

Supporting Information

Nickel Dual Photoredox Catalysis for the Synthesis of Aryl Amines

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UV/Vis Data for tpyNi Catalyst

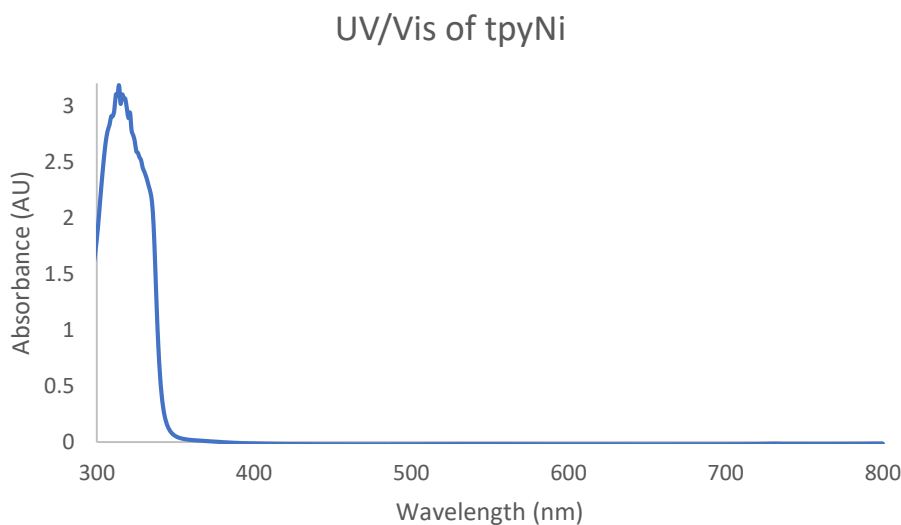


Figure SI-1. UV/Vis spectra of **tpyNi** catalyst used in the dual catalysis system. Spectra collected on a 1 mM solution of **tpyNi** in MeCN. Excitation wavelengths for cross-coupling reactions are between 400-500 nm with a maximum intensity at 480 nm.

Fluorescence Data

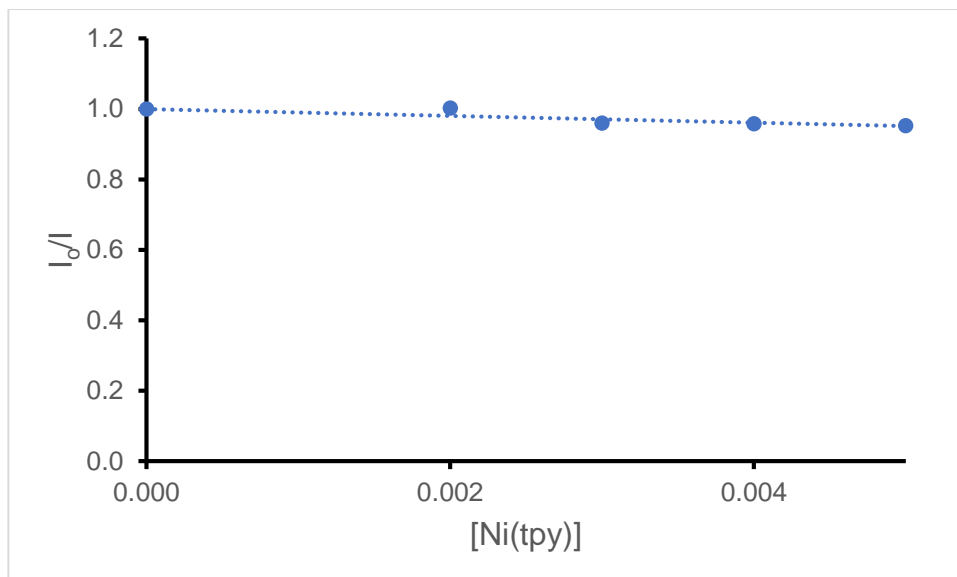


Figure SI-2. Stern-Volmer plot for the fluorescence of $\text{Ru}(\text{phen})_3^{2+}$ in the presence of varying amounts of tpyNi . $[\text{Ru}(\text{phen})_3^{2+}] = 0.005 \text{ mM}$. As evidenced by the straight line with no slope, the Ni catalyst does not quench the $\text{Ru}(\text{phen})_3^{2+}$ photocatalyst.

