Journal of Pharmacognosy and Phytochemistry

Available online at www.phytojournal.com

**E-ISSN:** 2278-4136
**P-ISSN:** 2349-8234
JPP 2015; 3(6): 140-144
Received: 11-02-2015
Accepted: 25-03-2015

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# A new Dihydronaphtaquinone from *Dianella ensifolia* L. Redout

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**Abstract**
A new dihydronaphtaquinone 2-hexyl-3-(2-hydroxyethyl)-2,3-dihydronaphtaquinone 1-4, which was named armandinol, was isolated from the leaves of Dianella ensifolia L.Redouté, together with two known quinones. The structure of the new compound was elucidated using spectroscopic methods, mainly 1D and 2D NMR.

**Keywords:** Dianella ensifolia; dihydronaphtaquinone; armandinol, NMR

## 1. Introduction
The genus Dianella belongs to the family Liliaceae, comprises about 21 species, distributed generally in Tropic Asia, Australia and the Pacific. Dianella ensifolia L.Redouté, species recorded in Madagascar was collected in a village which name is Betafo, not far from the capital. This plant is not really used in traditional Malagasy medicine. However, according to the local people, the leaves are used an infusion as an exciting brain cells and a remedy against constipation.
Although previous phytochemical research on Dianella ensifolia L.Redouté revealed phenolic and quinone compounds isolated from the root of the plant [1]. In our chemical investigation, a new dihydronaphtaquinone, 2 - hexyl -3 - (2-hydroxyethyl) -2, 3-dihydronaphtoquinone 1-4 (**1**) with two known quinones, chrysophanol (**2**) and isoeugenitol (**3**) were isolated from the leaves of Dianella ensifolia L. Redouté by column chromatograph. The structure of the new compound was elucidated using 1D and 2D NMR spectroscopic data. To the best of our knowledge, this is the first report on the existence of this compound from natural source.

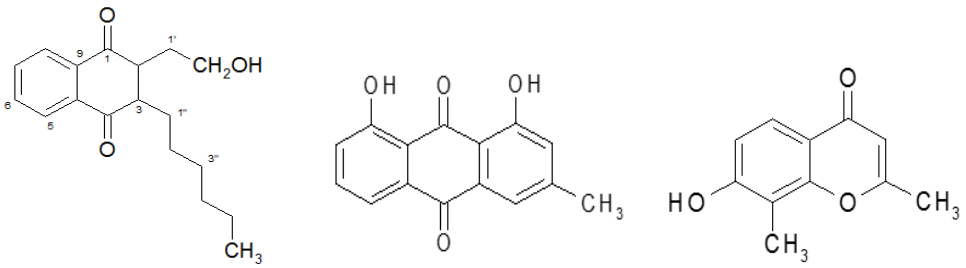



**Fig 1:** Structure of compound **1**, **2** and **3**

## 2. Materials and Methods
### 2.1. General
Melting points was measured with the melting point apparatus of Electrothermal and was not corrected. NMR spectra were recorded with a Brüker AV-400 and AV-500 with a cryoprobe for 1H, BBD, APT, HSQC, and HMBC. Chemical shift values are in δ(ppm) using the peak signals of the solvent $CDCl_3$ ($\delta_H$ 7.28; and $\delta_C$ 70.00) as reference, and coupling constants are reported in Hz. ESIMS data were measured with a Finnigan MAT95 spectrometer (70eV) with perfluorokerosene as a reference substance for HR-EI-MS. Column chromatography was performed on silica gel 60 (6.3-20 µm) (Merck, Darmstadt, Germany). Normal-phase silica gel 60 TLC plates (w/UV 254) were used for fraction detection. The spot were visualized using UV light at 254 nm and spraying with vanillin-sulfuric acid reagent.

### 2.2. Plant Material
The leaves of Dianella ensifolia were collected in august 2011 in one village next to Antananarivo, the capital of Madagascar. The plant was authenticated at the botanical and zoological park of Tsimbazaza Antananarivo Madagascar where a voucher specimen is deposited under the reference number DIA 011-215.

### 2.3 Extraction and Isolation
Powdered dried of leaves from Dianella ensifolia (400 g) were extracted with 96% EtOH at room temperature. Evaporation of EtOH under reduced pressure gave a brown residue (20, 67 g). The residue was later suspended in $H_2O$, and partitioned with Hexane, $CH_2Cl_2$ and n-BuOH. The Dichloromethane extract (3, 48g) was applied to a silica gel column with Hexane and Acetone as binary mixtures of increasing polarity afforded 12 fractions (Fr. F1-F12). Fr. F1 (Hexane – Acetone 95:05) was isolated on silica gel eluted with Hexane - Acetone step gradients (90:10→70:30) to give 4 subfractions (Fr. F5-1- F5-4). Further purification of Fr. F5-1 was applied to column chromatography on silica gel with $CH_2Cl_2$- Acetone (95:5→80:20) to obtain compound 1 (8.0 mg). Fr. F10 (Hexane – Acetone 5:5) was isolated on silica gel eluted with $CH_2Cl_2$ – Acetone (90:10→70:30) to obtain compound (**2)** (15 mg) and 3 (11 mg).

## 3. Results and Discussion
### 3.1. Structure elucidation
Compound (**1**) was yellow oil with melting point of 124-125 °C. Its molecular formula was determined as $C_{18}H_{24}O_3$, on the basis of the HR-MS (positive) at m/z 288.1766 (calc. 288.1745). Observation of symmetrically oriented four-spin AA'BB' type signals at δ= 7.57 ppm for H-6 and H-7 (ddd, J= 7.88, 7.37, 1.38Hz) and δ=7.69 ppm for H-5 and H-8 (ddd, J= 7.86, 1.38, 1 Hz) in the aromatic proton region of the $^1$H-NMR spectrum including a signal at 1,68 ppm for H-2 and H-3 (dddd, J= 9.12, 8.37, 4.11, 1.20 Hz) . The signal at δ=167,78 ppm attributed to two carbonyls carbon, two signals of an aromatic ring at δ=130.67 ppm and δ=128.62 ppm corresponding to four olefinics carbons in the $^{13}$C-NMR spectrum, suggested the presence of a dihydro-1,4-naphthaquinone skeleton having no substituent in the A-ring [2].

HSQC NMR showed that protons at δ = 7.69 ppm are attached by carbons at δ = 128.62 ppm (C-5, C-8) and protons at δ = 7.56 ppm are linked to the carbons at δ = 130.67 ppm (C-6, C-7). The signal at δ = 132.41 ppm, corresponding to quaternary carbons is attributed to the two carbons at positions C-9 and C-10. The signal at δ = 38.97 ppm is attributed to the carbon at positions C-2 and C-3.

The presence of a long chain moiety in the molecule was indicated by the peaks in the region of weak field. The signal at δ = 4.21 ppm (d, J= 6.31Hz) in $^1$H NMR and δ=68.17 ppm in $^{13}$C NMR spectra suggested the presence of an alcohol function (-$CH_2$OH). The correlations observed in HSQC and HMBC spectra (Figure 2) suggested that a linear chain –$(CH_2)_6$-$CH_3$ is fused to the 2,3-dihydro-1,4-naphthaquinone skeleton and a –$CH_2CH_2$OH group at C-3 and C-2 respectively. The signal at δ = 4.21 ppm (-$CH_2$OH) is correlated with the carbon at δ = 167.78 ppm (C-1, C-4), δ = 38.91 ppm (C-2) and δ = 30.91 ppm (C-1'). Additionally, the proton at δ = 1.68 ppm corresponding to the carbon at δ = 38.91 ppm (HSQC), are correlated with carbons at δ = 28.68 ppm (C-1'') and δ = 22.75 ppm (C-2'').

Thus, the structure of 1 was elucidated as an 2-heptyl-3-(2-hydroxyethyl)-2, 3-dihydronaphtaquinone 1-4 and named armandinol.

Additionally, chrysophanol (2) [3] and isoeugenitol (3) [1] were identified by comparing its $^1$H NMR data with literature.

