Supporting Information
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Concurrent $\alpha$-Iodination and $N$-Arylation of Cyclic $\beta$-Enaminones

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**Supplementary Information**

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General Information

$^1$H and $^{13}$C NMR spectra were recorded on a 500 MHz INOVA VARIAN or a 400 MHz BRUKER AVANCE spectrometer at 25 °C. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; qui, quintuplet; m, multiplet and dd, doublet of doublets. The coupling constants $J$, are reported in Hertz (Hz). Low-resolution mass spectra (LRMS) were obtained on an ion trap (Agilent 6310) spectrometer using electrospray ionization (ESI) in positive or negative mode. Melting points were determined with a national microMelting point apparatus without corrections. Organic solutions were concentrated by rotary evaporation below 40 °C in vacuum. TLC plates were visualized by exposure to ultraviolet light. 1, 2-Dichloroethane were dried by CaH$_2$ before use, other reagents and solvents were purchased as reagent grade and was used without further purification. Flash column chromatography was performed over silica gel 100-200 m and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE), or a mixture of methanol (M) and dichloromethane (D). A series of arylidene diacetates were prepared following the known procedure.[1]

Preparation of the Substrates

**General procedure A:**[2] A mixture of cyclohexane-1, 3-dione (10 mmol) or cyclopentane-1, 3-dione (10 mmol), substituted aniline (10 mmol) and acetic acid (10 mmol) was stirred at 80 °C under nitrogen atmosphere until TLC indicated the total consumption of the aniline. Then, the reaction mixture was purified by column
chromatography using a mixture of methanol and dichloromethane as eluent to afford substrate: 1a in 85% yield as yellow solid, m.p. 183–185 °C (ref. 186 °C);[3] 1b in 92% yield as white solid, m.p. 204–206 °C (ref. 203–204 °C);[4] 1c in 88% yield as yellow solid, m.p. 183–185 °C (ref. 184–185 °C);[5] 1f in 85% yield as yellow solid, m.p. 192–193 °C (ref. 190 °C);[4] 1h in 95% yield as white solid, m.p. 163–165 °C (ref. 164–166 °C);[6] 1i in 73% yield as yellow solid, m.p. 138–139 °C (ref. 140–141 °C);[7] 1j in 62% yield as yellow solid, m.p. 235–237 °C (ref. 236–237 °C).[6] The new compounds thus obtained were characterized as follows:

3-(4-Nitrophenylamino)cyclohex-2-enone (1d)

Following the general procedure A, 1d was purified by silica gel chromatography (2% M/D). \( R_f = 0.60 \) (M/D = 5/95). **Yield:** 80%, yellow solid, m.p. 177–182 °C. \(^1\text{H} \text{NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 8.18 \) (d, \( J = 9.0 \text{ Hz}, 2\text{H} \)), 7.27 (d, \( J = 9.0 \text{ Hz}, 2\text{H} \)), 5.83 (s, 1H), 2.57 (t, \( J = 6.0 \text{ Hz}, 3\text{H} \)), 2.41 (t, \( J = 6.4 \text{ Hz}, 2\text{H} \)), 2.14 – 1.99 (m, 2H).

3-(2,4-Difluorophenylamino)cyclohex-2-enone (1e)

Following the general procedure A, 1e was purified by silica gel chromatography (2% M/D). \( R_f = 0.66 \) (M/D = 5/95). **Yield:** 74%, yellow solid, m.p. 176–179 °C. \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.31 – 7.16 \) (m, 1H), 6.88 (m, 2H), 5.21 (s, 1H), 2.53 (t, \( J = 6.1 \text{ Hz}, 2\text{H} \)), 2.32 (t, \( J = 6.4 \text{ Hz}, 2\text{H} \)), 2.08 – 1.91 (m, 2H).

