Supporting Information for

2-Aminobenzaldehydes Synthesis by Rhodium(III)-Catalyzed C–H Amidation of Aldehydes with Dioxazolones

Chen-Fei Liu, Man Liu, Jun-Shu Sun, Chao Li,

and Lin Dong*

Table of Contents

1. General Methods
2. General Procedure for Synthesis of 2-aminobenzaldehydes
3. Synthetic Application of 2-aminobenzaldehydes
4. Determination of Products by LCMS Data
5. Characterization Data for Compounds
6. NMR Spectra
1. General Methods

NMR data were obtained for $^1$H at 400 MHz or 600 MHz, and for $^{13}$C at 100 MHz or 151 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl$_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrometer. TLC was performed on glass-backed silica plates. All benzaldehydes were commercially available. 1, 4, 2-Dioxazol-5-ones were prepared according to the literature procedures.[1,2]

2. General Procedure for Synthesis of 2-aminobenzaldehydes

Benzaldehyde 1a (5.3 mg, 0.05 mmol), 3-phenyl-1, 4, 2-dioxazol-5-one 2a (24.5 mg, 3.0 equiv.), [Cp*RhCl$_2$]$_2$ (1.6 mg, 5 mol %), AgSbF$_6$ (6.8 mg, 0.4 equiv.), Zn(OAc)$_2$·2H$_2$O (3.3 mg, 0.3 equiv.) and PhCOOH (6 mg, 1.0 equiv.) were stirred in DME (0.5 mL) at 120 ºC for 24 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:50) to give the product 3a as white solid (8.8 mg, 78%). The following products 3a, 3b, 3e, 3g, 3h, 3i, 3j and 8 have been reported by previous literatures,[3,4] therefore, only the $^1$H NMR was attached accordingly. About the following products 3j, 3k, 3m and 3p-3z the single peak can be observed in the $^1$H NMR illustrate that the amidation occured at the less hindered position.

**Caution:** With ethereal solvent, potentially explosive peroxides may be formed. Although the peroxides were not detected in the scale of 0.5 mmol, we’d like to remind the readers to pay attention to the possible peroxides when the reaction perform on a larger scale.

3. Synthetic Application of 2-aminobenzaldehydes

![Ethyl-1-benzoyl-7-bromo-2-imino-1,2-dihydroquinoline-3-carboxylate](image)

Ethyl-1-benzoyl-7-bromo-2-imino-1,2-dihydroquinoline-3-carboxylate 7: A mixture of aldehyde 3i (40 mg, 0.13 mmol, 1.0 equiv), molecular sieves 4 Å (40 mg), absolute ethanol (0.8 mL), ethylcyanoacetate (16.8 µL, 0.16 mmol, 1.2 equiv) and piperidine(0.2 µL, 2%, 2.6 µmol) in catalytic amount was stirred under argon at 60 ºC for 24 h. The solution was diluted with CH$_2$Cl$_2$ and molecular sieves were filtered on a pad of Celite. The mixture was concentrated under vacuum and the compound 7 was obtained as a yellow solid (44 mg, yield 83%) after purification by flash column chromatography on silica gel.
2,7-diphenylquinazoline 6: To a dried tube equipped with stir bar was added Aldehyde 3i (40 mg, 0.13 mmol, 1.0 equiv), 25% NH₃·H₂O (1.2 mL) and 2-propanol (0.8 mL). The reaction mixture was stirred at 100 °C for 12 h. Then the reaction mixture was cooled to room temperature and concentrated under vacuum and the compound 5 was obtained (34 mg, yield 92%) after purification by flash column chromatography on silica gel. A mixture of compound 5 (40 mg, 0.14 mmol, 1.0 equiv), PhB(OH)₂ (22.4 mg, 0.18 mmol, 1.3 equiv), Pd(OAc)₂ (1.2 mg, 0.13% mmol, 0.036 equiv), dppf (2.8 mg, 0.13% mmol, 0.036 equiv), CsCO₃ (92 mg, 0.28 mmol, 2 equiv) and 1,4-dioxane : H₂O (1.2 mL : 0.4 mL) was stirred under argon at 60 °C for 24 h. The solution was concentrated under vacuum and 6 was obtained (32 mg, yield 80%) after purification by flash column chromatography on silica gel (PE/EA: 100/1).

