Electronic Supplementary Information

Synthesis of acetamides using CO_2, methanol, H_2 and amines

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Experimental

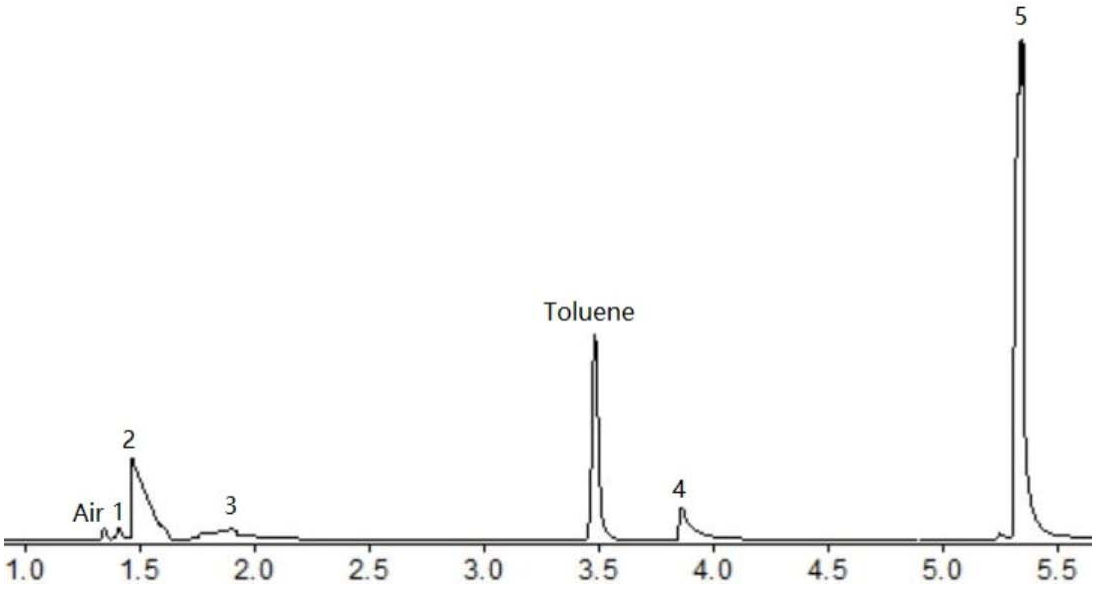
Chemicals

Dicarbonylacetylacetonato rhodium (I) ($Rh(acac)(CO)_2$, 99%), Tetracarbonyldi -μ-chlorodirhodium(I) ($Rh_2(CO)_4Cl_2$, Rh 50.1-52.9%), Rhodium(III) acetylacetonate ($Rh(acac)_3$, 98%), Rhodium, 5% on carbon(dry), Rhodium, 5% on alumina powder (reduced), Decacarbonyldirhenium ($Re_2(CO)_{10}$, 96%), Rhodium(III) chloride, anhydrous ($RhCl_3$, 99.9%), Rhodium(III) iodide (RhI_3, 99.9%), Tetramethylurea (TMU, 99%), 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, 98%), Lithium iodide (LiI, 99.95%), 1-methyl-2-pyrrolidinone (NMP, 99%), imidazole (99%), 4-methylimidazole(98%), Lithium tetrafluoroborate ($LiBF_4$, 98%), potassium iodide (KI, 99.9%), Dibromobis(triphenylphosphine)nickel(II) ($Ni(PPH_3)_2Br_2$, 99%), sodium iodide (NaI, 99.5%), sodium chloride (NaCl, 99.99%), potassium chloride(KCl, 99.99%), 1,2,3,4-Tetrahydroisoquinoline (97%), Morpholine (99%), N-Methylaniline (98%) were supplied by Alfa Aesar China Co., Ltd. Rhodium acetate dimer ($Rh_2(OAc)_4$, 99%), Ruthenium carbonyl ($Ru_3(CO)_{12}$, 98+%), Lithium bromide (LiBr, 99.5%), 1,3-Dimethyl-2-imidazolidinone (DMI, 98+%) were purchased from Adamas Reagent. Lithium chloride (LiCl, 98%), Dicobalt Octacarbonyl ($CO_2(CO)_8$, stabilized with 1-5% Hexane) were provided by TCI Shanghai Co., Ltd. Pyrrolidine (99%), Chloro(1,5-cyclooctadiene)rhodium(I) dimer ($Rh_2(1,5\text{-}cod)_2Cl_2$, 98%), Potassium fluoride(KF, 99%), Lithium Fluoride (LiF, 99%) was provided by Beijing InnoChem Science & Technology Co., Ltd. 1-Ethyl-2-pyrrolidinone (NEP, 99%), N-Methylcyclohexylamine (99%), 1-n-Octyl-2-pyrrolidone (NOP, 98%), Hexamethyleneimine (98%) were obtained from Aladdin Reagent. N,N-dimethylformamide (DMF, 99.5%), tetrahydrofuran (THF, 99.5%), and cyclohexane (99%) were purchased from J&K Scientific Ltd. Squalane (99%), dimethylammonium-dimethylcarbamate (DIMCARB), Purine(99%), Indole(99+%), Pyrrole(99%), Iodine (I_2, 99.5%) and dodecacarbonyl tetrairidium ($Ir_4(CO)_{12}$, 98+%) were bought from Acros Organics company. Methanol (99.5%) was obtained from Beijing Chemical Company. Toluene (99.8%) was provided by Xilong Chemical Co., Ltd. Methanol–^{13}C ($^{13}CH_3OH$, 99 atom% ^{13}C) and Methanol–^{18}O ($CH_3{}^{18}OH$, 95atom% ^{18}O) were obtained from Sigma-Aldrich Co. LLC. The CO_2 (99.99%), H_2 (99.99%) and CO (99.99%) were purchased from Beijing Analytical Instrument Company. All chemicals were used as received.

