Electronic Supplementary Information (ESI)

Selective synthesis of α,β-unsaturated aldehydes from allylic alcohols using oxidatively supplied hydrogen peroxide from electrochemical two-electron water oxidation

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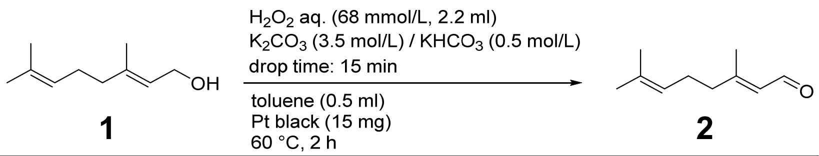
Contents

1. Oxidation of geraniol using aqueous H_2O_2 solution

Aqueous H_2O_2 solution was made by adding K_2CO_3 (3.5 mol/L) and $KHCO_3$ (0.5 mol/L) to an industrially purchased H_2O_2 and it was diluted to aqueous H_2O_2 solution (68 mmol/L) by an ion-exchange water.

Table S1. Screening of reaction time. [a]



Entry	Time(h)	conv. of 1 (%)[b]	Yield of 2 (%)[b]	selectivity(%)[c]
1		65	62	95
2	0.3	62	60	97
3		58	58	>99
4		81	81	>99
5	1	79	79	>99
6		76	76	>99
7		90	88	98
8	2	86	86	>99
9		94	93	>99
10		87	87	>99
11	3	87	87	>99
12		88	88	>99

[a]Reaction conditions are as follows: **1** (0.15 mmol), Pt black (15 mg), toluene (0.50 mL), H_2O_2 aq. by 2e-WOR (68 mmol/L, 2.2 ml, 0.15 mmol), 60 °C, 2.0 h. [b]Determined by GC analysis based on **1**. [c]Selectivity = (Yield of **2**) / (Conversion of **1**) x 100 (%).

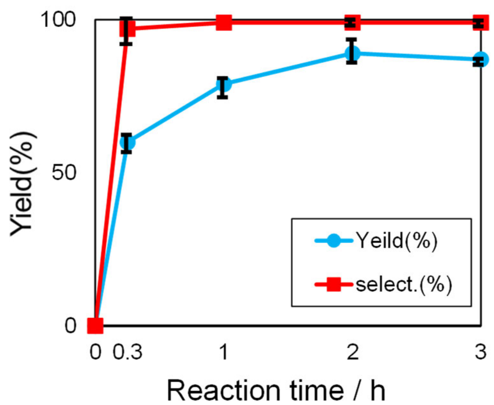


Fig. S1. Screening of reaction time (plots of yields of **2** and selectivity).

2. XRD spectra of (111) plane in Pt black

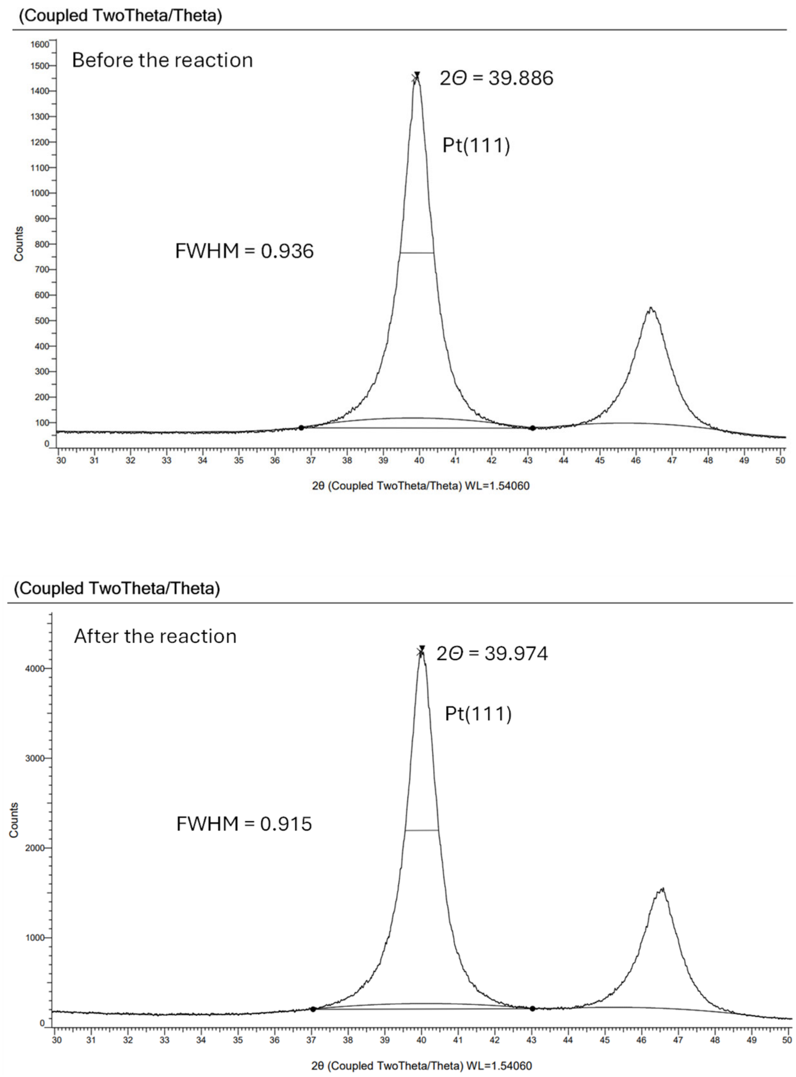


Fig. S2. XRD spectra of (111) plane in Pt black (upper: before the reaction, lower: after the reaction).

