# Photochemical nucleophile-olefin combination, aromatic substitution (photo-NOCAS) reaction: methanol, $\beta$ -myrcene, and 1,4-dicyanobenzene. Intramolecular cyclization of an ene-diene radical cation<sup>1</sup>

# Donald R. Arnold and Kimberly A. McManus

Abstract: The photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction of methanol, 7-methyl-3-methylene-1,6-octadiene ( $\beta$ -myrcene, 1), and 1,4-dicyanobenzene yields five 1:1:1 adducts: *cis*-2-(4-cyanophenyl)-4-(1-methoxy-1-methylethyl)-1-methylenecyclohexane (15), *trans*-2-(4-cyanophenyl)-4-(1-methoxy-1-methylethyl)-1-methylenecyclohexane (16), 1-(4-cyanophenyl)-4-(1-methoxy-1-methylethyl)cyclohexene (17), 4-[4-methoxy-3,3-dimethylcyclohex-(*E*)-1-ylidenyl]methylbenzonitrile (18), and 4-(1-vinyl-4-*trans*-methoxy-3,3-dimethylcyclohexyl)benzonitrile (19). All of these adducts are cyclic; variation in the product ratio as a function of methanol concentration indicates cyclization is occurring, 1,6-*endo*, with both the initially formed radical cation and with the intermediate  $\beta$ -alkoxyalkyl radicals. Evidence based upon comparison of the ionization and oxidation potential of  $\beta$ -myrcene with model alkenes and with conjugated dienes indicates the initial electron transfer involves the trisubstituted mono alkene moiety; the diene moiety, mono-substituted at a nodal position, has a higher oxidation potential. High-level ab initio molecular orbital calculations (MP2/6-31G\*//HF/6-31G\*) provide useful information regarding the nature (relative energies and charge and spin distribution) of the intermediate radical cations, which supports the proposed reaction mechanism.

Key words: photoinduced electron transfer, radicals, radical cations, β-myrcene, cyclization.

**Résumé** : La réaction photochimique de combinaison nucléophile–oléfine avec substitution aromatique (photo-NOCAS) entre le méthanol, le 7-méthyl-3-méthylène-octa-1,6-diène ( $\beta$ -myrcène, 1) et le 1,4-dicyanobenzène fournit cinq adduits 1:1:1: *cis*-2-(4-cyanophényl)-4-(1-méthoxy-1-méthyléthyl)-1-méthylènecyclohexane (15), *trans*-2-(4-cyanophényl)-4-(1-méthoxy-1-méthyléthyl)cyclohexène (17), 4-[4-méthoxy-3,3-diméthylcyclohex-(*E*)-1-ylidényl]méthylbenzonitrile (18) et le 4-(1-vinyl-4-*trans*-méthoxy-3,3-diméthylcyclohexyl)benzonitrile (19). Tous ces produits sont cycliques; les variations dans les rapports de produits en fonction de la concentration de méthanol indiquent que la cyclisation se produit, 1,6-*endo*, tant avec le cation radical formé initialement qu'avec les radicaux  $\beta$ -alkoxyalkyles intermédiaires. Des données obtenues sur la base d'une comparaison des potentiels d'ionisation et d'oxydation du  $\beta$ -myrcène avec ceux d'alcènes et de diènes conjugués indiquent que le transfert initial d'électron implique la portion trisubstituée du monoalcène; le potentiel d'oxydation de la portion diénique monosubstituée en position nodale est supérieur. Des calculs ab initio d'orbitales moléculaires à un niveau élevé (MP2/6-31G\*//HF/6-31G\*) fournissent des informations utiles relatives à la nature (énergies relatives et distributions de charge et de spin) des cations radicaux intermédiaires qui supportent le mécanisme réactionnel proposé.

Mots clés : transfert d'électron photoinduit, radicaux, cations radicaux, β-myrcène, cyclisation.

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# Introduction

The definition of the scope and limitations of the photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction has received considerable attention (1–3). This reaction has synthetic utility; yields of the nucleophile, olefin, aromatic (1:1:1) adducts can be high. The reaction is general for mono alkenes, and dienes, both conjugated and nonconjugated, and the reaction can incorporate a variety of nucleophiles; e.g., methanol, fluoride anion, cyanide anion, acetonitrile. Our understanding of the mechanism of this reaction has progressed to the point where the results from a new reaction can now provide useful fundamental information regarding the reactivity of the intermediates, i.e., radical cation, radical anion, and radical. A main objective of this project was to determine the probability and regiochemistry of intramolecular cyclization of the intermediate(s) involved during the reaction of a nonconjugated alkene – conjugated diene, 7-methyl-3-methylene-1,6octadiene ( $\beta$ -myrcene, 1).

Relevant examples of this reaction are shown in reactions [1]–[4] (2). The irradiation of an acetonitrile–methanol solution of 1,4-dicyanobenzene (2) and the unsymmetric mono

alkene, 2-methyl-2-butene (3), yields both regioisomeric 1:1:1 adducts (4, 5) in 70% yield (reaction [1]) (2*a*). The mechanism proposed for formation of the major (6:1) isomer, 3-(4-cyanophenyl)-2-methoxy-3-methylbutane (4), involves rapid equilibration of the initially formed distonic radical cation intermediates, followed by irreversible deprotonation, with preferential formation of the more stable  $\beta$ -alkoxyalkyl radical (2*a*, *b*).

Similar irradiation of an acetonitrile-methanol solution of 1,4-dicyanobenzene and 2-methyl-1,3-butadiene (6) gave four isomeric 1:1:1 adducts (reaction [2]) (2*c*). The major



**Table 1.** The dependence of the product ratio [(18 + 19)/(16 + 17)] from reaction [5] on the concentration of methanol.

[CH <sub>3</sub> OH] (M)	Product ratio
0.25	$0.64 \ (0.03)^a$
0.50	0.64 (0.04)
1.00	0.89 (0.02)
1.50	1.01 (0.03)
2.00	1.02 (0.01)

<sup>a</sup>Population standard deviation.

(8:1) adducts (7, 8, 9) result from combination of methanol with the diene radical cation at C-1, which again leads ultimately to the more stable allylic radical (2*b*).

The irradiation of an acetonitrile-methanol solution of 1,4-dicyanobenzene and 2,5-dimethyl-1,5-hexadiene (11) provides an example of cyclization of the intermediate radical cation (reaction [3]) (2*d*). The ratio of 1:1:1 adducts is dependent upon the methanol concentration; lowering the concentration of methanol favours radical cation cyclization, increasing the yield of 13. Cyclization, 1,6-endo, endo, of the initially formed alkene radical cation yields the more heavily substituted, more stable, 1,4-distonic radical cation intermediate, leading to the formation of 13.

A particularly interesting example of the photo-NOCAS reaction involves irradiation of an acetonitrile-methanol solution of 1.4-dicvanobenzene and 6,6-dimethyl-2methylenebicyclo[3.1.1]heptane ( $\beta$ -pinene) (14) (reaction [4]) (2e). In this case, the initially formed alkene radical cation cleaves an allylic cyclobutyl bond to give the distonic radical cation. The structures of the three 1:1:1 adducts (15, 16, 17) are consistent with reaction of this intermediate; no other 1:1:1 adducts were obtained. The adducts maintain optical activity, hence, the distonic radical cation does not cleave; cleavage of this distonic radical cation would yield the achiral radical cation of  $\beta$ -myrcene (1<sup>+-</sup>).

#### Results

An acetonitrile–methanol (3:1) solution of 1,4dicyanobenzene (2), biphenyl, serving as a codonor, and  $\beta$ myrcene (1) was irradiated with a medium-pressure mercury vapour lamp through Pyrex. Progress of the reaction was monitored by capillary column gas chromatography with a flame ionization detector (GC–fid). The reaction produced five 1:1:1 (methanol, 1, 2) photo-NOCAS adducts (reaction [5]). The yields were based upon complete conversion of 1,4-dicyanobenzene as the limiting reagent ( $\beta$ -myrcene

[5]



D (codonor) = biphenyl Ar = 4-cyanophenyl



Fig. 1. Variation in the product ratio  $\left[\frac{18 + 19}{16 + 17}\right]$  from

(1) was present in excess) and were calculated from the total weight of the combined products and the ratio of isomers determined by integrated peak (GC-fid) area. The ratio of adducts was not dependent upon the extent of conversion; these ratios remained constant during the irradiation.

Three of the adducts, *cis*-2-(4-cyanophenyl)-4-(1-methoxy-1-methylethyl)-1-methylenecyclohexane (**15**), *trans*-2-(4-cyanophenyl)-4-(1-methoxy-1-methylethyl)-1-methylenecyclohexane (**16**), and 1-(4-cyanophenylmethyl)-4-(1-methoxy-1-methylethyl)cyclohexene (**17**), were racemic mixtures of the enantiomeric adducts previously characterized from the reaction involving  $\beta$ -pinene (**14**) (reaction [4]) (2*e*). The major adducts were the new compounds: 4-[4-methoxy-3,3dimethylcyclohex-(*E*)-1-ylidenyl]methylbenzonitrile (**18**) and 4-(1-vinyl-4-*trans*-methoxy-3,3-dimethylcyclohexyl)benzonitrile (**19**).

