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(Z)-Ethyl 3-(4-chlorobenzamido)-2-cyano-3-(4-fluorophenyl)acrylateDehua Zhang,^{a*} Xiaoyan Zhang^b and Lijuan Guo^c

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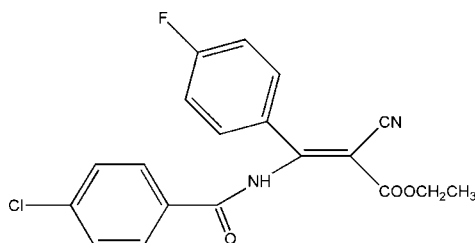
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.065; wR factor = 0.140; data-to-parameter ratio = 13.8.

The title compound, $\text{C}_{19}\text{H}_{14}\text{ClFN}_2\text{O}_3$, was prepared by the reaction of ethyl (*Z*)-3-amino-2-cyano-3-(4-fluorophenyl)acrylate and 4-chlorobenzoyl chloride. The dihedral angle between the chlorobenzene and fluorobenzene rings is $66.18(19)^\circ$. In addition to an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond, there are intermolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonding interactions, which stabilize the crystal structure.

Related literature

For the agrochemical activity of the title compound, see: Heller *et al.* (2004); Ibers & Hamilton (1964).



Experimental

Crystal data

$\text{C}_{19}\text{H}_{14}\text{ClFN}_2\text{O}_3$
 $M_r = 372.77$
 Monoclinic, $P2_1/c$
 $a = 6.1429(5)$ Å
 $b = 13.1555(6)$ Å
 $c = 22.9263(10)$ Å
 $\beta = 92.280(4)^\circ$

$V = 1851.27(19)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 298(2)$ K
 $0.40 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 Absorption correction: none
 23332 measured reflections

3259 independent reflections
 2138 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.140$
 $S = 1.07$
 3259 reflections

236 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O2}$	0.86	2.00	2.668 (3)	134
$\text{C3}-\text{H3}\cdots\text{N2}^{\text{i}}$	0.93	2.53	3.314 (5)	143
$\text{C6}-\text{H6}\cdots\text{O1}^{\text{ii}}$	0.93	2.41	3.170 (4)	140
$\text{C14}-\text{H14}\cdots\text{N2}^{\text{iii}}$	0.93	2.55	3.463 (5)	169

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$; (iii) $x + 1, y, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2277).

References

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supplementary materials

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(Z)-Ethyl 3-(4-chlorobenzamido)-2-cyano-3-(4-fluorophenyl)acrylate

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Comment

Recently, 2-cyanoacrylates have been extensively used as agrochemicals because of their unique mechanism of action and good environmental profiles. The title compound is useful as an inhibitor of *Pyricularia oryzae*, *Rhizoctonia solani*, *Botrytis cinerea* and *Gibberella zeae* (Heller *et al.*, 2004; Ibers & Hamilton, 1964).

In the title compound (Fig.1), all bond lengths and angles are unexceptional. The aromatic rings of the chlorobenzene and fluorobenzene groups form a dihedral angle of 66.18 (19)°. The molecular conformation is stabilized by an intramolecular N—H···O hydrogen bond (Table 1). The crystal packing is governed by C—H···O and C—H···N hydrogen interactions (Fig.2) resulting in a three-dimensional network.

Experimental

To a solution of ethyl (2Z)-3-amino-2-cyano-3-(4-fluorophenyl)acrylate (1.17 g, 0.0050 mol) in CH₂Cl₂ (18 ml), 4-chlorobenzoyl chloride (2.63 g, 0.015 mol) was added. Subsequently, Et₃N (1.52 g, 0.015 mol) was dropped into the solution under stirring. The reaction mixture was then heated to reflux, stirred for 4 h and cooled to room temperature. The reaction solution was filtered off and some white solid was separated. The organic phase was washed with water and then dried over Na₂SO₄. After removal of the solvent, a brown dope was obtained. The title compound was isolated by column chromatography using ethyl acetate/light petroleum (1:6 v/v) as eluent. Single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of an ethyl acetate/petroleum ether (3:1 v/v) solution after 45 days.

Refinement

All H atoms were placed at calculated positions and refined using a riding model, with C—H = 0.93-0.97 Å, N—H = 0.86 Å and with $U_{iso}(H) = 1.2 U_{eq}(C, N)$ or $1.5 U_{eq}(C)$ for methyl H atoms.

