Supplementary information for:

“Direct Alkenyl C-H Functionalization of Cyclic Enamines with Carboxylic Acids via Rh Catalysis Assisted by Hydrogen Bonding”

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General Experimental Section

Analytic methods.

$^{1}$H NMR, $^{13}$C NMR data were obtained on Bruker 400 M nuclear resonance spectrometers unless otherwise specified, respectively. CDCl$_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^{1}$H NMR spectrum as 0.00 ppm. The data of $^{1}$H NMR was reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiplet and $br$ = broad), coupling constant ($J$ values) in Hz and integration. Chemical shifts for $^{13}$C NMR spectra were recorded in ppm from TMS using the central peak of CDCl$_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200 - 300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin - layer chromatography (TLC) was performed on pre-coated, glass–backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS (ESI) analysis was performed by Analytical Instrumentation Center, Chengdu Institute of Biology, Chinese Academy of Sciences.

General preparation for chemicals.

Dicarbonylacetylacetonato rhodium(I) (99%), Chloro(1,5-cyclooctadiene)rhodium(I)(97%) dimer, Hydroxy(1,5-cyclooctadiene)rhodium(I)dimer,min.(97%), and Dicarbonylchlororhodium(I) dimer (97%)were purchased from Alfa Aesar. All the acids were purchased from Alfa Aesar. All the solvents were directly used from purchased without any further purification unless otherwise specified.
General Experimental Procedures

General procedure for preparation of enamine substrates 1

The substituted 2-aminepyridines were prepared as equations (S1-S3) below.

(Equation S1) 3-Hydropyridine (78.5 mmol, 7.46g) was added to ice cold H₂SO₄ (42 ml), concentrated HNO₃ (4 ml) was added dropwise while maintaining the temperature below 10 °C. After addition, the reaction was monitored by TLC until disappearance of the started material in about 4 h. The ice cold water was addition by caution and then it was neutralized to pH=6 by saturated potassium carbonate. It was cooled and then solid precipitated, it was filtered and washed with petroleum ether/EtOAc =10/1. Recrystallization in petroleum ether/EtOAc afforded yellow solid. The aqueous phase was extracted by EtOAc and combined with the mother solution and purified by flash chromatography on silica gel with petroleum ether/EtOAc (5:1). The two parts were combined to give desired product 8.25g.

2-Nitro-3-hydropyridine (20 mmol, 2.82g) and potassium carbonate (40 mmol, 5.52g) were half-dissolved in acetone (150 ml). Me₂SO₄[2] (26 mmol, 2.46 ml) or BnBr[3] (26 mmol, 3.09 ml) was added dropwise at 0 °C and stirred at room temperature until disappearance of the started material. It was quenched by water and the solvent was removed and extracted by EtOAc, dried over Na₂SO₄, evaporated in vacuum to afford crude product which was purified by flash chromatography on silica gel with ether/EtOAc (10:1) to produce the desired product. And finally the methyl ether was reduced by Pd/C, H₂ and benzyl ether was reduction by Fe/AcOH.

(Equation S2) The new prepared sodium methoxide (200 mmol, 10.8g) was mixed with 3,5-dichloropyridine (20 mmol, 2.96g) and dissolved in DMF (60 ml) in the atmosphere of N₂, it was heated to 80 °C for 36 h and then cooled to room temperature. The DMF was removed under reduced pressure and washed with water (20 ml), extracted by EtOAc, dried over Na₂SO₄, evaporated in vacuum to afford product which was purified by flash chromatography on silica gel with petroleum ether/EtOAc (10:1) to produce the desired product 1.81g.

3,5-Dimethoxyppyridine (10 mmol, 1.39g) was dissolved in concentrated H₂SO₄ (20 ml), HNO₃ (10.5 mmol, 0.675 ml) and H₂SO₄ (20 ml) were mixed and was added dropwise at 0 °C. It was stirred for 5 minutes and quenched by ice and extracted by...
EtOAc, dried over Na₂SO₄, evaporated in vacuum to afford crude product which was purified by flash chromatography on silica gel with petroleum ether/EtOAc (4:1) to produce the desired product 1.57 g. And finally it was reduction by Pd/C, H₂ in at room temperature.

(Equation S3)Br₂ (107.26 mmol, 5.50 ml) was added to 10% NaOH solution 50 ml 5-10 ºC. This sodium hypobromide solution was added over 2 h to a solution of 3-hydropyridine (105.15 mmol, 10 g) in 10% NaOH (50 ml).[6] The mixture was for additional 2 h. Acetic acid was added to bring the pH of the solution to between 6 and 7. The mixture was cooled to 5 ºC for 1 h, and product was filtered off. It was washed with water and dried in vacuo at 85 ºC to give the product 6.4 g as white solid. The methylation[2, 7], nitration[1, 8], debromide and reduction[8] to afford the desired product.

Substrates 1a-1j was prepared by condensation of 1,2-ketones with substituted arylamine or acetamide as equation below.[9]

(Equation S4)In a 50 mL round bottom flask, equipped with a condenser, 1,2-dione (10mmol), arylamine or acetic amide (10 mmol), alumina (10 g) and toluene (30mL) was stirred and heated to reflux for 36 h. Upon reaction completion, alumina was removed by filtration and washed with EtOAc. The organic phases were combined and concentrated under vacuum and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (20:1-4:1) to give substrates 1a-1j.
General Experimental Procedures and Characterizations

[Rh(cod)Cl]₂ (0.005 mmol, 2.4 mg) or [Rh(CO)₂Cl]₂ (0.005 mmol, 1.9 mg), enamine 1 (0.2 mmol), and carboxylic acid (0.24 mmol) were added to a Schlenk flask, which was then degassed with N₂ for three times. (tBuCO)₂O (0.3 mmol) and 2 mL of anhydrous toluene were added, and the reaction mixture was subsequently heated and kept at 140°C in oil bath for the indicated time with stirring. After cooling to room temperature, 1 mL of a concentrated ammonia solution was added. The mixture was directly subjected to column chromatograph on silica gel with petroleum ether/EtOAc (12:1-5:1) as eluent to afford the desired product 2 or 3.

General Experimental Procedures for 1 mmol scale

[Rh(cod)Cl]₂ (0.025 mmol, 12 mg) enamine 1c (1 mmol, 218.3 mg), and carboxylic acid (0.24 mmol) were added to a Schlenk flask, which was then degassed with N₂ for three times. (tBuCO)₂O (3 mmol, 0.305) and 10 mL of anhydrous toluene were added, and the reaction mixture was subsequently heated and kept at 140°C in oil bath for the indicated time with stirring. After cooling to room temperature, 4 mL of a concentrated ammonia solution was added. The mixture was directly subjected to column chromatograph on silica gel with petroleum ether/EtOAc (12:1-5:1) as eluent to afford the desired product 2 or 3.
The hydrolysis of enamine product

(Equation S5) In a sealed tube, substrate \(2a\) (0.2 mmol, 58.8 mg), TsOH (0.8 mmol, 137.8 mg) and toluene/H\(_2\)O (1/1, 4 ml) were stirred at 140°C for 36 h. After reaction completed, the mixture was extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with sat. NaHCO\(_3\) (10 mL) and brine (10 mL) and dried over Na\(_2\)SO\(_4\). The solvent was removed under vacuum and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (10:1) to give product \(4a\) (24.5 mg, 65%) as white solid, part of \(2a\) was recovered (14.7 mg, 25%).

