Ionic polyamide boosting Ru efficiency in reductive amination of carbonyl compounds

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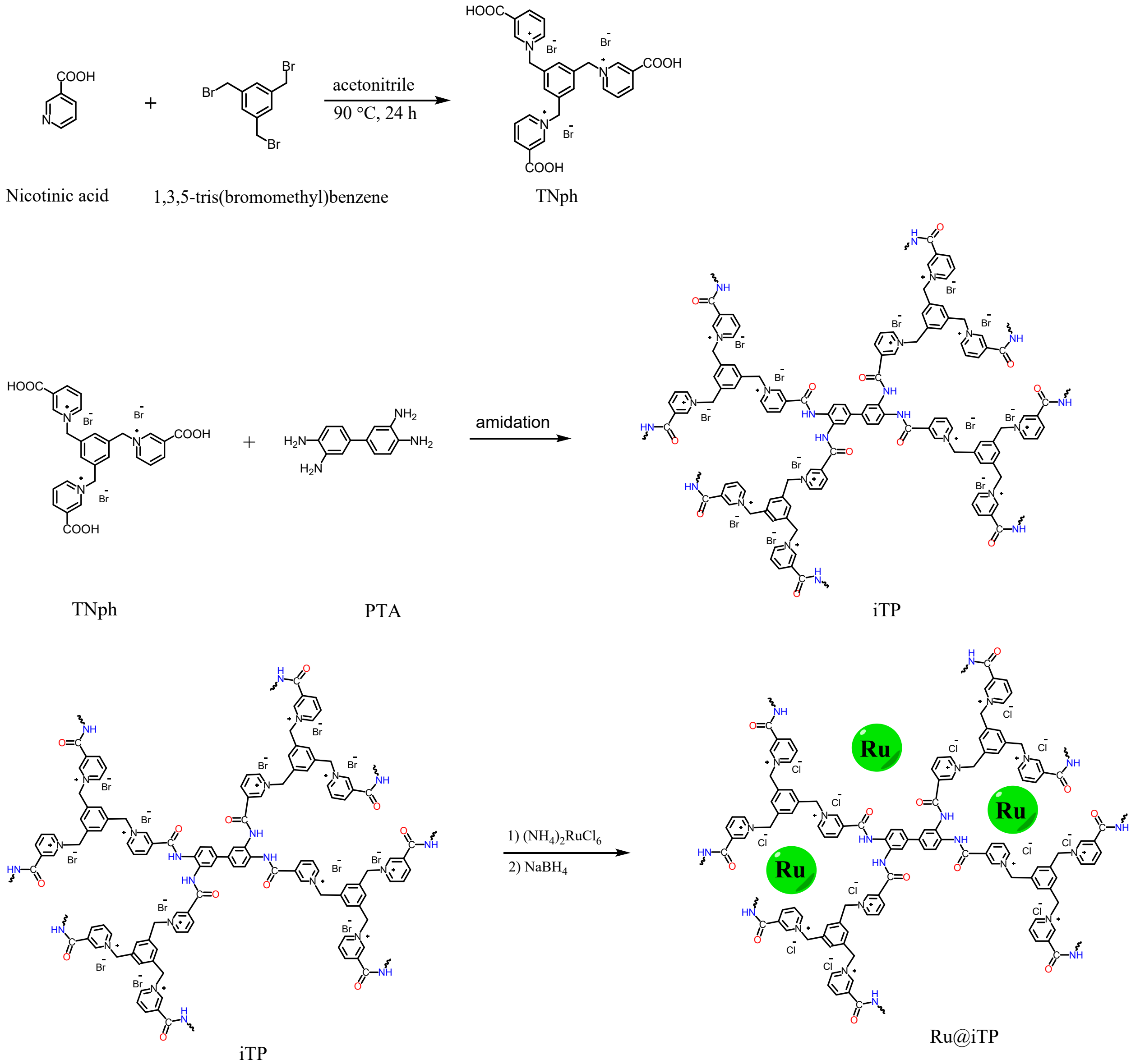
1. Experimental Section

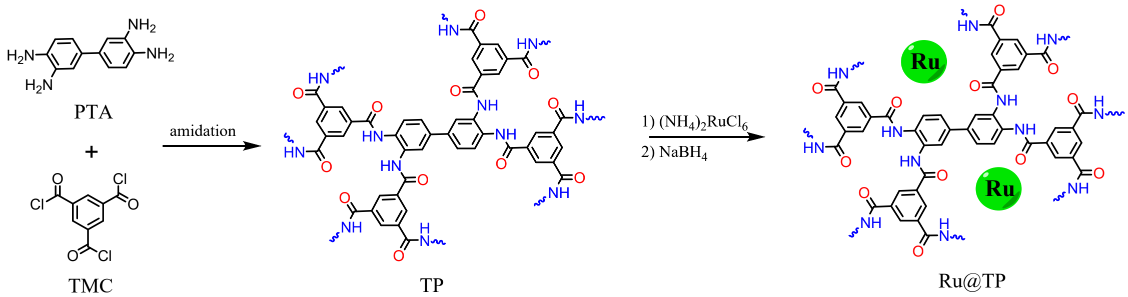
Materials

N,N-Dimethylformamide (99.5%), N-methyl pyrrolidone (99.5%), sodium borohydride (96%), methanol (99.5%), ethanol (99.8%), nicotinic acid (99%), dichloroethane (99.8 %), triethylamine (99.5 %), were purchased from Sinopharm Chemical Reagent Co. Ltd. Acetonitrile (99.5 %), thionyl chloride (99 %), 1,3,5-tris(bromomethyl)benzene (98 %), dodecane (99.5 %), 3,3'-Diaminobenzidine (99 %), NH_3/MeOH solution (7 M), cyclohexylamine (99.5 %), 1,3,5-benzenetricarbonyl chloride (98 %) cyclohexanone (99.8 %), were provided by Aladdin Chemical. octan-2-amine (98%), acetophenone (99%), 2,2',2''-(benzene-1,3,5-triyl)triacetic acid (98%), pentan-3-amine (98%), octan-2-one (98%), nonan-2-one (99%), cyclopentanamine (99%), cycloheptanone (99%), pentan-3-one (98%), 1-phenylpentan-1-one (98%), cyclohexanamine (99%), 4-phenylbutan-2-one (98%), 1-phenylethan-1-amine (98%), cyclopentanone (99%), 4-methylpentan-2-one (99%), benzaldehyde (99.5%), 2,3-dihydro-1H-inden-1-one (99%), 2,3-dihydro-1H-inden-1-amine (98%), octanal (99%), 4-methoxybenzaldehyde (99%), 3,4-dimethoxybenzaldehyde (98%), cyclohexanecarbaldehyde (97%), 4-bromobenzaldehyde (96%), 3-phenylpropanal (95%), 3-phenylpropan-1-amine (98%), nicotinaldehyde (98%), 4-(aminomethyl)-N,N-dimethylaniline (97%), cyclohexylmethanamine (97%), 4-bromobenzaldehyde (99%), octan-1-amine(99%), 4-(dimethylamino)benzaldehyde(99%), (4-fluorophenyl)methanamine (99%), (4-chlorophenyl)methanamine (98%), pyridin-3-ylmethanamine (99%), (4-methoxyphenyl)methanamine (98%), 3-methylbutanal (99%), 5-methylfuran-2-carbaldehyde (98%), (5-methylfuran-2-yl)methanamine (98%), 4-methylbenzaldehyde (99%), hexanal (99%), p-tolylmethanamine (98%), 1-(p-tolyl)ethan-1-amine (96%), hexan-1-amine (97%), 3-methylbutan-1-amine (99%), 1-(p-tolyl)ethan-1-one (95%), 3-chlorobenzaldehyde (98%), 3-methoxybenzaldehyde (98%) were provided by Aladdin Chemical, cycloheptanamine (99%), cyclohexanone (99.7%), 3,4-dihydronaphthalen-1(2H)-one (97%), 3,4-dihydronaphthalen-1(2H)-one (97%), 1,2,3,4-tetrahydronaphthalen-1-amine (98%), (3,4-dimethoxyphenyl)methanamine (97%), 4-methylbenzaldehyde (98%), undecan-6-one (98%), undecan-6-amine (98%) were purchased from Macklin Chemical.

2. Supplementary Schemes



Scheme S1. Schematically illustration for the preparation of Ru@iTP.



Scheme S2. Schematically illustration for the preparation of Ru@TP.

3. Supplementary Figures

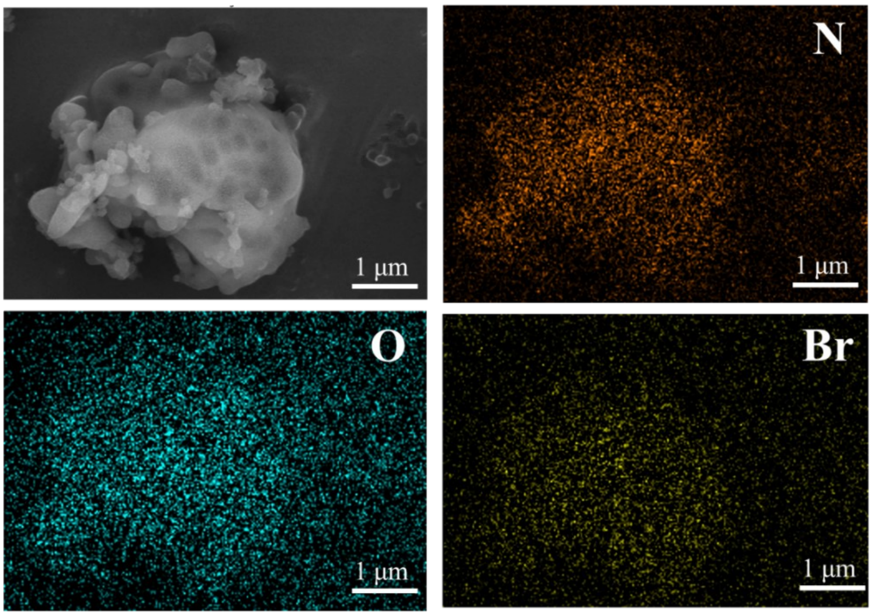


Fig. S1 SEM and elemental mapping images of N, O and Br for iTP.

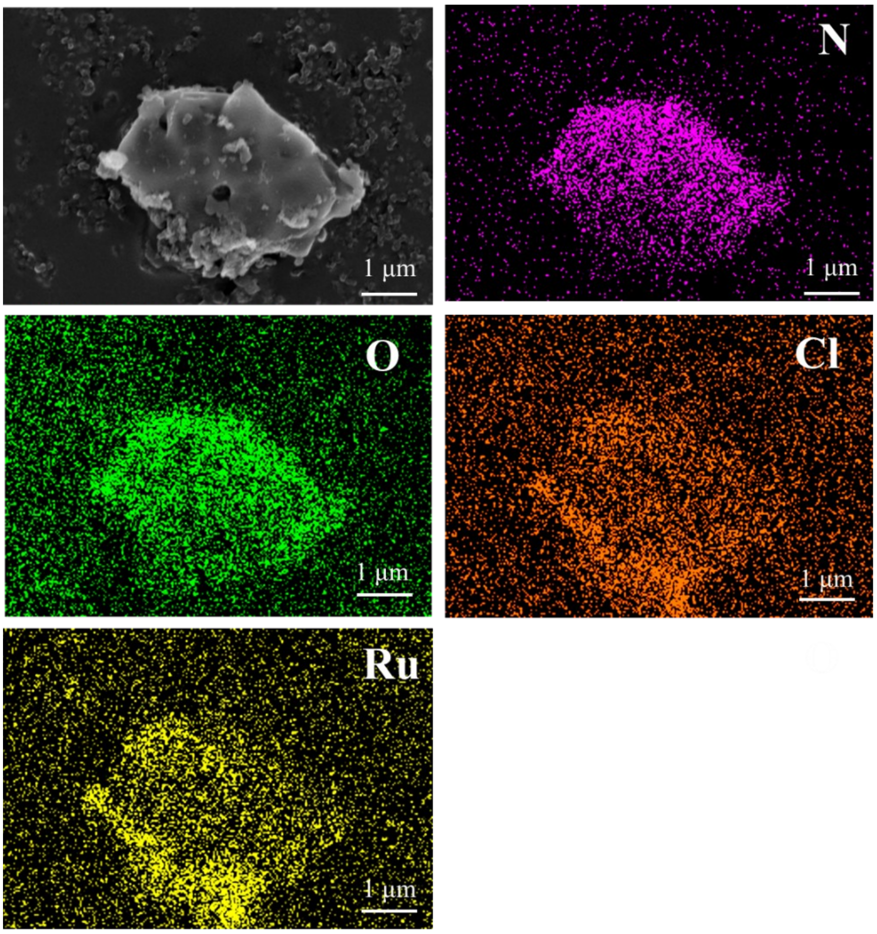


Fig.S2 SEM and elemental mapping images of N, O, Cl and Ru for 3%Ru@iTP.

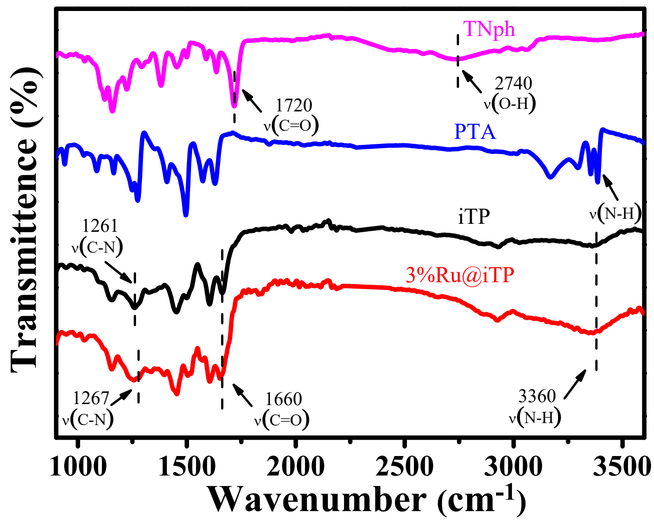


Fig. S3 FTIR spectra of PTA, TNph, iTP, and 3%Ru@iTP.

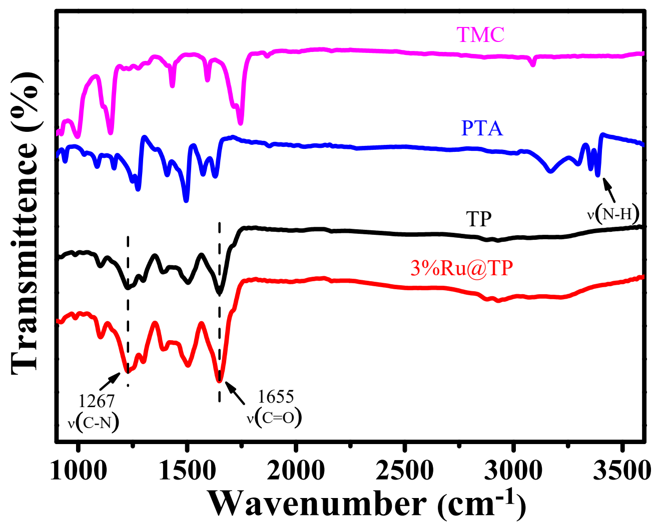


Fig. S4 FTIR spectra of PTA, TMC, TP, and 3%Ru@TP.

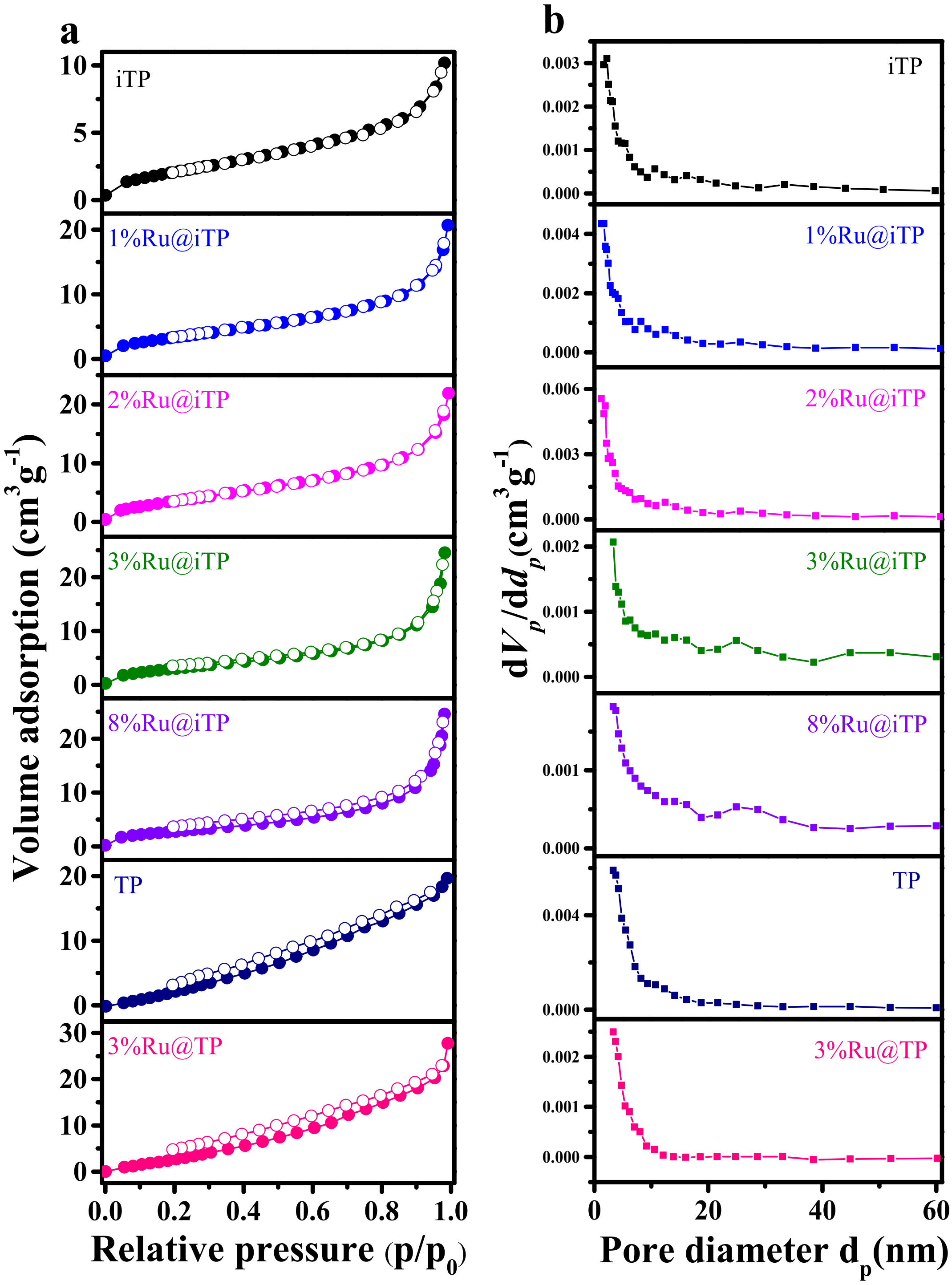


Fig. S5 (a) N_2 sorption isotherms and (b) pore size distribution curves of iTP, 1%Ru@iTP, 2%Ru@iTP, 3%Ru@iTP, 8%Ru@iTP, TP, and 3%Ru@TP.