Catalytic reaction

All the experiments were carried out in a 16mL Teflon-lined stainless steel reactor equipped with a magnetic stirrer. The inner diameter of the reactor was 18 mm. In a typical experiment, certain amounts of the Rh catalyst, promoters, the amine substrates, methanol or tracer (if used) and 2 mL solvent were added into the reactor. At room temperature, CO_2 and H_2 were charged sequentially into the reactor to desired pressure after the reactor was purged with 1 MPa CO_2 for three times. The reactor was placed in an air bath of constant temperature, and the magnetic stirrer was set at 800 rpm. After the reaction was complete, the reactor was cooled in an ice-water

bath. Then the residual gas was released slowly and collected in a gasbag. Using toluene as the internal standard, the reaction solution was analyzed by GC (Agilent 7890B) equipped with a flame ionization detector and a HP-5 capillary column (0.32 mm in diameter, 30 m in length). The liquid products were identified using GC-MS (Agilent-7890B-5977A) as well as by comparing the retention times with the standards in the GC traces. The yields of the products were calculated from the GC data. The gaseous samples were detected by a GC (Agilent 4890D) equipped with a TCD detector and a packed column (Carbon molecular sieve TDX-01, 3 mm in diameter and 1 m in length) using Argon as the carry gas.



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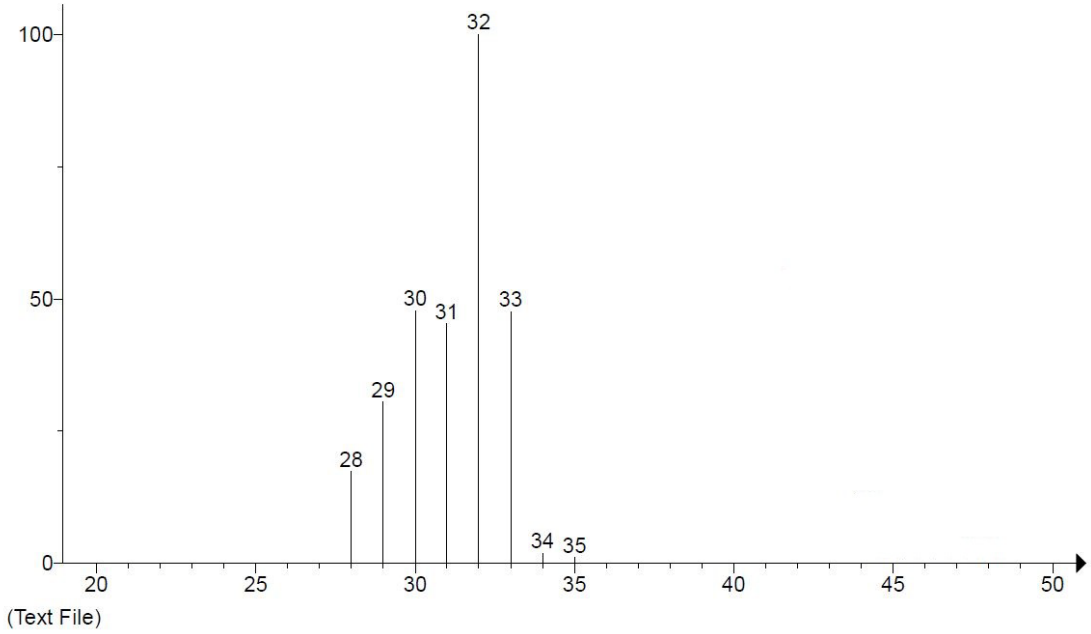

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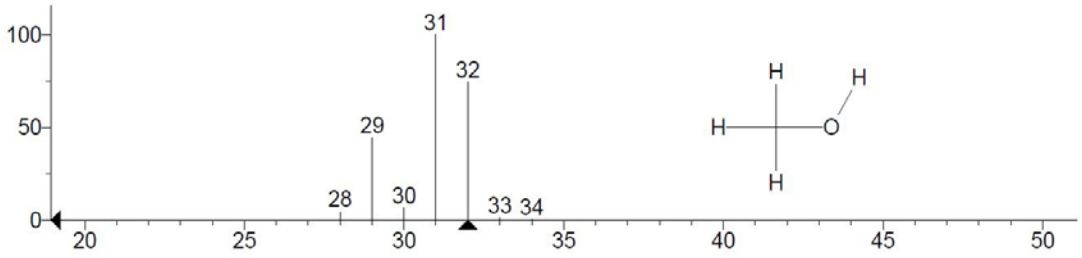