3. Time dependence of potential about oxidative H_2O_2 production on FTO anode

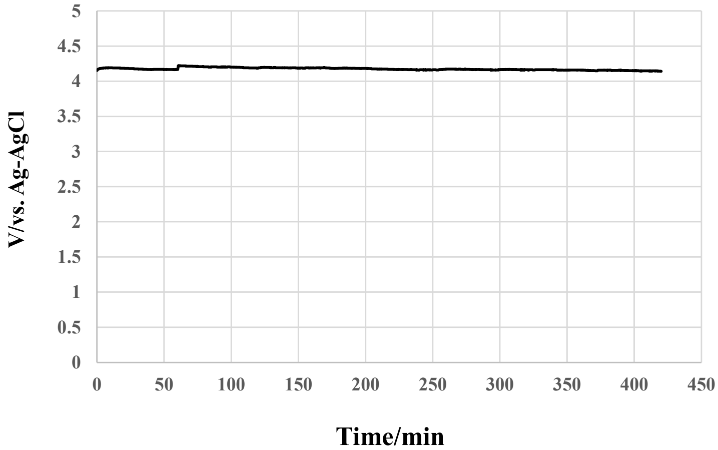


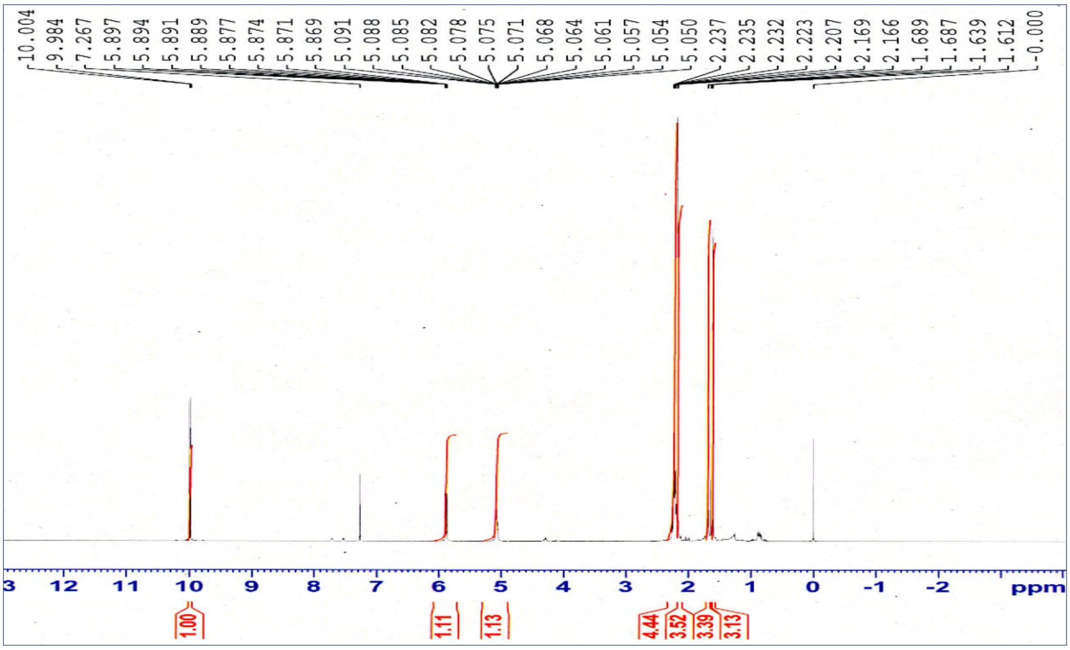
Fig. S3. Time dependence of potential about oxidative H_2O_2 production on FTO anode at constant current (50 mA). Aqueous solution (3.5 mol/L) of K_2CO_3/0.5mol/L $KHCO_3$ (pH 10.8) with an ice bath (3-5 °C).