4. Mechanistic Study

The benzaldehyde 1a and phenyl isocyanate I’ were performed under standard conditions in DME. The imine 4a’ was obtained in 37% yield.

The reaction mixtures were tested respectively by LCMS when 1a and 2a reacted under standard conditions in DCE or DME for 3 h. I’ and 4a’ were observed in DME (eq 9), while 4a’ was observed in DCE (eq 10).
We tested the reaction in the presence of 5%, 10%, 20% aniline, respectively (shown in below scheme a and b). Only low yields of 3a were obtained, while higher yields of 4a were obtained in the presence of aniline. It implied that in the presence of catalytic amount of aniline, the yield of 4a got a promotion, but the aniline catalyst may not work for the formation of 3a. Therefore, low yield of 3a indicated that **imine-directed ortho-amidation pathway did not work smoothly in this reaction system**, and the results of that were same as eqs 5,6 in the Scheme 4.
5. Characterization Data for Compounds

\(N\)-(2-formylphenyl)benzamide (3a). White solid, m.p. 77.1-79.9 °C, 24 h, 8.8 mg, 78% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 12.10 \text{ (s, 1H)}\), 10.01 (s, 1H), 8.97 (d, \(J = 8.4 \text{ Hz, 1H}\)), 8.09-8.07 (m, 2H), 7.74 (dd, \(J_1 = 7.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H}\)), 7.71-7.67 (m, 1H), 7.59-7.52 (m, 3H), 7.29 (dd, \(J_1 = 7.6 \text{ Hz, } J_2 = 0.8 \text{ Hz, 1H}\)) ppm. The structure has been reported by previous literatures\(^{[3,4]}\).

\(N\)-(2-((phenylimino)methyl)phenyl)benzamide (4a). White solid, m.p. 102.2-104.9 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 13.58 \text{ (s, 1H)}\), 9.02 (d, \(J = 8.8 \text{ Hz, 1H}\)), 8.66 (s, 1H), 8.13 (d, \(J = 7.6 \text{ Hz, 2H}\)), 7.56-7.44 (m, 7H), 7.34-7.19 (m, 4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 166.4, 163.2, 149.9, 140.6, 135.3, 134.4, 132.7, 131.8, 129.5, 128.6, 127.7, 126.8, 122.8, 121.3, 120.8, 120.0 \text{ ppm}\). ESI HRMS: calcd. for C\(_{20}\)H\(_{16}\)N\(_2\)O+H 301.1341, found 301.1347.
N-(2-formyl-3-methylphenyl)benzamide (3b). White solid, m.p. 109.0-110.2 °C, 24 h, 8.1 mg, 68% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 12.56\) (s, 1H), 10.52 (s, 1H), 8.83 (d, \(J = 8.4\) Hz, 1H), 8.08 (d, \(J = 7.2\) Hz, 2H), 7.57-7.43 (m, 4H), 6.97 (d, \(J = 7.2\) Hz, 1H), 2.70 (s, 3H) ppm. The structure has been reported by previous literatures(4).

N-(2-formyl-3-methoxyphenyl)benzamide (3c). White solid, m.p. 128.6, 128.4, 128.2, 127.9, 127.7 ppm. ESI LRMS: calcd. for \(\text{C}_{14}\text{H}_{13}\text{NO}^+\text{H} 282.0298,\) found 282.0296, 284.0270.

N-(3-bromo-2-formylphenyl)benzamide (3d). White solid, m.p. 138.1, 134.2, 132.4, 131.1, 112.2, 111.2, 105.2, 55.9 ppm. ESI LRMS: calcd. for \(\text{C}_{14}\text{H}_{16}\text{BrNO}^+\text{H} 303.9973,\) found 303.9977, 305.9961.

N-(3-bromo-2-((phenylimino)methyl)phenyl)benzamide (4d). Light yellow solid, m.p. 136.1, 134.5, 130.5, 129.6, 129.4, 128.7, 128.6, 128.4, 128.2, 127.9, 127.7, 127.5, 127.3, 122.0, 121.1, 120.4, 119.8, 119.7, 118.9, 100.3, 58.4 ppm. ESI LRMS: calcd. for \(\text{C}_{20}\text{H}_{15}\text{BrN}_{2}O^+\text{H} 379.0446,\) found 379.0443, 381.0427.

