Supporting Information

Efficient Synthesis of Biazoles by Aerobic Oxidative Homocoupling of Azoles
Catalyzed by Copper(I) / 2-pyridonate Catalytic System

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Experimental Section:

General: All reactions and manipulations were carried out by means of standard Schlenk techniques. \(^1\)H and \(^1\)C NMR spectra were recorded on JEOL ECS-400 and ECX-500 spectrometers. Column chromatography was carried out by using Wako-gel C-200. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Melting points were measured using a Yanagimoto melting point measurement apparatus. Solvents were dried by standard procedures and distilled prior to use. 1-(4-methylbenzyl)-1\(^H\)-imidazole (8), 1-(4-trifluorobenzyl)-1\(^H\)-imidazole (9), 1-(4-bromobenzyl)-1\(^H\)-imidazole (10), 1-(4-chlorobenzyl)-1\(^H\)-imidazole (11), 1-(3-chlorobenzyl)-1\(^H\)-imidazole (12), 1-(2-chlorobenzyl)-1\(^H\)-imidazole (13), were prepared according to the literature method. All other reagents are commercially available and were used without further purification.

Preparation of 2-pyridonate ligands: To an oven-dried, argon purged flask were added 1.0 mmol of functionalized hydroxypyridine (2-hydroxypyridine, 3-hydroxypyridine, 4-hydroxypyridine, phenol, 5-trifluoromethyl-2-hydroxypyridine, 5-nitro-2-hydroxypyridine, 6-methyl-2-hydroxypyridine, 5-methyl-2-hydroxypyridine, 4-methyl-2-hydroxypyridine, 3-methyl-2-hydroxypyridine, 3-methoxy-2-hydroxypyridine), 1.0 mmol of sodium ethoxide and ethanol (2.5 mL), respectively. The mixture was stirred at room temperature for 2 hours. Then the solvent was removed and residue was dried in vacuo to give a colorless or yellow solid.

Sodium 2-pyridonate (L1) \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta = 7.72\) (br, 1H, Ar-H ), 7.55 (t, 1H, \(J = 8.0\) Hz, Ar-H ), 6.54 (t, 1H, \(J = 5.3\) Hz, Ar-H ), 6.47 (d, 1H, \(J = 7.5\) Hz, Ar-H ).

Sodium 3-methoxy-2-pyridonate (L5) \(^1\)H NMR (400 MHz, D\(_2\)O): \(\delta = 7.17\) (br, 1H, Ar-H ), 7.04 (d, 1H, \(J = 7.6\) Hz, Ar-H ), 6.47 (br, 1H, Ar-H ), 3.76 (s, 3H, OCH\(_3\) ).

Sodium 3-methyl-2-pyridonate (L6) \(^1\)H NMR (400 MHz, D\(_2\)O): \(\delta = 7.50\) (d, 1H, \(J = 5.2\) Hz, Ar-H ), 7.44 (d, 1H, \(J = 5.2\) Hz, Ar-H ), 6.47 (t, 1H, \(J = 5.2\) Hz, Ar-H ), 2.06 (s, 3H, CH\(_3\) ).

Sodium 4-methyl-2-pyridonate (L7) \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta = 7.50\) (d, 1H, \(J = 6.0\) Hz, Ar-H ), 6.43 (d, 1H, \(J = 6.0\) Hz, Ar-H ), 6.37 (br, 1H, Ar-H ), 2.22 (s, 3H, CH\(_3\) ).

Sodium 5-methyl-2-pyridonate (L8) \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta = 7.55\) (s, 1H, Ar-H ), 7.44 (d, 1H, \(J = 9.0\) Hz, Ar-H ) 6.43 (d, 1H, \(J = 8.5\) Hz, Ar-H ), 2.12 (s, 3H, CH\(_3\) ).

Sodium 6-methyl-2-pyridonate (L9) \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta = 7.49\) (br, 1H, Ar-H ), 6.39 (br, 1H, Ar-H ), 6.31 (br, 1H, Ar-H ), 2.27 (br, 3H, CH\(_3\) ).

