SYNTHESIS OF RACEMIC 4[3-SPIRO-(2-HYDRO-1,4-
BENZOTHIAZINE/BENZOXAZINE)-CYCLOHEXANYL]
COUMARINS
The importance of spiro compounds as a flavoring and organoleptic agents is well documented. The work in this chapter deals with the synthesis of spiro heterocycles containing coumarin and benzazines. In view of this an attempt has been made to highlight the importance of spiro heterocycles.

Stereo specific synthesis of 2-substituted spirobicyclic thiazolidine lactam (1) has been reported by Subasinghe et al. which possess the carbomethoxy and the carbonyl functions, which are very similar to those observed in penicillin.

![Wiring Diagram](image)

Synthesis of chiral spiro-3-isoxazolin-5-one-3-oxides (2) (chiral nitrones) via a nitroketene intermediate and their asymmetric 1,3-dipolar cycloaddition reactions leading to EPC synthesis of modified aminoacids were reported by Katagiri and co-workers.3

![Chemical Structure](image)

The syntheses of novel soluble ditopic 1,10-phenanthroline ligands bearing a central spiro-[5,5] undecane or a spiro-[5,5] bifluorylidene (3) and (4) fragment and X-ray crystal structure of spiro[3,3]heptane-2,6-dispirofluorine have also been reported.
Synthesis of regioselective spiropyrrolidines (6)\textsuperscript{6} and (6a)\textsuperscript{7} via 1,3-dipolar cycloaddition reaction of N-metalated azomethine ylides were reported by G. Subramaniyano and Raghunathan. The spiro atom is a part of the dihydrochromone and pyrrolidine rings.

\[ \text{5} \]

Piperidine based spiro heterocycles with Indanone ring containing a \( \gamma \)-phenyl ring and a sulphonamide moiety were found to be antagonists of the human CCR5 receptor as anti-HIV-1 agents.\textsuperscript{8} Amongst these the most active compound was the \( m \)-chlorophenyl derivative with a \( N \)-\( \text{CH}_3 \) group (7).
Synthesis, stereochemistry and ring chain tautomerism of some new spiro-1,3-oxathianes (8) were presented by Terec et al.9

![Chemical structure of 8](image)

The 4-phenyl-5-isoxazolones and 4-phenyl-3-carboethoxy pyridines were spiro annealed10 in the form of compound (9).

![Chemical structure of 9](image)

The dihydrobenzofurans fused α-pyrone containing spiro compounds (10) and (11) have been isolated from *penicillium brevicompactum* and screened as allelopathic agents.11

![Chemical structure of 10 and 11](image)

A simple synthesis of spiro C6-annulated hydrocyclopenta [g] indolin-2-ones derivatives (12) were reported by Vladimir Kouznetsov et al.12

![Chemical structure of 12](image)

Chemoselective Michael reactions on pyroglutamates resulted in an expeditious synthesis of spiro bis-γ-lactamats as β-turn peptidomimetics13 (13).
A one-pot method under mild conditions was developed for the preparation of 9,9' (10H, 10'H)-spirobiacridines (14) and crystal structures of the compound was determined by Ooishi et al.\textsuperscript{14}

\begin{equation}
\begin{array}{c}
\text{BOC} \\
\begin{array}{c}
\longrightarrow \\
1) \text{t-BuLi, TMEDA}
\end{array} \\
\text{N-MEM-acridone} \\
2) \text{H}^+ \\
(R = H, OCH}_3 \\
3) \text{H}^+
\end{array}
\end{equation}

A novel three component reaction of isoquinoline and dimethyl acetylene dicarboxylate with 1,2 and 1,4-benzoquinones, afforded spiro[1,3]oxazino[2,2-a]isoquinoline\textsuperscript{15} derivatives (15) in high yields.

\begin{equation}
\begin{array}{c}
\text{C}_7H_7N \\
+ \bigg\{ \begin{array}{c}
\text{CO}_2Me \\
\text{CO}_2Me
\end{array} \bigg\} \\
\text{DME, } \text{Ac}^+ \\
\text{rt, 8 h, 78%}
\end{array}
\end{equation}

