Supporting Information

Formal [4+2] benzannulation of 2-alkenyl indoles with aldehydes: a route to structurally diverse carbazoles and bis-carbazoles

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**Experimental Section:**

**General:** All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen atmosphere. THF was obtained from Rankem India, and was freshly distilled over Na-benzophenone under nitrogen. All other solvents were obtained from Merck India and were dried according to the standard literature procedure. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized under UV light and dipping into KMnO₄ solution. Silica gel (particle size 100-200 mesh) was purchased from SRL India for performing column chromatography by using mixture of hexanes and ethylacetate eluent. NaH (60% dispersion in mineral oil), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and p-toluenesulfonic acid monohydrate, indole-2-carboxylic acid were received from Spectrochem Pvt. Ltd and used as it is. The ¹H NMR spectroscopic data were recorded with a Bruker 400 or 600 MHz instrument. ¹³C NMR spectra were similarly recorded at 100 or 150 MHz, using a broadband decoupled mode. The ¹H NMR spectroscopic data are reported relative to either CDCl₃ (δ = 7.26 ppm) and DMSO-d₆ (δ = 2.50 ppm). Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton signals in CDCl₃ (δ = 7.26, 77.16) and DMSO-d₆ (δ = 2.50, 39.52). Coupling constants (J) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublets m: multiplet, br: broad. Infrared (IR) spectra were recorded by Perkin Elmer FTIR spectrometer, and reported in terms of wave number (cm⁻¹). High resolution mass spectra (HRMS) were recorded in ESI (+ Ve) method.
Synthesis of Aldehydes:

All aldehydes are either commercially available or prepared by following reported synthetic method.\(^1\)

Synthesis of 2-Alkenyl Indoles:

2-Alkenyl indoles were prepared by following a reported procedure.\(^2\) To a 50 mL round bottom flask equipped with a reflux condenser, \(\text{ArCH}_2\text{PPh}_3\text{Br}\) (5.0 mmol, 2.5 equiv.) was taken. Then the reaction flask was evacuated under \textit{vacuo} and backfilled with nitrogen by using a Schlenk technique. This procedure was repeated twice. Then dry toluene (10.0 mL) was added under nitrogen, and the resulting mixture was cooled down to 0 °C. To the stirring solution, \(\text{NaH}\) (5.0 mmol, 2.5 equiv., 60% dispersion in mineral oil) was added portion wise at the same temperature under constant nitrogen pressure. After that it was allowed to warm to rt, and stirred at the same condition for 45 min. Subsequently, the solution of 1H-indole-2-carbaldehyde (2.0 mmol, 1.0 equiv.) in dry toluene (10.0 mL) was added and the resulting reaction mixture was heated at 80 °C for 2 h. After completion of the reaction as indicated by TLC, saturated aq. \(\text{NH}_4\text{Cl}\) solution (10.0 mL) was added to the reaction mixture. The aqueous layer was extracted with ethylacetate (3 x 10 mL), the combined organic layers were dried over \(\text{Na}_2\text{SO}_4\), and evaporated under reduced pressure. The crude residue was purified by column chromatography (5% ethylacetate/hexane) to afford substrates 1.

General Procedure I (GP I): Synthesis of Carbazoles by One-Pot Formal [4+2]-Benzannulation of 2-Alkenyl-Indoles with Aldehydes Using Oxygen as Sole Oxidant

To a 15 mL sealed pressure tube equipped with a magnetic stir bar benzenesulfinic acid (\(\text{PhSO}_2\text{H}\), 34.1 mg, 0.24 mmol, 1.2 equiv.), \(p\)-toluenesulfonic acid monohydrate (PTSA·\(\text{H}_2\text{O}\), 3.8 mg, 0.02 mmol, 0.10 equiv.), and 2-alkenyl indole 1 (0.20 mmol, 1.0 equiv.) were sequentially added. To this mixture, aldehyde 2 (0.3 mmol, 1.5 equiv.) dissolved in 1.2 mL
tetrahydrofuran (THF) was subsequently added at the room temperature. Finally, the resulting reaction mixture was stirred at 60 °C (for few particular substrates this step was performed at room temperature, please check individual examples). After complete consumption of starting material \(1\) (generally 50 to 75 min) as indicated by TLC, the reaction mixture was cooled down to room temperature. Then sodium hydride (20 mg, 0.50 mmol, 2.5 equiv.) and DBU (0.02 mmol, 3.0 µL, 0.20 M in THF, 10.0 mol %) were added successively and stirring was continued further at the room temperature. After complete consumption of sulfonylindole \(A\) as indicated by TLC, 2.0 mL of decalin was added to the reaction mixture and then the pressure tube was filled with molecular oxygen (purging of oxygen is not required). After that, it was heated to 180 °C. Upon complete consumption of 2,3-dialkenylindole \(B\) (generally 24 h to 72 h, check individual examples in Table S1) as indicated by TLC, ethyl acetate was added to the crude reaction mixture and then it was carefully transferred to a round bottom flask. Then the solvent was evaporated under \textit{vacuo} and the crude product was purified by silica gel column chromatography to afford the pure desired carbazoles \(3a-3s, 4a-4i,\) and \(5-7\).