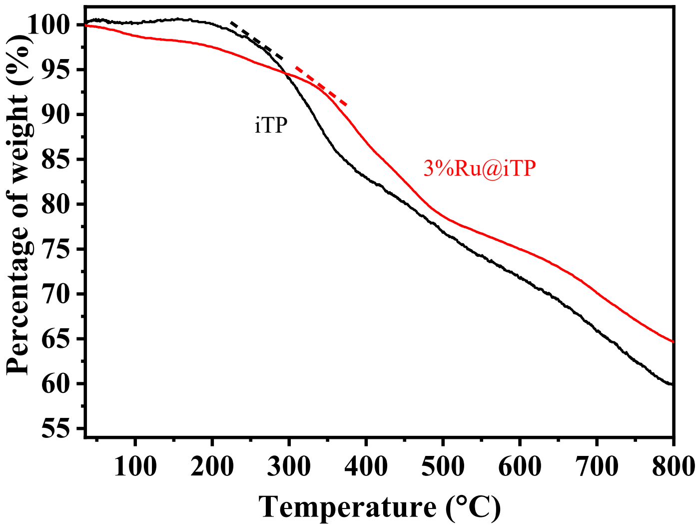


Fig. S6 TG curves of iTP and 3%Ru@iTP.

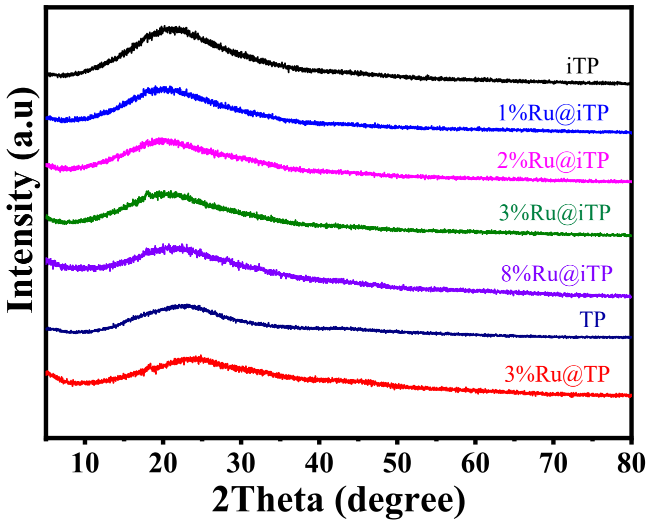


Fig. S7 XRD patterns of iTP, 1%Ru@iTP, 2%Ru@iTP, 3%Ru@iTP, 8%Ru@iTP, TP, and 3%Ru@TP.

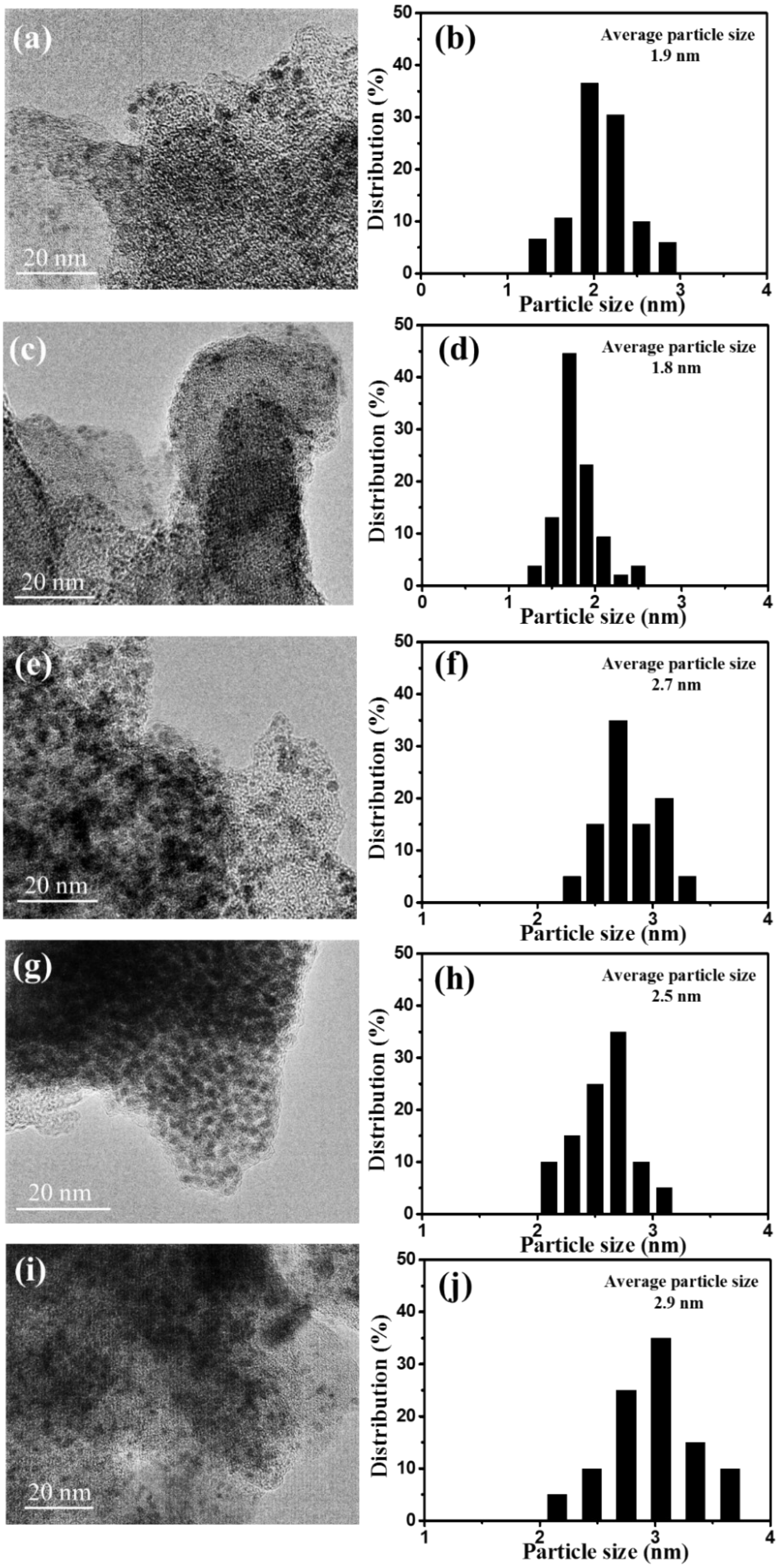


Fig. S8 (a) TEM image and (b) particle size distribution of 1%Ru@iTP, (c) TEM image and (d) particle size distribution of 2%Ru@iTP, (e) TEM image and (f) particle size distribution of 8%Ru@iTP, (g) TEM image and (h) particle size distribution of 3%Ru@TP, (i) TEM image and (j) particle size distribution of spent 3%Ru@TP.

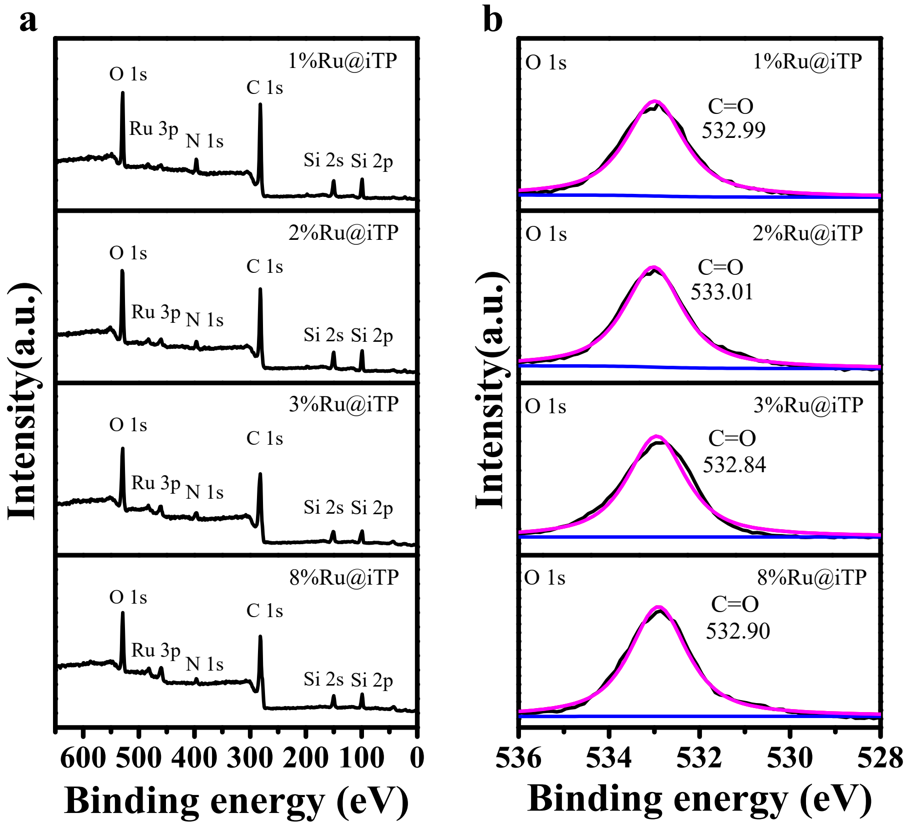


Fig. S9 (a) Survey scan and (b) O 1s XPS spectra of 1%Ru@iTP, 2%Ru@iTP, 3%Ru@iTP and 8%Ru@iTP.

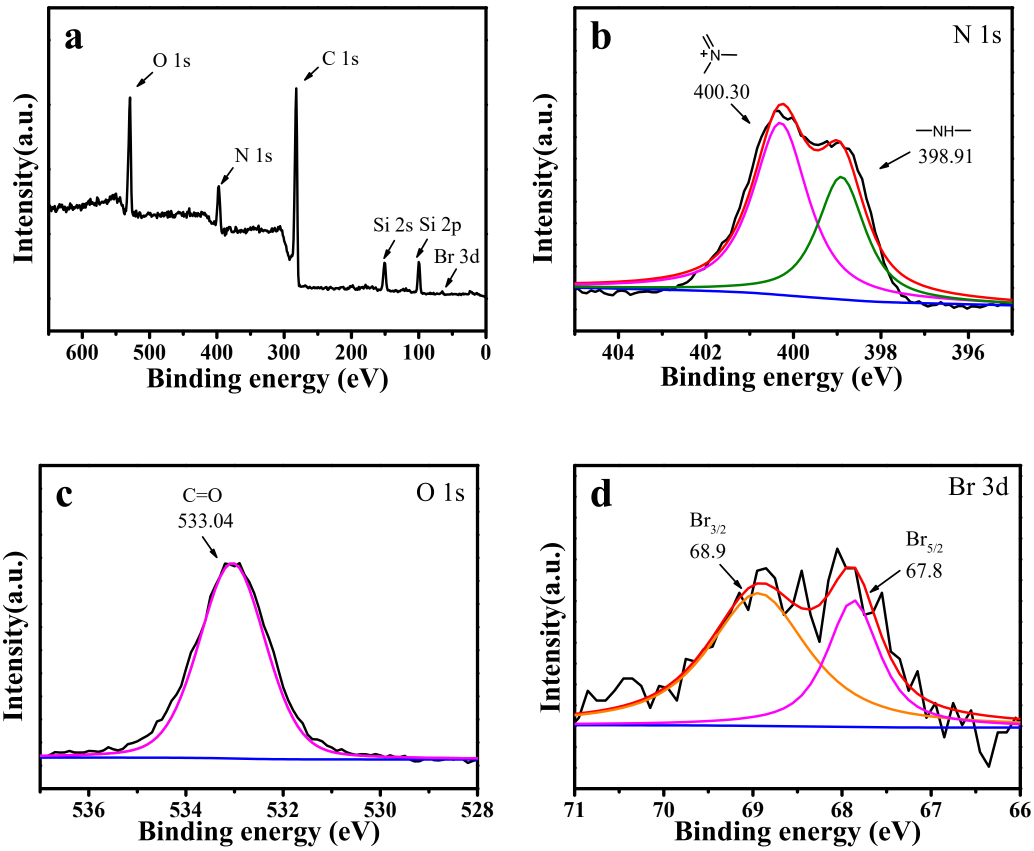


Fig. S10 (a) Survey scan, (b) N 1s, (c) O 1s, and (d) Br 3d XPS spectra of iTP.

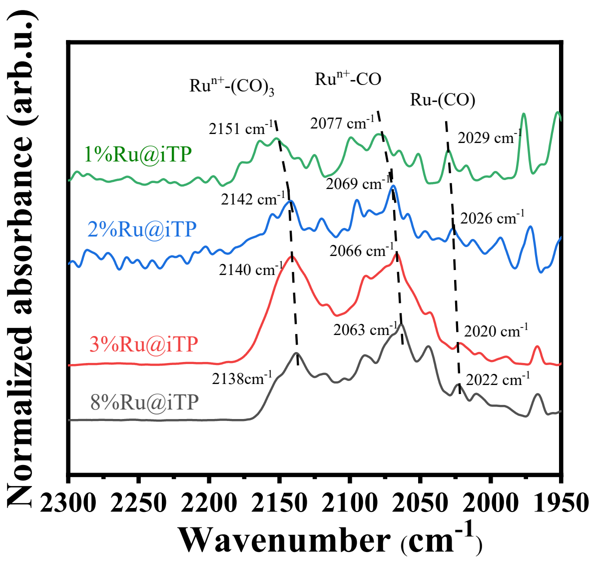


Fig. S11 CO-probed FT-IR spectra of 1%Ru@iTP, 2%Ru@iTP, 3%Ru@iTP and 8%Ru@iTP.

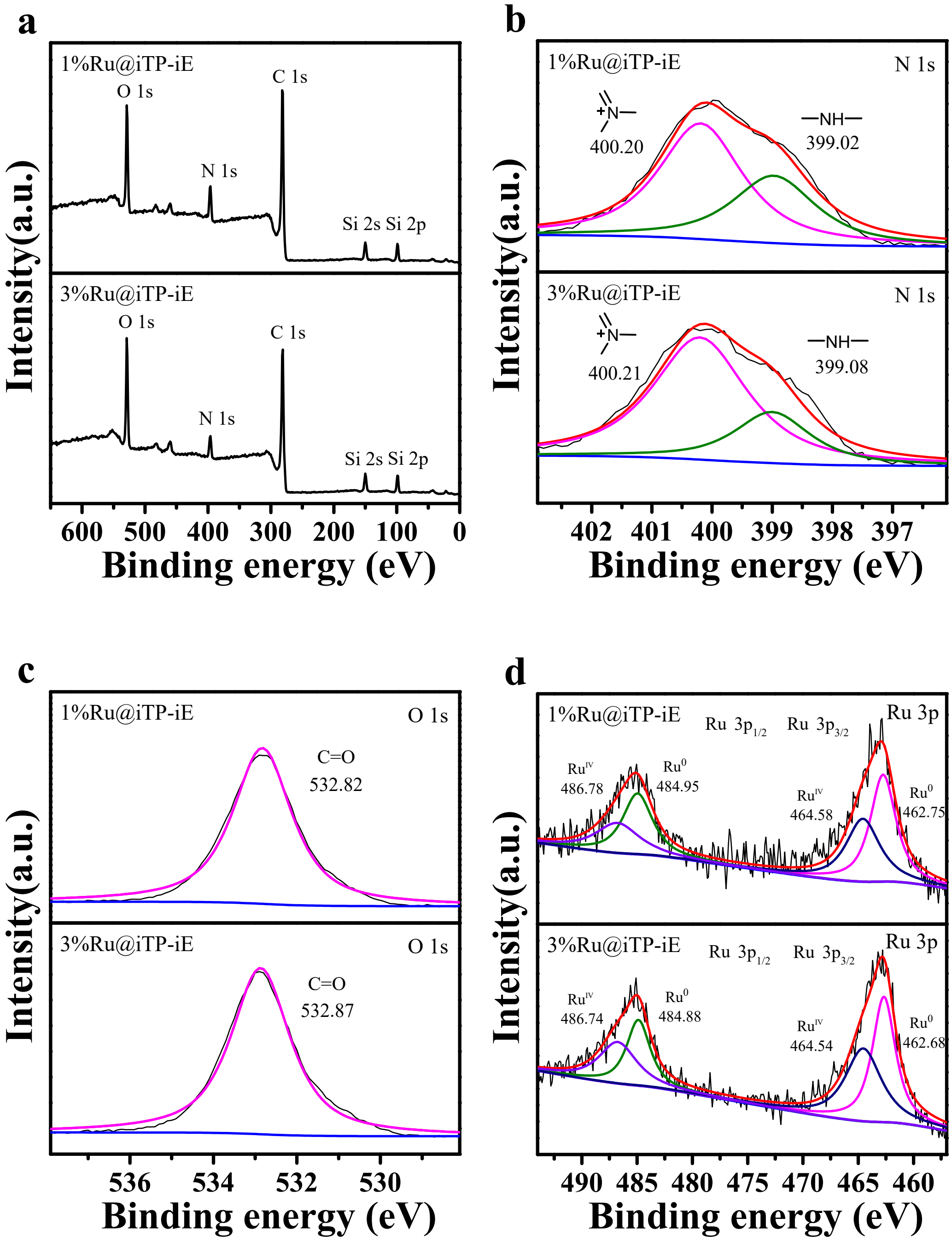


Fig. S12 (a) Survey scan, (b) N 1s, (c) O 1s and (d) Ru 3p XPS spectra of 1%Ru@iTP-iE and 3%Ru@iTP-iE.

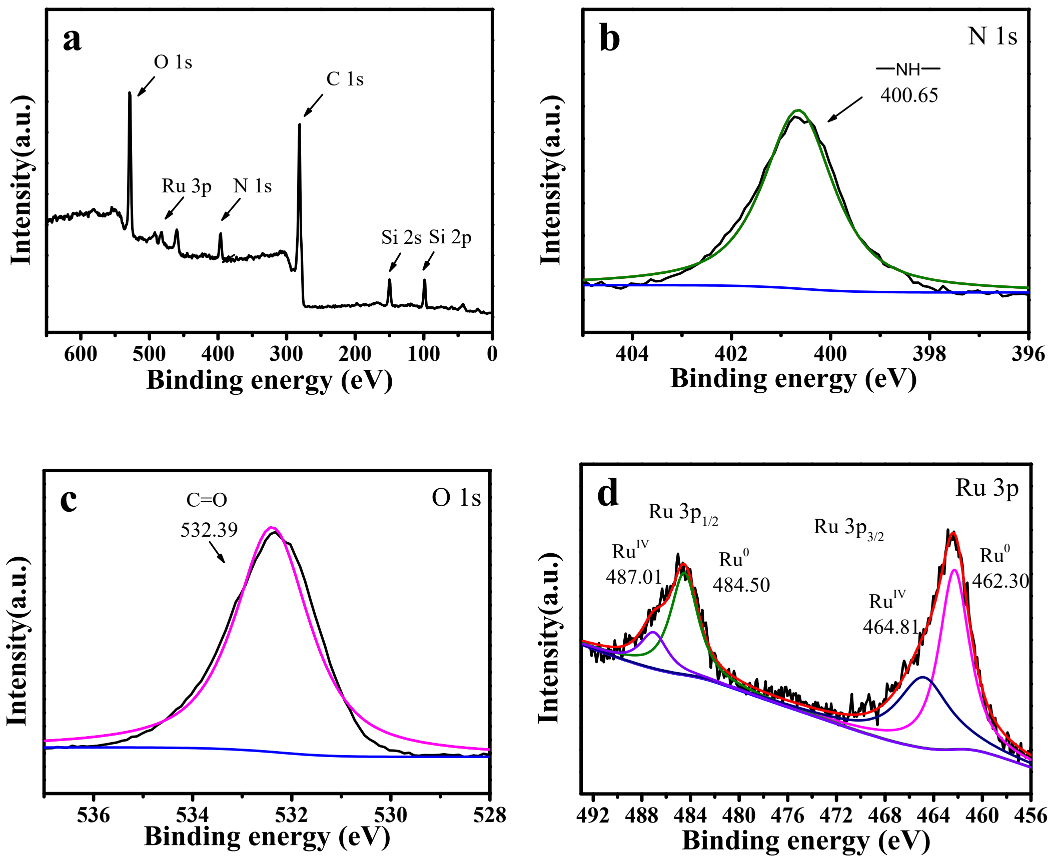


Fig. S13 (a) Survey scan; (b) N 1s, (c) O 1s, and (d) Ru 3p XPS spectra of 3%Ru@TP.

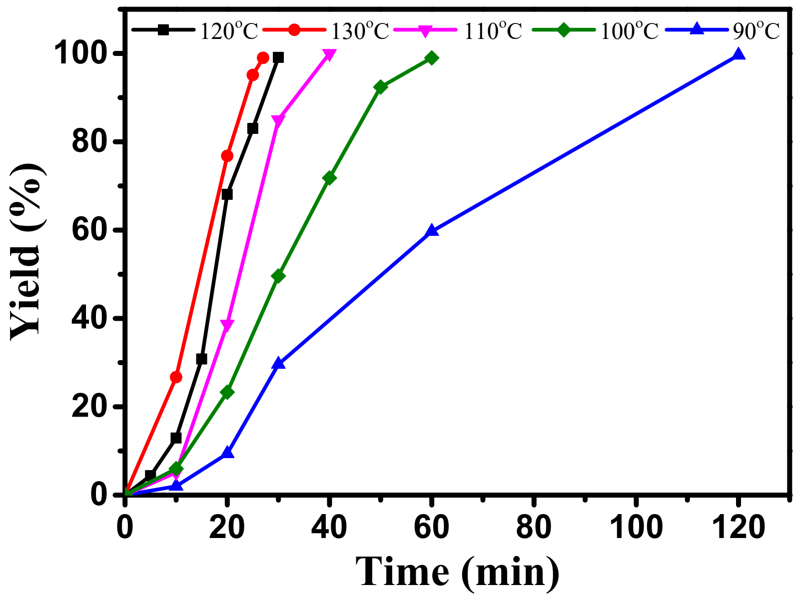
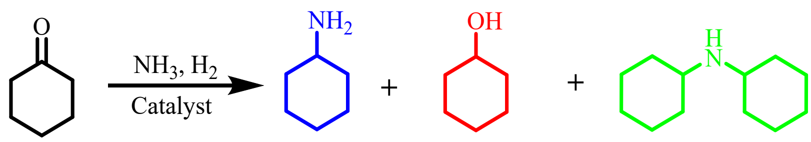


Fig. S14 Kinetic curves at different temperatures. Reaction conditions: 3%Ru@iTP (0.37 mol% Ru), cyclohexanone (0.5 mmol), MeOH (5 mL), H_2 (4 MPa), 120 °C, NH_3 (7 mmol).



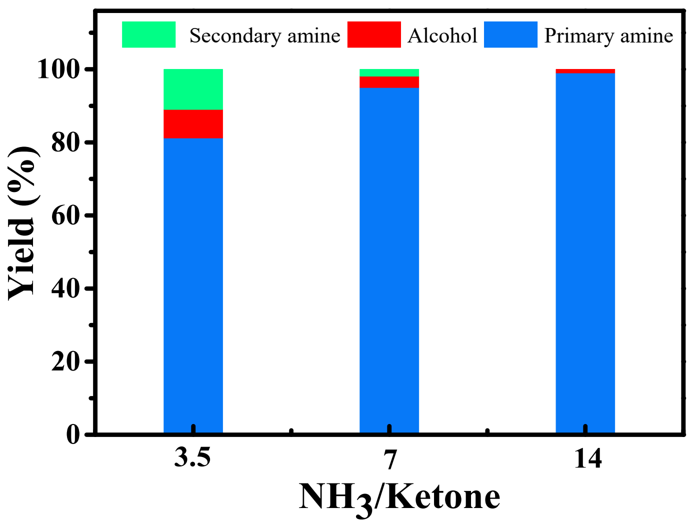


Fig. S15 Effect of ammonia. Reaction conditions: 3%Ru@iTP (0.37 mol%), cyclohexanone (0.5 mmol), MeOH (5 mL), H_2 (4 MPa), 120 °C, NH_3 (7 mmol).

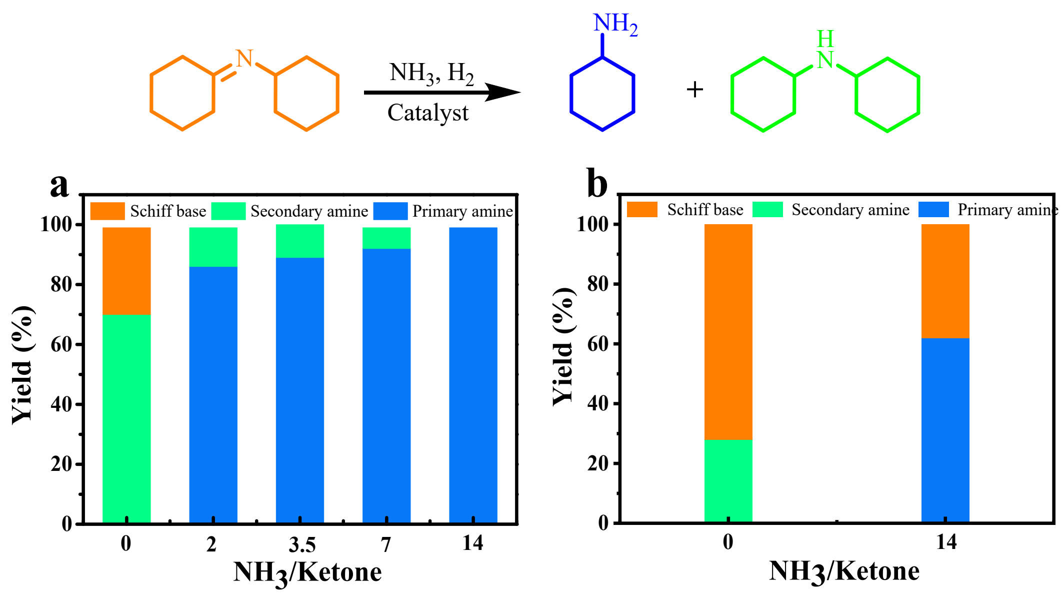


Fig. S16 Control experiments using Schiff base as the reactant over 3%Ru@iTP with different reaction time. Reaction conditions: Schiff base (0.5 mmol), H_2O (0.5 mmol), 3%Ru@iTP (0.37 mol% Ru), MeOH (5 mL), H_2 (4 MPa), 120 °C, (a) 30 min, (b) 5 min.

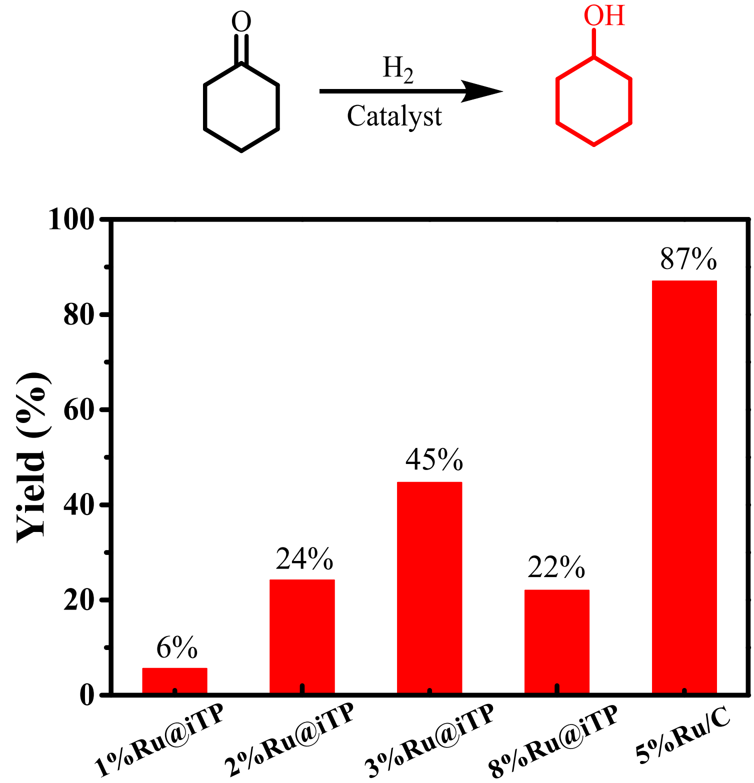


Fig. S17 Control experiments using cyclohexanone as the reactant over different catalysts. Reaction conditions: cyclohexanone (0.5 mmol), catalyst (0.37 mol% Ru), MeOH (5 mL), H_2 (4 MPa), 120 °C, 5 min.

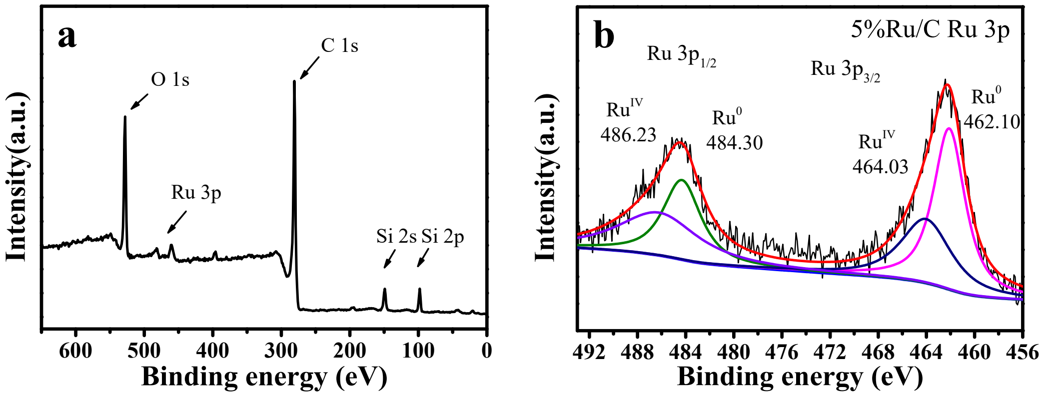


Fig. S18 (a) Survey scan; (b) Ru 3p XPS spectra of 5%Ru/C.

4. Supplementary Tables

Table S1 Textural properties

Entry	Catalyst	S_{BET} ^{I} (m^2/g)	V_p ^{II} (cm^3/g)	D_p ^{III} (nm)
1	iTP	7.7	0.016	8.1
2	1%Ru@iTP	12.8	0.031	9.7
3	2%Ru@iTP	14.1	0.032	9.2
4	3%Ru@iTP	11.7	0.037	9.8
5	8%Ru@iTP	10.6	0.038	9.9
6	TP	18.8	0.030	6.4
7	3%Ru@TP	12.3	0.042	7.3

^{I} BET surface area, ^{II}Total pore volume, ^{III}Average pore diameter.

Table S2 Element analyses

Entry	Sample	C (%)	N (%)	H (%)
1	iTP	69.31	12.61	6.245
2	1%Ru@iTP	68.89	12.53	6.244
3	2%Ru@iTP	66.81	12.08	6.024
4	3%Ru@iTP	64.66	11.72	6.150
5	8%Ru@iTP	60.66	11.10	5.923
6	TP	59.76	12.78	5.621
7	3%Ru@TP	57.22	12.11	5.371

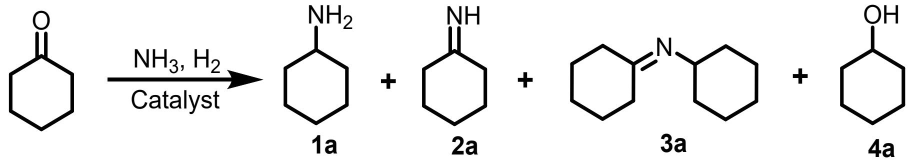


Table S3 Reductive amination of cyclohexanone over different catalysts [I]

Entry	Catalyst	Ru [II] (wt%)	Con. (%)	Yield (%)			
				1a	2a	3a	4a
1 [II]	1%Ru@iTP-iE	0.4	88	-	11	77	-
2 [II]	3%Ru@iTP-iE	0.6	94	-	5	89	-
3	3%Ru@TP-7th	2.16	99	49	2	48	1

[I] Reaction conditions: cyclohexanone (0.5 mmol), catalyst (0.37 mol% Ru), MeOH (5 mL), H_2 (4 MPa), NH_3 (7 mmol), 30 min. [II] After ion exchange with $(NH_4)_2RuCl_6$ thoroughly wash and dry then reduced by $NaBH_4$.

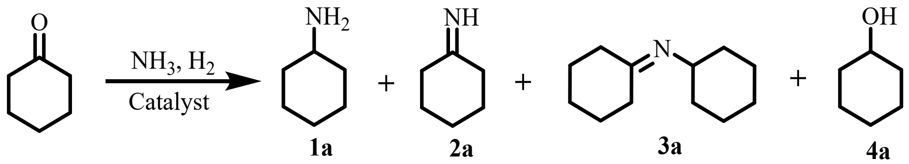


Table S4 Reductive amination of cyclohexanone over 3%Ru@iTP using different catalyst amount [I]

Entry	Catalyst amount (mg)	Conversion (%)	Yield (%)			
			1a	2a	3a	4a
1	1.7	93	6	18	69	0
2	3.4	94	31	7	55	1
3	5.1	95	51	6	37	1
4	6.7	＞99	99	-	-	1
5	8.5	＞99	99	-	-	1

[I] Reaction conditions: cyclohexanone (0.5 mmol), MeOH (5 mL), NH_3 (7 mmol), 30 min, 120 °C, H_2 (4 MPa).

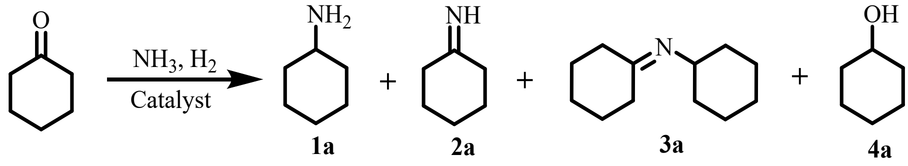


Table S5 Reductive amination of cyclohexanone over 3%Ru@iTP under different pressure [I]

Entry	H_2 (MPa)	Conversion (%)	Yield (%)			
			1a	2a	3a	4a
1	1	90	13	11	66	-
2	2	96	54	5	36	1
3	3	＞99	83	2	14	1
4	4	＞99	99	-	-	1
5	5	＞99	98	-	-	2

[I] Reaction conditions: cyclohexanone (0.5 mmol), catalyst (0.37 mol% Ru), MeOH (5 mL), NH_3 (7 mmol), 120 °C, 30 min.

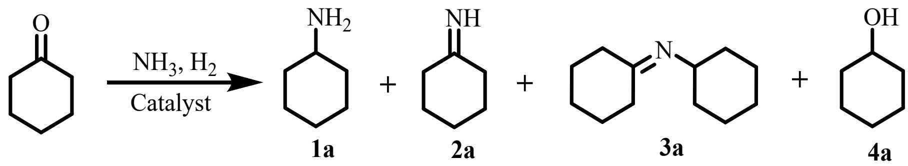


Table S6 Reductive amination of cyclohexanone over 3%Ru@iTP under different temperature [I]

Entry	T (°C)	Conversion (%)	Yield (%)			
			1a	2a	3a	4a
1	90	98	30	5	62	1
2	100	＞99	51	3	45	1
3	110	＞99	85	-	14	1
4	120	＞99	99	-	-	1
5	130	＞99	99	-	-	1

[I] Reaction conditions: cyclohexanone (0.5 mmol), catalyst (0.37 mol% Ru), MeOH (5 mL), H_2 (4 MPa), NH_3 (7 mmol), 30 min.

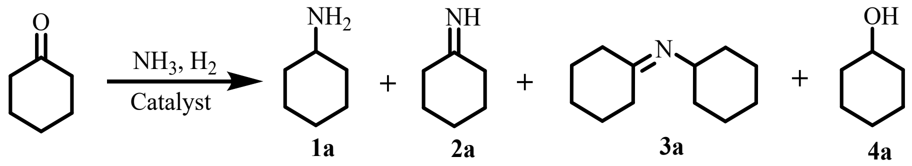


Table S7 Reductive amination of cyclohexanone over 3%Ru@iTP using different reaction time [I]

Entry	Time (min)	Conversion (%)	Yield (%)			
			1a	2a	3a	4a
1	5	86	4	18	63	1
2	10	93	13	10	69	1
3	15	96	31	7	57	1
4	20	97	72	3	21	1
5	25	98	83	3	11	1
6	30	＞99	99	-	-	1

[I] Reaction conditions: cyclohexanone (0.5 mmol), catalyst (0.37 mol% Ru), MeOH (5 mL), H_2 (4 MPa), NH_3 (7 mmol), 120 °C.

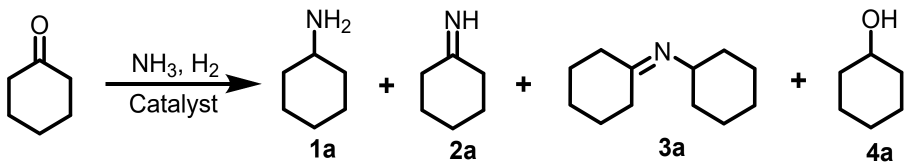


Table S8 Reductive amination of cyclohexanone over 2%Ru@iTP under different catalyst amount [I]

Entry	Catalyst amount (mg)	Con. (%)	Yield (%)			
			1a	2a	3a	4a
1	10	97	36	6	53	1
2	20	＞99	88	-	11	1

[I] Reaction conditions: cyclohexanone (0.5 mmol), 2%Ru@iTP (0.37 mol% Ru), MeOH (5 mL), H_2 (4 MPa), NH_3 (7 mmol), 120 °C, 30 min.

Table S9 Reported catalytic systems for RA of cyclohexanone with NH_3 and H_2

Entry	Catalyst	Cat. (mol%)	Reaction conditions	Yield% [I] /Yeld% [II]	TOF(h^{-1})[III]	Ref.
1	Ru/Nb_2O_5	0.4	NH_3 (0.1 MPa), H_2 (4 MPa),MeOH (5 ml), 90 °C, 1 h	96/94 (4)	240	1
2	Ru-NP	0.4	NH_3 (8 mmol), H_2 (2 MPa),MeOH (5 ml), 90 °C, 1 h	97/95 (5)	242	2
3	$RuCl_2(PPh_3)_3$	3	NH_3 (0.5 MPa), H_2 (4 MPa), t-amyl alcohol (1.5 ml), 130 °C, 30 h	86/-	1.1	3
4	Ru/TiP-100	0.2	NH_3 (0.6 MPa), H_2 (1.4 MPa), MeOH (5 ml), 30 °C, 6 h	97/92 (5)	81	4
5	Ru/ZrO_2-150	2.5	NH_3 (40 mmol), H_2 (1.2 MPa), EtOH (3 ml), 95 °C, 8 h	99/84 (5)	5	5
6	Ru_1/NC-900-800NH_3	0.25	NH_3 (0.5 MPa), H_2 (2 MPa), MeOH (3 g), 100 °C, 10 h	96/96 (5)	40	6
7	Ru/BN-e	0.6	NH_3 (4 mmol), H_2 (1 MPa), MeOH (7 ml), 90 °C, 5 h	99/95 (5)	33	7
8	Co-DABCO-TPA@C-800	3.5	NH_3 (0.5 MPa), H_2 (4 MPa), THF (3 ml), 120 °C, 15 h	92/90 (7)	2	8
9	3%Ru@iTP	0.37	NH_3 (7 mmol), H_2 (4 MPa), MeOH (5 ml), 120 °C, 0.5 h	99/98 (7)	535	This work
			NH_3 (7 mmol), H_2 (5 MPa), MeOH (5 ml), 180 °C, 0.25 h	96/-	1037	

[I] Yield of the fresh catalyst. [II] Yield of the spent catalyst after several recycling runs, number of cycles was shown in parentheses. [III] Turnover frequency (TOF) = (mol Product obtained)/(mol Metal×h).

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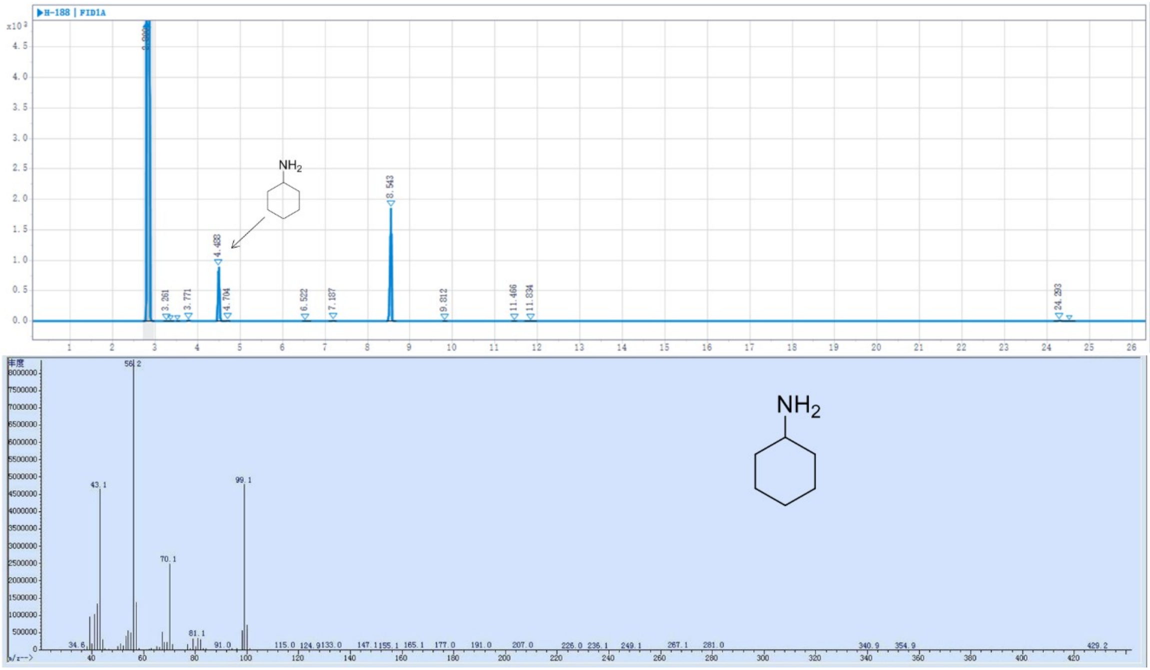
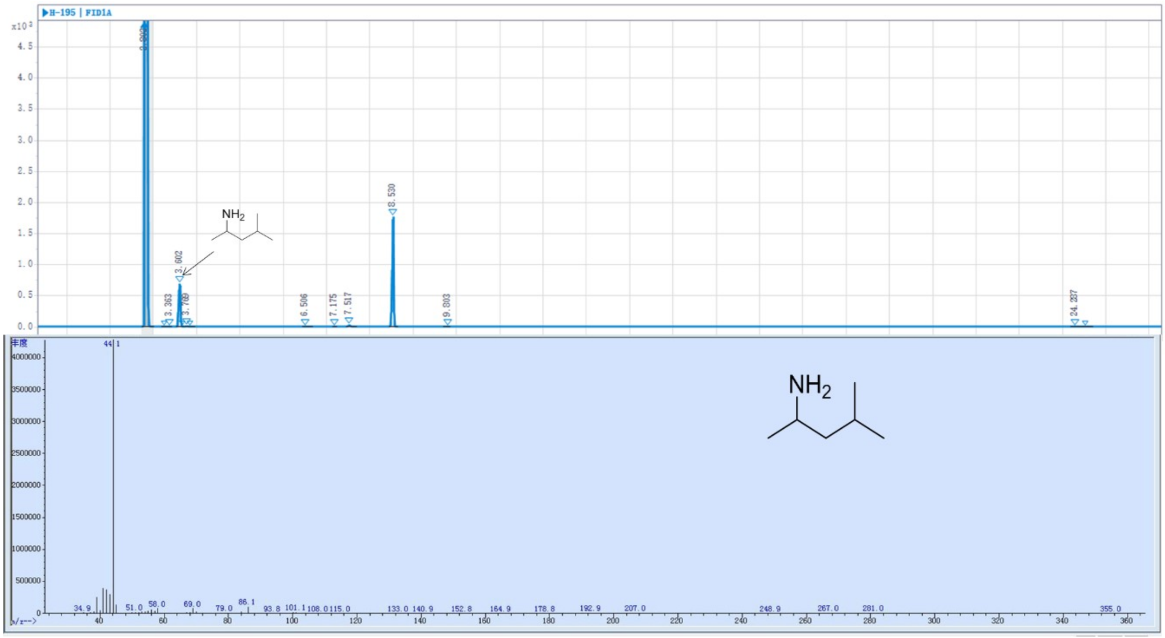
GC and MS spectra of products



GC and MS spectra of cyclohexanamine



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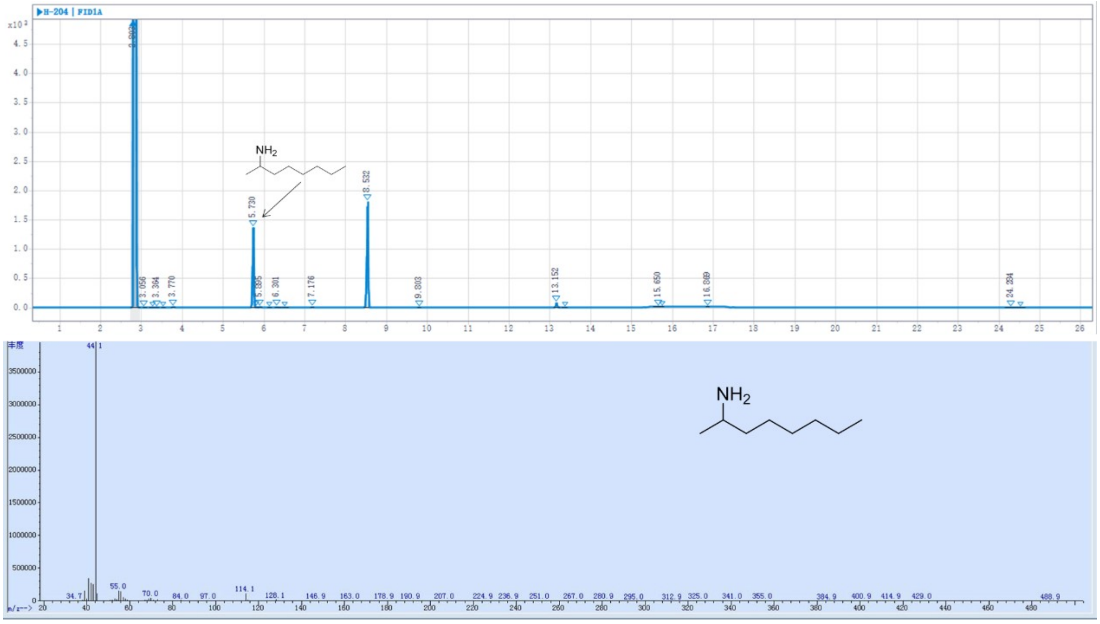

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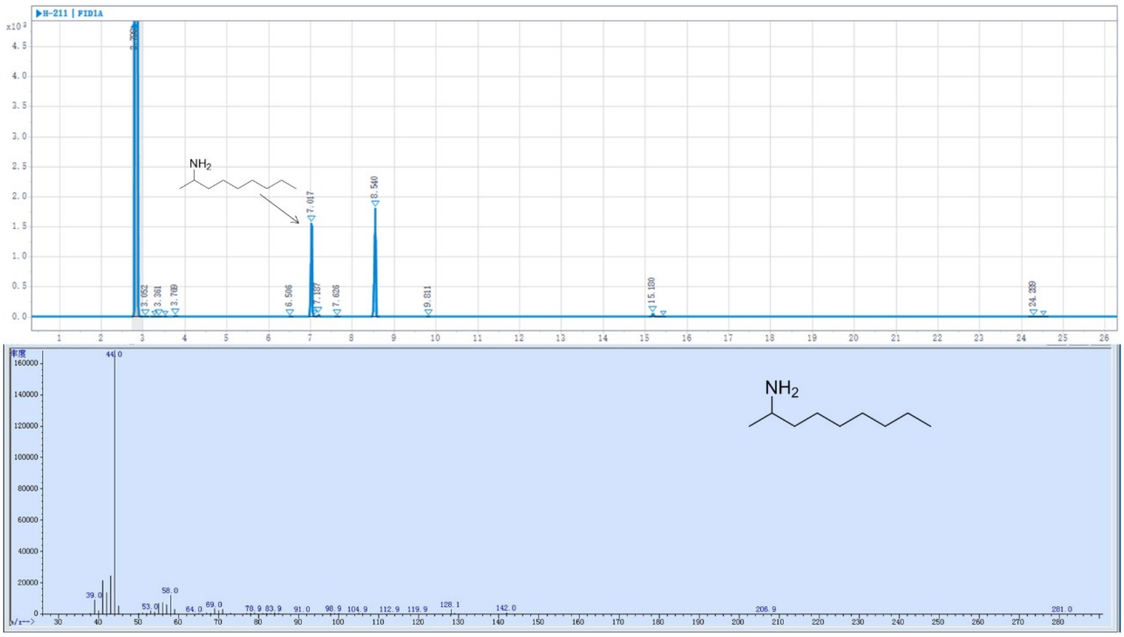
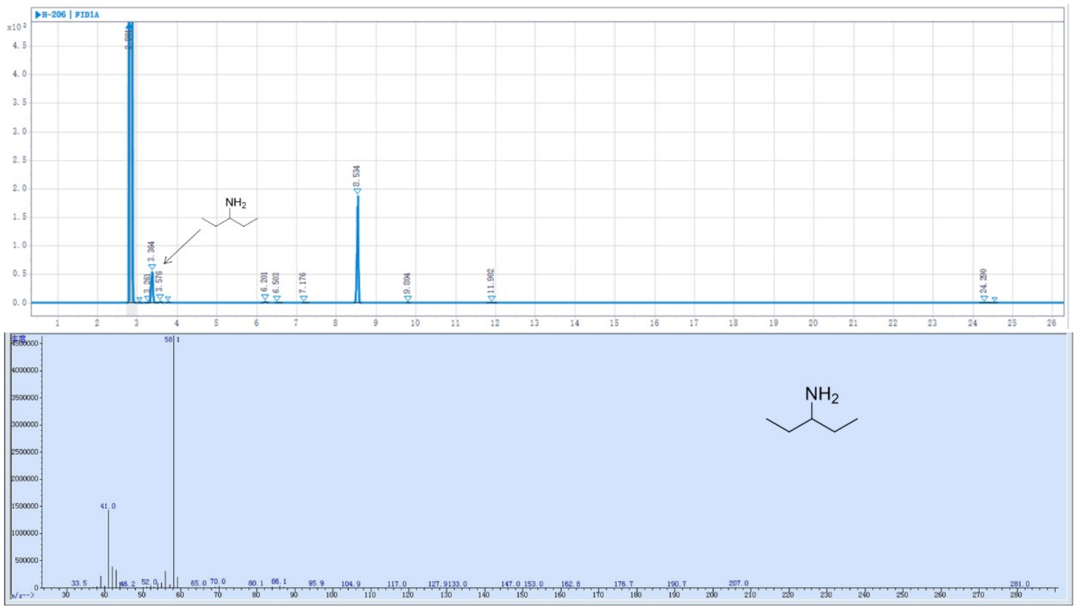