N-(2-formyl-4-methylphenyl)benzamide (3e). White solid, m.p. 120.0-120.8 °C, 24 h, 9.3 mg, 78% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 11.99\) (s, 1H), 9.96 (s, 1H), 8.85 (d, \(J = 8.4\) Hz, 1H), 8.07 (d, \(J = 6.8\) Hz, 2H), 7.57-7.48 (m, 5H), 2.42 (s, 3H) ppm. The structure has been reported by previous literatures(3,4).

N-(4-chloro-2-formylphenyl)benzamide (3f). White solid, m.p. 139.8-142.7 °C, 36 h, 6.2 mg, 48% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 11.97\) (s, 1H), 9.94 (s, 1H), 8.96(d, \(J = 8.8\) Hz, 1H), 8.05 (d, \(J = 7.2\) Hz, 2H), 7.70-7.53 (m, 5H) ppm; \(^1^C\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 194.6, 166.1, 139.8, 136.1, 135.1, 134.0, 132.4, 128.9, 128.1, 127.5, 123.0, 121.7 ppm. ESI LRMS: calcd. for \(\text{C}_{14}\text{H}_{16}\text{ClNO}^+\text{H} 282.0298,\) found 282.0296, 284.0270.
N-(2-formyl-5-methylphenyl)benzamide (3g). White solid, m.p. 131.0 °C, 24 h, 8.0 mg, 67% yield; 1H NMR (400 MHz, CDCl₃): δ = 12.11 (s, 1H), 9.93 (s, 1H), 8.81 (s, 1H), 8.09-8.06 (m, 2H), 7.61-7.51 (m, 4H), 7.07 (d, J = 7.6 Hz, 1H), 2.48 (s, 3H) ppm. The structure has been reported by previous literatures[3,4].

N-(2-formyl-5-methoxyphenyl)benzamide (3h). White solid, m.p. 118.0-119.9 °C, 24 h, 9.9 mg, 78% yield; 1H NMR (400 MHz, CDCl₃): δ = 12.38 (s, 1H), 9.81 (s, 1H), 8.59 (s, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.60-7.50 (m, 4H), 6.74 (dd, J₁ = 8.4 Hz, J₂ = 1.6 Hz, 1H), 3.94 (s, 3H) ppm. The structure has been reported by previous literatures[3,4].

N-(5-bromo-2-formylphenyl)benzamide (3i). White solid, m.p. 147.0-147.9 °C, 24 h, 6.5 mg, 43% yield; 1H NMR (400 MHz, CDCl₃): δ = 12.13 (s, 1H), 9.96 (s, 1H), 9.24 (s, 1H), 8.07 (d, J = 7.6 Hz, 2H), 7.63-7.54 (m, 4H), 7.42 (d, J = 8.0 Hz, 1H) ppm. The structure has been reported by previous literatures[4].

N-(5-bromo-2-((phenylimino)methyl)phenyl)benzamide (4i). White solid, m.p. 140.5-144.2 °C, 24 h, 3 mg, 16% yield; 1H NMR (400 MHz, CDCl₃): δ = 13.64 (s, 1H), 9.27 (d, J = 1.6 Hz, 1H), 8.60 (s, 1H), 8.11-8.09 (m, 2H), 7.56-7.27 (m, 10H) ppm. 13C NMR (100 MHz, CDCl₃): δ = 166.4, 162.2, 149.6, 141.3, 135.2, 134.9, 132.0, 128.7, 127.7, 127.6, 127.1, 126.0, 123.0, 120.8, 120.1 ppm. ESI HRMS: calcd. for C₂₀H₁₅BrN₂O⁺H 379.0446, found 379.0441, 381.0423.

N-(2-formyl-4,5-dimethoxyphenyl)benzamide (3j). White solid, m.p. 161.4-124.2 °C, 24 h, 12.5 mg, 82% yield; 1H NMR (400 MHz, CDCl₃): δ = 12.33 (s, 1H), 9.83 (s, 1H), 8.72 (s, 1H), 8.07 (d, J = 7.2 Hz, 2H), 7.58-7.52 (m, 3H), 7.10 (s, 1H), 4.06 (s, 3H), 3.95 (s, 3H) ppm. The structure has been reported by previous literatures[4].