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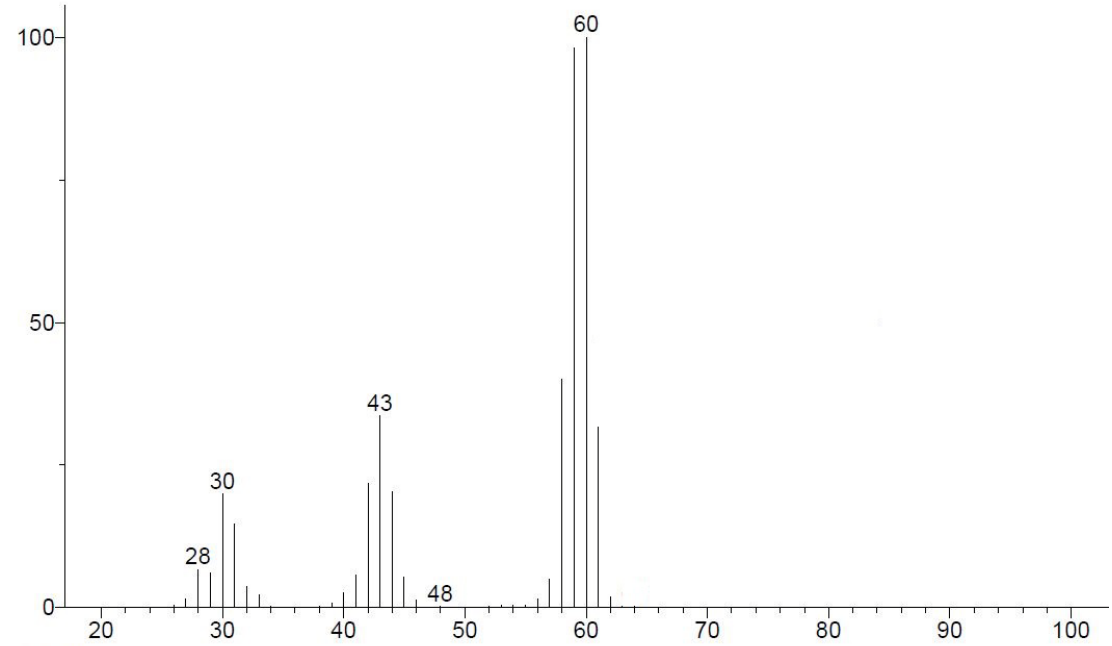

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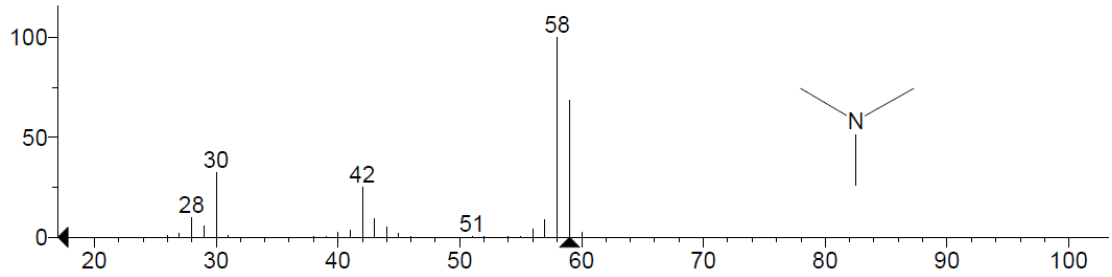

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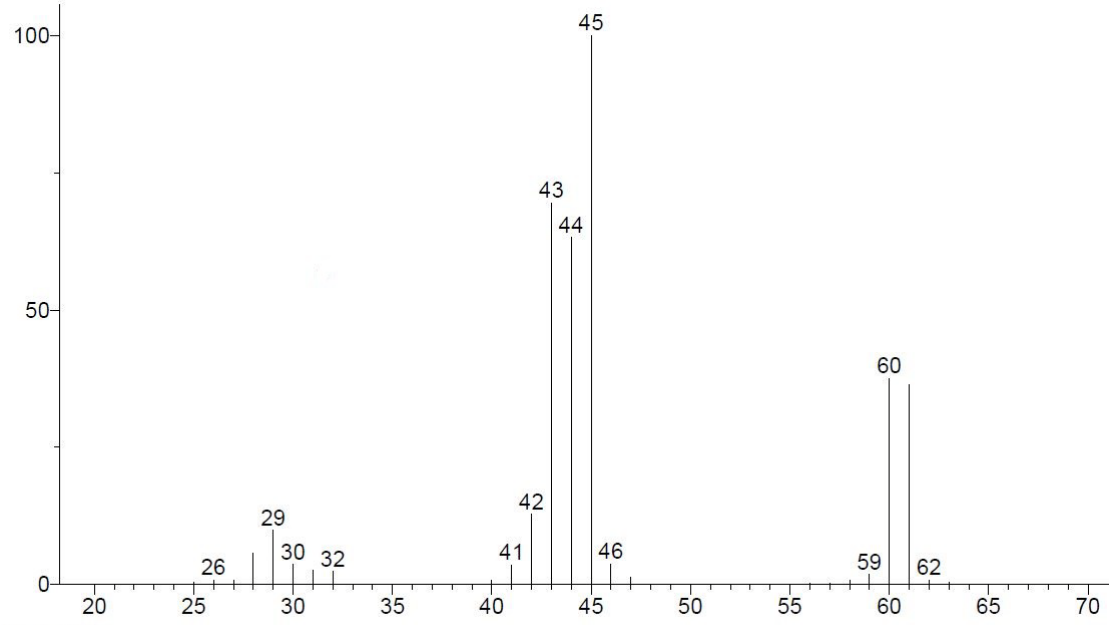

