Supporting Information

Investigating the radical properties of oxidized carbon materials under photo-irradiation: behavior of carbon radicals and their application in catalytic reactions

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1. General Information

All the chemicals used in this study were purchased from commercial sources and used as received unless otherwise mentioned. Kessil A360X tuna blue LED light with a wavelength centered at 470 nm was used. The intensity of blue LED light is 45-55×10^3 lux, measured using HD 2102.2 photo-radiometer. The products were quantified by gas chromatography-mass spectrometry (GCMS-QP2010 *Plus,* Shimadzu), equipped with a flame ionization detector (FID). ESR analysis was performed using an electron spin resonance spectrometer (JES-X310) with microwave frequency 9.542 GHz, modulation frequency 100 kHz, power 1 mW, and weep time 1 min. The functional groups on the surface of the oxidized carbon materials were recorded by Fourier transform infrared spectrophotometer (FTIR; Shimadzu IRTracer-100). The samples for the FTIR were dried and mixed with KBr and then pressed into 1.3 cm-diameter pellets. Freeze-drying of the oxidized carbon materials was performed using ADVANTEC DRZ350WC. The surface chemistry was performed using an X-ray photoelectron spectroscopy (XPS; JPS-9030) with a pass energy of 20 eV.

Various carbon materials such as graphite, activated carbon (AC), carbon black (CB), carbon nanotube (CNT), and nanodiamond (ND) were oxidized using the following procedure. Carbon material (1.0 g) was dispersed in 95% H_2SO_4 (30 mL). After cooling the mixture in an ice bath, $KMnO_4$ (3.0 g) was gradually added to the solution, keeping the temperature below 55 °C. The mixture was stirred at 35 °C for 2 h. The generated suspension was again cooled down, after which 60 mL of deionized water was added slowly to keep the temperature below 50 °C. The suspension was further treated by 30% aq. H_2O_2. The resulting suspension was purified by centrifugation with water five times and freeze-dried to afford oxidized carbon materials.

2. UV-visible Spectra

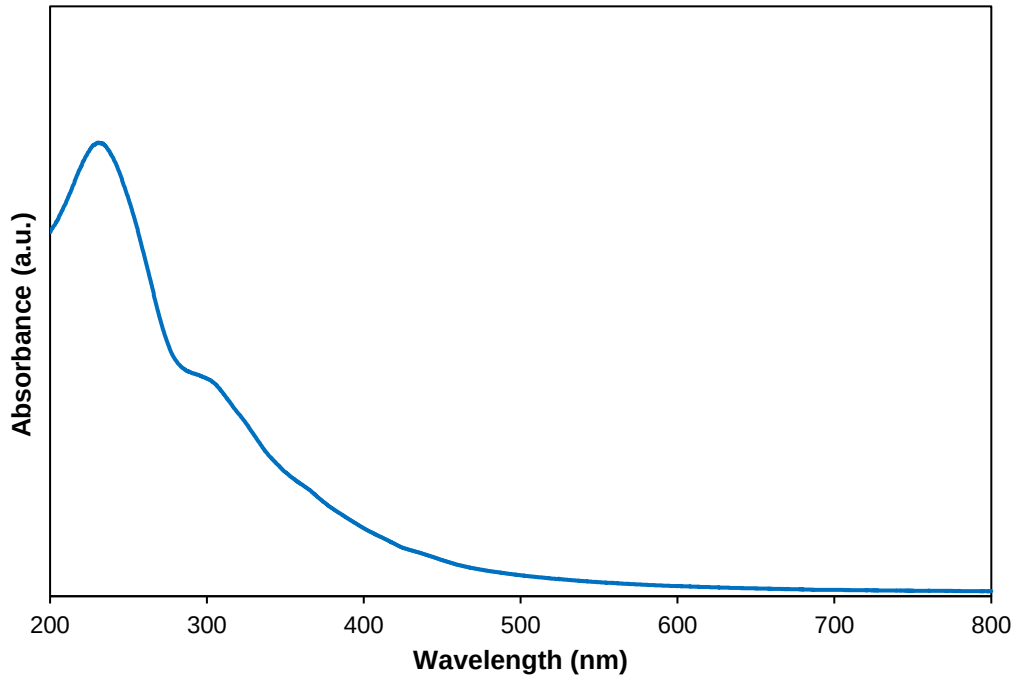


Figure S1. UV-vis absorption spectra of GO.

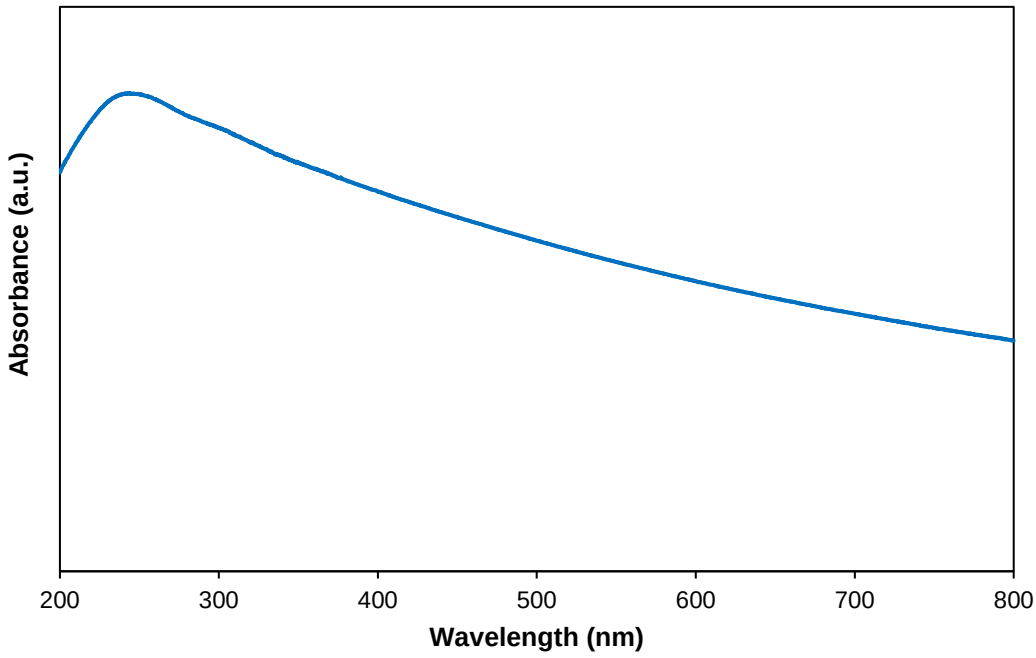


Figure S2. UV-vis absorption spectra of O-AC.

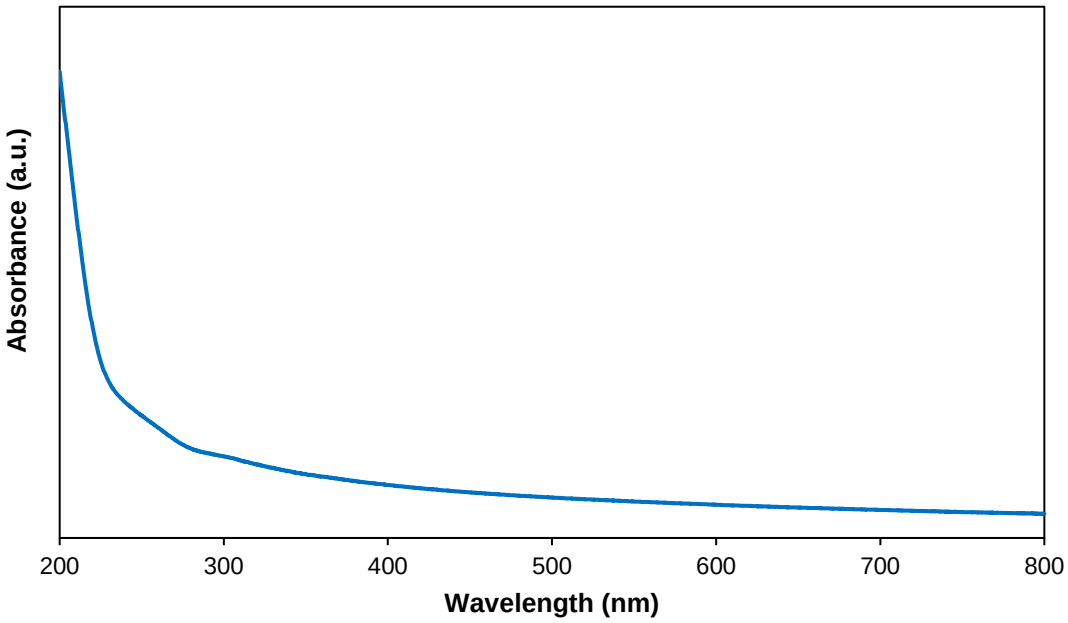


Figure S3. UV-vis absorption spectra of O-CB.

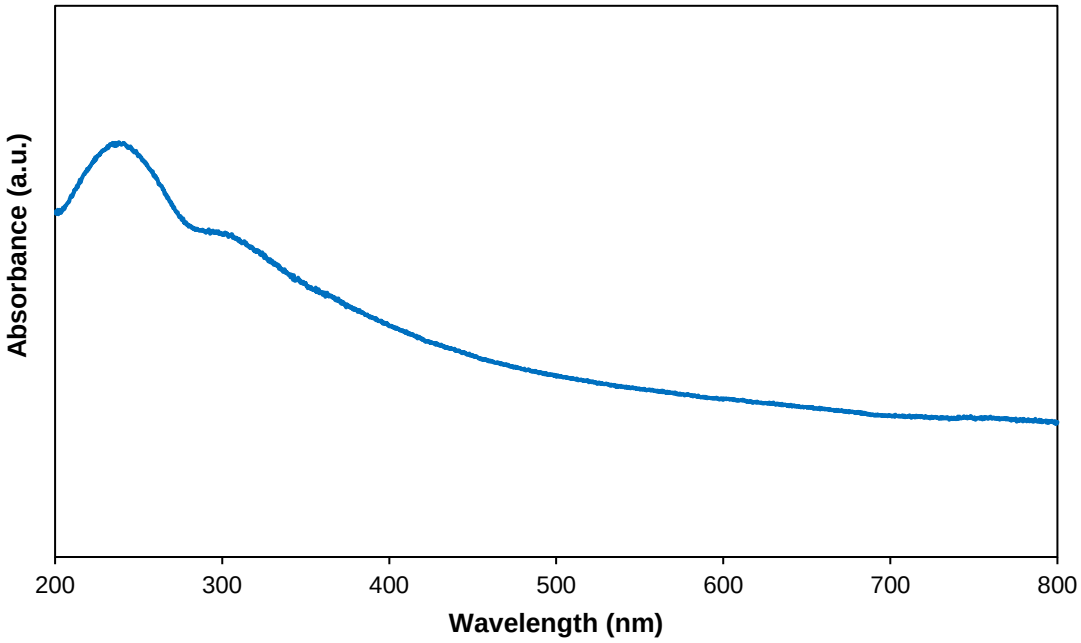


Figure S4. UV-vis absorption spectra of O-CNT.

