Supporting Information for

Synthesis of Carbazolones and 3-Acetylindoles via Oxidative C-N Bond Formation through PIFA-Mediated Annulation of 2-Aryl Enaminones

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Supplementary Material

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General Information

$^1$H and $^{13}$C NMR spectra were recorded on a 400 MHz spectrometer at 25 °C. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br, broad and dd, doublet of doublets. The coupling constants J, are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained on a Q-TOF micro spectrometer. Melting points were determined with a national micromelting point apparatus without corrections. TLC plates were visualized by exposure to ultraviolet light. 1,2-Dichloroethane were dried by CaH$_2$ before use, other reagents and solvents were purchased as reagent grade and were used without further purification. Flash column chromatography was performed over silica gel 200-300 m and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE), or a mixture of methanol (M) and dichloromethane (D).

General Procedure for the Preparation of 1$^{1-2}$

To a solution of 3-aryl-dione$^1$ (3.0 mmol) in toluene (30 mL) was added corresponding amine (6.0 mmol). The reaction mixture was stirred at reflux until TLC indicated the total consumption of 3-aryl-pentane-2,4-dione. The mixture was evaporated to partially remove the solvent. EA was used to extract the mixture and the combined organic phase, after dried with anhydrous Na$_2$SO$_4$, was evaporated to remove the solvent under vacuum and the residue was purified by flash chromatography to give the desired product 1.$^2$

General Procedure for the Preparation of 2

To a solution of correspond substrate 1 (2.0 mmol) in CH$_2$Cl$_2$ (30 mL) was added a solution of PIFA (2.4 mmol) in CH$_2$Cl$_2$ (10 mL) dropwise under ice-bath during about 30 min, TLC monitored the process, after the consumption of starting material, to the reaction mixture was added saturated aq. NaHCO$_3$ solution, raised the temperature to rt, the mixture was stirred for 10 min, CH$_2$Cl$_2$ was used to extract the mixture and the organic phase, after dried with anhydrous Na$_2$SO$_4$, was evaporated to remove the solvent, the residue was purified by flash chromatography to give the desired product 2.

General Procedure for the Preparation of 3$^{1-2}$
A mixture of 3-phenylpentane-2,4-dione \(^1\) (3.0 mmol), corresponding amine (6.0 mmol) in EtOH (30 mL) was stirred at reflux until TLC indicated the total consumption of 3-phenylpentane-2,4-dione. The mixture was evaporated to partially remove the solvent. EA was used to extract the mixture and the combined organic phase, after dried with anhydrous Na\(_2\)SO\(_4\), was evaporated to remove the solvent under vacuum. The residue was purified by flash chromatography to give the desired product 3.\(^2\)

**General Procedure for the Preparation of 4**

To a solution of corresponding substrate 3 (2.0 mmol) in CH\(_2\)Cl\(_2\) (30 mL) was added a solution of PIFA (2.4 mmol) in CH\(_2\)Cl\(_2\) (10 mL) dropwise under ice-bath during about 30 min, TLC monitored the process. After the consumption of starting material, saturated aq. NaHCO\(_3\) solution was added to the reaction mixture. The reaction mixture was warmed up to rt, stirred for 10 min. CH\(_2\)Cl\(_2\) was used to extract the mixture and the organic phase, after dried with anhydrous Na\(_2\)SO\(_4\), was evaporated to remove the solvent. The residue was purified by flash chromatography to give the desired product 4.

**\(^1\)H and \(^{13}\)C NMR Spectra of Substrates 1**

3-Amino-2-phenylcyclohex-2-enone (1a)\(^3\) Following the general procedure, 1a was purified by silica gel column chromatography (EA/PE = 20/80). \(R_f = 0.45\) (M/D = 80/20). Yield: 88%, yellow solid, mp 165-167 °C. \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta 7.32\) (t, \(J_\text{Harom} = 7.6\) Hz, 2H, Harom), 7.19 (t, \(J_\text{Harom} = 7.6\) Hz, 1H, Harom), 7.06 (d, \(J_\text{Harom} = 7.2\) Hz, 2H, H\(_{\text{arom}}\)), 6.64 (br, 1H, NH), 5.67 (br, 1H, NH), 2.47 (t, \(J_\text{CH2} = 6.4\) Hz, 2H, CH\(_2\)), 2.22 (t, \(J_\text{CH2} = 6.4\) Hz, 2H, CH\(_2\)), 1.88 (dd, \(J_\text{CH2} = 12.4, 6.4\) Hz, 2H, CH\(_2\)). HRMS (ESI) \(m/z\) calcd for C\(_{12}\)H\(_{13}\)N\(\text{NaO}^+\) [M + Na\(^+\)] 210.1025, found 210.1027.

