Supporting Information

Configurationally Stable Doubly-Bridged Biphenyl Azocines via Cu-Catalyzed Double Carbene Insertions into Corresponding Azepines

Steven Harthong, Elodie Brun, Stéphane Grass, Céline Besnard, Thomas Bürgi and Jérôme Lacour

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1. $^1$H, $^{13}$C NMR and HRMS analysis

![Chemical structure](image)

$^1$H NMR (300 MHz, CDCl$_3$)

![NMR spectrum](image)

$^{13}$C NMR (75 MHz, CDCl$_3$)

![NMR spectrum](image)
Submitter: HARTHONG
Sample name: SH122
Sample number: 4261
Operator: Eliane Sandmeier
Principal investigator: Dr. Sophie Michalet
Date of reception: 27/09/11
Date of certificate: 06/10/11
Data filename: SMS10GE-110930-ES-A001
Instrument: QSTAR Pulsar (AB/MDS Sciex)
Ionisation mode: ESI (positif)

<table>
<thead>
<tr>
<th>Expected Formula</th>
<th>Observed m/z [M+H]⁺</th>
<th>Expected m/z (amu)</th>
<th>Accuracy (ppm)</th>
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<tbody>
<tr>
<td>C₂₅H₂₄N₂</td>
<td>389.2002</td>
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<td>-2.6</td>
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</table>

Chemical Formula: C₂₅H₂₄N₂
Exact Mass: 388.19365

![Mass spectrum image]
$^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (101 MHz, CDCl₃)
Expected Formula | Observed m/z \([M+H]^+\) | Expected m/z (amu) | Accuracy (ppm)
---|---|---|---
\(C_{38}H_{57}N_2O_8\) | 649.2563 | 649.2544 | 2.9

SH94.1
Chemical Formula: \(C_{39}H_{58}N_2O_8\)
Exact Mass: 648.24717
^1H NMR (400 MHz, CDCl₃)

^13C NMR (101 MHz, CDCl₃)
### UNIVERSITY OF GENEVA
Faculty of Sciences
Sciences Mass Spectrometry

**Submitter:** HARTHONG  
**Sample name:** SH94.2  
**Sample number:** 4256  
**Operator:** Eliane Sandmeier  
**Principal investigator:** Dr. Sophie Michalet

**Date of reception:** 27/09/11  
**Date of certificate:** 06/10/11  
**Data filename:** SMS10GE-110930-ES-A001  
**Instrument:** QSTAR Pulsar (AB/MDS Sciex)  
**Ionisation mode:** ESI (positive)

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<tr>
<th>Expected Formula</th>
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</table>

![Chemical Structure](image)

**Chemical Formula:** C_{39}H_{37}N_{2}O_{8}  
**Exact Mass:** 648.24717

---

![Mass Spectrogram](image)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Submitter: HARTHONG
Sample name: SH139.1
Sample number: 4258
Operator: Eliane Sandmeier
Principal investigator: Dr. Sophie Michalet

Date of reception: 27/09/11
Date of certificate: 06/10/11
Data filename: SMS10GE-I110930-ES-A001
Instrument: QSTAR Pulsar (AB/MDS Sciex)
Ionisation mode: ESI (positive)

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Chemical Formula: C_{42}H_{45}N_{2}O_{8}
Exact Mass: 704.30977

SH 139.1

- TOP MS: 5.884 to 5.960 min from Sample 12 (peak 2581) of SMS10GE-I110930-ES-A001 (recalibrated).wff
  Max. 45 signal.

 peaks:
  705.31 1(1)
  706.32 0(1)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
<table>
<thead>
<tr>
<th>Expected Formula</th>
<th>Observed m/z [M+H]^+</th>
<th>Expected m/z (amu)</th>
<th>Accuracy (ppm)</th>
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<td>C_{42}H_{45}N_{2}O_{8}</td>
<td>705.3143</td>
<td>705.3170</td>
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</table>

![Chemical Structure](image)

