Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Highly economical and direct amination of sp^3 carbon using low-cost Nickel Pincer catalyst

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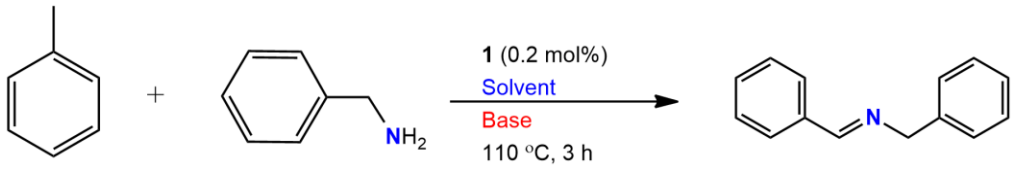
Supplementary Tables and Figures:

Table S1 The reaction of toluene with benzylamine using various solvents and bases catalyzed by **1**.[a]



Entry	Solvent	Base	TON	% GC Yield	Entry	Solvent	Base/oxidant	TON	% GC Yield
1	DMSO	KO^{t}Bu	46.0	9.2	11	DMSO	KOH	2.5	0.5
2	Toluene	KO^{t}Bu	10.5	2.1	12	DMSO	Cs_2CO_3	18.8	3.8
3	MTBE	KO^{t}Bu	NR	0.0	13	DMSO	DBU	8.6	1.7
4	*Iso*-butanol	KO^{t}Bu	NR	0.0	14	DMSO	[b]DMAP	17.4	3.5
5	Propylene carbonate	KO^{t}Bu	6.1	1.2	15	DMSO	DABCO	18.7	3.7
6	Trifluorotoluene	KO^{t}Bu	NR	0.0	16	DMSO	KO^{t}Bu	46.0	9.2
7	DMA	KO^{t}Bu	12.2	2.4	17	DMSO	Pyridine oxide	21.3	4.3
8	DMF	KO^{t}Bu	10.0	2.0	18	DMSO	Iodobenzene diacetate	6.6	1.3
9	Cyclohexane	KO^{t}Bu	NR	NR					
10	Acetonitrile	KO^{t}Bu	NR	NR					

[a]TONs and GC yields represent an average of two runs. TON and percent GC yield were measured by gas chromatography/mass spectrometry (GC/MS) using decane as an internal standard. No reaction (NR). [b]4-Dimethylaminopyridine.

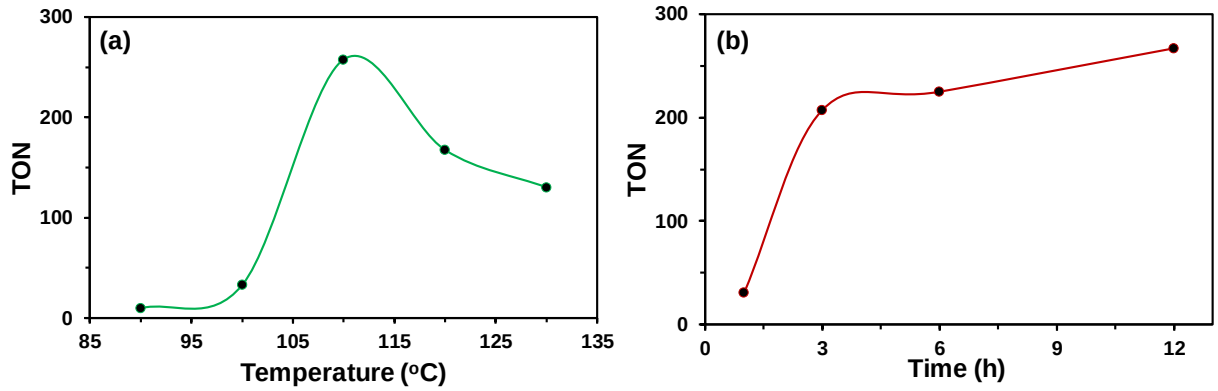


Fig. S1 Study of the effect of a) temperature (for 3 h) and b) time (at 110 °C) on C-N coupling reaction. Reaction conditions: **1** (2.0 mg, 3.46 μmol), benzylamine (183.5 mg, 1.71 mmol), toluene (157.8 mg, 1.71 mmol), KO^{t}Bu (0.31 eq., 55.0 mg, 0.49 mmol) and DMSO (1.0 mL) were used.

Synthesis of N-propylbenzenemethanamine:

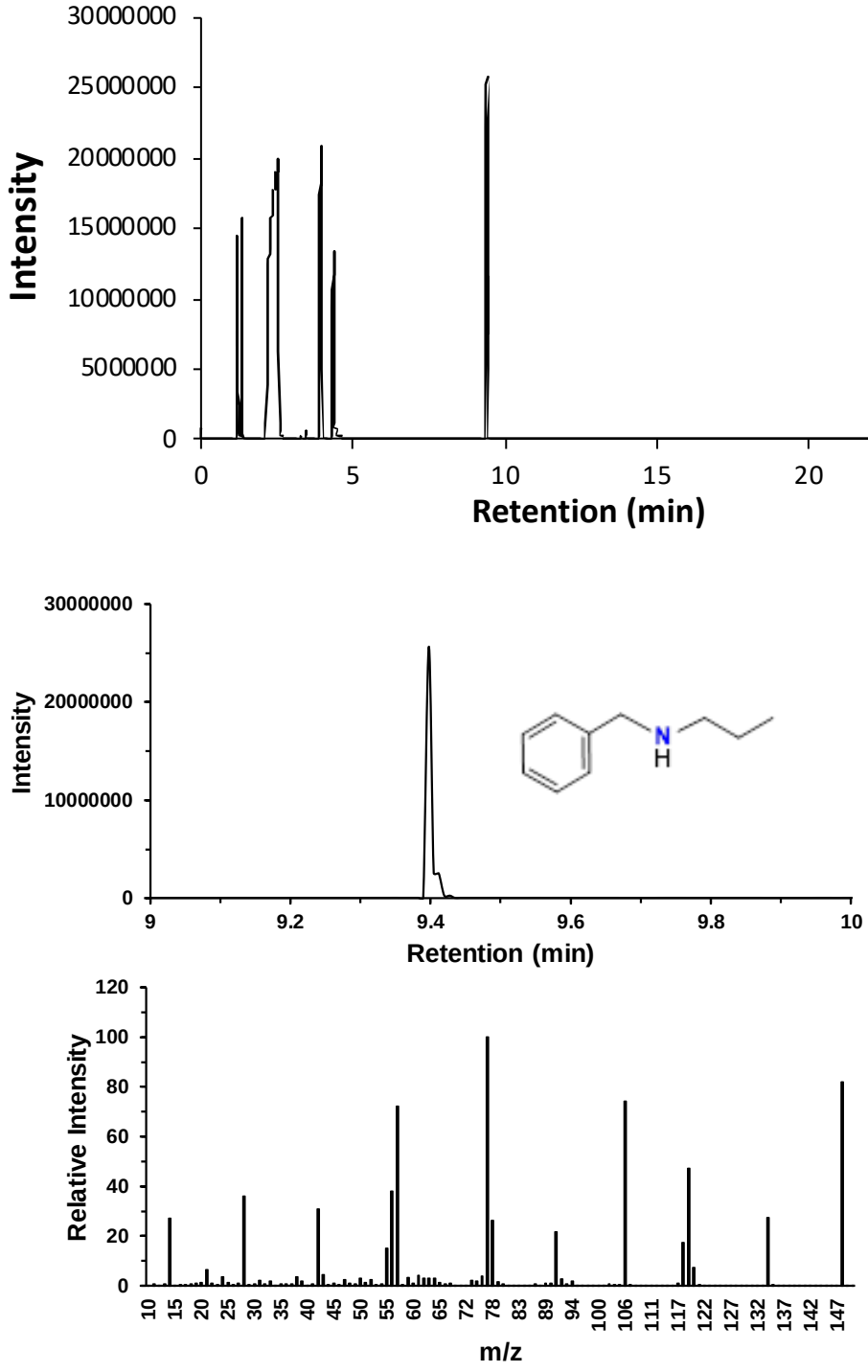


Fig. S2 GC/MS of the reaction between propylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-butylbenzenemethanamine:

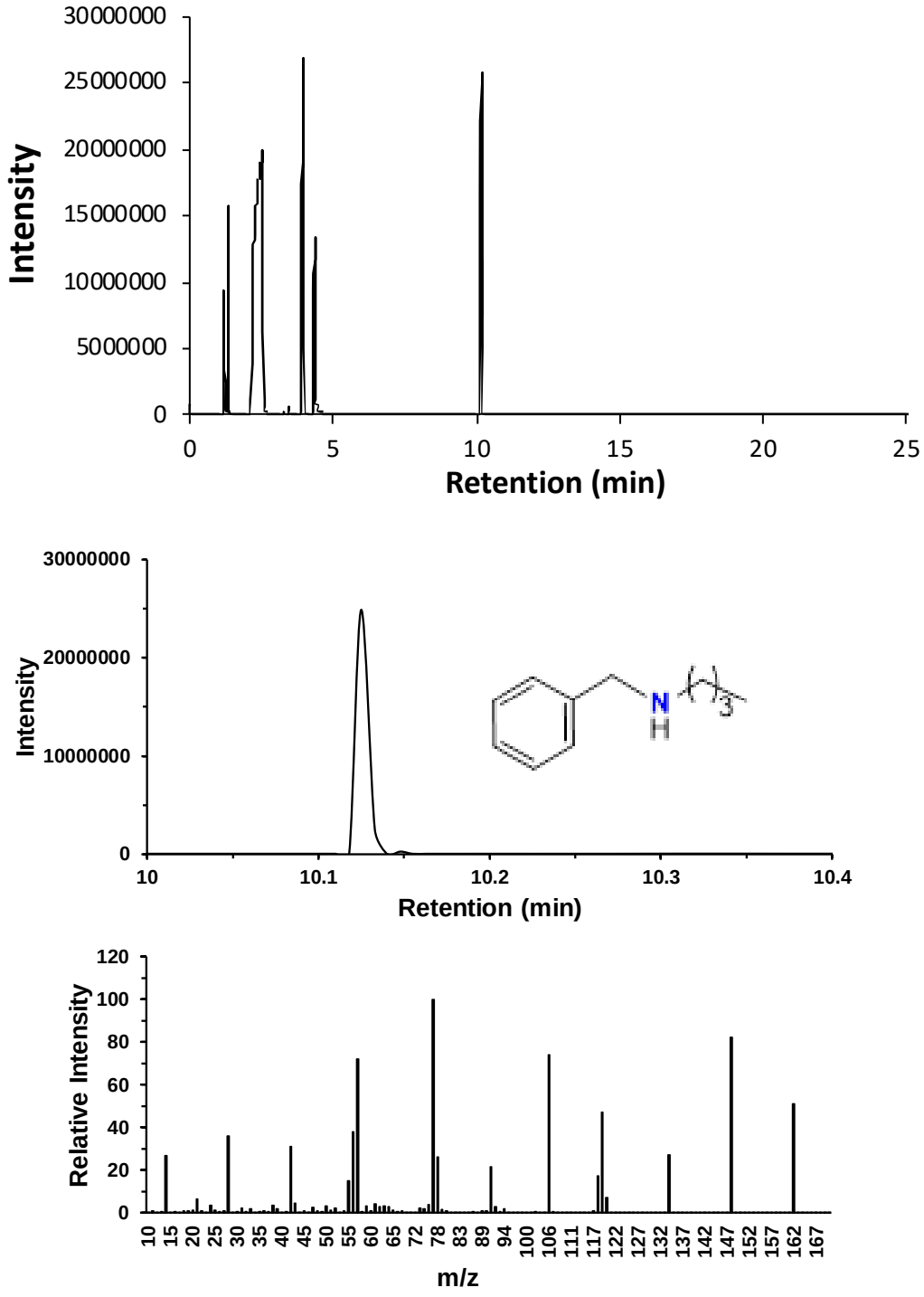


Fig. S3 GC/MS of the reaction between butylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-pentylbenzenemethanamine:

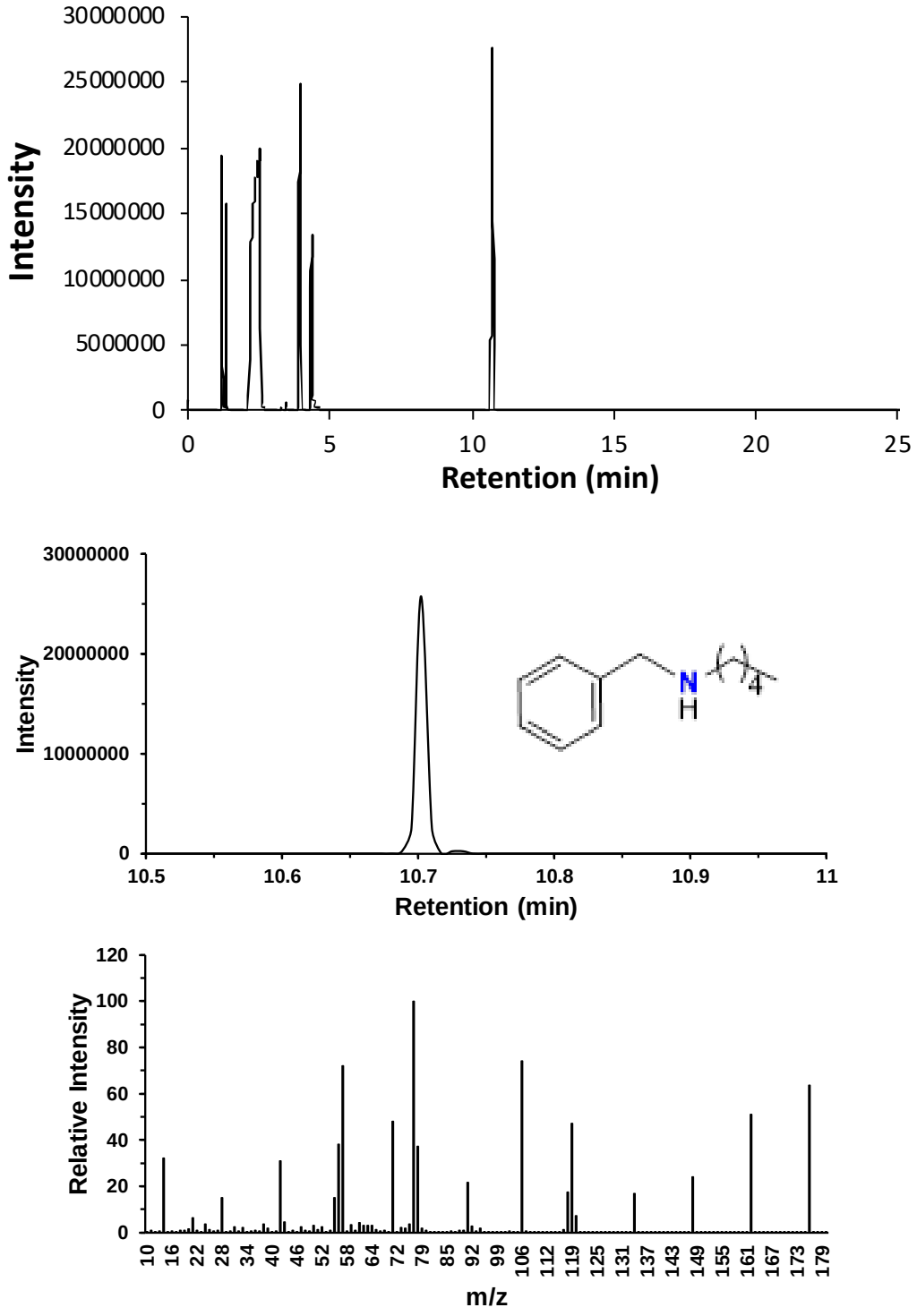


Fig. S4 GC/MS of the reaction between pentylamine and toluene. The sample was analyzed with decane as the internal standard.

Synthesis of N-hexylbenzenemethanamine:

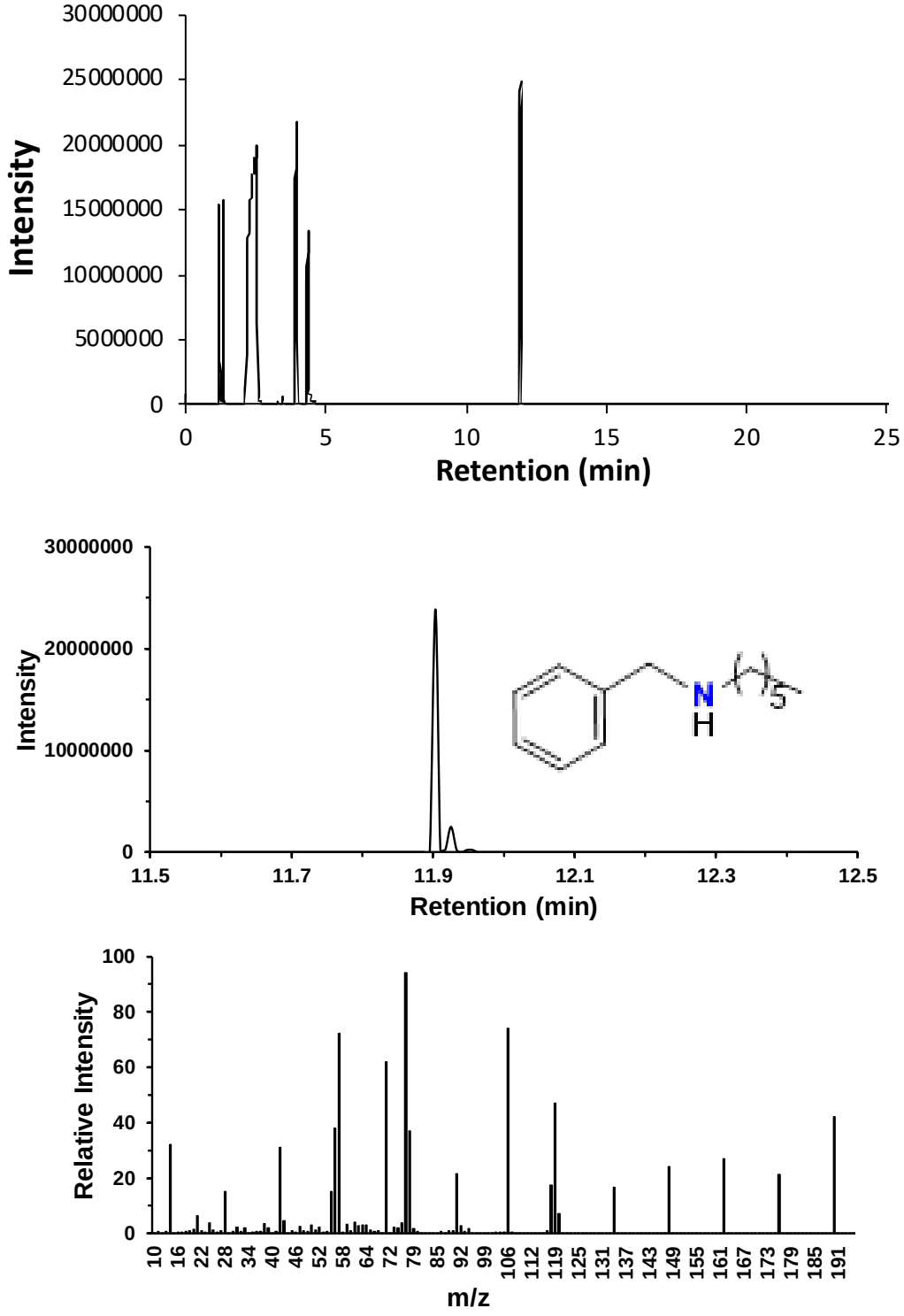


Fig. S5 GC/MS of the reaction between hexylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-heptylbenzenemethanamine:

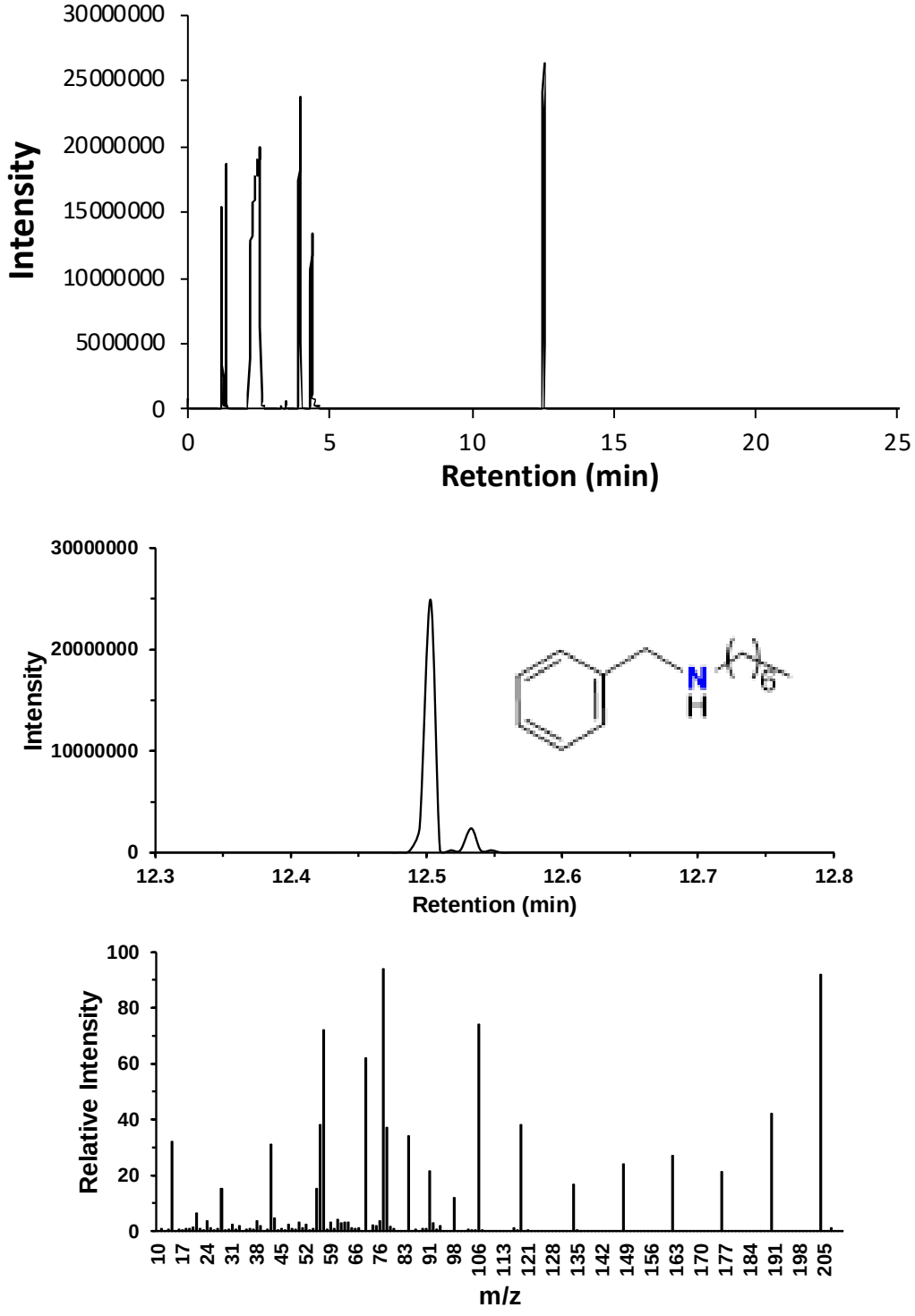


Fig. S6 GC/MS of the reaction between heptylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-octylbenzenemethanamine:

