Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Base-catalyzed Diastereoselective Trimerization of Trifluoroacetone

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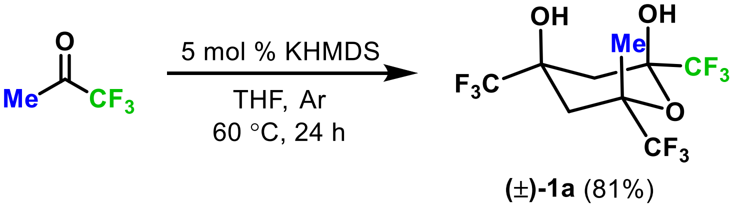
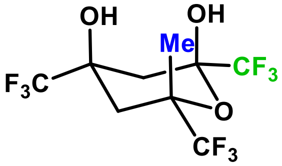
Materials and Methods

All reactions were carried out in flame-dried glassware under an atmosphere argon with magnetic stirring. Anhydrous tetrahydrofuran (THF), toluene (PhMe), diethyl ether (Et_2O), dichloromethane (DCM), and benzene were obtained by passing commercially available pre-dried, deoxygenated solvents through a column of activated alumina. All reagents were used directly from commercial suppliers (Sigma-Aldrich Co., Strem Chemicals Inc., Acros Organics, and Oakwood Products Inc.), unless otherwise noted. Reactions were monitored by thin-layer chromatography using EMD Millipore 60 F_{254} silica plates, visualizing with $KMnO_4$ staining solution, and also by GC-MS using a Shimadzu GC2010 gas chromatograph and connected Shimadzu QP2010S mass spectrometer. **NMR** spectra were recorded on either a Bruker – Biospin DRX 600, Bruker – DRX 500, or a Bruker – AMX 400. These instruments were calibrated using residual undeuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; $(CD_3)_2CO$: δ_H = 2.05 ppm, δ_C = 29.84 ppm, 206.26 ppm) as an internal reference. Data is reported as follows: chemical shift in parts per million (δ, ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constants (Hz). ^1J-couplings between ^{13}C and ^{19}F nuclei in the ^{13}C NMR spectra for the -CF_3 groups in the boranes are not determined, however, ^2J-couplings are reported. **LRMS** data was obtained by electron ionization (EI) using a Shimadzu GC2010 gas chromatograph and connected Shimadzu QP2010S mass spectrometer.

Synthesis and Characterization of Oxane (±)-1a†



To a flame-dried flask containing a stir bar and dry THF (29.5 mL) under an atmosphere of argon was added a 1M solution of KHMDS in THF (500 µL, 0.50 mmol, 0.05 equiv.). Trifluoroacetone (900 µL, 10.0 mmol, 1.0 equiv.) was added in one portion. The rubber septum was immediately replaced with a polymer cap that was parafilmed in place and the reaction heated to 60 °C for 24 hours. Upon completion, the reaction was quenched with an aqueous saturated solution of NH_4Cl and the organic layer separated. The aqueous layer was extracted once with EtOAc and the combined organics dried over Na_2SO_4 and concentrated to a viscous oil. After leaving this oil under high vacuum for ~30 minutes it solidified into a white crystalline product that was broken apart with a spatula and triturated with hexanes (2 x 5 mL). After drying, 904 mg of **1a** (81% yield) was obtained with a diastereomeric purity of >20:1.



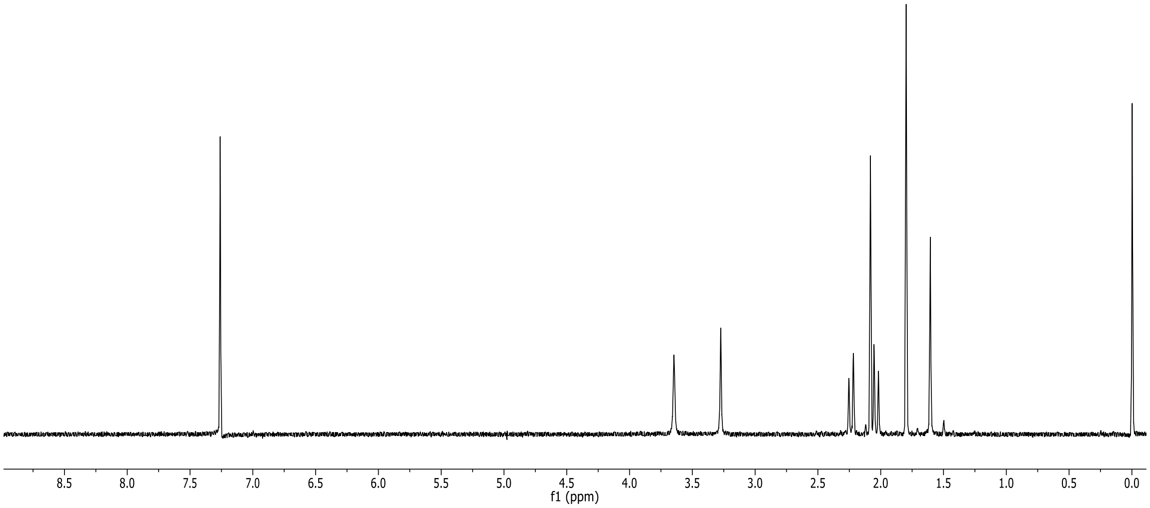
(±)-1a: (904 mg, 2.69 mmol, 81% yield, colorless shards). **^{1}H NMR*** (600 MHz, $CDCl_3$) δ 3.70 (s, 1H), 3.31 (s, 1H), 2.28 – 2.19 (m, 1H), 2.08 (d, *J* = 2.3 Hz, 2H), 2.04 (d, *J* = 14.4 Hz, 1H), 1.80 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 124.71 (q, *J* = 282.97 Hz), 124.42 (q, *J* = 284.14 Hz), 121.49 (q, *J* = 285.25 Hz), 94.83 (q, *J* = 34.0 Hz), 76.18 (q, *J* = 29.8 Hz), 70.89 (q, *J* = 30.3 Hz), 30.05, 29.83, 22.20. **^{19}F NMR** (376 MHz, MeOD) δ -86.27, -86.54, -88.43 (hexafluorobenzene reference at -164.90 ppm). **X-RAY**: (CCDC 1531815). **LRMS** (EI): 303 *m/z* $[M – 2(OH)]^+$; 267 *m/z* $[M – CF_3]^+$. **R_f** = 0.39 (1:4 EtOAc/hexanes). **MP** = 110.9 – 112.8 °C (crystallized from EtOAc).

†*Note:* When performed on 100 mmol scale at a concentration of 1M, 8.24 g (74% yield) of **1a** was obtained.

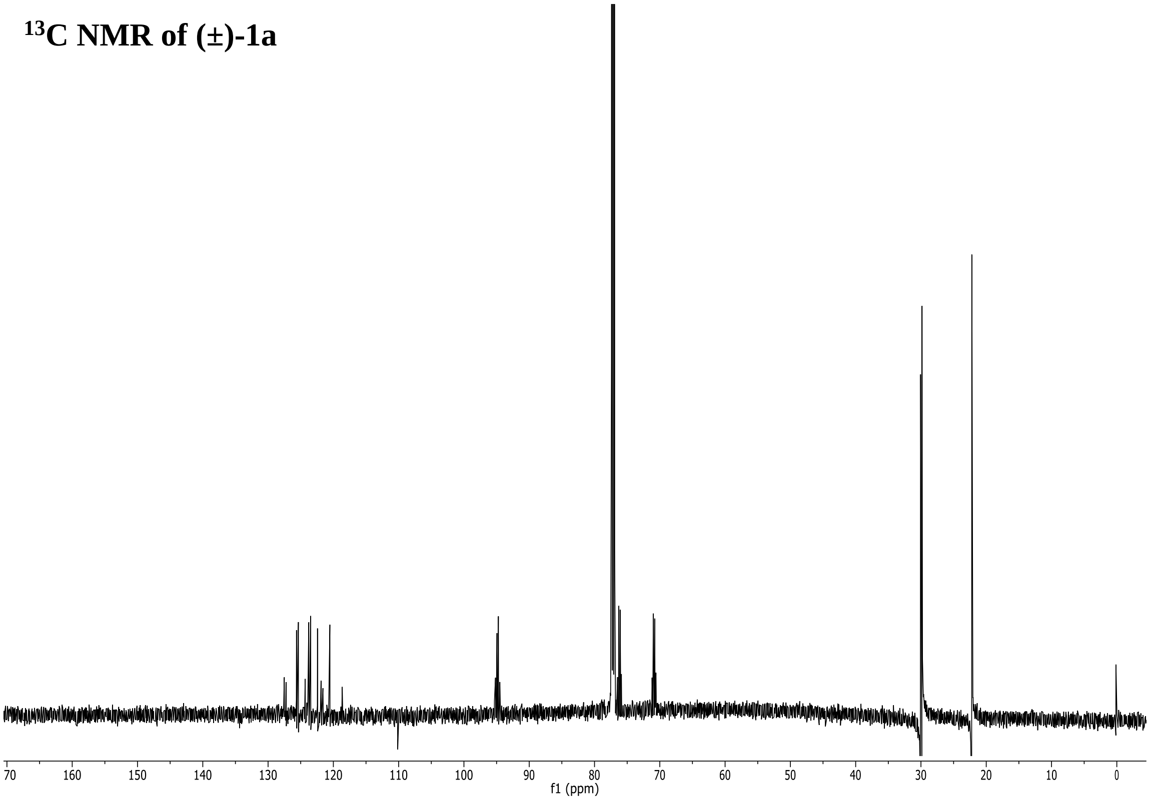
Note:* Alcoholic protons are not visible in MeOD: **^{1}H NMR (600 MHz, MeOD) δ 2.17 (dd, *J* = 14.1, 2.1 Hz, 1H), 2.00 (dd, *J* = 13.9, 2.1 Hz, 1H), 1.93 (d, *J* = 13.9 Hz, 1H), 1.86 (d, *J* = 14.1 Hz, 1H), 1.81 (d, *J* = 1.3 Hz, 3H).

^{1}H, ^{13}C, ^{19}F, and 2D NMR Spectra of Oxane (±)-1a

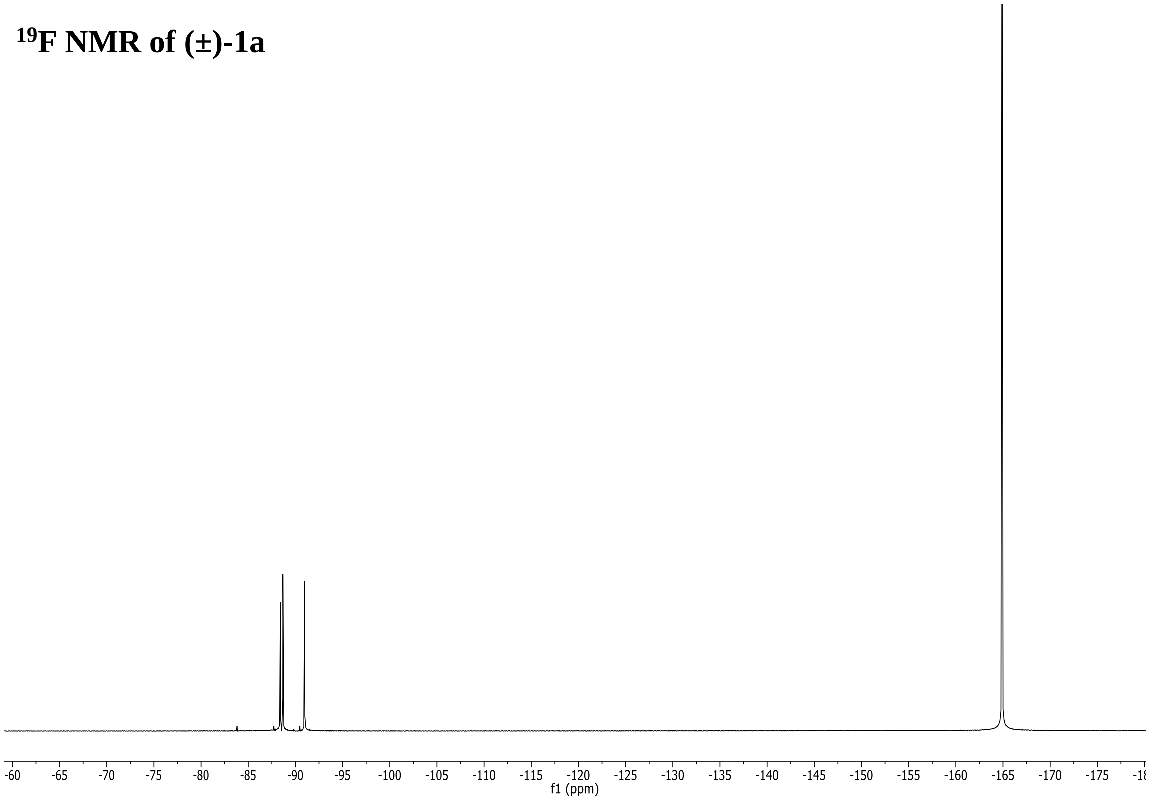
^{1}H NMR of (±)-1a



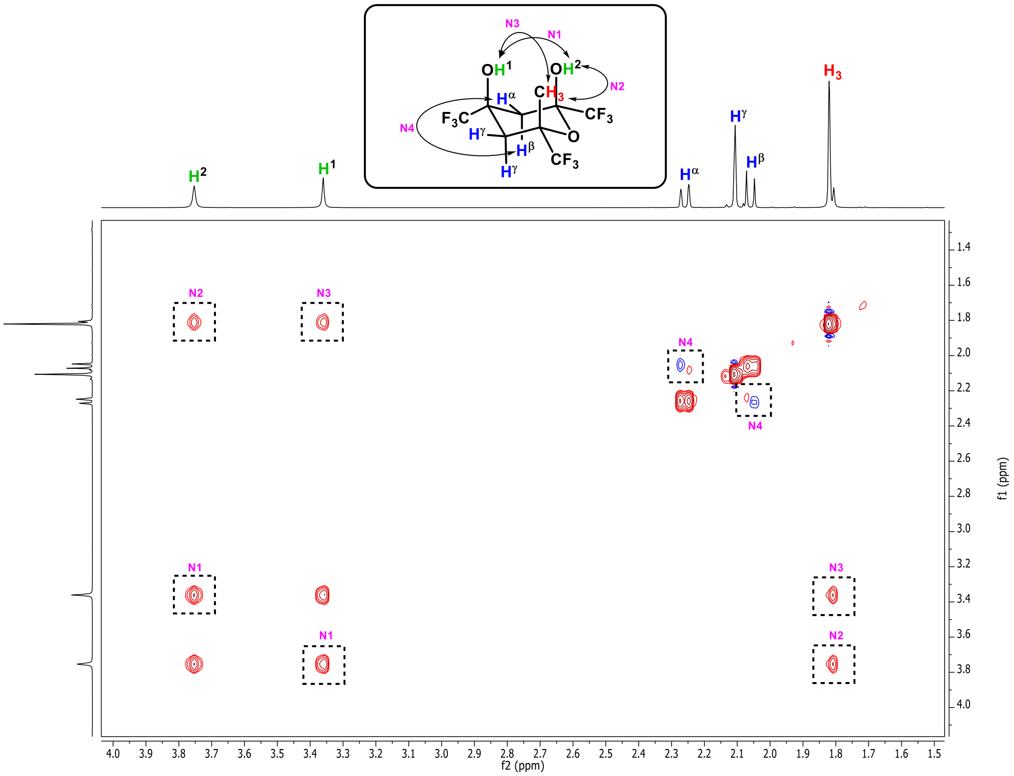
^{13}C NMR of (±)-1a



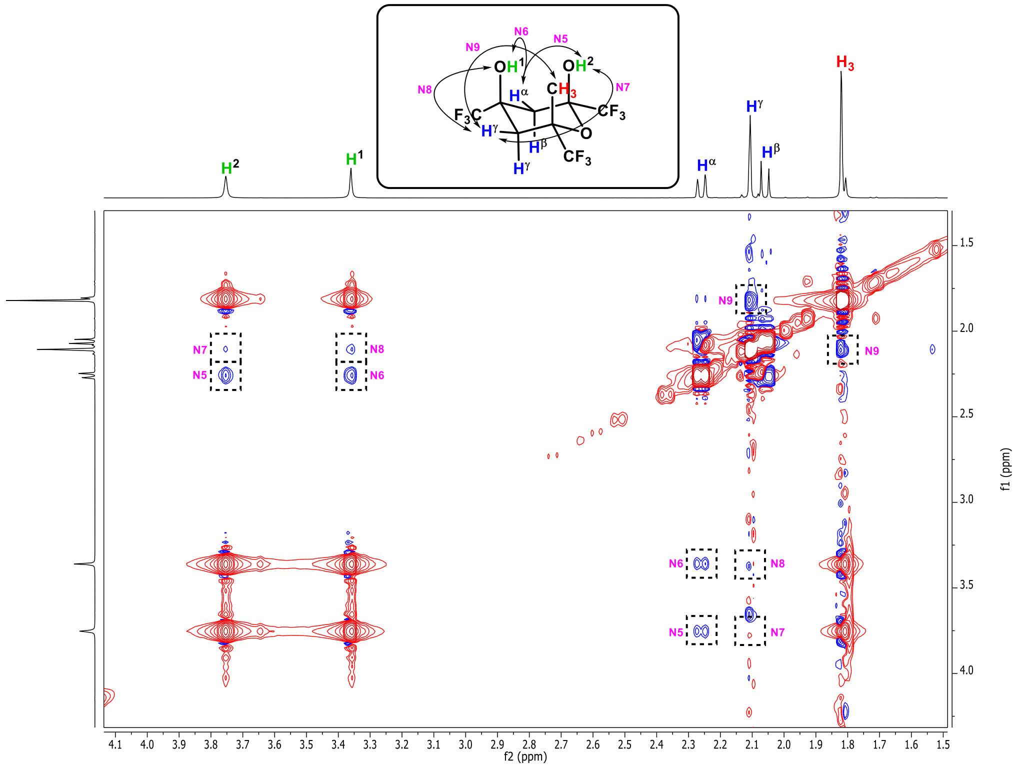
^{19}F NMR of (±)-1a



NOESY of **(±)-1a**: Strong correlations.



