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ONE-STEP SYNTHESIS OF 4(2′-BROMO PROPYL)-PHENOLS FROM NATURALLY OCCURING ALLYL ARYL ETHERS USING BORON TRIBROMIDE

Ajoy Kumar Bauri*

Bio-Organic Division, Bhabha Atomic Research Centre Trombay, Mumbai 400085, India.

***Corresponding Author: Ajoy Kumar Bauri**
Bio-Organic Division, Bhabha Atomic Research Centre Trombay, Mumbai 400085, India.

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ABSTRACT
A variety of naturally occurring allyl aryl ethers were demethylated at low temperature using 1.2 equivalent boron tribromide producing respective phenols along with hydro bromination of allylic double bonds. In general, boron tribromide is used as a demethylating agent to cleave the ether linkage to yield phenols. Notably, experimental result revealed that allyl aryl ethers would provide quantitative yield of 2-bromo alkyl phenols when 1.2 equivalent of boron tribromide was used as reagent. The respective alkyl bromo phenols were obtained in the enantiomeric ratio 1:1 as established by chiral HPLC.

KEYWORDS: Methyl ether of allyl benzene; boron tribromide; cryo-temperature; demethylation; hydro-bromination at allylic double bond.

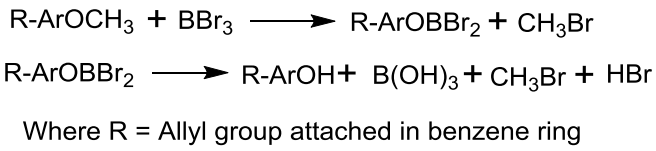
INTRODUCTION

Allyl aryl ethers were isolated from different natural resources and they were used as substrates to demethylate using boron tribromide. While demethylation using boron tribromide, it has been observed that cleavage of allyl ethers to form respective phenols along with hyro bromination of allylic double bond. Allylic double bond undergoes hydro bromination while on demethylation of allyl aryl ether using boron tribromide under cryogenic condition using dichloro-methane as solvent. A series of reaction has been carried out using different allyl aryl ethers to optimize the reaction condition and quantify the yield of the reaction products. The products were identified as a mixture of enantiomer in the ratio of 1:1 established by chiral HPLC.[1-6]

RESULT AND DISCUSSION

In general, boron tribromide is used as demethylating for aryl ethers or substituted aryl ethers. But when methyl ether of allyl benzene used as substrates for demethylation hydro-bromination reaction also took place at the double bond of allyl chain under these circumstances. When the mono or poly methyl allyl aryl ethers (having allylic group in irrespective positions of benzene ring) were used as substrates for demethylation with boron tribromide at low temperature, it produced aromatic phenol with simultaneous occurrence of hydro-bromination of double bond in allylic chain.[6-10] The demethylation time with simultaneous hydro-bromination for all the methyl ethers is about 12 h. Changing the alkyl group with the bulker group of the ethers does not affect the results.[1-5, 8]

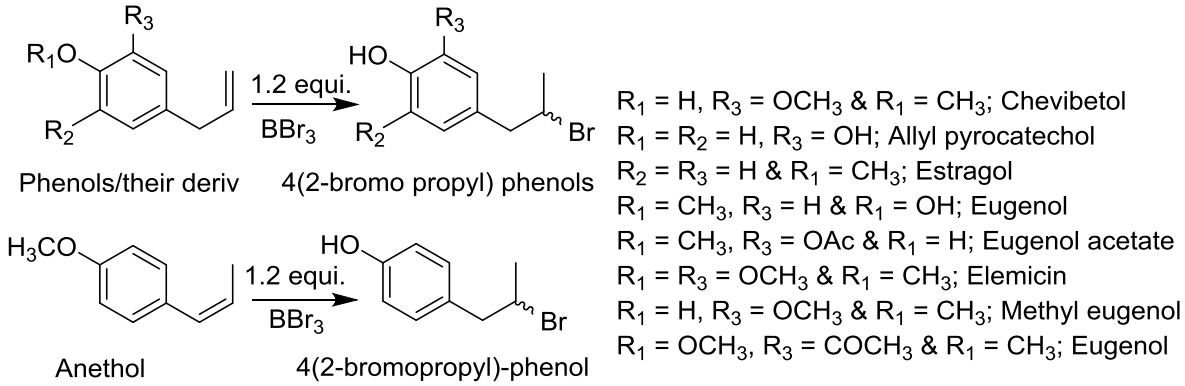
An efficient and single spot method for conversion alkyl aryl ether to with simultaneous hydro-bromination of allyl double bond using boron tribromide in dichloromethane at low temperature. In general, the reaction is depicted below.



Scheme 1: Demethylation reaction using BBr_3 as reagent.

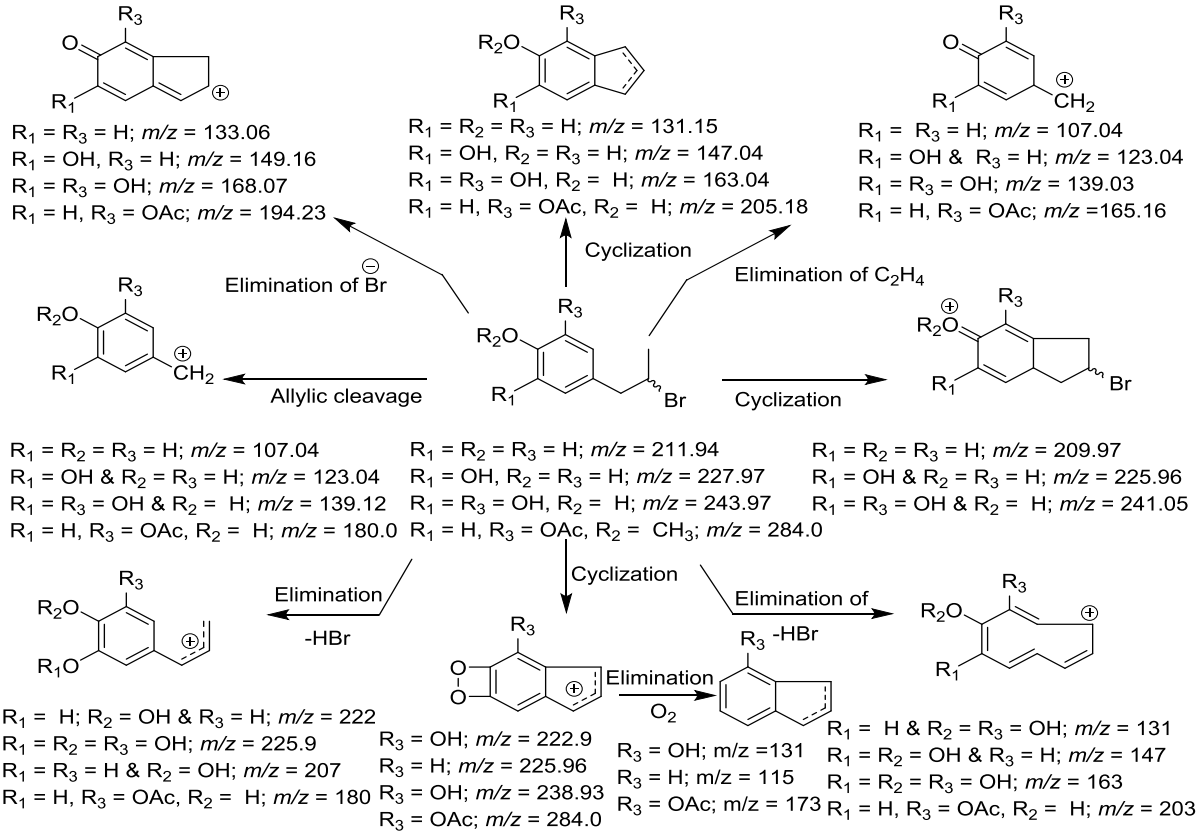
Boron tribromide (BBr_3) is a Lewis acid and one of the most well-known, highly utilized reagents for cleavage of aryl ether to respective phenols and often used in the production of pharmaceuticals in large scale production.[8] This reagent is frequently employed in a 1:1 stoichiometric ratio for ether cleavage up to three equivalents of anisole producing tri phenoxy borane $B(OPh)_3$ prior to hydrolysis along with hydrobromic acid (HBr) as by-product.[8, 9] Probably that HBr reacts with allylic double bond of generated allyl phenols to form bromo hydro phenols.[7-10]