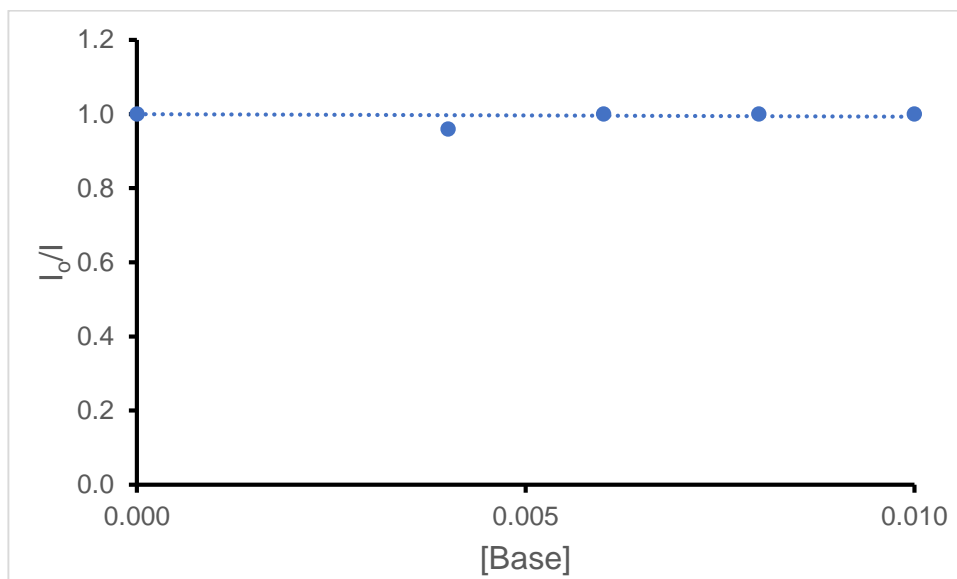


Figure SI-3. Stern-Volmer plot for the fluorescence of $\text{Ru}(\text{phen})_3^{2+}$ in the presence of varying amounts of K_3PO_4 . $[\text{Ru}(\text{phen})_3^{2+}] = 0.005 \text{ mM}$. As evidenced by the straight line with no slope, the K_3PO_4 base does not quench the $\text{Ru}(\text{phen})_3^{2+}$ photocatalyst.

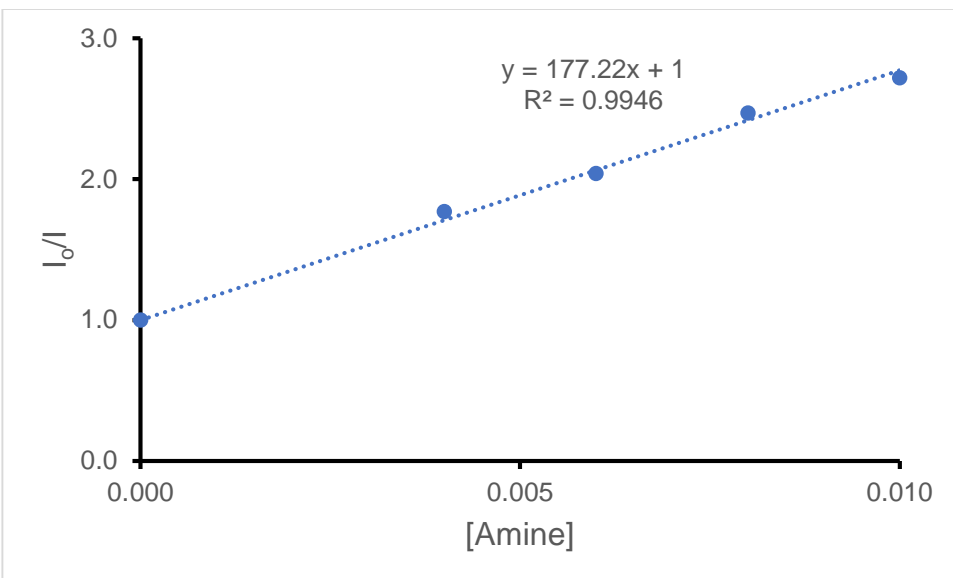


Figure SI-4. Stern-Volmer plot for the fluorescence quenching of Ru(phen)₃²⁺ in the presence of varying amounts of 4-methoxy-aniline. [Ru(phen)₃²⁺] = 0.005 mM. The aniline substrate clearly quenches the Ru(phen)₃²⁺ photocatalyst.