NOESY of **(±)-1a**: Weak correlations.



^{1}**H – ^{13}C HSQC** of **(±)-1a**: Proton identities were determined unequivocally using NOESY.

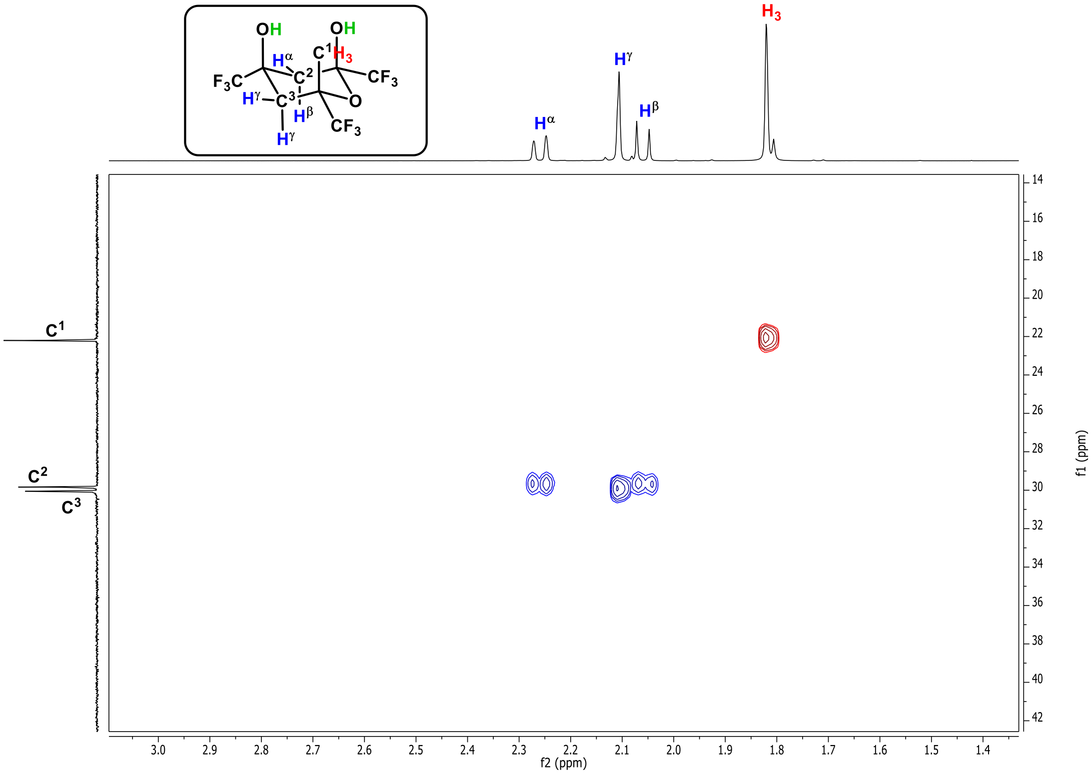
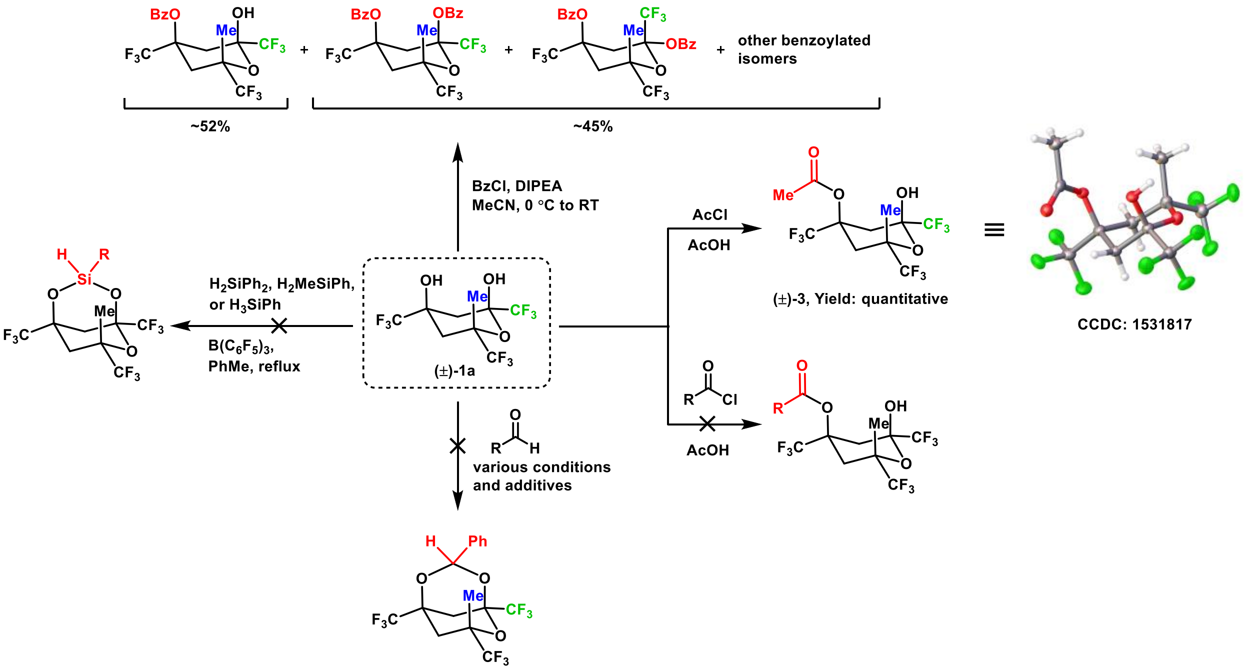
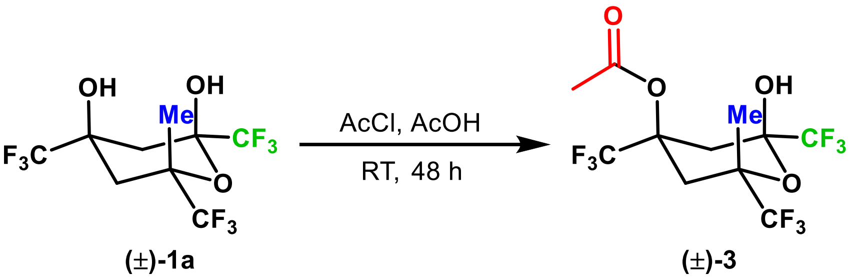


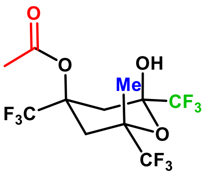
Figure S1: Attempted Derivatizations of Oxane (±)-1a



Synthesis and Characterization of Oxane (±)-3



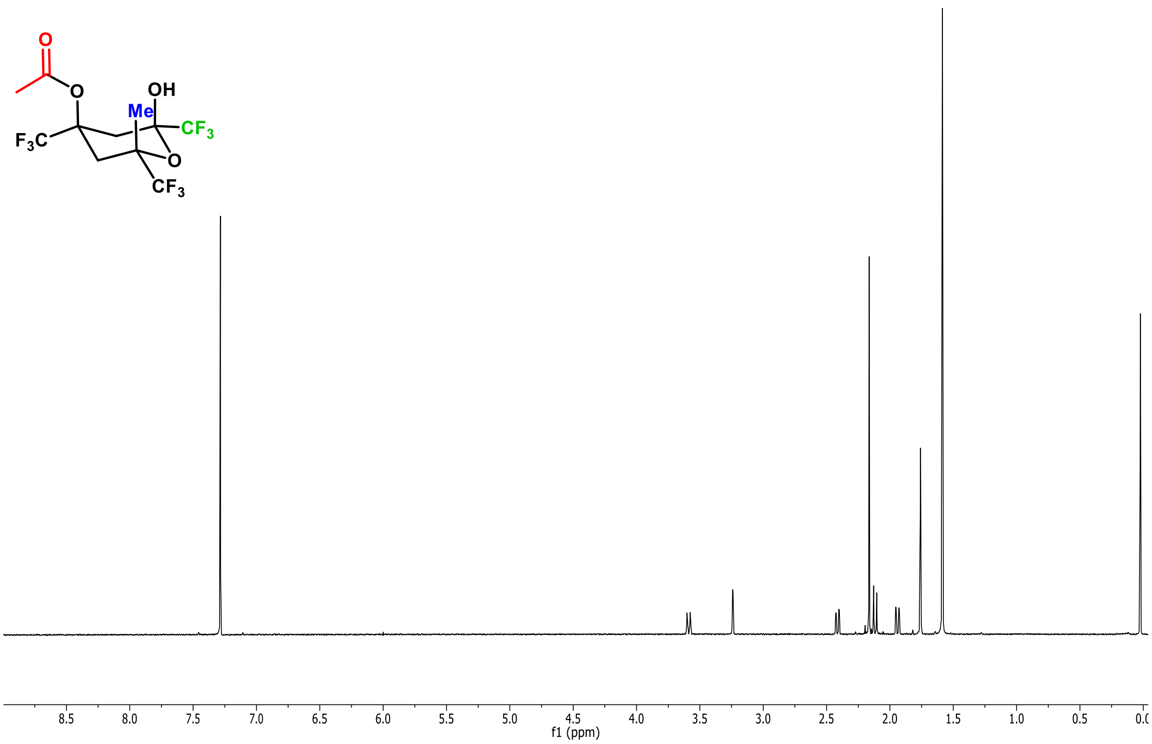
To oxane **(±)-1a** (100 mg, 0.30 mmol, 1.0 equiv.) in a 1 dram vial containing a stir bar was added AcCl (508 µL, 7.15 mmol, 24 equiv.) and AcOH (68 µL, 1.20 equiv., 4.0 equiv.). This mixture was stirred at room temperature for 48 hours under ambient conditions and subsequently concentrated with a stream of air. This was placed under high vacuum, triturated with hexanes (3 x 5 mL), and dried to give oxane **(±)-3** (110 mg, 98%).



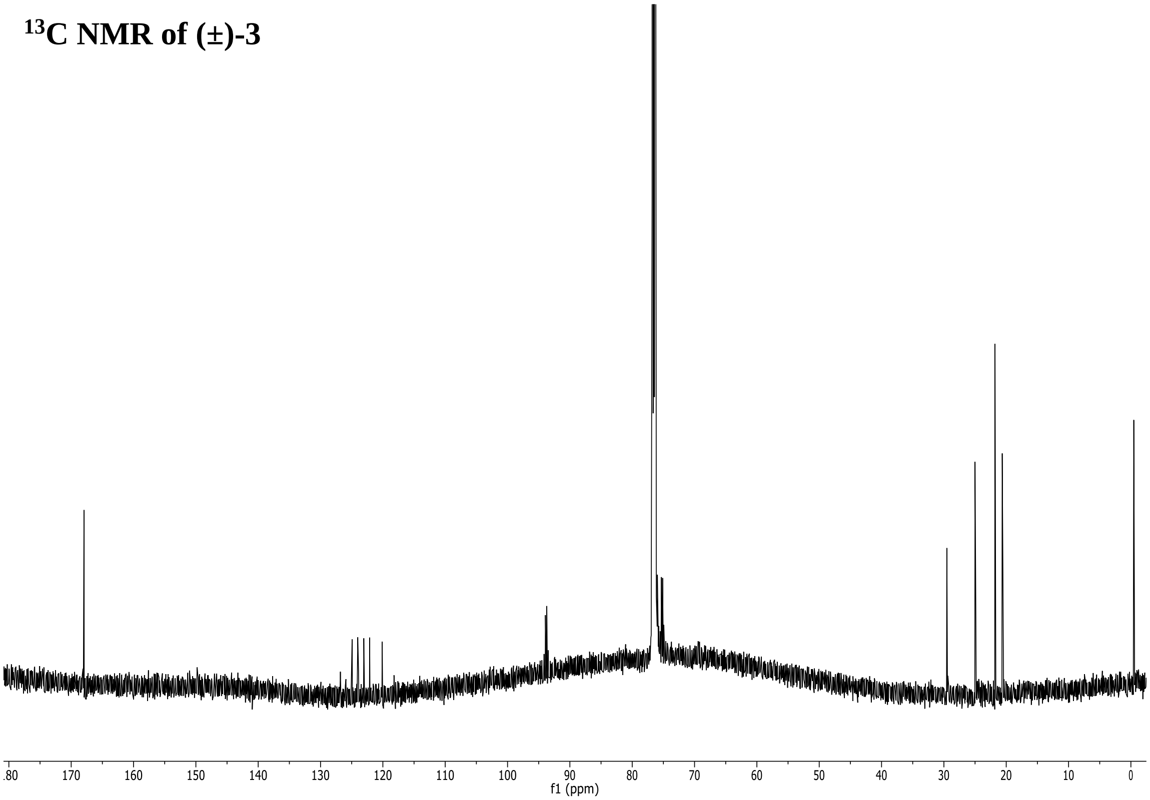
(±)-3: (110 mg, 0.298 mmol, 98% yield, white solid). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.62 – 3.52 (m, 1H), 3.22 (d, *J* = 2.2 Hz, 1H), 2.39 (dd, *J* = 14.5, 2.5 Hz, 1H), 2.14 (d, *J* = 0.7 Hz, 3H), 2.09 (d, *J* = 14.4 Hz, 1H), 1.92 (dd, *J* = 14.8, 2.2 Hz, 1H), 1.74 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.56, 129.11, 127.42, 126.54, 125.54, 124.64, 124.51, 123.67, 122.74, 122.62, 120.73, 118.83, 118.61, 94.32 (q, *J* = 32.5 Hz), 76.58 (q, *J* = 30.3 Hz), 75.74 (q, *J* = 29.6 Hz), 30.14, 25.62, 22.42, 21.26. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -81.61, -88.40, -91.00. **X-RAY**: (CCDC 1531817). **R$_f$** = 0.43 (1:4 EtOAc/hexanes)

