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## Structure Reports

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# (*E,E*)-2,5-Bis(4-*tert*-butylbenzylidene)-cyclopentanone

 Jian Wei,<sup>a,b</sup> Guang Liang,<sup>c</sup> Yuhong Gai<sup>c</sup> and Jingmei Lu<sup>a,b\*</sup>

<sup>a</sup>College of Life Science, Northeast Normal University, Changchun, Jilin Province 130024, People's Republic of China, <sup>b</sup>College of Life Science, Changchun Normal University, Changchun, Jilin Province 130017, People's Republic of China, and <sup>c</sup>College of Agriculture, Jilin Agricultural University, Changchun, Jilin Province 130118, People's Republic of China

Correspondence e-mail: lujingmei2008@hotmail.com

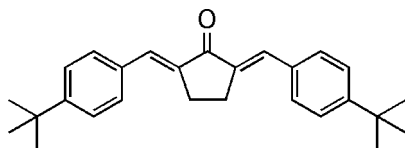
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.069;  $wR$  factor = 0.181; data-to-parameter ratio = 16.0.

The asymmetric unit of the title compound,  $\text{C}_{27}\text{H}_{32}\text{O}$ , contains two and a half molecules. In the crystal structure, one of the molecules lies on a crystallographic twofold rotation axis. The dihedral angles between the benzene rings are 12.17 (6), 16.29 (11) and 51.24 (8)° for the three molecules. The dihedral angles between the benzene rings of each molecule in the asymmetric unit are 12.17 (6) and 16.29 (11)°

## Related literature

For related literature, see: Began *et al.* (1999); Kawamori *et al.* (1999); Liang *et al.* (2008); Liang, Tian *et al.* (2007); Liang, Yang *et al.* (2007); Livingstone & Walker (2003); Poorichaya *et al.* (2007); Saiah (2008).



## Experimental

## Crystal data

$\text{C}_{27}\text{H}_{32}\text{O}$   
 $M_r = 372.53$   
 Monoclinic,  $C2/c$   
 $a = 41.246$  (7) Å  
 $b = 6.2930$  (10) Å  
 $c = 43.001$  (7) Å  
 $\beta = 94.243$  (4)°  
 $V = 11131$  (3) Å<sup>3</sup>  
 $Z = 20$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.07$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.50 \times 0.41 \times 0.18$  mm

## Data collection

Bruker SMART CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2002)  
 $T_{\min} = 0.761$ ,  $T_{\max} = 1.000$   
 (expected range = 0.752–0.989)  
 28046 measured reflections  
 10373 independent reflections  
 4318 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.128$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$   
 $wR(F^2) = 0.180$   
 $S = 0.86$   
 10373 reflections  
 648 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.18$  e Å<sup>-3</sup>

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; 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.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2667).

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**supplementary materials**

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## (*E,E*)-2,5-Bis(4-*tert*-butylbenzylidene)cyclopentanone

J. Wei, G. Liang, Y. Gai and J. Lu

### Comment

The title compound, (2*E*,5*E*)-2,5-bis(4-*tert*-butylbenzylidene)cyclopentanone (I), is one of the monocarbonyl analogues of curcumin designed and synthesized by our group. Curcumin has been found to possess a variety of pharmaceutical applications, for example, inhibiting the mutations and the formation of tumors, antioxidation, anti-inflammation, anti-virus, and decreasing total cholesterol and LDL cholesterol level (Began *et al.*, 1999; Kawamori *et al.*, 1999; Poorichaya *et al.*, 2007). In previous studies, curcumin was found to be able to effect the activity of enzyme 11-beta-hydroxysteroid dehydrogenase type-1 (11-beta-HSD1), which catalyzes glucocorticoid conversion between active form (corticosterone in rodents) and inactive form (dehydrocortisone in rodents) and then regulates downstream target genes leading to increased hepatic glucose production and lipolysis in adipose tissue (Livingstone & Walker, 2003; Saiah, 2008). According to the structural disadvantages of curcumin responsible for its weak pharmacokinetic profiles, a series of mono-carbonyl analogues were designed and synthesized (Liang *et al.*, 2008), and their 11-beta-HSD1-regulating activities *in vitro* were evaluated using intact Leydig cells. The title compound (I) showed an 11-beta-HSD1-regulating bioactivity with ED<sub>50</sub> = 3029 nM on 11-beta-HSD1 oxidase and IC<sub>50</sub> = 12278 nM against reductase of this enzyme, comparable to curcumin performs on 11-beta-HSD1 regulation (data not shown). Among these derivatives, some crystal structures are reported (Liang, Tian *et al.*, 2007; Liang, Yang *et al.*, 2007). In the present paper, we describe the crystal structure of compound (I). The geometrical parameters of title compound (I) are normal and there are three independent molecules. The dihedral angles between two benzene rings in each are 12.17 (6)°, 16.29 (11)°, 51.24 (8)°, respectively.

### Experimental

To a solution of 15 mmol 4-*tert*-butylbenzaldehyde in MeOH (10 ml) was added 7.5 mmol cyclopentanone. The solution was stirred at room temperature for 20 min, followed by added dropwise 2.0 mol/L NaOCH<sub>3</sub> (3.75 ml, 7.5 mmol) in methanol. The mixture was stirred at room temperature for 1.5 h and monitored with TLC. When the reaction was complete, the residue was poured into saturated NH<sub>4</sub>Cl solution and filtered. The precipitate was washed and purified by chromatography over silica gel using CH<sub>2</sub>Cl<sub>2</sub> / CH<sub>3</sub>OH as the eluent to afford the pure product (yield: 66.9%). Single crystals of (I) were grown in a CH<sub>2</sub>Cl<sub>2</sub>—CH<sub>3</sub>CH<sub>2</sub>OH mixture (5:1 *v/v*) by slow evaporation (mp 452–454 K). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.35 (18H, s, CH<sub>3</sub>), 3.11 (4H, s, CH<sub>2</sub>—CH<sub>2</sub>), 7.47 (4H, d, J=8.4 Hz, Ar—H(2,6)), 7.56 (4H, d, J=8.4 Hz, Ar—H(3,5)), 7.59 (2H, s, CH). ESI-MS *m/z*: 373.69 (*M*+1), calcd for C<sub>27</sub>H<sub>32</sub>O: 372.53.

### Refinement

The H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ .

## Figures

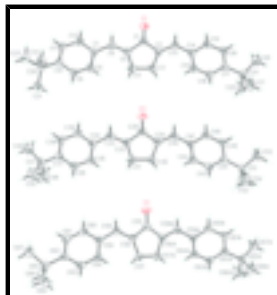


Fig. 1. The three independent molecules of (I), showing 30% displacement ellipsoids for the non-hydrogen atoms [symmetry code: (A)  $-x+1, y, -z+1/2$ ].



Fig. 2. Reaction scheme.

## (E,E)-2,5-Bis(4-*tert*-butylbenzylidene)cyclopentanone

### Crystal data

$C_{27}H_{32}O$

$M_r = 372.53$

Monoclinic,  $C2/c$

Hall symbol:  $-C 2yc$

$a = 41.246 (7) \text{ \AA}$

$b = 6.2930 (10) \text{ \AA}$

$c = 43.001 (7) \text{ \AA}$

$\beta = 94.243 (4)^\circ$

$V = 11131 (3) \text{ \AA}^3$

$Z = 20$

$F_{000} = 4040$

$D_x = 1.111 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2156 reflections

$\theta = 5.3\text{--}40.8^\circ$

$\mu = 0.07 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism, yellow

$0.50 \times 0.41 \times 0.18 \text{ mm}$

### Data collection

Bruker SMART CCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2) \text{ K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2002)

$T_{\min} = 0.761, T_{\max} = 1.000$

28046 measured reflections

10373 independent reflections

4318 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.128$

$\theta_{\max} = 25.5^\circ$

$\theta_{\min} = 1.9^\circ$

$h = -49 \rightarrow 36$

$k = -7 \rightarrow 7$

$l = -48 \rightarrow 52$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

|  |   |
|--|---|
| $R[F^2 > 2\sigma(F^2)] = 0.068$                                | $w = 1/[\sigma^2(F_o^2) + (0.0573P)^2]$   |
| $wR(F^2) = 0.180$  | where $P = (F_o^2 + 2F_c^2)/3$  |
| $S = 0.86$   | $(\Delta/\sigma)_{\max} = 0.011$  |
| 10373 reflections  | $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$   |
| 648 parameters   | $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$  |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 2008),<br>$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Secondary atom site location: difference Fourier map           | Extinction coefficient: 0.00016 (4)   |

### 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 ( $\text{\AA}^2$ )

|     | $x$         | $y$        | $z$         | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|------------|-------------|----------------------------------|
| O1  | 0.29393 (5) | 0.4048 (3) | 0.07533 (6) | 0.0780 (7)                       |
| O2  | 0.39495 (5) | 0.5016 (3) | 0.17171 (6) | 0.0781 (7)                       |
| O3  | 0.5000      | 0.4826 (5) | 0.2500      | 0.150 (2)                        |
| C1  | 0.29711 (7) | 0.5803 (5) | 0.06428 (7) | 0.0541 (8)                       |
| C2  | 0.27036 (7) | 0.7186 (5) | 0.05130 (7) | 0.0518 (8)                       |
| C3  | 0.28460 (7) | 0.9189 (5) | 0.03993 (7) | 0.0564 (8)                       |
| H3A | 0.2770      | 1.0396     | 0.0514      | 0.068*                           |
| H3B | 0.2782      | 0.9391     | 0.0180      | 0.068*                           |
| C4  | 0.32163 (7) | 0.9001 (5) | 0.04504 (7) | 0.0609 (9)                       |
| H4A | 0.3314      | 0.9010     | 0.0252      | 0.073*                           |
| H4B | 0.3305      | 1.0176     | 0.0576      | 0.073*                           |
| C5  | 0.32819 (7) | 0.6937 (4) | 0.06157 (7) | 0.0498 (8)                       |
| C6  | 0.35604 (7) | 0.6012 (5) | 0.07231 (7) | 0.0560 (8)                       |
| H6  | 0.3533      | 0.4710     | 0.0820      | 0.067*                           |
| C7  | 0.38955 (7) | 0.6671 (5) | 0.07152 (7) | 0.0504 (8)                       |
| C8  | 0.39985 (8) | 0.8547 (5) | 0.05871 (8) | 0.0693 (10)                      |
| H8  | 0.3844      | 0.9530     | 0.0512      | 0.083*                           |
| C9  | 0.43234 (8) | 0.9011 (5) | 0.05671 (7) | 0.0662 (10)                      |
| H9  | 0.4380      | 1.0308     | 0.0483      | 0.079*                           |
| C10 | 0.45680 (7) | 0.7603 (5) | 0.06689 (7) | 0.0501 (8)                       |
| C11 | 0.44633 (8) | 0.5780 (5) | 0.08082 (8) | 0.0676 (10)                      |
| H11 | 0.4618      | 0.4827     | 0.0893      | 0.081*                           |

## supplementary materials

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|      |             |            |              |             |
|------|-------------|------------|--------------|-------------|
| C12  | 0.41393 (8) | 0.5305 (5) | 0.08281 (8)  | 0.0669 (10) |
| H12  | 0.4083      | 0.4032     | 0.0920       | 0.080*      |
| C13  | 0.23963 (7) | 0.6558 (5) | 0.05233 (7)  | 0.0569 (9)  |
| H13  | 0.2373      | 0.5182     | 0.0597       | 0.068*      |
| C14  | 0.20898 (7) | 0.7645 (5) | 0.04394 (7)  | 0.0521 (8)  |
| C15  | 0.20580 (8) | 0.9549 (5) | 0.02837 (8)  | 0.0651 (9)  |
| H15  | 0.2242      | 1.0205     | 0.0216       | 0.078*      |
| C16  | 0.17589 (8) | 1.0512 (5) | 0.02251 (8)  | 0.0691 (10) |
| H16  | 0.1746      | 1.1799     | 0.0119       | 0.083*      |
| C17  | 0.14765 (7) | 0.9602 (5) | 0.03214 (7)  | 0.0516 (8)  |
| C18  | 0.15075 (8) | 0.7686 (5) | 0.04666 (8)  | 0.0693 (10) |
| H18  | 0.1322      | 0.7016     | 0.0530       | 0.083*      |
| C19  | 0.18059 (8) | 0.6705 (5) | 0.05234 (8)  | 0.0683 (10) |
| H19  | 0.1816      | 0.5382     | 0.0620       | 0.082*      |
| C20  | 0.49193 (7) | 0.8047 (5) | 0.06146 (7)  | 0.0586 (9)  |
| C21  | 0.50018 (8) | 1.0402 (6) | 0.06386 (8)  | 0.0873 (12) |
| H21A | 0.4866      | 1.1179     | 0.0487       | 0.121*      |
| H21B | 0.5226      | 1.0609     | 0.0600       | 0.121*      |
| H21C | 0.4965      | 1.0905     | 0.0844       | 0.121*      |
| C22  | 0.49753 (8) | 0.7297 (6) | 0.02807 (7)  | 0.0924 (13) |
| H22A | 0.4935      | 0.5797     | 0.0264       | 0.129*      |
| H22B | 0.5196      | 0.7589     | 0.0237       | 0.129*      |
| H22C | 0.4830      | 0.8039     | 0.0134       | 0.129*      |
| C23  | 0.51543 (7) | 0.6833 (5) | 0.08448 (8)  | 0.0813 (11) |
| H23A | 0.5115      | 0.7228     | 0.1054       | 0.112*      |
| H23B | 0.5374      | 0.7180     | 0.0806       | 0.112*      |
| H23C | 0.5121      | 0.5333     | 0.0818       | 0.112*      |
| C24  | 0.11478 (7) | 1.0750 (5) | 0.02828 (7)  | 0.0600 (9)  |
| C25  | 0.11316 (9) | 1.2364 (6) | 0.00167 (8)  | 0.0994 (13) |
| H25A | 0.0917      | 1.2959     | -0.0009      | 0.129*      |
| H25B | 0.1181      | 1.1670     | -0.0173      | 0.129*      |
| H25C | 0.1286      | 1.3477     | 0.0065       | 0.129*      |
| C26  | 0.08709 (8) | 0.9174 (6) | 0.02227 (10) | 0.1145 (16) |
| H26A | 0.0856      | 0.8292     | 0.0403       | 0.132*      |
| H26B | 0.0912      | 0.8303     | 0.0046       | 0.132*      |
| H26C | 0.0671      | 0.9933     | 0.0180       | 0.132*      |
| C27  | 0.10989 (8) | 1.1952 (5) | 0.05843 (8)  | 0.0823 (11) |
| H27A | 0.1092      | 1.0959     | 0.0753       | 0.113*      |
| H27B | 0.0898      | 1.2729     | 0.0562       | 0.113*      |
| H27C | 0.1276      | 1.2922     | 0.0628       | 0.113*      |
| C28  | 0.39418 (8) | 0.6813 (5) | 0.16108 (7)  | 0.0569 (9)  |
| C29  | 0.36451 (8) | 0.8006 (5) | 0.14964 (7)  | 0.0530 (8)  |
| C30  | 0.37431 (7) | 1.0141 (5) | 0.13873 (7)  | 0.0610 (9)  |
| H30A | 0.3645      | 1.1246     | 0.1507       | 0.073*      |
| H30B | 0.3673      | 1.0331     | 0.1169       | 0.073*      |
| C31  | 0.41147 (7) | 1.0257 (5) | 0.14342 (7)  | 0.0598 (9)  |
| H31A | 0.4208      | 1.0478     | 0.1236       | 0.072*      |
| H31B | 0.4180      | 1.1422     | 0.1572       | 0.072*      |
| C32  | 0.42270 (8) | 0.8190 (5) | 0.15740 (7)  | 0.0525 (8)  |