Typical procedure for demethylation using boron tribromide (BBr_3): To precooled stirred solution of aryl ether in dichloroethane at -40 ^{0}C was added a solution of boron tribromide under gentle flow of nitrogen, after that the reaction was stirred for 60 min. The ice bath was removed and the reaction was allowed to progress for another 12 h. The reaction mixture was quenched with ice cold water. The whole mixture was extracted thrice with dichloromethane in 100 mL separating funnel. The combined dichloroethane extract was washed with brine and dried over Na_2SO_4. The extract was evaporated using rota-vapour to yield crude product. The crude product was purified by column chromatography over silica gel to obtain desired product. The structural characterization of desired product has been carried out by spectroscopic and spectrometric methods.[8,10] The reactions were depicted below in scheme 1.



Scheme 2: Demethylation reaction of allyl aryl ethers using boron tribromide.

The mechanism of demethylation of tertiary alkyl ethers proceeds via formation of a complex between the boron centre and the ether oxygen followed by elimination of an alkyl bromide to yield a dibromo (organo) borane and finally boron hydroxide and hydrobromic acid. This hydrobromic acid reacts with the ally double bond to form 4(2-bromo propyl)-phenols according to Markovnikov rule.[11] The structural characterization of these products has been carried out by spectroscopic and spectrometric methods. The mass fragmentations of these products were depicted in the scheme 2 mentioned below.



Scheme 3: Interpretation of mass fragmentation of respective products.

Experimental section

The compounds used in the ether cleavage studies were either isolated from natural resources or chemically transformed isolated phenols to the respective methyl ether using exhaustive methylation using dimethyl sulphate in presence of ignited K_2CO_3 in dry acetone under refluxed condition over a span of time 12 h. The purity and structural characterization of these isolates were established by NMR, GC and LC studies.

Exhaustive methylation of naturally occurring isolated phenols: Naturally occurring isolated phenols were methylated using dimethyl sulphate in dry acetone in presence of ignited K_2CO_3 and freshly distilled $(CH_3)_2SO_4$ under refluxed condition for 12h with continuous stirring followed by usual work up to yield methyl ether of respective phenols. The methylated ether was used as substrates for BBr_3 reaction. Amongst them some of isolates are available as methylated products and this methylated allyl aryl ether was directly used as substrates for boron tribromide reaction.

General procedure for demethylation ether using boron tribromide: Synthons and 10 mL dichloromethane (DCM) were charged in a 25 mL three necked round bottom flask fitted with a magnetic stirrer in presence of argon atmosphere and maintained. The reactant mixture was cooled at -40 ^{o}C using acetone dry ice and boron tribromide was added through a septum with syringe. Cold bath was removed and reaction mixture was stirred for 30 min. The reaction mixture was quenched with ice cold water and extracted with dichloromethane followed by usual worked up. And dried over $MgSO_4$ and concentrated. This procedure was used for cleavage of all these substrates.

General experimental procedure

Boron tribromide was purchased from commercial source and used as received. Melting points were incorrected, IR spectra recorded neat on a Thermal Scientific Nicolet 670 spectrophotometer with Omnic software. Preparative TLC was performed on 0.50 mm thick silica gel 60 F_{254} layer with fluorescent indicator coated on 20 cm x 20 cm glass sheets. TLC plate visualization was accomplished with UV light (254 nm) UV spectra were measured on a Shimadzu UV160 A double beam spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian AR 500 NMR machine.

Isolation of allyl aryl phenols and allyl aryl ether from natural resources and their spectral data

Two allyl aryl phenols chevibetol and allyl pyrocatechol had been isolated from leaves extract of diethyl ether extract of *Piper beetle* by means of column chromatography over silica gel with gradient solvent with a binary mixture hexane and ethyl acetate. The structural characterization of the have carried out by means of spectroscopic and spectrometric methods. The spectral data were given below.

Chevibetol (**1**): Faint yellow liquid; possessed peculiar aromatic pungent smell. ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.00 (d, 1H, *J* = 8.2 Hz, H-6), 6.90 (d, 1H, *J* = 2.8 Hz, H-5), 6.87 (d, 1H, *J* = 8.0 Hz, *J* = 8.0 Hz, H-3) 5.96-5.89 (m, 1H, H-2′), 5.09-5.05 (m, 2H, H-3′), 3.81 (s, 3H, -OCH_3), 3.32 (dd, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 149.5 (C-1), 139.7 (C-2), 137.3 (C-4), 132.8 (C-3′), 126.8 (C-2′), 123.1 (C-5), 119.9 (C-6), 112.4 (C-3), 56.1 (-OCH_3), 39.3 (C-1′). EIMS: *m/z* (%) 206 [M^+] (not appeared), 175 (8.6), 164 (38.9), 149 (19.5), 132 (8.2), 121 (12.8), 107 (13.5), 103, 91 (40.9), 91 (100%, base peak), 77 (45.5), 65 (35.7), 51.0 (49.7).[13-14]

Allyl pyrocatechol (**2**): Pale yellow viscous liquid substance with pleasant aroma. ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.79 (d, 1H, *J* = 8.0 Hz, H-6), 6.71 (d, 1H, *J* = 2.2 Hz, H-5), 6.63 (d, 1H, *J* = 8.0 Hz, *J* = 8.0 Hz, H-3), 5.96-5.88 (m, 1H, H-2′), 5.08-5.03 (m, 2H, H-3′), 3.28 (dd, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 143.49 (C-1), 141.68 (C-2), 137.68 (C-4), 133.39 (C-3′), 121.15 (C-2′), 116.01 (C-5), 115.70 (C-6), 115.62 (C-3), 39.6 (C-1′). EIMS: m/z (%) 206 [M^+], (10.5), 164 (bsae peak, 100%), 149 (40.3), 131 (15.9), 121 (13.50), 103, 91 (14.7), 91 (23.8) 77 (12.9) , 65 (10.9), 55 (8.0).[13-14]

Characterization of allyl phenols from diethyl ether extract of star anise (Illicium verum)

Allyl aryl phenols named as anethole and estragole had been segregated from leaves extract of diethyl ether extract of star anise (in English) by means of column chromatography over silica gel with gradient solvent with a binary mixture hexane and ethyl acetate. The structural characterization of the have carried out by means of spectroscopic and spectrometric methods. The spectral data were given below.

