Supporting Information for

Regioselective $\pi$-Extension of Indoles With Rhodium Enalcarbenoids- Synthesis of Substituted Carbazoles

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1. General Methods:
All the reactions were performed in an oven-dried glassware under argon atmosphere. Solvents were dried using standard methods. Tetrahydrofuran and diethyl ether were dried over sodium-benzophenone ketyl. Acetonitrile, dichloromethane and toluene were distilled over calcium hydride. Unless otherwise stated, all the commercial reagents were used as received. Progress of the reaction was monitored by thin layer chromatography (Merck Silicagel 60 F-254, 0.25 nm, precoated plates on alumina). Column chromatographic purifications were performed on Merck silica gel (100-200 mesh). Melting points were recorded on a digital melting point apparatus and are uncorrected. Spectroscopic characterizations were carried at the Central Instrumentation Facility (CIF), Indian Institute of Science Education and Research (IISER) Bhopal. $^1$H-NMR spectra were recorded on Bruker Avance III FT-NMR spectrometers at 400 MHz, 500 or 700 MHz and $^{13}$C-NMR spectra were recorded at 101 MHz, 126 MHz or 176 MHz. $^1$H-NMR chemical shifts are reported in ppm relative to the TMS ($\delta=0$) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). $^{13}$CNMR chemical shifts are reported in ppm relative to the residual CDCl$_3$ signal ($\delta= 77.16$). IR spectra were recorded on a Perkin Elmer FT-IR spectrometer. HRMS data was obtained on a Bruker microTOFQII or Agilent 5975C high resolution mass spectrometers.

2. Preparation of Enaldiazo Esters 14a-c:

Synthesis of enaldiazo esters 14a-c was previously reported by us.$^{[1]}$
3. Preparation of Substituted Indole Starting Materials:

Indoles 13c-13g were purchased from Sigma-Aldrich. Known indoles 13a, 13b and 13h-l were prepared according to the literature procedures.\(^2\)
4. Optimization of π-Extension of Indoles:

A 0.15 M solution of 14a (0.6 mmol) was added slowly with a flow rate of 1 ml/h using a syringe pump to a solution of indole 13a (0.24 mmol), Rh\textsuperscript{II} catalyst and 5 mol% (±)-BINOL phosphoric acid 21 in appropriate solvent (2 ml) at temperature T. The reaction was continued for an additional 2 h. The solvent was evaporated under reduced pressure and the product was purified by silica gel flash column chromatography using ethyl acetate-petroleum ether as the eluent.

**Ethyl 9-benzyl-9H-carbazole-4-carboxylate (20):** Obtained as a yellow solid. Yield = 68%; R\textsubscript{f}=0.42 (Ethyl Acetate/Hexane : 4/96); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.84 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 8.1 Hz, 1H).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Rh\textsubscript{2}L\textsubscript{4} (mol %)</th>
<th>14a/13a</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
<td>1.5/1</td>
<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>42</td>
</tr>
<tr>
<td>2.</td>
<td>Rh\textsubscript{2}(Oct)\textsubscript{4}(2)</td>
<td>1.5/1</td>
<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>31</td>
</tr>
<tr>
<td>3.</td>
<td>Rh\textsubscript{2}(esp)\textsubscript{4}(2)</td>
<td>1.5/1</td>
<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>26</td>
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<tr>
<td>4.</td>
<td>Rh\textsubscript{2}(TFA)\textsubscript{4}(2)</td>
<td>1.5/1</td>
<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>14</td>
</tr>
<tr>
<td>5.</td>
<td>Rh\textsubscript{2}(DOSP)\textsubscript{4}(2)</td>
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<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>20</td>
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<tr>
<td>6.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
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<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>32</td>
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<tr>
<td>7.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
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<td>40</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>68</td>
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<td>8.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
<td>3/1</td>
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<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>69</td>
</tr>
<tr>
<td>9.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
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<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
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<tr>
<td>10.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
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<td>CHCl\textsubscript{3}</td>
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<td>11.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
<td>2.5/1</td>
<td>84</td>
<td>C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2}</td>
<td>&lt;5</td>
</tr>
<tr>
<td>12.</td>
<td>Rh\textsubscript{2}(OAc)\textsubscript{4}(2)</td>
<td>2.5/1</td>
<td>40</td>
<td>toluene</td>
<td>15</td>
</tr>
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</table>
Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H). 7.14 (d, J = 5.9 Hz, 2H), 7.01 – 6.96 (m, 2H), 5.44 (s, 2H), 4.46 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 168.2, 141.5, 141.4, 136.9, 129.0, 127.7, 127.0, 126.4, 126.0, 125.9, 124.9, 122.4, 121.7, 121.7, 119.7, 113.0, 108.7, 61.2, 46.5, 14.6; IR (neat): 3063, 2922, 2850, 1725, 1714, 1616, 1594 cm\-1; HRMS (APCI) m/z Calc. for C22H19NO2 [M+H] 330.1489, Found 330.1510.