4. NMR Spectra of α,β-unsaturated aldehydes

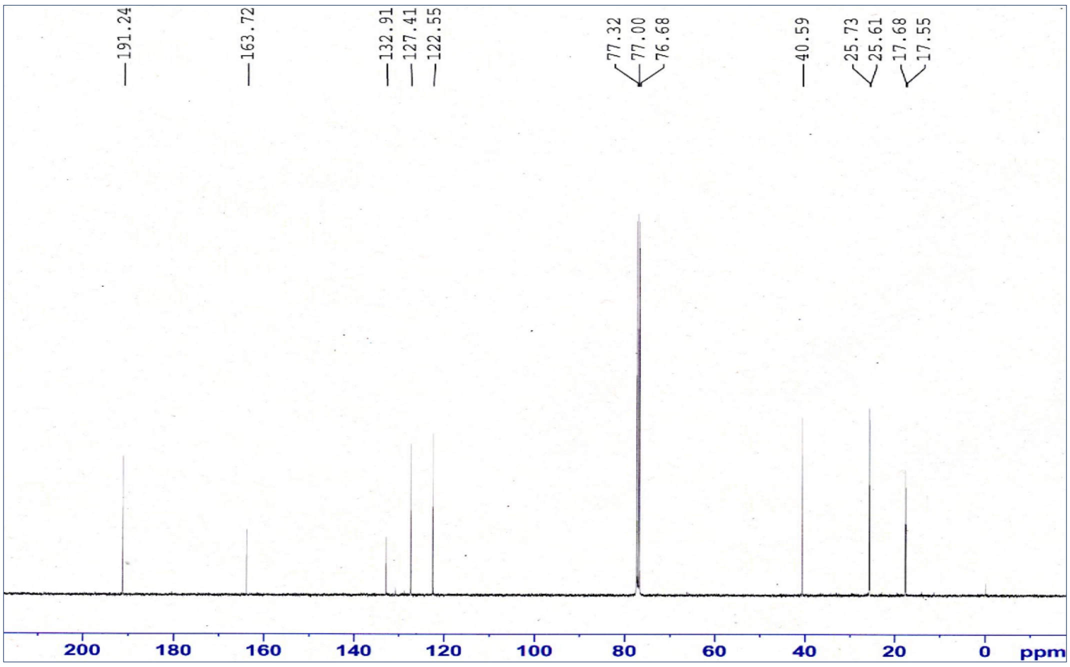
The NMR spectroscopic data of the synthesized compounds **2**, **10–15** agreed well with the NMR data reported by the production through another methods.[a-c]

Geranial (2)[a]

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)

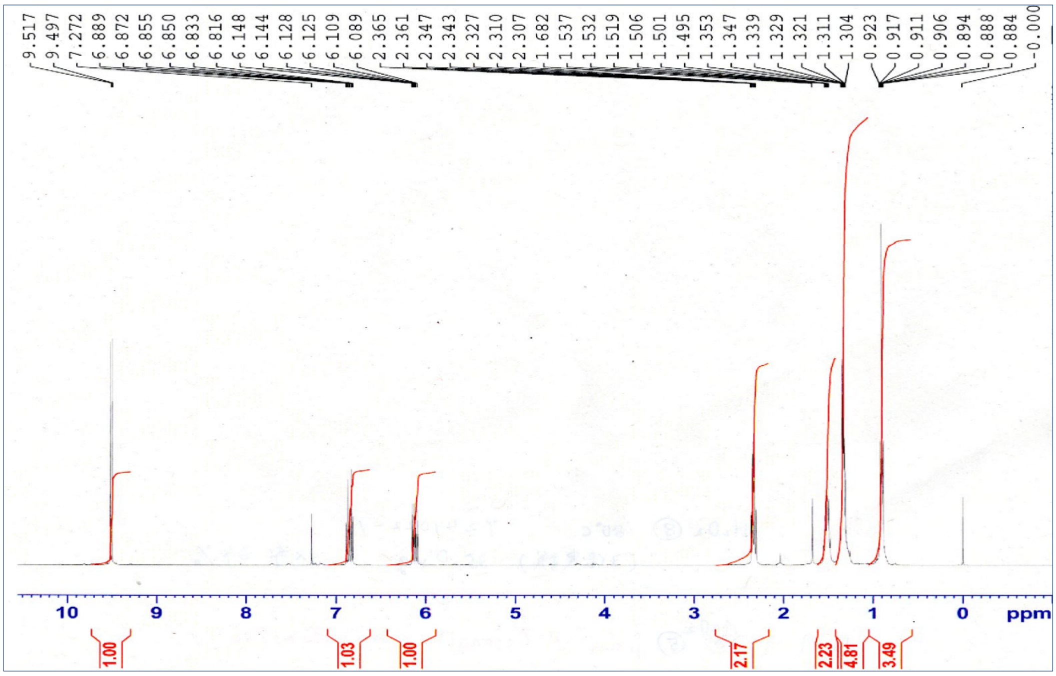


^{13}C NMR (100MHz, $CDCl_3$, 25 °C)

