Supplementary Information

F···HO intramolecular hydrogen bond forming five-membered rings hardly appears in monocyclic organofluorine compounds

Rodrigo A. Cormanich,[a] Matheus P. Freitas,*[,b] Cláudio F. Tormena[a] and Roberto Rittner[a]

[a] *Chemistry Institute, State University of Campinas, P.O. Box 6154, 13083-970, Campinas, SP, Brazil*

[b] *Chemistry Department, Federal University of Lavras, P. O. BOX 3037, 37200-000, Lavras, MG, Brazil.*

* E-mail: matheus@dqi.ufla.br

Table of Contents

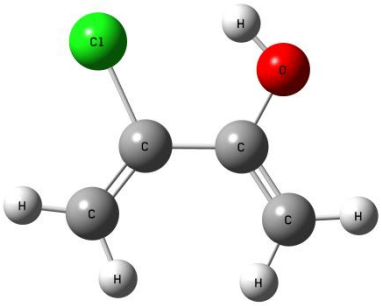
Chlorine derivatives

Table S1: Selected geometric parameters for compounds **1-Cl** to **10-Cl** (interatomic distances in angstroms and bond angles in degrees).

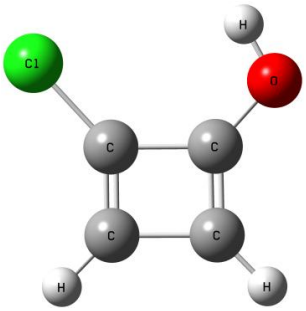
Compound	***r*(Cl···HO)**	***r*(Cl···O)**	**∠ O-C-C(Cl)**	**∠ Cl-C-C(O)**	**∠ C-C(Cl)-C(O)**	**∠ C-C(O)-C(Cl)**
1-Cl	**2.24**	**2.90**	**117.9**	**114.7**	**127.8**	**123.1**
2-Cl	3.23	3.65	132.2	132.3	89.8	90.8
3-Cl	3.31	3.62	139.7	135.7	89.1	90.7
4-Cl	2.56	3.13	124.4	120.9	114.2	111.8
5-Cl	2.58	3.15	123.8	121.0	110.9	108.5
6-Cl	2.72	3.25	127.4	124.2	108.5	107.0
7-Cl	2.74	3.26	127.4	124.4	107.2	105.8
8-Cl	2.36	2.99	119.7	116.6	122.4	118.9
9-Cl	2.41	3.01	123.1	118.2	121.6	118.4
10-Cl	2.27	2.92	117.6	113.1	131.1	124.3

Table S2: Electronic density and its Laplacian at the H-bond BCP (ρ_{HBCP} and $\nabla^2\rho_{HBCP}$, respectively) and hydroxyl hydrogen integrated atomic properties for the conformers **A** and **B** of 3-chlorobuta-1,3-dien-2-ol (**1-Cl**), obtained by QTAIM (in au).

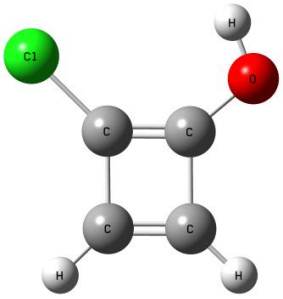
Conformer	ρ_{HBCP}	$\nabla^2\rho_{HBCP}$	q(H)	E(H)	M_1(H)	V(H)
A	0.025	+0.075	+0.599	-0.3450	0.159	0.018
B	-	-	+0.591	-0.3524	0.169	0.013



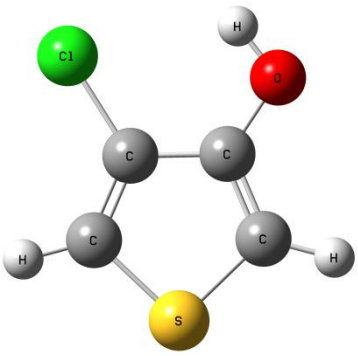
3-chlorobuta-1,3-dien-2-ol
(**1-Cl**)