Srinivas Peddi\textsuperscript{16} and co-workers have been reported the structural parameters for high 5-HT\textsubscript{2A} receptor affinity of spiro[9,10-dihydroanthracene]-9,3'-pyrolidine (16) (SPAMDA).

\begin{equation}
\begin{array}{c}
\text{NH} \\
\begin{array}{c}
\text{O}
\end{array}
\end{array}
\end{equation}

Synthesis and structural studies of a novel scaffold for drug\textsuperscript{17} discovery, a 4,5-dihydro-3H-spiro-[1,5-benzoazepine-2,4-piperidine] (17) was accomplished from \textit{ortho}-hydroxyacetophenone and \textit{N}-benzypiperidine.

\begin{equation}
\begin{array}{c}
\begin{array}{c}
\text{CH}_3 \\
\text{OH}
\end{array} \\
\begin{array}{c}
\text{N}
\end{array}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{H}_2\text{N} \\
\begin{array}{c}
\text{O}
\end{array}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{O}
\end{array}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{H}_2\text{C} \\text{O}_2\text{H}
\end{array}
\end{equation}
Synthesis of spiro bipyridopyrans (18) indolinospironaphtho-1,4-oxazines (19) and study of their X-Ray crystal structure, antitumoral and antiviral evaluation were reported by Silvana et al.\textsuperscript{18}

\[
\begin{align*}
\text{R} & = \text{Benzo, CH}_3 \\
X & = CH, N \\
R_1 & = \text{NO}_2, \text{OCH}_3
\end{align*}
\]

Synthesis and evaluation of some new spiro indoline-based heterocycles as potentially active antimicrobial agents\textsuperscript{19} (20), (21) and (22) was reported by Abdel Rahman et al.

\[
\begin{align*}
\text{R} & = \text{H, Boc, cbz}
\end{align*}
\]

A symmetric spiro-cyclization of a pyrolidine derivative was used as a key step for constructing novel rigid dimer (23) was reported by Planas et al.\textsuperscript{20}

\[
\begin{align*}
\text{R} & = \text{H, Boc, cbz}
\end{align*}
\]

Xie et al.\textsuperscript{21} have been reported the convenient synthesis of 1'-\textit{H}-spiro-[indoline-3, 4'-piperidine] and its derivatives (24).

\[
\begin{align*}
\text{R} & = \text{H, Boc, cbz}
\end{align*}
\]
Quantitative structure and aldose reductase inhibitory activity relationship of 1,2,3,4-tetrahydro pyrrolo[1,2-a]pyrazine-4-spiro-3-pyrrolidine-1,2',3,5'-tetrone derivatives (25) were reported by Kwangseok et al.\textsuperscript{22}

\[
\begin{array}{c}
R_3\quad R_4
\end{array}
\]

Regio and Stereoselective synthesis of bis-spiropyrazoline-5,3'-chroman (thiochroman)-4-one derivatives (26) and (26a) were presented by Dawood et al.\textsuperscript{23}

\[
\begin{array}{c}
\text{26} \\
\text{26a}
\end{array}
\]

Chattopadhyay et al.\textsuperscript{24} have reported a short new route to the chiral spirotetrahydrofurans (27).

\[
\begin{array}{c}
\text{27}
\end{array}
\]

A facile synthesis of new spiro thiazolo pyridazines (28) by 1,3-dipolar cycloaddition were reported by Abouricha et al.\textsuperscript{25}

\[
\begin{array}{c}
\text{29}
\end{array}
\]
In view of the above importance of the spiro heterocycles we have developed a methodology for the synthesis of a series of new spiro compound by nucleophilic substitution and intramolecular carbanion addition, across the potential dipolarophilic azomethine(C=N) group. This has been discussed under the present work.

**Present work**

The steps involved in the synthesis of the target molecules is presented in schemes I and II. The spiro atom, visualized as the carbonyl carbon of the cyclohexanone was converted into the azomethine group by its reaction with o-amino phenol and o-aminothiophenol to obtain the intermediates (2) and (4) respectively. The reaction of these intermediates with 4-bromomethylcoumarin in ethanol in the presence of potassium carbonate leads to the formation of coumarinyl spiro dihydroxazines (3) and (5) respectively.

