Electronic Supplementary Information

Photocatalytic oxidative amine coupling using polyhedral $SrTiO_3$ crystals

Zong-Li Chen and Michael H. Huang*
Department of Chemistry, National Tsing Hua University, Hsinchu 300044, Taiwan

Synthesis of $SrTiO_3$ crystals

To grow 138 nm $SrTiO_3$ cubes, 2.5 mL ethanol was first mixed with 0.031 mL of $TiCl_4$ solution. $TiCl_4$ source is already a solution. After stirring for 10 min on the heating agitator, 1 mL of an aqueous solution containing 0.084 g of solid $SrCl_2 \cdot 6H_2O$ compound was added. After stirring for 5 min, 3.7 mL of 3 M LiOH aqueous solution was introduced. The stirring process should be carried out in an ice bath at about 5 ºC, and an additional 30 min of stirring is required. Next, the mixture was transferred to a Teflon container placed in an autoclave. The autoclave was heated at a set temperature of 70 ºC for 3 h.

For the synthesis of 213 nm $SrTiO_3$ cubes, 1 mL of water and 1.5 mL of hexanol were mixed, followed the addition of 0.026 mL of $TiCl_4$ solution. After stirring for 10 min, 1 mL of an aqueous solution containing 0.070 g of $SrCl_2 \cdot 6H_2O$ was added and stirred for another 5 min. Next, 3.7 mL of a 3 M LiOH aqueous solution was introduced and stirred for 30 min. All steps should be carried out in an ice bath at 5 ºC. Then the solution was transferred to an autoclave and heated at 70 ºC in an oven for 3 h.

For {110}-truncated $SrTiO_3$ cubes, 2 mL of water, 0.85 mL of hexanol, and 0.208 mL of $TiCl_4$ solution were mixed for 10 min. Next, 1 mL of an aqueous solution containing 0.560 g of $SrCl_2 \cdot 6H_2O$ was added. After stirring for 5 min, 3.7 mL of a 3 M LiOH aqueous solution was added. Here all the processes were conducted at room temperature. After stirring for 30 min, the solution was transferred to a Teflon-covered autoclave and heated in an oven at 200 ºC for 20 h.

To make {100}-truncated $SrTiO_3$ rhombic dodecahedra, 2 mL of water, 0.85 mL of ethylene glycol, and 0.026 mL of $TiCl_4$ solution were mixed and stirred for 10 min. Next, 1 mL of aqueous solution containing 0.070 g of $SrCl_2 \cdot 6H_2O$ was introduced and stirred for 5 min. Then 3.7 mL of 3 M LiOH aqueous solution was introduced and stirred for 30 min. All processes were kept at room temperature. The solution was transferred to an autoclave and heated in an oven set at 200 ºC for 20 h.

Reactive species trapping experiment

For the trapping reagent experiments, the photocatalytic reaction steps are similar to those described. However, there are slight variations in the experimental procedure depending on the specific trapping reagent used. When using (2,2,6,6-

tetramethylpiperidin-1-yl)oxyl (TEMPO), it is important to note that TEMPO sublimes in a vacuum system. Therefore, TEMPO is first dissolved in acetonitrile and then injected into a 15 mL quartz test tube for the reaction. After the reaction, the standard treatment follows. However, to calculate the isolated yield, the crude product obtained is subjected to sublimation in a vacuum system using a heating water bath to remove the TEMPO reagent, and then it can be weighed.

When using tert-butanol, it is first dissolved in acetonitrile and injected into a quartz test tube. After the reaction, the standard treatment follows. Tert-butanol can be removed through rotary evaporation and a vacuum system. Therefore, from the isolated product, the yield can be calculated.

When using bicyclo[2.2.2]-1,4-diazaoctane (DABCO), it is important to note that DABCO is prone to hydrolysis and sublimation. Therefore, DABCO is first dissolved in acetonitrile and then injected into a quartz test tube for the reaction. After the reaction, the standard treatment follows. Here a vacuum system is not used. The crude product obtained after rotary evaporation can be subjected to NMR analysis to measure the conversion by calculating the integral value.

When using KI or $AgNO_3$, it is added together with $SrTiO_3$ crystals into a quartz test tube. The tube is then sealed with a serum stopper and subjected to vacuum and oxygen filling steps. KI is removed by centrifugation, and the organic layer is retained. A vacuum system is not used. After rotary evaporation, the crude product can be obtained and subjected to NMR analysis to measure the conversion by calculating the integral value.

Since 1,4-benzoquinone sublimes in a vacuum system, it is first dissolved in acetonitrile and injected into a quartz test tube for the reaction. The crude product obtained is purified using column chromatography to obtain the isolated product, which is then weighed to calculate the yield.

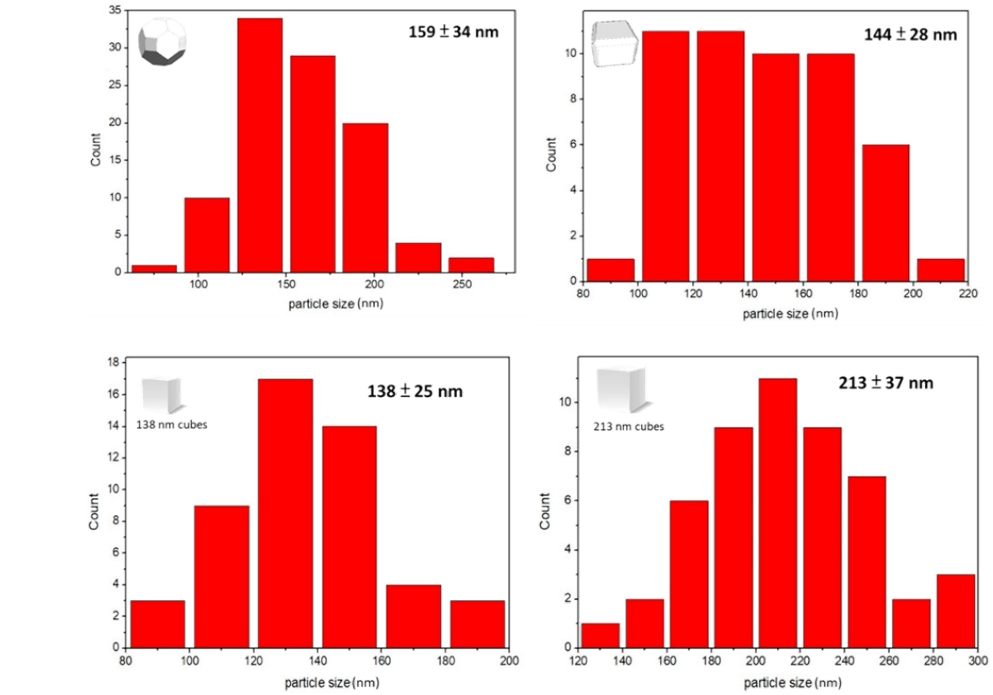


Fig. S1 Size distribution histograms of the synthesized $SrTiO_3$ crystals. Opposite {100} face length was used for the size measurements of the truncated rhombic dodecahedra.

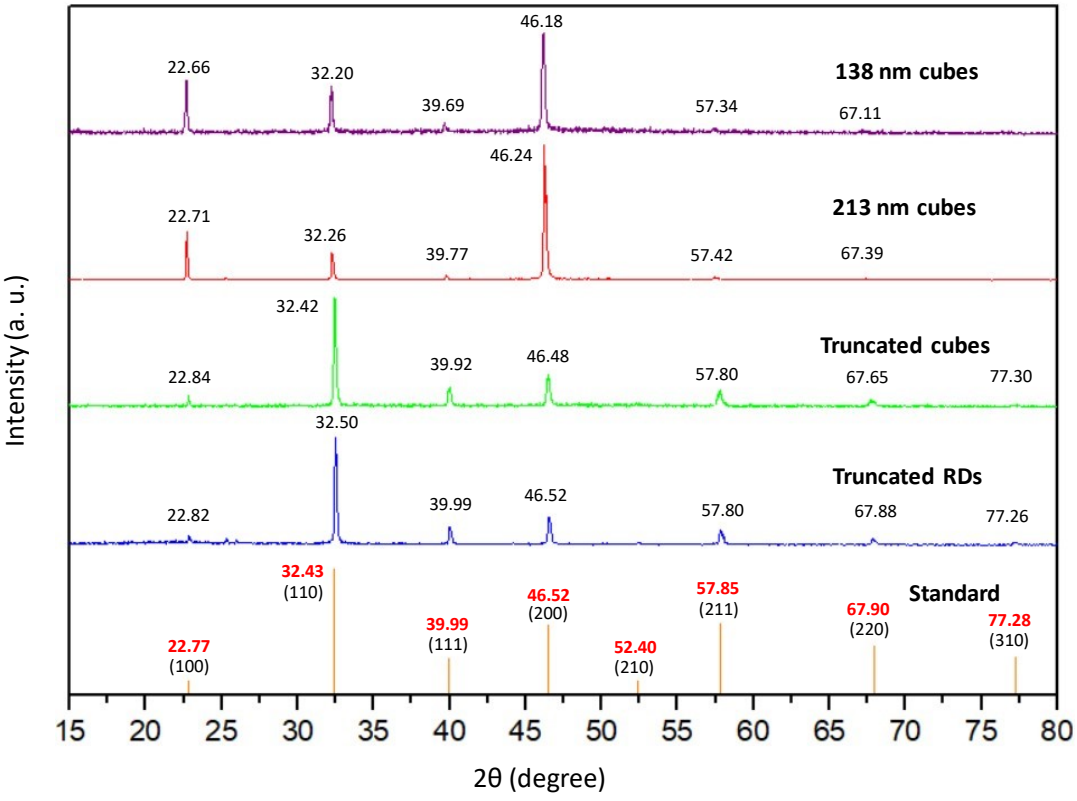


Fig. S2 XRD patterns of different $SrTiO_3$ crystals.

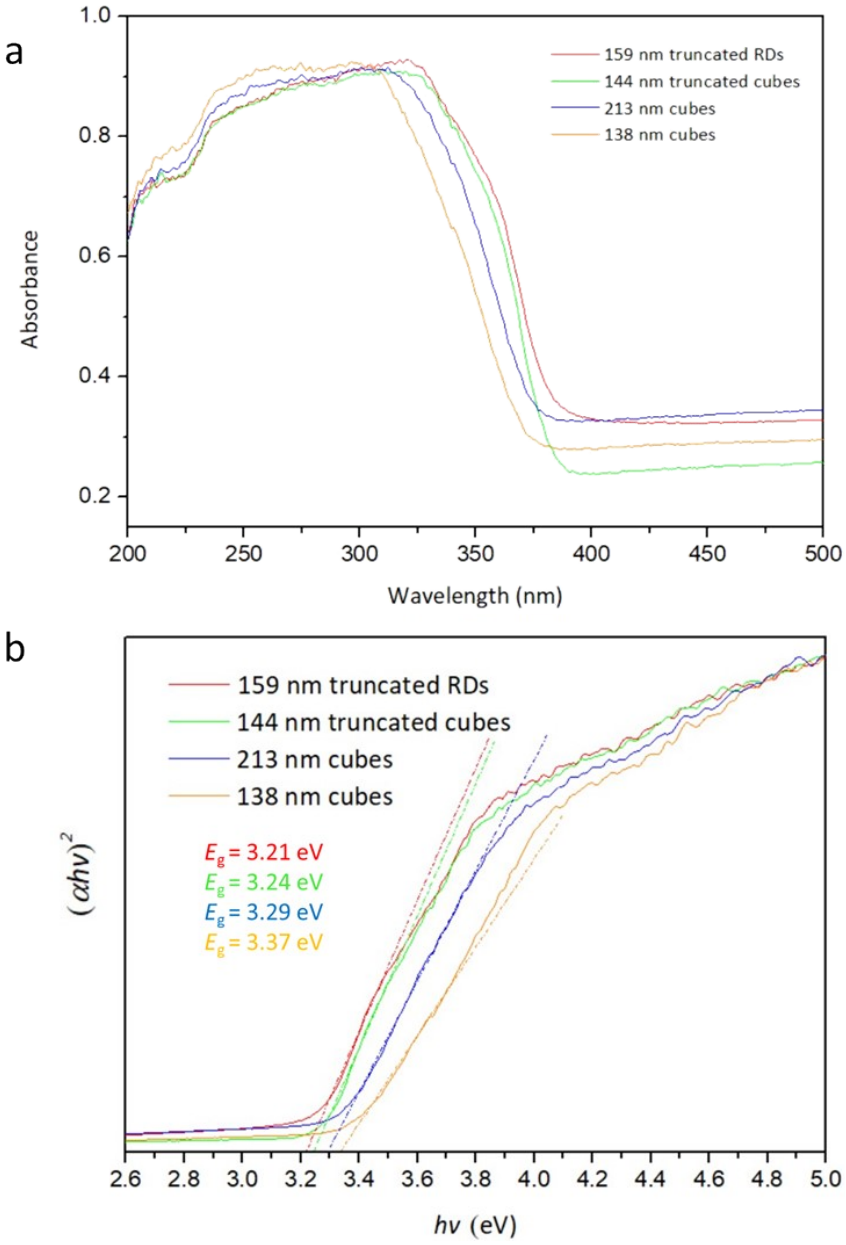


Fig. S3 (a) UV–vis absorption spectra of different $SrTiO_3$ crystals and (b) their corresponding Tauc plot.

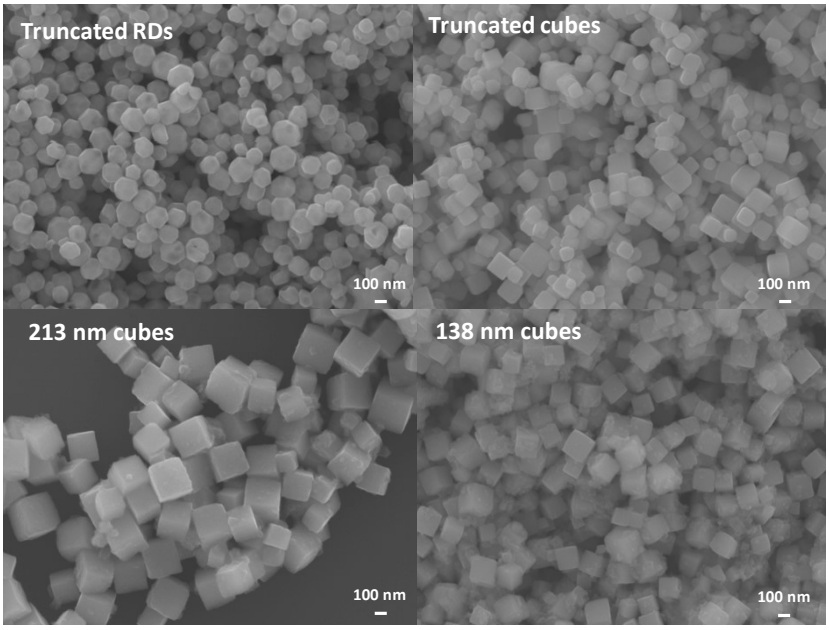
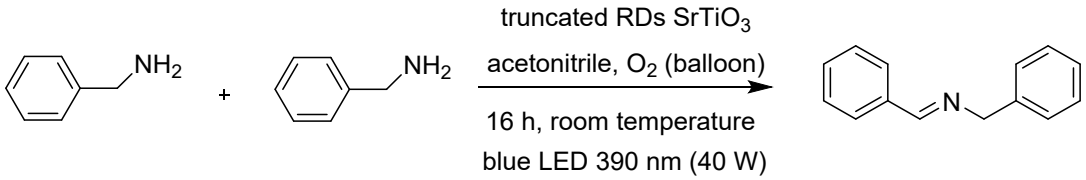


Fig. S4 SEM images of different $SrTiO_3$ crystals after the amine coupling reaction.

Table S1 Recycling Cycles to Product Yield[a,b]



entry	cycle	selectivity (%)	yield (%)
1	first	>99	>99
2	second	>99	80
3	third	>99	74

[a]Regent and condition: benzylamine (0.4 mmol), photocatalyst (4.0 mg), acetonitrile (3 mL), O_2 (1 atm). [b]Isolated yield.

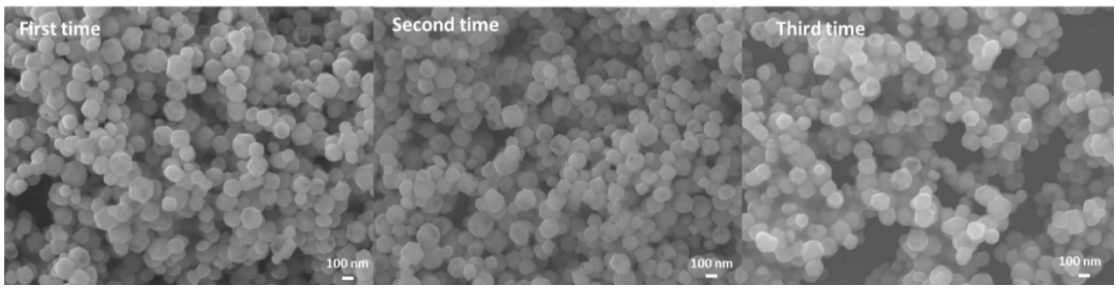


Fig. S5 SEM images of $SrTiO_3$ truncated rhombic dodecahedra after the recycling experiments.

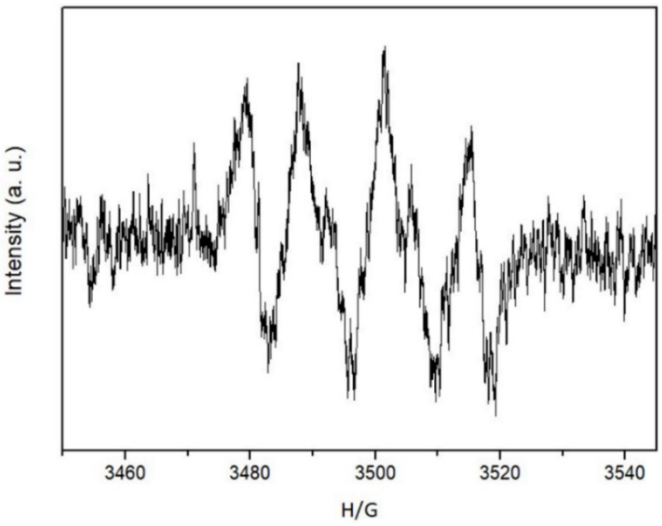


Fig. S6 EPR spectrum of photoirradiated truncated $SrTiO_3$ rhombic dodecahedra in acetonitrile.

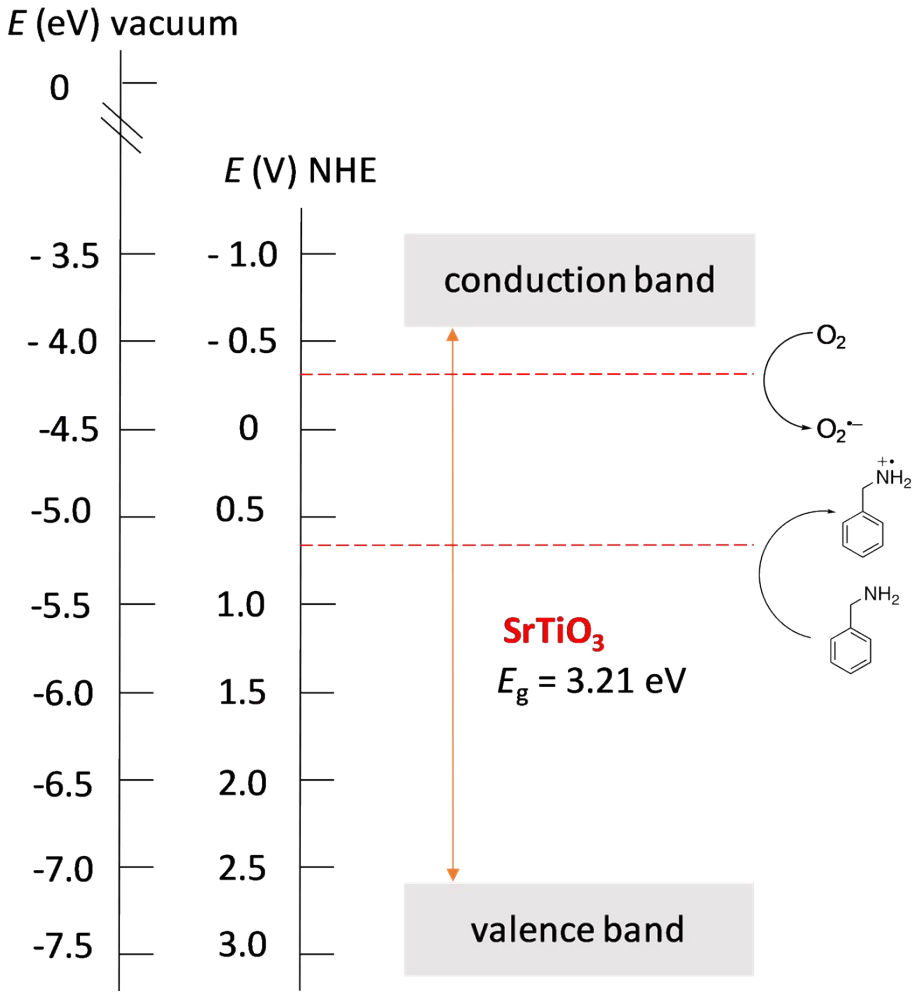
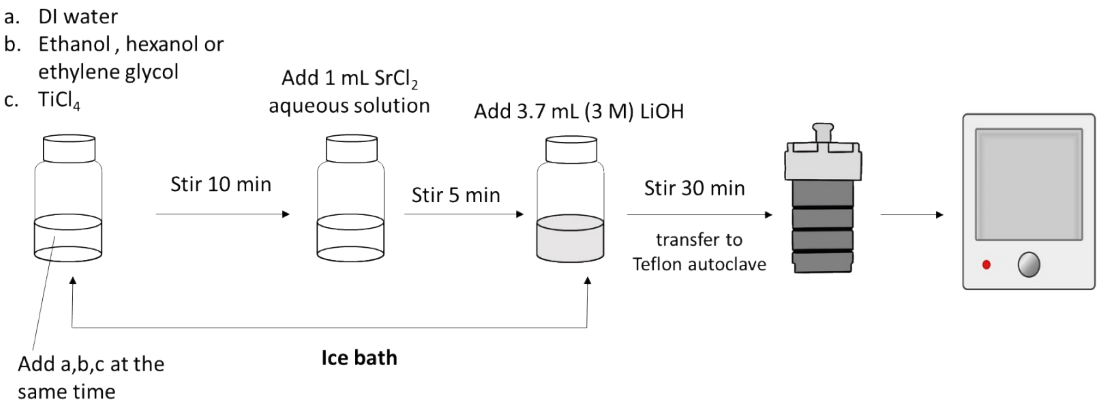


Fig. S7 Band diagram of {100}-truncated $SrTiO_3$ rhombic dodecahedra. Potentials of the reduction and oxidation half-reactions are marked.

138 nm	$TiCl_4$	Water	**Ethanol**	$SrCl_2{\cdot}6H_2O$	LiOH	Temperature	time
	0.031 mL	0 mL	2.5 mL	0.084 g	3.7 mL (3 M)	70 ℃	3 h
213 nm 	$TiCl_4$	Water	**Ethanol**	$SrCl_2{\cdot}6H_2O$	LiOH	Temperature	Time
	0.026 mL	1 mL	1.5 mL	0.070 g	3.7 mL (3 M)	70 ℃	3 h
144 nm 	$TiCl_4$	Water	**Hexanol**	$SrCl_2{\cdot}6H_2O$	LiOH	Temperature	Time
	0.208 mL	2 mL	0.85 mL	0.560 g	3.7 mL (3 M)	200 ℃	20 h
159 nm 	$TiCl_4$	Water	**Ethylene glycol**	$SrCl_2{\cdot}6H_2O$	LiOH	Temperature	Time
	0.026 mL	2 mL	0.85 mL	0.070 g	3.7 mL (3 M)	200 ℃	20 h



Scheme S1 Reaction conditions for the growth of different $SrTiO_3$ crystals.

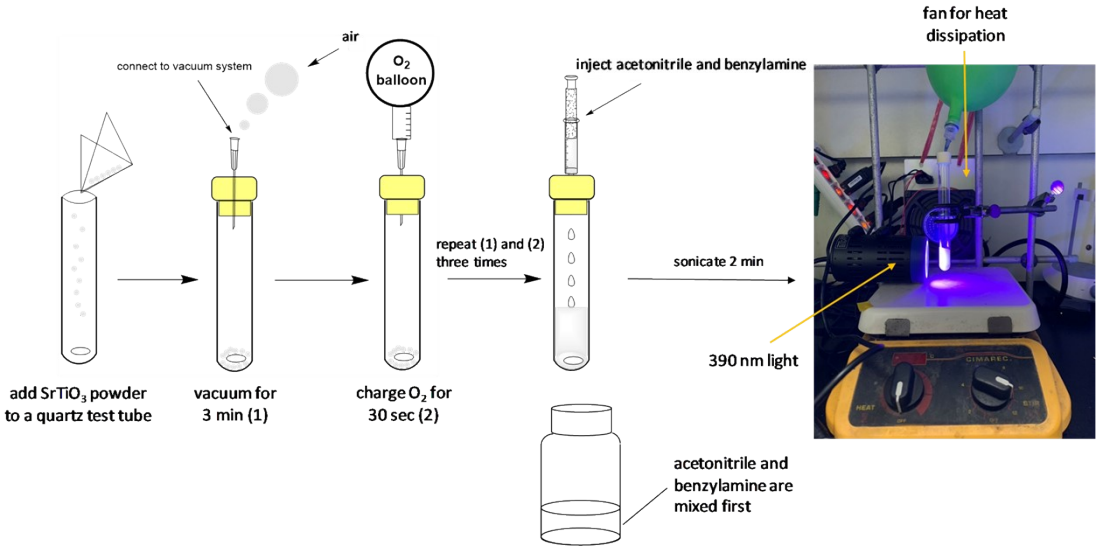


Fig. S8 Experimental process for photocatalytic amine coupling.

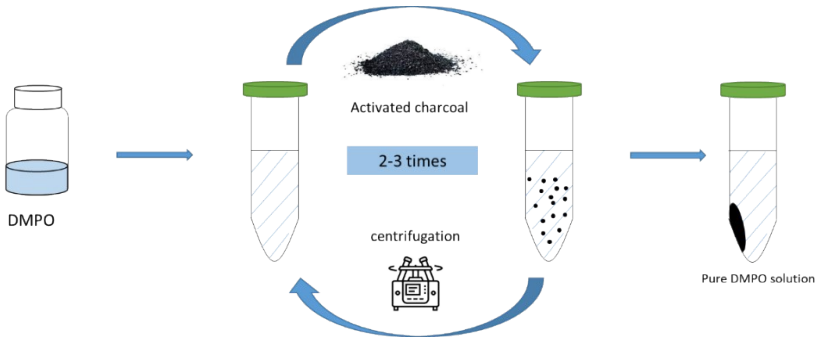


Fig. S9 Purification of the radical trapping agent DMPO.

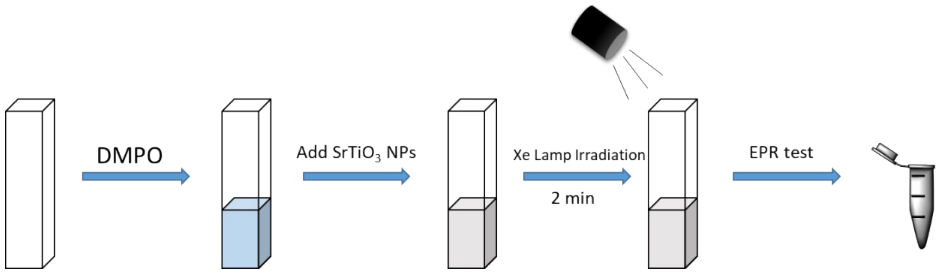
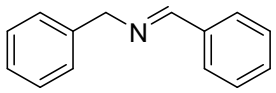


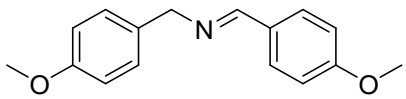
Fig. S10 Steps before EPR measurement.

Spectroscopic data of isolated products



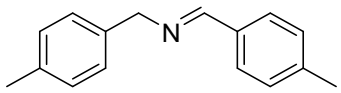
***(E)*-*N*-Benzylidenebenzylamine (2a)**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.79 (dd, *J* = 6.3, 3.0 Hz, 2H), 7.48–7.39 (m, 3H), 7.35 (d, *J* = 4.6 Hz, 5H), 4.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.96, 139.18, 136.04, 130.68, 128.51, 128.40, 128.20, 127.90, 126.90, 64.91.



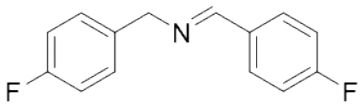
***(E)*-4-Methoxy-*N*-[(4-methoxyphenyl)methylene]benzenemethanamine (2b)**

Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.88 (dd, *J* = 16.3, 8.6 Hz, 4H), 4.71 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.63, 160.94, 158.60, 131.57, 129.77, 129.11, 113.92, 113.85, 64.29, 55.28, 55.22.



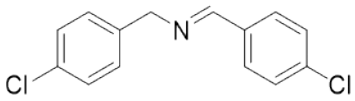
***(E)*-4-Methyl-N-[(4-methylphenyl)methylene]benzenemethanamine (2c)**

Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 8.0, 3.8 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 2H), 2.39 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.68, 140.93, 136.47, 136.31, 133.58, 129.26, 129.11, 128.21, 127.92, 64.73, 21.45, 21.05.



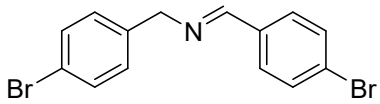
***(E)*-4-Fluoro-N-[(4-fluorophenyl)methylene]benzenemethanamine (2d)**

Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.78 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.30 (dd, *J* = 8.2, 5.4 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 4.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.58, 163.10, 160.51, 134.88, 132.26, 130.16, 130.07, 129.45, 129.37, 115.76, 115.54, 115.33, 115.12, 64.03.



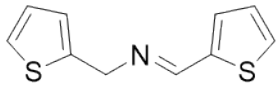
***(E)*-4-Chloro-N-[(4-chlorophenyl)methylene]benzenemethanamine (2e)**

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.19 (m, 4H), 4.76 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.74, 137.53, 136.75, 134.36, 132.69, 129.36, 129.16, 128.81, 128.52, 64.01.



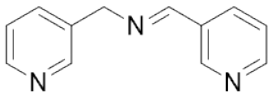
***(E)*-4-Bromo-N-[(4-bromophenyl)methylene]benzenemethanamine (2f)**

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 4.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.96, 138.00, 134.77, 131.82, 131.52, 129.62, 129.57, 125.30, 120.86, 64.11.



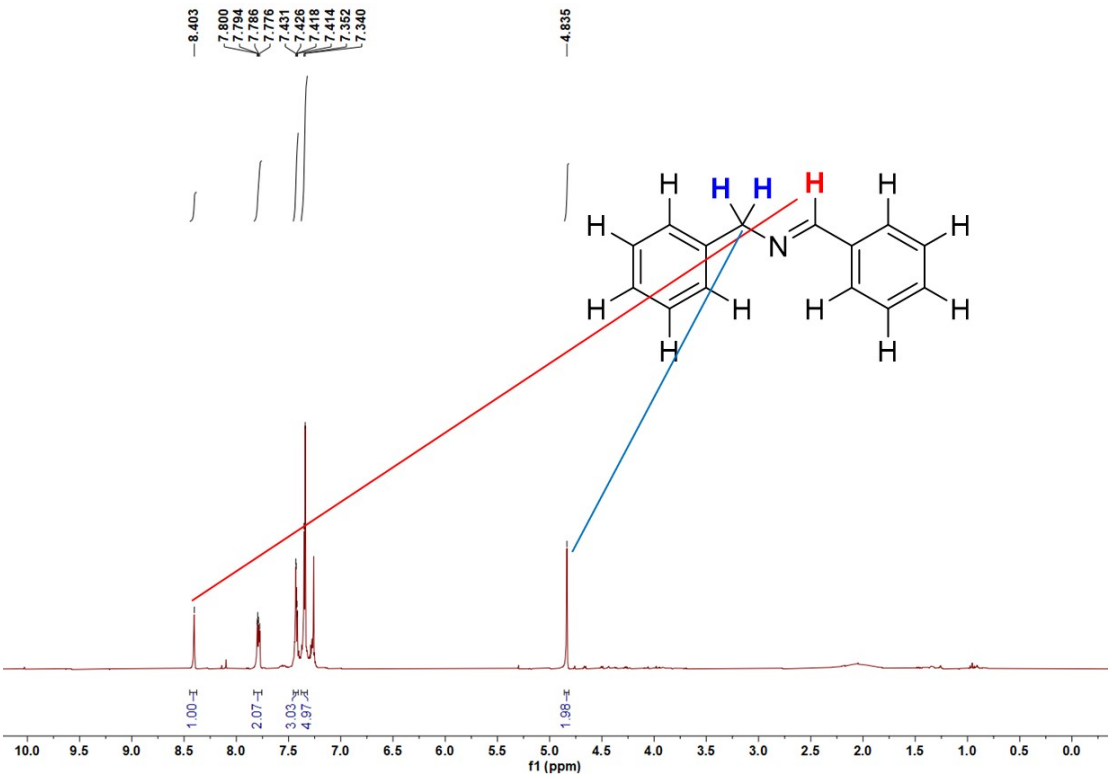
***(E)*-N-(2-Thienylmethylene)-2-thiophenemethanamine (2g)**

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.41 (d, *J* = 5.1 Hz, 1H), 7.33 (d, *J* = 3.5 Hz, 1H), 7.24 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.99 (d, *J* = 4.9 Hz, 2H), 4.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.34, 141.98, 141.44, 130.90, 129.24, 127.29, 126.78, 125.18, 124.71, 58.36.

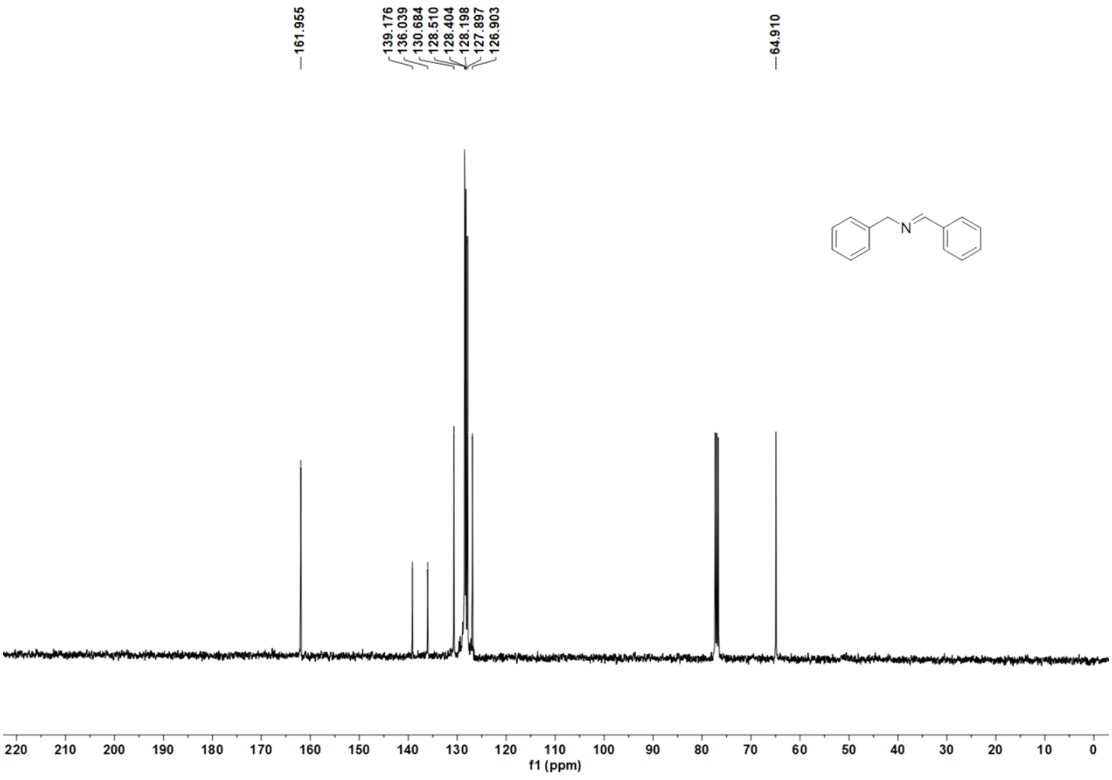


***(E)*-N-(3-Pyridinylmethylene)-3-pyridinemethanamine (2h)**

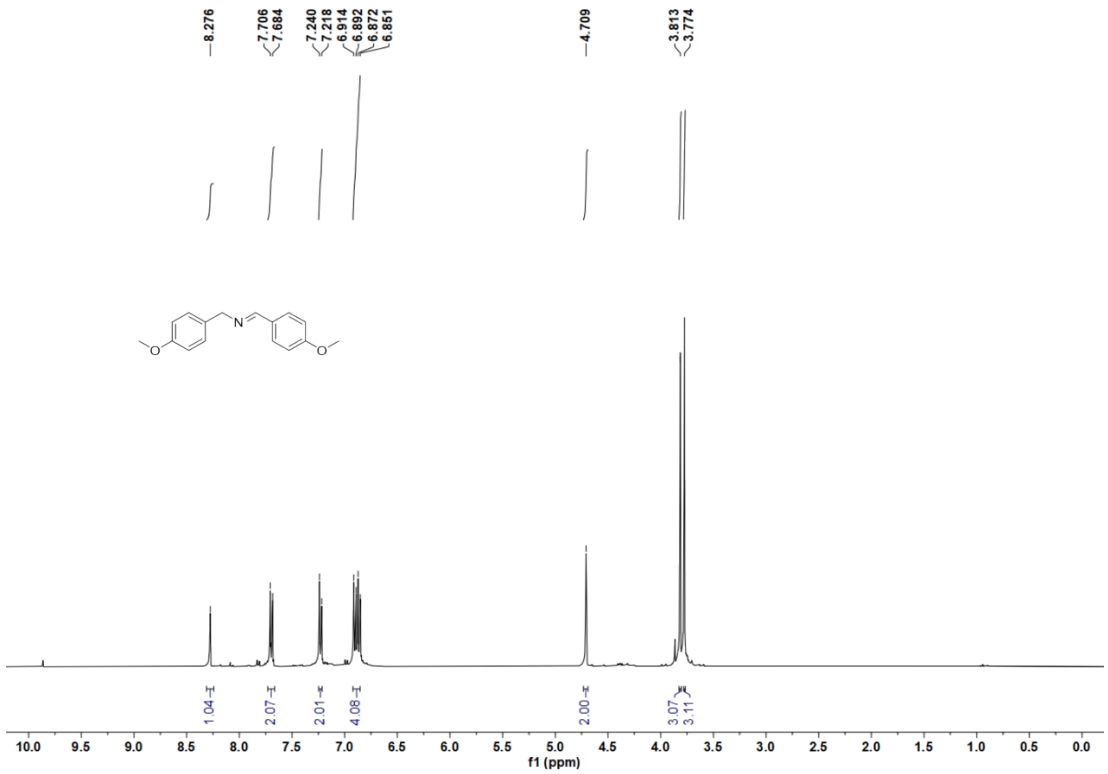
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.62 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.59–8.54 (m, 1H), 8.49 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.43 (d, *J* = 1.2 Hz, 1H), 8.12 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.65 (ddd, *J* = 7.8, 2.3, 1.6 Hz, 1H), 7.33 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.28 – 7.22 (m, 1H), 4.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.65, 151.62, 150.15, 149.11, 148.38, 135.53, 134.57, 134.32, 131.28, 123.62, 123.40, 62.31.



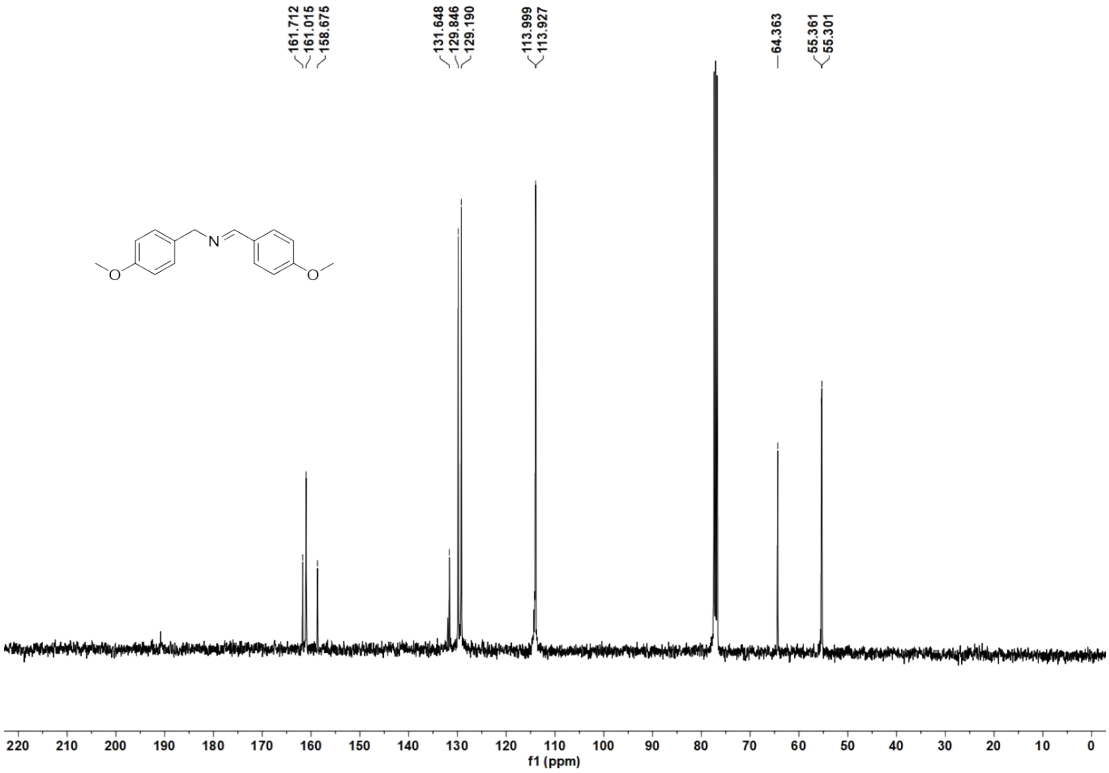
Spectrum S1 ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400 MHz).



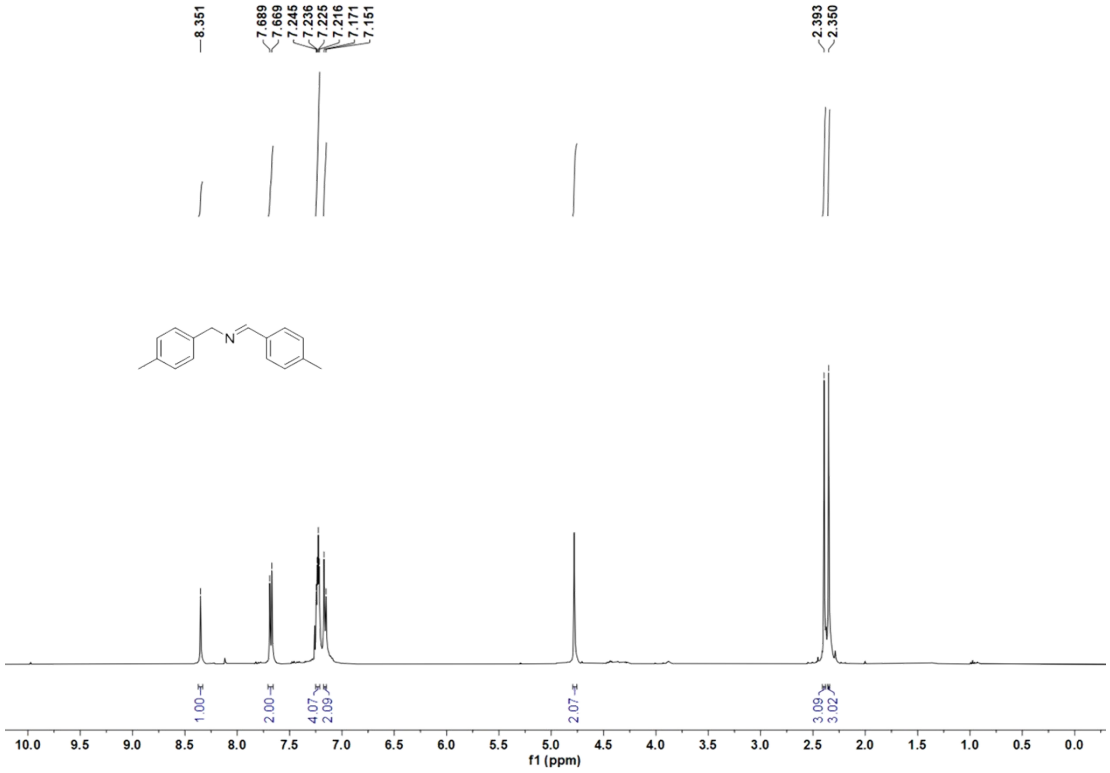
Spectrum S2 ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100 MHz).



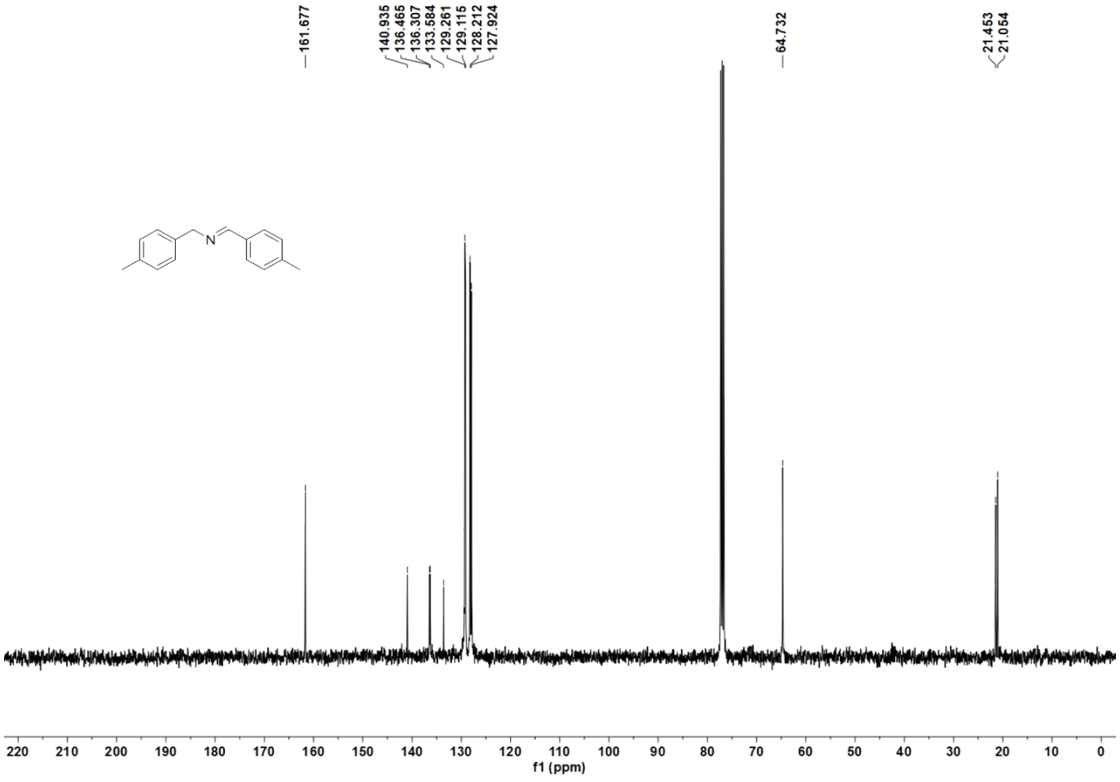
Spectrum S3 ^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz).



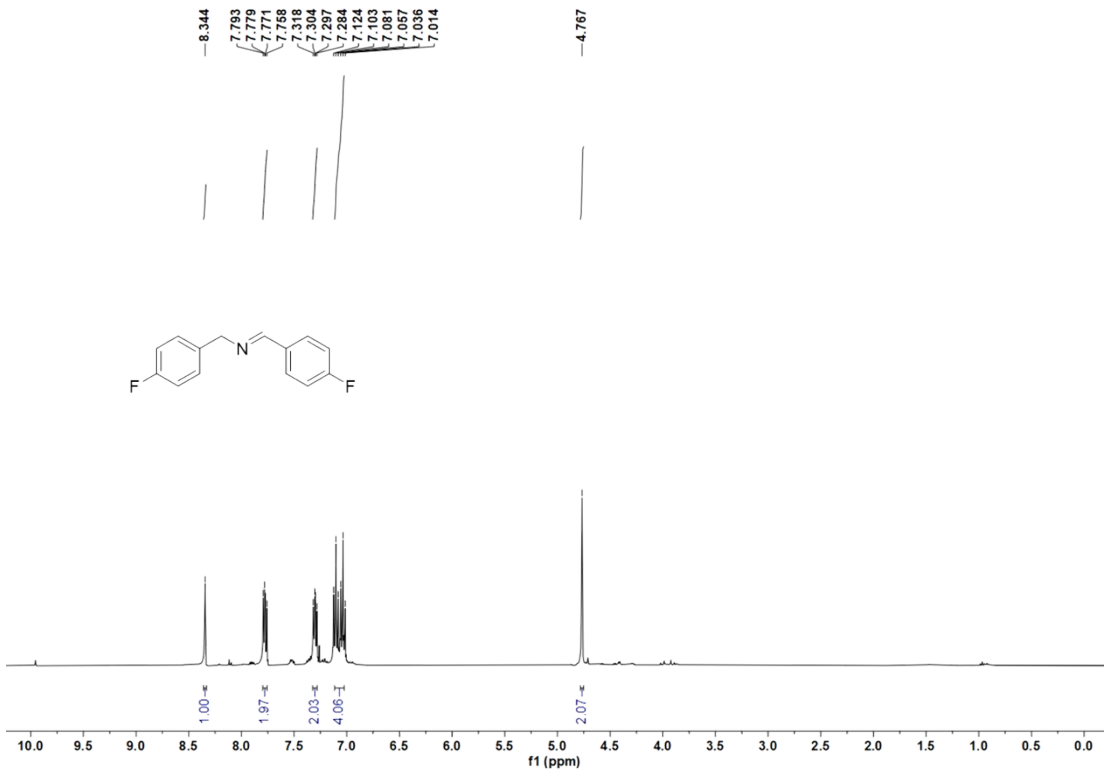
Spectrum S4 ^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100 MHz).



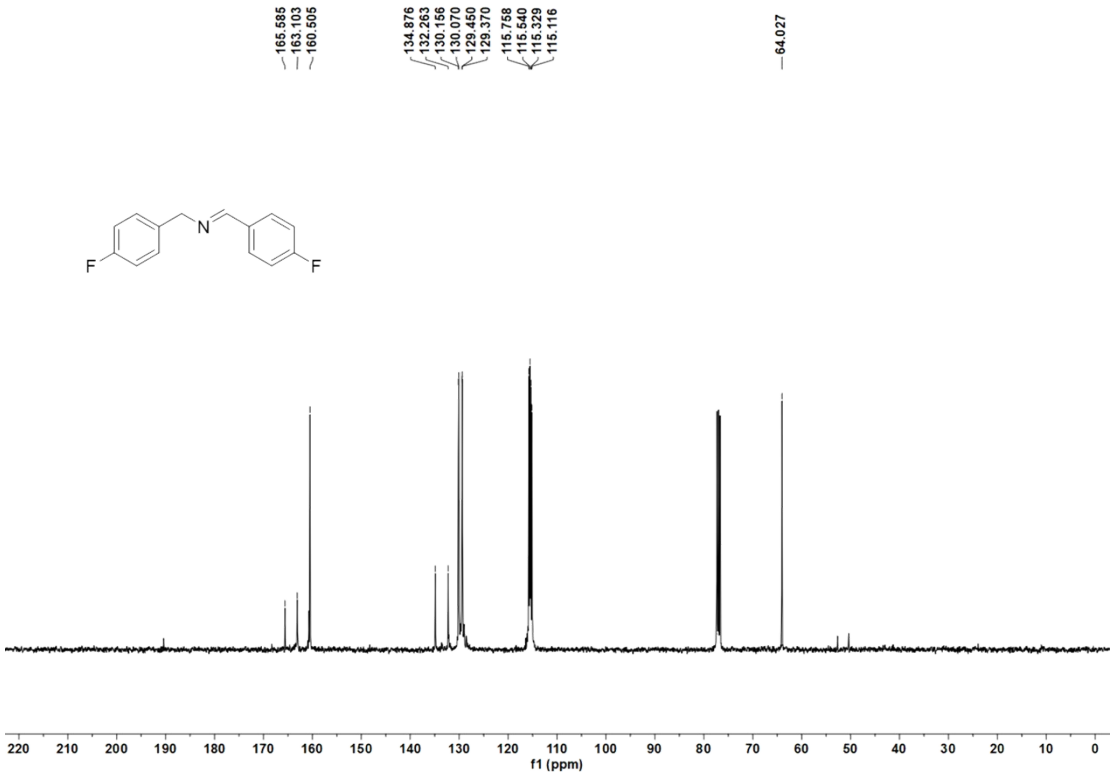
Spectrum S5 ^{1}H NMR spectrum of compound 2c ($CDCl_3$, 400 MHz).



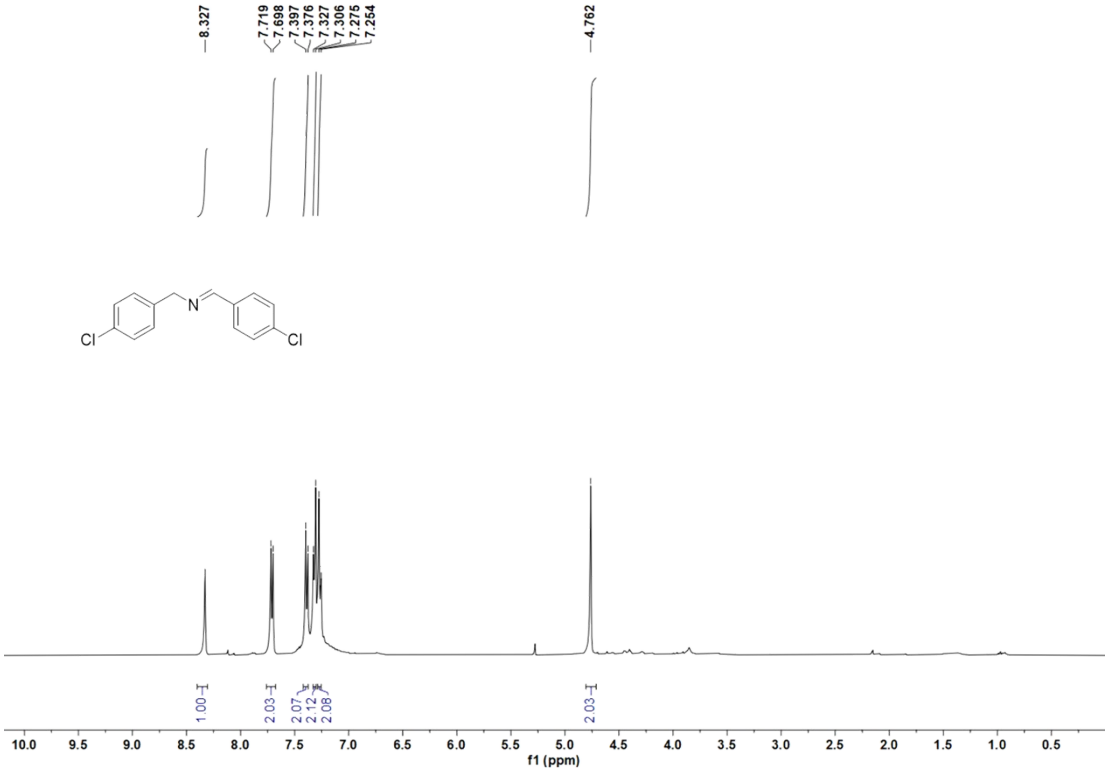
Spectrum S6 ^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100 MHz).



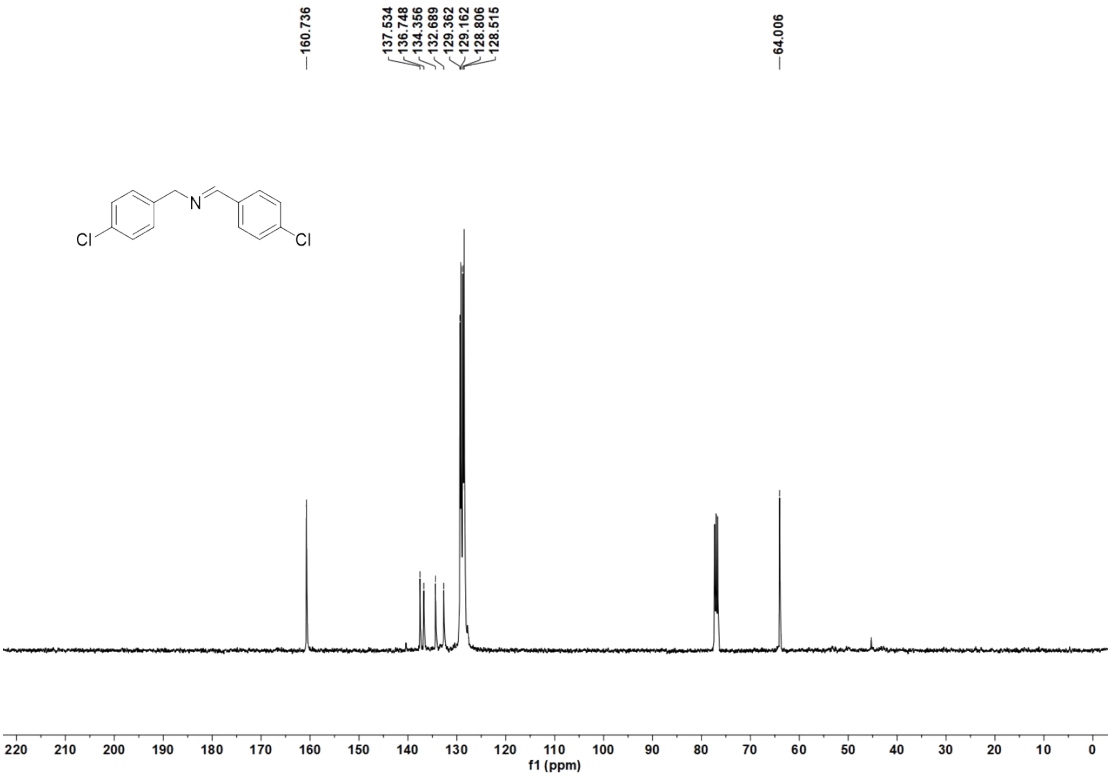
Spectrum S7 ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz).



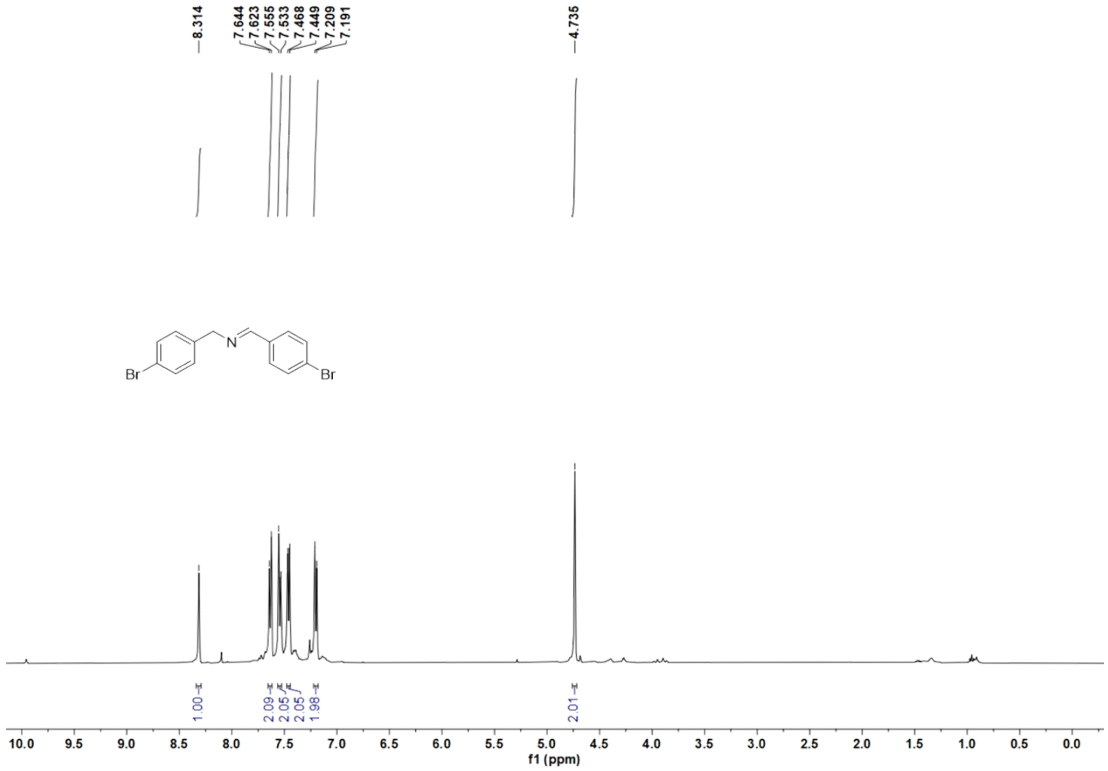
Spectrum S8 ^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 100 MHz).



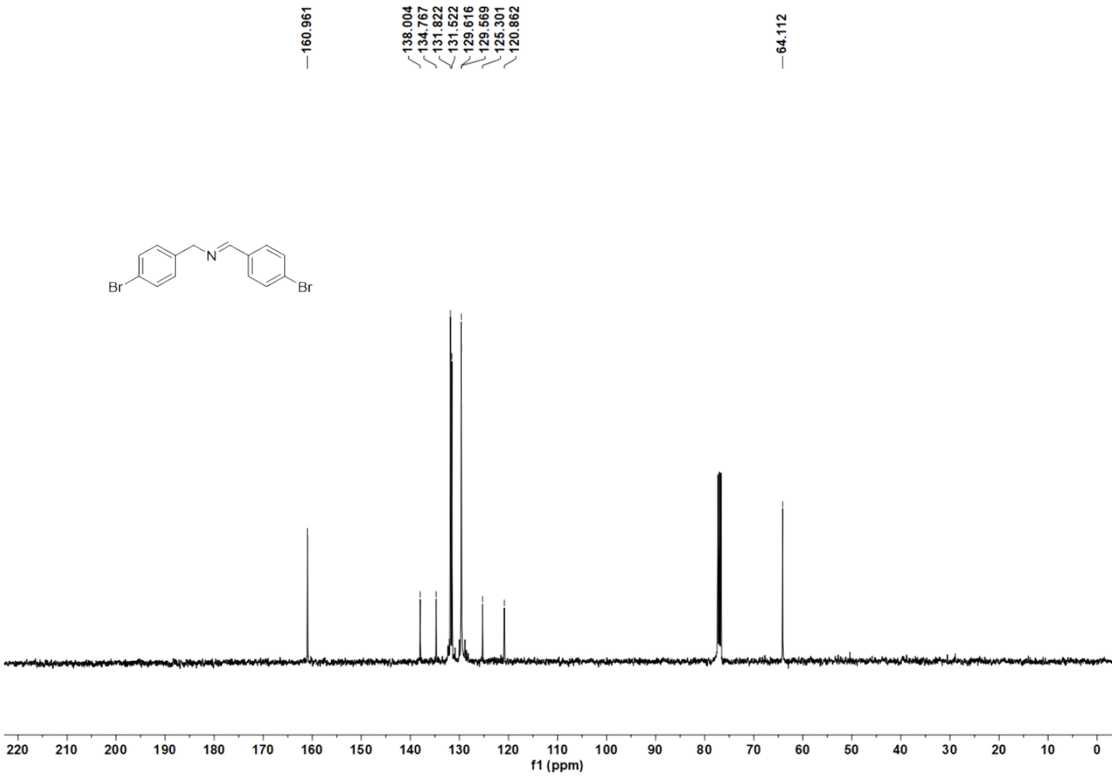
Spectrum S9 ^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz).



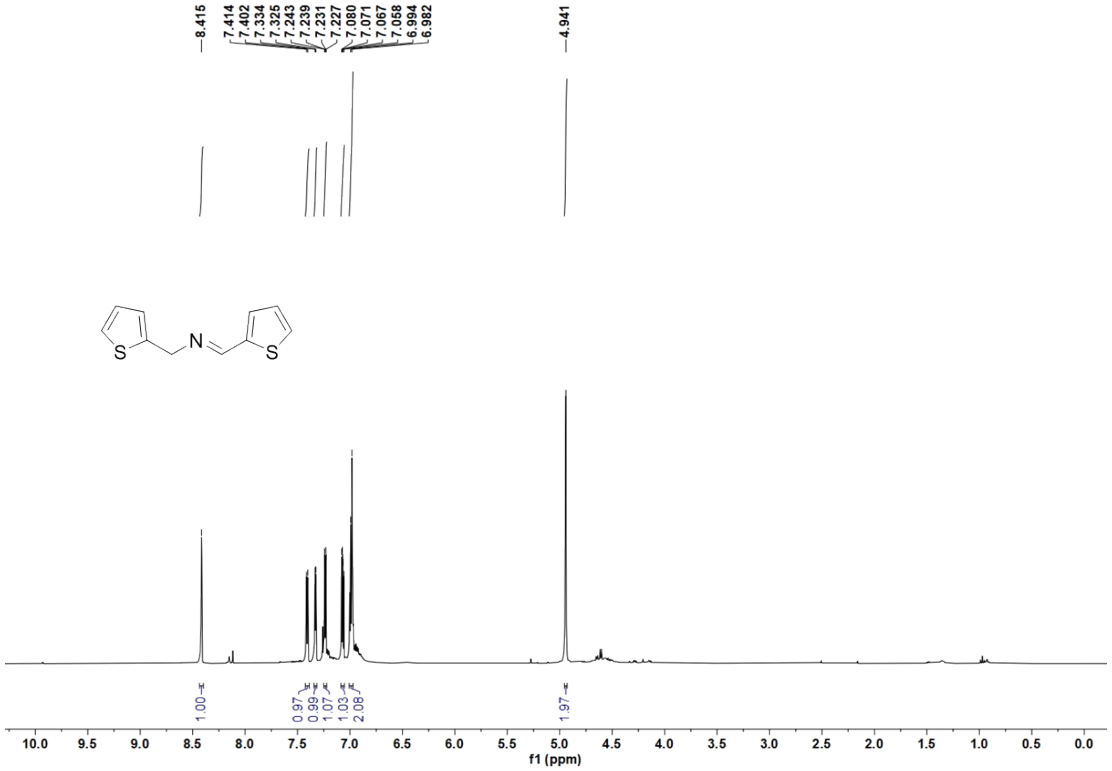
Spectrum S10 ^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz).



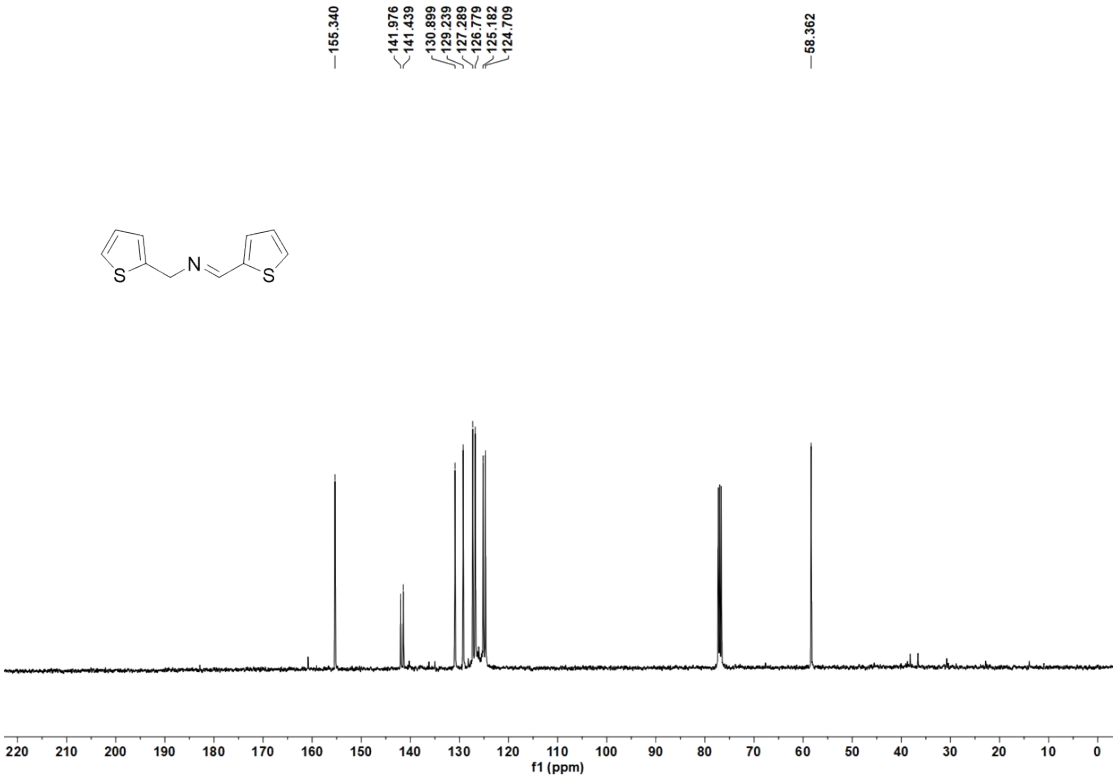
Spectrum S11 ^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz).



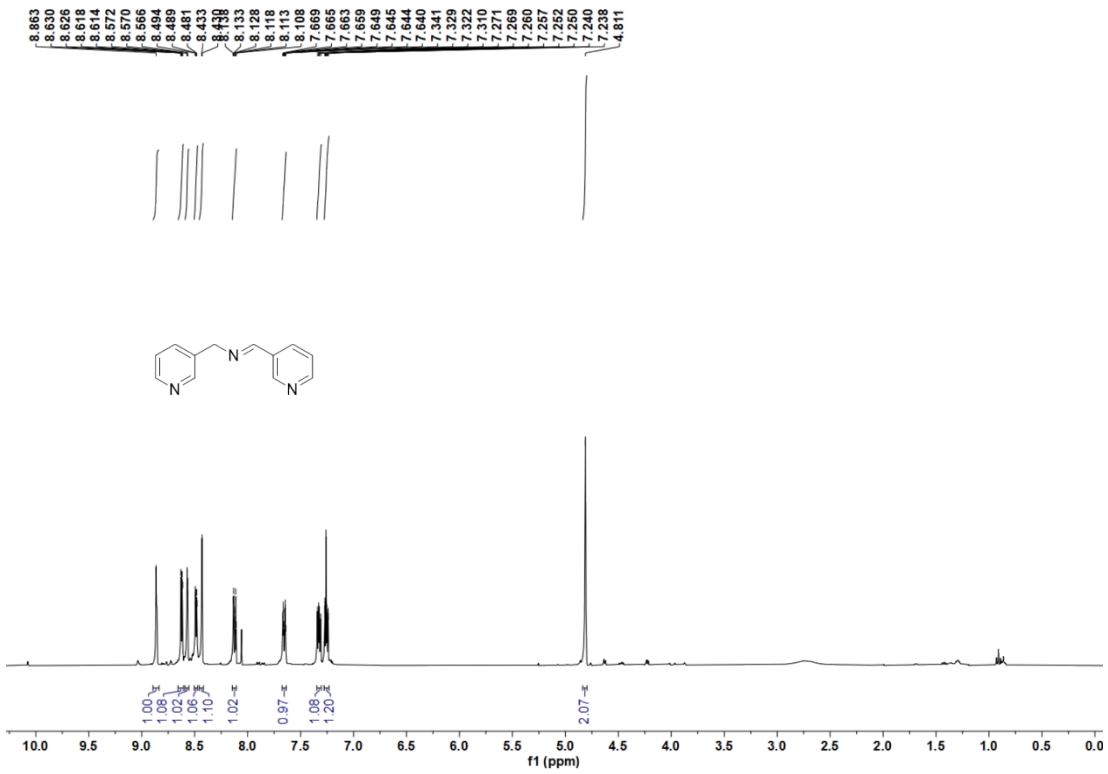
Spectrum S12 ^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz).



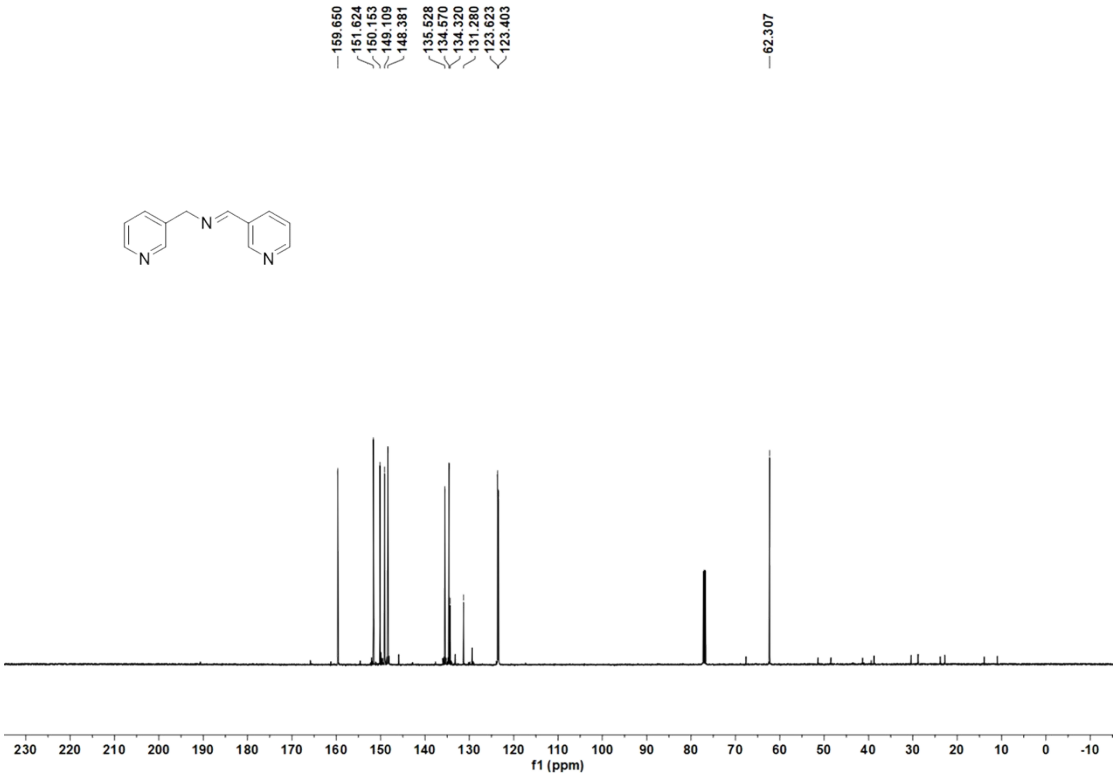
Spectrum S13 ^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz).



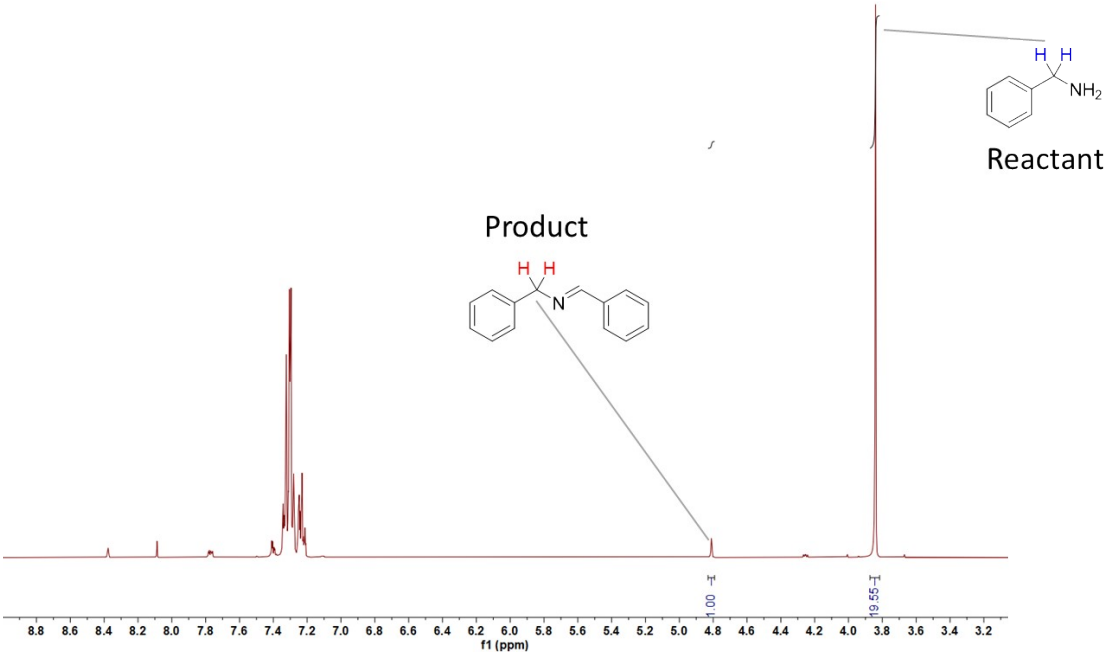
Spectrum S14 ^{13}C NMR spectrum of compound **2g** ($CDCl_3$, 100 MHz).



Spectrum S15 ^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz).



Spectrum S16 ^{13}C NMR spectrum of compound **2h** ($CDCl_3$, 100 MHz).



Spectrum S17 ^{1}H NMR spectrum of the starting material and product in the presence of KI as a hole scavenger.