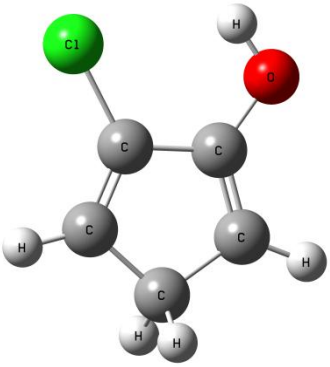
3-chlorocyclobuta-1,3-dien-2-ol
(**2-Cl**)



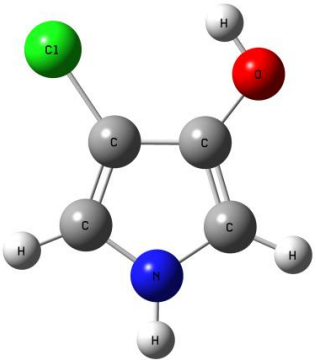
2-chlorocyclobuta-1,3-dienol
(**3-Cl**)



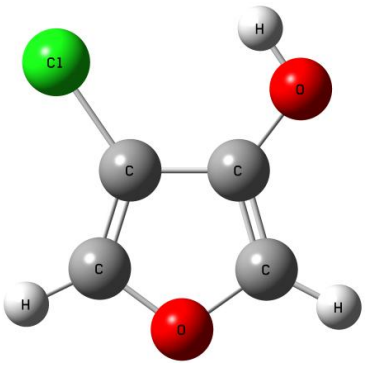
4-chlorothiophen-3-ol
(**4-Cl**)



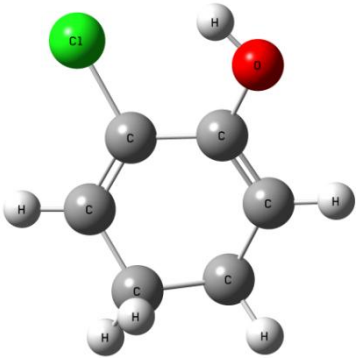
3-chlorocyclopenta-1,4-dien-2-ol
(**5-Cl**)



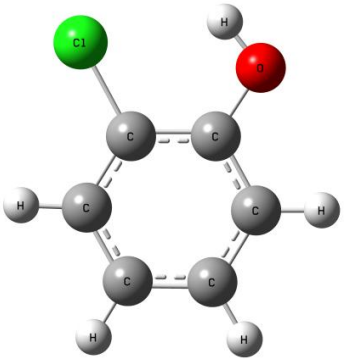
4-chloropyrrol-3-ol
(**6-Cl**)



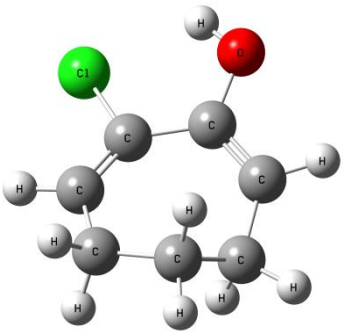
4-chlorofuran-3-ol
(**7-Cl**)



3-chlorocyclohexa-1,3-dien-2-ol
(**8-Cl**)

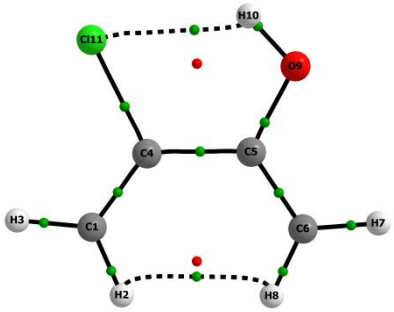


2-chlorophenol
(**9-Cl**)

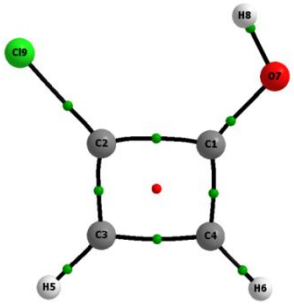


(**10-Cl**)

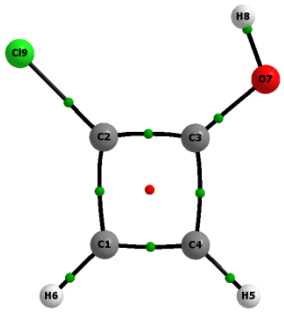
Figure S1: Geometric representations for the conformer **A** of compounds **1-Cl** to**10-Cl**.