5. Carbazole Synthesis by π-Extension of Indoles (Table 2):

\[
\text{RO}_2\text{C} \quad \text{N}_2 \quad + \quad \text{13} \quad \xrightarrow{2 \text{ mol% Rh}_2(\text{OAc})_4} \quad \text{22-39}
\]

General procedure:
An oven dried 10 ml round-bottom flask containing a stir bar under inert atmosphere was charged with Indole 13 (0.24 mmol), Rh2(OAc)4 (0.0048 mmol), 21 (0.012 mmol) and CH2Cl2 (2 ml) and heated to reflux. To the gently refluxing contents was added a solution of enaldiazo ester 14 (0.6 mmol) in CH2Cl2 (4 ml) over 4 h using a syringe pump. The reaction was continued at reflux for another 2 h, and the solvent was evaporated under reduced pressure. The crude material was purified by a silica gel flash column chromatography using ethyl acetate-petroleum ether as the eluent to furnish carbazole.

Ethyl 9-methyl-9H-carbazole-4-carboxylate (22): Obtained as a black solid. Yield = 64%; Rf=0.33 (Ethyl Acetate/Hexane : 3/97); 1H NMR (400 MHz, CDCl3) δ 8.90 (d, J = 8.1 Hz, 1H), 7.86 (dd, J = 7.4, 0.6 Hz, 1H), 7.55 (t, J = 8.7 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.27 (dd, J = 11.6, 4.3 Hz, 1H), 4.55 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.50 (t, J = 7.1 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 168.2, 141.8, 141.7,
126.7, 125.8, 124.6, 122.1, 121.5, 121.4, 119.3, 112.6, 108.3, 61.2, 29.2, 14.5; IR (neat): 3062, 2928, 2857, 1725, 1610, 1570 cm⁻¹; HRMS (LC) m/z Calc. for C₁₆H₁₅NO₂ [M+H] 254.1176, Found: 254.1186.

Ethyl 6-methoxy-9-methyl-9H-carbazole-4-carboxylate (23):
Obtained as a yellow solid. Yield = 50%; R°F = 0.35 (Ethyl Acetate/Hexane : 8/92); ¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 2.4 Hz, 1H), 7.83 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 8.9 Hz, 1H), 7.19 (dd, J = 8.9, 2.5 Hz, 1H), 4.53 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.84 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 153.6, 142.3, 137.1, 125.8, 124.5, 121.8, 121.8, 121.3, 116.6, 112.8, 108.9, 108.5, 61.2, 56.30, 29.41, 14.6; IR (neat): 3059, 2925, 2848, 1751, 1714, 1596, 1575, 1537 cm⁻¹; HRMS (LC) m/z Calc. for C₁₇H₁₇NO₃ [M+H] 284.1281, Found: 284.1286.