3-(3,4-Dimethylphenylamino)cyclohex-2-enone (1g)

Following the general procedure A, 1g was purified by silica gel chromatography (2% M/D). \( R_f = 0.62 \) (M/D = 5/95). **Yield:** 92%, red solid, m.p. 165–169 °C. \(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.47 \) (s, 1H), 7.02 (d, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 6.91 (s, 1H), 6.84 (d, \( J = 7.9 \text{ Hz}, 1\text{H} \)), 5.49 (s, 1H), 2.47 (t, \( J = 6.1 \text{ Hz}, 2\text{H} \)), 2.30 (t, \( J = 6.4 \text{ Hz}, 2\text{H} \)), 2.20 (s, 3H), 1.95 (dt, \( J = 12.3, 6.2 \text{ Hz}, 2\text{H} \)).
General procedure B: A mixture of cyclohexane-1, 3-dione (10 mmol), alkyl substituted amine (10 mmol) in toluene was stirred at 80 °C under nitrogen atmosphere until TLC indicated the total consumption of amine. Then, the solvent was removed under vacuum and the residue was purified by column chromatography using a mixture of methanol and dichloromethane as eluent to afford substrate: 1k in 85% yield as yellow solid, m.p. 123–126 °C (ref. 125–127 °C);[4] 1l in 88% yield as yellow solid, m.p. 94–96 °C (ref. 98–99 °C);[8] 1m in 73% yield as yellow solid, m.p. 153–155 °C (ref. 155–156 °C);[9] 4a in 85% yield as yellow solid, m.p. 49–51 °C (ref. 47–48 °C).[10] 4d in 72% yield as yellow solid, m.p. 38–40 °C (ref. 41–42 °C).[11]

Synthesis of α-Iodo Enaminones

General procedure: To a solution of the substrate 1 (1.0 mmol) in ClCH₂CH₂Cl (10 mL), was added a solution of aryliodine diacetate 2 (1.3 mmol) in ClCH₂CH₂Cl (10 mL) dropwise at 60 ºC under nitrogen atmosphere. After the addition, the reaction mixture was stirred at this temperature until the conversion was complete (as indicated by TLC). Then the mixture was cooled to room temperature, treated with saturated NaHCO₃ (40 mL) and extracted with CH₂Cl₂ (20 mL × 3). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure to remove the solvent. The given residue was purified by column chromatography using a mixture of PE and EA as eluent to afford the title compounds c.

3-(Diphenylamino)-2-iodocyclohex-2-enone (3a)

Following the general procedure, 3a was purified by silica gel chromatography (10% EA/PE). Rᵣ = 0.46 (EA/PE = 20/80). Yield: 85%, yellow solid, m.p. 106–108 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.32 (t, J = 7.9 Hz, 4H), 7.14 (t, J = 7.4 Hz, 2H), 7.02 (d, J = 7.7
2-Iodo-3-{phenyl[4-(trifluoromethyl)phenyl]amino}cyclohex-2-enone (3b)

Following the general procedure, 3b was purified by silica gel chromatography (10% EA/PE). $R_f = 0.45$ (EA/PE = 20/80).

Yield: 74%, yellow solid, m.p. 97–99 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47 – 7.30 (m, 4H), 7.26 – 7.10 (m, 3H), 7.10 – 7.03 (m, 2H), 2.78 – 2.65 (t, $J = 6.3$ Hz, 2H), 2.59 (t, $J = 6.0$ Hz, 2H), 2.08 – 1.92 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.05, 166.40, 144.31, 130.00, 127.43, 125.72, 125.22, 120.99, 120.79, 98.13, 37.04, 33.85, 21.79. LRMS (ESI): [M + Na$^+$] 455.8.

3-[(4-Bromophenyl)(phenyl)amino]-2-iodocyclohex-2-enone (3c)

Following the general procedure, 3c was purified by silica gel chromatography (10% EA/PE). $R_f = 0.46$ (EA/PE = 20/80).

Yield: 75%, yellow solid, m.p. 133–134 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42 (d, $J = 8.8$ Hz, 2H), 7.34 (t, $J = 7.8$ Hz, 2H), 7.18 (t, $J = 7.4$ Hz, 1H), 7.02 (d, $J = 7.5$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 2.70 (t, $J = 6.4$ Hz, 2H), 2.57 (t, $J = 6.0$ Hz, 2H), 2.05 – 1.86 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.06, 166.40, 144.48, 144.27, 132.61, 129.77, 126.47, 125.46, 117.61, 97.02, 37.04, 33.90, 21.79. LRMS (ESI): [M + Na$^+$] 490.1.

2-Iodo-3-[(4-nitrophenyl)(phenyl)amino]cyclohex-2-enone (3d)

Following the general procedure, 3d was purified by silica gel chromatography (20% EA/PE). $R_f = 0.23$ (EA/PE = 20/80).

Yield: 89%, yellow solid, m.p. 136–138 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (d, $J = 9.2$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz,
2H), 7.32 (t, J = 7.4 Hz, 1H), 7.22 – 7.11 (m, 2H), 6.94 (d, J = 9.2 Hz, 2H), 2.74 (t, J = 6.4 Hz, 2H), 2.59 (t, J = 5.9 Hz, 2H), 2.06-2.00 (m, 2H). $^{13}$C NMR (100 MHz, CDCl₃): δ 192.98, 165.55, 150.24, 142.81, 142.49, 130.32, 127.24, 126.18, 125.52, 121.37, 102.33, 36.99, 33.36, 21.69. LRMS (ESI): [M - H⁻] 432.8.

3-[(2,4-Difluorophenyl)(phenyl)amino]-2-iodocyclohex-2-enone (3e)

Following the general procedure, 3e was purified by silica gel chromatography (10% EA/PE). Rₕ = 0.43 (EA/PE = 20/80). Yield: 85%, yellow solid, m.p. 127–129 °C. $^1$H NMR (400 MHz, CDCl₃): δ 7.33 (t, J = 7.8 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.99 (d, J = 7.5 Hz, 2H), 6.92 – 6.82 (m, 2H), 2.67 (t, J = 6.4 Hz, 2H), 2.58 (t, J = 6.0 Hz, 2H), 1.99-1.93 (m, 2H). $^{13}$C NMR (100 MHz, CDCl₃): δ 193.06, 166.53, 161.98, 161.87, 159.51, 159.39, 158.95, 158.84, 156.43, 156.32, 144.70, 130.25, 130.16, 129.68, 129.40, 129.32, 125.49, 124.78, 112.32, 112.09, 105.41, 105.16, 104.92, 93.24, 36.93, 33.40, 21.61. LRMS (ESI): [M + H⁺] 426.2.

3-[(2-Chlorophenyl)(phenyl)amino]-2-iodocyclohex-2-enone (3f)

Following the general procedure, 3f was purified by silica gel chromatography (15% EA/PE). Rₕ = 0.35 (EA/PE = 20/80). Yield: 72%, yellow solid, m.p. 120–121 °C. $^1$H NMR (400 MHz, CDCl₃): δ 7.43 (m, 1H), 7.33–7.13 (m, 6H), 6.96 (s, 2H), 2.67 (t, J = 6.4 Hz, 2H), 2.53 (t, J = 6.0 Hz, 2H), 1.92–1.99 (m, 2H). $^{13}$C NMR (100 MHz, CDCl₃): δ 193.07, 165.89, 145.06, 142.46, 132.24, 130.97, 130.26, 129.42, 127.93, 127.63, 125.75, 125.23, 92.09, 36.86, 33.84, 21.46. LRMS (ESI): [M + H⁺] 424.2.

3-[(3,4-Dimethylphenyl)(phenyl)amino]-2-iodocyclohex-2-enone (3g)
Following the general procedure, 3g was purified by silica gel chromatography (10% EA/PE). $R_f = 0.45$ (EA/PE = 20/80).

