Nuclear Magnetic Resonance (NMR) Spectroscopy Special Focus on Proton Magnetic Resonance (^{1}H-NMR) Theory and Structural Elucidation

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ABSRACT

Nuclear Magnetic Resonance (NMR) spectroscopy stands as one of the most powerful analytical techniques for the non-destructive determination of molecular structures. This abstract explores the fundamental principles of NMR, specifically focusing on **Proton Magnetic Resonance (^{1}H-NMR)**, and evaluates its indispensable role in the structure elucidation of technical grade pesticides and their isomers.

Proton NMR Instrument at University Sophisticated Instrument Facility (USIF)

ALIGARH MUSLIM UNIVERSITY

Proton Nuclear Magnetic Resonance (^{1}H-NMR) is a sophisticated analytical technique used to determine the structure of organic molecules by observing the magnetic properties of hydrogen nuclei.

1. Working Principle

The principle of $^1\mathrm{H}$-NMR is based on the **nuclear spin** of protons.

- **Spin States:** Hydrogen nuclei ($^1\mathrm{H}$) possess a spin quantum number of $1/2$. In the absence of an external magnetic field, these spins are randomly oriented.
- **Alignment:** When placed in a strong external magnetic field (B_0), the nuclei align either with the field (lower energy, α-state) or against it (higher energy, β-state).

- **Resonance:** By applying radiofrequency (RF) radiation, the nuclei can "flip" from the α to the β state. This absorption of energy occurs at a specific frequency called the **Larmor frequency**.
- **Shielding:** Electrons surrounding the proton create local magnetic fields that oppose B_0. Protons in different chemical environments experience different net fields, leading to different **Chemical Shifts** (δ, measured in ppm).

2. Instrumentation

Modern NMR spectrometers typically utilize **Fourier Transform (FT-NMR)** technology:

- **Magnet:** A powerful superconducting magnet cooled by liquid helium.
- **Probe:** Holds the sample (usually dissolved in a deuterated solvent like $CDCl_3$) and contains the RF coils.
- **RF Transmitter:** Delivers a short pulse of radiofrequencies to excite all protons simultaneously.

- **Receiver:** Detects the **Free Induction Decay (FID)** signal as the nuclei return to equilibrium.
- **Computer:** Performs a Fourier Transform on the FID to convert the time-domain signal into a frequency-domain spectrum.

3. Structure Elucidation & Isomer Characterization

NMR provides four primary types of information to solve a structure:

1. **Chemical Shift (δ):** Indicates the electronic environment (e.g., aromatic, aliphatic, or near electronegative atoms).
2. **Integration:** The area under the peak is proportional to the number of protons contributing to that signal.

3. **Spin-Spin Splitting (Multiplicity):** Follows the $n + 1$ rule, revealing how many neighboring protons are present.
4. **Coupling Constants (J):** Measured in Hz; essential for distinguishing **cis/trans** isomers and diastereomers.

