Supporting Information


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Experimental Procedures

1. General Remarks
All air sensitive reactions were carried out under argon using flame-dried apparatus. Reactions were monitored by TLC on Merck silica gel 60 Å F TLC plates and visualised with 254 nm UV followed by aqueous 1% KMnO₄ or PMA. Column chromatography was performed using Sigma Aldrich 40–63 μm 60 Å 230–400 Å silica and the stated solvent system under slight positive pressure. Reaction and chromatography solvents were removed using a rotary evaporator equipped with a diaphragm pump. ¹H and ¹³C NMR spectroscopy was performed on a Bruker AV400 (400/100 MHz) spectrometer at 298 K in CDCl₃. Chemical shifts are quoted as δ values in ppm using residual solvent peaks as the reference. Coupling constants J are given in Hz and multiplicity is described as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad. HRMS data were obtained using a Bruker APEX III FT-ICR-MS with samples run in HPLC grade methanol. Electrospray mass spectrometry was performed on a directly injected Waters quadrupole MSD using ESI⁺ or ESI⁻ ionisation with MeOH as solvent. Infrared spectroscopy was performed on a Nicolet iS5 Laboratory FT-IR spectrometer and spectra of solids were acquired from films deposited by evaporation of CDCl₃ or DCM solutions. Absorption maxima (λmax) are quoted in wavenumbers (cm⁻¹) with the following abbreviations used to describe their intensity: s, strong; m, medium; w, weak; br, broad. All other starting materials and reagents were used as supplied from commercial sources.

2. Photochemical Set-Ups
Set-up A: as detailed in Angew. Chem., Int. Ed., 2015, 54, 4531, scaled to accommodate a 36 or 60 W Philips UVC PL36/10/4P lamp and with a reactor capacity of 120 mL.¹

Set-up B: as above but with a twin channel peristaltic pump drawing in separate streams of air and a solution of the starting material. Those streams are combined using a Y-connector giving to a segmented stream of air bubbles and the reaction solution which is passed into the photoreactor.

Set-up C (for scale-up): as above but with three reactors connected in series, each equipped with a 60 W Philips UVC PL36/10/4P lamp and with a Y-connector introducing air into the final photoreactor.

3. Cyclisation Procedures
9-Methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 4
Using flow photochemical set-up A: A solution of enaminone 5a (412 mg, 2.06 mmol) and iodine (25.4 mg, 0.100 mmol, 5 mol%) in MeCN (105 mL) was irradiated with a 36 W UVA lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo to a brown oil that was triturated with cold EIOAc to afford the title compound 4 (352 mg, 1.78 mmol, 86%) as an off-white solid.

Using flow photochemical set-up B: A solution of enaminone 5a (150 mg, 0.746 mmol) in MeCN (75 mL) was segmented with bubbles of air then irradiated with a 36 W UVA lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo then triturated with cold EIOAc to afford the title compound 4 (116 mg, 0.583 mmol, 78%) as a yellow solid.

Using flow photochemical set-up C: A solution of enaminone 5a (8.72 g, 43.3 mmol) in MeCN (1.45 L) was irradiated firstly with 2×60 W UVA lamps for a residence time of 1 h then by a 60 W UVA lamp under segmented flow with bubbles of air for a residence time of 15 min. The resulting solution was concentrated in vacuo then washed with cold EIOAc to afford the title compound 4 (6.64 g, 33.3 mmol, 77%) as a yellow solid. MP 193 – 194 °C (MeOH), Lit.20 195 – 196 °C (EIOAc/hexane). IR νmax (film, cm⁻¹): 2953 (br), 1630 (s), 1475 (s), 1093 (m). ¹H NMR (400 MHz, CDCl₃): δ 8.23 (1 H, m, ArH), 7.29 – 7.24 (3 H, m, 3 × ArH), 3.68 (3 H, s, CH₃), 2.91 (2 H, app. t, J = 6.2 Hz, CH₂), 2.58 (2 H, dd, J = 7.2, 5.7 Hz, CH₂), 2.24 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 193.6 (C), 151.8 (C), 137.3 (C), 124.6 (C), 122.8 (CH), 122.3 (CH), 121.4 (CH), 112.4 (C), 109.0 (CH), 37.7 (CH₂), 29.7 (CH₂), 23.1 (CH₂), 22.0 (CH₂) ppm. LRMS (ESI⁺): 200 [M+H⁺]: Data consistent with literature values.²
5-Methyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indol-1-one, 14

*Using flow photochemical set-up B:* A solution of dihydropyridine 17 (420 mg, 1.39 mmol) in MeCN (139 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for 30 min. To the resultant solution was added TFA (0.40 mL, 5.22 mmol) and after 15 h at RT, sat. NaHCO₃ (10 mL) was added. The aqueous phase was separated and washed with DCM (3 x 30 mL), then the combined organic phases were dried over MgSO₄, concentrated *in vacuo* and purified by column chromatography (20 – 40% acetone in DCM) to afford the *title compound* (175 mg, 0.875 mmol, 63%) as a yellow solid. **MP** 242 – 245 °C (acetone/CH₂Cl₂), Lit.²,³ 242 – 244 °C (petrol/CH₂Cl₂/MeOH). **¹H NMR** (400 MHz, CDCl₃): δ 8.17 (m, 1H, ArH), 7.34 – 7.24 (m, 3H, 3 x ArH), 5.73 (br s, 1H, NH), 3.70 (s, 3H, CH₃), 3.69 (t, J = 7.0 Hz, 2H, CH₂), 3.01 (t, J = 7.0 Hz, 2H, CH₂), 2.18 (s, 3H, CH₃) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 167.1 (C), 144.8 (C), 137.3 (C), 125.2 (C), 122.4 (CH), 121.9 (CH), 120.9 (CH), 109.2 (CH), 105.2 (C), 40.5 (CH₂), 29.9 (CH₃), 21.8 (CH₂) ppm. **LRMS** (ESI⁺): 201 ([M⁺H⁺], 100%). Data consistent with literature values.³

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*N-(Methoxymethyl)-1,2-dimethyl-1H-indole-3-carboxamide, 15*

*Using flow photochemical set-up B:* A solution of dihydropyridine 16 (173 mg, 0.865 mmol) in MeOH (86 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (50 – 80% EtOAc in petrol) to afford the *title compound* 16 (162 mg, 0.698 mmol, 81%) as a yellow solid. **MP:** 131 – 132 °C. **IR** νₘₓₙ (film, cm⁻¹): 3319 (br), 2931 (br), 1636 (s), 1545 (m), 1507 (m), 1473 (s), 1404 (m), 1225 (m), 1171 (m), 1116 (m), 1069 (m). **¹H NMR** (400 MHz, CDCl₃): δ 7.75 (1H, m, ArH), 7.35 (1H, m, ArH), 7.78 – 7.22 (2H, m, 2 x ArH), 6.62 (1H, br. s, NH), 4.97 (2H, d, J = 7.0 Hz, CH₂), 3.72 (3H, s, CH₃), 3.46 (3H, s, CH₃), 2.77 (3H, s, CH₃) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ 166.6 (C), 143.2 (C), 136.5 (C), 124.9 (C), 121.8 (CH), 121.4 (CH), 118.4 (CH), 109.7 (CH), 107.0 (C), 71.4 (CH₂), 55.9 (CH₃), 29.5 (CH₃), 11.7 (CH₃) ppm. **LRMS** (ESI⁺): 255 (40%, [M + Na⁺]), 233 (10%, [M + H⁺]), 172 (100%, [M – NHCH₂OCH₃]⁺). **HRMS** (ESI⁺): Found 255.1106, C₁₃H₁₅N₂NaO₂ [M + Na⁺] requires 255.1104.
Using flow photochemical set-up A: A solution of enaminone 5c (286 mg, 1.00 mmol) and iodine (12 mg, 0.05 mmol, 5 mol%) in MeCN (50 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% EtO in petrol) to afford the title compound 18c (231 mg, 0.810 mmol, 81%) as a yellow solid.

Using flow photochemical set-up B: A solution of enaminone 5c (265 mg, 0.923 mmol) in MeCN (92 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% EtO in petrol) to afford the title compound 18c (60 mg, 0.210 mmol, 23%) as a yellow solid. MP 143 – 144 °C (EtO/petrol), Lit.4 144 – 148 °C. IR νmax (film, cm⁻¹): 2977 (br), 1738 (s), 1663 (s), 1366 (s), 1350 (s), 1151 (s), 1139 (s). ¹H NMR (400 MHz, CDCl₃): δ 8.30 (1 H, m, ArH), 8.09 (1 H, m, ArH), 7.35 – 7.31 (2 H, m, 2 × ArH), 3.32 (2 H, app. t, J = 6.2 Hz, CH₃), 2.26 – 2.58 (2 H, m, CH₂), 2.24 (2 H, app. quin, J = 6.4 Hz, CH₂), 1.72 (9 H, s, 3 × CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 195.5 (C), 152.0 (C), 149.8 (C), 135.8 (C), 128.5 (C), 124.8 (CH), 124.3 (CH), 121.5 (CH), 117.3 (C), 115.1 (CH), 83.4 (C), 37.9 (CH₃), 28.2 (3 × CH₃), 25.9 (CH₂), 23.3 (CH₂) ppm. LRMS (ESI⁺): 286 [M+H]⁺. Data consistent with literature values.²

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9-Methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 3

To a solution of 18c (310 mg, 1.09 mmol) in DCM (10 mL) at RT was added TFA (5 mL) dropwise. After 48 hours, sat. Na₂CO₃ (50 mL) was added, then the aqueous phase was separated and extracted with DCM (3 × 50 mL). The organic phases were combined, dried over MgSO₄, concentrated under reduced pressure and purified by column chromatography (50 – 60% EtOAc/hexane) to afford the title compound 3 (167 mg, 0.903 mmol, 83%) as a white solid. MP 215 – 216 °C (EtOAc/hexane), Lit.4 216 – 217 °C. IR νmax (film, cm⁻¹): 3143 (br), 1623 (s), 1467 (s). ¹H NMR (400 MHz, CDCl₃): δ 9.03 (1 H, br s, NH), 8.23 (1 H, m, ArH), 7.36 (1 H, m, ArH), 7.28 – 7.22 (2 H, m, 2 × ArH), 3.00 (2 H, app. t, J = 6.2 Hz, CH₃), 2.61 (2 H, app. dd, J = 7.2, 5.6 Hz, CH₂), 2.25 (2 H, app. quin, J = 6.5 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 194.4 (C), 151.3 (C), 135.7 (C), 124.8 (C), 123.3 (C), 122.5 (CH), 121.5 (CH), 113.4 (C), 110.9 (CH), 38.1 (CH₂), 23.7 (CH₃), 23.5 (CH₂) ppm. LRMS (ESI⁺): 186 [M+H]⁺. Data consistent with literature values.⁴
9-Benzyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18d

Using flow photochemical set-up B: A solution of enaminone 5d (200 mg, 0.722 mmol) in MeCN (72 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated in vacuo and purified by column chromatography (50 – 70% EtOAc in petrol) to afford the title compound 18d (139 mg, 0.505 mmol, 70%) as a yellow solid. **MP** 148 – 151 °C (acetone/CH₂Cl₂), Lit. 148 – 150 °C (aq. EtOH). ¹H NMR (400 MHz, CDCl₃): δ 8.31 (1H, m, ArH), 7.35 – 7.21 (6H, m, 6 x ArH), 7.04 (2H, m, 2 x ArH), 5.35 (2H, s, CH₂), 2.89 (2H, app. t, J = 6.2 Hz, CH₂), 2.60 (2H, dd, J = 7.3, 5.8 Hz, CH₂), 2.25 (2H, app. quin., J = 6.4 Hz, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 194.0 (C), 151.8 (C), 137.2 (C), 136.0 (C), 129.1 (2 x CH), 127.9 (CH), 126.1 (2 x CH), 124.9 (C), 123.2 (CH), 122.7 (CH), 121.8 (CH), 113.2 (C), 109.6 (CH), 47.0 (CH₂), 37.9 (CH₂), 23.4 (CH₂), 22.3 (CH₂) ppm. **LRMS** (ESI⁺): 276 (100%, M+H⁺). Data consistent with literature values.³

9-Benzyl-2-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18f

Using flow photochemical set-up B: A solution of enaminone 5f (200 mg, 0.687 mmol) in MeCN (69 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 18f (137 mg, 0.474 mmol, 69%) as an off-white solid. **MP** 148 – 149 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.30 (1H, dt, J = 7.7, 1.1 Hz, ArH), 7.35 – 7.21 (6H, m, 6 x ArH), 7.06 – 7.01 (2H, m, 2 x ArH), 5.35 (2H, s, CH₂), 2.98 (1H, m, CHH), 2.64 (1H, dd, J = 15.8, 3.4 Hz, CHH), 2.58 – 2.47 (2H, m, CHH + CH), 2.36 (1H, dd, J = 16.0, 11.7 Hz, CHH), 1.19 (3H, d, J = 6.2 Hz, CH₃) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 193.7 (C), 151.7 (C), 137.4 (C), 136.0 (C), 129.1 (2 x CH), 127.9 (CH), 126.0 (2 x CH), 124.8 (C), 123.2 (CH), 122.8 (CH), 121.7 (CH), 112.8 (C), 109.7 (CH), 47.0 (CH₂), 46.2 (CH₂), 31.3 (CH₃), 30.3 (CH), 21.3 (CH₃) ppm. **LRMS** (ESI⁺): 290 [M+H⁺]. **HRMS** (ESI⁺): Found 290.1543, C₁₉H₁₃NO [M+H⁺] requires 290.1539.
9-Ethyl-2-phenyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18g

Using flow photochemical set-up B: A solution of enamino 5g (200 mg, 0.687 mmol) in MeCN (69 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated in vacuo and purified by column chromatography (20 – 60% EtOAc in petrol) to afford the title compound 18g (116 mg, 0.401 mmol, 58%) as a yellow solid. MP 177 – 179 °C.

\[ \text{IR } \nu_{\text{max}} \text{ (film, cm}^{-1}\text{): } 2980 \text{ (br), } 1639 \text{ (s), } 1475 \text{ (m), } 1454 \text{ (s), } 1131 \text{ (w), } 1098 \text{ (w).} \]

\[ ^1\text{H NMR} \text{ (400 MHz, CDCl}_3\text{): } \delta 8.31 \text{ (1H, m, ArH), } 7.41 \text{ – } 7.28 \text{ (8H, m, 8 x ArH), } 4.18 \text{ (2H, q, } J = 7.3 \text{ Hz, } \text{CH}_2\text{), } 3.65 \text{ (1H, app. tt, } J = 11.6, 4.8 \text{ Hz, CH), } 3.25 \text{ (1H, dd, } J = 16.8, 5.0 \text{ Hz, CHH), } 3.12 \text{ (1H, dd, } J = 16.8, 11.3 \text{ Hz, CHH), } 2.93 \text{ – } 2.86 \text{ (2H, m, CH}_2\text{), } 1.42 \text{ (3H, t, } J = 7.3 \text{ Hz, CH}_3\text{) ppm.} \]

\[ ^1\text{C NMR} \text{ (101 MHz, CDCl}_3\text{): } \delta 192.5 \text{ (C), } 150.5 \text{ (C), } 143.1 \text{ (C), } 136.7 \text{ (C), } 128.9 \text{ (2 x CH), } 127.2 \text{ (CH), } 126.9 \text{ (2 x CH), } 124.8 \text{ (C), } 123.2 \text{ (CH), } 122.8 \text{ (CH), } 121.9 \text{ (CH), } 112.5 \text{ (C), } 109.4 \text{ (CH), } 44.8 \text{ (CH}_2\text{), } 42.1 \text{ (CH), } 38.5 \text{ (CH}_2\text{), } 30.1 \text{ (CH}_2\text{), } 15.1 \text{ (CH}_3\text{) ppm.} \]

\[ \text{HRMS (ESI\textsuperscript{+}): } 290 \text{ [M+H\textsuperscript{+}] requires } 290.1539. \]

9-Benzyl-2-phenyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18h
Using flow photochemical set-up B: A solution of enaminoe 5h (200 mg, 0.567 mmol) in MeCN (57 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated in vacuo and purified by column chromatography (5 – 30% EtOAc in petrol) to afford the title compound 18h (85 mg, 0.242 mmol, 42%) as a yellow solid. MP 173-174 °C. IR νmax (film, cm⁻¹): 2981 (br), 2360 (m), 1647 (s), 1457 (s). ¹H NMR (400 MHz, CDCl₃): δ 8.34 (1H, dt, J = 7.6, 1.0 Hz, ArH), 7.38 – 7.23 (11H, m, 11 x ArH), 7.01 (2H, dd, J = 7.5, 1.8 Hz, 2 x ArH), 5.35 (2H, s, CH₂), 3.65 (1H, app. tt, J = 11.1, 4.8 Hz, CH₃), 3.21 (1H, dd, J = 16.9, 5.1 Hz, CH₃), 3.05 (1H, dd, J = 16.8, 11.0 Hz, CHH), 2.92 (1H, dd, J = 16.4, 11.6 Hz, CHH), 2.85 (1H, dd, J = 16.6, 4.7 Hz, CHH) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 192.6 (C), 150.7 (C), 143.0 (C), 137.5 (C), 135.8 (C), 129.1 (2 x CH), 128.8 (2 x CH), 127.9 (CH), 127.1 (CH), 126.9 (2 x CH), 124.7 (C), 123.4 (CH), 122.9 (CH), 121.8 (CH), 111.9 (C), 109.8 (CH), 47.0 (CH₃), 45.0 (CH₃), 42.0 (CH), 30.2 (CH₂) ppm. LRMS (ESI⁺): 352 [M+H⁺]. HRMS (ESI⁺): Found 352.1697, C₂₉H₂₂N⁰ [M+H⁺] requires 352.1696.

3.3.9-Trimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18i

Using flow photochemical set-up A: A solution of enaminoe 5i (285 mg, 1.24 mmol) and iodine (15.8 mg, 0.062 mmol, 5 mol%) in MeCN (62 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% Et₂O in petrol) to afford the title compound 18i (182 mg, 0.802 mmol, 65%) as an off-white oil.