Yield: 77%, yellow solid, m.p. 125–126 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31–7.27 (m, 2H), 7.12–7.06 (m, 2H), 6.98–6.96 (m, 2H), 6.87–6.70 (m, 2H), 2.66 (t, $J = 6.4$ Hz, 2H), 2.57 (t, $J = 6.0$ Hz, 2H), 2.24 (s, 3H), 2.22 (s, 3H), 1.98–1.92 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.04, 166.94, 145.48, 142.83, 137.89, 133.98, 130.59, 129.31, 127.04, 125.27, 124.52, 123.76, 123.43, 94.13, 37.01, 34.10, 21.81, 19.90, 19.31. LRMS (ESI): [M + H$^+$] 418.3.

2-Iodo-3-[(4-methoxyphenyl)(phenyl)amino]cyclohex-2-enone (3h)

Following the general procedure, 3h was purified by silica gel chromatography (20% EA/PE). $R_f = 0.29$ (EA/PE = 20/80).

Yield: 60%, yellow solid, m.p. 121–123 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31–7.27 (m, 2H), 7.10 (t, $J = 7.4$ Hz, 1H), 6.97 (t, $J = 9.2$ Hz, 4H), 6.86 (d, $J = 8.9$ Hz, 2H), 3.81 (s, 3H), 2.68 (t, $J = 6.4$ Hz, 2H), 2.56 (t, $J = 6.0$ Hz, 2H), 1.98–1.92 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.99, 166.85, 157.59, 145.64, 138.27, 129.38, 127.60, 125.06, 124.53, 114.89, 93.49, 55.63, 37.00, 34.11, 21.82. LRMS (ESI): [M + H$^+$] 420.0.

2-Iodo-3-[phenyl(p-tolyl)amino]cyclohex-2-enone (3i)

Following the general procedure, 3i was purified by silica gel chromatography (10% EA/PE). $R_f = 0.45$ (EA/PE = 20/80).

Yield: 85%, yellow solid, m.p. 128–130 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31–7.26 (m, 2H), 7.13–7.09 (m, 3H), 6.98 (d, $J = 7.7$ Hz, 2H), 6.92 (d, $J = 8.2$ Hz, 2H), 2.68 (t, $J = 6.5$ Hz, 2H), 2.57 (t, $J = 5.9$ Hz, 2H), 2.34 (s, 3H), 1.98–1.92 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.00, 166.90, 145.42, 142.67, 135.11, 130.13, 129.80, 125.72, 125.26, 124.67, 94.63, 37.01, 34.05, 21.79, 21.01. LRMS (ESI): [M + H$^+$] 404.2.
2-Iodo-3-[(4-methoxyphenyl)(4-nitrophenyl)amino]cyclohex-2-enone (3j)

Following the general procedure, 3j was purified by silica gel chromatography (25% EA/PE). \( R_f = 0.19 \) (EA/PE = 20/80).

**Yield**: 57%, yellow solid, m.p. 143–144 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.13 (d, \( J = 9.1 \) Hz, 2H), 7.12 (d, \( J = 8.8 \) Hz, 2H), 6.95 (d, \( J = 8.8 \) Hz, 2H), 6.85 (d, \( J = 9.1 \) Hz, 2H), 3.85 (s, 3H), 2.73 (t, \( J = 6.4 \) Hz, 2H), 2.57 (t, \( J = 5.9 \) Hz, 2H), 2.04–1.97 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 193.00, 165.37, 159.10, 150.55, 142.09, 135.35, 128.17, 125.51, 120.62, 115.67, 101.23, 55.76, 37.00, 33.26, 21.68.

**LRMS** (ESI): [M + H\(^{+}\)] 464.9.

3-[(Bis(4-bromophenyl)amino)-2-iodocyclohex-2-enone (3k)

Following the general procedure, 3k was purified by silica gel chromatography (10% EA/PE). \( R_f = 0.46 \) (EA/PE = 20/80).

