

Supporting Information

Cobalt(III) and Rhodium(III)-Catalyzed C-H Amidation and Synthesis of 4-Quinolones: C-H Activation Assisted by Weakly Coordinating and Functionalizable Enaminone

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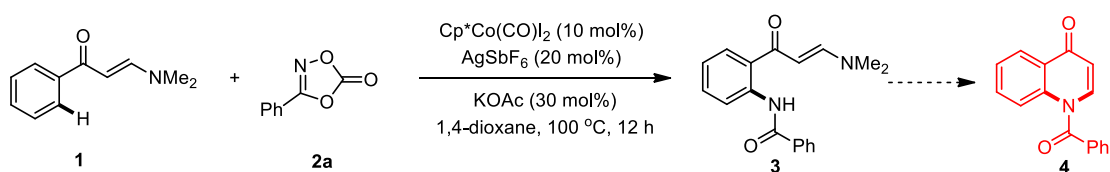
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I. General Considerations

All rhodium- and cobalt-catalyzed reactions were carried out in a nitrogen-filled dry box. ^1H and ^{13}C NMR spectra were recorded using CDCl_3 , $\text{DMSO}-d_6$, CD_3OD as a solvent on a 400 MHz spectrometer at 298 K. The chemical shift is given in dimensionless δ values and is frequency referenced relative to SiMe_4 in ^1H and ^{13}C NMR spectroscopy. High-resolution mass spectra were obtained on an Agilent Q-TOF 6540 spectrometer. All other solvents were obtained from commercial sources and were used as received.

II. Procedure for the cobalt- and rhodium-catalyzed C-H amidation of enaminones



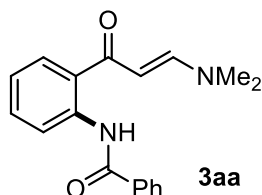
Reaction Conditions A (representative example): enaminone **1a** (35.1 mg, 0.2 mmol), $\text{CoCp}^*(\text{CO})\text{I}_2$ (9.5 mg, 10 mol %), AgNTf_2 (15.5 mg, 20 mol %), KOAc (6.0 mg, 30 mol %), and freshly prepared dioxazolone **2a** (50.0 mg, 0.3 mmol) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL) under N_2 . The reaction mixture was stirred for 12 h at 100 °C. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the product **3aa** as a yellow solid (54.6 mg, 93%).

Scale-up synthesis: enaminone **1a** (175 mg, 1 mmol), $\text{CoCp}^*(\text{CO})\text{I}_2$ (47.5 mg, 10 mol %), AgNTf_2 (77.5 mg, 20 mol %), KOAc (30 mg, 30 mol %), and dioxazolone **2a** (250 mg, 1.5 mmol) were weighed into a pressure tube, to which was added freshly prepared 1,4-dioxane (10 mL) under N_2 . The reaction mixture was stirred for 12 h at 100 °C. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the product **3aa** as a yellow solid (206 mg, 70%).

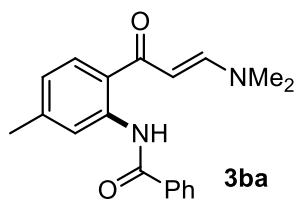
Reaction Conditions B: enaminone **1** (35.1 mg, 0.2 mmol), dioxazolone **2a** (50.0 mg,

0.3 mmol), [Cp*RhCl₂]₂ (4.9 mg, 4 mol %), AgSbF₆ (11 mg, 16 mol %), and AgOAc (6.7 mg, 20 mol %) were weighed into a pressure tube, to which was added 1,2-dichloromethane (2 mL) under N₂. The reaction mixture was stirred for 12 h at 100 °C. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired product.

Reaction Conditions C: enaminone **1** (35.1 mg, 0.2 mmol), dioxazolone **2a** (50.0 mg, 0.3 mmol), Cp*Co(CO)I₂ (9.5 mg, 10 mol %), AgSbF₆ (11.0 mg, 20 mol %), and AgOAc (6.7 mg, 20 mol %) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL) under N₂. The reaction mixture was stirred for 12 h at 100 °C. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired product.

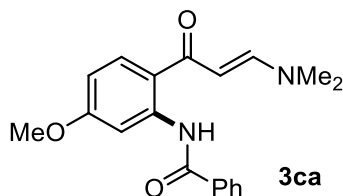


Conditions A (54.7 mg, 93%, yellow solid). ¹H NMR (400 MHz, CDCl₃) δ 13.10 (br s, 1H), 8.85 (d, *J* = 7.9 Hz, 1H), 8.10 – 8.07 (m, 2H), 7.83 – 7.80 (m, 2H), 7.56 – 7.40 (m, 4H), 7.12 – 7.08 (m, 1H), 5.72 (d, *J* = 12.2 Hz, 1H), 3.13 (s, 3H), 2.90 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.1, 165.6, 155.0, 140.2, 135.2, 132.2, 131.4, 129.0, 128.6, 127.3, 125.6, 122.3, 120.8, 93.3, 45.2 (br), 37.3 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for [C₁₈H₁₈N₂O₂+H]⁺ 295.1447, Found 295.1445.

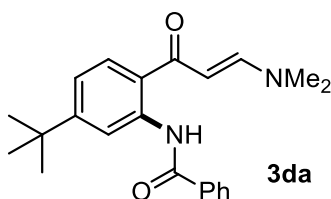


Conditions A (54.2 mg, 88%, white solid). ¹H NMR (400 MHz, CDCl₃) δ 13.22 (br s, 1H), 8.72 (s, 1H), 8.10 – 8.08 (m, 2H), 7.82 (d, *J* = 12.0 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.47 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.74 (d, *J* = 12.2 Hz, 1H), 3.16 (s, 3H), 2.93 (s, 3H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.2, 165.7, 154.7, 143.2, 140.5, 135.3, 131.4, 129.2, 128.6, 127.4, 123.1, 122.9, 121.2, 93.2, 45.2 (br),

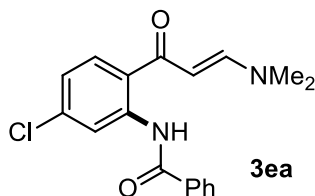
37.4 (br), 21.9. The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[C_{19}H_{20}N_2O_2+H]^+$ 309.1603, Found 309.1605.



Conditions A (60.3 mg, 93%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.71 (br, 1H), 8.61 (d, $J = 2.6$ Hz, 1H), 8.12 – 8.09 (m, 2H), 7.82 – 7.78 (m, 2H), 7.52 – 7.48 (m, 3H), 6.63 (dd, $J = 8.9, 2.6$ Hz, 1H), 5.72 (d, $J = 12.2$ Hz, 1H), 3.91 (s, 3H), 3.14 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 166.0, 162.8, 154.3, 143.1, 135.2, 131.5, 130.8, 128.6, 127.4, 117.8, 109.5, 104.2, 92.7, 55.4, 45.2 (br), 37.3 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[C_{19}H_{20}N_2O_3+H]^+$ 325.1552, Found 325.1556.

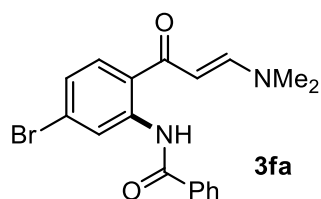


Conditions B (44.1 mg, 63%, white solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.22 (br, 1H), 8.99 (d, $J = 1.3$ Hz, 1H), 8.21 – 8.09 (m, 2H), 7.83 (d, $J = 12.2$ Hz, 1H), 7.83 (d, $J = 12.2$ Hz, 1H), 7.51 – 7.50 (m, 3H), 7.13 (dd, $J = 8.3, 1.4$ Hz, 1H), 5.76 (d, $J = 12.2$ Hz, 1H), 3.17 (s, 3H), 2.94 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 165.8, 156.3, 154.7, 140.5, 135.4, 131.4, 128.9, 128.6, 127.4, 122.8, 119.4, 118.0, 93.2, 45.2 (br), 37.4 (br), 35.2, 31.1. The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[C_{22}H_{26}N_2O_2+H]^+$ 351.2073, found 351.2070.