A plausible pathway for their formation is envisaged in terms of an initial allylic SN reaction leading to 4-thiophenoxy or 4-phenoxy intermediates. These intermediates contain an active methylene group, which can easily generate a carbanion stabilized as the enolate anion. An intramolecular attack on the azomethine carbon is stereoelectronically favoured followed by protonation at the nitrogen leading to the formation of the dihydrobenzazines. The racemic product obtained was characterized by various spectral methods.

The product isolation was done by filtration as dilution with water, which lead to the precipitation of coloured crystalline solids. The so obtained compounds are systematically named and numbered as follows.

4[3'-spiro (2'-hydro-1',4'-benzothiazino/benzoxazino)-cyclohexanyl] coumarin
* The substituent R is mentioned in tables.
Results and discussion

During the present investigation, a new spiro compound (3) has been synthesised by the reaction of 4-bromomethylcoumarin (1) with imine (2) prepared from cyclohexanone and o-aminothiophenol, which results in the formation (3).

Formation of (3a) (R= 6-CH₃) was supported by the appearance of NH band around 3293 cm⁻¹ and lactone carbonyl stretching band exhibited at 1701 m⁻¹ respectively (spectrum No.1). The spectral data are presented in table 1.
In the $^1$H NMR spectrum of above compound (3a) (R= 6-CH$_3$) (spectrum No.2), the CH$_3$ protons resonated as a singlet at 2.47 ppm whereas multiplet in the range of 1.25-1.67 is ppm due to cyclohexane ring protons. Another characteristic singlet for one proton at 4.31 ppm due to chiral C$_2$-H protons and NH appeared broad singlet at 4.37 ppm and it is D$_2$O exchanged (spectrum No.3), C$_3$-H of coumarin resonated as a singlet at 6.48 ppm, aromatic multiplet resonated in the range of 6.67-7.43 ppm. The results are summarized in the table 2. The 2D HOMO-COSY (spectrum No. 5) of the same compound was recorded for further confirmation and the mass, purity (96.2%) of the compound has been confirmed by LCMS (spectrum No.6) and HPLC (spectrum No.7). Finally it was confirmed by single X-ray diffraction study (Fig 1 and 2).

The formation of spiro biheterocycles (5a) (R= 6-CH$_3$) is confirmed by their IR spectra, which exhibit the lactone carbonyl stretching band at 1717 cm$^{-1}$, and the NH stretching band exhibited at 3387 cm$^{-1}$ respectively (spectrum No.11) and the results are summarised in table -1.

![Diagram of compound 5](image)

