Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Photocatalytic Organic Transformation by Layered Double Hydroxides: Highly Efficient and Selective Oxidation of Primary Aromatic Amines to Their Imines at Ambient Aerobic Condition

Xiu-Jie Yang,[a] Bin Chen,*[b] Xu-Bing Li,[b] Li-Qiang Zheng,*[a] Li-Zhu Wu,*[b] Chen-Ho Tung[a,b]

[a] Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, P. R. China

[b] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, the Chinese Academy of Science, Beijing 100190, P. R. China

Table of Contents

1. Materials.
2. Instruments and methods.
3. Synthesis of (Zn^{II}/Ti^{IV})LDH.
4. Catalytic procedure for oxidation of benzylamines.
5. Procedure for the oxidative three-component Ugi reaction.
6. Figure S1. N_2 adsorption-desorption isotherm (top) and pore size distribution curve (below) of (Zn^{II}/Ti^{IV})LDH.
7. Figure S2. Powder XRD pattern of (Zn^{II}/Ti^{IV})LDH with different molar ratios of Zn/Ti 4:1, 5:1 and 6:1, respectively.
8. Synthesis of (Mg^{II}/Al^{III})LDH.
9. Figure S3. Powder XRD pattern of (Mg^{II}/Al^{III})LDH.
10. Table S1. Chemical composition of LDHs.
11. Table S2. Control experiments of photocatalytic oxidation of benzylamine.
12. Figure S4. Reusability of (Zn^{II}/Ti^{IV})LDH for the photocatalytic oxidation of benzylamine.
13. Figure S5. Photographs taken for the detection of H_2O_2 in the photocatalytic oxidation of benzylamine.
14. Figure S6. UV-Vis diffuse reflectance spectrum of (Zn^{II}/Ti^{IV})LDH.
15. Figure S7. UV-Vis diffuse relectance spectrum of (Mg^{II}/Al^{III})LDH.
16. Figure S8. ^{1}H NMR spectra of the products.
17. References.

1. Materials

$Zn(NO_3)_2 \cdot 6H_2O$, urea, NaOH, Na_2CO_3, 2-thiophenemethylamine, dibenzylamine, 1,3,5-trimethoxybenzene, t-butylisonitrile, cinnamic acid, superoxide dismutase (SOD) were purchased from Acros. Other chemicals are of analytical grade without further purification unless otherwise noted. The ultrapure water with 18.2 MΩ·cm (Mettler Toledo, FE20, China) was used throughout the experiment.

2. Instruments and methods

High-resolution transmission electron microscopy (HR-TEM) was performed by JEM 2100F (operated at an accelerating voltage of 200 kV). Powder X-ray diffraction (XRD) patterns of the samples were collected using a Bruke D8 Focus under Cu-*Kα* irradiation (λ = 1.54056 Å), with a scan step of 0.02° and a scan range between 6 and 70°. Fourier transform infrared spectra were recorded on a Nicolet NEXUS 670 fourier transform infrared (FT-IR) spectrophotometer with the samples being pressed into KBr pellets. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrophotometer with Al-*Kα* radiation. The low temperature N_2 adsorption-desorption measurements were carried out using a Quadrasorb SI-MP. The samples were degassed for 1 day at 80℃ before the analysis. The specific surface area determination was calculated using the Brunaer-Emmett-Teller (BET) method based on the absorption isotherm. ^1H NMR spectra were run on a Bruke-400 spectrometer with tetramethylsilane as an internal standard. Mass spectra were recorded with ApexIII (7.0 tesla) FTICR mass spectrometer (Bruker). Elemental analyses were conducted on a Vario EI III analyzer and inductively coupled plasma atomic emission (ICP-AE) spectroscopy (Varian 710-OES) to determine the amount of C, H, N elements, and Mg, Al, Zn and Ti elements after the LDHs were dissolved in a HCl solution.

3. Synthesis of (Zn^{II}/Ti^{IV})LDH

The synthesis of (Zn^{II}/Ti^{IV})LDH is according to the procedure reported in the literature.[1] (Zn^{II}/Ti^{IV})LDH was prepared by coprecipitation of $Zn(NO_3)_2\cdot 6H_2O$ with titanium isopropoxide (Zn^{II}/Ti^{IV} = 6:1, $[Zn^{II} + Ti^{IV}]$ = 0.7 M) in urea (1M) solution under refluxing for 48 h. The products were collected by filtration, washed with distilled water, and dried at 60 °C overnight. (Zn^{II}/Ti^{IV})LDH with Zn^{II}/Ti^{IV} ratio of 4:1 and 5:1 was also prepared according to the same preparation procedure.

If not specified, (Zn^{II}/Ti^{IV})LDH in the paper refers to (Zn^{II}/Ti^{IV})LDH with Zn^{II}/Ti^{IV} ratio of 6:1. (Zn^{II}/Ti^{IV})LDH (4:1) and (Zn^{II}/Ti^{IV})LDH (5:1) refer to (Zn^{II}/Ti^{IV})LDH with Zn^{II}/Ti^{IV} ratio of 4:1 and 5:1, respectively.

4. Catalytic procedure for oxidation of benzylamines

The photocatalytic reaction was carried out in acetonitrile solution in air (1 atm) at room temperature. 0.2 mmol substrate and 20 mg LDH in 5 mL CH_3CN solution in a Pyrex reactor was irradiated with 500 W high-pressure mercury lamp (λ>300 nm) at air atmosphere. After irradiation, 16.8 mg (0.1 mmol) 1,3,5-trimethoxybenzene was added as the internal standard. LDH photocatalyst was removed by filtration, and the product was obtained after evaporation of the solvent. The chemical structure of the products were identified by ^1H NMR, and the reaction conversion and selectivity was calculated using 1,3,5-trimethoxybenzene as the internal standard.

5. Procedure for the oxidative three-component Ugi reaction

After the photocatalytic oxidation of primary aromatic amine to imine, the (Zn^{II}/Ti^{IV})LDH was removed by centrifugation, and solvent was removed by evaporation. Cinnamic acid (0.1 mmol), *t*-butylisocyanide (0.11 mmol) and CH_3OH (2 mL) were added to the flask containing imine product. After stirring at 60℃ for 48 h, the Ugi product was purified by column chromatography (petroleum ether/ethyl acetate = 6:1).

