

# (*E*)-1-(4,4''-Difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-(4-nitrophenyl)prop-2-en-1-one

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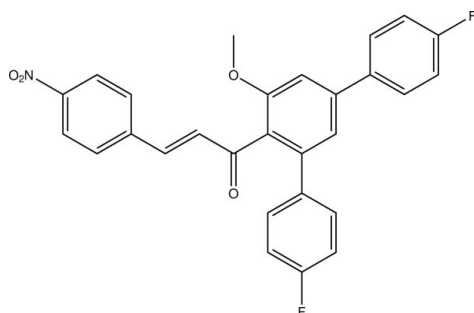
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Key indicators: single-crystal X-ray study; *T* = 200 K; mean  $\sigma(\text{C}-\text{C})$  = 0.002 Å; *R* factor = 0.045; *wR* factor = 0.114; data-to-parameter ratio = 17.2.

In the title compound,  $\text{C}_{28}\text{H}_{19}\text{F}_2\text{NO}_4$ , a polysubstituted terphenyl derivative bearing a Michael system, the  $\text{C}=\text{C}$  double bond has an *E* configuration. Two  $\text{C}-\text{H}\cdots\text{F}$  contacts connect molecules into inversion dimers. In addition, a  $\text{C}-\text{H}\cdots\pi$  as well as a  $\text{C}-\text{F}\cdots\pi$  contact can be identified. The shortest centroid-centroid distance between two aromatic rings is 3.9535 (8) Å, between one of the *para*-fluorobenzene rings and its symmetry-generated equivalent.

## Related literature

For the pharmacological importance of terphenyls, see: Liu (2006) and of chalcones, see: Dhar (1981); Dimmock *et al.* (1999); Satyanarayana *et al.* (2004). For our work on the synthesis of different chalcone derivatives, see: Samshuddin *et al.* (2011*a,b*); Fun *et al.* (2010*a,b*); Jasinski *et al.* (2010*a,b*); Baktir *et al.* (2011*a,b*). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



## Experimental

### Crystal data

$\text{C}_{28}\text{H}_{19}\text{F}_2\text{NO}_4$   
 $M_r$  = 471.44  
Monoclinic,  $P2_1/c$   
 $a$  = 23.3751 (7) Å  
 $b$  = 6.9098 (2) Å  
 $c$  = 13.7879 (5) Å  
 $\beta$  = 99.243 (2)°  
 $V$  = 2198.07 (12) Å<sup>3</sup>  
 $Z$  = 4  
Mo  $K\alpha$  radiation  
 $\mu$  = 0.11 mm<sup>-1</sup>  
 $T$  = 200 K  
0.58 × 0.44 × 0.17 mm

### Data collection

Bruker APEXII CCD diffractometer  
37111 measured reflections  
5462 independent reflections  
4899 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.026

### Refinement

$R[F^2 > 2\sigma(F^2)]$  = 0.045  
 $wR(F^2)$  = 0.114  
 $S$  = 1.05  
5462 reflections  
317 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}}$  = 0.32 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.24 e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C11–C16 ring.

| $D-\text{H}\cdots A$                                | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C25}-\text{H25}\cdots\text{F1}^{\text{i}}$   | 0.95         | 2.54               | 3.2165 (17) | 129                  |
| $\text{C33}-\text{H33}\cdots\text{Cg1}^{\text{ii}}$ | 0.95         | 2.91               | 3.4748 (15) | 119                  |
| $\text{C24}-\text{F1}\cdots\text{Cg1}^{\text{iii}}$ | 1.36 (1)     | 3.95 (1)           | 4.8373 (15) | 123 (1)              |

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

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2010); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2465).

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## supporting information

*Acta Cryst.* (2011). E67, o3179–o3180 [https://doi.org/10.1107/S1600536811045806]

**(*E*)-1-(4,4''-Difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-(4-nitrophenyl)-prop-2-en-1-one**

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### S1. Comment

Chalcones constitute an important family of substances belonging to flavonoids, a large group of natural and synthetic products with interesting physicochemical properties, biological activity and structural characteristics. They have been reported to possess many interesting pharmacological activities (Dhar, 1981) including anti-inflammatory, antimicrobial, antifungal, antioxidant, cytotoxic, antitumor and anticancer activities (Dimmock *et al.*, 1999; Satyanarayana *et al.*, 2004). In recent years, it has been reported that some terphenyls exhibit considerable biological activities (*e.g.* being potent anticoagulants, immunosuppressants, antithrombotics, neuroprotectives, specific 5-lipoxygenase inhibitors) and showing cytotoxic activities (Liu, 2006). In view of the pharmacological importance of terphenyls and chalcones, and in continuation of our work on synthesis of various derivatives of 4,4'-difluoro chalcone (Samshuddin *et al.*, 2011a/b, Fun *et al.*, 2010a/b, Jasinski *et al.*, 2010a/b, Baktır *et al.*, 2011a/b), the molecular and crystal structure of the title compound is reported.

