Electronic Supplementary Material (ESI) for RSC Advances.

Table S1. Calculated and experimental inversion barriers (kcal mol^{-1}) for aniline and its mono-halosubstituted derivatives.[a]

	B3LYP			MP2			Experimental		
Aniline	0.78			2.32			1.47[b], 1.61[c], 1.29[d], 1.50[e]		
	F	**Cl**	**Br**	**F**	**Cl**	**Br**	**F**	**Cl**	**Br**
o	0.64 (-0.14)	0.46 (-0.32)	0.45 (-0.33)	2.08 (-0.24)	2.18 (-0.14)	2.21 (-0.11)	1.49[f] (-0.01)	1.18[f] (-0.32)	1.10[f] (-0.40)
m	0.63 (-0.15)	0.63 (-0.15)	0.65 (-0.13)	2.04 (-0.28)	2.14 (-0.18)	2.13 (-0.19)	1.31[f] (-0.19)	1.30[f] (-0.20)	1.30[f] (-0.20)
p	0.90 (+0.12)	0.72 (-0.06)	0.69 (-0.09)	2.41 (+0.09)	2.36 (+0.04)	2.34 (+0.02)	1.72[f] (+0.22)	1.48[f] (-0.02)	1.47[f] (-0.03)

[a] Values in parentheses are the inversion barrier differences between aniline and its halo-derivatives.

[b] Ref. 38, microwave

[c] Ref. 44, vibrational IR

[d] Ref. 45, fluorescence

[e] Ref. 46, far-IR

[f] Ref. 47, far-IR

Table S2. Calculated and gas-phase experimental bond lengths (Å) and bond angles (degrees) for aniline, selected fluoroanilines and chloroanilines.

		N-H	N-C[g]	$(C-C)_{avg}$	H-N-H[g]
Aniline	Exp.[a]	1.001	1.402	1.396	111.2
	Cal.	1.009	1.398	1.396	112.2
o-Fluoroaniline	Exp.[b]	0.998	*1.410*	1.392	*111.0*
	Cal.	1.009	1.391	1.394	113.3
m-Fluoroaniline	Exp.[c]	1.00[e]	1.403	1.392	115.0
	Cal.	1.009	1.394	1.394	112.6
p-Fluoroaniline	Exp.[d]	1.02	1.420	1.390	111.9
	Cal.	1.010	1.401	1.393	111.8
o,o'-Difluoroaniline	Exp.[b]	1.003	1.410	1.390	*113.0*
	Cal.	1.009	1.385	1.392	114.7
o-Chloroaniline	Exp.[e]	1.004			113.8
	Cal.	1.009	1.386	1.396	114.0
m-Chloroaniline	Exp.[f]	1.001	1.399	1.397	114
	Cal.	1.009	1.394	1.395	112.6

[a] Refs. 38,39

[b] Ref. 54

[c] Ref. 41

[d] Refs. 51,52

[e] Ref. 42

[f] Ref. 53

[g] Assumed values used in relevant refs. are shown in italic.

Table S3. NBO analysis of the C_1-N_7 bond in aniline, fluoroanilines, chloroanilines and bromoanilines.