6. Figure S1

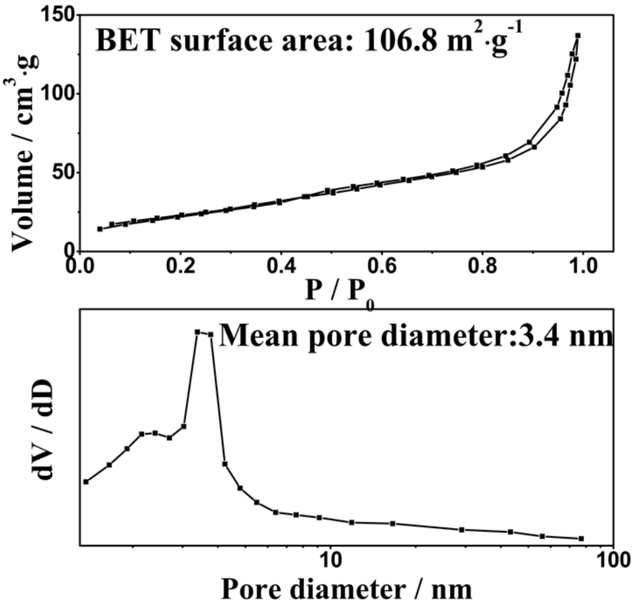


Figure S1 N_2 adsorption-desorption isotherm (top) and pore size distribution curve (below) of (Zn^{II}/Ti^{IV})LDH.

The surface area and pore-size distribution properties were measured by nitrogen adsorption-desorption isotherm curve. Figure S1 shows that the BET surface area is 106.8 $m^2 \cdot g^{-1}$, with the mean pore diameter is 3.4 nm.

7. Figure S2

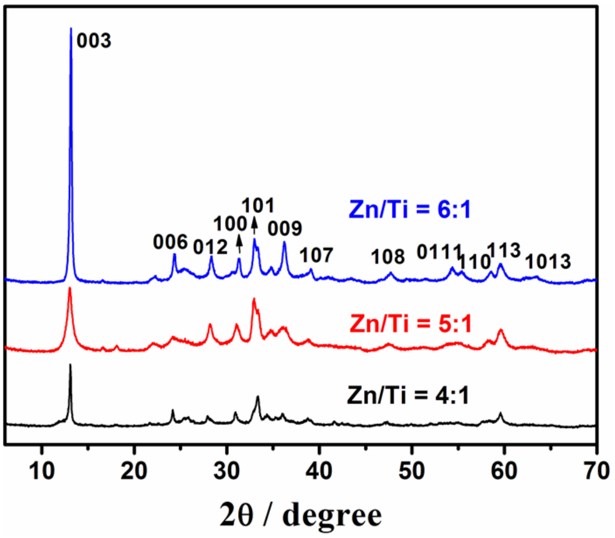


Figure S2 Powder XRD pattern of (Zn^{II}/Ti^{IV})LDH with different molar ratio of Zn^{II}/Ti^{IV} 4:1, 5:1 and 6:1, respectively.

8. Synthesis of (Mg^{II}/Al^{III})LDH

(Mg^{II}/Al^{III})LDH was prepared using coprecipitation method. $Mg(NO_3)_2 \cdot 6H_2O$ (0.02 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol) were dissolved in 50 mL deionized water (denoted as solution A), while NaOH (0.048 mol) and Na_2CO_3 (0.02 mol) were also dissolved in 50 mL water (solution B). Solution A and solution B were added simultaneously to a vessel maintaining the pH of the reaction mixture at 9. The mixture was aged 24 h at 60 °C. The solid was collected by centrifugation and washed three times with deionized water. The sample was dried at 60 °C overnight.

9. Figure S3

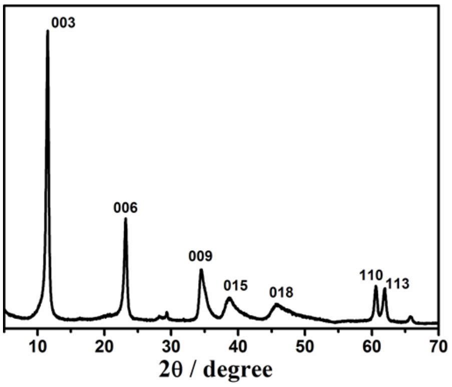


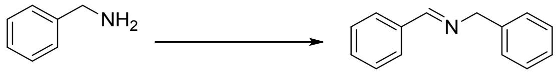
Figure S3 Powder XRD pattern of (Mg^{II}/Al^{III})LDH.

10. Table S1. Chemical composition of LDHs

Sample	Elemental content (wt%)					Formula[a]
	M^{II}	$M^{III/IV}$	$M^{II}/M^{III/IV}$	C	H	
(Zn^{II}/Ti^{IV})LDH (6:1)	43.86	5.27	6.14	1.79	3.26	$[Zn_{0.86}Ti_{0.14}(OH)_2](CO_3)_{0.14} \cdot 1.08H_2O$
(Zn^{II}/Ti^{IV})LDH (5:1)	42.47	5.97	5.18	1.49	3.52	$[Zn_{0.84}Ti_{0.16}(OH)_2](CO_3)_{0.16} \cdot 1.26H_2O$
(Zn^{II}/Ti^{IV})LDH (4:1)	39.53	8.23	3.63	2.06	3.27	$[Zn_{0.78}Ti_{0.22}(OH)_2](CO_3)_{0.22} \cdot 1.10H_2O$
(Mg^{II}/Al^{III})LDH	18.54	11.73	1.81	2.61	4.15	$[Mg_{0.64}Al_{0.36}(OH)_2](CO_3)_{0.18} \cdot 0.72H_2O$

[a] LDHs formulae are calculated based on elemental analyses and the general formula $[Zn^{II}_{1-x}Ti^{IV}_{x}(OH)_2]^{2x+}(CO_3^{2-})_x \cdot yH_2O$ for (Zn^{II}/Ti^{IV})LDH, $[Mg^{II}_{1-x}Al^{III}_{x}(OH)_2]^{x+}(CO_3^{2-})_{x/2} \cdot yH_2O$ for (Mg^{II}/Al^{III})LDH.

