Supporting Information

Synthesis of Functionalized Benzoxazines by Copper-Catalyzed C(sp³)-H Bond Functionalization of Acetonitrile with Olefinic Amides

Xue-Qiang Chu, Xiao-Ping Xu,* Hua Meng and Shun-Jun Ji*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, 215123, China. Fax: (+)86 512o 65880307; Tel: +86-512-65880307; E-mail: xuxp@suda.edu.cn; shunjun@suda.edu.cn

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General procedure for oxycyanomethylation of olefinic amides with acetonitrile

Olefinic amide 1 (0.2 mmol), acetonitrile 2 (2 mL), Cu(OTf)₂ (0.1 mmol), 1,10-phenanthroline (0.2 mmol), K₃PO₄ (0.6 mmol) and di-tert-butyl peroxide (0.5 mmol) was stirred at 140 °C under air in pressure-tight tube. Upon completion of the reaction (indicated by TLC), solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography purification afforded pure product 3 with petroleum/ethyl acetate as the eluent.
Table S1: Optimization of the reaction conditions

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<th>Oxidant (equiv)</th>
<th>Base (equiv)</th>
<th>Time (h)</th>
<th>Temp. (°C)</th>
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*Reaction conditions: 1a (0.2 mmol), 2a (2 mL), catalyst (1 equiv), base (3 equiv) and oxidant (2.5 equiv) at 140 °C under air; DTBP = di-tert-butyperoxide; TBPB = tert-butyperoxybenzoate; DCP = dicumyl peroxide; BPO = benzoyl peroxide. Yields were determined by GC with an internal standard (biphenyl) as the ratio between the formed products and the initial amount of limiting reactant. Isolated yields. Under air. Under Argon atmosphere.
Figure S1: Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO).
Analytical and spectral data for compounds:

3-(4-methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3aa): Yield = 64%. Yellow oil. IR (KBr) \( \nu \) = 3030, 2927, 2853, 2247, 1624, 1572, 1321, 1262, 1066, 764, 694 cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta \) = 8.16–8.10 (m, 2H), 7.54–7.44 (m, 3H), 7.36–7.31 (m, 2H), 7.25–7.21 (m, 1H), 7.08 (d, \( J = 7.5 \) Hz, 1H), 2.53–2.45 (m, 2H), 2.44–2.31 (m, 2H), 1.70 (s, 3H) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) = 156.0, 139.1, 132.5, 131.8, 129.5, 128.6, 128.0, 127.4, 127.3, 126.1, 122.5, 119.5, 79.7, 36.9, 28.3, 12.6 ppm. HRMS m/z: calcd for C\(_{18}\)H\(_{17}\)N\(_2\)O \([\text{M+H}]^+\) 277.1341, found: 277.1351.

3-(2-(4-methoxyphenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ba): Yield = 58%. Brown oil. IR (KBr) \( \nu \) = 2959, 2922, 2839, 2247, 1595, 1509, 1247, 1166, 1026, 768 cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta \) = 8.08 (d, \( J = 8.9 \) Hz, 2H), 7.36–7.27 (m, 2H), 7.23–7.17 (m, 1H), 7.06 (d, \( J = 7.8 \) Hz, 1H), 6.96 (d, \( J = 8.9 \) Hz, 2H), 3.87 (s, 3H), 2.53–2.42 (m, 2H), 2.42–2.31 (m, 2H), 1.68 (s, 3H) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) = 162.7, 156.0, 139.4, 129.8, 129.4, 127.3, 126.8, 125.7, 124.9, 122.5, 119.5, 113.9, 79.5, 55.6, 36.8, 28.2, 12.6 ppm. HRMS m/z: calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O \([\text{M+H}]^+\) 307.1447, found: 307.1455.

3-(2-(4-ethylphenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ca): Yield = 53%.
Yellow oil. IR (KBr) \( \nu = 2965, 2929, 2871, 2247, 1621, 1596, 1482, 1321, 1262, 1066, 842, 767 \) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 8.04 \) (d, \( J = 8.3 \) Hz, 2H), 7.34–7.25 (m, 4H), 7.25–7.18 (m, 1H), 7.07 (d, \( J = 7.5 \) Hz, 1H), 2.71 (q, \( J = 7.6 \) Hz, 2H), 2.52–2.42 (m, 2H), 2.43–2.32 (m, 2H), 1.69 (s, 3H), 1.27 (t, \( J = 7.6 \) Hz, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.2, 148.6, 139.3, 129.9, 129.4, 128.1, 128.1, 127.4, 127.1, 125.9, 122.5, 119.5, 79.5, 36.9, 29.1, 28.3, 15.6, 12.6 \) ppm. HRMS m/z: calcd for C\(_{20}\)H\(_{21}\)N\(_2\)O \([\text{M+H}]^+\) 305.1654, found: 305.1655.

