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# Quantum-chemical, spectroscopic and X-ray diffraction studies of (E)-2-[(2-Bromophenyl)iminomethyl]-4-trifluoromethoxyphenol

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# ABSTRACT

The Schiff base compound (E)-2-[(2-Bromophenyl)iminomethyl]-4-trifluoromethoxyphenol has been synthesised and characterised by IR, UV–vis, and X-ray single-crystal determination. The molecular geometry from X-ray determination of the title compound in the ground state has been compared using the Hartree–Fock (HF) and density functional theory (DFT) with the 6–311++G(d,p) basis set. The calculated results show that the DFT and HF can well reproduce the structure of the title compound. Using the TD-DFT and TD-HF methods, electronic absorption spectra of the title compound have been predicted and good agreement with the TD-DFT method and the experimental determination was found. The predicted nonlinear optical properties of the title compound are much greater than those of urea. In addition, DFT calculations of the title compound, molecular electrostatic potential (MEP), natural bond orbital (NBO), and thermodynamic properties were performed at B3LYP/6–311++G(d,p) level of theory.

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# 1. Introduction

Azomethines (known as Schiff-bases), having imine groups (CH=N) and benzene rings in the main chain alternately, and being  $\pi$ -conjugated, exhibit interest as materials for wide spectrum applications, particularly as corrosion inhibitors [1], catalyst carriers [2,3], thermo-stable materials [4–6], a metal ion complexing agents [7] and in biological systems [8–10]. Schiff base ligands consist of a variety of substituents with different electron-donating and electron-withdrawing groups, and therefore may exhibit interesting electro-chemical properties. The Schiff base compounds have been also under investigation during last years because of their potential applicability in optical communications and many of them have NLO behavior [11,12].

Schiff base compounds display interesting photochromic and thermochromic features in the solid state and can be classified in terms of these properties [13]. Photo- and thermochromism arise via H-atom transfer from the hydroxy O atom to the imine N atom [14,15]. Such proton-exchanging materials can be utilized for the design of various molecular electronic devices [16–18]. In general, *o*-hydroxy Schiff bases display two possible tautomeric forms, the enol-imine (OH) and the keto-amine (NH) forms (see Fig. 1). Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O–H…N in enol-imine

[19,20] and N-H···O in keto-amine [21,22] tautomers. Different methods were used to show the presence of the enol-imine and keto-amine forms, among them are UV-vis, IR, MS, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, and X-ray crystallography techniques [23–26]. Recently, we focused our attention on the synthesis and characterization of various Schiff base derivatives [27–29] and studied their special properties. To the best of our knowledge, neither the synthesis nor theoretical studies of the title compound of (E)-2-[(2-Bromophenyl)iminomethyl]-4-trifluoromethoxyphenol have been available until now. After synthesizing this compound we determined its crystal structure.

Investigations into the structural stability of these compounds using both experimental techniques and theoretical methods have been of interest for many years. With recent advances in computer hardware and software, it is possible to correctly describe the physico-chemical properties of molecules from first principles using various computational techniques [30]. In recent years, density functional theory (DFT) has been the shooting star in theoretical modeling. The development of ever better exchange-correlation functionals has made it possible to calculate many molecular properties with accuracies comparable to those of traditional correlated *ab initio* methods, at more favorable computational costs [31]. Literature surveys have revealed the high degree of accuracy of DFT methods in reproducing the experimental values in terms of geometry, dipole moment, vibrational frequency, etc. [32–37].

In this paper, we wish to report the synthesis, characterization and crystal structure of the Schiff base (E)-2-[(2-Bromophenyl)iminomethyl]-4-trifluoromethoxyphenol as well as

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**Fig. 1.** Tautomeric forms of the title compound.

the theoretical studies on it by using the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods. The interaction enegies, molecular electrostatic potential, thermodynamic and nonlinear optical properties of the title compound were investigated at the B3LYP/6-311++G(d,p) level. These calculations are valuable for providing insight into molecular properties of Schiff base compounds.

# 2. Experimental and computational methods

## 2.1. Physical measurements

The melting point was determined using a Gallenkamp melting point apparatus. The IR spectrum of the title compound was recorded in the range 4000–400 cm<sup>-1</sup> using a Schmadzu FTIR-8900 spectrophotometer with KBr pellets. The spectrum was recorded at room temperature with scanning speed of  $10 \text{ cm}^{-1} \text{ min}^{-1}$  and the spectral resolution of  $4.0 \text{ cm}^{-1}$ . The ultraviolet absorption spectra of the title compund were examined in the range 200–600 nm using a Unicam UV–vis spectrophotometer equipped with a 10 mm quartz cell. The UV pattern is taken from a  $1 \times 10^{-5}$  M solution of the title compound, dissolved in ethanol at  $20 \,^{\circ}$ C.

# 2.2. Synthesis

The compound (E)-2-[(2-Bromophenyl)iminomethyl]-4trifluoromethoxyphenol was prepared by reflux a mixture of a solution containing 2-hydroxy-5-(trifluoromethoxy) benzaldehyde (0.019 g; 0.092 mmol) in 20 ml ethanol and a solution containing 2-bromoaniline (0.016 g; 0.092 mmol) in 20 ml ethanol. The reaction mixture was stirred for 1 hunder reflux. The crystals of (E)-2-[(2-Bromophenyl)iminomethyl]-4-trifluoromethoxyphenol suitable for X-ray analysis were obtained from ethylalcohol by slow evaporation (Yield: % 68; M.P, 357–359 K).

# 2.3. Crystal structure determination

A colourless crystal of the compound with dimensions of  $0.04 \text{ mm} \times 0.18 \text{ mm} \times 0.45 \text{ mm}$  was mounted on goniometer of a STOE IPDS II diffractometer. Measurements were performed at room temperature (296K) using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The systematic absences and intensity symmetries indicated the monoclinic Pbca space group. A total of 19,487 reflection (1132 unique) within the  $\theta$  range of  $[1.5^{\circ} < \theta < 26.5^{\circ}]$  were collected in the *w* scan mode. Cell parameters were determined by using X-AREA software [38]. The intensities collected were corrected for Lorentz and polarization factors, absorption correction ( $\mu = 3.00 \text{ mm}^{-1}$ ) by integration method via X-RED32 software [38]. The structure was solved by direct methods using SHELXS-97 [39]. The maximum peaks and deepest hole observed in the final  $\Delta \rho$  map were 0.42 and -0.21 eÅ<sup>-3</sup>, respectively. The scattering factors were taken from SHELXL-97 [39]. The molecular graphics were done using ORTEP-3 for Windows [40]. All non-hydrogen atoms were refined anisotropically. The

refinement was carried out using the full matrix least squares method on the positional and anisotropic temperature parameters of non-hydrogen atoms corresponding to 194 crystallographic parameters. Atom H1 was located in a difference Fourier map and refined isotropically, and the other H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.93 Å for aromatic CH. The displacement parameters of the H atoms were fixed at  $U_{iso}(H) = 1.2U_{eq}(C)$  of their parent atoms. Details of the data collection conditions and the parameters of the refinement process are given in Table S1 (Supporting Information).

# 2.4. Computational methods

The molecular geometry is directly taken from the X-ray diffraction experimental result without any constraints. In the next step, the DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) with the 6–311++G(d,p) basis set and Hartree–Fock calculations with the 6–311++G(d,p) basis set using the Berny method [41,42] were performed with the Gaussian 03W software package [43]. The harmonic vibrational frequencies were calculated at the same level of theory for the optimized structures. Vibrational band assignments were made using the Gauss-View molecular visualisation program [44]. Additionally, the calculated vibrational frequencies were clarified by means of the potential energy distribution (PED) analysis and assignments of all the fundamental vibrational modes by using VEDA 4 program [45]. In order to investigate the atomic charge behavior of the title compound in solvent media, we also carried out optimization calculations in three solvents ( $\varepsilon$  = 78.39, H<sub>2</sub>O;  $\varepsilon$  = 24.55, C<sub>2</sub>H<sub>5</sub>OH;  $\varepsilon$  = 4.9, CHCl<sub>3</sub>) at the B3LYP/6–311++G(d,p) level using the Onsager [46] method. The electronic absorption spectra were calculated using the time-dependent density functional theory (TD-DFT) and Hartree–Fock (TD-HF) methods [47–50]. In addition, the electronic absorbtion spectra were calculated in ethanol solution with the Polarizable Continuum Model (PCM) [51–54] method.

To investigate the reactive sites of the title compound the MEP were evaluated using the B3LYP/6–311++G(d,p) method. MEP, V(r), at a given point r(x, y, z) in the vicinity of a molecule is defined in terms of the interaction energy between the electrical charge generated from the molecule's electrons and nuclei and a positive test charge (a proton) located at r. For the system studied the V(r) values were calculated as described previously using the equation [55],

$$V(r) = \frac{\sum Z_A}{|R_A - r|} - \frac{\int \rho(r')}{|r' - r|} d^3 r'$$
(1)

where  $Z_A$  is the charge of nucleus A, located at  $R_A$ ,  $\rho(r')$  is the electronic density function of the molecule, and r' is the dummy integration variable. The linear polarizability and first hyperpolarizability properties of the title compound were obtained from molecular polarizabilities based on theoretical calculations. In addition, the NBO analysis was performed at the B3LYP/6–311++G(d,p)



**Fig. 2.** (a) Ortep-3 diagram of the title compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. (b) The theoretical geometric structure of the title compound (B3LYP/6–311++G(d,p) level).

level by means of the NBO 3.1 program within the Gaussian 03W package [56].

# 3. Results and discussion

# 3.1. Description of the crystal structure

The title compound, an Ortep-3 view of which is shown in Fig. 2a, crystallizes in the orthorhombic space group *Pbca* with Z=8 in the unit cell. The asymmetric unit in the crystal structure contains only one molecule. The molecular structure of the title compound is approximately planar. The dihedral angle between the aromatic ring systems is  $1.2(3)^\circ$ . The imino group is coplanar with the hydroxyphenyl ring, as shown by the C9–C8–C7–N1 torsion angle of  $2.6(9)^\circ$ . It is also known that Schiff bases may exhibit photochromism depending on the planarity or non-planarity, respectively [57]. Therefore, the title compound may exhibit thermochromic properties.

The tautomerism appears in *ortho*-hydroxylated Schiff bases as a result of intramolecular proton transfer from oxygen atom to nitrogen atom. This proton transfer is resulted in two tautomeric structures as enol-imine and keto-amine forms in the solid state. These tautomeric forms are related to two types of intramolecular hydrogen bonds as  $O-H\cdots N$  in enol-imine form and  $N-H\cdots O$  in keto-amine form (Fig. 1). The C7–N1 and C9–O1 bonds of the title compound are the most important indicators of the tautomeric type. Because, the C2–O1 bond is of a double bond for the keto-amine tautomer, whereas this bond displays single bond character in enol-imine tautomer. In addition, the C7–N1 bond is also a double bond in enol-imine tautomer and of single bond lenght in keto-amine tautomer [58]. In the title compound, the enol-imine form is favored over the keto-amine form, as indicated by C9–O1 (1.328 (7)Å) and C7–N1 (1.262 [59]. The title compound is stabilized by  $O-H\cdots N$  and  $O-H\cdots Br$  type hydrogen bonds. There is a strong intramolecular  $O1-H1\cdots N1$ hydrogen bond involving hydroxyl atom O1 and imine atom N1, namely  $O1-H1\cdots N1$ , producing an S(6) ring motif [60] resulting in approximate planarity of the molecular skeleton  $[O\cdots N=2.600$ (6)Å]. The crystal structure is further stabilized by intramolecular  $O-H\cdots Br$  hydrogen bond, namely  $O1-H1\cdots Br1$  and the details of the hydrogen bonds are summarized in Table S2 (Supporting Information). In addition, there is also  $\pi-\pi$  interaction between the Cg2 ring in a neighboring molecule is 3.784 (4)Å at (1/2 - x, 1/2 + x, z)[Cg2 is the ring centroid of the C8/C13 ring]. A packing diagram of the title compound is shown in Fig. S3 (Supporting Information).

(trifluoromethoxy) phenol (C-O = 1.343 (3) and C-N = 1.269 (5) Å)

# 3.2. Optimized geometries

B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) calculations were performed on the title compound. The atomic numbering scheme the theoretical geometric structure of the title compound are shown in Fig. 2b. Calculated geometric parameters are listed in Table 1 along with the experimental data. When the X-ray structure of the title compound is compared with its optimized counterpart (Fig. S4; Supporting Information), conformational discrepancies are observed. The most remarkable discrepancies are found in the orientation of the bromophenyl ring of the title compound, which is defined by the torsion angles C7–N1–C1–C2 [177.3(7)°] and C7–N1–C1–C6 [-3.3(9)°]. These torsion angles have been calculated at  $133.18^{\circ}$  and  $-49.90^{\circ}$  for the HF/6-311++G(d,p) level, 141.52° and -41.81° for the B3LYP/6-311++G(d,p) level. Another difference with respect to the optimized structures is observed in the relative orientation of the trifluoromethoxy group. The methoxy group is almost perpendicular with the attached ring with C13-C12-O2-C14 and C11-C12-O2-C14 torsion angles of 90.0(8)° and -94.3(8)° for X-ray while the corresponding values are calculated as  $91.12^\circ$  and  $-92.66^\circ$  for HF and  $90.04^\circ$  and  $-94.26^\circ$  for B3LYP, respectively.

When the geometry of hydrogen bond in the optimized structures is examined, the proton donor group O1–H1 forms an intramolecular interaction with nitrogen atom N1, with a bond length of 1.91 Å and a bond angle of 141.44° for HF and a bond length of 1.76 Å and a bond angle of 145.80° for B3LYP (Table S2; Supporting Information). Similarly, another intramolecular H-bond, O1–H1…Br1, of length 3.49 Å and bond angle 142.28° for HF and of length 3.32 Å and bond angle 138.67° for B3LYP is also observed. The presence of the H-bond appears as an important property of the molecule, stabilizing its conformation in the crystal; as shown in the molecular modeling part, this is also visible in the model obtained for the molecule discussed.

It is well known that DFT-optimized bond lengths are usually longer and more accurate than HF due to the inclusion of electron correlation. On the contrary, according to our calculations, the HF method correlates well for the bond length compared with the B3LYP method (Table 1). The biggest difference between experimental and calculated bond lengths is about 0.033 Å for HF and 0.055 Å for B3LYP, the root mean square error (RMSE) is found to be 0.015 Å for HF and 0.026 Å for B3LYP, indicating that the bond lengths obtained by the HF method show a good correlation with the experimental values. For bond angles, the opposite was observed. As can be seen from Table 1, both the biggest difference Table 1

Table 1			
Selected	molecula	r structure	parameters

Parameters	Experimental	Calculated 6-311++G(d,p	
		HF	B3LYP
Bond lengths (Å)			
C1-C2	1.378 (6)	1.392	1.405
C1-C6	1.399(7)	1.391	1.404
C1-N1 C2_C3	1.405 (6)	1.404	1.402
C2-Br1	1.370(7)	1.582	1,550
C3-C4	1.384(8)	1.384	1.393
C4-C5	1.361 (8)	1.383	1.393
C5-C6	1.379(7)	1.383	1.389
C7-N1	1.262 (6)	1.258	1.286
C7-C8	1.433 (7)	1.466	1.450
(8-(9	1.400 (8)	1.401	1.420
C0-C15	1.400(8)	1.390	1.400
C9-C10	1.327 (8)	1.393	1.402
C10-C11	1.357 (9)	1.374	1.384
C11-C12	1.364 (8)	1.386	1.395
C12-C13	1.367 (8)	1.367	1.378
C12-02	1.422 (7)	1.389	1.411
C14-F2	1.283 (8)	1.302	1.333
C14-F1	1.295 (8)	1.314	1.350
C14-02	1.311(8) 1.212(9)	1.331	1.348
Max difference <sup>a</sup>	1.512(8)	0.033	0.055
RMSE		0.015	0.026
Devidence (a)			
Bond angles (°)	1174(E)	110 15	117.01
C2-C1-C0	117.4 (5)	120.21	117.81
C6-C1-N1	124.2(5)	121.56	120.12
C3-C2-C1	121.9 (5)	120.97	121.20
C3-C2-Br1	117.7 (4)	118.50	118.74
C1-C2-Br1	120.3 (4)	120.50	120.04
C2-C3-C4	119.9 (6)	120.08	119.92
C5-C4-C3	119.5 (6)	119.66	119.86
(4-(5-(6)))	120.7 (5)	120.05	120.00
01-C9-C8	122.1 (6)	123.25	122.23
C10-C9-C8	118.4 (6)	119.35	119.40
C11-C10-C9	121.9 (6)	120.63	120.55
C10-C11-C12	119.7 (6)	119.81	119.69
C11-C12-C13	121.1 (6)	120.49	121.11
C11-C12-O2	120.0 (6)	119.55	119.11
C13-C12-O2	118.7 (6)	119.84	119.61
C12-C13-C8 C5-C6-C1	1206(5)	120.57	120.00
F2-C14-02	120.0(3) 110.9(7)	108.13	107.97
F1-C14-O2	114.0 (7)	112.50	112.88
F2-C14-F1	108.0 (6)	108.35	108.30
N1-C7-C8	122.3 (5)	123.15	122.21
C9-C8-C13	119.1 (5)	119.11	119.14
C9-C8-C7	121.3 (5)	122.67	121.57
C13-C8-C7	119.6(5) 107.4(9)	118.21	119.28
F1-C14-F3	103.9(7)	108.23	106.14
02-C14-F3	112.1 (6)	112.39	112.78
C7-N1-C1	125.0 (5)	120.11	120.93
C14-02-C12	117.3 (5)	118.63	117.74
Max. difference <sup>a</sup>		4.89	4.07
RMSE		1.56	1.29
Torsion angles (°)			
C2-C1-N1-C7	177.3 (7)	133.18	141.52
C6-C1-N1-C7	-3.3 (9)	-49.90	-41.81
C13-C12-O2-C14	90.0 (8)	91.12	90.04
C11-C12-O2-C14	-94.3 (8)	-92.66	-94.26
LO-L/-NI-LI N1_C1_C2_Rr1	-1/8.8(5) 22(8)	177.93	1/6.11 _2.95
	(U)	2.00	2.55

<sup>a</sup> RMSE and maximum differences between the bond lengths and angles computed using theoretical methods and those obtained from X-ray diffraction.



Fig. 3. FT-IR spectrum of the title compound.

and the RMSE for the bond angles obtained by the B3LYP method are smaller than those determined by HF.

A logical method for globally comparing the structures obtained with the theoretical calculations is by superimposing the molecular skeleton on that obtained from X-ray diffraction, giving a RMSE of 2.229 Å for B3LYP and 2.247 Å for the HF method (Fig. S4; Supporting Information). According to these results, it may be concluded that the HF calculation well reproduce the bond lengths, while the B3LYP method is better at predicting the bond angles and 3-D geometry of the title compound. In spite of the differences, calculated geometric parameters represent a good approximation, and they are the bases for calculating other parameters, such as vibrational frequencies, electronic absorption spectra and molecular electrostatic potential, as described below.

# 3.3. IR spectroscopy

Harmonic vibrational frequencies of the title compound were calculated using the DFT/B3LYP and HF method with 6-311++G(d,p) basis set. The vibrational band assignments were made using the Gauss-View molecular visualisation program. Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of PEDs using VEDA 4 program [45]. In order to facilitate assignment of the observed peaks we have analyzed some vibrational frequencies and compared our calculated results of the title compound with their experimental ones and showed in Table 2. In order to improve the agreement between the calculated and the experimentally observed values, the calculated harmonic frequencies have been scale down via introduction of scaling factors. In this study four different scaling factors were used. For wavenumbers less than 1700 cm<sup>-1</sup>, factors of 0.983 at B3LYP level and 0.908 at HF level were used. For wavenumbers higher than 1700 cm<sup>-1</sup>, factors of 0.958 at B3LYP level and 0.910 at HF level were used [61].

The FT-IR spectra of the title compound were recorded in the 4000–400 cm<sup>-1</sup> region using KBr pellets on a Schmadzu FT-IR 8900 spectrophotometer and given in Fig. 3. The O–H group gives rise to three vibrations as stretching, in-plane bending and out-of-plane bending vibrations. The OH group vibrations are likely to be most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen-bonded species. The non-hydrogen-bonded or a free hydroxyl group absorb strongly in the 3550–3700 cm<sup>-1</sup> region [62]. Intramolecular hydrogen bonding if present in sixmembered ring system would reduce the O–H stretching band to 3200–3550 cm<sup>-1</sup> region [63]. In the case of unsubstituted phenol it has been shown that the frequency of OH stretching vibration in the gas phase is 3657 cm<sup>-1</sup> [64]. In our case the experimental OH stretching mode was observed at 3417 cm<sup>-1</sup>,

Та	bl	e	2

Comparison of the experimental and calculated vibrational frequencies (cm<sup>-1</sup>).

$\begin{tabular}{ c c c c } \hline HF & B1LYP \\ \hline HF & $	Experimental IR with KBr	Calculated at 6-311++(d,p)		Assignments (%PED <sup>a</sup> )	
341735763121 $\nu(O-H)(99)$ -30653073 $\nu_{1}(C-H)$ R2 (99)-30623069 $\nu_{1}(C-H)$ R2 (98)306830513060 $\nu_{1}(C-H)$ R2 (98)-30483055 $\nu_{1}(C-H)$ R2 (98)-30403048 $\nu_{1}(C-H)$ R2 (98)-30283038 $\nu_{1}(C-H)$ R1 (96)-30283038 $\nu_{1}(C-H)$ R1 (98)289829342912 $\nu_{1}$ mathematic (C-H) (99)162017031639 $\nu(C-H)$ R1 (22)157016021579 $\nu(C-C)$ R1 (15)148914831490 $\gamma(OH)$ (19) + $\gamma(C-H)$ R1 (22)147214651476 $\gamma(OH)$ (18)138113991360 $\gamma_{1}$ mathematic (C-H) (24)129313121255 $\nu_{1}$ (C-C) (10) + $\gamma(C-H)$ R1 (10)125712891225 $\nu_{1}$ (C-F) (18) + $\nu_{1}$ (C-N) (11)17212601178 $\nu(CO-CF_{3})$ (31) + $\nu_{4}$ (C-F) (19) + $\nu_{1}$ (C-N) (11)17212601178 $\nu(CO-CF_{3})$ (31) + $\nu_{4}$ (C-H) (21)15112231165 $\gamma(C-H)$ R2 (83)15310371022 $\nu_{1}$ (C-H) (10) + $\beta(CC)$ (20)900932892 $\beta_{1}$ (CON) (10) + $\tau_{1}$ (CCC) R1 (10)15410371022 $\nu_{1}$ (CC) (11) + $\omega_{1}$ (CCC) (21)155761751 $\omega(C-H)$ R2 (19)16666 $\nu(C-F_{1})$ (16) + $\beta(CC)$ (10) + $\alpha(FCF)$ (11) + $\delta(FCF)$ (12)1677566 $\beta(CC)$ (10)		HF	B3LYP		
-30653073 $\nu_{1}$ (C-H) B2 (99)-30623069 $\nu_{1}$ (C-H) R1 (94)306830513060 $\nu_{at}$ (C-H) R2 (98)-30403048 $\nu_{at}$ (C-H) R1 (96)-30283038 $\nu_{at}$ (C-H) R1 (96)-30283038 $\nu_{at}$ (C-H) R1 (96)162017031639 $\nu$ (C-H) (74)158616121595 $\nu$ (C-C-R) (44) + $\nu$ (C-C) R1 (10)158616121595 $\nu$ (C-C) R1 (15)148914831490 $\nu$ (OH) (19) + $\nu$ (C-H) R1 (22)147214651476 $\gamma$ (OH) (18)138113791405 $\nu$ (C-C) R1 (11) + $\nu$ (C-H) R1 (22)144114431456 $\gamma$ (OH) (18)138413591360 $\nu_{aipmair}$ (C-H) (48)129313121295 $\nu_{afc}$ (C-F) (18) + $\nu$ (C-N) (11)121712891225 $\nu_{a}$ (C-F) (20) + $\nu$ (C-C) (20) + $\nu$ (C-N) (11)117212801178 $\nu$ (CO-C) (37) + $\nu$ (C-H) (20)115112231165 $\gamma$ (C-H) R2 (83)103012191109 $\nu_{a}$ (C-H) (64) + $\delta$ (FOFC) (20)96510371022 $\nu$ (FO-C) (10) + $\beta$ (CCC) R1 (10)884900883 $\tau$ (HCCC) R1 (10)884900883 $\tau$ (HCCC) R1 (10)884900883 $\tau$ (HCCC) R1 (10) + $\sigma$ (FCF) (11) + $\delta$ (FOFC) (12)975761751 $\omega$ (C-H) R2 (59)735761751 $\omega$ (C-H) R2 (59)735761751	3417	3576	3121	ν(O–H) (99)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-	3065	3073	ν <sub>s</sub> (C–H) R2 (99)	
306830513060 $\nu_{st}(C-H) R2 (98)$ -30403048 $\nu_{st}(C-H) R2 (98)$ -30283038 $\nu_{st}(C-H) R1 (96)$ -30283038 $\nu_{st}(C-H) R1 (99)$ 162017031639 $\nu(C-R) (44) + \nu(C=C) R1 (10)$ 158616121595 $\nu(C=C) R1 (15)$ 157016021579 $\nu(C=C) R1 (15)$ 148914831490 $\gamma(OH) (19) + \gamma(C-H) R1 (22)$ 147214651476 $\gamma(C+H) R1 (11) + \gamma(C-H) R1 (22)$ 144114431456 $\gamma(OH) (18)$ 138113791405 $\nu(C-C) R1 (30) + \gamma(OH) (27)$ 15413591360 $\nu_{ainchich} (C-H) (148)$ 129313121295 $\nu_{phenn} (C-O) (37) + \gamma(C-H) R1 (10)$ 125712891225 $\nu_{s} (C-F_3) (39) + \nu(C-N) (11)$ 17212601178 $\nu(C-C) R1 (30) + \nu_{s} (C-F_3) (29)$ 15112231165 $\gamma(C-H) R2 (83)$ 103012191109 $\nu_{s} (C-F_3) (31) + \nu_{s} (C-F_3) (29)$ 96510371022 $\nu(R-C) (10) + \delta(CC) R1 (10)$ 88490083 $\tau(HOCC) R1 (14) + \delta(FC) (20)$ 96510371022 $\nu(R-C) (10) + \delta(CC) R1 (13) + \delta(OCC) R1 (16)$ 975761751 $(HOC) R1 (69)$ 755761751 $(HOC) R1 (16) + \delta(FC) (CO) (11) + \delta(FCC) (11) + \delta(FCC) (12) + \delta(OCC) R1 (16) + \delta(FCC) (11) + \delta(FCC) (12) + \delta(OCC) R1 (16) + \delta(FCC) (11) + \delta(FCC) (12) + \delta(OCC) R1 (16) + \delta(FCC) (11) + \delta(FCC) (12) + \delta(OCC) (11) + \delta(FCC) (12) + \delta(OCC) (11) + \delta(FCC) (12) + \delta$	-	3062	3069	ν <sub>s</sub> (C-H) R1 (94)	
-30483055 $\nu_{k}$ (C-H) R1 (98)-30283038 $\nu_{al}$ (C-H) R1 (96)289829342912 $\nu_{al}$ (C-H) R1 (98)152017031639 $\nu(C-R)$ (44) + $\nu(C-R)$ R1 (10)158616121595 $\nu(C-C)$ R2 (16)157016021579 $\nu(C-C)$ R1 (11)148914831490 $\gamma$ (0H) (19) + $\gamma$ (C-H) R1 (22)147214651476 $\gamma$ (C-H) R1 (11) + $\gamma$ (C-H) R2 (12)147313591360 $\nu_{tipend}$ (C-O) (37) + $\gamma$ (C-H) R1 (10)125712891205 $\nu_{pinend}$ (C-O) (37) + $\gamma$ (C-H) R1 (10)125712891225 $\nu_{sicc}$ (C-R) (16)12571201 $\nu$ (C-C) R1 (14) + $\nu$ (C-N) (11)12601178 $\nu$ (CO-CF <sub>3</sub> ) (11) + $\nu$ (C-H) (11)117212601178 $\nu$ (CO-CF <sub>3</sub> ) (11) + $\nu$ (C-N) (11)117212601178 $\nu$ (CO-CF <sub>3</sub> ) (11) + $\nu$ (C-N) (11)115112231165 $\gamma$ (C-H) R2 (83)103012191109 $\nu_{ab}$ (C-F) (10) + $\beta$ (CCC) R2 (11)96510371022 $\nu$ (C-C) R1 (14) + $\nu$ (C-R) (10)96510371022 $\nu$ (C-C) R1 (15)11511223165 $\gamma$ (C-H) R2 (83)103012191109 $\nu_{ab}$ (C-C) (10) + $\beta$ (CCC) R2 (54)96510371022 $\nu$ (C-C) (10) + $\beta$ (CCC) R2 (14)975761751 $\omega$ (C-H) R2 (95)755761751 $\omega$ (C-H) R2 (95)755761751	3068	3051	3060	$v_{\rm as}(C-H) R2 (98)$	
-30403048 $\nu_{uc}$ (C-H) R1 (96)-30283038 $\nu_{att}$ (C-H) R1 (98)289829342912Valphatic, (C-H) (99)162017031639 $\nu(C=N)$ (44) + $\nu(C=C)$ R1 (10)158616121555 $\nu(C=N)$ (44) + $\nu(C=C)$ R1 (10)148914831490 $\gamma(OH)$ (19) + $\gamma(C-H)$ R1 (22)147214651476 $\gamma(C-H)$ R1 (11) + $\gamma(C-H)$ R2 (12)147114431456 $\gamma(OH)$ (18)138113791405 $\nu(C-C)$ R1 (30) + $\gamma(OH)$ (27)135413591360 $\gamma_{aliphatic}$ (C-H) R1 (10)125712891225 $\nu_{bcend}$ (Co-C) (37) + $\gamma(C-H)$ R1 (10)12601178 $\nu(C-C)$ R1 (30) + $\nu(C-C)$ (11) + $\nu(C-N)$ (11)172112601178 $\nu(C-C)$ R1 (30) + $\nu(C-R)$ (10) + $\nu(C-N)$ (11)175112231165 $\gamma(C-H)$ R2 (83)103012191109 $\nu_{alic}$ (C-1) R1 (10)844900883 $\tau(HCC)$ R1 (51)826850816 $\tau(HOCC)$ R1 (10)884900883 $\tau(HCC)$ R1 (51)826850816 $\tau(HOCC)$ R1 (10)826850816 $\tau(HOCC)$ R1 (10)826850816 $\tau(HOCC)$ R1 (10)826651 $\nu(C-C)$ R1 (10) + $\pi(CCC)$ R1 (38) + $\delta(OCCC)$ R1 (16)755761751 $o(C-H)$ R2 (59)755761751 $o(C-H)$ R2 (59)755761751 $(C-H)$ R2 (10) + $\tau(HCC)$ R1 (10) + $\delta(FOFC)$ (12)<	-	3048	3055	$\nu_{\rm s}$ (C–H) R2 (98)	
-30283038 $\nu_{ac}(-H)$ R1 (98)289829342912 $\nu_{ainplatic}(C-H)$ (99)162017031639 $\nu(C=N)$ R4 (4+ $\nu(C=C)$ R1 (10)158616121595 $\nu(C=C)$ R2 (16)157016021579 $\nu(C=C)$ R1 (15)148914831490 $\nu(C=N)$ R4 (14)147214651476 $\nu(C+N)$ R4 (11)+ $\nu(C=H)$ R2 (12)147114431456 $\nu(OH)$ (18)138113791405 $\nu(C=C)$ R1 (30)+ $\nu(OH)$ (27)135413591360 $\nu_{aiptatic}$ (C-H) R1 (10)125712891225 $\nu_{bhend}$ (C-O) (37)+ $\nu(C=H)$ R1 (10)125712891225 $\nu_{aiptatic}$ (C-H) (14)+ $\nu(C=OCT_3)$ (18)+ $\nu(C=N)$ (11)117212601178 $\nu(C=C)$ R1 (30)+ $\nu(C=C)$ (20)115112231165 $\gamma(C+H)$ R2 (83)103012191109 $\nu_{aic}(C-H)$ (25)9431025983 $\beta_{aiptatic}$ (C-H)9431025983 $\beta_{aiptatic}$ (C-H)944900883 $\tau(HOCC)$ R1 (10)+ $\tau(HCCC)$ R1 (38)+ $\delta(OCC)$ R1 (16)755761751 $\omega(C-H)$ R2 (59)735741730 $\tau(HCCC)$ R1 (38)+ $\delta(OCC)$ R1 (38)+ $\delta(OCC)$ R1 (16)651698666 $\nu(C=F_1)$ (16)+ $\beta(CC)$ (10)+ $\omega(FCF)$ (11)+ $\delta(FOFC)$ (12)652646651 $\nu(B-O)$ (10)+ $\omega(FCF)$ (29)646651 $\nu(B-O)$ (10)+ $\omega(FCF)$ (29)748605 $\delta(FOC)$ (R1 (13)+ $\omega(FCF)$ (12)+ $\beta(OCC)$ (15)	-	3040	3048	$v_{\rm as}(C-H) R1 (96)$	
289829342912 $\nu_{idpustr.}(C-H)$ (99)162017031639 $\nu(C=N)$ (44) + $\nu(C=C)$ R1 (10)158616121595 $\nu(C=C)$ R1 (15)157016021579 $\nu(C=C)$ R1 (15)148914831490 $\gamma(OH)$ (19) + $\gamma(C-H)$ R1 (22)147214651476 $\gamma(C-H)$ R1 (11) + $\gamma(C-H)$ R2 (12)144114431456 $\gamma(OH)$ (13) + $\gamma(C-H)$ R1 (22)138113791405 $\nu(C-C)$ R1 (30) + $\gamma(OH)$ (27)135413591360 $\gamma_{alpatic}$ (C-H) R1 (10)125712891225 $\nu_{alc}$ (C-F <sub>3</sub> ) (20) + $\nu(C-C)$ (13) + $\nu(C-N)$ (11)120112751201 $\nu(C-C-F_3)$ (13) + $\nu(C-C)$ (10) + $\nu(C-C)$ (11) + $\nu(C-N)$ (11)17212601178 $\nu(CO-CF_3)$ (13) + $\nu_a(C-F_3)$ (29)115112231165 $\gamma(C+H)$ R2 (83)103012191109 $\nu_{ab}(C-F_3)$ (29)96510371022 $\nu(B-C-)$ (10) + $\beta(CCC)$ R2 (54)9431025983 $\beta_{alpatic}(C-H)$ 900932892 $\beta(CCN)$ (10) + $\tau(CCC)$ R1 (38) + $\delta(OCC)$ R1 (69)755761751 $\omega(C-H)$ R2 (59)735741730 $\tau(HCC)$ R1 (13) + $\nu(FCF)$ (11) + $\delta(FOFC)$ (12)680725696 $\beta(CCC)$ R2 (10)680725696 $\beta(CCC)$ R2 (10) + $\sigma(FCF)$ (11) + $\delta(FOFC)$ (12)651698666 $\nu(C-F)$ (13) + $\omega(FCF)$ (21) + $\beta(OCC)$ (16)662657 $\beta(FOFC)$ (24)670662597<	-	3028	3038	$v_{\rm as}(C-H) R1 (98)$	
162017031639 $\nu$ (C=N) (44) + $\nu$ (C=C) R1 (10)158616121595 $\nu$ (C=C) R2 (16)157016021579 $\nu$ (C=C) R1 (15)148914831490 $\gamma$ (OH) (19) + $\gamma$ (C-H) R1 (22)147214651476 $\gamma$ (C-H) R1 (11) + $\gamma$ (C-H) R2 (12)144114431456 $\gamma$ (OH) (18)138113791405 $\nu$ (C-C) R1 (30) + $\gamma$ (OH) R2 (12)135413591360 $\gamma$ alphatic (C-H) (48)129313121295 $\nu_{bheon}$ (C-G) (37) + $\gamma$ (C-H) R1 (10)125712891225 $\nu_{s}$ (C-F <sub>3</sub> ) (29) + $\nu$ (CO-CF <sub>3</sub> ) (18) + $\nu$ (C-N) (11)117212601178 $\nu$ (CO-CF <sub>3</sub> ) (31) + $\nu_{s}$ (C-F <sub>3</sub> ) (29)115112231165 $\gamma$ (C-H) R2 (83)103012191109 $\nu_{as}$ (C-F <sub>3</sub> ) (64) + $\delta$ (RDC) (20)96510371022 $\nu$ (BC-C) R1 (10)984900883 $\tau$ (HOCC) R1 (10)884900883 $\tau$ (HOCC) R1 (10)884900883 $\tau$ (HOCC) R1 (10)884900883 $\tau$ (HOCC) R1 (18) + $\delta$ (OCC) R1 (16)755761751 $\omega$ (C-H) R2 (59)735741730 $\tau$ (HOCC) R1 (18) + $\delta$ (OCC) R1 (16)680623666 $\nu$ (C-F <sub>3</sub> ) (16) + $\beta$ (CCC) R1 (38) + $\delta$ (OCC) R1 (16)681698666 $\nu$ (C-C) R1 (13) + $\omega$ (FCF) (11) + $\delta$ (FOFC) (12)662679 $\beta$ (CCC) R1 (13) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)743546646651744746 <td>2898</td> <td>2934</td> <td>2912</td> <td><math>v_{\text{aliphatic}}(C-H)</math> (99)</td>	2898	2934	2912	$v_{\text{aliphatic}}(C-H)$ (99)	
158616121595 $\nu$ (C=C) R2 (16)157016021579 $\nu$ (C=C) R1 (15)148914831490 $\gamma$ (OH) (19) + $\gamma$ (C-H) R1 (22)147214651476 $\gamma$ (C-H) R1 (11) + $\gamma$ (C-H) R2 (12)144114431456 $\gamma$ (OH) (18)138113791405 $\nu$ (C-C) R1 (30) + $\gamma$ (OH) (27)135413591360 $\gamma_{aliphatc}$ (C-H) (48)129313121295 $\nu_{phenol}$ (C-O) (37) + $\gamma$ (C-H) R1 (10)125712891225 $\nu_{5}$ (C-F <sub>3</sub> ) (20) + $\nu$ (CO-F <sub>3</sub> ) (18) + $\nu$ (C-N) (11)120112751201 $\nu$ (C-C) R1 (14) + $\nu$ (C-OF <sub>3</sub> ) (11) + $\nu$ (C-N) (11)117212601178 $\nu$ (CO-CF <sub>3</sub> ) (31) + $\nu_{5}$ (C-F <sub>3</sub> ) (29)115112231165 $\gamma$ (C-H) R2 (83)103012191109 $\nu_{ac}$ (C-F <sub>1</sub> ) (64) + $\delta$ (FOFC) (20)96510371022 $\nu$ (Br-C) (10) + $\beta$ (CCC) R1 (14) - $\beta$ (CC) R1 (14)900883r(HCCC) R1 (16)755761751 $\omega$ (C-H) R2 (59)735741751 $\omega$ (C-H) R2 (59)735741730r(HCCC) R1 (13) + $\delta$ (OCC) R1 (14) + $\delta$ (OCC) R1 (16)620623666 $\nu$ (C-C) (10) + $\beta$ (CCC) R1 (38) + $\delta$ (OCC) R1 (16)621648666 $\nu$ (C-C) (10) + $\beta$ (CCC) R2 49655623605 $\delta$ (FOFC) (24)670602597 $\beta$ (CCC) R1 (13) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)486481476 $\beta_{phenol}$ (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15) <td>1620</td> <td>1703</td> <td>1639</td> <td><math>\nu(C = N) (44) + \nu(C = C) R1 (10)</math></td>	1620	1703	1639	$\nu(C = N) (44) + \nu(C = C) R1 (10)$	
157016021579 $\nu$ (C=C) R1 (15)148914831490 $\gamma$ (OH) (19) + $\gamma$ (C-H) R1 (22)147214651476 $\gamma$ (C-H) R1 (11) + $\gamma$ (C-H) R2 (12)144114431456 $\gamma$ (OH) (18)138113791405 $\nu$ (C-C) R1 (30) + $\gamma$ (OH) (27)135413591360 $\gamma_{aliphatic}$ (C-H) (48)129313121295 $\nu_{phenal}$ (C-O) (37) + $\gamma$ (C-H) R1 (10)125712891225 $\nu_{s}$ (C-C-S) (20) + $\nu$ (CO-CS) (18) + $\nu$ (C-N) (11)117112751201 $\nu$ (C-C-R) (20) + $\nu$ (CO-CS) (11) + $\nu$ (C-N) (11)117212601178 $\nu$ (CO-CF <sub>3</sub> ) (20) + $\nu$ (CO-CF <sub>3</sub> ) (29)103012191109 $\nu_{as}$ (C-F <sub>3</sub> ) (64) + $\delta$ (FOFC) (20)96510371022 $\nu$ (Br-C) (10) + $\beta$ (CCC) R2 (54)9431025983 $\beta$ aliphatic(C-H)900932892 $\beta$ (CCN) (10) + $\tau$ (HCCC) R1 (10)884900883 $\tau$ (HCCC) R1 (51)826850816 $\tau$ (HCCC) R1 (59)755761751 $\omega$ (C-H) R2 (59)735741730 $\tau$ (HCCC) R1 (38) + $\delta$ (OCCC) R1 (16)620623666 $\nu$ (CC-R2 (10) + $\eta$ (CCC) R2 49651698666 $\nu$ (Br-C) (10) + $\beta$ (CCC) R2 49652623605 $\delta$ (FOCC) (44)654481476 $\beta$ phenel (ACC) R1 (13) + $\alpha$ (FCF) (21) + $\beta$ (OCC) (15)486481476 $\beta$ phenel (ACC) R1 (13) + $\alpha$ (FCF) (13)	1586	1612	1595	$\nu$ (C=C) R2 (16)	
148914831490 $\gamma(OH) (19) + \gamma(C-H) R1 (22)$ 147214651476 $\gamma(OH) R1 (11) + \gamma (C-H) R2 (12)$ 144114431456 $\gamma(OH) (18)$ 138113791405 $\nu(C-C) R1 (30) + \gamma(OH) (27)$ 135413591360 $\gamma_{aliphatic} (C-H) (48)$ 129313121295 $\nu_{phenol} (C-O) (37) + \gamma(C-H) R1 (10)$ 125712891225 $\nu_s (C-F_3) (20) + \nu (CO-CF_3) (18) + \nu (C-N) (11)$ 120112751201 $\nu (C-C) R1 (14) + \nu (C-C) (11) + \nu (C-N) (11)$ 117212601178 $\nu (CO-CF_3) (31) + \nu_s (C-F_3) (29)$ 115112231165 $\gamma (C-H) R2 (83)$ 103012191109 $\nu_{asl} (C-F_3) (64) + \delta (FOFC) (20)$ 96510371022 $\nu (B-C) (10) + \beta (CCC) R2 (54)$ 9431025983 $\beta_{aliphatic} (C-H)$ 900932892 $\beta (CCN) (10) + \tau (HCC) R1 (10)$ 884900883 $\tau (HCC) R1 (51)$ 826850816 $\tau (HOCC) R1 (69)$ 755761751 $\omega (C-H) R2 (59)$ 755761751 $\omega (C-H) R2 (59)$ 755761751 $\omega (C-H) R2 (59)$ 755696 $\beta (CCC) R1 (16) + \beta (CCC) R1 (38) + \delta (OCCC) R1 (16)$ 680725696 $\beta (CCC) R2 (12)$ 651698666 $\nu (E-F_1) (16) + \beta (CCC) (10) + \omega (FCF) (11) + \delta (FOFC) (12)$ 652613 $\nu (B-C) (10) + \beta (CCC) R2 49$ 655623605 $\delta (FOCT) (14) + \omega (FCF) (21) + \delta (CCC) (15)$	1570	1602	1579	ν(C=C) R1 (15)	
147214651476 $\gamma(C-H) R1 (11) + \gamma (C-H) R2 (12)$ 144114431456 $\gamma(OH) (18)$ 138113791405 $\nu(C-C) R1 (30) + \gamma(OH) (27)$ 135413591360 $\gamma_{aliphatic} (C-H) (48)$ 129313121295 $\nu_{phend} (C-O) (37) + \gamma(C-H) R1 (10)$ 125712891225 $\nu_s (C-F_3) (20) + \nu(CO-CF_3) (18) + \nu(C-N) (11)$ 120112751201 $\nu(C-C) R1 (14) + \nu(C-OCF_3) (11) + \nu(C-N) (11)$ 117212601178 $\nu(CO-CF_3) (31) + \nu_s (C-F_3) (29)$ 115112231165 $\gamma(C-H) R2 (83)$ 103012191109 $\nu_{asc} (C-F_3) (64) + \delta (FOC) (20)$ 96510371022 $\nu (Br-C) (10) + \beta (CCC) R2 (54)$ 9431025983 $\beta_{aliphatic} (C-H)$ 900932892 $\beta (CCN) (10) + \tau (HCCC) R1 (10)$ 884900883 $\tau (HCCC) R1 (51)$ 826850816 $\tau (HOCC) R1 (51)$ 826850816 $\tau (HOCC) R1 (10)$ 884900883 $\tau (HCCC) R1 (10) + \tau (CCC) R1 (38) + \delta (OCCC) R1 (16)$ 651698666 $\nu (C-F_2) (16) + \beta (COC) (10) + \omega (FCF) (11) + \delta (FOF) (12)$ 651698666 $\nu (C-F_2) (16) + \beta (COC) (10) + \omega (FCF) (11) + \delta (FOF) (12)$ 651623605 $\delta (FOFC) (44)$ 605623605 $\delta (FOFC) (44)$ 605623605 $\delta (FOFC) (24)$ 605623605 $\delta (FOFC) (21) + \beta (OCC) (15)$ 486481476 <t< td=""><td>1489</td><td>1483</td><td>1490</td><td><math>\gamma</math>(OH)(19)+<math>\gamma</math>(C–H)R1(22)</td></t<>	1489	1483	1490	$\gamma$ (OH)(19)+ $\gamma$ (C–H)R1(22)	
144114431456 $\gamma(OH)(18)$ 138113791405 $\nu(C-C) R1 (30) + \gamma(OH)(27)$ 135413591360 $\gamma_{aliphatic}(C-H)(48)$ 129313121295 $\nu_{phenol} (C-0)(37) + \gamma(C-H) R1 (10)$ 125712891225 $\nu_{5}(C-F_{3})(20) + \nu(C-CF_{3})(18) + \nu(C-N)(11)$ 117212601178 $\nu(C-C, R1 (14) + \nu(C-C)F_{3})(11) + \nu(C-N)(11)$ 117212601178 $\nu(CO-CF_{3})(31) + \nu_{5}(C-F_{3})(29)$ 115112231165 $\gamma(C-H) R2 (83)$ 103012191109 $\nu_{as}(C-F_{3})(64) + \delta(FOFC)(20)$ 96510371022 $\nu(Br-C) (10) + \beta(CCC) R2 (54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN) (10) + \tau(HCC) R1 (10)$ 884900883 $\tau(HCCC) R1 (51)$ 826850816 $\tau(HOCC) R1 (59)$ 755761751 $\omega(C-H) R2 (59)$ 755761730 $\tau(HCCC) R2 (10) + \tau(CCC) C1 (13) + \delta(OCC) R1 (16)$ 680725696 $\beta(CCC) R2 (12)$ 651698666 $\nu(C-F_{3}) (16) + \beta(CCC) (10) + \omega(FF) (11) + \delta(FOFC) (12)$ 652646651 $\nu(Br-C) (10) + \beta(CCC) R1 (38) + \delta(OCC) R1 (16)$ 655623605 $\delta(FOFC) (44)$ 700602597 $\beta(CCC) R1 (13) + \beta(PCC) (15) + \beta(OCC) (15)$ 486481476 $\gamma(CCC) R1 (18) + \delta(BrCCC) (15)$	1472	1465	1476	$\gamma$ (C–H) R1 (11)+ $\gamma$ (C–H) R2 (12)	
138113791405 $\nu(C-C) R1 (30) + \gamma(OH) (27)$ 135413591360 $\gamma_{alphatic} (C-H) (48)$ 129313121295 $\nu_{phenol} (C-O) (37) + \gamma(C-H) R1 (10)$ 125712891225 $\nu_s (C-F_3) (20) + \nu (CO-CF_3) (18) + \nu (C-N) (11)$ 120112751201 $\nu (C-C, R1 (14) + \nu (C-OCF_3) (11) + \nu (C-N) (11)$ 117212601178 $\nu (CO-F_3) (31) + \nu_s (C-F_3) (29)$ 103012191109 $\nu_a (C-F_3) (64) + \delta (FOFC) (20)$ 96510371022 $\nu (Br-C) (10) + \beta (CCC) R2 (54)$ 9431025983 $\beta_{alphatic} (C-H)$ 900882 $\beta (CCN) (10) + \tau (HCC) R1 (10)$ 884900883 $\tau (HCCC) R1 (51)$ 826850816 $\tau (HOCC) R1 (69)$ 735741730 $\tau (HCCC) R2 (10) + \tau (CCCC) R1 (38) + \delta (OCCC) R1 (16)$ 680725696 $\beta (CCC) R2 (10) + \tau (CCCC) R1 (38) + \delta (OCCC) R1 (16)$ 680725696 $\beta (CCC) R2 (10) + \tau (CCCC) R1 (38) + \delta (OCCC) R1 (16)$ 651698666 $\nu (C-F_3) (16) + \beta (CCC) (10) + \omega (FF) (11) + \delta (FOFC) (12)$ 651698666 $\nu (C-F_3) (16) + \beta (CCC) (10) + \omega (FF) (11) + \delta (FOFC) (12)$ 652623605 $\delta (FOFC) (44)$ 570602597 $\beta (CCC) R1 (13) + \omega (FF) (21) + \beta (OCC) (15)$ 485481476 $\beta _{phenol} (OCC) (16) + \omega (FF) (21) + \beta (OCC) (15)$	1441	1443	1456	γ(OH) (18)	
135413591360 $\gamma_{aliphatic}$ (C-H)(48)129313121295 $\nu_{phenol}$ (C-O)(37)+ $\gamma$ (C-H) R1 (10)125712891225 $\nu_s$ (C-F_3)(20)+ $\nu$ (CO-CF_3)(11)+ $\nu$ (C-N)(11)120112751201 $\nu$ (C-C-C) R1 (14)+ $\nu$ (C-OCF_3)(11)+ $\nu$ (C-N)(11)117212601178 $\nu$ (CO-CF_3)(31)+ $\nu_s$ (C-F_3)(29)115112231165 $\gamma$ (C-H) R2 (83)103012191109 $\nu_{as}$ (C-F_3)(64)+ $\delta$ (FOFC)(20)96510371022 $\nu$ (BC-C) (10)+ $\beta$ (CCC) R2 (54)9431025983 $\beta_{aliphatic}$ (C-H)900932892 $\beta$ (CCN) (10)+ $\tau$ (HCCC) R1 (10)884900883 $\tau$ (HCCC) R1 (51)884900883 $\tau$ (HCCC) R1 (59)755761751 $\omega$ (C-H) R2 (59)755761751 $\omega$ (C-H) R2 (59)755761751 $\omega$ (C-F_3) (16)+ $\beta$ (COC) (11)+ $\delta$ (COCC) R1 (18)+ $\delta$ (OCCC) R1 (16)680725696 $\beta$ (CCC) R2 (10)+ $\tau$ (CCCC) R1 (38)+ $\delta$ (OCCC) R1 (16)651698666 $\nu$ (Br-C) (10)+ $\beta$ (CCC) R2 49605623605 $\delta$ (FOFC) (44)570602597 $\beta$ (CCC) R1 (13)+ $\omega$ (FCF) (21)+ $\beta$ (OCC) (15)485464458 $\tau$ (CCCC) R1 (18)+ $\delta$ (BrCCC) (13)	1381	1379	1405	$\nu$ (C–C) R1 (30) + $\gamma$ (OH) (27)	
129313121295 $\nu_{phenol} (C-0) (37) + \gamma (C-H) R1 (10)$ 125712891225 $\nu_s (C-F_3) (20) + \nu (CO-CF_3) (11) + \nu (C-N) (11)$ 120112751201 $\nu (C-C) R1 (14) + \nu (C-OCF_3) (11) + \nu (C-N) (11)$ 117212601178 $\nu (CO-CF_3) (31) + \nu_s (C-F_3) (29)$ 115112231165 $\gamma (C-H) R2 (83)$ 103012191109 $\nu_a (C-F_3) (64) + \delta (FOFC) (20)$ 96510371022 $\nu (Br-C) (10) + \beta (CCC) R2 (54)$ 9431025983 $\beta_{alphatic} (C-H)$ 900932892 $\beta (CN) (10) + \tau (HCCC) R1 (10)$ 884900883 $\tau (HCCC) R1 (51)$ 826850816 $\tau (HCCC) R1 (51)$ 826850816 $\tau (HCCC) R2 (10) + \pi (CCCC) R1 (38) + \delta (OCCC) R1 (16)$ 680725696 $\beta (CCC) (10) + \omega (FCF) (11) + \delta (FOFC) (12)$ 651698666 $\nu (C-F_3) (16) + \beta (CCC) (10) + \omega (FCF) (11) + \delta (FOFC) (12)$ 652623605 $\delta (FOFC) (44)$ 700602597 $\beta (CCC) R1 (13) + \omega (FCF) (29)$ 486481476 $\beta _{phenol} (OCC) (16) + \omega (FCF) (21) + \beta (OCC) (15)$	1354	1359	1360	$\gamma_{\text{aliphatic}}$ (C–H) (48)	
125712891225 $v_s(C-F_3)(20) + v(CO-CF_3)(18) + v(C-N)(11)$ 120112751201 $v(C-C)R1(14) + v(C-OCF_3)(11) + v(C-N)(11)$ 117212601178 $v(CO-CF_3)(31) + v_s(C-F_3)(29)$ 115112231165 $\gamma(C-H)R2(83)$ 103012191109 $v_{as}(C-F_3)(64) + \delta(FOFC)(20)$ 96510371022 $v(Br-C)(10) + \beta(CCC)R2(54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN)(10) + \tau(HCC)R1(10)$ 884900883 $\tau(HCCC)R1(51)$ 826850816 $\tau(HOCC)R1(59)$ 755761751 $\omega(C-H)R2(59)$ 735741730 $\tau(HCCC)R1(38) + \delta(OCC)R1(16)$ 680725696 $\beta(CCC)R2(12)$ 651698666 $v(C-F_2)(16) + \beta(CCC)(10) + \omega(FCF)(11) + \delta(FOFC)(12)$ 622646651 $v(Br-C)(10) + \beta(CCC)R2 49$ 605623605 $\delta(FOFC)(44)$ 570602597 $\beta(CCC)R1(13) + \omega(FCF)(21) + \beta(OCC)(15)$ 435464458 $\tau(CCCC)R1(18) + \delta(BrCCC)(13)$	1293	1312	1295	$\nu_{\text{phenol}}$ (C–O) (37) + $\gamma$ (C–H) R1 (10)	
120112751201 $\nu(C-C) R1 (14) + \nu(C-OCF_3) (11) + \nu(C-N) (11)$ 117212601178 $\nu(CO-CF_3) (31) + \nu_s (C-F_3) (29)$ 115112231165 $\gamma(C-H) R2 (83)$ 103012191109 $\nu_{as}(C-F_3) (64) + \delta(FOFC) (20)$ 96510371022 $\nu(Br-C) (10) + \beta(CCC) R2 (54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN) (10) + \tau(HCCC) R1 (10)$ 884900883 $\tau(HCCC) R1 (51)$ 826850816 $\tau(HOCC) R1 (69)$ 755761751 $\omega(C-H) R2 (59)$ 735741730 $\tau(HCCC) R2 (10) + \tau(CCCC) R1 (38) + \delta(OCCC) R1 (16)$ 680725696 $\beta(CCC) R2 (12)$ 651698666 $\nu(C-F_3) (16) + \beta(COC) (10) + \omega(FCF) (11) + \delta(FOFC) (12)$ 622646651 $\nu(Br-C) (10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (29)$ 485481476 $\beta phento (OCC) (16) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCCC) R1 (18) + \delta(BFCCC) (13)$	1257	1289	1225	$v_{s}(C-F_{3})(20) + v(CO-CF_{3})(18) + v(C-N)(11)$	
117212601178 $\nu(CO-CF_3)(31) + \nu_s(C-F_3)(29)$ 115112231165 $\gamma(C-H) R2 (83)$ 103012191109 $\nu_{as}(C-F_3)(64) + \delta(FOFC)(20)$ 96510371022 $\nu(Br-C)(10) + \beta(CCC) R2 (54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN)(10) + \tau(HCCC) R1 (10)$ 884900883 $\tau(HCCC) R1 (51)$ 826850816 $\tau(HOCC) R1 (69)$ 755761751 $\omega(C-H) R2 (59)$ 735741730 $\tau(HCCC) R2 (10) + \tau(CCC) R1 (38) + \delta(OCCC) R1 (16)$ 680725696 $\beta(CCC) R2 (12)$ 651698666 $\nu(C-F_3) (16) + \beta(CCC) (10) + \omega(FCF) (11) + \delta(FOFC) (12)$ 622646651 $\nu(Br-C) (10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCCC) R1 (18) + \delta(BTCC) (13)$	1201	1275	1201	$\nu$ (C-C) R1 (14) + $\nu$ (C-OCF <sub>3</sub> ) (11) + $\nu$ (C-N) (11)	
115112231165 $\gamma(C-H) R2 (83)$ 103012191109 $\nu_{as}(C-F_3) (64) + \delta(FOFC) (20)$ 96510371022 $\nu(Br-C) (10) + \beta(CCC) R2 (54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN) (10) + \tau(HCC) R1 (10)$ 884900883 $\tau(HCCC) R1 (51)$ 826850816 $\tau(HOCC) R1 (69)$ 755761751 $\omega(C-H) R2 (59)$ 735741730 $\tau(HCCC) R2 (10) + \tau(CCCC) R1 (38) + \delta(OCCC) R1 (16)$ 680725696 $\beta(CCC) R2 (12)$ 651698666 $\nu(C-F_3) (16) + \beta(COC) (10) + \omega(FCF) (11) + \delta(FOFC) (12)$ 622646651 $\nu(Br-C) (10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (29)$ 486481476 $\beta_{phenol} (OCC) (16) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCC) R1 (18) + \delta(BrCCC) (13)$	1172	1260	1178	$v(CO-CF_3)(31) + v_s(C-F_3)(29)$	
103012191109 $\nu_{as}(C-F_3) (64) + \delta(FOFC) (20)$ 96510371022 $\nu(Br-C) (10) + \beta(CCC) R2 (54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN) (10) + \tau(HCCC) R1 (10)$ 884900883 $\tau(HCCC) R1 (51)$ 826850816 $\tau(HOCC) R1 (69)$ 755761751 $\omega(C-H) R2 (59)$ 735741730 $\tau(HCCC) R2 (10) + \tau(CCCC) R1 (38) + \delta(OCCC) R1 (16)$ 680725696 $\beta(CCC) R2 (12)$ 651698666 $\nu(C-F_3) (16) + \beta(CCC) (10) + \omega(FCF) (11) + \delta(FOFC) (12)$ 622646651 $\nu(Br-C) (10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (29)$ 486481476 $\beta_{phenol} (OCC) (16) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCC) R1 (18) + \delta(BrCCC) (13)$	1151	1223	1165	γ(C–H) R2 (83)	
96510371022 $\nu(Br-C)(10) + \beta(CCC) R2(54)$ 9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN)(10) + \tau(HCC) R1(10)$ 884900883 $\tau(HCCC) R1(51)$ 826850816 $\tau(HOCC) R1(69)$ 755761751 $\omega(C-H) R2(59)$ 735741730 $\tau(HCCC) R2(10) + \tau(CCCC) R1(38) + \delta(OCCC) R1(16)$ 680725696 $\beta(CCC) R2(12)$ 651698666 $\nu(C-F_3)(16) + \beta(COC)(10) + \omega(FCF)(11) + \delta(FOFC)(12)$ 622646651 $\nu(Br-C)(10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1(13) + \omega(FCF)(29)$ 486481476 $\beta_{phenol} (OCC)(16) + \omega(FCF)(21) + \beta(OCC)(15)$ 435464458 $\tau(CCC) R1(18) + \delta(BrCCC)(13)$	1030	1219	1109	$v_{as}(C-F_3)(64) + \delta(FOFC)(20)$	
9431025983 $\beta_{aliphatic}(C-H)$ 900932892 $\beta(CCN)(10) + \tau(HCCC) R1(10)$ 884900883 $\tau(HCCC) R1(51)$ 826850816 $\tau(HOCC) R1(69)$ 755761751 $\omega(C-H) R2(59)$ 735741730 $\tau(HCCC) R2(10) + \tau(CCCC) R1(38) + \delta(OCCC) R1(16)$ 680725696 $\beta(CCC) R2(12)$ 651698666 $\nu(C-F_3)(16) + \beta(COC)(10) + \omega(FCF)(11) + \delta(FOFC)(12)$ 622646651 $\nu(BT-C)(10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1(13) + \omega(FCF)(21) + \beta(OCC)(15)$ 435464458 $\tau(CCCC) R1(18) + \delta(BTCCC)(13)$	965	1037	1022	$\nu(Br-C)(10) + \beta(CCC) R2(54)$	
900932892 $\beta(CCN)(10) + \tau(HCCC) R1(10)$ 884900883 $\tau(HCCC) R1(51)$ 826850816 $\tau(HOCC) R1(69)$ 755761751 $\omega(C-H) R2(59)$ 735741730 $\tau(HCCC) R2(10) + \tau(CCCC) R1(38) + \delta(OCCC) R1(16)$ 680725696 $\beta(CCC) R2(12)$ 651698666 $\nu(C-F_3)(16) + \beta(COC)(10) + \omega(FCF)(11) + \delta(FOFC)(12)$ 622646651 $\nu(Br-C)(10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC)(44)$ 570602597 $\beta(CCC) R1(13) + \omega(FCF)(29)$ 486481476 $\beta_{phenol}(OCC)(16) + \omega(FCF)(21) + \beta(OCC)(15)$ 435464458 $\tau(CCCC) R1(18) + \delta(BrCCC)(13)$	943	1025	983	$\beta_{\text{aliphatic}}(C-H)$	
884900883 $\tau$ (HCCC) R1 (51)826850816 $\tau$ (HOCC) R1 (69)755761751 $\omega$ (C-H) R2 (59)735741730 $\tau$ (HCCC) R2 (10) + $\tau$ (CCCC) R1 (38) + $\delta$ (OCCC) R1 (16)680725696 $\beta$ (CCC) R2 (12)651698666 $\nu$ (C-F <sub>3</sub> ) (16) + $\beta$ (COC) (10) + $\omega$ (FCF) (11) + $\delta$ (FOFC) (12)622646651 $\nu$ (Br-C) (10) + $\beta$ (CCC) R2 49605623605 $\delta$ (FOFC) (44)570602597 $\beta$ (CCC) R1 (13) + $\omega$ (FCF) (29)486481476 $\beta$ phenol (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)435464458 $\tau$ (CCC) R1 (18) + $\delta$ (BrCCC) (13)	900	932	892	$\beta(CCN)(10) + \tau(HCCC) R1(10)$	
826850816 $\tau$ (HOCC) R1 (69)755761751 $\omega$ (C-H) R2 (59)735741730 $\tau$ (HCCC) R2 (10) + $\tau$ (CCCC) R1 (38) + $\delta$ (OCCC) R1 (16)680725696 $\beta$ (CCC) R2 (12)651698666 $\nu$ (C-F <sub>3</sub> ) (16) + $\beta$ (COC) (10) + $\omega$ (FCF) (11) + $\delta$ (FOFC) (12)622646651 $\nu$ (Br-C) (10) + $\beta$ (CCC) R2 49605623605 $\delta$ (FOFC) (44)570602597 $\beta$ (CCC) R1 (13) + $\omega$ (FCF) (29)486481476 $\beta$ phenol (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)435464458 $\tau$ (CCC) R1 (18) + $\delta$ (BrCCC) (13)	884	900	883	$\tau$ (HCCC) R1 (51)	
755761751 $\omega$ (C-H) R2 (59)735741730 $\tau$ (HCCC) R2 (10) + $\tau$ (CCCC) R1 (38) + $\delta$ (OCCC) R1 (16)680725696 $\beta$ (CCC) R2 (12)651698666 $\nu$ (C-F <sub>3</sub> ) (16) + $\beta$ (COC) (10) + $\omega$ (FCF) (11) + $\delta$ (FOFC) (12)622646651 $\nu$ (Br-C) (10) + $\beta$ (CCC) R2 49605623605 $\delta$ (FOFC) (44)570602597 $\beta$ (CCC) R1 (13) + $\omega$ (FCF) (29)486481476 $\beta_{phenol}$ (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)435464458 $\tau$ (CCC) R1 (18) + $\delta$ (BrCCC) (13)	826	850	816	$\tau$ (HOCC) R1 (69)	
735741730 $\tau(\text{HCCC}) \text{ R2} (10) + \tau(\text{CCCC}) \text{ R1} (38) + \delta(\text{OCCC}) \text{ R1} (16)$ 680725696 $\beta(\text{CCC}) \text{ R2} (12)$ 651698666 $\nu(\text{C-F}_3) (16) + \beta(\text{COC}) (10) + \omega(\text{FCF}) (11) + \delta(\text{FOFC}) (12)$ 622646651 $\nu(\text{Br-C}) (10) + \beta(\text{CCC}) \text{ R2} 49$ 605623605 $\delta(\text{FOFC}) (44)$ 570602597 $\beta(\text{CCC}) \text{ R1} (13) + \omega(\text{FCF}) (29)$ 486481476 $\beta_{\text{phenol}} (\text{OCC}) (16) + \omega(\text{FCF}) (21) + \beta(\text{OCC}) (15)$ 435464458 $\tau(\text{CCC}) \text{ R1} (18) + \delta(\text{BrCCC}) (13)$	755	761	751	ω(C-H) R2 (59)	
680725696 $\beta(CCC) R2 (12)$ 651698666 $\nu(C-F_3) (16) + \beta(COC) (10) + \omega(FCF) (11) + \delta(FOFC) (12)$ 622646651 $\nu(Br-C) (10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC) (44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (29)$ 486481476 $\beta_{phenol} (OCC) (16) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCC) R1 (18) + \delta(BrCCC) (13)$	735	741	730	$\tau$ (HCCC) R2 (10) + $\tau$ (CCCC) R1 (38) + $\delta$ (OCCC) R1 (16)	
651698666 $\nu(C-F_3)(16) + \beta(COC)(10) + \omega(FCF)(11) + \delta(FOFC)(12)$ 622646651 $\nu(Br-C)(10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC)(44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (29)$ 486481476 $\beta_{phenol} (OCC) (16) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCCC) R1 (18) + \delta(BrCCC) (13)$	680	725	696	$\beta$ (CCC) R2 (12)	
622646651 $\nu(Br-C)(10) + \beta(CCC) R2 49$ 605623605 $\delta(FOFC)(44)$ 570602597 $\beta(CCC) R1 (13) + \omega(FCF) (29)$ 486481476 $\beta_{phenol} (OCC) (16) + \omega(FCF) (21) + \beta(OCC) (15)$ 435464458 $\tau(CCCC) R1 (18) + \delta(BrCCC) (13)$	651	698	666	$\nu$ (C-F <sub>3</sub> )(16)+ $\beta$ (COC)(10)+ $\omega$ (FCF)(11)+ $\delta$ (FOFC)(12)	
605623605 $\delta$ (FOFC) (44)570602597 $\beta$ (CCC) R1 (13) + $\omega$ (FCF) (29)486481476 $\beta_{phenol}$ (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)435464458 $\tau$ (CCCC) R1 (18) + $\delta$ (BrCCC) (13)	622	646	651	$\nu(Br-C)(10) + \beta(CCC) R2 49$	
570602597 $\beta$ (CCC) R1 (13)+ $\omega$ (FCF) (29)486481476 $\beta_{phenol}$ (OCC) (16)+ $\omega$ (FCF) (21)+ $\beta$ (OCC) (15)435464458 $\tau$ (CCCC) R1 (18)+ $\delta$ (BrCCC) (13)	605	623	605	$\delta(\text{FOFC})$ (44)	
486       481       476 $\beta_{phenol}$ (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)         435       464       458 $\tau$ (CCCC) R1 (18) + $\delta$ (BrCCC) (13)	570	602	597	$\beta$ (CCC) R1 (13) + $\omega$ (FCF) (29)	
435 464 458 $\tau(CCCC) R1 (18) + \delta(BrCCC) (13)$	486	481	476	$\beta_{\text{phenol}}$ (OCC) (16) + $\omega$ (FCF) (21) + $\beta$ (OCC) (15)	
	435	464	458	$\tau$ (CCCC) R1 (18)+ $\delta$ (BrCCC) (13)	

<sup>a</sup> Potential energy distribution (PED), less than 10% are not shown.

 $\nu$ , stretching;  $\gamma$ , rocking;  $\omega$ , wagging;  $\beta$ , bending;  $\tau$ , torsion;  $\delta$ , out of plane bending; s, symmetric; as, asymmetric. *Abbreviations*: R1, trifluoromethoxyphenol ring; R2, Bromophenyl ring.

which have been calculated with the B3LYP and HF at 3121 and 3576 cm<sup>-1</sup>, respectively. Generally, the OH in-plane bending vibration in phenols lie in the region 1300–1400 cm<sup>-1</sup>. The strong bands at 1381–1489 cm<sup>-1</sup> in the FT-IR spectra corresponds to in-planebending vibration of OH group. The OH out-of-plane deformation vibration in phenols, in general lies in the region 517–710 cm<sup>-1</sup> [65]. The band at 826 cm<sup>-1</sup> in the FT-IR spectra corresponds to outof-plane bending mode of hydroxyl vibration. The calculated values of OH group vibrations show good agreement with the experimental results.

The characteristic region of  $1700-1500 \text{ cm}^{-1}$  can be used to identify the proton transfer of Schiff bases. Azomethine (C=N) bond stretching vibration was observed to be  $1620 \text{ cm}^{-1}$  experimentally, while that have been calculated at  $1703 \text{ cm}^{-1}$  for HF and  $1639 \text{ cm}^{-1}$  for B3LYP. The benzene ring modes predominantly involve C=C bonds and the vibrational frequency is associated with C=C stretching modes of carbon skeleton [62]. The bands observed at 1620, 1586 and  $1570 \text{ cm}^{-1}$ , which can be attributed to the C=C stretching vibrations, were calculated at 1701, 1612 and  $1602 \text{ cm}^{-1}$  for HF and at 1639, 1595 and  $1579 \text{ cm}^{-1}$  for B3LYP, respectively. The bands observed at 570, 680 and  $965 \text{ cm}^{-1}$  in the FT-IR spectra are ascribed to the vibration modes including the phenyl CCC angle bending. The theoretically computed values of the angles bending vibration modes show good agreement with the experimental values.

The aromatic C–H stretching, C–H in-plane bending and C–H out-of-plane bending vibrations appear in  $2900-3150 \text{ cm}^{-1}$ ,  $1100-1500 \text{ cm}^{-1}$  and  $750-1000 \text{ cm}^{-1}$  frequency ranges,

respectively [66]. The C–H aromatic stretching mode was observed at 3068 cm<sup>-1</sup> experimentally, and calculated at 3073–3038 cm<sup>-1</sup> for B3LYP and at 3065–3028 cm<sup>-1</sup> for HF. The band at 2898 cm<sup>-1</sup> correspond to the aliphatic C–H stretching mode. The C–H inplane bending vibration computed at 1490, 1476, 1295, 1165 and 1124 cm<sup>-1</sup> by B3LYP/6–311++G(d,p) method shows excellent agreement with FT-IR bands at 1489, 1472, 1293, 1151 and 1043 cm<sup>-1</sup>. The bands observed at 884, 755 and 735 cm<sup>-1</sup> in FT-IR spectra are assigned to C–H out-of-plane bending vibration for the title compound.

Another characteristic region of the Schiff bases derivative spectrum is 1100–1400 cm<sup>-1</sup>, which is attributed to C–O stretching vibrations. The Car-OH stretching vibration was observed at 1293 cm<sup>-1</sup> which confirms the presence of phenol group in the compound. Three strong infrared bands at 1257, 1172, and 1030 cm<sup>-1</sup> are assigned to the C-F stretching modes. According to the calculations, the first two bands are caused by symmetric CF<sub>3</sub> stretching modes and the latter is due to the asymmetric CF<sub>3</sub> stretching mode. Furthermore, the medium bands at 651, 570 and 486 cm<sup>-1</sup> in the IR spectrum of the title compund are assigned to CF<sub>3</sub> deformation modes. The C-Br vibrations are often found over a wide range of 480–1290 cm<sup>-1</sup> since its vibration is easily affected by the adjacent atoms or groups [67,68]. In FT-IR spectrum of the title compound the medium bands at 965 and 622 cm<sup>-1</sup> are assigned to C-Br stretching vibration coupled with ring deformation. The other vibrational frequencies can be seen in Table 2. The presence of O–H, C=N and C<sub>ar</sub>–O stretching vibrations strongly



Fig. 4. Correlation graphics of calculated and experimental frequencies of the title compound.

suggests that the title compound has the enol-imine form in the solid state.

To make a comparison with the experimental observations, we present correlation graphs in Fig. 4 based on the calculations. As we can see from correlation graphics in Fig. 4 experimental fundamentals are found to have a better correlation with HF than B3LYP. Besides, the vibrational frequencies calculated by B3LYP method are more compatible to experimental values with the exception of O–H stretching mode which has the correlation coefficient  $R^2 = 0.99873$ .

# 3.4. Electronic absorption spectra

The electronic absorption spectra of the title compound in ethanol solvent were recorded within the 200–600 nm range and a representative spectrum is shown in Fig. 5. As can be seen from the figure, electronic absorption spectra showed three bands at 348, 272 and 212 nm. The maximum absorption wavelength is assigned to intramolecular charge transfer band of the azomethine C=N group. These values are similar to those found for related Schiff base compounds [69,70].

The UV–visible spectrum of *ortho*-hydroxylated Schiff bases that exist mainly as enol-imine structure indicate the presence of a band at <400 nm, whereas compounds existing in the keto-amine form



**Fig. 5.** UV-vis spectra of title compound in ethanol solvent and the comparison of calculated transitions in gas phase and ethanol solvent with the experimental spectra.

show a new band, especially in polar and nonpolar solvents, at >400 nm [71–73]. In this study, any band belong to keto-amine form was not observed with a value greater than 400 nm, which indicates that the title compound is in enol form not in keto in ethanol solvent.

Electronic absorption spectra were calculated using the TD-DFT and TD-HF methods based on the B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) level optimized structures in gas phase, respectively. The calculated results are listed in Table 3 along with the experimental absorption spectra data. For TD-HF calculations, the absorption wavelengths are obtained at 257, 220 and 179 nm. It is obvious that these bands are not corresponding to the experimental results. For TD-DFT calculations, the theoretical absorption bands are predicted at 355, 280 and 215 nm and can easily be seen that they correspond to the experimental absorption ones. In addition to the calculations in gas phase, TD-DFT calculations of the title compound in ethanol solvent were performed using the PCM model. The PCM calculations reveal that the calculated absorption bands have slight blue-shifts (see Fig. 5) with values of 351, 278 and 214 nm comparing with the gas phase calculations of TD-DFT method. Thus, the TD-DFT method in the gas phase and in solvent media is convenient for predicting electronic absorption spectra.

According to the investigation on the frontier molecular orbital (FMO) energy levels of the title compound, we can find that the corresponding electronic transfers happened between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), HOMO–3 and LUMO, HOMO–1 and LUMO+3 orbitals, respectively. Fig. 6 shows the distributions and energy levels of the FMOs computed at the B3LYP/6–311++G(d,p) level for the title compound. Molecular orbital coefficient analyses based on optimized geometry indicate that, for the title compound, the frontier molecular orbitals are mainly composed of p-atomic orbitals, so aforementioned electronic transitions are mainly derived from the contribution of the  $\pi \rightarrow \pi^*$  band.

# 3.5. Atomic charge distributions in gas-phase and in solution-phase

The Mulliken atomic charges for the non-H atoms of the title compound calculated at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels in gas-phase are presented in Table S6 (Supporting Information). To investigate the solvent effect for the atomic charge distributions of the title compound, based on the B3LYP/6-311++G(d,p) model and Onsager reaction field model, three kinds of solvent (chloroform, ethanol and water) were

Experimental		TD-HF		TD-DFT		TD-PCM	
Wavelength (nm)	Abs.	Wavelength (nm)	Oscillator strength	Wavelength (nm)	Oscillator strength	Wavelength (nm)	Oscillator strength
348	0.18	257	0.48	354	0.34	351	0.48
272	0.20	220	0.02	280	0.26	278	0.27
212	0.44	206	0.02	215	0.21	214	0.30

 Table 3

 Experimental and theoretical electronic absorption spectra values.

selected and calculated values are also listed in Table S6 (Supporting Information).

The Mulliken atomic charges show that the O2 atom, the Br atom and the fluor atoms (F1, F2 and F3) have negative atomic charges in gas phase. On the other hand, it is found that, in the solution phase, the atomic charge values of the O2, Br1, F1 and F2 atoms are bigger than those in gas phase and while the atomic charge values will increase with increasing polarity of the solvent, the value for F3 decreases with increasing solvent polarity. The coordination of these atoms will changed in different solvents, which may be helpful when one wishes to use the title compound to construct interesting metal complexes with different coordinate geometries [74]. This calculated result is not only consistent with many reported experimental values [75–78], it also supports the original idea of our synthesis.

# 3.6. Molecular electrostatic potential

The MEP is related to the electronic density and is a very useful descriptor for determining the sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [79]. The electrostatic potential V(r) is also well suited for analysing processes based on the "recognition" of one molecule by another, as in drug–receptor, and enzyme–substrate interactions, because it is through their potentials that the two species first "see" each other [80,81].

To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, the MEP at the B3LYP/6-311++G(d,p) optimized geometry was calculated. The negative (red and yellow) regions of the MEP are related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity, as shown in Fig. 7. As can be seen from the figure, this molecule has several possible sites for electrophilic attack. Negative regions in the studied molecule are found around the phenol O1 atom, O2, Br1 and the fluor atoms of the CF3 group. Also, a negative electrostatic potential region is observed around the N1 atom. The negative V(r) values are -0.030 a.u. for O1. which is the most negative region. -0.019 a.u. for O2, -0.011 a.u. for Br1, -0.011, -0.013 and -0.010 a.u. for F1, F2 and F3 atoms, respectively, and -0.005 a.u. for N1 atom, which is the least negative region. However, a maximum positive region is localized on the C7-H7 bond with a value of +0.032 a.u., indicating a possible site for nucleophilic attack. According to these calculated results, the MEP map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information concerning the region from where the compound can undergo non-covalent interactions.

The MEP is best suited for identifying sites for intra- and intermolecular interactions [82]. When an intramolecular interaction takes place the electrostatic potential of the negative atom becomes less negative and the positive region on the other atom becomes less positive [82,83]. For the MEP surface in the studied molecule, the weak negative regions associated with the N1 and Br1 atoms and also the weak positive region by the nearby H1 atom are indicative of intramolecular (N1…H1–O1) and (Br1…H1–O1) hydrogen bondings.

# 3.7. Natural bond orbital (NBO) analysis

NBO analysis provides an efficient method for studying intraand inter-molecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [84]. The larger the  $E^{(2)}$  value, the more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency



**Fig. 6.** Molecular orbital surfaces and energy levels given in parantheses for the HOMO-3, HOMO-1, HOMO, LUMO and LUMO+3 of the title compound computed at B3LYP/6-311++G(d,p) level.



Fig. 7. Molecular electrostatic potential map calculated at B3LYP/6-311++G(d,p) level.

from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction.

In order to investigate the intramolecular interactions, the stabilization energies of the title compound were performed by using second-order perturbation theory. To investigate the solvent effect for the stabilization energies of the title compound, based on B3LYP/6–311++G(d,p) model and PCM model, three kinds of solvent were selected and calculated values were listed in Table 4. For each donor NBO(*i*) and acceptor NBO(*j*), the stabilization energy  $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated as [85,86]

$$E^{(2)} = -q_i \frac{(F_{ij})^2}{\varepsilon_i - \varepsilon_i} \tag{2}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$ ,  $\varepsilon_j$  are diagonal elements (orbital energies) and  $F_{ij}$  is the off-diagonal NBO Fock matrix element.

NBO analysis revealed that the  $n(N1) \rightarrow \sigma^*(O1-H1)$  interactions give the strongest stabilization to the system of the title compound by 33.61 kcal/mol and strengthen the intramolecular O1-H1…N1 hydrogen bond in gas phase. As shown in Table 4, the  $E^{(2)}$  value due to the  $n(N1) \rightarrow \sigma^*(O1-H1)$  orbital interaction increases with increasing dielectric constant of solvent. The result can be used to explain the enhancement of the O-H…N hydrogen bond strength with increase of solvent polarity. There is another NBO interaction of the  $n(Br1) \rightarrow \sigma^*(O1-H1)$  imply the existence of O1-H1…Br1 hydrogen bond which has the stabilization energy 0.21 kcal/mol in gas phase. The stabilization energies of the  $n(Br1) \rightarrow \sigma^*(O1-H1)$  orbital interactions is almost a constant as solvent polarity increases. Thus, it is apparent that O1-H1…N1 and O1-H1…Br1 interactions significantly influence crystal packing with this molecule.

# 3.8. Nonlinear optical effects

Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [87]. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [88–91].

The non-linear optical response of an isolated molecule in an electric field  $E_i(\omega)$  can be presented as a Taylor series expansion of the total dipole moment,  $\mu_{tot}$ , induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ii}E_i + \beta_{iik}E_iE_k + \cdots$$
(3)

where  $\alpha$  is the linear polarizability,  $\mu_0$  the permanent dipole moment and  $\beta_{ijk}$  are the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability is defined as [92]:

$$\alpha_{tot} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{4}$$

First hyperpolarizability is a third rank tensor that can be described by  $3 \times 3 \times 3$  matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry [93] ( $\beta_{XYY} = \beta_{YXY} = \beta_{YYZ} = \beta_{YZY} = \beta_{ZYY}$ ;... likewise other permutations also take same value). The output from Gaussian 03 provides 10 components of this matrix as  $\beta_{XXX}$ ,  $\beta_{XXY}$ ,  $\beta_{XYY}$ ,  $\beta_{YYZ}$ 

 $\beta_{xzz}$ ,  $\beta_{yzz}$ ,  $\beta_{zzz}$ , respectively. The components of the first hyperpolarizability can be calculated using the following equation [92]:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$
(5)

Using the *x*, *y* and *z* components of  $\beta$ , the magnitude of the first hyperpolarizability tensor can be calculated by:

$$\beta_{tot} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)} \tag{6}$$

The complete equation for calculating the magnitude of  $\beta$  from Gaussian 03W output is given as follows:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2}$$
(7)

The calculations of the total molecular dipole moment ( $\mu$ ), linear polarizability ( $\alpha$ ) and first-order hyperpolarizability ( $\beta$ ) from the Gaussian output have been explained in detail previously [94], and DFT/B3LYP has been extensively used as an effective method to investigate the organic NLO materials. To investigate the effects of basis sets on the NLO properties of the title compound, the  $\mu_{tot}$ ,  $\alpha_{tot}$  and  $\beta_{tot}$  were calculated by B3LYP method with 6–31G(d), 6–31+G(d), 6–31++G(d,p), 6–311+G(d), and 6–311++G(d,p) basis sets and listed in Table S8 (Supporting Information).

From Table S8 (Supporting Information), we see that calculated values of the  $\mu_{tot}$ ,  $\alpha_{tot}$  and  $\beta_{tot}$  slightly depend on the size of basis sets. Obtained values of the  $\mu_{tot}$  and  $\alpha_{tot}$  with 6–31G(d) basis set are smaller than those obtained with large size of basis sets. It is found that the calculated results of the  $\mu_{tot}$  and  $\alpha_{tot}$  for the basis sets from 6–31+G(d) to 6–311++G(d,p) have minor differences from each other. Since there are not any reported experimental values for the first hyperpolarizability of the title compound in the literature, it is difficult to conclude which basis set computes reliable values of  $\beta_{tot}$ .

Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for comparative purposes. The calculated values of  $\mu_{tot}$ ,  $\alpha_{tot}$  and  $\beta_{tot}$  for the title compound are 3.560-3.749 D, 29.266-33.548 Å<sup>3</sup> and  $3.445-3.946 \times 10^{-30}$  cm<sup>5</sup>/esu, which are grater than those of urea (the  $\mu_{tot}$ ,  $\alpha_{tot}$  and  $\beta_{tot}$  of urea are 1.373 D, 3.831 Å<sup>3</sup> and  $0.3728 \times 10^{-30}$  cm<sup>5</sup>/esu obtained by B3LYP/6-31G(d) method). Although the calculated values of  $\beta_{tot}$  are smaller than that of 4-(2,3,4-trihydroxybenzylideneamino)antipyrine ( $\beta_{tot} = 10.012 \times 10^{-30}$  cm<sup>5</sup>/esu calculated with B3LYP/6-31G(d) method) [87] and 4-(2,3-dichlorobenzylideneamino)antipyrine ( $\beta_{tot} = 25.191 \times 10^{-30}$  cm<sup>5</sup>/esu calculated with B3LYP/6-31G(d) method) [95]. These results indicate that the title compound is a good candidate of NLO material.

To understand this phenomenon in the context of molecular orbital theory, we examined the molecular HOMOs and molecular LUMOs of the title compound. The calculated energies gaps are also listed in Table S8 (Supporting Information). The HOMO-LUMO energy gaps were calculated as 3.981–4.074 eV for the title compound, 3.923 eV for 4-(2,3,4-trihydroxybenzylideneamino)antipyrine [87], 3.903 eV for 4-(2,3-dichlorobenzylidene amino)antipyrine [95]. It is also found as 8.205 eV for urea by B3LYP/6–31G(d) method.

As can be seen from the  $\beta_{tot}$  values for these compounds, there is an inverse relationship between first hyperpolarizability and HOMO–LUMO gap, allowing the molecular orbitals to overlap to have a proper electronic communication conjugation, which is a marker of the intramolecular charge transfer from the electron donating group through the  $\pi$ -conjugation system to the electron accepting group [96,97].

#### Table 4

Second-order perturbation theory analysis of the Fock matrix in NBO basis, calculated at B3LYP/6-311++G(d,p) level and PCM model.

Dielectric constant	Donor orbital (i)	Acceptor orbital (j) <sup>a</sup>	E <sup>(2)</sup> (kcal/mol) <sup>b</sup>	$\varepsilon_j - \varepsilon_i (a.u.)^c$	$F_{ij}$ (a.u.) <sup>d</sup>
Gas ( $\varepsilon = 1$ )	LP(1) N1	BD*(1) O1-H1	33.61	0.50	0.127
	LP(2) Br1	BD*(1) O1-H1	0.21	0.42	0.010
Chloroform ( $\varepsilon$ = 4.9)	LP(1) N1	BD*(1) O1-H1	34.35	0.50	0.128
	LP(2) Br1	BD*(1) O1-H1	0.22	0.43	0.010
Ethanol ( $\varepsilon$ = 24.55)	LP(1) N1	BD*(1) O1-H1	34.68	0.50	0.128
	LP(2) Br1	BD*(1) O1-H1	0.22	0.43	0.010
Water ( <i>ε</i> = 78.39)	LP(1) N1	BD*(1) O1-H1	34.71	0.50	0.128
	LP(2) Br1	BD*(1) O1-H1	0.22	0.43	0.010

<sup>a</sup> BD\*, antibonding orbital; LP, lone pair. For BD, (1) denotes  $\sigma$  orbital. For LP, (1) and (2) denote the first and the second lone pair electron, respectively.

<sup>b</sup>  $E^{(2)}$  means energy of hyper conjugative interactions.

<sup>c</sup> Energy difference between donor and acceptor *i* and *j* NBO orbitals.

<sup>d</sup>  $F_{ij}$  is the Fock matrix element between *i* and *j* NBO orbitals.

# Table 5

 $Thermodynamic \ properties \ at \ different \ temperatures \ at \ B3LYP/6-311++G(d,p) \ level.$ 

<i>T</i> (K)	$H_m^0$ (kcal/mol)	$C_{p,m}^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$S_m^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
200	6.00	48.70	120.51
250	8.80	59.35	132.97
298.15	12.00	69.32	144.63
300	12.13	69.69	145.07
350	15.96	79.37	156.86
400	20.25	88.17	168.31
450	24.96	96.04	179.39

## 3.9. Thermodynamic properties

To determine thermodynamical properties of the title compound, the standard thermodynamic functions: heat capacity  $(C_{p,m}^0)$ , entropy  $(S_m^0)$ , and enthalpy  $(H_m^0)$  based on the vibrational analysis at the B3LYP/6–311++G(d,p) level were obtained and are listed in Table 5. The table shows that the standard heat capacities, entropies, and enthalpies increase at any temperatures from 200.00 to 450.00 K, because the intensities of the molecular vibration increase with increasing temperature.

The correlation equations between these thermodynamic properties and temperature *T* are as follows:

$$C_{p,m}^{0} = 2.22995 + 0.28245T - 1.41884T^{2} \times 10^{-4} \quad (R^{2} = 0.99992)$$
(8)

$$S_m^0 = 67.30951 + 0.27953T - 6.7657T^2 \times 10^{-5}$$
 ( $R^2 = 1$ ) (9)

$$H_m^0 = -0.58244 + 0.01363T + 9.59433T^2 \times 10^{-5} \quad (R^2 = 0.99998)$$
(10)

Based on these relationships, the values of  $C_{p,m}^0$ ,  $S_m^0$ , and  $H_m^0$  can be obtained at any other temperatures and be helpful for the further studies of the title compound.

# 4. Conclusions

(E)-2-[(2-Bromophenyl)iminomethyl]-4-

trifluoromethoxyphenol has been synthesised and characterised by IR, UV–vis, and X-ray single-crystal diffraction. The X-ray, IR and UV–vis spectral data for the title compound show that the compound exists in the enol form, which is stabilized by the intramolecular O–H···N hydrogen bond. Although it is well known that DFT optimized bond lengths are usually longer and more accurate than HF because of inclusion of electron correlation, the HF method correlates better for the bond length compared

with the DFT according to our calculations. However, the DFT method seems to be more appropriate than the HF method for the obtaining the bond angles and 3D geometry of the title compound. For the calculation of vibrational frequencies, both the methods, DFT and HF, can predict the IR spectrum of title compound well. The TD-DFT calculations lead to much closer agreement with the experimental absorption spectra, both in the gas phase and in solvent media. Molecular orbital coefficient analyses suggest that the electronic spectrum correspond to the  $\pi \rightarrow \pi^*$  electronic transition. The MEP map shows that the negative potential sites are on electronegative atoms while the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can undergo non-covalent interactions. NBO analysis revealed that the  $n(N1) \rightarrow \sigma^*(O1-H1)$ interaction gives the strongest stabilization to the system. The predicted nonlinear optical (NLO) properties of the title compound are much greater than those of urea. The title compound is a good candidate as second-order nonlinear optical material. The correlations between the thermodynamic properties  $C_{p,m}^0$ ,  $S_m^0$ ,  $H_m^0$ and temperature T were also obtained. We hope our paper will be helpful for the design and synthesis of new materials.

# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.10.055.

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