Supplementary information

For the article entitled:

Mechanochemical synthesis of antifungal bis(benzoxaboroles)

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1. General Information

All materials were obtained from commercial sources, were of minimum 95% purity and used as received, without further purification. All chemicals were handled and reactions set up under air. Mechanochemical reactions were performed using Vibratory Micro Mill Pulverisette vibrational ball mill with an agate mortat and an agate milling ball. The samples were sonicated using Bandelin Sonorex RK 100 H bath and centrifuged using Hettich EBA 20 centrifuge.

TLC analyses were performed on Merck Silica gel 60 F_{254} aluminium sheets, visualized under UV light (254 nm), or by treatment with a staining solution followed by heating. Three staining solutions were used: acidic ethanolic solution of *p*-anisaldehyde, alkaline aqueous solution of potassium permanganate, or acidic ethanolic solution of curcumin.

^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded using Varian VNMRS 500 MHz spectrometer, equipped with a multinuclear z-gradient inverse probe head. In all experiments, the probe temperature was maintained at 25 °C. Standard 5 mm glass NMR tubes were used, except for some ^{11}B NMR experiments for which the samples were prepared in quartz tubes. Chemical shifts are reported relative to residual undeuterated solvent peak (^{1}H NMR), solvent signal (^{13}C NMR), or external references ($BF_3{\cdot}Et_2O$ in $CDCl_3$ for ^{11}B NMR and $CFCl_3$ in $CDCl_3$ for ^{19}F NMR). The signals are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, t = triplet, m = multiplet, br = broad signal), integration.

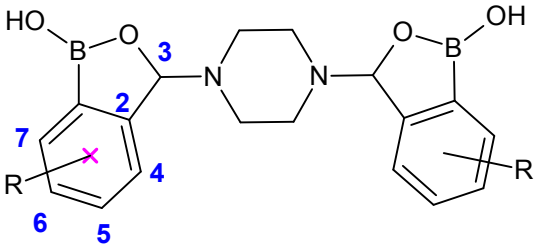
The low-resolution ^{1}H NMR spectra were recorded using Nanalysis NMReady-60E 60 MHz benchtop spectrometer.

FTIR spectra were recorded in transmission mode using Thermo Nicolet Avatar 370 spectrometer. The samples of the analysed compounds were mixed with potassium bromide and formed into pellets using hydraulic press. Analytically relevant absorption maxima (ν_{max}, cm^{-1}) are reported.

Melting points were determined in open capillary glass tubes using a melting point apparatus produced by Warsztat Elektromechaniczny J. Kawałkowski (Warszawa). As all the studied samples underwent degradation, the starting point was recorded when the sample started changing its colour, whereas the ending point when there was no further change in the samples' colour.

Elemental analyses were performed using CHNS Elementar Vario EL III apparatus. Each elemental composition is reported as an average of two analyses.

Microbiological studies involved eight fungal strains. *A. niger* LOCK 0440, *A. terreus* LOCK 64, *F. oxysporum* E95 and *C. albicans* LOCK 0001 were purchased from the Institute of Fermentation Technology and Microbiology, Technical University of Łódź, while *F. solani* F-454, and *P. ochrochloron* F-337 were obtained from the Czech Collection of Microorganism (CCM). *F. dimerum* DAE-1001, originally isolated from the surface of carrot seeds, was taken from the collection of microorganisms of the Department of Analytical and Ecological Chemistry, Faculty of Chemistry, Opole University. *C. tenuis* DSM-26797 were purchased from Leibniz-Institute DSMZ-German Collection of Microorganisms and Cell Cultures. *Aspergillus* and *Penicillium* strains were routinely maintained in potato dextrose agar while *Fusarium* strains grew in Czapek agar medium. Yeast *C. tenuis* and *C. albicans* were maintained in standard YPD agar medium. In case of filamentous fungi, the spore suspensions used as inocula were prepared by washing the surface of 10- to 14-day-old cultures with sterile 0.05% Tween solution in distilled (Milipore Q) water. These inocula were then quantified using a Thom's chamber. In case of yeast, one-day-old cultures were used directly for inoculation.