The C=C double of the Michael system is (*E*)-configured. The least-squares planes defined by the carbon atoms of the *para*-fluoro phenyl rings of the terphenyl moiety and its central phenyl ring enclose angles of 40.43 (6)° and 43.99 (6)°, respectively. The plane defined by the atoms of the nitro group is tilted by 13.56 (19)° with respect to the plane of the aromatic system it is bonded to (Fig. 1).

In the crystal, C–H⋯F contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the corresponding atoms are observed. These are supported by one of the hydrogen atoms in *ortho* position to a fluorine atom whose symmetry-generated equivalent acts as acceptor for this type of contact. In total, the molecules are connected to centrosymmetric dimers (Fig. 2). In terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the descriptor for the C–H⋯F contacts is  $R_2^2(8)$  on the unitary level. In addition, a C–H⋯ $\pi$  as well as a C–F⋯ $\pi$  contact can be identified. The shortest intercentroid distance between two aromatic systems is apparent between two of the *para*-fluoro phenyl moieties that are also part of the C–H⋯F contacts and was measured at 3.9535 (8) Å. Details about metrical parameters of the intermolecular contacts and their symmetry can be found in Table 1.

The packing of the title compound in the crystal is shown in Figure 3.

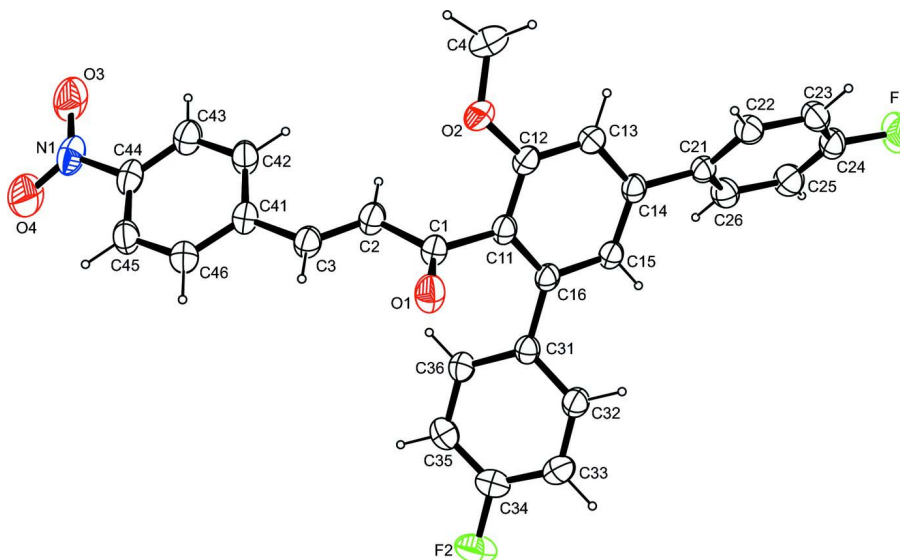
### S2. Experimental

To a mixture of 1-(4,4''-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl) ethanone (3.38 g, 0.01 mol) and 4-nitrobenzaldehyde (1.51 g, 0.01 mol) in 40 ml of ethanol, 10 ml of 10% sodium hydroxide solution was added and stirred at 5–10 °C for 3 h. The precipitate formed was collected by filtration and purified by recrystallization from ethanol (yield: 80%). Single crystals suitable for the X-ray diffraction study were grown from DMF–ethanol (*v:v* 1:1) by slow

evaporation at room temperature.

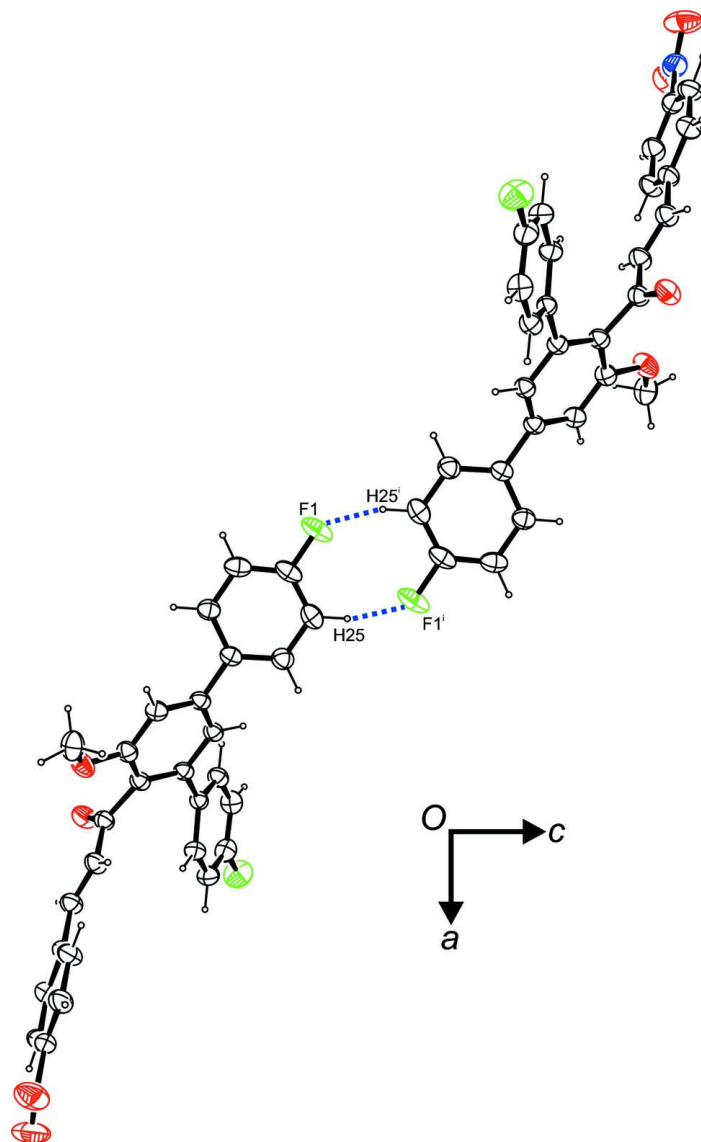
### S3. Refinement

Carbon-bound H atoms were placed in calculated positions (C—H 0.95 Å for aromatic and vinylic carbon atoms, C—H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with  $U(\text{H})$  set to  $1.2U_{\text{eq}}(\text{C})$ . The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density (HFIX 137 in the *SHELX* program suite (Sheldrick, 2008)), with  $U(\text{H})$  set to  $1.5U_{\text{eq}}(\text{C})$ .

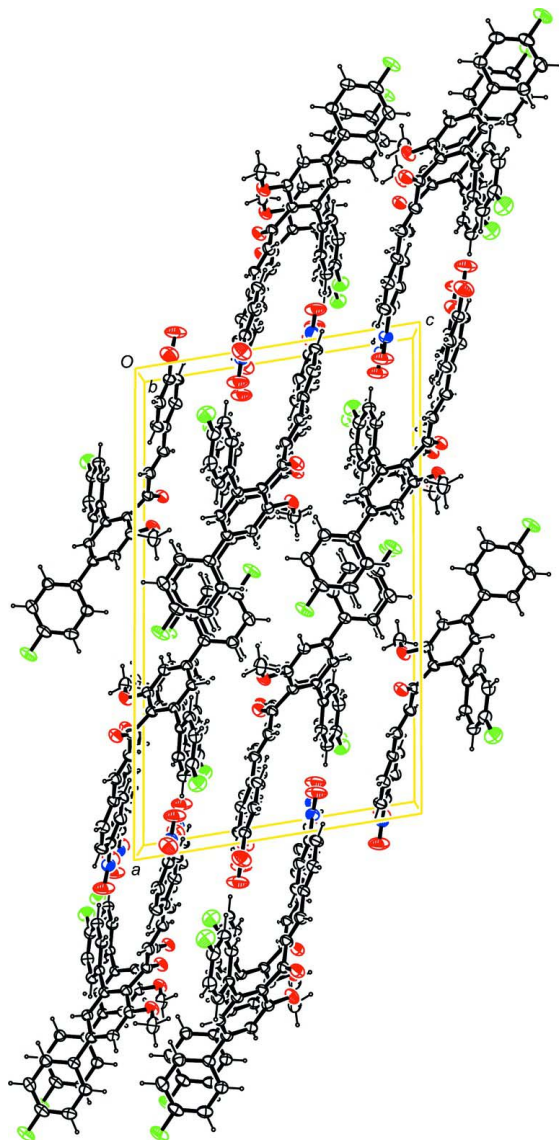


**Figure 1**

The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level).

**Figure 2**

Intermolecular contacts, viewed along  $[0\ 1\ 0]$ . Symmetry operator:  $^i -x + 1, -y + 2, -z$ .



**Figure 3**

Molecular packing of the title compound, viewed along [0 1 0] (anisotropic displacement ellipsoids drawn at 50% probability level).

**(*E*)-1-(4,4''-Difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)- 3-(4-nitrophenyl)prop-2-en-1-one**

*Crystal data*

$C_{28}H_{19}F_2NO_4$

$M_r = 471.44$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1/c$

$a = 23.3751\ (7)\ \text{\AA}$

$b = 6.9098\ (2)\ \text{\AA}$

$c = 13.7879\ (5)\ \text{\AA}$

$\beta = 99.243\ (2)^\circ$

$V = 2198.07\ (12)\ \text{\AA}^3$

$Z = 4$

$F(000) = 976$

$D_x = 1.425\ \text{Mg m}^{-3}$

Melting point: 489 K

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

Cell parameters from 9792 reflections

$\theta = 2.7\text{--}28.4^\circ$

$\mu = 0.11\ \text{mm}^{-1}$

$T = 200\ \text{K}$

Block, yellow

$0.58 \times 0.44 \times 0.17\ \text{mm}$

*Data collection*

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

37111 measured reflections

5462 independent reflections

4899 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 28.4^\circ$ ,  $\theta_{\text{min}} = 1.8^\circ$

