Electronic Supporting Information

Cp*Co(III)-Catalyzed Amidation of Olefinic and Aryl C-H Bonds: Highly Selective Synthesis of Enamides and Pyrimidones
Yuan Liu, *† Fang Xie † †, Ai-Qun Jia, * and Xingwei Li, *b

*State Key Laboratory of Marine Resource Utilization in South China Sea, Key Laboratory of Tropical Biological Resources of Ministry Education, Department of Pharmacy, Hainan University, Haikou 570228, China. E-mail: jiaaiqun@gmail.com

†Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: xwli@dicp.ac.cn.

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I. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in a N₂ filled glovebox. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ¹H and ¹³C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate/hexanes. N-methoxy-acrylamides¹ and dioxazolones² were prepared according to literature reports.

II. General procedures for the synthesis of compound 3,4 and 5

Typical Reaction Conditions for synthesis of 3: N-methoxy-acrylamide (0.2 mmol), dioxazolones (0.24 mmol), Cp*Co(CO)I₂ (5 mol%), AgNTf₂ (10 mol%), Zn(OAc)₂ (0.2 mmol) and DCE (2 mL) were charged into a pressure tube. The reaction mixture was stirred under N₂ at 40 °C for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA to afford the product 3.

(Z)-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

White solid, Yield 93% (55.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 12.38 (d, J = 10.0 Hz, 1H), 8.16 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.38 (m, 3H), 7.35 – 7.33 (m, 2H), 3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 164.7, 136.9, 134.9, 132.8, 132.4, 130.0, 129.2, 128.9, 128.5, 127.8, 110.9, 64.9. HRMS (ESI) Calcd for [C₁₇H₁₆N₂O₃+H]⁺ 297.1234, Found 297.1233.
(Z)-4-Fluoro-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

White solid, Yield 80% (50.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.39 (d, $J = 10.4$ Hz, 1H), 8.34 (s, 1H), 8.05 – 7.99 (m, 2H), 7.56 (d, $J = 10.4$ Hz, 1H), 7.43 – 7.35 (m, 3H), 7.35 – 7.30 (m, 2H), 7.20 – 7.14 (m, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5, 163.6, 136.7, 134.8, 130.3 (d, $J_{CF} = 9.0$ Hz), 129.9, 129.2, 128.6 (d, $J_{CF} = 3.0$ Hz) 128.5, 116.0 (d, $J_{CF} = 22.0$ Hz), 111.2, 64.8. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$FN$_2$O$_3$]+H] $^+$ 315.1139, Found 315.1139.

(Z)-4-Chloro-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

White solid, Yield 88% (58.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.42 (d, $J = 10.4$ Hz, 1H), 8.18 (s, 1H), 7.88 – 7.95 (m, 2H), 7.60 (d, $J = 10.4$ Hz, 1H), 7.49 – 7.46 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.32 (m, 2H), 3.82 (s, 3H). $^{13}$C NMR (100MHz, CDCl$_3$) δ 167.5, 163.6, 139.2, 136.6, 134.7, 130.8, 129.9, 129.20, 129.19, 129.15, 128.5, 111.4, 64.8. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$ClN$_2$O$_3$]+H] $^+$ 331.0844, Found 331.0844.

(Z)-4-Bromo-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

White solid, Yield 77% (57.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.42 (d, $J = 9.6$ Hz, 1H), 8.20 (s, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 10.4$ Hz, 1H), 7.43 – 7.41 (m, 2H), 7.34 – 7.32 (m, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5, 163.7, 136.5, 134.7, 132.1,
(Z)-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)-4-methylbenzamide
White solid, Yield 91% (56.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.33 (d, $J = 10.8$ Hz, 1H), 8.18 (s, 1H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 10.8$ Hz, 1H), 7.44 – 7.38 (m, 3H), 7.36 – 7.32 (m, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 3.81 (s, 3H), 2.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.6, 164.6, 143.6, 136.9, 135.0, 129.9, 129.54, 129.51, 129.1, 128.4, 127.8, 110.7, 64.8, 21.6. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_2$O$_3$+H]$^+$ 311.1390, Found 311.1392.

(Z)-4-(Tert-butyl)-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide
Colorless liquid, Yield 83% (58.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.33 (d, $J = 10.8$ Hz, 1H), 8.16 (s, 1H), 7.95 (m, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.51 (m, 2H), 7.45 – 7.37 (m, 3H), 7.35 – 7.33 (m, 2H), 3.81 (s, 3H), 1.36 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.6, 164.7, 156.5, 137.1, 135.0, 130.0, 129.6, 129.2, 128.4, 127.7, 125.8, 110.6, 64.8, 35.1, 31.1. HRMS (ESI) Calcd for [C$_{21}$H$_{24}$N$_2$O$_3$+H]$^+$ 353.1860, Found 353.1862.

(Z)-4-Methoxy-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide
White solid, Yield 83% (54.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.31 (d, $J = 10.8$ Hz, 1H), 8.14 (s, 1H), 7.97 (m, 2H), 7.63 (d, $J = 10.8$ Hz, 1H), 7.46 – 7.37 (m, 3H), 7.35 – 7.32 (m, 2H), 7.00 – 6.97 (m, 2H), 3.88 (s, 3H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.7, 164.2, 163.3, 137.2, 135.1, 130.0, 129.9, 129.2, 128.4, 124.7, 114.1, 110.3, 64.9, 55.5. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_2$O$_4$+H]$^+$ 327.1339, Found 327.1339.

(Z)-3-Fluoro-$N$-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

White solid, Yield 89% (56.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.39 (d, $J = 10.4$ Hz, 1H), 8.38 (s, 1H), 7.77 – 7.75 (m, 1H), 7.73 – 7.69 (m, 1H), 7.55 (d, $J = 10.4$ Hz, 1H), 7.52 – 7.45 (m, 1H), 7.43 – 7.36 (m, 3H), 7.34 – 7.25 (m, 3H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 163.5 (d, $J_{C,F} = 3.0$ Hz), 162.9 (d, $J_{C,F} = 247.0$ Hz), 136.4, 134.74, 134.68, 130.5 (d, $J_{C,F} = 8.0$ Hz), 129.9, 129.2, 128.6, 123.1 (d, $J_{C,F} = 3.0$ Hz), 119.8 (d, $J_{C,F} = 22.0$ Hz), 115.2 (d, $J_{C,F} = 23.0$ Hz), 111.6, 64.8. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$FN$_2$O$_3$+H]$^+$ 315.1139, Found 315.1140.

(Z)-3-Chloro-$N$-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

Colorless liquid, Yield 88% (58.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.37 (d, $J = 10.4$ Hz, 1H), 8.25 (s, 1H), 8.00 (t, $J = 1.6$ Hz, 1H), 7.87 – 7.85 (m, 1H), 7.59 – 7.54 (m, 2H), 7.46 – 7.38 (m, 4H), 7.34 – 7.32 (m, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 163.4, 134.6, 135.2, 134.7, 134.2, 132.8, 130.1, 129.9, 129.2, 128.6, 128.2, 125.6, 111.7, 64.8. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$ClN$_2$O$_3$+H]$^+$ 331.0844, Found 331.0846.
(Z)-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)-3-methylbenzamide

Colorless liquid, Yield 92% (57.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.28 (d, $J$ = 10.4 Hz, 1H), 8.26 (s, 1H), 7.81 – 7.79 (m, 2H), 7.60 (d, $J$ = 10.4 Hz, 1H), 7.43 – 7.36 (m, 5H), 7.35 – 7.32 (m, 2H), 3.81 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5, 164.9, 138.8, 136.8, 135.0, 133.6, 132.3, 129.9, 129.1, 128.7, 128.40, 128.39, 124.8, 110.9, 64.8, 21.4. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_2$O$_3$+H]$^+$ 311.1390, Found 311.1392.

(Z)-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)-3-(trifluoromethyl)benzamide

White solid, Yield 98% (71.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.47 (d, $J$ = 10.4 Hz, 1H), 8.37 (s, 1H), 8.30 (s, 1H), 8.14 (d, $J$ = 7.6 Hz, 1H), 7.85 (d, $J$ = 7.6 Hz, 1H), 7.65 (t, $J$ = 7.8 Hz, 1H), 7.57 (d, $J$ = 10.4 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.36 – 7.31 (m, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.3, 163.3, 136.3, 134.6, 133.4, 131.6 (q, $J_{C-F}$ = 32.0 Hz), 130.4, 129.9, 129.5, 129.3, 129.2, 128.6, 125.3 (q, $J_{C-F}$ = 3.0 Hz), 123.6 (q, $J_{C-F}$ = 271.0 Hz), 112.0, 64.8. HRMS (ESI) Calcd for [C$_{18}$H$_{15}$F$_3$N$_2$O$_3$+H]$^+$ 365.1108, Found 365.1110.

(Z)-2-Fluoro-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)benzamide

White solid, Yield 87% (54.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.30 (t, $J$ = 10.4 Hz, 1H), 8.33 (s, 1H), 8.10 (td, $J_1$ = 7.2 Hz, $J_2$ = 1.6 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.42 – 7.34 (m, 3H), 7.34 – 7.28 (m,
7H), 7.23 – 7.18 (m, 1H), 3.79 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.7, 161.7 (d, $J_{CF} = 3.0$ Hz), 161.1 (d, $J_{CF} = 251.0$ Hz), 135.6, 135.1, 134.5 (d, $J_{CF} = 9.0$ Hz), 132.1 (d, $J_{CF} = 1.0$ Hz), 129.9, 129.1, 128.4, 124.8 (d, $J_{CF} = 3.0$ Hz), 120.1 (d, $J_{CF} = 11.0$ Hz), 116.6 (d, $J_{CF} = 24.0$ Hz), 112.1, 64.7. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$FN$_2$O$_3$+H]$^+$ 315.1139, Found 315.1140.

![3am](Z)-N-methoxy-2-phenyl-3-(2-phenylacetamido)acrylamide

Colorless liquid, Yield 80% (49.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.25 (d, $J = 10.8$ Hz, 1H), 8.16 (s, 1H), 7.40 – 7.28 (m, 9H), 7.23 – 7.21 (m, 2H), 3.71 (s, 3H), 3.68 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.5, 166.9, 135.8, 134.9, 133.7, 129.8, 129.3, 129.10, 129.05, 128.4, 127.5, 110.9, 64.7. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_2$O$_3$+H]$^+$ 311.1390, Found 311.1389.

![3an](Z)-N-(3-(methoxyamino)-3-oxo-2-phenylprop-1-en-1-yl)thiophene-2-carboxamide

Yellow solid, Yield 52% (33.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.24 (d, $J = 10.6$ Hz, 1H), 8.24 (s, 1H), 7.78 – 7.77 (dd, $J_1 = 3.6$ Hz, $J_2 = 0.8$ Hz, 1H), 7.62 (dd, $J_1 = 4.8$ Hz, $J_2 = 0.8$ Hz, 1H), 7.52 (d, $J = 10.6$ Hz, 1H), 7.43 – 7.36 (m, 3H), 7.33 – 7.31 (m, 2H), 7.16 – 7.14 (m, 1H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 159.5, 137.7, 136.4, 134.8, 132.4, 129.94, 129.93, 129.2, 128.5, 128.1, 110.7, 64.8. HRMS (ESI) Calcd for [C$_{15}$H$_{14}$N$_2$O$_3$S+H]$^+$ 303.0798, Found 303.0798.

![3ba](Z)-N-(2-(4-fluorophenyl)-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide

White solid, Yield 91% (57.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.35 (d, $J = 10.8$ Hz, 1H), 8.22 (s, 1H), 8.02 – 7.98 (m, 2H), 7.61 – 7.56 (m, 2H), 7.52 – 7.49 (m, 2H), 7.33 – 7.28 (m, 2H), 7.13 – 7.07
(m, 2H), 3.81 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5, 164.7, 162.8 (d, $J_{C-F} = 247.0$ Hz), 137.0, 132.9, 132.2, 131.8 (d, $J_{C-F} = 8.0$ Hz), 130.8 (d, $J_{C-F} = 4.0$ Hz), 128.9, 127.8, 116.2 (d, $J_{C-F} = 22.0$ Hz), 109.8, 64.8. HRMS (ESI) Calcd for [C$_{17}$H$_{14}$F$_2$N$_2$O$_3$+H]$^+$ 315.1139, Found 315.1139.

(Z)-N-(2-(4-chlorophenyl)-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide

White solid, Yield 78% (51.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.35 (d, $J = 10.8$ Hz, 1H), 8.25 (s, 1H), 8.02–7.97 (m, 2H), 7.62–7.56 (m, 2H), 7.52–7.49 (m, 2H), 7.40–7.35 (m, 2H), 7.29–7.25 (m, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.3, 164.7, 137.1, 134.6, 133.3, 132.9, 132.2, 131.3, 129.4, 128.9, 127.8, 109.8, 64.9. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$ClN$_2$O$_3$+H]$^+$ 331.0844, Found 331.0841.

(Z)-N-(3-(methoxyamino)-3-oxo-2-(p-tolyl)prop-1-en-1-yl)benzamide

White solid, Yield 77% (47.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.35 (d, $J = 10.8$ Hz, 1H), 8.26 (s, 1H), 8.03–7.99 (m, 2H), 7.61–7.56 (m, 2H), 7.52–7.48 (m, 2H), 7.23–7.19 (m, 4H), 3.80 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.7, 164.7, 138.4, 136.5, 132.7, 132.4, 131.8, 129.9, 129.8, 128.9, 127.8, 110.9, 64.8, 21.2. HRMS (ESI) Calcd for [C$_{18}$H$_{17}$N$_2$O$_3$+H]$^+$ 311.1390, Found 311.1389.

(Z)-N-(2-(4-(tert-butyl)phenyl)-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide
White solid, Yield 54% (37.8 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 12.38 (d, \(J = 10.8\) Hz, 1H), 8.25 (s, 1H), 8.04 – 8.00 (m, 2H), 7.61 (d, \(J = 10.8\) Hz, 1H), 7.58 – 7.56 (m, 1H), 7.52 – 7.48 (m, 2H), 7.44 – 7.42 (m, 2H), 7.27 – 7.25 (m, 2H), 3.82 (s, 3H), 1.35 (s, 9H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.7, 164.7, 151.6, 136.6, 132.7, 132.5, 131.8, 129.6, 128.9, 127.8, 126.1, 110.9, 64.8, 34.7, 31.3. HRMS (ESI) Calcd for [C\(_{21}\)H\(_{24}\)N\(_2\)O\(_3\)+H]\(^+\) 353.1860, Found 353.1861.

![3fa](image)

(Z)-N-(3-(methoxyamino)-2-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)benzamide

White solid, Yield 77% (50.0 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 12.35 (d, \(J = 10.4\) Hz, 1H), 8.33 (s, 1H), 8.03 – 7.98 (m, 2H), 7.61 – 7.53 (m, 2H), 7.51 – 7.48 (m, 2H), 7.26 – 7.21 (m, 2H), 6.94 – 6.89 (m, 2H), 3.81 (s, 3 H), 3.80 (s, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.8, 164.6, 159.7, 136.3, 132.7, 132.4, 131.2, 128.8, 127.8, 126.8, 114.5, 110.6, 64.8, 55.3. HRMS (ESI) Calcd for [C\(_{18}\)H\(_{18}\)N\(_2\)O\(_4\)+H]\(^+\) 327.1339, Found 327.1340.

![3ga](image)

(Z)-N-(2-(3-fluorophenyl)-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide

White solid, Yield 98% (64.4 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 12.36 (d, \(J = 10.4\) Hz, 1H), 8.32 (s, 1H), 8.01 – 7.99 (m, 2H), 7.64 – 7.56 (m, 2H), 7.53 – 7.49 (m, 2H), 7.41 – 7.34 (m, 1H), 7.14 – 7.03 (m, 3H), 3.82 (s, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.1, 164.7, 162.9 (d, \(J_{CF} = 247.0\) Hz), 137.3, 137.1 (d, \(J_{CF} = 8.0\) Hz), 132.9, 132.2, 130.8 (d, \(J_{CF} = 9.0\) Hz), 128.9, 127.8, 125.6 (d, \(J_{CF} = 3.0\) Hz), 117.0 (d, \(J_{CF} = 22.0\) Hz), 115.5 (d, \(J_{CF} = 21.0\) Hz), 109.8 (d, \(J_{CF} = 1.0\) Hz), 64.9. HRMS (ESI) Calcd for [C\(_{19}\)H\(_{19}\)FN\(_2\)O\(_3\)+H]\(^+\) 315.1139, Found 315.1142.

![3ha](image)

(Z)-N-(2-(3-chlorophenyl)-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide
White solid, Yield 73% (48.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.35 (d, $J = 10.4$ Hz, 1H), 8.29 (s, 1H), 8.03 – 7.97 (m, 2H), 7.62 – 7.58 (m, 2H), 7.53 – 7.49 (m, 2H), 7.38 – 7.31 (m, 3H), 7.24 – 7.20 (m, 1H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 164.7, 137.4, 136.8, 135.0, 132.9, 132.2, 130.4, 130.0, 128.9, 128.6, 128.1, 127.8, 109.7, 64.9. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$ClN$_2$O$_3$ + H]$^+$ 331.0844, Found 331.0846.

$^{3}$ia ($^Z$)-N-(2-(3-bromophenyl)-3-(methoxyamino)-3-oxoprop-1-en-yl)benzamide

White solid, Yield 82% (61.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.35 (d, $J = 10.4$ Hz, 1H), 8.26 (s, 1H), 8.02 – 7.98 (m, 2H), 7.62 – 7.58 (m, 2H), 7.52 – 7.48 (m, 2H), 7.28 – 7.27 (m, 2H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.1, 164.7, 137.5, 137.0, 132.94, 132.88, 132.2, 131.6, 130.6, 128.9, 128.5, 127.8, 123.2, 109.6, 64.9. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$BrN$_2$O$_3$ + H]$^+$ 375.0339, Found 375.0338.

$^{3}$ja ($^Z$)-N-(3-(methoxyamino)-2-(3-methoxyphenyl)-3-oxoprop-1-en-yl)benzamide

White solid, Yield 90% (58.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.39 (d, $J = 10.6$ Hz, 1H), 8.35 (s, 1H), 8.02 – 8.00 (m, 2H), 7.65 – 7.56 (m, 2H), 7.52 – 7.48 (m, 2H), 7.31 (t, $J = 8.0$ Hz, 1H), 6.92 – 6.90 (m, 2H), 6.87 – 6.84 (m, 1H), 3.82 (s, 3H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 164.7, 160.0, 136.7, 136.2, 132.8, 132.4, 130.2, 128.9, 127.8, 122.1, 115.5, 114.0, 110.9, 64.8, 55.4. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_2$O$_4$ + H]$^+$ 327.1339, Found 327.1337.

$^{3}$ka ($^Z$)-N-(2-(2-fluorophenyl)-3-(methoxyamino)-3-oxoprop-1-en-yl)benzamide
White solid, Yield 80% (49.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.42 (d, $J = 10.4$ Hz, 1H), 8.24 (s, 1H), 8.03 – 7.98 (m, 2H), 7.62 – 7.57 (m, 2H), 7.52 – 7.49 (m, 2H), 7.41 – 7.34 (m, 1H), 7.31 – 7.27 (m, 1H), 7.21 – 7.17 (m, 1H), 7.15 – 7.11 (m, 1H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.9, 164.7, 160.5 (d, $J_{C,F} = 246.0$ Hz), 138.1, 132.9, 132.6 (d, $J_{C,F} = 2.0$ Hz), 132.2, 130.9 (d, $J_{C,F} = 8.0$ Hz), 128.9, 127.8, 124.9 (d, $J_{C,F} = 3.0$ Hz), 122.3 (d, $J_{C,F} = 16.0$ Hz), 116.3 (d, $J_{C,F} = 22.0$ Hz), 104.4, 64.8.

HRMS (ESI) Calcd for [C$_{17}$H$_{15}$F$_{2}$N$_{2}$O$_{3}$]+H$^+$ 315.1139, Found 315.1139.

![3la](image)

(Z)-N-(2-(2-chlorophenyl)-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide

White solid, Yield 78% (51.6 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.38 (d, $J = 10.4$ Hz, 1H), 8.07 (s, 1H), 8.02 – 8.01 (m, 2H), 7.62 – 7.53 (m, 2H), 7.52 – 7.49 (m, 2H), 7.47 – 7.45 (m, 1H), 7.37 – 7.31 (m, 3H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 164.7, 137.1, 135.4, 133.3, 132.88, 132.86, 132.2, 130.4, 130.2, 128.9, 127.9, 127.6, 108.5, 64.7. HRMS (ESI) Calcd for [C$_{17}$H$_{15}$ClN$_{2}$O$_{3}$]+H$^+$ 331.0844, Found 331.0845.

![3ma](image)

(Z)-N-(3-(methoxyamino)-3-oxo-2-(o-tolyl)prop-1-en-1-yl)benzamide

White solid, Yield 78% (47.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.39 (d, $J = 10.4$ Hz, 1H), 8.03 – 8.02 (m, 2H), 7.95 (s, 1H), 7.61 – 7.57 (m, 1H), 7.55 – 7.47 (m, 3H), 7.33 – 7.18 (m, 4H), 3.77 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 164.7, 138.2, 136.7, 133.5, 132.8, 132.4, 131.4, 130.7, 129.1, 128.9, 127.8, 126.7, 109.8, 64.7, 19.9. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_{2}$O$_{3}$]+H$^+$ 311.1390, Found 311.1392.

![3na](image)
(Z)-N-(2-benzyl-3-(methoxyamino)-3-oxoprop-1-en-1-yl)benzamide
Colorless liquid, Yield 89% (55.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.36 (d, $J = 10.4$ Hz, 1H), 8.06 (s, 1H), 8.01 (d, $J = 10.4$ Hz, 1H), 7.59 – 7.55 (m, 1H), 7.51 – 7.47 (m, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.25 (m, 3H), 3.66 (s, 3H), 3.58 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.7, 164.7, 137.8, 137.2, 132.5, 132.7, 132.4, 125.9, 125.8, 125.7, 128.8, 127.7, 109.2, 64.8, 22.7, 13.7. HRMS (ESI) Calcd for [C$_{18}$H$_{18}$N$_2$O$_3$+H]$^+$ 311.1390, Found 311.1397.

![30a](image)

(Z)-N-(2-(methoxycarbamoyl)but-1-en-1-yl)benzamide
White solid, Yield 76% (37.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.28 (d, $J = 10.3$ Hz, 1H), 8.52 (s, 1H), 8.03 – 7.95 (m, 2H), 7.61 – 7.50 (m, 2H), 7.53 – 7.43 (m, 2H), 3.86 (s, 3H), 2.23 (q, $J = 7.4$ Hz, 2H), 1.19 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.4, 164.7, 134.5, 132.58, 132.57, 128.8, 127.7, 109.2, 64.8, 22.7, 13.7. HRMS (ESI) Calcd for [C$_{13}$H$_{16}$N$_2$O$_3$+Na]$^+$ 271.1053, Found 271.1059.

![Diagram](image)

Typical Reaction Conditions for synthesis of 4: N-methoxy-acrylamide (0.2 mmol), dioxazolone (0.21 mmol), Cp*$\text{Co(CO)}_2$I$_2$ (2.5 mol%), AgNTf$_2$ (5 mol%), Zn(OAc)$_2$ (1.0 equiv) and DCE (2 mL) were charged into a pressure tube. The reaction mixture was stirred under N$_2$ at 110 ºC for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA to afford the product 4.

![4aa](image)

3-Methoxy-2,5-diphenylpyrimidin-4(3H)-one
Yellow solid, Yield 90% (50.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.95 – 7.91 (m, 2H), 7.77 – 7.73 (m, 2H), 7.57 – 7.43 (m, 5H), 7.41 – 7.37 (m, 1H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.5, 156.4, 149.0, 132.7, 131.4, 131.3, 129.6, 128.64, 128.56, 128.44, 128.42, 127.4, 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{14}$N$_2$O$_2$+H]$^+$ 279.1128, Found 279.1128.

![4ab]

2-(4-Fluorophenyl)-3-methoxy-5-phenylpyrimidine-4(3H)-one

Yellow solid, Yield 81% (48.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H), 8.00 – 7.97 (m, 2H), 7.75 – 7.73 (m, 2H), 7.48 – 7.44 (m, 2H), 7.41 – 7.38 (m, 1H), 7.23 – 7.18 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.6 (d, $\nu_{CF} = 252.0$ Hz), 157.4, 155.4, 148.8, 132.6, 132.1 (d, $\nu_{CF} = 9.0$ Hz), 128.7, 128.6, 128.4, 127.5, 127.3 (d, $\nu_{CF} = 3.0$ Hz), 115.7 (d, $\nu_{CF} = 22.0$ Hz), 64.0. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$FNO$_2$+H]$^+$ 297.1034, Found 297.1036.

![4ac]

2-(4-Chlorophenyl)-3-methoxy-5-phenylpyrimidine-4(3H)-one

Yellow solid, Yield 78% (48.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H), 7.94 – 7.89 (m, 2H), 7.75 – 7.71 (m, 2H), 7.52 – 7.42 (m, 4H), 7.42 – 7.36 (m, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.3, 155.4, 148.8, 137.8, 132.6, 131.1, 129.6, 128.8, 128.7, 128.6, 128.4, 127.7, 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$ClNO$_2$+H]$^+$ 313.0738, Found 313.0738.

![4ad]

2-(4-Bromophenyl)-3-methoxy-5-phenylpyrimidine-4(3H)-one

Yellow solid, Yield 80% (57.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H), 7.85 – 7.83 (m, 2H), 7.74 – 7.72 (m, 2H), 7.67 – 7.65 (m, 2H), 7.47 – 7.44 (m, 2H), 7.42 – 7.38 (m, 1H), 3.84 (s, 3H). $^{13}$C
NMR (100 MHz, CDCl$_3$) $\delta$ 157.3, 155.4, 148.8, 132.6, 131.8, 131.2, 130.1, 128.8, 128.6, 128.4, 127.7, 126.3, 64.2. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$BrN$_2$O$_2$+H]$^+$ 357.0233, Found 357.0231.

3-Methoxy-5-phenyl-2-(p-tolyl)pyrimidin-4(3H)-one

Yellow solid, Yield 74% (43.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (s, 1H), 7.87 – 7.83 (m, 2H), 7.75 – 7.73 (m, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.32 – 7.30 (m, 2H), 3.82 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.6, 156.6, 149.0, 142.0, 132.8, 129.6, 129.165, 129.162, 128.6, 128.5, 128.4, 127.0, 63.9, 21.6. One signal is missing due to overlap. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_2$+H]$^+$ 293.1285, Found 293.1287.

2-(4-(Tert-butyl)phenyl)-3-methoxy-5-phenylpyrimidin-4(3H)-one

Yellow solid, Yield 70% (46.6 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (s, 1H), 7.83 – 7.81 (m, 2H), 7.69 – 7.63 (m, 2H), 7.45 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.28 (m, 1H), 3.76 (s, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.6, 156.5, 149.0, 142.0, 132.8, 129.6, 129.165, 129.39, 128.35, 127.0, 125.5, 64.0, 35.0, 31.2. One signal is missing due to overlap. HRMS (ESI) Calcd for [C$_{21}$H$_{22}$N$_2$O$_2$+H]$^+$ 335.1754, Found 335.1757.

2-Methoxy-2-(4-methoxyphenyl)-5-phenylpyrimidin-4(3H)-one

Yellow solid, Yield 60% (36.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 8.00 – 7.95 (m, 2H), 7.75 – 7.73 (m, 2H), 7.47 – 7.42 (m, 2H), 7.40 – 7.37 (m, 1H), 7.03 – 6.99 (m, 2H), 3.89 (s, 3H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 157.6, 156.1, 149.1, 132.9, 131.6, 128.53, 128.47, 128.4, 126.5, 123.4, 113.9, 63.8, 55.5. HRMS (ESI) Calcd for [C$_{19}$H$_{16}$N$_2$O$_3$+H]$^+$ 309.1234, Found 309.1235.
3-Methoxy-5-phenyl-2-(4-(trifluoromethyl)phenyl)pyrimidin-4(3H)-one

Yellow solid, Yield 70% (48.1 mg).\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.15 (s, 1H), 8.07 (d, \(J = 8.0\) Hz, 2H), 7.79 (d, \(J = 8.4\) Hz, 2H), 7.77 – 7.72 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 1H), 3.85 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.2, 155.1, 148.7, 134.6, 133.0 (q, \(J_{C,F} = 33.0\) Hz), 132.4, 130.1, 128.9, 128.6, 128.4, 128.3, 125.4 (q, \(J_{C,F} = 11.0\) Hz), 123.7 (q, \(J_{C,F} = 270.0\) Hz), 64.3. HRMS (ESI) Calcd for [C\(_{18}\)H\(_{13}\)F\(_3\)N\(_2\)O\(_2\)+H]\(^+\) 347.1002, Found 347.1004.

4-(1-Methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)benzonitrile

Yellow solid, Yield 68% (41.4 mg).\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.14 (s, 1H), 8.08 – 8.06 (m, 2H), 7.83 – 7.81 (m, 2H), 7.75 – 7.73 (m, 2H), 7.49 – 7.40 (m, 3H), 3.86 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.0, 154.5, 148.6, 135.3, 132.3, 132.2, 130.3, 129.0, 128.7, 128.6, 128.4, 118.0, 115.0, 64.4. HRMS (ESI) Calcd for [C\(_{18}\)H\(_{13}\)N\(_2\)O\(_2\)+H]\(^+\) 304.1081, Found 304.1081.

2-(3-Fluorophenyl)-3-methoxy-5-phenylpyrimidin-4(3H)-one

Yellow liquid, Yield 92% (54.7 mg).\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.13 (s, 1H), 7.77 – 7.71 (m, 3H), 7.70 – 7.65 (m, 1H), 7.53 – 7.43 (m, 3H), 7.42 – 7.37 (m, 1H), 7.30 – 7.24 (m, 1H), 3.85 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.3 (d, \(J_{C,F} = 246.0\) Hz), 157.3, 155.1 (d, \(J_{C,F} = 2.0\) Hz), 148.8, 133.1 (d, \(J_{C,F} = 8.0\) Hz), 132.5, 130.2 (d, \(J_{C,F} = 8.0\) Hz), 128.8, 128.6, 128.4, 127.9, 125.4 (d, \(J_{C,F} = 3.0\) Hz), 118.5 (d, \(J_{C,F} = 21.0\) Hz), 116.8 (d, \(J_{C,F} = 24.0\) Hz), 64.2. HRMS (ESI) Calcd for [C\(_{17}\)H\(_{13}\)F\(_2\)N\(_2\)O\(_2\)+H]\(^+\) 297.1034, Found 297.1034.
2-(3-Chlorophenyl)-3-methoxy-5-phenylpyrimidin-4(3H)-one

Yellow solid, Yield 82% (50.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 7.95 – 7.93 (m, 1H), 7.86 – 7.82 (m, 1H), 7.75 – 7.73 (m, 2H), 7.55 – 7.52 (m, 1H), 7.49 – 7.43 (m, 3H), 7.42 – 7.37 (m, 1H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 155.1, 148.7, 134.5, 132.8, 132.5, 131.5, 129.74, 129.69, 128.8, 128.6, 128.4, 128.0, 127.7, 64.3. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$ClN$_2$O$_2$+H]$^+$ 313.0738, Found 313.0739.

2-Methoxy-5-phenyl-2-(m-tolyl)pyrimidin-4(3H)-one

Yellow solid, Yield 95% (55.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (s, 1H), 7.77 – 7.71 (m, 4H), 7.48 – 7.44 (m, 2H), 7.42 – 7.36 (m, 3H), 3.82 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.5, 156.8, 149.0, 138.3, 132.8, 132.1, 131.2, 130.0, 128.61, 128.56, 128.4, 128.3, 127.3, 126.6, 64.1, 21.5. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_2$+H]$^+$ 293.1285, Found 293.1287.

3-Methoxy-5-phenyl-2-(3-(trifluoromethyl)phenyl)pyrimidin-4(3H)-one

Yellow solid, Yield 75% (52.6 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25 (s, 1H), 8.17 – 8.15 (m, 2H), 7.84 – 7.82 (m, 1H), 7.77 – 7.72 (m, 2H), 7.66 (t, $J$ = 7.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.44 – 7.38 (m, 1H), 3.86 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 154.9, 148.7, 132.8, 132.4, 132.0, 131.1 ($q, J_{C,F} = 32.0$ Hz), 129.1, 128.9, 128.6, 128.4, 128.2, 128.0 ($q, J_{C,F} = 3.0$ Hz), 126.7 ($q, J_{C,F} = 4.0$ Hz), 123.7 ($q, J_{C,F} = 271.0$ Hz), 64.3. HRMS (ESI) Calcd for [C$_{18}$H$_{13}$F$_3$N$_2$O$_2$+H]$^+$ 347.1002, Found 347.1001.
2-(2-Fluorophenyl)-3-methoxy-5-phenylpyrimidin-4(3H)-one

Yellow solid, Yield 60% (35.8 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (s, 1H), 7.77 – 7.72 (m, 2H), 7.61 – 7.52 (m, 2H), 7.49 – 7.38 (m, 3H), 7.33 – 7.29 (m, 1H), 7.25 – 7.21 (m, 1H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.9 (d, $J_{C\text{-}F} = 251.0$ Hz), 157.1, 153.4, 148.7, 132.8 (d, $J_{C\text{-}F} = 9.0$ Hz), 132.5, 130.5 (d, $J_{C\text{-}F} = 2.0$ Hz), 128.8, 128.7, 128.6, 128.5, 124.3 (d, $J_{C\text{-}F} = 4.0$ Hz), 120.2 (d, $J_{C\text{-}F} = 15.0$ Hz), 116.1 (d, $J_{C\text{-}F} = 21.0$ Hz), 64.5 (d, $J_{C\text{-}F} = 1.0$ Hz). HRMS (ESI) Calcd for [C$_{17}$H$_{13}$FN$_2$O$_2$+H]$^+$ 297.1034, Found 297.1034.

2-Benzyl-3-methoxy-5-phenylpyrimidin-4(3H)-one

Yellow liquid, Yield 60% (35.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (s, 1H), 7.68 – 7.63 (m, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.33 (m, 5H), 7.32 – 7.26 (m, 1H), 4.20 (s, 2H), 3.86 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.8, 157.6, 148.7, 134.9, 132.7, 129.2, 128.9, 128.52, 128.51, 128.4, 127.6, 127.5, 64.3, 39.5. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_2$+H]$^+$ 293.1285, Found 293.1285.

3-Methoxy-5-phenyl-2-(thiophen-2-yl)pyrimidin-4(3H)-one

Yellow solid, Yield 55% (31.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 – 8.18 (m, 1H), 8.08 (s, 1H), 7.75 – 7.71 (m, 2H), 7.67 – 7.66 (m, 1H), 7.48 – 7.42 (m, 2H), 7.39 – 7.36 (m, 1H), 7.22 – 7.20 (m, 1H), 4.16 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.4, 150.5, 149.3, 133.4, 133.2, 133.0, 132.9, 128.6, 128.5, 128.4, 128.3, 125.8, 64.0. HRMS (ESI) Calcd for [C$_{15}$H$_{12}$N$_2$O$_2$S+H]$^+$ 285.0692, Found 285.0691.
5-(4-Fluorophenyl)-3-methoxy-2-phenylpyrimidin-4(3H)-one
Yellow solid, Yield 70% (41.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (s, 1H), 7.95 – 7.90 (m, 2H), 7.76 – 7.72 (m, 2H), 7.60 – 7.49 (m, 3H), 7.17 – 7.12 (m, 2H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.0 (d, $J_{C-F} = 247.0$ Hz), 157.4, 156.6, 148.7, 131.4, 131.2, 130.2 (d, $J_{C-F} = 8.0$ Hz), 129.5, 128.7 (d, $J_{C-F} = 3.0$ Hz), 128.5, 126.5, 115.6 (d, $J_{C-F} = 21.0$ Hz), 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$FN$_2$O$_2$+H]$^+$ 297.1034, Found 297.1035.

5-(4-Chlorophenyl)-3-methoxy-2-phenylpyrimidin-4(3H)-one
Yellow solid, Yield 70% (43.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (s, 1H), 7.95 – 7.90 (m, 2H), 7.73 – 7.68 (m, 2H), 7.60 – 7.49 (m, 3H), 7.45 – 7.40 (m, 2H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.3, 156.8, 148.9, 134.7, 131.5, 131.1, 129.7, 129.6, 128.8, 128.5, 126.2, 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$ClN$_2$O$_2$+H]$^+$ 313.0738, Found 313.0737.

3-Methoxy-2-phenyl-5-(p-tolyl)pyrimidin-4(3H)-one
Yellow solid, Yield 51% (29.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 7.95 – 7.90 (m, 2H), 7.66 – 7.64 (m, 2H), 7.59 – 7.48 (m, 3H), 7.28 – 7.26 (m, 2H), 3.81 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.5, 156.2, 148.5, 138.7, 131.34, 131.29, 129.8, 129.5, 129.3, 128.4, 128.3, 127.4, 64.0, 21.3. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_2$+H]$^+$ 293.1285, Found 293.1284.

5-(4-(Tert-butyl)phenyl)-3-methoxy-2-phenylpyrimidin-4(3H)-one
Yellow liquid, Yield 40% (24.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (s, 1H), 7.96 – 7.90 (m, 2H), 7.72 – 7.66 (m, 2H), 7.58 – 7.47 (m, 5H), 3.82 (s, 3H), 1.36 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.6, 156.3, 151.8, 148.6, 131.33, 131.30, 129.8, 129.5, 128.4, 128.1, 127.4, 125.6, 64.0, 34.7, 31.3. HRMS (ESI) Calcd for [C$_{21}$H$_{22}$N$_2$O$_2$+H]$^+$ 335.1754, Found 335.1755.
Yellow solid, Yield 60% (37.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (s, 1H), 7.94 – 7.89 (m, 2H), 7.75 – 7.69 (m, 2H), 7.58 – 7.49 (m, 3H), 7.02 – 6.96 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.0, 157.6, 155.9, 148.0, 131.4, 131.3, 129.7, 129.5, 128.4, 127.1, 125.1, 114.0, 64.0, 55.4. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_3$+H]$^+$ 309.1234, Found 309.1236.

Yellow solid, Yield 88% (52.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.96 – 7.91 (m, 2H), 7.60 – 7.49 (m, 5H), 7.44 – 7.39 (m, 1H), 7.42 – 7.35 (m, 2H), 3.82 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.8 (d, $J_{CF} = 244.0$ Hz), 157.2, 157.0, 149.3, 134.8 (d, $J_{CF} = 8.0$ Hz), 131.5, 131.1, 130.0 (d, $J_{CF} = 9.0$ Hz), 129.6, 128.5, 126.1 (d, $J_{CF} = 2.0$ Hz), 123.9 (d, $J_{CF} = 3.0$ Hz), 115.6 (d, $J_{CF} = 3.0$ Hz), 115.4 (d, $J_{CF} = 5.0$ Hz), 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$FN$_2$O$_2$+H]$^+$ 297.1034, Found 297.1035.

Yellow solid, Yield 71% (44.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 (s, 1H), 7.96 – 7.91 (m, 2H), 7.78 – 7.76 (m, 1H), 7.65 – 7.62 (m, 1H), 7.60 – 7.49 (m, 3H), 7.42 – 7.35 (m, 2H), 3.82 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 157.1, 149.3, 134.47, 134.46, 131.6, 131.1, 129.8, 129.6, 128.7, 128.5, 128.4, 126.5, 126.0, 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$ClN$_2$O$_2$+H]$^+$ 313.0738, Found 313.0740.
5-(3-Bromophenyl)-3-methoxy-2-phenylpyrimidin-4(3H)-one

Yellow solid, Yield 66% (47.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (s, 1H), 7.94 – 7.92 (m, 3H), 7.70 – 7.67 (m, 1H), 7.61 – 7.49 (m, 4H), 7.32 (t, $J = 7.9$ Hz, 1H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.2, 157.1, 149.3, 134.7, 131.58, 131.56, 131.3, 131.1, 130.0, 129.6, 128.5, 127.0, 125.9, 122.6, 64.1. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$BrN$_2$O$_2$+H]$^+$ 357.0233, Found 357.0233.

3-Methoxy-5-(3-methoxyphenyl)-2-phenylpyrimidin-4(3H)-one

Yellow liquid, Yield 77% (47.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.96 – 7.90 (m, 2H), 7.57 – 7.50 (m, 3H), 7.39 – 7.34 (m, 2H), 7.31 – 7.29 (m, 1H), 6.97 – 6.94 (m, 1H), 3.86 (s, 3H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.6, 157.4, 156.6, 149.1, 134.0, 131.4, 131.2, 129.56, 129.55, 128.5, 127.2, 120.7, 114.6, 113.9, 64.1, 55.4. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_3$+H]$^+$ 309.1234, Found 309.1233.

5-(2-Fluorophenyl)-3-methoxy-2-phenylpyrimidin-4(3H)-one

Yellow liquid, Yield 77% (45.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 1.6$ Hz, 1H), 7.95 – 7.93 (m, 2H), 7.65 – 7.49 (m, 4H), 7.41 – 7.36 (m, 1H), 7.26 – 7.15 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.1 (d, $J_{CF} = 248.0$ Hz), 157.3, 157.0, 151.2 (d, $J_{CF} = 5.0$ Hz), 131.49, 131.45, 131.2, 130.4 (d, $J_{CF} = 9.0$ Hz), 129.6, 128.5, 124.2 (d, $J_{CF} = 4.0$ Hz), 122.8 (d, $J_{CF} = 2.0$ Hz), 120.4 (d, $J_{CF} = 14.0$ Hz), 116.0 (d, $J_{CF} = 22.0$ Hz), 64.1. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$FNP$_2$O$_2$+H]$^+$ 297.1034, Found 297.1032.

5-(2-Chlorophenyl)-3-methoxy-2-phenylpyrimidin-4(3H)-one

Yellow solid, Yield 83% (51.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (s, 1H), 7.98 – 7.93 (m, 2H), 7.60 – 7.48 (m, 4H), 7.45 – 7.41 (m, 1H), 7.37 – 7.32 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz,
CDCl$_3$ δ 157.6, 156.8, 151.2, 134.0, 131.72, 131.68, 131.5, 131.2, 130.0, 129.7, 128.4, 126.9, 126.6, 64.1. One signal is missing due to overlap. HRMS (ESI) Calcd for [C$_{17}$H$_{13}$ClN$_2$O$_2$+H]$^+$ 313.0738, Found 313.0735.

![3-Methoxy-2-phenyl-5-(o-tolyl)pyrimidin-4(3H)-one](image)

**4ma**

3-Methoxy-2-phenyl-5-(o-tolyl)pyrimidin-4(3H)-one

Yellow liquid, Yield 85% (49.3 mg). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.86 – 7.82 (m, 2H), 7.81 (s, 1H), 7.51 – 7.41 (m, 3H), 7.26 – 7.19 (m, 2H), 7.17 – 7.14 (m, 2H), 3.69 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 157.1, 156.9, 150.4, 137.7, 132.9, 131.5, 131.2, 130.2, 130.1, 129.6, 129.1, 128.7, 128.3, 125.7, 63.9, 19.7. HRMS (ESI) Calcd for [C$_{18}$H$_{16}$N$_2$O$_2$+H]$^+$ 293.1285, Found 293.1288.

![5-Benzyl-3-methoxy-2-phenylpyrimidin-4(3H)-one](image)

**4na**

5-Benzyl-3-methoxy-2-phenylpyrimidin-4(3H)-one

Yellow liquid, Yield 82% (48.1 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 – 7.82 (m, 2H), 7.72 (s, 1H), 7.55 – 7.44 (m, 3H), 7.36 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 3.87 (s, 2H), 3.75 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.4, 156.0, 154.3, 150.4, 138.3, 131.4, 131.1, 129.4, 129.1, 128.7, 128.6, 128.4, 126.6, 64.0, 33.8. HRMS (ESI) Calcd for [C$_{19}$H$_{16}$N$_2$O$_2$+H]$^+$ 293.1285, Found 293.1284.

![3-Methoxy-5-methyl-2-phenylpyrimidin-4(3H)-one](image)

**4oa**

3-Methoxy-5-methyl-2-phenylpyrimidin-4(3H)-one

White solid, Yield 64% (29.8 mg). $^1$H NMR (400 MHz, CD$_3$OD) δ 7.90 – 7.89 (m, 1H), 7.83 – 7.79 (m, 2H), 7.61 – 7.50 (m, 3H), 3.71 (s, 3H), 2.12 (d, $J = 0.9$ Hz, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 159.4, 156.3, 148.6, 131.2, 130.9, 129.1, 128.0, 125.2, 63.2, 11.9. HRMS (ESI) Calcd for [C$_{15}$H$_{12}$N$_2$O$_2$+H]$^+$ 217.0972, Found 217.0974.
3-Methoxy-5-ethyl-2-phenylpyrimidin-4(3H)-one

White solid, Yield 67% (30.6 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.82 (m, 2H), 7.80 (s, 1H), 7.56 – 7.45 (m, 3H), 3.76 (s, 3H), 2.59 (q, $J$ = 8.0 Hz, 2H), 1.26 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.5, 155.6, 147.5, 131.5, 131.0, 130.7, 129.3, 128.3, 63.9, 21.1, 12.6. HRMS (ESI) Calcd for [C$_{13}$H$_{14}$N$_2$O$_2$+H]$^+$ 231.1128, Found 231.1126.

Typical Reaction Conditions for synthesis of 5: N-methoxy-acrylamide (0.2 mmol), dioxazolone (0.71 mmol), Cp$^*$Co(CO)$_2$I$_2$ (10 mol%), AgNTf$_2$ (40 mol%), Zn(OAc)$_2$ (0.2 mmol), 4 Å M.S. (100 mg) and DCE (2 mL) were charged into a pressure tube. The reaction mixture was stirred under N$_2$ at 130 ºC for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA to afford the product 5.

$N$-(2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 81% (64.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.77 (s, 1H), 8.50 (d, $J$ = 8.0 Hz, 1H), 8.14 (s, 1H), 7.92 (d, $J$ = 7.2 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 1H), 7.73 (d, $J$ = 7.2 Hz, 2H), 7.60 – 7.42 (m, 7H), 7.28 – 7.25 (m, 1H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.2, 157.2, 155.4, 146.9, 137.4, 134.7, 132.4, 132.2, 132.1, 130.9, 129.0, 128.9, 128.7, 128.4, 128.2, 127.2, 123.6, 123.2, 119.5, 64.6. HRMS (ESI) Calcd for [C$_{24}$H$_{16}$N$_5$O$_3$+H]$^+$ 398.1499, Found 398.1497.
4-Chloro-N-(5-chloro-2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 75% (70.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 11.17 (s, 1H), 8.65 (d, $J = 1.6$ Hz, 1H), 8.11 (s, 1H), 7.89 – 7.84 (m, 3H), 7.74 – 7.72 (m, 2H), 7.51 – 7.42 (m, 5H), 7.26 – 7.23 (m, 1H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.2, 157.0, 154.6, 146.4, 138.8, 138.74, 138.70, 132.8, 132.1, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 123.8, 122.7, 116.6, 64.6. HRMS (ESI) Calcd for [C$_{24}$H$_{17}$Cl$_2$N$_3$O$_3$+H]$^+$ 466.0720, Found 466.0717.

4-(Tert-butyl)-N-(5-(tert-butyl)-2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 80% (80.9 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.93 (s, 1H), 8.63 (s, 1H), 8.18 (s, 1H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.56 – 7.44 (m, 5H), 7.32 – 7.28 (m, 1H), 3.84 (s, 3H), 1.44 (s, 9H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.2, 157.4, 156.3, 155.7, 155.6, 147.1, 137.5, 132.4, 131.9, 130.6, 128.9, 128.6, 128.5, 127.7, 127.0, 125.9, 120.7, 120.2, 116.4, 64.5, 35.4, 35.1, 31.2, 31.1. HRMS (ESI) Calcd for [C$_{32}$H$_{35}$N$_3$O$_3$+H]$^+$ 510.2751, Found 510.2753.
4-Methoxy-N-(5-methoxy-2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 75% (69.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.41 (s, 1H), 8.28 (d, $J = 2.4$ Hz, 1H), 8.14 (s, 1H), 7.96 – 7.89 (m, 3H), 7.76 (d, $J = 7.2$ Hz, 2H), 7.51 – 7.44 (m, 3H), 7.02 (d, $J = 8.8$ Hz, 2H), 6.80 – 6.78 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 162.7, 157.4, 155.5, 146.9, 140.3, 132.5, 132.4, 129.1, 128.8, 128.6, 128.4, 127.2, 127.1, 114.1, 110.4, 110.3, 106.4, 64.2, 55.6, 55.5. One signal is missing due to overlap.

HRMS (ESI) Calcd for [C$_{26}$H$_{23}$N$_3$O$_5$+H]$^+$ 458.1710, Found 458.1708.

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3-Chloro-N-(4-chloro-2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 62% (58.3 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.84 (s, 1H), 8.40 (d, $J = 9.0$ Hz, 1H), 8.07 (s, 1H), 7.85 – 7.80 (m, 2H), 7.71 – 7.65 (m, 3H), 7.48 – 7.44 (m, 2H), 7.41 – 7.34 (m, 4H), 3.77 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.8, 157.0, 153.9, 146.6, 136.1, 135.9, 135.1, 132.4, 132.2, 131.9, 130.7, 130.3, 129.2, 129.1, 128.9, 128.7, 128.4, 127.6, 125.3, 124.2, 120.3, 64.8. HRMS (ESI) Calcd for [C$_{24}$H$_{17}$Cl$_2$N$_3$O$_3$+H]$^+$ 466.0720, Found 466.0721.

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$N$-(2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)-4-methylphenyl)-3-methylbenzamide

Yellow solid, Yield 75% (63.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.41 (s, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 8.15 (s, 1H), 7.76 – 7.74 (m, 3H), 7.69 – 7.68 (m, 2H), 7.50 – 7.38 (m, 6H), 3.84 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.4, 157.3, 155.6, 147.2, 138.7, 134.72, 134.68, 133.4, 133.1, 132.8, 132.3, 131.0, 128.9, 128.7, 128.6, 128.4, 128.064, 128.063, 123.9, 123.3, 120.0,
64.6, 21.5, 21.0. One signal is missing due to overlap. HRMS (ESI) Calcd for [C_{26}H_{23}N_{3}O_{3}+H]^+ 426.1812, Found 426.1813.

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\text{N-(2-(1-methoxy-6-oxo-5-phenyl-1,6-dihydropyrimidin-2-yl)thiophen-3-yl)thiophene-2-carboxamide}
\]

Yellow solid, Yield 57% (46.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 13.37 (s, 1H), 8.43 (d, $J = 5.6$ Hz, 1H), 8.15 (s, 1H), 7.78 – 7.74 (m, 3H), 7.66 (d, $J = 5.6$ Hz, 1H), 7.59 (d, $J = 4.8$ Hz, 1H), 7.49 – 7.45 (m, 2H), 7.42 – 7.38 (m, 1H), 7.20 – 7.16 (m, 1H), 4.21 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.2, 157.1, 152.6, 147.1, 145.5, 139.4, 133.5, 132.5, 131.3, 129.5, 128.6, 128.3, 128.1, 124.6, 122.4, 107.1, 64.6. One signal is missing due to overlap. HRMS (ESI) Calcd for [C_{20}H_{15}N_{3}S_{2}+H]^+ 410.0628, Found 410.0627.

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\text{N-(2-(5-(2-fluorophenyl)-1-methoxy-6-oxo-1,6-dihydropyrimidin-2-yl)phenyl)benzamide}
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Yellow solid, Yield 65% (53.5 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.78 (s, 1H), 8.52 (d, $J = 8.4$ Hz, 1H), 8.16 (s, 1H), 7.92 – 7.88 (m, 3H), 7.67 – 7.48 (m, 5H), 7.43 – 7.38 (m, 1H), 7.29 – 7.17 (m, 3H), 3.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.2, 160.0 (d, $J_{C,F} = 248.0$ Hz), 156.8, 156.1, 149.4 (d, $J_{C,F} = 5.0$ Hz), 137.5, 134.6, 132.5, 132.1, 131.5 (d, $J_{C,F} = 3.0$ Hz), 130.9, 130.8 (d, $J_{C,F} = 8.0$ Hz), 128.9, 127.2, 124.2 (d, $J_{C,F} = 4.0$ Hz), 123.6, 123.3 (d, $J_{C,F} = 2.0$ Hz), 123.1, 119.9 (d, $J_{C,F} = 14.0$ Hz), 119.3, 116.1 (d, $J_{C,F} = 22.0$ Hz), 64.6. HRMS (ESI) Calcd for [C_{24}H_{13}FN_{3}O_{3}+H]^+ 416.1405, Found 416.1406.
**5ca**

*N-(2-(5-(2-chlorophenyl)-1-methoxy-6-oxo-1,6-dihydropyrimidin-2-yl)phenyl)benzamide*

Yellow solid, Yield 61% (52.3 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.74 (s, 1H), 8.52 (d, \(J = 8.4\) Hz, 1H), 8.07 (s, 1H), 7.93 – 7.89 (m, 3H), 7.63 – 7.59 (m, 1H), 7.56 – 7.45 (m, 5H), 7.37 – 7.35 (m, 2H), 7.30 – 7.26 (m, 1H), 3.81 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.2, 156.7, 156.4, 149.6, 137.5, 134.6, 133.8, 132.5, 132.2, 131.7, 131.1, 130.9, 130.3, 130.1, 128.9, 127.2, 127.0, 126.9, 123.6, 123.2, 119.5, 64.6. HRMS (ESI) Calcd for [C\(_{24}\)H\(_{18}\)ClN\(_3\)O\(_3\)H]\(^+\) 432.1109, Found 432.1111.

**5da**

*N-(2-(1-methoxy-6-oxo-5-(o-tolyl)-1,6-dihydropyrimidin-2-yl)phenyl)benzamide*

Yellow solid, Yield 62% (50.8 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.79 (s, 1H), 8.51 (d, \(J = 8.4\) Hz, 1H), 7.96 (s, 1H), 7.94 – 7.89 (m, 3H), 7.62 – 7.48 (m, 4H), 7.34 – 7.26 (m, 5H), 3.80 (s, 3H), 2.32 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.2, 156.9, 155.9, 148.7, 137.5, 137.4, 134.6, 132.4, 132.2, 131.9, 130.9, 130.5, 130.1, 129.9, 129.1, 128.9, 127.1, 125.9, 123.6, 123.2, 119.5, 64.5, 20.1. HRMS (ESI) Calcd for [C\(_{25}\)H\(_{21}\)N\(_3\)O\(_3\)H]\(^+\) 412.1656, Found 412.1658.

**5ea**

*N-(2-(5-(4-fluorophenyl)-1-methoxy-6-oxo-1,6-dihydropyrimidin-2-yl)phenyl)benzamide*

Yellow solid, Yield 77% (63.3 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.72 (s, 1H), 8.49 (d, \(J = 8.0\) Hz, 1H), 8.11 (s, 1H), 7.91 (d, \(J = 7.6\) Hz, 2H), 7.87 (d, \(J = 8.0\) Hz, 1H), 7.76 – 7.70 (m, 2H), 7.61 – 7.49 (m, 4H), 7.28 – 7.25 (m, 1H), 7.17 – 7.13 (m, 2H), 3.80 (s, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.2,
163.1 (d, $J_{CF} = 247.0$ Hz), 157.2, 155.4, 146.8, 137.4, 134.7, 132.4, 132.2, 130.9, 130.3 (d, $J_{CF} = 8.0$ Hz), 128.9, 128.2 (d, $J_{CF} = 3.0$ Hz), 127.2, 127.1, 123.6, 123.2, 119.5, 115.7 (d, $J_{CF} = 22.0$ Hz), 64.6.

HRMS (ESI) Calcd for $[C_{25}H_{18}BrN_3O_4+H]^+$ 476.0604, Found 476.0602.

**5fa**

$N$-(2-(5-(3-bromophenyl)-1-methoxy-6-oxo-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 58% (54.4 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.68 (s, 1H), 8.48 (d, $J = 8.0$ Hz, 1H), 8.12 (s, 1H), 7.92 – 7.68 (m, 4H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.61 – 7.50 (m, 5H), 7.33 (t, $J = 8.0$ Hz, 1H), 7.29 – 7.25 (m, 1H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.3, 157.0, 155.9, 147.4, 137.4, 134.6, 134.2, 132.6, 132.2, 131.9, 131.2, 130.9, 130.1, 129.0, 127.1, 127.0, 126.7, 123.7, 123.3, 122.7, 119.4, 64.6. HRMS (ESI) Calcd for $[C_{24}H_{18}FN_3O_3+H]^+$ 416.1403, Found 416.1403.

**5ga**

$N$-(2-(1-methoxy-5-(3-methoxyphenyl)-6-oxo-1,6-dihydropyrimidin-2-yl)phenyl)benzamide

Yellow solid, Yield 72% (61.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.78 (s, 1H), 8.51 (d, $J = 8.4$ Hz, 1H), 8.15 (s, 1H), 7.92 – 7.90 (m, 2H), 7.88 (d, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.62 – 7.48 (m, 4H), 7.40 – 7.34 (m, 2H), 7.30 – 7.24 (m, 2H), 6.97 ($J_1 = 8.0$ Hz, $J_2 = 2.4$ Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.2, 159.7, 157.2, 155.4, 147.1, 137.4, 134.7, 133.6, 132.4, 132.1, 130.9, 129.7, 128.9, 127.9, 127.2, 123.6, 123.1, 120.7, 119.4, 114.8, 114.0, 64.6, 55.4. HRMS (ESI) Calcd for $[C_{25}H_{21}N_3O_4+H]^+$ 428.1603, Found 428.1603.

**III. Derivatization of amidated products**
4aa (27.8 mg, 0.1 mmol), 3-phenyl-1,4,2-dioxazol-5-one (24.5 mg, 0.15 mmol), [Cp*Co(CO)]₂ (2.4 mg, 0.005 mmol), AgN Tf₂ (7.8 mg, 0.02 mmol) and Zn(OAc)₂ (18.3 mg, 0.1 mmol) were dissolved in DCE (1 mL) under N₂ atmosphere. The mixture was stirred at 110°C overnight. After that the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA to afford compound 5aa as a yellow solid (32.2 mg, 81%).

4aa (27.8 mg, 0.1 mmol), diazo compound (27.9 mg, 0.15 mmol), [Cp*RhCl]₂ (2.5 mg, 0.004 mmol), AgSbF₆ (6.9 mg, 0.02 mmol) and Cu(OAc)₂ (18.2 mg, 0.1 mmol) were dissolved in DCE (1 mL) under N₂ atmosphere. The mixture was stirred at 80°C overnight. After that the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA to afford compound 6 as a yellow solid (38.0 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.79 – 7.74 (m, 2H), 7.73 – 7.68 (m, 1H), 7.63 – 7.56 (m, 2H), 7.51 – 7.44 (m, 3H), 7.41 (m, 1H), 4.85 (s, 1H), 4.22 (q, J = 7.2 Hz, 4H), 3.74 (s, 3H), 1.25 (t, J = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 167.8, 157.1, 156.2, 148.5, 132.5, 132.2, 131.4, 130.8, 130.1, 129.6, 128.8, 128.6, 128.5, 128.3, 127.9, 64.1, 62.0, 54.9, 14.0.
In a Schlenk tube, 2,5-Bis(4-(tert-butyl)phenyl)-3-methoxypyrimidin-4(3H)-one (78.0 mg, 0.2 mmol) was dissolved in dry THF (4 mL). SmI$_2$ solution (0.1 M in THF, 4.0 mL, 0.4 mmol) was added slowly via a syringe. The reaction mixture was stirred at RT about 2 h (The process of the reaction could be monitored by TLC analysis). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (DCM/MeOH = 95:5) to afford 7 as a white solid (47.1 mg, 65% yield). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 13.05 (s, 1H), 8.28 (s, 1H), 8.20 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 1.31 (s, 9H), 1.30 (s, 9H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 174.3, 155.71, 155.68, 152.8, 151.5, 130.4, 129.0, 128.0, 127.4, 125.9, 125.2, 124.4, 34.9, 34.6, 31.1, 30.9. HRMS (ESI) Calcd for [C$_{24}$H$_{28}$N$_2$O+H]$^+$ 361.2274, Found 361.2279.

![Chemical structure of 3ca and 8](image)

Compound 8 was prepared according to the above procedure of preparing 7. White solid, 61% yield $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 12.44 (d, $J = 10.0$ Hz, 1H), 7.97 (d, $J = 7.6$ Hz, 2H), 7.66 (d, $J = 10.0$ Hz, 1H), 7.60 – 7.56 (m, 1H), 7.52 – 7.48 (m, 2H), 7.40 – 7.38 (m, 2H), 7.33 – 7.31 (m, 2H), 5.84 (s, 1H), 5.58 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.8, 136.8, 135.1, 134.3, 132.8, 132.5, 131.2, 129.3, 128.9, 127.8. HRMS (ESI) Calcd for [C$_{16}$H$_{13}$N$_2$O$_2$Cl+H]$^+$ 301.0738, Found 301.0734.

![Chemical structures of 3aa, 4aa, and 4aa](image)

3aa (29.6 mg, 0.10 mmol), Zn(OAc)$_2$ (18.3 mg, 0.1 mmol) were dissolved in DCE (1 mL) under
N₂ atmosphere. The mixture was stirred at 110°C overnight. After that the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA to afford compound 4aa (15.3 mg, 55%).

3aa (29.6 mg, 0.1 mmol), [Cp*Co(CO)]₂ (1.2 mg, 0.0025 mmol), AgNTf₂ (1.9 mg, 0.005 mmol) and Zn(OAc)₂ (18.3 mg, 0.1 mmol) were dissolved in DCE (1 mL) under N₂ atmosphere. The mixture was stirred at 110°C overnight. After that the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using PE/EA to afford compound 4aa (23.1 mg, 83%).

**IV. Mechanistic Studies**

(a) **H/D Exchange Experiments**

![Chemical Reaction Diagram](image)

I (17.7 mg, 0.1 mmol), Cp*Co(CO)]₂ (2.4 mg, 0.005 mmol), AgNTf₂ (3.9 mg, 0.01 mmol), Zn(OAc)₂ (18.3 mg, 0.1 mmol), and D₂O (20 mg, 1 mmol) were dissolved in DCE (1 mL) under N₂ atmosphere. The reaction mixture was stirred at 40°C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford an oil, which was characterized by ¹H NMR spectroscopy.
A mixture of 1 (35.44 mg, 0.2 mmol), 2m (46.2 mg, 0.2 mmol), 2l (35.4 mg, 0.2 mmol), Cp*Co(CO)I₂ (2.1 mg, 0.005 mmol), AgNTf₂ (3.9 mg, 0.01 mmol), and Zn(OAc)₂ (36.7 mg, 0.2 mmol) were dissolved in DCE (2 mL) under N₂ atmosphere. The reaction mixture was stirred at 110°C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford 4am and 4al, which were characterized by ¹H NMR spectroscopy.
V. References


VI. NMR Spectra of Products

3aa
3ad
3al
4ad
4am
4ca
4ha

![Chemical Structure of 4ha](image)
4ia
4pa
5ac