CHAPTER 2

DIPOLAR CYCLOADDITION REACTIONS OF 2-OXOINDOLIN-3-YLIDENES

2.1. INTRODUCTION

The 1,3-dipolar cycloaddition reactions constitute one of the most important classes of organic reactions. The ease of generation of various dipoles and the highly regio and stereoselective nature of their addition to π systems have contributed to the universal acceptance of dipolar cycloadditions for the construction of highly complex and valuable heterocycles.¹

In the context of the general interest of our research group in developing novel heterocyclic synthesis using dipolar cycloadditions,² 2-oxoindolin-3-ylidenes (e.g. 1) were perceived as excellent dipolarophiles. Although the addition of various dipoles to these systems can potentially lead to novel spiroindolenin framework,³ not much effort has been made in this direction; the available data is mainly derived from the reactions of diazoalkanes⁴ and azomethine ylides.⁵⁻⁸

2.1.1. REACTION WITH DIAZOALKANES

The report on the addition of diazoalkanes to 2-oxoindolin-3-ylidenes in 1978 by Franke constitutes the first example of 1,3-dipolar cycloaddition to this system (Scheme 1).⁴
2.1.2. REACTION WITH AZOMETHINE YLIDES

There has been considerable work on the reaction of azomethine ylides with oxoindolinylidene derivatives. Grigg and co-workers have exploited the dipolarophilicity of oxoindolinylidenes in their study of various \textit{in situ} generated dipoles.\textsuperscript{5,6,9}

The oxoindolylidene 4, when treated with the iminothiocarbonate 5 in the presence of acetic acid in refluxing xylene, afforded a 1:1 mixture of \textit{cis} and \textit{trans} isomers of the cycloadduct 6, separable by fractional crystallization (Scheme 2).\textsuperscript{3a}
This cycloaddition is proposed to involve tautomeric generation of the azomethine ylide 7 (Scheme 3), followed by cycloaddition and then elimination of methane thiol from the initial cycloadduct.

![Scheme 3]

The azomethine ylides generated by thermal prototropy of imines undergo cycloaddition reaction with the oxoindolinylidene. Thus, the imine 8, when refluxed in xylene in the presence of oxoindolinylidene 4, afforded the cycloadducts 9 and 10 (Scheme 4).

![Scheme 4]

i. Xylene, 130 °C, 36 h, 84% (1.2:1)
Pyridoxal imine 11 also undergoes similar cycloaddition with 2-oxoindolinyldene acetate via an azomethine ylide (Scheme 5).\(^6\)

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{Ph-} \quad \text{CO}_2\text{Me} \\
\begin{array}{c}
\text{N} \\
\text{H}
\end{array} & \quad \begin{array}{c}
\text{OH} \\
\text{HOH}
\end{array} & \quad \begin{array}{c}
\text{MeO}_2\text{C} \\
\text{Ph}
\end{array} \\
\text{H} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

\[\xrightarrow{i. \text{ Xylene, } 130^\circ\text{C}, 5 \text{ days, } 49\%} \]

Scheme 5

The 2-oxoindolin-3-ylidene derivatives 4 and 13 reacted smoothly with nonstabilized azomethine ylide 14, generated by desilylation route from N-benzyl-N-(methoxymethyl)-N-[(trimethylsilyl)methyl]amine at room temperature, giving rise to cycloadducts 15 and 16, respectively in good yields (Scheme 6).\(^7\)

\[
\begin{align*}
\begin{array}{c}
\text{EWG} \quad \text{Ph} \\
\text{N}
\end{array} & \quad \begin{array}{c}
\text{Ph-} \\
\text{CO}_2\text{Me}
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
\text{N}
\end{array} & \quad \begin{array}{c}
\text{OH} \\
\text{HOH}
\end{array} & \quad \begin{array}{c}
\text{MeO}_2\text{C} \\
\text{Ph}
\end{array} \\
\text{H} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

\[\xrightarrow{i. \text{ Toluene, RT, } 24 \text{ h}} \]

Scheme 6

Nyerges et al. have reported the tandem \textit{in situ} generation and reaction of nitromethylene oxindole and azomethine ylide.\(^8\) When a mixture of oxindole 17
and isoquinolinium salt 18 was treated with 2 equivalents of triethylamine at
room temperature, the spiroindolenin system 19 was formed. The actual reacting
species are nitromethylene oxindole 13 and azomethine ylide 20 (Scheme 7).

![Scheme 7](image)

i. Et$_3$N, Toluene, RT, 1 h, 73-75%

Scheme 7

Recently, the reaction of oxoindolinylidene 1 with azomethine ylide was
made use of in the asymmetric synthesis of (+) and (-)-spirotryprostatins.$^{10}$ The
core pyrrolidinone ring of spirotryprostatin B 25 was formed through the
reaction of a chiral azomethine ylide 23 with the oxoindolinylidene 1
(Scheme 8).
2.1.3. REACTION WITH MISCELLANEOUS SYSTEMS

The metallo-1,3-dipoles generated from copper(II) and zinc(II) complexes undergo cycloaddition with oxoindolinyldene acetate to yield the corresponding cycloadducts. The reaction between the zinc complex 26 and the oxoindolinyldene 4 is illustrative (Scheme 9)."
An isolated example of the addition of benzonitrile oxide to oxoindolinylidene acetate is available in the literature (Scheme 10).4

\[
\begin{array}{c}
\text{EtO}_2\text{C} \\
\text{Ph} \\
\text{H} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{EtO}_2\text{C} \\
\text{C}_6\text{H}_5\text{CNO} \\
\text{H} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{EtO}_2\text{C} \\
\text{Ph} \\
\text{H} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{EtO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{H} \\
\text{H}
\end{array}
\]

Scheme 10

The above discussion reveals that 1,3-dipolar cycloaddition of carbonyl ylides to oxoindolinylidenes has remained unexplored. Conceivably, 1,3-dipolar cycloaddition reactions of carbonyl ylides to \(\pi\)-bonds offer a very convenient strategy for the synthesis of structurally complex oxygen heterocycles.11 Recent experiments in our laboratory have shown that carbonyl ylides can be added to isatins at room temperature yielding spiroindolenin systems (Scheme 11).2d

\[
\begin{array}{c}
\text{R} \\
\text{O} \\
\text{CHN}_2 \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{R}_2 \\
\text{N} \\
\text{O} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{R} \\
\text{R}_2 \\
\text{N} \\
\text{O} \\
\text{O}
\end{array}
\]

Scheme 11

Against this background, we have undertaken some investigations on the dipolar cycloaddition of carbonyl ylides to oxoindolinylidenes. The results of these investigations are delineated in the following section.
2.2. RESULTS AND DISCUSSION

The oxoindolinylidene acetates and carbonyl ylides selected for our study are shown in Figures 1 and 2.

![Figure 1](image1.png)

1, R = H; 34, R = Me; 35, R = Bn

![Figure 2](image2.png)

The oxoindolinylidene acetates were prepared from the corresponding isatins by Wittig reaction. The diazoketones required for our study were prepared from the appropriate carboxylic acids by known literature procedures (Scheme 12).
2.2.1. REACTION WITH SIX MEMBERED CARBONYL YLIDES

Our studies were initiated with the rhodium(II) acetate catalyzed decomposition of 1-diazo-5-phenyl-2,5-pentanedione 42 in the presence of 3-ethoxycarbonylmethylene-2-oxoindole 1. The reaction proceeded smoothly to afford endo and exo adducts 43 and 44 in a total yield of 98% (Scheme 13).
The cycloadducts were separated by column chromatography and characterized on the basis of spectroscopic data. The IR spectrum of the *endo* adduct 43 showed the -NH absorption band at 3225 cm\(^{-1}\) and the carbonyl absorption bands were observed at 1734 and 1707 cm\(^{-1}\). The regio and stereochemical assignment of the structure is derived from proton NMR analysis. In the \(^1\)H NMR spectrum, the -NH proton appeared as a singlet at \(\delta 8.18\) (exchangeable with D\(_2\)O). The bridgehead proton on C-1 appeared as a doublet at \(\delta 4.81\) (\(J = 8.1\) Hz) and the proton on C-7 resonated as a doublet at \(\delta 4.11\) (\(J = 8.4\) Hz). The possibility of this adduct being the other regioisomer was discarded on the basis of coupling constant of these protons. For the other regioisomer there will be no vicinal coupling for the bridgehead and angular protons. The observed coupling constant indicated that this is the *endo* adduct with the structure 43. In bicyclic systems, the bridgehead proton is expected to show a vicinal coupling of 4-8 Hz with the *exo* proton and a \(J\) value of 0-3 Hz is expected with an *endo* proton. Thus, the \(J\) value of 8.6 Hz in this compound indicates that this has the structure 43 with the proton on C-7 in the *exo* position. One of the protons of the methylene moiety (on C-3) displayed a multiplet centered at \(\delta 3.10\). The other proton on the same carbon appeared as a multiplet centered at \(\delta 2.71\) along with one of the protons of the other methylene group (C-4). The remaining proton on C-4 was visible as a multiplet centered at \(\delta 2.22\) integrating for one proton. The methyl protons of the ester group showed a triplet at \(\delta 0.81\) (3H, \(J = 7.1\) Hz). In the \(^{13}\)C NMR spectrum, the three carbonyl signals were observed at \(\delta 203.34\) (C-2), 179.50 (ester carbonyl) and 168.44 (lactam carbonyl). The bridgehead carbon C-1 appeared at \(\delta 82.25\) and the signal due to the other bridgehead carbon C-5 was discernible at \(\delta 87.75\). The signal due to the spirocarbon was seen at \(\delta 63.34\). These assignments were confirmed by 2D NMR spectrum. The \(^{13}\)C-\(^1\)H correlation spectrum was utilized
to assign the signals in the $^1$H and $^{13}$C NMR spectra and is illustrated in Figure 3.