$h = -31 \rightarrow 31$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 18$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.114$

$S = 1.05$

5462 reflections

317 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

$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 1.0552P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

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

|     | <i>x</i>     | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| F1  | 0.54918 (4)  | 0.89243 (16) | 0.09405 (8)  | 0.0577 (3)                       |
| F2  | 0.14304 (5)  | 0.02099 (15) | 0.26896 (8)  | 0.0585 (3)                       |
| O1  | 0.25621 (5)  | 0.57681 (15) | 0.56774 (8)  | 0.0428 (2)                       |
| O2  | 0.32555 (5)  | 1.02608 (15) | 0.54905 (8)  | 0.0426 (2)                       |
| O3  | -0.01724 (6) | 1.5042 (2)   | 0.61968 (11) | 0.0651 (4)                       |
| O4  | -0.06990 (5) | 1.2537 (2)   | 0.63545 (13) | 0.0765 (5)                       |
| N1  | -0.02455 (6) | 1.3295 (2)   | 0.62244 (10) | 0.0480 (3)                       |
| C1  | 0.25169 (5)  | 0.72612 (19) | 0.52066 (9)  | 0.0310 (3)                       |
| C2  | 0.20726 (6)  | 0.8734 (2)   | 0.53077 (10) | 0.0346 (3)                       |
| H2  | 0.2095       | 0.9969       | 0.5013       | 0.042*                           |
| C3  | 0.16442 (6)  | 0.8363 (2)   | 0.58026 (10) | 0.0348 (3)                       |
| H3  | 0.1650       | 0.7142       | 0.6121       | 0.042*                           |
| C4  | 0.35123 (8)  | 1.2132 (2)   | 0.55848 (11) | 0.0460 (3)                       |
| H4A | 0.3935       | 1.2006       | 0.5682       | 0.069*                           |
| H4B | 0.3397       | 1.2798       | 0.6151       | 0.069*                           |
| H4C | 0.3382       | 1.2882       | 0.4987       | 0.069*                           |
| C11 | 0.29155 (5)  | 0.76687 (18) | 0.44743 (9)  | 0.0291 (2)                       |
| C12 | 0.33024 (6)  | 0.92135 (18) | 0.46656 (9)  | 0.0314 (3)                       |
| C13 | 0.37199 (5)  | 0.95644 (19) | 0.40751 (9)  | 0.0314 (3)                       |
| H13 | 0.3990       | 1.0591       | 0.4228       | 0.038*                           |
| C14 | 0.37401 (5)  | 0.83985 (18) | 0.32563 (9)  | 0.0287 (2)                       |
| C15 | 0.33356 (5)  | 0.69187 (18) | 0.30343 (9)  | 0.0284 (2)                       |
| H15 | 0.3338       | 0.6170       | 0.2457       | 0.034*                           |
| C16 | 0.29257 (5)  | 0.65097 (17) | 0.36424 (9)  | 0.0274 (2)                       |
| C21 | 0.41994 (5)  | 0.86685 (17) | 0.26396 (9)  | 0.0292 (2)                       |
| C22 | 0.47750 (6)  | 0.89612 (19) | 0.30685 (10) | 0.0338 (3)                       |

