Supplementary material

The need to change the approach to the safe use of herbicides by developing chiral and environmentally friendly formulations: a series of enantioselective (R)- and (S)-phenylethylammonium chloroacetates

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1. Synthesis of QASs

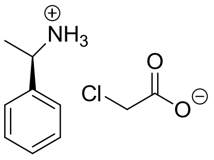
General: (*R*)-(+)- and (*S*)-(-)-1-phenylethylammonium chloro-, dichloro- and trichloroacetates were synthesized in the reaction of the corresponding chloro-, dichloro- and trichloroacetic acids with 10% excess of (*R*)-(+)- or (*S*)-(-)-1-phenylethylamine without solvent. In case of chloroacetates, the reactions were performed at room temperature, whereas in case of di- and trichloroacetates, the reactions were carried out in flasks immersed in a cooling ice-water bath. After the reaction was completed, the excess of amine was evaporated with a rotary vacuum evaporator. (*R*)-(+)- and (*S*)-(-)-1-Phenylethylammonium sulfates [(*R)*-SO_4, (*S)*-SO_4] were synthesized in the reaction of H_2SO_4 (aq. 25%) with (*R*)-(+)- or (*S*)-(-)-1-phenylethylamine in a 1:2 molar ratio without solvent.[1] The reactions were carried out at low temperature using a cooling ice-water bath, collected solids were dried and subjected to further analysis. Diisopropylammonium sulfate $(i\text{-}Pr_2NH^+)_2SO_4$ (DIPA-SO_4) was prepared in the reaction performed in chloroform according to the procedure used in the literature for tris(diisopropylammonium) sulfate-hydrogensulfate $[(i\text{-}Pr_2NH^+)_3(SO_4^{2-})(HSO_4^-)$ except that the amine and concentrated (95 %) sulfuric acid were used in a 2:1 molar ratio instead of 3:2 as in the original procedure.[2] A small amount of the sulfate-hydrogensulfate was detected in the crude reaction mixture (MS: m/z = 500.3039). Crystallization of the crude diisopropylammonium sulfate (DIPA-SO_4) was carried out in methanol instead of water[2] to avoid hydrolysis of the product to the sulfate-hydrogensulfate. The structure of DIPA-SO_4 was clearly confirmed by X-ray analysis (see below). Similar protocol for the DIPA-SO_4 synthesis, however, without use of any solvent, was performed by Reiß and Engel.[3]

Optical rotation values were measured in 100 mm cell on Perkin Elmer 241 MC under Na lamp radiation in MeOH. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 200, AV 500 spectrometers in $CDCl_3$, MeOD or D_2O with chemical shifts (δ) given in ppm relative to TMS as an internal standard. The low resolution FAB(+) and FAB(-) mass spectra (LSI, Cs^+, 13 keV) of pure compounds were obtained using a Finnigan Mat 95 spectrometer. High-resolution mass spectrometry (HRMS) measurements were performed using Finnigan Mat 95 and Synapt G2-Si mass spectrometer (Waters) equipped with an ESI source and quadrupole-Time-of-Flight mass analyser. The mass spectrometer was operated in the positive and negative ion detection modes. The measurement was performed with capillary voltage set to 2.7 kV and sampling cone to 20 V. The source temperature was 110 °C. The results of the measurements were processed using the MassLynx 4.1 software (Waters) incorporated with the instrument. Melting points were measured using Boetius apparatus. Elemental analysis was determined with an EuroVector analizator model 301.

[1] J. Cihelka, D. Havlíček, R. Gyepes, I. Němec, Z. Koleva, S-(−)-1-phenyl ethyl ammonium(1+) sulphate and S-(−)-1-phenyl ethyl ammonium(1+) hydrogen phosphate 2.5 hydrate, preparation and characterization of crystallographic, optical and dielectric properties, J. Mol. Struct., 2010, 980 (1-3), 31-38. DOI: 10.1016/j.molstruc.2010.06.033

[2] G. Sh. Mohammadnezhad, M. M. Amini, H. R. Khavasi, S. W. Ng, Tris(diiso-propyl-ammonium) hydrogensulfate sulfate, *Acta Cryst E*, 2008, 64 (8), 1564. DOI: 10.1107/S160053680802237X

[3] G. J. Reiß, J. S. Engel, Bis(diisopropylammonium) sulfate, Acta Cryst E, 2004, 60 (6), 985-987. DOI: 10.1107/S1600536804010645



(R)-MCA

(R)-(+)*-1-Phenylethylammonium chloroacetate** ((R)*-MCA**) m.p. 78-80 °C; $[\alpha]_{25}^{D}$= + 6.9 (1, MeOH); [1]H NMR (200 MHz, $CDCl_3$) δ (ppm) = 1.55 (d, 3H, J = 6.0 Hz, CH_3), 3.57 (d, 2H, J = 2.0 Hz, CH_2Cl), 4.24 (q, 1H, J = 8.0 Hz, CH), 7.29-7.41 (m, 5H, C_6H_5), 8.04 (br s, 3H, NH_3^+); [13]C NMR (126 MHz, $CDCl_3$) δ (ppm) = 21.08 (s, CH_3), 44.30 (s, CH_2), 51.18 (s, CH), 126.62 (s, 2 x C_{Ar}), 128.67 (s, C_{Ar}), 129.00 (s, 2 x C_{Ar}), 138.86 (s, C_{Ar}), 173.20 (s, COO^-); HRMS [TOF ES-] for $ClCH_2COO^-$, Calcd for $C_2H_2ClO_2$: 92.9743, Found: 92.9743; MS-FAB(-): m/z (%) = 93, 95 ($ClCH_2COO^-$, $^{35}Cl/^{37}Cl$, 30, 10); HRMS [TOF ES+] for $C_6H_5CH(CH_3)NH_3^+$, Calcd for $C_8H_{12}N$: 122.0970, Found: 122.0969; MS-FAB (+): m/z (%) = 122 [$C_6H_5CH(CH_3)NH_3^+$, 100]; Anal. Calcd for $C_{10}H_{14}ClNO_2$: C, 55.69; H, 6.54; N, 6.49; Cl, 16.44 Found: C, 55.72; H, 6.60; N, 6.51; Cl, 16.21.

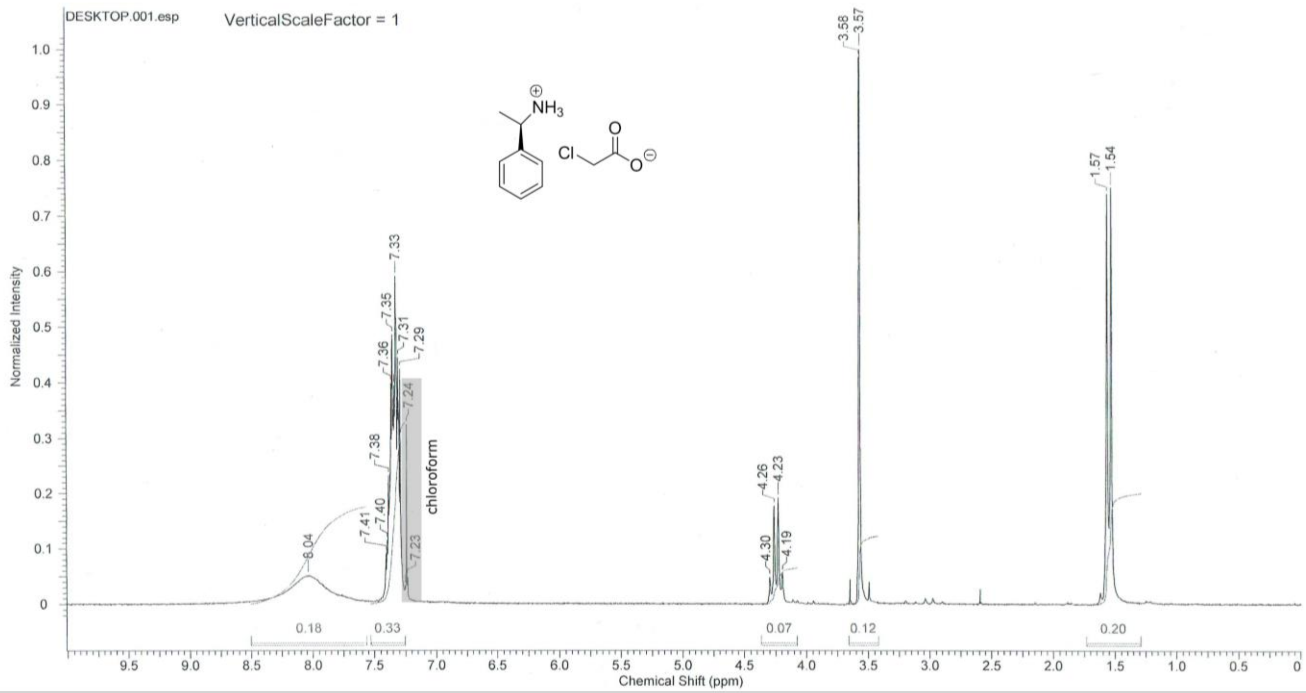


*Figure S1 [1]H NMR spectrum of **(R)-MCA**.*

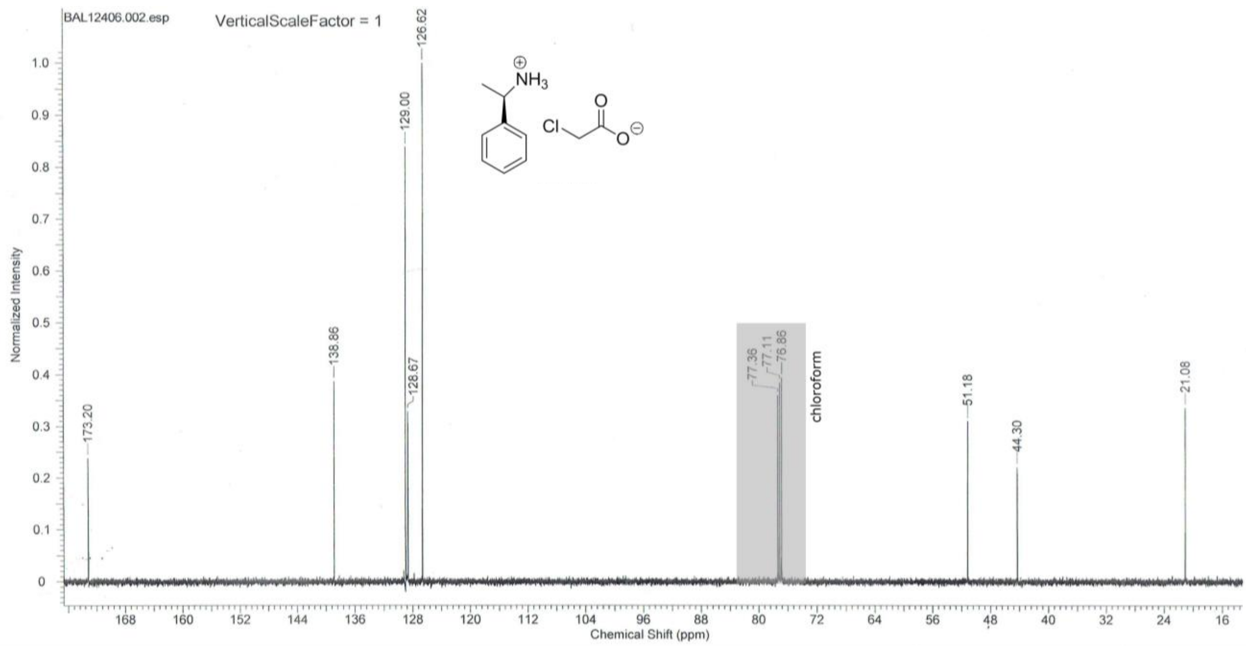
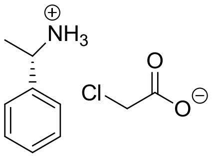


*Figure S2 [13]C NMR spectrum of **(R)-MCA**.*



***(S)*-MCA**

(S)*-(-)-1-Phenylethylammonium chloroacetate** ((S)*-MCA**) oil; ; $[\alpha]_{25}^{D}$= - 6.6 (1.7, MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 1.55 (d, 3H, J = 6.0 Hz, CH_3), 3.57 (s, 2H, CH_2Cl), 4.24 (q, 1H, J = 8.0 Hz, CH), 7.25-7.41 (m, 5H, C_6H_5), 7.76 (br s, 3H, NH_3^+); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 21.07 (s, CH_3), 44.31 (s, CH_2), 51.18 (s, CH), 126.65 (s, 2 x C_{Ar}), 128.67 (s, C_{Ar}), 129.00 (s, 2 x C_{Ar}), 138.86 (s, C_{Ar}), 173.19 (s, COO^-); MS-FAB (-): m/z (%) = 93, 95 ($ClCH_2COO^-$, $^{35}Cl/^{37}Cl$, 20, 7); MS-FAB (+): m/z (%) = 122 [$C_6H_5CH(CH_3)NH_3^+$, 100]; Anal. Calcd for $C_{10}H_{14}ClNO_2$: C, 55.69; H, 6.54; N, 6.49; Cl, 16.44 Found: C, 55.77; H, 6.62; N, 6.54; Cl, 16.20.

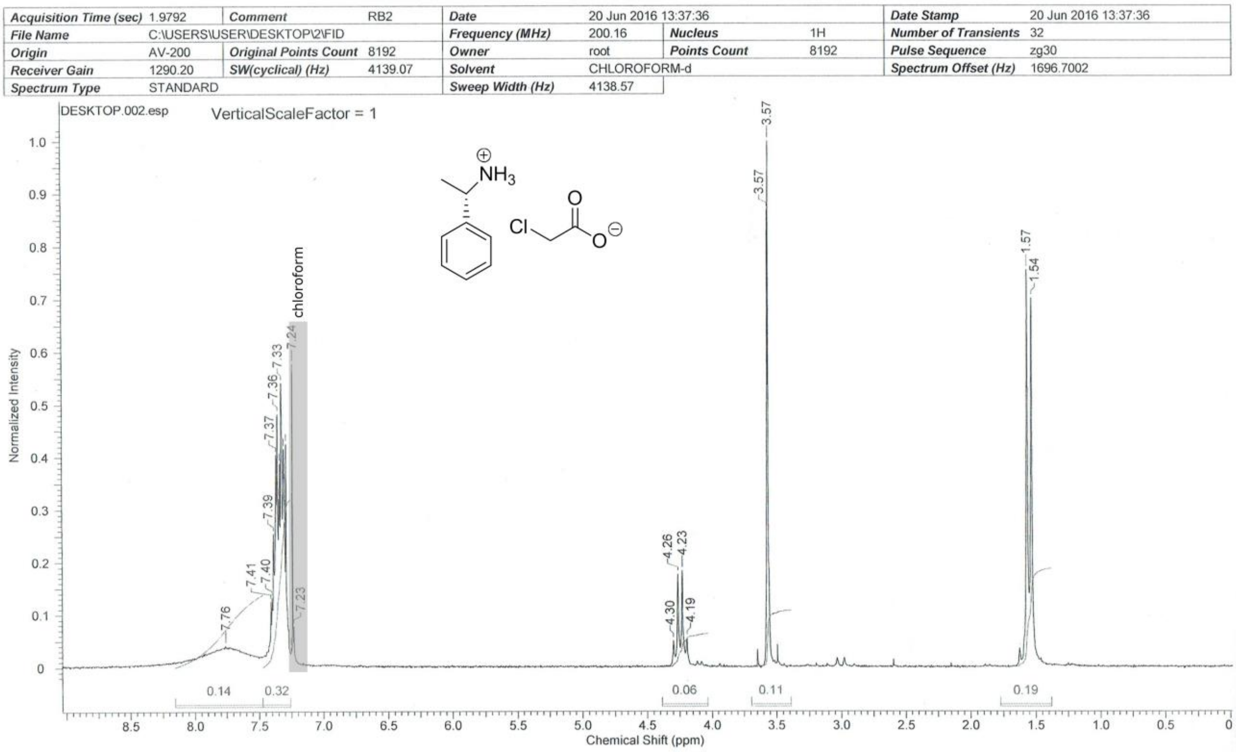


*Figure S3 ^{1}H NMR spectrum of **(S)-MCA**.*

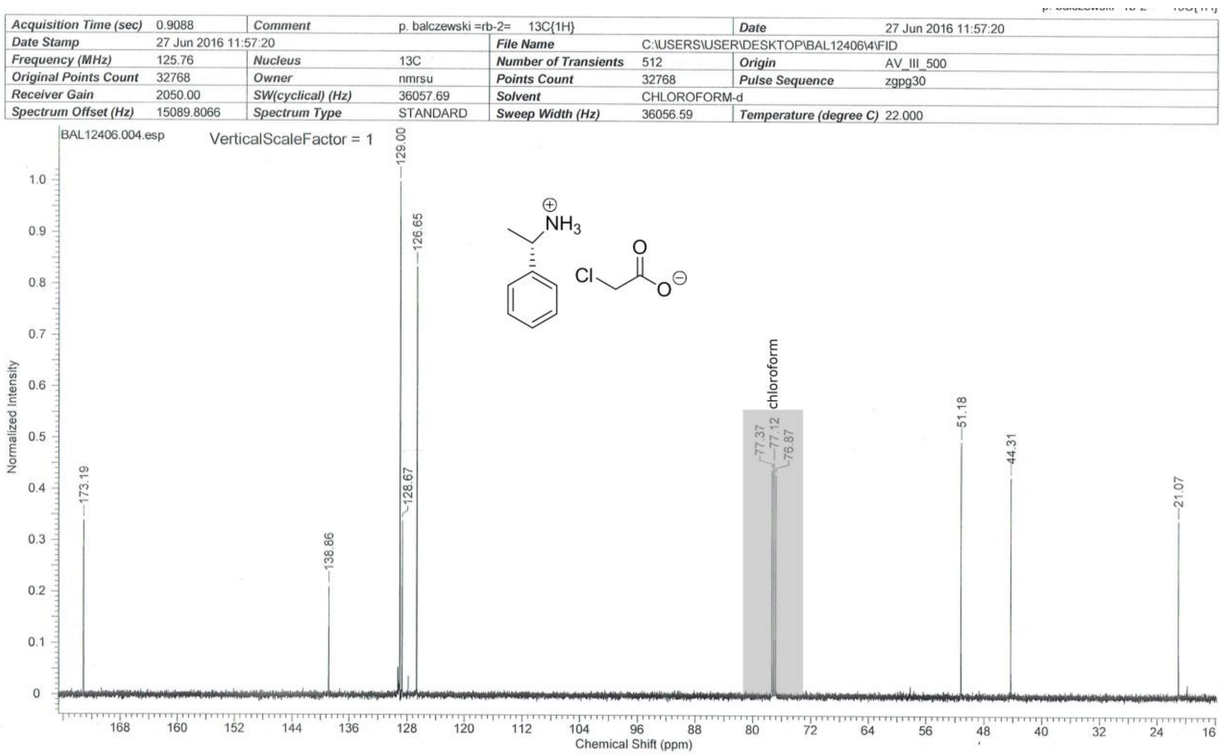
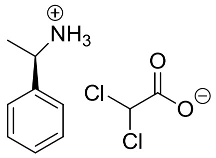


*Figure S4 ^{13}C NMR spectrum of **(S)-MCA**.*



(R)-DCA

(R)-(+)*-1-Phenylethylammonium dichloroacetate** ((R***)-**DCA**) m.p. 105-106 °C; ; $[\alpha]_{25}^{D}$= + 3.3 (1, MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 1.54 (d, 3H, J = 6.0 Hz, CH_3), 4.24 (q, 1H, J = 6.0 Hz, CH), 5.48 (s, 1H, Cl_2CH), 7.25-7.37 (m, 5H, C_6H_5); ^{13}C NMR (126 MHz, D_2O) δ (ppm) = 19.57 (s, CH_3), 50.89 (s, CH), 68.40 (s, Cl_2CH), 126.40 (s, 2 x C_{Ar}), 128.97 (s, C_{Ar}), 129.17 (s, C_{Ar}), 129.39 (s, C_{Ar}), 138.26 (s, C_{Ar}), 170.78 (s, COO^-); MS-FAB (-): m/z (%) = 93, 95 ($ClCH_2COO^-$, $^{35}Cl/^{37}Cl$, 20, 7); MS-FAB (+): m/z (%) = 122 [$C_6H_5CH(CH_3)NH_3^+$, 100]; Anal. Calcd for $C_{10}H_{13}Cl_2NO_2$: C, 48.02; H, 5.24; N, 5.60; Cl, 28.35 Found: C, 47.91; H, 5.47; N, 5.42; Cl, 28.34.

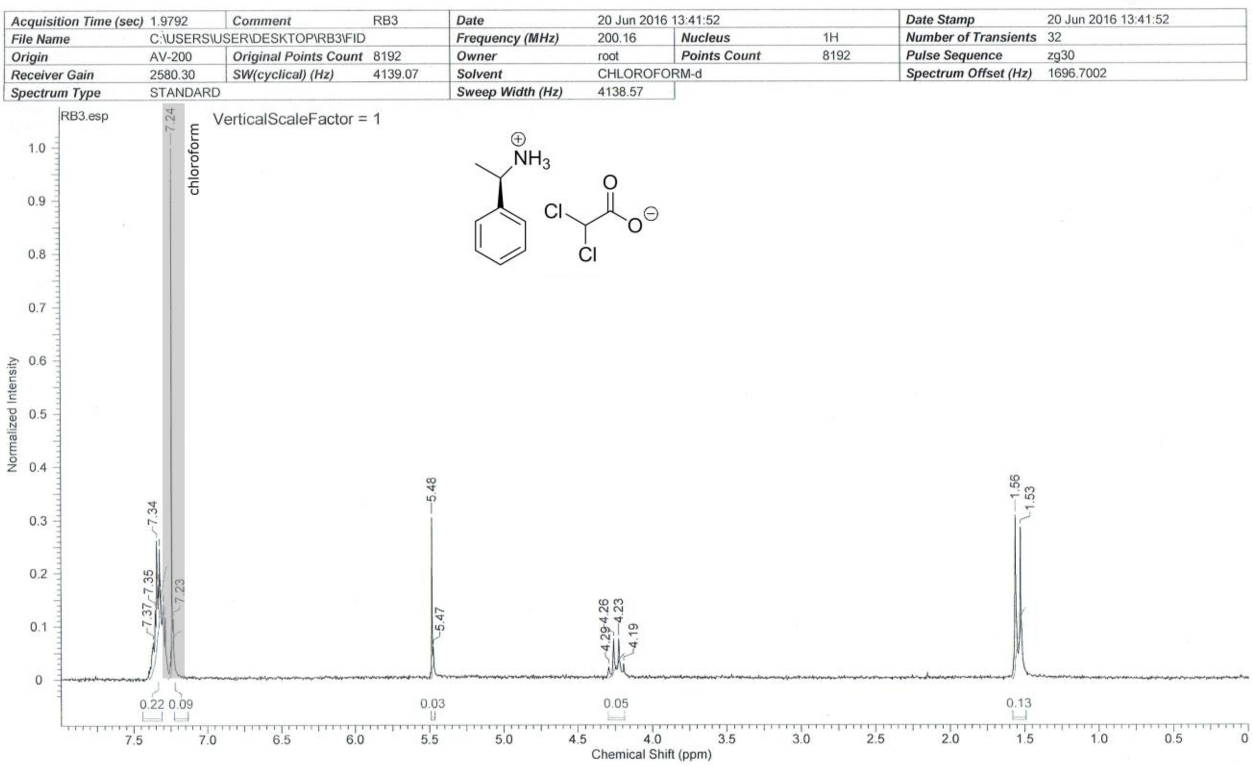


Figure S5 ^{1}H NMR spectrum of ***(R)-DCA***.

