Transition Metal-Free Approach Towards Synthesis of β-Carboline Tethered 1,3,4-Oxadiazoles via Oxidative C-O Bond Formation

Dharmender Singh\textsuperscript{a}, Sandip Kumar Tiwari\textsuperscript{b} and Virender Singh\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}Department of Chemistry, Dr B R Ambedkar National Institute of Technology (NIT) Jalandhar, 144011, Punjab, India.
\textsuperscript{b}Drug Discovery and Molecular Synthesis Lab, Centre of Biomedical Research, Sanjay Gandhi Postgraduate Institute of Medical Sciences (SGPGIIMS), Lucknow - 226014, Uttar Pradesh, India.

E-mail:- singhv@nitj.ac.in; Fax: (91) 172-2214692

Supporting Information

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1. Synthesis of Kumujian C and its derivatives

Scheme S1. Synthesis of Kumujian C

Scheme S2. Synthesis of 1-formyl-9H-pyrido[3,4-b]indole derivatives
**pH study during the course of oxidative C-O bond formation**: To probe the reaction mechanism and get evidence about the generation of HI acid during the course of reaction, the pH study of reaction medium was conducted in the absence of base. It was observed that at the start of reaction, the pH of medium was 10.03 after addition of benzohydrazone 1bA. After addition of iodine to reaction medium reduced the pH in acidic range (4.98) giving an inference of generation of HI. The continuous decrease in the pH of medium with the progress of reaction confirmed the generation of HI. It was found that after completion of reaction under base free conditions, the pH of reaction medium was 2.61. The pH for entries 4-7 were measured after cooling the reaction mixture to room temperature.

**Table S1. pH study during the course of oxidative C-O bond formation**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Time (min.)</th>
<th>pH of reaction medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Anhydrous DMSO, rt</td>
<td>00:00</td>
<td>9.84</td>
</tr>
<tr>
<td>2</td>
<td>Addition of 1bA in DMSO, rt</td>
<td>00:01</td>
<td>10.03</td>
</tr>
<tr>
<td>3</td>
<td>Addition of iodine (1.5 equiv.) to 1bA in DMSO, rt</td>
<td>00:02</td>
<td>4.98</td>
</tr>
<tr>
<td>4</td>
<td>After 3 h at 90 °C (15-20% conversion into 2bA)</td>
<td>03:00</td>
<td>4.18</td>
</tr>
<tr>
<td>5</td>
<td>After 9 h at 90 °C (40-45% conversion into 2bA)</td>
<td>09:00</td>
<td>3.14</td>
</tr>
<tr>
<td>6</td>
<td>After 16 h at 90 °C (95-98% conversion into 2bA)</td>
<td>16:00</td>
<td>2.61</td>
</tr>
<tr>
<td>7</td>
<td>After 16 h at 90 °C (95-98% conversion into 2bA) then 3 equiv. of Cs₂CO₃ was added to reaction mixture</td>
<td>16.05</td>
<td>8.68</td>
</tr>
</tbody>
</table>
Figure S1. $^1$H-NMR spectrum of 2aA.

Figure S2. $^{13}$C-NMR spectrum of 2aA.
Figure S3. $^1$H-NMR spectrum of 2aB.

Figure S4. $^{13}$C-NMR spectrum of 2aB.
Figure S5. $^1$H-NMR spectrum of 2aC.

Figure S6. $^{13}$C-NMR spectrum of 2aC.
Figure S7. $^1$H-NMR spectrum of 2aD.

Figure S8. $^{13}$C-NMR spectrum of 2aD.
Figure S9. $^1$H-NMR spectrum of 2aE.

Figure S10. $^{13}$C-NMR spectrum of 2aE.
Figure S11. $^{1}$H-NMR spectrum of 2aF.

Figure S12. $^{13}$C-NMR spectrum of 2aF.
Figure S13. $^1$H-NMR spectrum of 2aG.

Figure S14. $^{13}$C-NMR spectrum of 2aG.
Figure S15. $^1$H-NMR spectrum of 2aH.

Figure S16. $^{13}$C-NMR spectrum of 2aH.
Figure S17. $^1$H-NMR spectrum of 2aI.

Figure S18. $^{13}$C-NMR spectrum of 2aI.
Figure S19. $^1$H-NMR spectrum of 2aK.

Figure S20. $^{13}$C-NMR spectrum of 2aK.
Figure S21. $^1$H-NMR spectrum of 2iA.

Figure S22. $^{13}$C-NMR spectrum of 2iA.
Figure S23. $^1$H-NMR spectrum of 2kA.

Figure S24. $^{13}$C-NMR spectrum of 2kA.
**Figure S25.** $^1$H-NMR spectrum of 2kG.

**Figure S26.** $^{13}$C-NMR spectrum of 2kG.
Figure S27. $^1$H-NMR spectrum of 2kI.

Figure S28. $^{13}$C-NMR spectrum of 2kI.
Figure S29. $^1$H-NMR spectrum of 2bA.

Figure S30. $^{13}$C-NMR spectrum of 2bA.
Figure S31. $^1$H-NMR spectrum of 2cA.

Figure S32. $^{13}$C-NMR spectrum of 2cA.
Figure S33. $^1$H-NMR spectrum of 2dA.

Figure S34. $^{13}$C-NMR spectrum of 2dA.
Figure S35. $^1$H-NMR spectrum of 2eA.

Figure S36. $^{13}$C-NMR spectrum of 2eA.
Figure S37. $^1$H-NMR spectrum of 2fA.

Figure S38. $^{13}$C-NMR spectrum of 2fA.
Figure S39. $^1$H-NMR spectrum of 2gA.

Figure S40. $^{13}$C-NMR spectrum of 2gA.
Figure S41. $^1$H-NMR spectrum of 2jA.

Figure S42. $^{13}$C-NMR spectrum of 2jA.
Figure S43. $^1$H-NMR spectrum of 5A.

Figure S44. $^{13}$C-NMR spectrum of 5A.
Figure S45. $^1$H-NMR spectrum of 2kM.

Figure S46. $^{13}$C-NMR spectrum of 2kM.
Figure S47. $^1$H-NMR spectrum of 6.

Figure S48. $^{13}$C-NMR spectrum of 6.