Supplementary data for article:

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Reactivity of (*E*)-4-aryl-4-oxo-2-butenoic acid arylamides toward 2-mercaptoethanol. A LFER study

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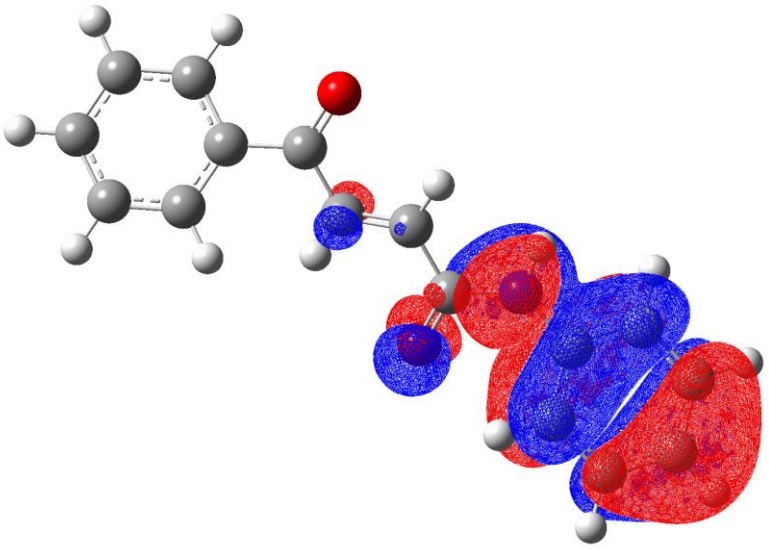
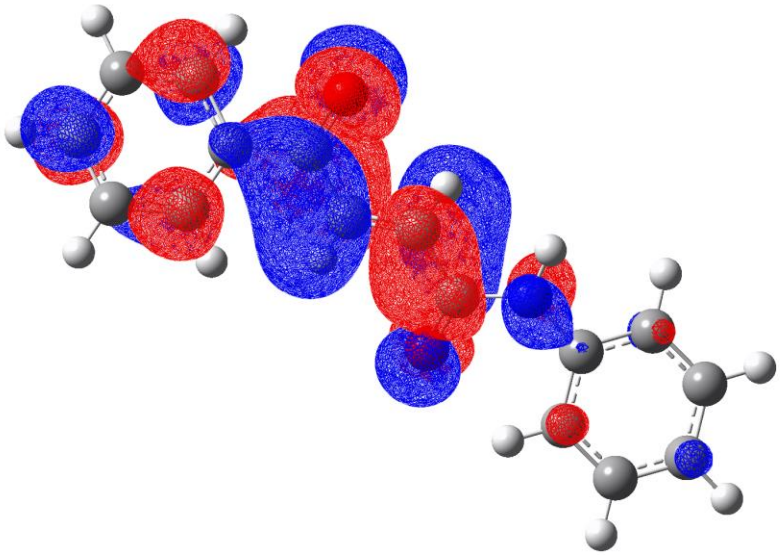


a)



b)

Figure S1. a) HOMO, and b) LUMO of the compound **1**, as obtained by MP2 calculations. Major part of LUMO orbital is located on Michael acceptor moiety of the molecule.

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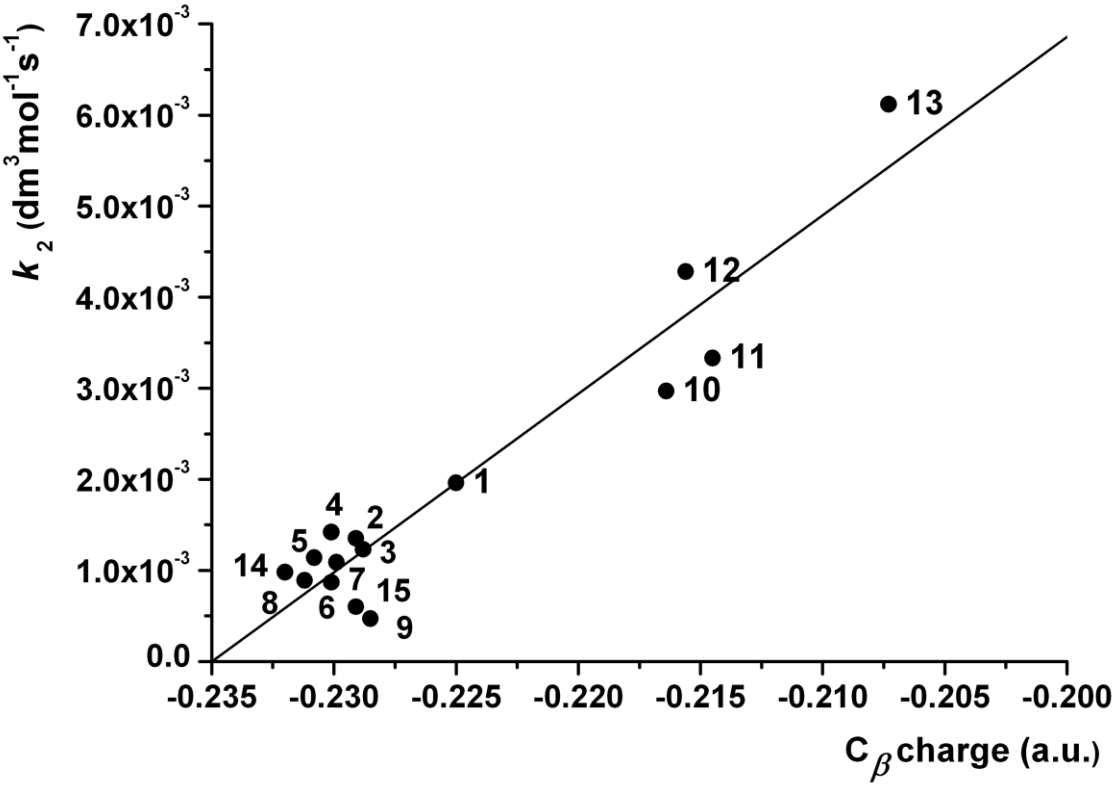
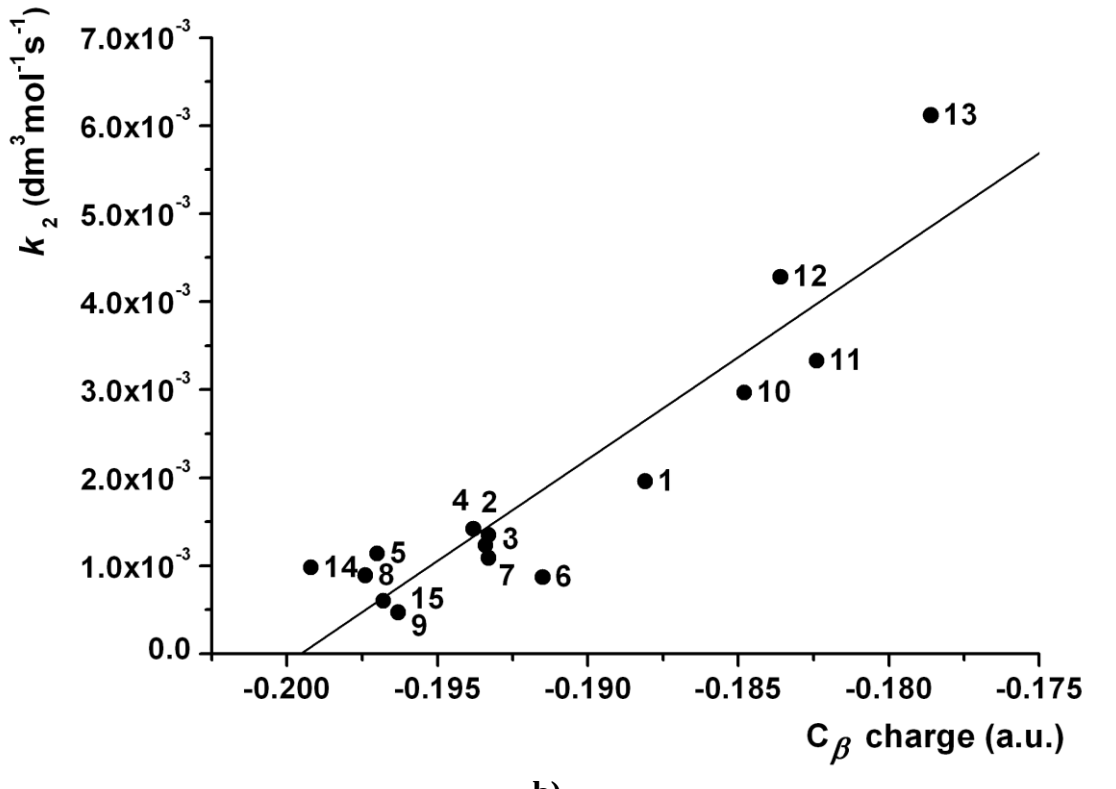
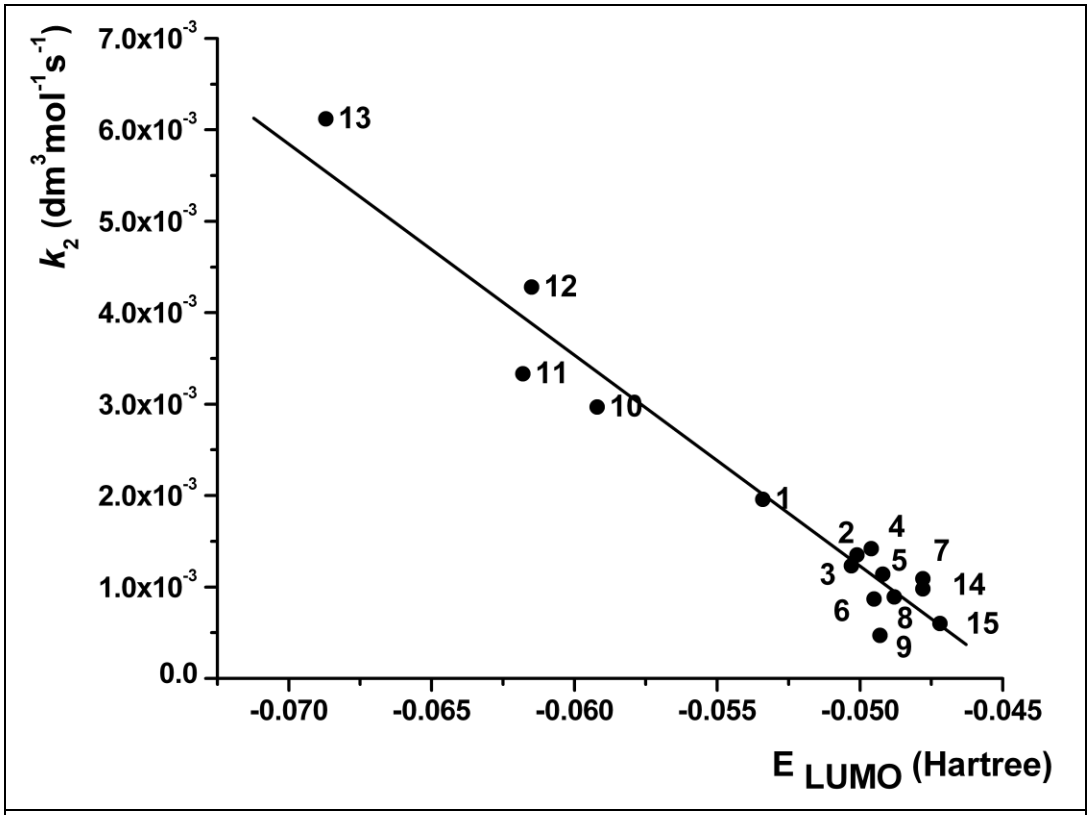


a)

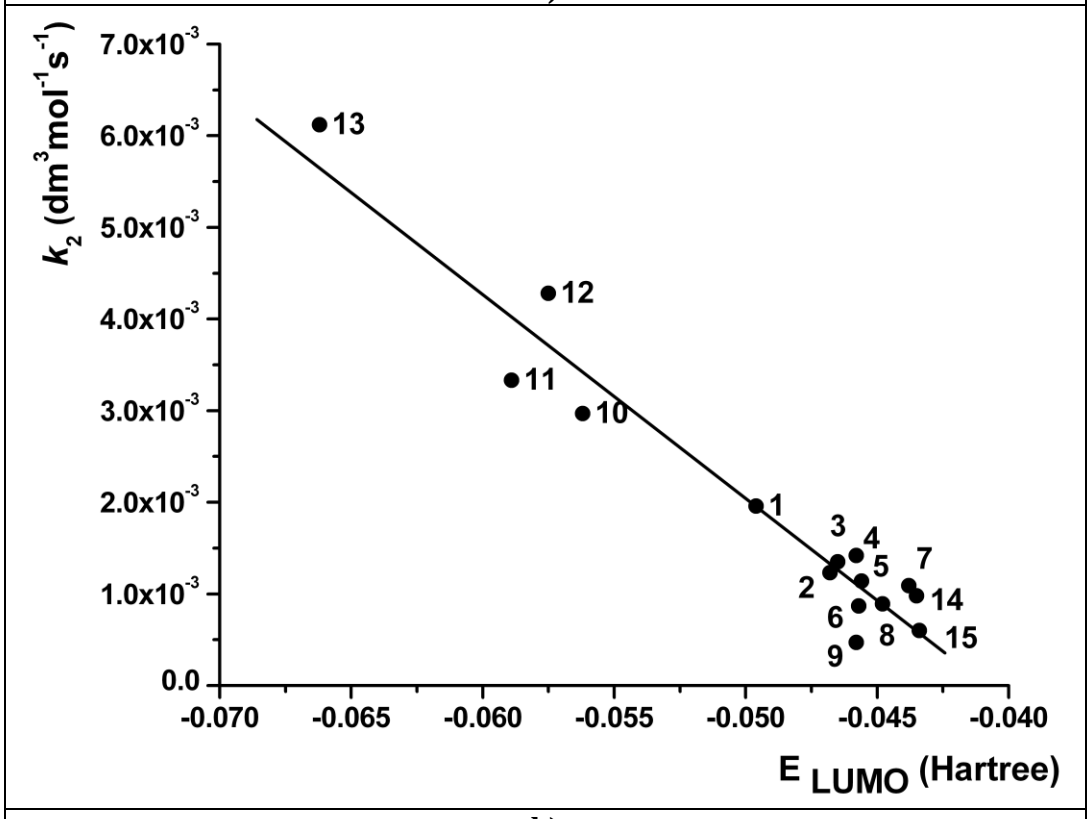


b)

Figure S2. Correlations between k_2 and Coulson atomic charges on C_β, as obtained by single point calculation by **a)** semiempirical MO PM6 (r = 0.955, n = 15, F = 134.55, slope = 0.1961, intercept = 0.0461), and **b)** semiempirical MO PM7 method (r = 0.918, n = 15, F = 70.14, slope = 0.2317, intercept = 0.0462), using geometries optimized on MP2 level of theory.



a)



b)

Figure S3. Correlations between k_2 and numerical values of LUMO orbitals, as obtained by single point calculation by **a)** semiempirical MO PM6 (r = 0.975, n = 15, F = 253.17, slope = –0.2356, intercept = –0.0106), and **b)** semiempirical MO PM7 method (r = 0.970, n = 15, F = 203.79, slope = –0.2222, intercept = 0.0090), using geometries optimized on MP2 level of theory.

Table S1. Experimental and predicted values of $\log(k_R/k_H)$, obtained according to Eq. 3 (Figure 5, main text).