Using flow photochemical set-up B: A solution of enaminoe 5i (231 mg, 1.01 mmol) in MeCN (101 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% EtOAc in petrol) to afford the title compound 18i (152 mg, 0.670 mmol, 67%) as an off-white oil. IR νmax (film, cm⁻¹): 2924 (br), 1637 (s), 1474 (s), 1456 (s), 1416 (m), 1067 (s). ¹H NMR (400 MHz, CDCl₃): δ 8.27 (1 H, m, ArH), 7.12 – 7.08 (3 H, m, 3 x ArH), 3.65 (3 H, s, CH₃), 2.92 (2 H, t, J = 6.3 Hz, CH₃), 2.08 (2 H, t, J = 6.3 Hz, CH₃), 1.24 (6 H, s, 2 x CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 198.9 (C), 150.3 (C), 137.7 (C), 131.0 (C), 125.2 (C), 122.7 (CH), 122.3 (CH), 121.4 (CH), 109.0 (CH), 41.4 (C), 36.9 (CH₃), 29.5 (CH₃), 24.4 (2 x CH₃), 19.4 (CH₂) ppm. LRMS (ESI⁺): 228 [M+H⁺]. Data consistent with literature values, though the product proved sensitive to column chromatography leading to some decomposition.²
9-Ethyl-3,3-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18j
Using flow photochemical set-up B: A solution of enamino 5j (200 mg, 0.823 mmol) in MeCN (82 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 18j as an off-white solid (146 mg, 0.606 mmol, 74%). **MP** 121 – 124 °C. **IR** ν\textsubscript{max} (film, cm\textsuperscript{-1}): 2961 (br), 2927 (w), 1640 (s), 1455 (s), 1067 (m), 753 (m). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}); δ 8.29 (1H, m, ArH), 7.33 (1H, m, ArH), 7.24 – 7.29 (2H, m, 2 x ArH), 4.16 (2H, q, J = 7.2 Hz, CH\textsubscript{2}), 2.97 (2H, t, J = 6.2 Hz, CH\textsubscript{2}), 2.12 (2H, t, J = 6.3 Hz, CH\textsubscript{2}). 1.43 (3H, t, J = 7.3 Hz, CH\textsubscript{3}). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}); δ 198.9 (C), 149.5 (C), 136.7 (C), 125.6 (C), 122.8 (CH), 122.4 (CH), 121.8 (CH), 110.9 (C), 109.1 (CH), 41.5 (C), 38.2 (CH\textsubscript{2}), 37.2 (CH\textsubscript{2}), 24.5 (2 x CH\textsubscript{3}), 19.4 (CH\textsubscript{3}), 15.0 (CH\textsubscript{3}) ppm. **LRMS (ESI\textsuperscript{+}):** 242 [M+H]+. **HRMS (ESI\textsuperscript{+}):** Found 242.1542, C\textsubscript{16}H\textsubscript{19}NO [M+H]\textsuperscript{+} requires 242.1539.

9-Benzy1-3,3-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18k
Using flow photochemical set-up B: A solution of enamino 5k (200 mg, 0.656 mmol) in MeCN (65 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 18k as a yellow solid (147 mg, 0.485 mmol, 75%). **MP** 171 – 173 °C (EtOAc/petrol). **IR** ν\textsubscript{max} (film, cm\textsuperscript{-1}): 2960 (w), 2925 (w), 1645 (s), 1456 (s), 1067 (m), 753 (m). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}); δ 8.32 (1H, d, J = 7.6 Hz, ArH), 7.35 – 7.21 (6H, m, 6 x ArH), 7.06 – 7.01 (2H, m, 2 x ArH), 5.34 (2H, s, CH\textsubscript{2}), 2.91 (2H, t, J = 6.3 Hz, CH\textsubscript{2}), 2.09 (2H, t, J = 6.3 Hz, CH\textsubscript{2}), 1.26 (6H, s, 2 x CH\textsubscript{3}). **MRMS (ESI\textsuperscript{+}):** Data consistent with literature values.\textsuperscript{5}
2,2,9-Trimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18I

Using flow photochemical set-up A: A solution of enamidine 5i (101 mg, 0.441 mmol) and iodine (5.6 mg, 0.022 mmol, 5 mol%) in MeCN (22 mL, 0.02 M) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% EtO in petrol) to afford the title compound 18I (75 mg, 0.330 mmol, 76%) as a yellow solid.

Using flow photochemical set-up B: A solution of enamidine 5i (130 mg, 0.568 mmol) in MeCN (57 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% EtO in petrol) to afford the title compound 18I (96 mg, 0.423 mmol, 71%) as a yellow solid. MP 118 – 119 °C (EtO/petrol), Lit.° 115 °C. IR νmax (film, cm⁻¹): 2954 (br), 1617 (m), 1549 (s), 1492 (m), 1382 (m), 1281 (s). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (1 H, m, ArH), 7.31 – 7.26 (3 H, m, 3 × ArH), 7.68 (3 H, s, CH₃), 7.47 (2 H, s, CH₃), 1.88 (6 H, s, 2 × CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 193.0 (C), 150.8 (C), 137.7 (C), 124.5 (C), 122.7 (CH), 122.5 (CH), 121.5 (CH), 113.4 (C), 109.1 (CH), 51.9 (CH₃), 36.1 (CH₃), 35.1 (CH₃), 29.8 (C), 24.4 (2 × CH₃) ppm. LRMS (ESI⁺): 228 [M+H]⁺. Data consistent with literature values.°
9-Ethyl-2,2-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18m

Using flow photochemical set-up B: A solution of enaminone 5m (200 mg, 0.823 mmol) in MeCN (82 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated in vacuo and purified by column chromatography (10 - 30% EtOAc in petrol) to afford the title compound 18m (131 mg, 0.544 mmol, 66%) as an off-white solid. **MP** 91 – 94 °C (EtOAc/petrol), Lit. 93 – 95 °C (Et2O/hexane). **IR** νmax (film, cm⁻¹): 2959 (br), 1644 (s), 1455 (s), 1092 (m), 748 (m). **¹H NMR** (400 MHz, CDCl₃): δ 8.26 (1H, m, ArH), 7.34 (1H, m, ArH), 7.30 – 7.27 (2H, m, 2 x ArH), 4.17 (2H, q, J = 7.3 Hz, CH₂), 2.80 (2H, s, CH₂), 2.49 (2H, s, CH₂), 1.41 (3H, t, J = 7.3 Hz, CH₃), 1.20 (6H, s, 2 x CH₃) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 193.1 (C), 150.3 (C), 136.6 (C), 124.8 (C), 122.8 (CH), 122.5 (CH), 121.7 (CH), 111.5 (C), 109.2 (CH), 51.9 (CH₂), 38.4 (CH₂), 36.1 (CH₂), 35.3 (C), 28.8 (2 x CH₃), 15.2 (CH₃) ppm. **LRMS (ESI⁺):** 242 [M+H]⁺. Data consistent with literature values.⁸

9-Benzyl-2,2-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 18n

Using flow photochemical set-up B: A solution of enaminone 5n (200 mg, 0.656 mmol) in MeCN (65 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 15 min. The resultant solution was concentrated in vacuo and purified by column chromatography (10 - 40% EtOAc in petrol) to afford the title compound 18n (135 mg, 0.446 mmol, 69%) as a yellow solid. **MP** 143 – 147 °C (EtOAc/petrol), Lit. 140 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.30 (1H, dt, J = 7.7, 1.1 Hz, ArH), 7.34 – 7.20 (6H, m, 6 x ArH), 7.05 – 6.99 (2H, m, 2 x ArH), 5.35 (2H, s, CH₂), 2.75 (2H, s, CH₂), 2.48 (2H, s, CH₂), 1.16 (6H, s, 2 x CH₃) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 193.4 (C), 150.9 (C), 137.4 (C), 136.0 (C), 129.0 (2 x CH), 127.9 (CH), 125.9 (2 x CH), 124.7 (C), 123.1 (CH), 122.7 (CH), 121.6 (CH), 111.9 (C), 109.7 (CH), 52.0 (CH₂), 46.9 (CH₂), 36.2 (CH₂), 35.4 (C), 28.7 (2 x CH₃) ppm. **LRMS (ESI⁺):** 304 [M+H]⁺. Data consistent with literature values.⁹
8,9-Dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20a

*Using flow photochemical set-up A:* A solution of enammon 19a (205 mg, 0.953 mmol) and iodine (12 mg, 0.05 mmol, 5 mol%) in dry MeCN (48 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtO in petrol) to afford the *title compound 20a* (73 mg, 0.343 mmol, 36%) as an off-white solid.

*Using flow photochemical set-up B:* A solution of enamnone 19a (350 mg, 1.63 mmol) in MeCN (163 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtO in petrol) to afford the *title compound 20a* (132 mg, 0.620 mmol, 38%) as an off-white solid. **MP** 165 – 166 °C (EtO/petrol); Lit.** 186 – 187 °C. **IR** ν max (film, cm⁻¹): 2940 (br), 1637 (s), 1465 (s), 1409 (m), 1105 (s). **1H NMR** (400 MHz, CDCl₃): δ 8.14 (1 H, d, J = 7.8 Hz, ArH), 7.14 (1 H, app. t, J = 7.6 Hz, ArH), 6.99 (1 H, d, J = 7.1 Hz, ArH), 3.96 (3 H, s, CH₃), 2.90 (2 H, app. t, J = 6.2 Hz, CH₂), 2.77 (3 H, s, CH₃), 2.63 (2 H, dd, J = 7.2, 5.8 Hz, CH₂), 2.24 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. **13C NMR** (100 MHz, CDCl₃): δ 193.8 (C), 153.1 (C), 136.3 (C), 126.5 (CH), 125.5 (C), 122.9 (CH), 121.0 (C), 119.9 (CH), 112.4 (C), 37.0 (CH₂), 33.3 (CH₃), 23.1 (CH₃), 22.4 (CH₂), 20.1 (CH₃) ppm. **LRMS (ESI⁺):** 236 [M + Na]⁺, 214 [M + H]⁺. Data consistent with literature values.**

5,9-Dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20b and 7,9-dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20b′

*Using flow photochemical set-up B:* A solution of enamnone 19b (290 mg, 1.26 mmol) in MeCN (126 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 40% EtO in petrol) to afford firstly *title compound 20b* (210 mg, 0.986 mmol, 51%) as an off-white solid. **MP:** 169 – 170 °C. **IR** ν max (film, cm⁻¹): 2933 (br), 1629 (s), 1476 (m), 1432 (m), 1087 (m). **1H NMR** (400 MHz, CDCl₃): δ 8.11 (1 H, d, J = 8.0 Hz, ArH), 7.10 (1 H, ddd, J = 8.0, 1.3, 0.6 Hz, ArH), 7.07 (1 H, m, ArH), 3.63 (3 H, s, CH₃), 2.86 (2 H, app. t, J = 6.3 Hz, CH₂), 2.53 (2 H, dd, J = 7.1, 5.9 Hz, CH₂), 2.49 (3 H, s, CH₃), 2.22 (2 H, app. quin, J = 6.5 Hz, CH₂) ppm. **13C NMR** (100 MHz, CDCl₃): δ 193.6 (C), 151.5 (C), 137.7 (C), 132.8 (C), 123.9 (CH), 122.4 (C), 121.1 (CH), 112.5 (C), 109.2...
(CH), 37.7 (CH₂), 29.6 (CH₂), 23.2 (CH₂), 22.0 (CH₂), 21.8 (CH₃) ppm. LRMS (ESI⁺): 236 [M + Na]⁺, 214 [M + H]⁺. HRMS (ESI⁺): Found 214.1232. C₆H₁₃NO [M+H]⁺ requires 214.1226. Followed by title compound 20b’ (123 mg, 0.577 mmol, 30%) as an off-white solid. MP: 185 – 186 °C. IR (film, cm⁻¹): 2932 (br), 1634 (s), 1480 (m), 1408 (m), 1021 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.15 (1 H, dd, J = 8.1, 7.3 Hz, ArH), 7.04 – 7.01 (2 H, m, 2 × ArH), 3.43 (3 H, s, CH₃), 2.98 (3 H, s, CH₃), 2.80 (2 H, app. t, J = 6.3 Hz, CH₂), 2.52 (2 H, dd, J = 7.0, 5.9 Hz, CH₂), 2.15 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 192.2 (C), 152.0 (C), 137.8 (C), 132.8 (C), 124.2 (CH), 124.1 (C), 123.0 (CH), 113.5 (C), 106.4 (CH), 38.8 (CH₂), 29.6 (CH₃), 23.0 (CH₂), 22.51 (CH₂), 22.45 (CH₃) ppm. LRMS (ESI⁺): 236 [M + Na]⁺, 214 [M + H]⁺. HRMS (ESI⁺): Found 214.1230, C₆H₁₃NO [M+H]⁺ requires 214.1226.

* NMR Spectra for 20b:

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6,9-Dimethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20c

Using flow photochemical set-up B: A solution of enamino 19c (388 mg, 1.81 mmol) in MeCN (180 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% Et₂O in petrol) to afford the title compound 20c (272 mg, 1.28 mmol, 71%) as an off-white solid. MP 160 – 161 °C (Et₂O/petrol), Lit. 166 – 169 °C. IR (film, cm⁻¹): 2926 (br), 1627 (s), 1459 (s), 1323 (m), 1092 (s). ¹H NMR
(400 MHz, CDCl₃): δ 8.06 (1 H, app. quin, J = 0.9 Hz, ArH), 7.19 (1 H, d, J = 8.2 Hz, ArH), 7.10 (1 H, dd, J = 8.3, 1.5 Hz, ArH), 3.68 (3 H, s, CH₃), 2.91 (2 H, app. t, J = 6.3 Hz, CH₂), 2.61 (2 H, dd, J = 7.2, 5.8 Hz, CH₂), 2.48 (3 H, s, CH₃), 2.24 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 193.8 (C), 152.4 (C), 135.8 (C), 132.5 (C), 124.8 (C), 124.5 (CH), 121.6 (CH), 112.1 (C), 108.8 (CH), 37.4 (CH₂), 29.9 (CH₃), 23.2 (CH₂), 22.2 (CH₂), 21.4 (CH₃) ppm. LRMS (ESI⁺): 236 [M + Na]⁺, 214 [M + H]⁺. Data consistent with literature values.¹⁰

8-Methoxy-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20d

Using flow photochemical set-up B: A solution of enaminone 19d (332 mg, 1.44 mmol) in MeCN (144 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 1 hour. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 20d (227 mg, 0.991 mmol, 69%) as an off-white solid. MP: 139 – 140 °C. IR νmax (film, cm⁻¹): 2938 (br), 1638 (s), 1613 (s), 1542 (s), 1264 (m), 1109 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.87 (1 H, dd, J = 7.9, 0.9 Hz, ArH), 7.15 (1 H, t, J = 7.9 Hz, ArH), 6.69 (1 H, dd, J = 8.0, 0.7 Hz, ArH), 3.95 (1 H, s, CH₃), 3.92 (1 H, s, CH₃), 2.84 (2 H, app. t, J = 6.2 Hz, CH₂), 2.92 (2 H, app. dd, J = 7.2, 5.8 Hz, CH₂), 2.22 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 193.8 (C), 151.7 (C), 147.1 (C), 126.9 (C), 126.5 (C), 122.0 (CH), 114.2 (CH), 112.6 (C), 104.4 (CH), 55.4 (CH₂), 37.7 (CH₂), 33.1 (CH₃), 23.1 (CH₃), 22.0 (CH₂) ppm. LRMS (ESI⁺): 252 [M + Na]⁺, 230 [M + H]⁺. HRMS (ESI⁺): Found 230.1179, C₁₄H₁₆NO₂ [M+H]⁺ requires 230.1176.
5-Methoxy-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20e

Using flow photochemical set-up B: A solution of enamino 19e (290 mg, 1.26 mmol) in MeCN (126 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 40% Et2O in petrol) to afford firstly title compound 20e (127 mg, 0.555 mmol, 44%) as an off-white solid. **MP:** 197 – 199 °C. IR *ν* max (film, cm⁻¹): 2950 (br), 1629 (s), 1476 (m), 1245 (m), 1080 (m). **1H NMR** (400 MHz, CDCl₃): δ 8.11 (1 H, d, *J* = 8.7 Hz, ArH), 6.91 (1 H, dd, *J* = 8.6, 2.2 Hz, ArH), 6.76 (1 H, d, *J* = 2.2 Hz, ArH), 3.88 (3 H, s, CH₃), 3.63 (3 H, s, CH₃), 2.89 (2 H, app. t, *J* = 6.2 Hz, CH₂), 2.55 – 2.53 (2 H, m, CH₂), 2.23 (2 H, app. quin, *J* = 6.5 Hz, CH₂) ppm. **13C NMR** (100 MHz, CDCl₃): δ 193.6 (C), 156.9 (C), 151.3 (C), 138.3 (C), 122.2 (CH), 118.7 (C), 112.6 (C), 110.8 (CH), 93.8 (CH), 55.7 (CH₃), 37.7 (CH₂), 29.8 (CH₃), 23.3 (CH₂), 22.1 (CH₂) ppm. **LRMS (ESI)⁺:** 230 [M + H⁺]. **HRMS (ESI)⁺:** Found 230.1176, C₄₁H₂₄NO₂ [M+H⁺]⁺ requires 230.1176. Followed by title compound 20e' (71 mg, 0.310 mmol, 25%) as a yellow solid. **MP:** 195 – 196 °C. IR *ν* max (film, cm⁻¹): 2933 (br), 1644 (s), 1479 (m), 1262 (s), 1144 (m). **1H NMR** (400 MHz, CDCl₃): δ 7.21 (1 H, t, *J* = 8.0 Hz, ArH), 6.90 (1 H, br. d, *J* = 8.2 Hz, ArH), 6.71 (1 H, d, *J* = 8.0 Hz, ArH), 3.99 (3 H, s, CH₃), 3.64 (3 H, s, CH₃), 2.88 (2 H, app. t, *J* = 6.3 Hz, CH₂), 2.57 (2 H, dd, *J* = 7.1, 5.9 Hz, CH₂), 2.18 (2 H, app. quin, *J* = 6.4 Hz, CH₂) ppm. **13C NMR** (100 MHz, CDCl₃): δ 191.7 (C), 154.3 (C), 151.1 (C), 139.4 (C), 124.1 (CH), 114.3 (C), 113.1 (C), 103.7 (CH), 102.3 (CH), 56.0 (CH₃), 38.7 (CH₂), 30.0 (CH₃), 22.8 (CH₂), 22.6 (CH₂) ppm. **LRMS (ESI)⁺:** 230 [M + H⁺]. **HRMS (ESI)⁺:** Found 230.1177, C₄₁H₂₄NO₂ [M+H⁺]⁺ requires 230.1176.
6-Methoxy-9-methyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20f

Using flow photochemical set-up A: A solution of enaminoe 19f (239 mg, 1.03 mmol) and iodine (13 mg, 0.05 mmol, 5 mol%) in dry MeCN (52 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 20f (193 mg, 0.842 mmol, 81%) as an off-white solid.

