

Supplementary data

Phenol-TiO₂ Complex Photocatalysis: Visible Light-Driven Selective Oxidation of Amines into Imines with Air

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1. Experimental Section

1.1. Reagents and solvents

All the reagents were obtained from commercial suppliers such as Sigma-Aldrich, Alfa Aesar and TCI, J&K Scientific, etc. The solvents were supplied by Merck, Fischer Scientific and Sinopharm Chemical Reagent Co., LTD. Benzyl- α , α - d_2 -amine was supplied by CDN Isotopes, Quebec, Canada. Anatase TiO_2 (Ishihara ST-01) used in this paper was purchased from Ishihara Sangyo Kaisha, LTD., Japan. All the reagents and solvents were directly used without further purification.

1.2 UV-visible spectra

The UV-visible absorption spectra of the solid samples were recorded on a Shimadzu UV-2700 UV-VIS spectrophotometer with a diffuse reflectance measurement accessory. The UV-visible absorption spectra of the solutions were also carried out with the same equipments with a normal operating mode.

1.3 PXRD

The phase composition of the anatase TiO_2 sample was identified by powder X-ray diffraction (PXRD) using a Bruker D8 Advances diffractometer.

1.4 BET

The specific surface areas were determined by N_2 physisorption by using an ASAP automated system and the Brunauer-Emmet-Teller (BET) method. Each sample was degassed under vacuum ($<1 \times 10^{-5}$ bar) in the Micromertics system at $120^\circ C$ for 12 h prior to N_2 physisorption.

1.5 ESR

The ESR experiments were carried out on an electron spin resonance (ESR) spectrometer (JEOL, JES-FA200). The phenol-TiO₂ complex photocatalyst under the standard conditions was irradiated in the light chamber of the ESR spectrometer irradiated by a high-pressure Hg lamp with a filter to select the band of 460 nm visible light.

1.6 GC and GC-MS

The gas chromatography (GC) quantitative measurements of conversions of substrates and selectivities of products were made on a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) using high pure N₂ as the carrier gas and an Agilent J & W DB-5 capillary column (30 m × 0.32 mm × 0.25 μm, 19091J-413).

GC-FID standard analysis conditions: injector temperature 250 °C, detector temperature 280 °C, column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 20 °C/min. The results were all obtained using a split mode with a split ratio is 30:1. For Table 4, entry 13, the sample was diluted to 1/10 with CH₃CN before analysis by GC-FID. For Table 5, entries 5–7, 9–11, column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 10 °C/min.

Gas chromatography–mass spectrometry (GC–MS) analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a Shimadzu GCMS-QP2010 Ultra electron ionization mass spectrometer using a Restek (Rxi®-5Sil

MS) capillary column (30 m × 0.25 mm × 0.25 μm) with high pure He as the carrier gas.

1.7 General procedure for the selective oxidation of amine into imine with air

TiO₂ (50 mg), phenol (0.008 eq, 2.4×10⁻³ mmol), benzylamine (0.3 mmol), TEMPO (0.05 eq, 0.015 mmol), chlorobenzene (10 μL), CH₃CN (1 mL) and a magnetic stirring bar were added to a 10 mL pyrex vessel. After 5 min of ultrasonication, the mixture was stirred for 1h in dark to reach adsorption equilibrium. For the oxidation of secondary amines, secondary amines (0.2 mmol), TiO₂ (50 mg), phenol(2.4×10⁻³ mmol), and TEMPO (0.015 mmol), were added to the reaction vessel. The 10 mL reaction Pyrex vessel was capped with butyl rubber septum. Then a rubber hole puncher was used to punch a hole in the rubber septum to connect with air to supply the oxygen demand in the experimental process. The reaction mixture was magnetically stirred at 1500 rpm and illuminated with blue LED in an air-conditioned room with additional electronic fan cooling to warrant the reaction temperature constantly at room temperature. At the end of reaction, the phenol-TiO₂ particles were separated from the reaction mixture by centrifugation and the products were quantitatively analyzed by gas chromatography (GC) equipped with a flame ionization detector (FID) using chlorobenzene as the internal standard. The structures of products were confirmed by comparison with the retention time with authentic samples and further confirmed by gas chromatography–mass spectrometry (GC-MS).

