Supporting Information

Visible Light-Driven Oxidative Coupling Reactions of Amines by Photoactive WS_2 Nanosheets

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Contents of Supporting Information:

1. Materials

All reagents and solvents used were obtained commercially and used without further purification. Tungsten (IV) sulfide (WS_2), bromobenzene, benzyl amine, all primary, secondary and aliphatic amines were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Tokyo Chemical Industry Co., LTD. (Tokyo, Japan). *N*-Methyl-2-pyrrolidone (NMP), acetonitrile (CH_3CN) and diethyl ether ($(C_2H_5)_2O$) were purchased from Dae-Jung Chemicals (Busan, Republic of Korea).

2. Instrumentation

The morphology and size of WS_2 nanosheets were characterized by transmission electron microscope (TEM, JEOL-2100F) and atomic force microscope (AFM, XE-100, Park systems, Korea). Raman spectra were measured by Raman Microscope (RENISHAW, RM-100) at laser excitation of 514.5 nm. The UV/Vis absorption spectra of WS_2 were measured using a UV/Vis spectrometer (UV-2600, Shimadzu, Japan). The photoluminescence spectra were obtained by a spectrofluorometer (Nano Log®, Horiba Scientific, Tokyo, Japan). The amount of catalyst was quantified by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, SPECTRO, SPECTRO ARCOS). The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of the reaction mixture were recorded by a 400 MHz spectrometer (BRUKER Bio Spin AG, Bruker model digital ADVANCE III 400). The IR analysis of imines was analyzed by fourier transform-infra red spectrocopy (Smart iTR^{TM} , Thermo Scientific).

3. PL response of WS_2 nanosheets to benzylamine

PL response of WS_2 nanosheets to benzylamine at various concentrations from 0.05 to 0.9 mM was measured by using a spectrofluorometric. A 5.46 μL of benzylamine (0.05 mM) was added into a 1 mL portion of WS_2/NMP solution, which was then stirred vigorously for 5 min at 25^{o}C. The PL spectrum of the resulting solution was taken at an excitation of 380 nm with an exposure time of 0.1 sec.

4. GC analysis

GC analysis was done by YL Instrument 6500GC equipped with FID detector and a HP-5 capillary column (5%-Phenyl-methylpolysiloxane, 30 m, 0.320 mm x 0.25 μm, Agilent) using argon as a carried gas. Standard analysis condition: oven temperature 100 °C, injector temperature 280°C, FID detector temperature 300°C, column temperature program 10 °C/min, final temperature 280 °C (holding for 3 min).

5. General procedure for synthesis of imine products for calibration curves

All imine products as GC standards were readily synthesized via condensation of aldehydes and amines.[1] For *N*-benzylidene benzylamine, 5 mmol of benzylamine, 5 mmol of benzaldehyde, and 0.5 mg of anhydrous $MgSO_4$ were added into 5 mL of CH_2Cl_2, and then the resulting mixture was stirred at room temperature for 5 h. After filtering out solid $MgSO_4$, the solvent was vaporized by using a rotary evaporator. Unreacted benzealdehyde and benzylamine were further removed under vacuum at 60°C. Other imine products were also obtained in the same way.

