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A versatile method of epoxide formation with the support of peroxy ionic liquids

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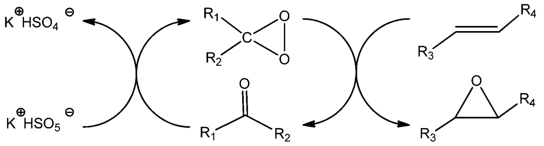
The application of the peroxy ionic liquid, 1-butyl-3-methylimidazolium peroxymonosulphate, as an oxidation agent and a solvent for the synthesis of epoxides was described. The 2.5-molar excess of the peroxy ionic liquid to olefin was applied. The reaction system consisted of 1,1,1-trifluoroacetone as an oxirane precursor, which was used with the molar ratio of 1 : 3 relative to olefin and water solution of $NaHCO_3$. Under these conditions the epoxidation of 4-bromocinnamic acid led to the epoxide formation at the ambient temperature in 30 minutes. Dioxiranes, generated from the peroxy ionic liquid and 1,1,1-trifluoroacetone, demonstrated encouraging potential for the epoxidation of a variety of other olefins: styrene, limonene, stilbene, linalyl acetate and a complex steroid molecule with high yields of final epoxides from 65–98%.

Introduction

Epoxides due to their high reactivity, which is caused by a highly strained tricyclic ring, under certain conditions and in the presence of a selected nucleophile, can be converted to a wide range of valuable derivatives.[1] Epoxides are important synthetic building blocks widely used in the chemical industry in the production of pharmaceutical products, flavours, fragrances, resins, adhesives or paints.[2–6]

Most epoxidation systems use catalysts based on transition metals (V, Mn, W, Ti, Re, *etc.*) which activate oxidants, such as H_2O_2 or hydroperoxides.[1] However, non-metal epoxidation using dioxiranes can also be performed. Dioxiranes are usually generated from the potassium peroxymonosulphate salt $KHSO_5$ and ketones as an efficient and remarkably versatile class of oxidants.[7] The commercial sources of $KHSO_5$ are low-cost industrial bulk chemicals, *e.g.*, the triple salt Oxone™ ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$). These products are stable oxidizing agents commonly used in the fine chemical synthesis; they are easy to handle, non-toxic and generate non-polluting by-products.[8] Epoxidations of olefins proceeding *via in situ* generated dioxiranes (Scheme 1) often require a range of pH 7–8,[9] higher pHs lead to rapid autodecomposition of Oxone™.[10] The *in situ* oxidation with dioxiranes presents many advantages, such as *e.g.* the possibility of regeneration of the parent ketones after the oxygen transfer. In early studies, a two-phase solvent system was employed, in which the solubility properties of alkene and ketone played a crucial role.[9]



Scheme 1 Catalytic cycle of oxidation by the ketone/Oxone™ method.

In our previous studies, alternative methods of the oxidation of ketones or alcohols with $KHSO_5$ were presented. The first method was based on the use of an alternative solvent, such as an ionic liquid, to dissolve $KHSO_5$ and eliminate water from the reaction system.[11] The work referred to above demonstrated that the use of homogenous conditions is critical for the oxidation of ketones with $KHSO_5$ to lactones, which was provided by ionic liquids. The second method used a phase transfer catalysis to avoid hydrolysis of lactones.[12]

Unique physical properties of ionic liquids, such as low volatility, thermal stability, make them attractive alternatives to organic solvents. Excellent solubility of organic and inorganic compounds in ionic liquids and the possibility of easy recycling of these salts have evoked wide interest in their application in the organic synthesis as solvents. The last decade brought much interest in task-specific ionic liquids, which are terms that refer to the potential design capacity of ionic liquids for chemical tasks.[13] Building on this, we demonstrated a new class of task-specific ionic liquids with peroxymonosulphate anions, *e.g.* 1-butyl-3-methylimidazolium salt (Scheme 2). The resulting salts were liquids at the room temperature and served as oxidants and solvents in the model oxidation of cyclohexanol to ε-caprolactone.[14]

Ionic liquids used as solvents in epoxidation reactions of a broad substrate scope with various oxidation agents were used

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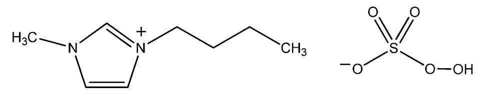


Scheme 2 1-Butyl-3-methylimidazolium peroxymonosulphate [bmim]-$[HSO_5]^-$.

to improve yield, selectivity or the rate of the reaction.[15,16] The epoxidation of alkenes by Oxone™ was also investigated in ionic liquids. To this aim 2-alkyl-3,4-dihydroisoquinolinium salts were used as catalysts.[17,18] The effectiveness of the reaction systems depended on the miscibility of the reagents with the ionic liquids.

The application of water miscible ionic liquids gave similar results to the conventional acetonitrile based systems.[17]

As presented above, new methods of epoxidation of alkenes are an ongoing area of research. This work is focused on the development of a versatile method of the epoxide ring formation using novel task-specific ionic liquids based on the peroxysulfate anion as both the oxidant and the solvent.

Results and discussion

For the initial study a model epoxidation of 4-bromocinnamic acid was chosen to determine crucial parameters for the epoxide ring formation. Among dioxiranes the most useful dimethyldioxirane and 1,1,1-trifluoroacetone (TFA) were used, as in their case high electronegativity of fluorine makes them a stronger epoxidising agent. From amongst the peroxymonosulphate ionic liquids 1-butyl-3-methylimidazolium salt [bmim][HSO_5] was chosen as a model oxidation agent. The use of [bmim][HSO_5] eliminated the addition of other solvents to the reaction system, while typical solvents like water–acetone or water–acetonitrile were used for comparative tests with Oxone™. Due to the short life of the *in situ* forming reactive dioxiranes, the reaction system required stabilization by the introduction of EDTA and maintaining the pH around 7–8 by the addition of $NaHCO_3$ (Table 1).

For comparison reasons the experiments were carried out with Oxone™. The order of the addition of the reagents was as follows: olefin and $NaHCO_3$ were suspended in the acetone–water mixture, then a water solution of EDTA was added. The molar ratio of olefin to $NaHCO_3$ was 1 : 15. Oxone™ was the last reagent which was introduced under vigorous stirring and allowed to react at 20–25 °C for an appropriate time. The reaction progress was monitored with ultra performance liquid chromatography (UPLC) (Table 1).

For the presented experiments, even if acetone was used as a solvent and the dioxirane precursor in a big excess (the molar ratio of olefin to acetone was 1 : 50) together with Oxone™ (the molar ratio of olefin to Oxone™ was 7), only 60% yield of epoxide was achieved in 4 h (Table 1, entry 1). In the next step, attempts to eliminate acetone using a more reactive dioxirane precursor, TFA with acetonitrile as a solvent, were performed. The molar ratio of olefin to TFA was 1 : 5 and even when Oxone™ was used in big excess, still the yield reached only 43% in 1 h (Table 1, entry 2).

The system was strengthened by the addition of the ionic liquid [bmim][HSO_5]. It is worth noting that in the first experiment the ionic liquid [bmim][HSO_5] (Table 1, entry 3) was added in the first step, together with water. Oxone™, as applied above, was the last component. The yield of epoxide was higher, but the reaction stopped after 4 h and a full conversion was not reached, probably because of the creation of a highly viscous mixture, very difficult to stir.

The use of the ionic liquids [bmim][HSO_5] with Oxone™ gave a much better conversion of 4-bromocinnamic acid compared to the reaction with Oxone™ alone in conventional solvents (Table 1, entry 3). These observations drive us to a conclusion that maybe there is a possibility of eliminating Oxone™ completely from the reaction mixture and performing this synthesis only in the presence of an ionic liquid. Additionally, we have observed that the order of the reagent addition may have a crucial role in the outcome of the reaction. Theoretically, an ionic liquid added as a thirst system component can react with the basic $NaHCO_3$ before it starts to react with ketone to form dioxirane. On the other hand, dioxiranes are very reactive species, and thus they are highly unstable. Therefore, it is necessary to avoid a situation where all of the formed dioxirane decomposes before it starts to react with olefin.

Table 1 Influence of reaction conditions on epoxidation of 4-bromocinnamic acid with Oxone™ or [bmim][HSO_5]

No.	Solvent	Source of dioxirane	Molar ratio olefin/$[HSO_5]^-$	Time	Yield of epoxide[c] [%]
1	H_2O–acetone[a]	Acetone	2.5 (Oxone™)	5 min	17
	H_2O–acetone[a]	Acetone	2.5 (Oxone™)	1 h	50
	H_2O–acetone[a]	Acetone	2.5 (Oxone™)	24 h	50
	H_2O–acetone[a]	Acetone	7 (Oxone™)	4 h	60
2	H_2O–acetonitrile[b]	TFA	5 (Oxone™)	5 min	20
	H_2O–acetonitrile[b]	TFA	5 (Oxone™)	24 h	20
	H_2O–acetonitrile[b]	TFA	7 (Oxone™)	5 min	20
	H_2O–acetonitrile[b]	TFA	7 (Oxone™)	1 h	43
3	H_2O–[bmim][HSO_5][b]	TFA	5 (Oxone™) + 7 [bmim][HSO_5]	5 min	60
	H_2O–[bmim][HSO_5][b]	TFA	5 (Oxone™) + 7 [bmim][HSO_5]	4 h	60
4	H_2O–[bmim][HSO_5][b]	TFA	7 [bmim][HSO_5]	5 min	88
	H_2O–[bmim][HSO_5][b]	TFA	7 [bmim][HSO_5]	30 min	99

[a] Reaction conditions: olefin (0.10 g, 0.44 mmol), $NaHCO_3$ (0.50 g, 6.60 mmol), 2 ml acetone/water (1 : 1 v/v), 1 ml water solution of EDTA (0.40 mol dm^{-3}), RT. [b] Reaction conditions: olefin (0.10 g, 0.44 mmol), $NaHCO_3$ (0.50 g, 6.60 mmol), 1 ml water, 1 ml acetonitrile, 1 ml water solution of EDTA (0.40 mol dm^{-3}), TFA (0.24 g, 2.20 mmol), RT. [c] Yield was determined by UPLC, no by-products were detected, only unreacted olefin was found.

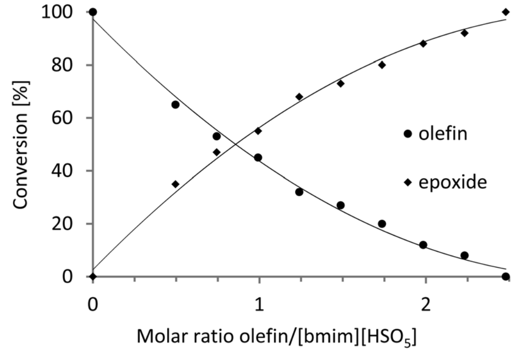


Fig. 1 Influence of the amount of the ionic liquid [bmim][HSO_5] on the conversion of 4-bromocinnamic acid and yield of epoxide in the presence of TFA and EDTA at RT.

Table 2 Influence of additives on the epoxidation of 4-bromocinnamic acid in the presence of TFA and [bmim][HSO_5][a]

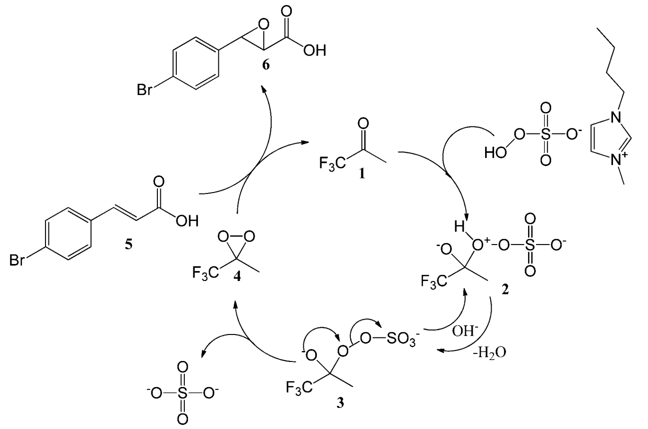
No.	EDTA [ml]	Water [ml]	Molar ratio olefin/$NaHCO_3$	Time [min]	Conversion of olefin [%]	Yield of epoxide[b] [%]
1	—	—	15	5	3	4
				30	6	6
2	1	1	—	5	0	0
				30	0	0
3	—	1	15	5	45	45
				30	100	99

[a] Reaction conditions: olefin (0.10 g, 0.44 mol), $NaHCO_3$ (0.50 g, 6.60 mmol), 1 ml water, 1 ml water solution of EDTA (0.40 mol dm^{-3}), TFA (0.24 g, 2.20 mmol), [bmim][HSO_5] (0.25 g, 1.10 mmol), RT. [b] Yield and conversion were determined by UPLC.

Table 3 Influence of the amount of TFA on the epoxidation of 4-bromocinnamic acid in the presence of $NaHCO_3$ and [bmim][HSO_5][a]

No.	Molar ratio olefin/TFA	Reaction time [h]	Conversion of olefin [%]	Yield of epoxide[b] [%]
1	5	0.5	100	99
2	3	0.5	100	99
3	2	0.5	90	91
4	1	0.5	60	60
		24	80	80
5	—[c]	24	0	0

[a] Olefin (0.10 g, 0.44 mol), $NaHCO_3$ (0.50 g, 6.60 mmol), 1 ml water, [bmim][HSO_5] (0.25 g, 1.10 mmol) RT. [b] Yield was determined by UPLC. [c] The reaction without TFA.



Scheme 3 Proposed mechanism for epoxidation of olefin with [bmim][HSO_5].

Taking the observation made in the last experiment into account (Table 1, entry 4) Oxone™ was eliminated from the system and [bmim][HSO_5] was added as the last reagent. This time we achieved our goal, the reaction was fast and a full conversion was observed after 30 minutes.

In order to determine the influence of crucial factors on the course of the model reaction several experiments under the conditions determined above (Table 1, entry 4) were performed. At first a sufficient amount of oxidizing agent was established. To this aim [bmim][HSO_5] was added to the reaction system in portions. After the addition of each portion the conversion of olefin and yield of the product were analyzed with UPLC (Fig. 1). The results lead to a conclusion that the necessary molar ratio of olefin to the ionic liquid to obtain almost 100% of the product is only 2.5.

In the next stage the impact of the presence of stabilizing agents: EDTA and $NaHCO_3$ as well as water on the reactivity of olefin was checked (Table 2). It was confirmed that the base and water are necessary to keep the desirable pH of the reaction system (Table 2, entry 3). However, when the reaction is carried out in the presence of [bmim][HSO_5] there is no need for further stabilization of dioxiranes by the EDTA complex.

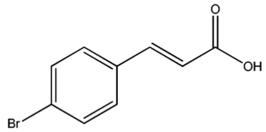
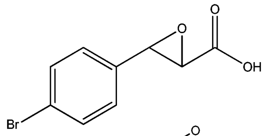
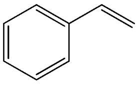
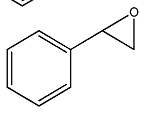
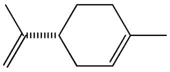
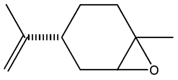
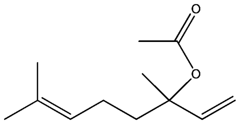
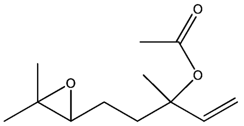
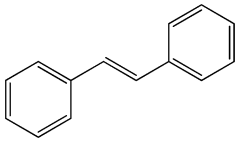
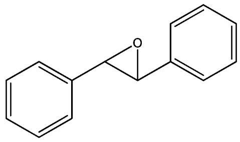
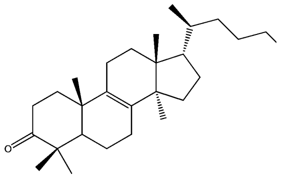
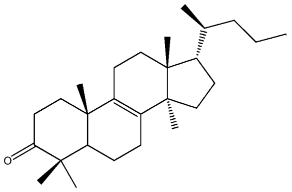
In the experiments presented above, the molar ratio of olefin to TFA was 1 : 5. The possibility of lowering the amount of ketone was also checked (Table 3). It was found that 3 equivalents of 1,1,1-trifluoroacetone are enough to reach a full conversion of olefin after 30 minutes. It was proved by Shi *et al.* that TFA forms much more stable dioxirane species compared to dimethyldioxirane. Even catalytic amounts of ketone were enough to obtain a satisfactory conversion, although the reaction requires several hours to be completed.[19] The reaction without the addition of TFA does not occur, which can be the proof of the necessity of formation of dioxirane during the reaction.

The proposed mechanism for the epoxidation of 4-bromocinnamic acid with [bmim][HSO_5] as an oxidant is presented in Scheme 3. In the first step the carbonyl group from TFA **1** is attacked by $[HSO_5]^-$ peracid anions to form intermediate **2**. In the next steps the formation of dioxirane **4** occurs. In the end the resulted dioxirane oxidises 4-bromocinnamic acid **5** to its epoxide **6**.

The new method has already shown a significant improvement in comparison with the conventional process of epoxidation it terms of yield and stabilization requirements. Another advantage of this method would be easy isolation of the product. After a simple aqueous work-up and extraction with ethyl acetate it is possible to isolate desired 3-(4-bromophenyl)oxirane-2-carboxylic acid with 98% yield and 99% purity (determined by NMR).

Finally, the most active reaction system was examined in the epoxidation of various olefins to determine its practical potential. A few derivatives which are commonly used for this type of reaction were selected: styrene, stilbene, limonene, linalyl acetate and also steroid structure (IMDA). The yields of epoxides obtained in the

Table 4 Epoxidation of selected olefins in the presence of TFA and [bmim][HSO_5][a]

No.	Olefin	Epoxide	Oxidising agent	Reaction time	Conversion of olefin[b] [%]	Yield of epoxide[b] [%]
1			*m*-CPBA [bmim][HSO_5]	30 min 30 min	80 100	80 99 (98)
2			*m*-CPBA [bmim][HSO_5]	30 min 30 min	60 100	60 99 (85)
3			*m*-CPBA [bmim][HSO_5]	1 h 1 h	100 100	50[c] 80[c] (65)
4			*m*-CPBA [bmim][HSO_5]	1 h 10 min	90 100	90 99 (90)
5			*m*-CPBA [bmim][HSO_5]	5 min 5 min	20 100	20 99 (72)
6			*m*-CPBA [bmim][HSO_5]	1 h 20 min	100 100	99 99 (70)

[a] Olefin (0.20 g, 0.88 mmol), $NaHCO_3$ (1.00 g, 12.12 mmol), 2 ml water, TFA (0.29 g, 2.64 mmol), [bmim][HSO_5] (0.50 g, 2.20 mmol), RT. [b] Yield and conversion were determined by UPLC/MS, in the parenthesis isolated yields. [c] 20% of the bisoxidised product was observed (determined by NMR).

reaction with a very strong oxidation agent *m*-chloroperbenzoic acid (*m*-CPBA) were also presented for comparison. Organic percarboxylic acids as typical oxidants are fairly expensive, often poorly-stable and hazardous, and this consequently limits their commercial application. Therefore, the new approach with relatively stable peroxy ionic liquids appears to be a very attractive alternative.

Styrene was oxidized to epoxide with the conversion of 60% in the presence of *m*-CPBA in 30 minutes. In comparison with the use of a liquid a complete conversion was observed using a peroxy ionic liquid within the same period of time (Table 4, entry 2). Similar results were observed with the epoxidation of limonene, where the use of the ionic liquid improved conversion of the reaction. In this process conversion was not completed mainly due to the fact that bisoxidised products were formed during this reaction (Table 4, entry 3). In the oxidation of linalyl acetate improvements of both the reaction time and conversion in comparison to the traditional method were observed (Table 4, entry 4). Stilbene was oxidized very rapidly (Table 4, entry 5). Just after 5 minutes a complete conversion was observed.

Encouraged with very good results we have tried to perform the reaction on a more complex system. In the case of a steroid molecule (iso-masticadienonic acid, Table 4, entry 6), the application of the peroxy ionic liquid led to a 5-times shorter reaction time compared to peracid. It is also worth mentioning that these types of derivatives are very attractive in terms of biological activity and epoxide can be treated as a versatile reagent for further functionalization.

Conclusions

A new and effective method of epoxidation of olefins in the presence of 1,1,1-trifluoroacetone and versatile peroxy ionic liquid was developed. Peroxy ionic liquid based on the 1-methyl-3-butylimidazolium cation bears the peroxy function in the ion structure as peroxymonosulphate $[HSO_5]^-$. Peroxymonosulphate ionic liquid does not contain the ballast of inorganic salts ($KHSO_4$ and K_2SO_4) against Oxone™, which results in an easier work-up and product purification. An ionic liquid acts as both an oxidant and a reaction medium. In this work it was demonstrated that using the developed method high yields of epoxides and short reaction times can be reached. Forevermore, epoxides can be easily isolated from the reaction mixture by simple extraction.

Experimental

Materials

1-Butyl-3-methylimidazolium bromide, sulfuric acid, Oxone™, acetone, 1,1,1-trifluoroacetone, acetonitrile, 4-bromocinnamic acid, styrene, stilbene, limonene, linalyl acetate, $NaHCO_3$, *m*-chloroperbenzoic acid and EDTA were purchased from Sigma Aldrich. Iso-masticadienonic acid was purchased from Angene International Limited. [bmim][HSO_5] was synthesized according to the literature procedure.[14]

Instrumentation

The structure and purity of all the synthesized substances were confirmed by the NMR analysis. ^{1}H NMR spectra were recorded on a Bruker 400 MHz in $CDCl_3$ or DMSO (internal standard TMS). All epoxides were characterised by comparing their NMR spectra with those of authentic samples. UPLC analyses were performed using a Shimadzu UPLC DAD detector and an Acquity UPLC HSS C18 column (Waters, 50 mm × 2.1 mm × 1.8 μm).

Methods

General method of the epoxidation reaction with [bmim][HSO_5]. Olefin (0.44 mmol) was suspended in 1 ml of water followed by the addition of solid $NaHCO_3$ (6.60 mmol) and TFA (1.32 mmol). Next [bmim][HSO_5] (1.10 mmol) was added dropwise and the reaction was stirred at RT. Periodically, 20 μl of the samples diluted with 1.5 ml of the acetonitrile–water mixture were collected during the reaction to monitor the progress of the reaction utilising UPLC. After the reaction was finished, the post-reaction mixture was filtered off and the residue was acidified with 1 M HCl in the ice bath, then 3 × 20 ml of ethyl acetate was added and extractions were performed. The organic layer was washed with brine and dried over Na_2SO_4. After evaporation of the solvent epoxides were obtained with 65–98% yields.

3-(4-Bromophenyl)oxirane-2-carboxylic acid (1). ^{1}H NMR (400 MHz, DMSO) δ 13.30 (s, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 4.14 (d, J = 1.8 Hz, 1H), 3.65 (d, J = 1.9 Hz, 1H).

2-Phenyloxirane (2). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16–7.45 (m, 5H), 3.82 (dd, J = 2.5 Hz, J = 4.3 Hz,1H), 3.16 (dd, J = 2.5 Hz, J = 4.3 Hz, 1H), 2.82 (dd, J = 2.5 Hz, J = 4.3 Hz, 1H).

1-Methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (3). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.13–2.27 (m, 7H), 1.55 (bs, 3H), 1.71 (s, 3H), 3.02 (t, H, J = 5.5 Hz), 4.75 (s, 2H).

5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-1-en-3-yl acetate (4). ^{1}H NMR (400 MHz, DMSO) δ 6.02–5.88 (m, 1H), 5.12 (ddt, J = 16.1, 11.0, 1.2 Hz, 2H), 2.66 (s, 1H), 1.96 (d, J = 0.7 Hz, 3H), 1.94–1.74 (m, 2H), 1.48 (m, 5H), 1.20 (d, J = 15.6 Hz, 6H).

2,3-Diphenyloxirane (5). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.95 (s, 2H), 7.40–7.8 (m, 10H).

2-Methyl-3-[(4*S*)-4-[(2*S*,11*S*,15*S*)-2,6,6,11,15-pentamethyl-5-oxotetracyclo[8.7.0.0^{2,7}.0^{11,15}]heptadec-1(10)-en-14-yl]pentyl] oxirane-2-carboxylic acid (6). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.11 (td, J = 1.3 Hz, 1H), 2.67–2.39 (m, 4H), 2.02 (ddd, J = 20.3, 10.1, 6.2 Hz, 6H), 1.94 (d, J = 1.3 Hz, 3H), 1.83–1.61 (m, 5H), 1.53 (ddd, J = 33.1, 18.6, 13.3 Hz, 6H), 1.35 (ddd, J = 15.6, 12.3, 9.9 Hz, 1H), 1.26 (d, J = 7.0 Hz, 3H), 1.13–1.03 (m, 8H), 0.93 (dd, J = 15.8, 3.3 Hz, 7H), 0.78 (s, 3H).

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