STEREOSELECTIVE SYNTHESIS OF SEVEN-MEMBERED RINGS USING INTRAMOLECULAR (4+3) CYCLOADDITION REACTIONS

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INTRAMOLECULAR (4+3) CYCLOADDITION REACTIONS

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STEREOSELECTIVE SYNTHESIS OF SEVEN-MEMBERED RINGS USING INTRAMOLECULAR (4+3) CYCLOADDITION REACTIONS

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ABSTRACT
Heterocyclic molecules containing seven-membered rings have importance in organic synthesis owing to their presence in some natural products and biologically active molecules. Furthermore, these scaffolds act as important tools for developing new drugs and biological probes. A stereoselective, intramolecular (4+3) cycloaddition of an oxidopyridinium ion has been developed. N-Alkylation of a nicotinate derivative followed by reaction under basic condition in acetonitrile afforded (4+3) cycloaddition products in excellent yield and high stereoselectivity. Substitution at the 3, 2-TMS, and 1, 3 positions of the diene resulted in 100% stereoselectivity.
CHAPTER ONE
(4+3) Cycloaddition Reactions

1.1 Introduction

(4+3) cycloaddition involves cyclization of 4-atoms of conjugated \( \pi \)-system with 3-atoms of \( \pi \)-system. \(^1\) (4+3) cycloaddition involving 6\( \pi \) electrons is symmetry allowed, based on the Woodward-Hoffmann rule. \(^2\) The cycloaddition of allylic cation and diene is an example of (4+3) cycloaddition reaction (Figure 1). (4+3) cycloaddition reaction is a robust method to construct seven-membered cyclic and heterocycle molecules from simple starting materials. \(^3\) Molecules containing seven-membered rings have significant importance in synthetic chemistry because there are many natural products and biologically active molecules that consist of a seven-membered cyclic or heterocyclic system. \(^4\)

![Figure 1. (4+3) Cycloaddition reaction.](image)

A facile synthesis of seven-membered cyclic or heterocyclic compounds is important because of its demand in drug development and understanding of the complex mechanism of the living system. \(^5\) Such synthesis is challenging compared to six-membered cyclic compounds because it is entropically disfavored and has a high ring strain. \(^6\) Figure 2 shows the ring strain of cyclic compounds with different ring sizes, developed by Alinger and
coworkers using the improved force-field method. Cycloaddition is one of the most common methods for the synthesis of cyclic compounds. (4+3) cycloaddition is well known for constructing a seven-membered cyclic and heterocyclic system because it is stereoselective, and step and atom economic method.

![Ring size vs strain energy of cycloalkanes](image)

**Figure 2.** The strain energy of cyclic compounds.

### 1.2 Mechanism and Stereochemistry

In 1984, Hoffmann reported three different mechanistic pathways for (4+3) cycloaddition reactions. The first, called Type A, follows a concerted path to make cyclic adducts (Figure 3a). The second (Type B) follows a stepwise mechanism (Figure 3b), while type
C undergoes a stepwise mechanism but fails to cyclize, resulting in electrophilic addition or substitution product (Figure 3c).

Figure 3: Types of (4+3) cycloaddition reactions. a) Type A b) Type B and c) Type C. Cramer and coworkers' theoretical studies of (4+3) cycloaddition reactions follow both concerted and stepwise pathways, depending upon the connectivity between a diene and allylic cation. Harmata proposed six types of connectivity possible in (4+3) cycloaddition reactions (Figure 4).^9

Figure 4. Different types of connectivity in (4+3) cycloaddition reactions.
In general, the (4+3) cycloaddition reactions are less stereoselective than Diels-Alder reactions due to complex stepwise mechanistic pathways. Allyl cations can have three different geometries, viz U, W, and sickle form (Figure 5a). These geometries also contribute to reduced stereoselectivity of (4+3) cycloaddition reactions that follow concerted pathways. Overall, the electrophilicity of the allyl cation, the nucleophilicity of the diene, and the solvent polarity contribute to the stereochemical outcome of the (4+3) cycloaddition reaction.

For concerted mechanistic pathway for the (4+3) cycloaddition reaction, two types of transition states are reported (Figure 5b). The first being an extended chair-like transition state that corresponds to exo cycloadducts. The second is a compact boat-like transition state corresponding to endo cycloadducts.

Figure 5. a) Geometry of allyl cation. b) extended and compact transition states.

1.3 Intramolecular (4+3) Cycloaddition Reactions

Intramolecular (4+3) cycloaddition reactions occur between a 4-atom diene and a 3-atom dienophile of the same molecule connected by a linker. A general scheme of intramolecular (4+3) cycloaddition reaction is shown in Figure 6. Fused seven-member compounds can be synthesized via intramolecular (4+3) cycloaddition reaction. Such
fused compounds are synthetically significant because there are a plethora of bioactive natural products that contain seven-membered fused systems (Figure 7).\textsuperscript{11}

\textbf{Figure 6.} General scheme of intramolecular (4+3) cycloaddition reactions.

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=0.3\textwidth]{image1} & \includegraphics[width=0.3\textwidth]{image2} & \includegraphics[width=0.3\textwidth]{image3} \\
Prostratin & Ingenol & (-)-englerin A \\
protein treatment of HIV & & anticancer drug candidate \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=0.3\textwidth]{image4} & \includegraphics[width=0.3\textwidth]{image5} & \includegraphics[width=0.3\textwidth]{image6} \\
Komaroviquinone & (+)-allycyathin B\textsubscript{2} & Frondosin A \\
& antibacterial agent & HIV-inhibitor \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=0.3\textwidth]{image7} & \includegraphics[width=0.3\textwidth]{image8} \\
Serratenediol & Cortistain A \\
\end{tabular}
\end{center}

\textbf{Figure 7.} Naturals products containing seven-membered fused systems.
1.4 Background: Intramolecular (4+3) cycloaddition reaction

In 1962, Fort reported the first (4+3) cycloaddition reaction between an \(\alpha\)-haloketone and furan (Scheme 1).\(^{12}\) The authors treated \(\alpha\)-chloro ketone 7 with 2,6-lutidine at room temperature to generate oxyallyl cations 8 that was trapped by furan. A diastereomeric mixture of cycloadduct 9 was obtained with an 18\% overall yield.

Scheme 1. (4+3) cycloaddition reaction between \(\alpha\)-halo ketone and furan.

In 1970, Noyori and coworkers reported the first intramolecular (4+3) cycloaddition of a dibromoketone (Scheme 2).\(^{13}\) The authors heated \(\alpha, \alpha'\) dibromoketone 10 in the presence of \(\text{Fe}_2(\text{CO})_9\) in benzene for three hours to obtain stereoselective cycloadduct 11 with 38\% yields.

Scheme 2. Intramolecular (4+3) cycloaddition of \(\alpha, \alpha'\) dibromoketone.

In 1988, Hoffmann and coworkers reported intramolecular (4+3) cycloaddition of alcohol 12 utilizing \(\text{TiCl}_4/\text{PhNHMe}\) in DCM at -78 °C to obtain diastereomeric cycloadducts 13 and 14 in 50:50 ratio with 20\% overall yield (Scheme 3).\(^{14}\) The authors reported a diastereomeric ratio of 39:61 for the cycloadducts 16 and 17 obtained by (4+3) cycloaddition of silyl ethers 15, in 30\% yields under similar conditions (Scheme 4).
In 1984, Fohlisch and coworkers reported intramolecular the (4+3) cycloaddition of gem-dichloroketones in excellent yield.\textsuperscript{15} The authors treated dichloroketone 18 with an excess of LiClO\textsubscript{4} and triethylamine at room temperature to obtain 76\% of cycloadducts 19 and 20. The cycloadducts were obtained with high stereoselectivity of 70:24:6:1 of 19-\(\alpha\)-Cl:19-\(\beta\)-Cl:20-\(\alpha\)-Cl:20-\(\beta\)-Cl (Scheme 5).