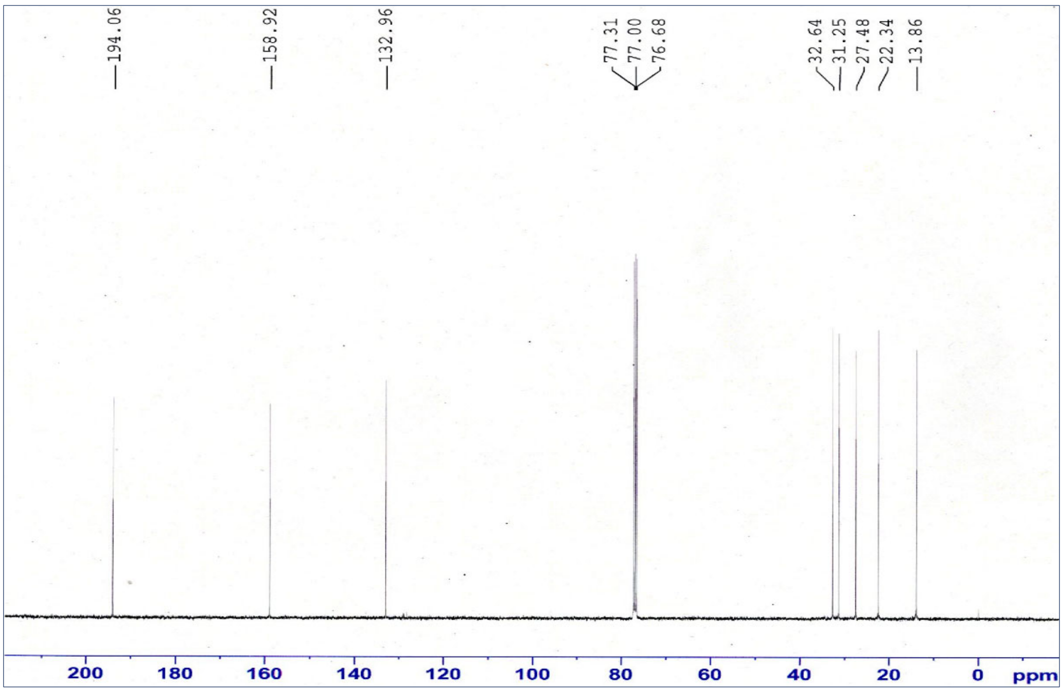


(*E*)-2-octen-1-al (10)[b]

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)

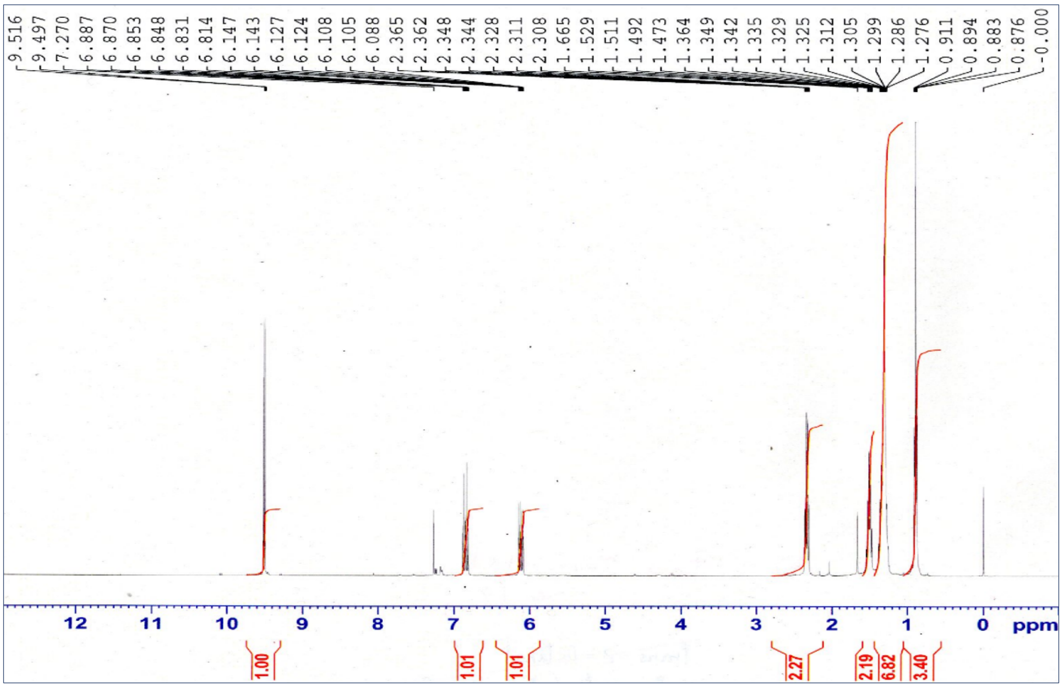


^{13}C NMR (100MHz, $CDCl_3$, 25 °C)

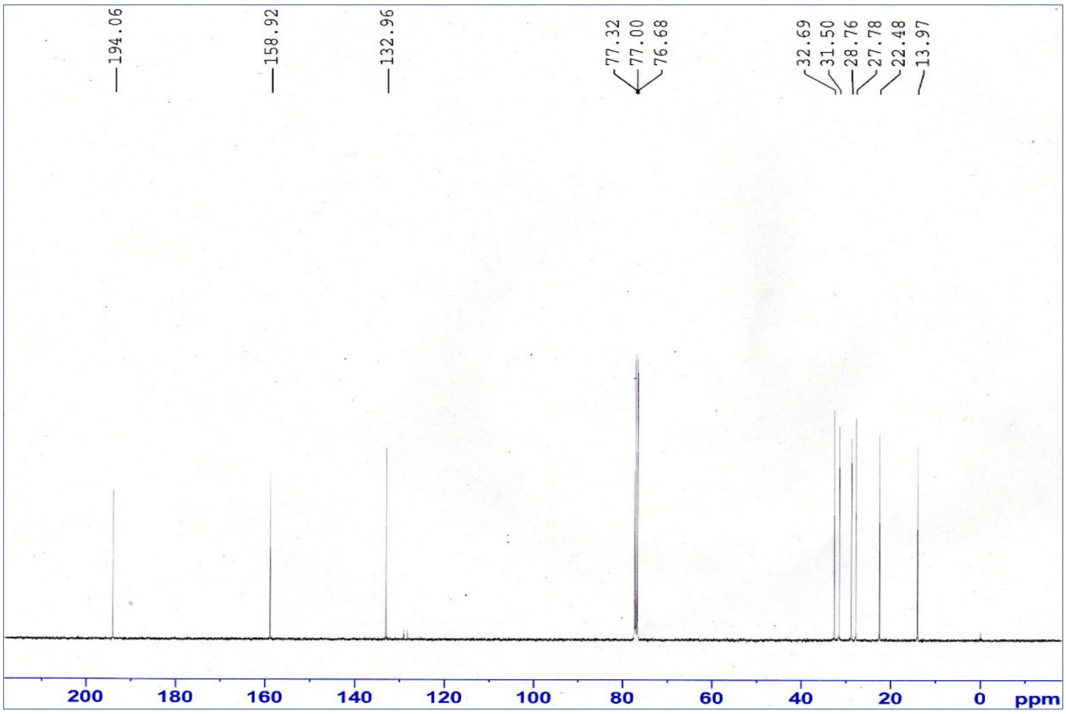


(*E*)-2-nonen-1-al (11)[b]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

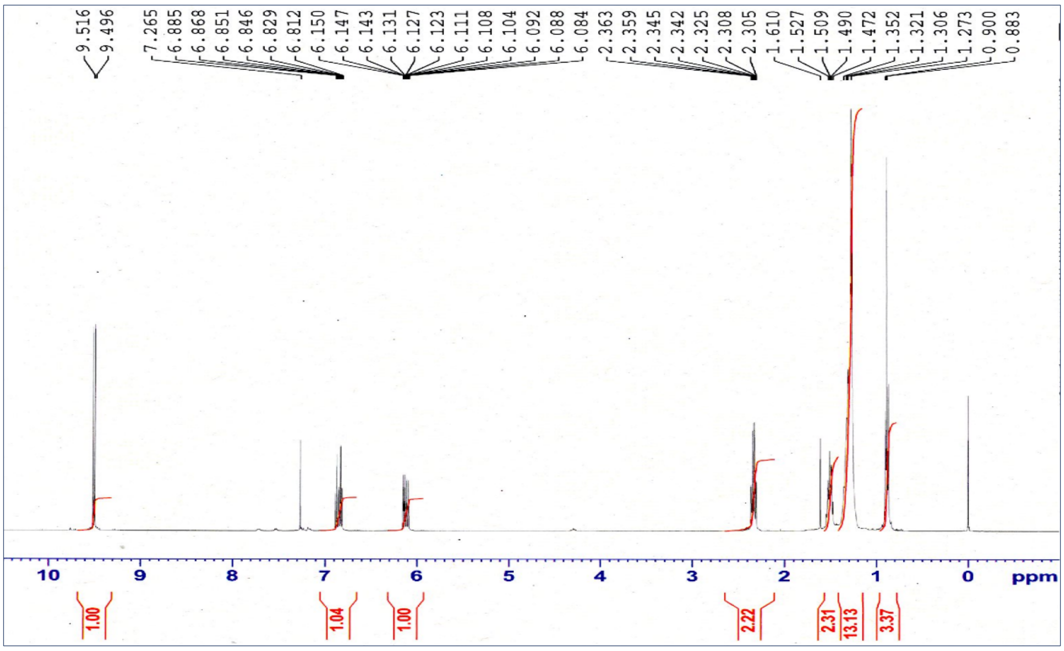


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

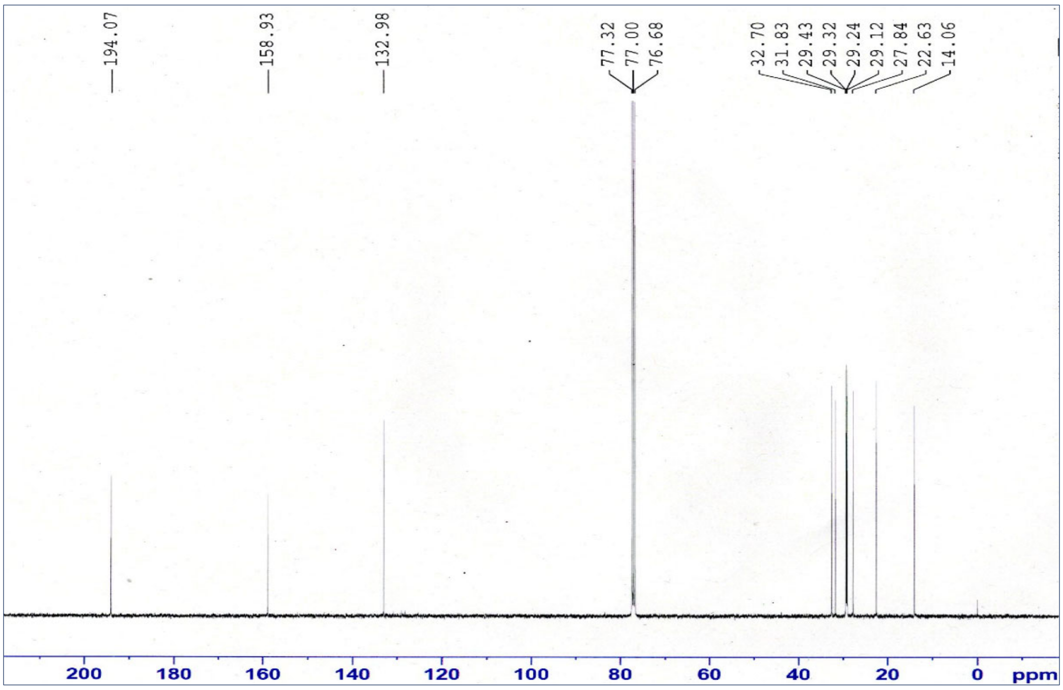


(*E*)-2-dodecen-1-al (12)[c]