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\text{O} \\
\text{C} \\
\text{N}
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3-(4-methyl-2-m-tolyl-4\(^H\)-benzo[\(d\)]\([1,3]\)oxazin-4-yl)propanenitrile (3da): Yield = 54%. Yellow oil. IR (KBr) \( \nu = 2958, 2919, 2850, 2247, 1624, 1573, 1482, 1263, 1077, 767, 714 \) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 7.94 \) (s, 1H), 7.91 (d, \( J = 6.7 \) Hz, 1H), 7.37–7.30 (m, 4H), 7.25–7.19 (m, 1H), 7.07 (d, \( J = 7.5 \) Hz, 1H), 2.54–2.49 (m, 2H), 2.43 (s, 3H), 2.42–2.31 (m, 2H), 1.70 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.3, 139.1, 138.3, 132.7, 132.4, 129.5, 128.5, 128.5, 127.4, 127.2, 126.0, 125.1, 122.5, 119.5, 79.7, 36.9, 28.3, 21.6, 12.6 \) ppm. HRMS m/z: calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O \([\text{M+H}]^+\) 291.1498, found: 291.1501.

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\begin{array}{c}
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\text{O} \\
\text{C} \\
\text{N}
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3-(2-(3-(dimethylamino)phenyl)-4-methyl-4\(^H\)-benzo[\(d\)]\([1,3]\)oxazin-4-yl)propanenitrile (3ea): Yield = 31%. Brown oil. IR (KBr) \( \nu = 2971, 2926, 2901, 2805, 2247, 1592, 1481, 1259, 1076, 994, 868, 767, 720, 683 \) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 7.51 \) (dd, \( J = 2.5, 1.6 \) Hz, 1H), 7.43 (d, \( J = 7.7 \) Hz, 1H), 7.36–7.28 (m, 3H), 7.24–7.20 (m, 1H), 7.07 (d, \( J = 7.6 \) Hz, 1H), 6.89 (dd, \( J = 8.0, 2.4 \) Hz, 1H), 3.03 (s, 6H), 2.57–2.44 (m, 2H), 2.43–2.33 (m, 2H), 1.70 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.8, 150.8, 139.3, 133.2, 129.4, 129.2, 127.6, 127.1, 126.1, 122.5, 119.6, 116.3, 116.1, 111.7, 79.5, 40.9, 36.9, 28.2, 12.6 ppm. HRMS m/z: calcd for C\(_{20}\)H\(_{22}\)N\(_3\)O \([\text{M+H}]^+\) 320.1763, found: 320.1757.
3-(2-(4-fluorophenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3fa): Yield = 57%. Yellow oil. IR (KBr) ν = 2972, 2927, 2901, 2248, 1635, 1598, 1482, 1320, 1152, 1066, 845, 807, 768, 710 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.17–8.10 (m, 2H), 7.37–7.29 (m, 2H), 7.26–7.21 (m, 1H), 7.17–7.10 (m, 2H), 7.08 (dd, J = 7.6, 0.9 Hz, 1H), 2.51–2.43 (m, 2H), 2.43–2.32 (m, 2H), 1.70 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 155.2, 139.0, 130.3, 130.2, 129.6, 128.7 (d, J = 2.9 Hz), 127.4, 127.2, 126.1, 122.6, 119.4, 115.7 (d, J = 21.8 Hz), 80.0, 36.9, 28.5, 12.7 ppm. ¹⁹F NMR (376MHz, CDCl₃): δ = -107.9 ppm. HRMS m/z: calcd for C₁₈H₁₆FN₂O [M+H]⁺ 295.1247, found: 295.1252.

3-(2-(4-chlorophenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ga): Yield = 64%. Yellow oil. IR (KBr) ν = 3034, 2973, 2928, 2853, 2248, 1921, 1623, 1595, 1485, 1401, 1320, 1262, 1169, 1088, 838, 767 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.10–8.03 (m, 2H), 7.46–7.40 (m, 2H), 7.37–7.29 (m, 2H), 7.24 (dd, J = 6.9, 1.9 Hz, 1H), 7.10–7.05 (m, 1H), 2.53–2.42 (m, 2H), 2.42–2.31 (m, 2H), 1.70 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 138.9, 138.1, 131.0, 129.6, 129.3, 128.9, 127.6, 127.3, 126.1, 122.6, 119.4, 80.0, 36.9, 28.5, 12.7 ppm. HRMS m/z: calcd for C₁₈H₁₆ClN₂O [M+H]⁺ 311.0952, found: 311.0949.