![Scheme 3. Intramolecular (4+3) cycloaddition of alcohol 12 using TiCl\(_4\)/PhNHMe.](image)

In 1988, Giguere and coworkers reported intramolecular (4+3) cycloaddition of allylic alcohol 21 utilizing triflic anhydride and 2,6-lutidine in DCM at -78 °C to afford cycloadduct 22 in 56\% yield and a trans: cis ratio of 65:35 (Scheme 6).\textsuperscript{16}

![Scheme 4. Intramolecular (4+3) cycloaddition of silyl ether 15 using TiCl\(_4\)/PhNHMe.](image)

![Scheme 5. Intramolecular (4+3) cycloaddition of gem-dichloro ketone 18](image)
In 1993, Harmata and Herron\textsuperscript{18} reported intramolecular (4+3) cycloaddition of the allylic sulfones 23 using AlMe\textsubscript{3} in DCM at -78 °C to obtain cycloadducts 24 and 25 in 77% yields and 17:10 diastereoselectivity (Scheme 7).\textsuperscript{17}

Scheme 6. Intramolecular (4+3) cycloaddition of allylic alcohol 21

Scheme 7. Intramolecular (4+3) cycloaddition of allylic sulfone 23

Then in 1995, Harmata and coworkers were the first to report a nonphotochemical intramolecular (4+3) cycloaddition reaction of a cyclic cation (Scheme 8).\textsuperscript{18} The authors synthesized five- to eight-membered cyclic oxyallylic cations tethered with furan 26 using LDA and triflyl chloride. Intramolecular (4+3) cycloaddition occurred in the presence of 3M LiClO\textsubscript{4} and triethylamine. Cycloadducts 27 and 28 were obtained in good yields and good to excellent stereoselectivity (Scheme 8).

In 1988, Harmata and coworkers demonstrated the stereoselective synthesis of cycloadduct 30 by utilizing 2-alkoxyallylic sulfones 29 in the presence of TiCl\textsubscript{4} in DCM at -78 °C with 74% yield (Scheme 9).\textsuperscript{19} The cycloadduct 30 was also formed by (4+3) cycloaddition of enol ether 31 with 58% yield, under similar conditions (Scheme 9).
In 1988, Schultz and coworker demonstrated the use of oxyallyl zwitterions, generated via photolysis, in the (4+3) cycloaddition reaction. The authors generated zwitterions from furan bridged 2,5-cyclohexadiene-l-one 32 utilizing 366 nm UV light in benzene (Scheme 10). The zwitterion underwent intramolecular (4+3) cycloaddition to afford cycloadduct 33 as a single diastereomer in 80% yield.

Scheme 8. Intramolecular (4+3) cycloaddition reaction of a cyclic cation.

Scheme 9. Intramolecular (4+3) cycloaddition reaction of a sulfone 29 and enol ether 31.

Scheme 10. Intramolecular (4+3) cycloaddition reaction via photolysis.
CHAPTER TWO

(4+3) Cycloaddition Reaction of N-Oxidopyridinium Ions

2.1 Introduction

Heterocyclic seven-membered fused systems such as 7-azabicyclo[4.3.1]decane is prevalent in bioactive natural products (Figure 8). Such fused ring compounds can be synthesized by (4+3) cycloaddition reactions utilizing N-oxidopyridinium ions. Alan Roy Katritzky was the first to explore the N-oxidopyridinium ions as a precursor for (4+3) cycloaddition reactions. The author demonstrated (4+3) cycloaddition of N-alkyl oxidopyridinium ions 34 and 36 with diene to afford heterocyclic seven-member fused cycloadducts 35 and 37, respectively (Scheme 11).

Figure 8. Natural products containing 7-azabicyclo[4.3.1]decane ring.

Inspired by Katritzky’s work, our group furthered the study of (4+3) cycloaddition using N-oxidopyridinium ions. In 2017, Harmata and coworkers reported a (4+3) cycloaddition
by heating methyl-5-hydroxynicotinate 38 in sealed tubes with several different dienes in the presence of triethylamine and acetonitrile at 85 °C (Scheme 12). The reaction resulted in good to excellent yields and high regioselectivity.

Scheme 11. (4+3) cycloaddition reactions of N-oxidopyridinium ions.

Scheme 12. (4+3) cycloaddition of a methyl-5-hydroxynicotinate. Although (4+3) cycloaddition of N-oxidopyridinium ions and symmetric diene afford regioselectivity, (4+3) cycloaddition involving asymmetric dienes was not very regioselective. In order to enhanced regioselectivity, intramolecular (4+3) cycloaddition of N-oxidopyridinium ions was considered. Harmata and coworkers synthesized the first example of intramolecular (4+3) cycloaddition of N-oxidopyridinium ion (Scheme 13).
The authors utilized a diene tethered N-oxidopyridinium ion 43 to afford a diastereomeric mixture of seven-membered fused cycloadducts 44 and 45 in a 1:1.19 ratio.

\[
\begin{align*}
\text{HO} & \quad \text{TEA (3eq)} \quad \text{MeCN, 85 °C,} \\
\text{N} & \quad \text{6 h, 84%} \\
\text{OTf} & \quad (1:1.9) \\
\end{align*}
\]

\[
\begin{align*}
43 & \quad \rightarrow \\
44 & \quad + \\
45 & \\
\end{align*}
\]

Scheme 13. Intramolecular (4+3) cycloaddition of N-oxidopyridinium ion.

2.2 Results and discussion

2.2.1 (4+3) cycloaddition reactions with 3-methyl substituted dienes

We wanted to develop a highly stereoselective and regioselective intramolecular (4+3) cycloaddition method. To achieve this goal, we tested various dienes with varying substituents such as alkyl, aryl, and trimethylsilane at different positions of the dienes. Intramolecular (4+3) cycloaddition using 3-methyl diene 46 afforded seven-membered fused adduct 48 in high yields and stereoselectivity (Scheme 14). The diene 46 was heated with 5-hydroxynicotinate 47 for 12 h. Next, the reaction mixture was dissolved in acetonitrile, followed by heating with triethylamine to afford the cycloadduct 48. The reaction was optimized by varying the base, solvent, reaction time, and reaction concentration (Table 1). High yields (80%) of cycloadduct were obtained with TEA as a base, acetonitrile as a solvent with a reaction time of 9 h, and a reaction concentration of 0.05 M. The cycloadduct 48 was characterized by X-ray crystallography (Figure 9). The crystals were grown in the 10:1 mixture of chloroform and hexane.
Scheme 14. Intramolecular (4+3) cycloadduct of 3-methyl substituted diene.

Table 1: Optimization of (4+3) cycloaddition reaction of N-oxidopyridinium ion with 3-methyl substituted dienes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Conc.</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>TEA</td>
<td>0.05M</td>
<td>CH₃CN</td>
<td>6</td>
<td>58</td>
</tr>
<tr>
<td>2.</td>
<td>TEA</td>
<td>0.05M</td>
<td>CH₃CN</td>
<td>9</td>
<td>80</td>
</tr>
<tr>
<td>3.</td>
<td>TEA</td>
<td>0.05M</td>
<td>CH₃CN</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>4.</td>
<td>PhCOONa</td>
<td>0.05M</td>
<td>CH₃CN</td>
<td>1</td>
<td>54</td>
</tr>
<tr>
<td>5.</td>
<td>PhCOONa</td>
<td>0.05M</td>
<td>CH₃CN</td>
<td>11</td>
<td>68</td>
</tr>
<tr>
<td>6.</td>
<td>PhCOONa</td>
<td>0.1M</td>
<td>H₂O</td>
<td>12</td>
<td>27</td>
</tr>
</tbody>
</table>

2.2.2 Intramolecular (4+3) cycloaddition reactions with 1-alkyl and 1-phenyl substituted dienes

To obtain enhanced stereoselectivity, intramolecular (4+3) cycloaddition of N-oxidopyridinium ion with dienes substituted at 1-position were considered. The diene with methyl substitution at the 1-position afforded highly selective exo cycloadduct, while diene with phenyl substitution at 1-position yielded was cycloadduct with moderate exo
selectivity (Scheme 15). The yield of cycloadducts 50 (R = Me) was low due to a 50:50 E,E : E,Z mixture of 49(a). The crystal structure of *exo* cycloadducts 51 (R = Me) was determined by single-crystal X-ray diffraction (Figure 10). After analyzing $^{13}$C nmr spectrums and crystal structures of cycloadduct 44, 45, 48 and 51(a), we found that the chemical shift of C-11 for *exo* cycloadduct was around 90 ppm and endo cycloadduct was around 103 ppm. Endo/exo stereochemistry of the rest of the cycloadduct were assigned based on the chemical shift of C-11 of $^{13}$C nmr spectrums.

![Crystal Structure](image)

**Figure 9.** X-ray crystal structure of *endo* cycloadduct 48.

**Scheme 15.** (4+3) cycloaddition of 1-methyl (and phenyl) substituted diene.
2.2.3 (4+3) cycloaddition reactions with 2-methyl and 2-trimethylsilane substituted dienes

The stereoselectivity of intramolecular (4+3) cycloaddition reactions with dienes substitution at 2-methyl and 2-trimethylsilane were determined (Scheme 16). Moderate exo to endo selectivity was observed with diene substituted with methyl at 2-position, whereas diene with trimethylsilane at 2-position demonstrated endo selectivity. Both the reactions yielded absolute regioselectivity.