(Equation S6) In a sealed tube, substrate \(2w\) (0.2 mmol), TsOH (0.8 mmol, 137.8 mg) and toluene/H\(_2\)O (1/1, 4 ml) were stirred at 140°C for 24 h. After reaction completed, the mixture was diluted with 10 mL water and extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with sat. NaHCO\(_3\) (30 mL) and brine (30 mL) and dried over Na\(_2\)SO\(_4\). The solvent was removed under vacuum and the residue was purified by flash chromatography eluting with petroleum ether/EtOAc (10:1) to give product \(4w\) (21.0 mg, 75%) as pale oil.
5-methyl-2-(pyridin-2-ylamino)cyclopent-2-enone
Compound 1a\[^9\] was obtained as amorphous solid. \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25 (dd, \(J = 5.2, 1.2\) Hz, 1H), 7.67 (t, \(J = 3.2\) Hz, 1H), 7.51 (dd, \(J = 8.4, 7.2, 2.0\) Hz, 1H), 6.78-6.75 (m, 2H), 6.70 (d, \(J = 8.4\) Hz, 1H), 2.95 (ddd, \(J = 18.4, 6.4, 3.2\) Hz, 1H), 2.50-2.42 (m, 1H), 2.27 (ddd, \(J = 18.4, 3.2, 2.0\) Hz, 1H), 1.23 (d, \(J = 7.6\) Hz, 3H). \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.25, 154.33, 147.88, 137.33, 137.05, 131.27, 115.39, 110.63, 37.83, 33.86, 16.36.

5-methyl-2-((3-methylpyridin-2-yl)amino)cyclopent-2-enone
Compound 1b was obtained as yellow oil. \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.14 (d, \(J = 4.0\) Hz, 1H), 7.83 (t, \(J = 2.8\) Hz, 1H), 7.34 (d, \(J = 6.8\) Hz, 1H), 6.72 (dd, \(J = 7.2, 5.2\) Hz, 1H), 6.66 (br, 1H), 2.96 (ddd, \(J = 18.0, 6.4, 3.2\) Hz, 1H), 2.51-2.43 (m, 1H), 2.31-2.27 (m, 1H), 2.25 (s, 3H), 1.24 (d, \(J = 7.6\) Hz, 3H). \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.50, 152.77, 145.29, 137.53, 136.88, 132.09, 118.33, 115.40, 37.80, 33.93, 16.82, 16.40. HRMS: m/z: [M + H]\(^+\) calculated for C\(_{15}\)H\(_{15}\)N\(_2\)O: 203.1179; found 203.1181.

2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Compound 1c was obtained as yellow solid. \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85-7.82 (m, 2H), 7.34 (br, 1H), 6.95 (dd, \(J = 7.6, 1.2\) Hz, 1H), 6.72 (dd, \(J = 8.0, 4.8\) Hz, 1H), 3.87 (s, 3H), 2.94 (ddd, \(J = 18.4, 6.4, 3.2\) Hz, 1H), 2.48-2.40 (m, 1H), 2.26 (ddd, \(J = 18.2, 3.2, 2.0\) Hz, 1H), 1.23 (d, \(J = 7.6\) Hz, 3H). \(^1^C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.27, 145.53, 142.95, 138.25, 136.75, 131.88, 114.73, 114.62, 55.26, 37.81, 33.90, 16.44. HRMS: m/z: [M + H]\(^+\) calculated for C\(_{12}\)H\(_{15}\)N\(_2\)O\(_2\): 219.1128; found 219.1132.
2-((3-(benzyloxy)pyridin-2-yl)amino)-5-methylcyclopent-2-enone
Compound 1d was obtained as yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85-7.84 (m, 2H), 7.47 (br, 1H), 7.43-7.33 (m, 5H), 6.99 (d, $J$ = 8.0 Hz, 1H), 6.67 (dd, $J$ = 7.6, 5.2 Hz, 1H), 5.14 (s, 2H), 2.95 (ddd, $J$ = 18.4, 6.4, 3.2 Hz, 1H), 2.48-2.41 (m, 1H), 2.27 (d, $J$ = 18.4 Hz, 1H), 1.24 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.17, 145.74, 141.84, 138.63, 136.69, 135.89, 131.89, 128.67, 128.14, 127.03, 116.48, 114.65, 70.21, 37.78, 33.88, 16.36.
HRMS: m/z: [M + H]$^+$ calculated for C$_{18}$H$_{19}$N$_2$O$_2$: 295.1441; found 295.1447.

2-((3,5-dimethoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Compound 1e was obtained as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73-7.72 (m, 1H), 7.48 (s, 1H), 7.11 (br, 1H), 6.65 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.94-2.87 (m, 1H), 2.43-2.38 (m, 1H), 2.23 (d, $J$ = 18.0 Hz, 1H), 1.20 (d, $J$ = 7.2 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.31, 150.25, 143.54, 140.06, 136.94, 130.00, 120.82, 105.82, 56.18, 55.38, 37.80, 33.78, 16.41.
HRMS: m/z: [M + H]$^+$ calculated for C$_{13}$H$_{17}$N$_2$O$_3$: 249.1234; found 249.1237.

2-((5-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Compound 1f was obtained as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J$ = 2.8 Hz, 1H), 7.54 (t, $J$ = 3.2 Hz, 1H), 7.17 (dd, $J$ = 8.8, 2.8 Hz, 1H), 6.68 (d, $J$ = 8.8 Hz, 1H), 6.62 (br, 1H), 3.81 (s, 3H), 2.93 (ddd, $J$ = 18.0, 6.4, 3.2 Hz, 1H), 2.49-2.41 (m, 1H), 2.26 (ddd, $J$=18.4, 2.8, 2.0 Hz, 1H), 1.23 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.34, 150.05, 148.71, 137.41, 132.81, 129.24, 125.17, 111.13, 56.10, 37.85, 33.73, 16.36.
HRMS: m/z: [M + H]$^+$ calculated for C$_{12}$H$_{15}$N$_2$O$_2$: 219.1128; found 219.1133.
N-(4-methyl-5-oxocyclopent-1-en-1-yl)acetamide
Compound 1g was obtained as white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76-7.74 (m, 2H), 2.87 (ddd, $J$=18.8, 6.0, 4.7Hz, 1H), 2.40-2.32 (m, 1H), 2.23-2.17 (m, 1H), 2.12 (s, 3H), 1.15 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (100MHz, CDCl$_3$) $\delta$ 206.45, 168.80, 139.23, 135.67, 37.72, 34.03, 23.60, 15.99.
HRMS: m/z: [M + H]$^+$ calculated for C$_8$H$_{12}$NO$_2$: 154.0863; found 154.0868.