Ethyl 9-benzyl-5-(benzyloxy)-9H-carbazole-4-carboxylate (24):
Obtained as a yellow solid. Yield = 70%; R°F = 0.77 (Ethyl Acetate/Hexane : 2/98); ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.4 Hz, 2H), 7.43 – 7.22 (series of m, 10H), 7.12 – 7.07 (m, 2H), 6.96 (d, J = 8.2 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 5.45 (s, 2H), 5.39 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 155.1, 141.5, 140.6, 137.4, 136.9, 129.8, 129.0, 128.7, 127.9, 127.7, 127.3, 126.5, 124.8, 119.0, 117.9, 111.6, 110.3, 102.9, 102.1, 70.6, 61.0, 46.8, 14.4; IR (neat): 3060, 2922, 2856, 1728 cm⁻¹; HRMS (LC) m/z Calc. for C₂₉H₂₅NO₃ [M+H] 436.1907, Found: 436.1907.

Benzyl 9-benzyl-9H-carbazole-4-carboxylate (25): Obtained as a white solid. Yield = 67%; R°F = 0.63 (Ethyl Acetate/Hexane : 4/96); ¹H NMR (500 MHz, CDCl₃) δ 8.97 (d, J = 8.2 Hz, 1H), 7.96 (dd, J = 7.6, 0.9 Hz, 1H), 7.60 – 7.38 (series of m, 9H), 7.31 - 7.25 (m, 4H), 7.15 – 7.10 (m, 2H), 5.59 (s, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 167.9, 141.5, 141.4, 136.8, 136.2, 129.0, 128.7, 128.5, 128.4, 127.7, 127.0, 126.3, 126.0, 125.5, 124.9,
122.7, 121.9, 121.7, 119.7, 113.3, 108.7, 67.0, 46.5; IR (neat): 3033, 2920, 2849, 1715, 1617, 1593, 1571 cm\(^{-1}\); HRMS (LC) m/z Calc. for C\(_{27}\)H\(_{21}\)NO\(_2\) [M+H]\(^{+}\) 392.1645, Found: 392.1669.

**Benzyl 9-methyl-9H-carbazole-4-carboxylate (26):** Obtained as a white solid. Yield = 66%; R\(_f\)=0.76 (Ethyl Acetate/Hexane : 5/95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.88 (d, \(J = 8.1\) Hz, 1H), 7.90 (dd, \(J = 7.5, 0.6\) Hz, 1H), 7.59 (d, \(J = 7.7\) Hz, 1H), 7.55 – 7.45 (m, 4H), 7.43 – 7.19 (m, 1H), 5.52 (s, 2H), 3.87 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.9, 141.8, 141.8, 136.3, 128.8, 128.5, 128.4, 126.8, 126.0, 125.4, 124.7, 122.4, 121.6, 121.5, 119.4, 112.8, 108.3, 67.0, 29.3; IR (neat): 3063, 2922, 2852, 1722, 1714, 1616, 1594, 1574 cm\(^{-1}\); HRMS (LC) m/z Calc. for C\(_{21}\)H\(_{17}\)NO\(_2\) [M+H]\(^{+}\) 354.0891 , Found: 354.0911.

**Benzyl 9-benzyl-6-methoxy-9H-carbazole-4-carboxylate (27):** Obtained as a pale yellow solid. Yield = 68%; R\(_f\)=0.65 (Ethyl Acetate/Hexane : 10/90); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.52 (d, \(J = 2.4\) Hz, 1H), 7.89 (d, \(J = 7.2\) Hz, 1H), 7.55 – 7.52 (m, 3H), 7.44 – 7.33 (m, 4H), 7.28 – 7.20 (m, 4H), 7.13 (dd, \(J = 8.9, 2.5\) Hz, 1H), 7.07 – 7.04 (m, 2H), 5.54 (s, 2H), 5.51 (s, 2H), 3.88 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.9, 153.8, 141.9, 137.0, 136.6, 136.3, 128.9, 128.8, 128.5, 127.7, 126.3, 125.4, 124.7, 122.4, 122.0, 121.6, 116.9, 113.4, 109.3, 108.4, 66.9, 56.1, 46.7; IR (neat): 3033, 2928, 2857, 1715, 1623, 1597, 1575 cm\(^{-1}\); HRMS (LC) m/z Calc. for C\(_{28}\)H\(_{23}\)NO\(_3\) [M+H]\(^{+}\) 422.1751, Found:422.1769. CCDC 1005568 contains crystallographic data.
Benzyl 9H-carbazole-4-carboxylate (28): Obtained as a yellow solid. Yield = 62%; Rf=0.50 (Ethyl Acetate/Hexane : 2/98); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.88 (d, J = 8.2 Hz, 1H), 8.28 (s, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.55 - 7.33 (series of m, 9H) 7.21 (d, J = 7.9 Hz, 1H), 5.53 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.9, 140.4, 140.3, 136.2, 128.8, 128.5, 128.4, 126.9, 125.9, 125.3, 124.8, 122.9, 122.1, 122.0, 119.8, 115.2, 110.4, 66.9; IR (neat): 3035, 2926, 2854, 1727, 1714, 1698, 1605, 1573 cm$^{-1}$; HRMS (LC) m/z Calc. for C$_{20}$H$_{15}$NO$_2$ [M+H] 302.1176, Found: 302.1160.

Benzyl 6-methoxy-9H-carbazole-4-carboxylate (29): Obtained as a yellow solid. Yield = 58%; Rf=0.43 (Ethyl Acetate/Hexane : 10/90); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.44 (d, J = 2.4 Hz, 1H), 8.15 (s, 1H), 7.89 (dd, J = 7.5, 0.6 Hz, 1H), 7.59 (dd, J = 8.0, 0.6 Hz, 1H), 7.51 (d, J = 7.2 Hz, 2H), 7.42 - 7.31 (m, 5H), 7.12 (dd, J = 8.8, 2.5 Hz, 1H), 5.51 (s, 2H), 3.86 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.8, 135.3, 135.3, 128.8, 128.4, 125.3, 124.7, 122.8, 122.5, 122.2, 117.1, 115.3, 111.0, 108.2, 66.9, 56.1; IR (neat): 3036, 2929, 2835, 1714, 1701, 1606, 1596 cm$^{-1}$; HRMS (LC) m/z Calc. for C$_{21}$H$_{17}$NO$_3$ [M+H] 332.1281, Found: 332.1268. CCDC 1005570 contains crystallographic data.

Benzyl 6-((tert-butyldimethylsilyl)oxy)-9H-carbazole-4-carboxylate (30): Obtained as a black solid. Yield = 52%; Rf=0.80 (Ethyl Acetate/Hexane : 2/98); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.41 (d, J = 2.3 Hz, 1H), 8.11 (s, 1H), 7.84 (dd, J = 7.5, 0.6 Hz, 1H), 7.55 - 7.31 (series of m, 7H) 7.27 (d, J = 8.7 Hz, 1H), 7.03 (dd, J = 8.6, 2.4 Hz,
**Benzyl 6-methyl-9H-carbazole-4-carboxylate (31):** Obtained as a pink solid. Yield = 67%; R_f=0.64 (Ethyl Acetate/Hexane : 4/96); ^1^H NMR (400 MHz, CDCl₃) δ 8.60 (s, 1H), 8.15 (s, 1H), 7.88 (dd, J = 7.6, 0.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.1 Hz, 2H), 7.43 – 7.30 (m, 5H), 7.27 (dd, J = 8.4, 1.0 Hz, 1H), 5.52 (s, 2H), 2.46 (s, 3H); ^1^C NMR (101 MHz, CDCl₃) δ 168.0, 140.7, 138.6, 136.3, 129.1, 128.8, 128.5, 128.4, 125.6, 125.4, 124.7, 122.9, 122.2, 121.9, 115.1, 110.1, 67.0, 21.8; IR (neat): 3028, 2924, 2854, 1714, 1700, 1607 cm⁻¹; HRMS (LC) m/z Calc. for C₂₁H₁₇NO₂ [M+H] 316.1332, Found: 316.1346.