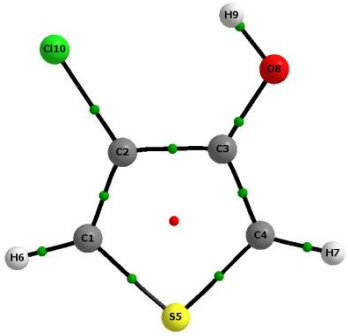
3-chlorobuta-1,3-dien-2-ol
(**1-Cl**)[a]



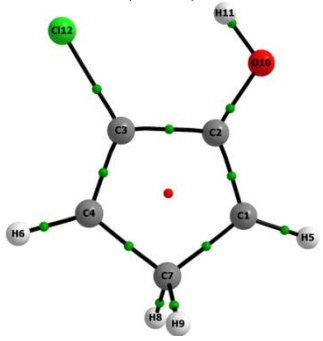
3-chlorocyclobuta-1,3-dien-2-ol
(**2-Cl**)



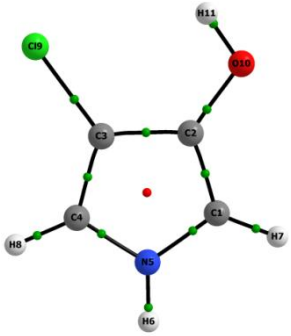
2-chlorocyclobuta-1,3-dienol
(**3-Cl**)



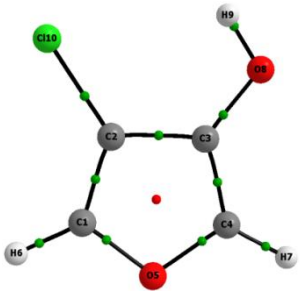
4-chlorothiophen-3-ol
(**4-Cl**)



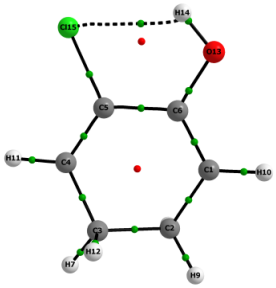
3-chlorocyclopenta-1,4-dien-2-ol
(**5-Cl**)



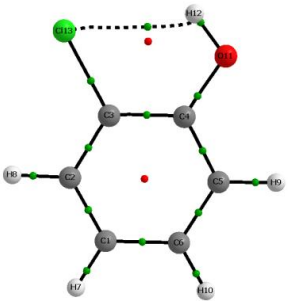
4-chloropyrrol-3-ol
(**6-Cl**)



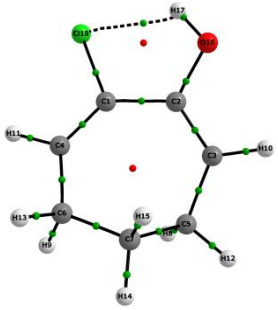
4-chlorofuran-3-ol
(**7-Cl**)



3-chlorocyclohexa-1,3-dien-2-ol
(**8-Cl**)



2-chlorophenol
(**9-Cl**)



7-chlorocyclohepta-1,6-dienol
(**10-Cl**)

[a] H···H interaction is unstable (ellipiticity = 1.370 au) and does not affect considerably the geometrical parameters of this compound.

Figure S2. Molecular graphs of compounds **1-Cl** to **10-Cl** (conformers **A**). Green points represent bond critical points (BCP) and red points indicate ring critical points (RCP).

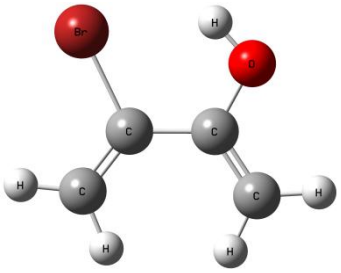
Bromine derivatives

Table S3: Selected geometric parameters for compounds **1-Br** to **10-Br** (interatomic distances in angstroms and bond angles in degrees).

