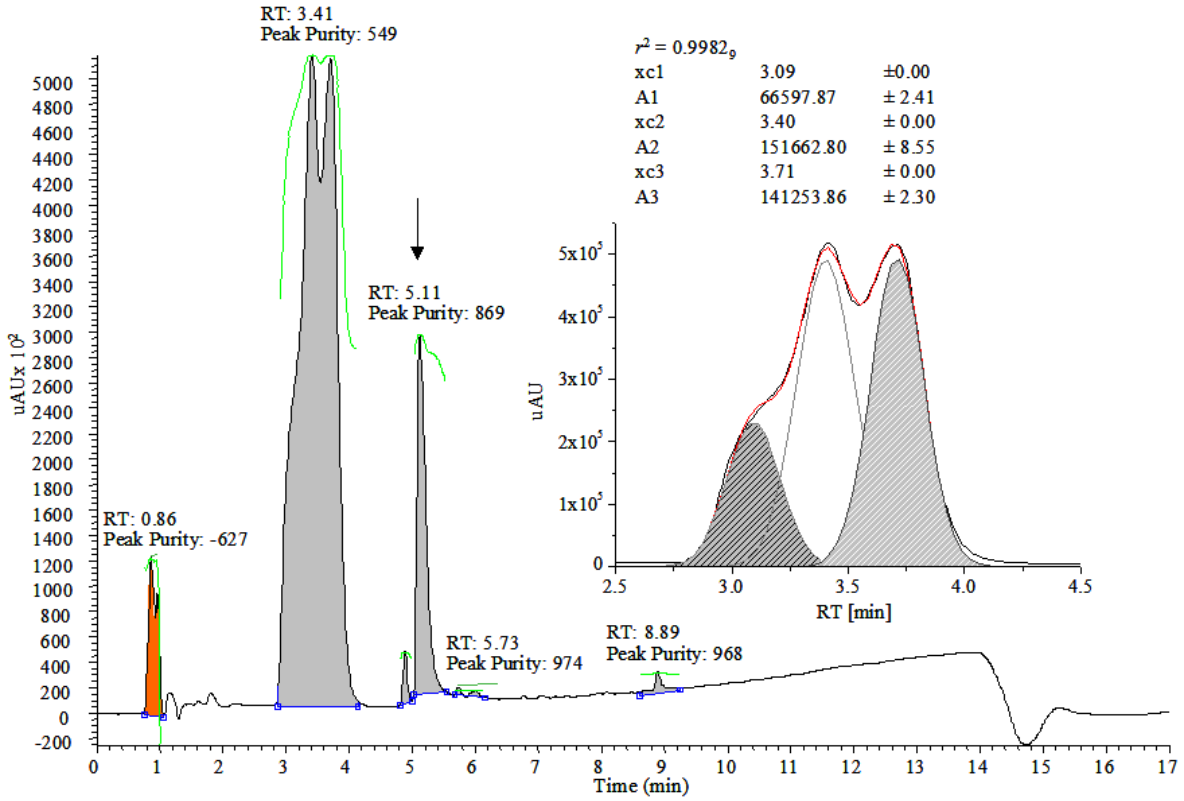
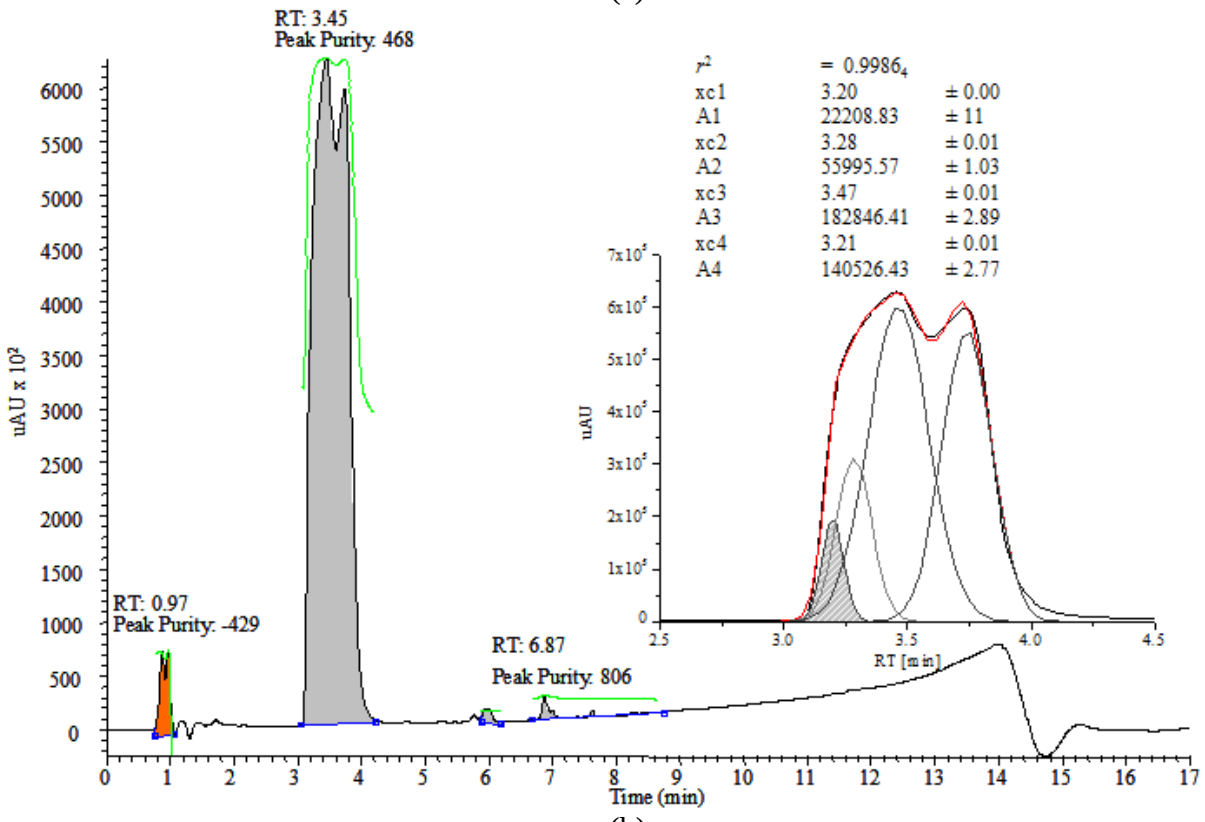