11. Table S2. Control experiments of photocatalytic oxidation of benzylamine.[a]



Entry	Catalyst[b]	Irradiation[c]	Atmosphere	Yield [%][d]
1	(Zn^{II}/Ti^{IV})LDH	√	1 atm air	97
2	(Zn^{II}/Ti^{IV})LDH	×	1 atm air	3
3	(Zn^{II}/Ti^{IV})LDH	√	1 atm argon	5
4	none	√	1 atm air	3
5	TiO_2 (P25)	√	1 atm air	85
6	ZnO	√	1 atm air	78
7	(Zn^{II}/Ti^{IV})LDH (4:1)	√	1 atm air	87
8	(Zn^{II}/Ti^{IV})LDH (5:1)	√	1 atm air	72
9	(Mg^{II}/Al^{III})LDH	√	1 atm air	87
10[e]	(Zn^{II}/Ti^{IV})LDH	√	1 atm air	2
11[f]	(Zn^{II}/Ti^{IV})LDH	√	1 atm air	46 (8)[g]
12	none	×	50 eqv. H_2O_2[h]	32
13	none	×	2 eqv. H_2O_2[h]	12
14	none	×	1 eqv. H_2O_2[h]	8

[a] Reaction condition: 0.2 mmol benzylamine, 5 mL CH_3CN, 5 h. [b] catalyst amount: 20 mg. [c] 500 W high pressure Hg lamp ($\lambda > 300$ nm). [d] Determined by ^1H NMR ($CDCl_3$) using 1,3,5-trimethoxybenzene as the internal standard. [e] Reaction carried out in 5 mL H_2O with the addition of SOD (superoxide dismutase). [f] Reaction carried out in 5 mL H_2O. [g] The data in the parentheses is the yield of benzaldehyde. [h] The amount of H_2O_2 added is relative to that of benzylamine.

12. Figure S4

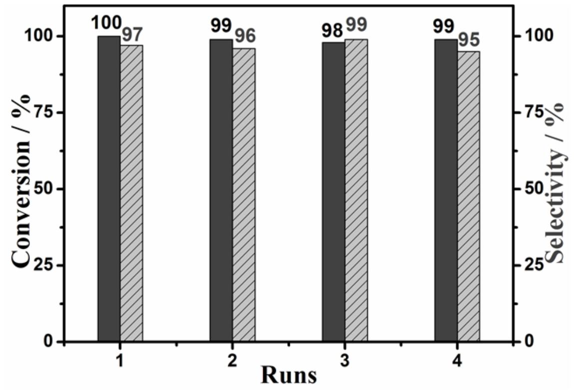


Figure S4. Reusability of (Zn^{II}/Ti^{IV})LDH photocatalyst for oxidation of benzylamine. Reaction conditions: benzylamine (0.2 mmol), 20 mg (Zn^{II}/Ti^{IV})LDH, 5 mL CH_3CN, 1 atm air, room temperature, 500 W high pressure Hg lamp □λ>300 nm), 5 h. (The black columns represent the conversion of the reaction, and the shadow ones represent the selectivity)

13. Figure S5

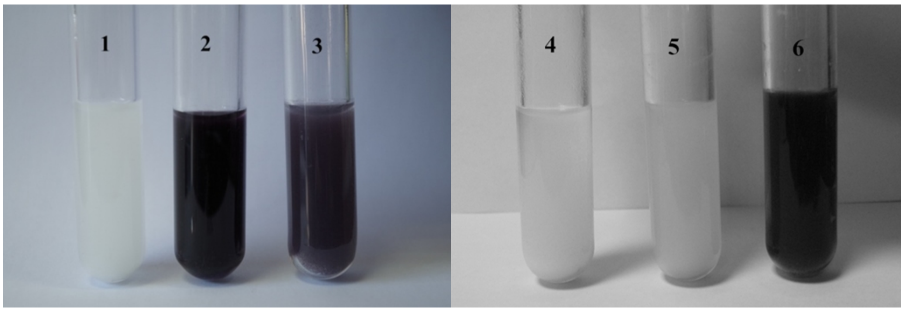


Figure S5 Photographs of (1) a solution containing starch (5 mg), KI (0.1 M) and acetic acid (0.1 M); (2) a solution of starch (5 mg), KI (0.1 M), acetic acid (0.1 M) and H_2O_2 (30%, 30 μL); solution of starch (5 mg), KI (0.1 M), acetic acid (0.1 M), benzylamine (0.2 mmol) with (3) (Zn^{II}/Ti^{IV})LDH (20 mg), (4) $MgCl_2$ (20 mg), (5) $AlCl_3$ (20 mg), (6) (Mg^{II}/Al^{III})LDH (20 mg) after irradiation for 1 h using 500 W high pressure mercury lamp (λ>300 nm) at air atmosphere. The solvent used herein is 5 mL CH_3CN/H_2O (4:1), H_2O was added to make KI soluble in the solution.

14. Figure S6

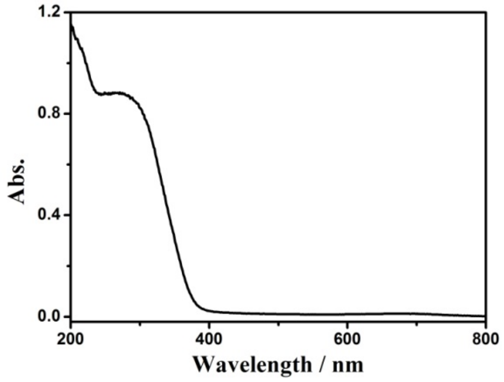


Figure S6 UV-Vis diffuse reflectance spectrum of (Zn^{II}/Ti^{IV})LDH.

15. Figure S7

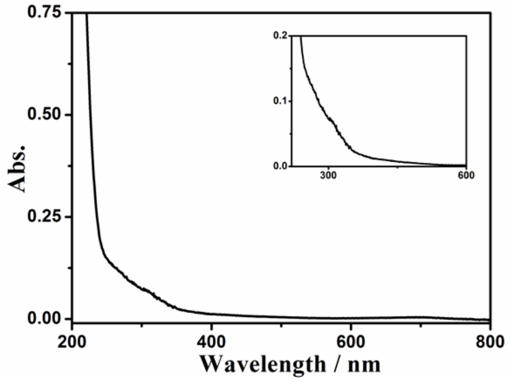
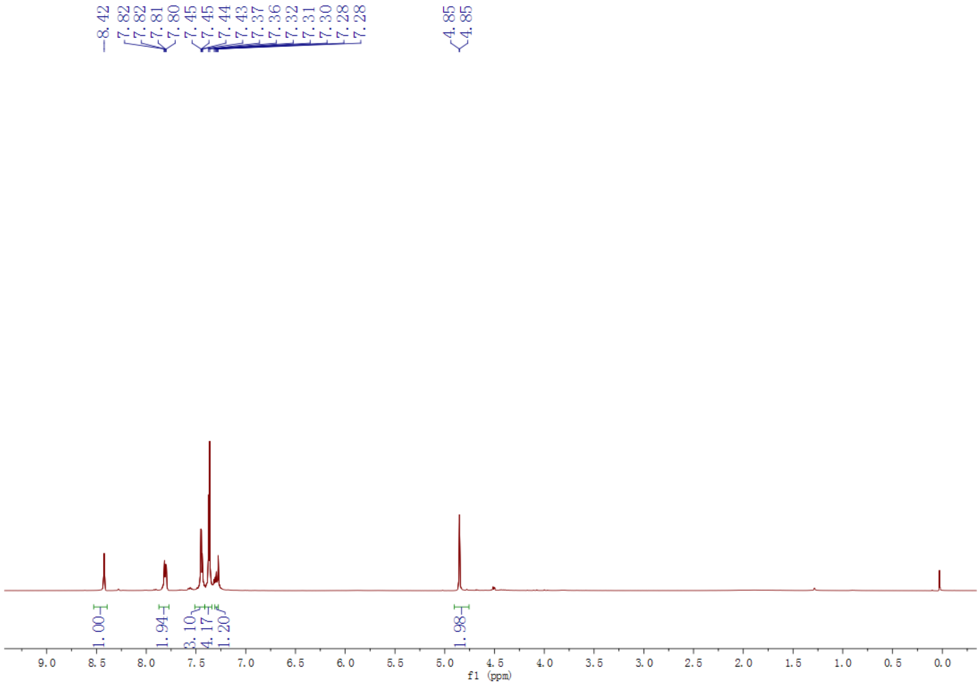


