Supporting Information (spectra copies) for

A mild and convenient protocol for the synthesis of quinoxalin-2(1H)-ones and benzimidazoles

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General information

For product purification by flash column chromatography, silica gel (200~300 mesh) and petroleum ether (bp. 60~90 °C) are used. All solvents were purified and dried by standard techniques. All experiments were conducted in open flask at room temperature, unless otherwise specified. All organic extracts were dried over Na₂SO₄. ¹H NMR and ¹³C NMR spectra were taken on Bruker AM-500 spectrometer with TMS as an internal standard and CDCl3 as solvent.

N-protected-o-phenylenediamines 1^1 were prepared according to literature procedures. The rest of chemicals were purchased from Beijing InnoChem Science&Technology Co., Ltd.

General Procedure 1: The Synthesis of N-protected-o-phenylenediamines¹



A 200 mL round-bottom flask equipped with stir bar was charged with Ophenylenediamine (15.0 mmol, 1.2 eq.) in DMF (50.0 mL) was added K_2CO_3 (30.0 mmol, 2.0 eq.) and benzyl bromide/iodomethane (10.0 mmol, 1.0 eq.) at room temperature for 8 h. The reaction mixture was extracted with ethyl acetate (100 mL), then the reaction solution was washed with water and saturated NaCl, dried over anhydrous Na_2SO_4 , the combined organic phases were filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography on 200-300 mesh silica gel.

General Procedure 2: The Synthesis of benzimidazoles/quinoxalin-2(1H)-ones and benzimidazoles



N-protected-*o*-phenylenediamine (1.0 eq., 0.6 mmol), α -hydroxy ketone/ α -ketoester/ α -ketoacid (1.0 eq., 0.6 mmol), CF₃COOH (1 eq., 0.6 mmol) with MeCN (2.0 mL) and magnetic stirrer were taken in open flask at room for 2 h. The reaction mixture was extracted with ethyl acetate (15.0 mL), the combined organic phases were dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by silica gel column chromatography on 200-300 mesh silica gel afforded benzimidazoles/quinoxalines.

General Procedure 3: Validation experiments

To investigate the rationality of the proposed mechanism, we employed GC-MS to analyze the reaction of *N*-benzyl-*o*-phenylenediamine (1a) with acetoin (2a). The results indicate that acetic acid may be derived from the oxidation of acetaldehyde during the reaction. Subsequently, we also investigated the reaction of *N*-benzyl-*o*phenylenediamine (1a) with 1-hydroxychlorohexyl phenyl ketone (2c), which resulted in the formation of cyclohexanone. These two experiments support our hypothesis regarding the reaction mechanism. Furthermore, in the reaction of *N*-benzyl-*o*phenylenediamine (1a) with ethyl 3-methyl-2-oxobutanoate (4a), we detected the formation of ethyl trifluoroacetate, suggesting that ethanol was generated during the process.

GC–MS analyses were performed using a 7000D GC/TQ instrument (Aglient). The reaction mixture were analyzed on a DB-FFAP column (60 m x 250 μ m x 0.25 μ m). Helium at a constant flow rate of 1.2 mL/min was used as carrier gas. The injector was held at 250°C. The temperature rise program of the gas chromatography parameter column incubator was as follows: the oven temperature was held at 50°C for 2 min, then programmed to 80°C for 2 min, and finally kept at 230°C for 3 min. The mass spectrum parameters were set as follows: EI source, ionization energy 70 eV, ion source temperature 230°C, and scanning range m/z 40–550. Compound analysis was carried out through the NIST database.



GC-MS analysis reports







S5



Characterization Data for substrates and products



*N*¹-benzylbenzene-1,2-diamine (1a)². ¹H NMR (500 MHz, CDCl₃): $\delta = 7.39 - 7.33$ (m, 4H), 7.29 - 7.28 (m, 1H), 6.81 - 6.78 (m, 1H), 6.71 - 6.66 (m, 3H), 4.30 (s, 2H), 3.67 (br, 1H), 3.32 (br, 2H). 13C NMR (125 MHz, CDCl₃): $\delta = 139.4$, 137.7, 134.1, 128.6 (2C), 127.8 (2C), 127.2, 120.7, 118.8, 116.5, 111.9.



 N^{1} -benzyl-4,5-dimethylbenzene-1,2-diamine (1b). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.39$ (d, J = 6.0 Hz, 2H), 7.34 (t, J = 5.5 Hz, 2H), 7.28 (d, J = 5.5 Hz, 1H), 6.53 (s, 1H), 6.49 (s, 1H), 4.27 (s, 2H), 3.29 (br, 3H), 2.14 (s, 3H), 2.13 (s, 3H). 13C NMR (125 MHz, CDCl₃): $\delta = 139.8$, 135.6, 132.0, 128.5, 128.1, 127.8, 127.1, 126.4, 118.4, 114.1, 77.3, 77.0, 76.8, 49.0, 19.3, 18.8.



 N^{1} -benzyl-4,5-difluorobenzene-1,2-diamine (1c). 1H NMR (500 MHz, CDCl₃): $\delta = 7.34$ (s, 4H), 7.29 (d, J = 2.5 Hz, 1H), 6.49 (t, J = 9.0 Hz, 1H), 6.42 (dd, J = 11.5 Hz, 7.5 Hz, 1H), 4.19 (s, 2H), 3.60 (br, 1H), 3.23 (br, 2H). 13C NMR (125 MHz, CDCl₃): $\delta = 145.4$ (d, J = 11.3 Hz, 1C), 141.9 (J = 11.3 Hz, 1C), 138.5, 133.9 (d, J = 6.3 Hz, 1C), 129.9 (d, J = 2.5 Hz, 1C), 128.7 (2C), 127.6, 127.5 (2C), 105.3 (d, J = 20.0 Hz, 1C), 101.2 (d, J = 21.3 Hz, 1C), 48.8.



