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Evaluation of *p*-benzoquinones derivatives as post-emergent plant growth inhibitor

Avaliação de derivados *p*-benzoquinonas como inibidores pós-emergentes do crescimento vegetal

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ABSTRACT

Eight *p*-benzoquinones derivatives (**1-8**) were synthesized and evaluated as photosynthesis and plant growth (dry biomass) inhibitors through *semi in vivo* and *in vivo* assay. The photosynthetic parameters provided by the JIP-test were based on the major steps of the photosynthetic process: photon absorption (ABS), energy capture (TR), electron transport (ET) and reduction of photosystem II (PS II) final acceptors (RE). Compounds **6**, **7** and **8** decresead the $PI_{(abs)}$ parameter by 82, 75, 42% and incresead the ET_0/CS_0 parameter by 37, 20 and 25%, respectively. These results suggested that **6-8** inhibit the electron transport chain at PS II in both *semi in vivo* and *in vivo* assays. Futhermore, compounds **6** and **7** reduced the plant growth by 52 and 77%, respectively. Therefore, the derivatives of *p*-benzoquinone not only demonstrated appreciable activity as inhibitors of photosynthesis by acting on the electron transport chain on the acceptor side of PS II, but also inhibit the plant growth.

Keywords: fluorescence of chlorophyll *a*, herbicide, JIP-test, photosystem II, plant growth.

RESUMO

Oito derivados de *p*-benzoquinonas (**1-8**) foram sintetizados e avaliados como inibidores da fotossíntese e do crescimento de plantas (biomassa seca) através de ensaios *semi-in vivo* e *in vivo*. Os parâmetros fotossintéticos fornecidos pelo JIP-teste foram baseados nas principais etapas do processo fotossintético: absorção de fótons (ABS), captura de energia (TR), transporte de elétrons (ET) e redução dos receptores finais do fotossistema II (FS II) (RE). Os compostos **6**, **7** e **8** reduzem o parâmetro $PI_{(abs)}$ em 82, 75, 42% e aumentam o parâmetro ET_0/CS_0 em 37, 20 e 25%, respectivamente. Estes resultados sugeriram que **6-8** inibem a cadeia transportadora de elétrons do FS II nos ensaios *semi in vivo* e *in vivo*. Além disso, os compostos **6** e **7** reduziram o crescimento das plantas em 52 e 77%, respectivamente. Portanto, os derivados da *p*-benzoquinona não apenas demonstraram apreciável atividade como inibidores da fotossíntese, atuando na cadeia de transporte de elétrons no lado aceitador do PS II, mas também inibem o crescimento vegetal.

Palavras chave: Clorofila *a*, herbicida, JIP-teste, fotossistema II, crescimento de planta.

1. INTRODUCTION

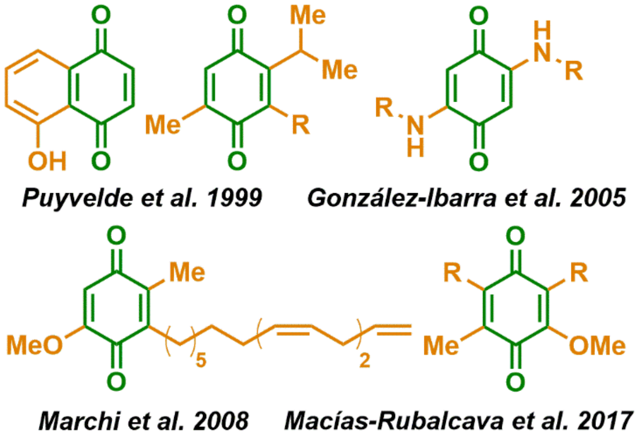
The demand for food has been increased concomitant to the rapid growth in the world population, therefore the control of weeds is essential, which are directly responsible for the reduction of crop production, due the competition for nutrients, water and space (de Carvalho et al., 2016; Sampaio et al., 2016). Herbicides represent a group of pesticide commonly used for the crops, and its frequently application in high doses, leads to a number of problems, such as the emergence of resistant weed species, soil and water contamination, damage the crops and more importantly impacts on human health (Gianessi, 2013; Varejão et al., 2014; Vítek et al., 2017). In this scenarion, it is necessary to develop such new weed control substances that must be efficient, selective, active in small doses and safer for crop, environment and humans.