2-((2-methoxyphenyl)amino)-5-methylcyclopent-2-enone
Compound 1h was obtained as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (d, $J$ = 7.6 Hz, 1H), 6.95-6.90 (m, 1H), 6.87-6.86 (d, $J$ = 4.0 Hz, 2H), 6.84 (br, 1H), 6.68 (t, $J$ = 3.2 Hz, 1H), 3.88 (s, 3H), 2.91 (ddd, $J$ = 18.0, 6.4, 3.2 Hz, 1H), 2.50-2.42 (m, 1H), 2.26-2.20 (m, 1H), 1.24 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.31, 147.96, 138.66, 131.52, 122.91, 120.69, 120.08, 114.17, 110.07, 55.49, 37.77, 33.30, 16.42.
HRMS: m/z: [M + H]$^+$ calculated for C$_{13}$H$_{16}$NO$_2$: 218.1176; found 218.1180.

2-((3-methoxypyridin-2-yl)amino)cyclopent-2-enone
Compound 1i was obtained as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (t, $J$ = 2.8 Hz, 1H), 7.83 (d, $J$ = 5.2 Hz, 1H), 7.37 (br, 1H), 6.95 (d, $J$ = 7.6 Hz, 1H), 6.72 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.87 (s, 3H), 2.69 (dd, $J$ = 7.6, 3.2 Hz, 2H), 2.45-2.43(m, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.69, 145.44, 142.96, 138.26, 137.90, 133.44, 114.64, 114.18, 55.27, 32.37, 24.57.
HRMS: m/z: [M + H]$^+$ calculated for C$_{11}$H$_{13}$N$_2$O$_2$: 205.0972; found 205.0978.
2-((3-methoxypyridin-2-yl)amino)cyclohex-2-enone
Compound 1j was obtained as yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (t, $J$ = 4.8 Hz, 1H), 7.86 (br, 1H), 7.77 (d, $J$ = 4.8 Hz, 1H), 6.91 (d, $J$ = 8.0 Hz, 1H), 6.66 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.87 (s, 3H), 2.59-2.52 (m, 4H), 2.02 (q, $J$=6.4 Hz, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 195.12, 146.48, 143.11, 137.78, 133.80, 123.76, 114.17, 113.91, 55.31, 37.60, 24.87, 22.80.
HRMS: m/z: [M + H]$^+$ calculated for C$_{12}$H$_{15}$N$_2$O$_2$: 219.1128; found 219.1130.
Characterization of Products in Details

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc = 4/1 as eluate and 2a was obtained as yellow solid (55.3 mg, 94%, condition A; 279.6 mg, 95%, 1 mmol scale). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47-7.47 (m, 2H), 7.36 (d, $J$ = 4.0 Hz, 1H), 7.28-7.21 (m, 3H), 6.94-6.91 (m, 2H), 6.56 (dd, $J$ = 8.0, 5.2 Hz, 1H), 3.88 (s, 3H), 3.33 (dd, $J$ = 17.2, 6.8 Hz, 1H), 2.72-2.62 (m, 2H), 1.32 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.65, 149.12, 144.47, 143.65, 137.94, 136.53, 132.90, 128.78, 127.62, 127.55, 114.80, 114.52, 55.22, 37.87, 36.29, 16.42. HRMS: m/z: [M + H]$^+$ calculated for C$_{18}$H$_{19}$N$_2$O$_2$: 295.1441; found 295.1442.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(p-tolyl)cyclopent-2-enone
Petroleum ether/EtOAc = 5/1 as eluate and 2b was obtained as yellow solid (55.5 mg, 90%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.40 (m, 3H), 7.06 (d, $J$ = 8.0 Hz, 2H), 6.93 (d, $J$ = 7.6 Hz, 1H), 6.84 (br, 1H), 6.57 (dd, $J$ = 8.0, 5.2 Hz, 1H), 3.89 (s, 3H), 3.31 (dd, $J$ = 17.2, 7.2 Hz, 1H), 2.70-2.61 (m, 2H), 2.32 (s, 3H), 1.31 (d, $J$ = 7.6 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.63, 150.38, 144.85, 143.56, 139.17, 138.05, 133.33, 132.49, 128.34, 127.66, 114.36, 114.36, 55.19, 37.74, 36.15, 21.36, 16.40. HRMS: m/z: [M + H]$^+$ calculated for C$_{19}$H$_{21}$N$_2$O$_2$: 309.1598; found 309.1609.
3-(4-methoxyphenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and 2c was obtained as yellow solid (59.0 mg, 91%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, J = 8.8 Hz, 2H), 7.43-7.42 (m, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.81 (br, 1H), 6.77 (d, J = 8.8 Hz, 2H), 6.57 (dd, J = 7.6, 5.2 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.31 (dd, J = 16.9, 7.2 Hz, 1H), 2.68 – 2.59 (m, 2H), 1.29 (d, J = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.55, 160.23, 150.71, 145.01, 143.56, 138.12, 131.76, 129.54, 128.66, 114.69, 114.26, 113.01, 55.20, 55.14, 37.63, 36.06, 16.50.

HRMS: m/z: [M + H]$^+$ calculated for C$_{19}$H$_{21}$N$_2$O$_3$: 325.1547; found 325.1554.

3-(4-fluorophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =5/1 as eluate and 2d was obtained as yellow solid (55.8 mg, 89%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, J = 8.8, 5.6 Hz, 2H), 7.36 (dd, J = 4.2, 1.2 Hz, 1H), 6.95-6.89 (m, 4H), 6.58 (dd, J = 8.0, 5.2 Hz, 1H), 3.89 (s, 3H), 3.30 (dd, J = 17.2, 7.2 Hz, 1H), 2.70-2.61 (m, 2H), 1.31 (d, J = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.49, 162.71 (d, J=248.3 Hz), 147.81, 144.30, 143.68, 137.85, 132.74 (d, J=3.3 Hz), 132.56, 129.67 (d, J = 8.3 Hz), 114.71 (d, J = 24.2 Hz), 114.66, 114.59, 55.20, 37.73, 36.25, 16.40.

HRMS: m/z: [M + H]$^+$ calculated for C$_{18}$H$_{18}$F$_2$N$_2$O$_2$: 313.1347; found 313.1358.
3-(4-chlorophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =5/1 as eluate and 2e was obtained as yellow solid (59.8 mg, 91%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.35 (m, 3H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.99 (br, 1H), 6.94 (dd, $J = 8.0$, 0.8 Hz, 1H), 6.58 (dd, $J = 8.0$, 5.2 Hz, 1H), 3.89 (s, 3H), 3.29 (dd, $J = 17.6$, 7.2 Hz, 1H), 2.68-2.61 (m, 2H), 1.31 (d, $J = 7.6$ Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.44, 146.82, 144.08, 143.71, 137.87, 135.16, 134.39, 132.92, 129.00, 127.65, 114.89, 114.83, 55.24, 37.78, 36.18, 16.41.
HRMS: m/z: [M + H]$^+$ calculated for C$_{18}$H$_{18}$ClN$_2$O$_2$: 329.1051; found 329.1065.