Using flow photochemical set-up B: A solution of enaminoe 19f (134 mg, 0.585 mmol) in MeCN (58 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 20f (33 mg, 0.144 mmol, 25%) as an off-white solid. MP 151 – 152 °C (Et2O/petrol). Lit.10 148 – 150 °C. IR \( \nu_{\text{max}} \) (film, cm\(^{-1}\)): 3335 (br), 2944 (br), 1723 (m), 1636 (s), 1477 (s), 1120 (s), 1090 (s). \(^1\)H NMR (400 MHz, CDC\(_2\)) \( \delta \): 7.76 (1 H, d, \( J = 2.6 \) Hz, ArH), 7.15 (1 H, d, \( J = 8.8 \) Hz, ArH), 6.88 (1 H, dd, \( J = 8.9,2.5 \) Hz, ArH), 3.89 (1 H, s, CH\(_3\)), 3.64 (3 H, s, CH\(_3\)), 2.87 (2 H, app. q, \( J = 6.2 \) Hz, CH\(_2\)), 2.54 (2 H, dd, \( J = 7.3,5.6 \) Hz, CH\(_3\)), 2.22 (2 H, app. quin, \( J = 6.4 \) Hz, CH\(_2\)) ppm. \(^13\)C NMR (100 MHz, CDC\(_2\)) \( \delta \): 193.7 (C), 156.3 (C), 151.2 (C), 132.2 (C), 125.4 (C), 112.8 (CH), 112.4 (C), 109.8 (CH), 103.3 (CH), 55.9 (CH\(_3\)), 37.8 (CH\(_2\)), 29.9 (CH\(_3\)), 23.2 (CH\(_3\)), 22.2 (CH\(_3\)) ppm. LRMS (ESI\(^+\)): 252 [M + Na]\(^+\), 230 [M + H]\(^+\). Data consistent with literature values.10

9-Methyl-6-trifluoromethyl-1,2,3,9-tetrahydro-4H-carbazol-4-one, 20g

Using flow photochemical set-up B: A solution of enaminoe 19g (213 mg, 0.792 mmol) in MeCN (79 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 50% Et\(_2\)O in petrol) to afford the title compound 20g (77 mg, 0.288 mmol, 37%, purity ~95%) as a yellow solid. MP: 198 – 200 °C. IR \( \nu_{\text{max}} \) (film, cm\(^{-1}\)): 2944 (br), 1641 (s), 1458 (s), 1327 (s), 1109 (s). \(^1\)H NMR (400 MHz, CDC\(_2\)) \( \delta \): 8.52 (1 H, br s, ArH), 7.50 (1 H, dd with fine splitting, \( J = 8.6,1.3 \) Hz, ArH), 7.35 (1 H, d with fine splitting, \( J = 8.6 \) Hz, ArH), 3.73 (3 H, s, CH\(_3\)), 2.95 (2 H, app. t, \( J = 6.2 \) Hz, CH\(_2\)), 2.58 (2 H, dd, \( J = 7.4,5.6 \) Hz, CH\(_3\)), 2.27 (2 H, app. quin, \( J = 6.4 \) Hz, CH\(_2\)) ppm. \(^13\)C NMR (100 MHz, CDC\(_2\)) \( \delta \): 193.7 (C), 153.4 (C), 138.8 (C), 125.0 (q, \( J_{CF} = 271 \) Hz, CF\(_3\)), 124.8 (q, \( J_{CF} = 32 \) Hz, C), 124.2 (C), 119.8 (q, \( J_{CF} = 3.7 \) Hz, CH), 119.1 (q, \( J_{CF} = 3.9 \) Hz, CH), 113.0 (C), 100.3 (CH), 37.7 (CH\(_2\)), 30.1 (CH\(_3\)), 23.1 (CH\(_3\)), 22.1 (CH\(_3\)) ppm. \(^{19}\)F NMR (376 MHz, CDC\(_2\)) \( \delta \): –60.74 (3 F, s, CF\(_3\)) ppm. LRMS (ESI\(^+\)): 268 [M + H]\(^+\). HRMS (ESI\(^+\)): Found 268.0951, C\(_{14}\)H\(_{13}\)F\(_3\)NO\(_2\) [M+H]\(^+\) requires 268.0944.

S16
6-Chloro-9-methyl-1,2,3,9-tetrahydro-4H-carbazole-4-one. 20h

Using flow photochemical set-up B: A solution of emaminone 19h (200 mg, 0.851 mmol) in MeCN (61 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated in vacuo and purified by column chromatography (50 – 60% EtOAc in petrol) to afford the title compound 20h (96 mg, 0.412 mmol, 49%) as an off-white solid. MP 209 – 212 °C (EtOAc/petrol), Lit.\textsuperscript{10} 215 – 216 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.17 (dd, J = 1.8, 0.9 Hz, 1H, ArH), 7.15 (dd, J = 8.6, 1.8 Hz, 1H, ArH), 7.13 (dd, J = 8.6, 0.8 Hz, 1H, ArH), 3.63 (s, 3H, CH\textsubscript{3}), 2.86 (2H, app. t, J = 6.2 Hz, CH\textsubscript{2}), 2.50 (2H, dd, J = 7.4, 5.6 Hz, CH\textsubscript{2}), 2.23 – 2.15 (2H, m, CH\textsubscript{2}) ppm. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 193.5 (C), 152.6 (C), 135.8 (C), 128.5 (C), 125.7 (C), 123.2 (CH), 121.2 (CH), 112.3 (C), 110.0 (CH), 37.7 (CH\textsubscript{3}), 30.0 (CH\textsubscript{2}), 23.2 (CH\textsubscript{2}), 22.2 (CH\textsubscript{2}) ppm. LRMS (ESI\textsuperscript{+}): 234 [M+H\textsuperscript{+}]. Data consistent with literature values,\textsuperscript{10}
Methyl 9-methyl-4-oxo-2,3,4,9-tetrahydro-1H-carbazole-6-carboxylate, 20k

Using flow photochemical set-up B: A solution of enamino 19k (200 mg, 0.778 mmol) in MeCN (39 mL) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 20k (144 mg, 0.560 mmol, 73%) as a white solid. **MP** 212 – 214 °C (EtOAc/petrol), Lit.11 214 – 217 °C. **1H NMR** (400 MHz, CDCl₃): δ 8.88 (1H, dd, J = 1.7, 0.6 Hz, ArH), 7.94 (1H, dd, J = 8.7, 1.7 Hz, ArH), 7.24 (1H, dd, J = 8.6, 0.6 Hz, ArH), 3.93 (3H, s, CH₃), 3.66 (3H, s, CH₃), 2.89 (2H, t, J = app. 6.2 Hz, CH₂), 2.54 (1H, dd, J = 7.3, 5.6 Hz, CH₂), 2.28 – 2.19 (2H, m, CH₂) ppm. **13C NMR** (101 MHz, CDCl₃): δ 193.4 (C), 167.8 (C), 153.1 (C), 139.8 (C), 124.4 (C), 124.3 (C), 124.2 (C), 123.7 (C), 113.2 (C), 108.6 (CH), 51.9 (CH₃), 37.7 (CH₂), 30.0 (CH₂), 23.0 (CH₂), 22.1 (CH₃) ppm. LRMS (ESI⁺): 258 [M+H⁺]. Data consistent with literature values.11

5-Benzyl-5,6,7,8-tetrahydro-9H-1,3]dioxolo[4,5-b]carbazol-9-one, 20l

Using flow photochemical set-up B: A solution of enamino 19l (340 mg, 1.08 mmol) in MeCN (108 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 20l (234 mg, 0.734 mmol, 68%) as an off-white solid. **MP**: 175 – 176 °C. **IR** νmax (film, cm⁻¹): 2945 (br), 1617 (m), 1546 (s), 1491 (s), 1396 (m), 1323 (m), 1268 (m), 1189 (m). **1H NMR** (400 MHz, CDCl₃): δ 7.72 (1 H, d, J = 0.5 Hz, ArH), 7.35 – 7.26 (3 H, m, 3 × ArH), 7.05 – 7.00 (2 H, m, 2 × ArH), 6.69 (1 H, d, J = 0.5 Hz, ArH), 5.94 (2 H, s, CH₂), 5.23 (2 H, s, CH₂), 2.84 (2 H, app. t, J = 6.2 Hz, CH₂), 2.56 (2 H, dd, J = 7.3, 5.7 Hz, CH₂), 2.21 (2 H, app. quin, J = 6.5 Hz, CH₂) ppm. **13C NMR** (100 MHz, CDCl₃): δ 193.9 (C), 150.0 (C), 145.4 (C), 144.8 (C), 135.8 (C), 132.0 (C), 129.1 (2 × CH), 127.9 (CH), 126.0 (2 × CH), 118.9 (C), 113.3 (C), 109.4 (CH), 100.92 (CH), 91.2 (CH), 47.2 (CH₂), 37.8 (CH₂), 23.4 (CH₂), 22.3 (CH₃) ppm. LRMS (ESI⁺): 342 [M + Na⁺]; 320 [M + H⁺]. HRMS (ESI⁺): Found 320.1284, C₂₀H₁₇NO₂ [M+H⁺] requires 320.1281.

S18
1-(1,2-Dimethyl-1H-benzo[g]indol-3-yl)ethan-1-one, 20m

Using flow photochemical set-up A: A solution of enaminone 19m (330 mg, 1.33 mmol) in MeCN (133 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% Et₂O in petrol) to afford the title compound 20m (181 mg, 0.727 mmol, 56%) as an off-white solid. **MP**: 201 – 202 °C. **IR** ν_max (film, cm⁻¹): 2935 (br), 1636 (s), 1528 (m), 1458 (m), 1417 (m). **¹H NMR** (400 MHz, CDCl₃): δ 8.43 (1 H, d, J = 8.6 Hz, ArH), 8.40 (1 H, dd, J = 8.6, 0.7 Hz, ArH), 7.99 (1 H, app. dd, J = 8.1, 1.5 Hz, ArH), 7.69 (1 H, d, J = 8.6 Hz, ArH), 7.54 (1 H, ddd, J = 8.4, 7.0, 1.5 Hz, ArH), 7.47 (1 H, ddd, J = 8.1, 6.9, 1.2 Hz, ArH), 4.09 (3 H, s, CH₃), 2.93 (2 H, t, J = app. 6.2 Hz, CH₂), 2.60 (2 H, dd, J = 7.4, 5.6 Hz, CH₂), 2.27 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ 194.6 (C), 150.2 (C), 131.8 (C), 130.9 (C), 129.5 (CH), 125.7 (CH), 123.9 (CH), 123.8 (CH), 122.5 (C), 122.3 (C), 120.8 (CH), 120.4 (CH), 113.2 (C), 37.7 (CH₃), 34.7 (CH₃), 23.2 (CH₂), 22.4 (CH₃) ppm. **LRMS** (ESI⁺): 250 [M + H⁺]. **HRMS (ESI⁺)**: Found 250.1233, C₁₇H₁₈NO [M+H⁺] requires 250.1226.

4-Methyl-3,4-dihydrocyclopenta[b]indol-1(2H)-one, 22a

Using flow photochemical set-up B: A solution of enaminone 21a (214 mg, 1.14 mmol) in MeCN (114 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 60W UVC lamp for a residence time of 2 hour. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% Et₂O in petrol) to afford the title compound 22a (75 mg, 0.405 mmol, 35%) as a yellow solid. **MP**: 211 – 212 °C (Et₂O/petrol), Lit 24 214 – 216 °C. **IR** ν_max (film, cm⁻¹): 2922 (br), 1669 (s), 1476 (m), 1132 (m). **¹H NMR** (400 MHz, CDCl₃): δ 7.94 (1 H, dt, J = 7.5,
1.2 Hz, ArH), 7.33 – 7.25 (3 H, m, 3 × ArH), 3.74 (3 H, s, CH₃), 3.03 – 2.96 (4 H, m, 2 × CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 195.1 (C), 168.2 (C), 143.1 (C), 123.4 (CH), 122.3 (CH), 121.5 (C), 121.0 (CH), 119.4 (C), 109.9 (CH), 40.7 (CH₂), 30.6 (CH₃), 20.5 (CH₃) ppm. LRMS (ES⁺): 186 [M+H⁺]. Data consistent with literature values.²

5-Methyl-6,7,8,9-tetrahydropyrolo[3,2-b]indol-10(5H)-one, 22b
Using flow photochemical set-up A: A solution of enammine 21b (310 mg, 1.44 mmol) and iodine (18 mg, 0.07 mmol, 5 mol%) in dry MeCN (72 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 22b (170 mg, 0.798 mmol, 56%) as a yellow oil. IR νmax (film, cm⁻¹): 2932 (br), 1697 (m), 1606 (s), 1470 (s), 1409 (s), 1127 (m), 1094 (m). ¹H NMR (400 MHz, CDCl₃): δ 8.46 (1 H, m, ArH), 7.28 – 7.24 (3 H, m, 3 × ArH), 3.71 (3 H, s, CH₃), 3.08 (2 H, app. dd, J = 7.0, 5.5 Hz, CH₂), 2.83 – 2.80 (2 H, m, CH₂), 2.09 – 2.03 (2 H, m, CH₂), 1.97 – 1.91 (2 H, m, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.6 (C), 148.0 (C), 136.8 (C), 126.9 (C), 122.8 (CH), 122.4 (CH), 122.3 (CH), 115.2 (C), 108.8 (CH), 43.7 (CH₂), 29.9 (CH₂), 26.6 (CH₂), 25.0 (CH₂), 22.2 (CH₂) ppm. LRMS (ES⁺): 214 [M+H⁺]. HRMS (ES⁺): Found 214.1231, C₁₉H₂₂NO [M+H⁺] requires 214.1226.

4,5,6,7,10,11-Hexahydroazepino[3,2-j]carbazol-12(9H)-one, 22f
Using flow photochemical set-up B: A solution of enammine 21f (240 mg, 1.00 mmol) in MeCN (100 mL, 0.01 M) was segmented with bubbles of air then irradiated with a 60W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtOAc in petrol)
Using high-performance liquid chromatography (HPLC), a solution of 

\[ \text{H+)I} \] 119.4 (9.5, 5.3, 4.9, 3.9, 3.8, 3.0, 2.9, 2.7, 2.5, 2.2, 1.6, \text{ppm). LRM1 (ES-): 174 (M+H+). Data consistent with literature values.} \]
Using flow photochemical set-up A: A solution of enaminone 23b (160 mg, 0.847 mmol) in MeCN (420 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 24b (97 mg, 0.519 mmol, 61%) as a yellow solid. MP 108 – 109 °C (EtO/petrol), Lit.\textsuperscript{12b} 113 – 114 °C (EtOH). IR \textsuperscript{\textsubscript{\textnu}}max (film, cm\textsuperscript{-1}): 2924 (br), 1634 (s), 1511 (m), 1400 (s). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}); δ 7.98 (1 H, m, ArH), 7.36 (1 H, m, ArH), 7.30 – 7.27 (2 H, m, 2 \times ArH), 3.74 (3 H, s, CH\textsubscript{3}), 2.81 (3 H, s, CH\textsubscript{3}), 2.71 (3 H, s, CH\textsubscript{3}) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}); δ 194.8 (C), 145.5 (C), 136.7 (C), 126.3 (C), 122.1 (2 \times CH), 120.7 (CH), 114.1 (C), 109.6 (CH), 31.5 (CH\textsubscript{3}), 29.5 (CH\textsubscript{3}), 12.7 (CH\textsubscript{3}) ppm. LRMS (ESI\textsuperscript{+}): 188 [M + H]\textsuperscript{+}. Data consistent with literature values.\textsuperscript{12}

3-Acetyl-1-benzyl-2-methyldione, 24c

Using flow photochemical set-up A: A solution of enaminone 23c (130 mg, 0.491 mmol) in MeCN (250 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 24c (76 mg, 0.289 mmol, 58%) as a yellow solid. MP 100 – 101 °C (EtO/petrol), Lit.\textsuperscript{13b} 107 – 109 °C (MeOH). IR \textsuperscript{\textnu}max (film, cm\textsuperscript{-1}): 2922 (br), 1636 (s), 1515 (m), 1454 (m), 1406 (s). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}); δ 8.04 (1 H, m, ArH), 7.35 – 7.20 (6 H, m, 6 \times ArH), 7.02 – 6.98 (2 H, m, 2 \times ArH), 5.39 (2 H, s, CH\textsubscript{3}), 2.75 (3 H, s, CH\textsubscript{3}), 2.73 (3 H, s, CH\textsubscript{3}) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}); δ 194.8 (C), 144.9 (C), 136.5 (C), 136.1 (C), 129.0 (2 \times CH), 127.7 (CH), 126.4 (C), 125.9 (2 \times CH), 122.3 (CH), 122.1 (CH), 120.8 (CH), 114.7 (C), 110.0 (CH), 46.4 (CH\textsubscript{3}), 31.7 (CH\textsubscript{3}), 12.7 (CH\textsubscript{3}) ppm. LRMS (ESI\textsuperscript{+}): 264 [M + H]\textsuperscript{+}. Data consistent with literature values.\textsuperscript{13}
3-Acetyl-1-methyl-2-phenylindole, 24d

*Using flow photochemical set-up A:* A solution of enamino 23d (150 mg, 0.598 mmol) in MeCN (300 mL, 0.002 M) was irradiated with a 36W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (30 – 70% EtOAc in petrol) to afford the *title compound* 24d (100 mg, 0.402 mmol, 67%) as an off-white oil. **IR** {ν} (film, cm⁻¹): 3054 (br), 2970 (w), 1635 (s), 1345 (s). **¹H NMR** (400 MHz, CDCl₃): δ 8.51 (1 H, m, ArH), 7.58 – 7.55 (3 H, m, 3 × ArH), 7.45 – 7.43 (2 H, m, 2 × ArH), 7.38 – 7.34 (3 H, m, 3 × ArH), 3.52 (3 H, s, CH₃), 1.98 (3 H, s, CH₃) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ 194.6 (C), 146.5 (C), 136.6 (C), 132.2 (C), 130.2 (2 × CH), 129.7 (CH), 128.8 (2 × CH), 126.7 (C), 123.4 (CH), 122.81 (CH), 122.78 (CH), 115.9 (C), 109.4 (CH), 30.8 (CH₃), 30.1 (CH₃) ppm. **LRMS (ESI⁺):** 272 [M + Na⁺], 250 [M + H⁺]. Data consistent with literature values.¹²

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3-Benzoyl-1,2-dimethylindole, 24e

*Using flow photochemical set-up A:* A solution of 23e (401 mg, 1.60 mmol) in MeCN (800 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 40 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (60 – 100% DCM/petrol) to afford the *title compound* 24e (248 mg, 1.00 mmol, 63%) as an off-white solid. **IR** {ν} (film, cm⁻¹): 3056 (br), 1716 (s), 1597 (s), 1401 (s), 1228 (s). **¹H NMR** (400 MHz, CDCl₃): δ 7.78 – 7.75 (2 H, m, 2 × ArH), 7.56 (1 H, m, ArH), 7.48 – 7.44 (2 H, m, 2 × ArH), 7.32 (2 H, m, 2 × ArH), 7.22 (1 H, app. td, J = 7.6, 1.2 Hz, ArH), 7.08 (1 H, dd, J = 8.0, 7.1, 1.1 Hz, ArH), 3.76 (3 H, s, CH₃), 2.61 (3 H, s, CH₃) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ 192.9 (C), 144.7 (C), 141.6 (C), 136.5 (C), 132.4 (CH), 129.1 (2 × CH), 128.2 (2 × CH), 127.1 (C), 122.0 (CH), 121.4 (CH), 121.0 (CH), 113.6 (C), 109.1 (CH), 29.7 (CH₃), 12.5 (CH₃) ppm. **LRMS (ESI⁺):** 250 [M + H⁺]. Data consistent with literature values.¹⁴
3-Acetyl-1,2,5-trimethylindole, 2f