The $^1$H NMR spectra of the compound are in total agreement with the proposed structure (5) and is confirmed by $^1$H NMR spectra (spectrum No.12). The multiplet in the range 1.05-1.85 ppm is due to cyclohexane protons, singlet at 2.42 ppm is due to 6-CH$_3$ of coumarin. Chiral proton resonated as a singlet at 4.62 ppm and singlet at 6.21 ppm is due to C$_3$-H of coumarin and NH resonated as a singlet at 6.41 ppm, which was disappeared on D$_2$O exchange. The aromatic protons resonated as a multiplet in the range 6.52-8.12 ppm and results are summarised in table -2.
Table-1: IR data of compounds (3a-3f and 5a-5d)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>X</th>
<th>R</th>
<th>$\nu_{C=O}\text{cm}^{-1}$ Lactone</th>
<th>$\nu_{N-H}\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>S</td>
<td>6-CH$_3$</td>
<td>1701</td>
<td>3293</td>
</tr>
<tr>
<td>3b</td>
<td>S</td>
<td>7-CH$_3$</td>
<td>1708</td>
<td>3302</td>
</tr>
<tr>
<td>3c</td>
<td>S</td>
<td>6-OCH$_3$</td>
<td>1705</td>
<td>3315</td>
</tr>
<tr>
<td>3d</td>
<td>S</td>
<td>6-Cl</td>
<td>1705</td>
<td>3310</td>
</tr>
<tr>
<td>3e</td>
<td>S</td>
<td>5,6-Benzo</td>
<td>1715</td>
<td>3308</td>
</tr>
<tr>
<td>3f</td>
<td>S</td>
<td>7,8-Benzo</td>
<td>1713</td>
<td>3298</td>
</tr>
<tr>
<td>5a</td>
<td>O</td>
<td>6-CH$_3$</td>
<td>1717</td>
<td>3387</td>
</tr>
<tr>
<td>5b</td>
<td>O</td>
<td>7-CH$_3$</td>
<td>1713</td>
<td>3288</td>
</tr>
<tr>
<td>5c</td>
<td>O</td>
<td>6-OCH$_3$</td>
<td>1716</td>
<td>3325</td>
</tr>
<tr>
<td>5d</td>
<td>O</td>
<td>6-Cl</td>
<td>1714</td>
<td>3317</td>
</tr>
</tbody>
</table>
Table-2: *H NMR data of compounds (3a-3f and 5a-5d)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>X</th>
<th>R</th>
<th>Chemical Shift (δ ppm) 300 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>S</td>
<td>6-CH₃</td>
<td>1.25-1.67(m, 10H, Cyclohexane), 2.47(s, 3H, 6-CH₃), 4.31(s, 1H, chiral CH), 4.37(s, 1H, NH, D₂O Exchanged), 6.48(s, 1H, C₃-H), 6.67-7.43(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>3b</td>
<td>S</td>
<td>7-CH₃</td>
<td>1.27-1.69(m, 10H, Cyclohexane), 2.49(s, 3H, 6-CH₃), 4.33(s, 1H, chiral CH), 4.36(s, 1H, NH, D₂O Exchanged), 6.45(s, 1H, C₃-H), 6.67-7.45(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>3c</td>
<td>S</td>
<td>6-OCH₃</td>
<td>1.22-1.61(m, 10H, Cyclohexane), 3.89(s, 3H, 6-OCH₃), 4.24(s, 1H, chiral CH), 4.36(s, 1H, NH, D₂O Exchanged), 6.50(s, 1H, C₃-H), 6.66-7.32(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>3d</td>
<td>S</td>
<td>6-Cl</td>
<td>1.24-1.67(m, 10H, Cyclohexane), 4.32(s, 1H, chiral CH), 4.35(s, 1H, NH, D₂O Exchanged), 6.45(s, 1H, C₃-H), 6.67-7.46(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>3e</td>
<td>S</td>
<td>5,6-Benz</td>
<td>1.27-1.47(m, 10H, Cyclohexane), 4.87(s, 1H, chiral CH), 4.22(s, 1H, NH, D₂O Exchanged), 6.34(s, 1H, C₃-H), 6.54-8.21(m, 10H, Ar-H)</td>
</tr>
<tr>
<td>3f</td>
<td>S</td>
<td>7,8-Benz</td>
<td>1.25-1.66(m, 10H, Cyclohexane), 4.31(s, 1H, chiral CH), 4.37(s, 1H, NH, D₂O Exchanged), 6.48(s, 1H, C₃-H), 6.66-7.48(m, 10H, Ar-H)</td>
</tr>
<tr>
<td>5a</td>
<td>O</td>
<td>6-CH₃</td>
<td>1.05-1.85(m, 10H, Cyclohexane), 2.42(s, 3H, 6-CH₃), 4.62(s, 1H, chiral CH), 6.21(s, 1H, C₃-H), 6.41(s, 1H, NH), 6.52-8.12(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>5b</td>
<td>O</td>
<td>7-CH₃</td>
<td>1.05-1.87(m, 10H, Cyclohexane), 2.45(s, 3H, 7-CH₃), 4.65(s, 1H, chiral CH), 6.23(s, 1H, C₃-H), 6.38(s, 1H, NH), 6.55-8.21(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>5c</td>
<td>O</td>
<td>6-OCH₃</td>
<td>1.12-1.81(m, 10H, Cyclohexane), 3.79(s, 3H, 6-OCH₃), 4.54(s, 1H, chiral CH), 6.46(s, 1H, NH, D₂O Exchanged), 6.32(s, 1H, C₃-H), 6.56-8.14(m, 7H, Ar-H)</td>
</tr>
<tr>
<td>5d</td>
<td>O</td>
<td>6-Cl</td>
<td>1.04-1.97(m, 10H, Cyclohexane), 4.52(s, 1H, chiral CH), 6.46(s, 1H, NH, D₂O Exchanged), 6.32(s, 1H, C₃-H), 6.57-8.11(m, 7H, Ar-H)</td>
</tr>
</tbody>
</table>
\(^{13}\)C NMR (\(\delta\) ppm, 300 MHz) spectrum of the compounds.

