Supporting Information
for
Development of a method for the synthesis of 2,4,5-trisubstituted oxazoles composed of carboxylic acid, amino acid, and boronic acid

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General information, Table S1, experimental procedure and characterization data for products, and $^1$H and $^{13}$C NMR spectra

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1. General methods

Nuclear magnetic resonance (\textsuperscript{1}H NMR \(400\) MHz or \(600\) MHz, \textsuperscript{13}C NMR \(100\) MHz or \(125\) MHz) spectra were determined on a JEOL JNM-ECS400 spectrometer and JEOL JNM-ECS600 spectrometer. Chemical shifts for \textsuperscript{1}H NMR are reported as \(\delta\) values relative to tetramethylsilane as the internal standard and coupling constants are in hertz (Hz). The following abbreviations are used for spin multiplicity: \(s =\) singlet, \(d =\) doublet, \(t =\) triplet, \(m =\) multiplet, \(br =\) broad. Chemical shifts for \textsuperscript{13}C NMR were reported in ppm relative to the center line of a triplet at 77.16 ppm for deuteriochloroform. NMR yields were determined by quantitative NMR spectroscopy using 1,3,5-trimethoxybenzene, coumarin or 6-methylcoumarin as the internal standard. Mass spectra were measured on a JMS-T100TD AccuTOF TLC (DART-MS) and JMS-SX102A (FAB). Melting points were determined with a Yanagimoto melting point apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F\textsubscript{254}. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 N (spherical, neutral, 40-100 mesh).

Reagents and solvents were purchased from Tokyo Chemical Industry (TCI), Nacalai Tesque, Aldrich, and Wako Pure Chemical Industries and were used without further purification unless otherwise noted. Dehydrated 1,4-dioxane, 1,2-dimethoxyethane, toluene and xylene were purchased from commercial sources and distilled over metal sodium before use. All reactions sensitive to oxygen or moisture were conducted under a \textsubscript{2}N atmphere.
2. Table S1. The results of experiments for Suzuki-Miyaura coupling under other conditions.

![Chemical structure]

| Entry | Metal cat. | Base | Additive | Solvent | Time | Yield |
|-------|------------|------|----------|---------|------|-------|
| 1     | NiCl₂(dppf) | K₃PO₄ | 4a (2 equiv) | toluene (0.10 M) | 36 h | 6     |
| 2     | NiCl₂(dppf) | K₃PO₄ | 4a (7 equiv) | toluene | 3 h  | 66    |
| 3     | NiCl₂(dppf) | K₃PO₄ | LiCl (3 equiv) | toluene | 24 h | 31    |
| 4     | NiCl₂(dppf) | K₃PO₄ | LiCl (2 equiv) | toluene | 24 h | 49    |
| 5     | NiCl₂(dppf) | K₃PO₄ | LiCl (4 equiv) | toluene | 3 h  | 65    |
| 6     | NiCl₂(dppf) | K₃PO₄ | LiCl (5 equiv) | toluene | 24 h | 36    |
| 7     | NiCl₂(dppf) | K₃PO₄ | LiCl (3 equiv) | toluene | 3 h  | 67    |
| 8     | NiCl₂(dppf) | K₃PO₄ | LiI (3 equiv) | toluene | 20 h | 0     |
| 9     | NiCl₂(dppf) | K₃PO₄ | CuI (5 mol %) | toluene | 19 h | 0     |
| 10    | NiCl₂(dppf) | K₃PO₄ | LiCl (3 equiv) | Bu₄NI (0.5 equiv) | toluene | 20 h | 5     |
| 11    | NiCl₂(dppf) | K₃PO₄ | CuI (3 equiv) | toluene | 19 h | 0     |
| 12    | NiCl₂(dppf) | Cs₂CO₃ | LiCl (3 equiv) | toluene | 19 h | 20    |
| 13    | NiCl₂(dppf) | Li₂CO₃ | LiCl (3 equiv) | toluene | 26 h | 0     |
| 14    | NiCl₂(dppf) | K₃PO₄ | LiCl (3 equiv) | toluene | 5 min | 32 |
| 15    | NiCl₂(dppf) | K₃PO₄ | LiCl (3 equiv) | xylene 139 °C | 4 h | 53 |
| 16    | NiCl₂(dppf) | K₃PO₄ | LiCl (3 equiv) | dppf (5 mol %) | toluene | 4 h | 65 |