![Figure 10: X-crystal structure of exo cycloadduct 50 (R = Me).](image)

**Scheme 16.** (4+3) cycloaddition of 2-methyl (and trimethylsilane) substituted diene.
2.2.4 (4+3) cycloaddition reactions with 1,2-dialkyl and 1,3-dimethyl, and 6-methyl substituted dienes

The stereoselectivity of intramolecular (4+3) cycloaddition reactions with dienes substituted with 1,2-dialkyl, 1,3-dimethyl and 6-methyl were also determined (Scheme 17). The excellent endo to exo selectivity was observed with a 1,2-dialkyl substitution, whereas the diene with 1,3-dimethyl substitution leads to complete endo selectivity. The diene with 6-methyl substitution afforded moderate exo to endo selectivity. The yield of cycloadducts 56 and 57 were low due 60: 40 ratio of \( E,E : E,Z \) mixture of 55. Also, the ratio \( EE : E,Z \) mixture of 58 was 60: 40, which was responsible for the low yield of 59. The crystal structure of the endo cycloadduct 61 was determined by single-crystal X-ray diffraction (Figure 11). By analyzing \(^1\)H nmr spectrum of 61 and 62, we found that the Chemical shift of both methy groups was the same, which indicated similar stereochemistry of both methyl groups.
Scheme 17. (4+3) cycloaddition of 1,2-dialkyl, 1,3-dimethyl and 6-methyl substituted diene.

2.3 Conclusion

Mostly stereoselective intramolecular (4+3) cycloaddition reactions of an N-oxidopyridinium ion were developed. Intramolecular (4+3) cycloaddition reaction of an N-oxidopyridinium ion with 3-methyl, 2-TMS, and 1,3-dimethyl substituted dienes demonstrated absolutely stereoselectivity. The stereoselectivity of intramolecular (4+3) cycloaddition reaction of an N-oxidopyridinium ion with 1-methyl and 1,2-dialkyl substituted dienes was excellent. All these reactions were 100% regioselective. Controlling stereoselectivity was the main challenge of (4+3) cycloaddition reactions of
N-oxidopyridinium ions, which has been addressed by our intramolecular (4+3) cycloaddition of N-oxidopyridinium ions.
CHAPTER 3  EXPERIMENTAL

3.1 General information

All reactions were carried out under the argon atmosphere. All reaction flasks were covered by a rubber septum. Syringes and long needles were used to transfer reactive liquid reagents. All glassware was dried in the oven. HPLC grade Tetrahydrofuran from fisher was distilled over sodium with benzophenone, As well as acetonitrile from fisher was distilled over CaH₂, and HPLC grade diethyl ether and dichloromethane dried over molecular sieves were used to run reactions. Silica gel plates from Sigma Aldrich were used for Thin-layer chromatography (TLC). 230-400 mesh silica gels, a nitrogen atmosphere, and HLC grade solvent were used for flash chromatography. Bruker DRX-500 (500MHz) and DRX-600 (600MHz) were used to recode ¹H and ¹³C NMR spectrum.

CDCl₃ with TMS and MeOD were used as NMR solvent. CDCl₃ (7.26 ppm) was used as a reference for ¹H NMR and CDCl₃ (77.0ppm) for ¹³C NMR. Infrared spectra were obtained on a ThermoScientific Nicolet Summit PRO FTIR spectrometer either as a neat liquid film using CDCl₃ as a solvent.

3.2 Intramolecular (4+3) cycloaddition reactions of N oxydopiridinium Ions

3.2.1 General procedure of ethyl (4aS,8R,9aR)-5-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate

(E)-5-methylhepta-4,6-dien-1-ol (0.4 g, 3.17 mmole) was dissolved in 6.3 mL dichloromethane (DCM) at room temperature under argon atmosphere. Then tosyl
chloride (0.72g, 3.80mmole) was added. After that DMAP (3.8 mg, 0.03 mmole) was added, triethylamine (.43 g, 4.27 mmole) and stirred 12 hours. After reaction completed, it was quenched with water and extracted with dichloromethane, dried over Na$_2$SO$_4$, passed and concentrated under reduced pressure at room temperature. The crude mixture was purified by column chromatography (5-30% Et$_2$O/Hexane) to get (E)-5-methylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate 46 with 79% yields.

(E)-5-methylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate 46 (0.05 g, 0.17 mmole) was added to ethyl 5-hydroxynicotinate (0.03 g, 0.18 mmole) and stirred for overnight at 80°C. After completion, the resulting N-methyloxidopyridinium ion was dissolved in acetonitrile (3.6 mL, 0.05 M) and trimethylamine (0.07 mL, 0.53 mmole). The reaction mixture was heated in a sealed tube for 9 hours. After the reaction finished, it was quenched with 10% hydrochloric acid solution, extracted with dichloromethane, dried over Na$_2$SO4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (10-40% Ethyl acetate/Hexane) to get a solid white cycle product 48. Cycloadduct 48 was recrystallized in CHCl$_3$ and hexane (10% Hexane/Chloroform).

![Chemical structure of (E)-5-methylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate 46](attachment:structure.png)

(E)-5-methylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate (46). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.28 (dd, J = 17.4, 10.6 Hz, 1H), 5.31 (t, J = 7.4 Hz, 1H), 5.07 (d, J = 17.3 Hz, 1H), 4.92 (d, J = 10.7 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 2.43 (s, 3H), 2.16 (q, J = 7.4 Hz, 2H), 1.72 (p, J = 6.9 Hz, 2H), 1.66 (s,
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 144.8, 141.2, 135.4, 133.2, 130.5, 129.9, 127.9, 111.3, 77.4, 77.2, 76.9, 70.0, 29.0, 24.0, 21.7, 11.7. IR (CDCl$_3$) 2930, 1598, 1357, 1172, 924, 813, 661, 553 cm$^{-1}$. HRMS calcd for (C$_{15}$H$_{20}$O$_3$S)Na$: 303.1025$, found: 303.1021.

ethyl (4aR,8R,9aR)-5-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (48): mp $= 118-119$ °C. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 (s, 1H), 5.46 (ddt, J = 8.8, 4.4, 1.6 Hz, 1H), 4.44 – 4.07 (m, 2H), 3.50 (ddt, J = 16.0, 10.8, 2.1 Hz, 2H), 3.36 – 3.22 (m, 1H), 3.19 – 3.13 (m, 1H), 2.96 (ddd, J = 15.3, 11.0, 8.6 Hz, 1H), 2.75 – 2.65 (m, 1H), 2.16 – 2.04 (m, 2H), 1.86 – 1.77 (m, 1H), 1.74 (ddd, J = 12.9, 6.7, 4.3 Hz, 2H), 1.68 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 204.7, 167.2, 144.5, 140.5, 124.1, 102.8, 72.1, 59.9, 53.5, 43.6, 43.1, 33.0, 27.6, 26.7, 18.8, 14.8. IR (film) $\nu_{\text{max}}$ = 2940, 2859, 2259, 2246, 1733, 1677, 1596, 1478, 1441, 1318, 1240 cm$^{-1}$. HRMS calcd for (C16H21O3N Na$^+$): 298.141365, found: 298.141128.

(4E,6E)-octa-4,6-dien-1-yl 4-methylbenzenesulfonate (49a). $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.79 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 7.9 Hz, 4H), 6.33 – 6.15 (m, 1H), 6.05 – 5.83 (m, 3H), 5.68 (dq, J = 13.8, 6.7 Hz, 1H), 5.56 (dq, J = 14.0, 7.0 Hz, 1H), 5.38 (dt, J = 14.2, 7.1 Hz, 1H), 5.14 (dt, J = 10.7, 7.7 Hz, 1H), 4.03 (dt, J = 8.6, 6.3 Hz, 4H), 2.45 (s, 6H), 2.20 (q, J = 7.5 Hz, 2H), 2.08 (q, J = 7.3 Hz, 2H), 1.81 – 1.69 (m, 10H). $^{13}$C
NMR (126 MHz, CDCl$_3$) $\delta$ 145.00, 144.96, 133.55, 133.53, 132.08, 131.56, 130.49, 130.4, 130.2, 130.1, 129.5, 128.3, 128.2, 128.1, 127.1, 126.9, 77.1, 70.3, 70.1, 30.0, 29.2, 28.9, 28.5, 23.8, 22.0, 18.6, 18.3. IR (CDCl$_3$) 2926, 1364, 1176, 907, 729, 665, 555 cm$^{-1}$.

