Supporting Information

An Enantio- and Diastereoselective Chemoenzymatic Synthesis of α-Fluoro β-Hydroxy Carboxylic Esters

James K. Howard, Marion Müller, Alan Berry,* and Adam Nelson*

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Table of Contents

General Information 2

Cloning, expression and purification of the *trans*-o-hydroxybenzylidene pyruvate hydratase/aldolase (HBPA) from *Pseudomonas putida* 3

Substrate screen 7

Optimisation of the aldolase-catalysed reaction 8

Illustrative $^{19}$F NMR spectra of crude products of reactions 9

Key NMR data of the esters 3 10

Synthetic methods and data 11

General method and data for Mosher’s ester analysis 22

NMR Spectra of products 30

X-Ray crystallography data 66
General Information

All non-aqueous reactions were carried out under an atmosphere of nitrogen. Solvents were removed under reduced pressure using a Büchi rotary evaporator and a Vacuubrand PC2001 Vario diaphragm pump. THF and CH$_2$Cl$_2$ were dried and purified by means of a Pure Solv MD solvent purification system (Innovative Technology Inc.). All other solvents used were of chromatography or analytical grade. Commercially available starting materials were obtained from Sigma–Aldrich, Alfa Aesar and Fluorochem. Flash column chromatography was carried out using silica (35-70 μm particles) according to the method of Still, Kahn and Mitra. Thin layer chromatography was carried out on commercially available pre-coated aluminium plates (Merck silica 2880 Kieselgel 60F254).

Optical rotation measurements were carried out at the sodium D-line (589 nm) on a Schmidt + Haensch Polatronic H532 polarimeter instrument. IR spectra were recorded on a PerkinElmer One FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker MaXis Impact spectrometer with electrospray ionisation (ESI) source. $^1$H, $^{13}$C and $^{19}$F NMR spectral data were collected on a Bruker Advance500 or DPX300 spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to the residual solvent peak. Melting points were determined on a Reichert hot stage microscope and are uncorrected. X-ray crystal structures were recorded at 120K on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector and connected to an Oxford Cryostream low temperature device using mirror monochromated Cu Kα radiation (λ = 1.54184 Å) from a Microfocus Nova X-ray source. The structures were solved by direct methods using SHELXS$^1$ and refined by a full matrix least squares technique based on F$^2$ using SHELXL97.$^2$ Molecular properties were calculated with the open access web tool LLAMA (https://llama.leeds.ac.uk/).

1. W. C. Still, M. Kahn and A. Mitra, J. Org. Chem., 1978, 43, 2923.

2. G. M. Sheldrick, Acta Crystallogr. A, 2008, 64, 112-122.
Cloning, expression and purification of the trans-o-hydroxybenzylidene pyruvate hydratase/aldolase (HBPA) from Pseudomonas putida

A synthetic gene encoding the Pseudomonas putida trans-o-hydroxybenzylidene pyruvate hydratase/aldolase (HBPA) (UniProt code: Q51947) codon-optimised for expression in E. coli was obtained from GenScript (Supplementary Figure 1). The synthetic gene also encoded a N-terminal hexa-histidine tag to aid protein purification and the gene was flanked by EcoRI and PstI restriction sites upstream and downstream of the gene, respectively. The synthetic gene was digested with EcoRI and PstI and was ligated into the expression vector pKK223-3 (Pharmacia) previously digested with the same enzymes. The resulting expression plasmid was designated pKHBA (Supplementary Figure 2) and was transformed into E. coli BL21(DE3).

For expression, cells containing the expression plasmid were grown overnight in 2 × YT media (16 g/L tryptone, 10 g/L yeast extract and 5 g/L sodium chloride) supplemented with 50 µg/mL ampicillin. This culture was then used to inoculate 1L of the same medium and the culture was grown to an optical density (OD_{600nm}) of 0.5-0.7. IPTG was then added to a final concentration of 0.1 mM and growth was continued for a further 17 h at 37 °C. Cells were harvested by centrifugation (12,000 g for 70 min at 4 °C) and were stored at −80 °C until further use. Frozen cells from 1 L of culture were suspended in 40 ml of 50 mM Tris-HCl buffer (pH 7.4) containing 500 mM NaCl and 20 mM imidazole. The cells were then lysed at 30 Kpsi using a Constant Cell Disruption System. Cell debris was removed by centrifugation (21,000 g for 70 min at 4 °C). The supernatant was added to nickel-loaded chelating Sepharose fast flow resin (~ 5 ml) in a 50 ml Falcon tube and the resin was gently agitated for 1 h at 4 °C before centrifugation (3,250 g for 5 min). The resin was subsequently washed four times with wash buffer (50 mM Tris-HCl buffer, pH 7.4 containing 500 mM NaCl and 20 mM imidazole) before elution of the enzyme with ~175 ml of 50 mM Tris-HCl buffer (pH 7.4) containing 500 mM NaCl and 500 mM imidazole. The eluted protein was then dialysed overnight at 4 °C against 25 mM MES buffer (pH 6.0). The eluted protein was shown to be partially-purified by SDS-PAGE (Supplementary Figure 3) and ESI-MS (Supplementary Figure 4) analysis demonstrated that the purified protein had a molecular mass of 37588.3 Da compared with the expected molecular mass of 37588.9 Da deduced from the amino acid sequence (Supplementary Figure 5).
**Supplementary Figure 1.** Gene sequence, adapted to the bias of *E. coli*, encoding the *Pseudomonas putida* trans-o-hydroxybenzylidene pyruvate hydratase aldolase (HBPA). The sequence also contains information for a N-terminal hexa-histidine tag (blue).
Supplementary Figure 2. Plasmid map of pKHBPA derived from pKK223-3 containing the gene for HBPA. Additionally the plasmid contains the IPTG inducible tac promoter, two rrnB terminators, an ampicillin resistance marker, and the pBR322 origin of replication.

Supplementary Figure 3. SDS-PAGE analysis of the stages of nickel purification of HBPA. Lane 1: soluble cell fraction, lane 2: protein standard, lane 3: non-resin bound protein, lane 4: 1st wash step, lane 5: 2nd wash step, lane 6: 3rd wash step, lane 7: 4th wash step, lane 8: 1st elution step, lane 9: 2nd elution step and lane 10: both elution steps combined.
**Supplementary Figure 4.** Deconvoluted ESI-MS spectrum illustrating the observed mass of 37,588 for partially-purified *P. putida* HBPA.

**Supplementary Figure 5.** Amino acid sequence for *P. putida* HBPA.
Substrate screen

Screen conditions: In an NMR tube, β-fluoropyruvic acid sodium salt (0.25 mmol in 12.5 mM aq. MES buffer, final conc. 25 mM) followed by aldehyde (0.55 mmol in 25 mM aq. MES buffer, final conc. 27.5 mM) was added to trans-ortho-hydroxybenzylidene.pyruvate hydratase aldolase (1 mg/mL enzyme in 25 mM MES buffer, pH 6.0, final vol. 1 mL), and the reaction mixture was left to stand at r.t. for 24 h. Conversions were measured on analysis of the $^{19}$F NMR spectrum of the reaction at 24 h by integration of those resonances corresponding to both the keto and hydrate forms of the products compared to the keto and hydrate form of residual fluoropyruvate.

Supplementary Table 1: Conversions of Aldolase reaction for those aldehyde substrates screened.

| Entry | Aldehyde | Conversion after 24 h | Entry | Aldehyde | Conversion after 24 h | Entry | Aldehyde | Conversion after 24 h |
|-------|----------|----------------------|-------|----------|----------------------|-------|----------|----------------------|
| 1     | ![1a](image) | 96%                  | 12    | ![1l](image) | 95%                  | 26    | ![1w](image) | 4%                   |
| 2     | ![1b](image) | 92%                  | 13    | ![1m](image) | 84%                  | 27    | ![1x](image) | 15%                  |
| 3     | ![1c](image) | 79%                  | 14    | ![1n](image) | 82%                  | 28    | ![1y](image) | 37%                  |
| 4     | ![1d](image) | 91%                  | 15    | ![1o](image) | 11%                  | 26    | ![1z](image) | 9%                   |
| 5     | ![1e](image) | 58%                  | 16    | ![1p](image) | 6%                   | 27    | ![1aa](image) | 0%                   |
| 6     | ![1f](image) | 92%                  | 17    | ![1q](image) | 0%                   | 28    | ![1ab](image) | 0%                   |
| 7     | ![1g](image) | 91%                  | 18    | ![1r](image) | 26%                  | 29    | ![1ac](image) | 46%                  |
| 8     | ![1h](image) | 77%                  | 19    | ![1s](image) | 23%                  | 30    | ![1ad](image) | 42%                  |
| 9     | ![1i](image) | 77%                  | 20    | ![1t](image) | 7%                   |       |          |                      |
| 10    | ![1j](image) | 76%                  | 21    | ![1u](image) | 0%                   |       |          |                      |
| 11    | ![1k](image) | 78%                  | 22    | ![1v](image) | 86%                  |       |          |                      |
Optimisation of the aldolase-catalysed reaction

**Supplementary Table 2:** Conditions examined for the aldolase-catalysed reaction

![Chemical reaction diagram](attachment:image.png)

| Entry | Pyruvate Equiv. | Aldehyde Equiv. | [Enzyme] (mg/mL) | Solvent | Conversion % |
|-------|-----------------|-----------------|------------------|---------|--------------|
| 1     | 1.0             | 2.0             | -                | 25mM MES buffer | <1%          |
| 2     | 1.0             | 2.0             | 1.00             | 25mM MES buffer | 92%          |
| 3     | 1.0             | 1.1             | 1.00             | 25mM MES buffer | 92%          |
| 4     | **1.0**         | **1.1**         | **0.20**         | 25mM MES buffer | **89%**      |
| 5     | 1.0             | 1.1             | 0.05             | 25mM MES buffer | 40%          |
| 6     | **1.0**         | **1.1**         | **0.20**         | DMSO: 25mM MES buffer (10:90) | **85%**     |
| 7     | 1.0             | 1.1             | 0.20             | DMSO: 25mM MES buffer (20:80) | 83%          |
| 8     | 1.0             | 1.1             | 0.20             | DMSO: 25mM MES buffer (50:50) | 16%          |
| 9     | 1.0             | 1.1             | 0.20             | EtOH: 25mM MES buffer (10:90) | 13%          |
| 10    | 1.0             | 1.1             | 0.20             | EtOH: 25mM MES buffer (20:80) | 1%           |
| 11    | 1.0             | 1.1             | 0.20             | EtOH: 25mM MES buffer (50:50) | <1%          |
| 12    | 1.0             | 1.1             | 0.20             | THF: 25mM MES buffer (10:90) | 14%          |
| 13    | 1.0             | 1.1             | 0.20             | THF: 25mM MES buffer (20:80) | 1%           |
| 14    | 1.0             | 1.1             | 0.20             | THF: 25mM MES buffer (50:50) | <1%          |
Supplementary Figure 6: Panel A: 282 MHz $^{19}$F spectrum of fluoropyruvate in its keto and hydrated forms in 25 mM pH 6.0 MES buffer. Panel B: Addition of 0.1 mol% HBPA results, after 24 hr, in the appearance of double doublets corresponding to the keto and hydrated forms of the major (93%) and minor (7%) diastereomers 5f. Panel C: Addition of H$_2$O$_2$ results in a dramatic simplification of the spectrum, with single double doublet resonances corresponding to each diastereomer 6f. Panel D: Purified ester 3f.
### Key NMR data of the esters 3

#### Supplementary Table 3: NMR data for the syn-diastereomers

| Compound | \( \delta F \) | \( \delta 2-\text{H} \) | \( \delta 3-\text{H} \) | \( ^2J_{HF} \) | \( ^3J_{HF} \) | \( ^3J_{HH} \) |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|
| 3a       | -206.9         | 5.34           | 5.34           | 47.4           | 24.3           | 2.4            |
| 3b       | -201.1         | 5.14           | 5.27           | 48.2           | 22.8           | 4.3            |
| 3c       | -202.1         | 5.10           | 5.25           | 48.0           | 23.1           | 4.0            |
| 3d       | -206.7         | 5.25           | 5.23           | 47.9           | 22.6           | 2.4            |
| 3e       | -203.8         | 4.99           | 5.18           | 47.7           | 23.7           | 3.4            |
| 3f       | -203.8         | 5.05           | 5.17           | 47.9           | 23.1           | 3.0            |
| 3g       | -206.7         | 5.25           | 5.25 – 5.13    | 46.9           | 24.4           | 2.4            |
| 3h       | -207.3         | 5.29           | 5.22           | 46.9           | 24.7           | 2.2            |
| 3i       | -205.8         | 5.13 – 5.55    |                | 47.9           | 25.4           | n.m.           |
| 3j       | -206.6         | 5.36 – 5.13    |                | 45.1           | 22.6           | n.m.           |
| 3k       | -206.4         | 5.29           | 5.22           | 47.9           | 24.7           | 2.7            |
| 3l       | -206.4         | 5.10           | 5.26           | 47.9           | 25.4           | 2.5            |
| 3m       | -206.4         | 5.36           | 5.38           | 47.9           | 22.6           | 2.7            |
| 3n       | -206.9         | 5.40           | 5.50           | 46.8           | 24.4           | 2.3            |

