Electronic Supplementary Information

Ionic liquids with dual pesticidal function

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Experimental section

Materials:(*R,S)*-[1-(4-chlorophenyl)-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl)-3-pentanol] (Tebuconazole), (±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (Propiconazole), 4-chloro-2-methylphenoxyacetic acid (MCPA), 4-chloro-2-methylphenoxypropionic acid (MCPP), 2,4-dichlorophenoxyacetic acid (2,4-D), 3,6-dichloro-2-metoxybenzoic acid (Dicamba) were obtained in the industry as a technical sample and crystallized before use.

General: ^{1}H NMR spectra were recorded on a Mercury Gemini 300 spectrometer operating at 400 MHz with TMS as the internal standard. ^{13}C NMR spectra were obtained with the same instrument at 100MHz. CHN elemental analyses were performed at the Adam Mickiewicz University, Poznan (Poland).

Density was determined using an Automatic Density Meter DDM2911 with a mechanical oscillator method. The density of the samples (about 2.0 mL) was measured with respect to controlled temperature conditions via Peltier, at 25^{o}C. The apparatus was calibrated using deionized water as the reference substance. After each series of measurements, the densimeter was washed by two kinds of solvents and dried.

Viscosity was determined using a rheometer (Rheotec RC30-CPS) with cone-shaped geometry (C50-2). The viscosity of the samples (about 1.5 mL) was measured with respect to temperature, from 20 to 80°C.

Refractive index was determined using Automatic Refractometer J357 with electronic temperature control.

Synthesis of tebuconazole and propiconazole based salts: Tebuconazole or Propiconazole was dissolved in methanol, then a stoichiometric amount of organic acid was added and the mixture was stirred for 4 h at room temperature. After evaporation of methanol, the product was washed 3 times with 20 mL of hexane. The product was dried under vacuum at 60°C for 10 h.

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

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 2H); 1.77 (m, 1H); 2.19 (s, 3H); 2.52 (m, 2H); 4.35 (m, 2H); 4.72 (s, 2H); 6.85 (d, J = 12.6 Hz, 1H); 7.17 (m, 2H); 7.22 (m, 2H); 7.30 (s, 2H); 8.04 (s, 1H); 8.54 (s, 1H); 13.09 (s, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 15.83; 25.45; 29.29; 36.07; 37.97; 53.49; 64.93; 75.41; 112.86;126.28; 128.18; 130.04; 142.05; 145.34; 150.68; 154.81; 170.12.

Elemental analysis calc. (%) for $C_{25}H_{31}Cl_2N_3O_4$ (508.44): C 59.06; H 6.15; N 8.26. Found: C 59.35; H 6.41; N 8.38.

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

^{1}H NMR (DMSO-d_6) δ (ppm) 0.92 (s, 9H); 1.53 (d, J = 6.8 Hz, 2H); 1.92 (m, 1H); 2.18 (s, 3H); 2.30 (s, 2H); 2.52 (m, 2H); 4.35 (m, 2H); 4.82 (d, J = 6.7 Hz, 2H); 6.78 (d, J = 8.9 Hz, 1H); 7.12 (m, 2H); 7.21 (m, 2H); 7.30 (m, 2H); 8.03 (s, 1H); 8.54 (s, 1H); 13.09 (m, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 15.83; 18.33; 25.45; 29.28; 36.06; 37.96; 53.49; 72.05; 75.40; 113.38; 126.27; 128.17; 130.03; 142.04; 145.33; 150.67; 154.56; 172.96.

Elemental analysis calc. (%) for $C_{26}H_{33}Cl_2N_3O_4$ (522.46): C 59,77; H 6,37; N 8,04. Found: C 59.38; H 6.19; N 8.32.