N-(6-formylbenzo[d][1,3]dioxol-5-yl)benzamide (3k). Yellow solid, m.p. 182.1-183.5 °C, 24 h, 9.3 mg, 44% yield; 1H NMR (400 MHz, CDCl₃): δ = 12.44 (s, 1H), 9.76 (s, 1H), 8.60 (s, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.58-7.51 (m, 3H), 7.07 (s, 1H), 6.10 (s, 2H) ppm; 13C NMR (100 MHz, CDCl₃): δ = 193.1, 154.2, 139.7, 132.2, 128.8, 127.5, 116.0, 113.0, 102.4, 101.3 ppm. ESI HRMS: calcd. for C₁₅H₁₅NO₄⁺H 270.0766, found 270.0766.

N-(1-formynaphthalen-2-yl)benzamide (3l). Yellow solid, m.p. 196.7-197.3 °C, 24 h, 9.9 mg, 72% yield; 1H NMR (400 MHz, CDCl₃): δ = 13.14 (s, 1H), 11.10 (s, 1H), 9.17 (d, J = 9.2 Hz, 1H), 8.49 (d, J = 8.8 Hz, 1H), 8.15-8.12 (m, 3H), 7.88 (d, J = 8.0 Hz, 1H), 7.66-7.49 (m, 5H) ppm; 13C NMR (100 MHz, CDCl₃): δ = 193.0, 193.0, 166.7, 143.0, 137.8, 134.4, 133.7, 132.4, 129.6, 129.4, 129.0, 128.9, 127.8, 125.2, 119.7, 112.9 ppm. ESI HRMS: calcd. for C₁₈H₁₃NO₂⁺H 276.1025, found 276.1025.
\[ \text{N-(1-acetylnaphthalen-2-yl)benzamide (3m). Yellow solid, m.p. 142.9-145.3} \]
\[ \text{C, 24 h, 24 h, 8.0 mg, 58% yield; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 11.90 \text{ (s, 1H)}, 10.14 \text{ (s, 1H)}, 9.35 \text{ (s, 1H)}, 8.25 \text{ (s, 1H)}, 8.11 \text{ (dd, } J = 7.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 2H)}, 7.91 \text{ (d, } J = 8.8 \text{ Hz, 2H)}, 7.66-7.46 \text{ (m, 5H) ppm; } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 195.8, 166.0, 140.4, 137.2, 135.8, 134.5, 132.0, 130.5, 129.0, 128.9, 128.7, 128.1, 127.4, 125.9, 123.1, 117.4 \text{ ppm. ESI HRMS: calcd. for C}_{13}\text{H}_{13}\text{NO}_2\text{+H 276.1025, found 276.1030.} \]

\[ \text{N-(2-formylthiophen-3-yl)benzamide (3n). White solid, m.p. 97.9-103.7} \]
\[ \text{C, 24 h, 3.1 mg, 27% yield; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 11.63 \text{ (s, 1H)}, 9.79 \text{ (s, 1H)}, 8.37 \text{ (d, } J = 5.2 \text{ Hz, 1H)}, 8.03 \text{ (d, } J = 7.6 \text{ Hz, 2H)}, 7.77 \text{ (d, } J = 5.2 \text{ Hz, 1H)}, 7.62-7.52 \text{ (m, 3H) ppm; } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 184.5, 164.8, 145.2, 136.5, 133.1, 132.5, 128.9, 127.6, 123.1, 121.4 \text{ ppm. ESI HRMS: calcd. for C}_{13}\text{H}_9\text{NO}_2\text{S+H 232.0432, found 232.0430.} \]

\[ \text{N-(3-acetylnaphthalen-2-yl)benzamide (3o). White solid, m.p. 110.3-114.9} \]
\[ \text{C, 24 h, 3.4 mg, 21% yield; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 12.43 \text{ (s, 1H)}, 9.93 \text{ (s, 1H)}, 8.06-8.04 \text{ (m, 2H)}, 7.65-7.61 \text{ (m, 1H)}, 7.58-7.54 \text{ (m, 2H)}, 7.24 \text{ (d, } J = 5.6 \text{ Hz, 1H)}, 6.83 \text{ (d, } J = 5.6 \text{ Hz, 1H) ppm; } ^{13}\text{C NMR (151 MHz, CDCl}_3\text{): } \delta = 187.2, 164.1, 150.3, 132.9, 131.3, 128.9, 128.9, 127.5, 127.5, 127.5, 127.5, 125.0, 122.3, 117.1 \text{ ppm. ESI HRMS: calcd. for C}_{13}\text{H}_9\text{NO}_2\text{S+Na 254.0252, found 254.0253.} \]