^{1}H, ^{13}C, and ^{19}F NMR Spectra of Oxane (±)-3

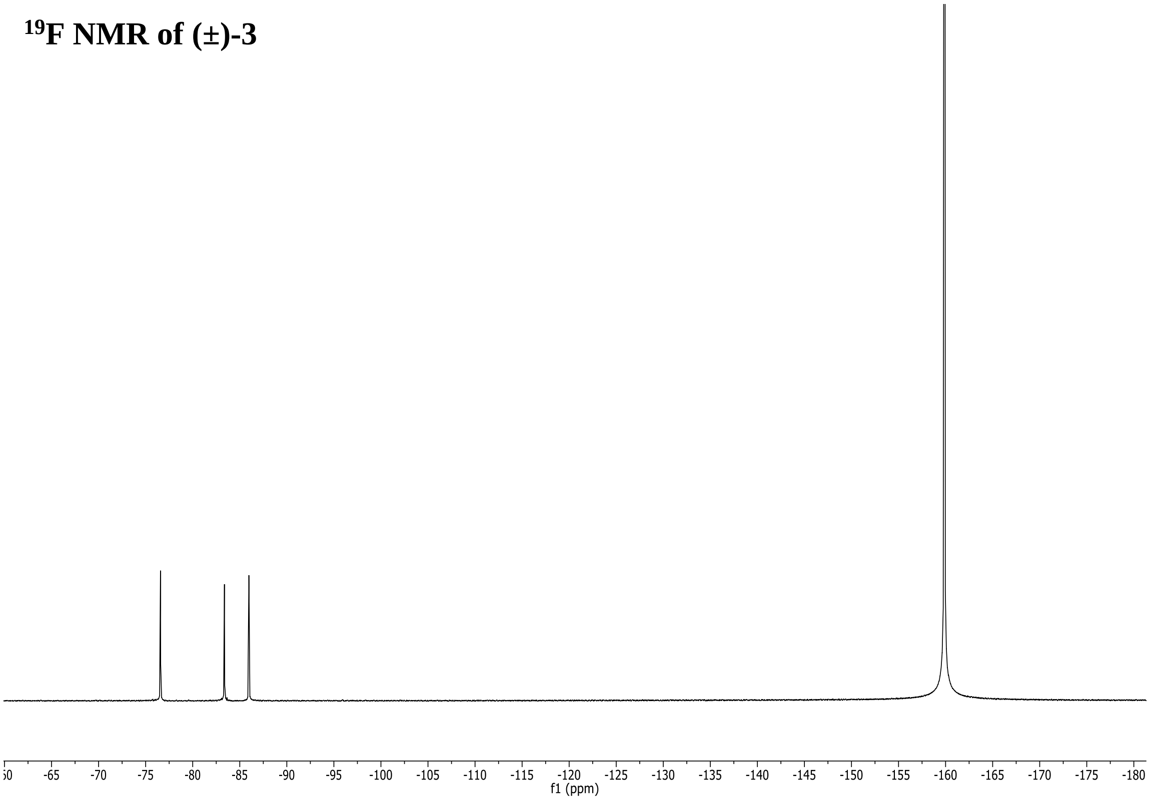
^{1}H NMR of (±)-3



^{13}C NMR of (±)-3



^{19}F NMR of (±)-3



-65
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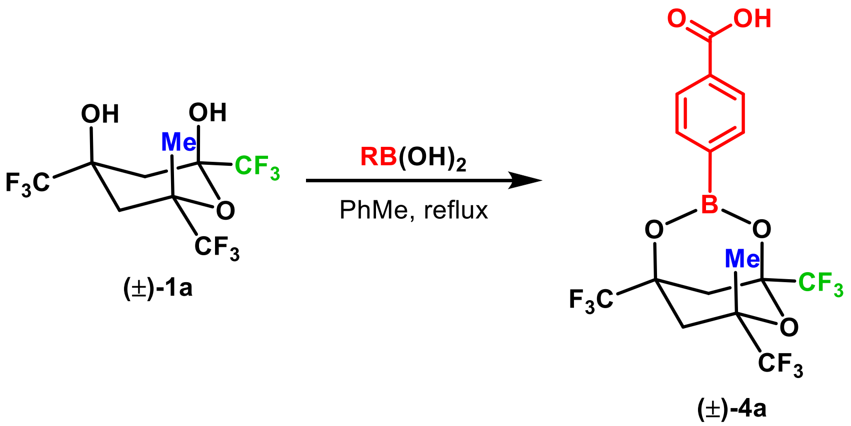
f1 (ppm)

Synthesis and Characterization of Borates (±)-4a-4j

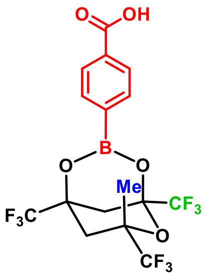


Standard procedure for 4a – 4f

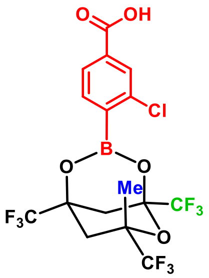
Oxane **(±)-1a** (100 mg, 0.30 mmol, 1.0 equiv.) and 4-carboxyphenylboronic acid (49 mg, 0.30 mmol, 1.0 equiv.) were added to a 1 dram vial equipped with a stir bar under ambient conditions. Dry toluene (1.5 mL) was added and the reaction heated to 110 °C for 24 hours. Upon completion, the solution was cooled, concentrated, and azeotroped with additional toluene (3 x 4 mL) to remove residual water. This delivered a reasonably pure white solid which was triturated with hexanes (2 x 3 mL) to give borane **(±)-4a** (116 mg, 83%) as a white solid.

Standard procedure for 4g – 4j

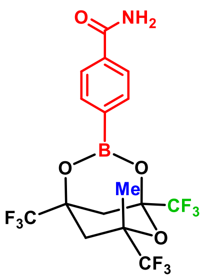
Same as above procedure, except no trituration.



(±)-4a: (116 mg, 0.249 mmol, 83% yield, white solid). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.17 – 8.14 (m, 2H), 8.00 – 7.97 (m, 2H), 2.40 (d, J = 14.6 Hz, 1H), 2.35 – 2.30 (m, 2H), 2.27 (d, J = 12.8 Hz, 1H), 1.52 (s, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 170.89, 134.17, 132.36, 129.02, 128.82, 128.05, 126.91, 125.72, 125.03, 123.85, 123.16, 123.04, 121.99, 121.17, 119.30, 117.42, 92.90 (q, J = 35.9 Hz), 75.61 (q, J = 30.3 Hz), 71.55 (q, J = 32.9 Hz), 31.72, 28.55, 23.29. **^{19}F NMR** (376 MHz, CDCl$_3$) δ -87.67, -88.18, -89.80. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.

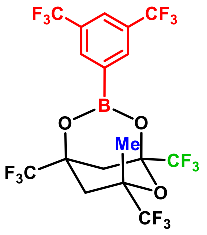


(±)-4b: (129 mg, 0.258 mmol, 86% yield, white solid). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.11 (d, J = 1.5 Hz, 1H), 7.99 (dd, J = 7.8, 1.5 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 2.42 (d, J = 14.6 Hz, 1H), 2.34 (d, J = 13.0 Hz, 3H), 2.28 (d, J = 12.7 Hz, 1H), 1.60 (d, J = 1.3 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 170.19, 140.64, 136.85, 133.68, 131.61, 130.43, 130.02, 129.19, 128.48, 128.37, 127.55, 125.63, 125.45, 124.36, 123.76, 122.50, 121.70, 119.83, 93.00 (q, J = 36.4 Hz), 75.45 (q, J = 30.5 Hz), 71.75 (q, J = 32.9 Hz), 31.79, 28.43, 23.50. **^{19}F NMR** (376 MHz, CDCl$_3$) δ -87.49, -88.12, -89.73. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.

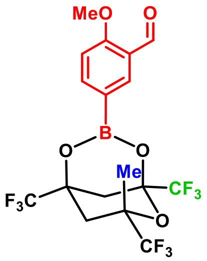


(±)-4c:* (120 mg, 0.258 mmol, 86% yield, white solid). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.97 – 7.93 (m, 1H), 7.87 – 7.83 (m, 1H), 7.28 – 7.23 (m, 1H), 7.20 – 7.13 (m, 1H), 6.13 (s, 1H), 5.83 (s, 1H), 2.44 – 2.23 (m, 4H), 1.51 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ δ 168.96, 138.02, 137.14, 135.04, 132.20, 129.18, 128.80, 128.37, 127.48, 126.93, 125.65, 125.44, 124.48, 123.78, 122.61, 121.79, 119.92, 93.10 (q, *J* = 36.0 Hz), 75.59 (q, *J* = 30.4 Hz), 71.72 (q, *J* = 32.7 Hz), 31.71, 28.54, 23.26. **^{19}F NMR** (376 MHz, CDCl$_3$) δ (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.

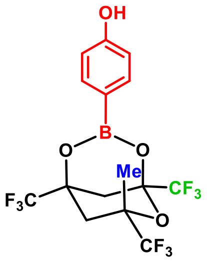
**Note: Hexanes is present in ^{1}H-NMR and ^{13}C-NMR spectra and is ommitted from the characterization above. Heating under high vacuum (60 °C at ~100 mTorr) for 24 hours failed to remove residual hexanes. Dissolution in other solvents (EtOAc, Et$_2$O, DCM) and evaporation resulted in their deposition into product material. These solvents were also unable to be removed under high vacuum.*



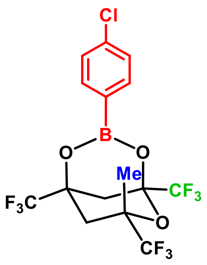
(±)-4d: (107 mg, 0.192 mmol, 64% yield, white solid). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 8.25 (dd, *J* = 2.0, 1.0 Hz, 2H), 8.05 (tt, *J* = 1.7, 0.9 Hz, 1H), 2.43 (d, *J* = 14.7 Hz, 1H), 2.39 – 2.28 (m, 3H), 1.52 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 134.46, 131.89 (q, *J* = 33.5 Hz), 127.42, 126.50 (m, *J* = 3.7 Hz), 126.19, 126.04, 125.55, 124.32, 124.23, 123.67, 123.52, 122.45, 122.43, 121.80, 121.65, 120.62, 120.58, 119.78, 117.90, 93.32 (q, *J* = 36.3 Hz), 75.68 (q, *J* = 30.6 Hz), 72.11 (q, *J* = 32.9 Hz), 31.71, 28.55, 23.51. **^{19}F NMR** (376 MHz, CDCl$_3$) δ -66.10, -87.51, -88.11, -89.67. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.



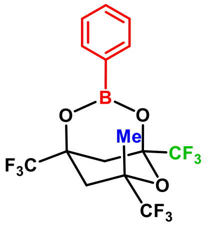
(±)-4e: (77 mg, 0.160 mmol, 54% yield, tan solid). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 10.48 (s, 1H), 8.33 (d, *J* = 1.8 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.99 (s, 3H), 2.40 – 2.34 (m, 1H), 2.31 – 2.26 (m, 2H), 2.23 (d, *J* = 12.5 Hz, 1H), 1.49 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 189.71, 165.12, 142.52, 135.96, 128.75, 127.57, 126.38, 125.70, 124.72, 124.51, 123.82, 123.70, 122.64, 121.95, 121.83, 119.95, 118.08, 111.49, 93.02 (q, *J* = 35.9 Hz), 75.54 (q, *J* = 30.4 Hz), 71.57 (q, *J* = 32.6 Hz), 55.99, 31.71, 28.57, 23.21. **^{19}F NMR** (376 MHz, CDCl$_3$) δ -87.67, -88.21, -89.80. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.



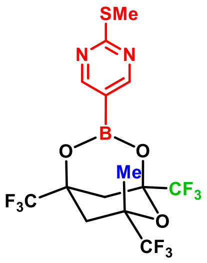
(±)-4f: (85 mg, 0.194 mmol, 65% yield, white solid). **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.80 – 7.76 (m, 2H), 6.89 – 6.84 (m, 2H), 5.06 (s, 1H), 2.35 (d, *J* = 14.4 Hz, 1H), 2.29 – 2.19 (m, 3H), 1.51 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl$_3$) δ 159.66, 137.05, 136.71, 128.30, 127.62, 126.93, 126.76, 126.49, 125.77, 124.62, 123.89, 122.75, 121.91, 120.04, 115.26, 115.01, 92.70 (q, *J* = 35.6 Hz), 75.31 (q, *J* = 29.8 Hz), 71.37 (q, *J* = 32.7 Hz), 31.70, 28.58, 23.16. **^{19}F NMR** (376 MHz, CDCl$_3$) δ -87.85, -88.24, -89.95. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.



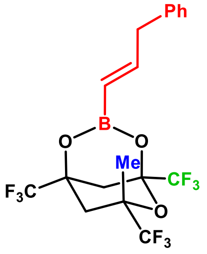
(±)-4g: (123 mg, 0.270 mmol, 90% yield, viscous yellow liquid). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.43 – 7.38 (m, 2H), 2.41 – 2.33 (m, 1H), 2.32 – 2.21 (m, 3H), 1.50 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.53, 136.13, 129.19, 128.62, 128.38, 126.37, 125.68, 125.45, 124.50, 123.80, 123.69, 122.64, 121.93, 121.81, 119.94, 118.06, 93.05 (q, *J* = 35.8 Hz), 75.56 (q, *J* = 30.3 Hz), 71.61 (q, *J* = 32.6 Hz), 31.70, 28.55, 23.23. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.76, -88.22, -89.87. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.



(±)-4h: (125 mg, 0.296 mmol, 99% yield, brown solid). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.57 – 7.53 (m, 1H), 7.42 (tq, *J* = 7.1, 0.8 Hz, 2H), 2.37 (d, *J* = 14.5 Hz, 1H), 2.31 – 2.26 (m, 2H), 2.24 (d, *J* = 13.1 Hz, 1H), 1.52 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 134.77, 132.97, 128.73, 128.19, 127.84, 127.14, 126.45, 125.74, 124.58, 123.86, 123.76, 122.71, 121.88, 120.84, 120.01, 118.13, 93.00 (q, *J* = 37.0 Hz), 75.55 (q, *J* = 30.3 Hz), 71.49 (q, *J* = 32.5 Hz), 31.72, 28.58, 23.21. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.80, -88.22, -89.90. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.



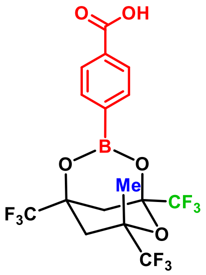
(±)-4i: (132 mg, 0.282 mmol, 94% yield, yellow wax). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.82 (s, 2H), 2.59 (s, 3H), 2.45 – 2.34 (m, 2H), 2.34 – 2.24 (m, 2H), 1.52 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.69, 162.66, 129.18, 128.37, 127.43, 126.18, 125.56, 125.44, 124.31, 123.69, 123.51, 122.44, 121.64, 120.57, 119.76, 93.11 (q, *J* = 36.4 Hz), 75.62 (q, *J* = 30.6 Hz), 71.86 (q, *J* = 33.1 Hz), 31.70, 28.62, 23.38, 14.24. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.67, -88.14, -89.80. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.

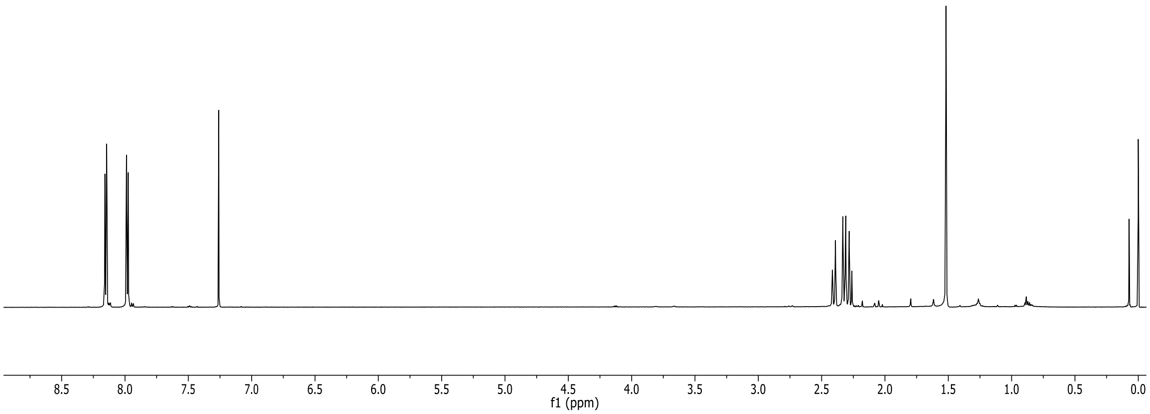


(±)-4j: (123 mg, 0.266 mmol, 89% yield, yellow wax). **^{1}H NMR** (^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.19 – 7.15 (m, 2H), 6.94 (dt, *J* = 17.7, 6.3 Hz, 1H), 5.44 (dt, *J* = 17.7, 1.7 Hz, 1H), 3.52 (dd, *J* = 6.4, 1.6 Hz, 2H), 2.27 (d, *J* = 14.2 Hz, 1H), 2.20 – 2.10 (m, 3H), 1.52 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.12, 137.87, 128.45, 128.14, 128.06, 127.00, 126.00, 125.85, 125.77, 125.13, 123.90, 123.25, 123.07, 122.03, 121.38, 121.20, 119.32, 117.45, 92.04 (q, *J* = 35.9 Hz), 74.75 (q, *J* = 30.4 Hz), 70.42 (q, *J* = 32.6 Hz), 41.54, 31.03, 27.83, 22.54. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -87.89, -88.26, -89.99. (hexafluorobenzene reference at -164.90 ppm). **R$_f$** = Unstable to silica and neutral alumina.