GC and MS spectra of nonan-2-amine



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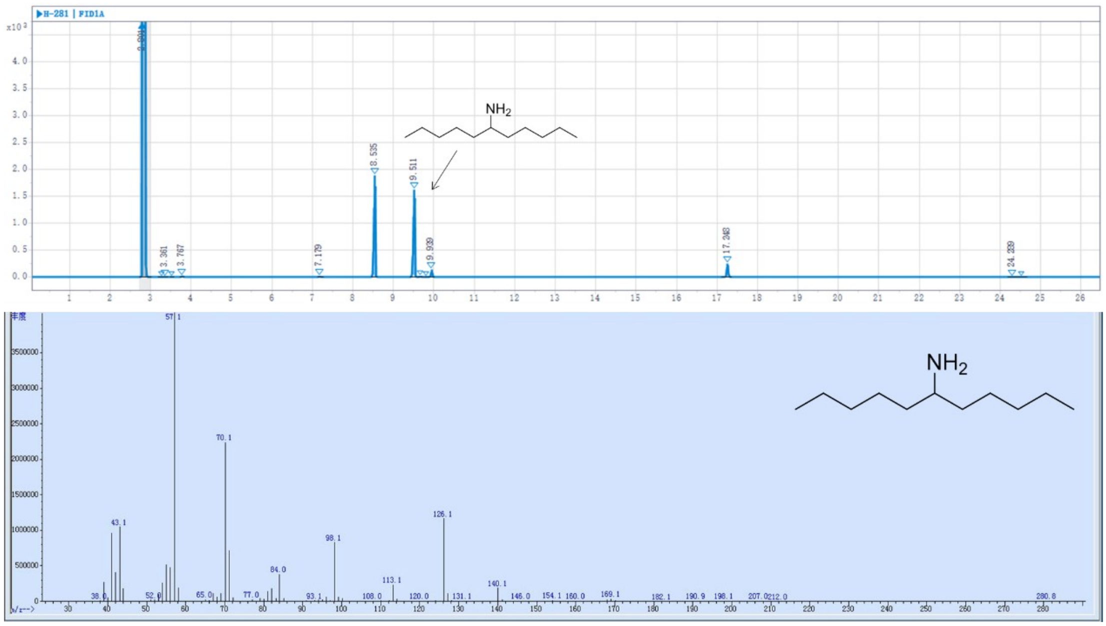
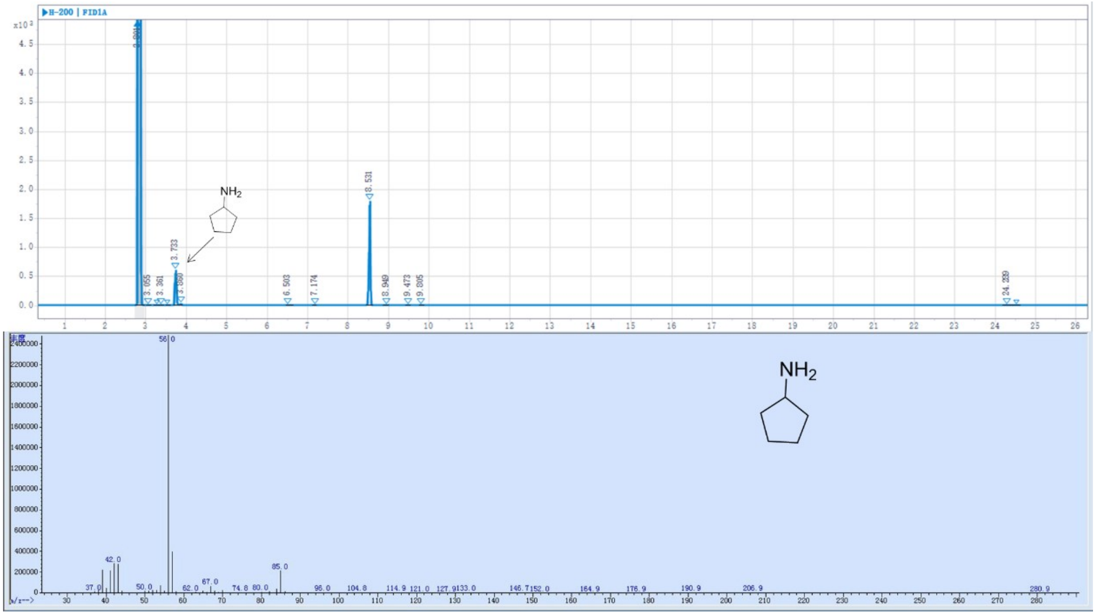
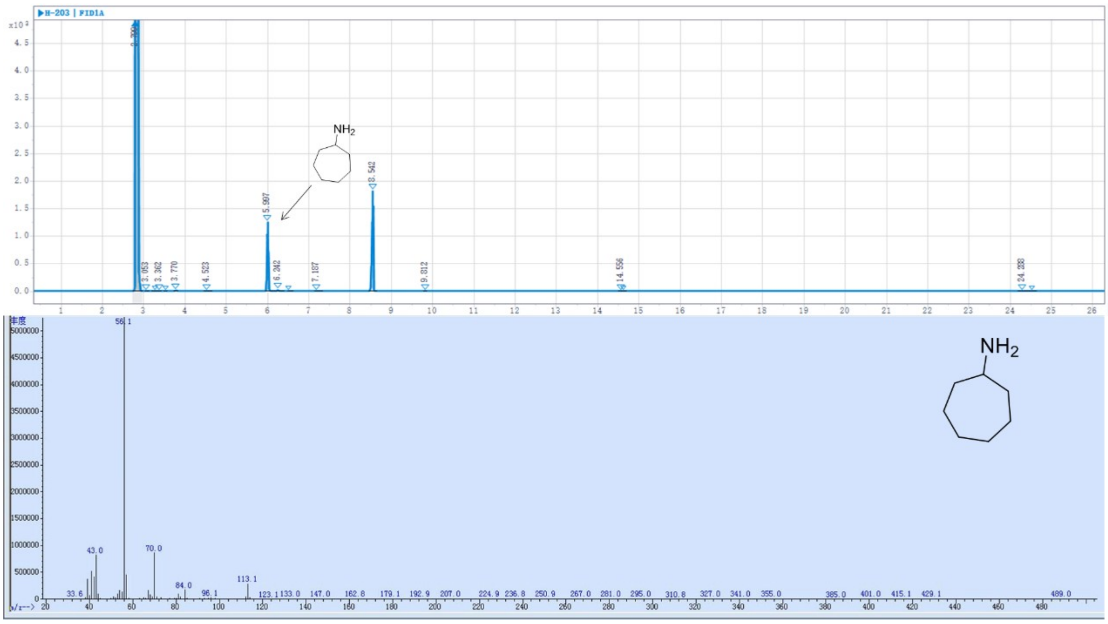


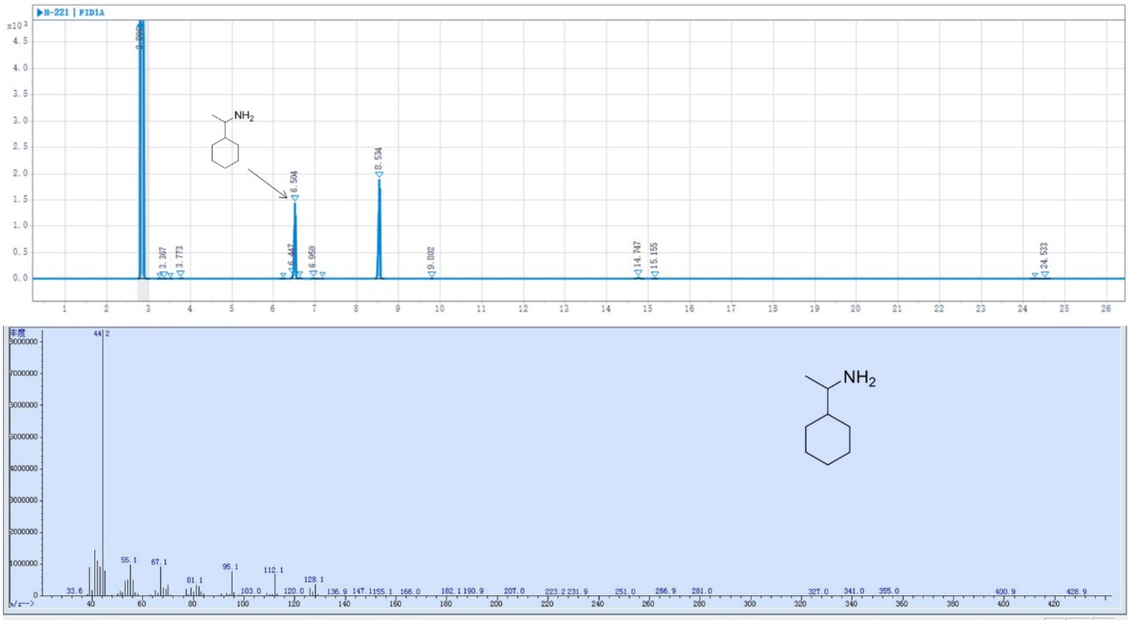
GC and MS spectra of undecan-6-amine



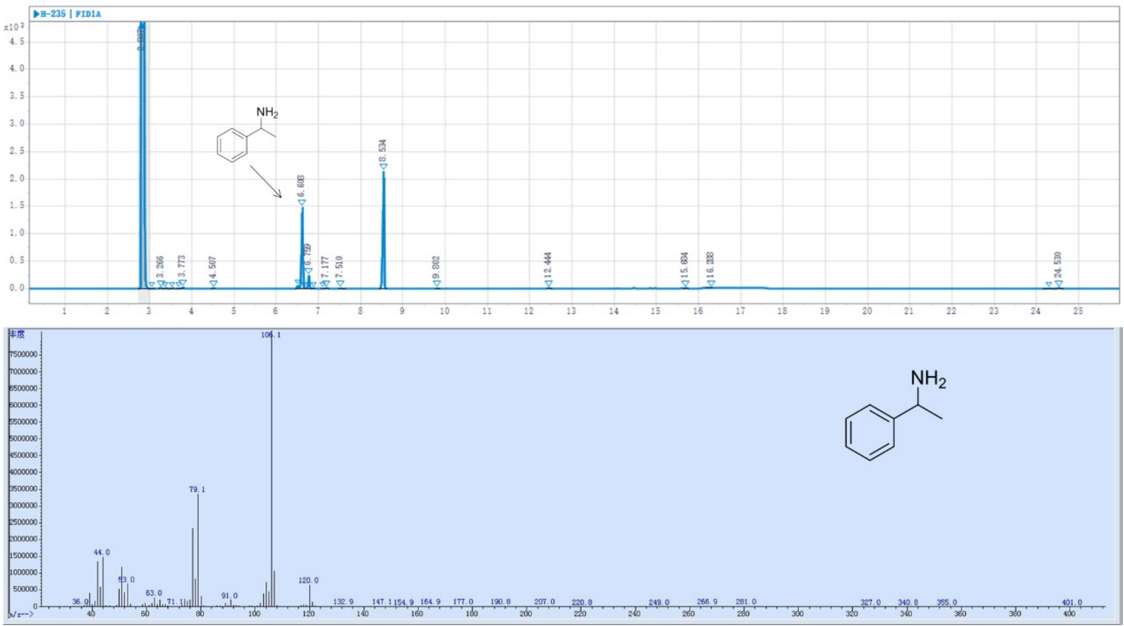
GC and MS spectra of 4-methylpentan-2-amine



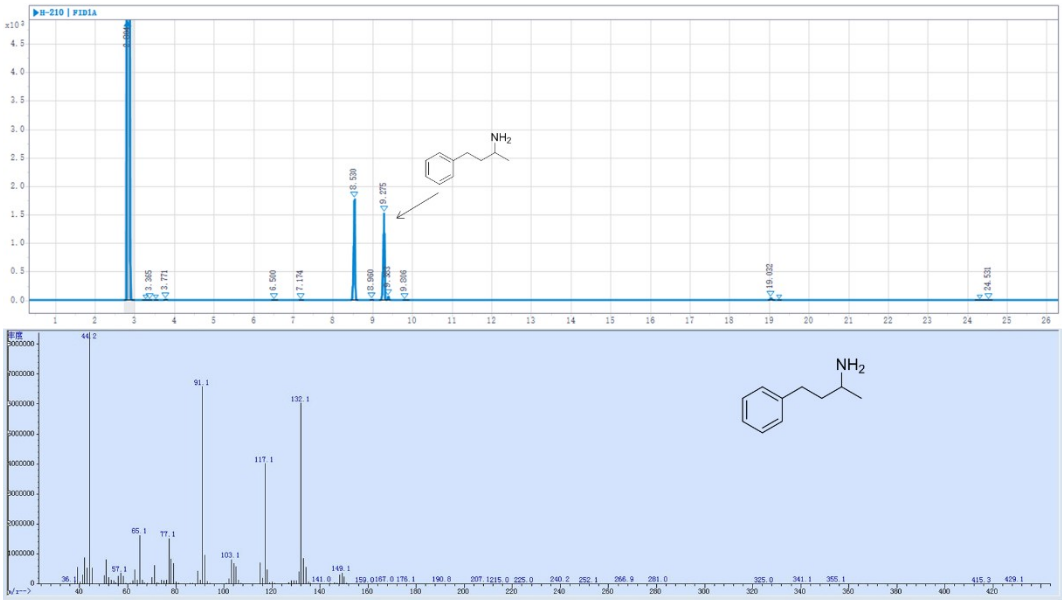
GC and MS spectra of cycloheptanamine



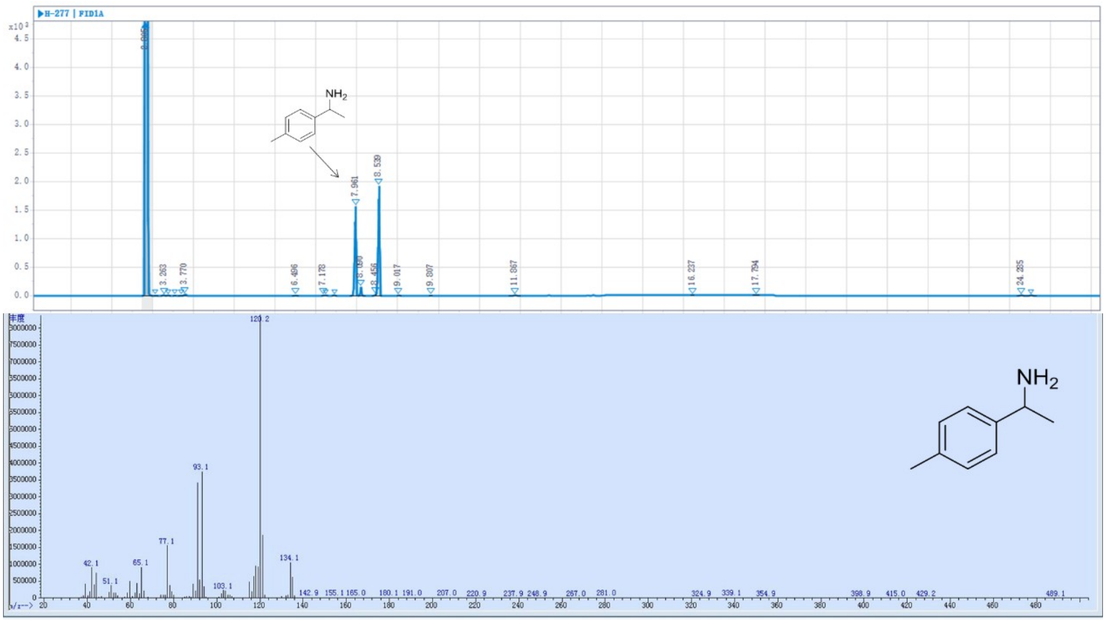
GC and MS spectra of 1-cyclohexylethan-1-amine