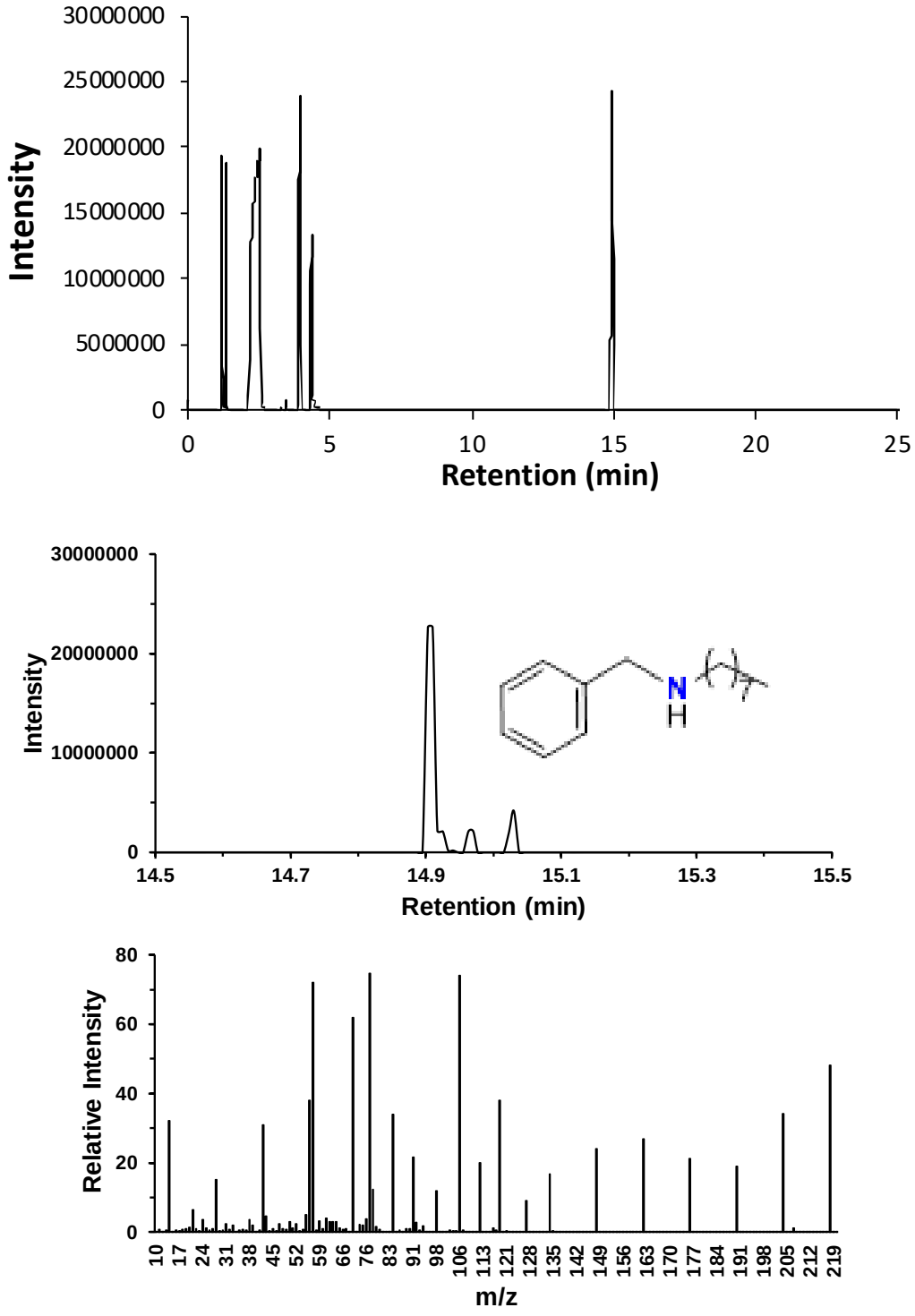


Fig. S7 GC/MS of the reaction between octylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-nonylbenzenemethanamine:

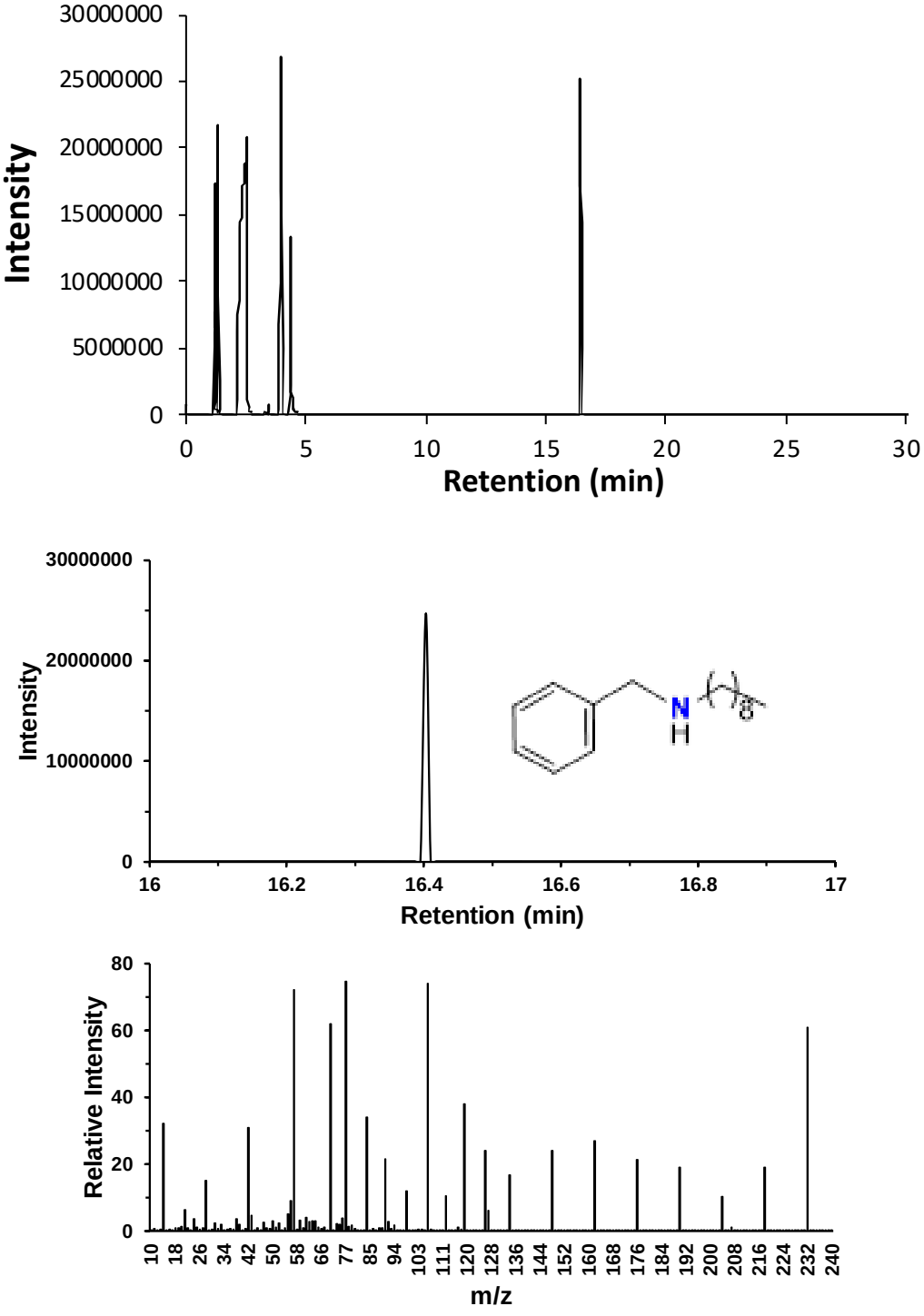


Fig. S8 GC/MS of the reaction between nonylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-decylbenzenemethanamine:

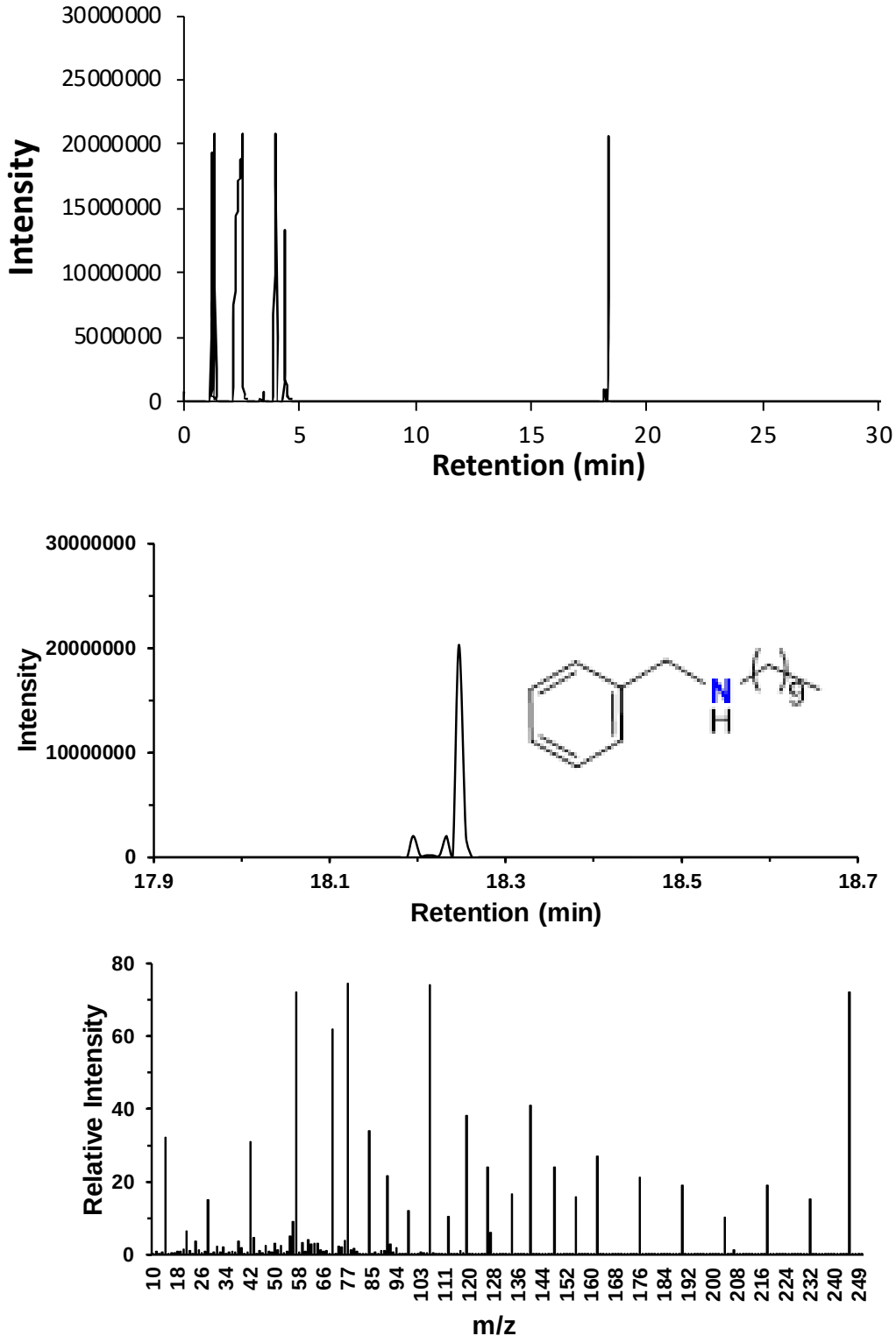


Fig. S9 GC/MS of the reaction between decylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-phenylbenzenemethanamine:

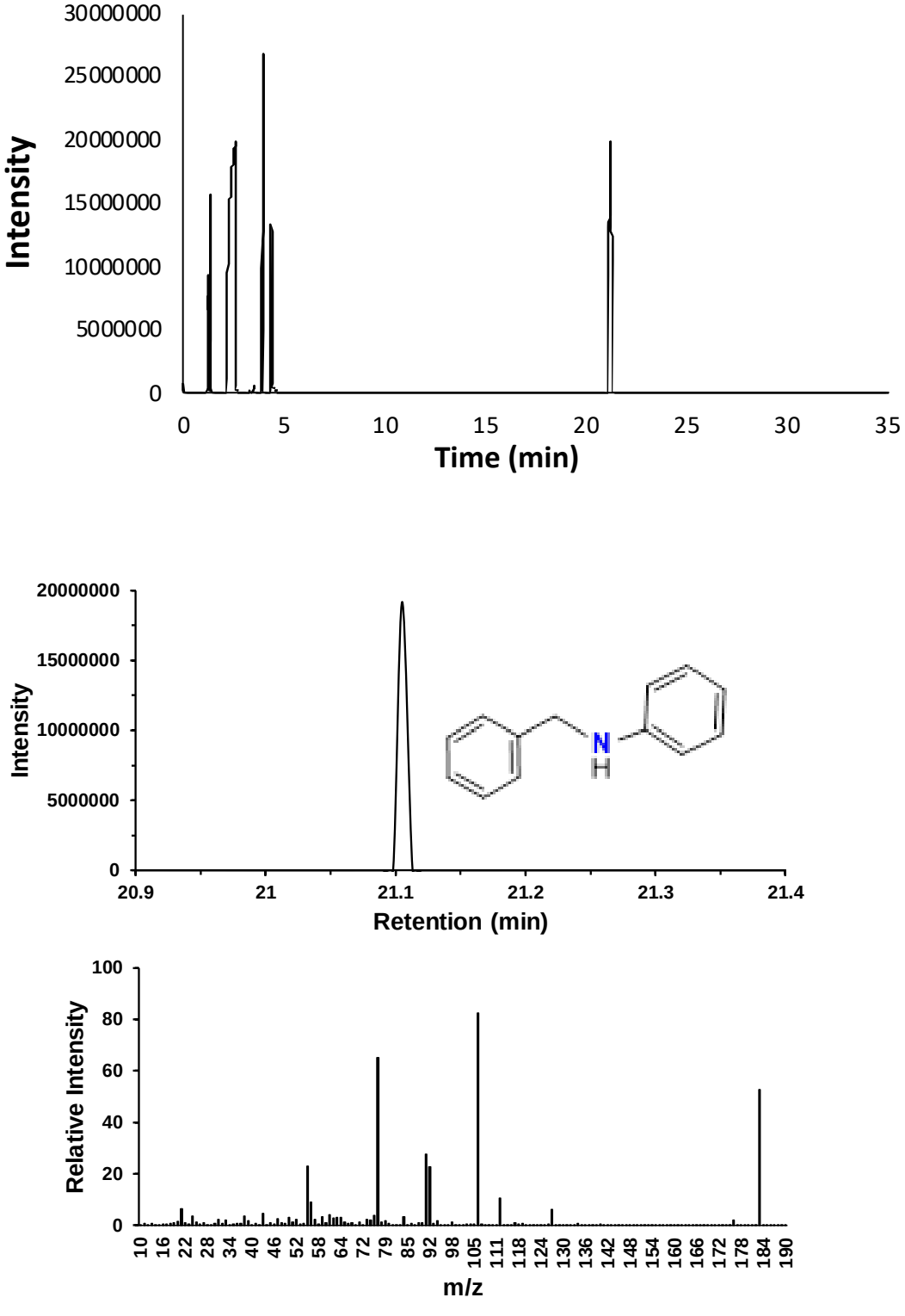


Fig. S10 GC/MS of the reaction between aniline and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of dibenzylamine:

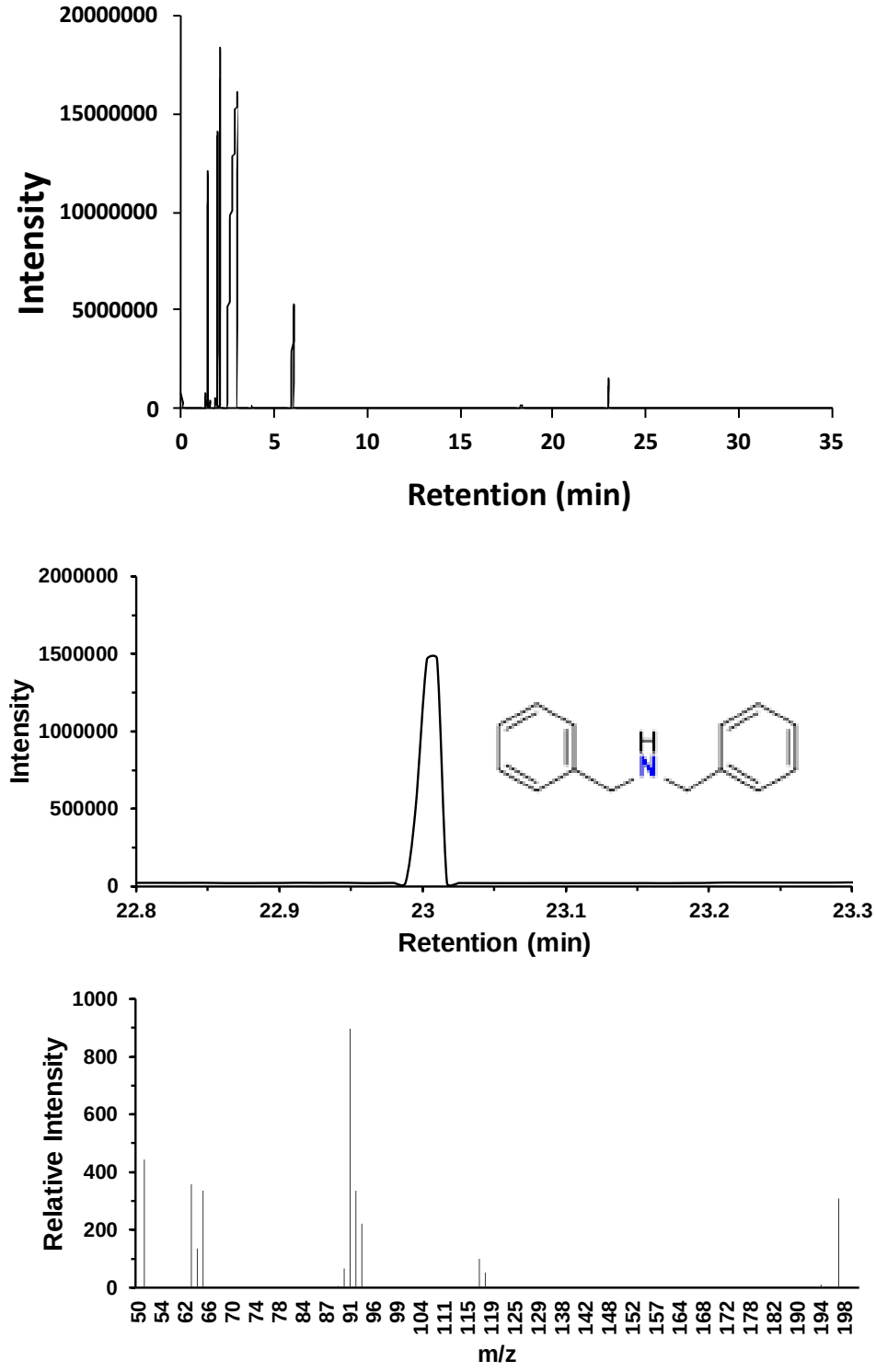


Fig. S11 GC/MS of the reaction between benzylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of α-methyl-N-(phenylmethyl)benzenemethanamine:

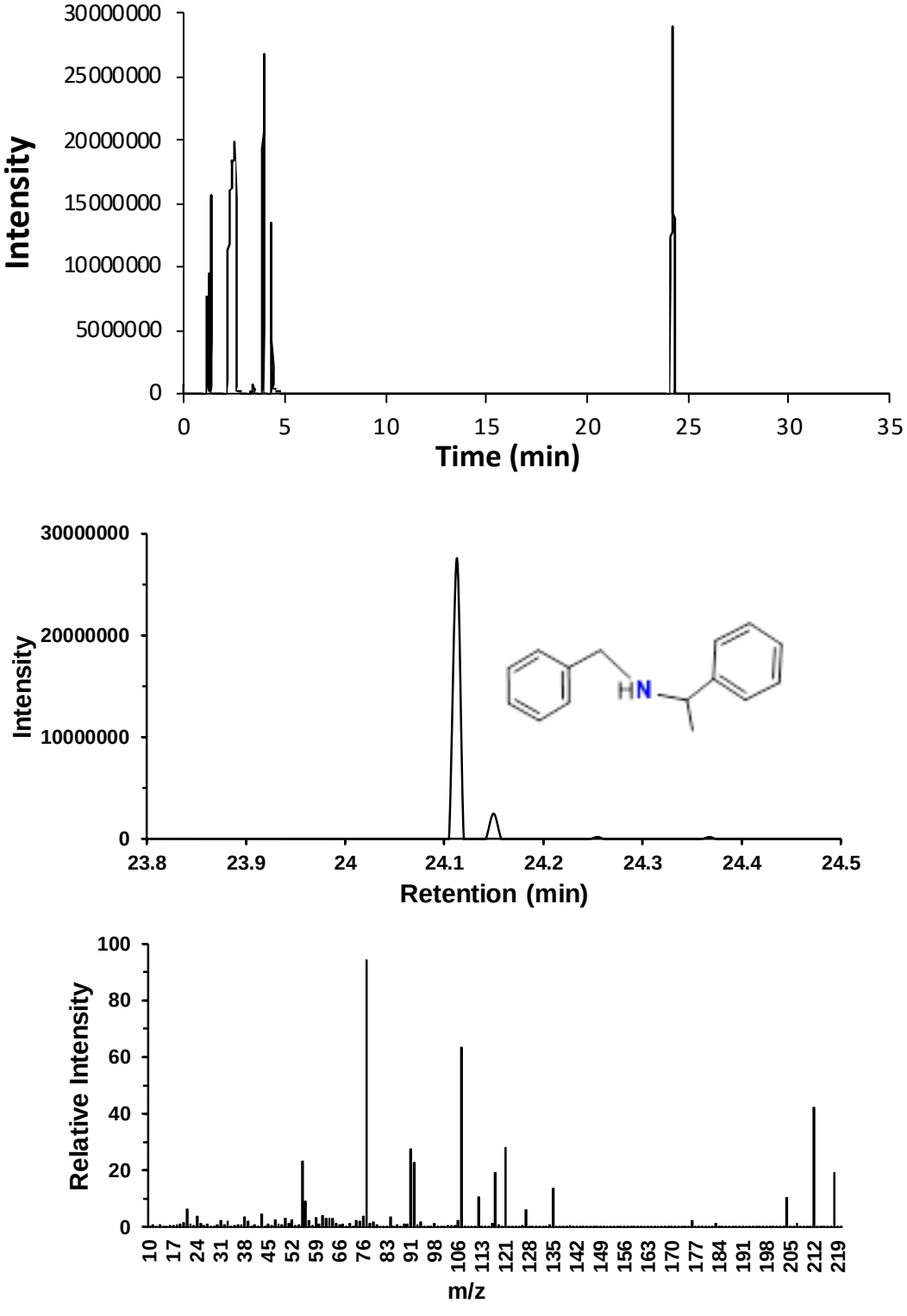


Fig. S12 GC/MS of the reaction between α-methylbenzylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(3-methylbutyl)benzenemethanamine:

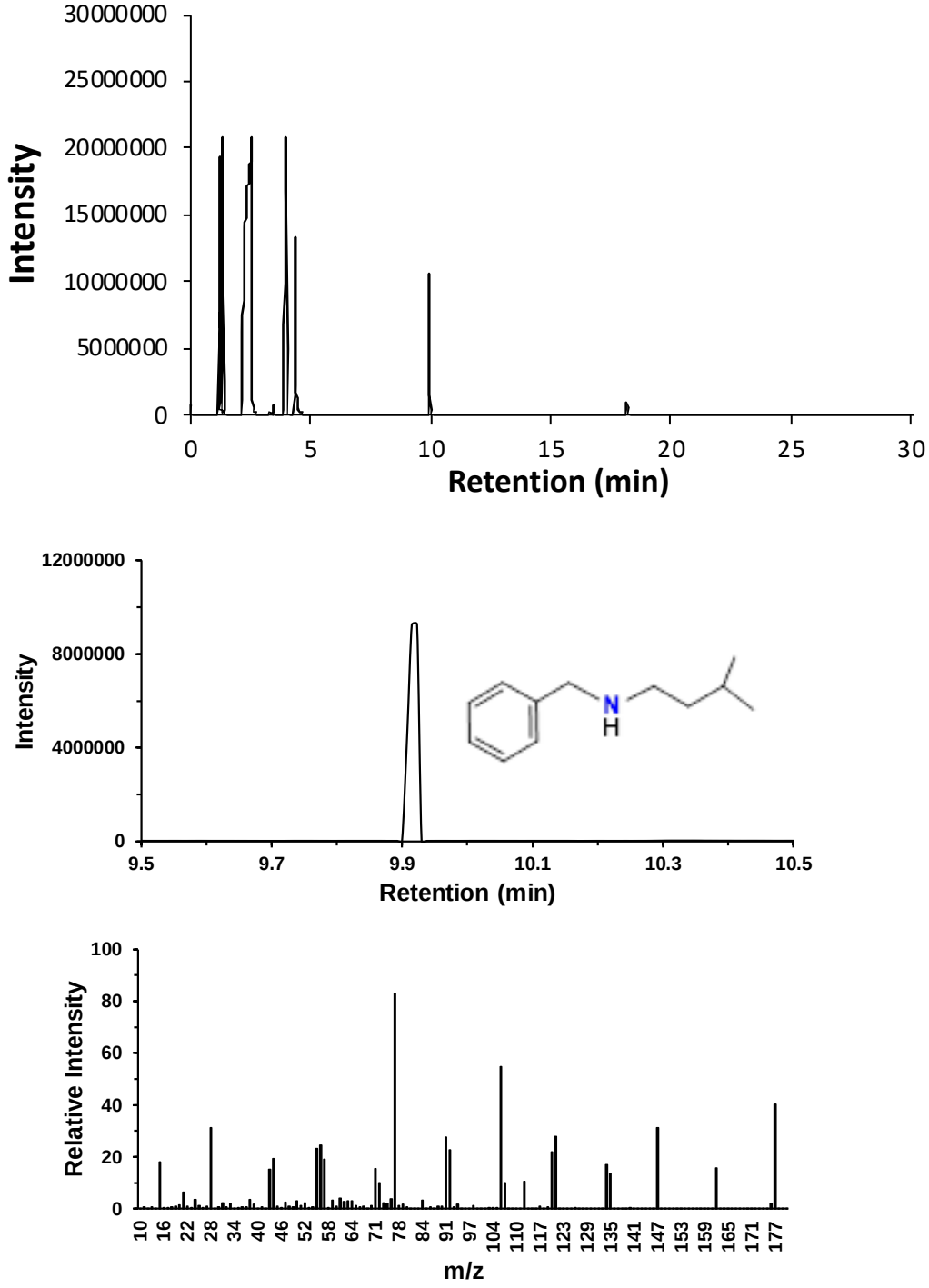


Fig. S13 GC/MS of the reaction between isoamylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of pyrrolidine:

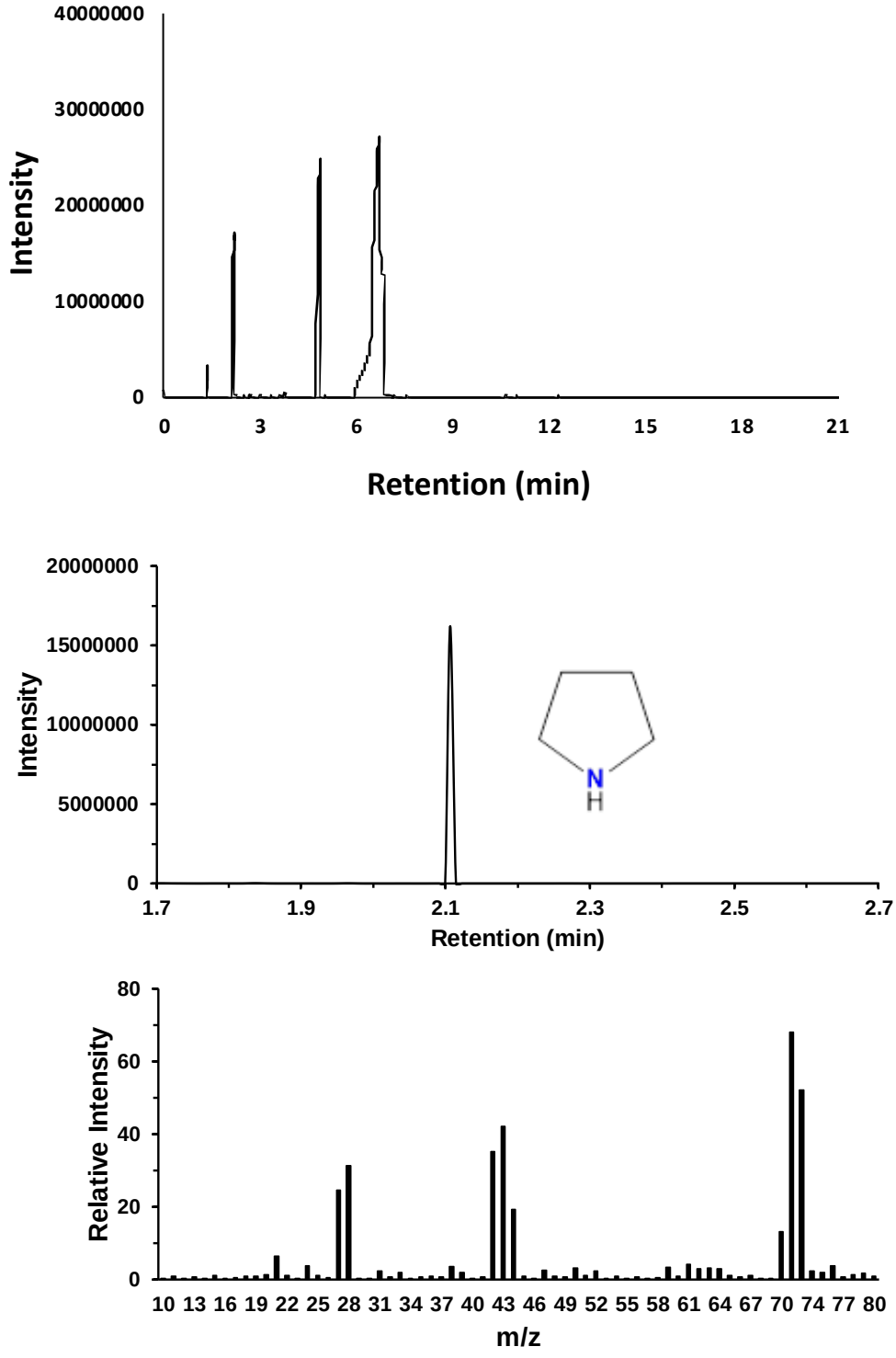


Fig. S14 GC/MS of the cyclization of butylamine. The sample was analyzed with decane as an internal standard.

Synthesis of 1-methylpyrrolidine:

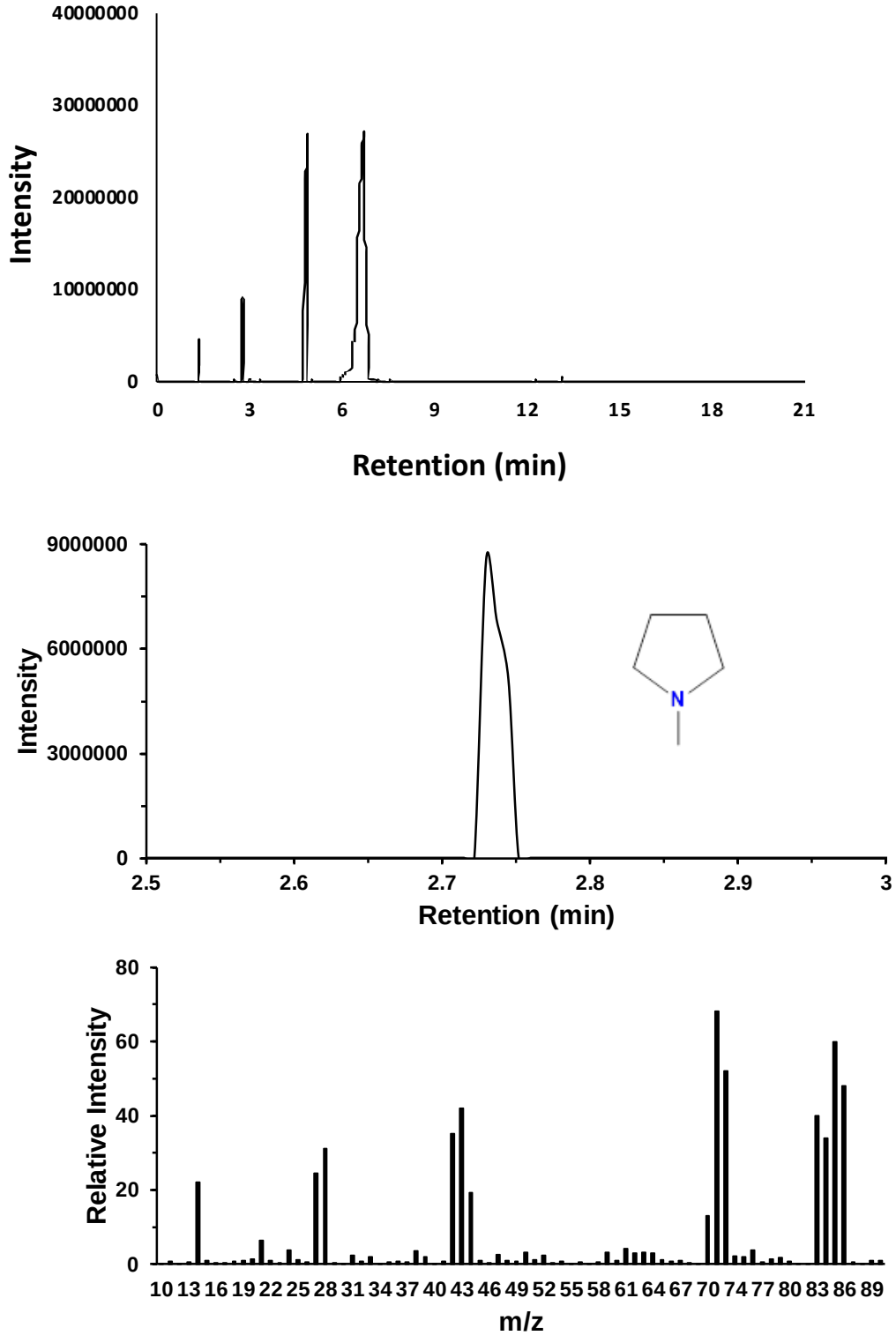


Fig. S15 GC/MS of the cyclization of butylmethylamine. The sample was analyzed with decane as an internal standard.

Synthesis of 1-ethylpyrrolidine:

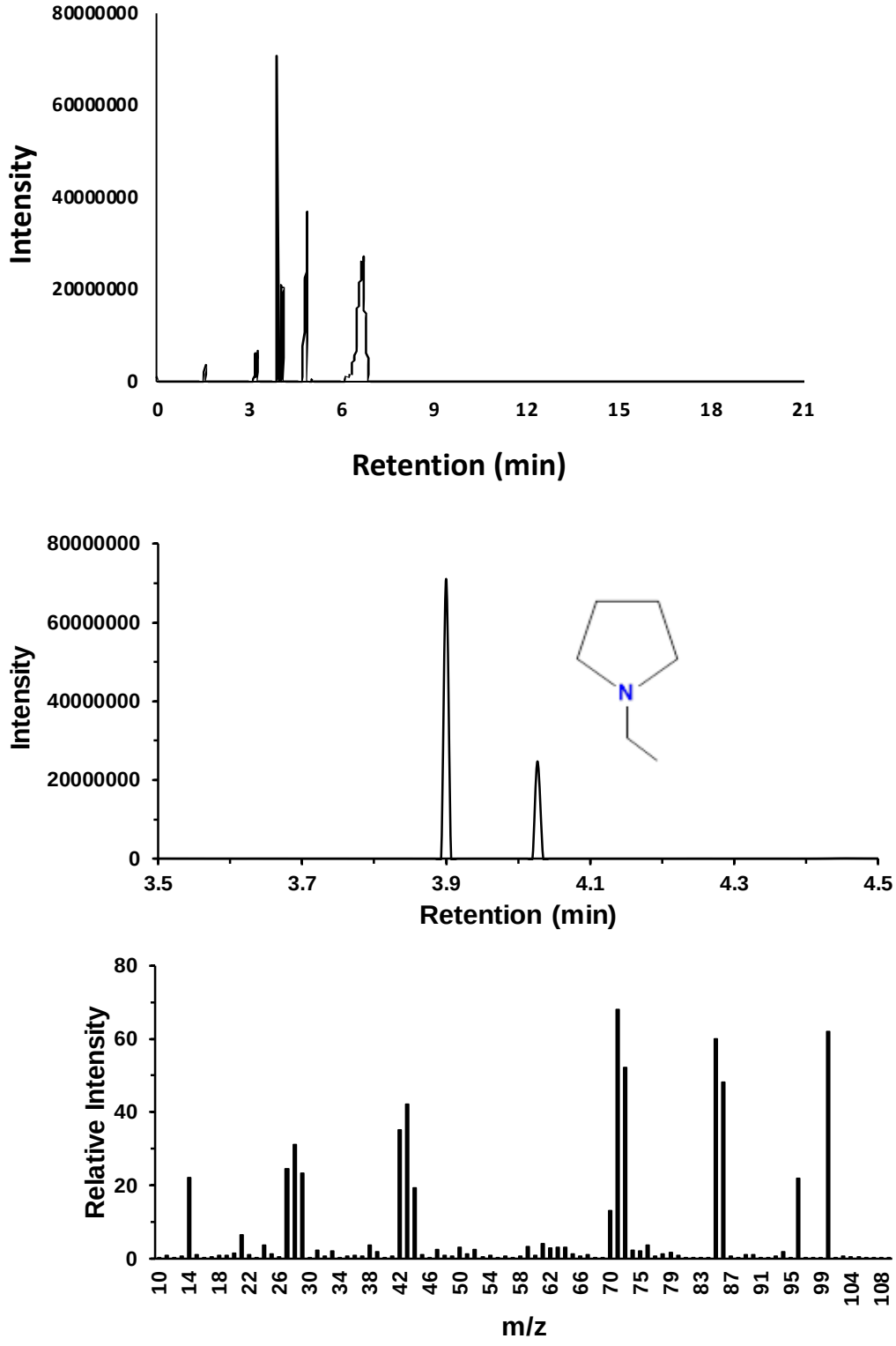


Fig. S16 GC/MS of the cyclization of butylethylamine. The sample was analyzed with decane as an internal standard.

Synthesis of 1-butylpyrrolidine:

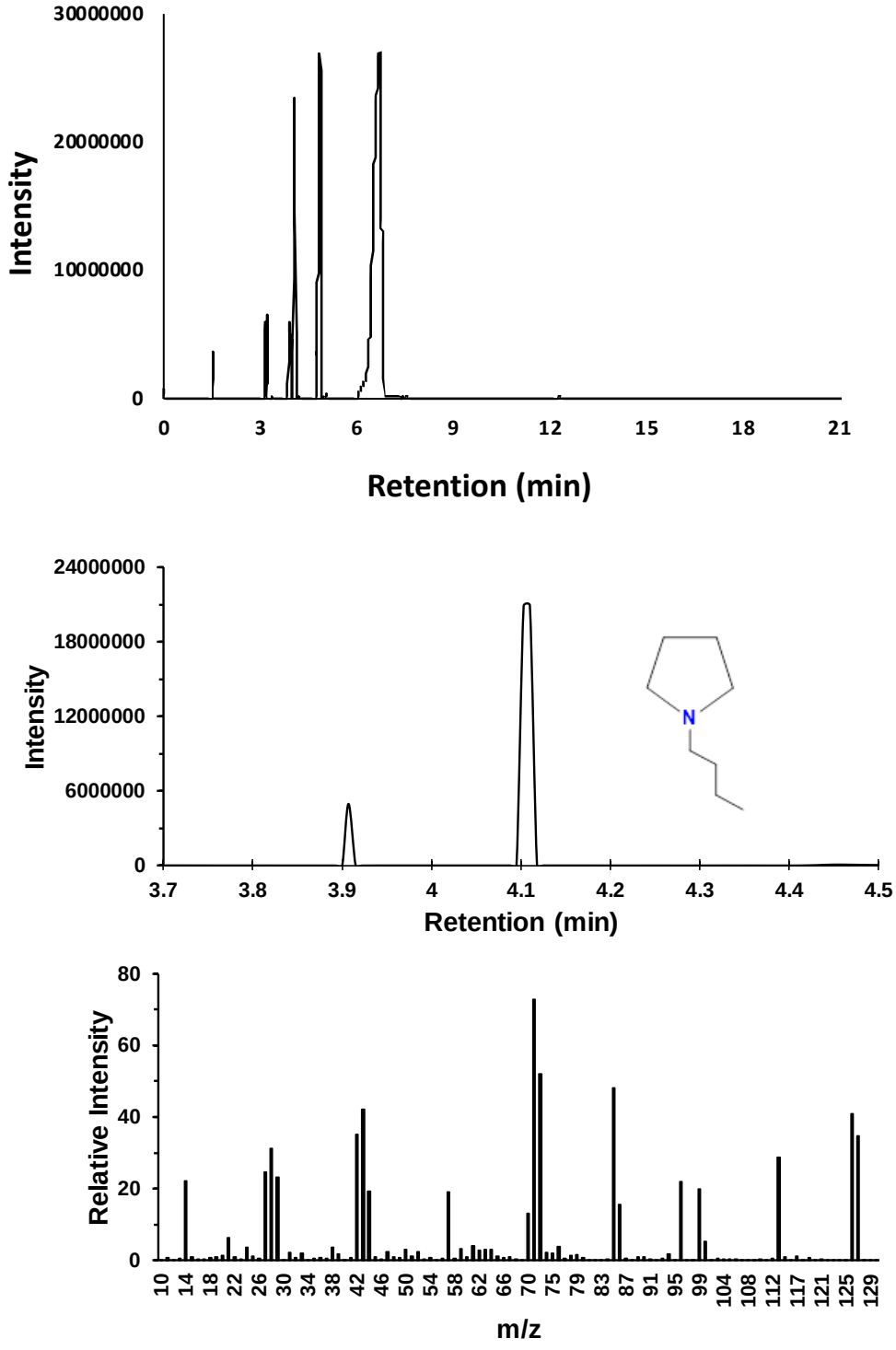


Fig. S17 GC/MS of the cyclization of di-butylamine. The sample was analyzed with decane as an internal standard.

Synthesis of piperdine:

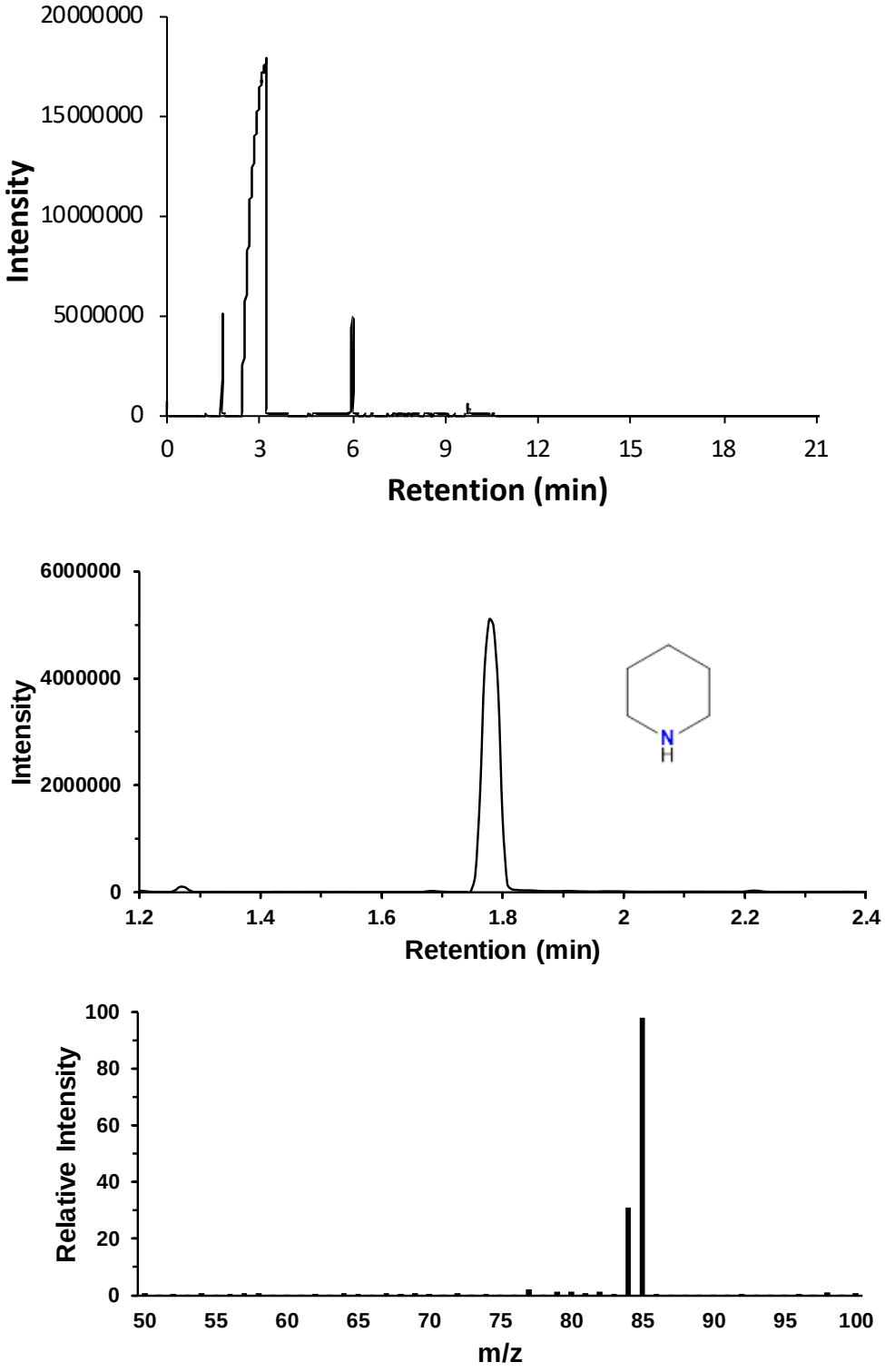


Fig. S18 GC/MS of the cyclization of pentylamine. The sample was analyzed with decane as an internal standard.

Synthesis of 2-methylpiperdine:

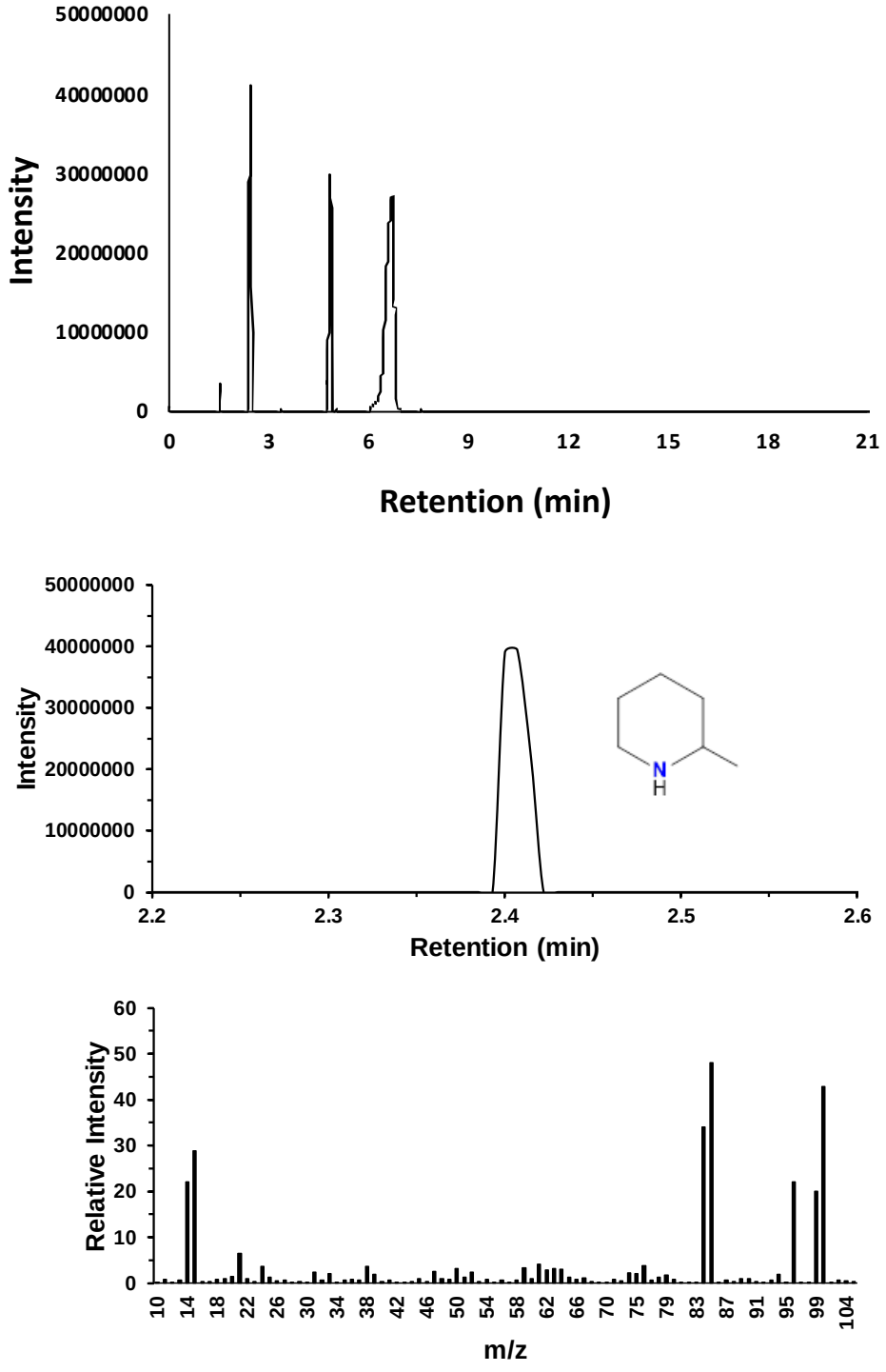


Fig. S19 GC/MS of the cyclization of hexylamine. The sample was analyzed with decane as an internal standard.