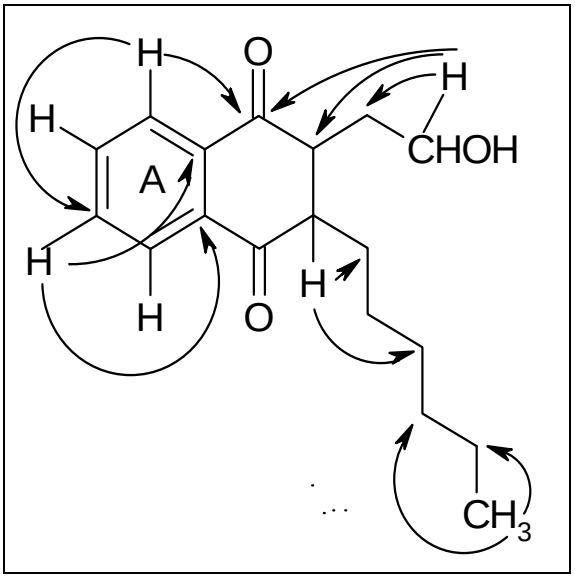


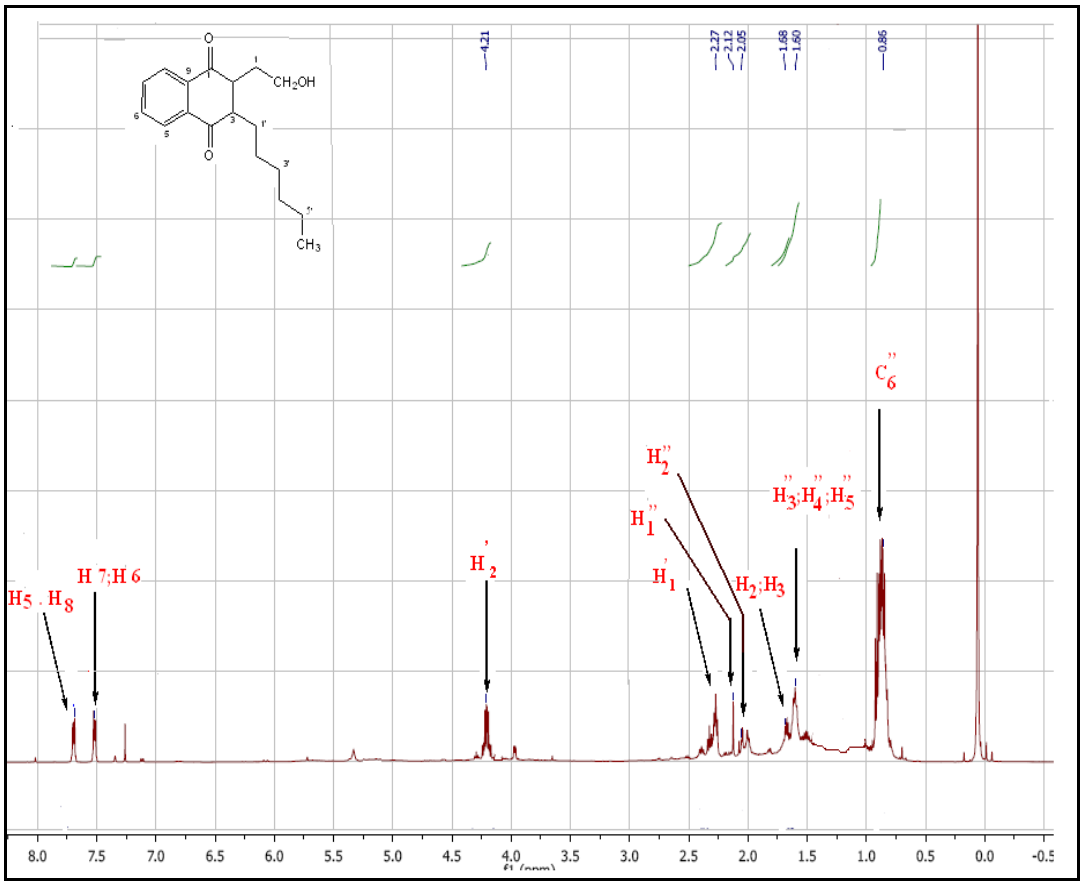

**Fig 2:** The key HMBC correlations of compound 1.

### 3.2 Antioxidant activity
Qualitative antioxidant assay was performed by the standard TLC- DPPH method [4]. The compounds 1, 2 and 3 were spotted on a TLC plate and air dried, then plates were sprayed with 0.002% ethanolic DPPH (2, 2-Diphenyl-1-picrylhydrazyl) solution using an atomizer. Positive activity was detected with the three compounds by the pale yellow spots on a reddish purple background due to the decolourization of DPPH by the antioxidant. Ascorbic acid and gallic acid were used as the positive control [5, 6, 7].

