Supporting Information

Tuneable access to indole, indolone and cinnoline derivatives from a common 1,4-diketone Michael acceptor

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I. **GC-MS study and related spectra.**

We found important to make sure that indole 6b actually resulted from a 1,2-addition and not from a degradation of indolone 7b. For this purpose indolone 7b was refluxed overnight (16h) with 3 mol% of acetic acid in toluene as in entry 5 of table 1 from the paper (conditions to produce mainly the indole) and the reaction was followed by GC-MS.

![GC chromatogram for indolone 7b](image1)

MS spectra for indolone 7b peak at $t = 24.33$ min, $M = 253$.  

![MS spectra for indolone 7b](image2)
After 16h of reaction, only indolone 7b is detected. No traces of indole 6b. We carry on the reaction up to 24h to check.
GC chromatogram after 24h of reaction:

After 24h of reaction, only indolone 7b is detected. No traces of indole 6b.

So under these conditions, indolone 7b remained unchanged, with no trace of indole 6b detected, indicating that the indole was formed intramolecularly by 1,2-addition of the intermediately formed imine to the Michael acceptor (Schema 5 from the paper).
II. General Experimental Methods

All chemicals were used as received otherwise notice.

All the NMR spectra were recorded on a Bruker Advance III 400, 300 or 200 wide bore. $^1$H and $^{13}$C spectra were recorded respectively at 400 MHz and 101 MHz or 300 MHz and 76 MHz or 200 MHz and 50 MHz. $^{19}$F spectra were recorded at 376 MHz. $^{31}$P spectra were recorded at 162 MHz. $^1$H and $^{13}$C chemical shifts were reported in ppm from the residual solvent peak. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, td = triplet of doublet, q = quadruplet, p = pentuplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, m = multiplet), coupling constant $J$ (Hz) and integration.

High-resolution mass spectra (HMRS) were recorded on a Bruker micrOTOF-Q spectrometer.

Gas chromatography-mass spectrometry (GC-MS) spectra were recorded on a Shimadzu QP2010.

Chromatography purifications were performed on a Fluka 60 silica column (0.063-0.2 mm) or a Grace Reveleris™ with Reveleris™ flash cartridges silica 40 µM.

Analytical thin layer chromatography was performed on Merck Silica Gel 60 F254 plates.

The irradiation with microwave was carried out in the cavity of a Discover system from CEM.

III. Generals procedures

a. General procedure A for the preparation of hydroxyalkylocyclohex-2-en-1-one 1a-b

DMAP (15 mmol, 0.20 equiv) was added to a solution of cyclohex-2-en-1-one (75 mmol, 1 equiv) or 4,4-dimethylcyclohex-2-en-1-one (75 mmol, 1 equiv) and (HCHO)$_{aq}$ (75 mmol, 1 equiv) in 15 mL of THF. The reaction mixture was stirred for 24 h at room temperature followed by the addition of a solution of HCl (1N) (50 mL). The organic phase was collected and the aqueous phase was extracted 3 times with CH$_2$Cl$_2$ (3 x 30 mL). The organic phases were combined and dried over Na$_2$SO$_4$. The solvent was evaporated and the crude product
was purified by silica gel chromatography diethylether/petroleum ether 75/25. 1a and 1b were prepared according to literature methods [1].

**b. General procedure B for the preparation of acetyloxalkylcyclohex-2-en-1-one 2a-b**

DMAP (5 mmol, 0.12 equiv) was added to a solution of 2-hydroxymethylcyclohex-2-en-1-one 1a (40 mmol, 1 equiv) or 2-(hydroxymethyl)-4,4-dimethylcyclohex-2-en-1-one 1b (40 mmol, 1 equiv), acetic anhydride (40 mmol, 1 equiv) and Et₃N (40 mmol, 1 equiv) at 0°C. After 10 min the reaction mixture was stirred for 2 h at room temperature followed by the addition of a solution of HCl (1N) (50 mL). The organic phase was collected and the aqueous phase was extracted 3 times with CH₂Cl₂ (3 x 30 mL). The organic phases were combined and dried over Na₂SO₄. The solvent was evaporated and the crude product was purified by silica gel chromatography diethyl ether/petroleum ether 75/25. 2a and 2b were prepared according to literature methods [2].

**c. General procedure C for the preparation of nitroalkylcyclohex-2-en-1-one 3a-d**

To a solution of 2-(acetyloxymethyl)cyclohex-2-en-1-one 2a (10 mmol, 1 equiv) or (2-(acetyloxymethyl)-4,4-dimethylcyclohex-2-en-1-one 2b (10 mmol, 1 equiv) in 15 mL EtOH, were added nitroalkane (12 mmol, 1.2 equiv) and Et₃N (12 mmol, 1.2 equiv). The reaction mixture was heated under reflux and stirred for 24 h then dried over Na₂SO₄. The solvent was evaporated and the crude product was purified by silica gel chromatography diethylether/petroleum ether 50/50. 3a and 3b were prepared according to literature methods [2,3].

**d. General procedure D for the 1,4-diketones 5a-d from Nef reaction**

To a solution of sodium (15.51 mmol, 1 equiv) in anhydrous ethanol (15 mL), were added 2-(2-nitroalkyl)cyclohex-2-en-1-one 3 (5.17 mmol, 0.33 equiv) dissolved in 10 mL of absolute ethanol. The reaction mixture was stirred for 3h at room temperature. Then, 3 mL of H₂SO₄ dissolved in 10 mL of absolute ethanol was introduced at -50°C. After 1h, 10 mL of water were added at -50°C and the reaction mixture was cooled to room temperature. After the completion of the reaction, the solvent was evaporated under reduced pressure and the reaction mixture was extracted three times with 50 mL of dichloromethane. The recombined organic phases were washed with a solution of NaOH (1 %) then dried with Na₂SO₄ or MgSO₄ and the solvent was evaporated under reduced pressure. The crude material was
purified by silica gel column chromatography or Flash chromatography to afford the desired product [4].

e. General procedure E for the preparation of ylides 4a-g

A solution of PPh₃ (6.4 mmol, 1.01 equiv) and bromide derivatives (6.3 mmol, 1 equiv) in 13 mL THF was heated under reflux and stirred for 4 hours. Then, the reaction mixture was cooled to room temperature and the crude phosphonim bromide was filtered, washed with THF (3 x 20 mL). Then, 25 mL of CH₂Cl₂ and aqueous NaOH (20w%, 25 mL) were added and the mixture was stirred for 10 minutes. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure to give the corresponding phosphonium ylide [5].

f. General procedure F for the 1,4-diketones 5e-k from Wittig reaction

To a solution of compound 3 (1 equiv) in CH₂Cl₂ or toluene (0.20 mol/L), were added cyclohexane-1,2-dione (1.05 equiv). The reaction mixture was heated under reflux and stirred for 48 hours and 2 days at room temperature. After the completion of the reaction, the solvent was evaporated under reduced pressure and the crude material was purified by flash chromatography to afford the desired product [6].

g. General procedure G for the preparation of indoles 6a-l

To a solution of 1,4-diketone 5 (0.54 mmol, 1 equiv) in 4 mL toluene, were added acetic acid (3 mol %, 1.7 µL) and primary amine (0.81 mmol, 1.5 equiv). The reaction mixture was heated under reflux and stirred for 16h. After the completion of the reaction, the reaction was dried over MgSO₄ and the solvent was evaporated under reduced pressure. Then the crude material was purified by flash chromatography using silica cartridge to afford the desired product.

h. General procedure H for the preparation of indolone derivatives (1,5,6,7-tetrahydroindol-4-ones) 7b, 7d and 7g-k

To a solution of 1,4-diketone 5 (1 equiv) in butanol (C = 0.1 M), was added primary amine (1.5 equiv). The reaction mixture was stirred and heated inside a microwave cavity at 100 °C for 3h. After 3 hours, the reaction mixture was cooled and dried over MgSO₄ and the solvent
was evaporated under reduced pressure. Then the crude material was purified by flash chromatography using silica cartridge to afford the desired product.

i. General procedure I for the preparation of cinnoline derivatives (5,6,7,8-tetrahydrocinnolines) 8a-k

To a solution of 1,4-diketones 5 (1 mmol, 1 equiv) in 6 mL of absolute ethanol, were added hydrazine monohydrate (1.5 mmol, 1.5 eq, 75 mg) and 3 mol % (1.7 μL) acetic acid (AcOH). The reaction mixture was heated under reflux and stirred for 16 hours. After the completion of the reaction, the reaction was dried with MgSO₄ and the solvent was evaporated under reduced pressure. Then the crude material was purified by flash chromatography to afford the desired product.

IV. Characterisation data

a. Hydroxyalkylcyclohex-2-en-1-one 1a-b

- 2-(Hydroxymethyl)cyclohex-2-en-1-one (1a) [1]

Compound 1a was prepared according to the general procedure A using cyclohex-2-en-1-one (75 mmol, 7.2 mL), DMAP (15 mmol, 1.83 g) and (HCHO)ₐq (75 mmol, 15 mL) in 15 mL THF. The title compound was obtained after silica gel chromatography as a yellow oil. The spectral data are in good agreement with previous reports [1]. Yield = 80 % (7.5 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. Rₓ = 0.60 (diethyl ether/petroleum ether 75/25).

₁H NMR (300 MHz, CDCl₃) δ = 1.94-2.02 (m, 2H), 2.34-2.52 (m, 4H), 4.21 (s, 2H), 6.90 (t, J = 4.1 Hz, 1H).

- 2-(Hydroxymethyl)-4,4-dimethylcyclohex-2-en-1-one (1b) [7]

Compound 1b was prepared according to the general procedure A using 4,4-dimethylcyclohex-2-en-1-one (20 mmol, 2.5 g), DMAP (4 mmol, 0.48 g) and (HCHO)ₐq (20 mmol, 4 mL) in 4 mL THF. The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 82 % (2.5 g). The spectral data are in good agreement with previous
reports [7]. Yield = 80 % (7.5 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. \( R_f = 0.60 \) (diethyl ether/petroleum ether 75/25).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 1.12 \) (s, 6H), 1.81 (t, \( J = 6.9 \) Hz, 2H), 2.43 (t, \( J = 6.8 \) Hz, 2H), 4.16 (s, 2H), 6.57 (s, 1H).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 200.4 \) (C), 155.8 (CH), 135.2 (C), 61.4 (CH\(_2\)), 35.9 (CH\(_2\)), 34.6 (CH\(_2\)), 32.8 (C), 27.8 (2 \times CH\(_3\)).

b. Acetyloxalkylocyclohex-2-en-1-one 2a-b

- **2-(Acetyloxymethyl)cyclohex-2-en-1-one (2a)**[2]

Compound 2a was prepared according to the general procedure B using 2-(hydroxymethyl)cyclohex-2-en-1-one 1a (40 mmol, 5.04 g), acetic anhydride (40 mmol, 4.08 g) and Et\(_3\)N (40 mmol, 4.04 g). The title compound was obtained after silica gel chromatography as a yellow oil. The spectral data are in good agreement with previous reports [2]. Yield = 80 % (5.37 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. \( R_f = 0.40 \) (diethyl ether/petroleum ether 50/50).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta = 1.96 \) (s, 3H), 2.00-2.16 (m, 2H), 2.17-2.50 (m, 4H), 4.22 (s, 2H), 6.96 (t, \( J = 4.1 \) Hz, 1H).

- **2-(Acetyloxymethyl)-4,4-dimethylcyclohex-2-en-1-one (2b)**

Compound 2b was prepared according to the general procedure B using 2-(hydroxymethyl)-4,4-dimethylocyclohex-2-en-1-one 1b (20 mmol, 3.04 g), acetic anhydride (20 mmol, 2.04 g) and Et\(_3\)N (20 mmol, 2.02 g). Yield = 82 % (3.2 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. \( R_f = 0.40 \) (diethyl ether/petroleum ether 50/50).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 1.16 \) (s, 6H), 1.82-1.87 (m, 2H), 2.05 (s, 3H), 2.43-2.49 (m, 2H), 4.67 (d, \( J = 1.2 \) Hz, 2H), 6.63 (s, 1H).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 21.1 \) (CH\(_3\)), 27.9 (2 \times CH\(_3\)), 33.1 (C), 34.6 (CH\(_2\)), 36.0 (CH\(_2\)), 61.5 (CH\(_2\)), 131.5 (C), 157.5 (CH), 170.7 (C), 197.9 (C).

HRMS (ESI, m/z) calcd for C\(_{11}\)H\(_{17}\)O\(_3\) [M+H]\(^+\) = 197.1172 found 197.1186 and for C\(_{11}\)H\(_{16}\)NaO\(_3\) [M+Na]\(^+\) = 219.0992 found 219.1038.
c. Nitroalkylcyclohex-2-en-1-one 3b-d

- **2-(2-Nitropropyl)cyclohex-2-en-1-one (3a) [2]**

  Compound 3a was prepared according to the general procedure C using 2-(acetyloxymethyl)cyclohex-2-en-1-one 2a (10 mmol, 1.6 g) and nitroethane (12 mmol, 0.9 g) in 15 mL EtOH. The title compound was obtained after silica gel chromatography as a brown oil. The spectral data are in good agreement with previous reports [2]. Yield = 56 % (1.02 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. \( R_f = 0.50 \) (diethyl ether/petroleum ether 50/50).

