

Supporting Information
For

Direct synthesis of hydrazones by visible light mediated aerobic oxidative
cleavage of C=C bond

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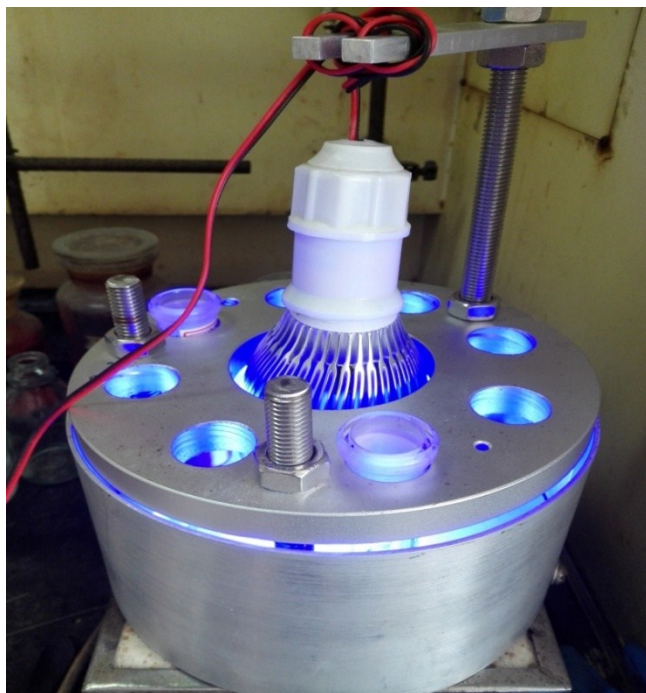
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1. General Information

Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H (400MHz) and ^{13}C NMR (100MHz) data were recorded on Bruker AVANCE II 400MHz spectrometer using CDCl_3 as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^1H NMR spectra was recorded with tetramethylsilane ($\delta = 0.00$ ppm) as internal reference; ^{13}C NMR spectra was recorded with CDCl_3 ($\delta = 77.00$ ppm) as internal reference.

Reaction Apparatus:

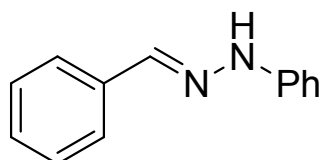
Photochemical reactions were carried out under visible light irradiation by a blue led bulb at room temperature.



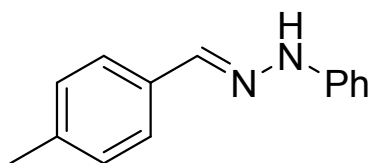
2. General procedures for synthesis of 3aa-3al and 3ba-3bl

To a solution of aryl hydrazines (0.5 mmol) and alkene (1.5 mmol) in MeCN (1.5 mL) was added Methylene Blue (0.01mmol) and 2, 6-lutidine (0.5 mmol). The reaction mixture was stirred at room temperature under air atmosphere (open vial) and irradiated by blue LED (7 W) for 8 h. The reaction was monitored by thin layer chromatography (TLC). When the reaction was completed, it was diluted with water and extracted with ethyl acetate 3 times. Removal of solvent followed by column chromatography afforded desired products.

3. Compound characterizations

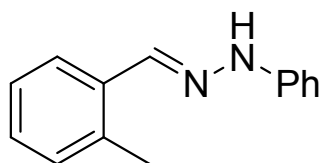


(E)-1-benzylidene-2-phenylhydrazine (**3aa**).^[1] Petroleum ether/ethyl acetate = 20:1, white solid, 75% yield (150 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.70 (m, 3H), 7.35-7.39 (m, 2H), 7.28-7.32 (m, 3H), 7.11-7.13 (m, 2H), 6.87 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 137.3, 135.3, 129.3, 128.6, 128.4, 126.2, 120.1, 112.8.

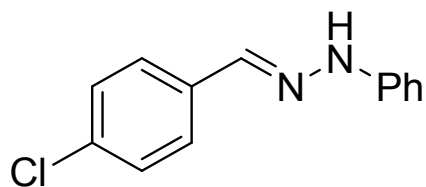


(E)-1-(4-methylbenzylidene)-2-phenylhydrazine (**3ab**).^[1] Petroleum ether/ethyl acetate = 20:1, white solid, 78% yield (156 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.57-7.59 (m, 2H), 7.29-7.33 (m, 2H), 7.20-7.22

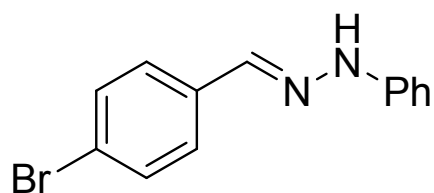
(m, 2H), 7.12-7.15 (m, 2H), 6.90 (t, $J = 7.2$ Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 138.4, 137.6, 132.5, 129.3, 129.3, 126.1, 119.9, 112.7, 21.4.



(E)-1-(2-methylbenzylidene)-2-phenylhydrazine **(3ac)**.^[2] Petroleum ether/ethyl acetate = 20:1, white solid, 62% yield (124 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.84-7.86 (m, 1H), 7.31 (t, $J = 8.0$ Hz, 2H), 7.20-7.25 (m, 3H), 7.12-7.14 (m, 2H), 6.90 (t, $J = 7.2$ Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 136.3, 135.4, 133.1, 130.8, 129.3, 128.1, 126.4, 126.1, 120.0, 112.7, 20.2.

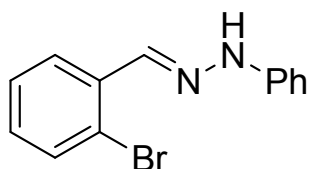


(E)-1-(4-chlorobenzylidene)-2-phenylhydrazine **(3ad)**.^[3] Petroleum ether/ethyl acetate = 20:1, white solid, 70% yield (140 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.58-7.63 (m, 4H), 7.29-7.36 (m, 4H), 7.11-7.13 (m, 2H), 6.92 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 135.8, 133.9, 133.8, 129.3, 128.8, 127.2, 120.3, 112.8.

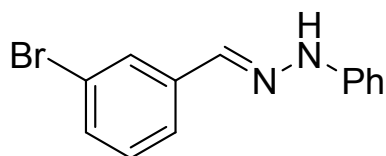


(E)-1-(4-bromobenzylidene)-2-phenylhydrazine **(3ae)**.^[3] Petroleum

ether/ethyl acetate = 20:1, white solid, 76% yield (152 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.58 (s, 1H), 7.49-7.54 (m, 4H), 7.29-7.33 (m, 2H), 7.11-7.13 (m, 2H), 6.92 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.3, 135.8, 134.2, 131.7, 129.3, 127.5, 122.1, 120.3, 112.8.

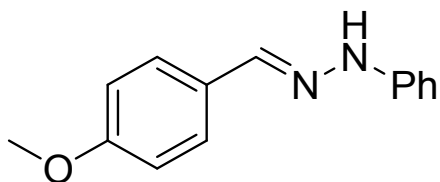


(E)-1-(2-bromobenzylidene)-2-phenylhydrazine **(3af)**.^[3] Petroleum ether/ethyl acetate = 20:1, white solid, 61% yield (120 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.05-8.07 (m, 2H), 7.84 (s, 1H), 7.51-7.54 (m, 1H), 7.27-7.33 (m, 3H), 7.11-7.15 (m, 3H), 6.89 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 135.6, 134.0, 132.8, 129.2, 129.2, 127.3, 126.8, 122.5, 120.3, 112.7.