\[ \text{Figure 3. } ^{13}\text{C}-^1\text{H COSY spectrum of 43} \]

The figure clearly shows all the $^1$H-$^{13}$C connectivities. Of these, the most diagnostic are the connections between $\delta$ 33.05-2.22 (2.76), 33.83-2.71 (3.07), 55.32-4.11 and 82.25-4.88. All the other signals in $^1$H and $^{13}$C NMR spectra were in good agreement with the assigned structure.
The IR spectrum of the *exo* adduct 44 showed two strong bands at 1735 and 1700 cm\(^{-1}\). The -NH absorption band was observed at 3219 cm\(^{-1}\). In the \(^1\)H NMR spectrum, the bridgehead proton on C-1 and the proton on C-7 appeared as doublets at \(\delta 5.18\) \((J = 3.1 \text{ Hz})\) and 3.82 \((J = 3.1 \text{ Hz})\), respectively. The low coupling constant of 2.9 Hz between the bridgehead proton and the angular proton (on C-7) indicated that the carboxylate group is *exo*. The -OCH\(_2\) protons were seen as a quartet at \(\delta 3.65\) \((J = 6.9 \text{ Hz})\). The methylene protons on C-3 displayed a broad multiplet centered at \(\delta 3.16\), whereas the protons on the other methylene moiety appeared as two separate multiplets at \(\delta 2.64\) and 2.25 integrating for one proton each. The methyl protons of the ester functionality gave a triplet at \(\delta 0.62\) \((J = 7.1 \text{ Hz})\). The -NH proton was visible at \(\delta 8.35\) as a singlet (exchangeable with D\(_2\)O). In the \(^{13}\)C NMR spectrum, the signals due to the three carbonyl groups were visible at \(\delta 205.75, 176.85\) and 167.91. The bridgehead carbons C-1 and C-5 displayed signals at \(\delta 81.00\) and 90.05, respectively. The spiro carbon gave a peak at \(\delta 63.01\). Finally, the assigned structure was unequivocally established by single crystal X-ray analysis (Figure 4).
Under similar experimental conditions, the reaction of oxoindolinyldene derivatives 34-36 with the diazoketone 42 furnished similar spiro-oxabicyclic compounds. The results are summarized in Table 1.

The cycloadducts were separated by column chromatography and characterized by spectroscopic methods. The adducts 49 and 50 were obtained as mixture after column chromatography and were separated by Pasteur style physical separation. All these compounds 45-50 showed characteristic carbonyl absorptions in their IR spectra and typical proton and carbon signals in the NMR spectra.

Figure 4. X-ray structure of 44
Table 1. Cycloaddition reactions of diazoketone 42 with oxoindolinyldenenes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxoindolinyldene</th>
<th>Time (h)</th>
<th>Products</th>
<th>Yield (%)* (Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="34" /></td>
<td>2</td>
<td><img src="image2" alt="45" /> <img src="image3" alt="46" /></td>
<td>87 (98)* (2:1)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image4" alt="35" /></td>
<td>1</td>
<td><img src="image5" alt="47" /> <img src="image6" alt="48" /></td>
<td>89 (97)* (2:1)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image7" alt="36" /></td>
<td>0.5</td>
<td><img src="image8" alt="49" /> <img src="image9" alt="50" /></td>
<td>97 (2:1)</td>
</tr>
</tbody>
</table>

Reaction Conditions: Rh$_2$(OAc)$_4$, RT, Argon, *Isolated Yield, *Yield based on recovered oxoindolinyldene is given in parantheses.

Subsequent to these investigations, we became interested in the dipolar addition of the thienyl substituted carbonyl ylide 38 with the oxoindolinyldenenes. The rhodium(II) acetate catalyzed decomposition of 1-diazo-5-(2-thienyl)-2,5-pentanedione 51 in a toluene solution of oxoindolinyldene 1 afforded the cycloadducts 52 and 53 in high yields (Scheme 14).
After chromatographic purification, the exo and endo adducts were obtained as a mixture in 2:1 ratio. These isomers were separated by fractional crystallization. The assignment of the structure is based on spectroscopic analysis. The IR spectrum of the endo adduct 52 showed the -NH absorption at 3318 cm⁻¹. The absorption due to the carbonyl groups were seen at 1737 and 1716 cm⁻¹. In the ¹H NMR spectrum, a singlet due to the -NH proton, exchangeable with D₂O, was seen at δ 8.43. The proton on the bridgehead carbon C-1 resonated as a doublet at δ 4.80 (J = 8.3 Hz) and the proton on the adjacent carbon C-7 displayed a doublet at δ 4.17 (J = 8.3 Hz). One of the methylene protons on the carbon α to the carbonyl group (C-3) gave a multiplet.
centered at $\delta 3.10$ whereas, the other proton on the same carbon resonated along with one of the protons of the neighbouring methylene group to give a broad multiplet centered at $\delta 2.70$. The other proton on C-4 appeared as a multiplet centered at $\delta 2.38$. In the $^{13}$C NMR spectrum, the three carbonyl groups were discernible at $\delta 202.50, 179.41$ and $168.53$ corresponding to the keto, ester and lactam moieties, respectively. The signal due to the spirocarbon was observed at $\delta 63.74$. All the other signals were in good agreement with the assigned structure.

The adduct 53 showed the -NH absorption band at 3171 cm$^{-1}$ in IR spectrum and the carbonyl absorption bands were seen at 1740 and 1696 cm$^{-1}$. The bridgehead proton on C-1 and the proton on the $\alpha$ carbon C-7 appeared as doublets at $\delta 5.17 (J = 1.3$ Hz) and $3.82 (J = 2.8$ Hz), respectively. In the $^{13}$C NMR spectrum, the signals corresponding to the carbonyl groups were visible at $\delta 204.96, 176.25$ and $167.73$ and the spiro carbon displayed the signal at $\delta 63.55$. The two bridgehead carbons C-1 and C-5 gave peaks at $\delta 81.46$ and $89.19$, respectively. All the other signals in the $^1$H and $^{13}$C NMR spectra were in good agreement with the assigned structure.

Under similar experimental conditions, oxoindolinylidene acetates 34, 35 and 36 also underwent facile 1,3-dipolar cycloaddition with the carbonyl ylide 38 formed by the rhodium(II) acetate catalyzed decomposition of the diazoketone 51. The results of these experiments are summarized in Table 2. As usual, separation of the cycloadducts was effected by column chromatography followed by fractional crystallization. In the case of bromocompounds 57 and 58, the final separation of the isomers was carried out by Pasteur style physical separation.
Table 2. Reaction of oxoindolinylidenes with the diazocompound 51

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxoindolinylidene</th>
<th>Time (h)</th>
<th>Products</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt; (Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="34.png" alt="Image" /></td>
<td>1.5</td>
<td><img src="54.png" alt="Image" /></td>
<td>95 (1:0)</td>
</tr>
<tr>
<td>2</td>
<td><img src="35.png" alt="Image" /></td>
<td>1</td>
<td><img src="55.png" alt="Image" /> <img src="56.png" alt="Image" /></td>
<td>88 (98)* (1.1:1)</td>
</tr>
<tr>
<td>3</td>
<td><img src="36.png" alt="Image" /></td>
<td>0.5</td>
<td><img src="57.png" alt="Image" /> <img src="58.png" alt="Image" /></td>
<td>70 (82)* (2:1)</td>
</tr>
</tbody>
</table>

R<sup>a</sup> = CO<sub>2</sub>Et, R' = thienyl

Reaction conditions: Rh<sub>2</sub>(OAc)<sub>4</sub>, Toluene, RT, Argon, *Isolated yield, *Yield based on recovered oxoindolinylidene is given in parantheses.