Using flow photochemical set-up A: A solution of the crude enaminoine 23f (195 mg, 0.961 mmol) in MeCN (480 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% Et2O in petrol) to afford the title compound 24f (122 mg, 0.607 mmol, 64%) as a yellow solid. IR νmax (film, cm⁻¹): 2919 (br), 1635 (s), 1511 (m), 1487 (m), 1402 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.77 (1 H, dt, J = 1.6, 0.8 Hz, ArH), 7.22 (1 H, d, J = 8.4 Hz, ArH), 7.09 (1 H, dd, J = 8.3, 1.6 Hz, ArH), 7.68 (3 H, s, CH₃), 2.76 (3 H, s, CH₃); 2.68 (3 H, s, CH₃). ²H NMR (100 MHz, CDCl₃): δ 194.6 (C), 145.0 (C), 135.0 (C), 131.3 (C), 126.5 (C), 123.3 (CH), 120.6 (CH), 113.8 (C), 109.1 (CH), 31.6 (CH₃), 29.5 (CH₃), 21.7 (CH₃), 12.7 (CH₃) ppm. LRMS (ESI⁺): 202 [M + H]⁺. Data consistent with literature values.¹²

3-Acetyl-1,2-dimethyl-5-trifluoromethylindole, 24g

Using flow photochemical set-up A: A solution of the crude enaminoine 23g (171 mg, 0.665 mmol) in MeCN (335 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% Et₂O in petrol) to afford the title compound 24g (80 mg, 0.314 mmol, 47%) as a yellow solid. MP: 141 – 142 °C. IR νmax (film, cm⁻¹): 3081 (br), 1630 (s), 1326 (s), 1140 (s), 1103 (s). ¹H NMR (400 MHz, CDCl₃): δ 8.30 (1 H, m, ArH), 7.20 (1 H, ddd, J = 8.6, 1.7, 0.7 Hz, ArH), 7.39 (1 H, br. d, J = 8.6 Hz, ArH), 3.75 (3 H, s, CH₃), 2.80 (3 H, s, CH₃), 2.69 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 194.1 (C), 146.5 (C), 137.9 (C), 129.2 (C), 127.8 (CF₃, JCF = 270 Hz), 125.8 (C), 124.2 (C, JCF = 32.3 Hz), 118.9 (CH, JCF = 3.2 Hz), 118.3 (CH, JCF = 3.9 Hz), 109.6 (CH), 31.6 (CH₃), 29.8 (CH₃), 12.7 (CH₃) ppm. ¹⁹F(H) NMR (376 MHz, CDCl₃): −60.71 (3 F, s, CF₃) ppm. LRMS (ESI⁺): 256 [M + H]⁺. HRMS (ESI⁺): Found 256.0948, C₁₇H₁₆F₃NO [M+H]⁺ requires 256.0944.
3-Acetyl-1,2-dimethyl-5-methoxyindole, 24h

Using flow photochemical set-up A: A solution of the crude enamnone 23h (187 mg, 0.854 mmol) in MeCN (427 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtO in petrol) to afford the title compound 24h (113 mg, 0.521 mmol, 61%) as an off-white solid. IR νmax (film, cm⁻¹): 2934 (br), 1629 (s), 1486 (s), 1404 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.53 (1 H, d, J = 2.3 Hz, ArH), 7.20 (1 H, d, J = 8.8 Hz, ArH), 6.89 (1 H, dd, J = 8.8, 2.5 Hz, ArH), 3.90 (3 H, s, CH₃), 3.66 (3 H, s, CH₃), 2.73 (3 H, s, CH₃), 2.64 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 194.1 (C), 155.8 (C), 145.0 (C), 131.7 (C), 127.1 (C), 114.1 (C), 111.1 (CH), 110.0 (CH), 103.9 (CH), 55.9 (CH₃), 31.4 (CH₃), 29.6 (CH₃), 12.8 (CH₃) ppm. LRMS (ESI⁺): 218 [M + H⁺]: Data consistent with literature values.¹⁵
3-Acetyl-1-methyl-1H-benzo[g]indole, 24i
Using flow photochemical set-up A: A solution of the crude enamino 23i (298 mg, 1.32 mmol) in MeCN (662 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtO in petrol) to afford the title compound 24i (203 mg, 0.910 mmol, 69%) as an off-white solid. **MP:** 161 °C (dec.). **IR** \(\nu_{\text{max}}\) (film, cm\(^{-1}\)): 3109 (br), 1639 (s), 1533 (m), 1359 (m), 1126 (m). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.52 (1 H, d, \(J = 8.8\) Hz, ArH), 8.42 (1 H, br d, \(J = 8.6\) Hz, ArH), 7.99 (1 H, app. dd, \(J = 8.0, 1.3\) Hz, ArH), 7.69 (1 H, d, \(J = 8.7\) Hz, ArH), 7.62 (1 H, s, CH), 7.57 (1 H, ddd, \(J = 8.4, 6.9, 1.5\) Hz, ArH), 7.49 (1 H, ddd, \(J = 8.1, 6.9, 1.2\) Hz, ArH), 4.30 (3 H, s, CH\(_3\)). 13C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 193.5 (C), 134.5 (CH), 131.8 (C), 131.0 (C), 129.3 (CH), 125.8 (CH), 124.2 (CH), 124.1 (C), 123.9 (CH), 122.7 (C), 121.4 (CH), 120.4 (CH), 117.1 (C), 39.3 (CH\(_3\)), 27.7 (CH\(_3\)) ppm. **LRMS** (ESI\(^+\)): 224 [M + H]\(^+\). **HRMS** (ESI\(^+\)): Found 224.1072, C\(_{16}\)H\(_{14}\)NO [M+H]\(^+\) requires 224.1070.

3-Acetyl-1,5-dimethylindole, 24j
Using flow photochemical set-up A: A solution of the crude enamino 23j (170 mg, 0.899 mmol) in MeCN (900 mL, 0.001 M) was irradiated with a 60W UVC lamp for a residence time of 60 min. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% EtO in petrol) to afford the title compound 24j (130 mg, 0.695 mmol, 78%) as a yellow solid. **IR** \(\nu_{\text{max}}\) (film, cm\(^{-1}\)): 2944 (br), 1635 (s), 1466 (s), 1388 (m). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.18 (1 H, app. br d, \(J = 1.6\) Hz, ArH), 7.66 (1 H, s, CH), 7.23 (1 H, d, \(J = 8.3\) Hz, ArH), 7.14 (1 H, d, \(J = 8.3, 1.7\) Hz, ArH), 3.82 (3 H, s, CH\(_3\)), 2.51 (3 H, s, CH\(_3\)), 2.50 (3 H, s, CH\(_3\)) ppm. **13C NMR** (100 MHz, CDCl\(_3\)): \(\delta\) 193.0 (C), 135.84 (C), 135.77 (CH), 132.2 (C), 126.4 (C), 124.8 (CH), 122.2 (CH), 116.5 (C), 109.2 (CH), 33.5 (CH\(_3\)), 27.5 (CH\(_3\)), 21.5 (CH\(_3\)) ppm. **LRMS** (ESI\(^+\)): 188 [M + H]\(^+\). Data consistent with literature values.\(^{12}\)
Methyl 1,2-dimethyl-1H-indole-3-carboxylate, 24k

Using flow photochemical set-up A: A solution of the crude ester 27k (217 mg, ~1.00 mmol) in MeCN (500 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated \textit{in vacuo} and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 28k (99 mg, 0.488 mmol, 46%, over 2 steps) as an off-white solid. \textbf{IR} \textit{v}_{\text{max}} (film, cm\textsuperscript{-1}): 2948 (br), 1689 (s), 1533 (m), 1437 (m), 1213 (s), 1159 (m), 1104 (m). \textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}): \textit{s} 8.11 (1 H, m, ArH), 7.31 (1 H, m, CH), 7.26 – 7.22 (2 H, m, 2 × ArH), 3.94 (3 H, s, CH\textsubscript{3}), 3.71 (3 H, s, CH\textsubscript{3}), 2.78 (3 H, s, CH\textsubscript{3}) ppm. \textbf{13C NMR} (100 MHz, CDCl\textsubscript{3}): \textit{s} 166.6 (C), 145.3 (C), 136.5 (C), 126.5 (C), 122.0 (CH), 121.6 (CH), 121.4 (CH), 109.0 (CH), 103.8 (CH), 50.7 (CH\textsubscript{3}), 29.6 (CH\textsubscript{3}), 11.9 (CH\textsubscript{3}) ppm. \textbf{LRMS} (ES\textsuperscript{+}): 204 [M + H]\textsuperscript{+}. Data consistent with literature values.\textsuperscript{2}

3-Formyl-1,2-dimethylindole, 24l

Using flow photochemical set-up A: A solution of enaminal 23l (201 mg, 1.15 mmol) in MeCN (574 mL, 0.002 M) was irradiated with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated \textit{in vacuo} and purified by column chromatography (40 – 70% EtOAc in petrol) to afford the title compound 24l (118 mg, 0.682 mmol, 59%) as a yellow oil. \textbf{IR} \textit{v}_{\text{max}} (film, cm\textsuperscript{-1}): 2965 (br), 1745 (m), 1648 (s), 1325 (s), 1035 (s). \textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}): \textit{s} 10.17 (1 H, s, CH\textsubscript{2}), 8.27 (1 H, m, ArH), 7.31 – 7.28 (3 H, m, 3 × ArH), 3.71 (3 H, s, CH\textsubscript{3}), 2.69 (3 H, s, CH\textsubscript{3}) ppm. \textbf{13C NMR} (100 MHz, CDCl\textsubscript{3}): \textit{s} 184.1 (CH), 147.6 (C), 137.0 (CH), 125.7 (C), 123.1 (CH), 122.8 (CH), 120.8 (C), 114.2 (C), 109.2 (CH), 29.6 (CH\textsubscript{3}), 10.6 (CH\textsubscript{3}) ppm. \textbf{LRMS} (ES\textsuperscript{+}): 174 [M + H]\textsuperscript{+}. Data consistent with literature values.\textsuperscript{16}
Dimethyl 1-methyl-1H-indole-2,3-dicarboxylate, 24m

*Using flow photochemical set-up A:* A solution of diester 23m (97 mg, 0.411 mmol) and acetic acid (10 drops) in MeCN (250 mL, 0.002 M) was with a 60W UVC lamp for a residence time of 20 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (10 – 30% EtOAc in petrol) to afford the title compound 24m (71 mg, 0.258 mmol, 63%) as a yellow solid. **IR** ν<sub>max</sub> (film, cm<sup>-1</sup>): 2981 (br), 1699 (s), 1531 (m), 1243 (s), 1209 (s), 1103 (s). **1H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.15 (1 H, d, J = 7.9, 1.1 Hz, ArH), 7.38 – 7.36 (2 H, m, 2 × ArH), 7.30 (1 H, m, ArH), 4.50 (2 H, q, J = 7.1 Hz, CH₂), 4.40 (2 H, q, J = 7.1 Hz, CH₂), 3.85 (3 H, s, CH₃), 1.44 (3 H, t, J = 7.2 Hz, CH₃), 1.42 (3 H, t, J = 7.2 Hz, CH₃) ppm. **13C NMR** (100 MHz, CDCl<sub>3</sub>): δ 164.1 (C), 162.8 (C), 136.7 (C), 135.0 (C), 125.4 (C), 124.3 (CH), 122.5 (CH), 122.3 (CH), 110.0 (CH), 108.0 (C), 62.3 (CH₂), 60.2 (CH₂), 31.3 (CH₃), 14.4 (CH₃), 14.0 (CH₃) ppm. **LRMS (ESI<sup>+</sup>):** 298 [M + Na]<sup>+</sup>, 276 [M + H]<sup>+</sup>. Data consistent with literature values.<sup>17</sup>

9-Methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one, 28a

*Using flow photochemical set-up A:* A solution of enamine 27a (262 mg, 1.32 mmol) and iodine (16.3 mg, 0.066 mmol, 5 mol%) in dry MeCN (262 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated *in vacuo* and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 30a (186 mg, 0.935 mmol, 71%) as an off-white solid. **MP** 95 – 96 °C (EtOAc/petrol), Lit.:<sup>18</sup> 95 – 97 °C. **IR** ν<sub>max</sub> (film, cm<sup>-1</sup>): 2927 (br), 1648 (s), 1470 (m), 1430 (m), 1410 (m), 1231 (m), 1158 (m), 1074 (m), 997 (s), 921 (s), 879 (s), 802 (s), 737 (s), 693 (s), 597 (s), 528 (s), 472 (s), 439 (s), 410 (s).
1186 (m). \textit{H NMR} (400 MHz, CDCl$_3$): $\delta$ 7.76 (1 H, dt, $J = 8.1, 0.9$ Hz, ArH), 7.42 (1 H, ddd, $J = 8.6, 6.7, 1.1$ Hz, ArH), 7.35 (1 H, dd, $J = 8.4, 0.5$ Hz, ArH), 7.35 (1 H, ddd, $J = 8.0, 6.9, 1.1$ Hz, ArH), 4.08 (3 H, s, CH$_3$), 3.03 (2 H, app. t, $J = 6.1$ Hz, CH$_2$), 2.66 (2 H, dd, $J = 7.3, 5.7$ Hz, CH$_2$), 2.23 (2 H, app. quin, $J = 6.5$ Hz, CH$_2$) ppm. \textit{13C NMR} (100 MHz, CDCl$_3$): $\delta$ 192.2 (C), 139.6 (C), 130.3 (C), 129.1 (C), 126.6 (CH), 124.6 (C), 121.2 (CH), 119.9 (CH), 110.2 (CH), 39.9 (CH$_2$), 31.4 (CH$_3$), 24.7 (CH$_2$), 21.8 (CH$_3$) ppm. LRMS (ESI$^+$): 200 [M + H]$^+$. Data consistent with literature values.$^{18}$

9-Benzyl-2,3,4,9-tetrahydro-1H-carbazol-1-one, 28b

Using flow photochemical set-up A: A solution of enaminone 27b (96 mg, 0.391 mmol) and iodine (5 mg, 0.02 mmol, 5 mol%) in dry MeCN (78 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 –40% EtOAc/petrol) to afford the title compound 28b (71 mg, 0.289 mmol, 73%) as a yellow solid. MP 107 – 108 °C (EtOAc/petrol), Lit.$^{19}$ 108 – 109 °C. IR $\nu_{\text{max}}$ (film, cm$^{-1}$): 2929 (br), 1652 (s), 1453 (m), 1262 (m). \textit{H NMR} (400 MHz, CDCl$_3$): $\delta$ 7.69 (1 H, dd, $J = 8.1, 1.0$ Hz, ArH), 7.40 –7.35 (2 H, m, 2 × ArH), 7.27 – 7.12 (6 H, m, 6 × ArH), 5.84 (2 H, s, CH$_3$), 3.07 (2 H, app. t, $J = 6.1$ Hz, CH$_2$), 2.67 (2 H, dd, $J = 7.3, 5.7$ Hz, CH$_2$), 2.26 (2 H, app. quin, $J = 6.3$ Hz, CH$_2$) ppm. \textit{13C NMR} (100 MHz, CDCl$_3$): $\delta$ 192.0 (C), 139.4 (C), 138.4 (C), 130.0 (C), 129.1 (C), 128.5 (2 × CH), 127.1 (CH), 126.9 (C), 126.7 (2 × CH), 125.1 (C), 121.4 (CH), 120.3 (CH), 110.9 (CH), 47.9 (CH$_2$), 40.0 (CH$_2$), 24.7 (CH$_2$), 21.9 (CH$_3$) ppm. LRMS (ESI$^+$): 246 [M + H]$^+$. Data consistent with literature values.$^{19}$

6-Methoxy-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one, 28c
Using flow photochemical set-up A: A solution of enammine 27c (296 mg, 1.28 mmol) and iodine (16.3 mg, 0.06 mmol, 5 mol%) in dry MeCN (64 mL, 0.02 M) under argon was irradiated with a 36W UVC lamp for a residence time of 30 min. The resulting solution was concentrated in vacuo and purified by column chromatography (20 – 40% EtOAc in petrol) to afford the title compound 28c (200 mg, 0.873 mmol, 66%) as a yellow solid. MP: 153 – 154 °C. IR νmax (film, cm⁻¹): 2938 (br), 1647 (s), 1493 (s), 1206 (s).

\(^1\)H NMR (400 MHz, CDCl₃): δ 7.25 (1 H, dd, J = 9.1, 0.5 Hz, ArH), 7.08 (1 H, dd, J = 9.1, 2.5 Hz, ArH), 7.01 (1 H, br. d, J = 2.3 Hz, ArH), 4.04 (3 H, s, CH₃), 3.88 (3 H, s, CH₃), 2.98 (2 H, app. t, J = 6.1 Hz, CH₂), 2.64 (2 H, dd, J = 7.4, 5.6 Hz, CH₂), 2.21 (2 H, app. quin, J = 6.5 Hz, CH₂) ppm. \(^1\)C NMR (100 MHz, CDCl₃): δ 192.1 (C), 154.2 (C), 135.3 (C), 130.7 (C), 128.2 (C), 124.6 (C), 118.3 (CH), 111.2 (CH), 101.0 (CH), 55.7 (CH₃), 39.9 (CH₃), 31.5 (CH₃), 24.7 (CH₂), 21.8 (CH₂) ppm. LRMS (ESI⁺): 230 [M + H⁺]. HRMS (ESI⁺): Found 230.1182, C₁₆H₁₆NO₂ [M+H⁺] requires 230.1176.