R = H (**1**), R = 4-F (**2**), R = 5-F (**3**),

R = 6-F (**4**), R = 7-F (**5**), R = 7-CHO (**6**)

Fig.1. Compounds under study with atom numbering scheme.

2. ^{1}H and ^{13}C NMR Spectra of Novel Compounds

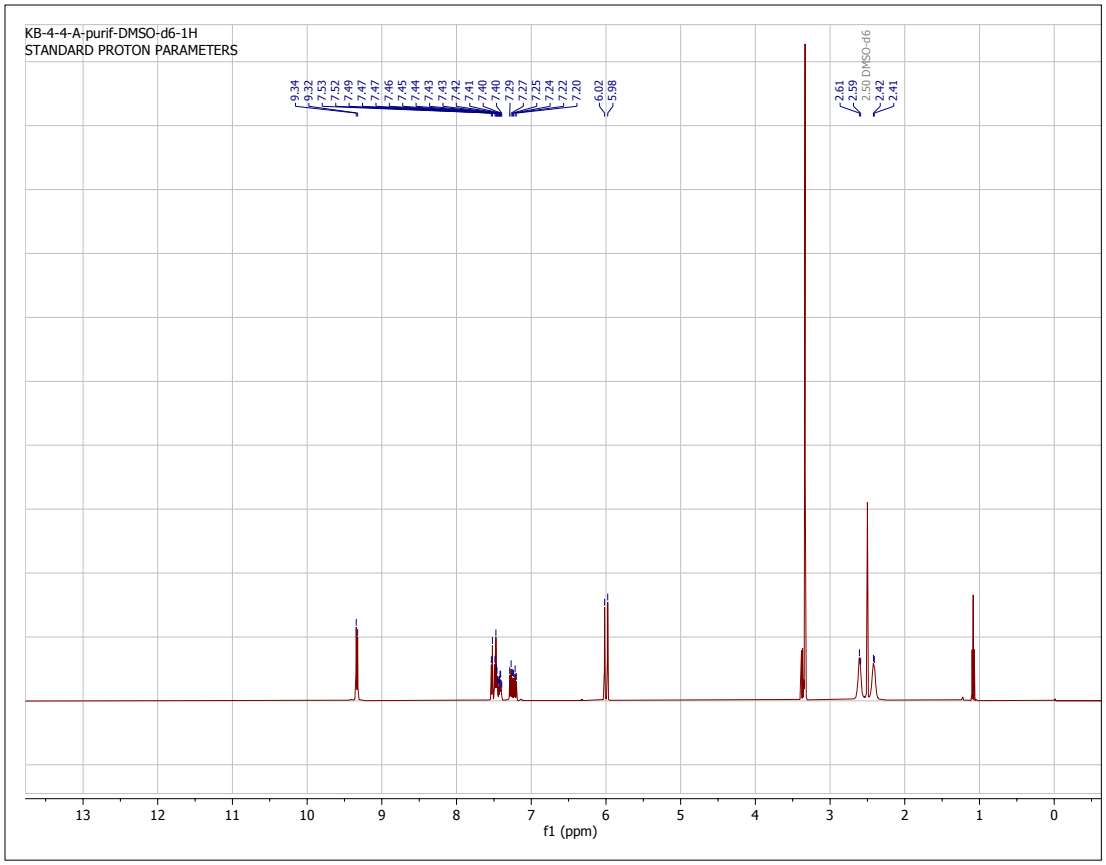


Fig. 2. ^{1}H NMR spectrum of **2**.