2.2.2. REACTION WITH FIVE MEMBERED CARBONYL YLIDE

After having studied the reactivity of oxoindolinylidenes towards six membered carbonyl ylides, we turned our attention to the reaction of oxoindolinylidene acetates towards a five membered carbonyl ylide. The carbonyl ylide precursor 62 was prepared from the corresponding carboxylic
acid which in turn was prepared from ethyl acetoacetate and 1,2-dibromoethane (Scheme 15).\(^\text{15}\)

\[
\begin{array}{c}
\text{Br} \\
\text{Br} \\
\text{59}
\end{array}
+ 
\begin{array}{c}
\text{EtO} \equiv \text{CH}_3 \\
\text{Br} \\
\text{60}
\end{array}
\xrightarrow{i}
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{61}
\end{array}
\]

\[
\begin{array}{c}
\text{EtO}_2 \text{C} \\
\text{62}
\end{array}
\xrightarrow{ii}
\begin{array}{c}
\text{O} \\
\text{CH}_3 \\
\text{CHN}_2
\end{array}
\xrightarrow{iii}
\begin{array}{c}
\text{Me} \\
\text{39}
\end{array}
\]

i. NaOH, H\(_2\)O; ii. (a) ClCO\(_2\)Me, Et\(_3\)N (b) CH\(_2\)N\(_2\); iii. Rh\(_2\)(OAc)\(_4\)

Scheme 15

When a solution of 1-acetyl-1-diazoacetyl cyclopropane 62 and oxoindolinyldene 1 was treated with catalytic amount of rhodium(II) acetate at room temperature, the reaction afforded all the four possible isomeric products as shown in Scheme 16.

\[
\begin{array}{c}
\text{O} \\
\text{EtO}_2 \text{C} \\
\text{63}
\end{array}
+ 
\begin{array}{c}
\text{CHN}_2 \\
\text{62}
\end{array}
\xrightarrow{i}
\begin{array}{c}
\text{Me} \\
\text{64}
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{EtO}_2 \text{C} \\
\text{66}
\end{array}
\]

i. Rh\(_2\)(OAc)\(_4\), Toluene, Argon, RT, 30 min, 93% (2:2:3:2)

Scheme 16
The products were separated by column chromatography and fractional crystallization. The \textit{exo} adducts 64 and 66 were obtained as a mixture after chromatography. Further separation of these products was effected by fractional crystallization. The structures of the products were ascertained on the basis of spectroscopic analysis. The FT-IR spectrum of the adduct 63 showed the -NH absorption band at 3193 cm\(^{-1}\) and the carbonyl absorption peaks were seen at 1762 and 1709 cm\(^{-1}\). In the \(^{1}\text{H}\) NMR spectrum, the -NH proton (exchangeable with D\(_2\)O) resonated to give a singlet at \(\delta 8.98\). The bridgehead proton on C-1 and the proton on C-6 displayed a doublet at \(\delta 4.89 (J = 5.6 \text{ Hz}, 1\text{H})\) and \(3.99 (J = 5.6 \text{ Hz}, 1\text{H})\), respectively. The coupling constant of these protons is characteristic of the \textit{endo} adduct 63. The bridgehead methyl group gave a singlet at \(\delta 1.18\). The characteristic carbonyl signals in the \(^{13}\text{C}\) NMR spectrum were observed at \(\delta 208.49, 179.97\) and \(167.79\).

The \textit{exo} isomer 64 exhibited the -NH absorption band at 3204 cm\(^{-1}\) and the carbonyl absorption peaks at 1763 and 1710 cm\(^{-1}\). In the \(^{1}\text{H}\) NMR spectrum, the bridgehead proton displayed a singlet at \(\delta 5.10\) and the proton on the vicinal carbon showed a singlet at \(\delta 3.61\).\(^{\text{a}}\) The carbonyl groups displayed \(^{13}\text{C}\) signals at \(\delta 210.25, 176.51\) and \(168.45\).

In the IR spectrum of the cycloadduct 65, characteristic -NH and carbonyl absorption peaks were seen at 3281 and 1730 cm\(^{-1}\), respectively. The -NH proton signal was visible at \(\delta 9.02\) in \(^{1}\text{H}\) NMR spectrum. The bridgehead proton and the methine proton appeared as singlets at \(\delta 4.53\) and \(3.66\) respectively. In the \(^{13}\text{C}\) NMR spectrum, the carbonyl signals were observed at \(\delta 207.36, 180.03\) and \(168.15\).

The \textit{exo} adduct 66 displayed the -NH absorption band at 3187 cm\(^{-1}\) and the carbonyl absorptions were seen at 1747 and 1707 cm\(^{-1}\) in the IR spectrum. In the \(^{1}\text{H}\) NMR spectrum, the -NH signal was observed at \(\delta 9.04\). The bridgehead

\(^{\text{a}}\) In high resolution NMR, these protons showed a vicinal coupling of 0.8 Hz.
proton resonated to give a singlet at $\delta$ 4.27 and the methine proton was discernible at $\delta$ 3.56. The $^{13}$C NMR spectrum showed the carbonyl peaks at $\delta$ 207.56, 175.98 and 167.97.

These assignments were confirmed with the help of detailed $^1$H NMR analysis. NOESY and nOe difference experiments were carried out on these samples to assign the resonances and to establish the molecular structure.

The adduct 64 showed characteristic coupling of 0.8 Hz for the bridge-head proton which indicated that the protons involved are attached to vicinal carbons in the norbornane framework and that the proton on the adjacent carbon is on the endo side of the bicyclic system. NOESY spectrum showed cross peaks between H15-Me17, Me17-H15, Me17-H16 and H4-H5. The nOe intensities measured by difference nOe experiments and the NOESY spectrum are shown in Figures 5a and 5b.

The structure of 65 was ascertained with the help of NOESY and nOe difference experiments. The characteristic NOESY cross peaks observed are shown in Figure 6a.
The endo structure of the adduct was confirmed by the nOe of H13-H5 = 5% which is possible only if the aromatic ring is endo. The nOe difference spectrum is displayed in Figure 6b.
The reaction of N-methyl and N-benzyl oxoindolinyldenes 34 and 35 with the diazoketone 62 followed a similar course. The results of these experiments are given in Table 3.
Table 3. Reaction of oxoindolinylidenes with the diazocompound 62

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxoindolinylidene</th>
<th>Time (h)</th>
<th>Products</th>
<th>Yield %(^a) (Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\text{34} \quad \text{EtO}_2\text{C} \quad \text{Me} \quad \text{N} \quad \text{Me} )</td>
<td>0.5</td>
<td>(\text{67} \quad \text{68} )</td>
<td>93 (3:2:3:2)</td>
</tr>
<tr>
<td>2</td>
<td>(\text{35} \quad \text{Bn} \quad \text{N} \quad \text{N} \quad \text{Me} )</td>
<td>1</td>
<td>(\text{69} \quad \text{70} \quad \text{71} \quad \text{72} )</td>
<td>98 (1:1:1)</td>
</tr>
</tbody>
</table>

Reaction conditions: \(\text{Rh}_2(\text{OAc})_4\), Toluene, RT, Argon, \(^a\) Isolated yield.
As in the previous experiment, the products were separated by column chromatography followed by fractional crystallization. The structure of the products was assigned by spectroscopic methods and by correlating with the adducts 63, 64, 65 and 66.

For the sake of completeness, addition of a seven membered carbonyl ylide to the oxoindolinylidene 1 was attempted. However, the reaction afforded only an inseparable mixture of exo and endo adducts in very low yields. The reaction was not pursued further.

2.2.3. THEORETICAL CALCULATIONS

Frontier molecular orbital theory generally rationalizes the regioselectivity of most 1,3-dipolar cycloaddition reactions. The HOMO of the dipole is dominant in reaction with electron deficient dipolarophiles, whereas, LUMO of the dipole is the controlling molecular orbital in reactions with electron rich dipolarophiles. In order to explain the observed mode of addition, we have carried out some theoretical calculations using semi-empirical PM3 method with the aid of TITAN software (version 1). The correlation diagram for the reaction of oxoindolinylidene 1 with the carbonyl ylide 37 is given in Figure 7 as an illustrative example.
From the correlation diagram in Figure 7, it is clear that the most favorable interaction is HOMO(dipole)-LUMO(dipolarophile) interaction. HOMO(dipole)-LUMO(dipolarophile) and LUMO(dipole)-HOMO(dipolarophile) interactions are symmetry allowed. However, the LUMO(dipole)-HOMO(dipolarophile) interaction is unimportant due to the large energy gap compared to the other. Thus, it is a HOMO controlled reaction according to Sustmann's classification of 1,3-dipolar cycloaddition reactions.\textsuperscript{16}

In conclusion, we have shown that highly functionalized spiroindolenin systems can be synthesized using the simple one step addition of carbonyl ylides to oxoindolinylidene derivatives. It is conceivable that the cycloadducts may be amenable to a number of useful synthetic transformations.
2.3. EXPERIMENTAL DETAILS

All reactions were carried out in oven dried glassware under an atmosphere of argon, unless otherwise mentioned. Analytical thin layer chromatography was performed on silica gel TLC plates. Purification by column chromatography was carried out using silica gel (100-200 mesh). Mixtures of ethyl acetate and hexane were used as eluents. After the chromatographic separation, the solvents were removed using a Büchi-EL rotary evaporator. Melting points were recorded on Fisher Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Bomem MB series FT-IR spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded on Brüker 300 MHz NMR spectrometer using chloroform-d as solvent, unless otherwise mentioned. The chemical shifts are given in $\delta$ scale with tetramethyldisilane as internal standard. High-resolution mass spectra were recorded on a Finnigan MAT model 8430 instrument. Elemental analyses were done using Perkin-Elmer 2400 CHNS Analyzer. All solid products were purified by recrystallization from an appropriate solvent system. Solvents used for the experiments (toluene, ether and dichloromethane) were distilled and dried by employing standard procedures.