|     |             |              |              |            |
|-----|-------------|--------------|--------------|------------|
| H22 | 0.4870      | 0.9087       | 0.3762       | 0.041*     |
| C23 | 0.52104 (6) | 0.9071 (2)   | 0.24956 (11) | 0.0386 (3) |
| H23 | 0.5602      | 0.9277       | 0.2787       | 0.046*     |
| C24 | 0.50613 (6) | 0.8877 (2)   | 0.14999 (11) | 0.0394 (3) |
| C25 | 0.45022 (7) | 0.8625 (2)   | 0.10411 (11) | 0.0410 (3) |
| H25 | 0.4413      | 0.8524       | 0.0346       | 0.049*     |
| C26 | 0.40697 (6) | 0.8522 (2)   | 0.16222 (10) | 0.0356 (3) |
| H26 | 0.3678      | 0.8348       | 0.1319       | 0.043*     |
| C31 | 0.25194 (5) | 0.48643 (18) | 0.33831 (9)  | 0.0278 (2) |
| C32 | 0.27220 (6) | 0.31378 (19) | 0.30383 (10) | 0.0331 (3) |
| H32 | 0.3119      | 0.3038       | 0.2968       | 0.040*     |
| C33 | 0.23598 (6) | 0.1566 (2)   | 0.27957 (10) | 0.0384 (3) |
| H33 | 0.2501      | 0.0399       | 0.2556       | 0.046*     |
| C34 | 0.17884 (6) | 0.1751 (2)   | 0.29133 (11) | 0.0390 (3) |
| C35 | 0.15653 (6) | 0.3426 (2)   | 0.32347 (10) | 0.0381 (3) |
| H35 | 0.1168      | 0.3510       | 0.3300       | 0.046*     |
| C36 | 0.19314 (5) | 0.4991 (2)   | 0.34611 (10) | 0.0329 (3) |
| H36 | 0.1781      | 0.6168       | 0.3672       | 0.039*     |
| C41 | 0.11626 (6) | 0.9660 (2)   | 0.59044 (9)  | 0.0334 (3) |
| C42 | 0.11732 (6) | 1.1622 (2)   | 0.56648 (11) | 0.0388 (3) |
| H42 | 0.1500      | 1.2140       | 0.5423       | 0.047*     |
| C43 | 0.07152 (6) | 1.2819 (2)   | 0.57750 (11) | 0.0407 (3) |
| H43 | 0.0725      | 1.4158       | 0.5623       | 0.049*     |
| C44 | 0.02418 (6) | 1.2015 (2)   | 0.61122 (10) | 0.0378 (3) |
| C45 | 0.02118 (6) | 1.0089 (2)   | 0.63473 (11) | 0.0414 (3) |
| H45 | −0.0122     | 0.9574       | 0.6568       | 0.050*     |
| C46 | 0.06796 (6) | 0.8922 (2)   | 0.62547 (11) | 0.0395 (3) |
| H46 | 0.0672      | 0.7595       | 0.6433       | 0.047*     |

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

|     | $U^{11}$   | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$   | $U^{23}$    |
|-----|------------|-------------|-------------|-------------|------------|-------------|
| F1  | 0.0536 (6) | 0.0593 (6)  | 0.0704 (6)  | 0.0013 (5)  | 0.0407 (5) | 0.0106 (5)  |
| F2  | 0.0576 (6) | 0.0439 (5)  | 0.0721 (7)  | −0.0193 (4) | 0.0047 (5) | −0.0043 (5) |
| O1  | 0.0448 (5) | 0.0411 (5)  | 0.0462 (6)  | 0.0121 (4)  | 0.0186 (4) | 0.0126 (4)  |
| O2  | 0.0513 (6) | 0.0372 (5)  | 0.0438 (5)  | −0.0048 (4) | 0.0208 (5) | −0.0128 (4) |
| O3  | 0.0632 (8) | 0.0562 (8)  | 0.0811 (9)  | 0.0269 (6)  | 0.0276 (7) | 0.0082 (7)  |
| O4  | 0.0345 (6) | 0.0864 (11) | 0.1117 (12) | 0.0079 (6)  | 0.0207 (7) | −0.0264 (9) |
| N1  | 0.0370 (6) | 0.0639 (9)  | 0.0438 (7)  | 0.0154 (6)  | 0.0084 (5) | −0.0087 (6) |
| C1  | 0.0300 (6) | 0.0330 (6)  | 0.0312 (6)  | 0.0043 (5)  | 0.0084 (5) | −0.0003 (5) |
| C2  | 0.0362 (6) | 0.0341 (6)  | 0.0355 (6)  | 0.0077 (5)  | 0.0118 (5) | 0.0020 (5)  |
| C3  | 0.0340 (6) | 0.0346 (7)  | 0.0373 (6)  | 0.0057 (5)  | 0.0102 (5) | 0.0005 (5)  |
| C4  | 0.0619 (9) | 0.0356 (7)  | 0.0392 (7)  | 0.0010 (7)  | 0.0041 (7) | −0.0078 (6) |
| C11 | 0.0281 (5) | 0.0288 (6)  | 0.0316 (6)  | 0.0060 (5)  | 0.0085 (4) | 0.0021 (5)  |
| C12 | 0.0337 (6) | 0.0283 (6)  | 0.0331 (6)  | 0.0051 (5)  | 0.0082 (5) | −0.0022 (5) |
| C13 | 0.0303 (6) | 0.0278 (6)  | 0.0368 (6)  | 0.0015 (5)  | 0.0071 (5) | −0.0007 (5) |
| C14 | 0.0266 (5) | 0.0281 (6)  | 0.0322 (6)  | 0.0056 (4)  | 0.0076 (4) | 0.0032 (5)  |
| C15 | 0.0287 (5) | 0.0277 (6)  | 0.0300 (5)  | 0.0044 (4)  | 0.0076 (4) | −0.0005 (4) |



|     |            |            |            |             |            |             |
|-----|------------|------------|------------|-------------|------------|-------------|
| C16 | 0.0259 (5) | 0.0254 (5) | 0.0313 (6) | 0.0057 (4)  | 0.0063 (4) | 0.0019 (4)  |
| C21 | 0.0293 (6) | 0.0244 (5) | 0.0353 (6) | 0.0026 (4)  | 0.0099 (5) | 0.0021 (5)  |
| C22 | 0.0324 (6) | 0.0314 (6) | 0.0383 (6) | −0.0004 (5) | 0.0078 (5) | 0.0018 (5)  |
| C23 | 0.0304 (6) | 0.0328 (7) | 0.0544 (8) | −0.0012 (5) | 0.0123 (6) | 0.0049 (6)  |
| C24 | 0.0419 (7) | 0.0304 (6) | 0.0522 (8) | 0.0017 (5)  | 0.0264 (6) | 0.0075 (6)  |
| C25 | 0.0490 (8) | 0.0402 (7) | 0.0370 (7) | −0.0005 (6) | 0.0166 (6) | 0.0052 (6)  |
| C26 | 0.0344 (6) | 0.0365 (7) | 0.0367 (7) | 0.0003 (5)  | 0.0082 (5) | 0.0047 (5)  |
| C31 | 0.0278 (5) | 0.0292 (6) | 0.0270 (5) | 0.0034 (4)  | 0.0061 (4) | 0.0025 (4)  |
| C32 | 0.0338 (6) | 0.0314 (6) | 0.0354 (6) | 0.0047 (5)  | 0.0093 (5) | 0.0008 (5)  |
| C33 | 0.0464 (8) | 0.0290 (6) | 0.0400 (7) | 0.0031 (5)  | 0.0074 (6) | −0.0016 (5) |
| C34 | 0.0422 (7) | 0.0347 (7) | 0.0389 (7) | −0.0082 (6) | 0.0026 (5) | 0.0026 (5)  |
| C35 | 0.0297 (6) | 0.0443 (8) | 0.0402 (7) | −0.0026 (5) | 0.0057 (5) | 0.0018 (6)  |
| C36 | 0.0287 (6) | 0.0341 (6) | 0.0364 (6) | 0.0039 (5)  | 0.0071 (5) | −0.0005 (5) |
| C41 | 0.0314 (6) | 0.0382 (7) | 0.0322 (6) | 0.0051 (5)  | 0.0100 (5) | −0.0004 (5) |
| C42 | 0.0365 (7) | 0.0412 (7) | 0.0420 (7) | 0.0062 (6)  | 0.0164 (5) | 0.0044 (6)  |
| C43 | 0.0423 (7) | 0.0414 (7) | 0.0405 (7) | 0.0105 (6)  | 0.0124 (6) | 0.0039 (6)  |
| C44 | 0.0307 (6) | 0.0505 (8) | 0.0324 (6) | 0.0105 (6)  | 0.0055 (5) | −0.0059 (6) |
| C45 | 0.0319 (6) | 0.0518 (9) | 0.0433 (7) | −0.0012 (6) | 0.0142 (5) | −0.0064 (6) |
| C46 | 0.0383 (7) | 0.0389 (7) | 0.0440 (7) | 0.0006 (6)  | 0.0146 (6) | −0.0018 (6) |

*Geometric parameters (Å, °)*

|         |             |         |             |
|---------|-------------|---------|-------------|
| F1—C24  | 1.3630 (15) | C22—C23 | 1.3870 (18) |
| F2—C34  | 1.3586 (16) | C22—H22 | 0.9500      |
| O1—C1   | 1.2145 (16) | C23—C24 | 1.368 (2)   |
| O2—C12  | 1.3673 (15) | C23—H23 | 0.9500      |
| O2—C4   | 1.4230 (18) | C24—C25 | 1.368 (2)   |
| O3—N1   | 1.221 (2)   | C25—C26 | 1.3889 (18) |
| O4—N1   | 1.2209 (19) | C25—H25 | 0.9500      |
| N1—C44  | 1.4698 (18) | C26—H26 | 0.9500      |
| C1—C2   | 1.4764 (17) | C31—C32 | 1.3949 (17) |
| C1—C11  | 1.5063 (16) | C31—C36 | 1.3985 (17) |
| C2—C3   | 1.3243 (18) | C32—C33 | 1.3848 (19) |
| C2—H2   | 0.9500      | C32—H32 | 0.9500      |
| C3—C41  | 1.4630 (17) | C33—C34 | 1.377 (2)   |
| C3—H3   | 0.9500      | C33—H33 | 0.9500      |
| C4—H4A  | 0.9800      | C34—C35 | 1.372 (2)   |
| C4—H4B  | 0.9800      | C35—C36 | 1.3832 (19) |
| C4—H4C  | 0.9800      | C35—H35 | 0.9500      |
| C11—C12 | 1.3965 (18) | C36—H36 | 0.9500      |
| C11—C16 | 1.4022 (17) | C41—C46 | 1.3939 (19) |
| C12—C13 | 1.3890 (17) | C41—C42 | 1.397 (2)   |
| C13—C14 | 1.3939 (17) | C42—C43 | 1.3802 (19) |
| C13—H13 | 0.9500      | C42—H42 | 0.9500      |
| C14—C15 | 1.3930 (17) | C43—C44 | 1.384 (2)   |
| C14—C21 | 1.4844 (16) | C43—H43 | 0.9500      |
| C15—C16 | 1.3997 (16) | C44—C45 | 1.374 (2)   |
| C15—H15 | 0.9500      | C45—C46 | 1.381 (2)   |