^1H NMR (400 MHz, $CDCl_3$, 25 °C)

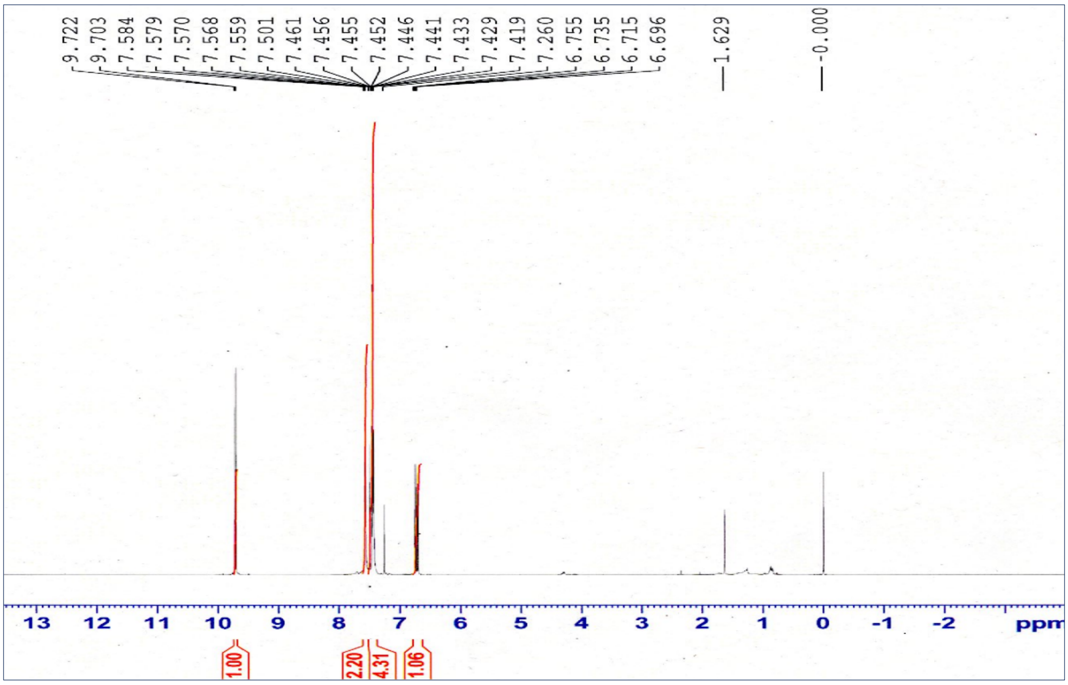


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

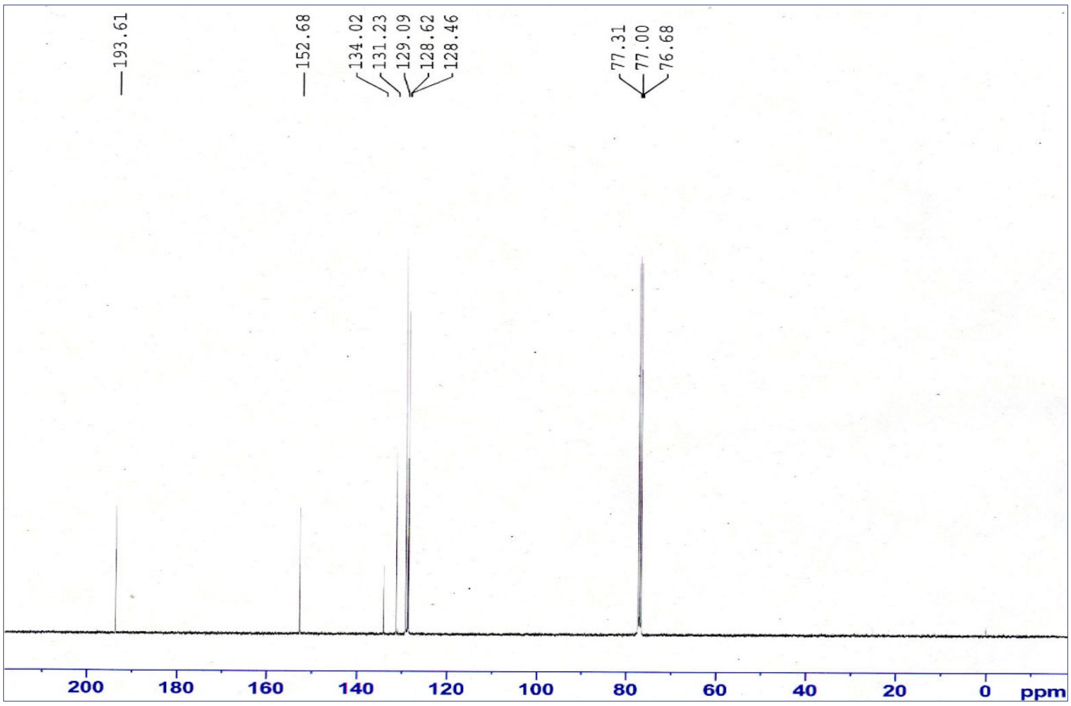


(*E*)-cinnamaldehyde (13)[b]