3-Amino-2-p-tolylcyclohex-2-enone (1b) Following the general procedure, 1b was purified by silica gel column chromatography (EA/PE = 50/50). \(R_f = 0.32\) (EA/PE = 90/10). Yield: 90%, yellow solid, mp 212-214 °C. \(^1\)H NMR (400 MHz, DMSO) \(\delta 7.12\) (d, \(J_\text{Harom} = 7.6\) Hz, 2H, H\(_{\text{arom}}\)), 6.95 (d, \(J_\text{Harom} = 8.0\) Hz, 2H, H\(_{\text{arom}}\)), 6.59 (br, 1H, NH), 5.61 (br, 1H, NH), 2.46 (t, \(J_\text{CH2} = 6.0\) Hz, 2H, CH\(_2\)), 2.29 (s, 3H, CH\(_3\)), 2.20 (t, \(J_\text{CH2} = 6.4\) Hz, 2H, CH\(_2\)), 1.94-1.79 (m, 2H, CH\(_2\)). \(^{13}\)C NMR (100 MHz, DMSO): \(\delta 192.38, 162.31, 135.06, 133.15, 131.43, 129.16, 110.39, 37.25, 29.14, 21.53, 21.27.\)
3-Amino-2-(3,4-dimethoxyphenyl)cyclohex-2-enone (1c) Following the general procedure, 1c was purified by silica gel column chromatography (EA). Rf = 0.40 (M/D = 5/95). Yield: 43%, yellow solid, mp 203-205 °C. 1H NMR (400 MHz, DMSO) δ 6.90 (d, J = 8.0 Hz, 1H, H arom), 6.62-6.53 (m, 2H, H arom), 5.75 (br, 2H, NH2), 3.74 (s, 3H, CH3), 3.70 (s, 3H, CH3), 2.45 (t, J = 6.4 Hz, 2H, CH2), 2.21 (t, J = 6.4 Hz, 2H, CH2). 13C NMR (100 MHz, DMSO): δ 192.14, 162.42, 148.90, 147.45, 128.64, 123.65, 115.33, 112.32, 110.48, 55.94, 55.73, 37.27, 29.13, 21.52. LRMS (ESI) m/z calcd for C13H15NNaO+ [M + Na+] 224.1046, found 224.1048.

3-Amino-2-(3-fluorophenyl)cyclohex-2-enone (1d) Following the general procedure, 1d was purified by silica gel column chromatography (EA/PE = 80/20). Rf = 0.30 (M/D = 10/90). Yield: 57%, white solid, mp 90-91 °C. 1H NMR (400 MHz, CDCl3) δ 8.06 (d, J = 13.6 Hz, 1H, H arom), 7.31 (t, J = 8 Hz, 1H, H arom), 6.93-6.85 (m, 2H, H arom), 6.14 (br, 1H, NH2), 5.84 (br, 1H, NH2) 2.45 (t, J = 6.0 Hz, 2H, CH2), 2.38 (t, J = 6.0 Hz, 2H, CH2). 13C NMR (100 MHz, CDCl3): δ 194.51, 163.17 (d, J C-F = 239.2 Hz), 163.15, 137.05 (d, J C-F = 7.9 Hz), 130.22 (d, J C-F = 8.6 Hz), 126.67, 118.10(d, J C-F = 10.1 Hz), 112.64 (d, J C-F = 20.7 Hz), 111.4, 36.65, 29.16 21.17. HRMS (ESI) m/z calcd for C12H12FNNaO+ [M + Na+] 228.0795, found 228.0795.

3-Amino-2-(3-(trifluoromethyl)phenyl)cyclohex-2-enone (1e) Following the general procedure, 1e was purified by silica gel column chromatography (EA/PE = 80/20). Rf = 0.40 (EA/PE = 95/5). Yield: 63%, white solid, mp 109-110 °C. 1H NMR (400 MHz, CDCl3) δ 7.48-7.38 (m, 2H, H arom), 7.37-7.32 (m, 1H, H arom), 7.26-7.22 (m, 1H, H arom), 2.37-2.34 (m, 4H, CH2), 1.96-1.91 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3): δ 194.74, 164.52, 135.65, 134.70, 129.18, 128.04, 124.08 (q, J C-F = 270.8 Hz), 123.63 (q, J C-F = 3.6 Hz), 110.35, 36.13, 28.73, 20.97. HRMS (ESI) m/z calcd for C13H12F3NNaO+ [M + Na+] 278.0763, found 278.0765.

3-Amino-2-(4-nitrophenyl)cyclohex-2-enone (1f) Following the general procedure, 1f was purified by silica gel column chromatography (EA/PE = 80/20). Rf = 0.35 (M/D = 5/95). Yield: 37%, yellow solid, mp 127-129 °C. 1H NMR (400 MHz, DMSO) δ 8.16 (d, J = 8.8 Hz, 2H, H arom), 7.37 (d, J = 8.8 Hz, 2H, H arom), 6.94 (br, 1H, NH), 6.35 (br, 1H, NH), 2.52 (t, J = 6.4 Hz, 2H, CH2),
2.26 (t, J = 6.4 Hz, 2H, CH2), 1.91-1.85 (m, 2H, CH2). 13C NMR (100 MHz, DMSO): δ 191.88, 163.71, 145.58, 144.73, 132.85, 123.48, 108.56, 37.09, 29.53, 21.25. HRMS (ESI) m/z calcd for C12H12N2NaO3+ [M + Na+] 255.0740, found 255.0741.