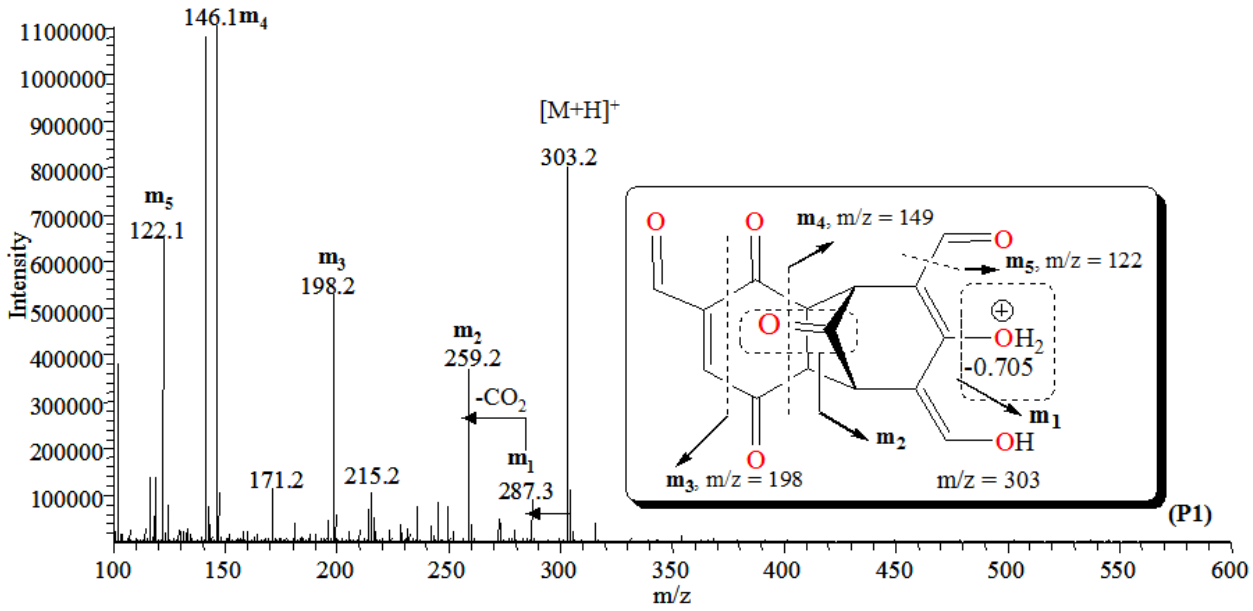
SUPPORTING MATERIALS