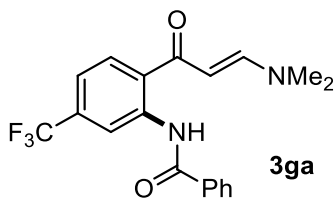


Conditions A (64.8 mg, 99%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.30 (br,

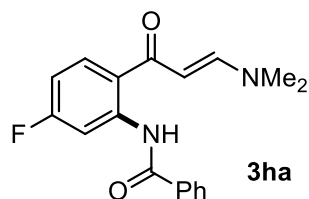
1H), 8.95 (s, 1H), 8.06 – 8.05 (m, 2H), 7.80 (d, $J = 12.0$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.50 – 7.48 (m, 3H), 7.02 (d, $J = 8.2$ Hz, 1H), 5.64 (d, $J = 12.0$ Hz, 1H), 3.14 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.0, 165.6, 155.2, 141.5, 138.0, 134.8, 131.7, 130.1, 128.6, 127.4, 123.5, 122.2, 120.5, 92.8, 45.3 (br), 37.4 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_2+\text{H}]^+$ 329.1057, Found 329.1059.



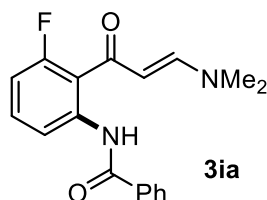
Conditions A (67.7 mg, 91%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.25 (br, 1H), 9.11 (d, $J = 1.7$ Hz, 1H), 8.06 – 8.05 (m, 2H), 7.81 (d, $J = 12.1$ Hz, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.54 – 7.47 (m, 3H), 7.18 (dd, $J = 8.5, 1.7$ Hz, 1H), 5.63 (d, $J = 12.1$ Hz, 1H), 3.15 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.1, 165.6, 155.2, 141.4, 134.8, 131.7, 130.2, 128.6, 127.4, 126.6, 125.2, 124.0, 123.4, 92.8, 45.3 (br), 37.4 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{BrN}_2\text{O}_2+\text{H}]^+$ 373.0552, Found 373.0551.



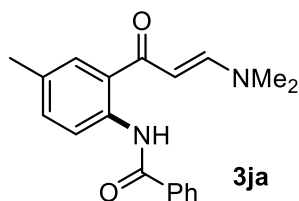
Conditions A (69.5 mg, 96%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.09 (br, 1H), 9.21 (s, 1H), 8.07 (d, $J = 6.7$ Hz, 2H), 7.88 – 7.85 (m, 2H), 7.54 – 7.51 (m, 3H), 7.31 (d, $J = 8.0$ Hz, 1H), 5.68 (d, $J = 12.1$ Hz, 1H), 3.19 (s, 3H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 165.8, 155.7, 140.6, 134.7, 133.3 (q, $J_{\text{C-F}} = 32.0$ Hz), 131.8, 129.3, 128.7, 128.2, 127.4, 123.7 (q, $J_{\text{C-F}} = 271.2$ Hz), 118.7 (q, $J_{\text{C-F}} = 3.7$ Hz), 117.8 (q, $J_{\text{C-F}} = 3.4$ Hz), 93.2, 45.4 (br), 37.5 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_2+\text{H}]^+$ 363.1320, Found 363.1321.



Conditions A (54.9 mg, 88%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.43 (br, 1H), 8.69 (dd, $J = 12.1, 2.5$ Hz, 1H), 8.08 – 8.06 (m, 2H), 7.85 – 7.80 (m, 2H), 7.55 – 7.48 (m, 3H), 6.80 – 7.75 (m, 1H), 5.68 (d, $J = 12.1$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.1, 165.9, 164.7 (d, $J_{\text{C-F}} = 248.7$ Hz), 155.0, 142.8 (d, $J_{\text{C-F}} = 12.5$ Hz), 134.9, 131.7, 131.07 (d, $J_{\text{C-F}} = 10.3$ Hz), 128.7, 127.4, 121.6 (d, $J_{\text{C-F}} = 2.9$ Hz), 109.1 (d, $J_{\text{C-F}} = 22.0$ Hz), 107.8 (d, $J_{\text{C-F}} = 27.5$ Hz), 92.9, 45.3 (br), 37.4 (br). HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{FN}_2\text{O}_3+\text{H}]^+$ 313.1352, Found 313.1356.

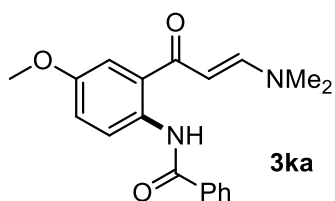


Conditions B (30.0 mg, 48%, white solid). ^1H NMR (400 MHz, CDCl_3) δ 12.04 (br, 1H), 8.48 (d, $J = 8.1$ Hz, 1H), 8.01 (d, $J = 6.9$ Hz, 2H), 7.86 (s, 1H), 7.53 – 7.47 (m, 3H), 7.38 (dd, $J = 14.6, 8.2$ Hz, 1H), 6.86 – 6.82 (m, 1H), 5.62 (dd, $J = 12.1, 3.3$ Hz, 1H), 3.17 (s, 3H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 165.4, 155.0, 140.0, 134.8, 131.8, 131.7 (two overlapping signals), 128.6, 127.3, 117.3 (d, $J_{\text{C-F}} = 16.6$ Hz), 116.9 (d, $J_{\text{C-F}} = 1.1$ Hz), 110.6 (d, $J_{\text{C-F}} = 24.3$ Hz), 98.6, 45.3 (br), 37.4 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{FN}_2\text{O}_2+\text{H}]^+$ 313.1352, Found 313.1355.

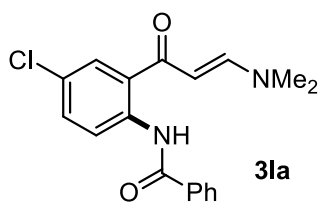


Conditions A (48.7 mg, 79%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 12.92 (br, 1H), 8.72 (d, $J = 8.4$ Hz, 1H), 8.08 – 8.06 (m, 2H), 7.83 (d, $J = 12.2$ Hz, 1H), 7.60 (s,

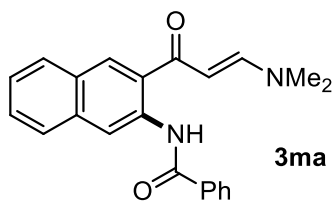
1H), 7.50 – 7.48 (m, 3H), 7.30 (d, $J = 8.3$ Hz, 1H), 5.73 (d, $J = 12.2$ Hz, 1H), 3.16 (s, 3H), 2.94 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.4, 165.4, 155.0, 137.8, 135.4, 132.9, 131.6, 131.3, 129.3, 128.6, 127.3, 125.7, 120.8, 93.4, 45.2 (br), 37.4 (br), 20.9. The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2+\text{H}]^+$ 309.1603, Found 309.1601.



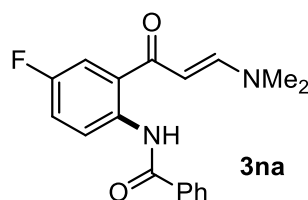
Conditions A (40.8%, 63%, yellow solid). ^1H NMR (400 MHz, DMSO) δ 13.08 (s, 1H), 8.60 (d, $J = 9.1$ Hz, 1H), 7.95 – 7.90 (m, 3H), 7.62 – 7.55 (m, 3H), 7.47 (d, $J = 2.9$ Hz, 1H), 7.14 (dd, $J = 9.1, 2.9$ Hz, 1H), 5.88 (d, $J = 12.0$ Hz, 1H), 3.83 (s, 3H), 3.21 (s, 3H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 189.1, 164.0, 156.1, 154.5, 135.0, 133.1, 131.8, 128.9, 127.3, 126.9, 121.6, 117.1, 114.6, 92.5, 55.6, 45.0 (br), 37.6 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3+\text{H}]^+$ 325.1552, Found 325.1552.