**Benzyl 7-methyl-9H-carbazole-4-carboxylate (32):** Obtained as a pink solid. Yield = 66%; R_f=0.72 (Ethyl Acetate/Hexane : 3/97); ^1^H NMR (400 MHz, CDCl₃) δ 8.69 (d, J = 8.2 Hz, 1H), 8.18 (s, 1H), 7.92 – 7.88 (m, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.1 Hz, 2H), 7.44 – 7.31 (m, 4H), 7.27 (d, J = 7.2 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 5.52 (s, 2H), 2.56 (s, 3H); ^1^C NMR (101 MHz, CDCl₃) δ 167.8, 140.3, 139.7, 136.3, 128.8, 128.5, 128.4, 127.5, 125.5, 124.7, 123.6, 123.0, 122.7, 121.6, 119.9, 119.3, 115.2, 66.9, 17.0; IR (neat): 3028, 2924, 2854, 1714, 1700, 1607 cm⁻¹; HRMS (LC) m/z Calc. for C₂₁H₁₇NO₂ [M+H] 316.1332, Found: 316.1343.

**Ethyl 6-methyl-9H-carbazole-4-carboxylate (33):** Obtained as a pink solid. Yield = 60%; R_f=0.75 (Ethyl Acetate/Hexane : 4/96); ^1^H NMR (400 MHz, CDCl₃)
δ 8.64 (s, 1H), 8.15 (s, 1H), 7.83 (dd, J = 7.5, 0.7 Hz, 1H), 7.57 (dd, J = 8.0, 0.6 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.28 (dd, J = 8.3, 1.0 Hz, 1H), 4.54 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃ δ 168.2, 140.7, 138.6, 129.1, 128.4, 125.8, 125.5, 124.7, 122.6, 122.3, 121.8, 114.8, 110.1, 61.2, 21.9, 14.6; IR (neat): 3032, 2921, 2857, 1696, 1649, 1605; HRMS (LC) m/z Calc. for C₁₆H₁₅NO₂ [M+H]254.1176, Found : 256.1194.

![Ethyl 7-methyl-9H-carbazole-4-carboxylate](image)

**Ethyl 7-methyl-9H-carbazole-4-carboxylate (34):** Obtained as a pink solid. Yield =61%; R_f=0.72 (Ethyl Acetate/Hexane : 4/96); ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, J = 8.2 Hz, 1H), 8.17 (s, 1H), 7.85 (dd, J = 7.5, 0.5 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.1 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 4.53 (q, J = 7.1 Hz, 2H), 2.56 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 140.3, 139.7, 127.4, 126.0, 124.7, 123.4, 122.8, 122.5, 121.6, 119.9, 119.3, 115.0, 61.2, 17.0, 14.6; IR (neat): 3054, 2925, 2855, 1717, 1696, 1606, 1590 cm⁻¹; HRMS (LC) m/z Calc. for C₁₆H₁₅NO₂ [M+H] 254.1176, Found : 256.1162.
6. Carbazole Synthesis by Twofold $\pi$-Extension of Pyrroles (Table 3):

The first $\pi$-extension of pyrrole to 7-substituted indole 35 was carried according to our reported procedure. The 2nd $\pi$-extension in 35 was carried according to the general procedure described for table 2 (page# S5). The yields reported are for the 2nd $\pi$-extension of indole 35 to 4,8-disubstituted carbazoles 36-38.

5-benzyl 1-ethyl 9H-carbazole-1,5-dicarboxylate (36): Obtained as a white solid. Yield = 47%; $R_f$=0.63; (Ethyl Acetate/Hexane: 3/97). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.36 (s, 1H), 9.20 (d, $J$ = 8.0 Hz, 1H), 8.17 (dd, $J$ = 7.6, 1.0 Hz, 1H), 8.01 (dd, $J$ = 7.6, 0.8 Hz, 1H), 7.74 (dd, $J$ = 8.0, 0.8 Hz, 1H), 7.57 (d, $J$ = 7.3 Hz, 2H), 7.51 (t, $J$ = 7.8 Hz, 1H), 7.45 (dd, $J$ = 10.1, 4.6 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.29 (d, $J$ = 4.5 Hz, 1H), 5.55 (s, 2H), 4.52 (q, $J$ = 7.1 Hz, 2H), 1.51 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.8, 167.5, 141.0, 140.6, 136.2, 131.7, 128.8, 128.5, 128.5, 128.4, 125.5, 125.4, 123.6, 123.3, 121.4, 118.9, 115.8, 111.6, 67.0, 61.1, 14.6; IR (neat): 3417, 3042, 2919, 2857, 1664 cm$^{-1}$; HRMS (LC) $m/z$ calc. for C$_{23}$H$_{19}$NO$_4$ [M+H] 374.1387, Found: 374.1399.
5-ethyl 1-methyl 9H-carbazole-1,5-dicarboxylate (37): Obtained as a white solid. Yield = 45%; Rf=0.64; (Ethyl Acetate/Hexane : 4/94). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.27 (s, 1H), 9.17 (d, $J = 8.0$ Hz, 1H), 8.11 (d, $J = 7.6$ Hz, 1H), 7.92 (d, $J = 7.5$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 7.9$ Hz, 1H), 4.52 (q, $J = 7.1$ Hz, 2H), 4.01 (s, 3H), 1.48 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.2, 167.8, 140.9, 140.6, 131.7, 128.5, 125.9, 125.6, 123.4, 123.4, 121.3, 118.9, 115.6, 111.3, 61.3, 52.1, 14.6; IR (neat): 3417, 2928, 2857, 1690, 1570 cm$^{-1}$; HRMS (LC) m/z calc. for C$_{17}$H$_{15}$NO$_4$ [M+H] 298.1074, Found: 298.1098.

Dimethyl 9H-carbazole-1,5-dicarboxylate (38): Obtained as a white solid. Yield = 48%; Rf=0.55; (Ethyl Acetate/Hexane: 3/97). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.31 (s, 1H), 9.18 (d, $J = 8.1$ Hz, 1H), 8.17 – 8.13 (m, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 1H), 7.31 (t, $J = 7.9$ Hz, 1H), 4.09 (s, 3H), 4.05 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 168.2, 168.1, 140.9, 140.5, 131.6, 128.5, 125.6, 125.4, 123.5, 123.3, 121.2, 119.0, 115.7, 111.3, 52.3, 52.1; IR (neat): 3410, 2925, 2857, 1680 cm$^{-1}$; HRMS (LC) m/z calc. for C$_{16}$H$_{13}$NO$_4$ [M+H] 284.0917, Found: 284.0935. CCDC 1005569 contains crystallographic data.
7. Synthetic Applications of $\pi$-Extension:

A: Synthesis of 40-an analogue of hepatitis C virus replication inhibitor 4:

Scheme S1: Synthesis of an analogue 40 of hepatitis C virus replication inhibitor 4 via $\pi$-extension of indole

**Ethyl 9H-carbazole-4-carboxylate (39):** Prepared by following the general procedure of $\pi$-extension. Obtained as a pale yellow liquid. Yield = 52%; $R_f$=0.53 (Ethyl Acetate/Hexane : 3/97); $^1$H NMR (500 MHz, CDCl₃) $\delta$ 8.95 – 8.91 (m, 1H), 8.40 (s, 1H), 7.91 (dd, $J = 7.5$, 1.1 Hz, 1H), 7.53 (dd, $J = 8.1$, 1.1 Hz, 1H), 7.49 (ddd, $J = 8.2$, 7.1, 1.2 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.40 – 7.36 (m, 1H), 7.32 – 7.27 (m, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl₃) $\delta$ 168.3, 140.4, 140.3, 126.8, 125.7, 125.6, 124.8, 122.6, 122.0, 121.8, 119.7, 115.0, 110.5, 61.3, 14.5; IR (neat): 3029, 2921, 2718, 1726, 1715, 1697 cm⁻¹; HRMS (LC) $m/z$ Calc. for C₁₅H₁₃NO₂ [M+H]$^+$ 240.1019, Found: 240.1002.