Table S1. The influence of the amount of TEMPO on the selective aerobic oxidation benzylamine to imine under visible light irradiation^[a].

Entry	TEMPO[μ mol]	Conv.[%] ^[b]	Sel.[%] ^[b]
1	0	39	98
2	3	48	94
3	6	68	81
4	9	77	97
5	12	83	97
6	15	83	99
7	18	93	99

[a] Reaction conditions: benzylamine (0.3 mmol), phenol (0.0024 mmol), TiO₂ (50 mg), air (1 atm), blue LED irradiation (3 W \times 4), CH₃CN (1 mL), 0.5 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table S2. The influence of different LED_s on the selective aerobic oxidation benzylamine to imine under visible light irradiation^[a].

Entry	LED	λ_{max} (nm)	Conv.[%] ^[b]	Sel.[%] ^[b]
1	Red	630	0	0
2	Yellow	590	0	0
3	Green	530	3	99
4	Blue	460	83	99
5	Violet	400	67	94
6	White	Continuous	15	95
7	Warm light	Continuous	4	84

[a] Reaction conditions: benzylamine (0.3 mmol), phenol (0.0024 mmol), TiO₂ (50 mg), TEMPO (0.0015 mmol), LED irradiation (3 W \times 4), air (1 atm), CH₃CN (1 mL), 0.5 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

Table S3. The influence of the solvent on the selective aerobic oxidation benzylamine to imine under visible light irradiation^[a].

Entry	Solvent	Conv.[%] ^[b]	Sel.[%] ^[b]
1	CH ₃ CN	83	99
2	BTF ^[b]	48	98
3	EtOAc	26	95
4	PhMe	52	99
5	DCM	31	99
6	1,4-Dioxane	60	90

[a] Reaction conditions: amine (0.3 mmol), TiO₂ (50 mg), phenol (0.0024 mmol), TEMPO (0.0015 mmol), air (1 atm), blue LED irradiation (3 W×4), 0.5 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine. [c] BTF, benzotrifluoride; EtOAc, ethyl acetate; PhMe, toluene; DCM, dichloromethane.

Table S4. The influence different TiO₂ on the selective aerobic oxidation benzylamine to imine under visible light irradiation ^[a]

Entry	TiO ₂	Crystal phase	Conv.[%] ^[b]	Sel.[%] ^[b]
1	TiO ₂ (ST-01)	Anatase	83	99
2	TiO ₂ (Alfa)	Anatase	67	99
3	TiO ₂ (P25)	Anatase/rutile	67	99
4	TiO ₂ (P90)	Anatase/rutile	84	96

[a] Reaction conditions: benzylamine (0.3 mmol), phenol (0.0024 mmol), TiO₂ (50 mg), TEMPO (0.0015 mmol), LED irradiation (3 W×4), air (1 atm), CH₃CN (1 mL), 0.5 h. [b] Determined by GC-FID using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylidenebenzylamine.