6. Supplementary Figures and Tables

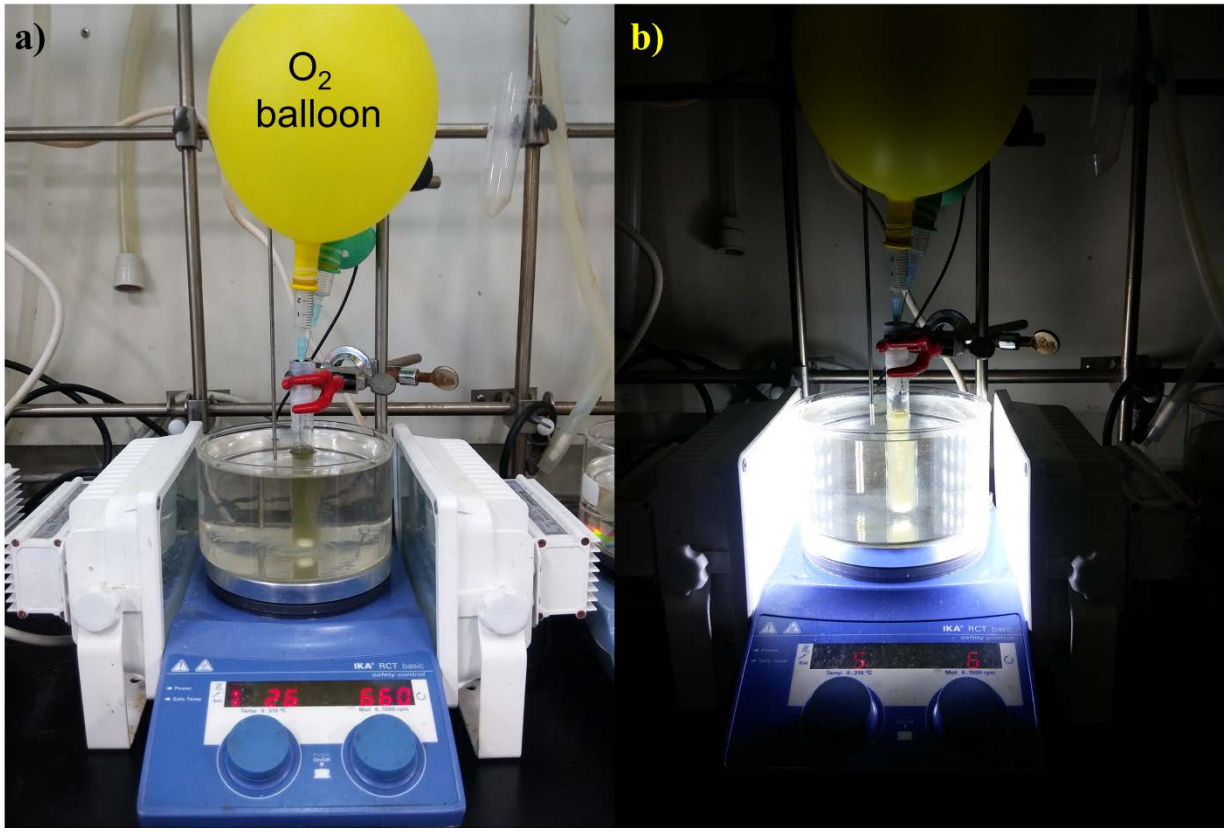


Figure S1. Photos of an experimental set-up for photocatalysis. a) Before, and b) After visible light irradiation.