**Preparation of 40:**

Prepared using the literature procedure reported by Beigelman et. al. A solution of carbazole 39 (0.4 mmol), 3-nitro-5-fluorotoluene (0.4 mmol) and anhydrous cesium carbonate (0.5 mmol) in dry DMF (5 mL) was stirred at 35 °C for 14 h. The reaction mixture was extracted with ethyl acetate and washed with water, brine and dried over anhydrous sodium sulfate. Purification by silica gel column chromatography using 5% ethyl acetate-hexane gave N-
arylcarbazole 40 as a white solid. Yield = 74%; Rf=0.65; (Ethyl Acetate/Hexane : 80/20); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.95 (d, \(J = 8.1\) Hz, 1H), 8.37 (d, \(J = 2.2\) Hz, 1H), 8.27 (dd, \(J = 8.5, 2.4\) Hz, 1H), 7.94 – 7.91 (m, 1H), 7.53 (d, \(J = 8.6\) Hz, 1H), 7.44 (dt, \(J = 16.0, 4.4\) Hz, 2H), 7.33 (dd, \(J = 11.3, 4.0\) Hz, 1H), 7.15 (d, \(J = 7.7\) Hz, 1H), 6.98 (d, \(J = 8.1\) Hz, 1H), 4.57 (q, \(J = 7.1\) Hz, 2H), 2.06 (s, 3H), 1.51 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.0, 148.0, 141.9, 141.4, 141.4, 139.8, 130.8, 127.5, 127.0, 126.4, 126.2, 125.5, 123.6, 122.9, 122.3, 122.3, 120.9, 113.7, 109.4, 61.5, 18.1, 14.6; IR (neat): 3020, 2926, 2900, 1630, 1425 cm\(^{-1}\); HRMS (LC) \(m/z\) calc. for C\(_{22}\)H\(_{18}\)N\(_2\)O\(_4\) [M+H] 375.1339, Found: 1375.1323.

B: Synthesis of 41- an analogue of sPLA2 inhibitor 5:

![Reaction diagram]

The sPLA2 inhibitor 5\(^{[4]}\) analogue 41 was prepared by \(\pi\)-extension of 13b with 14a according to the general procedure of \(\pi\)-extension.

**Ethyl 9-benzyl-5-(benzyloxy)-9H-carbazole-4-carboxylate (41):**
Prepared by following the general procedure of \(\pi\)-extension. Obtained as a yellow solid. Yield = 71%; Rf=0.77 (Ethyl Acetate/Hexane : 2/98); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 7.4\) Hz, 2H), 7.43 – 7.35 (m, 3H), 7.32 (dd, \(J = 9.1, 2.9\) Hz, 2H), 7.29 – 7.25 (m, 2H), 7.24 (s, 2H), 7.12 – 7.07 (m, 2H), 6.96 (d, \(J = 8.2\) Hz, 1H), 6.66 (d, \(J = 8.0\) Hz, 1H), 5.45 (s, 2H), 5.39 (s, 2H), 4.14 (q, \(J = 7.1\) Hz, 2H), 1.28 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.8, 155.1, 142.9, 140.6, 137.4, 136.9, 129.8, 129.0, 128.7, 127.9, 127.7, 127.3, 126.5,
124.8, 119.0, 117.9, 111.6, 110.3, 102.9, 102.1, 70.6, 61.0, 46.8, 14.4; IR (neat): 3060, 2922, 2856, 1728 cm⁻¹; HRMS (LC) m/z Calc. for C₂₉H₂₅NO₃ [M+H] 436.1907, Found: 436.1907.

