Supporting information for:

**Copper catalyzed synthesis of valuable heterocyclic
compounds using a tandem oxidation process approach**

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General information

^1H and ^{13}C NMR spectra were recorded on a 400 or 100 MHz instrument using CDCl_3 as an internal standard unless otherwise stated. Data are expressed in parts per million relative to the residual solvent. All J values are given in Hz. Radial chromatography was performed with the solvent system delivered by gravity flow using a 1mm layer of silica gel. All microwave reactions were performed using the CEM Focused MicrowaveTM Synthesis system which uses an infrared sensor located below the cavity floor to measure temperature. All synthesized compounds are known and the appropriate literature references have been provided.

General Procedure

1.) 2-Phenylquinoxaline (3a)

2-hydroxyacetophenone (0.068g, 0.50mmol), *o*-phenylenediamine (0.054g, 0.50 mmol), copper acetate monohydrate (10mg, 0.050mmol) and TEMPO (7.8mg, 0.050 mmol) were dissolved in DMF (2 ml) in a microwave tube equipped with a stirrer bar. The mixture was irradiated for 30 minutes at 110°C under open vessel conditions. Water was added to the mixture and the resulting solution was then extracted with dichloromethane and concentrated to produce the crude product, which was

subsequently purified using radial chromatography to produce the title compound as an orange solid (0.097g, 94%) mp = 80 – 81°C.

¹H NMR: 7.50-7.61 (3H, m), 7.72-7.82 (2H, m), 8.15 (2H, m), 8.24 (2H, m), 9.34 (1H, s).

¹³C NMR: 127.5, 129.0, 129.1, 129.5, 129.6, 130.1, 130.2, 136.8, 141.5, 142.3, 143.3, 151.9.

Data consistent with literature values.¹

2.) 2-Methylquinoxaline (3b)

Under microwave irradiation

Synthesized using the procedure for **3a** except using hydroxyacetone (0.037g, 0.50 mmol) and *o*-phenylenediamine (0.054g, 0.50mmol). The crude mixture was purified using radial chromatography to produce the title compound as an orange oil (0.045 g, 63%).

Under room temperature

Hydroxyacetone (0.037g, 0.50mmol), o-phenylenediamine (0.054g, 0.50mmol), copper acetate monohydrate (10mg, 0.050mmol) and TEMPO (7.81mg, 0.050mmol) were dissolved in DMF (2ml) and stirred at room temperature overnight. Water was added to the mixture and the resulting solution was then extracted with dichloromethane and concentrated to produce the crude product, which was subsequently purified using radial chromatography to produce the title compound as orange oil (0.063g, 88%).

¹H NMR: 2.79 (3H, s), 7.70 – 7.78 (2H, m), 8.04 – 8.12 (2H, m), 8.78 (1H, s).

¹³C NMR: 22.8, 128.7, 129.1, 129.3, 130.2, 141.2, 142.2, 146.3, 153.9.

Data consistent with literature values.²

3.) 2,3-Diphenylquinoxaline (3c)

Synthesized using the procedure for **3a** except using benzoin (0.106g, 0.50mmol) and o-phenylenediamine (0.054g, 0.50mmol). The crude mixture was purified using

radial chromatography to produce the title compound as a white solid (0.128g, 91%)
mp = 124°C.

¹H NMR: 7.34 – 7.39 (6H, m), 7.52 – 7.55 (4H, m), 7.80 (2H, m), 8.22 (2H, m).

¹³C NMR: 128.4, 128.9, 129.5, 129.9, 130.0, 139.2, 141.2, 153.5.

Data consistent with literature values.¹

4.) 2-Phenyl-6,7-dimethylquinoxaline (3d)

Synthesized using the procedure for **3a** except using 2-hydroxyacetophenone (0.068 g, 0.50mmol) and 4,5-dimethyl-1,2-phenylenediamine (0.068g, 0.50mmol). The crude mixture was purified using radial chromatography to produce the title compound as an orange solid (0.112g, 96%) mp = 121°C.

¹H NMR: 2.53 (6H, s), 7.48-7.60 (3H, m), 7.90 (2H, m), 8.18 (2H, m), 9.24 (1H, s).