* NMR yield.
* The reaction was conducted using sealed tube.
3. Experimental procedure and characterization data for products

**General procedure for the preparataion of (3aa):**

To a solution of benzoic acid 1a (2.2 g, 18.0 mmol) and N-methylmorpholine (396 µL, 3.60 mmol) in 1,4-dioxane/H₂O (100 mL:50 mL) was added DMT-MM (5.23 g, 18.9 mmol) at room temperature. After stirring for 15 min, a solution of alanine 2a (1.76 g, 19.8 mmol) and aq 1 M NaOH (19.8 mL, 19.8 mmol) was added. After the reaction was completed (monitored by TLC), N-methylmorpholine (3.96 mL, 36.0 mmol) and DMT-MM (14.9 g, 54 mmol) were added in order. After stirring for 3 h, the reaction mixture was diluted in EtOAc (100 mL) and washed with aq 1 M HCl (40 mL), sat. aq NaHCO₃ (40 mL), and brine (30 mL). The organic layer was dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc:hexane = 7:3) to give oxazole 3aa in 78% yield.

**5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methyl-2-phenyloxazole (3aa)**

Yield: 78%. White solid. ¹H NMR (400MHz, CDCl₃): δ 7.98-7.92 (m, 2H), 7.47-7.40 (m, 3H), 4.03 (s, 6H), 2.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 174.1, 172.6, 154.9, 146.4, 130.2, 128.8, 127.3, 125.8, 120.6, 55.9, 10.4; HRMS (DART+) Calcd for C₁₅H₁₅N₄O₄⁺ ([M+H]+): 315.1093, Found: 315.1093.

**5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-2-(4-methoxyphenyl)-4-methyloxazole (3ba)**

Yield: 69%. Colorless crystal (recrystallization from CH₂Cl₂ and hexane). mp: 164-166 °C. ¹H NMR (400MHz, CDCl₃): δ 7.88 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 4.03 (s, 6H), 3.85 (s, 3H), 2.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 174.2, 172.6, 154.9, 146.4, 130.2, 128.8, 127.3, 125.8, 120.6, 55.5, 10.5; HRMS (DART+) Calcd for C₁₆H₁₇N₄O₅⁺ ([M+H]+): 345.1199, Found: 345.1202; Anal. Calcd for C₁₆H₁₆N₄O₅: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.78; H, 4.64; N, 16.46.

**5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-2-(4-formylphenyl)-4-methyloxazole (3ca)**

Yield: 60%. Colorless crystal (recrystallization from EtOAc and hexane). mp: 109-111 °C. ¹H NMR (600 MHz, CDCl₃): δ 10.06 (s, 1H), 8.11 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.2 Hz, 2H), 4.05 (s, 6H), 2.18 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 191.6, 174.2, 172.6, 153.7, 147.3, 137.2, 130.2, 126.3, 121.9, 56.1, 10.5; HRMS (DART+) Calcd for C₁₆H₁₅N₄O₅⁺ ([M+H]+): 343.1042, Found: 343.1023; Anal. Calcd for C₁₆H₁₄N₄O₅: C, 56.14; H, 4.12; N, 16.37. Found: C, 55.89; H, 4.17; N, 16.48.
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methyl-2-phenyloxazole (3da)

Yield: 54%. Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.31-7.25 (m, 2H), 7.23-7.18 (m, 3H), 4.02 (s, 6H), 3.09-3.04 (m, 2H), 3.01-2.96 (m, 2H), 2.04 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 174.1, 172.6, 157.4, 146.0, 140.3, 128.6, 128.4, 126.4, 118.7, 55.9, 33.0, 30.4, 10.2; HRMS (DART+) Calcd for C$_{17}$H$_{18}$N$_4$O$_4$ ($[M+H]^+$): 343.1406, Found: 343.1392; Anal. Calcd for C$_{17}$H$_{19}$N$_4$O$_4$: C, 59.64; H, 5.30; N, 16.37. Found: C, 59.99; H, 5.46; N, 16.28.