*Chemical Formula: C_{42}H_{45}N_{2}O_{8}*

*Exact Mass: 704.36977*
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Submitter: HARTHONG
Sample name: SH119
Sample number: 4262
Operator: Eliane Sandmeier
Principal investigator: Dr. Sophie Michalet

Date of reception: 27/09/11
Date of certificate: 06/10/11
Data filename: SMS10GE-110930-ES-A001
Instrument: QSTAR Pulsar (AB/MDS Sciex)
Ionisation mode: ESI (positive)

<table>
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<th>Expected Formula</th>
<th>Observed m/z [M+H]⁺</th>
<th>Expected m/z (amu)</th>
<th>Accuracy (ppm)</th>
</tr>
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<td>C_{25}H_{24}N_{3}O_{4}</td>
<td>402.1698</td>
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Chemical Formula: C_{25}H_{24}N_{3}O_{4}
Exact Mass: 401.16271

SH119
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Submitter: HARTHONG
Sample name: SH147
Sample number: 4260
Operator: Eliane Sandmeier
Principal investigator: Dr. Sophie Michalet
Date of reception: 27/09/11
Date of certificate: 06/10/11
Data filename: SMS10GE-110930-ES-A001
Instrument: QSTAR Pulsar (AB/MDS Sciex)
Ionisation mode: ESI (positive)

<table>
<thead>
<tr>
<th>Expected Formula</th>
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<th>Expected m/z (amu)</th>
<th>Accuracy (ppm)</th>
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<td>-0.1</td>
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Chemical Formula: C_{27}H_{28}N_{4}O_{4}
Exact Mass: 429.19401

---

Image: Mass spectrum of SH147
2. Vibrational circular dichroism (VCD)

*Experimental method.* IR and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm\(^{-1}\)) in front of the photoelastic modulator was used to enhance the signal/noise ratio. Solutions of 4 mg of (+)-4B and (-)-4B, respectively, in 200 ml CD\(_2\)Cl\(_2\) were prepared and measured in a transmission cell equipped with CaF\(_2\) windows and a 200 mm spacer. CD\(_2\)Cl\(_2\) served as reference. For both for the sample and the reference 8400 scans at 4 cm\(^{-1}\) resolution were averaged. The reference was subtracted from the sample spectrum.

*Computational method.* Density functional theory (DFT) as implemented in Gaussian03 was used to study the conformation and to calculate the corresponding IR and VCD spectra. The calculations were performed using the b3lyp functional (A.D. Becke, J.Chem.Phys. 98 (1993) 5648-5652, C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789.) and a 6-31G(d) basis set. (R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54 (1971) 724). Prior to the calculation of the spectra all degrees of freedom were completely relaxed. IR and VCD spectra were constructed from calculated dipole and rotational strengths assuming Gaussian band shape with a half-width at half-maximum of 5 cm\(^{-1}\). Frequencies were scaled by a factor of 0.96. All calculations were performed for the gas phase species.

*Conformational analysis.* Calculations were performed for the (Ra)-4B enantiomer. The doubly-bridged biphenyl framework is quite rigid. However, the four ester groups bear conformational freedom. In principle for each ester group the methyl can be oriented up or down leading to \(4^2 = 16\) conformers. Due to the symmetry of the compound some of these possibilities are identical leading to a total of 10 distinguishable conformers (see table). Based on their energy and the corresponding Boltzmann factors four conformers were identified with relative abundance of more than 10%
(according to their Boltzmann factor at 298 K). The Boltzmann average of these four conformers was compared to the experimental spectrum.

Table: Possible conformers of 4B due to the conformational freedom of the ester groups. 16 principle possibilities arise however, due to symmetry only 10 are distinguishable. The relative energy of these conformers is given as well as the corresponding fractions according to the Boltzmann factors.

<table>
<thead>
<tr>
<th>conformer</th>
<th>redundant conformer</th>
<th>Energy difference with respect to most stable conformer (kcal/mol)</th>
<th>Fraction according to Boltzmann distribution (298K)</th>
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<tbody>
<tr>
<td>ddddd</td>
<td></td>
<td>1.42</td>
<td>0.026</td>
</tr>
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<td>dddu</td>
<td></td>
<td>0.81</td>
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<tr>
<td>ddud</td>
<td></td>
<td>2.26</td>
<td>0.006</td>
</tr>
<tr>
<td>dduu</td>
<td></td>
<td>0.59</td>
<td>0.107</td>
</tr>
<tr>
<td>duud</td>
<td></td>
<td>1.67</td>
<td>0.017</td>
</tr>
<tr>
<td>dudu</td>
<td></td>
<td>0.23</td>
<td>0.195</td>
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<td>duuu</td>
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<td>0.06</td>
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<td>uudd</td>
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<td></td>
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</tr>
<tr>
<td>uudu</td>
<td>duuu</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Structure of calculated conformers
Figure: Calculated VCD spectra for the four most stable conformers of (Rα)-4B. UUUU (black trace, most stable conformer), DUUU (red trace), DUDU (green trace) and DDUU (blue trace).

Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K.

Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov,
G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y.
Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez,
3. CSP-HPLC Traces

CSP-HPLC Traces for 3a

Racemic:

Column Chiralpak IA, Hexane/i-PrOH/Ethanolamine = 98:1.998:0.002, flow 1 ml/min, 23 °C.

(+)-R<sub>R</sub>-3a:

Column Chiralpak IA, Hexane/i-PrOH/Ethanolamine = 98:1.998:0.002, flow 1 ml/min, 23 °C.
(-)-S$_2$-3a:

Column Chiralpak IA, Hexane/i-PrOH/Ethanolamine = 98:1.998:0.002, flow 1 ml/min, 23 °C.

CSP-HPLC Traces for 4B

Racemic:

Column Chiralpak IA, Hexane/i-PrOH = 80:20, flow 1 ml/min, 23 °C.
(-)-4B:
Column Chiralpak IA, Hexane/i-PrOH = 80:20, flow 1 ml/min, 23 °C.

(+)-4B:
Column Chiralpak IA, Hexane/i-PrOH = 80:20, flow 1 ml/min, 23 °C.
CSP-HPLC Traces for 5B

Racemic:
Column Chiralpak IB, Hexane/i-PrOH = 90:10, flow 1 ml/min, 23 °C.

(–)-5B:
Column Chiralpak IB, Hexane/i-PrOH = 90:10, flow 1 ml/min, 23 °C.
(+)-5B:
Column Chiralpak IB, Hexane/i-PrOH = 90:10, flow 1 ml/min, 23 °C.

Enantiospecificity
Enantioenriched $R_a$-3a:

![R-3a (ee 49%)](image)

Column Chiralpak IA, Hexane/i-PrOH/Ethanolamine = 98:1.998:0.002, flow 1 ml/min, 23 °C.
Enantioenriched (+)-4B:

Column Chiralpak IA, Hexane/i-PrOH = 80:20, flow 1 ml/min, 23 °C.

Enantioenriched (+)-5B:

Column Chiralpak IB, Hexane/i-PrOH = 90:10, flow 1 ml/min, 23 °C.
4. Racemization barrier determination of 3a

Circular dichroism “Time course” measurements were recorded at 70 °C, 75 °C, 80 °C and 85 °C during 10 min with solutions in CH\textsubscript{3}CN (1.5.10\textsuperscript{-5} M). Measurements were performed at 220 nm. The kinetic constant at each temperature was calculated considering first order kinetics.

**CD / UV compounds 3a**

![Graph showing CD / UV compounds 3a](image)

- **70 °C**
  - \( \ln([a]/[a_0]) \)
  - \( y = -5.03E-04 + 6.31E-02 \)
  - \( R^2 = 1.78E-01 \)

- **75 °C**
  - \( \ln([a]/[a_0]) \)
  - \( y = -9.04E-04 - 2.06E-01 \)
  - \( R^2 = 1.97E-01 \)

- **80 °C**
  - \( \ln([a]/[a_0]) \)
  - \( y = -2.17E-03 - 1.40E-01 \)
  - \( R^2 = 8.56E-01 \)

- **85 °C**
  - \( \ln([a]/[a_0]) \)
  - \( y = -3.12E-03 + 5.09E-02 \)
  - \( R^2 = 6.90E-02 \)
<table>
<thead>
<tr>
<th>T [°C]</th>
<th>T [K]</th>
<th>1000/T</th>
<th>k</th>
<th>ln(k)</th>
<th>R-Square</th>
<th>DG</th>
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<td>2.9142</td>
<td>-5.03E-04</td>
<td>-7.584</td>
<td>0.362</td>
<td>138.6 kJ/mol</td>
<td>1.0977 h</td>
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<tr>
<td>75</td>
<td>348.15</td>
<td>2.9723</td>
<td>-9.04E-04</td>
<td>-7.008</td>
<td>0.445</td>
<td>140.6 kJ/mol</td>
<td>0.7789 h</td>
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<tr>
<td>80</td>
<td>353.15</td>
<td>2.9317</td>
<td>-2.17E-03</td>
<td>-6.132</td>
<td>0.667</td>
<td>141.2 kJ/mol</td>
<td>0.3853 h</td>
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<tr>
<td>85</td>
<td>358.15</td>
<td>2.7921</td>
<td>-3.12E-03</td>
<td>-5.769</td>
<td>0.532</td>
<td>141.9 kJ/mol</td>
<td>0.1905 h</td>
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</tbody>
</table>

slope = \(-15.63 ± 3.57\) \(\text{kJ/mol} \cdot \text{K}^{-1}\) 
intercept = \(37.55 ± 10.10\) Ln(A)

\(E_a\) = 129.9 ± 29.7 kJ/mol \(= 31.1 ± 7.1\) kcal/mol 
\(A\) = \(3.0E+16 ± 8.1E+15\)

\(\Delta H^\# = E_a - RT\) = 127.4 ± 29.1 kJ/mol \(= 30.5 ± 7.0\) kcal/mol
\(\Delta S^\# = R \ln(A)\) = 62.3 ± 16.6 J.K\(^{-1}\).mol\(^{-1}\) \(= 14.9 ± 4.0\) cal.K\(^{-1}\).mol\(^{-1}\)
\(\Delta G^\# = RT\ln(A)\) = 108.9 ± 34.0 kJ/mol \(= 26.0 ± 8.1\) kcal/mol

![](image)
5. Enantiomerization barriers determination (VT-NMR) of 7 and 8B

Mono azepine 7

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>T [K]</th>
<th>1000/T</th>
<th>k</th>
<th>ln(k)</th>
</tr>
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<tbody>
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<td>-80</td>
<td>193</td>
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</table>

slope= -5.41 ± 0.01 \quad \text{Ea/R} \quad \text{Li}(A)
intercept= 28.82 ± 0.08

\[ T = 25 \quad ^{°}\text{C} \]

\[ E_a = 45.0 \pm 0.1 \quad \text{kJ/mol} \quad 10.8 \pm 0.0 \quad \text{kcal/mol} \]

\[ A = 3.3E+12 \pm 6.2E+09 \]

\[ \Delta H = E_a - RT \]
\[ \Delta S = R \left[ \ln \left( \frac{A}{k \cdot T} \right) \right] - 1 \]

Mono azocine 8B

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>T [K]</th>
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<th>k</th>
<th>ln(k)</th>
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</table>

slope= -7.27 ± 0.46 \quad \text{Ea/R} \quad \text{Li}(A)
intercept= 23.65 ± 1.25

\[ T = 25 \quad ^{°}\text{C} \]

\[ E_a = 60.4 \pm 3.6 \quad \text{kJ/mol} \quad 14.5 \pm 0.9 \quad \text{kcal/mol} \]

\[ A = 2.3E+10 \pm 1.2E+09 \]

\[ \Delta H = E_a - RT \]
\[ \Delta S = R \left[ \ln \left( \frac{A}{k \cdot T} \right) \right] - 1 \]

\[ \Delta G = \frac{\Delta H - \Delta S}{T} \]
6. X-ray structure determination

Data were collected on a Supernova Diffractometer using Kα radiation. Details on data collection and structure refinement can be found in Table 1. Asymmetric units, with anisotropic displacement ellipsoids depicted at 50 percent probability levels can be found in Figure 1. For 5b, a disordered cyclohexane molecule was modelled using three different molecules. The occupancy of these molecules were first refined (with restraint to make their sum equal to one) with Uiso =0.05 and then fixed to the refined value. The major component (B with occupancy 0.5) was then restrained anisotropically whereas one of the remaining component was restrained isotropically (F with occupancy 0.27) and the last one, whose displacement parameters badly behaved (D with occupancy 0.3) was refined with one isotropic displacement parameter for the whole molecule. For all these molecules restraints were applied on distances and angles and on 1-4 distances to fix the chair conformation. (Without the restraints, due to the disorder, the molecules tended to be flat).

Data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.”

<table>
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<th>CCDC number</th>
<th>3a</th>
<th>4b</th>
<th>5b</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C28H24N2</td>
<td>C38H36N2O8</td>
<td>C44H48N2O8</td>
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<tr>
<td>Formula weight</td>
<td>388.49</td>
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<tr>
<td>Temperature / K</td>
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<td>180.0</td>
</tr>
<tr>
<td>Crystal system</td>
<td>trigonal</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3c</td>
<td>C2/c</td>
<td>P-1</td>
</tr>
<tr>
<td>α/°, β/°, γ/°</td>
<td>90.00, 90.00, 120.00</td>
<td>90.00, 97.684(5), 90.00</td>
<td>113.458(4), 96.828(3), 101.427(3)</td>
</tr>
<tr>
<td>Volume / Å³</td>
<td>9322.5(3)</td>
<td>3342.3(4)</td>
<td>1894.68(12)</td>
</tr>
<tr>
<td>Z</td>
<td>18</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>ρcalc / mg mm⁻³</td>
<td>1.246</td>
<td>1.289</td>
<td>1.285</td>
</tr>
<tr>
<td>μ / mm⁻¹</td>
<td>0.556</td>
<td>0.744</td>
<td>0.714</td>
</tr>
<tr>
<td>F(000)</td>
<td>3708</td>
<td>1368</td>
<td>780</td>
</tr>
<tr>
<td>Crystal size / mm³</td>
<td>0.3 × 0.3 × 0.2</td>
<td>0.2 × 0.2 × 0.2</td>
<td>0.15×0.1×0.02</td>
</tr>
<tr>
<td>20 range for data collection</td>
<td>10.86 to 146.6°</td>
<td>8.94 to 139.9°</td>
<td>6.5 to 146.6°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-33 ≤ h ≤ 34, -30 ≤ k ≤ 32, -16 ≤ l ≤ 16</td>
<td>-19 ≤ h ≤ 19, -12 ≤ k ≤ 15, -19 ≤ l ≤ 20</td>
<td>-12 ≤ h ≤ 12, -16 ≤ k ≤ 17, -18 ≤ l ≤ 18</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2057[R(int) = 0.0203]</td>
<td>3162[R(int) = 0.0174]</td>
<td>7466[R(int) = 0.0233]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2057/0/138</td>
<td>3162/0/271</td>
<td>7466/102/534</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.044</td>
<td>1.033</td>
<td>1.023</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ(I)]</td>
<td>R1 = 0.0394, wR2 = 0.1012</td>
<td>R1 = 0.0342, wR2 = 0.0879</td>
<td>R1 = 0.0453, wR2 = 0.1281</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R1 = 0.0432, wR2 = 0.1045</td>
<td>R1 = 0.0387, wR2 = 0.0923</td>
<td>R1 = 0.0511, wR2 = 0.1352</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.158/-0.283</td>
<td>0.223/-0.166</td>
<td>0.391/-0.298</td>
</tr>
</tbody>
</table>

Table S1: Crystallographic data.
**Fig**: Asymmetric unit (anisotropic displacement ellipsoids at 50 percent probability levels)