	Fluoroanilines	Chloroanilines	Bromoanilines
Molecule	Average Hybridization	Average Hybridization	Average Hybridization
aniline	C_1 ($sp^{2.05}$); N_7 ($sp^{2.47}$)	C_1 ($sp^{2.05}$); N_7 ($sp^{2.47}$)	C_1 ($sp^{2.05}$); N_7 ($sp^{2.47}$)
o	C_1 ($sp^{2.04}$); N_7 ($sp^{2.42}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.38}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.37}$)
m	C_1 ($sp^{2.04}$); N_7 ($sp^{2.43}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.43}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.43}$)
p	C_1 ($sp^{2.04}$); N_7 ($sp^{2.49}$)	C_1 ($sp^{2.05}$); N_7 ($sp^{2.45}$)	C_1 ($sp^{2.05}$); N_7 ($sp^{2.45}$)
o,m	C1 ($sp^{2.04}$); N7 ($sp^{2.39}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.35}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.34}$)
o,p	C_1 ($sp^{2.03}$); N_7 ($sp^{2.45}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.37}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.35}$)
o,m'	C_1 ($sp^{2.03}$); N_7 ($sp^{2.39}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.34}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.33}$)
o,o'	C_1 ($sp^{2.02}$); N_7 ($sp^{2.38}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.29}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.27}$)
m,p	C_1 ($sp^{2.04}$); N_7 ($sp^{2.46}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.42}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.42}$)
m,m'	C_1 ($sp^{2.04}$); N_7 ($sp^{2.39}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.39}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.39}$)
o,m,p	C_1 ($sp^{2.03}$); N_7 ($sp^{2.42}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.35}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.33}$)
o,m,m'	C_1 ($sp^{2.03}$); N_7 ($sp^{2.36}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.31}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.31}$)
o,m,o'	C_1 ($sp^{2.02}$); N_7 ($sp^{2.36}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.25}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.24}$)
o,p.m'	C_1 ($sp^{2.03}$); N_7 ($sp^{2.42}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.35}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.34}$)
o,p,o'	C_1 ($sp^{2.02}$); N_7 ($sp^{2.42}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.28}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.26}$)
m,p,m'	C_1 ($sp^{2.04}$); N_7 ($sp^{2.42}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.40}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.39}$)
o,m,p,m'	C_1 ($sp^{2.03}$); N_7 ($sp^{2.39}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.32}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.30}$)
o,m,m',o'	C_1 ($sp^{2.02}$); N_7 ($sp^{2.32}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.23}$)	C_1 ($sp^{2.04}$); N_7 ($sp^{2.21}$)
o,p,m',o'	C_1 ($sp^{2.02}$); N_7 ($sp^{2.39}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.26}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.23}$)
o,m,p,m',o'	C_1 ($sp^{2.01}$); N_7 ($sp^{2.36}$)	C_1 ($sp^{2.03}$); N_7 ($sp^{2.23}$)	C_1 ($sp^{2.05}$); N_7 ($sp^{2.20}$)

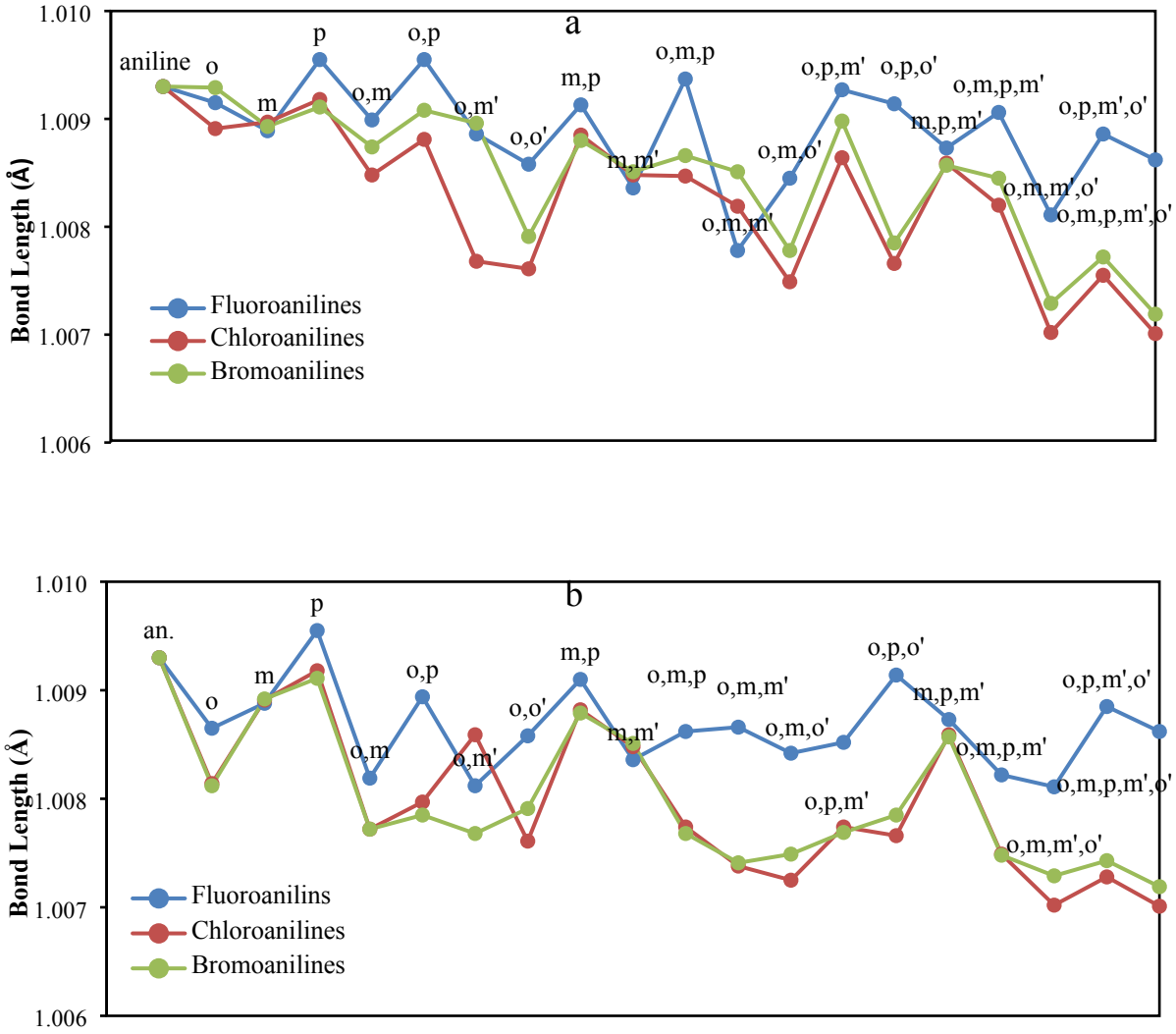

Figure S1: Optimized N-H bond lengths (Å) of H-atom at the side of the ring (a) with more halogen substituents and (b) with less halogen substituents for aniline, fluoroanilines, chloroanilines and bromoanilines.

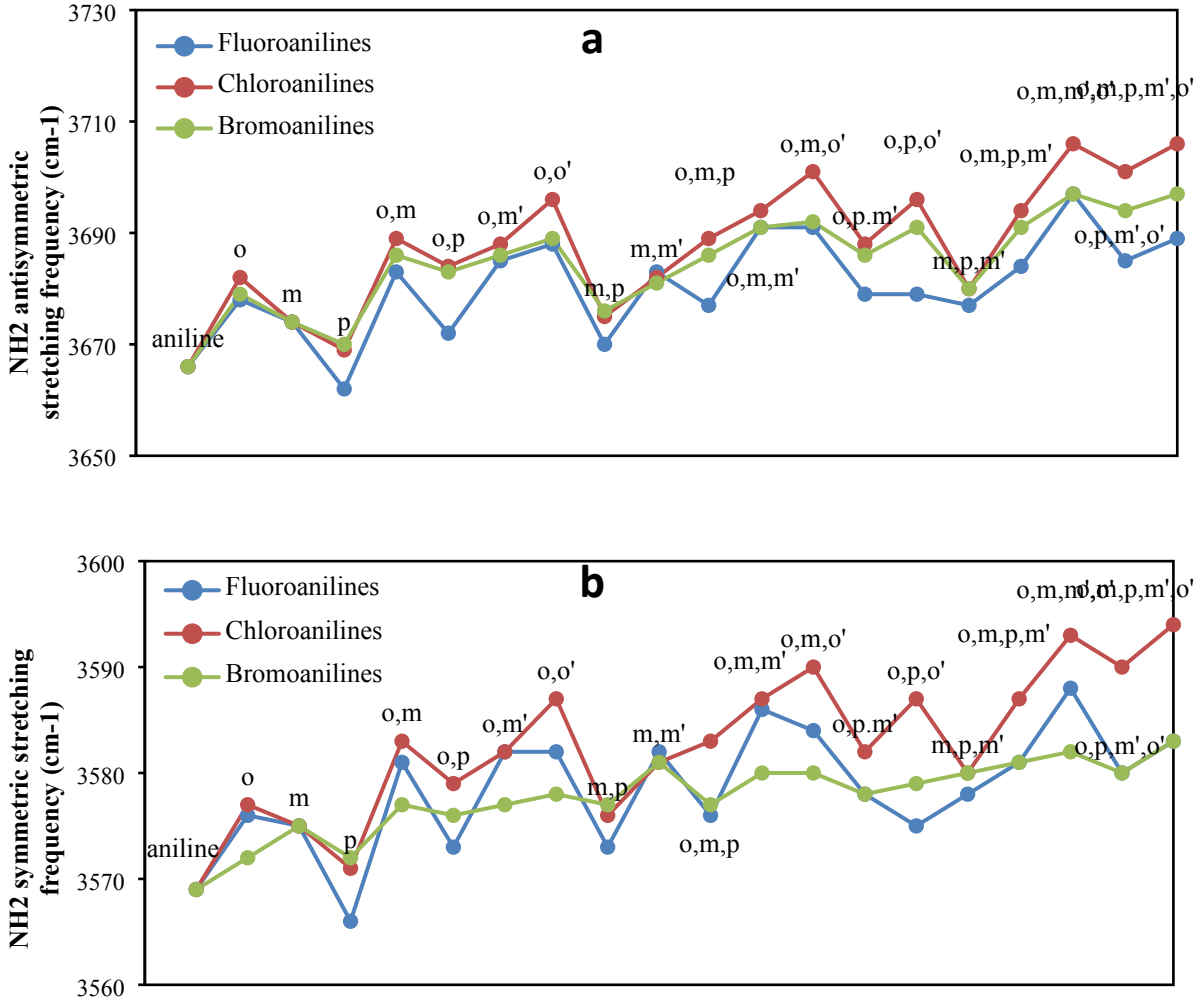

Figure S2**:** Calculated NH_2 (a) antisymmetric and (b) symmetric stretching vibrational frequencies (cm^{-1}) for aniline, fluoroanilines, chloroanilines and bromoanilines

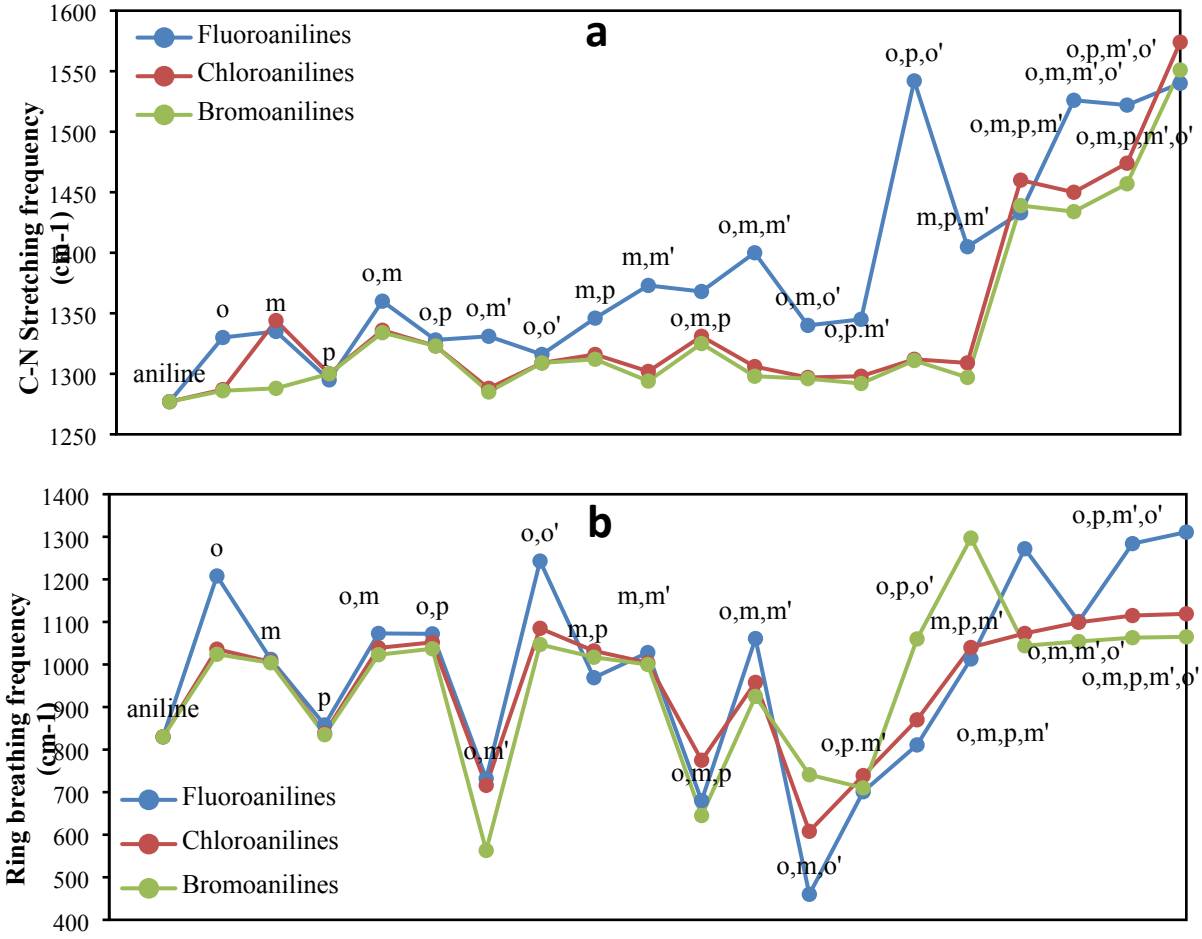

Figure S3**:** Calculated (a) C-N and (b) ring breathing vibrational frequencies (cm^{-1}) for aniline, fluoroanilines, chloroanilines and bromoanilines

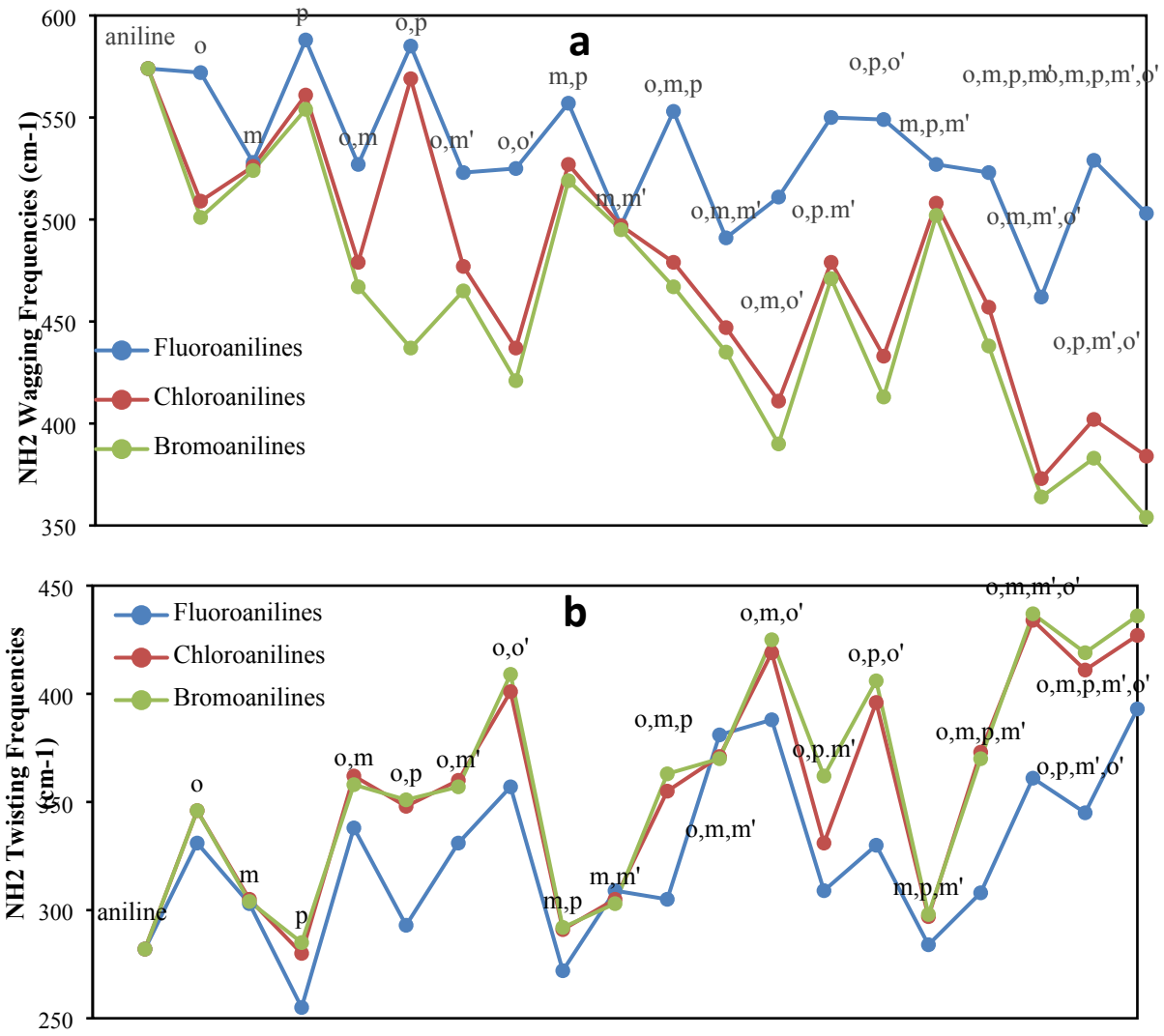

Figure S4: Calculated NH_2 (a) wagging and (b) twisting vibrational frequencies (cm^{-1}) for aniline, fluoroanilines, chloroanilines and bromoanilines.

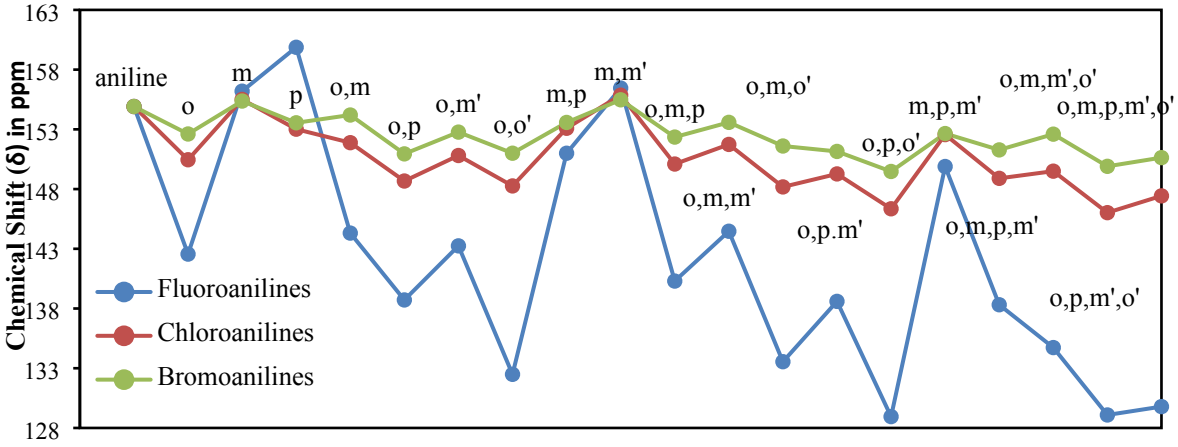

Figure S5: ^{13}C chemical shift (δ) of C_1 carbon atom of aniline, fluoroaniline, chloroaniline and bromoaniline derivatives.

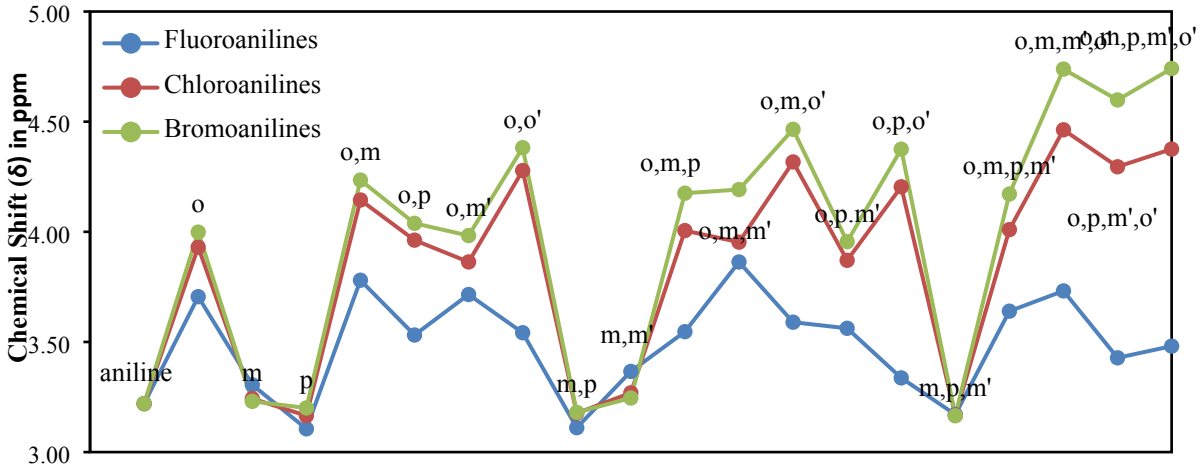

Figure S6: ^{1}H chemical shift (δ) of H_{13} hydrogen atom of aniline, fluoroaniline, chloroaniline and bromoaniline derivatives.

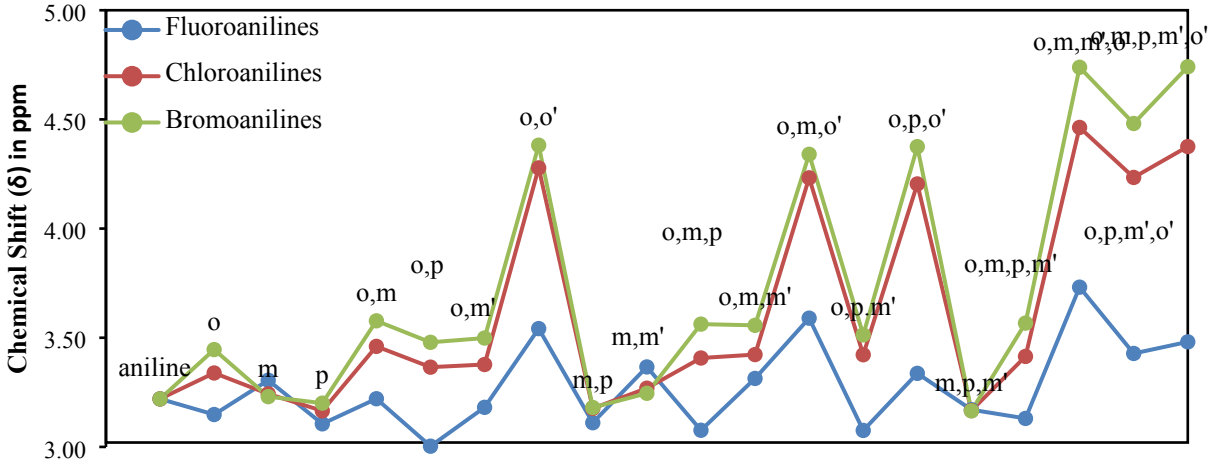

Figure S7: ^{1}H chemical shift (δ) of H_{14} hydrogen atom of aniline, fluoroaniline, chloroaniline and bromoaniline derivatives.