|      |             |            |              |             |
|------|-------------|------------|--------------|-------------|
| C33  | 0.45271 (8) | 0.7498 (5) | 0.16590 (7)  | 0.0591 (9)  |
| H33  | 0.4536      | 0.6132     | 0.1742       | 0.071*      |
| C34  | 0.48430 (8) | 0.8524 (5) | 0.16440 (7)  | 0.0572 (9)  |
| C35  | 0.48909 (8) | 1.0564 (5) | 0.15346 (8)  | 0.0651 (9)  |
| H35  | 0.4712      | 1.1402     | 0.1474       | 0.078*      |
| C36  | 0.51997 (9) | 1.1379 (5) | 0.15140 (8)  | 0.0693 (10) |
| H36  | 0.5221      | 1.2766     | 0.1444       | 0.083*      |
| C37  | 0.54771 (8) | 1.0213 (6) | 0.15933 (7)  | 0.0596 (9)  |
| C38  | 0.54279 (8) | 0.8225 (6) | 0.17108 (8)  | 0.0700 (10) |
| H38  | 0.5608      | 0.7416     | 0.1778       | 0.084*      |
| C39  | 0.51227 (8) | 0.7368 (5) | 0.17340 (7)  | 0.0656 (9)  |
| H39  | 0.5103      | 0.5996     | 0.1811       | 0.079*      |
| C40  | 0.33520 (8) | 0.7134 (5) | 0.15129 (7)  | 0.0575 (9)  |
| H40  | 0.3354      | 0.5726     | 0.1579       | 0.069*      |
| C41  | 0.30296 (8) | 0.8035 (5) | 0.14442 (7)  | 0.0542 (8)  |
| C42  | 0.29618 (8) | 0.9955 (5) | 0.13020 (7)  | 0.0650 (9)  |
| H42  | 0.3131      | 1.0715     | 0.1223       | 0.078*      |
| C43  | 0.26539 (8) | 1.0797 (5) | 0.12713 (7)  | 0.0621 (9)  |
| H43  | 0.2621      | 1.2104     | 0.1173       | 0.075*      |
| C44  | 0.23909 (7) | 0.9745 (5) | 0.13833 (6)  | 0.0487 (8)  |
| C45  | 0.24561 (8) | 0.7785 (5) | 0.15148 (8)  | 0.0692 (10) |
| H45  | 0.2286      | 0.7013     | 0.1589       | 0.083*      |
| C46  | 0.27610 (8) | 0.6926 (5) | 0.15411 (8)  | 0.0697 (10) |
| H46  | 0.2791      | 0.5573     | 0.1625       | 0.084*      |
| C47  | 0.58159 (8) | 1.1126 (6) | 0.15588 (8)  | 0.0694 (10) |
| C48  | 0.58196 (9) | 1.2481 (8) | 0.12684 (10) | 0.116 (2)   |
| H48A | 0.5704      | 1.3778     | 0.1298       | 0.133*      |
| H48B | 0.5717      | 1.1721     | 0.1094       | 0.133*      |
| H48C | 0.6040      | 1.2803     | 0.1229       | 0.133*      |
| C49  | 0.60698 (9) | 0.9422 (7) | 0.15397 (13) | 0.115 (2)   |
| H49A | 0.6092      | 0.8657     | 0.1733       | 0.132*      |
| H49B | 0.6274      | 1.0063     | 0.1500       | 0.132*      |
| H49C | 0.6005      | 0.8460     | 0.1373       | 0.132*      |
| C50  | 0.59097 (9) | 1.2498 (6) | 0.18397 (10) | 0.1174 (16) |
| H50A | 0.5930      | 1.1627     | 0.2023       | 0.136*      |
| H50B | 0.5745      | 1.3556     | 0.1861       | 0.136*      |
| H50C | 0.6114      | 1.3181     | 0.1813       | 0.136*      |
| C51  | 0.20573 (7) | 1.0771 (5) | 0.13858 (7)  | 0.0539 (8)  |
| C52  | 0.19933 (8) | 1.2366 (5) | 0.11190 (8)  | 0.0842 (11) |
| H52A | 0.2155      | 1.3465     | 0.1136       | 0.116*      |
| H52B | 0.1782      | 1.2984     | 0.1131       | 0.116*      |
| H52C | 0.2003      | 1.1649     | 0.0923       | 0.116*      |
| C53  | 0.17837 (8) | 0.9136 (6) | 0.13635 (9)  | 0.0906 (12) |
| H53A | 0.1798      | 0.8295     | 0.1179       | 0.126*      |
| H53B | 0.1578      | 0.9854     | 0.1354       | 0.126*      |
| H53C | 0.1803      | 0.8230     | 0.1543       | 0.126*      |
| C54  | 0.20421 (8) | 1.1991 (5) | 0.16945 (8)  | 0.0819 (11) |
| H54A | 0.2071      | 1.1016     | 0.1866       | 0.113*      |
| H54B | 0.1835      | 1.2676     | 0.1699       | 0.113*      |

## supplementary materials

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|      |             |            |              |             |
|------|-------------|------------|--------------|-------------|
| H54C | 0.2211      | 1.3041     | 0.1711       | 0.113*      |
| C55  | 0.5000      | 0.6744 (8) | 0.2500       | 0.0757 (15) |
| C56  | 0.47090 (8) | 0.8110 (5) | 0.24588 (7)  | 0.0558 (8)  |
| C57  | 0.48172 (6) | 1.0344 (4) | 0.24519 (7)  | 0.0578 (9)  |
| H57A | 0.4701      | 1.1193     | 0.2596       | 0.069*      |
| H57B | 0.4776      | 1.0929     | 0.2244       | 0.069*      |
| C58  | 0.44126 (8) | 0.7242 (5) | 0.24475 (7)  | 0.0621 (9)  |
| H58  | 0.4408      | 0.5766     | 0.2457       | 0.075*      |
| C59  | 0.40947 (8) | 0.8272 (5) | 0.24219 (7)  | 0.0541 (8)  |
| C60  | 0.38304 (8) | 0.7181 (5) | 0.25263 (8)  | 0.0692 (10) |
| H60  | 0.3861      | 0.5811     | 0.2604       | 0.083*      |
| C61  | 0.35248 (8) | 0.8073 (5) | 0.25171 (8)  | 0.0694 (10) |
| H61  | 0.3356      | 0.7305     | 0.2595       | 0.083*      |
| C62  | 0.34621 (7) | 1.0063 (5) | 0.23968 (7)  | 0.0508 (8)  |
| C63  | 0.37253 (8) | 1.1119 (5) | 0.22831 (7)  | 0.0576 (9)  |
| H63  | 0.3692      | 1.2456     | 0.2194       | 0.069*      |
| C64  | 0.40330 (8) | 1.0253 (5) | 0.22976 (7)  | 0.0570 (9)  |
| H64  | 0.4202      | 1.1027     | 0.2222       | 0.068*      |
| C65  | 0.31284 (8) | 1.1083 (5) | 0.24011 (7)  | 0.0554 (8)  |
| C66  | 0.30633 (8) | 1.2711 (6) | 0.21395 (8)  | 0.0984 (13) |
| H66A | 0.3220      | 1.3839     | 0.2164       | 0.128*      |
| H66B | 0.2848      | 1.3282     | 0.2148       | 0.128*      |
| H66C | 0.3081      | 1.2033     | 0.1942       | 0.128*      |
| C67  | 0.28577 (8) | 0.9443 (6) | 0.23752 (10) | 0.1012 (14) |
| H67A | 0.2864      | 0.8687     | 0.2182       | 0.132*      |
| H67B | 0.2652      | 1.0144     | 0.2381       | 0.132*      |
| H67C | 0.2886      | 0.8461     | 0.2546       | 0.132*      |
| C68  | 0.31128 (8) | 1.2240 (6) | 0.27122 (8)  | 0.0887 (12) |
| H68A | 0.3141      | 1.1236     | 0.2880       | 0.123*      |
| H68B | 0.2905      | 1.2922     | 0.2719       | 0.123*      |
| H68C | 0.3282      | 1.3289     | 0.2733       | 0.123*      |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| O1  | 0.0684 (16) | 0.0598 (15) | 0.107 (2)   | -0.0006 (13) | 0.0149 (13) | 0.0237 (15)  |
| O2  | 0.0815 (17) | 0.0480 (14) | 0.106 (2)   | 0.0022 (13)  | 0.0130 (14) | 0.0113 (14)  |
| O3  | 0.081 (3)   | 0.036 (2)   | 0.332 (7)   | 0.000        | 0.016 (3)   | 0.000        |
| C1  | 0.059 (2)   | 0.050 (2)   | 0.055 (2)   | 0.0021 (18)  | 0.0105 (16) | 0.0025 (17)  |
| C2  | 0.054 (2)   | 0.053 (2)   | 0.049 (2)   | 0.0001 (18)  | 0.0108 (15) | -0.0013 (16) |
| C3  | 0.054 (2)   | 0.058 (2)   | 0.058 (2)   | -0.0018 (17) | 0.0104 (16) | 0.0071 (16)  |
| C4  | 0.057 (2)   | 0.062 (2)   | 0.064 (2)   | 0.0006 (17)  | 0.0066 (16) | 0.0128 (18)  |
| C5  | 0.051 (2)   | 0.051 (2)   | 0.0484 (19) | 0.0035 (17)  | 0.0133 (15) | 0.0062 (15)  |
| C6  | 0.064 (2)   | 0.057 (2)   | 0.048 (2)   | 0.0030 (18)  | 0.0105 (16) | 0.0040 (16)  |
| C7  | 0.054 (2)   | 0.053 (2)   | 0.0443 (19) | 0.0046 (17)  | 0.0059 (15) | 0.0060 (15)  |
| C8  | 0.053 (2)   | 0.069 (2)   | 0.086 (3)   | 0.0052 (19)  | 0.0015 (18) | 0.022 (2)    |
| C9  | 0.057 (2)   | 0.066 (2)   | 0.076 (3)   | -0.0001 (19) | 0.0036 (18) | 0.0237 (19)  |
| C10 | 0.052 (2)   | 0.059 (2)   | 0.0396 (18) | 0.0071 (17)  | 0.0036 (14) | -0.0024 (16) |