The diazoketones were prepared from the corresponding carboxylic acids following the literature procedures. $^{13,14}$

**General procedure for the rhodium(II) catalyzed cycloaddition reaction of 1-diazoalkane diones with oxoindolinyldienes**

A toluene solution of oxoindolinyldene acetate and 1.5 equivalents of appropriate diazokanedione was purged with argon. To this solution, catalytic amount of rhodium(II) acetate (2 mg) was added and stirred under argon atmosphere at room temperature. When the reaction was over (as indicated by TLC), the solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica gel using the appropriate hexane-ethyl acetate mixture as the eluent to give the pure cycloadducts. Wherever
necessary, further separation of the isomeric products was carried out by fractional crystallization. The products were identified on the basis of spectroscopic data.

**Cycloadducts 43 and 44**

A solution of oxoindolinyldene acetate 1 (0.217 g, 1 mmol) and 1-diazooxo-5-phenyl-2,5-pentanedione 42 (0.303 g, 1.5 mmol) in toluene (15 mL) was treated with catalytic amount of rhodium(II) acetate at room temperature under an atmosphere of argon and was stirred for 45 min. On completion of the reaction, toluene was removed under reduced pressure in a rotary evaporator. The residue on chromatography on a silica gel column (100-200 mesh) using 10% ethyl acetate-hexane as eluent afforded the *endo* adduct 43 (0.203 g, 52%) as an off-white crystalline solid and the *exo* adduct 44 (0.180 g, 46%) as colorless crystalline solid. The products were further purified by recrystallization from ethyl acetate-hexane solvent system.

**Ethyl (1'R,3R,5'S,7'S)-7'-1,2-dihydro-2,2'-dioxo-5'-phenyl spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 43**

Recrystallized from ethyl acetate-hexane, mp. 164 °C (decomposed)

IR (KBr) $\nu_{(\text{max})}$: 3225, 1734, 1707, 1619, 1473, 1446, 1372, 1347, 1303, 1185, 1160, 1029 cm$^{-1}$.

$^1$H NMR: $\delta$ 8.18 (s, 1H, exchangeable with D$_2$O), 7.45 (d, $J$ = 7.5 Hz, 1H), 7.32 (t, $J$ = 7.3 Hz, 1H), 7.12 (brs, 5H), 6.86 (d, $J$ = 7.6 Hz, 2H), 4.81 (d, $J$ = 8.1 Hz, 1H), 4.11 (d, $J$ = 8.4 Hz, 1H), 3.85-3.79 (m, 2H), 3.13-3.07 (m, 1H), 2.81-2.67 (m, 2H), 2.24-2.15 (m, 1H), 0.81 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR: $\delta$ 203.34, 179.50, 168.44, 142.63, 140.51, 129.74, 127.88, 127.64, 123.76, 122.43, 110.38, 87.75, 82.25, 63.34, 61.25, 55.32, 33.83, 33.05, 13.65.

Anal. calcd. for C$_{23}$H$_{21}$NO$_3$: C, 70.57; H, 5.40; N, 3.57. Found: C, 70.76; H, 5.42; N, 3.73.
Ethyl (1'R,3S,5'S,7'R)-7'-1,2-dihydro-2,2'-dioxo-5'-phenyl spiro[3H-indole-3,6'-[8]oxabicyc[3.2.1]octane]-7'-carboxylate 44

Recrystallized from ethyl acetate-hexane, mp. 195-197 °C.

IR (KBr) ν_{max}: 3219, 1735, 1700, 1619, 1473, 1447, 1372, 1345, 1303, 1242, 1188, 1160 cm^{-1}.

^{1}H NMR : δ 8.35 (s, 1H), 7.10-6.90 (m, 7H), 6.70 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 5.18 (d, J = 3.1 Hz, 1H), 3.82 (d, J = 3.1 Hz, 1H), 3.65 (q, J = 6.9 Hz, 2H), 3.25-3.08 (m, 2H), 2.69-2.60 (m, 1H), 2.30-2.17 (m, 1H), 0.62 (t, J = 7.1 Hz, 3H).

^{13}C NMR : δ 205.75, 176.85, 167.91, 141.30, 139.82, 129.16, 128.38, 127.84, 127.19, 126.56, 123.31, 122.24, 108.70, 90.05, 81.00, 63.01, 61.27, 57.26, 33.34, 31.92, 13.34.

X-RAY Crystal data: C_{23}H_{20}NO_{5}.H_{2}O Fw: 408.42. Crystal size: 0.40 x 0.36 x 0.12 mm^{3}, Monoclinic, Space group: P2(1)/n. Unit cell dimensions a = 8.8733(4) Å, α = 90°, b = 14.8316(7) Å, β = 97.245(4)°; c = 15.4797(8) Å, γ = 90°. R indices (all data) R1 = 0.0873, wR2 = 0.1461. Volume, Z = 2020.94(17) Å^{3}, 4. D calc. = 1.342 mg/m^{3}. F (000) = 860. Absorption Coefficient = 0.098 mm^{-1}. Reflections collected = 38290. λ = 0.71073 Å. (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995).

Cycloadducts 45 and 46

Treatment of 1-diazo-5-phenyl-2,5-pentane dione 42 (0.303 g, 1.5 mmol) with 3-ethoxycarbonyl methylene-2-oxoindoline 34 (0.231 g, 1 mmol) in toluene (10 mL), in the presence of a catalytic amount of rhodium(II) acetate at room temperature for 2 h followed by chromatographic purification of the product afforded the adduct 45 (0.231 g, 57%) as a pale yellow semi-solid and the adduct 46 (0.121 g, 30%) as colorless crystals.
Ethyl (1'R,3R,5'S,7'S)-7'-1,2-dihydro-2,2'-dioxo-1-methyl-5'-phenyl spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 45

IR (KBr) $\nu_{(\text{max})}$: 1723 (broad band), 1611, 1493, 1470, 1375, 1331, 1194, 1160, 1028 cm$^{-1}$.

$^1$H NMR: $\delta$ 7.49-7.38 (m, 2H), 7.13-7.11 (m, 5H), 6.76 (d, $J = 7.7$ Hz, 2H), 4.85 (d, $J = 8.3$ Hz, 1H), 4.15 (d, $J = 8.4$ Hz, 1H), 3.91-3.75 (m, 2H), 3.16-3.04 (m, 1H), 2.74-2.60 (m, 2H) 2.67 (s, 3H), 2.23-2.16 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR: $\delta$ 204.25, 176.92, 168.53, 145.29, 140.24, 129.65, 127.50, 125.18, 122.21, 108.60, 87.78, 82.40, 63.09, 61.05, 54.52, 33.45, 32.89, 25.79, 13.59.

Ethyl (1'R,3S,5'S,7'R)-7'-1,2-dihydro-2,2'-dioxo-1-methyl-5'-phenyl spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 46

Recrystallized from ethyl acetate-hexane solvent system, mp. 180-182 °C.

IR (KBr) $\nu_{(\text{max})}$: 1741, 1702, 1607, 1469, 1378, 1351, 1133, 1094, 1025 cm$^{-1}$.

$^1$H NMR: $\delta$ 7.03-6.96 (m, 7H), 6.72 (t, $J = 7.5$ Hz, 1H), 6.54 (d, $J = 7.7$ Hz, 1H), 5.17 (d, $J = 1.7$ Hz, 1H), 3.80 (d, $J = 3.1$ Hz, 1H), 3.60-3.53 (m, 2H), 3.30 (s, 3H), 3.26-3.09 (m, 2H), 2.68-2.59 (m, 1H), 2.26-2.17 (m, 1H), 0.57 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR: $\delta$ 205.76, 174.83, 167.89, 142.91, 141.32, 128.32, 127.73, 127.06, 123.18, 122.23, 107.10, 89.87, 62.60, 61.02, 57.00, 33.30, 31.83, 26.72, 13.32.

Cycloadducts 47 and 48

Treatment of 1-diazo-5-phenyl-2,5-pentane dione 42 (0.303 g, 1.5 mmol) with 3-ethoxycarbonylmethylene-2-oxoindoline 35 (0.307 g, 1 mmol) in toluene (10 mL), in the presence of a catalytic amount of rhodium(II) acetate at room temperature for 1 h followed by chromatographic purification of the product afforded the adduct 47 (0.274 g, 57%) as an off-white crystalline solid and the adduct 48 (0.154 g, 32%) as a colorless solid.
Ethyl(1'R,3R,5'S,7'S)-7'-1,2-dihydro-2,2'-dioxo-5'-phenyl-1-(phenylmethyl)
spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 47
Recrystallized from CH$_2$Cl$_2$-hexane, mp. 168-170 °C.