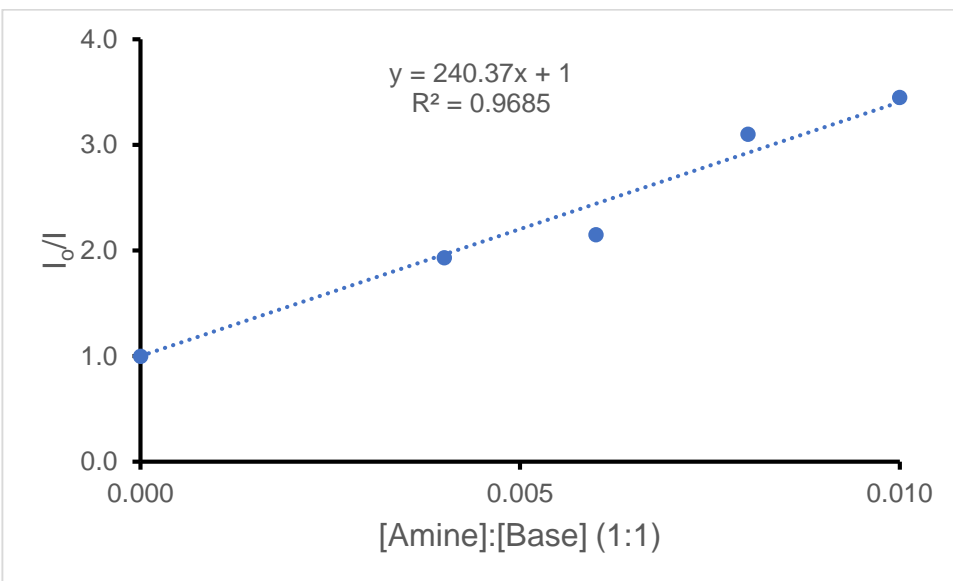


Figure SI-5. Stern-Volmer plot for the fluorescence quenching of Ru(phen)₃²⁺ in the presence of varying amounts of 4-methoxy-aniline and K₃PO₄. [Ru(phen)₃²⁺] = 0.005 mM. Addition of base does not have a considerable effect on the fluorescence quenching of Ru(phen)₃²⁺ by 4-methoxy-aniline.

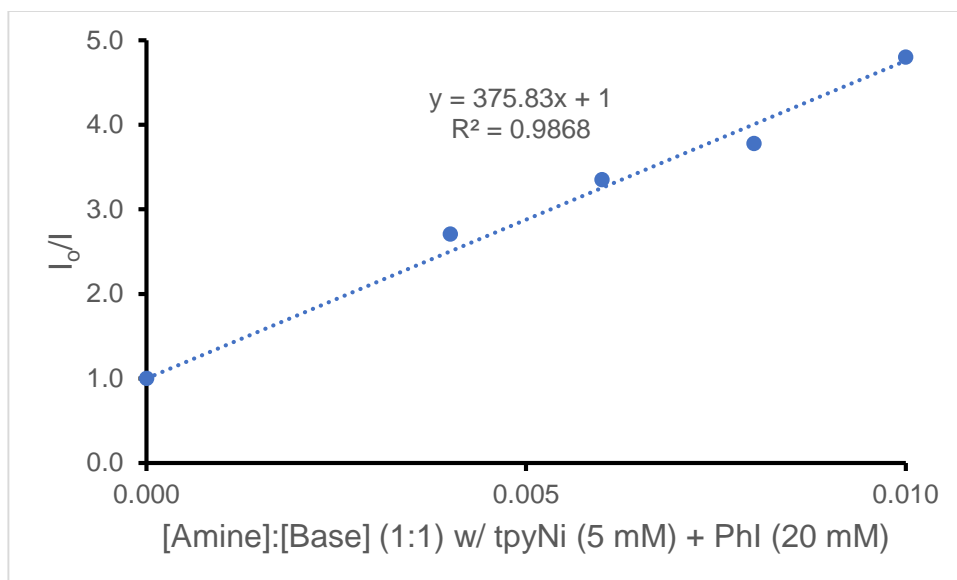
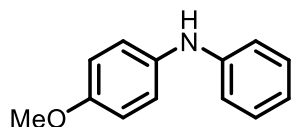
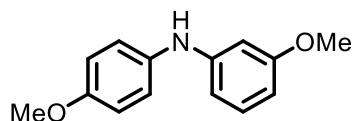


Figure SI-6. Stern-Volmer plot for the fluorescence quenching of $\text{Ru}(\text{phen})_3^{2+}$ in the presence of tpyNi catalyst, iodobenzene, and varying amounts of 4-methoxyaniline and K_3PO_4 . $[\text{Ru}(\text{phen})_3^{2+}] = 0.005 \text{ mM}$. Aniline quenching of the photocatalyst appears to be the dominating quenching mechanism in the entire reaction mixture.