2-(tert-Butyl)-5-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methylxazole (3ea)

Yield: 71%. White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.02 (s, 6H), 2.05 (s, 3H), 1.36 (d, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 174.2, 172.7, 164.5, 145.8, 118.1, 55.9, 33.9, 28.4, 10.4; HRMS (DART+) Calcd for C$_{13}$H$_{19}$N$_4$O$_4$ ($[M+H]^+$): 295.1406, Found: 295.1400; Anal. Calcd for C$_{13}$H$_{18}$N$_4$O$_4$: C, 53.05; H, 6.16; N, 19.4. Found: C, 52.90; H, 6.21; N, 19.07.

1,4-Bis(5-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-2-phenyloxazole-2-yl)benzene (3fa)

Yield: 65%. White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (s, 4H), 4.04 (s, 12H), 2.16 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 174.2, 172.7, 154.3, 146.8, 128.6, 126.3, 121.3, 56.1, 10.6. HRMS (FAB+) Calcd for C$_{24}$H$_{23}$N$_8$O$_8$ ($[M+H]^+$): 551.1639, Found: 551.1633.

4-Benzyl-5-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-2-phenyloxazole (3ab)

Yield: 78%. Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.98-7.93 (m, 2H), 7.44-7.40 (m, 3H), 7.28-7.24 (m, 2H), 7.23-7.19 (m, 2H), 7.17-7.13 (m, 1H), 3.96 (s, 6H), 3.88 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 174.0, 172.6, 155.3, 147.0, 137.7, 130.4, 129.0, 128.8, 128.4, 127.4, 126.5, 126.1, 123.5, 56.0, 31.6; HRMS (DART+) Calcd for C$_{24}$H$_{23}$N$_8$O$_8$ ($[M+H]^+$): 391.1406, Found: 391.1383; Anal. Calcd for C$_{24}$H$_{24}$N$_8$O$_8$: C, 64.48; H, 4.86; N, 14.03.

5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-isopropyl-2-phenyloxazole (3ac)

Yield: 83%. Colorless oil. $^1$H NMR (CDCl$_3$): $\delta$ 7.98-7.92 (m, 2H), 7.45-7.39 (m, 3H), 4.02 (s, 6H), 2.89 (sep, $J = 6.9$ Hz, 1H), 1.27 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (CDCl$_3$): $\delta$ 174.2, 173.1, 155.0, 145.0, 130.2, 129.8, 128.8, 127.6, 126.0, 56.0, 14.03.
25.6, 21.2; HRMS (DART+) Calcd for C\(_{17}\)H\(_{19}\)N\(_4\)O\(_4\)\(^{+}\): 343.1406, Found: 343.1406; Anal. Calcd for C\(_{17}\)H\(_{18}\)N\(_4\)O\(_4\): C, 59.64; H, 5.30; N, 16.37. Found: C, 59.32; H, 5.49; N, 16.08.

5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-isobutyl-2-phenyloxazole (3ad)

Yield: 70%. Colorless oil. \(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.98-7.93 (m, 2H), 7.46-7.40 (m, 3H), 4.02 (s, 6H), 2.36 (d, \(J = 7.2\) Hz, 2H), 2.07 (m, 1H), 0.95 (d, \(J = 6.5\) Hz, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 174.1, 172.9, 155.0, 146.9, 130.2, 128.8, 127.5, 125.9, 124.1, 55.9, 33.9, 27.7, 22.4; HRMS (ESI+) Calcd for C\(_{18}\)H\(_{21}\)N\(_4\)O\(_4\)\(^{-}\): 357.1563, Found: 357.1580.