IR (KBr) $\nu$($\text{max}$): 1737, 1719, 1610, 1492, 1467, 1368, 1179, 1029 cm$^{-1}$.

$^1$H NMR : $\delta$ 7.47 (d, $J$ = 7.5 Hz, 1H), 7.28-7.07 (m, 10H), 6.71 (m, 2H),
6.62 (d, $J$ = 7.7 Hz, 1H), 4.88 (d, $J$ = 8.3 Hz, 1H), 4.58 (d, $J$ =
15.7 Hz, 1H), 4.38 (d, $J$ = 15.7 Hz, 1H), 4.24 (d, $J$ = 8.4 Hz, 1H),
3.89-3.68 (m, 2H), 3.19-3.07 (m, 1H), 2.87-2.79 (m, 1H), 2.73-
2.64 (m, 1H), 2.31-2.20 (m, 1H), 0.74 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR : $\delta$ 203.20, 177.50, 168.45, 144.66, 140.56, 135.03, 128.59,
128.01, 127.61, 127.41, 127.01, 125.26, 124.62, 124.06, 122.37,
109.55, 87.56, 82.18, 62.87, 61.09, 56.07, 44.00, 34.12, 33.15,
13.56.

Anal calcd. for C$_{30}$H$_{27}$N$_{2}$O$_5$: C, 74.82; H, 5.65; N, 2.90. Found: C, 74.87; H,
5.76; N, 2.93.

Ethyl(1'R,3S,5'S,7'R)-7'-1,2-dihydro-2,2'-dioxo-5'-phenyl-1-(phenylmethyl)
spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 48
Recrystallized from ethyl acetate-hexane, mp. 165-167 °C.

IR (KBr) $\nu$($\text{max}$): 1740, 1702, 1607, 1468, 1377, 1350, 1094, 1025 cm$^{-1}$.

$^1$H NMR : $\delta$ 7.36-7.29 (m, 5H), 7.03-6.86 (m, 7H), 6.68 (t, $J$ = 7.3 Hz,
1H), 6.51 (d, $J$ = 7.7 Hz, 1H), 5.19 (d, $J$ = 2.9 Hz, 1H), 5.09 (d, $J$
= 15.3 Hz, 1H), 4.86 (d, $J$ = 15.2 Hz, 1H), 3.88 (d, $J$ = 2.9 Hz,
1H), 3.61-3.49 (m, 2H), 3.29-3.14 (m, 2H), 2.70-2.61 (m, 1H),
2.27-2.16 (m, 1H), 0.39 (t, $J$ = 7.0 Hz, 3H).

$^{13}$C NMR : $\delta$ 205.57, 175.02, 167.87, 142.14, 141.19, 135.67, 128.73,
128.18, 127.88, 127.68, 127.07, 126.23, 123.37, 122.17, 108.07,
90.09, 81.10, 62.50, 61.11, 57.21, 44.38, 33.33, 32.08, 13.11.

Anal calcd. for C$_{30}$H$_{27}$N$_{2}$O$_5$: C, 74.82; H, 5.65; N, 2.90. Found: C, 74.88; H,
5.67; N, 2.93.
Cycloadducts 49 and 50

Treatment of 1-diazo-5-phenyl-2,5-pentane dione 42 (0.303 g, 1.5 mmol) with 5-bromo-3-ethoxycarbonyl methylene-2-oxoindoline 36 (0.296 g, 1 mmol) in toluene (20 mL), in presence of a catalytic amount of rhodium(II) acetate at room temperature for 30 min followed by chromatographic purification of the product afforded the *endo* adduct 49 (0.310 g, 66%) a colorless crystalline solid and the *exo* adduct 50 (0.146 g, 31%) as an off-white crystalline solid.

Ethyl (1'R,3R,5'S,7'S)-7'-5-bromo-1,2-dihydro-2,2'-dioxo-5'-phenyl spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 49

Recrystallized from ethyl acetate-hexane solvent system, mp. 240-242 °C.

IR (KBr) \( \nu_{\text{max}} \): 3306, 1730, 1699, 1619, 1474, 1445, 1372, 1311, 1241, 1187, 1034 cm\(^{-1}\).

\(^1\)H NMR : \( \delta \) 8.13 (s, 1H), 7.53-7.47 (m, 2H), 7.12 (brs, 4H), 6.94-6.85 (m, 1H), 6.75 (d, \( J = 8.2 \) Hz, 1H), 4.80 (d, \( J = 8.4 \) Hz, 1H), 4.06 (d, \( J = 8.3 \) Hz, 1H), 3.93-3.91 (m, 2H), 3.03-2.94 (m, 1H), 2.80-2.62 (m, 2H), 2.31-2.23 (m, 1H), 0.91 (t, \( J = 6.9 \) Hz, 3H).

\(^13\)C NMR : \( \delta \) 203.15, 178.89, 168.26, 141.61, 140.13, 132.62, 128.82, 127.95, 127.85, 127.04, 123.80, 115.03, 111.69, 87.89, 82.26, 63.48, 61.67, 55.19, 33.35, 32.84, 13.80.

Ethyl (1'R,3S,5'S,7'R)-7'-5-bromo-1,2-dihydro-2,2'-dioxo-5'-phenyl spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 50

Recrystallized from ethyl acetate-hexane solvent system, mp. 225-227 °C.

IR (KBr) \( \nu_{\text{max}} \): 3170, 3107, 1737, 1704, 1617, 1471, 1447, 1305, 1268, 1184, 1029 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)+DMSO-\( d_6 \)) : \( \delta \) 9.99 (s, 1H), 7.07-6.99 (m, 7H), 6.49 (d, \( J = 8.2 \) Hz, 1H), 5.15 (d, \( J = 1.2 \) Hz, 1H), 3.80 (d, \( J = 2.9 \) Hz, 1H), 3.76-3.66 (m, 2H), 3.24-3.07 (m, 2H), 2.68-2.59 (m, 1H), 2.22-2.16 (m, 1H), 0.71 (t, \( J = 7.1 \) Hz, 3H).
Chapter 2

$^{13}$C NMR : $\delta$ 205.53, 176.26, 167.67, 140.90, 140.00, 131.14, 130.85, 128.99, 128.20, 127.77, 127.23, 123.12, 113.93, 110.40, 89.79, 80.86, 63.07, 61.31, 57.12, 33.15, 31.67, 13.29.

Cycloadducts 52 and 53

Treatment of 1-diazo-5-(2-thienyl)-2,5-pentane dione 51 (0.312 g, 1.5 mmol) with 3-ethoxycarbonylmethylene-2-oxoindoline 1 (0.217 g, 1 mmol) in toluene (15 mL), in the presence of a catalytic amount of rhodium(II) acetate at room temperature for 30 min followed by chromatographic purification of the product afforded 0.460 g of the cycloadduct as a mixture of endo and exo isomers. Further separation of the isomers was effected by fractional crystallization.

Ethyl (1'R,3R,5'S,7'S)-7'-1,2-dihydro-2,2'-dioxo-5'-(2-thienyl)-spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 52

Recrystallised from CH$_2$Cl$_2$-hexane solvent system, mp. 190 °C (decomposed).

IR (KBr) $\nu_{(max)}$: 3318, 1737, 1716, 1615, 1470, 1378, 1346, 1301, 1242, 1190 cm$^{-1}$.

$^1$H NMR : $\delta$ 8.43 (s, 1H, exchangeable with D$_2$O), 7.43-7.33 (m, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 4.4$ Hz, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.74 (t, $J = 6.7$ Hz, 1H), 6.42 (d, $J = 2.5$ Hz, 1H), 4.80 (d, $J = 8.3$ Hz, 1H), 4.17 (d, $J = 8.3$ Hz, 1H), 3.91-3.78 (m, 2H), 3.17-3.04 (m, 1H), 2.77-2.63 (m, 2H), 2.42-2.31 (m, 1H), 0.83 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR : $\delta$ 202.50, 179.41, 168.53, 142.87, 142.67, 129.86, 126.42, 125.69, 124.40, 124.15, 122.50, 122.44, 110.65, 87.36, 82.63, 63.74, 54.86, 35.09, 33.06, 13.69.

Anal. Calcd. for C$_{21}$H$_{19}$NO$_5$S: C, 63.46; H, 4.81; N, 3.52; S, 8.06. Found: C, 63.48; H, 4.78; N, 3.82; S, 8.10.

Ethyl (1'R,3S,5'S,7'R)-7'-1,2-dihydro-2,2'-dioxo-5'-(2-thienyl)-spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 53
Recrystallized from CH₂Cl₂-hexane, mp. 180 °C (decomposed).

IR (KBr) ν(max): 3171, 1740, 1474, 1194 cm⁻¹.