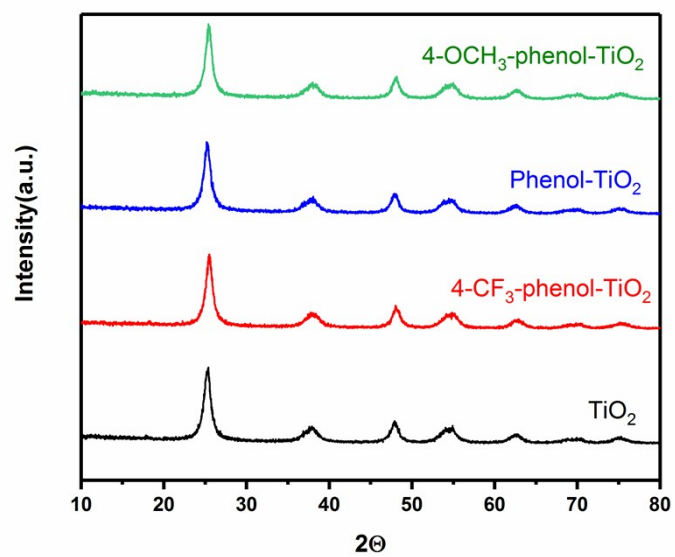


Figure S1. The XRD patterns of anatase TiO₂ and Surface ligand -TiO₂

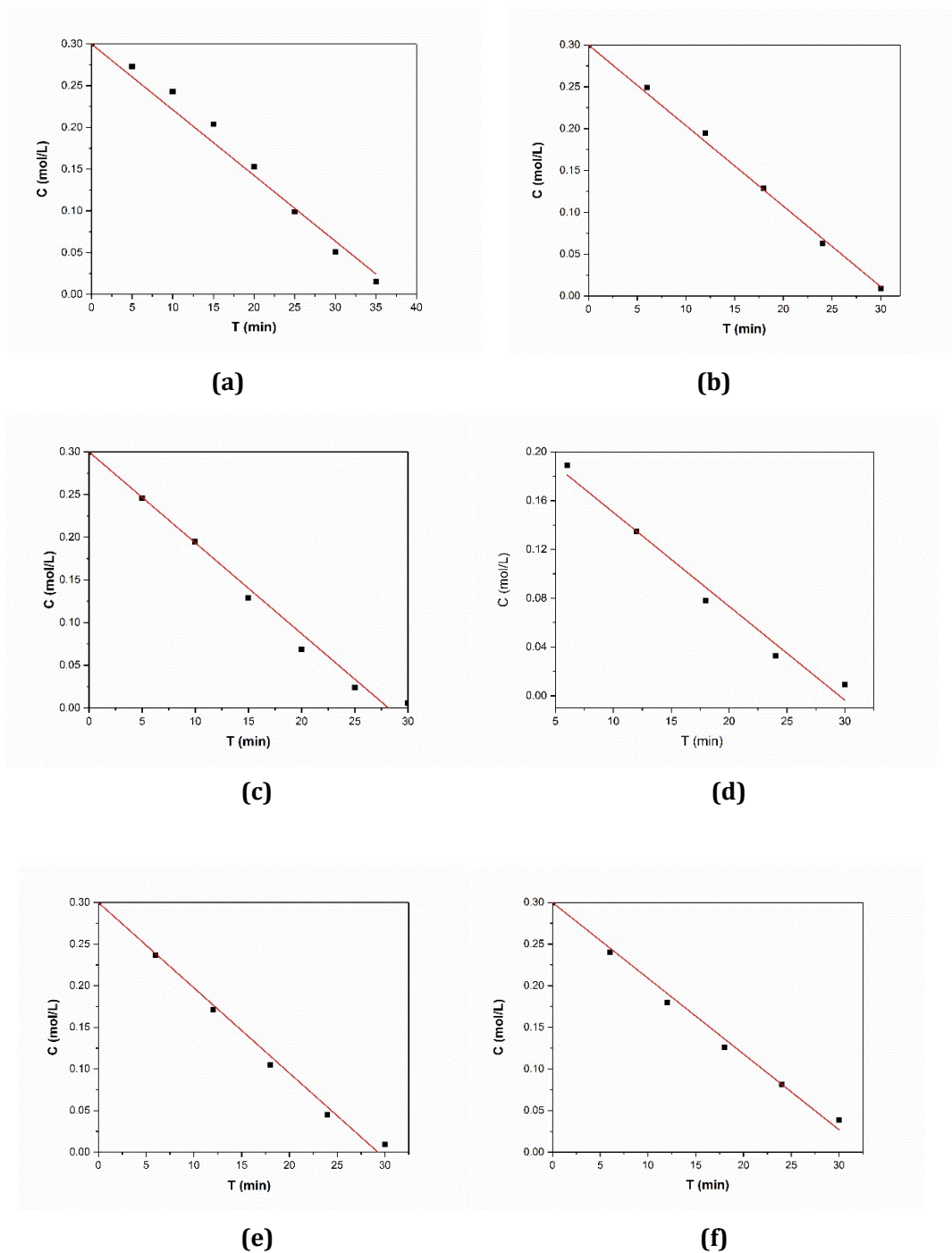
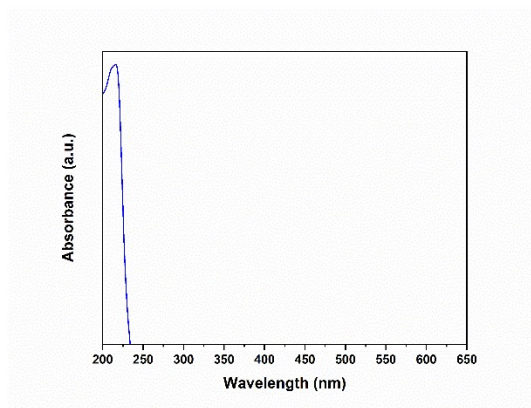
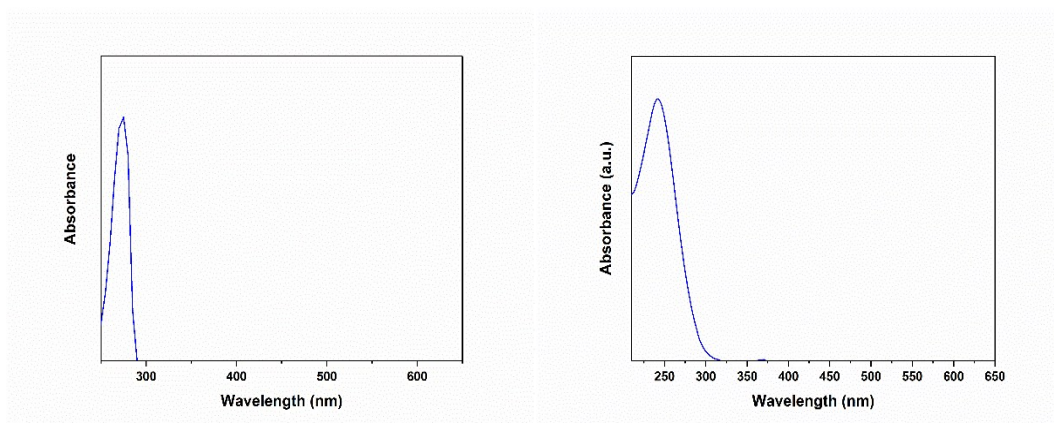


Figure S2. The reaction kinetic profiles for the visible light photocatalytic oxidation of 4-substituted benzylamines. **a**, H; **b**, CH₃; **c**, OCH₃; **d**, Cl; **e**, F; **f**, Br.

Reaction conditions: amine (0.3 mmol), phenol (2.4×10^{-3} mmol), TiO₂ (50 mg), TEMPO (0.0015 mmol), air (1 atm), blue LED irradiation (3 W \times 4), CH₃CN (1 mL), yield of *N*-benzylidenebenzylamine was determined by GC-FID.



(a)



(b)

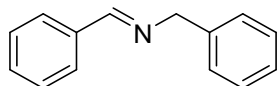
(c)

Figure S3. UV-visible absorbance of spectroscopy of benzylamine (a), phenol (b), TEMPO (c)

S4. ^1H NMR, ^{13}C NMR and HRMS data

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C NMR spectroscopy). Chemical shifts (δ) were reported in ppm, and coupling constants (J) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Unless otherwise stated, CDCl_3 (^1H NMR: 7.26 ppm; ^{13}C NMR: 77.1 ppm) was used as the solvent.

***N*-benzylidenebenzylamine**



Yield: 87%;

^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 7.84 (d, $J = 3.4$ Hz, 2H), 7.49–7.43 (m, 3H), 7.40 (d, $J = 3.3$ Hz, 4H), 7.35–7.28 (m, 1H), 4.88 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.26, 139.48, 136.33, 131.00, 128.83, 128.72, 128.51, 128.21, 127.22, 65.25.

HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$ 196.10480, found: 196.11385.

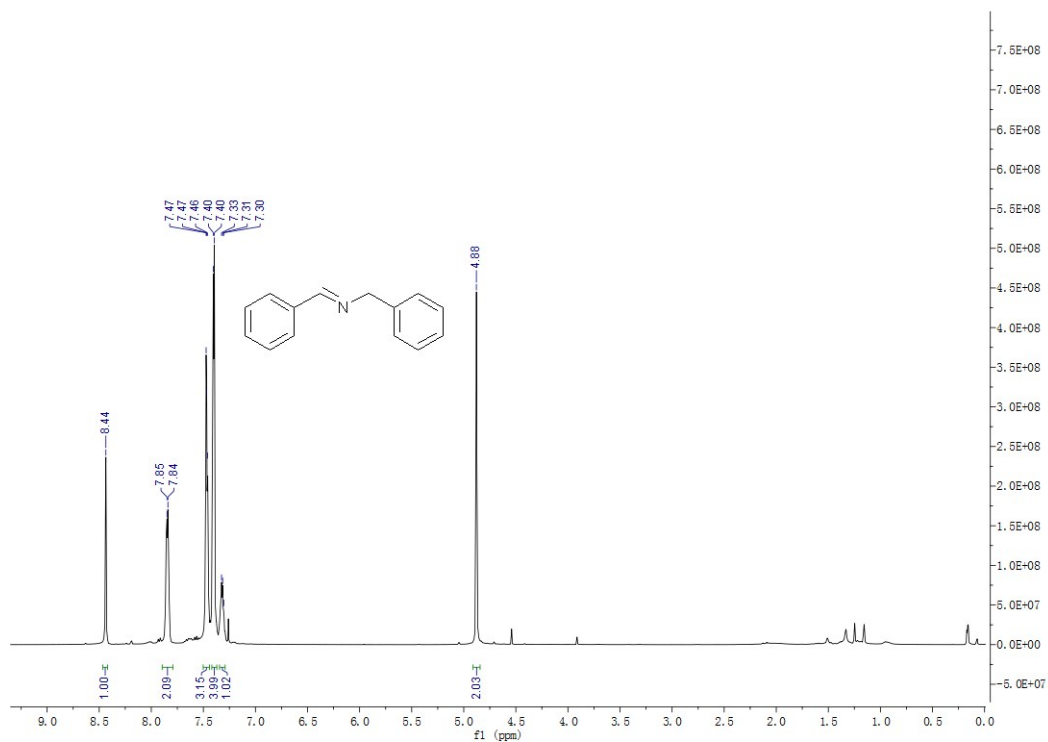


Figure S4. The ^1H NMR spectra of *N*-benzylidenebenzylamine

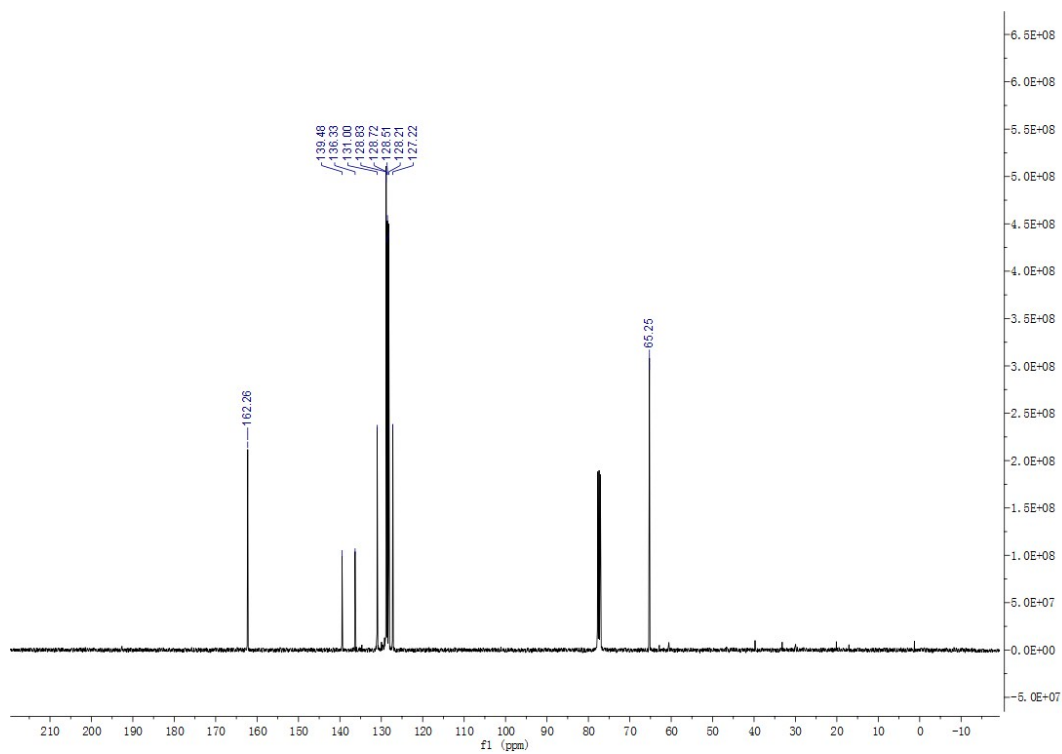


Figure S5. The ^{13}C NMR spectra of *N*-benzylidenebenzylamine

LXJ #17 RT: 0.09 AV: 1 NL: 1.48E8
F: FTMS + p ESI Full ms [50.00-600.00]

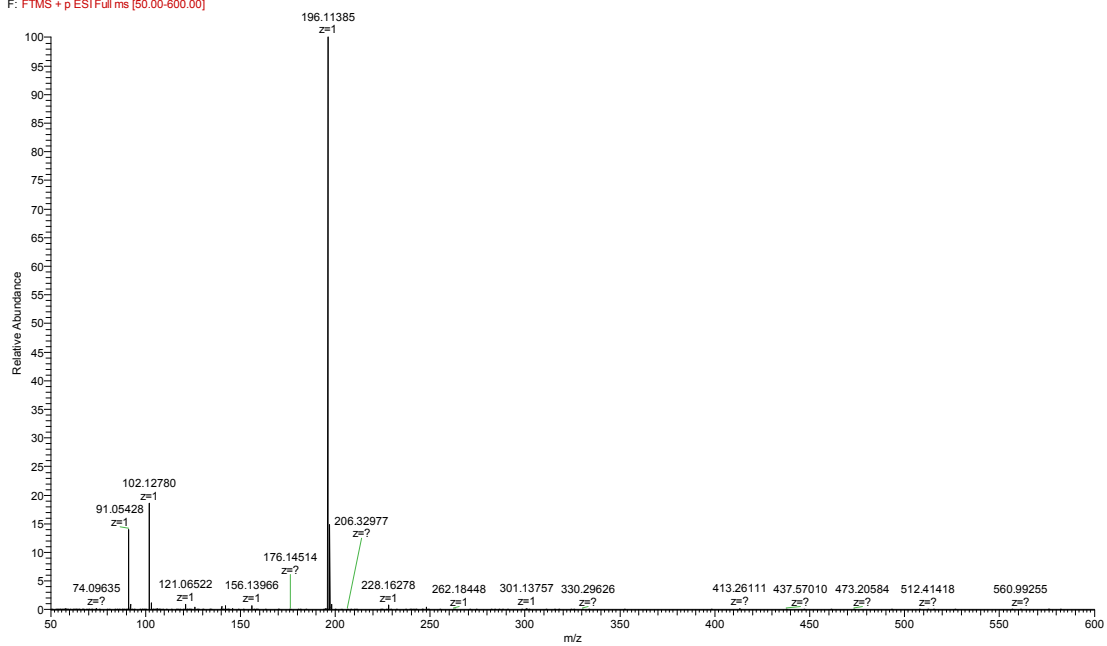


Figure S6. The HRMS spectra of *N*-benzylidenebenzylamine