Sodium 5-(trifluoromethyl) -2-pyridonate (L10) \(^1\)H NMR (400 MHz, D\(_2\)O): \(\delta = 8.08\) (s, 1H, Ar-H ), 7.61 (d, 1H, \(J = 7.2\) Hz, Ar-H ), 6.38 (d, 1H, \(J = 7.2\) Hz, Ar-H ).

Sodium 5-nitro-2-pyridonate (L11) \(^1\)H NMR (500 MHz, D\(_2\)O): \(\delta = 8.84\) (br, 1H, Ar-H ), 8.18 (br, 1H, Ar-H ), 6.39 (br, 1H, Ar-H ).

Procedure for the homocoupling of 1-methyl-1\(^H\)-imidazole shown in Table 1: To an oven-dried, argon purged two-necked flask were added sodium 2-pyridonate (0.04 mmol, 2.0 or 1.0 mol%), Cu-catalyst (0.02 mmol, 2.0 or 1.0 mol%), 1-methyl-1\(^H\)-imidazole (1.0 or 2.0 mmol), and \(p\)-xylene (4 mL). The flask was sealed and preheated at 140 \(^\circ\)C under argon for...
about 1 minute and then the mixture was stirred at 140 °C under open air for 20 h. The mixture was cooled to room temperature. The solvent was removed in vacuo and the crude reaction mixture was diluted with chloroform and filtered through a filter-paper. Chloroform was removed in vacuo and 1,3,5-trimethoxybenzene was added as an internal standard for NMR analysis. The yield of 1,1’-dimethyl-1'H,1'H’-2,2’-biimidazole (1) was calculated by \(^1\)H-NMR analysis in chloroform-d.

**General Procedure for the oxidative homocoupling of various azoles shown in Table 2 and 3:** To an oven-dried, argon purged flask were added sodium 5-methyl-2-pyridonate (L8) (0.04 mmol, 2.0 mol%), CuCl (0.02 mmol, 1.0 mol%), an azole (2.00 mmol) and \(p\)-xylene (4 mL). The flask was sealed and preheated at 140 °C under argon for about 1 minutes and then the mixture was stirred at 140 °C under open air for 20 h. The mixture was cooled to room temperature. The solvent was removed in vacuo and the crude reaction mixture was diluted with chloroform and filtered through a filter-paper. The filtrate was concentrated by evaporation and purified by a silica gel column chromatography.

**Stoichiometric reaction of CuCl with sodium 5-methyl-2-pyridonate (L8) to afford copper compound 21:**

\[
\text{CuCl} + \text{Na} \begin{array}{c} \text{N} \\ \end{array} \text{ONa} \xrightarrow{\text{p-xylene, reflux, 2h}} \text{copper compound 21}
\]

To an oven-dried, argon purged two-necked flask were added CuCl (1.5 mmol), sodium 5-methyl-2-pyridonate (1.5 mmol) and \(p\)-xylene (10 mL). The suspension was heated under reflux in an oil bath for 2 h under argon. Then the mixture was cooled to room temperature and washed with, MeOH, (5 mL, 2 times) and Et₂O (5 mL, 2 times). Drying in vacuum gave a yellow solid (21) (229.1 mg, 89%). M. p.: 192 °C (dec.). \(^1\)H NMR (500 MHz, D₂O) \(\delta\) 7.65 (d, 1H, \(J = 9.0\) Hz), 7.37 (s, 1H), 6.61 (d, 1H, \(J = 9.5\) Hz), 2.15 (s, 3H). \(^13\)C NMR (125.7 MHz, D₂O) \(\delta\) 163.7, 146.5, 132.5, 119.3, 118.2, 16.0. Anal.Calcd for CuC₆H₆NO: C, 41.98; H, 3.52; N, 8.16. Found: C, 41.74; H, 3.53; N, 8.11.
Aerobic oxidative homocoupling of N-methylimidazole catalyzed by the copper compound 21:

\[ \text{N-methylimidazole} \xrightarrow{(1.0 \text{ mol\% Cu})} \text{1a} \]