¹H NMR : δ 8.12 (s, 1H, exchangeable with D₂O), 7.11 (d, J = 7.4 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.92-6.91 (m, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.67-6.64 (m, 3H), 5.17 (d, J = 1.2 Hz, 1H), 3.82 (d, J = 2.8 Hz, 1H), 3.68 (q, J = 7.1 Hz, 2H), 2.70-2.62 (m, 1H), 2.41-2.39 (m, 1H), 0.63 (t, J = 7.1 Hz, 3H).

¹³C NMR : δ 204.96, 176.25, 167.73, 143.54, 140.00, 128.79, 128.63, 126.68, 126.26, 123.73, 122.28, 121.91, 108.83, 89.19, 81.46, 63.55, 61.35, 56.92, 33.31, 33.09, 13.34.

Anal. Calcd. for C₂₁H₁₉NO₅S·H₂O: C, 60.71; H, 5.10; N, 3.37; S, 7.71. Found: C, 60.57; H, 5.15; N, 3.67; S, 7.96.

Ethyl (1'R,3R,5'S,7'S)-7'-1,2-dihydro-2,2'-dioxo-1-methyl-5'-(2-thienyl)-spiro[3H-indole-3,6' [8]oxabicyclo[3.2.1]octane]-7'-carboxylate 54

Treatment of 1-diazo-5-(2-thienyl)-2,5-pentane dione 51 (0.312 g, 1.5 mmol) with 3-ethoxycarbonylmethylene-2-oxoindoline 34 (0.231 g, 1 mmol) in toluene (10 mL), in the presence of a catalytic amount of rhodium(II) acetate at room temperature for 1.5 h followed by chromatographic purification of the product afforded 0.390 g (95%) of the cycloadduct 54 as a white crystalline solid which was recrystallized from CH₂Cl₂-hexane solvent system, mp. 122-124 °C.

IR (KBr) ν(max): 1743, 1719, 1609, 1493, 1468, 1376, 1350, 1189, 1157, 1098 cm⁻¹.

¹H NMR : δ 7.46-7.34 (m, 2H), 7.14-7.10 (m, 2H), 6.80 (d, J = 5.9 Hz, 2H), 6.41 (d, J = 3.1 Hz, 1H), 4.85 (d, J = 8.2 Hz, 1H), 4.22 (d, J = 8.2 Hz, 1H), 3.88-3.81 (m, 2H), 3.13-3.05 (m, 1H), 2.83 (s, 3H), 2.72-2.64 (m, 2H), 2.41-2.35 (m, 1H), 0.83 (t, J = 7.0 Hz, 3H).
Chapter 2

$^{13}$C NMR : $\delta$ 202.59, 176.85, 168.53, 145.53, 142.57, 129.86, 126.11, 125.40, 124.27, 123.71, 122.50, 122.34, 108.38, 87.49, 82.79, 63.49, 54.33, 35.02, 33.04, 26.15, 13.70.

Anal. Calcd. for C$_{22}$H$_{21}$NO$_5$S: C, 64.22; H, 5.14; N, 3.40; S, 7.79. Found: C, 64.09; H, 5.22; N, 3.81; S, 8.14.

Cycloadducts 55 and 56

Treatment of 1-diazo-5-(2-thienyl)-2,5-pentane dione 51 (0.312 g, 1.5 mmol) with 3-ethoxycarbonylmethylene-2-oxoindoline 35 (0.307 g, 1 mmol) in toluene (10 mL), in presence of a catalytic amount of rhodium(II) acetate at room temperature for 1 h followed by chromatographic purification of the product afforded the adduct 55 (0.278 g, 57%) as an off-white crystalline solid and the adduct 56 (0.156 g, 32%) as colorless crystals.

Ethyl(1'R,3R,5'S,7'S)-7'-1,2-dihydro-2,2'-dioxo-1-(phenylmethyl)-5'(2-thienyl)-spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 55

Recrystallized from ethyl acetate-hexane, mp. >300 °C.

IR (KBr) $\nu$(max): 1742, 1716, 1609, 1488, 1462, 1372, 1178, 1018 cm$^{-1}$.

$^1$H NMR : $\delta$ 7.45 (d, $J$ = 7.4 Hz, 1H), 7.24-7.08 (m, 8H), 6.84-6.78 (m, 2H), 6.65 (d, $J$ = 7.6 Hz, 1H), 6.47 (d, $J$ = 2.4 Hz, 1H), 4.86 (d, $J$ = 8.4 Hz, 1H), 4.68 (d, $J$ = 15.7 Hz, 1H), 4.50 (d, $J$ = 15.7 Hz, 1H), 4.29 (d, $J$ = 8.4 Hz, 1H), 3.87-3.72 (m, 2H), 3.19-3.07 (m, 1H), 2.81-2.65 (m, 1H), 2.45-2.34 (m, 1H), 0.75 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR : $\delta$ 202.40, 177.26, 168.37, 144.83, 142.70, 135.12, 129.78, 128.66, 127.51, 127.12, 126.43, 125.40, 124.45, 123.90, 122.97, 122.40, 109.64, 87.17, 82.49, 82.49, 63.28, 61.19, 55.64, 44.16, 35.49, 33.21, 13.59.

Ethyl (1'R,3S,5'S,7'R)-7'-1,2-dihydro-2,2'-dioxo-1-(methylphenyl)-5'(2-thienyl)-spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 56

Recrystallized from ethylacetate-hexane, mp. 184-186 °C.
IR (KBr) $\nu_{(\text{max})}$: 1735, 1705, 1610, 1489, 1467, 1370 cm$^{-1}$.

$^1$H NMR: $\delta$ 7.37-7.29 (m, 5H), 7.12 (d, $J = 7.3$ Hz, 1H), 6.96 (t, $J = 7.6$ Hz, 1H), 6.88-6.86 (m, 1H), 6.76 (t, $J = 7.5$ Hz, 1H), 6.58-6.53 (m, 2H), 6.47-6.46 (m, 1H), 5.21 (d, $J = 15.2$ Hz, 1H), 5.17 (d, $J = 1.2$ Hz, 1H), 4.78 (d, $J = 15.4$ Hz, 1H), 3.87 (d, $J = 3.0$ Hz, 1H), 3.70-3.50 (m, 2H), 3.28-3.15 (m, 2H), 2.69-2.63 (m, 1H), 2.43-2.32 (m, 1H), 0.38 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR: $\delta$ 204.87, 174.43, 167.71, 143.43, 142.21, 135.62, 128.72, 128.45, 127.91, 127.75, 126.35, 126.10, 123.67, 122.23, 122.08, 108.25, 89.26, 81.55, 63.02, 61.23, 56.86, 44.40, 33.34, 30.86, 13.70.

Cycloadducts 57 and 58

Treatment of 1-diazo-5-(2-thienyl)-2,5-pentane dione 51 (0.312 g, 1.5 mmol) with 3-ethoxycarbonyl methylene-2-oxoindoline 36 (0.296 g, 1 mmol) in toluene (20 mL), in presence of a catalytic amount of rhodium(II) acetate at room temperature for 30 min followed by chromatographic purification of the product afforded the adducts 57 and 58 as a mixture in the ratio 2:1. The endo and exo isomers were separated by crystallization and Pasteur style physical separation.

Ethyl (1'R,3R,5'S,7'S)-7'-5-bromo-1,2-dihydro-2,2'-dioxo-5'-(2-thienyl)-spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 57

Recrystallized from ethyl acetate-hexane, mp. 212-214 °C.

IR (KBr) $\nu_{(\text{max})}$: 3298, 1741, 1708, 1616, 1475, 1434, 1303, 1276, 1182 cm$^{-1}$.

$^1$H NMR: $\delta$ 9.44 (s, 1H), 7.49-7.44 (m, 2H), 7.12-7.10 (m, 1H), 6.82-6.78 (m, 2H), 6.50-6.49 (m, 1H), 4.80 (d, $J = 8.4$ Hz, 1H), 4.17 (d, $J = 8.4$ Hz, 1H), 3.98-3.87 (m, 2H), 3.06-2.97 (m, 1H), 2.76-2.65 (m, 2H), 2.45-2.34 (m, 1H), 0.90 (t, $J = 7.1$ Hz, 3H).
**Chapter 2**

\[ ^{13}C \text{NMR} \quad \delta \quad 202.24, \ 178.45, \ 168.22, \ 142.65, \ 132.57, \ 128.58, \ 126.38, \ 126.26, \ 124.34, \ 122.62, \ 114.40, \ 111.84, \ 87.30, \ 82.55, \ 63.64, \ 61.54, \ 54.77, \ 34.96, \ 32.92, \ 13.70. \]

**Ethyl (1'R,3R,5'S,7'R)-7'-5-bromo-1,2-dihydro-2,2'-dioxo-5'-(2-thienyl)-spiro[3H-indole-3,6'-[8]oxabicyclo[3.2.1]octane]-7'-carboxylate 58**

Recrystallized from ethyl acetate-hexane, mp. 180 °C (decomposed).

IR (KBr) \( \nu_{\text{max}} \): 3301, 1728, 1701, 1618, 1474, 1302, 1183 cm\(^{-1}\).