#### Supplementary Table 4: NMR data for the anti-diastereomers

| Compound | F     | \( ^2J_{HF} \) | \( ^3J_{HF} \) | \( ^3J_{HH} \) |
|----------|-------|----------------|----------------|----------------|
| 3a’      | n.m.  | n.m.           | n.m.           | n.m.           |
| 3b’      | n.m.  | n.m.           | n.m.           | n.m.           |
| 3c’      | n.m.  | n.m.           | n.m.           | n.m.           |
| 3d’      | -197.4| 46.2           | 18.0           |                |
| 3e’      | -198.0| 48.2           | 17.7           |                |
| 3f’      | -196.5| 47.9           | 15.5           |                |
| 3g’      | -197.7| 48.5           | 16.2           |                |
| 3h’      | -197.6| 48.4           | 16.3           |                |
| 3i’      | n.m.  | n.m.           | n.m.           | n.m.           |
| 3j’      | -199.9| 45.1           | 16.9           |                |
| 3k’      | -199.7| 47.9           | 19.7           |                |
| 3l’      | n.m.  | n.m.           | n.m.           | n.m.           |
| 3m’      | -198.6| 47.9           | 19.7           |                |
| 3n’      | -197.5| 47.7           | 17.2           |                |

n.m. = not measurable
Synthetic Methods and data

General procedure A: β-fluoropyruvic acid sodium salt (0.50 mmol in 25 mM aq. MES buffer, final conc. 25 mM) followed by aldehyde (0.55 mmol in 25 mM aq. MES buffer, final conc. 27.5 mM) was added to trans-ortho-hydroxybenzylidenepyruvate hydratase aldolase (250 μg/mL enzyme in 25 mM MES buffer, pH 6.0, final vol. 20 mL), and the reaction mixture was left to stand at r.t. for 24 h before the addition of solution of H₂O₂ (30% aq. solution, 150 μL). After 30 min of vigorous stirring, the reaction mixture was cooled to 0 °C and Na₂S₂O₅ (solid) was slowly added, before the water was removed in vacuo to reveal a crude product. SOCl₂ (200 μL, 1.03 mmol) was slowly added to a suspension of the crude product in EtOH (10 mL) at 0 °C and stirred at r.t. for 4 h before being cooled to 0 °C and made alkaline with NaHCO₃ (sat. aq. sol). The resulting mixture was extracted with EtOAc (3 × 10 mL), the combined organic layers were washed with H₂O (2 × 30 mL), dried (MgSO₄), filtered and concentrated in vacuo to reveal a crude product.

General procedure B: Modified General Procedure A, where aldehyde was dissolved in 1 mL DMSO and added to the biotransformation.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(2-pyrazinyl)propionate (3a)

Produced by general procedure A, followed by purification by flash chromatography eluting with 55:45 EtOAc—Hexane to yield the propionate 3a (76.0 mg, 71%, d.r. >98:<2) as a colourless solid (compound crystallised as colourless plates from Et₂O/pentane). m.p. 73-75 °C; Rf 0.30 (55:45 EtOAc—Hexane); [α]²³_D +91.2 (MeOH, c 1.8); syn: ¹⁹F NMR (282 MHz, CDCl₃) δ −206.9 (dd, ²JHF 47.4 and ³JHF 24.3); ¹H NMR (300 MHz, CDCl₃) δ 8.81 (1H, s, pyrazine 3-H), 8.57-8.54 (2H, m, pyrazine 5-H and pyrazine 6-H), 5.34 (1H, dd, ²JHF 47.4 and ³JHF 24.3, 2-H), 5.34 (1H, dd, ²JHF 24.3 and ³JHF 24.3, 3-H), 4.31 (2H, q, ³JHF 7.2, ethyl 1-H₂), 1.30 (3H, t, ³JHF 7.2, ethyl 2-H₂), ¹³C NMR (75 MHz, CDCl₃) δ 167.4 (d, ²JCF 24.0, C-1), 152.7 (d, ¹JCF 1.9, pyrazine C-2), 144.3 (s, pyrazine C-5), 143.4 (s, pyrazine C-3), 143.3 (s, pyrazine C-6), 90.3 (d, ¹JCF 191.1, C-2), 72.2 (d, ²JCF 20.5, C-3), 62.2 (s, ethyl C-1), 14.2 (s, ethyl C-2); νmax/cm⁻¹ (ATR) 3215, 2983, 1737, 1402, 1209, 1068, 1018; HRMS (ESI) m/z [M+H] calcd for C₉H₁₂FN₃O₃: 215.082647, found: 215.082572, 0.3 ppm error.
(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(o-hydroxyphenyl)propionate (3b)

Produced by general procedure A on a 0.25 mmol scale, followed by purification by flash chromatography eluting with 30:70 EtOAc—Hexane to yield the propionate 3b (40.3 mg, 71%, d.r. >98:<2) as a colourless oil. R<sub>f</sub> 0.30 (30:70 EtOAc—Hexane); [α]<sup>D</sup> +59.1 (MeOH, c 0.33); syn: <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ −201.1 (dd, <sup>2</sup>J<sub>HF</sub> 48.2 and <sup>3</sup>J<sub>HF</sub> 22.8); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.40 (1H, br s, Ar OH), 7.19 (1H, dt, <sup>3</sup>J<sub>HH</sub> 7.8 and <sup>4</sup>J<sub>HH</sub> 1.5, Ar 4-H), 7.09-7.06 (1H, m, Ar 6-H), 6.89-6.84 (2H, m, Ar 3-H and Ar 5-H), 5.27 (1H, dd, <sup>3</sup>J<sub>HF</sub> 22.8 and <sup>3</sup>J<sub>HH</sub> 4.3, 3-H), 5.14 (1H, dd, <sup>2</sup>J<sub>HF</sub> 48.2 and <sup>3</sup>J<sub>HH</sub> 4.3, 2-H), 4.24-4.13 (2H, m, ethyl 1-H<sub>2</sub>), 1.19 (3H, t, <sup>3</sup>J<sub>HH</sub> 7.2, ethyl 2-H<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.1 (d, <sup>2</sup>J<sub>CF</sub> 24.0, C-1), 155.3 (s, Ar C-2), 130.0 (s, Ar C-4), 127.9 (s, Ar C-6), 122.0 (d, <sup>3</sup>J<sub>CF</sub> 3.7, Ar C-1), 120.4 (s, Ar C-5), 117.0 (s, Ar C-3), 91.0 (d, <sup>1</sup>J<sub>CF</sub> 189.7, C-2), 73.9 (d, <sup>2</sup>J<sub>CF</sub> 21.0, C-3), 62.2 (s, ethyl C-1), 13.9 (s, ethyl C-2); ν<sub>max</sub>/cm<sup>−1</sup> (ATR) 3383, 2982, 1736, 1457; HRMS (ESI) m/z [M+Na] calcd for C<sub>11</sub>H<sub>13</sub>FNaO<sub>4</sub>: 251.069008, found: 251.069201, 0.8 ppm error.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(5-chloro-o-hydroxyphenyl)propionate (3c)

Produced by general procedure B, followed by purification by flash chromatography eluting with 20:80 EtOAc—Hexane to yield the propionate 3c (77.8 mg, 60%, d.r. >98:<2) as a colourless amorphous solid. R<sub>f</sub> 0.30 (20:80 EtOAc—Hexane); [α]<sup>D</sup> +60.3 (MeOH, c 1.0); syn: <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ −202.1 (dd, <sup>2</sup>J<sub>HF</sub> 48.0 and <sup>3</sup>J<sub>HF</sub> 23.1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.14 (1H, dd, <sup>4</sup>J<sub>HH</sub> 2.6, Ar H-6), 6.78 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.6, Ar 3-H), 5.25 (1H, dd, <sup>3</sup>J<sub>HF</sub> 23.1 and <sup>3</sup>J<sub>HH</sub> 4.0, 3-H), 5.10 (1H, dd, <sup>2</sup>J<sub>HF</sub> 48.0 and <sup>3</sup>J<sub>HH</sub> 4.0, 2-H), 4.23 (2H, q, <sup>3</sup>J<sub>HH</sub> 7.1, ethyl 1-H<sub>2</sub>), 1.23 (3H, t, <sup>3</sup>J<sub>HH</sub> 7.2, ethyl 2-H<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.0 (d, <sup>2</sup>J<sub>CF</sub> 24.3, C-1), 153.8 (s, Ar C-2), 129.7 (s, Ar C-4), 127.6 (s, Ar C-6), 125.2 (s, Ar C-5), 123.8 (d, <sup>3</sup>J<sub>CF</sub> 3.3, Ar C-1), 118.3 (s, Ar C-3), 90.7 (d, <sup>1</sup>J<sub>CF</sub> 191.6, C-2), 73.0 (d, <sup>2</sup>J<sub>CF</sub> 20.7, C-3), 62.5 (s, ethyl C-1), 14.0 (s, ethyl C-2); ν<sub>max</sub>/cm<sup>−1</sup> (ATR) 2984, 1734, 1420, 1211, 1104, 817; HRMS (ESI) m/z [M+Na] calcd for C<sub>11</sub>H<sub>12</sub>ClFNaO<sub>4</sub>: 285.030035, found 285.030273, −0.8 ppm error.
(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(2-pyridyl)propionate (3d)

Produced by general procedure A, followed by purification by flash chromatography eluting with 60:40 EtOAc—Hexane to yield the propionate 3d (53.9 mg, 51%, d.r. 93:7) as a colourless oil. $R_f$ 0.30 (60:40 EtOAc—Hexane); $\left[\alpha\right]_D^{21} +84.9$ (MeOH, c 1.6); anti: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −197.4 (dd, $^2J_{HF}$ 46.2 and $^3J_{HF}$ 18.0); syn: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −206.7 (dd, $^2J_{HF}$ 47.9 and $^3J_{HF}$ 22.6); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.56-8.53 (1H, m, pyridine 6-H), 7.73 (1H, td, $^3J_{HH}$ 7.8 and $^4J_{HH}$ 1.7, pyridine 4-H), 7.43 (1H, d, $^3J_{HH}$ 7.8, pyridine 3-H), 7.27-7.23 (1H, m, pyridine 5-H), 5.25 (1H, dd, $^2J_{HF}$ 47.4 and $^3J_{HH}$ 2.4, 2-H), 5.23 (1H, dd, $^3J_{HH}$ 24.6 and $^3J_{HH}$ 2.4, 3-H), 4.27 (2H, apparentqd, $^3J_{HH}$ 7.2 and $^3J_{HH}$ 1.2, ethyl 1-H$_2$), 1.27 (3H, t, $^3J_{HH}$ 7.2, ethyl 2-H$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.6 (d, $^2J_{CF}$ 24.0, C-1), 156.2 (d, $^3J_{CF}$ 1.5, pyridine C-2), 148.5 (s, pyridine C-6), 137.1 (s, pyridine C-4), 123.3 (s, pyridine C-5), 120.9 (s, pyridine C-3), 90.8 (d, $^1J_{CF}$ 190.5, C-2), 72.9 (d, $^2J_{CF}$ 20.2, C-3), 61.9 (s, ethyl C-1), 14.1 (s, ethyl C-2); $\nu_{max}$/cm$^{-1}$ 3169, 2984, 1738, 1593, 1208, 1063; HRMS (ESI) $m/z$ [M+H] calcd for C$_{16}$H$_{13}$FNO$_3$: 214.087398, found 214.087735, −1.6 ppm error.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(3-pyridyl)propionate (3e)