5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-(2-(methylthio)ethyl)-2-phenyloxazole (3ae)

Yield: 70%. White solid. \(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.98-7.92 (m, 2H), 7.45-7.41 (m, 3H), 4.03 (s, 6H), 2.86-2.81 (m, 2H), 2.82-2.77 (m, 2H), 2.12 (s, 3H); \(^{13}\)C NMR (150 Hz, CDCl\(_3\)): \(\delta\) 174.8, 172.8, 155.3, 146.7, 130.4, 128.9, 127.3, 126.0, 123.2, 56.0, 32.4, 25.5, 15.6; HRMS (DART+) Calcd for C\(_{19}\)H\(_{19}\)N\(_4\)O\(_4\)S\(^{+}\): 375.1127, Found: 375.1105; Anal. Calcd for C\(_{17}\)H\(_{18}\)N\(_4\)O\(_4\)S: C, 54.53; H, 4.85; N, 14.96. Found: C, 54.46; H, 4.91; N, 14.86.

5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-2,4-diphenyloxazole (3af)

Yield: 78%. Yellow solid. \(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.09-8.02 (m, 2H), 7.85-7.81 (m, 2H), 7.50-7.45 (m, 3H), 7.43-7.37 (m, 2H), 7.32-7.27 (m, 1H), 3.97 (s, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 174.1, 172.5, 155.2, 145.8, 130.5, 130.0, 128.8, 128.7, 128.0, 127.8, 127.1, 126.1, 126.0, 125.8, 125.6, 123.8, 55.9; HRMS (DART+) Calcd for C\(_{20}\)H\(_{19}\)N\(_4\)O\(_4\)\(^{+}\): 377.1250, Found: 377.1238.
General procedure for the synthesis of 5

**Conditions A:** To a round-bottom flask equipped with a reflux condenser were added 5-(triazinyl)oxazole 3aa (100 mg, 0.318 mmol), phenylboronic acid (4a, 155 mg, 1.27 mmol), NiCl2(dppf) (10.9 mg, 0.0159 mmol), K3PO4 (473 mg, 2.23 mmol), LiCl (40.4 mg, 0.954 mmol) and toluene (2.3 mL) in N2. After the reaction mixture was stirred at 110 °C for 3 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted in CH2Cl2 (10 mL), filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (CH2Cl2:hexane = 70:30) to give 5aaa as a white solid.

**Conditions B:** To a screw-capped tube was added 5-(triazinyl)oxazole 3aa (100 mg, 0.318 mmol), 4-ethoxycarbonylphenylboronic acid (4b, 246 mg, 1.27 mmol), NiCl2(dppf) (10.9 mg, 0.0159 mmol), K3PO4 (473 mg, 2.23 mmol), LiCl (40.4 mg, 0.954 mmol), DPPF (8.8 mg, 0.0159 mmol) and toluene (2.3 mL) in N2. After the mixture was stirred at 110 °C for 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted in CH2Cl2 (10 mL), filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc:hexane = 10:90) to give 5aab (62.5 mg, 64%) as a white solid.

**4-Methyl-2,5-diphenyloxazole (5aaa)**

![Image of 4-Methyl-2,5-diphenyloxazole](image)

Synthesized under conditions A in 68% yield. White solid. 1H NMR (400 MHz, CDCl3): δ 8.12-8.06 (m, 2H), 7.72-7.66 (m, 2H), 7.50-7.41 (m, 5H), 7.37-7.30 (m, 1H), 2.51 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 159.5, 145.6, 133.5, 130.3, 129.3, 128.94, 128.91, 127.8, 127.6, 126.4, 125.5, 13.7; HRMS (DART+) Calcd for C16H14NO+ ([M+H]+): 236.1075, Found: 236.1065.