Anethole (**3**): Yellow liquid with pleasant aroma having molecular formula $C_{10}H_{12}O$ established by mass spectrometry. It is present as major constituent in diethyl ether of star anise. The spectral characterization of this component has been carried out spectroscopic and spectrometric methods. The spectral data of anethole is given below.

^{1}H NMR ($CDCl_3$, 200 MHz): δ_H 7.28 (dd, 1H, *J* = 8.2 & 2.2 Hz, H-6), 6.84 (dd, 1H, *J* = 8.2 & 2.2 Hz, H-5), 6.39 (dd, 1H, *J* = 8.2 Hz), 6.17-6.03 (m, 1H, H-2′), 3.80 (s, 3H, OCH_3), 1.87 (d, 2H, J = 6.6 Hz, H-1′). δ_C ^{13}C NMR ($CDCl_3$, 50 MHz): 158.5 (C-1), 130.6 (C-3′), 130.3 (C-4), 126.7 (C-2 & C-6), 123.1 (C-2′), 111.7 (C-2 & C-6), 54.9 (-OCH_3), 18.2 (C-1′). LRESI (positive mode): obs. *m/z* value 171.099 au; calc. m/z 171.079.[14]

Estragole (**4**): A viscus yellow liquid with pleasant aroma having molecular formula $C_{10}H_{12}O$ established by mass spectrometry. It is a viscus yellow liquid with pleasant aroma having molecular formula $C_{10}H_{12}O$ established by mass spectrometry. It is also present as

major constituent in star anise. The spectral characterization of this component has been carried out spectroscopic and spectrometric methods. The spectral data estragole is given below.

^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.12 (dd, 2H, *J* = 8.2 & 2.2 Hz, H-6), 6.85 (dd, 2H, *J* = 8.2 & 2.2 Hz, H-3 & H-5), 5.98-5.92 (m, 1H, H-2′), 5.08-5.04 (m, 2H, H-3′), 3.80 (s, 3H, -OCH_3), 3.34 (dd, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 158.1 (C-1), 138.0 (C-2′), 132.2 (C-4), 129.6 (C-3 & C-5), 115.5 (C-1′), 113.9 (C-2 & C-6), 55.3 (-OCH_3), 39.4 (benzylic C-3′).[13-17]

IR spectrum (neat), ν_{max}: 3365 (brs peak, OH), 3010, 2931, 2857, 1713, 1605, 1522, 1445, 1282, 1196, 916, 818, 793. LRESI (positive mode): obs. *m/z* 17.099 au; calc. *m/z* 171.079 au.

Characterization of allyl phenols isolated from diethyl ether extract of clove

Eugenol and its acetate had been separated from diethyl ether extract of dried bud of *S. aromatica* by means of column chromatography over silica gel with gradient solvent with a binary mixture hexane and ethyl acetate. The structural characterization of them have been carried out by means of spectroscopic and spectrometric methods. The spectral data were given below.

Eugenol (**5**): A viscus dark yellow liquid owing pleasant aroma; molecular formula $C_{10}H_{12}O$ established by mass spectrometry. ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.84 (d, 1H, *J* = 8. Hz, H-6), 6.69 (dd, 1H, *J* = 8.2 & 2.2 Hz, H-5 & H-3), 5.98-5.92 (m, 1H, H-2′), 5.10 - 5.04 (m, 2H, H-1`), 3.87 (s, 3H, -OCH_3), 3.32 (d, 2H, H-3′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 146.5 (C-1), 144.0 (C-2), 137.9 (C-4), 122.6 (C-2′), 121.3 (C-1), 115.6 (C-5), 114.3 (C-6), 111.2 (C-3), 56.9 (-OCH_3), 40.0 (C-3′). EIMS *m/z* (%): 51 (5.2), 66 (3.4), 77.00 (6.4), 91(3.1), 109 (1.4), 122 (12.2), 137 (100, base peak), 166.1 (23.5) [M^+].[13-17]

Eugenol acetate (**6**): Pale yellow liquid; owing plesant aroma; present substaintial amount in clove. ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H 6.95 (d, 1H, *J* = 8.2 Hz, H-6), 6.78 (d, 1H, *J* = 2.2 Hz, H-5), 6.76 (d, 1H, *J* = 2.2 Hz, H-3), 5.99-5.91 (m, 1H, H-2′), 5.12-5.07 (m, 2H, H-2′), 3.81 (s, 3H, -OCH_3), 3.37 (d, 2H, H-3′), 2.30 (s, 3H, >$COCH_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 169.2 (-$COCH_3$), 150.8 (C-1), 138.9 (C-2), 137.9 (C-4), 122.4 (C-1′), 120.6 (C-6), 116.1 (C-5), 112.6 (C-3), 55.7 (-OCH_3), 40.0 (C-3′), 20.6 (>$COCH_3$). HRESI-MS (positive mode): obs. *m/z* 193.3188 au ; cal. *m/z* 193.086 au.[8-11]

Characterization of allyl phenol isolated from rhizome of *Acorus calamus*

A pale-yellow liquid substance separated from diethyl ether extract of dry rhizome of *Acoras calamus* (vach) by means of column chromatography over silica gel with gradient solvent with a binary mixture hexane and ethyl acetate. It was present as major ingredient. The structural characterization of the constituent has been carried out by means of spectroscopic and spectrometric methods and identified as elemicin. The spectral data of elemicin were given below.

Elemicin (**7**): Pecuilar sented pale yeollow liquid; molecula formula $C_{12}H_{16}O_3$ and mass 208.110 au determined by HR-ESI-MS study. ^{1}H NMR ($CDCl_3$, 200 MHz): δ_H 6.84 (d, 1H, *J* = 2.2 Hz, H-4), 6.53 (d, 1H, *J* = 2.2 Hz, H-6), 5.80-5.735 (m, 1H, H-3′), 5.54-5.33 (m, 1H, H-2′), 3.90 (s, 3H, OCH_3), 3.84 (s, OCH_3, 3H), 3.81 (s, OCH_3, 3H), 1.85 (d, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 50 MHz): δ_C 150.79 (C-2), 147.87 (C-1), 141.55 (C-3), 124.3 (C-2′), 124.1 (C-5), 117.1 (C-1′), 113.1 (C-4), 96.6 (C-6), 55.6 (C_2-OCH_3), 55.1 (C_1-OCH_3), 54.9 (C_3-OCH_3), 13.7 (C-3′).[14-17]

Spectral data of demethylated products of allyl aryl ethers isolated from different spices and medicinal plants