1,3-Dimethyl-2-(1-oxo-propyl)indole, 28d

Using flow photochemical set-up A: A solution of enammine 27d (200 mg, 1.00 mmol) in MeCN (500 mL) was irradiated with a 36W UVC lamp for a residence time of 30 min. The resultant solution was concentrated in vacuo and purified by column chromatography (5 – 40% EtOAc in hexanes) to afford the title compound 28d as a yellow solid (79 mg, 0.393 mmol, 39%). MP 110 – 111 °C (EtOAc/hexane), Lit.\(^\text{20}\) 113 – 114 °C. \(^1\)H NMR (400 MHz, CDCl₃): δ 7.69 (1H, dt, J = 8.2, 0.9 Hz, ArH), 7.41 – 7.34 (2H, m, 2 x ArH), 7.16 (1H, ddd, J = 8.0, 6.1, 1.8 Hz, ArH), 3.98 (3H, s, CH₃), 2.98 (2H, q, J = 7.2 Hz, CH₂), 2.65 (3H, s, CH₃), 1.27 (3H, t, J = 7.3 Hz, CH₃) ppm. \(^1\)C NMR (101 MHz, CDCl₃): δ 196.1 (C), 138.9 (C), 133.7 (C), 127.3 (C), 125.7 (CH), 120.8 (CH), 119.8 (CH), 118.4 (C), 110.1 (CH), 36.3 (CH₃), 32.6 (CH₃), 11.9 (CH₃), 8.4 (CH₃) ppm. LRMS (ESI⁺): 202 [M+H⁺]. Data consistent with literature values.\(^\text{20}\)
4. Preparation of Starting Materials

3-(Methylphenylmino)cyclohex-2-en-1-one, 5a

N-methylaniline (3.42 g, 32.0 mmol), 1,3-cyclohexanedicarboxylate 12 (3.58 g, 32.0 mmol) and pTSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 20% acetone/DCM) to afford the title compound 5a (5.15 g, 25.6 mmol, 80%) as a yellow solid. IR νmax (film, cm⁻¹): 2939 (br), 1609 (s), 1549 (s), 1489 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.38 (2 H, m, 2 × ArH), 7.32 (1 H, ddt, J = 8.2, 6.6, 1.2 Hz, ArH), 7.15 – 7.11 (2 H, m, 2 × ArH), 5.33 (1 H, s, CH), 3.24 (3 H, s, CH₃), 2.31 (2 H, d, J = 7.1, 6.0 Hz, CH₂), 2.21 (2 H, app. t, J = 6.2 Hz, CH₂), 1.89 (2 H, app. quin, J = 6.5 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.5 (C), 165.1 (C), 145.3 (C), 129.7 (2 × CH), 122.4 (CH), 127.1 (2 × CH), 100.5 (CH), 40.7 (CH₂), 36.0 (CH₃), 28.5 (CH₂), 22.5 (CH₂) ppm. LRMS (ESI⁺): 202 [M+H⁺]. Data consistent with literature values.²¹

4-(Methylphenylmido)-5,6-dihydropyridin-2(1H)-one, 16

N-methylaniline (1.00 mL, 9.23 mmol), piperidine-2,4-dione (1.02 g, 9.01 mmol) and pTSA (30 mg, 0.174 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (5 – 15% acetone/DCM) to afford the title compound 16 (1.47 g, 7.27 mmol, 81%) as a yellow solid. MP: 156 – 157 °C. IR νmax (film, cm⁻¹): 3174 (br), 2950 (br), 1628 (s), 1568 (s), 1475 (m), 1387 (m), 1136 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (2 H, t, J = 7.6 Hz, 2 × ArH), 7.26 (1 H, m, ArH), 7.09 (2 H, br d, J = 7.5 Hz, 2 × ArH), 5.90 (1 H, br s, NH), 4.93 (1 H, br s, CH), 3.29 (2 H, br t, J = 5.9 Hz, CH₂), 3.19 (3 H, s, CH₃), 2.24 (2 H, br t, J = 6.7 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 170.7 (C), 157.4 (C), 145.4 (C), 129.4 (2 × CH), 127.0 (2 × CH), 126.8 (CH), 91.3 (CH), 40.4 (CH₃), 39.4 (CH₂), 27.4 (CH₂) ppm. LRMS (ESI⁺): 405 [2M+H⁺], 203 [M+H⁺]. HRMS (ESI⁺): Found 203.1180, C₉H₁₂N₂O [M+H⁺] requires 203.1179.
tert-Butyl 4-(methyl(phenyl)amino)-6-oxo-3,6-dihydropyridine-1(2H)-carboxylate, 17

To a solution of 16 (514 mg, 2.54 mmol) in dry THF at −78 °C was added NaH (203 mg, 5.08 mmol). After warming to RT over 1 hour, Di-tert-butyl dicarbonate (742 mg, 3.30 mmol) was added. The resulting solution was heated to 40 °C for 22 h then cooled to RT and sat. NH₄Cl (14 mL) and Et₂O (30 mL) were added. The aqueous phase was separated and extracted with Et₂O (2 × 30 mL) then the organic phases were combined, dried over MgSO₄, concentrated in vacuo and purified by column chromatography (0 – 30% acetone in DCM) to afford the title compound 17 (420 mg, 1.39 mmol, 55%) as a red oil. **H NMR (400 MHz, CDCl₃):**  δ 7.43 – 7.37 (2H, m, 2 × ArH), 7.31 (1H, m, ArH), 7.12 – 7.09 (2H, m, 2 × ArH), 5.02 (1H, s, CH), 3.76 (2H, t, J = 6.3 Hz, CH₂), 3.23 (3H, s, CH₃), 2.8 (2H, t, J = 6.4 Hz, CH₂), 1.53 (9H, s, 3 × CH₃) ppm. **¹³C NMR (101 MHz, CDCl₃):** δ 166.2 (C), 159.1 (C), 152.9 (C), 144.9 (C), 129.7 (2 × CH), 127.1 (C), 127.0 (2 × CH), 93.1 (CH), 82.0 (C), 42.7 (CH₂), 40.6 (CH₃), 28.2 (3 × CH₂), 28.0 (CH₃) ppm. LRMS (ESI⁺): 303 [M+H⁺], 247 [M⁺-H2O⁺]. **HRMS (ESI⁺):** Found 325.1529, C₁₇H₂₂N₂NaO₃ [M+Na⁺] requires 325.1523.

3-(Ethybenzyl(phenyl)amino)cyclohex-2-en-1-one, 5b

N-Ethylaniline (1.26 mL, 10.0 mmol), 1,3-cyclohexanediol (1.12 g, 10.0 mmol) and pTSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 5b (1.74 g, 8.08 mmol, 81%) as a yellow solid. IR νmax (film, cm⁻¹): 2949 (br), 1603 (s), 1548 (s), 1256 (s), 1190 (s), 1132 (s). **H NMR (400 MHz, CDCl₃):**  δ 7.42 – 7.37 (2H, m, 2 × ArH), 7.31 (1H, m, ArH), 7.12 – 7.09 (2H, m, 2 × ArH), 5.33 (1H, s, CH), 3.62 (2H, q, J = 7.2, Hz, CH₂), 2.28 (2H, dd, J = 7.1, 6.0 Hz, CH₂), 2.16 (2H, app. t, J = 6.2 Hz, CH₂), 1.87 (2H, app. quin, J = 6.4 Hz, CH₂), 1.16 (3H, t, J = 7.2 Hz, CH₃) ppm. **¹³C NMR (100 MHz, CDCl₃):** δ 197.4 (C), 164.3 (C), 143.6 (C), 129.6 (2 × CH), 128.1 (2 × CH), 127.6 (CH), 99.7 (CH), 47.5 (CH₂), 35.9 (CH₃), 85.8 (CH₂), 22.4 (CH₃), 11.9 (CH₃) ppm. LRMS (ESI⁺): 431 [2M+H⁺], 216 [M+H⁺]. Data is consistent with literature values.¹
tert-Butyl (3-oxocyclohex-1-en-1-yl)(phenyl)carbamate, 5c
To a solution of 3-(phenylamino)cyclohex-2-en-1-one (730 mg, 3.90 mmol), di-tert-butyl dicarbonate (1275 mg, 5.85 mmol) in dry MeCN (20 mL) under argon was added DMAP (48 mg, 0.4 mmol). The reaction mixture was stirred at RT for 16 h. The resulting solution was concentrated in vacuo then purified by column chromatography (70 – 90% EtOAc/PetO) to afford the title compound 5c (671 mg, 3.03 mmol, 81%) as a off-white solid. IR ν_max (film, cm⁻¹): 2970 (br), 1716 (s), 1644 (s), 1582 (s), 1243 (s), 1152 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.36 (2 H, m, 2 × ArH), 7.31 (1 H, m, ArH), 7.12 – 7.08 (2 H, m, 2 × ArH), 5.42 (1 H, app. s, CH), 2.81 (2 H, td, J = 6.1, 0.7 Hz, CH₃), 2.35 (2 H, dd, J = 7.1, 6.1 Hz, CH₃), 2.02 (2 H, app. quin, J = 6.4 Hz, CH₃). 1.39 (9 H, s, 3 × CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 199.2 (C), 162.7 (C), 152.3 (C), 140.5 (C), 129.3 (2 × CH), 127.9 (2 × CH), 127.7 (CH), 116.7 (CH), 82.6 (C), 36.6 (CH₃), 29.5 (CH₃), 27.9 (3 × CH₃), 22.9 (CH₂) ppm. LRMS (ESI⁺): 288 [M+H]⁺: Data is consistent with literature values.²⁵

3-(Benzyl)(phenyl)amino)cyclohex-2-en-1-one, 5d
A solution of N-benzylaniline (916 mg, 5.00 mmol), 1,3-cyclohexadiene (561 mg, 5.00 mmol) and pTSA (5 mg) in toluene (50 mL) was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (5 – 30% acetone in DCM) to afford the title compound 5d (1.15 g, 4.14 mmol, 83%) as a yellow oil. IR ν_max (film, cm⁻¹): 2981 (br), 2360 (w), 1617 (m), 1558 (s), 1187 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.40 - 7.28 (5H, m, 5 × ArH) 7.27 – 7.12 (5H, m, 5 × ArH), 5.40 (1H, s, CH), 4.84 (2H, s, CH₂) 2.33 (2H, dd, J = 5.5, 1.3 Hz, CH₃), 2.30 (2H, dd, J = 6.0, 1.1 Hz, CH₃), 1.93 (2H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 197.7
3-(Ethyl(phenyl)amino)-5-methylcyclohex-2-en-1-one, 5e

A solution of N-ethylaniline (0.63 mL, 5.00 mmol), 5-methyl-1,3-cyclohexadiene (0.63 g, 5.00 mmol) and pTSA (5 mg) in toluene was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% acetone in DCM) to afford the title compound 5e (796 mg, 3.47 mmol, 69%) as a yellow solid. 

**MP** 104-105 °C. 
**IR** ν_max (film, cm⁻¹): 2954 (br), 1615 (m), 1548 (s), 1251 (m). ¹H NMR (400 MHz, CDCl₃): 5.746 – 7.40 (2H, m, 2 × ArH), 7.35 (1H, t, J = 7.5, 1.3 Hz, ArH), 7.12 (2H, d with fine splitting, J = 7.1 Hz, 2 × ArH), 5.34 (1H, s, CH), 3.72 – 3.56 (2H, m, CH₂), 2.37 (1H, ddd, J = 16.0, 3.8, 1.7 Hz, CHH), 2.19 – 2.09 (2H, m, CHH + CH), 2.00 (1H, dd, J = 15.8, 11.4 Hz, CHH), 1.91 (1H, dd, J = 17.6, 11.4 Hz, CHH), 1.18 (3H, t, J = 7.2 Hz, CH₃), 0.97 (3H, d, J = 6.4 Hz, CH₃) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 197.6 (C), 163.7 (C), 143.7 (C), 129.7 (2 × CH), 128.1 (2 × CH), 127.6 (CH), 99.6 (CH), 47.7 (CH₂), 44.4 (CH₂), 36.7 (CH₂), 29.9 (CH), 21.2 (CH₃), 11.9 (CH₃) ppm. **LRMS (ESI⁺):** 230 [M+H]⁺. 


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(C), 165.0 (C), 144.4 (C), 136.3 (C), 129.6 (2 × CH), 128.7 (2 × CH), 127.7 (2 × CH), 127.5 (CH), 127.4 (CH), 126.9 (2 × CH), 101.6 (CH), 56.7 (CH₃), 36.0 (CH₂), 28.6 (CH₂), 22.5 (CH₂) ppm. **LRMS (ESI⁺):** 278 [M+H]⁺. Data is consistent with literature values.²³
A solution of N-benzyllaniline (1.10 g, 6.00 mmol), 5-methyl-1,3-cyclohexadiene (631 mg, 5.00 mmol) and pTSA (5 mg) in toluene (50 mL) was heated at reflux for 18 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 50% acetone in DCM) to afford the title compound 5f (1.38 g, 4.74 mmol, 95%) as an orange oil. IR \( \nu_{\text{max}} \) (film, cm\(^{-1}\)): 2954 (br), 1622 (m), 1557 (s), 1233 (m), 701 (m). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.40 – 7.34 (2H, m, 2 × ArH), 7.34 – 7.24 (4H, m, 4 × ArH), 7.22 – 7.18 (2H, m, 2 × ArH), 7.16 – 7.11 (2H, m, 2 × ArH), 5.40 (1H, s, CH), 4.84 (2H, s, CH\(_2\)), 2.38 (1H, ddd, J = 16.0, 3.9, 1.2 Hz, CHH), 2.32 (1H, ddd, J = 16.3, 4.0, 1.2 Hz, CHH), 2.17 (1H, m, CH), 2.05 (1H, dd, J = 11.5, 10.6 Hz, CHH), 2.01 (1H, dd, J = 11.2, 9.9 Hz, CHH), 0.99 (3H, dd, J = 6.4 Hz, CH\(_3\)) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 197.6 (C), 164.3 (C), 144.4 (C), 136.2 (C), 129.6 (2 × CH), 128.7 (2 × CH), 127.7 (2 × CH), 127.5 (CH), 127.4 (CH), 126.9 (2 × CH), 101.3 (CH), 56.8 (CH\(_2\)), 44.3 (CH\(_2\)), 36.8 (CH\(_3\)), 29.9 (CH), 21.1 (CH\(_3\)) ppm. LRMS (ESI\(^+\)): 292 [M+H]\(^+\). HRMS (ESI\(^+\)): Found 292.1701, \( C_{20} H_{25} NO \) [M+H]\(^+\) requires 292.1696.

A solution of N-ethylaniline (0.63 mL, 5.00 mmol), 5-phenyl-1,3-cyclohexadiene (0.94 g, 5.00 mmol) and pTSA (5 mg) in toluene (70 mL) was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% acetone in DCM) to afford the title compound 5g (1.31 g, 4.50 mmol, 89%) as an off-white solid. IR \( \nu_{\text{max}} \) (film, cm\(^{-1}\)): 2977 (br), 1615 (m), 1550 (s), 1492 (m), 1453 (m), 1254 (m). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.40 (2H, ddd, J = 8.4, 7.2, 1.0 Hz, 2 × ArH), 7.33 – 7.28 (3H, m, 3 × ArH), 7.22 (1H, tt, J = 7.2, 1.3 Hz, ArH), 7.18 (2H, ddd, J = 7.8, 1.6 Hz, 2 × ArH), 7.12 (2H, dd, J = 7.8, 1.6 Hz, 2 × ArH), 5.43 (1H, s, CH), 3.76 – 3.58 (2H, m, CH\(_2\)), 3.27 (1H, m, CH), 2.60 – 2.54 (2H, m, CH\(_2\)), 2.42 (1H, ddd, J = 16.9, 11.1, 0.9 Hz, CHH), 2.37 (1H, dd, J = 16.9, 4.8 Hz, CHH), 1.21 (3H, t, J = 7.1 Hz, CH\(_3\)) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 196.6 (C), 163.3 (C), 143.5 (C), 143.4 (C), 129.8 (2 × CH), 128.7 (2 × CH), 128.0 (CH), 127.8 (2 × CH), 126.9 (CH), 126.8 (2 × CH), 99.7 (CH), 47.9 (CH\(_2\)), 43.1 (CH\(_3\)).
5-(Benzyl(phenyl)amino)-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one, 5h

A solution of N-benzylaniline (916 mg, 5.00 mmol), 5-phenyl-1,3-cyclohexadione (941 mg, 5.00 mmol) and pTSA (5 mg) in toluene (50 mL) was heated at reflux for 16 h. The resulting solution was concentrated in vacuo and purified by column chromatography (0 – 30% acetone in DCM) to afford the title compound 5h (1.70 g, 4.81 mmol, 96%) as an orange oil. \( \text{IR } \nu_{\text{max}} \text{ (film, } \text{cm}^{-1}) \): 2981 (br), 2359 (br), 1617 (m), 1550 (s), 1493 (m), 1236 (m), 757 (m), 698 (s). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.38 – 7.27 (7H, m, 7 \times \text{ArH}), 7.27 – 7.12 (8H, m, 8 \times \text{ArH}), 5.50 (1H, s, CH), 4.87 (2H, s, CH\(_2\)), 3.33 (1H, m, CH), 2.61 – 2.53 (4H, m, 2 \times \text{CH}_2) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 196.7 (C), 163.7 (C), 144.3 (C), 136.1 (C), 129.8 (C), 129.7 (2 \times \text{CH}), 128.7 (2 \times \text{CH}), 128.7 (2 \times \text{CH}), 127.6 (2 \times \text{CH}), 127.5 (CH), 126.9 (2 \times \text{CH}), 126.9 (CH), 126.8 (2 \times \text{CH}), 101.5 (CH), 57.0 (CH\(_2\)), 43.1 (CH\(_2\)), 40.7 (CH), 36.2 (CH\(_2\)) ppm. \( \text{LRMS (ESI}^+\) : 354 ((M+H)^+), 100%). \( \text{HRMS (ESI}^+\) : Found 354.1860. \( \text{C}_{29}\text{H}_{25}\text{NO} \) [M+H]^+ requires 354.1852.

6,6-Dimethyl-3-(methyl(phenyl)amino)cyclohex-2-en-1-one, 5i

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S36
N-methylaniline (0.96 mL, 8.87 mmol), 6,6-dimethyl-3-(methyl(phenyl)amino)cyclohex-2-en-1-one (1.035 g, 7.43 mmol) and pTSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 5i (1.35 g, 5.90 mmol, 80%) as a white solid. MP: 90 – 91 °C. IR νmax (film, cm⁻¹): 2924 (br), 1648 (m), 1546 (s), 1392 (m), 1191 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.36 (2 H, m, 2 × ArH), 7.29 (1 H, m, ArH), 7.14 – 7.10 (2 H, m, 2 × ArH), 5.18 (1 H, s, CH), 3.21 (3 H, s, CH₃), 2.22 (2 H, t, J = 6.3 Hz, CH₂), 1.71 (2 H, t, J = 6.4 Hz, CH₂), 1.10 (6 H, s, 2 × CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 202.5 (C), 163.1 (C), 145.4 (C), 129.6 (2 × CH), 127.3 (CH), 127.1 (2 × CH), 99.0 (CH), 40.6 (CH₃), 39.0 (C), 36.3 (CH₂), 25.5 (CH₂), 24.8 (2 × CH₃) ppm. LRMS (ESI⁺): 230 [M+H⁺], 252 [M+Na⁺]. HRMS (ESI⁺): Found 354.1860, C₁₃H₂₃NO [M+H⁺] requires 354.1539.

3-(Ethyl(phenyl)amino)-6,6-dimethylcyclohex-2-en-1-one, 5j

A solution of N-ethylaniline (1.26 mL, 10.0 mmol), 4,4-dimethyl-1,3-cyclohexadione (701 mg, 5.00 mmol) and pTSA (5 mg) in toluene (40 mL) was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% acetone in DCM) to afford the title compound 5j (1.10 g, 4.52 mmol, 90%) as a yellow oil. IR νmax (film, cm⁻¹): 2971 (br), 2359 (br), 1616 (w), 1558 (s), 1211 (m), 702 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.38 (2H, m, 2 × ArH), 7.34 (1H, m, ArH), 7.16 – 7.08 (2H, m, 2 × ArH), 5.26 (1H, s, CH), 3.64 (2H, q, J = 7.1 Hz, CH₂), 3.20 (2H, t, J = 6.3 Hz, CH₂), 1.72 (2H, t, J = 6.3 Hz, CH₂), 1.18 (2H, t, J = 7.2 Hz, CH₂), 1.12 (6H, s, 2 × CH₃) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 202.5 (C), 162.6 (C), 143.7 (C), 129.7 (2 × CH), 128.3 (2 × CH), 127.6 (CH), 98.3 (CH), 47.5 (CH₂), 39.0 (C), 36.3 (CH₂), 25.7 (CH₂), 24.9 (2 × CH₂), 12.1 (CH₂) ppm. LRMS (ESI⁺): 244 [M+H⁺]. HRMS (ESI⁺): Found 244.1702, C₁₃H₂₃NO [M+H⁺] requires 244.1696.