**4-Methyl-2-phenyl-5-(4-ethoxycarbonylphenyl)oxazole (5aab)**

![Image of 4-Methyl-2-phenyl-5-(4-ethoxycarbonylphenyl)oxazole](image)

Synthesized under conditions B in 64% yield (6 h). White solid. 1H NMR (600 MHz, CDCl3): δ 8.15-8.11 (m, 2H), 8.11-8.07 (m, 2H), 7.77-7.72 (m, 2H), 7.51-7.43 (m, 3H), 4.41 (q, J = 7.2 Hz, 2H), 2.54 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); 13C NMR (150 MHz, CDCl3): δ 166.3, 160.2, 144.8, 135.7, 133.3, 130.6, 130.2, 129.2, 129.0, 127.3, 126.5, 124.8, 61.2, 14.5, 14.0; HRMS (DART+) Calcd for C19H18NO3 ([M+H]+): 308.1287, Found: 308.1297; Anal. Calcd for C19H18NO3: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.27; H, 5.70; N, 4.45.

**4-Methyl-5-(4-methoxyphenyl)-2-phenyloxazole (5aac)**

![Image of 4-Methyl-5-(4-methoxyphenyl)-2-phenyloxazole](image)

Synthesized under conditions B in 67% yield (6 h). White solid. 1H NMR (600 MHz, CDCl3): δ 8.09-8.04 (m, 2H), 7.63-7.58 (m, 2H), 7.48-7.39 (m, 3H), 7.02-6.97 (m, 2H), 3.85 (s, 3H), 2.46 (s, 3H); 13C NMR (150 MHz, CDCl3): δ 159.3, 159.0, 145.7, 132.0, 130.1, 128.9, 127.7, 127.0, 126.2, 122.1, 144.4, 55.5, 13.5; HRMS (DART+) Calcd for C15H16NO3 ([M+H]+): 266.1181, Found: 266.1205.
4-Methyl-5-(2-naphyl)-2-phenyloxazole (5aad)

Synthesized under conditions A in 77% yield (1 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.16-8.09 (m, 3H), 7.94-7.88 (m, 2H), 7.87-7.80 (m, 2H), 7.55-7.43 (m, 5H), 2.59 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.7, 145.8, 134.0, 133.5, 132.7, 130.4, 128.9, 128.7, 128.3, 127.9, 127.6, 126.8, 126.7, 126.5, 126.4, 124.4, 123.3, 13.9; HRMS (DART+) Calcd for C$_{20}$H$_{16}$NO ([M+H]+): 286.1232, Found: 286.1231. Anal. Calcd for C$_{20}$H$_{15}$NO: C, 84.19; H, 5.30; N, 4.91. Found: C, 83.95; H, 5.36; N, 4.87.

4-Methyl-2-phenyl-5-(4-tolyl)oxazole (5aae)

Synthesized under conditions A in 71% yield (6 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.10-8.06 (m, 2H), 7.60-7.56 (m, 2H), 7.49-7.41 (m, 3H), 7.30-7.25 (m, 2H), 2.48 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.2, 145.8, 137.7, 132.8, 130.2, 129.6, 128.9, 127.7, 126.5, 126.3, 125.5, 21.5, 13.6; HRMS (DART+) Calcd for C$_{17}$H$_{16}$NO ([M+H]+): 250.1232, Found: 250.1243.

4-Methyl-2-phenyl-5-(2-tolyl)oxazole (5aaf)

Synthesized under conditions B in 46% yield (6 h). Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.08-8.03 (m, 2H), 7.48-7.40 (m, 3H), 7.40-7.36 (m, 1H), 7.35-7.25 (m, 3H), 2.42 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 160.2, 146.2, 137.6, 134.3, 131.0, 130.2, 129.9, 129.1, 128.9, 128.2, 127.8, 126.2, 125.9, 20.7, 12.6; HRMS (DART+) Calcd for C$_{17}$H$_{16}$NO ([M+H]+): 250.1232, Found: 250.1251. Anal. Calcd for C$_{17}$H$_{13}$NO: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.13; H, 6.27; N, 5.43.

4-Methyl-2-phenyl-5-(3-thienyl)oxazole (5aag)

Synthesized under conditions B in 68% yield (6 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.08-8.04 3(m(2H), 7.51-7.47 (m, 1H), 7.47-7.39 (m, 5H), 2.44 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.0, 143.0, 132.5, 130.2, 130.1, 128.9, 127.5, 126.6, 126.2, 125.2, 120.6, 13.1; HRMS (DART+) Calcd for C$_{14}$H$_{12}$NOS ([M+H]+): 242.0640, Found: 242.0668. Anal. Calcd for C$_{14}$H$_{11}$NOS: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.73; H, 4.79; N, 5.61.