3-(4-bromophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =5/1 as eluate and 2f was obtained as yellow solid (47.0 mg, 63%, condition A; 59.0 mg, 79%, condition B). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.29 (m, 5H), 6.99 (br, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 6.59 (dd, $J = 7.6$, 4.8 Hz, 1H), 3.89 (s, 3H), 3.29 (dd, $J = 17.2$, 7.2 Hz, 1H), 2.69-2.61 (m, 2H), 1.31 (d, $J = 7.2$ Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.48, 146.82, 144.05, 143.73, 137.89, 135.63, 132.97, 130.62, 129.24, 122.79, 114.93, 114.88, 55.26, 37.80, 36.14, 16.40.
HRMS: m/z: [M + H]$^+$ calculated for C$_{18}$H$_{18}$BrN$_2$O$_2$: 373.0546; found 373.0555.

4-(2-((3-methoxypyridin-2-yl)amino)-4-methyl-3-oxocyclopent-1-en-1-yl)benzonitrile
Petroleum ether/EtOAc =4/1 as eluate and 2g was obtained as yellow solid (33.2 mg, 52%, condition A; 58.8 mg, 92%, condition B). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49-7.43 (m, 4H), 7.25 (d, $J$ = 5.2 Hz, 1H), 7.18 (br, 1H), 6.96 (d, $J$ = 8.0 Hz, 1H), 6.60 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.91 (s, 3H), 3.30 (dd, $J$ = 17.2, 7.2 Hz, 1H), 2.71-2.65 (m, 2H), 1.33 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.28, 143.92, 143.25, 141.83, 137.51, 133.92, 131.02, 128.03, 118.92, 115.43, 115.17, 111.13, 55.32, 37.95, 36.13, 16.37.

HRMS: m/z: [M + H]$^+$ calculated for C$_{19}$H$_{18}$N$_3$O$_2$: 320.1394; found 320.1399.

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2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(4-(trifluoromethyl)phenyl)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and 2h was obtained as yellow solid (29.0 mg, 40%, condition A; 52.2 mg, 72%, condition B). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52-7.45 (m, 4H), 7.27 (dd, $J$ = 5.2, 1.2 Hz, 1H), 7.09 (br, 1H), 6.95 (dd, $J$ = 7.9, 1.2 Hz, 1H), 6.58 (dd, $J$ = 8.0, 5.2 Hz, 1H), 3.90 (s, 3H), 3.32 (dd, $J$ = 17.2, 7.2 Hz, 1H), 2.75-2.64 (m, 2H), 1.33 (d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.49, 145.03, 143.84, 143.68, 140.56, 137.68, 133.68, 129.87 (q, $J$ = 32.1 Hz), 127.77, 124.25 (q, $J$ = 3.8 Hz), 124.02 (q, $J$ = 270.6 Hz), 115.14, 114.05, 55.28, 37.94, 36.31, 16.38.

HRMS: m/z: [M + H]$^+$ calculated for C$_{39}$H$_{18}$F$_3$N$_2$O$_2$: 363.1315; found 363.1318.

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2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(m-tolyl)cyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and 2i was obtained as yellow solid (56.7 mg, 92%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, $J$ = 4.8 Hz, 1H), 7.29-7.28 (m, 2H), 7.14-7.07 (m, 2H), 6.94 (d, $J$ = 7.6 Hz, 1H), 6.88 (br, 1H), 6.57 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.32 (dd, $J$ = 17.2, 6.8 Hz, 1H), 2.71-2.61 (m, 2H), 2.24 (s, 3H), 1.32 (d, $J$ = 7.4 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.61, 149.15, 144.54, 143.67, 137.99, 137.00, 136.30, 132.89, 129.55, 128.25, 127.41, 124.91, 114.78, 114.45, 55.22, 37.84, 36.29, 21.26, 16.40.

HRMS: m/z: [M + H]$^+$ calculated for C$_{19}$H$_{21}$N$_2$O$_2$: 309.1598; found 309.1613.

3-(3-methoxyphenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and 2j was obtained as faint yellow solid (59.7 mg, 92%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 4.8 Hz, 1H), 7.16 (t, $J$ = 7.6 Hz, 1H), 7.09 (d, $J$ = 7.6 Hz, 1H), 7.01 (s, 1H), 6.93 (d, $J$ = 8.0 Hz, 1H), 6.89 (br, 1H), 6.82 (dd, $J$ = 8.0, 2.0 Hz, 1H), 6.58 (dd, $J$ = 7.6, 4.8 Hz, 1H), 3.87 (s, 3H), 3.57 (s, 3H), 3.31 (dd, $J$ = 17.2, 6.8 Hz, 1H), 2.71-2.62 (m, 2H), 1.31 (d, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.64, 158.81, 148.84, 144.47, 143.70, 138.02, 137.68, 133.04, 128.49, 120.19, 115.17, 114.85, 114.62, 112.80, 55.25, 54.89, 37.85, 36.32, 16.38.

HRMS: m/z: [M + H]$^+$ calculated for C$_{19}$H$_{21}$N$_2$O$_3$: 325.1547; found 325.1549.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(3-nitrophenyl)cyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and 2k was obtained as yellow solid (29.2 mg, 43%, condition B). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19-8.18 (m, 1H), 8.08 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.67 (d, $J$ = 7.6 Hz, 1H), 7.36 (t, $J$ = 8.0 Hz, 1H), 7.23-7.21 (m, 2H), 6.96 (dd, $J$ = 7.6, 0.8 Hz, 1H), 6.58 (dd, $J$ = 8.0, 5.2 Hz, 1H), 3.93 (s, 3H), 3.36 (dd, $J$ = 17.2, 7.2 Hz, 1H), 2.77-2.67 (m, 2H), 1.33 (d, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.32, 147.42, 144.13, 143.36, 142.59, 138.79, 137.44, 133.78, 133.52, 128.04, 122.68, 122.52, 115.44, 115.30, 55.40, 37.94, 36.18, 16.43.

HRMS: m/z: [M + H]$^+$ calculated for C$_{18}$H$_{18}$N$_3$O$_4$: 340.1292; found 340.1295.
2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(o-tolyl)cyclopent-2-enone
Petroleum ether/EtOAc =5/1 as eluate and 2l was obtained as yellow solid (20.4 mg, 33%, condition B). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32-7.30 (m, 1H), 7.19-7.12 (m, 2H), 7.10 (dd, \(J = 5.2, 1.2\) Hz, 1H), 7.01 (d, \(J = 6.8\) Hz, 1H), 6.87 (br, 1H), 6.82 (dd, \(J = 8.0, 0.8\) Hz, 1H), 6.47 (dd, \(J = 7.8, 4.8\) Hz, 1H), 3.81 (s, 3H), 3.20 (dd, \(J = 17.6, 6.8\) Hz, 1H), 2.71-2.58 (m, 2H), 2.06 (s, 3H), 1.33 (d, \(J = 7.2\) Hz, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.14, 148.48, 143.86, 142.99, 138.94, 137.48, 135.30, 134.14, 129.53, 127.56, 126.43, 124.99, 114.69, 114.64, 55.15, 39.02, 38.46, 19.83, 16.50.
HRMS: m/z: [M + H]^+ calculated for C\(_{19}\)H\(_{21}\)N\(_2\)O\(_2\): 309.1598; found 309.1613.