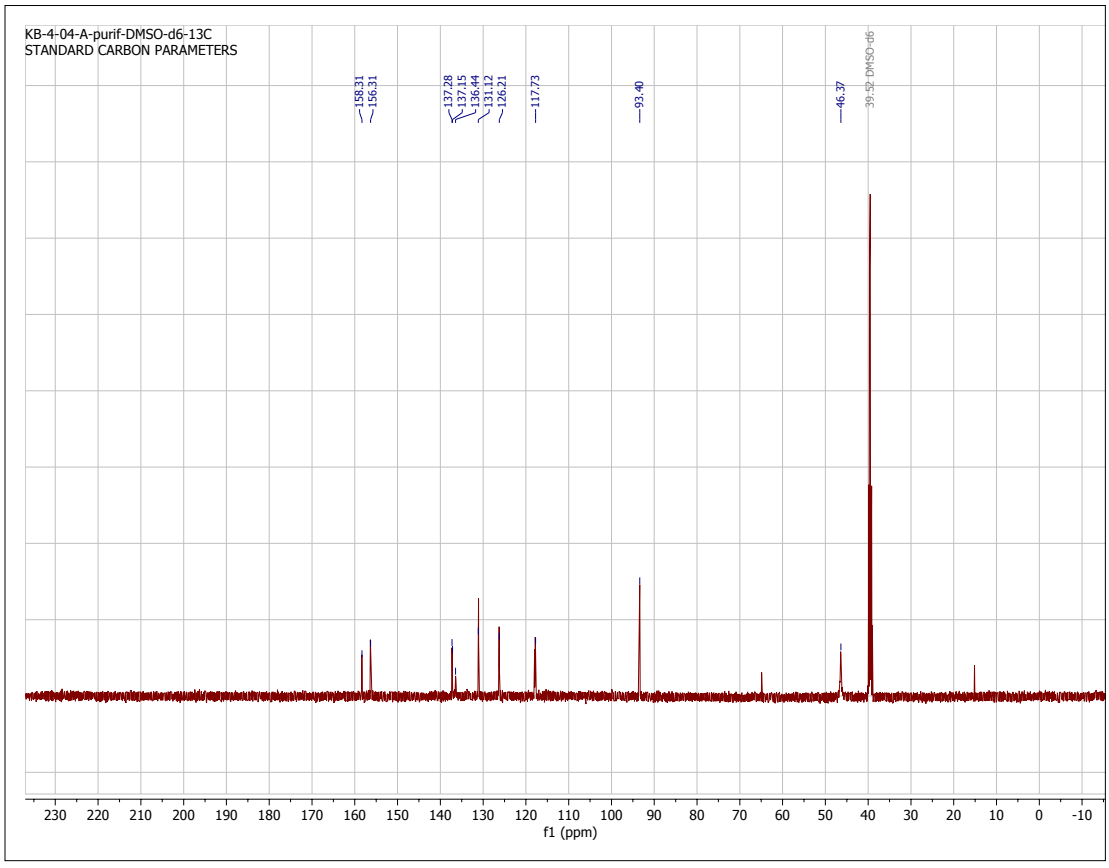


Fig. 3. ^{13}C NMR spectrum of **2**.