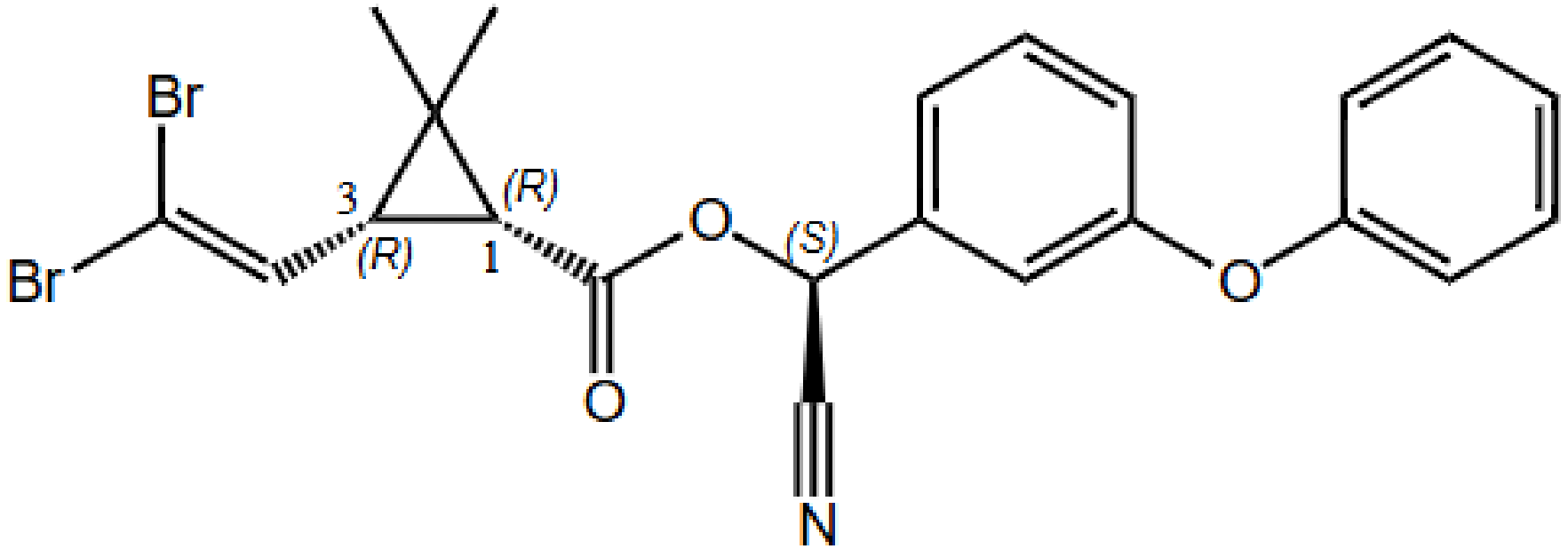
4. Special Reference: Deltamethrin Technical Isomers

Deltamethrin is a potent pyrethroid insecticide. It has three chiral centers, leading to 8 possible stereoisomers, though the technical "active" form is specifically the **(1R, 3R, αS)** isomer.

Isomer Characterization via ^{1}H-NMR:

- **The α-Proton:** The proton on the carbon bearing the cyano ($-CN$) group is a critical diagnostic marker. In the active isomer, this typically appears as a singlet around **6.3–6.7 ppm**.

Deltamethrin



(*S*)-cyano(3-phenoxyphenyl)methyl (1*R*,3*R*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-1-carboxylate

- **Cyclopropane Ring Protons:** The $H-1$ and $H-3$ protons on the cyclopropane ring show specific coupling. For the **cis** configuration (found in Deltamethrin), the coupling constant $J_{1,3}$ is typically **8–9 Hz**, whereas **trans** isomers show a smaller J value (~5 Hz).
- **Gem-Dimethyl Groups:** The two methyl groups on the cyclopropane ring are diastereotopic and appear as two distinct singlets in the **1.2–1.3 ppm** region.
- **Aromatic Region:** The phenoxyphenyl group yields complex multiplet patterns between **7.0–7.6 ppm**.

Deltamethrin ($C_{22}H_{19}Br_2NO_3$) is a highly potent synthetic pyrethroid insecticide that contains three chiral centers (two on the cyclopropane ring, one at the α-cyano benzyl position), leading to eight potential stereoisomers.

The commercial, highly active insecticide consists of a single stereoisomer: **(S)-α-cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate** (also known as *cis*-deltamethrin, or *1R-cis-*αS).

1. **[1R,3R,αS] - Deltamethrin** (Active)
2. **[1R,3R,αR]** - αR-Deltamethrin
3. **[1R,3S,αS]** - *trans*-Deltamethrin
4. **[1R,3S,αR]** - αR-*trans*-Deltamethrin
5. **[1S,3S,αS]** - Enantiomer of Deltamethrin
6. **[1S,3S,αR]** - Enantiomer of αR-Deltamethrin
7. **[1S,3R,αS]** - Enantiomer of *trans*-Deltamethrin
8. **[1S,3R,αR]** - Enantiomer of αR-*trans*-Deltamethrin

General Structural Features

The structure comprises two main parts linked by an ester bond:

- **Acid moiety:** 2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylic acid.
- **Alcohol moiety:** α-cyano-3-phenoxybenzyl alcohol.