Figure S7 UV-Vis diffuse reflectance spectrum of (Mg^{II}/Al^{III})LDH.

16. Figure S8

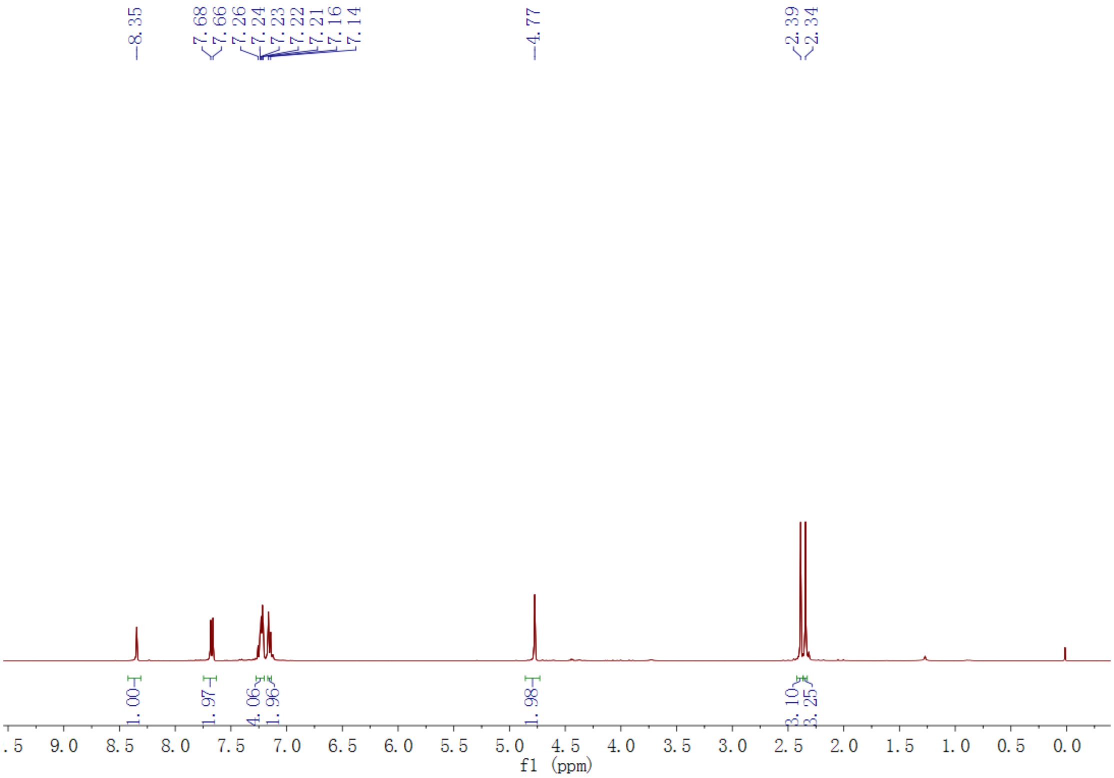
(1) *N*-benzyliden-1-phenylmethanamine

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.81 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.44 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.37 (d, *J* = 4.5 Hz, 4H), 7.32 – 7.24 (m, 1H), 4.85 (d, *J* = 0.9 Hz, 2H).



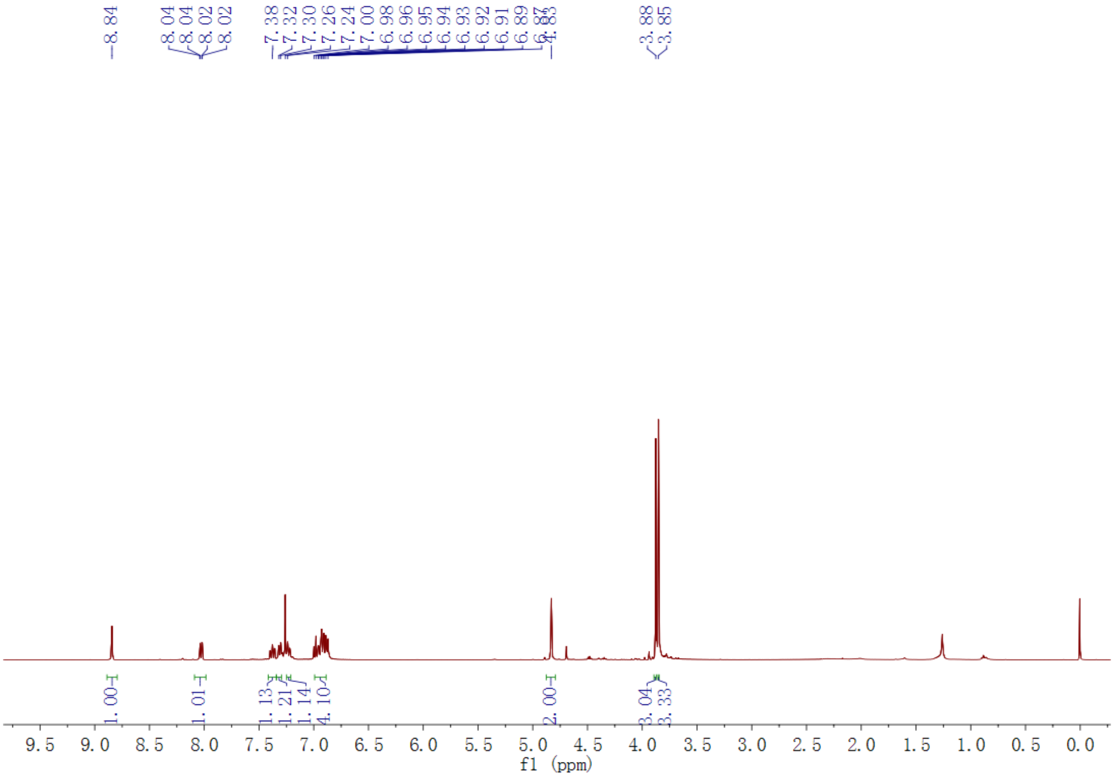
(2) *N*-(4-methylbenzyliden)-1-p-tolylmethanamine

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.35 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.18 (m, 4H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.77 (s, 2H), 2.39 (s, 3H), 2.34 (s, 3H).



