The halogen effect on the ^{13}C NMR chemical shift in substituted benzenes

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1 Experimental ^{13}C NMR chemical shifts

Table S1: Experimental carbon 1 ^{13}C NMR chemical shifts[a,b] for *ortho* (*o*-), *meta* (*m*-), and *para* (*p*-) isomers of the X-R-benzene compounds in $CDCl_3$ and DMSO-d_6.

	F		Cl		Br		I	
R	$CDCl_3$	DMSO	$CDCl_3$	DMSO	$CDCl_3$	DMSO	$CDCl_3$	DMSO
H	163.10	162.20	134.47	133.10	122.73	121.70	94.59	94.82
o-NH_2	151.94	150.67	119.47	117.03	109.53	107.41	84.36	83.06
m-NH_2	164.12	163.30	135.00	133.38	123.26	122.06	95.13	95.12
p-NH_2	156.69	154.18	123.34	118.66	110.42	105.97	79.56	75.62
o-NO_2	155.73	154.61	127.32	124.81	114.69	112.82	86.41	87.69
m-NO_2	162.56	161.72	135.69	134.00	123.09	122.02	93.68	94.87
p-NO_2	166.46	165.72	141.60	140.09	130.20	129.35	102.89	104.40

[a] in ppm. [b] Experimental error is 0.1 ppm.

2 DFT benchmark

Different combinations of DFT functionals (B3LYP, KT2, BP86, or PBE0), basis sets (TZ2P or QZ4P) and inclusion or not of solvation model (COSMO - chloroform) were performed to choice the most accurate level of theory for the C1 chemical shifts calculations. The results for B3LYP, KT2, and BP86 are showed in Table S2 and S3, while data obtained by PBE0 are in Table S4 and S5.

Table S2: Percentage errors (in %) of the C1 chemical shifts calculated at the B3LYP, KT2, and BP86 functionals using TZ2P or QZ4P basis sets in isolated-phase or $CHCl_3$ (COSMO) for X-R-benzene compounds. Errors were determined in comparison to experimental data (Table S1).

		B3LYP				KT2				BP86			
		TZ2P		QZ4P		TZ2P		QZ4P		TZ2P		QZ4P	
R	X	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$
H	F	3.65	3.32	3.27	2.96	3.86	3.50	4.67	4.35	4.33	4.00	4.55	4.25
	Cl	5.84	4.71	5.39	4.30	5.65	4.56	5.90	4.83	6.79	5.70	6.35	5.28
	Br	7.81	6.77	7.41	6.51	8.07	6.98	8.36	7.38	9.61	8.54	9.23	8.29
	I	9.86	9.34	10.23	9.92	13.70	13.01	15.04	14.46	15.18	14.51	15.53	14.99
	Average	6.79	6.04	6.58	5.92	7.82	7.01	8.49	7.76	8.98	8.19	8.92	8.20
o-NH_2	F	3.03	2.98	2.13	2.09	4.66	4.42	4.61	4.38	4.35	4.21	3.84	3.71
	Cl	3.88	3.43	2.73	2.45	5.46	4.80	4.56	4.08	5.30	4.71	3.82	3.36
	Br	5.86	5.40	5.09	4.86	7.92	7.18	7.42	6.86	8.29	7.61	7.22	6.72
	I	7.70	7.17	7.11	7.16	13.57	13.10	13.84	13.57	13.63	13.06	12.99	12.63
	Average	5.12	4.75	4.27	4.14	7.90	4.88	5.11	4.72	5.39	4.90	6.97	6.61
m-NH_2	F	3.78	3.43	3.47	3.13	3.64	3.28	4.73	4.33	4.13	3.79	4.52	4.16
	Cl	6.11	4.81	5.71	4.47	5.22	4.04	5.62	4.39	6.23	4.99	5.87	4.59
	Br	7.92	6.76	7.63	6.59	7.24	6.05	7.76	6.63	8.65	7.45	8.41	7.28
	I	10.17	9.42	10.68	10.06	12.46	11.63	13.97	13.17	13.67	12.87	14.11	13.29
	Average	7.00	6.11	6.87	6.06	7.14	6.25	8.02	7.13	8.17	7.28	8.23	7.33
p-NH_2	F	2.80	2.38	2.30	1.86	3.95	3.47	4.26	3.74	3.94	3.47	3.64	3.14
	Cl	4.82	2.91	3.69	1.77	5.88	3.94	5.06	2.97	6.24	4.13	4.69	2.50
	Br	6.44	4.58	5.40	3.72	7.94	5.90	7.15	5.11	8.69	6.59	7.23	5.14
	I	8.30	6.75	7.05	5.65	13.66	11.66	13.37	11.27	13.94	11.81	12.60	10.46
	Average	5.59	4.16	4.61	3.25	7.86	6.24	7.46	5.77	8.20	6.50	7.04	5.31

Table S3: Percentage errors (in %) of the C1 chemical shifts calculated at the B3LYP, KT2, and BP86 functionals using TZ2P or QZ4P basis sets in isolated-phase or $CHCl_3$ (COSMO) for X-R-benzene compounds. Errors were determined in comparison to experimental data (Table S1).

		B3LYP				KT2				BP86			
		TZ2P		QZ4P		TZ2P		QZ4P		TZ2P		QZ4P	
R	X	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$	isolated	$CHCl_3$
	F	4.96	4.18	4.57	3.80	5.70	5.45	6.06	6.01	5.87	5.66	5.77	4.87
	Cl	6.40	5.58	6.06	5.16	8.21	7.47	8.56	7.93	7.31	6.66	6.69	6.17
o-NO_2	Br	8.95	8.22	11.44	7.94	12.57	11.19	13.11	12.86	13.63	10.35	10.28	9.96
	I	12.78	12.53	13.40	13.39	21.10	21.40	22.85	23.24	20.07	20.01	20.12	20.38
	Average	8.27	7.63	8.87	7.57	11.90	11.38	12.65	12.51	11.72	10.67	10.72	10.35
	F	3.02	2.57	2.92	2.52	3.67	3.19	4.61	4.30	4.23	3.75	4.53	4.23
	Cl	4.63	3.51	4.63	3.62	4.94	4.03	5.50	4.75	6.28	5.25	6.07	5.22
m-NO_2	Br	6.48	5.37	6.52	5.58	7.49	6.49	8.10	7.37	9.13	8.06	8.97	8.18
	I	8.25	7.59	9.20	8.75	13.44	12.77	15.19	14.88	14.99	14.27	15.62	15.24
	Average	5.60	4.76	5.82	5.12	7.39	6.62	8.35	7.83	8.66	7.83	8.80	8.22
	F	3.42	3.78	3.35	3.79	3.72	3.98	4.64	5.10	4.18	4.50	4.46	4.95
	Cl	5.71	6.26	5.52	6.26	5.28	5.94	5.85	6.77	6.46	7.18	6.27	7.22
p-NO_2	Br	7.80	8.73	7.77	9.01	7.98	9.08	8.63	10.12	9.52	10.64	9.43	10.88
	I	10.97	13.79	11.33	14.55	14.20	17.18	15.93	19.47	15.71	18.85	16.35	19.93
	Average	6.98	8.14	6.99	8.40	7.80	9.05	8.76	10.37	8.97	10.29	9.13	10.75

Table S4: Percentage errors (in %) of the C1 chemical shifts calculated at the PBE0 functional using TZ2P or QZ4P basis sets in isolated-phase or $CHCl_3$ (COSMO) for X-R-benzene compounds. Errors were determined in comparison to experimental data (Table S1).

		PBE0					
		TZ2P		QZ4P		TZ2P/$CHCl_3$	TZ2P/$CHCl_3$
R	X	isolated	$CHCl_3$	isolated	$CHCl_3$	Extra functions[a]	Extra functions[a] + f_{XC}[b]
H	F	2.07	1.66	1.74	1.32	1.71	1.68
	Cl	3.39	2.22	2.97	1.87	3.07	2.83
	Br	5.23	4.09	4.78	3.78	4.87	3.16
	I	7.64	6.98	8.07	7.55	7.86	1.54
	Average	4.58	3.74	4.39	3.63	4.38	2.30
o-NH_2	F	1.18	0.97	0.31	0.12	1.30	1.27
	Cl	0.68	0.08	0.37	0.83	1.26	1.05
	Br	2.42	1.73	1.36	0.97	2.77	1.13
	I	4.49	3.60	3.58	3.50	4.73	1.42
	Average	2.19	1.60	1.41	1.36	2.52	1.22
m-NH_2	F	2.25	1.80	1.98	1.51	1.86	1.83
	Cl	3.70	2.41	3.38	2.15	3.27	3.04
	Br	5.43	4.15	5.04	3.92	4.92	3.24
	I	8.82	8.01	8.60	7.84	8.08	1.93
	Average	5.05	4.09	4.75	3.86	4.53	2.51
p-NH_2	F	1.08	0.49	0.56	0.05	0.84	0.82
	Cl	2.02	0.11	0.92	1.17	1.22	1.01
	Br	3.47	1.30	2.23	0.21	2.58	0.74
	I	5.68	3.61	4.22	2.27	4.50	2.84
	Average	3.06	1.38	1.98	0.93	2.29	1.35

[a] Diffuse (AddDiffuseFit) and fit (FitType QZ4P) functions were added. [b] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the SO contribution.

Table S5: Percentage errors (in %) of the C1 chemical shifts calculated at the PBE0 functional using TZ2P or QZ4P basis sets in isolated-phase or $CHCl_3$ (COSMO) for X-R-benzene compounds. Errors were determined in comparison to experimental data (Table S1).

		PBE0					
		TZ2P		QZ4P		TZ2P/$CDCl_3$	TZ2P/$CDCl_3$
R	X	isolated	$CDCl_3$	isolated	$CDCl_3$	Extra functions[a]	Extra functions[a] + f_{XC}[b]
	F	3.63	2.82	2.56	2.33	2.96	2.90
	Cl	4.50	3.44	4.10	3.03	4.28	3.99
o-NO_2	Br	7.19	6.06	9.11	5.53	6.64	4.67
	I	11.83	11.11	12.20	11.57	11.79	4.42
	Average	6.79	5.86	6.99	5.62	6.42	4.00
	F	1.60	1.11	1.53	1.08	1.38	1.36
	Cl	2.41	1.30	2.45	1.45	2.42	2.18
m-NO_2	Br	4.31	3.17	4.24	3.26	4.20	2.44
	I	6.73	6.00	7.57	7.04	7.13	0.52
	Average	3.76	2.90	3.95	3.21	3.78	1.63
	F	1.99	2.22	1.94	2.26	2.39	2.34
	Cl	3.40	3.81	3.27	3.83	4.58	4.34
p-NO_2	Br	5.45	6.15	5.28	6.24	6.84	5.18
	I	8.93	11.24	9.26	11.90	11.27	5.50
	Average	4.94	5.86	4.94	6.06	6.27	4.34

[a] Diffuse (AddDiffuseFit) and fit (FitType QZ4P) functions were added. [b] Terms from the DFT exchange-correlation response kernel (f_{XC}) were included to improve the SO contribution.

3 Individual contributions of the C1 shielding

Table S6 displays the decomposition of the C1 isotropic NMR shielding constants into the diamagnetic, paramagnetic, and spin-orbit contributions.

Table S6: The C1 shielding $(\sigma^{\text{total}})^{a,b}$ and the diamagnetic $(\sigma^{\text{dia}})^{a}$, paramagnetic $(\sigma^{\text{para}})^{a}$, and spin-orbit $(\sigma^{\text{SO}})^{a}$ contributions obtained for X-R-benzene compounds.

R	X	σ^{dia}	σ^{para}	σ^{SO}	σ^{total}
H	F	241.53	-225.51	1.31	17.33
	Cl	250.51	-209.25	3.77	45.03
	Br	247.87	-206.51	17.13	58.49
	I	251.92	-203.47	41.73	90.18
o-NH_2	F	242.38	-214.26	1.24	29.36
	Cl	251.10	-191.85	3.34	62.59
	Br	248.25	-188.81	14.73	74.17
	I	252.09	-184.49	35.06	102.66
m-NH_2	F	240.72	-225.96	1.29	16.05
	Cl	249.91	-209.41	3.68	44.18
	Br	247.26	-206.38	16.84	57.72
	I	251.40	-203.12	40.64	88.92
p-NH_2	F	241.73	-217.84	1.26	25.15
	Cl	250.69	-195.65	3.66	58.70
	Br	248.02	-191.28	17.03	73.77
	I	252.21	-184.99	41.54	108.76
o-NO_2	F	240.98	-219.31	1.17	22.84
	Cl	249.63	-202.56	3.29	50.36
	Br	246.66	-199.83	16.29	63.12
	I	250.56	-199.46	42.09	93.19
m-NO_2	F	240.98	-223.94	1.21	18.25
	Cl	250.39	-209.63	3.31	44.07
	Br	247.74	-207.03	16.28	56.99
	I	251.97	-205.16	42.17	88.98
p-NO_2	F	241.28	-229.83	1.15	12.60
	Cl	250.57	-218.81	3.14	34.90
	Br	247.89	-217.49	15.69	46.09
	I	252.38	-218.19	40.32	74.51

[a] in ppm. [b] $\sigma^{\text{total}} = \sigma^{\text{dia}} + \sigma^{\text{para}} + \sigma^{\text{SO}}$.

4 NLMO contributions to the C1 shielding

NLMO contributions for diamagnetic, paramagnetic, and spin-orbit terms of the C1 shielding are displayed in Table S7 - S15 for X-R-benzenes.

Table S7: NLMO contributions[a] to σ^{dia} term of the C1 shielding for X-benzenes.

Parent	X-benzene			
NBO	F	Cl	Br	I
CR (C1)	203.44	203.45	203.47	203.48
CR (C2-C6)[b]	0.04	0.04	0.04	0.04
CR (X)[c]	-0.01	-0.01	-0.02	-0.07
$LP_1(X)$	1.95	1.75	1.39	1.24
$LP_2(X)$	1.12	1.31	1.11	1.12
$LP_3(X)$	1.34	1.18	1.03	1.07
$\sigma_{C1\text{-}C2}$	8.44	10.09	10.50	11.53
$\sigma_{C1\text{-}C6}$	8.44	10.09	10.50	11.53
$\sigma_{C2\text{-}C3}$	0.47	0.53	0.56	0.51
$\sigma_{C3\text{-}C4}$	-0.13	-0.10	-0.10	-0.10
$\sigma_{C4\text{-}C5}$	-0.13	-0.10	-0.10	-0.10
$\sigma_{C5\text{-}C6}$	0.47	0.53	0.56	0.51
$\pi_{C\text{-}C}$[d]	18.94	19.57	19.67	19.57
$\sigma_{C1\text{-}X}$	-4.08	0.88	-2.15	0.11
$\sigma_{C2\text{-}H}$	0.52	0.54	0.58	0.59
$\sigma_{C3\text{-}H}$	0.07	0.11	0.09	0.11
$\sigma_{C4\text{-}H}$	0.05	0.05	0.05	0.04
$\sigma_{C5\text{-}H}$	0.07	0.11	0.10	0.12
$\sigma_{C6\text{-}H}$	0.52	0.54	0.58	0.60
all σ^*	0.00	0.00	0.01	0.03
all π^*	0.00	0.00	0.00	-0.01
$\sum_{total}$[e]	241.53	250.51	247.87	251.92

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of three π orbitals. [e] Sum of all NLMO contributions.

Table S8: NLMO contributions[a] to σ^{para} term of the C1 shielding for X-benzenes.

Parent	X-benzene			
NBO	F	Cl	Br	I
CR (C1)	-0.05	-0.03	0.01	0.03
CR (C2-C6)[b]	-1.05	-1.09	-1.21	-1.26
CR (X)[c]	0.00	0.04	-0.01	-0.01
$LP_1(X)$	-6.85	-4.47	-4.05	-3.70
$LP_2(X)$	-0.38	-0.60	0.33	1.27
$LP_3(X)$	-1.37	-3.32	-3.03	-3.23
σ_{C1-C2}	-73.30	-65.03	-65.52	-65.77
σ_{C1-C6}	-73.30	-65.03	-65.52	-65.77
σ_{C2-C3}	-1.32	-1.14	-0.91	-0.67
σ_{C3-C4}	0.05	-0.14	-0.21	-0.39
σ_{C4-C5}	0.05	-0.14	-0.21	-0.39
σ_{C5-C6}	-1.31	-1.14	-0.91	-0.67
π_{C-C}[d]	-27.04	-14.77	-10.63	-6.64
σ_{C1-X}	-31.96	-41.80	-41.71	-41.95
σ_{C2-H}	-3.05	-4.41	-5.39	-6.04
σ_{C3-H}	-0.55	-0.68	-0.86	-0.94
σ_{C4-H}	-0.48	-0.41	-0.43	-0.35
σ_{C5-H}	-0.55	-0.68	-0.86	-0.95
σ_{C6-H}	-3.05	-4.41	-5.39	-6.04
all σ^*	0.00	0.00	0.00	0.00
all π^*	0.00	0.00	0.00	0.00
$\sum_{total}$[e]	-225.51	-209.25	-206.51	-203.47

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of three π orbitals. [e] Sum of all NLMO contributions.

Table S9: NLMO contributions[a] to σ^{SO} term of the C1 shielding for X-benzenes.

Parent	X-benzene			
NBO	F	Cl	Br	I
CR (C1)	0.88	1.54	6.02	15.59
CR (C2-C6)[b]	0.00	0.00	0.03	0.00
CR (X)[c]	0.00	0.01	0.04	0.16
$LP_1(X)$	0.04	0.17	0.99	2.50
$LP_2(X)$	0.00	0.00	0.02	0.04
$LP_3(X)$	-0.01	0.00	0.02	0.08
$\sigma_{C1\text{-}C2}$	0.07	0.09	1.00	-0.52
$\sigma_{C1\text{-}C6}$	0.07	0.09	1.00	-0.52
$\sigma_{C2\text{-}C3}$	0.02	0.02	-0.02	-0.05
$\sigma_{C3\text{-}C4}$	0.00	-0.01	-0.03	-0.03
$\sigma_{C4\text{-}C5}$	0.00	-0.01	-0.03	-0.03
$\sigma_{C5\text{-}C6}$	0.02	0.02	-0.02	-0.05
$\pi_{C\text{-}C}$[d]	-0.01	-0.01	0.25	0.36
$\sigma_{C1\text{-}X}$	0.07	0.49	1.35	9.56
$\sigma_{C2\text{-}H}$	-0.01	-0.04	0.01	-0.09
$\sigma_{C3\text{-}H}$	-0.01	0.00	0.01	-0.11
$\sigma_{C4\text{-}H}$	0.00	0.00	0.00	0.00
$\sigma_{C5\text{-}H}$	-0.01	0.00	0.01	-0.11
$\sigma_{C6\text{-}H}$	-0.01	-0.04	0.01	-0.09
$\sigma^*_{C1\text{-}C2}$	0.01	0.12	0.57	1.75
$\sigma^*_{C1\text{-}C6}$	0.01	0.12	0.57	1.75
$\sigma^*_{C1\text{-}X}$	0.20	1.24	5.35	11.58
all other σ^*	0.00	0.00	0.02	0.09
all π^*	-0.02	-0.03	-0.04	-0.13
$\sum_{total}$[e]	1.31	3.77	17.13	41.73

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of three π orbitals. [e] Sum of all NLMO contributions.

Table S10: NLMO contributions[a] to σ^{dia} term of the C1 shielding for X-NH_2-benzenes.

Parent	*o*-X-NH_2				*m*-X-NH_2				*p*-X-NH_2			
NBO	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR (C1)	203.40	203.41	203.43	203.44	203.45	203.46	203.48	203.49	203.41	203.42	203.44	203.45
CR (C2-C6)[b]	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
CR (X)[c]	-0.01	-0.02	-0.03	-0.07	-0.02	-0.02	-0.02	-0.07	-0.01	-0.02	-0.03	-0.07
CR (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LP_1(X)	1.92	1.72	1.38	1.23	1.94	1.74	1.39	1.24	1.93	1.73	1.39	1.24
LP_2(X)	1.15	1.26	1.06	1.06	1.10	1.27	1.08	1.10	1.11	1.31	1.11	1.12
LP_3(X)	1.26	1.16	1.04	1.08	1.33	1.17	1.04	1.07	1.28	1.13	1.02	1.05
LP (N)	0.60	0.69	0.70	0.70	0.19	0.15	0.15	0.16	0.23	0.25	0.25	0.09
$\sigma_{C1\text{-}C2}$	7.73	9.61	9.89	10.79	7.82	9.64	10.02	11.11	8.31	9.99	10.36	11.46
$\sigma_{C1\text{-}C6}$	9.40	10.79	11.13	12.11	8.50	10.28	10.67	11.79	8.31	9.99	10.36	11.46
$\sigma_{C2\text{-}C3}$	0.54	0.54	0.57	0.54	0.49	0.54	0.57	0.52	0.40	0.46	0.49	0.44
$\sigma_{C3\text{-}C4}$	-0.14	-0.11	-0.11	-0.11	-0.05	-0.04	-0.03	-0.03	-0.04	-0.04	-0.03	-0.03
$\sigma_{C4\text{-}C5}$	-0.13	-0.11	-0.10	-0.10	-0.15	-0.13	-0.13	-0.12	-0.04	-0.04	-0.03	-0.03
$\sigma_{C5\text{-}C6}$	0.55	0.60	0.63	0.57	0.42	0.49	0.52	0.47	0.40	0.46	0.49	0.44
$\pi_{C\text{-}C}$[d]	19.50	20.05	20.16	20.06	18.73	19.40	19.51	19.41	19.41	20.05	20.17	20.24
$\sigma_{C1\text{-}X}$	-4.05	0.76	-2.35	-0.12	-4.09	0.80	-2.21	-0.01	-4.06	0.78	-2.22	0.00
$\sigma_{C2\text{-}H}$	-	-	-	-	0.58	0.59	0.63	0.63	0.49	0.52	0.54	0.57
$\sigma_{C2\text{-}R}$	0.08	0.09	0.11	0.12	-	-	-	-	-	-	-	-
$\sigma_{C3\text{-}H}$	0.07	0.11	0.10	0.12	-	-	-	-	0.11	0.15	0.14	0.16
$\sigma_{C3\text{-}R}$	-	-	-	-	-0.05	-0.03	-0.04	-0.03	-	-	-	-
$\sigma_{C4\text{-}H}$	0.05	0.04	0.04	0.04	0.07	0.07	0.07	0.06	-	-	-	-
$\sigma_{C4\text{-}R}$	-	-	-	-	-	-	-	-	-0.04	-0.04	-0.04	-0.04
$\sigma_{C5\text{-}H}$	0.07	0.10	0.10	0.11	0.06	0.10	0.09	0.10	0.12	0.15	0.14	0.16
$\sigma_{C6\text{-}H}$	0.49	0.50	0.55	0.57	0.54	0.56	0.60	0.61	0.49	0.52	0.54	0.57
$\sigma_{N\text{-}H}$[e]	-0.14	-0.13	-0.10	-0.11	-0.18	-0.17	-0.18	-0.17	-0.12	-0.12	-0.12	-0.12
all σ^*	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.02
all π^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01
$\sum_{total}$[f]	242.38	251.10	248.25	252.09	240.72	249.91	247.26	251.40	241.73	250.69	248.02	252.21

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of three π orbitals. [e] Sum of $\sigma_{N\text{-}H}$ contributions. [f] Sum of all NLMO contributions.

Table S11: NLMO contributions[a] to σ^{para} term of the C1 shielding for X-NH_2-benzenes.

Parent	*o*-X-NH_2				*m*-X-NH_2				*p*-X-NH_2			
NBO	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR (C1)	-0.03	-0.02	0.01	0.03	-0.06	-0.04	0.00	0.02	-0.07	-0.04	-0.01	0.02
CR (C2-C6)[b]	-1.07	-1.10	-1.25	-1.37	-1.06	-1.10	-1.25	-1.32	-0.96	-1.02	-1.15	-1.21
CR (X)[c]	0.00	0.04	-0.01	0.02	0.00	0.03	-0.01	0.00	0.00	0.04	0.00	0.02
CR (N)	-0.01	-0.02	-0.03	-0.04	-0.01	-0.01	-0.01	-0.02	0.00	-0.01	0.01	-0.01
LP_1(X)	-6.16	-3.93	-3.55	-3.20	-7.05	-4.60	-4.14	-3.77	-6.52	-4.11	-3.69	-3.37
LP_2(X)	-0.43	-0.71	0.04	0.72	-0.50	-0.58	0.38	1.38	-0.56	-0.57	0.33	1.23
LP_3(X)	-1.15	-2.81	-2.44	-2.55	-1.30	-3.29	-3.01	-3.24	-1.28	-2.96	-2.56	-2.47
LP (N)	-0.99	0.18	-0.06	0.26	-0.80	-0.75	-0.79	-0.83	-0.59	0.23	0.40	0.17
$\sigma_{C1\text{-}C2}$	-65.42	-57.84	-59.87	-61.39	-74.09	-65.17	-66.06	-65.97	-69.71	-60.03	-60.56	-60.25
$\sigma_{C1\text{-}C6}$	-69.35	-60.35	-59.67	-59.21	-74.03	-64.80	-64.31	-63.65	-69.71	-60.03	-60.56	-60.25
$\sigma_{C2\text{-}C3}$	-1.74	-1.66	-1.61	-1.54	-1.12	-0.91	-0.66	-0.38	-1.27	-1.16	-0.90	-0.67
$\sigma_{C3\text{-}C4}$	0.12	-0.05	-0.06	-0.19	-0.16	-0.29	-0.36	-0.57	-0.08	-0.24	-0.32	-0.50
$\sigma_{C4\text{-}C5}$	0.09	-0.09	-0.16	-0.33	-0.12	-0.31	-0.37	-0.61	-0.08	-0.24	-0.32	-0.50
$\sigma_{C5\text{-}C6}$	-1.18	-1.05	-0.86	-0.63	-1.19	-1.05	-0.83	-0.61	-1.27	-1.16	-0.90	-0.67
$\pi_{C\text{-}C}$[d]	-29.21	-14.48	-10.06	-5.18	-25.55	-13.64	-9.43	-5.42	-27.05	-12.93	-8.17	-2.28
$\sigma_{C1\text{-}X}$	-30.14	-38.25	-38.03	-37.87	-32.06	-43.03	-43.36	-44.41	-31.43	-41.36	-40.52	-40.32
$\sigma_{C2\text{-}H}$	-	-	-	-	-2.89	-4.35	-5.31	-6.01	-2.90	-4.22	-5.18	-5.87
$\sigma_{C2\text{-}R}$	-2.25	-2.53	-2.36	-2.03	-	-	-	-	-	-	-	-
$\sigma_{C3\text{-}H}$	-0.37	-0.42	-0.57	-0.63	-	-	-	-	-0.56	-0.69	-0.87	-0.97
$\sigma_{C3\text{-}R}$	-	-	-	-	-0.32	-0.36	-0.39	-0.42	-	-	-	-
$\sigma_{C4\text{-}H}$	-0.47	-0.41	-0.44	-0.36	-0.49	-0.41	-0.45	-0.38	-	-	-	-
$\sigma_{C4\text{-}R}$	-	-	-	-	-	-	-	-	-0.38	-0.30	-0.29	-0.25
$\sigma_{C5\text{-}H}$	-0.75	-0.90	-1.03	-1.12	-0.47	-0.64	-0.81	-0.91	-0.56	-0.69	-0.87	-0.97
$\sigma_{C6\text{-}H}$	-2.75	-4.09	-5.16	-5.94	-2.77	-4.16	-5.23	-5.99	-2.90	-4.22	-5.18	-5.87
$\sigma_{N\text{-}H}$[e]	-1.00	-1.36	-1.64	-1.94	0.08	0.05	0.02	-0.01	0.06	0.06	0.03	0.00
all σ^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
all π^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sum_{total}$[f]	-214.26	-191.85	-188.81	-184.49	-225.96	-209.41	-206.38	-203.12	-217.84	-195.65	-191.28	-184.99

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of three π orbitals. [e] Sum of $\sigma_{N\text{-}H}$ contributions. [f] Sum of all NLMO contributions.

Table S12: NLMO contributions[a] to σ^{SO} term of the C1 shielding for X-NH_2-benzenes.

Parent	*o*-X-NH_2				*m*-X-NH_2				*p*-X-NH_2			
NBO	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR (C1)	0.88	1.44	5.35	13.58	0.87	1.50	5.97	15.37	0.85	1.49	6.12	15.74
CR (C2-C6)[b]	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.02
CR (X)[c]	0.00	0.01	0.03	0.14	0.00	0.01	0.03	0.16	0.00	0.01	0.04	0.16
CR (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LP_1(X)	0.04	0.15	0.90	2.22	0.04	0.16	1.00	2.48	0.04	0.17	1.01	2.50
LP_2(X)	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.03	0.00	0.00	0.02	0.03
LP_3(X)	0.00	0.00	0.02	0.06	0.00	0.00	0.02	0.08	0.00	0.00	0.02	0.07
LP (N)	0.00	0.00	0.02	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
$\sigma_{C1\text{-}C2}$	0.04	0.03	-0.20	-1.06	0.07	0.09	0.05	-0.47	0.08	0.13	0.09	-0.41
$\sigma_{C1\text{-}C6}$	0.06	0.11	0.16	-0.19	0.09	0.14	0.16	-0.28	0.08	0.13	0.09	-0.41
$\sigma_{C2\text{-}C3}$	0.01	-0.01	-0.08	-0.39	0.01	0.02	0.05	-0.05	0.02	0.02	0.07	-0.02
$\sigma_{C3\text{-}C4}$	0.00	0.00	0.01	0.03	0.00	-0.01	-0.01	-0.02	0.00	-0.01	-0.01	-0.03
$\sigma_{C4\text{-}C5}$	0.00	-0.01	-0.01	-0.03	0.00	-0.01	-0.01	-0.05	0.00	-0.01	-0.01	-0.03
$\sigma_{C5\text{-}C6}$	0.02	0.02	0.08	0.01	0.02	0.02	0.07	-0.04	0.02	0.02	0.07	-0.02
$\pi_{C\text{-}C}$[d]	-0.01	0.00	0.24	0.40	-0.01	0.00	0.23	0.32	-0.01	-0.01	0.19	0.21
$\sigma_{C1\text{-}X}$	0.06	0.44	2.94	8.56	0.07	0.47	3.15	9.24	0.06	0.48	3.26	9.65
$\sigma_{C2\text{-}H}$	-	-	-	-	-0.01	-0.05	-0.08	-0.11	-0.02	-0.05	-0.09	-0.13
$\sigma_{C2\text{-}R}$	0.00	-0.01	-0.02	0.01	-	-	-	-	-	-	-	-
$\sigma_{C3\text{-}H}$	0.00	0.01	-0.02	-0.06	-	-	-	-	0.00	0.00	-0.04	-0.09
$\sigma_{C3\text{-}R}$	-	-	-	-	0.00	0.00	-0.02	-0.04	-	-	-	-
$\sigma_{C4\text{-}H}$	0.00	0.00	0.00	0.01	0.00	0.00	-0.01	-0.01	-	-	-	-
$\sigma_{C4\text{-}R}$	-	-	-	-	-	-	-	-	0.00	0.00	0.00	0.00
$\sigma_{C5\text{-}H}$	-0.01	0.00	-0.05	-0.12	-0.01	0.00	-0.05	-0.12	0.00	0.00	-0.04	-0.09
$\sigma_{C6\text{-}H}$	-0.01	-0.05	-0.08	-0.12	-0.01	-0.05	-0.09	-0.14	-0.02	-0.05	-0.09	-0.13
$\sigma_{N\text{-}H}$[e]	-0.01	-0.05	-0.20	-0.44	0.00	0.00	0.00	-0.03	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}C2}$	-0.02	0.08	0.50	1.60	0.00	0.09	0.50	1.61	0.00	0.10	0.56	1.68
$\sigma^*_{C1\text{-}C6}$	0.03	0.12	0.51	1.36	0.03	0.13	0.61	1.74	0.00	0.10	0.56	1.68
$\sigma^*_{C1\text{-}X}$	0.19	1.10	4.67	9.53	0.19	1.19	5.25	10.94	0.19	1.16	5.22	11.20
all other σ^*	0.00	0.00	0.01	0.03	0.00	0.00	0.04	0.15	0.00	0.00	0.02	0.10
all π^*	-0.03	-0.04	-0.05	-0.11	-0.02	-0.02	-0.04	-0.12	-0.01	-0.02	-0.04	-0.10
$\sum_{total}$[f]	1.24	3.34	14.73	35.06	1.29	3.68	16.84	40.64	1.26	3.66	17.03	41.54

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of three π orbitals. [e] Sum of $\sigma_{N\text{-}H}$ contributions. [f] Sum of all NLMO contributions.

Table S13: NLMO contributions[a] to σ^{dia} term of the C1 shielding for X-NO_2-benzenes.

Parent	*o*-X-NO_2				*m*-X-NO_2				*p*-X-NO_2			
NBO	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR (C1)	203.41	203.42	203.44	203.46	203.42	203.44	203.45	203.47	203.44	203.46	203.47	203.49
CR (C2-C6)[b]	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.03	0.03	0.03	0.03
CR (X)[c]	0.15	-0.05	-0.05	-0.03	0.05	-0.02	-0.03	-0.05	0.01	-0.04	-0.02	-0.03
CR (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CR (O)[d]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LP_1(X)	1.96	1.74	1.38	1.21	1.96	1.75	1.39	1.24	1.97	1.77	1.41	1.25
LP_2(X)	1.24	1.36	1.12	1.08	1.17	1.39	1.16	1.16	1.16	1.37	1.14	1.14
LP_3(X)	1.40	1.34	1.18	1.19	1.41	1.27	1.12	1.13	1.55	1.35	1.19	1.19
LP_1(O)[d]	0.74	0.71	0.71	0.71	0.41	0.41	0.40	0.40	0.32	0.32	0.32	0.32
LP_2(O)[d]	-0.27	-0.16	-0.17	-0.20	-0.16	-0.16	-0.16	-0.15	-0.14	-0.14	-0.14	-0.14
LP_3(O)	0.13	0.11	0.11	0.11	0.01	0.04	0.04	0.04	0.02	0.02	0.02	0.02
$\sigma_{C1\text{-}C2}$	6.25	7.88	8.14	8.90	7.76	9.51	9.89	10.97	8.54	10.15	10.60	11.72
$\sigma_{C1\text{-}C6}$	9.32	10.44	10.67	11.65	8.22	9.88	10.30	11.36	8.54	10.15	10.60	11.72
$\sigma_{C2\text{-}C3}$	0.68	0.69	0.73	0.70	0.33	0.38	0.41	0.35	0.39	0.45	0.47	0.43
$\sigma_{C3\text{-}C4}$	-0.12	-0.10	-0.10	-0.10	-0.02	0.00	0.00	0.01	-0.10	-0.08	-0.07	-0.07
$\sigma_{C4\text{-}C5}$	-0.12	-0.10	-0.10	-0.09	-0.15	-0.13	-0.13	-0.12	-0.10	-0.08	-0.07	-0.07
$\sigma_{C5\text{-}C6}$	0.50	0.58	0.60	0.53	0.45	0.51	0.53	0.49	0.39	0.45	0.47	0.43
$\pi_{C\text{-}C}$[e]	18.36	19.14	19.23	19.08	18.88	19.45	19.56	19.45	18.22	18.87	18.98	18.87
$\sigma_{C1\text{-}X}$	-3.76	1.52	-1.37	1.18	-3.97	1.35	-1.59	0.79	-4.19	1.14	-1.93	0.57
$\sigma_{C2\text{-}H}$	-	-	-	-	0.57	0.60	0.64	0.65	0.51	0.53	0.58	0.62
$\sigma_{C2\text{-}R}$	0.43	0.37	0.38	0.35	-	-	-	-	-	-	-	-
$\sigma_{C3\text{-}H}$	0.07	0.09	0.06	0.10	-	-	-	-	0.11	0.16	0.14	0.15
$\sigma_{C3\text{-}R}$	-	-	-	-	0.07	0.08	0.08	0.08	-	-	-	-
$\sigma_{C4\text{-}H}$	0.05	0.05	0.05	0.04	0.08	0.08	0.08	0.07	-	-	-	-
$\sigma_{C4\text{-}R}$	-	-	-	-	-	-	-	-	0.05	0.05	0.05	0.05
$\sigma_{C5\text{-}H}$	0.06	0.11	0.10	0.12	0.05	0.09	0.08	0.10	0.11	0.16	0.14	0.15
$\sigma_{C6\text{-}H}$	0.50	0.49	0.55	0.57	0.48	0.51	0.55	0.56	0.51	0.54	0.57	0.60
$\sigma_{N\text{-}O}$[f]	-0.23	-0.22	-0.22	-0.22	-0.11	-0.11	-0.11	-0.11	-0.10	-0.10	-0.10	-0.10
$\pi_{N\text{-}O}$	0.20	0.19	0.19	0.19	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
all σ^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
all π^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sum_{total}$[g]	240.98	249.63	246.66	250.56	240.98	250.39	247.74	251.97	241.28	250.57	247.89	252.38

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of contributions from two oxigen atoms. [e] Sum of three π orbitals. [f] Sum of $\sigma_{N\text{-}O}$ contributions. [g] Sum of all NLMO contributions.

Table S14: NLMO contributions[a] to σ^{para} term of the C1 shielding for X-NO_2-benzenes.

Parent	*o*-X-NO_2				*m*-X-NO_2				*p*-X-NO_2			
NBO	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR (C1)	-0.03	-0.01	0.01	0.03	-0.07	-0.05	-0.01	0.01	-0.09	-0.06	-0.02	0.00
CR (C2-C6)[b]	-1.11	-1.16	-1.30	-1.39	-0.98	-1.04	-1.18	-1.26	-0.91	-0.96	-1.12	-1.21
CR (X)[c]	-0.01	-0.02	-0.06	-0.06	0.06	0.02	-0.10	0.03	0.00	0.00	0.00	0.00
CR (N)	-0.02	-0.02	-0.03	-0.04	-0.01	-0.01	-0.02	-0.02	-0.01	-0.01	-0.01	0.02
CR (O)[d]	-0.04	-0.04	-0.05	-0.05	-0.03	-0.03	-0.04	-0.05	-0.02	-0.04	-0.04	-0.04
LP_1(X)	-7.68	-5.23	-4.63	-4.12	-7.34	-4.79	-4.25	-3.78	-7.64	-5.05	-4.48	-4.03
LP_2(X)	-0.09	-0.64	0.13	0.95	-0.58	-0.74	0.18	1.13	-0.72	-0.87	0.02	0.94
LP_3(X)	-1.36	-3.90	-3.91	-4.68	-1.41	-3.81	-3.67	-4.17	-1.57	-4.24	-4.26	-5.16
LP_1(O)[d]	-0.89	-0.95	-1.04	-1.09	-0.49	-0.53	-0.51	-0.66	-0.44	-0.48	-0.56	-0.64
LP_2(O)[d]	-1.59	-1.33	-1.53	-1.86	-0.32	-0.35	-0.46	-0.53	-0.34	-0.36	-0.44	-0.48
LP_3(O)	-0.51	-0.53	-0.52	-0.48	-0.39	-0.35	-0.41	-0.46	-0.29	-0.31	-0.39	-0.45
$\sigma_{C1\text{-}C2}$	-67.92	-60.14	-61.50	-61.93	-72.88	-63.24	-64.27	-63.18	-73.45	-63.09	-63.08	-62.07
$\sigma_{C1\text{-}C6}$	-72.00	-62.64	-60.08	-59.10	-71.76	-61.87	-60.41	-59.64	-73.45	-63.09	-63.08	-62.07
$\sigma_{C2\text{-}C3}$	-1.58	-1.74	-1.65	-1.75	-1.19	-1.13	-0.83	-0.59	-1.76	-1.64	-1.36	-1.08
$\sigma_{C3\text{-}C4}$	0.18	0.08	0.04	-0.05	-0.17	-0.30	-0.34	-0.49	-0.09	-0.19	-0.23	-0.44
$\sigma_{C4\text{-}C5}$	0.16	-0.06	-0.16	-0.35	-0.18	-0.35	-0.43	-0.67	-0.09	-0.19	-0.23	-0.44
$\sigma_{C5\text{-}C6}$	-1.39	-1.24	-1.18	-0.94	-1.48	-1.45	-1.29	-1.11	-1.76	-1.64	-1.36	-1.09
$\pi_{C\text{-}C}$[e]	-24.59	-12.51	-8.31	-4.98	-25.21	-13.87	-9.95	-6.60	-25.19	-14.97	-11.21	-8.52
$\sigma_{C1\text{-}X}$	-33.98	-44.80	-47.46	-50.89	-34.00	-47.59	-48.95	-51.68	-36.93	-53.85	-55.62	-59.80
$\sigma_{C2\text{-}H}$	-	-	-	-	-2.69	-4.02	-4.89	-5.55	-2.54	-3.85	-4.89	-5.68
$\sigma_{C2\text{-}R}$	-1.28	-1.05	-0.66	-0.15	-	-	-	-	-	-	-	-
$\sigma_{C3\text{-}H}$	-0.71	-0.66	-0.81	-0.84	-	-	-	-	-0.24	-0.40	-0.58	-0.69
$\sigma_{C3\text{-}R}$	-	-	-	-	-0.02	-0.03	-0.06	-0.10	-	-	-	-
$\sigma_{C4\text{-}H}$	-0.50	-0.44	-0.48	-0.42	-0.48	-0.42	-0.44	-0.38	-	-	-	-
$\sigma_{C4\text{-}R}$	-	-	-	-	-	-	-	-	0.00	0.02	0.02	0.02
$\sigma_{C5\text{-}H}$	-0.59	-0.75	-0.84	-0.91	-0.36	-0.55	-0.70	-0.79	-0.23	-0.40	-0.57	-0.70
$\sigma_{C6\text{-}H}$	-2.43	-3.61	-4.76	-5.46	-2.52	-3.82	-4.90	-5.67	-2.54	-3.85	-4.89	-5.68
$\sigma_{N\text{-}O}$[f]	0.19	0.35	0.44	0.44	0.28	0.36	0.49	0.58	0.24	0.30	0.44	0.54
$\pi_{N\text{-}O}$	0.46	0.48	0.51	0.54	0.28	0.33	0.41	0.47	0.25	0.37	0.48	0.60
all σ^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
all π^*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sum_{total}$[g]	-219.31	-202.56	-199.83	-199.46	-223.94	-209.63	-207.03	-205.16	-229.83	-218.81	-217.49	-218.19

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of contributions from two oxigen atoms. [e] Sum of three π orbitals. [f] Sum of $\sigma_{N\text{-}O}$ contributions. [g] Sum of all NLMO contributions.

Table S15: NLMO contributions[a] to σ^{SO} term of the C1 shielding for X-NO_2-benzenes.

Parent	*o*-X-NO_2				*m*-X-NO_2				*p*-X-NO_2			
NBO	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
CR (C1)	0.90	1.59	6.36	16.58	0.86	1.48	6.31	16.44	0.82	1.37	6.11	15.73
CR (C2-C6)[b]	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CR (X)[c]	-0.10	-0.55	-2.11	-2.73	-0.10	-0.53	-1.88	-2.51	-0.11	-0.49	-1.77	-2.52
CR (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CR (O)[d]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LP_1(X)	0.05	0.19	1.07	2.54	0.04	0.16	1.05	2.63	0.03	0.14	1.01	2.52
LP_2(X)	-0.01	-0.02	-0.06	-0.04	0.00	0.00	0.02	0.03	0.00	0.00	0.02	0.04
LP_3(X)	-0.01	-0.01	0.02	0.09	0.00	0.00	0.02	0.09	0.00	-0.01	0.01	0.07
LP_1(O)[d]	0.00	0.00	-0.01	-0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
LP_2(O)[d]	-0.02	-0.03	-0.11	-0.23	0.00	0.00	-0.01	-0.05	0.00	-0.02	-0.04	-0.08
LP_3(O)	0.00	0.00	-0.02	-0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma_{C1\text{-}C2}$	0.04	0.02	-0.12	-0.85	0.10	0.14	0.10	-0.33	0.15	0.27	0.40	0.25
$\sigma_{C1\text{-}C6}$	0.08	0.16	0.38	0.25	0.12	0.25	0.40	0.24	0.15	0.27	0.40	0.25
$\sigma_{C2\text{-}C3}$	0.00	0.00	-0.03	-0.23	0.01	0.01	0.03	-0.07	0.01	0.02	0.07	-0.01
$\sigma_{C3\text{-}C4}$	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	-0.02	0.00	-0.01	-0.01	-0.04
$\sigma_{C4\text{-}C5}$	0.00	-0.01	0.00	-0.03	-0.01	-0.01	-0.01	-0.04	0.00	-0.01	-0.01	-0.04
$\sigma_{C5\text{-}C6}$	0.02	0.03	0.12	0.08	0.02	0.03	0.11	0.06	0.01	0.02	0.07	-0.01
$\pi_{C\text{-}C}$[e]	-0.01	0.00	0.32	0.59	0.00	0.00	0.29	0.45	-0.01	0.00	0.30	0.58
$\sigma_{C1\text{-}X}$	0.08	0.53	3.73	11.11	0.06	0.52	3.56	10.63	0.05	0.49	3.39	10.08
$\sigma_{C2\text{-}H}$	-	-	-	-	-0.02	-0.04	-0.07	-0.08	-0.02	-0.07	-0.12	-0.22
$\sigma_{C2\text{-}R}$	-0.01	-0.01	-0.01	-0.01	-	-	-	-	-	-	-	-
$\sigma_{C3\text{-}H}$	0.00	0.00	-0.03	-0.09	-	-	-	-	-0.01	0.00	-0.04	-0.10
$\sigma_{C3\text{-}R}$	-	-	-	-	0.00	0.00	0.00	-0.02	-	-	-	-
$\sigma_{C4\text{-}H}$	0.00	0.00	0.00	0.01	0.00	0.00	-0.01	0.00	-	-	-	-
$\sigma_{C4\text{-}R}$	-	-	-	-	-	-	-	-	0.00	0.00	-0.01	-0.01
$\sigma_{C5\text{-}H}$	-0.01	0.01	-0.04	-0.10	-0.01	0.00	-0.05	-0.11	-0.01	0.00	-0.04	-0.10
$\sigma_{C6\text{-}H}$	-0.01	-0.13	-0.16	-0.32	-0.02	-0.08	-0.13	-0.25	-0.02	-0.07	-0.12	-0.22
$\sigma_{N\text{-}O}$[f]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\pi_{N\text{-}O}$	0.00	0.00	-0.02	-0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sigma^*_{C1\text{-}C2}$	-0.05	0.06	0.59	2.18	-0.05	0.03	0.38	1.47	-0.02	0.08	0.51	1.61
$\sigma^*_{C1\text{-}C6}$	0.06	0.16	0.57	1.39	0.04	0.17	0.73	1.97	-0.02	0.08	0.51	1.61
$\sigma^*_{C1\text{-}X}$	0.20	1.33	5.92	12.25	0.19	1.20	5.46	11.62	0.18	1.11	5.11	11.04
all other σ^*	0.00	0.00	-0.01	-0.01	0.00	0.01	0.04	0.16	0.00	0.00	0.02	0.09
all π^*	-0.03	-0.03	-0.06	-0.18	-0.02	-0.03	-0.06	-0.15	-0.03	-0.03	-0.08	-0.20
$\sum_{total}$[g]	1.17	3.29	16.29	42.09	1.21	3.31	16.28	42.17	1.15	3.14	15.69	40.32

[a] in ppm. [b] Sum of core carbon 2-6 contributions. [c] Sum of all core X contributions. [d] Sum of contributions from two oxigen atoms. [e] Sum of three π orbitals. [f] Sum of $\sigma_{N\text{-}O}$ contributions. [g] Sum of all NLMO contributions.

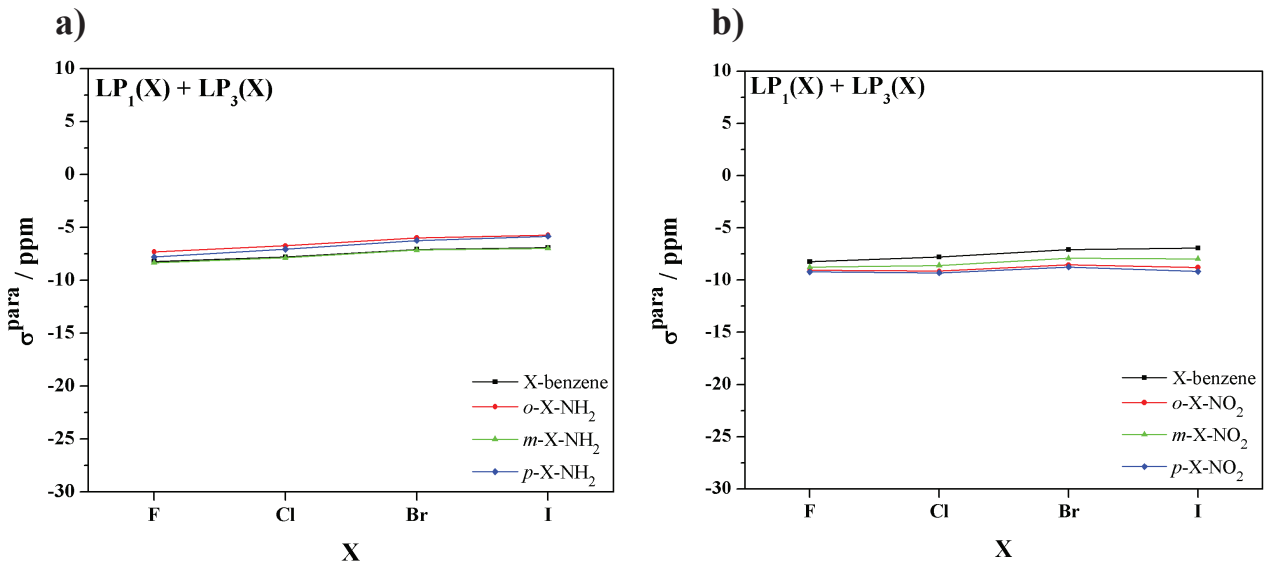

Figure S1: Sum of $LP_1(X)$ and $LP_3(X)$ orbital contributions to the isotropic σ^{para} term of the C1 shielding for X-benzenes, X-NH_2-benzenes **(a)**, and X-NO_2-benzenes **(b)** (in ppm).

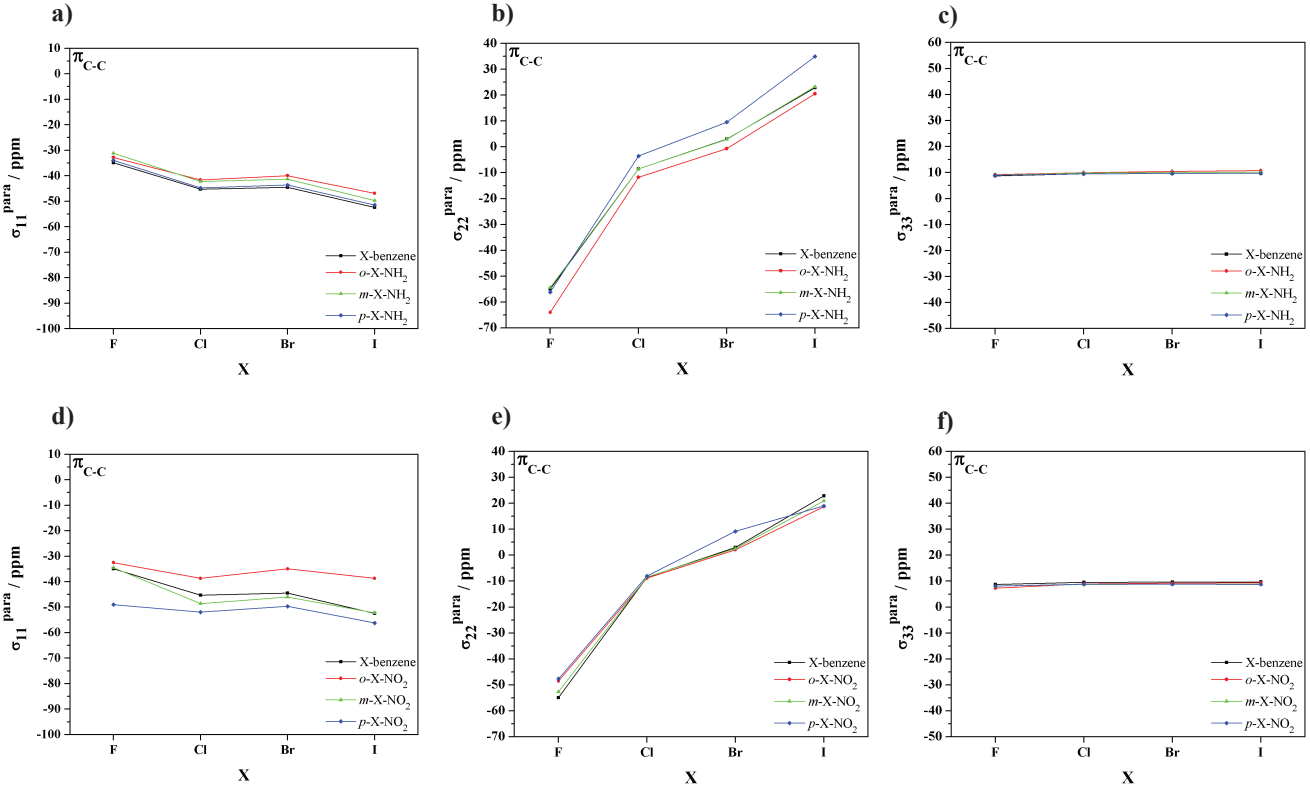

Figure S2: $\pi_{C\text{-}C}$ NLMO contributions to σ_{11} (**a**, **d**), σ_{22} (**b**, **e**), and σ_{33} (**c**, **f**) components of the C1 σ^{para} for X-R-benzenes (in ppm). Top row: NH_2 substituent. Bottom row: NO_2 substituent. Each value refers to the sum of contribution from three $\pi_{C\text{-}C}$ orbitals.

Table S16: Atomic hybrid contributions percentage of C1 (%C1) to $\sigma^*_{\text{C1-X}}$ antibonding NBO for X-R-benzenes.

	%C1			
R	F	Cl	Br	I
H	71.87	56.38	53.52	47.70
o-NH_2	71.95	56.75	54.01	48.36
m-NH_2	71.99	56.59	53.77	47.96
p-NH_2	71.86	56.52	53.71	47.97
o-NO_2	71.08	54.60	51.29	44.98
m-NO_2	71.47	55.51	52.44	46.40
p-NO_2	71.64	55.65	52.57	46.51

Table S17: CMO π contributions to the σ_{22} component of the σ^{para} term associated with $\pi_{\text{C-C}} - \sigma^*_{\text{C1-X}}$ interactions for X-R-benzenes.

	CMO π-1				CMO π-2				CMO π-3			
R	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
H	-10.19	-47.27	-41.47	-30.99	-0.90	-0.80	-0.82	-0.80	-40.16	17.54	38.34	69.84
o-NH_2	-6.65	-36.75	-33.89	-25.22	-25.65	11.53	24.76	38.07	-30.96	-2.44	3.45	24.66
m-NH_2	-3.31	-31.88	-24.18	-22.66	-30.84	13.34	30.58	53.05	-4.86	2.36	4.93	13.66
p-NH_2	-6.00	-33.83	-26.42	-18.27	-0.86	-0.78	-0.79	-0.46	-32.50	12.01	25.82	59.46
o-NO_2	-10.31	-43.46	-37.93	-28.31	-2.61	-2.52	-2.75	-1.65	-36.28	18.31	39.26	63.09
m-NO_2	-7.89	-43.40	-36.95	-27.45	-1.58	-0.40	-0.41	-1.00	-37.92	19.56	40.51	65.79
p-NO_2	-8.24	-44.25	-37.68	-27.91	-0.82	-0.75	-0.76	-0.75	-35.54	19.24	39.00	60.64

Table S18: CMOs $\sigma^*_{\text{C1-X}}$ energies (in eV) for X-R-benzenes.

	CMO $\sigma^*_{\text{C1-X}}$			
R	F	Cl	Br	I
H	4.61	1.18	0.03	-0.67
o-NH_2	4.57	1.29	0.07	-0.63
m-NH_2	4.66	1.19	0.08	-0.63
p-NH_2	4.51	1.29	0.11	-0.57
o-NO_2	5.10	0.88	-0.27	-0.94
m-NO_2	4.62	0.96	-0.21	-0.91
p-NO_2	4.76	1.02	-0.17	-0.89

Table S19: CMOs π-1, π-2 and π-3 energies (in eV) for X-R-benzenes.

	CMO π-1				CMO π-2				CMO π-3			
R	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
H	-10.64	-11.52	-11.30	-11.12	-7.73	-7.74	-7.75	-7.70	-7.36	-7.26	-7.19	-6.89
o-NH_2	-11.04	-11.84	-11.68	-11.56	-7.40	-7.33	-7.27	-7.04	-6.30	-6.30	-6.31	-6.26
m-NH_2	-11.21	-11.69	-11.58	-11.47	-7.39	-7.31	-7.24	-6.96	-6.33	-6.34	-6.35	-6.30
p-NH_2	-11.06	-11.64	-11.52	-11.42	-7.67	-7.69	-7.70	-7.65	-6.16	-6.16	-6.17	-6.08
o-NO_2	-11.16	-12.05	-11.83	-11.64	-8.29	-8.18	-8.16	-8.14	-7.89	-7.71	-7.59	-7.22
m-NO_2	-11.18	-11.97	-11.77	-11.61	-8.36	-8.36	-8.35	-8.29	-7.89	-7.72	-7.59	-7.21
p-NO_2	-11.19	-11.98	-11.77	-11.60	-8.27	-8.26	-8.25	-8.20	-8.00	-7.81	-7.68	-7.28

Table S20: CMOs π^*-1, π^*-2 and π^*-3 energies (in eV) for X-R-benzenes.

	CMO π^*-1				CMO π^*-2				CMO π^*-3			
R	F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
H	-0.60	-0.62	-0.64	-0.64	-0.26	-0.59	-0.63	-0.60	3.91	3.64	3.49	3.07
o-NH_2	-0.35	-0.53	-0.56	-0.57	0.06	-0.05	-0.08	-0.07	4.19	3.90	3.80	3.80
m-NH_2	-0.36	-0.54	-0.57	-0.58	0.06	-0.12	-0.14	-0.13	3.75	3.60	3.40	3.03
p-NH_2	-0.57	-0.57	-0.59	-0.56	0.19	-0.12	-0.15	-0.17	4.01	3.73	3.63	3.19
o-NO_2	-0.82	-1.04	-1.06	-1.09	-0.30	-0.57	-0.59	-0.52	3.72	3.30	3.22	2.94
m-NO_2	-0.83	-1.04	-1.06	-1.06	-0.13	-0.27	-0.29	-0.26	3.61	3.40	3.28	2.92
p-NO_2	-1.05	-1.05	-1.06	-1.02	0.00	-0.28	-0.30	-0.30	3.73	3.49	3.37	3.75

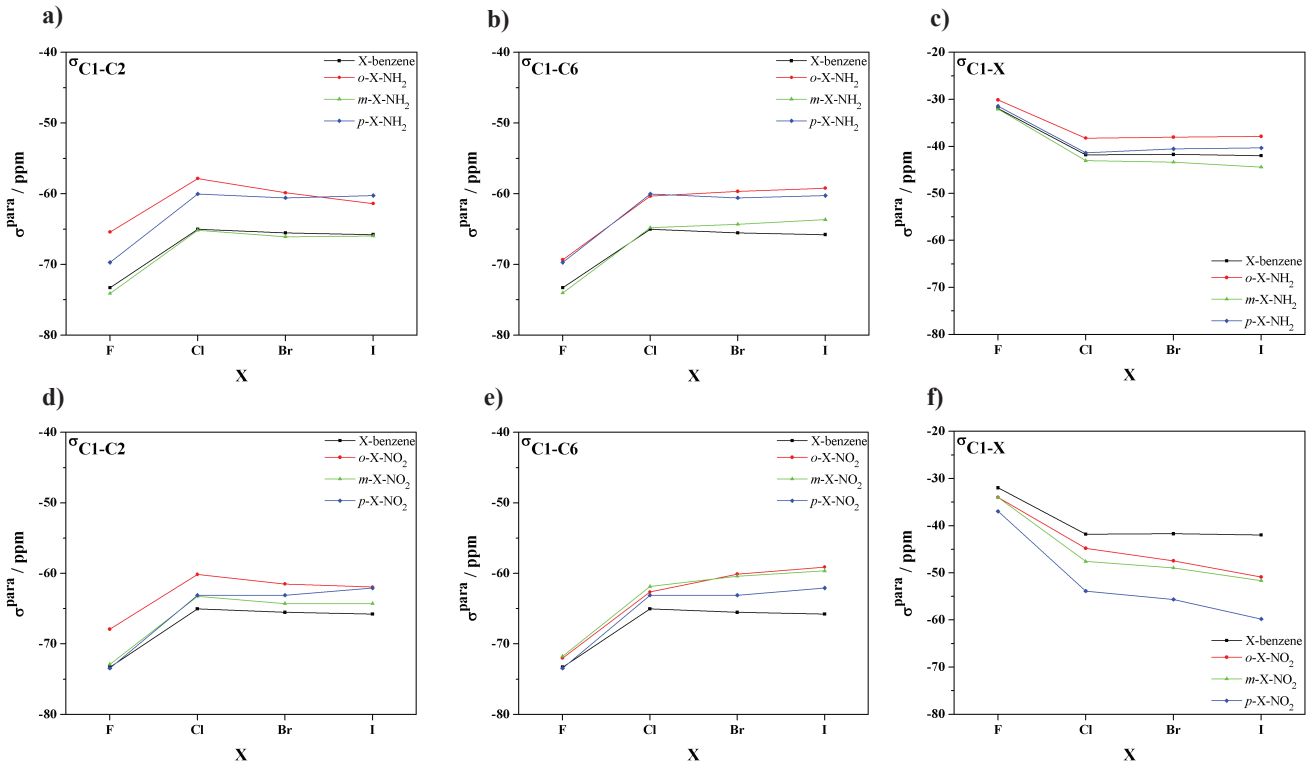

Figure S3: $\sigma_{C1\text{-}C2}$ (**a**, **d**), $\sigma_{C1\text{-}C6}$ (**b**, **e**), and $\sigma_{C1\text{-}X}$ (**c**, **f**) NLMO contributions to the isotropic σ^{para} term of the C1 shielding for X-R-benzenes (in ppm). Top row: NH_2 substituent. Bottom row: NO_2 substituent.

Table S21: Parent NBO percentage of $\sigma_{C1\text{-}C2}$ and $\sigma_{C1\text{-}C6}$ NLMOs for X-R-benzenes.

	$\sigma_{C1\text{-}C2}$				$\sigma_{C1\text{-}C6}$			
R	F	Cl	Br	I	F	Cl	Br	I
H	99.3593	99.2845	99.2915	99.2683	99.3593	99.2845	99.2915	99.2683
o-NH_2	99.0923	99.0296	99.0451	99.0297	99.2849	99.2053	99.2123	99.1862
m-NH_2	99.2290	99.1493	99.1536	99.1271	99.3289	99.2416	99.2458	99.2193
p-NH_2	99.3278	99.2496	99.2554	99.2311	99.3278	99.2496	99.2554	99.2311
o-NO_2	99.1680	99.0356	99.0420	99.0249	99.1859	99.0350	99.0236	98.9721
m-NO_2	99.0981	99.0275	99.0303	99.0030	99.3787	99.2965	99.2993	99.2728
p-NO_2	99.3752	99.2976	99.3011	99.2726	99.3752	99.2976	99.3011	99.2726

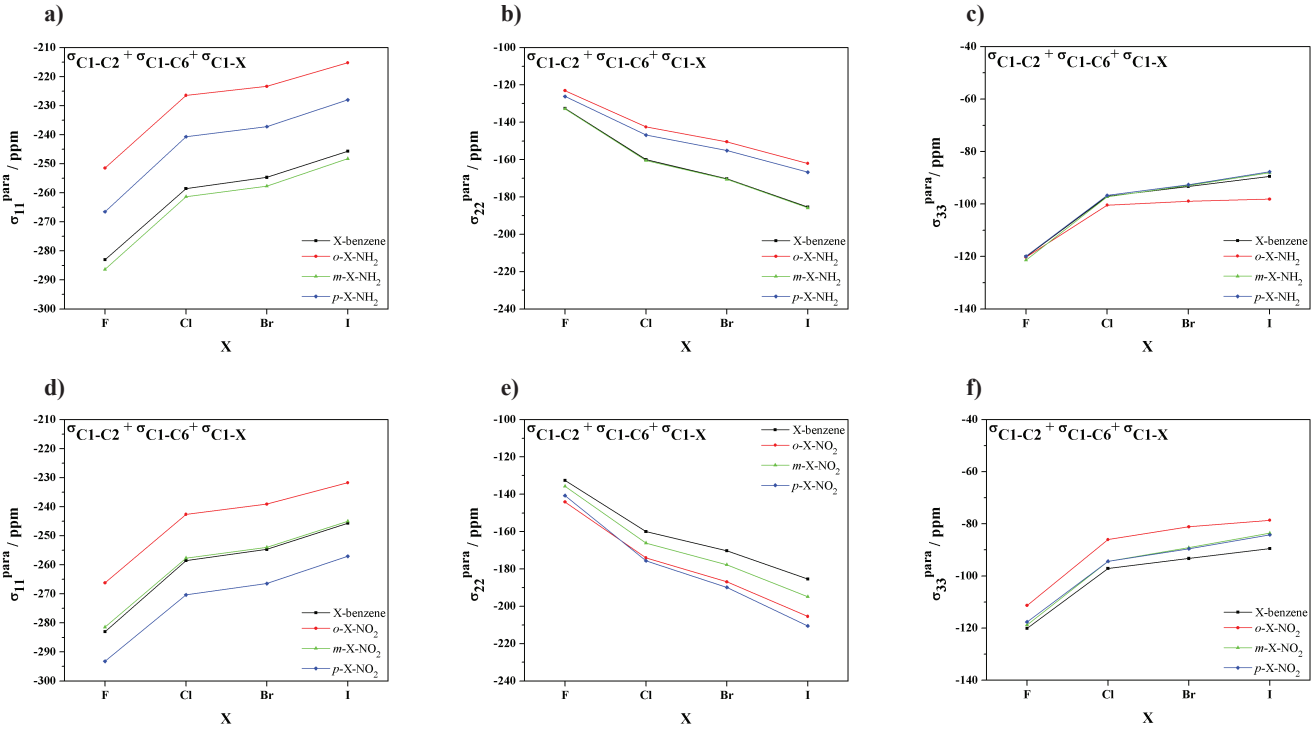

Figure S4: Sum of $\sigma_{C1\text{-}C2}$, $\sigma_{C1\text{-}C6}$, and $\sigma_{C1\text{-}X}$ NLMO contributions to σ_{11} (**a**, **d**), σ_{22} (**b**, **e**), and σ_{33} (**c**, **f**) components of the σ^{para} term of the C1 shielding tensor for X-R-benzenes (in ppm). Top row: NH_2 substituent. Bottom row: NO_2 substituent.

Table S22: Atomic hybrid contributions of the carbon of interest (%C1) to $\sigma_{C1\text{-}X}$ NLMOs for X-R-benzenes.

	$\sigma_{C1\text{-}X}$			
R	F	Cl	Br	I
H	28.07	43.36	46.10	51.70
o-NH_2	27.99	43.01	45.64	51.08
m-NH_2	27.96	43.14	45.84	51.42
p-NH_2	28.08	43.23	45.92	51.45
o-NO_2	28.86	45.11	48.27	54.30
m-NO_2	28.47	44.22	47.16	52.96
p-NO_2	28.30	44.09	47.03	52.86

Table S23: $\sigma^*_{C1\text{-}X}$ NBO occupations for X-benzene and X-NH_2-benzenes.

	$\sigma_{C1\text{-}X}$			
X	H	*o*-NH_2	*m*-NH_2	*p*-NH_2
F	0.03362	0.02945	0.03300	0.03313
Cl	0.03241	0.03035	0.03214	0.03136
Br	0.03657	0.03511	0.03632	0.03515
I	0.03640	0.03665	0.03617	0.03479

5 *Δ*VDD atomic charges

σ contributions for *Δ*VDD atomic charges (in me$^-$) for X-NH_2-benzenes (Fig. S5) and X-NO_2-benzenes (Fig. S6) calculated in relation to X-benzene values caused by the formation of the C-N bond.

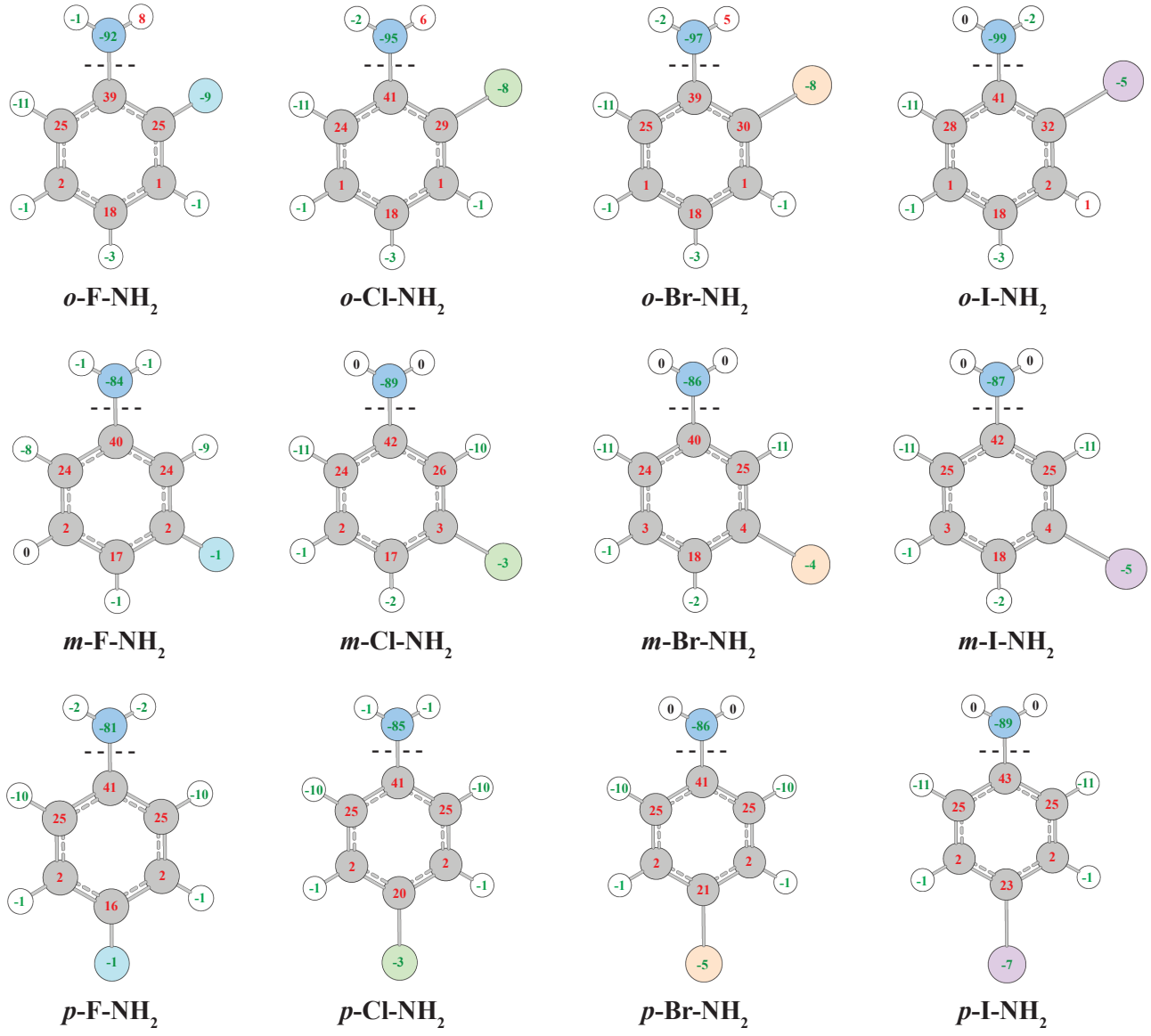

Figure S5: The σ contribution for *Δ*VDD atomic charges (in me$^-$) for X-NH_2-benzenes calculated in relation to X-benzene values caused by the formation of the C-N bond. Negative values indicate accumulation of electronic density, while positive values denote electron density depletion and positive charge accumulation.

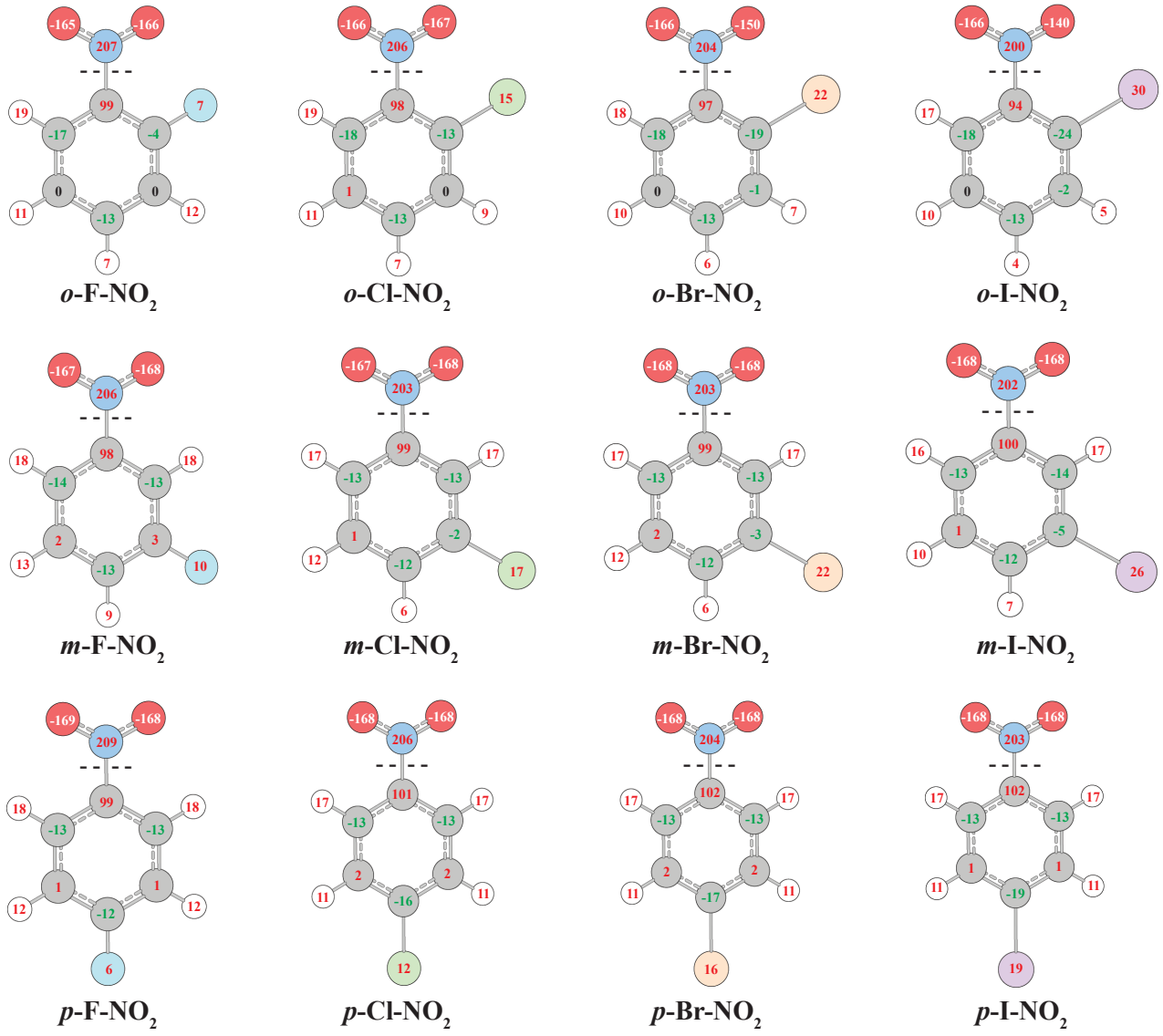

Figure S6: The σ contribution for ΔVDD atomic charges (in me$^-$) for X-NO_2-benzenes calculated in relation to X-benzene values caused by the formation of the C-N bond. Negative values indicate accumulation of electronic density, while positive values denote electron density depletion and positive charge accumulation.

Table S24: Atomic hybrid contributions (%) of C1 and C2 to the $\sigma_{C1\text{-}C2}$ NLMO for X-benzene and X-NO_2-benzenes.

	X-benzene		*o*-X-NO_2-benzene		*m*-X-NO_2-benzene		*p*-X-NO_2-benzene	
X	%C1	%C2	%C1	%C2	%C1	%C2	%C1	%C2
F	49.54	49.90	48.44	50.82	48.88	50.31	49.52	49.94
Cl	50.33	49.06	49.22	49.93	49.61	49.52	50.30	49.09
Br	49.94	49.45	48.84	50.32	49.20	49.94	49.89	49.51
I	49.43	49.93	48.32	50.83	48.66	50.45	49.34	50.02

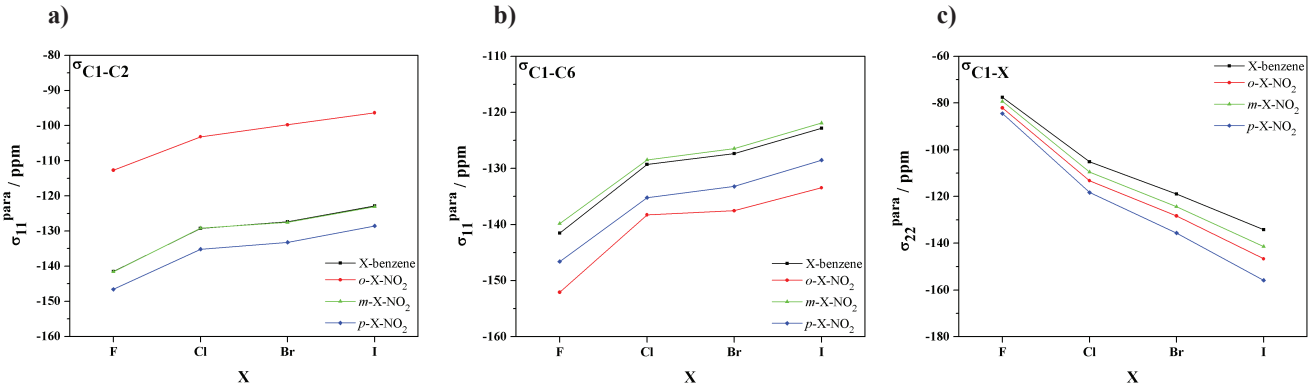

Figure S7: $\sigma_{C1\text{-}C2}$ (**a**), and $\sigma_{C1\text{-}C6}$ (**b**) NLMO contributions to σ_{11} component, and $\sigma_{C1\text{-}X}$ (**c**) NLMO contributions to σ_{22} component of the σ^{para} mechanism for C1 of the X-NO_2-benzenes (in ppm).

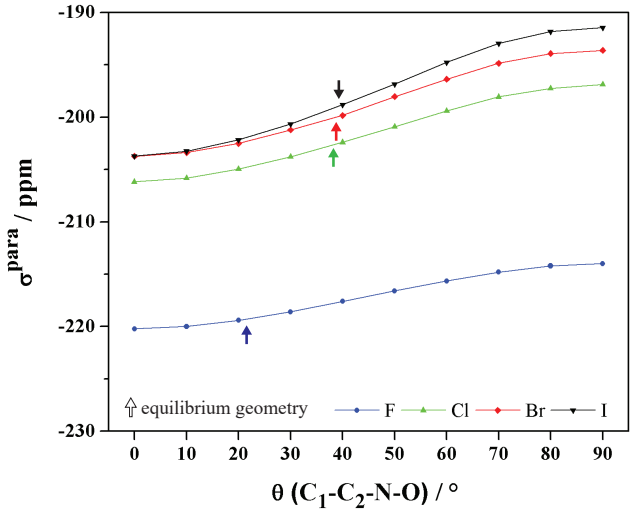

Figure S8: The σ^{para} mechanism of the C1 shielding tensor *versus* the dihedral angle C_1-C_2-N-O (θ) for *o*-X-NO_2-benzene (in ppm). The arrows indicate the torsional angle and shielding in the equilibrium geometry.