¹³C NMR: 20.3, 20.3, 127.3, 128.1, 128.6, 129.0, 129.8, 137.1, 140.1, 140.5, 140.7, 141.2, 142.2, 151.0.

Data consistent with literature.²

5.) 2,3-Diphenyl-6,7-dimethylquinoxaline (3e)

Synthesized using the procedure for **3a** except using benzoin (0.106g, 0.50mmol) and 4,5-dimethyl-1,2-phenylenediamine (0.068g, 0.50mmol). The crude mixture was purified using radial chromatography to produce the title compound as an orange solid (0.132 g, 85%) mp = 174 – 175°C.

¹H NMR: 2.53, (6H, s), 7.31-7.38 (6H, m), 7.49-7.54 (4H, m), 7.94 (2H, s).

¹³C NMR: 20.3, 128.1, 128.2, 128.5, 129.9, 139.9, 140.6, 140.9, 152.3.

Data consistent with literature.²

6.) 2-Phenyl-benzo[g]quinoxaline (3f)

Synthesized using the procedure for **3a** except using 2-hydroxyacetophenone (0.068 g, 0.50 mmol) and naphthalene-2,3-diamine (0.079 g, 0.50 mmol). The crude mixture was purified using radial chromatography to produce the title compound as an orange solid (0.092 g, 69%) mp = 162°C.

¹H NMR: 7.49-7.62 (5H, m), 8.04-8.11 (2H, m), 8.25 (2H, d, *J* = 7.0 Hz), 8.65 (s, 1H), 8.68 (s, 1H), 9.35 (s, 1H)

¹³C NMR: 126.6, 126.8, 127.5, 127.6, 127.9, 128.4, 128.5, 128.8, 129.1, 133.6, 134.1, 136.7, 138.1, 138.7, 144.4, 151.7.

Data consistent with literature.³

7.) 2,3-Diphenyl-benzo[*g*]quinoxaline (3g)

Synthesized using the procedure for **3a** except using benzoin (0.106g, 0.50mmol) and 2,3-naphthalenediamine (0.079g, 0.50mmol). The crude mixture was purified using radial chromatography to produce the title compound as an orange solid (0.098g, 59%), mp 183 – 185°C

¹H NMR: 7.28 – 7.32 (6H, m), 7.40 – 7.45 (6H, m), 7.96 (2H, m), 8.60 (2H, s)

¹³C NMR: 126.7, 127.5, 128.2, 128.5, 129.0, 129.8, 134.0, 137.9, 139.2, 154.1.

Data consistent with literature.⁴

8.) 2,3-Dihydro-5,6-diphenylpyrazine (3h)

Synthesized using the procedure for **3a** except using benzoin (0.106g, 0.50mmol) and ethylenediamine (0.030g, 0.50mmol). The crude mixture was purified using radial chromatography to produce the title compound as an orange solid (0.108g, 92%), mp 163 - 165°C

¹H NMR (400 MHz, DMSO): 3.64 (4H, s), 7.33 – 7.42 (10H, m).

¹³C NMR (100 MHz, DMSO): 46.2, 128.7, 128.9, 130.9, 138.6, 160.3.

Data consistent with literature.²

9.) 2,3-Diphenylpyrazine (3i)

Benzoin (0.054g, 0.50mmol), ethylenediamine (0.030g, 0.50mmol), copper acetate monohydrate (10mg, 0.05mmol), TEMPO (7.8mg, 0.05mmol) and sulfur (0.032g, 1 mmol) were added to 2ml DMF in a microwave tube equipped with a stirrer bar. The mixture^{*} was irradiated for 30 minutes at 110°C under open vessel conditions. Water was added to the mixture and the resulting solution was then extracted with dichloromethane and concentrated to produce the crude product, which was subsequently purified using radial chromatography to produce the title compound as an orange solid (0.108g, 94%) mp = 123 – 125°C.

¹H NMR (400 MHz, DMSO): 7.36 – 7.40 (6H, m), 7.43 – 7.46 (4H, m), 8.79 (2H, s).

¹³C NMR (100 MHz, DMSO): 129.3, 129.6, 130.4, 139.4, 143.4, 152.8.

Data consistent with literature.²

^{*} The phrase “mixture” is left undefined as elemental sulfur displays limited solubility in dimethylformamide. Nevertheless, under these conditions excellent yields were observed.

References

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