^1H NMR Spectrum of Active Deltamethrin

The proton NMR spectrum of the active isomer (in CD_3CN/H_2O or similar solvents) features distinct signals for its structural components:

- **Aromatic Region (δ 7.00 - 7.50 ppm):** Contains 9 protons from the 3-phenoxybenzyl group.
- **α-cyano proton (H9/H_{benzyl}):** Appears as a singlet (or highly shifted multiplet) between δ 6.30 - 6.70 ppm.
- **Olefinic proton (H4/H_{vinyl}):** Appears as a doublet (typically $J \approx 8 - 10$ Hz) between δ 6.30 - 6.70 ppm.
- **Cyclopropane protons (H1, H3):** Two doublets of doublets located between δ 1.50 - 2.50 ppm, with characteristic coupling constants representing *cis* (larger J) or *trans* (smaller J) relationships.
- **Gem-dimethyl protons (6H):** Two singlets around δ 1.20 - 1.30 ppm.

NMR Differentiation of Isomers

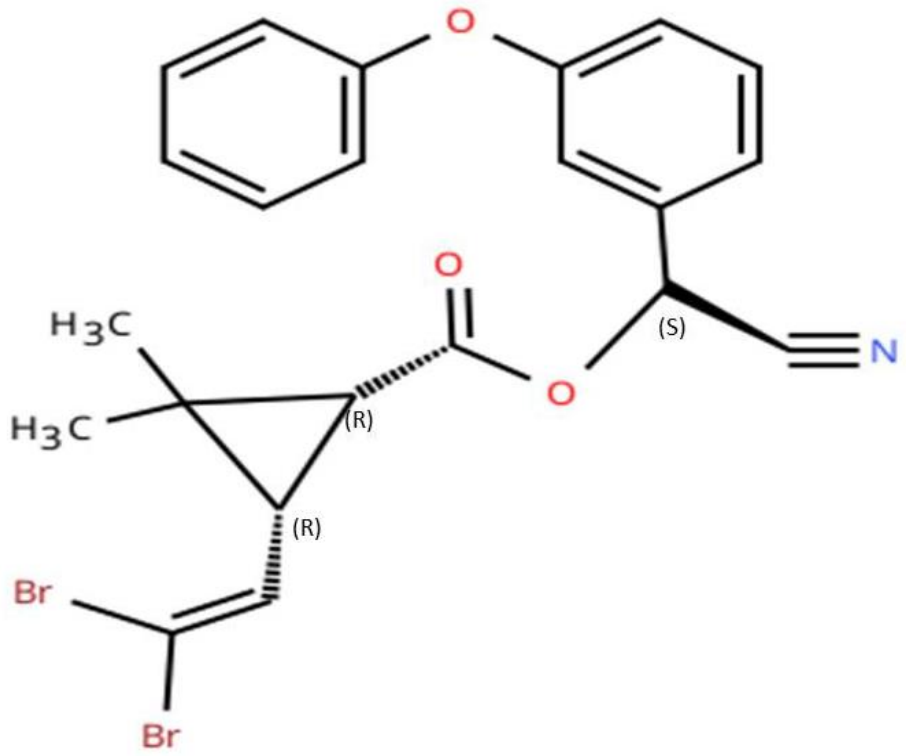
NMR is used to distinguish the isomers, particularly *cis* vs *trans* at the cyclopropane ring:

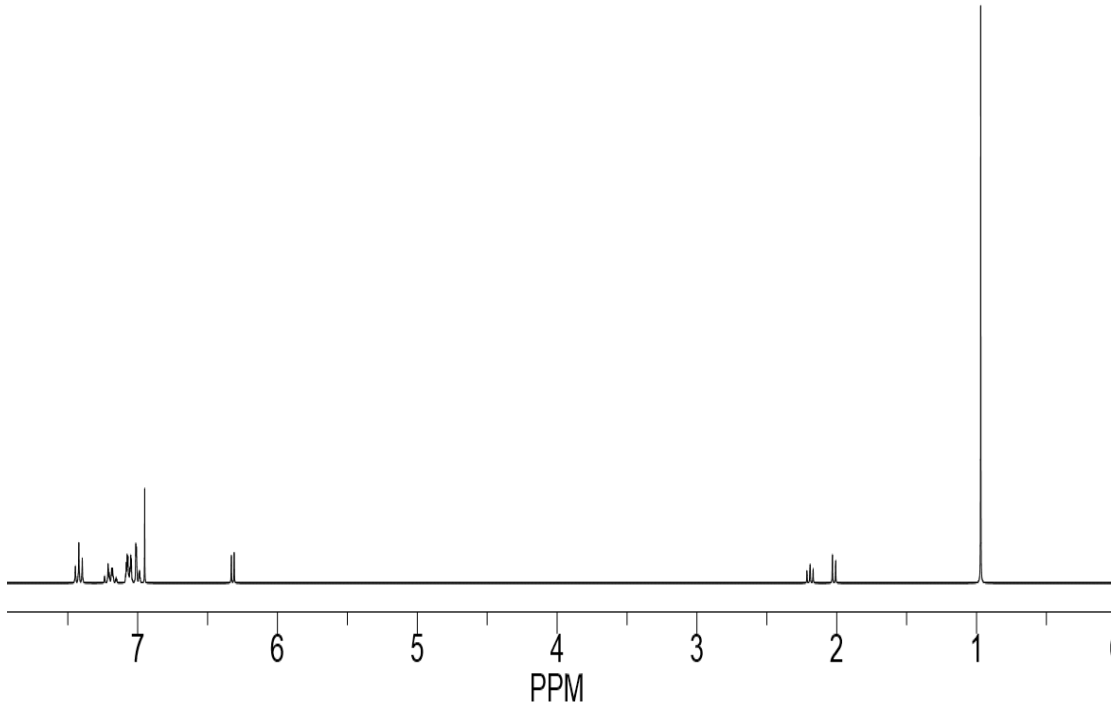
- **cis-isomers (Deltamethrin):** The cyclopropane ring protons have a smaller coupling constant ($J_{1,3} \approx 5 - 6$ Hz).
- **trans-isomers:** The coupling constant between ring protons is larger ($J_{1,3} \approx 6 - 8$ Hz).

The α-cyano group causes the α-proton signal to be highly deshielded, and its chemical shift is sensitive to the configuration (αR vs α S).

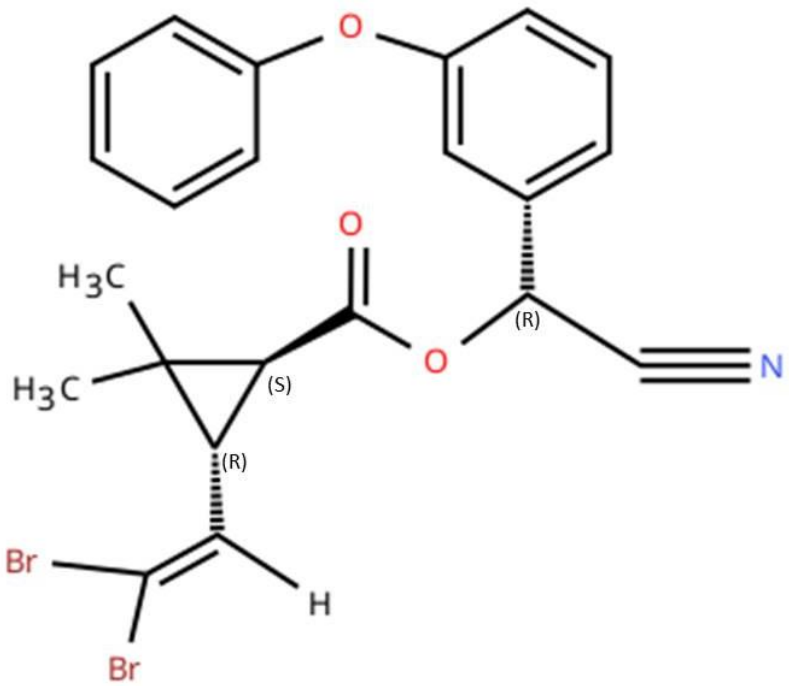
Below are the ^{1}HNMR spectra of Deltamethrin and several of its key isomers