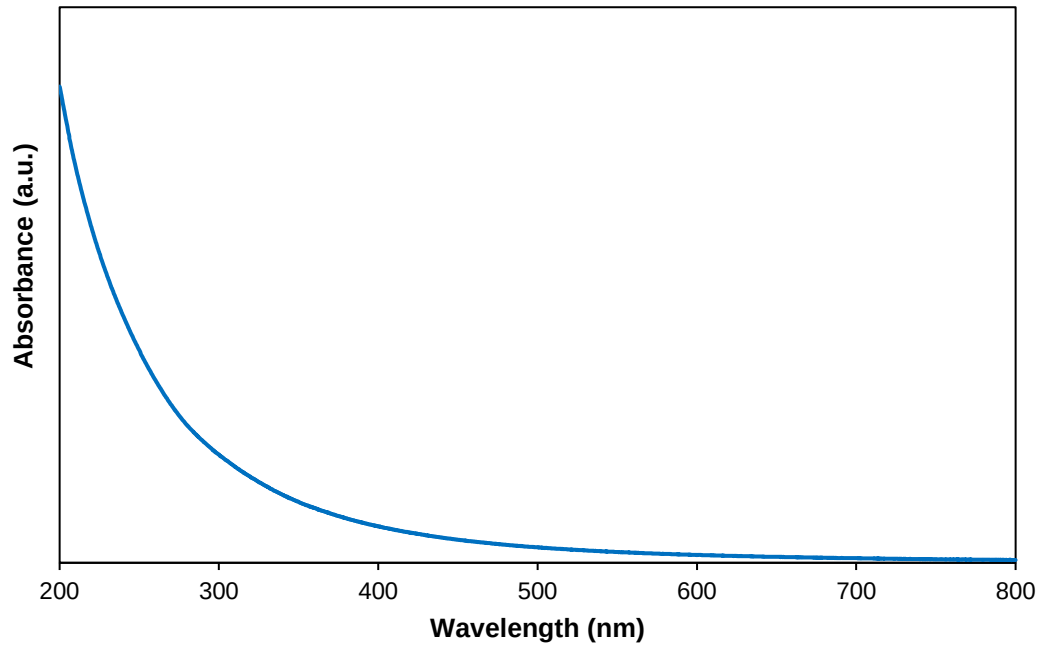


Figure S5. UV-vis absorption spectra of O-ND.

3. XPS Survey Spectra

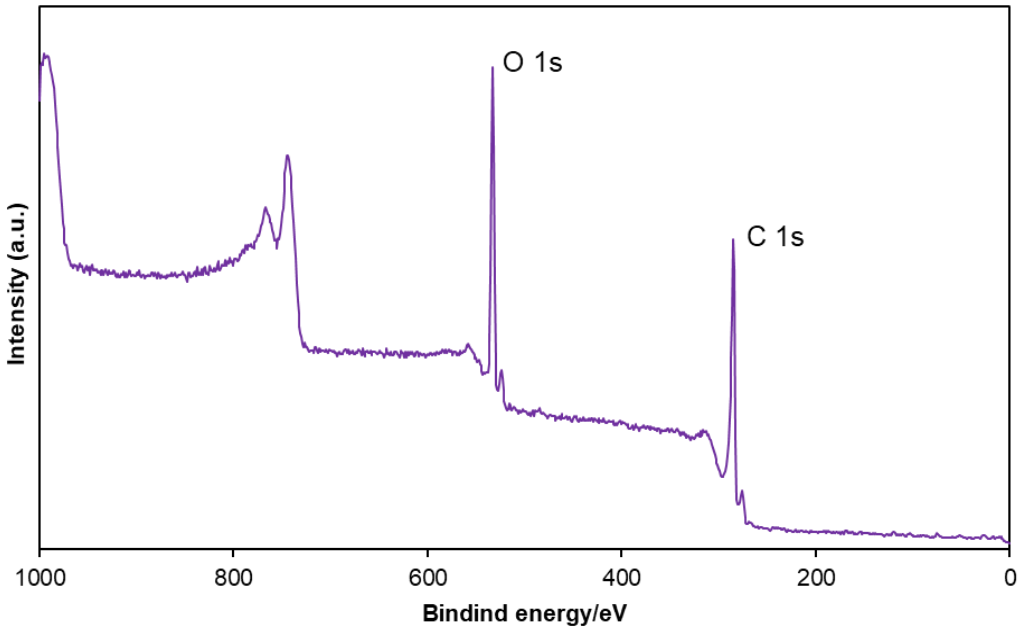


Figure S6. XPS survey spectra of O-AC.

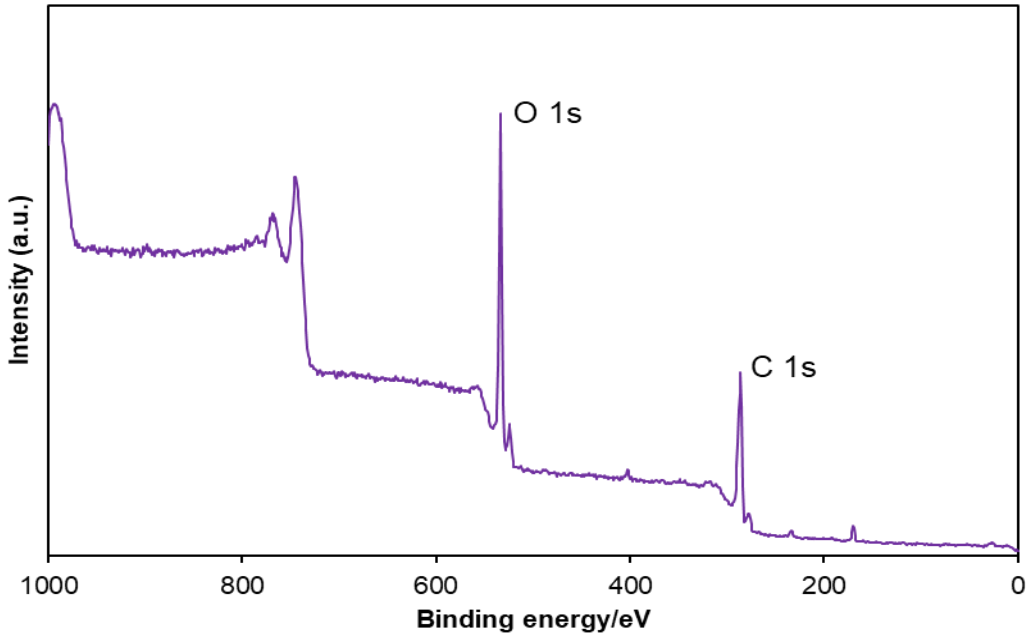


Figure S7. XPS survey spectra of O-CB.

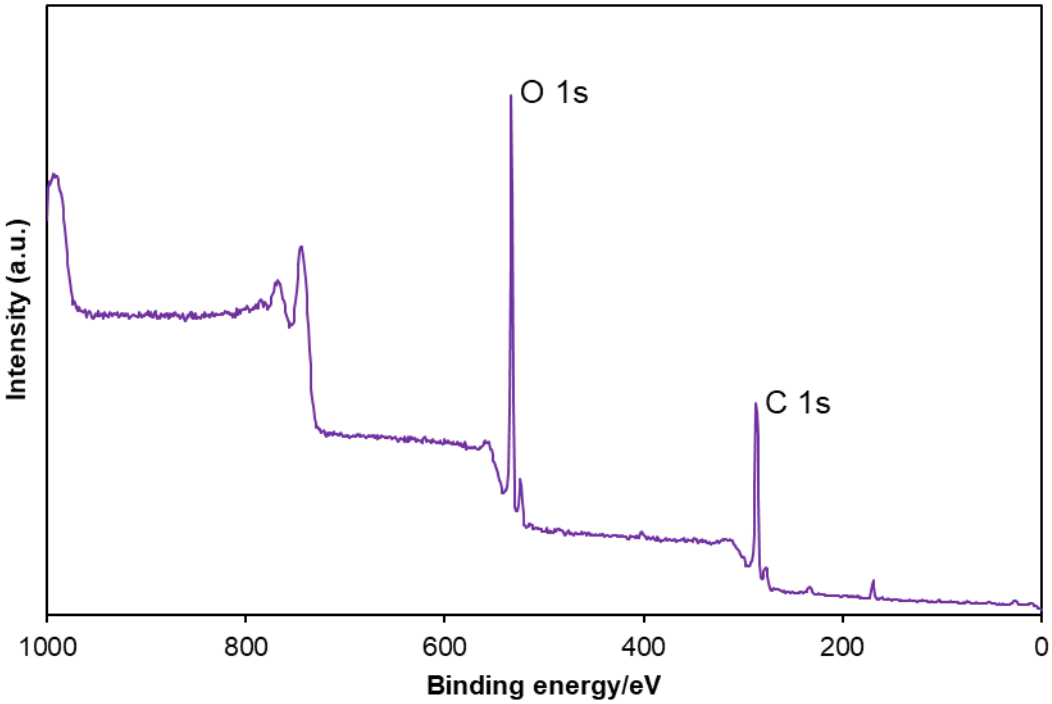


Figure S8. XPS survey spectra of O-CNT.