**Yield**: 71%, yellow solid, m.p. 152–154 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.43 (d, \( J = 8.7 \) Hz, 4H), 6.88 (d, \( J = 8.7 \) Hz, 4H), 2.70 (t, \( J = 6.5 \) Hz, 2H), 2.56 (t, \( J = 5.9 \) Hz, 2H), 2.02–1.96 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.88, 165.83, 143.69, 132.80, 126.45, 118.14, 98.22, 36.96, 33.71, 21.74. **LRMS** (ESI): [M + H\(^{+}\)] 545.6.

2-Iodo-3-[(3-nitrophenyl)(4-nitrophenyl)amino]cyclohex-2-enone (3l)

Following the general procedure, 3l was purified by silica gel chromatography (25% EA/PE). \( R_f = 0.13 \) (EA/PE = 20/80).

**Yield**: 57%, yellow solid, m.p. 167–169 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.85–8.22 (m, 2H), 8.10 (dd, \( J = 8.1, 1.2 \) Hz, 1H), 7.94 (t, \( J = 2.0 \) Hz, 1H), 7.62-7.57 (m, 1H), 7.51–7.40 (m, 1H), 7.07-7.05 (m, 2H), 2.79 (t, \( J = 6.4 \) Hz, 2H), 2.63 (t, \( J = 5.9 \) Hz, 2), 2.12-2.07 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.55, 164.59, 149.85, 149.11, 144.15, 143.94, 131.05, 130.45, 126.00, 122.26, 120.75, 119.57, 105.19, 36.87, 33.62, 21.79. **LRMS** (ESI): [M - H\(^{+}\)] 477.7.
3-[(2,4-Difluorophenyl)(4-nitrophenyl)amino]-2-iodocyclohex-2-enone (3m)

Following the general procedure, 3m was purified by silica gel chromatography (20% EA/PE). \( R_f = 0.25 \) (EA/PE = 20/80). **Yield:** 63%, yellow solid, m.p. 165–168 °C. **\( ^1\)H NMR (400 MHz, CDCl\(_3\))**: \( \delta \) 8.17 (m, 2H), 7.35 – 7.20 (m, 1H), 7.05 – 6.79 (m, 4H), 2.73 (t, \( J = 6.2 \) Hz, 2H), 2.60 (t, \( J = 6.0 \) Hz, 2), 2.13 – 1.96 (m, 2H). **\( ^{13}\)C NMR (100 MHz, CDCl\(_3\))**: \( \delta \) 192.91, 164.78, 160.65, 156.97, 149.65, 143.11, 130.57, 130.48, 125.67, 120.73, 113.12, 112.91, 106.34, 106.09, 105.84, 101.35, 36.92, 32.82, 21.59. **LRMS (ESI):** [M + H\(^+\)] 470.9.

3-[(2-Chlorophenyl)(3-nitrophenyl)amino]-2-iodocyclohex-2-enone (3n)

Following the general procedure, 3n was purified by silica gel chromatography (20% EA/PE). \( R_f = 0.22 \) (EA/PE = 20/80). **Yield:** 85%, yellow solid, m.p. 146–149 °C. **\( ^1\)H NMR (400 MHz, CDCl\(_3\))**: \( \delta \) 7.92 (dd, \( J = 8.2, 1.3 \) Hz, 1H), 7.64 (m, 1H), 7.50 (m, 2H), 7.34 (m, 2H), 7.27 – 7.10 (m, 2H), 2.72 (t, \( J = 6.1 \) Hz, 2H), 2.52 (t, \( J = 5.9 \) Hz, 2H), 2.01 (m, 2H). **\( ^{13}\)C NMR (100 MHz, CDCl\(_3\))**: \( \delta \) 192.96, 164.97, 149.43, 145.96, 140.91, 132.94, 131.72, 130.61, 130.32, 129.49, 129.13, 128.69, 118.77, 118.04, 96.25, 37.24, 33.48, 21.43. **LRMS (ESI):** [M + H\(^+\)] 468.9.