(a)

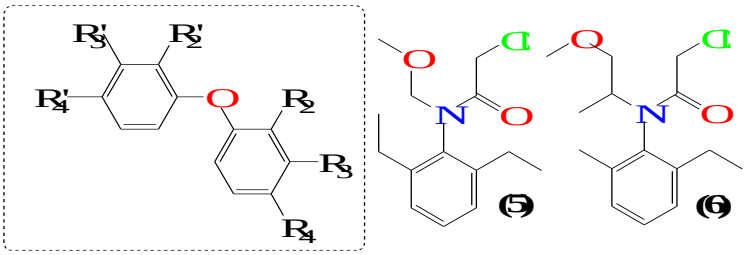


(b)



(c)

Figure S1. Mass chromatograms of 2,5-dihydroxy benzaldehyde (a) and DHA (b) in solvent mixture acetonitrile:methanol 1:1 at recalculated pH = 8.5; Curve fitted patterns within the retention times 2.5–4.5 min (small figures) according [ref. 7 in the main text]; The chemometric data about the peak positions (xc_i) and the integral areas (A_i), where i = 1–4; r^2–regression coefficient; ESI-MS spectra of interacion product labeled as P1; Chemical diagram and mass spectrometric fragmentation schemes; The theoretical q_O(NBO) values, defining the proton accepting positions in the molecular ionic fragments (c).



Scheme S1. Chemical diagrams of studied herbicides (**1**)–(**6**).

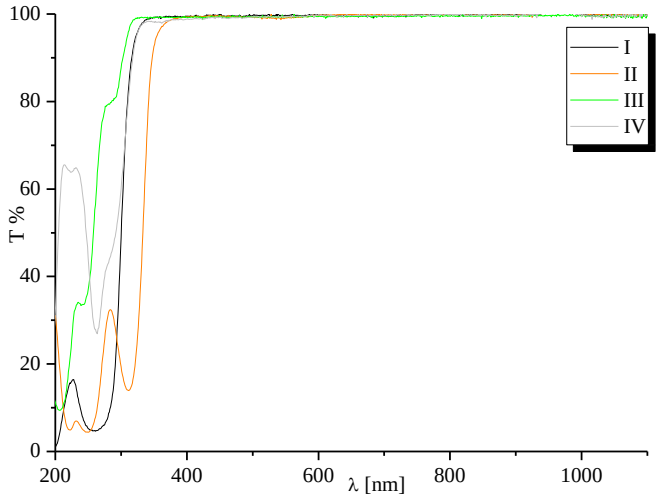


Figure S2. Transmission spectra of **I–IV**

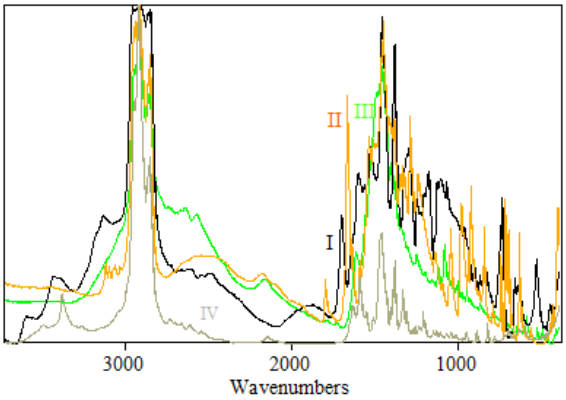


Figure S3. IR-spectra in nujol mull of the matrixes I – IV

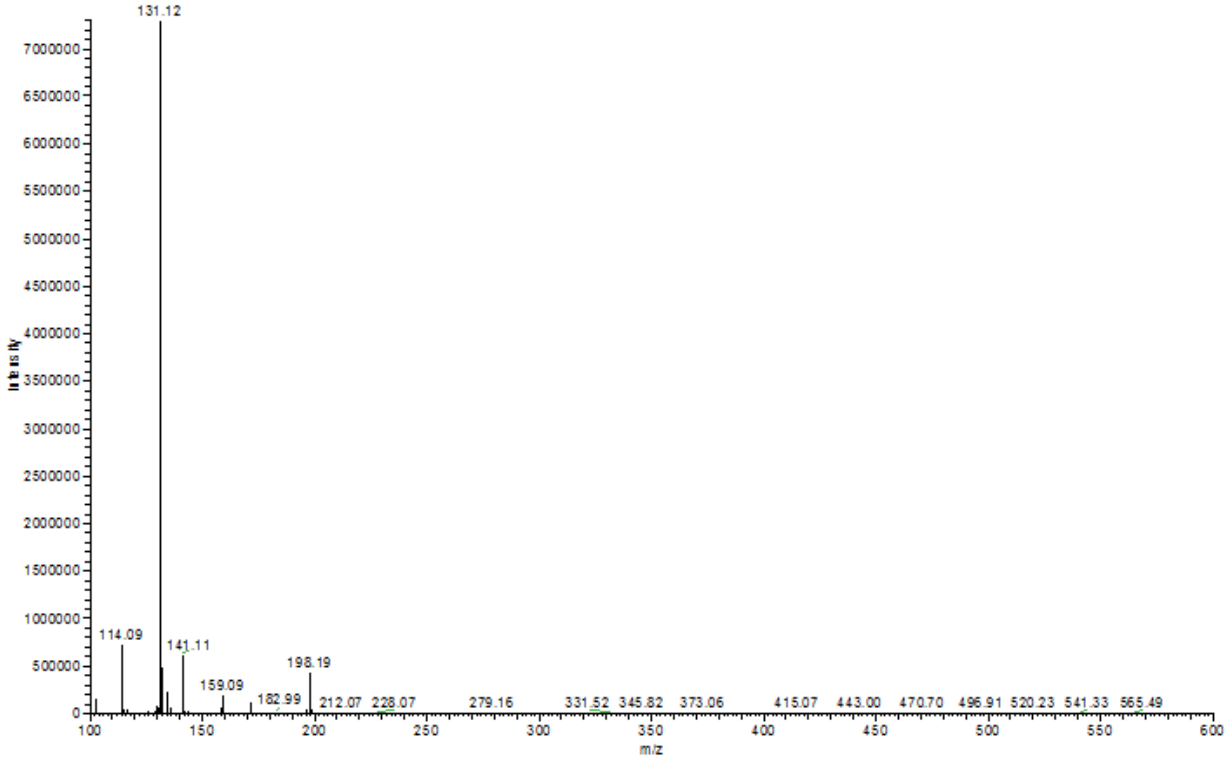