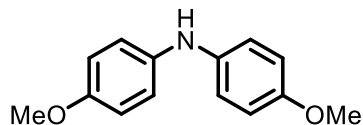
Spectral Data



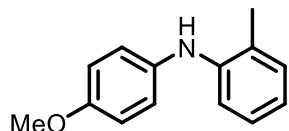
4-methoxy-N-phenylaniline (1): Yield: 0.066 g, 76%. ^1H NMR (300 MHz, CDCl_3) δ : 7.14 (t, 2H), 7.09 (d, 2H), 6.96-6.72 (m, 5H), 5.39 (br s, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 152.8, 145.3, 139.9, 132.2, 128.0, 117.5, 116.4, 114.8, 55.7. Spectra match previous reports.¹



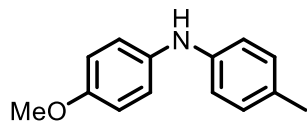
3-methoxy-N-(4-methoxyphenyl)aniline (2): Yield: 0.107 g, 93%. ^1H NMR (300 MHz, CDCl_3) δ : 7.19 (t, 1H), 6.94 (d, 2H), 6.84 (d, 2H), 6.80-6.77 (m, 2H), 6.50 (d, 1H), 5.35 (br s, 1H), 3.69 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 160.1, 155.2, 138.4, 130.8, 129.9, 123.0, 117.8, 113.8, 55.4, 55.3. Spectra match previous reports.²



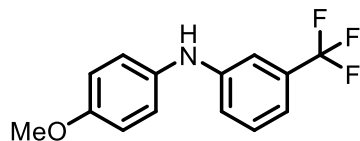
bis(4-methoxyphenyl)amine (3): Yield: 0.105 g, 91%. ^1H NMR (300 MHz, CDCl_3) δ : 7.5 (d, 4H), 6.61 (d, 4H), 6.59 (s, 1H), 3.70 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 159.5, 138.2, 124.4, 114.2, 55.6 ppm. Spectra match previous reports.³



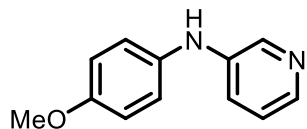
N-(4-methoxyphenyl)-2-methylaniline (4): Yield: 0.035 g, 30%. ^1H NMR (300 MHz, CDCl_3) δ : 7.19 (d, 1H), 7.15-6.97 (m, 4H), 6.95-6.73 (m, 3H), 5.18 (br s, 1H), 3.81 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 161.6, 147.1, 138.9, 129.8, 128.2, 127.4, 124.4, 119.5, 114.2, 55.6, 28.1. Spectra match previous reports.⁴



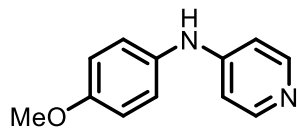
4-methoxy-N-(p-tolyl)aniline (5): Yield: 0.066 g, 62%. ^1H NMR (300 MHz, CDCl_3) δ : 7.81 (d, 2H), 7.20 (d, 2H), 7.04-6.87 (m, 4H), 5.40 (s, 1H), 3.75 (s, 3H), 2.10 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 156.2, 146.0, 134.3, 131.9, 131.5, 123.5, 117.8, 115.5, 55.6, 16.9 ppm. Spectra match previous reports.²



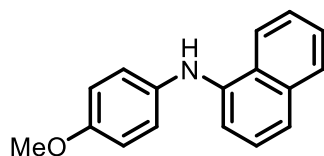
N-(4-methoxyphenyl)-3-(trifluoromethyl)aniline (6): Yield: 0.110 g, 86%. ^1H NMR (300 MHz, CDCl_3) δ : 7.21-7.19 (t, 1H), 7.04-7.00 (m, 5H), 6.84-6.81 (d, 2H), 5.57 (br s, 1H), 3.75 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 156.1, 146.0, 134.3, 131.9, 131.5, 129.8, 123.5, 117.8, 115.6, 115.5, 111.3, 55.6 ppm. Spectra match previous reports.⁵