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

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 2H); 1.85 (m, 1H); 2.55 (m, 2H); 4.35 (m, 2H); 4.85 (s, 1H); 4.97 (s, 1H); 7.11 (t, J = 10.2 Hz, 1H); 7.28 (m, 2H); 7.37 (m, 2H); 7.57 (s, 2H); 8.04 (s, 1H); 8.54 (s, 1H); 13.17 (m, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 25.45; 29.27; 36.05; 37.96; 53.49; 65.22; 75.40; 114.89; 127.89; 128.16; 130.02; 142.03; 145.33; 150.66; 152.38; 169.55.

Elemental analysis calc. (%) for $C_{24}H_{28}Cl_3N_3O_4$ (528.86): C 54.51; H 5.34; N 7.95. Found: C 54.22; H 5.12; N 7.63.

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

^{1}H NMR (DMSO-d_6) δ (ppm) 0.93 (s, 9H); 1.62 (m, 2H); 1.95 (m, 1H); 2.54 (m, 2H); 3.86 (m, 3H); 4.35 (m, 2H); 7.15 (d, J = 8.3 Hz, 1H); 7.28 (m, 2H); 7.36 (m, 2H); 7.57 (s, 1H); 7.61 (s, 1H); 8.04 (s, 1H); 8.53 (s, 1H); 13.16 (s, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 25.45; 29.27; 36.05; 37.96; 53.49; 62.00; 75.40; 126.18; 128.16; 130.02; 131.53; 142.03; 145.33; 150.66; 152.47; 165.17.

Elemental analysis calc. (%) for $C_{24}H_{28}Cl_3N_3O_4$ (528,86): C 54.51; H 5.34; N 7.95; Found: C 54.78; H 5.66; N 7.60.

*(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazol-4-ium 4-chloro-2-methylphenoxyacetate (**5**)*

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (t, J = 4.26 Hz, 3H); 1.23 (m, 4H); 2.19 (s, 3H); 3.23 (m, 1H); 3.89 (m, 2H); 4.69 (m, 4H); 6.83 (d, J = 8.80 Hz, 1H); 7.14 (m, 1H); 7.22 (m, 1H); 7.36 (m, 2H); 7.64 (d, J = 5.39 Hz, 1H); 7.85 (d, J = 10.21 Hz, 1H); 8.41 (s, 1H); 13.07 (s, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 13.82; 15.73; 18.45; 34.36; 53.48; 64.92; 69.48; 76.23; 77.27; 124.23; 126.25; 128.40; 130.44; 132.45; 135.51; 145.65; 150.72; 154.71; 170.05.

Elemental analysis calc. (%) for $C_{24}H_{26}Cl_3N_3O_5$ (542.84): C 53.10; H 4.83; N 7.74; Found: C 53.41; H 4.58; N 7.38.

*(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazol-4-ium 2-(4-chloro-2-methylphenoxy)propionate (**6**)*

^{1}H NMR (DMSO-d_6) δ (ppm) 0.85 (m, 3H); 1.2 (m, 4H); 1.52 (d, J = 9.8 Hz, 3H); 2.18 (s, 3H); 3.23 (s, 1H); 3.89 (m, 2H); 4.73 (m, 2H); 4.85 (m, 1H); 6.78 (d, J = 6.9 Hz, 1H); 7.12 (m, 1H); 7.30 (m, 1H); 7.37 (m, 2H); 7.63 (d, J = 6.6 Hz, 1H); 7.87 (d, J = 10.2 Hz, 1H); 8.41 (s, 1H); 13.11 (s, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 13.82; 15.75; 18.41; 34.33; 53.48; 64.95; 69.46; 76.24; 77.25; 106.49; 124.24; 126.22; 128.41; 130.43; 132.44; 135.56; 145.65; 150.78; 154.74; 170.01.

Elemental analysis calc. (%) for $C_{25}H_{28}Cl_3N_3O_5$ (556.87): C 53.92; H 5.07; N 7.55; Found: C 53.65; H 5.40; N 7.88.