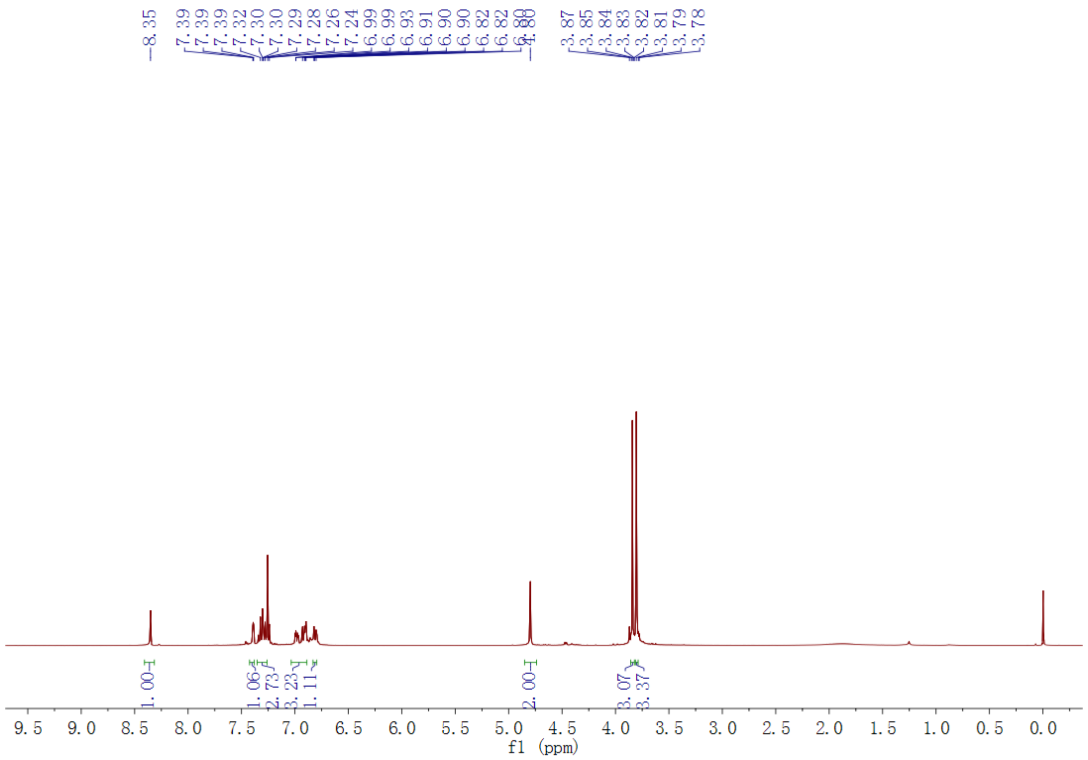
(3) *N*-(2-methoxybenzyliden)-1-(2-methoxyphenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.03 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.22 (dd, *J* = 9.7, 8.2 Hz, 1H), 7.03 – 6.84 (m, 4H), 4.83 (s, 2H), 3.88 (s, 3H), 3.85 (s, 3H).



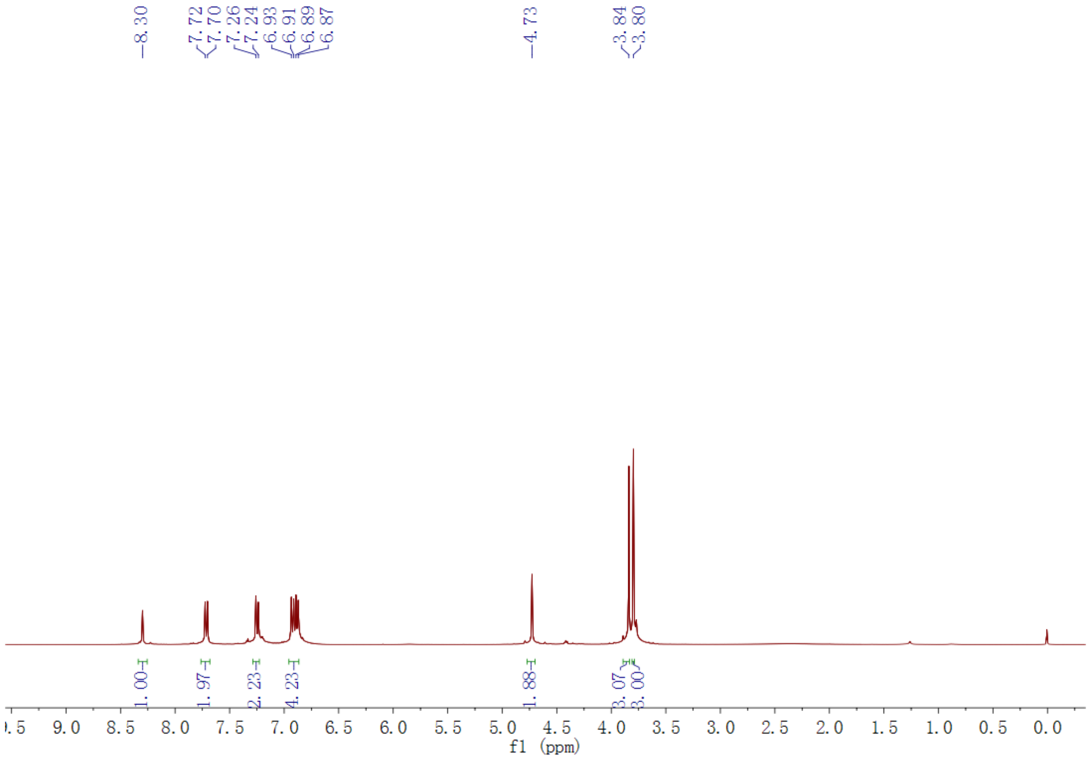
(4) *N*-(3-methoxybenzyliden)-1-(3-methoxyphenyl)methanamine

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.35 (s, 1H), 7.42 – 7.38 (m, 1H), 7.35 – 7.26 (m, 3H), 7.03 – 6.89 (m, 3H), 6.81 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.80 (s, 2H), 3.86 – 3.82 (m, 3H), 3.81 (s, 3H).