HRMS calcd for (C$_{15}$H$_{20}$O$_3$)Na$^+$ : 303.1025, found: 303.1020.

[Structure diagram]

ethyl 7-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (50a). $\text{mp} = 119$-$124^\circ\text{C}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 (s, 1H), 5.64 – 5.45 (m, 1H), 5.34 (dt, $J = 12.6$, 2.0 Hz, 1H), 4.12 (qq, $J = 11.0$, 7.1 Hz, 2H), 3.70 (t, $J = 2.3$ Hz, 1H), 3.55 (t, $J = 3.3$ Hz, 1H), 3.45 (dd, $J = 12.0$, 3.3 Hz, 1H), 3.23 (td, $J = 12.6$, 3.3 Hz, 1H), 2.53 (p, $J = 2.8$ Hz, 1H), 2.41 (tt, $J = 7.3$, 3.8 Hz, 1H), 2.06 (dt, $J = 10.2$, 3.1 Hz, 1H), 1.85 (dd, $J = 8.8$, 3.6 Hz, 1H), 1.63 (s, 1H), 1.60 – 1.55 (m, 1H), 1.25 (dt, $J = 7.1$, 3.4 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 206.9, 168.7, 146.3, 138.6, 130.8, 90.5, 67.6, 59.5, 53.1, 50.9, 39.5, 37.8, 32.3, 22.0, 22.0, 14. IR (CDCl$_3$) 2935, 2859, 2248, 1172, 1674, 1615, 1443, 1235, 1172, 1141, 1078, 905, 724, 646 cm$^{-1}$. HRMS calcd for (C$_{16}$H$_{21}$NO$_3$)H$^+$ : 276.1594, found: 276.1590.

(4$E$,6$E$)-7-phenylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate (49b). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 7.5$ Hz, 2H), 7.36 – 7.16 (m, 5H), 6.96 (ddd, $J = 15.6$, 11.1, 1.2 Hz, 1H), 6.50 (d, $J = 15.5$ Hz, 1H), 6.14 (dd, $J = 11.8$, 9.9 Hz, 1H).
Hz, 1H), 5.36 (dt, J = 10.9, 7.7 Hz, 1H), 4.05 (t, J = 6.3 Hz, 2H), 2.36 (s, 3H), 2.32 (qd, J = 7.6, 1.6 Hz, 2H), 1.86 – 1.72 (m, 2H). 13C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.9, 137.5, 133.2, 133.1, 130.4, 130.4, 130.1, 128.8, 128.0, 127.8, 126.6, 124.0, 70.0, 29.0, 24.0, 21.8. IR (CDCl<sub>3</sub>) 3024, 2930, 1598, 1492, 1448, 1356, 1172, 1069, 916, 812, 730, 691, 661, 553 cm<sup>-1</sup>. HRMS calcd for (C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>S)Na<sup>+</sup>: 365.1182, found: 365.1176.

![Chemical Structure](image)

**ethyl (4aR,7S,8S,9aR)-9-oxo-7-phenyl-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (50b). mp = 176-178°C.**

1H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.48 (s, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.18 (d, J = 7.6 Hz, 2H), 5.94 (ddd, J = 13.1, 7.5, 3.1 Hz, 1H), 5.63 (d, J = 13.2 Hz, 1H), 4.26 (dd, J = 10.7, 7.1 Hz, 1H), 4.24 – 4.20 (m, 1H), 4.17 (dt, J = 10.5, 7.1 Hz, 1H), 3.76 (dd, J = 3.3, 1.6 Hz, 1H), 3.64 (t, J = 3.2 Hz, 1H), 3.54 – 3.46 (m, 2H), 3.23 (td, J = 12.8, 3.0 Hz, 1H), 2.74 (s, 1H), 2.31 – 2.10 (m, 1H), 2.04 (s, 1H), 1.87 – 1.83 (m, 1H), 1.71 – 1.59 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H). 13C NMR (151 MHz, CDCl<sub>3</sub>) δ 203.4, 140.0, 133.3, 132.4, 128.8, 128.3, 127.2, 66.9, 66.2, 59.7, 53.4, 53.3, 49.9, 36.4, 32.5, 31.9, 23.0, 22.6, 15.6, 15.0, 14.4. IR (neat) 2936, 2249, 1740, 729, 723, 645, 522, 481 cm<sup>-1</sup>. HRMS calcd for (C<sub>21</sub>H<sub>23</sub>NO<sub>3</sub>)Na<sup>+</sup>: 360.1570, found: 360.1568.
ethyl (4aS,7R,8S,9aR)-9-oxo-7-phenyl-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (51b). \( \text{mp} = 181-183^\circ \text{C} \). \( ^1 \text{H} \) NMR (600 MHz, CDCl\(_3\)) \( \delta \): 7.47 (s, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.22 – 7.18 (m, 1H), 5.95 (dtd, \( J = 13.1, 2.9, 1.1 \) Hz, 1H), 5.48 (ddt, \( J = 13.1, 3.3, 1.7 \) Hz, 1H), 3.83 (td, \( J = 3.1, 1.4 \) Hz, 1H), 3.76 (td, \( J = 3.6, 3.1, 1.1 \) Hz, 1H), 3.72 (dq, \( J = 10.9, 7.2 \) Hz, 1H), 3.61 (p, \( J = 3.3 \) Hz, 1H), 3.49 (dtd, \( J = 13.0, 4.4, 1.5 \) Hz, 1H), 3.33 – 3.17 (m, 1H), 2.64 (p, \( J = 3.0 \) Hz, 1H), 2.16 – 2.07 (m, 1H), 1.97 – 1.77 (m, 2H), 1.69 – 1.56 (m, 1H), 0.76 (s, 3H). \( ^{13} \text{C} \) NMR (151 MHz, CDCl\(_3\)) \( \delta \): 205.8, 143.6, 135.5, 131.9, 128.9, 128.4, 126.8, 90.1, 67.5, 60.6, 59.2, 53.0, 52.1, 49.9, 38.6, 32.4, 21.9, 14.4, 14.2. IR (neat) 2935 2857, 1720, 1672, 1618, 1447, 1168, 1140, 1078, 759, 700 cm\(^{-1}\). HRMS calcd for \((\text{C}_{21}\text{H}_{23}\text{NO}_3)\text{Na}^+\): 338.1750, found: 338.1746.

\( \text{(E)} \)-6-methylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate (52a). \( ^1 \text{H} \) NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.75 (t, \( J = 6.9 \) Hz, 2H), 7.30 (t, \( J = 7.0 \) Hz, 2H), 6.01 (dd, \( J = 15.7, 5.9 \) Hz, 1H), 5.46 (dt, \( J = 15.0, 7.0 \) Hz, 1H), 4.81 (dd, \( J = 17.8, 5.7 \) Hz, 2H), 3.99 (q, \( J = 6.5 \) Hz, 2H), 2.39 (dd, \( J = 7.6, 3.4 \) Hz, 3H), 2.10 (q, \( J = 7.3 \) Hz, 2H), 1.71 (dd, \( J = 13.2, 6.6 \) Hz, 1H).
Hz, 5H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.9, 141.8, 134.3, 134.3, 133.2, 130.0, 128.4, 128.0, 128.0, 115.2, 115.2, 69.9, 28.6, 28.5, 21.7, 21.7, 18.7. IR (CDCl$_3$) 2954, 1600, 1357, 1174, 916, 812, 727, 662, 552. HRMS calcd for (C$_{15}$H$_{20}$O$_3$S)Na$^+$: 303.1025, found: 303.1020.

![Chemical Structure](image)

ethyl (4aR,8R,9aR)-6-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (53a). mp = 113-116°C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.58 – 7.37 (m, 1H), 5.57 – 5.43 (m, 1H), 4.31 – 4.10 (m, 2H), 3.53 (dt, J = 11.0, 2.7 Hz, 1H), 3.48 (dt, J = 13.9, 3.2 Hz, 1H), 3.34 – 3.23 (m, 1H), 3.15 – 3.09 (m, 1H), 2.87 – 2.76 (m, 1H), 2.57 (q, J = 9.5, 9.1 Hz, 1H), 2.33 (dt, J = 15.2, 2.9 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.77 – 1.72 (m, 6H), 1.29 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 204.9, 167.4, 144.8, 139.7, 126.1, 102.9, 72.7, 60.1, 53.3, 43.3, 41.9, 39.1, 29.4, 27.1, 25.8, 14.9. IR (CDCl$_3$) 2935, 2247, 1735, 1677, 1596, 1445, 1319, 1254, 1179, 1140, 916, 729, 527. HRMS calcd for (C$_{16}$H$_{21}$O$_3$N)H$^+$: 276.1594, found: 276.1590.
ethyl (4aS,8R,9aR)-6-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (54a). mp = 119-121°C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 (s, 1H), 5.32 – 5.04 (m, 1H), 4.37 – 3.99 (m, 2H), 3.71 (td, \(J = 3.0, 1.3\) Hz, 1H), 3.51 (dt, \(J = 5.2, 3.2\) Hz, 1H), 3.46 – 3.38 (m, 1H), 3.28 – 3.13 (m, 1H), 2.64 (dd, \(J = 15.9, 5.1\) Hz, 1H), 2.47 (p, \(J = 2.9\) Hz, 1H), 2.19 (dd, \(J = 15.8, 3.2\) Hz, 1H), 2.07 – 1.96 (m, 1H), 1.94 – 1.76 (m, 2H), 1.73 (dd, \(J = 2.6, 1.4\) Hz, 3H), 1.67 (s, 1H), 1.33 – 1.19 (m, 3H). \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 206.8, 167.8, 145.8, 138.3, 125.6, 92.8, 68.3, 59.4, 53.2, 45.0, 38.0, 37.6, 32.8, 29.9, 22.1, 14.9. IR (CDCl\(_3\)) 2939, 2251, 1675, 1620, 1444, 1277, 1171, 1140, 1087, 918, 713. HRMS calcd for (C\(_{16}\)H\(_{21}\)O\(_3\)N)Na\(^+\) : 298.1413, found: 298.1410.

(E)-6-(trimethylsilyl)hepta-4,6-dien-1-yl 4-methylbenzenesulfonate (52b). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.87 – 7.64 (m, 2H), 7.54 – 7.17 (m, 2H), 6.53 – 5.88 (m, 1H), 5.77 – 5.50 (m, 2H), 5.32 (d, \(J = 3.2\) Hz, 1H), 4.02 (dd, \(J = 6.9, 5.7\) Hz, 2H), 2.44 (d, \(J = 4.1\) Hz, 3H), 2.26 – 2.07 (m, 2H), 1.75 (dd, \(J = 7.6, 6.3\) Hz, 2H), 0.12 (s, 9H). \(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 149.0, 144.9, 136.6, 130.3, 130.2, 130.1, 128.2, 127.2, 70.1, 29.2, 28.9, 21.9, -0.6. IR (CDCl\(_3\)) 2970, 1364, 1249, 1175, 966, 908, 839, 729. HRMS calcd for (C\(_{17}\)H\(_{26}\)O\(_3\)SSi)Na\(^+\) : 361.1264, found: 361.1260.
ethyl (4aR,8R,9aR)-9-oxo-6-(trimethylsilyl)-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocycloheptab[pyridine-10-carboxylate (53a). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (s, 1H), 5.76 (dt, J = 3.2, 1.6 Hz, 1H), 4.11 (dq, J = 8.7, 7.1 Hz, 2H), 3.72 (td, J = 3.1, 1.4 Hz, 1H), 3.61 (dt, J = 5.6, 3.1 Hz, 1H), 3.42 (dd, J = 13.3, 4.4 Hz, 1H), 3.32 – 3.15 (m, 1H), 3.04 (dd, J = 15.8, 5.3 Hz, 1H), 2.28 – 2.31 (m, 1H), 2.21 – 2.10 (m, 1H), 1.99 (m, 1H), 1.96 – 1.77 (m, 2H), 1.62 (s, 1H), 1.25 (t, J = 7.1 Hz, 3H), 0.00 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 206.9, 167.6, 145.3, 145.1, 139.5, 93.3, 67.9, 59.4, 53.2, 46.0, 37.62, 34.0, 32.8, 22.5, 15.0, -2.0. IR (CDCl₃) 1167, 1178, 901, 716, 650. HRMS calcd for (C₁₈H₂₇O₃NSi)H⁺: 334.1833, found: 334.1830.

(E)-5-(cyclohex-1-en-1-yl)pent-4-en-1-yl 4-methylbenzenesulfonate (55). ¹H NMR (500 MHz, Chloroform-d) δ 7.78 (d, J = 8.0 Hz, 8H), 7.34 (d, J = 7.9 Hz, 8H), 5.94 (d, J = 15.4 Hz, 2H), 5.79 – 5.69 (m, 1H), 5.61 (d, J = 4.3 Hz, 2H), 5.56 (s, 1H), 5.36 (dt, J = 14.9, 6.9 Hz, 2H), 5.11 (dt, J = 11.6, 7.3 Hz, 1H), 4.03 (q, J = 6.4 Hz, 8H), 2.44 (s, 13H), 2.06 (ddd, J = 29.9, 10.0, 4.5 Hz, 18H), 1.73 (p, J = 6.9 Hz, 7H), 1.69 – 1.54 (m, 10H). ¹³C NMR (126 MHz, CDCl₃) δ 144.9, 144.9, 144.9, 135.6, 135.4, 135.2, 135.1, 133.5, 133.5, 133.5, 133.4, 133.3, 130.1, 128.3, 128.3, 128.2, 128.1, 127.2, 124.2, 70.4, 70.2, 29.8, 29.2, 29.1, 28.2, 28.1, 28.7, 26.1, 25.8, 25.0, 24.8, 23.1, 22.9, 22.8, 22.4, 21.9, 18.9.
ethyl 11-oxo-2,3,4,4a,6,7,8,9,9a,10,11,11a-dodecahydro-1,10-ethenobenzocyclohepta[1,2-b]pyridine-12-carboxylate (56)

IR (CDCl$_3$) 2931, 1721, 1681, 1557, 1264, 1243, 1123, 1095, 917, 762, 536. HRMS calcd for (C$_{19}$H$_{25}$O$_3$N)$^+_{Na}$: 338.1726, found: 338.1726.

(4E,6E)-5-methylocta-4,6-dien-1-yl 4-methylbenzenesulfonate (58). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.78 (d, J = 8.2 Hz, 6H), 7.33 (d, J = 8.1 Hz, 7H), 6.55 – 6.23 (m, 1H), 5.99 (dd, J = 15.4, 1.9 Hz, 3H), 5.79 – 5.64 (m, 1H), 5.57 (dq, J = 15.8, 6.6 Hz, 3H), 5.17 (t, J = 7.5 Hz, 2H), 5.06 (t, J = 7.6 Hz, 1H), 4.02 (t, J = 6.4 Hz, 6H), 2.44 (s, 10H), 2.14
(p, J = 7.8, 7.4 Hz, 7H), 1.79 (dd, J = 6.6, 1.7 Hz, 3H), 1.76 – 1.68 (m, 18H), 1.65 (s, 7H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 144.9, 144.9, 135.9, 135.3, 133.7, 133.5, 133.4, 130.1, 130.1, 128.36, 128.2, 127.6, 126.2, 125.9, 123.1, 70.3, 70.3, 29.3, 29.1, 24.1, 23.3, 21.9, 20.8, 18.9, 18.5, 12.7. IR (neat) 2951, 1357, 1173, 1097, 906, 726, 662, 552. HRMS calcd for (C$_{16}$H$_{22}$O$_3$S)Na$^+$ : 317.1181, found: 317.1186.

ethyl (4aR,7S,8S,9aR)-5,7-dimethyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (59). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 (s, 1H), 5.14 (dt, J = 3.5, 1.6 Hz, 1H), 4.51 – 4.02 (m, 2H), 3.50 (dd, J = 13.9, 4.2 Hz, 1H), 3.25 (ddd, J = 16.7, 9.4, 3.9 Hz, 1H), 3.12 (dd, J = 9.4, 2.4 Hz, 1H), 3.06 (t, J = 2.4 Hz, 1H), 2.77 – 2.62 (m, 1H), 2.38 (ddq, J = 6.7, 4.7, 2.4 Hz, 1H), 2.06 (dt, J = 8.6, 2.5 Hz, 1H), 1.88 – 1.69 (m, 3H), 1.68 (t, J = 2.1 Hz, 3H), 1.46 (d, J = 7.2 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 204.3, 167.5, 144.9, 138.5, 131.6, 102.2, 71.5, 60.1, 53.5, 52.3, 43.6, 40.7, 27.7, 26.7, 24.4, 18.8, 14.8. IR (neat) 2941, 1731, 1683, 1578, 1274, 1250, 1133, 1059, 911, 726, 573. HRMS calcd for (C$_{17}$H$_{23}$O$_3$N)H$^+$ : 290.1750, found: 290.1748.

(E)-2-methylhepta-4,6-dien-1-yl 4-methylbenzenesulfonate (60). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.87 – 7.73 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.22 (dt, J = 17.0, 10.2 Hz, 1H), 5.96 (dd, J = 15.3, 10.4 Hz, 1H), 5.50 (dt, J = 14.9, 7.3 Hz, 1H), 5.05 (d, J = 17.0 Hz,
1H), 4.96 (d, J = 10.1 Hz, 1H), 3.84 (qd, J = 9.4, 5.7 Hz, 2H), 2.43 (s, 3H), 2.17 – 2.06 (m, 1H), 1.90 (ddt, J = 25.8, 13.0, 6.9 Hz, 2H), 0.88 (d, J = 6.7 Hz, 3H). $^{13}$C NMR (126 MHz, CDC$_3$) δ 144.9, 137.0, 133.5, 131.4, 130.1, 128.1, 128.1, 115.8, 74.4, 35.8, 33.2, 18.8, 16.4, 13.5. IR (CDCl$_3$) 2953, 1598, 1356, 1174, 909, 725, 553. cm$^{-1}$. HRMS calcd for (C$_{15}$H$_{20}$O$_3$S)Na$^+$ : 303.1025, found: 303.1020.

![Structure](image)

ethyl (3S,4aR,8S,9aR)-3-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-
ethenocyclohepta[b]pyridine-10-carboxylate (61). mp = 112-115°C. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 (s, 1H), 5.77 (td, J = 6.8, 5.3, 2.7 Hz, 2H), 4.37 – 4.02 (m, 2H), 3.53 (dt, J = 10.9, 2.2 Hz, 1H), 3.45 (dd, J = 13.8, 5.3 Hz, 1H), 3.10 (dd, J = 9.2, 2.4 Hz, 1H), 3.07 – 2.97 (m, 1H), 2.86 (dd, J = 13.7, 11.8 Hz, 1H), 2.69 (dddd, J = 11.9, 8.8, 6.1, 2.2 Hz, 1H), 2.15 (ddt, J = 32.8, 12.9, 2.8 Hz, 2H), 2.01 – 1.84 (m, 1H), 1.41 (q, J = 12.1 Hz, 1H), 1.28 (td, J = 7.0, 1.2 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 205.0, 167.3, 145.0, 133.1, 130.7, 102.9, 72.8, 60.3, 60.1, 43.7, 41.3, 37.7, 33.4, 33.15, 18.9, 14.9. IR (CDCl$_3$) 1734, 1675, 1597, 1142, 913, 729. HRMS calcd for (C$_{16}$H$_{21}$O$_3$N)Na$^+$ : 298.1413, found: 298.1411.
ethyl (3S,4aS,8S,9aR)-3-methyl-9-oxo-2,3,4,4a,7,8,9,9a-octahydro-1,8-ethenocyclohepta[b]pyridine-10-carboxylate (62) mp = 116-120°C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 (s, 1H), 5.72 (ddd, J = 11.6, 7.6, 2.9 Hz, 1H), 5.42 (ddd, J = 12.8, 3.4, 1.7 Hz, 1H), 4.42 – 3.94 (m, 2H), 3.70 (dq, J = 3.5, 1.7 Hz, 1H), 3.56 (q, J = 3.9 Hz, 1H), 3.38 (dt, J = 13.3, 3.0 Hz, 1H), 2.77 (ddd, J = 12.6, 9.5, 4.9 Hz, 2H), 2.55 – 2.42 (m, 1H), 2.16 (dt, J = 16.4, 3.4 Hz, 1H), 2.03 (ddt, J = 13.2, 3.6, 2.0 Hz, 1H), 1.92 (td, J = 11.6, 6.6 Hz, 1H), 1.50 (td, J = 12.7, 4.1 Hz, 1H), 1.25 (td, J = 7.1, 1.2 Hz, 3H), 0.89 (d, J = 6.5 Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 207.2, 167.7, 145.5, 132.4, 130.2, 93.5, 67.1, 60.0, 59.5, 45.3, 41.3, 37.4, 32.9, 27.9, 18.8, 14.9. IR (CDCl\(_3\)) 1719, 1680, 1623, 1260, 1154. HRMS calcd for (C\(_{16}\)H\(_{21}\)O\(_3\)N)\(\text{H}^+\) : 276.1594, found: 276.1590.
3.3 Preparation of Dienes

3.3.1 Synthesis of (E)-5-methylhepta-4,6-dien-1-ol (67)

Pent-4-en-1-ol 63 (2 g, 23.22 mmol, 1.0 eq) was dissolved in dry DMF (23.22 ml), was cooled at 0 °C. Then tert-butyldimethylsilyl chloride (4.60 g, 30.19 mmol, 1.3 eq) and imidazole (2.06 g, 30.19 mmol, 1.3 eq) were added. After that the reaction mixture was stirred for 19 hours at room temperature. Then the reaction mixture was quenched with 100 mL and then extracted with Et₂O (3 x 150 mL). The extracted organic layers were combined and washed with a saturated solution of NH₄Cl, brine, and water. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (5% Et₂O in Pentane) and rotavap to afford as a clear oil. The tert-butyldimethyl(pent-4-en-1-yloxy)silane 64 was afforded with 97% yields (4.56 g), and the ¹H and ¹³C NMR spectrums matched with the literature spectrum.²³

In an oven-dried round bottle flask, tert-butyldimethyl(pent-4-en-1-yloxy)silane 64 (2.00 g, 10.0 mmol), methylvinylketone (2.48 mL, 30.0 mmol) and Grubbs catalyst 2nd Generation (424.5 mg, 0.5 mmol) were dissolved in DCM (40 mL). The solution was then refluxed for 5 hours. Then the reaction mixture filtered through celite and rotavap. The product was purified by flash chromatography (5-20% E₂O in pentane) and rotavap
to afford as a cleat oil. \((E)-7-((\text{tert-butyldimethylsilyl})\text{oxy})\text{hept-3-en-2-one} 65\) was afforded with 45% yields (1.1 g), and the \(\text{\(^1\)H}\) and \(\text{\(^{13}\)C}\) NMR spectrums matched with the literature spectrum.\(^{24}\)

In an oven-dried round bottle flask, Methyltriphenylphosphonium bromide (2.06 g, 5.77 mmol) was suspended in anhydrous THF (15 mL) at 0 °C and degassed for 5 minutes. After that n-BuLi (2.5 M in hexanes, 2.74 mL, 6.21 mmol) was added and stirred for 30 minutes. \((E)-7-((\text{tert-butyldimethylsilyl})\text{oxy})\text{hept-3-en-2-one}\) (1.0 g, 4.12 mmol) dissolved in 2.5 mL THF was then added and stirred for 3 hours. Then 10 mL water was added to quench the reaction. Then extracted with Et\(_2\)O (3 x 30 mL). The extracted organic layers were combined and washed with brine. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was then dissolved in THF, and TBAF (1.0M in THF, 4.12 mL, 4.12 mmol) was added and stirred for 3 hours at room temperature. Then water was added to quench the reaction. The reaction mixture was extracted with Et\(_2\)O (3 x 30 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (10-40% E\(_2\)O in Pentane) and rotavap to afford as a clear oil. \((E)-5\)-methylhepta-4,6-dien-1-ol 67 was afforded with 45% yields (0.23 g), and the \(\text{\(^1\)H}\) and \(\text{\(^{13}\)C}\) NMR spectrums matched with the literature spectrum.\(^{24}\)
3.3.2 Synthesis of 4,6-Octadien-1-ol (72)

Butane-1,4-diol 68 (13.0 g, 144.25 mmol) and t-butyldimethylsilyl chloride (10.85 g, 71.98 mmol) were dissolved in 250 mL DCM. The solution was then cooled at 0 °C, and triethylamine (10.0 mL, 72 mmol) was added dropwise. After 2 hours, a 150 mL saturated solution of ammonium chloride was added to quench the reaction. The organic layer was separated, washed with 100 mL water, dried over Na₂SO₄, and concentrated in rotavap. The crude product was clean enough for the next step.