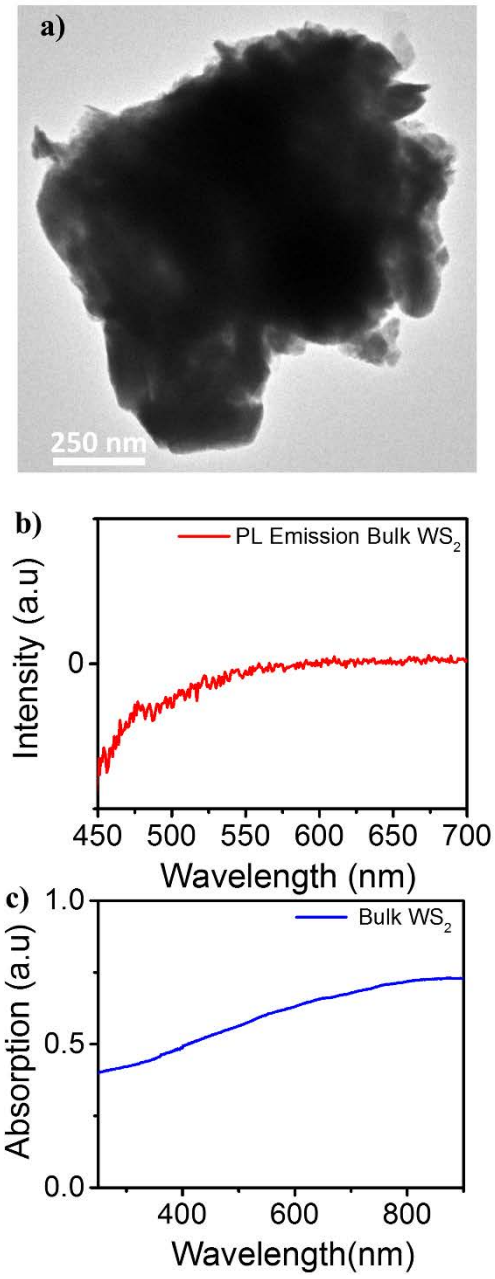


Figure S2. a) TEM image, b) fluorescence spectra and c) UV-Vis absorption of bulk WS_2.

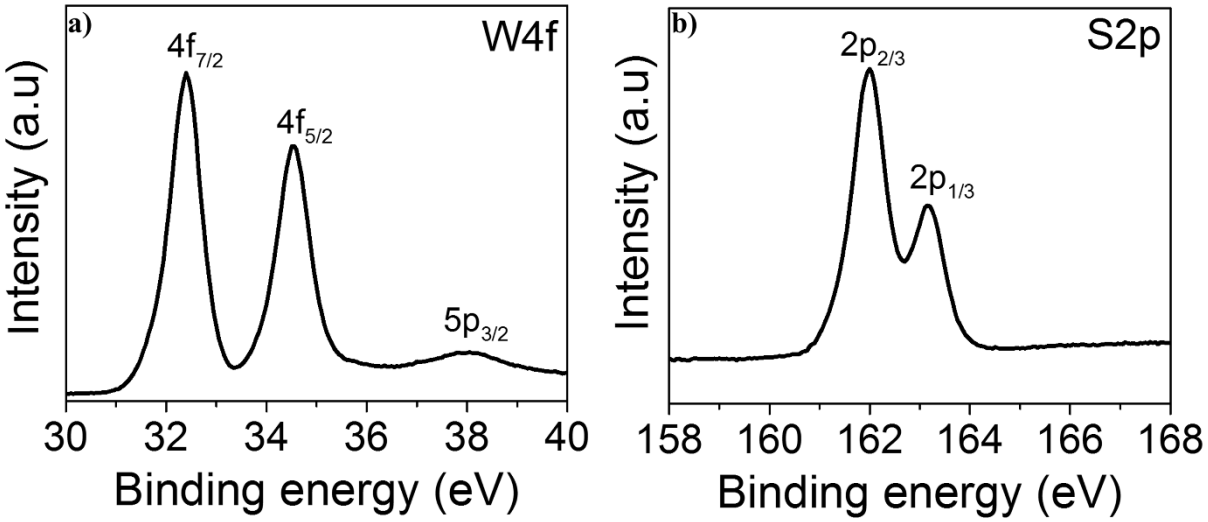


Figure S3. XPS spectra of 2H-WS_2 Nanosheets: (a) W4f spectrum, showing strong peaks of $W4f_{7/2}$ and $W4f_{5/2}$ at 32.4 and 34.55 eV, respectively, and a weak peak of $W5p_{3/2}$ at 37.9 eV. (b) S2p spectrum, showing two peaks of $S2p_{3/2}$ and $S2p_{1/3}$ at 161.9 and 163.2 eV.[2]