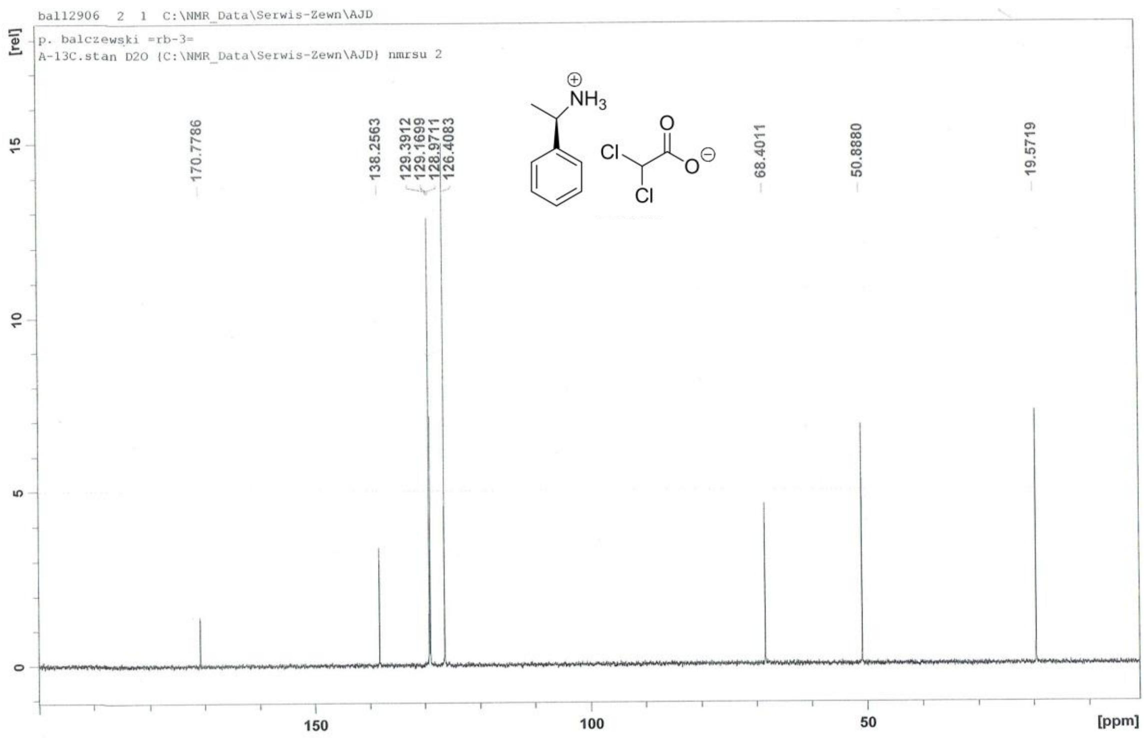
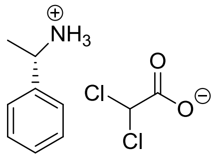


Figure S6 ^{13}C NMR spectrum of ***(R)-DCA***.



***(S)*-DCA**

(S)-(-)*-1-Phenylethylammonium dichloroacetate** ((S)*-DCA**) m.p. 104-105 °C; ; $[\alpha]^{D}_{25}$= - 3.2 (1, MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 1.57 (d, 3H, J = 8.0 Hz, CH_3), 4.26 (q, 1H, J = 6.0 Hz, CH), 5.49 (s, 1H, Cl_2CH), 7.25-7.36 (m, 5H, C_6H_5); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 21.38 (s, CH_3), 51.53 (s, CH), 68.84 (s, Cl_2CH), 126.56 (s, 2 x C_{Ar}), 128.65 (s, C_{Ar}), 129.04 (s, 2 x C_{Ar}), 139.28 (s, C_{Ar}), 169.74 (s, COO^-); MS-FAB (-): m/z (%) = 127, 129, 131 (Cl_2CHCOO^-, ^{35}Cl/^{37}Cl, 100, 68, 10); 255, 257, 259, 261 [2($Cl_2CH_2COO^-$) + 1, ^{35}Cl/^{37}Cl, 38, 50, 29, 6]; MS-FAB (+): m/z (%) = 122 [$C_6H_5CH(CH_3)NH_3^+$, 100]; Anal. Calcd for $C_{10}H_{13}Cl_2NO_2$: C, 48.02; H, 5.24; N, 5.60; Cl, 28.35 Found: C, 48.17; H, 5.31; N, 5.63; Cl, 28.38.

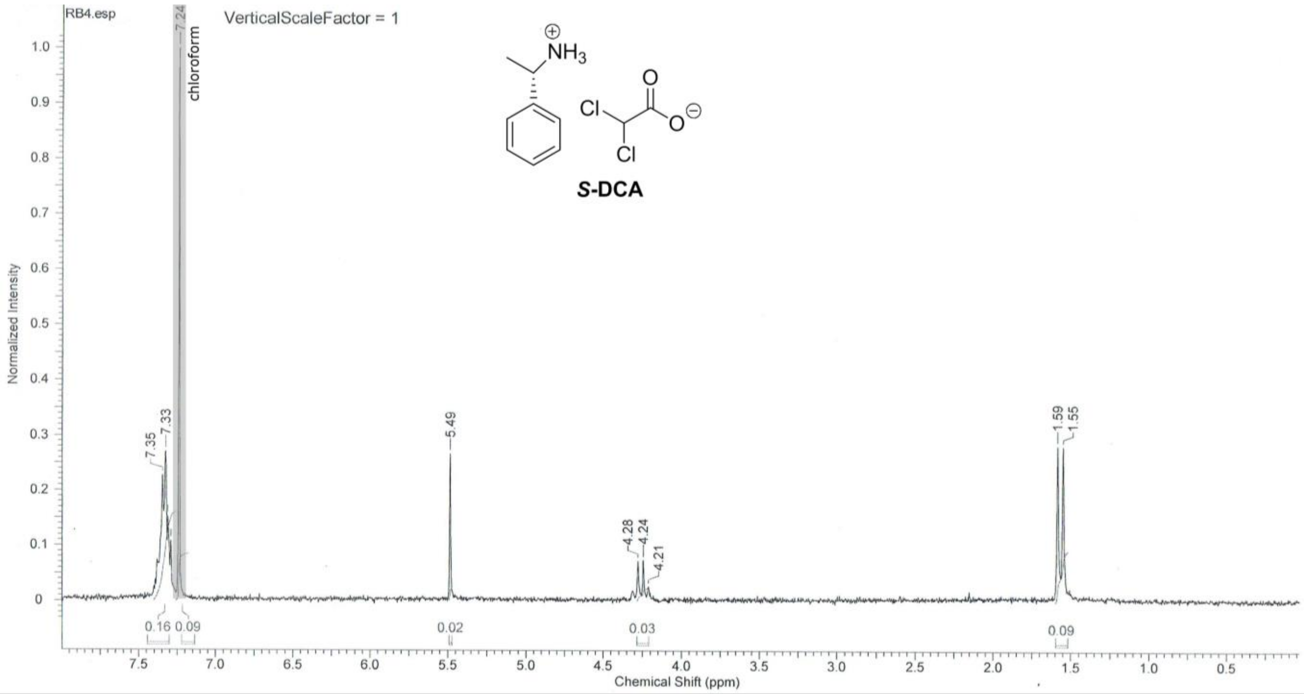


*Figure S7 ^{1}H NMR spectrum of **(S)-DCA**.*

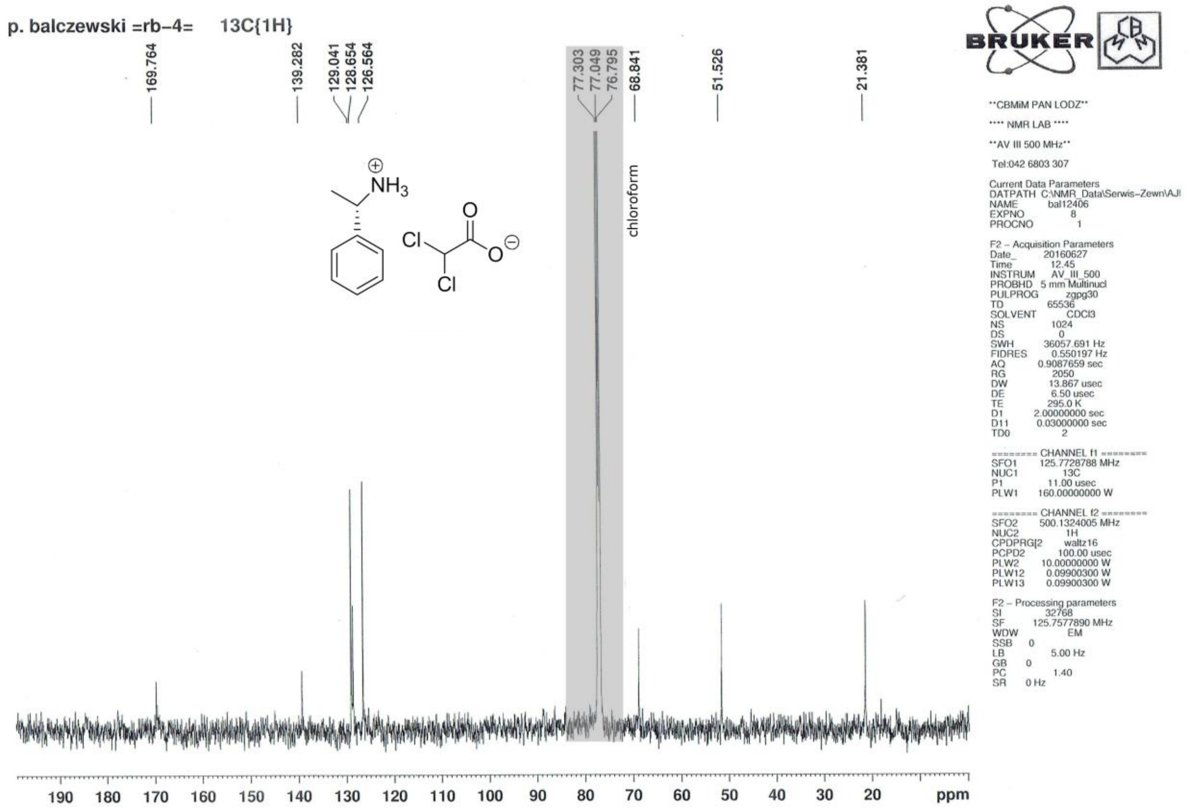
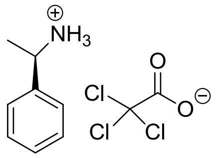


*Figure S8 ^{13}C NMR spectrum of **(S)-DCA**.*



(R)-TCA

(R)*-(+)-1-Phenylethylammonium trichloroacetate** ((R)*-TCA**) m.p. 82-84 °C; ; $[\alpha]_{25}^{D}$= + 11.4 (1, MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 1.55 (d, 3H, J = 6.0 Hz, CH_3), 4.24 (q, 1H, J = 6.0 Hz, CH), 5.59 (br s, 3H, NH_3^+), 7.25-7.39 (m, 5H, C_6H_5); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 20.97 (s, CH_3), 51.78 (s, CH), 95.74 (s, CCl_3), 126.88 (s, 2 x C_{Ar}), 128.77 (s, C_{Ar}), 129.03 (s, 2 x C_{Ar}), 138.83 (s, C_{Ar}), 165.78 (s, COO^-); MS-FAB (-): m/z (%) = 161, 163, 165, 167 (Cl_3CCOO^-, $^{35}Cl/^{37}Cl$, 100, 95, 30, 7); 323, 325, 327, 329, 331, 333 [2(Cl_3CCOO^-) + 1, $^{35}Cl/^{37}Cl$, 20, 42, 30, 17, 6, 3]; MS-FAB (+): m/z (%) = 122 [$C_6H_5CH(CH_3)NH_3^+$, 100]; Anal. Calcd for $C_{10}H_{12}Cl_3NO_2$: C, 42.21; H, 4.25; N, 4.92; Found: C, 42.35; H, 4.31; N, 4.96.

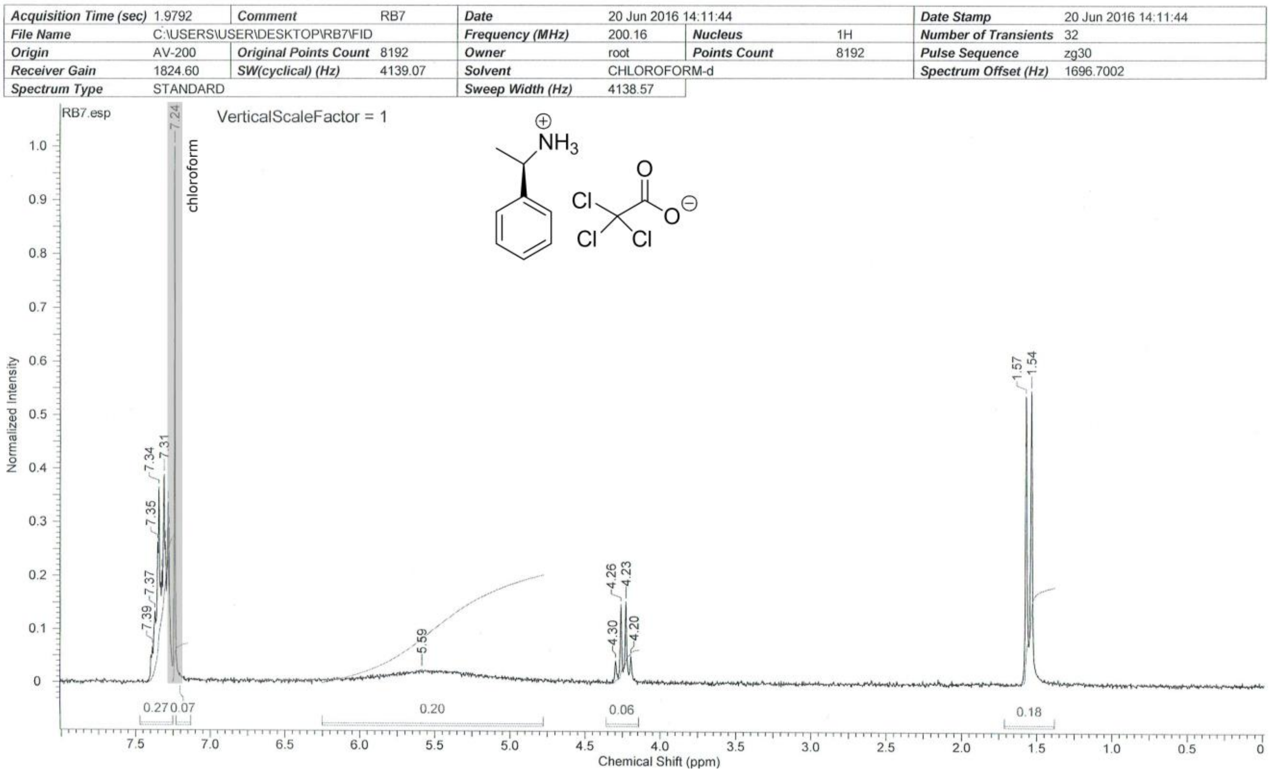


*Figure S9 ^{1}H NMR spectrum of **(R)-TCA**.*

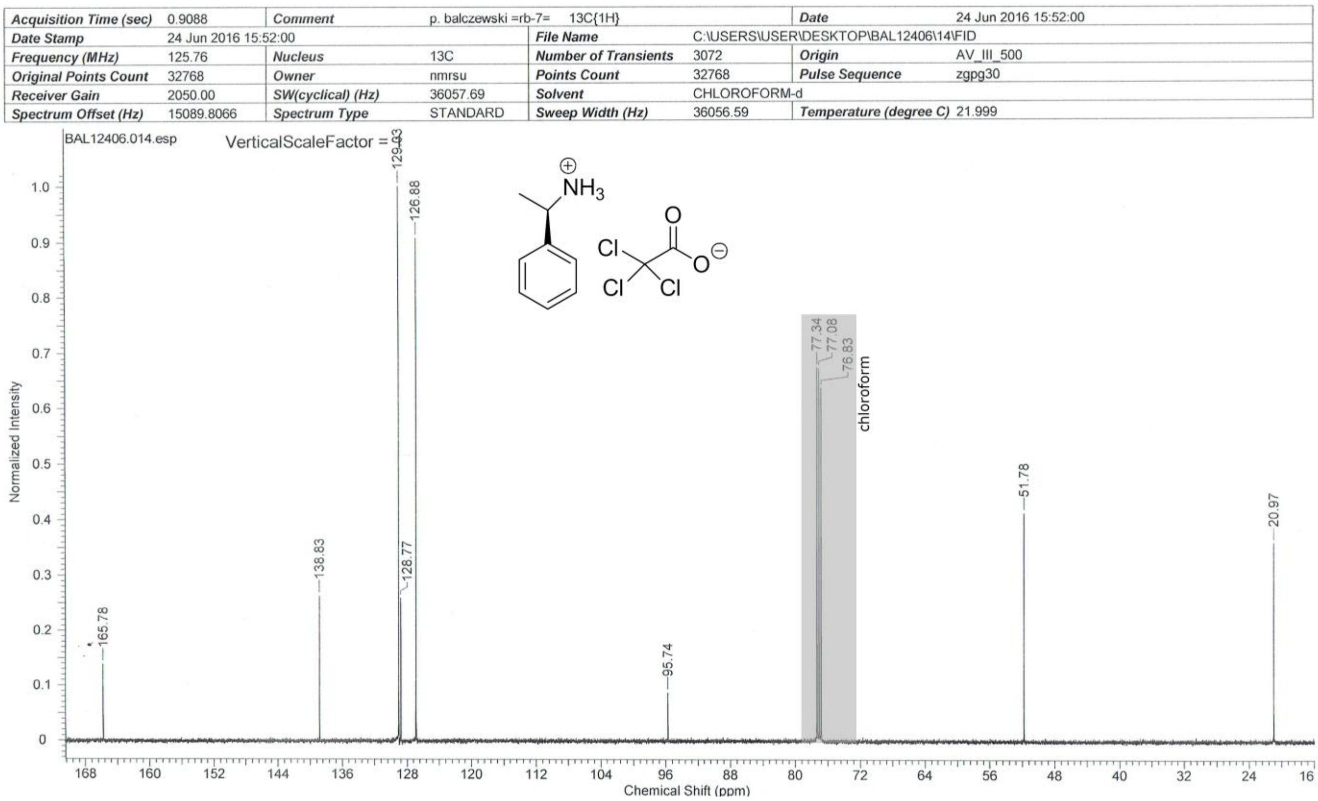
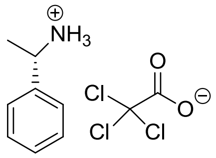


*Figure S10 ^{13}C NMR spectrum of **(R)-TCA**.*



***(S)*-TCA**

(S)*-(-)-1-Phenylethylammonium trichloroacetate** ((S)*-TCA**) m.p. 81-83 °C; ; $[\alpha]_{25}^{D}$= - 11.9 (1, MeOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) = 1.55 (d, 3H, J = 6.0 Hz, CH_3), 4.26 (q, 1H, J = 8.0 Hz, CH), 7.26-7.37 (m, 5H, C_6H_5); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 21.14 (s, CH_3), 51.20 (s, CH), 95.73 (s, CCl_3), 126.80 (s, 2 x C_{Ar}), 128.73 (s, C_{Ar}), 129.03 (s, 2 x C_{Ar}), 139.05 (s, C_{Ar}), 165.85 (s, COO^-); MS-FAB (-): m/z (%) = 161, 163, 165, 167 (Cl_3CCOO^-, $^{35}Cl/^{37}Cl$, 100, 96, 31, 4); 323, 325, 327, 329, 331, 333 [2(Cl_3CCOO^-) + 1, $^{35}Cl/^{37}Cl$, 24, 48, 35, 17, 4, 1]; MS-FAB (+): m/z (%) = 122 [$C_6H_5CH(CH_3)NH_3^+$, 100]; Anal. Calcd for $C_{10}H_{12}Cl_3NO_2$: C, 42.21; H, 4.25; N, 4.92; Found: C, 42.39; H, 4.42; N, 5.01.

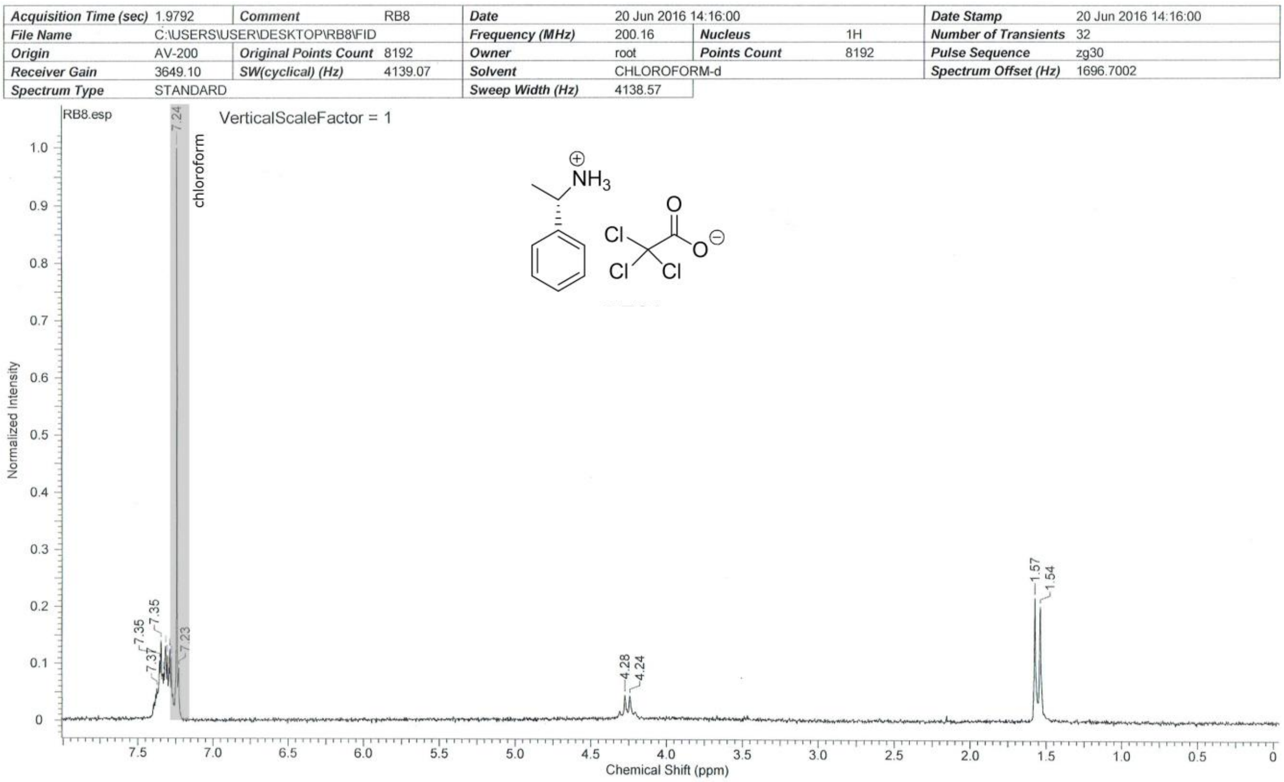


*Figure S11 ^{1}H NMR spectrum of **(S)-TCA**.*

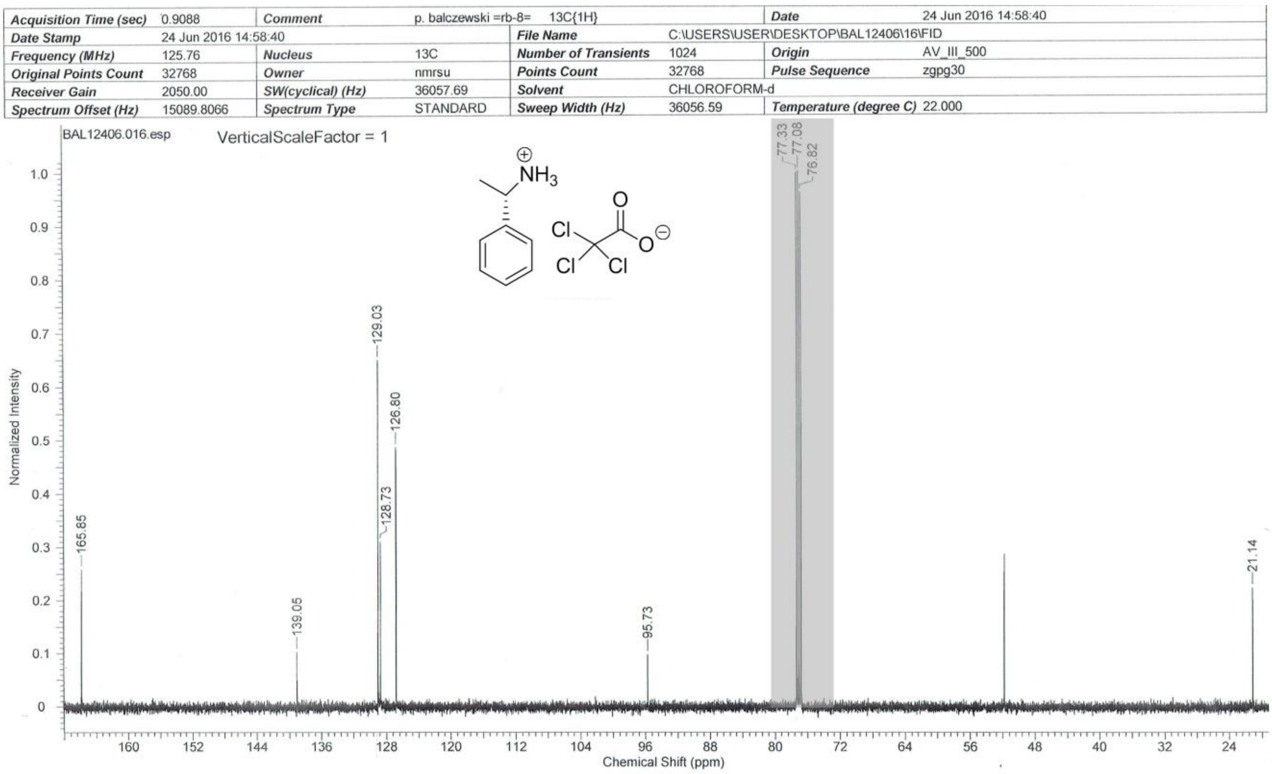
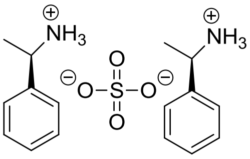


*Figure S12 ^{13}C NMR spectrum of **(S)-TCA**.*



***(R)*-SO$_4$**

(R)*-(+)-1-Phenylethylammonium sulfate** ((R)*-SO$_4$**) m.p. 242-248 °C; ; $[\alpha]_{25}^{D}$= + 4.5 (1, MeOH); ^{1}H NMR (200 MHz, MeOD) δ (ppm) = 1.62 (d, 6H, J = 8.0 Hz, 2 x CH_3), 4.46 (q, 2H, J = 6.0 Hz, 2 x CH), 7.35-7.48 (m, 10H, 2 x C_6H_5); ^{13}C NMR (50 MHz, MeOD) δ (ppm) = 19.55 (s, 2 x CH_3), 50.78 (s, 2 x CH), 126.34 (s, 2 x C_{Ar}), 128.47 (s, 4 x C_{Ar}), 128.76 (s, 4 x C_{Ar}), 138.77 (s, 2 x C_{Ar}); HRMS [TOF ES+] for [M+1, 100], Calcd for $C_{16}H_{25}N_2O_4S$: 341.1535, Found: 341.1542; Anal. Calcd for $C_{16}H_{24}N_2O_4S$: C, 56.45; H, 7.11; N, 8.23; S, 9.42; Found: C, 56.72; H, 7.12; N, 8.21; S, 9.48.