\[ \text{2-chloro-N-(2-formyl-4,5-dimethoxyphenyl)benzamide (3p). Yellow solid, m.p. 152.9-155.5} \]
\[ \text{C, 24 h, 9.6 mg, 60% yield; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 11.80 \text{ (s, 1H)}, 9.77 \text{ (s, 1H)}, 8.66 \text{ (s, 1H)}, 7.65 \text{ (dd, } J_1 = 7.2 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H)}, 7.49 \text{ (dd, } J_1 = 8.0 \text{ Hz, } J_2 = 1.2 \text{ Hz, 1H)}, 7.44 \text{ (dd, } J_1 = 7.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H)}, 7.41-7.36 \text{ (m, 1H)}, 7.10 \text{ (s, 1H)}, 4.06 \text{ (s, 3H)}, 3.95 \text{ (s, 3H) ppm; } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 193.2, 166.0, 155.5, 144.9, 137.1, 135.7, 131.4, 130.7, 129.3, 127.1, 116.5, 115.0, 103.4, 56.5, 56.3 \text{ ppm. ESI HRMS: calcd. for C}_{16}\text{H}_{14}\text{ClNO}_3\text{+H 320.0690, found 320.0698.} \]

\[ \text{N-(2-formyl-4,5-dimethoxyphenyl)-3-methylbenzamide (3q). Yellow solid, m.p. 139.0-139.8} \]
\[ \text{C, 24 h, 12.7 mg, 80% yield; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 12.31 \text{ (s, 1H)}, 9.83 \text{ (s, 1H)}, 8.70 \text{ (s, 1H)}, 7.65-7.61 \text{ (m, 2H)}, 7.40 \text{ (t, } J = 8.0 \text{ Hz, 1H)}, 7.13-7.10 \text{ (m, 2H)}, 4.05 \text{ (s, 3H)}, 3.94 \text{ (s, 3H)}, 3.90 \text{ (s, 3H) ppm; } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 193.5, 166.0, 160.0, 155.7, 144.6, 137.8, 135.7, 129.9, 119.3, 118.9, 116.5, 115.0, 112.2, 103.1, 56.4, 56.2, 55.4 \text{ ppm. ESI HRMS: calcd. for C}_{17}\text{H}_{17}\text{NO}_3\text{+H 300.1236, found 300.1238.} \]

\[ \text{3-bromo-N-(2-formyl-4,5-dimethoxyphenyl)benzamide (3s). Yellow solid, m.p. 162.8-163.8} \]
\[ \text{C, 24 h, 9.5 mg, 52% yield; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 11.71 \text{ (s, 1H)}, 9.77 \text{ (s, 1H)}, 8.64 \text{ (s, 1H)}, 7.67 \text{ (dd, } J_1 = 8.0 \text{ Hz, } J_2 = 1.2 \text{ Hz, 1H)}, 7.60 \text{ (dd, } J_1 = 7.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H)}, 7.43 \text{ (td, } J_1 = 7.6 \text{ Hz, } J_2 = 1.2 \text{ Hz, 1H)}, 7.34 \text{ (td, } J_1 = 7.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H)}, 7.09 \text{ (s, 1H),} \]

8
4.05 (s, 3H), 3.94 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.2, 191.6, 166.8, 163.0, 155.5, 149.3, 144.9, 144.0, 137.9, 137.1, 134.4, 133.9, 131.7, 129.1, 127.7, 119.8, 116.5, 115.0, 103.3, 56.6, 56.3 ppm. ESI HRMS: calcd. for C$_{16}$H$_{14}$BrNO$_3$Na 386.0004, found 386.0005, 387.9954.

$N$-(2-formyl-4,5-dimethoxyphenyl)-4-methylbenzamide (3t). Light yellow solid, m.p. 146.7-149.5 °C, 24 h, 13.0 mg, 81% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 12.27 (s, 1H), 9.83 (s, 1H), 8.72 (s, 1H), 7.96 (d, $J$ = 8.4 Hz, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.09 (s, 1H), 4.05 (s, 3H), 3.94 (s, 3H), 2.43 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.5, 166.2, 155.7, 144.5, 142.8, 138.1, 131.5, 129.5, 127.4, 116.5, 114.9, 103.1, 56.4, 56.2, 21.5 ppm.