|             |             |             |             |
|-------------|-------------|-------------|-------------|
| C16—C31     | 1.4877 (17) | C45—H45     | 0.9500      |
| C21—C26     | 1.3905 (18) | C46—H46     | 0.9500      |
| C21—C22     | 1.3948 (18) |             |             |
| C12—O2—C4   | 117.90 (11) | F1—C24—C23  | 118.25 (14) |
| O4—N1—O3    | 123.89 (14) | F1—C24—C25  | 118.59 (14) |
| O4—N1—C44   | 117.61 (15) | C23—C24—C25 | 123.16 (12) |
| O3—N1—C44   | 118.49 (14) | C24—C25—C26 | 118.00 (13) |
| O1—C1—C2    | 122.49 (12) | C24—C25—H25 | 121.0       |
| O1—C1—C11   | 120.47 (11) | C26—C25—H25 | 121.0       |
| C2—C1—C11   | 117.04 (11) | C25—C26—C21 | 121.16 (13) |
| C3—C2—C1    | 121.13 (13) | C25—C26—H26 | 119.4       |
| C3—C2—H2    | 119.4       | C21—C26—H26 | 119.4       |
| C1—C2—H2    | 119.4       | C32—C31—C36 | 118.13 (12) |
| C2—C3—C41   | 126.04 (13) | C32—C31—C16 | 119.80 (11) |
| C2—C3—H3    | 117.0       | C36—C31—C16 | 122.07 (11) |
| C41—C3—H3   | 117.0       | C33—C32—C31 | 121.69 (12) |
| O2—C4—H4A   | 109.5       | C33—C32—H32 | 119.2       |
| O2—C4—H4B   | 109.5       | C31—C32—H32 | 119.2       |
| H4A—C4—H4B  | 109.5       | C34—C33—C32 | 117.75 (13) |
| O2—C4—H4C   | 109.5       | C34—C33—H33 | 121.1       |
| H4A—C4—H4C  | 109.5       | C32—C33—H33 | 121.1       |
| H4B—C4—H4C  | 109.5       | F2—C34—C35  | 118.84 (13) |
| C12—C11—C16 | 119.70 (11) | F2—C34—C33  | 118.30 (13) |
| C12—C11—C1  | 117.89 (11) | C35—C34—C33 | 122.85 (13) |
| C16—C11—C1  | 122.35 (11) | C34—C35—C36 | 118.63 (12) |
| O2—C12—C13  | 123.57 (12) | C34—C35—H35 | 120.7       |
| O2—C12—C11  | 115.19 (11) | C36—C35—H35 | 120.7       |
| C13—C12—C11 | 121.16 (11) | C35—C36—C31 | 120.91 (12) |
| C12—C13—C14 | 119.49 (12) | C35—C36—H36 | 119.5       |
| C12—C13—H13 | 120.3       | C31—C36—H36 | 119.5       |
| C14—C13—H13 | 120.3       | C46—C41—C42 | 118.89 (12) |
| C15—C14—C13 | 119.48 (11) | C46—C41—C3  | 119.20 (13) |
| C15—C14—C21 | 119.62 (11) | C42—C41—C3  | 121.91 (12) |
| C13—C14—C21 | 120.87 (11) | C43—C42—C41 | 120.79 (13) |
| C14—C15—C16 | 121.49 (11) | C43—C42—H42 | 119.6       |
| C14—C15—H15 | 119.3       | C41—C42—H42 | 119.6       |
| C16—C15—H15 | 119.3       | C42—C43—C44 | 118.22 (14) |
| C15—C16—C11 | 118.55 (11) | C42—C43—H43 | 120.9       |
| C15—C16—C31 | 118.84 (11) | C44—C43—H43 | 120.9       |
| C11—C16—C31 | 122.61 (11) | C45—C44—C43 | 122.82 (13) |
| C26—C21—C22 | 118.52 (12) | C45—C44—N1  | 119.22 (13) |
| C26—C21—C14 | 120.55 (11) | C43—C44—N1  | 117.96 (14) |
| C22—C21—C14 | 120.83 (11) | C44—C45—C46 | 118.19 (13) |
| C23—C22—C21 | 120.84 (13) | C44—C45—H45 | 120.9       |
| C23—C22—H22 | 119.6       | C46—C45—H45 | 120.9       |
| C21—C22—H22 | 119.6       | C45—C46—C41 | 121.07 (14) |
| C24—C23—C22 | 118.31 (13) | C45—C46—H46 | 119.5       |