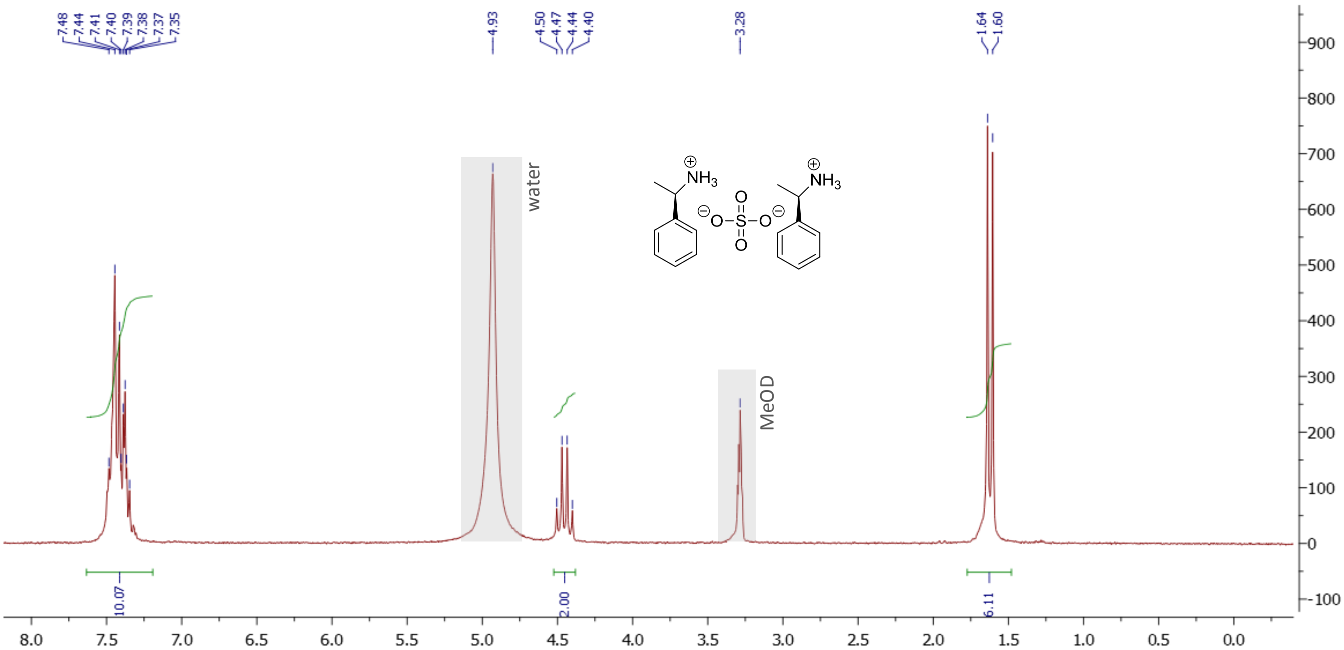


*Figure S13 ^{1}H NMR spectrum of **(R)-SO$_4$**.*

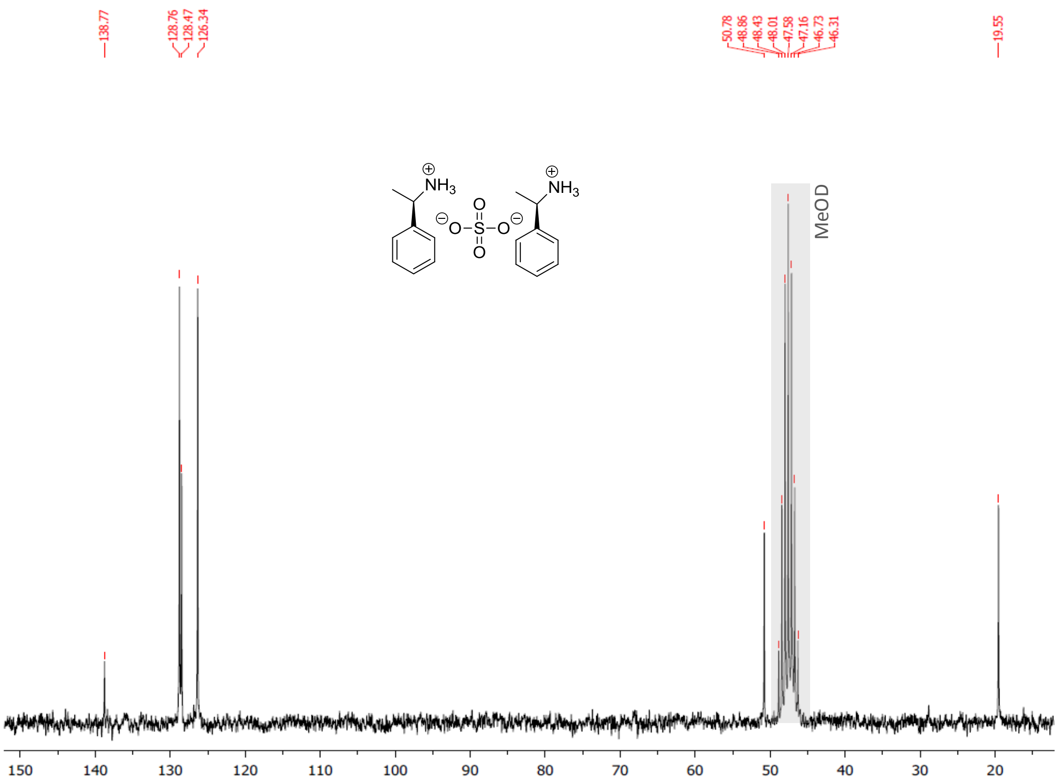


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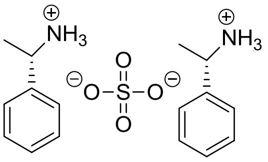
*Figure S14 ^{13}C NMR spectrum of **(R)-SO$_4$**.*



(*S*)-SO$_4$

(*S*)-(-)-1-Phenylethylammonium sulfate ((***S***)**-SO$_4$**) m.p. 241-248 °C; ; $[\alpha]_{25}^{D}$= - 4.8 (1, MeOH); ^{1}H NMR (200 MHz, MeOD) δ (ppm) = 1.62 (d, 6H, J = 6.0 Hz, 2 x CH$_3$), 4.45 (q, 2H, J = 8.0 Hz, 2 x CH), 7.36-7.49 (m, 10H, 2 x C$_6$H$_5$); ^{13}C NMR (50 MHz, MeOD) δ (ppm) = 18.24 (s, 2 x CH$_3$), 49.50 (s, 2 x CH), 125.05 (s, 2 x C$_{Ar}$), 127.21 (s, 4 x C$_{Ar}$), 127.49 (s, 4 x C$_{Ar}$), 137.47 (s, 2 x C$_{Ar}$); HRMS [TOF ES+] for [M+1, 100], Calcd for $C_{16}H_{25}N_2O_4S$: 341.1535, Found: 341.1543; Anal. Calcd for $C_{16}H_{24}N_2O_4S$: C, 56.45; H, 7.11; N, 8.23; S, 9.42, Found: C, 56.69; H, 7.10; N, 8.24; S, 9.50.

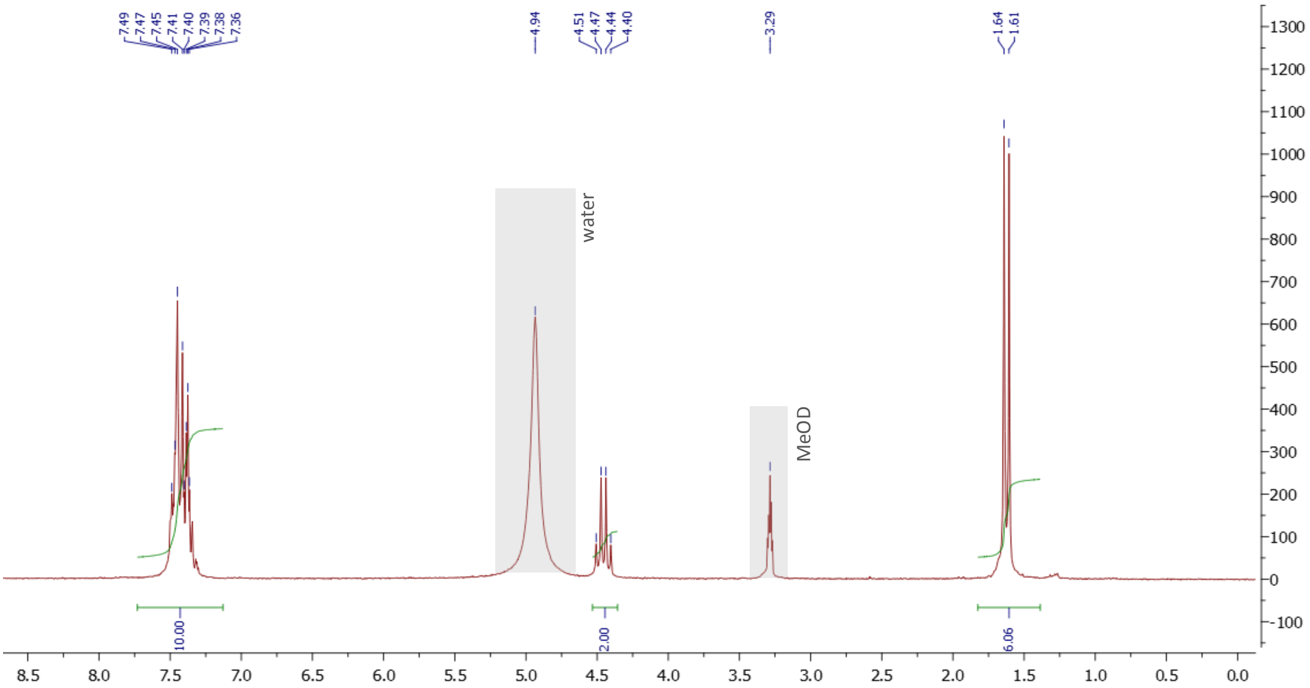


*Figure S15 ^{1}H NMR spectrum of **(S)-SO$_4$**.*

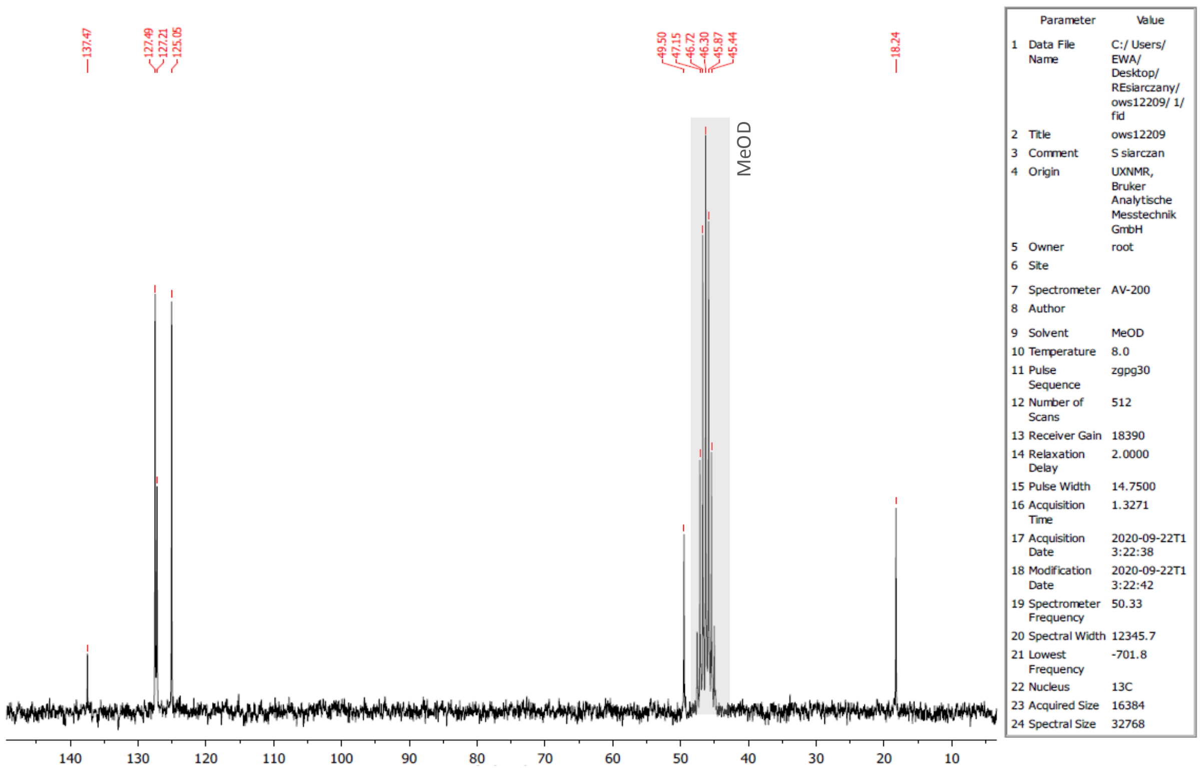
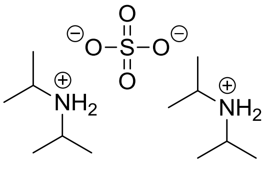


*Figure S16 ^{13}C NMR spectrum of **(S)-SO$_4$**.*



DIPA-SO_4

Diisopropylammonium sulfate (**DIPA-SO_4**) m.p. 182-185 °C; ^{1}H NMR (200 MHz, MeOD) δ (ppm) = 1.32 (d, 24H, J = 8.0 Hz, 4 x CH_3), 4.96 (s, 4H, 4 x CH); ^{13}C NMR (50 MHz, MeOD) δ (ppm) = 18.00 (s, 4 x CH_3), 46.79 (s, 4 x CH); HRMS [TOF ES+] for [M+1, 100]: Calcd: 301.2161; Found: 301.2161; HRMS [TOF ES+] for 102 [$C_6H_{16}N^+$, 100], Calcd: 102.1283, Found: 102.1279; Anal. Calcd for $C_{12}H_{32}N_2O_4S$: C, 47.97; H, 10.73; N, 9.32; S, 10.67; Found: C, 47.91; H, 10.53; N, 9.35; S, 11.02.

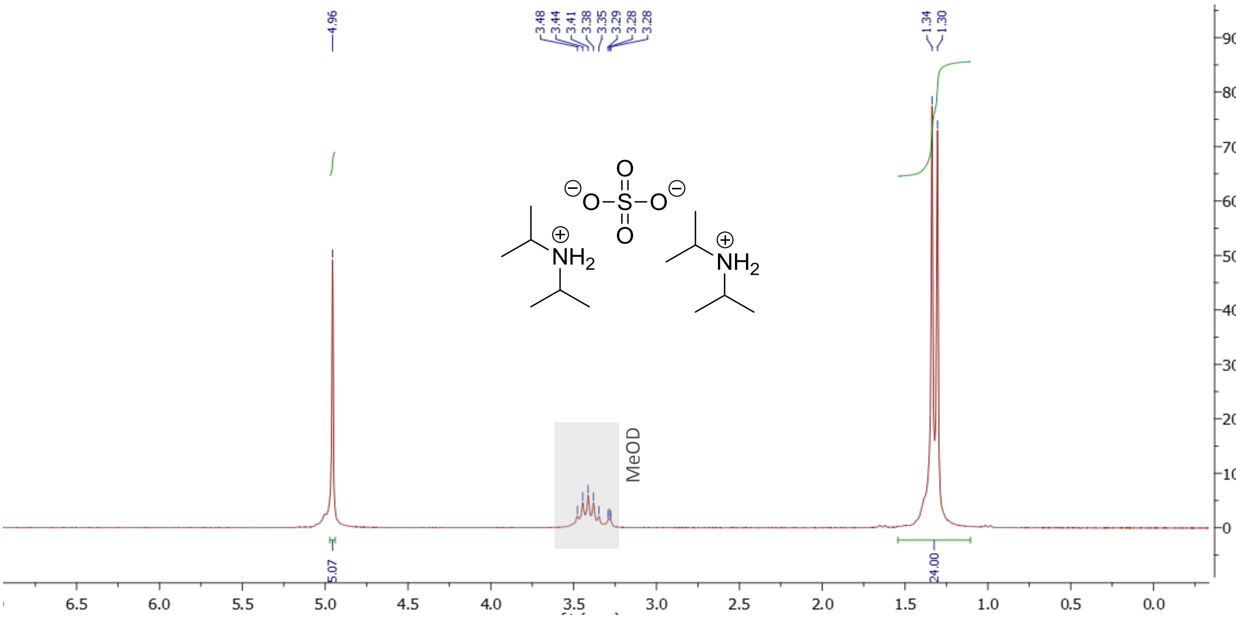


*Figure S17a ^{1}H NMR spectrum of **DIPA-SO_4**.*

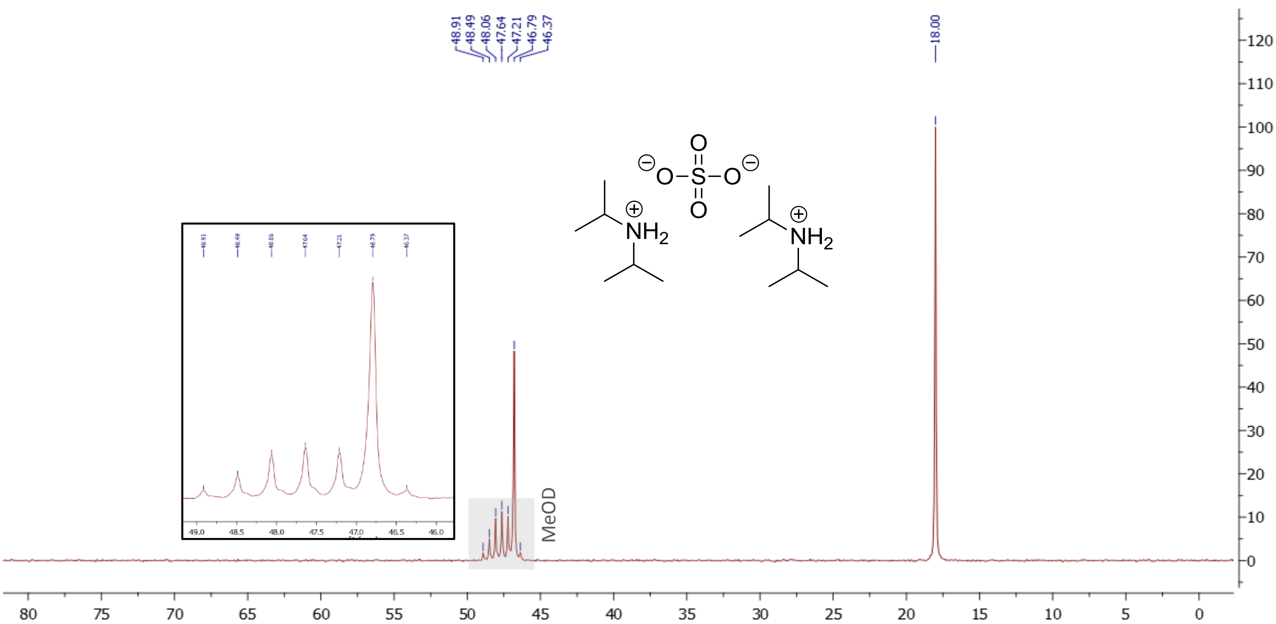


*Figure S17b ^{13}C NMR spectrum of **DIPA-SO_4**.*

2. X-ray crystal structure determination of diisopropylammonium sulfate (DIPA-SO_4)

Crystallographic data for DIPA-SO_4: $2C_6H_{16}N^+\cdot SO_4^{2-}$, M=300.46, monoclinic, $P2_1/n$, a = 8.7824(2) Å, b = 8.82350(10) Å, c = 22.0837(4) Å, β = 95.202(2) °, V = 1704.25(5) $Å^3$, Z = 4, Dc = 1.171 g/cm^3, F(000)=664, crystal size 0.55x0.48x0.36 mm. Diffraction data were collected at 293(2) K, using an Oxford Diffraction Xcalibur^{TM}3 diffractometer (graphite-monochromated CuKα radiation, CCD detector). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXS-97 and SHELXL-97, respectively. The disorder on oxygen atoms of SO_4^{2-} anion was refined over two positions with the occupancy factor for the major component of 0.854(8). All non-hydrogen atoms were refined anisotropically. H atoms of methyl groups were positioned geometrically and constrained to ride on their parent atoms, with C-H distances of 0.96 Å and with U_{iso} values of 1.5Ueq(C). All other hydrogen atoms were located in a difference Fourier maps and refined isotropically with N-H and C-H distances in the ranges of 0.79(2)-0.92(2) Å and 0.91(2)-0.98(2) Å, respectively. R1=0.0349 and wR2=0.0960 for 2879 reflections with $F^2 > 2\sigma(F^2)$ and 226 parameters; R1=0.0366 and wR2=0.0979 for 3063 unique reflections, S=1.035. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC: 2073361.

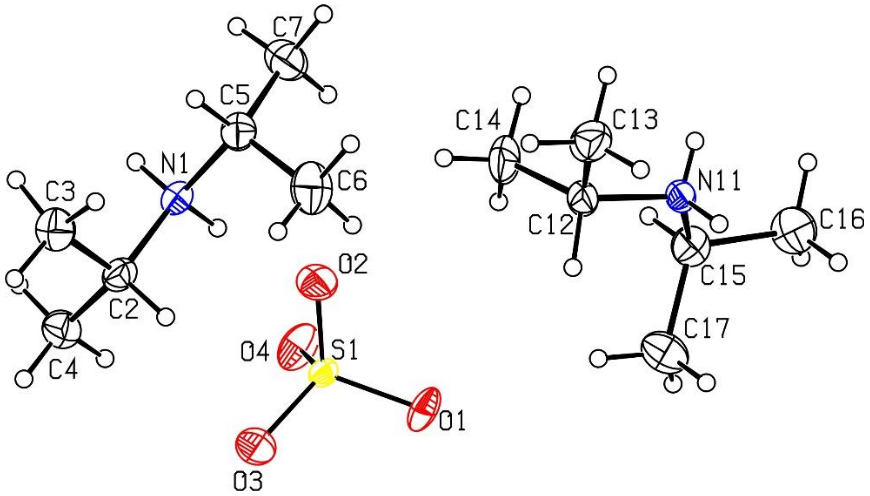


Figure. S18. A view of the asymmetric part of unit cell of DIPA-SO_4 with the atom numbering scheme and displacement ellipsoids drawn at the 30 % probability level. The minor component on oxygen atoms of SO_4^{2-} anion has been omitted for clarity.

3. Phytotoxicity studies

Table S1. Variations in the yield of fresh weight (FW, g/pot), dry weight (DW, g/g f.m.) and germination for spring barley as the effect of increasing concentration of quaternary ammonium salts (QASs) in soil (in mg/kg of soil d.w.). Data are means ± SD from 3 independent experiments. Values denoted with the same letters do not differ statistically at the level of $p<0.05$ (Tukey's HSD test).

IL		**Concentration of QAS [mg/kg of soil d.w.]**								
		0	**1**	**10**	**100**	**200**	**400**	**800**	**1000**	**$LSD_{0.95}$**
Spring barley										
(*R*)-MCA	FW	4.495±0.047 ^{a}	4.258±0.135 ^{ab}	4.368±0.461 ^{ab}	4.781±0.177 ^{a}	4.743±0.151 ^{a}	4.811±0.097 ^{a}	3.800±0.139 ^{b}	2.327±0.144 ^{c}	0.212
	DW	0.0790±0.0039 ^{bc}	0.0789±0.0033 ^{bc}	0.0780±0.0020 ^{c}	0.0773±0.0031 ^{c}	0.0759±0.0013 ^{c}	0.0755±0.0029 ^{c}	0.0842±0.0032 ^{b}	0.1041±0.0035 ^{a}	0.0030
	sprouts	20 ^{a}	20 ^{a}	18±1 ^{b}	20 ^{a}	20 ^{a}	20 ^{a}	19±1 ^{ab}	19±1 ^{ab}	1
(*S*)-MCA	FW	4.495±0.47 ^{a}	4.398±0.105 ^{a}	4.364±0.260 ^{a}	4.064±0.237 ^{a}	4.570±0.420 ^{a}	4.842±0.213 ^{a}	4.534±0.477 ^{a}	3.210±0.296 ^{b}	0.230
	DW	0.790±0.0039 ^{b}	0.0771±0.0020 ^{b}	0.0786±0.0021 ^{b}	0.0766±0.0020 ^{b}	0.0735±0.0090 ^{b}	0.0752±0.0024 ^{b}	0.0783±0.0036 ^{b}	0.0895±0.0026 ^{a}	0.0041
	sprouts	20 ^{a}	20±1 ^{a}	19±2 ^{ab}	18±1 ^{b}	19±1 ^{ab}	20 ^{a}	20 ^{a}	19±1 ^{ab}	1
(*R*)-DCA	FW	5.083±0.086 ^{a}	4.941±0.169 ^{a}	4.956±0.256 ^{a}	5.064±0.390 ^{a}	5.011±0.127 ^{a}	4.499±0.092 ^{a}	3.406±0.218 ^{b}	3.277±0.378 ^{b}	0.250
	DW	0.757±0.0041 ^{c}	0.0735±0.0030 ^{c}	0.0715±0.0028 ^{c}	0.0756±0.0010 ^{c}	0.0711±0.0028 ^{c}	0.0751±0.0030 ^{c}	0.0863±0.0019 ^{b}	0.1069±0.0018 ^{a}	0.0027
	sprouts	19±1 ^{a}	19±1 ^{a}	19±1 ^{a}	20 ^{a}	19±1 ^{a}	19±1 ^{a}	19±1 ^{a}	20 ^{a}	1
(*S*)-DCA	FW	5.083±0.089 ^{a}	5.327±0.245 ^{a}	4.973±0.481 ^{a}	5.620±0.310 ^{a}	-	-	-	5.539±0.477 ^{a}	0.476
	DW	0.0757±0.0041 ^{a}	0.0739±0.0026 ^{a}	0.0746±0.0019 ^{a}	0.0733±0.0033 ^{a}	-	-	-	0.0736±0.0039 ^{a}	0.0042
	sprouts	19±1 ^{ab}	20 ^{a}	19±1 ^{b}	20 ^{a}	-	-	-	19±1 ^{ab}	1
(*R*)-SO_4	FW	3.815±0.140 ^{ab}	3.514±0.235 ^{abc}	3.957±0.047 ^{a}	3.686±0.091 ^{ab}	3.763±0.052 ^{ab}	3.067±0.059 ^{abc}	2.384±0.182 ^{bc}	2.193±0.233 ^{c}	0.154
	DW	0.0746±0.0024 ^{c}	0.0764±0.0014 ^{c}	0.0744±0.0043 ^{c}	0.0809±0.0028 ^{c}	0.0765±0.0020 ^{c}	0.0783±0.0020 ^{c}	0.0891±0.0010 ^{c}	0.1029±0.0026 ^{a}	0.0025
	sprouts	19±1 ^{a}	19±1 ^{a}	20 ^{a}	18 ^{a}	18±2 ^{a}	19±2 ^{a}	18±1 ^{a}	19±2 ^{a}	1
(*S*)-SO_4	FW	3.815±0.140 ^{a}	3.555±0.015 ^{a}	3.770±0.057 ^{a}	3.532±0.091 ^{a}	-	-	-	3.573±0.131 ^{a}	0.133
	DW	0.746±0.0024 ^{c}	0.0769±0.0016 ^{bc}	0.0780±0.0010 ^{abc}	0.0810±0.0021 ^{a}	-	-	-	0.0808±0.0015 ^{ab}	0.0024
	sprouts	19±1 ^{a}	17±1 ^{a}	19 ^{a}	19±1 ^{a}	-	-	-	18 ^{a}	1
DIPA-SO_4	FW	3.645±0.050 ^{a}	3.855±0.168 ^{a}	4.055±0.079 ^{a}	4.177±0.100 ^{a}	-	-	-	3.724±0.024 ^{a}	0.132
	DW	0.0753±0.0016 ^{a}	0.0712±0.0013 ^{a}	0.0730±0.0014 ^{a}	0.0770±0.0047 ^{a}	-	-	-	0.0738±0.0010 ^{a}	0.0032
	sprouts	19±1 ^{a}	18 ^{a}	19 ^{a}	19 ^{a}	-	-	-	19±1 ^{a}	1
		Concentration of QAS [mg/kg of soil d.w.]								
		0	**1**	**10**	**20**	**40**	**80**	**100**	**1000**	
(*R*)-TCA	FW	5.155±0.039 ^{a}	4.968±0.088 ^{a}	4.697±0.070 ^{a}	3.973±0.089 ^{b}	1.724±0.467 ^{c}	0.348±0.002 ^{d}	0.175±0.042 ^{d}	-	0.207
	DW	0.0724±0.0024 ^{d}	0.0743±0.0024 ^{d}	0.0771±0.0022 ^{d}	0.0842±0.0021 ^{c}	0.1047±0.0059 ^{b}	0.1285±0.0055 ^{a}	0.1357±0.0008 ^{a}	-	0.0037
	sprouts	19±1 ^{a}	20±1 ^{a}	20±1 ^{a}	19±1 ^{a}	20 ^{a}	20 ^{a}	20 ^{a}	19±1 ^{a}	0
(*S*)-TCA	FW	5.155±0.039 ^{a}	5.191±0.180 ^{a}	5.321±0.231 ^{a}	3.633±0.197 ^{b}	2.595±0.523 ^{c}	1.495±0.083 ^{d}	0.645±0.044 ^{d}	-	0.269
	DW	0.0724±0.0024 ^{d}	0.0725±0.0026 ^{d}	0.0781±0.0031 ^{d}	0.0870±0.0024 ^{c}	0.0981±0.0041 ^{b}	0.1165±0.0037 ^{a}	0.1192±0.0037 ^{a}	-	0.0036
	sprouts	19±1 ^{a}	20±1 ^{a}	20±1 ^{a}	20±1 ^{a}	20±1 ^{a}	20±1 ^{a}	20 ^{a}	19±1 ^{a}	1

Table S2. Variations in the yield of fresh weight (FW, g/pot), dry weight (DW, g/g f.m.) and germination for common radish as the effect of increasing concentration of quaternary ammonium salts (QASs) in soil (in mg/kg of soil d.w.). Data are means ± SD from 3 independent experiments. Values denoted with the same letters do not differ statistically at the level of $p<0.05$ (Tukey's HSD test).

IL		**Concentration of QAS [mg/kg of soil d.w.]**								
		0	**1**	**10**	**100**	**200**	**400**	**800**	**1000**	**$LSD_{0.95}$**
Common radish										
(*R*)-MCA	FW	5.134±0.857 ^{a}	5.065±0.131 ^{a}	4.716±0.141 ^{a}	3.736±0.189 ^{a}	5.107±0.697 ^{a}	4.216±0.353 ^{a}	0.490±0.514 ^{b}	-	0.510
	DW	0.0530±0.0022 ^{c}	0.0522±0.0011 ^{c}	0.0530±0.0026 ^{c}	0.0534±0.0011 ^{c}	0.0547±0.0022 ^{c}	0.0642±0.0011 ^{b}	0.1200±0.0011 ^{a}	-	0.0019
	sprouts	18 ^{a}	17±1 ^{a}	17±1 ^{a}	18±1 ^{a}	19±1 ^{a}	19±1 ^{a}	6±4 ^{b}	0±1 ^{c}	2
(*S*)-MCA	FW	5.052±0.042 ^{a}	5.447±0.395 ^{a}	4.618±0.188 ^{ab}	4.806±0.138 ^{ab}	5.104±0.385 ^{a}	4.198±0.335 ^{ab}	3.506±0.295 ^{b}	-	0.314
	DW	0.0530±0.0022 ^{b}	0.0506±0.0029 ^{b}	0.0538±0.0022 ^{b}	0.0547±0.0014 ^{b}	0.0554±0.0035 ^{b}	0.0588±0.0039 ^{b}	0.0791±0.0121 ^{a}	-	0.0057
	sprouts	18 ^{a}	19±2 ^{a}	17±1 ^{a}	18±2 ^{a}	18±1 ^{a}	18 ^{a}	17±2 ^{a}	0±1 ^{b}	1
(*R*)-DCA	FW	5.824±0.642 ^{a}	6.109±0.612 ^{a}	5.542±0.455 ^{a}	5.457±0.310 ^{a}	5.927±0.402 ^{a}	4.456±0.392 ^{ab}	3.275±0.193 ^{bc}	1.808±0.166 ^{c}	0.442
	DW	0.0540±0.0022 ^{c}	0.0535±0.0026 ^{c}	0.0512±0.0025 ^{c}	0.0560±0.0009 ^{bc}	0.0526±0.0031 ^{c}	0.0581±0.0013 ^{bc}	0.0646±0.0050 ^{b}	0.1172±0.0165 ^{a}	0.0064
	sprouts	17±2 ^{a}	18±2 ^{a}	16±1 ^{a}	17±1 ^{a}	19±1 ^{a}	17±1 ^{a}	16±1 ^{a}	17±2 ^{a}	1
(*S*)-DCA	FW	5.824±0.642 ^{a}	5.371±0.263 ^{ab}	5.264±0.001 ^{ab}	5.412±0.0053 ^{ab}	5.542±0.111 ^{ab}	5.883±0.182 ^{a}	5.244±0.238 ^{ab}	4.523±0.186 ^{b}	0.091
	DW	0.0540±0.0022 ^{b}	0.0569±0.0015 ^{ab}	0.0537±0.0020 ^{b}	0.0550±0.0017 ^{a}	0.0552±0.0044 ^{a}	0.0544±0.0024 ^{b}	0.0569±0.0035 ^{ab}	0.0599±0.0022 ^{a}	0.0027
	sprouts	18±1 ^{ab}	17±1 ^{ab}	16±1 ^{b}	17±1 ^{ab}	19±1 ^{a}	19±1 ^{ab}	18±1 ^{ab}	18±1 ^{ab}	1
(*R*)-SO_4	FW	6.354±0.334 ^{ab}	6.008±0.121 ^{ab}	6.569±0.111 ^{ab}	6.643±0.116 ^{a}	5.731±0.138 ^{abc}	5.449±0.177 ^{bc}	4.757±0.347 ^{cd}	4.213±0.122 ^{d}	0.212
	DW	0.0523±0.0018 ^{b}	0.0559±0.0034 ^{b}	0.0557±0.0009 ^{b}	0.0567±0.0014 ^{b}	0.0560±0.0020 ^{b}	0.0588±0.0014 ^{b}	0.0613±0.0037 ^{b}	0.0922±0.0086 ^{a}	0.0037
	sprouts	19±2 ^{a}	19±1 ^{a}	19±1 ^{a}	20 ^{a}	19±2 ^{a}	19±1 ^{a}	17±1 ^{a}	20 ^{a}	1
(*S*)-SO_4	FW	6.354±0.334 ^{ab}	7.042±0.137 ^{a}	6.727±0.212 ^{ab}	5.808±0.039 ^{ab}	5.187±0.015 ^{ab}	4.947±0.025 ^{ab}	4.767±0.0003 ^{ab}	4.336±0.105 ^{b}	0.158
	DW	0.0523±0.0018 ^{c}	0.0549±0.0005 ^{c}	0.0532±0.0030 ^{c}	0.0573±0.0009 ^{bc}	0.0586±0.0009 ^{abc}	0.0587±0.0021 ^{abc}	0.0634±0.004 ^{ab}	0.655±0.0039 ^{a}	0.0025
	sprouts	19±1 ^{a}	19±1 ^{a}	19±1 ^{a}	19±1 ^{a}	18 ^{a}	18±1 ^{a}	18±1 ^{a}	19±1 ^{a}	1
DIPA-SO_4	FW	6.507±0.155 ^{abc}	6.702±0.144 ^{a}	6.595±0.195 ^{ab}	6.096±0.085 ^{abcd}	5.551±0.059 ^{bcde}	5.483±0.107 ^{cde}	5.369±0.029 ^{de}	4.598±0.022 ^{e}	0.150
	DW	0.0537±0.0012 ^{ab}	0.0524±0.0017 ^{b}	0.0500±0.0021 ^{b}	0.0541±0.0013 ^{ab}	0.0533±0.0017 ^{b}	0.0542±0.0016 ^{ab}	0.0583±0.0024 ^{a}	0.583±0.0017 ^{a}	0.0018
	sprouts	19±1 ^{a}	19±1 ^{a}	19±1 ^{a}	19 ^{a}	18±1 ^{a}	18±1 ^{a}	18±1 ^{a}	18±1 ^{a}	1
		Concentration of QAS [mg/kg of soil d.w.]								
		0	**1**	**10**	**20**	**40**	**80**	**100**	**1000**	
(*R*)-TCA	FW	8.430±0.441 ^{ab}	8.512±0.640 ^{a}	8.481±0.281 ^{ab}	7.991±0.578 ^{abc}	7.403±0.253 ^{bc}	7.081±0.284 ^{c}	7.031±0.356 ^{c}	3.770±0.180 ^{d}	0.420
	DW	0.0503±0.0010 ^{cd}	0.0491±0.0015 ^{d}	0.0524±0.0017 ^{cd}	0.0530±0.0018 ^{c}	0.0575±0.0024 ^{b}	0.0569±0.0023 ^{b}	0.0593±0.0025 ^{b}	0.0810±0.0028 ^{a}	0.0021
	sprouts	20 ^{a}	20 ^{a}	20 ^{a}	20±1 ^{a}	20 ^{a}	20 ^{a}	20 ^{a}	20±1 ^{a}	0
(*S*)-TCA	FW	8.430±0.441 ^{a}	7.800±0.222 ^{ab}	8.387±0.435 ^{a}	8.359±0.100 ^{a}	7.725±0.520 ^{ab}	6.832±0.15 ^{b}	6.830±0.397 ^{b}	2.581±0.532 ^{c}	0.369
	DW	0.0503±0.0010 ^{b}	0.0516±0.0013 ^{b}	0.0498±0.0016 ^{b}	0.0523±0.0014 ^{b}	0.0538±0.0015 ^{b}	0.0557±0.0015 ^{b}	0.0584±0.0005 ^{b}	01298±0.0281 ^{a}	0.0101
	sprouts	20 ^{a}	20 ^{a}	20±1 ^{a}	20 ^{a}	20±1 ^{a}	19±1 ^{a}	20 ^{a}	20±1 ^{a}	1

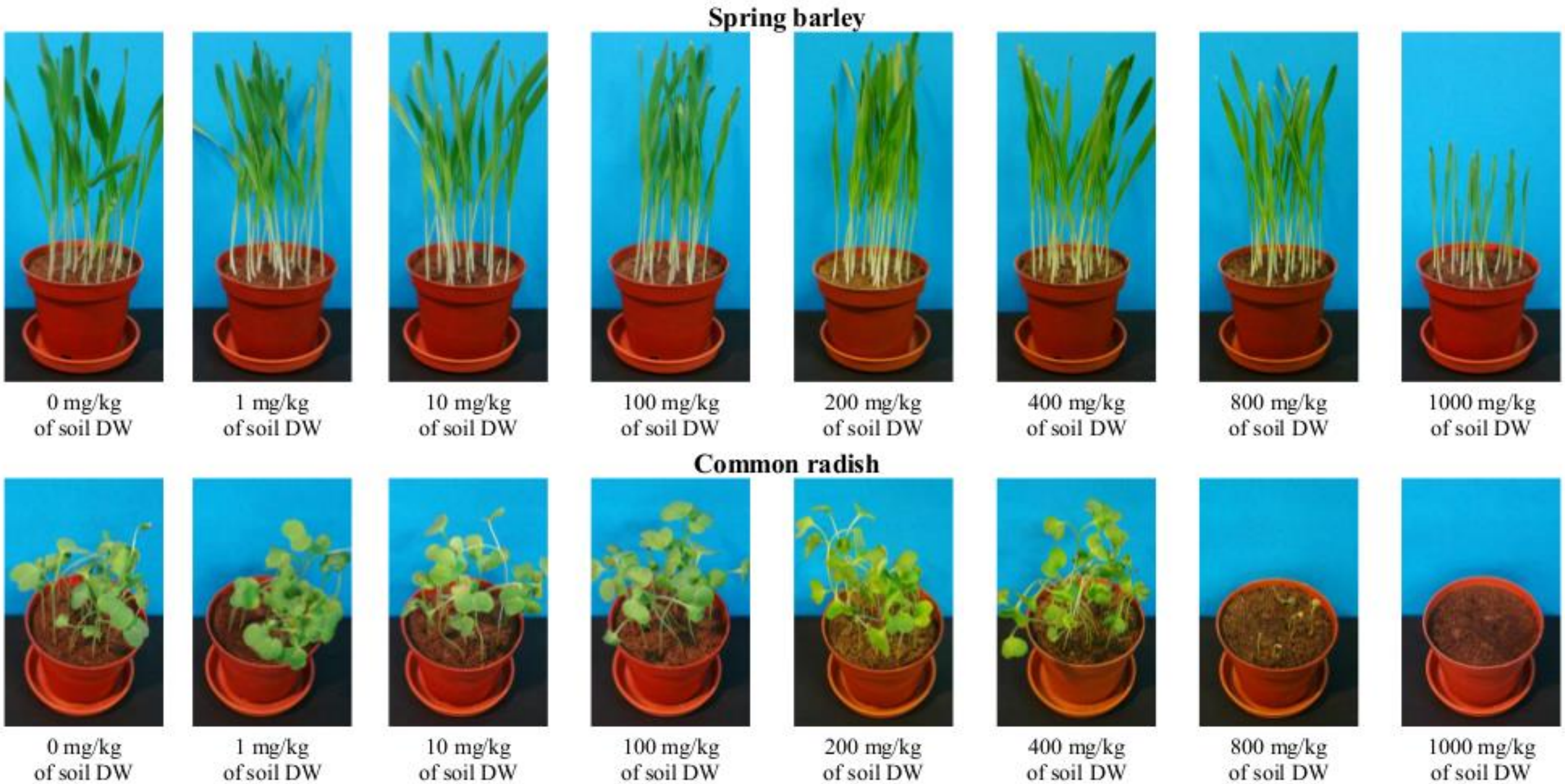


*Figure S19. Digital photographs of plants seedlings in soil treated with aqueous solutions of **(R)-MCA**.*

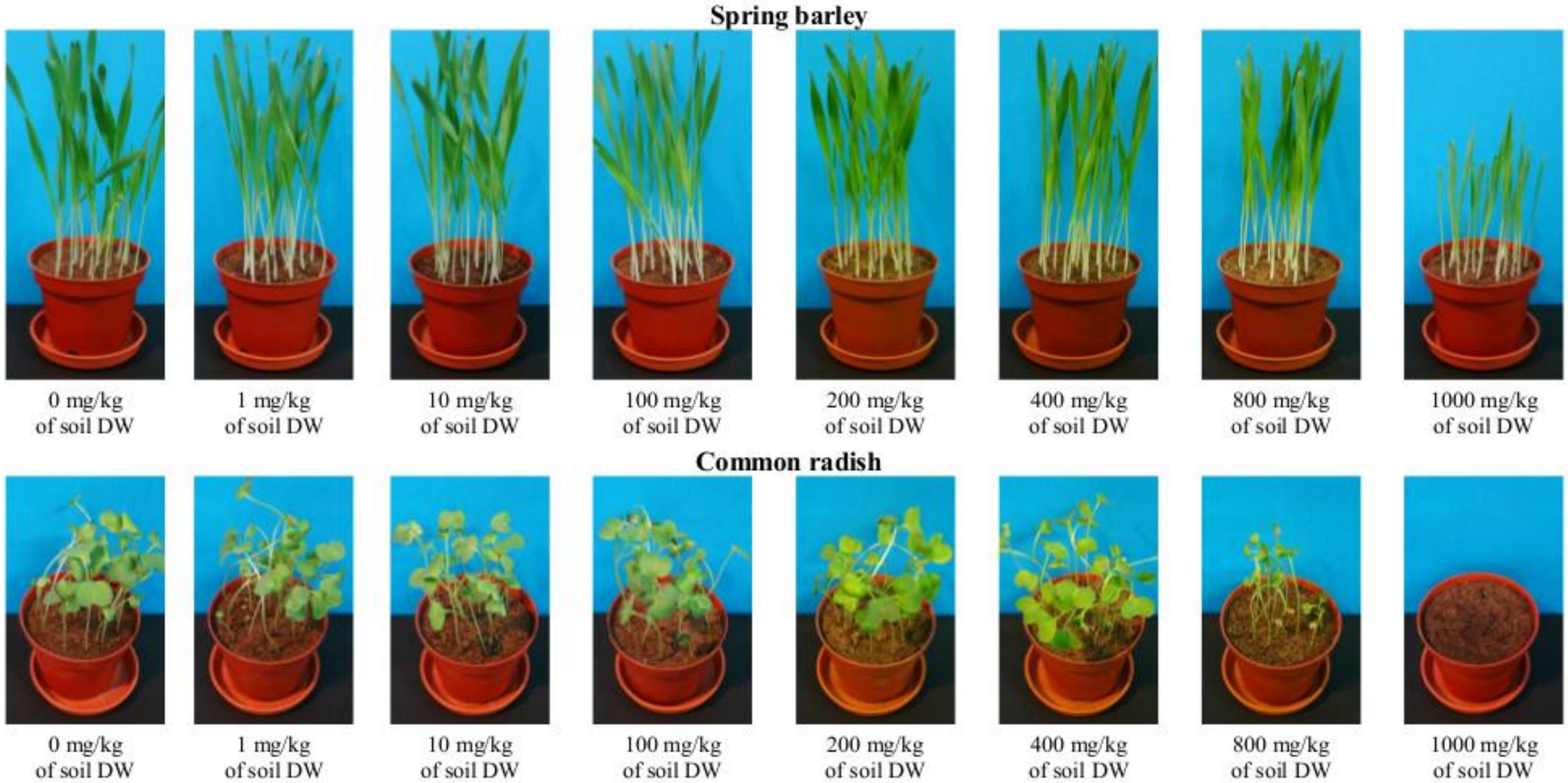


*Figure S20. Digital photographs of plants seedlings in soil treated with aqueous solutions of **(S)-MCA**.*

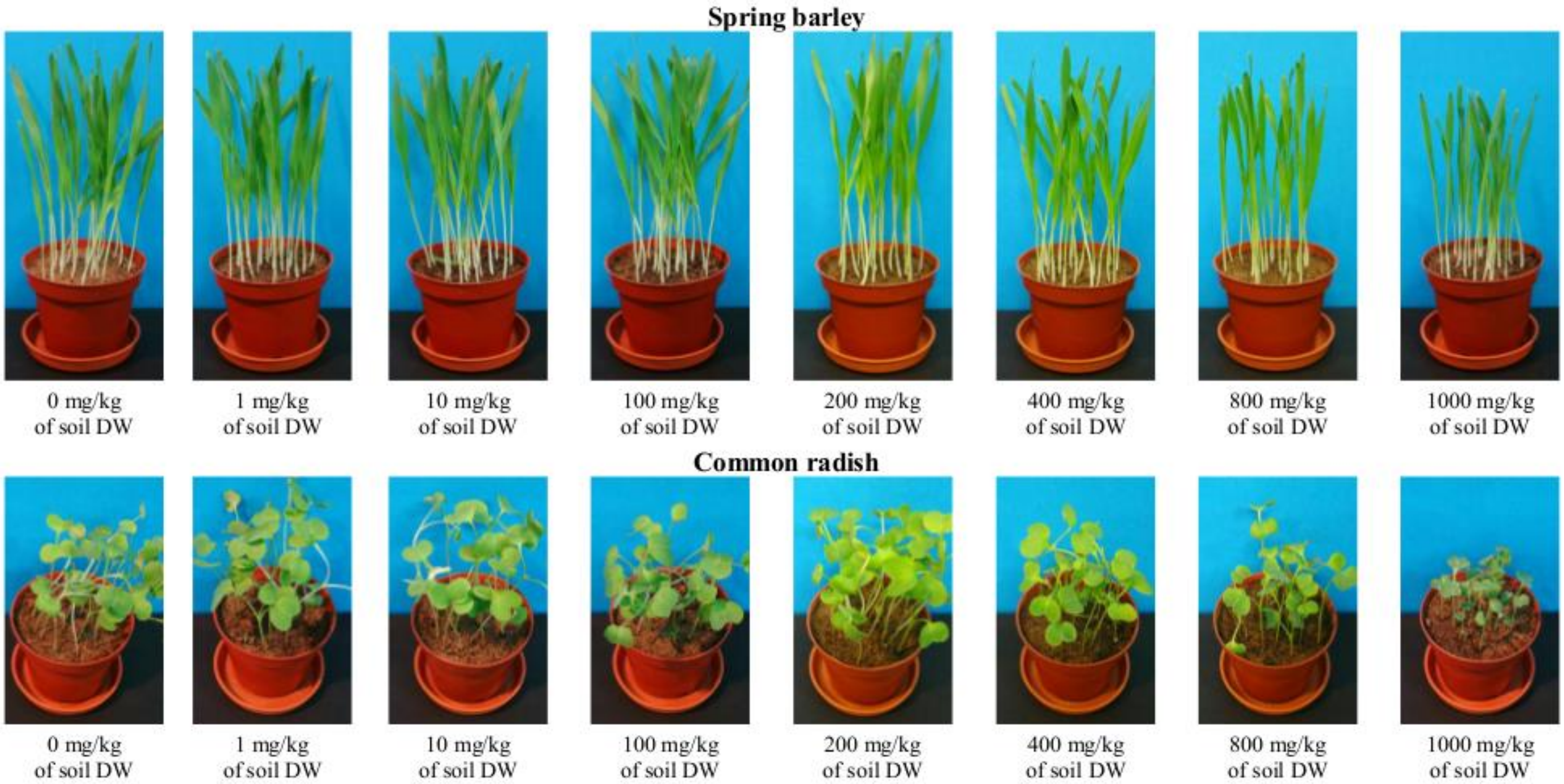


Figure S21. Digital photographs of plants seedlings in soil treated with aqueous solutions of ***(R)-DCA.***

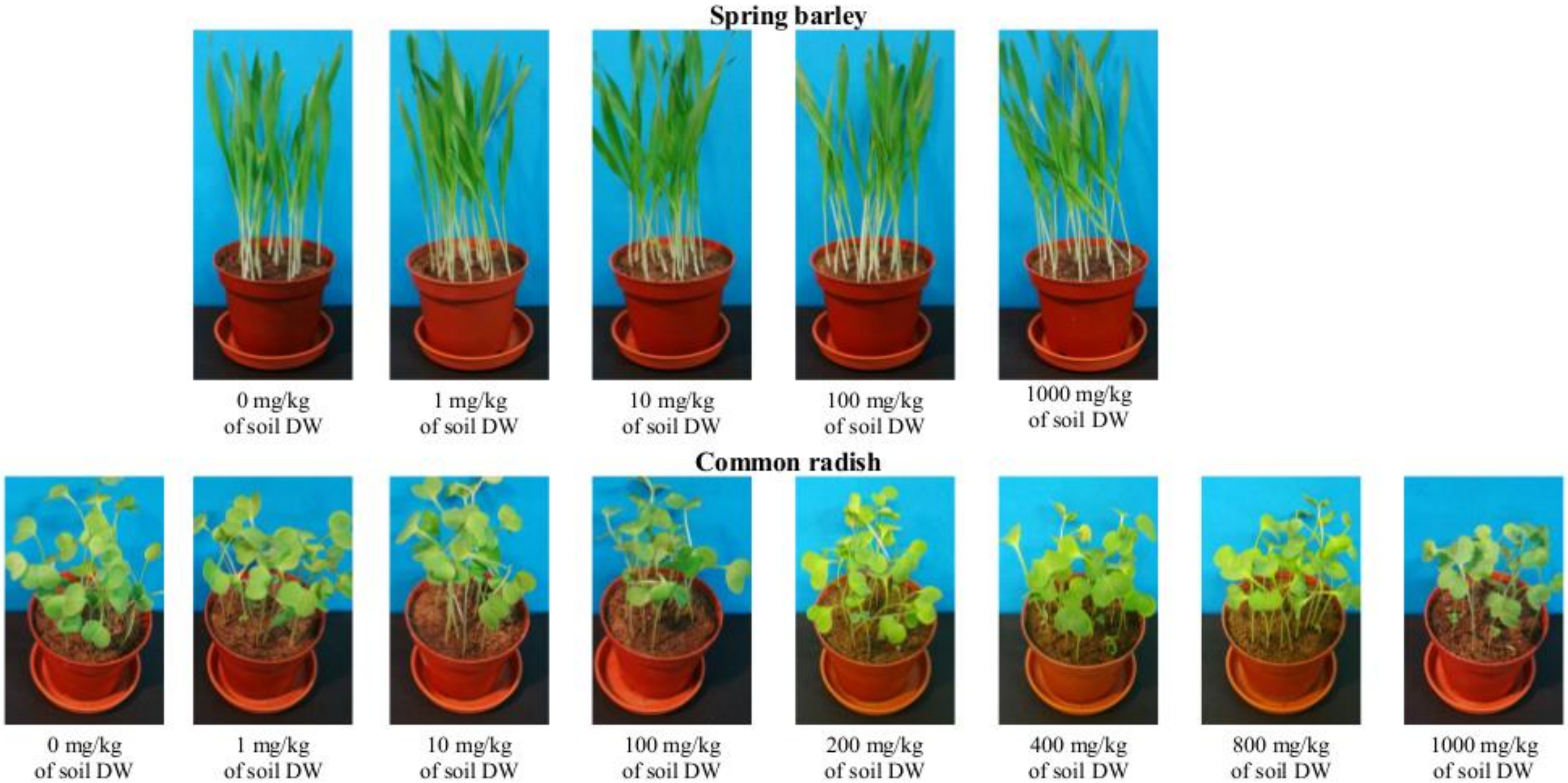


Figure S22. Digital photographs of plants seedlings in soil treated with aqueous solutions of ***(S)-DCA****.*

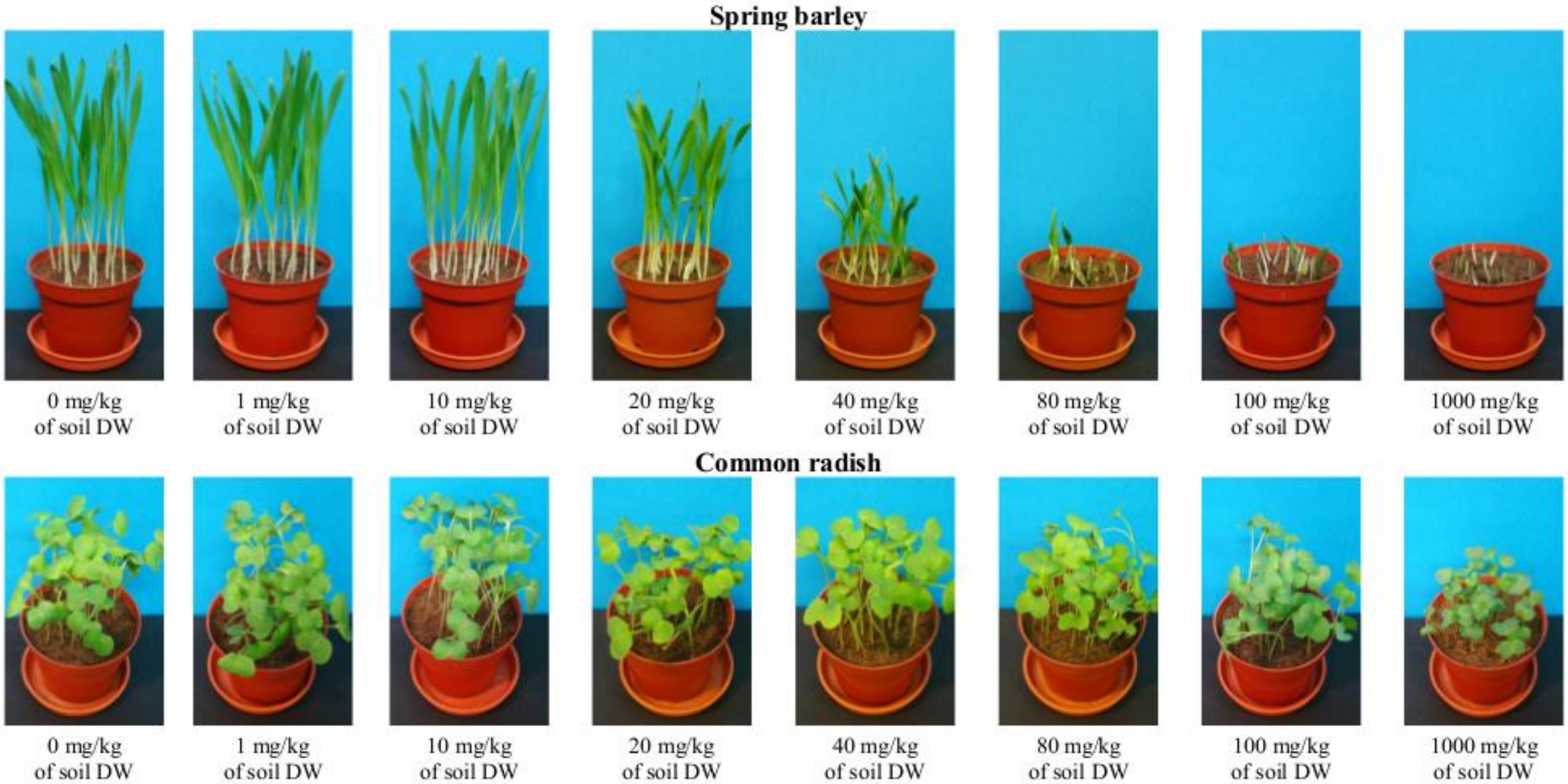


Figure S23. Digital photographs of plants seedlings in soil treated with aqueous solutions of ***(R)-TCA****.*

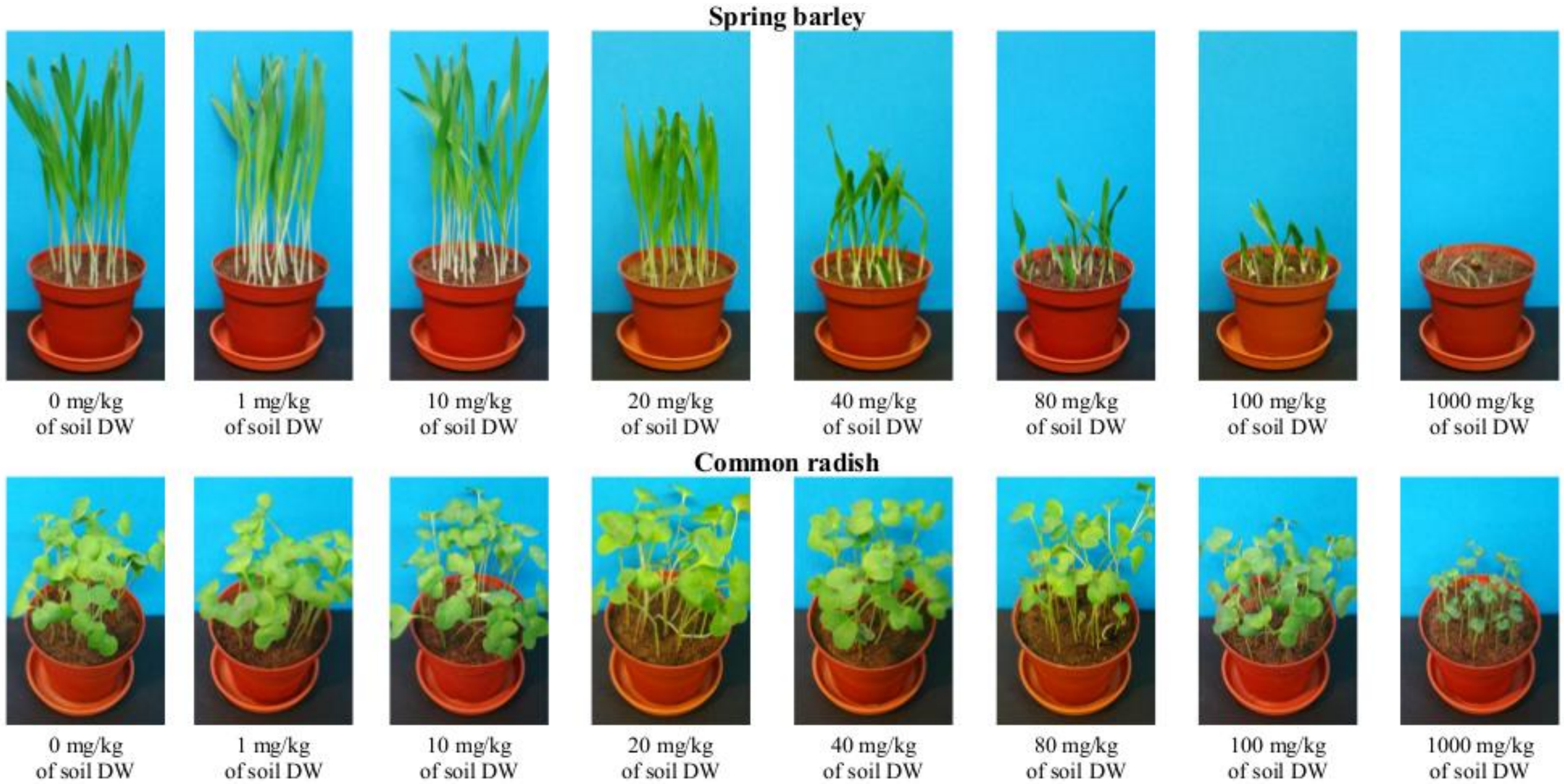


Figure S24. Digital photographs of plants seedlings in soil treated with aqueous solutions of ***(S)-TCA****.*

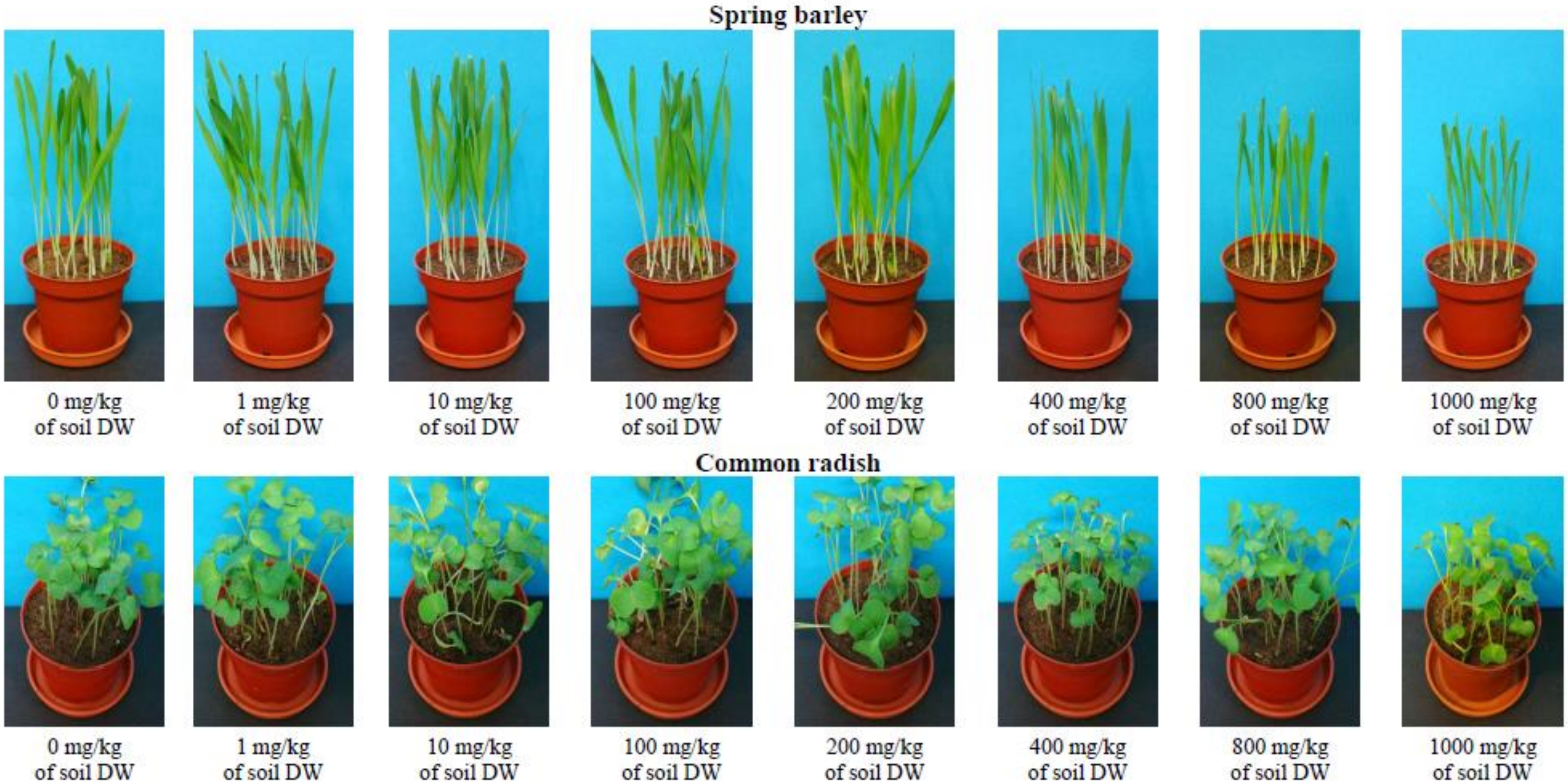


*Figure S25. Digital photographs of plants seedlings in soil treated with aqueous solutions of **(R)-SO_4**.*

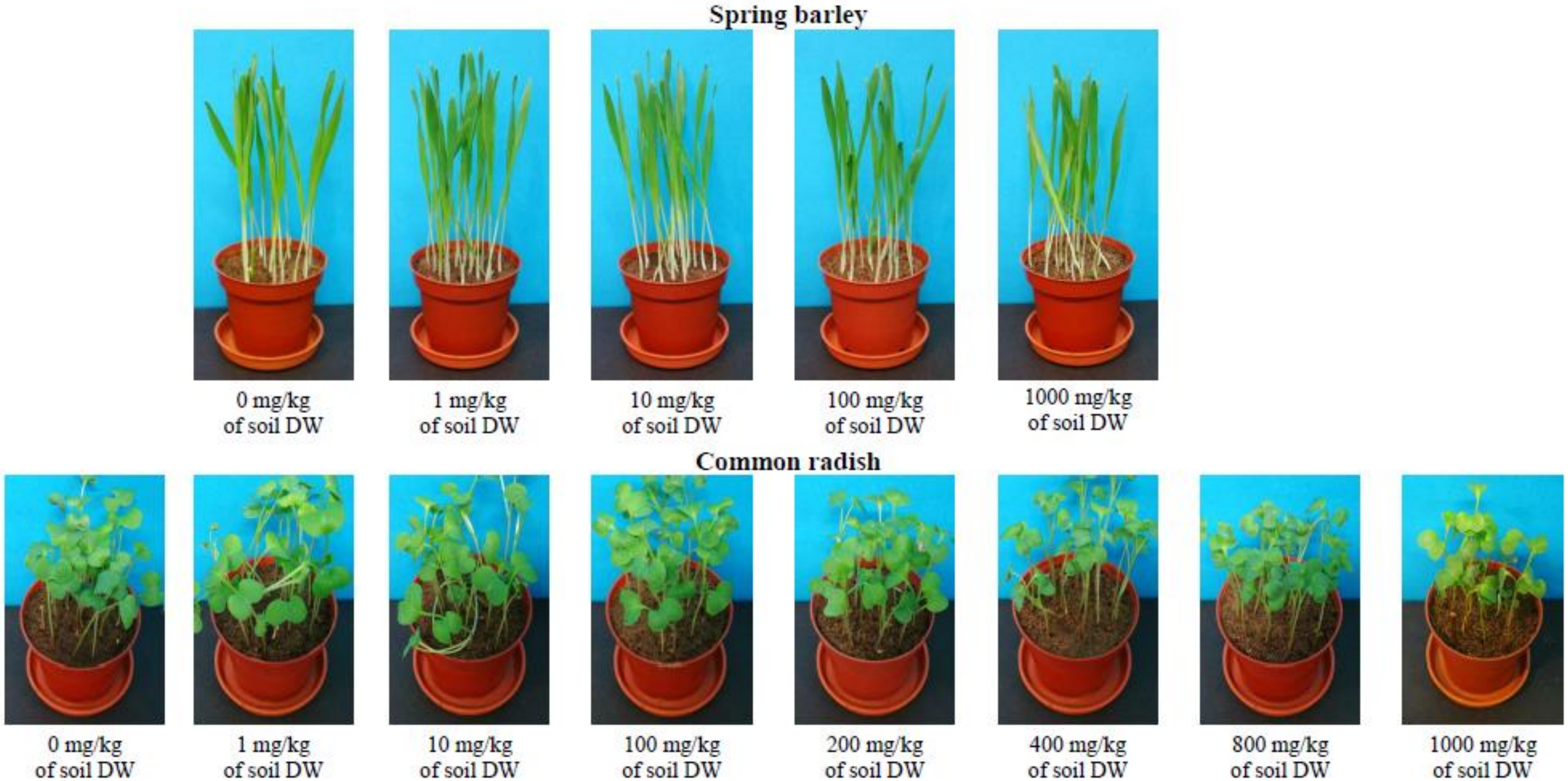


Figure S26. Digital photographs of plants seedlings in soil treated with aqueous solutions of ***(S)-SO$_4$****.*

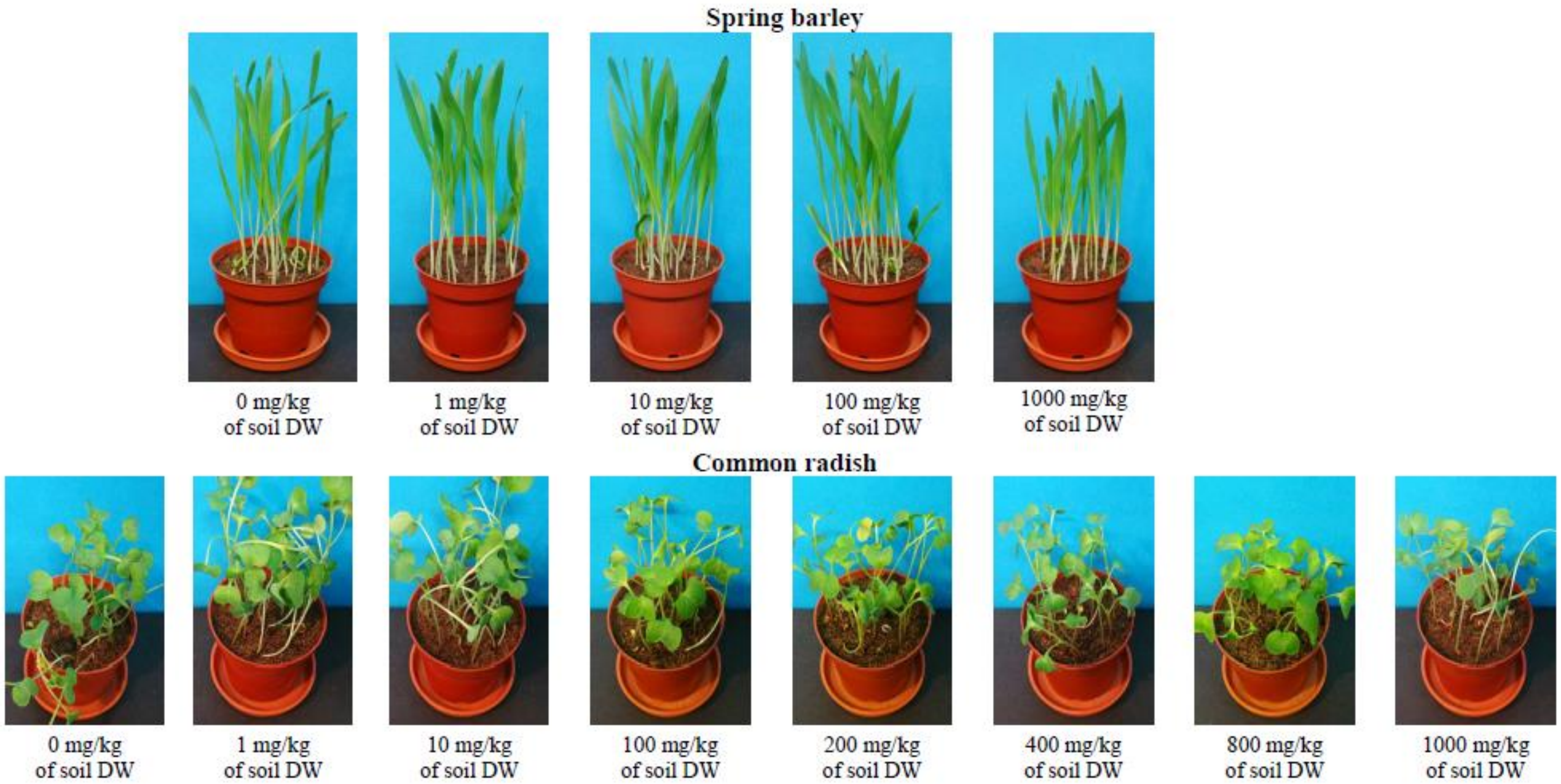


Figure S27. Digital photographs of plants seedlings in soil treated with aqueous solutions of ***DIPA-SO₄****.*

4. Herbicidal activity

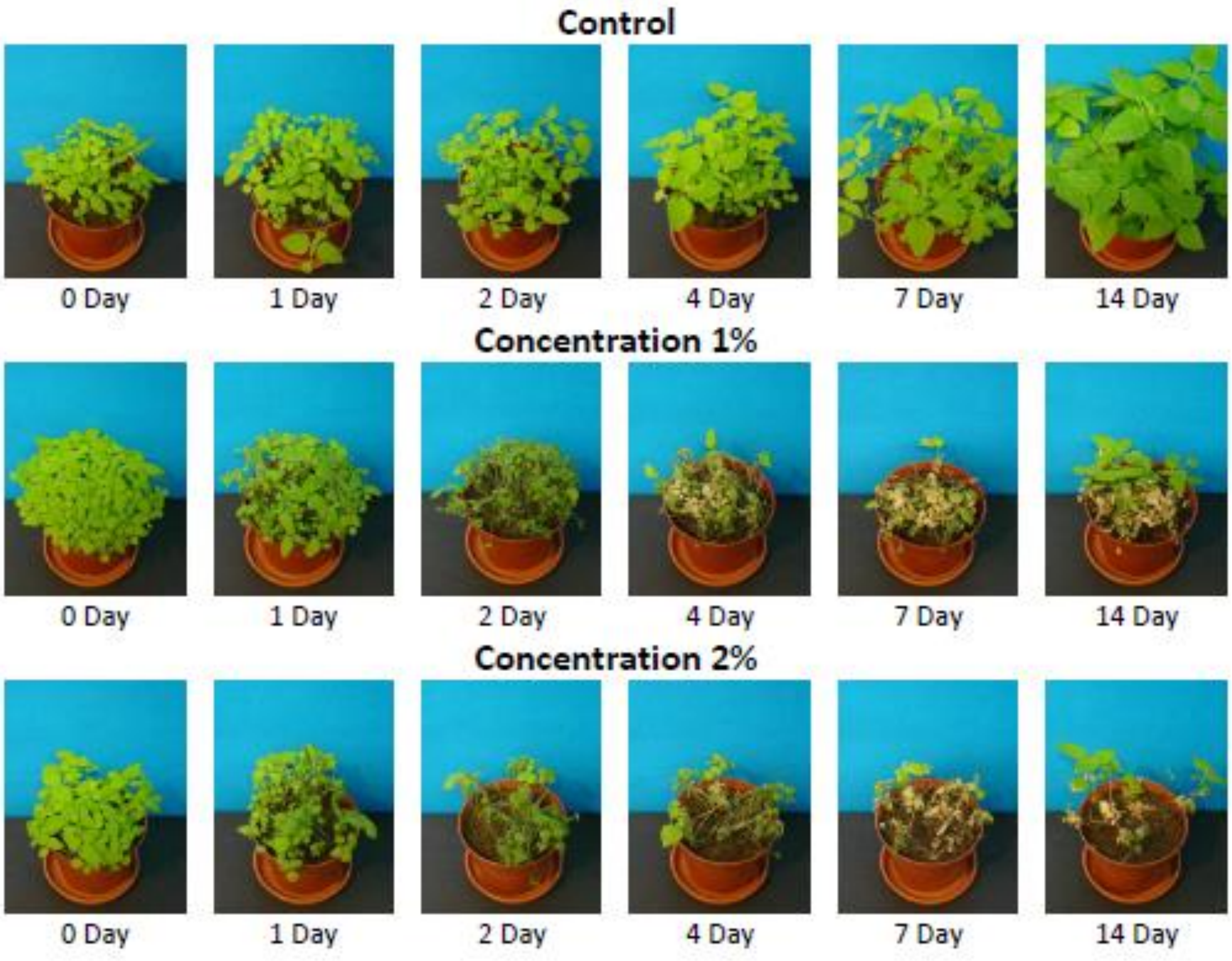


Figure S28. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***(R)-MCA****.*

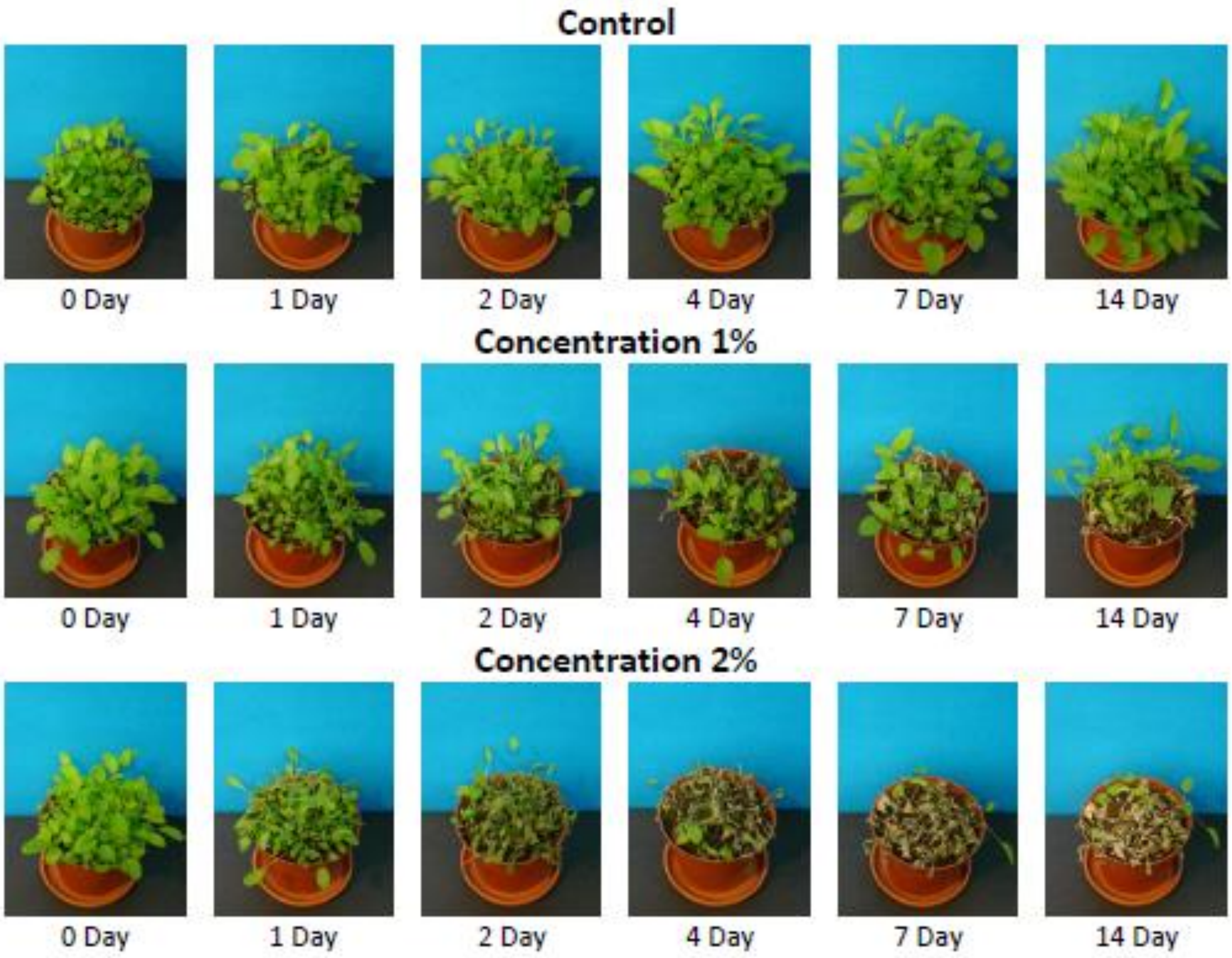


Figure S29. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of ***(R)-MCA****.*

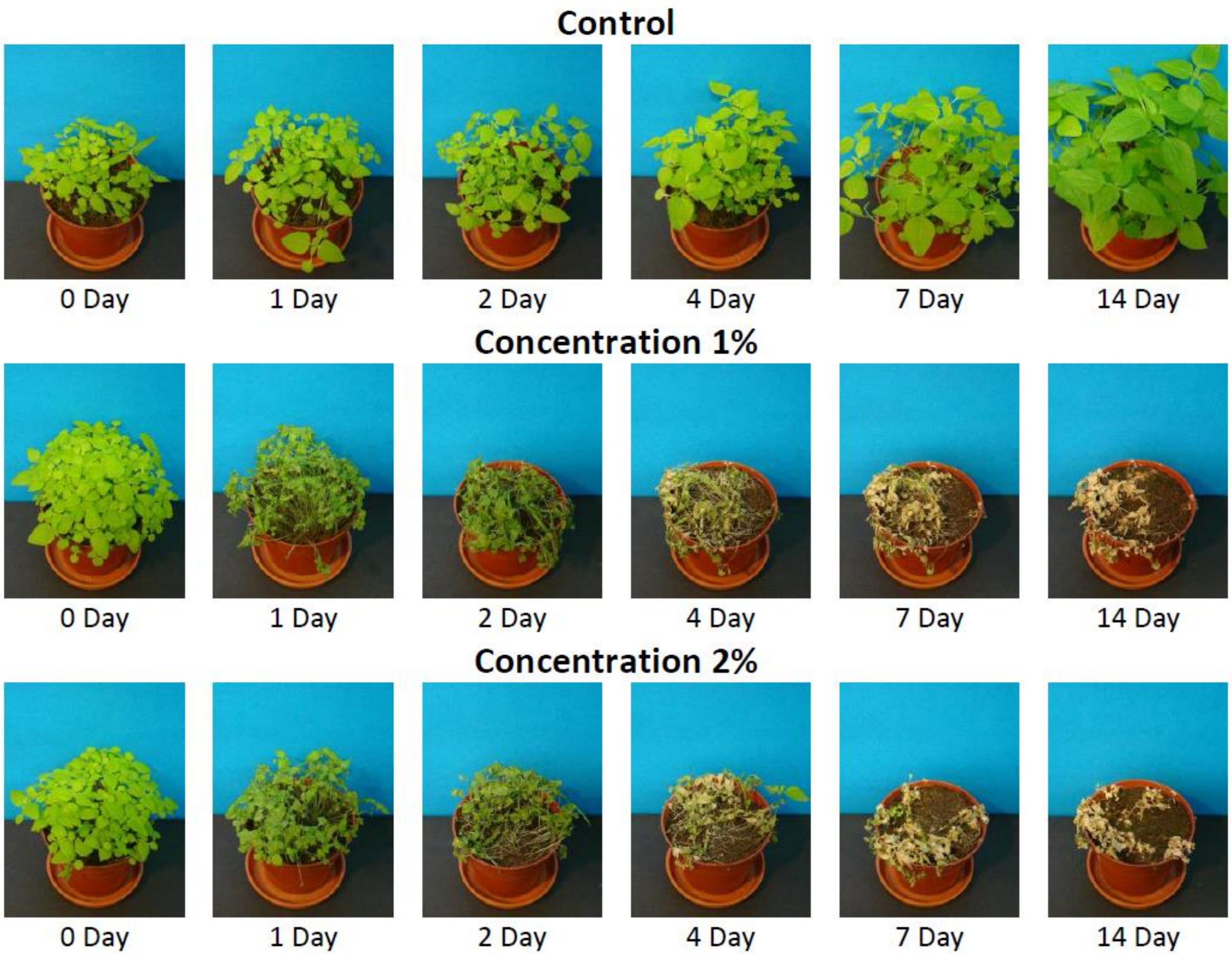


Figure S30. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***(S)-MCA****.*

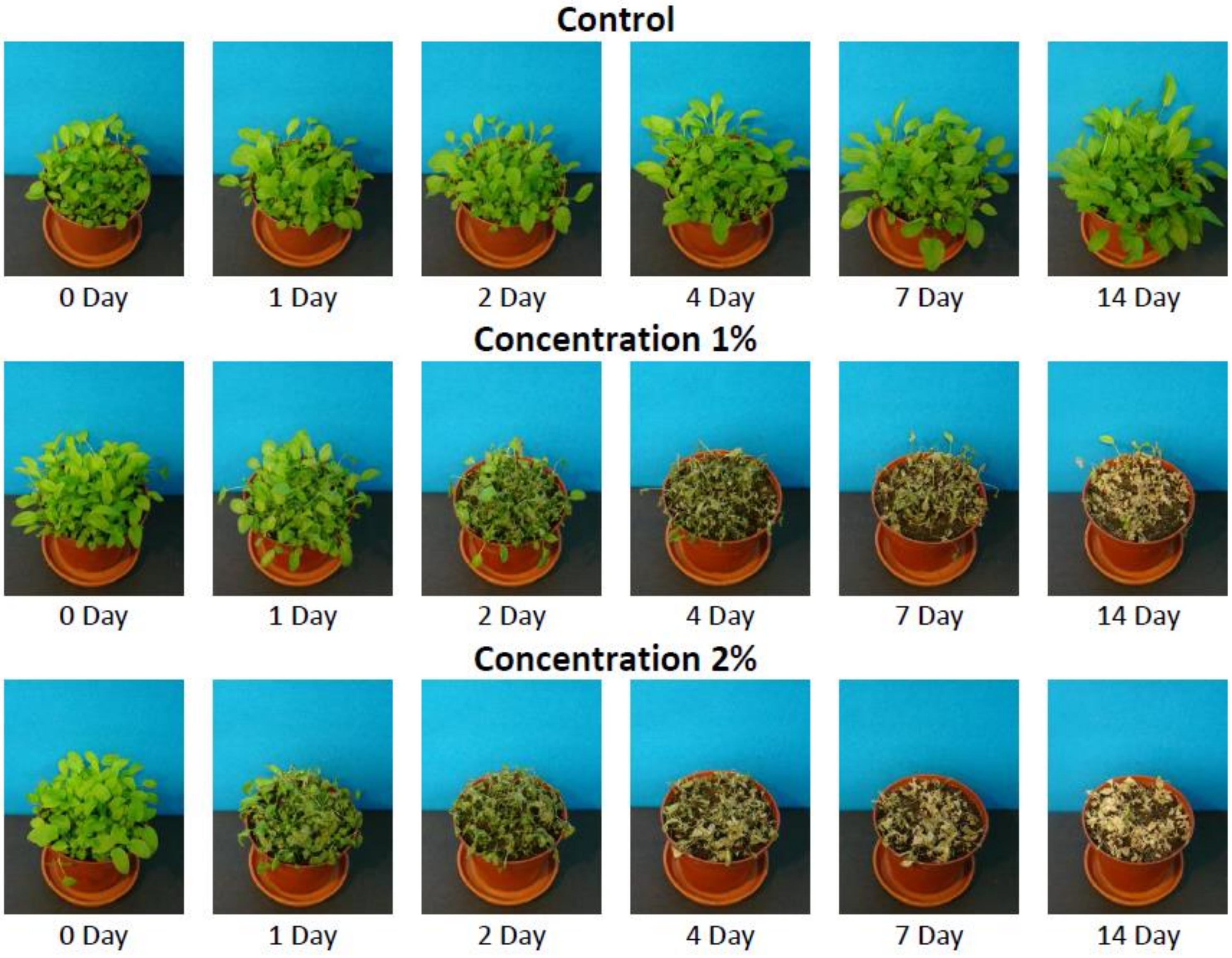


*Figure S31. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of **(S)-MCA**.*

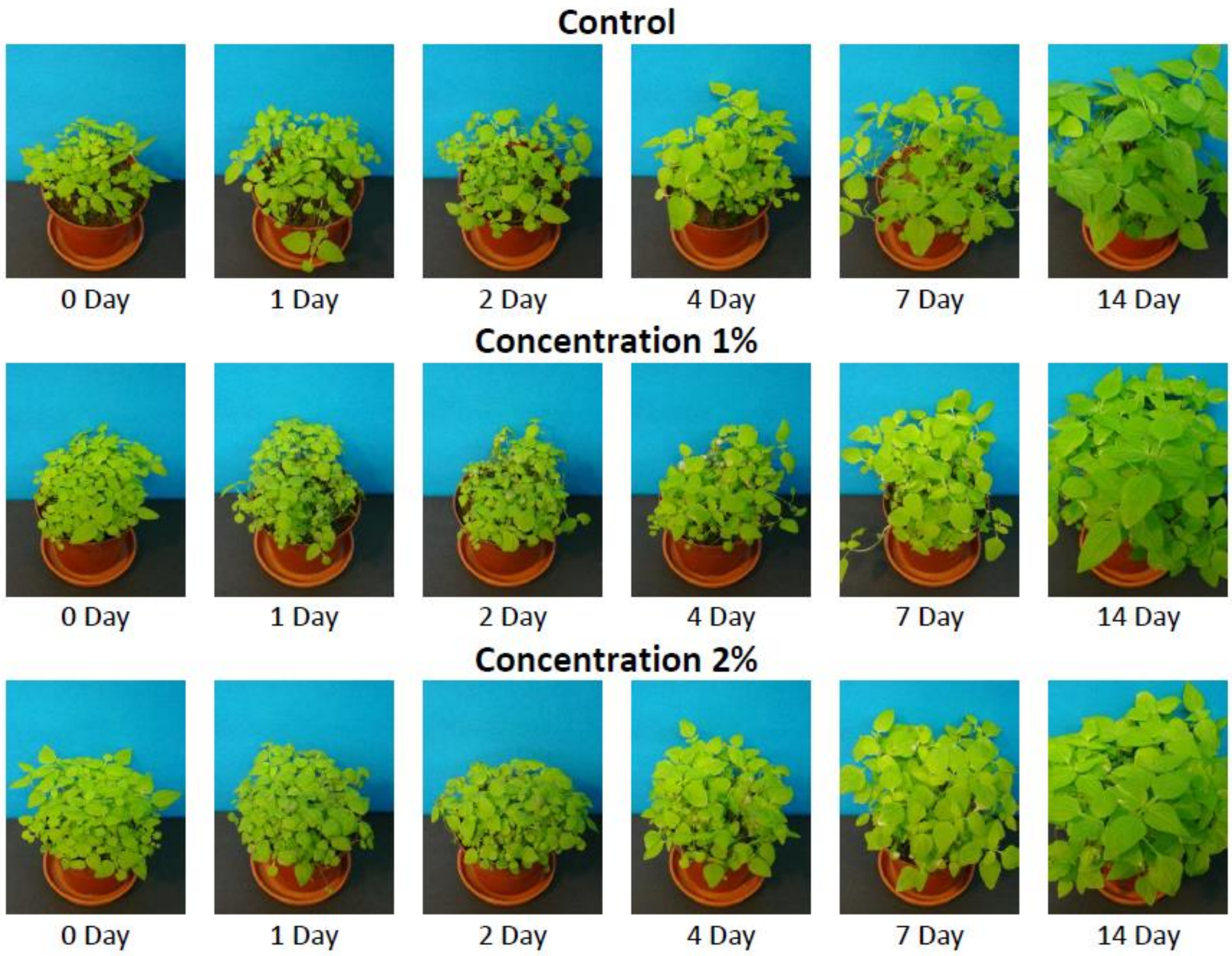


*Figure S32. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of **(R)-DCA**.*

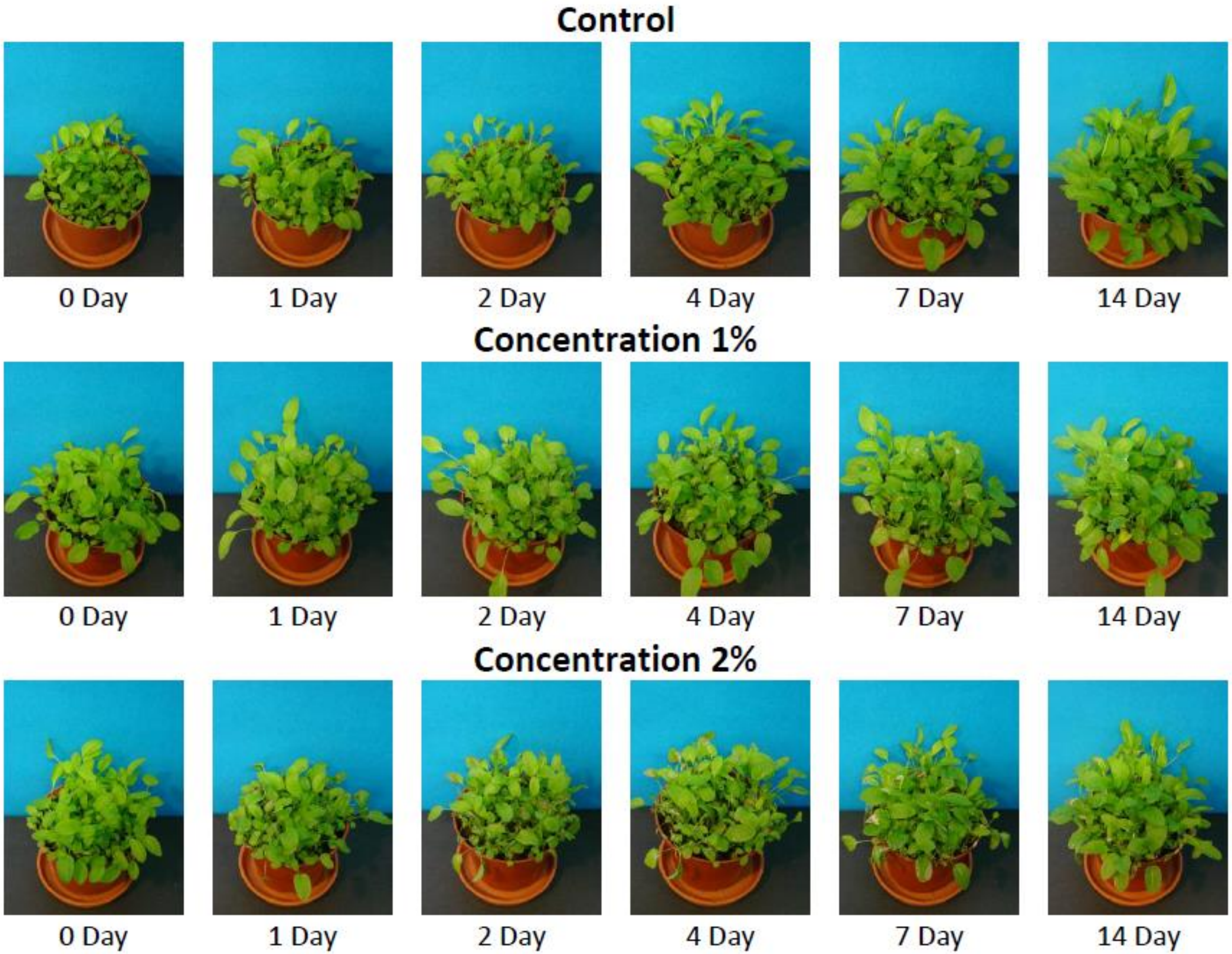


Figure S33. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of ***(R)-DCA****.*

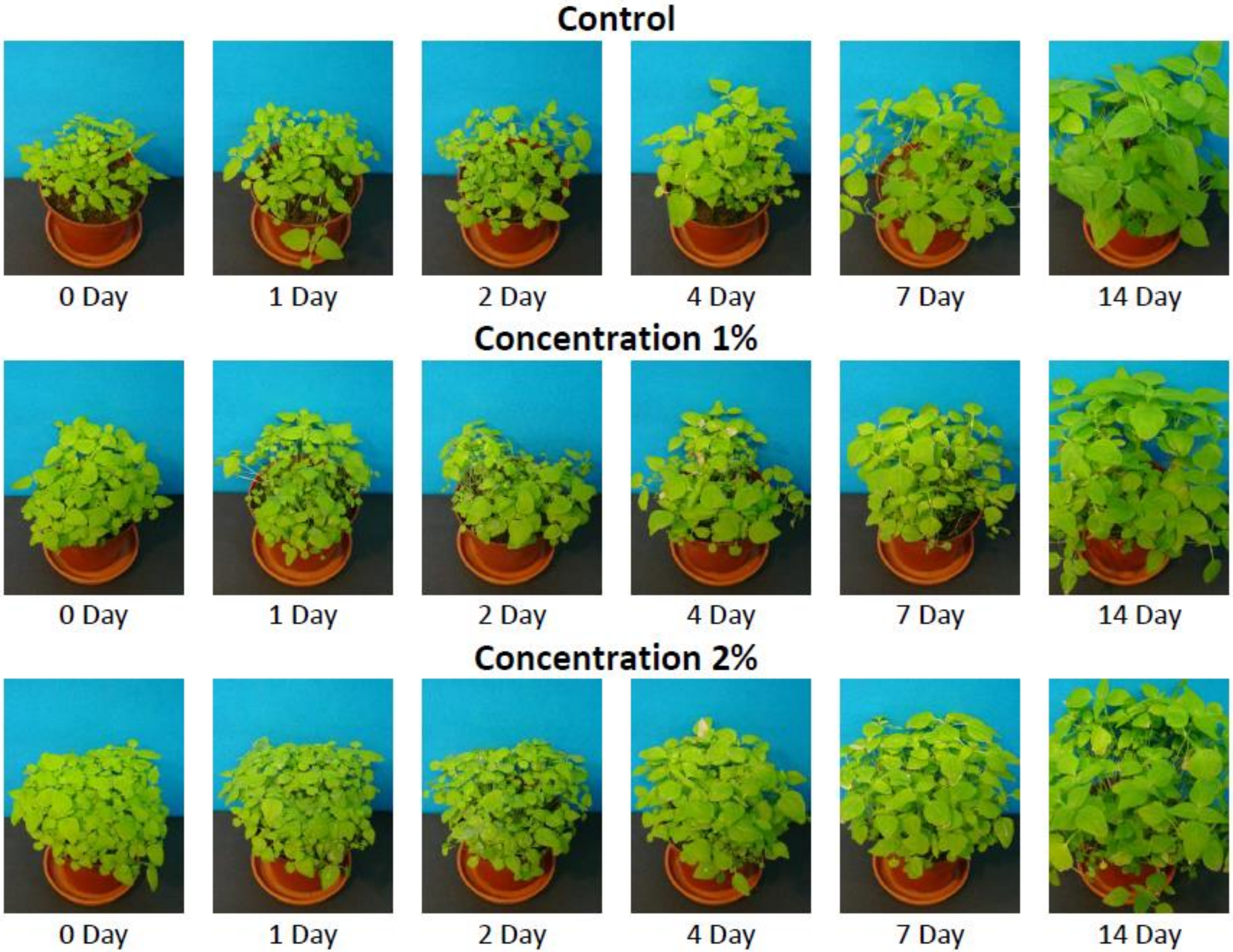


*Figure S34. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of **(S)-DCA**.*

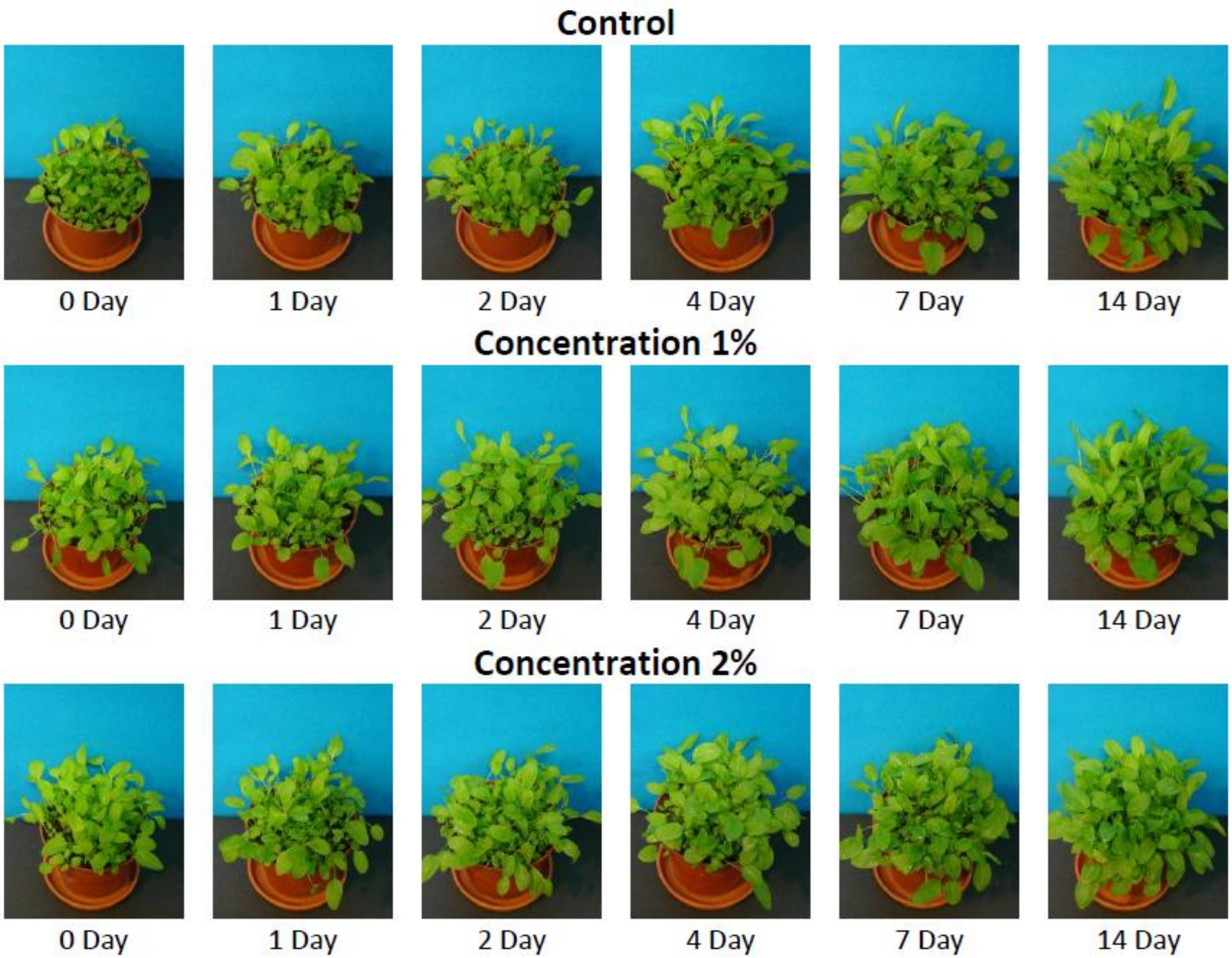


Figure S35. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of ***(S)-DCA****.*

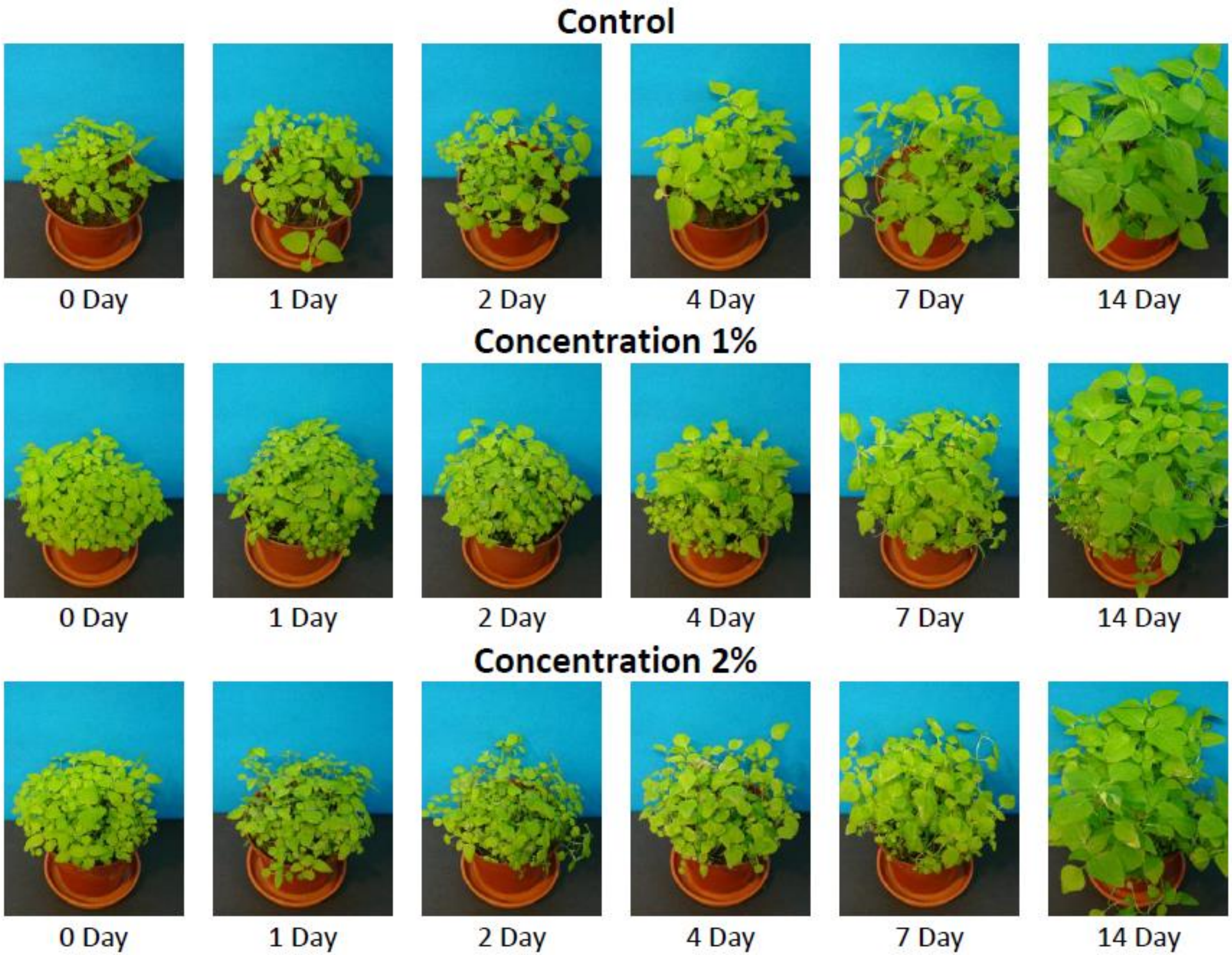


Figure S36. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***(R)-TCA****.*

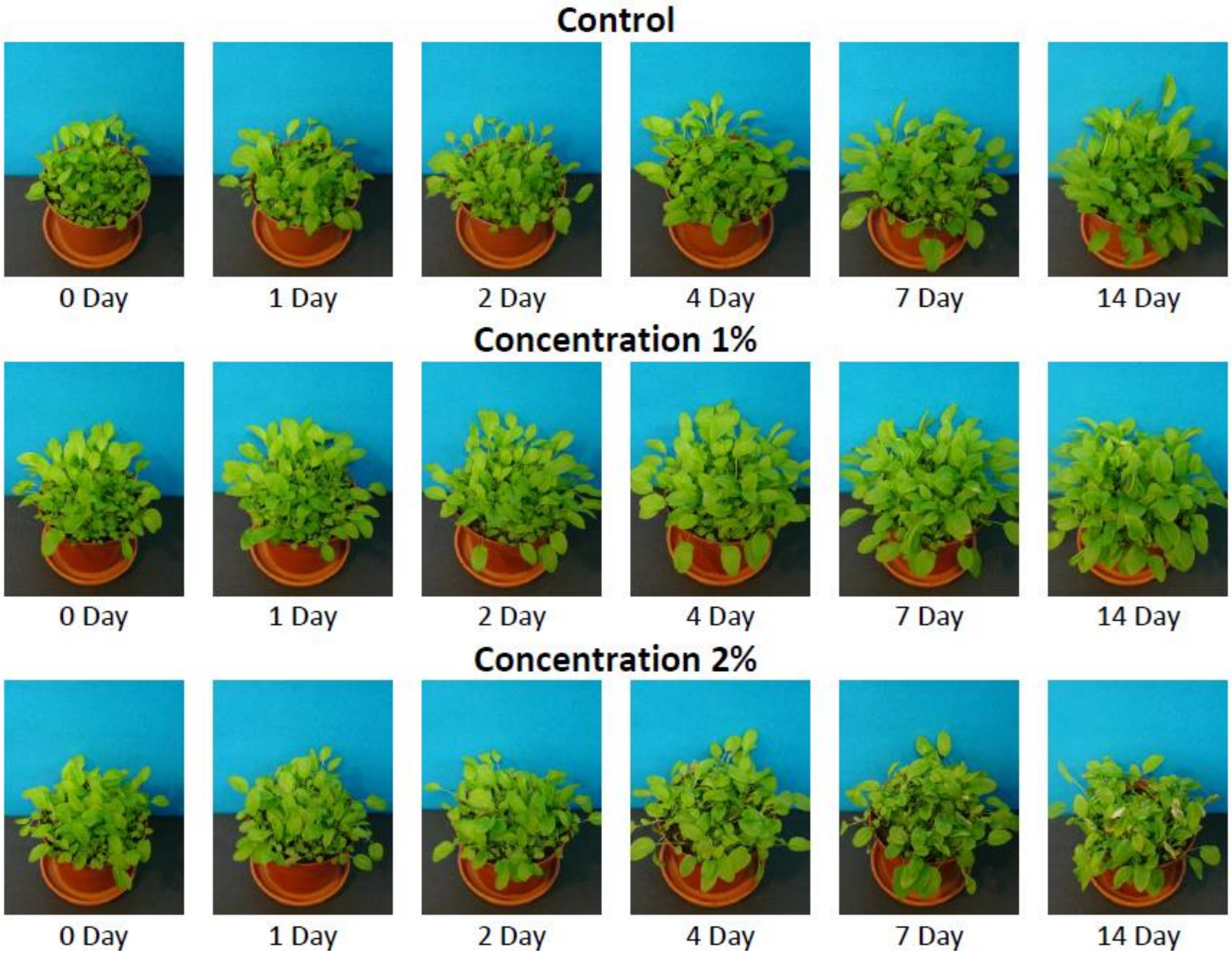


Figure S37. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of ***(R)-TCA****.*

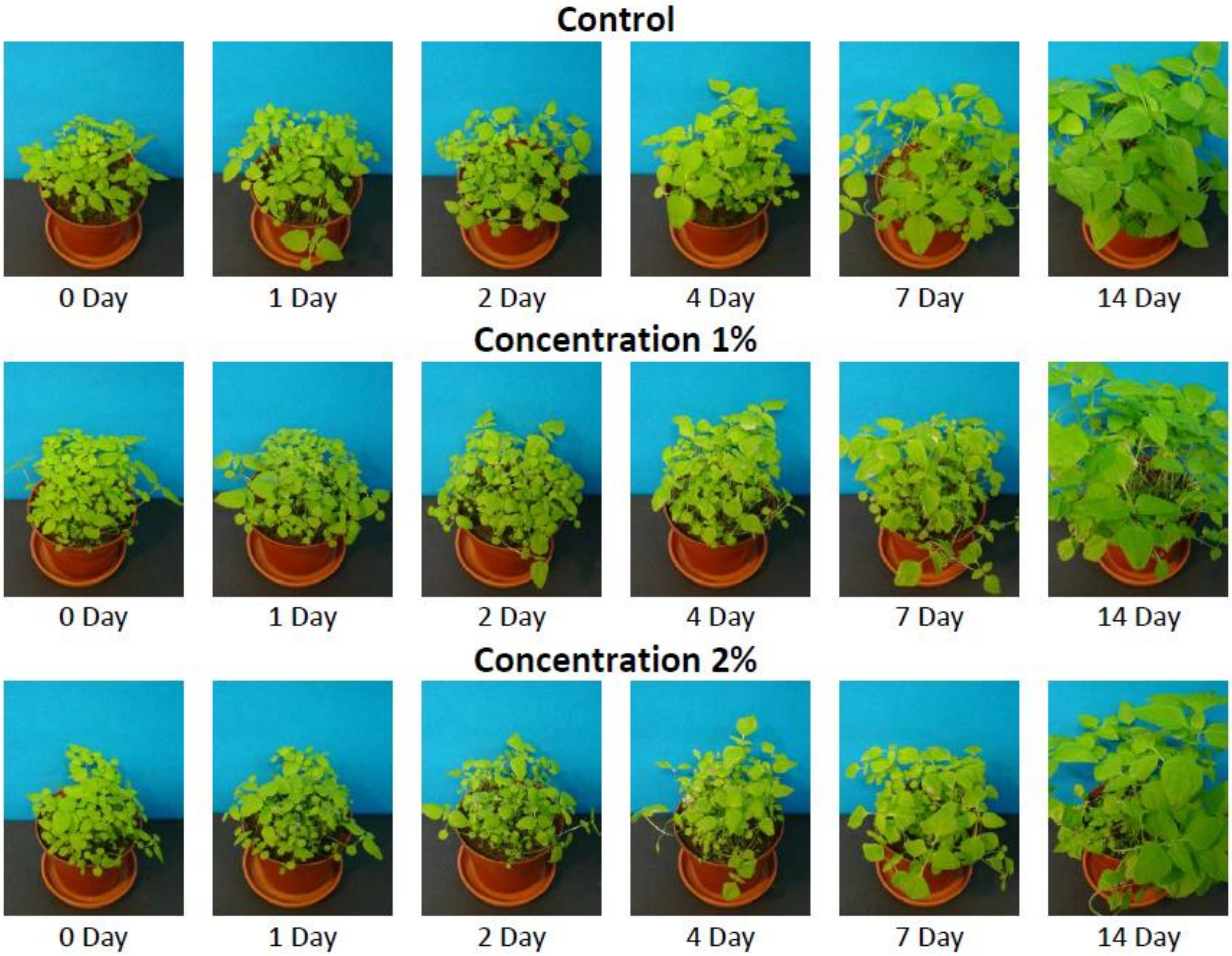


Figure S38. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***(S)-TCA****.*

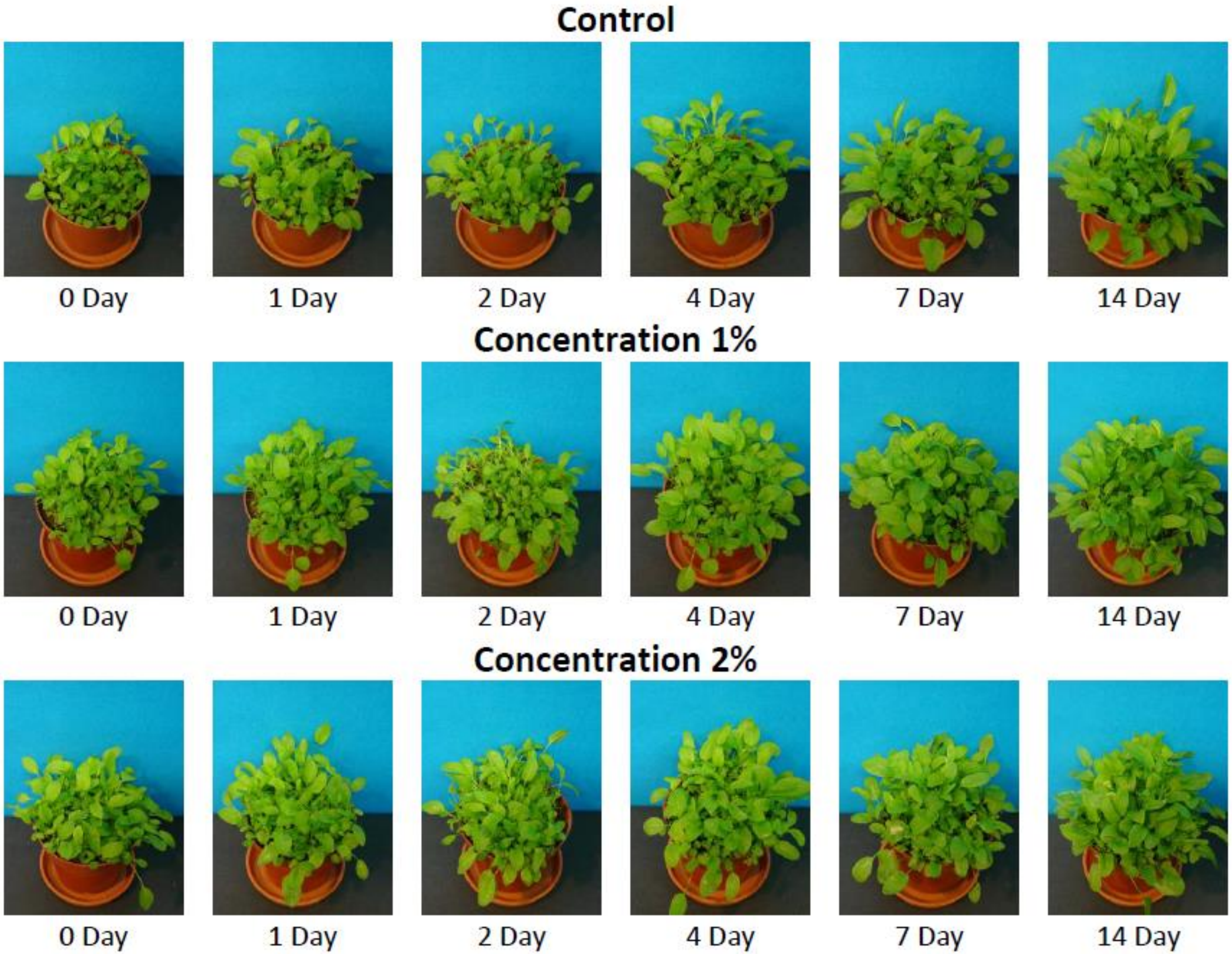


*Figure S39. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of **(S)-TCA**.*

