# **Supporting Information**

for

# "The Synthesis and Structural Analysis of 2-Quinuclidonium Tetrafluoroborate"

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Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Norcamphor, 3-chloroperbenzoic acid (m-CPBA), lithium aluminum hydride, sodium azide, trifluoroacetic acid (TFA), trifluoromethanesulfonimide, di-tertbutyl dicarbonate (Boc<sub>2</sub>O) and tetrafluoroboric acid in Et<sub>2</sub>O solution were purchased from Sigma-Aldrich Chemical Company and used as received. p-Toluenesulfonyl chloride was purchased from EM Science Inc. and purified prior to use. Triethylamine was purchased from Sigma-Aldrich Chemical Company and freshly distilled prior to use. Trifluoromethanesulfonic acid was purchased from SynQuest Laboratories, Inc. and used as received. 1,1-Dihydro-1,1,1-triacetoxy-1,2-benzoiodooxol-3(1H)-one (Dess-Martin periodinane, DMP) was prepared by known method<sup>1</sup>. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, anisaldehyde or KMnO<sub>4</sub> staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm. <sup>1</sup>H and <sup>13</sup>C, NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz and 75 MHz, respectively). <sup>1</sup>H NMR spectra were reported relative to Me<sub>4</sub>Si ( $\delta$  0.0 ppm) or residual CHCl<sub>3</sub> ( $\delta$  7.26 ppm) or CHD<sub>2</sub>CN ( $\delta$  1.94 ppm). <sup>13</sup>C NMR were reported relative to CDCl<sub>3</sub> (δ 77.0 ppm) and CD<sub>3</sub>CN (δ 118.69 ppm), respectively. FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm<sup>-1</sup>). High resolution mass spectra were obtained from the Caltech Mass Spectral Facility.

# Procedure for the Synthesis of Ketoazide (7).

### 2-Oxabicyclo[3.2.1]octan-3-one (10); CAS # 5724-61-8<sup>2</sup>

To a mixture of *m*-CPBA (77%, 28.8 g, 129 mmol) and NaHCO<sub>3</sub> (20.7 mmol, 246 mmol) in DCM (800 mL) was slowly added a solution of norcamphor **9** (13.5 g, 123 mmol) in DCM (200 mL) over 10 min at 20 °C. After stirring for 20 h at 20 °C, the reaction mixture was filtered to remove insoluble material and the filtrate was concentrated in vacuo to give a pale yellow oil, which was dissolved with AcOEt (200 mL) and washed 10% aqueous solution of Na<sub>2</sub>SO<sub>3</sub> (100 mL). The aqueous layer was extracted with AcOEt repeatedly (2 x 100 mL) and the combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> solution (100 mL), brine (100 mL), dried over MgSO<sub>4</sub> and concentrated under reduced pressure to afford a crude pale yellow semi solid (15.3 g). A solution of a crude product (include 10% of undesired isomer) in DCM (100 mL) was washed with aqueous 1 M NaOH repeatedly (1 x 100 mL, 2 x 50 mL), brine (100 mL), dried over MgSO<sub>4</sub> and concentrated in vacuo to give 12.2 g (79% yield) of desired bicyclic lactone **10** as a pale yellow semi solid. <sup>1</sup>H NMR (300 MHZ, CDCl<sub>3</sub>)  $\delta$  4.86 (m, 1H), 2.73 (ddd, *J* = 18.3, 4.8, 2.1 Hz, 1H), 2.55 (m, 1H), 2.48 (dt, *J* = 18.3, 2.1 Hz, 1H), 2.17 (m, 1H), 2.04-1.85 (m, 3H), 1.80-1.60 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  170.8 (C=O), 80.9 (CHO), 40.6 (CH<sub>2</sub>), 35.8 (CH<sub>2</sub>), 32.4 (CH<sub>2</sub>), 31.8 (CH), 29.2 (CH<sub>2</sub>); IR (Neat film, NaCl) 2945, 1730, 1375, 1223, 1196, 1129, 1069, 1016, 1000, 978 cm<sup>-1</sup>; HRMS (EI) *m/z* calc'd for C<sub>7</sub>H<sub>10</sub>O<sub>2</sub> [M<sup>+</sup>]: 126.0681, found 126.0679.