3-(Benzyl(4-nitrophenyl)amino)-2-iodocyclohex-2-enone (3o)

Following the general procedure, 3o was purified by silica gel chromatography (20% EA/PE). \( R_f = 0.22 \) (EA/PE = 20/80). **Yield:** 84%, yellow solid, m.p. 104–108 °C. **\( ^1\)H NMR (400 MHz, DMSO)**: \( \delta \) 8.15 – 8.03 (m, 2H), 7.36 (m, 4H), 7.34 – 7.23 (m, 1H), 7.03 – 6.93 (m, 2H), 5.03 (s, 2H), 2.70 (t, \( J = 5.9 \) Hz, 2H), 2.66 – 2.59 (m, 2H), 1.96 (m, 2H). **\( ^{13}\)C NMR (100 MHz, CDCl\(_3\))**: \( \delta \) 192.93, 166.91, 150.13, 141.01, 136.28, 129.25, 128.19, 127.04, 126.01, 116.14, 105.48, 54.95, 36.75, 32.99, 21.69. **LRMS (ESI):** [M + K\(^+\)] 486.9.
3-[Benzyl(3-nitrophenyl)amino]-2-iodocyclohex-2-enone (3p)

Following the general procedure, **3p** was purified by silica gel chromatography (25% EA/PE). \( R_f = 0.15 \) (EA/PE = 20/80).

**Yield**: 90%, yellow oil. \( ^1H \) NMR (400 MHz, DMSO): \( \delta \) 7.79 – 7.72 (m, 1H), 7.70 (t, \( J = 2.2 \) Hz, 1H), 7.53 (t, \( J = 8.2 \) Hz, 1H), 7.42 (d, \( J = 3.0 \) Hz, 1H), 7.41 – 7.33 (m, 4H), 7.28 (dd, \( J \) = 10.8, 4.2 Hz, 1H), 5.11 (s, 2H), 2.80 (t, \( J = 5.9 \) Hz, 2H), 2.67 – 2.55 (m, 2H), 1.99 – 1.79 (m, 2H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 193.06, 167.00, 149.41, 146.77, 136.79, 130.25, 129.28, 128.09, 126.79, 125.95, 116.96, 114.69, 99.16, 55.89, 36.74, 32.76, 21.49. \( \text{LRMS (ESI)}: [M + K^+] 487.0 \)

3-[Benzyl(4-bromophenyl)amino]-2-iodocyclohex-2-enone (3q)

Following the general procedure, **3q** was purified by silica gel chromatography (20% EA/PE). \( R_f = 0.30 \) (EA/PE = 20/80).

**Yield**: 57%, yellow solid, m.p. 112–114 °C. \( ^1H \) NMR (400 MHz, DMSO): \( \delta \) 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 7.29 – 7.21 (m, 1H), 7.01 – 6.95 (m, 2H), 5.05 (s, 2H), 2.75 (t, \( J = 5.9 \) Hz, 2H), 2.58 – 2.52 (m, 2H), 1.89 – 1.78 (m, 2H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.84, 167.48, 145.33, 137.67, 132.55, 129.16, 127.86, 126.81, 123.74, 116.22, 94.73, 56.64, 36.75, 32.96, 21.50. \( \text{LRMS (ESI)}: [M + H^+] 482.0 \)

3-[Benzyl(2-chlorophenyl)amino]-2-iodocyclohex-2-enone (3r)

Following the general procedure, **3r** was purified by silica gel chromatography (20% EA/PE). \( R_f = 0.23 \) (EA/PE = 20/80).

**Yield**: 62%, yellow solid, m.p. 107–108 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.59 – 6.85 (m, 9H), 5.06 (s, 2H), 2.60 (m 4H), 1.83 (m, 2H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.54, 167.11, 143.79, 137.51, 131.77, 130.77, 129.05, 128.09, 127.90, 127.69, 127.23, 126.72, 86.70, 57.66, 36.39, 32.67, 20.96. \( \text{LRMS (ESI)}: [M + H^+] 437.9 \).
Methyl-4-\([\text{benzyl}(2\text{-ido-3-oxocyclohex-1-enyl)}\text{amino}]\text{benzoate (3s)}\)

Following the general procedure, 3s was purified by silica gel chromatography (25% EA/PE). \(R_f = 0.19\) (EA/PE = 20/80).