## supplementary materials

|     |           |             |             |              |              |              |
|-----|-----------|-------------|-------------|--------------|--------------|--------------|
| C11 | 0.056 (2) | 0.070 (2)   | 0.077 (3)   | 0.0150 (19)  | 0.0045 (18)  | 0.017 (2)    |
| C12 | 0.059 (2) | 0.060 (2)   | 0.082 (3)   | 0.0062 (19)  | 0.0071 (19)  | 0.0227 (19)  |
| C13 | 0.055 (2) | 0.055 (2)   | 0.062 (2)   | 0.0012 (18)  | 0.0118 (16)  | 0.0019 (16)  |
| C14 | 0.054 (2) | 0.053 (2)   | 0.049 (2)   | -0.0008 (17) | 0.0067 (15)  | 0.0050 (16)  |
| C15 | 0.053 (2) | 0.070 (2)   | 0.075 (3)   | -0.0006 (19) | 0.0177 (17)  | 0.0171 (19)  |
| C16 | 0.063 (2) | 0.070 (2)   | 0.075 (3)   | 0.005 (2)    | 0.0118 (19)  | 0.0223 (19)  |
| C17 | 0.054 (2) | 0.056 (2)   | 0.0454 (19) | 0.0002 (17)  | 0.0033 (15)  | 0.0007 (16)  |
| C18 | 0.055 (2) | 0.076 (3)   | 0.077 (3)   | -0.0073 (19) | 0.0105 (18)  | 0.024 (2)    |
| C19 | 0.055 (2) | 0.064 (2)   | 0.086 (3)   | -0.0021 (19) | 0.0052 (19)  | 0.0267 (19)  |
| C20 | 0.053 (2) | 0.075 (2)   | 0.048 (2)   | 0.0003 (19)  | 0.0033 (15)  | -0.0044 (18) |
| C21 | 0.068 (3) | 0.098 (3)   | 0.097 (3)   | -0.013 (2)   | 0.012 (2)    | -0.006 (2)   |
| C22 | 0.072 (3) | 0.148 (4)   | 0.060 (3)   | 0.001 (2)    | 0.0227 (19)  | -0.015 (2)   |
| C23 | 0.058 (2) | 0.114 (3)   | 0.072 (3)   | 0.012 (2)    | 0.0023 (18)  | 0.010 (2)    |
| C24 | 0.058 (2) | 0.067 (2)   | 0.055 (2)   | 0.0061 (18)  | -0.0008 (16) | 0.0030 (18)  |
| C25 | 0.099 (3) | 0.126 (3)   | 0.073 (3)   | 0.041 (3)    | 0.006 (2)    | 0.031 (2)    |
| C26 | 0.062 (3) | 0.101 (3)   | 0.175 (5)   | -0.005 (2)   | -0.030 (3)   | -0.027 (3)   |
| C27 | 0.074 (3) | 0.100 (3)   | 0.074 (3)   | 0.014 (2)    | 0.012 (2)    | -0.008 (2)   |
| C28 | 0.069 (2) | 0.049 (2)   | 0.055 (2)   | 0.0024 (19)  | 0.0134 (17)  | -0.0054 (17) |
| C29 | 0.064 (2) | 0.048 (2)   | 0.048 (2)   | 0.0015 (18)  | 0.0161 (16)  | -0.0042 (15) |
| C30 | 0.067 (2) | 0.059 (2)   | 0.058 (2)   | 0.0008 (18)  | 0.0115 (17)  | 0.0045 (17)  |
| C31 | 0.062 (2) | 0.059 (2)   | 0.059 (2)   | -0.0003 (18) | 0.0093 (16)  | 0.0041 (17)  |
| C32 | 0.061 (2) | 0.046 (2)   | 0.052 (2)   | 0.0036 (18)  | 0.0117 (16)  | -0.0029 (16) |
| C33 | 0.073 (2) | 0.052 (2)   | 0.054 (2)   | 0.0012 (19)  | 0.0167 (17)  | -0.0035 (16) |
| C34 | 0.065 (2) | 0.058 (2)   | 0.049 (2)   | 0.0037 (19)  | 0.0109 (16)  | -0.0072 (17) |
| C35 | 0.060 (2) | 0.061 (2)   | 0.075 (3)   | 0.0040 (19)  | 0.0121 (18)  | -0.0022 (19) |
| C36 | 0.075 (3) | 0.061 (2)   | 0.074 (3)   | -0.006 (2)   | 0.015 (2)    | 0.0010 (19)  |
| C37 | 0.065 (2) | 0.062 (2)   | 0.052 (2)   | -0.001 (2)   | 0.0042 (17)  | -0.0049 (17) |
| C38 | 0.058 (2) | 0.079 (3)   | 0.072 (3)   | 0.005 (2)    | -0.0030 (18) | 0.004 (2)    |
| C39 | 0.065 (2) | 0.061 (2)   | 0.071 (3)   | 0.006 (2)    | 0.0033 (18)  | 0.0053 (18)  |
| C40 | 0.069 (2) | 0.049 (2)   | 0.056 (2)   | -0.0004 (18) | 0.0148 (17)  | 0.0010 (16)  |
| C41 | 0.064 (2) | 0.051 (2)   | 0.049 (2)   | -0.0018 (18) | 0.0099 (16)  | 0.0044 (16)  |
| C42 | 0.060 (2) | 0.069 (2)   | 0.068 (2)   | -0.0015 (19) | 0.0192 (17)  | 0.0224 (19)  |
| C43 | 0.069 (2) | 0.055 (2)   | 0.064 (2)   | -0.0048 (19) | 0.0135 (18)  | 0.0155 (17)  |
| C44 | 0.059 (2) | 0.051 (2)   | 0.0366 (18) | -0.0042 (17) | 0.0027 (14)  | 0.0015 (15)  |
| C45 | 0.063 (2) | 0.063 (2)   | 0.082 (3)   | -0.0110 (19) | 0.0137 (19)  | 0.021 (2)    |
| C46 | 0.068 (3) | 0.050 (2)   | 0.091 (3)   | -0.007 (2)   | 0.004 (2)    | 0.0208 (19)  |
| C47 | 0.055 (2) | 0.081 (3)   | 0.071 (3)   | -0.008 (2)   | -0.0033 (18) | -0.004 (2)   |
| C48 | 0.093 (3) | 0.177 (6)   | 0.095 (4)   | -0.069 (4)   | -0.007 (3)   | 0.087 (4)    |
| C49 | 0.070 (3) | 0.120 (4)   | 0.180 (7)   | 0.003 (3)    | 0.057 (4)    | -0.020 (4)   |
| C50 | 0.101 (3) | 0.139 (4)   | 0.109 (4)   | -0.046 (3)   | -0.010 (3)   | -0.020 (3)   |
| C51 | 0.058 (2) | 0.058 (2)   | 0.046 (2)   | -0.0061 (17) | 0.0041 (15)  | 0.0049 (16)  |
| C52 | 0.083 (3) | 0.104 (3)   | 0.065 (3)   | 0.017 (2)    | 0.0042 (19)  | 0.029 (2)    |
| C53 | 0.066 (3) | 0.096 (3)   | 0.109 (3)   | -0.017 (2)   | -0.002 (2)   | 0.005 (2)    |
| C54 | 0.086 (3) | 0.093 (3)   | 0.068 (3)   | 0.014 (2)    | 0.010 (2)    | -0.005 (2)   |
| C55 | 0.076 (4) | 0.038 (3)   | 0.114 (5)   | 0.000        | 0.017 (3)    | 0.000        |
| C56 | 0.065 (2) | 0.0397 (19) | 0.063 (2)   | -0.0012 (17) | 0.0130 (17)  | -0.0012 (16) |
| C57 | 0.063 (2) | 0.0414 (19) | 0.070 (2)   | -0.0032 (15) | 0.0114 (18)  | 0.0011 (16)  |
| C58 | 0.073 (3) | 0.0409 (19) | 0.073 (2)   | 0.0005 (19)  | 0.0110 (18)  | -0.0013 (17) |
| C59 | 0.070 (2) | 0.0397 (19) | 0.054 (2)   | -0.0034 (17) | 0.0093 (17)  | -0.0054 (16) |

## supplementary materials

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| C60 | 0.075 (3) | 0.044 (2) | 0.090 (3)   | -0.006 (2)   | 0.013 (2)   | 0.0126 (18)  |
| C61 | 0.066 (3) | 0.059 (2) | 0.085 (3)   | -0.0039 (19) | 0.0184 (19) | 0.015 (2)    |
| C62 | 0.064 (2) | 0.047 (2) | 0.0414 (19) | -0.0034 (17) | 0.0048 (15) | -0.0054 (15) |
| C63 | 0.078 (3) | 0.047 (2) | 0.048 (2)   | -0.0015 (19) | 0.0051 (17) | 0.0064 (16)  |
| C64 | 0.068 (2) | 0.050 (2) | 0.055 (2)   | -0.0060 (18) | 0.0155 (17) | 0.0035 (16)  |
| C65 | 0.064 (2) | 0.057 (2) | 0.045 (2)   | -0.0012 (18) | 0.0024 (15) | -0.0043 (16) |
| C66 | 0.101 (3) | 0.122 (3) | 0.071 (3)   | 0.033 (3)    | 0.004 (2)   | 0.027 (2)    |
| C67 | 0.069 (3) | 0.091 (3) | 0.142 (4)   | -0.006 (2)   | -0.006 (2)  | -0.011 (3)   |
| C68 | 0.085 (3) | 0.112 (3) | 0.070 (3)   | 0.021 (2)    | 0.011 (2)   | -0.021 (2)   |

### *Geometric parameters (Å, °)*

|         |           |          |           |
|---------|-----------|----------|-----------|
| O1—C1   | 1.213 (3) | C35—C36  | 1.382 (4) |
| O2—C28  | 1.219 (3) | C35—H35  | 0.9300    |
| O3—C55  | 1.207 (5) | C36—C37  | 1.381 (4) |
| C1—C5   | 1.479 (4) | C36—H36  | 0.9300    |
| C1—C2   | 1.482 (4) | C37—C38  | 1.370 (4) |
| C2—C13  | 1.331 (4) | C37—C47  | 1.528 (4) |
| C2—C3   | 1.489 (4) | C38—C39  | 1.380 (4) |
| C3—C4   | 1.532 (3) | C38—H38  | 0.9300    |
| C3—H3A  | 0.9700    | C39—H39  | 0.9300    |
| C3—H3B  | 0.9700    | C40—C41  | 1.456 (4) |
| C4—C5   | 1.496 (4) | C40—H40  | 0.9300    |
| C4—H4A  | 0.9700    | C41—C42  | 1.374 (4) |
| C4—H4B  | 0.9700    | C41—C46  | 1.399 (4) |
| C5—C6   | 1.339 (4) | C42—C43  | 1.374 (4) |
| C6—C7   | 1.446 (4) | C42—H42  | 0.9300    |
| C6—H6   | 0.9300    | C43—C44  | 1.387 (4) |
| C7—C12  | 1.383 (4) | C43—H43  | 0.9300    |
| C7—C8   | 1.383 (4) | C44—C45  | 1.375 (4) |
| C8—C9   | 1.381 (4) | C44—C51  | 1.521 (4) |
| C8—H8   | 0.9300    | C45—C46  | 1.366 (4) |
| C9—C10  | 1.389 (4) | C45—H45  | 0.9300    |
| C9—H9   | 0.9300    | C46—H46  | 0.9300    |
| C10—C11 | 1.379 (4) | C47—C49  | 1.505 (5) |
| C10—C20 | 1.511 (4) | C47—C50  | 1.512 (4) |
| C11—C12 | 1.378 (4) | C47—C48  | 1.513 (4) |
| C11—H11 | 0.9300    | C48—H48A | 0.9600    |
| C12—H12 | 0.9300    | C48—H48B | 0.9600    |
| C13—C14 | 1.459 (4) | C48—H48C | 0.9600    |
| C13—H13 | 0.9300    | C49—H49A | 0.9600    |
| C14—C15 | 1.374 (4) | C49—H49B | 0.9600    |
| C14—C19 | 1.384 (4) | C49—H49C | 0.9600    |
| C15—C16 | 1.381 (4) | C50—H50A | 0.9600    |
| C15—H15 | 0.9300    | C50—H50B | 0.9600    |
| C16—C17 | 1.388 (4) | C50—H50C | 0.9600    |
| C16—H16 | 0.9300    | C51—C53  | 1.524 (4) |
| C17—C18 | 1.359 (4) | C51—C52  | 1.533 (4) |
| C17—C24 | 1.534 (4) | C51—C54  | 1.539 (4) |

|           |           |                      |           |
|-----------|-----------|----------------------|-----------|
| C18—C19   | 1.383 (4) | C52—H52A             | 0.9600    |
| C18—H18   | 0.9300    | C52—H52B             | 0.9600    |
| C19—H19   | 0.9300    | C52—H52C             | 0.9600    |
| C20—C21   | 1.523 (4) | C53—H53A             | 0.9600    |
| C20—C23   | 1.536 (4) | C53—H53B             | 0.9600    |
| C20—C22   | 1.545 (4) | C53—H53C             | 0.9600    |
| C21—H21A  | 0.9600    | C54—H54A             | 0.9600    |
| C21—H21B  | 0.9600    | C54—H54B             | 0.9600    |
| C21—H21C  | 0.9600    | C54—H54C             | 0.9600    |
| C22—H22A  | 0.9600    | C55—C56 <sup>i</sup> | 1.476 (4) |
| C22—H22B  | 0.9600    | C55—C56              | 1.476 (4) |
| C22—H22C  | 0.9600    | C56—C58              | 1.337 (4) |
| C23—H23A  | 0.9600    | C56—C57              | 1.476 (4) |
| C23—H23B  | 0.9600    | C57—C57 <sup>i</sup> | 1.534 (5) |
| C23—H23C  | 0.9600    | C57—H57A             | 0.9700    |
| C24—C26   | 1.520 (4) | C57—H57B             | 0.9700    |
| C24—C27   | 1.527 (4) | C58—C59              | 1.460 (4) |
| C24—C25   | 1.528 (4) | C58—H58              | 0.9300    |
| C25—H25A  | 0.9600    | C59—C64              | 1.373 (4) |
| C25—H25B  | 0.9600    | C59—C60              | 1.391 (4) |
| C25—H25C  | 0.9600    | C60—C61              | 1.378 (4) |
| C26—H26A  | 0.9600    | C60—H60              | 0.9300    |
| C26—H26B  | 0.9600    | C61—C62              | 1.372 (4) |
| C26—H26C  | 0.9600    | C61—H61              | 0.9300    |
| C27—H27A  | 0.9600    | C62—C63              | 1.392 (4) |
| C27—H27B  | 0.9600    | C62—C65              | 1.520 (4) |
| C27—H27C  | 0.9600    | C63—C64              | 1.379 (4) |
| C28—C32   | 1.479 (4) | C63—H63              | 0.9300    |
| C28—C29   | 1.488 (4) | C64—H64              | 0.9300    |
| C29—C40   | 1.334 (4) | C65—C67              | 1.518 (4) |
| C29—C30   | 1.489 (4) | C65—C68              | 1.529 (4) |
| C30—C31   | 1.532 (4) | C65—C66              | 1.530 (4) |
| C30—H30A  | 0.9700    | C66—H66A             | 0.9600    |
| C30—H30B  | 0.9700    | C66—H66B             | 0.9600    |
| C31—C32   | 1.492 (4) | C66—H66C             | 0.9600    |
| C31—H31A  | 0.9700    | C67—H67A             | 0.9600    |
| C31—H31B  | 0.9700    | C67—H67B             | 0.9600    |
| C32—C33   | 1.337 (4) | C67—H67C             | 0.9600    |
| C33—C34   | 1.460 (4) | C68—H68A             | 0.9600    |
| C33—H33   | 0.9300    | C68—H68B             | 0.9600    |
| C34—C35   | 1.387 (4) | C68—H68C             | 0.9600    |
| C34—C39   | 1.394 (4) |                      |           |
| O1—C1—C5  | 126.1 (3) | C34—C35—H35          | 119.3     |
| O1—C1—C2  | 125.7 (3) | C37—C36—C35          | 122.5 (3) |
| C5—C1—C2  | 108.2 (3) | C37—C36—H36          | 118.7     |
| C13—C2—C1 | 119.8 (3) | C35—C36—H36          | 118.7     |
| C13—C2—C3 | 131.5 (3) | C38—C37—C36          | 115.7 (3) |
| C1—C2—C3  | 108.7 (3) | C38—C37—C47          | 122.7 (3) |