Photosynthesis is one of the fundamental physiological processes for the plant development and it has been widely studied to evaluate plant performance as well as its behaviour in stress environments such as high and low temperature, water deficit and flooding, herbicide action and others. OJIP test is a method that has been widely applied to detect the effects of abiotic stresses caused by the photosynthetic process of higher plants (Je et al., 2018; Rapacz et al., 2015; Urban et al., 2017; Xiang et al., 2013; Zushi and Matsuzoe, 2017). This method is based on the quantification of chlorophyll *a* (Chl *a*) fluorescence emission, being able to provide large numbers of information and accurate data of the functioning of the photosynthetic apparatus, especially the protein complex of photosystem II (PS II). Furthermore, this is a fast, simple and non-invasive technique, which can also be used for the *in vivo* assays (Baker, 2008).

Among the many applications of plant performance studies in a stress environment, the Chl *a* fluorescence technique has been employed as a tool for the development of new substances with photosynthesis inhibitory action (King-Díaz, B. Soares, M. , G. F. da Silva, M. , Lotina-Hennsen, B. and Veiga, 2014; Mendes et al., 2019; Veiga et al., 2013). The effects of photosynthetic apparatus on a number of compounds as well as synthetic compounds has been studied. The investigation showed that many of them are competing with partially reduced plastoquinone B for the site in the D1 protein, thus interrupting the electron flow between the photosystems (Dan Hess, 2000; Stirbet and Govindjee, 2011).

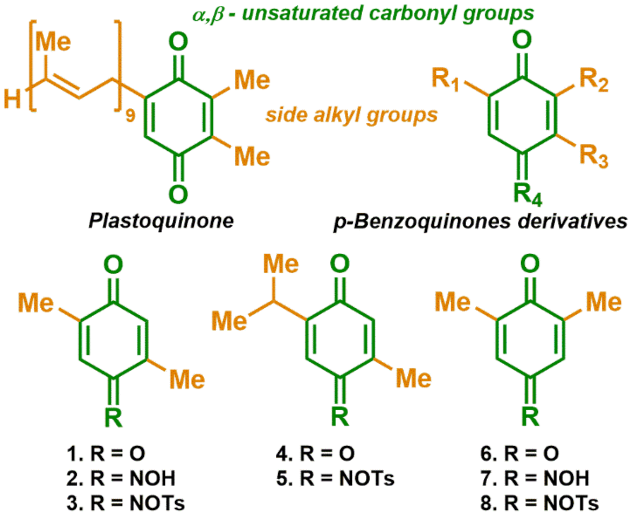
Quinones are a class of organic compounds consisting of a six-carbon cyclic dione containing two double bonds, which are the general constituents of the many biologically relevant molecules (Abraham et al., 2011; Lindsey et al., 2004; Molfetta et al., 2005; Sagnou et al., 2009; Yezerski et al., 2007) such as plastoquinone and phylloquinone that are electron acceptors in the electron transport chains during the process of photosynthesis. Due to the structural similarity of *p*-benzoquinones derivatives to plastoquinone that has a system of two α,β-unsaturated carbonyl groups and a side alkyl groups, it is interesting to study this class of compounds as inhibitors of photosynthesis. Puyvelde *et al.* showed that the 3-hydroxythymoquinone inhibits the growth and germination of the grass weed *Agrostis capillaris* down to 250 μM (Van Puyvelde et al., 1999). González-Ibarra *et al*. demonstrated the herbicidal activity of 2,5-diamino-*p*-benzoquinone derivatives on photosystem I (PS I) and PS II (González-Ibarra et al., 2005). Marchi *et al*. described the activity of sorgoleone, a natural product isolated from root exudates of *Sorghum bicolor,* as an inhibitor of PS II (Marchi et al., 2008). Recently, Macías-Rubalcava *et al*. investigated the mechanism of the photosynthesis light reactions of the secondary metabolites produced by the endophytic fungus *Xylaria feejeensis* strain SM3e-1b, isolated from *Sapium macrocarpum* (**Figure 1**) (Macías-Rubalcava et al., 2017).

Figure 1. Natural and synthetic molecules containing *p*-benzoquinone scaffold that are herbicidal active.