### 3-(2-Hydroxyethyl)cyclopentanol (11); CAS # 61478-09-9<sup>3</sup>

To a stirred suspension of LiAlH<sub>4</sub> (3.67 g, 96.7 mmol) in dry Et<sub>2</sub>O (300 mL) was slowly added a solution of a bicyclic lactone **10** (12.2 g, 96.7 mmol) in dry Et<sub>2</sub>O (100 mL) over 10 min at 0 °C. After stirring for 1 h at ambient temperature, the reaction was quenched by the addition of saturated aqueous Na<sub>2</sub>SO<sub>4</sub> solution (50 mL) at 0 °C and the mixture was stirred for 30 min. MgSO<sub>4</sub> (30 g) was added to the white suspension and the resulting mixture was stirred for further 30 min. The insoluble white solid was separated by filtration and the filtrate was concentrated in vacuo to afford 12.3 g (98% yield) of desired diol **11** as a colorless oil. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  4.23 (br s, 2H), 4.02 (m, 1H), 3.36 (t, *J* = 6.6 Hz, 2H), 1.95 (m, 1H), 1.78 (m, 1H), 1.68-1.52 (m, 2H), 1.52-1.38 (m, 3H), 1.24 (m, 1H), 1.00 (m, 1H); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>)  $\delta$  71.7 (CHOH), 60.1 (CH<sub>2</sub>OH), 42.0 (CH<sub>2</sub>), 39.8 (CH<sub>2</sub>), 34.9 (CH<sub>2</sub>), 34.4 (CH), 30.0 (CH<sub>2</sub>); IR (Neat film, NaCl) 3326, 2946, 1435, 1346, 1054, 1007 cm<sup>-1</sup>; HRMS (EI) *m/z* calc'd for C<sub>7</sub>H<sub>12</sub>O [M – H<sub>2</sub>O]<sup>+</sup>: 112.0888, found 112.0898.

#### 2-(3-Hydroxycyclopentyl)ethyl 4-methylbenzenesulfonate (12).

To a solution of diol **11** (3.05 g, 23.5 mmol) in DCM (50 mL) was added TsCl (4.94 g, 25.9 mmol) and  $Et_3N$  (3.61 mL, 25.9 mmol) at ambient temperature. After stirring for 48 h at ambient temperature, the resulting suspension was concentrated in vacuo and the residue was purified by the flash column chromatography (eluent, hexanes/AcOEt) to give 4.93

g (74% yield) of desired monotosylate **12** as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.21 (m, 1H), 3.98 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.23 (s, 1H), 2.01 (m, 1H), 1.84 (m, 1H), 1.76-1.48 (m, 5H), 1.30 (m, 1H), 1.07 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  144.6 (Ar C), 132.8 (Ar C), 129.7 (Ar CH), 127.7 (Ar CH), 73.1 (CHOH), 69.8 (CH<sub>2</sub>OTs), 41.5 (CH<sub>2</sub>), 35.2 (CH<sub>2</sub>), 35.0 (CH<sub>2</sub>), 34.3 (CH), 29.7 (CH<sub>2</sub>), 21.5 (ArCH<sub>3</sub>); IR (Neat film, NaCl) 3379, 2953, 1598, 1446, 1356, 1176, 1097, 1041, 996, 959, 886, 816, 767, 665 cm<sup>-1</sup>; HRMS (FAB, Pos.) *m/z* calc'd for C<sub>14</sub>H<sub>21</sub>O<sub>4</sub>S [M+H]<sup>+</sup>: 285.1161, found 285.1169.

#### 3-(2-Azidoethyl)cyclopentanol (13).

To a solution of tosylate 12 (9.48 g, 33.3 mmol) in dry DMF (33 mL) was added sodium azide (2.28 g, 35.0 mmol) and the mixture was heated with stirring for 1 h. After the reaction mixture was cooled with ice bath,  $Et_2O$  (50 mL) was added to this mixture and this suspension was stirred for 10 min. The precipitate was filtered off and the filtrate was concentrated in vacuo. The crude residue was purified by