**Note:** It should be noted that, for all the cases the TLC of the last step were checked after 36 h. Sometimes the 2,3-dialkenylindole \(B\) and the corresponding carbazole product show same \(R_f\) values in TLC but the textures of these two spots are easily distinguishable by dipping in to \(\text{KMnO}_4\) solution or anisal staining agent or under UV-light. TLC-spot of the electrolycized intermediates \(C\) are generally come just below the carbazole products \(3-7\). If electrolycized products \(C\) is still remaining in the reaction mixture after 36 h, the reaction mixture was again filled with molecular oxygen and reaction was continued at 180 °C until complete consumption of the electrolycized products \(C\) to carbazoles.

For \(3s\) \(\text{CH}_2\text{Cl}_2\) was used in place of THF. The first step was conducted using 0.4 equiv PTSA·H₂O and 1.5 equiv \(\text{PhSO}_2\text{H}\) and in second step 3.0 equiv \(\text{NaH}\) was used along with 0.1 equiv DBU.

The \(^1\text{H}\) and \(^{13}\text{C}\) spectral data of the following carbazoles (Table S1) are in agreement with our previously reported values;\(^2\) and \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of these compounds are provided at the end of the supporting information.

**Table S1.** Carbazoles known in the literature.

<table>
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<tr>
<th>Compound number</th>
<th>Time for last step (in h)</th>
<th>Amount isolated in mg (0.20 mmol scale)</th>
<th>Yield (%)</th>
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<td>(3a)</td>
<td>36</td>
<td>49.7</td>
<td>78</td>
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The titled compound 3c was synthesized according to the GP I by using (E)-2-styryl-1H-indole (43.9 mg, 0.20 mmol, 1.0 equiv.) and 4-methoxyphenylacetaldehyde (45.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 36 h. The carbazole 3c (48.1 mg, 0.14 mmol, 69%) was isolated as a yellow solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 11.32 (br s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.10 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.45 (s, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.28 - 7.15 (m, 6H), 7.08 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 3.72 (s, J = 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm) 157.49, 142.38, 140.49, 139.07, 137.96, 134.52, 131.04, 129.82, 127.92, 126.24, 125.77, 122.30, 121.99, 121.90, 120.49, 118.72, 113.31, 112.41, 111.06, 54.97. FTIR: ʋ_max (neat)/ cm⁻¹ = 3250, 2926, 2856, 1661, 1238, 1024, 745. HRMS (ESI): calculated for C₂₅H₁₉NO₃Na ([M+Na⁺]: 372.1359; found 372.1348.

3-(4-Methoxyphenyl)-2-phenyl-9H-carbazole (3l): The titled compound 3l was synthesized according to the GP I by using (E)-2-styryl-1H-indole (43.9 mg, 0.20 mmol, 1.0 equiv.) and 4-((4-methoxybenzyl)oxy)butanal (62.5 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 36 h. The carbazole 3l (43.3 mg, 0.11 mmol,
53%) was isolated as a pale yellow oil after column chromatography on silica gel by using 6% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): δ (ppm) 11.16 (br s, 1H), 8.09 (d, $J = 7.8$ Hz, 1H), 8.06 (s, 1H), 7.48 – 7.44 (m, 3H), 7.40 – 7.37 (m, 4H), 7.23 (s, 1H), 7.17 – 7.12 (m, 3H), 6.84 (d, $J = 7.8$ Hz, 2H), 4.28 (s, 2H), 3.72 (s, 3H), 3.50 (t, $J = 7.2$ Hz, 2H), 2.94 (t, $J = 7.2$ Hz, 2H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): δ (ppm) 158.60, 142.24, 140.30, 139.67, 138.37, 130.42, 129.32, 129.04, 128.15, 126.81, 126.16, 125.55, 122.09, 121.89, 121.05, 120.21, 118.54, 113.57, 111.85, 110.97, 71.33, 70.50, 55.04, 33.0. FTIR: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3411, 3058, 2923, 2853, 1611, 1512, 1244, 1033, 702. HRMS (ESI): calculated for C$_{28}$H$_{25}$NO$_2$Na ([M+Na]$^+$): 430.1778; found 430.1751.