Produced by general procedure A, followed by purification by flash chromatography eluting with EtOAc to yield the propionate 3e (31.0 mg, 29%, d.r. 83:17) as a colourless oil. $R_f$ 0.35 (EtOAc); $\left[\alpha\right]_D^{21} +48.2$ (MeOH, c 0.9); anti: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −198.0 (dd, $^2J_{HF}$ 48.2 and $^3J_{HF}$ 17.7); syn: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ −203.8 (dd, $^2J_{HF}$ 47.7 and $^3J_{HF}$ 23.7); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.56-8.43 (2H, m, pyridine 2-H and pyridine 6-H), 7.86-7.76 (1H, m, pyridine 4-H), 7.33-7.27 (1H, m, pyridine 5-H), 5.18 (1H, dd, $^3J_{HH}$ 23.7 and $^3J_{HH}$ 3.4, 3-H), 4.99 (1H, dd, $^2J_{HF}$ 47.7 and $^3J_{HH}$ 3.4, 2-H), 4.22 (2H, apparentqd, $^3J_{HH}$ 7.2 and $^3J_{HH}$ 1.5, ethyl 1-H$_2$), 1.22 (3H, t, $^3J_{HH}$ 7.2, ethyl 2-H$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.6 (d, $^2J_{CF}$ 24.0, C-1), 149.2 (s, pyridine C-6), 147.8 (s, pyridine C-2), 135.2 (s, pyridine C-4), 134.8 (d, $^3J_{CF}$ 3.0, pyridine C-3), 123.7 (s, pyridine C-5), 91.4 (d, $^1J_{CF}$ 192.0, C-2), 71.6 (d, $^2J_{CF}$ 19.5, C-3), 62.1 (s, ethyl C-1), 14.1 (s, ethyl C-2); $\nu_{max}$/cm$^{-1}$ (ATR) 3098, 2984, 1738, 1427, 1210, 1027, 729; HRMS (ESI) $m/z$ [M+H] calcd for C$_{16}$H$_{13}$FNO$_3$: 214.087398, found 214.087074, −1.5 ppm error.
(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(4-pyridyl)propionate (3f)

Produced by general procedure A, followed by purification by flash chromatography eluting with EtOAc to yield the propionate 3f (61.1 mg, 57%, d.r. 90:10) as an off white amorphous solid (compound crystallised as colourless plates from Et2O/pentane). m.p. 58-61 °C; Rf 0.25 (EtOAc); [α]D22 +42.1 (MeOH, c 2.1); anti: 19F NMR (282 MHz, CDCl3) δ −196.5 (dd, 8JHF 47.9 and 9JHF 15.5); syn: 19F NMR (282 MHz, CDCl3) δ −204.2 (dd, 8JHF 47.4 and 9JHF 23.1); 1H NMR (500 MHz, CDCl3) δ 8.57 (2H, d, JHH 5.1, pyridine 2-H and pyridine 6-H), 7.37 (2H, d, JHH 5.3, pyridine 3-H and pyridine 5-H), 5.17 (1H, dd, JHH 23.1 and JHH 3.0, 3-H), 5.05 (1H, dd, 8JHF 47.4 and 9JHF 3.0, 2-H), 4.31-4.22 (2H, m, ethyl 1-H2), 1.26 (3H, t, JCH 7.0, ethyl 2-H3); 13C NMR (75 MHz, CDCl3) δ 167.5 (d, 8JCF 24.0, C-1), 149.8 (s, pyridine C-2 and pyridine C-5), 147.8 (s, pyridine C-4), 121.6 (s, pyridine C-3 and pyridine C-5), 90.8 (d, JCF 192.7, C-2), 72.5 (d, JCF 20.2, C-3), 62.3 (s, ethyl C-1), 14.1 (s, ethyl C-2); νmax/cm−1 (ATR) 3087, 2985, 1756, 1605, 1214, 1062; HRMS (ESI) m/z [M+H]+ calcd for C16H13FNO: 214.087398, found: 214.087106, −1.4 ppm error.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(5-bromo-pyridin-2-yl)propionate (3g)

Produced by general procedure B, followed by purification by flash chromatography eluting with 30:70 EtOAc—Hexane to yield the propionate 3g (110.5 mg, 76%, d.r. 94:6) as a colourless amorphous solid. Rf 0.35 (30:70 EtOAc—Hexane); [α]D26 +71.1 (MeOH, c 1.1); anti: 19F NMR (282 MHz, CDCl3) δ −197.7 (dd, 8JHF 48.5 and 9JHF 16.2); syn: 19F NMR (282 MHz, CDCl3) δ −206.7 (dd, 8JHF 46.9 and 9JHF 24.4); 1H NMR (300 MHz, CDCl3) δ 8.62 (1H, dd, 8JHH 2.3 and 9JHH 0.7, pyridine 6-H), 7.86 (1H, dd, 8JHH 8.4 and 9JHH 2.3, pyridine 4-H), 7.37 (1H, dd, 8JHH 8.4 and 9JHH 0.7, pyridine 3-H), 5.25 (1H, dd, 8JHH 46.9 and 9JHH 2.4, 2-H), 5.25-5.13 (1H, m, 3-H), 4.29 (2H, apparent qd, 3JHH 7.2 and JHH 0.8, ethyl 1-H2), 4.18 (1H, bd, 3JHH 8.0, OH), 1.29 (3H, t, 3JHH 7.2, ethyl 2-H3); 13C NMR (75 MHz, CDCl3) δ 167.6 (d, 8JCF 24.6, C-1), 155.3 (d, 3JCF 2.4, pyridine C-2), 149.8 (s, pyridine C-6), 139.7 (s, pyridine C-4), 122.4 (s, pyridine C-3), 120.2 (s, pyridine C-5), 90.4 (d, 1JCF 192.1, C-2), 72.9 (d, 2JCF 21.0, C-3), 62.1 (s, ethyl C-1), 14.1 (s, ethyl C-2); νmax/cm−1 (ATR) 2982, 1738, 1466, 1210, 1064, 1008; HRMS (ESI) m/z [M+H]+ calcd for C16H12BrFNO3: 291.997910, found 291.997864, 0.2 ppm error.
(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(4-chloro-pyridin-2-yl)propionate (3h)

Produced by general procedure B, followed by purification by flash chromatography eluting with 30:70 EtOAc—Hexane to yield the propionate 3h (46.5 mg, 38%, d.r. 92:8) as a colourless amorphous solid. Rt 0.30 (30:70 EtOAc—Hexane); [α]D 27 +75.6 (MeOH, c 1.9); anti: 19F NMR (282 MHz, CDCl3) δ −197.6 (dd, 2JHF 48.4 and 3JHF 16.3); syn: 19F NMR (282 MHz, CDCl3) δ −207.3 (dd, 2JHF 46.9 and 3JHF 24.7); 1H NMR (300 MHz, CDCl3) δ 8.46 (1H, d, 3JHH 5.2, pyridine 6-H), 7.50 (1H, d, 4JHH 1.9, pyridine 3-H), 7.27 (1H, dd, 3JHH 5.2 and 4JHH 1.9, pyridine 5-H), 5.29 (1H, dd, 2JHF 46.9 and 3JHH 2, 2-H), 5.22 (1H, dd, 3JHF 24.7 and 3JHH 2, 2-H), 4.30 (2H, apparent qd, 3JHH 7.2 and JHH 1.0, ethyl 1-H2), 1.30 (3H, t, 3JHH 7.2, ethyl 2-H3); 13C NMR (75 MHz, CDCl3) δ 167.6 (d, 2JCF 24.6, C-1), 158.5 (d, 3JC5 2.0, pyridine C-2), 149.5 (s, pyridine C-6), 145.3 (s, pyridine C-4), 123.7 (s, pyridine C-3), 121.6 (s, pyridine C-5), 90.5 (d, 1JCF 192.2, C-2), 73.0 (d, 2JCF 20.6, C-3), 62.1 (s, ethyl C-1), 14.1 (s, ethyl C-2); νmax/cm−1 (ATR) 2983, 1738, 1578, 1373, 1212, 1064; HRMS (ESI) m/z [M+H] calcd for C10H13ClFNO3: 248.04826, found 248.048565, 0.6 ppm error.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(2-quinolyl)propionate (3i)

Produced by general procedure B, followed by purification by flash chromatography eluting with 20:80 EtOAc—Hexane to yield the propionate 3i (33.1 mg, 25%, d.r. >98:<2) as an orange amorphous solid. Rt 0.25 (20:80 EtOAc—Hexane); [α]D 27 +25.8 (MeOH, c 2.0); syn: 19F NMR (282 MHz, CDCl3) δ −205.8 (dd, 2JHF 47.9 and 3JHF 25.4); 1H NMR (300 MHz, CDCl3) δ 8.21 (1H, d, 3JHH 8.5, quinoline 4-H), 8.08 (1H, dd, 3JHH 8.5 and 4JHH 1.2, quinoline 8-H), 7.84 (1H, dd, 3JHH 8.2 and 4JHH 1.5, quinoline 5-H), 7.74 (1H, dd, 3JHH 8.5, 3JHH 7.0 and 4JHH 1.5, quinoline 7-H), 7.57 (1H, ddd, 3JHH 8.2, 3JHH 7.0 and 4JHH 1.2, quinoline 6-H), 7.48 (1H, d, 3JHH 8.5, quinoline 3-H), 5.13-5.55 (2H, m, 2-H and 3-H), 4.32 (2H, apparent qd, 3JHH 7.1 and JHH 1.0, ethyl 1-H2), 1.29 (3H, t, 3JHH 7.1, ethyl 2-H3); 13C NMR (75 MHz, CDCl3) δ 167.6 (d, 2JCF 24.0, C-1), 155.8 (d, 2JCF 1.5, quinoline C-2), 146.6 (s, quinoline C-9), 137.6 (s, quinoline C-4), 130.2 (s, quinoline C-8), 129.0 (s, quinoline C-7), 127.9 (s, quinoline C-10), 127.7 (s, quinoline C-5), 127.0 (s, quinoline C-6), 118.1 (s, quinoline C-3), 90.5 (d, 1JCF 192.7, C-2), 72.9 (d, 2JCF 21.0, C-3), 62.0 (s, ethyl C-1), 14.2 (s, ethyl C-2); νmax/cm−1 (ATR) 3285, 1737, 1329; HRMS (ESI) m/z [M+H] calcd for C14H13FNO3: 264.103048, found 264.103252, −0.8 ppm error.
(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(1,3-oxazol-4-yl)propionate (3j)

Produced by general procedure A, followed by purification by flash chromatography eluting with 45:55 EtOAc—Hexane to yield the propionate 3j (42.9 mg, 43%, d.r. 94: 6) as a colourless oil. Rf 0.30 (45:55 EtOAc—Hexane); [α]_D^20 +49.8 (MeOH, c 0.7); anti: ¹⁹F NMR (282 MHz, CDCl₃) δ −199.9 (dd, ²J_HF 45.1 and ³J_HF 16.9); syn: ¹⁹F NMR (282 MHz, CDCl₃) δ −206.6 (dd, ²J_HF 45.1 and ³J_HF 22.6); ¹H NMR (300 MHz, CDCl₃) δ 7.89 (1H, d, ⁴J_HH 1.1, oxazole 2-H), 7.74-7.73 (1H, m, oxazole 5-H), 5.36-5.13 (2H, m, 2-H and 3-H), 4.29 (2H, q, ³J_HF 7.1, ethyl 1-H), 3.64 (1H, br s, OH), 1.29 (3H, t, ³J_HH 7.1, ethyl 2-H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6 (d, ²J_CF 24.0, C-1), 151.5 (s, oxazole C-2), 138.6 (d, ³J_CF 2.2, oxazole C-4), 136.7 (d, ³J_CF 2.2, oxazole C-5), 89.7 (d, ¹J_CF 189.7, C-2), 67.9 (d, ¹J_CF 21.0, C-3), 62.1 (s, ethyl C-1), 14.1 (s, ethyl C-2); ν_max/cm⁻¹ 3140, 1740, 1511, 1213, 1060; HRMS (ESI) m/z [M+H] calcd for C₈H₁₁FNO₄: 204.066662, found 204.066261, 2.0 ppm error.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(2-methyl-1,3-oxazol-4-yl)propionate (3k)

Produced by general procedure A, followed by purification by flash chromatography eluting with 45:55 EtOAc—Hexane to yield the propionate 3k (48 mg, 48%, d.r. 93: 7) as a colourless amorphous solid. Rf 0.30 (45:55 EtOAc—Hexane); [α]_D^20 +41.4 (MeOH, c 1.2); anti: ¹⁹F NMR (282 MHz, CDCl₃) δ −199.7 (dd, ²J_HF 47.9 and ³J_HF 19.7); syn: ¹⁹F NMR (282 MHz, CDCl₃) δ −206.4 (dd, ²J_HF 47.9 and ³J_HF 25.4); ¹H NMR (300 MHz, CDCl₃) δ 7.56 (1H, s, oxazole 5-H), 5.19 (1H, dd, ²J_HF 47.4 and ³J_HH 27.2, 2-H), 5.10 (1H, ddd, ³J_HH 24.9, ¹J_HH 2.7 and ¹J_HH 1.2, 3-H), 4.26 (2H, q, ³J_HH 7.1, ethyl 1-H), 2.41 (3H, s, CH₃), 1.28 (3H, t, ³J_HH 7.1, ethyl 2-H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6 (d, ¹J_CF 24.0, C-1), 162.2 (s, oxazole C-2), 138.7 (d, ¹J_CF 2.2, oxazole C-4), 135.9 (d, ¹J_CF 189.7, C-2), 67.7 (d, ¹J_CF 19.5, C-3), 62.0 (s, ethyl C-1), 14.1 (s, ethyl C-2), 13.8 (s, CH₃); ν_max/cm⁻¹ 3259, 1741, 1579, 1292, 1069; HRMS (ESI) m/z [M+H] calcd for C₉H₁₃FNO₄: 218.082313, found 218.082077, 1.1 ppm error.
(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(5-methyl-1,2-oxazol-3-yl)propionate (3l)