3-(2-(4-bromophenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ha): Yield = 55%. Yellow oil. IR (KBr) ν = 2967, 2926, 2852, 2247, 1622, 1483, 1320, 1261, 1068, 1009, 835,
767 cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 7.99\) (d, \(J = 8.6\) Hz, 2H), 7.59 (d, \(J = 8.6\) Hz, 2H), 7.34 (td, \(J = 7.9, 3.6\) Hz, 2H), 7.24 (dd, \(J = 10.4, 3.5\) Hz, 1H), 7.07 (d, \(J = 7.7\) Hz, 1H), 2.54 – 2.42 (m, 2H), 2.43 – 2.31 (m, 2H), 1.69 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.2, 138.9, 131.8, 131.5, 129.6, 129.5, 127.6, 127.3, 126.6, 126.1, 122.6, 119.4, 80.1, 36.8, 28.5, 12.6\) ppm. HRMS m/z: calcd for C\(_{18}\)H\(_{16}\)BrN\(_2\)O \([\text{M+H}]^+\) 355.0447, found: 355.0457.

![Image](https://via.placeholder.com/150)

3-(2-(3-iodophenyl)-4-methyl-4\(^H\)-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ia): Yield = 49%.

Yellow oil. IR (KBr) \(\nu = 3061, 2972, 2901, 2247, 1622, 1597, 1417, 1316, 1076, 870, 766, 710\) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.45\) (t, \(J = 1.6\) Hz, 1H), 8.13–8.05 (m, 1H), 7.85–7.82 (m, 1H), 7.38–7.30 (m, 2H), 7.27–7.23 (m, 1H), 7.19 (t, \(J = 7.9\) Hz, 1H), 7.10–7.04 (m, 1H), 2.52–2.31 (m, 4H), 1.70 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.4, 140.6, 138.7, 136.7, 134.5, 130.2, 129.6, 127.7, 127.3, 127.1, 126.2, 122.6, 119.3, 94.2, 80.2, 36.8, 28.5, 12.7\) ppm. HRMS m/z: calcd for C\(_{18}\)H\(_{16}\)IN\(_2\)O \([\text{M+H}]^+\) 403.0308, found: 403.0308.

![Image](https://via.placeholder.com/150)

3-(4-methyl-2-(4-(methylsulfonyl)phenyl)-4\(^H\)-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ja): Yield = 58%.

White solid. M.p. 137.7–138.6 °C. IR (KBr) \(\nu = 2925, 2852, 2251, 1623, 1597, 1297, 1261, 1150, 1066, 957, 770\) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.39–8.32\) (m, 2H), 8.08–8.02 (m, 2H), 7.42–7.36 (m, 2H), 7.34–7.29 (m, 1H), 7.11 (d, \(J = 7.3\) Hz, 1H), 3.11 (s, 3H), 2.55–2.47 (m, 2H), 2.46–2.36 (m, 2H), 1.75 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.1, 143.0, 138.5, 137.6, 129.8, 128.8, 128.3, 127.3, 126.6, 122.7, 119.2, 80.6, 44.7, 36.9, 28.7, 12.7\) ppm. HRMS m/z: calcd for C\(_{19}\)H\(_{16}\)N\(_2\)O\(_3\)S \([\text{M+H}]^+\) 355.1117, found: 355.1117.
3-(4-methyl-2-(4-nitrophenyl)-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ka): Yield = 54%. Yellow solid. M.p. 84.5–85.6 °C. (KBr) v = 2927, 2852, 2247, 1625, 1519, 1344, 1317, 1264, 1067, 862, 760, 703 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.35–8.27 (m, 4H), 7.41–7.35 (m, 2H), 7.33–7.27 (m, 1H), 7.10 (d, J = 7.7 Hz, 1H), 2.53–2.45 (m, 2H), 2.45–2.34 (m, 2H), 1.73 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 153.9, 149.8, 138.4, 138.3, 129.8, 128.9, 128.4, 127.2, 126.6, 123.7, 122.7, 119.2, 80.7, 77.6, 77.2, 76.9, 36.9, 28.7, 12.7 ppm. HRMS m/z: calcd for C₁₈H₁₆N₃O₃ [M+H]+ 322.1192, found: 322.1192.