Figure S4. ESI-MS spectrum of **II**

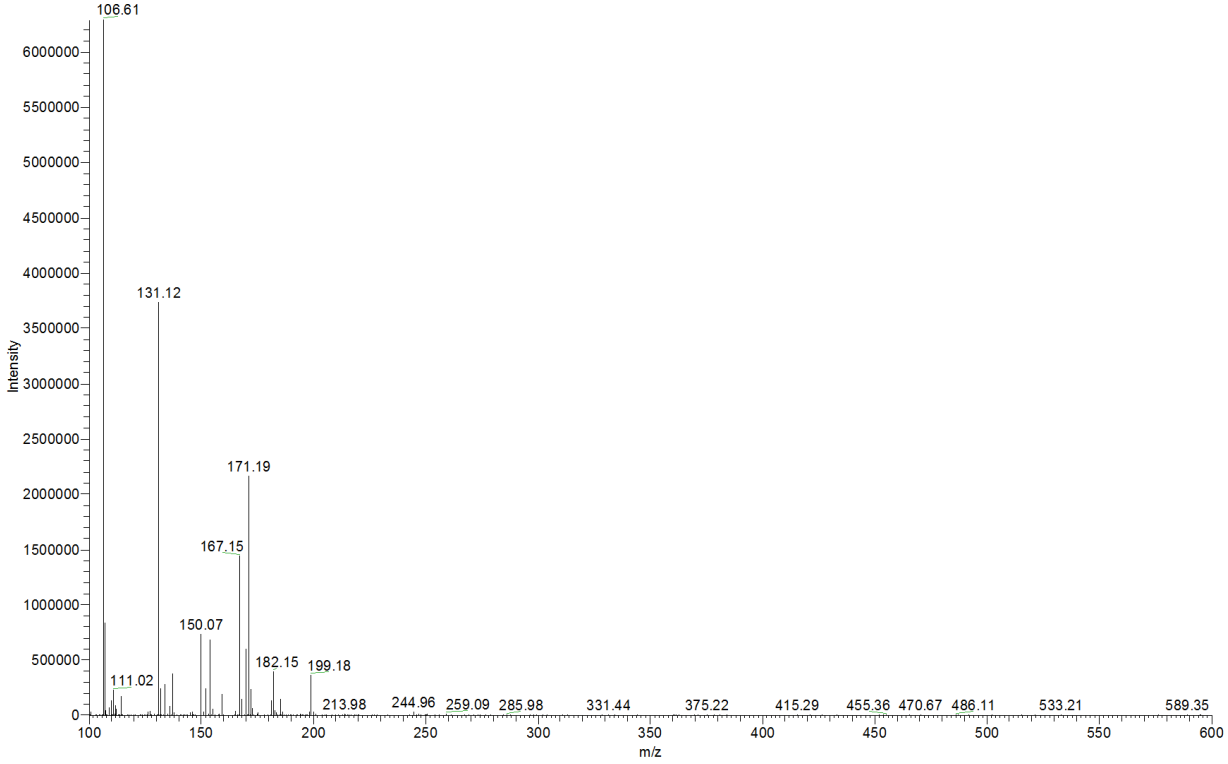
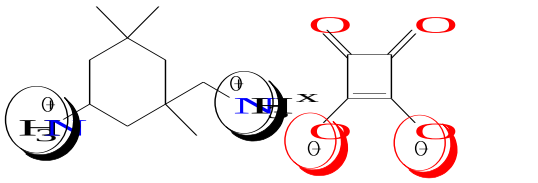


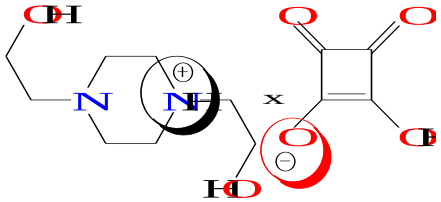
Figure S5. ESI-MS spectrum of isophorone amino nitrimine

Table S1. Crystallographic refinment data

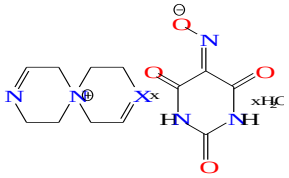
	(I)	**(III)**	**(IV)**
Empirical formula	$C_{14}H_{24}N_2O_4$	$C_{12}H_{20}N_{20}O_6$	$C_{16}H_{20}N_9O_{19}$
M_r	430.41	288.30	498.41
Crystal size	0.28×0.18×0.13	0.33×0.28×0.14	0.11×0.07×0.04
Crystal system	Orthrhombic	Monoclinic	Monoclinic
Space group	P *c a* 2_1	$P2_1/c$	C2/*c*
T [K]	300(2)	293(2)	300(2)
λ [Å]	0.71073	0.71073	0.71073
a [Å]	13.520(3)	8.573(5)	26.766(6)
b [Å]	8.4840(19)	8.663(5)	11.962(2)
c [Å]	13.632(3)	10.021(5)	7.0676(16)
α [°]	90	90	90
β [°]	90	121.11(4)	100.866(7)
γ [°]	90	90	90
V [Å]	1563.6(6)	637.2(6)	2222.2(8)
Z	4	2	4
μ [mm^{-1}]	0.088	0.121	0.126
ρ_{calc} [mg m^{-3}]	1.208	1.503	1.490
2θ [°]	25.14	24.25	25.06
Reflections collected	8444	5583	10169
Goodness-of-fit on F^2	0.990	1.026	1.222
R_1 [$I>2\sigma(I)$]	0.0441	0.0880	0.0866