|                 |              |                 |              |
|-----------------|--------------|-----------------|--------------|
| C24—C23—H23     | 120.8        | C41—C46—H46     | 119.5        |
| C22—C23—H23     | 120.8        |                 |              |
| O1—C1—C2—C3     | −10.8 (2)    | C23—C24—C25—C26 | −1.4 (2)     |
| C11—C1—C2—C3    | 168.41 (13)  | C24—C25—C26—C21 | 0.0 (2)      |
| C1—C2—C3—C41    | −176.23 (13) | C22—C21—C26—C25 | 1.2 (2)      |
| O1—C1—C11—C12   | −114.27 (15) | C14—C21—C26—C25 | −175.06 (12) |
| C2—C1—C11—C12   | 66.55 (15)   | C15—C16—C31—C32 | 41.00 (16)   |
| O1—C1—C11—C16   | 62.98 (18)   | C11—C16—C31—C32 | −138.88 (12) |
| C2—C1—C11—C16   | −116.20 (13) | C15—C16—C31—C36 | −138.17 (12) |
| C4—O2—C12—C13   | 20.49 (19)   | C11—C16—C31—C36 | 41.95 (17)   |
| C4—O2—C12—C11   | −162.74 (12) | C36—C31—C32—C33 | −1.30 (19)   |
| C16—C11—C12—O2  | 179.64 (11)  | C16—C31—C32—C33 | 179.50 (12)  |
| C1—C11—C12—O2   | −3.03 (17)   | C31—C32—C33—C34 | −0.5 (2)     |
| C16—C11—C12—C13 | −3.51 (18)   | C32—C33—C34—F2  | −179.18 (12) |
| C1—C11—C12—C13  | 173.82 (11)  | C32—C33—C34—C35 | 1.6 (2)      |
| O2—C12—C13—C14  | 178.94 (12)  | F2—C34—C35—C36  | −179.97 (12) |
| C11—C12—C13—C14 | 2.35 (19)    | C33—C34—C35—C36 | −0.7 (2)     |
| C12—C13—C14—C15 | 1.00 (18)    | C34—C35—C36—C31 | −1.2 (2)     |
| C12—C13—C14—C21 | −176.80 (11) | C32—C31—C36—C35 | 2.18 (19)    |
| C13—C14—C15—C16 | −3.23 (18)   | C16—C31—C36—C35 | −178.64 (12) |
| C21—C14—C15—C16 | 174.59 (11)  | C2—C3—C41—C46   | 165.67 (14)  |
| C14—C15—C16—C11 | 2.07 (17)    | C2—C3—C41—C42   | −14.6 (2)    |
| C14—C15—C16—C31 | −177.81 (11) | C46—C41—C42—C43 | 0.2 (2)      |
| C12—C11—C16—C15 | 1.28 (17)    | C3—C41—C42—C43  | −179.47 (13) |
| C1—C11—C16—C15  | −175.93 (11) | C41—C42—C43—C44 | −1.1 (2)     |
| C12—C11—C16—C31 | −178.84 (11) | C42—C43—C44—C45 | 0.5 (2)      |
| C1—C11—C16—C31  | 3.96 (18)    | C42—C43—C44—N1  | −179.77 (13) |
| C15—C14—C21—C26 | 41.97 (17)   | O4—N1—C44—C45   | −12.8 (2)    |
| C13—C14—C21—C26 | −140.23 (13) | O3—N1—C44—C45   | 166.21 (15)  |
| C15—C14—C21—C22 | −134.25 (13) | O4—N1—C44—C43   | 167.52 (15)  |
| C13—C14—C21—C22 | 43.55 (17)   | O3—N1—C44—C43   | −13.5 (2)    |
| C26—C21—C22—C23 | −1.07 (19)   | C43—C44—C45—C46 | 1.0 (2)      |
| C14—C21—C22—C23 | 175.23 (12)  | N1—C44—C45—C46  | −178.73 (13) |
| C21—C22—C23—C24 | −0.3 (2)     | C44—C45—C46—C41 | −1.9 (2)     |
| C22—C23—C24—F1  | −177.96 (12) | C42—C41—C46—C45 | 1.3 (2)      |
| C22—C23—C24—C25 | 1.6 (2)      | C3—C41—C46—C45  | −178.97 (13) |
| F1—C24—C25—C26  | 178.13 (13)  |                 |              |

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 is the centroid of the C11—C16 ring.

| $D\cdots H\cdots A$                | $D\cdots H$ | $H\cdots A$ | $D\cdots A$ | $D\cdots H\cdots A$ |
|------------------------------------|-------------|-------------|-------------|---------------------|
| C25—H25 $\cdots$ F1 <sup>i</sup>   | 0.95        | 2.54        | 3.2165 (17) | 129                 |
| C33—H33 $\cdots$ Cg1 <sup>ii</sup> | 0.95        | 2.91        | 3.4748 (15) | 119                 |
| C24—F1 $\cdots$ Cg1 <sup>iii</sup> | 1.36 (1)    | 3.95 (1)    | 4.8373 (15) | 123 (1)             |

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