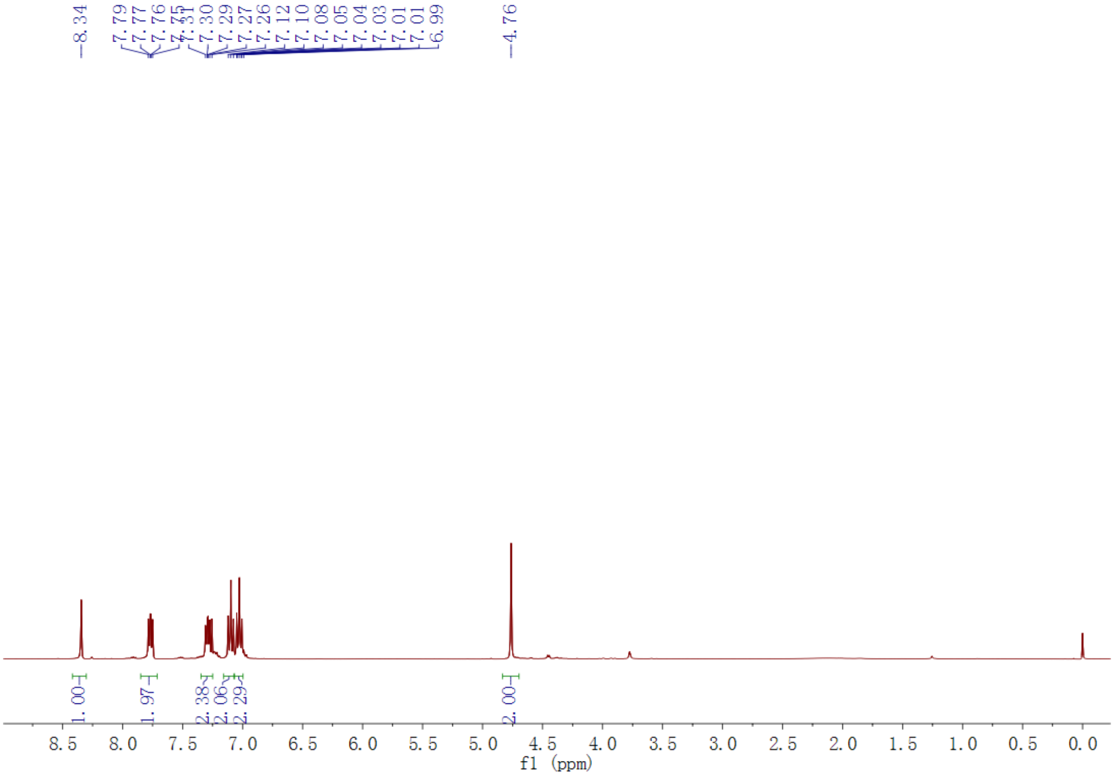
(5) *N*-(4-methoxybenzyliden)-1-(4-methoxyphenyl)methanamine

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (s, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 9.1 Hz, 2H), 6.90 (dd, *J* = 16.8, 8.6 Hz, 4H), 4.73 (s, 2H), 3.84 (s, 3H), 3.80 (s, 3H).



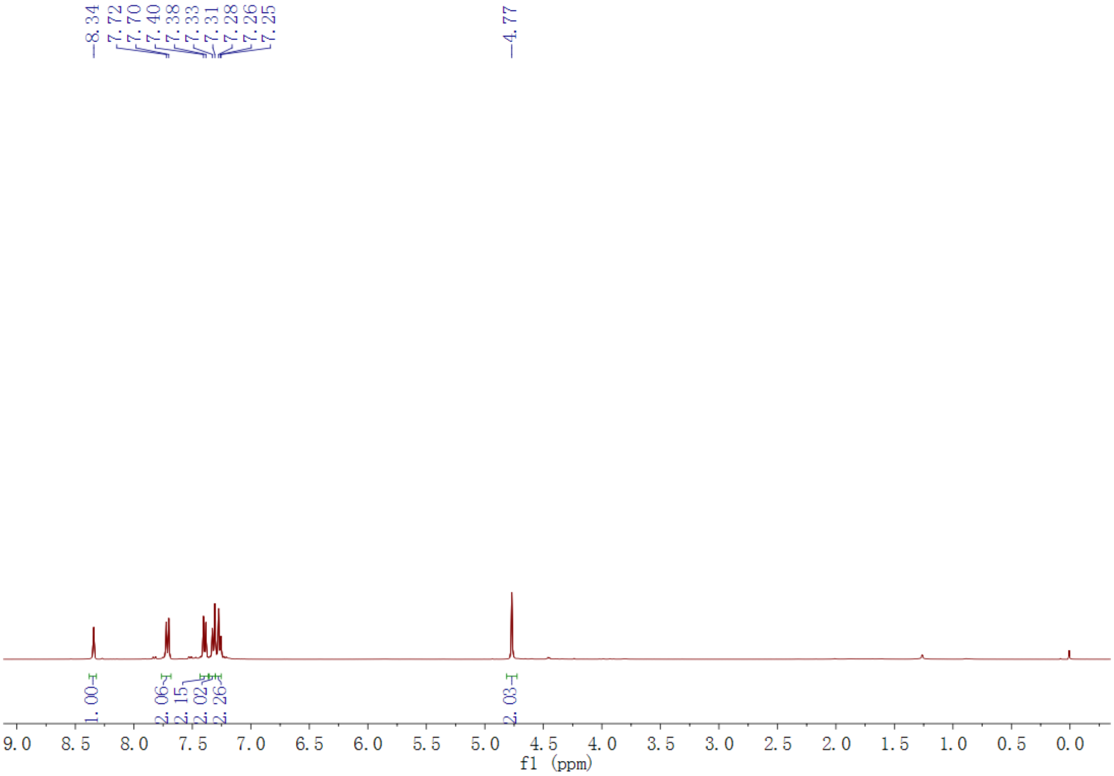
(6) *N*-(4-fluorobenzyliden)-1-(4-fluorophenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.85 – 7.71 (m, 2H), 7.35 – 7.25 (m, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 7.07 – 7.00 (m, 2H), 4.76 (s, 2H).