Produced by general procedure B, followed by purification by flash chromatography eluting with 20:80 EtOAc—Hexane to yield the propionate 3l (76.1 mg, 70%, d.r. >98:<2) as a colourless amorphous solid. Rt 0.3 (30:70 EtOAc—Hexane); [α]_{D}^{25} +38.0 (MeOH, c 1.4); syn: \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ −206.4 (dd, \(^{2}\)J\(_{HF}\) 47.9 and \(^{3}\)J\(_{HF}\) 25.4); \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) δ 6.12 (1H, s, isoxazole 4-H), 5.26 (1H, d, \(^{3}\)J\(_{HF}\) 25.5, 3-H), 5.10 (1H, dd, \(^{2}\)J\(_{HF}\) 47.2 and \(^{3}\)J\(_{HF}\) 2.5, 2-H), 4.27 (2H, q, \(^{3}\)J\(_{HF}\) 7.2, ethyl 1-H\(_2\)), 3.88 (1H, br d, \(^{3}\)J\(_{HF}\) 7.5, OH), 2.39 (3H, s, CH\(_3\)) 1.27 (3H, t, \(^{3}\)J\(_{HF}\) 7.2, ethyl 2-H\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 170.3 (s, isoxazole C-5), 167.2 (d, \(^{2}\)J\(_{CF}\) 24.0, C-1), 162.5 (d, J\(_{CF}\) 2.2, isoxazole C-3), 100.6 (d, J\(_{CF}\) 1.5, isoxazole C-4), 90.0 (d, J\(_{CF}\) 181.2, C-2), 67.4 (d, \(^{2}\)J\(_{CF}\) 20.2, C-3), 62.2 (s, ethyl C-1), 14.0 (s, ethyl C-2), 12.2 (s, CH\(_3\)); \(\nu\)\(^{\max}\)/cm\(^{-1}\) (ATR) 3144, 2985, 1742, 1603, 1213, 1068, 731; HRMS (ESI) m/z [M+H] calcd for C\(_9\)H\(_{13}\)FNO\(_4\): 218.082313, found 218.082620, −1.4 ppm error.

(2R3S)-Ethyl 2-fluoro-3-hydroxy-3-(1,3-thiazol-4-yl)propionate (3m)

Produced by general procedure A, followed by purification by flash chromatography eluting with 45:55 EtOAc—Hexane to yield the propionate 3m (44.0 mg, 41%, d.r. 94:6) as a colourless oil. Rt 0.30 (45:55 EtOAc—Hexane); [α]_{D}^{25} +70.7 (MeOH, c 2.0); anti: \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ −198.6 (dd, \(^{2}\)J\(_{HF}\) 47.9 and \(^{3}\)J\(_{HF}\) 19.7); syn: \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) δ −206.4 (dd, \(^{2}\)J\(_{HF}\) 47.9 and \(^{3}\)J\(_{HF}\) 22.6); \(^{1}\)H NMR (300 MHz, CDCl\(_3\)) δ 8.80 (1H, d, \(^{4}\)J\(_{HH}\) 2.1, thiazole 2-H), 7.43 (1H, dd, \(^{4}\)J\(_{HH}\) 2.1 and \(^{4}\)J\(_{HH}\) 1.0, thiazole 5-H), 5.38 (1H, ddd, \(^{3}\)J\(_{HH}\) 23.7, \(^{3}\)J\(_{HH}\) 2.7 and \(^{4}\)J\(_{HH}\) 1.0, 3-H), 5.36 (1H, dd, \(^{2}\)J\(_{HF}\) 47.7 and \(^{3}\)J\(_{HF}\) 2.7, 2-H), 4.29 (2H, q, \(^{3}\)J\(_{HH}\) 7.1, ethyl 1-H\(_2\)), 3.32 (1H, br s, OH), 1.29 (3H, t, \(^{3}\)J\(_{HH}\) 7.1, ethyl 2-H\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 167.7 (d, \(^{2}\)J\(_{CF}\) 24.7, C-1), 155.0 (d, \(^{3}\)J\(_{CF}\) 2.2, thiazole C-4), 153.5 (s, thiazole C-2), 116.1 (s, thiazole C-5), 90.3 (d, \(^{2}\)J\(_{CF}\) 190.5, C-2), 71.0 (d, \(^{2}\)J\(_{CF}\) 20.2, C-3), 62.1 (s, ethyl C-1), 14.1 (s, ethyl C-2); \(\nu\)\(^{\max}\)/cm\(^{-1}\) (ATR) 3144, 2985, 1754, 1373, 1298, 1065 cm\(^{-1}\); HRMS (ESI) m/z [M+H] calcd for C\(_8\)H\(_{11}\)FNO\(_3\): 218.082313, found 220.043552, −1.2 ppm error.
(2R3R)-Ethyl 2-fluoro-3-hydroxy-3-(1,3-thiazol-2-yl)propionate (3n)

Produced by general procedure A, followed by purification by flash chromatography eluting with 40:60 EtOAc—Hexane to yield the propionate 3n (44.0 mg, 41%, d.r. 93:7) as a colourless oil. \( R_t \) 0.20 (40:60 EtOAc—Hexane); [\( \alpha \)]\text{D}\text{+} 65.0 (MeOH, c 2.0); \textit{anti}: \({ }^{19} \text{F} \) NMR (282 MHz, CDCl\textsubscript{3}) \( \delta \) –197.5 (dd, \( J_{\text{HF}} \) 47.7 and \( J_{\text{HF}} \) 17.2); \textit{syn}: \({ }^{19} \text{F} \) NMR (282 MHz, CDCl\textsubscript{3}) \( \delta \) –206.9 (dd, \( J_{\text{HF}} \) 46.8 and \( J_{\text{HF}} \) 24.4); \( ^1 \text{H} \) NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 7.76 (1H, d, \( J_{\text{HH}} \) 3.3, thiazole 4-H), 7.35 (1H, d, \( J_{\text{HH}} \) 3.3, thiazole 5-H), 5.50 (1H, dd, \( J_{\text{HF}} \) 24.4 and \( J_{\text{HF}} \) 3.3-H), 5.40 (1H, dd, \( J_{\text{HF}} \) 46.8 and \( J_{\text{HF}} \) 2.3, 2-H), 4.64 (1H, br s, OH), 4.29 (2H, apparent qd, \( J_{\text{HF}} \) 7.2 and \( J_{\text{HH}} \) 0.8, ethyl 1-H\text{Z}), 1.29 (3H, t, \( J_{\text{CF}} \) 7.1, ethyl 2-H\text{Z}); \( ^{13} \text{C} \) NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 169.8, C\text{S}; 220.043819, found 220.043885, 0.3 ppm error.

(2R3S)-Ethyl 2-fluoro-3-(5-bromo-pyridin-2-yl)-3-\{[(JS4S)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carbonyloxy}propanoate (7g)

Propionate 3g (64.2 mg, 0.22 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (1.1 mL, ~0.2 M) and cooled to 0 °C. Pyridine (55 \textmu L, 0.68 mmol) was added to the reaction mixture follow by (1S)-(−)-camphamic chloride (72.3 mg, 0.33 mmol). The reaction warmed to rt over 1 h and was left for 18 h. After this time water was added and the resulting mixture was extracted with ethyl acetate, dried (MgSO\textsubscript{4}), filtered, and concentrated \textit{in vacuo} to reveal a crude product. The product was purified by flash chromatography eluting with 30:70 EtOAc—Hexane to yield the propionate 7g (84.7 mg, 0.18 mmol, 81%) as a colourless solid (compound crystallised as colourless needles from Et\textsubscript{2}O/pentane). m.p. 137-139 °C; \( R_t \) 0.3 (30:70 EtOAc—Hexane); [\( \alpha \)]\text{D}\text{+} 31.1 (CHCl\textsubscript{3}, c 0.6); \( ^{19} \text{F} \) NMR (282 MHz, CDCl\textsubscript{3}) –205.3 (dd, \( J_{\text{HF}} \) 46.2 and \( J_{\text{HF}} \) 24.5); \( ^1 \text{H} \) NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 8.66 (1H, d, \( J_{\text{HH}} \) 2.3, pyridine 6-H), 7.87 (1H, dd, \( J_{\text{HF}} \) 8.4 and \( J_{\text{HF}} \) 2.3, pyridine 4-H), 7.29 (1H, d, \( J_{\text{HH}} \) 8.4, pyridine 3-H), 6.44 (1H, dd, \( J_{\text{HF}} \) 24.5 and \( J_{\text{HF}} \) 2.7, 3-H), 5.47 (1H, dd, \( J_{\text{HF}} \) 46.2 and \( J_{\text{HF}} \) 2.7, 2-H), 4.26 (2H, apparent qd, \( J_{\text{HF}} \) 7.2 and \( J_{\text{HH}} \) 3.9, ethyl 1-H\text{Z}), 2.48 (1H, ddd, \( J_{\text{HF}} \) 13.3, \( J_{\text{HH}} \) 10.7 and \( J_{\text{HH}} \) 4.3, camphamic 6-H),
2.12 (1H, ddd, J_HH 13.5, J_HH 9.3 and J_HH 4.5 Hz, camphanic 6-H), 1.96 (1H, ddd, J_HH 13.1, J_HH 10.7 and J_HH 4.5, camphanic 5-H), 1.73 (1H, ddd, J_HH 13.3, J_HH 9.3 and J_HH 4.2, camphanic 5-H), 1.31 (3H, t, J_HH 7.1, ethyl 2-H), 1.13 (3H, s, camphanic 4'-H), 1.11 (3H, s, camphanic 7'-H), 0.98 (3H, s, camphanic 7'-H); 13C NMR (75 MHz, CDCl3) δ 154.1 (s, Ar C), 152.5 (d, J_CF 27.5, pyridine C), 150.7 (s, pyridine C), 139.8 (s, pyridine C), 122.7 (s, pyridine C), 120.9 (s, pyridine C), 88.3 (d, J_HF 194.0, C), 75.2 (d, J_CF 18.7, C), 62.5 (s, ethyl C), 54.9 (s, camphanic C), 31.0 (s, camphanic C), 29.0 (s, camphanic C), 16.7 (s, camphanic C), 14.1 (s, ethyl C), 9.7 (s, camphanic C); ν_max/cm⁻¹ (ATR) 2971, 1788, 1466, 1260; HRMS (ESI) m/z [M+H] calcd for C_{20}H_{23}BrFNO_6: 472.076554, found 472.076980, −0.9 ppm error.

(2R3S)-2-Fluoro-3-hydroxy-3-(5-chloro-o-hydroxyphenyl)propanol (8c)

Propionate 3c (36.7 mg, 0.14 mmol) was dissolved in THF (2.8 mL, 50 mM) and cooled to 0 °C before the addition of a solution of LiAlH₄ (154 μL, 0.15 mmol, 1 M in THF). After 30 min the reaction mixture was slowly warmed to room temperature and stirred for a further 1.5 h. The reaction mixture was cooled to 0 °C and quenched with H₂O (150 μL), followed by NaOH (150 μL) and let warm to rt over 15 min. After this time H₂O (200 μL) was added and the reaction was dried (MgSO₄), filtered through a pad of celite, and concentrated in vacuo to reveal a crude product. The product was purified by flash chromatography eluting with 50:8:1 CH₂Cl₂—EtOH—NH₃OH to yield the diol 8c (26.7 mg, 0.12 mmol, 87%) as a colourless oil. Rᵣ 0.34 (50:8:1 CH₂Cl₂—EtOH—NH₃OH); [α]_D^{22} +41.0 (MeOH, c 0.89); ¹⁹F NMR (282 MHz, MeOD) δ −202.5 (ddt, J_HF 48.2, J_HF 27.5 and J_HF 20.3); ¹H NMR (300 MHz, MeOD) δ 7.35 (1H, d, J_HH 2.7, Ar 6-H), 7.09 (1H, dd, J_HH 8.7 and J_HH 2.7, Ar 4-H), 6.75 (1H, d, J_HH 8.7, Ar 3-H), 5.1 (1H, dd, J_HF 20.3 and J_HH 4.7, 3-H), 4.64 (1H, ddd, J_HF 48.2, J_HH 6.7, J_HH 4.7 and J_HH 3.4, 2-H), 3.86-3.57 (2H, m, 1-H₂); ¹³C NMR (75 MHz, MeOD) δ 154.1 (s, Ar C), 130.0 (d, J_CF 4.7, Ar C), 129.2 (s, Ar C), 128.8 (s, Ar C), 125.3 (s, Ar C), 117.4 (s, Ar C), 96.8 (d, J_CF 178.0, C), 68.6 (d, J_CF 19.5, C), 62.8 (d, J_CF 23.0, C); ν_max/cm⁻¹ (ATR) 3366, 2937, 2476, 2070, 1584, 1329; HRMS (ESI) m/z [M+H] calcd for C_{9}H_{8}CIFO_{3}: 219.022974, found 219.022381, 2.7 ppm error.

