Supporting Information

BF₃·OEt₂-Mediated Nucleophilic Fluorocyclization of Sulfonyl 3-Methylene-oxabenzocyclooctan-6-ones. Diastereocontrolled Synthesis of Benzofused Fluorooxabicyclo[4.2.1]nonanes

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Compound 4b (\(^1\)H-NMR spectral data)
Compound 4b (\(^{13}\text{C}-\text{NMR spectral data}\))

Pulse Sequence: s2pu1
UNITYplus-400 *unity400*
Date: Dec 23, 2015
Solvent: CDCl3
Ambient temperature
Total 224 repetitions

\[
\text{Me}
\]

\[
\begin{align*}
192.866 & \quad 91.698 \\
187.719 & \quad 138.483 \\
131.382 & \quad 124.382 \\
124.382 & \quad 124.382 \\
76.251 & \quad 76.251 \\
79.176 & \quad 77.318 \\
51.613 & \quad 51.613 \\
32.717 & \quad 23.717 \\
11.506 & \quad 11.506
\end{align*}
\]

ppm
Compound 4c (¹H-NMR spectral data)
Compound 4c ($^{13}$C-NMR spectral data)

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Nov 28 2019
Solvent: CDCl$_3$
Ambient Temperature
Total 256 repetitions
Compound 4d (\textsuperscript{1}H-NMR spectral data)
Compound 4d ($^{13}$C-NMR spectral data)
Compound 4e (¹H-NMR spectral data)
Compound 4e ($^{13}$C-NMR spectral data)
Compound 4f (\(^1\)H-NMR spectral data)

NC1681202
Pulse Sequence: spul
UNITYplus-400 "unity400"
Date: Dec. 3 2013
Solvent: CHCl3
Ambient Temperature
Total 32 replications

[Chemical Structure Image]

[1H-NMR Spectral Data Image]
Compound 4f ($^{13}$C-NMR spectral data)
Compound 4g (1H-NMR spectral data)
Compound 4g (\textsuperscript{13}C-NMR spectral data)
Compound 4h (¹H-NMR spectral data)
Compound 4h ($^{13}$C-NMR spectral data)

Pulse Sequence: s2pul
UNITYplus-600 "unity400"
Date: Dec 20 2010
Solvent: CDCl3
Ambient Temperature
Total 512 repetitions

[Chemical structure and $^{13}$C-NMR spectrum image]
Compound 4i (¹H-NMR spectral data)
Compound 4i ($^{13}$C-NMR spectral data)
Compound 4j (\(^1\)H-NMR spectral data)
Compound 4j ($^{13}$C-NMR spectral data)
Compound 4k (\textsuperscript{1}H-NMR spectral data)
Compound 4k ($^{13}$C-NMR spectral data)
Compound 4l (\(^1\)H-NMR spectral data)
Compound 4l ($^{13}$C-NMR spectral data)
Compound 4m (1H-NMR spectral data)
Compound 4m ($^{13}$C-NMR spectral data)
Compound 4n (¹H-NMR spectral data)
Compound 4n (\(^{13}\text{C}-\text{NMR} \) spectral data)
Compound 4o (¹H-NMR spectral data)
Compound 4o (\(^{13}\text{C}-\text{NMR}\) spectral data)
Compound 4p (¹H-NMR spectral data)
Compound 4p ($^{13}$C-NMR spectral data)
Compound 4q (¹H-NMR spectral data)
Compound 4q ($^{13}$C-NMR spectral data)
Compound 4r (¹H-NMR spectral data)
Compound 4r ($^{13}$C-NMR spectral data)
Compound 4s (¹H-NMR spectral data)
Compound 4s (\textsuperscript{13}C-NMR spectral data)
Compound 4t ($^1$H-NMR spectral data)
Compound 4t (\(^{13}\text{C}-\text{NMR spectral data}\))
Compound 4u (1H-NMR spectral data)
Compound 4u ($^{13}$C-NMR spectral data)

Pulse Sequence: s2pul
UNITYplus-400 "unity-400"
Date: Jan 3 2020
Solvent: CDCl3
Ambient temperature
Total 3584 repetitions

-181.812
-155.207
-129.966
-128.898
-127.725
-125.639
-124.298
-124.073
-76.234
-71.318
-76.482
-72.472
-33.460
-21.240
Compound 4v (¹H-NMR spectral data)
Compound 4v ($^{13}$C-NMR spectral data)
Compound 4w (¹H-NMR spectral data)

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Mar 20
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

[Chemical structure image]

[1H-NMR spectrum image]
Compound 4w ($^{13}$C-NMR spectral data)
Compound 4x (¹H-NMR spectral data)
Compound 4x ($^{13}$C-NMR spectral data)
Compound 4y (¹H-NMR spectral data)

Pulse Sequence: a2pul
UNITYplus-400 "unity400"
Date: Jan 18 2020
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

[Chemical structure image]
Compound 4y ($^{13}$C-NMR spectral data)
Compound 4z (¹H-NMR spectral data)

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Nov 6 2020
Solvent: CDCl₃
Ambient temperature
Total 32 repetitions

[Chemical structure image]

[Graph showing NMR spectral data]

ppm
Compound 4z (\(^{13}\)C-NMR spectral data)
Compound 4aa (\(^1\)H-NMR spectral data)
Compound 4aa (\(^{13}\text{C}-\text{NMR spectral data}\))
Compound 6a (\(^1\)H-NMR spectral data)
Compound 6a ($^{13}$C-NMR spectral data)
Compound 5a (¹H-NMR spectral data)
Compound 5a ($^{13}$C-NMR spectral data)

Pulse Sequence: s2pu3
UNITYplus-600 "unity400"
Date: Dec 20 2019
Solvent: CDCl₃
Ambient temperature
Total 560 repetitions

![NMR Spectrum](image)
Compound 5b (¹H-NMR spectral data)
Compound 5b (\textsuperscript{13}C-NMR spectral data)

NMR spectrum of Compound 5b showing the \textsuperscript{13}C-NMR spectral data. The spectrum includes a variety of peaks in the range of 20 to 200 ppm, indicating the presence of different carbon environments within the molecule. The peaks are labeled with their corresponding chemical shifts, providing insight into the structural details of the compound.
Compound 5c (\(^1\)H-NMR spectral data)
Compound 5c (\(^{13}\text{C}\)-NMR spectral data)
Compound 5d (¹H-NMR spectral data-1)
Compound 5d (\(^{13}\)C-NMR spectral data)
Compound 5e (¹H-NMR spectral data-1)
Compound 5e (¹H-NMR spectral data-2)
Compound 5e ($^{13}$C-NMR spectral data)
Compound 5f (\(^1\)H-NMR spectral data)
Compound 5f ($^{13}$C-NMR spectral data)
Compound 5g (\(^1\)H-NMR spectral data)
Compound 5g ($^{13}$C-NMR spectral data)

NC1130NB
Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Dec 10 2013
Solvent: CDCl3
Ambient temperature
Total 448 repetitions
Compound 5h (1H-NMR spectral data)
Compound 5h ($^{13}$C-NMR spectral data)
Compound 5i (\(^1\)H-NMR spectral data)
Compound 5i (\(^{13}\)C-NMR spectral data)
Compound 5j (¹H-NMR spectral data)
Compound 5j (\(^{13}\)C-NMR spectral data)
Compound 5k (¹H-NMR spectral data)
Compound 5k ($^{13}$C-NMR spectral data)

NC1212NR
Pulse Sequence: s2pu1
UNITYplus-400 "unity400"
Date: Dec 24 2013
Solvent: CDCl3
Ambient temperature
Total 1152 repetitions
Compound 5l ('H-NMR spectral data-1)
Compound 5l (\(^1\)H-NMR spectral data-2)
Compound 5l (\(^{13}\)C-NMR spectral data)
Compound 5m (1H-NMR spectral data)
Compound 5m ($^{13}$C-NMR spectral data)
Compound 5n (¹H-NMR spectral data-1)
Compound 5n (1H-NMR spectral data-2)
Compound 5n (\(^{13}\text{C}-\text{NMR} \) spectral data)
Compound 5o ('H-NMR spectral data-1)
Compound 5o \((^1\text{H}-\text{NMR spectral data-2})\)
Compound 5o ($^{13}$C-NMR spectral data)
Compound 5p (\(^1\text{H}-\text{NMR spectral data}\))
Compound 5p ($^{13}$C-NMR spectral data)
Compound 5q ($^1$H-NMR spectral data)
Compound 5q (\textsuperscript{13}C-NMR spectral data)
Compound 5r (1H-NMR spectral data-1)
Compound 5r (\textsuperscript{1}H-NMR spectral data-2)
Compound 5r ($^{13}$C-NMR spectral data)
Compound 5r-1 (¹H-NMR spectral data)
Compound 5r-1 (\(^{13}\text{C}\)-NMR spectral data)

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Mar 6 2020
Solvent: CDC13
Ambient temperature
Total 32000 repetitions

[Diagram of compound structure]

[Chemical shifts: 180, 160, 140, 120, 100, 80, 60, 40, 20 ppm]

S-101
Compound 5s (¹H-NMR spectral data)
Compound 5s (\(^{13}\)C-NMR spectral data)
Compound 6t (¹H-NMR spectral data)
Compound 6t ($^{13}$C-NMR spectral data)
Compound 5u ($^1$H-NMR spectral data)
Compound 5u ($^{13}$C-NMR spectral data)
Compound 5v (1H-NMR spectral data)
Compound 5v ($^{13}$C-NMR spectral data)
Compound 5y (¹H-NMR spectral data)
Compound 5y $^{13}$C-NMR spectral data

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Apr 13 2010
Solvent: CDC13
Ambient temperature
Total 9248 repetitions
Compound 7a (\textsuperscript{1}H-NMR spectral data)
Compound 7a \((^{13}\text{C}-\text{NMR spectral data})\)
Compound 7b (¹H-NMR spectral data)
Compound 7b ($^{13}$C-NMR spectral data)
Compound 9 (¹H-NMR spectral data)
Compound 9 ($^{13}$C-NMR spectral data)
X-ray crystal data of compound 4l (CCDC 2003255)

Sample preparation: A solution of compound 4l (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
Empirical formula  
Formula weight  
Temperature  
Wavelength  
Crystal system  
Space group  
Unit cell dimensions  
Volume  
Z  
Density (calculated)  
Absorption coefficient  
F(000)  
Crystal size  
Theta range for data collection  
Index ranges  
Reflections collected  
Independent reflections  
Completeness to theta = 25.242°  
Absorption correction  
Max. and min. transmission  
Refinement method  
Data / restraints / parameters  
Goodness-of-fit on F²  
Final R indices [I>2sigma(I)]  
R indices (all data)  
Extinction coefficient  
Largest diff. peak and hole  

C19 H17 F O4 S  
360.38  
113(2) K  
0.71073 Å  
Monoclinic  
P 1 21/c 1  
a = 9.0958(2) Å  
b = 11.0238(3) Å  
c = 16.3016(3) Å  
α = 90°.  
β = 98.035(2°).  
γ = 90°.  
1618.52(6) Å³  
4  
1.479 Mg/m³  
0.233 mm⁻¹  
752  
0.25 x 0.2 x 0.1 mm³  
2.237 to 26.990°.  
-11<=h<=11, -13<=k<=14, -20<=l<=20  
16444  
3383 [R(int) = 0.0259]  
100.0 %  
Semi-empirical from equivalents  
1.00000 and 0.47803  
Full-matrix least-squares on F²  
3383 / 0 / 235  
1.037  
R1 = 0.0332, wR2 = 0.0755  
R1 = 0.0415, wR2 = 0.0783  
n/a  
0.333 and -0.384 e.Å⁻³
X-ray crystal data of compound 5d (CCDC 2003256)

Sample preparation: A solution of compound 5d (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C19 H19 F O3 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>346.40</td>
</tr>
<tr>
<td>Temperature</td>
<td>113(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8.1798(3) Å</td>
</tr>
<tr>
<td>α = 88.093(4)°</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>8.2382(4) Å</td>
</tr>
<tr>
<td>β = 81.665(4)°</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>12.9438(7) Å</td>
</tr>
<tr>
<td>γ = 73.510(4)°</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>827.50(7) Å</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.390 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.220 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>364</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.3 x 0.25 x 0.25 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.578 to 27.055°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10&lt;=h&lt;=10, -10&lt;=k&lt;=7, -16&lt;=l&lt;=16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>12519</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3425 [R(int) = 0.0379]</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.00000 and 0.56378</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3425 / 0 / 219</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.060</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0375, wR2 = 0.0928</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0459, wR2 = 0.0971</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.009(2)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.300 and -0.426 e.Å⁻³</td>
</tr>
</tbody>
</table>
Sample preparation: A solution of compound 5j (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
Formula weight 194.24
Temperature 113(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions
\[ a = 10.5216(3) \, \text{Å} \quad \alpha = 114.737(2)^\circ. \]
\[ b = 14.9812(4) \, \text{Å} \quad \beta = 100.424(2)^\circ. \]
\[ c = 15.0603(3) \, \text{Å} \quad \gamma = 104.503(2)^\circ. \]
Volume 1974.08(9) Å³
Z 8
Density (calculated) 1.307 Mg/m³
Absorption coefficient 0.192 mm⁻¹
F(000) 824
Crystal size 0.2 x 0.2 x 0.15 mm³
Theta range for data collection 2.114 to 27.076°.
Index ranges
\[-13 \leq h \leq 13, \quad -18 \leq k \leq 19, \quad -19 \leq l \leq 19\]
Reflections collected 33783
Independent reflections 8215 [R(int) = 0.0422]
Completeness to theta = 25.242° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.57917
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 8215 / 0 / 493
Goodness-of-fit on F² 1.079
Final R indices [I>2sigma(I)] R1 = 0.0432, wR2 = 0.1083
R indices (all data) R1 = 0.0626, wR2 = 0.1150
Extinction coefficient n/a
Largest diff. peak and hole 0.463 and -0.462 e.Å⁻³
X-ray crystal data of compound 5l (CCDC 2003258)

**Sample preparation**: A solution of compound 5l (30 mg) in CH$_2$Cl$_2$ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

**Crystal measurement**: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
Empirical formula C19 H18 F2 O3 S
Formula weight 364.39
Temperature 113(2) K
Wavelength 0.71073 Å
Crystal system Orthorhombic
Space group P2₁2₁2₁
Unit cell dimensions
a = 5.88630(10) Å  \( \alpha = 90^\circ \)
b = 9.4890(2) Å  \( \beta = 90^\circ \)
c = 29.6414(7) Å  \( \gamma = 90^\circ \)
Volume 1655.62(6) Å³
Z 4
Density (calculated) 1.462 Mg/m³
Absorption coefficient 0.232 mm⁻¹
F(000) 760
Crystal size 0.25 x 0.25 x 0.2 mm³
Theta range for data collection 2.254 to 27.000°.
Index ranges -7≤h≤7, -12≤k≤12, -33≤l≤37
Reflections collected 31130
Independent reflections 3504 [R(int) = 0.0346]
Completeness to theta = 25.242° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.42029
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 3504 / 115 / 227
Goodness-of-fit on F² 1.034
Final R indices [I>2sigma(I)] R1 = 0.0314, wR2 = 0.0767
R indices (all data) R1 = 0.0336, wR2 = 0.0780
Absolute structure parameter 0.00(2)
Extinction coefficient n/a
Largest diff. peak and hole 0.324 and -0.282 e.Å⁻³
Sample preparation: A solution of compound 5m (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
Empirical formula  \( \text{C}_{19}\text{H}_{18}\text{Cl}\text{FO}_3\text{S} \)
Formula weight  380.84
Temperature/K  113(2)
Crystal system  monoclinic
Space group  \( \text{P2}_1/c \)
\( a/\text{Å} \)  14.9529(3)
\( b/\text{Å} \)  7.52540(10)
\( c/\text{Å} \)  15.8144(3)
\( \alpha/^\circ \)  90.00
\( \beta/^\circ \)  106.409(2)
\( \gamma/^\circ \)  90.00
Volume/Å\(^3\)  1707.06(5)
\( Z \)  4
\( \rho_{\text{calc}}/\text{g/cm}^3 \)  1.482
\( \mu/\text{mm}^{-1} \)  0.372
\( F(000) \)  792.0
Crystal size/\text{mm}^3  0.2 \times 0.2 \times 0.2
Radiation  \( \text{MoK}\alpha (\lambda = 0.71073) \)
2\( \Theta \) range for data collection/\(^\circ\)  5.32 to 52
Index ranges  \(-18 \leq h \leq 17, -9 \leq k \leq 9, -19 \leq l \leq 17 \)
Reflections collected  31146
Independent reflections  3362 [\( R_{\text{int}} = 0.0313, R_{\sigma} = 0.0181 \)]
Data/restraints/parameters  3362/0/227
Goodness-of-fit on \( F^2 \)  1.062
Final R indexes [I>=2\( \sigma \) (I)]  \( R_1 = 0.0307, wR_2 = 0.0783 \)
Final R indexes [all data]  \( R_1 = 0.0343, wR_2 = 0.0799 \)
Largest diff. peak/hole / e Å\(^3\)  0.30/-0.39
X-ray crystal data of compound 6a (CCDC 2003260)

Sample preparation: A solution of compound 6a (30 mg) in CH$_2$Cl$_2$ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
Empirical formula: C13 H16 O4 S
Formula weight: 268.32
Temperature: 113(2) K
Wavelength: 0.71073 Å
Crystal system: Monoclinic
Space group: P 1 21/n 1
Unit cell dimensions:
\[a = 8.1912(3) \text{ Å}, \quad \alpha = 90^\circ.\]
\[b = 6.0583(2) \text{ Å}, \quad \beta = 92.806(4)^\circ.\]
\[c = 25.2332(11) \text{ Å}, \quad \gamma = 90^\circ.\]
Volume: 1250.69(8) Å³
Z: 4
Density (calculated): 1.425 Mg/m³
Absorption coefficient: 0.263 mm⁻¹
F(000): 568
Crystal size: 0.25 x 0.2 x 0.2 mm³
Theta range for data collection: 2.580 to 27.034°.
Index ranges: -10≤h≤10, -7≤k≤7, -31≤l≤29
Reflections collected: 10768
Independent reflections: 2550 [R(int) = 0.0372]
Completeness to theta = 25.242°: 98.3 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.00000 and 0.47989
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 2550 / 0 / 173
Goodness-of-fit on F²: 1.195
Final R indices [I>2sigma(I)]: R1 = 0.0854, wR2 = 0.2050
R indices (all data): R1 = 0.0921, wR2 = 0.2070
Extinction coefficient: n/a
Largest diff. peak and hole: 1.228 and -0.464 e.Å⁻³
X-ray crystal data of compound 7a (CCDC 2003261)

Sample preparation: A solution of compound 7a (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_{16}H_{22}O_3S$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>294.39</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>113(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>5.5686(2)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>9.5682(3)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>15.1726(5)</td>
</tr>
<tr>
<td>$\alpha$/°</td>
<td>105.346(3)</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>92.676(2)</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>102.631(3)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>756.02(5)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$/g/cm³</td>
<td>1.293</td>
</tr>
<tr>
<td>$\mu$/mm⁻¹</td>
<td>0.219</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>316.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.15 × 0.1 × 0.1</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo Kα ($\lambda = 0.71073$)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>4.548 to 54.142</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 ≤ h ≤ 6, -12 ≤ k ≤ 11, -19 ≤ l ≤ 19</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16987</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3170 [R_{int} = 0.0451, R_{sigma} = 0.0366]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3170/0/191</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.088</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>$R_1 = 0.0572$, $wR_2 = 0.1449$</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>$R_1 = 0.0670$, $wR_2 = 0.1489$</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.61/-0.38</td>
</tr>
</tbody>
</table>
Sample preparation: A solution of compound 7b (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
<table>
<thead>
<tr>
<th><strong>Empirical formula</strong></th>
<th>C₁₈H₁₇FO₃S</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula weight</strong></td>
<td>332.38</td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>113(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>6.87130(10)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>10.4176(3)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>11.8932(3)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td>99.558(2)</td>
</tr>
<tr>
<td><strong>β/°</strong></td>
<td>105.692(2)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td>96.770(2)</td>
</tr>
<tr>
<td><strong>Volume/Å³</strong></td>
<td>796.26(3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>ρ calc/g/cm³</strong></td>
<td>1.386</td>
</tr>
<tr>
<td><strong>µ/mm⁻¹</strong></td>
<td>0.226</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>348.0</td>
</tr>
<tr>
<td><strong>Crystal size/mm³</strong></td>
<td>0.15 × 0.15 × 0.1</td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td><strong>2Θ range for data collection/°</strong></td>
<td>3.64 to 52</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>12550</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>3134 [R_int = 0.0226, Rsigma = 0.0250]</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>3134/0/209</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.076</td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;=2σ (I)]</strong></td>
<td>R₁ = 0.0416, wR₂ = 0.1025</td>
</tr>
<tr>
<td><strong>Final R indexes [all data]</strong></td>
<td>R₁ = 0.0484, wR₂ = 0.1059</td>
</tr>
<tr>
<td><strong>Largest diff. peak/hole / e Å⁻³</strong></td>
<td>0.71/-0.52</td>
</tr>
</tbody>
</table>
X-ray crystal data of compound 9 (CCDC 2008547)

Sample preparation: A solution of compound 9 (30 mg) in CH₂Cl₂ (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement: X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.
Empirical formula \( \text{C}_{19}\text{H}_{23}\text{ClO}_{4}\text{S} \)

Formula weight 389.36

Temperature/K 113(2)

Crystal system monoclinic

Space group \( \text{P2}_1/\text{n} \)

\( a/\text{Å} \) 14.5435(3)

\( b/\text{Å} \) 6.0581(2)

\( c/\text{Å} \) 20.5872(4)

\( \alpha/^\circ \) 90.00

\( \beta/^\circ \) 93.464(2)

\( \gamma/^\circ \) 90.00

Volume/\( \text{Å}^3 \) 1810.54(8)

\( Z \) 4

\( \rho_{\text{calc}} \text{g/cm}^3 \) 1.428

\( \mu/\text{mm}^{-1} \) 0.353

\( F(000) \) 825.0

Crystal size/\( \text{mm}^3 \) 0.3 \( \times \) 0.3 \( \times \) 0.2

Radiation MoK\( \alpha \) (\( \lambda = 0.71073 \))

2\( \Theta \) range for data collection/\(^\circ\) 3.96 to 54.14

Index ranges

\(-18 \leq h \leq 18, -6 \leq k \leq 7, -26 \leq l \leq 25\)

Reflections collected 38190

Independent reflections 3861 \([R_{\text{int}} = 0.0328, R_{\text{sigma}} = 0.0190]\)

Data/restraints/parameters 3861/0/231

Goodness-of-fit on \( F^2 \) 1.072

Final R indexes \([I\geq2\sigma(I)]\) \( R_1 = 0.0332, wR_2 = 0.0874 \)

Final R indexes [all data] \( R_1 = 0.0379, wR_2 = 0.0898 \)

Largest diff. peak/hole / e \( \text{Å}^{-3} \) 0.38/-0.35