1d

N^{*I*}-methylbenzene-1,2-diamine (1d)³. ¹H NMR (500 MHz, CDCl₃): $\delta = 6.87 - 6.84$ (m, 1H), 6.72 - 6.65 (m, 3H), 3.32 (br, 3H), 2.86 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 138.9, 134.02, 120.9, 118.4, 116.3, 110.9, 77.3, 77.0, 76.7, 30.9.$



*N*¹,4,5-trimethylbenzene-1,2-diamine (1e). ¹H NMR (500 MHz, CDCl₃): $\delta = 6.49$ (s, 1H), 6.44 (s, 1H), 3.19 (br, 3H), 2.81 (s, 3H), 2.18 (s, 3H), 2.12 (s, 3H).¹³C NMR (125 MHz, CDCl₃): $\delta = 136.7$, 131.7, 128.0, 125.8, 118.2, 113.1, 77.3, 77.0, 76.8, 31.2, 19.2, 18.7.



4,5-difluoro-*N*^{*I*}-methylbenzene-1,2-diamine (1f). ¹H NMR (500 MHz, CDCl₃): $\delta = 6.53$ (dd, J = 11.0 Hz, 8.0 Hz, 1H), 6.42 (dd, J = 12.0 Hz, 7.5 Hz, 1H), 3.23 (br, 3H), 2.81 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 145.7$ (d, J = 11.3 Hz, 1C), 141.7 (d, J = 12.5 Hz, 1C), 135.4 (d, J = 6.3 Hz, 1C), 129.6 (d, J = 5.0 Hz, 1C), 105.2 (d, J = 20.0 Hz, 1C), 100.2 (d, J = 22.5 Hz, 1C), 31.2.



N^{*I*}-phenylbenzene-1,2-diamine (1g)⁴. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.23 - 7.18$ (m, 2H), 7.12 - 7.11 (m,1H), 7.02 - 7.00 (m, 1H), 6.83 - 6.72 (m, 5H). ¹³C NMR (125

MHz, CDCl₃) δ = 145.3, 141.9, 129.3 (2C), 128.5, 125.7, 124.9, 119.3, 119.1, 116.1, 115.2 (2C).



1-benzyl-2-methyl-1H-benzo[d]imidazole (3a)⁵. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.71(d, J = 7.5 \text{ Hz}, 1\text{H}), 7.21(s, 4\text{H}), 7.15(s, 2\text{H}), 6.97 (d, J = 5.0 \text{ Hz}, 2\text{H}), 5.16 (s, 2\text{H}), 2.47 (s, 3\text{H}).$ ¹³C NMR (125 MHz, CDCl₃): $\delta = 151.6, 142.2, 135.5, 135.1, 128.7(2\text{C}), 127.6, 125.9(2\text{C}), 122.0, 121.7, 118.7, 109.1, 46.6, 13.6.$



1-benzyl-2,5,6-trimethyl-1H-benzo[d]imidazole (3b)^{5. 1}H NMR (500 MHz, CDCl₃): $\delta = 7.47(s, 1H), 7.23-7.22(m, 3H), 6.98-6.94 (m, 3H), 5.14 (s, 2H), 2.45(s, 3H), 2.32 (s, 3H), 2.28 (s, 3H).$ ¹³C NMR (125 MHz, CDCl₃): $\delta = 150.6, 140.9, 135.9, 133.7, 130.8, 130.3, 128.6(2C), 127.4, 125.8(2C), 118.9, 109.3, 46.5, 20.2, 19.9, 13.5.$



1-benzyl-2-ethyl-5,6-difluoro-1H-benzo[d]imidazole (3c). ¹H NMR (500 MHz, CDCl₃): δ = 7.34 - 7.31 (m, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.89 (d, *J* = 6.0 Hz, 2H), 6.85 - 6.82 (m, 1H), 5.11 (s, 2H), 2.41 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 153.3, 148.3 (dd, *J* = 22.5 Hz, 12.5 Hz, 1C), 146.4 (dd, *J* = 18.8 Hz, 15.0 Hz, 1C), 137.5 (d, *J* = 10.0 Hz, 1C), 134.8, 130.4 (d, *J* = 11.2 Hz, 1C), 128.9 (2C), 127.9, 125.9 (2C), 106.1 (d, *J* = 18.8 Hz, 1C), 97.4 (d, *J* = 22.5 Hz, 1C), 47.2, 13.7.



1-benzyl-2-ethyl-1H-benzo[d]imidazole (3d)⁶. ¹H NMR (500 MHz, CDCl₃): δ = 7.66 (d, *J* = 10.0 Hz, 1H), 7.09 (s, 4H), 7.02 (s, 2H), 6.85 (d, *J* = 5.0 Hz, 2H), 5.06 (s, 2H), 2.65 (q, *J* = 15.0 Hz, 5.0 Hz, 2H), 1.26 (t, *J* = 5.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 156.0, 142.3, 135.7, 135.2, 128.6 (2C), 127.5, 125.8 (2C), 122.0, 121.6, 118.9, 46.4, 20.6, 11.4.



1-benzyl-2-ethyl-5,6-dimethyl-1H-benzo[d]imidazole (3e): ¹H NMR (500 MHz, CDCl₃) δ = 7.40 (s, 1H), 7.07 - 7.05 (m, 3H), 6.83 - 6.79 (m, 3H), 4.99 (s, 2H), 2.59 (q, J = 7.5 Hz, 15.0 Hz, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 1.21 (t, J = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 155.0, 140.7, 135.9, 133.6, 130.7 130.1, 128.4 (2C), 127.2, 125.6 (2C), 118.9, 109.3, 46.1, 20.1, 20.0, 19.8, 11.3.



1-benzyl-2-ethyl-5,6-difluoro-1H-benzo[d]imidazole (3f). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.38$ (t, J = 9.5 Hz, 1H), 7.17 - 7.16 (m, 1H), 6.89 - 6.88 (m, 1H), 6.82 (t, J = 8.0 Hz, 1H), 5.13 (s, 2H), 2.72 - 2.70 (m, 2H), 1.27 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 157.8$, 148.3 (dd, J = 25.0 Hz, 15.0 Hz, 1C), 146.4 (dd, J = 23.8 Hz, 15.0 Hz, 1C), 137.5 (d, J = 10.0 Hz, 1C), 135.0, 130.5 (d, J = 11.3 Hz, 1C), 128.9 (2C), 127.9, 125.8 (2C), 106.3 (d, J = 20.0 Hz, 1C), 97.4 (d, J = 22.5 Hz, 1C), 46.9, 20.8, 11.3.

