

## Crystal structure of 2-chloro-1-(6-fluoro-3,4-dihydro-2H-chromen-2-yl)ethanone

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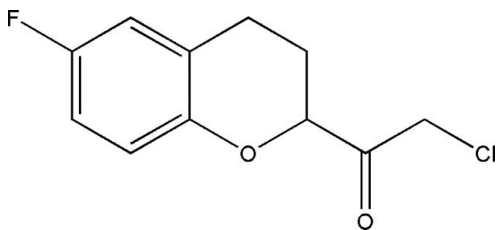
In the title molecule,  $C_{11}H_{10}ClFO_2$ , the benzene ring, the F atom and the O atom of the dihydropyran ring are essentially coplanar, with an r.m.s. deviation of 0.007 Å. The dihydropyran ring is in a half-chair conformation. In the crystal, molecules are linked by pairs of weak C—H... $\pi$  hydrogen bonds, forming inversion dimers.

**Keywords:** crystal structure; chromene; dihydropyran ring; hydrogen bonding; dimer formation; neбиволол intermediate.

**CCDC reference:** 992910

## 1. Related literature

For the application of the title compound as a key intermediate in the preparation of neбиволол, which is useful in treating essential hypertension, see: Raffaella *et al.* (2011).



## 2. Experimental

## 2.1. Crystal data

|                              |   |
|------------------------------|---|
| $C_{11}H_{10}ClFO_2$         | $V = 998.2 (6) \text{ \AA}^3$             |
| $M_r = 228.64$               | $Z = 4$                                   |
| Monoclinic, $P2_1/c$         | Mo $K\alpha$ radiation                    |
| $a = 9.704 (3) \text{ \AA}$  | $\mu = 0.37 \text{ mm}^{-1}$              |
| $b = 9.720 (3) \text{ \AA}$  | $T = 296 \text{ K}$                       |
| $c = 10.804 (4) \text{ \AA}$ | $0.20 \times 0.20 \times 0.20 \text{ mm}$ |
| $\beta = 101.637 (7)^\circ$  |   |

## 2.2. Data collection

|  |  |
|--|--|
| Rigaku SCXmini diffractometer  | 5810 measured reflections              |
| Absorption correction: multi-scan<br>( <i>CrystalClear</i> ; Rigaku, 2005) | 1940 independent reflections           |
| $T_{\min} = 0.983$ , $T_{\max} = 0.983$                                    | 1701 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.037$               |

## 2.3. Refinement

|                                 |  |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.058$ | 136 parameters                                       |
| $wR(F^2) = 0.169$               | H-atom parameters constrained                        |
| $S = 1.06$                      | $\Delta\rho_{\text{max}} = 0.87 \text{ e \AA}^{-3}$  |
| 1940 reflections                | $\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$ |

Table 1

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C1–C6 ring.

| $D-H\cdots A$              | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------|-------|-------------|-------------|---------------|
| C11—H11B...Cg <sup>i</sup> | 0.97  | 2.76        | 3.457 (3)   | 129           |

Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5719).

## References

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- Raffaella, V., Paolo, M., Livius, C. & Johnny, F. (2011). US 7960572, B2. Rigaku. (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

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## Crystal structure of 2-chloro-1-(6-fluoro-3,4-dihydro-2H-chromen-2-yl)ethanone

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### S1. Comment

The title compound is a key intermediate in preparing nebivolol, which is useful in treating essential hypertension (Raffaella, *et al.*, 2011). As part of our interest in these types of materials, we report herein the crystal structure of the title compound.