4-Methyl-2-(4-methoxyphenyl)-5-phenyloxazole (5baa)

Synthesized under conditions B in 68% yield (6 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.08-8.04 3(m(2H), 7.51-7.47 (m, 1H), 7.47-7.39 (m, 5H), 2.44 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.0, 143.0, 132.5, 130.2, 130.1, 128.9, 127.5, 126.6, 126.2, 125.2, 120.6, 13.1; HRMS (DART+) Calcd for C$_{14}$H$_{12}$NOS ([M+H]+): 242.0640, Found: 242.0668. Anal. Calcd for C$_{14}$H$_{11}$NOS: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.73; H, 4.79; N, 5.61.
Synthesized under conditions A in 69% yield (4 h). White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04-7.99 (m, 2H), 7.69-7.64 (m, 2H), 7.49-7.42 (m, 2H), 7.34-7.28 (m, 1H), 7.00-6.95 (m, 2H), 3.86 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.4, 159.6, 145.0, 133.3, 129.5, 128.9, 128.0, 127.5, 125.3, 120.4, 114.3, 55.5, 13.7; HRMS (DART+) Calcd for C$_{17}$H$_{16}$NO$_2$ ([M+H]+): 266.1181, Found: 266.1175.

2-(4-Formylphenyl)-4-methyl-5-phenyloxazole (5caa)

![Chemical structure image]

Synthesized under conditions A in 64% yield (4 h). White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.1 (s, 1H), 8.28-8.22 (m, 2H), 8.01-7.96 (m, 2H), 7.74-7.68 (m, 2H), 7.53-7.46 (m, 2H) 7.41-7.34 (m, 1H), 2.53 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.7, 158.1, 146.8, 137.1, 134.3, 132.6, 130.3, 129.1, 128.8, 128.3, 126.7, 125.7, 13.7; HRMS (DART+) Calcd for C$_{17}$H$_{16}$NO$_2$ ([M+H]+): 264.1025, Found: 264.1054; Anal. Calcd for C$_{17}$H$_{16}$NO$_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.50; H, 5.05; N, 5.31.

4-Methyl-2-phenethyl-5-phenyloxazole (5daa)

![Chemical structure image]

Synthesized under conditions A in 68% yield (2 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.58-7.53 (m, 2H), 7.44-7.39 (m, 2H), 7.32-7.27 (m, 3H), 7.26-7.19 (m, 3H), 3.16-3.10 (m, 2H) 3.11-3.05 (m, 2H), 2.40 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 162.0, 145.2, 140.6, 131.7, 129.4, 128.8, 128.7, 128.4, 127.5, 126.5, 125.3, 33.4, 30.2, 13.4; HRMS (DART+) Calcd for C$_{18}$H$_{19}$NO ([M+H]+): 264.1388, Found: 264.1395; Anal. Calcd for C$_{18}$H$_{19}$NO: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.00; H, 6.64; N, 5.28.

4-Methyl-2-tert-butyl-5-phenyloxazole (5eaa)

![Chemical structure image]

Synthesized under conditions A in 73% yield (4 h). Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61-7.55 (m, 2H), 7.46-7.39 (m, 2H), 7.32-7.25 (m, 1H), 2.40 (s, 3H), 1.43 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 169.3, 144.7, 131.3, 129.7, 128.8, 127.3, 125.3, 33.7, 28.8, 13.4; HRMS (DART+) Calcd for C$_{18}$H$_{19}$NO ([M+H]+): 216.1387. Found: 216.1387.