Although the herbicidal activity of benzoquinones derivatives has been described in literature, most of these compounds have a complex molecular structure or high molecular weight that make it difficult to use these substances for crop protection. Thus, our aim in this work is to evaluate *p*-benzoquinones and their nitrogen derivatives as inhibitors of photosynthesis, plant growth and seed germination (**Figure 2**). The compounds **1-8** have an alkyl groups on different positions at *p*-benzoquinone motif and has a low molecular weight that might facilitate their access to the site of action, and can be synthetized in few steps using an accessible synthetic approach (Uliana et al., 2014).

Figure 2. Plastoquinone and *p*-benzoquinone derivatives **1-8**.



2. MATERIALS AND METHODS

2.1 P-BENZOQUINONE DERIVATIVES

Compounds **1-8** were synthetized as described by Uliana *et al.* (Uliana et al., 2014, 2008). Stock solutions of **1-8** were prepared using dimethyl sulfoxide (DMSO). Maximum concentration of solvent in the media was less than 1%.

2.2 CHL A FLUORESCENCE MEASUREMENT IN SPINACH LEAF DISCS

Ten spinach (*S. oreaceae)* leaf discs measuring 1 cm diameter were placed in Petri dishes containing 20 mL of modified Krebs solution: 115 mM NaCl, 5.9 mM KCl, 1.2 mM $MgCl_2$, 1.2 mM KH_2PO_4, 1.2 mM Na_2SO_4, 2.5 mM $CaCl_2$, 25 mM $NaHCO_3$ and pH was adjusted for 7.4. The Petri dishes were incubated for 12 hours at room temperature. Compounds **1-8** were added in DMSO solutions at different concentrations (100, 200 and 300 µM) for each Petri dish and incubated for 6 additional hours; then, the discs were dark adapted during 30 min. Negative and positive controls were performed using DMSO and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU), respectively. Chl *a* fluorescence was measured at room temperature with the Hansatech Fluorescence Handy PEA (Plant Efficiency Analyzer). Fluorescence photosynthetic results were obtained as Chl *a* fluorescence measurements in thylakoids, using the Biolyzer HP3 (Sampaio et al., 2018).

2.3 CHL A FLUORESCENCE DETERMINATION IN INTACT *LYCOPERSICON LYCOPERSICUM* LEAVES

Seeds of *Lycopersicon lycopersicum* were grown in 12 cm diameter pots containing 50:50 w/w soil/vermiculite and watered daily in a greenhouse at room temperature. After 15 days, the plants were selected for similar size and were manually sprayed with a solution of **1-8** (150, 200 and 300 µM) in an aqueous solution containing 0.05% v/v of Tween-20. The control group was sprayed with distilled water containing the same amount of DMSO and Tween-20 (Mendes et al., 2019). After 24, 48 and 72 hours of treatment, plants were adapted at the dark for 30 min and Chl *a* fluorescence was measured at room temperature with the Hansatech Fluorescence Handy PEA (Plant Efficiency Analyzer).

2.2.3 Measurement of JIP-test transients

The Chl *a* fluorescence transient was measured using Handy-PEA® fluorimeter (Plant Effiecient Analyze) at room temperature, employing a saturating red-light pulse (650 nm) by 2 s at 3.000 µmol $m^{-2}s^{-1}$ (Aguilar et al., 2008). Further, primary fluorescence parameters of OJIP curve were calculated based on a range of biophysical parameters, which quantify the photosynthetic apparatus through the JIP-test.

Compounds **1-8** activities (150 and 300 µM) on PS II were evaluated based on 18 photosynthetic parameters derived from the OJIP transients and the results were shown in radar charts. All calculated parameters were compared to negative control. Quantum, de-excitation, phenomenological and performance index parameters were calculated using the JIP-test and any parameter variation greater than 20% compared to control were considered significant.

The evaluated parameters were calculated and extracted by employing the software Biolyzer_HP3 (*Laboratory of Bioenergetics*). These parameters are based on the main events of the photosynthesis and associated to the PS II, which represent the activities of reaction center, phenomenological flows by cross section, quantum yields, performance index, as well as photochemical and non-photochemical de-excitation (Chen et al., 2011; Strasser et al., 2004).