Synthesis of 1-pentylpiperdine:

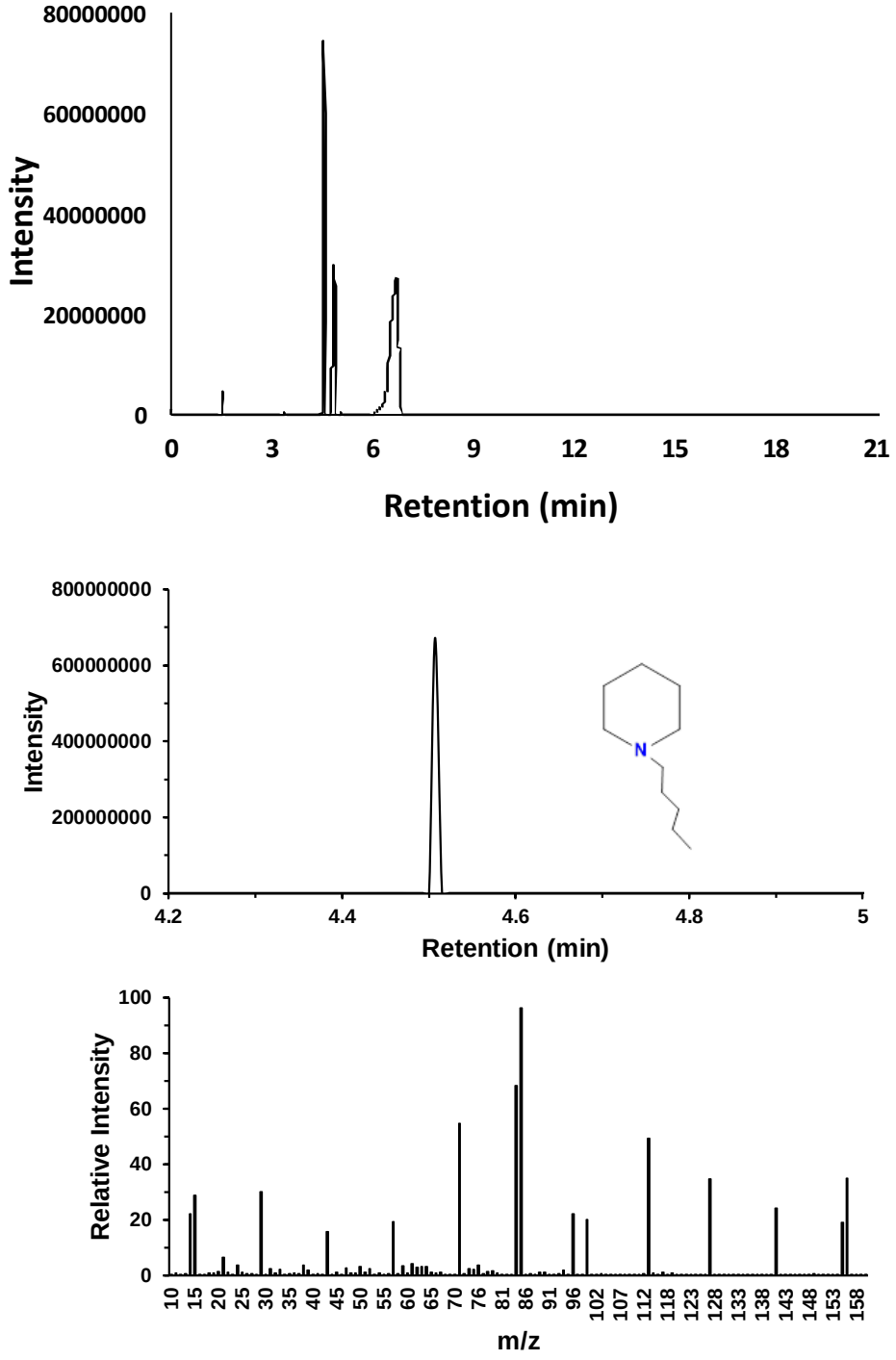


Fig. S20 GC/MS of the cyclization of di-pentylamine. The sample was analyzed with decane as an internal standard.

Synthesis of 2-ethylpiperdine:

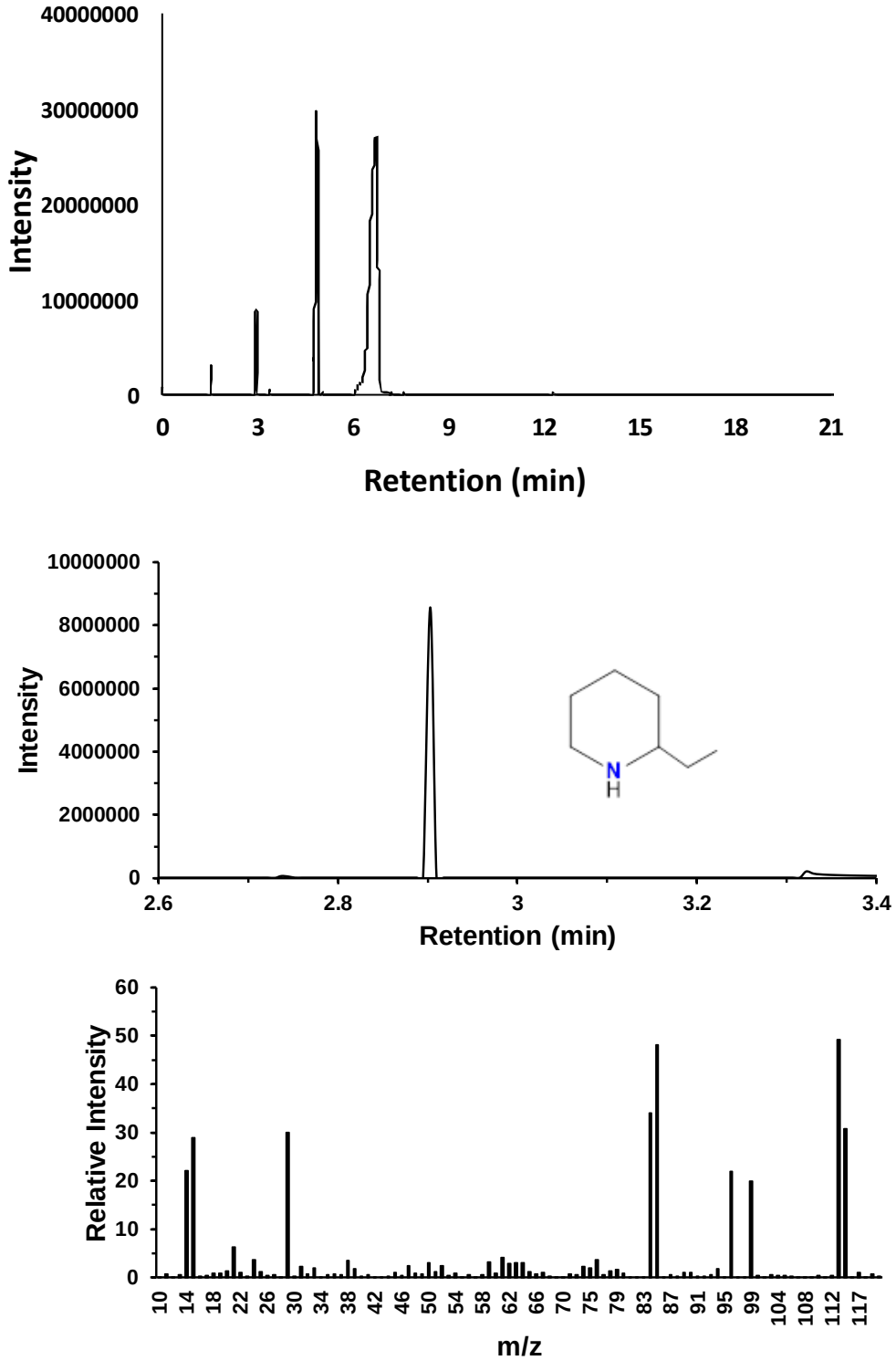


Fig. S21 GC/MS of the cyclization of heptylamine. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)-1-butylamine:

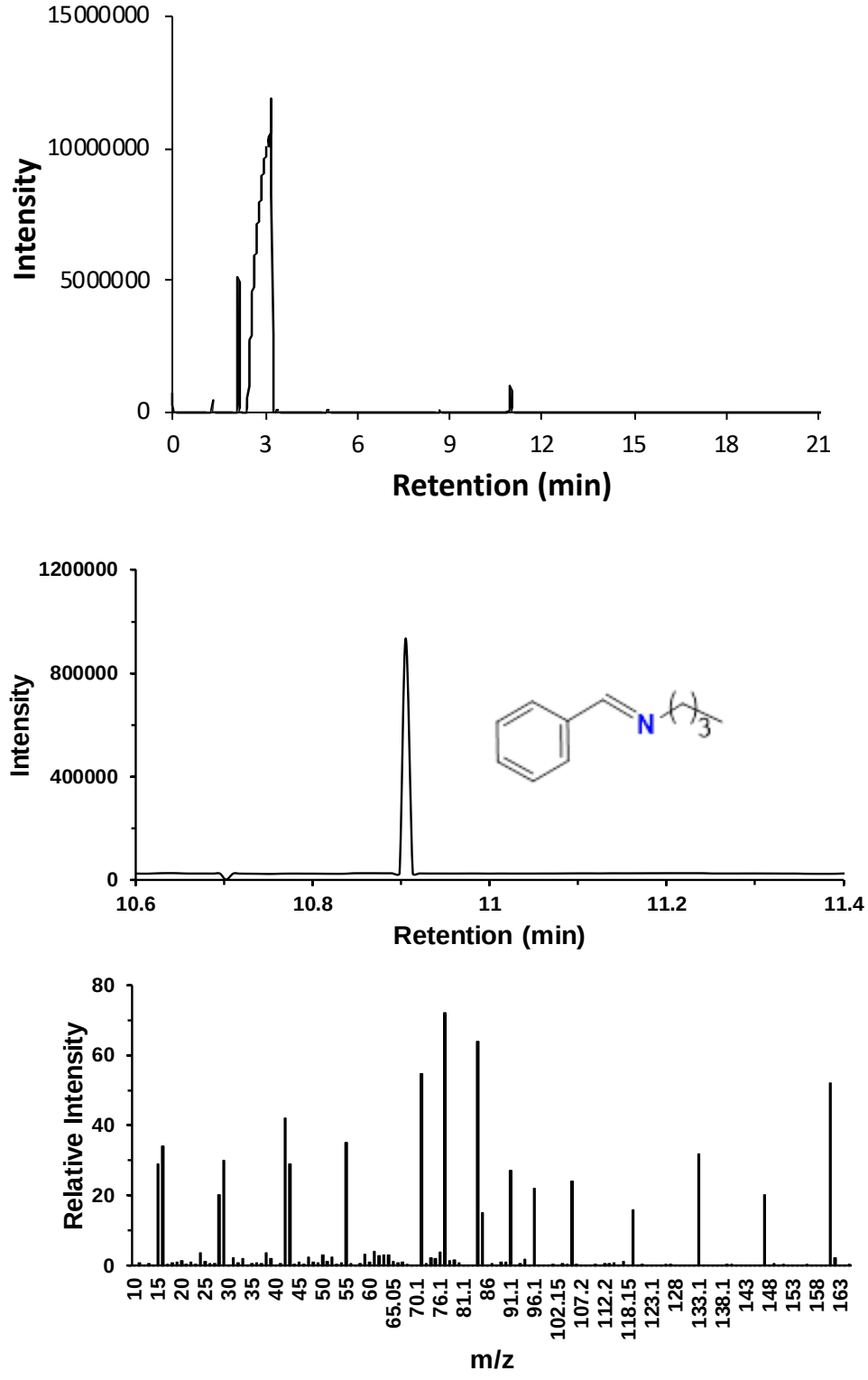


Fig. S22 GC/MS of the reaction between butylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)-1-hexylamine:

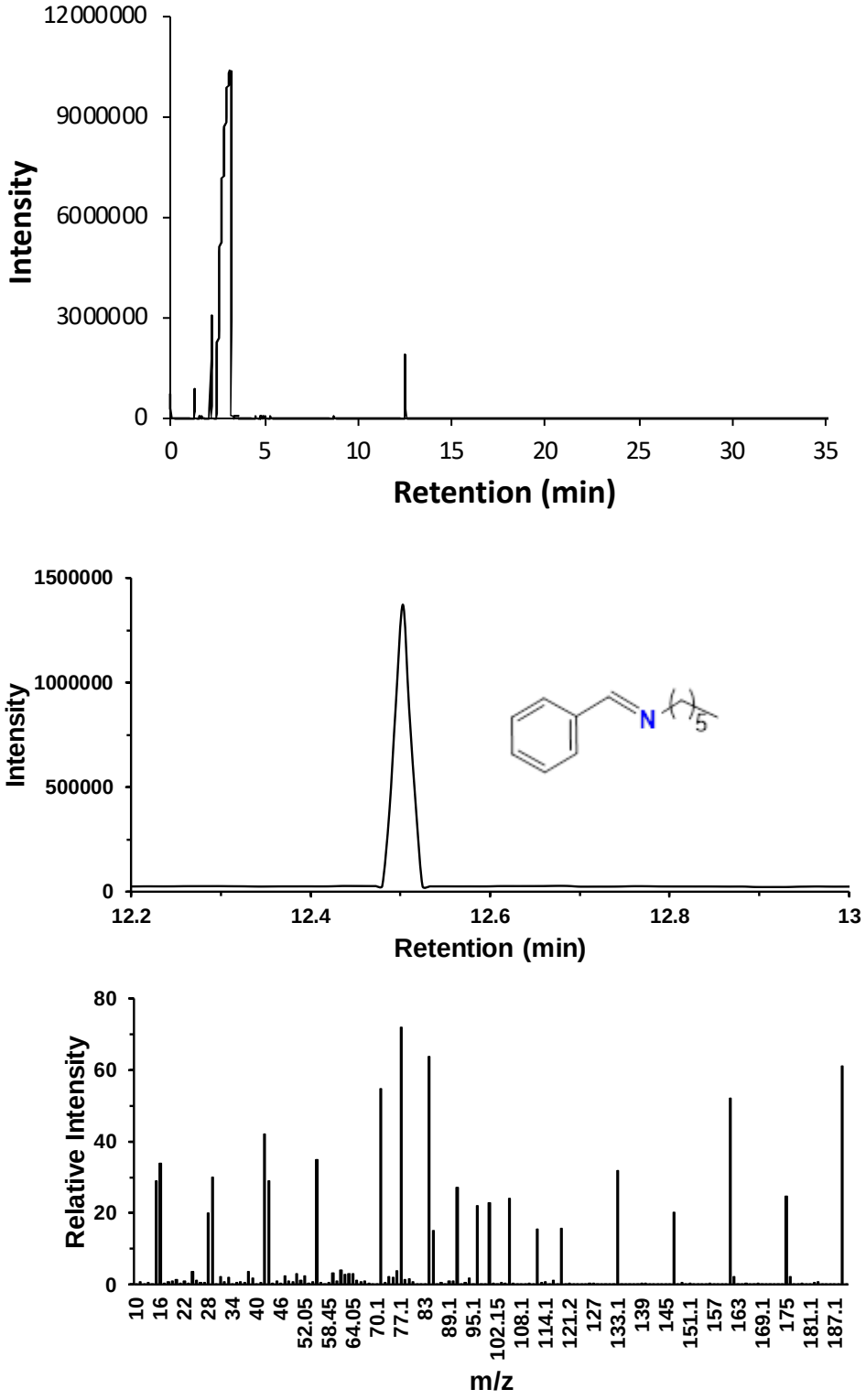


Fig. S23 GC/MS of the reaction between hexylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)-1-heptylamine:

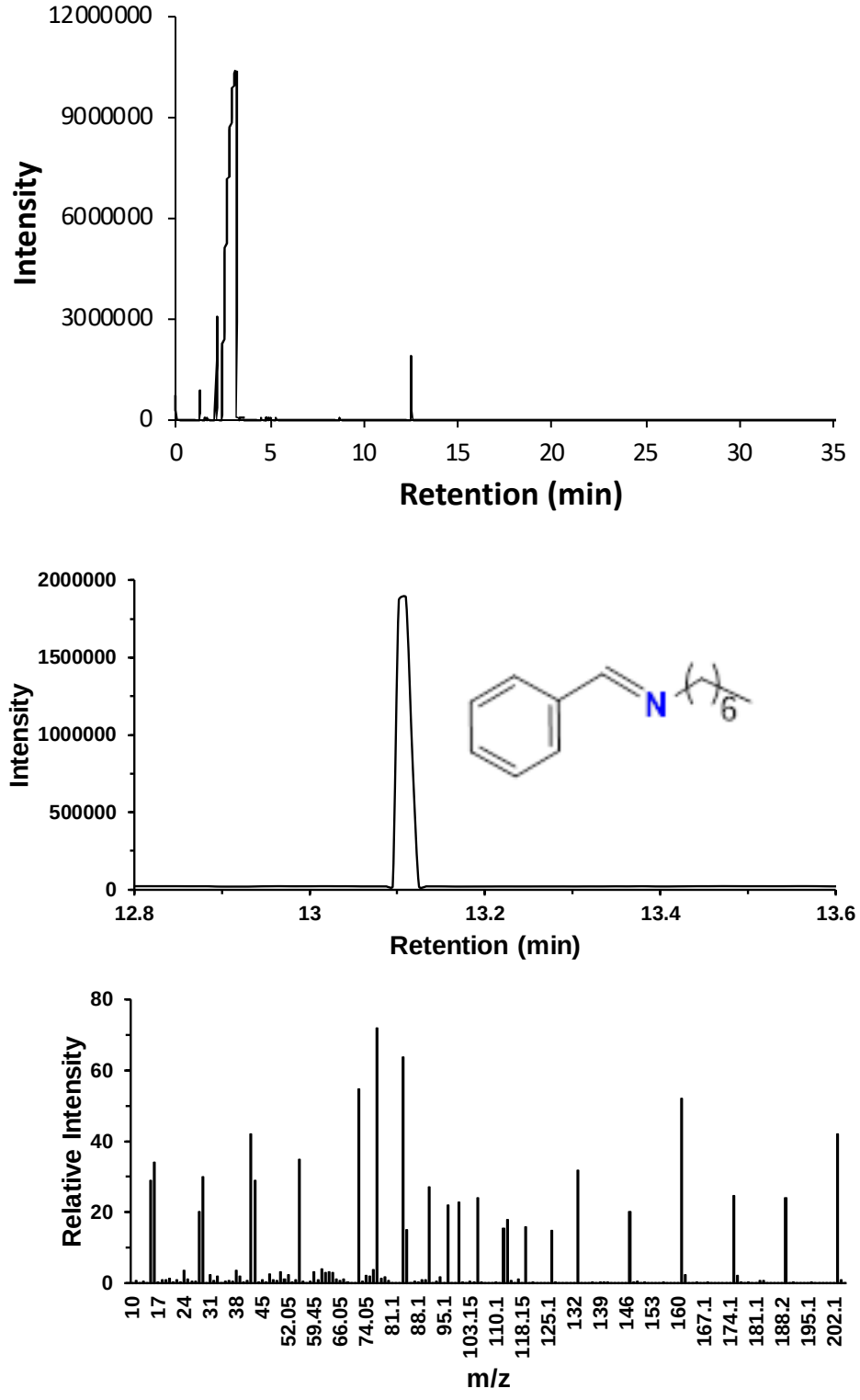


Fig. S24 GC/MS of the reaction between heptylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)-1-octylamine:

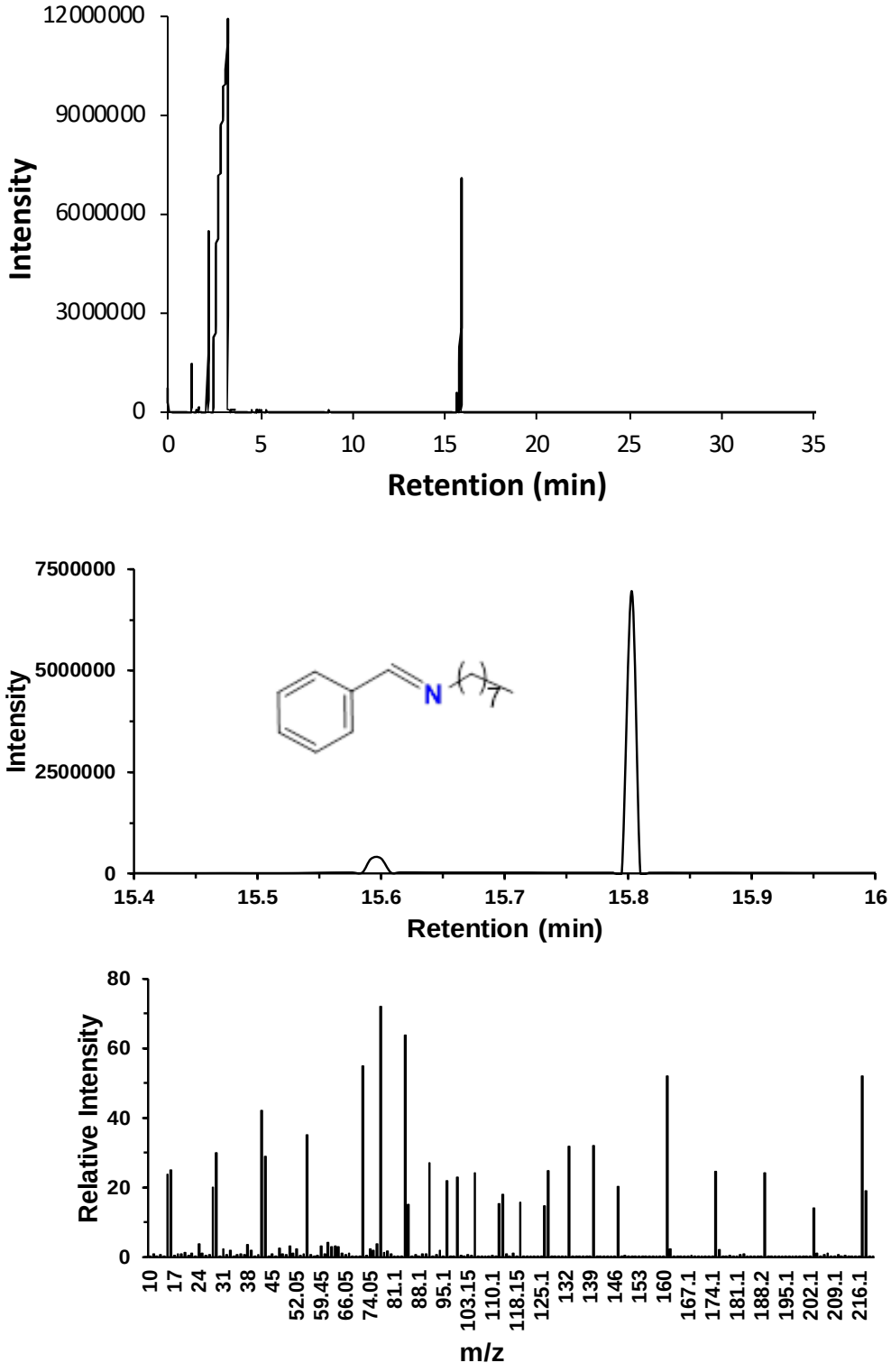


Fig. S25 GC/MS of the reaction between octylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)-1-nonylamine:

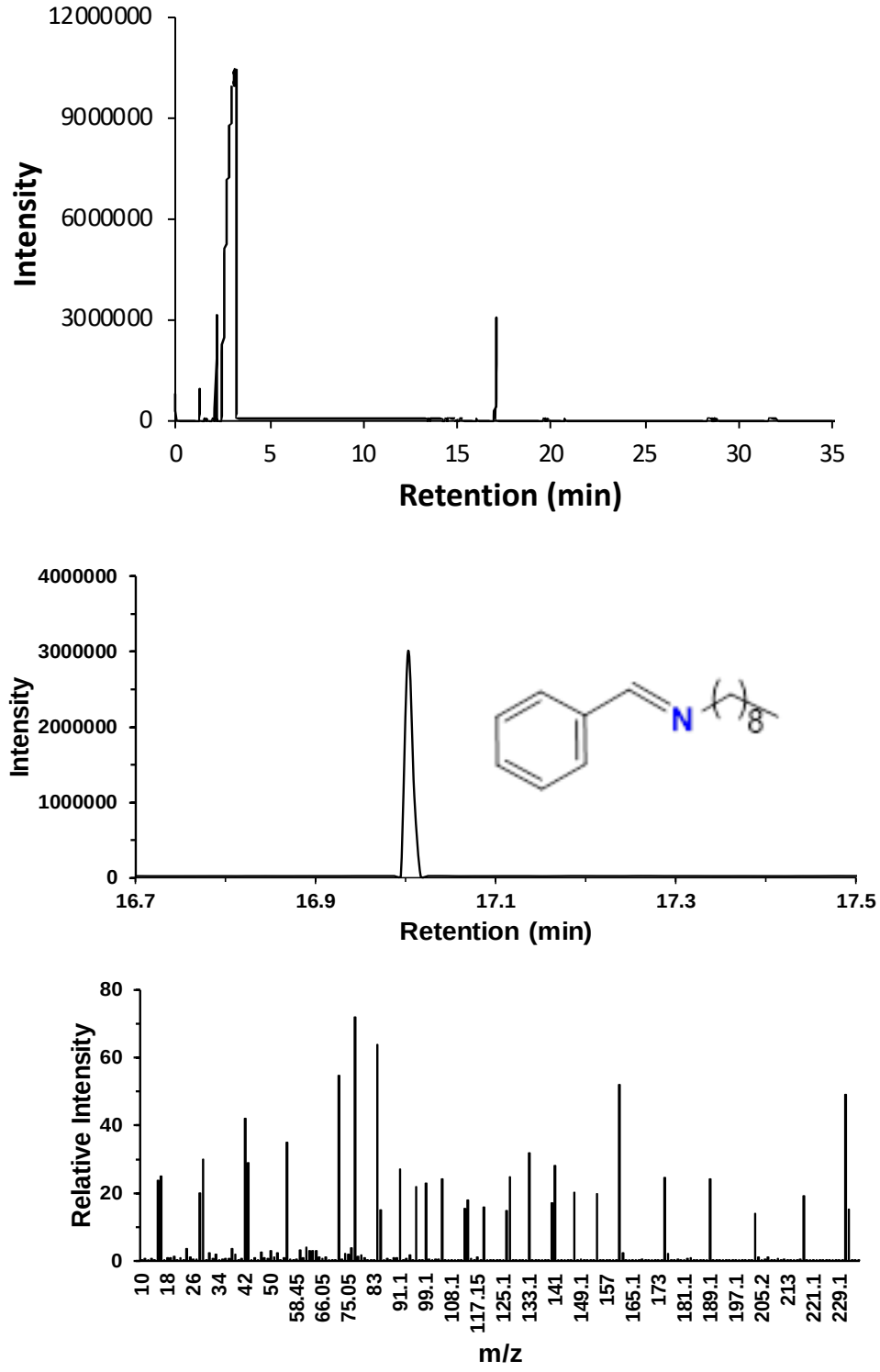


Fig. S26 GC/MS of the reaction between nonylamine and toluene. Toluene (1 eq., 157.6 mg, 1.71 mmol), nonylamine (1 eq., 247.9 mg, 1.71 mmol) at 110 ºC, 3 h. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)-1-decylamine:

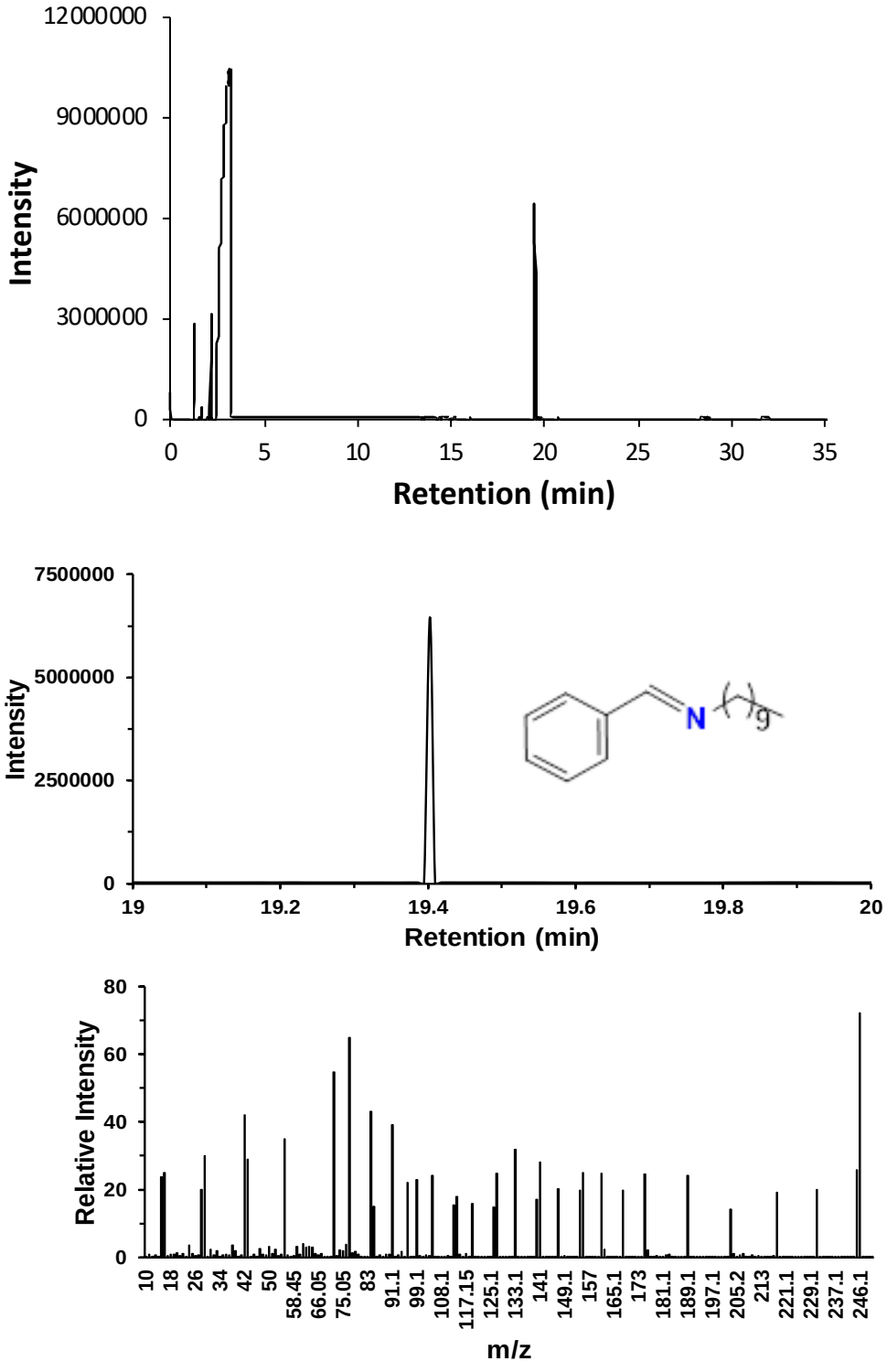


Fig. S27 GC/MS of the reaction between decylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of α-methyl-N-(phenylmethylene)benzenemethanamine:

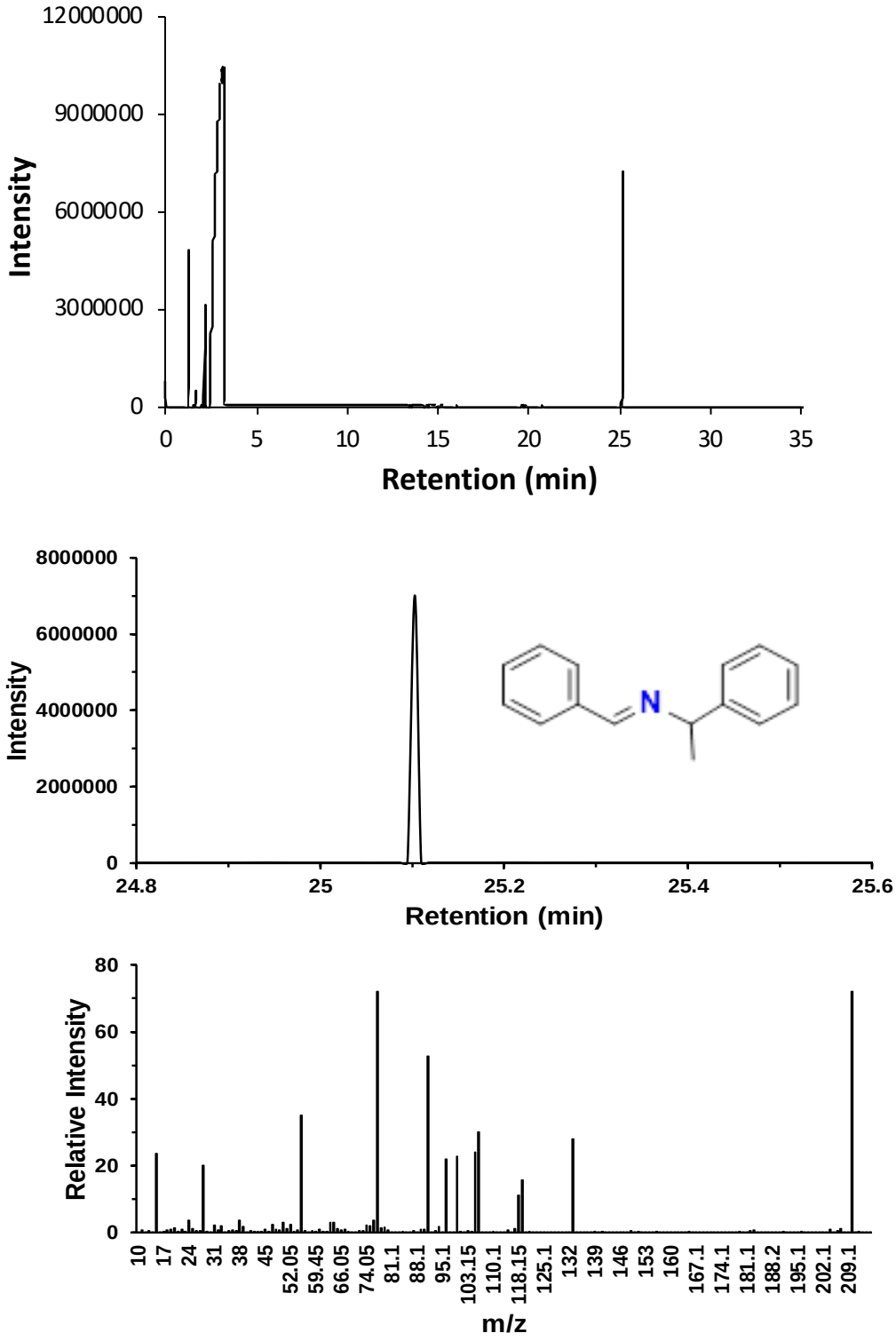


Fig. S28 GC/MS of the reaction between α-methylbenzylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)benzenamine:

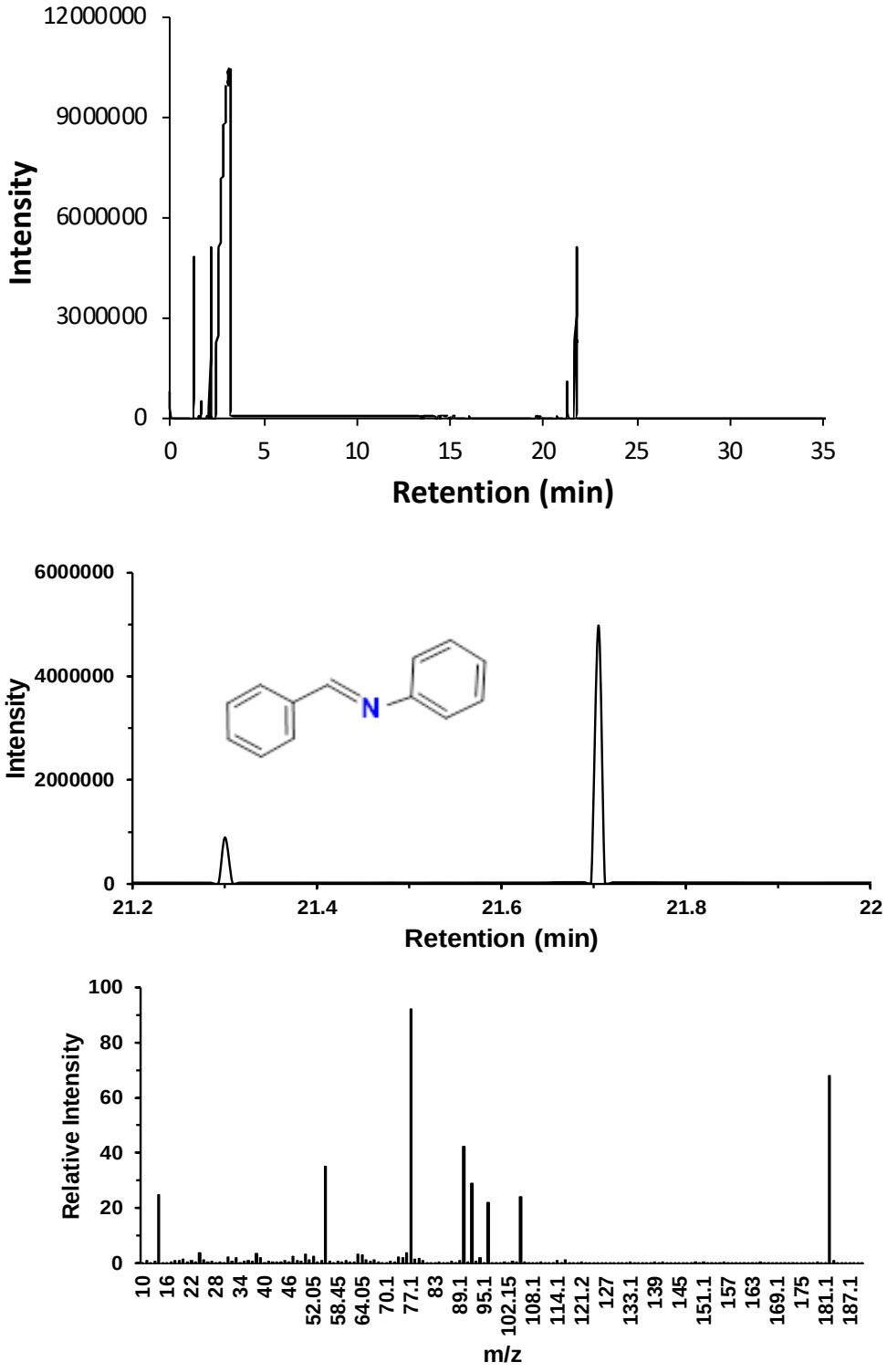


Fig. S29 GC/MS of the reaction between aniline and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(phenylmethylene)benzenemethanamine:

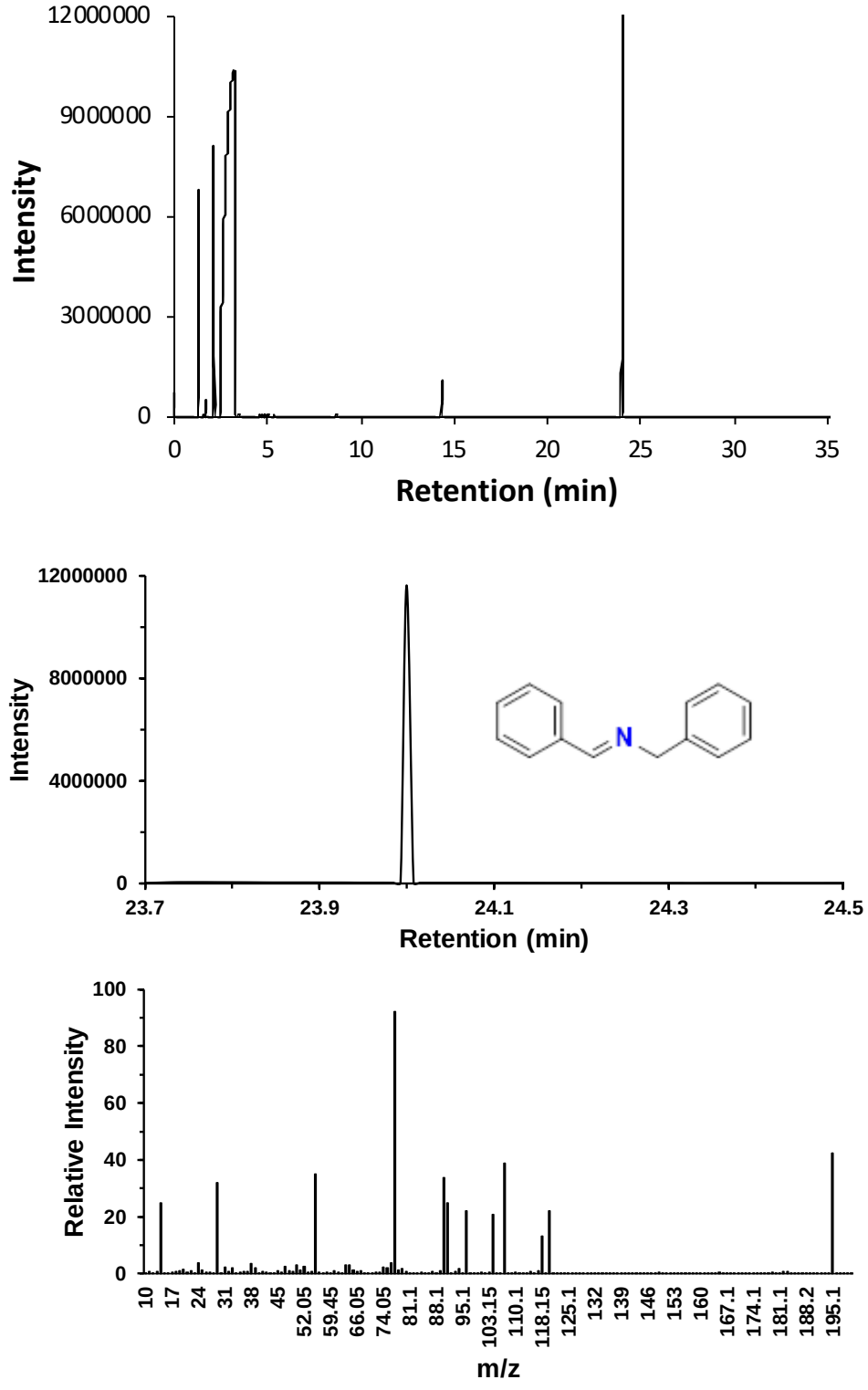


Fig. S30 GC/MS of the reaction between benzylamine and toluene. The sample was analyzed with decane as an internal standard.

Synthesis of 3-amino-N-propylbezenemethanamine:

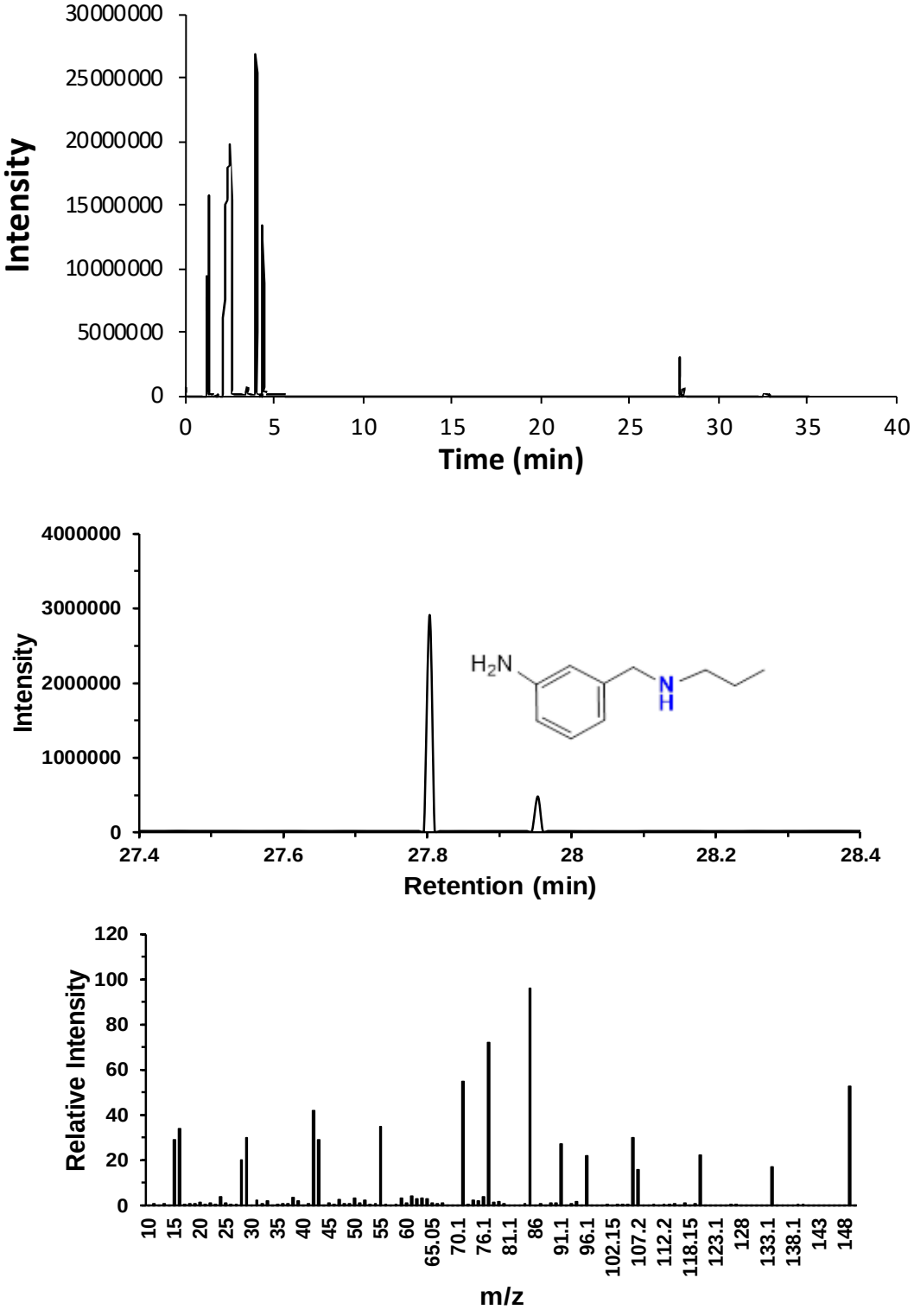


Fig. S31 GC/MS of the reaction between propylamine and m-toluidine. The sample was analyzed with decane as an internal standard.