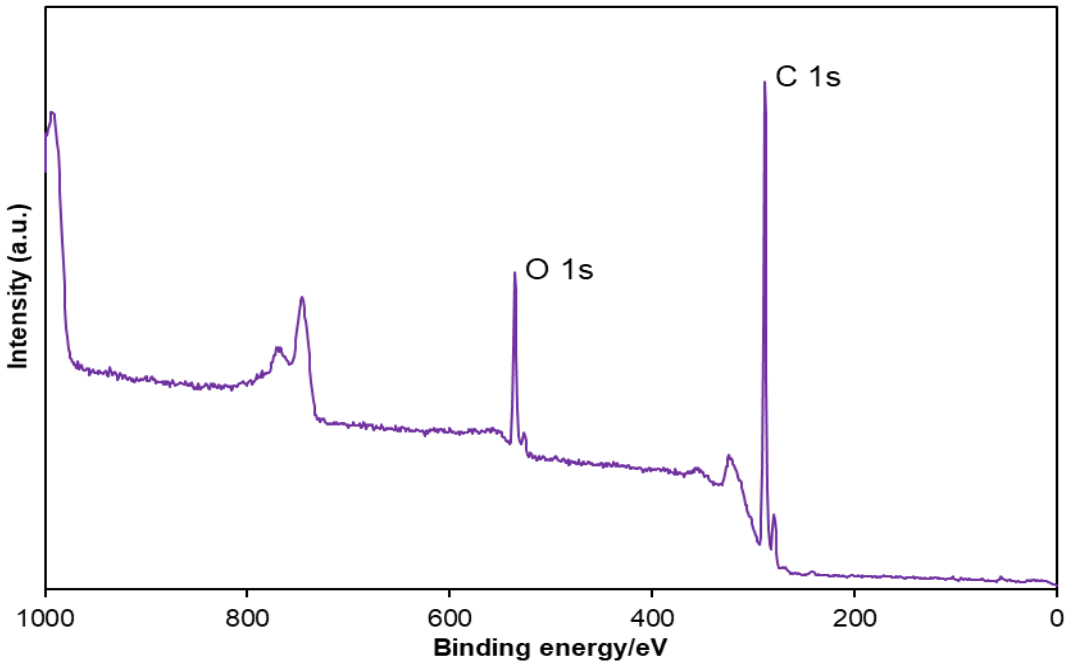


Figure S9. XPS survey spectra of O-ND.

4. ESR Spectra of GO for Stability Test

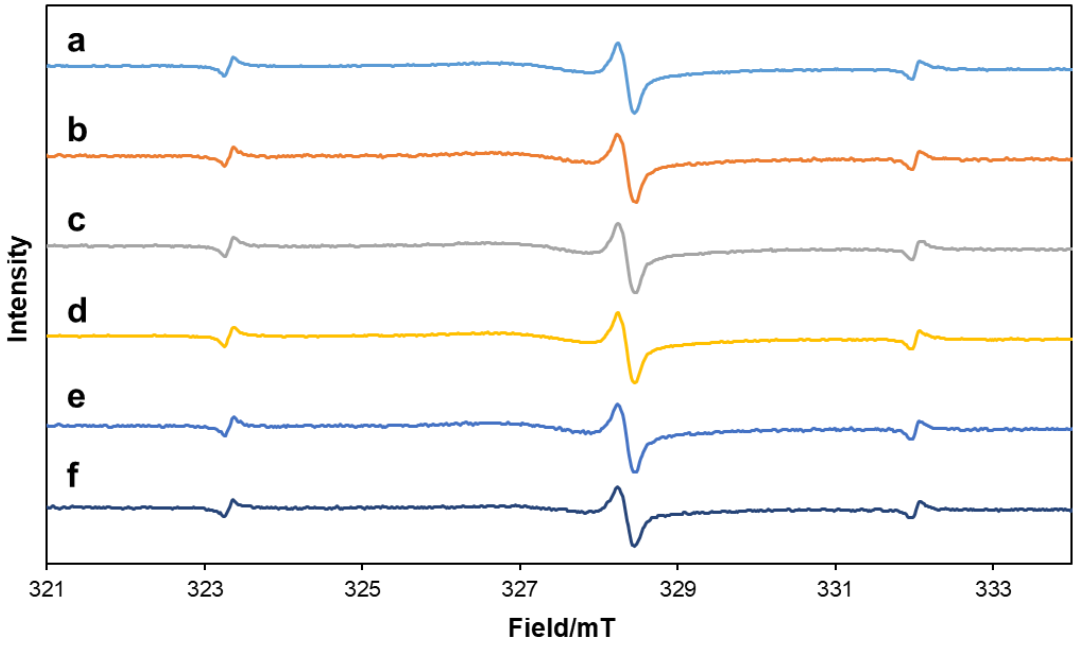


Figure S10. ESR spectra of GO after (a) 1st month, (b) 2nd month, (c) 3rd month, (d) 4th month, (e) 5th month, and (f) 6th month.

5. Typical Procedure for Amine Functionalization of GO (Am-GO)

GO (300 mg) was dispersed in distilled water (150 mL) in a glass beaker using an ultrasonic probe sonicator. In a separate beaker, n-butylamine (450 mg) was dispersed in 45 mL water via bath sonication for 10 min. The GO suspension was then transferred to a 500 mL round bottom flask in which the n-butylamine suspension was also moved and the mixture was stirred in an oil bath at 80 °C for 20 h. The black solution eventually obtained was left to stand undisturbed for 24 h after which it showed a separation of the functionalized GO from the solvent suggesting its hydrophobic nature. The functionalized GO was then extracted via centrifugation. The obtained solid product was purified by centrifugation with water five times and freeze-dried to afford the pure amine functionalized GO.

6. FTIR Spectra and Photochemical Properties of Am-GO

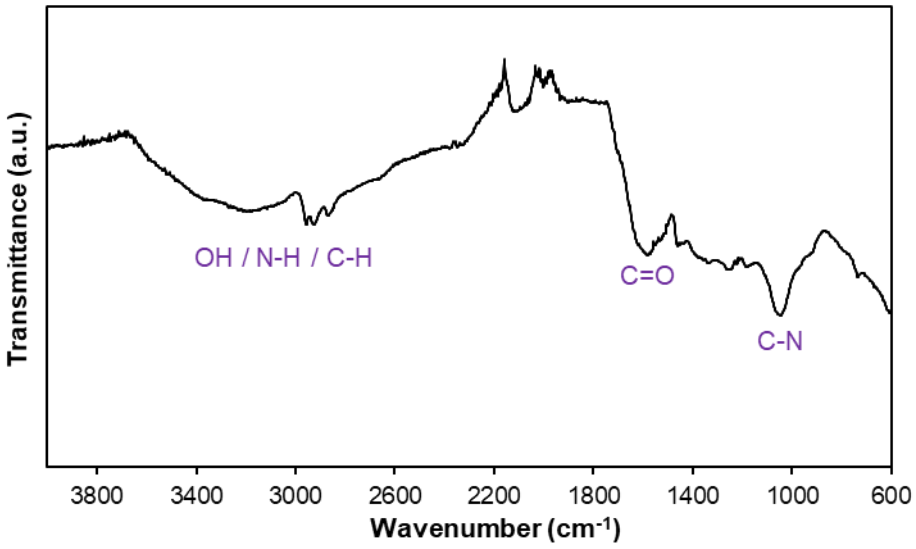


Figure S11. FTIR spectra of Am-GO.

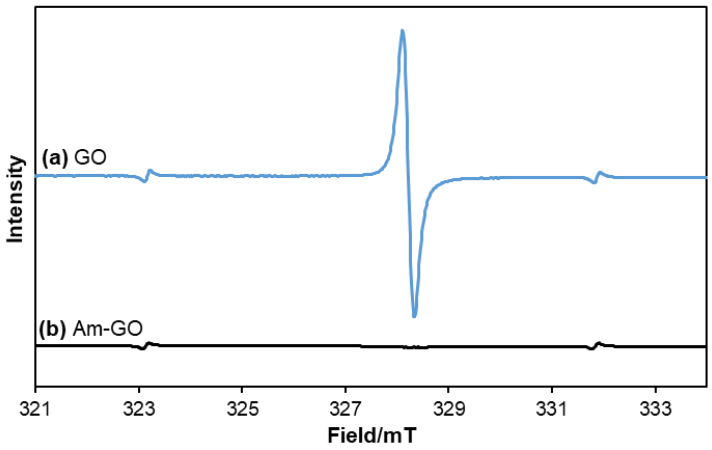


Figure S12. ESR spectra of (a) GO and (b) Am-GO after blue LED irradiation. The standard Mn^{2+} peaks are observed at 323 and 332 mT.

7. XPS Spectra at C 1s Region of GO and Am-GO

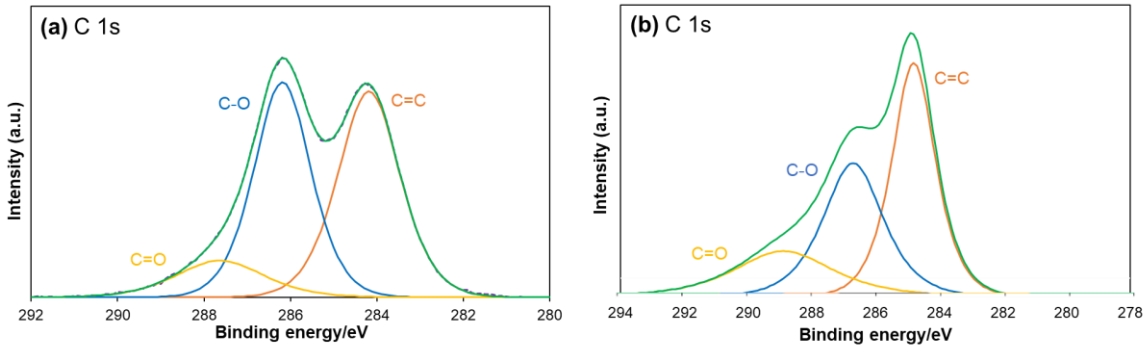


Figure S13. XPS spectra at C 1s region of (a) GO and (b) Am-GO.

8. XPS Survey and N 1s Spectra of Am-GO

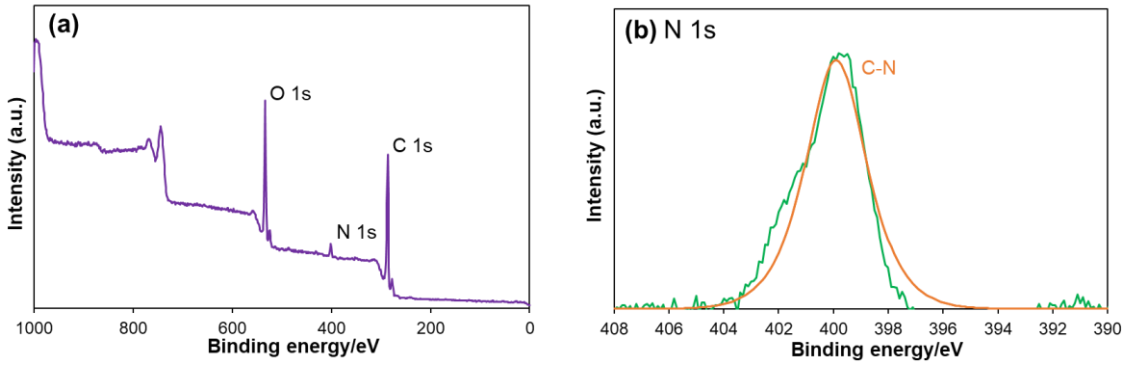
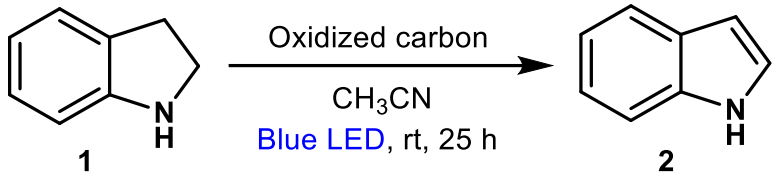


Figure S14. XPS spectra (a) survey and (b) N 1s region of Am-GO.

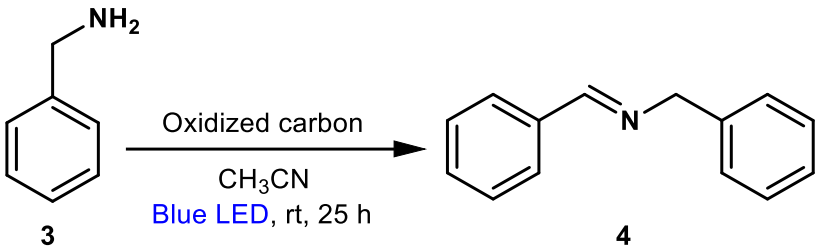
9. Typical Procedure of Dehydrogenation of Indoline

The mixture of indoline **1** (0.2 mmol), oxidized carbon (5 mg), and CH_3CN (1.0 mL) was stirred with irradiating Blue LED light under an air atmosphere at room temperature for 25 h. After the reaction, the reaction mixture was analyzed by GC using n-dodecane as an internal standard.



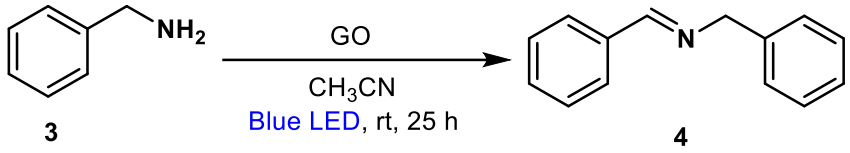
10. Typical Procedure of Oxidative Coupling of Benzylamine

The mixture of benzylamine **3** (0.2 mmol), oxidized carbon (5 mg), and CH_3CN (1.0 mL) was stirred with irradiating Blue LED light under an air atmosphere at room temperature for 25 h. After the reaction, the reaction mixture was analyzed by GC using n-dodecane as an internal standard. Then product was separated from the reaction mixture by centrifugation and removed from the solvent by evaporation. Finally, the product was purified by flash column chromatography. Imines are known to be unstable when exposed to water/moisture. As a result, the synthesis and purification processes at a 0.2 mmol scale resulted in imine decomposition. Consequently, the NMR spectra shown below are not pure. This is why we have determined the product yields using gas chromatography.



11. Screening of Reaction Conditions

Table S1 Screening Reaction Conditions of Oxidative Coupling of Benzylamine[a]

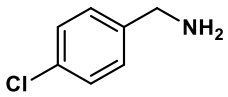
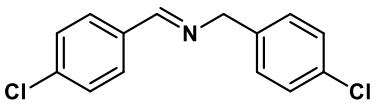
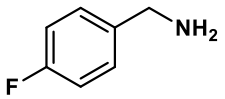
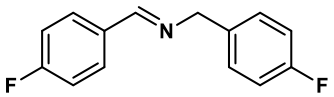
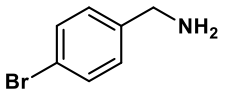
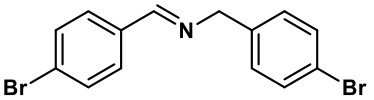
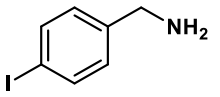
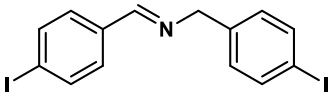
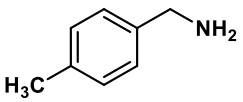
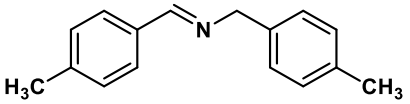
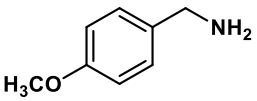
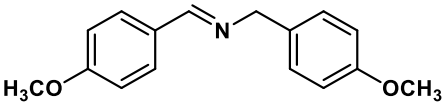
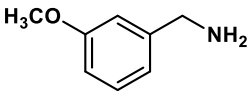
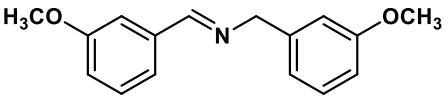
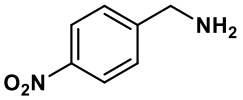
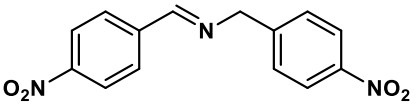


entry	GO (mg)	time (hour)	solvent	yield (%)[b]
1	5	5	CH_3CN	30
2	5	10	CH_3CN	51
3	5	15	CH_3CN	70
4	5	20	CH_3CN	80
5	**5**	**25**	**CH_3CN**	**88±2[c]**
6	5	30	CH_3CN	90
7	3	25	CH_3CN	72
8	6	25	CH_3CN	90
9	10	25	CH_3CN	88
10	5	25	DMF	61
11	5	25	THF	55

[a]Reaction conditions: benzylamine **3** (0.2 mmol), GO (5 mg), CH_3CN (1.0 mL) under air atmosphere at room temperature, irradiation of blue LED for 25 h. [b]GC yield. [c]n=3.

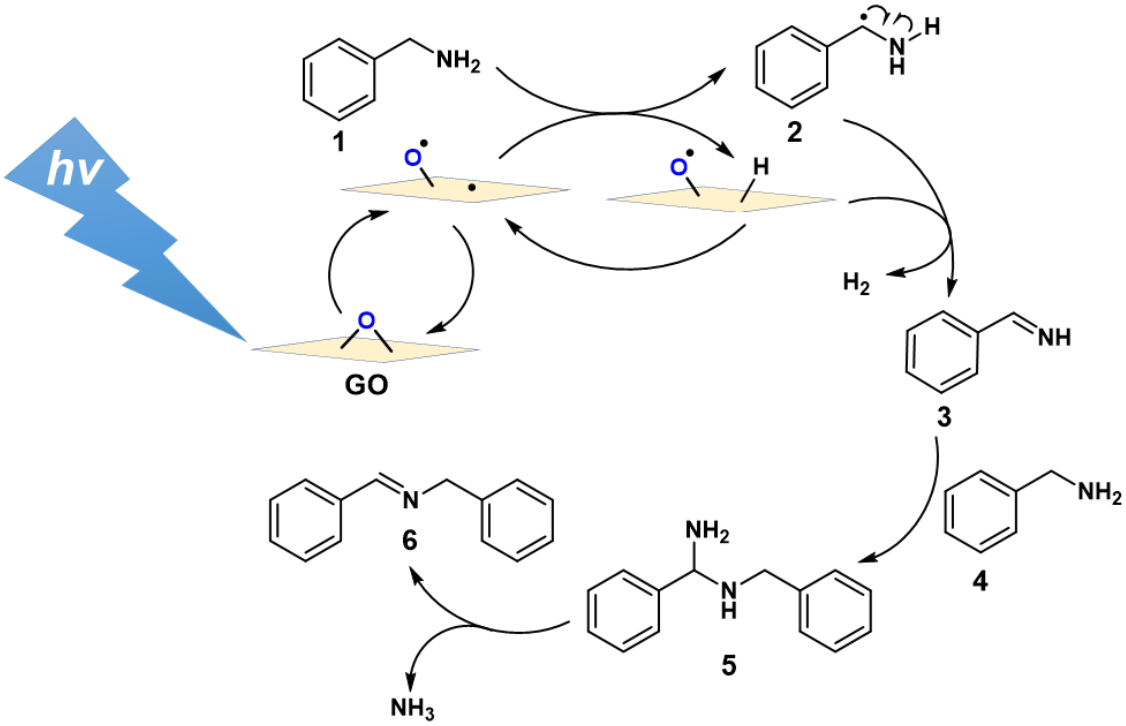
12. Substrate Scope

Table S2 Substrate scope using GO as photocatalyst[a]

Entry	Substrate	Product	Yield[b] (%)
1	 **3a**	 **4a**	90
2	 **3b**	 **4b**	88
3	 **3c**	 **4c**	90
4	 **3d**	 **4d**	88
5	 **3e**	 **4e**	87
6	 **3f**	 **4f**	87
7	 **3g**	 **4g**	86
8	 **3h**	 **4h**	86

[a]Reaction conditions: benzylamine derivatives **3** (0.2 mmol), GO (5 mg), CH_3CN (1.0 mL) under air atmosphere at room temperature, irradiation of blue LED for 25 h. [b]GC yield.

13. Mechanism



Scheme S1. The proposed reaction mechanism for GO catalyzed oxidative coupling of benzylamine.

14. EI-Mass Spectra of Product 4

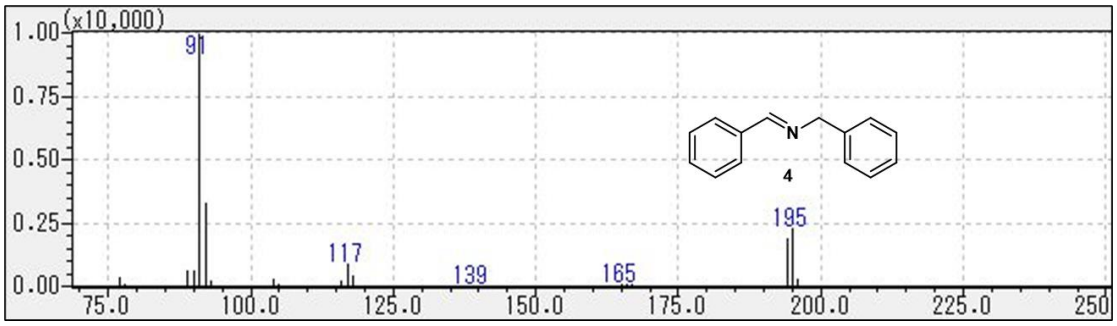


Figure S15. EI-Mass spectra of Product **4**.

15. NMR Spectra of Product 4a-h

N-benzyl-1-phenylmethanimine (4)

^{1}H NMR ($CDCl_3$) δ ppm: 8.4 (s, 1H), 7.80-7.81 (d, 2H), 7.41-7.44 (m, 3H), 7.30-7.37 (m, 4H,), 7.26-7.39 (m, 1H), 4.8 (s, 2H).

^{13}C NMR ($CDCl_3$) δ ppm: 162.14, 139.41, 136.26, 130.90, 127.12, 128.11-129.12, 65.18.

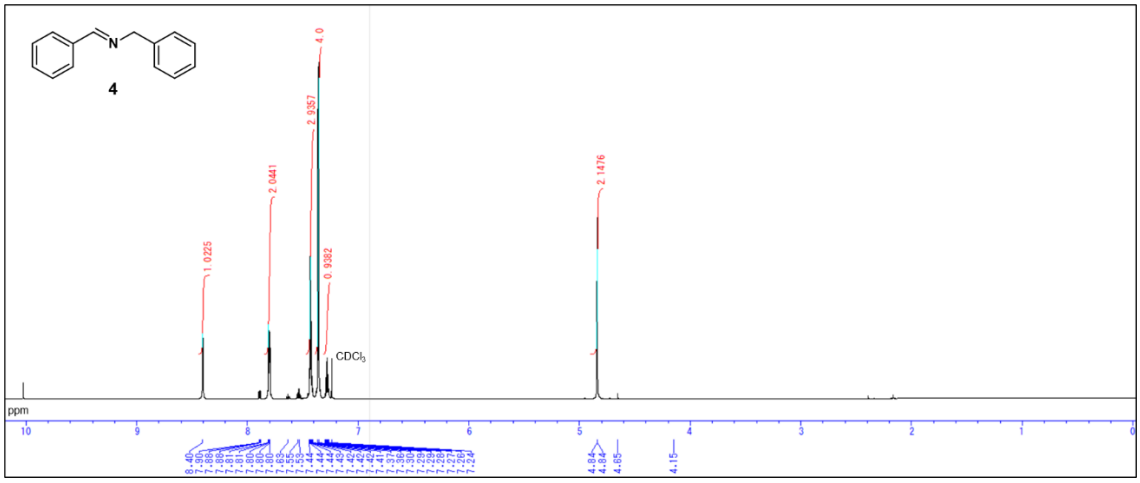


Figure S16: ^{1}H NMR spectra of product **4**.

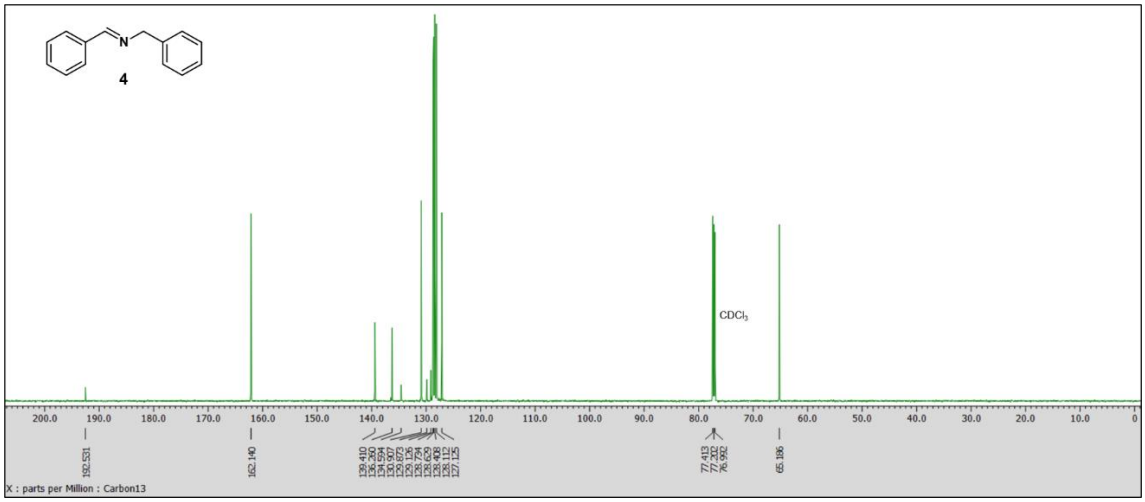


Figure S17. ^{13}C NMR spectra of product **4**.

N-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (4a)

^{1}H NMR ($CDCl_3$) δ ppm: 8.47 (s, 1H), 7.80-7.81 (d, 2H), 7.45-7.46 (d, 2H), 7.32-7.36 (m, 4H,), 4.76 (s, 2H).

^{13}C NMR ($CDCl_3$) δ ppm: 160.79, 138.88, 136.1, 135.30, 129.37, 129.61, 128.06, 128.39 63.55.

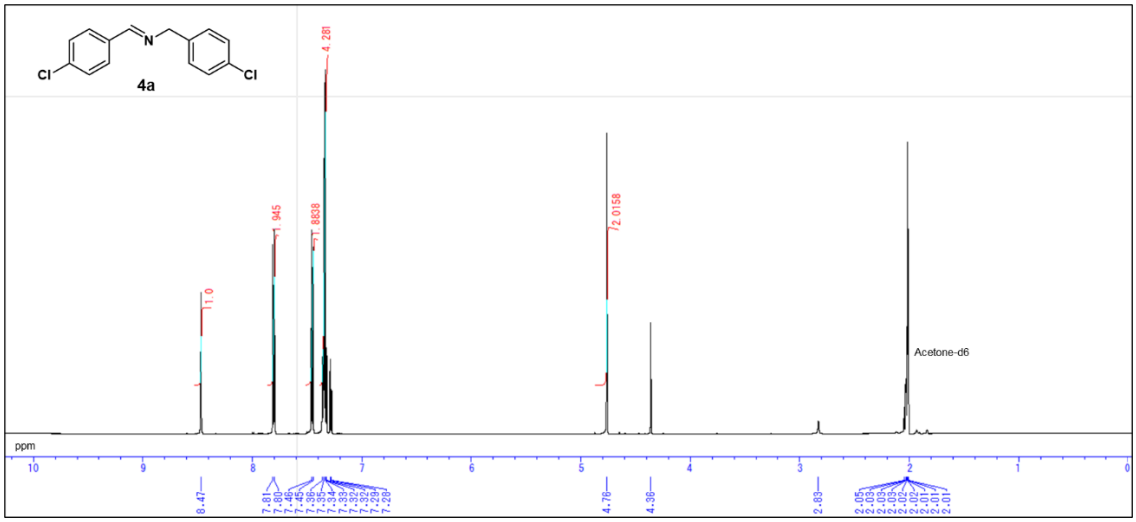


Figure S18: ^{1}H NMR spectra of product **4a**.

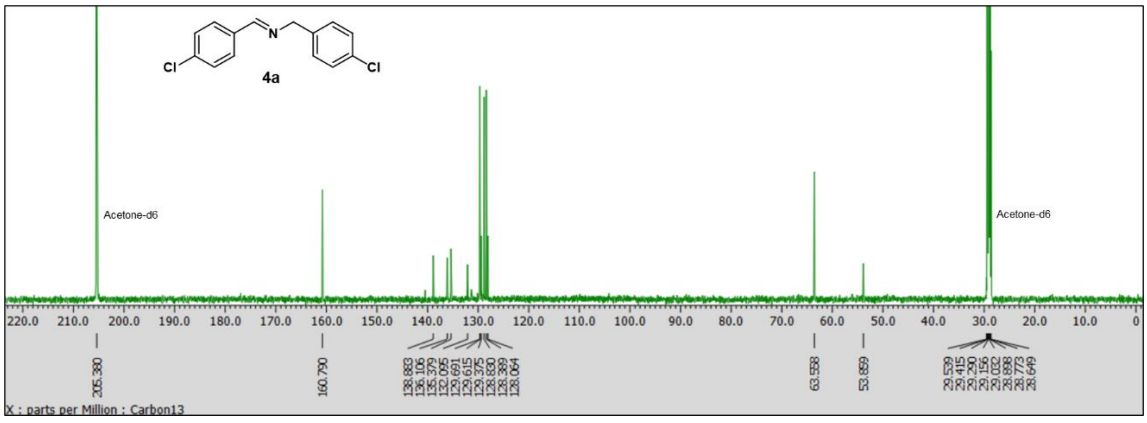


Figure S19: ^{13}C NMR spectra of product **4a**.

N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (4b)

^{1}H NMR ($CDCl_3$) δ ppm: 8.31 (s, 1H), 7.73-7.75 (m, 2H), 7.27-7.29 (m, 2H), 7.2-7.24 (m, 2H), 7.05-7.09 (m, 2H), 4.73 (s, 2H).

^{13}C NMR ($CDCl_3$) δ ppm: 165.34, 163.68, 160.87, 137.81, 132.87, 130.30, 129.33, 128.71, 115.77, 64.21.

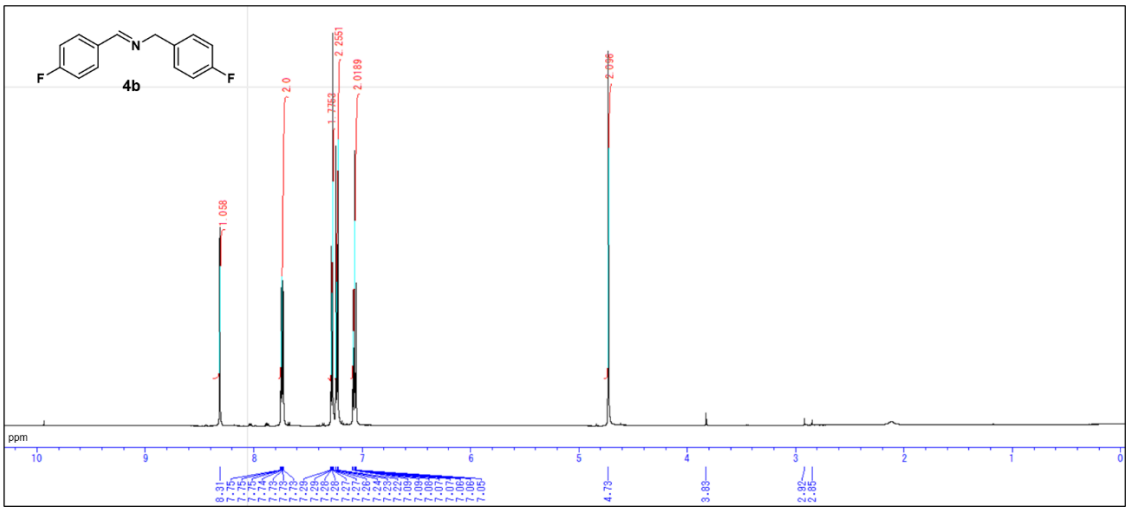


Figure S20: ^{1}H NMR spectra of product **4b**.

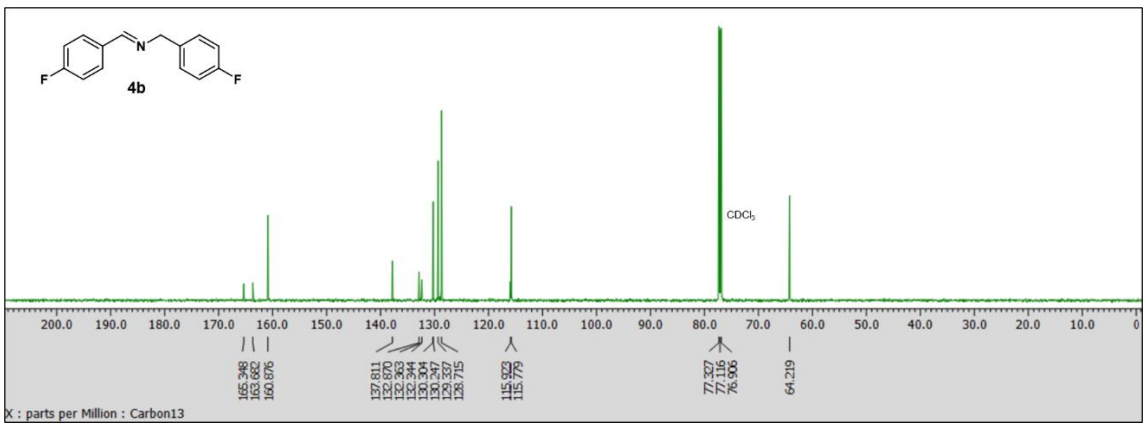


Figure S21: ^{13}C NMR spectra of product **4b**.

N-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (4c)

^{1}H NMR ($CDCl_3$) δ ppm: 8.51 (s, 1H), 7.83-7.85 (d, 2H), 7.48-7.50 (d, 2H), 7.36-7.40 (m, 4H), 4.80 (s, 2H).

^{13}C NMR ($CDCl_3$) δ ppm: 160.79, 138.88, 136.10, 135.37, 129.37, 129.61, 128.06, 128.39 63.55.

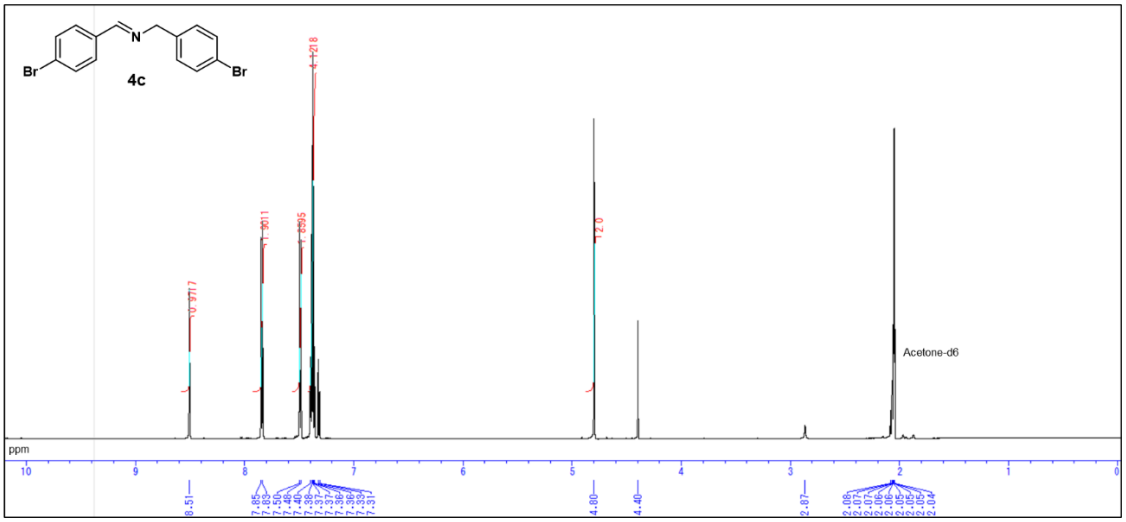


Figure S22: ^{1}H NMR spectra of product **4c**.

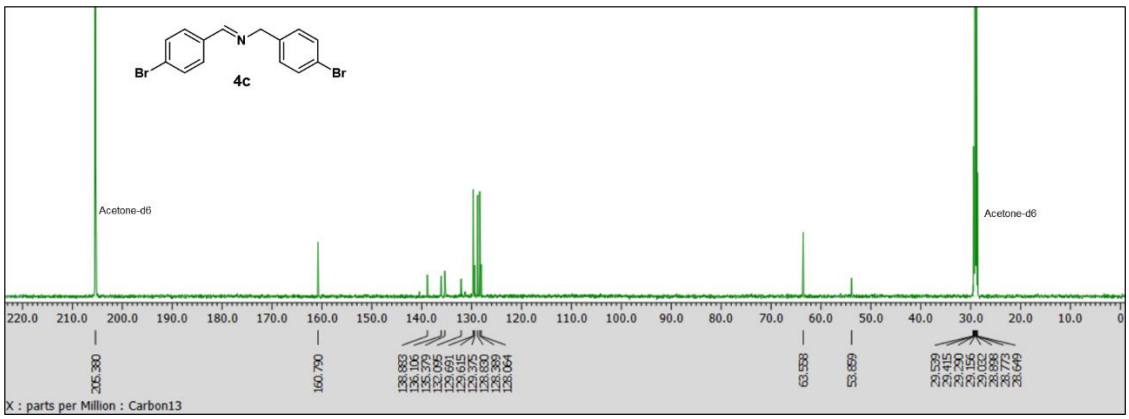


Figure S23: ^{13}C NMR spectra of product **4c**.

N-(4-iodobenzyl)-1-(4-iodophenyl)methanimine (4d)

^{1}H NMR ($CDCl_3$) δ ppm: 8.33 (s, 1H), 7.74-7.77 (m, 2H), 7.28-7.31 (m, 2H), 7.24-7.26 (m, 2H,), 7.07-7.11 (m, 2H), 4.75 (s, 2H).

^{13}C NMR ($CDCl_3$) δ ppm: 165.35, 163.69, 160.88, 137.81, 132.87, 130.24, 129.34, 128.71, 115.92, 64.21.

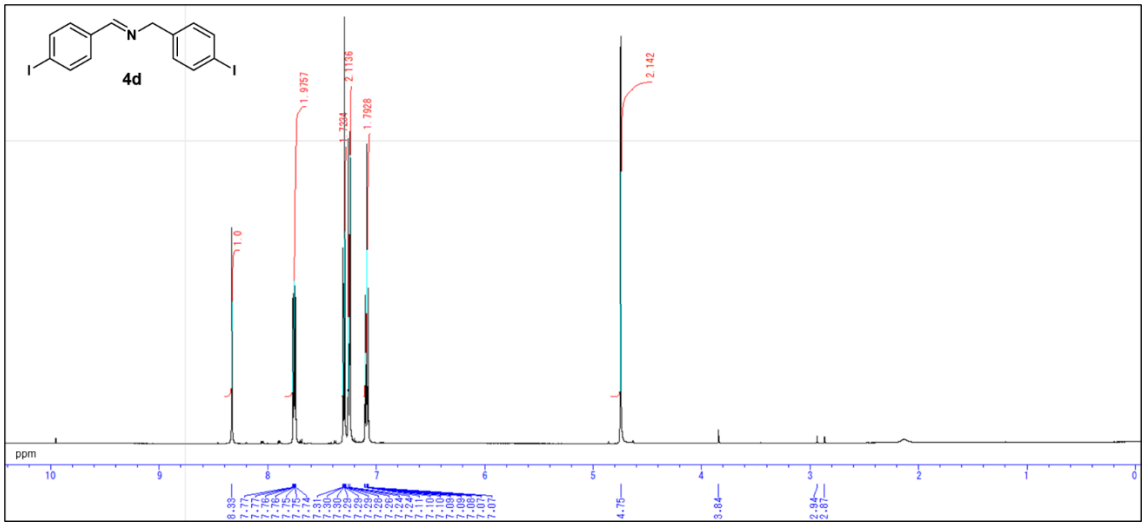


Figure S24: ^{1}H NMR spectra of product **4d**.

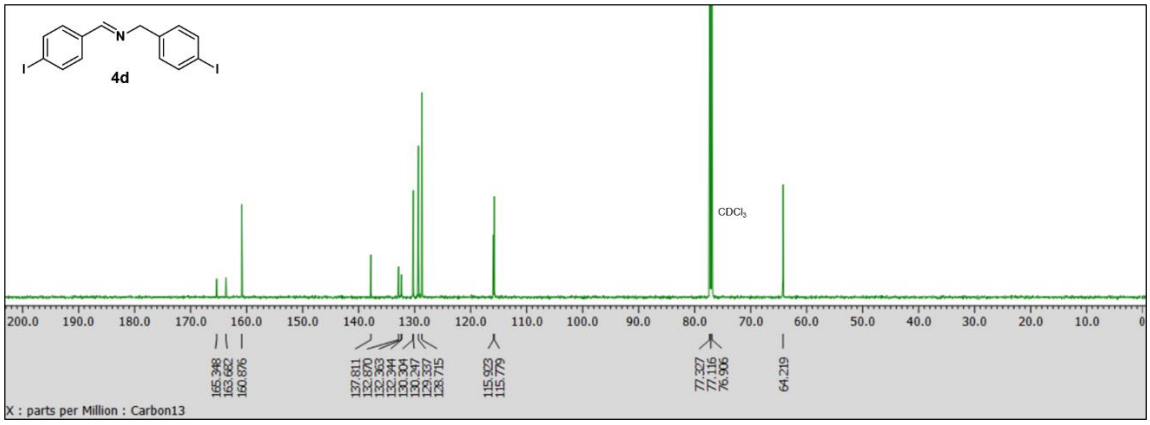


Figure S25: ^{13}C NMR spectra of product **4d**.

N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (4e)

^{1}H NMR ($CDCl_3$) δ ppm: 8.28 (s, 1H), 7.68-7.70 (m, 2H), 7.26-7.28 (m, 2H), 7.22-7.24 (m, 2H,), 6.89-6.91 (m, 2H), 4.71 (s, 2H), 3.81 (s, 6H).

^{13}C NMR ($CDCl_3$) δ ppm: 161.91, 161.74, 138.22, 132.70, 129.96, 129.01, 128.71, 128.59, 114.12, 64.24, 55.46.

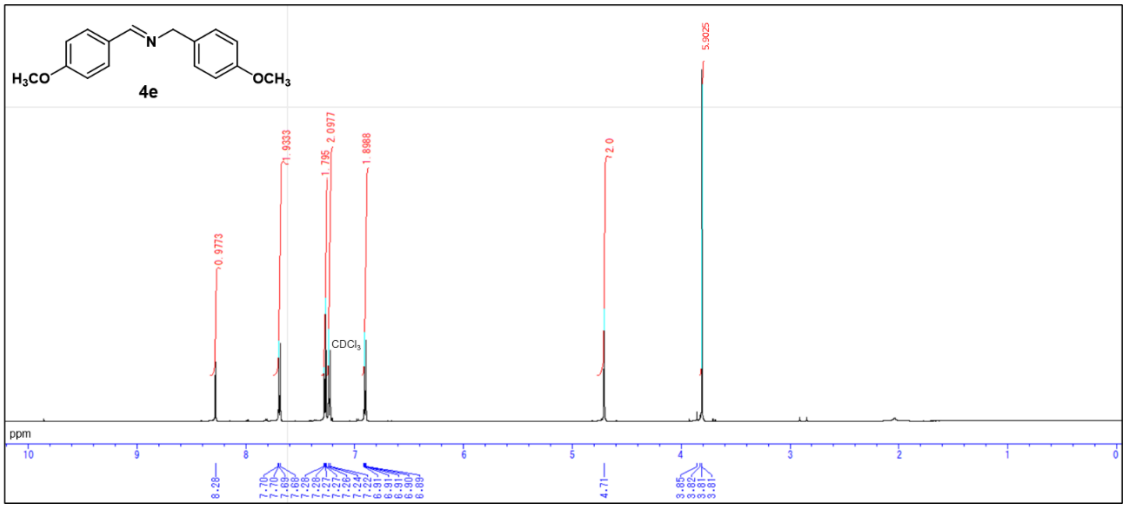


Figure S26: ^{1}H NMR spectra of product **4e**.

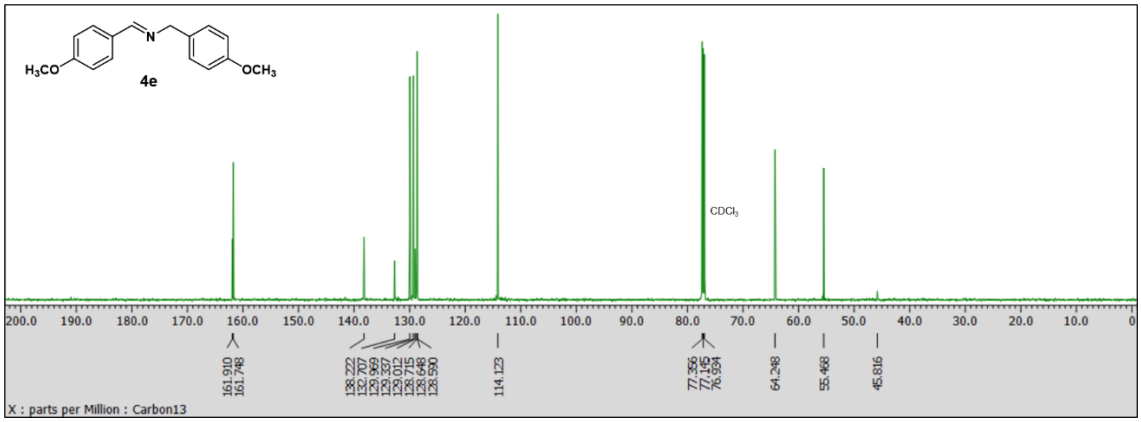


Figure S27: ^{13}C NMR spectra of product **4e**.

N-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine (4f)

^{1}H NMR ($CDCl_3$) δppm: 8.32 (s, 1H), 7.74-7.76 (m, 2H), 7.35-7.36 (m, 3H), 7.26-7.29 (m, 1H,), 7.93-7.95 (m, 2H), 4.80 (s, 2H), 3.82 (s, 6H).

^{13}C NMR ($CDCl_3$) δ ppm: 161.85, 161.53, 139.68, 132.13, 130, 129.20, 128.75, 128.12, 127.06, 113.52, 65.08, 55.45.

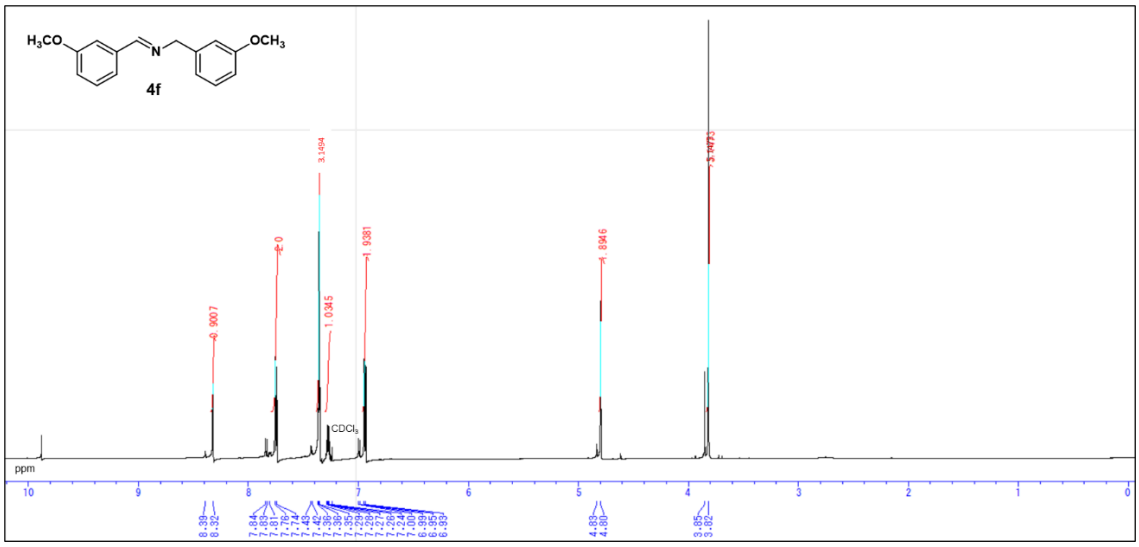


Figure S28: ^{1}H NMR spectra of product **4f**.

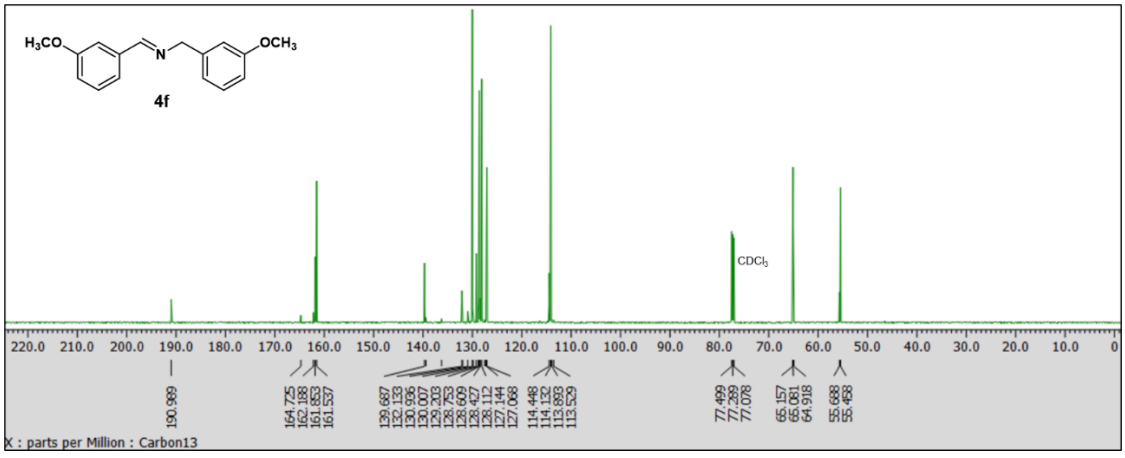


Figure S29: ^{13}C NMR spectra of product **4f**.

N-(4-methylbenzyl)-1-(p-tolyl)methanimine (4g)

^{1}H NMR ($CDCl_3$) δppm: 8.43 (s, 1H), 7.70-7.72 (d, 2H), 7.34-7.38 (m, 4H), 7.30-7.33 (m, 2H,), 4.75 (s, 2H), 2.36 (s, 6H).

^{13}C NMR ($CDCl_3$) δ ppm: 161.84, 140.96, 139.23, 134.06, 131.99, 129.75, 129.41, 128.23, 128.12, 63.67, 20.69.

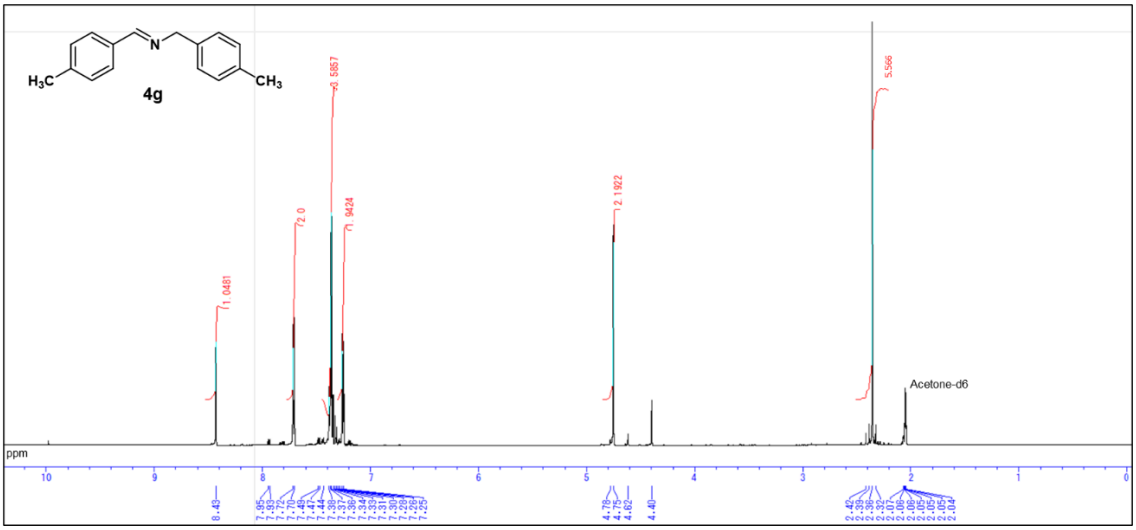


Figure S30: ^{1}H NMR spectra of product **4g**.

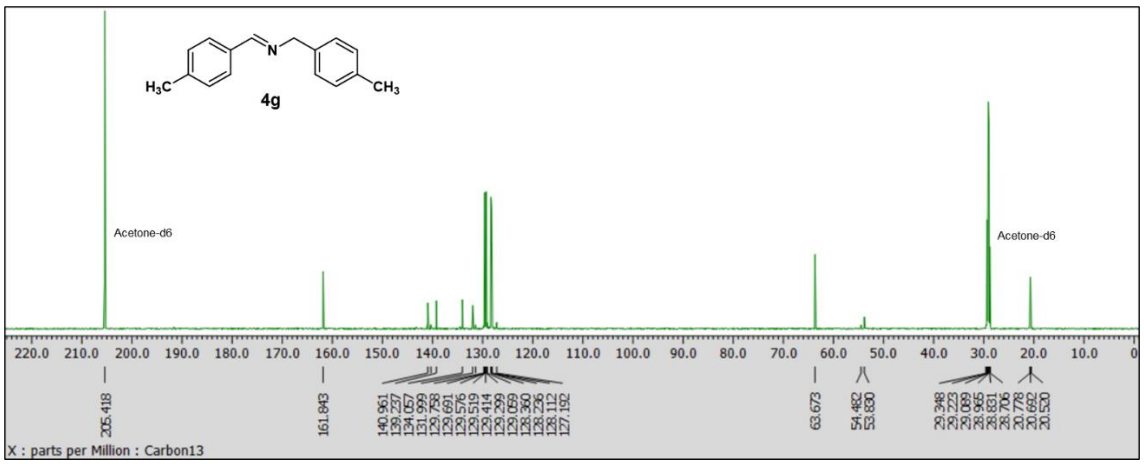


Figure S31: ^{13}C NMR spectra of product **4g**.

N-(4-nitrobenzyl)-1-(4-nitrophenyl)methanimine (4h)

^{1}H NMR ($CDCl_3$) δppm: 8.50 (s, 1H), 7.77-7.79 (d, 2H), 7.64-7.66 (d, 2H), 7.36-7.40 (m, 4H,), 4.80 (s, 2H).

^{13}C NMR ($CDCl_3$) δ ppm: 160.79, 138.88, 136.1, 135.30, 129.37, 129.61, 128.83, 128.39, 128.06, 63.55.

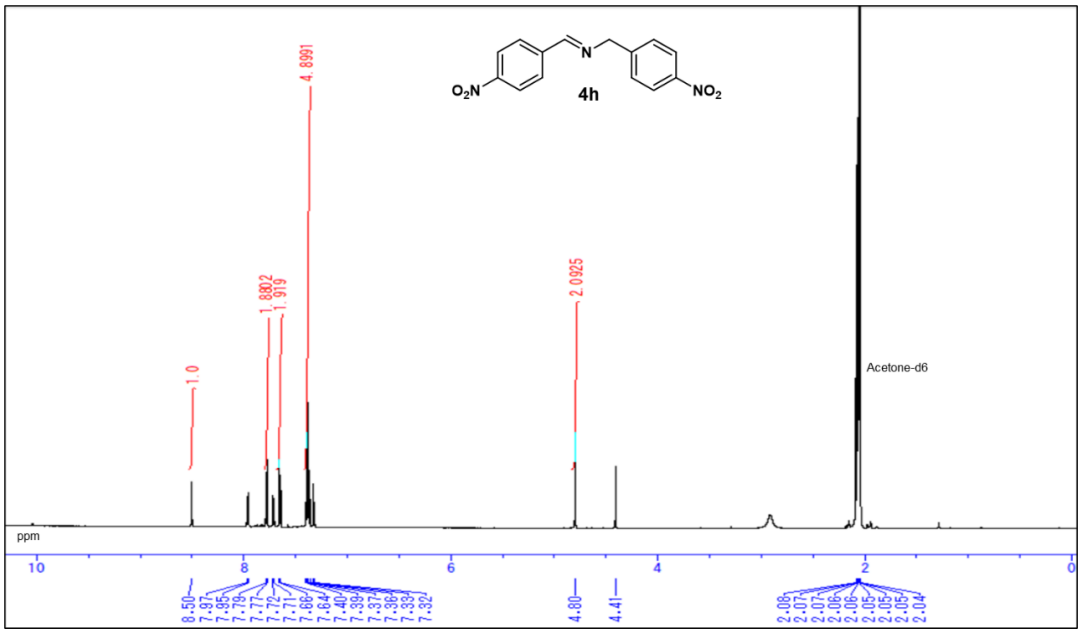


Figure S32: ^{1}H NMR spectra of product **4h**.

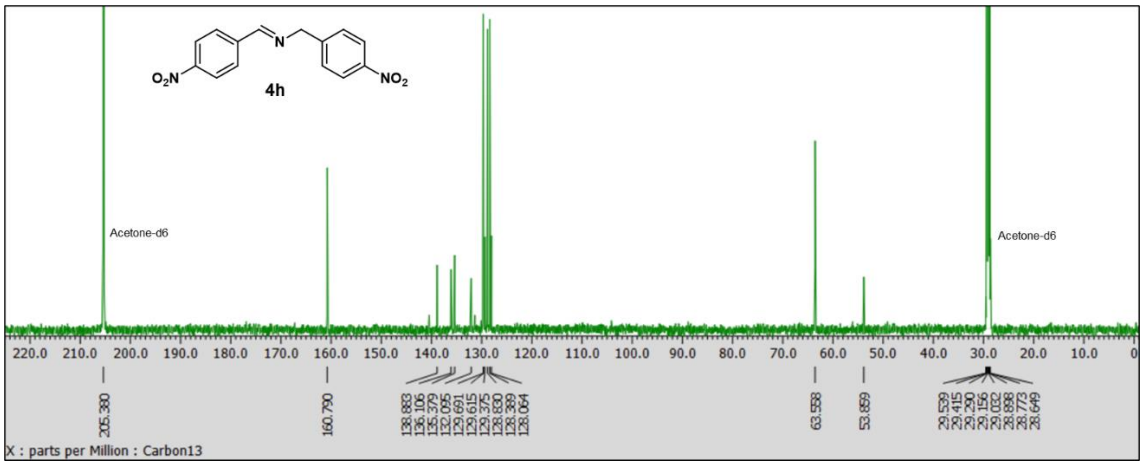


Figure S33: ^{13}C NMR spectra of product **4h**.

16. References

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