The ratio of products [(18 + 19)/(16 + 17)] was dependent upon the initial concentration of methanol. (The yield of 15 was too low for an accurate measurement.) Irradiations were carried out in Pyrex tubes (5 mm) under conditions similar to those used for the preparative scale reaction described above. The concentration of methanol was varied (0.25-2.0 M). The concentrations of the other reactants were the same as in the preparative scale reaction. The ratio [(18 + 19)/(16 + 17)] of products was determined from the corresponding integrated peak (GC–fid) areas (Table 1 and Fig. 1). An increase in methanol concentration caused an increase in the yield of 18 and 19 relative to 16 and 17. At the lower range of methanol concentration ( $\leq 0.5 \text{ M}$ ) the ratio of



15(1%) + 16(3%) + 17(4%)

Fig. 2. The X-ray crystal structure of 4-[4-methoxy-3,3-dimethylcyclohex-(*E*)-1-ylidenyl]methylbenzoic acid (18a).<sup>3</sup>



products remained constant. The ratios (18/19) and (16/17) were independent of methanol concentration.

#### Structural assignments

Products 15, 16, and 17 were shown to have identical gas chromatographic retention times and mass spectra as the previously characterized adducts (2e).

Compound **18** was identified as 4-[4-methoxy-3,3dimethylcyclohex-(*E*)-1-ylidenyl]-methylbenzonitrile. The typical AA'XX' pattern in the aromatic region of the <sup>1</sup>H nmr spectrum is indicative of the 4-cyanophenyl group. The presence of the trisubstituted alkene is supported by a triplet (5.20 ppm), representing a vinyl proton with typical coupling (7.3 Hz) to a geminal methylene, and a doublet (3.43 ppm), representing this geminal methylene, arylsubstituted. The doublet of doublets at 2.93 ppm represents the axial proton of the methoxy-substituted methine ( ${}^{3}J_{4ax-5ax}$ = 8.5 Hz,  ${}^{3}J_{4ax-5eq}$  = 3.7 Hz). The <sup>1</sup>H nmr also exhibits two singlets at 0.84 and 0.94 ppm indicative of two nonequivalent methyl groups.

The  ${}^{13}$ C nmr spectrum of **18** exhibits a doublet (85.91 ppm), which indicates a methine group substituted by the methoxy group. There is a lower field triplet (47.93 ppm), which is consistent with an aryl-substituted methylene group (carbons adjacent to the 4-cyanophenyl group tend to occur between 37–55 ppm (1, 2)). The  ${}^{13}$ C nmr spectrum also exhibits a doublet (120.12 ppm) for the vinyl methine and a singlet (138.77 ppm) for the quaternary vinyl carbon, further supporting the existence of the trisubstituted alkene.

The assigned overall structure and stereochemistry of **18** was substantiated by X-ray crystallography. The nitrile group in compound **18** was converted to a carboxylic acid; 4-[4-methoxy-3,3-dimethylcyclohex-(E)-1-ylidenyl]methylbenzoic acid (**18a**). The <sup>1</sup>H nmr spectrum of the nitrile (**18**) and this carboxylic acid (**18a**) are almost identical; the X-ray analysis of **18a** (Fig. 2) provides firm evidence for the structure of the initial product (**18**).<sup>3</sup>

Compound 19 was identified as 4-(1-vinyl-4-transmethoxy-3,3-dimethylcyclohexyl)benzonitrile. The typical AA'XX' pattern in the aromatic region of the <sup>1</sup>H nmr spectrum is indicative of the 4-cyanophenyl group. The presence of the terminal alkene is supported by two doublets and a doublet of doublets (4.87, 5.03, and 5.86 ppm) in the vinyl proton region. The distorted four-line multiplet at 2.81 ppm represents the axial proton of the methoxy-substituted methine. Individual coupling constants were not obtained; however, based on the width of the multiplet at half-height (13 Hz), this proton is axial. Typical equatorial-axial and equatorial-equatorial couplings range from 0 to 3 Hz; if this proton were equatorial, the separation of the outer lines of a four-line multiplet would be, at most, 6 Hz. The <sup>1</sup>H nmr spectrum also exhibits two singlets at 0.72 and 0.96 ppm indicative of two nonequivalent methyl groups.

A nuclear Overhauser enhancement (NOE) experiment proved the aryl group was *trans* to the methoxy group on the cyclohexyl ring. When the methyl protons at 0.72 ppm were irradiated, a NOE was observed for the proton of the methoxy-substituted methine, the methoxy-methyl protons, and the methyl protons (0.96 ppm). When the methyl protons at 0.96 ppm were irradiated, a NOE was observed for

<sup>&</sup>lt;sup>3</sup>X-ray crystallographic data for **18a** may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2. Details of data collection, structural analysis and refinement, and tables of interatomic distances and bond angles have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

the methoxy–methyl protons, the vinyl protons, and the methyl protons (0.72 ppm). Based on the evidence that the proton of the methoxy-substituted methine is axial, vide supra, the methoxy group is equatorial, the aryl group is equatorial, i.e., the *trans* configuration.

The  ${}^{13}$ C nmr spectrum of compound **19** exhibits a doublet (85.58 ppm) indicative of a methine group substituted by the methoxy group. There is a lower field singlet (44.31 ppm), which is consistent with an aryl-substituted quaternary carbon. This spectrum also exhibits a triplet (112.52 ppm) for the vinyl methylene and a doublet (146.73 ppm) for the vinyl methine, thus further supporting the existence of the terminal mono-substituted alkene.

#### Calculations

Ab initio molecular orbital calculations were carried out, using the GAUSSIAN 94 package of programs (4), to obtain fully optimized structures (HF/6-31G\*) of  $\beta$ -myrcene (1) and the radical cations 1<sup>++</sup>, 1a<sup>++</sup>, and 1b<sup>++</sup>. The results of these calculations, optimized structures, and spin and charge density distribution obtained from Mulliken population analysis, are listed in Tables 2 and 3. The total energies, corrected for spin contamination, were obtained from single point calculations with Møller–Plesset perturbation theory (MP2) using the HF/6-31G\* optimized structures (5). The results of an extensive stochastic search, using the molecular mechanics program (MM3-94 (6)), identified 24 conformers of  $\beta$ -myrcene (1); the more stable conformers are described in Table 4.

# Discussion

A mechanism for the formation of **15**, **16**, and **17** involves cyclization of the initially formed radical cation of myrcene (**1**<sup>+</sup>) to the distonic radical cation (**1a**<sup>+</sup>) (Scheme 1). This distonic radical cation is identical to that formed upon cleavage of the  $\beta$ -pinene radical cation (**14**<sup>+</sup>). An alternative mode of cyclization of **1**<sup>+</sup> yields the distonic radical cation **1b**<sup>+</sup>, which leads to formation of **18** and **19**. The regiochemistry of these adducts requires reaction of these distonic radical cations — tertiary or secondary alkyl cation with methanol and the allylic radical with the radical anion of **1**,4-dicyanobenzene (**2**<sup>-</sup>). At lower methanol concentrations ( $\leq 0.5$  M) cyclization of the radical cation dominates, the product ratio [(**18** + **19**)/(**16** + **17**)] is relatively small (0.64), 1,6-endo, exo cyclization of **1**<sup>+</sup> to **1a**<sup>+</sup> is favoured.

The results from the molecular orbital calculations are consistent with these observations (Table 3). The distonic radical cation  $1a^{++}$  has most of the positive charge density on the tertiary carbocation (C7, C8, and C9), while the spin density is delocalized over the allylic radical (C2 and C10). Similarly, the distonic radical cation  $1b^{++}$  has greatest positive charge on C6, and the spin density is delocalized over the allylic radical (C1 and C3). It seems likely that the alternative modes of cyclization of the initially formed  $\beta$ -myrcene radical cation,  $1^{++}$ , are dependent upon conformational factors. The rate of the intermolecular reaction of a diene radical cation with the precursor diene is rapid,  $10^8-10^9$  M<sup>-1</sup> s<sup>-1</sup> (3a). Nevertheless, the molecular orbital calculations indicate that the major mode of cyclization of  $1^{++}$  yields the more stable distonic radical cation  $1a^{++}$ . The calculations also indicate that cyclization is significantly

exothermic, -21.6 kcal mol<sup>-1</sup> for  $\mathbf{1}^+$  to  $\mathbf{1a}^+$  and -11.3 kcal mol<sup>-1</sup> for  $\mathbf{1}^+$  to  $\mathbf{1b}^+$ , consistent with the lack of reversibility.

At higher methanol concentrations the product ratio [(18 +(19)/(16 + 17) increases; for the preparative runs (6 M methanol) this ratio becomes 1.7. Under these conditions, reaction of the radical cation  $(1^+)$  with methanol competes with cyclization; the measured bimolecular rate constant for reaction of diene radical cations with methanol (>10<sup>9</sup>  $M^{-1} s^{-1}$ ) is consistent (3a). Now the product ratio is controlled by the addition of methanol to the radical cation  $1^{+}$  at the alternative sites, C7 or C6, to yield the  $\beta$ -alkoxyalkyl radicals, 1c<sup> $\cdot$ </sup> or 1d' (Scheme 2). As expected, based upon the product ratio from reaction (1), addition of methanol to the alkene radical cation at C6, with subsequent formation of the more stable tertiary radical (1d), is favoured, relative to addition at C7, to give the secondary radical (1c). Both of these  $\beta$ alkoxyalkyl radicals then cyclize 1,6-endo on the way to the observed products.