S37
3-(Benzyl(phenyl)amino)-6,6-dimethylcyclohex-2-en-1-one, 5k
A solution of N-benzylaniline (916 mg, 5.00 mmol), 4,4-dimethyl-1,3-cyclohexadiene (701 mg, 5.00 mmol) and pTSA (5 mg) in toluene (50 mL) was heated at reflux for 16 h. The resulting solution was concentrated in vacuo and purified by column chromatography (0 – 30% acetone in DCM) to afford the title compound 5k (1.23 g, 4.03 mmol, 80%) as a yellow solid. **MP** 95 – 98 °C. **IR** ν<sub>max</sub> (film, cm<sup>−1</sup>): 2980 (br), 1622 (m), 1559 (s), 1205 (m). **<sup>1</sup>H NMR** (400 MHz, CDCl₃): δ 7.39 – 7.27 (5H, m, 5 × ArH), 7.25 (1H, m, ArH), 7.23 – 7.19 (2H, m, 2 × ArH), 7.16 – 7.12 (2H, m, 2 × ArH), 5.29 (1H, s, CH), 4.84 (2H, s, CH₂) 2.35 (2H, t, J = 6.3 Hz, CH₂), 1.77 (2H, t, J = 6.3 Hz, CH₂), 1.12 (6H, s, 2 × CH₃) ppm. **<sup>13</sup>C NMR** (101 MHz, CDCl₃): δ 202.7 (C), 163.0 (C), 144.5 (C), 136.6 (C), 129.6 (2 × CH), 128.7 (2 × CH), 127.8 (2 × CH), 127.4 (CH), 126.9 (2 × CH), 100.1 (CH), 56.5 (CH₂), 39.1 (C), 36.1 (CH₂), 25.5 (CH), 24.6 (2 × CH₃) ppm. **LRMS (ESI<sup>+</sup>):** 306 [M+H]<sup>+</sup>. Data is consistent with literature values.²⁴

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5,5-Dimethyl-3-(methyl(phenyl)amino)cyclohex-2-en-1-one, 5l
N-methylaniline (0.93 mL, 8.60 mmol), 5,5-dimethylcyclohexane-1,3-dione (1.00 g, 7.14 mmol) and pTSA (50 mg, 0.291 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 5l (1.37 g, 6.03 mmol, 83%) as a yellow solid. **IR** ν<sub>max</sub> (film, cm<sup>−1</sup>): 2950 (br), 1615 (m), 1552 (s), 1394 (m). **<sup>1</sup>H NMR** (400 MHz, CDCl₃): δ 7.44 – 7.39 (2H, m, 2 × ArH), 7.32 (1H, m, ArH), 7.12 – 7.09 (2H, m, 2 × ArH), 5.34 (1H, s, CH), 3.24 (3H, s, CH₃), 2.17 (2H, s, CH₂), 2.06 (2H, s, CH₂), 0.99 (6H, s, 3 × CH₃) ppm. **<sup>13</sup>C NMR** (100 MHz, CDCl₃): δ 197.1 (C), 163.4 (C), 145.4 (C), 129.7 (2 × CH), 127.4 (CH), 127.2 (2 × CH), 99.4 (CH), 49.8 (CH₂), 42.1 (CH₂), 41.0 (CH₂), 33.1 (C), 28.3 (2 × CH₃) ppm. **LRMS (ESI<sup>+</sup>):** 230 [M+H]<sup>+</sup>. Data is consistent with literature values.²⁵
3-(Ethyl(phenyl)amino)-5,5-dimethylcyclohex-2-en-1-one

A solution of N-ethylaniline (1.89 mL, 15.00 mmol), 5,5-dimethyl-1,3-cyclohexadiene (701 mg, 5.00 mmol) and pTSA (5 mg) in toluene was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% acetone in DCM) to afford the title compound 5m (590 mg, 2.42 mmol, 49%) as an off-white solid. **MP** 116–119 °C. **IR** (film, cm⁻¹): 2957 (br.), 1541 (s), 1491 (m), 1252 (s), 1129 (m), 702 (m). **¹H NMR** (400 MHz, CDCl₃): δ 7.48 – 7.40 (2H, m, 2 × ArH), 7.36 (1H, m, ArH), 7.13 – 7.08 (2H, m, 2 × ArH), 5.37 (1H, s, CH), 3.66 (2H, q, J = 7.1 Hz, CH₂), 2.18 (2H, s, CH₂), 2.03 (2H, s, CH₂), 1.19 (3H, t, J = 7.1 Hz, CH₃), 1.00 (6H, s, 2 × CH₃) ppm. **¹³C NMR** (101 MHz, CDCl₃): δ 197.0 (C), 162.9 (C), 143.7 (C), 129.8 (2 × CH), 128.1 (2 × CH), 127.7 (CH), 98.8 (CH), 49.6 (CH₂), 47.8 (CH₂), 42.2 (CH₂), 33.2 (C), 28.3 (2 × CH₂), 12.0 (CH₃) ppm. **LRMS (ESI⁺):** 244 [M+H]⁺. Data is consistent with literature values.²⁶

3-(Benzyl(phenyl)amino)-5,5-dimethylcyclohex-2-en-1-one, 5n

A solution of N-benzylaniline (1.50 g, 8.19 mmol), dimedone (701 mg, 5.00 mmol) and pTSA (5 mg) in toluene (50 mL) was heated at reflux for 57 h. The resulting solution was concentrated in vacuo and purified by...
column chromatography (10 – 50% acetone in DCM) to afford the title compound 5n (953 mg, 3.12 mmol, 62%) as a yellow solid. MP 112-113 °C. IR ν\text{max} (film, cm\textsuperscript{-1}): 2957 (br), 2359 (br), 1622 (m), 1558 (s), 1492 (m), 1236 (m). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.40 – 7.35 (m, 2H, 2 × ArH), 7.34 – 7.25 (m, 3H, 3 × ArH), 7.26 – 7.20 (m, 3H, 3 × ArH), 7.15 – 7.11 (m, 2H, 2 × ArH), 5.41 (s, 1H, CH), 4.85 (s, 2H, CH\textsubscript{2}) 2.18 (s, 4H, 2 × CH\textsubscript{2}). 1.02 (s, 6H, 2 × CH\textsubscript{3}) ppm. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 197.2 (C), 163.1 (C), 144.5 (C), 136.3 (C), 129.7 (2 × CH), 128.7 (2 × CH), 127.5 (CH), 127.4 (CH), 126.8 (2 × CH), 100.8 (CH), 56.9 (CH\textsubscript{2}), 49.8 (CH\textsubscript{2}), 42.3 (CH\textsubscript{2}), 33.3 (C), 28.3 (2 × CH\textsubscript{2}) ppm. LRM\textsuperscript{S} (ES\textsuperscript{+}): 306 [M+H]\textsuperscript{+}. Data is consistent with literature values.\textsuperscript{27}

3-(Methyl(o-tolyl)amino)cyclohex-2-en-1-one, 19a
2-Methy-N-methylaniline (0.56 mL, 4.51 mmol), 1,3-cyclohexanedione (510 mg, 4.55 mmol) and pTSA (60 mg, 0.348 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19a (731 mg, 3.40 mmol, 76%) as a yellow oil. IR ν\text{max} (film, cm\textsuperscript{-1}): 2947 (br), 1615 (m), 1548 (s), 1490 (m), 1396 (m), 1322 (m), 1266 (m), 1188 (m). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.27 – 7.21 (3 H, m, 3 × ArH), 7.05 (1 H, m, ArH), 5.39 (1 H, s, CH), 3.14 (3 H, s, CH\textsubscript{3}), 2.30 (2 H, br t, J = 5.9 Hz, CH\textsubscript{2}), 2.18 (3 H, s, CH\textsubscript{3}), 2.18 – 2.02 (2 H, m, CH\textsubscript{2}), 1.90 – 1.87 (2 H, m, CH\textsubscript{2}) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 197.4 (C), 165.3 (C), 143.9 (C), 135.7 (C), 131.4 (CH), 128.2 (2 × CH), 127.8 (CH), 127.3 (CH), 99.2 (CH), 39.4 (CH\textsubscript{2}), 36.0 (CH\textsubscript{2}), 28.0 (CH\textsubscript{2}), 22.4 (CH\textsubscript{2}), 17.3 (CH\textsubscript{3}) ppm. LRM\textsuperscript{S} (ES\textsuperscript{+}): 238 [M+Na]\textsuperscript{+}, 216 [M+H]\textsuperscript{+}. Data is consistent with literature values.\textsuperscript{10}
3-(Methyl(m-tolyl)amino)cyclohex-2-en-1-one, 19b

3-Methy-N-methylaniline (1.12 mL, 8.86 mmol), 1,3-cyclohexanedione (898 mg, 8.02 mmol) and pTSA (60 mg, 0.349 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19b (1.187 g, 5.52 mmol, 69%) as a yellow oil. IR \( \nu_{\text{max}} \) (film, cm\(^{-1}\)): 2952 (br), 1605 (s), 1549 (s). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.26 (1 H, t, \( J = 7.6 \) Hz, ArH), 7.10 (1 H, app. br d, \( J = 7.6 \) Hz, ArH), 6.93 – 6.90 (2 H, m, 2 × ArH), 5.28 (1 H, s, CH), 3.20 (3 H, s, CH\(_3\)H), 2.35 (3 H, s, CH\(_3\)H), 2.28 (2 H, app. t, \( J = 6.1 \) Hz, CH\(_2\)), 2.20 (2 H, t, \( J = 6.2 \) Hz, CH\(_2\)), 2.49 (3 H, s, CH\(_3\)H), 1.87 (2 H, quin, \( J = 6.4 \) Hz, CH\(_2\)) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 197.4 (C), 165.0 (C), 145.2 (C), 139.7 (C), 129.3 (CH), 128.1 (CH), 127.6 (CH), 123.9 (CH), 100.2 (CH), 40.6 (CH\(_3\)), 36.0 (CH\(_3\)), 28.4 (CH\(_3\)), 22.4 (CH\(_3\)), 21.2 (CH\(_3\)) ppm. LRMS (ESI\(^+\)): 238 [M+Na\(^+\)], 216 [M+H\(^+\)]. HRMS (ESI\(^+\)): Found 216.1388, C\(_9\)H\(_8\)NO [M+H\(^+\)] requires 216.1383.

3-(Methyl(p-tolyl)amino)cyclohex-2-en-1-one, 19c

4-Methy-N-methylaniline (1.0 mL, 7.92 mmol), 1,3-cyclohexanedione (733 mg, 6.54 mmol) and pTSA (60 mg, 0.349 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19c (1.075 g, 5.00 mmol, 77%) as a yellow solid. IR \( \nu_{\text{max}} \) (film, cm\(^{-1}\)): 2940 (br), 1606 (s), 1559 (s), 1508 (s), 1370 (s). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.20 – 7.17 (2 H, m, 2 × ArH), 7.01 – 6.98 (2 H, m, 2 × ArH), 5.29 (1 H, s, CH), 3.20 (3 H, s, CH\(_3\)H), 2.35 (3 H, s, CH\(_3\)H), 2.28 (2 H, dd, \( J = 6.2 \), 6.4 Hz, CH\(_2\)), 2.19 (2 H, t, \( J = 6.2 \) Hz, CH\(_2\)), 2.24 (2 H, quin, \( J = 6.4 \) Hz, CH\(_2\)) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 197.4 (C), 165.2 (C), 142.7 (C), 137.3 (C), 130.2 (2 × CH), 126.8 (2 × CH), 100.1 (CH), 40.7 (CH\(_3\)), 36.0 (CH\(_3\)), 28.4 (CH\(_3\)), 22.4 (CH\(_3\)), 20.9 (CH\(_3\)) ppm. LRMS (ESI\(^+\)): 453 [2M+Na\(^+\)], 216 [M+H\(^+\)]. Data is consistent with literature values.\(^{21}\)
3-({2-Methoxyphenyl}(methyl)amino)cyclohex-2-en-1-one, 19d
2-Methoxy-N-methylaniline (956 mg, 6.98 mmol), 1,3-cyclohexanedione (782 mg, 6.98 mmol) and pTSA (60 mg, 0.349 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19d (1.27 g, 5.50 mmol, 79%) as a yellow oil. IR \( v_{\text{max}} \) (film, cm\(^{-1}\)): 2943 (br), 1615 (m), 1546 (s), 1496 (m), 1246 (m), 1186 (m). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.30 (1 H, ddd, \( J = 8.3, 7.3, 1.8 \) Hz, ArH), 7.08 (1 H, dd, \( J = 7.9, 1.8 \) Hz, ArH), 6.97 – 6.93 (2 H, m, 2 x ArH), 5.34 (1 H, br s, CH), 3.82 (1 H, s, CH\(_3\)), 3.13 (1 H, s, CH\(_3\)), 2.28 (2 H, dd, \( J = 7.1, 5.9 \) Hz, CH\(_2\)), 2.20 – 2.00 (2 H, br s, CH\(_2\)), 1.86 (2 H, br s, CH\(_2\)) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 197.4 (C), 166.1 (C), 155.2 (C), 133.5 (C), 128.1 (CH), 128.9 (CH), 120.9 (CH), 112.0 (CH), 99.4 (CH), 55.5 (CH\(_3\)), 39.7 (CH\(_3\)), 36.0 (CH\(_3\)), 27.6 (CH\(_2\)), 22.2 (CH\(_2\)) ppm. LRMS (ESI\(^+\)): 463 \([M+H]^+\); 232 \([M+H]^+\). HRMS (ESI\(^+\)): Found 232.1336, \( \text{C}_{10}\text{H}_{10}\text{NO}_2 \) [M+H] requires 232.1332.

3-({3-Methoxyphenyl}(methyl)amino)cyclohex-2-en-1-one, 19e
3-Methoxy-N-methylaniline (600 mg, 4.38 mmol), 1,3-cyclohexanedione (448 mg, 4.00 mmol) and pTSA (30 mg, 0.174 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19e (758 mg, 3.28 mmol, 82%) as a yellow oil. IR \( v_{\text{max}} \) (film, cm\(^{-1}\)): 2948 (br), 1613 (s), 1596 (s), 1550 (s), 1489 (s), 1247 (s), 1216 (s), 1186 (s). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.30
(1 H, t, J = 8.1 Hz, ArH), 6.85 (1 H, ddd, J = 8.4, 2.5, 0.9 Hz, ArH), 6.71 (1 H, ddd, J = 7.8, 2.0, 0.9 Hz, ArH), 6.66 (1 H, t, J = 2.2 Hz, ArH), 5.32 (1 H, s, CH3), 3.81 (3 H, s, CH3), 3.22 (3 H, s, CH3), 2.30 (2 H, app. dd, J = 7.0, 6.0 Hz, CH2), 2.24 (2 H, t, J = 6.2 Hz, CH2), 1.89 (2 H, quin, J = 6.4 Hz, CH2) ppm. 13C NMR (100 MHz, CDCl3): δ 197.5 (C), 165.0 (C), 160.5 (C), 146.4 (C), 130.3 (CH), 119.3 (CH), 113.0 (CH), 112.9 (CH), 100.4 (CH), 55.4 (CH3), 40.6 (CH2), 28.4 (CH2), 22.5 (CH2) ppm. LRMS (ESI+): 463 [2M+H]+, 254 [M+Na]+, 232 [M+H]+. HRMS (ESI+): Found 232.1339, C4H40NO2 [M+H]+ requires 232.1332.

3-((4-Methoxyphenyl)(methyl)amino)cyclohex-2-en-1-one, 19f
4-Methoxy-N-methylaniline (1.48 g, 10.8 mmol), 1,3-cyclohexanedione (1.00 g, 8.93 mmol) and pTSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19f (1.83 g, 7.92 mmol, 88%) as a yellow oil. IR νmax (film, cm⁻¹): 2939 (br), 1611 (s), 1551 (s), 1507 (s), 1238 (s), 1158 (s). 1H NMR (400 MHz, CDCl3): δ 7.03 – 6.99 (2 H, m, 2 x ArH), 7.89 – 6.85 (2 H, m, 2 x ArH), 5.24 (1 H, s, CH), 3.78 (3 H, s, CH3), 3.16 (3 H, s, CH3), 2.25 (2 H, dd, J = 7.2, 5.9 Hz, CH2), 2.16 (2 H, t, J = 6.2 Hz, CH2), 1.84 (2 H, quin, J = 6.5 Hz, CH2) ppm. 13C NMR (100 MHz, CDCl3): δ 197.2 (C), 165.4 (C), 158.2 (C), 138.0 (C), 128.0 (2 x CH), 114.6 (2 x CH), 99.9 (CH), 55.4 (CH3), 40.7 (CH2), 35.9 (CH2), 28.3 (CH2), 22.3 (CH2) ppm. LRMS (ESI+): 463 [2M+H]+, 232 [M+H]+. Data consistent with literature values.
3-(Methyl(4-trifluoromethylphenyl)amino)cyclohex-2-en-1-one, 19g
N-Methyl-4-(trifluoromethyl)aniline (1.00 g, 5.71 mmol), 1,3-cyclohexanedione (608 mg, 5.43 mmol) and pTSA (150 mg, 0.87 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19g (968 mg, 3.66 mmol, 67%) as an orange solid. MP: 60 – 61 °C. IR νmax (film, cm⁻¹): 2952 (br), 1607 (m), 1553 (s), 1320 (s), 1104 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.67 (2 H, dd, J = 8.4 Hz, 2 × ArH), 7.27 (2 H, d, J = 8.3 Hz, 2 × ArH), 5.34 (1 H, s, CH), 3.26 (3 H, s, CH₃), 2.32 (2 H, dd, J = 6.9, 6.1 Hz, CH₂), 2.24 (2 H, t, J = 6.1 Hz, CH₂), 1.92 (2 H, quin, J = 6.6 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.7 (C), 164.2 (C), 148.4 (C), 129.3 (q, JCF = 33 Hz, C), 127.5 (2 × CH), 126.8 (q, JCF = 3.7 Hz, 2 × CH), 123.6 (q, JCF = 272.2 Hz, CH), 101.9 (CH), 40.6 (CH₂), 36.0 (CH₂), 28.5 (CH₂), 22.5 (CH₂) ppm. ¹⁹F NMR (376 MHz, CDCl₃): –62.81 (3 F, s, CF₃) ppm. LRMS (ESI⁺): 292 [M+Na]⁺, 270 [M+H]⁺. HRMS (ESI⁺): Found 270.1100, C₁₈H₁₇F₂NO₂ [M+H]⁺ requires 270.1107.

