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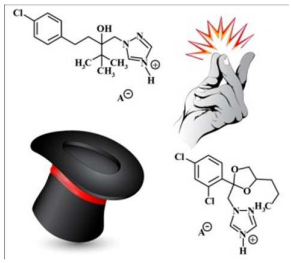

A new, cheap and efficient method, which may be used to obtain ILs by modifying commonly used fungicides, was presented.

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ARTICLE

Known triazole fungicides - new trick

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Tebuconazole and propiconazole were converted into salts by reaction with inorganic and organic acids. Numerous novel salts were obtained as a result, many of which could be characterized as protic ionic liquids. Their thermal stability and biological activity against a fungal species of *Fusarium culmorum*, *Microdochium nivale*, *Sclerotinia sclerotiorum* and *Botrytis cinerea* (in concentration range from 10 up to 1000 ppm) were assessed in the framework of this study. The evaluation revealed that high antifungal activity of the synthesized tebuconazole- and propiconazole-based salts, which may be classified as new triazole fungicides, was preserved. Physical properties of the obtained salts have changed significantly, thus creating new application possibilities of known triazole fungicides.

Introduction

Tebuconazole - (*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol and propiconazole - (±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazole represent the group of popular triazole fungicides used in agriculture to treat pathogenic plant fungi. Triazoles have been introduced in the 1970s and soon became the dominant group of fungicides. Despite this, the resistance of pathogenic fungi to these substances develops relatively slowly.[1] According to the World Health Organization toxicity classification, tebuconazole is listed as Class III (slightly hazardous) and propiconazole as Class II (moderately toxic).[2] Both of these fungicides belong to the inhibitors of sterol 14α-demethylation and they are widely used as foliar applications on cereals, fruits, vegetable, tea plants, ornamentals and as seed treatments.[3] Tebuconazole and propiconazole have a single site mode of action and they are components of many different products dedicated to agriculture and plant disease control. These fungicides exhibit systemic action and they are able to move *via* the xylem to different plant tissues, even those which were not directly treated with the compound.[4] High activity towards species such as *Botrytis cinerea*, *Sclerotinia sclerotiorum*, *Alternaria* spp. and *Leptosphaeria* spp. makes these triazoles very effective at low doses. Tebuconazole is a white crystalline powder with water solubility equal to 0.032 g/L at 20 ºC and propiconazole is a yellowish oil with water solubility equal to 0.099 g/L at 20 ºC. Commercial formulas of tebuconazole and propiconazole require the formation of emulsion in water, which can limit some potential applications. Aside from their high biological activity, tebuconazole and propiconazole have been successfully used in extraction of metals[5,6] and acids,[7] however structures of the latter have not been well described.

Ionic liquids (ILs) are a very attractive group of compounds. Variety of structures and unique properties thereof contribute to numerous uses in many different fields. Since ILs are characterized by low melting points and negligible volatility, they have found use as green solvents, non-toxic and easy to recycle.[8–13] Chemicals converted to ILs exhibit improved properties, making their use easier and more effective.[14] They are efficient food deterrents,[15] herbicides[14,16–18] and herbicide-plant regulators.[19,20] There are some examples of fungicidal ILs described in literature,[21–25] hence this manuscript is focused on presenting a new, cheap and efficient method, which may be used to obtain ILs by modifying the existing structures of commonly used fungicides.

Results and discussion

Tebuconazole- and propiconazole-based salts were synthesized in one step reaction with organic or inorganic acids (Fig. 1).

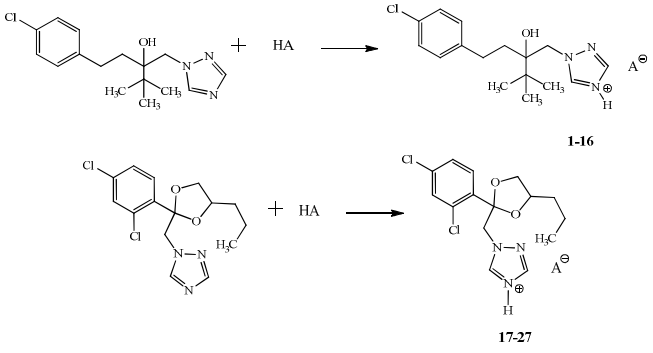

Fig. 1 Synthesis of tebuconazole and propiconazole based salts.

The acids used for the synthesis were characterized by various pKa values (from -7 for hydrochloric acid, to +3.86 for D,L-lactic acid). Reactions were conducted at room temperature with high yields (exceeding 90%). The progress of each reaction was monitored by changes in pH value of acids solutions in methanol. In case of all of obtained salts, the equilibrium state was reached after 15 to 45

minutes from adding tebuconazole or propiconazole, depending on the pKa value of the acid. For strong acids, with a pKa value ≤ 2, the reaction time was approx. 15-20 minutes, while for acids, with a pKa value > 2, the reaction time was extended to 40-45 minutes. The synthesized salts were dried under vacuum (10 mbar) at 45 ºC for 10 h and stored over P_4O_{10}. The water contents of the dried salts were measured by Karl-Fischer method and found to be less than 500 ppm. The obtained salts were stable in air and in contact with water or the tested organic solvents. They were insoluble in hexane and water but soluble in acetone, dichloromethane, DMSO and low molecular weight alcohols (methanol, 2-propanol).

The synthesized salts (hydrochlorides, dihydrogen citrates, dodecylbenzenesulfonates, methanesulfonates, *p*-toluenesulfonate, benzenesulfonates, oxalate, tetrafluoroborate, methoxyacetates, L-tartrate, nitrates, dihydrogen phosphate, maleates, D,L-lactate, itaconate, malate, hydrogen sulfate, 4-methylbenzenesulfonate), the corresponding reaction yields and melting points were presented in Table 1.

Table 1 Prepared tebuconazole (**1-16**) and propiconazole (**17-27**) based salts

Salt	Anion	Yield [%]	M_p [ºC]
1	hydrochloride – [Cl]	92	192-194[a]
2	dihydrogen citrate	99	liquid
3	dodecylbenzenesulfonate	98	wax
4	methanesulfonate	98	150-152
5	4-methylbenzenesulfonate	92	172-174
6	benzenesulfonate	93	137-139
7	oxalate	98	80-83
8	tetrafluoroborate – [BF_4]	99	121-123
9	methoxyacetate	92	liquid
10	L-tartrate	99	wax
11	nitrate – [NO_3]	96	180-182
12	dihydrogen phosphate – [H_2PO_4]	98	112-116
13	maleate	98	120-123
14	D,L-lactate	97	liquid
15	itaconate	98	86-90
16	malate	98	87-90
17	nitrate – [NO_3]	99	113-115[b]
18	hydrochloride – [Cl]	97	102-104
19	hydrogen sulfate – [HSO_4]	99	liquid
20	4-methylbenzenesulfonate	96	wax
21	Dodecylbenzenesulfonate	98	liquid
22	Methanesulfonate	99	wax
23	Benzenesulfonate	99	wax
24	dihydrogen citrate	99	liquid
25	Methoxyacetate	92	liquid
26	D,L-lactate	97	liquid
27	Maleate	98	liquid

Lit. [a]126-128 ºC,[7] [b]133.5 ºC.[26]

Among the obtained tebuconazole-based salts (**1**-**16**), two of them (**1**, **3**) have been previously reported in literature.[7,26] The synthesized salts were crystalline solids with narrow range of melting points (**1**, **4**-**8**, **11**-**13**, **15**-**16**), waxes (**3**, **10**) or liquids (**2**, **9**, **14**). 8 out of the total 16 obtained salts can be described as protic ILs (melting points < 100 °C). Propiconazole-based salts **17** and **18** were obtained as crystalline solids, **20**, **22**, **23** were waxes and the remaining salts were liquids. Salts **19**–**27** can be described as protic ILs. Propiconazole nitrate (**17**) has been previously described in literature as a solid with a melting point of 133.5 ºC. The difference between the melting point values can be caused by using pure nitric acid instead of a mixture of nitric acid with acetic acid.[3]

The synthesized salts were thermally stable, as confirmed by the data presented in Table 2.

Table 2 Thermal transitions and decomposition temperatures[a] of prepared salts

Salt	T_g [a]	T_c [b]	T_m [c]	$T_{onset\ 5\%}$ [d]	$T_{onset\ 50\%}$ [d]
1	5	-	191	189	196/320
2	21	-	-	168	195/340
3	8	-	83	251	322
4	-	141	153	170	308/465
5	-	-	174	242	295
6	39	127	144	252	322
7	-0.4	-	81	163	189/320
9	-1.4	-	-	167	175/340
10	24	-	-	192	208/314
11	-	-	182	182	185/260
12	59	-	115	243	304
13	15	-	130	152	308
14	-3.6	-	-	176	238/315
15	4.3	-	81	182	215/360
16	8.9	-	93	198	333
17	-18	-	114	150	155/328
18	-21	48	100	146	148/328
19	-11	-	-	183	284
20	26	-	-	266	323
21	-4.5	-	-	262	328
22	13	-	-	219	318
23	12	-	-	262	339
24	12	-	-	168	190/320
25	-30	-	-	166	188/336
26	-23	-	-	171	180/300

T in [ºC], [a] glass transition temperature, [b] crystallization temperature, [c] melting point on heating, [d] decomposition temperatures as $T_{onset5\%}$ to 5 wt% and $T_{onset50\%}$ to 50 wt% mass loss, first and second decomposition.

The glass transition temperature values ranged from -30 to 59 ºC (except for **4**, **5**, **11**). The glass transition temperature for propiconazole was at -24 ºC, whereas for tebuconazole the value could not be determined.

Highest thermal stability among tebuconazole-based salts was observed for benzenesulfonate (**6**) with the $T_{onset\ 5\%}$ value at 252 ºC and $T_{onset\ 50\%}$ value at 322 ºC. For sulfonates (3-**6**), the thermal stability order may be established as following: methanesulfonate < *p*-toluenesulfonate < dodecylbenzenesulfonate < benzenesulfonate. Additionally, an exothermal effect was observed (270 J/g) for methanesulfonate (**4**) during its decomposition. For nitrate (**11**), the melting point reached the same value as the decomposition temperature (182 ºC). In general, two steps of thermal decomposition were observed for most of tebuconazole-based salts. The highest thermal stability among propiconazole-based salts was observed for 4-methylbenzenesulfonate (**20**) wiat the $T_{onset5\%}$ value at 266 ºC and $T_{onset\ 50\%}$ value at 322 ºC. An exothermal decomposition (115 J/g) was observed for nitrate (**17**). Two steps of thermal decomposition were observed for propiconazole-based salts **17, 18, 24-26**. In case of sulfonates (**20**-**23**) only hydrogensulfonate (**20**) exhibited two steps of thermal decomposition.

Decomposition temperatures for tebuconazole amounted to 302 ºC for $T_{onset5\%}$ and 364 ºC for $T_{onset50\%}$, while those for propiconazole amounted to 265 ºC for $T_{onset5\%}$ and 322 ºC for $T_{onset50\%}$, with marked differences from values established for synthesized salts **1**-**26**.
Viscosities of the prepared salts were determined for protic ILs **21**, **25** and **26**. The measured values ranged from 0.805 Pa·s (for **25**, at 20 ºC) to 45.781 Pa·s (for **21**, at 25 ºC, the test was impossible to conduct at lower temperature). Viscosity values strongly depended on temperature. The largest change was noted for **21,** with a decrease of viscosity value to 0.111 Pa·s at 80 ºC, as shown in Figure 2.

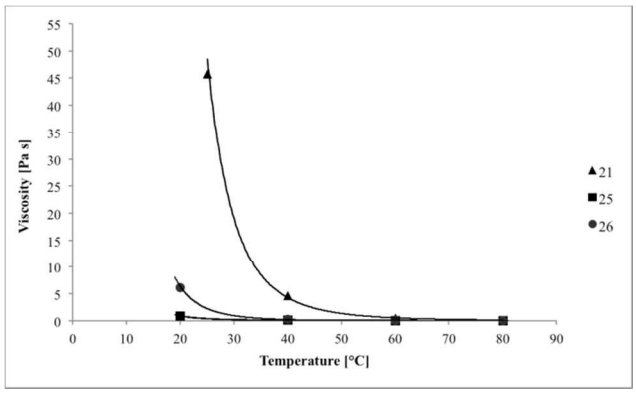

Fig. 2 Viscosity of protic ILs: ▲ – 21, ■ – 25, ● – 26.

Determination of density values for the obtained ILs was challenging due to their high viscosity. The values measured for **25** and **26** amounted to 1.2741 and 1.2777 g/mL at 20 ºC, respectively, and decreased in sequence with increasing temperature to 40 ºC (1.2557 and 1.2596 g/mL), 60 ºC (1.2370 and 1.2410 g/mL) and 80 ºC (1.2178 and 1.2217 g/mL).
Results presented in the Table 3 show that the tested tebuconazole-based salts **5** and **6** were active against *B. cinerea*, *F. culmorum* and *M. nivale.*

Table 3 Inhibition of the growth of *Botrytis cinerea, Fusarium culmorum* and *Microdochium nivale* due to tebuconazole based salts

Object	The growth of *B. cinerea* mycelium [cm]			The growth of *F. culmorum* mycelium [cm]			The growth of *M. nivale* mycelium [cm]		
	10 [ppm]	100 [ppm]	1000 [ppm]	10 [ppm]	100 [ppm]	1000 [ppm]	10 [ppm]	100 [ppm]	1000 [ppm]
Control	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
5	0.0	0.0	0.0	0.1	0.0	0.0	0.3	0.0	0.0
6	1.0	0.0	0.0	1.5	0.0	0.0	2.9	0.0	0.0
Tebu 250 EW[a]	0.0	0.0	0.0	0.8	0.0	0.0	1.2	0.0	0.0
LSD $_{(P=0.05)}$	0.29	0.15	0.08	0.10	0.17	-	0.27	0.15	0.14

[a] *commercial fungicides containing tebuconazole.*

Significant differences between the inhibition of fungal growth for control and the tested salts were observed in all cases. Complete inhibition of mycelium growth was observed at concentrations of 100 and 1000 ppm. Slight mycelial growth of *F. culmorum* and *M. nivale* was noticed when the tested salts **5** and **6** were used at a concentration of 10 ppm, while growth of *B. cinerea* was observed in the presence of 10 ppm of benzenesulfonate (**6**).
Salts **10**, **12**-**16**, **20**, **25**-**27** at a concentration of 100 and 1000 ppm completely inhibited the growth of *S. sclerotiorum*, *F. culmorum* and *M. nivale,* as shown in Table 4.

Table 4 Inhibition of the growth of *Sclerotinia sclerotiorum, Fusarium culmorum* and *Microdochium nivale* due to tebuconazole and propiconazole based salts

Object	The growth of *S. sclerotiorum* mycelium [cm]			The growth of *F. culmorum* mycelium [cm]			The growth of *M. nivale* mycelium [cm]		
	10 [ppm]	100 [ppm]	1000 [ppm]	10 [ppm]	100 [ppm]	1000 [ppm]	10 [ppm]	100 [ppm]	1000 [ppm]
Control	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
10	3.7	0.0	0.0	1.3	0.0	0.0	2.3	0.0	0.0
12	4.6	0.0	0.0	4.6	0.0	0.0	3.4	0.0	0.0
13	2.5	0.0	0.0	0.5	0.0	0.0	1.3	0.0	0.0
14	2.1	0.0	0.0	0.4	0.0	0.0	1.3	0.0	0.0
15	4.2	0.0	0.0	2.2	0.0	0.0	2.7	0.0	0.0
16	0.1	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0
20	1.8	0.0	0.0	0.5	0.0	0.0	0.4	0.0	0.0
25	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
26	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
27	2.1	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0
Tebu 250 EW[a]	4.6	0.0	0.0	0.5	0.0	0.0	2.4	0.0	0.0
Bumper 250 EC[b]	0.6	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
LSD $_{(P=0.05)}$	0.21	-	-	0.16	-	-	0.47	-	-

commercial fungicides containing [a] *tebuconazole and* [b] *propiconazole.*

At the concentration of 10 ppm the activity of the tested salts varied depending on both the salt and the fungus. Salts **25** and **26** completely inhibited the growth of all fungi, maleate (**27**) and Bumper 250 EC inhibited only *M. nivale*, while malate (**16**) caused total inhibition of growth for *F. culmorum*. On the other hand dihydrogen phosphate (**12**) and itaconate (**15**) did not exhibit activity against *S. sclerotiorum*, *F. culmorum* and *M. nivale*. After application of other salts at a concentration of 10 ppm a differentiated growth of fungi was observed. The results presented in the Table 5 show that the tested salts **17**-**19**, **21**, **23** and **24** as well as commercial products Tebu 250 EW and Bumper 250 EC completely inhibited the growth of *B. cinerea*, *F. culmorum* and *M. nivale* at a concentration of 100 and 1000 ppm. At the concentration of 10 ppm

the growth of all the tested fungi was completely inhibited by salts **19** and **21** as well as Bumper 250 EC.
The ionic liquids **23** and **24** caused a complete inhibition of growth for *B. cinerea* and *M. nivale*, whereas ionic liquids **17** and **18** inhibited only *B. cinerea*.

Table 5 Inhibition of the growth of *Botrytis cinerea, Fusarium culmorum* and *Microdochium nivale* due to propiconazole based salts

Object	The growth of *B. cinerea* mycelium [cm]			The growth of *F. culmorum* mycelium [cm]			The growth of *M. nivale* mycelium [cm]		
	10 [ppm]	100 [ppm]	1000 [ppm]	10 [ppm]	100 [ppm]	1000 [ppm]	10 [ppm]	100 [ppm]	1000 [ppm]
Control	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
17	0.0	0.0	0.0	0.1	0.0	0.0	0.2	0.0	0.0
18	0.0	0.0	0.0	0.1	0.0	0.0	1.1	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
21	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
23	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
24	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Tebu 250 EW[a]	0.0	0.0	0.0	0.1	0.0	0.0	1.2	0.0	0.0
Bumper 250 EC[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LSD $_{(P=0.05)}$	0.28	0.28	0.28	0.09	0.08	0.07	0.19	0.16	0.16

commercial fungicides containing [a] tebuconazole and [b] propiconazole.

The obtained results indicate that the synthesized tebuconazole- and propiconazole-based salts preserved high activity towards fungi, which is a characteristic trait of the precursor compounds. The cation created by the addition of a proton to the nitrogen atom is responsible for the fungicidal activity. It was previously established, that a substituent in the tebuconazole cation, which is bigger than a proton (i.e. methyl, benzyl or alkyl), contributes to a decrease of the fungicidal activity.[27] The obtained propiconazole-based salts were more effective compared to the tebuconazole-based salts. In the case of the latter an influence of the anion on the biological activity was observed. The dihrydogen phosphate and itaconate anions seem to decrease the efficiency of the synthesized salts.
Overall, novel protic ILs exhibiting strong fungicidal properties were obtained. The proposed method for designing new, third generation ILs[28,29] was found to be efficient. This potentially opens up new possibilities of employing the commonly used active compounds in a modified form.

Conclusions

Synthesis of tebuconazole- and propiconazole-based salts was conducted with use of both organic and inorganic acids. New salts were obtained with high yields. Chemical modification of the triazole structure resulted in changed psychical properties. 17 of synthesized salts can be described as protic ILs. The obtained tebuconazole- and propiconazole-based salts are active against fungal species of *Fusarium culmorum*, *Microdochium nivale*, *Sclerotinia sclerotiorum* and *Botrytis cinerea* at a level equivalent to known triazole fungicides. The method presented in this study can be used to improve the physical properties of triazole fungicides and make their use easier and more efficient. The synthesized triazolium ILs do not exhibit a tendency to complex metals and their biodegradability will also change compared to the precursor compound.[30]

Experimental

Materials
Tebuconazole and propiconazole (both technical grade) were used without further purification. Hydrochloric acid (37%), citric acid (99%), 4-dodecylbenzenesulfonic acid (≥95%), methanesulfonic acid (≥99.5%), 4-methylbenzenesulfonate acid monohydrate (≥98.5%), benzenesulfonic acid (90%), oxalic acid (98%), tetrafluoroboric acid (48% in water), sulfuric acid (95-98%), methoxyacetic acid (98%), lactic acid (85%), L-tartaric acid (≥99%), nitric acid (70%), phosphoric acid (85% in water), maleic acid (≥99%) as well as malic acid (≥98%) were purchased from Sigma Aldrich and Fluka, and used as received.
Synthesis
The corresponding acid was first dissolved in methanol, then a stoichiometric amount of tebuconazole or propiconazole was added. The reaction was performed at room temperature, until equilibrium was reached. The progress of the reaction and the equilibrium states of the reactions were determined by changes in observed pH values for reaction mixtures. Upon evaporation of the solvent, the product was washed with water and hexane. Finally, the obtained salts were dried under vacuum (10 mbar) at 45 ºC for 10 h.
Analysis
^{1}H NMR spectra were recorded on a Mercury Gemini 300 spectrometer operating at 300 MHz with TMS as the internal standard. ^{13}C NMR spectra were obtained with the same instrument at 75 MHz (the spectra are available in ESI). CHN elemental analyses were performed at the Adam Mickiewicz University, Poznan (Poland). The water content was determined by using an Aquastar volumetric Karl Fischer titration with Composite 5 solution as the titrant and anhydrous methanol as a solvent. Melting point values were obtained by visual observation *via* hot-plate apparatus. Densities measurements were carried using an Automatic Density Meter DDM2911 with a mechanical oscillator method. The densities of the samples (about 2.0 mL) were measured with respect to temperature controlled conditions *via* Peltier, at 25 ºC. Viscosity measurements were performed using a rheometer (Rheotec RC30-CPS) with cone-shaped geometry (C50-2). The viscosities of the samples (about 1.5 mL) were measured with respect to temperature, from 20 to 90 ºC. Determination of refractive index values was carried out using Automatic Refractometer J357 with electronic temperature control.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol chloride (1)
^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.63 (m, 1H); 1.79 (m, 1H); 2.05 (m, 1H); 2.54 (s, 1H); 2.63 (m, 1H); 4.51 (d, J = 2.2 Hz, 2H); 7.19 (d, J = 8.3 Hz, 2H); 7.31 (d, J = 8.4, 2H); 8.81 (s, 1H); 9.64 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.60; 29.53; 36.39; 38.09; 54.82; 75.15; 128.22; 130.08; 130.24; 141.80; 143.77; 145.67.
Elemental analysis calc. (%) for $C_{16}H_{23}Cl_2N_3O$ (344,28): C 55.82; H 6.78; N 12.21. Found: C 56.12; H 6.40; N 12.51.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol dihydrogen citrate (2)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.64 (m, 1H); 1.80 (m, 1H); 1.91 (m, 1H); 2.55 (m, 2H); 2.72 (m, 4H) 4.47 (d, *J* = 2.2 Hz, 2H); 7.16 (d, *J* = 8.2 Hz, 2H); 7.28 (m, 2H); 8.03 (s, 1H); 8.53 (s, 1H); 12.5 (m, 2H). ^{13}C NMR (DMSO-d_6) δ (ppm): 25.60; 29.52; 36.39; 54.82; 75.14; 128.22; 130.07; 141.79; 143.76, 145.66.

Elemental analysis calc. (%) for $C_{22}H_{30}ClN_3O_8$ (499.94): C 52.85, H 6.05, N 8.40. Found: C 53.47; H 6.42; N 8.79.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol 4-dodecylbenzenesulfonate (3)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.81 (m, 3H); 0.95 (s, 9H); 1.06 (m, 16H); 1.19 (m, 3H); 1.64 (m, 2H); 1.80 (m, 2H); 2.00 (m, 2H); 2.41 (t, *J* = 3.6 Hz, 1H); 2.64 (m, 2H); 4.53 (d, *J* = 2.2 Hz, 2H); 7.10 (d, *J* = 8.9 Hz, 2H); 7.17 (d, *J* = 12.3 Hz, 2H); 7.29 (d, *J* = 8.2 Hz, 2H); 7.53 (d, *J* = 8.5 Hz, 2H); 8.73 (s, 1H); 9.42 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm): 13.91; 22.09; 22.26; 25.51; 29.12; 29.52; 31.29; 36.4; 54.67; 75.1; 125.56; 128.19; 130.04; 141.72; 143.99; 146.05.

Elemental analysis calc. (%) for $C_{34}H_{52}ClN_3O_4S$ (634.31): C 64.38, H 8.26, N 6.62. Found: C 63.99; H 8.57; N 6.24.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol methanesulfonate (4)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.96 (s, 9H); 1.60 (m, 1H); 1.79 (m, 1H); 2.08 (m, 1H); 2.49 (s, 3H); 2.58 (m, 2H); 4.48 (m, 2H); 7.18 (m, 2H); 7.30 (m, 2H); 8.69 (s, 1H); 9.36 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.53; 29.49; 36.36; 54.59; 75.14; 128.23; 130.06; 141.78; 144.10, 146.42.

Elemental analysis calc. (%) for $C_{17}H_{26}ClN_3O_4S$ (403.92): C 50.55, H 6.49, N 10.40. Found: C 50.17; H 6.88; N 10.87.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol 4-methylbenzenesulfonate (5)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.96 (s, 9H); 1.60 (m, 1H); 1.80 (m, 1H); 2.08 (m, 1H); 2.29 (s, 3H); 2.58 (m, 2H); 4.49 (m, 2H); 7.15 (m, 4H); 7.19 (m, 2H); 7.29 (m, 2H); 8.81 (s, 1H); 9.50 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 20.83; 25.55; 29.54; 36.43; 54.79; 75.11; 125.55; 128.71; 130.27; 138.20; 141.71; 143.88; 144.91, 145.69.

Elemental analysis calc. (%) for $C_{23}H_{30}ClN_3O_4S$ (480.02): C 57.55, H 6.30, N 8.75. Found: C 57.17; H 5.98; N 8.41.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol benzenesulfonate (6)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.96 (s, 9H); 1.60 (m, 1H); 1.80 (m, 1H); 2.12 (m, 1H); 2.59 (m, 2H); 4.49 (m, 2H); 7.17 (m, 2H); 7.32 (m, 5H); 7.66 (m, 2H); 8.83 (s, 1H); 9.53 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.55; 29.56; 36.45; 54.84; 75.10; 125.53; 127.82; 128.24; 128.80; 130.08; 130.29; 141.71; 143.84; 145.53; 147.69.

Elemental analysis calc. (%) for $C_{22}H_{28}ClN_3O_4S$ (465.99): C 56.70, H 6.06, N 9.02. Found: C 56.33; H 6.34; N 8.78.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol oxalate (7)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 1H); 1.79 (m, 1H); 1.91 (m, 1H); 2.52 (s, 1H); 2.56 (m, 1H); 4.34 (m, 2H); 7.15 (d, *J* = 8.5 Hz, 2H); 7.30 (d, *J* = 8.5 Hz, 2H); 8.04 (s, 1H); 8.54 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.46; 29.28; 36.06; 37.98; 53.51; 75.41; 128.18; 130.04; 130.16; 142.05; 145.34; 150.66; 161.38.

Elemental analysis calc. (%) for $C_{18}H_{24}ClN_3O_5$ (397.85): C 54.34; H 6.08; N 10.56. Found: C 54.72; H 5.66; N 10.19.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol tetrafluoroborate (8)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.96 (s, 9H); 1.62 (m, 1H); 1.82 (m, 1H); 2.06 (m, 1H); 2.51 (t, *J* = 3.6 Hz, 1H); 2.62 (m, 1H); 4.45 (m, 2H); 7.19 (d, *J* = 8.2 Hz, 2H); 7.29 (m, 2H); 8.55 (s, 1H); 9,17 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.51; 29.47; 36.34; 54.35; 75.21; 128.23; 130.17; 141.81; 144.32, 147.25. ^{19}F NMR (DMSO-d_6) δ (ppm) 148.65.

Elemental analysis calc. (%) for $C_{16}H_{23}BClF_4N_3O$ (395,63): C 48.57, H 5.86, N 10.62. Found: C 48.92; H 5.16; N 10.35.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol methoxyacetate (9)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 1H); 1.79 (m, 1H); 1.92 (m, 1H); 2.52 (s, 1H); 3.31 (s, 3H); 3.95 (s, 2H); 4.34 (m, 1H); 7.15 (d, *J* = 8.5 Hz, 2H); 7.30 (d, *J* = 8.5 Hz, 2H); 8.04 (s, 1H); 8.54 (s, 1H); 12.66 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.44; 29.27; 36.04; 37.96; 53.49; 58.27; 68.88; 75.40; 128.16; 130.02; 130.16; 142.04; 145.32; 150.66; 171.54.

Elemental analysis calc. (%) for $C_{19}H_{28}ClN_3O_4$ (383.87): C 56.32; H 6.83; 10.95. Found: C 55.94; H 7.20; N 10.57.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol L-tartrate (10)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.94 (s, 9H); 1.63 (m, 1H); 1.80 (m, 1H); 1.92 (m, 1H); 2.53 (s, 1H); 2.57 (m, 1H); 4.37 (m, 2H); 4.38 (s, 2H); 7.15 (d, *J* = 8.4 Hz, 2H); 7.30 (d, *J* = 8.5 Hz, 2H); 8.05 (s, 1H); 8.55 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.46; 29.30; 36.07; 37.98; 53.55; 72.23; 75.44; 128.18; 130.03; 130.19; 142.03; 145.34; 150.64; 173.21.

Elemental analysis calc. (%) for $C_{22}H_{28}ClN_3O_7$ (457.91): C 54.37; H 6.64; N 8.65. Found: C 54.67; H 6.99; N 8.98.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol nitrate (11)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.98 (s, 9H); 1.66 (m, 1H); 1,85 (m, 1H); 2.01 (m, 1H); 2.43 (t, *J* = 3.8 Hz, 1H); 2.62 (m, 1H); 4.50 (m, 2H); 7.20 (d, *J* = 8.4 Hz, 2H); 7.30 (m, 2H); 8.46 (s, 1H); 9.24 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.56; 29.49; 36.41; 54.29; 75.27; 128.26; 130.21; 141.61; 143.72, 146.89.

Elemental analysis calc. (%) for $C_{16}H_{23}ClN_4O_4$ (370.83): C 51.82, H 6.25, N 15.10. Found: C 52.11; H 6.89; N 15.39.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol dihydrogen phosphate (12)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 1H); 1.79 (m, 1H); 1.91 (m, 1H); 2.53 (s, 1H); 2.56 (m, 1H); 4.34 (m, 2H); 7.15 (d, *J* = 8.3 Hz, 2H); 7.30 (d, *J* = 8.4 Hz, 2H); 8.04 (s, 1H); 8.54 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.46; 29.27; 36.04; 37.98; 53.50; 75.41; 128.17; 130.04; 130.16; 142.05; 145.34; 150.66.

Elemental analysis calc. (%) for $C_{16}H_{25}ClN_3O_5P$ (405.81): C 47.35; H 6.21; N 10.35. Found: C 47.69; H 5.85; N 10.70.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol maleate (13)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.61 (m, 1H); 1.79 (m, 1H); 1.92 (m, 1H); 2.52 (s, 1H); 2.56 (m, 1H); 4.34 (m, 2H); 6.30 (s, 2H), 7.15 (d, *J* = 8.5 Hz, 2H); 7.30 (d, *J* = 8.4 Hz, 2H); 8.05 (s, 1H); 8.55 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.48; 29.30; 36.08; 38.00; 53.55; 75.43; 128.21; 130.06; 130.19; 130.24; 142.06; 145.33; 150.58; 166.78.

Elemental analysis calc. (%) for $C_{20}H_{26}ClN_3O_5$ (423.89): C 56.67; 6.18; N 9.91. Found: C 56.30; H 6.79; N 10.26.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol D,L-lactate (14)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.92 (s, 9H); 1.29 (m, 3H); 1.44 (m, 1H); 1.64 (m, 1H); 1.81 (m, 1H); 1.91 (m, 1H); 2.56 (m, 1H); 4.08 (m, 1H); 4.47 (d, *J* = 2.2 Hz, 2H); 7.16 (d, *J* = 8.2 Hz, 2H); 7.29 (m, 2H); 8.05 (s, 1H); 8.54 (s, 1H); 12.5 (m, 1H). ^{13}C NMR (DMSO-d_6) δ ppm): 25.60; 29.52; 36.39; 54.82; 75.14; 128.22; 130.07; 141.79; 143.76, 145.66.

Elemental analysis calc. (%) for $C_{19}H_{28}ClN_3O_4$ (397.90): C 56.67; H 6.18; N 9.91. Found: C 56.88; H 5.79; N 10.27.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol itaconate (15)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 1H); 1.79 (m, 1H); 1.92 (m, 1H); 2.52 (s, 1H); 2.56 (m, 1H); 3.24 (s, 2H); 4.34 (m, 2H); 5.72 (d, *J* = 1.5 Hz, 1H); 6.14 (d, *J* = 1.6 Hz, 1H); 7.15 (d, *J* = 8.5 Hz, 2H); 7.29 (d, *J* = 8.5 Hz, 2H); 8.04 (s, 1H); 8.53 (s, 1H); 12.48 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.49; 29.31; 36.09; 37.46; 38.01; 53.54; 75.46; 127.40; 128.22; 130.07; 130.21; 135.48; 142.07; 145.37; 150.69; 167.57; 172.05.
Elemental analysis calc. (%) for $C_{21}H_{28}ClN_3O_5$ (437.92): C 57.60; 6.44; 9.60. Found: C 57.00; H 6.06; N 9.27.

(*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-[(1*H*-1,2,4-triazol-4-ium)-1-ylmethyl]pentan-3-ol malate (16)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 1H); 1.79 (m, 1H); 1.91 (m, 1H); 2.56 (m, 3H); 3.66 (m, 2H); 4.33 (m, 3H); 7.15 (d, *J* = 8.5 Hz, 2H); 7.29 (d, *J* = 8.5 Hz, 2H); 8.04 (s, 1H); 8.54 (s, 1H); 12.45 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 25.50; 29.33; 36.11; 38.02; 53.58; 67.09; 75.48; 128.23; 130.08; 130.23; 142.08; 145.38; 150.70; 171.92; 174.70.
Elemental analysis calc. (%) for $C_{20}H_{28}ClN_3O_6$ (441.91): C 54.36; H 6.39; N 9.51. Found: C 53.99; H 6.69; N 9.12.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium nitrate (17)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.30 (m, 4H); 3.27 (s, 1H); 3.91 (m, 3H); 4.85 (m, 2H); 7.44 (m, 2H); 7.66 (m, 1H); 8.41 (s, 1H); 9.14 (s, 1H); 11.86 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.81; 18.44; 34.35; 54.03; 69.64; 76.31; 77.51; 106.11; 127.26; 130.41; 132.48; 135.58; 144.65; 147.78.
Elemental analysis calc. (%) for $C_{15}H_{18}Cl_2N_4O_5$ (405.23): C 44.46; H 4.48; N 13.83. Found: C 44.83; H 4.62; N 13.53.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium chloride (18)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.20-1.40 (m, 4H); 3.29 (s, 1H); 3.91 (m, 2H); 4.84 (m, 2H); 7.40-7.47 (m, 2H); 7.67 (m, 1H); 8.39 (d, *J* = 12.4 Hz, 2H); 9.13 (d, *J* = 4.07 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.84; 18.40; 39.52; 69.56; 76.32; 77.47; 106.13; 127.33; 130.03; 130.63; 132.52; 134.54; 135.18; 144.58; 147.91.
Elemental analysis calc. (%) for $C_{15}H_{18}Cl_3N_3O_2$ (378.68): C 47.58; H 4.79; N 11.10. Found: C 47.22; H 5.10; N 11.36.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium hydrogen sulfate (19)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.30 (m, 4H); 3.30 (s, 1H); 3.92 (m, 2H); 4.88 (m, 2H); 7.43 (m, 2H); 7.67 (s, 1H); 8.60 (d, *J* = 15.1 Hz, 1H); 9.39 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.91; 18.44; 39.50; 69.66; 76.44; 77.67; 106.05; 127.35; 130.19; 130.74; 132.60; 134.74; 135.08; 144.39; 146.59.
Elemental analysis calc. (%) for $C_{15}H_{19}Cl_2N_3O_6S$ (440.30): C 40.92; H 4.35; N 9.54. Found: C 40.51; H 4.01; N 9.88.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium 4-methylbenzenesulfonate (20)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.85 (m, 3H); 1.28 (m, 4H); 2.30 (s, 3H); 3.27 (m, 1H); 3.89 (m, 2H); 4.84 (m, 2H); 7.17 (m, 2H); 7.45 (m, 4H); 7.67 (m, 1H); 8.48 (d, *J* = 16.6 Hz, 1H); 9.23 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.80; 18.34; 20.82; 34.14; 69.54; 76.30; 77.51; 106.03; 125.55; 127.34; 128.27; 130.05; 130.62; 132.50; 134.58; 135.07; 138.24; 144.86; 147.21.
Elemental analysis calc. (%) for $C_{22}H_{25}Cl_2N_3O_5S$ (514.42): C 51.37; H 4.90; N 8.17. Found: C 51.71; H 4.53; N 7.85.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium dodecylbenzenesulfonate (21)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.82 (m, 3H); 0.85 (m, 3H); 1.11 (m, 4H); 1.24 (m, 16H); 1.54 (m, 4H); 2.52 (m, 2H); 3.18 (m, 1H); 3.90 (m, 2H); 4.85 (m, 2H); 7.15 (m, 2H); 7.43 (m, 2H); 7.56 (m, 1H); 7.76 (m, 2H); 8.47 (d, *J* = 15.4 Hz, 1H); 9.27 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.93; 18.36; 22.09; 27.09; 29.05; 31.31; 34.14; 34.45; 36.33; 37.73; 69.55; 76.31; 77.52; 106.03; 125.58; 126.18; 126.80; 127.32; 130.06; 130.61; 132,51; 134.59; 135.05; 144.46; 145.11; 147.09.
Elemental analysis calc. (%) for $C_{33}H_{47}Cl_2N_3O_5S$ (668.71): C 59.27; H 7.08; N 6.28. Found: C 59.66; H 7.29; N 6.00.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium methanesulfonate (22)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.29 (m, 4H); 2.54 (s, 3H); 3.29 (m, 1H); 3.91 (m, 2H); 4.86 (m, 2H); 7.48 (m, 2H); 8.46 (d, *J* = 21.7 Hz, 1H); 9.25 (d, *J* = 6.6 Hz, 1H); 10.90 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.89; 18.43; 34.22 69.61; 76.37; 77.58; 106.08; 127.42; 130.11; 130.70; 132.57; 134.66; 135.11; 144.53; 147.12.
Elemental analysis calc. (%) for $C_{16}H_{21}Cl_2N_3O_5S$ (438.33): C 43.94; H 4.61; N 9.61. Found: C 44.31; H 5.00; N 9.26.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium benzenesulfonate (23)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.84 (m, 3H); 1.29 (m, 4H); 3.18 (m, 1H); 3.89 (m, 2H); 4.85 (m, 2H); 7.34 (m, 5H); 7.46 (m, 2H); 7.66 (m, 1H); 8.52 (d, *J* = 13.2 Hz, 1H); 9.26 (d, *J* = 7,1 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.83; 18.36; 34.17; 69.55; 76.31; 77.53; 106.01; 125.53; 127.38; 127.82; 128.80; 130.07; 130.66; 132.51; 134.61; 135.05; 144.45; 147.03.
Elemental analysis calc. (%) for $C_{21}H_{23}Cl_2N_3O_5S$ (500.40): C 50.41; H 4.63; N 8.40. Found: C 50.06; H 7.02; N 8.07.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium dihydrogen citrate (24)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.31 (m, 4H); 2.69 (m, 5H); 3.24 (m, 1H); 3.61 (d, *J* = 19.6 Hz, 1H); 3.89 (m, 2H); 4.85 (m, 2H); 7.47 (m, 2H); 7.64 (m, 1H); 7.87 (d, *J* =10.4 Hz, 1H); 8.43 (d, *J* = 1.9 Hz, 1H); 10.70 (s, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.93; 18.57; 34.32; 42.90; 53.51; 69.63; 72.57; 76.32; 77.48; 106.52; 127.27; 130.38; 132.51; 135.67; 145.49; 150.80; 171.33; 171.42; 174.88.
Elemental analysis calc. (%) for $C_{21}H_{25}Cl_2N_3O_9$ (534.34): C 49.63; H 5.11; N 7.89. Found: C 49.99; H 5.44; N 7.58.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium methoxyacetate (25)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.32 (m, 4H); 3.30 (m, 4H); 3.95 (m, 4H); 4.74 (m, 2H); 7.45 (m, 2H); 7.64 (s, 1H); 7.88 (d, *J* = 10.5 Hz, 1H); 8.42 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.79; 18.40; 39.50; 53.39; 58.25; 68.87; 69.50; 76.23; 106.41; 127.13; 129.90; 130.53; 132.49; 134.16; 135.55; 145.34; 150.67; 171.54.
Elemental analysis calc. (%) for $C_{18}H_{23}Cl_2N_3O_5$ (432.30): C 50.01; H 5.36; N 9.72. Found: C 49.69; H 4.97; N 10.00.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium D,L-lactate (26)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.29 (m, 7H); 3.24 (m, 1H); 3.89 (m, 1H); 4.06 (m, 2H); 4.74 (m, 2H); 7.42 (m, 2H); 7.64 (s, 1H); 7.88 (d, *J* =10.1 Hz, 1H); 8.43 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.81; 18.44; 20.46; 34.17; 65.82; 69.53; 76.26; 77.34; 106.45; 127.18; 129.93; 130.55; 132.52; 134.37; 135.56; 145.36; 150.69; 176.38.
Elemental analysis calc. (%) for $C_{18}H_{23}Cl_2N_3O_5$ (432.30): C 50.01; H 5.36; N 9.72. Found: C 50.35; H 5.72; N 9.38.

(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazol-4-ium maleate (27)

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.30 (m, 4H); 3.21 (m, 1H); 3.91 (m, 2H); 4.75 (m, 2H); 6.33 (m, 2H); 7.40 (m, 2H); 7.67 (s, 1H); 7.89 (d, *J* = 10.2 Hz, 1H); 8.44 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ (ppm) 13.83; 18.46; 39.50; 69.58; 76.31; 106.49; 127.20; 128.64; 129.95; 130.59; 131.22; 131.57; 132.57; 134.43; 145.38; 150.69; 166.92.

Elemental analysis calc. (%) for $C_{19}H_{21}Cl_2N_3O_6$ (458.29): C 49.79; H 4.62; N 9.17. Found: C 49.49; H 4.89; N 8.85.

Thermal stability

Thermal transition temperatures were determined by DSC, with a Mettler Toledo Star^e DSC1 (Leicester, UK) unit, under nitrogen. Samples (between 5 and 15 mg) were placed in aluminum pans and heated from 25 to 120 ºC at a heating rate of 10 ºC /min, cooled with an intracooler at a cooling rate of 10 ºC /min to -100 ºC, then heated again to 120 ^{o}C. Thermogravimetric analysis was performed using a Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK), under nitrogen. Samples (between 2 and 10 mg) were placed in aluminium pans and heated from 30 to 450 ºC at a heating rate of 10 ºC/min.

Antifungal activity

Four species of fungi were used: *Fusarium culmorum*, *Sclerotinia sclerotiorum*, *Microdochium nivale* and *Botrytis cinerea* (obtained from the Institute of Plant Protection-NRI collection). The sample of tested salts was dissolved in 4 mL of methanol, isopropanol or water, then added to a sterile medium (PDA – *Potato Dextrose Agar*, Difco^{TM}) and cooled to 50 ºC. The concentration of the studied salt in the medium was 10, 100 or 1000 ppm. Liquid medium containing the tested salts was distributed on the Petri dishes (diameter of 50 mm). The 4 mm disks of the examined fungi were placed in the center of the Petri dish. In the control sample, the fungi were grown on PDA with the addition of sterile water. The tested salts were compared with commercial fungicides (Tebu 250 EW and Bumper 250 EC) containing tebuconazole or propiconazole as an active substance. The plates were incubated in room temperature until the mycelium in the control reached the edge of the Petri dish. Afterwards, the diameter of the mycelium was measured, subtracting the initial diameter of the disc with the fungus (4 mm). Four replications were performed for each experimental sample. The results were subjected to Student-Newman-Keuls's analysis to test for significant differences between control and samples with addition of ILs.

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Notes and references

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