**2-Phenyl-3-(2-(prop-2-yn-1-yloxy)ethyl)-9H-carbazole (3m):**

The titled compound 3m was synthesized according to the GP I by using (E)-2-styryl-1H-indole (43.9 mg, 0.20 mmol, 1.0 equiv.) and 4-(prop-2-yn-1-yloxy)butanal (38.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 24 h. The carbazole 3m (27.5 mg, 0.08 mmol, 42%) was isolated as a colourless oil after column chromatography on silica gel by using 6% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): δ (ppm) 11.17 (br s, 1H), 8.11 (d, $J = 7.8$ Hz, 1H), 8.07 (s, 1H), 7.48 – 7.45 (m, 3H), 7.41 – 7.36 (m, 4H), 7.25 (s, 1H), 7.16 (t, $J = 7.2$ Hz, 1H), 4.02 (d, $J = 2.4$ Hz, 2H), 3.55 (t, $J = 7.5$ Hz, 2H), 2.92 (t, $J = 7.5$ Hz, 2H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): δ (ppm) 142.21, 140.33, 139.71, 138.42, 129.31, 128.21, 126.87, 125.89, 125.59, 122.10, 121.93, 121.01, 120.25, 118.58, 111.92, 111.0, 80.39, 77.0, 70.24, 57.23, 32.76. FTIR: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3410, 3058, 2923, 2113, 1612, 1465, 1087, 702. HRMS (ESI): calculated for C$_{23}$H$_{20}$NO ([M+H]$^+$): 326.1539; found 326.1553.

**3-(4-((4-Methoxybenzyl)oxy)-2-methylbutyl)-2-phenyl-9H-carbazole (3p):**

The titled compound 3p was synthesized according to the GP I by using (E)-2-styryl-1H-indole (43.9 mg, 0.20 mmol, 1.0 equiv.) and 6-((4-methoxybenzyl)oxy)-4-methylhexanal (75.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 60 h. The carbazole 3p (66.4 mg, 0.15 mmol, 74%) was isolated as a yellow oil after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): δ (ppm) 11.16 (br s, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.96 (s, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.38 – 7.34 (m, 4H), 7.24 (s,
1H), 7.15 – 7.12 (m, 3H), 6.84 (d, J = 8.4 Hz, 2H), 4.19 (s, 2H), 3.71 (s, 3H), 3.18 – 3.15 (m, 2H), 2.77 (dd, J = 13.2, 6.3 Hz, 1H), 2.52 (dd, J = 13.2, 7.8 Hz, 1H), 1.62 – 1.56 (m, 1H), 1.45 – 1.40 (m, 1H), 1.18 – 1.12 (m, 1H), 0.65 (d, J = 6.6 Hz, 3H). 13C NMR (150 MHz, DMSO-d6): δ (ppm) 158.61, 142.70, 140.34, 139.88, 138.24, 130.58, 129.40, 129.05, 128.75, 128.06, 126.64, 125.48, 122.23, 121.75, 121.20, 120.22, 118.49, 113.55, 111.95, 110.96, 71.41, 67.56, 55.02, 40.46, 35.91, 31.52, 19.55.

FTIR: νmax(neat)/ cm⁻¹ = 3402, 2927, 2857, 1612, 1512, 1244, 1026, 993, 702.

HRMS (ESI): calculated for C₃₁H₃₂NO₂ ([M+H]+): 450.2428; found 450.2439.