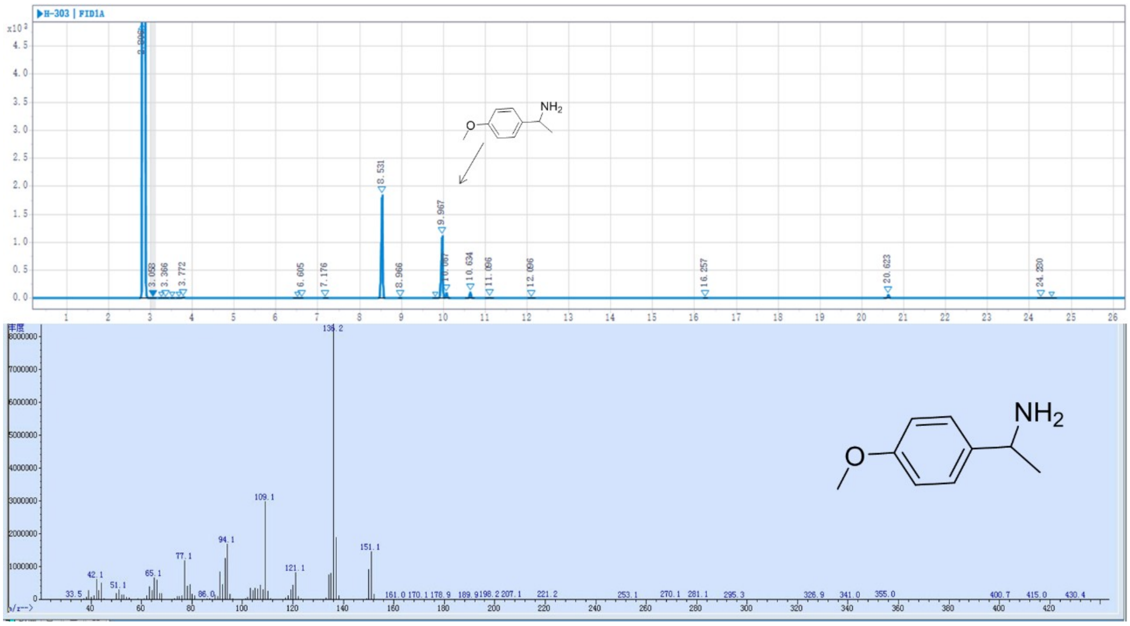
GC and MS spectra of 1-phenylethan-1-amine



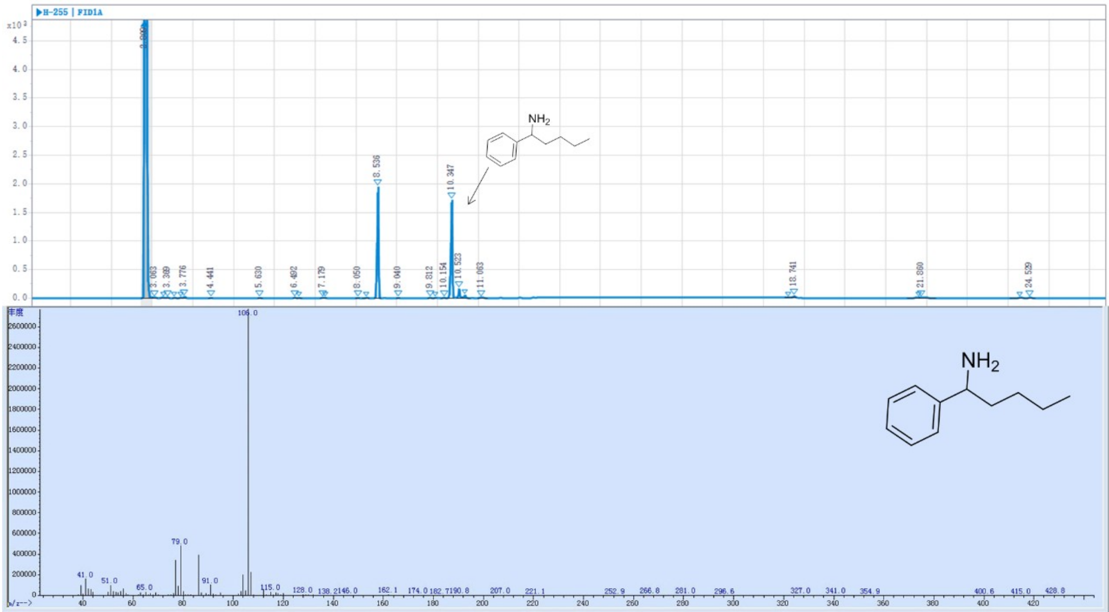
GC and MS spectra of 4-phenylbutan-2-amine



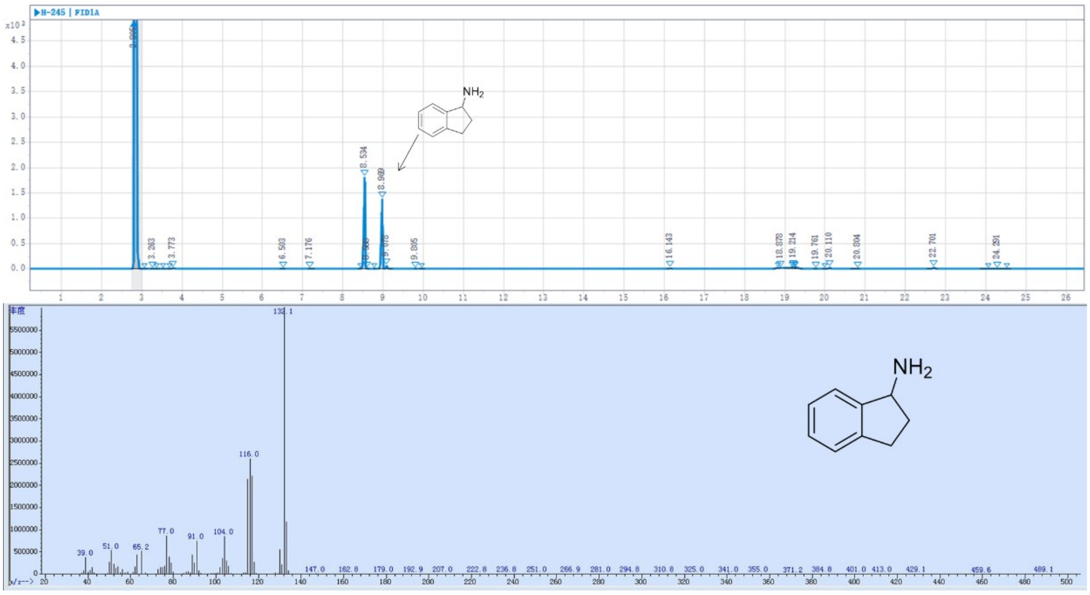
GC and MS spectra of 1-(p-tolyl)ethan-1-amine



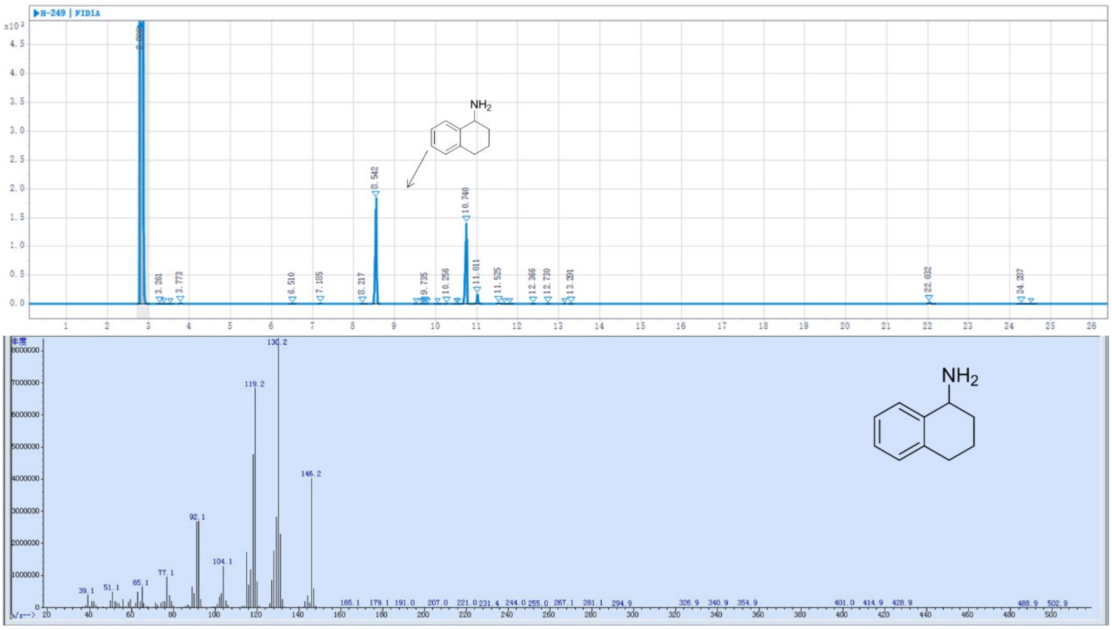
GC and MS spectra of 1-(4-methoxyphenyl)ethan-1-amine



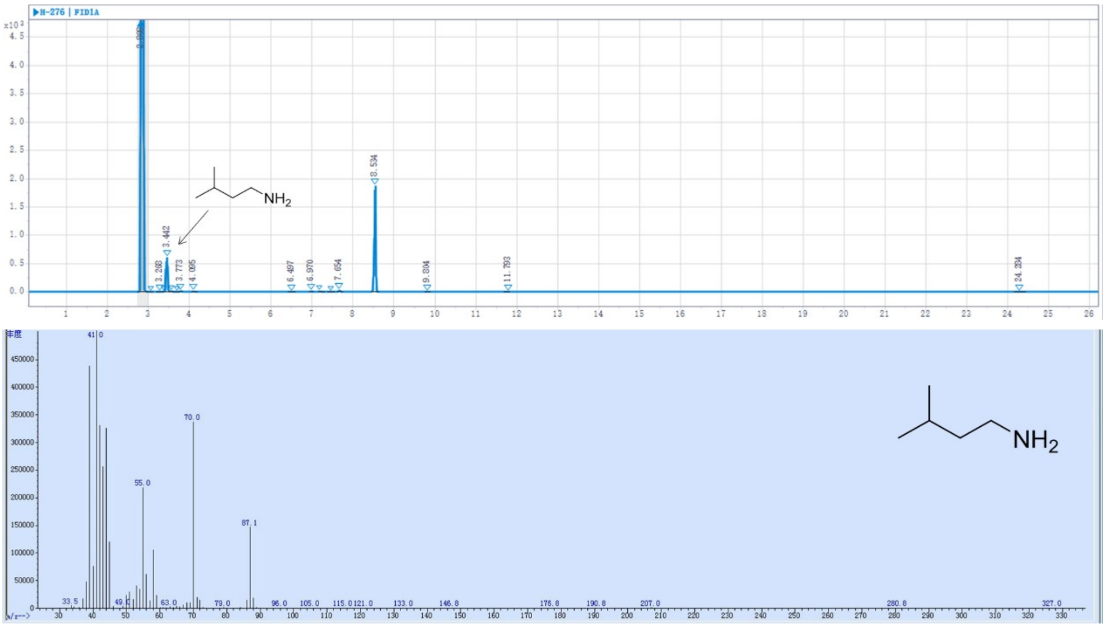
GC and MS spectra of 1-phenylpentan-1-amine



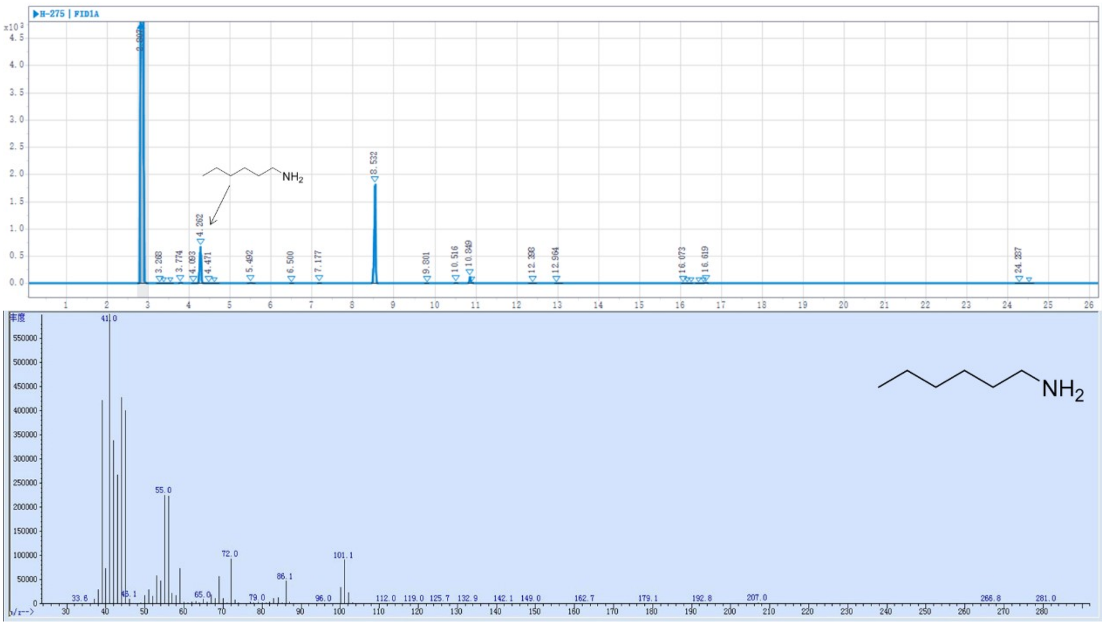
GC and MS spectra of 2,3-dihydro-1H-inden-1-amine



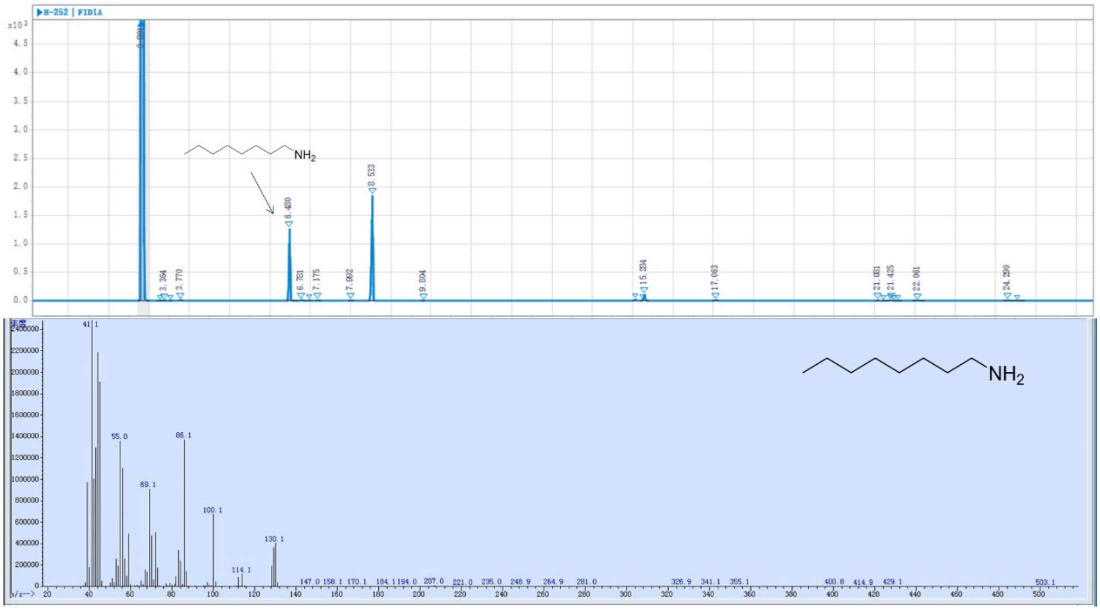
GC and MS spectra of 1,2,3,4-tetrahydronaphthalen-1-amine



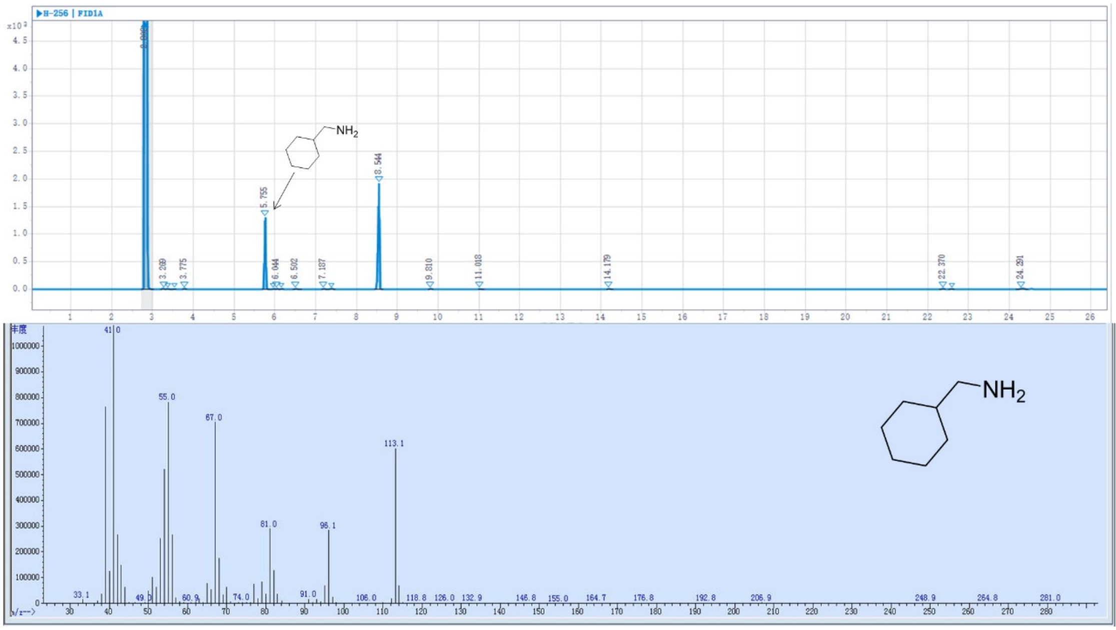
GC and MS spectra of 3-methylbutan-1-amine