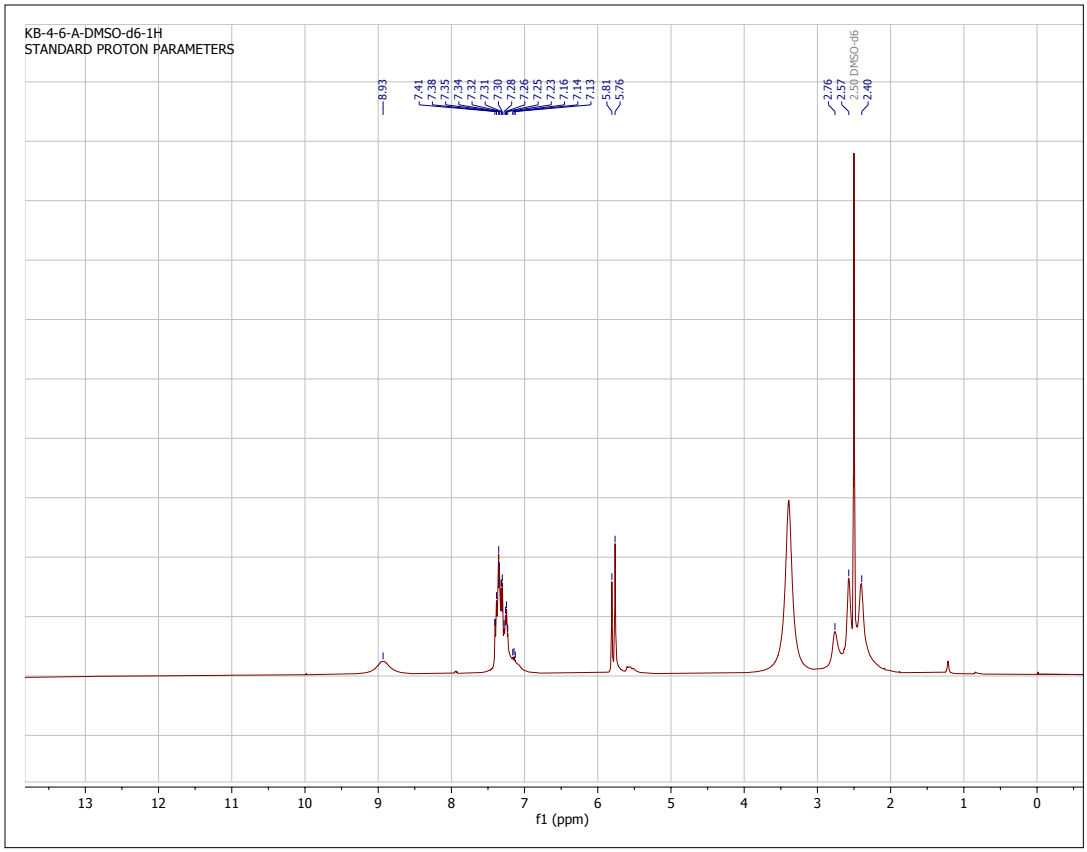


Fig. 4. ^{1}H NMR spectrum of **4**.