I



II



III

Scheme S2. Chemical diagram of the crystals **I**–**III**

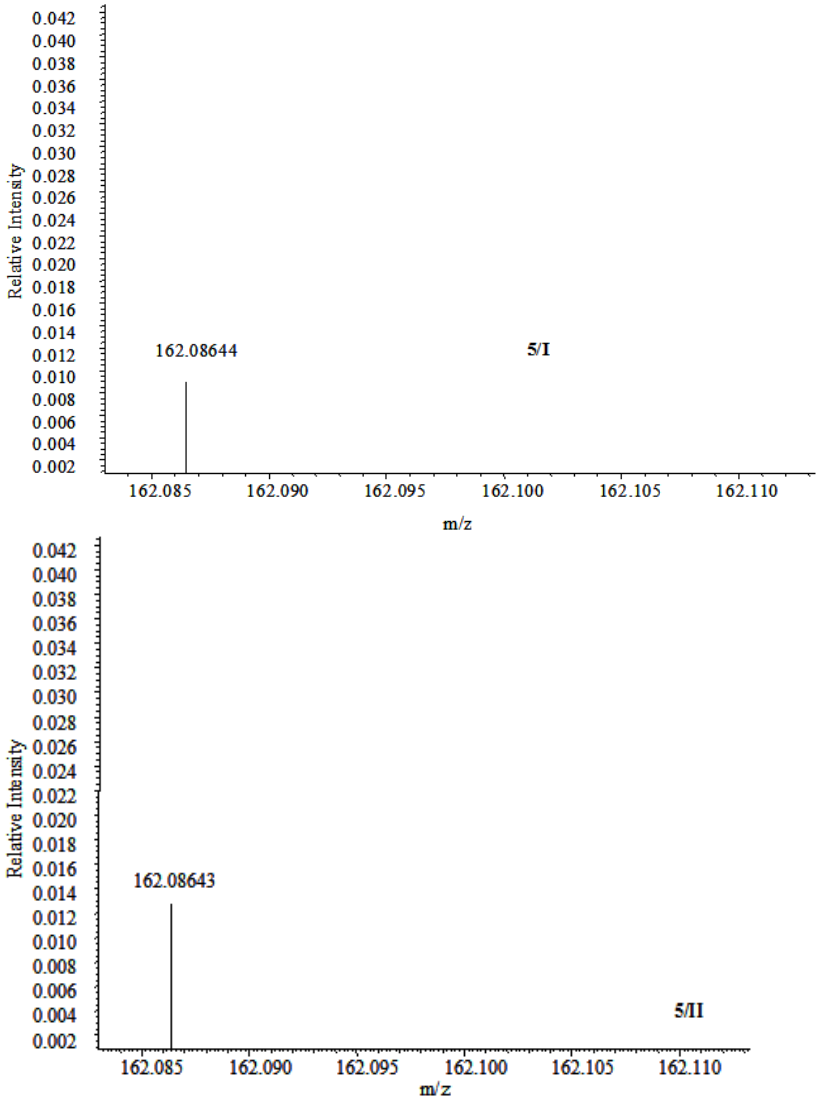
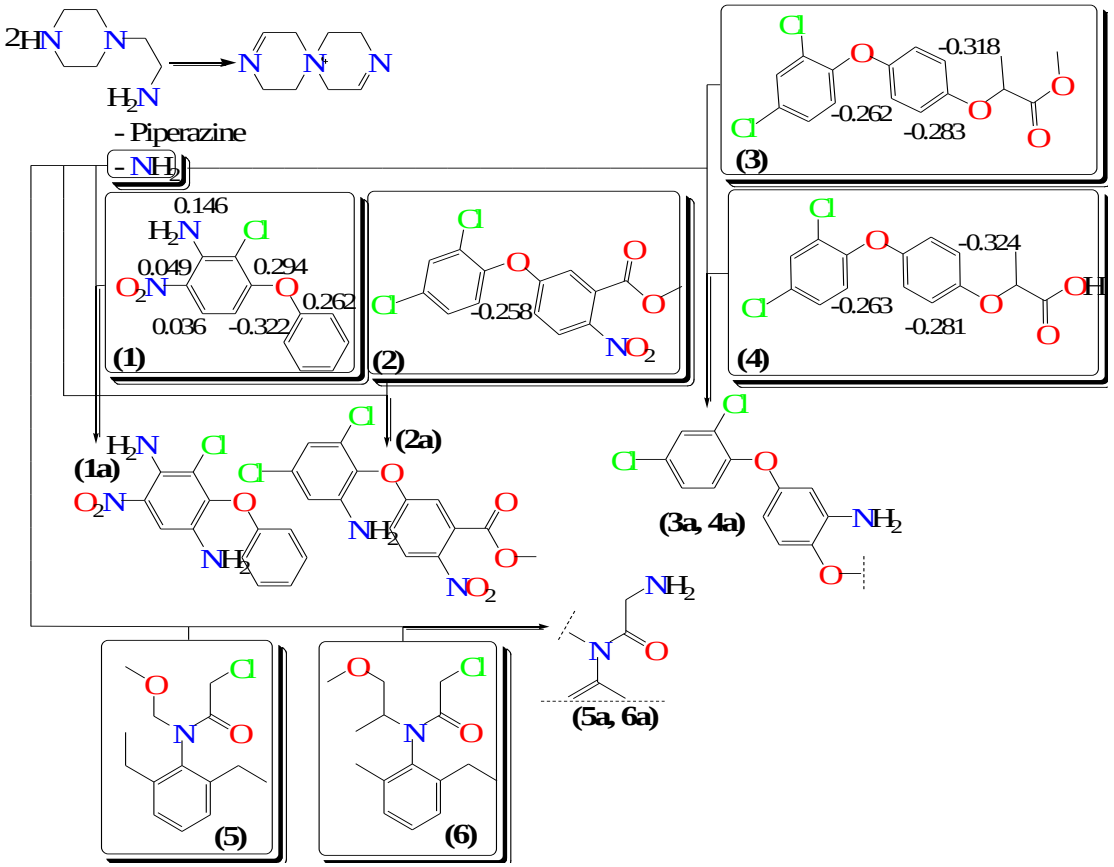