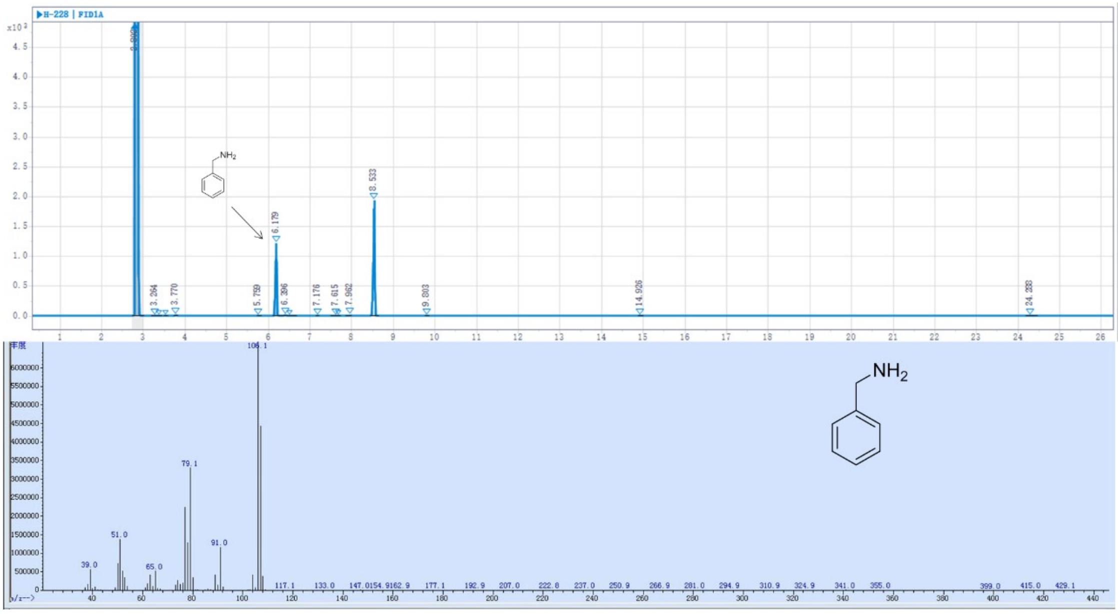
GC and MS spectra of hexan-1-amine



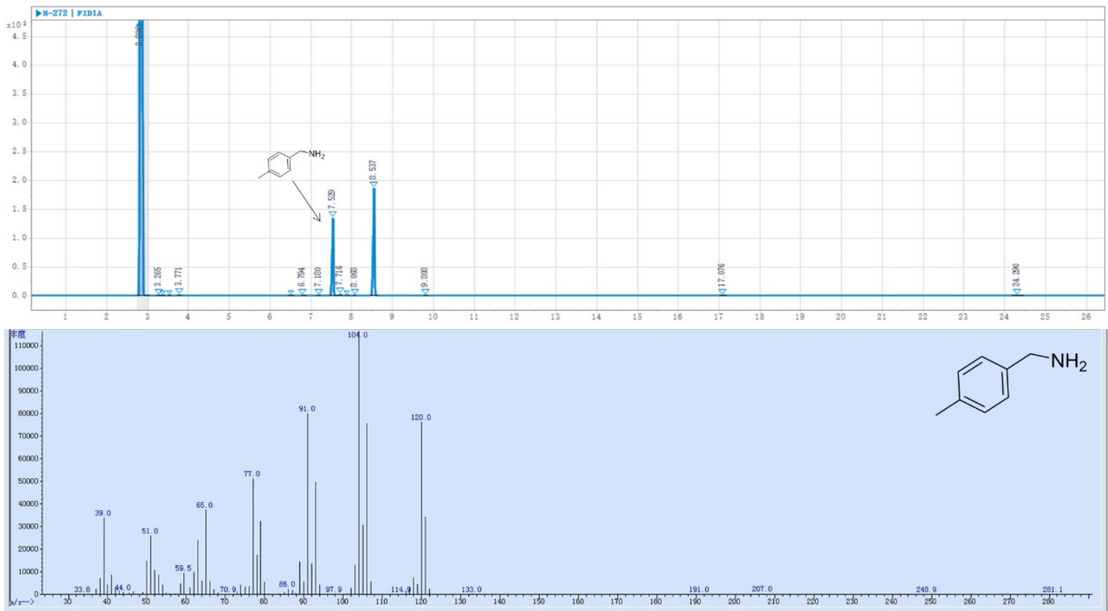
GC and MS spectra of octan-1-amine



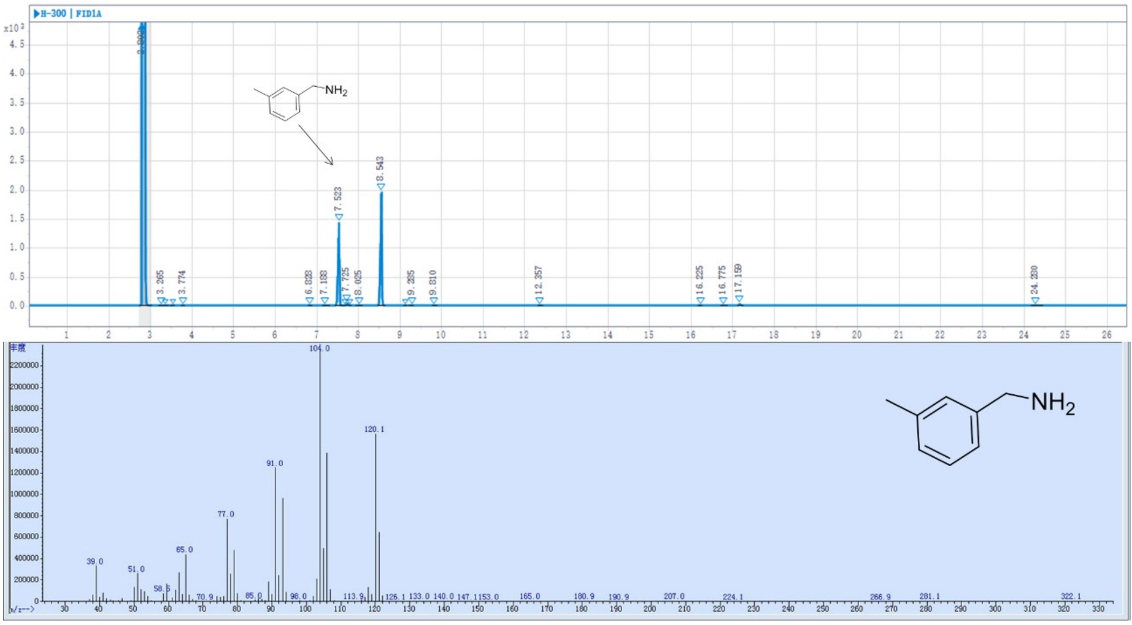
GC and MS spectra of cyclohexylmethanamine



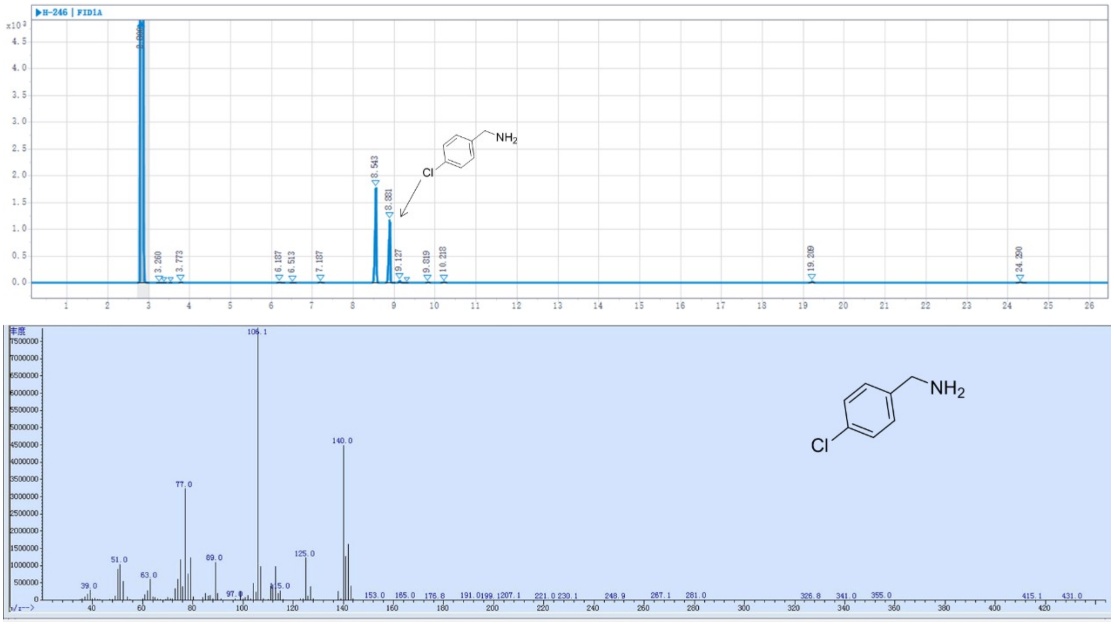
GC and MS spectra of phenylmethanamine



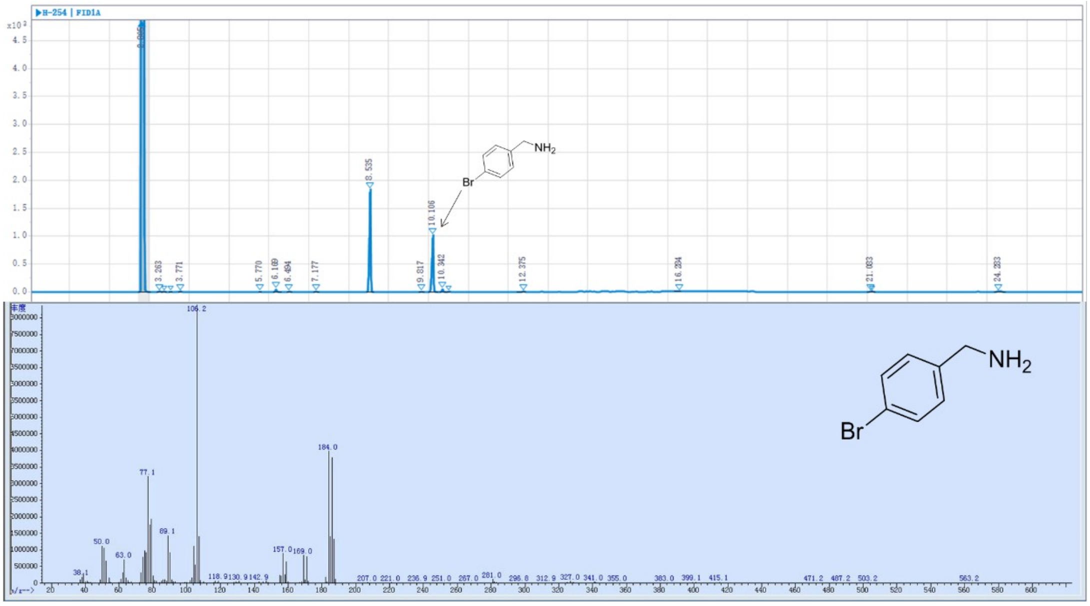
GC and MS spectra of p-tolylmethanamine



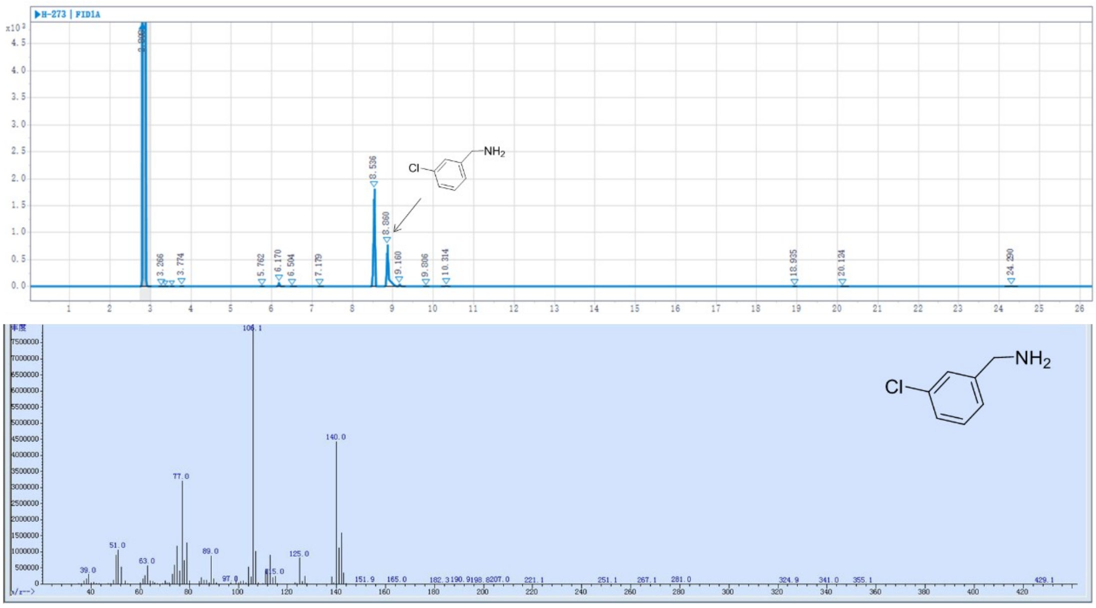
GC and MS spectra of m-tolylmethanamine



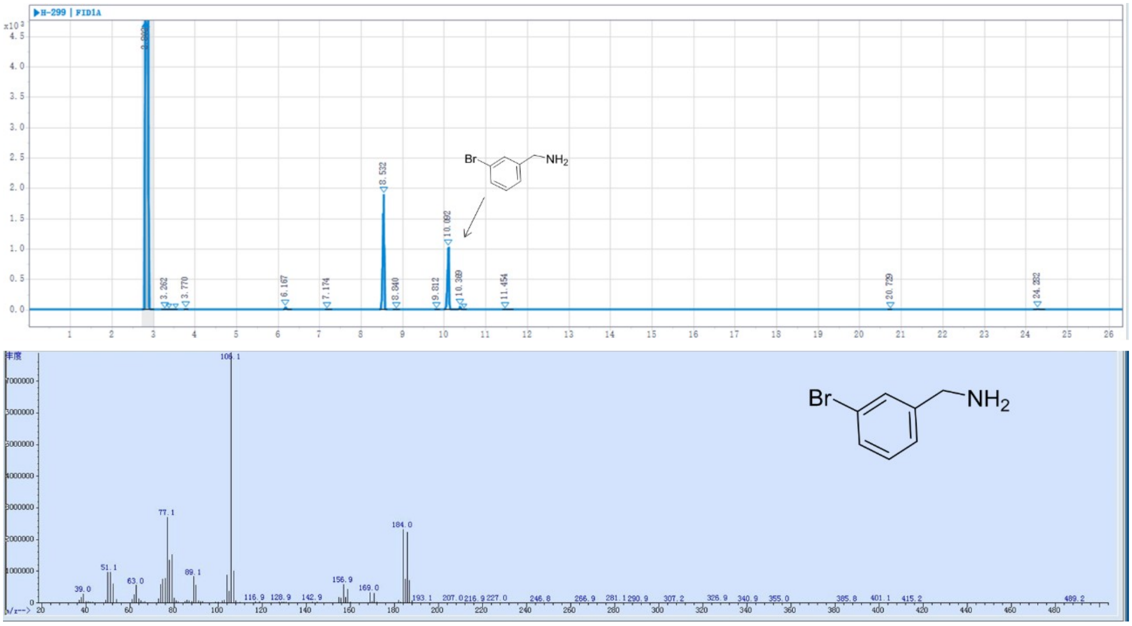
GC and MS spectra of (4-chlorophenyl)methanamine



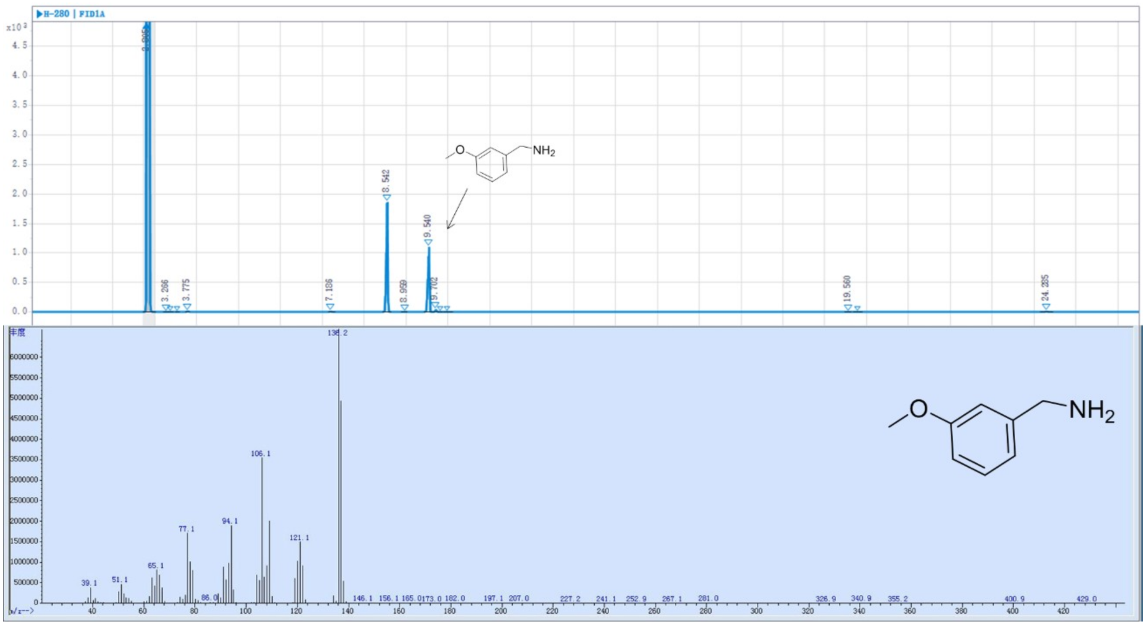
GC and MS spectra of (4-bromophenyl)methanamine