## supplementary materials

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|             |           |               |           |
|-------------|-----------|---------------|-----------|
| C2—C3—C4    | 107.5 (2) | C36—C37—C47   | 121.6 (3) |
| C2—C3—H3A   | 110.2     | C37—C38—C39   | 123.0 (3) |
| C4—C3—H3A   | 110.2     | C37—C38—H38   | 118.5     |
| C2—C3—H3B   | 110.2     | C39—C38—H38   | 118.5     |
| C4—C3—H3B   | 110.2     | C38—C39—C34   | 121.1 (3) |
| H3A—C3—H3B  | 108.5     | C38—C39—H39   | 119.4     |
| C5—C4—C3    | 106.2 (2) | C34—C39—H39   | 119.4     |
| C5—C4—H4A   | 110.5     | C29—C40—C41   | 130.3 (3) |
| C3—C4—H4A   | 110.5     | C29—C40—H40   | 114.9     |
| C5—C4—H4B   | 110.5     | C41—C40—H40   | 114.9     |
| C3—C4—H4B   | 110.5     | C42—C41—C46   | 115.6 (3) |
| H4A—C4—H4B  | 108.7     | C42—C41—C40   | 125.9 (3) |
| C6—C5—C1    | 119.3 (3) | C46—C41—C40   | 118.5 (3) |
| C6—C5—C4    | 131.4 (3) | C43—C42—C41   | 122.6 (3) |
| C1—C5—C4    | 109.2 (3) | C43—C42—H42   | 118.7     |
| C5—C6—C7    | 131.6 (3) | C41—C42—H42   | 118.7     |
| C5—C6—H6    | 114.2     | C42—C43—C44   | 121.6 (3) |
| C7—C6—H6    | 114.2     | C42—C43—H43   | 119.2     |
| C12—C7—C8   | 115.7 (3) | C44—C43—H43   | 119.2     |
| C12—C7—C6   | 119.0 (3) | C45—C44—C43   | 115.9 (3) |
| C8—C7—C6    | 125.2 (3) | C45—C44—C51   | 121.8 (3) |
| C9—C8—C7    | 122.3 (3) | C43—C44—C51   | 122.1 (3) |
| C9—C8—H8    | 118.9     | C46—C45—C44   | 122.7 (3) |
| C7—C8—H8    | 118.9     | C46—C45—H45   | 118.7     |
| C8—C9—C10   | 122.1 (3) | C44—C45—H45   | 118.7     |
| C8—C9—H9    | 119.0     | C45—C46—C41   | 121.5 (3) |
| C10—C9—H9   | 119.0     | C45—C46—H46   | 119.2     |
| C11—C10—C9  | 115.1 (3) | C41—C46—H46   | 119.2     |
| C11—C10—C20 | 123.8 (3) | C49—C47—C50   | 108.2 (3) |
| C9—C10—C20  | 121.1 (3) | C49—C47—C48   | 107.9 (4) |
| C12—C11—C10 | 122.9 (3) | C50—C47—C48   | 108.7 (3) |
| C12—C11—H11 | 118.5     | C49—C47—C37   | 112.5 (3) |
| C10—C11—H11 | 118.5     | C50—C47—C37   | 108.6 (3) |
| C11—C12—C7  | 121.8 (3) | C48—C47—C37   | 110.9 (3) |
| C11—C12—H12 | 119.1     | C47—C48—H48A  | 109.5     |
| C7—C12—H12  | 119.1     | C47—C48—H48B  | 109.5     |
| C2—C13—C14  | 131.5 (3) | H48A—C48—H48B | 109.5     |
| C2—C13—H13  | 114.3     | C47—C48—H48C  | 109.5     |
| C14—C13—H13 | 114.3     | H48A—C48—H48C | 109.5     |
| C15—C14—C19 | 116.6 (3) | H48B—C48—H48C | 109.5     |
| C15—C14—C13 | 125.4 (3) | C47—C49—H49A  | 109.5     |
| C19—C14—C13 | 118.0 (3) | C47—C49—H49B  | 109.5     |
| C14—C15—C16 | 121.6 (3) | H49A—C49—H49B | 109.5     |
| C14—C15—H15 | 119.2     | C47—C49—H49C  | 109.5     |
| C16—C15—H15 | 119.2     | H49A—C49—H49C | 109.5     |
| C15—C16—C17 | 121.5 (3) | H49B—C49—H49C | 109.5     |
| C15—C16—H16 | 119.3     | C47—C50—H50A  | 109.5     |
| C17—C16—H16 | 119.3     | C47—C50—H50B  | 109.5     |
| C18—C17—C16 | 116.8 (3) | H50A—C50—H50B | 109.5     |

|               |           |                            |             |
|---------------|-----------|----------------------------|-------------|
| C18—C17—C24   | 121.3 (3) | C47—C50—H50C               | 109.5       |
| C16—C17—C24   | 121.8 (3) | H50A—C50—H50C              | 109.5       |
| C17—C18—C19   | 122.0 (3) | H50B—C50—H50C              | 109.5       |
| C17—C18—H18   | 119.0     | C44—C51—C53                | 112.3 (3)   |
| C19—C18—H18   | 119.0     | C44—C51—C52                | 112.2 (3)   |
| C18—C19—C14   | 121.5 (3) | C53—C51—C52                | 108.0 (3)   |
| C18—C19—H19   | 119.3     | C44—C51—C54                | 108.2 (2)   |
| C14—C19—H19   | 119.3     | C53—C51—C54                | 108.3 (3)   |
| C10—C20—C21   | 112.4 (3) | C52—C51—C54                | 107.6 (3)   |
| C10—C20—C23   | 112.0 (3) | C51—C52—H52A               | 109.5       |
| C21—C20—C23   | 108.2 (3) | C51—C52—H52B               | 109.5       |
| C10—C20—C22   | 107.4 (2) | H52A—C52—H52B              | 109.5       |
| C21—C20—C22   | 108.2 (3) | C51—C52—H52C               | 109.5       |
| C23—C20—C22   | 108.4 (3) | H52A—C52—H52C              | 109.5       |
| C20—C21—H21A  | 109.5     | H52B—C52—H52C              | 109.5       |
| C20—C21—H21B  | 109.5     | C51—C53—H53A               | 109.5       |
| H21A—C21—H21B | 109.5     | C51—C53—H53B               | 109.5       |
| C20—C21—H21C  | 109.5     | H53A—C53—H53B              | 109.5       |
| H21A—C21—H21C | 109.5     | C51—C53—H53C               | 109.5       |
| H21B—C21—H21C | 109.5     | H53A—C53—H53C              | 109.5       |
| C20—C22—H22A  | 109.5     | H53B—C53—H53C              | 109.5       |
| C20—C22—H22B  | 109.5     | C51—C54—H54A               | 109.5       |
| H22A—C22—H22B | 109.5     | C51—C54—H54B               | 109.5       |
| C20—C22—H22C  | 109.5     | H54A—C54—H54B              | 109.5       |
| H22A—C22—H22C | 109.5     | C51—C54—H54C               | 109.5       |
| H22B—C22—H22C | 109.5     | H54A—C54—H54C              | 109.5       |
| C20—C23—H23A  | 109.5     | H54B—C54—H54C              | 109.5       |
| C20—C23—H23B  | 109.5     | O3—C55—C56 <sup>i</sup>    | 125.6 (2)   |
| H23A—C23—H23B | 109.5     | O3—C55—C56                 | 125.6 (2)   |
| C20—C23—H23C  | 109.5     | C56 <sup>i</sup> —C55—C56  | 108.8 (4)   |
| H23A—C23—H23C | 109.5     | C58—C56—C55                | 120.0 (3)   |
| H23B—C23—H23C | 109.5     | C58—C56—C57                | 131.7 (3)   |
| C26—C24—C27   | 108.8 (3) | C55—C56—C57                | 108.2 (3)   |
| C26—C24—C25   | 108.4 (3) | C56—C57—C57 <sup>i</sup>   | 106.69 (17) |
| C27—C24—C25   | 107.8 (3) | C56—C57—H57A               | 110.4       |
| C26—C24—C17   | 111.0 (3) | C57 <sup>i</sup> —C57—H57A | 110.4       |
| C27—C24—C17   | 108.2 (2) | C56—C57—H57B               | 110.4       |
| C25—C24—C17   | 112.5 (3) | C57 <sup>i</sup> —C57—H57B | 110.4       |
| C24—C25—H25A  | 109.5     | H57A—C57—H57B              | 108.6       |
| C24—C25—H25B  | 109.5     | C56—C58—C59                | 129.4 (3)   |
| H25A—C25—H25B | 109.5     | C56—C58—H58                | 115.3       |
| C24—C25—H25C  | 109.5     | C59—C58—H58                | 115.3       |
| H25A—C25—H25C | 109.5     | C64—C59—C60                | 116.6 (3)   |
| H25B—C25—H25C | 109.5     | C64—C59—C58                | 124.9 (3)   |
| C24—C26—H26A  | 109.5     | C60—C59—C58                | 118.5 (3)   |
| C24—C26—H26B  | 109.5     | C61—C60—C59                | 121.8 (3)   |
| H26A—C26—H26B | 109.5     | C61—C60—H60                | 119.1       |
| C24—C26—H26C  | 109.5     | C59—C60—H60                | 119.1       |

## supplementary materials

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|               |            |                 |            |
|---------------|------------|-----------------|------------|
| H26A—C26—H26C | 109.5      | C62—C61—C60     | 122.0 (3)  |
| H26B—C26—H26C | 109.5      | C62—C61—H61     | 119.0      |
| C24—C27—H27A  | 109.5      | C60—C61—H61     | 119.0      |
| C24—C27—H27B  | 109.5      | C61—C62—C63     | 116.0 (3)  |
| H27A—C27—H27B | 109.5      | C61—C62—C65     | 121.8 (3)  |
| C24—C27—H27C  | 109.5      | C63—C62—C65     | 122.2 (3)  |
| H27A—C27—H27C | 109.5      | C64—C63—C62     | 122.3 (3)  |
| H27B—C27—H27C | 109.5      | C64—C63—H63     | 118.8      |
| O2—C28—C32    | 125.8 (3)  | C62—C63—H63     | 118.8      |
| O2—C28—C29    | 126.2 (3)  | C59—C64—C63     | 121.3 (3)  |
| C32—C28—C29   | 108.1 (3)  | C59—C64—H64     | 119.3      |
| C40—C29—C28   | 120.1 (3)  | C63—C64—H64     | 119.3      |
| C40—C29—C30   | 131.0 (3)  | C67—C65—C62     | 111.9 (3)  |
| C28—C29—C30   | 108.9 (3)  | C67—C65—C68     | 108.0 (3)  |
| C29—C30—C31   | 107.1 (2)  | C62—C65—C68     | 108.0 (2)  |
| C29—C30—H30A  | 110.3      | C67—C65—C66     | 108.2 (3)  |
| C31—C30—H30A  | 110.3      | C62—C65—C66     | 112.6 (3)  |
| C29—C30—H30B  | 110.3      | C68—C65—C66     | 107.9 (3)  |
| C31—C30—H30B  | 110.3      | C65—C66—H66A    | 109.5      |
| H30A—C30—H30B | 108.6      | C65—C66—H66B    | 109.5      |
| C32—C31—C30   | 106.8 (2)  | H66A—C66—H66B   | 109.5      |
| C32—C31—H31A  | 110.4      | C65—C66—H66C    | 109.5      |
| C30—C31—H31A  | 110.4      | H66A—C66—H66C   | 109.5      |
| C32—C31—H31B  | 110.4      | H66B—C66—H66C   | 109.5      |
| C30—C31—H31B  | 110.4      | C65—C67—H67A    | 109.5      |
| H31A—C31—H31B | 108.6      | C65—C67—H67B    | 109.5      |
| C33—C32—C28   | 120.5 (3)  | H67A—C67—H67B   | 109.5      |
| C33—C32—C31   | 130.4 (3)  | C65—C67—H67C    | 109.5      |
| C28—C32—C31   | 109.1 (3)  | H67A—C67—H67C   | 109.5      |
| C32—C33—C34   | 130.9 (3)  | H67B—C67—H67C   | 109.5      |
| C32—C33—H33   | 114.5      | C65—C68—H68A    | 109.5      |
| C34—C33—H33   | 114.5      | C65—C68—H68B    | 109.5      |
| C35—C34—C39   | 116.2 (3)  | H68A—C68—H68B   | 109.5      |
| C35—C34—C33   | 125.1 (3)  | C65—C68—H68C    | 109.5      |
| C39—C34—C33   | 118.7 (3)  | H68A—C68—H68C   | 109.5      |
| C36—C35—C34   | 121.4 (3)  | H68B—C68—H68C   | 109.5      |
| C36—C35—H35   | 119.3      |                 |            |
| O1—C1—C2—C13  | 2.8 (5)    | C28—C32—C33—C34 | 179.3 (3)  |
| C5—C1—C2—C13  | -177.0 (3) | C31—C32—C33—C34 | 0.0 (5)    |
| O1—C1—C2—C3   | -179.5 (3) | C32—C33—C34—C35 | 1.1 (5)    |
| C5—C1—C2—C3   | 0.8 (3)    | C32—C33—C34—C39 | -176.3 (3) |
| C13—C2—C3—C4  | 179.5 (3)  | C39—C34—C35—C36 | 0.7 (5)    |
| C1—C2—C3—C4   | 2.1 (3)    | C33—C34—C35—C36 | -176.8 (3) |
| C2—C3—C4—C5   | -4.1 (3)   | C34—C35—C36—C37 | 1.4 (5)    |
| O1—C1—C5—C6   | -0.8 (5)   | C35—C36—C37—C38 | -3.4 (5)   |
| C2—C1—C5—C6   | 178.9 (3)  | C35—C36—C37—C47 | 178.0 (3)  |
| O1—C1—C5—C4   | 176.9 (3)  | C36—C37—C38—C39 | 3.5 (5)    |
| C2—C1—C5—C4   | -3.4 (3)   | C47—C37—C38—C39 | -178.0 (3) |
| C3—C4—C5—C6   | -178.1 (3) | C37—C38—C39—C34 | -1.5 (5)   |

|                 |            |                               |              |
|-----------------|------------|-------------------------------|--------------|
| C3—C4—C5—C1     | 4.6 (3)    | C35—C34—C39—C38               | -0.6 (5)     |
| C1—C5—C6—C7     | 176.5 (3)  | C33—C34—C39—C38               | 177.0 (3)    |
| C4—C5—C6—C7     | -0.5 (6)   | C28—C29—C40—C41               | 173.8 (3)    |
| C5—C6—C7—C12    | -175.7 (3) | C30—C29—C40—C41               | -3.6 (6)     |
| C5—C6—C7—C8     | 0.7 (5)    | C29—C40—C41—C42               | 10.0 (5)     |
| C12—C7—C8—C9    | 1.3 (5)    | C29—C40—C41—C46               | -167.0 (3)   |
| C6—C7—C8—C9     | -175.2 (3) | C46—C41—C42—C43               | 3.5 (5)      |
| C7—C8—C9—C10    | 1.3 (5)    | C40—C41—C42—C43               | -173.6 (3)   |
| C8—C9—C10—C11   | -3.8 (5)   | C41—C42—C43—C44               | 0.0 (5)      |
| C8—C9—C10—C20   | 173.7 (3)  | C42—C43—C44—C45               | -2.4 (5)     |
| C9—C10—C11—C12  | 4.1 (5)    | C42—C43—C44—C51               | 172.6 (3)    |
| C20—C10—C11—C12 | -173.4 (3) | C43—C44—C45—C46               | 1.3 (5)      |
| C10—C11—C12—C7  | -1.7 (5)   | C51—C44—C45—C46               | -173.7 (3)   |
| C8—C7—C12—C11   | -1.1 (5)   | C44—C45—C46—C41               | 2.2 (5)      |
| C6—C7—C12—C11   | 175.6 (3)  | C42—C41—C46—C45               | -4.5 (5)     |
| C1—C2—C13—C14   | 174.1 (3)  | C40—C41—C46—C45               | 172.8 (3)    |
| C3—C2—C13—C14   | -3.0 (6)   | C38—C37—C47—C49               | 23.2 (5)     |
| C2—C13—C14—C15  | 10.0 (5)   | C36—C37—C47—C49               | -158.4 (4)   |
| C2—C13—C14—C19  | -169.6 (3) | C38—C37—C47—C50               | -96.5 (4)    |
| C19—C14—C15—C16 | 2.4 (5)    | C36—C37—C47—C50               | 81.9 (4)     |
| C13—C14—C15—C16 | -177.2 (3) | C38—C37—C47—C48               | 144.1 (4)    |
| C14—C15—C16—C17 | 0.1 (5)    | C36—C37—C47—C48               | -37.5 (5)    |
| C15—C16—C17—C18 | -2.2 (5)   | C45—C44—C51—C53               | -33.2 (4)    |
| C15—C16—C17—C24 | 174.6 (3)  | C43—C44—C51—C53               | 152.1 (3)    |
| C16—C17—C18—C19 | 1.5 (5)    | C45—C44—C51—C52               | -155.1 (3)   |
| C24—C17—C18—C19 | -175.2 (3) | C43—C44—C51—C52               | 30.2 (4)     |
| C17—C18—C19—C14 | 1.1 (5)    | C45—C44—C51—C54               | 86.3 (4)     |
| C15—C14—C19—C18 | -3.0 (5)   | C43—C44—C51—C54               | -88.4 (3)    |
| C13—C14—C19—C18 | 176.6 (3)  | O3—C55—C56—C58                | 6.5 (3)      |
| C11—C10—C20—C21 | -147.0 (3) | C56 <sup>i</sup> —C55—C56—C58 | -173.5 (3)   |
| C9—C10—C20—C21  | 35.7 (4)   | O3—C55—C56—C57                | -176.10 (15) |
| C11—C10—C20—C23 | -24.8 (4)  | C56 <sup>i</sup> —C55—C56—C57 | 3.90 (15)    |
| C9—C10—C20—C23  | 157.9 (3)  | C58—C56—C57—C57 <sup>i</sup>  | 167.2 (3)    |
| C11—C10—C20—C22 | 94.1 (4)   | C55—C56—C57—C57 <sup>i</sup>  | -9.8 (4)     |
| C9—C10—C20—C22  | -83.2 (4)  | C55—C56—C58—C59               | 177.1 (3)    |
| C18—C17—C24—C26 | -36.4 (4)  | C57—C56—C58—C59               | 0.4 (6)      |
| C16—C17—C24—C26 | 147.1 (3)  | C56—C58—C59—C64               | 24.2 (5)     |
| C18—C17—C24—C27 | 83.0 (4)   | C56—C58—C59—C60               | -156.7 (3)   |
| C16—C17—C24—C27 | -93.6 (4)  | C64—C59—C60—C61               | -2.5 (5)     |
| C18—C17—C24—C25 | -158.0 (3) | C58—C59—C60—C61               | 178.3 (3)    |
| C16—C17—C24—C25 | 25.4 (4)   | C59—C60—C61—C62               | 1.8 (5)      |
| O2—C28—C29—C40  | 1.9 (5)    | C60—C61—C62—C63               | 0.3 (5)      |
| C32—C28—C29—C40 | -178.0 (3) | C60—C61—C62—C65               | -177.1 (3)   |
| O2—C28—C29—C30  | 179.8 (3)  | C61—C62—C63—C64               | -1.7 (4)     |
| C32—C28—C29—C30 | 0.0 (3)    | C65—C62—C63—C64               | 175.7 (3)    |
| C40—C29—C30—C31 | 178.1 (3)  | C60—C59—C64—C63               | 1.1 (5)      |
| C28—C29—C30—C31 | 0.5 (3)    | C58—C59—C64—C63               | -179.7 (3)   |
| C29—C30—C31—C32 | -0.7 (3)   | C62—C63—C64—C59               | 1.0 (5)      |

## supplementary materials

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|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| O2—C28—C32—C33  | 0.3 (5)    | C61—C62—C65—C67 | -31.6 (4)  |
| C29—C28—C32—C33 | -179.9 (3) | C63—C62—C65—C67 | 151.2 (3)  |
| O2—C28—C32—C31  | 179.7 (3)  | C61—C62—C65—C68 | 87.2 (4)   |
| C29—C28—C32—C31 | -0.4 (3)   | C63—C62—C65—C68 | -90.0 (3)  |
| C30—C31—C32—C33 | -179.9 (3) | C61—C62—C65—C66 | -153.7 (3) |
| C30—C31—C32—C28 | 0.7 (3)    | C63—C62—C65—C66 | 29.0 (4)   |

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

Fig. 1

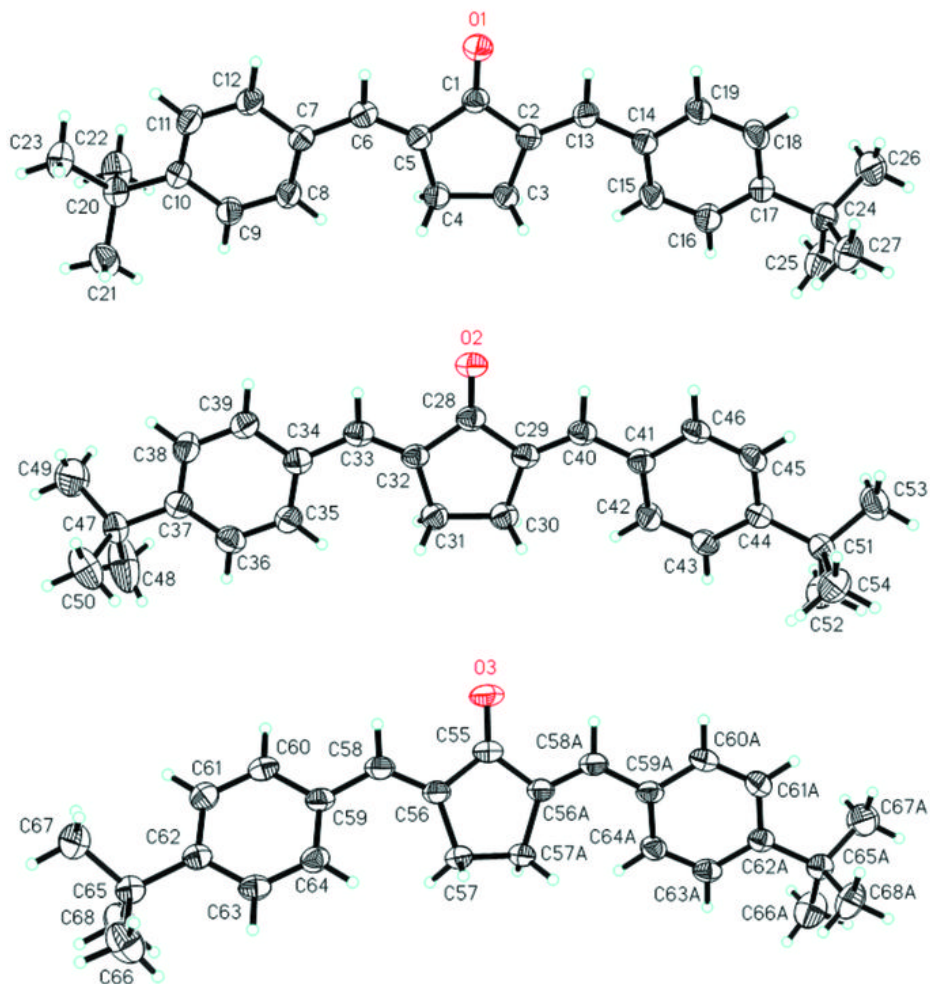


Fig. 2