Figures

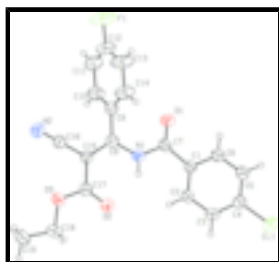


Fig. 1. The molecular structure of The title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

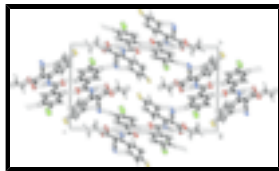


Fig. 2. Packing diagram of the title compound, viewed approximately along the *a* axis. Hydrogen bonds are shown as dashed lines.

(Z)-Ethyl 3-(4-chlorobenzamido)-2-cyano-3-(4-fluorophenyl)acrylate

Crystal data

$C_{19}H_{14}ClFN_2O_3$	$F_{000} = 768$
$M_r = 372.77$	$D_x = 1.337 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 6.1429 (5) \text{ \AA}$	Cell parameters from 1253 reflections
$b = 13.1555 (6) \text{ \AA}$	$\theta = 3.1\text{--}20.3^\circ$
$c = 22.9263 (10) \text{ \AA}$	$\mu = 0.24 \text{ mm}^{-1}$
$\beta = 92.280 (4)^\circ$	$T = 298 (2) \text{ K}$
$V = 1851.27 (19) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.40 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2138 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.053$
Monochromator: graphite	$\theta_{\text{max}} = 25.0^\circ$
$T = 298(2) \text{ K}$	$\theta_{\text{min}} = 1.8^\circ$
phi and ω scans	$h = -7 \rightarrow 7$
Absorption correction: none	$k = -15 \rightarrow 15$
23332 measured reflections	$l = -24 \rightarrow 27$
3259 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.065$	H-atom parameters constrained
$wR(F^2) = 0.140$	$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 1.3651P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
3259 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
236 parameters	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
	Extinction correction: none

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4513 (5)	0.4421 (2)	0.11848 (12)	0.0510 (7)
C2	0.4752 (5)	0.3939 (2)	0.17187 (14)	0.0613 (9)
H2	0.3761	0.4064	0.2006	0.074*
C3	0.6452 (6)	0.3273 (3)	0.18272 (14)	0.0670 (9)
H3	0.6599	0.2942	0.2185	0.080*
C4	0.7924 (5)	0.3099 (2)	0.14056 (15)	0.0626 (9)
C5	0.7716 (6)	0.3559 (3)	0.08732 (15)	0.0696 (9)
H5	0.8718	0.3431	0.0589	0.084*
C6	0.6006 (6)	0.4213 (2)	0.07632 (14)	0.0673 (9)
H6	0.5848	0.4523	0.0399	0.081*
C7	0.2778 (5)	0.5173 (2)	0.10220 (14)	0.0582 (8)
C8	-0.0191 (5)	0.6171 (2)	0.14507 (13)	0.0531 (8)
C9	-0.0435 (5)	0.6899 (2)	0.09582 (13)	0.0557 (8)
C10	-0.2251 (6)	0.6897 (3)	0.05965 (16)	0.0790 (11)
H10	-0.3308	0.6400	0.0642	0.095*
C11	-0.2547 (7)	0.7618 (3)	0.01659 (16)	0.0873 (12)
H11	-0.3779	0.7598	-0.0083	0.105*
C12	-0.1070 (8)	0.8340 (3)	0.01079 (16)	0.0870 (13)
C13	0.0819 (9)	0.8367 (3)	0.04453 (19)	0.1072 (16)
H13	0.1867	0.8863	0.0388	0.129*
C14	0.1124 (7)	0.7635 (3)	0.08740 (17)	0.0879 (12)
H14	0.2395	0.7638	0.1108	0.106*
C15	-0.1571 (5)	0.6200 (2)	0.18996 (13)	0.0539 (8)
C16	-0.3251 (6)	0.6945 (3)	0.18956 (14)	0.0667 (9)
C17	-0.1424 (5)	0.5506 (2)	0.24042 (13)	0.0561 (8)
C18	-0.3118 (6)	0.4975 (3)	0.32660 (15)	0.0742 (10)
H18A	-0.1840	0.5102	0.3518	0.089*
H18B	-0.3126	0.4264	0.3155	0.089*
C19	-0.5130 (7)	0.5229 (4)	0.35748 (17)	0.1065 (15)
H19A	-0.5114	0.5937	0.3677	0.160*
H19B	-0.5193	0.4826	0.3923	0.160*
H19C	-0.6383	0.5088	0.3324	0.160*
Cl1	1.00991 (17)	0.22922 (8)	0.15591 (5)	0.0969 (4)