2,2'-(1, 4-Phenylene) bis(4-methyl-5-phenyloxazole) (5faa)

![Chemical structure image]

Synthesized under conditions B in 63% yield (6 h). Yellow solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.18 (s, 4H), 7.75-7.68 (m, 4H), 7.52-7.45 (m, 4H), 7.39-7.32 (m, 2H), 2.53 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 158.9, 146.1, 133.9, 129.1, 129.0, 128.7, 128.0, 126.7, 125.6, 13.7. HRMS (FAB+) Calcd for C$_{38}$H$_{37}$N$_2$O$_2$ ([M+H]+): 393.1603, Found: 393.1591.

4-Benzyl-2,5-diphenyloxazole (5aba)


Synthesized under conditions A in 60% (4 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.13-8.09 (m, 2H), 7.69-7.64 (m, 2H), 7.49-7.40 (m, 5H), 7.36-7.27 (m, 5H), 7.24-7.19 (m, 1H), 4.22 (s, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 160.0, 146.7, 138.7, 135.9, 130.4, 129.0, 128.91, 128.88, 128.7, 128.6, 128.2, 127.6, 126.5, 125.8, 33.3; HRMS (DART+) Calcd for C$_{22}$H$_{18}$NO ([M+H]$^+$): 312.1388, Found: 312.1390.

4-Isopropyl-2,5-diphenyloxazole (5aca)$^5$

Synthesized under conditions B in 54% yield (6 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.13-8.07 (m, 2H), 7.68-7.62 (m, 2H), 7.49-7.40 (m, 5H), 7.37-7.31 (m, 1H), 3.29 (d, $J = 6.8$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.9, 144.1, 143.5, 130.1, 129.6, 128.9, 128.8, 128.0, 127.8, 126.5, 126.1, 22.2; HRMS (DART+) Calcd for C$_{18}$H$_{18}$NO ([M+H]$^+$): 264.1388, Found: 264.1394.

4-Isobutyl-2,5-diphenyloxazole (5ada)

Synthesized under conditions B in 62% yield (6 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.12-8.07 (m, 2H), 7.72-7.67 (m, 2H), 7.48-7.40 (m, 5H), 7.35-7.30 (m, 1H), 2.71 (d, $J = 7.3$ Hz, 2H), 2.22 (d, $J = 6.5$ Hz, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.6, 146.0, 137.5, 130.2, 129.5, 128.9, 128.8, 127.81, 127.77, 126.4, 125.8, 36.3, 28.5, 22.7; HRMS (DART+) Calcd for C$_{19}$H$_{20}$NO ([M+H]$^+$): 278.1545, Found: 278.1535; Anal. Calcd for C$_{19}$H$_{19}$NO: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.19; H, 6.93; N, 5.00.

4-(2-(Methylthio)ethyl)-2,5-diphenyloxazole (5aea)

Synthesized under conditions A in 62% yield (4 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.11-8.06 (m, 2H), 7.72-7.67 (m, 2H), 7.50-7.42 (m, 5H), 7.38-7.33 (m, 1H), 3.15-3.10 (m, 2H), 2.99-2.94 (m, 2H), 2.17 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 159.9, 146.1, 136.1, 130.4, 129.02, 128.99, 128.89, 128.2, 127.6, 126.5, 125.9, 33.1, 27.8, 15.9; HRMS (DART+) Calcd for C$_{18}$H$_{18}$NOS ([M+H]$^+$): 296.1109, Found: 296.1110.

2,4,5-Triphenyloxazole (5afa)$^6$

Synthesized under conditions B in 47% yield (6 h). White solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.18-8.13 (m, 2H), 7.75-7.65 (m, 4H), 7.51-7.44 (m, 3H), 7.43-7.31 (m, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 160.3, 145.7, 136.9, 132.7, 130.5, 129.1, 128.9, 128.82, 128.76, 128.69, 128.4, 128.3, 127.5, 126.7, 126.6; HRMS (DART+) Calcd for C$_{22}$H$_{16}$NO ([M+H]$^+$): 298.1232, Found: 298.1227
4. References
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5. $^1$H and $^{13}$C NMR spectra
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methyl-2-phenyloxazole (3aa)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-2-(4-methoxyphenyl)-4-methylloxazole (3ba)
5-(5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-2-(4-formylphenyl)-4-methylloxazole (3ca)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methyl-2-phenyloxazole (3da)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
2-\((t\text{er}-\text{t})\text{-Butyl}\)-5-\(((4,6\text{-dimethoxy-1,3,5\text{-triazin-2-yl})\text{oxy})\text{-4-methyl}\text{oxazole (3ea)}