**\(^1\)H NMR** (CDCl\(_3\)+DMSO-d\(_6\)):

\( \delta \) 10.36 (s, 1H), 7.15 (s, 1H), 7.15-7.11 (m, 1H), 6.96-6.94 (m, 1H), 6.67-6.62 (m, 2H), 6.53 (m, 1H), 5.11 (d, \( J = 1.5 \) Hz, 1H), 3.78 (d, \( J = 2.9 \) Hz, 1H), 3.78-3.66 (m, 2H), 3.14-3.09 (m, 2H), 2.66-2.56 (m, 1H), 2.37-2.30 (m, 1H), 0.69 (t, \( J = 7.2 \) Hz, 3H).

\[ ^{13}C \text{NMR} \quad \delta \quad 204.56, \ 175.43, \ 167.39, \ 142.96, \ 140.25, \ 130.92, \ 128.85, \ 126.10, \ 123.65, \ 121.69, \ 113.66, \ 110.42, \ 88.80, \ 81.16, \ 63.38, \ 61.23, \ 56.53, \ 33.03, \ 32.82, \ 13.13. \]

Anal calcd. for C\(_2\)H\(_{18}\)NO\(_5\)SBr: C, 52.95; H, 3.80; N, 2.94; S, 6.73. Found: C, 52.65; H, 4.09; N, 2.96; S, 6.68.

**Cycloadducts 63, 64, 65 and 66**

Treatment of 1-acetyl-1-diazoacetyl cyclopropane 62 (0.228 g, 1.5 mmol) with 3-ethoxycarbonyl methylene-2-oxoindoline 1 (0.217 g, 1 mmol) in toluene (15 mL), in presence of a catalytic amount of rhodium(II) acetate at room temperature for 30 min followed by chromatographic purification afforded the adducts 63 (0.070 g, 20%) and 65 (0.106 g, 31%) as colorless crystalline solids. The adducts 64 and 66 were obtained as a mixture of regioisomers (0.141 g, 41%, 1:1) and were separated by fractional crystallization.

**Ethyl(1'R,3''R,4'R,5'S)-1''',2'''-dihydro-1''-methyl-2''',3'''-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-6',3'''-[3H]-indole]-5'''-carboxylate 63**

Recrystallized from CH\(_2\)Cl\(_2\)-hexane, mp. 224-226 °C.
Chapter 2

IR (KBr) \( \nu_{\text{max}} \): 3193, 3086, 1762, 1709, 1472, 1381, 1333, 1189, 1140, 1104 cm\(^{-1}\).

\(^1\)H NMR : \( \delta \) 8.98 (s, 1H, exchangeable with D\(_2\)O), 7.26-7.19 (m, 1H), 7.09 (d, \( J = 7.5 \) Hz, 1H), 6.98-6.89 (m, 2H), 4.89 (d, \( J = 5.6 \) Hz, 1H), 3.99 (d, \( J = 5.6 \) Hz, 1H), 3.85-3.78 (m, 2H), 1.62-1.59 (m, 1H), 1.18 (s, 3H), 1.12-1.06 (m, 1H), 0.92-0.85 (m, 1H), 0.80 (t, \( J = 7.1 \) Hz, 3H), 0.74-0.69 (m, 1H).

\(^1\)C NMR : \( \delta \) 208.49, 179.97, 167.79, 141.86, 129.13, 128.01, 124.74, 121.35, 110.02, 90.54, 81.76, 61.11, 60.91, 54.28, 38.72, 15.45, 14.39, 13.68, 13.56.

Ethyl (1'R,3'S,4'R,5'R)-1",2"-dihydro-1'-methyl-2",3'-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-6',3''-[3H]-indole]-5'-carboxylate

Recrystallized from CHCl\(_3\)-hexane, mp. 143-145 °C.

IR (KBr) \( \nu_{\text{max}} \): 3204, 3089, 1763, 1710, 1617, 1473, 1390, 1339, 1219 cm\(^{-1}\).

\(^1\)H NMR : \( \delta \) 9.07 (s, 1H), 7.31-7.22 (m, 2H), 7.04-6.99 (m, 1H), 6.89 (d, \( J = 7.6 \) Hz, 1H), 5.10 (s, 1H), 3.71 (q, \( J = 7.1 \) Hz, 2H), 3.61 (s, 1H), 1.64-1.59 (m, 1H), 1.13-0.92 (m, 3H), 0.86 (s, 3H), 0.67 (t, \( J = 7.1 \) Hz, 3H).

\(^1\)C NMR : \( \delta \) 210.25, 176.51, 168.45, 140.90, 129.31, 128.93, 125.99, 122.70, 109.53, 90.84, 81.82, 62.25, 61.07, 55.49, 35.83, 14.67, 14.35, 14.18, 13.48.

Anal. Calcd. for C\(_{19}\)H\(_{19}\)NO\(_5\).H\(_2\)O: C, 63.50; H, 5.89; N, 3.89. Found: C, 63.93; H, 5.41; N, 3.36.

Ethyl (1'R,3"R,4'S,6'S)-1",2"-dihydro-1'methyl-2",3'-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-5',3''-[3H]-indole]-6'-carboxylate

Recrystallized from CHCl\(_3\)-hexane solvent system, mp. 95-97 °C.

IR (KBr) \( \nu_{\text{max}} \): 3281, 2984, 1730, 1612, 1472, 1331, 1201, 1041 cm\(^{-1}\).
Chapter 2

\(^1\)H NMR: \( \delta 9.18 (s, 1H), 7.22 (d, J = 7.6 \text{ Hz}, 1H), 6.98-6.91 (m, 2H), 6.76 (d, J = 7.4 \text{ Hz}, 1H), 4.53 (s, 1H), 3.76-3.65 (m, 2H), 3.66 (s, 1H), 1.87-1.80 (m, 1H), 1.58 (s, 3H), 1.42-1.35 (m, 1H), 1.12-1.05 (m, 1H), 0.90-0.83 (m, 1H), 0.63 (t, J = 7.1 \text{ Hz}, 3H).

\(^13\)C NMR: \( \delta 207.36, 180.03, 168.15, 141.34, 129.19, 125.33, 124.63, 122.28, 110.14, 86.67, 86.56, 60.33, 60.14, 56.28, 37.07, 17.57, 14.52, 14.45, 13.39.


Ethyl(1'R,3'S,4'S,6'R)-1',2'-dihydro-1'methyl-2'',3'-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-5',3''-[3H]-indole]-6'-carboxylate 66

Recrystallized from CHCl\(_3\)-hexane, mp. 188-190 °C.

IR (KBr) \( \nu_{(\text{max})} \): 3187, 1747, 1707, 1619, 1470, 1340, 1183, 1032 cm\(^{-1}\).

\(^1\)H NMR: \( \delta 9.04 (s, 1H), 7.41 (d, J = 7.4 \text{ Hz}, 1H), 7.25-7.20 (m, 1H), 7.00 (t, J = 7.5 \text{ Hz}, 1H), 6.90 (d, J = 7.6 \text{ Hz}, 1H), 4.27 (s, 1H), 3.62 (q, J = 7.0 \text{ Hz}, 2H), 3.56 (s, 1H), 1.64 (s, 3H), 1.56-1.43 (m, 2H), 1.24-1.19 (m, 1H), 0.90-0.85 (m, 1H), 0.66 (t, J = 7.1 \text{ Hz}, 3H).

\(^13\)C NMR: \( \delta 207.56, 175.98, 167.97, 141.08, 129.24, 129.08, 125.63, 122.72, 109.79, 87.21, 86.76, 60.24, 60.07, 59.17, 40.65, 14.98, 14.03, 13.79, 13.47.

Cycloadducts 67, 68, 69, and 70

Treatment of 1-acetyl-1-diazoacetyl cyclopropane 62 (0.228 g, 1.5 mmol) with 3-ethoxycarbonyl methylene-2-oxoindoline 34 (0.231 g, 1 mmol) in toluene (15 mL), in presence of a catalytic amount of rhodium(II) acetate at room temperature for 30 min followed by chromatographic purification afforded the adducts 67 (0.099 g, 28%) and 69 (0.067 g, 19%) as colorless crystalline solids. The adducts 68 and 70 were obtained as a mixture of regioisomers
(0.163 g, 46%) and were separated by fractional crystallization. The cycloadduct 68 was obtained as colorless crystals and 70 as a pale yellow oil.

**Ethyl (1'R,3"R,4'R,5'S)-1",2"-dihydro-1',1"-dimethyl-2",3'-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-6',3"-[3H]-indole]-5'-carboxylate 67**

Recrystallized from EtOAc-hexane, mp. 169-171 °C.

IR (KBr) \( \nu_{(\text{max})} \): 1758, 1712, 1613, 1492, 1374, 1350, 1265, 1188, 1141, 1091 cm\(^{-1}\).

\(^1\)H NMR: \( \delta \) 7.30-7.25 (m, 1H), 7.10 (d, \( J = 7.4 \) Hz, 1H), 6.95 (t, \( J = 7.6 \) Hz, 1H), 6.82 (d, \( J = 7.7 \) Hz, 1H), 4.87 (d, \( J = 5.6 \) Hz, 1H), 3.96 (d, \( J = 5.6 \) Hz, 1H), 3.84-3.72 (m, 2H), 3.28 (s, 3H), 1.62-1.55 (m, 1H), 1.11-1.01 (m, 1H), 1.07 (s, 3H), 0.94-0.87 (m, 1H), 0.77 (t, \( J = 7.1 \) Hz, 3H), 0.69-0.62 (m, 1H).

\(^13\)C NMR: \( \delta \) 208.66, 177.31, 161.81, 144.57, 129.03, 127.64, 124.24, 121.26, 107.86, 90.40, 81.71, 60.71, 60.46, 54.28, 38.75, 26.65, 15.37, 14.36, 13.59, 13.35.


**Ethyl (1'R,3"S,4'R,5'R)-1",2"-dihydro-1',1"-dimethyl-2",3'-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-6',3"-[3H]-indole]-5'-carboxylate 68**

Recrystallized from CH\(_2\)Cl\(_2\)-MeOH, mp. 119-121°C.

IR (KBr) \( \nu_{(\text{max})} \): 1752, 1708, 1609, 1467, 1576, 1342, 1209, 1089 cm\(^{-1}\).

\(^1\)H NMR: \( \delta \) 7.34-7.27 (m, 2H), 7.03 (t, \( J = 7.5 \) Hz, 1H), 6.81 (d, \( J = 7.6 \) Hz, 1H), 5.08 (s, 1H), 3.68-3.61 (m, 2H), 3.57 (s, 1H), 3.23 (s, 3H), 1.68-1.64 (m, 1H), 1.11-0.94 (m, 3H), 0.81 (s, 3H), 0.62 (t, \( J = 7.1 \) Hz, 3H).
$^{13}$C NMR : δ 210.05, 173.92, 168.36, 143.72, 128.75, 125.65, 122.57, 107.55, 90.53, 81.58, 61.58, 60.78, 55.60, 43.88, 29.24, 26.69, 14.66, 14.03, 13.33.

Anal. Calcd. for C$_{20}$H$_{21}$NO$_5$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.59; H, 5.95; N, 4.42.

Ethyl (1'R,3'R,4'S,6'S)-1''-dihydro-1','1''-dimethyl-2'',3''-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-5',3''-[3H]-indole]-6'-carboxylate 69

Recrystallized from hexane-ethyl acetate, mp. 164-166 °C.

IR (KBr) $v_{(\text{max})}$: 1748, 1728, 1611, 1497, 1472, 1377, 1332, 1194, 1178, 1154, 1035 cm$^{-1}$.

$^1$H NMR : δ 7.30-7.26 (m, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.82 (t, $J = 7.7$ Hz, 1H), 6.76 (d, $J = 7.5$ Hz, 1H), 4.43 (s, 1H), 3.68-3.63 (m, 2H), 3.28 (s, 3H), 1.84-1.77 (m, 1H), 1.74-1.61 (m, 1H), 1.55 (s, 3H), 1.39-1.37 (m, 1H), 1.10-1.04 (m, 1H), 0.58 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR : δ 207.62, 177.34, 168.19, 144.12, 129.18, 125.09, 124.18, 122.26, 107.97, 86.66, 86.53, 60.29, 60.15, 55.66, 37.05, 26.85, 17.54, 14.54, 14.40, 13.33.

Ethyl (1'R,3''S,4'S,6'R)-1''-dihydro-1','1''-dimethyl-2'',3''-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-5',3''-[3H]-indole]-6'-carboxylate 70

IR (KBr) $v_{(\text{max})}$: 1744, 1715, 1611, 1492, 1470, 1374, 1349, 1335, 1183, 1135 cm$^{-1}$.

$^1$H NMR : δ 7.45 (d, $J = 7.5$ Hz, 1H), 7.34-7.28 (m, 1H), 7.07-7.02 (m, 1H), 6.83 (d, $J = 7.3$ Hz, 1H), 4.23 (s, 1H), 3.67-3.57 (m, 2H), 3.55 (s, 1H), 3.24 (s, 3H), 1.64 (s, 3H), 1.52-1.42 (m, 1H), 1.28-1.20 (m, 1H), 0.90-0.83 (m, 2H), 0.62 (t, $J = 7.0$ Hz, 3H).
Cycloadducts 71, 72 and 73

Treatment of 1-acetyl-1-diazoacetyl cyclopropane 62 (0.228 g, 1.5 mmol) with 3-ethoxycarbonyl methylene-2-oxoindoline 35 (0.307 g, 1 mmol) in toluene (10 mL), in the presence of a catalytic amount of rhodium(II) acetate at room temperature for 1 h followed by chromatographic purification afforded the adducts 71 (0.147 g, 34%). The adducts 72 and 73 were obtained as a mixture of regioisomers (0.276 g, 64%). On fractional crystallization, 72 was obtained as pale yellow oil and 73 as colorless crystals.

Ethyl (1'R,3'R,4'R,5'S)-1'' ,2''-dihydro-1'-methyl-1''-(phenylmethyl)-2'' ,3''-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-6',3''-[3H]-indole]-5'-carboxylate 71
Recrystallized from ethyl acetate-hexane, mp. 198-200 °C.
IR (KBr) ν(max): 1766, 1742, 1612, 1492, 1462, 1381, 1354, 1184, 1140 cm⁻¹.

^1^H NMR : δ 7.28 (brs, 5H), 7.17-7.07 (m, 2H), 6.89 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 4.97 (s, 2H), 4.89 (d, J = 5.6 Hz, 1H), 4.05 (d, J = 5.6 Hz, 1H), 3.81-3.73 (m, 2H), 1.61-1.55 (m, 1H), 1.26-1.24 (m, 1H), 1.11 (s, 3H), 1.10-1.05 (m, 1H), 0.91-0.87 (m, 1H), 0.69 (t, J = 7.1 Hz, 3H).

^1^3^C NMR : δ 208.63, 177.53, 167.79, 143.72, 135.43, 128.93, 128.78, 127.62, 127.23, 124.46, 121.28, 109.06, 90.53, 81.68, 60.70, 60.40, 54.89, 44.16, 38.90, 15.43, 14.49, 13.61, 13.53.

Ethyl (1'R,3''S,4'R,5'R)-1'',2''-dihydro-1'-methyl-1''-(phenylmethyl)-2'',3''-dioxodispiro[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-6',3''-[3H]-indole]-5'-carboxylate 72
IR (KBr) ν(max): 1758, 1715, 1611, 1487, 1467, 1368, 1210, 1179, 1035 cm⁻¹.
$^1$H NMR: $\delta$ 7.43 (d, $J = 7.4$ Hz, 1H), 7.34-7.27 (m, 5H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.97 (t, $J = 7.5$ Hz, 1H), 6.68 (t, $J = 6.8$ Hz, 1H), 5.09 (s, 1H), 5.07 (d, $J = 15.7$ Hz, 1H), 4.78 (d, $J = 15.5$ Hz, 1H), 3.66 (s, 1H), 3.63-3.51 (m, 2H), 1.67-1.58 (m, 1H), 1.10-0.87 (m, 3H), 0.83 (s, 3H), 0.45 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR: $\delta$ 209.96, 174.08, 168.33, 142.66, 135.58, 128.64, 127.66, 127.13, 125.66, 122.82, 108.69, 90.68, 81.65, 60.83, 60.29, 55.63, 44.00, 35.75, 14.71, 14.20, 13.94, 13.16.

Ethyl (1'R,3"R,4'S,6'S)-1",2"-dihydro-1'-methyl-1"-(phenylmethyl)-2",3"-dioxodispersio[cyclopropane-1,2'-[7]oxabicyclo[2.2.1]heptane-S',3"-[3H]-indole]-6'-carboxylate 73

Recrystallized from CH$_2$Cl$_2$-MeOH, mp. 200-202 °C.

IR (KBr) $\nu_{(\text{max})}$: 1745, 1072, 1609, 1491, 1372, 1348, 1086 cm$^{-1}$.

$^1$H NMR: $\delta$ 7.28-7.25 (m, 5H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.90 (t, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 7.4$ Hz, 1H), 6.68 (d, $J = 7.7$ Hz, 1H), 5.17 (d, $J = 15.7$ Hz, 1H), 4.80 (d, $J = 15.7$ Hz, 1H), 4.49 (s, 1H), 3.75 (s, 1H), 3.64-3.62 (m, 2H), 1.86-1.82 (m, 1H), 1.58 (s, 3H + m, 1H), 1.41-1.39 (m, 1H), 1.11-1.07 (m, 1H), 0.48 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR: $\delta$ 207.67, 177.58, 168.25, 143.15, 135.43, 129.07, 128.77, 127.75, 127.15, 124.99, 124.26, 122.30, 109.20, 86.76, 86.58, 60.60, 60.24, 55.71, 44.16, 37.13, 17.56, 14.58, 14.53, 13.27.

2.4. REFERENCES