3-Amino-5,5-dimethyl-2-phenylcyclohex-2-enone (1g) Following the general procedure, 1g was purified by silica gel column chromatography (EA/PE = 80/20). Rf = 0.40 (EA/PE = 95/5). Yield: 73%, white solid, mp 112-114 °C. 1H NMR (400 MHz, CDCl3) δ 7.34 (t, J = 8.8 Hz, 2H, H arom), 7.22-7.19 (m, 2H, H arom), 7.14-7.12 (m, 1H, H arom), 4.72 (br, 2H, NH2), 2.30 (s, 4H, CH2), 1.13 (s, 6H, CH2). 13C NMR (100 MHz, CDCl3) δ 194.18, 151.21, 136.31, 124.69, 123.19, 122.50, 121.18, 111.92, 111.33, 77.38, 77.06, 76.74, 52.31, 37.34, 35.81, 28.64. HRMS (ESI) m/z calcd for C14H17NNaO+ [M + Na+] 238.1202, found 238.1205.

3-Amino-2-(naphthalen-2-yl)cyclohex-2-enone (1h) Following the general procedure, 1h was purified by silica gel column chromatography (EA/PE = 95/5). Rf = 0.40 (EA/PE = 95/5). Yield: 69%, white solid, mp 192-193 °C. 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 8.0 Hz, 1H, H arom), 7.78-7.73 (m, 2H, H arom), 7.59 (s, 1H, H arom), 7.43-7.41 (m, 2H, H arom), 7.23 (t, J = 12 Hz, 1H, H arom), 4.72 (br, 2H, NH2), 2.43 (t, J = 6.0 Hz, 4H, CH2), 2.02-1.96 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3): δ 194.74, 161.38, 133.76, 132.49, 132.19, 129.49, 129.19, 128.38, 127.71, 127.60, 125.81, 125.77, 36.74, 29.26, 21.26. HRMS (ESI) m/z calcd for C16H15NNaO+ [M + Na+] 260.1046, found 260.1047.

3-(Methylamino)-2-phenylcyclohex-2-enone (1i) Following the general procedure, 1i was purified by silica gel column chromatography (EA/PE = 90/10). Rf = 0.35 (EA/PE = 95/5). Yield: 81%, white solid, mp 92-94 °C. 1H NMR (400 MHz, CDCl3) δ 7.38 (t, J = 7.6 Hz, 2H, H arom), 7.26 (dd, J = 10.4, 4.4 Hz, 1H, H arom), 7.14 (d, J = 7.2 Hz, 2H, H arom), 4.78 (br, 1H, NH), 2.81 (s, 3H, CH3), 2.56 (t, J = 6.4 Hz, 2H, CH2), 2.47-2.40 (m, 2H, CH2), 2.10-2.04 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3): δ 193.18, 162.59, 134.95, 131.36, 129.02, 126.96, 112.58, 36.55, 29.98, 25.20, 21.15. HRMS (ESI) m/z calcd for C13H15NNaO+ [M + Na+] 224.1046, found 224.1048.

3-(Methylamino)-2-p-tolylcyclohex-2-enone (1j) Following the general procedure, 1j was purified by silica gel column chromatography (EA/PE = 80/20). Rf = 0.54 (M/D = 5/95). Yield: 93%, white solid, mp 129-130 °C. 1H NMR (400 MHz, CDCl3) δ 7.20 (d, J = 7.6 Hz, 2H, H arom),
6-(Propylamino)-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (1k) Following the general procedure, 1b was recrystallized from EA/PE as a white solid. Rf = 0.56 (M/D = 5/95). Yield: 62%, m.p. 118 °C. 1H NMR (400MHz, CDCl3) δ 7.39 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.3 Hz, 2H), 4.76 (br, 1H), 3.07 (dd, J = 12.9, 6.4 Hz, 2H), 2.54 (dd, J = 21.0, 14.9 Hz, 2H), 2.43 (t, J = 6.4 Hz, 2H), 2.12 -1.99 (m, 2H), 1.53-1.37 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 193.12, 161.91, 135.06, 131.30, 129.00, 126.90, 112.45, 44.74, 36.67, 25.38, 23.64, 21.30, 11.11. HRMS (ESI) m/z calcd for C15H19NNaO+ [M + Na+] 252.1359, found 252.1360.

2-Phenyl-3-(phenylamino)cyclohex-2-enone (1l) Following the general procedure, 1l was purified by silica gel column chromatography (EA/PE = 5/95). Rf = 0.51 (EA/PE = 60/40). Yield: 87%, white solid, mp 127-129 °C. 1H NMR (400 MHz, CDCl3) δ 7.44 (t, J = 7.6 Hz, 2H, H arom), 7.33-7.26 (m, 4H, H arom), 7.18 (t, J = 7.6 Hz, 1H, H arom), 7.01 (d, J = 8.0 Hz, 2H, H arom), 6.46 (s, 1H, H arom). 2.60 (t, J = 6.4 Hz, 2H, CH2), 2.52 (t, J = 6.4 Hz, 2H, CH2), 2.07-2.01 (m, 2H, CH2). LRMS (ESI) m/z calcd for C36H34N2NaO2+ [2M + Na+] 549.2, found 549.2.

3-(4-Methoxyphenylamino)-2-phenylcyclohex-2-enone (1m) Following the general procedure, 1m was purified by silica gel column chromatography. Rf = 0.40 (EA/PE = 10/90). Yield: 63%, white solid, mp 67-69 °C. 1H NMR (400 MHz, CDCl3) δ 7.46 (t, J = 7.2 Hz, 7.6 Hz, 2H, H arom), 7.29-7.36 (m, 3H, H arom), 7.01 (d, J = 8.0 Hz, 2H, H arom), 6.87 (d, J = 8.0 Hz, 2H, H arom), 6.46 (br, 1H, NH), 3.82 (s, 3H, CH3), 2.66 (t, J = 6.4 Hz, 2H, CH2), 2.54 (t, J = 6.0 Hz, 2H, CH2), 2.06-2.02 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3) δ 194.38, 160.25, 158.01, 134.56, 131.25, 131.00, 129.16, 127.47, 127.27, 114.38, 114.32, 37.07, 26.75, 21.77. HRMS (ESI) m/z calcd for C19H19NNaO2+ [M + Na+] 316.1308, found 316.1308.

3-(4-Nitrophenylamino)-2-phenylcyclohex-2-enone (1n) Following the general procedure, 1n was purified by silica gel column chromatography. Rf = 0.50 (EA/PE = 10/90). Yield: 87%, yellow
solid, mp 132-134 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 8.0 Hz, 2H, H arom), 7.45 (t, J = 8.0 Hz, 2H, H arom), 7.35 (t, J = 8.0 Hz, 1H, H arom), 7.21 (d, J = 8.0 Hz, 2H, H arom), 6.99 (d, J = 8.0 Hz, 2H, H arom), 6.64 (br, 1H, NH), 2.80 (t, J = 6.0 Hz, 2H, CH₂), 2.59 (t, J = 6.0 Hz 2H, CH₂), 2.15 (d, J = 4.5 Hz, 2H, CH₂). ¹³C NMR (100 MHz, DMSO) δ 195.54, 156.08, 147.13, 135.38, 131.36, 131.20, 128.04, 127.58, 126.67, 124.60, 120.45, 37.90, 29.90, 21.40. HRMS (ESI) m/z calcd for C₁₈H₁₆N₂NaO₃⁺ [M + Na⁺] 331.1053, found 331.1057.

¹H and ¹³C NMR spectra of Carbazolones 2

2,3-Dihydro-1H-carbazol-4(9H)-one (2a) Following the general procedure, 2a was purified by silica gel column chromatography (EA/PE = 60/40). Rf = 0.50 (EA/PE = 80/20). Yield: 90%, white solid, mp 224-226 °C. ¹H NMR (400 MHz, DMSO) δ 7.94 (d, J = 6.8 Hz, 1H, H arom), 7.39 (d, J = 6.8 Hz, 1H, H arom), 7.26-6.94 (m, 2H, H arom), 2.96 (t, J = 6.0 Hz, 2H, CH₂), 2.48-2.36 (m, 2H, CH₂), 2.17-2.06 (m, 2H, CH₂). LRMS (ESI) m/z calcd for C₁₂H₁₁NNaO⁺ [M + Na⁺] 208.1, found 208.1.

7-Methyl-2,3-dihydro-1H-carbazol-4(9H)-one (2b) Following the general procedure, 2b was purified by silica gel column chromatography (EA/PE = 60/40). Rf = 0.29 (EA/PE = 60/40). Yield: 90%, white solid, mp>250 °C. ¹H NMR (400 MHz, DMSO) δ 7.81 (d, J = 8.0 Hz, 1H, H arom), 7.18 (s, 1H, H arom), 6.96 (d, J = 7.6 Hz, 1H, H arom), 2.93 (t, J = 6.0 Hz, 2H, CH₂), 2.45-2.33 (m, 5H, CH₂, CH₃), 2.11 (dd, J = 12.4, 6.2 Hz, 2H, CH₂). ¹³C NMR (100 MHz, DMSO): δ 193.17, 152.30, 136.74, 132.04, 123.45, 122.76, 120.33, 112.17, 111.90, 38.23, 23.92, 23.17, 21.78. HRMS (ESI) m/z calcd for C₁₃H₁₃NNaO⁺ [M + Na⁺] 222.0889, found 222.0892.

6,7-Dimethoxy-2,3-dihydro-1H-carbazol-4(9H)-one (2c) Following the general procedure, 2c was purified by silica gel column chromatography (EA/PE = 10/90). Rf = 0.40 (EA/PE = 20/80). Yield: 67%, white solid, mp 230-231 °C. ¹H NMR (400MHz, DMSO) δ 11.56 (br, 1H, NH), 7.44 (s, 1H, H arom), 6.94 (s, 1H, H arom), 3.78 (s, 3H, CH₃), 3.76 (s, 3H, CH₃), 2.91 (t, J = 6.0 Hz, 2H, CH₂), 2.39 (t, J = 6.0 Hz, 2H, CH₂), 2.10 (dd, J = 12.0, 5.9 Hz, 2H, CH₂). ¹³C NMR (100 MHz, DMSO) δ 193.20, 150.87, 147.07, 146.34, 130.39, 117.68, 112.33, 112.17, 111.90, 38.23, 23.92, 23.17, 21.78. HRMS (ESI) m/z calcd for C₁₄H₁₆NO₃⁺ [M + H⁺] 246.1125, found 246.1127.

6-Fluoro-2,3-dihydro-1H-carbazol-4(9H)-one (2d) Following the general procedure, 2d was
purified by silica gel column chromatography (EA/PE = 10/90). \( R_f = 0.55 \) (EA/PE = 20/80). Yield: 65\%, white solid, mp > 250 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 12.52 (br, 1H, NH), 8.24 (s, 1H, \( H_{\text{arom}} \)), 7.61 (d, \( J = 8.4 \) Hz, 1H, \( H_{\text{arom}} \)), 7.49 (d, \( J = 8.4 \) Hz, 1H, \( H_{\text{arom}} \)), 3.02 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)), 2.48 (t, \( J = 6.4 \) Hz, 2H, CH\(_2\)), 2.17-2.14 (m, 2H, CH\(_2\)). LRMS (ESI) m/z calcd for C\(_{12}\)H\(_{10}\)FNO\(^+\) [M + H\(^+\)] 204.1, found 204.0.

**8-Fluoro-2,3-dihydro-1\(H\)-carbazol-4(9\(H\))-one (2d)** Following the general procedure, 2d′ was purified by silica gel column chromatography (PE). \( R_f = 0.75 \) (EA/PE = 20/80). Yield: 22\%, white solid, mp 224-226 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 12.11 (br, 1H, NH), 8.25 (d, \( J = 7.6 \) Hz, 1H, \( H_{\text{arom}} \)), 7.51 (d, \( J = 7.6 \) Hz, 1H, \( H_{\text{arom}} \)), 7.33 (t, \( J = 7.6, 7.6 \) Hz, 1H, \( H_{\text{arom}} \)), 3.04 (t, \( J = 6.4 \) Hz, 2H, CH\(_2\)), 2.48 (t, \( J = 6.8 \) Hz, 2H, CH\(_2\)), 2.15-2.01 (m, 2H, CH\(_2\)). 13C NMR (100 MHz, DMSO) \( \delta \) 193.29, 158.88 (d, \( J_{\text{C-F}} = 233 \) Hz), 154.28, 132.91, 125.48, 113.14 (d, \( J_{\text{C-F}} = 9.7 \) Hz), 110.63 (d, \( J_{\text{C-F}} = 25.5 \) Hz), 105.76, 105.51, 37.23, 23.76, 23.23. LRMS (ESI) m/z calcd for C\(_{12}\)H\(_{10}\)FNO\(^+\) [M + H\(^+\)] 204.1, found 204.3.

**6-(Trifluoromethyl)-2,3-dihydro-1\(H\)-carbazol-4(9\(H\))-one (2e)** Following the general procedure, 2e was purified by silica gel column chromatography (PE). \( R_f = 0.60 \) (EA/PE = 10/90). Yield: 49\%, white solid, mp 207-209 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 11.96 (br, 1H, NH), 7.60 (m, 1H, \( H_{\text{arom}} \)), 7.40 (m, 1H, \( H_{\text{arom}} \)), 7.01 (m, 1H, \( H_{\text{arom}} \)), 2.96 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)), 2.43 (t, \( J = 6.0 \) Hz, 2H, CH\(_2\)), 2.13 (m, 2H, CH\(_2\)). LRMS (ESI) m/z calcd for C\(_{13}\)H\(_{10}\)F\(_3\)NO\(^+\) [M + H\(^+\)] 254.1, found 254.1.

**8-(Trifluoromethyl)-2,3-dihydro-1\(H\)-carbazol-4(9\(H\))-one (2e′)** Following the general procedure, 2e′ was purified by silica gel column chromatography (PE). \( R_f = 0.70 \) (EA/PE = 10/90). Yield: 41\%, white solid, mp 183-185 °C. \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 12.34 (br, 1H, NH), 7.76 (d, \( J = 8.0 \) Hz, 1H, \( H_{\text{arom}} \)), 7.11 (m, 1H, \( H_{\text{arom}} \)), 7.02 (m, 1H, \( H_{\text{arom}} \)), 2.98 (t, \( J = 6.4 \) Hz, 2H, CH\(_2\)), 2.45 (t, \( J = 6.4 \) Hz, 2H, CH\(_2\)), 2.13 (m, 2H, CH\(_2\)). 13C NMR (100 MHz, DMSO) \( \delta \) 193.62, 154.95, 138.17, 125.78(q, \( J_{\text{C-F}} = 243 \) Hz), 124.68, 122.92, 119.51 (q, \( J_{\text{C-F}} = 3.3 \) Hz), 117.47 (q, \( J_{\text{C-F}} = 3.5 \) Hz), 112.87, 38.11, 23.71, 23.16. HRMS (ESI) m/z calcd for C\(_{13}\)H\(_{11}\)F\(_3\)NO\(^+\) [M + H\(^+\)] 254.0787, found 254.0789.

**7-Nitro-2,3-dihydro-1\(H\)-carbazol-4(9\(H\))-one (2f)** Following the general procedure, 2f was
purified by silica gel column chromatography (EA/PE = 50/50). Rf = 0.40 (EA/PE = 70/30). Yield: 79%, yellow solid, mp > 250 °C. 1H NMR (400 MHz, DMSO) δ 12.52 (br, 1H, NH), 8.24 (d, J = 1.2 Hz, 1H, H aromatic), 8.30 (d, J = 1.4 Hz, 1H, H aromatic), 8.07 (m, 2H, H aromatic), 3.06 (t, J = 6.0 Hz, 2H, CH2), 2.48 (t, J = 6.4 Hz, 2H, CH2), 2.16 (m, 2H, CH2). LRMS (ESI) m/z calcd for C12H10N2NaO3+ [M + Na+] 253.1, found 253.4.

2,2-Dimethyl-2,3-dihydro-1H-carbazol-4(9H)-one (2g) Following the general procedure, 2g was purified by silica gel column chromatography (PE). Rf = 0.70 (EA/PE = 10/90). Yield: 87%, white solid, mp 212-214 °C. 1H NMR (400 MHz, CDCl3) δ 9.82 (br, 1H, NH), δ 8.23 (m, 1H, H aromatic), 7.41 (m, 2H, H aromatic), 7.25 (m, 2H, H aromatic), 2.87 (s, 2H, CH2), 2.51 (s, 2H, CH2), 1.17 (s, 6H, CH3). LRMS (ESI) m/z calcd for C14H15NNaO+ [M + Na+] 236.1, found 236.5.

8,9,10,11-Tetrahydro-7H-benzo[a]carbazol-7-one (2h) Following the general procedure, 2h was purified by silica gel column chromatography (PE). Rf = 0.70 (EA/PE = 20/80). Yield: 84%, white solid, mp 92-94 °C. 1H NMR (400 MHz, CDCl3) δ 9.26 (br, 1H, NH), δ 8.36 (d, J = 8.8 Hz, 1H, H aromatic), 7.70 (d, J = 8.8 Hz, 1H, H aromatic), 7.57 (t, J = 8.8 Hz, 1H, H aromatic), 7.48 (t, J = 8.8 Hz, 1H, H aromatic), 3.12 (t, J = 6.4 Hz, 2H, CH2), 2.67 (t, J = 6.4 Hz, 2H, CH2), 2.33 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3) δ 194.75, 161.38, 133.76, 132.50, 132.19, 129.50, 129.20, 128.38, 127.72, 127.61, 125.82, 125.76, 112.64, 36.75, 29.27, 21.27. HRMS (ESI) m/z calcd for C16H14NO+ [M + Na+] 258.1070, found 258.1071.

9-Methyl-2,3-dihydro-1H-carbazol-4(9H)-one (2i) Following the general procedure, 2i was purified by silica gel column chromatography (EA/PE = 40/60). Rf = 0.29 (EA/PE = 50/50). Yield: 82%, white solid, mp 205-207 °C. 1H NMR (400 MHz, DMSO) δ 8.30-8.22 (m, 1H, H aromatic), 7.34-7.23 (m, 3H, H aromatic), 3.72 (s, 3H, CH3), 2.94 (t, J = 6.0 Hz, 2H, CH2), 2.61-2.57 (m, 2H, CH2), 2.30-2.23 (m, 2H, CH2). LRMS (ESI) m/z calcd for C13H13NNaO+ [M + Na+] 222.1, found 222.3.

7,9-Dimethyl-2,3-dihydro-1H-carbazol-4(9H)-one (2j) Following the general procedure, 2j was purified by silica gel column chromatography (EA/PE = 10/90). Rf = 0.54 (EA/PE = 20/80). Yield: 74%, white solid, mp 239-241 °C. 1H NMR (400MHz, CDCl3) δ 8.10 (d, J = 8.0 Hz, 1H, H aromatic), 7.17-7.01 (m, 2H, H aromatic), 3.63 (s, 3H, CH3), 2.93-2.84 (m, 2H, CH2), 2.58-2.51 (m, 2H, CH2), 2.48 (s, 3H, CH3), 2.25-2.19 (m, 2H, CH2). 13C NMR (100 MHz, CDCl3) δ 193.65, 151.39, 137.81,
132.88, 124.08, 122.48, 121.29, 112.67, 109.22, 37.84, 29.76, 23.36, 22.19, 21.89. HRMS (ESI) m/z calcd for C\textsubscript{14}H\textsubscript{15}NNaO\textsuperscript{+} [M + Na\textsuperscript{+}] 236.1046, found 236.1046.

9-Propyl-2,3-dihydro-1\textsubscript{H}-carbazol-4(9\textsubscript{H})-one (2k) Following the general procedure, 2k was purified by silica gel column chromatography (EA/PE = 15/85). R\textsubscript{f} = 0.42 (EA/PE = 50/50). Yield: 31%, yellow solid, mp 153-155 °C. \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}) \(\delta\) 8.27 (dd, \(J\) = 6.0, 2.5 Hz, 1H, Harom), 7.35 -7.22 (m, 3H, Harom), 4.07 (t, \(J\) = 7.3 Hz, 2H, NCH\textsubscript{2}), 2.94 (t, \(J\) = 6.2 Hz, 2H, CH\textsubscript{2}), 2.66 -2.52 (m, 2H, CH\textsubscript{2}), 2.26 (p, \(J\) = 6.3 Hz, 2H, CH\textsubscript{2}), 1.85 (h, \(J\) = 7.4 Hz, 2H, CH\textsubscript{2}), 0.97 (t, \(J\) = 7.4 Hz, 3H, CH\textsubscript{3}). HRMS (ESI) m/z calcd for C\textsubscript{15}H\textsubscript{17}NNaO\textsuperscript{+} [M + Na\textsuperscript{+}] 250.1202, found 250.1207.

9-Phenyl-2,3-dihydro-1\textsubscript{H}-carbazol-4(9\textsubscript{H})-one (2l)\textsuperscript{10} Following the general procedure, 2l was purified by silica gel column chromatography (EA/PE = 10/90). R\textsubscript{f} = 0.70 (EA/PE = 30/70). Yield: 73%, solid, mp 153-154 °C. \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}) \(\delta\) 8.32 (d, \(J\) = 7.6 Hz, 2H, H arom), 7.65-7.48 (m, 1H, Harom ), 7.40 (d, \(J\) = 7.6 Hz, 1H, H arom), 7.31 (t, \(J\) = 7.6 Hz, 1H, H arom), 7.22 (t, \(J\) = 7.6 Hz, 1H, H arom), 7.16 (d, \(J\) = 8.0 Hz, 2H, H arom), 2.82 (t, \(J\) = 6.4 Hz, 2H, CH\textsubscript{2}), 2.65 (t, \(J\) = 6.4 Hz, 2H, CH\textsubscript{2}), 2.27-2.17 (m, 2H, CH\textsubscript{2}). LRMS (ESI) m/z calcd for C\textsubscript{36}H\textsubscript{30}N\textsubscript{2}NaO\textsubscript{2}\textsuperscript{+} [2M + Na\textsuperscript{+}] 545.2, found 545.2.

9-(4-Methoxyphenyl)-2,3-dihydro-1\textsubscript{H}-carbazol-4(9\textsubscript{H})-one (2m) Following the general procedure, 2m was purified by silica gel column chromatography (PE). R\textsubscript{f} = 0.60 (EA/PE = 20/80). Yield: 76%, solid, mp 123-125 °C. \textsuperscript{1}H NMR (400MHz, DMSO) \(\delta\) 8.32 (d, \(J\) = 7.6 Hz, 1H, H arom), 7.28-7.32 (m, 3H, H arom ), 7.20-7.24 (m, 1H, H arom), 7.08-7.14 (m, 3H, H arom), 3.93 (s, 3H, CH\textsubscript{3}), 2.80 (t, \(J\) = 6.4 Hz, 2H, CH\textsubscript{2}), 2.64 (t, \(J\) = 6.4 Hz, 2H, CH\textsubscript{2}), 2.22 (m, 2H, CH\textsubscript{2}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 194.31, 159.72, 152.36, 138.46, 128.72, 128.40, 124.63, 123.29, 122.84,121.49, 114.99, 113.27, 110.42, 56.66, 38.10, 23.02, 23.01. HRMS (ESI) m/z calcd for C\textsubscript{19}H\textsubscript{17}NNaO\textsuperscript{2+} [M + Na\textsuperscript{+}] 314.1151, found 314.1151.

9-(4-Nitrophenyl)-2,3-dihydro-1\textsubscript{H}-carbazol-4(9\textsubscript{H})-one (2n) Following the general procedure, 2n was purified by silica gel column chromatography (PE). R\textsubscript{f} = 0.50 (EA/PE = 20/80). Yield: 70%, yellow solid, mp 166-168 °C. \textsuperscript{1}H NMR (400MHz, CDCl\textsubscript{3}) \(\delta\) 8.46 (d, \(J\) = 8.0 Hz, 2H, H arom), 8.32 (d, \(J\) = 8.0 Hz, 1H, H arom ), 7.63 (d, \(J\) = 8.0 Hz, 2H, H arom), 7.34 (t, \(J\) = 8.0 Hz, 1H, H arom),
7.26 (t, J = 8.0 Hz, 1H, H arom), 7.21 (d, J = 8.0 Hz, 1H, H arom), 2.87 (t, J = 6.0 Hz, 2H, CH2), 2.63 (t, J = 6.0 Hz, 2H, CH2), 2.27-2.21 (m, 2H, CH2). 13C NMR (100 MHz, DMSO) δ 194.09, 152.71, 147.23, 141.74, 137.24, 128.73, 125.74, 125.06, 124.15, 123.60, 121.16, 113.79, 110.94, 38.14, 23.56, 23.09. HRMS (ESI) m/z calcd for C18H14N2NaO3 [M + Na+] 329.0897, found 329.0898.

1H and 13C NMR Spectra of Substrates 3

3-Phenyl-4-(propylamino)pent-3-en-2-one (3a) Following the general procedure, 3a was purified by silica gel column chromatography (PE). Rf = 0.58 (EA/PE = 20/80). Yield: 22%, yellow oil. 1H NMR (400 MHz, CDCl3) δ 12.10 (br, 1H, NH), 7.33 (t, J = 7.6 Hz, 2H, H arom), 7.29-7.23 (m, 1H, H arom), 7.15 (d, J = 7.6 Hz, 2H, H arom), 3.26 (dd, J = 12.8, 6.7 Hz, 2H, CH2), 1.81 (s, 3H, CH3), 1.74 (s, 3H, CH3), 1.62 (m, 2H, CH2), 1.04 (t, J = 7.6 Hz, 3H, CH3). 13C NMR (100 MHz, CDCl3) δ 194.00, 162.53, 141.17, 132.29, 128.45, 126.41, 109.20, 45.22, 29.03, 16.74, 11.56. HRMS (ESI) m/z calcd for C14H19NNaO+ [M + Na+] 240.1359, found 240.1362.

4-(Benzylamino)-3-phenylpent-3-en-2-one (3b) Following the general procedure, 3b was purified by silica gel column chromatography (PE). Rf = 0.46 (EA/PE = 20/80). Yield: 58%, yellow oil. 1H NMR (400MHz, CDCl3) δ 12.35 (br, 1H, NH), 7.40-7.23 (m, 8H, H arom), 7.16 (d, J = 7.2 Hz, 2H, H arom), 4.52 (d, J = 5.8 Hz, 2H, CH2), 1.84 (s, 3H, CH3), 1.71 (s, 3H, CH3). 13C NMR (100 MHz, CDCl3) δ 195.00, 162.27, 140.99, 138.06, 132.24, 128.86, 128.51, 126.90, 126.54, 110.07, 47.23, 29.27, 16.85. HRMS (ESI) m/z calcd for C18H19NNaO+ [M + Na+] 288.1359, found 288.1361.

3-Phenyl-4-(phenylamino)pent-3-en-2-one (3c) Following the general procedure, 3c was purified by silica gel column chromatography (EA/PE = 10/90). Rf = 0.3 (EA/PE = 10/90). Yield: 87%, white solid, mp 105-107 °C. 1H NMR (400MHz, CDCl3) δ 7.43-7.09 (m, 10H, H arom), 1.90 (s, 3H, CH3), 1.74 (s, 3H, CH3). LRMS (ESI) m/z calcd for C17H17NNaO+ [M + Na+] 274.1, found 274.0.

1H and 13C NMR Spectra of 3-Acetylindoles 4

9-Propyl-2,3-dihydro-1H-carbazol-4(9H)-one (4a) Following the general procedure, 4a was purified by silica gel column chromatography (EA/PE = 40/60). Rf = 0.42 (EA/PE = 50/50). Yield:
74%, yellow solid, mp 153-155 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (dd, $J = 6.0, 2.4$ Hz, 1H, H$_{arom}$), 7.35-7.22 (m, 3H, H$_{arom}$), 4.07 (t, $J = 7.6$ Hz, 2H, CH$_2$), 2.94 (t, $J = 6.4$ Hz, 2H, CH$_2$), 2.66-2.52 (m, 2H, CH$_2$), 2.26 (p, $J = 6.4$ Hz, 2H, CH$_3$), 1.85 (h, $J = 7.6$ Hz, 2H, CH$_2$), 0.97 (t, $J = 7.6$ Hz, 3H, CH$_3$). HRMS (ESI) m/z calcd for C$_{15}$H$_{17}$NNaO$^+$ [M + Na$^+$] 250.1202, found 250.1207.

1-(1-Benzyl-2-methyl-1H-indol-3-yl)ethanone (4b)$^{11}$ Following the general procedure, 4b was purified by silica gel column chromatography (EA/PE = 10/90). $R_f$ = 0.48 (EA/PE = 20/80). Yield: 73%, white solid, mp 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J = 8.0$ Hz, 1H, H$_{arom}$), 7.29-7.20 (m, 6H, H$_{arom}$), 6.99 (d, $J = 7.0$ Hz, 2H, H$_{arom}$), 5.38 (s, 2H, CH$_2$), 2.74 (s, 3H, CH$_3$), 2.59 (s, 3H, CH$_3$). 13C NMR (100 MHz, CDCl$_3$) $\delta$ 194.88, 145.11, 137.82, 136.25, 129.85, 129.05, 128.32, 126.23, 122.42, 122.40, 122.04, 115.09, 110.88, 31.73, 13.95. HRMS (ESI) m/z calcd for C$_{18}$H$_{17}$NNaO$^+$ [M + Na$^+$] 286.1202, found 286.1202.

1-(2-Methyl-1-phenyl-1H-indol-3-yl)ethanone (4c) Following the general procedure, 4c was purified by silica gel column chromatography (EA/PE = 10/90). $R_f$ = 0.51 (EA/PE = 20/80). Yield: 86%, solid, mp 130-132 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J = 8.0$ Hz, 1H, H$_{arom}$), 7.65-7.51 (m, 3H, H$_{arom}$), 7.38-7.24 (m, 3H, H$_{arom}$), 7.17 (t, $J = 7.0$ Hz, 1H, H$_{arom}$), 7.03 (d, $J = 8.0$ Hz, 1H, H$_{arom}$), 2.74 (s, 3H, CH$_3$), 2.59 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.88, 145.11, 137.82, 136.25, 129.85, 129.05, 128.32, 126.23, 122.42, 122.40, 122.04, 115.09, 110.88, 31.73, 13.95. HRMS (ESI) m/z calcd for C$_{17}$H$_{15}$NNaO$^+$ [M + Na$^+$] 272.1046, found 272.1047.

References:


**1H and 13C NMR Spectra of 1**
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O

NH₂

1a

O

NH₂

1b

ppm (δ)

ppm (δ)

S14
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$^1$H and $^{13}$C NMR Spectra of Carbazolones 2

2a

2b
$^1$H and $^{13}$C NMR Spectra of 3
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