\text{\(^1\text{H NMR (400 MHz, CDCl}_3\)}

\text{\(^{13}\text{C NMR (100 MHz, CDCl}_3\)}
1,4-Bis(5-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methyloxazol-2-yl)benzene (3fa)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
4-Benzyl-5-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-2-phenyloxazole (3ab)

\[\text{\textsuperscript{1}H NMR (600 MHz, CDCl}_3\text{)}\]

\[\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{)}\]
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-isopropyl-2-phenyloxazole (3ac)
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-isobutyl-2-phenyloxazole (3ad)
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-(2-(methylthio)ethyl)-2-phenyloxazole (3ae)

$^1$H NMR (600 MHz, CDCl₃)

$^{13}$C NMR (150 MHz, CDCl₃)
5-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-2,4-diphenyloxazole (3af)

\[ \text{\(^1\)H NMR (600 MHz, CDCl\textsubscript{3})} \]

\[ \begin{align*}
\text{Ph} & \quad \text{O} \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{O} \quad \text{Me} \\
\text{O} & \quad \text{Me} \\
\end{align*} \]

\text{3af}

\[ \text{\(^1\)C NMR (150 MHz, CDCl\textsubscript{3})} \]

\[ \begin{align*}
\text{Ph} & \quad \text{O} \quad \text{N} \quad \text{N} \\
\text{N} & \quad \text{O} \quad \text{Me} \\
\text{N} & \quad \text{O} \quad \text{Me} \\
\end{align*} \]

\text{3af}
4-Methyl-2,5-diphenyloxazole (5aaa)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
4-Methyl-2-phenyl-5-(4-ethoxycarbonylphenyl)oxazole (5aab)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-5-(4-methoxyphenyl)-2-phenyloxazole (5aac)

\(^1\)H NMR (600 MHz, CDCl\(_3\))

\(^{13}\)C NMR (150 MHz, CDCl\(_3\))
4-Methyl-5-(2-naphtyl)-2-phenyloxazole (5aad)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-2-phenyl-5-(4-tolyl)oxazole (5aae)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-2-phenyl-5-(2-tolyl)oxazole (5aaf)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-2-phenyl-5-(3-thienyl)oxazole (5aag)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-2-(4-methoxyphenyl)-5-phenyloxazole (5baa)

\[ \text{1H NMR (600 MHz, CDCl}_3) \]

\[ \text{13C NMR (150 MHz, CDCl}_3) \]

S30
2-(4-Formylphenyl)-4-methyl-5-phenyloxazole (5caa)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-2-phenethyl-5-phenyloxazole (5daa)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Methyl-2-tert-butyl-5-phenyloxazole (5eaa)

\[ \text{\textsuperscript{1}H NMR (600 MHz, CDCl}_3\text{)} \]

\[ \text{\textsuperscript{13}C NMR (150 MHz, CDCl}_3\text{)} \]
2, 2’-(1,4-Phenylene) bis(4-methyl-5-phenyl)oxazole (5faa)

$^1$H NMR (600 MHz, CDCl$_3$)

5faa

$^{13}$C NMR (150 MHz, CDCl$_3$)

5faa
4-Benzyl-2,5-diphenyloxazole (5aba)

$^1$H NMR (600 MHz, CDCl$_3$)

![NMR spectrum](image)

$^{13}$C NMR (150 MHz, CDCl$_3$)

![NMR spectrum](image)
4-Isopropyl-2,5-diphenyloxazole (5aca)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
4-Isobutyl-2,5-diphenyloxazole (5ada)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)

S37
4-(2-(Methylthio)ethyl)-2,5-diphenyloxazole (5aea)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
2,4,5-Triphenyloxazole (5afa)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)

S39