Demethylated chevibetol (**1a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.80 (d, 1H, *J* = 10 Hz, H-6), 6.73 (d, 1H, *J* = 2.2 Hz, H-3), 6.50 (dd, 1H, *J* = 10 & 2.2 Hz, H-5), 4.26-4.22 (m, 1H, H-3′), 3.12 (dd, 1H, *J* = 8.8, & 2.2 Hz, Ha-2′), 2.99-2.92 (dd, 1H, *J* = 8.8, & 2.2 Hz, Hb-2′) 1.69 (d, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 143.5 (C-1), 142.4 (C-2), 131.8 (C-4), 121.9 (C-6), 116.4 (C-5), 115.4 (C-3), 51.1 (C-2′), 46.9 (C-3′), 25.7 (C-1′).[8-11]

Demethylated methyl ester of allyl pyrocatechol (**2a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.80 (d, 1H, *J* = 10 Hz, H-6), 6.73 (d, 1H, *J* = 2.2 Hz, H-3), 6.50 (dd, 1H, *J* = 10 & 2.2 Hz, H-5), 4.26-4.22 (m, 1H, H-3′), 3.12 (dd, 1H, *J* = 8.8, & 2.2 Hz, Ha-2′), 2.99-2.92 (dd, 1H, *J* = 8.8, & 2.2 Hz, Hb-2′), 1.69 (d, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 143.5 (C-1), 142.4 (C-2), 131.8 (C-4), 121.9 (C-6), 116.4 (C-5), 115.4 (C-3), 51.1 (C-2′), 46.9 (C-3′), 25.7 (C-1′).

Demethylated anethole (**3a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.07 (d, 1H, *J* = 8.8 & 2.2 Hz, H-4), 6.78 (d, 2H, *J* = 8.8 & 2.2 Hz, H-6), 6.14 (brs, 1H, OH), 4.25 (m, 2H, H-3′), 3.17-3.12 (m, 2H), 1.69 (M, 3H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 154.5 (C-1), 130.9 (C-4), 130.5 (C-3 & C-5), 115.4 (C-2 & C6), 51.3 (C-2′), 46.7 (C-3′), 25.6 (C-1′).[8-11]

Demethylated ergasole (**4a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.07 (d, 2H, *J* = 8.8 & 2.2 Hz, H-4), 6.78 (d, 2H, *J* = 8.8 & 2.2 Hz, H-6), 6.14 (brs, 1H, OH), 4.25 (m, 1H, H-2′), 3.17-3.12 (dd, 1H, *J* = 8.8, 6.6 & 2.2 Hz, Ha-3′), 3.01-2.97 (dd, 1H, *J* = 8.8, 6.6 & 2.2 Hz, Hb-3′),1.68 (d, 3H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 154.5 (C-1), 130.9 (C-4), 130.5 (C-3 & C-5), 115.4 (C-2 & C6), 51.3 (C-2′), 46.7 (C-3′), 25.6 (C-1′).[8-11]

Demethylated eugenol (**5a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.80 (d, 1H, *J* = 10 Hz, H-6), 6.73 (d, 1H, *J* = 2.2 Hz, H-3), 6.50 (dd, 1H, *J* = 10 & 2.2 Hz, H-5), 4.26-

4.22 (m, 1H, H-3′), 3.12 (dd, 1H, *J* = 8.8, & 2.2 Hz, Ha-2′), 2.99-2.92 (dd, 1H, *J* = 8.8, & 2.2 Hz, Hb-2′) 1.69 (d, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 143.5 (C-1), 142.4 (C-2), 131.8 (C-4), 121.9 (C-6), 116.4 (C-5), 115.4 (C-3), 51.1 (C-2′), 46.9 (C-3′), 25.7 (C-1′).[8-11]

Demethylated eugenol acetate (**6a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.80 (d, 1H, *J* = 10 Hz, H-6), 6.73 (d, 1H, *J* = 2.2 Hz, H-3), 6.50 (dd, 1H, *J* = 10 Hz & 2.2 Hz, H-5), 4.26-4.22 (m, 1H, H-3′), 3.12 (dd, 1H, *J* = 8.8 Hz & 2.2 Hz, Ha-2′), 2.99-2.92 (dd, 1H, *J* = 8.8, & 2.2 Hz, Hb-2′), 2.34 (s, 3H, >$COCH_3$), 1.69 (d, 2H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 143.5 (C-1), 142.4 (C-2), 131.8 (C-4), 121.9 (C-6), 116.4 (C-5), 115.4 (C-3), 51.1 (C-2′), 46.9 (C-3′), 37.4 (>$COCH_3$), 25.7 (C-1′).[8-11]

Demethylated elemicin (**7a**): ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 6.73 (d, 1H, *J* = 2.2 Hz, H-3), 6.50 (d, 1H, *J* = 2.2 Hz, H-5), 4.26-4.22 (m, 1H, H-3′), 3.12 (dd, 1H, *J* = 8.8, & 2.2 Hz, H_a-2′), 2.99-2.92 (dd, 1H, *J* = 8.8, & 2.2 Hz, H_b-2′) 1.69 (d, 3H, *J* = 6.6 Hz, H-1′). ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 143.5 (C-1& C-3), 142.4 (C-2), 131.8 (C-4), 121.9 (C-6), 116.4 (C-5), 115.4 (C-3), 51.1 (C-2′), 46.9 (C-3′), 25.7 (C-1′).[8-11]

Annexure: Supplimentary information

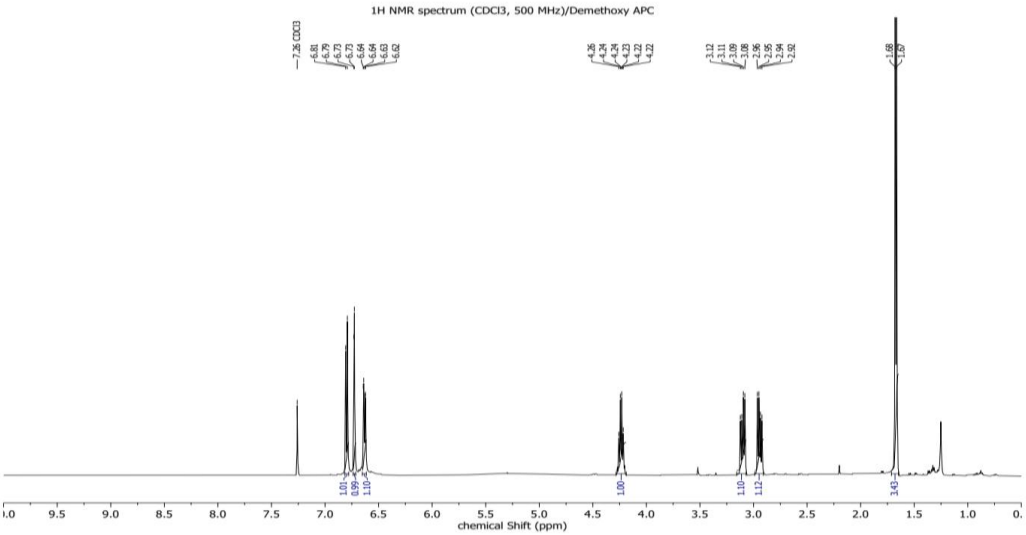


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4(2-bromo propyl) catechol.

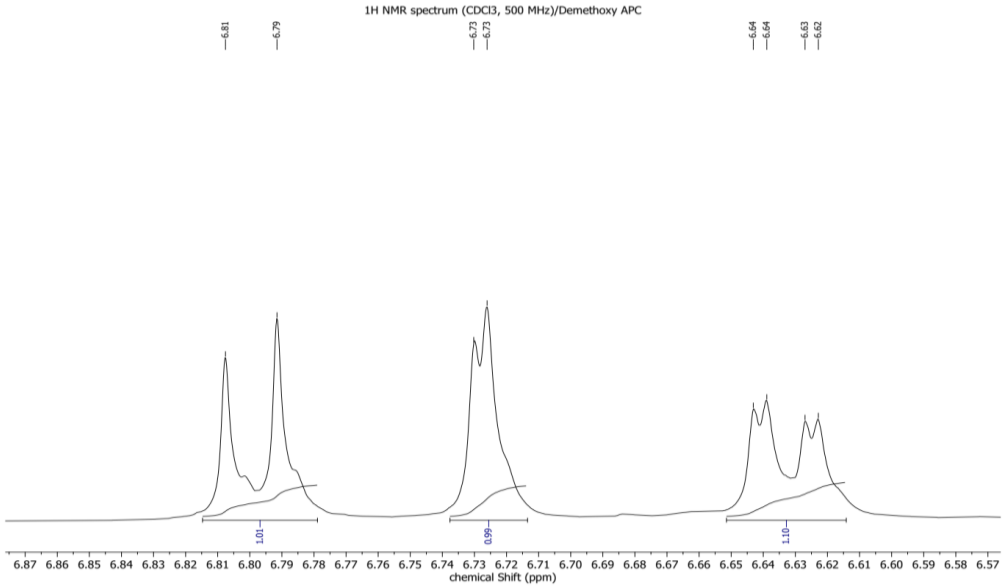


Figure S2: Expansion of ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4(2-bromo propyl) catechol.

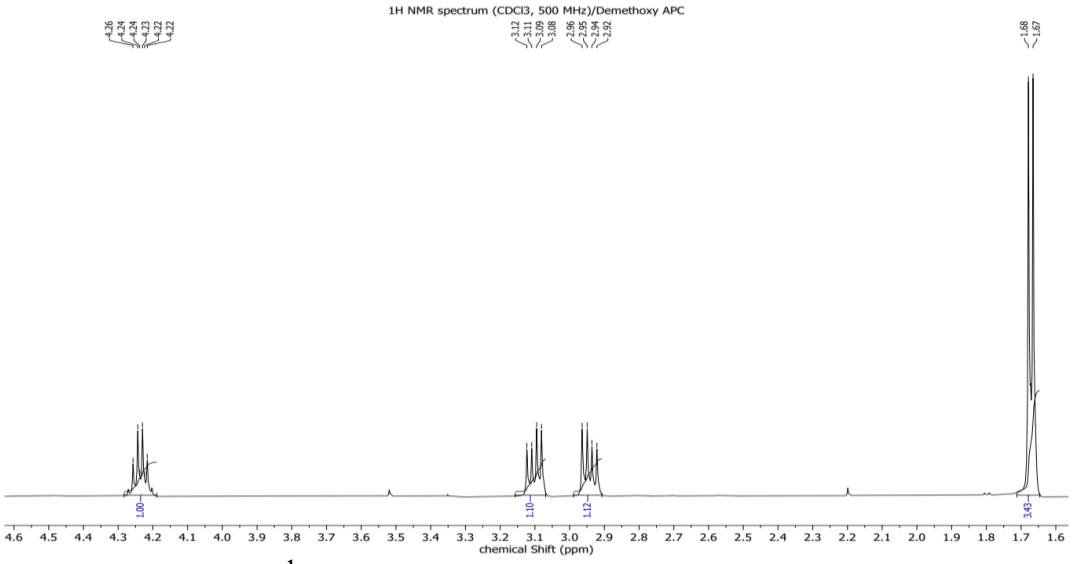


Figure S3: Expansion of ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4(2-bromo propyl) catechol.

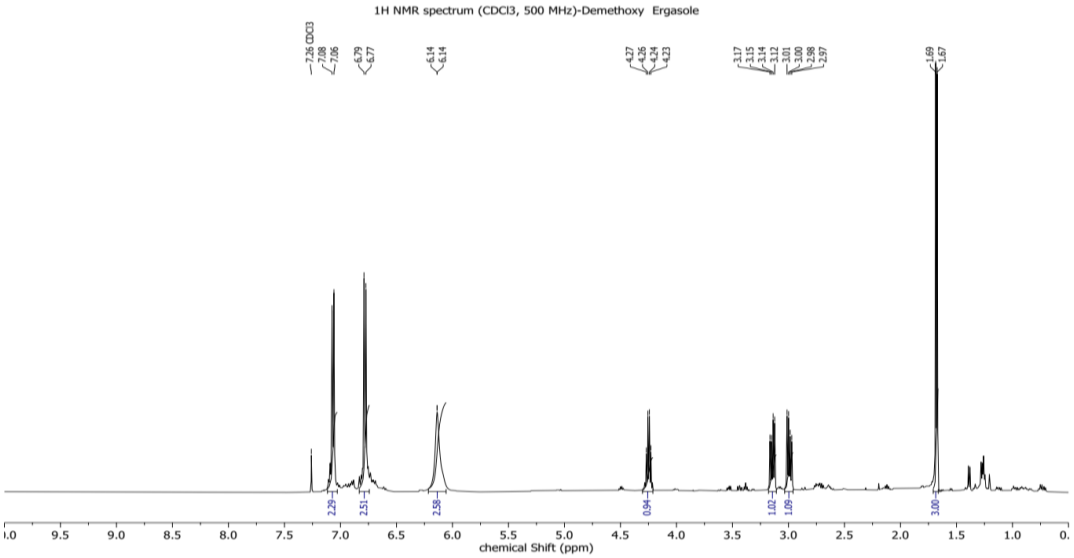


Figure S4: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4(2-bromo propyl) phenol.

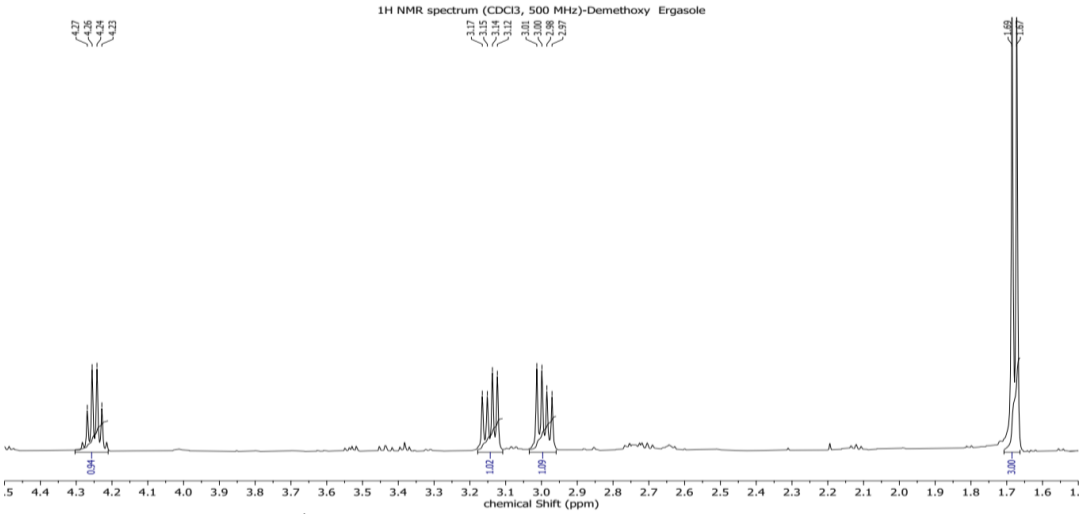


Figure S4: Expansion of ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4(2-bromo propyl) phenol.

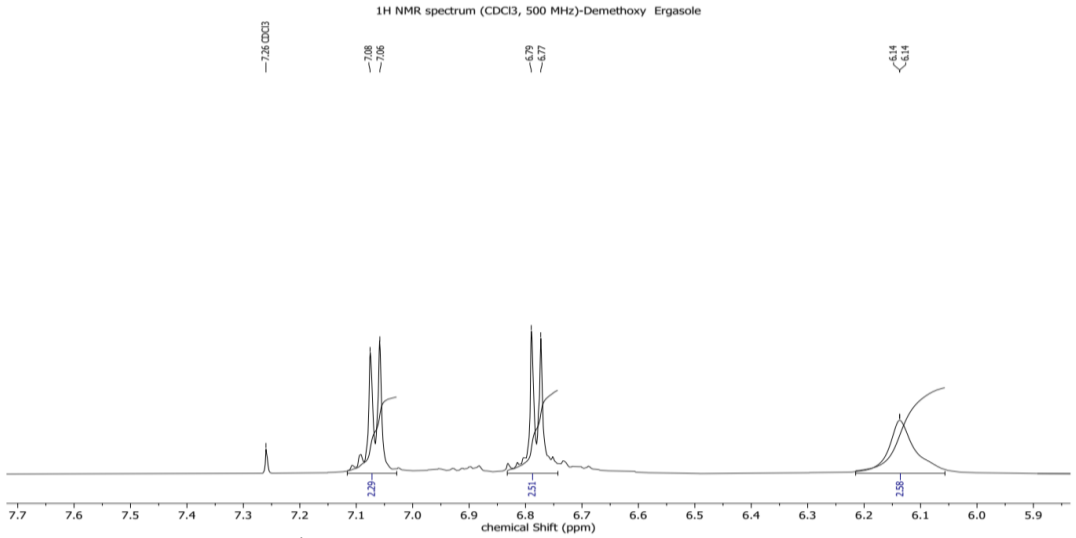


Figure S5: Expansion of ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of 4(2-bromo propyl) phenol.

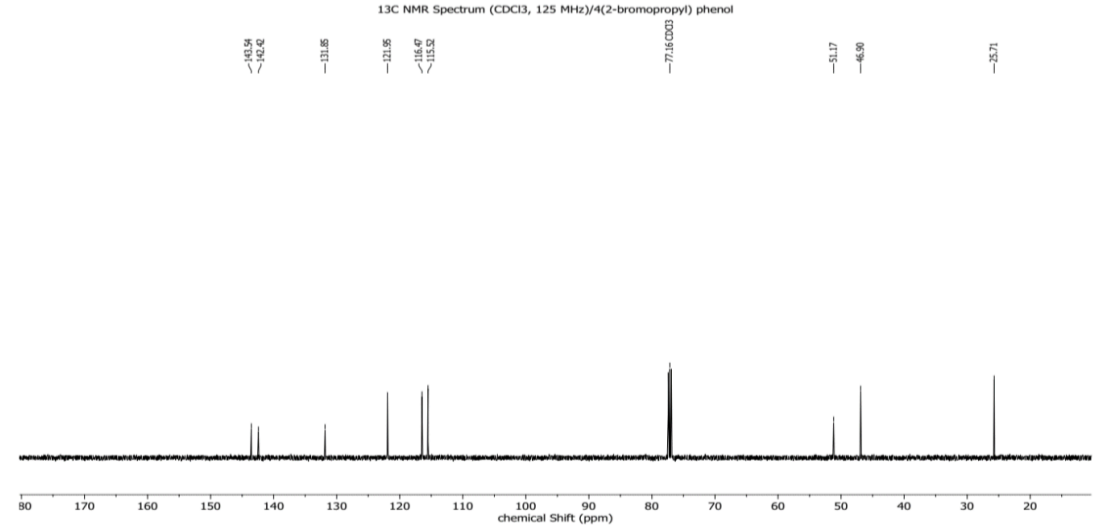


Figure S6: ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4(2-bromo propyl) catechol.

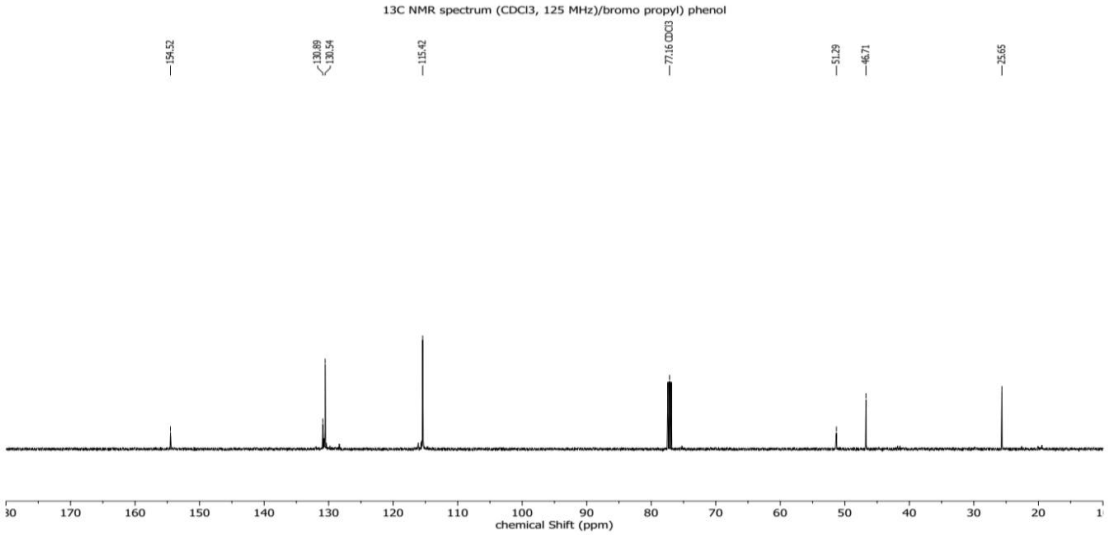


Figure S7: ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of 4(2-bromo propyl) phenol.