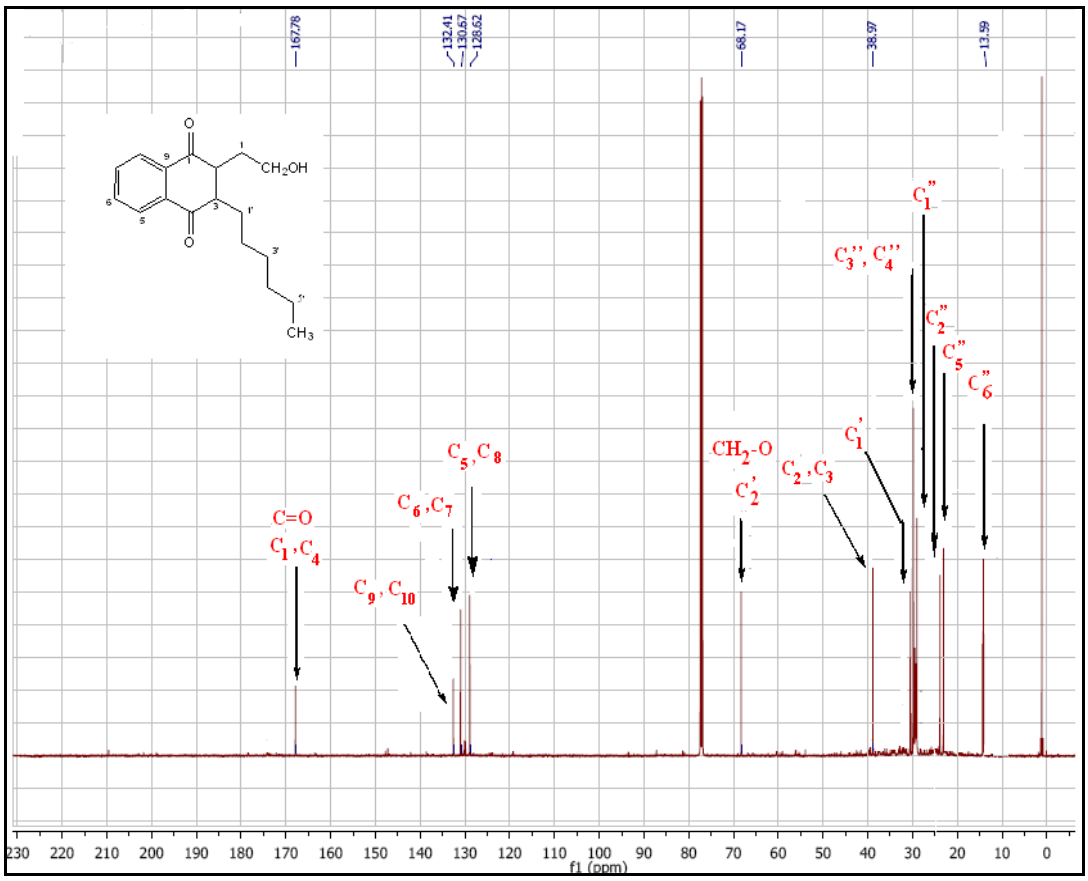
**Table 1:** $^1$H (500 Mhz) and $^{13}$C (100 Mhz) NMR chemical shifts for compound **1** in $CDCl_3$, [a,b]

| Carbon | 1H | 13C |
|---|---|---|
| 1 | | 167,78 |
| 2 | 1,68 m (9.12, 8.41, 4.11, 1.2) | 38,97 |
| 3 | 1,68 m (9.12, 8.41, 4.11, 1.2) | 38,97 |
| 4 | | 167,78 |
| 5 | 7,69 d (7.86, 1.38) | 128,62 |
| 6 | 7,56 t (7.88, 7.37, 1.38) | 130,67 |
| 7 | 7,56 t (7.88, 7.37, 1.38) | 130,67 |
| 8 | 7,69 d (7.86, 1.38) | 128,62 |
| 9 | | 132,41 |
| 10 | | 132,41 |
| 1' | 4,21 | 68,17 |
| 2' | 2,27 | 30,91 |
| 1'' | 2,12 | 28,69 |
| 2'' | 2,05 | 22,75 |
| 3'' | 1,68 | 29,36 |
| 4'' | 1,60 | 29,36 |
| 5'' | 1,60 | 21,34 |
| 6'' | 0,86 t | 13,59 |

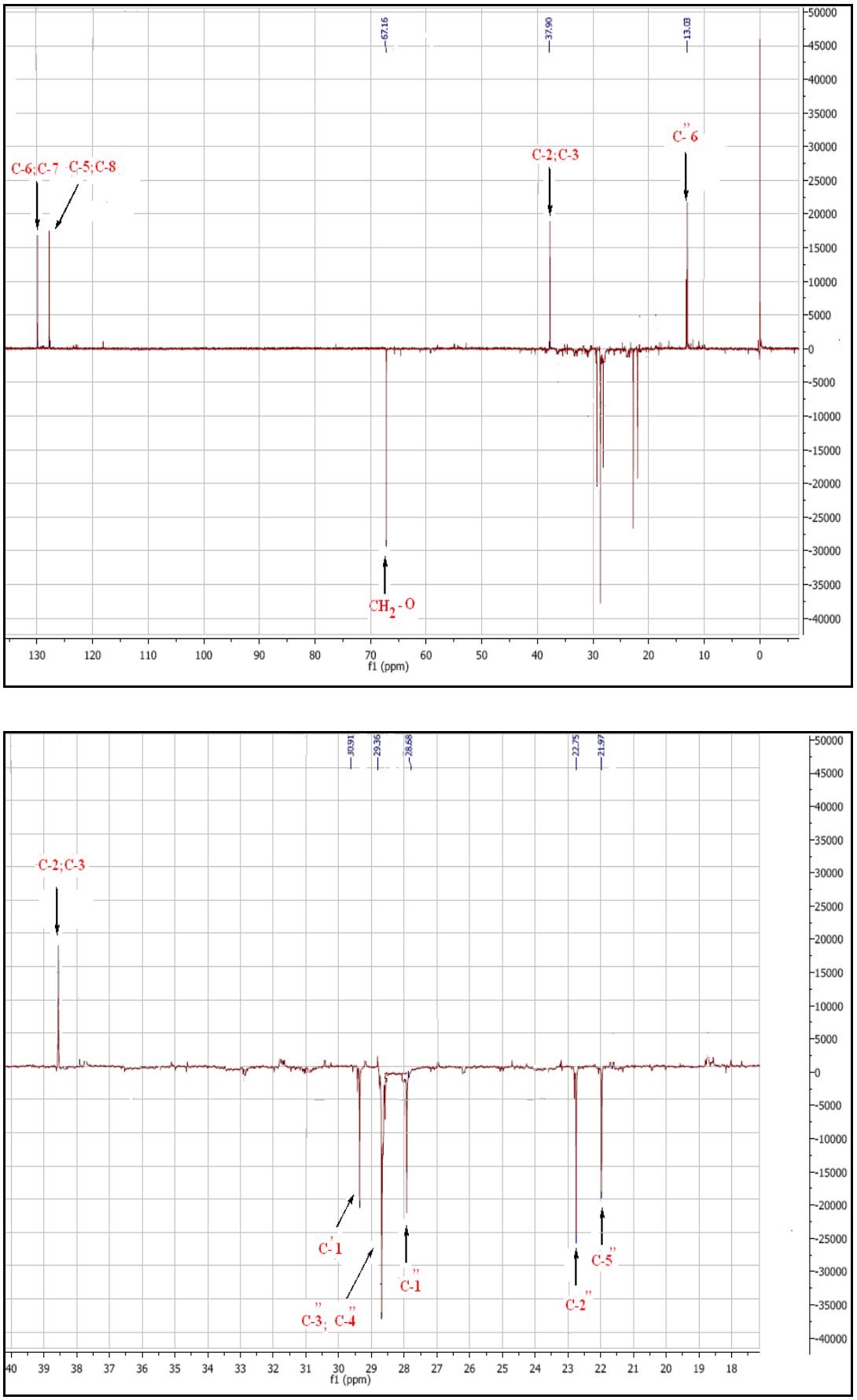
[a] Assignments were confirmed by 2D experiments.
[b] δ ppm, 500MHz for $^1$H and 100 Mhz for $^{13}$C; multiplicities values (Hz) in parenthese.



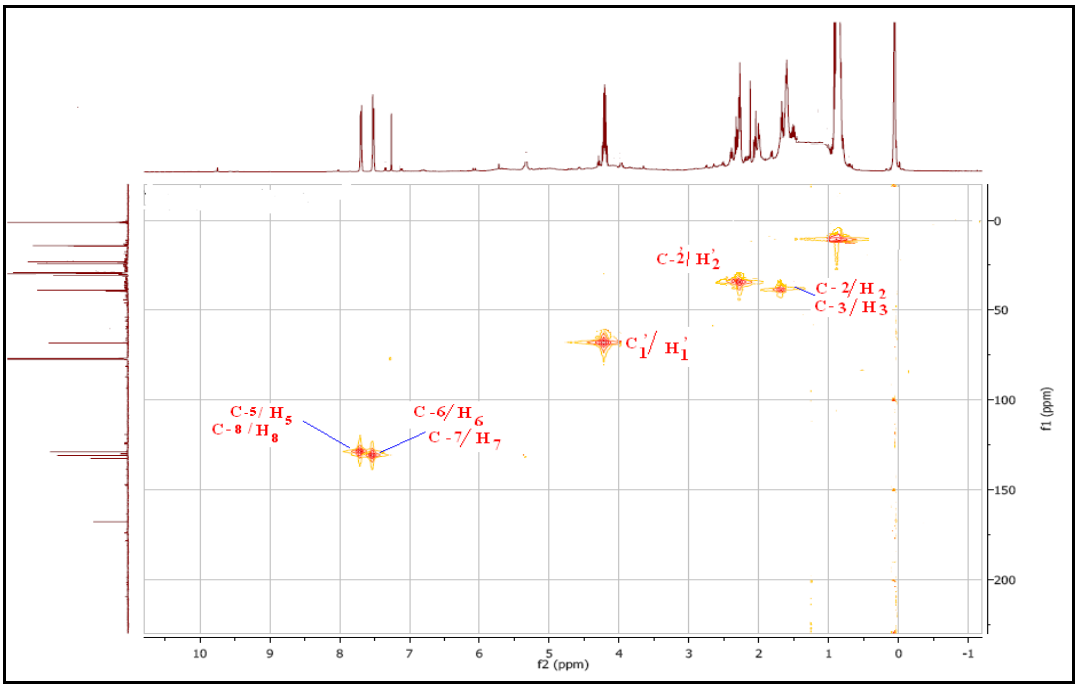

**S1:** [1]H-NMR spectrum of compound 1



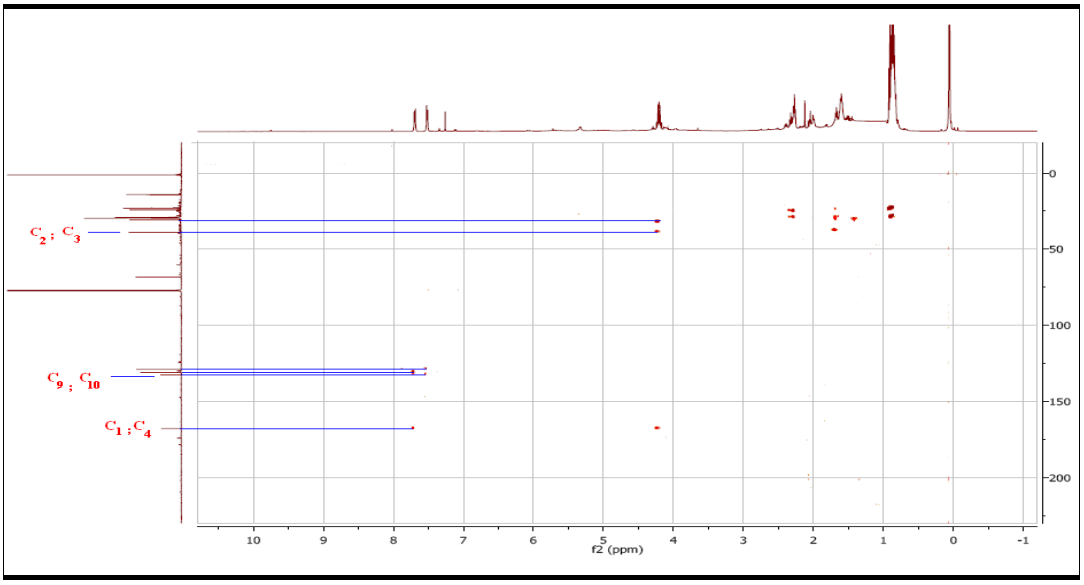

**S2:** [13]C-NMR spectrum of compound 1




**S3:** DEPT spectra of compound 1




**S4:** HSQC spectrum of compound 1




**S5:** HMBC spectrum of compound 1

**4. Acknowledgments**

The authors are grateful to the financial support of D.A.A.D (Deutscher Akademischer Austauschdienst) from its re-invitation program to Dr. Rivoarison Randrianasolo and to the Organic Chemistry Institute of the University of Hanover for EIMS and NMR spectra.

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