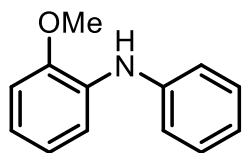
N-(4-methoxyphenyl)pyridin-3-amine (7): Yield: 0.075 g, 75%. ^1H NMR (300 MHz, CDCl_3) δ : 7.81 (d, 1H), 7.60 (d, 1H), 7.23 (dd, 1H), 7.05-7.00 (m, 1H), 7.05 (d, 2H), 6.93 (d, 2H), 5.85 (br s, 1H), 3.80 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): 161.6, 139.4, 137.5, 130.3, 127.7, 127.5, 124.4, 114.2, 55.6 ppm. Spectra match previous reports.²



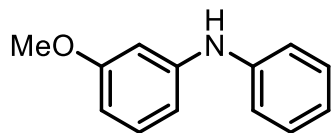
N-(4-methoxyphenyl)pyridin-4-amine (8): Yield: 0.075 g, 75%. ^1H NMR (300 MHz, CDCl_3) δ : 8.45 (d, 2H), 7.92 (d, 1H), 6.80 (m, 1H), 6.70 (d, 2H), 6.50(d, 2H), 5.82 (br s, 1H), 3.72 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 155.7, 144.5, 139.9, 125.3, 120.8, 120.5, 116.4, 114.8, 114.1, 55.4 ppm. Spectra match previous reports.⁶



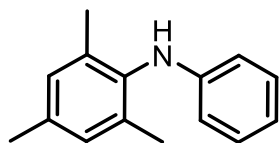
N-(4-methoxyphenyl)naphthalen-1-amine (9): Yield: 0.100 g, 80%. ^1H NMR (300 MHz, CDCl_3) δ : 7.96 (d, 2H), 7.64 (d, 1H), 7.38-7.04 (m, 6H), 7.00 (d, 2H), 5.60 (br s, 1H), 3.68 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 161.6, 147.2, 134.4, 129.3, 128.7, 128.0, 126.9, 126.8, 126.6, 126.4, 125.9, 124.5, 114.3, 55.6 ppm. Spectra match previous reports.⁷



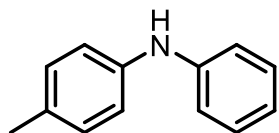
2-methoxy-N-phenylaniline (10): Yield: 0.078g, 78%. ^1H NMR (300 MHz, CDCl_3) δ : 7.35-7.29 (m, 3H), 7.25-7.18 (m, 2H), 6.99 (t, 1H), 6.74-6.69 (m, 3H), 6.35 (br s, 1H), 3.89 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 147.3, 136.1, 130.9, 129.8, 121.0, 120.8, 118.4, 118.2, 115.0, 110.4, 55.4. Spectra match previous reports.⁸



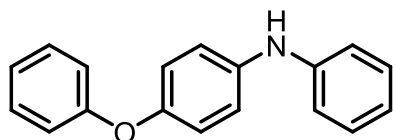
3-methoxy-N-phenylaniline (11): Yield: 0.096 g, 96%. ^1H NMR (300 MHz, CDCl_3) δ : 7.35-7.30 (m, 2H), 7.18 (m, 1H), 7.12-7.06 (m, 2H), (6.92 m, 1H) 6.38 (m, 2H), 6.35 (m, 1H), 6.00 (br s, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 160.7, 147.7, 142.7, 130.1, 129.3, 121.2, 118.0, 107.9, 103.9, 101.1, 55.1. Spectra match previous reports.⁴



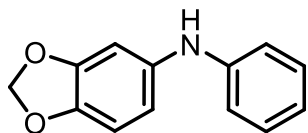
2,4,6-trimethyl-N-phenylaniline (12): Yield: 0.076 g, 72%. ^1H NMR (300 MHz, CDCl_3) δ : 7.18 (t, 2H), 6.90 (s, 2H), 6.84-6.72 (m, 1H), 6.67 (d, 2H), 5.09 (s, 1H), 2.35 (s, 3H), 2.17 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ : 148.6, 137.6, 135.4, 135.3, 130.1, 121.0, 120.7, 22.0, 20.0. Spectra match previous reports.⁴