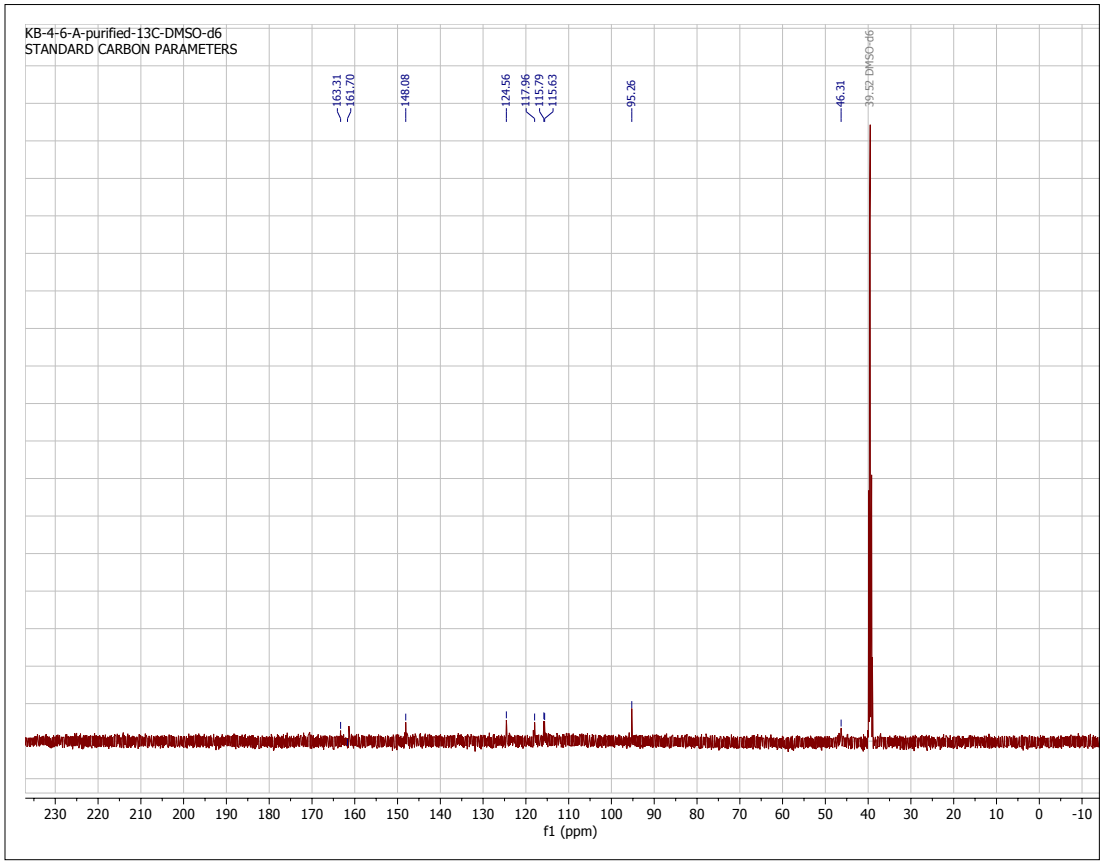


Fig. 5. ^{13}C NMR spectrum of **4**.

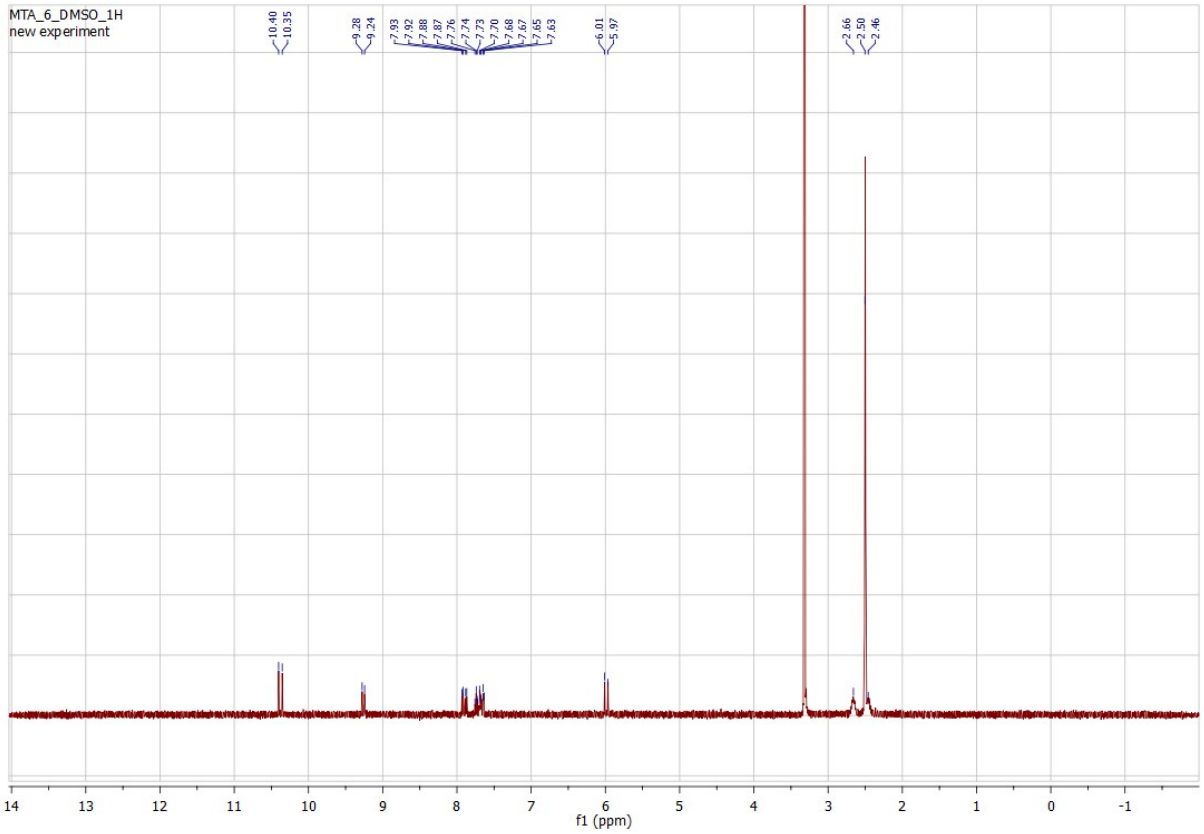


Fig. 6. ^{1}H NMR spectrum of **6**.