Adduct **18** results from cyclization of the radical cation (Scheme 1) or radical (Scheme 2) at C10 of the diene moiety. The *E*-configuration of this adduct (**18**) clearly indicates this diene had the s-*trans* conformation. The result of an extensive stochastic search for conformers of  $\beta$ -myrcene (**1**), using the molecular mechanics program (MM3-94 (6)), is consistent with reaction of this conformation (Table 4). Conformer 3 has close approach between C7 and C10, required for cyclization to **1b**<sup>+\*</sup>, and the s-*trans* conformation of the diene. Conformers 6 and 8 have close approach between C1 and C6 required for cyclization to **1a**<sup>+\*</sup>. None of the low-energy conformers have the s-*cis* conformation and close approach of C7-C10 or C1-C6. The fully optimized (ab initio) structures of  $\beta$ -myrcene (1) and of the  $\beta$ -myrcene radical cation (**1**<sup>+\*</sup>) are similar (Table 4).

Clearly, none of the products from reaction 5 involve initial addition of the nucleophile, methanol, to the conjugated diene moiety. This was, at first, a surprise; however, there is convincing evidence that formation of the trialkylsubstituted mono-ene radical cation (C6, C7) is energetically favoured (1*b*). The oxidation potentials and the ionization potentials of  $\beta$ -myrcene (1) and of the model compounds 2methyl-2-butene (3) and 2-methyl-1,3-butadiene (6) are summarized in Table 5. The radical cation of the trialkylsubstituted mono-ene moiety (C5, C6, C7, C8, C9) is more stable than that at the conjugated diene moiety (C1, C2, C3, C10, C4). The molecular orbital calculations support this conclusion; the charge density of radical cation, 1<sup>++</sup>, is largely on C6, C7, C8, and C9, while the spin density is on C6 and C7 (Table 3).

#### Conclusions

Photoinduced electron transfer, from 7-methyl-3methylene-1,6-octadiene ( $\beta$ -myrcene, 1) to 1,4dicyanobenzene, in acetonitrile-methanol, leads to formation of five 1:1:1 (photo-NOCAS) adducts (15–19). All of these adducts are cyclic; both the initially formed radical cation and the intermediate  $\beta$ -alkoxyalkyl radicals cyclize. The preferred modes of cyclization are for the radical cation 1<sup>+</sup>, 1,6-*endo, exo* and 1,6-*endo, endo*, and for the radicals, 1c<sup>-</sup> and 1d<sup>-</sup>, 1,6-*endo*. The observed products, the measured oxidation and ionization potentials, and the molecular orbital

β-Myrcene (1)           C1-C2         1.323         C1-C2-C3         126.8         C4-C3-C2-C1         -0.1           C3-C3         1.480         C2-C3-C4         117.5         C5-C4-C3         177.1           C3-C4         1.515         C3-C4-C5         116.4         C7-C6-C5-C4         114.0           C4-C5         1.534         C4-C5-C6         111.4         C8-C7-C6-C5         -118.0           C5-C6         1.507         C5-C6-C7         128.9         C9-C7-C6-C5         0.1           C6-C7         1.325         C6-C7-C8         120.8         C10-C3-C2-C1         179.8           C7-C8         1.511         C6-C7-C9         125.4         -0.7         22-C3         147.9         C2-C3-C4         116.5         C5-C4-C3-C2         -178.1           C3-C10         1.325         C2-C3-C10         119.7         C5-C4-C3-C2         -177.6           C4-C5         1.547         C4-C5-C6         110.0         C7-C6-C5         -177.6           C4-C5         1.547         C4-C5-C6         110.0         C7-C6-C5         -177.6           C4-C5         1.547         C4-C5-C6         110.0         C7-C6-C5         -178.1           C5-C6         1.547	Bond length (Å)		Bond angle (deg)		Dihedral angle (deg	Dihedral angle (deg)	
C1C2 1.323 C1-C2-C3 126.8 C4-C3-C2-C1 -0.1 C2C3 1.480 C2-C3-C4 117.5 C5-C4-C3-C2 -180.0 C3C1 1.326 C2-C3-C10 118.6 C6-C5-C4-C3 177.1 C3C4 1.515 C3-C4-C5 116.4 C7-C6-C5-C4 114.0 C4C5 1.534 C4-C5-C6 111.4 C8-C7-C6-C5 -0.1 C6C7 1.325 C6-C7 128.9 C9-C7-C6-C5 0.1 C6C7 1.325 C6-C7-C8 120.8 C10-C3-C2-C1 179.8 C7C8 1.511 C6-C7-C9 125.4 C7C9 1.510 PMyrcene radical cation (1 <sup>+</sup> ) C1C2 1.322 C1-C2-C3 126.8 C4-C3-C2-C1 -0.7 C3C3 1.479 C2-C3-C4 116.5 C5-C4-C3-C2 -178.1 C3C10 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3C10 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3C4 1.515 C3-C4-C5 114.4 C6-C5-C4-C3 -177.6 C4C5 1.547 C4-C5-C6 110.0 C7-C6-C5 -177.6 C4C5 1.547 C4-C5-C6 110.0 C7-C6-C5 -177.6 C4C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 -178.1 C7C9 1.492 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7C9 1.492 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7C9 1.492 C6-C7-C9 118.4 FMyrcene cyclized, distonic, radical cation (1a <sup>+</sup> ) C1C2 1.507 C1-C2-C3 125.3 C1-C6-C5 -46.9 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6-C7 -173.2 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6-C7 -173.2 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6-C7 -173.2 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6-C7 -173.2 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6-C5 -46.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C1 94.7 C1C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C3C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 3.90 C3C10 1.513 C3-C4-C5 113.2 C8-C7-C10 11.2 C7C8 1.534 C8-C7-C10 111.2 C9-C7-C10-C6 129.8 C7C9 1.536 C9-C7-C10			β-1	Myrcene (1)			
C2—C3 1.480 C2-C3-C4 117.5 C5-C4-C3-C2 -180.0 C3—C10 1.326 C2-C3-C10 118.6 C6-C3-C4-C3 177.1 C3—C4 1.515 C3-C4-C5 116.4 C7-C6-C5-C4 114.0 C4—C5 1.534 C4-C5-C6 111.4 C8-C7-C6-C5 -180.0 C5—C6 1.507 C5-C6-C7 128.9 C9-C7-C6-C5 0.1 C6—C7 1.325 C6-C7-C8 120.8 C10-C3-C2-C1 179.8 C7—C8 1.511 C6-C7-C9 125.4 C7—C9 1.510 C1—C2 1.322 C1-C2-C3 126.8 C4-C3-C2-C1 -0.7 C2—C3 1.479 C2-C3-C4 116.5 C5-C4-C3-C2 -178.1 C3—C10 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3—C10 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3—C4 1.515 C3-C4-C5 114.4 C6-C5-C4-C3 -177.6 C4—C5 1.547 C4-C5-C6 110.0 C7-C6-C5 -177.6 C4—C5 1.547 C4-C5-C6 110.0 C7-C6-C5 -1.8 C7—C8 1.488 C4-C3-C10 123.8 C8-C7-C6-C5 -177.6 C4—C5 1.547 C4-C5-C6 120.1 C10-C3-C2-C1 179.1 C7—C9 1.492 C6-C7 127.0 C9-C7-C6-C5 1.8 C7—C8 1.488 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7—C9 1.492 C6-C7-0 121.5 C8-C7-C9 118.4 <b>FMyrcene cyclized, distonic, radical cation (1a*)</b> C1—C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 -46.9 C2—C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C7 -173.2 C3—C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3—C10 1.398 C2-C3-C4 120.1 C3-C2-C1C 15.9 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 15.9 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 15.9 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5—C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -7.5 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5—C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -7.5 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5—C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -7.2 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5—C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -7.5 C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5—C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -7.5 C4—C5 1.532 C4-C3-C10 118.9 C8-C7-C6-C5 -2.6 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C6-C7-C9 119.4 C5-C4-C3-10.6 112.4 C7—C10 1.540	C1—C2	1.323	C1-C2-C3	126.8	C4-C3-C2-C1	-0.1	
C3-C10 1.326 C2-C3-C10 118.6 C6-C5-C4-C3 177.1 C3-C4 1.515 C3-C4-C5 116.4 C7-C6-C5-C4 114.0 C4-C5 1.534 C4-C5-C6 111.4 C8-C7-C6-C5 -180.0 C5-C6 1.507 C5-C6-C7 128.9 C9-C7-C6-C5 0.1 C6-C7 1.325 C6-C7-C8 120.8 C10-C3-C2-C1 179.8 C7-C8 1.511 C6-C7-C9 125.4 C7-C9 1.510 $\begin{array}{c} \beta \text{Myrcene ratical cation (1^+)} \\ C1-C2 1.322 C1-C2-C3 126.8 C4-C3-C2-C1 -0.7 C3-C3 1.479 C2-C3-C4 116.5 C5-C4-C3-C2 -178.1 C3-C10 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3-C4 1.515 C3-C4-C5 114.4 C6-C5-C4-C3 -177.6 C4-C5 1.547 C4-C5-C6 110.0 C7-C6-C5-C4 -115.3 C5-C6 1.485 C4-C3-C10 123.8 C8-C7-C6-C5 -177.6 C6-C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7-C8 1.488 C4-C3-C10 123.8 C8-C7-C6-C5 -177.6 C6-C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7-C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 \begin{array}{c} \beta -Myrcene cyclized, distonic, radical cation (1a^+) \\ \hline C1-C2 1.507 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C5 -46.9 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C3 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 179.1 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 -713.2 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 -6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 -6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5 -24.6 C6-C7-C9 118.5 C10-C3-C2-C1 -7.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C3-C10 118.9 C8-C7-C6-C1 -85.5 C6-C7-C9 118.5 C10-C3-C2-C1 179.0 C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C6-C7 2 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C3-C4 1.513 C3-C4-C5 112.6 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C3-C4 1.513 C3-C4-C5 112.6 C9-C7-C6-C5 193.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -39.0 C3-C10 1.515 C3-C10-C7 115.2 C2$	C2—C3	1.480	C2-C3-C4	117.5	C5-C4-C3-C2	-180.0	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3—C10	1.326	C2-C3-C10	118.6	C6-C5-C4-C3	177.1	
C4-C5 1.534 C4-C5-C6 111.4 C8-C7-C6-C5 -180.0 C5-C6 1.507 C5-C6-C7 128.9 C9-C7-C6-C5 0.1 C6-C7 1.325 C6-C7-C8 120.8 C10-C3-C2-C1 179.8 C7-C8 1.511 C6-C7-C9 125.4 C7-C9 1.510 $\beta$ Myrcene ratical cation (1 <sup>+</sup> ) C1-C2 1.322 C1-C2-C3 126.8 C4-C3-C2-C1 -0.7 C2-C3 1.479 C2-C3-C4 116.5 C5-C4-C3-C2 -178.1 C3-C1 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3-C4 1.515 C3-C4-C5 114.4 C6-C5-C4-C3 -177.6 C4-C5 1.547 C4-C5-C6 110.0 C7-C6-C5-C4 -115.3 C5-C6 1.485 C4-C3-C10 123.8 C8-C7-C6-C5 1.77.6 C6-C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7-C8 1.488 C6-C7-C9 121.5 C7-C9 1.492 C6-C7-C9 121.5 C7-C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1a <sup>*</sup> ) C1-C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1-C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C5 1.98 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 7.32 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C4 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C4 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5 -246-C5 -246-C5 C6-C7-C9 119.9 C3-C4-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -35.5 C6-C7-C9 119.9 C3-C4-C5-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5 -266-C5 C6-C7-C9 119.9 C3-C4-C5-C1 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -85.5 C6-C7-C9 119.9 C3-C4-C5-C1 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C5 -266-C5 C6-C7-C9 119.9 C3-C7-C6-C1 -85.5 C6-C7-C9 119.9 C3-C7-C6-C1 -85.5 C6-C7-C9 119.9 C3-C7-C6-C1 -85.5 C6-C7-C9 119.9 C3-C7-C6-C1 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -175.9 C7-C9 1.536 C1-C2-C3 126.7 C1-C2-C3-C10-C7 -17.7 C4-C5 1.533 C3-C4-C5 115.3 C3-C4-C5 115.3 C7-C9 1.8.5 C10-C7-C6 39.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -17.7 C4-C5 1.534 C3-C4-C5 115.2 C3-C7-C10-C6 129.8 C7-C9 1.536 C3-C7-C10 1112.4 C5-C7-C10-C6 129.8 C7-C9 1.536 C3-C7-C10	C3—C4	1.515	C3-C4-C5	116.4	C7-C6-C5-C4	114.0	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4—C5	1.534	C4-C5-C6	111.4	C8-C7-C6-C5	-180.0	
C6-C7         1.325         C6-C7-C8         120.8         C10-C3-C2-C1         179.8           C7-C8         1.511         C6-C7-C9         125.4         179.8           C7-C9         1.510         FMyrcene radical cation (1")           C1-C2         1.322         C1-C2-C3         126.8         C4-C3-C2-C1         -0.7           C2-C3         1.479         C2-C3-C4         116.5         C5-C4-C3-C2         -178.1           C3-C10         1.325         C2-C3-C4         116.5         C5-C4-C3-C10         2.1           C3-C4         1.515         C3-C4-C5         114.4         C6-C5-C4-C3         -177.6           C4-C5         1.547         C4-C5-C6         110.0         C7-C6-C5         1.8           C5-C6         1.485         C4-C3-C10         123.8         C8-C7-C6         1.8           C7-C8         1.488         C6-C7-C9         121.5         -         C8-C7-C9         118.4           C1-C2         1.507         C1-C2-C3         125.3         C1-C6-C5         19.8         C2-C1-C6-C7         173.2           C3-C4         1.519         C2-C1-C6         10.0         C2-C3-C4         19.8         C3-C10         1.38         C3-C10         1.59	C5—C6	1.507	C5-C6-C7	128.9	C9-C7-C6-C5	0.1	
C7-C8         1.511         C6-C7-C9         125.4           C7-C9         1.510         β-Myreene radical cation (1 <sup>+</sup> )           C1-C2         1.322         C1-C2-C3         126.8         C4-C3-C2         -177.6           C2-C3         1.479         C2-C3-C4         116.5         C5-C4-C3-C1         -177.6           C3-C10         1.325         C2-C3-C10         119.7         C5-C4-C3-C10         2.1           C3-C4         1.515         C3-C4-C5         114.4         C6-C5-C4-C3         -177.6           C4-C5         1.547         C4-C5-C6         110.0         C7-C6-C5-C4         -115.3           C5-C6         1.485         C4-C3-C10         123.8         C8-C7-C6-C5         1.8           C7-C8         1.488         C6-C7-C8         120.1         C10-C3-C2-C1         179.1           C7-C8         1.488         C6-C7-C9         118.4             C1-C2         1.507         C1-C6-C7         103.7         C2-C1-C6-C7         -173.2           C3-C10         1.398         C2-C1-C6         110.0         C2-C3-C4         65.9           C4-C5         1.519         C2-C1-C6         100.0         C2-C3-C4         15.9	C6—C7	1.325	C6-C7-C8	120.8	C10-C3-C2-C1	179.8	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C7—C8	1.511	C6-C7-C9	125.4			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	С7—С9	1.510					
C1C2 1.322 C1-C2-C3 126.8 C4-C3-C2-C1 -0.7 C2C3 1.479 C2-C3-C4 116.5 C5-C4+C3-C2 -178.1 C3C10 1.325 C2-C3-C10 119.7 C5-C4+C3-C10 2.1 C3C4 1.515 C3-C4-C5 114.4 C6-C5-C4+C3 -177.6 C4C5 1.547 C4-C5-C6 110.0 C7-C6-C5-C4 -115.3 C5C6 1.485 C4-C3-C10 123.8 C8-C7-C6-C5 -177.6 C6C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7C8 1.488 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 PMyrcene cyclized, distonic, radical cation (1a*) C1C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C2C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C5 -46.9 C2C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1 179.1 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 153.2 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C6-C7-C8 12.16 C9-C7-C6-C5 153.2 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C6-C7-C8 12.16 C9-C7-C6-C5 153.2 C6-C7-C8 12.16 C9-C7-C6-C5 153.2 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C7-C9 1.4400 C2-C3-C10 121.5 C2-C3-C10 -1.2 C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10-7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7 163.6 C3-C4 1.540			β-Myrcene	radical catio	on (1 <sup>+</sup> )		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C1—C2	1.322	C1-C2-C3	126.8	C4-C3-C2-C1	-0.7	
C3-C10 1.325 C2-C3-C10 119.7 C5-C4-C3-C10 2.1 C3-C4 1.515 C3-C4-C5 114.4 C6-C5-C4-C3 -177.6 C4-C5 1.547 C4-C5-C6 110.0 C7-C6-C5-C4 -115.3 C5-C6 1.485 C4-C3-C10 123.8 C8-C7-C6-C5 -17.6 C6-C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7-C8 1.488 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7-C9 1.492 C6-C7-C9 118.4 <b>β-Myrcene cyclized, distonic, radical cation (1a<sup>+</sup>)</b> C1-C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1-C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C7 -173.2 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 59.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1 -2.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 14.69 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -34.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 119.9 C9-C7-C6-C5 153.2 C7-C9 1.536 C1-C7-C10 113.2	C2—C3	1.479	C2-C3-C4	116.5	C5-C4-C3-C2	-178.1	
C3-C4         1.515         C3-C4-C5         114.4         C6-C5-C4-C3         -177.6           C4-C5         1.547         C4-C5-C6         110.0         C7-C6-C5-C4         -115.3           C5-C6         1.485         C4-C3-C10         123.8         C8-C7-C6-C5         -177.6           C6-C7         1.414         C5-C6-C7         127.0         C9-C7-C6-C5         1.8           C7-C8         1.488         C6-C7-C9         121.5         C8-C7-C9         118.4           C1-C2         1.507         C1-C2-C3         125.3         C1-C6-C5-C4         66.0           C1-C6         1.577         C1-C6-C5         199.8         C2-C1-C6-C5         -46.9           C2-C3         1.389         C1-C6-C7         103.7         C2-C1-C6-C5         19.8           C3-C10         1.398         C2-C3-C4         120.1         C3-C2-C1         -5.9           C4-C5         1.529         C2-C3-C4         120.1         C3-C2-C1         19.8           C3-C10         1.398         C2-C3-C4         120.1         C3-C2-C1         -5.12           C5-C6         1.534         C3-C4-C5         112.7         C4-C3-C2-C1         -2.2           C6-C7         14.6         <	C3—C10	1.325	C2-C3-C10	119.7	C5-C4-C3-C10	2.1	
C4C5 1.547 C4-C5-C6 110.0 C7-C6-C5-C4 -115.3 C5C6 1.485 C4-C3-C10 123.8 C8-C7-C6-C5 -177.6 C6C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7C8 1.488 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1a <sup>+</sup> ) C1C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C5 19.8 C3C1 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5C6 1.534 C3-C4-C5 109.1 C7-C6-C5 -41.59 C4C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5C6 1.534 C3-C4-C5 109.1 C7-C6-C5 -26.6 C6-C7-C9 118.9 C8-C7-C6-C1 94.7 C7C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C6-C7-C8 121.6 C9-C7-C6-C5 153.2 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C4-C5 -161.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1b <sup>+</sup> ) C1C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C3C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C10-C3-C4-C5 -25.0 C3C10 1.515 C3-C10-7 115.5 C4-C3-C10 -22.0 C4C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C4C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6-C7-C9 1.947 C6-C7-C10 113.2 C8-C7-C10 -7.7 C4C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 129.8 C7C8 1.594 C8-C7-C10 112.4 C7C9 1.540	C3—C4	1.515	C3-C4-C5	114.4	C6-C5-C4-C3	-177.6	
C5-C6 1.485 C4-C3-C10 123.8 C8-C7-C6-C5 -177.6 C6-C7 1.414 C5-C6-C7 127.0 C9-C7-C6-C5 1.8 C7-C8 1.488 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7-C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 <b>FMyrcene cyclized, distonic, radical cation (1a*)</b> C1-C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1-C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C7 -173.2 C3-C1 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C1 120.9 C3-C4-C5-C6 -51.2 C5-C6 1.534 C3-C4-C5 110.20 C3-C4-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 112.9 C3-C4-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 -94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -17.7 C4-C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6-C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7-C8 1.540	C4—C5	1.547	C4-C5-C6	110.0	C7-C6-C5-C4	-115.3	
C6-C7         1.414         C5-C6-C7         127.0         C9-C7-C6-C5         1.8           C7-C8         1.488         C6-C7-C8         120.1         C10-C3-C2-C1         179.1           C7-C9         1.492         C6-C7-C9         121.5         C8-C7-C9         118.4 <b>β-Myrcene cyclized, distonic, radical cation (1a*) Geometry C1-C2-C3</b> 125.3         C1-C6-C5-C4         66.0           C1-C2         1.507         C1-C6-C5         109.8         C2-C1-C6-C5         -46.9           C2-C3         1.389         C1-C6-C7         103.7         C2-C1-C6-C7         -173.2           C3-C4         1.519         C2-C1-C6         110.0         C2-C3-C4-C5         19.8           C3-C10         1.398         C2-C3-C10         120.9         C3-C4-C5-C6         -51.2           C5-C6         1.534         C3-C4-C5         112.7         C4-C3-C2-C1         -2.2           C6-C7         1.469         C4-C5-C6         109.1         C7-C6-C5-C4         -175.9           C7-C8         1.478         C4-C3-C10         118.9         C8-C7-C6-C1         -85.5           C6-C7-C8         121.6         C9-C7-C6-C5         153.2         C8-C7-C9         119.9         C9-C7-C6-C5<	C5—C6	1.485	C4-C3-C10	123.8	C8-C7-C6-C5	-177.6	
C7C8 1.488 C6-C7-C8 120.1 C10-C3-C2-C1 179.1 C7C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1a <sup>+</sup> ) C1C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C7 -173.2 C3C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4C5 1.529 C2-C3-C1 120.9 C3-C4-C5-C6 -51.2 C5C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C1 94.7 C7C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C4-C5 1532 C2-C3-C10 121.5 C2-C3-C10 -1.2 C3C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3C10 1.515 C3-C10-C7 115.5 C4-C3-C10 -1.7 C2C3 1.400 C2-C3-C10 121.5 C2-C3-C10 -1.2 C3C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3C10 1.515 C3-C10-C7 115.5 C4-C3-C10 -71.7 C4C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -71.7 C4C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7C8 1.594 C8-C7-C10 112.4 C7C9 1.540	C6—C7	1.414	C5-C6-C7	127.0	C9-C7-C6-C5	1.8	
C7-C9 1.492 C6-C7-C9 121.5 C8-C7-C9 118.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1a <sup>+</sup> ) C1-C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1-C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C7 -173.2 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C1 94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C2-C1 179.0 C10-C3-C2-C1 179.0 C10-C3-C4-C5 -161.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1b <sup>+</sup> ) C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -17.7 C4-C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6-C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7-C8 1.594 C8-C7-C10 112.4 C7-C10 1.540	C7—C8	1.488	C6-C7-C8	120.1	C10-C3-C2-C1	179.1	
C8-C7-C9118.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1a*)C1C21.507C1-C2-C3125.3C1-C6-C5-C466.0C1C61.577C1-C6-C5109.8C2-C1-C6-C5-46.9C2C31.389C1-C6-C7103.7C2-C1-C6-C7-173.2C3C41.519C2-C1-C6110.0C2-C3-C4-C519.8C3C101.398C2-C3-C4120.1C3-C2-C1-C615.9C4C51.529C2-C3-C10120.9C3-C4-C5-C6-51.2C5C61.534C3-C4-C5112.7C4-C3-C2-C1-2.2C6C71.469C4-C5-C6109.1C7-C6-C5-C4-175.9C7C81.478C4-C3-C10118.9C8-C7-C6-C5-26.6C6-C7-C8121.6C9-C7-C6-C5153.2C6-C7-C9119.9C9-C7-C6-C5153.2C7C91.477C5-C6-C7117.4C8-C7-C6-C5-161.4 <b>BMyrcene cyclized, distonic, radical cation (1b*)</b> C1C21.386C1-C2-C3126.7C1-C2-C3-C10-1.2C2C31.400C2-C3-C10121.5C2-C3-C10-1.2C2C31.400C2-C3-C10121.5C2-C3-C10-1.2C2C31.400C2-C3-C10121.5C2-C3-C10-1.2C2C31.400C2-C3-C10121.5C4-C3-C10-C763.6C3C41.513C3-C10-C7115.5C4-C3-C10-C7-17.7C4C51.533C4-C3-C10119.4	С7—С9	1.492	C6-C7-C9	121.5			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			C8-C7-C9	118.4			
C1-C2 1.507 C1-C2-C3 125.3 C1-C6-C5-C4 66.0 C1-C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C7 -173.2 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C1 94.7 C6-C7-C9 119.9 C9-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C1 179.0 C10-C3-C4-C5 -161.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1b <sup>+</sup> ) C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7 163.6 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10 -22.0 C6-C7 C1 1.447 C6-C7-C10 113.2 C8-C7-C10 -22.0 C6-C7 C1 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7-C8 1.594 C8-C7-C10 112.4 C7-C10 1.540		f	-Myrcene cyclized,	distonic, radi	ical cation (1a <sup>+*</sup> )		
C1-C6 1.577 C1-C6-C5 109.8 C2-C1-C6-C5 -46.9 C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C7 -173.2 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C8 121.6 C9-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -17.7 C4-C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6-C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7-C8 1.594 C8-C7-C10 112.4 C7-C10 1.540	C1—C2	1.507	C1-C2-C3	125.3	C1-C6-C5-C4	66.0	
C2-C3 1.389 C1-C6-C7 103.7 C2-C1-C6-C7 -173.2 C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C4-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C4-C5 -161.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1b <sup>+</sup> ) C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -17.7 C4-C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6-C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7-C8 1.594 C8-C7-C10 112.4 C7-C10 1.540	C1—C6	1.577	C1-C6-C5	109.8	C2-C1-C6-C5	-46.9	
C3-C4 1.519 C2-C1-C6 110.0 C2-C3-C4-C5 19.8 C3-C10 1.398 C2-C3-C4 120.1 C3-C2-C1-C6 15.9 C4-C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 -51.2 C5-C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 -2.2 C6-C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 -175.9 C7-C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7-C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 -26.6 C6-C7-C8 121.6 C9-C7-C6-C1 -85.5 C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C4-C5 -161.4 $\beta$ -Myrcene cyclized, distonic, radical cation (1b <sup>+</sup> ) C1-C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 -1.2 C2-C3 1.400 C2-C3-C10 121.5 C2-C3-C10-C7 163.6 C3-C4 1.513 C3-C4-C5 113.1 C3-C10-C7-C6 39.0 C3-C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 -17.7 C4-C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 -22.0 C6-C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 -108.1 C7-C8 1.594 C8-C7-C10 111.2 C9-C7-C10-C6 129.8 C7-C9 1.536 C9-C7-C10 112.4 C7-C10 1.540	C2—C3	1.389	C1-C6-C7	103.7	C2-C1-C6-C7	-173.2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3—C4	1.519	C2-C1-C6	110.0	C2-C3-C4-C5	19.8	
C4—C5 1.529 C2-C3-C10 120.9 C3-C4-C5-C6 $-51.2$ C5—C6 1.534 C3-C4-C5 112.7 C4-C3-C2-C1 $-2.2$ C6—C7 1.469 C4-C5-C6 109.1 C7-C6-C5-C4 $-175.9$ C7—C8 1.478 C4-C3-C10 118.9 C8-C7-C6-C1 94.7 C7—C9 1.477 C5-C6-C7 117.4 C8-C7-C6-C5 $-26.6$ C6-C7-C8 121.6 C9-C7-C6-C1 $-85.5$ C6-C7-C9 119.9 C9-C7-C6-C5 153.2 C8-C7-C9 118.5 C10-C3-C2-C1 179.0 C10-C3-C4-C5 $-161.4$ <b>β-Myrcene cyclized, distonic, radical cation (1b</b> <sup>+</sup> ) C1—C2 1.386 C1-C2-C3 126.7 C1-C2-C3-C10 $-1.2$ C2—C3 1.400 C2-C3-C10 121.5 C2-C3-C10 C7 163.6 C3—C4 1.513 C3-C4-C5 113.1 C3-C10-C7 C6 39.0 C3—C10 1.515 C3-C10-C7 115.5 C4-C3-C10-C7 $-17.7$ C4—C5 1.533 C4-C3-C10 119.4 C5-C4-C3-C10 $-22.0$ C6—C7 1.447 C6-C7-C10 113.2 C8-C7-C10-C6 $-108.1$ C7—C9 1.536 C9-C7-C10 112.4 C7—C10 1.540	C3—C10	1.398	C2-C3-C4	120.1	C3-C2-C1-C6	15.9	
C5-C61.534C3-C4-C5112.7C4-C3-C2-C1-2.2C6-C71.469C4-C5-C6109.1C7-C6-C5-C4-175.9C7-C81.478C4-C3-C10118.9C8-C7-C6-C194.7C7-C91.477C5-C6-C7117.4C8-C7-C6-C5-26.6C6-C7-C9119.9C9-C7-C6-C1-85.5C6-C7-C9119.9C9-C7-C6-C5153.2C8-C7-C9118.5C10-C3-C2-C1179.0C1-C21.386C1-C2-C3126.7C1-C2-C3-C10-1.2C2-C31.400C2-C3-C10121.5C2-C3-C10-C7163.6C3-C41.513C3-C4-C5113.1C3-C10-C7163.6C3-C101.515C3-C10-C7115.5C4-C3-C10-22.0C6-C71.447C6-C7-C10113.2C8-C7-C10-22.0C6-C71.447C6-C7-C10113.2C8-C7-C10-C6-108.1C7-C81.594C8-C7-C10112.4C7-C10-C6129.8C7-C91.536C9-C7-C10112.4C7-C10-C6129.8	C4—C5	1.529	C2-C3-C10	120.9	C3-C4-C5-C6	-51.2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C5—C6	1.534	C3-C4-C5	112.7	C4-C3-C2-C1	-2.2	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C6—C7	1.469	C4-C5-C6	109.1	C7-C6-C5-C4	-175.9	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C7—C8	1.478	C4-C3-C10	118.9	C8-C7-C6-C1	94.7	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C7—C9	1.477	C5-C6-C7	117.4	C8-C7-C6-C5	-26.6	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			C6-C7-C8	121.6	C9-C7-C6-C1	-85.5	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			C6-C7-C9	119.9	C9-C7-C6-C5	153.2	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			C8-C7-C9	118.5	C10-C3-C2-C1	179.0	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					C10-C3-C4-C5	-161.4	
C1C2       1.386       C1-C2-C3       126.7       C1-C2-C3-C10       -1.2         C2C3       1.400       C2-C3-C10       121.5       C2-C3-C10-C7       163.6         C3C4       1.513       C3-C4-C5       113.1       C3-C10-C7-C6       39.0         C3C10       1.515       C3-C10-C7       115.5       C4-C3-C10-C7       -17.7         C4C5       1.533       C4-C3-C10       119.4       C5-C4-C3-C10       -22.0         C6C7       1.447       C6-C7-C10       113.2       C8-C7-C10-C6       -108.1         C7C8       1.594       C8-C7-C10       111.2       C9-C7-C10-C6       129.8         C7C9       1.536       C9-C7-C10       112.4       C7C10       12.4		Ê	-Myrcene cyclized,	distonic, radi	ical cation (1b <sup>+*</sup> )		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C1-C2	1.386	C1-C2-C3	126.7	C1-C2-C3-C10	-1.2	
C3-C4       1.513       C3-C4-C5       113.1       C3-C10-C7-C6       39.0         C3-C10       1.515       C3-C10-C7       115.5       C4-C3-C10-C7       -17.7         C4-C5       1.533       C4-C3-C10       119.4       C5-C4-C3-C10       -22.0         C6-C7       1.447       C6-C7-C10       113.2       C8-C7-C10-C6       -108.1         C7-C8       1.594       C8-C7-C10       111.2       C9-C7-C10-C6       129.8         C7-C9       1.536       C9-C7-C10       112.4       C7-C10       12.4	$C^2 - C^3$	1.400	C2-C3-C10	121.5	C2-C3-C10-C7	163.6	
C3—C10       1.515       C3-C10-C7       115.5       C4-C3-C10-C7       -17.7         C4—C5       1.533       C4-C3-C10       119.4       C5-C4-C3-C10       -22.0         C6—C7       1.447       C6-C7-C10       113.2       C8-C7-C10-C6       -108.1         C7—C8       1.594       C8-C7-C10       111.2       C9-C7-C10-C6       129.8         C7—C9       1.536       C9-C7-C10       112.4       C7-C10       112.4	C3—C4	1.513	C3-C4-C5	113.1	C3-C10-C7-C6	39.0	
C4-C5       1.533       C4-C3-C10       119.4       C5-C4-C3-C10       -22.0         C6-C7       1.447       C6-C7-C10       113.2       C8-C7-C10-C6       -108.1         C7-C8       1.594       C8-C7-C10       111.2       C9-C7-C10-C6       129.8         C7-C9       1.536       C9-C7-C10       112.4       C7-C10       112.4	C3-C10	1.515	C3-C10-C7	115.5	C4-C3-C10-C7	-17.7	
C6-C7       1.447       C6-C7-C10       113.2       C8-C7-C10-C6       -108.1         C7-C8       1.594       C8-C7-C10       111.2       C9-C7-C10-C6       129.8         C7-C9       1.536       C9-C7-C10       112.4       C7-C10       112.4	C4—C5	1.533	C4-C3-C10	119.4	C5-C4-C3-C10	-22.0	
C7—C8       1.594       C8-C7-C10       111.2       C9-C7-C10-C6       129.8         C7—C9       1.536       C9-C7-C10       112.4         C7—C10       1.540	C6—C7	1.447	C6-C7-C10	113.2	C8-C7-C10-C6	-108.1	
C7—C9 1.536 C9-C7-C10 112.4 C7—C10 1.540	C7—C8	1.594	C8-C7-C10	111.2	C9-C7-C10-C6	129.8	
C7—C10 1.540	C7—C9	1.536	C9-C7-C10	112.4	0, 0, 010 00		
	C7—C10	1.540					

**Table 2.** Optimized (HF/6-31G\*) structures for  $\beta$ -myrcene (1),  $\beta$ -myrcene radical cation (1<sup>+•</sup>),  $\beta$ -myrcene cyclized, distonic, radical cations (1a<sup>+•</sup> and 1b<sup>+•</sup>).

calculations all indicate the trisubstituted mono alkene moiety is the site of the initially formed radical cation  $1^+$ , not the conjugated diene. Cyclization of this radical cation is significantly exothermic and is irreversible. The observed products and the molecular orbital calculations indicate that on the cyclized, distonic radical cation intermediates,  $1a^+$ and  $1b^+$ , the positive charge density is largely on the tertiary and secondary alkyl moiety, and the spin density is delocalized on the allylic radical. The addition of methanol to the initially formed radical cation follows the established pattern for alcohol addition to mono alkenes; addition occurs preferentially to ultimately yield the more heavily substituted, more stable,  $\beta$ -alkoxyalkyl radical. Cyclization of these radicals, **1c** and **1d**, occur 1,6-endo.

		Charge	Spin
	Atom	density	density
β-Myrcene radical cation, $1^{+}$ ( $E = -388.91912$ )			
10	1	-0.026	-0.000
#U II	2	0.065	0.002
3	3	0.102	0.005
4 2	4	0.043	0.030
5	5	0.058	-0.068
6	6	0.253	0.610
	7	0.187	0.451
8 7 9	8	0.183	-0.015
. †	9	0.187	-0.014
1-	10	-0.051	-0.000
β-Myrcene cyclized, distonic, radical cation, $1a^{+}$ (E =	= -388.953 51)		
10	1	0.060	-0.068
1,	2	0.029	0.914
3	3	0.073	-0.788
4 2	4	0.066	0.049
5 1	5	0.059	-0.008
6	6	-0.050	0.010
$\sim$	7	0.323	-0.001
8 7 9	8	0.211	0.000
+	9	0.211	0.000
1a •	10	0.017	0.892
β-Myrcene cyclized, distonic, radical cation, $1b^+$ ( $E =$	= -388.937 18)		
1	1	0.023	0.854
2	2	0.040	-0.787
	3	0.016	1.027
4 10	4	0.092	-0.072
	5	0.110	0.012
5 7 9	6	0.476	0.001
6 - 8	7	-0.198	0.011
	8	0.180	-0.002
+ 15 *	9	0.151	-0.000
ui ui	10	0.110	-0.073

Table 3. Charge and spin density distribution on the radical cations 1<sup>++</sup>, 1a<sup>++</sup>, and 1b<sup>++</sup>.<sup>a</sup>

<sup>a</sup>Spin and charge densities include hydrogens summed into heavy atoms.

# **Experimental**

#### **General information**

The <sup>1</sup>H and <sup>13</sup>C nmr spectra were obtained from a Bruker AC 250 F spectrometer. Spectra were recorded in parts per million and frequencies are relative to tetramethylsilane. Infrared spectra (ir) were recorded on a Nicolet 205 FTIR and are reported in wave numbers (cm<sup>-1</sup>). Elemental analyses were performed by Canadian Microanalytical Service Ltd., B.C. Exact mass determinations were obtained using a CEC 21-110 mass spectrometer at Dalhousie University, Halifax, NS. Melting points were determined using a Cybron Corporation Thermolyne apparatus with a digital thermocouple and are corrected. Product yields and progress of the reactions were determined using a Hewlett-Packard (HP) 5890 gas chromatograph with a DB-1701 fused silica WCOT column (30 m  $\times$  0.25 mm, 0.25  $\mu$ m film thickness) and a calibrated flame ionization detector (GC-fid) and are based upon 1,4-dicyanobenzene (2) as the limiting reagent. An HP 3392A integrator was interfaced with the GC-fid to obtain peak areas. An HP 5890 gas chromatograph with a 5% phenyl methyl silicone fused silica WCOT column (25 m × 0.20 mm, 0.33 µm film thickness) interfaced with an HP 5970 mass selective detector (GC-MS) was also used for product analyses. Mass spectra are reported as m/z (relative intensity). Separation of product mixtures was generally carried out using preparative medium-pressure liquid chromatography (mplc) (1*a*). The mplc consists of a 2.5 cm × 1 m column packed with thin-layer chromatography (TLC) grade silica gel (without binder) (Rose Scientific Ltd., cat. 81632) at a pressure of 19 psi using helium (1 psi = 6.9 kPa). Connected to the mplc was a uv spectrophotometer – fraction collector collecting ca. 10 mL fractions.

#### Materials

Acetonitrile (Fisher ACS grade) was distilled twice, first from sodium hydride and then from phosphorus pentoxide. It was then passed through a column of basic alumina,

	Energy diff.	C1—C6	C7—C10	C1—C7	C6—C10	C1-C2-C3-C10
Conformer	(kJ/mol)	(Å)	(Å)	(Å)	(Å)	(°)
Stochastic sea	arch, molecular me	echanics (MM	3, 94 (6))			
1	0.000	4.74	5.81	5.10	4.66	177.44
2	0.371	4.73	5.34	6.01	4.67	176.85
3	3.687	4.66	3.63	4.96	3.38	177.45
4	3.932	6.00	5.77	6.65	4.65	2.54
5	4.014	6.01	5.31	7.12	4.64	2.73
6	4.417	3.41	5.25	3.83	4.01	176.30
7	4.432	4.62	4.19	5.91	3.37	178.30
8	4.990	3.44	4.31	3.72	4.06	177.47
9	6.716	4.49	4.34	4.36	4.08	3.34
Ab initio mol	ecular orbital theo	ory (UHF/6-31	G*) (4)			
		5.34	5.43	6.28	4.44	179.8
β-Myrcene rad	dical cation $(1^+)$ ,	ab initio mole	cular orbital the	ory (UHF/6-3	(4) (1G*)	
		5.30	5.42	6.30	4.38	179.1

Table 4.  $\beta$ -Myrcene (1) conformers.

Scheme 1. Cyclization of the initially formed  $\beta$ -myrcene radical cation, to give the distonic radical cation, followed by reaction of the distonic radical cation with nucleophile (methanol) and with the aromatic radical anion.



refluxed over calcium hydride for 24 h (under a nitrogen atmosphere), fractionally distilled (under nitrogen), and stored over molecular sieves (3 Å) (7). Methanol was distilled and then stored over molecular sieves (4 Å). 1,4-Dicyanobenzene (2) (Aldrich) was purified by treatment with Norite in methylene chloride, followed by recrystallization from 95% ethanol. Tetraethylammonium perchlorate (TEAP) (Aldrich) was recrystallized three times from water and then dried in a vacuum oven for 15 h, 70°C, 0.25 Torr (1 Torr = 133.3 Pa). Myrcene (1) (technical grade) was obtained from the Aldrich Chemical Co. and purified by vacuum distillation. Biphenyl (Eastman Kodak Co.) was recrystallized from methanol.

### Irradiation

The irradiation was carried out on an acetonitrile-methanol (3:1) solution consisting of myrcene (1), 1,4dicyanobenzene (2), and biphenyl. Solutions were irradiated in either 2 cm i.d. Pyrex tubes or 5 mm Pyrex nmr tubes, which were degassed by nitrogen ebullition. These samples were irradiated at 10°C using a CGE 1 MW mediumpressure mercury vapour lamp contained in a water-cooled quartz immersion well.

#### Cyclic voltammetric measurements

Cyclic voltammetry was used to obtain the oxidation potential of myrcene (1). The apparatus has been described (8). The working electrode was a platinum sphere (1 mm diameter), and the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (sce), which was connected to the solution (TEAP 0.1 M, acetonitrile) through a Luggin capillary. The alkene concentration was ca. 0.005 M. Since the anodic wave was irreversible, the half-wave potential was taken as 0.028 V before the anodic peak potential (9).

#### Formation of the methanol, $\beta$ -myrcene (1), 1,4dicyanobenzene (2) photo-NOCAS adducts 15, 16, 17, 18, and 19: reaction [5]

A solution of  $\beta$ -myrcene (1) (10.0 mL, 8.0 g, 0.059 mol), 1,4-dicyanobenzene (2) (3.7 g, 0.029 mol), and biphenyl (2.3 g, 0.015 mol) in acetonitrile-methanol (3:1) (240 mL) was degassed by nitrogen ebullition and irradiated for 9 days using a 1 kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was chromatographed (mplc) using a linear solvent gradient (hexanes – 10% diethyl ether, 90% hexanes). Isolation of the adducts was achieved via further chromatography using mplc and a linear solvent gradient (hexanes – 1% diethyl ether, 99% hexanes). The five 1:1:1 adducts were eluted in Scheme 2. Reaction of the initially formed  $\beta$ -myrcene radical cation with nucleophile (methanol), to give the radical, followed by cyclization of the radical and reaction with the aromatic radical anion.

**Table 5.** Calculated and experimental oxidation potentials and ionization potentials of  $\beta$ -myrcene (1) and model systems.

	IP v (calcd.) <sup><math>a</math></sup>	IP a (calcd.) <sup><math>b</math></sup>	$E^{OX}_{1/2}$ (V)
2-Methyl-2-	8.68 <sup>d</sup> (8.93)	(8.27)	2.03 <sup>e</sup>
butene (3)			
2-Methyl-1,3-	$8.89^d$ (8.67)	(8.45)	$2.25^{f}$
butadiene (6)			
β-Myrcene (1)	$8.68^g$ (8.65)	8.36 (8.24)	2.12
	$8.92^{h}$		

<sup>*a*</sup> Experimental vertical ionization potential; calculated vertical ionization potential in parentheses, taken from the eigenvalue of the HOMO.

<sup>b</sup> Experimental adiabatic ionization potential; calculated adiabatic ionization potential in parentheses, taken as the difference between the calculated total energy of the minimized neutral molecule and the minimized radical cation.

<sup>c</sup> Measured (CV) oxidation potential (vs. sce).

<sup>d</sup> Reference 10.

<sup>e</sup> Reference 2a.

<sup>f</sup> Reference 2c.

<sup>g</sup> HOMO.

<sup>h</sup> The second band.

the order **19**, **18**, **16**, **17**, and **15**. Adducts **15–17** were found to be identical, mass spectra and GC retention times, with photo-NOCAS adducts previously characterized from  $\beta$ pinene (**14**) (2*e*), *cis*-2-(4-cyanophenyl)-4-(1-methoxy-1methylethyl)-1-methylenecyclohexane (**15**, 1%), *trans*-2-(4cyanophenyl)-4-(1-methoxy-1-methylethyl)-1-methylenecyclohexane (**16**, 3%), 1-(4-cyanophenylmethyl)-4-(1-methoxy-1-methylethyl)cyclohexene (**17**, 4%).

#### 4-(1-Vinyl-4-trans-methoxy-3,3-dimethylcyclohexyl]benzonitrile (19)

The yield of **19** was 5%; infrared (Nicolet 205) v: 3082 (w), 2930 (s), 2875 (m), 2822 (m), 2228 (s), 1632 (w), 1605 (m), 1504 (m), 1461 (m), 1408 (w), 1388 (w), 1363 (m), 1186 (m), 1101 (s), 1040 (w), 1019 (w), 997 (w), 915 (m), 835 (m); <sup>1</sup>H nmr (250.13 MHz, CDCl<sub>3</sub>),  $\delta_{TMS}$ : 0.72 (s, 3H, CH<sub>3</sub>), 0.96 (s, 3H, CH<sub>3</sub>), 1.71–1.97 (m, 5H, cyclohexyl H's), 2.20 (m, 1H, cyclohexyl H), 2.81 (m, 1H, H of methoxy-

substituted carbon (4-H)), 3.36 (s, 3H, OCH<sub>3</sub>), 4.87 (d, 1H,  ${}^{3}J_{1'-2'trans} = 17.7$  Hz, vinyl H (2'trans-H)), 5.03 (d, 1H,  ${}^{3}J_{1'-2'cis}$  $J_{1-2trans}^{-2}$  = 10.7 Hz, vinyl H (2/cis-H)), 5.86 (dd, 1H,  ${}^{3}J_{1'-2'trans}^{-2}$  = 10.7 Hz,  ${}^{3}J_{1'-2'trans}^{-2}$  = 10.7 Hz,  ${}^{3}J_{1'-2'trans}^{-2}$  = 10.7 Hz, vinyl H (1'-H)), 7.45 (d, 2H,  ${}^{3}J_{2'-3'}^{-3}$  = 8.5 Hz,  ${}^{3}J_{5'-6'}^{-2}$  = 8.5 Hz, H's adjacent to alkylsubstituted aryl carbon (2'-H, 6'-H)), 7.58 (d, 2H,  ${}^{3}J_{2'-3'}$  = 8.5 Hz,  ${}^{3}J_{5'-6'} = 8.5$  Hz, H's adjacent to cyano-substituted aryl carbon (3'-H, 5'-H)). The NOE experiment: the methyl protons at 0.72 and 0.96 ppm were irradiated. When the methyl protons at 0.72 ppm were irradiated, an NOE was observed for the proton of the methoxy-substituted methine, the methoxy-methyl protons, and the methyl protons (0.96 ppm). When the methyl protons at 0.96 ppm were irradiated, an NOE was observed for the methoxy-methyl protons, the vinyl protons, and the methyl protons (0.72 ppm). <sup>13</sup>C nmr (62.90 MHz, CDCl<sub>3</sub>), δ: 22.12 (t), 24.03 (q), 29.44 (q), 30.17 (t), 36.17 (s), 44.31 (s), 47.42 (t), 57.37 (q, OCH<sub>3</sub>), 85.58 (d, CH, methoxy-substituted), 109.50 (s, quaternary aryl carbon, cyano-substituted), 112.52 (t, alkene CH<sub>2</sub>), 119.06 (s, CN), 127.27 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 131.98 (d, aromatic CH adjacent to cyano-substituted carbon), 146.73 (d, alkene CH), 153.38 (s, quaternary aryl carbon, alkyl-substituted); MS, m/z: 55(14), 58(22), 71(100), 115(15), 116(19), 121(17), 127(16), 140(18), 154(22), 155(13), 166(20), 181(13), 194(52), 195(13), 237(17). Exact mass calcd. for C<sub>18</sub>H<sub>23</sub>NO: 269.1780; found: 269.1773.

# 4-[4-Methoxy-3,3-dimethylcyclohex-(E)-1-ylidenyl]methylbenzonitrile (18)

The yield of **18** was 7%; infrared (Nicolet 205) v: 2969 (s), 2950 (s), 2870 (m), 2822 (m), 2228 (s), 1607 (m), 1504 (m), 1452 (m), 1184 (m), 1101 (s), 823 (m); <sup>1</sup>H nmr (250.13 MHz, CDCl<sub>3</sub>),  $\delta_{\text{TMS}}$ : 0.84 (s, 3H, CH<sub>3</sub>), 0.94 (s, 3H, CH<sub>3</sub>), 1.38–1.55 (m, 1H, <sup>3</sup>J<sub>4ax-5ax</sub> = 8.5 Hz, <sup>3</sup>J<sub>5ax-6eq</sub> = 5.5 Hz, axial H of methylene group (5ax-H)), 1.77–2.08 (m, 4H, <sup>2</sup>J<sub>6ax-6eq</sub> = 13.7 Hz, <sup>2</sup>J<sub>2ax-2eq</sub> = 13.4 Hz, <sup>3</sup>J<sub>5eq-6eq</sub> = 5.5 Hz, <sup>3</sup>J<sub>4ax-5eq</sub> = 3.7 Hz, H of methylene groups on ring (2ax-, 2eq-, 5eq-, 6ax-H)), 2.46 (dt, 1H, <sup>2</sup>J<sub>6ax-6eq</sub> = 13.7 Hz,

 ${}^{3}J_{5ax-6eq} = 5.5$  Hz,  ${}^{3}J_{5eq-6eq} = 5.5$  Hz, equatorial H of methylene group on ring (6eq-H)), 2.93 (dd, 1H,  ${}^{3}J_{4ax-5ax} = 8.5$  Hz,  ${}^{3}J_{4ax-5eq} = 3.7$  Hz, CH group, methoxy-substituted (4ax-H)),  $^{4ax-seq}$  517 III, 513 group, integrating 518 Jack (in III), 513 group, and (in III), 513 (in Group, aryl-substituted (8-H)), 5.20 (i, 1H,  $^{3}J_{7-8} = 7.3$  Hz, Vinyl H (7-H)), 7.27 (d, 2H,  $^{3}J_{2'-3'} = 8.5$  Hz,  $^{3}J_{5'-6'} = 8.5$  Hz, H's adjacent to alkyl-substituted aryl carbon (2'-H, 6'-H)), 7.56 (d, 2H,  ${}^{3}J_{2'-3'} = 8.5$  Hz,  ${}^{3}J_{5'-6'} = 8.5$  Hz, H's adjacent to cyano-substituted aryl carbon (3'-H, 5'-H));  ${}^{13}$ C nmr (62.90 MHz, CDCl<sub>3</sub>),  $\delta$ : 21.61 (q), 25.00 (t), 25.78 (t), 27.52 (q), 33.87 (t), 37.17 (s), 47.93 (t, CH<sub>2</sub>, aryl-substituted), 57.52 (q, OCH<sub>3</sub>), 85.91 (d, CH, methoxy-substituted), 109.59 (s, quaternary aryl carbon, cyano-substituted), 119.18 (s, CN), 120.12 (d, vinyl CH), 129.08 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.22 (d, aromatic CH adjacent to cyano-substituted carbon), 138.77 (s), 147.53 (s); MS, m/z: 55(27), 67(26), 71(25), 77(22), 79(23), 93(34), 116(55), 121(83), 154(44), 167(23), 180(22), 194(64),195(24), 237(100). Anal. calcd. for C<sub>18</sub>H<sub>23</sub>NO: C 80.26, H 8.61, N 5.20; found: C 79.90, H 8.78, N 4.91.

# Preparation of 4-[4-methoxy-3,3-dimethylcyclohex-(*E*)-1-ylidenyl]methylbenzoic acid (18a)

4-[4-Methoxy-3,3-dimethylcyclohex-(E)-1-ylidenyl]methylbenzonitrile (**18**) (0.041 g, 0.15 mmol) and 4 mL of a 40% sodium hydroxide solution was refluxed for 2 days. This mixture was cooled and extracted with dichloromethane. The aqueous layer was acidified with hydrochloric acid (conc.) and extracted twice with benzene. Evaporation of the solvent left a white solid (0.026 g, 0.090 mmol), which was recrystallized from hexanes.

# 4-[4-Methoxy-3,3-dimethylcyclohex-(E)-1-ylidenyl]methylbenzoic acid (18a)

The yield of 18a was 60%: the melting point was 112-113°C; infrared (Nicolet 205) v: 2967 (s), 2938 (s), 2900 (m), 2871 (m), 2821 (m), 2674 (w), 2544 (w), 1682 (s), 1608 (m), 1572 (w), 1425 (s), 1318 (m), 1290 (s), 1182 (m), 1101 (s), 951 (w); <sup>1</sup>H nmr (250.13 MHz, CDCl<sub>3</sub>),  $\delta_{TMS}$ : 0.86 (s, 3H, CH<sub>3</sub>), 0.95 (s, 3H, CH<sub>3</sub>), 1.39–1.56 (m, 1H,  ${}^{3}J_{4ax-5ax}$ (5, 51, CH<sub>3</sub>), 0.25 (5, 51, CH<sub>3</sub>), 1.65 (1.6, 1.65 (1.1, 1.4,  $t_{4ax-3ax}$ = 8.6 Hz,  ${}^{3}J_{5ax-6eq}$  = 5.5 Hz, axial H of methylene group (5ax-H)), 1.80–2.06 (m, 4H,  ${}^{2}J_{6ax-6eq}$  = 13.7 Hz,  ${}^{2}J_{2ax-2eq}$  = 13.6 Hz,  ${}^{3}J_{5eq-6eq}$  = 5.5 Hz,  ${}^{3}J_{4ax-5eq}$  = 3.7 Hz, H of methy-lene groups on ring (2ax-, 2eq-, 5eq-, 6ax-H)), 2.49 (m, 1H,  ${}^{2}J_{6ax-6eq} = 13.7$  Hz,  ${}^{3}J_{5ax-6eq} = 5.5$  Hz,  ${}^{3}J_{5eq-6eq} = 5.5$  Hz, equatorial H of methylene group on ring (6eq-H)), 2.94 (dd, <sup>1</sup>H,  ${}^{3}J_{4ax-5ax} = 8.6$  Hz,  ${}^{3}J_{4ax-5eq} = 3.7$  Hz, CH group, methoxy-substituted (4ax-H)), 3.38 (s, 3H, OCH<sub>3</sub>), 3.44 (d, 2H,  ${}^{3}J_{7-8} = 7.3$  Hz, CH<sub>2</sub> group, aryl-substituted (8-H)), 5.24 (t, 1H,  ${}^{3}J_{7-8} = 7.3$  Hz, vinyl H (7-H)), 7.27 (d, 2H,  ${}^{3}J_{2'-3'} =$ 8.1 Hz,  ${}^{3}J_{5'-6'} = 8.1$  Hz, H's adjacent to alkyl-substituted aryl carbon (2'-H, 6'-H)), 8.02 (d, 2H,  ${}^{3}J_{2'-3'} = 8.1$  Hz,  ${}^{3}J_{5'-6'} =$ 8.1 Hz, H's adjacent to cyano-substituted aryl carbon (3'-H, 5'-H)); <sup>13</sup>C nmr (62.90 MHz, CDCl<sub>3</sub>), δ: 21.52 (q), 25.06 (t), 25.83 (t), 27.58 (q), 33.90 (t), 37.19 (s), 48.04 (t, CH<sub>2</sub>, arylsubstituted), 57.53 (q, OCH<sub>3</sub>), 86.14 (d, CH, methoxysubstituted), 120.79 (d, vinyl CH), 126.90 (s, quaternary aryl carbon, COOH-substituted), 128.46 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 130.41 (d, aromatic CH adjacent to COOH-substituted carbon), 138.13 (s), 148.43 (s), 172.13 (s, C=O of COOH); MS, m/z: 55(26),

77(35), 79(27), 91(36), 93(36), 107(31), 121(78), 128(37), 129(50), 135(30), 141(41), 211(30), 213(50), 256(100). X-ray data: see footnote 3.

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