Synthesis of 3-nitro-N-propylbezenemethanamine:

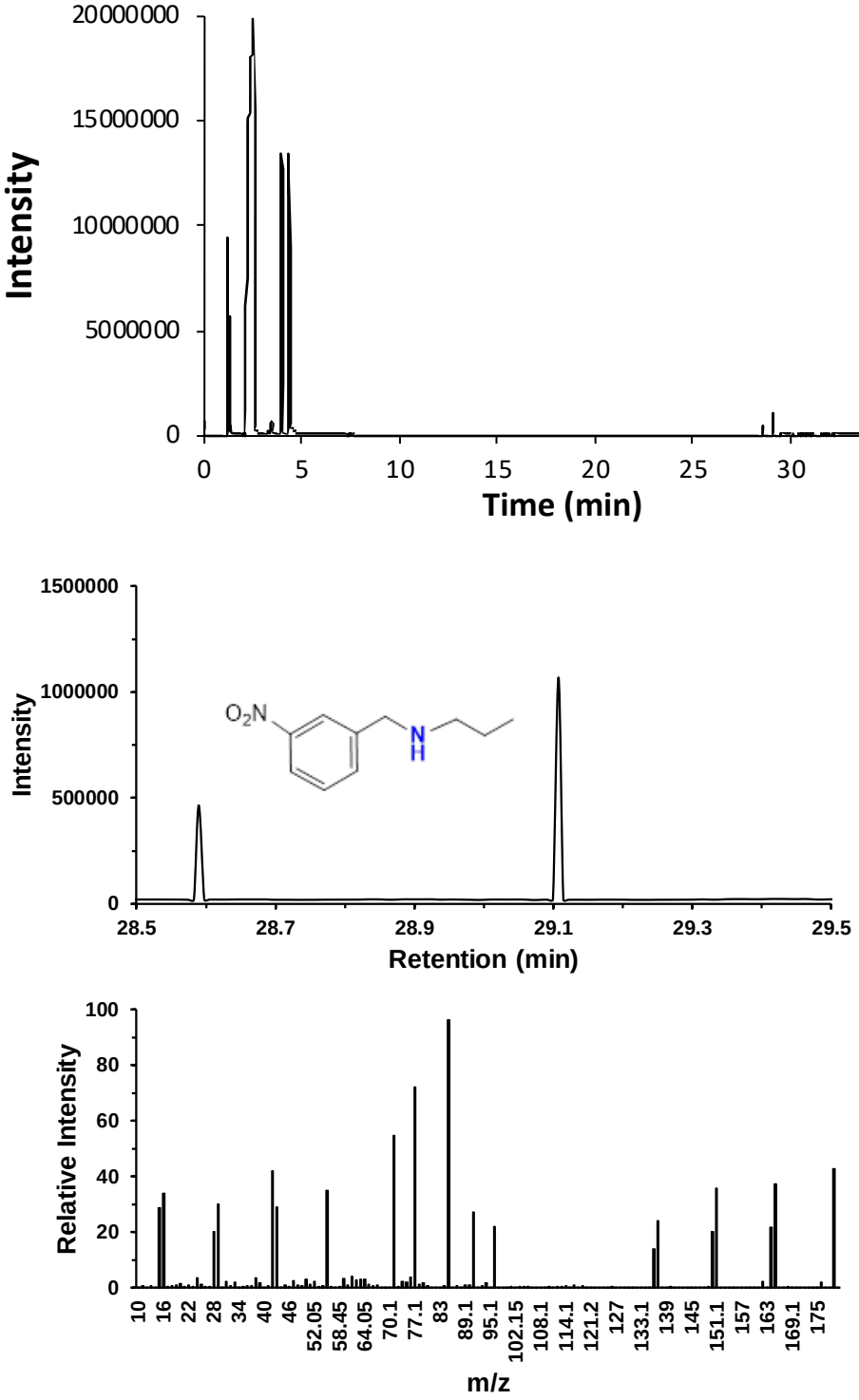


Fig. S32 GC/MS of the reaction between propylamine and m-nitrotoluene. The sample was analyzed with decane as an internal standard.

Synthesis of 3-methoxy-N-propylbenzenemethanamine:

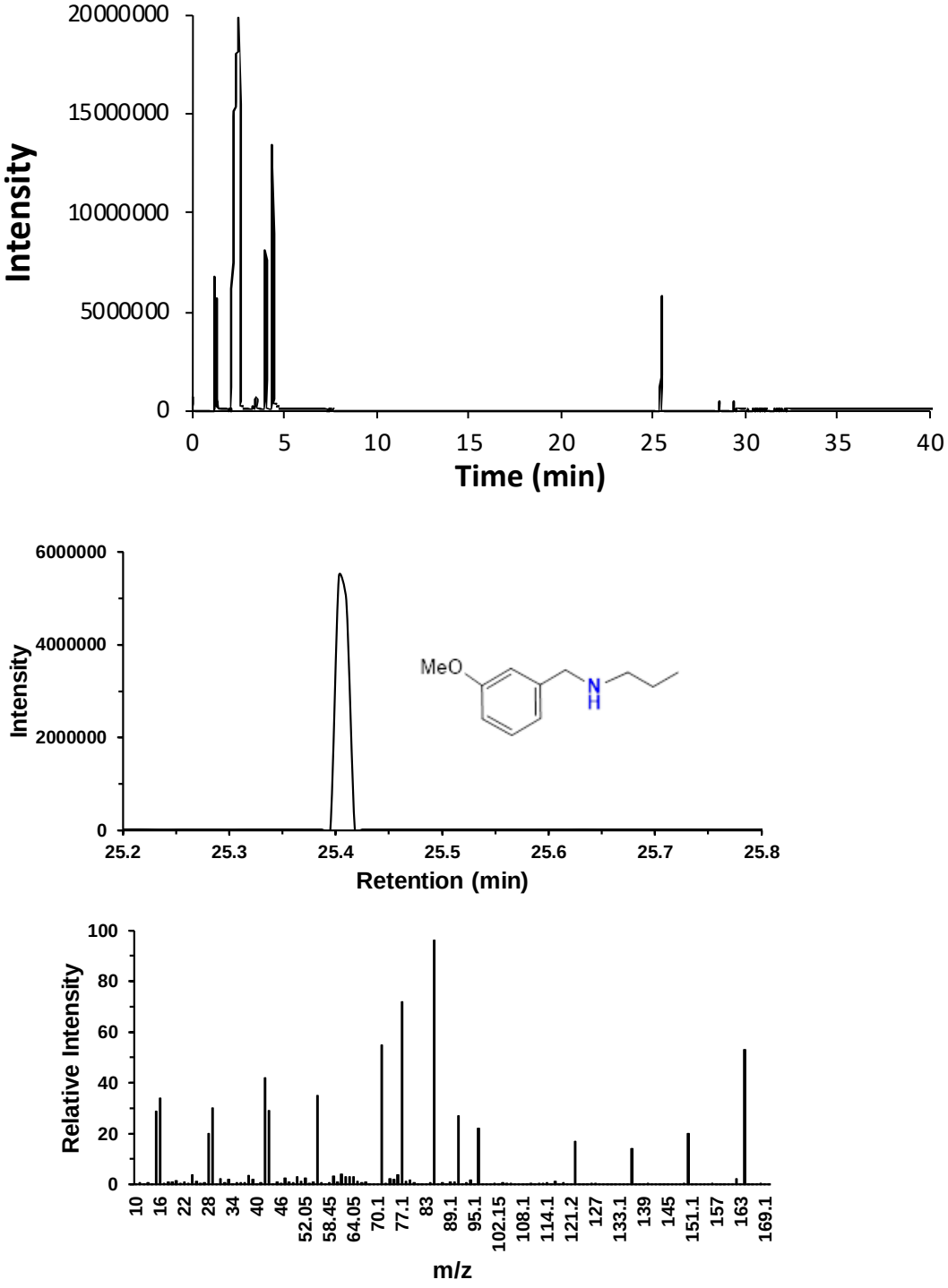


Fig. S33 GC/MS of the reaction between propylamine and m-anisole. The sample was analyzed with decane as an internal standard.

Synthesis of N-hexyl-4-methyl-benzenemethanamine:

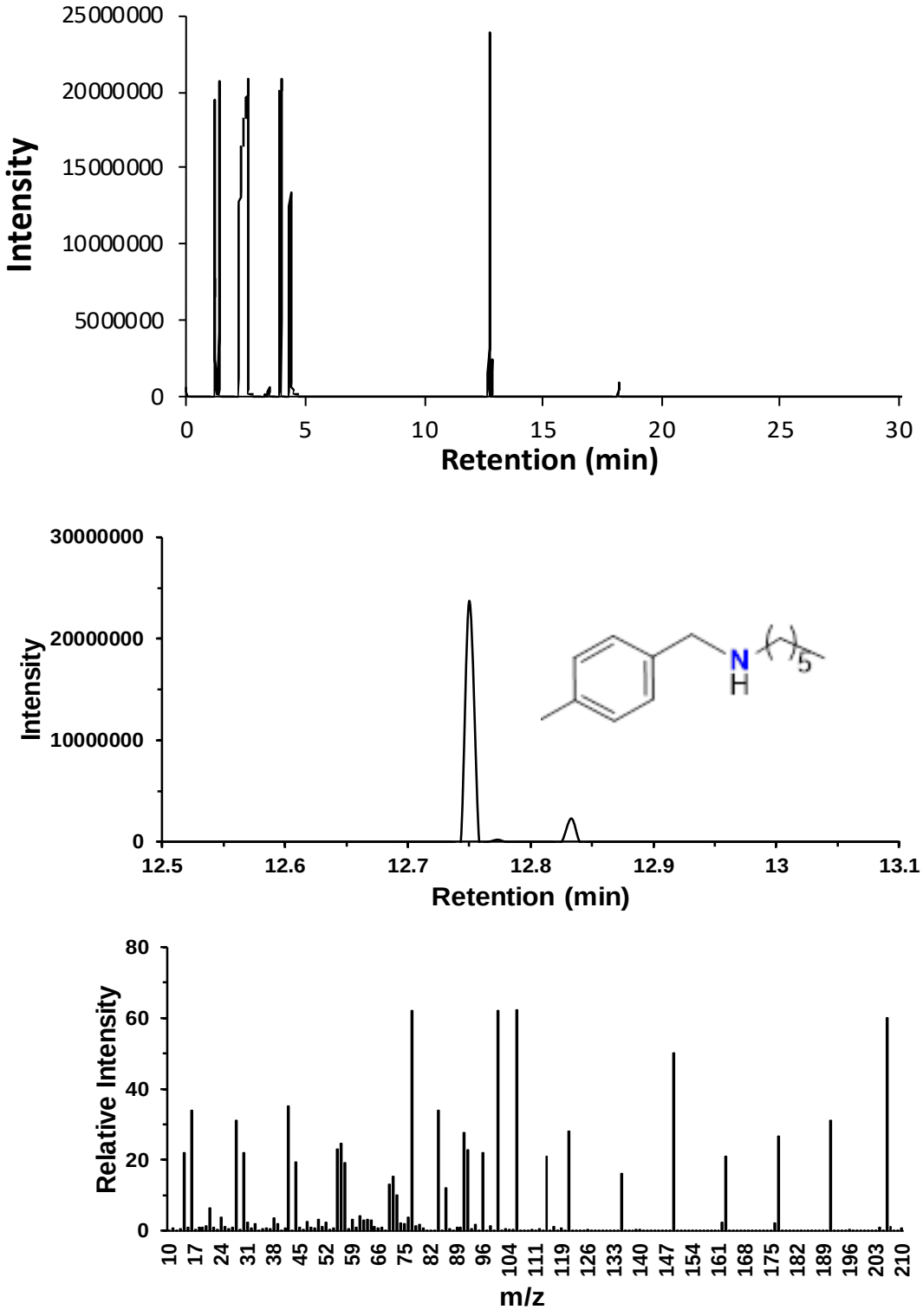


Fig. S34 GC/MS of the reaction between hexylamine and p-xylene. The sample was analyzed with decane as an internal standard.

Synthesis of N-hexyl-α-methylbenzenemethanamine:

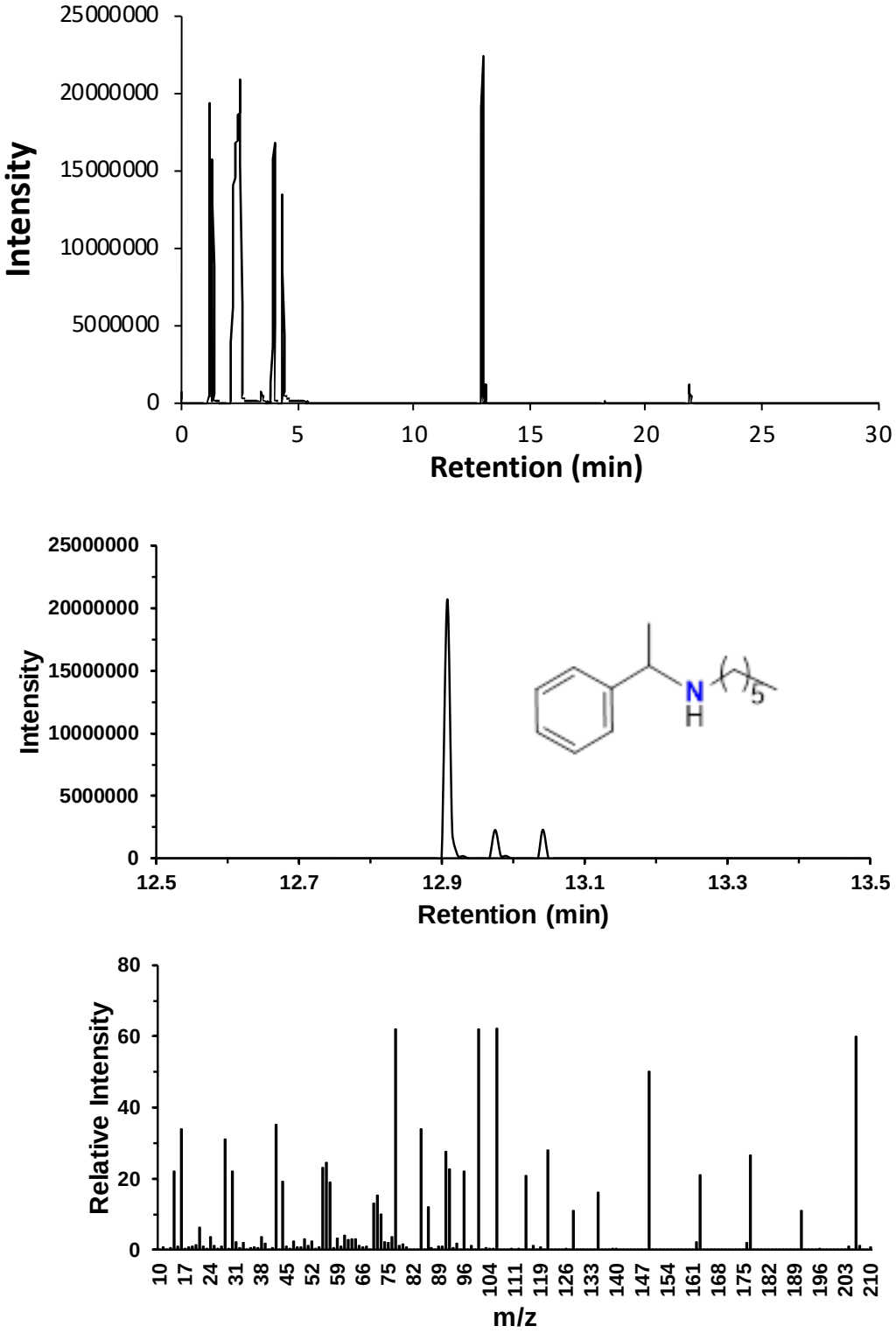


Fig. S35 GC/MS of the reaction between hexylamine and ethylbenzene. The sample was analyzed with decane as an internal standard.

Synthesis of N-hexyl-(1-vinylcyclohexyl)amine:

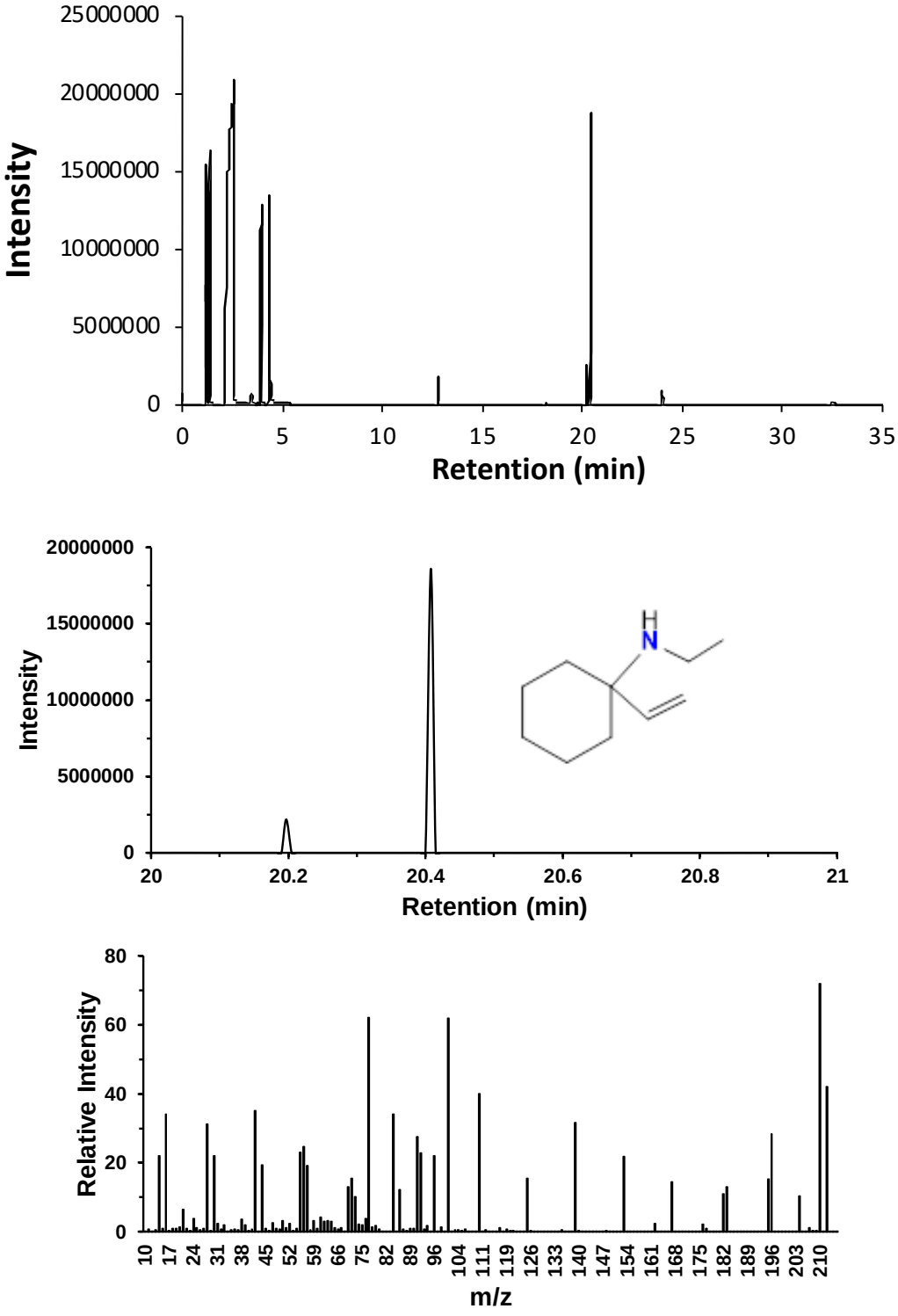


Fig. S36 GC/MS of the reaction between hexylamine and vinylcyclohexane. The sample was analyzed with decane as an internal standard.

Synthesis of N-hexylcyclohexanamine:

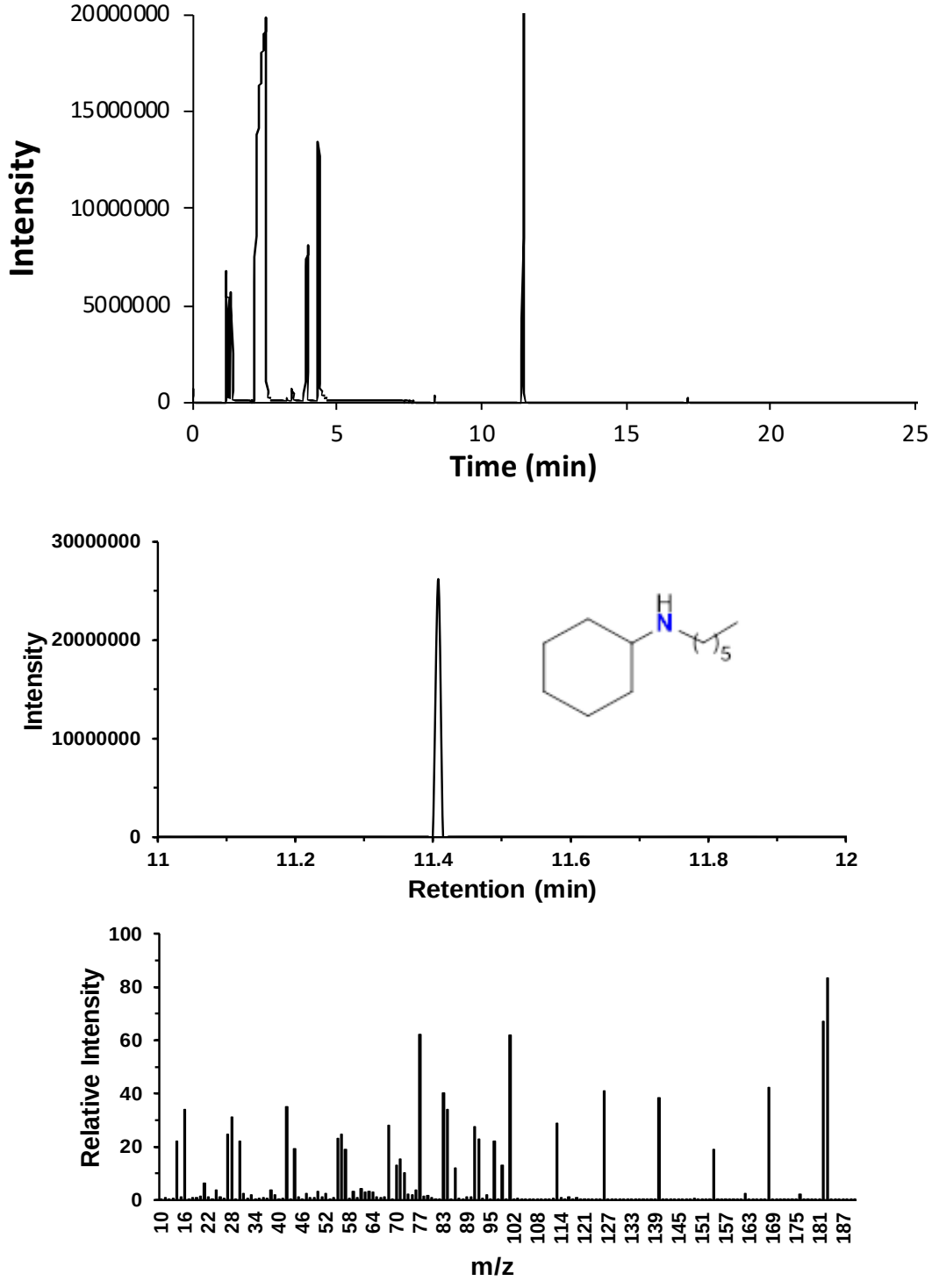


Fig. S37 GC/MS of the reaction between hexylamine and cyclohexane. The sample was analyzed with decane as an internal standard.