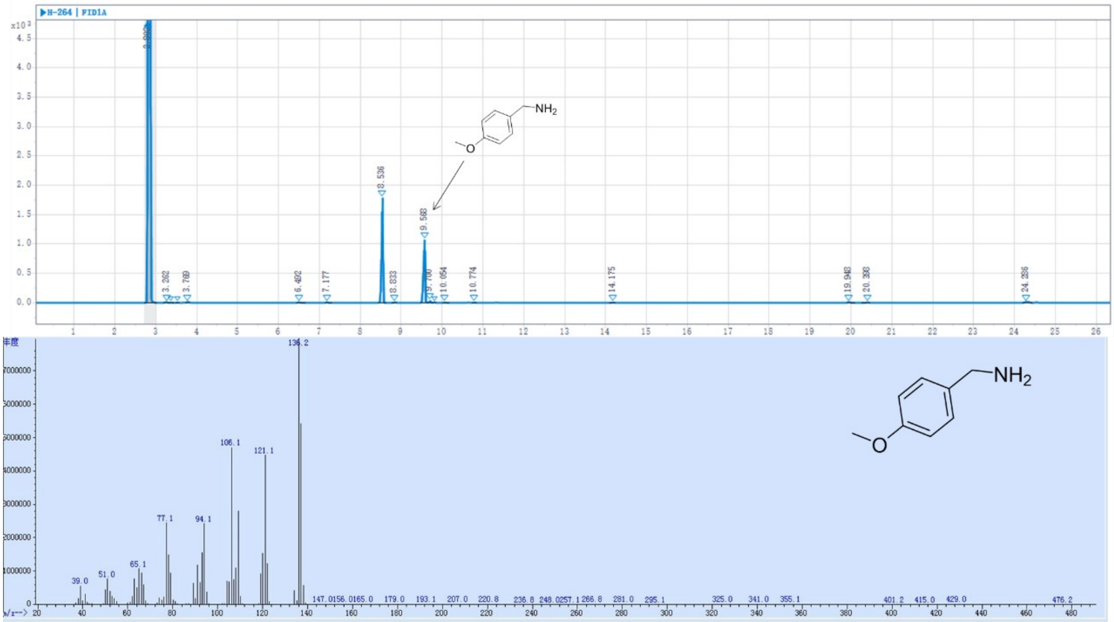
GC and MS spectra of (3-chlorophenyl)methanamine



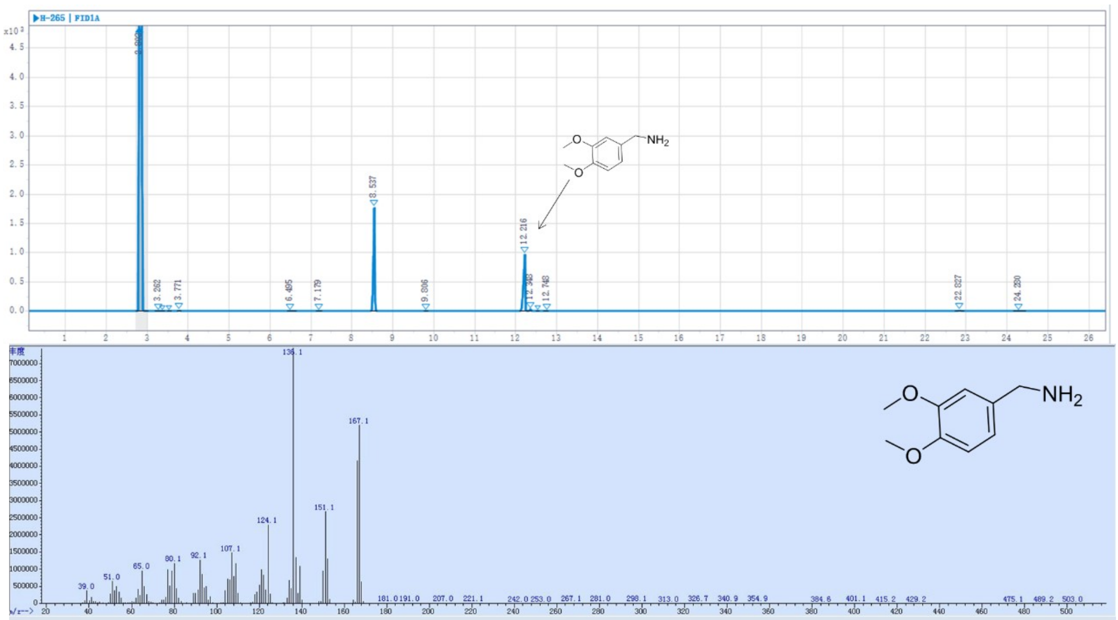
GC and MS spectra of (3-bromophenyl)methanamine



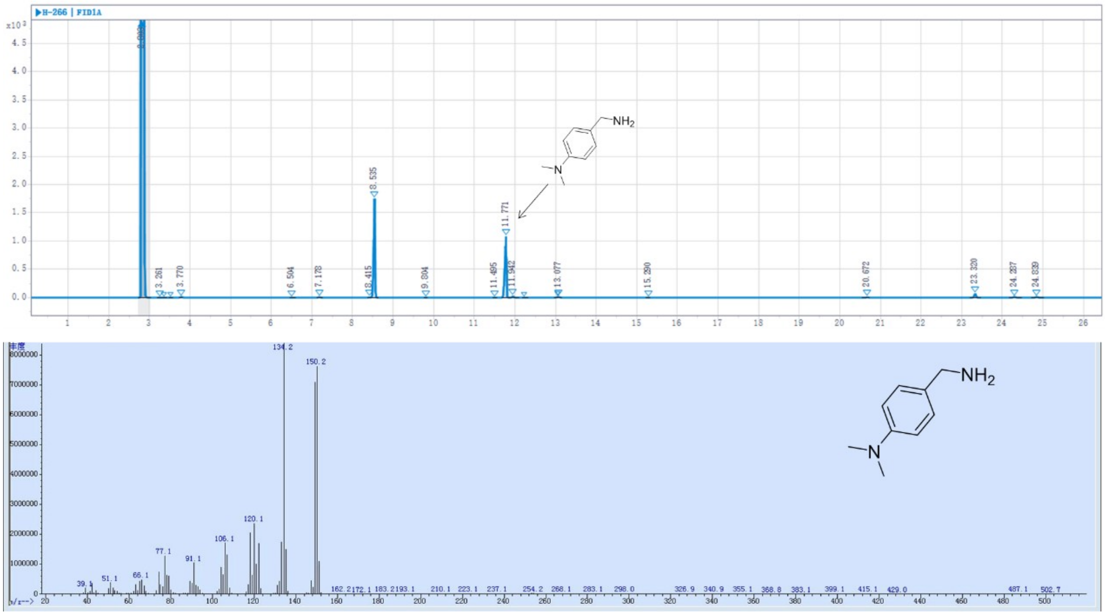
GC and MS spectra of (3-methoxyphenyl)methanamine



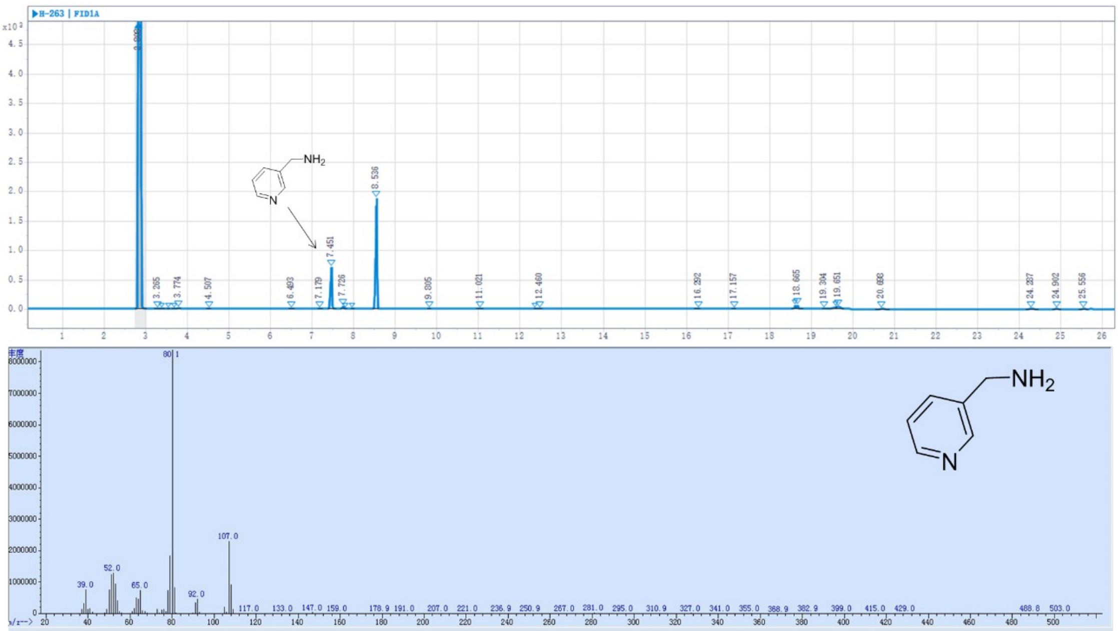
GC and MS spectra of (4-methoxyphenyl)methanamine



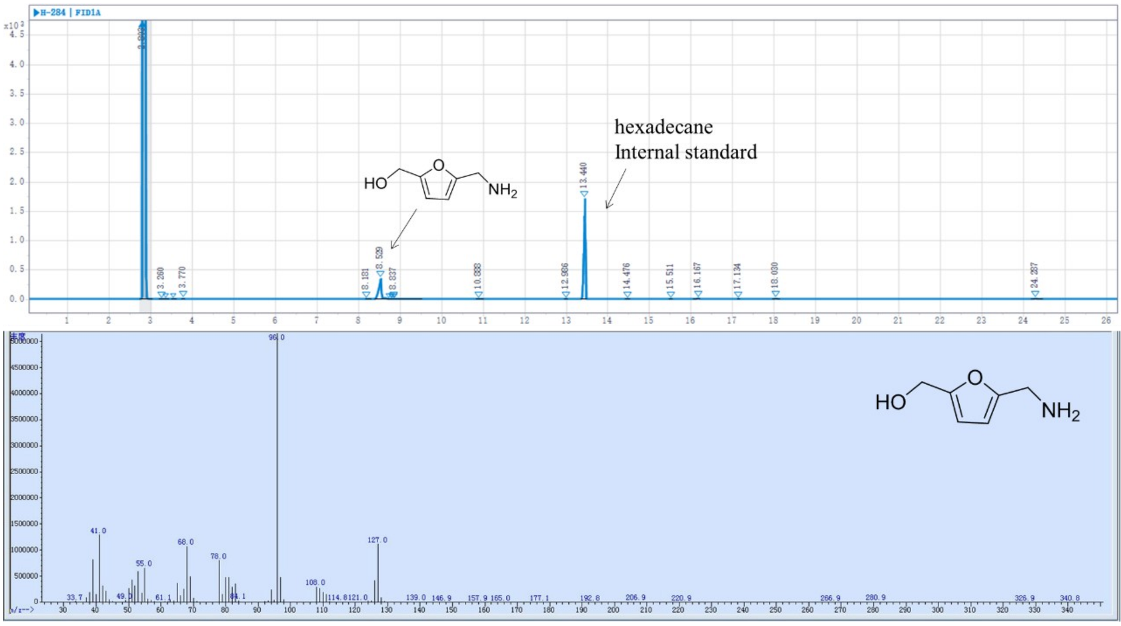
GC and MS spectra of (3,4-dimethoxyphenyl)methanaminee



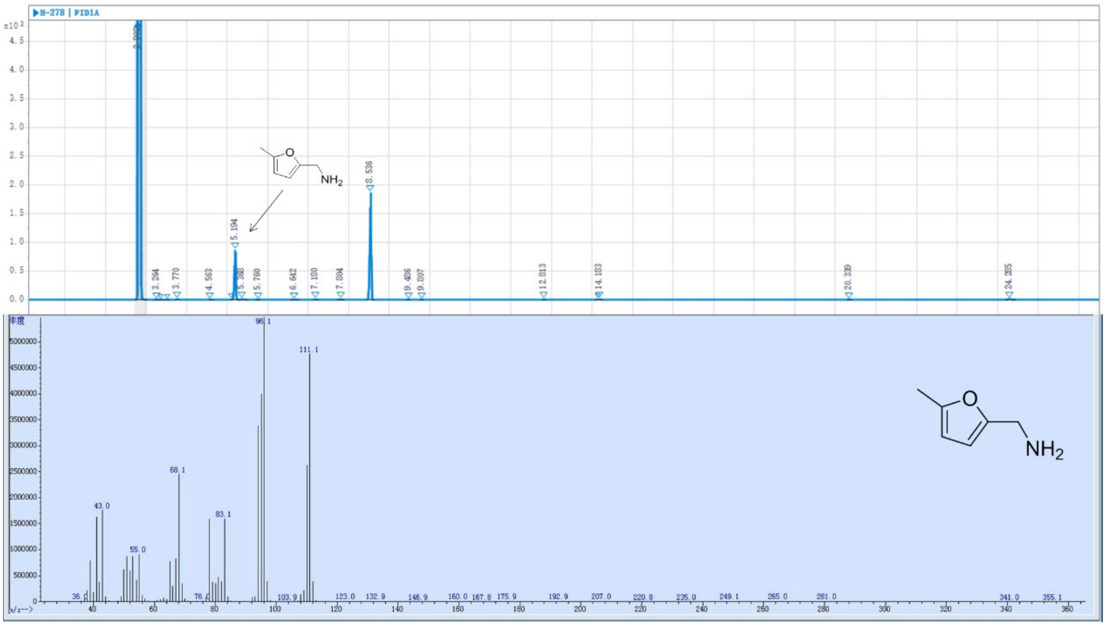
GC and MS spectra of 4-(aminomethyl)-N,N-dimethylaniline



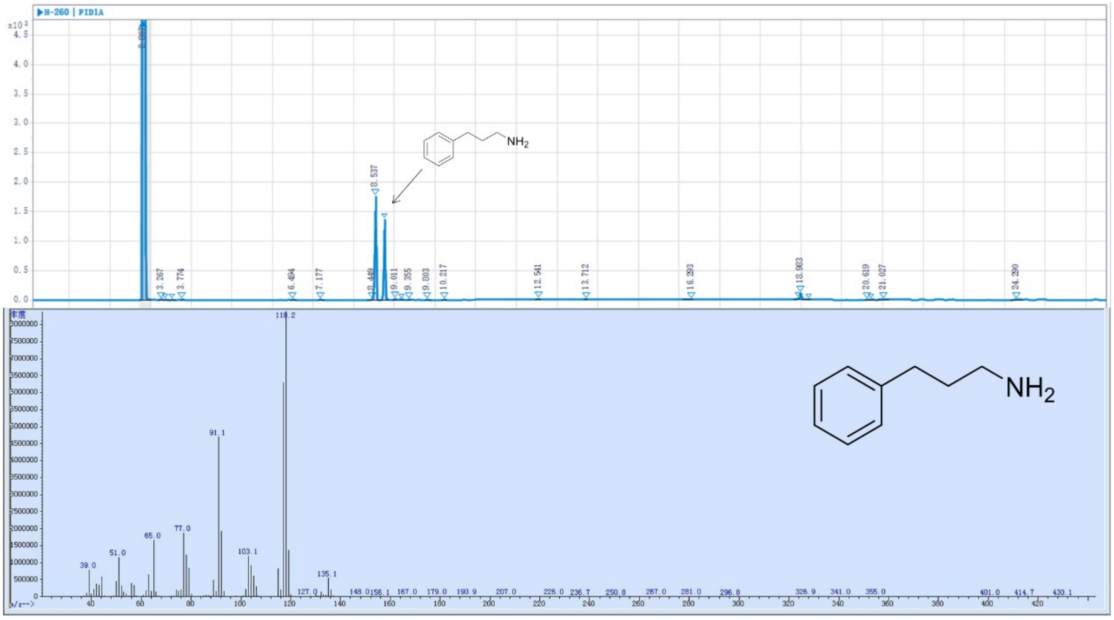
GC and MS spectra of pyridin-3-ylmethanamine



GC and MS spectra of (5-(aminomethyl)furan-2-yl)methanol



GC and MS spectra of (5-methylfuran-2-yl)methanamine



GC and MS spectra of 3-phenylpropan-1-amine