To an oven-dried, argon purged two-necked flask were added the copper compound 21 (3.2 mg, 2.0 mol\% Cu), 1-methyl-1H-imidazole (2.00 mmol), and \( p \)-xylene (4 mL). The flask was sealed and preheated at 140 °C under argon for about 1 minute and then the mixture was stirred at 140 °C under open air for 20 h. The mixture was cooled to room temperature. The solvent was removed in vacuo and the crude reaction mixture was diluted with chloroform and filtered through a filter-paper. Chloroform was removed in vacuo and 1,3,5-trimethoxybenzene was added as an internal standard for NMR analysis. The yield of 1,1'-dimethyl-1H,1H'-2,2'-biimidazole (1a) was calculated by the integration in \(^1\)H-NMR analysis in chloroform-d.
**Explanation of a Plausible Mechanism:**

Although the mechanism for the CuCl/2-pyridonate catalyzed aerobic oxidative homo-coupling of azoles is not completely clear so far, a plausible one is shown in Scheme S1. The reaction would start with the formation of a Cu(I) species A bearing 2-pyridonate as a ligand by the reaction of CuCl with sodium 2-pyridonate. Then, 2-pyridonate ligand-promoted C-H activation of azole would occur to afford a Cu(I) species B which would be oxidized by oxygen to form a Cu(III)-oxo species C. Subsequent hydrogen transfer from hydroxyl group in the ligand to copper-oxo moiety would occur to afford a Cu(III) species D. Ligand promoted C-H activation of azole followed by dehydration would proceed to give a bis-imidazolyl Cu(III) species E. Reductive elimination would take place to give the corresponding biazoles and regenerate the Cu(I) species A.

Scheme S1. A plausible mechanism
Data for the Products of oxidative homocoupling of azoles:

1,1’-dimethyl-1\textit{H},1\textit{H}’-2,2’-biimidazole (1a): Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 1a as a colorless solid (152.2 mg, 95% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.11 (d, 2H, \( J \) = 1.0 Hz, Im-H), 6.96 (d, 2H, \( J \) = 1.0 Hz, Im-H), 4.04 (s, 6H, CH\textsubscript{3}). \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}) \( \delta \) 138.82, 127.96, 122.74, 35.49.

1,1’-diethyl-1\textit{H},1\textit{H}’-2,2’-biimidazole (2a): Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (3:1) to give product 2a as a colorless solid (182.2 mg, 96% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.12 (d, 2H, \( J \) = 1.0 Hz, Im-H), 7.02 (d, 2H, \( J \) = 1.0 Hz, Im-H), 4.50 (q, 4H, \( J \) = 7.5 Hz, CH\textsubscript{2}), 1.41 (t, 6H, \( J \) = 7.5 Hz, CH\textsubscript{3}). \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}) \( \delta \) 138.04, 128.24, 120.56, 42.63, 16.63.

1,1’-di-n-butyl-1\textit{H},1\textit{H}’-2,2’-biimidazole (3a): Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:1) to give 3a as a pale yellow oil (221.0 mg, 90% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.11 (s, 2H, Im-H), 6.99 (s, 2H, Im-H), 4.44 (t, 4H, \( J \) = 7.5 Hz, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.74-1.68 (m, 4H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.30-1.25 (m, 4H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 0.89-0.86 (t, 6H, \( J \) = 7.5 Hz, CH\textsubscript{3}). \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}) \( \delta \) 138.24, 128.05, 47.20, 33.25, 19.81, 13.73.

1,1’-divinyl-1\textit{H},1\textit{H}’-2,2’-biimidazole (4a): Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:1) to give 4a as a colorless solid (117.5 mg, 63% yield). M. p.: 125-126\textdegree C, \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 8.02 (q, 2H, \( J \) = 8.0 Hz, CH=CH\textsubscript{2}), 7.37 (d, 2H, \( J \) = 1Hz, Im-H), 7.17 (d, 2H, \( J \) = 1 Hz, Im-H), 5.28 (dd, 2H, \( J \) = 16.0 Hz, 1.5 Hz, CH=CH\textsubscript{2}), 4.95 (dd, 2H, \( J \) = 8.0 Hz, \( J \) = 1.5 Hz, CH=CH\textsubscript{2}). \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}) \( \delta \) 137.3, 131.3, 129.6, 117.1, 102.5. Anal.Calcd for C\textsubscript{10}H\textsubscript{10}N\textsubscript{4}: C, 64.50; H, 5.41; N, 30.09. Found; C, 64.59; H, 5.38; N, 30.04.