2.3 DRY BIOMASS DETERMINATION

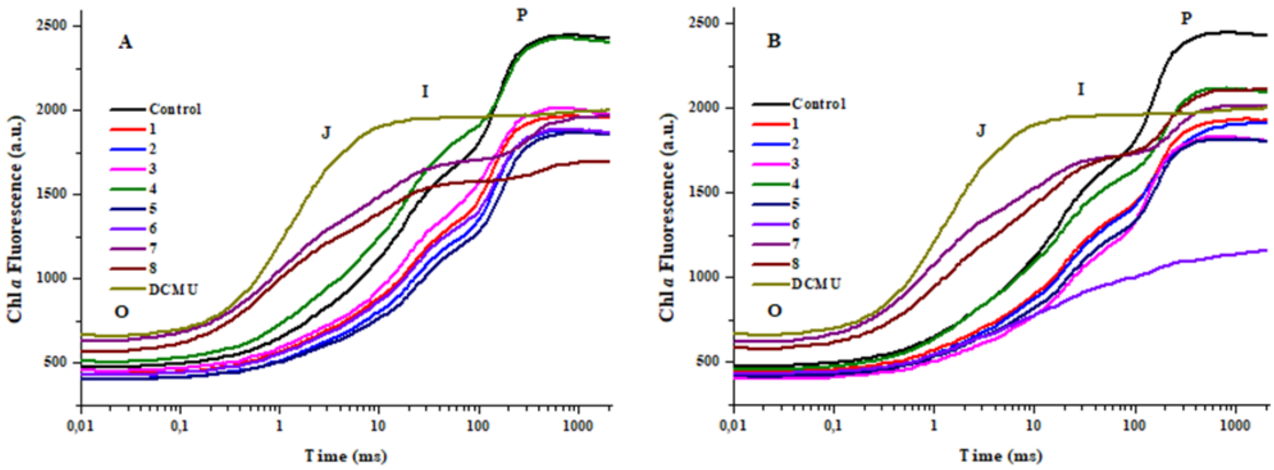
To evaluate the effect of **1-8** in *Licopersicum lycopersicum* plants growth, after 14 days, shoot dry weight (SDW in grams) were measured. SDW was determined by drying all components in an oven at 65 ºC for 20 days. Negative and positive controls were performed using DMSO and DCMU, respectively. Experiments were conducted with 3 replicates. SDW was measured using an analytical balance (Torres-Romero et al., 2008).

3. RESULTS AND DISCUSSION

3.1 CHL A FLUORESCENCE ASSAY ON SPINACH LEAF DISCS (SEMI IN VIVO)

Chl *a* fluorescence assay has been used as a tool to evaluate the effects on photosynthetic apparatus in plants when submitted to enviroment stresses, as well as to provide detailed information about the structure and function of PS II. The effects of **1-8** on PS II were evaluated through Chl *a* fluorescence induction curve (**Figure 3**).

Figure 3. Chlorophyll *a* fluorescence OJIP transient curves mesuared on spinach leaf discs of **1-8** at 150 µM (**A**) and 300 µM (**B**). The OJIP curves of the negative (DMSO) and positive (DCMU) controls are also shown.



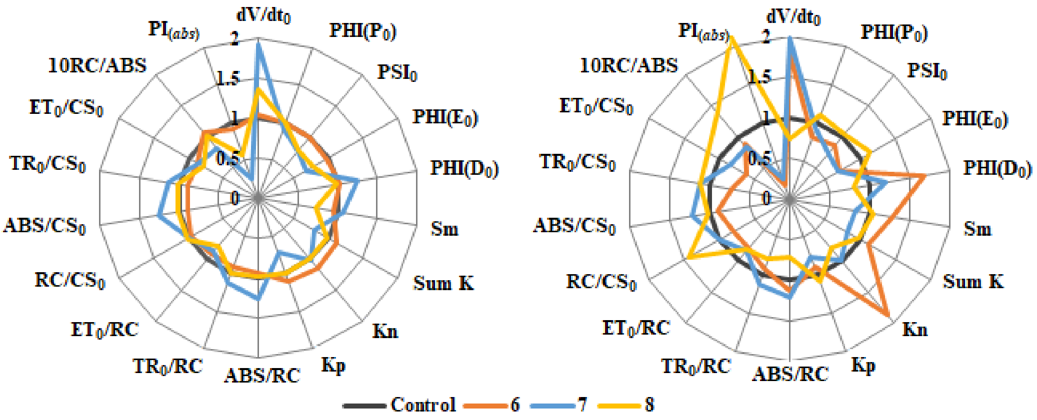
Among the tested compounds, **6-8** showed appreciable results compared to the negative control (DMSO) at 150 and 300 µM, demonstrating an electron chain blockade activity, similar to DCMU, which increased fluorescence yield in the first 2 ms of illumination (J level), converting the standard transient into an OJ curve (Morales-Flores et al., 2007).