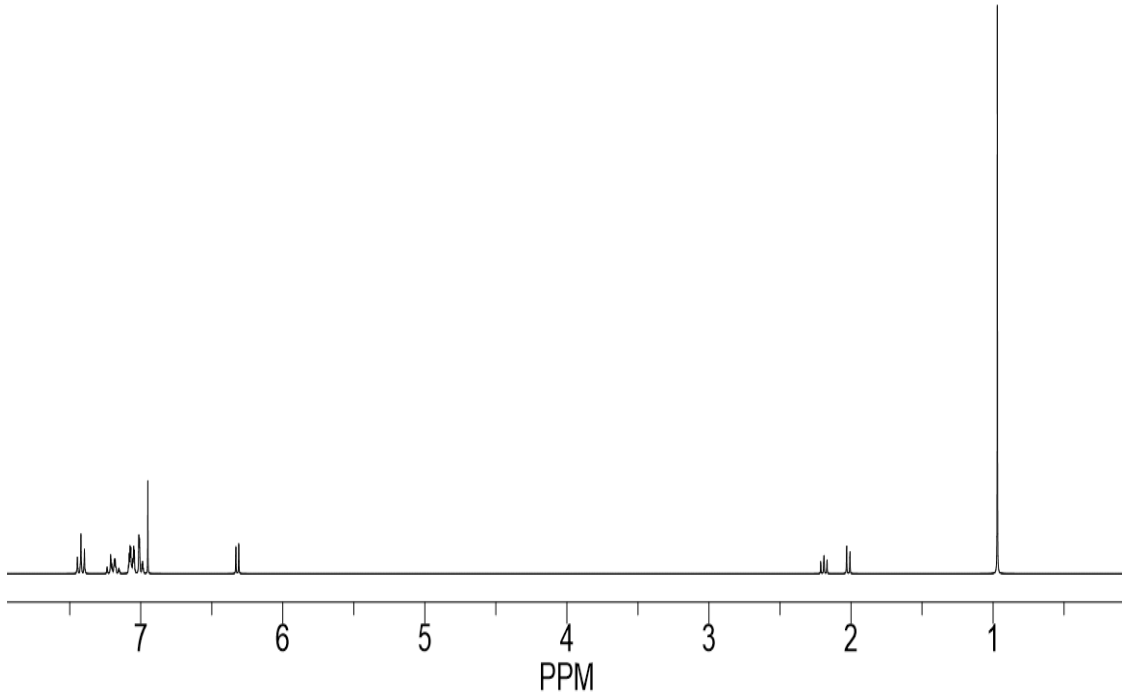
1. (S)-cyano(3-phenoxyphenyl)methyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-1-carboxylate