*(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazol-4-ium 2,4-dichlorophenoxyacetate (**7**)*

^{1}H NMR (DMSO-d_6) δ (ppm) 0.86 (m, 3H); 1.22 (m, 4H); 3.24 (s, 1H); 3.91 (m, 2H); 4.74 (m, 2H); 4.85 (m, 2H); 7.09 (d, J = 9.0 Hz, 1H); 7.33 (m, 1H); 7.39 (m, 2H); 7.57 (m, 1H); 7.65 (m, 1H); 7.86 (s, 1H); 8.42 (s, 1H); 13.11 (s, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 13.81; 18.42; 34.31; 53.44; 65.17; 69.49; 76.21; 77.28; 114.88; 124.2; 127.3; 129.4; 130.51; 132.39; 135.52; 145.35; 150.78; 152.35; 169.55.

Elemental analysis calc. (%) for $C_{23}H_{23}Cl_4N_3O_5$ (563.26): C 49.04; H 4.12; N 7.46; Found: C 49.35; H 4.38; N 7.78.

*(±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazol-4-ium 3,6-dichloro-2-methoxybenzoate (**8**)*

^{1}H NMR (DMSO-d_6) δ (ppm) 0.85 (m, 3H); 1.22 (m, 4H); 3.23 (m, 1H); 3.84 (m, 5H); 4.73 (m, 2H); 7.32 (m, 2H); 7.40 (m, 2H); 7.65 (m, 1H); 7.85 (s, 1H); 8.42 (s, 1H); 13.21 (s, 1H).

^{13}C NMR (DMSO-d_6) δ (ppm) 13.72; 18.46; 34.33; 53.43; 61.92; 69.47; 76.21; 77.28; 106.38; 125.92; 127.99; 129.61; 130.29; 132.37; 135.52; 145.18; 150.66; 152.43; 165.20.

Elemental analysis calc. (%) for $C_{23}H_{23}Cl_4N_3O_5$ (563.26): C 49.04; H 4.12; N 7.46; Found: C 48.76; H 4.33; N 7.19.

Thermal analysis: Thermal transition temperatures of prepared salts 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 ^{o}C at a heating rate of 10 ^{o}C min^{-1} and cooled with an intracooler at a cooling rate of 10 $^\circ$C min^{-1} to -100 ^{o}C and 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 aluminum pans and heated from 30 to 450 ^{o}C at a heating rate of 10 ^{o}C min^{-1}.

Antifungal activity: The biological activity was tested in two experiments with respect to four fungi species: *Fusariumculmorum* (KZF-5), *Microdochiumnivale* (KZF-7), *Botrytis cinerea* (KZF-12) and*Sclerotiniasclerotiorum* (KZF-14) from Institute of Plant Protection-NRI collection.

The sample of tested salts was dissolved in 4 mL of methanol (**1**-**4**) or isopropanol (**5**-**8**) and then added to sterile medium (PDA – *Potato Dextrose Agar*, Difco^{TM}), cooled to 50 ºC. The salt concentration in the medium was 10, 100 and 1000 ppm. Liquid medium containing

tested salts was overlaid on the Petri dishes of diameter 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 methanol or isopropanol.The tested salts were compared to fungicide Tebu 250 EW or Bumper 250 EC containing Tebuconazole or Propiconazole as an active substance, respectively. The plates were incubated at room temperature until mycelia in the control reached the edge of Petri dish. Then, the diameter of mycelia was measured, subtracting the initial diameter of the disc with fungus (4 mm). Four replications were performed for each experiment. The results were subjected to Student-Newman-Keuls's analysis to test for significant differences between control and samples with addition of salts.

Herbicidal activity:

Greenhouse studies

White mustard (*Sinapis alba L.*) and common lambsquarters (*Chenopodium album L.*) were grown in 0.5 L plastic pots filled with a mixture of peat-based potting material and sandy loam soil (3:1) containing 3% of organic matter. Greenhouse temperature was 20±2 ^{o}C, humidity was 60% and 16/8 day/night hours. Plants were thinned to four per pot within 10-14 days after emergence. When plants reached 4-5 leaf stage they were sprayed with tested compounds at sublethal rates to obtain incomplete control which help differentiate among studied salts. The salts were applied using a moving nozzle sprayer with flat fan nozzle TeeJet 1102 delivering 200 L/ha at 0.2 MPa air pressure.