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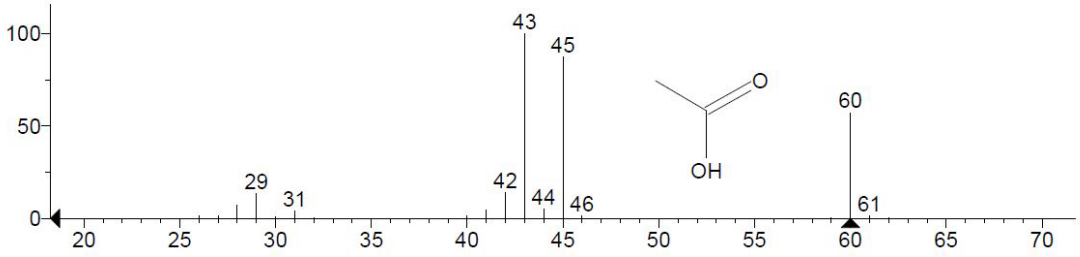

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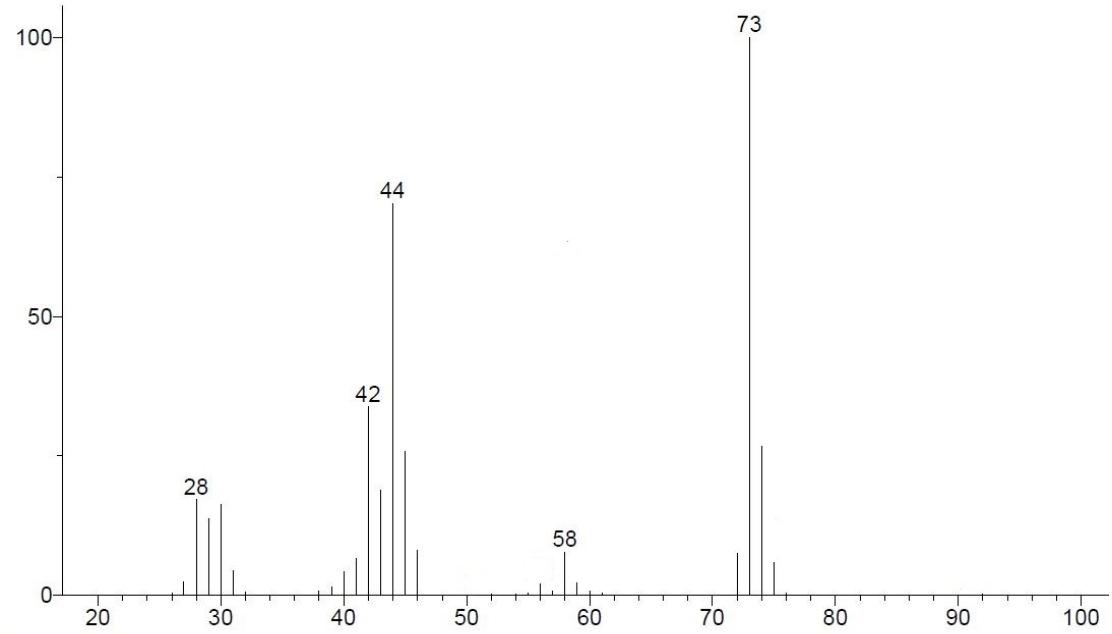

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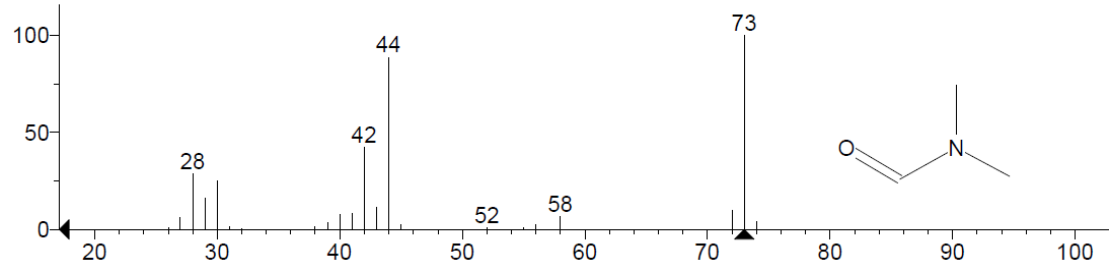