flash SiO<sub>2</sub> column chromatography to afford 4.78 g (92% yield) of azidoalcohol **13** as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.32 (m, 1H), 3.28 (t, *J* = 6.9 Hz, 1H), 2.18 (ddd, *J* = 12.9, 8.1, 6.3 Hz, 1H), 2.00-1.60 (m, 7H), 1.51-1.34 (m, 1H), 1.19 (dddd, *J* = 12.9, 8.7, 5.4, 1.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  72.9 (CHOH), 50.3 (CH<sub>2</sub>), 41.6 (CH<sub>2</sub>), 35.3 (CH), 35.2 (CH<sub>2</sub>), 34.9 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>); IR (Neat film, NaCl) 3351, 2948, 2097, 1439, 1343, 1265, 1103, 997 cm<sup>-1</sup>; HRMS (FAB, Pos.) *m/z* calc'd for C<sub>7</sub>H<sub>14</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 156.1137, found 156.1128.

#### 3-(2-Azidoethyl)cyclopentanone (7).

To a suspension of DMP (3.73 g, 8.80 mmol) in DCM (20 mL) was slowly added a solution of azidoalcohol **13** (1.24 g, 8.00 mmol) in DCM (20 mL) over 5 min at 0 °C. The resulting reaction mixture was stirred at ambient temperature until complete consumption of **13**. After 1 h stirring, the mixture was diluted with 100 mL of Et<sub>2</sub>O and the insoluble material was removed by filtration. The filtrate was then washed with 100 mL of saturated aqueous NaHCO<sub>3</sub> solution and the aqueous layer was extracted with 50 mL of Et<sub>2</sub>O. The combined organic layers were washed with water, brine, dried over MgSO<sub>4</sub> and concentrated in vacuo. The crude residue was purified by flash SiO<sub>2</sub> column chromatography to afford 1.14 g (7.44 mmol, 93% yield) of ketoazide 7 as a colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.36 (t, *J* = 7.1 Hz, 2H), 2.50-2.10 (m, 5H), 1.90-1.70 (m, 3H), 1.54 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  218.5 (C=O), 49.8 (CH<sub>2</sub>), 44.7 (CH<sub>2</sub>), 38.3 (CH<sub>2</sub>), 34.5 (CH), 34.4 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>); IR (Neat film, NaCl) 2933, 2098, 1741, 1458, 1405, 1357, 1265, 1161 cm<sup>-1</sup>; HRMS (EI) *m/z* calc'd for C<sub>7</sub>H<sub>11</sub>N<sub>3</sub>O [M<sup>+</sup>]: 153.0902, found 153.0899.

#### Intramolecular Schmidt Reaction of Ketoazide (7) with TFA.

A solution of ketoazide 7 (235 mg, 1.54 mmol) in TFA (3 mL) was stirred for 3 h at 60 °C under drv nitrogen atmosphere. After cooling, 3 mL of dry MeOH was added to the reaction mixture and this mixture was stirred for further 1 h at ambient temperature. The resulting mixture was concentrated in vacuo to give a mixture of amino ester TFA salts (14 and 15). This amino ester was then treated with (Boc)<sub>2</sub>O (0.46 mL, 3.08 mmol, 2.0 eq.) in CHCl<sub>3</sub> (3 mL) and sat. NaHCO<sub>3</sub> aq. (3 mL). After 14 h stirring, the aqueous phase of the reaction mixture was separated and extracted with CHCl<sub>3</sub>. The combined organic layers were dried over  $MgSO_4$  and concentrated under the reduced pressure to give crude oil, which was purified by flash column chlomatography (eluent; Hexanes-AcOEt) to give 222 mg of Boc protected amino ester 16 (56% yield) and 134 mg of 17 (34% yield) as a colorless oil. Spectra data for 16; <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CDCl}_3) \delta 4.07 \text{ (br d, } J = 13.2 \text{ Hz}, 2\text{H}), 3.67 \text{ (s, 3H)}, 2.71 \text{ (m, 2H)}, 2.24 \text{ (d, } J = 6.9 \text{ Hz}, 2\text{H}),$ 1.92 (m, 1H), 1.73-1.58 (m, 3H), 1.45 (s, 9H), 1.26-1.06 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) & 172.7 (CO<sub>2</sub>CH<sub>3</sub>), 154.6 (NCO<sub>2</sub>t-Bu), 79.2 (C(CH<sub>3</sub>)<sub>3</sub>), 51.3 (CO<sub>2</sub>CH<sub>3</sub>), 43.5 (NCH<sub>2</sub>), 40.7 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 32.9 (CH), 31.6 (CHCH<sub>2</sub>CH<sub>2</sub>N), 28.3(C(CH<sub>3</sub>)<sub>3</sub>); IR (Neat film, NaCl) 2976, 2931, 2851, 1739, 1694, 1424, 1366, 1315, 1289, 1241, 1161, 1122, 1014, 968, 950, 866, 770 cm<sup>-1</sup>; HRMS (EI) m/z calc'd for  $C_{13}H_{23}NO_4$  [M<sup>+</sup>]: 257.1627, found 257.1616. Spectra data for 17; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.68 (s, 3H), 3.53 (dd, J = 10.5, 7.2 Hz, 1H), 3.45 (m, 1H), 3.24 (ddd, J = 10.5, 9.6, 7.2 Hz, 1H), 2.87 (dd, J = 10.5, 9.6, 7.2 Hz, 1H), 3.85 (dd, J = 10.5, 9.6, 7.2 10.5, 9.0 Hz, 1H), 2.34 (t, J = 7.8 Hz, 2H), 2.10 (m, 1H), 1.99 (m, 1H), 1.71 (g, J = 7.8 Hz, 2H), 1.45 (s, 9H), 1.45 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 173.5 (CO<sub>2</sub>CH<sub>3</sub>), 154.4 (NCO<sub>2</sub>t-Bu), 78.9 (C(CH<sub>3</sub>)<sub>3</sub>), 51.5 (CO<sub>2</sub>CH<sub>3</sub>), 51.0 (NCH<sub>2</sub>CH), 45.4 (NCH<sub>2</sub>CH<sub>2</sub>), 38.0 (NCH<sub>2</sub>CH), 32.5 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 31.1 (NCH<sub>2</sub>CH<sub>2</sub>), 28.4 (C(CH<sub>3</sub>)<sub>3</sub>), 28.1 (CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); IR (Neat film, NaCl) 2975, 2872, 1740, 1694, 1479, 1405, 1366, 1258, 1170, 1124, 882, 773 cm<sup>-1</sup>; HRMS (EI) m/z calc'd for C<sub>13</sub>H<sub>23</sub>NO<sub>4</sub> [M<sup>+</sup>]: 257.1627, found 257.1623.

### Procedure for the Synthesis of 2-Quinuclidonium tetrafluoroborate (1•HBF<sub>4</sub>).

A 10 mL tube equipped with stir bar and three-way stopcock was flame-dried under vacuum, backfilled with dry nitrogen, and charged with ketoazide 7 (306 mg, 2.00 mmol, 1.0 equiv) and dry ether (4 mL). To this solution was added ethereal HBF<sub>4</sub> (54 wt%, 0.55 mL, 4.00 mmol, 2.0 equiv) at 0 °C and the resulting mixture was stirred at ambient temperature until gas evolution ceased (3 h). The supernatant of the resulting suspension was removed by syringe and the remaining white solid was washed with dry ether (3 x 3 mL) and dried under vacuum. The resulting crude solid was then dissolved with 4 mL of dry acetonitrile and this solution was transferred to a 10 mL test tube, which was placed in septum sealed 200 mL Erlenmeyer flask. Dry Et<sub>2</sub>O (10 mL) was then added to Erlenmeyer flask outside of the tube, and the resulting flask was settled in a desiccator ( $P_2O_5$ ) at ambient temperature until the crystals were formed (6 days). After the mother liquor was removed by syringe, the solid was washed with dry Et<sub>2</sub>O (3 x 5 mL) and dried under vacuum to afford 164 mg (0.770 mmol, 38% vield) of 2-quinuclidonium tetrafluoroborate 1•HBF<sub>4</sub> as a colorless crystals; mp 185-200 °C dec.; <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, TMS = 0 ppm)  $\delta$  8.02 (br, 1H, N<sup>+</sup>H), 3.85-3.60 (m, 4H, NCH<sub>2</sub>), 2.99 (d, J = 3.0 Hz, 2H, COCH<sub>2</sub>), 2.51 (sept. J = 3.0 Hz, 1H, CH<sub>2</sub>CH), 2.10-1.90 (m, 4H, CH<sub>2</sub>CH); <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN, CD<sub>3</sub>CN = 118.69 ppm)  $\delta$  175.9 (C=O), 48.1 (CH<sub>2</sub>), 40.1 (CH<sub>2</sub>), 25.7 (CH), 22.7 (CH<sub>2</sub>); IR (KBr) 3168, 2981, 1822, 1468, 1398, 1336, 1312, 948, 823, 799, 766, 716 cm<sup>-1</sup>; HRMS (FAB, Pos.) m/z calc'd for C<sub>7</sub>H<sub>12</sub>NO [M+H]<sup>+</sup> 126.0919, found 126.0920. The obtained 2-quinuclidonium tetrafluoroborate 1•HBF<sub>4</sub> was recrystallized from CH<sub>3</sub>CN-Et<sub>2</sub>O to provide suitable crystals for X-ray analysis.

#### Procedure for the Reactivity Study of (1•HBF<sub>4</sub>) with 5 equiv of D<sub>2</sub>O.

To an oven dried NMR tube (8 inch) equipped with septum was charged **1**•**HBF**<sub>4</sub> (13.4 mg, 0.0629 mmol) and 0.75 mL of acetonitrile-d<sub>3</sub> under N<sub>2</sub> atmosphere. To this was added D<sub>2</sub>O (5.7  $\mu$ L, 0.315 mmol, 5.0 equiv) in one portion. After the cap was wrapped in parafilm, the tube was well shaken and the resulting tube was transferred to the probe of NMR spectrometer operating at ambient temperature. The ratio of **1**•**HBF**<sub>4</sub> to product amino acid was determined by the integral values of <sup>1</sup>H NMR spectra.

#### References

1. Dess, D. B.; Martin, J. C. J. Am. Chem. Soc. 1991, 113, 7277.

2. House, H. O.; Haack, J. L.; McDaniel, W. C.; VanDerveer, D. J. Org. Chem. 1983, 48, 1643.

3. Jung, M. E.; Speltz, L. M. J. Am. Chem. Soc. 1976, 98, 7882.

# X-ray crystallographic structure of 1•HBF<sub>4</sub>



Figure 1. ORTEP drawing of 1•HBF<sub>4</sub> (shown with 50% probability ellipsoids, BF<sub>4</sub><sup>-</sup> is omitted for clarity)

**Note:** Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 296767.

Empirical formula	$\left[\mathrm{C}_{7}\mathrm{H}_{12}\mathrm{NO}\right]^{+}\mathrm{BF}_{4}^{-}$
Formula weight	212.99
Crystallization Solvent	Acetonitrile/diethylether
Crystal Habit	Block
Crystal size	0.30 x 0.26 x 0.20 mm <sup>3</sup>
Crystal color	Colorless
Data Coll	ection
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
$\theta$ range for 11113 reflections used in lattice determination	2.61 to 33.10°
Unit cell dimensions	a = 12.5134(6)  Å b = 7.8049(4)  Å c = 18.4921(9)  Å
Volume	1806.05(15) Å <sup>3</sup>
Z	8
Crystal system	Orthorhombic
Space group	$Pca2_1$
Density (calculated)	1.567 Mg/m <sup>3</sup>
F(000)	880
$\theta$ range for data collection	2.20 to 33.53°
Completeness to $\theta = 33.53^{\circ}$	93.3%
Index ranges	$-18 \le h \le 18, -10 \le k \le 11, -28 \le l \le 28$
Data collection scan type	$\omega$ scans at 5 $\phi$ settings
Reflections collected	28405
Independent reflections	6413 [ $R_{int} = 0.0717$ ]
Absorption coefficient	0.156 mm <sup>-1</sup>
Absorption correction	None
Max. and min. transmission	0.9694 and 0.9546

# Table 1. Crystal data and structure refinement for 1•HBF<sub>4</sub> (CCDC 296767).

#### Table 1 (cont.)

# **Structure solution and Refinement**

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6413 / 7 / 281
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F <sup>2</sup>	3.203
Final R indices [I>2 $\sigma$ (I), 4707 reflections]	R1 = 0.0831, wR2 = 0.1590
R indices (all data)	R1 = 0.1122, wR2 = 0.1667
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	1.4(13)
Largest diff. peak and hole	1.434 and -1.240 e.Å <sup>-3</sup>

# **Special Refinement Details**

This compound crystallizes in the orthorhombic space group  $Pca2_1$  with Z = 8. Interestingly, it has been reported that very high correlation coefficients can be observed during least-squares refinement if certain conditions are present.<sup>1</sup> In addition to two molecules in the asymmetric unit, these two molecules need to be related by a local center of symmetry and that center needs to lie near x = 1/8 and y = 1/4. If these conditions are met; and they are here, then the correlation coefficients between atoms related by the local center will be very high and consequently the standard uncertainty of parameters derived from least-squares will also be high. Therefore the errors presented in this report are uncharacteristically high considering the quality of the data. These conditions also give rise to high R-factors and Goodness-of-fit. However, the connectivity of the molecule is unambiguous.

Refinement of  $F^2$  against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on  $F^2$ , conventional R-factors (R) are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma$  ( $F^2$ ) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

<sup>&</sup>lt;sup>1</sup> Marsh, R. E., Schomaker, V. and Herbstein, F. H. Arrays with Local Centers of Symmetry in Space Groups Pca2<sub>1</sub> and Pna2<sub>1</sub>. Acta Cryst., 1998, B54, 921-924.



Figure 2. Crystal packing of 1•HBF<sub>4</sub>.

	Х	у	Z	U <sub>eq</sub>	Occ
O(1A)	4301(2)	411(3)	1929(2)	17(1)	1
N(1A)	6163(3)	120(3)	1883(2)	17(1)	1
C(1A)	5100(3)	311(4)	2278(2)	9(1)	1
C(2A)	5257(3)	346(4)	3079(2)	12(1)	1
C(3A)	6441(3)	177(4)	3244(3)	17(1)	1
C(4A)	6848(3)	-1533(5)	2935(2)	20(1)	1
C(5A)	6656(3)	-1563(4)	2113(2)	19(1)	1
C(6A)	6895(3)	1584(5)	2069(2)	21(1)	1
C(7A)	7075(3)	1626(5)	2877(2)	20(1)	1
O(1B)	1805(3)	4894(4)	682(2)	54(1)	1
N(1B)	3636(3)	4873(3)	717(2)	19(1)	1
C(1B)	2590(4)	4902(5)	340(3)	38(1)	1
C(2B)	2751(4)	5013(6)	-462(3)	44(2)	1
C(3B)	3962(4)	5053(4)	-630(3)	23(1)	1
C(4B)	4467(4)	3401(6)	-344(2)	28(1)	1
C(5B)	4307(3)	3329(5)	496(2)	26(1)	1
C(6B)	4270(3)	6501(5)	553(2)	21(1)	1
C(7B)	4457(4)	6611(5)	-265(2)	27(1)	1
B(1A)	9178(4)	4903(4)	2571(3)	17(1)	1
F(1A)	9462(2)	3292(3)	2643(2)	59(1)	1
F(2A)	8220(2)	5116(3)	2201(2)	38(1)	1
F(3A)	9069(2)	5789(4)	3231(2)	40(1)	1
F(4A)	9968(2)	5789(3)	2178(1)	29(1)	1
B(1B)	6695(5)	21(5)	34(4)	24(1)	1
F(1B)	5723(2)	-120(3)	408(2)	37(1)	1
F(2B)	6510(4)	762(8)	-633(3)	36(2)	0.472(7)
F(3B)	7443(5)	824(8)	433(3)	50(2)	0.472(7)
F(4B)	7048(5)	-1648(8)	-141(4)	56(2)	0.472(7)
F(2C)	6866(6)	1795(8)	173(6)	126(4)	0.528(7)
F(3C)	7481(6)	-768(9)	379(5)	94(3)	0.528(7)
F(4C)	6572(5)	-464(12)	-643(3)	72(3)	0.528(7)

Table 2. Atomic coordinates (x 10<sup>4</sup>) and equivalent isotropic displacement parameters ( $Å^2x$  10<sup>3</sup>) for 1•HBF<sub>4</sub> (CCDC 296767). U(eq) is defined as the trace of the orthogonalized U<sup>ij</sup> tensor.

$\overline{O(1A)-C(1A)}$	1.192(4)	O(1B)-C(1B)	1.168(6)
N(1A)-C(6A)	1.504(5)	N(1B)-C(1B)	1.484(6)
N(1A)-C(5A)	1.512(5)	N(1B)-C(5B)	1.524(5)
N(1A)-C(1A)	1.526(5)	N(1B)-C(6B)	1.529(5)
C(1A)-C(2A)	1.495(5)	C(1B)-C(2B)	1.499(7)
C(2A)-C(3A)	1.518(5)	C(2B)-C(3B)	1.547(7)
C(3A)-C(4A)	1.539(5)	C(3B)-C(7B)	1.523(6)
C(3A)-C(7A)	1.539(5)	C(3B)-C(4B)	1.530(6)
C(4A)-C(5A)	1.540(6)	C(4B)-C(5B)	1.567(6)
C(6A)-C(7A)	1.511(6)	C(6B)-C(7B)	1.533(6)
$\mathbf{D}(1 \mathbf{A}) \mathbf{E}(1 \mathbf{A})$	1 214(4)	$\mathbf{D}(1\mathbf{D}) \mathbf{E}(2\mathbf{C})$	1 225(0)
B(1A) - F(1A) D(1A) - F(2A)	1.314(4) 1.200(6)	D(1D)-F(3C)	1.323(9)
B(1A)-F(2A)	1.390(6)	B(1B)-F(4C)	1.316(9)
B(1A)-F(3A)	1.410(6)	B(1B)-F(3B)	1.346(8)
B(1A)-F(4A)	1.409(5)	B(1B)-F(2B)	1.381(9)
		B(IB)-F(IB)	1.404(7)
		B(1B)-F(4B)	1.413(7)
		B(1B)-F(2C)	1.424(8)
C(6A)-N(1A)-C(5A)	110.3(3)	C(1B)-N(1B)-C(5B)	111.8(3)
C(6A)-N(1A)-C(1A)	110.3(3)	C(1B)-N(1B)-C(6B)	110.6(3)
C(5A)-N(1A)-C(1A)	107.8(3)	C(5B)-N(1B)-C(6B)	108.5(3)
O(1A)-C(1A)-C(2A)	130.2(3)	O(1B)-C(1B)-N(1B)	119.1(4)
O(1A)-C(1A)-N(1A)	118.6(3)	O(1B)-C(1B)-C(2B)	130.5(5)
C(2A)-C(1A)-N(1A)	111.2(3)	N(1B)-C(1B)-C(2B)	110.3(4)
C(1A)-C(2A)-C(3A)	109.1(3)	C(1B)-C(2B)-C(3B)	109.3(4)
C(2A)-C(3A)-C(4A)	108.9(3)	C(7B)-C(3B)-C(4B)	110.6(4)
C(2A)-C(3A)-C(7A)	110.5(3)	C(7B)-C(3B)-C(2B)	109.0(4)
C(4A)-C(3A)-C(7A)	107.6(4)	C(4B)-C(3B)-C(2B)	108.6(4)
C(3A)-C(4A)-C(5A)	109.2(3)	C(3B)-C(4B)-C(5B)	108.6(4)
N(1A)-C(5A)-C(4A)	109.2(3)	N(1B)-C(5B)-C(4B)	108.0(3)
N(1A)-C(6A)-C(7A)	109.5(3)	N(1B)-C(6B)-C(7B)	108.8(3)
C(6A)-C(7A)-C(3A)	110.1(3)	C(3B)-C(7B)-C(6B)	109.3(4)
F(1A)-B(1A)-F(2A)	113.5(4)	F(3C)-B(1B)-F(4C)	114.3(7)
F(1A)-B(1A)-F(3A)	114.1(5)	F(3B)-B(1B)-F(2B)	114.3(5)
F(2A)-B(1A)-F(3A)	106.5(4)	F(3C)-B(1B)-F(1B)	111.7(6)
F(1A)-B(1A)-F(4A)	109.4(4)	F(4C)-B(1B)-F(1B)	110.1(5)
F(2A)-B(1A)-F(4A)	107.0(4)	F(3B)-B(1B)-F(1B)	111.6(6)
F(3A)-B(1A)-F(4A)	105.9(3)	F(2B)-B(1B)-F(1B)	109.1(5)
		F(3B)-B(1B)-F(4B)	109.7(6)
		F(2B)-B(1B)-F(4B)	103.6(6)
		F(1B)-B(1B)-F(4B)	108.1(4)
		F(3C)-B(1B)-F(2C)	104.6(6)
		F(4C)-B(1B)-F(2C)	118.0(7)
		F(1B)-B(1B)-F(2C)	96.7(5)

Table 3. Bond lengths [Å] and angles [°] for 1•HBF<sub>4</sub> (CCDC 296767).

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
O(1A)	120(12)	160(10)	242(15)	3(9)	-11(11)	14(8)
N(1A)	189(19)	211(16)	124(18)	2(11)	38(15)	34(10)
C(1A)	92(10)	57(8)	109(10)	-3(7)	6(8)	-19(7)
C(2A)	111(18)	113(14)	143(18)	-21(11)	1(13)	14(10)
C(3A)	180(20)	165(17)	180(20)	-18(13)	20(18)	24(12)
C(4A)	168(17)	161(17)	257(19)	41(15)	-17(16)	111(13)
C(5A)	98(15)	188(16)	270(20)	-56(14)	82(14)	1(13)
C(6A)	59(14)	225(18)	340(20)	59(16)	16(16)	-36(12)
C(7A)	158(17)	183(16)	260(20)	-17(15)	-15(16)	-66(14)
O(1B)	210(18)	1110(30)	302(19)	-42(18)	48(15)	-69(15)
N(1B)	120(18)	272(17)	170(20)	6(12)	29(15)	-3(10)
C(1B)	250(20)	560(30)	330(20)	-61(18)	-42(18)	-28(18)
C(2B)	320(30)	790(40)	210(20)	10(20)	-40(19)	7(19)
C(3B)	200(20)	340(20)	150(20)	61(13)	29(19)	22(13)
C(4B)	390(20)	340(20)	122(17)	-14(16)	7(17)	-22(17)
C(5B)	400(20)	185(17)	190(19)	1(15)	8(17)	26(16)
C(6B)	260(20)	186(17)	170(18)	-35(13)	47(15)	-23(14)
C(7B)	350(20)	235(19)	230(20)	10(16)	63(18)	48(16)
B(1A)	150(20)	151(18)	200(30)	19(13)	30(20)	-9(11)
F(1A)	211(11)	123(9)	1450(30)	173(15)	230(15)	66(9)
F(2A)	244(15)	695(19)	206(16)	-32(11)	-32(14)	96(10)
F(3A)	273(13)	703(19)	219(12)	-152(14)	-5(11)	-5(13)
F(4A)	209(10)	368(12)	298(11)	68(11)	126(10)	-109(10)
B(1B)	230(30)	270(20)	230(30)	17(16)	0(20)	-15(14)
F(1B)	294(16)	592(18)	232(17)	-60(10)	0(14)	-75(10)
F(2B)	330(30)	550(40)	220(30)	70(30)	30(20)	40(30)
F(3B)	480(30)	490(40)	510(40)	-100(30)	-10(30)	-160(30)
F(4B)	480(40)	400(30)	810(50)	-180(30)	60(30)	90(30)
F(2C)	740(50)	230(30)	2820(120)	140(50)	-270(60)	-90(30)
F(3C)	550(40)	690(50)	1590(80)	110(50)	-230(50)	270(40)
F(4C)	550(40)	1400(80)	230(30)	-140(40)	110(20)	-270(50)

Table 4. Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>4</sup>) for 1•HBF<sub>4</sub> (CCDC 296767). The anisotropic displacement factor exponent takes the form:  $-2\pi^2$  [ h<sup>2</sup> a<sup>\*2</sup>U <sup>11</sup> + ... + 2 h k a<sup>\*</sup> b<sup>\*</sup> U<sup>12</sup> ]

D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)
N(1A)-H(1A)F(1B)	0.93	1.86	2.789(6)	174.3
N(1A)-H(1A)F(3B)	0.93	2.55	3.171(7)	124.7
N(1B)-H(1B)F(2A)#1	0.93	1.86	2.792(6)	175.4
N(1B)-H(1B)F(4A)#1	0.93	2.59	3.215(5)	124.9

Table 5.	Hydrogen	bonds f	for 1	•HBF <sub>4</sub>	(CCDC	296767)	[Å and <sup>c</sup>	'].
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Symmetry transformations used to generate equivalent atoms: #1 x-1/2,-y+1,z

# Spectra data of reported compounds.

















Supporting Information for Tani and Stoltz









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