supplementary materials

F1	-0.1365 (6)	0.90693 (18)	-0.03083 (11)	0.1356 (11)
N1	0.1499 (4)	0.54859 (19)	0.14698 (10)	0.0595 (7)
H1	0.1799	0.5216	0.1805	0.071*
N2	-0.4597 (6)	0.7536 (3)	0.19023 (14)	0.0981 (12)
O1	0.2500 (5)	0.5501 (2)	0.05344 (10)	0.0940 (9)
O2	0.0048 (4)	0.49015 (17)	0.24988 (10)	0.0701 (6)
O3	-0.3085 (4)	0.56200 (16)	0.27479 (9)	0.0628 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0583 (19)	0.0492 (16)	0.0460 (17)	-0.0001 (14)	0.0068 (15)	0.0007 (14)
C2	0.065 (2)	0.064 (2)	0.056 (2)	0.0058 (17)	0.0166 (17)	0.0054 (16)
C3	0.076 (2)	0.070 (2)	0.055 (2)	0.0070 (19)	0.0057 (18)	0.0142 (17)
C4	0.066 (2)	0.0532 (18)	0.069 (2)	0.0047 (16)	0.0076 (18)	0.0025 (16)
C5	0.077 (2)	0.073 (2)	0.061 (2)	0.0152 (19)	0.0198 (18)	0.0022 (18)
C6	0.085 (3)	0.066 (2)	0.0522 (19)	0.0133 (19)	0.0115 (18)	0.0070 (16)
C7	0.069 (2)	0.0603 (19)	0.0460 (19)	0.0017 (16)	0.0124 (16)	0.0019 (15)
C8	0.060 (2)	0.0509 (17)	0.0482 (18)	0.0018 (15)	-0.0006 (15)	-0.0051 (14)
C9	0.064 (2)	0.0523 (18)	0.0514 (18)	0.0036 (16)	0.0030 (16)	-0.0038 (15)
C10	0.083 (3)	0.086 (3)	0.067 (2)	-0.013 (2)	-0.011 (2)	0.013 (2)
C11	0.093 (3)	0.099 (3)	0.067 (2)	0.003 (3)	-0.025 (2)	0.008 (2)
C12	0.137 (4)	0.056 (2)	0.066 (2)	0.008 (2)	-0.021 (3)	0.0120 (19)
C13	0.150 (4)	0.066 (2)	0.102 (3)	-0.032 (3)	-0.038 (3)	0.026 (2)
C14	0.109 (3)	0.069 (2)	0.083 (3)	-0.014 (2)	-0.032 (2)	0.012 (2)
C15	0.060 (2)	0.0543 (17)	0.0471 (18)	0.0084 (15)	0.0011 (15)	-0.0003 (14)
C16	0.073 (2)	0.077 (2)	0.050 (2)	0.019 (2)	0.0033 (17)	0.0008 (17)
C17	0.057 (2)	0.0577 (19)	0.0537 (19)	0.0008 (16)	0.0027 (16)	-0.0077 (16)
C18	0.086 (3)	0.076 (2)	0.060 (2)	-0.013 (2)	0.0093 (19)	0.0138 (18)
C19	0.095 (3)	0.155 (4)	0.072 (3)	0.002 (3)	0.028 (2)	0.021 (3)
Cl1	0.0849 (7)	0.0965 (7)	0.1095 (8)	0.0329 (6)	0.0085 (6)	0.0214 (6)
F1	0.226 (3)	0.0791 (16)	0.0970 (18)	0.0063 (18)	-0.0458 (19)	0.0293 (14)
N1	0.0694 (18)	0.0653 (16)	0.0443 (14)	0.0139 (14)	0.0072 (13)	0.0055 (12)
N2	0.105 (3)	0.122 (3)	0.068 (2)	0.053 (2)	0.0133 (19)	0.0078 (19)
O1	0.110 (2)	0.119 (2)	0.0542 (15)	0.0513 (17)	0.0204 (14)	0.0236 (15)
O2	0.0746 (16)	0.0726 (14)	0.0636 (14)	0.0142 (13)	0.0100 (12)	0.0111 (12)
O3	0.0666 (14)	0.0682 (13)	0.0543 (13)	0.0006 (11)	0.0105 (11)	0.0010 (11)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.381 (4)	C11—C12	1.324 (5)
C1—C6	1.386 (4)	C11—H11	0.9300
C1—C7	1.491 (4)	C12—F1	1.361 (4)
C2—C3	1.378 (4)	C12—C13	1.369 (6)
C2—H2	0.9300	C13—C14	1.383 (5)
C3—C4	1.369 (4)	C13—H13	0.9300
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.364 (4)	C15—C16	1.423 (5)
C4—Cl1	1.732 (3)	C15—C17	1.473 (4)