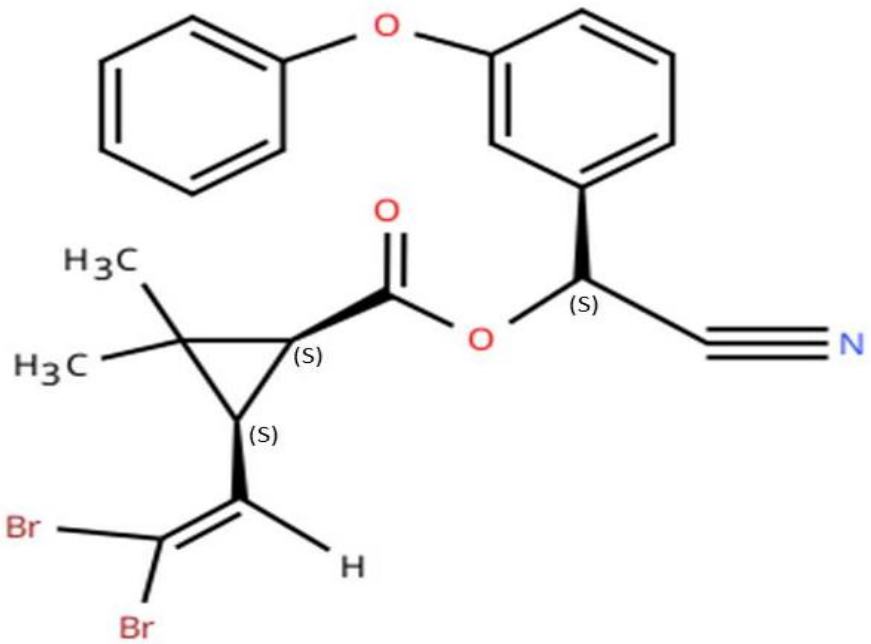


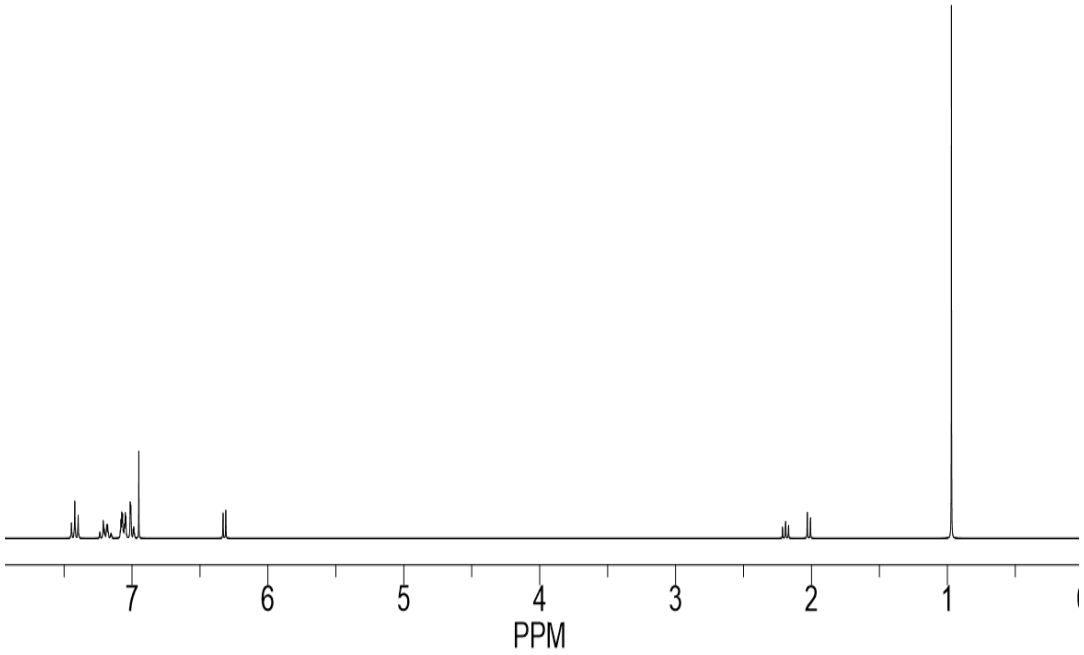
2. (R)-cyano(3-phenoxyphenyl)methyl (1S,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-1-carboxylate