Spectrum No. 4 (3a):

\[ \text{C}_7 - 161, \text{C}_3 - 113, \text{C}_4 - 132, \text{C}_5 - 117, \text{C}_6 - 127, \text{C}_7 - 123, \text{C}_8 - 126, \text{C}_9 - 139, \text{C}_{10} - 154, \text{C}_{11} - 21, \text{C}_{12} - 41, \text{C}_{13} - 51, \text{C}_{14} - 119, \text{C}_{15} - 117, \text{C}_{16} - 119.2, \text{C}_{17} - 115, \text{C}_{18} - 134, \text{C}_{19} - 152, \text{C}_{20} - 35, \text{C}_{21} - 25, \text{C}_{22} - 38, \text{C}_{23} - 21, \text{C}_{24} - 25. \]

Spectrum No. 10 (3c):

\[ \text{C}_2 - 161, \text{C}_3 - 113, \text{C}_4 - 127, \text{C}_5 - 108, \text{C}_6 - 126, \text{C}_7 - 119, \text{C}_8 - 120, \text{C}_9 - 139, \text{C}_{10} - 156, \text{C}_{11} - 56, \text{C}_{12} - 42, \text{C}_{13} - 51, \text{C}_{14} - 119, \text{C}_{15} - 117, \text{C}_{16} - 116, \text{C}_{17} - 118, \text{C}_{18} - 148, \text{C}_{19} - 153, \text{C}_{20} - 35, \text{C}_{21} - 21, \text{C}_{22} - 38, \text{C}_{23} - 21, \text{C}_{24} - 25. \]
Chapter 6

Wavenumbers (cm⁻¹)

Spectrum No. 1: IR (KBr) of compound 3a.

Spectrum No. 2: 'H NMR spectrum of compound 3a in CDCl₃.

Spectrum No. 1: IR (KBr) of compound 3a.

Spectrum No. 2: 'H NMR spectrum of compound 3a in CDCl₃.
Spectrum No. 3: $^1$H NMR spectrum of compound 3a in CDCl$_3$+D$_2$O.

Spectrum No. 4: $^{13}$C NMR spectrum of compound 3a in CDCl$_3$. 
Spectrum No. 5: 2D HOMO-COSY of compound 3a in CDCl₃.
Peak List for "TWC of DAD Spectral Data: from Sample 4 (IN0580-060A) of Data290805.wiff"

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Area (mAU x min)</th>
<th>% Area</th>
<th>Height (mAU)</th>
<th>% Height</th>
<th>Width (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2894</td>
<td>2335.9419</td>
<td>3.5002</td>
<td>964.6015</td>
<td>3.7777</td>
</tr>
<tr>
<td>2</td>
<td>2.2788</td>
<td>908.8385</td>
<td>1.7618</td>
<td>379.1461</td>
<td>1.4848</td>
</tr>
<tr>
<td>3</td>
<td>2.3423</td>
<td>6.349348</td>
<td>95.1381</td>
<td>94.7375</td>
<td>0.1733</td>
</tr>
</tbody>
</table>

Spectrum No. 6: LCMS of compound 3a. MPS – SCIEX – API-2000
Spectrum No.7: HPLC of the compound 3a. Agilent1100 Series
Spectrum No. 8: IR (KBr) of compound 3c.

Spectrum No. 9: 1H NMR of compound 3c in CDCl₃.
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Spectrum No. 11: IR (KBr) of compound 5a.

Spectrum No. 10: $^{13}$C NMR of compound 3c in CDCl$_3$.

Spectrum No.11: IR (KBr) of compound 5a.

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Spectrum No. 12: $^1$H NMR of compound 5a in CDCl$_3$. 
X-Ray crystal of the compound (3a): Crystals of the compound suitable for diffraction studies were grown from ethanol by slow evaporation technique. The preparative ORETEP diagram is given below.

Fig 1: ORTEP diagram of compound (3a)

Fig 2: Molecular packing diagram of compound (3a)
The synthesis of substituted 4-[3'-spiro cyclohexane 1',4'-benzothiazino/benzoxazino]coumarins (3) and (5) involved the following steps. Commercial samples were used after purification.