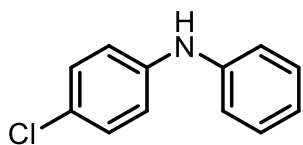
4-methyl-N-phenylaniline (13): Yield: 0.057 g, 62%. ^1H NMR (300 MHz, CDCl_3) δ : 7.19 (t, 2H), 6.90 (d, 2H), 6.60 (m, 4H), 6.52 (t, 1H), 5.30 (br s, 1H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 143.8, 140.2, 131.1, 129.7, 129.1, 127.8, 116.2, 115.3, 20.4. Spectra match previous reports.²



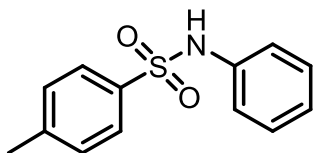
4-phenoxy-N-phenylaniline (14): Yield: 0.114 g, 88%. ^1H NMR (300 MHz, CDCl_3) δ : 7.23-6.86 (m, 14H) 3.51 (br s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ : 158.9, 148.6, 142.6, 130.0, 129.6, 129.5, 122.0, 121.1, 120.9, 117.2, 116.2. Spectra match previous reports.⁹



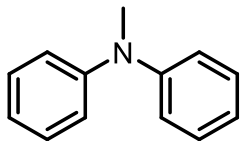
N-phenylbenzo[d][1,3]dioxol-5-amine (15): Yield: 0.077 g, 73%. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 7.57-7.52 (m 2H), 6.96-6.94 (m, 3H), 6.69-6.60 (m, 2H), 6.32-6.30 (m, 1H), 6.00 (s, 2H), 5.89 (s, 1H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 148.2, 141.4, 140.4, 120.9, 116.7, 111.9, 108.6, 101.7, 101.0 ppm. Spectra match previous reports.¹⁰



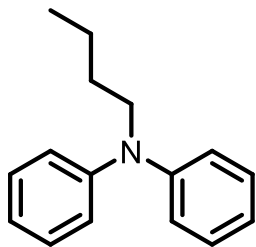
4-chloro-N-phenylaniline (16): Yield: 0.038 g, 35%. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 7.31 (m, 2H), 7.10-7.13 (d, 2H), 6.93-7.01 (d, 2H), 6.68-6.76 (m, 3H), 5.34 (s, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 143.9, 143.6, 129.3, 128.0, 122.1, 118.9, 115.1. Spectra match previous reports.⁴



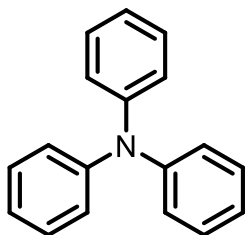
4-methyl-N-phenylbenzenesulfonamide (17): Yield: 0.075 g, 65%. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 7.69 (d, 2H), 7.33-7.28 (m, 4H), 7.09-7.06 (m, 3H), 2.02 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 171.0, 139.8, 139.3, 137.4, 130.2, 127.4, 30.8. Spectra match previous reports.¹¹



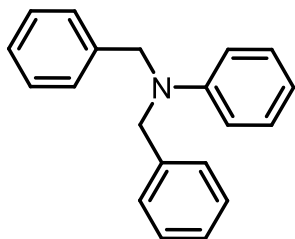
N-methyl-N-phenylaniline (18): Yield: 0.076 g, 83%. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 7.25 (t, 4H), 6.80 (dd, 4H), 6.70 (dd, 2H), 2.90 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ : 149.4, 129.2, 117.3, 112.4, 30.7. Spectra match previous reports.²



N-butyl-N-phenylaniline (19): Yield: 0.075 g, 67%. ^1H NMR (300 MHz, CDCl_3) δ : 7.26-7.01 (m, 10H), 3.04-3.02 (t, 2H), 1.60-1.40 (m, 4H), 0.91-0.88 (t, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 146.7, 128.4, 127.3, 125.6, 41.8, 29.8, 18.4, 12.0. Spectra match previous reports.¹²



Triphenylamine (20): Yield: 0.087 g, 71%. ^1H NMR (300 MHz, CDCl_3) δ : 7.33-6.80 (m, 15H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 143.2, 129.3, 122.1, 118.1, 117.8 ppm. Spectra match previous reports.¹⁴



N,N-dibenzylaniline (21): Yield: 0.070 g, 51%. ^1H NMR (300 MHz, CDCl_3) δ : 7.43-7.37 (m, 12H), 7.34-7.28 (m, 3H), 3.87 (s, 4H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 156.8, 140.4, 128.5, 128.3, 128.2, 126.9, 116.7, 112.4, 53.2. Spectra match previous reports.¹³

References

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