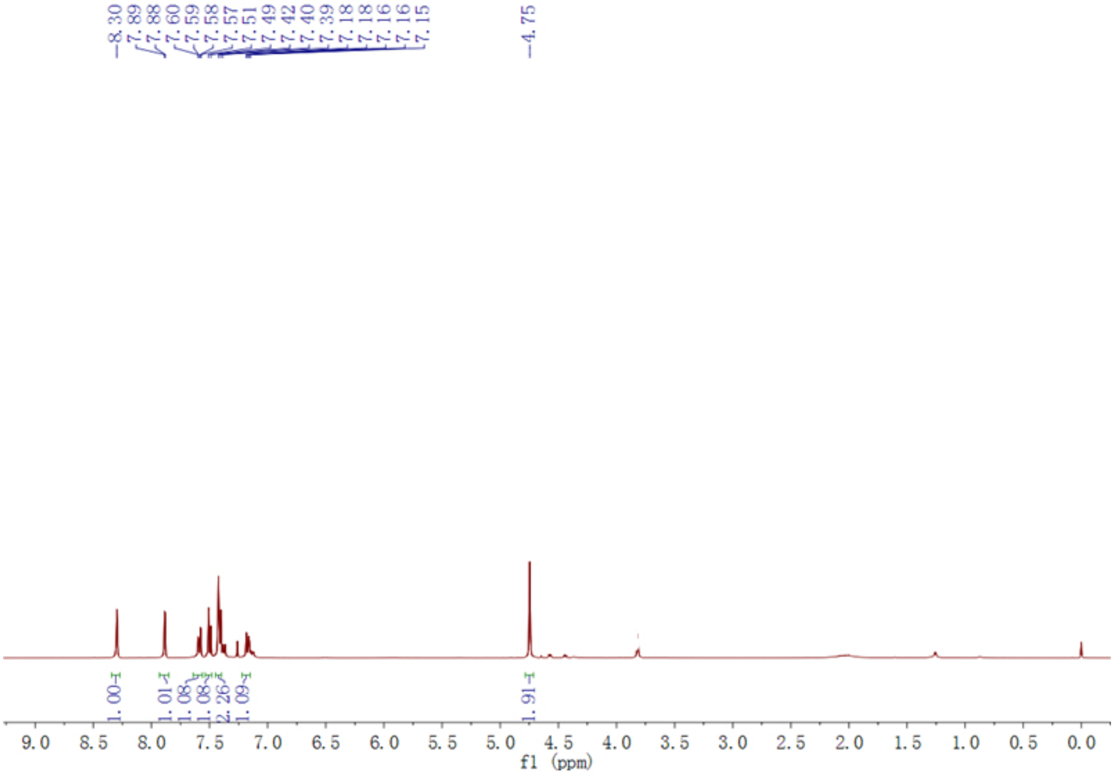
(7) *N*-(4-chlorobenzyliden)-1-(4-chlorophenyl)methanamine

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.34 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.23 (m, 2H), 4.77 (s, 2H).



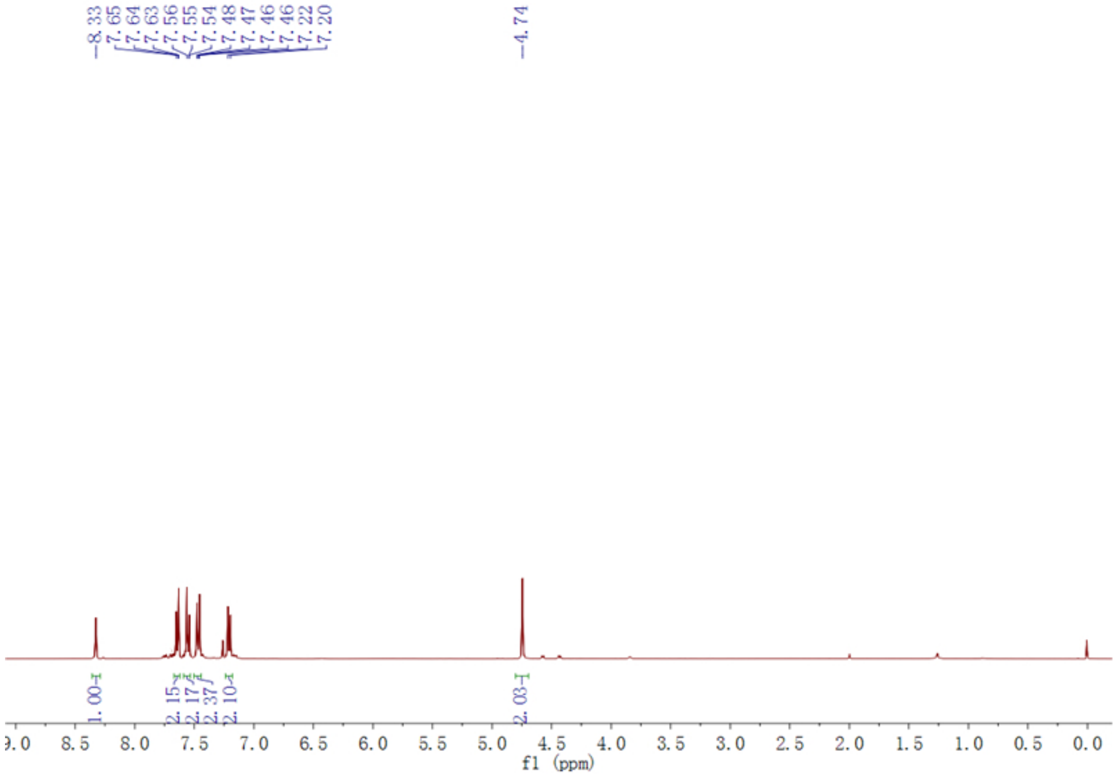
(8) *N*-(3,4-dichlorobenzyliden)-1-(3,4-dichlorophenyl)methanamine

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.30 (s, 1H), 7.88 (d, *J* = 1.7 Hz, 1H), 7.59 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.75 (s, 2H).