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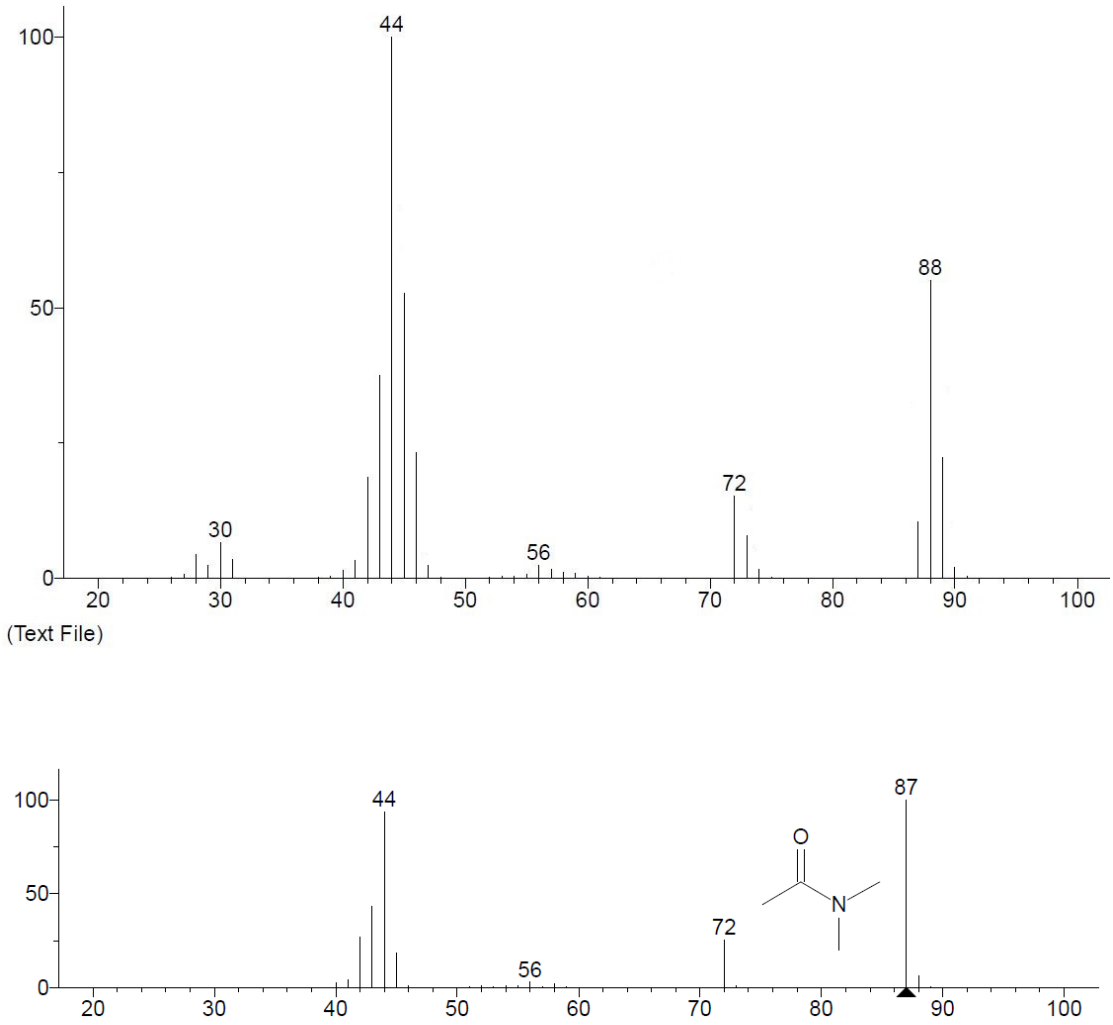
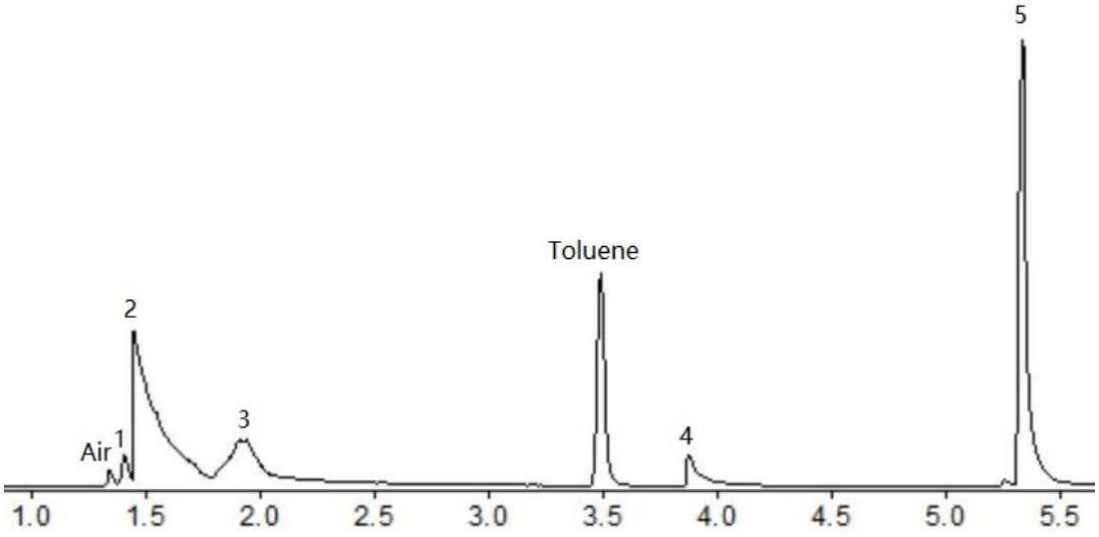


Fig. S1 The GC-MS spectra of reaction solution using $^{13}CH_3OH$ instead of CH_3OH. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes：

According to fragment analysis, the CH_3 group of methanol substrate was firstly transferred into acetic acid intermediate, and finally to acetamide product. In addition, obvious exchange of CH_3 group between methanol and the amine substrate was observed.



