Regioselective Synthesis of Novel 7-5-8-Fused Oxabridged Tricyclic Molecules via Consecutive Dipolar Cycloaddition of Pentafulvenes with 3-Oxidopyrylium Betaines

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This paper is dedicated with respect to Dr. Bert Fraser-Reid on the occasion of his 72nd birthday.

Abstract: Pentafulvenes undergo consecutive dipolar cycloadditions with various substituted oxidopyrylium betaines resulting in the formation of a new class of structurally interesting 7-5-8-fused oxabridged tricyclic molecules.

Key words: Pentafulvenes, oxidopyrylium betaines, consecutive dipolar cycloaddition, 7-5-8-fused tricyclic molecules

The design and synthesis of novel polycyclic molecules with structurally interesting skeletons has been a fascinating and inspiring area and continues to be a major challenge in organic synthesis.1 In this context, the development of efficient and novel synthetic routes to medium sized heterocycles is a worthy endeavor due to the presence of such systems in many biologically and structurally interesting natural products.2 The well-known entropic and enthalpic factors associated with the formation of medium-sized rings make the synthesis of these ring systems a challenging problem in synthetic organic chemistry. The conformations of the medium-sized rings strongly affect the reactivity and hence a number of synthetic routes to these systems through conformationally constrained oxabridged systems have been reported in literature.3 The oxabicyclic products can be manipulated stereoselectively in a variety of ways so as to unmask the embedded medium-sized carbocycles. Recent reports by Sun et al.4 have shown that some oxabridged cyclooctanoid natural products, Lancifodilactones, exhibit cytotoxic and excellent anti-HIV activity. Moreover, a number of biologically active natural and synthetic cyclooctanoid molecules are known in the literature and some of them are shown in Figure 1. The interesting biological activities combined with the synthetic challenges have served to make them interesting targets in a number of synthetic studies.

Inspired by the versatile reactivity pattern of pentafulvenes in cycloaddition reactions,5 we undertook an investigation of its reactivity with 3-oxidopyrylium betaines. Pentafulvenes are known to act as 2π, 4π,7 or 6π8 components in cycloaddition reactions, whereas 3-oxidopyryliu-

Figure 1  Some biologically active cyclooctanoids

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um betaines have been well utilized in the synthesis of cycloheptanoids. Our preliminary results have shown that pentafullvenes undergo facile [6+3] cycloaddition with 3-oxidopyrylium betaines leading to the formation of 5-8-fused oxabridged cyclooctanoids.

In order to extend our methodology towards the construction of more complex and structurally interesting polycyclic systems, we investigated the cycloaddition of 6,6-dimethyl fulvene with excess pyranulose acetate, expecting a one-pot multiple cycloaddition. But to our dismay, the reaction afforded an intractable mixture of products. Our next attempt involved the reaction of 3-oxidopyrylium betaine with the 5-8-fused oxabridged cyclooctanoid, formed from the initial [6+3] cycloaddition. The reaction afforded a separable mixture of 7-5-8-fused oxabridged tricyclic systems in 81% yield. The reaction is illustrated in Scheme 1.

The products were characterized on the basis of spectral analysis. The a and b protons of the seven-membered ring in 4a and 4b resonated as a doublet and a double doublet at δ = 6.07, 7.15 ppm and at δ = 5.84, 6.64 ppm, respectively. The endo protons of the ring junction appeared as multiplets centered at δ = 3.70, 3.27 ppm in 4a and at δ = 3.72, 3.48 ppm in 4b. The major difference observed in 1H NMR of 4a and 4b is in the chemical shift of the a and b protons. Similar reactivity was observed with the [6+6] adduct 3 and various substituted 3-oxidopyrylium betaines. The results are summarized in Table 1. The structure of the adducts were unambiguously confirmed by single crystal X-ray analysis of 4b (Figure 2 and Table 1; entries 1 and 2). It is interesting to note that the second cycloaddition occurs only in the cyclopentadiene part, leaving the a,b-unsaturated ketone part unreacted. The single crystal X-ray analysis clearly showed that 4b and 5a are syn:anti and syn:syn oxabridged compounds. The difference in chemical shift value of the a and b protons of the seven-membered rings can be attributed to the presence of the carbonyl group in close proximity to these protons. This change in chemical shift value was found to be general in all other examples studied. The consecutive dipolar cycloaddition reaction was carried out with 6,6-pentamethylene fulvene and the results are summarized in Table 2.

The results obtained validate the methodology as a practical and rapid approach to polycyclic systems containing multiple oxabridges. These novel 7-5-8-fused tricyclic systems were obtained through consecutive dipolar cycloaddition of a single fulvene molecule with two molecules of 3-oxidopyrylium betaine. A variety of 7-5-8-fused tricyclic systems can be prepared by using appropriately functionalized fulvenes and betaines. The presence of the oxabridge offers rigidity to the molecule and hence functionalities can be introduced to these rigid molecular scaffolds in stereoselective fashion by virtue of its conformational rigidity. The oxabicyclic products can be stereoselectively manipulated in a number of ways and those that unmask the embedded cyclooctanoid and cycloheptanoid skeleton are of particular interest.

It is clear from the X-ray crystal structure of 5a (Figure 2) that it has a bowl-shaped framework and can be efficiently utilized in the synthesis of novel supramolecular systems. Currently, there is lot of interest in the synthesis of molecules that have the ability to bind and signal the presence of anions as well as transport such species across vesicles and cell membranes. The functional groups effective for
### Table 1  Consecutive Dipolar Cycloaddition of 6,6-Dimethylfulvene with 3-Oxidopyrylium Betaines

<table>
<thead>
<tr>
<th>Entry</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Products (ratio)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>syn:anti 4a:4b 2:1</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5a:5b 3:1</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6a:6b 3.4:1</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>7a:7b 3.4:1</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>8b:9a 1:3</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9a:9b 3:1</td>
<td>63</td>
</tr>
</tbody>
</table>

*Reaction conditions: (i) Fulvene (1 equiv), pyranulose acetate 1 (1.2 equiv), Et<sub>3</sub>N (1.2 equiv), CHCl<sub>3</sub>, 6 h; (ii) pyranulose acetate 2 (1.2 equiv), Et<sub>3</sub>N (1.2 equiv), CHCl<sub>3</sub>, 6 h.*
the binding can be effectively attached to the 7-5-8-oxa-
bridged molecule due to the presence of potentially amen-
able functional groups. The cleft-like frameworks are
known for their inherently high degree of structural order.
Appending receptor motifs to this type of rigid framework
allows them to be oriented in a specific, predetermined to-
pographical relationship. The novel 7-5-8-fused oxabridged framework can be easily synthesized by the
consecutive dipolar cycloaddition of pentafulvenes and
can be efficiently utilized in the synthesis of a new family
of conformationally preorganized supramolecular systems.
In conclusion, we have developed a novel and efficient
methodology for the synthesis of novel and versatile 7-5-
8-fused oxabridged tricyclic systems. To the best of our
knowledge, this is the first report of a 7-5-8-oxabridged
tricyclic system. It is to be noted that the lancifodilactones
shown in Figure 1 have a highly oxygenated 7-5-8-fused
system and both show excellent anti-HIV activity. The 7-
5-8-fused oxabridged systems described in this paper are

Table 2 Consecutive Dipolar Cycloaddition of 6,6-Pentamethylene Fulvene with 3-Oxidopyrylium Betaines

<table>
<thead>
<tr>
<th>Entry</th>
<th>R1</th>
<th>R2</th>
<th>Products (ratio)</th>
<th>syn:anti</th>
<th>syn:syn</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>10a:10b 3:1</td>
<td>85</td>
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<td></td>
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<tr>
<td>2</td>
<td>H</td>
<td>CH3</td>
<td>11a:11b 2.9:1</td>
<td>84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>CH(CH3)2</td>
<td>12a:12b 3:1:1</td>
<td>74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>(CH2)3CH3</td>
<td>13a:13b 2.9:1</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Reaction conditions: (i) Fulvene (1 equiv), pyranulose acetate 1 (1.2 equiv), Et3N (1.2 equiv), CHCl3, 6 h (ii) pyranulose acetate 2 (1.2 equiv), Et3N (1.2 equiv), CHCl3, 6 h.
potentially amenable to a number of synthetic transformations. Investigations of the potential of these molecules in the synthesis of novel biologically active chemical entities and macrocycles are in progress and will be reported in due course.

All reactions were conducted in oven-dried glassware. Solvents used for the experiments were distilled and dried as specified. Pyranulose acetate and fulvenes were prepared according to the literature procedures. All other reagents were purchased from local suppliers. All reactions were monitored by TLC (Silica gel 60 F254, 0.25 mm, Merck), visualization was effected with UV and/or by developing in iodine or basic potassium permanganate. Chromatography refers to open column chromatography on silica gel (100–200 mesh). Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (1H) and 75 (13C) MHz on a Bruker Advance DPX 300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (1H) or CDCl3 (13C) as internal standards. IR spectra were recorded on a Bomem MB series FT-IR spectrometer, absorptions are reported in cm⁻¹. Elemental analyses were performed on a Perkin-Elmer-2400 Elemental Analyzer. The single crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 100(2) K. The X-ray generator was operated at 50 kV and 30 mA using MoKα radiation. The data was reduced using SAINTPLUS and an empirical absorption correction was applied using the package SADABS. XPREP was used to determine the space group. The crystal structure was solved by direct methods using SHELXS-97 and refined by full matrix least squares methods using SHELXL-97. Molecular and packing diagrams were generated using ORTEP-III and PLATON. All the hydrogen atoms of the compound were set in calculated positions and refined as riding atoms.

**Typical Procedure for the Synthesis of 4a and 4b**

Dimethyl fulvene (250 mg, 2.36 mmol), pyranulose acetate (441.8 mg, 2.86 mmol) and dry Et3N (285.8 mg, 2.86 mmol) were taken in Dimethyl fulvene (250 mg, 2.36 mmol), pyranulose acetate (441.8 mg, 2.86 mmol) and dry Et3N (285.8 mg, 2.86 mmol) were taken in dimethylformamide (10 mL) and the mixture was subjected to chromatography [silica gel (100–200 mesh), EtOAc–hexane, 3:1] to afford the products 4a and 4b in a 2:1 ratio as white crystalline solids (120 mg, 81% combined yield).

**4a**

White crystalline solid; mp 169–171 °C.

IR (KBr): 2929, 2918, 1447, 1379, 1247, 1153, 1072, 1037, 920 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.15 (dd, J1 = 4.2 Hz, J2 = 9.6 Hz, 1 H), 6.93 (dd, J1 = 4.2 Hz, J2 = 10.5 Hz, 1 H), 6.07 (d, J = 9.9 Hz, 1 H), 5.97 (d, J = 10.5 Hz, 1 H), 4.98–5.02 (m, 1 H), 4.56 (d, J = 8.7 Hz, 1 H), 4.17 (d, J = 4.2 Hz, 1 H), 4.05 (s, 1 H), 3.68–3.73 (m, 1 H), 3.25–3.29 (m, 1 H), 2.20–2.24 (m, 1 H), 2.04–2.11 (m, 1 H), 1.18 (s, 3 H), 0.93 (s, 3 H).

13C NMR (75 MHz, CDCl3): δ = 195.1, 193.1, 150.7, 147.6, 146.4, 128.7, 128.4, 123.9, 84.7, 77.1, 76.3, 75.0, 55.6, 40.3, 37.5, 29.4, 27.4, 21.9.

HRMS (EI): m/z calcd for C18H18O4: 298.1205; found: 298.1153.

**4b**

White crystalline solid; mp 166–168 °C.

IR (KBr): 2960, 2918, 1447, 1379, 1247, 1153, 1072, 1039, 920 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 6.96 (dd, J1 = 4.2 Hz, J2 = 10.2 Hz, 1 H), 6.64 (dd, J1 = 4.5 Hz, J2 = 9.9 Hz, 1 H), 5.93 (d, J = 10.5 Hz, 1 H), 5.84 (d, J = 10.2 Hz, 1 H), 4.71–4.74 (m, 1 H), 4.57 (d, J = 8.7 Hz, 1 H), 4.43 (s, 1 H), 4.21 (d, J = 4.2 Hz, 1 H), 3.69–3.74 (m, 1 H), 3.45–3.52 (m, 1 H), 2.29–2.39 (m, 1 H), 1.82–1.88 (m, 1 H), 1.32 (s, 3 H), 0.85 (s, 3 H).

13C NMR (75 MHz, CDCl3): δ = 196.0, 195.8, 152.0, 148.4, 146.4, 128.1, 127.4, 123.7, 84.2, 77.4, 76.8, 75.7, 57.8, 41.4, 37.3, 30.1, 27.5, 22.6.

HRMS (EI): m/z calcd for C18H18O4: 298.1205; found: 298.1168.

**Compounds 5a and 5b**

Total yield: 80%; ratio 5a:5b, 3:1.

**5a**

White crystalline solid; mp 193–195 °C.

IR (KBr): 2963, 2939, 1693, 1681,1455, 1375, 1204, 1128, 1072, 1033, 925 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = (4.5 Hz, 1 H), 6.93 (dd, J1 = 4.2 Hz, J2 = 10.5 Hz, 1 H), 6.05 (d, J = 9.6 Hz, 1 H), 5.96 (d, J = 10.8 Hz, 1 H), 4.95–4.99 (m, 1 H), 4.17 (d, J = 4.2 Hz, 1 H), 4.05 (s, 1 H), 3.76–3.79 (m, 1 H), 2.79–2.86 (m, 1 H), 2.18–2.24 (m, 1 H), 2.01–2.07 (m, 1 H), 1.48 (s, 3 H), 1.30 (s, 3 H), 0.85 (s, 3 H).

**5b**

White crystalline solid; mp 140–142 °C.

IR (KBr): 2967, 2926, 1693, 1456, 1377, 1265, 1199, 1072, 1037, 926 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 6.96 (dd, J1 = 4.2 Hz, J2 = 10.2 Hz, 1 H), 6.71 (dd, J1 = 4.5 Hz, J2 = 9.9 Hz, 1 H), 5.94 (d, J = 10.2 Hz, 1 H), 5.83 (d, J = 9.9 Hz, 1 H), 4.67–4.71 (m, 1 H), 4.42 (s, 1 H), 4.21 (d, J = 3.9 Hz, 1 H), 3.77–3.83 (m, 1 H), 2.98–3.07 (m, 1 H), 2.29–2.39 (m, 1 H), 1.79–1.86 (m, 1 H), 1.48 (s, 3 H), 1.30 (s, 3 H), 0.85 (s, 3 H).

**Compounds 6a and 6b**


**6a**

Pale-yellow crystalline solid; mp 135–137 °C.

IR (KBr): 2963, 2929, 1693, 1685, 1469, 1380, 1231, 1183, 1076, 1042, 924 cm⁻¹.

1H NMR (300 MHz, CDCl3): δ = 7.09 (dd, J1 = 4.5 Hz, J2 = 9.6 Hz, 1 H), 6.92 (dd, J1 = 4.2 Hz, J2 = 10.5 Hz, 1 H), 6.02 (d, J = 9.6 Hz, 1 H), 5.95 (d, J = 10.8 Hz, 1 H), 4.92–4.96 (m, 1 H), 4.16 (d, J = 4.2 Hz, 1 H), 4.07 (s, 1 H), 3.68–3.71 (m, 1 H), 2.97–3.05 (m, 1 H), 2.03–2.28 (m, 4 H), 1.18 (s, 3 H), 1.00–1.08 (m, 6 H), 0.92 (s, 3 H).

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**Compounds 7a and 7b**


**Compounds 9a and 9b**

Total yield: 63%; ratio 9a:9b, 1:3.

**Compounds 10a and 10b**

Total yield: 85%; ratio 10a:10b, 3:1.

**Compound 8b**

Total yield: 60%; pale-yellow crystalline solid; mp 173–175 °C.

**Compounds 10c and 10d**

Total yield: 93%; ratio 10c:10d, 1:1.
11a White crystalline solid: mp 249–252 °C.

IR (KBr): 2924, 2856, 1693, 1681, 1442, 1373, 1256, 1180, 1121, 1071, 1044, 949 cm⁻¹.

¹³C NMR (75 MHz, CDCl₃): δ = 196.1, 151.9, 148.3, 146.5, 129.2, 127.5, 123.9, 84.2, 77.2, 75.7, 70.5, 58.0, 41.5, 40.0, 32.3, 30.4, 29.8, 25.4, 21.8, 21.4.

HRMS (EI): m/z calcd for C₂₁H₂₂O₂: 338.1518; found: 338.1577.

Compounds 11a and 11b

Total yield: 84%; ratio 11a:11b, 2.9:1.

11b Pale-yellow crystalline solid; mp 163–165 °C.

IR (KBr): 2929, 2856, 1693, 1455, 1372, 1249, 1076, 1036, 1003, 986, 949 cm⁻¹.

¹³C NMR (300 MHz, CDCl₃): δ = 201.0, 193.9, 150.6, 147.5, 144.8, 129.7, 128.5, 123.9, 89.7, 77.4, 75.3, 69.9, 56.5, 47.2, 41.1, 32.3, 30.9, 29.9, 25.3, 21.6, 21.3, 20.2.

HRMS (EI): m/z calcd for C₂₂H₂₄O₂: 352.1675; found: 352.1595.

Compounds 12a and 12b

Total yield: 74%; ratio 12a:12b, 3:1:1.

12a Pale-yellow crystalline solid: mp 235–237 °C.

IR (KBr): 2934, 2856, 1686, 1452, 1376, 1256, 1070, 1037, 1018, 946 cm⁻¹.

¹³C NMR (300 MHz, CDCl₃): δ = 6.91–6.96 (m, 1 H), 6.54 (dd, J₁ = 4.5 Hz, J₂ = 9.6 Hz, 1 H), 5.87–5.89 (m, 1 H), 5.71–5.76 (m, 1 H), 4.72 (s, 1 H), 4.61 (d, J = 4.8 Hz, 1 H), 4.31 (s, 1 H), 3.72 (s, 1 H), 2.89–2.96 (m, 1 H), 2.23–2.33 (m, 2 H), 1.18–1.41 (m, 10 H).

HRMS (EI): m/z calcd for C₂₃H₂₄O₄: 376.1753; found: 376.1752.

12b Pale-yellow crystalline solid: mp 155–157 °C.

IR (KBr): 2929, 2861, 1688, 1457, 1383, 1245, 1076, 1037, 1016, 944 cm⁻¹.

¹³C NMR (300 MHz, CDCl₃): δ = 7.02 (dd, J₁ = 3.9 Hz, J₂ = 10.2 Hz, 1 H), 6.56–6.61 (m, 1 H), 5.96 (d, J = 10.5 Hz, 1 H), 5.74–5.78 (m, 1 H), 4.79 (s, 1 H), 4.65–4.68 (m, 1 H), 4.38 (s, 1 H), 3.63–3.69 (m, 1 H), 3.16–3.18 (m, 1 H), 2.29–2.39 (m, 1 H), 2.07–2.16 (m, 2 H), 1.28–1.62 (m, 10 H), 1.04–1.06 (m, 6 H).

¹³C NMR (75 MHz, CDCl₃): δ = 198.21, 196.32, 151.3, 148.5, 146.7, 129.8, 128.8, 124.2, 93.6, 77.7, 76.2, 70.8, 58.7, 44.9, 41.3, 32.6, 32.2, 31.8, 30.0, 25.7, 22.1, 21.7, 18.3, 17.7.

HRMS (EI): m/z calcd for C₂₃H₂₄O₄: 376.1753; found: 376.1752.

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References


(11) X-ray crystal data for 4b: CCDC 282936; Empirical formula C_{19}H_{18}O_{4}; Formula weight 298.32; T = 273 (2) K, λ = 0.71073 Å; Crystal system = triclinic; Space group P-1; Unit cell dimensions a = 6.5522 (11) Å, α = 97.335 (3)°, b = 8.6272 (15) Å, β = 103.040 (3)°, c = 13.763 (2) Å, γ = 102.074 (3)°; V = 728.6 (2) Å³; Z = 2; D_{calc} = 1.360 Mg/m³; Absorption coefficient 0.096 mm⁻¹; F(000) = 316; Crystal size 0.24 × 0.16 × 0.10 mm; Theta range for data collection 1.54° to 28.23°; Index ranges –8 ≤ h ≤ 7, –10 ≤ k ≤ 11, –17 ≤ l ≤ 16; Reflections collected 4440; Independent reflections 3240[R(int)] = 0.0186; Refinement method Full-matrix least-squares on F²; Data/restraints/parameters 3240/0/211; Goodness-of-fit on F² 1.046; Final R indices [1 > 2σ(I)] R1 = 0.0685, wR2 = 0.1777; R indices (all data) R1 = 0.1065, wR2 = 0.2234; Largest diff. peak and hole 0.486 and –0.287 e·Å⁻³.

(12) X-ray crystal data for 5a: CCDC 285388; Empirical formula C_{19}H_{20}O_{4}; Formula weight 312.35, T = 273 (2) K, λ = 0.71073 Å; Crystal system = orthorhombic; Space group Pbca; Unit cell dimensions a = 13.3749 (14) Å, α = 90°, b = 12.4231 (13) Å, β = 90°, c = 18.502 (2) Å, γ = 90°; V = 3074.2 (6) Å³; Z = 8; D_{calc} = 1.350 Mg/m³; Absorption coefficient 0.094 mm⁻¹; F(000) = 1328; Crystal size 0.14 × 0.14 × 0.06 mm; Theta range for data collection 2.20° to 25.00°; Index ranges –14 ≤ h ≤ 15, –14 ≤ k ≤ 14, –22 ≤ l ≤ 12; Reflections collected 14337; Independent reflections 2701 [R(int)] = 0.0533; Refinement method Full-matrix least-squares on F²; Data/restraints/parameters 2701/0/121; Goodness-of-fit on F² 1.187; Final R indices [1 > 2σ(I)] R1 = 0.0678, wR2 = 0.1324; R indices (all data) R1 = 0.0861, wR2 = 0.1399; Largest diff. peak and hole –0.243 and –0.187 e·Å⁻³.