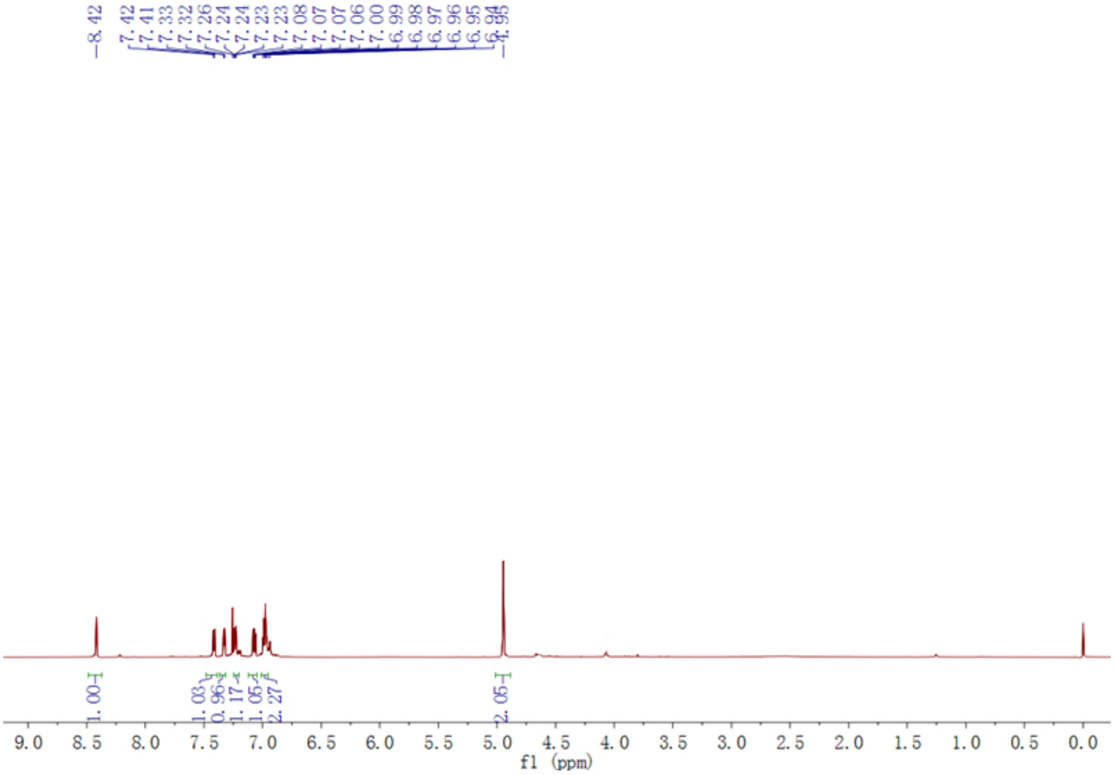
(9) *N*-(4-bromobenzyliden)-1-(4-bromophenyl)methanamine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.68 – 7.61 (m, 2H), 7.59 – 7.53 (m, 2H), 7.50 – 7.43 (m, 2H), 7.19 (dd, *J* = 13.4, 5.5 Hz, 2H), 4.74 (s, 2H).



(10) *N*-thenyliden-1-thenylmethanamine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.41 (d, *J* = 5.0 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.27 – 7.18 (m, 1H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.02 – 6.95 (m, 2H), 4.95 (s, 2H).



(11) *N*-Benzyl-N-(2-tert-butylamino)-2-oxo-1-phenylethyl)cinnamamide

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (dd, *J* = 15.6, 8.7 Hz, 1H), 7.42 – 7.23 (m, 10H), 7.19 – 7.10 (m, 3H), 7.01 (d, *J* = 6.7 Hz, 2H), 6.72 (d, *J* = 15.3 Hz, 1H), 6.13 (s, 1H), 5.75 (s, 1H), 4.93 (d, *J* = 17.9 Hz, 1H), 4.70 (d, *J* = 17.9 Hz, 1H), 1.35 (s, 9H).

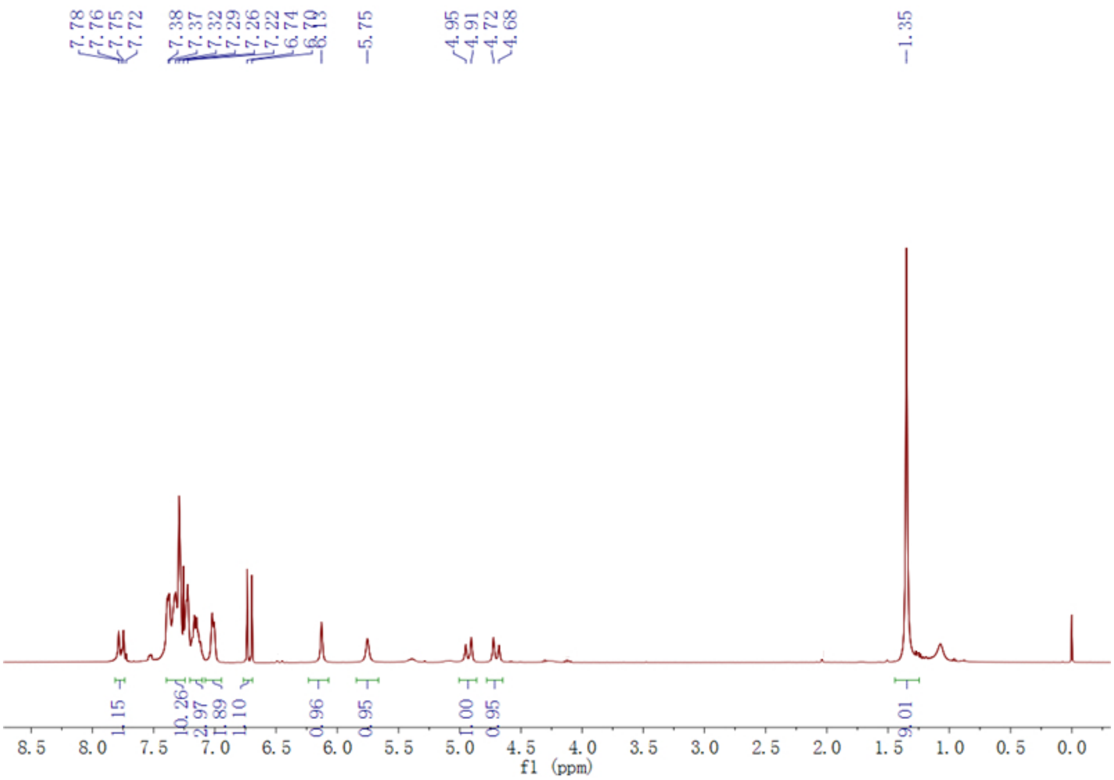


Figure S8 ^{1}H NMR spectra of (1) N-benzyliden-1-phenylmethanamine; (2) N-(4-methylbenzyliden)-1-p-tolylmethanamine; (3) N-(2-methoxybenzyliden)-1- (2-methoxyphenyl)methanamine; (4) N-(3-methoxybenzyliden)-1-(3-methoxyphenyl) methanamine; (5) N-(4-methoxybenzyliden)-1-(4-methoxyphenyl)methanamine; (6) N-(4-fluorobenzyliden)-1-(4-fluorophenyl)methanamine; (7) N-(4-chlorobenzyliden) -1-(4-chlorophenyl)methanamine; (8) N-(3,4-dichlorobenzyliden)-1- (3,4-dichlorophenyl)methanamine; (9) N-(4-bromobenzyliden)-1-(4-bromophenyl) methanamine; (10) N-thenyliden-1-thenylmethanamine; (11) N-Benzyl-N- (2-tert-butylamino)-2-oxo-1-phenylethyl)cinnamamide.

17. Reference:

[1] C. G. silva, Y. Bouizi, V. Fornés and H. García, *J. Am. Chem. Soc.*, 2009, **131**, 13833.