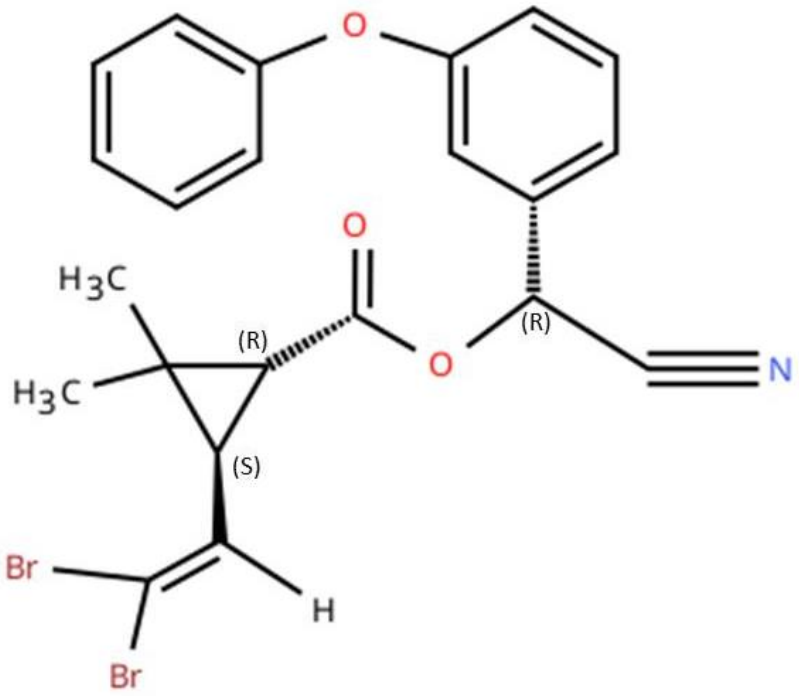


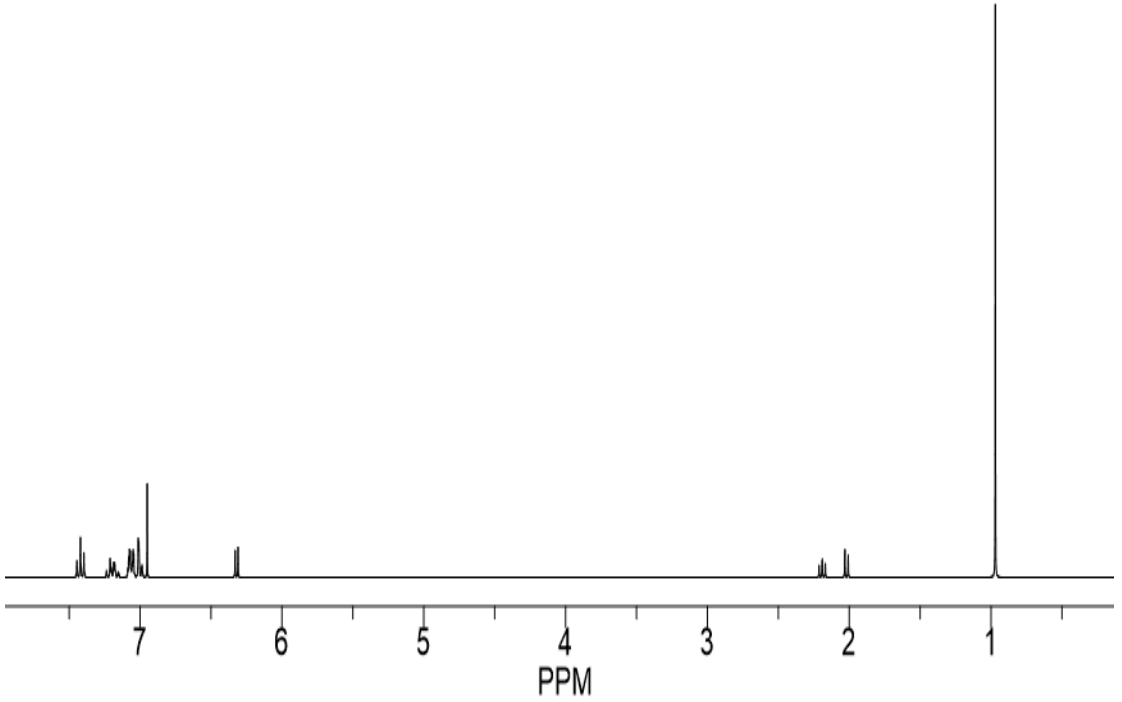
3. (S)-cyano(3-phenoxyphenyl)methyl (1S,3S)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-1-carboxylate





4. (R)-cyano(3-phenoxyphenyl)methyl (1R,3S)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane-1-carboxylate





THANK YOU