**Yield:** 65%, yellow oil. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta 7.95 \) (d, \(J = 8.9\) Hz, 2H), 7.38 – 7.28 (m, 5H), 7.27 (s, 1H), 6.86 (d, \(J = 5.0\) Hz, 2H), 5.04 (s, 2H), 3.86 (s, 3H), 2.68 – 2.62 (m, 4H), 2.04 – 1.93 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta 193.25, 167.60, 166.84, 149.33, 137.26, 131.42, 129.20, 129.13, 127.88, 126.86, 123.28, 118.56, 100.56, 55.50, 52.10, 36.84, 32.99, 29.89, 21.58.\) LRMS (ESI): [M+K\(^+\)] 499.8; [M - H\(^+\)] 460.9.

2-Iodo-3-\([\text{(4-nitrophenyl)(phenethyl)}\text{amino}]\text{cyclohex-2-enone (3t)}\)

Following the general procedure, 3t was purified by silica gel chromatography (20% EA/PE). \(R_f = 0.23\) (EA/PE = 20/80).

**Yield:** 86%, yellow solid, m.p. 127–129 \(^\circ\)C. \(^1\)H NMR (400 MHz, DMSO): \(\delta 8.18 – 8.09\) (m, 2H), 7.34 (q, \(J = 8.0\) Hz, 4H), 7.25 (t, \(J = 7.0\) Hz, 1H), 6.99 (d, \(J = 9.3\) Hz, 2H), 3.98 – 3.85 (m, 2H), 3.05 – 2.92 (m, 2H), 2.61 (dt, \(J = 11.7, 6.1\) Hz, 4H), 2.04 – 1.90 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta 192.97, 166.94, 149.74, 140.79, 138.01, 129.03, 128.97, 127.32, 126.14, 115.56, 105.75, 52.85, 36.79, 35.08, 32.46, 21.75.\) LRMS (ESI): [M + H\(^+\)] 463.4.

3-\([\text{Cyclohexyl(4-nitrophenyl)}\text{amino}]\text{-2-iodocyclohex-2-enone (3u)}\)

Following the general procedure, 3u was purified by silica gel chromatography (20% EA/PE). \(R_f = 0.30\) (EA/PE = 20/80).

**Yield:** 35%, yellow solid, m.p. 146–149 \(^\circ\)C. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta 8.06\) (d, \(J = 9.3\) Hz, 2H), 6.56 (d, \(J = 9.3\) Hz, 2H), 3.90 – 3.70 (m, 1H), 2.68 (t, \(J = 6.1\) Hz, 2H), 2.53 (t, \(J = 5.9\) Hz, 2H), 2.08 (m, 4H), 1.93 – 1.77 (m, 2H), 1.76 – 1.66 (m, 1H), 1.58 (m, 1H), 1.37 (m,
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.85, 165.57, 149.21, 139.48, 126.29, 113.98, 112.69, 59.17, 36.82, 34.20, 31.36, 26.27, 25.90, 21.96. LRMS (ESI): [M + H$^+$] 440.9.

3-(Diphenylamino)-2-iodocyclopent-2-enone (3v)

Following the general procedure, 3v was purified by silica gel chromatography (20% EA/PE). $R_f = 0.30$ (EA/PE = 30/70). **Yield:** 75%, yellow solid, m.p. 152–155 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (t, $J = 7.6$ Hz, 4H), 7.28 (dd, $J = 12.5$, 5.1 Hz, 2H), 7.20 (d, $J = 7.5$ Hz, 4H), 2.77 – 2.68 (m, 2H), 2.64 – 2.54 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 201.43, 173.29, 143.77, 129.61, 128.16, 127.44, 32.50, 31.71, 0.20. LRMS (ESI): [M + H$^+$] 375.8.