3-(2-methoxyphenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =4/1 as eluate and 2m was obtained as faint yellow solid (58.4 mg, 90%, condition A). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.28-7.23 (m, 2H), 7.08 (br, 1H), 6.91 (td, \(J = 7.6, 0.4\) Hz, 1H), 6.84 (dd, \(J = 7.6, 1.2\) Hz, 1H), 6.72 (d, \(J = 8.4\) Hz, 1H), 6.48 (dd, \(J = 7.6, 4.8\) Hz, 1H), 3.83 (s, 3H), 3.54 (s, 3H), 3.28 (dd, \(J = 17.6, 7.2\) Hz, 1H), 2.71-2.63 (m, 2H), 1.31 (d, \(J = 7.6\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.07, 156.25, 144.60, 144.29, 142.98, 137.74, 134.35, 129.63, 127.65, 127.45, 119.93, 114.36, 113.96, 110.19, 55.13, 54.62, 38.34, 37.74, 16.14.
HRMS: m/z: [M + H]^+ calculated for C\(_{19}\)H\(_{21}\)N\(_2\)O\(_2\): 325.1547; found 325.1551.
3-(2-fluorophenyl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc =5/1 as eluate and 2n was obtained as yellow solid (57.5 mg, 92%, condition A). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (td, J = 7.6, 1.6 Hz, 1H), 7.25-7.19 (m, 1H), 7.15 (dd, J=5.2, 1.6 Hz, 1H), 7.13 (br, 1H), 7.03 (td, J = 7.6, 0.8 Hz, 1H), 6.88-6.83 (m, 2H), 6.51 (dd, J = 7.6, 4.8 Hz, 1H), 3.85 (s, 3H), 3.28 (dd, J = 17.2, 6.8 Hz, 1H), 2.73-2.61 (m, 2H), 1.32 (d, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 207.14, 160.46 (d, J=249.0 Hz), 143.93, 143.29, 140.04, 137.35, 134.06, 129.71 (d, J = 8.5 Hz), 128.08 (d, J = 4.2 Hz), 126.85 (d, J = 14.7 Hz), 123.14 (d, J = 3.3 Hz), 115.03, 114.92 (d, J = 22.1 Hz), 114.74, 114.66, 55.19, 38.10, 37.43, 16.28.

HRMS: m/z: [M + H]⁺ calculated for C₁₈H₁₈FN₂O₂: 313.1347; found 313.1357.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(thiophen-2-yl)cyclopent-2-enone

Petroleum ether/EtOAc =4/1 as eluate and 2o was obtained as yellow solid (57.1 mg, 95%, condition A). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, J = 4.8, 0.8 Hz, 1H), 7.45 (dd, J = 5.2, 0.8 Hz, 1H), 7.33 (dd, J=3.6, 0.8 Hz, 1H), 7.05 (dd, J = 5.2, 4.0 Hz, 1H), 6.98 (dd, J=8.0, 1.2 Hz, 1H), 6.65 (dd, J = 7.6, 4.8 Hz, 1H), 6.51 (br, 1H), 3.90 (s, 3H), 3.39 (dd, J = 17.2, 7.6 Hz, 1H), 2.74-2.66 (m, 2H), 1.31 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 206.73, 149.36, 145.80, 143.61, 138.42, 137.71, 131.69, 130.13, 128.78, 126.93, 115.09, 114.64, 55.35, 37.98, 35.74, 16.53.

HRMS: m/z: [M + H]⁺ calculated for C₁₆H₁₇N₂O₂S: 301.1005; found 301.1008.
3-((furan-2-yl)-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc =6/1 as eluate and Zp was obtained as brown oil (54.0 mg, 95%, condition A). \(^1\)H NMR (400 MHz, CDCl₃) δ 7.60 (dd, \(J = 5.2, 1.6\) Hz, 1H), 7.43 (s, 1H), 6.96 (dd, \(J = 8.0, 1.2\) Hz, 1H), 6.85 (br, 1H), 6.66 (dd, \(J = 8.0, 5.2\) Hz, 1H), 6.44-6.42 (m, 2H), 3.88 (s, 3H), 3.29 (dd, \(J = 17.2, 6.8\) Hz, 1H), 2.69-2.57 (m, 2H), 1.29 (d, \(J = 7.2\) Hz, 3H).
\(^13\)C NMR (100 MHz, CDCl₃) δ 206.20, 150.74, 145.05, 143.85, 143.62, 139.29, 138.19, 130.89, 115.00, 114.81, 114.15, 112.01, 55.23, 37.70, 33.41, 16.39.
HRMS: m/z: [M + H]+ calculated for C₁₆H₁₇N₂O₃: 285.1234; found 285.1238.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(pyridin-3-yl)cyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and Zq was obtained as yellow solid (29.5 mg, 50%, condition A; 53.2 mg, 90%, condition B). \(^1\)H NMR (400 MHz, CDCl₃) δ 8.62 (d, \(J = 1.6\) Hz, 1H), 8.44 (dd, \(J = 4.8, 1.2\) Hz, 1H), 7.66 (dt, \(J=8.0, 2.0\) Hz, 1H), 7.28 (dd, \(J = 4.8, 1.2\) Hz, 1H), 7.17-7.13 (m, 2H), 6.94 (dd, \(J = 7.6, 1.2\) Hz, 1H), 6.58 (dd, \(J = 7.6, 4.8\) Hz, 1H), 3.90 (s, 3H), 3.34 (dd, \(J = 16.8, 6.8\) Hz, 1H), 2.73-2.64 (m, 2H), 1.33 (d, \(J = 7.2\)Hz, 3H).
\(^13\)C NMR (100 MHz, CDCl₃) δ 207.23, 148.89, 148.74, 143.91, 143.61, 143.37, 137.64, 134.58, 133.46, 132.96, 122.34, 115.16, 115.09, 55.29, 37.84, 35.85, 16.42.
HRMS: m/z: [M + H]+ calculated for C₁₇H₁₈N₃O₂: 296.1394; found 296.1399.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(pyridin-4-yl)cyclopent-2-enone
Petroleum ether/EtOAc =4/1 as eluate and 2r was obtained as yellow solid (33.1 mg, 56%, condition B). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 6.0$ Hz, 2H), 7.28 (dd, $J = 4.8$, 1.2 Hz, 1H), 7.20 (dd, $J = 4.8$, 1.2 Hz, 2H), 7.15 (br, 1H), 6.96 (dd, $J = 8.0$, 0.8 Hz, 1H), 6.59 (dd, $J = 8.0$, 5.2 Hz, 1H), 3.90 (s, 3H), 3.29 (dd, $J = 17.6$, 7.2 Hz, 1H), 2.71-2.63 (m, 2H), 1.32 (d, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.38, 149.01, 144.57, 143.86, 143.27, 142.40, 137.61, 134.40, 121.66, 115.48, 115.21, 55.31, 37.95, 35.84, 16.32.