ESI HRMS: calcd. for C$_{17}$H$_{17}$NO$_3$+H 300.1236, found 300.1241.

4-chloro-$N$-(2-formyl-4,5-dimethoxyphenyl)benzamide (3u). Light brown, solid, m.p. 165.3-168.7 °C, 24 h, 9.6 mg, 60% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 12.32 (s, 1H), 9.83 (s, 1H), 8.67 (s, 1H), 8.00 (d, $J$ = 8.4 Hz, 2H), 7.50 (d, $J$ = 8.4 Hz, 2H), 7.11 (s, 1H), 4.05 (s, 3H), 3.95 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.6, 165.0, 155.7, 144.8, 138.6, 137.7, 132.7, 129.2, 128.8, 116.5, 114.9, 103.1, 56.5, 56.3 ppm.

ESI HRMS: calcd. for C$_{16}$H$_{14}$ClNO$_3$+H 320.0690, found 320.0683, 322.0670.

4-bromo-$N$-(2-formyl-4,5-dimethoxyphenyl)benzamide (3v). Light yellow solid, m.p. 168.3-171.2 °C, 24 h, 9.3 mg, 51% yield; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 12.33 (s, 1H), 9.83 (s, 1H), 8.67 (s, 1H), 7.93 (d, $J$ = 8.4 Hz, 2H), 7.67 (d, $J$ = 8.4 Hz, 2H), 7.11 (s, 1H), 4.05 (s, 3H), 3.95 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.6, 165.1, 155.7, 144.8, 137.7, 133.1, 132.1, 129.0, 127.1, 116.5, 114.9, 103.1, 56.5, 56.3 ppm.

ESI HRMS: calcd. for C$_{16}$H$_{14}$BrNO$_3$+H 364.0184, found 364.0186, 366.0169.

$N$-(2-formyl-4,5-dimethoxyphenyl)-4-methoxybenzamide (3w). Yellow solid, m.p. 151.8-152.1 °C, 24 h, 8.7 mg, 55% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 12.25 (s, 1H), 9.83 (s, 1H), 8.71 (s, 1H), 8.04 (d, $J$ = 8.4 Hz, 2H), 7.09 (s, 1H), 7.02 (d, $J$ = 8.8 Hz, 2H), 4.05 (s, 3H), 3.95 (s, 3H), 3.89 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.5, 165.8, 162.8, 155.7, 144.4, 138.3, 129.4, 126.6, 116.5, 114.8, 114.1, 103.0, 56.4, 56.2, 55.4 ppm. ESI HRMS: calcd. for C$_{17}$H$_{15}$NO$_3$+H 316.1185, found 316.1183.

$N$-(4,5-dimethoxy-2-(((4-methoxyphenyl)imino)methyl)phenyl)-4-methoxybenzamide (4w). Yellow solid, m.p. 185.8-187.3 °C, 24 h, 3.6 mg, 17% yield; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 13.64 (s, 1H), 8.79 (s, 1H), 8.54 (s, 1H), 8.08 (d, $J$ = 8.4 Hz, 2H), 7.27-7.25 (m, 2H), 6.97 (t, $J$ = 7.8 Hz, 5H), 4.02 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H) ppm; $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ = 165.9, 162.3, 160.2, 158.4, 151.9, 144.1, 143.3, 136.2, 129.4, 127.7, 121.7, 115.6, 114.6, 113.9, 113.7, 103.5, 56.2, 56.1, 55.5, 55.4 ppm. ESI HRMS: calcd. for C$_{28}$H$_{32}$N$_2$O$_5$+H 421.1763, found 421.1769.
**N-(2-formyl-4,5-dimethoxyphenyl)-2-naphthamide (3x).** Yellow solid, m.p. 173.9-174.4 °C, 24 h, 7.7 mg, 46% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 12.49$ (s, 1H), 9.87 (s, 1H), 8.77 (s, 1H), 8.60 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 8.04-7.97 (m, 2H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.62-7.55 (m, 2H), 7.12 (s, 1H), 4.07 (s, 3H), 3.95 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.5$, 166.2, 155.7, 144.6, 138.0, 135.1, 132.7, 131.5, 129.4, 128.8, 128.6, 128.1, 127.7, 126.8, 123.5, 116.5, 115.0, 103.2, 56.5, 56.3 ppm. ESI HRMS: calcd. for C$_{20}$H$_{17}$NO$_{4}$+H 336.1236, found 336.1240.