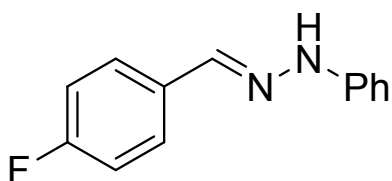


(E)-1-(3-bromobenzylidene)-2-phenylhydrazine **(3ag)**. Petroleum ether/ethyl acetate = 20:1, white solid, 54% yield (110 mg), mp: 135-136 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.69 (s, 1H), 7.51-7.57 (m, 2H), 7.39-7.41 (m, 1H), 7.20-7.31 (m, 3H), 7.10-7.12 (m, 2H), 6.90 (t, $J = 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 137.4, 135.2, 131.1, 130.1, 129.3, 128.7, 124.8, 122.8, 120.5, 112.8. IR (film) ν/cm^{-1} 3220 (s), 3047 (s), 2865 (w), 890 (w), 760 (m), 695 (m). MS (ESI, m/z) 275.0 (M + H⁺), 297.0 (M + Na⁺).

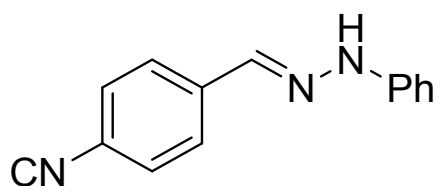
Anal. calcd for $C_{13}H_{11}BrN_2$: C, 56.75; H, 4.03; N, 10.18. Found: C, 56.48; H, 4.23; N, 10.08.



(E)-1-(4-methoxybenzylidene)-2-phenylhydrazine (3ah).^[2] Petroleum ether/ethyl acetate = 15:1, yellow solid, 65% yield (130 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.62 (m, 3H), 7.46 (s, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.11-7.13 (m, 2H), 6.87-6.94 (m, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 144.9, 137.4, 129.2, 128.1, 127.5, 119.7, 114.0, 112.6, 55.3.

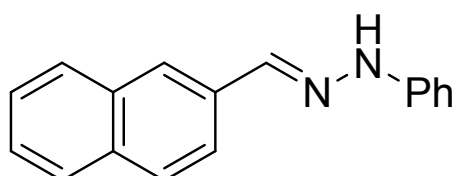


(E)-1-(4-fluorobenzylidene)-2-phenylhydrazine (3ai).^[3] Petroleum ether/ethyl acetate = 20:1, white solid, 72% yield (144 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.68 (m, 3H), 7.28-7.31 (m, 2H), 7.05-7.13 (m, 4H), 6.89 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 246.6 Hz), 144.6, 136.1, 131.5 (d, J = 3.3 Hz), 129.3, 127.7 (d, J = 8.1 Hz), 120.1, 115.6 (d, J = 22.0 Hz), 112.7.

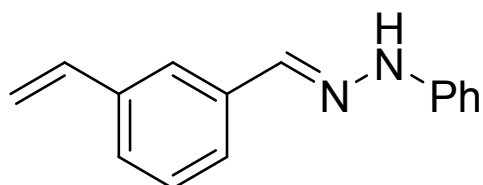


(E)-4-((2-phenylhydrazono)methyl)benzonitrile (3aj).^[3] Petroleum

ether/ethyl acetate = 10:1, yellow solid, 63% yield (120 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.71-7.74 (m, 2H), 7.62-7.64 (m, 3H), 7.30-7.34 (m, 2H), 7.14-7.16 (m, 2H), 6.95 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 139.8, 134.3, 132.3, 129.4, 126.2, 121.0, 119.0, 113.0, 110.8.

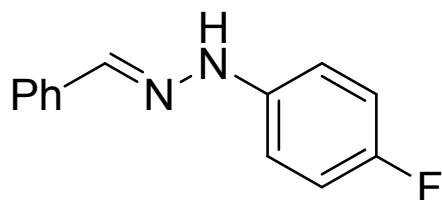


(E)-1-(naphthalen-2-ylmethylene)-2-phenylhydrazine (3ak).^[4] Petroleum ether/ethyl acetate = 15:1, white solid, 52% yield (100 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.81 (d, $J = 8.8$ Hz, 1H), 8.34 (s, 1H), 7.82-7.91 (m, 3H), 7.49-7.64 (m, 3H), 7.32-7.36 (m, 2H), 7.19-7.21 (m, 2H), 6.92 (t, $J = 7.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 136.9, 134.0, 130.6, 130.3, 129.4, 129.0, 128.7, 126.7, 126.3, 125.9, 125.4, 124.4, 120.1, 112.8.

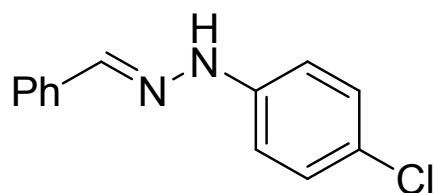


(E)-1-phenyl-2-(3-vinylbenzylidene)hydrazine (3al). Petroleum ether/ethyl acetate = 15:1, white solid, 73% yield (140 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.70 (m, 2H), 7.55 (d, $J = 6.8$ Hz, 1H), 7.27-7.35 (m, 4H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.88 (t, $J = 7.2$ Hz, 1H), 6.75 (dd, $J_1 = 10.8$ Hz, $J_2 = 17.6$ Hz, 1H), 5.81 (dd, $J_1 = 0.8$ Hz, $J_2 = 18.0$ Hz, 1H), 5.30 (dd, $J_1 = 0.8$ Hz, $J_2 = 10.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 137.9, 137.1, 136.6, 135.5, 129.3, 128.8, 126.1, 125.6, 124.0, 120.2, 114.3, 112.8. IR (film) ν/cm^{-1} 3314 (w), 1595 (vs),

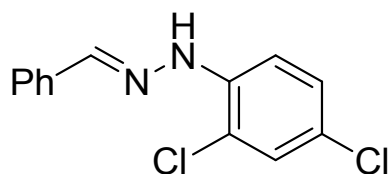
1506 (vs), 1247 (vs), 1131 (vs), 913 (m), 749 (m). MS(ESI, m/z) 223.1 (M + H⁺), 245.1 (M + Na⁺). Anal.calcd for C₁₅H₁₄N₂: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.92; H, 6.23; N, 12.85.



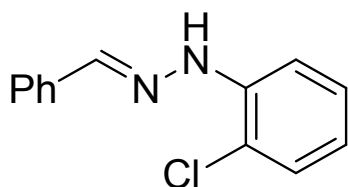
(E)-1-benzylidene-2-(4-fluorophenyl)hydrazine (3ba).^[1] Petroleum ether/ethyl acetate = 15:1, white solid, 72% yield (144 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.65-7.67 (m, 2H), 7.37-7.40 (m, 2H), 7.31 (t, J = 8.8 Hz, 1H), 7.06-7.09 (m, 2H), 7.00 (t, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.3 (d, J = 235.9 Hz), 141.0, 137.5, 135.1, 128.6, 128.5, 126.1, 115.8 (d, J = 22.5 Hz), 113.7 (d, J = 7.1 Hz).



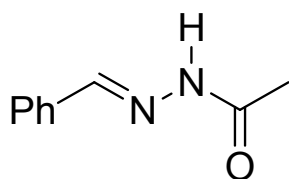
(E)-1-benzylidene-2-(4-chlorophenyl)hydrazine (3bb).^[2] Petroleum ether/ethyl acetate = 20:1, white solid, 74% yield (140 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.66 (m, 3H), 7.35-7.39 (m, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.20-7.24 (m, 2H), 7.03-7.05 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 137.9, 135.0, 129.2, 128.7, 128.6, 126.2, 124.6, 113.8.



(E)-1-benzylidene-2-(2,4-dichlorophenyl)hydrazine (3bc). Petroleum ether/ethyl acetate = 20:1, white solid, 63% yield (130 mg), mp: 127-128 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.68 (m, 3H), 7.59 (s, 1H), 7.32-7.44 (m, 3H), 7.28-7.30 (m, 2H), 6.89 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.1, 138.9, 134.6, 133.1, 130.7, 129.0, 128.7, 126.4, 122.5, 114.2, 112.1. IR (film) ν /cm⁻¹ 3230 (s), 3084 (s), 2960 (m), 758 (w), 690 (w). MS(ESI, *m/z*) 265.0 (M + H⁺), 287.0 (M + Na⁺). Anal. calcd for C₁₃H₁₀Cl₂N₂: C, 58.89; H, 3.80; N, 10.57. Found: C, 58.63; H, 4.03; N, 10.48.

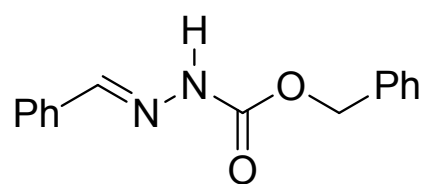


(E)-1-benzylidene-2-(2-chlorophenyl)hydrazine (3bd). Petroleum ether/ethyl acetate = 20:1, white solid, 52% yield (104 mg), mp: 122-123 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.85 (s, 1H), 7.64-7.71 (m, 3H), 7.39-7.43 (m, 2H), 7.32-7.36 (m, 1H), 7.24-7.30 (m, 2H), 6.81 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 139.5, 134.9, 129.0, 128.8, 128.6, 127.9, 126.4, 120.0, 116.8, 114.2. IR (film) ν /cm⁻¹ 3215 (m), 3051 (s), 2884 (s), 745 (w), 690 (m). MS(ESI, *m/z*) 231.1 (M + H⁺), 253.1 (M + Na⁺). Anal. calcd for C₁₃H₁₁ClN₂: C, 67.68; H, 4.81; N, 12.14. Found: C, 67.63; H, 4.63; N, 12.02.

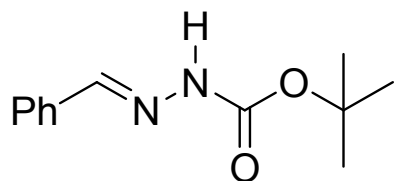


(E)-N'-benzylideneacetohydrazide (3be). Petroleum ether/ethyl acetate =

3:1, yellow oil, 55% yield (110 mg). ^1H NMR (400 MHz, CDCl_3) δ 10.80 (s, 1H), 7.90 (s, 1H), 7.68-7.68 (m, 2H), 7.39 (m, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 144.1, 133.9, 130.0, 128.7, 127.1, 20.3. IR (film) ν/cm^{-1} 3197 (m), 2976 (s), 2864 (w), 1671 (vs), 1607 (s), 760 (w), 690 (m). MS (ESI, m/z) 163.1 ($\text{M} + \text{H}^+$), 185.1 ($\text{M} + \text{Na}^+$). Anal. calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}$: C, 66.65; H, 6.21; N, 17.27. Found: C, 66.63; H, 6.32; N, 17.02.

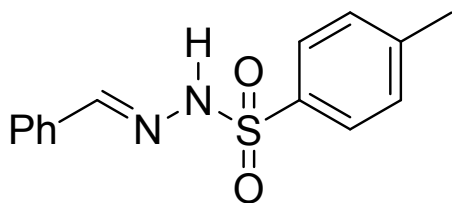


benzyl (E)-2-benzylidenehydrazine-1-carboxylate (3bf).^[5] Petroleum ether/ethyl acetate = 2:1, yellow oil, 63% yield (120 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.86 (s, 1H), 7.67-7.69 (m, 2H), 7.34-7.43 (m, 8H), 5.27 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 135.8, 133.6, 130.0, 128.5, 128.5, 128.3, 128.3, 127.2, 67.4.

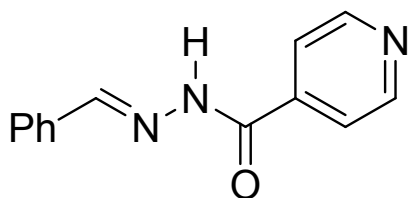


(E)-tert-butyl 2-benzylidenehydrazinecarboxylate (3bg). Petroleum ether/ethyl acetate = 3:1, yellow oil, 68% yield (130 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (s, 1H), 7.67-7.90 (m, 2H), 7.36-7.37 (m, 3H), 1.55 (s, 9H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 152.9, 143.6, 135.1, 129.8, 129.2, 126.9, 79.9, 28.6. IR (film) ν/cm^{-1} 3250 (s), 2978 (w), 1703 (vs), 1529 (s), 1258 (s), 1053 (m), 761 (w), 694 (w). MS(ESI, m/z) 221.1 ($\text{M} + \text{H}^+$), 243.1 ($\text{M} + \text{Na}^+$).

Anal. calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.27; H, 7.59; N, 12.93.

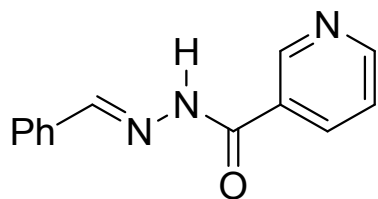


(E)-N'-benzylidene-4-methylbenzenesulfonohydrazide (3bh). Petroleum ether/ethyl acetate = 3:1, white solid, 69% yield (140 mg), mp: 143-145 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.88-7.90 (m, 2H), 7.80 (s, 1H), 7.54-7.56 (m, 2H), 7.27-7.34 (m, 5H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 144.2, 135.2, 133.2, 130.3, 129.7, 128.5, 127.9, 127.3, 21.5. IR (film) ν/cm^{-1} 3226 (s), 2923 (w), 2856 (w), 1371 (m), 1157 (vs), 814 (w), 699 (w). MS (ESI, m/z) 275.1 (M + H⁺), 297.1 (M + Na⁺). Anal. calcd for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21. Found: C, 61.07; H, 5.32; N, 10.03.

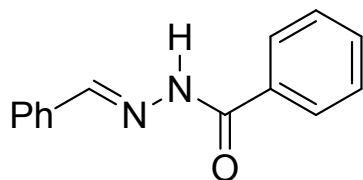


(E)-N'-benzylideneisonicotinohydrazide (3bi). Petroleum ether/ethyl acetate = 1:2, yellow oil, 71% yield (140 mg). 1H NMR (400 MHz, $(CD_3)_2SO$) δ 12.08 (s, 1H), 8.78 (d, $J = 6.0$ Hz, 2H), 8.46 (s, 1H), 7.81-7.82 (m, 2H), 7.73-7.76 (m, 2H), 7.46-7.47 (m, 3H). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 162.2, 150.8, 149.6, 140.9, 134.5, 130.9, 129.4, 127.7, 122.0. IR (film) ν/cm^{-1} 3427 (w), 3200 (m), 2917 (m), 1680 (vs), 1566 (vs), 769 (w), 690 (m). MS (ESI, m/z) 226.1 (M + H⁺), 248.1 (M + Na⁺). Anal. calcd for $C_{13}H_{11}N_3O$: C, 69.32; H,

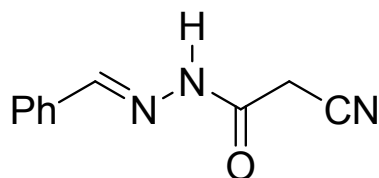
4.92; N, 18.66. Found: C, 69.07; H, 5.13; N, 18.53.



(E)-N'-benzylidenenicotinohydrazide (3bj).^[1] Petroleum ether/ethyl acetate = 1:2, yellow oil, 66% yield (130 mg). ¹H NMR (400 MHz, CDCl₃) δ 10.94-11.95 (m, 1H), 9.18-9.25 (m, 1H), 8.63-8.76 (m, 1H), 8.08-8.47 (m, 2H), 7.19-7.58 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 152.1, 150.6, 148.6, 135.8, 133.3, 130.4, 128.9, 128.4, 127.5, 123.3.



(E)-N'-benzylidenebenzohydrazide (3bk).^[6] Petroleum ether/ethyl acetate = 3:1, yellow oil, 77% yield (150 mg). ¹H NMR (400 MHz, (CD₃)₂SO) δ 11.86 (s, 1H), 8.45 (s, 1H), 7.90-7.92 (m, 2H), 7.72-7.73 (m, 2H), 7.44-7.59 (m, 6H). ¹³C NMR (100 MHz, (CD₃)₂SO) δ 163.6, 148.3, 134.8, 133.9, 132.2, 130.6, 129.3, 129.0, 128.1, 127.6.

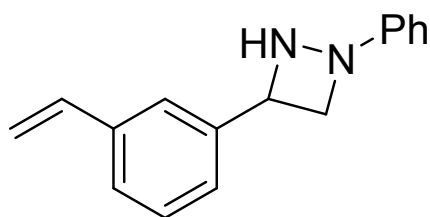


(E)-N'-benzylidene-2-cyanoaceto-hydrazide (3bl). Petroleum ether/ethyl acetate = 1:1, yellow oil, 53% yield (100 mg). ¹H NMR (400 MHz, (CD₃)₂SO) δ 11.80 (s, 1H), 8.00 (s, 1H), 7.68-7.70 (m, 2H), 7.41-7.43 (m, 3H), 4.21 (s, 2H). ¹³C NMR (100 MHz, (CD₃)₂SO) δ 165.3, 144.9, 134.3, 130.6, 129.2, 127.5,

116.5, 24.8. IR (film) ν/cm^{-1} 3215 (s), 2922 (m), 2260 (w), 1672 (vs), 758 (w), 690 (w). MS(ESI, m/z) 188.1 (M + H⁺), 210.1 (M + Na⁺). Anal. calcd for C₁₀H₉N₃O: C, 64.16; H, 4.85; N, 22.45. Found: C, 64.09; H, 5.03; N, 22.23.

4. Synthesis of intermediate 6

To a solution of aryl hydrazines (0.5 mmol) and alkene (1.5 mmol) in MeCN (1.5 mL) was added Methylene Blue (0.01mmol) and 2, 6-Dimethylpyridine (0.5 mmol). The reaction mixture was stirred at room temperature under air atmosphere (open vial) and irradiated by blue LED (7 W) for 3 h. Then it was diluted with water and extracted with ethyl acetate 3 times. Removal of solvent followed by column chromatography afforded intermediate **6** (31 mg, 26%).

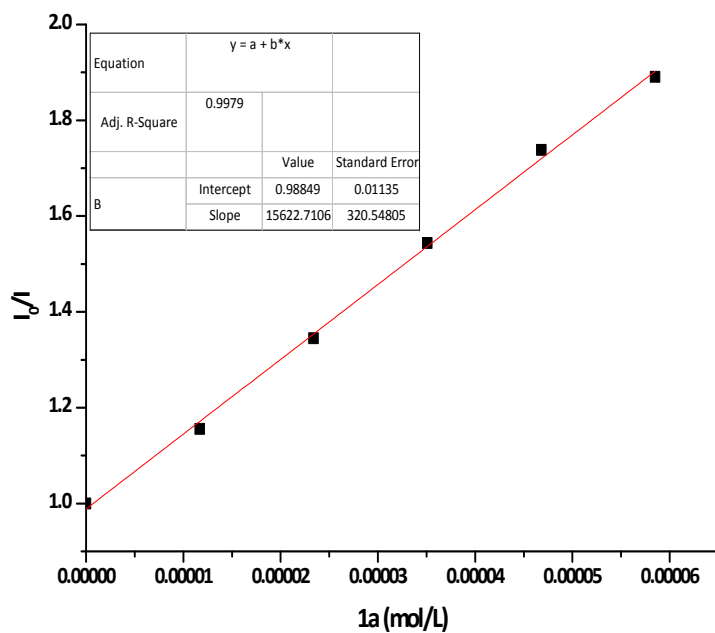
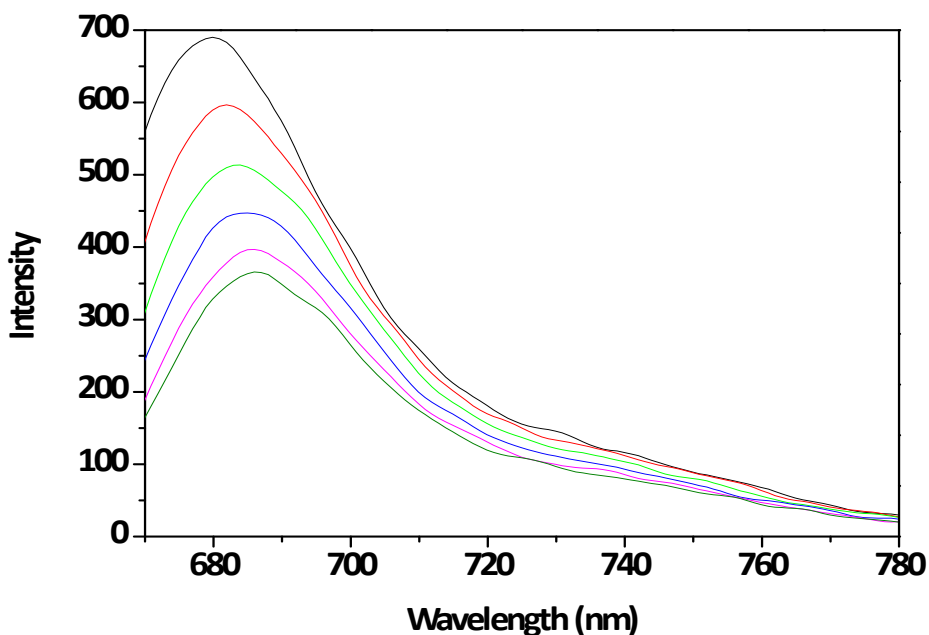


Petroleum ether/ethyl acetate = 25:1, white oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.29-7.40 (m, 4H), 7.20-7.25 (m, 3H), 7.13-7.15 (m, 2H), 6.73 (dd, $J_1= 17.6$ Hz, $J_2= 10.8$ Hz, 1H), 5.76 (dd, $J_1= 17.6$ Hz, $J_2= 0.4$ Hz, 1H), 5.28 (dd, $J_1= 10.8$ Hz, $J_2= 0.8$ Hz, 1H), 5.14-5.17 (m, 1H), 3.19 (dd, $J_1= 14.0$ Hz, $J_2= 7.6$ Hz, 1H), 2.97 (dd, $J_1= 13.6$ Hz, $J_2= 6.0$ Hz, 1H). MS (ESI, m/z) 237.1 (M + H⁺), 259.1 (M + Na⁺).

5. Luminescence quenching by compound 1a

A Varian Cary Eclipse fluorescence spectrometer was used to record the emission intensities. All the solutions were excited at 664 nm and the emission intensity at 685

nm was observed. CH_3CN was degassed with a stream of N_2 for 30 min. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of Methylene Blue in CH_3CN was collected. Then, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 685 nm.



6. References

- (1) Lundgren R J, Stradiotto M. *Angewandte Chemie International Edition*, **2010**, 49(46): 8686-8690.
- (2) Hu J R, Zhang W J, Zheng D G. *Tetrahedron*, **2013**, 69(46): 9865-9869.
- (3) Török B, Sood A, Bag S, et al. *Biochemistry*, **2013**, 52(7): 1137.
- (4) La Regina G, Gatti V, Piscitelli F, et al. *ACS combinatorial science*, **2010**, 13(1): 2-6.
- (5) Gan W, Moon P J, Clavette C, et al. *Organic letters*, **2013**, 15(8): 1890-1893.
- (6) Morales S, Aceña J L, García Ruano J L, et al. *The Journal of Organic Chemistry*, **2016**, 81(20): 10016-10022.

7. Spectroscopic Data for Products