1. Preparation of substituted 4-bromomethyl coumarins (1)

2. Preparation of 4-[3'-spiro (2'-hydro-1',4'-benzothiazino/benzoxazino)cyclohexane-yl]coumarins (3) and (5).

1. Preparation of substituted 4-bromomethyl coumarins (1).

The above compounds were prepared according to literature method given in experimental part A of chapter-2.

2. Preparation of 4-[3'-spiro (2'-hydro-1', 4'-benzothiazine/benzoxazine)cyclohexane-yl]coumarins (3) and (5).

A mixture of anhydrous potassium carbonate (0.02 mol), Schiff base (2/4) (0.01 mol) and dry ethanol was stirred for 30 min. To this added substituted 4-bromomethyl coumarins (1) (0.01 mol) and then the reaction mixture were refluxed on water-bath for 12 hrs. Filter the hot solution, cool and added to crushed ice. Solid separated was filtered washed with HCl (1:1) (15 ml) and then water, crystallized from ethanol table -3.
### Table-3: Physical and Analytical data of compounds (3a-3f and 5a-5d)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>R</th>
<th>X</th>
<th>M.P (°C)</th>
<th>Yield (%)</th>
<th>Mol. Formula</th>
<th>Analysis Found (Calcd)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>6-CH₃</td>
<td>S</td>
<td>205</td>
<td>75</td>
<td>C_{23}H_{23}NO₂S</td>
<td>73.20 (73.18) 6.17 (6.14) 3.73 (3.71)</td>
</tr>
<tr>
<td>3b</td>
<td>7-CH₃</td>
<td>S</td>
<td>222</td>
<td>71</td>
<td>C_{23}H_{23}NO₂S</td>
<td>73.20 (73.18) 6.17 (6.14) 3.73 (3.71)</td>
</tr>
<tr>
<td>3c</td>
<td>6-OCH₃</td>
<td>S</td>
<td>208</td>
<td>68</td>
<td>C_{23}H_{23}NO₂S</td>
<td>70.22 (70.20) 5.91 (5.89) 3.58 (3.56)</td>
</tr>
<tr>
<td>3d</td>
<td>6-Cl</td>
<td>S</td>
<td>182</td>
<td>65</td>
<td>C_{22}H_{28}ClNO₂S</td>
<td>66.42 (66.40) 5.08 (5.07) 3.54 (3.52)</td>
</tr>
<tr>
<td>3e</td>
<td>5,6-Benzo</td>
<td>S</td>
<td>118</td>
<td>70</td>
<td>C_{24}H_{23}NO₂S</td>
<td>75.52 (75.51) 5.63 (5.61) 3.42 (3.39)</td>
</tr>
<tr>
<td>3f</td>
<td>7,8-Benzo</td>
<td>S</td>
<td>123</td>
<td>73</td>
<td>C_{24}H_{23}NO₂S</td>
<td>75.52 (75.51) 5.63 (5.61) 3.42 (3.39)</td>
</tr>
<tr>
<td>5a</td>
<td>6-CH₃</td>
<td>O</td>
<td>105</td>
<td>63</td>
<td>C_{22}H₂₃NO₃</td>
<td>74.63 (74.63) 6.42 (6.41) 3.89 (3.88)</td>
</tr>
<tr>
<td>5b</td>
<td>7-CH₃</td>
<td>O</td>
<td>142</td>
<td>62</td>
<td>C_{22}H₂₃NO₂O</td>
<td>76.44 (76.43) 6.42 (6.41) 3.90 (3.88)</td>
</tr>
<tr>
<td>5c</td>
<td>6-OCH₃</td>
<td>O</td>
<td>126</td>
<td>56</td>
<td>C_{23}H₂₃NO₄</td>
<td>73.21 (73.19) 6.16 (6.14) 3.72 (3.71)</td>
</tr>
<tr>
<td>5d</td>
<td>6-Cl</td>
<td>O</td>
<td>153</td>
<td>53</td>
<td>C_{22}H₂₃ClNO₃</td>
<td>69.21 (69.20) 5.29 (5.28) 3.69 (3.67)</td>
</tr>
</tbody>
</table>

All the compounds have been recrystallised from ethanol.
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