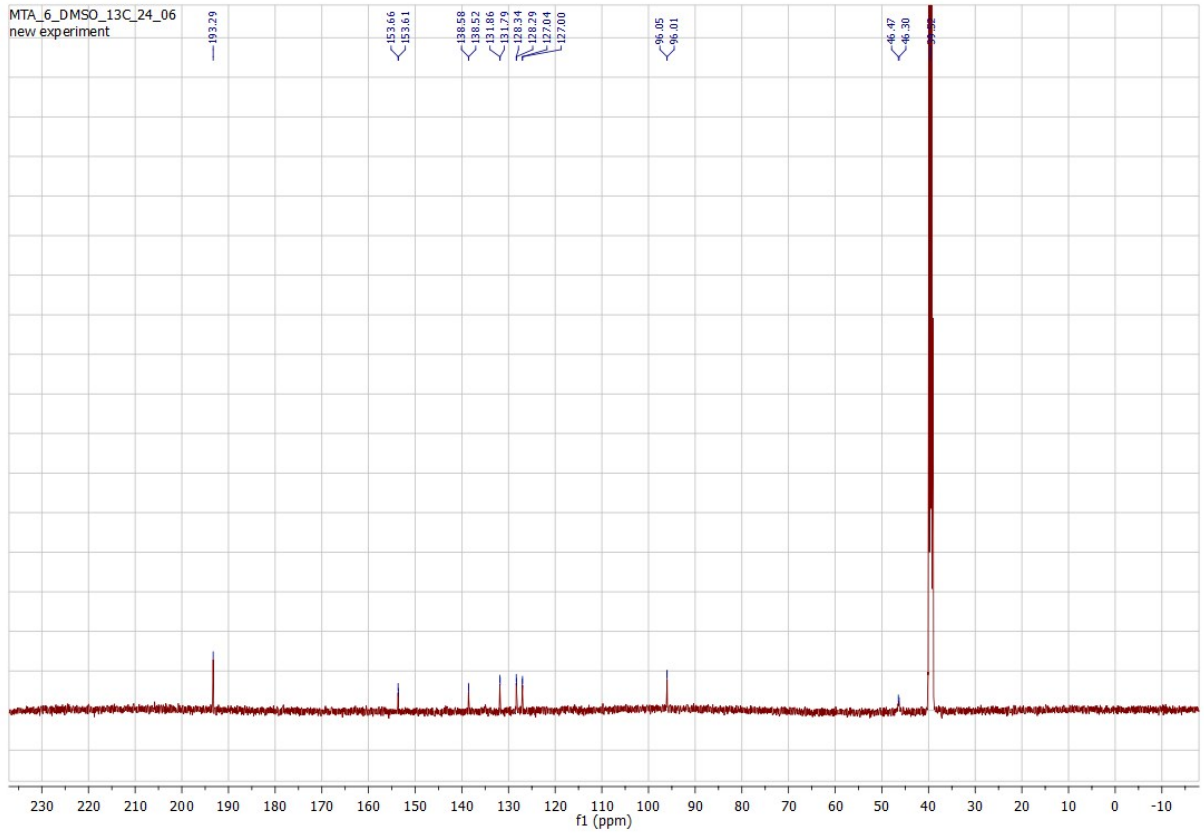
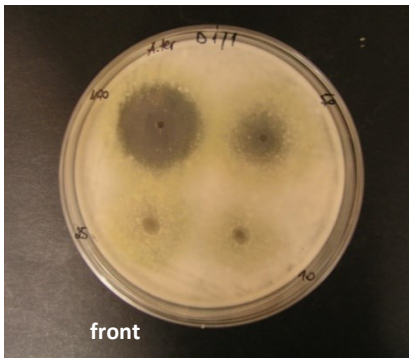
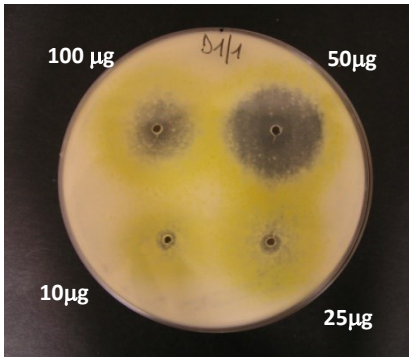


Fig. 6. ^{13}C NMR spectrum of **6**.