Comp. Nº	$\log(k_R/k_H)$	
	Experimental	**Predicted**
1	0	0.0378
2	–0.1619	–0.0986
3	–0.2024	–0.1077
4	–0.1400	–0.1440
5	–0.2354	–0.2364
8	–0.3429	–0.4002
9	–0.6202	–0.6714
10	0.1805	0.0924
11	0.2302	0.2470
12	0.3392	0.2470
13	0.4945	0.5121
14	–0.3010	–0.2765
15	–0.5141	–0.4749

Table S2. Experimentally determined second-order rate constants (k_2, $dm^3\ mol^{-1}s^{-1}$) for the addition of 2-mercaptoethanol to compounds **1-15**, calculated charges on C_β in a.u. (Figure 1, main text), and values of HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) in Hartrees. Calculation obtained in vacuum.

Comp. Nº	k_2 ($\cdot 10^{-3}$)	PM6			PM7			MP2		
		Coulson Charge C_β	HOMO	LUMO	Coulson Charge C_β	HOMO	LUMO	Mulliken Charge C_β	HOMO	LUMO
1	1.96 (±0.11)	–0.2250	–0.3382	–0.0534	–0.1881	–0.3370	–0.0496	–0.2353	–0.3214	0.0212
2	1.35 (±0.17)	–0.2291	–0.3370	–0.0501	–0.1933	–0.3359	–0.0465	–0.2362	–0.3204	0.0243
3	1.23 (±0.10)	–0.2288	–0.3370	–0.0503	–0.1934	–0.3359	–0.0468	–0.2386	–0.3201	0.0246
4	1.42 (±0.10)	–0.2301	–0.3368	–0.0496	–0.1938	–0.3356	–0.0458	–0.2363	–0.3203	0.0245
5	1.14 (±0.05)	–0.2308	–0.3364	–0.0492	–0.1970	–0.3354	–0.0456	–0.2372	–0.3199	0.0250
6	0.87 (±0.03)	–0.2301	–0.3371	–0.0495	–0.1915	–0.3359	–0.0457	–0.2235	–0.3207	0.0232
7	1.09 (±0.12)	–0.2299	–0.3365	–0.0478	–0.1933	–0.3353	–0.0438	–0.2238	–0.3205	0.0250
8	0.89 (±0.01)	–0.2312	–0.3363	–0.0488	–0.1974	–0.3351	–0.0448	–0.2372	–0.3197	0.0254
9	0.47 (±0.03)	–0.2285	–0.3368	–0.0493	–0.1963	–0.3359	–0.0458	–0.2372	–0.3203	0.0247
10	2.97 (±0.31)	–0.2164	–0.3410	–0.0592	–0.1848	–0.3403	–0.0562	–0.2296	–0.3250	0.0137
11	3.33 (±0.22)	–0.2145	–0.3416	–0.0618	–0.1824	–0.3408	–0.0589	–0.2293	–0.3253	0.0113
12	4.28 (±0.51)	–0.2156	–0.3411	–0.0615	–0.1836	–0.3400	–0.0575	–0.2302	–0.3245	0.0127
13	6.12 (±0.78)	–0.2073	–0.3438	–0.0687	–0.1786	–0.3431	–0.0662	–0.2252	–0.3281	0.0033
14	0.98 (±0.03)	–0.2320	–0.3304	–0.0478	–0.1992	–0.3306	–0.0435	–0.2388	–0.3111	0.0271
15	0.60 (±0.01)	–0.2291	–0.3271	–0.0472	–0.1968	–0.3264	–0.0434	–0.2366	–0.3091	0.0269

Table S3. Statistical values of correlations between rate constants (k_2) and the descriptors obtained from optimized geometries (Charges on C_β atom, HOMO, and LUMO); *r* – Correlation coefficient, *n* – Number of compounds in correlation, *F* – Fischer F test.

	PM6			PM7			MP2		
	Coulson Charge C_β	HOMO	LUMO	Coulson Charge C_β	HOMO	LUMO	Mulliken Charge C_β	HOMO	LUMO
r	0.955, 0.954*	0.959	0.975	0.918, 0.903*	0.951	0.970	0.945	0.953	0.969
n	15	13	15	15	13	15	13	13	15
F	134.55	125.55	253.17	70.14	103.59	203.79	83.41	110.52	196.72

* Correlation coefficient obtained with Mulliken charge