Compound **6** at 300 µM increased F_0 intensity up to 300 ms followed by a rapid decay. This behavior is related to the electron donor side inhibition of the PS II. The appearance of a transient K-band indicates that the electron flow was blocked before the introduction of the quinones pool, maintaining an action in the center of silent reaction at the water oxidation site (Chen et al., 2016).

The OJIP polyphase curves of **7** and **8** showed significant fluorescence increasement at J level that associated with a final fluorescence intensity decreasement at I-P phase, indicated that **7** and **8** inhibit electron transport chain at PS II. In addition, the reduced quinone A (Q_A^-) accumulation may suggest an action on the electron acceptor side of PS II, as similar behavoir to the commercial herbicide DCMU (Paunov et al., 2018; Zhong et al., 2019).

The performance index ($PI_{(abs)}$) is the most sensitive parameter for plant damage detection and quantification, as it is related to three of the main photochemical processes: absorption, capture and transfer of the excitation energy (Appenroth et al., 2001; Šimić et al., 2014). Compounds **6-8** showed appreciable inhibitory activity on photosynthesis by decreasing $PI_{(abs)}$ and an increasing dV/dt_0 parameter (**Figure 4**).

Figure 4. Radar charts of the effects of **6-8** on Chl *a* fluorescence parameters calculated from the OJIP curve in spinach sheet discs at 150 µM (**A**) and 300 µM (**B**).



Compound **6** reduced the parameters $PI_{(abs)}$, ET_0/RC, ET_0/CS_0 and TR_0/CS_0 by 82, 22, 37, 28 and 12%, respectively, at 300 µM. Furthermore, the increasement of dV/dt_0, $PHI(D_0)$, Kn and Sm parameters by 80, 69, 87 and 29, respectively, that implies the energy absorbed by the system has been released as heat.

Compound **7** decresead $PI_{(abs)}$ parameter by 74% and incresead dV/dt_0 parameter by 95% at both concentrations. At 300 µM, the reduction of PSI_0, $PHI(E_0)$ and active reaction center number (10RC/ABS) parameter by 26, 31 and 20%, respectively, indicating that part of the energy trapped in the reaction centers was dissipated as heat instead of being used in quinone pool reduction.

The variation of 10RC/ABS parameter observed by **6** and **7** indicates that the RCs, which are responsible for all the redox process between the donors and acceptors of electron transport chain was reduced. Addicionally, the increasement of ABS/RC and ABS/CS_0 parameters means that part of RCs was inactivated, and thus the number of absorbed photons was consequently reduced by an excess of energy in the system (Franić et al., 2018).

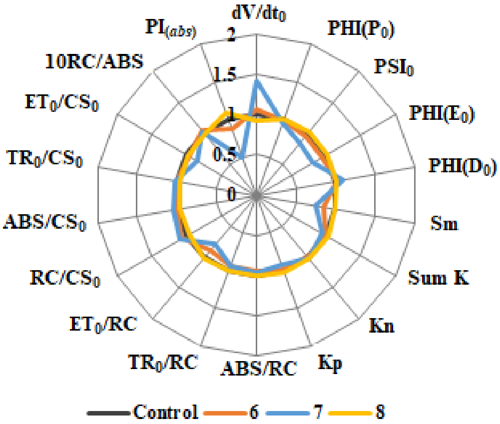
At 150 µM, compound **8** decreased $PI_{(abs)}$ parameter by 42% and incresead dV/dt_0 parameter by 37%. The parameters correlated with reaction center (RC), cross section (CS) and quantum yield (PHI) were also evaluated and the reducion of electron transport by cross section (ET_0/CS_0) by 25% and reaction center (Et_0/RC) by 22% suggests that the efficiency of electron transport beyond the Q_A

site was reduced by the compound **8**, indicating that the stress observed by the decrease of the PI$_{(abs)}$ is directly associated with electron flow blockage at the PS II acceptor side. The increase of PI$_{(abs)}$ parameter at 300 µM by **8** indicates that the stress caused to the system may be temporary and the damage is considered as reversible (Diagro et al., 2018).

3.2 *IN VIVO* ASSAYS

To evaluate the *p*-benzoquinone derivatives activity *in vivo*, compounds **6-8** were sprayed at 150 and 300 µM on *Lycopersicon lycopersicum* plants. After 24, 48 and 72 h of treatment, the Chl *a* fluorescence transients were measured and the JIP-parameters were calculated with Biolyser HP software. The results showed that the effects of **6** and **7** (300 µM) on *L. lycopersicum* were significant at 72 h. The activity of **8** was similar to negative control (**Figure 5**). The *in vivo* activity evaluation is conditioned with the plant structure, which implies the time required for compounds to reach the thylakoid, as it is necessary to overcome the natural barriers such as cell wall.

Figure 5. Radar chart of the effects of **6-8** on Chl *a* fluorescence parameters calculated from the OJIP curve on *L. lycopersicum* plants at 300 µM.



Although **6** reduced PI$_{(abs)}$ parameter by 25%, the slight variations in other parameters make it not possible to localize the compound activity on photosynthetic apparatus. Compound **7** reduced PI$_{(abs)}$ parameter by 50% and increased dV/dt$_0$ parameter by 42%. Furthermore, **7** decreased ET$_0$/RC, ET$_0$/CS, PSI$_0$ and PHI(E$_0$) parameters by 22, 15, 17 and 20%, respectively, indicating the electron flow on photosynthetic process was reduced.

The electron transport blockage is related to damages on the protein complexes responsible for redox reactions that occur at photosynthetic process. This behavior corroborates with the *semi in vivo* assay. Thus, compound **7** showed appreciable photosynthesis inhibitory activity by blocking electron transport in PS II of the *L. lycopersicum* species.

3.3 DRY BIOMASS

Dry biomass of *L. lycopersicum* plants was weighed after 15 days of treatment with **6-8** at 150 and 300 µM, in the absence of compounds (negative control) and with DCMU (positive control) (**Table 1**).

Tabel 1. Effect of **6-8** on dry biomass production estimated by measuring the dry weight of *L. lycopersicom* plants.

Treatment	**[ ]**[a]	**Dry biomass**[b]	**%**
Control	-	0.8656±0.0432	100
6	150	0.4664±0.0233	54
	300	0.4463±0.0223	52
7	150	0.8234±0.0411	95
	300	0.2030±0.0101	23
8	150	0.8959±0.0447	104
	300	0.8563±0.0428	99

[a] (µM). [b] (grams). data were expressed as means ± S.DE (standard errors).

Compounds **6** and **7** at 150 µM inhibited plant growth by 46 and 5%, respectively. At 450 µM, the best result was achieved for **7**, reducing the dry biomass by 77%. Compound **8** does not demonstrate any activity on plant growth.

Plant growth is directily related to the photosynthesis process and the CO_2 assimilation capacity of the plants. The plant growth inhibition observed through dry biomass reduction indicates a decrease of photosynthetic and CO_2 fixation activity, suggesting that the ATP and NADPH production were also reduced, promoting an inadequate plant development (Bacarin et al., 2010).

The results of the dry biomass assay corroborate the PS II inhibitor activities demonstrated by the Chl *a* fluorescence assay, indicating that **7** has an action as a post-emergent herbicide blocking the electron transfer process at PS II in the plant.

5. CONCLUSION

This work shows the evaluation of *p*-benzoquinone derivatives (**1-8**) as photosynthesis and plant growth inhibitors. The best result was obtained for 4-(hydroxyimino)-2,6-dimethylcyclohexa-2,5-dien-1-one (**7**), which inactivated the RC on PSII, blocking the electron flow from reduced quinone A to quinone B. Compound **7** acts as a post-emergent herbicide since the dry biomass was reduced by 77% at 300 μM, corroborating the fluorescence results.

The 2,6 dissubstituted p-benzoquinones (**6-8**) showed better results than 2,5 dissubstituted derivatives (**1-5**), indicating that the presence of alkyl groups at these positions is important for the biological activity. In addition, the presence of electron withdrawing groups at the carbonyl group also increases the herbicide activity. The optimization of these features is a future goal of our group in further development of new herbicide prototypes.

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