Non-heme iron catalysis in C=C, C—H, and CH$_2$ oxidation reactions. Oxidative transformations on terpenoids catalyzed by Fe(bpmen)(OTf)$_2$

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ABSTRACT

The oxidation of terpene olefins with hydrogen peroxide in the presence of the non-hemo catalyst **5a** afforded mixtures of epoxides whose composition was dependent upon the oxidation protocol used in each case. With terpenoid enones, the mixtures obtained evolved from clean epoxidation of α-ionone **23** to the clean allylic oxidation of damascone **28** due to the progressive deactivation of the electron density on the double bonds present in this series.

The oxidation of bicyclic and tricyclic terpenoids afforded oxidation products coming from epoxidation, to olefin degradation, methyne and methylene activation products. Probably, the most attractive result was the synthesis of the Magnus lactone **46**, from the tricyclic ether **45**, with 88% yield and 100% conversion.

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1. Introduction

Iron catalysis has emerged as an attractive research area in recent years.[1] Iron has a number of advantages over other transition metals usually employed in catalysis; it is relatively non-toxic, abundant, cheap, and environmentally friendly.[2] As a consequence, iron-based catalyst systems have been applied in numerous organic transformations such as carbon—carbon,[3] carbon—heteroatom,[4] hetero—heteroatom bond-forming reactions,[5] atom transfer radical polymerizations,[6] reductions,[7] and oxidations.[8]

The selective oxidation of hydrocarbons under mild conditions constitutes a major challenge of modern chemistry.[9] Non-heme iron enzymes, such as methane monooxygenase[10] and Rieske dioxygenases,[11] catalyze such reactions and have inspired the development of synthetic models as alkane oxidation catalysts.[12] Exceptional non-heme iron catalysts are those that are architecturally reminiscent of the active sites in non-heme enzymes found in nature. Mononuclear iron complexes synthesized from tris(picolyl)amine (tpa, **1**. Fig. 1),[9b] the tetradentate bpmen ligand scaffold (**2a**),[12c,13] or from substituted pyridine ligand **3**,[14] act as very efficient catalysts, using the environmentally friendly H$_2$O$_2$ as the oxidant in several oxidative transformations, such as the oxidation of alkanes[15] or alkenes.[16] Complex **4** has been shown to selectively oxidize methine groups

to tertiary alcohols.[17] Furthermore, iron salts in combination with peroxides and appropriate additives also show catalytic activity in oxidation reactions of alkanes, alkenes or arenes and in epoxidation reactions.[18]

Terpenes are cheap and are often chiral precursors to fragrances, flavors, drugs, and agrochemicals.[19] Oxy functionalization of terpenes frequently starts with a selective epoxidation. Although catalytic epoxidation is currently the main pathway used to obtain many commodities and fine chemicals, the synthesis of major terpene oxides still employs the stoichiometric peracid route. In designing a catalytic alternative, we assumed that the use of H$_2$O$_2$ in the presence of Fe(bpmen)(OTf)$_2$ (**5a**)[13c] (bpmen: [N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-diaminomethane]; OTf: trifluoromethanesulfonate) could be appropriate for the development of an alternative, more affordable and sustainable method to access functionalized terpene derivatives.

2. Results and discussion

As part of a research project aimed at the study of hydrogen peroxide-promoted oxidative transformations of highly valuable starting materials in the presence of Fe(II) non-heme complexes, we recently reported our results on the oxidative transformations of steroid enones.[20] We now report our results on terpenoid olefins, enones and polycyclic substrates. The oxidation reactions were carried out at room temperature with the progressive addition of

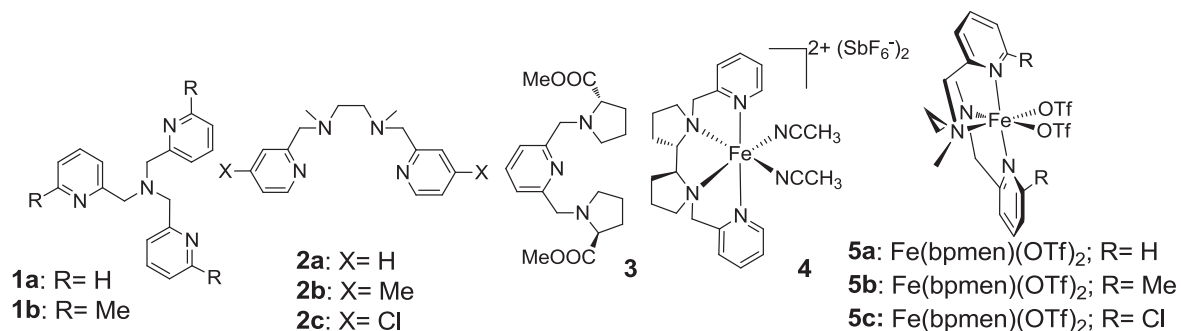* Corresponding author. E-mail address: fcobmjo@usal.es (F.A. Bermejo).

Fig. 1. Examples of ligand and non-heme iron(II) oxidation catalysts.

hydrogen peroxide in the open air (see Experimental part). The reactions were followed by TLC and were stopped after 10 min (protocol A), and after 30 min (protocol B). The product mixtures resulting from the substrate oxidation reactions were fractionated by column chromatography and identified by comparing their ^{1}H NMR and ^{13}C NMR spectra with the data in the literature. Tables 1–3 summarize our results.
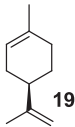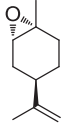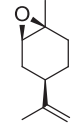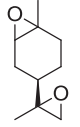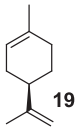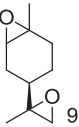
2.1. Terpenoid olefins

The oxidation reactions of the terpenoid olefins (geranyl acetate **6**, farnesyl acetate **9**, nerol acetate **12**, linalool acetate **16**, and R-(+)-limonene **19**) with H_2O_2 in the presence of **5a** led to mixtures of monoepoxides and diepoxides, depending on the degree of unsaturation of the olefinic substrate. Generally speaking, by using

Table 1
Catalytic oxidation of trisubstituted and terminal olefins by Fe(bpmen)(OTf)$_2$[a]

Entry	Diolefin	Catalyst (%)	Oxidant (equiv)	Conversion[b] (%)	Yield[c] (%)
1	**6**	5	1	80	**7** 40% (50%) **8** 20% (25%)
2	**9**	5	1	80	**10** 40% (50%) **11** 20% (25%)
3	**12**	5	1	84	**13** 51% (60%) **14** 9% (11%) **15** 10% (12%)
4[d]	**12**	15	3	100	**15** 41% (41%)
5	**16**	5	1	80	**17** 68% (85%)
6[d]	**16**	15	3	100	**17** 12% (12%) **18** 23% (23%)

Table 1 (*continued*)

Entry	Diolefin	Catalyst (%)	Oxidant (equiv)	Conversion[b] (%)	Yield[c] (%)
7[e]	**19**	5	1	100	**20** 70% (70%) **21** 7% (7%) **22** 9% (9%)
8[d]	**19**	15	3	100	**22**[f] 90% (90%)

[f] Diastereomeric mixture of diepoxides.