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

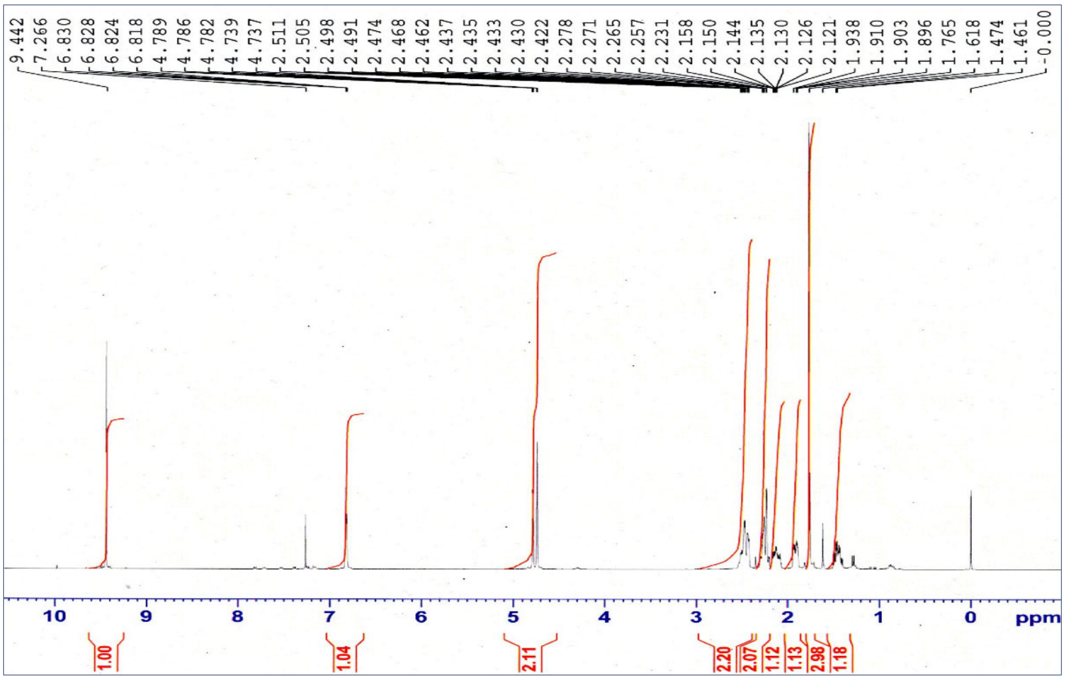


^{13}C NMR (100MHz, $CDCl_3$, 25 °C)

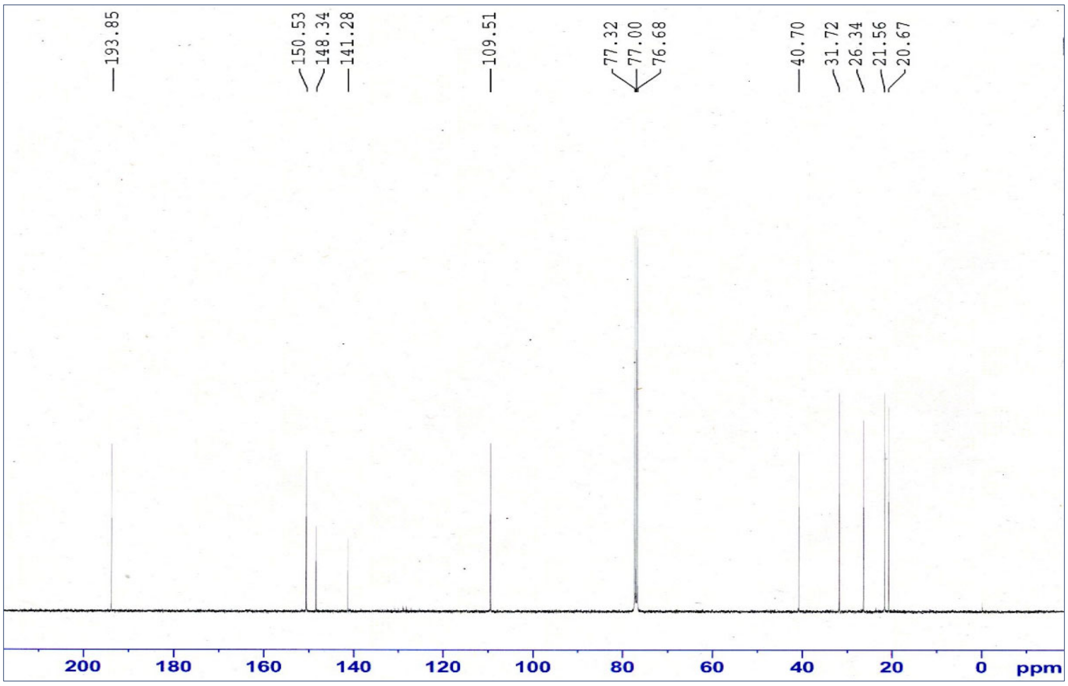


Perillaldehyde (14)[b]