Tested salts were dissolved in a water and ethanol 1:1 (v/v) mixture in an amount corresponding to 170 g MCPA, 2,4-D or MCPP per 1 ha. Efficacy of tested salts was compared with reference herbicides containing potassium and sodium salts of MCPA (Chwastox Extra 300 SL), dimethylammonium salt of 2,4-D (Aminopielik Standard 600 SL) and dimethylammonium salt of Dicamba (Dikamba 480 SL).

The plots were arranged in a completely randomized setup with four replications. Fresh weight of plants was determined two weeks after treatment. Data were expressed as percent of fresh weight reduction compared with control (non-sprayed plants).

Field experiments

Field studies were conducted in Sosnicowice (Poland) in winter wheat on a sandy soil at pH 5.93 and 1.7% of organic matter. The area of individual plots was approx. 20 m^2. The experiments were laid out as a randomized block with four replicates. All treatments were applied using backpack sprayer with TeeJet XR 11003 flat fan nozzles with a water volume of 300 L ha^{-1} and an operating pressure of 0.2 MPa. The applications were made at growth stage 31 (1 node detectable of wheat plants) at rates of 170 g ha^{-1} MCPA or 2,4-D to obtain incomplete control. The efficiency of the tested salts was evaluated visually two and four weeks after treatment (WAT), comparing the weed infestation of individual weed species on each plot treated by the herbicide with relevant check plot (no herbicide), according to EPPO Standard No. PP 1/93(3). Data were presented in the percent using a scale of 0 (no control) to 100% (complete weed destruction).The selectivity of tested compounds to the crop plants was also determined visually.

Biodegradation:

Microorganisms

A bacterial consortium with a high biodegradation potential towards studied salts was isolated from petroleum-contaminated soil. The genetic characterization of the bacterial consortium based on the analysis of 16s rRNA sequences[1] revealed the following taxa: *Alcaligenes*(AlcP), *Sphingobacterium*(SphiP), *Citrobacter*(CKK), *Achromobacter*(AchrP), *Comamonadaceae*(ComP), *Pseudomonas* (PseuP), *Variovorax*(VariP). Preparation of the preculture and subsequent cultivation conditions were carried out as described recently.[2]

Preparation of biodegradation tests

The biodegradation tests were carried out in loosely closed Erlenmeyer flasks, with 50 mL of the mineral medium and approx. 0.025 g of the studied salt, which was a sole source of carbon and energy. The initial inoculum was adjusted to reach an OD_{600} value of 0.1±0.01 by adding approx. 1 mL of dense cell suspension from the aerobically grown preculture. The cultivation was carried out at 25 °C and 120 rpm for 30 days. The samples were prepared in triplicates. Samples lacking biomass served as control to account for potential abiotic losses. After finishing the biodegradation tests, the biomass was separated by centrifugation (10.000 g for 10 min) and was rinsed three times with the methanol (3x1 mL). The aliquotes were combined with the supernatant. About 10 mL of the supernatant were subjected to ultrasound-assisted extraction with methanol (3 x 1 mL). The extracts were combined, filtered through a 0.2 μm PTFE syringe filter, diluted with a methanol:water solution (80:20 v/v) and subjected to determination of residual salts with the use of HPLC-MS (UltiMate 3000 RSLC, Dionex, with a Hypersil GOLD column 100 mm x 2.1 mm I.D.; 1.9 μm and an API 4000 QTRAP triple quadrupole mass spectrometer, AB Sciex).

1. B. Wyrwas, Ł. Chrzanowski, Ł. Ławniczak, A. Szulc, P. Cyplik, W. Białas, A. Szymański, A. Hołderna-Odachowska, *J. Hazard. Mater.***2011**, *197*, 97-103.