C5—C6	1.374 (4)	C16—N2	1.135 (4)
C5—H5	0.9300	C17—O2	1.217 (4)
C6—H6	0.9300	C17—O3	1.322 (4)
C7—O1	1.204 (4)	C18—O3	1.461 (4)
C7—N1	1.380 (4)	C18—C19	1.487 (5)
C8—C15	1.360 (4)	C18—H18A	0.9700
C8—N1	1.374 (4)	C18—H18B	0.9700
C8—C9	1.484 (4)	C19—H19A	0.9600
C9—C10	1.363 (4)	C19—H19B	0.9600
C9—C14	1.381 (5)	C19—H19C	0.9600
C10—C11	1.376 (5)	N1—H1	0.8600
C10—H10	0.9300		
C2—C1—C6	118.5 (3)	C11—C12—F1	120.2 (4)
C2—C1—C7	125.2 (3)	C11—C12—C13	122.1 (4)
C6—C1—C7	116.3 (3)	F1—C12—C13	117.7 (4)
C3—C2—C1	120.4 (3)	C12—C13—C14	118.1 (4)
C3—C2—H2	119.8	C12—C13—H13	121.0
C1—C2—H2	119.8	C14—C13—H13	121.0
C4—C3—C2	119.7 (3)	C9—C14—C13	120.8 (4)
C4—C3—H3	120.2	C9—C14—H14	119.6
C2—C3—H3	120.2	C13—C14—H14	119.6
C5—C4—C3	121.2 (3)	C8—C15—C16	119.2 (3)
C5—C4—C11	119.9 (3)	C8—C15—C17	123.8 (3)
C3—C4—C11	119.0 (3)	C16—C15—C17	117.0 (3)
C4—C5—C6	119.1 (3)	N2—C16—C15	178.8 (4)
C4—C5—H5	120.5	O2—C17—O3	123.6 (3)
C6—C5—H5	120.5	O2—C17—C15	124.5 (3)
C5—C6—C1	121.2 (3)	O3—C17—C15	111.9 (3)
C5—C6—H6	119.4	O3—C18—C19	107.2 (3)
C1—C6—H6	119.4	O3—C18—H18A	110.3
O1—C7—N1	121.3 (3)	C19—C18—H18A	110.3
O1—C7—C1	122.9 (3)	O3—C18—H18B	110.3
N1—C7—C1	115.7 (3)	C19—C18—H18B	110.3
C15—C8—N1	119.2 (3)	H18A—C18—H18B	108.5
C15—C8—C9	120.7 (3)	C18—C19—H19A	109.5
N1—C8—C9	120.1 (3)	C18—C19—H19B	109.5
C10—C9—C14	118.1 (3)	H19A—C19—H19B	109.5
C10—C9—C8	121.1 (3)	C18—C19—H19C	109.5
C14—C9—C8	120.6 (3)	H19A—C19—H19C	109.5
C9—C10—C11	121.1 (4)	H19B—C19—H19C	109.5
C9—C10—H10	119.4	C8—N1—C7	128.6 (3)
C11—C10—H10	119.4	C8—N1—H1	115.7
C12—C11—C10	119.7 (4)	C7—N1—H1	115.7
C12—C11—H11	120.2	C17—O3—C18	117.1 (3)
C10—C11—H11	120.2		
C6—C1—C2—C3	0.5 (5)	C10—C11—C12—C13	3.4 (7)
C7—C1—C2—C3	-178.5 (3)	C11—C12—C13—C14	-2.7 (7)
C1—C2—C3—C4	0.8 (5)	F1—C12—C13—C14	179.3 (4)

