Supporting Information for

Reductive amination of ketones/aldehydes with amines using $BH_3N(C_2H_5)_3$ as reductant

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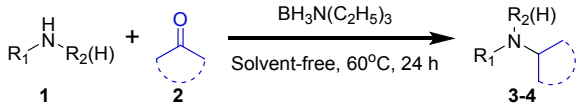
1. General information

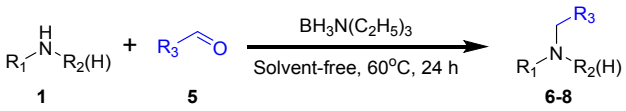
All reagents are analytically pure agents purchased from Energy Chemical and are used without further purification unless otherwise stated. Deuterated solvents Deuterated reagents are provided by Energy Chemical, China. The yields were determined using Shimadzu GC 2014 gas chromatography using dodecane as an internal standard. The substrates and their corresponding products also were decided by an Agilent 7890B/5977 GC-MS. The NMR spectra were recorded on a JNM-ECZ-400 spectrometer at 128 MHz (^{11}B NMR). The chemical shifts are given in ppm, which are referenced to $BF_3 \cdot Et_2O$ (^{11}B NMR).

2. Typical procedure for the reductive amination of amines and ketones



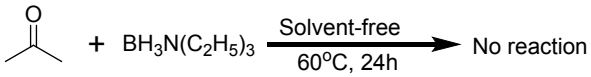
In a typical procedure, amines (**1**, 1.0 mmol), ketones (**2**, 3.0 mmol), and $BH_3N(C_2H_5)_3$ (1.0 mmol) were charged into a 20 mL high-pressure Schlenk flask under ambient temperature and pressure. Then, the mixture was stirred at 60°C for 24 h. When the reaction was finished, the reactor was cooled to room temperature. The yields were resolved by Shimadzu GC 2014 gas chromatography, and the substrates and their corresponding products also were decided by an Agilent 7890B/5977 GC-MS.

3. Typical procedure for the reductive amination of amines and aldehydes



In a typical procedure, amines (**1**, 1.0 mmol), aldehydes (**5**, 3.0 mmol), and $BH_3N(C_2H_5)_3$ (1.0 mmol) were charged into a 20 mL high-pressure Schlenk flask under ambient temperature and pressure. Then, the mixture was stirred at 60°C for 24 h. When the reaction was finished, the reactor was cooled to room temperature. The yields were resolved by Shimadzu GC 2014 gas chromatography, and the substrates and their corresponding products also were decided by an Agilent 7890B/5977 GC-MS.

4. Reaction of acetone and $BH_3N(C_2H_5)_3$



Acetone (3.0 mmol) and $BH_3N(C_2H_5)_3$ (1.0 mmol) were charged into a 20 mL high-pressure Schlenk flask under ambient temperature and pressure. Then, the mixture was stirred at 60°C for 24

h. When the reaction was finished, the reactor was cooled to room temperature. Approximately 0.1 mL of the mixture was dissolved in 0.5 mL of $CDCl_3$ and used for the ^{11}B NMR experimental analysis (**Fig. S1**). For the control experiment, approximately 0.1 mL of the $BH_3N(C_2H_5)_3$ was dissolved in 0.5 mL of $CDCl_3$ and used for the ^{11}B NMR experimental analysis (**Fig. S2**). The result indicate that $BH_3N(C_2H_5)_3$ does not react with acetone.

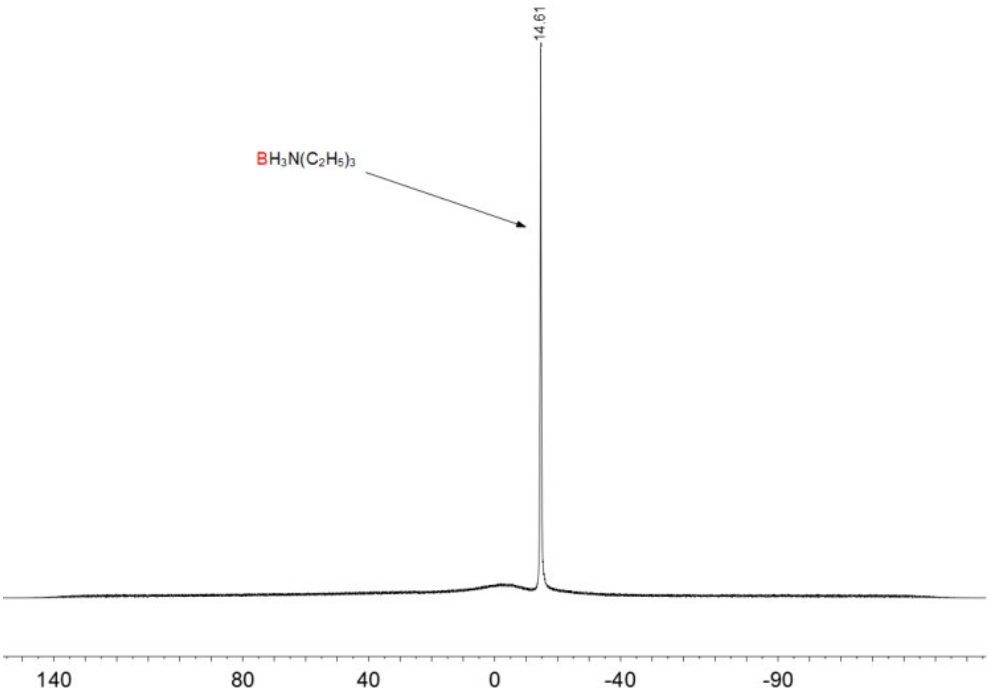


Fig. S1 The ^{11}B NMR spectra for the reaction of acetone and $BH_3N(C_2H_5)_3$.

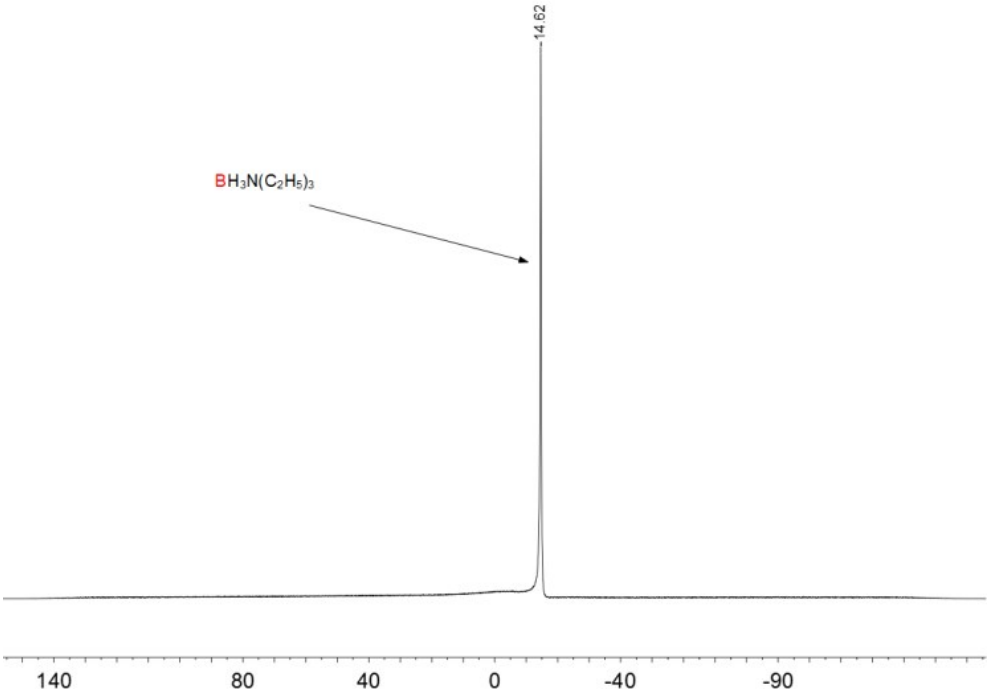
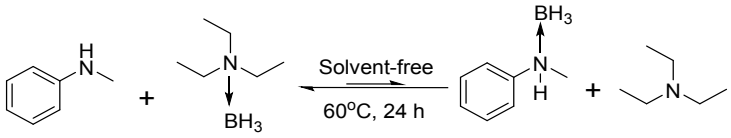


Fig. S2 The ^{11}B NMR spectra for the $BH_3N(C_2H_5)_3$.

5. Reaction of *N*-methylaniline and $BH_3N(C_2H_5)_3$



The *N*-methylaniline (1.0 mmol) and $BH_3N(C_2H_5)_3$ (1.0 mmol) were charged into a 20 mL high-pressure Schlenk flask under ambient temperature and pressure. Then, the mixture was stirred at 60°C for 24 h. When the reaction was finished, the reactor was cooled to room temperature. Approximately 0.1 mL of the mixture was dissolved in 0.5 mL of $CDCl_3$ and used for ^{11}B NMR experimental analysis (**Fig. S3**). The result indicate that $BH_3N(C_2H_5)_3$ reacts with N-methylaniline to form $BH_3NHR_1R_2$ (R_1=CH_3, R_2=C_6H_5). In addition, we also studied ^{11}B NMR of other amines (e.g., 1,2,3,4-tetrahydroquinoline, indoline, and dipropylamine) after their reactions with $BH_3N(C_2H_5)_3$ (**Fig. S4-S6**).

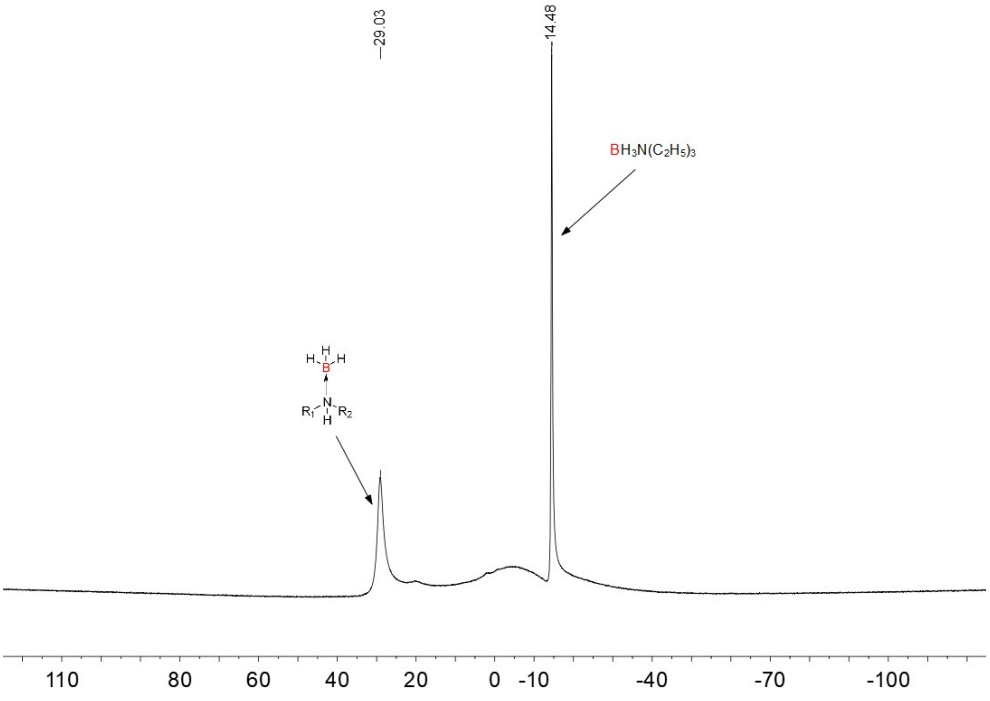


Fig. S3 The ^{11}B NMR spectra for the reaction of *N*-methylaniline and $BH_3N(C_2H_5)_3$.

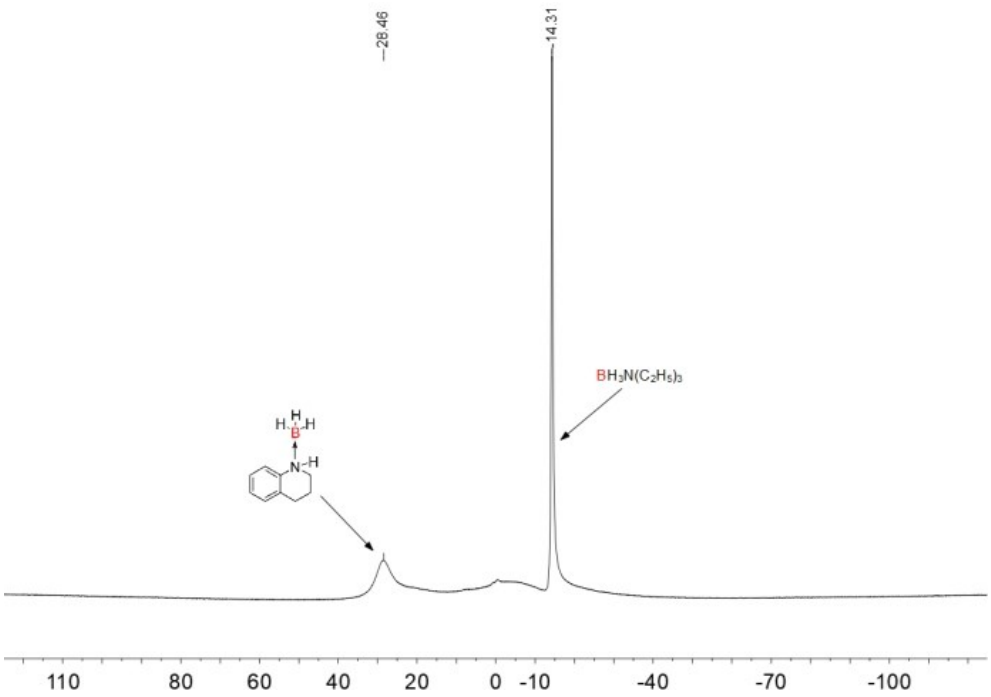


Fig. S4 The ^{11}B NMR spectra for the reaction of 1,2,3,4-tetrahydroquinoline and $BH_3N(C_2H_5)_3$.

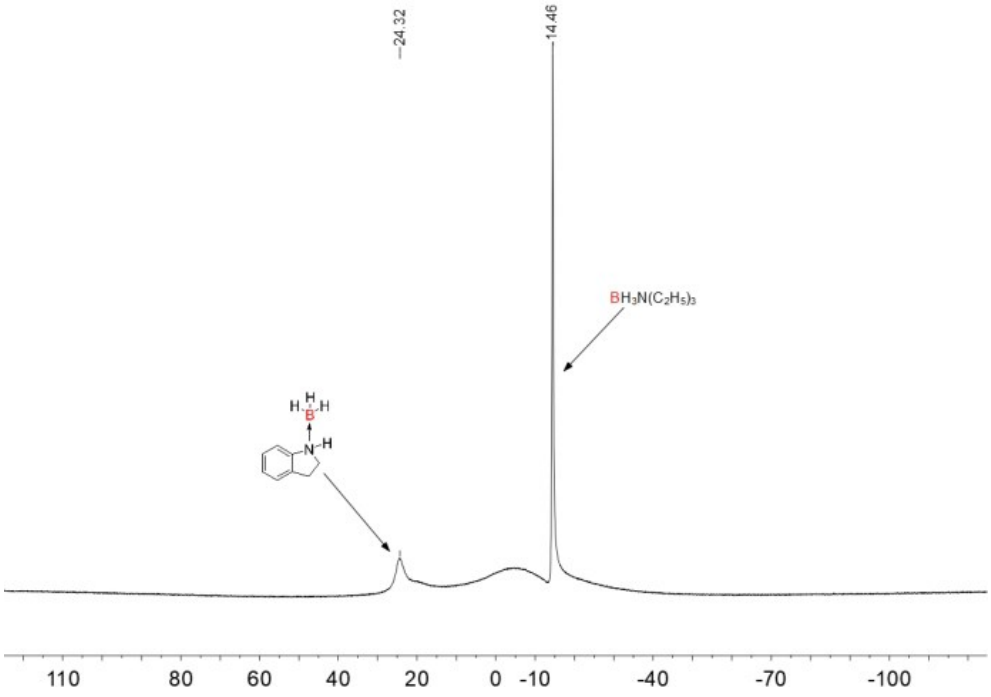


Fig. S5 The ^{11}B NMR spectra for the reaction of indoline and $BH_3N(C_2H_5)_3$.

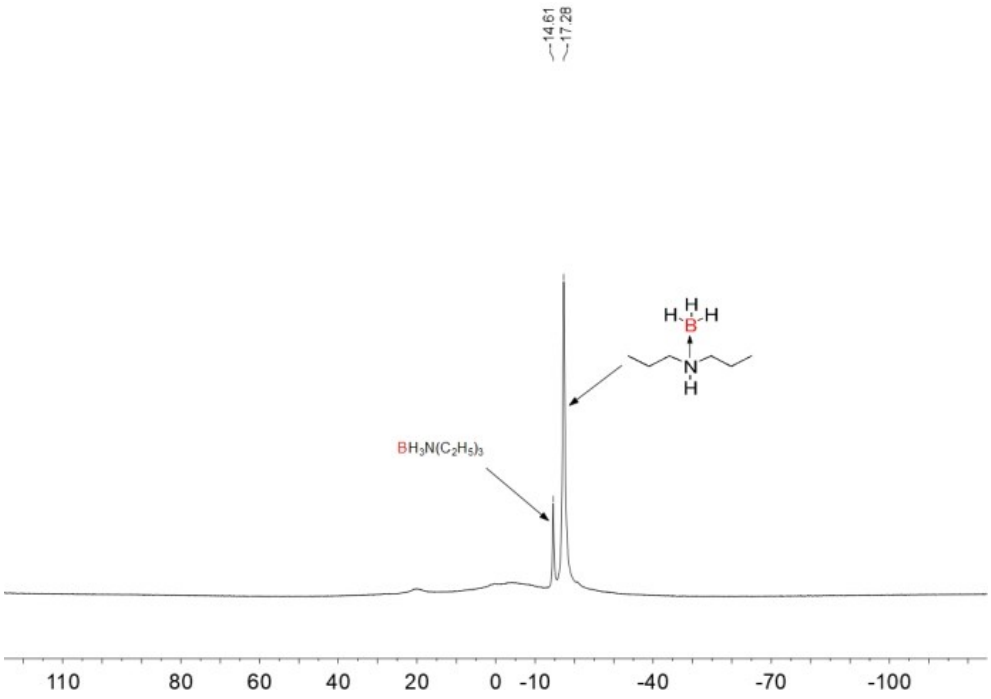
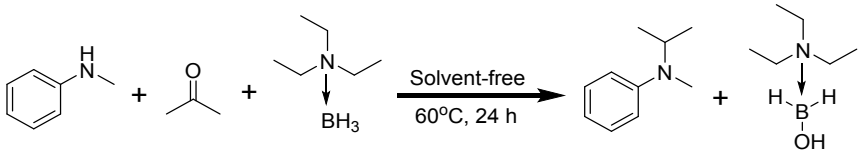


Fig. S6 The ^{11}B NMR spectra for the reaction of dipropylamine and $BH_3N(C_2H_5)_3$.

6. Reaction of *N*-methylaniline, acetone, and $BH_3N(C_2H_5)_3$



The *N*-methylaniline (1.0 mmol), acetone (3.0 mmol), and $BH_3N(C_2H_5)_3$ (1.0 mmol) were charged into a 20 mL high-pressure Schlenk flask under ambient temperature and pressure. Then, the mixture was stirred at 60°C for 24 h. When the reaction was finished, the reactor was cooled to room temperature. Approximately 0.1 mL of the mixture was dissolved in 0.5 mL of $CDCl_3$ and ^{11}B NMR experimental analysis (**Fig. S7**). A new peak at a chemical shift of 0.59 ppm in ^{11}B NMR was found after the reaction of *N*-methylaniline, acetone, and $BH_3N(C_2H_5)_3$, suggesting that oxidation product of $BH_2(OH)N(C_2H_5)_3$ was generated.

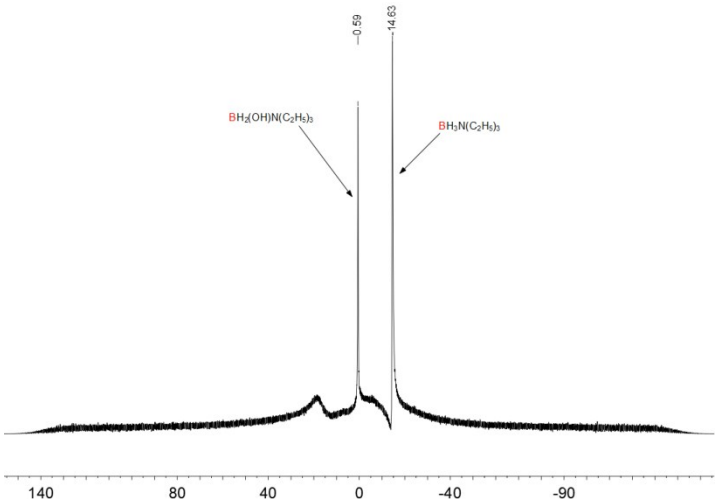
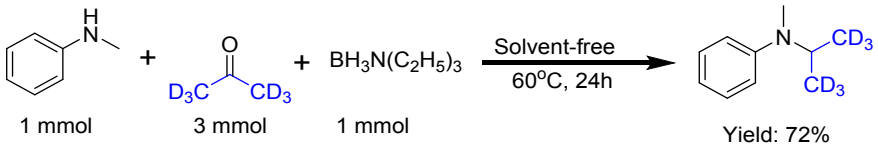


Fig. S7 The ^{11}B NMR spectra for the reaction of *N*-methylaniline, acetone, and $BH_3N(C_2H_5)_3$.

7. Isotope labeling experiment with acetone-d_6



The *N*-methylaniline (1.0 mmol), acetone-d_6 (3.0 mmol), and $BH_3N(C_2H_5)_3$ (1.0 mmol) were charged into a 20 mL high-pressure Schlenk flask under ambient temperature and pressure. Then, the mixture was stirred at 60°C for 24 h. When the reaction was finished, the reactor was cooled to room temperature. The yields were resolved by Shimadzu GC 2014 gas chromatography, and the substrates and their corresponding products also were decided by an Agilent 7890B/5977 GC-MS (**Fig. S8**). The residue was directly purified by preparative TLC on silica, eluting with petroleum ether and ethyl acetate to give **3a** and **3a-d_6**, both yellow liquids, and thestructure confirmed by NMR (**Fig. S9 and S10**).

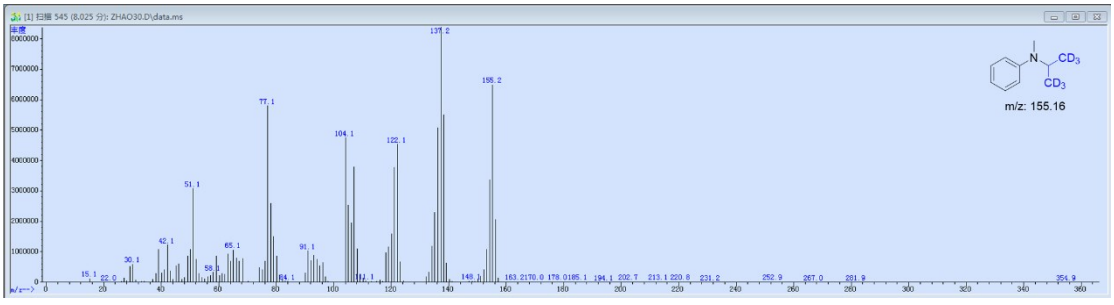
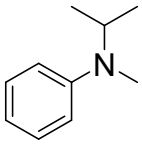
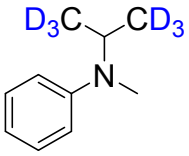


Fig. S8 The GC/MS information for the reductive amination product of acetone-d_6 with *N*-methylaniline.



3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 2H), 6.79 (d, J = 8.1 Hz, 2H), 6.69 (t, J = 7.1 Hz, 1H), 4.08 (dt, J = 19.4, 6.4 Hz, 1H), 2.72 (s, 3H), 1.15 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.30 (s), 129.24 (s), 116.55 (s), 113.46 (s), 49.05 (s), 29.92 (s), 19.45 (s).



3a-*d*$_6$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 6.7 Hz, 2H), 7.03 (d, J = 7.5 Hz, 3H), 3.31 (s, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.06 (s), 130.02 (s), 129.84 (s), 122.53 (s), 61.17 (s), 41.43 (s).

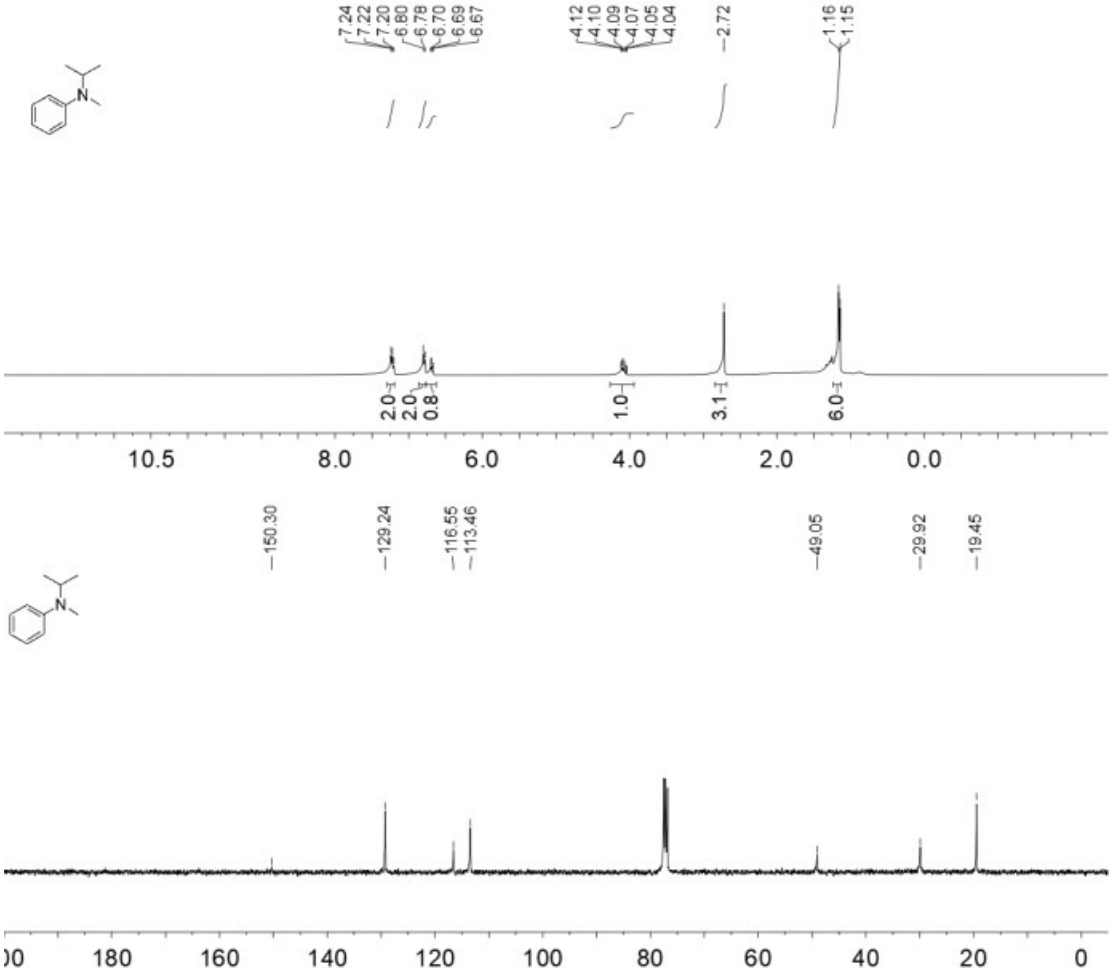


Fig. S9 The ^{1}H NMR and ^{13}C NMR of **3a**.

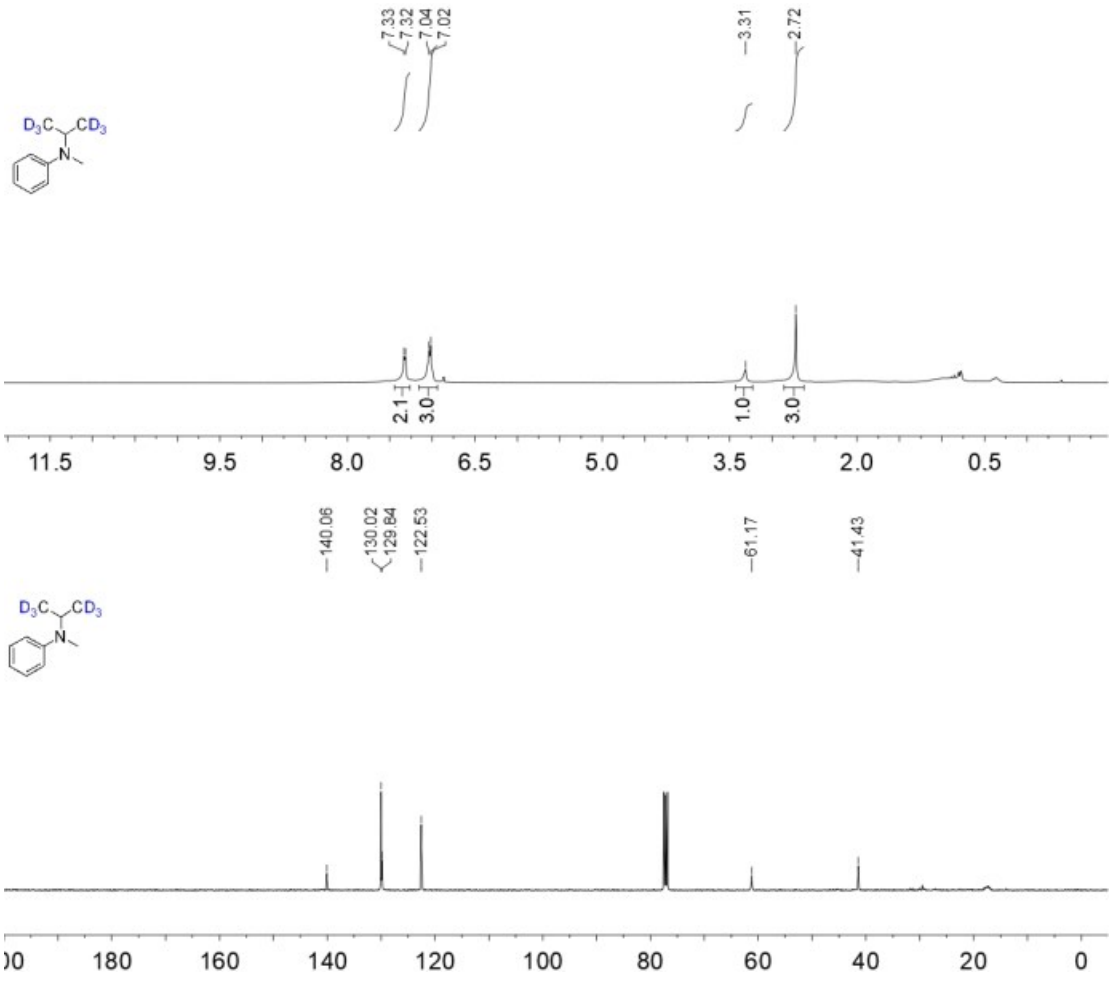
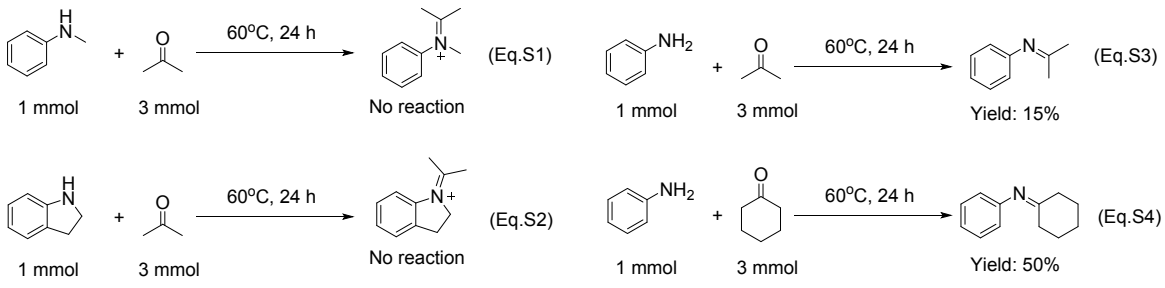


Fig. S10 The ^{1}H NMR and ^{13}C NMR of **3a-*d*$_6$**.



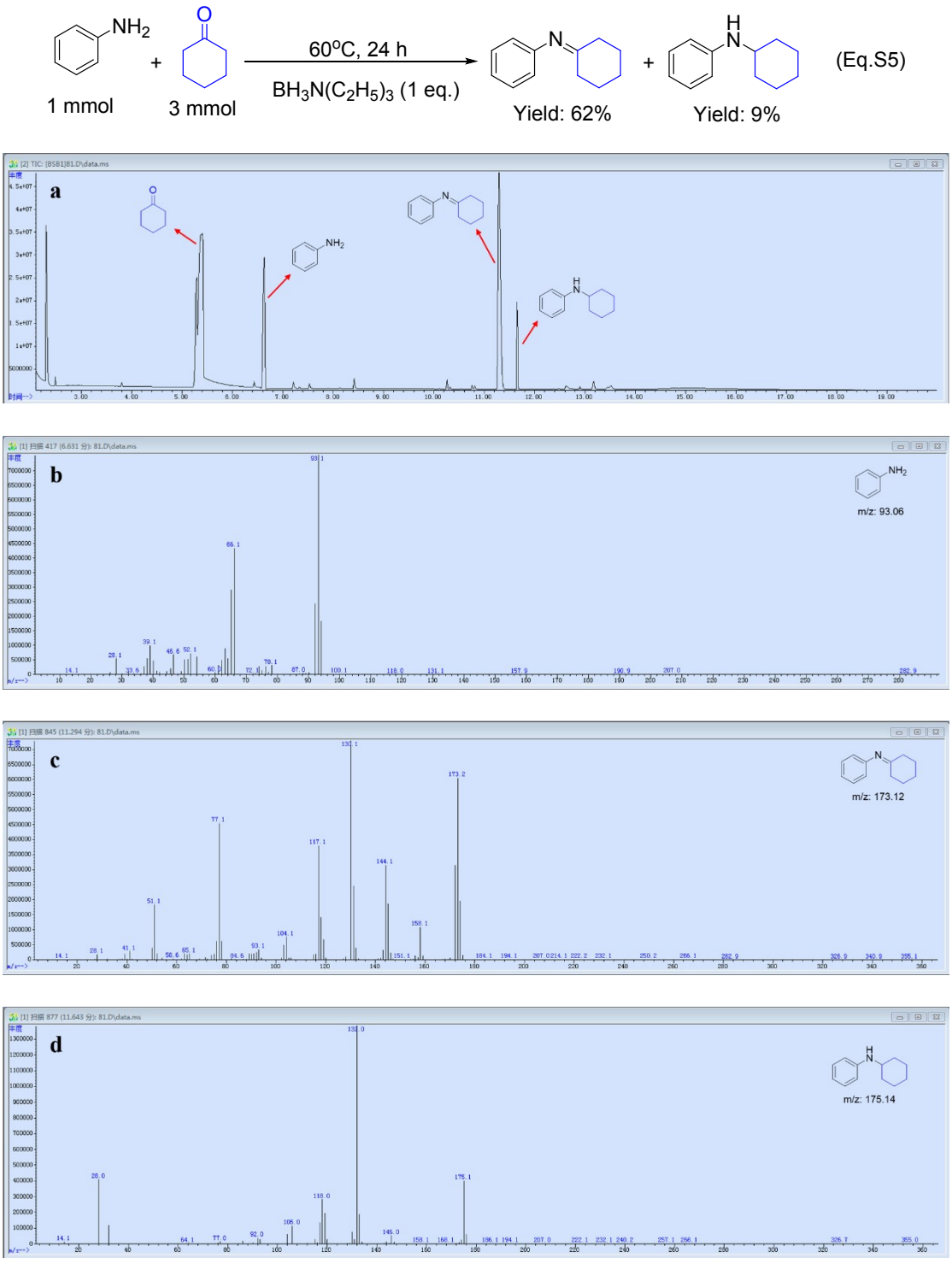
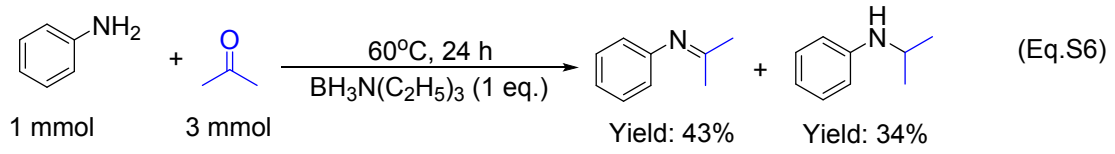


Fig. S11 (a) Typical GC-MS analysis of the reductive amination reaction of cyclohexanone (**2b**) with aniline. Retention time (min): (b) 6.631 min, (c) 11.294 min, (d) 11.643 min.



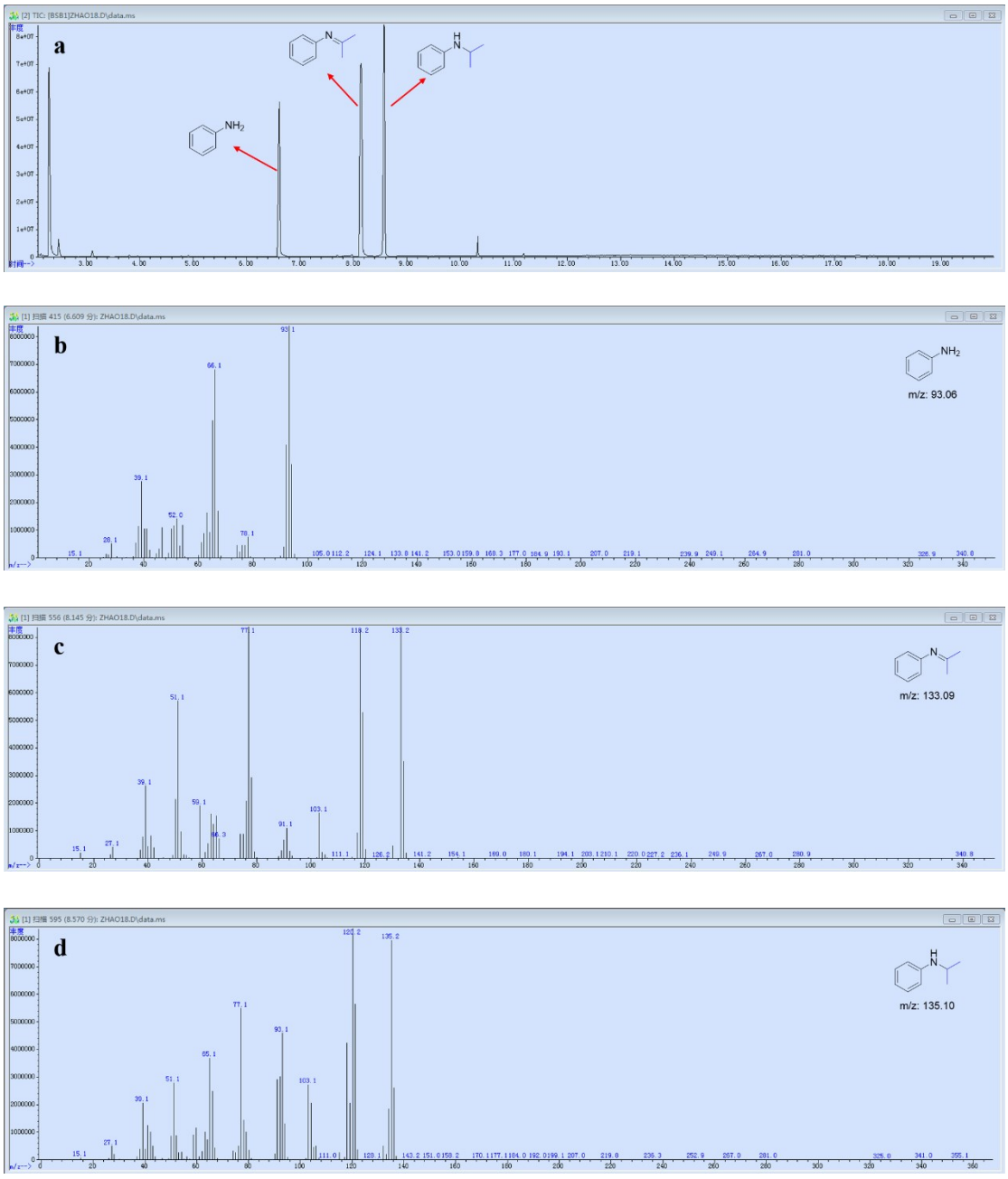
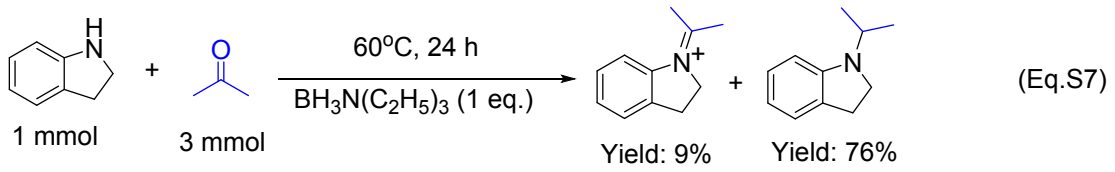


Fig. S12 (a) Typical GC-MS analysis of the reductive amination reaction of acetone (**2a**) with aniline. Retention time (min): (b) 6.609 min, (c) 8.145 min, (d) 8.570 min.



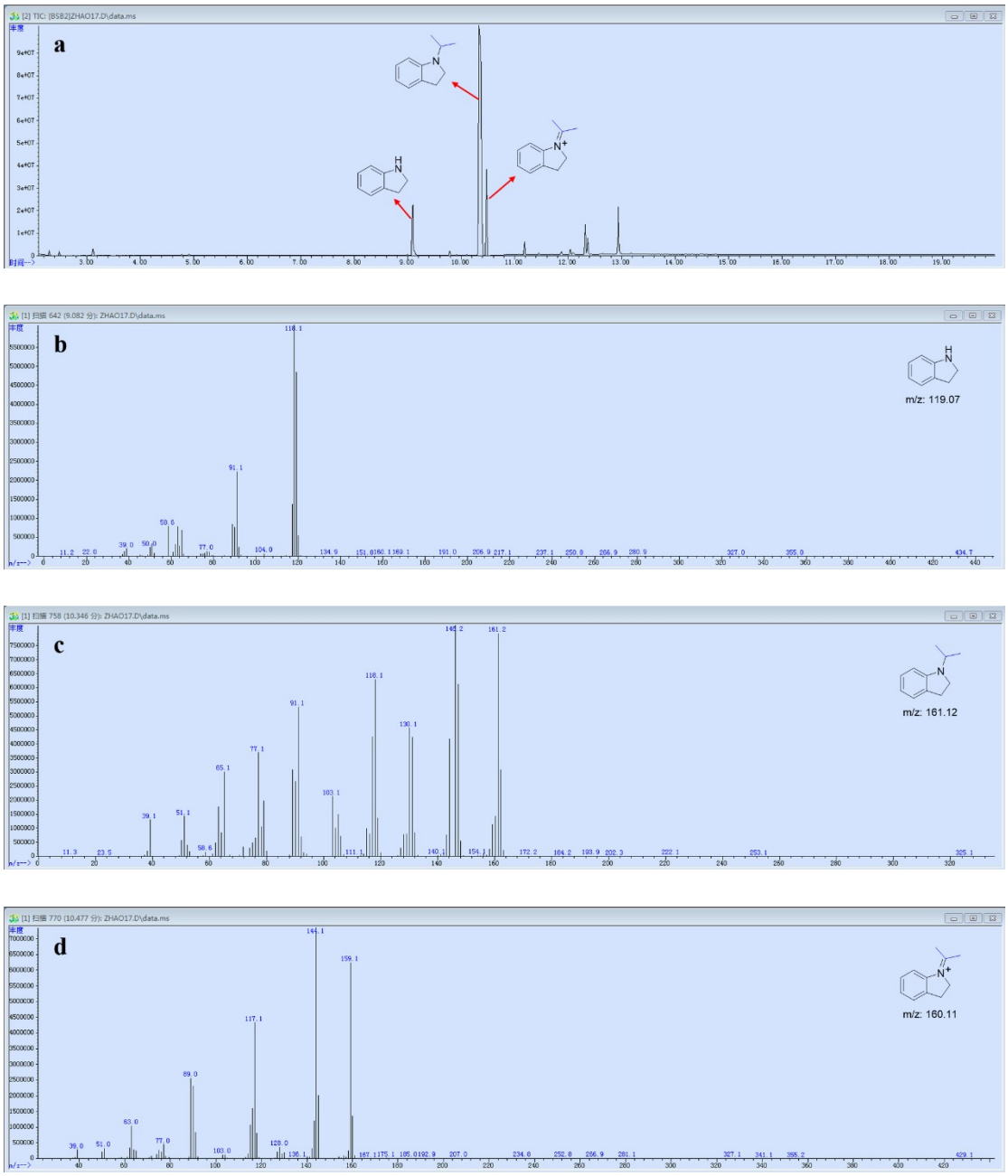
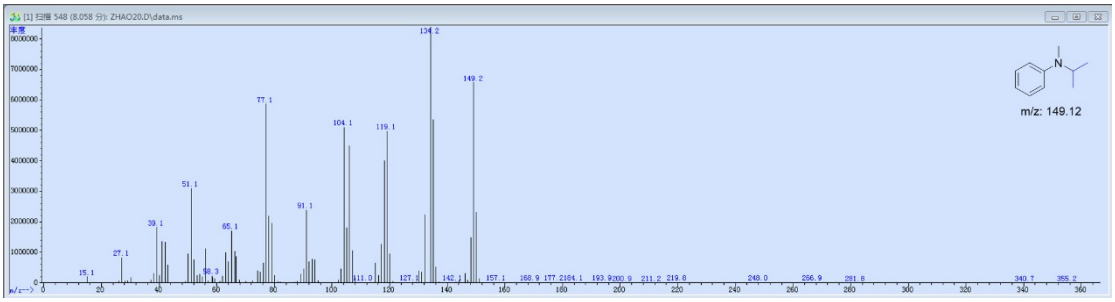


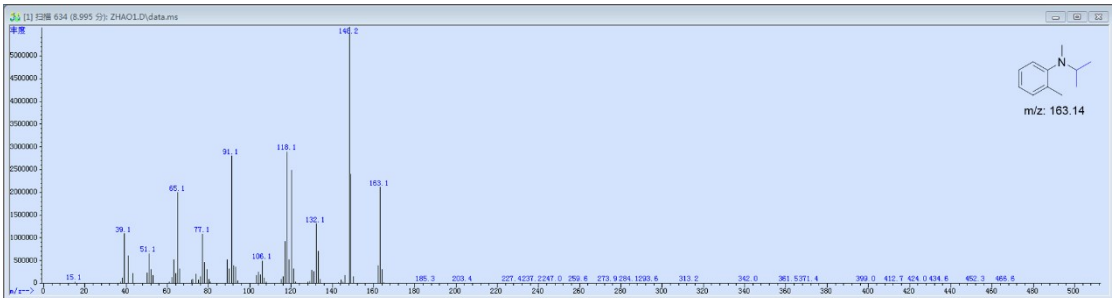
Fig. S13 (a) Typical GC-MS analysis of the reductive amination reaction of acetone (**2a**) with indoline. Retention time (min): (b) 9.082 min, (c) 10.346 min, (d) 10.477 min.

8. GC-MS analysis data

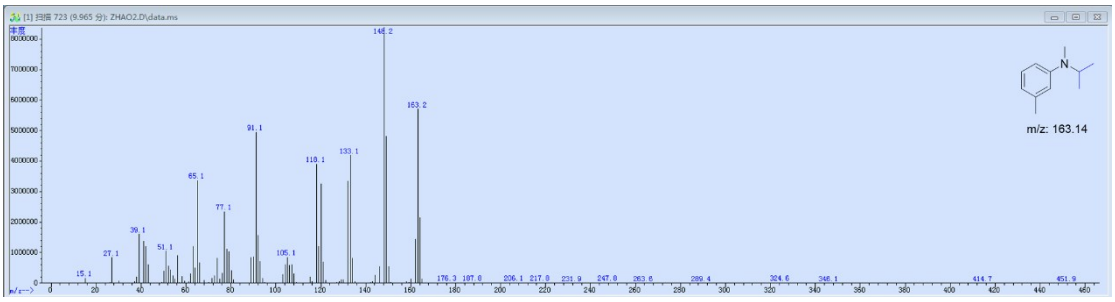
Scheme S1 The GC-MS information of **3a**.



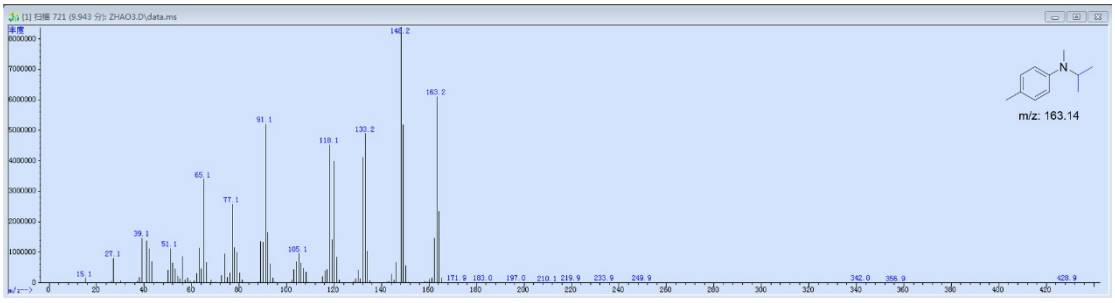
Scheme S2 The GC-MS information of **3b**.



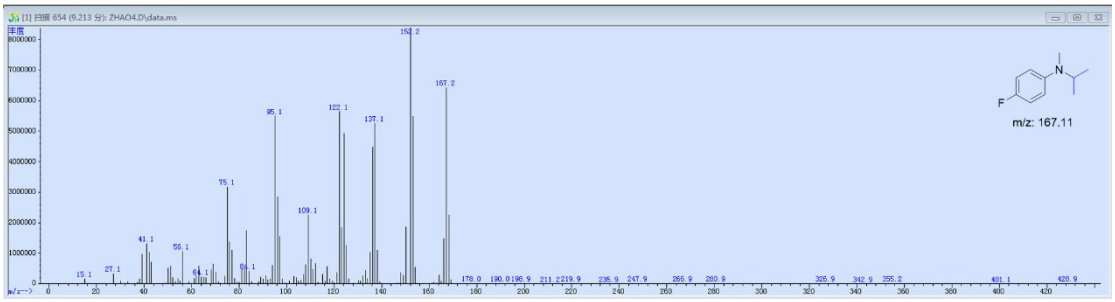
Scheme S3 The GC-MS information of **3c**.



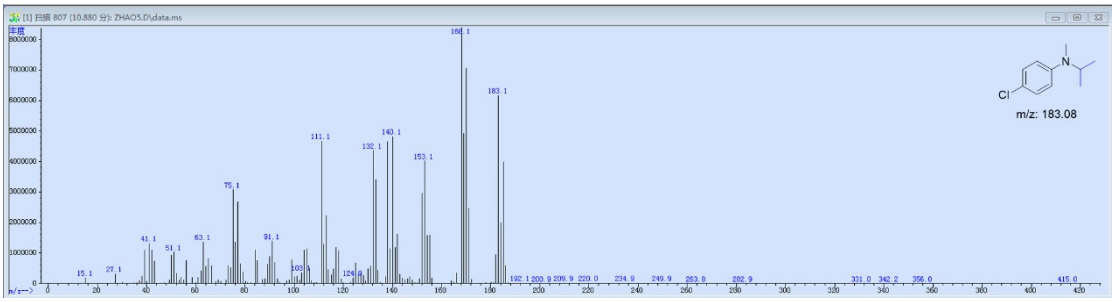
Scheme S4 The GC-MS information of **3d**.



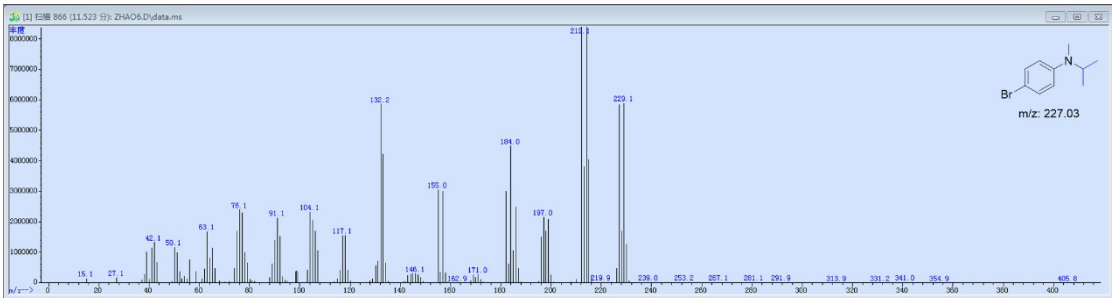
Scheme S5 The GC-MS information of **3e**.