3-(4-Chlorophenyl)(methyl)amino)cyclohex-2-en-1-one, 19h
A solution of 4-chloro-N-methylaniline (1.196 g, 8.45 mmol), 1,3-cyclohexadiene (901 mg, 8.04 mmol) and pTSA (20 mg) in toluene (100 mL) was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 30% acetone in DCM) to afford the title compound 19h (1.44 g, 6.11 mmol, 76%) as a white solid. MP 162–164 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.31 (2H, d, J = 8.8 Hz, 2 × ArH), 7.01 (2H, d, J = 8.8 Hz, 2 × ArH), 5.24 (1H, s, CH), 3.14 (3H, s, CH₃), 2.24 (2H, dd, J = 7.1, 6.0 Hz, CH₂), 2.14 (2H, app. t, J = 6.2 Hz, CH₂), 1.88 – 1.80 (2H, m, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 197.8 (C), 164.5 (C), 143.9 (C), 133.1 (C), 129.9 (2 × CH), 128.5 (2 × CH), 101.2 (CH), 40.7 (CH₂), 36.1 (CH₂), 28.5 (CH₂), 22.5 (CH₂) ppm. LRMS (ESI⁺): 236 [M[(Cl)+H]⁺]. Data is consistent with literature values.¹⁹
Methyl 4-(methyl(3-oxocyclohex-1-en-1-yl)amino)benzoate, 19k
A solution of methyl-4-(methylamino)benzoate (991 mg, 6.00 mmol), 1,3-cyclohexa-dione (611 mg, 5.00 mmol) and pTSA (10 mg) in toluene (50 mL) was heated at reflux for 17 h. The resulting solution was concentrated in vacuo and purified by column chromatography (10 – 50% acetone in DCM) to afford the title compound 19k (1.06 g, 4.09 mmol, 82%) as a yellow solid. **MP** 111–113 °C. **IR** ν_max (film, cm⁻¹): 2950 (w), 1719 (m), 1573 (s), 1273 (m). ¹H NMR (400 MHz, CDCl₃): δ 8.09 (2H, d, J = 8.7 Hz, 2 × ArH), 7.22 (2H, d, J = 8.7 Hz, 2 × ArH), 5.37 (1H, s, CH), 3.95 (3H, s, CH₃), 3.28 (3H, s, CH₃), 2.34 (2H, dd, J = 7.0, 6.0 Hz, CH₂), 2.26 (2H, t, J = 6.2 Hz, CH₂), 1.92 (2H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 197.8 (C), 166.1 (C), 164.3 (C), 149.3 (C), 131.1 (2 × CH), 128.3 (C), 126.9 (2 × CH), 101.9 (CH), 52.4 (CH₂), 40.7 (CH₃), 36.1 (CH₂), 28.6 (CH₃), 22.6 (CH₃) ppm. **LRMS** (ESI⁺): Found 260.1285, C₂₃H₂₃NO₃ [M+H]⁺ requires 260.1281.

3-(Benzo[d][1,3]dioxol-5-yl(phenyl)amino)cyclohex-2-en-1-one, 19l
N-Benzylbenzo[d][1,3]dioxol-5-amine (787 mg, 3.47 mmol), 1,3-cyclohexanedione (350 mg, 3.13 mmol) and pTSA (50 mg, 0.290 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19l (802 mg, 2.50 mmol, 81%) as an off-white oil. **IR** ν_max (film, cm⁻¹): 3391 (br), 2962 (br), 1607 (m), 1546 (s), 1481 (s), 1235 (m), 1183 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.30 – 7.16 (5 H, m, 5 × ArH), 6.70 (1 H, d, J = 8.0 Hz, ArH), 6.57 – 6.54 (2 H, m, 2 × ArH), 5.93 (2 H, s, CH₂), 5.33 (1 H, s, CH), 4.74 (2 H, s, CH₂), 2.31 (2 H, t, J = 6.2 Hz, CH₂), 2.26 (2 H, t, J = 6.5 Hz, CH₂), 1.89 (2 H, app. quin, J = 6.1 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.4 (C), 165.2 (C), 148.1 (C), 146.7 (C), 137.9 (C), 136.1 (C), 128.5 (2 × CH), 127.3 (CH), 126.8 (2 × CH), 126.9 (C), 126.9 (2 × CH), 101.9 (CH), 52.4 (CH₂), 40.7 (CH₃), 36.1 (CH₂), 28.6 (CH₃), 22.6 (CH₃) ppm. **LRMS** (ESI⁺): Found 260.1285, C₂₃H₂₃NO₃ [M+H]⁺ requires 260.1281.
121.0 (CH), 108.6 (CH), 108.3 (CH), 101.6 (CH₂), 101.1 (CH), 56.2 (CH₂), 35.8 (CH₂), 28.2 (CH₂), 22.3 (CH₃) ppm. LRMS (ESI⁺): 665 [2M+Na]⁺, 344 [M+Na]⁺, 322 [M+H]⁺. HRMS (ESI⁺): Found 322.1438, C₂₉H₂₆NO₃ [M+H]⁺ requires 322.1444.

3-(Methyl(naphthalen-2-yl)amino)cyclohex-2-en-1-one, 19m
N-Methyl(naphthalen-1-amine (1.07 g, 6.81 mmol), 1,3-cyclohexanedione (692 mg, 6.18 mmol) and pTSA (50 mg, 0.290 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 19m (1.16 g, 4.62 mmol, 75%) as an off-white oil. IR νmax (film, cm⁻¹): 2946 (br), 1615 (m), 1549 (s), 1396 (m), 1322 (m), 1190 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.93 (1 H, m, ArH), 7.86 (1 H, d, J = 8.2 Hz, ArH), 7.69 (1 H, m, ArH), 7.59 – 7.53 (2 H, m, 2 × ArH), 7.49 (1 H, dd, J = 8.3, 7.3 Hz, ArH), 7.31 (1 H, dd, J = 7.2, 1.1 Hz, ArH), 5.54 (1 H, s, CH), 3.31 (3 H, s, CH₃), 2.30 (2 H, t, J = 6.5 Hz, CH₂), 2.17 (1 H, br, CHH), 1.89 – 1.79 (3 H, m, CH₃ + CHH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.1 (C), 165.4 (C), 141.1 (C), 134.2 (C), 130.1 (C), 128.3 (CH), 128.1 (CH), 127.1 (CH), 126.4 (CH), 125.4 (CH), 125.0 (CH), 121.8 (CH), 99.1 (CH), 40.1 (CH₂), 35.7 (CH₂), 27.4 (CH₂), 22.0 (CH₃) ppm. LRMS (ESI⁺): 525 [2M+Na]⁺, 503 [M+H]⁺, 274 [M+Na]⁺, 252 [M+H]⁺. HRMS (ESI⁺): Found 252.1383, C₁₂H₁₃NO [M+H]⁺ requires 252.1389.

3-(Methyl(phenyl)amino)cyclopent-2-en-1-one, 21a
N-Methylaniline (1.16 mL, 10.7 mmol), 1,3-cyclopentanedione (960 mg, 9.80 mmol) and pTSA (30 mg, 0.174 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The
resulting solution was concentrated in vacuo then purified by column chromatography (10 – 20% acetone/DCM) to afford the title compound 21a (1.42 g, 7.59 mmol, 78%) as a yellow solid. IR (film, cm⁻¹): 3050 (br), 2924 (br), 1648 (s), 1541 (s), 1191 (m).  

³¹H NMR (400 MHz, CDCl₃): δ 7.49 – 7.44 (2 H, m, 2 × ArH), 7.37 (1 H, m, ArH), 7.27 – 7.24 (2 H, m, 2 × ArH), 5.17 (1 H, s, CH), 3.39 (3 H, br s, CH₃), 2.55 (2 H, br s, CH₂), 2.44 – 2.42 (2 H, m, CH₂) ppm. ³¹C NMR (100 MHz, CDCl₃): δ 204.0 (C), 177.0 (C), 144.6 (C), 129.5 (2 × CH), 127.4 (CH), 126.0 (2 × CH), 102.1 (CH), 41.0 (CH₃), 34.2 (CH₃), 28.1 (CH₂) ppm. LRMS (ESI⁺): 188 [M+H]⁺. Data is consistent with literature values.²⁸

3-(Methyl(phenyl)amino)cyclohept-2-en-1-one, 21b
N-Methylaniline (1.00 mL, 9.22 mmol), 1,3-cycloheptanedicarbonyl (0.88 mL, 7.68 mmol) and pTSA (150 mg, 0.87 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 21b (1.10 g, 5.12 mmol, 66%) as a yellow oil. IR (film, cm⁻¹): 2949 (br), 1602 (m), 1546 (s), 1257 (m), 1199 (m). ³¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.36 (2 H, m, 2 × ArH), 7.28 (1 H, m, ArH), 7.11 – 7.08 (2 H, m, 2 × ArH), 5.41 (1 H, s, CH₃), 3.20 (3 H, s, CH₃), 2.57 – 2.54 (2 H, m, CH₂), 2.42 – 2.39 (2 H, m, CH₂), 1.83 – 1.77 (2 H, m, CH₂), 1.72 – 1.65 (2 H, m, CH₂) ppm. ³¹C NMR (100 MHz, CDCl₃): δ 202.0 (C), 163.8 (C), 146.3 (C), 129.6 (2 × CH), 127.0 (3 × CH), 105.3 (CH), 42.0 (CH₃), 40.5 (CH₂), 29.4 (CH₂), 24.0 (CH₂), 21.1 (CH₂) ppm. LRMS (ESI⁺): 238 [M+Na]⁺, 216 [M+H]⁺. HRMS (ESI⁺): Found 216.1383, C₁₁H₁₈NO [M+H]⁺ requires 216.1388.
3-(Indolin-1-yl)cyclohex-2-en-1-one, 21d
Indoline (1.2 mL, 10.7 mmol), 1,3-cyclohexanedione (1.14 g, 10.2 mmol) and pTSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 21f (1.85 g, 8.70 mmol, 81%) as a brown solid. **MP:** 81 – 82 °C. **IR** νmax (film, cm⁻¹): 2942 (br), 1617 (s), 1541 (s), 1460 (s), 1254 (s). **¹H NMR** (400 MHz, CDCl₃): δ 7.20 (1 H, d, J = 7.3, 1.1, 0.98 Hz, ArH), 7.17 – 7.10 (2 H, m, 2 × ArH), 6.94 (1 H, td, J = 7.2, 1.5 Hz, ArH), 5.43 (1 H, s, CH), 3.89 (2 H, t, J = 8.3 Hz, CH₂), 3.14 (2 H, t, J = 8.1 Hz, CH₂), 2.86 (2 H, t, J = 6.2 Hz, CH₂), 2.39 (2 H, dd, J = 7.2, 5.9 Hz, CH₂), 2.08 (2 H, quin, J = 6.7 Hz, CH₂) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ 197.5 (C), 160.9 (C), 143.5 (C), 133.5 (C), 127.2 (CH), 125.6 (CH), 122.5 (CH), 114.3 (CH), 103.6 (CH), 51.1 (CH₂), 28.7 (CH₂), 27.5 (CH), 23.0 (CH₂) ppm. **LRMS (ESI⁺):** 236 [M+Na⁺], 214 [M+H⁺]. **HRMS** (ESI⁺): Found 214.1226, C₉H₁₀NO [M+H⁺] requires 214.1231.

![NMR spectrum of 21d](image)

3-(3,4-Dihydroquinolin-1(2H)-yl)cyclohex-2-en-1-one, 21e
1,2,3,4-tetrahydroquinoline (1.2 mL, 9.56 mmol), 1,3-cyclohexanedione (1020 mg, 9.11 mmol) and pTSA (150 mg, 1.00 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 21e (1.99 g, 8.78 mmol, 92%) as a yellow oil. **IR** νmax (film, cm⁻¹): 2946 (br), 1610 (m), 1542 (s), 1487 (s), 1181 (s). **¹H NMR** (400 MHz, CDCl₃): δ 7.16 – 7.13 (2 H, m, 2 × ArH), 7.05 (1 H, m, ArH), 6.99 (1 H, m, ArH), 5.53 (1 H, s, CH), 3.55 (2 H, t, J = 6.6 Hz, CH₂), 2.65 (2 H, t, J = 6.2 Hz, CH₂), 2.56 (2 H, t, J = 6.0 Hz, CH₂), 2.37 (2 H, dd, J = 6.9, 6.1 Hz, CH₂), 1.99 – 1.93 (4 H, m, 2 × CH₂) ppm. **¹³C NMR** (100 MHz, CDCl₃): δ 197.9 (C), 184.6 (C), 139.1 (C), 134.4 (C), 128.1 (CH), 124.5 (CH), 124.4 (CH), 104.2 (CH), 47.4 (CH₂), 36.5 (CH₂), 29.3 (CH₂), 27.0 (CH₂), 24.6 (CH₂), 23.3 (CH₂) ppm. **LRMS (ESI⁺):** 250 [M+Na⁺], 228 [M+H⁺]. **HRMS** (ESI⁺): Found 228.1389, C₁₉H₁₅NO [M+H⁺] requires 228.1383.

![NMR spectrum of 21e](image)
3-(2,3,4,5-Tetrahydro-1H-benzo[b]azepin-1-yl)cyclohex-2-en-1-one, 21f
2,3,4,5-Tetrahydro-1H-benzo[b]azepine (939 mg, 6.39 mmol), 1,3-cyclohexanedione (680 mg, 6.07 mmol) and pTSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 30% acetone/DCM) to afford the title compound 21f (1.23 g, 5.10 mmol, 84%) as a yellow oil. IR νmax (film, cm⁻¹): 2940 (br), 1615 (m), 1541 (s), 1488 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.22 (3 H, br s, 3 × ArH), 7.06 (1 H, m, ArH), 5.45 (1 H, br s, CH), 4.06 (1 H, br, CH₂H), 3.04 (1 H, br, CHH), 2.21 – 2.62 (2 H, m, CH₂), 2.40 – 2.27 (3 H, m, CH₂ + CHH), 2.03 – 1.65 (6 H, m, 3 × CH₃), 1.43 (1 H, br s, CHH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 197.5 (C), 163.0 (C), 143.9 (C), 140.5 (C), 130.1 (CH), 127.9 (CH), 127.5 (CH), 127.1 (CH), 98.4 (CH), 50.1 (CH₂), 36.0 (CH₃), 33.8 (CH₂), 28.5 (CH₂), 26.4 (CH₂), 26.1 (CH₃), 22.4 (CH₂) ppm. LRMS (ES⁺): 264 [M+Na⁺], 242 [M+H⁺]. HRMS (ES⁺): Found 242.1539, C₁₉H₂₄NO [M+H⁺] requires 242.1546.

(E)-4-(Methyl(phenyl)amino)but-3-en-2-one, 23a
A solution of 3-butyn-2-one (0.94 mL, 12.02 mmol) in EtOH (10 mL) was added N-methylaniline (1.08 mL, 9.98 mmol). After 16 h at RT the resulting solution was concentrated in vacuo then purified by column chromatography (30 – 60% EtOAc/petrol) to afford the title compound 23a (1.63 g, 0.95 mmol, 95%) as a yellow oil. IR νmax (film, cm⁻¹): 3465 (br), 3040 (br), 1544 (s), 1494 (s), 1346 (m), 1251 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.87 (1 H, d, J = 13.2 Hz, =CH), 7.37 – 7.31 (2 H, m, 2 × ArH), 7.15 – 7.11 (3 H, m, 3 × ArH), 5.40 (1 H, d, J = 13.2 Hz, =CH), 3.25 (3 H, s, CH₃), 2.17 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 196.1 (C), 148.2 (CH), 146.3 (C), 129.4 (2 × CH), 124.6 (2 × CH), 120.2 (CH), 101.7 (CH), 36.8 (CH₃), 28.1 (CH₃) ppm. LRMS (EI): 175 (75%, M⁺), 160 (100%, [M-Me⁺]), 132 (90%), 117 (73%). Data is consistent with literature values.²⁹
(E)-4-(Methyl(phenyl)amino)pent-3-en-2-one, 23b

N-Methylaniline (1.19 mL, 11.0 mmol), 2,4-pentanedione (1.02 mL, 9.95 mmol) and pTSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 40% Et₂O/petrol) to afford the title compound 23b (1.27 g, 6.72 mmol, 67%) as a yellow oil. IR (film, cm⁻¹): 3409 (br), 2934 (br), 1604 (s), 1508 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.38 (2 H, m, 2 × ArH), 7.30 (1 H, m, ArH), 7.11 (1 H, m, ArH), 5.29 (1 H, s, CH), 3.24 (3 H, s, CH₃), 2.30 (3 H, s, CH₃). 13C NMR (100 MHz, CDCl₃): δ 195.3 (C), 160.7 (C), 145.9 (C), 129.5 (2 × CH), 127.13 (2 × CH), 127.07 (CH), 97.5 (CH), 41.0 (CH₂), 31.8 (CH₃), 18.0 (CH₃) ppm. LRMS (ESI⁺): 212 [M+Na]⁺, 190 [M+H]⁺.

(E)-4-(Benzy(phenyl)amino)pent-3-en-2-one, 23c

A solution of N-benzylaniline (1.83 g, 10.00 mmol), 2,4-pentanedione (1.23 mL, 12.00 mmol) and pTSA (10 mg) in toluene (100 mL) were heated at reflux under a soxhlet filled with 4Å molecular sieves for 40 h then cooled to RT. The resulting solution was concentrated in vacuo and purified by column chromatography (0 to 20%
EtOAc in hexanes) to give the title compound 23c (1.12 g, 4.22 mmol, 42%) as a yellow solid. IR ν_max (film, cm⁻¹): 3030 (br), 1526 (s), 1490 (m), 1417 (m), 1176 (m), 698 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.31 (4H, m, 4 × ArH), 7.30 – 7.22 (4H, m, 4 × ArH), 7.17 – 7.12 (2H, m, 2 × ArH), 5.35 (1H, s, CH), 4.87 (2H, s, CH₂), 2.42 (3H, s, CH₃), 2.01 (3H, s, CH₃) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 195.4 (C), 160.3 (C), 144.7 (C), 136.4 (C), 129.3 (2 × CH), 128.3 (2 × CH), 127.4 (2 × CH), 127.0 (CH), 126.9 (CH), 126.4 (2 × CH), 98.5 (CH), 86.4 (CH₂), 31.7 (CH₃), 17.6 (CH₃) ppm. LRMS (EI): 265 (33%, M⁺), 248 (77%), 222 (70%), 118 (80%), 91 (100%). HRMS (EI): Found 265.1464, C₁₂H₁₃NO [M⁺] requires 265.1461.