3-(2-Methyl-4-(phenylthio)butyl)-2-phenyl-9H-carbazole (3q):

The titled compound 3q was synthesized according to the GP I by using (E)-2-styryl-1H-indole (43.9 mg, 0.20 mmol, 1.0 equiv.) and 4-methyl-6-(phenylthio)hexanal (67.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 52 h. The carbazole 3q (58.4 mg, 0.14 mmol, 69%) was isolated as a white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. 1H NMR (600 MHz, DMSO-d6): δ (ppm) 11.17 (br s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.96 (s, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.44 – 7.42 (m, 2H), 7.39 – 7.34 (m, 4H), 7.24 (s, 1H), 7.21 – 7.19 (m, 2H), 7.16 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 7.8 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 2.80 (dd, J = 13.2, 6.3 Hz, 1H), 2.64 (t, J = 7.8 Hz, 2H), 2.52 (dd, J = 13.2, 7.8 Hz, 1H), 1.62 – 1.57 (m, 1H), 1.43 – 1.37 (m, 1H), 1.25 – 1.19 (m, 1H), 0.69 (d, J = 6.0 Hz, 3H). 13C NMR (150 MHz, DMSO-d6): δ (ppm) 142.60, 140.31, 139.80, 138.27, 136.39, 129.38, 128.88, 128.48, 128.09, 127.91, 126.67, 125.48, 125.40, 122.20, 121.72, 121.25, 120.23, 118.49, 111.97, 110.96, 40.05, 35.33, 33.62, 29.86, 19.31. FTIR: νmax(neat)/ cm⁻¹ = 3404, 3057, 2953, 1612, 1464, 1239, 1024, 995, 735. HRMS (ESI): calculated for C₂₉H₂₇NSNa ([M+Na]+): 444.1756; found 444.1752.

3-Butyl-6-chloro-2-phenyl-9H-carbazole (4a):

The titled compound 4a was synthesized according to the GP I by using (E)-5-chloro-2-styryl-1H-indole (50.7 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 78 h. The carbazole 4a (41.7 mg, 0.12 mmol, 63%) was isolated as a white solid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. 1H NMR (600 MHz, DMSO-d6): δ (ppm) 11.30 (br s, 1H), 8.21 (d, J = 2.4 Hz, 1H), 8.07 (s, 1H), 7.48 (d, J = 9.0 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.39 – 7.35 (m, 4H), 7.24 (s, 1H), 2.65 (t, J = 8.1 Hz,
2H), 1.45 – 1.39 (m, 2H), 1.18 – 1.12 (m, 2H), 0.73 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): δ (ppm) 142.34, 140.31, 138.77, 138.72, 130.70, 129.23, 128.13, 126.87, 125.22, 123.57, 122.81, 121.12, 120.84, 119.87, 112.40, 112.06, 33.52, 32.37, 21.94, 13.70. FTIR: $\nu$$_{max}$(neat)/ cm$^{-1}$ = 3421, 3059, 2928, 2857, 1633, 1235, 1071, 806. HRMS (ESI): calculated for C$_{22}$H$_{21}$ClN ([M+H]$^+$): 334.1357; found 334.1351.

3-Butyl-2-(p-tolyl)-9H-carbazole (4b): The titled compound 4b was synthesized according to the GP I by using (E)-2-(4-methylstyril)-1H-indole (46.7 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 78 h. The carbazole 4b (44.5 mg, 0.14 mmol, 71%) was isolated as a yellow solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): δ (ppm) 11.09 (br s, 1H), 8.10 (d, J = 7.2 Hz, 1H), 7.99 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.27 – 7.24 (m, 4H), 7.21 (s, 1H), 7.14 (t, J = 7.2 Hz, 1H), 2.68 (t, J = 7.8 Hz, 2H), 2.37 (s, 3H), 1.47 – 1.42 (m, 2H), 1.21 – 1.15 (m, 2H), 0.76 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): δ (ppm) 140.24, 139.59, 139.33, 138.13, 135.63, 130.19, 129.06, 128.59, 125.30, 122.18, 121.76, 120.19, 120.10, 118.34, 111.76, 110.83, 33.65, 32.37, 21.92, 20.72, 13.67. FTIR: $\nu$$_{max}$(neat)/ cm$^{-1}$ = 3413, 3023, 2923, 2855, 1611, 1464, 1236, 819, 742. HRMS (ESI): calculated for C$_{23}$H$_{24}$N ([M+H]$^+$): 314.1903; found 314.1894.