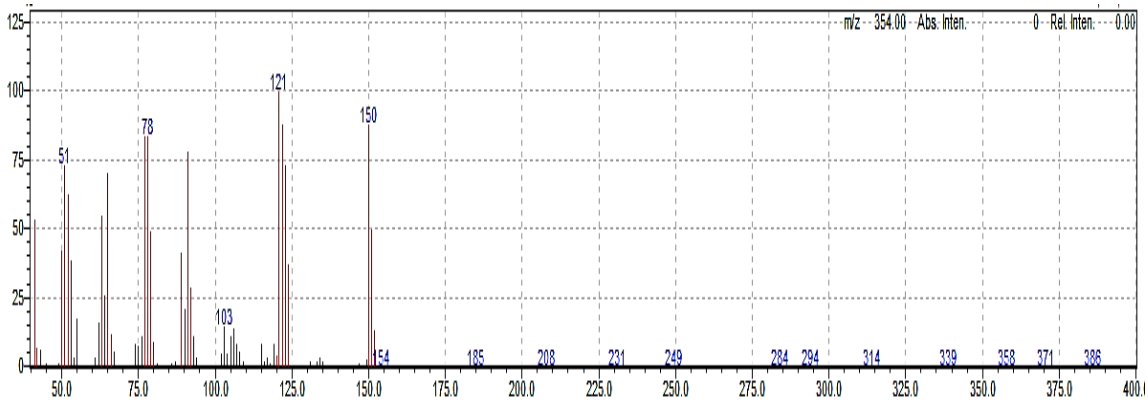


Figure S8: EIMS spectra of 4(2-bromo propyl) catechol.

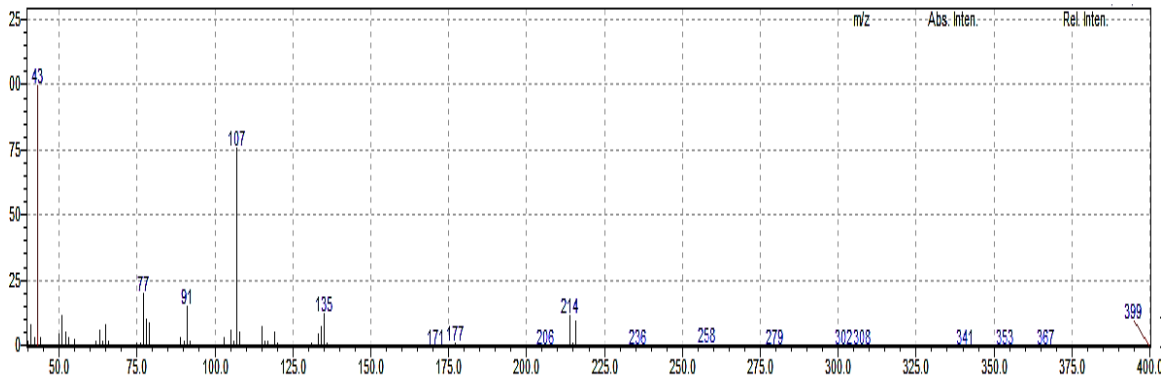


Figure S9: EIMS spectra of 4(2-bromo propyl) 2-methoxy phenol.

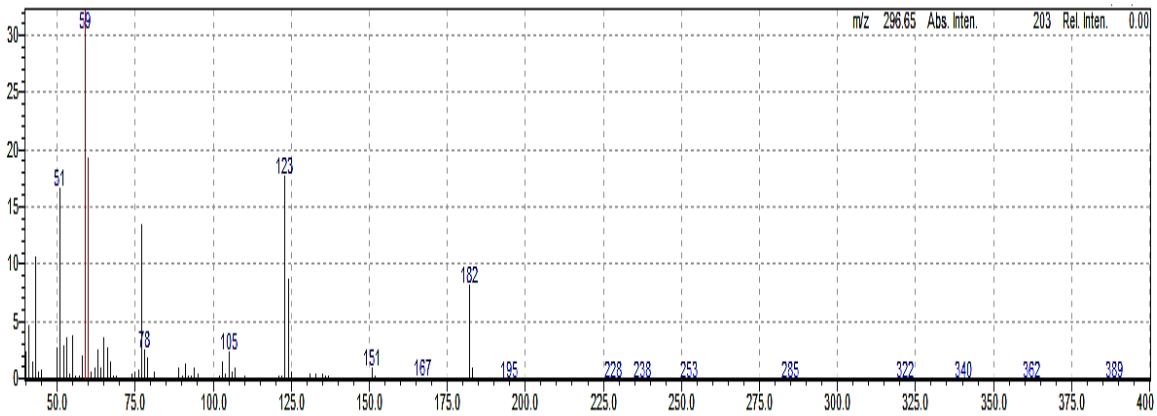


Figure S10: EIMS spectra of bromo propyl phenols obtained from allyl pyrocatechol.

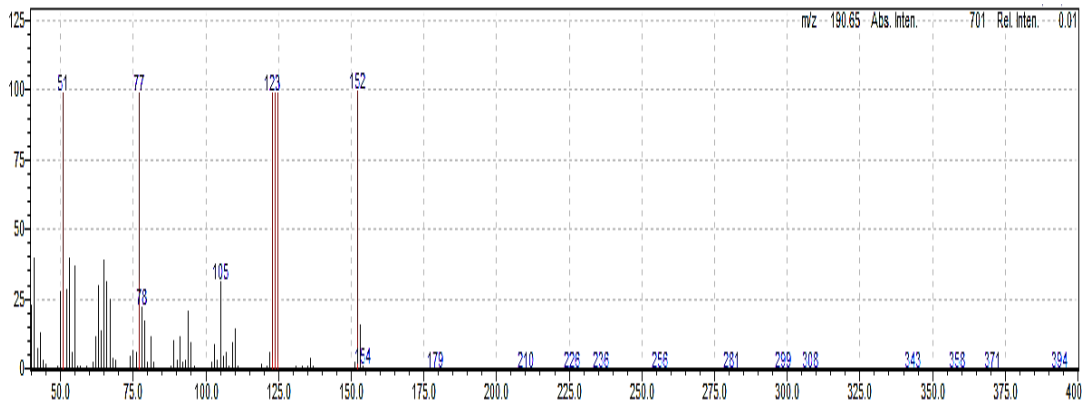


Figure S11: EIMS spectra of bromo propyl phenol obtained from eugenol.

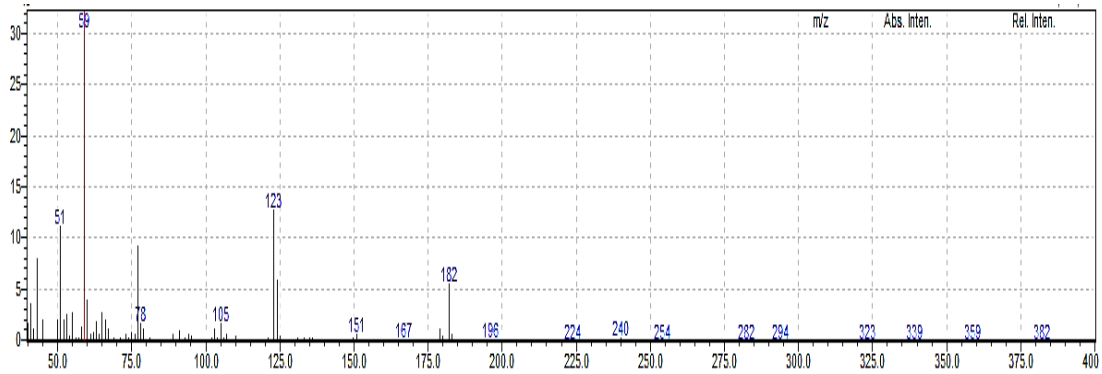


Figure S12: EIMS spectra of bromo propyl phenols methyl eugenol.