1-benzyl-2-phenyl-1H-benzo[d]imidazole (3g)⁷. ¹H NMR (500 MHz, CDCl₃): δ = 7.87 (d, *J* = 7.5 Hz, 1H), 7.69(d, *J* = 5.5 Hz, 2H), 7.46 (s, 3H), 7.32 (d, *J* = 7.0 Hz, 4H), 7.24 - 7.21 (m, 2H), 7.10 (d, *J* = 5.5 Hz, 2H), 5.45 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 154.1, 143.2, 136.4, 136.0, 130.1, 129.9 (2C), 129.1(d, *J* = 26.3 Hz, 2C), 128.7 (2C), 127.7, 125.9 (2C), 123.0, 126.6, 120, 110.5, 48.3.



1-benzyl-5,6-dimethyl-2-phenyl-1H-benzo[d]imidazole (3h)¹. ¹H NMR (500 MHz, CDCl₃): δ = 7.66 - 7.62 (m, 3H), 7.42 (s, 3H), 7.32 - 7.28 (m, 3H), 7.10 - 70.8 (m, 2H), 6.97 (s, 1H), 5.39 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 153.3, 141.7, 136.7, 134.6, 132.2, 131.5, 130.3, 129.6, 129.1 (2C), 129.0 (2C), 128.6 (2C), 127.6 (2C), 125.8, 120.0, 110.5.



1-benzyl-5,6-difluoro-2-phenyl-1H-benzo[d]imidazole (3i)^{1.} ¹H NMR (500 MHz, CDCl₃): $\delta = 7.67 - 7.65$ (m, 2H), 7.61 (t, J = 9.5 Hz, 1H), 7.47 -7.46 (m, 2H), 7.35 - 7.34 (m, 3H), 7.08 -7.07 (m, 2H), 6.95 (t, J = 7.0 Hz, 1H), 5.40 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 155.6$, 149.1 (t, J = 15.0 Hz, 1C), 147.2 (t, J = 15.0 Hz 1C), 138.3 (d, J = 10.0 Hz, 1C), 135.5, 131.3 (d, J = 10.0 Hz, 1C), 130.2, 129.5, 129.2 (2C), 129.1 (2C), 128.9 (2C), 128.1, 125.9 (2C), 107.2 (d, J = 18.8 Hz, 1C), 98.5 (d, J = 23.8 Hz, 1C), 48.7.

1,2-dimethyl-1H-benzo[d]imidazole (3j)^{7. 1}H NMR (500 MHz, CDCl₃): δ = 7.66 (dd, J = 5.0 Hz, 2.0 Hz, 1H), 7.20 (d, J = 2.5 Hz, 1H), 3.58 (s, 3H), 2.51 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 151.6, 142.3, 135.5, 121.7, 121.5, 118.6, 108.6, 29.5, 13.5.



1,2,5,6-tetramethyl-1H-benzo[d]imidazole (3k): ¹H NMR (500 MHz, CDCl₃): δ = 7.39 (s, 1H), 6.91 (s, 1H), 3.45 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 150.4, 140.5, 133.8, 130.3, 129.8, 118.5, 108.8, 29.1,

5,6-difluoro-1,2-dimethyl-1H-benzo[d]imidazole (3l). ¹H NMR (500 MHz, CDCl₃) $\delta = 7.38$ (dd, J = 10.5 Hz, 7.0 Hz, 1H), 6.97 (dd, J = 10.0 Hz, 7.0 Hz, 1H), 3.62 (s, 3H), 2.53 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) $\delta = 153.2$, 148.1 (dd, 23.7 Hz, 15.0 Hz, 1C), 146.2 (dd, 21.2 Hz, 15.0 Hz, 1C), 137.1 (d, 11.2 Hz, 1C), 130.7 (d, 11.2 Hz, 1C), 105.7 (d, 20.0 Hz, 1C), 96.7 (d, 22.5 Hz, 1C), 29.7.



2-ethyl-1-methyl-1H-benzo[d]imidazole (3m)⁸. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.57$ (d, J = 6.0 Hz, 1H), 7.05-6.99 (m, 3H), 3.33 (s, 3H), 2.60 (q, J = 15.0 Hz, 7.5 Hz, 2H), 1.25 (t, J = 8.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 155.7$, 141.8, 135.2, 121.4, 121.1, 118.3, 108.4 (2C), 28.8, 20.2, 11.0.



2-ethyl-1,5,6-trimethyl-1H-benzo[d]imidazole (3n). ¹H NMR (500 MHz, CDCl₃): δ = 7.45 (s, 1H), 6.93 (s, 1H), 3.47 (s, 3H), 2.73 (q, *J* = 15.0 Hz, 7.5 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.37 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 154.8, 140.5, 133.9, 130.2, 129.7, 118.7, 108.7, 28.9, 20.2, 20.0, 19.7, 11.2.



2-ethyl-5,6-difluoro-1-methyl-1H-benzo[d]imidazole (30). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.30$ (dd, J = 10.5 Hz, 7.5 Hz, 1H), 6.85 (dd, J = 10.0 Hz, 7.5 Hz, 1H), 3.50 (s, 3H), 2.72 (q, J = 15.0 Hz, 7.5 Hz, 2H), 1.30 (t, J = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 157.6$, 148.0 (dd, J = 30 Hz, 15.0 Hz, 1C), 146.1 (dd, J = 27.5 Hz, 15.0 Hz, 1C), 137.1 (d, J = 10.0 Hz, 1C), 130.8 (d, J = 11.3 Hz, 1C), 105.9 (d, J = 20.0 Hz, 1C), 96.6 (d, J = 23.8 Hz, 1C), 29.4, 20.5, 11.0.



1-methyl-2-phenyl-1H-benzo[d]imidazole (3p)⁹. ¹H NMR (500 MHz, CDCl₃): δ = 7.67 (d, J = 6.5 Hz, 1H), 7.54 (d, J = 5.0 Hz, 2H), 7.28 (s, 3H), 7.11 (s, 3H), 3.54 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 153.3, 142.4, 136.2, 129.7, 129.4, 129.0 (2C), 128.3 (2C), 122.4, 122.1, 119.3, 109.4, 31.2.



1,5,6-trimethyl-2-phenyl-1H-benzo[d]imidazole (3q)^{1. 1}H NMR (500 MHz, CDCl₃): $\delta = 7.74$ (d, J = 6.5 Hz, 2H), 7.57 (s, 1H), 7.50 (d, J = 7.0 Hz, 3H), 7.15 (s, 1H), 3.81 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 152.9$, 141.5,

135.2, 131.9, 131.2, 130.5, 129.4, 129.3 (2C), 128.6 (2C), 119.8, 109.8, 31.6, 20.6, 20.3.



5,6-difluoro-1-methyl-2-phenyl-1H-benzo[d]imidazole (3r). ¹H NMR (500 MHz, CDCl₃): δ = 7.73 (s, 2H), 7.60 - 7.54 (m, 4H), 7.18 -7.17 (m, 1H), 3.83 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 155.2, 149.1 (dd, *J* = 36.3 Hz, 15.0 Hz, 1C), 147.1 (dd, *J* = 33.8 Hz, 16.3 Hz, 1C), 138.0 (d, *J* = 10.0 Hz, 1C), 131.9 (d, *J* = 11.3 Hz, 1C), 130.0, 129.7, 129.3 (2C), 128.8 (2C), 107.1 (d, *J* = 20.0 Hz, 1C), 97.6 (d, *J* = 22.5 Hz, 1C), 23.0.



2-methyl-1-phenyl-1H-benzo[d]imidazole (3s)¹⁰. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.75$ (d, J = 8.0 Hz, 1H), 7.57-7.48 (m, 3H), 7.35 (d, J = 7.5 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 151.5$, 142.6, 136.4, 136.1, 129.9 (2C), 128.8, 127.2 (2C), 122.6, 122.4, 119.0, 109.9, 14.4.



2-ethyl-1-phenyl-1H-benzo[d]imidazole (3t)¹¹. ¹H NMR (500 MHz, CDCl₃): δ = 7.79 (d, *J* = 8.0 Hz, 1H), 7.58 - 7.50 (m, 3H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 2.80 (q, *J* = 15.0 Hz, 7.5 Hz, 2H), 1.35 (t, *J* = 7.5 Hz, 3H). ¹³CNMR (125 MHz, CDCl₃): δ = 156.2, 142.5, 136.5, 136.0, 129.8 (2C), 128.8, 127.2 (2C), 122.5, 122.2, 119.0, 109.8, 21.2, 12.0.



1,2-diphenyl-1H-benzo[d]imidazole (3u)¹². ¹HNMR (500 MHz, CDCl₃): δ = 7.89 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 7.0 Hz, 2H), 7.44 (d, J = 7.0 Hz, 3H), 7.30 - 7.22 (m, 8H). ¹³CNMR (125 MHz, CDCl₃): δ = 152.2, 142.9, 137.1, 136.8, 129.7 (d, J = 13.8 Hz) (2C), 129.3 (2C), 128.4, 128.1 (2C), 127.2 (2C), 123.2, 122.8, 119.7, 110.3



1-benzyl-3-isopropylquinoxalin-2(1H)-one (5a). ¹HNMR (500 MHz, CDCl₃): $\delta = 7.85$ (d, J = 7.0 Hz, 1H), 7.37 (t, J = 6.5 Hz, 2H), 7.31 - 7.21 (m, 7H), 5.50 (s, 2H), 3.72 - 3.67 (m, 1H), 1.36 (s, 3H), 1.35 (s, 3H). ¹³CNMR (125 MHz, CDCl₃): $\delta = 165.1$, 154.5, 135.4, 133.0, 132.3, 129.9, 129.4, 128.9 (2C), 127.6, 126.8 (2C), 123.4, 114.2, 45.8, 31.2, 20.2 (2C).



1-benzyl-3-isopropyl-6,7-dimethylquinoxalin-2(1H)-one (5b). ¹HNMR (500 MHz, CDCl₃): δ = 7.62 (s, 1H), 7.30 (d, *J* = 6.5 Hz, 2H), 7.26 - 7.22 (m, 4H), 6.99 (s, 1H), 5.47 (s, 2H), 3.69 - 3.64 (m, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H). ¹³CNMR (125 MHz, CDCl₃): δ = 163.9, 154.6, 139.0, 135.7, 132.3, 131.4, 130.3, 130.0, 128.8 (2C), 127.5, 126.8 (2C), 114.7, 45.7, 31.0, 20.5, 20.3 (2C), 19.0.



1-benzyl-6,7-difluoro-3-isopropylquinoxalin-2(1H)-one (5c). ¹HNMR (500 MHz, CDCl₃): δ = 7.58 - 7.55 (m, 1H), 7.26 - 7.17 (m, 3H), 7.14 - 7.12 (m, 2H), 6.92 (dd, *J* = 11.0 Hz, 7.0 Hz, 1H), 5.34 (s, 2H), 3.60 - 3.55 (m, 1H), 1.25 (s, 3H), 1.24 (s, 3H). ¹³CNMR (125 MHz, CDCl₃): δ = 165.6, 154.1, 151.8 (d, *J* = 2.5 Hz, 1C), 129.1 (2C), 128.0, 126.8 (2C), 117.5 (d, *J* = 17.5 Hz, 1C), 102.9 (d, *J* = 22.5 Hz, 1C), 46.4, 31.3, 20.1 (2C).



1-benzyl-3-propylquinoxalin-2(1H)-one (5d)¹⁶. ¹H NMR (500 MHz, CDCl₃): δ = 7.84 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.31 - 7.23 (m, 7H), 5.50 (s, 2H), 2.99 (t, J = 7.0 Hz, 2H), 1.90 - 1.85 (m, 2H), 1.07(t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 161.3, 155.0, 135.3, 133.0, 132.4, 129.7 (2C), 129.5, 128.9, 127.6, 126.8 (2C), 123.5, 114.3, 45.8, 36.2, 20.2, 14.1.



1-benzyl-6,7-dimethyl-3-propylquinoxalin-2(1H)-one (5e). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.59$ (s, 1H), 7.29 (d, J = 5.5 Hz, 2H), 7.23 (s, 3H), 6.99 (s, 1H), 5.45 (s, 2H), 2.95 - 2.94 (m, 2H), 2.29 (s, 3H), 2.28 (s, 3H), 1.86 - 1.85 (m, 2H), 1.06 (t, J = 6.5 Hz, 3H). ¹³C NMR (125MHz, CDCl₃): $\delta = 159.9$, 155.0, 139.0, 135.6, 132.4, 131.3, 130.4, 129.8, 128.8 (2C), 127.5, 126.8 (2C), 114.5, 45.6, 36.1, 20.4, 20.2, 19.0, 14.0.



1-benzyl-6,7-difluoro-3-propylquinoxalin-2(1H)-one (5f). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.57 - 7.53$ (m, 1H), 7.25 - 7.18 (m, 3H), 7.14 - 7.13 (m, 2H), 6.95 - 6.91 (m, 1H), 5.34 (s, 2H), 2.88 (t, J = 7.0 Hz, 2H), 1.79 - 1.75 (m, 2H), 0.99 (t, J = 6.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 161.8$ (d, J = 2.5 Hz, 1C), 154.6, 151.8 (d, J = 13.8 Hz, 1C), 147.6 (d, J = 13.8 Hz, 1C), 134.5, 129.5 (d, J = 10.0 Hz, 1C), 129.3 (d, J = 11.3 Hz, 1C), 129.1 (2C), 128.0, 126.8 (2C), 117.3 (d, J = 17.5 Hz, 1C), 103.0 (d, J = 22.5 Hz, 1C), 46.4, 36.1, 19.9, 14.0.



1-benzyl-3-butylquinoxalin-2(1H)-one (5g)¹⁷. ¹H NMR (500 MHz, CDCl₃): δ = 7.84 (dd, J = 1.5 Hz, 8.0, 1H), 7.40 - 7.37 (m, 1H),7.33 - 7.22 (m, 7H), 5.50 (s, 2H), 3.03 - 2.99 (m, 2H), 1.85 - 1.79 (m, 2H), 1.54 - 1.47 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H). ¹³C NMR (125MHz, CDCl₃): δ =161.5, 155.0, 135.3, 133.0, 132.4, 129.7, 129.4,128.9, 127.6, 126.8, 123.5, 114.3, 45.8, 34.1, 29.0, 22.7, 14.0.



1-benzyl-3-butyl-6,7-dimethylquinoxalin-2(1H)-one. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.59$ (s, 1H), 7.28 (d, J = 5.5 Hz, 2H), 7.23 (s, 3H), 6.99 (s, 1H), 5.45 (s, 2H), 2.97 (d, J = 6.0 Hz, 2H), 2.27 (s, 6H), 1.81 - 1.80 (m, 2H), 1.49 - 1.48 (m, 2H), 0.98 - 0.97 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 160.0$, 154.9, 139.0, 135.5, 132.3, 131.3, 130.3, 129.8, 128.7 (2C), 127.4, 126.8 (2C), 114.7, 45.6, 33.9, 28.9, 22.7, 20.4, 19.0, 13.9.



1-benzyl-3-butyl-6,7-difluoroquinoxalin-2(1H)-one. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.57 - 7.54$ (m, 1H), 7.26 - 7.21 (m, 3H), 7.14 - 7.13 (m, 2H), 6.95 - 6.92 (m, 1H), 5.34 (s, 2H), 2.90 (t, J = 7.0 Hz, 2H), 1.72 (t, J = 6.5 Hz, 2H), 1.41 (q, J = 13.5 Hz, 7.0 Hz, 2H), 0.91 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 162.0$ (d, J = 3.8 Hz, 1C), 154.5, 149.8 (d, J = 13.8 Hz, 1C), 145.6 (d, J = 13.8 Hz, 1C), 134.5, 129.5 (d, J = 8.8 Hz, 1C), 129.3 (d, J = 8.8 Hz, 1C), 129.1 (2C), 128.0, 126.8 (2C), 117.4 (d, J = 18.8 Hz, 1C), 103.0 (d, J = 22.5 Hz, 1C), 46.4, 33.9, 28.7, 22.7, 13.9.



1-benzyl-3-cyclohexylquinoxalin-2(1H)-one (5j)¹⁴: ¹H NMR (500 MHz, CDCl₃): δ = 7.84 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.0 Hz, 1H), 7.31 - 7.22 (m, 7H), 5.49 (s, 2H), 3.40 (q, J = 19.5 Hz, 11.5Hz, 1H), 2.01 (d, J = 11.5 Hz, 2H), 1.88 (d, J = 12.5 Hz, 2H), 1.78 (d, J = 12.5 Hz, 1H), 1.60 (t, J = 16.0 Hz, 2H), 1.48 (q, J = 25.5 Hz, 12.5 Hz, 2H), 1.36 - 1.29 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 164.4, 154.6, 135.5, 133.2, 132.2, 129.9, 129.3, 128.9 (2C), 127.6, 126.9 (2C), 123.4, 114.2, 45.9, 40.8, 30.6 (2C), 26.3 (2C), 26.2.



1-benzyl-3-cyclohexyl-6,7-dimethylquinoxalin-2(1H)-one (5k)¹⁵. ¹H NMR (500 MHz, CDCl₃): δ = 7.60 (s, 1H), 7.28 (d, *J* = 6.0Hz, 2H), 7.23 (d, *J* = 5.5 Hz, 3H), 6.99 (s, 1H), 5.45 (s, 2H), 3.37 (t, *J* = 11.0 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.0 (d, *J* =

11.0 Hz, 2H), 1.87(d, J = 10.5 Hz, 2H), 1.76 (d, J = 11.5 Hz, 1H), 1.59 (dd, J = 24.0 Hz, 12.0 Hz, 2H), 1.47(q, J = 25.0 Hz, 12.5 Hz, 2H), 1.35 - 1.30 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 163.1$, 154.5, 138.9, 135.7, 132.2, 131.5, 130.1, 129.9,128.8 (2C), 127.4, 126.8 (2C), 114.6, 45.7, 40.6, 30.6 (2C), 26.3, 26.1, 20.4, 19.0.



1-benzyl-3-cyclohexyl-6,7-difluoroquinoxalin-2(1H)-one (5l). ¹H NMR (500 MHz, CDCl₃): δ = 7.63 (t, *J* = 9.5 Hz, 1H), 7.35 - 7.28 (m, 3H), 7.22 - 7.21 (m, 2H), 7.01 (dd, *J* = 11.0 Hz, 7.0 Hz, 1H), 5.41 (s, 2H), 3.37 (dd, *J* = 11.0 Hz, 3.0 Hz, 1H), 2.00 - 1.99 (m, 2H), 1.89 - 1.87 (m, 2H), 1.79 - 1.77 (m, 1H), 1.59 - 1.43 (m, 4H), 1.35 - 1.27 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 164.9 (d, *J* = 12.5 Hz, 1C), 154.1, 151.7 (d, *J* = 14.3 Hz, 1C), 147.5 (d, *J* = 13.8 Hz, 1C), 134.6, 129.4 (d, *J* = 7.1 Hz, 1C), 129.2 (d, *J* = 8.3 Hz, 1C), 129.1 (2C), 127.9, 126.8 (2C), 117.4 (d, *J* = 17.5 Hz, 1C), 102.7 (d, *J* = 23.0 Hz, 1C), 46.4, 40.8, 30.5 (2C), 26.2 (2C), 26.1.



3-isopropyl-1-methylquinoxalin-2(1H)-one (5m)¹⁶. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.83$ (d, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 3.69(s, 3H), 3.66 - 3.60 (m, 1H), 1.33 (s, 3H), 1.31(s, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 164.8$, 154.4, 132.8, 132.6, 129.7, 129.3, 123.3, 113.3, 31.1, 28.9, 20.1 (2c).



3-isopropyl-1,6,7-trimethylquinoxalin-2(1H)-one (5n). ¹H NMR (500 MHz, CDCl₃) $\delta = 7.60$ (s, 1H), 7.03 (s, 1H), 3.66 (s, 3H), 3.63 - 3.53 (m, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 163.6$, 154.5, 138.9, 132.1, 131.1, 130.9, 129.8, 114.0, 31.0, 28.8, 20.4, 20.2 (2c), 19.0.



6,7-difluoro-3-isopropyl-1-methylquinoxalin-2(1H)-one (50). ¹H NMR (500 MHz, CDCl₃): δ = 7.65 (t, *J* = 9.5 Hz, 1H), 7.09 (dd, *J* = 11.0 Hz, 7.0 Hz, 1H), 3.61 - 3.56 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 165.5 (d, *J* = 3.8 Hz, 1C), 154.0, 151.9 (d, *J* = 15.0 Hz, 1C), 147.5 (d, *J* = 13.8 Hz, 1C), 130.1 (d, *J* = 8.8 Hz, 1C), 129.0 (d, *J* = 8.8 Hz, 1C), 117.4 (d, *J* = 17.5 Hz, 1C), 102.1 (d, *J* = 23.8 Hz, 1C), 31.2, 29.5, 20.0 (2C).



1-methyl-3-propylquinoxalin-2(1H)-one (5p)¹⁶. ¹H NMR (500 MHz, CDCl₃): $\delta =$

7.81 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.0 Hz, 1H), 7.31 (t, J = 7.0 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 3.68 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H), 1.83 (q, J = 14.5 Hz, 7.0 Hz, 2H), 1.05 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 160.1$, 154.7, 133.9, 132.5, 129.4, 129.3, 123.3, 113.4, 36.1, 28.8, 20.0, 13.9.



1,6,7-trimethyl-3-propylquinoxalin-2(1H)-one (5q): ¹H NMR (500 MHz, CDCl₃): δ = 7.57 (s, 1H), 7.03 (s, 1H), 3.66 (s, 3H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 1.81 (q, *J* = 15.0 Hz, 7.5 Hz, 2H), 1.04 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 159.7, 154.9, 139.0, 132.2, 131.0, 131.0, 129.64, 114.0, 77.3, 77.0, 76.7, 36.1, 28.8, 20.4, 20.2, 19.1, 14.0,



6,7-difluoro-1-methyl-3-propylquinoxalin-2(1H)-one (5r). ¹H NMR (500 MHz, CDCl₃): δ = 7.62 (dd, *J* = 9.5 Hz, 8.5 Hz, 1H), 7.10 (dd, *J* = 11.0 Hz, 7.0 Hz, 1H), 3.66 (s, 3H), 2.88 (t, *J* = 7.0 Hz, 2H), 1.82 - 1.78 (m, 2H), 1.04 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 161.6 (d, *J* = 3.8 Hz, 1C), 154.4, 151.8 (d, *J* = 13.8 Hz, 1C), 147.4 (d, *J* = 13.8 Hz, 1C), 117.2 (d, *J* = 17.5 Hz, 1C), 102.1 (d, *J* = 22.5 Hz, 1C), 36.0, 29.4, 19.8, 13.9.



3-butyl-1-methylquinoxalin-2(1H)-one (5s)¹⁷. ¹H NMR (500 MHz, CDCl₃): δ = 7.81 (d, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.33 - 7.26 (m, 2H), 3.68 (s, 3H), 2.94 (t, *J* = 7.5 Hz, 2H), 1.77 (t, *J* = 6.0 Hz, 2H), 1.47 (q, *J* = 14.0 Hz, 7.0 Hz, 2H), 0.97 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 161.2, 154.7, 132.9, 132.6, 129.4, 129.3, 123.3, 113.4, 33.9, 28.9, 28.8, 22.6 (2C), 13.8.



3-butyl-1,6,7-trimethylquinoxalin-2(1H)-one (5t)¹⁷. ¹H NMR (500 MHz, CDCl₃): δ = 7.56 (s, 1H), 7.02 (s, 1H), 3.65(s, 3H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 2.33 (s, 3H), 1.76 (t, *J* = 7.0 Hz, 2H), 1.46 (q, *J* = 14.5 Hz, 7.0 Hz, 2H), 0.97 (t, *J* = 7.0 Hz, 3H)

¹³C NMR (125 MHz, CDCl₃): δ = 159.9, 154.8, 139.0, 132.2, 131.0, 130.9, 129.6, 114.0, 33.9,28.9, 28.8, 22.6, 20.3, 19.0, 13.9.



3-butyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one (5u)¹⁷. ¹H NMR (500 MHz, CDCl₃): δ = 7.63 (dd, J = 10.0 Hz, 8.5 Hz, 1H), 7.09 (dd, J = 11.5 Hz, 7.0 Hz, 1H), 3.65 (s, 3H), 2.91(t, J = 7.5 Hz, 2H), 1.78 - 1.72 (m, 2H), 1.46 (q, J = 15 Hz, 7.5 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 161.8 (d, J = 3.8 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H).

1C), 154.4, 151.8 (d, *J* = 13.8 Hz, 1C), 147.5 (d, *J* = 13.8 Hz, 1C), 130.1 (d, *J* = 8.8 Hz, 1C), 128.9 (d, *J* = 6.3 Hz, 1C), 117.2 (d, *J* = 16.3 Hz, 1C), 102.1 (d, *J* = 22.5 Hz, 1C), 33.9, 29.5, 28.6, 22.6, 13.9.



3-cyclohexyl-1-methylquinoxalin-2(1H)-one (5v)¹⁵. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.84$ (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.0 Hz, 1H), 7.29 - 7.26 (m, 1H), 3.70 (s, 3H), 3.36 - 3.32 (m, 1H), 1.96 (d, J = 11.5 Hz, 2H), 1.87 (d, J = 12.0 Hz, 2H), 1.77 (d, J = 12.0Hz, 1H), 1.57 (dd, J = 22.0 Hz, 9.5 Hz, 2H), 1.47(dd, J = 25.0 Hz, 12.5 Hz, 2H), 1.35 - 1.30 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 164.3$, 154.6, 132.9, 132.8, 129.8, 129.4, 123.4, 113.4, 40.8, 30.5(2C), 29.0, 26.3(2C), 26.1.



3-cyclohexyl-1,6,7-trimethylquinoxalin-2(1H)-one (5w)¹⁸. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.60$ (s, 1H), 7.03 (s, 1H), 3.66 (s, 3H), 3.34 - 3.30 (m, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 1.94 (d, J = 11.0 Hz, 2H), 1.86 (d, J = 10.5 Hz, 2H), 1.76 (d, J = 12.0 Hz, 1H), 1.59 - 1.45 (m, 4H), 1.34 - 1.26 (m, 4H). ¹³C NMR (125MHz, CDCl₃): $\delta = 163.0$, 154.6, 138.9, 132.1, 131.2, 130.8, 129.8, 114.0, 40.6, 30.5 (2C), 28.9, 26.3 (2C), 26.1, 20.4, 19.0.



3-cyclohexyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one (5x)¹⁴. ¹H NMR (500 MHz, CDCl₃): δ =7.64 (q, *J* =10.0 Hz, 8.5 Hz, 1H), 7.08 (q, *J* = 11.0 Hz, 7.0 Hz, 1H), 3.65 (s, 3H), 3.32 - 3.28 (m, 1H), 1.93 (d, *J* = 10.0 Hz, 2H), 1.86 (d, *J* = 11.5 Hz, 2H), 1.76 (d, *J* = 12.5 Hz, 1H), 1.55 - 1.41 (m, 4H), 1.33 - 1.26 (m, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 164.8 (d, *J* = 2.5 Hz), 154.0, 151.8 (d, *J* = 15.0 Hz), 149.8 (d, *J* = 13.8 Hz), 147.4 (d, *J* = 13.8 Hz), 145.5 (d, *J* = 13.8 Hz), 129.9 (d, *J* = 8.8 Hz), 129.1 (d, *J* = 6.3 Hz), 117.3 (d, *J* = 17.5 Hz), 102.0 (d, *J* = 22.5 Hz), 40.7, 30.4 (2C), 29.5, 26.2 (2C), 26.1.



1,3-dibenzylquinoxalin-2(1H)-one (7a)¹⁹. ¹H NMR (500 MHz, CDCl₃): δ = 7.84 (d, *J* = 7.0 Hz, 1H), 7.49 (d, *J* = 6.5 Hz, 2H), 7.37 - 7.18 (m, 11H), 5.43 (s, 2H), 4.32 (s, 2H). ¹³CNMR (125 MHz, CDCl₃): δ = 159.4, 154.8, 137.0, 135.2, 133.0, 132.6, 130.0, 129.8, 129.5 (2C), 128.5 (2C), 128.4 (2C), 127.6, 126.8 (2C), 126.5, 123.5, 114.3, 45.9, 40.7.



1,2-dibenzyl-1H-benzo[d]imidazole (8a)⁶. ¹H NMR (500 MHz, CDCl₃): δ = 7.81 (d, J = 7.5 Hz, 1H), 7.24 - 7.18 (m, 11H), 6.92 (s, 2H), 5.17 (s, 2H), 4.25 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 153.3, 142.6, 136.0, 135.7, 128.8 (2C), 128.7 (2C), 128.4 (2C), 127.8, 126.9, 126.1 (2C), 122.5, 122.1, 119.6, 109.6, 47.0, 34.5.



1-benzyl-3-(tert-butyl)quinoxalin-2(1H)-one (7b)¹⁶. ¹H NMR (500 MHz, CDCl₃): δ = 7.82 (d, *J* = 7.5 Hz, 1H), 7.34, 16 (m, 8H), 5.46 (s, 2H), 1.54 (s, 9H). ¹³CNMR (125 MHz, CDCl₃): δ = 165.3, 153.6, 135.5, 132.6, 132.3, 130.1, 129.4, 128.8 (2C), 127.4, 126.6 (2C), 123.1, 113.9, 45.4, 39.5, 27.9 (3C).



1-benzyl-2-(tert-butyl)-1H-benzo[d]imidazole (8b)¹⁰. ¹H NMR (500 MHz, CDCl₃) δ = 7.80 (d, J = 7.5 Hz, 1H), 7.27 - 7.20 (m, 4H), 7.11 (t, J = 7.0 Hz, 1H), 6.97 (q, J = 19.5 Hz, 8.0 Hz, 3H), 5.60 (s, 2H), 1.52 (s, 9H). ¹³CNMR (125 MHz, CDCl₃): δ = 161.1, 141.7, 136.6, 136.2, 128.8 (2C), 127.4, 125.6 (2C), 122.4, 121.9, 119.5, 109.9, 48.6, 34.1, 29.8 (3C).



1-benzyl-3-(tert-butyl)quinoxalin-2(1H)-one (7c). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.62$ (d, J = 9.0 Hz, 1H), 7.32 - 7.25 (m, 3H), 7.19 (d, J = 7.0 Hz, 2H), 6.97 (dd, J = 11.0 Hz, 7.0 Hz, 1H), 5.40 (s, 2H), 1.51 (s,9H). ¹³CNMR (125 MHz, CDCl₃): $\delta = 160.0$ (d, J = 2.5 Hz, 1C), 153.2, 151.8 (d, J = 15.0 Hz, 1C), 147.4 (d, J = 13.8 Hz, 1C), 134.7, 129.7 (d, J = 7.5 Hz, 1C), 129.0 (2C), 128.6 (d, J = 7.5 Hz, 1C), 127.8, 126.6 (2C), 117.6 (d, J = 17.5 Hz, 1C), 102.5 (d, J = 22.5 Hz, 1C), 46.0, 39.6, 27.8 (3C).



1-benzyl-2-(tert-butyl)-5,6-difluoro-1H-benzo[d]imidazole (8c). ¹H NMR (500 MHz, CDCl₃): δ = 7.54 (dd, J = 10.0 Hz, 7.0 Hz, 1H), 7.31 - 7.27 (m, 3H), 6.94 (d, J = 6.0 Hz, 2H), 6.74 (dd, J = 9.5 Hz, 7.0 Hz, 1H), 5.55 (s, 2H), 1.51 (s, 9H). ¹³CNMR (125MHz, CDCl3): δ = 162.7, 148.6 (dd, J = 28.8 Hz, 16.3 Hz, 1C), 146.7 (dd, J = 26.3 Hz, 16.3 Hz, 1C), 136.8 (d, J = 10.0 Hz, 1C), 135.3, 131.8 (d, J = 10.0 Hz, 1C), 129.0 (2C), 127.8, 125.6 (2C), 106.9 (d, J = 20.0 Hz, 1C), 98.1 (d, J = 23.8 Hz, 1C), 49.0, 34.2, 29.6 (3C).



1-benzyl-3-(tert-butyl)-6,7-dimethylquinoxalin-2(1H)-one (7d). ¹H NMR (500 MHz, CDCl₃): δ = 7.59 (s, 1H), 7.28 - 7.26 (m, 2H), 7.20 (s, 3H), 6.95 (s, 1H), 5.43 (s, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.52 (s, 9H). ¹³CNMR (125 MHz, CDCl₃): δ = 164.1,

153.6, 139.0, 135.8, 132.0, 130.7, 130.6, 130.2, 128.7 (2C), 127.3, 126.6 (2C), 114.4, 77.3, 77.0, 76.7, 45.3, 39.3, 28.0 (3C), 20.4, 19.0.



3-benzyl-1-methylquinoxalin-2(1H)-one (7e)¹⁹. ¹H NMR (500 MHz, CDCl₃) δ = 7.84 (d, *J* = 7.5 Hz, 1H), 7.50 - 7.46 (m, 3H), 7.33 - 7.19 (m, 5H), 4.26 (s, 2H), 3.64 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 159.3, 154.7, 137.0, 133.3, 132.7, 129.9, 129.8, 129.5(2C), 128.4(2C), 126.5, 123.5, 113.5, 40.7, 29.1.



3-(tert-butyl)-1-methylquinoxalin-2(1H)-one (7f)¹⁶. ¹H NMR (500 MHz, CDCl₃): δ = 7.80 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 14.5 Hz, 1H), 7.26 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 3.63 (s, 3H), 1.50 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ = 165.0, 153.5, 133.1, 131.9, 129.9, 129.3, 122.9, 113.0, 39.3, 28.5, 27.7 (3C).



3-(tert-butyl)-1,6,7-trimethylquinoxalin-2(1H)-one (7g)¹⁸. ¹H NMR (500 MHz, CDCl₃): δ = 7.58 (s, 1H), 7.01 (s, 1H), 3.63 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 1.48 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ = 163.9, 153.7, 133.1, 139.0, 131.9, 131.2, 130.5, 130.1, 113.8, 39.2, 28.6, 27.9 (3C), 20.4, 19.0.



33-(tert-butyl)-6,7-difluoro-1-methylquinoxalin-2(1H)-one (7h)¹⁸. ¹H NMR (500 MHz, CDCl₃): δ = 7.63 (t, *J* = 8.5 Hz, 1H), 7.07 (dd, *J* = 11.0 Hz, 7.5 Hz, 1H), 3.63 (s, 3H), 1.46 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ = 165.9 (d, *J* = 3.8 Hz, 1C), 153.2, 151.9 (d, *J* = 13.8 Hz, 1C), 147.3 (d, *J* = 13.8 Hz), 130.5 (d, *J* = 7.5 Hz), 128.4(d, *J* = 7.5 Hz, 1C), 117.6 (d, *J* = 17.5 Hz, 1C), 101.8 (d, *J* = 22.5 Hz), 39.5, 29.2, 27.7 (3C).

Copies of the ¹H and ¹³C NMR Spectra













































































































S73





S75





S77









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