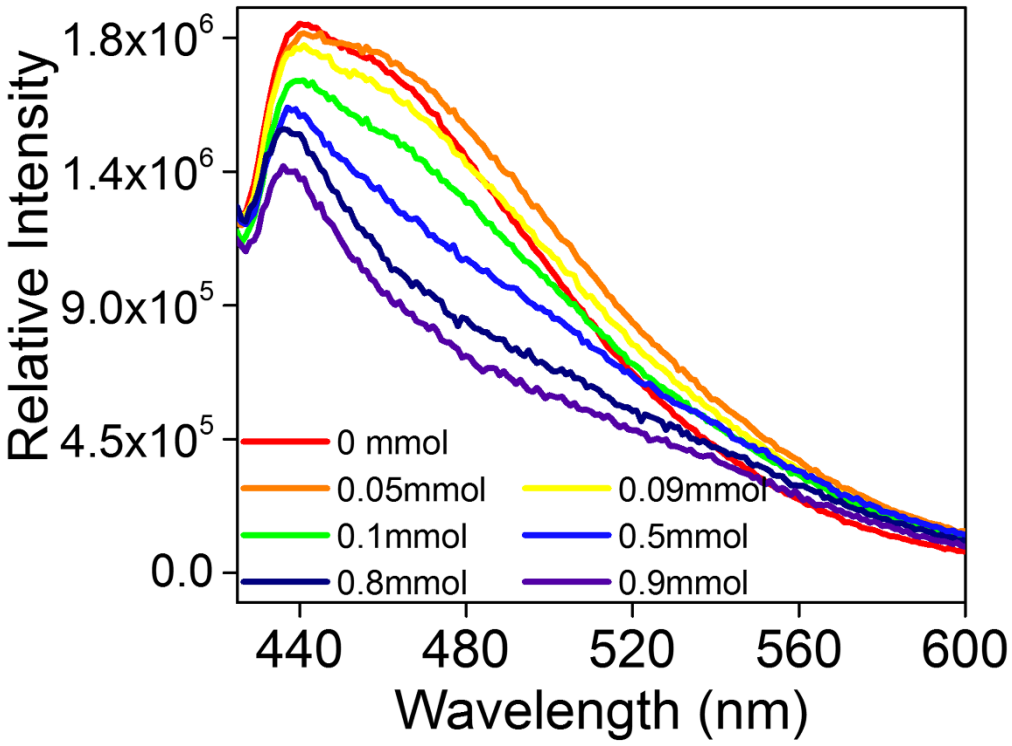


Figure S4. PL response of WS_2 nanosheets to benzylamine at various concentrations, showing that the WS_2 PL was gradually quenched by benzylamine as its concentration increased.