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)

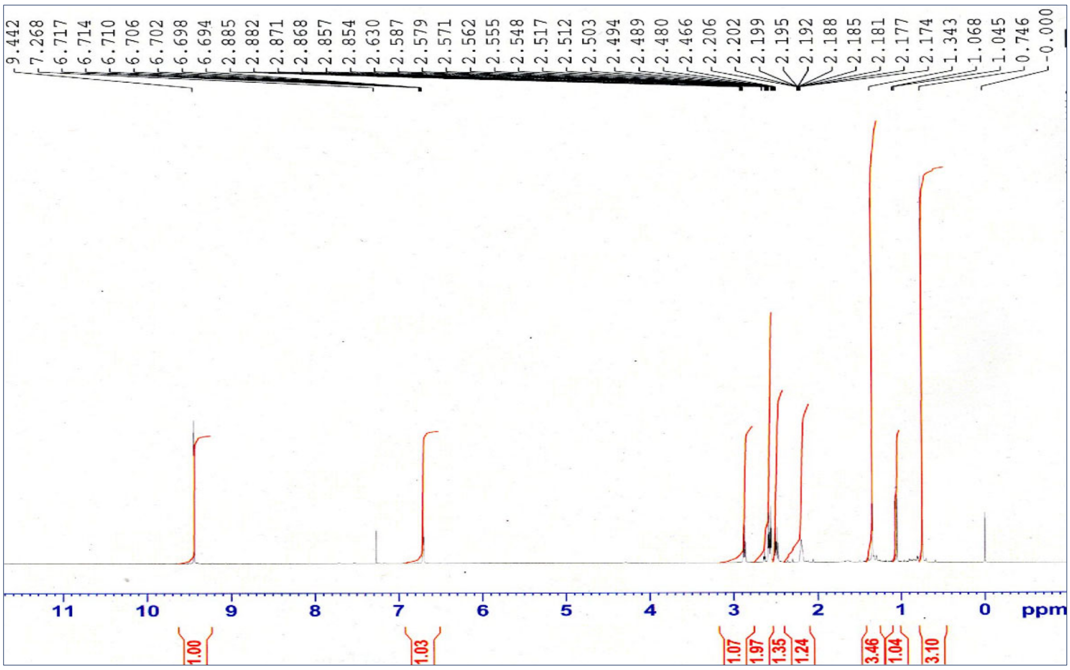


^{13}C NMR (100MHz, $CDCl_3$, 25 °C)

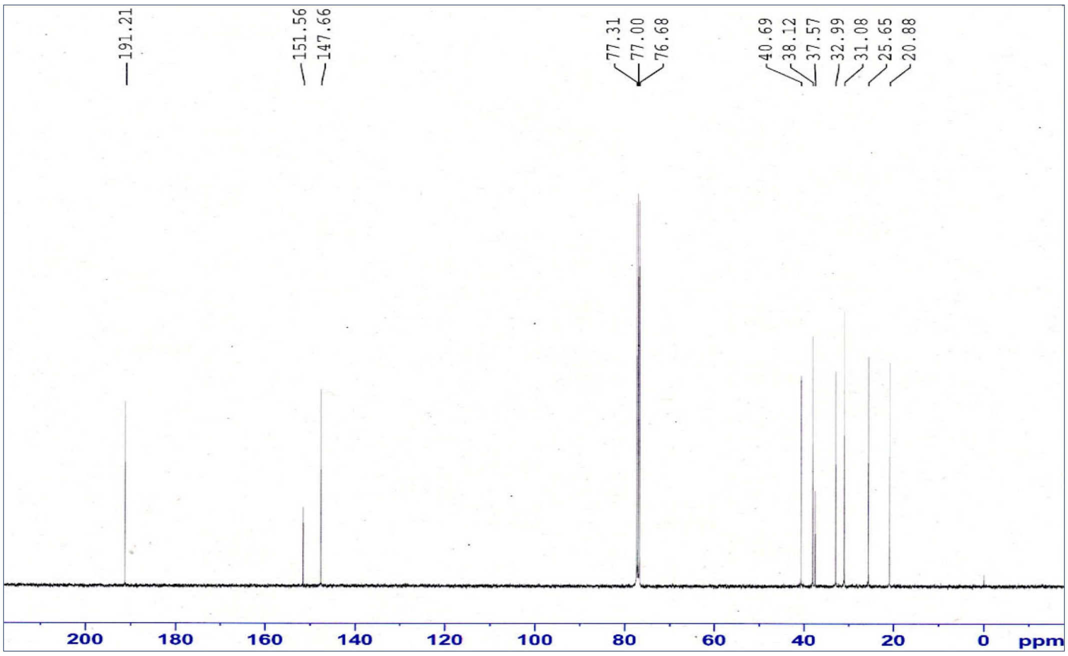


Myrtenal (15)[b]

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)



Ref. (a) J. Holz, S. Doerfelt and A. Börner, *Adv. Synth. Catal.*, 2017, **359**, 4379; (b) SDBSWeb: https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology(AIST), Nov. 15, 2024); (c) T. Yoshida, M. Murai, M. Abe, N. Ichimaru, T. Harada, T. Nishioka and H. Miyoshi, *Biochem.*, 2007, **46**, 10365.