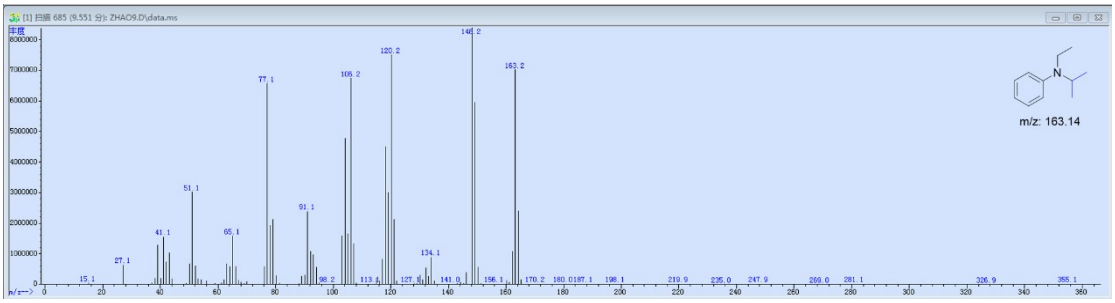
Scheme S6 The GC-MS information of **3f**.



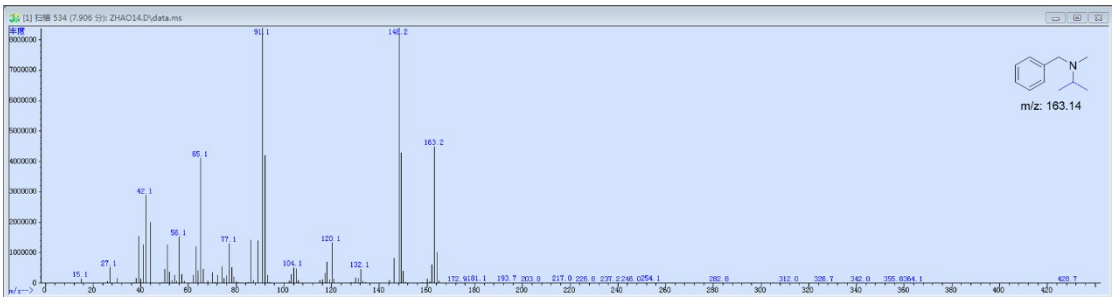
Scheme S7 The GC-MS information of **3g**.



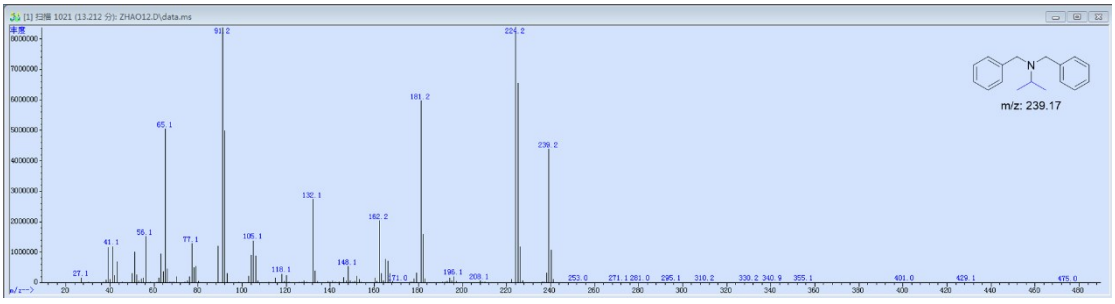
Scheme S8 The GC-MS information of **3i**.



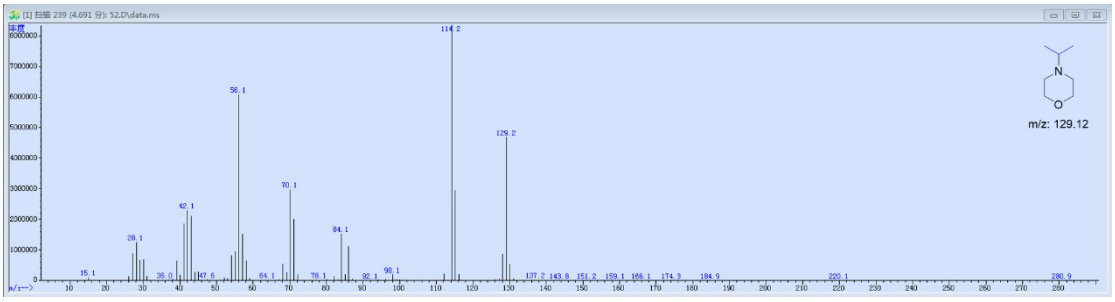
Scheme S9 The GC-MS information of **3k**.



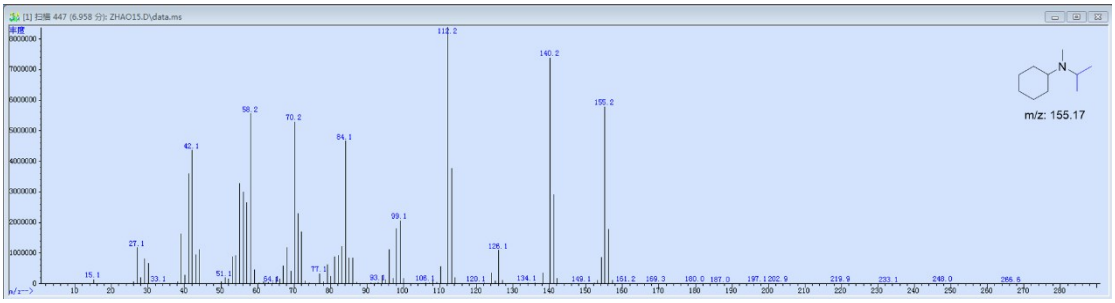
Scheme S10 The GC-MS information of **3l**.



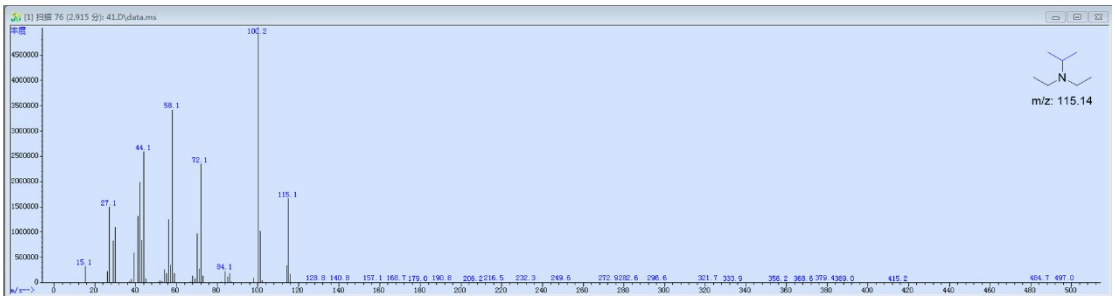
Scheme S11 The GC-MS information of **3m**.



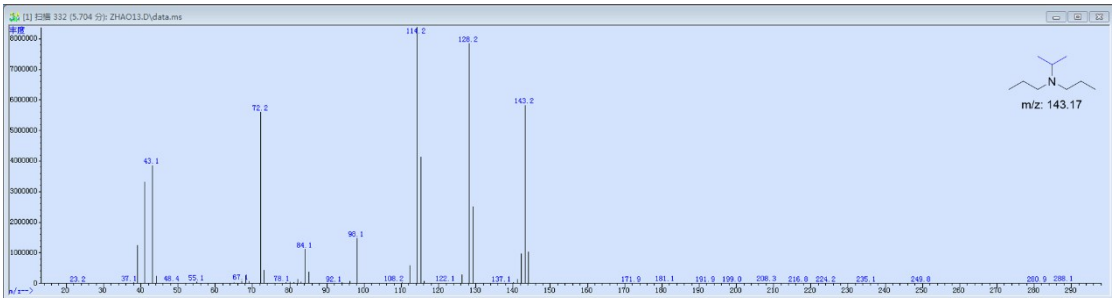
Scheme S12 The GC-MS information of **3n**.



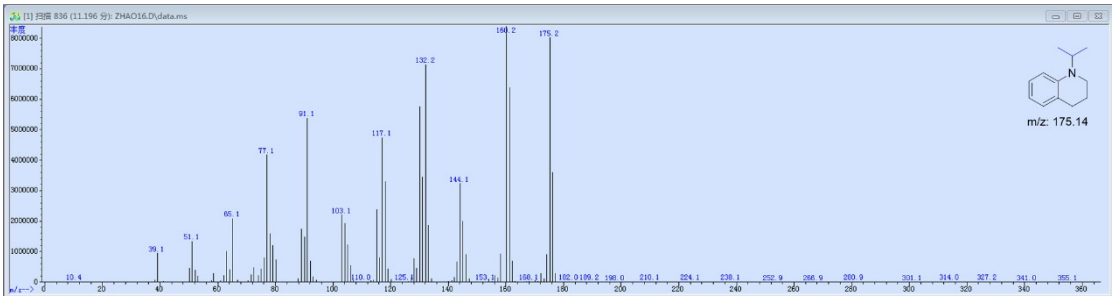
Scheme S13 The GC-MS information of **3o**.



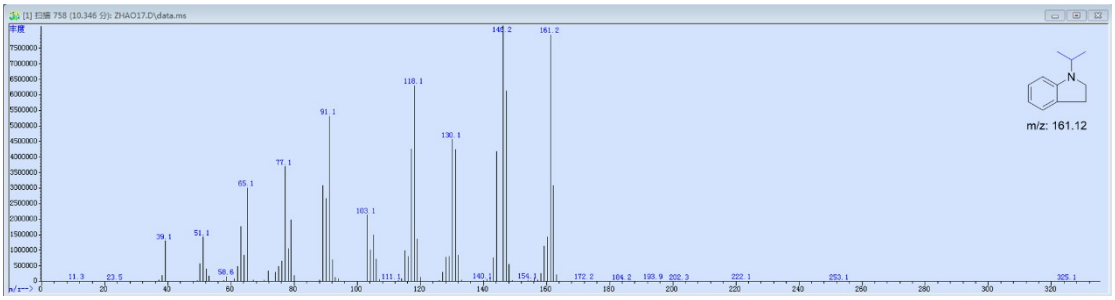
Scheme S14 The GC-MS information of **3p**.



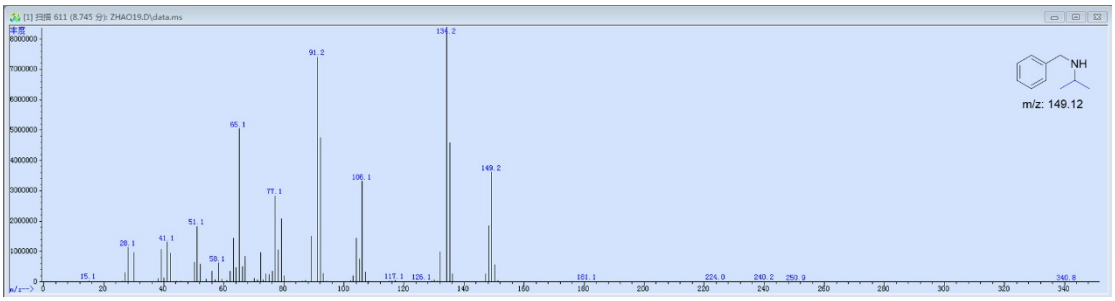
Scheme S15 The GC-MS information of **3q**.



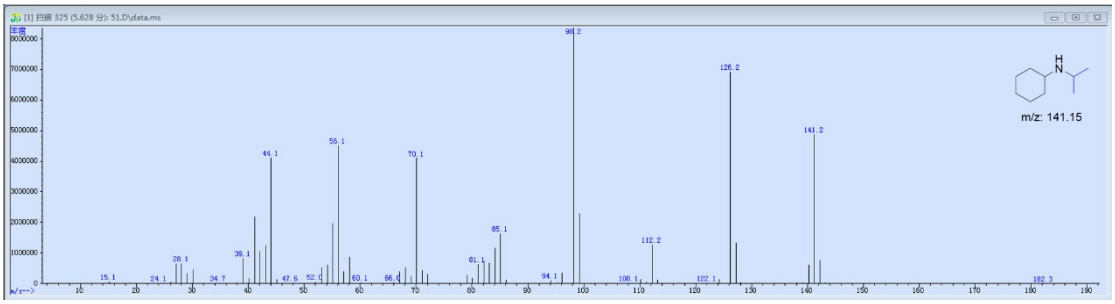
Scheme S16 The GC-MS information of **3r**.



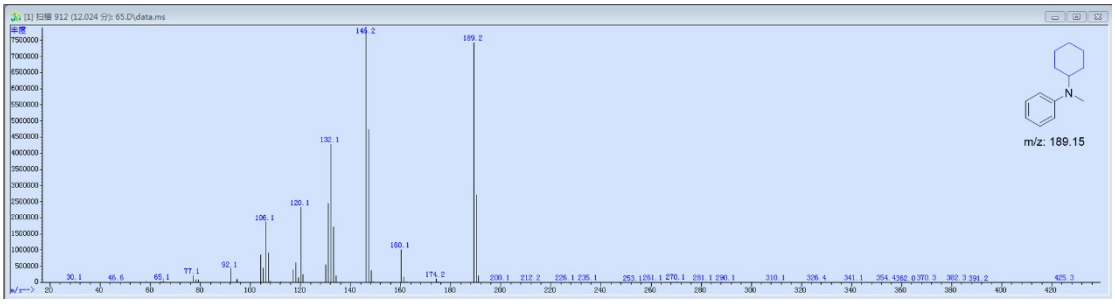
Scheme S17 The GC-MS information of **3s**.



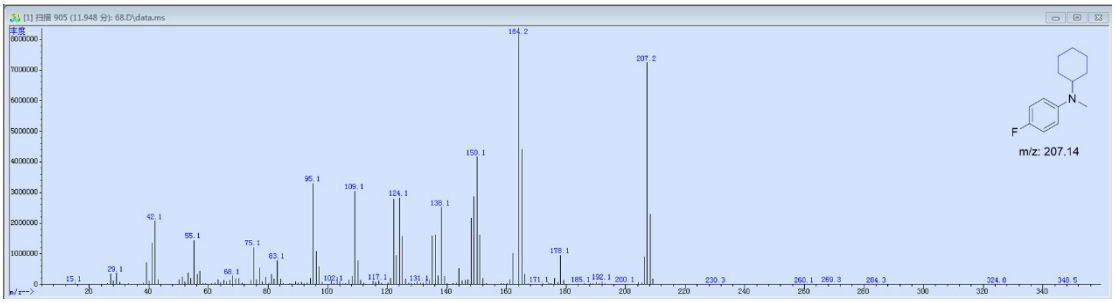
Scheme S18 The GC-MS information of **3t**.



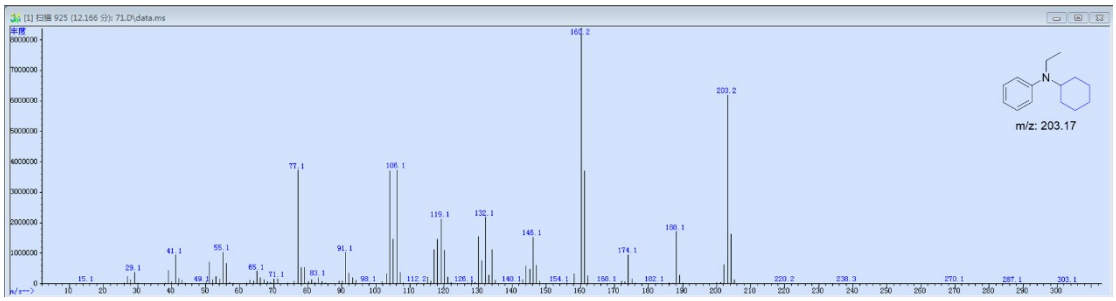
Scheme S19 The GC-MS information of **4a**.



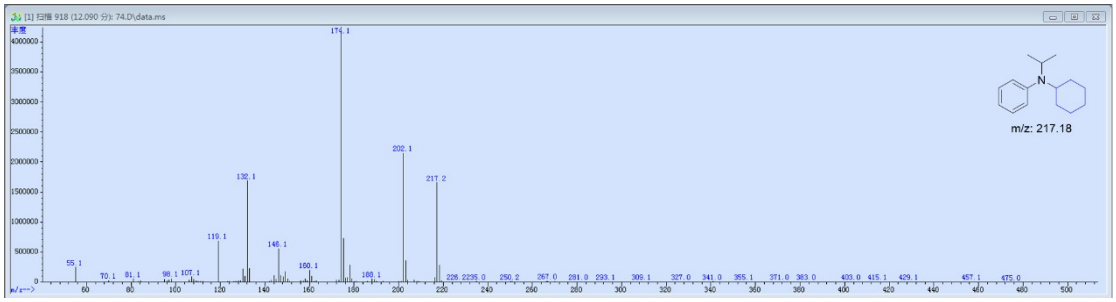
Scheme S20 The GC-MS information of **4b**.



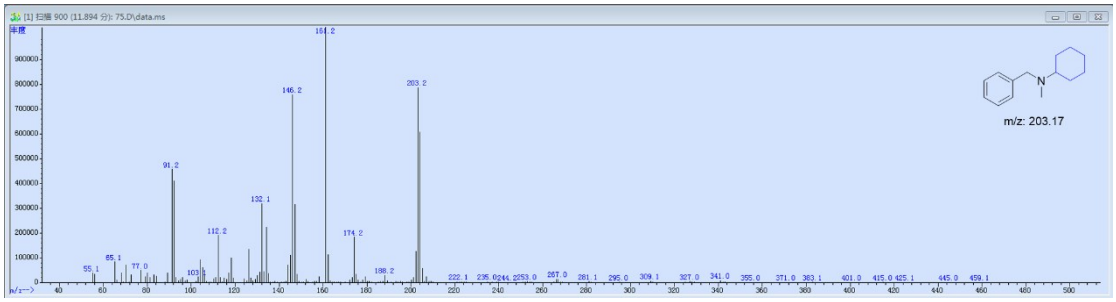
Scheme S21 The GC-MS information of **4d**.



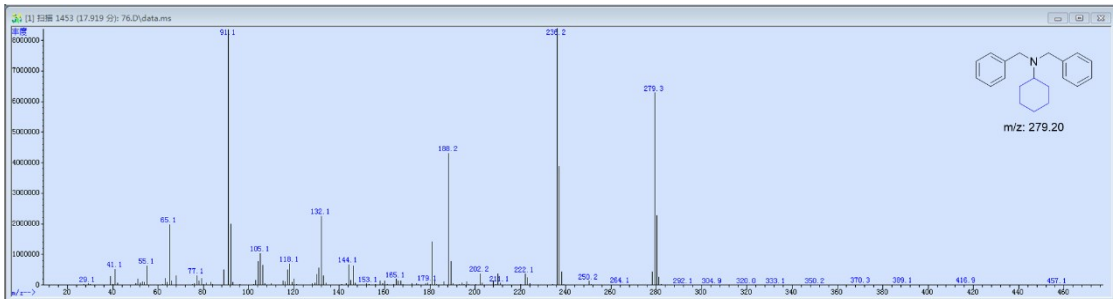
Scheme S22 The GC-MS information of **4e**.



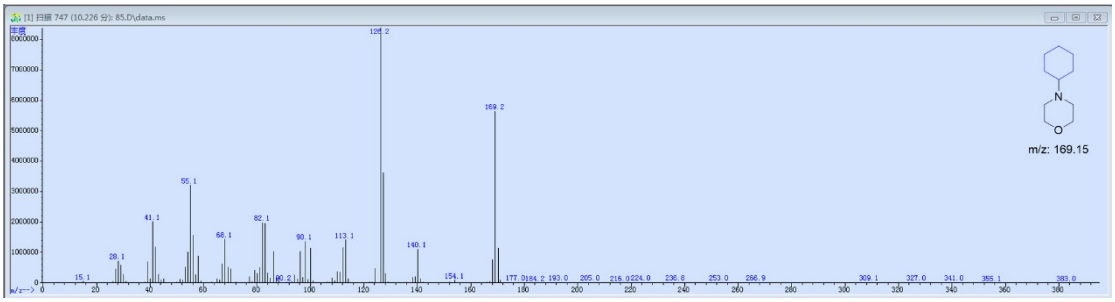
Scheme S23 The GC-MS information of **4f**.



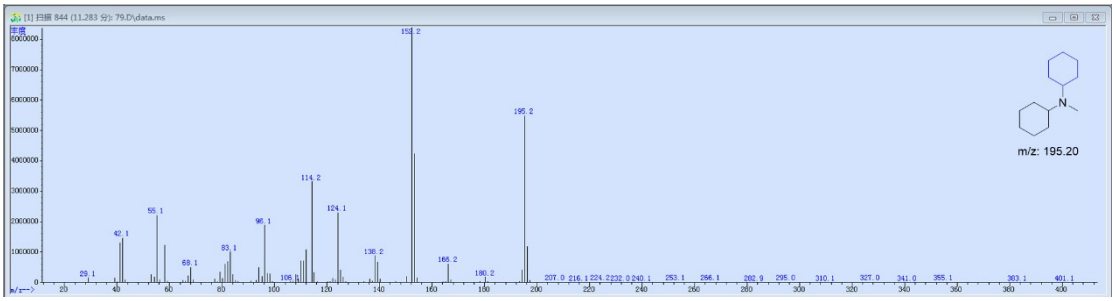
Scheme S24 The GC-MS information of **4g**.



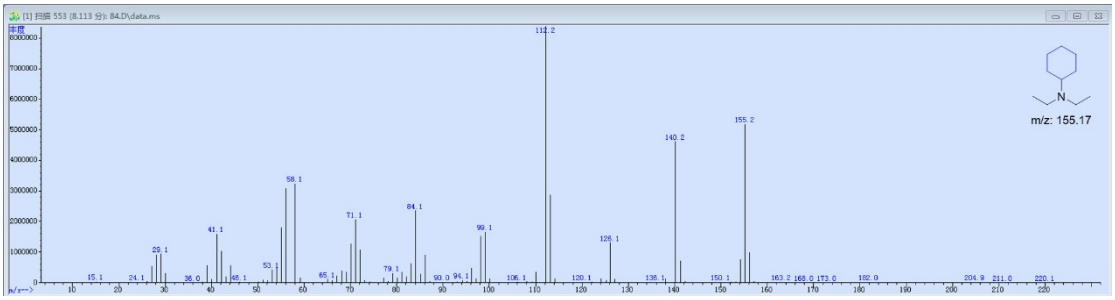
Scheme S25 The GC-MS information of **4h**.



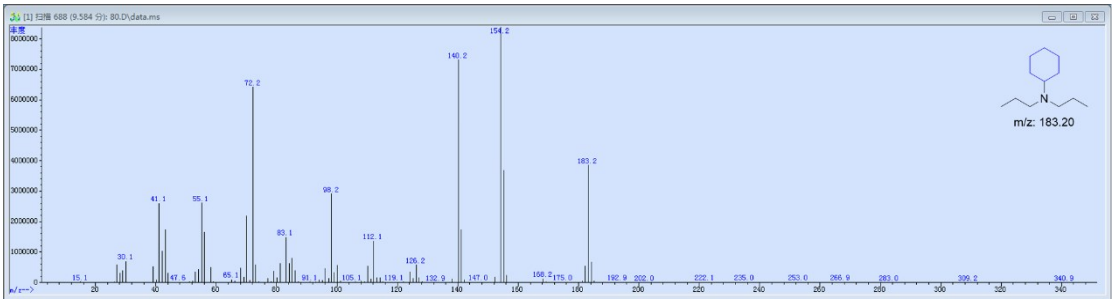
Scheme S26 The GC-MS information of **4i**.



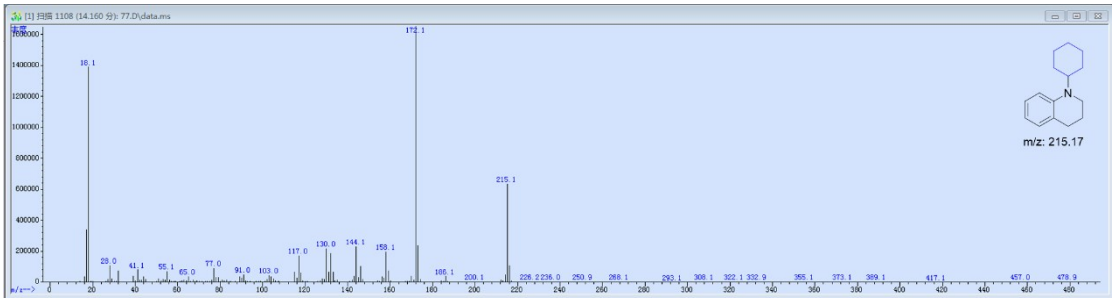
Scheme S27 The GC-MS information of **4j**.



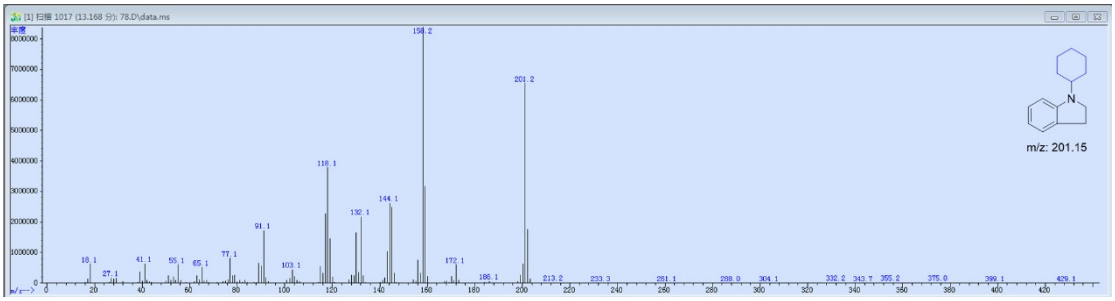
Scheme S28 The GC-MS information of **4k**.



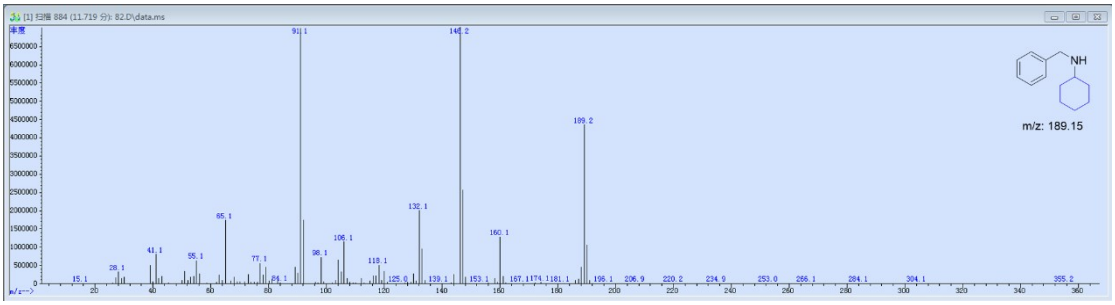
Scheme S29 The GC-MS information of **4l**.



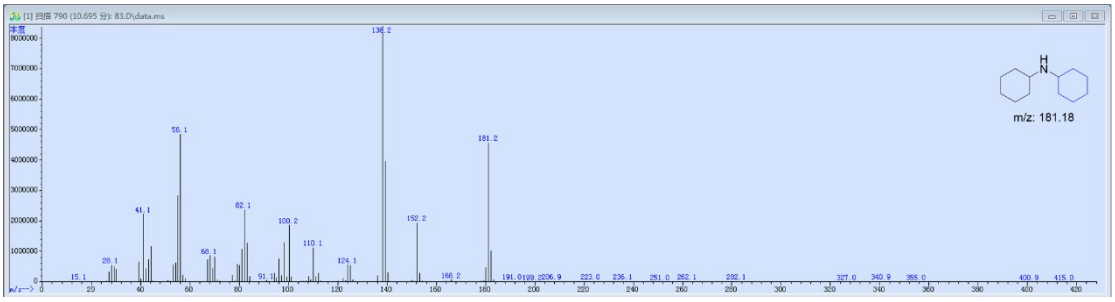
Scheme S30 The GC-MS information of **4m**.



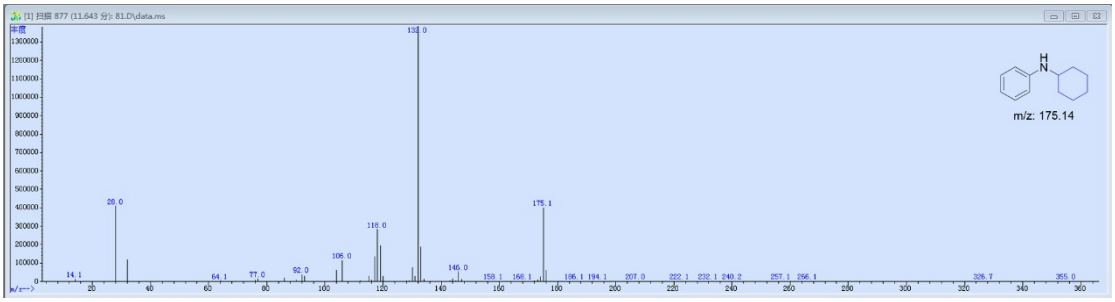
Scheme S31 The GC-MS information of **4n**.



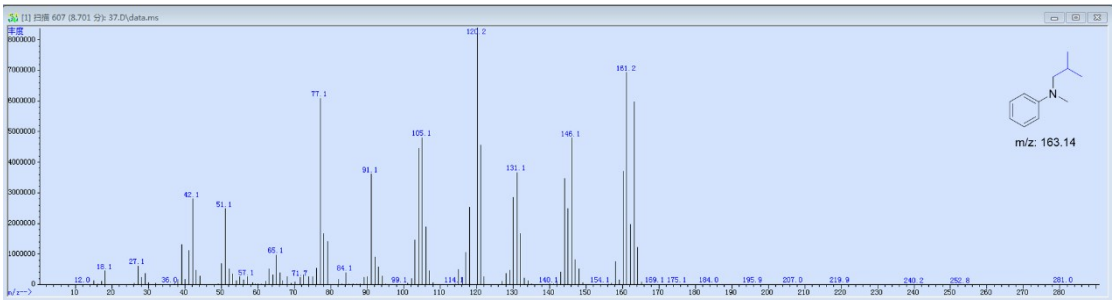
Scheme S32 The GC-MS information of **4o**.



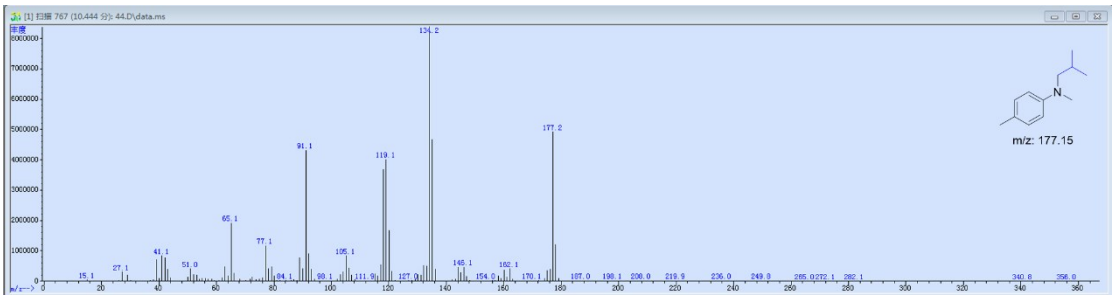
Scheme S33 The GC-MS information of **4p**.



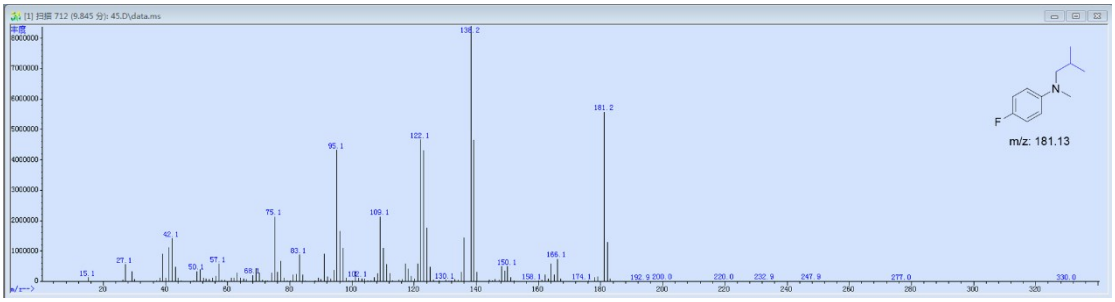
Scheme S34 The GC-MS information of **6a**.



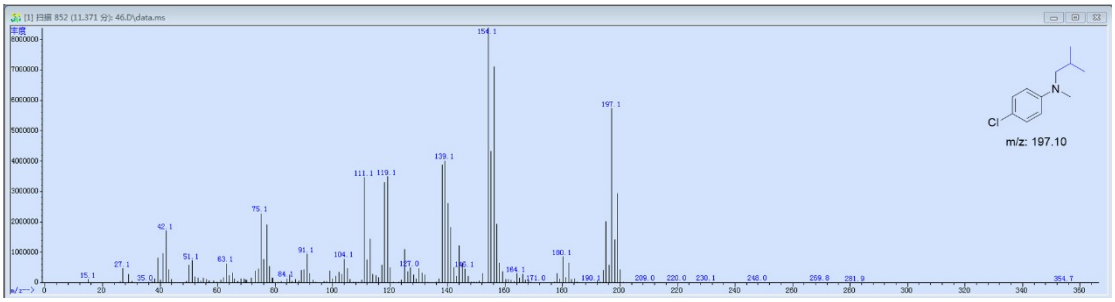
Scheme S35 The GC-MS information of **6b**.



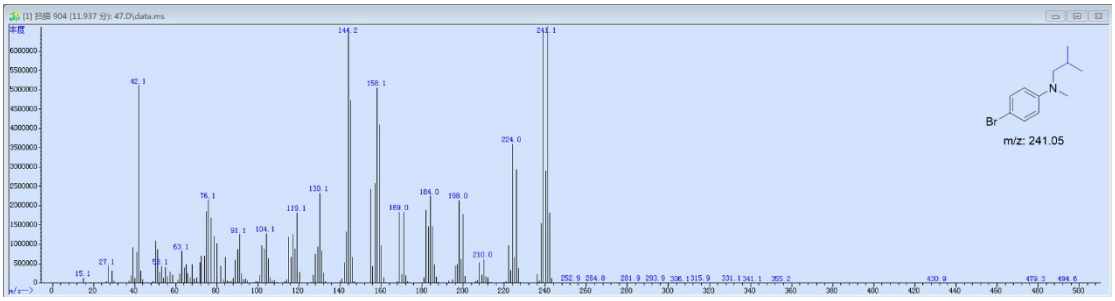
Scheme S36 The GC-MS information of **6c**.



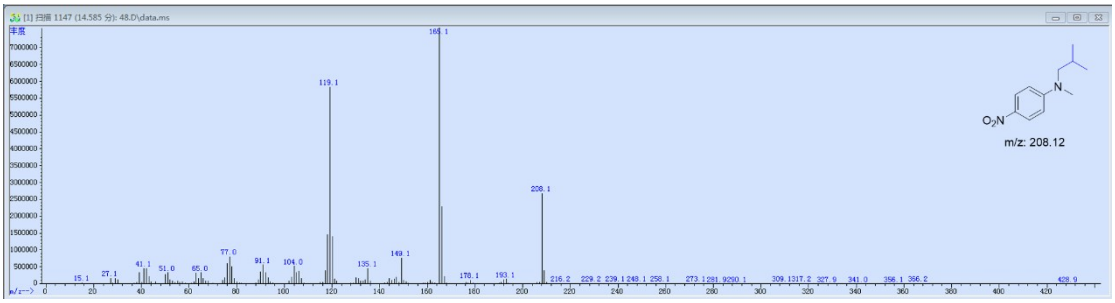
Scheme S37 The GC-MS information of **6d**.



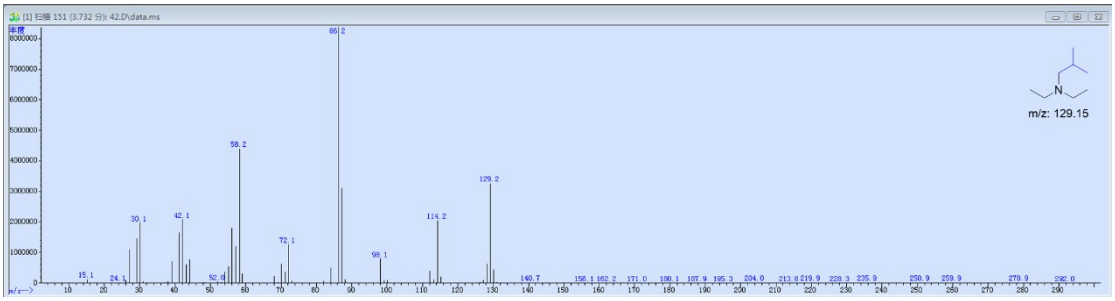
Scheme S38 The GC-MS information of **6e**.



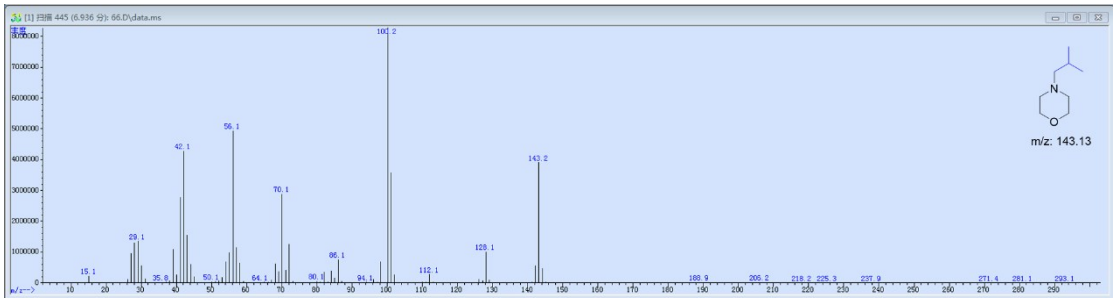
Scheme S39 The GC-MS information of **6f**.



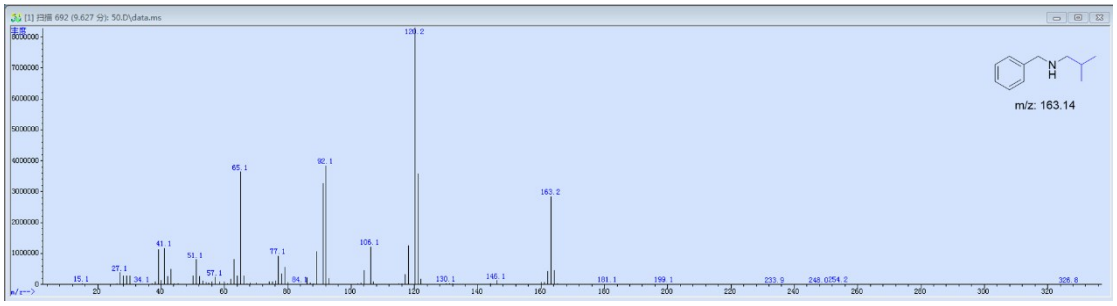
Scheme S40 The GC-MS information of **6g**.



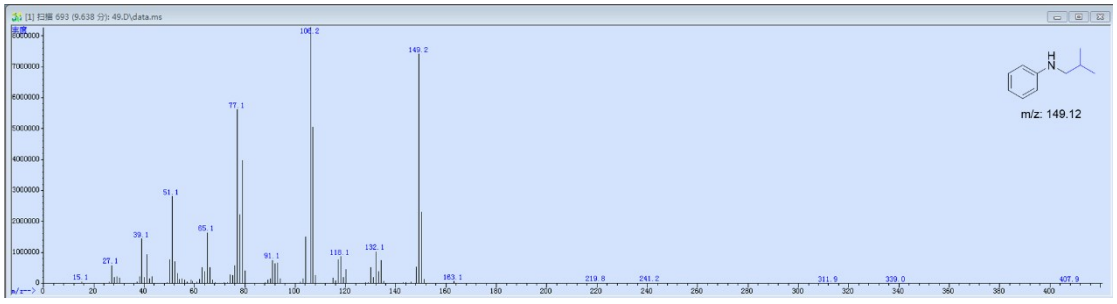
Scheme S41 The GC-MS information of **6h**.



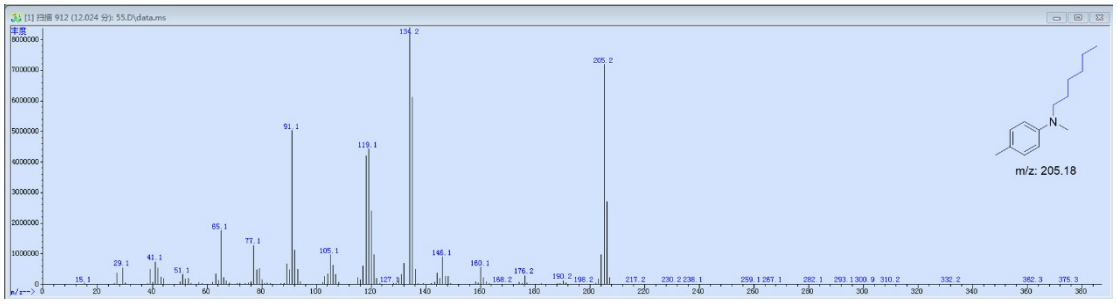
Scheme S42 The GC-MS information of **6i**.



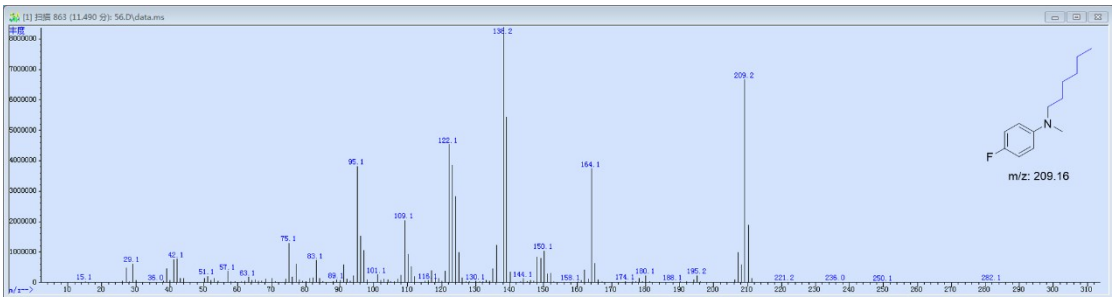
Scheme S43 The GC-MS information of **6j**.



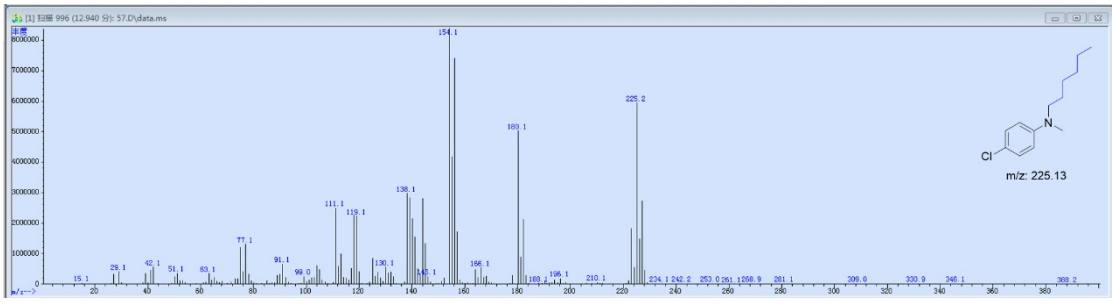
Scheme S44 The GC-MS information of **7a**.



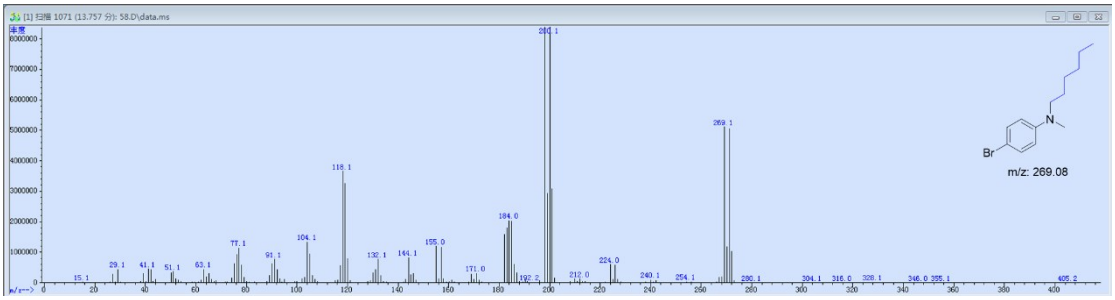
Scheme S45 The GC-MS information of **7b**.



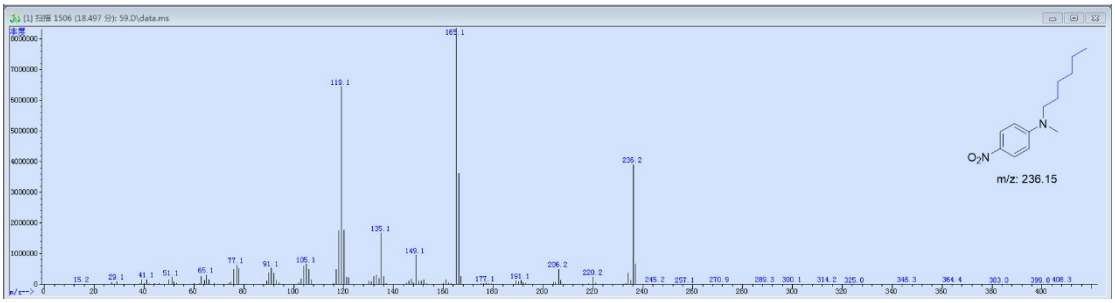
Scheme S46 The GC-MS information of **7c**.



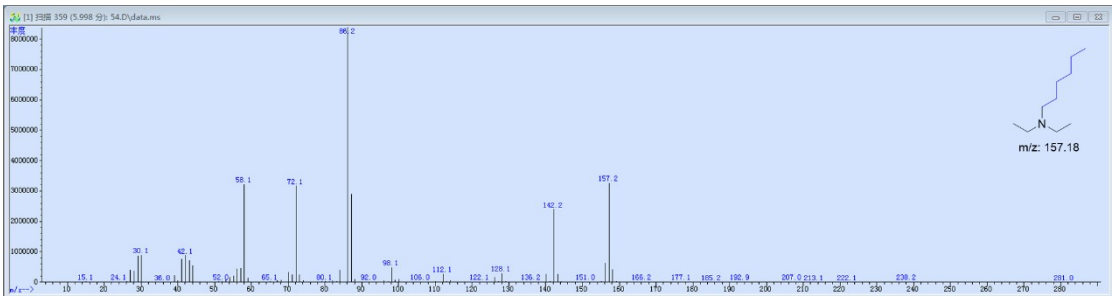
Scheme S47 The GC-MS information of **7d**.



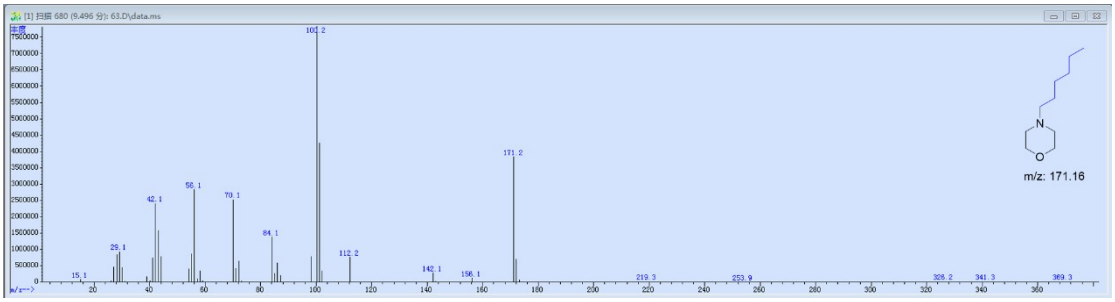
Scheme S48 The GC-MS information of **7e**.



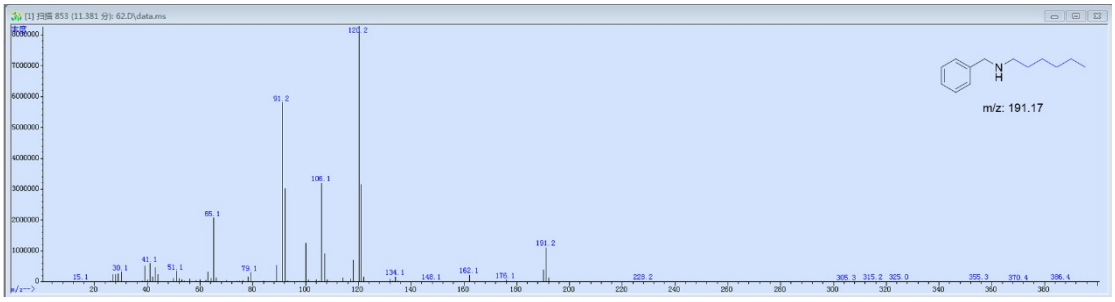
Scheme S49 The GC-MS information of **7f**.



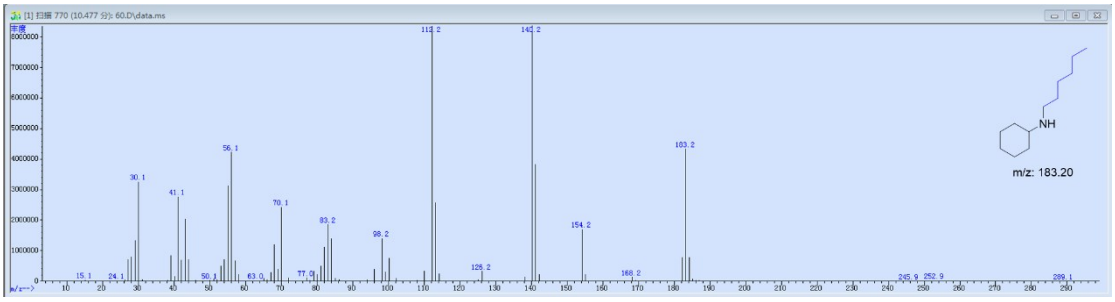
Scheme S50 The GC-MS information of **7g**.



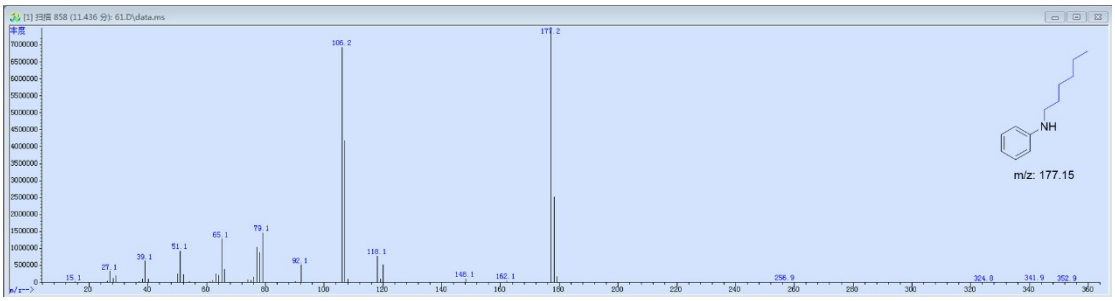
Scheme S51 The GC-MS information of **7h**.



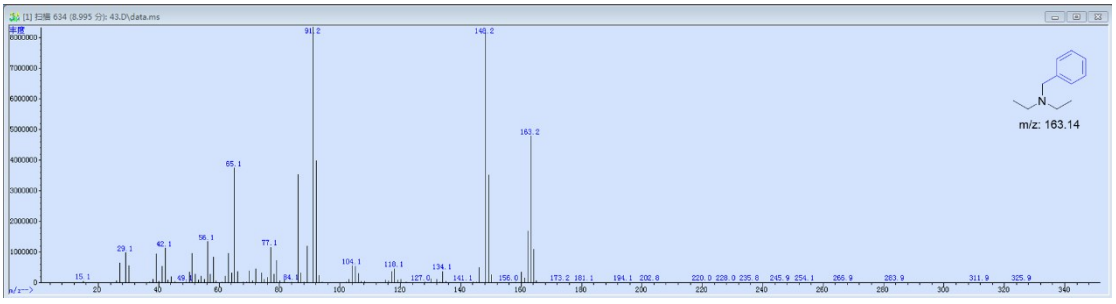
Scheme S52 The GC-MS information of **7i**.



Scheme S53 The GC-MS information of **7j**.



Scheme S54 The GC-MS information of **8a**.



Scheme S55 The GC-MS information of **8b**.