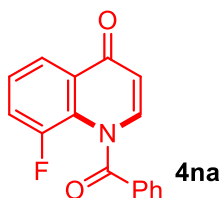
Conditions B (58.3 mg, 89%, yellow solid). ^1H NMR (700 MHz, CDCl_3) δ 12.94 (br, 1H), 8.82 (d, $J = 9.0$ Hz, 1H), 8.05 – 8.04 (m, 2H), 7.85 (d, $J = 12.1$ Hz, 1H), 7.74 (d, $J = 2.4$ Hz, 1H), 7.53 – 7.48 (m, 3H), 7.43 (dd, $J = 8.9, 2.4$ Hz, 1H), 5.65 (d, $J = 12.1$ Hz, 1H), 3.19 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 189.8, 165.6, 155.5, 138.9, 135.0, 131.9, 131.7, 128.7, 127.4, 127.2, 127.1, 127.0, 122.3, 93.0, 45.4 (br), 37.6 (br). HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_2+\text{H}]^+$ 329.1057, Found 329.1052.



Conditions B (53.0mg, 77%, yellow solid). ^1H NMR (700 MHz, CDCl_3) δ 12.85 (br, 1H), 9.28 (s, 1H), 8.30 (s, 1H), 8.13 – 8.12 (m, 2H), 7.87 (s, 1H), 7.85 (d, J = 3.6 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.52 – 7.50 (m, 4H), 7.40 (t, J = 7.4 Hz, 1H), 5.86 (d, J = 12.2 Hz, 1H), 3.16 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 165.6, 155.2, 136.3, 135.3, 131.4, 130.1, 128.7, 128.4, 128.1, 127.7, 127.3, 126.9, 125.1, 117.7, 93.8, 45.3 (br), 37.5 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_2+\text{H}]^+$ 345.1603, Found 345.1601.

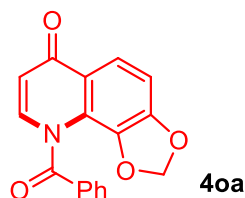


Conditions C (7.0 mg, 11%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 12.81 (br, 1H), 8.82 (dd, J = 9.2, 5.4 Hz, 1H), 8.06 – 8.04 (m, 2H), 7.86 (d, J = 12.1 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.22 – 7.17 (m, 1H), 5.65 (d, J = 12.1 Hz, 1H), 3.21 (s, 3H), 2.97 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 189.9, 165.5, 157.5 (d, $J_{\text{C-F}}$ = 227.4 Hz), 155.5, 136.5 (d, $J_{\text{C-F}}$ = 2.4 Hz), 135.1, 131.6, 128.7, 127.4, 127.31 (d, $J_{\text{C-F}}$ = 4.9 Hz), 122.7 (d, $J_{\text{C-F}}$ = 7.2 Hz), 118.8 (d, $J_{\text{C-F}}$ = 21.6 Hz), 115.2 (d, $J_{\text{C-F}}$ = 23.0 Hz), 93.1, 45.5 (br), 37.6 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{FN}_2\text{O}_2+\text{H}]^+$ 313.1352, Found 313.1356.

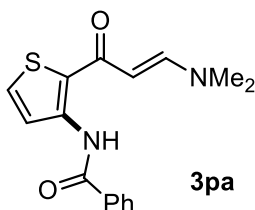


Conditions C (18.2 mg, 34%, white solid). ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 7.9 Hz, 1H), 7.85 – 7.81 (m, 3H), 7.85 – 7.81 (m, 1H), 7.70 – 7.67 (m, 2H), 7.54 – 7.50 (m, 1H), 7.44 – 7.39 (m, 1H), 6.28 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz,

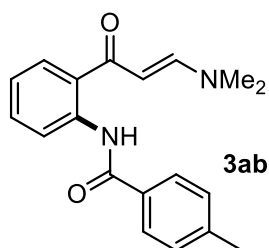
CDCl₃) δ 177.93 (d, J = 2.4 Hz, 3H), 169.3, 152.2 (d, $J_{\text{C-F}}$ = 251.2 Hz), 139.2, 134.6, 130.8 (d, J = 4.1 Hz, 3H), 130.3, 129.2, 128.71, 128.70 (d, $J_{\text{C-F}}$ = 9.9 Hz), 125.9 (d, $J_{\text{C-F}}$ = 7.9 Hz), 122.1 (d, $J_{\text{C-F}}$ = 3.4 Hz), 118.9 (d, $J_{\text{C-F}}$ = 19.9 Hz), 111.4. HRMS (ESI) Calcd for [C₁₆H₁₀FNO₂+H]⁺ 268.0774, Found 268.0775.



Conditions C (14.6 mg, 25%, yellow solid). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.5 Hz, 1H), 7.86 – 7.84 (m, 2H), 7.71 – 7.69 (m, 1H), 7.56 – 7.52 (m, 1H), 7.56 – 7.52 (m, 2H), 7.04 (d, J = 8.5 Hz, 1H), 6.16 (d, J = 8.2 Hz, 1H), 5.93 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 168.2, 151.3, 138.6, 136.2, 134.3, 131.3, 130.4, 129.1, 124.1, 122.5, 121.8, 110.8, 108.0, 102.3. HRMS (ESI) Calcd for [C₁₇H₁₀FNO₄+H]⁺ 294.0761, Found 294.0765.

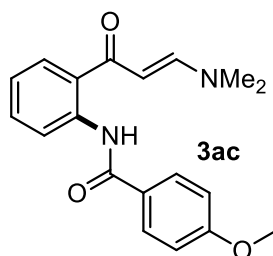


Conditions A (52.8 mg, 88%, yellow solid). ¹H NMR (400 MHz, CDCl₃) δ 12.87 (br, 1H), 8.33 (d, J = 5.4 Hz, 1H), 8.07 (d, J = 6.8 Hz, 2H), 7.79 (d, J = 12.1 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.39 (d, J = 5.4 Hz, 1H), 5.43 (d, J = 12.1 Hz, 1H), 3.15 (s, 3H), 2.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 183.4, 164.4, 153.3, 143.5, 134.1, 131.8, 128.7, 128.3, 127.5, 123.0, 121.4, 93.1, 45.1 (br), 37.4 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for [C₁₆H₁₆N₂O₂S+H]⁺ 301.1011, Found 301.1012.

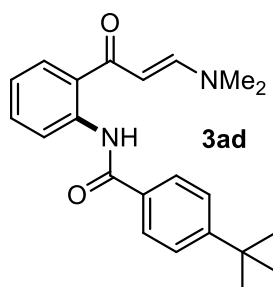


Conditions A (46.2 mg, 75%, yellow solid). ¹H NMR (400 MHz, CDCl₃) δ 12.97 (br,

1H), 8.83 (d, $J = 8.3$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.82 (t, $J = 9.1$ Hz, 1H), 7.84 – 7.80 (m, 2H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 2.0$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 5.73 (d, $J = 12.2$ Hz, 1H), 3.17 (s, 3H), 2.93 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.3, 165.7, 155.0, 141.9, 140.4, 132.5, 132.2, 129.3, 129.0, 127.4, 125.7, 122.1, 120.9, 93.5, 45.3 (br), 37.4 (br), 21.5. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2+\text{H}]^+$ 309.1603, Found 309.1602.

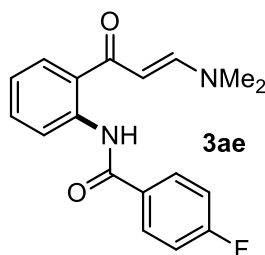


Conditions A (55.7 mg, 86%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.98 (s, 1H), 9.81 (d, $J = 8.3$ Hz, 1H), 9.04 (d, $J = 8.7$ Hz, 2H), 8.82 – 8.72 (m, 2H), 8.46 (t, $J = 7.7$ Hz, 1H), 8.06 (t, $J = 7.5$ Hz, 1H), 7.97 (d, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 12.2$ Hz, 1H), 4.84 (s, 3H), 4.14 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.3, 165.2, 162.2, 154.9, 140.5, 132.2, 129.2, 129.0, 127.6, 125.5, 122.0, 120.7, 113.8, 93.4, 55.3, 45.2 (br), 37.3 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3+\text{H}]^+$ 325.1552, Found 325.1559.

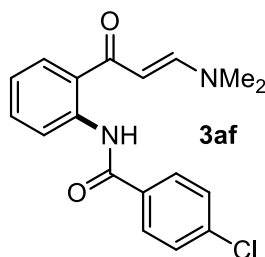


Conditions A (65.8 mg, 94%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 12.98 (br, 1H), 8.83 (d, $J = 8.3$ Hz, 1H), 8.01 (d, $J = 8.3$ Hz, 2H), 7.85 – 7.80 (m, 2H), 7.52 – 7.50 (m, 3H), 7.09 (t, $J = 7.5$ Hz, 1H), 5.73 (d, $J = 12.2$ Hz, 1H), 3.16 (s, 3H), 2.92 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.3, 165.7, 154.9, 140.4, 132.5, 132.2, 129.0, 127.2 (two overlapping signals), 125.7, 125.6, 122.1, 120.9, 93.4, 45.2 (br), 37.4 (br), 34.9, 31.1. The broadening of the Me signals is likely due to partially

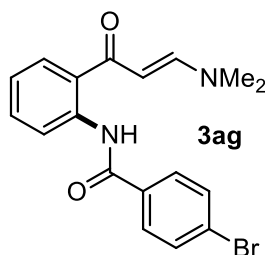
hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[C_{22}H_{26}N_2O_2+H]^+$ 351.2073, Found 351.2070.



Conditions A (49.2 mg, 79%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.13 (br, 1H), 8.80 (d, $J = 8.3$ Hz, 1H), 8.10 – 8.07 (m, 2H), 7.84 – 7.80 (m, 2H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.18 – 7.07 (m, 3H), 5.74 (d, $J = 12.2$ Hz, 1H), 3.16 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 164.5 (d, $J_{C-F} = 250.1$ Hz), 164.4, 155.0, 140.3, 132.3, 131.5 (d, $J_{C-F} = 3.0$ Hz), 129.8 (d, $J_{C-F} = 9.0$ Hz), 129.1, 125.5, 122.3, 120.8, 115.5 (d, $J_{C-F} = 21.7$ Hz), 93.3, 45.3 (br), 37.4 (br). HRMS (ESI) Calcd for $[C_{18}H_{17}FN_2O_2+H]^+$ 313.1352, Found 313.1357.

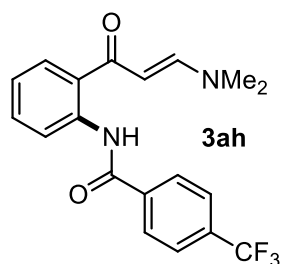


Conditions A (36.7 mg, 56%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.17 (br, 1H), 8.80 (d, $J = 8.3$ Hz, 1H), 8.01 (d, $J = 8.5$ Hz, 2H), 7.85 – 7.81 (m, 2H), 7.50 – 7.45 (m, 3H), 7.10 (t, $J = 7.5$ Hz, 1H), 5.74 (d, $J = 12.2$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 164.5, 155.1, 140.3, 137.7, 133.8, 132.4, 129.1, 128.9, 128.8, 125.5, 122.5, 120.8, 93.3, 45.3 (br), 37.4 (br). HRMS (ESI) Calcd for $[C_{18}H_{17}ClN_2O_2+H]^+$ 329.1057, Found 329.1058.

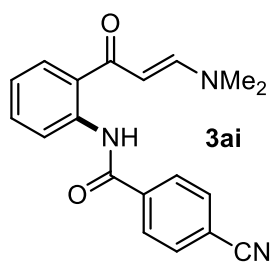


Conditions A (65.6 mg, 88%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.19 (br,

1H), 8.80 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 8.1$ Hz, 2H), 7.85 – 7.82 (m, 2H), 7.62 (d, $J = 8.1$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 7.3$ Hz, 1H), 5.74 (d, $J = 12.1$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.2, 164.6, 155.1, 140.2, 134.2, 132.4, 131.8, 129.1 (two overlapping signals), 126.2, 125.5, 122.5, 120.8, 93.2, 45.3 (br), 37.4 (br). HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{BrN}_2\text{O}_2+\text{H}]^+$ 373.0552, Found 373.0555.

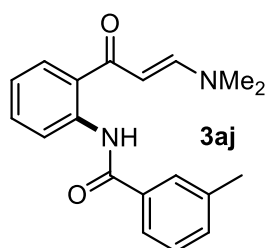


Conditions A (37.6 mg, 52%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.34 (br, 1H), 8.82 (d, $J = 8.1$ Hz, 1H), 8.18 (d, $J = 7.5$ Hz, 2H), 7.87– 7.75 (m, 4H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.13 (t, $J = 7.2$ Hz, 1H), 5.76 (d, $J = 11.9$ Hz, 1H), 3.19 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.2, 164.2, 155.2, 140.1, 138.7, 133.0 (q, $J_{\text{C-F}} = 32.1$ Hz), 132.4, 129.1, 127.9 (two overlapping signals), 125.7 (q, $J_{\text{C-F}} = 3.7$ Hz), 125.5, 122.7, 120.9, 93.2, 45.4 (br), 37.5 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_2+\text{H}]^+$ 363.1320, Found 363.1322.

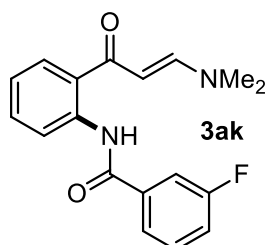


Conditions A (43.4 mg, 68%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.5 (br, 1H), 8.79 (d, $J = 8.3$ Hz, 1H), 8.16 (d, $J = 8.2$ Hz, 2H), 7.87 – 7.77 (m, 4H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 5.76 (d, $J = 12.1$ Hz, 1H), 3.20 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 163.5, 155.3, 134.0, 139.3, 132.5, 132.4, 129.1, 128.1, 125.4, 122.9, 120.8, 118.3, 114.8, 93.1, 45.4 (br), 37.5 (br). The broadening of the Me signals is likely due to partially hindered rotation along the

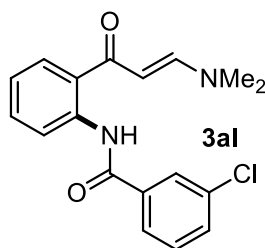
C(alkenyl)-N bond. HRMS (ESI) Calcd for $[C_{19}H_{17}N_3O_2+H]^+$ 320.1399, Found 320.1399.



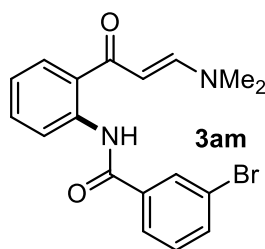
Conditions A (53.6 mg, 87%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 12.96 (br, 1H), 8.82 (d, $J = 8.3$ Hz, 1H), 7.89 – 7.80 (m, 4H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.40 – 7.32 (m, 2H), 7.10 (t, $J = 7.5$ Hz, 1H), 5.73 (d, $J = 12.2$ Hz, 1H), 3.17 (s, 3H), 2.93 (s, 1H), 2.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 165.9, 155.0, 140.3, 138.3, 135.2, 132.24, 132.20, 129.0, 128.4, 128.3, 125.7, 124.2, 122.2, 120.9, 93.4, 45.3 (br), 37.4 (br), 21.4. The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[C_{19}H_{20}N_2O_2+H]^+$ 309.1603, Found 309.1600.



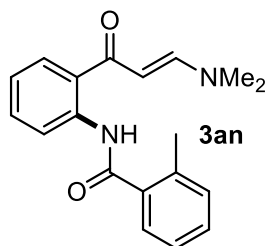
Conditions A (52.4 mg, 84%, yellow solid). 1H NMR (400 MHz, $CDCl_3$) δ 13.20 (br, 1H), 8.81 (d, $J = 8.3$ Hz, 1H), 7.95 – 7.68 (m, 4H), 7.51 – 7.44 (m, 2H), 7.21 (td, $J = 8.3, 2.0$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 5.75 (d, $J = 12.2$ Hz, 1H), 3.19 (s, 3H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 164.2, 162.8 (d, $J_{C-F} = 245.2$ Hz), 155.1, 140.1, 137.7 (d, $J_{C-F} = 6.8$ Hz), 132.3, 130.2 (d, $J_{C-F} = 7.7$ Hz), 129.1, 125.5, 122.8 (d, $J_{C-F} = 2.3$ Hz), 122.5, 120.8, 118.4 (d, $J_{C-F} = 21.3$ Hz), 114.8 (d, $J_{C-F} = 22.8$ Hz), 93.2, 45.3 (br), 37.4 (s). HRMS (ESI) Calcd for $[C_{18}H_{17}FN_2O_2+H]^+$ 313.1352, Found 313.1358.



Conditions A (59.7 mg, 91%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.19 (br, 1H), 8.79 (d, $J = 8.3$ Hz, 1H), 8.07 (s, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.85 – 7.81 (m, 2H), 7.50 – 7.40 (m, 3H), 7.11 (t, $J = 7.6$ Hz, 1H), 5.74 (d, $J = 12.2$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 164.2, 155.1, 140.1, 137.2, 134.8, 132.3, 131.5, 129.9, 129.1, 128.0, 125.6, 125.2, 122.6, 120.9, 93.2, 45.3 (br), 37.4 (br). The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_2 + \text{H}]^+$ 329.1057, Found 329.1053.

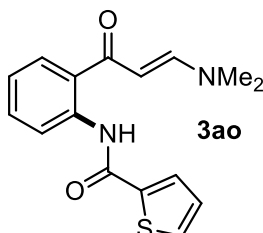


Conditions A (67.1 mg, 90%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.20 (br, 1H), 8.79 (d, $J = 8.3$ Hz, 1H), 8.23 (s, 1H), 7.98 (d, $J = 7.7$ Hz, 1H), 7.86 – 7.82 (m, 2H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.11 (t, $J = 7.4$ Hz, 1H), 5.74 (d, $J = 12.2$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 164.1, 155.1, 140.1, 137.4, 134.4, 132.3, 131.0, 130.1, 129.1, 125.6 (two overlapping signals), 122.9, 122.6, 120.9, 93.2, 45.3 (br), 37.4 (br). HRMS (ESI) Calcd for $[\text{C}_{18}\text{H}_{17}\text{BrN}_2\text{O}_2 + \text{H}]^+$ 373.0552, Found 373.0551.

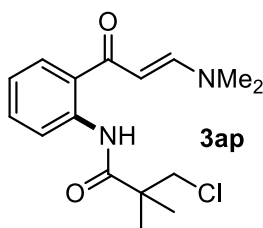


Conditions A (28.3 mg, 46%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 12.30 (br,

1H), 8.81 (d, $J = 8.2$ Hz, 1H), 7.80 – 7.74 (m, 2H), 7.63 (d, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.34 – 7.23 (m, 3H), 7.11 (t, $J = 7.4$ Hz, 1H), 5.70 (d, $J = 12.2$ Hz, 1H), 3.15 (s, 3H), 2.93 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 168.5, 155.0, 140.0, 136.9, 136.8, 132.2, 131.2, 130.0, 129.0, 127.2, 126.0, 125.9, 122.4, 120.9, 93.5, 45.2 (br), 37.4 (s), 20.3. HRMS (ESI) Calcd for $[\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2+\text{H}]^+$ 309.1603, Found 309.1606.



Conditions A (50.4 mg, 84%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 13.16 (br, 1H), 8.74 (d, $J = 8.3$ Hz, 1H), 7.85 – 7.80 (m, 3H), 7.52 – 7.44 (m, 2H), 7.13 – 7.06 (m, 2H), 5.75 (d, $J = 12.2$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.2, 160.4, 155.0, 141.0, 140.3, 132.4, 130.5, 129.1, 128.4, 127.8, 125.2, 122.2, 120.7, 93.3, 45.3 (br), 37.4 (br). HRMS (ESI) Calcd for $[\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}+\text{H}]^+$ 301.1011, Found 301.1009.



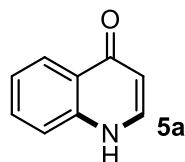
Conditions A (56.2 mg, 91%, yellow solid). ^1H NMR (400 MHz, CDCl_3) δ 12.38 (br, 1H), 8.68 (d, $J = 8.3$ Hz, 1H), 7.82 – 7.77 (m, 2H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 5.71 (d, $J = 12.2$ Hz, 1H), 3.74 (s, 2H), 3.19 (s, 3H), 2.95 (s, 3H), 1.45 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 174.1, 154.9, 139.9, 132.2, 129.0, 125.7, 122.3, 120.8, 93.3, 53.0, 45.6, 45.3 (br), 37.4 (br), 23.5. The broadening of the Me signals is likely due to partially hindered rotation along the C(alkenyl)-N bond. HRMS (ESI) Calcd for $[\text{C}_{16}\text{H}_{21}\text{ClN}_2\text{O}_2+\text{H}]^+$ 309.1370, Found 309.1371.

III. Synthesis of NH 4-Quinolones

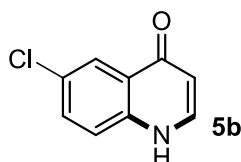
Reaction Conditions A: enaminone **1a** (35.1 mg, 0.2 mmol), $\text{CoCp}^*(\text{CO})\text{I}_2$ (9.5 mg,

10 mol %), AgNTf₂ (15.5 mg, 20 mol %), KOAc (6.0 mg, 30 mol %), and dioxazolone **2a** (50.0 mg, 0.3 mmol) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL) under N₂. The reaction mixture was stirred for 12 h at 100 °C. After removal of 1,4-dioxane under reduced pressure, THF (3 mL) was added followed by addition of HCl (2 M, 0.5 mL). The mixture was stirred at 30 °C for 12 h. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired product **5a** (85% yield).

Reaction Conditions B: enaminone (0.2 mmol), dioxazolone **2a** (50.0 mg, 0.3 mmol), [Cp*RhCl₂]₂ (4.9 mg, 4 mol%), AgSbF₆ (11 mg, 16 mol%), and AgOAc (6.7 mg, 20 mol %) were weighed into a pressure tube, to which was added 1,2-dichloromethane (2 mL) under N₂. The reaction mixture was stirred for 12 h at 100 °C. After complete removal of 1,2-dichloromethane under reduced pressure, THF (3 mL) was added followed by addition of HCl (2 M, 0.5 mL). The mixture was stirred at 30 °C for 12 h. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired product.



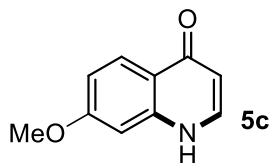
Conditions A (24.7 mg, 85%, white solid). ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.76 (br, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 7.1, 6.1 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.03 (d, *J* = 7.4 Hz, 1H). ¹³C NMR (100 MHz, DMSO) δ 176.9, 140.0, 139.4, 131.6, 125.8, 124.9, 123.0, 118.2, 108.7. HRMS (ESI) Calcd for [C₉H₇NO+H]⁺ 146.0606, Found 146.0605.



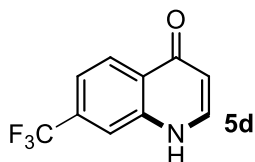
Conditions A (23 mg, 64%, yellow solid). ¹H NMR (400 MHz, CD₃OD) δ 8.19 (d, *J* = 2.1 Hz, 1H), 7.97 (d, *J* = 7.3 Hz, 1H), 7.67 (*J* = 8.9, 2.2 Hz, 1H), 7.57 (d, *J* = 8.9 Hz, 1H), 6.33 (d, *J* = 7.3 Hz, 1H). The NH signal was missing due to exchange. ¹³C NMR

(100 MHz, CD₃OD) δ 179.5, 141.7, 140.0, 133.8, 131.1, 127.7, 125.3, 121.6, 110.1.

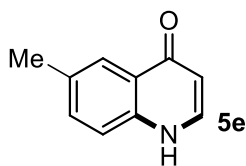
HRMS (ESI) Calcd for [C₉H₇ClNO+H]⁺ 180.0216, Found 180.0217.



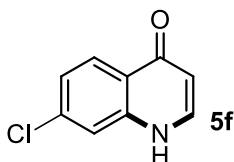
Conditions A (23.5 mg, 67%, yellow solid). ¹H NMR (400 MHz, CD₃OD) δ 8.11 (d, *J* = 9.1 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 1H), 6.98 (dd, *J* = 9.1, 2.0 Hz, 1H), 6.90 (s, 1H), 6.24 (d, *J* = 7.3 Hz, 1H), 3.89 (s, 3H). The NH signal was missing due to exchange. ¹³C NMR (100 MHz, MeOD) δ 180.3, 164.6, 143.5, 141.0, 127.9, 121.0, 116.2, 109.5, 99.6, 56.2. HRMS (ESI) Calcd for [C₁₀H₉NO₂+H]⁺ 176.0712, Found 176.0712.



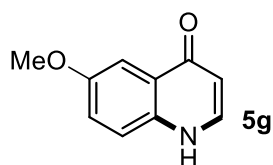
Conditions A (18.9 mg, 54%, yellow solid). ¹H NMR (400 MHz, CD₃OD) δ 8.40 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.89 (s, 1H), 7.62 (*J* = 8.6, 1.2 Hz, 1H), 6.38 (d, *J* = 7.4 Hz, 1H). The NH signal was missing due to exchange. ¹³C NMR (100 MHz, CD₃OD) δ 180.0, 142.5, 141.1, 134.8 (q, *J*_{C-F} = 32.6 Hz), 128.7, 128.1, 125.0 (q, *J*_{C-F} = 270.3 Hz), 120.8 (q, *J*_{C-F} = 3.3 Hz), 117.2 (q, *J*_{C-F} = 3.1 Hz), 111.0. HRMS (ESI) Calcd for [C₁₀H₆F₃NO+H]⁺ 176.0712, Found 176.0711.



Conditions A (24.1 mg, 76%, yellow solid). ¹H NMR (400 MHz, CD₃OD) δ 8.03 (s, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.55 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 7.2 Hz, 1H), 2.47 (s, 3H). The NH signal was missing due to exchange. ¹³C NMR (100 MHz, CD₃OD) δ 180.5, 141.0, 139.6, 135.6, 135.2, 126.6, 125.2, 119.4, 109.5, 21.3. HRMS (ESI) Calcd for [C₁₀H₉NO+H]⁺ 160.0762, Found 160.0762.

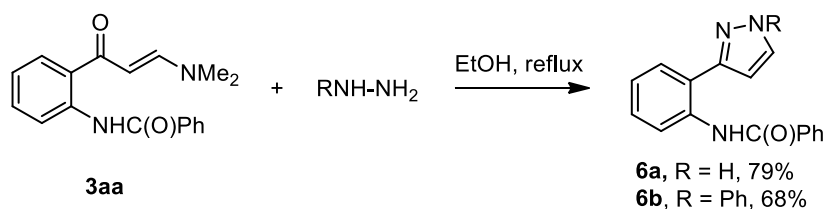


Conditions B (29.5 mg, 82%, yellow solid). ^1H NMR (400 MHz, DMSO- d_6) δ 11.87 (s, 1H), 8.13 (d, J = 8.7 Hz, 1H), 8.05 – 7.92 (m, 1H), 7.64 (d, J = 1.7 Hz, 1H), 7.37 (dd, J = 8.7, 1.8 Hz, 1H), 6.10 (d, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 176.4, 140.9, 140.1, 136.3, 127.4, 124.5, 123.5, 117.5, 109.4. HRMS (ESI) Calcd for $[\text{C}_9\text{H}_6\text{ClNO}+\text{H}]^+$ 180.0216, Found 180.0218

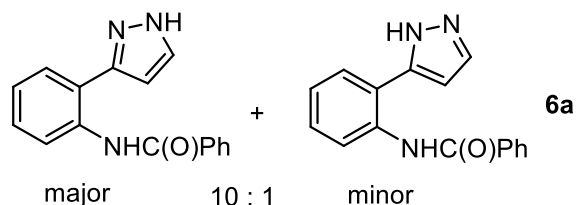


Conditions A (21.0 mg, 60%, yellow solid). ^1H NMR (400 MHz, CD_3OD) δ 7.93 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 2.8 Hz, 1H), 7.54 (d, J = 9.1 Hz, 1H), 7.35 (dd, J = 9.1, 2.9 Hz, 1H), 6.33 (d, J = 7.1 Hz, 1H), 3.90 (s, 3H). The NH signal was missing due to exchange. ^{13}C NMR (100 MHz, CD_3OD) δ 180.0, 158.3, 140.2, 136.3, 127.8, 124.8, 121.2, 108.8, 104.7, 56.1. HRMS (ESI) Calcd for $[\text{C}_{10}\text{H}_9\text{NO}_2+\text{H}]^+$ 176.0712, Found 176.0711. HRMS (ESI) Calcd for $[\text{C}_{10}\text{H}_9\text{NO}_2+\text{H}]^+$ 176.0712, Found 176.0711.

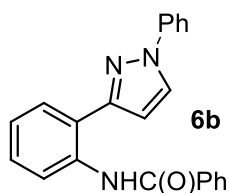
IV. Derivatization of an Amidated Product.



To a solution of **3aa** (58.8 mg, 0.2 mmol) in ethanol (3 mL) was added hydrazine hydrate (15.6 mg, 1.5 equiv), and the mixture was heated at 100°C (oil bath temperature) for overnight. The solution was extracted three times with dichloromethane (5 mL). The organic layer was washed with brine (10 mL), dried over MgSO_4 , and the solvent was removed under reduced pressure to afford the crude product. The residue was purified by silica gel chromatography using PE/EA to afford the product **6a** as a yellow solid.



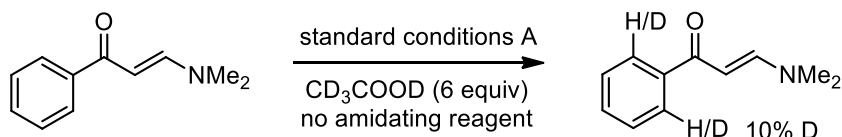
Selected signals: ^1H NMR (400 MHz, acetone- d_6): δ 12.67 (br, 2H, major), 12.2 (br, 1H, minor), 8.95 (d, J = 8.2 Hz, major), 8.90 (dd, J = 8.4, 1.0 Hz, 1H, minor), 8.19 – 8.17 (m, 2H, major), 8.15 – 8.14 (m, 1H, minor), 8.02 (d, J = 2.6 Hz, 1H, major), 7.96 (d, J = 2.3 Hz, 1H, minor), 7.89 (dd, J = 7.8, 1.5 Hz, 1H, major), 7.84 (J = 7.8, 1.5 Hz, 1H, minor), 6.94 (d, J = 2.0 Hz, 1H, major), 6.84 (d, J = 2.6 Hz, 1H, minor). ^{13}C NMR (101 MHz, acetone- d_6) δ 165.0, 151.3, 137.0, 135.7, 131.5, 129.9, 128.7, 128.1, 128.0, 127.8, 127.6, 127.4, 123.1, 120.5, 120.4, 120.3, 103.5, 103.3. HRMS (ESI) Calcd for $[\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}+\text{H}]^+$ 264.1137, Found 264.1133.



Product **6b** was isolated as a yellow solid (68%) ^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, J = 8.3 Hz, 1H), 7.97 (s, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.30 – 7.18 (m, 5H), 7.19 – 7.07 (m, 2H), 6.60 (d, J = 1.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.0, 140.8, 139.2, 138.2, 136.0, 134.3, 132.0, 130.8, 130.2, 129.0, 128.8, 127.6, 126.8, 124.3, 123.7, 121.5, 121.1, 109.1. HRMS (ESI) Calcd for $[\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}+\text{H}]^+$ 340.1450, Found 340.1454.

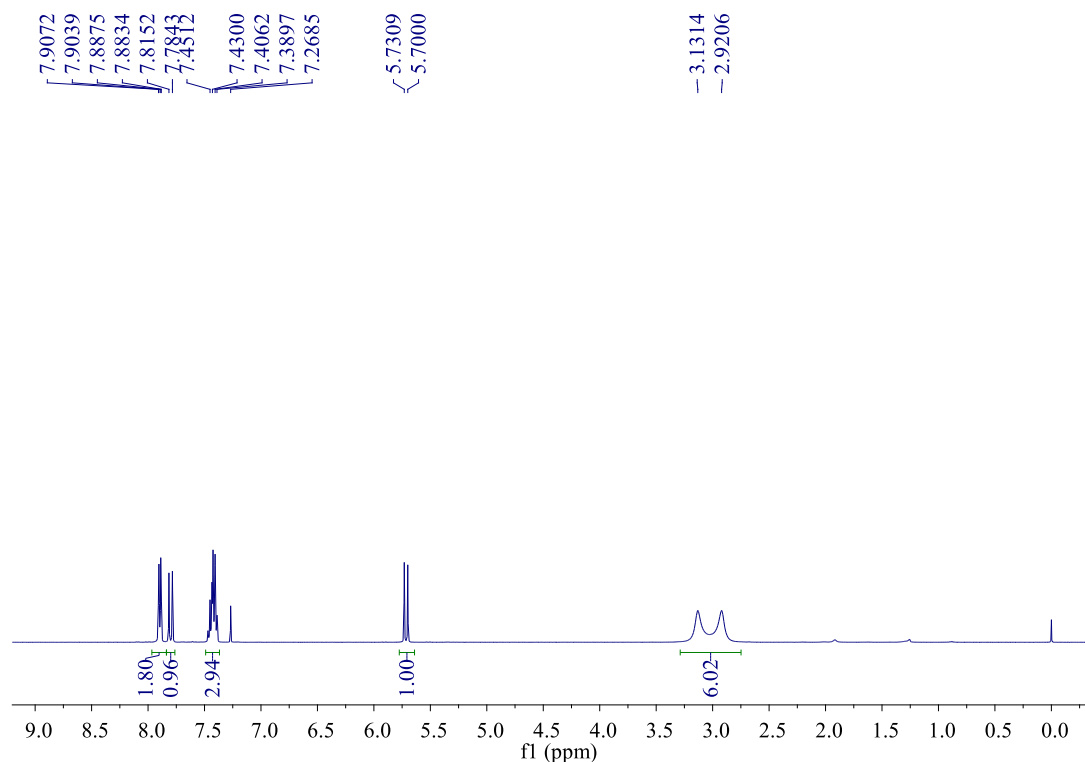
V. Mechanistic Studies

a. H/D exchange experiment

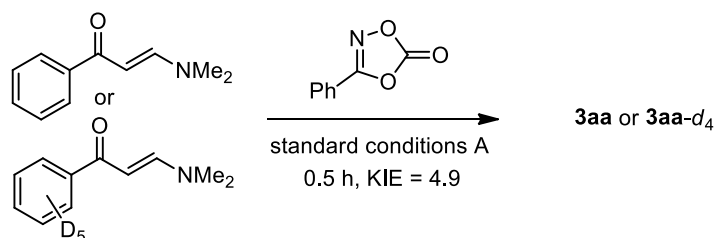


A mixture of enaminone **1** (35.1 mg, 0.2 mmol), $\text{CoCp}^*(\text{CO})\text{I}_2$ (9.5 mg, 10 mol %), AgNTf_2 (15.5 mg, 20 mol%), KOAc (6.0 mg, 30 mol %), and acetic acid- d_4 (76.8 mg, 6 equiv) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL)

under N₂. The ratio of H/D was determined on the basis of ¹H NMR analysis.

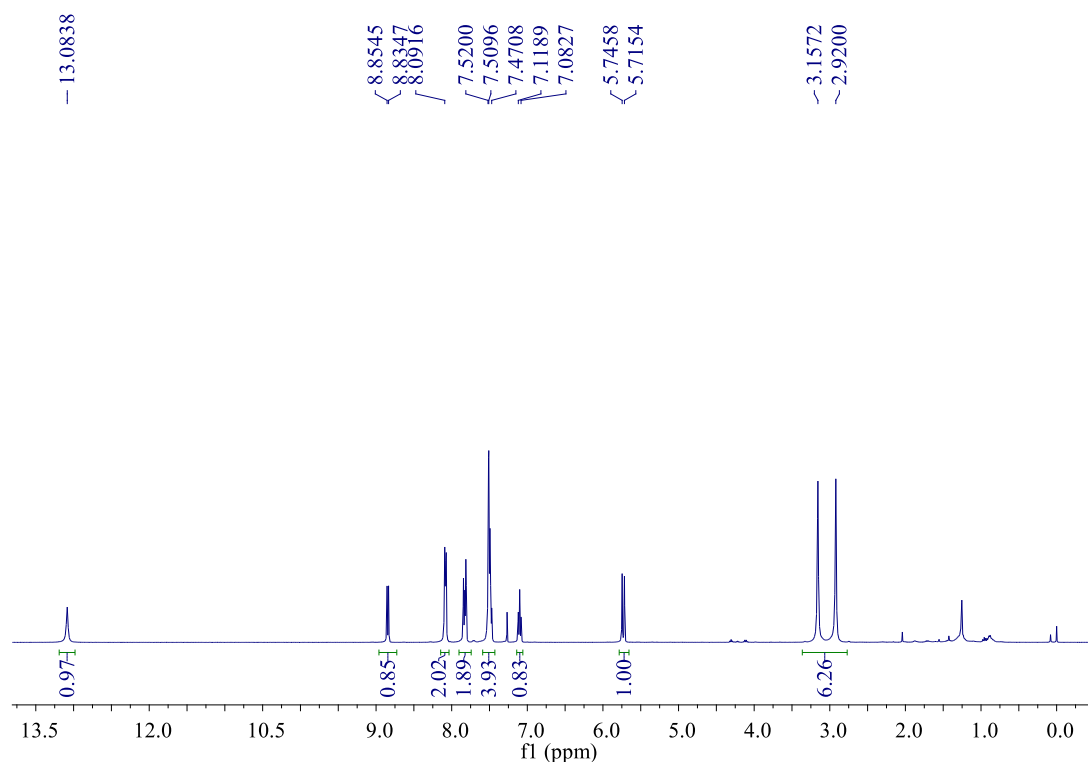


b. Intramolecular KIE experiments

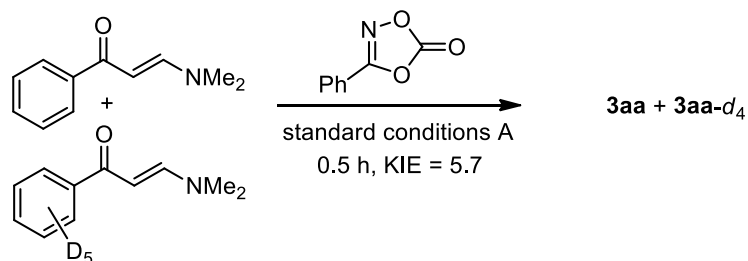


A mixture of enaminone **1a** (35.1 mg, 0.2 mmol), CoCp*(CO)I₂ (9.5 mg, 10 mol %), AgNTf₂ (15.5 mg, 20 mol %), KOAc (6.0 mg, 30 mol %), and dioxazolone **2a** (50.0 mg, 0.3 mmol) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL) under N₂. To another tube were added enaminone-*d*₅ **1a-d₅** (36.0 mg, 0.2 mmol), CoCp*(CO)I₂ (9.5 mg, 10 mol %), AgNTf₂ (15.5 mg, 20 mol %), KOAc (6.0 mg, 30 mol%), and dioxazolone **2a** (50.0 mg, 0.3 mmol) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL) under N₂. These two reaction mixtures were stirred side-by-side in the same oil bath at 50 °C for 0.5 h. The reactions tubes were quenched at 0 °C and these two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified by silica gel chromatography using PE/EA to afford the mixed product. KIE value (*k_H*/*k_D* = 4.9)

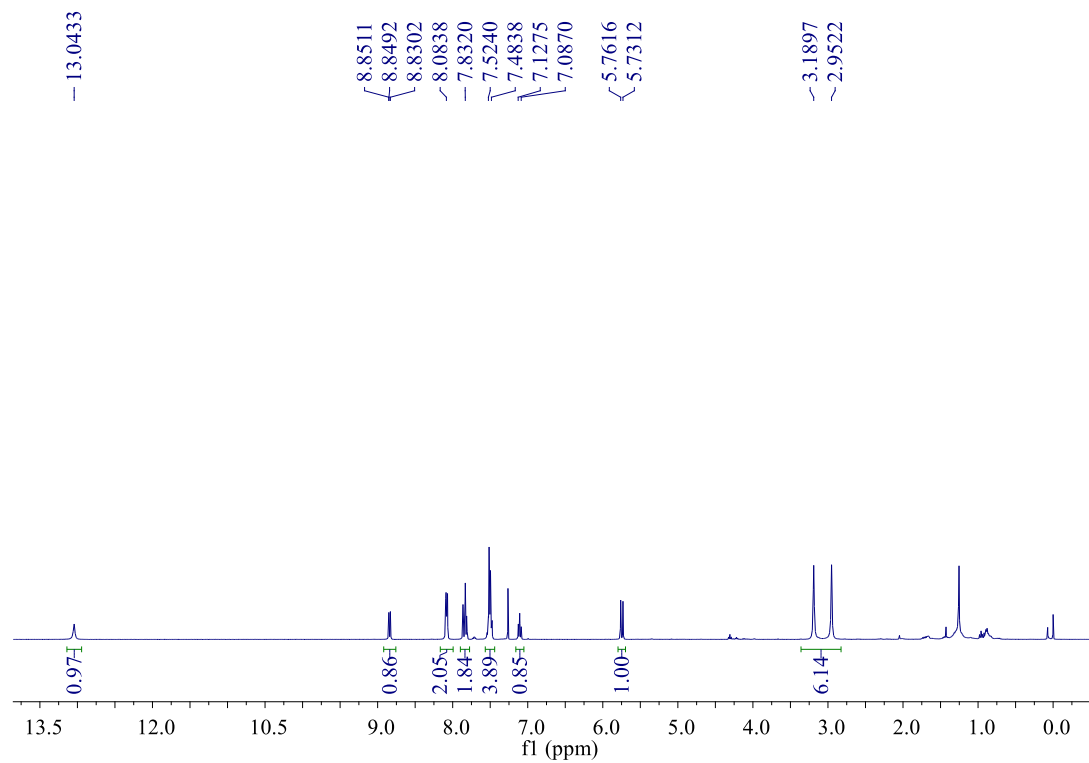
was determined on the basis of ^1H NMR analysis.



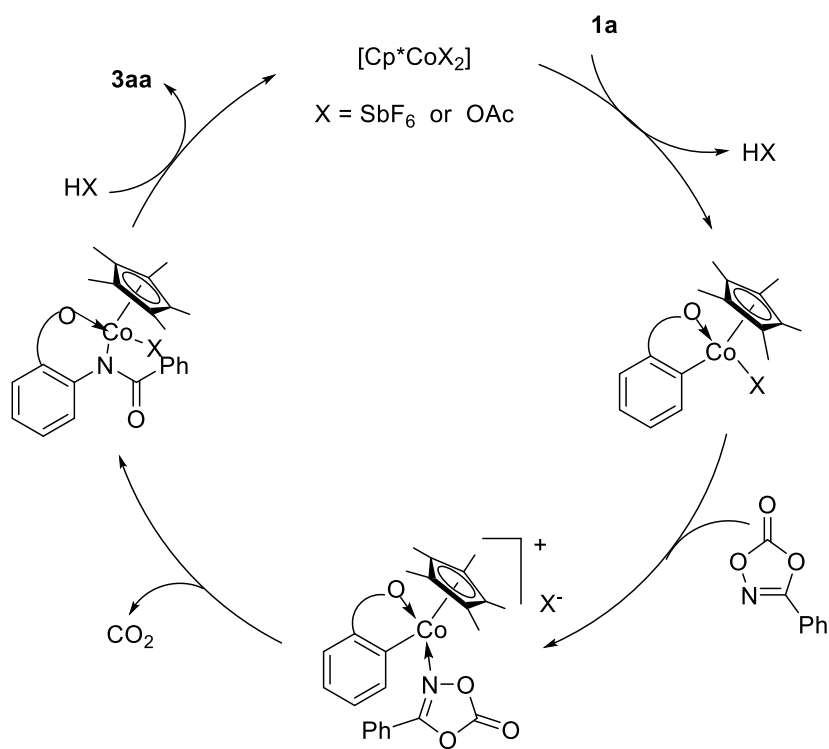
c. Intermolecular KIE experiments



An equimolar mixture of enaminone **1a** (35.1 mg, 0.2 mmol), enaminone **1a-d₅** (36.0 mg, 0.2 mmol), $\text{CoCp}^*(\text{CO})\text{I}_2$ (9.5 mg, 10 mol %), AgNTf_2 (15.5 mg, 20 mol %), KOAc (6.0 mg, 30 mol %), and dioxazolone **2a** (50.0 mg, 0.3 mmol) were weighed into a pressure tube, to which was added 1,4-dioxane (2 mL) under N_2 . The reaction mixture was stirred at 50 °C for 0.5 h. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired products. KIE value ($k_{\text{H}}/k_{\text{D}} = 5.7$) was determined on the basis of ^1H NMR analysis.



d. A proposed catalytic cycle for the coupling of 1a and 2a.



VI. NMR Spectra