**N-(2-formyl-4,5-dimethoxyphenyl)-2-phenylacetamide (3y).** White solid, m.p. 117.8-119.6 °C, 24 h, 8.7 mg, 58% yield; $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 11.33$ (s, 1H), 9.67 (s, 1H), 8.49 (s, 1H), 7.41-7.32 (m, 5H), 7.00 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.77 (s, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.0$, 170.7, 155.4, 144.5, 137.4, 134.0, 129.6, 128.9, 127.4, 116.3, 114.7, 103.0, 56.4, 56.2, 45.6 ppm. ESI HRMS: calcd. for C$_{17}$H$_{18}$NO$_{3}$+Na 322.1055, found 322.1056.

**N-(2-formyl-4,5-dimethoxyphenyl)furan-2-carboxamide (3z).** White solid, m.p. 154.0-154.5 °C, 24 h, 3.0 mg, 22% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 11.99$ (s, 1H), 9.81 (s, 1H), 8.60 (s, 1H), 8.15 (s, 1H), 7.51 (s, 1H), 7.08 (s, 1H), 6.91 (s, 1H), 4.03 (s, 3H), 3.94 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.5$, 161.6, 155.7, 145.8, 144.6, 144.2, 137.8, 123.4, 116.4, 114.5, 108.4, 102.9, 56.4, 56.2 ppm. ESI HRMS: calcd. for C$_{14}$H$_{13}$NO$_{3}$+H 276.0872, found 276.0819.

**2-(4-bromophenyl)quinazoline (5).** White solid, m.p. 172.9-175.3 °C, 24 h, 34 mg, 92% yield; $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 9.43$ (s, 1H), 8.59 (d, $J = 6.0$ Hz, 2H), 8.28 (s, 1H), 7.79 (d, $J = 9.0$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.54-7.52 (m, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 161.8$, 160.3, 151.4, 137.6, 131.1, 130.9, 130.9, 128.9, 128.7, 128.6, 128.3, 122.1 ppm. ESI HRMS: calcd. for C$_{14}$H$_{9}$BrN$_{2}$+H 285.0027, found 285.0021.

**2,7-diphenyquinazoline (6).** White solid, m.p. 211.3-212.8 °C, 24 h, 32 mg, 80% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.49$ (s, 1H), 8.63 (d, $J = 6.8$ Hz, 2H), 8.31 (s, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 2H), 7.56-7.47 (m, 6H) ppm; $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 161.4$, 160.1, 151.1, 146.8, 139.6, 138.0, 130.6, 129.1, 128.6, 128.5, 128.5, 127.6, 127.5, 127.0, 126.1, 122.5 ppm. ESI HRMS: calcd. for C$_{20}$H$_{14}$N$_{2}$+H 283.1235, found 283.1251.

**ethyl 1-benzoyl-7-bromo-2-imino-1,2-dihydroquinoline-3-carboxylate (7).** White solid, m.p. 161.3-162.8 °C, 24 h, 43 mg, 83% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 11.90$ (s, 1H), 8.87 (s, 1H), 8.32 (d, $J = 1.2$ Hz, 1H), 8.11-8.09 (m, 2H), 7.67 (d, $J = 8.8$ Hz, 1H), 7.60-7.51 (m, 4H), 4.49 (q, $J = 7.2$ Hz,
2H), 1.48 (t, J = 7.2 Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 166.9, 164.4, 149.5, 142.2, 134.7, 132.2, 131.1, 129.6, 129.8, 127.6, 127.5, 122.7, 112.7, 77.3, 77.0, 76.7, 62.5, 14.2\) ppm. ESI HRMS: calcd. for C\(_{19}\)H\(_{15}\)BrN\(_2\)O\(_3\)H 399.0344, found 399.0343, 401.0330.

2-phenyl-4H-benzo[d][1,3]oxazin-4-one (8). White solid, m.p. 121.9-124.7 °C, 24 h, 22 mg, 76% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.32 (d, J = 7.6\) Hz, 2H), 8.25 (d, \(J = 7.6\) Hz, 1H), 7.83 (d, \(J = 7.2\) Hz, 1H), 7.70 (d, \(J = 8.0\) Hz, 1H), 7.60-7.58 (m, 4H) ppm. The structure has been reported by previous literatures\(^{4}\).

References

6. NMR Spectra of Amidation Compounds and Structure Determination
33