HRMS: m/z: [M + H]$^+$ calculated for C$_{17}$H$_{18}$N$_3$O$_2$: 296.1394; found 296.1401.

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2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(naphthalen-2-yl)cyclopent-2-enone

Petroleum ether/EtOAc =6/1 as eluate and 2s was obtained as yellow solid (57.9 mg, 84%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (s, 1H), 7.76 (d, $J = 9.2$ Hz, 2H), 7.61 (s, 2H), 7.48-7.43 (m, 2H), 7.25 (d, $J = 4.8$ Hz, 1H), 7.04 (br, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 6.52 (dd, $J = 7.6$, 5.2 Hz, 1H), 3.91 (s, 3H), 3.45 (dd, $J = 16.8$, 6.8 Hz, 1H), 2.83 (dd, $J = 17.2$, 2.0 Hz, 1H), 2.75-2.68 (m, 1H), 1.36 (d, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.62, 148.59, 144.56, 143.64, 137.99, 134.26, 133.28, 133.15, 132.63, 128.57, 127.44, 126.98, 126.67, 126.60, 126.03, 125.57, 114.84, 114.62, 55.26, 37.91, 36.44, 16.49.

HRMS: m/z: [M + H]$^+$ calculated for C$_{22}$H$_{21}$N$_2$O$_2$: 345.1598; found 345.1603.

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(E)-2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-(prop-1-en-1-yl)cyclopent-2-enone

Petroleum ether/EtOAc =6/1 as eluate and 2t was obtained as brown oil (43.9 mg, 85%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 5.2$ Hz, 1H), 6.96-6.93 (m, 2H), 6.78 (br, 1H), 6.68 (dd, $J = 7.6$, 4.8 Hz, 1H), 6.19-6.10 (m, 1H), 3.87 (s, 3H), 3.03 (dd, $J = 16.8$, 6.8 Hz, 1H), 2.58-2.50 (m, 1H), 2.34 (dd, $J = 17.2$, 2.4 Hz, 1H), 1.88 (d, $J = 6.8$ Hz, 3H), 1.23 (d, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.09, 148.30, 145.63, 143.18, 138.08, 131.76, 131.54, 128.75, 114.84, 114.71, 55.27, 37.60, 33.15, 19.14, 16.69.

HRMS: m/z: [M + H]$^+$ calculated for C$_{15}$H$_{19}$N$_2$O$_2$: 259.1441; found 259.1441.
(E)-2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-styrylcyclopent-2-enone
Petroleum ether/EtOAc = 5/1 as eluate and 2u was obtained as yellow solid (55.1 mg, 86%, condition A; 285.1 mg, 89%, 1 mmol scale). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $J$ = 16.4 Hz, 1H), 7.79 (d, $J$ = 5.2 Hz, 1H), 7.46 (d, $J$ = 7.6 Hz, 2H), 7.32 (t, $J$ = 7.4 Hz, 2H), 7.27-7.23 (m, 1H), 7.15 (br, 1H), 6.99 (d, $J$ = 8.0 Hz, 1H), 6.86 (d, $J$ = 16.4 Hz, 1H), 6.76 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.19 (dd, $J$ = 16.4, 6.8 Hz, 1H), 2.66-2.58 (m, 1H), 2.49 (dd, $J$ = 16.4, 2.0 Hz, 1H), 1.30 (d, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 206.71, 144.95, 144.44, 138.01, 137.16, 133.28, 131.53, 128.65, 128.27, 127.12, 126.27, 115.35, 115.11, 55.34, 37.63, 33.06, 16.75.
HRMS: m/z: [M + H]$^+$ calculated for C$_{20}$H$_{21}$N$_2$O$_2$: 321.1598; found 321.1607.

2-((3-methoxypyridin-2-yl)amino)-3,5-dimethylcyclopent-2-enone
Petroleum ether/EtOAc = 7/1 as eluate and 2v was obtained as pale oil (44.1 mg, 95%, condition A). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, $J$ = 4.8 Hz, 1H), 6.93 (d, $J$ = 7.6 Hz, 1H), 6.66 (dd, $J$ = 8.0, 5.2 Hz, 1H), 6.56 (br, 1H), 3.88 (s, 3H), 2.91 (dd, $J$ = 18.0, 6.8 Hz, 1H), 2.55-2.48 (m, 1H), 2.26 (d, $J$ = 18.0 Hz, 1H), 2.17 (s, 3H), 1.23 (d, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.43, 144.95, 144.44, 138.01, 137.16, 133.28, 131.53, 128.65, 128.27, 127.12, 126.27, 115.35, 115.11, 55.19, 39.30, 38.32, 19.44, 16.34.
HRMS: m/z: [M + H]$^+$ calculated for C$_{13}$H$_{17}$N$_2$O$_2$: 233.1285; found 233.1278.

3-ethyl-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc = 7/1 as eluate and 2w was obtained as pale oil (44.8 mg, 91%, condition A; 234.0 mg, 95%, 1.0 mmol scale). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.69 (dd, $J$ = 16.4 Hz, 1H), 7.46 (d, $J$ = 7.6 Hz, 1H), 7.32 (t, $J$ = 7.4 Hz, 2H), 7.27-7.23 (m, 1H), 7.15 (br, 1H), 6.99 (d, $J$ = 8.0 Hz, 1H), 6.86 (d, $J$ = 16.4 Hz, 1H), 6.76 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.19 (dd, $J$ = 16.4, 6.8 Hz, 1H), 2.66-2.58 (m, 1H), 2.49 (dd, $J$ = 16.4, 2.0 Hz, 1H), 1.30 (d, $J$ = 7.6 Hz, 3H), 1.13 (d, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.43, 144.95, 144.44, 138.01, 137.16, 133.28, 131.53, 128.65, 128.27, 127.12, 126.27, 115.35, 115.11, 55.34, 37.63, 33.06, 16.75, 16.75.
HRMS: m/z: [M + H]$^+$ calculated for C$_{20}$H$_{21}$N$_2$O$_2$: 321.1598; found 321.1607.