*(E)-4-(Methyl(phenyl)amino)-4-phenylbut-3-en-2-one, 23d*

To a solution of 4-phenylbut-3-yn-2-one (0.50 mL, 3.44 mmol) in EtOH (10 mL) was added N-methylaniline (0.44 mL, 3.5 mmol). After 16 h at RT, the resulting solution was concentrated in vacuo then purified by column chromatography (40 – 50% EtOAc/petrol) to afford the title compound 23d (803 mg, 3.2 mmol, 91%) as a yellow oil. IR ν_max (film, cm⁻¹): 3058 (br), 1527 (s), 1487 (s), 1386 (m), 1258 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.27 – 7.20 (7 H, m, 7 × ArH), 7.13 – 6.97 (3 H, m, 3 × ArH), 5.49 (1 H, br s, CH), 3.28 (3 H, br s, CH₃), 1.71 (3 H, br s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 196.8 (C), 161.6 (C), 146.3 (C), 136.1 (C), 129.7 (2 × CH), 129.1 (CH), 128.8 (CH), 128.59 (CH), 128.1 (2 × CH), 127.0 (CH), 125.9 (CH), 105.4 (CH), 50.0 (CH₂), 29.9 (CH₃) ppm. LRMS (ESI⁺): 274 [M+Na⁺], 252 [M+H⁺]. HRMS (ESI⁺): Found 252.1389, C₁₁H₁₄NO [M+H⁺] requires 252.1383.
(E)-3-(Methylphenylamino)-1-phenylbut-2-en-1-one, 23e
N-methylaniline (1.63 mL, 15.0 mmol), 1-phenyl-1,3-butanedione (2.44 g, 15.0 mmol) and pTSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet extractor filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (20 – 50 % EtOAc/petrol) to afford the title compound 23e (2.45 g, 9.76 mmol, 65%) as a yellow oil contaminated with some impurities due to hydrolysis on column chromatography. IR νmax (film, cm⁻¹): 2923 (br), 1526 (s), 1215 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.89 – 7.56 (2 H, m, 2 × ArH), 7.47 – 7.39 (5 H, m, 5 × ArH), 7.33 (1 H, m, ArH), 7.18 – 7.15 (2 H, m, 2 × ArH), 5.94 (1 H, s, CH), 3.36 (3 H, s, CH₃), 2.27 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 188.8 (C), 162.8 (C), 145.9 (C), 142.5 (C), 130.5 (2 × CH), 129.7 (2 × CH), 128.0 (2 × CH), 127.3 (2 × CH), 127.1 (2 × CH), 94.7 (CH), 41.2 (CH₃), 18.7 (CH₃) ppm. LRMS (EI): 251 (M⁺, 20%), 234 (50%), 146 (100%), 106 (60%). HRMS (EI): Found 251.1299, C₁₁H₁₇NO M⁺ requires 251.1305.

(E)-4-(Methyl(p-toly)amino)pent-3-en-2-one, 23f
4-Methyl-N-methylaniline (1.26 mL, 9.98 mmol), 2,4-pentanedione (1.33 mL, 13.0 mmol) and pTSA (150 mg, 0.870 mmol) in toluene (150 mL) were heated at reflux under a soxhlet extractor filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 40% EtOAc/petrol) to afford the title compound 23f (1.44 g, 7.09 mmol, 71%) as a yellow oil contaminated with ca. 3 mol% 4-methyl-N-methylaniline due to hydrolysis during column chromatography. IR νmax (film, cm⁻¹): 2920 (br), 1643 (m), 1530 (s), 1413 (m), 1182 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.20 – 7.17 (2 H, m, 2 × ArH), 6.99 – 6.96 (2 H, m, 2 × ArH), 5.25 (1 H, s, CH), 3.21 (3 H, s, CH₃), 2.36 (3 H, s, CH₃), 2.28 (3 H, s, CH₃), 2.11 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 195.3 (C), 161.0 (C), 143.3 (C), 137.0 (C), 130.2 (2 × CH), 126.9 (2 × CH), 97.2 (CH), 41.1 (CH₃), 31.8 (CH₃), 21.0 (CH₃), 18.0 (CH₃) ppm. LRMS (EI): 203 (100%, M⁺), 188 (100%), 160 (100%), 144 (100%). HRMS (EI): Found 203.1305, C₁₁H₁₇NO M⁺ requires 203.1305.
(E)-4-(Methyl(4-(trifluoromethyl)phenyl)amino)pent-3-en-2-one, 23g
4-Trifluoromethyl-N-methylaniline (1.41 mL, 9.98 mmol), 2,4-pentanediene (1.12 mL, 11.0 mmol) and pTSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxlet filled with 4Å molecular sieves for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (10 – 40% EtO/petrol) to afford the title compound 23g (1.57 g, 6.11 mmol, 61%) as a yellow oil contaminated with ~10 mol% 4-trifluoromethyl-N-methylaniline due to hydrolysis during column chromatography. IR νmax (film, cm⁻¹): 2929 (br), 1541 (s), 1513 (s), 1324 (s), 1126 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.67 – 7.65 (2 H, m, 2 × ArH), 7.24 – 7.22 (2 H, m, 2 × ArH), 5.34 (1 H, s, CH), 3.25 (3 H, s, CH₃), 2.30 (3 H, s, CH₃), 2.13 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 195.8 (C), 159.6 (C), 149.1 (C), 128.9 (C, JCF = 33 Hz), 127.5 (2 × CH), 126.7 (2 × CH, JCF = 3.7 Hz), 123.8 (C, JCF = 272.2 Hz), 99.4 (CH), 40.9 (CH₃), 32.0 (CH₃), 18.2 (CH₃) ppm. ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -62.73 (3 F, s, CF₃) ppm. LRMS (El): 257 (35%, M⁺), 242 (99%), 214 (100%). HRMS (El): Found 256.0944, C₁₃H₁₂F₃NO [M–H]⁺ requires 256.0949.
(E)-4-((4-Methoxyphenyl)(methyl)amino)pent-3-en-2-one, 23h
4-methoxy-N-methylaniline (1.40 g, 10.2 mmol), 2,4-pentanedione (1.04 mL, 10.2 mmol) and pTSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a soxhlet filled with 4Å MS for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (50 – 70 % EtOAc/petrol) to afford the title compound 23h (1.58 g, 7.21 mmol, 71%) as a yellow oil. IR νmax (film, cm⁻¹): 2952 (br), 1534 (m), 1503 (s), 1419 (m), 1243 (m), 1182 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.03 – 6.99 (2 H, m, 2 × ArH), 6.92 – 6.88 (2 H, m, 2 × ArH), 5.23 (1 H, s, CH), 3.82 (3 H, s, CH₃), 3.20 (3 H, s, CH₃), 2.28 (3 H, s, CH₃), 2.21 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 195.3 (C), 161.3 (C), 158.4 (C), 138.7 (C), 128.2 (2 × CH), 114.7 (2 × CH), 97.1 (CH), 55.5 (CH₃), 41.2 (CH₃), 31.8 (CH₃), 17.9 (CH₃) ppm. LRMS (EI): 219 (40%, M⁺), 176 (50%), 161 (100%). HRMS (EI): Found 219.1254, C₁₃H₁₂NO₂ M⁺ requires 219.1254.

(E)-4-(Methyl(naphthalen-1-yl)amino)but-3-en-2-one, 23i
To a solution of but-3-en-2-one (0.28 mL, 3.58 mmol) in EtOH (10 mL) was added N-methylnaphthalen-1-amine (559 mg, 3.58 mmol). After 16 h at RT, the resulting solution was concentrated in vacuo then purified by column chromatography (20 – 40% EtOAc/petrol) to afford the title compound 23i (450 mg, 2.00 mmol, 56%) as a yellow oil. IR νmax (film, cm⁻¹): 3491 (br), 3054 (br), 1605 (s), 1548 (s), 1267 (m), 1250 (m). ¹H NMR (400 MHz, CDCl₃): δ 7.91 (1 H, m, ArH), 7.85 – 7.75 (3 H, m, 2 × ArH + CH), 7.47 – 7.35 (2 H, m, 2 × ArH), 7.48 (1 H, m, ArH), 7.32 (1 H, d, J = 7.1 Hz, ArH), 5.50 (1 H, br s, CH), 3.36 (3 H, br s, CH₃), 2.18 (3 H, br s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 196.0 (C), 152.0 (CH), 144.0 (C), 134.7 (C), 129.1 (C), 128.6 (CH), 127.9 (CH), 127.1 (CH), 126.6 (CH), 125.6 (CH), 123.2 (CH), 122.6 (CH), 100.4 (CH), 39.3 (CH₃), 27.7 (CH₃) ppm. LRMS (EI): 225 (86%, M⁺), 210 (95%), 182 (100%), 167 (78%). HRMS (EI): Found 225.1148, C₁₃H₁₂NO M⁺ requires 225.1148.
(E)-4-(Methyl(p-tolyl)amino)but-3-en-2-one, 23j
To a solution of but-3-en-2-one (0.41 mL, 5.25 mmol) in EtOH (10 mL) was added 4-methyl-N-methylaniline (0.63 mL, 5.23 mmol). After 16 h at RT, the resulting solution was concentrated in vacuo then purified by column chromatography (20 – 50% EtOAc/petrol) to afford the title compound 23j (775 mg, 4.10 mmol, 82%) as an off-white solid. IR νmax (film, cm⁻¹): 2918 (br), 1550 (s), 1509 (s), 1252 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.78 (1 H, d, J = 13.2 Hz, CH), 7.09 – 7.05 (2 H, m, 2 × ArH), 6.97 – 6.93 (2 H, m, 2 × ArH), 5.31 (1 H, d, J = 13.1 Hz, CH), 3.15 (3 H, s, CH₃), 2.24 (3 H, s, CH₃), 2.10 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 195.6 (C), 148.3 (CH), 143.7 (C), 134.2 (C), 129.7 (2 × CH), 120.0 (2 × CH), 100.9 (CH), 36.8 (CH₃), 27.8 (CH₃), 20.4 (CH₃) ppm. LRMS (ESI⁺): 212 [M+Na⁺], 190 [M+H⁺]. HRMS (ESI⁺): Found 190.1230, C₁₂H₁₃NO [M+H⁺] requires 190.1226.

Methyl (E)-3-(methyl(phenyl)amino)but-2-enolate, 23k
To a mixture of methyl acetoacetate (1.26 mL, 11.7 mmol) and N-methylaniline (1.26 mL, 11.6 mmol) was added Yb(OTf)₃ (20 mg). The reaction mixture was stirred at RT for 16 h then 50 mL DCM and 50 mL water was added. The aqueous phase was separated and extracted with DCM (2 × 50 mL). The organic phases were combined, dried over MgSO₄ and concentrated in vacuo to afford the title compound 23k (1.46 g, 8.24 mmol, 71%) as a yellow oil that was used without further purification due to its sensitivity towards hydrolysis under column chromatography.

(E)-3-(Methyl(phenyl)amino)but-2-enal, 23l
To a solution of but-2-ynal (680 mg, 10.0 mmol) in EtOH (10 mL) was added N-methylaniline (1.26 mL, 10.0 mmol). After stirred 16 h at 50 °C, the resulting solution was concentrated in vacuo then purified by column chromatography (20 – 50% EtOAc/petrol) to afford the title compound 23i (1360 mg, 7.77 mmol, 78%) as a yellow solid. IR νmax (film, cm⁻¹): 2931 (br), 1615 (s), 1553 (s), 1493 (s), 1190 (s). ¹H NMR (400 MHz, CDCl₃): δ 9.59 (1 H, d, J = 8.2 Hz, CH), 7.40 – 7.35 (2 H, m, 2 × ArH), 7.30 (1 H, m, CH), 7.11 – 7.07 (2 H, m, 2 × ArH), 5.27 (1 H, d, J = 8.2 Hz, CH), 3.23 (3 H, s, CH₃), 2.09 (3 H, s, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 187.9 (CH), 162.9 (C), 145.1 (C), 129.6 (2 × CH), 127.5 (CH), 126.9 (2 × CH), 102.8 (CH), 41.0 (CH₃), 16.2 (CH₃) ppm. LRMS (ESI⁺): 198 [M+Na⁺], 176 [M+H⁺]. HRMS (ESI⁺): Found 176.1070, C₇H₇NO [M+H⁺] requires 176.1072.

Diethyl 2-(methyl(phenyl)amino)maleate, 23m
To a solution of diethyl acetylenedicarboxylate (0.96 mL, 6.00 mmol) in water (20 mL) was added N-methylaniline (0.65 mL, 6.01 mmol). After 16 h at RT, DCM (20 mL) was added then the aqueous phase was separated and extracted with further DCM (2 × 20 mL). The organic phases were combined, dried over MgSO₄, concentrated in vacuo and purified by column chromatography (20 – 60% EtOAc/petrol) to afford the title compound 23m (1.63 g, 5.88 mmol, 95%) as an off-white oil. IR νmax (film, cm⁻¹): 2978 (br), 1728 (s), 1687 (m), 1560 (s), 1127 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.30 (2 H, m, 2 × ArH), 7.26 – 7.18 (3 H, m, 3 × ArH), 4.78 (1 H, s, CH), 4.09 (2 H, q, J = 7.5 Hz, CH₂), 4.08 (2 H, q, J = 7.5 Hz, CH₂), 3.19 (3 H, s, CH₃), 1.21 (3 H, t, J = 7.2 Hz, CH₃), 1.06 (3 H, t, J = 7.2 Hz, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 167.1 (C), 164.5 (C), 154.0 (C), 144.5 (C), 129.2 (2 × CH), 127.2 (CH), 126.6 (2 × CH), 88.4 (CH), 61.6 (CH₂), 59.2 (CH₂), 40.7 (CH₃), 14.3 (CH₃), 13.5 (CH₃) ppm. LRMS (ESI⁺): 300 [M+Na⁺], 278 [M+H⁺]. Data is consistent with literature values.²¹
2-(Methyl(phenyl)amino)cyclohex-2-en-1-one, 27a

N-Methylaniline (0.7 mL, 6.50 mmol), 1,2-cyclohexanedione (730 mg, 6.51 mmol) and pTSA (50 mg) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (50 – 80% EtOAc/hexane) to afford the title compound 27a (1.09 g, 5.42 mmol, 83%) as an off-white solid. IR (film, cm⁻¹): 2944 (br), 1680 (s), 1596 (S), 1497 (S). ¹H NMR (400 MHz, CDCl₃): δ 7.22 – 7.17 (2 H, m, 2 x ArH), 6.80 – 6.70 (4 H, m, 3 x ArH + CH), 3.08 (3 H, s, CH₃), 2.58 – 2.52 (4 H, m, 2 x CH₂), 2.10 (2 H, app. quin, J = 6.4 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 196.4 (C), 149.0 (C), 144.7 (C), 143.0 (CH), 128.8 (2 x CH), 118.4 (CH), 114.8 (2 x CH), 39.44 (CH₃), 39.35 (CH₂), 26.0 (CH₂), 22.9 (CH₂) ppm. LRMS (ESI⁺): 202 ([M+H]+, 100%). Data is consistent with literature values.²²

2-(Benzyl(phenyl)amino)cyclohex-2-en-1-one, 27b

N-Benzylaniline (1.45 g, 7.90 mmol), 1,2-cyclohexanedione (886 mg, 7.91 mmol) and pTSA (150 mg, 0.872 mmol) in toluene (150 mL) were heated at reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (50 – 90% EtOAc/petrol) to afford the title compound 27b (1.44 g, 5.20 mmol, 66%) as a yellow solid. MP: 156 – 157 °C. IR (film, cm⁻¹): 2929 (br), 1672 (s), 1596 (m), 1496 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.24 – 7.17 (4 H, m, 3 x ArH + 1 H), 7.11 (1 H, m, ArH), 7.05 – 7.00 (2 H, m, 2 x ArH), 6.74 (1 H, m, ArH), 6.62 (1 H, tt, J = 7.3, 1.1 Hz, ArH), 6.58 – 6.54 (2 H, m, 2 x ArH), 4.57 (2 H, s, CH₂), 2.43 – 2.39 (2 H, m, CH₂), 2.32 (2 H, td, J = 6.0, 4.5 Hz, CH₂), 1.90 (2 H, app. quin, J = 6.1 Hz, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 196.4 (C), 148.4 (C), 146.1 (CH), 142.7 (C), 139.0 (C), 128.7 (2 x CH), 128.3 (2 x CH), 126.8 (2 x CH), 126.7 (CH), 118.1 (CH), 114.1 (2 x CH), 55.4 (CH₂), 39.2 (CH₂), 25.9 (CH₂), 22.6 (CH₂) ppm. LRMS (ESI⁺): 300 [M+Na]+, 278 [M+H]+.
2-((4-Methoxyphenyl)(methyl)amino)cyclohex-2-en-1-one, 27c

4-Methoxy-N-methyl-aniline (670 mg, 4.67 mmol), 1,2-cyclohexanedione (822 mg, 7.34 mmol) and pTSA (50 mg, 0.33 mmol) in toluene (150 mL) were heated under reflux under a Dean-Stark trap for 16 h then cooled to RT. The resulting solution was concentrated in vacuo then purified by column chromatography (50–80% EtOAc/hexane) to afford the title compound 27c (878 mg, 3.80 mmol, 78%) as an off-white solid. IR νmax (film, cm⁻¹): 2938 (br), 1680 (s), 1506 (s), 1237 (s). ¹H NMR (400 MHz, CDCl₃): δ 6.81 – 6.74 (4 H, m, 4 × ArH), 6.51 (1 H, t, J = 4.5 Hz, =CH), 3.75 (3 H, s, CH₃), 3.02 (3 H, s, CH₂), 2.53 – 2.48 (4 H, m, 2 × CH₂), 2.08 – 2.02 (2 H, m, CH₂) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 196.4 (C), 153.7 (C), 145.3 (C), 143.5 (C), 137.0 (CH), 118.8 (2 × CH), 114.4 (2 × CH), 55.5 (CH₃), 40.6 (CH₂), 39.5 (CH₂), 25.8 (CH₂), 23.0 (CH₃) ppm. LRMS (ESI⁺): 232 [M+H]⁺. Data is consistent with literature values.¹³

(E)-4-(Methyl(phenyl)amino)hex-4-en-3-one, 27d

The title compound was prepared following a modified literature procedure.¹² A solution of N-methyl-aniline (1.11 mL, 10.0 mmol), 3,4-hexanedione (5.86 mL, 50.0 mmol) and pTSA (95 mg) in toluene (50 mL) was heated at reflux under a soxhlet containing 4 Å molecular sieves for 25 h. The resultant solution was diluted with ethyl acetate (30 mL), washed with water (2 × 50 mL), dried over MgSO₄, concentrated in vacuo and purified by column chromatography (5 – 30% EtOAc in petrol) to give the title compound 27d as a yellow oil (1.52 g, 7.48 mmol, 75%). IR νmax (CDCl₃, cm⁻¹): 2980 (br), 1683 (m), 1598 (s), 1500 (s), 1339 (w), 749 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.23 (2H, dd, J = 8.8, 7.2 Hz, 2 × ArH), 6.81 (1H, q, J = 7.0 Hz, CH), 6.75 (1H, tt, J = 7.3, 1.0 Hz, ArH), 6.60 (2H, dd, J = 8.9, 1.0 Hz, 2 × ArH), 3.13 (3H, s, CH₃), 2.43 (2H, q, J = 7.2 Hz, CH₂), 1.75 (3H, d, J = 7.1 Hz, CH₃), 1.01 (3H, t, J = 7.2 Hz, CH₂) ppm. ¹³C NMR (101 MHz, CDCl₃): δ 201.5 (CO), 147.6 (C), 145.1 (C), 134.9 (CH), 129.3 (CH), 117.3 (CH), 111.9 (CH), 38.1 (CH₃), 31.8 (CH₂), 13.6 (CH₃), 7.9 (CH₃) ppm. LRMS (ESI⁺): 204 [(M+H)⁺, 100%]. Data is consistent with literature values.³⁴
References