4-Oxo-2-(phenylamino)pent-2-en-3-yl acetate (5a)

Following the general procedure, 5a was purified by silica gel chromatography (10% EA/PE). $R_f = 0.46$ (EA/PE = 20/80). **Yield:** 85%, yellow solid, m.p. 102–104 °C. $^1$H NMR (400 MHz, DMSO): $\delta$ 7.51 (dd, $J = 4.8$, 2.5 Hz, 3H), 7.35 (dd, $J = 7.7$, 1.9 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.22 (s, 3H). LRMS (ESI): [M + K$^+$] 271.9.

(E)-2-Amino-4-oxopent-2-en-3-yl acetate (5b)

Following the general procedure, 5b was purified by silica gel chromatography (10% EA/PE). $R_f = 0.27$ (EA/PE = 30/70). **Yield:** 73%, yellow oil, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.24 (s, 3H), 2.02 (s, 3H), 1.87 (s, 3H). LRMS (ESI): [M + K$^+$] 195.9.

(E)-2-(Benzylamino)-4-oxopent-2-en-3-yl acetate (5c)

Following the general procedure, 5c was purified by silica gel chromatography (10% EA/PE). $R_f = 0.41$ (EA/PE = 30/70). **Yield:** 58%, viscous oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.36–7.25 (m, 5H), 4.46 (d, $J = 10$ Hz, 2H), 2.23 (s, 3H), 2.01 (s, 3H), 1.85 (s, 3H). 

**LRMS (ESI):** [M + Na$^+$] 269.9.

**(E)-2-(Methylamino)-4-oxopent-2-en-3-yl acetate (5d)**

Following the general procedure, 5d was purified by silica gel chromatography (10% EA/PE). $R_f = 0.46$ (EA/PE = 30/70). **Yield:** 72%, viscous oil, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.94 (d, $J = 5.2$ Hz, 3H), 2.23 (s, 3H), 1.96 (s, 3H), 1.87 (s, 3H). **LRMS (ESI):** [M + H$^+$] 172.0.
Reference


X-ray structure and data of 3a

Table 1. Crystal data and structure refinement for r90601f.

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Z, Calculated density  4,  1.657 Mg/m^3

Absorption coefficient  2.051 mm^-1

F(000)  768

Crystal size  0.24 x 0.20 x 0.18 mm

Theta range for data collection  2.39 to 25.02 deg.

Limiting indices  -10<=h<=12, -16<=k<=16, -13<=l<=14

Reflections collected / unique  12524 / 2741 [R(int) = 0.0324]

Completeness to theta = 25.02  99.2 %

Absorption correction  Semi-empirical from equivalents

Max. and min. transmission  0.7090 and 0.6388

Refinement method  Full-matrix least-squares on F^2

Data / restraints / parameters  2741 / 0 / 190

Goodness-of-fit on F^2  1.065

Final R indices [I>2sigma(I)]  R1 = 0.0200, wR2 = 0.0511

R indices (all data)  R1 = 0.0226, wR2 = 0.0521

Largest diff. peak and hole  0.314 and -0.663 e.A^-3
Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (A$^2 x 10^3$) for r90601f.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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Table 3. Bond lengths [Å] and angles [deg] for r90601f.

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Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å^2 x 10^3) for r90601f.
The anisotropic displacement factor exponent takes the form:
\[-2 \pi^2 \left[ h^2 a^{*2} U_{11} + \ldots + 2 h k a^{*} b^{*} U_{12} \right] \]

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for r90601f.

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Table 6. Torsion angles [deg] for r90601f.

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N(1)-C(13)-C(18)-C(17)  179.8(2)

Symmetry transformations used to generate equivalent atoms:
Table 7. Hydrogen bonds for r90601f [Å and deg.].

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