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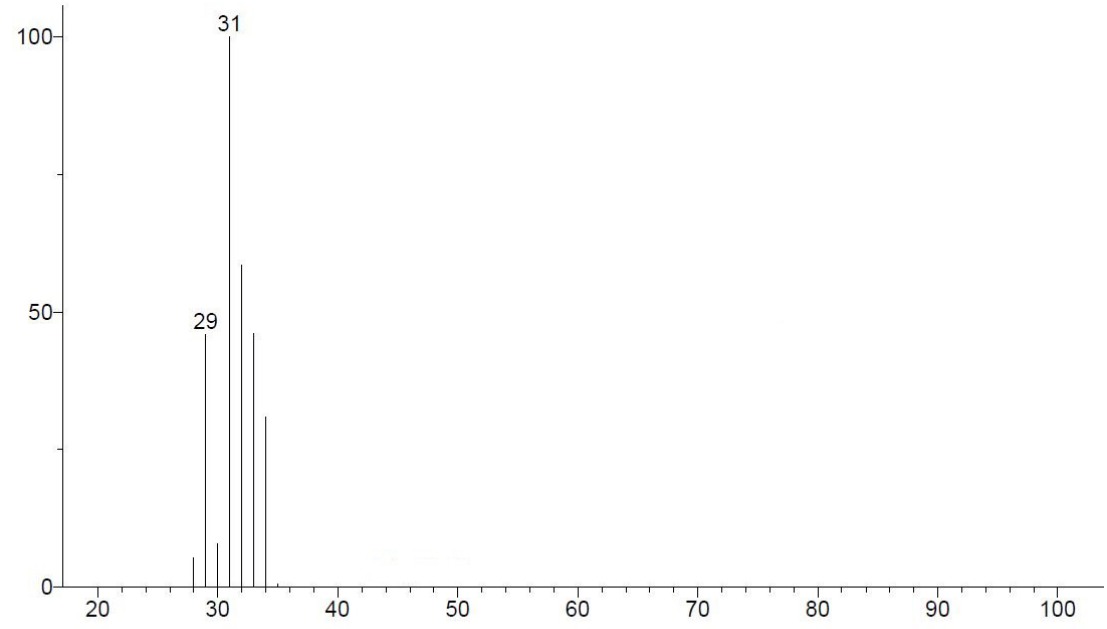

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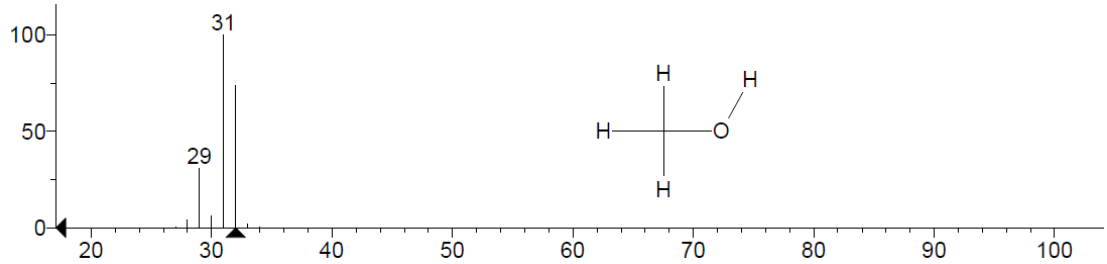

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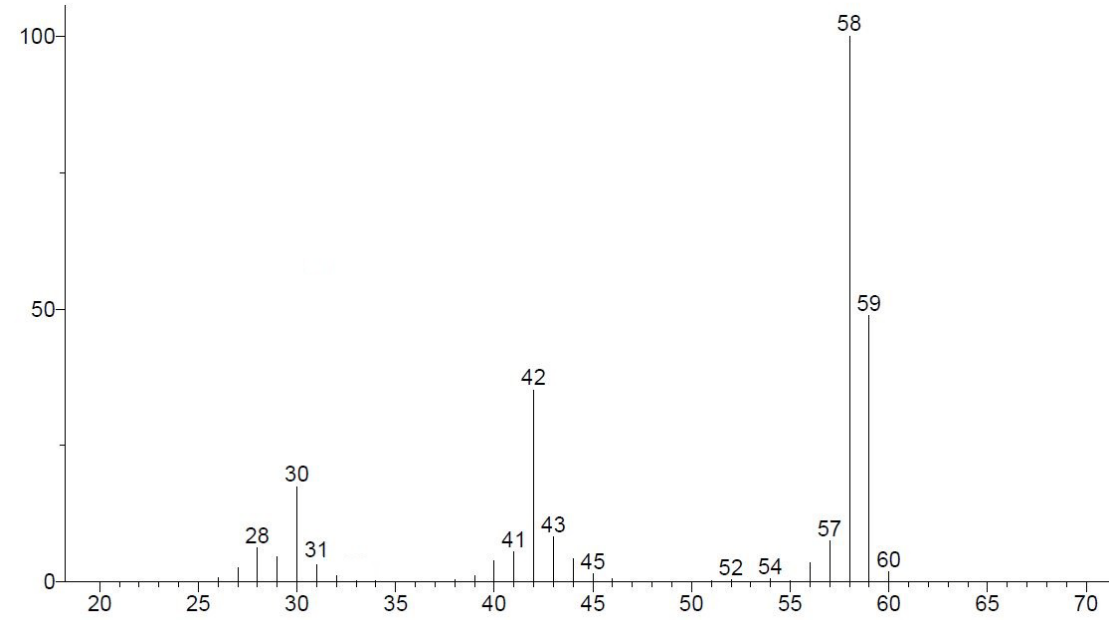

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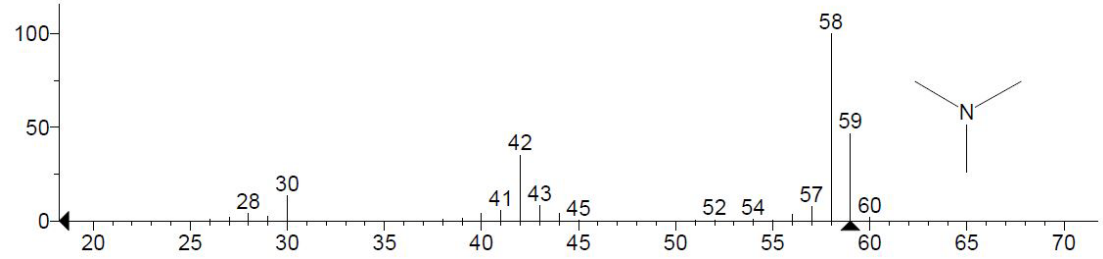

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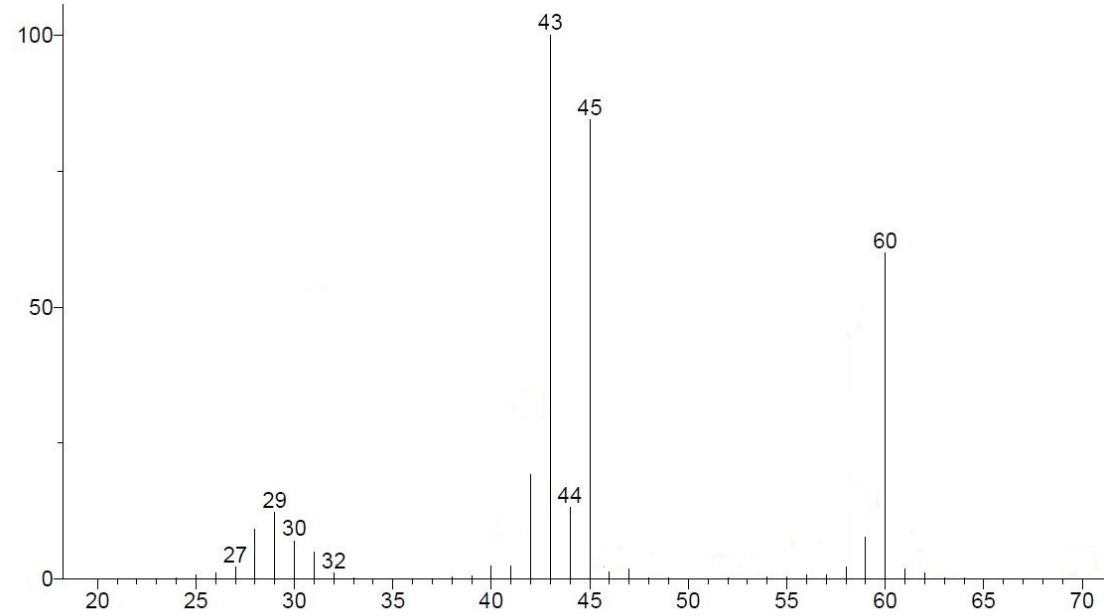

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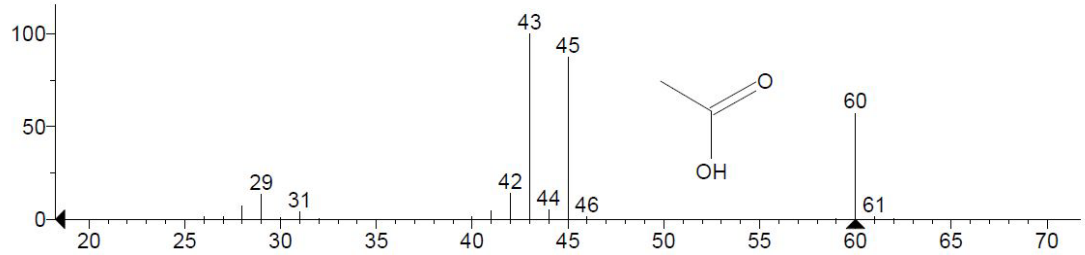

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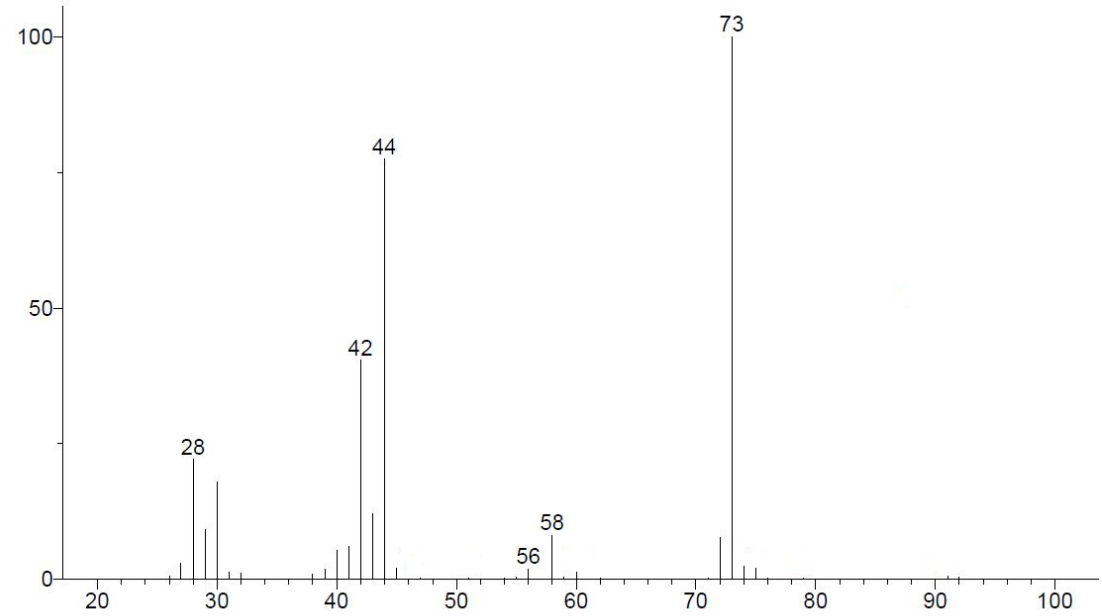