The crude 4-((tert-butyldimethylsilyl)oxy)butan-1-ol 69 (2.45g, 12.0 mmol), phosphorous triphenyl (3.78 g, 14.4 mmol) and imidazole (1.22 g, 18.0 mmol) were dissolved in 30 mL dichloromethane at 0 °C. Then iodine (4.11 g, 16.2mmol) was added to the reaction mixture and stirred at room temperature for 4 hours. Then the reaction mixture filtered through celite and rotavap. The product was purified by flash chromatography (5-10% Et₂O in Pentane) and rotavap to afford as a cleat oil. tert-butyl(4-iodobutoxy) dimethylsilane 70 afforded 76% yields (g), and the ¹H and ¹³C NMR spectrums matched with the literature spectrum.²⁵
t-Butyl(4-iodobutoxy)dimethylsilane (2.35 g, 7.85 mol) was mixed with triphenylphosphine (2.06 g, 7.85 mol) and heated neat at 80 °C for 16 hr. The reaction mixture becomes sticky white solid. Then 18 mL dry THF was added under argon atmosphere and cooled at 0 °C. Then n-BuLi (2.5 M in hexanes, 3.20 mL, 7.85 mmol) was added to (4-((tert-butyldimethylsilyl)oxy)butyl)triphenyl-l4-phosphane (71) and stirred for 30 minutes. After that, the crotonaldehyde (0.60 mL, 7.13 mmol) in 2.5 mL THF was added very slowly to the reaction mixture and stirred for 6 hours. Then 10 mL water was added to quench the reaction. Then extracted with Et2O (3 x 30 mL). The extracted organic layers were combined and washed with brine. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was then dissolved in THF, and TBAF (1.0M in THF, 15 mL, 15 mmol) was added and stirred for 3 hours at room temperature. Then water was added to quench the reaction. The reaction mixture was extracted with Et2O (3 x 30 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (10-40% Et2O in Pentane) and rotavap to afford as a cleat oil. 4,6-Octadien-1-ol 72 was afforded with 51% yields (0.46 g), and the 1H and 13C NMR spectrums matched with the literature spectrum.26

3.3.3 Synthesis of (4E,6E)-7-phenylhepta-4,6-dien-1-ol (76)
Triphenylphosphine (13.44 g, 51.24 mmol) and ethyl-4-bromobutanoate 73 (10.19 g, 52.26 mmol) were dissolved in 50 mL toluene and refluxed overnight. After that, the reaction mixture was cooled at room temperature and rotavap. (4-ethoxy-4-oxobutyl)triphenylphosphonium bromide 74 was obtained as a sticky white solid with quantitative yields. Then K$_2$CO$_3$ (28.33 g, 204.96 mmol) and toluene (100 mL) were added to (4-ethoxy-4-oxobutyl)triphenylphosphonium bromide 74. The mixture was heated to 65 °C and stirred for 10 minutes. After that, trans-cinnamaldehyde (26.0 mL, 204.96 mmol) was added and stirred for 7 hours. Then the reaction mixture was cooled at room temperature, 300 mL water was added and extracted with Ethyl acetate (3 x 150 mL). After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (0-20% Ethyl acetate in Hexane) and rotavap to afford as a clear oil. The ethyl (3E,5E)-6-phenylhexa-3,5-dienoate 75 was afforded with 46 % yields ( 5.1 g), and the $^1$H and $^{13}$C NMR spectrums matched with the literature spectrum.\textsuperscript{27}

In an oven-dried round bottle flask, lithium aluminum hydride (165 mg, 4.34 mmol) was suspended in 11 mL THF and cool to 0oC. Then ethyl (3E,5E)-6-phenylhexa-3,5-dienoate ( 0.5 g, 2.17 mmol) was added dropwise to the reaction mixture. After that, the reaction mixture was slowly warm to room temperature and stirred overnight. 10 mL of water was added dropwise to quench the reaction mixture, filtered through celite, and concentrated. The product was purified by flash chromatography (10-40% E2O in pentane) and rotavap to afford as a cleat oil. (4E,6E)-7-phenylhepta-4,6-dien-1-ol 76 was afforded with 86 % yields ( 0.35 g), and the $^1$H and $^{13}$C NMR spectrums matched with the literature spectrum.\textsuperscript{27}
3.3.4 Synthesis of (E)-6-methylhepta-4,6-dien-1-ol (79)

4-((tert-butyldimethylsilyl)oxy)butan-1-ol 69 (4.56 g, 22.30 mmol), PCC (8.63 g, 40.14 mmol) were dissolved in 50 mL CH₂Cl₂ and stirred at room temperature for overnight. Then the reaction mixture was filtered through celite and concentrated. The product was purified by flash chromatography (10% E₂O in pentane) and rotavap to afford as a clear oil. 4-((tert-butyldimethylsilyl)oxy)butanal 77 was afforded with 20 % yields (0.93 g), and the ¹H and ¹³C NMR spectrums matched with the literature spectrum.²⁸

(2-methylallyl)diphenylphosphate oxide 78 (1.46 g, 5.68 mmol) was dissolved in 14.2 mL THF at cooled to -78 °C. Then HMPA (2.0 mL, 11.5 mmol) and n-BuLi (2.5 M in hexanes, 2.5 mL, 5.68 mmol) was added to phosphine oxide and stirred for half an hour. A solution of 4-((tert-butyldimethylsilyl)oxy)butanal (1.15 g, 5.68 mmol) in THF (3.8 mL) was added and stirred for hours. Then 10 mL water was added to quench the reaction. Then extracted with Et₂O (3 x 15 mL). The extracted organic layers were combined and washed with brine. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was then dissolved in THF, and TBAF (1.0M in THF, 6.8 mL, 6.81 mmol) was added and stirred for 3 hours at room
temperature. Then water was added to quench the reaction. The reaction mixture was extracted with Et₂O (3× 10 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (10-40 % E₂O in pentane) and rotavap to afford as a cleat oil. (E)-6-methylhepta-4,6-dien-1-ol 79 was afforded with 31% yields (0.14 g), and the ¹H and ¹³C NMR spectrums matched with the literature spectrum.²⁸

**3.3.5 Synthesis of (E)-6-(trimethylsilyl)hepta-4,6-dien-1-ol (81)**

Ethynyltrimethylsilane (80) (0.7 mL, 5.0 mmol), pent-4-en-1-ol (1.5 mL, 15.0 mmol) and Hoveyda-Grubbs catalyst, 2nd generation (212 mg, 0.25 mmol) were dissolved in ClCH₂-CH₂Cl and stirred for 8 hours at 60 °C. Then the reaction mixture filtered through celite and rotavap. The product was purified by flash chromatography (0-35% E₂O in pentane) and rotavap to afford as a cleat oil. (E)-6-(trimethylsilyl)hepta-4,6-dien-1-ol 81 was afforded with 83% yields (0.76 g).³²

**3.3.6 Synthesis of (cyclohex-1-en-1-yl)pent-4-en-1-ol (85)**
Cycloheptene 82 (2 mL, 20.8 mmol), RuCl₃ (0.15 g, 0.73 mmol), NaIO₄ (6.8 g, 31.2 mmol) were dissolved in ClCH₂-CH₂Cl (83 mL) and water (83 mL) at room temperature and stirred for 1 hour. Then the reaction mixture was quenched with 100 mL saturated solution of NaS₂O₃ and then extracted with Ethyl acetate (3 x 50 mL). The extracted organic layers were combined and washed with brine and water. After that, heptanendial 83 was dried over anhydrous sodium sulfate, filtered, and concentrated. Crude heptanendial (1.28 g, 10.0 mmol) was transferred into a round bottle flask and dissolved in 50 mL CH₂Cl₂. Then 13.4 mL piperidine and 10 mL acetic acid were added to the solution and stirred at room temperature for 15 minutes. DI water was added to the reaction mixture to quench and then extracted with Et₂O (3 x 30 mL). The extracted organic layers were combined and washed with 1M HCl, a saturated solution of sodium bicarbonate and brine. The crude product was dried over anhydrous sodium sulfate, filtered, and concentrated. Then the crude product was purified by flash chromatography (10% Et₂O in Hexane) and rotavap to afford as a clear oil. The cyclohex-1-ene-1-carbaldehyde 84 was afforded with 72% yields (0.8 g), and the ¹H and ¹³C NMR spectrums matched with the literature spectrum.²⁹,³⁰

In an oven-dried round bottle flask, 7 mL THF was added to ((4-((tert-butyldimethylsilyl)oxy)butyl)triphenylphosphonium iodine (1.7 g, 2.99 mmol) and cooled at 0 °C. Then n-BuLi (2.5 M in hexanes, 1.22 mL, 2.99 mmol) was added to (4-((tert-butyldimethylsilyl)oxy)butyl) triphenyl-l4-phosphane iodide (1.7 g 2.99 mmol) and stirred for 30 minutes. After that, the cyclohex-1-ene-1-carbaldehyde (0.3 g, 2.72 mmol) dissolved in 1 mL THF was added very slowly to the reaction mixture and stirred for 6 hours. Then 10 mL water was added to quench the reaction and then extracted with Et₂O
(3 x 10 mL). The extracted organic layers were combined and washed with brine. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was then dissolved in THF, and TBAF (1.0M in THF, 4.5 mL, 4.50 mmol) was added and stirred for 3 hours at room temperature. Then water was added to quench the reaction. The reaction mixture was extracted with Et₂O (3 x 10 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (5-40% Et₂O in Pentane) and rotavap to afford as a cleat oil. 5-(cyclohex-1-en-1-yl)pent-4-en-1-ol 85 was afforded with 83% yields (0.74 g). 

1H NMR (500 MHz, CDCl₃) δ 6.04 (d, J = 15.7 Hz, 1H), 5.62 (d, J = 4.4 Hz, 1H), 5.52 (dt, J = 14.9, 7.0 Hz, 1H), 3.63 (dd, J = 7.7, 5.3 Hz, 2H), 2.12 (dq, J = 29.6, 6.6, 6.0 Hz, 4H), 1.96 – 1.88 (m, 1H), 1.67 – 1.52 (m, 8H). 13C NMR (126 MHz, CDCl₃) δ 135.7, 134.3, 127.7, 125.8, 62.68, 32.8, 29.4, 26.0, 24.8, 22.9, 22.8. HRMS calcd for (C₁₁H₁₈O)Na⁺ : 189.1249, found: 189.1248.

3.3.7 Synthesis of 5-methylocta-4,6-dien-1-ol (86)

In an oven-dried round bottle flask, 14.7 mL THF was added to ((4-((tert-butyldimethylsilyl)oxy)butyl)triphenylphosphonium iodide 71 (3.7 g, 6.40 mmol) and cooled at 0 °C. Then n-BuLi (2.5 M in hexanes, 2.7 mL, 6.40 mmol) was added to ((4-((tert-butyldimethylsilyl)oxy)butyl)triphenylphosphonium iodide and stirred for 30 minutes. After that, the (E)-pent-3-en-2-one (0.63 mL, 6.40 mmol) dissolved in 1 mL
THF was added slowly to the reaction mixture and stirred for 6 hours. Then 10 mL water was added to quench the reaction and then extracted with Et₂O (3 x 30 mL). The extracted organic layers were combined and washed with brine. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The product was then dissolved in THF, and TBAF (1.0M in THF, 13 mL, 13 mmol) was added and stirred for 3 hours at room temperature. Then water was added to quench the reaction. Then the reaction mixture was extracted with Et₂O (3 x 30 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (5-40% Et₂O in pentane) and rotavap to afford as a cleat oil. 5-methyllocta-4,6-dien-1-ol 86 was afforded with 83% yields (0.74 g). ¹H NMR (600 MHz, CDCl₃) δ 6.03 (dd, J = 15.5, 2.3 Hz, 1H), 5.55 (dq, J = 15.5, 6.6 Hz, 1H), 5.32 (t, J = 7.6 Hz, 1H), 3.83 – 3.41 (m, 2H), 2.17 (dq, J = 22.5, 7.4 Hz, 2H), 1.73 (dd, J = 6.8, 2.0 Hz, 3H), 1.70 – 1.68 (m, 3H), 1.60 (pd, J = 6.9, 2.7 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 136.1, 134.3, 129.4, 122.4, 62.4, 32.8, 24.6, 18.4, 12.6. HRMS calcd for (C₉H₁₆O)Na⁺: 163.1093, found: mass not observed.

3.3.8 Synthesis of (E)-2-methylhepta-4,6-dien-1-ol (90)

ethyl 2-methylpent-4-enoate (0.86 g, 6.05 mmol), crotonaldehyde (1.6 mL, 18.14 mmol) and Hoveyda-Grubbs catalyst, 2nd generation (1.9 g, 3 mmol) were dissolved in CH₂Cl₂
and stirred for 24 hours at 40 °C. Then the reaction mixture filtered through celite and rotavap. The product was purified by flash chromatography (5-20% Et2O in Pentane) and rotavap to afford as a cleat oil. ethyl (E)-2-methyl-6-oxohex-4-enoate 88 was afforded with 65% yields (0.65 g), and the 1H and 13C NMR spectrums matched with the literature spectrum.31

In an oven-dried round bottle flask, 3.4 mL THF was added to Methyltriphenyl phosphonium iodide (2.13 g, 5.26 mmol) under argon at 0°C and degas for five minutes. Then NaHMDS (2 M in THF, 2.63 mL, 5.26 mmol) was added to the reaction mixture and stirred for half an hour. After that, ethyl (E)-2-methyl-6-oxohex-4-enoate (0.60 g, 3.51 mmol) dissolved in 1 mL THF was added to the reaction mixture and stirred for 5 hours. Then 10 mL water was added to quench the reaction, then extracted with Et2O (3 x 20 mL). The extracted organic layers were combined and washed with brine. After that, it was dried over anhydrous sodium sulfate, filtered, and concentrated. The product was purified by flash chromatography (10% Et2O in pentane) and rotavap to afford as a clear oil. ethyl (E)-2-methylhepta-4,6-dienoate 89 was afforded with 81% yields (0.52 g), and the 1H and 13C NMR spectrums matched with the literature spectrum.31

In an oven-dried round bottle flask, lithium aluminum hydride (117 mg, 3.10 mmol) was suspended in 15.5 mL THF and cool to 0 °C. Then ethyl (3E,5E)-6-phenylhexa-3,5-dienoate (0.52 g, 3.10 mmol) was added dropwise to the reaction mixture. After that, the reaction mixture was slowly warm to room temperature and stirred overnight. 10 mL of water was added dropwise to quench the reaction mixture, filtered through celite, and concentrated. The crude product was purified by flash chromatography (10-40% Et2O in pentane) and rotavap to afford as a cleat oil. (E)-2-methylhepta-4,6-dien-1-ol 90 was
afforded with 63% yields (0.25 g), and the $^1$H and $^{13}$C NMR spectrums matched with the literature spectrum.\textsuperscript{31}
APPENDIX I

$^1$H NMR and $^{13}$C NMR Spectra
(62)
APPENDIX II: X-RAY CRYSTAL STRUCTURE
Table 1. Crystal data and structure refinement for RR-III-24-A2.

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Table 1. Crystal data and structure refinement for RR-11-120-A1.

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<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.317 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.090 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>592</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.34 x 0.2 x 0.14 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.222 to 30.222°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11 ( \leq h \leq 11 ), -16 ( \leq k \leq 16 ), -21 ( \leq l \leq 21 )</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>28412</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3923 [R(int) = 0.0286]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7460 and 0.7095</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3923 / 0 / 244</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.028</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0368, wR2 = 0.0944</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0469, wR2 = 0.1008</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.420 and -0.204 e.Å⁻³</td>
</tr>
</tbody>
</table>
Table 1. Crystal data and structure refinement for RR-IV-30-A1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>s1</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C16 H21 N O3</td>
</tr>
<tr>
<td>Formula weight</td>
<td>275.34</td>
</tr>
<tr>
<td>Temperature</td>
<td>150.0 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.14970(10) Å, a = 106.5551(7)°, b = 9.3307(2) Å, b = 96.6879(8)°, c = 12.2461(2) Å, c = 108.8479(7)°</td>
</tr>
<tr>
<td>Volume</td>
<td>721.26(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.268 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.704 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>296</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.23 x 0.22 x 0.12 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.869 to 74.150°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-8&lt;=h&lt;=8, -11&lt;=k&lt;=11, -15&lt;=l&lt;=15</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>22024</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2843 [R(int) = 0.0179]</td>
</tr>
<tr>
<td>Completeness to theta = 67.679°</td>
<td>97.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7538 and 0.7023</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2843 / 0 / 244</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.045</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0347, wR2 = 0.0929</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0360, wR2 = 0.0941</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.228 and -0.243 e.Å⁻³</td>
</tr>
</tbody>
</table>
REFERENCES