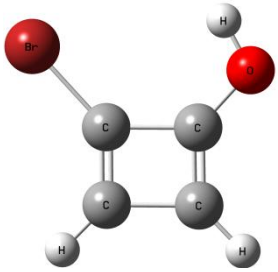
Compound	*r*(Br···HO)	*r*(Br···O)	∠ O-C-C(Br)	∠ Br-C-C(O)	∠ C-C(Br)-C(O)	∠ C-C(O)-C(Br)
1-Br	**2.34**	**3.03**	**118.5**	**115.4**	**127.6**	**122.9**
2-Br	3.31	3.76	132.1	132.6	89.5	90.9
3-Br	3.38	3.72	139.5	135.4	88.8	90.9
4-Br	2.64	3.24	124.8	121.2	114.1	111.8
5-Br	2.66	3.26	124.1	121.3	110.8	108.5
6-Br	2.80	3.36	127.6	124.3	108.4	107.0
7-Br	2.82	3.37	127.5	124.6	107.0	105.8
8-Br	2.46	3.11	120.2	117.1	122.3	118.8
9-Br	2.50	3.13	123.6	118.6	121.5	118.4
10-Br	2.38	3.05	118.2	113.5	131.0	123.8

Table S4: Electronic density and its Laplacian at the H-bond BCP (ρ_{HBCP} and $\nabla^2\rho_{HBCP}$, respectively) and hydroxyl hydrogen integrated atomic properties for the conformers **A** and **B** of 3-bromobuta-1,3-dien-2-ol (**1-Br**), obtained by QTAIM (in au).

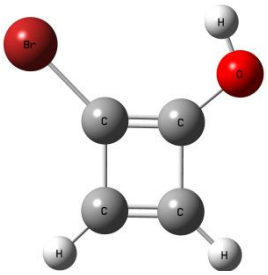
Conformer	ρ_{HBCP}	$\nabla^2\rho_{HBCP}$	q(H)	E(H)	M_1(H)	V(H)
A	0.024	+0.063	+0.591	-0.3470	0.165	0.018
B	-	-	+0.590	-0.3524	0.169	0.013



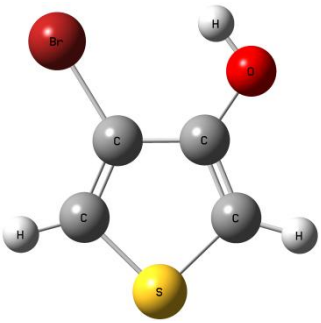
3-bromobuta-1,3-dien-2-ol
(**1-Br**)



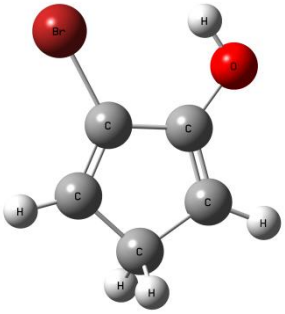
3-bromocyclobuta-1,3-dien-2-ol
(**2-Br**)



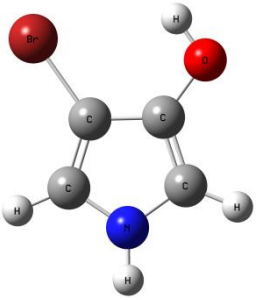
2-bromocyclobuta-1,3-dienol
(**3-Br**)



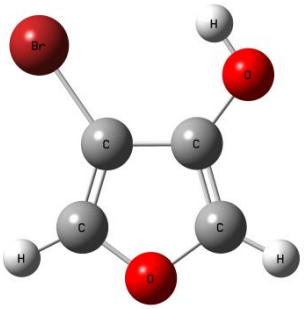
4-bromothiophen-3-ol
(**4-Br**)



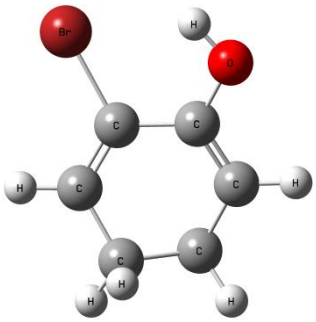
3-bromocyclopenta-1,4-dien-2-ol
(**5-Br**)



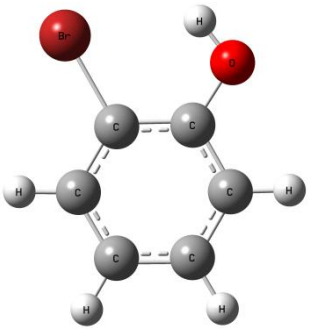
4-bromopyrrol-3-ol
(**6-Br**)



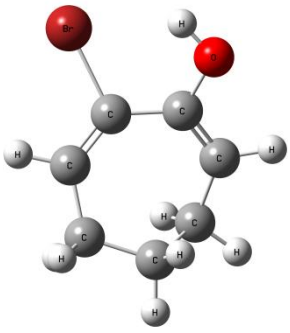
4-bromofuran-3-ol
(**7-Br**)



3-bromocyclohexa-1,3-dien-2-ol
(**8-Br**)

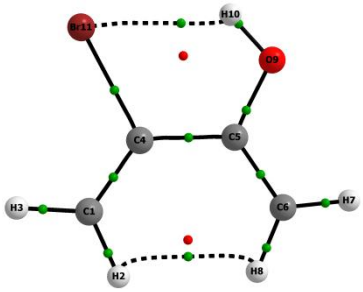


2-bromophenol
(**9-Br**)

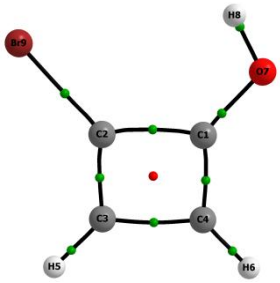


7-bromocyclohepta-1,6-dienol
(**10-Br**)

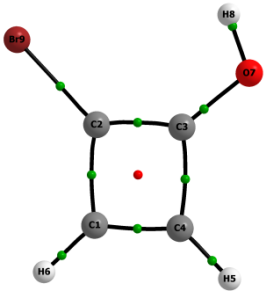
Figure S3: Geometric representations for the conformer **A** of compounds **1-Br** to**10-Br**.



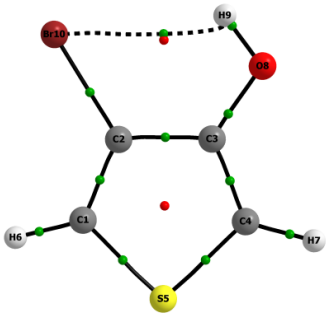
3-bromobuta-1,3-dien-2-ol
(**1-Br**)[a]



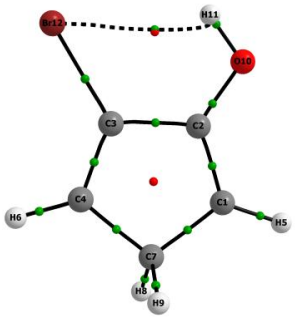
3-bromocyclobuta-1,3-dien-2-ol
(**2-Br**)



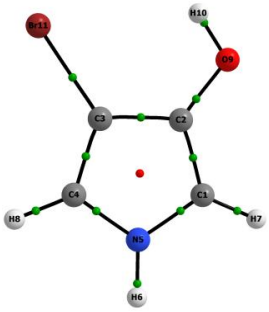
2-bromocyclobuta-1,3-dienol
(**3-Br**)



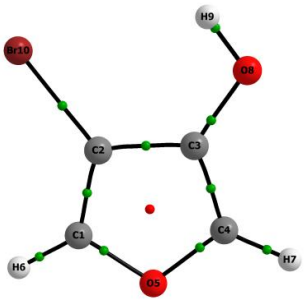
4-bromothiophen-3-ol
(**4-Br**)



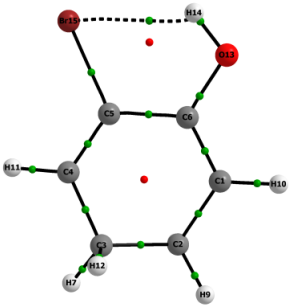
3-bromocyclopenta-1,4-dien-2-ol
(**5-Br**)



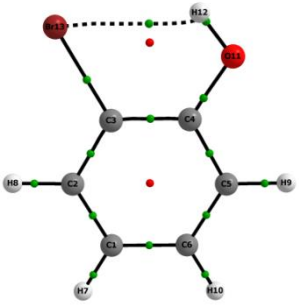
4-bromopyrrol-3-ol
(**6-Br**)



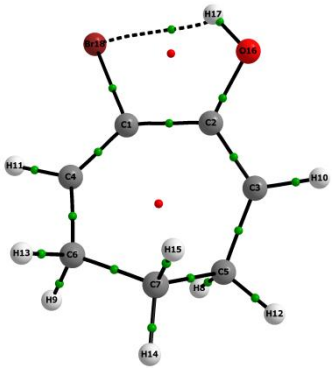
4-bromofuran-3-ol
(**7-Br**)



3-bromocyclohexa-1,3-dien-2-ol
(**8-Br**)



2-bromophenol
(**9-Br**)



7-bromocyclohepta-1,6-dienol
(**10-Br**)

[a] H···H interaction is unstable (ellipiticity c.a. 1.000 au) and does not affect considerably the geometrical parameters in this compound.

Figure S4. Molecular graphs of compounds **1-Br** to **10-Br** (conformer **A**). Green points represent bond critical points (BCP) and red points indicate ring critical points (RCP).

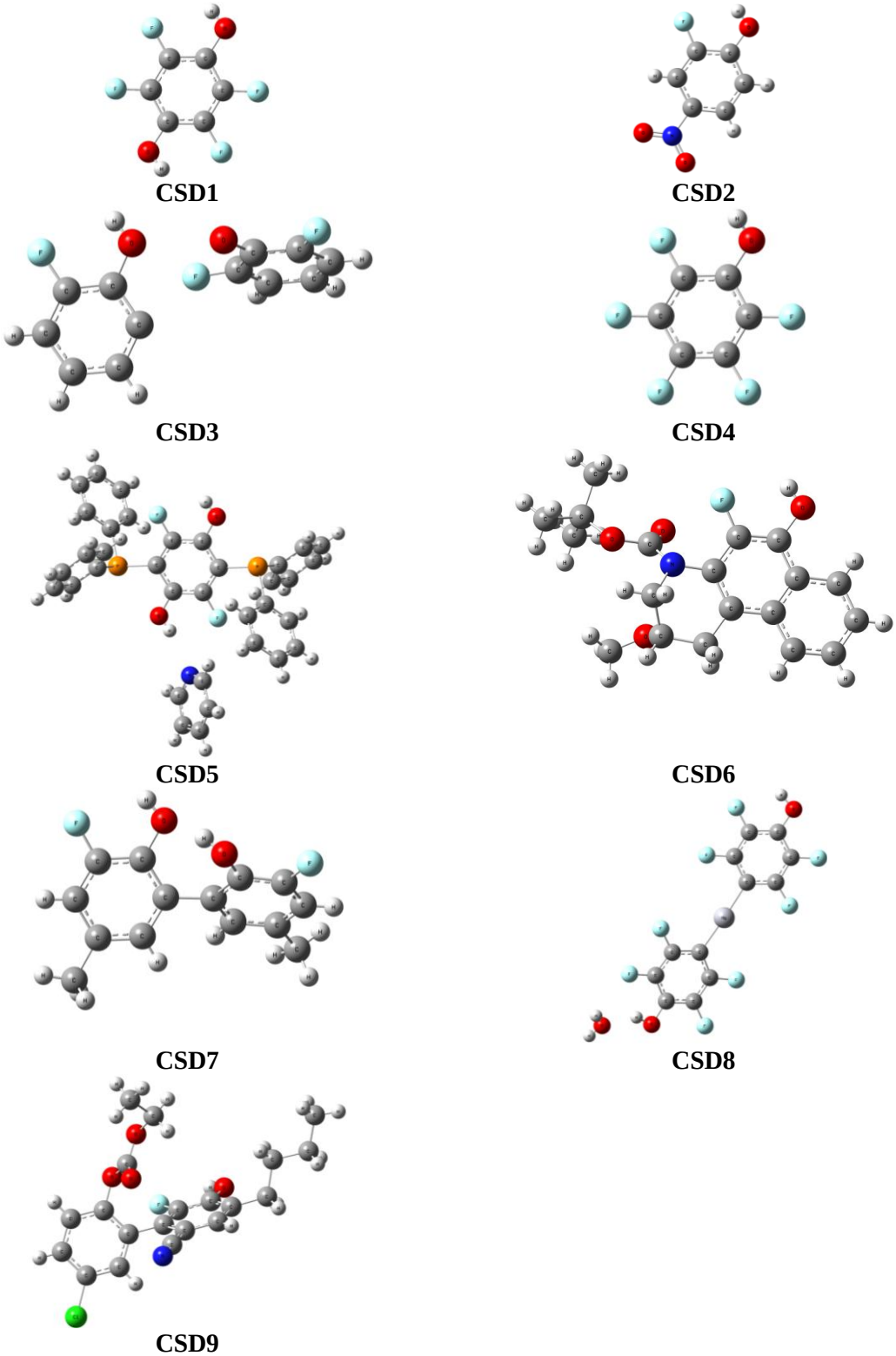


Figure S5: Structure and geometrical representation of 2-fluorophenol derivatives obtained from the Cambridge Structural Database.

Table S5: Selected geometric parameters for the reference compound **1** and of 2-fluorophenol derivatives obtained from the Cambridge Structural Database (interatomic distances in angstroms and bond angles in degrees).

Compound	*r*(F···HO)	*r*(F···O)	∠O-C-C(F)	∠F-C-C(O)	∠C-C(F)-C(O)	∠C-C(O)-C(F)
1	**1.990**	**2.575**	**115.7**	**111.2**	**130.0**	**124.3**
CSD1	2.374	2.774	123.3	118.9	121.4	117.4
CSD2	2.319	2.738	122.6	116.8	123.1	118.2
CSD3	2.345	2.690	119.9	117.9	122.2	118.5
CSD4	2.447	2.774	123.1	119.0	121.7	117.6
CSD5	2.277	2.704	120.4	117.8	122.8	120.9
CSD6	2.335	2.725	122.8	118.1	122.8	118.9
CSD7	2.291	2.719	121.7	116.6	123.1	118.9
CSD8	2.278	2.798	124.5	117.9	121.4	117.2
CSD9	2.300	2.739	122.1	117.6	123.9	119.7

References of compounds obtained from the Cambridge Structural Database (CSD):

CSD1: Thalladi, V. R.; Weiss, H. C.; Boese, R.; Nangia, A.; Desiraju, G. R. *Acta Crist.* **1999**, *B55*, 1005.

CSD2: Chambers, R. D.; Fox, M. A.; Sandford, G.; Trmcic, G.; Goeta, A., *J. Fluor. Chem.*, **2007**, *128*, 29.

CSD3: Oswald, I. D. H.; Allan, D. R.; Motherwell, W. D. S.; Parsons, S., *Struct. Sci.*, **2005**, *61*, 69.

CSD4: Gdaniec, M., *Crist. Eng. Comm.*, **2007**, *9*, 286.

CSD5: Pignotti, L. R.; Kongprakaiwoot, N.; Brennessel, W. W.; Baltrusaitis, J.; Luck, R. L.; Urnezius, E., *J. Organomet. Chem.*, **2008**, *693*, 3263.

CSD6: Boger, D. L.; Brunette, S. R.; Garbaccio, R. M., *J. Org. Chem.*, **2001**, *66*, 5163.

CSD7: Kirste, A.; Nieger, M.; Malkowsky, I. M.; Stecker, F.; Fischer, A.; Waldvogel, S. R., *Chem. Eur. J.*, **2009**, *15*, 2273.

CSD8: Deacon, G. b.; Felder, P. W.; Junk, P. C.; Buschbaum, K. M.; Ness, T. J.; Quitmann, C. C., *Inorg. Chem. Acta*, **2005**, *358*, 4389.

CSD9: Ibad, M. F.; Abid, O. R.; Adeel, M.; Nawaz, M.; Wolf, V.; Villinger, A.; Langer, P., *J. Org. Chem.*, **2010**, *75*, 8315.