3-(2-(2-chlorophenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3la): Yield = 25%. Yellow oil. IR (KBr) v = 3058, 2926, 2855, 2248, 1600, 1565, 1485, 1461, 1345, 1245, 1155, 1066, 822, 758 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.80 (dd, J = 8.0, 1.7 Hz, 1H), 7.44–7.39 (m, 1H), 7.37–7.33 (m, 1H), 7.28–7.25 (m, 2H), 7.09 (dd, J = 7.9, 1.3 Hz, 1H), 7.01 (dd, J = 8.3, 0.9 Hz, 1H), 6.93–6.88 (m, 1H), 2.54–2.47 (m, 2H), 2.46–2.37 (m, 2H), 1.74 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 161.5, 158.5, 136.6, 134.2, 129.8, 127.7, 126.9, 124.9, 122.9, 119.2, 118.9, 117.8, 113.8, 80.6, 36.8, 28.3, 12.6 ppm. HRMS m/z: calcd for C₁₈H₁₆ClN₂O [M+H]+ 311.0952, found: 311.0953.

3-(4-methyl-2-(2-nitrophenyl)-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ma): Yield = 42%. Yellow oil. IR (KBr) v = 3070, 2977, 2854, 2248, 2227, 1634, 1529, 1484, 1445, 1350,
1322, 1118, 862, 769 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.98 (dd, J = 7.6, 1.5 Hz, 1H), 7.81 (dd, J = 7.9, 1.3 Hz, 1H), 7.69–7.61 (m, 2H), 7.36–7.32 (m, 1H), 7.30–7.26 (m, 2H), 7.05 (dd, J = 7.8, 1.4 Hz, 1H), 2.53–2.39 (m, 2H), 2.39–2.26 (m, 2H), 1.69 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.4 149.3, 138.1 132.5, 131.5, 131.2 129.6, 128.3, 127.8, 126.9, 126.4, 124.0, 122.8, 119.4, 81.6, 37.2, 28.9, 12.6 ppm. HRMS m/z: calcd for C₁₈H₁₆N₃O₃ [M+H]⁺ 322.1192, found: 322.1194.

3-(2-(2,4-dinitrophenyl)-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3na): Yield = 18%. Yellow solid. M.p. 127.2–128.9 °C. IR (KBr) ν = 2920, 2850, 2247, 1592, 1346, 1052, 832, 767, 738 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.61 (d, J = 2.1 Hz, 1H), 8.49 (dd, J = 8.6, 2.2 Hz, 1H), 8.28 (d, J = 8.6 Hz, 1H), 7.40–7.28 (m, 3H), 7.10–7.02 (m, 1H), 2.49–2.40 (m, 2H), 2.39–2.30 (m, 2H), 1.71 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 152.2, 149.5, 148.8, 137.5, 132.7, 132.6, 129.9, 129.1, 126.9, 126.8, 126.5, 122.9, 119.5, 82.5, 77.6, 77.2, 76.9, 37.1, 29.1, 12.6 ppm. HRMS m/z: calcd for C₁₈H₁₃N₄O₅ [M+H]⁺ 367.1043, found: 367.1034.

3-(2-(4-methyl-2-(naphthalen-2-yl)-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3oa): Yield = 55%. Yellow oil. IR (KBr) ν = 3057, 2968, 2927, 2247, 1619, 1593, 1570, 1482, 1318, 1264, 1064, 957, 864, 769, 749 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.59 (s, 1H), 8.25 (dd, J = 8.7, 1.7 Hz, 1H), 8.00–7.96 (m, 1H), 7.89 (t, J = 8.8 Hz, 2H), 7.60–7.51 (m, 2H), 7.41–7.33 (m, 2H), 7.26 (q, J = 2.0 Hz, 1H), 7.13–7.09 (m, 1H), 2.60–2.49 (m, 2H), 2.50–2.35 (m, 2H), 1.76 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 156.1, 139.2, 135.2, 132.9, 129.8, 129.6, 129.3, 129.5, 128.3, 128.0, 127.9, 127.5, 127.4, 126.8, 126.1, 124.6, 122.6, 119.5, 79.9, 36.9, 28.4, 12.7 ppm. HRMS m/z: calcd for C₂₂H₁₉N₂O [M+H]⁺ 327.1498, found: 327.1494.
3-(4-methyl-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3pa): Yield = 47%. Yellow oil. IR (KBr) \( \tilde{\nu} = 3100, 2072, 2926, 2852, 2247, 1619, 1592, 1481, 1424, 1262, 1059, 1032, 850, 767, 715 \) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 7.73 \) (dd, \( J = 3.7, 1.2 \) Hz, 1H), 7.51 (dd, \( J = 5.0, 1.2 \) Hz, 1H), 7.35–7.27 (m, 2H), 7.24–7.18 (m, 1H), 7.12 (dd, \( J = 5.0, 3.7 \) Hz, 1H), 7.06 (dd, \( J = 7.6, 1.0 \) Hz, 1H), 2.56–2.43 (m, 2H), 2.42–2.33 (m, 2H), 1.70 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 152.7, 139.0, 136.9, 130.8, 130.1, 129.5, 128.0, 127.5, 127.1, 126.9, 125.8, 122.6, 119.4, 80.1, 36.7, 28.0, 12.5 \) ppm. HRMS m/z: calcd for C\(_{16}\)H\(_{15}\)N\(_2\)OS \([\text{M+Na}]^+\) 283.0906, found: 283.0908.

3-(2,4-diphenyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3qa): Yield = 36%. Yellow solid. M.p. 98.2–99.8 °C. IR (KBr) \( \tilde{\nu} = 3059, 2927, 2246, 1517, 1445, 1318, 1248, 1024, 766, 696 \) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 8.22 \) (d, \( J = 7.2 \) Hz, 2H), 7.54–7.45 (m, 3H), 7.38 (dd, \( J = 12.0, 7.0 \) Hz, 2H), 7.28 (dd, \( J = 9.8, 6.7 \) Hz, 8H), 2.86–2.77 (m, 2H), 2.63–2.51 (m, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.1, 142.1, 139.0, 132.2, 132.0, 129.9, 128.9, 128.7, 128.7, 128.1, 127.1, 126.3, 126.0, 125.6, 124.1, 119.5, 82.8, 77.6, 77.2, 76.9, 36.5, 13.2 \) ppm. HRMS m/z: calcd for C\(_{23}\)H\(_{19}\)N\(_2\)O \([\text{M+H}]^+\) 339.1498, found: 339.1497.

3-(2,4-dimethyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ra): Yield = 26%. Yellow oil. IR (KBr) \( \tilde{\nu} = 3064, 2973, 2855, 2247, 1640, 1522, 1484, 1376, 1263, 1082, 754 \) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta = 7.32–7.28 \) (m, 1H), 7.23–7.14 (m, 2H), 7.01 (dd, \( J = 7.6, 1.3 \) Hz, 1H), 6.87 (dd, \( J = 10.7, 7.6 \) Hz, 1H), 2.55–2.46 (m, 2H), 2.32–2.24 (m, 2H). HRMS m/z: calcd for C\(_{18}\)H\(_{17}\)N\(_2\)OS \([\text{M+Na}]^+\) 251.0726, found: 251.0727.
3-(2-tert-butyl-4-methyl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3sa): Yield = 26%.

Yellow solid. M.p. 57.2–58.4 °C. IR (KBr) ν = 2976, 2929, 2866, 2250, 1633, 1487, 1448, 1374, 1267, 1144, 1080, 955, 870, 777, 709 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.28 (dd, J = 7.2, 1.5 Hz, 1H), 7.22–7.15 (m, 2H), 7.01–6.96 (m, 1H), 2.44–2.35 (m, 2H), 2.35–2.26 (m, 2H), 1.54 (s, 3H), 1.26 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 167.2, 139.1, 129.3, 127.0, 126.9, 125.8, 122.3, 119.6, 78.7, 37.5, 36.4, 28.3, 27.6, 12.6 ppm. HRMS m/z: calcd for C₁₆H₂₁N₂O [M+H]+ 257.1654, found: 257.1656.

(E)-3-(4-methyl-2-styryl-4H-benzo[d][1,3]oxazin-4-yl)propanenitrile (3ua): Yield = 25%.

Yellow oil. IR (KBr) ν = 3060, 3026, 2965, 2852, 2247, 1567, 1481, 1260, 1076, 768, 696 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.55 (dd, J = 7.9, 1.3 Hz, 2H), 7.50 (d, J = 16.1 Hz, 1H), 7.41–7.31 (m, 4H), 7.26–7.20 (m, 2H), 7.08–7.04 (m, 1H), 6.67 (d, J = 16.1 Hz, 1H), 2.56–2.43 (m, 2H), 2.42–2.33 (m, 2H), 1.68 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 156.6, 139.3, 135.4, 129.9, 129.6, 129.1, 127.9, 127.6, 127.4, 125.9, 122.6, 122.0, 119.5, 79.4, 36.8, 28.3, 12.6 ppm. HRMS m/z: calcd for C₂₀H₁₉N₂O [M+H]+ 303.1498, found: 303.1505.
The $^1$H, $^{13}$C spectra of compounds:
**N O C H 3**

**Cl**