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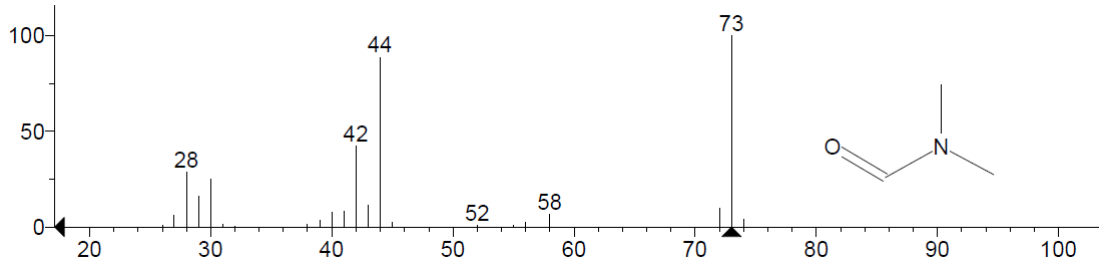

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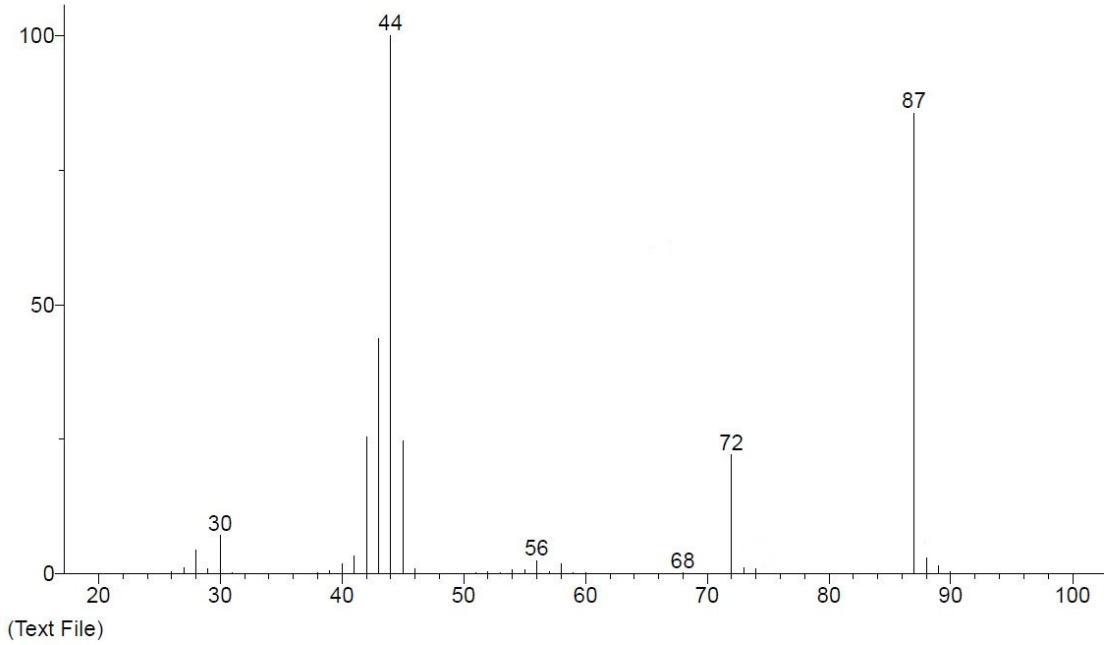

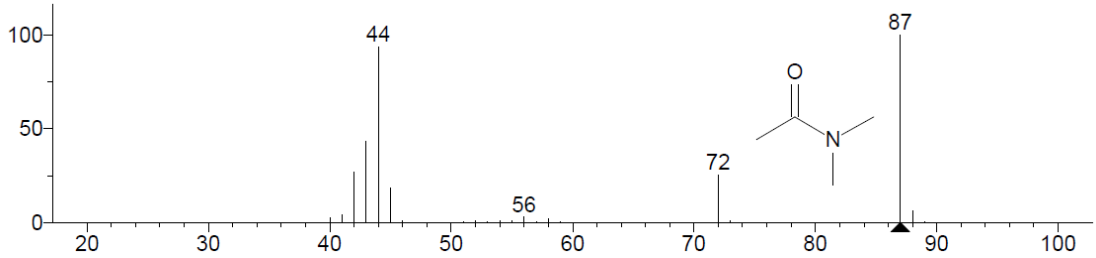

Fig. S2 The GC-MS spectra of reaction solution using $CH_3{}^{18}OH$ instead of CH_3OH. Other reaction conditions were the same as that of entry 1 in Table 1.

Notes：

According to fragment analysis, the OH group in the methanol substrate broke away during the reaction, and the O atom in the acetamide product was from CO_2.