1,1’-di(4-methoxyphenyl)-1\textit{H},1\textit{H}’-2,2’-biimidazole (5a): Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 5a as a colorless solid (266.1 mg, 77% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.22 (d, 2H, \( J \) = 1.0 Hz, Im-H), 7.02 (d, 2H, \( J \) = 1.0 Hz, Im-H), 6.75-6.70 (m, 8H, Ar-H), 3.79 (s, 6H, CH\textsubscript{3}). \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}) \( \delta \) 158.95, 137.81, 130.45, 129.73, 125.60, 121.63, 114.26, 55.67.

1,1’-dibenzyl-1\textit{H},1\textit{H}’-2,2’-biimidazole (7a): Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:1) to give 7a as a pale yellow solid (291.6 mg, 92% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.24-7.23 (m, 6H, Ar-H), 7.12 (d, 2H, \( J \) = 1.0 Hz, Im-H), 7.04-7.03 (m, 4H, Ar-H), 6.93 (d, 2H, \( J \) = 1.0 Hz, Im-H), 5.71 (s, 4H, CH\textsubscript{3}). \textsuperscript{13}C NMR (125.7 MHz, CDCl\textsubscript{3}) \( \delta \)
138.41, 137.46, 128.80, 128.53, 127.76, 127.58, 121.57, 50.94.

1,1’-di(4-methylbenzyl)-1H,1H'-2,2'-biimidazole (8a):
Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 8a as a pale red solid (294.2 mg, 86% yield). M.p.: 154-155 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.12 (s, 2H, Im-H), 7.04 (d, 4H, J = 7.5 Hz, Ar-H), 6.94-6.92 (m, 6H, Ar-H and Im-H), 5.63 (s, 4H, CH₂). ¹³C NMR (125.7 MHz, CDCl₃) δ 138.43, 137.48, 134.44, 129.46, 128.47, 127.69, 121.48, 50.75. Anal. Calcd for C₂₂H₂₂N₄: C, 77.16; H, 6.48; N, 16.36. Found: C, 77.39; H, 6.31; N, 16.45.

1,1’-di(4-trifluoromethylbenzyl)-1H,1H'-2,2'-biimidazole (9a):
Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:1) to give 9a as a pale red solid (379.7 mg, 88% yield). M.p.: 122-123 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, 4H, J = 8.0 Hz, Ar-H), 7.15-7.13 (m, 6H, Ar-H and Im-H), 6.95 (d, 2H, J = 1.0 Hz, Im-H), 5.85 (s, 4H, CH₂). ¹³C NMR (125.7 MHz, CDCl₃) δ 141.54, 138.25, 130.10 (q, J = 32.8 Hz, C-F coupling), 128.86, 127.65, 125.76, 124.08 (q, J = 271.8 Hz, C-F coupling), 121.85, 50.56. Anal. Calcd for C₂₂H₁₆F₆N₄: C, 58.67; H, 3.58; N, 12.44. Found: C, 59.14; H, 3.93; N, 12.07.

1,1’-di(4-bromobenzyl)-1H,1H'-2,2'-biimidazole (10a):
Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:1) to give 10a as a pale yellow solid (414.9 mg, 90% yield). M.p.: 149-150 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, 4H, J = 8.0 Hz, Ar-H), 7.12 (d, 2H, J = 1.0 Hz, Im-H), 6.93 (d, 2H, J = 1.5 Hz, Ar-H), 5.66 (s, 4H, CH₂). ¹³C NMR (125.7 MHz, CDCl₃) δ 138.20, 136.46, 131.92, 129.24, 128.66, 121.83, 121.68, 50.37. Anal. Calcd for C₂₂H₁₆Br₂N₄: C, 50.87; H, 3.42; N, 11.87. Found: C, 50.89; H, 3.38; N, 11.54.