3-ethyl-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone
Petroleum ether/EtOAc = 7/1 as eluate and 2w was obtained as pale oil (44.8 mg, 91%, condition A; 234.0 mg, 95%, 1.0 mmol scale). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.69 (dd, $J$ = 16.4 Hz, 1H), 7.46 (d, $J$ = 7.6 Hz, 1H), 7.32 (t, $J$ = 7.4 Hz, 2H), 7.27-7.23 (m, 1H), 7.15 (br, 1H), 6.99 (d, $J$ = 8.0 Hz, 1H), 6.86 (d, $J$ = 16.4 Hz, 1H), 6.76 (dd, $J$ = 7.6, 5.2 Hz, 1H), 3.90 (s, 3H), 3.19 (dd, $J$ = 16.4, 6.8 Hz, 1H), 2.66-2.58 (m, 1H), 2.49 (dd, $J$ = 16.4, 2.0 Hz, 1H), 1.30 (d, $J$ = 7.6 Hz, 3H), 1.13 (d, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.43, 144.95, 144.44, 138.01, 137.16, 133.28, 131.53, 128.65, 128.27, 127.12, 126.27, 115.35, 115.11, 55.34, 37.63, 33.06, 16.75, 16.75.
HRMS: m/z: [M + H]$^+$ calculated for C$_{20}$H$_{21}$N$_2$O$_2$: 321.1598; found 321.1607.
5.2, 0.8 Hz, 1H), 6.90 (dd, J = 8.0, 0.8 Hz, 1H), 6.64 (dd, J = 8.0, 5.2 Hz, 1H), 6.50 (br, 1H), 3.85 (s, 3H), 2.90 (dd, J = 18.0, 6.8 Hz, 1H), 2.59 (q, J = 7.6 Hz, 2H), 2.52-2.45 (m, 1H), 2.23 (d, J = 18.0 Hz, 1H), 1.21 (d, J = 7.2 Hz, 3H), 1.13 (t, J = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.78, 162.27, 146.17, 143.04, 138.04, 133.38, 114.64, 114.18, 55.19, 38.15, 36.16, 25.81, 16.43, 11.08.

HRMS: m/z: [M + H]$^+$ calculated for C$_{14}$H$_{19}$N$_2$O$_2$: 247.1441; found 247.1450.

2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-tridecylcyclopent-2-enone

Petroleum ether/EtOAc = 7/1 as eluate and 2x was obtained as pale oil (51.0 mg, 64%, condition A; 66.2 mg, 83%, condition B). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (dd, J = 5.2, 1.2 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.64 (dd, J = 7.6, 4.8 Hz, 1H), 6.51 (br, 1H), 3.86 (s, 3H), 2.89 (dd, J = 18.4, 6.8 Hz, 1H), 2.57 (t, J=7.6 Hz, 2H), 2.52-2.45 (m, 1H), 2.23 (d, J = 18.0 Hz, 1H), 1.56-1.51 (m, 2H), 1.24-1.2 (m, 23H), 0.87 (t, J = 6.8 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.74, 161.24, 146.17, 143.06, 138.07, 133.76, 114.61, 114.15, 55.19, 38.19, 36.87, 32.76, 31.87, 29.74, 29.64, 29.60(s, 2C), 29.58, 29.47, 29.37, 29.31, 26.80, 22.64, 16.49, 14.07.

HRMS: m/z: [M + H]$^+$ calculated for C$_{25}$H$_{41}$N$_2$O$_2$: 401.3163; found 401.3177.

3-Benzyl-2-((3-methoxypyridin-2-yl)amino)-5-methylcyclopent-2-enone

Petroleum ether/EtOAc = 6/1 as eluate and 2y was obtained as brown oil (51.8 mg, 84%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J = 4.8 Hz, 1H), 7.29-7.25 (m, 2H), 7.22 (m, 3H), 6.94 (d, J = 7.6 Hz, 1H), 6.69-6.66 (m, 2H), 4.03 (s, 2H), 3.88 (s, 3H), 2.74 (dd, J = 18.0, 6.8 Hz, 1H), 2.48-2.42 (m, 1H), 2.08 (d, J = 18.0 Hz, 1H), 1.16 (d, J = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.84, 157.38, 146.01, 143.23, 138.47, 138.03, 134.05, 129.15, 128.43, 126.29, 114.84, 114.50, 55.29, 39.14, 38.27, 36.58, 16.33.

HRMS: m/z: [M + H]$^+$ calculated for C$_{25}$H$_{21}$N$_2$O$_2$: 309.1598; found 309.1604.
2-((3-methoxypyridin-2-yl)amino)-5-methyl-3-phenethylcyclopent-2-enone
Petroleum ether/EtOAc = 5/1 as eluate and 2z was obtained as pale oil (48.4 mg, 75%, condition A; 54.8 mg, 85%, condition B). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (dd, \(J = 5.2, 1.6\) Hz, 1H), 7.26-7.23 (m, 2H), 7.19-7.13 (m, 3H), 6.93 (dd, \(J = 8.0, 1.2\) Hz, 1H), 6.68 (dd, \(J = 8.0, 5.2\) Hz, 1H), 6.59 (br, 1H), 3.87 (s, 3H), 2.98-2.86 (m, 5H), 2.54-2.44 (m, 1H), 2.21 (dd, \(J = 18.0, 1.6\) Hz, 1H), 1.19 (d, \(J = 7.2\) Hz, 3H). 
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.58, 158.40, 146.02, 141.59, 138.03, 134.04, 128.28, 128.21, 125.89, 114.71, 114.38, 55.19, 38.15, 37.38, 34.72, 32.80, 16.40.
HRMS: m/z: [M + H]^+ calculated for C\(_{20}\)H\(_{23}\)N\(_2\)O\(_2\): 323.1754; found 323.1768.

5-methyl-3-phenyl-2-(pyridin-2-ylamino)cyclopent-2-enone
Petroleum ether/EtOAc = 5/1 as eluate and 3a was obtained as yellow solid (21.1 mg, 40%, condition A). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.09 (d, \(J = 4.4\) Hz, 1H), 7.52-7.49 (m, 2H), 7.30-7.24 (m, 4H), 6.76 (br, 1H), 6.76 (dd, \(J = 5.6, 6.8\) Hz, 1H), 6.13 (d, \(J = 8.4\) Hz, 1H), 3.31 (dd, \(J = 17.6, 7.2\) Hz, 1H), 2.70-2.63 (m, 2H), 1.33 (d, \(J = 7.6\) Hz, 3H). 
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.28, 153.42, 148.03, 147.11, 136.94, 135.48, 133.39, 129.42, 128.25, 127.63, 115.57, 109.90, 37.82, 36.08, 16.57.
HRMS: m/z: [M + H]^+ calculated for C\(_{17}\)H\(_{17}\)N\(_2\)O: 265.1335; found 265.1340.