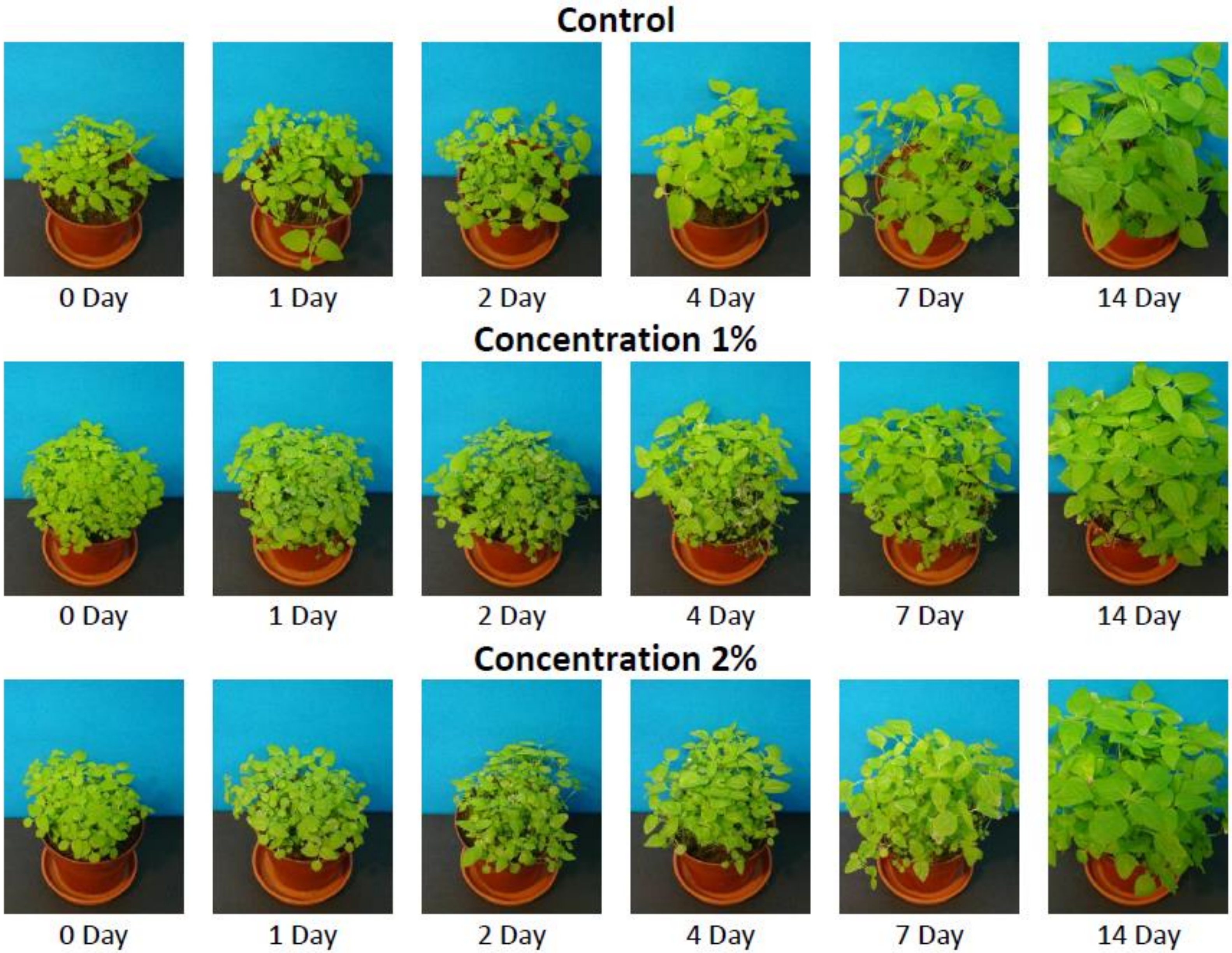


Figure S40. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***(R)-SO_4***.

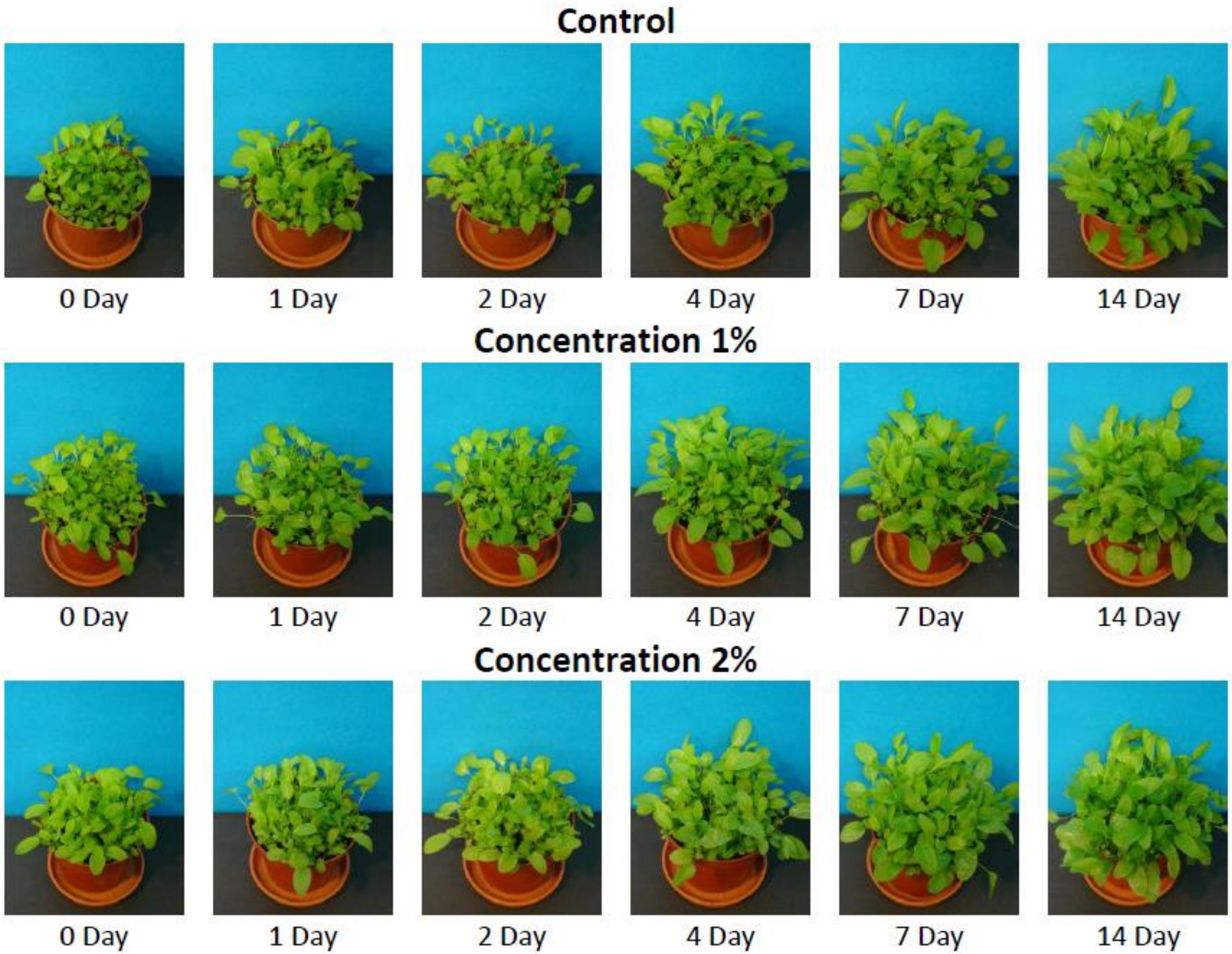


*Figure S41. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of **(R)-SO$_4$**.*

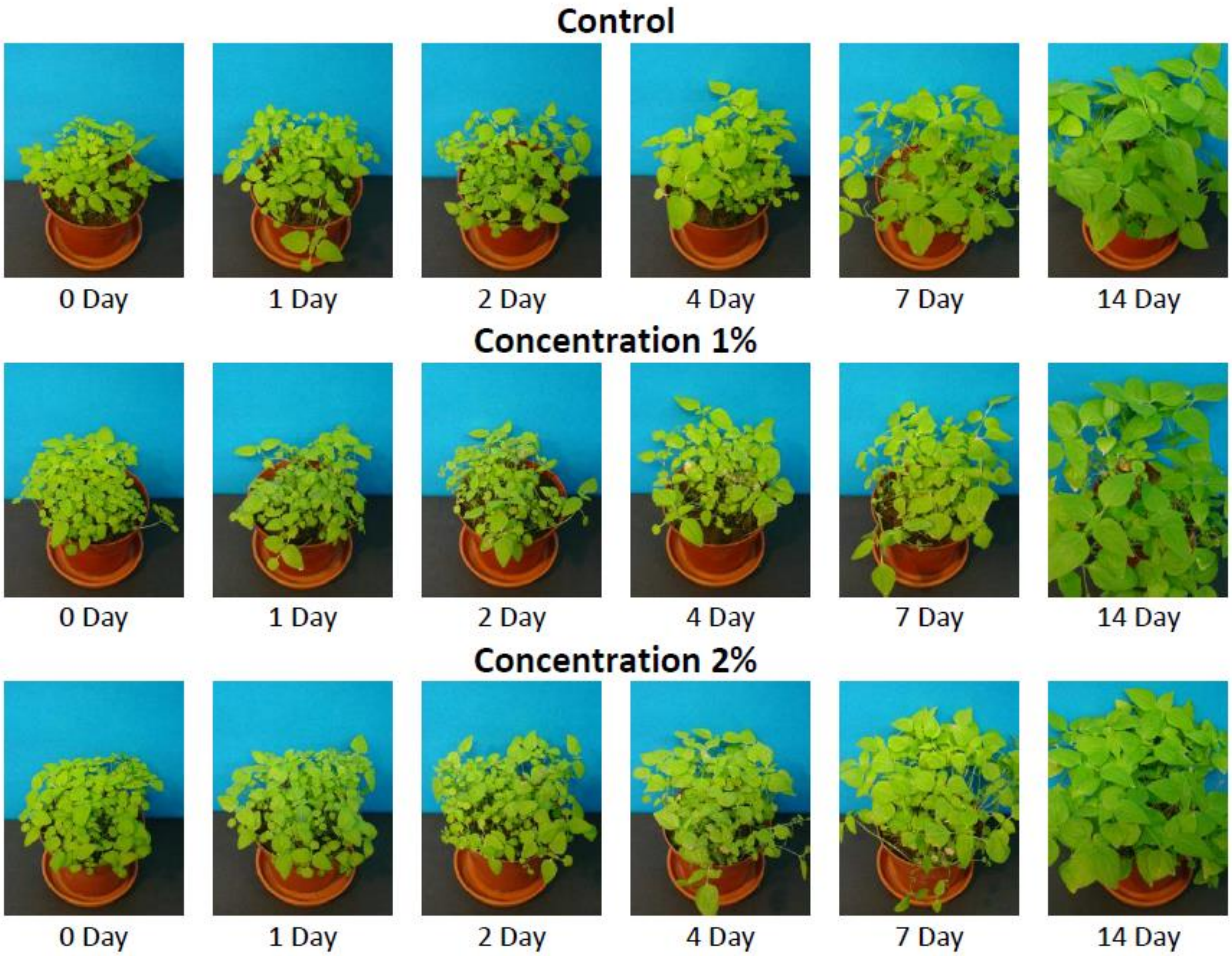


Figure S42. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***(S)-SO_4****.*

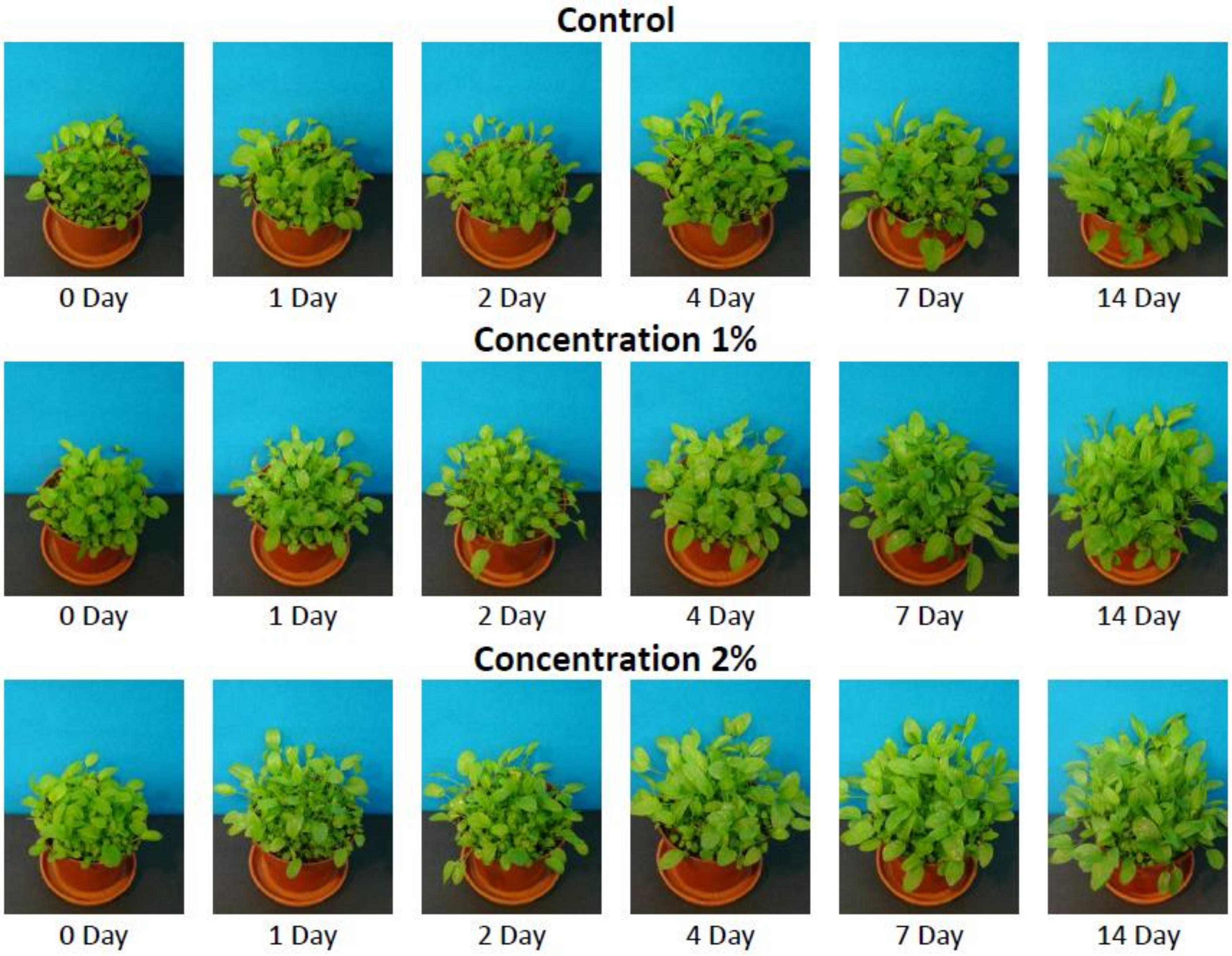


Figure S43. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of ***(S)-SO$_4$****.*

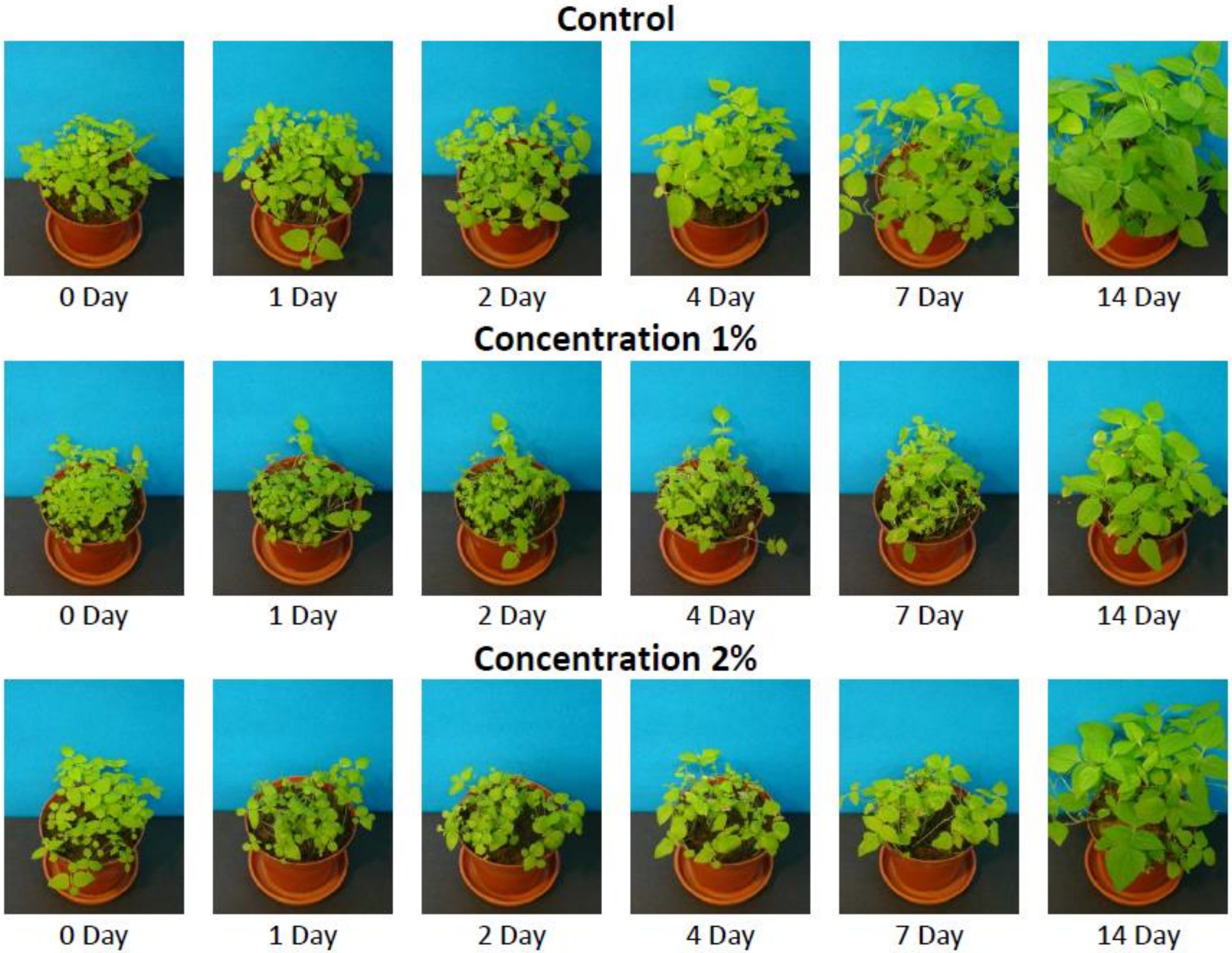


Figure S44. Digital photographs of gallant soldier after the spraying of 1% and 2% aqueous solutions of ***DIPA-SO$_4$****.*

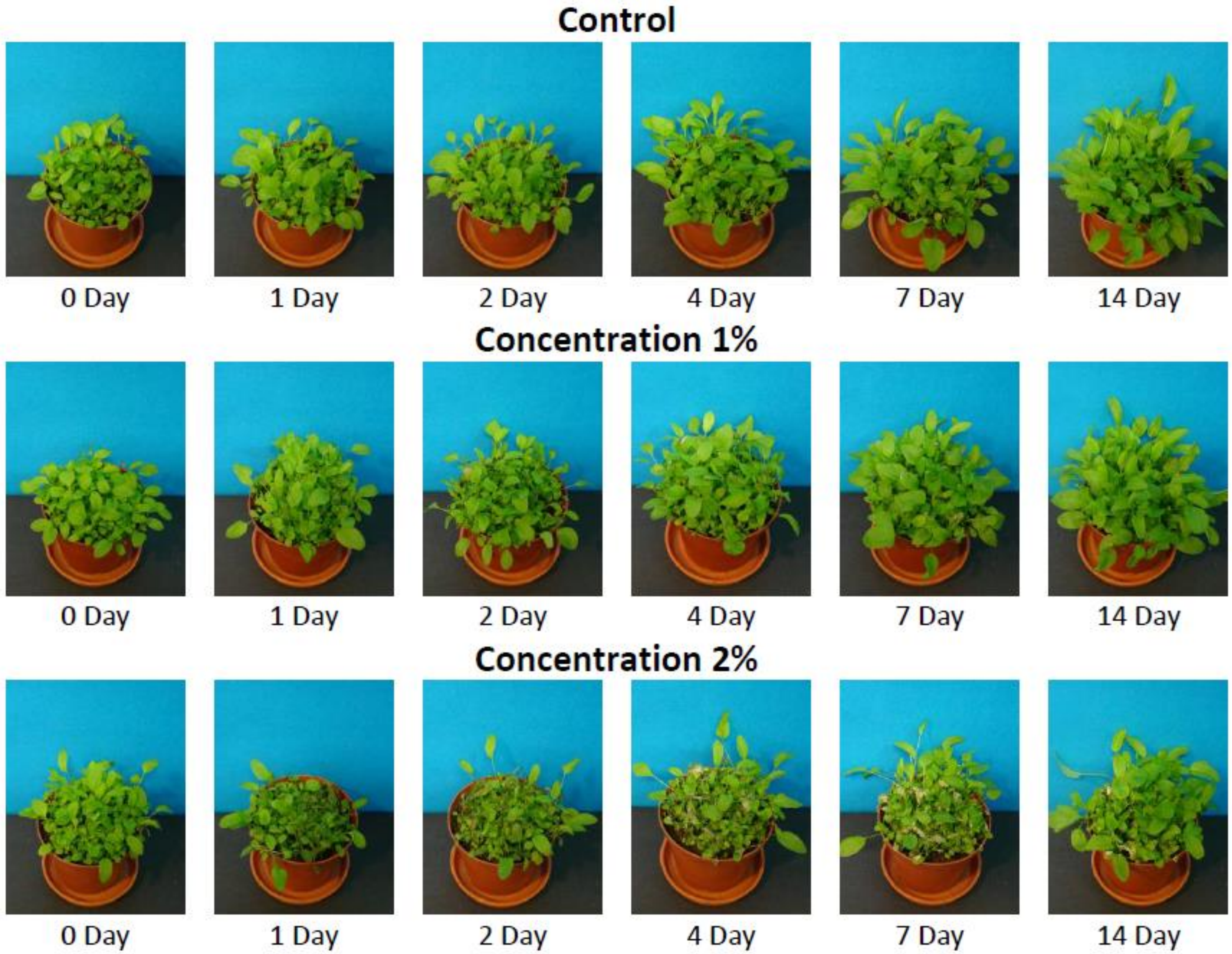


Figure S45. Digital photographs of common sorrel after the spraying of 1% and 2% aqueous solutions of ***DIPA-SO$_4$****.*