2. Ł. Chrzanowski, M. Dziadas, Ł. Ławniczak, P. Cyplik, W. Białas, A. Szulc, P. Lisiecki, H. Jeleń, *Biores. Technol*. **2012**, *111*, 328-335.

Results

All of the prepared ILs were characterized by ^{1}H and ^{13}C NMR and elemental analysis.Proton chemicalshifts in ^{1}H NMR spectra wereobserved for twoprotons in 1,2,4-triazole ring in the range of 8.03-8.04 and 8.53-8.54 ppm for tebuconazole-basedILs, and of 7.85-7.88 and 8.41-8.42 ppm for propiconazole-basedILs. A characteristicsignal of the proton near the positivelychargednitrogen atom in the triazolate ring was alsoobserved in the range of 13.07-13.21 ppm.

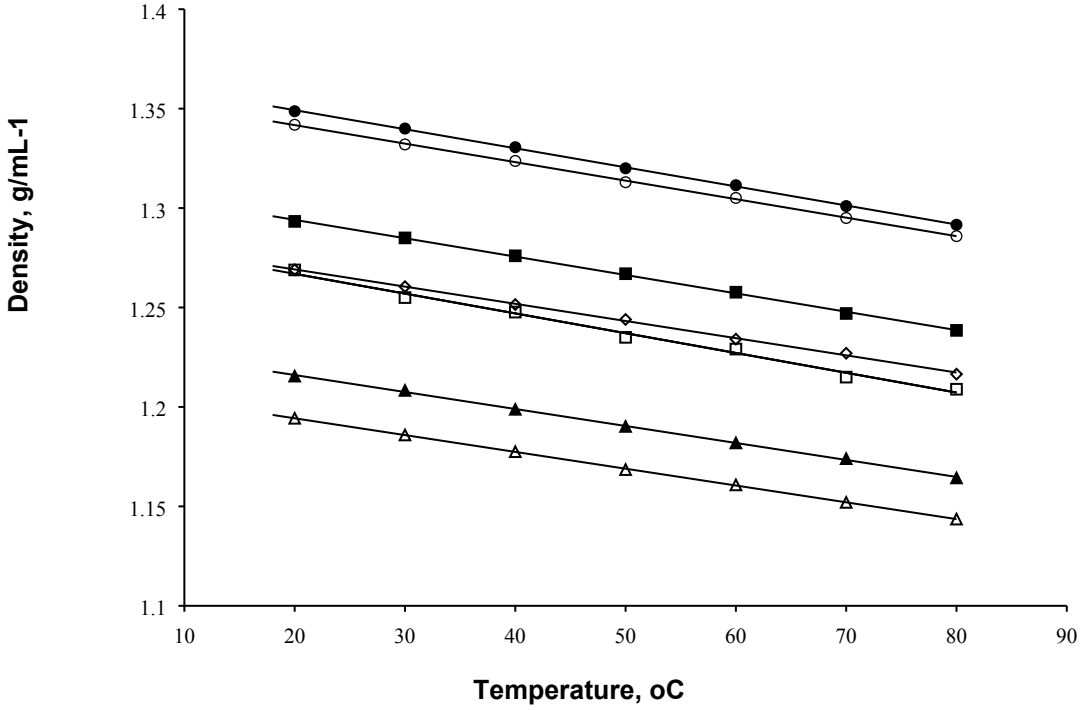

Fig. 1. Changes in the density value of the synthesized ILs as a function of temperature: ▲ – **1**, Δ – **2**, ◊ – **4**, ■ – **5**, □ – **6**, ● – **7**, ○ – **8**.

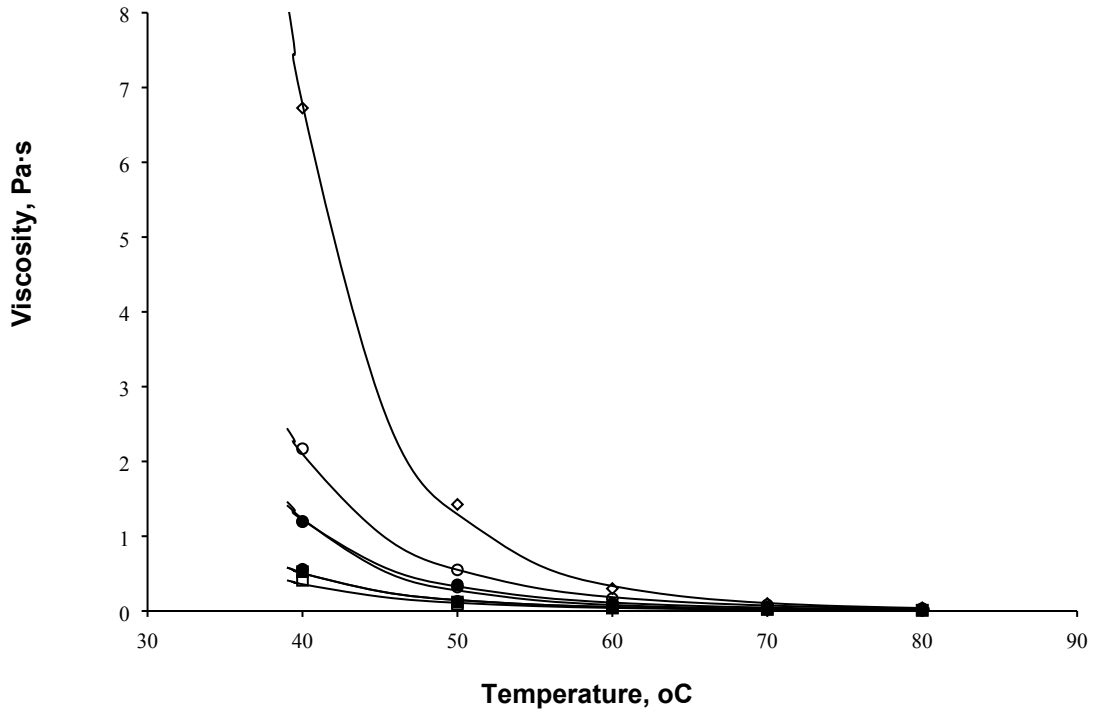

Fig. 2. Changes in the viscosity of prepared ILs as a function of temperature: ▲ – **1**, Δ – **2**, ◊ – **4**, ■ – **5**, □ – **6**, ● – **7**, ○ – **8**.

Table 1. Growth inhibition of *Fusariumculmorum* and *Microdochiumnivale*bytebuconazole-based ILs.

IL	*F. culmorum* [cm]			*M. nivale* [cm]		
	10[a]	100[a]	1000[a]	10[a]	100[a]	1000[a]
Control	4.6	4.6	4.6	4.6	4.6	4.6
1	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.2	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.0	0.0	0.2	0.0	0.0
Tebu	0.0	0.0	0.0	0.4	0.0	0.0
$LSD_{(P=0.05)}$	-	-	-	0.05	-	-

[a] in ppm.

Table 2. Growth inhibition of *Fusariumculmorum*, *Microdochiumnivale*, *Botrytis cinerea*and *Sclerotiniasclerotiorum*bypropiconazole-based ILs.

IL	*F. culmorum* [cm]			*M. nivale* [cm]			*B. cinerea* [cm]			*S. sclerotiorum* [cm]		
	10[a]	100[a]	1000[a]	10[a]	100[a]	1000[a]	10[a]	100[a]	1000[a]	10[a]	100[a]	1000[a]
Control	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
5	0.4	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	1.3	0.0	0.0
6	0.3	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0
7	0.4	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	1.3	0.0	0.0
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0
Bumper	0.4	0.0	0.0	0.1	0.0	0.0	0.8	0.1	0.0	0.8	0.0	0.0
$LSD_{(P=0.05)}$	0.13	-	-	0.19	-	-	0.16	0.13	-	0.71	-	-

[a]inppm.