(2R3S)-2-Fluoro-3-hydroxy-3-(4-pyridinyl)propanol (8f)
Propionate 3f (137.1 mg, 0.64 mmol) was dissolved in THF (12.8 mL, 50 mM) and cooled to 0 °C before the addition of a solution of LiAlH₄ (707 μL, 0.7 mmol, 1 M in THF). After 30 min the reaction mixture was slowly warmed to room temperature and stirred for a further 1.5 h. The reaction mixture was cooled to 0 °C and quenched with H₂O (700 μL), followed by NaOH (700 μL) and let warm to rt over 15 min. After this time H₂O (1 mL) was added and the reaction was dried (MgSO₄), filtered through a pad of celite, and concentrated in vacuo to reveal a crude product. The product was purified by flash chromatography eluting with 50:8:1 CH₂Cl₂—EtOH—NH₃·H₂O to yield the diol 8f (83.6 mg, 0.49 mmol, 76%) as a colourless oil. Rt 0.25 (50:8:1 CH₂Cl₂—EtOH—NH₃·H₂O); [α]²⁴D +36.1 (MeOH, c 1); ¹⁹F NMR (282 MHz, CD₂OD) δ −203.0 (ddt, 2JHF 47.7, 3JHF 25.9 and 3JHF 20.6); ¹H NMR (300 MHz, CD₂OD) δ 8.52 (2H, d, 3JHH 6.2, pyridine 2-H and pyridine 5-H), 7.52 (2H, d, 3JHH 6.2, pyridine 3-H and pyridine 4-H), 4.95 (1H, dd, 3JHH 20.9 and 3JHH 4.1, 3-H), 4.63 (1H, ddt, 2JHF 47.7, 3JHH 6.3 and 3JHH 3.9, 2-H), 3.78-3.47 (2H, m, 1-H₂), 13C NMR (75 MHz, CD₂OD) δ 152.8 (s, pyridine C-4), 149.9 (s, pyridine C-2 and pyridine C-6), 123.5 (s, pyridine C-3 and pyridine C-5), 97.0 (d, 1JCF 179.6, C-2), 72.1 (d, 2JCF 20.1, C-3), 62.1 (d, 2JCF 23.2, C-1); νmax/cm⁻¹ (ATR) 3313, 2458, 1606, 1416; HRMS (ESI) m/z [M+H] calcd for C₈H₁₁FNO₂: 172.076833, found 172.076994, 0.9 ppm error.

(2R3S)-2-Fluoro-3-hydroxy-3-(5-methyl-1,2-oxazol-3-yl)propanol (8l)

Propionate 3l (52.5 mg, 0.24 mmol) was dissolved in THF (5.1 mL, 50 mM) and cooled to 0 °C before the addition of a solution of LiBH₄ (142 μL, 0.28 mmol, 2 M in THF). After 30 min the reaction mixture was slowly warmed to room temperature and stirred for a further 1.5 h. The reaction mixture was cooled to 0 °C and quenched with H₂O (250 μL), followed by NaOH (250 μL) and let warm to rt over 15 min. After this time H₂O (300 μL) was added and the reaction was dried (MgSO₄), filtered through a pad of celite, and concentrated in vacuo to reveal a crude product. The product was purified by flash chromatography eluting with 50:8:1 CH₂Cl₂—EtOH—NH₃·H₂O to yield the diol 8l (21.1 mg, 0.12 mmol, 50%) as a colourless oil. Rt 0.46(50:8:1 CH₂Cl₂—EtOH—NH₃·H₂O); [α]²⁴D +16.3 (MeOH, c 0.9); ¹⁹F NMR (282 MHz, MeOD) δ −203.07 (ddt, 2JHF 46.2, 3JHF 25.4 and 3JHF 20.3); ¹H NMR (300 MHz, MeOD) δ 6.20 (1H, s, isoxazole 4-H), 4.92 (1H, dd, 2JHF 20.3 and 2JHH 4.5, 3-H), 4.62 (1H, ddt, 2JHF 48.0, 2JHH 6.1 and 2JHH 4.5, 2-H), 3.85-3.64 (2H, m, 1-H₂), 2.42 (3H, d, J 0.9, CH₃); ¹³C NMR (75 MHz, MeOD) δ 171.4 (s, isoxazole C-5), 165.5 (s, isoxazole C-3), 101.6 (s, isoxazole...
C-4), 96.2 (d, $^1J_{CF}$ 179.1, C-2), 66.8 (d, $^2J_{CF}$ 20.7, C-3), 61.9 (d, $^2J_{CF}$ 23.4, C-1), 11.9 (s, CH$_3$); ν$_{max}$/cm$^{-1}$ (ATR) 3353, 2476, 2070, 1584, 1329; HRMS (ESI) $m/z$ [M+H] calcd for C$_7$H$_{11}$FNO$_3$: 176.071748, found 176.071503, 1.4 ppm error.
General method and data for Mosher’s ester analysis

(2S or 2R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride ((S or R)-MTPA-Cl) (2.2 equiv.), pyridine (3.5 equiv.) and the selected propionate were dissolved in CH₂Cl₂ at 0 °C. The reaction mixture was stirred and the reaction was monitored by TLC until completion (~18 h). The resulting mixture was extracted with CH₂Cl₂ (3 × 5 mL), the combined organic layers were washed with H₂O (20 mL), dried (MgSO₄), filtered and concentrated in vacuo to reveal a crude product. The ¹⁹F NMR analysis was performed on the crude reaction mixtures.

Supplementary Table 5: ¹⁹F resonances for Mosher’s ester analysis

| Entry | Propionate | Parent Propionate | R-Isomer   | S-Isomer   |
|-------|------------|-------------------|------------|------------|
| 1     | 3a         |                   | -206.9     | -204.95    | -204.78    |
| 2     | 3b         |                   | -201.1     | -203.18    | -202.19    |
| 3     | 3c         |                   | -202.1     | -205.16    | -205.48    |
| 4     | 3d         |                   | -206.7     | -205.42    | -205.33    |
| 5     | 3e         |                   | -203.8     | -203.76    | -202.76    |
| 6     | 3f         |                   | -203.8     | -203.50    | -202.55    |
| 7     | 3g         |                   | -206.7     | -205.23    | -205.14    |
| 8     | 3h         |                   | -207.3     | -205.53    | -205.39    |
| 9     | 3i         |                   | -205.8     | -204.54    | -204.66    |
| 10    | 3j         |                   | -206.6     | -203.55    | -203.41    |
| 11    | 3k         |                   | -206.4     | -203.70    | -203.95    |
| 12    | 3l         |                   | -206.4     | -203.79    | -203.61    |
| 13    | 3m         |                   | -206.4     | -203.39    | -203.44    |
| 14    | 3n         |                   | -206.9     | -203.33    | -203.13    |
\textbf{\textsuperscript{19}F NMR of Mosher’s Esters}

From \textbf{3a}

\begin{center}
\includegraphics[width=\textwidth]{image1.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{image2.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{image3.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{image4.png}
\end{center}

From \textbf{3b}

\begin{center}
\includegraphics[width=\textwidth]{image5.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{image6.png}
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\begin{center}
\includegraphics[width=\textwidth]{image7.png}
\end{center}

\begin{center}
\includegraphics[width=\textwidth]{image8.png}
\end{center}
From 3c

From 3d
From 3g

From 3h
From 3i

From 3j
NMR Spectra of products

(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(2-pyrazinyl)propionate (3a)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(o-hydroxyphenyl)propionate (3b)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(5-chloro-o-hydroxyphenyl)propionate (3c)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(2-pyridyl)propionate (3d)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(3-pyridyl)propionate (3e)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(4-pyridyl)propionate (3f)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(5-bromo-pyridin-2-yl)propionate (3g)
(2R,3S)-Ethyl 2-fluoro-3-hydroxy-3-(4-chloro-pyridin-2-yl)propionate (3h)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(2-quinolyl)propionate (3i)
(2R,3S)Ethyl 2-fluoro-3-hydroxy-3-(1,3-oxazol-4-yl)propionate (3j)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(2-methyl-1,3-oxazol-4-yl)propionate (3k)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(5-methyl-1,2-oxazol-3-yl)propionate (3l)
(2R3S)Ethyl 2-fluoro-3-hydroxy-3-(1,3-thiazol-4-yl)propionate (3m)
(2R3R)Ethyl 2-fluoro-3-hydroxy-3-(1,3-thiazol-2-yi)propionate (3n)
(2R3S)-Ethyl 2-fluoro-3-(5-bromo-pyridin-2-yl)-3-[(JS4S)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carbonyloxy]propanoate (7g)
(2R3S)2-Fluoro-3-hydroxy-3-(5-chloro-5-hydroxyphenyl)propanol (8c)
(2R3S)2-Fluoro-3-hydroxy-3-(4-pyridinyl)propanol (8f)
(2R,3S)-2-Fluoro-3-hydroxy-3-(5-methyl-1,2-oxazol-3-yl)propanol (8I)
Table 1 Crystal data and structure refinement for 3a.

| Identification code | 3a |
|---------------------|----|
| Empirical formula   | C₉H₁₁FN₂O₃ |
| Formula weight      | 214.20 |
| Temperature/K       | 120.01(10) |
| Crystal system      | monoclinic |
| Space group         | P2₁ |
| a/Å                 | 5.9629(4) |
| b/Å                 | 11.2240(6) |
| c/Å                 | 7.7429(4) |
| α/°                 | 90 |
| β/°                 | 97.530(5) |
| γ/°                 | 90 |
| Volume/Å³           | 513.74(5) |
| Z                   | 2 |
| ρ calc/g/cm³        | 1.385 |
| μ/mm⁻¹              | 1.001 |
| F(000)              | 224.0 |
| Crystal size/mm³    | 0.29 x 0.11 x 0.05 |
| Radiation           | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 11.528 to 148.766 |
| Index ranges        | -7 ≤ h ≤ 7, -13 ≤ k ≤ 14, -9 ≤ l ≤ 9 |
| Reflections collected | 4784 |
| Independent reflections | 2033 [Rint = 0.0468, Rsigma = 0.0451] |
| Data/restraints/parameters | 2033/1/141 |
| Goodness-of-fit on F² | 1.032 |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0457, wR₂ = 0.1182 |
| Final R indexes [all data] | R₁ = 0.0472, wR₂ = 0.1210 |
| Largest diff. peak/hole / e Å⁻³ | 0.24/-0.24 |
| Flack parameter     | -0.10(17) |
### Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3a. U(eq) is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

| Atom | x   | y     | z     | U(eq) |
|------|-----|-------|-------|-------|
| F1   | 4290(3) | 4877.6(17) | 7301(2) | 33.6(4) |
| O1   | 7923(4) | 5527.4(18) | 9907(3) | 27.3(5) |
| N1   | 9092(4) | 4306(2) | 5795(3) | 26.9(5) |
| C1   | 8937(5) | 4397(2) | 7486(4) | 23.8(5) |
| O2   | 2958(4) | 6964(2) | 8437(3) | 36.2(5) |
| N2   | 10350(5) | 2436(2) | 8089(3) | 29.9(6) |
| C2   | 9546(5) | 3461(3) | 8635(4) | 27.2(6) |
| O3   | 5993(4) | 7879.0(19) | 7577(3) | 29.6(5) |
| C3   | 10492(6) | 2346(3) | 8635(4) | 31.7(6) |
| C4   | 9879(5) | 3277(3) | 8115(4) | 24.3(5) |
| C5   | 8060(5) | 5569(2) | 8115(4) | 27.2(6) |
| O4   | 5993(4) | 7879.0(19) | 7577(3) | 29.6(5) |
| C6   | 10492(6) | 2346(3) | 8635(4) | 31.7(6) |
| C7   | 9879(5) | 3277(3) | 8115(4) | 24.3(5) |
| C8   | 8060(5) | 5569(2) | 8115(4) | 27.2(6) |
| C9   | 5993(4) | 7879.0(19) | 7577(3) | 29.6(5) |

### Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3a. The Anisotropic displacement factor exponent takes the form: \(-2\pi^2[a^2 b^2 c^2 U_{11} + 2hka^*b^*U_{12} + ...].

| Atom | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|--------|--------|--------|--------|--------|--------|
| F1   | 25.9(8) | 26.0(8) | 47.9(10) | -2.6(7) | 1.3(7) | -7.0(7) |
| O1   | 30.4(11) | 20.5(9) | 30.8(10) | -3.6(8) | 3.0(8) | -4.3(8) |
| N1   | 29.0(12) | 22.7(11) | 29.4(11) | 3.5(9) | 4.7(9) | 0.2(9) |
| C1   | 20.7(12) | 19.9(12) | 30.9(13) | -0.9(10) | 3.2(9) | -3.2(9) |
| O2   | 23.8(10) | 35.5(11) | 50.5(13) | -5.1(10) | 9.7(9) | -1.5(9) |
| N2   | 33.3(13) | 21.7(11) | 35.4(12) | 1.5(9) | 6.4(10) | 1.5(9) |
| C2   | 29.2(14) | 22.6(12) | 29.7(13) | 0.2(11) | 3.7(10) | -1.1(11) |
| O3   | 27.3(11) | 21.2(9) | 41.1(11) | -2.7(8) | 8.4(8) | 1.3(8) |
| C3   | 35.5(16) | 23.2(13) | 37.4(15) | -1.5(11) | 8.6(12) | 3.6(11) |
| C4   | 30.1(15) | 29.7(14) | 30.2(13) | -0.8(11) | 7.1(11) | 1.6(11) |
| C5   | 22.8(12) | 18.2(11) | 28.7(13) | -1.7(10) | 1(1) | -2.6(9) |
| C6   | 24.0(13) | 22.4(13) | 31.6(14) | -1.7(10) | 4.5(11) | -1.5(11) |
| C7   | 22.7(13) | 24.4(13) | 31.3(13) | -2.3(10) | 1.7(10) | 0.5(10) |
| C8   | 31.0(15) | 24.5(14) | 41.7(15) | -6.5(12) | 4.4(12) | 3.6(11) |
| C9   | 36.3(16) | 22.6(12) | 44.8(17) | -0.5(13) | -1.5(13) | 2.6(12) |
Table 4 Bond Lengths for 3a.

| Atom | Atom | Length/Å |
|------|------|----------|
| F1   | C6   | 1.386(3) |
| O1   | C5   | 1.401(4) |
| N1   | C1   | 1.328(4) |
| N1   | C4   | 1.334(4) |
| C1   | C2   | 1.394(4) |
| C1   | C5   | 1.401(4) |
| O2   | C7   | 1.333(4) |
| N1   | C1   | 1.328(4) |
| O1   | C5   | 1.463(3) |
| N2   | C2   | 1.336(4) |
| C2   | C1   | 1.394(4) |
| C5   | C6   | 1.532(4) |
| C1   | C5   | 1.519(4) |
| C6   | C7   | 1.521(4) |
| O2   | C7   | 1.202(4) |
| N2   | C2   | 1.336(4) |

Table 5 Bond Angles for 3a.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C1   | N1   | C4   | 116.5(2) |
| N1   | C1   | C2   | 121.7(3) |
| N1   | C1   | C5   | 117.0(2) |
| C2   | C1   | C5   | 121.3(2) |
| C3   | N2   | C2   | 121.4(3) |
| N2   | C2   | C1   | 121.6(3) |
| N1   | C4   | C3   | 122.0(3) |
| O1   | C5   | C6   | 110.8(2) |

Table 6 Torsion Angles for 3a.

| A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|---------|
| F1  | C6  | C7  | O2  | 1.6(4)  |
| F1  | C6  | C7  | O3  | -177.7(2) |
| O1  | C5  | C6  | F1  | -65.9(3) |
| O1  | C5  | C6  | C7  | 53.4(3) |
| N1  | C1  | C2  | N2  | 1.1(4) |
| N1  | C1  | C5  | O1  | 178.3(2) |
| N1  | C1  | C5  | C6  | 56.9(3) |
| C1  | N1  | C4  | C3  | 0.4(4) |
| C1  | C5  | C6  | F1  | 55.9(3) |
| C1  | C5  | C6  | C7  | 175.2(2) |
| N2  | C3  | C4  | N1  | -0.7(5) |
| C2  | C1  | C5  | O1  | -1.6(3) |
| C2  | C1  | C5  | C6  | -179.8(2) |

| A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|---------|
| C2  | C1  | C5  | O1  | -1.6(3) |
| C2  | C1  | C5  | C6  | -179.8(2) |
| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H2   | 9390 | 3551 | 9807 | 33    |
| H3   | 11017| 1640 | 5962 | 38    |
| H4   | 10020| 3182 | 4084 | 36    |
| H5   | 9100 | 6209 | 7886 | 28    |
| H6   | 5863 | 5936 | 5874 | 31    |
| H8A  | 5301 | 9013 | 9455 | 39    |
| H8B  | 3638 | 9151 | 7712 | 39    |
| H9A  | 6620 | 9950 | 6364 | 53    |
| H9B  | 8216 | 9853 | 8136 | 53    |
| H9C  | 6167 | 10740| 7952 | 53    |
| H1   | 8440(80) | 6070(50) | 10410(60) | 42(12) |
X-Ray crystallography data for compound 3f (CCDC 1456912)

![Molecule structure](Image)

| Crystal data and structure refinement for 3f. |
|---------------------------------------------|
| Identification code | 3f |
| Empirical formula | C₁₀H₁₂NO₃F |
| Formula weight | 213.21 |
| Temperature/K | 120.00(10) |
| Crystal system | monoclinic |
| Space group | P2₁ |
| a/Å | 7.71880(12) |
| b/Å | 15.58529(13) |
| c/Å | 9.12133(13) |
| α/° | 90 |
| β/° | 114.0345(18) |
| γ/° | 90 |
| Volume/Å³ | 1002.16(3) |
| Z | 4 |
| ρ calc g/cm³ | 1.4130 |
| μ/mm⁻¹ | 0.994 |
| F(000) | 449.8 |
| Crystal size/mm³ | 0.21 × 0.12 × 0.09 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 10.62 to 148.9 |
| Index ranges | -9 ≤ h ≤ 9, -19 ≤ k ≤ 19, -11 ≤ l ≤ 11 |
| Reflections collected | 20519 |
| Independent reflections | 3793 [R(int) = 0.0456, Rsigma = 0.0331] |
| Data/restraints/parameters | 3793/1/283 |
| Goodness-of-fit on F² | 0.722 |
| Final R indexes [I>2σ (I)] | R₁ = 0.0436, wR₂ = 0.1440 |
| Final R indexes [all data] | R₁ = 0.0440, wR₂ = 0.1468 |
| Largest diff. peak/hole / e Å⁻³ | 0.47/-0.21 |
| Flack parameter | 0.07(11) |
Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for 3f. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom | x     | y     | z      | U(eq)   |
|------|-------|-------|--------|---------|
| O1   | 5676(2)| 2757.5(10) | 6482.0(18) | 25.6(3) |
| F1   | 5440.9(19) | 3046.9(9) | 3440.5(17) | 32.4(3) |
| C2   | 2272(3)  | 3119.8(11) | 6643(2)   | 19.6(4) |
| N1   | -897(3)  | 2679.3(11) | 6140(2)   | 21.5(4) |
| O3   | 577(2)   | 3118.4(10) | 1883.8(18) | 29.0(4) |
| O2   | 2468(3)  | 2223.0(14) | 1299(3)   | 46.5(5) |
| C5   | -812(3)  | 2112.1(12) | 5057(2)   | 20.4(4) |
| C7   | 3780(3)  | 3071.8(12) | 3692(2)   | 21.0(4) |
| C4   | 782(3)   | 2015.9(11) | 4731(2)   | 18.2(4) |
| C3   | 2355(3)  | 2534.6(11) | 5528(2)   | 16.4(4) |
| C6   | 4091(3)  | 2480.8(12) | 5139(2)   | 19.1(4) |
| C8   | 2211(3)  | 2759.2(13) | 2140(2)   | 23.7(4) |
| C1   | 632(3)   | 3165.8(12) | 6912(2)   | 22.1(4) |
| C9   | -1051(4) | 2752.1(17) | 507(3)    | 35.2(5) |
| C10  | -2801(4) | 3105(2)   | 578(3)    | 43.9(6) |
| O4   | 6035(2)  | 212.8(10)  | 6819.4(19) | 24.7(3) |
| F2A  | 8612(2)  | -183.3(12) | 9857(2)   | 33.9(4) |
| O6   | 5323(2)  | -59.7(9)   | 11440.8(16) | 24.0(3) |
| N2   | -223(3)  | 386.9(10)  | 7194(2)   | 21.2(4) |
| O5   | 7820(3)  | 808.1(15)  | 11936(3)  | 48.6(5) |
| C12  | 2856(3)  | 1028.9(11) | 8557(2)   | 19.8(4) |
| C15  | 535(3)   | -115.2(13) | 6424(2)   | 22.0(4) |
| C11  | 951(3)   | 955.4(12)  | 8253(2)   | 21.2(4) |
| C13  | 3626(3)  | 494.4(11)  | 7753(2)   | 18.0(4) |
| C18  | 6719(3)  | 276.9(13)  | 11143(3)  | 24.5(4) |
| C14  | 2433(3)  | -95.1(12)  | 6661(2)   | 20.1(4) |
| C19  | 4992(4)  | 335.7(13)  | 12767(3)  | 28.1(5) |
| C16  | 5736(3)  | 501.1(12)  | 8158(2)   | 20.9(4) |
| C20  | 3133(4)  | -7.0(16)   | 12680(3)  | 34.6(5) |
| F2B  | 6279(10) | -88.8(3)   | 9227(8)   | 34.0(14) |
| C17  | 6768(3)  | -87.1(13)  | 9611(3)   | 25.6(4) |
Table 3 Anisotropic Displacement Parameters (Å²×10³) for 3f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2\text{a}^*\text{b}^*U_{11}+\text{2hka}^*\text{b}^*U_{12}+\ldots]$. 

| Atom | U₁₁ | U₁₂ | U₁₃ | U₂₂ | U₂₃ | U₃₃ | U₄₄ | U₅₅ | U₆₆ |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| O1   | 14.4(7) | 43.9(8) | 19.7(7) | -2.3(5) | 8.0(6) | -5.6(5) |
| F1   | 20.5(7) | 52.8(7) | 28.6(7) | -1.2(5) | 14.9(6) | 8.0(6) |
| C2   | 18.0(9) | 23.8(8) | 18.2(9) | -3.1(6) | 8.4(8) | -1.9(6) |
| N1   | 18.2(8) | 28.8(7) | 19.2(8) | -0.1(6) | 9.3(8) | 0.6(6) |
| O3   | 22.2(8) | 45.3(9) | 17.3(7) | 4.8(6) | 5.8(7) | 1.7(6) |
| O2   | 39.7(12) | 62.4(12) | 34.8(10) | 5.2(9) | 12.4(10) | -22.0(8) |
| C5   | 18.0(9) | 23.8(8) | 18.2(9) | -3.1(6) | 8.4(8) | -1.9(6) |
| C7   | 17.3(10) | 24.2(8) | 19.5(9) | -2.6(6) | 7.3(8) | 0.4(6) |
| C4   | 17.7(10) | 19.0(8) | 17.1(8) | -0.5(6) | 6.2(8) | 0.8(6) |
| C3   | 15.7(9) | 18.4(7) | 14.7(8) | -0.4(6) | 5.9(8) | 1.7(6) |
| C6   | 18.1(10) | 22.2(8) | 18.2(8) | 1.0(6) | 8.7(8) | -0.2(6) |
| C8   | 26.7(11) | 29.4(9) | 16.6(9) | -3.0(7) | 10.5(9) | 0.1(6) |
| C1   | 22.9(11) | 25.1(9) | 20.0(9) | 0.8(7) | 10.5(9) | -2.3(6) |
| C9   | 31.9(13) | 46.3(13) | 27.7(11) | 0.1(9) | 12.4(11) | -6.6(9) |
| C10  | 26.0(13) | 78.2(18) | 21.9(11) | 5.7(12) | 3.9(11) | -8.3(11) |
| O4   | 16.3(7) | 39.5(8) | 20.8(7) | -4.4(5) | 10.1(6) | -6.8(6) |
| F2A  | 16.3(8) | 59.7(10) | 28.0(8) | 11.5(6) | 11.3(8) | 7.7(7) |
| O6   | 31.8(8) | 22.9(6) | 18.2(7) | -0.8(5) | 11.0(7) | -1.7(5) |
| N2   | 19.4(9) | 25.6(7) | 21.6(9) | 0.9(6) | 11.3(8) | 2.1(6) |
| O5   | 34.4(11) | 77.8(14) | 33.3(10) | -24.7(9) | 13.6(10) | -27.6(9) |
| C12  | 21.9(10) | 21.3(8) | 15.4(8) | 1.2(7) | 6.7(8) | -0.7(6) |
| C15  | 22.2(11) | 22.7(8) | 22.3(10) | -4.5(6) | 10.3(9) | -4.3(6) |
| C11  | 20.3(11) | 25.4(8) | 18.8(9) | 4.4(6) | 8.9(9) | 1.9(6) |
| C13  | 16.8(9) | 21.4(8) | 15.8(8) | 0.8(6) | 6.5(8) | 2.9(6) |
| C18  | 18.4(11) | 35.1(1) | 16.7(9) | 3.3(8) | 3.5(9) | -2.8(7) |
| C14  | 22(1) | 21.3(8) | 19.1(9) | -0.1(7) | 10.6(8) | -1.5(6) |
| C19  | 36.1(13) | 33.9(10) | 16.1(1) | 1.5(8) | 12.4(10) | -1.7(7) |
| C16  | 18.4(10) | 28.8(8) | 15.5(9) | -1.7(7) | 7.0(8) | -4.4(6) |
| C20  | 43.4(15) | 39.2(11) | 28.3(12) | -1.8(10) | 22.1(12) | 1.3(9) |
| F2B  | 36(4) | 31(3) | 28(3) | 14(3) | 6(3) | 6(3) |
| C17  | 21.7(11) | 32.7(10) | 20.6(9) | 6.4(8) | 6.9(9) | -2.7(8) |
Table 4 Bond Lengths for 3f.

| Atom | Atom | Length/Å |
|------|------|----------|
| O1   | C6   | 1.401(3) |
| F1   | C7   | 1.392(2) |
| C2   | C3   | 1.386(3) |
| C2   | C1   | 1.386(2) |
| N1   | C5   | 1.347(3) |
| N1   | C1   | 1.337(3) |
| O3   | C8   | 1.311(3) |
| O3   | C9   | 1.482(3) |
| O2   | C8   | 1.204(3) |
| C5   | C4   | 1.387(2) |
| C7   | C6   | 1.546(2) |
| C7   | C8   | 1.521(3) |
| C4   | C3   | 1.392(2) |
| C3   | C6   | 1.521(2) |
| C9   | C10  | 1.484(3) |
| O4   | C16  | 1.405(2) |
| F2A  | C17  | 1.356(2) |
| O6   | C18  | 1.322(3) |
| O6   | C19  | 1.470(2) |
| N2   | C15  | 1.335(2) |
| N2   | C11  | 1.352(3) |
| O5   | C18  | 1.196(3) |
| O6   | C18  | 1.322(3) |
| N2   | C11  | 1.352(3) |
| O5   | C18  | 1.196(3) |
| C12  | C11  | 1.386(3) |
| C12  | C13  | 1.392(2) |
| C15  | C14  | 1.392(3) |
| C13  | C14  | 1.392(3) |
| C13  | C16  | 1.517(2) |
| C18  | C17  | 1.523(3) |
| C19  | C20  | 1.503(3) |
| C16  | C17  | 1.540(3) |
| F2B  | C17  | 1.310(4) |

Table 5 Bond Angles for 3f.

| Atom | Atom | Angle/° |
|------|------|---------|
| C1   | C2   | 118.84(18) |
| C1   | N1   | 117.54(16) |
| C9   | O3   | 114.11(17) |
| C4   | C5   | 122.75(17) |
| C6   | C7   | 106.92(16) |
| C8   | C7   | 105.99(15) |
| C8   | C6   | 113.07(16) |
| C3   | C4   | 119.10(16) |
| C4   | C3   | 118.31(16) |
| C6   | C3   | 121.02(16) |
| C6   | C4   | 120.64(15) |
| C7   | C6   | 109.84(15) |
| C3   | C6   | 108.52(14) |
| C3   | C7   | 108.74(15) |
| O2   | C8   | 125.4(2) |
| C7   | C8   | 111.87(17) |
| C7   | C8   | 122.7(2) |
| N1   | C1   | 123.45(17) |
| C10  | C9   | 107.03(19) |
| C19  | O6   | 115.61(16) |
| C11  | N2   | 116.75(17) |
| C13  | C12  | 119.38(17) |
| C14  | C15  | 118.26(17) |
| C16  | C12  | 112.03(17) |
| C17  | C18  | 111.57(18) |
| C17  | C18  | 122.4(2) |
| C13  | C14  | 118.26(16) |
| C20  | C19  | 106.88(18) |
| C13  | C16  | 109.07(16) |
| C17  | C16  | 110.29(15) |
| C17  | C16  | 109.44(15) |
| C16  | C17  | 111.75(15) |
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3f.

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H1   | 6634(6)| 2700(20)| 6312(15)| 38.5(5) |
| H2   | 3299(3)| 3475.3(11)| 7199(2)| 23.6(4) |
| H5   | -1866(3)| 1770.6(12)| 4506(2)| 24.5(4) |
| H7   | 3520(3)| 3659.9(12)| 3925(2)| 25.2(5) |
| H4a  | 800(3)| 1610.3(11)| 3989(2)| 21.9(4) |
| H6   | 4278(3)| 1887.8(12)| 4877(2)| 22.9(4) |
| H1a  | 594(3)| 3555.6(12)| 7670(2)| 26.5(5) |
| H9a  | -982(4)| 2911.2(17)| -496(3)| 42.3(6) |
| H9b  | -1044(4)| 2131.0(17)| 579(3)| 42.3(6) |
| H10a | -3892(4)| 2878(14)| -300(20)| 65.9(9) |
| H10b | -2850(20)| 2946(15)| 1577(15)| 65.9(9) |
| H10c | -2800(20)| 3719(2)| 500(30)| 65.9(9) |
| H4   | 7140(14)| 300(20)| 6964(19)| 37.1(5) |
| H12  | 3614(3)| 1431.5(11)| 9291(2)| 23.8(4) |
| H15  | -259(3)| -504.2(13)| 5680(2)| 26.4(5) |
| H11  | 458(3)| 1314.0(12)| 8804(2)| 25.5(5) |
| H14  | 2893(3)| -466.0(12)| 6104(2)| 24.1(4) |
| H19a | 6008(4)| 188.5(13)| 13788(3)| 33.7(6) |
| H19b | 4937(4)| 955.3(13)| 12657(3)| 33.7(6) |
| H16  | 6221(3)| 1087.6(12)| 8423(2)| 25.0(5) |
| H20a | 2136(6)| 157(13)| 11677(12)| 51.8(8) |
| H20b | 3195(12)| -621.3(19)| 12760(30)| 51.8(8) |
| H20c | 2880(16)| 225(12)| 13549(16)| 51.8(8) |
| H17  | 6153(3)| -651.0(13)| 9398(3)| 30.7(5) |
| H17a | 8106(3)| -59.8(13)| 9784(3)| 30.7(5) |

Table 7 Atomic Occupancy for 3f.

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|------|-----------|------|-----------|------|-----------|
| F2A  | 0.800000  | F2B  | 0.200000  | H17  | 0.800000  |
| H17a | 0.200000  |      |           |      |           |
X-Ray crystallography data for compound 7g (CCDC 1456913)

![Image of a molecular structure]

Table 1 Crystal data and structure refinement for 7g.

| Parameter                              | Value                        |
|----------------------------------------|------------------------------|
| Identification code                    | 7g                           |
| Empirical formula                      | C\(_{20}\)H\(_{23}\)NO\(_6\)FBr |
| Formula weight                         | 472.30                       |
| Temperature/K                          | 120.00(10)                   |
| Crystal system                         | orthorhombic                 |
| Space group                            | P\(_{2}\)\(_1\)\(_2\)\(_1\)\(_2\)\(_1\) |
| a/Å                                    | 7.75381(7)                   |
| b/Å                                    | 13.37013(12)                 |
| c/Å                                    | 19.3857(2)                   |
| \(\alpha/^{\circ}\)                   | 90                           |
| \(\beta/^{\circ}\)                    | 90                           |
| \(\gamma/^{\circ}\)                   | 90                           |
| Volume/Å\(^3\)                         | 2009.70(3)                   |
| Z                                      | 4                            |
| \(\rho_{\text{calc}}\) g/cm\(^3\)    | 1.561                        |
| \(\mu\) mm\(^{-1}\)                  | 3.206                        |
| F(000)                                 | 968.0                        |
| Crystal size/mm\(^3\)                 | 0.31 \times 0.09 \times 0.03 |
| Radiation                              | CuK\(\alpha\) (\(\lambda = 1.54184\)) |
| 2\(\theta\) range for data collection/\(^{\circ}\) | 8.032 to 148.706             |
| Index ranges                           | -7 \(\leq h \leq 9\), -15 \(\leq k \leq 16\), -24 \(\leq l \leq 23\) |
| Reflections collected                  | 20678                        |
| Independent reflections                | 4079 [\(R_{\text{int}} = 0.0622, R_{\text{sigma}} = 0.0418\)] |
| Data/restraints/parameters             | 4079/0/266                   |
| Goodness-of-fit on F\(^2\)             | 0.875                        |
| Final R indexes \([I>2\sigma(I)]\)     | \(R_1 = 0.0374, wR_2 = 0.1003\) |
| Final R indexes \([\text{all data}]\)  | \(R_1 = 0.0385, wR_2 = 0.1021\) |
| Largest diff. peak/hole / e Å\(^{3}\) | 0.61/-0.46                   |
| Flack parameter                        | -0.035(11)                   |
Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for $7g$. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom | $x$     | $y$     | $z$     | $U_{eq}$  |
|------|---------|---------|---------|-----------|
| Br1  | 6381.3(5) | 2241.4(3) | 1070.5(2) | 22.32(15) |
| F1   | 13802(3)  | 4604.2(16) | 2325.4(11) | 22.0(4)   |
| O1   | 13223(4)  | 7175(2)   | 2021.9(19) | 35.3(8)   |
| N1   | 9456(4)   | 4562(3)   | 1707.7(17) | 21.3(6)   |
| C1   | 8188(5)   | 3900(3)   | 1642(2)   | 21.5(7)   |
| O2   | 15558(3)  | 6266.4(19) | 2309.1(14) | 18.5(5)   |
| C2   | 8308(5)   | 3102(3)   | 1188.0(18) | 18.4(7)   |
| O3   | 13651(3)  | 5144.5(18) | 965.6(12)  | 16.7(5)   |
| C3   | 9777(5)   | 2961(3)   | 802.1(19)  | 19.1(7)   |
| O4   | 12511(4)  | 6139(2)   | 139.7(15)  | 24.2(6)   |
| C4   | 11124(5)  | 3635(3)   | 882.4(18)  | 18.4(7)   |
| O5   | 15962(3)  | 4493.0(17) | 38.4(13)   | 16.3(5)   |
| C5   | 10891(5)  | 4438(3)   | 1323.0(17) | 15.0(6)   |
| O6   | 17951(4)  | 3634(2)   | -563.0(15) | 22.0(6)   |
| C6   | 12163(5)  | 5288(3)   | 1399.4(17) | 15.0(6)   |
| O7   | 12851(5)  | 5431(3)   | 2124.9(18) | 17.4(7)   |
| C7   | 13913(5)  | 6391(3)   | 2147.5(18) | 18.4(7)   |
| C8   | 16666(5)  | 7197(3)   | 2323(2)    | 23.2(7)   |
| C9   | 18332(6)  | 6939(3)   | 2589(2)    | 27.8(8)   |
| C10  | 13672(5)  | 5641(2)   | 361.5(17)  | 14.7(6)   |
| C11  | 15408(4)  | 5536(3)   | 13.2(18)   | 14.6(6)   |
| C12  | 16840(5)  | 6145(3)   | 371.7(19)  | 18.5(7)   |
| C13  | 18303(5)  | 6063(3)   | -171(2)    | 21.3(8)   |
| C14  | 17498(5)  | 5444(3)   | -766.2(19) | 16.5(7)   |
| C15  | 17247(5)  | 4412(3)   | -452.8(18) | 16.4(7)   |
| C16  | 15582(5)  | 5800(3)   | -758.0(17) | 14.8(6)   |
| C17  | 14406(5)  | 5183(3)   | -1228.8(19)| 21.4(7)   |
| C18  | 15333(5)  | 6907(3)   | -931.9(18) | 19.3(7)   |
| C19  | 18510(6)  | 5441(3)   | -1431(2)   | 23.5(7)   |
Table 3 Anisotropic Displacement Parameters ($\text{Å}^2\times10^3$) for 7g. The Anisotropic displacement factor exponent takes the form: $-2\pi^2\left[h^2a^*U_{11}+2hka^*b^*U_{12}+\ldots\right]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| Br1  | 18.3(2)  | 22.3(2)  | 26.4(2)  | -0.16(14)| -2.42(14)| -7.78(14)|
| F1   | 23.8(12)| 16.5(9)  | 25.7(10)| 5.5(8)   | -8.1(9)  | -1.6(9)  |
| O1   | 30.2(16)| 18.8(14)| 57.2(16)| 5.6(13)  |-19.4(15)|  0.9(12)|
| N1   | 12.1(14)| 25.8(15)| 26.1(15)|-4.7(13)  |  2.9(12)| -1.6(13)|
| C1   | 14.3(17)| 24.6(18)| 25.6(17)|-3.6(14)  |  3.3(14)| -2.3(14)|
| O2   | 12.8(13)| 16.6(12)| 26.1(12)|-0.1(10)  | -1(1)   | -2.3(10)|
| C2   | 15.6(16)| 18.9(15)| 20.8(15)|  2.5(12) | -2.5(13)| -3.8(13)|
| O3   | 11.4(12)| 21.5(12)| 17.1(11)|  3.4(9)  |  1.8(9) |  2.0(9)  |
| C3   | 21.4(18)| 17.5(16)| 18.4(15)|-3.0(13)  | -2.1(13)|  0.9(13) |
| O4   | 15.3(13)| 33.3(15)| 24.1(13)|  8.3(11) |  3.8(10)|  9.1(12)|
| C4   | 15.2(18)| 21.0(16)| 19.0(15)|-2.1(13)  | -0.4(13)|  2.0(14)|
| O5   | 13.8(12)| 15.7(10)| 19.3(11)|  2.6(9)  |  4.3(9) |  3.6(9)  |
| C5   | 11.3(16)| 18.1(15)| 15.5(14)|  3.4(12)|  0.9(12)|  0.8(12)|
| O6   | 19.3(13)| 18.7(13)| 28.1(13)|  2.4(10)|  5.3(11)|  5.8(10)|
| C6   | 12.5(16)| 17.2(15)| 15.4(15)|-0.4(12)  |  2.3(12)|  0.9(12)|
| C7   | 14.8(17)| 19.3(16)| 18.2(16)|  1.7(13)|  0.7(12)| -1.1(14)|
| C8   | 16.7(19)| 17.9(16)| 20.6(16)|  2.3(12)| -3.2(13)|  0.0(14)|
| C9   | 23.1(19)| 19.1(16)| 27.5(17)|  1.4(13)|  0.6(15)| -8.8(16)|
| C10  | 19.4(19)| 30.0(19)| 34(2)   | -3.0(15)| -5.5(16)| -8.2(15)|
| C11  | 11.2(16)| 15.2(14)| 17.6(14)|-1.7(12)  |  2.8(13)|  0.7(12)|
| C12  | 8.3(15) | 16.0(15)| 19.4(15)|-0.3(13)  |  2.4(12)| -0.2(12)|
| C13  | 12.6(16)| 23.3(17)| 19.5(16)|-5.3(13)  | -1.6(13)|  0.1(13)|
| C14  | 12.5(18)| 23.2(17)| 28.2(18)| -4.9(13)| -2.6(14)| -4.1(13)|
| C15  | 11.9(17)| 15.6(16)| 21.9(16)|-2.7(13)  |  4.1(13)| -0.6(13)|
| C16  | 12.7(16)| 18.4(17)| 18.0(16)|-1.3(12)  |  0.3(13)| -0.8(12)|
| C17  | 11.9(16)| 16.9(16)| 15.7(15)|  0.8(12)|  1.7(12)| -0.4(12)|
| C18  | 19.6(18)| 23.2(18)| 21.3(17)|-3.2(13)  | -2.3(14)| -1.7(14)|
| C19  | 19.3(17)| 18.0(16)| 20.7(16)|  3.3(13)|  3.6(13)|  1.3(13)|
| C20  | 20.8(18)| 23.1(17)| 26.6(18)|  3.0(14)|  9.3(16)|  1.2(15)|
| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Br1  | C2   | 1.899(4) | C5   | C6   | 1.512(5) |
| F1   | C7   | 1.385(4) | O6   | C16  | 1.194(5) |
| O1   | C8   | 1.201(5) | C6   | C7   | 1.517(5) |
| N1   | C1   | 1.329(5) | C7   | C8   | 1.526(5) |
| N1   | C5   | 1.349(5) | C9   | C10  | 1.503(6) |
| C1   | C2   | 1.386(5) | C11  | C12  | 1.512(5) |
| O2   | C8   | 1.324(5) | C12  | C13  | 1.542(5) |
| O2   | C9   | 1.470(4) | C12  | C17  | 1.542(5) |
| C2   | C3   | 1.376(5) | C13  | C14  | 1.552(5) |
| O3   | C6   | 1.441(4) | C14  | C15  | 1.551(5) |
| O3   | C11  | 1.346(4) | C15  | C16  | 1.519(5) |
| C3   | C4   | 1.388(5) | C15  | C17  | 1.560(5) |
| O4   | C11  | 1.200(5) | C15  | C20  | 1.508(5) |
| C4   | C5   | 1.384(5) | C17  | C18  | 1.531(5) |
| O5   | C12  | 1.461(4) | C17  | C19  | 1.529(5) |
| O5   | C16  | 1.383(4) |       |      |          |

Table 5 Bond Angles for 7g.

| Atom | Atom | Atom | Angle/° |
|------|------|------|---------|
| C1   | N1   | C5   | 118.3(3) |
| N1   | C1   | C2   | 121.6(4) |
| C8   | O2   | C9   | 114.2(3) |
| C1   | C2   | Br1  | 119.3(3) |
| C3   | C2   | C1   | 120.4(3) |
| C3   | C2   | Br1  | 120.2(3) |
| C11  | O3   | C6   | 116.9(3) |
| C2   | C3   | C4   | 118.2(3) |
| C5   | C4   | C3   | 118.3(3) |
| C16  | O5   | C12  | 105.3(3) |
| N1   | C5   | C4   | 123.0(3) |
| N1   | C5   | C6   | 113.0(3) |
| C4   | C5   | C6   | 123.9(3) |
| O3   | C6   | C5   | 111.5(3) |
| O3   | C6   | C7   | 106.0(3) |
| C5   | C6   | C7   | 114.6(3) |
| F1   | C7   | C6   | 110.3(3) |
| F1   | C7   | C8   | 112.1(3) |
| C6   | C7   | C8   | 108.8(3) |
| O1   | C8   | O2   | 126.0(4) |
| O1   | C8   | C7   | 119.2(3) |
| O2   | C8   | C7   | 114.9(3) |
| O2   | C9   | C10  | 107.2(3) |
| O3   | C11  | C12  | 110.7(3) |
| O4   | C11  | O3   | 125.2(3) |
|       |      |      |         |
Table 6 Torsion Angles for 7g.

| A | B   | C | D   | Angle/° | A | B   | C | D   | Angle/° |
|---|-----|---|-----|---------|---|-----|---|-----|---------|
| Br1 | C2   | C3 | C4   | 177.1(3) | C9 | O2   | C8 | C7   | 179.5(3) |
| F1  | C7   | C8 | O1   | -176.0(4) | C11 | O3  | C6 | C5   | 98.9(3) |
| F1  | C7   | C8 | O2   | 4.0(4)    | C11 | O3  | C6 | C7   | -135.9(3) |
| N1  | C1   | C2 | Br1  | -175.4(3) | C11 | C12 | C13 | C14  | -169.1(3) |
| N1  | C1   | C2 | C3   | 1.7(6)    | C11 | C12 | C17 | C15  | -175.3(3) |
| N1  | C5   | C6 | O3   | -178.2(3) | C11 | C12 | C17 | C18  | -59.0(4) |
| N1  | C5   | C6 | C7   | 61.4(4)   | C11 | C12 | C17 | C19  | 66.8(4) |
| C1  | N1   | C5 | C4   | -2.3(5)   | C12 | O5  | C16 | O6   | -179.0(3) |
| C1  | N1   | C5 | C6   | 175.0(3)  | C12 | O5  | C16 | C15  | 1.5(3) |
| C1  | C2   | C3 | C4   | 0.1(5)    | C12 | C13 | C14 | C15  | 1.1(4) |
| C2  | C3   | C4 | C5   | -2.8(5)   | C13 | C12 | C17 | C15  | 57.1(3) |
| O3  | C6   | C7 | F1   | -59.0(4)  | C13 | C12 | C17 | C18  | 173.3(3) |
| O3  | C6   | C7 | C8   | 64.4(4)   | C13 | C12 | C17 | C19  | -60.8(4) |
| O3  | C11 | C12 | O5   | 45.7(4)   | C13 | C14 | C15 | C16  | -67.5(3) |
| O3  | C11 | C12 | C13  | -72.3(4)  | C13 | C14 | C15 | C17  | 34.8(4) |
| O3  | C11 | C12 | C17  | 164.0(3)  | C13 | C14 | C15 | C20  | 167.2(3) |
| C3  | C4   | C5 | N1   | 4.1(5)    | C14 | C15 | C16 | O5   | 68.9(3) |
| C3  | C4   | C5 | C6   | -172.9(3) | C14 | C15 | C16 | O6   | -110.6(5) |
| O4  | C11 | C12 | O5   | -137.5(4) | C14 | C15 | C17 | C12  | -54.4(3) |
| O4  | C11 | C12 | C13  | 104.5(4)  | C14 | C15 | C17 | C18  | -171.0(3) |
| O4  | C11 | C12 | C17  | -19.2(5)  | C14 | C15 | C17 | C19  | 64.0(4) |
| C4  | C5   | C6 | O3   | -0.9(5)   | C16 | O5  | C12 | C11  | 162.7(3) |
| C4  | C5   | C6 | C7   | -121.3(4) | C16 | O5  | C12 | C13  | -75.0(3) |
| O5  | C12 | C13 | C14  | 70.8(3)   | C16 | O5  | C12 | C17  | 34.7(3) |
| O5  | C12 | C17 | C15  | -53.7(3)  | C16 | C15 | C17 | C12  | 51.9(3) |
| O5  | C12 | C17 | C18  | 62.6(4)   | C16 | C15 | C17 | C18  | -64.8(4) |
| O5  | C12 | C17 | C19  | -171.5(3) | C16 | C15 | C17 | C19  | 170.3(3) |
| C5  | N1   | C1 | C2   | -0.6(6)   | C17 | C12 | C13 | C14  | -37.7(3) |
| C5  | C6   | C7 | F1   | 64.4(4)   | C17 | C15 | C16 | O5   | -36.2(3) |
| C5  | C6   | C7 | C8   | -172.2(3) | C17 | C15 | C16 | O6   | 144.4(4) |
| C6  | O3   | C11 | O4   | -4.9(5)   | C20 | C15 | C16 | O5   | -165.0(3) |
| C6  | O3   | C11 | C12  | 171.9(3)  | C20 | C15 | C16 | O6   | 15.6(6) |
| C6  | C7   | C8 | O1   | 61.7(5)   | C20 | C15 | C17 | C12  | 176.3(3) |
| C6  | C7   | C8 | O2   | -118.3(3) | C20 | C15 | C17 | C18  | 59.7(4) |
| C8  | O2   | C9 | C10  | 173.8(3)  | C20 | C15 | C17 | C19  | -65.3(4) |
| C9  | O2   | C8 | O1   | -0.4(6)   |       |       |       |       |         |
| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H1   | 7197 | 3973 | 1907 | 26    |
| H3   | 9866 | 2428 | 496  | 23    |
| H4   | 12158| 3549 | 646  | 22    |
| H6   | 11590| 5908 | 1258 | 18    |
| H7   | 11871| 5504 | 2440 | 21    |
| H9A  | 16020| 7684 | 2623 | 28    |
| H9B  | 16646| 7480 | 1863 | 28    |
| H10A | 18846| 6443 | 2296 | 42    |
| H10B | 18239| 6680 | 3050 | 42    |
| H10C | 19039| 7528 | 2592 | 42    |
| H13A | 17172| 5848 | 808  | 22    |
| H13B | 16495| 6834 | 446  | 22    |
| H14A | 18650| 6720 | -332 | 26    |
| H14B | 19301| 5724 | 20   | 26    |
| H18A | 14560| 4484 | -1131| 32    |
| H18B | 14697| 5311 | -1702| 32    |
| H18C | 13226| 5365 | -1148| 32    |
| H19A | 14138| 7080 | -884 | 29    |
| H19B | 15696| 7028 | -1398| 29    |
| H19C | 16010| 7308 | -623 | 29    |
| H20A | 18703| 6117 | -1578| 35    |
| H20B | 17873| 5088 | -1779| 35    |
| H20C | 19599| 5116 | -1358| 35    |