

Supporting Information

Merging of the photocatalyst decatungstate and naphthalene diimide in hybrid structure for oxidative coupling of amines

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Supplementary Methods:

General methods

All air- and moisture-sensitive solutions and chemicals were handled under a argon atmosphere. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all reagents were commercially available and used as received without further purification. TLC was performed with Merck TLC Silica gel60 F₂₅₄ plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. Deactivated silica gel was prepared by addition of 15 mL Et₃N to 1 L of silica gel. Elemental analysis of the compound was recorded on Elementar Vario EL cube elemental analyzer. Powder X-ray diffraction (PXRD) intensities were performed at room temperature on a Bruker D8 ADVANCE X-Ray diffractometer at 40 kV, 50 mA for a Cu-target tube and a graphite monochromator. A Mettler Toledo equipment in the range 30-800°C with a ramp rate of 10 °C/min was used to carry out thermogravimetric analysis (TGA) experiment in nitrogen atmosphere. Fourier infrared (IR) spectra were measured on a NICOLET 5700 spectrometer using KBr disks dispersed with sample powders. Nuclear magnetic resonance (NMR) spectrum was measured on a Bruker Avance III 400 NMR spectrometer. UV-vis spectra were performed on a Varian Cary 500 UV-Vis spectrophotometer. The XPS experiments were carried out using Thermo Fisher ESCALAB250 spectrometer with Al_{Kα} X-ray source ($\lambda = 8.357 \text{ \AA}$).

Procedure and characterization for oxidative coupling of amines

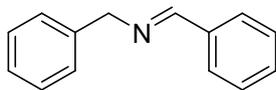
General Procedure:

An oven-dried 10 mL reaction tube equipped with a stir bar was charged with amines (0.4 mmol) and compound 1 (3.42 mg, 0.002 mmol, 0.5 mol%) in air. Anhydrous DMF (2.0 mL) was added by a “Titan” brand 1000 μ L pipettor to the reaction tube. The mixture was exposed to a 100 W white LED lamp placed at a distance of 10 cm and stirred for 24 hours at room temperature. Reaction progress was monitored by TLC. The mixture was extracted with ethyl acetate (10 mL \times 3). The combined organic layer was washed with brine, dried over Na₂SO₄, and the combined solutions were concentrated under reduced pressure. Assay yield determined by ¹H NMR spectroscopy of the crude reaction mixtures using C₂H₂Cl₄ as an internal standard. The crude product was purified by flash chromatography with loading it onto a deactivated silica gel column. (deactivated silica gel was

prepared by the addition of 15 mL of Et₃N to 1 L of silicagel).

Product Characterization:

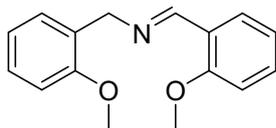
(*E*)-*N*-benzyl-1-phenylmethanimine (2a**):**



The reaction was performed following the General Procedure with phenylmethanamine **1a** (42.86 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2a** (37.88 mg, 97% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.41 (t, *J* = 1.6 Hz, 1H), 7.81 – 7.78(m, 2H), 7.45 – 7.41(m, 3H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.29 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.84 (d, *J* = 1.6 Hz, 2H) ppm; ¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 162.1, 139.3, 136.1, 130.8, 128.6, 128.5, 128.3, 128.0, 127.0, 65.1 ppm.

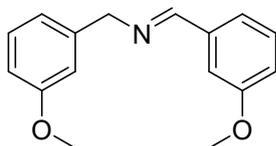
(*E*)-*N*-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (2b**):**



The reaction was performed following the General Procedure with (2-methoxyphenyl)methanamine **1b** (54.88 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2b** (50.04 mg, 98% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 1.2 Hz, 1H), 8.03 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.37 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.30 (ddd, *J* = 7.6, 2.0, 1.2 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.99 – 6.85 (m, 4H), 4.83 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 158.8, 158.4, 157.1, 131.9, 129.1, 128.1, 128.0, 127.5, 124.8, 120.8, 120.5, 111.0, 110.2, 59.7, 55.5, 55.4 ppm.

(*E*)-*N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (2c**):**

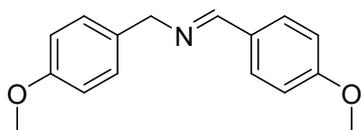


The reaction was performed following the General Procedure with (3-methoxyphenyl)methanamine **1c** (54.88 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2c** (45.96 mg, 90% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.34 (t, *J* = 1.2 Hz, 1H), 7.39 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.32 – 7.24 (m, 3H), 6.98 (ddd, *J* = 7.6, 2.8, 1.6 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.81 (ddd, *J* = 8.0, 2.4, 0.8 Hz, 1H), 4.79 (d, *J* =

1.6 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 162.1, 159.9, 159.8, 140.8, 137.5, 129.6, 129.6, 121.7, 120.4, 117.7, 113.6, 112.5, 111.6, 64.9, 55.4, 55.2 ppm.

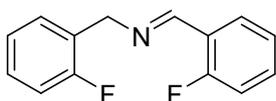
(*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (2d**):**



The reaction was performed following the General Procedure with (4-methoxyphenyl)methanamine **1d** (54.88 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2d** (42.38 mg, 83% yield) as a colorless oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 6.92 – 6.85 (m, 4H), 4.71 (s, 2H), 3.81 (d, $J = 0.8$ Hz, 3H), 3.77 (d, $J = 0.8$ Hz, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, Chloroform-*d*) δ 161.7, 161.1, 158.6, 131.6, 129.9, 129.2, 129.1, 114.0, 113.9, 64.4, 55.4, 55.3 ppm.

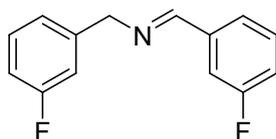
(*E*)-*N*-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (2e**):**



The reaction was performed following the General Procedure with (2-fluorophenyl)methanamine **1e** (50.06 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2e** (45.32 mg, 98% yield) as a colorless oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, $J = 1.6$ Hz, 1H), 8.03 (td, $J = 7.6, 1.6$ Hz, 1H), 7.42–7.35 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.03 (m, 4H), 4.87 (t, $J = 1.2$ Hz, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 163.6, 162.0, 161.1, 159.6, 156.1 (d, $J_{\text{C-F}} = 5.0$ Hz), 132.5 (d, $J_{\text{C-F}} = 8.5$ Hz), 130.2 (d, $J_{\text{C-F}} = 4.4$ Hz), 128.9 (d, $J_{\text{C-F}} = 8.1$ Hz), 127.8 (d, $J_{\text{C-F}} = 2.8$ Hz), 126.1 (d, $J_{\text{C-F}} = 14.8$ Hz), 124.4 (d, $J_{\text{C-F}} = 3.2$ Hz), 124.2 (d, $J_{\text{C-F}} = 3.7$ Hz), 123.7 (d, $J_{\text{C-F}} = 9.0$ Hz), 115.8 (d, $J_{\text{C-F}} = 21.2$ Hz), 115.3 (d, $J_{\text{C-F}} = 21.3$ Hz), 58.6 (d, $J_{\text{C-F}} = 2.9$ Hz) ppm.

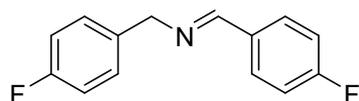
(*E*)-*N*-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (2f**):**



The reaction was performed following the General Procedure with (3-fluorophenyl)methanamine **1f** (50.06 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2f** (43.94 mg, 95% yield) as a colorless oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, J = 1.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.38 (td, J = 8.0, 5.2 Hz, 1H), 7.30 (td, J = 8.0, 6.0 Hz, 1H), 7.15–7.09 (m, 2H), 7.05 (dt, J = 9.6, 2.0 Hz, 1H), 6.95 (td, J = 8.8, 2.8 Hz, 1H), 4.80 (s, 2H) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 164.3 (d, $J_{\text{C-F}}$ = 5.6 Hz), 161.8 (d, $J_{\text{C-F}}$ = 4.9 Hz), 161.1 (d, $J_{\text{C-F}}$ = 2.9 Hz), 141.6 (d, $J_{\text{C-F}}$ = 7.3 Hz), 138.3 (d, $J_{\text{C-F}}$ = 7.3 Hz), 130.2 (d, $J_{\text{C-F}}$ = 8.1 Hz), 130.0 (d, $J_{\text{C-F}}$ = 8.1 Hz), 124.5 (d, $J_{\text{C-F}}$ = 2.9 Hz), 123.4 (d, $J_{\text{C-F}}$ = 2.9 Hz), 117.9 (d, $J_{\text{C-F}}$ = 21.8 Hz), 114.8 (d, $J_{\text{C-F}}$ = 21.9 Hz), 114.4 (d, $J_{\text{C-F}}$ = 22.2 Hz), 114.0 (d, $J_{\text{C-F}}$ = 21.1 Hz), 64.2 (d, $J_{\text{C-F}}$ = 2.1 Hz).

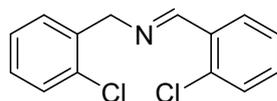
(*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (2g):



The reaction was performed following the General Procedure with (4-fluorophenyl)methanamine **1g** (50.06 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2g** (43.01 mg, 93% yield) as a colorless oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.34 (t, J = 1.6 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.32 – 7.27 (m, 2H), 7.13 – 7.00 (m, 4H), 4.76 (s, 2H) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 165.7, 163.2 (d, $J_{\text{C-F}}$ = 4.3 Hz), 160.8, 160.6, 134.9 (d, $J_{\text{C-F}}$ = 3.3 Hz), 132.3 (q, $J_{\text{C-F}}$ = 3.0 Hz), 130.2 (d, $J_{\text{C-F}}$ = 8.8 Hz), 129.5 (d, $J_{\text{C-F}}$ = 8.1 Hz), 115.8 (d, $J_{\text{C-F}}$ = 21.9 Hz), 115.3 (d, $J_{\text{C-F}}$ = 21.3 Hz), 64.2 ppm.

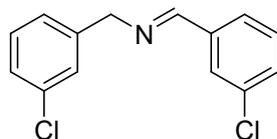
(*E*)-*N*-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (2h):



The reaction was performed following the General Procedure with (2-chlorophenyl)methanamine **1h** (56.64 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2h** (47.55 mg, 90% yield) as a colorless oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.87 (d, J = 1.6 Hz, 1H), 8.11 (dd, J = 7.6, 1.6 Hz, 1H), 7.43 – 7.31 (m, 4H), 7.30 – 7.18 (m, 3H), 4.93 (d, J = 1.2 Hz, 2H) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 159.8, 136.9, 135.3, 133.4, 133.1, 131.8, 129.9, 129.7, 129.4, 128.5, 128.4, 127.1, 127.0, 62.2 ppm.

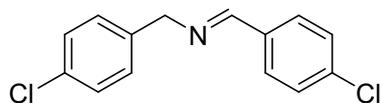
(*E*)-*N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (2i):



The reaction was performed following the General Procedure with (3-chlorophenyl)methanamine **1i** (56.64 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2i** (48.08 mg, 91% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.32 (t, *J* = 1.6 Hz, 1H), 7.81 (t, *J* = 1.6 Hz, 1H), 7.62 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.42 – 7.29 (m, 3H), 7.28 – 7.20 (m, 3H), 4.77 (d, *J* = 1.2 Hz, 2H) ppm; ¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 161.0, 141.0, 137.6, 134.9, 134.4, 131.0, 130.0, 129.8, 128.1, 128.0, 127.3, 126.7, 126.1, 64.3 ppm.

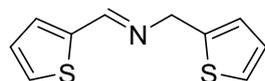
(*E*)-*N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (2j**):**



The reaction was performed following the General Procedure with (4-chlorophenyl)methanamine **1j** (56.64 mg, 0.4 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2j** (50.19 mg, 95% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.33 (t, *J* = 1.2 Hz, 1H), 7.70 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.38 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.31 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.27 – 7.24 (m, 2H), 4.86 (t, *J* = 0.8 Hz, 2H) ppm; ¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 160.9, 137.6, 136.9, 134.4, 132.9, 129.5, 129.3, 129.0, 128.7, 64.2 ppm.

(*E*)-1-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine (2k**):**



The reaction was performed following the General Procedure with thiophen-2-ylmethanamine **1k** (27.44 mg, 0.2 mmol). The crude material was purified by flash chromatography on deactivated silica gel (eluted with EtOAc : hexanes = 1:25) to give the product **2k** (33.17 mg, 80% yield) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (t, *J* = 1.2 Hz, 1H), 7.41 (dt, *J* = 5.2, 1.2 Hz, 1H), 7.32 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.23 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.06 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.99 – 6.95 (m, 2H), 4.94 (t, *J* = 1.2 Hz, 2H) ppm; ¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 155.5, 142.1, 141.5, 131.1, 129.5, 127.5, 127.0, 125.4, 124.9, 58.5 ppm.

Table S1. Crystallographic data and structure refinement details for compound **1**.

Complex	1
Chemical formula	C ₂₄ H ₃₃ N ₅ O ₂₁ W ₅ Zn
formula weight	1712.17
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> (Å)	11.6641(6)
<i>b</i> (Å)	12.2880(6)
<i>c</i> (Å)	17.5529(6)
α (deg)	104.503(4)
β (deg)	102.541(4)
γ (deg)	105.931(4)
<i>V</i> (Å ³)	2228.95(19)
<i>Z</i>	2
ρ_{calc} (g/cm ³)	2.551
μ (Mo K α) (mm ⁻¹)	13.454
F(000)	1560
collected reflns	15783
unique reflns/ <i>R</i> _{int}	7317/0.0273
no. of observations	6072
GOF	1.042
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0346, 0.0932
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0450, 0.0972

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

Table S2. Photocatalytic oxidation of benzylamine to imine over different material catalysts

Catalyst	Light source	Conditions	Conversion	Ref.
PCN-222	Xe lamp	r.t. air, 1 h, 0.1 mmol benzylamine, 5 mg PCN-222, 3 mL CH ₃ CN	100%	S1
NH ₂ -MIL-125 (Ti)	visible light	r.t. O ₂ , 12 h, 0.1 mmol benzylamine, 5 mg catalyst, 2 mL CH ₃ CN	73%	S2
Zn-PDI	Xe lamp (500 W)	r.t. air, 4 h, 1 mmol benzylamine, 0.01 mmol Zn-PDI, 5 mL CH ₃ CN	74%	S3
FJI-Y10	Xe lamp (300 W)	40 °C, O ₂ , 6 h, 1.0 mmol benzylamine, 10 mg FJI-Y10, 5 mL DMF	100%	S4
Zn-MOF	Xe arc lamp (300 W)	r.t. O ₂ , 1 h, 0.2 mmol benzylamine, 5 mg Zn-MOF, 1 mL CH ₃ CN	99%	S5
Zn-bpydc	Xe lamp (300 W) with full spectrum	25 °C, air, 4 h, 0.5 mmol benzylamine, 10 mg Zn-bpydc, 5 mL DMF	99.7%	S6
Mn-MOF	Xe lamp (300 W)	r.t. O ₂ , 1 h, 0.2 mmol benzylamine, 6 mg Mn-MOF, 1 mL DMA/DMF	99%	S7
Cd(dcbpy)	Xe lamp (300 W) with full spectrum	25 °C, air, 7 h, 0.48 mmol benzylamine, 10 mg catalyst, 5 mL DMF	99%	S8
RPF-30-Er	100 W warming lamp	25 °C, O ₂ , 18 h, 0.05 mmol benzylamine, 10 mol% catalyst, 1 mL CH ₃ CN	76%	S9
NNU-45	Xe lamp (300 W)	r.t. O ₂ , 160 min, 0.2 mmol benzylamine, 4 mg catalyst, 1 mL DMSO	99%	S10
NH ₂ -UiO-66	Xe lamp (350 W) with full spectrum	r.t. air, 10 h, 0.1 mmol benzylamine, 15 mg NH ₂ -UiO-66, 5 mL CH ₃ CN	83%	S11
Pd(1.0)/MIL-125-NH ₂	Xe lamp (300 W) 360–780 nm	r.t. O ₂ , 3 h, 0.05 mmol benzylamine, 5 mg photocatalyst, 2 mL CH ₃ CN	94.08%	S12
Ru(bpy) ₃ @MIL-125	Xe lamp (300 W)	r.t. air, 3 h, 0.1 mmol benzylamine, 5 mg catalyst, 3 mL CH ₃ CN	100%	S13
CNUIO-5	Xe lamp (300 W)	r.t. O ₂ , 5 h, 0.05 mmol benzylamines, 5 mg CNUIO-5, 5 mL CH ₃ CN	58.9%	S14
CdS@MIL-101	Xe lamp (300 W)	Ice bath, air, 9 h, 0.1 mmol benzylamine, 50 mg catalyst, 2 mL toluene	100%	S15
Zn ₂ (DPNDI)(W ₁₀ O ₃₂)(DMA) ₆	LED lamp (100W)	r.t. air, 24 h, 0.2 mmol benzylamine, 3.42 mg catalyst, 5 mL DMF	99%	This work

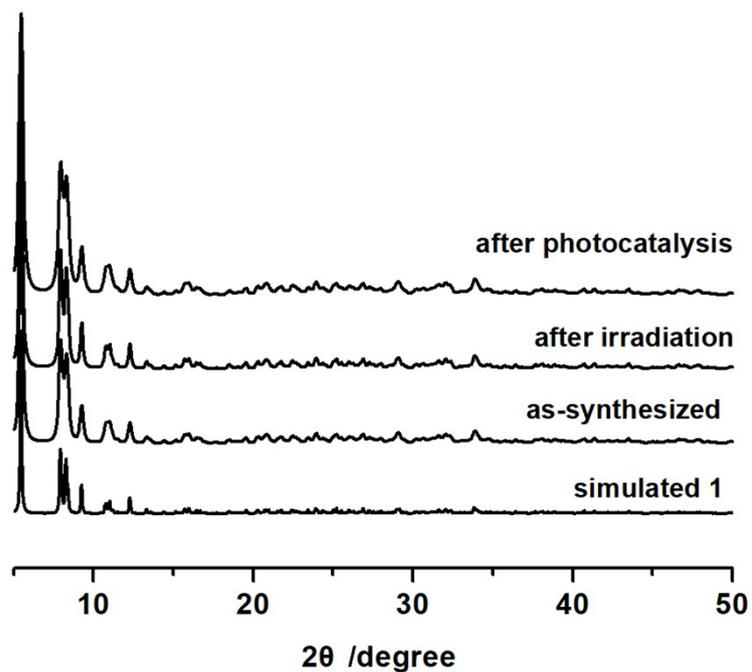


Figure S1. The XRD patterns of compound 1 after different treatment.

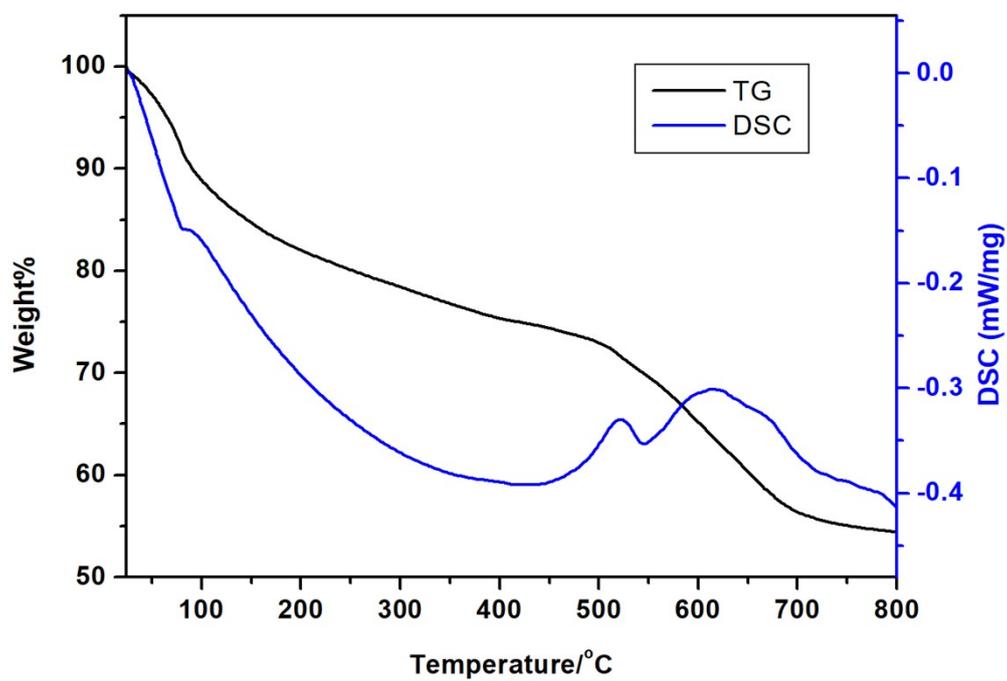


Figure S2. TGA and DSC curves of compound 1 under N_2 atmosphere with a heating rate of $10^\circ C/min$.

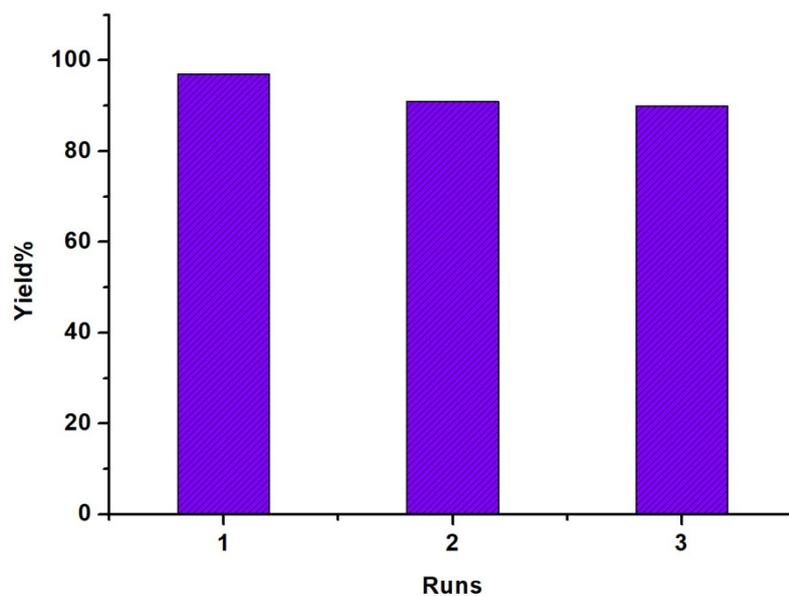


Figure S3. The recycle experiments for oxidative coupling of amines by using compound 1 as catalyst.

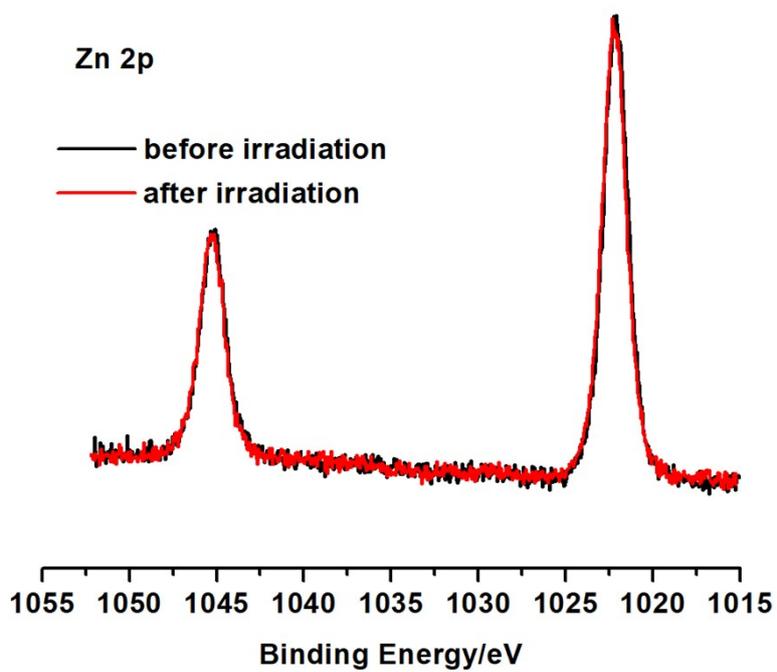


Figure S4. Zn 2p XPS core-level spectra of compound 1 before and after irradiation.

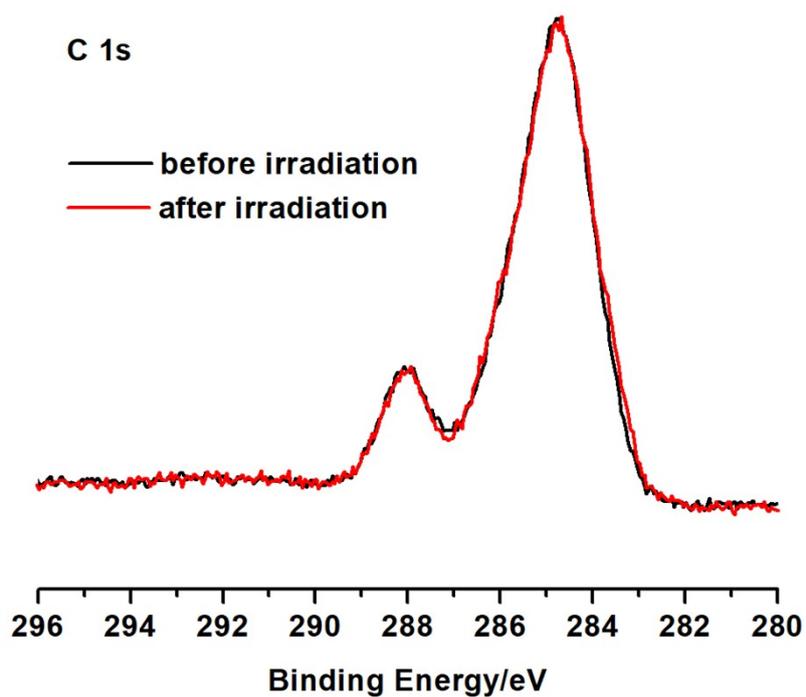


Figure S5. C 1s XPS core-level spectra of compound 1 before and after irradiation.

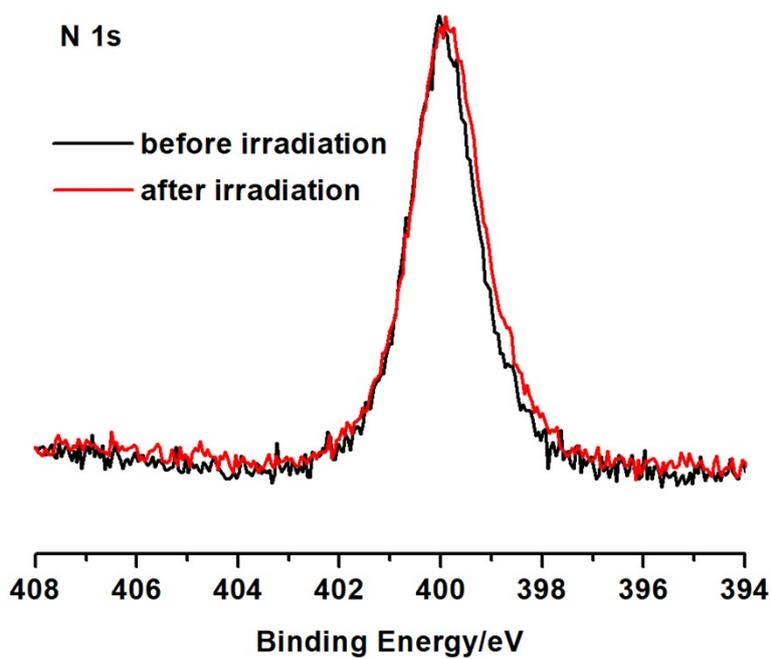


Figure S6. N 1s XPS core-level spectra of compound 1 before and after irradiation.

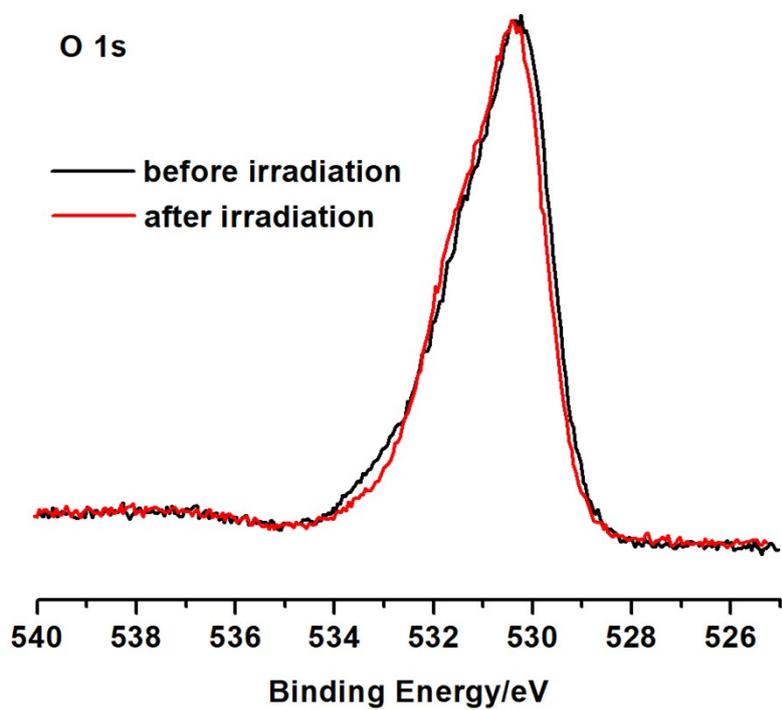


Figure S7. O 1s XPS core-level spectra of compound 1 before and after irradiation.

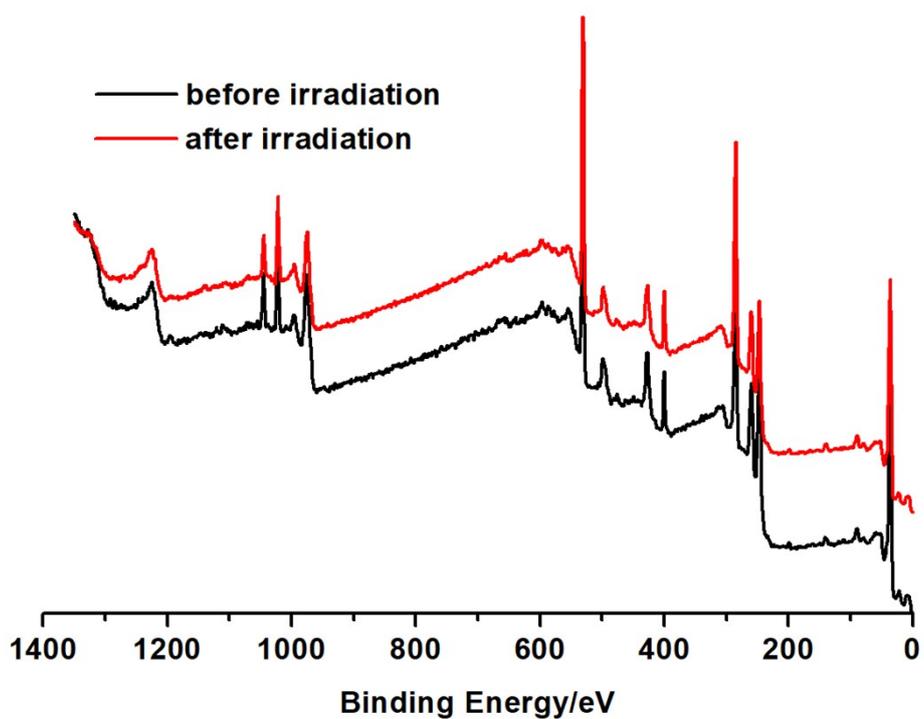


Figure S8. Survey XPS core-level spectra of compound 1 before and after irradiation.

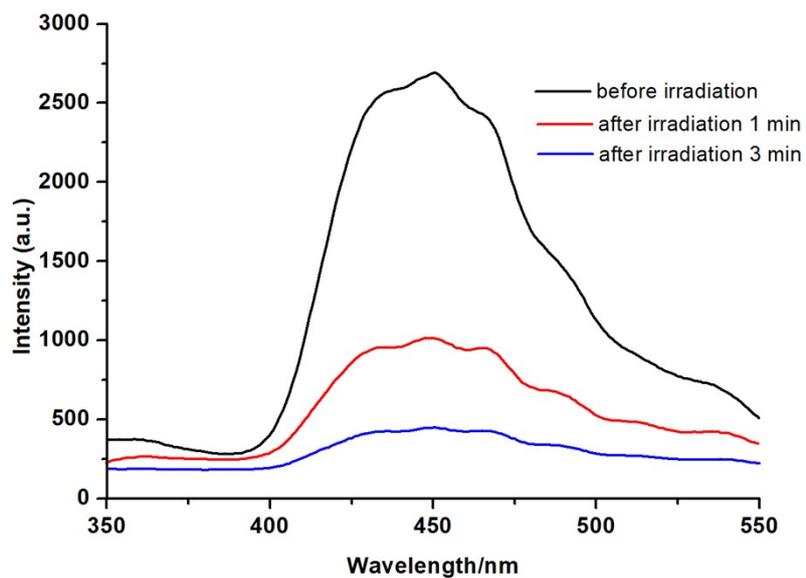


Figure S9. Fluorescence spectra of compound 1 at room temperature in air ($\lambda_{\text{ex}} = 300$ nm).

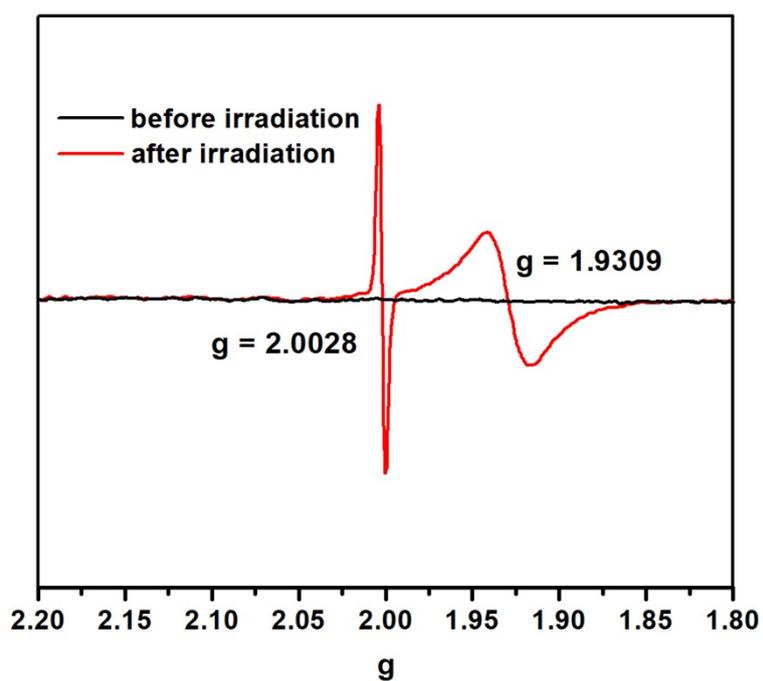


Figure S10. EPR spectra of the original and colored sample of compound 1.

NMR Spectra

Figure S11. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-benzyl-1-phenylmethanimine (**2a**):

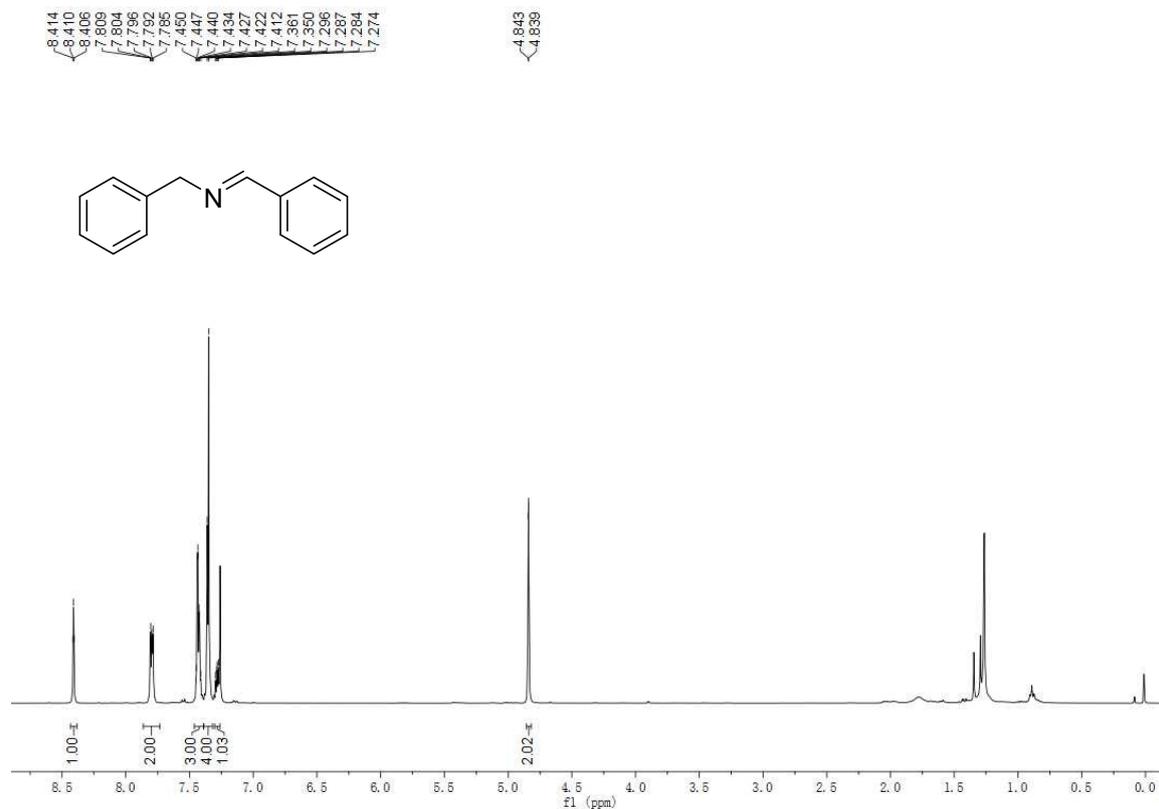


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-benzyl-1-phenylmethanimine (**2a**):

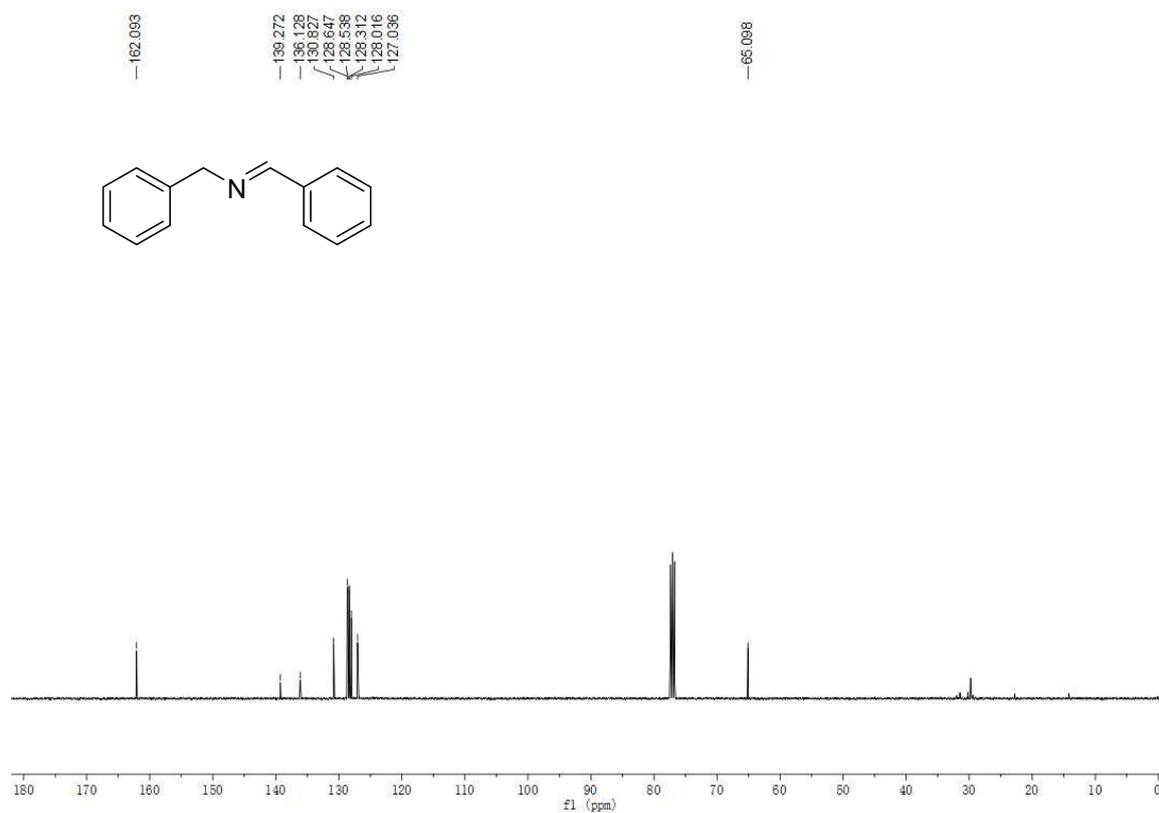


Figure S13. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (**2b**):

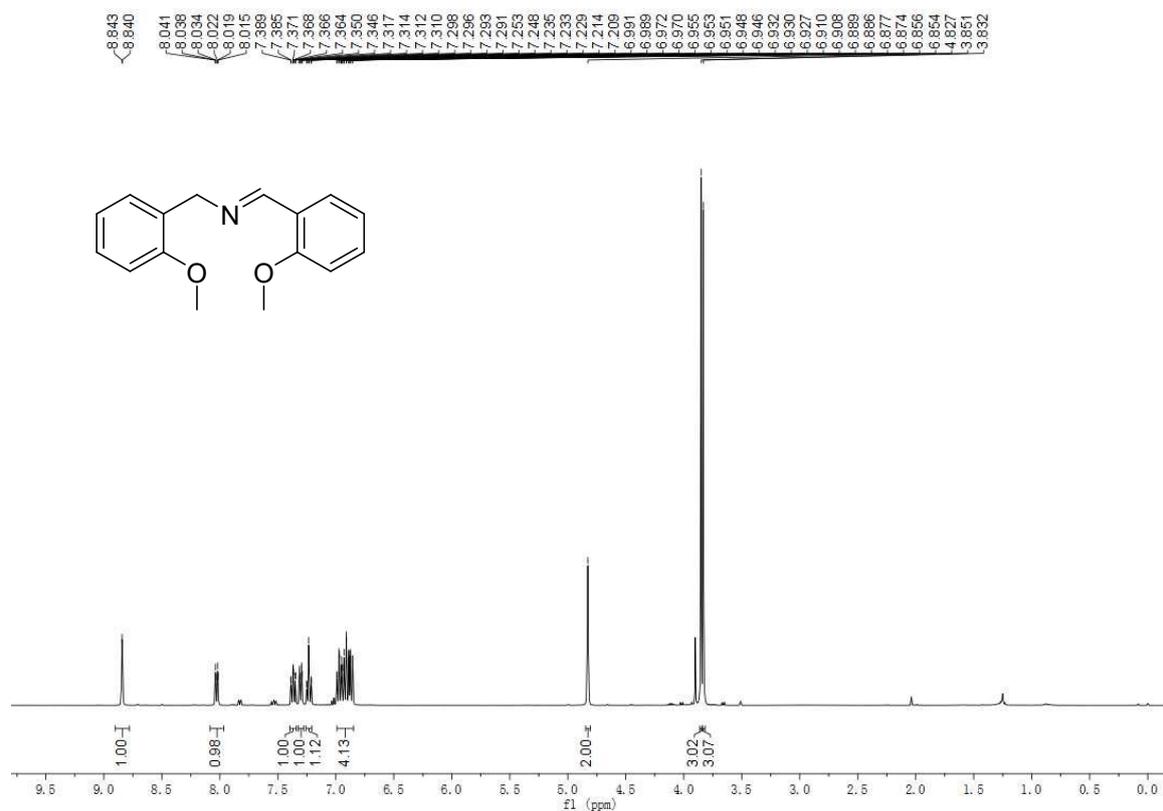


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(2-methoxybenzyl)-1-(2-methoxyphenyl)methanimine (**2b**):

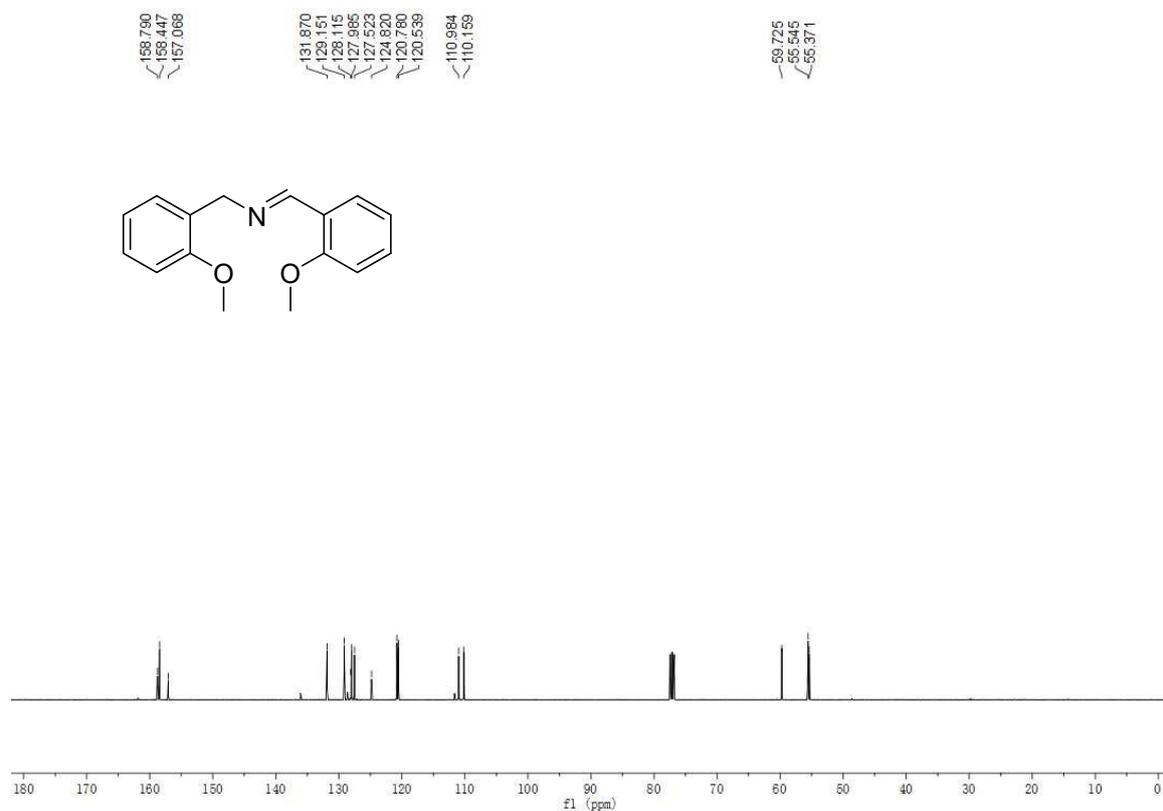


Figure S15. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (**2c**):

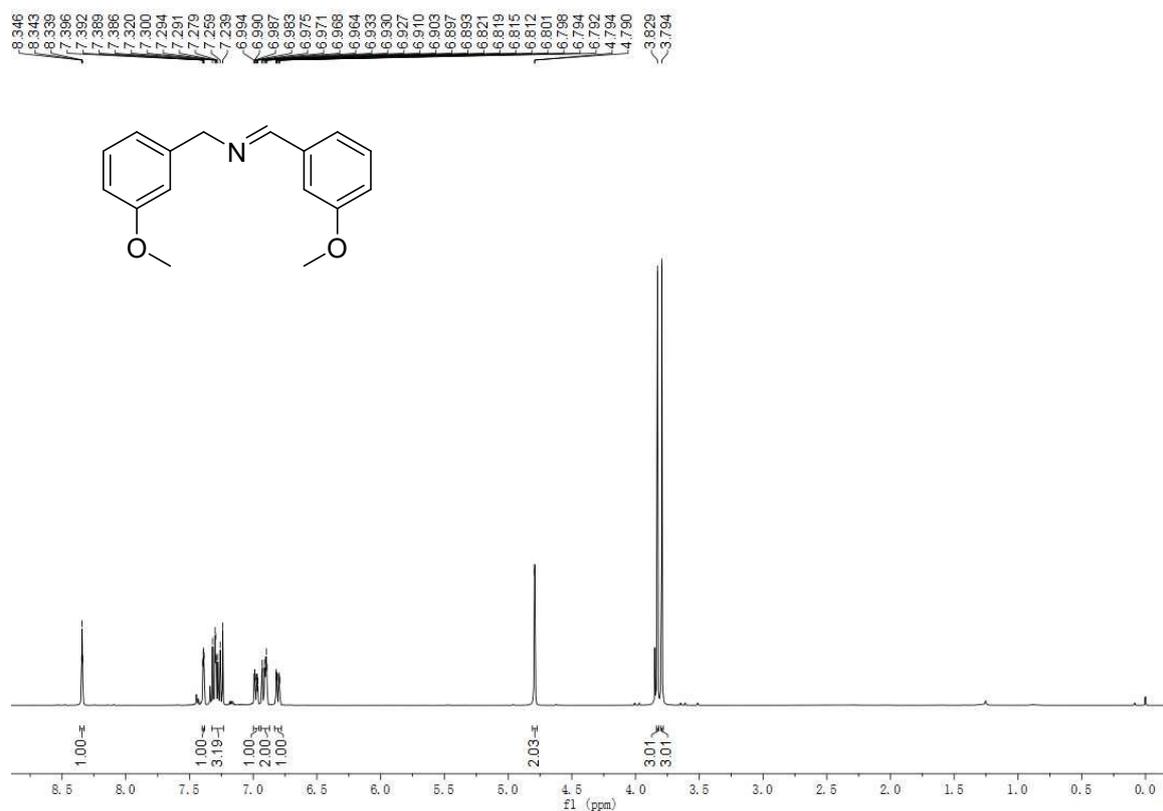


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (**2c**):

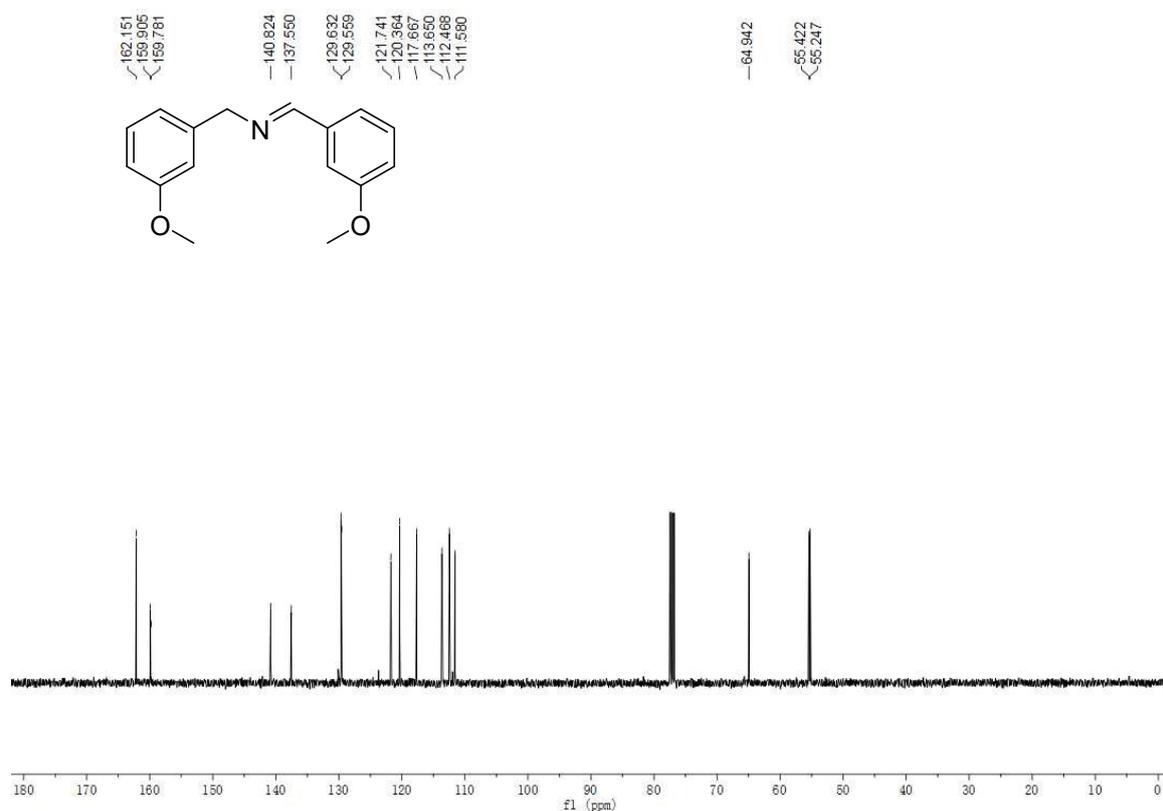


Figure S17. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (**2d**):

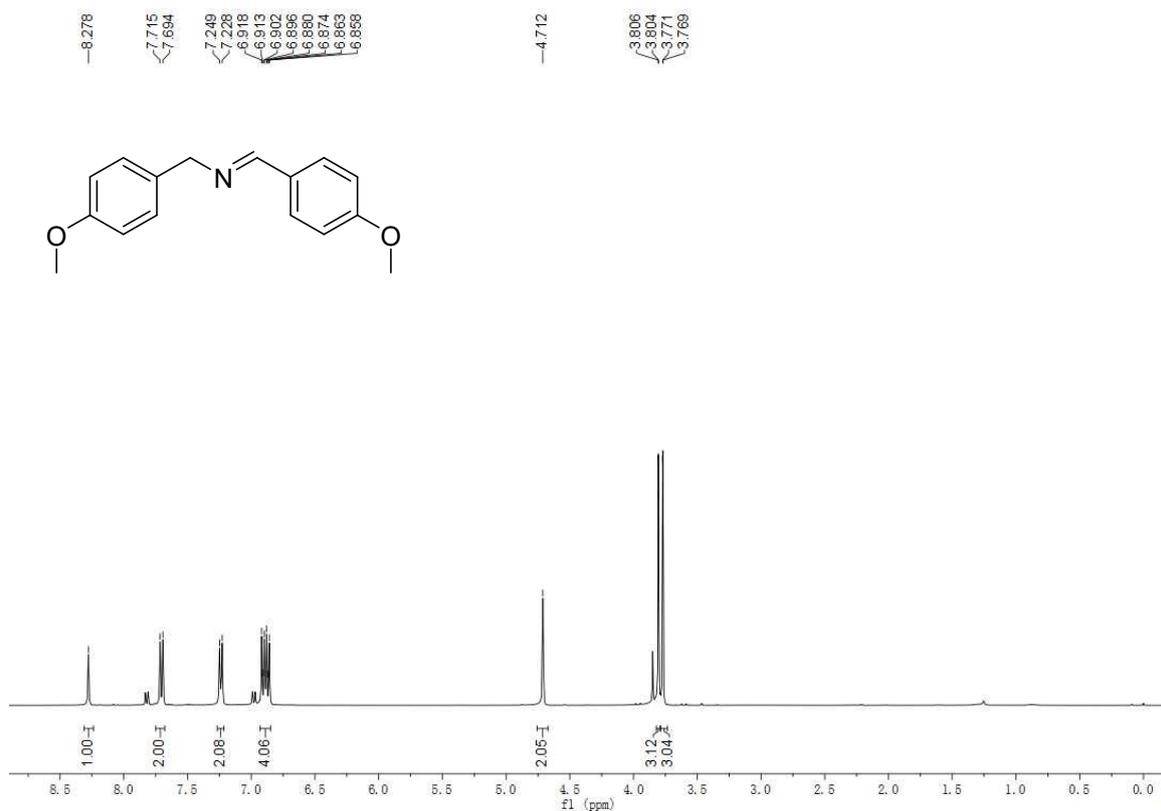


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (**2d**):

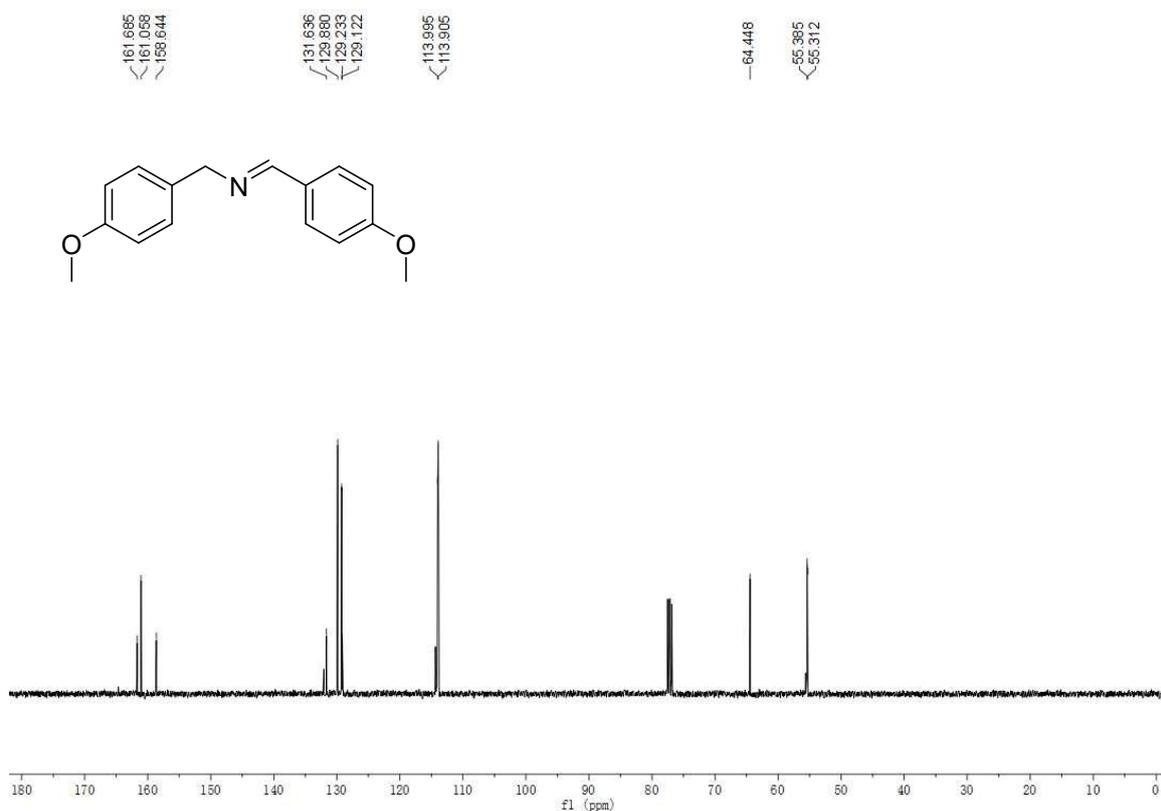


Figure S19. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (**2e**):

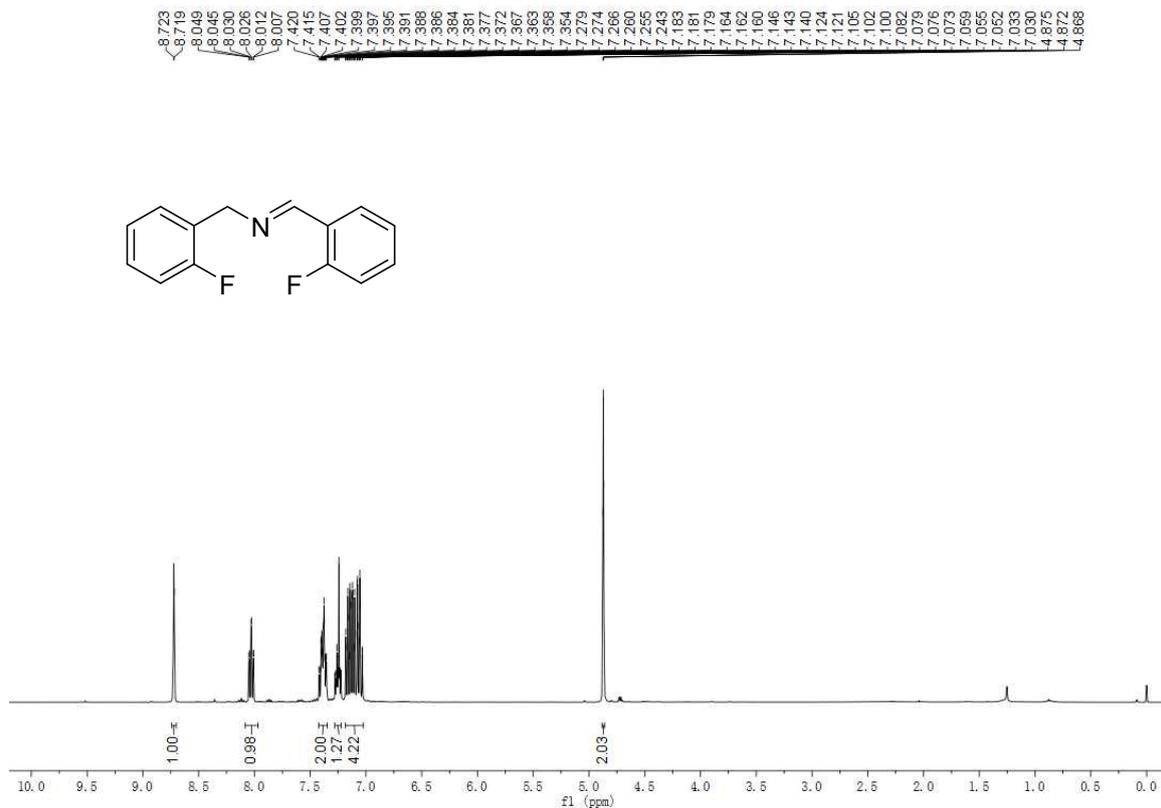


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-fluorobenzyl)-1-(2-fluorophenyl)methanimine (**2e**):

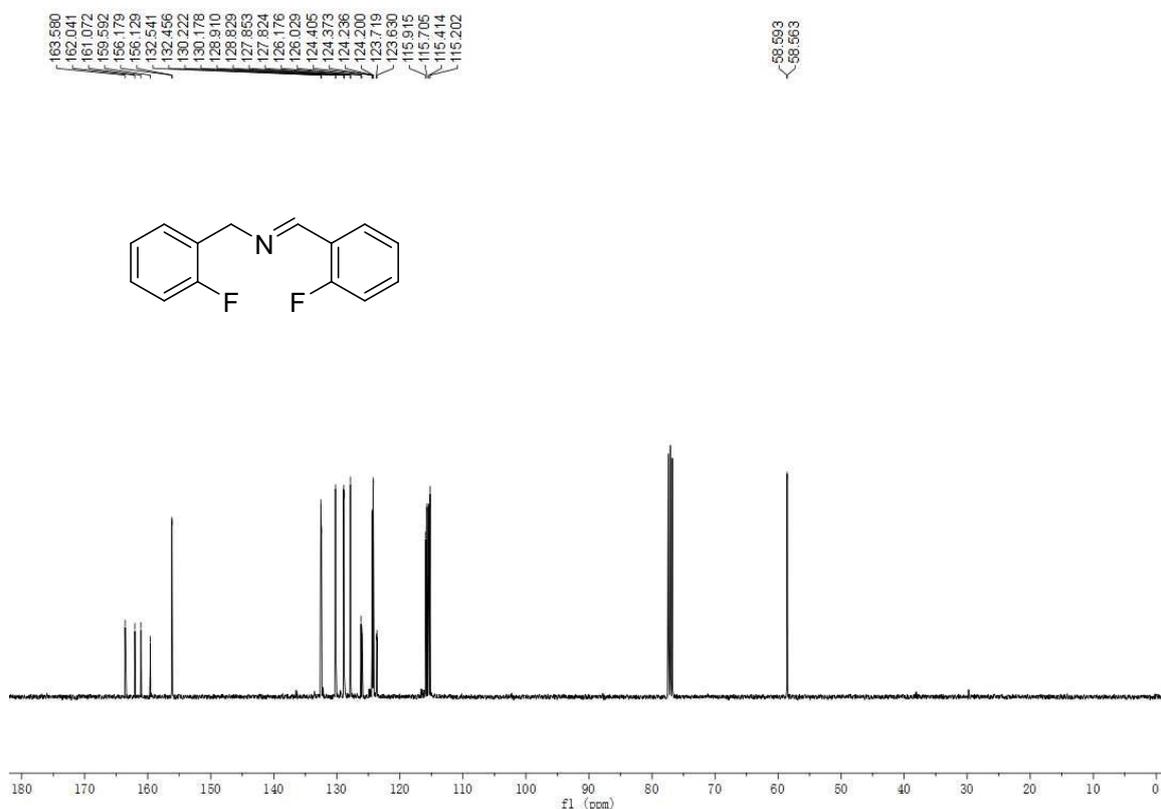


Figure S21. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (**2f**):

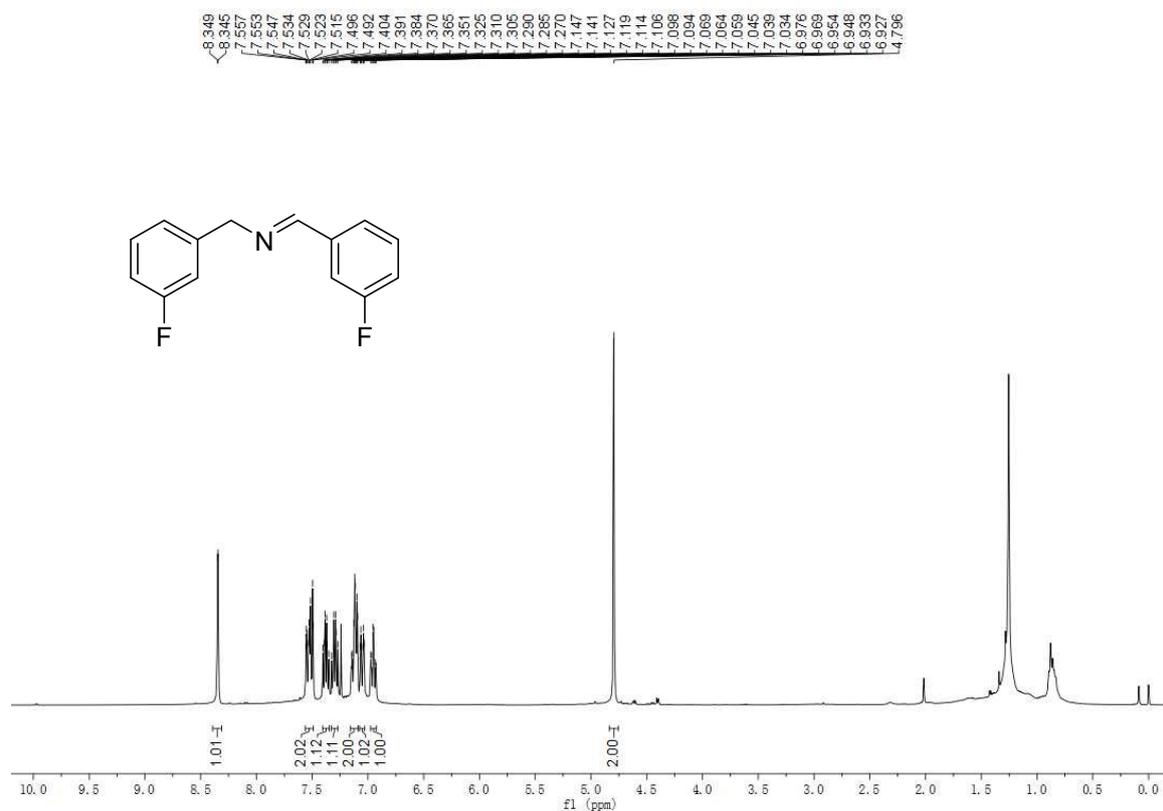


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (**2f**):

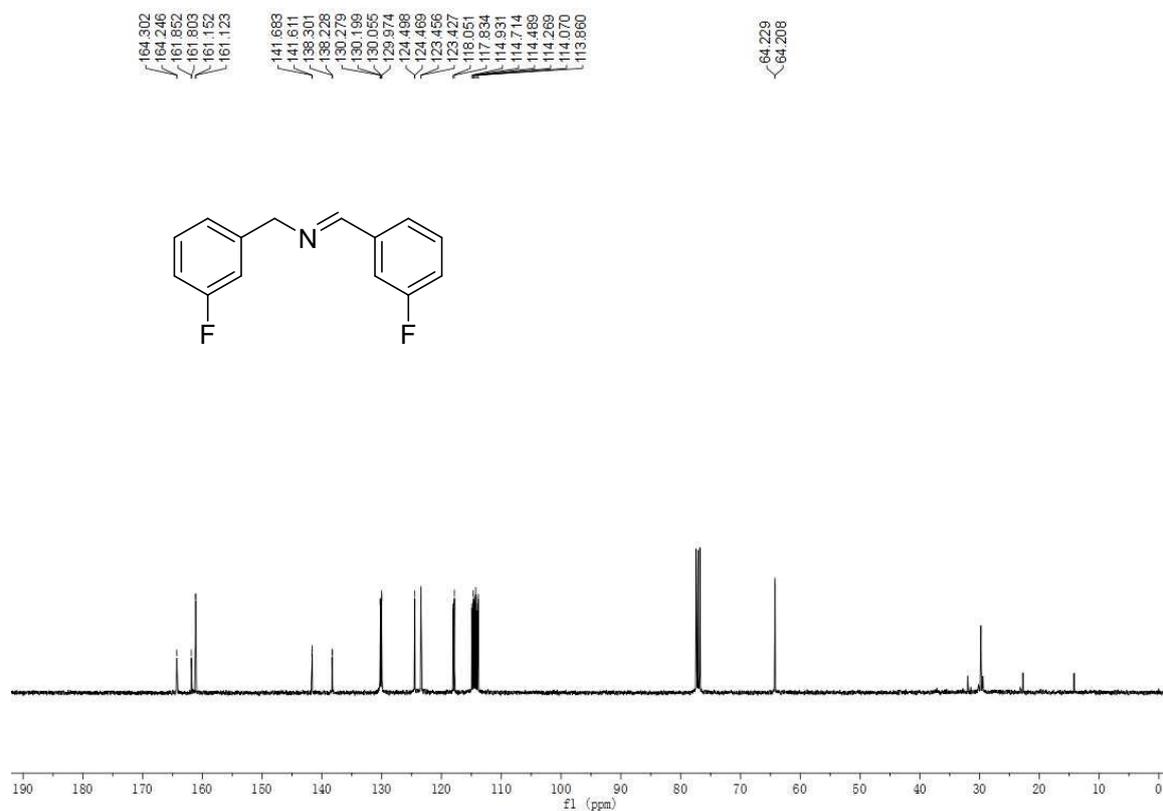


Figure S23. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (2g):

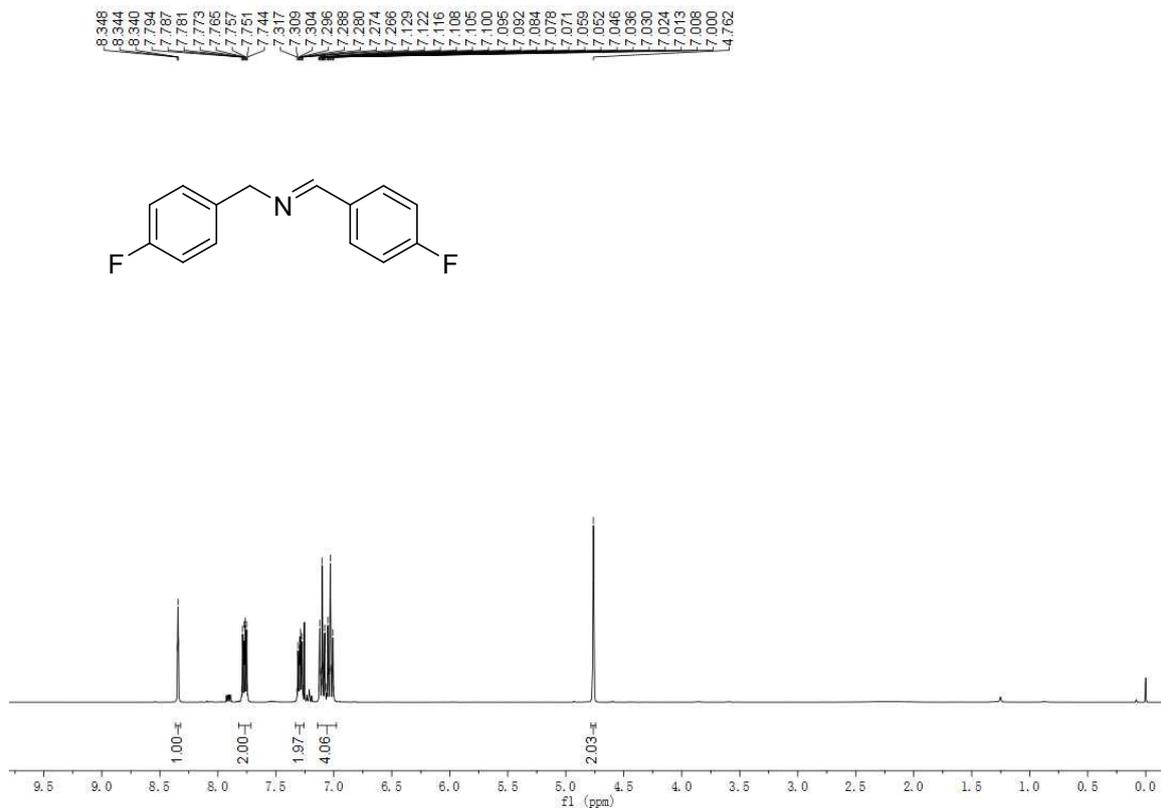


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (2g):

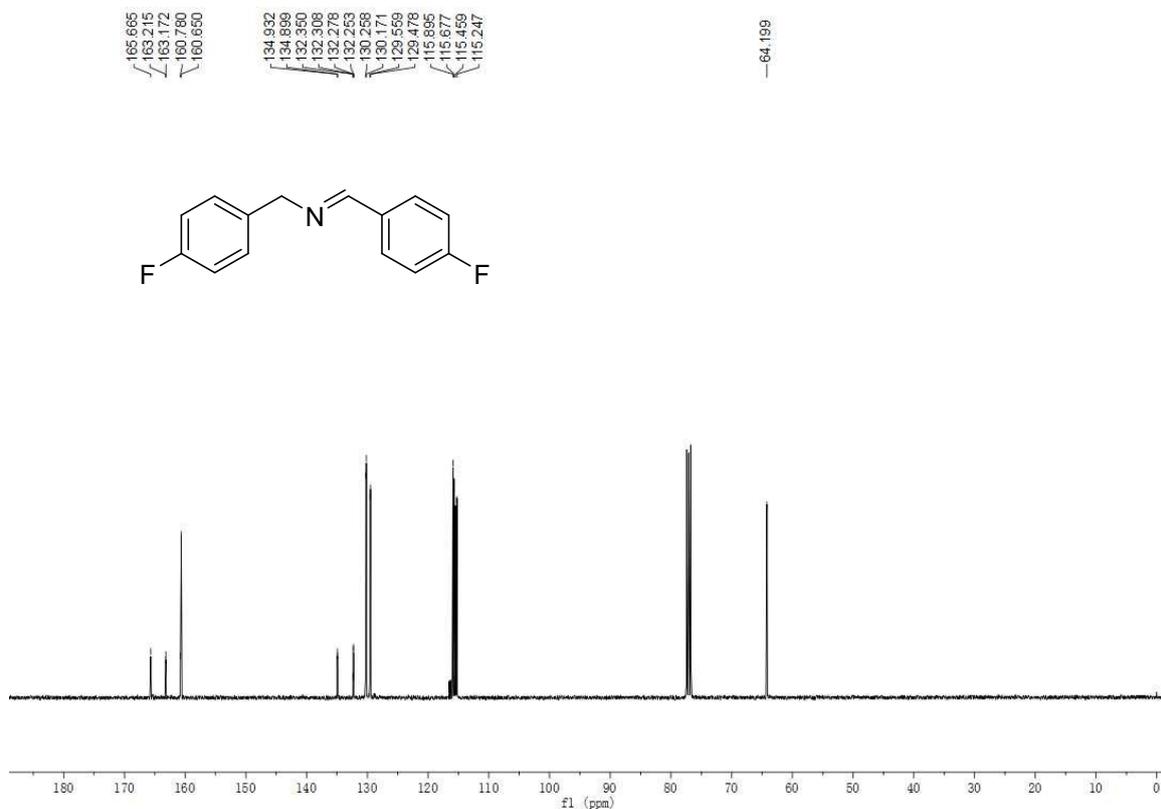


Figure S25. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (**2h**):

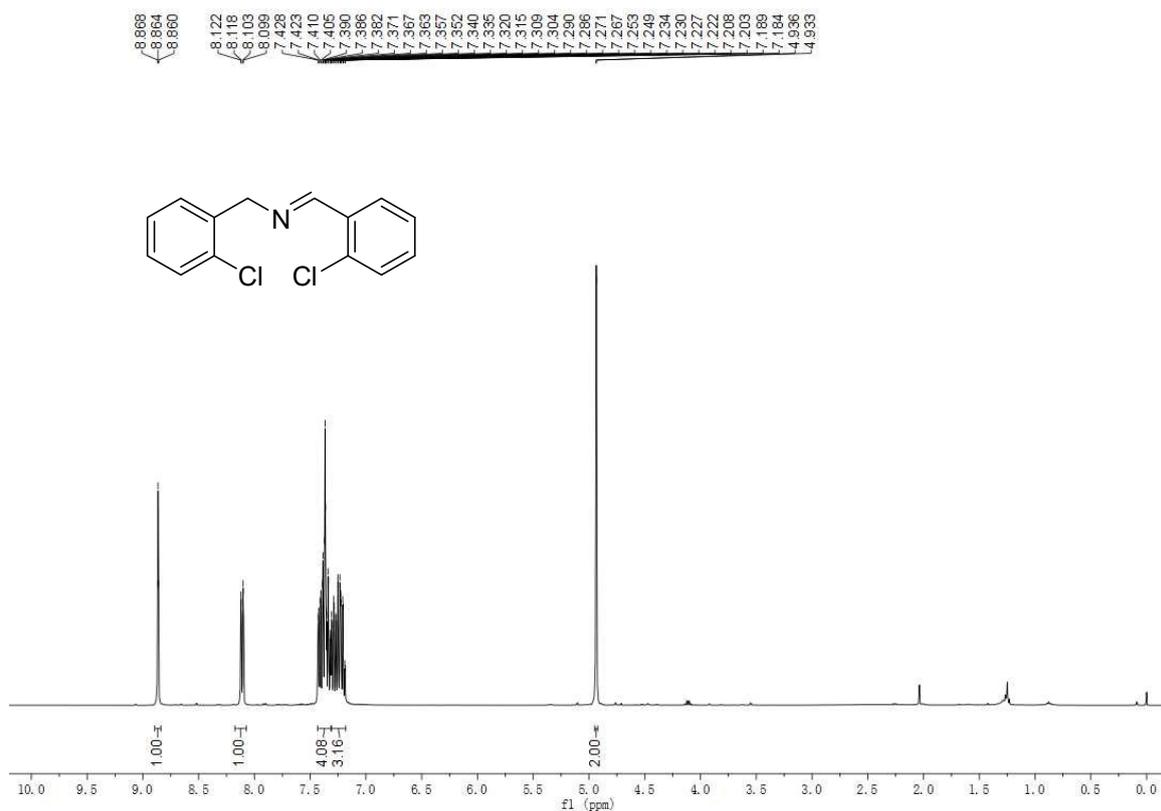


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(2-chlorobenzyl)-1-(2-chlorophenyl)methanimine (**2h**):

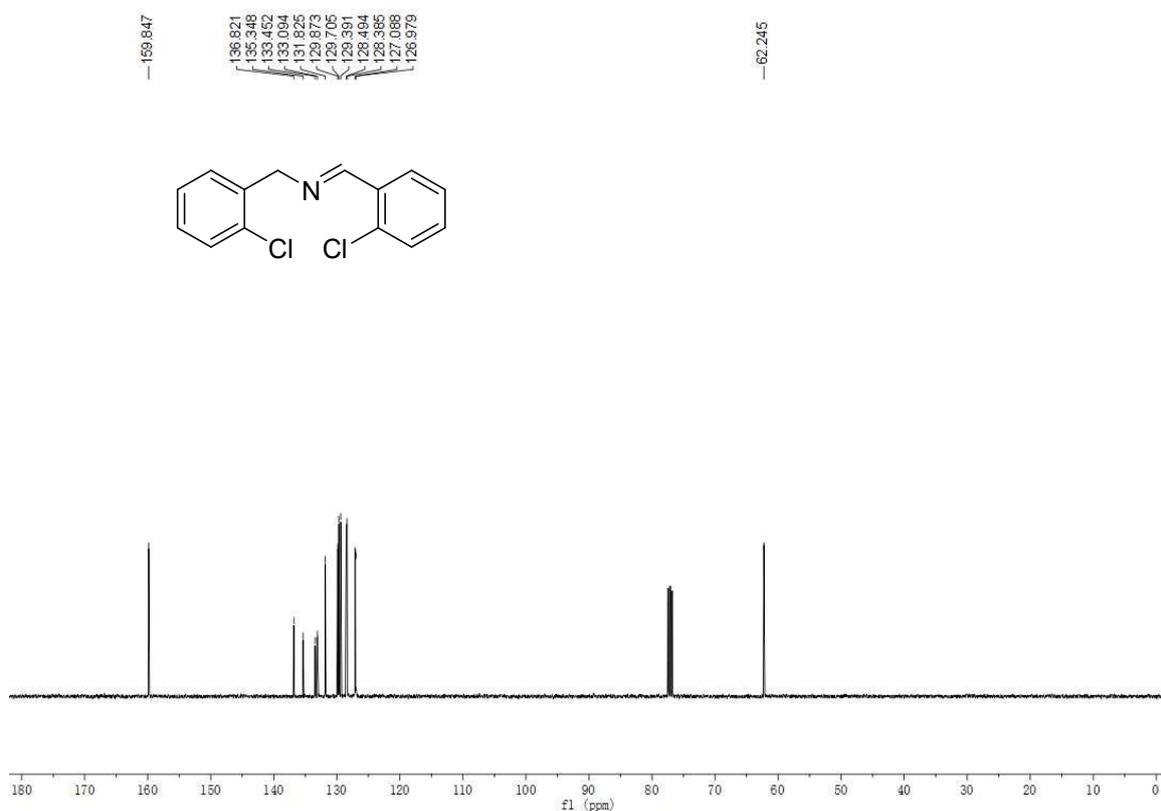


Figure S27. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (**2i**):

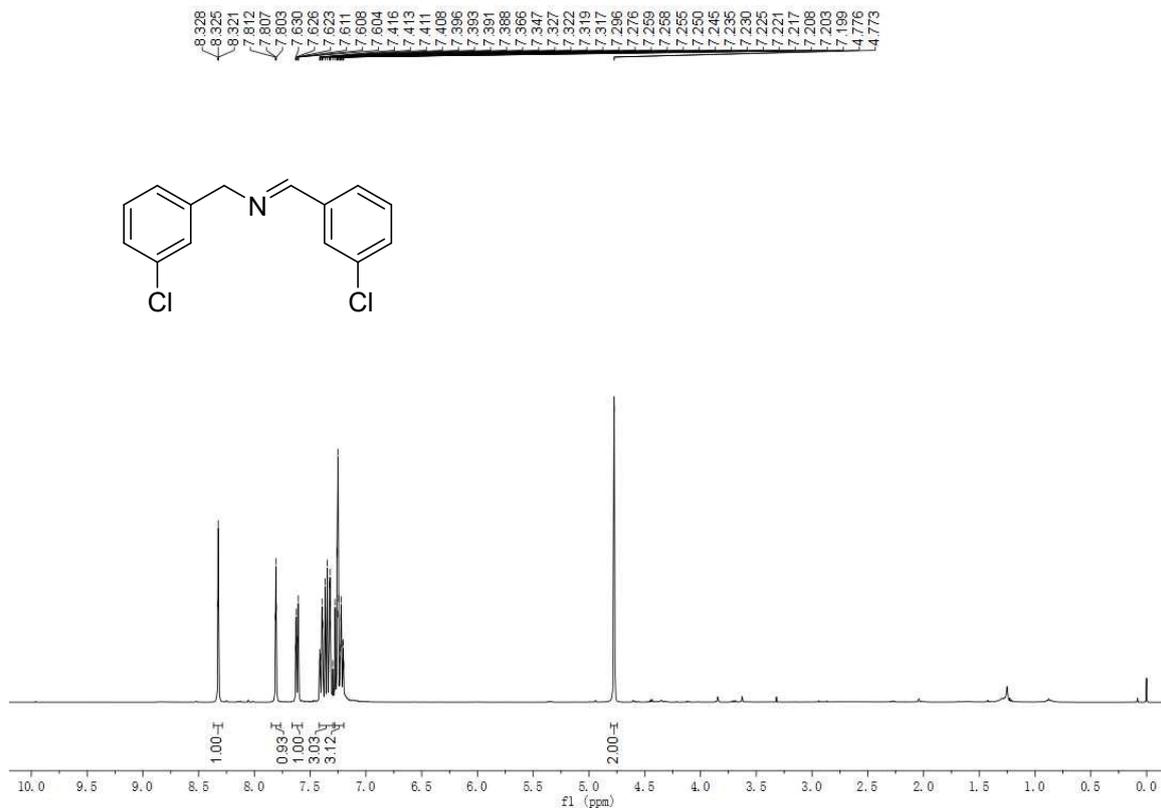


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(3-chlorobenzyl)-1-(3-chlorophenyl)methanimine (**2i**):

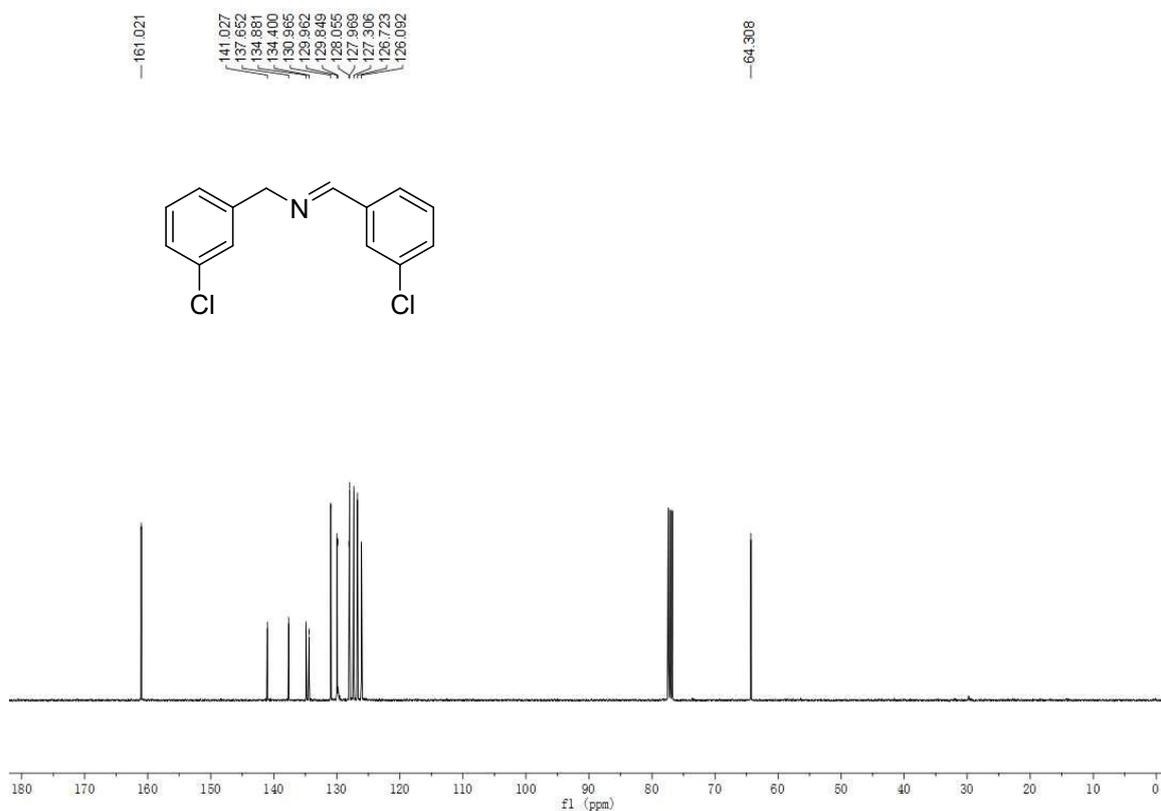


Figure S29. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (**2j**):

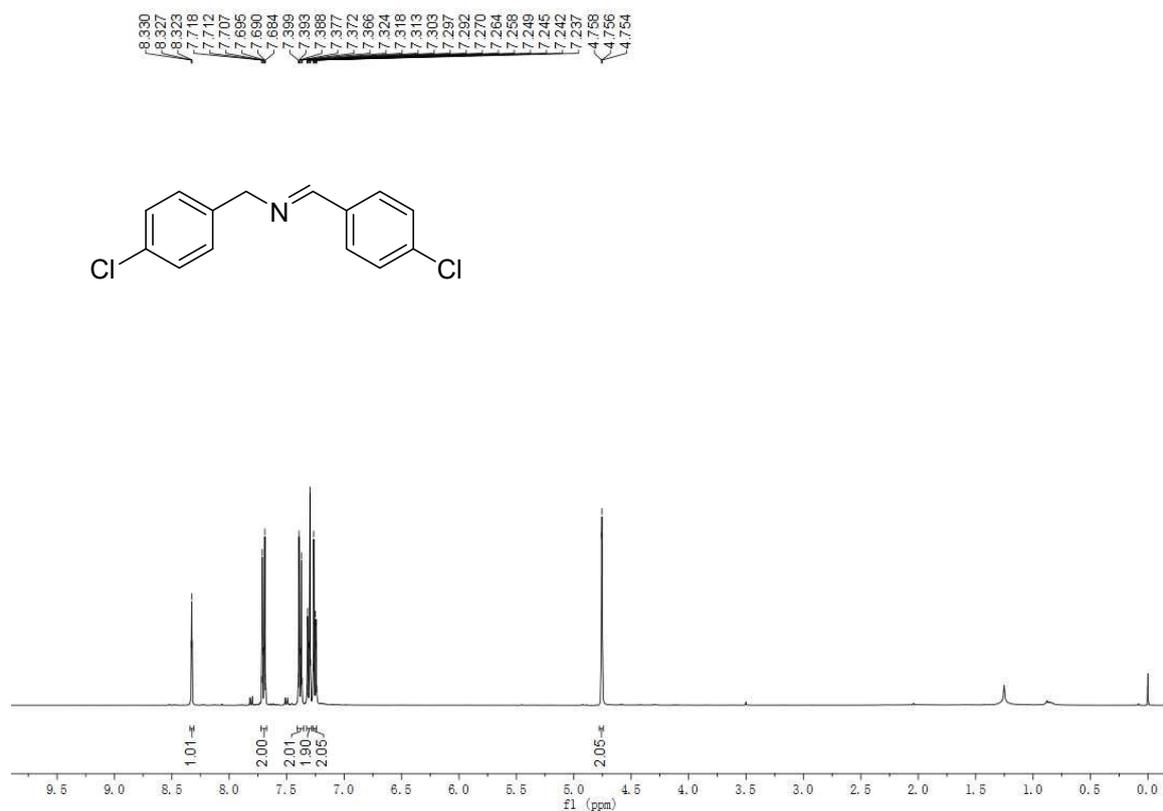


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (**2j**):

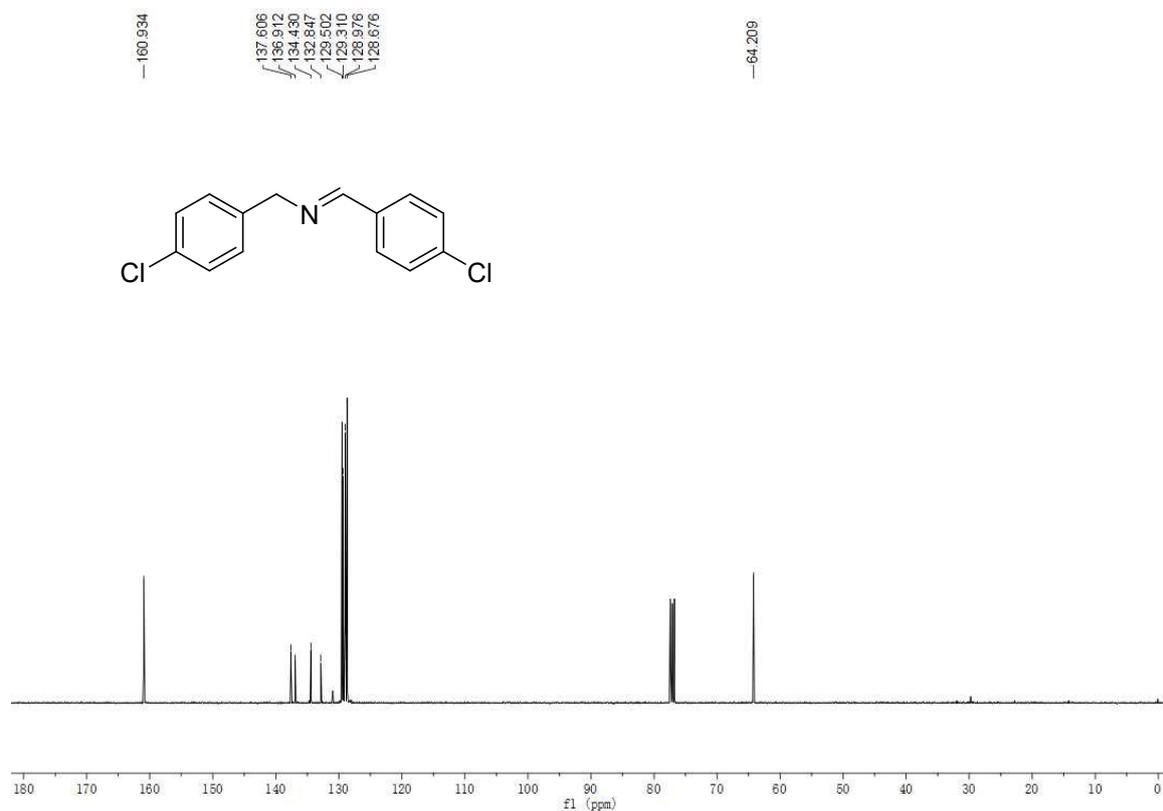


Figure S31. ^1H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-1-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine (2k):

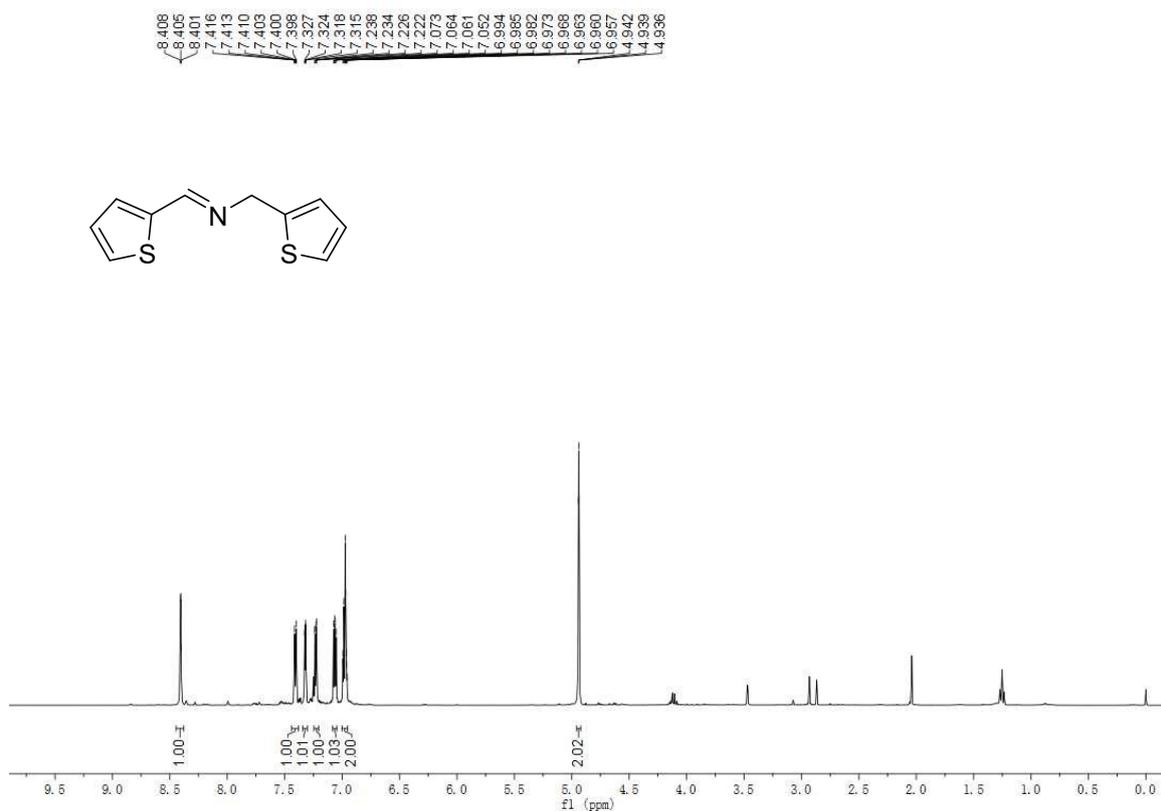
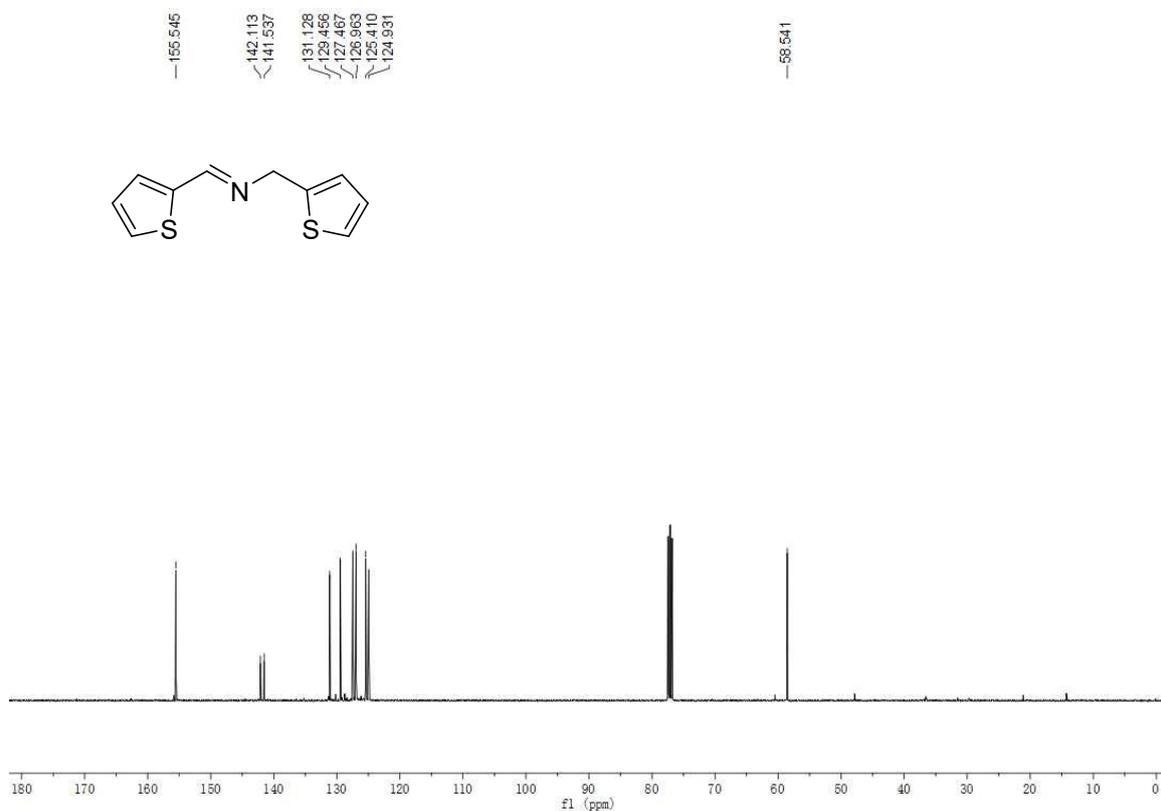


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-1-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine (2k):



References

- S1. C. Xu, H. Liu, D. Li, J.-H. Su and H.-L. Jiang, *Chem. Sci.*, 2018, 9, 3152–3158
- S2. D. Sun, L. Ye and Z. Li, *Appl. Catal., B*, 2015, 164, 428–432.
- S3. L. Zeng, T. Liu, C. He, D. Shi, F. Zhang and C. Duan, *J. Am. Chem. Soc.*, 2016, 138, 3958–3961.
- S4 F.-J. Zhao, G. Zhang, Z. Ju, Y.-X. Tan and D. Yuan, *Inorg. Chem.*, 2020, 59, 3297–3303.
- S5. P. Chen, Z. Guo, X. Liu, H. Lv, Y. Che, R. Bai, Y. Chi and H. Xing, *J. Mater. Chem. A*, 2019, 7, 27074–27080.
- S6. Y. Sha, J. Zhang, D. Tan, F. Zhang, X. Cheng, X. Tan, B. Zhang, B. Han, L. Zheng and J. Zhang, *Chem. Commun.*, 2020, 56, 10754–10757.
- S7. H. Liu, Z. Guo, H. Lv, X. Liu, Y. Che, Y. Mei, R. Bai, Y. Chi and H. Xing, *Inorg. Chem. Front.*, 2020, 7, 1016–1025.
- S8. J. Shi, J. Zhang, T. Liang, D. Tan, X. Tan, Q. Wan, X. Cheng, B. Zhang, B. Han, L. Liu and F. Zhang, *ACS Appl. Mater. Interfaces*, 2019, 11, 30953–30958.
- S9. L. M. Aguirre-Dí'az, N. Snejko, M. Iglesias, F. Sanchez, E. Gutierrez-Puebla and M. A. Monge, *Inorg. Chem.*, 2018, 57, 6883–6892.
- S10. H. Wei, Z. Guo, X. Liang, P. Chen, H. Liu and H. Xing, *ACS Appl. Mater. Interfaces*, 2019, 11, 3016–3023.
- S11. R. Liu, S. Meng, Y. Ma, L. Niu, S. He, X. Xu, B. Su, D. Lu, Z. Yang and Z. Lei, *Catal. Commun.*, 2019, 124, 108–112.
- S12. T. Wang, X. Tao, Y. Xiao, G. Qiu, Y. Yang and B. Li, *Catal. Sci. Technol.*, 2020, 10, 138–146.
- S13. X. Yang, T. Huang, S. Gao and R. Cao, *J. Catal.*, 2019, 378, 248–255.
- S14. S. Zhang, K. Chen, W. Peng and J. Huang, *New J. Chem.*, 2020, 44, 3052–3061.
- S15. R. Wu, S. Wang, Y. Zhou, J. Long, F. Dong and W. Zhang, *ACS Appl. Nano Mater.*, 2019, 2, 6818–6827.