Synthesis of N-(4-methylbenzyl)-3-phenylpropan-1-amine:

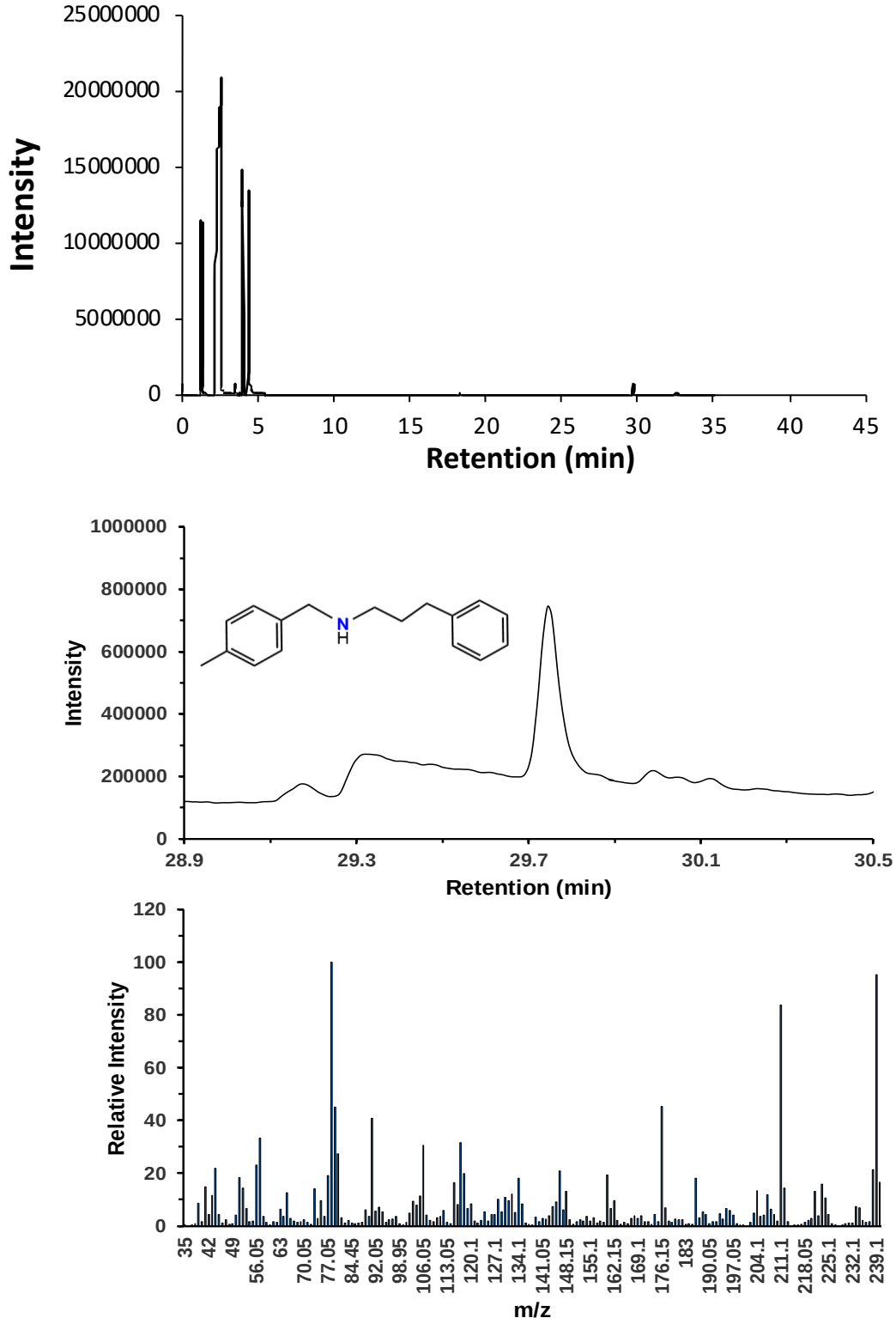


Fig. S38 GC/MS of the reaction between 3-phenylpropylamine and p-xylene. The sample was analyzed with decane as an internal standard.

Synthesis of N-(4-(tert-butyl)benzyl)-3-phenylpropan-1-amine:

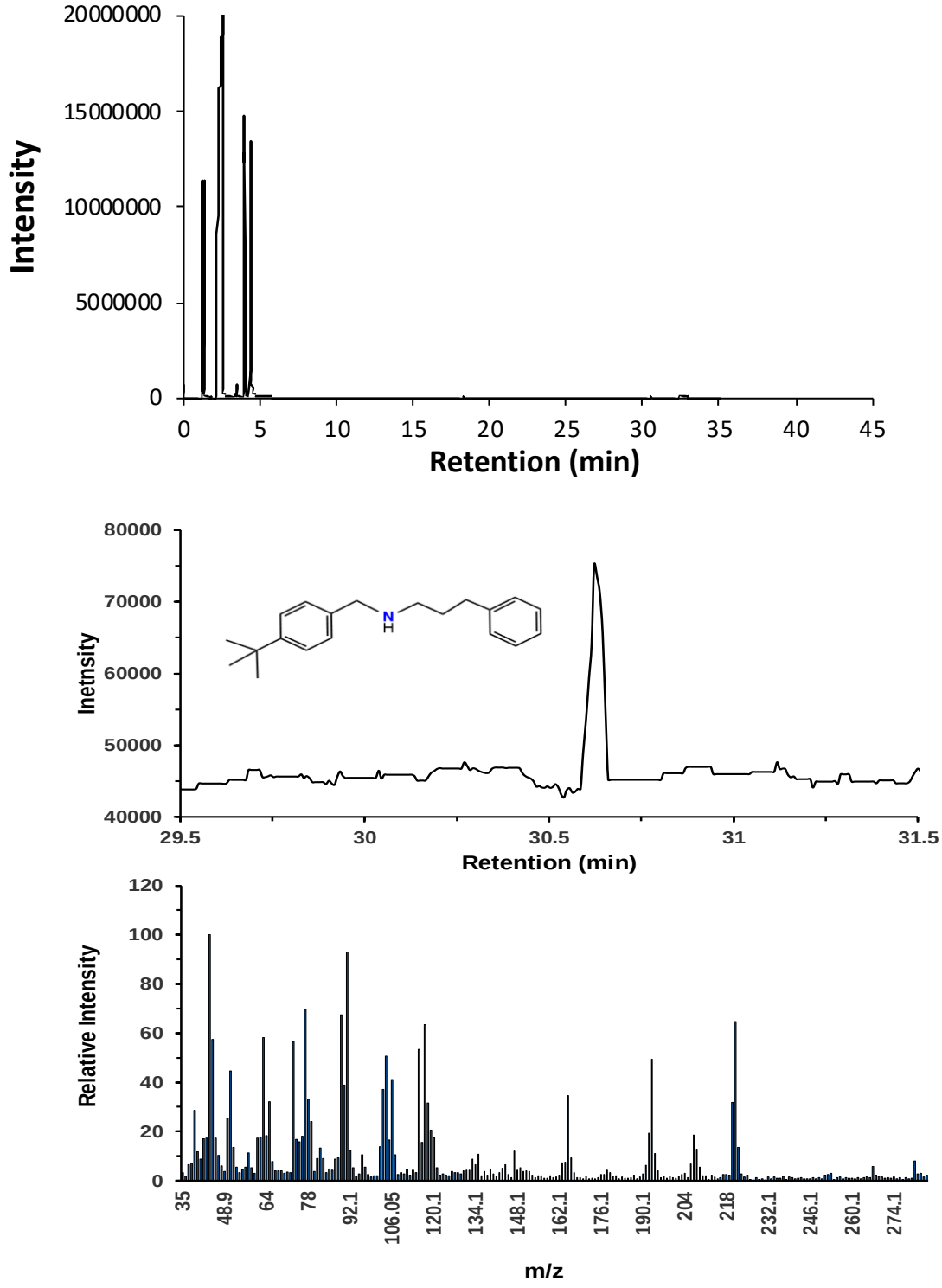


Fig. S39 GC/MS of the reaction between 3-phenylpropylamine and 4-tert-butyltoluene. The sample was analyzed with decane as an internal standard.

Synthesis of N-phenylbenzenemethanamine-d:

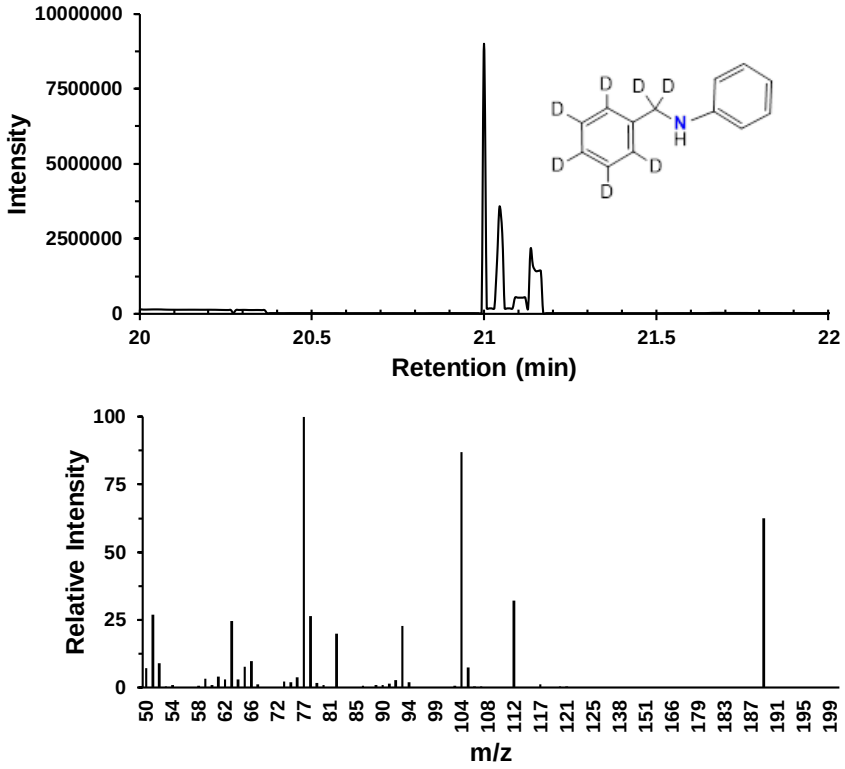


Fig. S40 GC/MS of the reaction between aniline and toluene-d^8. The sample was analyzed with decane as an internal standard.

Synthesis of N-propylbezenemethanamine-d:

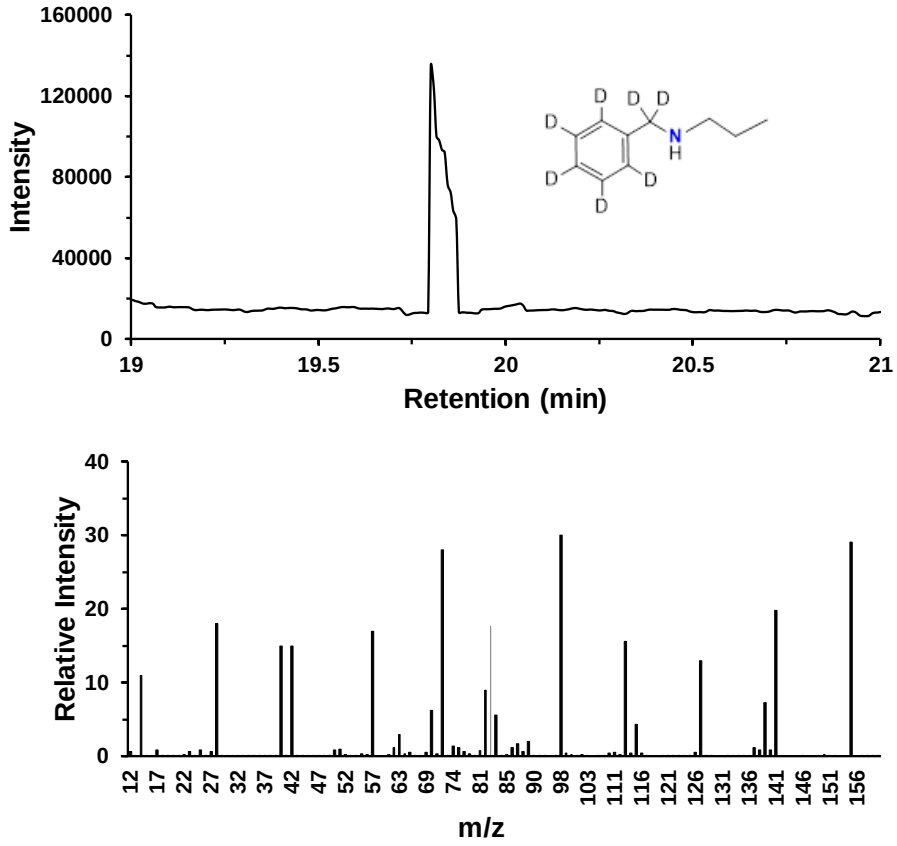


Fig. S41 GC/MS of the reaction between propylamine and toluene-d^8. The sample was analyzed with decane as an internal standard.

Synthesis of N-hexylbezenemethanamine-d:

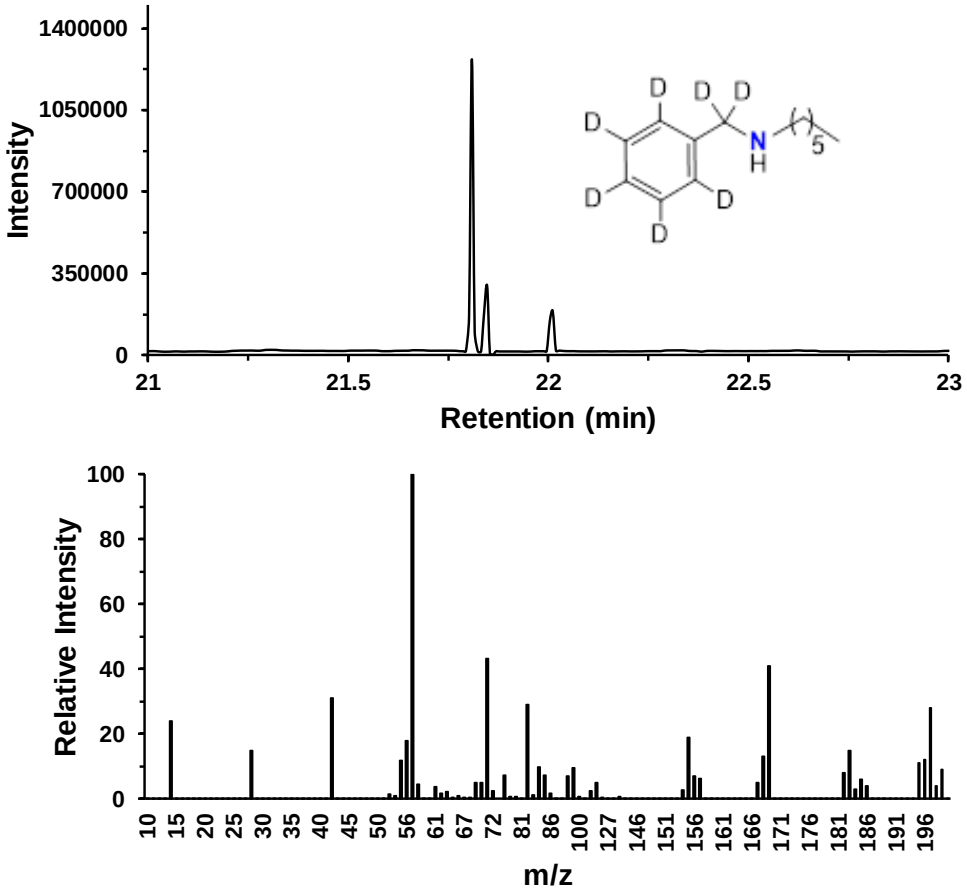


Fig. S42 GC/MS of the reaction between hexylamine and toluene-d^8. The sample was analyzed with decane as an internal standard.

Synthesis of dibenzylamine-d:

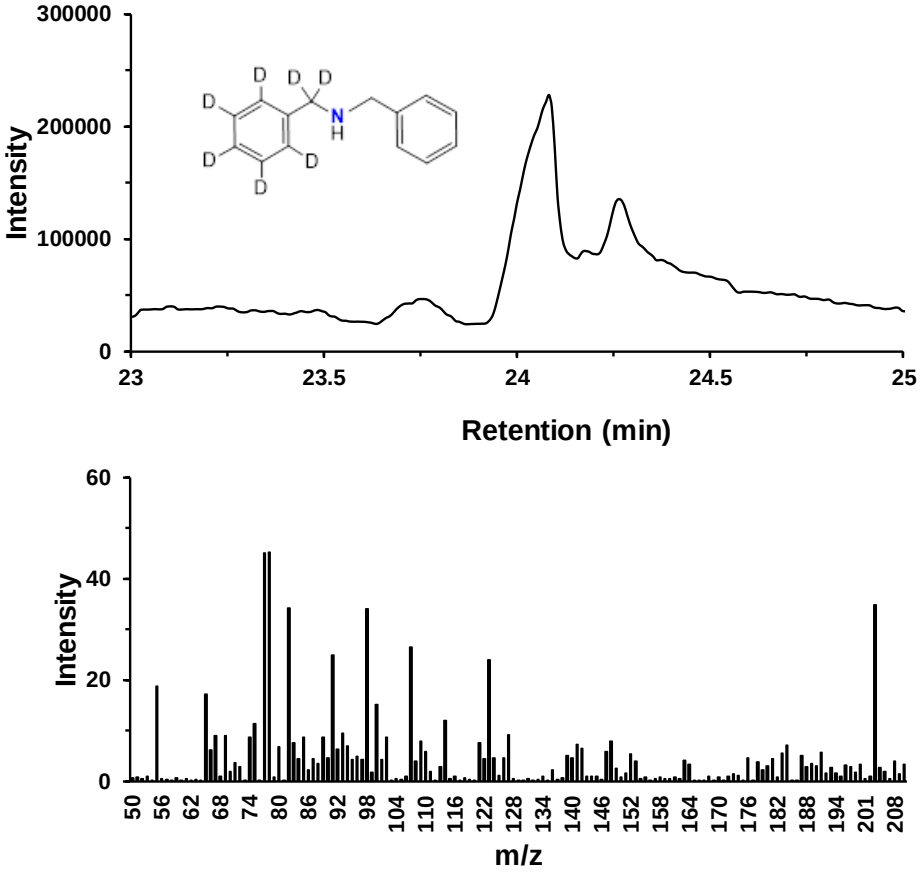


Fig. S43 GC/MS of the reaction between benzylamine and toluene-d^8. The sample was analyzed with decane as an internal standard.

Synthesis of cyclizine:

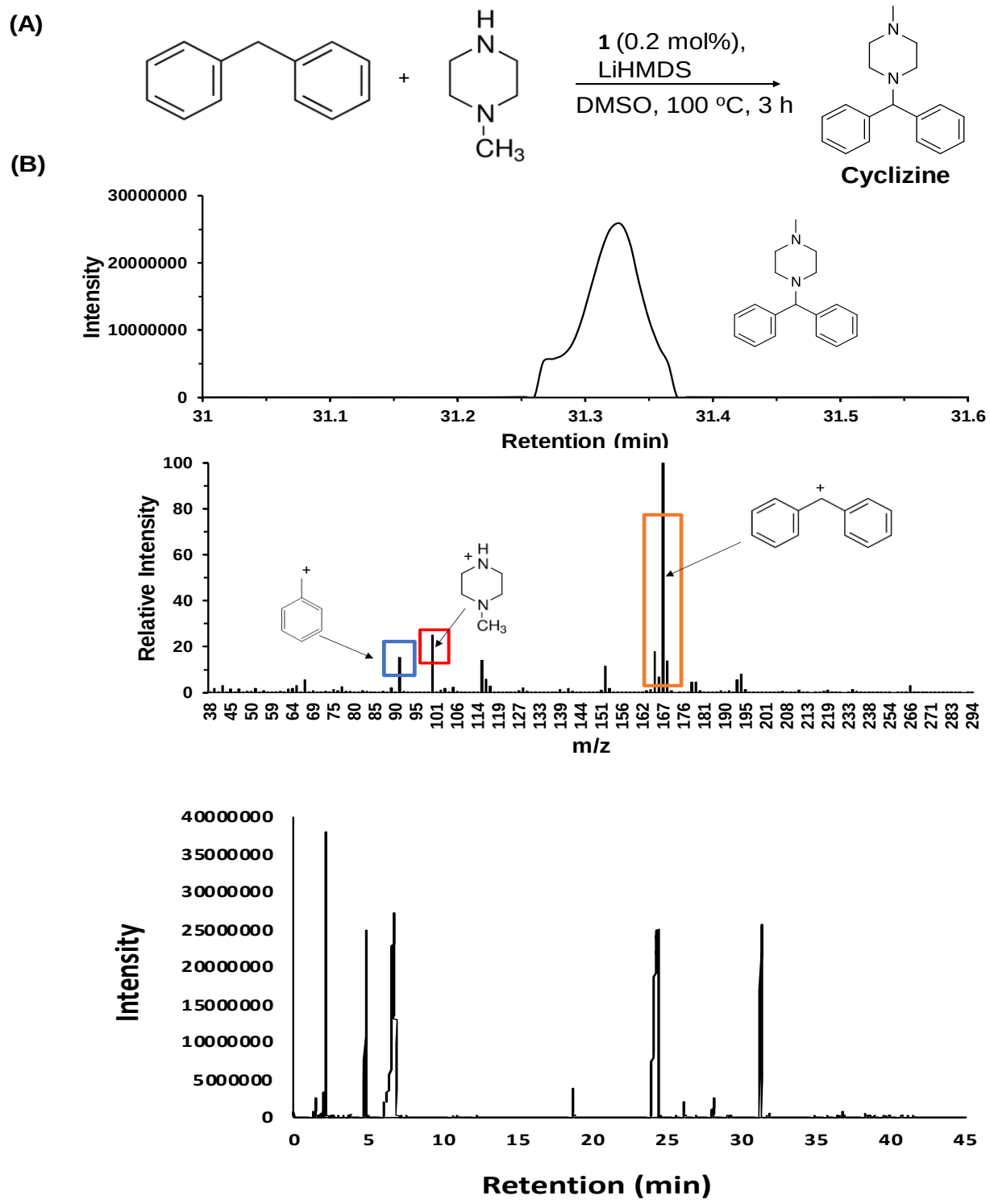


Fig. S44 A) One-step synthesis of cyclizine using **1** and B) GC/MS of cyclizine (M_w 266).