Figure S6. UV-MALDI-MS data of **5**, embedded in crystals of **I** and **II**, respectively



Scheme S3. Proposed mechanisms (resp. products of formation) of the formation the chemically modified herbicides under the interaction with the 2-Piperazin-1-yl-ethylamine in the strong acidic medium; The proposed mechanisms of interactions were based on the theoretical NBO analysis evaluated by the shown q_X(NBO) values, where X = O, N and C. The derivatives 1–4 are described in terms of the S_E reaction, since ether formed piperazine acted as base yielded the protonated forms in the presence of the acid. In contrast the 5 and 6 yielded the corresponding amines after the dechlorination at the S_N2 reaction

Experimental

Computational methods

Quantum chemical calculations

Quantum chemical GAUSSIAN 09 and Dalton2011 program packages [1a,b] are used. The geometries of the studied herbicides and MS species are optimized employing B3PW91, and M06-2X functional. The calculations of the molecular vibrations are utilized at 6-31+G(d,p), aug-cc-pVDZ and triple-ζ quality TZVP, triple-ζ plus double polarization TZ2P basis set, Los Alamos National Laboratory's 2 double-ζ as well as quasirelativistic effective core pseudo potentials from Stuttgart-Dresden. The UV-VIS spectra are calculated, using TDDFT method at above levels, PCM approach and mixed solvation model [1]. The chemical reactivity and proton accepting ability was evaluated by the NBO analysis [1].

Statistical and mathematical methods (Chemometrics)

The experimental and theoretical spectroscopic data are processed with a view to determine the peak positions and the integral intensities by R4Cal Open Office STATISTICs for Windows 7 program package, according the mathematical procedures and algorithms described in [2]. The statistical significance of each regression coefficient is evaluated by the statistical methods [2].

References

[1] (a) M. Frisch, et al. Gaussian 09, Gaussian, Inc., Pittsburgh, PA, 2009; (b) Dalton2011 Program Package; http://www.daltonprogram.org/download.html; (c) Y. Zhao, D. Truhlar, *Accts Chem. Res*. 2008, **41**, 157; (d) Y. Zhao, D. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215; (e) S. Grimme, A. Bahlmann, G. Haufe, *Chirality* 2002, **14**, 793; (f) S. Grimme, F. Neese, *J. Chem. Phys.* 2007, **127**, 154116; (g) D. Crawford, *Theor. Chem. Acc.* 2006, **115**, 227; (h) F. de Proft, P. Geerlings, *Chem. Rev.* 2001, **101**, 1451; (i) P. Stephens, D. McCann, J. Cheeseman, M. Frisch, *Chirality* 2005, **17**, S52; (j) P. Stephens, F. Devlin, J. Cheeseman, M. Frisch, O. Bortolini, P. Besse, *Chirality* 2003, **15**, S57; (j) P.vR. Schleyer, P. Schreiner (Eds.-in-Chief), N. Allinger, T. Clark, J. Gasteiger, P. Kollman, H. Schaefer III (Eds.), Encyclopedia of Computational Chemistry, Wiley, 1998, Vols. 1–5; (k) B. Ivanova, M. Spiteller, *Nat. Prod. Commun*. 2012, **7**, 157; (l) B. Ivanova, M. Spiteller, *J. Mol. Struct*. 2012, **1012**, 189; (m) B. Ivanova, M. Spiteller, *Biopolymers,* 2012, **97**, 134; (n) B. Ivanova, M. Spiteller, *J. Mol. Struct.* 2012, **1024**, 18

[2] (a) http://de.openoffice.org/; (b) C. Kelley, (1999) Iterative Methods for Optimization, SIAM Frontiers in Applied Mathematics, 18; (c) K. Madsen, H. Nielsen, O. Tingleff (2004) Informatics and Mathematical Modelling, 2nd Ed., DTU Press.