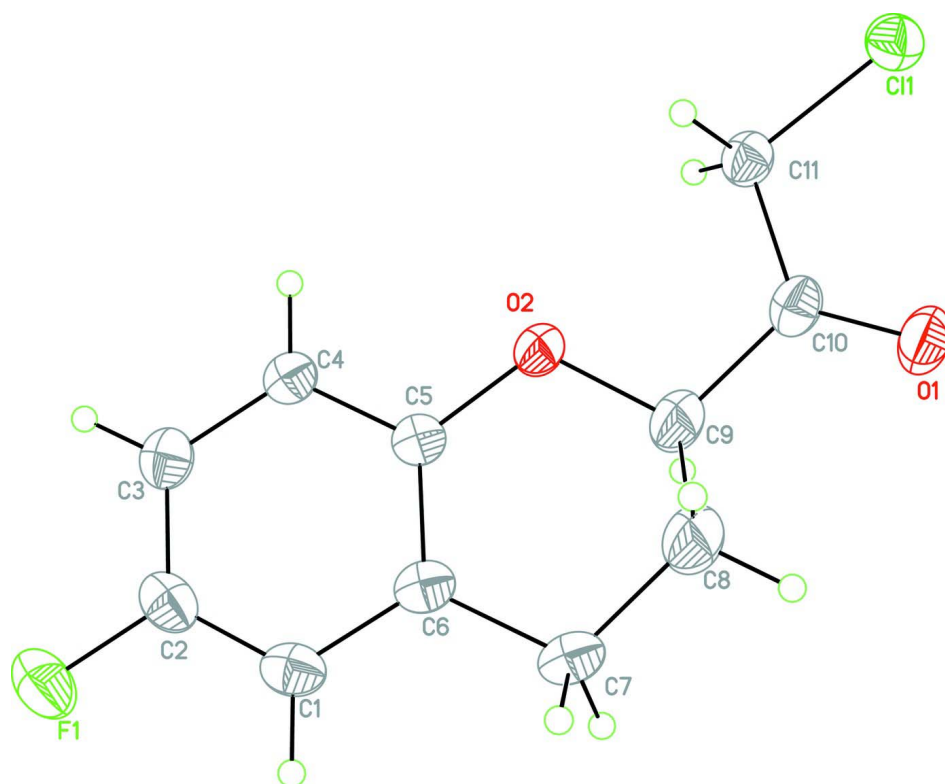
The molecular structure of the title compound is shown in Fig.1. Atoms F1 and O2 atoms are approximately coplanar with the benzene ring, with an r.m.s deviation of 0.007 Å. The dihydropyran ring is in a half-chair conformation. In the crystal, molecules are linked by pairs of weak C—H $\cdots$  $\pi$  hydrogen bonds forming inversion dimers (Fig. 2).

### S2. Experimental

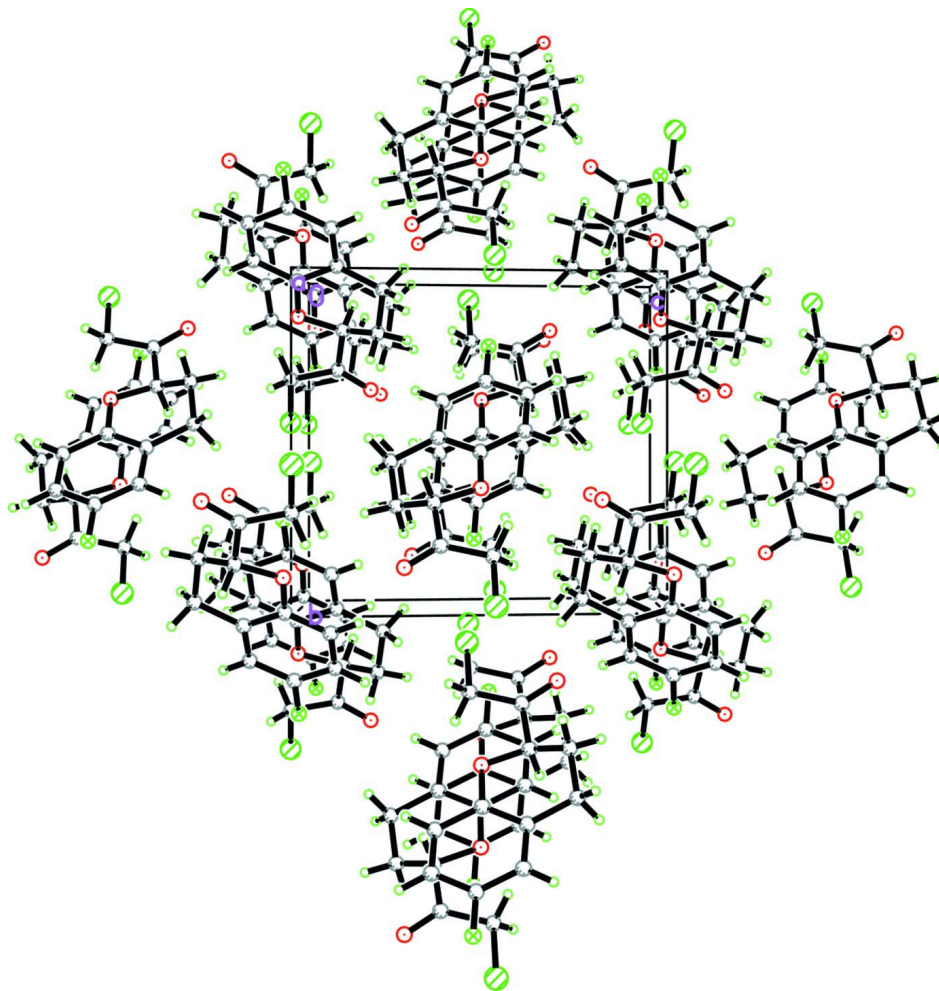
The title compound was provided by Changzhou Siyao Pham, Ltd (Changzhou, Jiangsu). Crystals of it suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution.

