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Abstract

Abstract: New *meso*-bis(quinolin-3-yl) porphyrins derivatives were synthesized from quinolin-3-carboxaldehydes derivatives and dipyrromethane in 1:1 ratio in CH₂Cl₂ at room temperature catalyzed by TFA and DDQ. Synthesized porphyrins were obtained with a low yield.

Keywords: Quinoline; porphyrins; dipyrromethane

Introduction

The porphyrin core has been a fascinating heterocyclic organic macrocycle as an interesting building unit for the design of new supramolecular assemblies and coordination polymers [1]. The extremely remarkable properties of highly conjugated macrocycles have led to their unique roles in diverse fields ranging from photomedicines [2] to dye sensitized solar cells that are well addressed in recent reviews [3-5]. Substituted nitrogen heterocyclic porphyrins are of particular interest [6]. As they provide sites for metal coordination, hydrogen bonding, alkylation and modulating electronic properties [7]. Several quinoline derivatives have been found to possess useful biological activities such as bactericidal [8], antitumor [9], antimalarial [10], antiinflammatory [11]. The benzo and hetero fused quinolines are known to bind to DNA topoisomerase and display cytotoxic and antitumor activities [12].

Results and Discussion

The synthesis of new macromolecules type *trans*-A₂B₂ porphyrins possessing aromatic moieties as 2-hydroxyquinoline and 2-chloro-5,8-dimethoxyquinoline were synthesized within two reaction steps (Scheme 1). In the first step, key precursors, 3-nitrophenyl dipyrromethane and aromatic aldehydes **A-1**, **A-2** were synthesized following literature reported conventional procedure [13], involved the synthesis of *trans*-A₂B₂-porphyrins via condensation of aryl aldehydes with *meso*-aryl dipyrromethane in the presence of trifluoroacetic acid (TFA) followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidizing agent.

Starting quinoline aldehydes was synthesized by Vilsmeier-Haack cyclization [14] and *meso*-dipyrromethane by modified procedure literature [15]. The reaction of aldehydes, with dipyrromethane gave rise to the corresponding porphyrin with a low yield of **P-1** and trace amount of **P-2**. Evaluation of reaction was followed by TLC and UV spectrophotometer. The desired A₂B₂-porphyrins, **P-1**, **P-2** were identified by ¹H-NMR and mass spectroscopy.

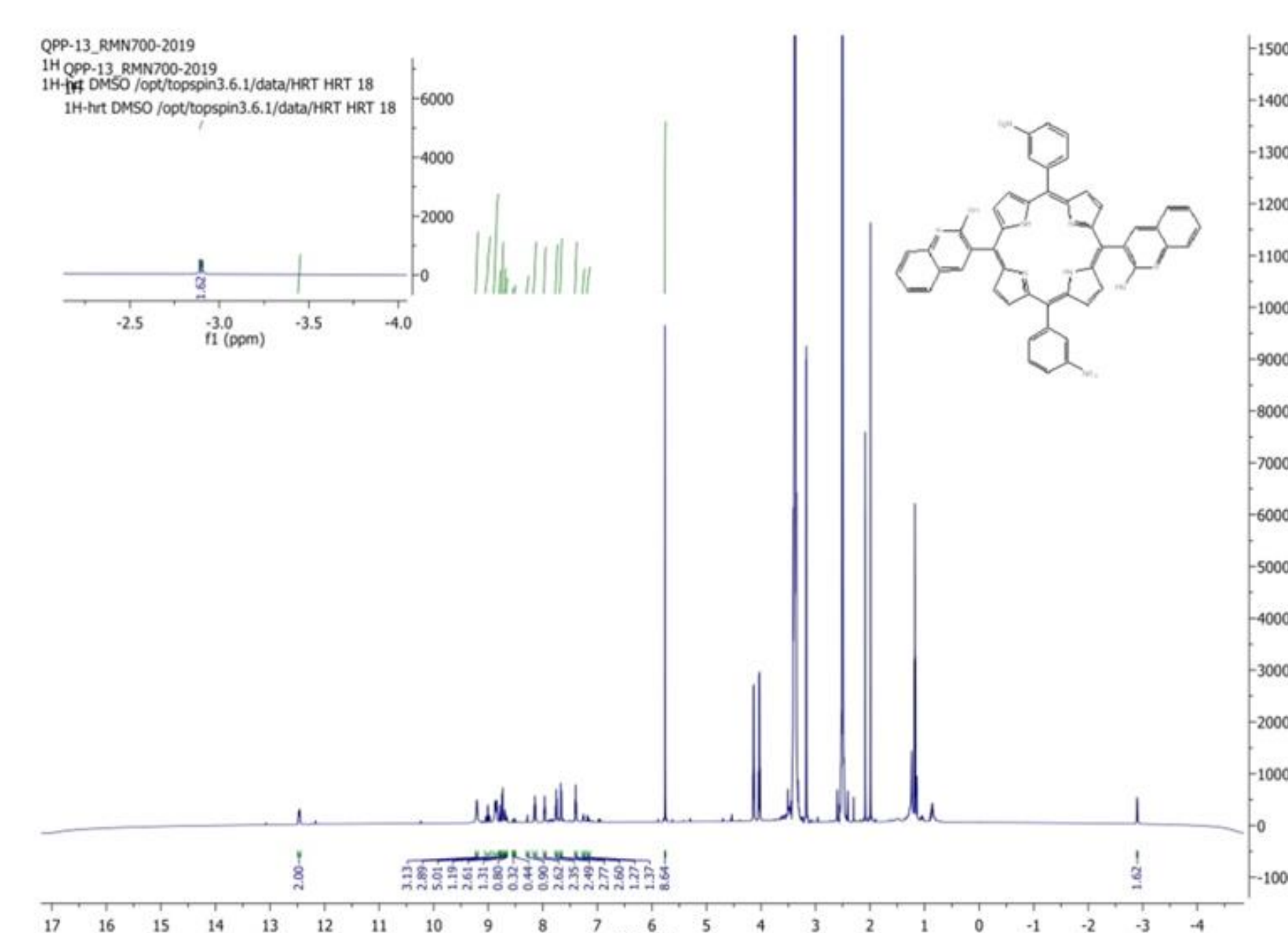
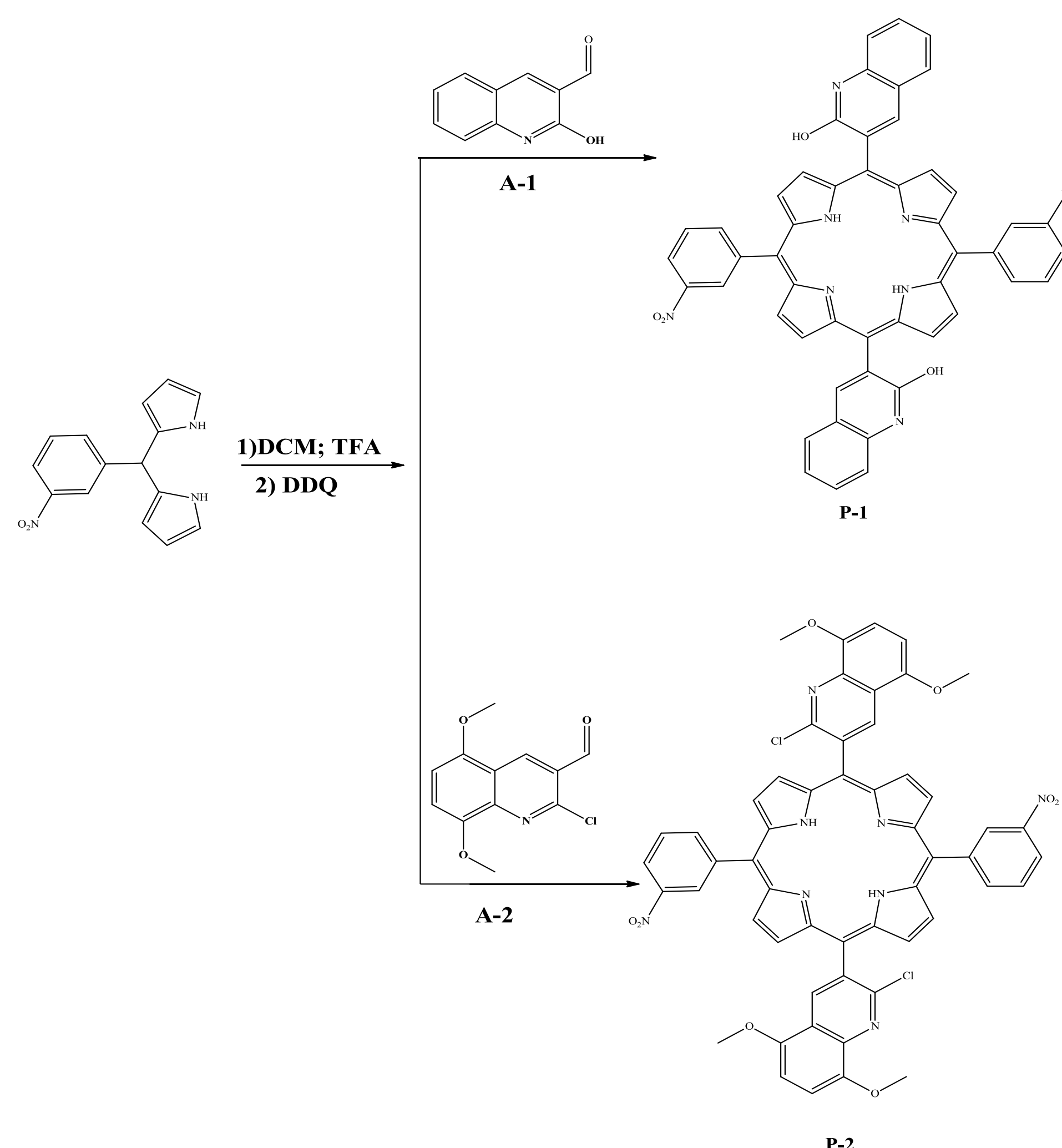


Figure 1. ¹H-NMR spectra of porphyrin **P-1**

Methods and Materials

Aldehyde (100 mmol) and dipyrromethane (200 mmol) were dissolved in DCM (40 mL) and stirred for 2 mins followed by addition of trifluoroacetic acid (5 μL). The reaction mixture was stirred under nitrogen atmosphere for 4 hrs at room temperature in dark. After that 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 300 mmol) was added and reaction mixture was stirred for another 3 hours under air. Formation of the desired porphyrin was identified by Observation of brown color spot on TLC (in 30% DCM/hexane). The crude reaction mixture was subjected to silica gel column to filter off excess DDQ and other oligomeric products using 100% DCM. Further purification was carried out with a neutral alumina column chromatography and the desired porphyrins (**P-1**, **P-2**) were eluted with 20–30% DCM/hexane.



Scheme 1. Formation of *trans*-A₂B₂ porphyrins **P-1**, **P-2**

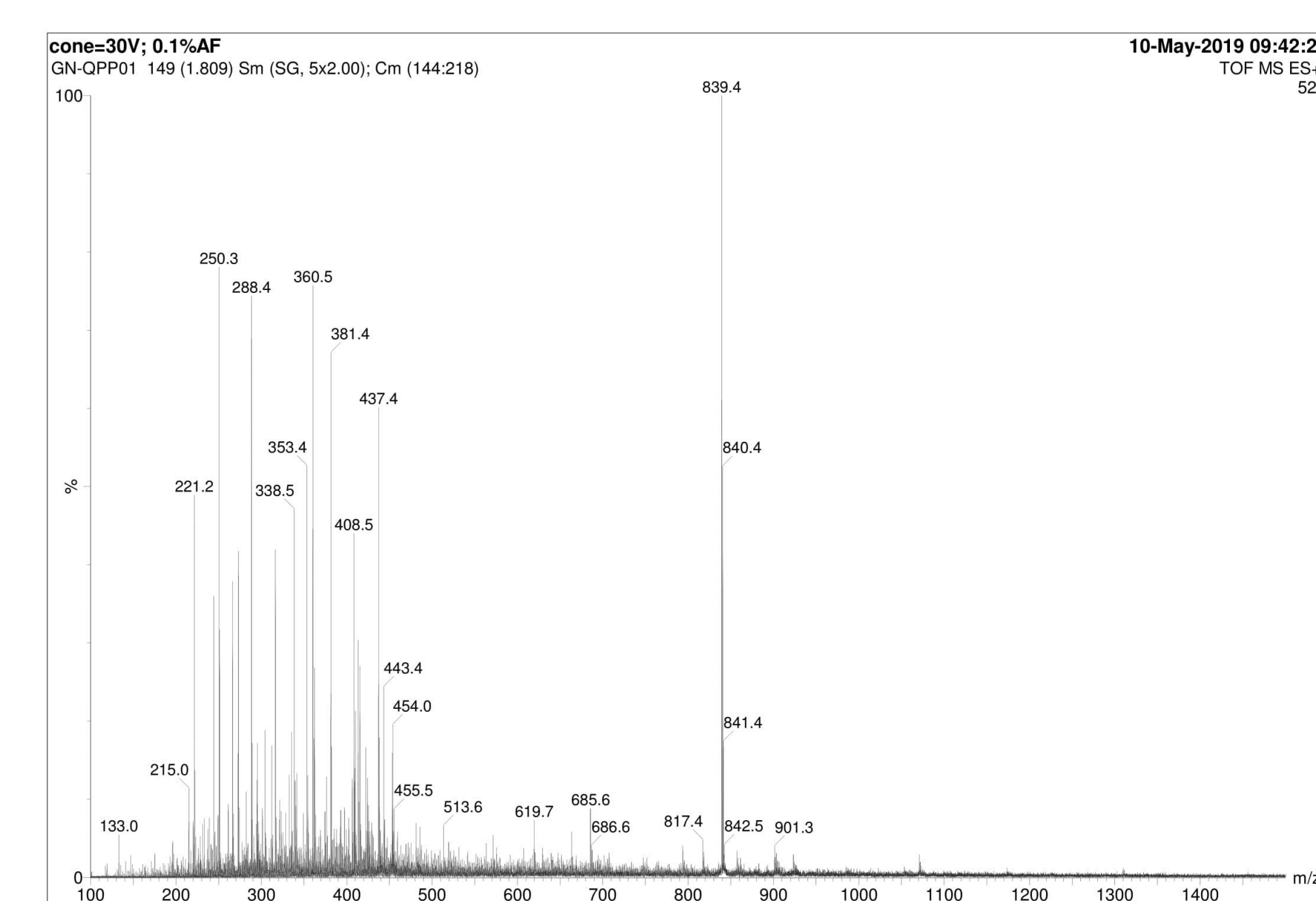


Figure 2. Mass spectroscopy **P-2**

Conclusion

In summary, we report the synthesis of *trans*-A₂B₂ porphyrins can be effectively synthesized from dipyrromethanes and quinoline aldehyde derivatives. Usually, the low yield of this reaction is being studied in order to improve it, as well as the use of other type of aldehydes is being carried out.

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