  \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta = 1.53 \) (d, \( J = 6.7 \) Hz, 3H), 1.94-2.03 (m, 2H), 2.36 (q, \( J = 4.8 \) Hz, 2H), 2.42-2.45 (m, 2H), 2.55-2.63 (m, 1H), 2.73-2.81 (m, 1H), 4.71-4.86 (m, 1H), 6.80 (t, \( J = 4.1 \) Hz, 1H).

- **2-(2-Nitrobutyl)cyclohex-2-en-1-one (3b)**

  Compound 3b was prepared according to the general procedure C using 2-(acetyloxymethyl)cyclohex-2-en-1-one 2a (10 mmol, 1.6 g) and nitropropane (12 mmol, 1.1 g) in 15 mL EtOH. The title compound was obtained after silica gel chromatography as a brown oil. Yield = 48 % (0.94 mg). Chromatography conditions: diethyl ether/petroleum ether 50/50. \( R_f = 0.50 \) (diethyl ether/petroleum ether 50/50).

  \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta = 0.96 \) (t, \( J = 7.4 \) Hz, 3H), 1.77-1.85 (m, 1H), 1.91-2.03 (m, 3H), 2.32-2.37 (m, 2H), 2.41-2.46 (m, 2H), 2.48-2.53 (m, 1H), 2.78-2.87 (m, 1H), 4.56-4.64 (m, 1H), 6.78 (t, \( J = 4.1 \) Hz, 1H).

  \(^1\)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 10.4 \) (CH\(_3\)), 23.0 (CH\(_2\)), 26.2 (CH\(_2\)), 27.4 (CH\(_2\)), 35.0 (CH\(_2\)), 38.3 (CH\(_2\)), 89.5 (CH), 134.3 (C), 149.5 (CH), 199.0 (C).

  HRMS (ESI, m/z) calcd for C\(_{10}\)H\(_{15}\)NNaO\(_3\) \([\text{M+Na}]^+\) = 220.0944 found 220.0965.

- **4,4-Dimethyl-2-(2-nitropropyl)cyclohex-2-en-1-one (3c)**

  Compound 3c was prepared according to the general procedure C using (2-(acetyloxymethyl)-4,4-dimethylcyclohex-2-en-1-one 2b (10 mmol, 1.96 g) and nitroethane (12 mmol, 0.9 mg) in 15 mL EtOH. The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 58 % (1.21 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. \( R_f = 0.50 \) (diethyl ether/petroleum ether 50/50).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.09 (d, J = 8.4 \text{ Hz}, 6\text{H}), 1.48 (d, J = 6.6 \text{ Hz}, 3\text{H}), 1.79 (t, J = 6.8 \text{ Hz}, 2\text{H}), 2.39-2.72 (m, 3\text{H}), 2.72 (dd, J = 4.4, 13.8 \text{ Hz}, 1\text{H}), 4.68-4.73 (m, 1\text{H}), 6.39 (s, 1\text{H}).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 18.9 (\text{CH}_3), 27.47 (\text{CH}_3), 27.51 (\text{CH}_3), 32.9 (\text{C}), 34.2 (\text{CH}_2), 35.7 (\text{CH}_2), 35.8 (\text{CH}_2), 82.5 (\text{CH}), 130.9 (\text{C}), 158.4 (\text{CH}), 198.3 (\text{C}).

HRMS (ESI, m/z) calcd for C\(_{11}\)H\(_{17}\)NNaO\(_3\) [M+Na]\(^+\) = 234.1101 found 234.1110 and for C\(_{11}\)H\(_{17}\)NKO\(_3\) [M+K]\(^+\) = 250.0840 found 250.0836.

- **4,4-Dimethyl-2-(2-nitropropyl)cyclohex-2-en-1-one (3d)**

Compound 3d was prepared according to the general procedure C using (2-(acetyloxymethyl)-4,4-dimethylcyclohex-2-en-1-one 2b (10 mmol, 1.96 g) and nitropropane (12 mmol, 1.07 g) in 15 mL EtOH. The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 61 % (1.31 g). Chromatography conditions: diethyl ether/petroleum ether 50/50. \(R_f = 0.50\) (diethyl ether/petroleum ether 50/50).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 0.95 (t, J = 7.4 \text{ Hz}, 3\text{H}), 1.11 (d, J = 8.7 \text{ Hz}, 6\text{H}), 1.81 (t, J = 6.9 \text{ Hz}, 3\text{H}), 1.90-2.00 (m, 1\text{H}), 2.36 (dd, J = 10.6, 13.8 \text{ Hz}, 1\text{H}), 2.45 (td, J = 3.2, 6.6 \text{ Hz}, 2\text{H}), 1.81 (dd, J = 3.6, 13.8 \text{ Hz}, 1\text{H}), 4.51-4.58 (m, 1\text{H}), 6.40 (s, 1\text{H}).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 10.4 (\text{CH}_3), 27.3 (\text{CH}_2), 27.8 (\text{CH}_3), 27.9 (\text{CH}_2), 33.3 (\text{CH}_2), 34.6 (\text{CH}_2), 34.7 (\text{C}), 36.1 (\text{CH}_2), 89.7 (\text{CH}), 131.2 (\text{CH}), 158.7 (\text{C}), 198.7 (\text{C}).

HRMS (ESI, m/z) calcd for C\(_{12}\)H\(_{19}\)NaO\(_3\) [M+Na]\(^+\) = 248.1257 found 248.1295.

d. Ylides 4a-g

- **3,3-Dimethyl-1-(triphenylphosphoranylidene)butan-2-one (4a) [8,9]**

Compound 4a was prepared according to the general procedure E using 1-bromo-3,3-dimethylbutan-2-one (14 mmol, 2.5 g) and PPh\(_3\) (14.1 mmol, 3.70 g) in 30 mL THF. Basic aqueous treatment (aqueous NaOH - 20\%w, 58 mL) of the isolated phosphonium bromine yielded the phosphonium ylide 4a without purification as a yellow solid. The spectral data are in good agreement with previous reports [8,9]. Yield = 50 % (2.65 g).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.15 (s, 9\text{H}), 3.74 (d, J_{PH} = 27.1 \text{ Hz}, 1\text{H}), 7.21-7.37 (m, 9\text{H}), 7.47-7.60 (m, 6\text{H}). R_f = 0.05 \text{(EtOAc 100 \%)}.\)
• **1-Phenyl-2-(triphenylphosphoranylidene)ethan-1-one (4b)** [5]

Compound 4b was prepared according to the general procedure E using 2-bromo-1-phenylethan-1-one (25 mmol, 5 g) and PPh$_3$ (25.25 mmol, 6.72 g) in 54 mL THF. Basic aqueous treatment (aqueous NaOH - 20w%, 104 mL) of the isolated phosphonium bromine yielded the phosphonium ylide 4b without purification as a white solid. The spectral data are in good agreement with previous reports [5]. Yield = 93% (8.81 g).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 4.45 (d, $J_{PH}$ = 24.4 Hz, 1H), 7.30-7.38 (m, 3H), 7.37-7.62 (m, 9H), 7.64-7.82 (m, 6H), 7.92-8.05 (m, 2H). R$_f$ = 0.05 (EtOAc 100%).

• **1-([1,1'-Biphenyl]-4-yl)-2-(triphenylphosphoranylidene)ethan-1-one (4c)** [10]

Compound 4c was prepared according to the general procedure E using 1-([1,1'-biphenyl]-4-yl)-2-bromoethan-1-one (10 mmol, 2.75 g) and PPh$_3$ (10.1 mmol, 2.67 g) in 22 mL THF. Basic aqueous treatment (aqueous NaOH - 20w%, 42 mL) of the isolated phosphonium bromine yielded the phosphonium ylide 4c without purification as a yellow solid. The spectral data are in good agreement with previous reports [10]. Yield = 66% (3 g).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 4.39 (d, $J_{PH}$ = 24.4 Hz, 1H), 7.20-7.26 (m, 1H), 7.34-7.42 (m, 7H), 7.43-7.55 (m, 8H), 7.62-7.69 (m, 7H), 7.97 (d, $J$ = 7.9 Hz, 2H). R$_f$ = 0.05 (EtOAc 100%).

• **1-(4-Iodophenyl)-2-(triphenylphosphoranylidene)ethan-1-one (4d)** [11]

Compound 4d was prepared according to the general procedure E using 2-bromo-1-(4-iodophenyl)ethan-1-one [5,12] (9.3 mmol, 3 g) and PPh$_3$ (9.4 mmol, 2.46 g) in 20 mL THF. Basic aqueous treatment (aqueous NaOH - 20w%, 38 mL) of the isolated phosphonium bromine yielded the phosphonium ylide 4d without purification as a yellow solid. The spectral data are in good agreement with previous reports [11]. Yield = 86% (3.8 g).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 4.39 (d, $J_{PH}$ = 23.5 Hz, 1H), 7.43-7.49 (m, 6H), 7.53-7.56 (m, 3H), 7.65-7.75 (m, 10H). R$_f$ = 0.05 (EtOAc 100%).

• **1-(4-Fluorophenyl)-2-(triphenylphosphoranylidene)ethan-1-one (4e)** [5,13]

Compound 4e was prepared according to the general procedure E using 2-bromo-1-(4-fluorophenyl)ethan-1-one (5 mmol, 1.1 g) and PPh$_3$ (5.1 mmol, 1.34 g) in 11 mL THF. Basic
aqueous treatment (aqueous NaOH - 20w%, 21 mL) of the isolated phosphonium bromine yielded the phosphonium ylide $4e$ without purification as a white solid. The spectral data are in good agreement with previous reports [5,13]. Yield = 85 % (1.70 g).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 4.27 (d, $J_{PH} = 24.0$ Hz, 1H), 6.86-6.96 (m, 2H), 7.36-7.40 (m, 6H), 7.42-7.51 (m, 3H), 7.55-7.69 (m, 6H), 7.82-7.92 (m, 2H). R$_f$ = 0.05 (EtOAc 100 %).

- **1-(Thiophen-2-yl)-2-(triphenylphosphoranylidene)ethan-1-one ($4f$)**

Compound $4f$ was prepared according to the general procedure E using 2-bromo-1-(thiophen-2-yl)ethan-1-one[14,15] (7.8 mmol, 1.60 g) and PPh$_3$ (7.9 mmol, 2.1 g) in 17 mL THF. Basic aqueous treatment (aqueous NaOH - 20w%, 32 mL) of the isolated phosphonium bromine yielded the phosphonium ylide $4f$ without purification as a yellow solid. The spectral data are in good agreement with previous reports.[4] Yield = 65 % (1.73 g).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 4.23 (d, $J_{PH} = 21.2$ Hz, 1H), 6.93-6.96 (m, 1H), 7.17-7.23 (m, 1H), 7.38-7.42 (m, 6H), 7.44-7.53 (m, 4H), 7.59-7.68 (m, 6H). R$_f$ = 0.05 (EtOAc 100 %).

- **1-(Pyridin-2-yl)-2-(triphenylphosphoranylidene)ethan-1-one ($4g$)**

Compound $4g$ was prepared according to the general procedure E using 2-(2-bromoacetyl)pyridin-1-ium bromide[16] (20 mmol, 4 g) and PPh$_3$ (20.2 mmol, 5.30 g) in 44 mL THF. Basic aqueous treatment (aqueous NaOH - 20w%, 82 mL) of the isolated phosphonium bromine yielded the phosphonium ylide $4g$ without purification as a yellow solid. Yield = 47 % (3.60 g). R$_f$ = 0.05 (EtOAc 100 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 4.97-5.20 (m, 1H), 7.06 (dd, $J = 7.6$, 5.0 Hz, 1H), 7.23-7.30 (m, 6H), 7.31-7.38 (m, 3H), 7.54 (dd, $J = 13.0$, 7.5 Hz, 7H), 7.94 (d, $J = 7.9$ Hz, 1H), 8.38 (d, $J = 4.7$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta =$ 51.8 (d, $J_{C-P} = 111.1$ Hz, CH, P=CH), 120.6 (d, $J_{C-P} = 1.6$ Hz, CH), 124.2 (CH), 126.7 (d, $J_{C-P} = 91.3$ Hz, 3 x C), 128.9 (d, $J_{C-P} = 12.3$ Hz, 6 x CH), 132.2 (d, $J_{C-P} = 3.0$ Hz, 3 x CH), 133.3 (d, $J_{C-P} = 10.3$ Hz, 6 x CH), 136.6 (CH), 148.1 (CH), 157.6 (d, $J_{C-P} = 14.1$ Hz, C), 182.9 (d, $J_{C-P} = 4.8$ Hz, C, C=O). $^{31}$P ($^1$H) NMR (CDCl$_3$, 162 MHz) $\delta =$ 17.4.

HRMS (ESI, m/z) calcd for C$_{25}$H$_{21}$NOP [M+H]$^+$ = 382.1355 found 382.1378 and for C$_{25}$H$_{20}$NNaOP [M+Na]$^+$ = 404.1175 found 404.1195.
1,4-Dicetones 5a-k

- **2-(2-Oxopropyl)cyclohex-2-en-1-one (5a)**

  Compound 5a was prepared according to the general procedure D using 2-(2-nitropropyl)cyclohex-2-en-1-one 3a (5.17 mmol, 0.90 g). The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 69% (540 mg). Chromatography conditions: diethyl ether/petroleum ether 75/25. R_f = 0.40 (diethyl ether/petroleum ether 75/25).

  \[ \text{H NMR (200 MHz, CDCl}_3 \text{) } \delta = 2.03 \text{ (p, } J = 6.2 \text{ Hz, 2H), 2.19 (s, 3H), 2.34-2.53 (m, 4H), 3.27 (s, 2H), 6.81 (t, } J = 4.2 \text{ Hz, 1H).} \]

  1^3C NMR (75 MHz, CDCl_3) \[ \delta = 22.9 \text{ (CH}_2 \text{), 26.0 \text{ (CH}_2 \text{), 29.9 \text{ (CH}_3 \text{), 37.8 \text{ (CH}_2 \text{), 44.3 \text{ (CH}_2 \text{), 134.0 \text{ (C), 148.9 \text{ (CH), 198.5 \text{ (C), 206.9 \text{ (C).}}} \]

  HRMS (ESI, m/z) calcd for C_9H_12NaO_2 [M+Na]^+ = 175.0730 found 175.0737.

- **2-(2-Oxobutyl)cyclohex-2-en-1-one (5b)**

  Compound 5b was prepared according to the general procedure D using 2-(2-nitrobutyl)cyclohex-2-en-1-one 3b (5.17 mmol, 1.02 g). The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 73% (630 mg). Chromatography conditions: diethyl ether/petroleum ether 75/25. R_f = 0.45 (diethyl ether/petroleum ether 75/25).

  \[ \text{H NMR (300 MHz, CDCl}_3 \text{) } \delta = 0.97 \text{ (t, } J = 7.3 \text{ Hz, 3H), 1.92-2.00 \text{ (m, 2H), 2.33-2.49 (m, 4H), 2.44 (q, } J = 7.3 \text{ Hz, 2H), 3.18 (s, 2H), 6.74 (t, } J = 4.1 \text{ Hz, 1H).} \]

  1^3C NMR (75 MHz, CDCl_3) \[ \delta = 7.7 \text{ (CH}_3 \text{), 22.9 \text{ (CH}_2 \text{), 26.1 \text{ (CH}_2 \text{), 35.9 \text{ (CH}_2 \text{), 37.9 \text{ (CH}_2 \text{), 43.0 \text{ (CH}_2 \text{), 134.3 \text{ (C), 148.7 \text{ (CH), 198.5 \text{ (C), 208.6 \text{ (C).}}} \]

  HRMS (ESI, m/z) calcd for C_{16}H_{14}NaO_2 [M+Na]^+ = 189.0886 found 189.0917.

- **4,4-Dimethyl-2-(2-oxopropyl)cyclohex-2-en-1-one (5c)**

  Compound 5c was prepared according to the general procedure D using 4,4-dimethyl-2-(2-nitropropyl)cyclohex-2-en-1-one 3c (5.17 mmol, 1.10 g). The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 87% (810 mg). Chromatography
conditions: diethyl ether/petroleum ether 75/25. R_f = 0.40 (diethyl ether/petroleum ether 75/25).

^1^H NMR (400 MHz, CDCl_3) δ = 1.14 (s, 6H), 1.84 (t, J = 6.8 Hz, 2H), 2.13 (s, 3H), 2.44 (t, J = 6.8 Hz, 2H), 3.18 (s, 2H), 6.43 (s, 1H).

^1^3^C NMR (101 MHz, CDCl_3) δ = 27.9 (2 x CH_3), 29.9 (CH_3), 33.3 (C), 34.3 (CH_2), 36.2 (CH_2), 44.1 (CH_2), 131.1 (C), 158.1 (CH), 198.3 (C), 205.8 (C).

HRMS (ESI, m/z) calcd for C_{11}H_{16}NaO_2 [M+Na]^+ = 203.1043 found 203.1087.

• 4,4-Dimethyl-2-(2-oxobutyl)cyclohex-2-en-1-one (5d)

Compound 5d was prepared according to the general procedure D using 4,4-dimethyl-2-(2-nitrobutyl)cyclohex-2-en-1-one 3d (5.17 mmol, 1.16 g). The title compound was obtained after silica gel chromatography as a yellow oil. Yield = 61 % (611 mg). Chromatography conditions: diethyl ether/petroleum ether 75/25. R_f = 0.40 (diethyl ether/petroleum ether 75/25).

^1^H NMR (400 MHz, CDCl_3) δ = 0.97 (t, J = 7.3 Hz, 3H), 1.11 (s, 6H), 1.81 (t, J = 6.7 Hz, 2H), 2.39-2.45 (m, 4H), 3.14 (s, 2H), 6.41 (s, 1H).

^1^3^C NMR (101 MHz, CDCl_3) δ = 7.7 (CH_3), 27.9 (2 x CH_3), 33.3 (C), 34.2 (CH_2), 35.8 (CH_2), 36.2 (CH_2), 42.9 (CH_2), 131.1 (C), 157.9 (CH), 198.3 (C), 208.4 (C).

HRMS (ESI, m/z) calcd for C_{12}H_{19}O_2 [M+H]^+ = 195.1380 found 195.1339 and for C_{12}H_{18}NaO_2 [M+Na]^+ = 217.1199 found 217.1223.

• Indoles 6a-l

• 2-(3,3-Dimethyl-2-oxobutyl)cyclohex-2-en-1-one (5e)

Compound 5e was prepared according to the general procedure F using 3,3-dimethyl-1-(triphenylphosphoranylidene)butan-2-one 4a (7.4 mmol, 2.65 g) and cyclohexan-1,2-dione (7.77 mmol, 0.87 g) in 37 mL CH_2Cl_2. The title compound was obtained after flash chromatography as a yellow oil. Yield = 46 % (0.66 g). Flash chromatography conditions: column 40g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. R_f = 0.40 (cyclohexane/EtOAc 50/50).
\[ ^1\text{H NMR (400 MHz, CDCl}_3) \delta = 1.17 (s, 9H), 2.01 (p, J = 6.3 Hz, 2H), 2.37-2.49 (m, 4H), 3.34 (s, 2H), 6.73 (t, J = 4.3 Hz, 1H). \]

\[ ^{13}\text{C NMR (101 MHz, CDCl}_3) \delta = 23.1 (\text{CH}_2), 26.2 (\text{CH}_2), 26.6 (3 \text{ x CH}_3), 37.7 (\text{CH}_2), 38.1 (\text{CH}_2), 44.5 (C), 134.9 (C), 148.5 (CH), 198.5 (C), 213.1 (C). \]

HRMS (ESI, m/z) calcd for C_{12}H_{18}NaO_2 [M+Na]^+ = 217.1199 found 217.1240.

**2-(2-Oxo-2-phenylethyl)cyclohex-2-en-1-one (5f)**

Compound 5f was prepared according to the general procedure F using 1-phenyl-2-(triphenylphosphoranylidene)ethan-1-one 4b (23 mmol, 8.80 g) and cyclohexan-1,2-dione (24.15 mmol, 2.7 g) in 115 mL CH_2Cl_2. The title compound was obtained after flash chromatography as a yellow oil. Yield = 73 % (3.58 g). Flash chromatography conditions: column 40 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. \( R_f = 0.40 \) (cyclohexane/EtOAc 50/50).

\[ ^1\text{H NMR (400 MHz, CDCl}_3) \delta = 2.05 (dt, J = 12.4, 6.1 Hz, 2H), 2.40-2.45 (m, 2H), 2.47-2.52 (m, 2H), 3.85 (s, 2H), 6.87 (t, J = 4.2 Hz, 1H), 7.45(dd, J = 7.6, 7.6 Hz, 2H), 7.49-7.60 (m, 1H), 7.97 (dd, J = 8.4, 1.3 Hz, 2H). \]

\[ ^{13}\text{C NMR (76 MHz, CDCl}_3) \delta = 23.1 (\text{CH}_2), 26.3 (\text{CH}_2), 38.1 (\text{CH}_2), 39.0 (\text{CH}_2), 128.5 (2 \text{ x CH}), 128.7 (2 \text{ x CH}), 133.2 (\text{CH}), 134.2 (C), 136.8 (C), 148.7 (CH), 197.7 (C), 198.4 (C). \]

HRMS (ESI, m/z) calcd for C_{14}H_{14}NaO_2 [M+Na]^+ = 237.0886 found 237.0893 and for C_{14}H_{14}KO_2 [M+K]^+ = 253.0625 found 253.0629.

**2-(2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)cyclohex-2-en-1-one (5g)**

Compound 5g was prepared according to the general procedure F using 1-([1,1'-biphenyl]-4-yl)-2-(triphenylphosphoranylidene)ethan-1-one 4c (4.25 mmol, 1.94 g) and cyclohexan-1,2-dione (4.46 mmol, 0.5 g) in 21 mL CH_2Cl_2. The title compound was obtained after flash chromatography as a yellow solid. Yield = 57 % (700 mg). mp 135°C. Flash chromatography conditions: column 40g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. \( R_f = 0.40 \) (cyclohexane/EtOAc 50/50).

\[ ^1\text{H NMR (400 MHz, CDCl}_3) \delta = 2.02-2.09 (m, 2H), 2.44(td, J = 6.0, 4.4 Hz, 2H), 2.48-2.53 (m, 2H), 3.83 (s, 2H), 6.89 (t, J = 4.2 Hz, 1H), 7.39 (dd, J = 7.3, 7.3 Hz, 1H), 7.47 (dd, J = 7.4, 7.4 Hz, 2H), 7.62 (d, J = 7.1 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H). \]
\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta = 23.1\) (CH\(_2\)), 26.3 (CH\(_2\)), 38.2 (CH\(_2\)), 39.0 (CH\(_2\)), 127.3 (2 x CH), 127.4 (2 x CH), 128.3 (CH), 129.0 (2 x CH), 129.1 (2 x CH), 134.3 (C), 136.5 (C), 140.0 (C), 145.9 (C), 148.9 (CH), 197.3 (C), 198.4 (C).

HRMS (ESI, m/z) calcd for C\(_{20}\)H\(_{18}\)NaO\(_2\) [M+Na]\(^{+}\) = 313.1199 found 313.1199 and for C\(_{20}\)H\(_{18}\)KO\(_2\) [M+K]\(^{+}\) = 329.0938 found 329.0943.

- **2-(2-(4-Iodophenyl)-2-oxoethyl)cyclohex-2-en-1-one (5h)**

Compound 5h was prepared according to the general procedure F using 1-(4-iodophenyl)-2-(triphenylphosphoranylidene)ethan-1-one 4d (7.62 mmol, 3.85 g) and cyclohexan-1,2-dione (8 mmol, 0.90 g) in 38 mL CH\(_2\)Cl\(_2\). The title compound was obtained after flash chromatography as a yellow solid. Yield = 58 % (1.50 g). mp 85°C. Flash chromatography conditions: column 40g, flow rate = 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. R\(_f\) = 0.40 (cyclohexane/EtOAc 50/50).

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 2.05\) (p, \(J = 6.3\) Hz, 2H), 2.43 (q, \(J = 5.3\) Hz, 2H), 2.49 (t, \(J = 6.7\) Hz, 2H), 3.79 (s, 2H), 4.67 (t, \(J = 4.3\) Hz, 1H), 7.68 (d, \(J = 8.2\) Hz, 2H), 7.81 (d, \(J = 8.1\) Hz, 2H).

\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta = 23.1\) (CH\(_2\)), 26.3 (CH\(_2\)), 38.1 (CH\(_2\)), 38.9 (CH\(_2\)), 101.2 (C), 129.3 (2 x CH), 134.0 (C), 136.1 (C), 138.0 (2 x CH), 149.1 (CH), 197.0 (C), 198.4 (C).

HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{13}\)INaO\(_2\) [M+Na]\(^{+}\) = 362.9852 found 362.9896.

- **2-(2-(4-Fluorophenyl)-2-oxoethyl)cyclohex-2-en-1-one (5i)**

Compound 5i was prepared according to the general procedure F using 1-(4-fluorophenyl)-2-(triphenylphosphoranylidene)ethan-1-one 4e (4.3 mmol, 1.70 g) cyclohexan-1,2-dione (4.15 mmol, 0.50 g) in 22 mL CH\(_2\)Cl\(_2\). The title compound was obtained after flash chromatography as a yellow oil. Yield = 50 % (0.5 g). Flash chromatography conditions: column 40g, flow rate = 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. R\(_f\) = 0.40 (cyclohexane/EtOAc 50/50).

\(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta = 2.03\) (p, \(J = 6.1\) Hz, 2H), 2.36-2.44 (m, 2H), 2.45-2.50 (m, 2H), 3.79 (s, 2H), 6.86 (t, \(J = 4.1\) Hz, 1H), 7.10 (dd, \(J = 8.9, 8.4\) Hz, 2H), 7.93-8.03 (m, 2H).

\(^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta = 23.1\) (CH\(_2\)), 26.3 (CH\(_2\)), 38.1 (CH\(_2\)), 38.9 (CH\(_2\)), 115.0 (d, \(J = 21.8\) Hz, 2 x CH), 131.1 (d, \(J_{C,F} = 9.4\) Hz, 2 x CH), 133.2 (d, \(J_{C,F} = 3.1\) Hz, C), 134.0 (C), 149.0 (CH), 165.8 (d, \(J_{C,F} = 254.6\) Hz, C), 196.1 (C), 198.4 (C).
$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -105.3$ (s).

HRMS (ESI, m/z) calcd for C$_{14}$H$_{14}$FO$_2$ [M+H]$^+$ = 233.0972 found 233.0973.

- **2-(2-Oxo-2-(thiophen-2-yl)ethyl)cyclohex-2-en-1-one (5j)**

Compound 5j was prepared according to the general procedure F using 1-(thiophen-2-yl)-2-(triphenylphosphoranylidene)ethan-1-one 4f (3.6 mmol, 1.38 g) and cyclohexan-1,2-dione (3.32 mmol, 371 mg) in 18 mL CH$_2$Cl$_2$. The title compound was obtained after flash chromatography as a yellow solid. Yield = 51 % (400 mg). mp 60°C. Flash chromatography conditions: column 40g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. $R_f = 0.40$ (cyclohexane/EtOAc 50/50).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.02$ (p, $J = 6.1$ Hz, 2H), 2.34-2.42(m, 2H), 2.44-2.51 (m, 2H), 3.77 (s, 2H), 6.91 (t, $J = 4.2$ Hz, 1H), 7.10 (dd, $J = 5.0$, 3.8 Hz, 1H), 7.61 (dd, $J = 4.9$, 1.2 Hz, 1H), 7.78 (dd, $J = 3.8$, 1.2 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 23.0$ (CH$_2$), 26.3 (CH$_2$), 38.1 (CH$_2$), 39.4 (CH$_2$), 128.2 (CH), 132.7 (CH), 133.7 (C), 133.9 (CH), 144.0 (C), 149.1 (CH), 190.4 (C), 198.2 (C).

HRMS (ESI, m/z) calcd for C$_{12}$H$_{13}$O$_2$S [M+H]$^+$ = 221.0631 found 221.0594 and for C$_{12}$H$_{12}$NaO$_2$S [M+Na]$^+$ = 243.0450 found 243.0488.

- **2-(2-Oxo-2-(pyridin-2-yl)ethyl)cyclohex-2-en-1-one (5k)**

Compound 5k was prepared according to the general procedure F using 1-(pyridin-2-yl)-2-(triphenylphosphoranylidene)ethan-1-one 4g (4 mmol, 1.52 g) and cyclohexan-1,2-dione (4.2 mmol, 470 mg) in 20 mL toluene. The title compound was obtained after flash chromatography as a yellow solid. Yield = 61 % (522 mg). mp 76°C. Flash chromatography conditions: column 40g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. $R_f = 0.40$ (cyclohexane/EtOAc 50/50).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.02$ (p, $J = 6.1$ Hz, 2H), 2.37-2.41(m, 2H), 2.43-2.50 (m, 2H), 4.07 (s, 2H), 6.82 (t, $J = 4.1$ Hz, 1H), 7.42 (ddd, $J = 7.6$, 4.8, 1.3 Hz, 1H), 7.77 (ddd, $J = 7.7$, 7.7, 1.7 Hz, 1H), 7.96 (ddd, $J = 7.9$, 1.1, 1.1 Hz, 1H), 8.63 (ddd, $J = 4.8$, 1.8, 0.9 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 23.4$ (CH$_2$), 26.5 (CH$_2$), 38.4 (CH$_2$), 39.1 (CH$_2$), 122.3 (CH), 127.5 (CH), 135.1 (C), 137.2 (CH), 148.9 (CH), 149.2 (CH), 153.5 (C), 198.7 (C), 199.1 (C).
HRMS (ESI, m/z) calcd for C_{13}H_{14}NO_{2} [M+H]^+ = 216.1019 found 216.1043 and for C_{13}H_{13}NNaO_{2} [M+Na]^+ = 238.0838 found 238.0877.

g. **Indoles 6a-l**

- **1-Benzyl-2-methyl-1H-indole (6a)**

Compound 6a was prepared according to the general procedure G using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (0.59 mmol, 90 mg) and benzylamine (0.88 mmol, 94 mg) in 4.5 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 54 % (65 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.50 (cyclohexane/EtOAc 90/10).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta = 2.35 \text{ (s, 3H), 5.29 \text{ (s, 2H), 6.31 \text{ (s, 1H), 6.96 \text{ (d, J = 6.5 Hz, 2H), 7.04-7.10 \text{ (m, 2H), 7.17-7.25 \text{ (m, 4H), 7.51-7.57 \text{ (m, 1H).}}}} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta = 12.9 \text{ (CH}_3), 47.0 \text{ (CH}_2), 100.6 \text{ (CH), 109.3 \text{ (CH), 119.7 \text{ (CH), 119.8 \text{ (CH), 120.9 \text{ (CH), 126.1 \text{ (2 x CH), 127.4 \text{ (CH), 128.3 \text{ (C), 128.9 \text{ (2 x CH), 136.8 \text{ (C), 137.3 \text{ (C), 138.0 \text{ (C).}}}} \]

HRMS (APCI, m/z) calcd for C_{16}H_{16}N [M+H]^+ = 222.1277 found 222.1305.

- **1-Benzyl-2-ethyl-1H-indole (6b)**

Compound 6b was prepared according to the general procedure G using -(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and phenylmethanamine (0.81 mmol, 86 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 47 % (60 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.50 (cyclohexane/EtOAc 90/10).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \delta = 1.24 \text{ (t, J = 7.4 Hz, 3H), 2.61 \text{ (q, J = 7.8 Hz, 2H), 5.24 \text{ (s, 2H), 6.28 \text{ (s, 1H), 6.88 \text{ (d, J = 7.2 Hz, 2H), 6.97-7.04 \text{ (m, 2H), 7.12-7.19 \text{ (m, 4H), 7.48-7.52 \text{ (m, 1H).}}}} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \delta = 12.7 \text{ (CH}_3), 20.1 \text{ (CH}_2), 46.5 \text{ (CH}_2), 98.7 \text{ (CH), 104.3 \text{ (CH), 119.6 \text{ (CH), 120.0 \text{ (CH), 121.0 \text{ (CH), 126.1 \text{ (2 x CH), 127.3 \text{ (CH), 128.3 \text{ (C), 128.9 \text{ (2 x CH), 137.4 \text{ (C), 138.1 \text{ (C), 143.0 \text{ (C).}}}} \]
HRMS (APCI, m/z) calcd for C_{17}H_{18}N [M+H]^+ = 236.1434 found 236.1429 and for C_{17}H_{17}NNa [M+Na]^+ = 258.1253 found 258.1275.

• **2-Ethyl-1-phenethyl-1H-indole (6c)**

Compound 6c was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and 2-phenethylamine (0.81 mmol, 98 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 47% (63 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.50 (cyclohexane/EtOAc 90/10).

1H NMR (400 MHz, CDCl_3) δ = 1.19 (t, J = 7.6 Hz, 3H), 2.42 (q, J = 7.4 Hz 2H), 2.94 (t, J = 7.6 Hz, 2H), 4.19 (t, J = 7.6 Hz, 2H), 6.16 (s, 1H), 6.99-7.03 (m, 3H), 7.07 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 7.7 Hz, 1H).

13C NMR (101 MHz, CDCl_3) δ = 12.6 (CH3), 19.8 (CH2), 36.5 (CH2), 44.9 (CH2), 98.1 (CH), 109.0 (CH), 119.4 (CH), 120.0 (CH), 120.7 (CH), 126.8 (CH), 128.4 (C), 128.8 (2 x CH), 129.0 (2 x CH), 136.5 (C), 138.8 (C), 142.8 (C).

HRMS (APCI, m/z) calcd for C_{18}H_{20}N [M+H]^+ = 250.1590 found 250.1597.

• **2-Ethyl-1-(4-methoxybenzyl)-1H-indole (6d)**

Compound 6d was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and 4-methoxybenzylamine (0.81 mmol, 111 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 43% (62 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.50 (cyclohexane/EtOAc 90/10).

1H NMR (400 MHz, CDCl_3) δ = 1.24 (t, J = 7.5 Hz, 3H), 2.62 (q, J = 7.5 Hz, 2H), 3.67 (s, 3H), 5.18 (s, 2H), 6.26 (s, 1H), 6.71 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.97-7.05 (m, 2H), 7.13 (d, J = 7.1 Hz, 1H), 7.50 (dd, J = 6.9, 1.7 Hz, 1H).

13C NMR (101 MHz, CDCl_3) δ = 11.5 (CH3), 18.9 (CH2), 44.8 (CH2), 54.2 (CH3), 97.4 (CH), 108.2 (CH), 113.1 (2 x CH), 118.4 (CH), 118.8 (CH), 119.7 (CH), 126.1 (2 x CH), 127.1 (C), 128.9 (C), 136.2 (C), 141.8 (C), 157.7 (C).

HRMS (ESI, m/z) calcd for C_{19}H_{19}NNaO [M+Na]^+ = 288.1359 found 288.1370.
• **2-Ethyl-1-(1-phenylethyl)-1H-indole (6e)**

Compound 6e was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and methylbenzylamine (0.81 mmol, 98 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 41 % (55 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.50 (cyclohexane/EtOAc 90/10).

1H NMR (400 MHz, CDCl3) δ = 1.33 (t, J = 7.4 Hz, 3H), 1.93 (d, J = 7.1 Hz, 3H), 2.66-2.77 (m, 2H), 5.73 (q, J = 7.1 Hz, 2H), 6.32 (s, 1H), 6.89-6.96 (m, 2H), 6.97-7.04 (m, 1H), 7.15 (d, J = 7.5 Hz, 2H), 7.20-7.30 (m, 3H), 7.53 (d, J = 7.8 Hz, 1H).

13C NMR (101 MHz, CDCl3) δ = 13.2 (CH3), 18.7 (CH3), 20.9 (CH2), 52.3 (CH), 99.0 (CH), 111.5 (CH), 119.2 (CH), 120.0 (CH), 120.4 (CH), 126.4 (2 x CH), 127.4 (CH), 128.7 (2 x CH), 128.7 (C), 128.9 (CH), 135.8 (C), 141.6 (C), 143.0 (C).

HRMS (APCI, m/z) calcd for C18H20N [M+H]⁺ = 250.1590 found 250.1628.

• **2-Ethyl-1-(furan-2-ylmethyl)-1H-indole (6f)**

Compound 6f was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and 3-furylmethylamine (0.81 mmol, 79 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 54 % (66 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.50 (cyclohexane/EtOAc 90/10).

1H NMR (400 MHz, CDCl3) δ = 1.35 (t, J = 7.4 Hz, 3H), 2.78 (q, J = 7.4 Hz, 2H), 5.16 (s, 2H), 6.01 (d, J = 3.3 Hz, 1H), 6.21 (dd, J = 3.3, 1.8 Hz, 1H), 6.28 (s, 1H), 7.06 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 1.3 Hz, 1H), 7.32 (dd, J = 8.2, 8.2 Hz, 1H), 7.53 (dd, J = 7.7, 7.7 Hz, 1H).

13C NMR (101 MHz, CDCl3) δ = 13.0 (CH3), 19.9 (CH2), 40.1 (CH2), 98.7 (CH), 107.4 (CH), 109.2 (CH), 110.4 (CH), 119.6 (CH), 119.9 (CH), 120.9 (CH), 128.3 (C), 137.1 (C), 142.2 (CH), 142.6 (C), 151.0 (C).

**1,3-Bis(2-ethyl-1H-indol-1-yl)propane (6g)**

Compound 6g was prepared according to the adapted general procedure G using -(2-oxobutyl)cyclohex-2-en-1-one 5b (0.91 mmol, 1 equiv, 152 mg) and 1,3-diaminopropane (0.45 mmol, 0.5 equiv, 34 mg) in 8 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 46 % (68 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.50 (cyclohexane/EtOAc 90/10).

1H NMR (400 MHz, CDCl_3) \( \delta = 1.31 \) (t, \( J = 7.4 \) Hz, 6H), 2.18-2.26 (m, 2H), 2.62 (q, \( J = 7.4 \) Hz, 4H), 4.09 (t, \( J = 7.2 \) Hz, 4H), 6.28 (s, 2H), 7.04-7.08 (m, 2H), 7.09-7.15 (m, 4H), 7.55 (d, \( J = 7.5 \) Hz, 2H).

13C NMR (101 MHz, CDCl_3) \( \delta = 13.1 \) (2 x CH₃), 20.3 (2 x CH₂), 31.0 (CH₂), 40.8 (2 x CH₂), 99.0 (2 x CH), 109.1 (2 x CH), 119.8 (2 x CH), 120.5 (2 x CH), 121.2 (2 x CH), 128.6 (2 x C), 137.0 (2 x C), 142.6 (2 x C).

HRMS (APCI, m/z) calcd for C_{23}H_{27}N_{2} \([M+H]^+\) = 331.2169 found 331.2162.

**3-(2-Ethyl-1H-indol-1-yl)-N,N-dimethylpropan-1-amine (6h)**

Compound 6h was prepared according to the general procedure G using using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (1 mmol, 166 mg) and 3-(dimethylamino)-1-propylamine (1.5 mmol, 153 mg) in 7.5 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 46 % (96 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.30 (cyclohexane/EtOAc 60/40).

1H NMR (400 MHz, CDCl_3) \( \delta = 1.38 \) (t, \( J = 7.4 \) Hz, 3H), 1.92-1.99 (m, 2H), 2.28 (s, 6H), 2.35 (t, \( J = 7.0 \) Hz, 2H), 2.77 (q, \( J = 7.5 \) Hz, 2H), 4.14 (t, \( J = 7.3 \) Hz, 2H), 6.27 (s, 1H), 7.06 (t, \( J = 7.4 \) Hz, 1H), 7.13 (t, \( J = 7.6 \) Hz, 1H), 7.30 (d, \( J = 8.2 \) Hz, 1H), 7.54 (d, \( J = 7.7 \) Hz, 1H).

13C NMR (101 MHz, CDCl_3) \( \delta = 12.8 \) (CH₃), 20.0 (CH₂), 28.0 (CH₂), 41.0 (CH₂), 45.3 (2 x CH₃), 56.7 (CH₂), 98.2 (CH), 109.1 (CH), 119.3 (CH), 120.0 (CH), 120.7 (CH), 128.3 (C), 136.8 (C), 142.7 (C).

HRMS (ESI, m/z) calcd for C_{13}H_{23}N_{2} \([M+H]^+\) = 231.1856 found 231.1842.
• 4-(2-(2-Methyl-1H-indol-1-yl)ethyl)morpholine (6i)

Compound 6i was prepared according to the general procedure G using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (1 mmol, 152 mg) and 4-(2-aminoethyl)morpholine (1.5 mmol, 195 mg) in 7.5 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 50 % (122 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. \( R_f = 0.30 \) (cyclohexane/EtOAc 60/40).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3^) \delta = 2.55 \text{ (s, 3H), 2.60 (t, } J = 7.4 \text{ Hz, 4H), 2.75 (t, } J = 6.7 \text{ Hz, 2H), 3.82 (t, } J = 7.5 \text{ Hz, 4H), 4.30 (t, } J = 6.5 \text{ Hz, 2H), 6.34 (s, 1H), 7.16 (ddd, } J = 8, 7, 1.1 \text{ Hz, 1H), 7.24 (ddd, } J = 8.2, 7.1, 1.3 \text{ Hz, 1H), 7.37 (dd, } J = 8.1, 1 \text{ Hz, 1H), 7.62 (d, } J = 7.7 \text{ Hz, 1H).} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3^) \delta = 12.9 \text{ (CH}_3^), 41.1 \text{ (CH}_2^), 54.2 \text{ (CH}_2^), 58.0 \text{ (CH}_2^), 67.0 \text{ (CH}_2^), 100.3 \text{ (CH), 108.9 (CH), 119.5 (CH), 119.9 (CH), 120.6 (CH), 128.3 (C), 136.5 (C), 136.6 (C).} \]

HRMS (ESI, m/z) calcd for C\textsubscript{15}H\textsubscript{21}N\textsubscript{2}O \([M+H]^+ = 245.1648 \) found 245.1676.

• 4-(2-(2-Ethyl-1H-indol-1-yl)ethyl)morpholine (6j)

Compound 6j was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (1 mmol, 166 mg) and 4-(2-aminoethyl)morpholine (1.5 mmol, 195 mg) in 8 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 47 % (118 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. \( R_f = 0.30 \) (cyclohexane/EtOAc 60/40).

\[ ^1H \text{ NMR (200 MHz, CDCl}_3^) \delta = 1.38 \text{ (t, } J = 7.5 \text{ Hz, 3H), 2.50 (t, } J = 6.7 \text{ Hz, 4H), 2.64 (t, } J = 6.7 \text{ Hz, 2H), 2.77 (q, } J = 7.4 \text{ Hz, 2H), 3.71 (t, } J = 6.5 \text{ Hz, 4H), 4.20 (t, } J = 6.7 \text{ Hz, 2H), 6.26 (s, 1H), 7.00-7.19 (m, 2H), 7.28 (d, } J = 7.9 \text{ Hz, 1H), 7.53 (d, } J = 7.9 \text{ Hz, 1H).} \]

\[ ^{13}C \text{ NMR (50 MHz, CDCl}_3^) \delta = 12.7 \text{ (CH}_3^), 20.0 \text{ (CH}_2^), 40.9 \text{ (CH}_2^), 54.2 \text{ (2 x CH}_2^), 57.9 \text{ (CH}_2^), 67.0 \text{ (2 x CH}_2^), 98.3 \text{ (CH), 108.9 (CH), 119.4 (CH), 120.0 (CH), 120.7 (CH), 128.3 (C), 136.7 (C), 142.6 (C).} \]

HRMS (ESI, m/z) calcd for C\textsubscript{16}H\textsubscript{23}N\textsubscript{2}O \([M+H]^+ = 259.1805 \) found 259.1804.
**2-Methyl-1-(pyridin-4-ylmethyl)-1H-indole (6k)**

Compound 6k was prepared according to the general procedure G using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (1 mmol, 152 mg) and 4-(aminomethyl)pyridine (1.5 mmol, 162 mg) in 7.5 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 53 % (118 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.35$ (s, 3H), 5.27 (s, 2H), 6.38 (s, 1H), 6.85 (d, $J = 5.8$ Hz, 2H), 7.09-7.15 (m, 3H), 7.55-7.63 (m, 1H), 8.49 (d, $J = 6.1$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 12.7$ (CH$_3$), 45.5 (CH$_2$), 101.2 (CH), 108.9 (CH), 120.0 (CH), 120.1 (2 x CH), 121.1 (CH), 121.2 (CH), 128.3 (C), 137.4 (C), 147.1 (C), 147.3 (C), 150.3 (2 x CH).

HRMS (ESI, m/z) calcd for C$_{15}$H$_{15}$N$_2$ [M+H]$^+$ = 223.1230 found 223.1229.

**2-Ethyl-1-(pyridin-4-ylmethyl)-1H-indole (6l)**

Compound 6l was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (1 mmol, 166 mg) and 4-(aminomethyl)pyridine (1.5 mmol, 162 mg) in 7.5 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 52 % (110 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

$^1$H NMR (200 MHz, CDCl$_3$) $\delta = 1.24$ (t, $J = 7.4$ Hz, 3H), 2.57 (q, $J = 7.4$ Hz, 2H), 5.21 (s, 2H), 6.31 (s, 1H), 6.76 (d, $J = 5.4$ Hz, 2H), 7.03 (d, $J = 3.2$ Hz, 3H), 7.45-7.59 (m, 1H), 8.40 (d, $J = 5.8$ Hz, 2H).

$^{13}$C NMR (50 MHz, CDCl$_3$) $\delta = 12.7$ (CH$_3$), 20.0 (CH$_2$), 45.5 (CH$_2$), 99.3 (CH), 108.9 (CH), 120.0 (CH), 120.2 (CH), 121.1 (2 x CH), 121.3 (CH), 128.3 (C), 137.1 (C), 142.6 (C), 147.3 (C), 150.3 (2 x CH).

HRMS (ESI, m/z) calcd for C$_{16}$H$_{17}$N$_2$ [M+H]$^+$ = 237.1386 found 237.1371.
h. Indolones 7a-k

- **1-Benzyl-2-methyl-1,5,6,7-tetrahydro-4H-indol-4-one (7a)**

Compound 7a was prepared according to the general procedure G using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (0.59 mmol, 90 mg) and benzylamine (0.88 mmol, 94 mg) in 4.5 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 10 % (14 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

1H NMR (400 MHz, CDCl3) δ = 2.08-2.13 (m, 2H), 2.14 (s, 3H), 2.48 (t, J = 7.4 Hz, 2H), 2.63 (t, J = 6.2 Hz, 2H), 5.03 (s, 2H), 6.35 (s, 1H), 6.92 (d, J = 7.5 Hz, 2H), 7.29-7.35 (m, 3H).

13C NMR (101 MHz, CDCl3) δ = 12.1 (CH3), 22.1 (CH2), 23.8 (CH2), 37.8 (CH2), 47.2 (CH2), 103.8 (CH), 120.1 (CH), 125.7 (2 x CH), 127.6 (C), 129.0 (2 x CH), 130.7 (C), 136.7 (C), 143.8 (C), 194.1 (C).

HRMS (ESI, m/z) calcd for C16H18NO [M+H]+ = 240.1383 found 240.1409 and calcd for C16H17NNaO [M+Na]+ = 262.1202 found 262.1234.

- **1-Benzyl-2-ethyl-1,5,6,7-tetrahydro-4H-indol-4-one (7b)**

Compound 7b was prepared according to the general procedure H using -(2-oxobutyl)cyclohex-2-en-1-one 5b (0.42 mmol, 70 mg) and phenylmethanamine (0.63 mmol, 67 mg) in 10 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 63 % (67 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

1H NMR (400 MHz, CDCl3) δ = 1.19 (t, J = 7.5 Hz, 3H), 2.10 (p, J = 6.9 Hz, 2H), 2.41-2.46 (m, 2H), 2.62 (t, J = 6.3 Hz, 2H), 5.04 (s, 2H), 6.38 (s, 1H), 6.88-6.92 (m, 2H), 7.26-7.34 (m, 3H).

13C NMR (101 MHz, CDCl3) δ = 12.4 (CH3), 19.4 (CH2), 22.1 (CH2), 23.9 (CH2), 37.9 (CH2), 47.1 (CH2), 102.0 (CH), 120.1 (C), 125.7 (2 x CH), 127.7 (CH), 129.1 (2 x CH), 136.9 (C), 137.3 (C), 144.1 (C), 194.3 (C).

HRMS (ESI, m/z) calcd for C17H20NO [M+H]+ = 254.1539 found 254.1491.
• 2-Ethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (7c)

Compound 7c was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and 2-phenethylamine (0.81 mmol, 98 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 11 % (15 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 1.26 (t, $J = 7.4$ Hz, 3H), 1.91-1.96 (m, 2H), 2.28 (t, $J = 6.2$ Hz , 2H), 2.35 (t, $J = 7.1$ Hz, 2H), 2.48 (q, $J = 7.4$ Hz, 2H), 2.90 (t, $J = 7.0$ Hz, 2H), 3.97 (t, $J = 7.0$ Hz, 2H), 6.32 (s, 1H), 6.97 (d, $J = 7.7$ Hz, 2H), 7.24-7.26 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 12.5 (CH$_3$), 19.4 (CH$_2$), 22.0 (CH$_2$), 23.9 (CH$_2$), 37.2 (CH$_2$), 37.8 (CH$_2$), 45.6 (CH$_2$), 102.1 (CH), 119.7 (C), 127.1 (CH), 128.9 (2 x CH), 129.0 (2 x CH), 136.5 (C), 137.8 (C), 144.1 (C), 194.3 (C).

HRMS (ESI, m/z) calcd for C$_{18}$H$_{22}$NO $[M+H]^+$ = 268.1696 found 268.1676 and for C$_{18}$H$_{21}$NNaO $[M+Na]^+$ = 290.1515 found 290.1491.

• 2-Ethyl-1-(4-methoxybenzyl)-1,5,6,7-tetrahydro-4H-indol-4-one (7d)

Compound 7d was prepared according to the general procedure H using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.30 mmol, 50 mg) and 4-methoxybenzylamine (0.45 mmol, 62 mg) in 9 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 48 % (41 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 1.21 (t, $J = 7.4$ Hz, 3H), 2.11 (p, $J = 6.2$ Hz, 2H), 2.42-2.48 (m, 4H), 2.63 (t, $J = 6.2$ Hz, 2H), 3.78 (s, 3H), 4.97 (s, 2H), 6.38 (s, 1H), 6.84 (s, 4H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 12.5 (CH$_3$), 19.5 (CH$_2$), 22.2 (CH$_2$), 24.0 (CH$_2$), 37.9 (CH$_2$), 46.7 (CH$_2$), 55.4 (CH$_3$), 102.0 (CH), 114.5 (2 x CH), 120.1 (C), 127.0 (2 x CH), 128.9 (C), 137.3 (C), 144.1 (C), 159.2 (C), 194.3 (C).

HRMS (ESI, m/z) calcd for C$_{18}$H$_{22}$NO$_2$ [M+H]$^+$ = 284.1645 found 284.1629 and for C$_{18}$H$_{21}$NNaO$_2$ [M+Na]$^+$ = 306.1464 found 306.1442.
2-Ethyl-1-(1-phenylethyl)-1,5,6,7-tetrahydro-4H-indol-4-one (7e)

Compound 7e was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and methylbenzylamine (0.81 mmol, 98 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 13% (19 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. $R_f = 0.30$ (cyclohexane/EtOAc 60/40).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 1.22$ (t, $J = 7.4$ Hz, 3H), 1.88 (d, $J = 7.2$ Hz, 3H), 1.95-2.04 (m, 2H), 2.22-2.29 (m, 2H), 2.37-2.41 (m, 2H), 2.50-2.63 (m, 2H), 5.50 (q, $J = 7.2$ Hz, 2H), 6.38 (s, 1H), 7.04-7.07 (m, 2H), 7.28-7.36 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 13.2$ (CH$_3$), 19.7 (CH$_3$), 20.7 (CH$_2$), 24.1 (CH$_2$), 24.5 (CH$_2$), 38.1 (CH$_2$), 53.2 (CH), 102.6 (CH), 121.0 (2 x CH), 126.3 (C), 127.9 (2 x CH), 129.2 (CH), 137.7 (C), 141.2 (C), 144.0 (C), 194.7 (C).

HRMS (ESI, m/z) calcd for C$_{18}$H$_{22}$NO $[M+H]^+ = 268.1696$ found 268.1699 and for C$_{18}$H$_{21}$NNaO $[M+Na]^+ = 290.1515$ found 290.1519.

2-Ethyl-1-(furan-2-ylmethyl)-1,5,6,7-tetrahydro-4H-indol-4-one (7f)

Compound 7f was prepared according to the general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.54 mmol, 90 mg) and 3-furylmethylamine (0.81 mmol, 79 mg) in 4 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 13% (17 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. $R_f = 0.30$ (cyclohexane/EtOAc 60/40).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 1.25$ (t, $J = 7.4$ Hz, 3H), 2.14 (p, $J = 6.3$ Hz, 2H), 2.43-2.47 (m, 2H), 2.55-2.63 (m, 2H), 2.80 (t, $J = 6.2$ Hz, 2H), 4.93 (s, 2H), 6.10 (dd, $J = 3.3, 0.9$ Hz , 1H), 6.30-6.32 (m, 2H), 7.35 (dd, $J = 1.9, 0.8$ Hz, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 12.3$ (CH$_3$), 19.4 (CH$_2$), 22.1 (CH$_2$), 23.8 (CH$_2$), 37.8 (CH$_2$), 40.8 (CH$_2$), 101.8 (CH), 107.9 (CH), 110.6 (CH), 120.1 (C), 137.0 (C), 142.9 (CH), 144.0 (C), 149.8 (C), 194.2 (C).

HRMS (ESI, m/z) calcd for C$_{15}$H$_{18}$NO$_2$ $[M+H]^+ = 244.1332$ found 244.1347 and for C$_{15}$H$_{17}$NNaO$_2$ $[M+Na]^+ = 266.1151$ found 266.1164.
• 1-(4-Bromobenzyl)-2-methyl-1,5,6,7-tetrahydro-4H-indol-4-one (7g)

Compound 7g was prepared according to the general procedure H using -(2-oxopropyl)cyclohex-2-en-1-one 5a (0.33 mmol, 50 mg) and (4-bromophenyl)methanamine (0.49 mmol, 91 mg) in 8 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 51 % (54 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

\[ \text{1H NMR} (400 \text{ MHz, CDCl}_3) \delta = 2.08-2.13 (m, 2H), 2.12 (s, 3H), 2.45 (t, J = 6.9 Hz, 2H), 2.61 (t, J = 6.2 Hz, 2H), 4.97 (s, 2H), 6.34 (s, 1H), 6.79 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H). \]

\[ \text{13C NMR} (101 \text{ MHz, CDCl}_3) \delta = 12.2 (\text{CH}_3), 22.2 (\text{CH}_2), 24.0 (\text{CH}_2), 38.0 (\text{CH}_2), 46.8 (\text{CH}_2), 104.1 (\text{CH}), 120.4 (\text{C}), 121.7 (\text{C}), 127.5 (2 \times \text{CH}), 130.7 (\text{C}), 132.3 (2 \times \text{CH}), 135.9 (\text{C}), 143.7 (\text{C}), 194.1 (\text{C}). \]

HRMS (ESI, m/z) calcd for C_{16}H_{16}BrNNaO [M+Na]^+ = 340.0307 found 340.0297.

• 1-(Furan-2-ylmethyl)-2-methyl-1,5,6,7-tetrahydro-4H-indol-4-one (7h)

Compound 7h was prepared according to the general procedure H using -(2-oxopropyl)cyclohex-2-en-1-one 5a (0.33 mmol, 50 mg) and furan-2-ylmethanamine (0.49 mmol, 47 mg) in 8 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 56 % (42 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

\[ \text{1H NMR} (400 \text{ MHz, CDCl}_3) \delta = 2.14 (p, J = 6.3 Hz, 2H), 2.26 (s, 3H), 2.44 (t, J = 6.2 Hz, 2H), 2.79 (t, J = 6.2 Hz, 2H), 4.92 (s, 2H), 6.12 (d, J = 3.0 Hz, 1H), 6.27 (s, 1H), 6.31 (dd, J = 3.3, 1.9 Hz, 1H), 7.35 (d, J = 1.6 Hz, 1H). \]

\[ \text{13C NMR} (101 \text{ MHz, CDCl}_3) \delta = 12.2 (\text{CH}_3), 22.1 (\text{CH}_2), 23.8 (\text{CH}_2), 37.9 (\text{CH}_2), 40.9 (\text{CH}_2), 103.7 (\text{CH}), 107.9 (\text{CH}), 111.0 (\text{CH}), 120.1 (\text{C}), 130.6 (\text{C}), 142.9 (\text{CH}), 143.9 (\text{C}), 149.8 (\text{C}), 194.1 (\text{C}). \]

HRMS (ESI, m/z) calcd for C_{14}H_{16}NO_2 [M+H]^+ = 230.1176 found 230.1201 and for C_{14}H_{15}NNaO_2 [M+Na]^+ = 252.0995 found 252.0984.
**1-(Pyridin-4-ylmethyl)-2-ethyl-1,5,6,7-tetrahydro-4H-indol-4-one (7i)**

Compound 7i was prepared according to the general procedure H using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (0.59 mmol, 90 mg) and 4-(aminomethyl)pyridine (0.89 mmol, 96 mg) in 15 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 51% (72 mg). Flash chromatography conditions: column 24 g, flow rate = 20 mL/min, cyclohexane/EtOAc 100/0 to 0/100. Rf = 0.11 (EtOAc 100%).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 2.15 (s, 3H), 2.19-2.11 (m, 2H), 2.49 (t, J = 6.2 Hz, 2H), 2.62 (t, J = 6.2 Hz, 2H), 5.05 (s, 2H), 6.40 (s, 1H), 6.86 (d, J = 5.5 Hz, 2H), 8.59 (d, J = 5.7 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 11.8 (CH$_3$), 22.0 (CH$_2$), 23.7 (CH$_2$), 37.7 (CH$_2$), 46.2 (CH$_2$), 104.4 (CH), 120.56 (2 x CH), 120.59 (C), 130.3 (C), 143.2 (C), 145.9 (C), 150.5 (2 x CH), 193.6 (C).

HRMS (APCI, m/z) calcd for C$_{15}$H$_{17}$N$_2$O [M+H]$^+$ = 241.1335 found 241.1344.

**2-Methyl-1-phenethyl-1,5,6,7-tetrahydro-4H-indol-4-one (7j)**

Compound 7j was prepared according to the general procedure H using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (0.33 mmol, 50 mg) and 2-phenylethan-1-amine (0.49 mmol, 59 mg) in 8 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 50% (42 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 1.93 (p, J = 6.3 Hz ,2H), 2.16 (s, 3H), 2.27 (t, J = 6.2 Hz, 2H), 2.36 (t, J = 6.2 Hz, 2H), 2.91 (t, J = 6.9 Hz, 2H), 3.97 (t, J = 6.9 Hz, 2H), 6.27 (s, 1H), 6.96 (dd, J = 7.3, 2.2 Hz, 2H), 7.21-7.29 (m, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 12.1 (CH$_3$), 22.0 (CH$_2$), 23.8 (CH$_2$), 37.1 (CH$_2$), 37.8 (CH$_2$), 45.7 (CH$_2$), 103.9 (CH), 119.8 (C), 127.1 (CH), 128.8 (2 x CH), 129.0 (2 x CH), 130.1 (C), 137.7 (C), 143.9 (C), 194.1 (C).

HRMS (ESI, m/z) calcd for C$_{17}$H$_{20}$NO [M+H]$^+$ = 254.1539 found 254.1544 and for C$_{17}$H$_{19}$NNaO [M+Na]$^+$ = 276.1359 found 276.135.
1-Phenethyl-2-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (7k)

Compound 7k was prepared according to the general procedure H using 2-(2-oxo-2-phenylethyl)cyclohex-2-en-1-one 5f (0.23 mmol, 50 mg) and 2-phenylethan-1-amine (0.34 mmol, 41 mg) in 7 mL butanol. The title compound was obtained after flash chromatography as a yellow oil. Yield = 54 % (40 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. Rf = 0.30 (cyclohexane/EtOAc 60/40).

1H NMR (400 MHz, CDCl3) δ = 2.00 (p, J = 6.3 Hz, 2H), 2.37-2.46 (m, 4H), 2.68 (t, J = 7.1 Hz, 2H), 4.11 (t, J = 7.1 Hz, 2H), 6.58 (s, 1H), 6.82 (dd, J = 6.5, 3.0 Hz, 2H), 7.18-7.22 (m, 3H), 7.35-7.47 (m, 5H).

13C NMR (101 MHz, CDCl3) δ = 22.3 (CH2), 23.8 (CH2), 37.0 (CH2), 38.0 (CH2), 46.2 (CH2), 106.2 (CH), 120.3 (C), 127.0 (CH), 128.0 (CH), 128.7 (2 x CH), 128.8 (2 x CH), 128.9 (2 x CH), 129.4 (2 x CH), 132.8 (C), 135.7 (C), 137.6 (C), 146.1 (C), 194.4 (C).

HRMS (ESI, m/z) calcd for C22H22NO [M+H]+ = 316.1696 found 316.1719 and for C22H21NNaO [M+Na]+ = 338.1515 found 338.1502.

i. Cinnolines 8a-k

3-Methyl-5,6,7,8-tetrahydrocinnoline (8a)

Compound 8a was prepared according to the general procedure I using 2-(2-oxopropyl)cyclohex-2-en-1-one 5a (1 mmol, 152 mg). The title compound was obtained after flash chromatography as a yellow oil. Yield = 82 % (121 mg). Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. Rf = 0.20 (EtOAc 100 %).

1H NMR (300 MHz, CDCl3) δ = 1.79-1.86 (m, 2H), 1.88-1.96 (m, 2H), 2.61 (s, 3H), 2.75 (t, J = 6.1 Hz, 2H), 3.09 (t, J= 6.4 Hz, 2H), 7.00 (s, 1H).

13C NMR (75 MHz, CDCl3) δ = 21.7 (CH3), 21.9 (CH2), 22.6 (CH2), 27.9 (CH2), 29.7 (CH2), 126.6 (CH), 137.1 (C), 157.2 (C), 158.3 (C).

HRMS (ESI, m/z) calcd for C9H13N2 [M+H]+ = 149.1073 found 149.1105 for C9H12N2Na [M+Na]+ = 171.0893 found 171.0913.
**3-Ethyl-5,6,7,8-tetrahydrocinnoline (8b)**

Compound 8b was prepared according to the general procedure I using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (1 mmol, 166 mg). The title compound was obtained after flash chromatography as a yellow oil. Yield = 90 % (146 mg). Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. Rf = 0.20 (EtOAc 100 %).

$^1$H NMR (300 MHz, CDCl$_3$) δ = 1.23 (t, $J$ = 6 Hz, 3H), 1.67-1.75 (m, 2H), 1.78-1.86 (m, 2H), 2.67 (t, $J$ = 6.3 Hz, 2H), 2.82 (q, $J$ = 7.6 Hz, 2H), 2.99 (t, $J$ = 6.4 Hz, 2H), 6.90 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ = 14.3 (CH$_3$), 22.3 (CH$_2$), 23.0 (CH$_2$), 28.4 (CH$_2$), 29.3 (CH$_2$), 30.1 (CH$_2$), 125.8 (CH), 137.5 (C), 158.8 (C), 162.9 (C).

HRMS (APCI, m/z) calcd for C$_{10}$H$_{15}$N$_2$ [M+H]$^+$ = 163.1230 found 163.1268.

**3,6,6-Trimethyl-5,6,7,8-tetrahydrocinnoline (8c)**

Compound 8c was prepared according to the general procedure I using 4,4-dimethyl-2-(2-oxopropyl)cyclohex-2-en-1-one 5c (1 mmol, 176 mg). The title compound was obtained after flash chromatography as a yellow oil. Yield = 86% (151 mg). Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. Rf = 0.20 (EtOAc 100 %).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 0.97 (s, 6H), 1.68 (t, $J$ = 6.9 Hz, 2H), 2.47 (s, 2H), 2.58 (s, 3H), 3.09 (t, $J$ = 6.9 Hz, 2H), 6.93 (s, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 21.8 (CH$_3$), 26.6 (CH$_2$), 27.9 (2 x CH$_3$), 29.2 (C), 35.3 (CH), 42.0 (CH$_2$), 127.2 (CH), 136.5 (C), 157.3 (C), 157.5 (C).

HRMS (ESI, m/z) calcd for C$_{11}$H$_{17}$N$_2$ [M+H]$^+$ = 177.1386 found 177.1418.

**3-Ethyl-6,6-dimethyl-5,6,7,8-tetrahydrocinnoline (8d)**

Compound 8d was prepared according to the general procedure I using 4,4-dimethyl-2-(2-oxobutyl)cyclohex-2-en-1-one 5d (1 mmol, 190 mg). The title compound was obtained after flash chromatography as a yellow solid. Yield = 92 % (175 mg). mp 38°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. Rf = 0.20 (EtOAc 100 %).
\( ^{1} \text{H NMR} \ (400 \text{ MHz, CDCl} \_3) \ \delta = 0.99 \ (s, \ 6\text{H}), \ 1.31 \ (t, \ J = 7.6 \text{ Hz, } 3\text{H}), \ 1.70 \ (t, \ J = 6.9 \text{ Hz, } 2\text{H}), \ 2.50 \ (s, \ 2\text{H}), \ 2.90 \ (q, \ J = 7.6 \text{ Hz, } 2\text{H}), \ 3.12 \ (t, \ J = 6.9 \text{ Hz, } 2\text{H}), \ 6.94 \ (s, \ 1\text{H}). \)

\( ^{13} \text{C NMR} \ (101 \text{ MHz, CDCl} \_3) \ \delta = 14.0 \ (\text{CH}_3), \ 26.7 \ (\text{CH}_2), \ 27.9 \ (2 \times \text{CH}_3), \ 29.0 \ (\text{CH}_2), \ 29.2 \ (\text{C}), \ 35.4 \ (\text{CH}_2), \ 42.1 \ (\text{CH}_2), \ 126.0 \ (\text{CH}), \ 136.5 \ (\text{C}), \ 158.0 \ (\text{C}), \ 162.2 \ (\text{C}). \)

HRMS (ESI, m/z) calcd for C\(_{12}\)H\(_{19}\)N\(_2\) [M+H]\(^{+}\) = 191.1543 found 191.1583.

- **3-(Tert-butyl)-5,6,7,8-tetrahydrocinnoline (8e)**

Compound 8e was prepared according to the general procedure I using 2-(3,3-dimethyl-2-oxobutyl)cyclohex-2-en-1-one 5e (1 mmol, 194 mg). The title compound was obtained after flash chromatography as a white solid. Yield = 77 % (146 mg), mp 102°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. \( R_f = 0.20 \) (EtOAc 100 %).

\( ^{1} \text{H NMR} \ (400 \text{ MHz, CDCl} \_3) \ \delta = 1.37 \ (s, \ 9\text{H}), \ 1.70-1.81 \ (m, \ 2\text{H}), \ 1.82-1.94 \ (m, \ 2\text{H}), \ 2.72 \ (t, \ J = 6.4 \text{ Hz, } 2\text{H}), \ 3.05 \ (t, \ J = 6.5 \text{ Hz, } 2\text{H}), \ 7.09 \ (s, \ 1\text{H}). \)

\( ^{13} \text{C NMR} \ (101 \text{ MHz, CDCl} \_3) \ \delta = 22.4 \ (\text{CH}_2), \ 23.0 \ (\text{CH}_2), \ 28.6 \ (\text{CH}_2), \ 30.1 \ (\text{CH}_2), \ 30.4 \ (3 \times \text{CH}_3), \ 36.7 \ (\text{C}), \ 123.0 \ (\text{CH}), \ 137.0 \ (\text{C}), \ 158.4 \ (\text{C}), \ 167.9 \ (\text{C}). \)

HRMS (ESI, m/z) calcd for C\(_{12}\)H\(_{19}\)N\(_2\) [M+H]\(^{+}\) = 191.1543 found 191.1533 and for C\(_{12}\)H\(_{18}\)N\(_2\)Na [M+Na]\(^{+}\) = 213.1362 found 213.1350.

- **3-Phenyl-5,6,7,8-tetrahydrocinnoline (8f)**

Compound 8f was prepared according to the general procedure I using 2-(2-oxo-2-phenylethyl)cyclohex-2-en-1-one 5f (1 mmol, 214 mg). The title compound was obtained after flash chromatography as a yellow solid. Yield = 81 % (170 mg), mp 86°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. \( R_f = 0.20 \) (EtOAc 100 %).

\( ^{1} \text{H NMR} \ (400 \text{ MHz, CDCl} \_3) \ \delta = 1.81-1.90 \ (m, \ 2\text{H}), \ 1.91-2.01 \ (m, \ 2\text{H}), \ 2.84 \ (t, \ J = 6.3 \text{ Hz, } 2\text{H}), \ 3.17 \ (t, \ J = 6.4 \text{ Hz, } 2\text{H}), \ 7.41-7.51 \ (m, \ 4\text{H}), \ 8.00-8.06 \ (m, \ 2\text{H}). \)

\( ^{13} \text{C NMR} \ (101 \text{ MHz, CDCl} \_3) \ \delta = 22.2 \ (\text{CH}_2), \ 22.8 \ (\text{CH}_2), \ 28.5 \ (\text{CH}_2), \ 30.1 \ (\text{CH}_2), \ 124.0 \ (\text{CH}), \ 127.1 \ (2 \times \text{CH}), \ 129.1 \ (2 \times \text{CH}), \ 129.7 \ (\text{CH}), \ 137.0 \ (\text{C}), \ 137.8 \ (\text{C}), \ 157.2 \ (\text{C}), \ 159.9 \ (\text{C}). \)
HRMS (ESI, m/z) calcd for C\textsubscript{14}H\textsubscript{15}N\textsubscript{2} [M+H]\textsuperscript{+} = 211.1230 found 211.1240 and for C\textsubscript{14}H\textsubscript{14}N\textsubscript{2}Na [M+Na]\textsuperscript{+} = 233.1049 found 233.1045.

- **3-([1,1'-Biphenyl]-4-yl)-5,6,7,8-tetrahydrocinnoline (8g)**

Compound 8g was prepared according to the general procedure I using 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)cyclohex-2-en-1-one 5g (1 mmol, 290 mg). The title compound was obtained after flash chromatography as a yellow solid. Yield = 86 % (246 mg). mp 145°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. R\textsubscript{f} = 0.20 (EtOAc 100 %).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 1.82-1.86 (m, 2H), 1.91-1.97 (m, 2H), 2.82 (t, J = 6.4 Hz, 2H), 3.16 (t, J = 6.4 Hz, 2H), 7.36 (dd, J = 7.3, 7.3 Hz, 1H), 7.42-7.50 (m, 3H), 7.64 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.3 Hz, 2H).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ = 22.0 (CH\textsubscript{2}), 22.6 (CH\textsubscript{2}), 28.3 (CH\textsubscript{2}), 29.9 (CH\textsubscript{2}), 123.4 (CH), 127.1 (2 x CH), 127.3 (2 x CH), 127.5 (2 x CH), 127.7 (CH), 128.9 (2 x CH), 136.7 (C), 137.4 (C), 140.4 (C), 142.2 (C), 156.9 (C), 159.3 (C).

HRMS (ESI, m/z) calcd for C\textsubscript{20}H\textsubscript{19}N\textsubscript{2} [M+H]\textsuperscript{+} = 287.1543 found 287.1559 and for C\textsubscript{20}H\textsubscript{18}N\textsubscript{2}Na [M+Na]\textsuperscript{+} = 309.1362 found 309.1335.

- **3-(4-Iodophenyl)-5,6,7,8-tetrahydrocinnoline (8h)**

Compound 8g was prepared according to the general procedure I using 2-(2-(4-iodophenyl)-2-oxoethyl)cyclohex-2-en-1-one 5h (1 mmol, 340 mg). The title compound was obtained after flash chromatography as a yellow solid. Yield = 82 % (275.5 mg). mp 155°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. R\textsubscript{f} = 0.20 (EtOAc 100 %).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 1.82-1.91 (m, 2H), 1.93-2.01 (m, 2H), 2.85 (t, J = 6.6 Hz, 2H), 3.17 (t, J = 6.4 Hz, 2H), 7.47 (s, 1H), 7.73-7.90 (m, 4H).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ = 22.01 (CH\textsubscript{2}), 22.6 (CH\textsubscript{2}), 28.4 (CH\textsubscript{2}), 30.0 (CH\textsubscript{2}), 96.1 (C), 123.4 (CH), 128.7 (2 x CH), 136.4 (C), 137.7 (C), 138.2 (2 x CH), 156.2 (C), 159.8 (C).

HRMS (ESI, m/z) calcd for C\textsubscript{14}H\textsubscript{13}IN\textsubscript{2} [M+H]\textsuperscript{+} = 337.0196 found 337.0235 and for C\textsubscript{14}H\textsubscript{13}IN\textsubscript{2}Na [M+Na]\textsuperscript{+} = 359.0016 found 358.9992.
3-(4-Fluorophenyl)-5,6,7,8-tetrahydrocinnoline (8i)

Compound 8i was prepared according to the general procedure I using 2-(2-(4-fluorophenyl)-2-oxoethyl)cyclohex-2-en-1-one 5i (1 mmol, 232 mg). The title compound was obtained after flash chromatography as a yellow solid. Yield = 92% (210 mg). mp 130°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. Rf = 0.20 (EtOAc 100 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.77-1.89 (m, 2H), 1.90-2.01 (m, 2H), 2.82 (t, $J = 6.6$ Hz, 2H), 3.15 (t, $J = 6.4$ Hz, 2H), 7.15 (dd, $J = 8.7, 8.7$ Hz, 2H), 7.43 (s, 1H), 8.01 (dd, $J = 8.9, 5.4$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 22.0 (CH$_2$), 22.6 (CH$_2$), 28.4 (CH$_2$), 29.9 (CH$_2$), 115.9 (d, $J_{C-H} = 21.7$ Hz, 2 x CH), 123.4 (CH), 128.8 (d, $J_{C-H} = 8.4$ Hz, 2 x CH), 133.1 (d, $J_{C-H} = 3.1$ Hz, C), 137.6 (C), 156.1 (C), 159.4 (C), 163.9 (d, $J_{C-H} = 249.1$ Hz, C).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -112.3-112.2 (m).

HRMS (ESI, m/z) calcd for C$_{14}$H$_{13}$FN$_2$Na [M+Na]$^+$ = 251.0955 found 251.1039.

3-(Thiophen-2-yl)-5,6,7,8-tetrahydrocinnoline (8j)

Compound 8j was prepared according to the general procedure I using 2-(2-oxo-2-(thiophen-2-yl)ethyl)cyclohex-2-en-1-one 5j (1 mmol, 220 mg). The title compound was obtained after flash chromatography as a yellow solid. Yield = 87% (188 mg). mp 172°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. Rf = 0.20 (EtOAc 100 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.81-1.87 (m, 2H), 1.90-1.98 (m, 2H), 2.81 (t, $J = 6.3$ Hz, 2H), 3.12 (t, $J = 6.4$ Hz, 2H), 7.12 (dd, $J = 5.0, 3.7$ Hz, 1H), 7.40 (s, 1H), 7.42 (dd, $J = 5.3, 1.1$ Hz, 1H), 7.59 (dd, $J = 3.7, 1.2$ Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 22.4 (CH$_2$), 22.9 (CH$_2$), 28.7 (CH$_2$), 30.3 (CH$_2$), 122.3 (CH), 125.7 (CH), 128.3 (CH), 128.8 (CH), 137.8 (C), 141.7 (C), 153.2 (C), 159.7 (C).

HRMS (ESI, m/z) calcd for C$_{12}$H$_{12}$N$_2$S [M+H]$^+$ = 239.0613 found 239.0610.

3-(Pyridin-2-yl)-5,6,7,8-tetrahydrocinnoline (8k)

Compound 8k was prepared according to the general procedure I using 2-(2-oxo-2-(pyridin-2-yl)ethyl)cyclohex-2-en-1-one 5k (1 mmol, 284 mg). The title compound was obtained after
flash chromatography as a yellow solid. Yield = 87 % (198 mg). mp 91°C. Flash chromatography conditions: column 12 g, flow rate= 20 mL/min, cyclohexane/EtOAc 100/0 to 50/50. R_f = 0.20 (EtOAc 100 %).

^1^H NMR (400 MHz, CDCl_3) δ = 1.78-1.89 (m, 2H), 1.89-2.00 (m, 2H), 2.87 (t, J = 6.4 Hz, 2H), 3.18 (t, J = 6.4 Hz, 2H), 7.33 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 7.83 (ddd, J = 7.7, 7.7, 1.8 Hz, 1H), 8.17 (s, 1H), 8.63 (d, J = 7.9, 1H), 8.66 (m, 1H).

^13^C NMR (101 MHz, CDCl_3) δ = 22.1 (CH_2), 22.6 (CH_2), 28.3 (CH_2), 30.1 (CH_2), 121.5 (CH), 124.1 (CH), 124.3 (CH), 137.2 (CH), 137.9 (C), 149.3 (CH), 154.3 (C), 156.3 (C), 160.7 (C).

HRMS (ESI, m/z) calcd for C_{13}H_{14}N_3 [M+H]^+ = 212.1182 found 212.1204 and for C_{13}H_{13}N_3Na [M+Na]^+ = 234.1002 found 234.1005.

j. 2-Ethyl-1-(3-(2-ethyl-1H-indol-1-yl)propyl)-1,5,6,7-tetrahydro-4H-indol-4-one 9

- 2-Ethyl-1-(3-(2-ethyl-1H-indol-1-yl)propyl)-1,5,6,7-tetrahydro-4H-indol-4-one (9)

Compound 9 was prepared according to the adapted general procedure G using 2-(2-oxobutyl)cyclohex-2-en-1-one 5b (0.91 mmol, 1 equiv, 152 mg) and 1,3-diaminopropane (0.45 mmol, 0.5 equiv, 34 mg) in 8 mL toluene. The title compound was obtained after flash chromatography as a yellow oil. Yield = 13 % (20 mg). Flash chromatography conditions: column 12 g, flow rate = 18 mL/min, cyclohexane/EtOAc 100/0 to 65/35. R_f = 0.30 (cyclohexane/EtOAc 60/40).

^1^H NMR (400 MHz, CDCl_3) δ = 1.19 (t, J = 7.4 Hz, 3H), 1.37 (t, J = 7.4 Hz, 3H), 2.04-2.08 (m, 2H), 2.09-2.17 (m, 2H), 2.37 (q, J = 8.4 Hz, 2H), 2.42-2.47 (m, 2H), 2.50 (t, J = 6.2 Hz, 2H), 2.70 (q, J = 7.4 Hz, 2H), 3.73 (t, J = 7.2 Hz, 2H), 4.12 (t, J = 7.2 Hz, 2H), 6.31 (s, 1H), 7.05-7.09 (m, 1H), 7.12-7.15 (m, 2H), 7.26 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H).

^13^C NMR (101 MHz, CDCl_3) δ = 12.5 (CH_3), 12.8 (CH_3), 19.4 (CH_2), 20.1 (CH_2), 22.0 (CH_2), 23.9 (CH_2), 31.2 (CH_2), 37.7 (CH_2), 40.0 (CH_2), 41.2 (CH_2), 90.1 (CH), 102.1 (CH), 108.7 (CH), 119.7 (CH), 120.1 (C), 120.3 (CH), 121.1 (CH), 128.4 (C), 136.62 (C), 136.64 (C), 136.7 (C), 142.1 (C), 194.1 (C).

HRMS (ESI, m/z) calcd for C_{23}H_{29}N_2O [M+H]^+ = 349.2274 found 349.2237.
V. NMR spectra
a. 2-(Acetyloxymethyl)-4,4-dimethylcyclohex-2-en-1-one 2b.
b. Nitroalkylcyclohex-2-en-1-one 3b-d.
• 2-(2-Nitrobutyl)cyclohex-2-en-1-one 3b

1H NMR

13C NMR
• 4,4-Dimethyl-2-(2-nitropropyl)cyclohex-2-en-1-one 3c

![1H NMR spectrum](image)

![13C NMR spectrum](image)
4,4-Dimethyl-2-2-nitropropylcyclohex-2-en-1-one 3d
c. 1-(Pyridin-2-yl)-2-(triphenylphosphoranylidene)ethan-1-one 4g.
d. 1,4-Dicetones 5a-k.
• 2-(2-Oxopropyl)cyclohex-2-en-1-one 5a

[Chemical structure images]

**H NMR

5a

**C NMR

5a
2-(2-Oxobutyl)cyclohex-2-en-1-one 5b

$^1$H NMR

$^{13}$C NMR
• 4,4-Dimethyl-2-(2-oxopropyl)cyclohex-2-en-1-one 5c

$^1$H NMR

$^{13}$C NMR
• 4,4-Dimethyl-2-(2-oxobutyl)cyclohex-2-en-1-one 5d

\[ \text{\H NMR} \]

\[ \text{\C NMR} \]
• 2-(3,3-Dimethyl-2-oxobutyl)cyclohex-2-en-1-one 5e

1H NMR

\[ \text{5e} \]

\[ \text{O} - \text{O} - \text{O} - \text{O} \]

\[ \text{13C NMR} \]

\[ \text{5e} \]
• 2-(2-Oxo-2-phenylethyl)cyclohex-2-en-1-one 5f

![1H NMR](image)

![13C NMR](image)
• 2-(2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)cyclohex-2-en-1-one 5g

1H NMR

13C NMR

5g
• 2-(2-(4-Iodophenyl)-2-oxoethyl)cyclohex-2-en-1-one 5h

\[ \text{O} \]

\[ \text{O} \]

\[ \text{I} \]

\[ \text{I} \]

\[ \text{1H NMR} \]

\[ 5h \]

\[ \text{13C NMR} \]

\[ 5h \]
- 2-(2-(4-Fluorophenyl)-2-oxoethyl)cyclohex-2-en-1-one 5i

**1H NMR**

**13C NMR**
$^{19}$F NMR

5i

![Chemical Structure](attachment:image.png)
- 2-(2-Oxo-2-(thiophen-2-yl)ethyl)cyclohex-2-en-1-one 5j

\[
\begin{align*}
\text{H NMR} \\
\text{5j}
\end{align*}
\]

\[
\begin{align*}
\text{C NMR} \\
\text{5j}
\end{align*}
\]
• 2-(2-Oxo-2-(pyridin-2-yl)ethyl)cyclohex-2-en-1-one 5k

1H NMR

13C NMR
e. Indoles 6a-l.
- 1-Benzyl-2-methyl-1H-indole 6a

1H NMR 6a

13C NMR 6a
• 1-Benzyl-2-ethyl-1H-indole 6b

1H NMR 6b

13C NMR 6b
• 2-Ethyl-1-phenethyl-1H-indole 6c

$^1$H NMR

$^1$H NMR

$^{13}$C NMR

$^{13}$C NMR
• 2-Ethyl-1-(4-methoxybenzyl)-1H-indole 6d

1H NMR

6d

13C NMR

6d
- 2-Ethyl-1-(1-phenylethyl)-1,5,6,7-tetrahydro-4H-indol-4-one 6e

1H NMR

\[ \text{N} \]

13C NMR

\[ \text{N} \]
- 2-Ethyl-1-(furan-3-ylmethyl)-1H-indole 6f
• 1,3-Bis(2-ethyl-1H-indol-1-yl)propane 6g

1H NMR 6g

13C NMR 6g
• 3-(2-Ethyl-1H-indol-1-yl)-N,N-dimethylpropan-1-amine 6h

\[ \text{\(1^H\) NMR} \]

\[ \text{\(13C\) NMR} \]
- 4-(2-(2-Methyl-1H-indol-1-yl)ethyl)morpholine 6i

1H NMR

\[ \text{1H NMR} \]

\[ \text{13C NMR} \]

\[ \text{13C NMR} \]
4-(2-(2-Ethyl-1H-indol-1-yl)ethyl)morpholine 6j

**1H NMR**

**13C NMR**
• 2-Methyl-1-(pyridin-4-ylmethyl)-1H-indole 6k

1H NMR
6k

13C NMR
6k
• 2-Ethyl-1-(pyridin-4-ylmethyl)-1H-indole 6l

1H NMR 6l

13C NMR 6l
f. Indolones 7a-k.
- 1-Benzyl-2-methyl-1,5,6,7-tetrahydro-4H-indol-4-one 7a

{1H NMR}

{13C NMR}
• 1-Benzyl-2-ethyl-1,5,6,7-tetrahydro-4H-indol-4-one 7b
• 2-Ethyl-1-phenethyl-1,5,6,7-tetrahydro-4H-indol-4-one 7c

1H NMR

13C NMR
- 2-Ethyl-1-(4-methoxybenzyl)-1,5,6,7-tetrahydro-4H-indol-4-one 7d

1H NMR 7d

13C NMR 7d
• 2-Ethyl-1-(1-phenylethyl)-1,5,7-tetrahydro-4H-indol-4-one 7e

\[ \text{1H NMR} \]

\[ \text{13C NMR} \]
• 2-Ethyl-1-(furan-3-ylmethyl)-1,5,6,7-tetrahydro-4H-indol-4-one 7f

\[ \text{O} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{N} \]

**1H NMR 7f**

**13C NMR 7f**
- 1-(4-Bromobenzyl)-2-methyl-1,5,6,7-tetrahydro-4H-indol-4-one 7g
• 1-(Furan-2-ylmethyl)-2-methyl-1,5,6,7-tetrahydro-4H-indol-4-one 7h

\[ \text{1H NMR} \quad 7h \]

\[ \text{13C NMR} \quad 7h \]
- 1-(Pyridin-4-ylmethyl)-2-ethyl-1,5,6,7-tetrahydro-4H-indol-4-one 7i
• 2-Methyl-1-phenethyl-1,5,6,7-tetrahydro-4H-indol-4-one 7j

\[ \text{\H NMR} \]

\[ \text{\C NMR} \]

\[ \text{7j} \]

\[ \text{7j} \]
- 1-Phenethyl-2-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one 7k

$^1$H NMR

$^{13}$C NMR
g. 2-ethyl-1-(3-(2-ethyl-1H-indol-1-yl)propyl)-1,5,7-tetrahydro-4H-indol-4-one 9.
h. Cinnolines 8a-k.
• 3-Methyl-5,6,7,8-tetrahydrocinnoline 8a

1H NMR

13C NMR
• 3-Ethyl-5,6,7,8-tetrahydrocinnoline 8b
• 3,6,6-Trimethyl-5,6,7,8-tetrahydrocinnoline 8c

1H NMR

13C NMR
- 3-Ethyl-6,6-dimethyl-5,6,7,8-tetrahydrocinnoline 8d

\[\text{\textsuperscript{1}H NMR} \]

\[\text{\textsuperscript{13}C NMR} \]

\[\text{8d} \]
• 3-(Tert-butyl)-5,6,7,8-tetrahydrocinnone 8e

1H NMR
8e

13C NMR
8e
• 3-Phenyl-5,6,7,8-tetrahydrocinoline 8f

\[ \text{1H NMR} \]

\[ \text{13C NMR} \]
• 3-[(1,1'-Biphenyl)-4-yl]-5,6,7,8-tetrahydrocinnoline 8g

$^1$H NMR

$^{13}$C NMR
• 3-(4-Iodophenyl)-5,6,7,8-tetrahydrocinnoline 8h
• 3-(4-Fluorophenyl)-5,6,7,8-tetrahydrocinnoline 8i

\[ \text{1H NMR} \]

\[ 8i \]

\[ \text{13C NMR} \]

\[ 8i \]
$^{19}$F NMR
8i

![NMR Spectrum](image_url)
• 3-(Thiophen-2-yl)-5,6,7,8-tetrahydrocinnoline 8j

**1H NMR**

**13C NMR**
• 3-(Pyridin-2-yl)-5,6,7,8-tetrahydrocinnoline 8k

$^1$H NMR

8k

N
N

$^{13}$C NMR

8k

N
N
VI. References