1,1’-di(4-chlorobenzyl)-1H,1H'-2,2'-biimidazole (11a):
Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 11a as a pale yellow solid (348.1 mg, 90% yield). M.p.: 161-162 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.20 (d, 4H, J = 8.0 Hz, Ar-H), 7.12 (d, 2H, J = 1.5 Hz, Im-H), 6.93 (d, 2H, J = 1.5 Hz, Ar-H), 5.69 (d, 2H, J = 1.5 Hz, Im-H), 5.68 (s, 4H, CH₂). ¹³C NMR (125.7 MHz, CDCl₃) δ 139.49, 138.25, 134.69, 130.15, 128.76, 128.09, 127.70, 125.67, 121.69, 50.44. Anal. Calcd for C₂₂H₁₆Cl₂N₄: C, 62.67; H, 4.21; N, 14.62. Found: C, 62.73; H, 4.22; N, 14.67.

1,1’-di(3-chlorobenzyl)-1H,1H'-2,2'-biimidazole (12a):
Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 12a as a pale yellow solid (318.4 mg, 83% yield). M.p.: 106-107 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.23-7.10 (m, 8H, Ar-H and Im-H), 6.92-6.94 (m, 4H, Ar-H and Im-H), 5.73 (s, 4H, CH₂). ¹³C NMR (125.7 MHz, CDCl₃) δ 139.49, 138.25, 134.69, 130.15, 128.76, 128.09, 127.70, 125.67, 121.69, 50.44. Anal. Calcd for C₂₂H₁₆Cl₂N₄: C, 62.67; H, 4.21; N, 14.62. Found: C, 62.46; H, 4.37; N, 14.59.
1,1’-di(2-chlorobenzyl)-1<sup>H</sup>,1<sup>H</sup>’-2,2’-biimidazole (13a):

Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 13a as a pale yellow solid (313.1 mg, 81% yield). M.p.: 157-158 °C, 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 (d, 2H, J = 8.0 Hz, Ar-H), 7.21 (t, 2H, J = 7.5 Hz, Ar-H), 7.12 (s, 2H, Im-H), 7.11 (t, 2H, J = 7.5 Hz, Ar-H), 6.95 (s, 2H, Im-H), 6.87 (d, 2H, J = 8.0 Hz, Ar-H), 5.89 (s, 4H, CH<sub>2</sub>). 13C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 138.58, 135.27, 133.26, 129.73, 129.34, 129.19, 128.72, 127.34, 121.66, 48.67. Anal. Calcd for C<sub>22</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>: C, 62.67; H, 4.21; N, 14.62. Found: C, 62.67; H, 4.17; N, 14.54.

1,1’-dimethyl-1<sup>H</sup>,1<sup>H</sup>’-2,2’-bibenzo[d]imidazole (14a):

Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:5) to give 14a as a colorless solid (224.1 mg, 85% yield). 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, 2H, J = 8.0 Hz, Ar-H), 7.48 (d, 2H, J = 8.0 Hz, Ar-H), 7.42-7.35 (m, 4H, Ar-H), 4.32 (s, 6H, CH<sub>3</sub>). 13C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 143.36, 142.68, 136.33, 124.06, 122.98, 120.43, 110.21, 32.56.

4,4’-diphenyl-2,2’-bioxazole (15a):

Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:5) to give product 15a as a colorless solid (241.9 mg, 84% yield). M.p.: 249-250 °C, 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 2H, Im-H), 7.87 (d, 4H, J = 7.5 Hz, Ar-H), 7.46 (t, 4H, J = 7.5 Hz, Ar-H), 7.38 (t, 2H, J = 7.5 Hz, Ar-H). 13C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 151.32, 142.97, 135.12, 129.94, 128.95, 128.89, 125.97. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.99; H, 4.20; N, 9.72. Found: C, 75.39; H, 4.48; N, 9.45.

2,2’-bibenzo[d]oxazole (16a):

Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:5) to give product 16a as a colorless solid (216.4 mg, 92% yield). 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, 2H, J = 8.0 Hz, Ar-H), 7.73 (d, 2H, J = 8.0 Hz, Ar-H), 7.55–7.47 (m, 4H, Ar-H). 13C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 152.03, 151.13, 141.31, 127.70, 125.92, 121.67, 111.63.