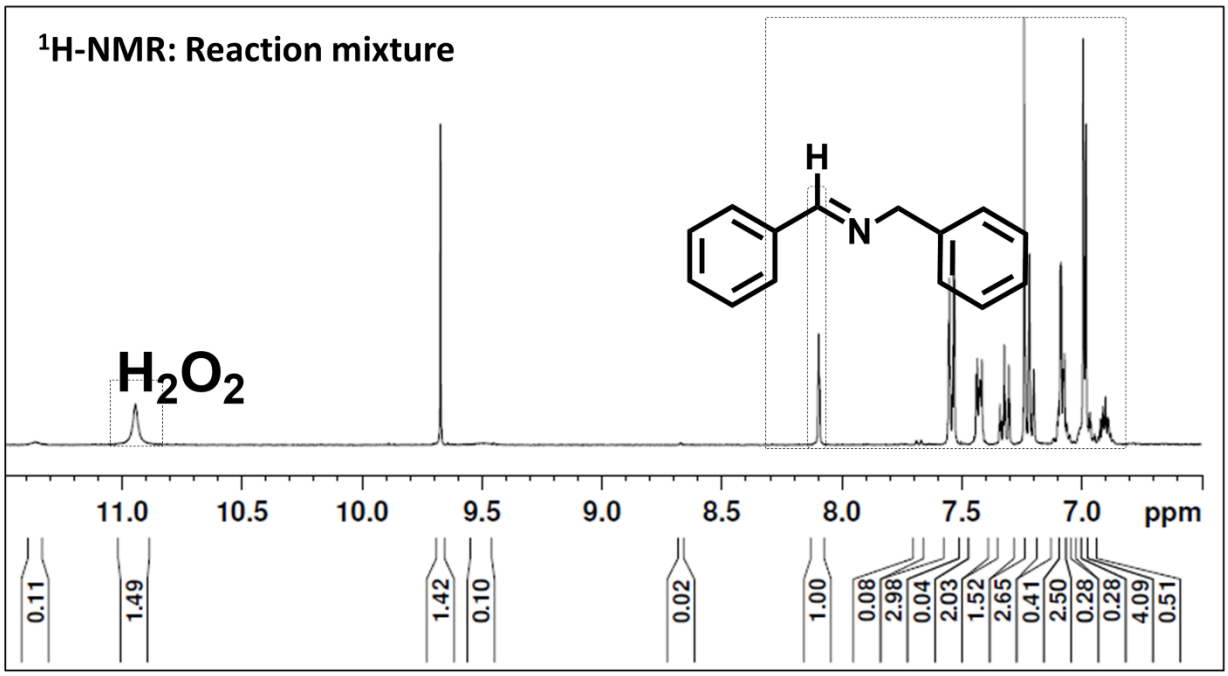


Figure S5. ^{1}H NMR spectrum of the reaction mixture for the oxidative coupling reaction of benzylamine photocatalyzed by WS_2 nanosheets, showing the peak of H_2O_2 (10.95 ppm) formed as a byproduct during the reaction.

Table S1. Recovered amount of WS_2 nanosheets after each round of oxidative coupling reaction of benzylamine

Cycles	**Initial amount**	**1st**	**2nd**	**3rd**	**4th**
Amount recovered after each cycle	1.2 mg	0.795 mg	0.536 mg	0.415 mg	0.482 mg

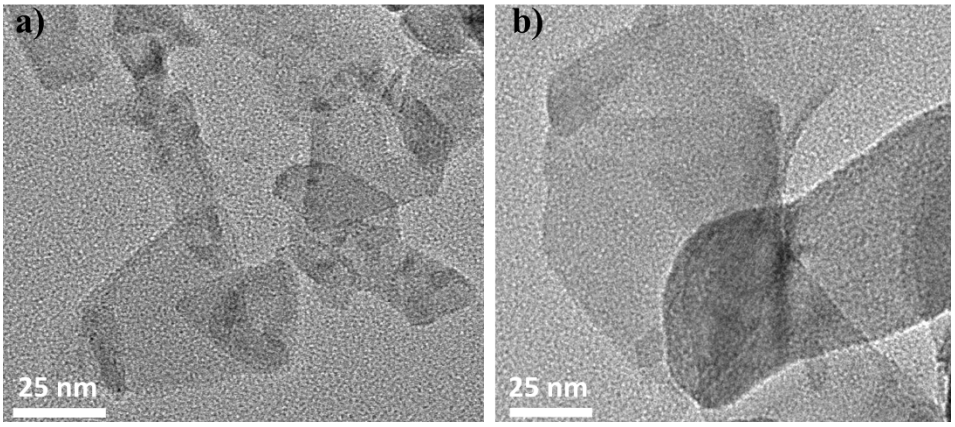
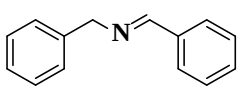
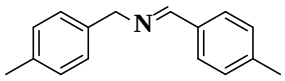


Figure S6. TEM images of WS_2 nanosheets (a) before and (b) after recycling them five times in the oxidative coupling of benzylamine.

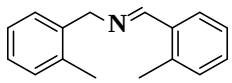
7. Characterization of pure imine products



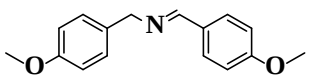
***N*-Benzylidine-*p*-benzylamine:** (Yellow liquid, GC RT: 11.29 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.35 (s, 1H), 7.79 – 7.74 (m, 2H), 7.39 (d, J = 2.2 Hz, 3H), 7.32 (d, J = 4.4 Hz, 4H), 7.24 (s, 1H), 4.80 (d, J = 1.3 Hz, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 162.09, 139.40, 136.25, 130.88, 128.72, 128.61, 128.39, 128.09, 127.10, 65.16 ppm; **FT-IR:** *v* = 3027/3085, 2840/2872/2732, 1643, 1580 cm^{-1}.



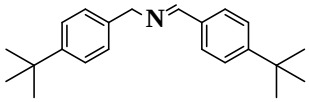
***N*-(4-Methylbenzylidine)-*p*-methylbenzylamine:** (Yellow solid, GC RT: 13.66 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.30 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4, 2H), 7.18 (d, *J* = 8.0, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ =161.18, 141.06, 136.57, 136.45, 133.70, 129.41, 129.26, 128.37, 128.07, 64.87, 21.61, 21.22 ppm; **FT-IR:** *v* = 3048/3022, 2913/2854/2732, 1638, 1571, 811, 794 cm^{-1}.



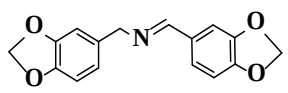
***N*-(2-Methylbenzylidine)-*o*-methylbenzylamine:** (Yellow liquid, GC RT: 13.29 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.63 (s, 1H), 7.92 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.32 – 7.10 (m, 7H), 4.80 (s, 2H), 2.47 (s, 3H), 2.37 (s, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 160.66, 137.84, 137.73, 136.20, 134.34, 130.93, 130.37, 130.23, 128.40, 127.84, 127.17, 126.30, 126.20, 63.41, 19.52, 19.42 ppm; **FT-IR:** *v* = 3063/3021, 2920/2879/2864, 1635, 1570, 754, 741 cm^{-1}.



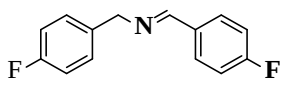
***N*-(4-Methoxybenzylidine)-*p*-methoxybenzylamine:** (Yellow liquid, GC RT: 16.64 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.26 (s, 1H), 7.72 – 7.66 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.93 – 6.83 (m, 4H), 4.70 (s, 2H), 3.79 (s, 3H), 3.75 (s, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 161.72, 160.99, 158.70, 131.74, 129.89, 129.24, 114.03, 113.95, 64.49, 55.40, 55.33 ppm; **FT-IR:** *v* = 3034/3006, 2957/2909/2835, 1640, 1577, 869, 830, 814 cm^{-1}.



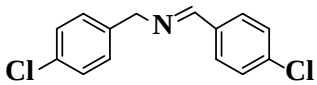
***N*-(4-(*tert*-Butyl)benzylidine)-*p*-(*tert*-butyl)benzylamine:** (Yellow liquid, GC RT: 17.83 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.35 (s, 1H), 7.73 – 7.69 (m, 2H), 7.44 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 2H),4.77 (s, 2H), 1.33 (s, 2H), 1.31 (s, 9H), 1.30 (s, 9H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ =161.77, 154.18, 149.87, 136.61, 133.73, 129.83, 128.23, 127.89, 127.82, 125.65, 125.50, 64.97, 35.03, 34.60, 31.56, 31.38, 31.22 ppm; **FT-IR:** *v* = 3058/3025, 2960/2902/2867, 1644, 1570, 848, 827, 803 cm^{-1}.



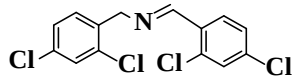
1-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)methanimine: (White solid, GC RT: 18.49 min); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.21 (s, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.76 (d, *J* = 1.0 Hz, 2H), 5.97 (s, 2H), 5.91 (s, 2H), 4.66 (d, *J* = 1.1 Hz, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ =160.96, 150.03, 148.37, 147.84, 146.62, 133.45, 131.08, 124.67, 121.13, 108.71, 108.31, 108.13, 106.78, 101.57, 101.02, 64.61 ppm; **FT-IR:** *v* = 3074/3027, 2892/2875/2778, 1645, 1560, 920, 874, 863 cm^{-1}.



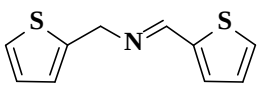
***N*-(4-Fluorobenzylidine)-*p*-fluorobenzylamine:** (Yellow liquid, GC RT: 11.16 min); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 7.78 – 7.74 (m, 2H), 7.32 – 7.21 (m, 2H), 7.12 – 7.04 (m, 2H), 7.03 – 6.96 (m, 2H), 4.75 (s, 1H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 165.65, 163.31,163.26,160.88, 160.62, 135.10, 135.07, 132.48, 132.45, 130.32, 130.32, 129.61, 129.54, 115.93, 115.72, 115.51, 115.30, 64.22 ppm; **FT-IR:** *v* = 3039/3005, 2753, 1601, 1507, 1155, 819, 873 cm^{-1}.



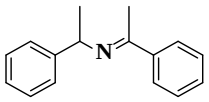
***N*-(4-Chlorolbenzylidine)-*p*-chlorobenzylamine:** (White solid, GC RT: 15.39 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.31 (s, 1H), 7.72 – 7.65 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 4.74 (s, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ =160.98, 137.76, 137.00, 134.58, 131.02, 129.61, 129.41, 129.07, 128.78, 64.30 ppm; **FT-IR:** *v* = 3064/3028, 2875/2856/2818, 1641, 1570, 824, 811, 799 cm^{-1}.



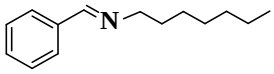
***N*-(2,4-Dichlorobenzylidine)-*o,p*-dichlorobenzylamine:** (White solid, GC RT: 17.79 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.78 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.21 (m, 2H), 4.86 (s, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 58.98, 137.48, 135.98, 135.47, 134.11, 133.59, 131.66, 130.60, 130.57, 130.45, 129.78, 129.47, 129.30, 128.11, 127.75, 127.37, 61.70 ppm; **FT-IR:** *v* = 3090/3025, 2901/2850/2807, 1641, 1584, 861, 834, 819, 802, 773 cm^{-1}.



1-(Thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanimine: (Yellow liquid, GC RT: 11.64 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.38 (d, J = 1.2 Hz, 1H), 7.38 (dt, J = 5.0, 1.0 Hz, 1H), 7.29 (dd, J = 3.6, 1.1 Hz, 1H), 7.21 (dd, J = 4.9, 1.5 Hz, 1H), 7.04 (dd, J = 5.0, 3.6 Hz, 1H), 6.99 – 6.92 (m, 2H), 4.92 (s, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 155.52, 142.19, 141.64, 131.13, 129.44, 127.50, 126.99, 125.38, 124.93, 58.61, ppm; **FT-IR:** *v* = 3058/3025, 2960/2902/2867, 1644, 1570, 861, 834, 819, 802, 773 cm^{-1}.



1-Phenyl-*N*-(1-phenylethyl)ethan-1-imine: (Yellow liquid, GC RT: 11.83 min,); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.99 – 7.91 (m, 2H), 7.59 – 7.49 (m, 1H), 7.45 (ddt, *J* = 8.2, 6.6, 1.1 Hz, 2H), 7.39 – 7.26 (m, 4H), 7.26 – 7.17 (m, 1H), 4.10 (q, *J* = 6.6 Hz, 1H), 2.59 (s, 3H), 1.37 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ =165.03, 137.15, 133.17, 129.48, 128.63, 128.53, 128.43, 128.37, 128.23, 126.87, 126.85, 126.74, 125.75, 59.90, 25.19, 15.66 ppm; **FT-IR:** *v* = 3060/3025, 2962/2923/2866, 1684, 1581, 759, 700, 690 cm^{-1}.



***N*-heptyl-1-phenylmethanimine:** (Yellow liquid, GC RT: 10.14 min); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.26 (s, 1H), 7.74-7.70 (m, 2H), 7.44 – 7.35 (m, 3H), 3.62-3.58 (m, 2H), 1.72-1.69 (m, 2H), 1.31-1.24 (m, 8H), 0.88 (t, J = 6.6 Hz, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 160.88, 136.47, 130.59, 128.71, 128.17, 61.97, 31.99, 31.09, 29.30, 27.49, 22.82, 14.28 ppm; **FT-IR:** *v* = 3063/3025, 2956/2926/2853, 1646, 1580, 826, 753, 692 cm^{-1}.

(1) Liu, L.; Zhang, S.; Fu, X.; Yan, C.-H., *Chem. Commun.* **2011,** *47*, 10148-10150.

(2) Lee, Y.-H.; Yu, L.; Wang, H.; Fang, W.; Ling, X.; Shi, Y.; Lin, C.-T.; Huang, J.-K.; Chang, M.-T.; Chang, C.-S.; Dresselhaus, M.; Palacios, T.; Li, L.-J.; Kong, J., *Nano Lett.* **2013,** *13*, 1852-1857.