8. Mechanistic Studies

To probe the mechanism of the reaction, the π-extension was carried with indole, enaldiazo ester 14a, 2 mol% Rh₂(OAc)₄ and 5 mol % (±)-21 at different temperatures in CDCl₃ solvent and progress of the reaction was monitored by thin layer chromatography (TLC) and ¹H-NMR data. At 10 °C, the reaction did not proceed even after 10 hours. However, the reaction was proceeded at room temperature (25 °C) as well as at 40 °C. But, no intermediate formation was detected by ¹H-NMR studies and by TLC analysis.

(a) NMR study at room temperature (25 °C):

An oven dried 10 ml round-bottom flask containing a stir bar under inert atmosphere was charged with Indole (0.24 mmol), Rh₂(OAc)₄ (0.0048 mmol), (±)-21 (0.012 mmol) and CDCl₃ (2 ml). To the gently stirring contents at rt (25 °C) was added a solution of enaldiazo ester 14a (0.3 mmol) in CDCl₃ (2 ml) with a flow rate of 1 ml/h using a syringe pump. The reaction was monitored by thin layer chromatography (TLC) and ¹H-NMR data. As shown in the below NMR spectral data no intermediate was detected after 0.6 eq. as well as 1.2 eq. of 14a addition.
39 (ethyl carbazole-4-carboxylate)

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 2 h addition + 11 h stirring at RT

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 2 h addition +1 h stirring at RT

14a (0.6 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 1 h addition at RT

14a

indole
39 (ethyl carbazole-4-carboxylate)

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 2 h addition + 11 h stirring at RT

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 2 h addition +1 h stirring at RT

14a (0.6 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 1 h addition at RT

14a

indole
(b) NMR study at 40 °C:

An oven dried 10 ml round-bottom flask containing a stir bar under inert atmosphere was charged with Indole (0.24 mmol), Rh$_2$(OAc)$_4$ (0.0048 mmol), (±)-21 (0.012 mmol) and CDCl$_3$ (2 ml). To the gently stirring contents at 40 °C was added a solution of enaldiazo ester 14a (0.3 mmol) in CDCl$_3$ (2 ml) with a flow rate of 1 ml/h using a syringe pump. The reaction was monitored by thin layer chromatography (TLC) and $^1$H-NMR data. As shown in the below NMR spectral data no intermediate was detected after 0.6 eq. as well as 1.2 eq. of 14a addition.
39 (ethyl carbazole-4-carboxylate)

14a (2.5 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 2h addition at 40 oC

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 1h addition at 40 oC

14a + Rh2(OAc)4 (DCM, 40 oC) [blank reaction]
39 (ethyl carbazole-4-carboxylate)

14a (2.5 eq) + Indole (1 eq) + Rh2(OAc)4 + 21

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 21

14a + Rh2(OAc)4 (DCM, 40 °C) [blank reaction]

Indole
39 (ethyl carbazole-4-carboxylate)

14a (2.5 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 2h addition at 40 oC

14a (1.2 eq) + Indole (1 eq) + Rh2(OAc)4 + 21 : 1h addition at 40 oC

14a

Indole

14a + Rh2(OAc)4 (DMF, 40 oC) [Blank reaction]
9. References:


10. NMR Spectra:

![NMR Spectrum Image]

20/400 MHz/CDCl₃
23/400 MHz/CDCl₃
BnO₂C

28/400 MHz/CDCl₃

S37
36/500 MHz/CDCl$_3$
BnO₂C

36/126 MHz/CDCl₃

14.67
EtO₂C

CO₂Me

37/400 MHz/CDCl₃

S53
38/500 MHz/CDCl₃
EtO₂C

39/500 MHz/CDCl₃
40/101 MHz/CDCl₃
DEPT-135
41/101 MHz/CDCl₃
DEPT-135

S64