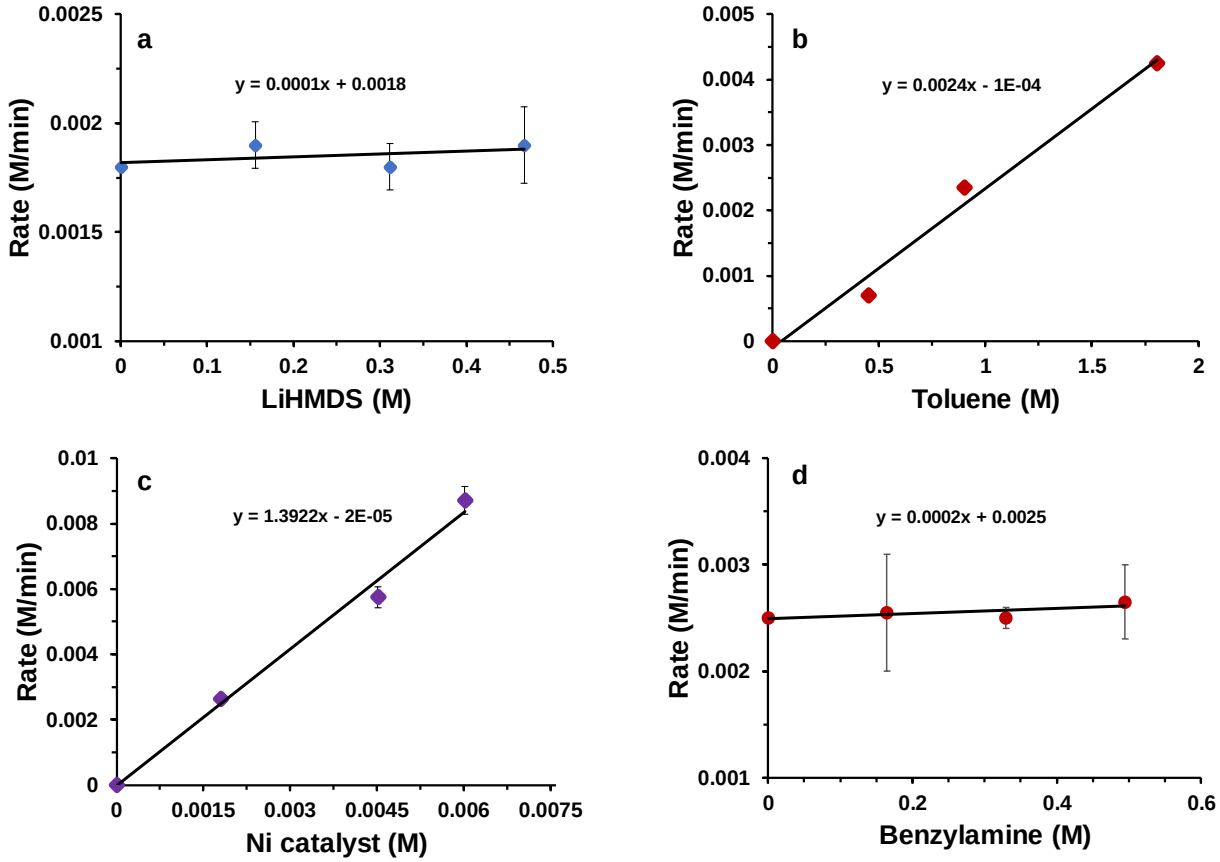


Fig. S45 Effect of a) LiHMDS, b) toluene, c) **1**, and d) benzylamine concentrations on the rate of dibenzylamine product yield at 110 °C.

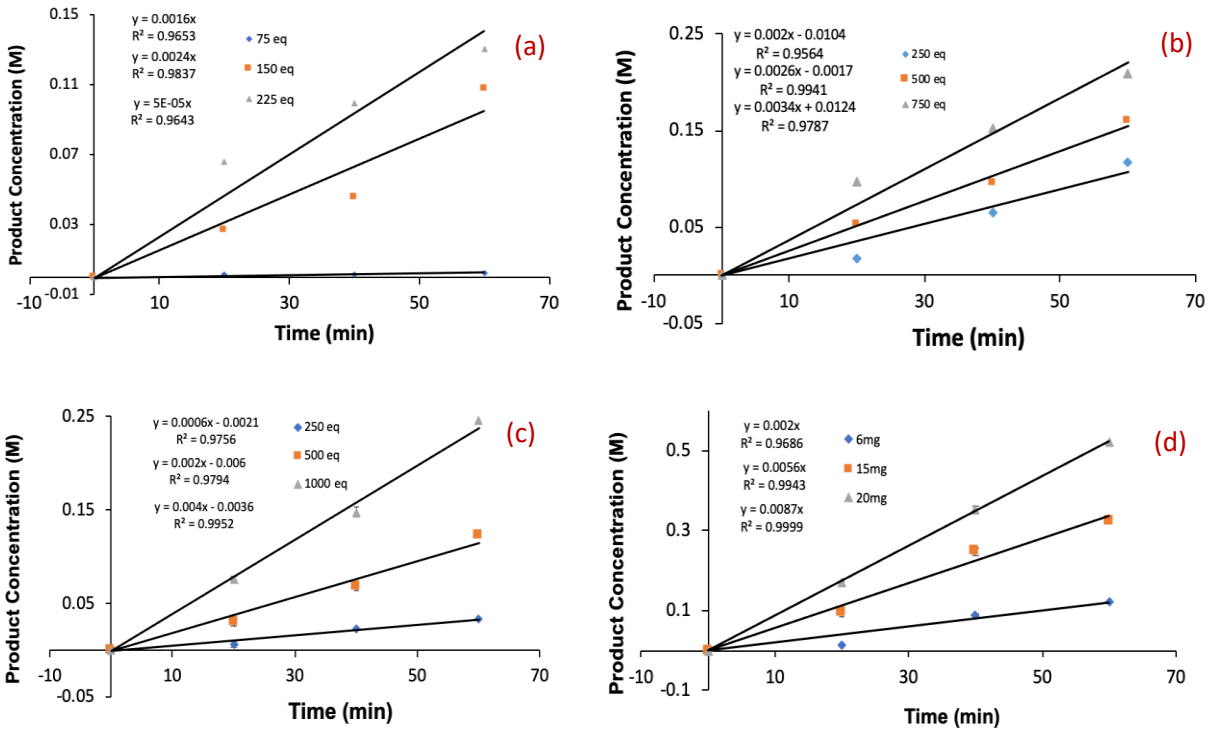


Fig. S46 Formation of benzylamine product in increasing concentrations of a) base (0.16–0.47 M), b) benzylamine (0.16–0.49 M), c) toluene substrate (0.45–1.80 M) and d) catalyst loads (1.2-4.0 mol %). The inset term "eq" represents the molar equivalent amount of starting reagent with respect to one molar equivalent of catalyst **1** (2.0 mg; 3.46 µmol) used in the reaction. The reactions were performed in DMSO (5.0 mL) at 110 ^{o}C. Data represents an average of two runs.

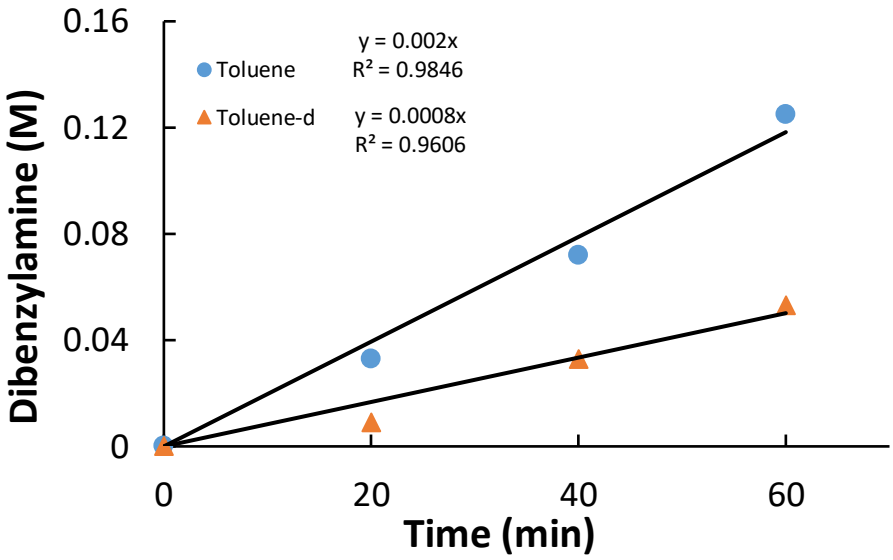


Fig. S47 The plot of product concentration vs. time using toluene and toluene-d8 over 1 h catalyzed by **1** in presence of LiHMDS at 110 °C.

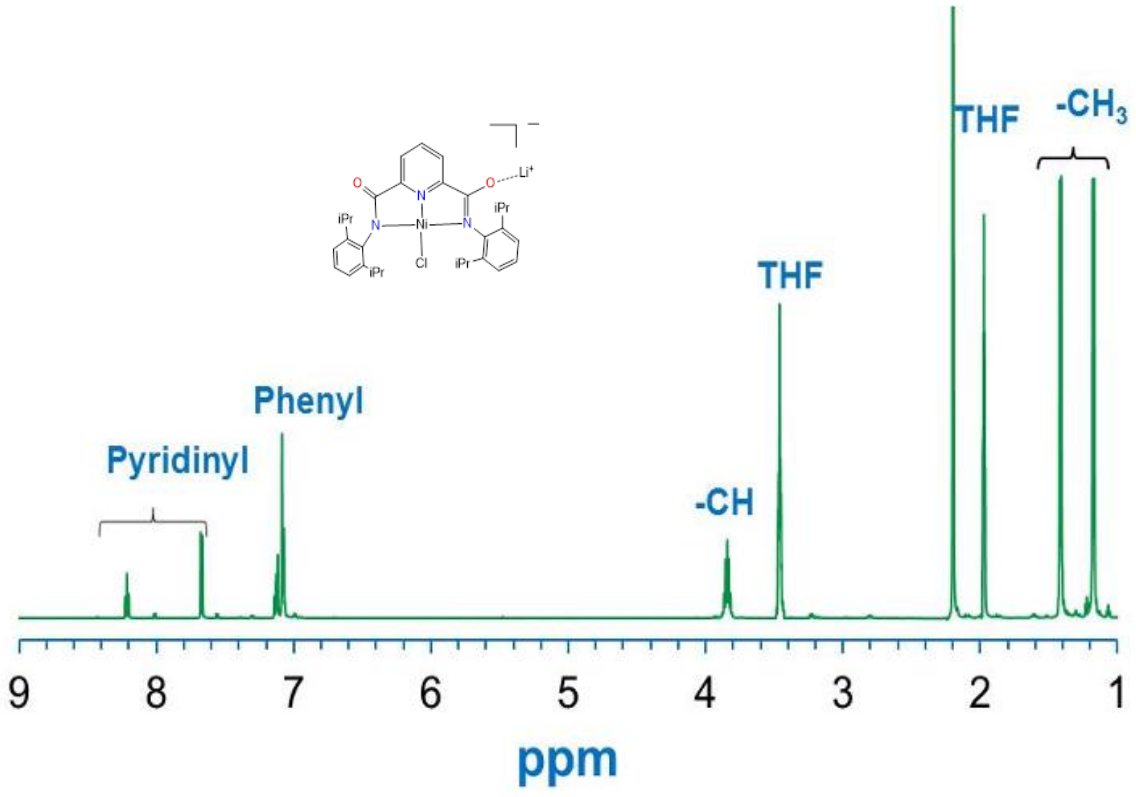


Fig. S48 ^{1}H NMR of nickel (II) complex (**1**).

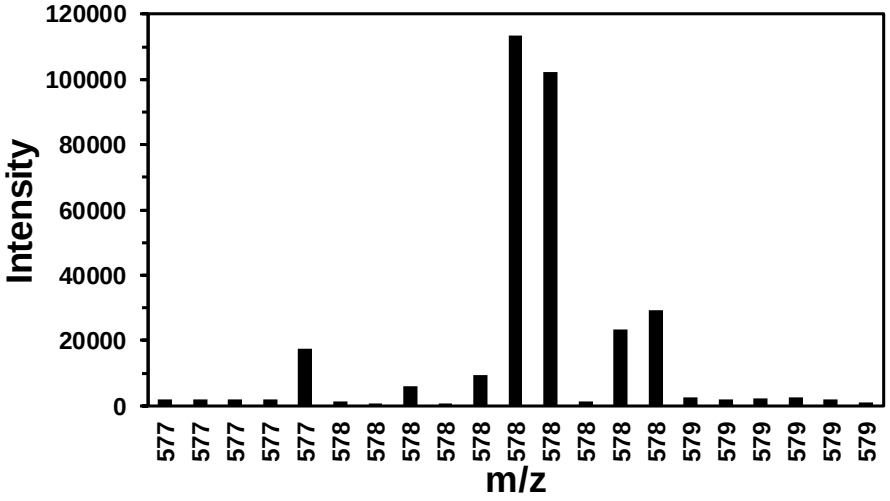


Fig. S49 ESI-MS of nickel (II) complex (**1**); negative ion mode; m/z 578.

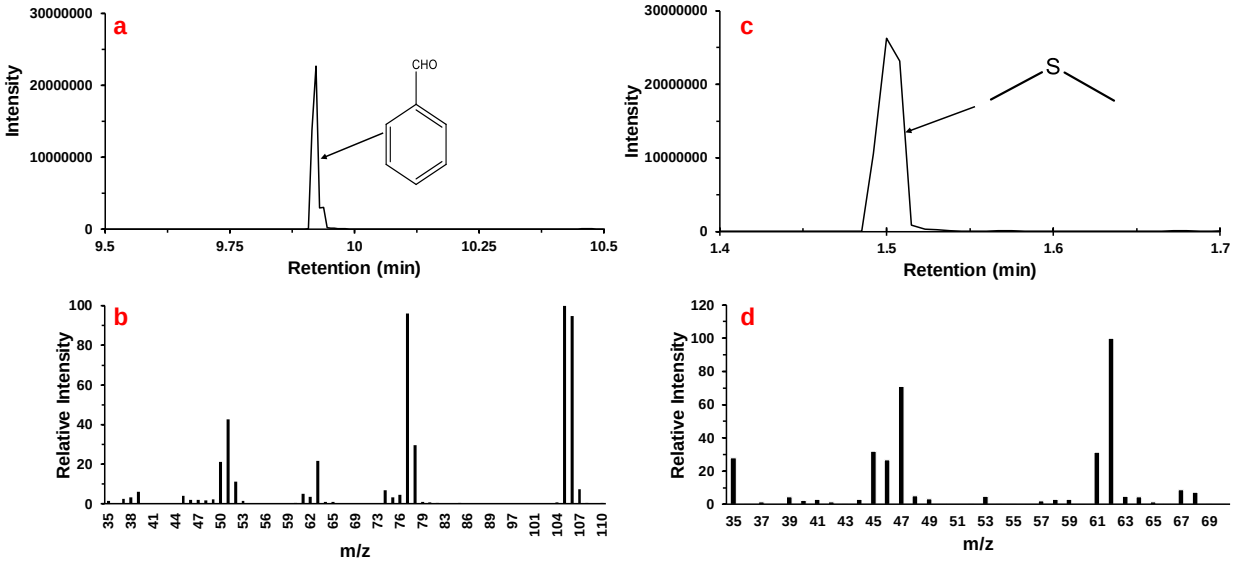
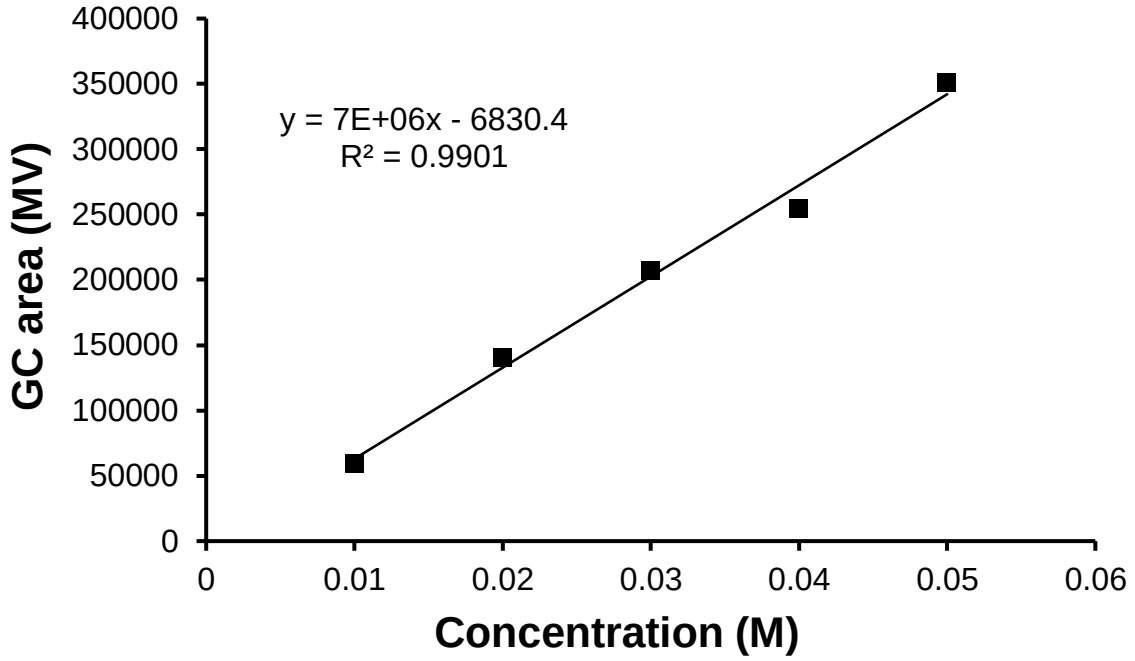


Fig. S50 GC/MS analysis of benzaldehyde (a and b) and dimethyl sulfide (c and d) formed during the reaction of toluene in the presence of **1** and KO^{t}Bu. Samples were analyzed using an internal standard of decane.

Calibration curve for GC analysis.

Dibenzylamine (3j) (purity 98.55%) was purchased from SD fine chemical India. Accurately 246.25 mg of dibenzylamine was taken in 25.00 mL volumetric flask (grade A) and dissolved and made the volume with methanol (HPLC grade, purity 99.95%). Using this stock solution of 0.05 (M) respective standard solutions of 0.01, 0.02, 0.03, 0.04 (M) were made in 10.00 mL volumetric flasks with methanol solvent. All the 5 flasks were inverted to ensure complete dissolution. 1.0 μL of each solution was injected in GC and collected the area under the curve of the peak. Area under the peak was plotted in respect to the concentration of each solution. Slope and intercept were measured after the linear fit of the data points. Regression (R^2) value 0.9901 signifies the high degree of linear fitness with the data points.

GC condition: Shimadzu 2010, HP-5 column (30 m x 0.25mm x 1.00 μm), FID (250°C), Injection temp. 250 ºC. Temperature 80 ºC at 15 ºC/min until 200 ºC, 5 ºC/min until 300 ºC, 5 min hold. RT 21.3 min.



Conc. (M)	GC area in mV
0.01	59104
0.02	140512
0.03	207312
0.04	254700
0.05	350905

Fig. S51 GC calibration curve for various concentrations of benzylamine.

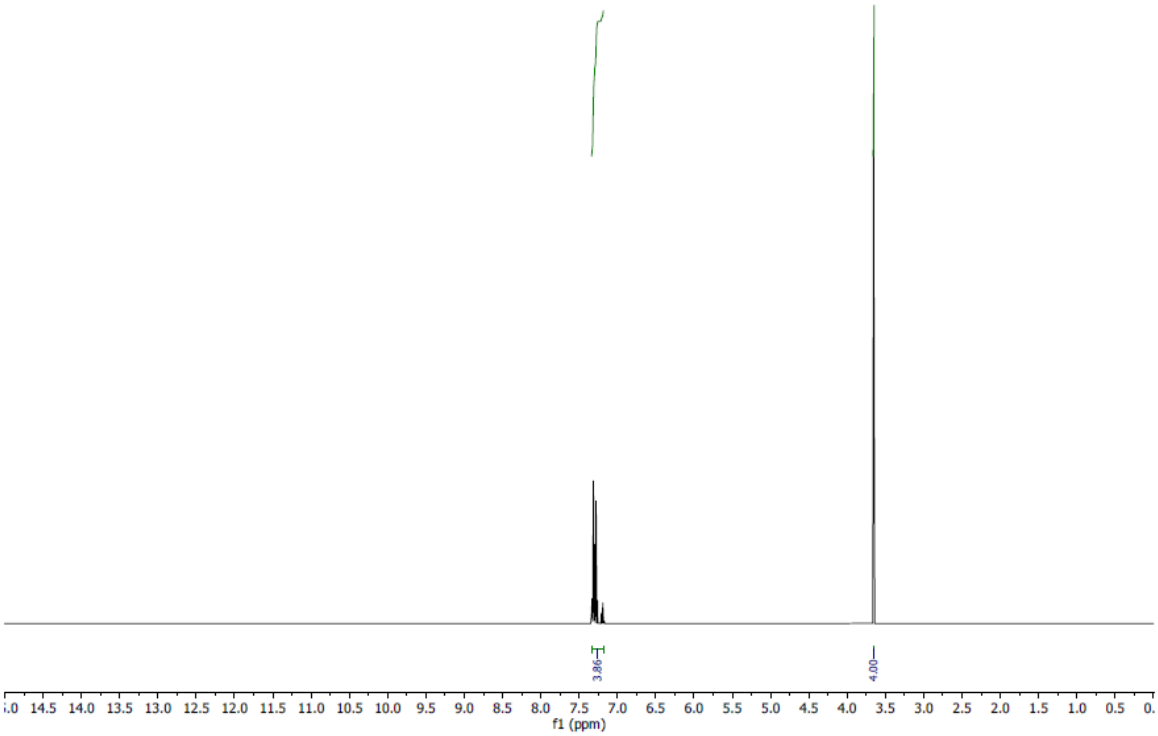


Fig. S52 ^{1}H NMR of dibenzylamine (3j).

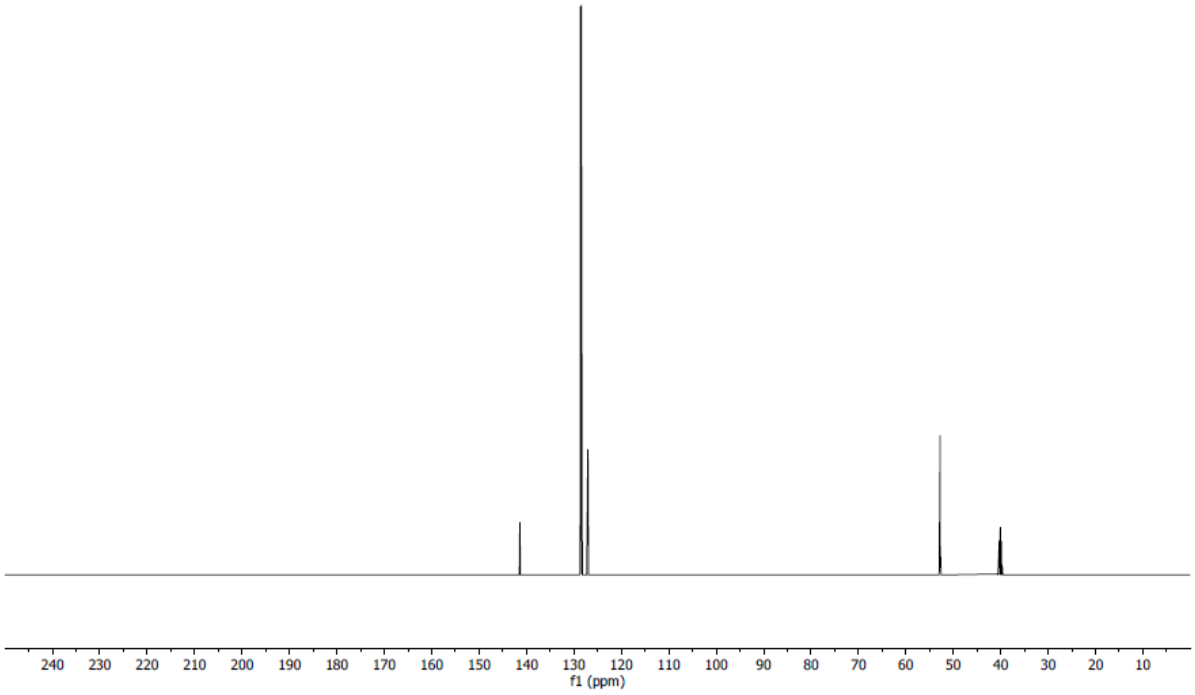
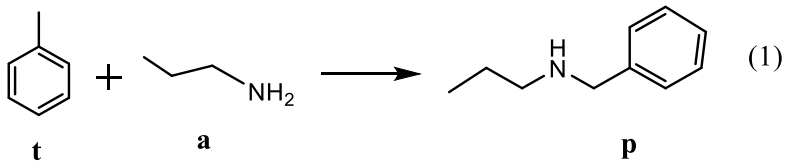


Fig. S53 ^{13}C NMR of dibenzylamine (3j).

Thermodynamic parameter calculation

Changes of Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH) under reaction conditions were calculated using ASPEN plus v10 to check spontaneity of reaction mentioned in eq 1. Data presented in Table S2 indicate that the reaction is thermodynamically controlled. Therefore, such an inherent limitation of yield could be overcome by higher catalyst loading.



t a p (1)

Table S2 Calculation of thermodynamic parameter for the eq. 1.

Temperature (°C)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS KJ/K
110	0.000136	-0.00108	-3.2×10^{-06}