5-methyl-2-((3-methylpyridin-2-yl)amino)-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc = 5/1 as eluate and 3b was obtained as yellow solid (10.0 mg, 18%, condition A). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63 (d, \(J = 3.6\) Hz, 1H), 7.40-7.38 (m, 2H), 7.32 (dd, \(J = 7.2, 1.8\) Hz, 1H), 7.24-7.18 (m, 3H), 6.57 (dd, \(J = 7.2, 5.2\) Hz, 1H), 6.27 (br, 1H), 3.35 (dd, \(J = 17.6, 7.6\) Hz, 1H), 2.73-2.65 (m, 2H), 2.30 (s, 3H), 1.34 (d, \(J = 7.2\) Hz, 3H). 
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 207.73, 151.99, 147.48, 144.93, 137.66, 136.61, 133.51, 128.70, 127.59, 127.50, 119.99, 115.76, 37.90, 36.31, 17.34, 16.47.
2-((3-(benzyloxy)pyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc =5/1 as eluate and 3d was obtained as yellow oil (42.2 mg, 57%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (dd, $J = 7.2, 5.2$ Hz, 4H), 7.43-7.36 (m, 4H), 7.27-7.22 (m, 3H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.96 (br, 1H), 6.55 (dd, $J = 8.0, 5.2$ Hz, 1H), 5.14 (s, 2H), 3.33 (dd, $J = 17.6, 7.2$ Hz, 1H), 2.72-2.62 (m, 2H), 1.32 (d, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.62, 149.42, 144.93, 142.76, 138.46, 136.47, 133.06, 128.45, 128.71, 128.28, 127.63, 127.54, 116.71, 114.52, 70.37, 37.92, 36.29, 16.41.
HRMS: m/z: [M + H]$^+$ calculated for C$_{24}$H$_{23}$N$_2$O$_2$: 371.1754; found 371.1755.

2-((3,5-dimethoxy-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc =3/1 as eluate and 3e was obtained as yellow solid (48.7 mg, 75%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.44 (m, 2H), 7.25-7.22 (m, 3H), 7.03 (d, $J = 2.4$ Hz, 1H), 6.72 (br, 1H), 6.65 (d, $J = 2.4$ Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.31 (dd, $J = 17.2, 7.2$ Hz, 1H), 2.71-2.61 (m, 2H), 1.31 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100MHz, CDCl$_3$) δ 207.80, 150.29, 147.29, 144.93, 142.76, 138.74, 136.63, 133.21, 128.57, 127.63, 127.51, 120.74, 105.92, 56.12, 55.41, 37.84, 36.21, 16.45.
HRMS: m/z: [M + H]$^+$ calculated for C$_{29}$H$_{22}$N$_2$O$_3$: 325.1547; found 325.1547.

2-((5-methoxypyridin-2-yl)amino)-5-methyl-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc =4/1 as eluate and 3f was obtained as yellow solid (8.8 mg, 15%, condition A). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J = 2.8$ Hz, 1H), 7.47-7.44 (m, 2H),
7.28-7.27 (m, 3H), 6.87 (dd, J = 8.8, 2.8 Hz, 1H), 6.64 (br, 1H), 6.10 (d, J = 8.8 Hz, 1H), 3.72 (s, 3H), 3.28 (dd, J = 17.2, 7.2 Hz, 1H), 2.68-2.62 (m, 2H), 1.33 (d, J = 7.6 Hz, 3H).

13C NMR (100 MHz, CDCl3) δ 207.42, 150.33, 147.44, 144.59, 135.68, 133.88, 133.84, 129.10, 128.14, 127.59, 123.62, 110.71, 56.05, 37.79, 36.04, 16.60.

HRMS: m/z: [M + H]+ calculated for C18H19N2O2: 295.1441; found 295.1447.

2-((3-methoxypyridin-2-yl)amino)-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc =5/1 as eluate and 3i was obtained as yellow solid (54.4 mg, 97%, condition A). 1H NMR (400 MHz, CDCl3) δ 7.49 (d, J = 6.8 Hz, 2H), 7.35 (d, J = 4.8 Hz, 1H), 7.24-7.23 (m, 3H), 6.93-6.90 (m, 2H), 6.56 (dd, J = 7.6, 5.2 Hz, 1H), 3.87 (s, 3H), 3.08 (t, J=4.4 Hz, 2H), 2.62 (t, J=4.4 Hz, 2H).

13C NMR (100 MHz, CDCl3) δ 204.94, 151.08, 144.39, 143.59, 137.87, 136.42, 134.04, 128.82, 127.55, 127.46, 114.79, 114.53, 55.16, 32.36, 26.96.

HRMS: m/z: [M + H]+ calculated for C17H17N2O2: 281.1285; found 281.1286.

2-((3-methoxypyridin-2-yl)amino)-[1,1'-biphenyl]-3-ol
Petroleum ether/EtOAc =5/1 as eluate and 3j was obtained as pale oil (21.6 mg, 37%, condition B). 1H NMR (400 MHz, CDCl3) δ 8.12-8.10 (m, 3H), 7.82 (dd, J = 8.0, 0.8 Hz, 1H), 7.66 (dd, J = 7.2, 0.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.44 (t, J=7.6 Hz, 1H), 7.39-7.35 (m, 1H), 6.79-6.75 (m, 1H), 6.66 (d, J = 7.2 Hz, 1H), 4.05 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 149.19, 143.38, 141.85, 138.40, 133.21, 130.03, 129.41, 128.43, 127.29, 124.67, 121.55, 117.65, 110.29, 109.45, 103.95, 55.94.

HRMS: m/z: [M + H]+ calculated for C18H17N2O2: 293.1285; found 293.1287.

2-hydroxy-5-methyl-3-phenylcyclopent-2-enone
Petroleum ether/EtOAc =15/1 as eluate and 4a was obtained as white solid (24.5 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J$ = 7.2 Hz, 2H), 7.47-7.43 (m, 2H), 7.38 (t, $J$ = 7.6 Hz, 1H), 6.20 (br, 1H), 3.16 (dd, $J$ = 16.8, 6.4 Hz, 1H), 2.65-2.57 (m, 1H), 2.47 (dd, $J$ = 16.8, 1.6 Hz, 1H), 1.30 (d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 205.66, 146.92, 136.43, 133.82, 129.43, 128.61, 127.77, 36.61, 32.71, 16.62.

HRMS: m/z: [M + H]$^+$ calculated for C$_{12}$H$_{13}$O$_2$: 189.0910; found 189.0913.

Petroleum ether/EtOAc =15/1 as eluate and 4w$^9$ was obtained as pale oil (21.0 mg, 75%). 4w$_1$:4w$_2$=0.57:1. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4w$_1$ 6.09 (br, 1H), 2.69 (dd, $J$ = 17.6, 6.4 Hz, 1H), 2.46-2.38 (m, 3H), 2.07-2.04 (m, 1H), 1.18 (d, $J$ = 7.6 Hz, 3H); 4w$_2$ 6.12 (br, 1H), 2.59 (dd, $J$ = 17.6, 6.0 Hz, 1H), 2.35-2.30 (m, 1H), 2.12-2.07 (m, 1H), 2.00 (s, 3H), 1.86-1.76 (m, 1H), 1.46-1.35 (m, 1H), 0.93 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 4w$_1$ 206.22, 148.06, 146.93, 37.34, 33.98, 21.59, 16.43, 11.23; 4w$_2$ 205.25, 148.30, 143.34, 44.17, 33.95, 24.33, 14.22, 11.13.
Reference