3-Butyl-2-(4-methoxyphenyl)-9H-carbazole (4c): The titled compound 4c was synthesized according to the GP I by using (E)-2-(4-methoxystyril)-1H-indole (49.9 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 60 h. The carbazole 4c (34.5 mg, 0.10 mmol, 52%) was isolated as a white solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): δ (ppm) 11.07 (br s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.99 (s, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.20 (s, 1H), 7.13 (t, J = 7.3 Hz, 1H), 7.01 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 2.68 (t, J = 7.8 Hz, 2H), 1.47 – 1.42 (m, 2H), 1.22 – 1.16 (m, 2H), 0.77 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): δ (ppm) 158.04, 140.22, 139.06, 138.14, 134.74, 130.33, 130.24, 125.26, 122.18, 121.66, 120.17, 120.08, 118.33, 113.43, 111.85, 111.82, 55.05, 33.61, 20.66, 13.67. FTIR: $\nu$$_{max}$(neat)/ cm$^{-1}$ = 3413, 3023, 2923, 2855, 1611, 1464, 1236, 819, 742. HRMS (ESI): calculated for C$_{23}$H$_{24}$N ([M+H]$^+$): 314.1903; found 314.1894.
(neat)/ cm$^{-1}$ = 3250, 2927, 2857, 1609, 1464, 1238, 1025, 830. **HRMS (ESI)**: calculated for C$_{23}$H$_{24}$NO ([M+H]$^+$): 330.1852; found 330.1795.

3-Butyl-2-(2-fluorophenyl)-9H-carbazole (4d):

The titled compound 4d was synthesized according to the **GP I** by using (E)-2-(2-fluorostyryl)-1H-indole (47.5 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 36 h. The carbazole 4d (36.3 mg, 0.11 mmol, 57%) was isolated as a white solid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ (ppm) 11.15 (br s, 1H), 8.13 (d, $J$ = 7.8 Hz, 1H), 8.04 (s, 1H), 7.48 (d, $J$ = 8.4 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.40 – 7.37 (m, 2H), 7.32 – 7.29 (m, 2H), 7.25 (s, 1H), 7.15 (t, $J$ = 7.8 Hz, 1H), 2.57 (br s, 2H), 1.44 – 1.39 (m, 2H), 1.18 – 1.12 (m, 2H), 0.72 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ (ppm) 159.16 (d, $J$ = 242.6 Hz), 140.28, 137.95, 132.60, 132.04 (d, $J$ = 3.2 Hz), 130.93, 129.52 (d, $J$ = 16.8 Hz), 129.35 (d, $J$ = 7.9 Hz), 125.58, 124.26 (d, $J$ = 3.2 Hz), 122.47, 122.07, 120.24, 120.03, 118.47, 115.35 (d, $J$ = 22.5 Hz), 112.14, 110.95, 33.22, 32.43, 21.79, 13.55. **FTIR**: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3252, 2926, 2856, 1612, 1466, 992, 745. **HRMS (ESI)**: calculated for C$_{22}$H$_{21}$FN ([M+H]$^+$): 318.1653; found 318.1659.

3-Butyl-2-(naphthalen-1-yl)-9H-carbazole (4e):

The titled compound 4e was synthesized according to the **GP I** by using (E)-2-(2-(naphthalen-1-yl)vinyl)-1H-indole (53.9 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 78 h. The carbazole 4e (58.1 mg, 0.17 mmol, 83%) was isolated as a yellowish gummy liquid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. $^1$H NMR (600 MHz, DMSO-d$_6$): $\delta$ (ppm) 11.15 (br s, 1H), 8.15 (d, $J$ = 7.8 Hz, 1H), 8.09 (s, 1H), 7.99 (d, $J$ = 8.4 Hz, 1H), 7.96 (d, $J$ = 8.4 Hz, 1H), 7.60 (t, $J$ = 7.5 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.44 (d, $J$ = 6.6 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.25 (s, 1H), 7.17 (t, $J$ = 7.5 Hz, 1H), 2.50 – 2.45 (m, 1H), 2.31 – 2.26 (m, 1H), 1.34 – 1.29 (m, 2H), 1.03 – 0.97 (m, 2H), 0.55 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, DMSO-d$_6$): $\delta$ (ppm) 140.33, 139.99, 138.12, 137.21, 133.12, 132.17, 131.33, 128.26, 127.38, 127.16, 126.17, 125.88, 125.82, 125.60, 125.44, 122.34, 122.32, 120.31, 120.16, 118.59, 112.43, 111.04, 33.50, 32.66, 21.78, 13.58. **FTIR**: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3415, 3043, 2925, 2857, 1610, 1465, 1235, 863.

3-Butyl-2-(thiophen-2-yl)-9H-carbazole (4f):
The titled compound 4f was synthesized according to the GP I by using (E)-2-(2-(thiophen-2-yl)vinyl)-1H-indole (45.0 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 36 h. The carbazole 4f (51.2 mg, 0.17 mmol, 84%) was isolated as a pale yellow solid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. 

**1H NMR** (600 MHz, DMSO-d$_6$): δ (ppm) 11.17 (br s, 1H), 8.11 (d, $J$ = 7.8 Hz, 1H), 8.02 (s, 1H), 7.59 (dd, $J$ = 4.8, 1.8 Hz, 1H), 7.47 (d, $J$ = 8.4 Hz, 1H), 7.41 (s, 1H), 7.38 (t, $J$ = 7.8 Hz, 1H), 7.16 – 7.13 (m, 3H), 2.82 (t, $J$ = 8.1 Hz, 2H), 1.54 – 1.49 (m, 2H), 1.30 – 1.24 (m, 2H), 0.83 (t, $J$ = 7.2 Hz, 3H).

**13C NMR** (150 MHz, DMSO-d$_6$): δ (ppm) 143.38, 140.50, 138.08, 131.00, 130.95, 127.43, 126.54, 125.82, 122.54, 122.03, 120.81, 120.41, 118.63, 112.78, 111.04, 133.92, 32.63, 22.12, 13.82. 

**FTIR**: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3398, 3049, 2927, 2868, 1607, 1448, 1235, 749. 

**HRMS (ESI)**: calculated for C$_{20}$H$_{20}$NS ([M+H]$^+$): 306.1311; found 306.1307.

3-Butyl-1-phenyl-9H-carbazole (4g):

The titled compound 4g was synthesized according to the GP I by using 2-(1-phenylvinyl)-1H-indole (43.9 mg, 0.20 mmol, 1.0 equiv.) and 1-hexanal (30.0 mg, 0.30 mmol, 1.50 equiv.). The final step was conducted over 36 h. The carbazole 4g (40.8 mg, 0.14 mmol, 68%) was isolated as a colourless oil after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. 

**1H NMR** (600 MHz, DMSO-d$_6$): δ (ppm) 10.94 (br s, 1H), 8.10 (d, $J$ = 7.8 Hz, 1H), 7.93 (s, 1H), 7.71 (d, $J$ = 8.4 Hz, 2H), 7.57 (t, $J$ = 7.5 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 1H), 7.45 (t, $J$ = 7.2 Hz, 1H), 7.35 (t, $J$ = 7.5 Hz, 1H), 7.24 (s, 1H), 7.14 (t, $J$ = 7.5 Hz, 1H), 2.79 (t, $J$ = 7.8 Hz, 2H), 1.71 – 1.66 (m, 2H), 1.41 – 1.35 (m, 2H), 0.93 (t, $J$ = 7.5 Hz, 3H). 

**13C NMR** (150 MHz, DMSO-d$_6$): δ (ppm) 140.55, 138.79, 135.39, 133.11, 128.96, 128.37, 127.19, 126.54, 125.82, 122.54, 122.03, 120.81, 120.41, 118.63, 112.78, 111.04, 133.92, 32.63, 22.12, 13.82. 

**FTIR**: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3400, 2926, 2856, 1650, 1498, 992. 

**HRMS (ESI)**: calculated for C$_{22}$H$_{22}$N ([M+H]$^+$): 300.1747; found 300.1750.

3-Butyl-1-(thiophen-2-yl)-9H-carbazole (4h):

The titled compound 4h was synthesized according to the GP I by using 2-(1-(thiophen-2-yl)vinyl)-1H-indole (34.0 mg, 0.15 mmol, 1.0 equiv.) and 1-hexanal (23.0 mg, 0.23 mmol, 1.50 equiv.). The final step was conducted over 36 h. The carbazole 4h (16.0 mg, 0.05 mmol, 35%) was isolated as a colourless
oil after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. \textbf{\textsuperscript{1}H NMR} (600 MHz, DMSO-$d_6$): $\delta$ (ppm) 10.99 (br s, 1H), 8.11 (d, $J = 7.8$ Hz, 1H), 7.93 (s, 1H), 7.66 (dd, $J = 4.8$, 1.2 Hz, 1H), 7.62 (br s, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.34 (s, 1H), 7.30 – 7.28 (m, 1H), 7.16 (t, $J = 7.4$ Hz, 1H), 2.77 (t, $J = 7.2$ Hz, 2H), 1.69 – 1.64 (m, 2H), 1.40 – 1.34 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, DMSO-$d_6$): $\delta$ (ppm) 140.64, 140.57, 134.71, 133.23, 128.42, 125.76, 125.68, 125.54, 125.39, 123.98, 122.35, 120.17, 119.23, 118.95, 117.38, 111.82, 34.84, 34.05, 21.91, 13.93. \textbf{FTIR}: $\nu_{\text{max}}$ (neat)/ cm$^{-1} = 3400, 2926, 2856, 1635, 1450, 1234, 735$. \textbf{HRMS (ESI)}: calculated for C$_{20}$H$_{20}$NS ([M+H]$^+$): 306.1311; found 306.1307.

3-Butyl-1,2-diphenyl-9H-carbazole (4i):

The titled compound 4i was synthesized according to the \textbf{GP I} by using (E)-2-(1,2-diphenylvinyl)-1H-indole (50.0 mg, 0.17 mmol, 1.0 equiv.) and 1-hexanal (25.0 mg, 0.25 mmol, 1.50 equiv.). The final step was conducted over 24 h. The carbazole 4i (36.3 mg, 0.10 mmol, 57%) was isolated as a colourless sticky liquid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. \textbf{\textsuperscript{1}H NMR} (600 MHz, DMSO-$d_6$): $\delta$ (ppm) 10.42 (br s, 1H), 8.13 (d, $J = 7.8$ Hz, 1H), 8.04 (s, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.33 (t, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.5$ Hz, 2H), 7.20 – 7.12 (m, 7H), 7.07 (d, $J = 7.2$ Hz, 2H), 2.54 – 2.51 (m, 2H), 1.45 – 1.40 (m, 2H), 1.18 – 1.12 (m, 2H), 0.71 (t, $J = 7.5$ Hz, 3H). \textbf{\textsuperscript{13}C NMR} (150 MHz, DMSO-$d_6$): $\delta$ (ppm) 140.64, 140.24, 137.87, 137.71, 136.78, 131.19, 130.66, 130.43, 128.01, 127.26, 126.50, 126.08, 125.34, 124.30, 122.33, 121.79, 120.04, 119.18, 118.50, 111.50, 33.69, 33.24, 22.06, 13.64. \textbf{FTIR}: $\nu_{\text{max}}$ (neat)/ cm$^{-1} = 3250, 2955, 2857, 1601, 1498, 1223, 996, 698$. \textbf{HRMS (ESI)}: calculated for C$_{28}$H$_{26}$N ([M+H]$^+$): 376.2060; found 376.2055.

References:


$^1$H and $^{13}$C NMR Spectra of Compound 3a (600 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3b (400 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3c (400 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3d (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3e (400 MHz, DMSO-d$_6$)

[Image of NMR spectra]
$^1$H and $^{13}$C NMR Spectra of Compound 3f (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3g (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3h (400 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3i (600 MHz, DMSO-d$_6$)
\(^{1}H\) and \(^{13}C\) NMR Spectra of Compound 3j (600 MHz, DMSO-d\(_6\))
$^1$H and $^{13}$C NMR Spectra of Compound 3k (600 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3l (600 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3m (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3n (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3o (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3p (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3q (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3r (600 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 3s (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4a (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4b (600 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4c (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4d (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4e (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4f (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4g (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4h (600 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 4i (600 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 5 (400 MHz, DMSO-$d_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 6 (400 MHz, DMSO-d$_6$)
$^1$H and $^{13}$C NMR Spectra of Compound 7 (600 MHz, DMSO-d$_6$)