2,2’-bibenzo[d]thiazole (17a):

Purification was performed by column chromatography on silica gel eluting with EtOAc (100%) to give 17a as a colorless solid (218.2 mg, 81% yield). M.p.: 239-240 °C (dec.), 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.17 (d, 2H, J = 8.0 Hz, Ar-H), 8.00 (d, 2H, J = 8.0 Hz, Ar-H), 7.57 (t, 2H, J = 7.0 Hz, Ar-H), 7.50 (t, 2H, J = 7.0 Hz, Ar-H). 13C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 161.63, 153.65, 135.90, 126.94, 126.73, 124.18, 122.14. Anal. Calcd for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>: C, 62.66; H, 3.00; N, 10.44. Found: C, 62.63; H, 2.97; N, 10.42.

4,4’-dimethyl-2,2’-bithiazole (18a):

Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:5) to give 18a as a pale green solid (180.9 mg, 91% yield). 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.96 (s, 4H, Im-H), 2.51 (s, 6H, CH<sub>3</sub>). 13C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 160.96, 154.30, 115.56, 17.32.
4,4’,5,5’-tetramethyl-2,2’-bithiazole (19a): Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:5) to give 19a as a colorless solid (209.1 mg, 92% yield). $^1$H NMR (500 MHz, CDCl₃) δ 2.39 (s, 6H, CH₃), 2.36 (s, 6H, CH₃). $^{13}$C NMR (125.7 MHz, CDCl₃) δ 157.23, 149.68, 128.30, 14.96, 11.76.

(4,4’-dimethyl-2,2’-bithiazole-5,5’-diyl)bis(methylene) dipropionate (20a): Purification was performed by column chromatography on silica gel eluting with EtOAc/Hexane (1:1) to give 20a as a colorless solid (367.6 mg, 98% yield). M.p.: 118-119 °C. $^1$H NMR (500 MHz, CDCl₃) δ 4.26 (t, 4H, OCH₂), 3.10 (t, 4H, Im-CH₂), 2.41 (s, 6H, Im-CH₃), 2.08 (s, 6H, COCH₃). $^{13}$C NMR (125.7 MHz, CDCl₃) δ 170.97, 158.36, 150.74, 129.34, 64.04, 26.31, 21.08, 15.20. Anal. Calcd for C₁₆H₂₀N₂O₄S₂: C, 52.15; H, 5.47; N, 7.66. Found: C, 52.11; H, 5.43; N, 7.59.

X-ray Structure Analysis of 14a: Diffraction data for 14a were obtained with a Rigaku RAXIS RAPID instrument. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied. The structures were solved by direct method⁵,⁶ and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature.⁷ Hydrogen atoms were located on the idealized positions. The calculations were performed using the program system CrystalStructure.⁸,⁹ ORTEP drawing of 14a is shown in Figure S1. The crystal data and details are shown in CIF file.

![Figure S1. ORTEP drawings of 1,1’-dimethyl-1H,1H’-2,2’-bibenzo[d]imidazole (14a) with 50% thermal probability ellipsoids.](image-url)
$^1$H NMR of 1a

$^13$C NMR of 1a
$^1$H NMR of 5a

$^{13}$C NMR of 5a


$^1$H NMR of 7a

$^{13}$C NMR of 7a
$\text{\textsuperscript{13}C NMR of 8a}$

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$\text{\textsuperscript{13}C NMR of 8a}$
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$^{1}H$ NMR of 11a

$^{13}C$ NMR of 11a
$^1$H NMR of 13a

$^{13}$C NMR of 13a
\[ ^{13}\text{C NMR of 15a} \]

**Diagram 1:**

![Diagram 1](image1)

**Diagram 2:**

![Diagram 2](image2)
$^1$H NMR of 17a

$^{13}$C NMR of 17a
$^{1}H$ NMR of 18a

\[ \text{Structure Image} \]

$^{13}C$ NMR of 18a

\[ \text{Structure Image} \]
$^{13}$C NMR of 20a

$^1$H NMR of 20a

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$^1$H NMR of Active copper compound 21

$^{13}$C NMR of Active copper compound 21
Reference: