Syntheses of N-Alkylated Carbazolones via Pd(OAc)$_2$-mediated Intramolecular Coupling of N-Substituted 3-(Arylamino)cyclohex-2-enones

Wenying Bi, Xiliu Yun, Yanfeng Fan, Xiuxiang Qi, Yunfei Du,* Jianhui Huang*

*Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

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**General Information**

$^1\text{H}/^{13}\text{C}$ NMR spectra were recorded on a BRUKER AVANCE 400 MHz spectrometer. $^1\text{H}$: Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: 7.27 ppm, (CD$_3$)$_2$SO: 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, br = broad, m = multiplet), integration coupling constants ($J$) in Hz and assignment. $^{13}\text{C}$ spectra were with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: 77.0 ppm, (CD$_3$)$_2$SO: 40.0 ppm). Low-resolution mass spectrometry (ESI) was performed on an ion trap (Agilent 6310) spectrometer. Melting points (uncorrected) were obtained on a national micro melting point apparatus.

Flash column chromatography was performed on silica gel (SiO$_2$, 200-300 Mesh) and the eluent was a mixture of EtOAc and petroleum ether (PE), or a mixture of MeOH and DCM. Thin layer chromatography plates (GF254, $50 \times 100$ mm) were visualized by exposure to ultraviolet light (254 nm). All solvents and reagents were purified using standard, laboratory techniques according to methods published in “Purification of Laboratory Chemicals” by Armarégo and Perrin (Pergamon Press 1996).
Synthesis of the Substrates

General procedure\(^1\): To a solution of 3-(arylamino)cyclohex-2-enones \(1\) (10 mmol) in anhydrous DMF (50 mL) was added NaH (25 mmol) slowly at 0 °C. The mixture was stirring at room temperature for 2 h before methyl iodide or benzyl chloride (25 mmol) was added dropwise to the mixture. TLC was used to monitor the reaction progress. After the consumption of starting material, the reaction mixture was extracted by ethyl acetate (25 mL \(\times\) 3). The organic phase was combined, dried (anhydrous \(\text{Na}_2\text{SO}_4\)). After filtration, the solvent was removed under reduced pressure to give the crude product. The residue was purified by flash column chromatography (MeOH/DCM = 2/98 or EtOAc/PE = 70/30) on silica gel to give the desired products 2a-n, which were characterized as follows:

3-[Methyl(phenyl)amino]cyclohex-2-enone (2a)\(^2\)

Following the general procedure, 2a was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. \(R_f\) = 0.40 (MeOH/DCM = 5/95). Yield: 81%, yellow solid, mp 74-76 °C. \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.42 (t, \(J = 7.0\) Hz, 2H, ArH), 7.32 (t, \(J = 7.0\) Hz, 1H, ArH), 7.14 (d, \(J = 7.0\) Hz, 2H, ArH), 5.32 (s, 1H, COCH), 3.24 (s, 3H, NCH\(_3\)), 2.31 (t, \(J = 6.0\) Hz, 2H, COCH\(_2\)), 2.22 (t, \(J = 6.0\) Hz, 2H, CH\(_2\)), 1.93-1.88 (m, 2H, CH\(_2\)). \(^13\text{C}\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.6, 165.0, 145.3, 129.7, 127.5, 127.1, 100.5, 40.7, 36.1, 28.5, 22.5. LRMS (ESI): m/z calcd for C\(_{13}\)H\(_{15}\)NO\[^+\] [M + H\(^+\)] 202.1, found [M + H\(^+\)] 202.0, [M + Na\(^+\)] 224.0.
3-[(4-Bromophenyl)(methyl)amino]cyclohex-2-enone (2b)

Following the general procedure, 2b was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. \( R_f = 0.35 \) (MeOH/DCM = 5/95). Yield: 77%, yellow solid, mp 160-162 °C.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \( \delta \) 7.54 (d, \( J = 9.0 \) Hz, 2H, ArH), 7.03 (d, \( J = 9.0 \) Hz, 2H, ArH), 5.31 (s, 1H, COCH), 3.22 (s, 3H, NCH\(_3\)), 2.31 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.21 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)).

\[ ^13C \text{ NMR (100 MHz, CDCl}_3\]: \( \delta \) 197.6, 164.5, 144.4, 132.9, 128.9, 121.1, 101.3, 40.7, 36.1, 28.5, 22.5. LRMS (ESI): m/z calcd for C\(_{13}\)H\(_{14}\)\( ^{81}\)BrNO\(^+\) [M + H\(^+\)] 281.0, found [M + H\(^+\)] 281.9, [M + Na\(^+\)] 303.9.

3-[(4-Chlorophenyl)(methyl)amino]cyclohex-2-enone (2c)

Following the general procedure, 2c was purified by flash column chromatography (EtOAc/PE = 70/30) on silica gel. \( R_f = 0.52 \) (MeOH/DCM = 5/95). Yield: 92%, white solid, mp 157-158 °C. \( ^1H \text{ NMR (400 MHz, DMSO): } \delta \) 7.50 (d, 2H, ArH), 7.30 (d, 2H, ArH), 5.04 (s, 1H, COCH), 3.18 (s, 3H, NCH\(_3\)), 2.23 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.10 (t, \( J = 7.0 \) Hz, 2H, CH\(_2\)), 1.82-1.76 (m, 2H, CH\(_2\)).

\[ ^13C \text{ NMR (100 MHz, DMSO): } \delta \) 195.6, 164.6, 144.6, 131.8, 130.0, 129.5, 100.7, 40.8, 36.4, 28.2, 22.5. LRMS (ESI): m/z calcd for C\(_{13}\)H\(_{14}\)\( ^{35}\)ClNO\(^+\) [M + H\(^+\)] 236.1, found [M + H\(^+\)] 236.5, [M + Na\(^+\)] 258.6, [2M + Na\(^+\)] 493.6.

3-[Methyl(p-tolyl)amino]cyclohex-2-enone (2d)

Following the general procedure, 2d was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. \( R_f = 0.35 \) (MeOH/DCM = 5/95). Yield: 72%, colorless oil. \( ^1H \text{ NMR (400 MHz, CDCl}_3\]: \( \delta \) 7.21 (d, \( J = 8.0 \) Hz, 2H, ArH), 7.02 (d, \( J = 8.0 \) Hz, 2H, ArH), 5.31 (s, 1H, COCH), 3.22 (s, 3H, NCH\(_3\)), 2.38 (s, 3H, ArCH\(_3\)), 2.30 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.21 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)).

\[ ^13C \text{ NMR (100 MHz, CDCl}_3\]: \( \delta \) 197.5, 165.3, 142.7, 137.4, 130.2, 126.8, 100.2, 40.8, 36.0, 28.5, 22.5, 21.0.
LRMS (ESI): m/z calcd for C$_{14}$H$_{17}$NO$^+$ [M + H$^+$] 216.1, found 216.0.

3-[(4-Methoxyphenyl)(methyl)amino]cyclohex-2-enone (2e)

Following the general procedure, 2e was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. $R_f$ = 0.42 (MeOH/DCM = 5/95). Yield: 79%, white solid, mp 99-100°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.06 (d, $J$ = 9.0 Hz, 2H, ArH), 6.91 (d, $J$ = 9.0 Hz, 2H, ArH), 5.29 (s, 1H, COCH), 3.83 (s, 3H, OCH$_3$), 3.21 (s, 3H, NCH$_3$), 2.30 (t, $J$ = 6.0 Hz, 2H, COCH$_2$), 2.21 (t, $J$ = 6.0 Hz, 2H, CH$_2$), 1.92-1.86 (m, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.4, 165.5, 158.6, 138.1, 128.2, 114.7, 100.0, 55.5, 40.9, 36.0, 28.4, 22.4. LRMS (ESI): m/z calcd for C$_{14}$H$_{17}$NO$_2$$^+$ [M + H$^+$] 232.1, found [M + H$^+$] 232.1, [M + Na$^+$] 254.1.

3-[Methyl(4-nitrophenyl)amino]cyclohex-2-enone (2f)

Following the general procedure, 2f was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. $R_f$ = 0.36 (MeOH/DCM = 5/95). Yield: 84%, yellow solid, mp 127-129°C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.29 (d, $J$ = 9.0 Hz, 2H, ArH), 7.32 (d, $J$ = 9.0 Hz, 2H, ArH), 5.41 (s, 1H, COCH), 3.32 (s, 3H, NCH$_3$), 2.36 (t, $J$ = 6.0 Hz, 2H, COCH$_2$), 2.31 (t, $J$ = 6.0 Hz, 2H, CH$_2$), 1.99-1.93 (m, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.9, 163.3, 151.0, 145.7, 127.4, 125.1, 103.9, 40.7, 36.2, 28.7, 22.7. LRMS (ESI): m/z calcd for C$_{13}$H$_{14}$N$_2$O$_3$$^+$ [M + H$^+$] 247.1, found [M + H$^+$] 247.2, [M + Na$^+$] 269.1.

3-[(2-Bromophenyl)(methyl)amino]cyclohex-2-enone (2g)

Following the general procedure, 2g was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. $R_f$ = 0.40 (MeOH/DCM = 5/95). Yield: 69%, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.67 (d, $J$ = 7.5 Hz, 1H, ArH), 7.42 (t, $J$ = 7.5 Hz, 1H, ArH), 7.27 (d, $J$ = 7.5 Hz, 2H, ArH), 5.39 (s, 1H, COCH), 3.15 (s, 3H, NCH$_3$), 2.30 (br s, 2H, COCH$_2$), 2.07-1.98 (m, 2H, CH$_2$), 1.90 (br s, 2H, CH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.7, 164.8, 143.8, 133.7, 129.8, 129.7, 128.9, 123.4, 99.8, 39.3, 36.1, 27.9, 22.3. LRMS
(ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{BrNO}^+ [M + H^+]$ 281.0, found [M + H$^+$] 281.8, [M + Na$^+$] 303.9.

3-[(2-Chlorophenyl)(methyl)amino]cyclohex-2-enone (2h)

Following the general procedure, 2h was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. $R_f$ = 0.41 (MeOH/DCM = 5/95). Yield: 75%, brown oil. $^1\text{H NMR (400 MHz, CDCl}_3$): $\delta$ 7.51-7.48 (m, 1H, ArH), 7.35-7.33 (m, 2H, ArH), 7.25-7.23 (m, 1H, ArH), 5.41 (s, 1H, COCH), 3.17 (s, 3H, NCH$_3$), 2.32 (br s, 2H, COCH$_2$), 2.08-1.91 (m, 4H, CH$_2$). $^{13}\text{C NMR (100 MHz, CDCl}_3$): $\delta$ 197.7, 164.9, 142.3, 133.3, 130.7, 129.8, 129.4, 128.2, 100.1, 39.4, 36.1, 27.8, 22.3. LRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClNO}^+ [M + H^+]$ 236.1, found [M + H$^+$] 236.2, [M + Na$^+$] 258.0.

3-[(Methyl(o-tolyl)amino]cyclohex-2-enone (2i)

Following the general procedure, 2i was purified by flash column chromatography (EtOAc/PE = 70/30) on silica gel. $R_f$ = 0.45 (MeOH/DCM = 5/95). Yield: 84%, brown oil. $^1\text{H NMR (400 MHz, CDCl}_3$): $\delta$ 7.28-7.22 (m, 3H, ArH), 7.07-7.05 (m, 1H, ArH), 5.38 (s, 1H, COCH), 3.14 (s, 3H, NCH$_3$), 2.31 (t, $J = 6.0$ Hz, 2H, COCH$_2$), 2.16 (s, 3H, ArCH$_3$), 2.12-1.82 (m, 4H, CH$_2$). $^{13}\text{C NMR (100 MHz, CDCl}_3$): $\delta$ 197.5, 165.3, 143.8, 135.6, 131.4, 128.2, 127.8, 127.3, 99.1, 39.4, 36.1, 28.0, 22.4, 17.3. LRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{17}\text{NO}^+ [M + H^+]$ 216.1, found [M + H$^+$] 216.2, [M + Na$^+$] 230.1.

3-((3-Fluorophenyl)(methyl)amino)cyclohex-2-enone (2j)

Following the general procedure, 2j was purified by flash column chromatography (EtOAc/PE = 70/30) on silica gel. $R_f$ = 0.63 (MeOH/DCM = 5/95). Yield: 75%, light yellow solid, mp 101-102°C. $^1\text{H NMR (400 MHz, DMSO)}$: $\delta$ 7.49-7.46 (m, 1H, ArH), 7.21-7.14 (m, 3H, ArH), 5.07 (s, 1H, COCH), 3.19 (s, 3H, NCH$_3$), 2.26 (br s, 2H, COCH$_2$), 2.12 (br s, 2H, CH$_2$), 1.80 (br s, 2H, CH$_2$). $^{13}\text{C NMR (100 MHz, DMSO)}$: $\delta$ 195.7, 164.5, 162.8 (d, $J_{C-F} = 244$ Hz), 147.3 (d, $J_{C-F} = 10$ Hz), 131.5 (d, $J_{C-F} = 10$ Hz), 123.9, 115.0 (d, $J_{C-F} =$
22 Hz), 114.4 (d, J_{C-F} = 22 Hz), 100.8, 40.8, 36.4, 28.2, 22.6. **LRMS (ESI):** m/z calcd for C_{13}H_{14}FNO^{+} [M + H^{+}] 220.1, found 220.1.

### 3-[Benzyl(3-nitrophenyl)amino]cyclohex-2-enone (2k)

Following the general procedure, 2k was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. \( R_f = 0.40 \) (MeOH/DCM = 5/95). **Yield:** 88%, orange oil. **\(^1\)H NMR (400 MHz, CDCl\(_3\)):** \( \delta \) 8.14 (ddd, \( J = 8.0, 2.0, 1.0 \) Hz, 1H, ArH), 8.04 (t, \( J = 2.0 \) Hz, 1H, ArH), 7.56 (t, \( J = 8.0 \) Hz, 1H, ArH), 7.49 (ddd, \( J = 8.0, 2.0, 1.0 \) Hz, 1H, ArH), 7.36-7.32 (m, 2H, ArH), 7.28 (tt, \( J = 7.0, 2.0 \) Hz, 1H, ArH), 7.20-7.18 (m, 2H, ArH), 5.38 (s, 1H, COCH), 4.89 (s, 2H, NCH\(_2\)), 2.39 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.34 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)), 2.02-1.96 (m, 2H, CH\(_2\)). **\(^{13}\)C NMR (100 MHz, CDCl\(_3\)):** \( \delta \) 197.8, 163.9, 148.8, 145.3, 135.6, 133.9, 130.5, 128.9, 127.8, 126.7, 122.8, 122.1, 103.4, 56.4, 36.0, 28.5, 22.4. **LRMS (ESI):** m/z calcd for C\(_{19}\)H\(_{18}\)N\(_2\)O\(_3\)\([\text{M} + \text{H}^+]\) 323.1, found [2M + Na\(^+\)] 667.4.

### 3-(Methyl(3-(trifluoromethyl)phenyl)amino)cyclohex-2-enone (2l)

Following the general procedure, 2l was purified by flash column chromatography (EtOAc/PE = 70/30) on silica gel. \( R_f = 0.55 \) (MeOH/DCM = 5/95). **Yield:** 89%, light brown solid, mp 75-76 °C. **\(^1\)H NMR (400 MHz, DMSO):** \( \delta \) 7.70-7.67 (m, 3H, ArH), 7.62-7.59 (m, 1H, ArH), 5.06 (s, 1H, COCH), 3.23 (s, 3H, NCH\(_3\)), 2.26 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.13 (t, \( J = 7.0 \) Hz, 2H, CH\(_2\)), 1.81 (m, 2H, CH\(_2\)). **\(^{13}\)C NMR (100 MHz, DMSO):** \( \delta \) 195.8, 146.5, 146.4, 132.0, 131.2, 130.8 (q, \( J = 32 \) Hz), 124.4 (q, \( J = 4 \) Hz), 124.2 (q, \( J = 271 \) Hz), 124.1 (q, \( J = 4 \) Hz), 101.1, 40.8, 36.3, 28.2, 22.6. **LRMS (ESI):** m/z calcd for C\(_{14}\)H\(_{14}\)F\(_3\)NO\(^+\) [M + H\(^+\)] 270.1, found [M + H\(^+\)] 270.6, [M + Na\(^+\)] 292.4, [2M + Na\(^+\)] 561.1.

### 3-[(2,4-Difluorophenyl)(methyl)amino]cyclohex-2-enone (2m)

Following the general procedure, 2m was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. \( R_f = 0.40 \) (MeOH/DCM = 5/95). **Yield:** 75%,
white solid, mp 133-134 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.22-7.16 (m, 1H, ArH), 6.97-6.91 (m, 2H, ArH), 5.32 (s, 1H, COCH), 3.19 (s, 3H, NCH\textsubscript{3}), 2.32 (t, \(J = 7.0\) Hz, 2H, COCH\textsubscript{2}), 2.19 (br s, 2H, CH\textsubscript{2}), 1.96-1.90 (m, 2H, CH\textsubscript{2}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 197.5, 165.0, 161.7 (dd, \(J_{C-F} = 249, 11\) Hz), 158.4 (dd, \(J_{C-F} = 251, 12\) Hz), 130.4 (dd, \(J_{C-F} = 10, 2\) Hz), 128.8 (dd, \(J_{C-F} = 13, 4\) Hz), 112.2 (dd, \(J_{C-F} = 22, 4\) Hz), 105.2 (dd, \(J_{C-F} = 26, 24\) Hz), 100.9, 40.0, 35.9, 27.4, 22.1. LRMS (ESI): m/z calcd for C\textsubscript{13}H\textsubscript{13}F\textsubscript{2}NO\textsuperscript{+} [M + H\textsuperscript{+}] 238.1, found [M + H\textsuperscript{+}] 238.1, [M + Na\textsuperscript{+}] 260.0.

3-[Benzyl(3,4-dimethylphenyl)amino]cyclohex-2-enone (2n)

Following the general procedure, 2n was purified by flash column chromatography (MeOH/DCM = 2/98) on silica gel. \(R_f = 0.50\) (MeOH/DCM = 5/95). Yield: 71%, white solid, mp 112-114 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.33-7.21 (m, 5H, ArH), 7.10 (d, \(J = 8.0\) Hz, 1H, ArH), 6.92 (s, 1H, ArH), 6.86 (d, \(J = 8.0\) Hz, 1H, ArH), 5.36 (s, 1H, COCH), 4.81 (s, 2H, NCH\textsubscript{2}), 2.33-2.28 (m, 4H, CH\textsubscript{2}), 2.24 (s, 3H, CH\textsubscript{3}), 2.23 (s, 3H, CH\textsubscript{3}), 1.94-1.88 (m, 2H, CH\textsubscript{2}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 197.6, 165.3, 142.2, 138.2, 136.5, 136.2, 130.6, 128.7, 128.6, 127.4, 126.9, 124.9, 101.2, 56.8, 36.1, 28.7, 22.5, 19.9, 19.4. LRMS (ESI): m/z calcd for C\textsubscript{21}H\textsubscript{23}NO\textsuperscript{+} [M + H\textsuperscript{+}] 306.2, found [M + H\textsuperscript{+}] 306.2.
Synthesis of \(N\)-substituted 2,3-dihydro-1\(H\)-carbazol-4(9\(H\))-ones

**General procedure:** To a solution of \(N\)-substituted 3-(arylamino)cyclohex-2-enones 2a-n (1 mmol) in acetic acid (15 mL) was added Pd(OAc)\(_2\) (0.1 mmol) and the resulting solution was heated at 100 °C passed through oxygen flow (1.0 L/min). TLC was used to monitor the reaction progress. After the consumption of starting material, the reaction mixture was extracted by ethyl acetate (15 mL \(\times\) 3). The organic phase was combined, dried (anhydrous Na\(_2\)SO\(_4\)). After filtration, the solvent was removed under reduced pressure to give the crude product. The residue was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel to give the desired products 3a-n which were characterized as follows:

**9-Methyl-2,3-dihydro-1\(H\)-carbazol-4(9\(H\))-one (3a)**

Following the general procedure, after 1 h, 3a was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. \(R_f = 0.45\) (EtOAc/PE = 40/60). **Yield:** 81%, white solid, mp 195-196 °C. **\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \(\delta\) 8.27-8.23 (m, 1H, ArH), 7.33-7.27 (m, 3H, ArH), 3.72 (s, 3H, NCH\(_3\)), 2.95 (t, \(J = 6.0\) Hz, 2H, COCH\(_2\)), 2.62 (t, \(J = 6.0\) Hz, 2H, CH\(_2\)), 2.30-2.23 (m, 2H, CH\(_2\)). **LRMS** (ESI): \(m/z\) calcd for C\(_{13}\)H\(_{13}\)NO\(^+\) [M + H\(^+\)] 200.1, found [M + H\(^+\)] 200.1, [M + Na\(^+\)] 222.0.
6-Bromo-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3b)

Following the general procedure, after 11 h, 3b was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. Rf = 0.40 (EtOAc/PE = 40/60). **Yield:** 79%, brown solid, mp 230-231 °C. **1H NMR (400 MHz, CDCl3):** δ 8.38 (d, J = 2.0 Hz, 1H, ArH), 7.34 (dd, J = 9.0, 2.0 Hz, 1H, ArH), 7.18 (d, J = 9.0 Hz, 1H, ArH), 3.68 (s, 3H, NCH3), 2.92 (t, J = 6.0 Hz, 2H, COCH2), 2.56 (t, J = 6.0 Hz, 2H, CH2), 2.28-2.22 (m, 2H, CH2). **13C NMR (100 MHz, CDCl3):** δ 193.8, 153.0, 137.6, 134.9, 127.2, 125.8, 124.4, 111.8, 110.8, 37.7, 35.6, 23.1, 21.9. **LRMS (ESI):** m/z calcd for C13H12BrNO [M + H+] 280.0, found 280.0.

6-Chloro-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3c)4

Following the general procedure, after 12 h, 3c was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. Rf = 0.38 (EtOAc/PE = 40/60). **Yield:** 62%, white solid, mp 215-216 °C. **1H NMR (400 MHz, DMSO):** δ 7.94 (d, J = 2.0 Hz, 1H, ArH), 7.59 (d, J = 9.0 Hz, 1H, ArH), 7.26 (dd, J = 9.0, 2.0 Hz, 1H, ArH), 7.18 (s, 3H, NCH3), 3.74 (s, 3H, NCH3), 3.00 (t, J = 6.0 Hz, 2H, COCH2), 2.44 (t, J = 6.0 Hz, 2H, CH2), 2.17-2.11 (m, 2H, CH2). **LRMS (ESI):** m/z calcd for C13H12ClNO [M + H+] 234.1, found [M + H+] 233.7, [2M + Na+] 489.4.

6,9-Dimethyl-2,3-dihydro-1H-carbazol-4(9H)-one (3d)3

Following the general procedure, after 4 h, 3d was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. Rf = 0.50 (EtOAc/PE = 40/60). **Yield:** 85%, white solid, mp 166-168 °C. **1H NMR (400 MHz, CDCl3):** δ 8.06 (s, 1H, ArH), 7.18 (d, J = 8.0 Hz, 1H, ArH), 7.09 (dd, J = 8.0, 1.0 Hz, 1H, ArH), 3.67 (s, 3H, NCH3), 2.91 (t, J = 6.0 Hz, 2H, COCH2), 2.57 (t, J = 6.0 Hz, 2H, CH2), 2.47 (s, 3H, ArCH3), 2.27-2.21 (m, 2H, CH2). **LRMS (ESI):** m/z calcd for C14H15NO [M + H+] 214.1, found 214.1.
6-Methoxy-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3e)

Following the general procedure, after 3.5 h, 3e was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. 

Rf = 0.45 (EtOAc/PE = 40/60). Yield: 83%, white solid, mp 148-150 °C. 1H NMR (400 MHz, CDCl3): δ 7.75 (br s, 1H, ArH), 7.18 (d, J = 8.0 Hz, 1H, ArH), 6.89 (d, J = 8.0 Hz, 1H, ArH), 3.90 (s, 3H, OCH3), 3.67 (s, 3H, NCH3), 2.90 (br s, 2H, COCH2), 2.56 (br s, 2H, CH2), 2.25-2.24 (m, 2H, CH2). LRMS (ESI): m/z calcd for C14H15NO2 [M + H+] 230.1, found [M + H+] 230.1, [M + Na+] 252.1.

9-Methyl-6-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3f)

Following the general procedure, after 24 h, 3f was purified by flash column chromatography (Et OAc/PE = 25/75) on silica gel. Rf = 0.42 (EtOAc/PE = 40/60). Yield: 65%, yellow solid, mp 235-236 °C. 1H NMR (400 MHz, CDCl3): δ 8.92 (d, J = 2.0 Hz, 1H, ArH), 8.04 (dd, J = 9.0, 2.0 Hz, 1H, ArH), 7.27 (d, J = 9.0 Hz, 1H, ArH), 3.76 (s, 3H, NCH3), 2.98 (t, J = 6.0 Hz, 2H, COCH2), 2.59 (t, J = 6.0 Hz, 2H, CH2), 2.33-2.27 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3): δ 193.3, 154.7, 143.4, 140.2, 124.0, 118.4, 117.9, 113.9, 109.1, 37.7, 30.3, 23.0, 22.2. LRMS (ESI): m/z calcd for C13H12N2O3 [M + H+] 245.1, found [M + H+] 245.0.

8-Bromo-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3g)

Following the general procedure, after 12 h, 3g was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. Rf = 0.41 (EtOAc/PE = 40/60). Yield: 40%, brown solid, mp 133-135 °C. 1H NMR (400 MHz, DMSO): δ 8.09 (dd, J = 8.0, 1.0 Hz, 1H, ArH), 7.41 (d, J = 8.0 Hz, 1H, ArH), 7.08 (t, J = 8.0 Hz, 1H, ArH), 4.03 (s, 3H, NCH3), 2.98 (t, J = 6.0 Hz, 2H, COCH3), 2.44 (t, J = 7.0 Hz, 2H, CH2), 2.17-2.10 (m, 2H, CH2). 13C NMR (100 MHz, DMSO): δ 193.2, 155.2, 133.7, 128.2, 128.1, 123.9, 120.4, 111.8, 103.8, 37.9, 33.6, 23.0, 22.2. LRMS (ESI): m/z calcd for C13H12BrNO [M + H+] 279.0, found [M + H+] 279.5, [M + Na+] 301.0, [2M + Na+] 579.0.
8-Chloro-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3h)

Following the general procedure, after 7 h, 3h was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. \( R_f = 0.40 \) (EtOAc/PE = 40/60). Yield: 25%, white solid, mp 141-144 °C.

\(^{1}\text{H NMR (400 MHz, DMSO)}\): \( \delta \) 8.02 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.23 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.15 (t, \( J = 8.0 \) Hz, 2H, ArH), 4.03 (s, 3H, NCH\(_3\)), 2.99 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.44 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)), 2.17-2.11 (m, 2H, CH\(_2\)).

\(^{13}\text{C NMR (100 MHz, DMSO)}\): \( \delta \) 193.3, 155.1, 132.6, 128.0, 124.7, 123.5, 119.9, 116.6, 111.9, 37.9, 33.5, 23.0, 22.1. LRMS (ESI): m/z calcd for C\(_{13}\)H\(_{11}\)ClNO\(^{+}\) [M + H\(^+\)] 234.1, found [M + Na\(^+\)] 256.5, [2M + Na\(^+\)] 489.4.

8,9-Dimethyl-2,3-dihydro-1H-carbazol-4(9H)-one (3i)

Following the general procedure, after 12 h, 3i was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. \( R_f = 0.55 \) (EtOAc/PE = 40/60). Yield: 34%, brown solid, mp 186-187 °C.

\(^{1}\text{H NMR (400 MHz, DMSO)}\): \( \delta \) 7.89 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.03 (t, \( J = 7.0 \) Hz, 1H, ArH), 6.93 (d, \( J = 7.0 \) Hz, 1H, ArH), 3.95 (s, 3H, NCH\(_3\)), 2.96 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.74 (s, 3H, ArCH\(_3\)), 2.40 (t, \( J = 7.0 \) Hz, 2H, CH\(_2\)), 2.15-2.09 (m, 2H, CH\(_2\)).

\(^{13}\text{C NMR (100 MHz, DMSO)}\): \( \delta \) 193.1, 153.5, 136.2, 125.9, 125.7, 122.4, 122.0, 118.8, 111.7, 37.9, 33.5, 23.3, 22.2, 20.0. LRMS (ESI): m/z calcd for C\(_{14}\)H\(_{15}\)NO\(^+\) [M + H\(^+\)] 214.1, found [M + Na\(^+\)] 236.5, [2M + Na\(^+\)] 449.2.

5/7-Fluoro-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3j)

Following the general procedure, after 8 h, 3j (7-F) was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel.

\(^{5}\text{-F: } R_f = 0.50 \) (EtOAc/PE = 40/60). Yield: 30%, white solid, mp 188-189 °C.

\(^{1}\text{H NMR (400 MHz, DMSO)}\): \( \delta \) 7.37 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.23 (td, \( J = 8.0, 5.0 \) Hz, 1H, ArH), 6.94 (dd, \( J = 11.0, 8.0 \) Hz, 1H, ArH), 3.74 (s, 3H, NCH\(_3\)), 3.00 (t, \( J = 6.0 \) Hz, 2H, COCH\(_2\)), 2.44 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)), 2.15-2.09 (m, 2H, CH\(_2\)).

\(^{13}\text{C NMR (100 MHz, DMSO)}\): \( \delta \) 190.6, 155.8 (d, \( J_{C,F} = 249 \) Hz), 153.8, 140.7
(d, $J_{\text{C-F}} = 12$ Hz), 123.9 (d, $J_{\text{C-F}} = 7$ Hz), 112.5 (d, $J_{\text{C-F}} = 23$ Hz), 111.1 (d, $J_{\text{C-F}} = 6$ Hz), 108.0 (d, $J_{\text{C-F}} = 21$ Hz), 107.0 (d, $J_{\text{C-F}} = 4$ Hz), 38.6, 30.8, 22.9, 22.2. LRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{FNO}^+$ [M + H$^+$] 218.1, found [M + Na$^+$] 240.2.

**7-F**: $R_f = 0.40$ (EtOAc/PE = 40/60). **Yield**: 39%, brown solid, mp 174-176 °C. **$^1$H NMR (400 MHz, DMSO)**: δ 7.95 (dd, $J = 8.0$, 6.0 Hz, 1H), 7.45 (dd, $J = 10.0$, 2.0 Hz, 1H), 7.06-7.01 (m, 1H, ArH), 3.71 (s, 3H, NCH$_3$), 2.98 (t, $J = 6.0$ Hz, 2H, COCH$_2$), 2.42 (s, $J = 6.0$ Hz, 2H, CH$_2$), 2.16-2.10 (m, 2H, CH$_2$). **$^{13}$C NMR (100 MHz, DMSO)**: δ 193.1, 159.7 (d, $J_{\text{C-F}} = 235$ Hz), 154.2 (d, $J_{\text{C-F}} = 2$ Hz), 138.0 (d, $J_{\text{C-F}} = 12$ Hz), 121.6 (d, $J_{\text{C-F}} = 10$ Hz), 121.2, 111.7, 110.3 (d, $J_{\text{C-F}} = 24$ Hz), 97.8 (d, $J_{\text{C-F}} = 27$ Hz), 37.8, 30.5, 23.3, 21.9. LRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{12}\text{FNO}^+$ [M + H$^+$] 218.1, found [M + Na$^+$] 240.3.

**9-Benzyl-7-nitro-2,3-dihydro-1H-carbazol-4(9H)-one (3k)**

Following the general procedure, after 22 h, 3k was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. $R_f = 0.57$ (EtOAc/PE = 40/60). **Yield**: 61%, yellow solid, mp 134-136 °C. **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 8.37 (d, $J = 9.0$ Hz, 1H, ArH), 8.24 (s, 1H, ArH), 8.17 (d, $J = 9.0$ Hz, 1H, ArH), 7.36-7.32 (m, 3H, ArH), 7.03 (d, $J = 7.0$ Hz, 2H, ArH), 5.42 (s, 2H, NCH$_2$), 2.95 (t, $J = 6.0$ Hz, 2H, COCH$_2$), 2.63 (t, $J = 6.0$ Hz, 2H, CH$_2$), 2.31-2.25 (m, 2H, CH$_2$). **$^{13}$C NMR (100 MHz, CDCl$_3$)**: δ 193.7, 156.1, 144.1, 136.2, 134.9, 129.7, 129.4, 128.4, 126.0, 121.7, 118.2, 113.5, 106.4, 47.5, 37.8, 23.1, 22.6. LRMS (ESI): m/z calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3^+$ [2M + Na$^+$] 663.4.

**9-Methyl-7-(trifluoromethyl)-2,3-dihydro-1H-carbazol-4(9H)-one (3l)**

Following the general procedure, after 27 h, 3l was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. $R_f = 0.41$ (EtOAc/PE = 40/60). **Yield**: 55%, white solid, mp 206-207 °C. **$^1$H NMR (400 MHz, DMSO)**: δ 8.17 (d, $J = 8.0$ Hz, 1H, ArH), 7.98 (s, 1H, ArH), 7.51 (d, $J = 8.0$ Hz, 1H, ArH), 3.82 (s, 3H, NCH$_3$), 3.04 (t, $J = 6.0$ Hz, 2H, COCH$_2$),
2.46 (t, J = 6.0 Hz, 2H, CH2), 2.19-2.13 (m, 2H, CH2). \(^{13}\)C NMR (100 MHz, DMSO): \(\delta\) 193.3, 156.1, 136.8, 127.3, 125.6 (q, J = 270 Hz), 123.3 (q, J = 31 Hz), 121.1, 118.8 (q, J = 4 Hz), 111.8, 108.4 (q, J = 4 Hz), 37.9, 30.6, 23.1, 22.0. LRMS (ESI): m/z calcd for C\(_{14}\)H\(_{12}\)F\(_3\)NO\(^+\) [M + H\(^+\)] 268.1, found [M + H\(^+\)] 268.7, [M + Na\(^+\)] 290.4, [2M + Na\(^+\)] 557.0.

**6,8-Difluoro-9-methyl-2,3-dihydro-1H-carbazol-4(9H)-one (3m)**

Following the general procedure, after 16 h, 3m was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. \(R_f = 0.37\) (EtOAc/PE = 40/60). Yield: 63%, brown solid, mp 141-143 °C.

\(^1\)H NMR (400 MHz, DMSO): \(\delta\) 7.52 (dd, J = 9.0, 2.0 Hz, 1H, ArH), 7.10 (ddd, J = 12.0, 9.0, 2.0 Hz, 1H, ArH), 3.87 (d, J = 2.0 Hz, 3H, NCH\(_3\)), 2.98 (t, J = 6.0 Hz, 2H, COCH\(_2\)), 2.44 (t, J = 6.0 Hz, 2H, CH\(_2\)), 2.17-2.10 (m, 2H, CH\(_2\)). \(^{13}\)C NMR (100 MHz, DMSO): \(\delta\) 193.2, 158.1 (dd, J\(_{C-F}\) = 236, 10 Hz), 155.8, 148.9 (dd, J\(_{C-F}\) = 246, 14 Hz), 127.8 (dd, J\(_{C-F}\) = 12, 6 Hz), 121.7 (dd, J\(_{C-F}\) = 8, 1 Hz), 112.5 (dd, J\(_{C-F}\) = 5, 1 Hz), 102.0 (dd, J\(_{C-F}\) = 24, 4 Hz), 98.8 (dd, J\(_{C-F}\) = 30, 23 Hz), 37.7, 33.0 (d, J\(_{C-F}\) = 6 Hz), 23.0, 21.8. LRMS (ESI): m/z calcd for C\(_{13}\)H\(_{11}\)F\(_2\)NO\(^+\) [M + H\(^+\)] 236.1, found [M + H\(^+\)] 236.6, [M + Na\(^+\)] 258.5, [2M + Na\(^+\)] 493.1.

**9-Benzyl-6,7-dimethyl-2,3-dihydro-1H-carbazol-4(9H)-one (3n)**

Following the general procedure, after 8 h, 3n was purified by flash column chromatography (EtOAc/PE = 25/75) on silica gel. \(R_f = 0.50\) (EtOAc/PE = 40/60). Yield: 77%, white solid, mp 175-176 °C. \(^1\)H NMR (400 MHz, DMSO): \(\delta\) 7.81 (s, 1H, ArH), 7.34-7.30 (m, 3H, ArH), 7.25 (t, J = 7.0 Hz, 1H, ArH), 7.09 (d, J = 7.0 Hz, 2H, ArH), 5.44 (s, 2H, NCH\(_2\)), 2.92 (t, J = 6.0 Hz, 2H, COCH\(_2\)), 2.42 (t, J = 6.0 Hz, 2H, CH\(_2\)), 2.28 (s, 3H, ArCH\(_3\)), 2.27 (s, 3H, ArCH\(_3\)), 2.13-2.07 (m, 2H, CH\(_2\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 193.9, 151.1, 136.3, 136.1, 132.2, 131.6, 129.0, 127.8, 126.0, 123.1, 122.0, 112.8, 110.0, 46.9, 37.9, 23.5, 22.3, 20.7, 19.9. LRMS (ESI): m/z calcd for C\(_{21}\)H\(_{21}\)NO\(^+\) [M + H\(^+\)] 304.1, found 304.5.
References


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