supplementary materials

C2—C3—C4—C5	-1.3 (5)	C10—C9—C14—C13	1.9 (6)
C2—C3—C4—C11	177.9 (3)	C8—C9—C14—C13	-174.7 (4)
C3—C4—C5—C6	0.6 (5)	C12—C13—C14—C9	0.0 (7)
C11—C4—C5—C6	-178.6 (3)	N1—C8—C15—C16	176.6 (3)
C4—C5—C6—C1	0.7 (5)	C9—C8—C15—C16	-0.5 (5)
C2—C1—C6—C5	-1.3 (5)	N1—C8—C15—C17	-2.5 (5)
C7—C1—C6—C5	177.8 (3)	C9—C8—C15—C17	-179.7 (3)
C2—C1—C7—O1	-172.5 (3)	C8—C15—C17—O2	7.0 (5)
C6—C1—C7—O1	8.5 (5)	C16—C15—C17—O2	-172.2 (3)
C2—C1—C7—N1	8.1 (5)	C8—C15—C17—O3	-173.4 (3)
C6—C1—C7—N1	-170.9 (3)	C16—C15—C17—O3	7.4 (4)
C15—C8—C9—C10	-64.0 (4)	C15—C8—N1—C7	164.6 (3)
N1—C8—C9—C10	118.9 (4)	C9—C8—N1—C7	-18.2 (5)
C15—C8—C9—C14	112.5 (4)	O1—C7—N1—C8	0.0 (5)
N1—C8—C9—C14	-64.7 (4)	C1—C7—N1—C8	179.4 (3)
C14—C9—C10—C11	-1.2 (6)	O2—C17—O3—C18	-0.1 (4)
C8—C9—C10—C11	175.4 (3)	C15—C17—O3—C18	-179.7 (3)
C9—C10—C11—C12	-1.4 (6)	C19—C18—O3—C17	-179.3 (3)
C10—C11—C12—F1	-178.6 (4)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2	0.86	2.00	2.668 (3)	134
C3—H3 \cdots N2 ⁱ	0.93	2.53	3.314 (5)	143
C6—H6 \cdots O1 ⁱⁱ	0.93	2.41	3.170 (4)	140
C14—H14 \cdots N2 ⁱⁱⁱ	0.93	2.55	3.463 (5)	169

Symmetry codes: (i) $-x, y-1/2, -z+1/2$; (ii) $-x+1, -y+1, -z$; (iii) $x+1, y, z$.

Fig. 1

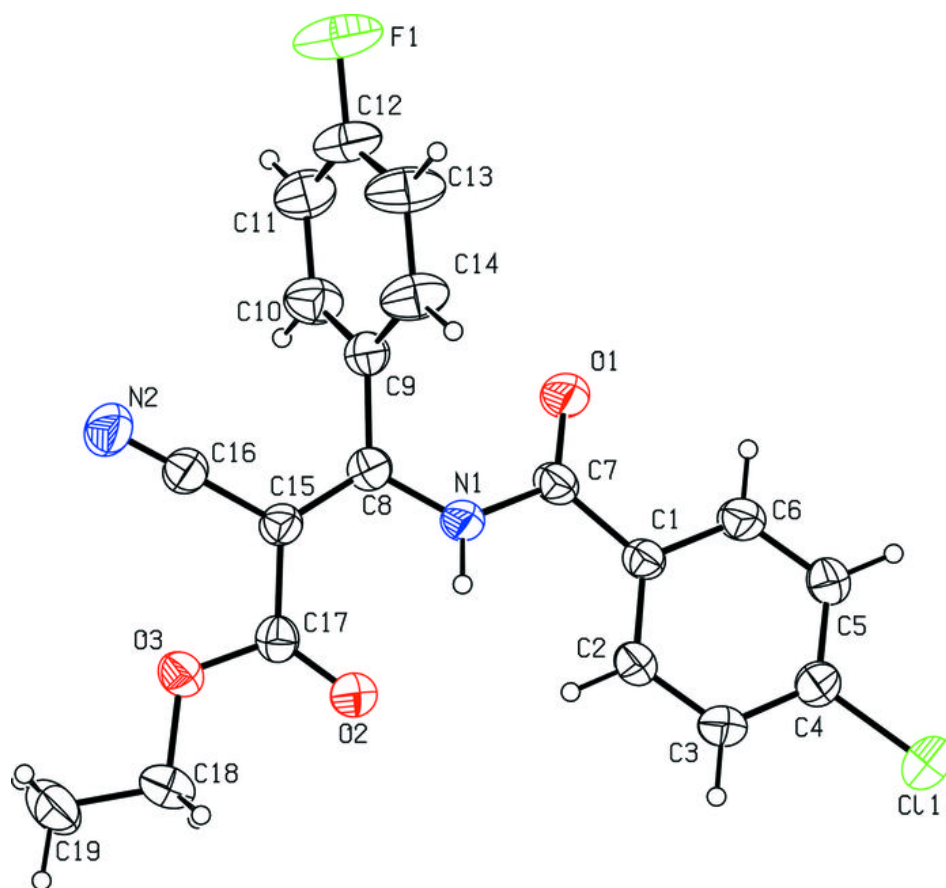


Fig. 2

