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2-Allyloxy-5-chlorobenzoic acid

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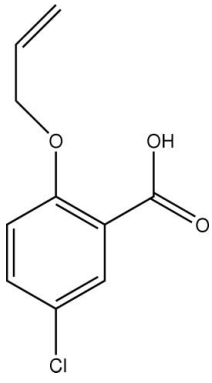
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.125; data-to-parameter ratio = 13.6.

The title compound, $C_{10}H_9ClO_3$, is an ether derived from salicylic acid. The asymmetric unit contains one independent molecule that is linked through centrosymmetrically related O—H···O hydrogen bonds by carboxyl pairing. The compound was prepared as a model for the analysis of the influence of electrostatic stabilization and intramolecular hydrogen bonding in [3,3]-sigmatropic Claisen reactions, such as the chorismate-to-prephenate rearrangement, catalyzed by chorismate mutase.

Related literature

For related literature, see: Castro (2004); Colapietro & Domenicano (1982); Jones *et al.* (1984); White *et al.* (1958); Zhang *et al.* (2005); Ziegler (1977).



Experimental

Crystal data

$C_{10}H_9ClO_3$
M_r = 212.62
Monoclinic, $P2_1/c$
a = 8.800 (1) Å
b = 15.201 (2) Å
c = 7.372 (1) Å
β = 98.469 (3)°
V = 975.4 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 293 (2) K
0.47 × 0.26 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
1848 measured reflections
1732 independent reflections
1405 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.125
S = 1.06
1732 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* in *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2372).

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supplementary materials

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2-Allyloxy-5-chlorobenzoic acid

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Comment

The intramolecular Claisen rearrangement of chorismate to prephenate, catalyzed by chorismate mutase, represents a rare case of a [3,3] sigmatropic shift reaction in live organisms and corresponds to a key step in the pathway to form aromatic amino acids in plants, bacteria and fungi (Ziegler, 1977; Castro, 2004; Zhang *et al.*, 2005). This unimolecular reaction occurs at the active site of the enzyme without formation of an enzyme-substrate covalent intermediate and it has been proposed that the transition state structures in the gas phase, water and enzyme are characteristic of a concerted pericyclic rearrangement. Since we are interested in the systematic analysis of the influence of electrostatic stabilization and intramolecular hydrogen bonding in [3,3] sigmatropic Claisen rearrangements, a series of ethers derived from salicylic acid has been synthesized. The 2-allyloxy-5-chlorobenzoic acid (I) is a new synthesized compound and here we report its X-ray crystal structure.

A projection of the crystal structure and the numbering of the non-hydrogen atoms are shown in Fig. 1 and the selected bond lengths and angles are given in Table 1. The data in Table 1 show that in the aromatic ring the C3—C4, C4—C5 and C5—C6 bonds are the strongest (shortest) C⋯C ring bonds, probably as a consequence of electronic effects and the strain induced by *ortho*-substitution at C1 and C2. The carboxyl and ether groups are planar, but they are not perfectly coplanar with the aromatic ring plane and deviate by 8.1 (3)° for carboxyl and by 15.0 (2)° for ether. The electron withdrawing influence of the carboxyl group weakens the C1—C2 and C2—C3 bonds which made them longer than the other ring bonds. These effects are similar to those found in *p*-chlorobenzoic acid (II) (Colapietro & Domenicano, 1982). The Cl atom in (I) has a small effect on the C3—C4—C5 angle [120.4 (2)°], but the COOH group reduces the C1—C2—C3 angle from 120° (normal benzene ring) to 119.37 (19)°. The effect is opposite to that found in compound (II), where the C3—C4—C5 angle is 122.0° and C1—C2—C3 angle is 120.1°. This evidently results from the presence of the allyloxy group in (I), lengthening both C1—C2 and C1—C6 bonds, and reducing the C2—C1—C6 angle to 118.9 (2)°. Closely similar effects are observed for 2-methoxymethoxybenzoic acid, where the *ortho*-substituent is electronically and sterically similar (Jones *et al.*, 1984).

A pair of molecules of (I) is connected through the carboxyl groups by centrosymmetric hydrogen bonds (O1—H1···O2^{i}, O1···O2^{i} 2.636 (2) Å, < (O1—H1···O2^{i}) 167.2°, symmetry code is: −*x*, −*y*, −*z*), which are stacked into sheets along *a* axis (Fig. 2). There is some interaction between O2 and O3 atoms with 2.622 (2) Å distance, a distance which - though short - is fairly normal for systems like this with the plane of the COOH group close to coplanar with the ring and is probably a consequence of the crystal-packing forces.

Experimental

Preparation of 2-allyloxy-5-chlorobenzoic Acid followed closely the procedure of White *et al.* (1958). A mixture of 8.63 g (50 mmol) of 5-chlorosalycilic acid, 6.05 g (0.05 mole) of allyl bromide, 8.29 g (60 mmol) of dry, powdered potassium carbonate, and sufficient dry acetone (about 30 ml) to give an easily stirred mass was stirred and refluxed for eight hours. Then the mixture was filtered, acidified with diluted acetic acid and the acetone removed by distillation under reduced

pressure. The residue was initially purified by crystallization from acetone water (m.p. 75–76°C). Colorless crystals of (I) were grown from aqueous solution by slow evaporation at room temperature.

Refinement

All non-H atoms were refined with anisotropic displacement parameters. H atom of the carboxylic moiety was found from Fourier map. This H atom was treated with riding model and they U_{eq} fixed at 1.2 times of the parent atom. H atoms bonded to C atoms were added at their calculated positions and included in the structure factor caculations, with C—H distances and U_{eq} taken from default of the refinement program.

Figures

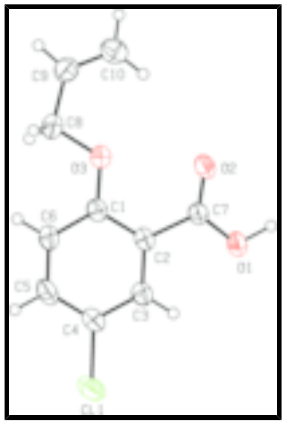


Fig. 1. Molecular structure of (I) with labeling scheme. Ellipsoids at 40% probability level.

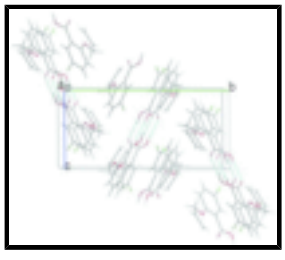


Fig. 2. Packing of (I) showing the pair of molecules connected through hydrogen bonds and stacked along *a* axis.

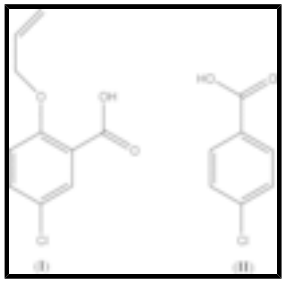


Fig. 3. Schematic representations of the structures of (I) and (II).

2-Allyloxy-5-chlorobenzoic acid

Crystal data

$C_{10}H_9ClO_3$	$F_{000} = 440$
$M_r = 212.62$	$D_x = 1.448$ Mg m^{-3}

Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 8.800$ (1) Å	Cell parameters from 25 reflections
$b = 15.201$ (2) Å	$\theta = 5.6$–17.1°
$c = 7.372$ (1) Å	$\mu = 0.37$ mm^{-1}
$\beta = 98.469$ (3)°	$T = 293$ (2) K
$V = 975.4$ (2) Å^3	Irregular block, colourless
$Z = 4$	0.47 × 0.26 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.018$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.1^\circ$
Monochromator: graphite	$\theta_{min} = 2.3^\circ$
$T = 293$(2) K	$h = -10 \rightarrow 0$
$\omega/2\theta$ scans	$k = 0 \rightarrow 18$
Absorption correction: none	$l = -8 \rightarrow 8$
1848 measured reflections	3 standard reflections
1732 independent reflections	every 200 reflections
1405 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.125$	$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1732 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0102 (3)	0.14496 (14)	0.5102 (3)	0.0390 (5)
C2	0.1059 (2)	0.09010 (13)	0.4234 (3)	0.0368 (5)
C3	0.2527 (3)	0.07040 (14)	0.5121 (3)	0.0400 (5)
H3	0.3161	0.0334	0.4562	0.048*
C4	0.3046 (3)	0.10546 (15)	0.6823 (3)	0.0426 (5)
C5	0.2134 (3)	0.16168 (16)	0.7646 (3)	0.0522 (6)
H5	0.2504	0.1864	0.8779	0.063*
C6	0.0676 (3)	0.18149 (16)	0.6798 (3)	0.0500 (6)
H6	0.0066	0.2197	0.7363	0.060*

C7	0.0576 (2)	0.05211 (14)	0.2379 (3)	0.0386 (5)
O1	0.1500 (2)	−0.00428 (13)	0.1857 (2)	0.0702 (6)
H1	0.1171	−0.0215	0.0586	0.084*
O2	−0.0616 (2)	0.07367 (13)	0.1405 (2)	0.0694 (6)
O3	−0.13381 (18)	0.15949 (11)	0.4243 (2)	0.0472 (4)
C8	−0.2398 (3)	0.20355 (17)	0.5228 (3)	0.0486 (6)
H8A	−0.2133	0.2654	0.5364	0.058*
H8B	−0.2356	0.1781	0.6441	0.058*
C9	−0.3964 (3)	0.19380 (16)	0.4193 (3)	0.0495 (6)
H9	−0.4751	0.2238	0.4642	0.059*
C10	−0.4343 (3)	0.14708 (17)	0.2713 (3)	0.0551 (6)
H10A	−0.3595	0.1159	0.2214	0.066*
H10B	−0.5362	0.1449	0.2157	0.066*
Cl1	0.48749 (7)	0.07853 (4)	0.79134 (8)	0.0581 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0422 (11)	0.0380 (11)	0.0363 (11)	−0.0039 (9)	0.0043 (9)	−0.0040 (8)
C2	0.0446 (12)	0.0340 (10)	0.0312 (10)	−0.0033 (9)	0.0035 (9)	−0.0022 (8)
C3	0.0463 (13)	0.0368 (11)	0.0365 (11)	−0.0008 (9)	0.0043 (9)	−0.0032 (9)
C4	0.0484 (12)	0.0425 (12)	0.0344 (11)	−0.0052 (9)	−0.0022 (9)	−0.0002 (9)
C5	0.0588 (15)	0.0575 (15)	0.0374 (12)	−0.0080 (11)	−0.0021 (11)	−0.0139 (11)
C6	0.0525 (14)	0.0524 (14)	0.0449 (13)	−0.0009 (11)	0.0065 (11)	−0.0196 (11)
C7	0.0421 (12)	0.0396 (11)	0.0334 (11)	0.0025 (9)	0.0028 (9)	−0.0051 (9)
O1	0.0670 (12)	0.0902 (14)	0.0474 (10)	0.0327 (10)	−0.0119 (9)	−0.0334 (9)
O2	0.0665 (12)	0.0895 (14)	0.0450 (10)	0.0326 (10)	−0.0159 (9)	−0.0296 (9)
O3	0.0440 (9)	0.0566 (10)	0.0404 (8)	0.0059 (7)	0.0040 (7)	−0.0128 (7)
C8	0.0501 (13)	0.0502 (13)	0.0466 (13)	0.0038 (10)	0.0108 (10)	−0.0117 (10)
C9	0.0488 (14)	0.0522 (13)	0.0484 (14)	0.0053 (11)	0.0105 (11)	0.0014 (11)
C10	0.0548 (14)	0.0587 (15)	0.0505 (14)	−0.0049 (12)	0.0034 (11)	0.0047 (11)
Cl1	0.0576 (4)	0.0596 (4)	0.0501 (4)	0.0019 (3)	−0.0152 (3)	−0.0042 (3)

Geometric parameters (Å, °)

C1—O3	1.349 (3)	C7—O2	1.225 (3)
C1—C6	1.393 (3)	C7—O1	1.279 (3)
C1—C2	1.405 (3)	O1—H1	0.9752
C2—C3	1.392 (3)	O3—C8	1.430 (3)
C2—C7	1.488 (3)	C8—C9	1.481 (3)
C3—C4	1.378 (3)	C8—H8A	0.9700
C3—H3	0.9300	C8—H8B	0.9700
C4—C5	1.373 (3)	C9—C10	1.303 (3)
C4—Cl1	1.738 (2)	C9—H9	0.9300
C5—C6	1.375 (4)	C10—H10A	0.9300
C5—H5	0.9300	C10—H10B	0.9300
C6—H6	0.9300		
O3—C1—C6	123.2 (2)	O2—C7—O1	122.0 (2)

O3—C1—C2	117.89 (18)	O2—C7—C2	122.61 (19)
C6—C1—C2	118.9 (2)	O1—C7—C2	115.36 (19)
C3—C2—C1	119.37 (19)	C7—O1—H1	110.9
C3—C2—C7	117.91 (19)	C1—O3—C8	118.45 (17)
C1—C2—C7	122.72 (19)	O3—C8—C9	108.60 (19)
C4—C3—C2	120.3 (2)	O3—C8—H8A	110.0
C4—C3—H3	119.8	C9—C8—H8A	110.0
C2—C3—H3	119.8	O3—C8—H8B	110.0
C5—C4—C3	120.4 (2)	C9—C8—H8B	110.0
C5—C4—Cl1	120.26 (17)	H8A—C8—H8B	108.4
C3—C4—Cl1	119.34 (18)	C10—C9—C8	126.1 (2)
C4—C5—C6	120.2 (2)	C10—C9—H9	116.9
C4—C5—H5	119.9	C8—C9—H9	116.9
C6—C5—H5	119.9	C9—C10—H10A	120.0
C5—C6—C1	120.7 (2)	C9—C10—H10B	120.0
C5—C6—H6	119.6	H10A—C10—H10B	120.0
C1—C6—H6	119.6		

Fig. 1

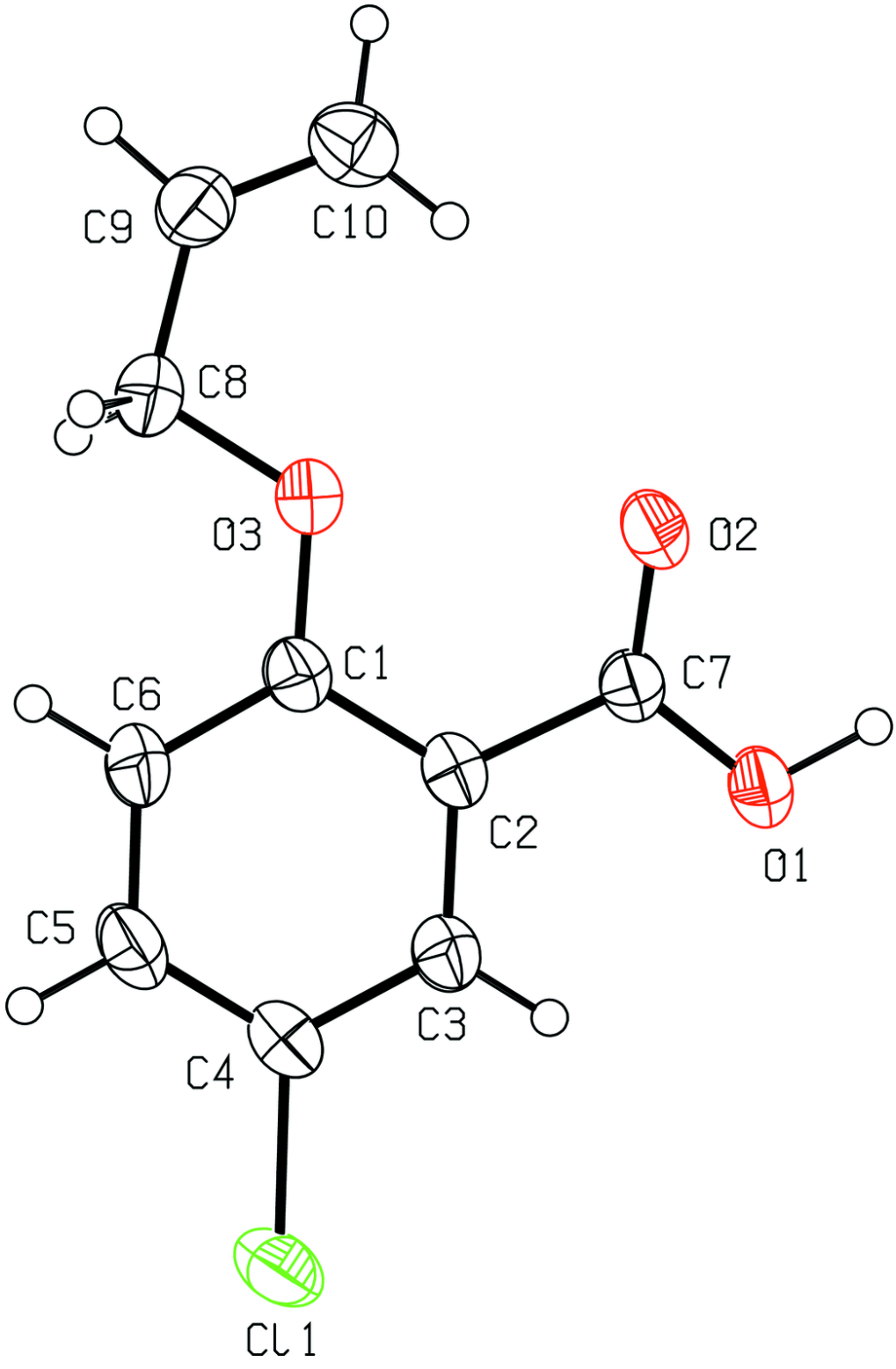


Fig. 2

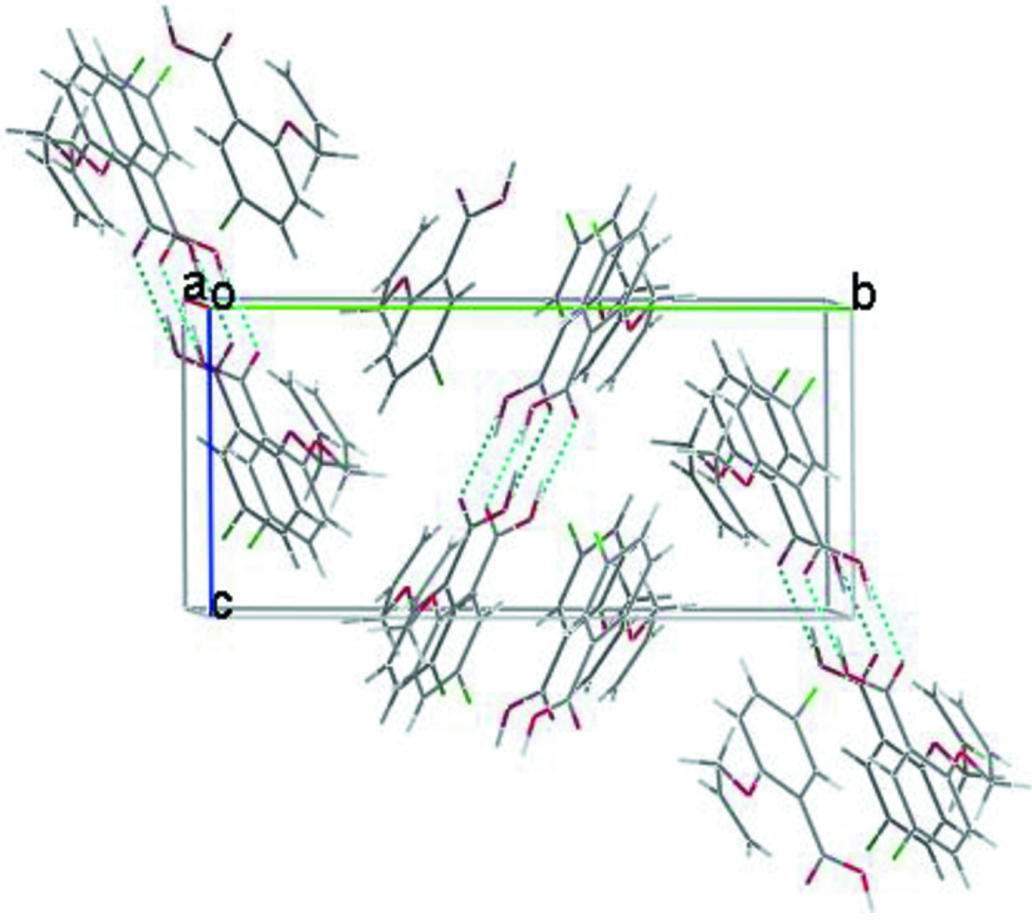
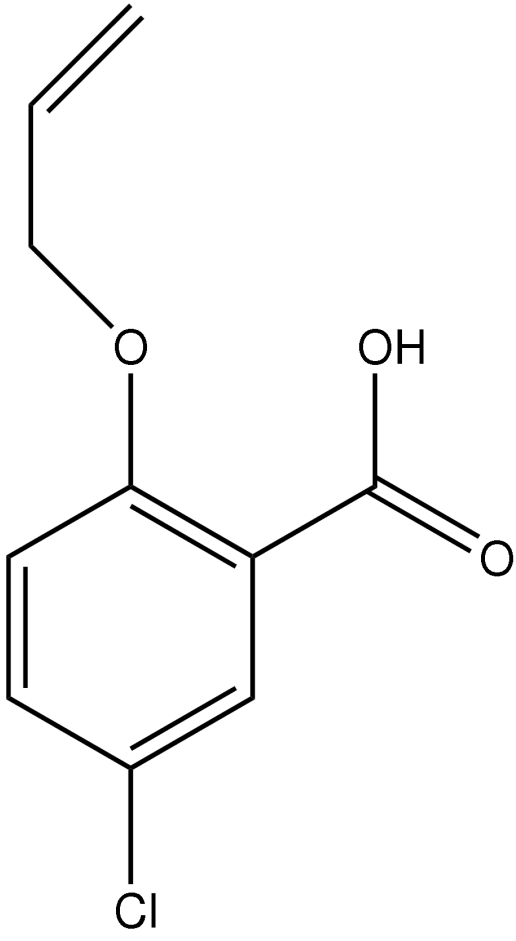
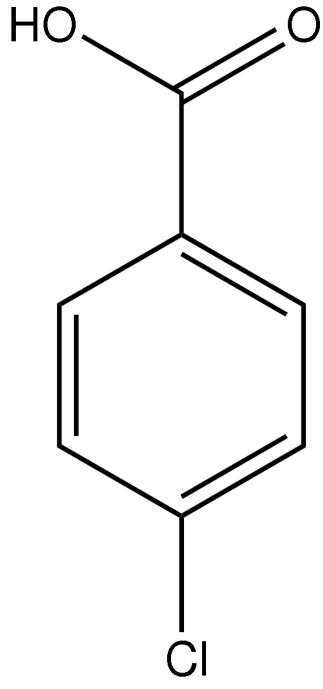


Fig. 3



(I)



(II)