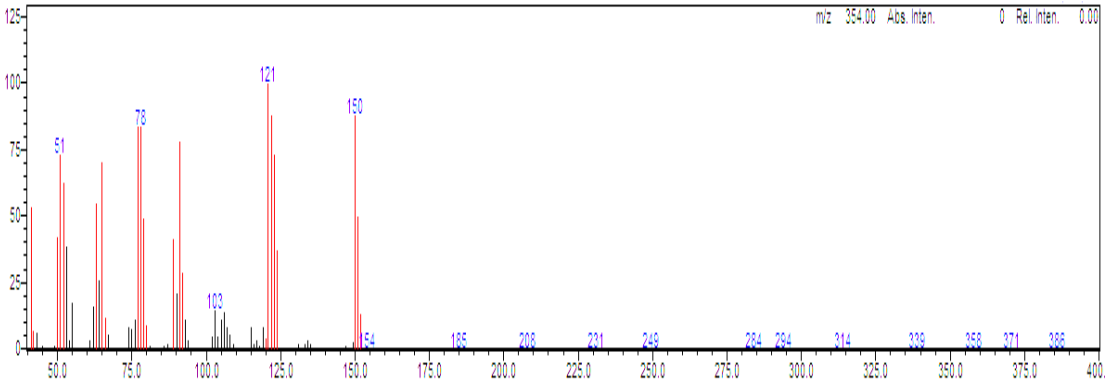


Figure S13: EIMS spectra of bromo alkyl phenols obtained from chevibetol.

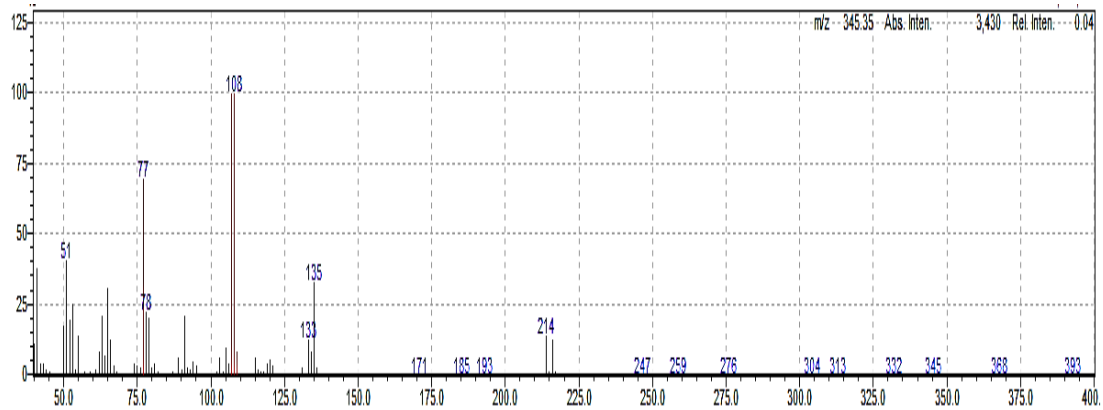


Figure S14: EIMS spectra of bromo propyl phenol obtained from phenols elemicin.

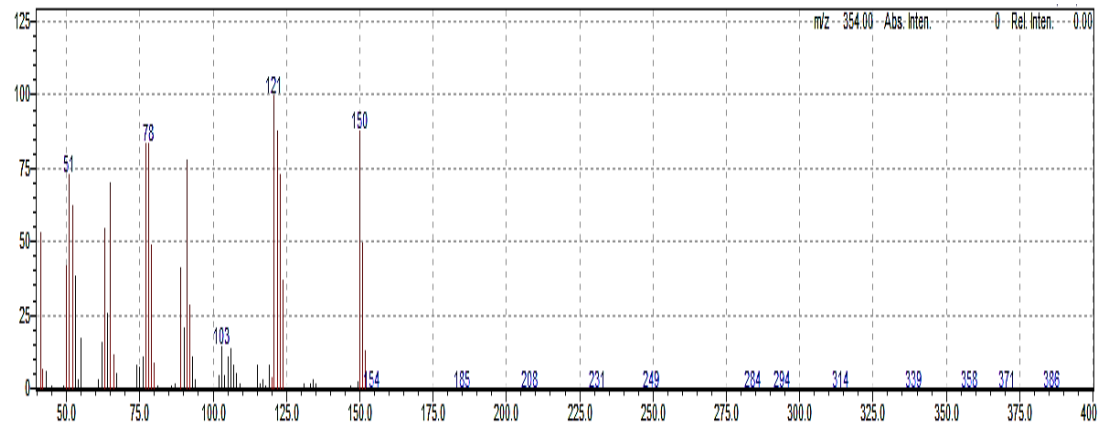


Figure S15: EIMS spectra of bromo alkyl phenols obtained from allyl pyrocatechol.

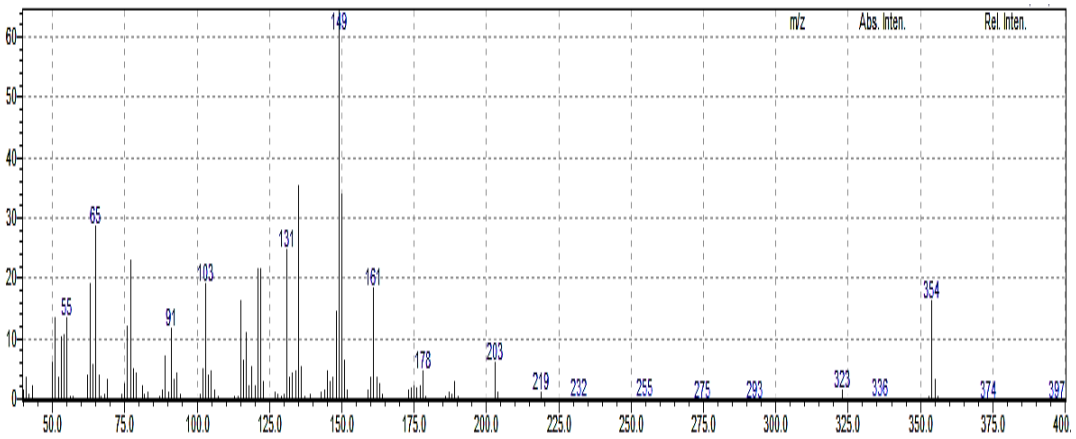


Figure S16: EIMS spectra of bromo alkyl phenols obtained from eugenol acetate.

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Conflict of interest

The author declares that there is no conflict of interest regarding the publication of this article.

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