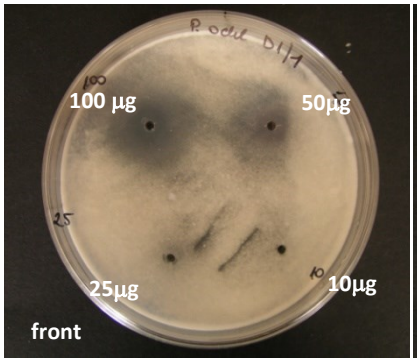
3. Pictures of chosen results of diffusion agar method

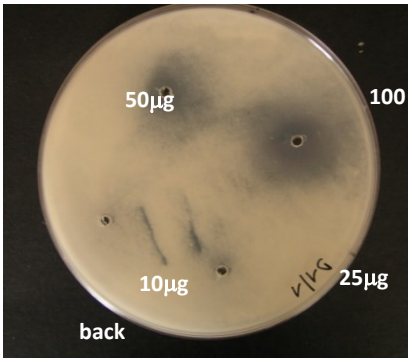
a) *Aspergillusterreus*, compound **2**, 100 µg, 50 µg, 25 µg, 10 µg



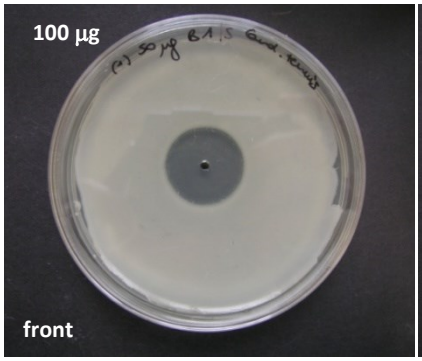


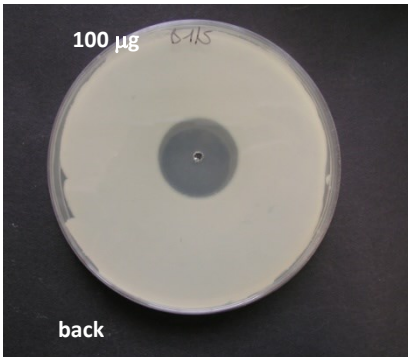
b) *Penicillium ochrochloron*, compound **2**, 100 µg, 50 µg, 25 µg, 10 µg



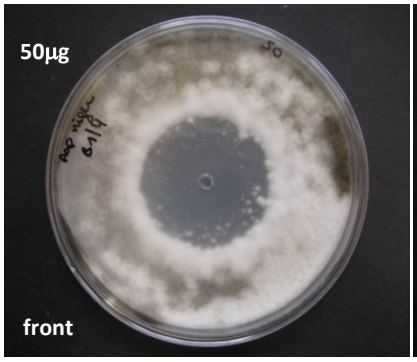


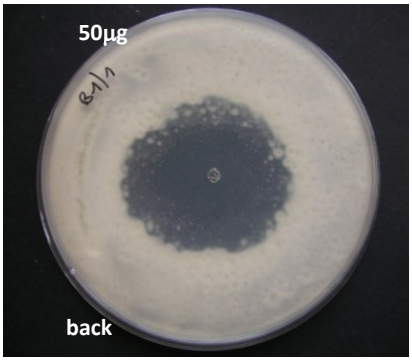
c) *Candida tenuis,* compound **3**, 50 µg





d) *Aspergillus niger,* compound **3**, 50 µg





e) *Fusarium solani,* compound **3**, 100 µg, 50 µg, 25 µg