[a] In all cases AcOH was used as additive for the catalyst, as described in Experimental section.

[b] Conversion was determined by GC or ^{1}H NMR analysis of the crude product.
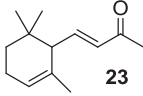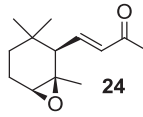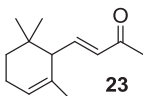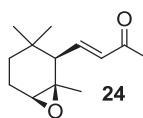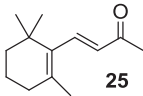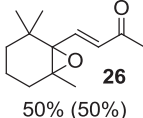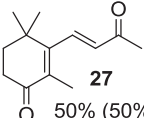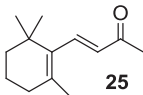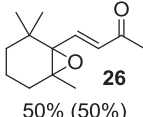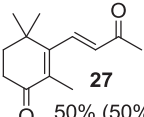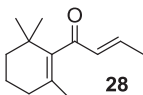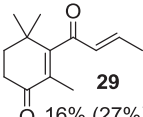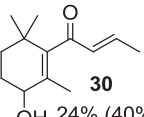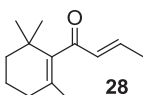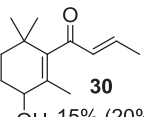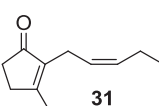
[c] Isolated yield based on starting substrate; isolated yield based on conversion is shown in brackets.

[d] The percentages of the mixture components were determined by GC/MS (see Experimental section).

[e] The reaction was run under Ar.
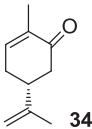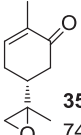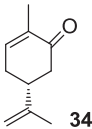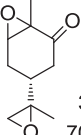
Table 2
Catalytic oxidation of enones by Fe(bpmen)(OTf)$_2$[a]

Entry	Enone	Catalyst (%)	Oxidant (equiv)	Conversion[b] (%)	Yield[c] (%)
1	**23**	5	1	100	**24** 100% (100%)
2	**23**	15	3	100	**24** 100% (100%)
3	**25**	5	1	100	**26** 50% (50%) **27** 50% (50%)
4	**25**	15	3	100	**26** 50% (50%) **27** 50% (50%)
5	**28**	5	1	60	**29** 16% (27%) **30** 24% (40%)
6	**28**	15	3	75	**29** 60% (80%) **30** 15% (20%)
7	**31**	5	1	94	(±)**32** 80% (85%)

(*continued on next page*)

Table 2 (*continued*)

Entry	Enone	Catalyst (%)	Oxidant (equiv)	Conversion[b] (%)	Yield[c] (%)
8	**31**	15	3	100	(±)**32** 10% (10%) **33**[d] 15% (15%)
9	**34**	5	1	74	**35**[e] 74% (100%)
10	**34**	15	3	70	**36**[f] 70% (100%)

[d] Mixture of diastereomeric epoxy *threo* diols.
[e] Product **35** was isolated as a 1:1 mixture of diastereoisomers.
[f] Product **36** was isolated as a mixture of different diastereoisomers.
  [a] In all cases AcOH was used as additive for the catalyst, as described in Experimental section.
  [b] Conversion was determined by GC or ^{1}H NMR analysis of the crude product.
  [c] Isolated yield based on starting substrate; isolated yield based on conversion is shown in brackets.

Table 3
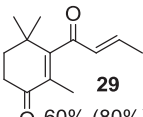Catalytic oxidation of bicyclic and tricyclic monoterpenes by Fe(bpmen)(OTf)$_2$[a]
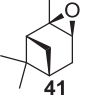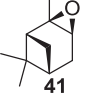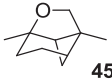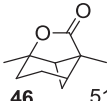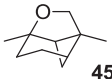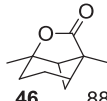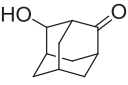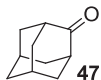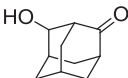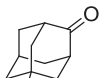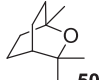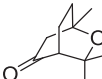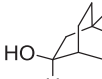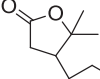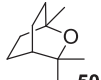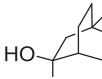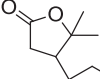
Entry	Monoterpene	Catalyst (%)	Oxidant (equiv)	Conversion[b] (%)	Yield[c] (%)
1	**40**	5	1	100	**41** 50% (50%)
2	**40**	15	3	100	**41** 50% (50%)
3[d]	**42**	5	1	91	**43** 64% (70%) **44** 10% (11%)
4[d]	**42**	15	3	98	**43** 75% (77%) **44** 12% (12%)
5	**45**	5	1	60	**46** 51% (85%)
6	**45**	15	3	100	**46** 88% (88%)
7	**47**	5	1	50	**48** 20% (40%) **49** 7% (14%)

Table 3 (*continued*)

Entry	Monoterpene	Catalyst (%)	Oxidant (equiv)	Conversion[b] (%)	Yield[c] (%)
8	**47**	15	3	100	**48** 40% (40%) **49** 27% (27%)
9	**50**	5	1	34	**51** 20% (59%) **52** 8% (23%) **53** 2% (5%)
10	**50**	15	3	63	**51** 41% (64%) **52** 8% (13%) **53** 5% (7%)

[a] In all cases AcOH was used as additive for the catalyst, as described in Experimental section.

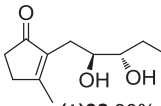[b] Conversion was determined by GC or ^{1}H NMR analysis of the crude product.

[c] Isolated yield based on starting substrate; isolated yield based on conversion is shown in brackets.

[d] The percentages of the mixture components were determined by GC/MS (see Experimental section).

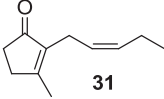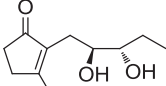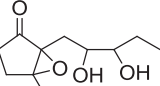1 equiv of the oxidant and 5% of the catalyst, the terminal tri-substituted monoepoxide was the major isolated product [**7** (50%), **10** (50%), **13** (60%), and **17** (85%)] (Table 1; entries 1, 2, 3, and 5, respectively). In the case of *R*-(+)-limonene **19** (Table 1, entry 8), the trisubstituted epoxides **20** (70%) and **21** (7%) were obtained, although they were contaminated with the diepoxide **22** (9%). It is clear that by using 1 equiv of oxidant we were looking for chemoselection among the double bonds within the molecule, and, evidently, the terminal trisubstituted double bond is the most activated one in all cases. Increasing the amount of oxidant (3 equiv) and that of the catalyst (15%) led to the isolation of the diepoxides [**15** (41%), **18** (23%), and **22** (90%)] as the major products (Table 1; entries 4, 6, and 8, respectively).

The stereoselectivity of epoxidation in the case of *R*-(+)-limonene (+)-**19** is interesting since it furnished the *cis*-*R*-(+)-limonene oxide **20** (70%) as the major component of the mixture with the trans diastereomer **21** (7%) (Table 1, entry 7). Both (+)- and (−)-limonene oxides are available commercially and are relatively inexpensive, but they are marketed as a 1:1 mixture of the *cis*- and *trans*-epoxides. Owing to the difficulty involved in the separation of limonene oxide diastereomers by physical means, synthetic routes to pure limonene oxide have been attempted by many research groups.[21]

In all cases, increasing the amounts of both the oxidant and the catalyst led to general product degradation, and the yields of the isolated oxidation products were rather poor. This trend was in accordance with previous observations with some cholestane derivatives.[20]

2.2. Terpenoid enones

We next focused our attention on the oxidation of different types of diterpenoid enones (Table 2). The α- and β-ionones (**23** and **25**, respectively) showed a difference of the behavior of the endocyclic double bond. The α-ionone **23** led quantitatively to the *cis* epoxide **24** under the two different protocols (Table 2, entries 1 and 2). The assignment of the configuration of **24** was achieved by using dimensional techniques, namely COSY (^{1}H/^{1}H), HMQC (^{1}H/^{13}C) and HMBC (^{1}H/^{13}C-long range) experiments, as well as by DEPT techniques (see Supplementary data), and was also based on the data in

the literature given for similar cases.[22] However, due to a stereo-electronic effect the endocyclic double bond in β-ionone **25** is now deactivated, and competition in the epoxidation leading to **26** by the allylic oxidation leading to the diketone **27** was observed. Increasing the amounts of oxidant and catalyst did not interfere in the results since both products **26** and **27** were isolated, in both cases with 50% yield (Table 2, entries 3 and 4). The yields observed for the oxidation products **26** and **27** were confusing, since their formation required more than 1 equiv of oxidant. However, when the reaction was run under inert atmosphere the yield of **27** decreased dramatically and the corresponding allylic alcohol was obtained in 30% yield. This change suggests the role of molecular oxygen in this transformation.

Owing to the proximity of the carbonyl to the cyclohexene ring in damascone **28**, the deactivation of both double bonds present in the molecule is evident. The oxidation of **28** led to the isolation of the allylic oxidation products **29** and **30**, with different yields (**29**/**30**=27:40 vs **29**/**30**=80:20), depending on the protocol used in each case (Table 2, entries 5 and 6). Conversion was higher in the latter case (75%).

We assumed that owing to the progressive deactivation of the electronic density on the double bonds present in the α-, β-ionone, and damascone series, the oxidative transformations under the conditions described above evolved from a clean epoxidation (α-ionone) to a clean allylic oxidation (damascone). The oxidation reaction of *cis*-jasmone **31** with hydrogen peroxide (1 equiv) in the presence of catalyst **5a** (5%) led to the isolation of the *threo* diol (±)-**32** with 85% yield and 94% conversion (Table 2 entry 7). In order to confirm the relative stereochemistry of (±)-**32**, *cis*-jasmone epoxidation was performed with *m*-chloro-peroxybenzoic acid, affording the desired racemic epoxide (±)-**37**, which by treatment with hydrochloric acid led to the same *threo* diol (±)-**32** with quantitative yields (Scheme 1).[23] The spectroscopic properties obtained for both reaction products and their corresponding acetonides (±)-**38** were superimposable. However, the *erythro* diol (−)-**39** was obtained from *cis*-jasmone under Sharpless dihydroxylation conditions,[24] with 76% yield. The spectroscopic properties obtained for (−)-**39** (^{1}H NMR: δ_{HA}=3.53 ppm; δ_{HB}=3.33 ppm; J_{HH}=4 Hz; ^{13}C NMR: δ_{CA}=73 ppm; δ_{CB}=75 ppm) were perceptibly different from those obtained for (±)-**32** (^{1}H NMR: δ_{HA}=3.43 ppm;
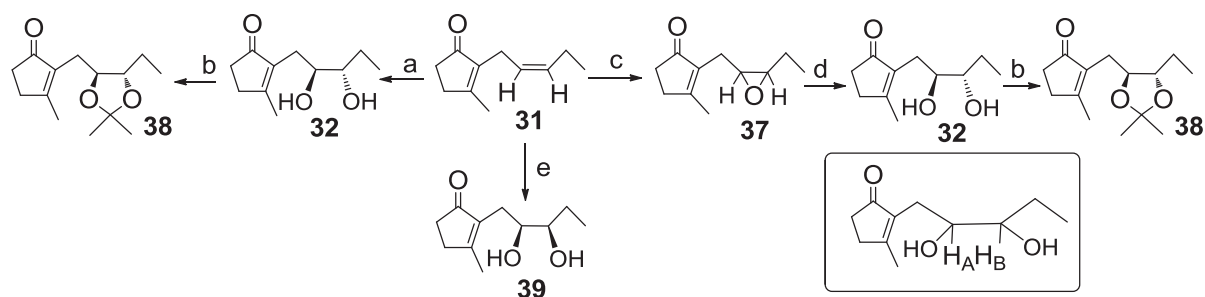
Scheme 1. Reagents and conditions: (a) H_2O_2, **5a**, AcOH, rt, 85%; (b) DMP, pTsOH, CH_2Cl_2, 90%; (c) m-CPBA, $NaHCO_3$, CH_2Cl_2, 99%; HCl/H_2O, THF; (d) HCl, H_2O, $CHCl_3$, 85%; (e) ADmixβ, H_2O, ^tBuOH, 76%.

δ_{HB}=3.17 ppm; J_{HH}=6 Hz; ^{13}C NMR: δ_{CA}=72 ppm; δ_{CB}=74 ppm), ratifying the proposed threo relative configuration of the isolated product (±)-**32**.

The stereochemical outcome of the oxidative transformation of cis-jasmone (**31**; Table 2, entry 7) may be explained in two different ways.

First, the water-assisted hydrolytic cleavage of epoxides, leading to trans-diols under similar reaction conditions, has been invoked earlier for cis-2-heptene. However, this was only argued to account for the formation of very small amounts of product.[25] In our case, however, the threo diol (±)-**32** was isolated in high yields (80%) and its formation took place shortly after the reaction had started. Thus, it is clear that its formation was not caused during the work-up protocol. In our opinion, the water-assisted hydrolytic cleavage of the precursor epoxide under the reaction conditions might not be ruled out.

However, the stereochemistry of (±)-**32** also suggests the participation of an oxidized olefin species capable of fast epimerization during the oxidation process. A possible explanation may be drawn in terms of a high-valent hydroxy-oxoiron intermediate [**2a**]Fe^V(O)OH (**A**), analogous to that invoked by Que and co-workers,[26] to form a carbon radical intermediate (**B**), which undergoes the closure of the carbon–oxygen bond to (**C**) after isomerization, leading to the threo diol (±)-**32** (Fig. 2).

The epoxidation of α-pinene under standard peracid conditions may lead to the isomerization and/or hydrolysis of both the reactant and the product, furnishing a complex mixture of β-pinene, 3-carene, camphene, campholenic aldehyde, α-terpineol, and so on.[27] In our case, the oxidation of (−)-α-pinene **40** under either protocol A or B (Table 3, entries 1 and 2) afforded (−)-α-pinene oxide **41**, with 50% yield in both cases, the rest of the reaction mixture being an unsolvable mixture of degradation products. In the case of (−)-β-pinene **42**, however, the oxidation reaction under protocol A conditions occurred with 91% conversion and furnished a mixture of (+)-nopinone **43** (70%) as the major product, and (+)-trans-dihydromyrtenal **44** (11%),[28] present in only minor amounts (Table 3, entry 3). Due to the fact that all these transformations are run in the open air, molecular oxygen must play a role in the transformation of **42** into **43** and **44**, since the oxidative cleavage of a carbon–carbon double bond clearly does require more than 1 equiv of oxidant. Increasing the amounts of oxidant (3 equiv) and catalyst (15%) afforded the same mixture of compounds, with higher yields [**43** (77%) and **44** (12%), respectively] and 98% of conversion (Table 3, entry 4). The formation of nopinone **43** and cis-dihydromyrtenal **44** has been described previously for the noncatalytic oxidation of β-pinene with nitrous oxide.[29]

Fig. 2. Possible mechanism for the oxidative transformations of cis-jasmone.

Increasing the amount of the oxidant (3 equiv) and the catalyst (15%) afforded a mixture of (±)-**32** (10%) and a diastereomeric mixture of epoxy threo diols **33** (15%) that was impossible to elucidate by conventional chromatographic methods. As usual, the oxidative degradation of the substrate under protocol B conditions afforded rather poor yields of the oxidation products. Finally, the oxidation of R-(−)-carvone (−)-**34** with hydrogen peroxide (1 equiv) in the presence of the catalyst **5a** (5%) led to the isolation of the carvone oxide **35** with 74% yield as a 1:1 mixture of diastereoisomers and the increase in oxidant (3 equiv) and catalyst (15%) led to the cis/trans diastereomeric mixture of diepoxides **36** with 70% yield (Table 2, entries 9 and 10).

2.3. Bicyclic and tricyclic monoterpenes

We next undertook the oxidative transformations of several monoterpene representatives of the pinane, adamantane, 2-oxabicyclo[2.2.2]octane, and oxatricyclo[4.3.0.0^{3,9}]nonane skeletons. Our results are summarized in Table 3.

Treatment of the tricyclic terpenoid ether (+)-**45**[30] with hydrogen peroxide (1 equiv) and catalyst **5a** (5%) afforded the Magnus lactone (+)-**46**[31] with 85% yield and 60% of conversion (Table 3, entry 5). Upon increasing the amounts of oxidant (3 equiv) and catalyst (15%) the same transformation afforded (+)-**46**, with 88% yield and no recovery of the starting material (Table 3, entry 6). This result is particularly attractive because the reaction is much milder and faster than the conventional protocol of heating (+)-**45** with CrO$_3$ and acetic acid at 100 °C to deliver the lactone with 72% yield.[30,31]

The oxidation of bicyclic systems represents an interesting case of site selectivity in C–H activation. The well-known propensity of adamantane to undergo oxidation is an interesting peculiarity that has made it a bench-mark for C–H activation, and numerous examples of its oxidation have been documented.[32] Under protocol A (Table 3, entry 7) the 2-adamantanone **47** afforded a mixture of the tertiary and secondary hydroxy derivatives **48** (40%) and **49** (14%), with 50% of conversion. However, with 3 equiv of H_2O_2 in the presence of catalyst **5a** (15%) (Table 3, entry 8) a mixture of the same hydroxy derivatives **48** (40%) and **49** (27%) was obtained, with

total conversion of the starting material. Clearly, the presence of the carbonyl group at position C-2 distorts the normal C−H activation trend in this type of carbon skeleton.[33] Eucalyptol (1,8-cineole) **50** has been found to be oxidized at high rates to 2β-hydroxy-1,8-cineole by rat and human liver and lung microsomal P450 enzymes.[34] On the other hand, several hydroxy derivatives of 1,8-cineole have been identified as metabolites of different insect species[35] and synthetic attempts at the regiospecific functionalization of this interesting monoterpene are also available.[36]

The reduced selectivity observed in the ease of oxidation of the tertiary bridgehead position for bicyclo[2.2.2]octane compared to that observed for adamantane[37] led us to study the reaction of 1,8-cineole with H_2O_2 in the presence of catalyst **5a** to see if our method could bring any new fruitful contribution to the topic of C−H activation on that particular type of substrate. Unfortunately, and quite unlike the results obtained with the tricyclic ether **45**, the oxidative transformation of **50** by reaction with hydrogen peroxide (1 equiv) in the presence of catalyst **5a** (5%) afforded a mixture of the 3-oxo-1,8-cineole **51** (59%),[36] the 3β-hydroxy-1,8-cineole **52** (23%),[38] and 5,5-dimethyl-4-(3-oxobutyl)-2(3H)-dihydrofuranone **53** (5%),[39] with a rather low conversion (34%) (Table 3, entry 9).

Nevertheless, the increase in both, oxidant (3 equiv) and catalyst (15%) furnished a mixture of **51** (64%), **52** (13%), and **53** (7%),[40] with higher oxoselectivity and higher level of conversion (63%) (Table 3, entry 10). The structure of the secondary alcohol **52** has been assigned by comparison of its spectroscopic data [^{1}H NMR: δ=4.46 ppm (1H, dd, HCOH), ^{13}C NMR: δ=65.49 ppm (d, C-3), and MS $C_{10}H_{18}O_2Na$: m/z=193.1208] with those described for the same compound and its C-3 epimer in the literature.[38]

3. Conclusions

The oxidation of terpene olefins with hydrogen peroxide in the presence of the non-hemo catalyst **5a** furnished mixtures of epoxides whose composition was dependent upon the oxidation protocol used. Upon addition of 1 equiv of oxidant in the presence of catalyst **5a** (5%) most of the substrates (geranyl acetate **6**, farnesyl acetate **9**, nerol acetate **12**, and linalool acetate **16**. Table 1) afforded the terminal trisubstituted epoxides as the major oxidation products (6,7-epoxygeranyl acetate **7**, 10,11-epoxyfarnesyl acetate **10**, 6,7-epoxyneryl acetate **12**, and 6,7-epoxy-linalyl acetate **16**). Interestingly, the isolation of 2,3-epoxynerol and 2,3-epoxygeraniol has been reported on using porphyrin metallic complexes.[41] Increasing the amount of the oxidant (3 equiv) and catalyst (15%) led to the diepoxides as the major products.

The oxidation of limonene **19** yielded the mixture of monoepoxides **20** and **21** with high stereoselectivity (**20**/**21**=10:1. Table 1 entry 7), which is noticeably higher than some reported results for oxidations in the presence of zeolite-entrapped Mn(III) porphyrin complexes.[42]

With terpenoid enones (Table 2) by using of 1 equiv of the oxidant and 5% of the catalyst the oxidative transformation evolved from clean epoxidation in the case of α-ionone **23** to clean allylic oxidation in the case of damascone **28**, due to the progressive deactivation of the electronic density on the double bonds present in this series. The *cis*-jasmone **31** afforded the *threo* diol (±)-**32** with 85% yield under protocol A, and the same product (±)-**32** (10%) contaminated with the epoxide diol **33** (15%) under protocol B.

The oxidation of bicyclic and tricyclic terpenoids afforded oxidation products coming from epoxidation (**41**), to olefin degradation (**43**), methyne (**49**), and methylene (**46** and **48**) activation products. Probably, the most attractive result was the synthesis of the Magnus lactone **46** from the tricyclic ether **45**, with 88% yield and 100% conversion. This transformation represents a remarkable improvement in the reaction conditions and yields for the preparation of this tricyclic lactone.[30]

The oxidation of 1,8-cineole provided the 3-oxo-1,8-cineole **51** as the major isolated product (Table 3, entries 9 and 10). The stereoselective formation of 3β-hydroxy-1,8-cineole **52** is similar to that obtained with several porphyrin complexes.[43]

Generally speaking we observed many degradation products on the alicyclic polyolefinic terpenes under protocol B conditions.

4. Experimental section

4.1. General experimental methods

^{1}H NMR spectra were measured at either 200 or 400 MHz and ^{13}C NMR spectra were measured at 50 or 100 MHz in $CDCl_3$ and referenced to TMS (^{1}H) or solvent (^{13}C), except where indicated otherwise. HRMS determinations were recorded at the Mass Spectrometry Service of the University of Salamanca, Spain, in an Applied Biosystems QSTAR XL with ESI ionization. The GC/MS analysis of the reaction mixtures was performed using an Agilent MS 220 gas chromatograph and a GC7890A mass selective detector. The DB5 column was 30 m long, of 0.25 mm internal diameter and a 0.25 μm layer thickness, using helium as a carrier gas. The sample program started at 50 °C as an initial temperature, and after 5 min the temperature has raised to 270 °C with a 10 °C/min gradient, and was maintained for additional 5 min. The components of mixtures were identified by comparing their full mass spectra and retention times with the corresponding data for reference compounds at the National Institute of Standard Technologies database (NIST 2011). Chemicals and solvents were obtained from commercial sources and used as received with the exception of tetrahydrofuran, which was distilled from sodium and benzophenone. The yields reported are for chromatographically pure isolated products unless mentioned otherwise. Preparation of the catalyst Fe(bpmen)(OTf)$_2$ (**5a**) was achieved according to the literature.[13c]

4.2. Protocol A (5 mol % of catalyst)

A 10 mL round-bottomed flask was loaded with 0.75 mL of a 0.33 M AcOH solution in CH_3CN, Fe(bpmen)(OTf)$_2$ (15.6 mg, 0.025 mmol, 5 mol %), and substrate (0.5 mmol, 1.0 equiv). The solution was stirred vigorously at room temperature. A 0.13 M solution of H_2O_2 in CH_3CN (4 mL, 1.2 equiv) was added dropwise via a syringe. After the addition had been completed, the reaction mixture was stirred for an additional 10 min period. Then, a NaHCO$_3$ saturated aqueous solution was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, evaporated under reduced pressure, and purified by flash chromatography.

4.3. Iterative protocol B (15 mol % of catalyst)

A 50 mL round bottom flask was charged with 0.75 mL of a 0.33 M AcOH solution in CH_3CN, Fe(bpmen)(OTf)$_2$ (15.6 mg, 0.025 mmol, 5 mol %), and substrate (0.5 mmol, 1.0 equiv). The solution was stirred vigorously at room temperature. A 0.13 M solution of H_2O_2 in CH_3CN (4 mL, 1.2 equiv) was added dropwise via syringe. After stirring for 10 min, 0.5 mL of a 0.5 M AcOH solution in CH_3CN and Fe(bpmen)(OTf)$_2$ (15.6 mg, 0.025 mmol, 5 mol %) was added. This was followed by dropwise addition of H_2O_2 (30 wt %, 68 μL, 0.6 mmol, 1.2 equiv) in CH_3CN (4 mL, 0.13 M). A third addition was performed for a total of 15 mol % Fe(bpmen)(OTf)$_2$, 1.5 equiv of AcOH, and 3.6 equiv of H_2O_2. After the last 10 min of stirring NaHCO$_3$ saturated aqueous solution was added and the mixture was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, evaporated under reduced pressure and purified by flash chromatography.

4.4. Geranyl acetate 6,7-oxide 7

^{1}H NMR (CDCl$_3$): δ=1.24 (s, 3H), 1.29 (s, 3H), 1.64 (m, 2H), 1.70 (s, 3H), 2.03 (s, 3H), 2.11 (m, 2H), 2.68 (t, J=6 Hz, 1H), 4.57 (d, J=7 Hz, 2H), 5.36 (t, J=7 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=15.75 (q), 18.03 (q), 20.31 (q), 24.11 (q), 26.35 (d), 35.47 (d), 57.66 (s), 60.52 (d), 63.19 (t), 118.20 (t), 140.53 (s), 170.33 (s) ppm. ESI-MS: m/z 235.0 [M+Na].

4.5. Geranyl acetate 2,3-6,7-dioxide 8

^{1}H NMR (CDCl$_3$): δ=1.31 (s, 3H), 1.35 (s, 3H), 2.09 (s, 3H), 2.71 (m, 1H), 3.02 (m, 1H), 4.21 (m, 2H) ppm. ^{13}C NMR (CDCl$_3$): δ=17.2 (q), 18.9 (q), 21.0 (q), 24.8 (q), 24.6 (d), 24.8 (d), 58.5 (s), 59.5 (s), 60.4 (t), 63.5 (d), 64.0 (t), 171.1 (s) ppm. ESI-MS: m/z 251.1 [M+Na].

4.6. Farnesyl acetate 10,11-oxide 10

^{1}H NMR (CDCl$_3$): δ=1.18 (s, 3H), 1.24 (s, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 2.03 (s, 3H), 2.68 (t, J=6.2 Hz, 1H), 4.55 (d, J=6.6 Hz, 2H), 5.09 (m, 1H), 5.35 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=15.3 (q), 15.8 (q), 20.3 (q), 24.2 (q), 25.0 (q), 26.7 (t), 27.8 (t), 35.6 (t), 39.0 (t), 60.4 (s), 60.5 (t), 62.4 (d), 117.7 (d), 123.0 (d), 133.9 (s), 140.5 (s), 170.4 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{17}$H$_{28}$O$_3$Na: 303.1930, experimental: 303.1926.

4.7. Farnesyl acetate 6,7-10,11-dioxide 11

^{1}H NMR (CDCl$_3$): δ=1.27 (s, 3H), 1.30 (s, 3H), 1.32 (s, 3H), 1.72 (s, 3H), 2.04 (s, 3H), 2.72 (m, 2H), 4.58 (d, J=7 Hz, 2H), 5.36 (m, 1H) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{17}$H$_{28}$O$_4$Na: 319.1879, experimental: 319.1874.

4.8. Nerol 6,7-oxide 13

^{1}H NMR (CDCl$_3$): δ=1.25 (s, 3H), 1.29 (s, 3H), 1.58 (m, 2H), 1.76 (s, 3H), 2.02 (s, 3H), 2.23 (t, J_1=7.8 Hz, J_2=8.2 Hz, 2H), 2.69 (t, J_1=J_2=6.2 Hz, 1H), 4.56 (d, J=7.4 Hz, 2H), 5.38 (t, J_1=7.2 Hz, J_2=7.4 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=18.9 (q), 21.2 (q), 23.6 (q), 25.0 (q), 27.7 (t), 29.0 (t), 58.6 (s), 61.0 (t), 63.9 (d), 119.9 (d), 141.9 (s), 171.2 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{12}$H$_{20}$O$_3$Na: 235.1304, experimental: 235.1289.

4.9. Nerol 2,3-oxide 14

^{1}H NMR (CDCl$_3$): δ=1.34 (s, 3H), 1.61 (s, 3H), 1.69 (s, 3H), 2.10 (s, 3H), 2.98 (dd, J_1=7.4 Hz, J_2=4.3 Hz, 1H), 4.00 (dd, J_1=12.1 Hz, J_2=7.4 Hz, 1H), 4.33 (dd, J_1=12.1 Hz, J_2=4.3 Hz, 1H), 5.08 (t, J_1=6.8 Hz, J_2=7.0 Hz, 1H) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{12}$H$_{20}$O$_3$Na: 235.1304, experimental: 235.1300.

4.10. Nerol 2,3-6,7-dioxide 15

^{1}H NMR (CDCl$_3$): δ=1.25 (s, 3H), 1.31 (s, 3H), 1.34 (s, 3H), 2.10 (s, 3H), 2.73 (m, 1H), 3.01 (m, 1H), 4.07 (m, 1H), 4.32 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=18.8 (q), 21.0 (q), 22.1 (q), 25.0 (q), 25.3 (t), 30.0 (t), 60.6 (s), 61.0 (d), 63.0 (t), 63.1 (d), 63.7 (s), 171.0 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{12}$H$_{20}$O$_4$Na: 251.1253, experimental: 251.1236.

4.11. Linalool 6,7-oxide 17

^{1}H NMR (CDCl$_3$): δ=1.23 (s, 3H), 1.27 (s, 3H), 1.53 (s, 3H), 1.97 (s, 3H), 2.67 (t, J_1=J_2=6.4 Hz, 1H), 5.15 (m, 2H), 5.93 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=18.7 (q), 22.3 (q), 23.6 (t), 23.8 (q), 25.0 (q), 36.5 (t), 58.5 (s), 64.2 (d), 82.5 (s), 113.7 (t), 141.7 (d), 170.0 (s) ppm. ESI-

HRMS (M$^+$+Na): calculated for C$_{12}$H$_{20}$O$_3$Na: 235.1304, experimental: 235.1303.

4.12. *cis* Limonene 1,2-oxide 20 and *trans* limonene 1,2-oxide 21

^{1}H NMR (CDCl$_3$): δ=1.31 (s, 3H), 1.65 (s, 3H), 2.99 (d, J=5.6 Hz, 1H, cis), 3.04 (t, J_1=J_2=2.2 Hz, 1H, trans), 4.66 (s, 2H) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{10}$H$_{16}$ONa: 175.1093, experimental: 175.1101.

4.13. Limonene 1,2-8,9-dioxide 22

^{1}H NMR (CDCl$_3$): δ=1.24 (s, 3H), 1.29 (s, 3H), 2.52 (m, 1H), 2.99 (m, 1H), 4.74 (s, 2H) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{10}$H$_{16}$O$_2$Na: 191.1042, experimental: 191.1036.

4.14. *trans* α-Ionone 1,2-oxide 24

^{1}H NMR (CDCl$_3$): δ=0.74 (s, 3H), 0.92 (s, 3H), 1.24 (s, 3H), 2.29 (s, 3H), 3.09 (t, J=2 Hz, 1H), 6.06 (d, J=16 Hz, 1H), 6.68 (dd, J_1=16 Hz, J_2=10 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=21.6 (t), 23.9 (q), 26.3 (q), 27.4 (q), 27.8 (q), 28.4 (t), 31.1 (s), 52.4 (d), 59.4 (d), 82.2 (s), 133.9 (d), 146.2 (d), 198.6 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{13}$H$_{20}$O$_2$Na: 231.1355, experimental: 231.1356.

4.15. β-Ionone 2,3-oxide 26

^{1}H NMR (CDCl$_3$): δ=0.92 (s, 3H), 1.11 (s, 6H), 2.27 (s, 3H), 6.24 (d, J=15.8 Hz, 1H), 6.97 (d, J=15.8 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=17.8 (t), 21.0 (q), 26.0 (q), 26.1 (q), 28.4 (q), 29.9 (t), 33.7 (s), 35.6 (t), 66.0 (s), 70.8 (s), 132.6 (d), 142.8 (d), 197.7 (s) ppm. ESI-MS: m/z 209.0 [M+H], 231.0 [M+Na].

4.16. (*E*)-2,4,4-Trimethyl-3-(3-oxobut-1-en-1-yl)cyclohex-2-enone 27

^{1}H NMR (CDCl$_3$): δ=1.18 (s, 6H), 1.79 (s, 3H), 2.34 (s, 3H), 6.14 (d, J=16.5 Hz, 1H), 7.18 (d, J=16.5 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=13.6 (q), 27.5 (q), 28.1 (q), 34.4 (t), 35.7 (s), 37.5 (s), 77.4 (s), 131.6 (s), 133.7 (d), 140.5 (d), 157.9 (s), 197.6 (s), 198.8 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{13}$H$_{18}$O$_2$Na: 229.1199, experimental: 229.1202.

4.17. (*E*)-3-(But-2-enoyl)-2,4,4-trimethylcyclohex-2-enone 29

^{1}H NMR (CDCl$_3$): δ=1.18 (s, 6H), 1.61 (s, 3H), 1.95 (m, 8H), 2.55 (dd, J_1=7.6 Hz, J_2=6.6 Hz, 2H), 6.17 (dd, J_1=12.4 Hz, J_2=1.8 Hz, 1H), 6.73 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=13.3 (q), 18.9 (q), 27.4 (2q), 34.4 (t), 34.9 (s), 38.2 (t), 129.6 (s), 133.0 (d), 148.2 (d), 161.0 (s), 198.0 (s), 199.1 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{13}$H$_{18}$O$_2$Na: 229.1199, experimental: 229.1190.

4.18. (*E*)-1-(3-Hydroxy-2,6,6-trimethylcyclohex-1-en-1-yl)but-2-en-1-one 30

^{1}H NMR (CDCl$_3$): δ=1.02 (s, 6H), 1.63 (s, 3H), 1.90 (dd, J_1=4.8 Hz, J_2=1.4 Hz, 3H), 3.98 (t, J=4.8 Hz, 1H), 6.17 (dd, J_1=12.4 Hz, J_2=1.8 Hz, 1H), 6.73 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=18.1 (q), 18.6 (q), 27.8 (q), 28.8 (t), 29.0 (q), 34.1 (s), 34.8 (s), 69.1 (d), 131.2 (s), 134.1 (d), 143.7 (s), 146.8 (d), 201.2 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{13}$H$_{20}$O$_2$Na: 231.1355, experimental: 231.1355.

4.19. 2-[(2RS,3RS)-2,3-Dihydroxypentyl]-3-methylcyclopent-2-enone (±)-32

^{1}H NMR (CDCl$_3$): δ=0.92 (t, J=7 Hz, 3H), 1.48 (m, 2H), 2.08 (s, 3H), 2.53 (m, 4H), 3.19 (m, 3H), 3.45 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=10.4 (q), 17.6 (q), 26.4 (t), 28.4 (t), 32.3 (t), 34.4 (t), 72.7 (d), 74.8 (d), 137.5 (s), 174.9 (s), 212.4 (s) ppm. ESI-MS: m/z 199.0 [M+H], 221.0 [M+Na]. IR: ν=3404, 2960, 2922, 2875, 1681, 1636 cm^{-1}.

4.20. 1-[(2R,3R)-2,3-Dihydroxypentyl]-5-methyl-6-oxabicyclo[3.1.0]hexan-2-one 33

^{1}H NMR (CDCl$_3$): δ=0.92 (t, J=7.8 Hz, 3H), 1.33 (s, 3H), 3.35 (t, J=6.2 Hz, 1H), 3.75 (s, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=10.4 (q), 15.8 (q), 24.2 (t), 33.6 (t), 33.6 (t), 34.9 (t), 66.9 (d), 73.6 (d), 74.1 (s), 81.0 (s), 219.5 (s) ppm. ESI-MS: m/z 237.0 [M+Na].

4.21. Carvone 8,9-oxide 35

^{1}H NMR (CDCl$_3$): δ=1.28 (s, 3H), 1.74 (s, 3H), 6.69 (dd, J$_1$=4.8 Hz, J$_2$=3.8 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=15.8 (q), 18.5 (q), 27.9 (t), 40.1 (t), 40.9 (d), 52.6 (t), 58.0 (s), 135.8 (s), 144.1 (d), 198.9 (s) ppm.

4.22. Carvone 1,2-8,9-dioxide 36

^{1}H NMR (CDCl$_3$): δ=1.25 (d, J=0.8 Hz, 3H), 1.39 (s, 3H), 2.62 (dd, J$_1$=5 Hz, J$_2$=0.8 Hz, 1H), 3.41 (d, J=3 Hz, 1H) ppm.

4.23. α-Pinene oxide 42

^{1}H NMR (CDCl$_3$): δ=0.90 (s, 3H), 1.25 (s, 3H), 1.30 (s, 3H), 1.57 (d, J=9.0 Hz, 1H), 1.68 (m, 1H), 1.80 (m, 1H), 1.88 (m, 2H), 1.97 (m, 1H), 3.02 (d, J=4 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=20.3 (q), 22.6 (q), 26.0 (t), 26.9 (q), 27.8 (t), 39.9 (d), 40.7 (s), 45.2 (d), 57.0 (d), 60.5 (s) ppm.

4.24. (+)-Nopinone 43

^{1}H NMR (CDCl$_3$): δ=0.84 (s, 3H), 1.32 (s, 3H), 1.55 (d, J=10.2 Hz, 1H), 1.8–2.7 (m, 7H) ppm. ^{13}C NMR (CDCl$_3$): δ=21.36 (t), 22.06 (q), 25.23 (t), 25.85 (q), 32.74 (t), 40.37 (d), 41.16 (s), 57.95 (d), 215.00 (s) ppm. ESI-MS: m/z 138.9 [M+H].

4.25. 6,9-Dimethyl-8-oxo-7-oxatricyclo[4.3.0.0^{3,9}]nonane Magnus lactone 46

^{1}H NMR (CDCl$_3$): δ=1.29 (s, 3H), 1.38 (s, 3H), 1.63 (d, J=10 Hz, 1H), 1.82 (s, 4H), 2.0–2.5 (m, 4H) ppm. ^{13}C NMR (CDCl$_3$): δ=16.47 (q), 23.27 (t), 23.34 (t), 25.11 (q), 29.86 (t), 42.47 (d), 49.77 (d), 52.18 (s), 88.48 (s), 179.57 (s) ppm. ESI-MS: m/z 166.9 [M+H].

4.26. (1S,3R,4R,5R,7S)-4-Hydroxyadamantan-2-one 48

^{1}H NMR (CDCl$_3$): δ=3.40 (t, J$_1$=1.6 Hz, J$_2$=1.0 Hz, 1H), 3.91 (br s, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=27.3 (d), 30.1 (d), 30.3 (t), 38.6 (t), 38.6 (t), 44.4 (t), 45.4 (d), 45.4 (d), 68.7 (d), 208.8 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{10}$H$_{14}$O$_2$Na: 189.0886, experimental: 189.0895.

4.27. (1R,3S,5S,7S)-5-Hydroxyadamantan-2-one 49

^{1}H NMR (CDCl$_3$): δ=2.91 (br s, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=30.0 (d), 38.3 (t), 38.3 (t), 44.3 (t), 45.2 (t), 45.2 (t), 47.1 (d), 47.1 (d), 67.5 (s), 217.0 (s) ppm. ESI-MS: m/z 189.0 [M+Na], 167.0 [M+H].

4.28. (1R,4R)-1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octan-5-one 51

^{1}H NMR (CDCl$_3$): δ=1.14 (s, 3H), 1.24 (s, 3H), 1.31 (s, 3H), 2.18 (t, J$_1$=6.6 Hz, J$_2$=2.6 Hz, 1H), 2.28 (s, 1H), 2.34 (d, J=2.6 Hz, 1 Hz) ppm. ^{13}C NMR (CDCl$_3$): δ=18.4 (t), 26.4 (q), 27.1 (q), 30.5 (t), 30.8 (q), 49.3 (t), 52.0 (d), 73.8 (s), 73.8 (s), 213.5 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{10}$H$_{16}$O$_2$Na: 191.1043, experimental: 191.1042.

4.29. (1R,4S)-1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octan-5-ol 52

^{1}H NMR (CDCl$_3$): δ=1.06 (s, 3H), 1.20 (s, 3H), 1.26 (s, 3H), 2.17 (s, 2H), 4.45 (m, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=14.1 (t), 27.3 (q), 28.5 (q), 29.2 (q), 31.2 (t), 40.5 (d), 43.0 (t), 65.4 (d), 71.1 (s), 73.5 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{10}$H$_{18}$O$_2$Na: 193.1199, experimental: 193.1208.

4.30. 5,5-Dimethyl-4-(3-oxobutyl)dihydrofuran-2(3H)-one 53

^{1}H NMR (CDCl$_3$): δ=1.06 (s, 3H), 1.20 (s, 3H), 1.26 (s, 3H), 2.16 (d, J=3 Hz, 1H), 2.26 (d, J=2.5 Hz, 1H), 2.74 (t, J$_1$=2.5 Hz, J$_2$=3 Hz, 1H), 2.83 (t, J$_1$=2.5 Hz, J$_2$=3 Hz, 1H) ppm. ^{13}C NMR (CDCl$_3$): δ=19.7 (q), 22.0 (t), 28.1 (q), 28.8 (q), 28.9 (t), 36.7 (d), 41.1 (t), 74.5 (s), 181.9 (s), 210.4 (s) ppm. ESI-HRMS (M$^+$+Na): calculated for C$_{10}$H$_{16}$O$_3$Na: 207.0991, experimental: 207.1008.

4.31. Retention times indexes of the compounds (NIST 2011)

16,757 (**15**), 26,992 (**18**), 13,432 (**44**).

Acknowledgements

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.02.013.

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