### S3. Refinement

All H atoms were positioned geometrically and treated as riding with C—H = 0.93 Å (aryl), C—H = 0.97 Å (methylene) and C—H = 0.98 Å (methine) with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ .

**Figure 1**

The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.



**Figure 2**

Part of the crystal structure viewed along the *a* axis.

**2-Chloro-1-(6-fluoro-3,4-dihydro-2*H*-chromen-2-yl)ethanone**

*Crystal data*

$C_{11}H_{10}ClFO_2$

$M_r = 228.64$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.704 (3) \text{ \AA}$

$b = 9.720 (3) \text{ \AA}$

$c = 10.804 (4) \text{ \AA}$

$\beta = 101.637 (7)^\circ$

$V = 998.2 (6) \text{ \AA}^3$

$Z = 4$

$F(000) = 472$

$D_x = 1.521 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1940 reflections

$\theta = 2.1\text{--}26.0^\circ$

$\mu = 0.37 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism, colourless

$0.20 \times 0.20 \times 0.20 \text{ mm}$

*Data collection*

Rigaku SCXmini  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution:  $13.6612 \text{ pixels mm}^{-1}$

CCD\_Profile\_fitting scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.983$ ,  $T_{\max} = 0.983$   
 5810 measured reflections  
 1940 independent reflections  
 1701 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.037$

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.1^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -11 \rightarrow 11$   
 $l = -12 \rightarrow 13$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.169$   
 $S = 1.06$   
 1940 reflections  
 136 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.087P)^2 + 0.9962P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.87 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|      | $x$         | $y$         | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|--------------|----------------------------------|
| C11  | 0.29999 (8) | 0.06003 (8) | 0.46282 (7)  | 0.0520 (3)                       |
| O2   | 0.6337 (2)  | 0.3728 (2)  | 0.50089 (17) | 0.0446 (5)                       |
| F1   | 1.0157 (2)  | 0.7779 (2)  | 0.4805 (2)   | 0.0693 (6)                       |
| C5   | 0.7331 (3)  | 0.4738 (3)  | 0.5024 (2)   | 0.0370 (6)                       |
| C1   | 0.9201 (3)  | 0.6183 (3)  | 0.6021 (3)   | 0.0465 (7)                       |
| H1   | 0.9827      | 0.6483      | 0.6738       | 0.056*                           |
| C6   | 0.8247 (3)  | 0.5141 (3)  | 0.6117 (3)   | 0.0399 (6)                       |
| C4   | 0.7381 (3)  | 0.5330 (3)  | 0.3864 (3)   | 0.0415 (6)                       |
| H4   | 0.6773      | 0.5026      | 0.3137       | 0.050*                           |
| C3   | 0.8324 (3)  | 0.6361 (3)  | 0.3789 (3)   | 0.0476 (7)                       |
| H3   | 0.8355      | 0.6776      | 0.3019       | 0.057*                           |
| C7   | 0.8214 (3)  | 0.4463 (3)  | 0.7360 (3)   | 0.0504 (7)                       |
| H7A  | 0.9162      | 0.4203      | 0.7767       | 0.060*                           |
| H7B  | 0.7865      | 0.5112      | 0.7906       | 0.060*                           |
| C11  | 0.4282 (3)  | 0.1895 (3)  | 0.4699 (3)   | 0.0433 (6)                       |
| H11A | 0.4958      | 0.1617      | 0.4197       | 0.052*                           |
| H11B | 0.3834      | 0.2735      | 0.4335       | 0.052*                           |
| C10  | 0.5040 (3)  | 0.2175 (3)  | 0.6024 (3)   | 0.0458 (7)                       |
| C2   | 0.9219 (3)  | 0.6765 (3)  | 0.4875 (3)   | 0.0483 (7)                       |
| O1   | 0.4794 (3)  | 0.1587 (3)  | 0.6926 (2)   | 0.0607 (6)                       |

|     |            |            |            |             |
|-----|------------|------------|------------|-------------|
| C9  | 0.6086 (4) | 0.3338 (5) | 0.6206 (3) | 0.0700 (11) |
| H9  | 0.5568     | 0.4116     | 0.6465     | 0.084*      |
| C8  | 0.7298 (5) | 0.3218 (5) | 0.7187 (4) | 0.0829 (14) |
| H8A | 0.7849     | 0.2438     | 0.7006     | 0.099*      |
| H8B | 0.6999     | 0.3028     | 0.7974     | 0.099*      |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C11 | 0.0554 (5)  | 0.0483 (5)  | 0.0536 (5)  | −0.0019 (3)  | 0.0140 (3)   | −0.0035 (3)  |
| O2  | 0.0478 (11) | 0.0536 (12) | 0.0315 (9)  | −0.0070 (9)  | 0.0054 (8)   | 0.0040 (8)   |
| F1  | 0.0627 (12) | 0.0574 (12) | 0.0896 (15) | −0.0171 (10) | 0.0197 (11)  | −0.0058 (11) |
| C5  | 0.0363 (13) | 0.0358 (13) | 0.0388 (14) | 0.0062 (10)  | 0.0070 (11)  | −0.0012 (10) |
| C1  | 0.0396 (14) | 0.0454 (16) | 0.0528 (16) | 0.0045 (12)  | 0.0052 (12)  | −0.0122 (13) |
| C6  | 0.0376 (13) | 0.0417 (14) | 0.0398 (14) | 0.0112 (11)  | 0.0062 (11)  | −0.0056 (11) |
| C4  | 0.0409 (14) | 0.0452 (15) | 0.0380 (14) | 0.0029 (11)  | 0.0073 (11)  | −0.0007 (11) |
| C3  | 0.0486 (16) | 0.0464 (16) | 0.0505 (16) | 0.0062 (13)  | 0.0159 (13)  | 0.0041 (13)  |
| C7  | 0.0517 (17) | 0.0602 (19) | 0.0357 (14) | 0.0038 (14)  | 0.0007 (12)  | −0.0048 (13) |
| C11 | 0.0477 (15) | 0.0429 (14) | 0.0399 (14) | 0.0034 (12)  | 0.0100 (12)  | 0.0038 (11)  |
| C10 | 0.0455 (15) | 0.0534 (17) | 0.0388 (14) | 0.0048 (13)  | 0.0091 (12)  | 0.0093 (12)  |
| C2  | 0.0417 (15) | 0.0381 (14) | 0.067 (2)   | −0.0003 (11) | 0.0159 (14)  | −0.0067 (13) |
| O1  | 0.0602 (13) | 0.0790 (16) | 0.0427 (12) | −0.0096 (12) | 0.0101 (10)  | 0.0160 (11)  |
| C9  | 0.078 (2)   | 0.092 (3)   | 0.0366 (16) | −0.028 (2)   | 0.0032 (15)  | 0.0125 (17)  |
| C8  | 0.088 (3)   | 0.108 (3)   | 0.0448 (19) | −0.035 (3)   | −0.0046 (18) | 0.022 (2)    |

*Geometric parameters (Å, °)*

|          |           |               |           |
|----------|-----------|---------------|-----------|
| C11—C11  | 1.761 (3) | C3—H3         | 0.9300    |
| O2—C5    | 1.374 (3) | C7—C8         | 1.492 (5) |
| O2—C9    | 1.416 (4) | C7—H7A        | 0.9700    |
| F1—C2    | 1.354 (3) | C7—H7B        | 0.9700    |
| C5—C6    | 1.383 (4) | C11—C10       | 1.497 (4) |
| C5—C4    | 1.389 (4) | C11—H11A      | 0.9700    |
| C1—C2    | 1.364 (5) | C11—H11B      | 0.9700    |
| C1—C6    | 1.391 (4) | C10—O1        | 1.194 (4) |
| C1—H1    | 0.9300    | C10—C9        | 1.506 (5) |
| C6—C7    | 1.501 (4) | C9—C8         | 1.420 (5) |
| C4—C3    | 1.370 (4) | C9—H9         | 0.9800    |
| C4—H4    | 0.9300    | C8—H8A        | 0.9700    |
| C3—C2    | 1.370 (5) | C8—H8B        | 0.9700    |
| C5—O2—C9 | 115.5 (2) | C10—C11—H11A  | 109.2     |
| O2—C5—C6 | 122.7 (2) | C11—C11—H11A  | 109.2     |
| O2—C5—C4 | 115.9 (2) | C10—C11—H11B  | 109.2     |
| C6—C5—C4 | 121.3 (3) | C11—C11—H11B  | 109.2     |
| C2—C1—C6 | 120.1 (3) | H11A—C11—H11B | 107.9     |
| C2—C1—H1 | 120.0     | O1—C10—C11    | 123.6 (3) |
| C6—C1—H1 | 120.0     | O1—C10—C9     | 119.5 (3) |

|             |           |            |           |
|-------------|-----------|------------|-----------|
| C5—C6—C1    | 117.7 (3) | C11—C10—C9 | 116.7 (2) |
| C5—C6—C7    | 120.9 (3) | F1—C2—C1   | 119.0 (3) |
| C1—C6—C7    | 121.4 (3) | F1—C2—C3   | 118.6 (3) |
| C3—C4—C5    | 120.1 (3) | C1—C2—C3   | 122.4 (3) |
| C3—C4—H4    | 119.9     | O2—C9—C8   | 115.8 (3) |
| C5—C4—H4    | 119.9     | O2—C9—C10  | 108.5 (3) |
| C2—C3—C4    | 118.3 (3) | C8—C9—C10  | 118.1 (3) |
| C2—C3—H3    | 120.8     | O2—C9—H9   | 104.2     |
| C4—C3—H3    | 120.8     | C8—C9—H9   | 104.2     |
| C8—C7—C6    | 111.3 (2) | C10—C9—H9  | 104.2     |
| C8—C7—H7A   | 109.4     | C9—C8—C7   | 114.2 (3) |
| C6—C7—H7A   | 109.4     | C9—C8—H8A  | 108.7     |
| C8—C7—H7B   | 109.4     | C7—C8—H8A  | 108.7     |
| C6—C7—H7B   | 109.4     | C9—C8—H8B  | 108.7     |
| H7A—C7—H7B  | 108.0     | C7—C8—H8B  | 108.7     |
| C10—C11—C11 | 112.2 (2) | H8A—C8—H8B | 107.6     |

*Hydrogen-bond geometry (Å, °)*

C<sub>g</sub> is the centroid of the C1—C6 ring.

| <i>D</i> —H... <i>A</i>                         | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---|-------------|---------------|-----------------------|-------------------------|
| C11—H11 <i>B</i> ...C <sub>g</sub> <sup>i</sup> | 0.97        | 2.76          | 3.457 (3)             | 129                     |

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .