Supporting information

Capturing electronic substituent effect with effective atomic orbitals

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Table 1: Boyd&Boyd electronegativities and occupations of the $2p_{C\text{-}H/X}$ eff-AO of the ipso-carbon and the σ-type eff-AO of the substituent in the mono-substituted benzene ring.

Substituent	X(Boyd&Boyd)	$2p_{C\text{-}H/X}$ eff-AO	σ-type eff-AO Substituent
SH	2.65	0.3666	0.4377
SiH_3	1.90	0.4243	0.1904
CF_3	2.71	0.3350	0.4949
COOH	2.63	0.3464	0.4704
$COOCH_3$	2.64	0.3500	0.4664
CN	2.69	0.3092	0.5225
$COCH_3$	2.59	0.3618	0.4378
COH	2.60	0.3634	0.4402
NO_2	3.22	0.2288	0.6555
$CHCH_2$	2.58	0.3615	0.4424
C_6H_5	2.58	0.3610	0.4417
CH_3	2.55	0.3633	0.4462
CH_2CH_3	2.55	0.3670	0.4377
NMe_2	3.13	0.2125	0.6666
NH_2	3.12	0.2185	0.6596
OH	3.55	0.1552	0.7536
OCH_3	3.53	0.1549	0.7533
SCH_3	2.65	0.3744	0.4222
$NHCH_3$	3.13	0.2128	0.6661
COCl	2.66	0.3355	0.4890

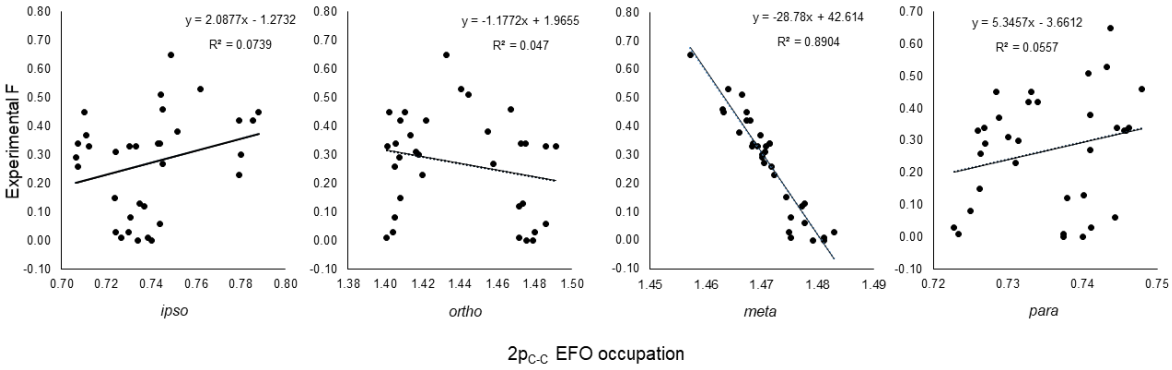

Figure 1: F parameter vs. occupation of the $2p_{C\text{-}C}$ eff-AO at carbon in ipso-, ortho-, meta- and para-positions for the mono-substituted benzene set.

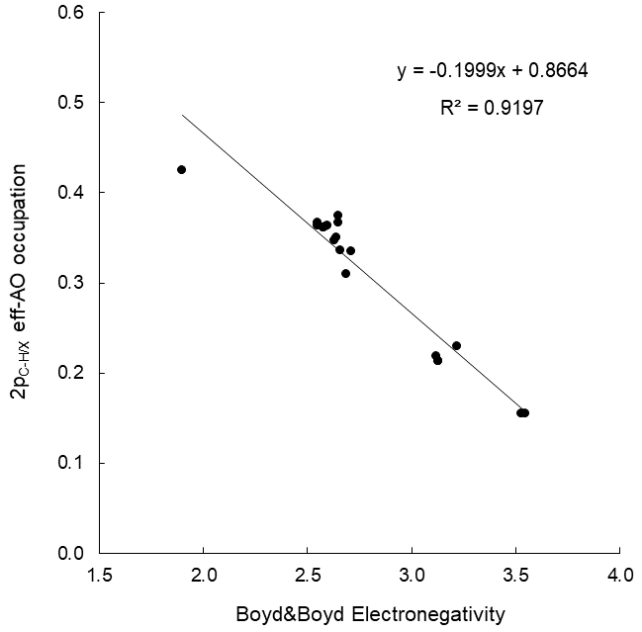

Figure 2: Correlation between the Boyd&Boyd electronegativity scale and the occupation of the $2p_{C\text{-}H/X}$ eff-AO of the ipso carbon in mono-substituted benzene derivatives.

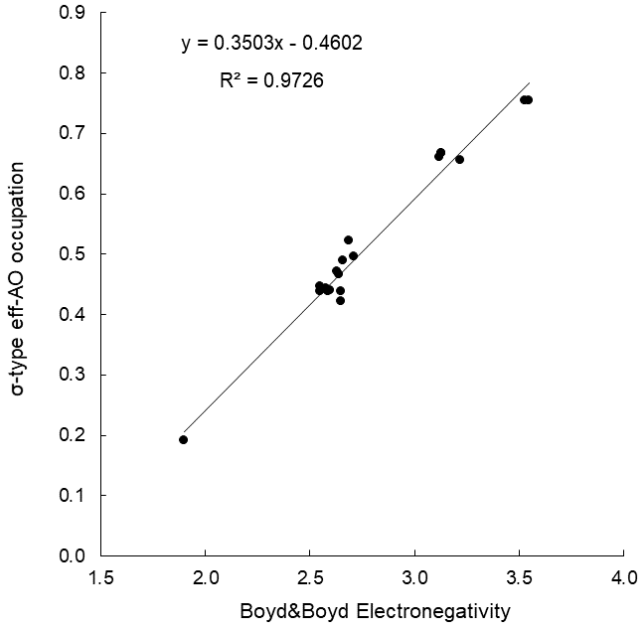

Figure 3: Correlation between the Boyd&Boyd electronegativity scale and the occupation of the σ-type eff-AO of the substituent in mono-substituted benzene derivatives.

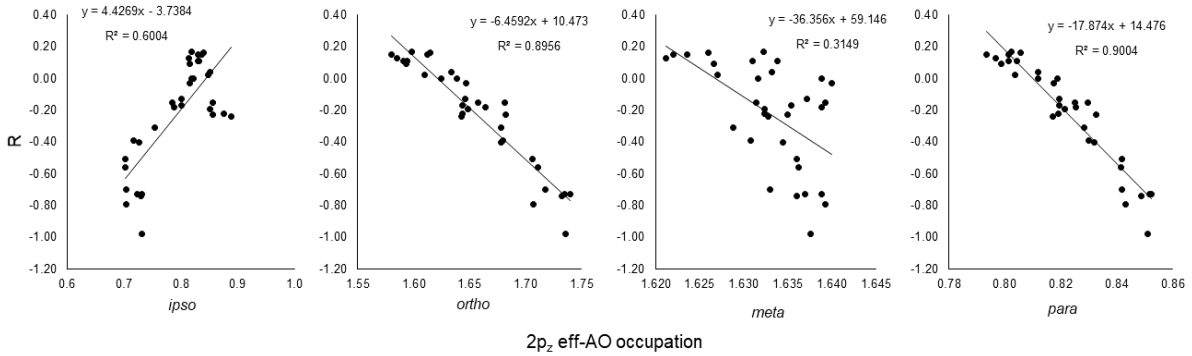

Figure 4: R parameter vs. occupation of the $2p_z$ eff-AO at carbon in ipso-, ortho-, meta- and para-positions for the mono-substituted benzene derivatives.

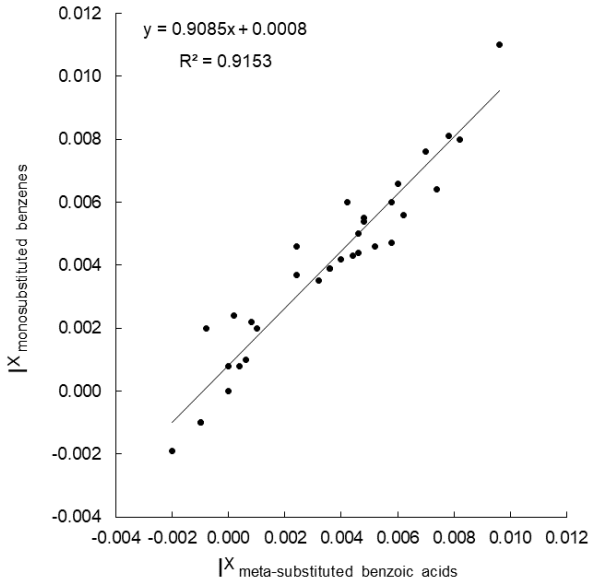

Figure 5: Correlation between the I^X descriptor using the unique meta position (see main text) in the meta-substituted benzoic acids with I^X values obtained for mono-substituted benzene derivatives.

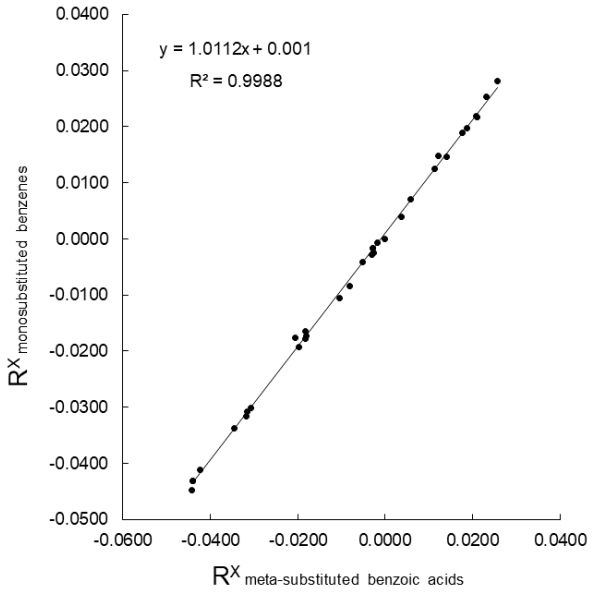

Figure 6: Correlation between the R^X descriptor in the meta-substituted benzoic acids with R^X values obtained for mono-substituted benzene derivatives.

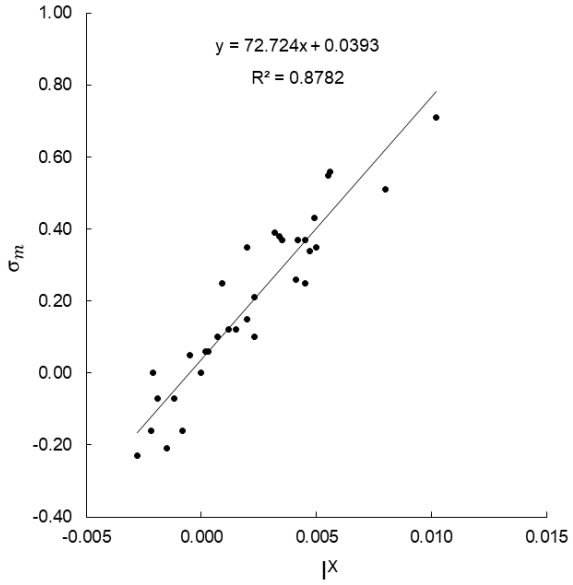

Figure 7: Correlation between the I^X descriptor in the meta-substituted benzoic acids with experimental σ_m values.

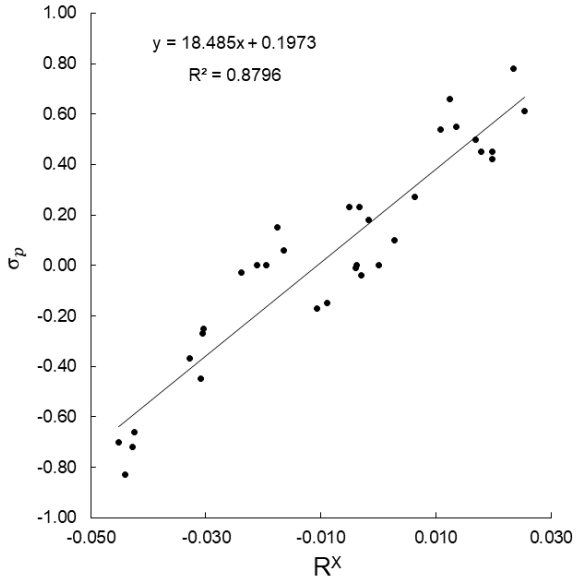

Figure 8: Correlation between the R^X descriptor in the para-substituted benzoic acids with experimental σ_p values.