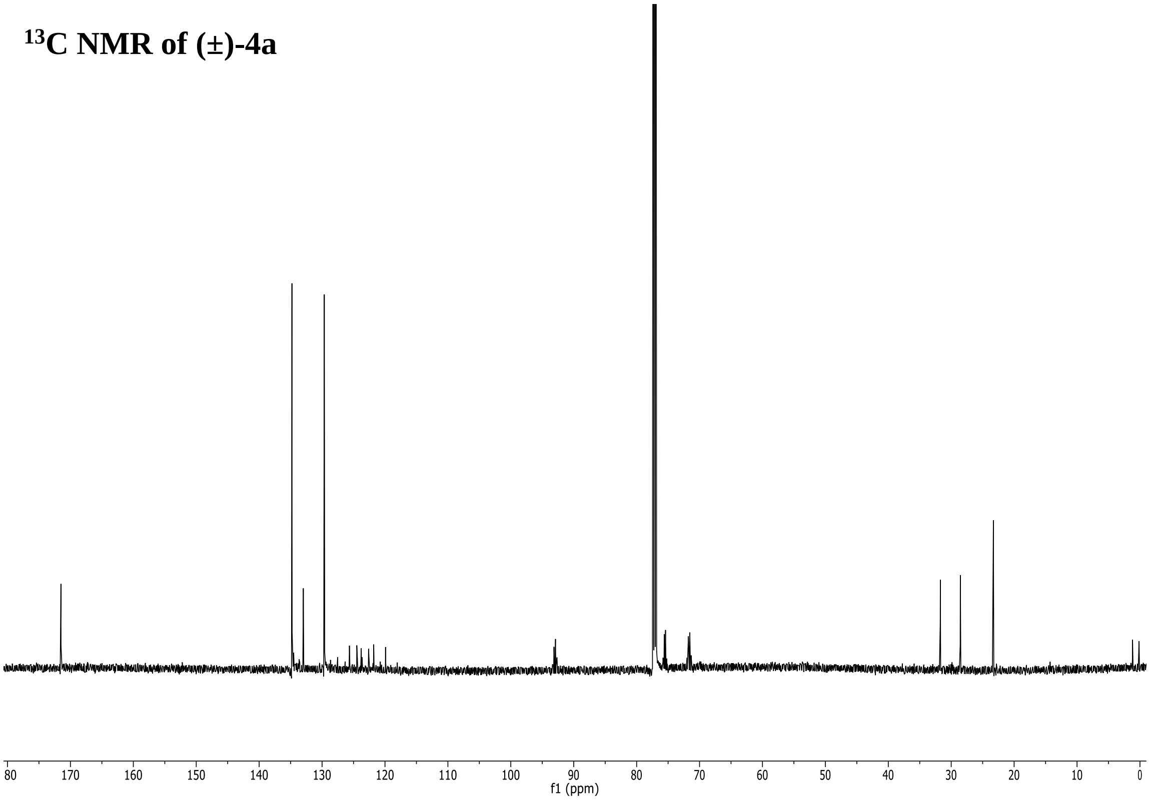
^{1}H, ^{13}C, and ^{19}F NMR Spectra of Borates (±)-4a-4j

^{1}H NMR of (±)-4a

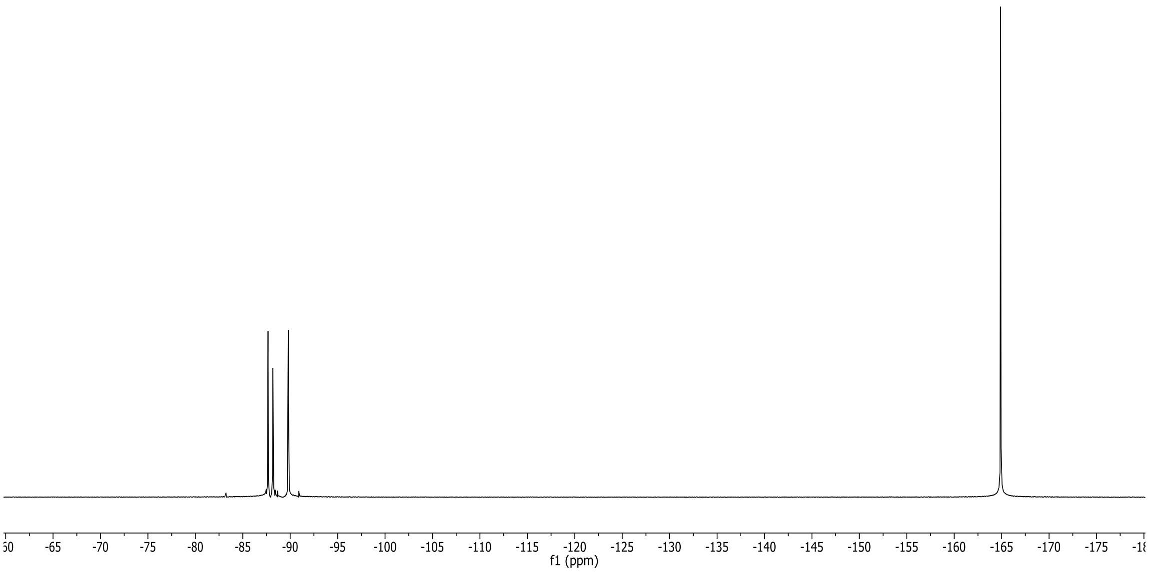




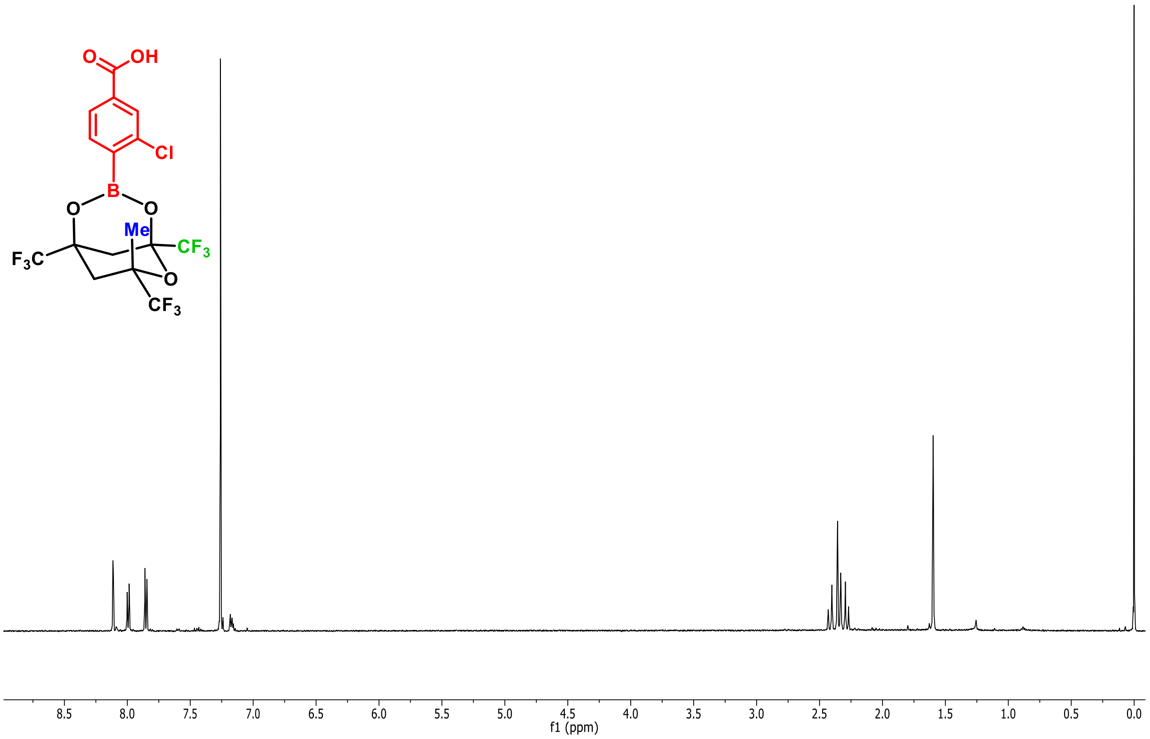
^{13}C NMR of (±)-4a



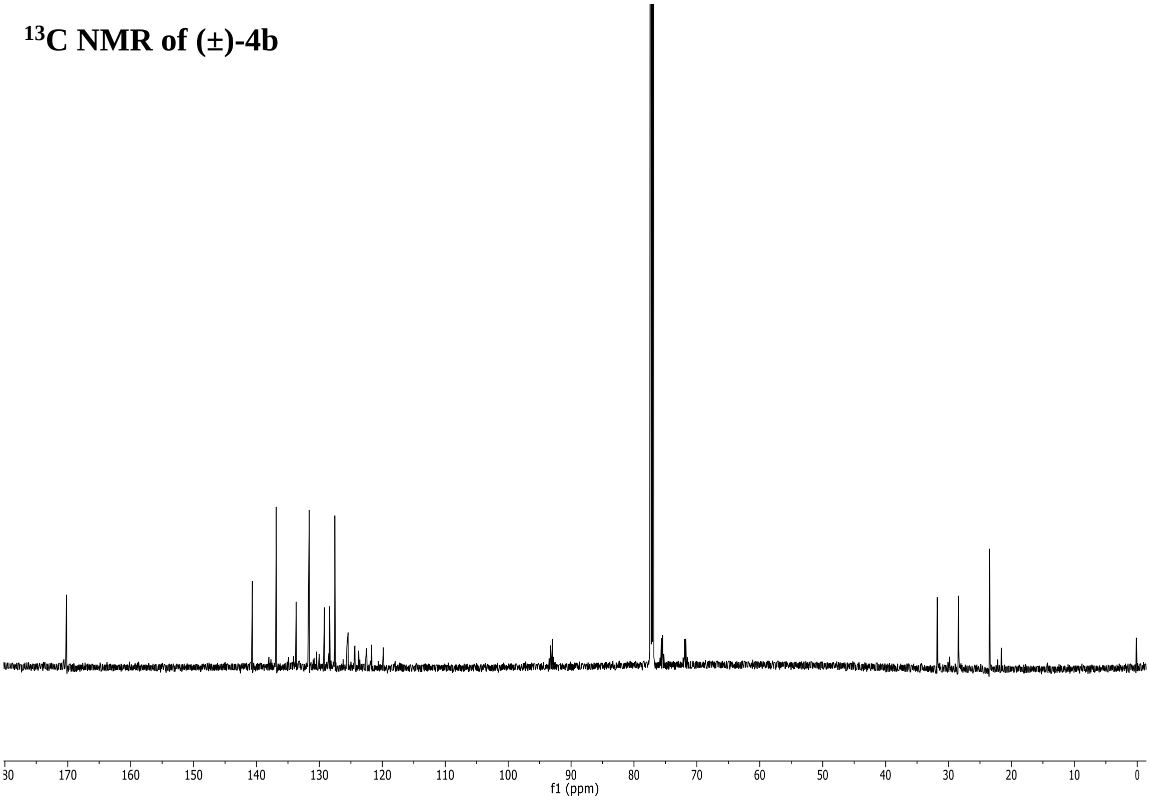
^{19}F NMR of (±)-4a



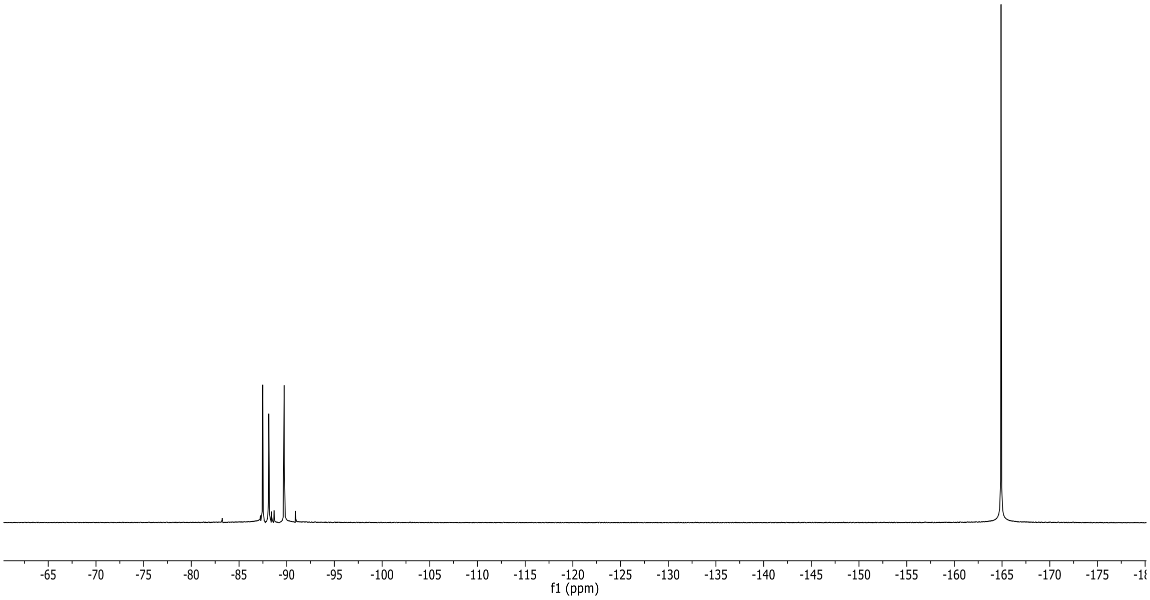
^{1}H NMR of (±)-4b



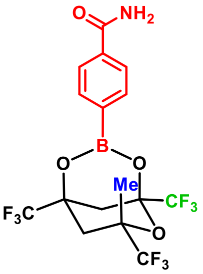
^{13}C NMR of (±)-4b

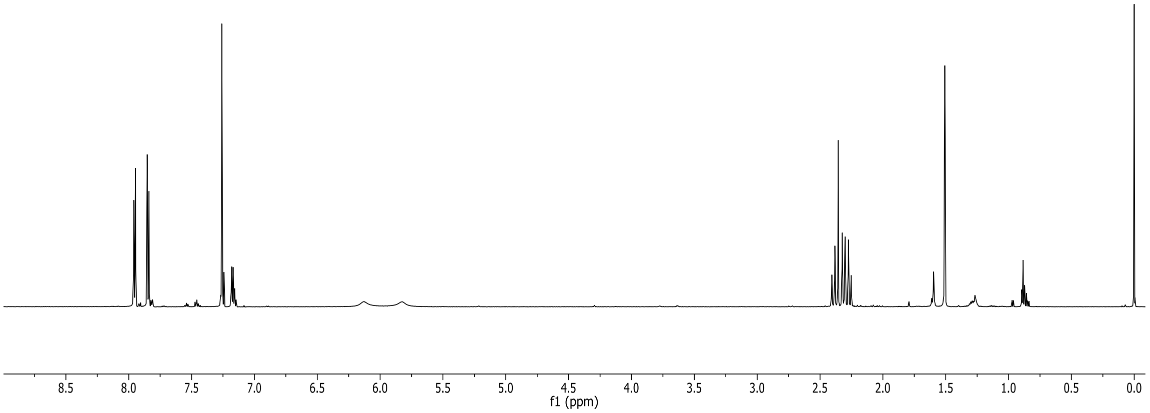


^{19}F NMR of (±)-4b

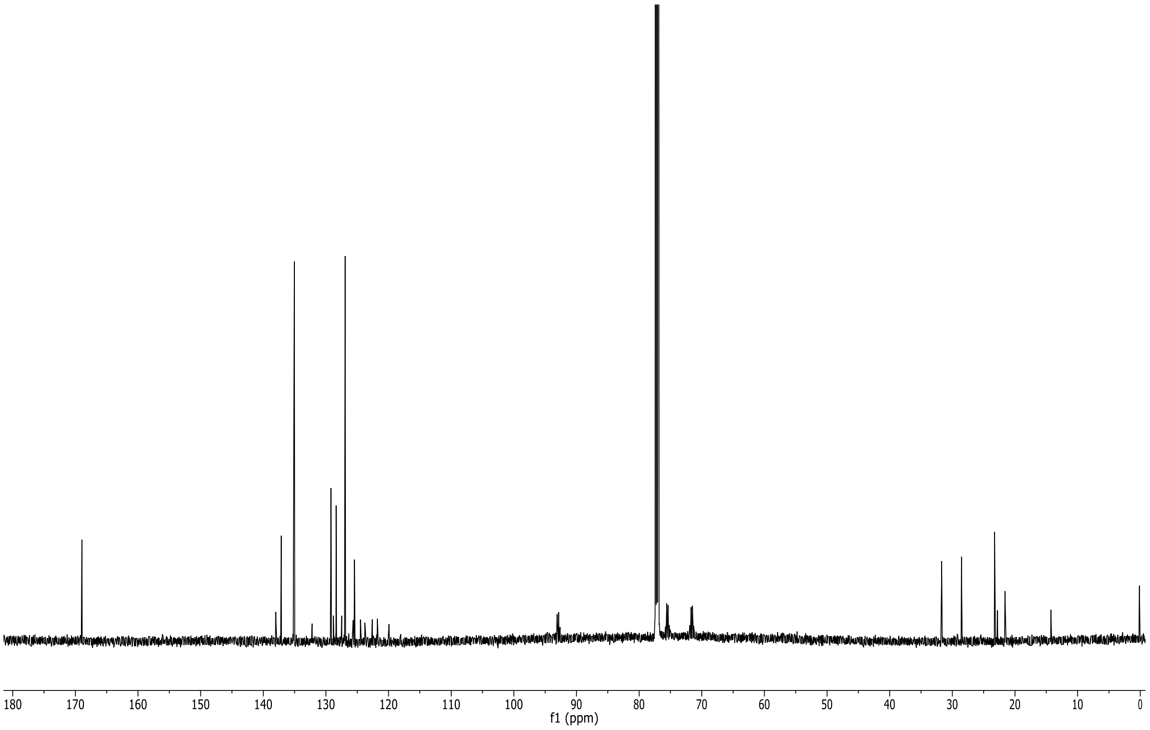


^{1}H NMR of (±)-4c – *Hexanes is present (unable to remove, see characterization above)*

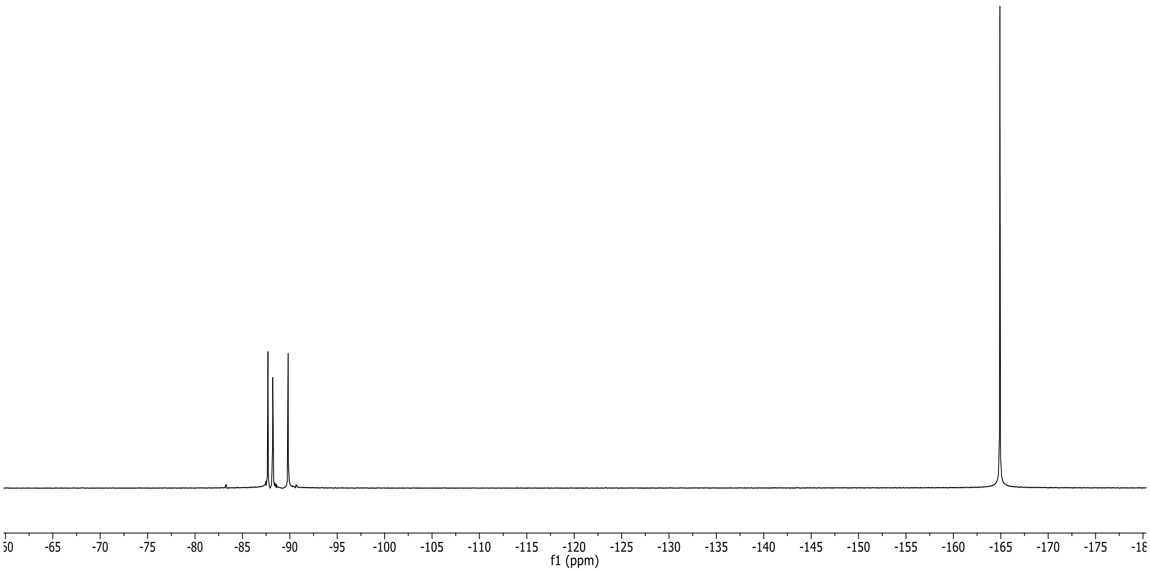




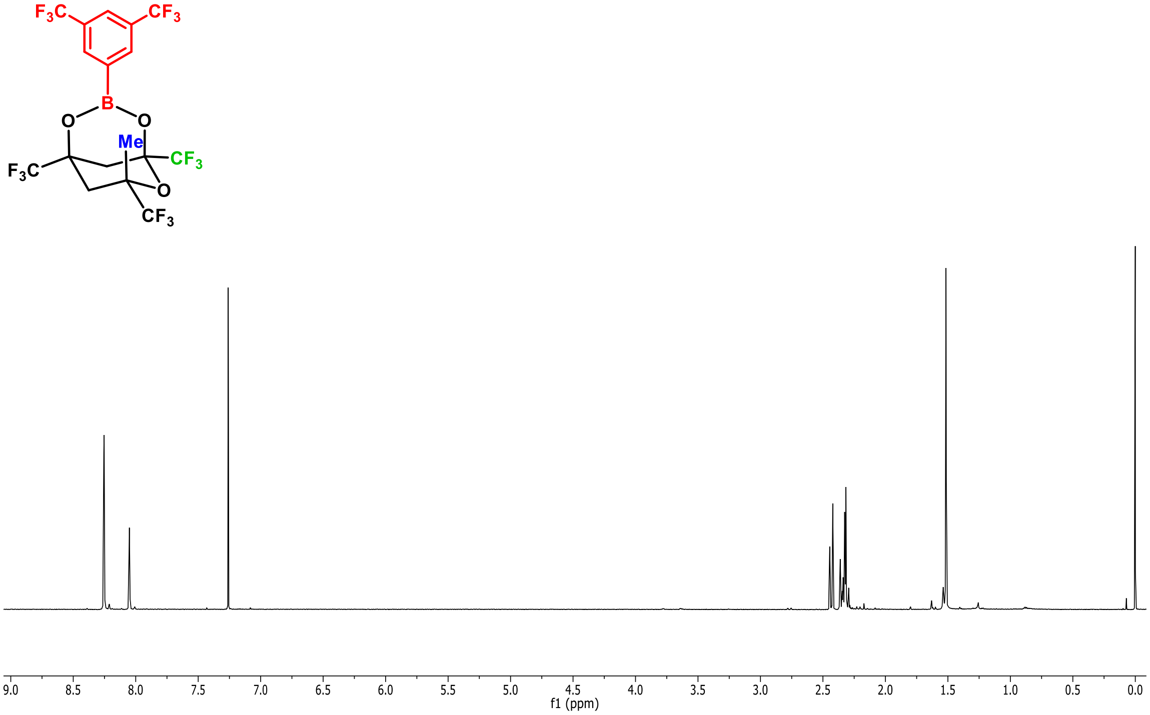
^{13}C NMR of (±)-4c – *Hexanes is present (unable to remove, see characterization above)*



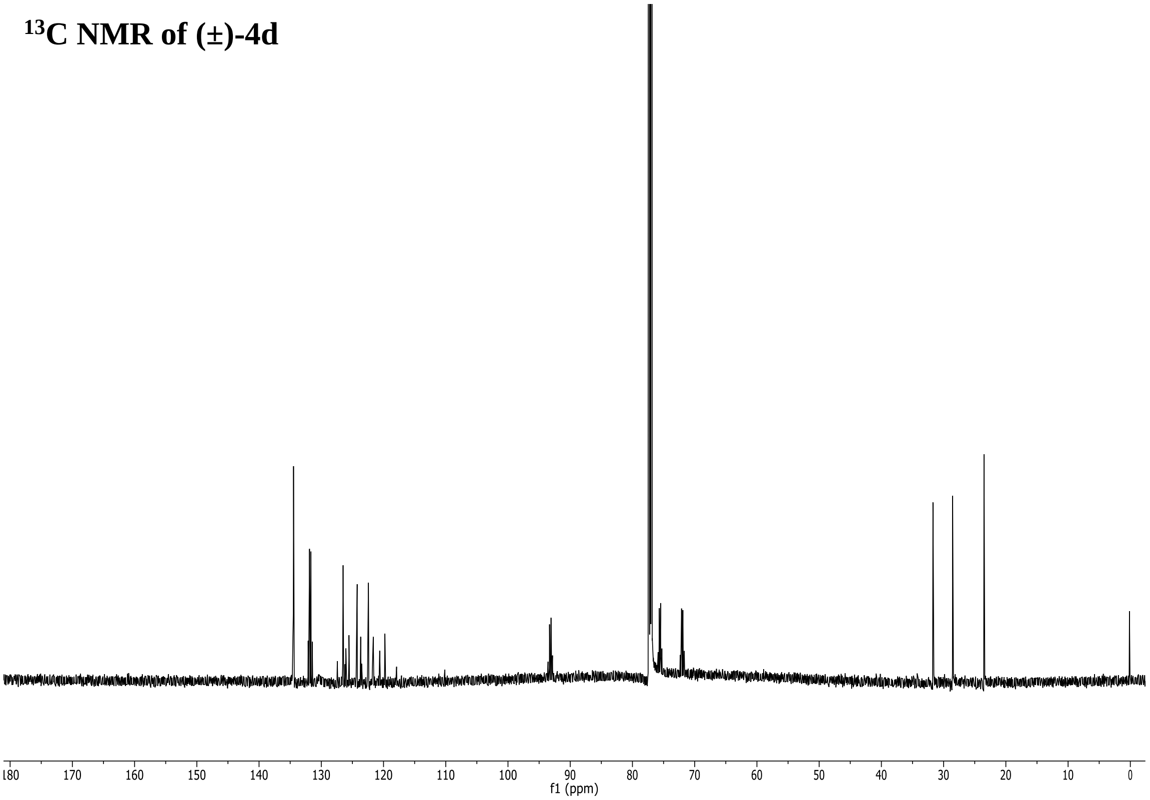
^{19}F NMR of (±)-4c



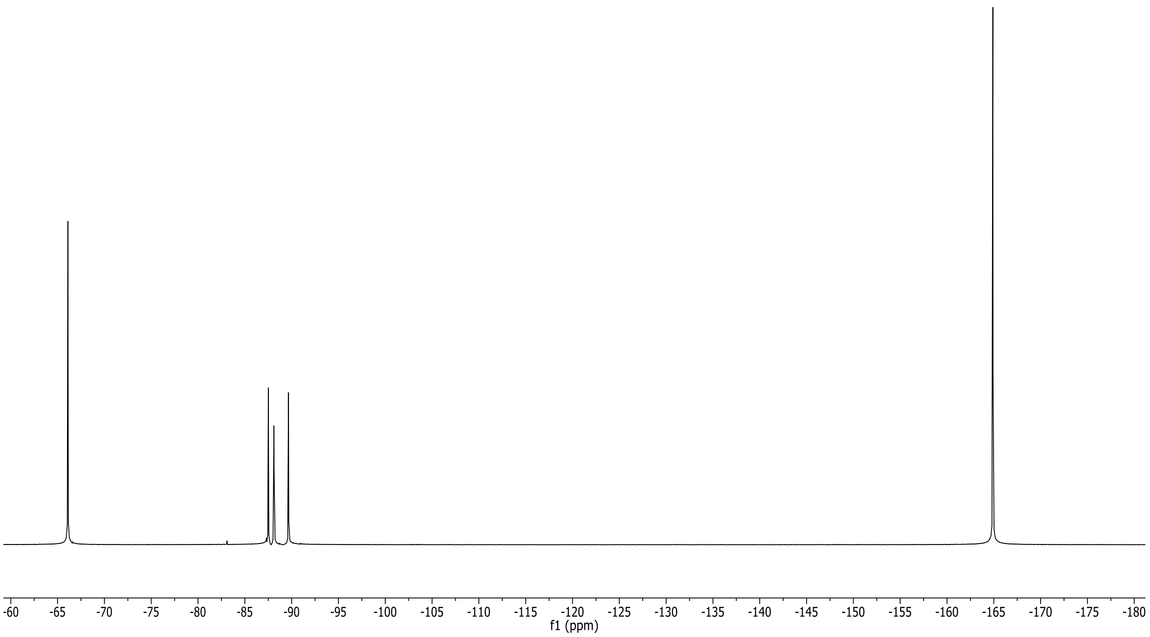
^{1}H NMR of (±)-4d



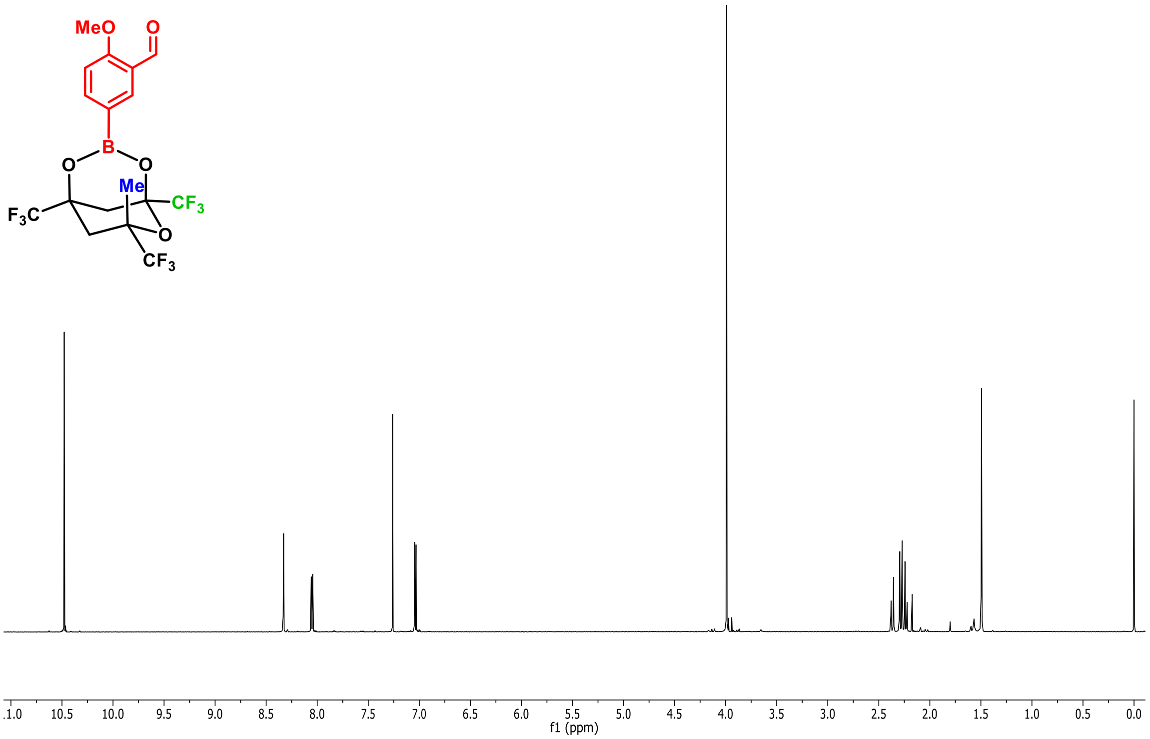
^{13}C NMR of (±)-4d



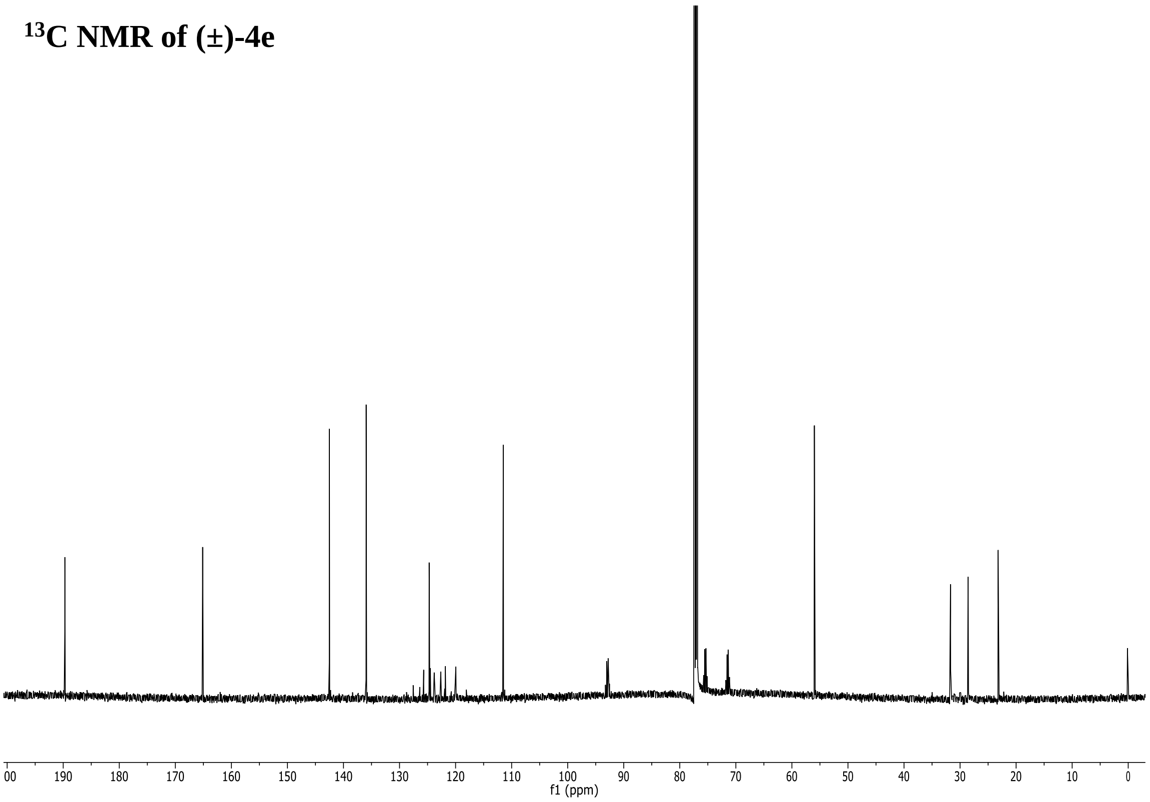
^{19}F NMR of (±)-4d



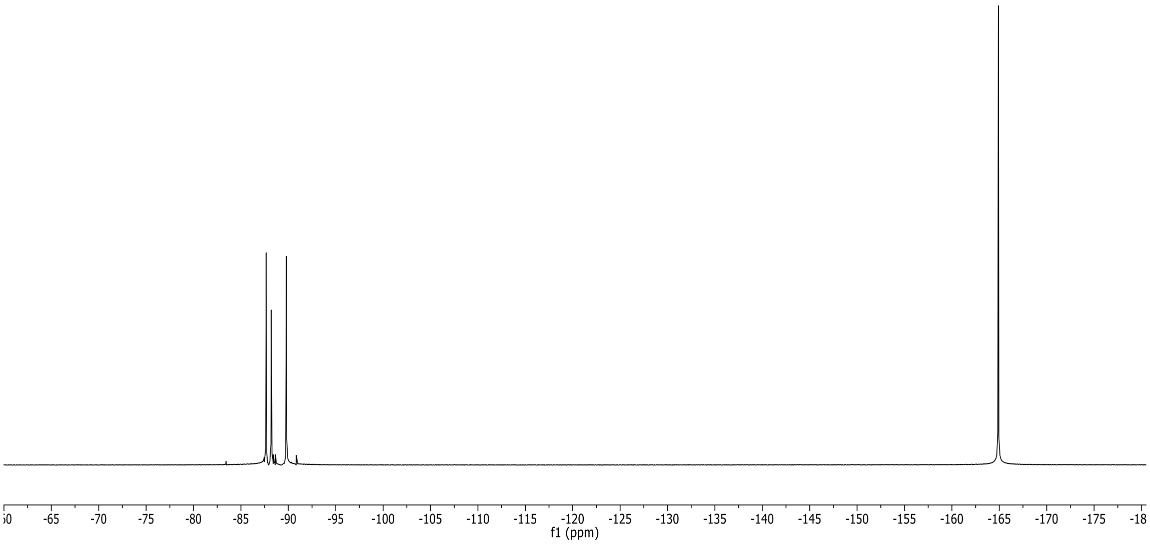
^{1}H NMR of (±)-4e



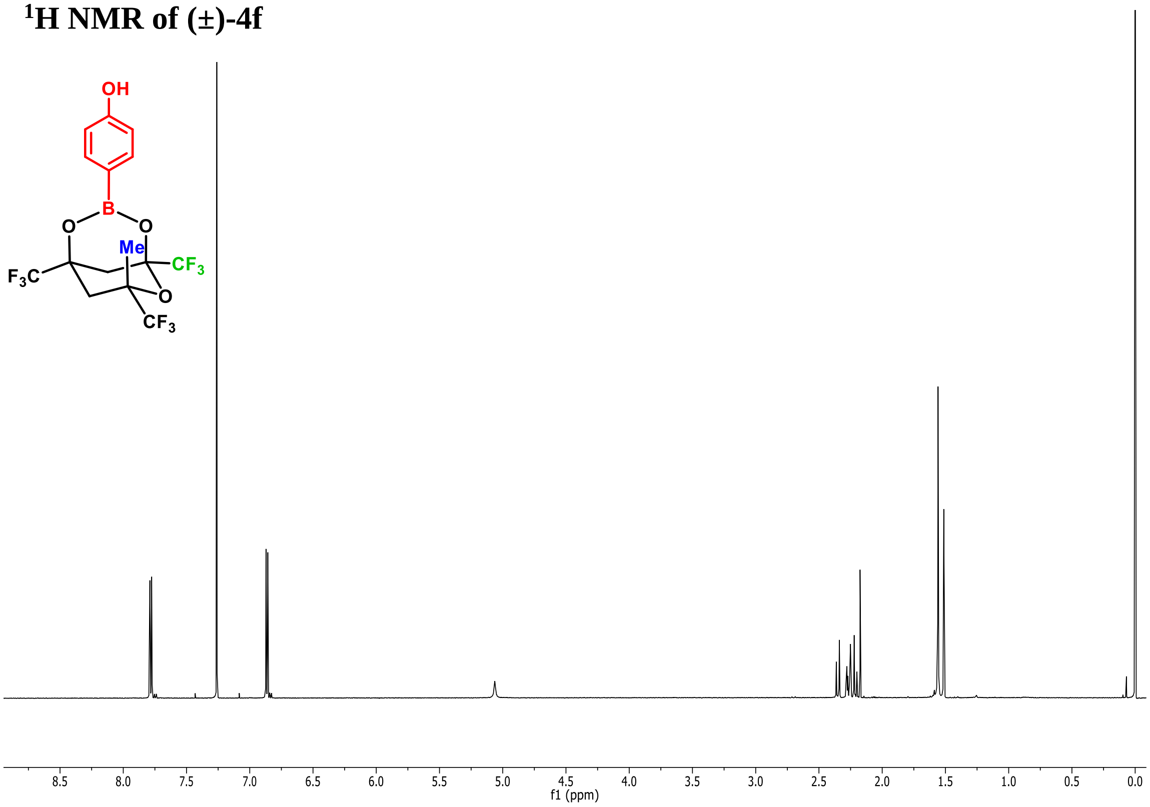
^{13}C NMR of (±)-4e



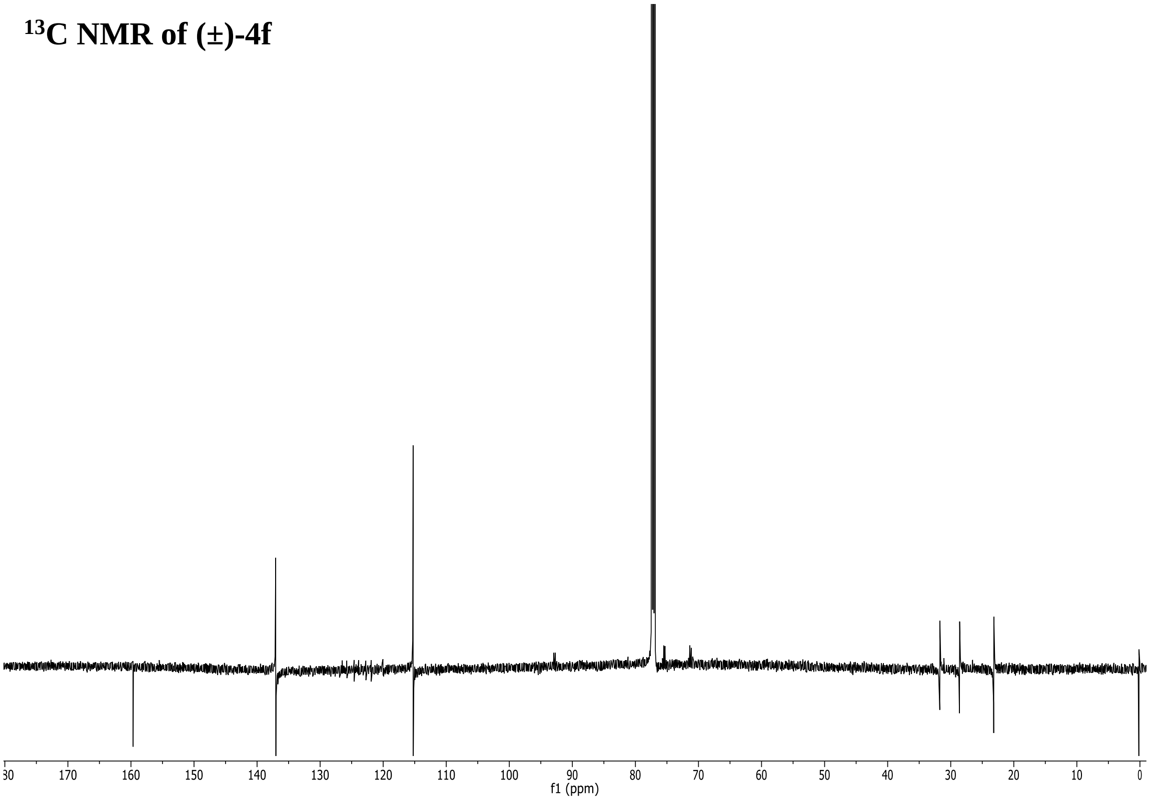
^{19}F NMR of (±)-4e



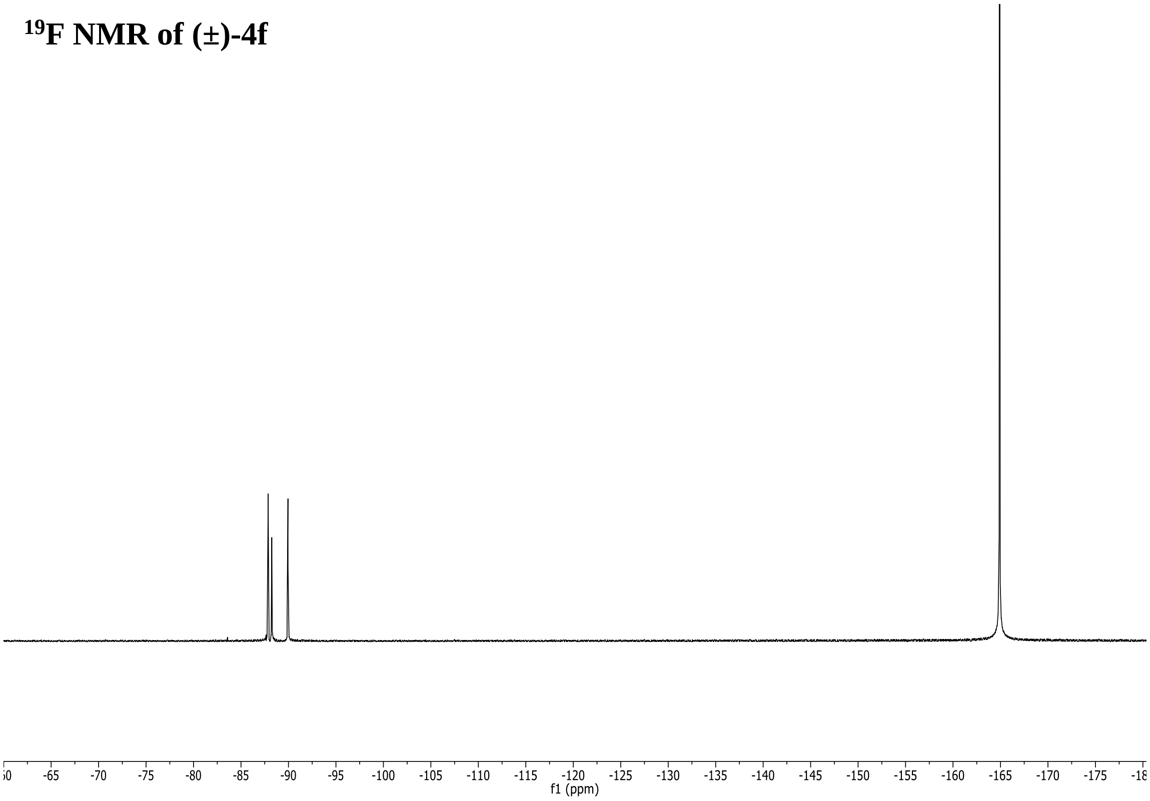
^{1}H NMR of (±)-4f



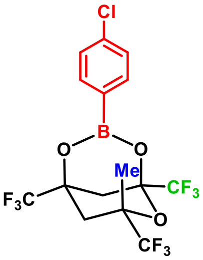
^{13}C NMR of (±)-4f

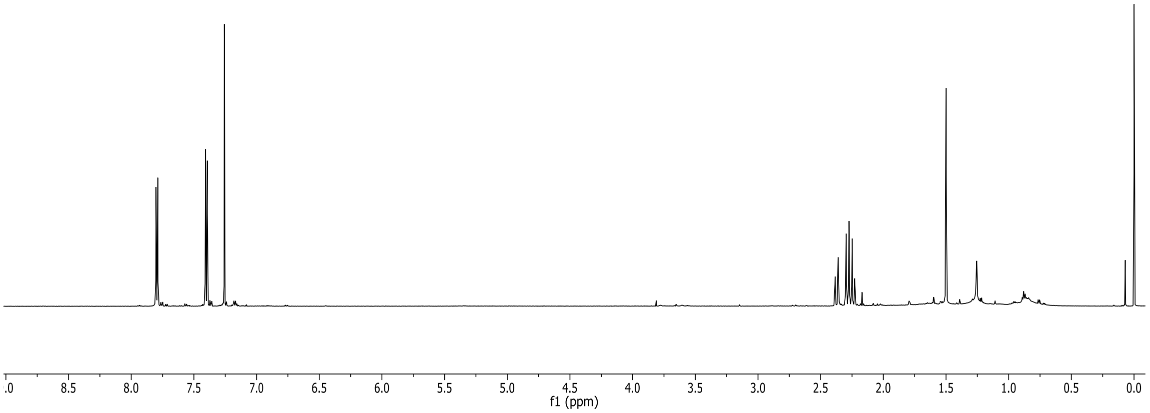


^{19}F NMR of (±)-4f

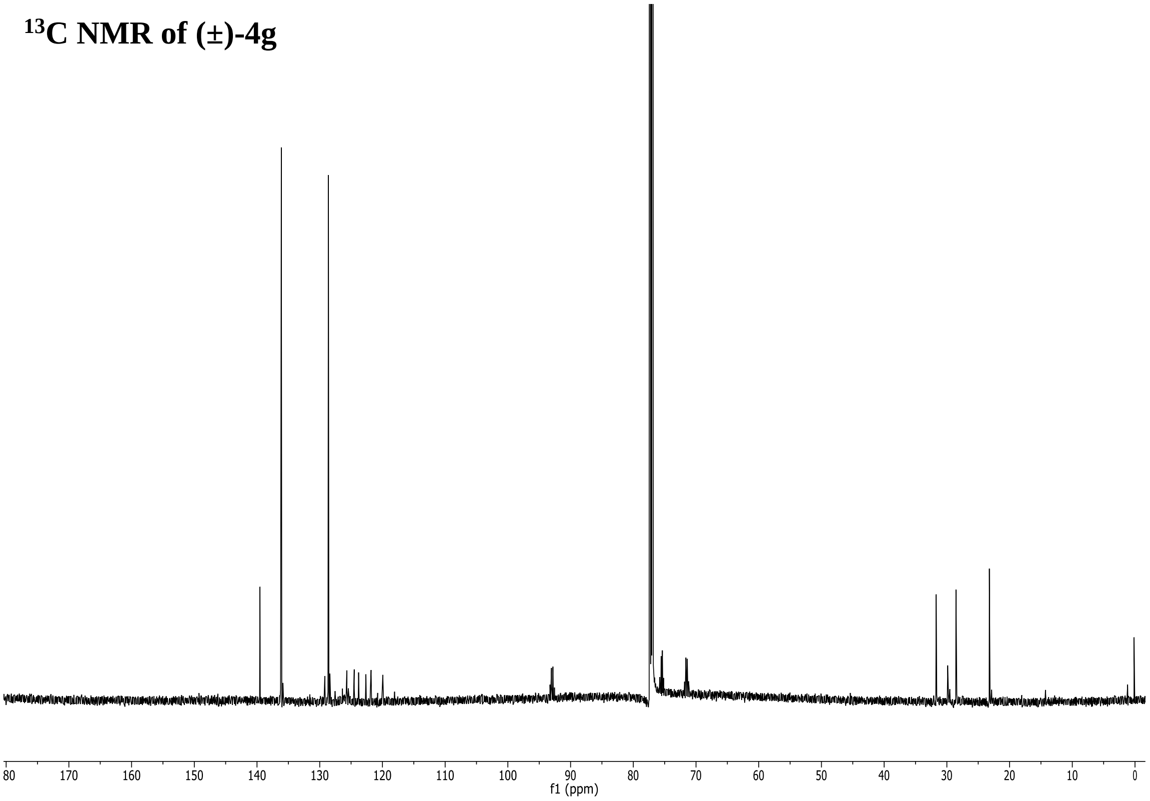


^{1}H NMR of (±)-4g

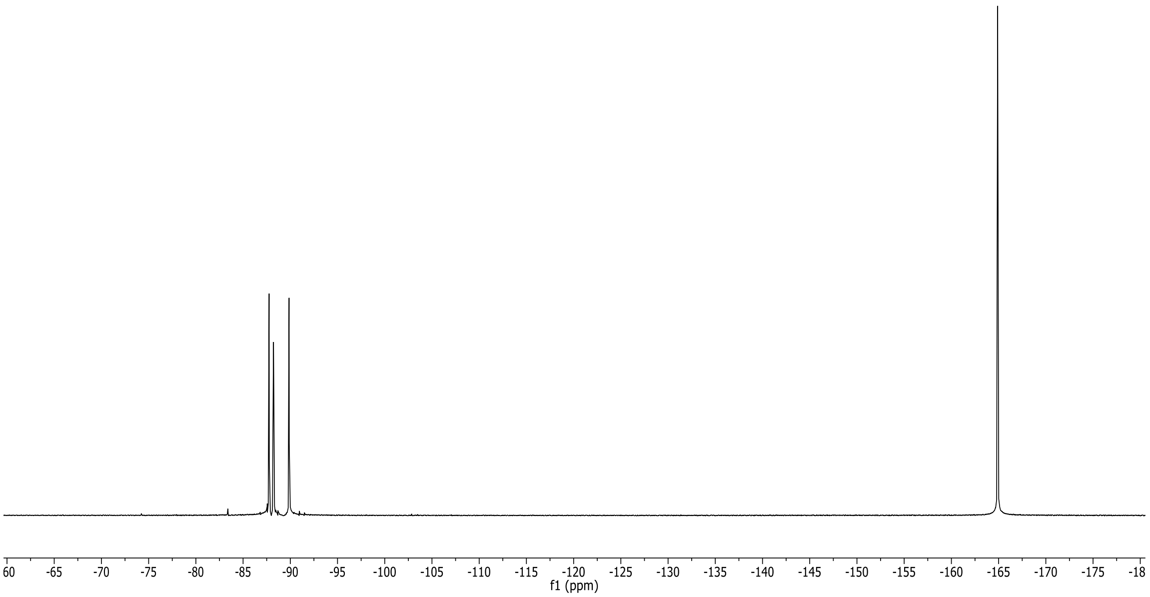




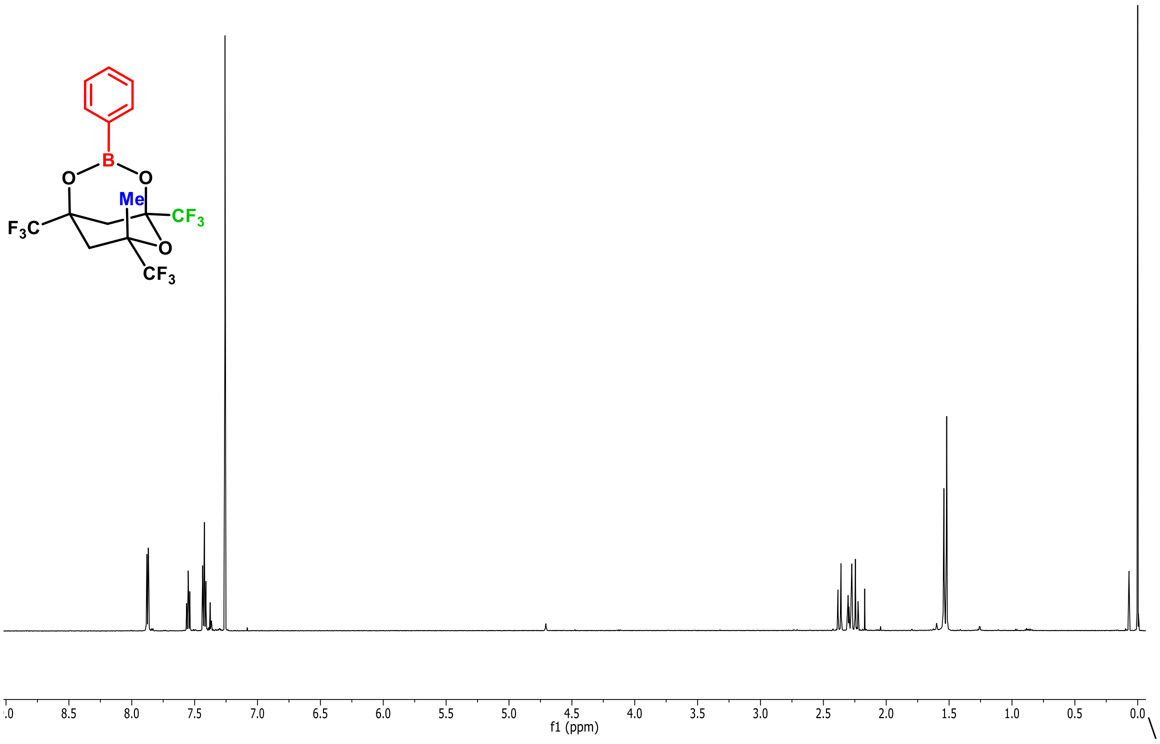
^{13}C NMR of (±)-4g



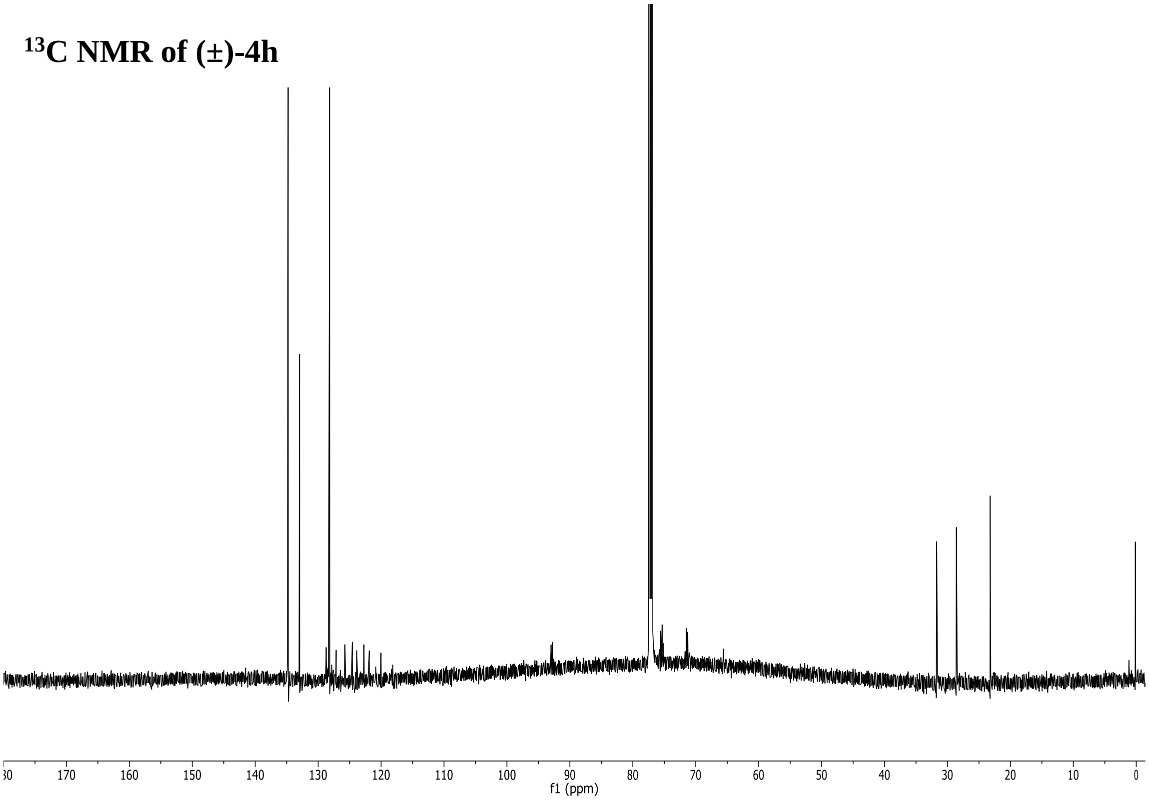
^{19}F NMR of (±)-4g



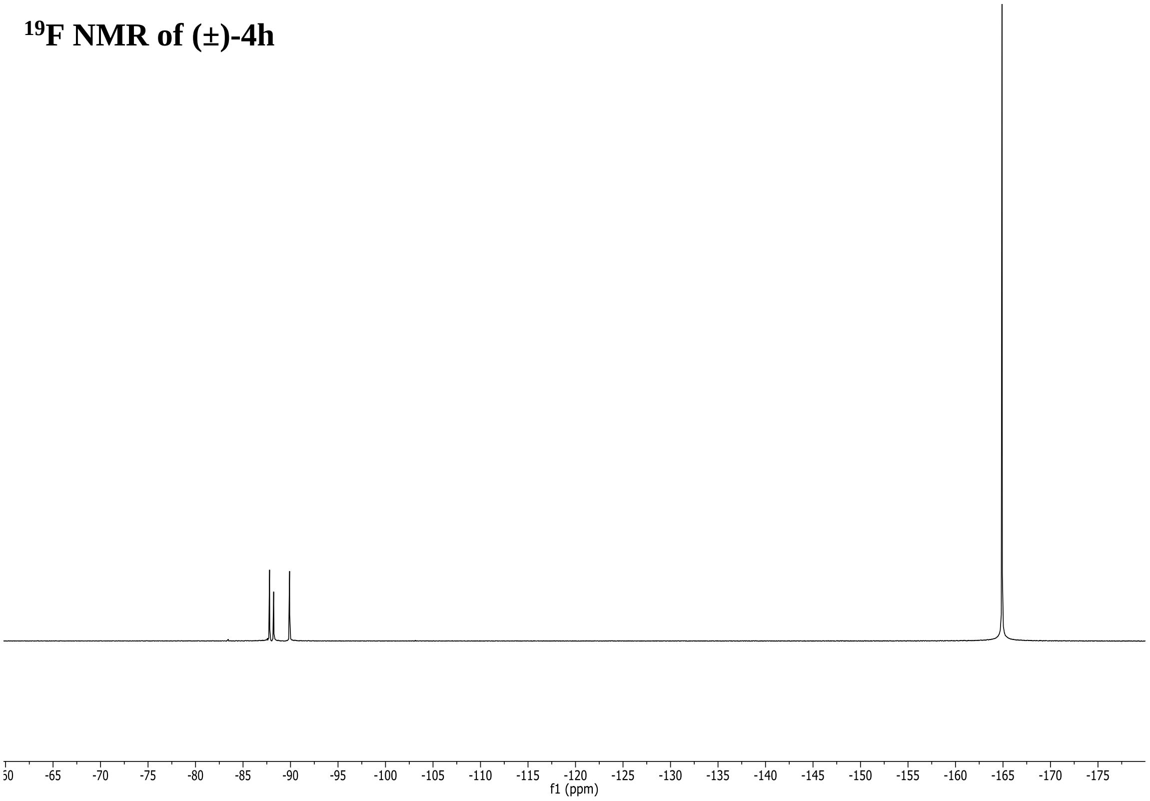
^{1}H NMR of (±)-4h



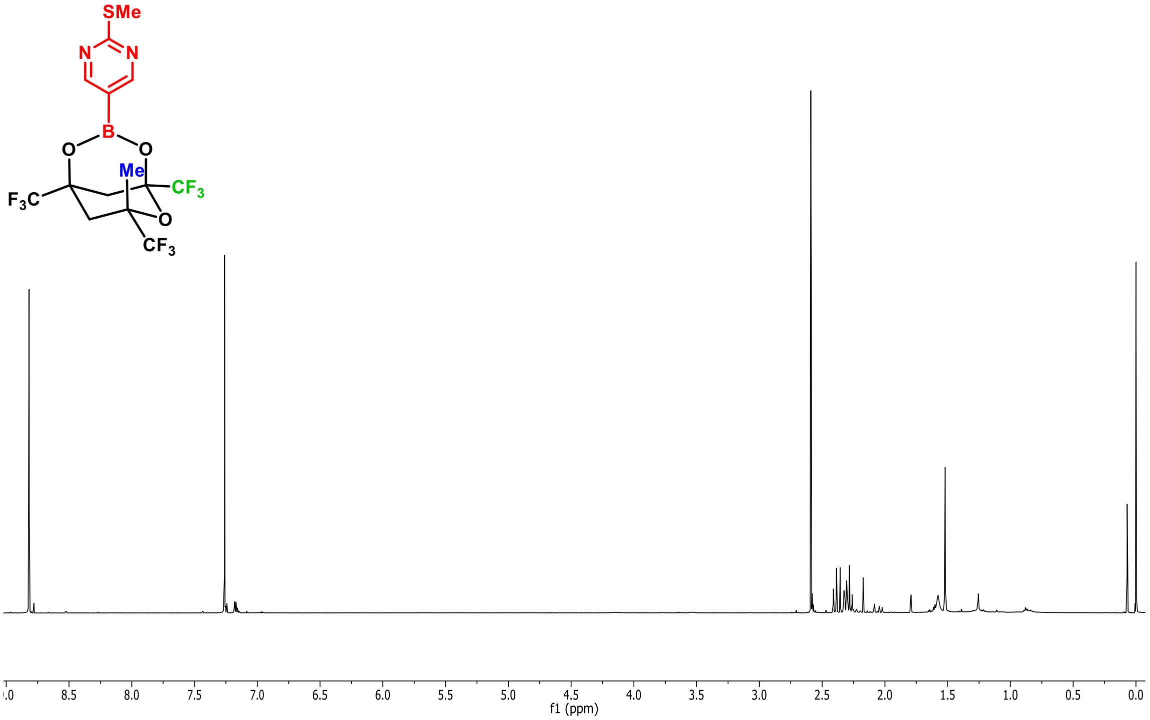
^{13}C NMR of (±)-4h



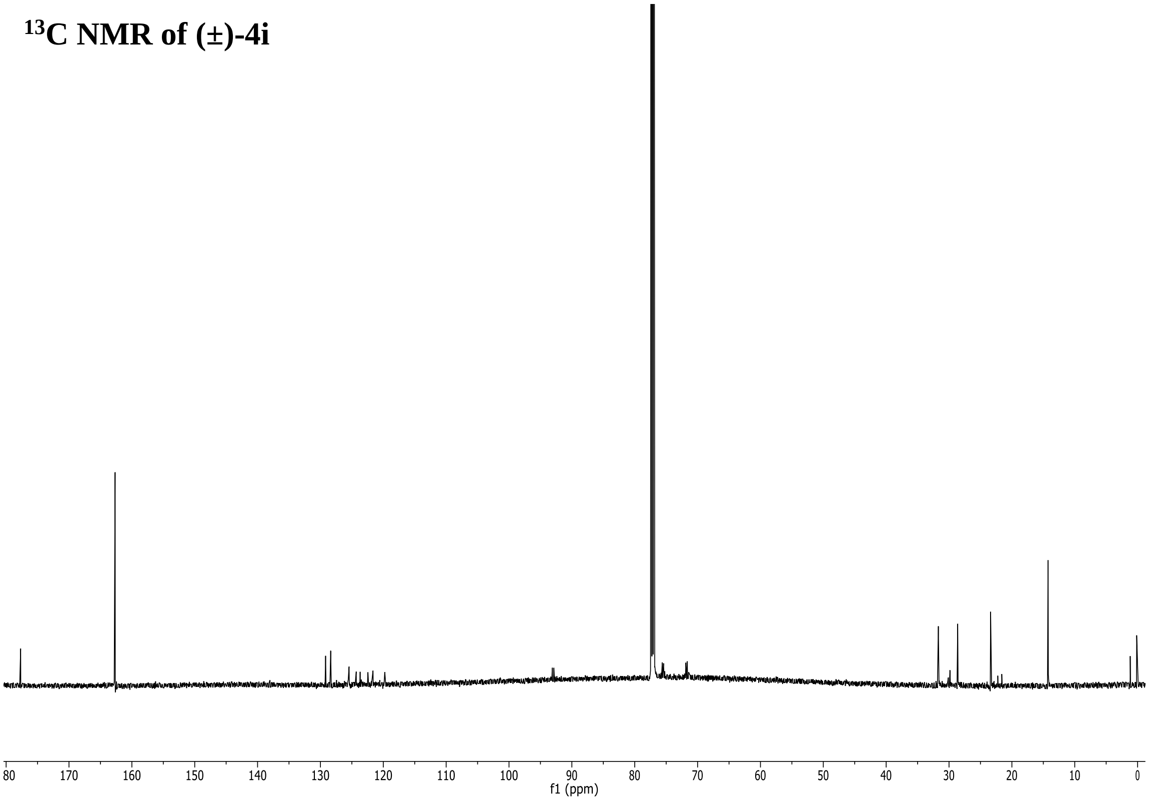
^{19}F NMR of (±)-4h



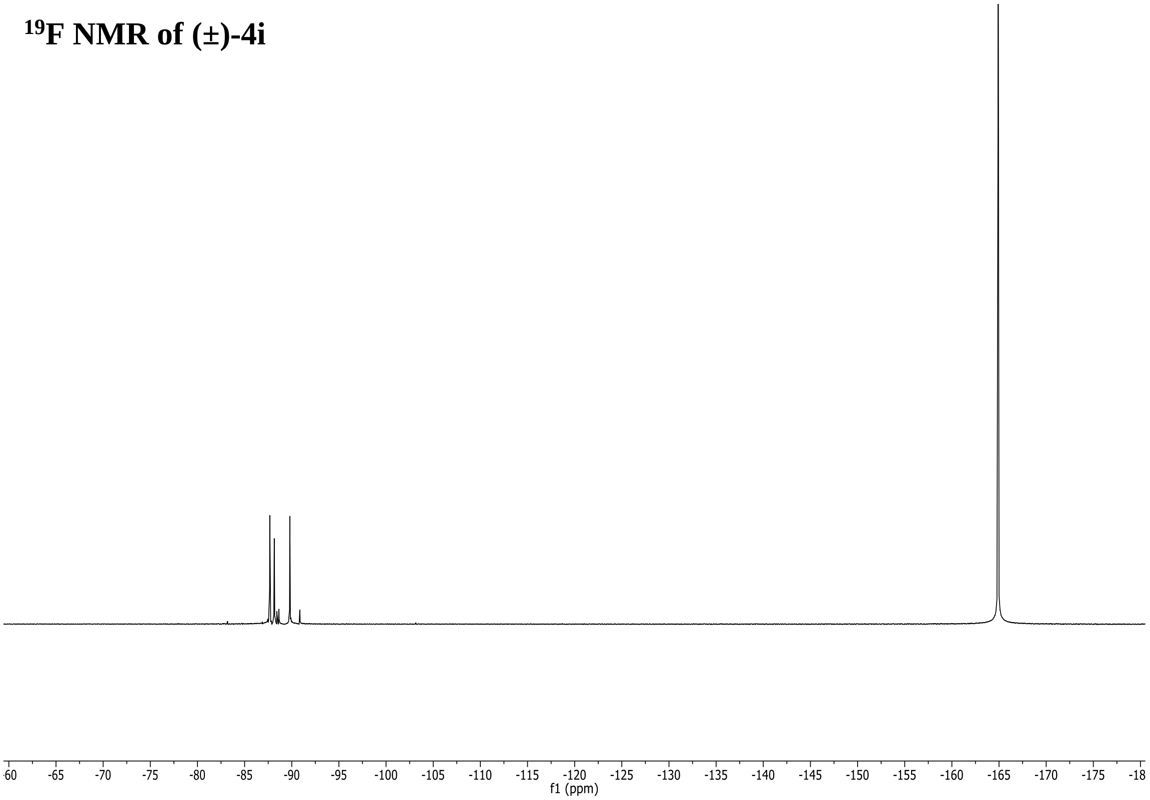
^{1}H NMR of (±)-4i



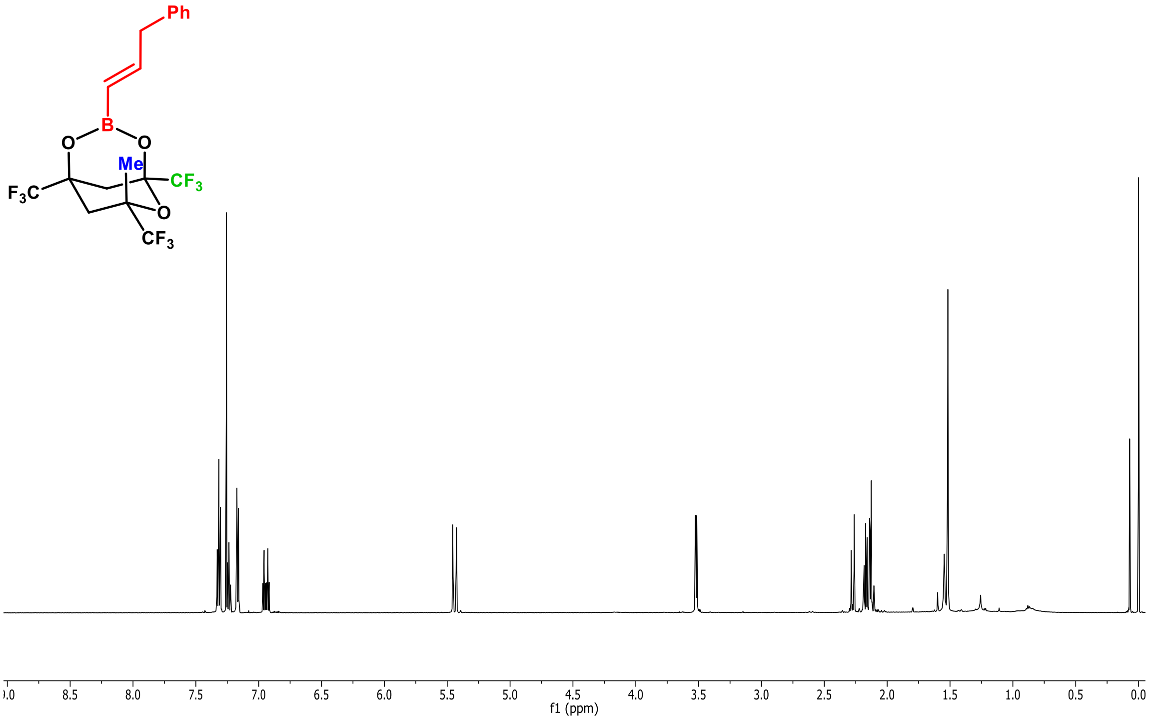
^{13}C NMR of (±)-4i



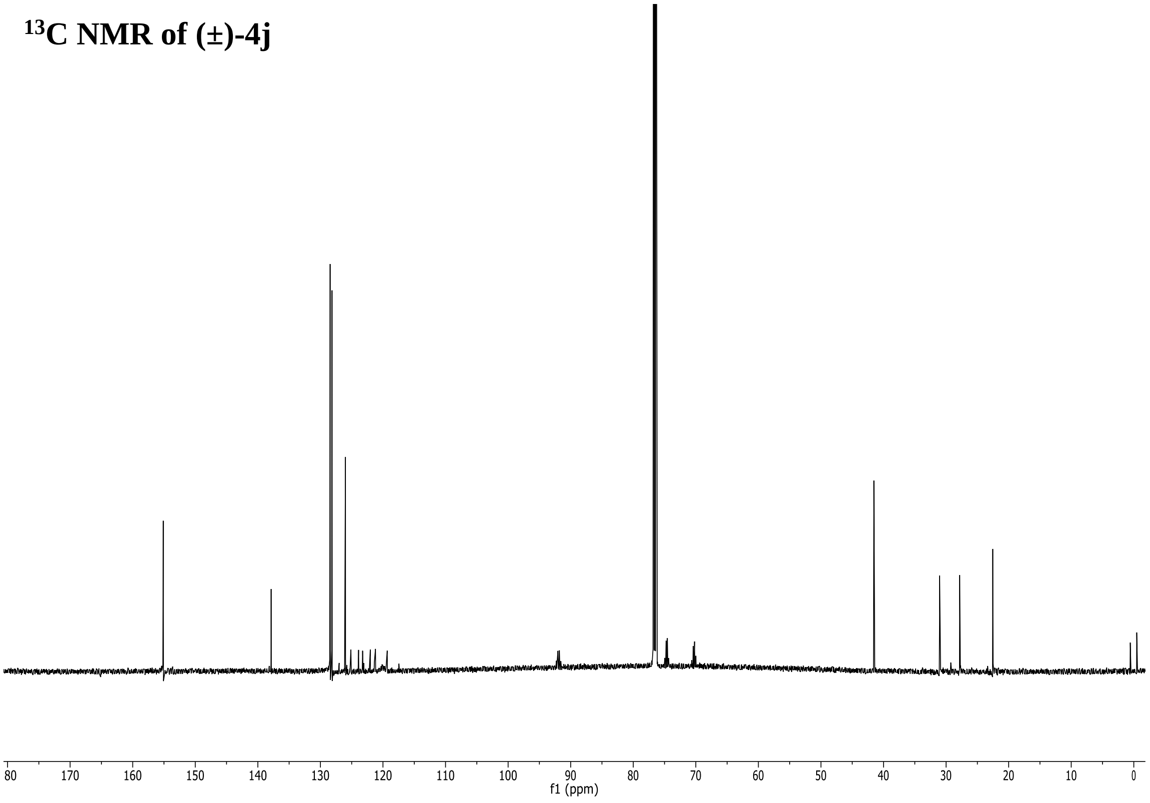
^{19}F NMR of (±)-4i



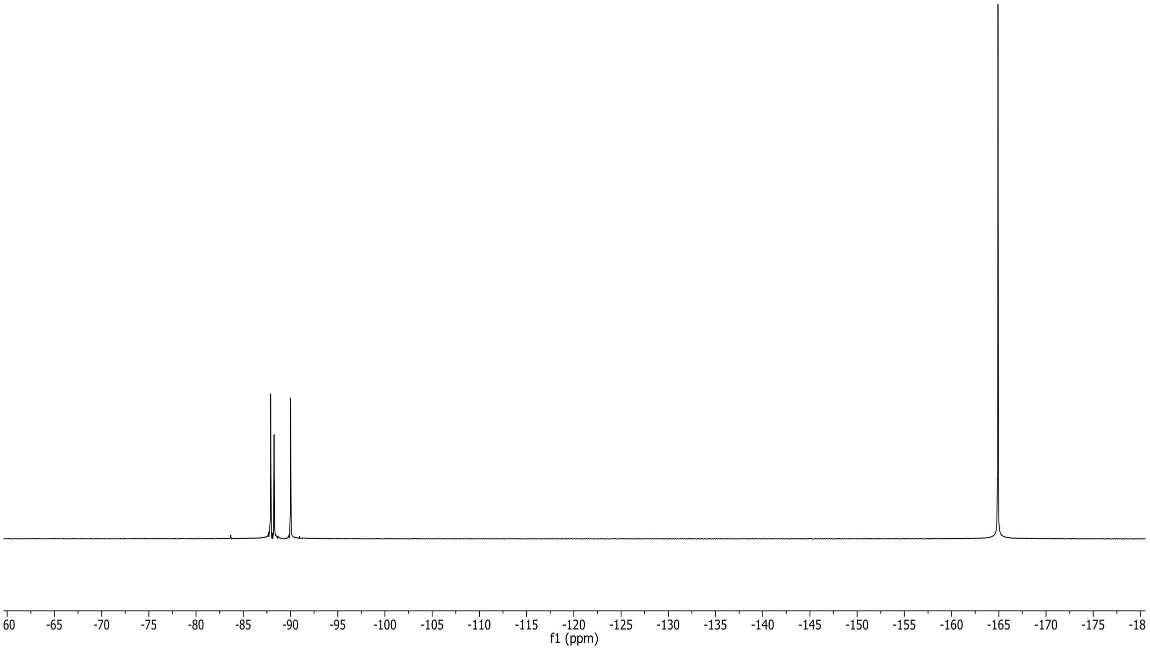
^{1}H NMR of (±)-4j



^{13}C NMR of (±)-4j



^{19}F NMR of (±)-4j



Crystallographic Data

Figure S2: Compound (±)-1a

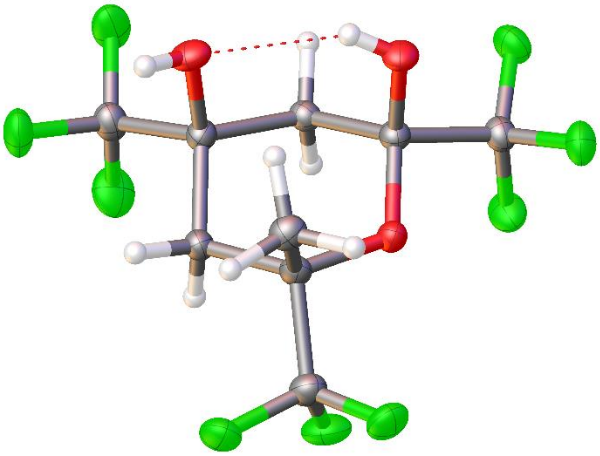


Table 1. Crystal data and structure refinement for (±)-1a

Identification code	dawson01_a	
Empirical formula	C9 H9 F9 O3	
Formula weight	336.16	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 7.8200(13) Å	α= 90°.
	b = 9.4398(16) Å	β= 97.709(9)°.
	c = 16.743(3) Å	γ = 90°.
Volume	1224.8(4) $Å^3$	
Z	4	
Density (calculated)	1.823 Mg/m^3	
Absorption coefficient	0.219 mm^{-1}	
F(000)	672	
Crystal size	0.2 x 0.1 x 0.05 mm^3	
Theta range for data collection	2.455 to 28.336°.	
Index ranges	-10<=h<=10, -12<=k<=12, -19<=l<=22	
Reflections collected	12258	
Independent reflections	3040 [R(int) = 0.0430]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2627 and 0.2206	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3040 / 0 / 199	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1002	
R indices (all data)	R1 = 0.0572, wR2 = 0.1080	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.440 and -0.251 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (±)-1a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3974(1)	7375(1)	6535(1)	27(1)
F(2)	1781(1)	6730(1)	5694(1)	27(1)
F(3)	4350(1)	6393(1)	5407(1)	28(1)
F(9)	8520(1)	4187(1)	7335(1)	32(1)
F(8)	8252(1)	1951(1)	7072(1)	32(1)
F(4)	470(1)	1416(1)	5326(1)	35(1)
F(6)	2306(1)	-86(1)	5906(1)	32(1)
F(7)	7887(1)	3489(1)	6109(1)	32(1)
F(5)	2953(2)	1193(1)	4922(1)	35(1)
O(3)	5166(1)	4657(1)	6659(1)	20(1)
O(1)	2446(2)	5054(1)	7060(1)	22(1)
O(2)	1892(2)	2260(1)	6840(1)	24(1)
C(2)	2577(2)	3804(1)	5811(1)	18(1)
C(7)	3381(2)	6371(2)	6008(1)	21(1)
C(1)	3392(2)	4909(2)	6409(1)	18(1)
C(4)	4785(2)	2076(1)	6436(1)	19(1)
C(3)	2868(2)	2336(1)	6186(1)	18(1)
C(5)	5680(2)	3269(2)	6965(1)	19(1)
C(8)	2145(2)	1208(2)	5577(1)	24(1)
C(9)	7595(2)	3230(2)	6867(1)	25(1)
C(6)	5514(2)	3131(2)	7860(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for (±)-1a

F(1)-C(7)	1.3345(18)
F(2)-C(7)	1.3346(19)
F(3)-C(7)	1.3390(19)
F(9)-C(9)	1.3421(19)
F(8)-C(9)	1.3386(18)
F(4)-C(8)	1.3348(19)
F(6)-C(8)	1.3394(18)
F(7)-C(9)	1.341(2)
F(5)-C(8)	1.338(2)
O(3)-C(1)	1.4150(18)
O(3)-C(5)	1.4440(17)
O(1)-C(1)	1.4039(19)
O(1)-H(1)	0.71(3)
O(2)-C(3)	1.419(2)
O(2)-H(2)	0.77(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(1)	1.525(2)
C(2)-C(3)	1.5254(19)
C(7)-C(1)	1.535(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(3)	1.521(2)
C(4)-C(5)	1.541(2)
C(3)-C(8)	1.529(2)
C(5)-C(9)	1.528(2)
C(5)-C(6)	1.528(2)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(1)-O(3)-C(5)	118.20(11)
C(1)-O(1)-H(1)	112(3)
C(3)-O(2)-H(2)	113(2)

H(2A)-C(2)-H(2B)	108.3
C(1)-C(2)-H(2A)	109.9
C(1)-C(2)-H(2B)	109.9
C(1)-C(2)-C(3)	108.99(12)
C(3)-C(2)-H(2A)	109.9
C(3)-C(2)-H(2B)	109.9
F(1)-C(7)-F(2)	107.74(12)
F(1)-C(7)-F(3)	107.70(12)
F(1)-C(7)-C(1)	111.67(13)
F(2)-C(7)-F(3)	107.17(13)
F(2)-C(7)-C(1)	110.52(13)
F(3)-C(7)-C(1)	111.82(12)
O(3)-C(1)-C(2)	112.69(12)
O(3)-C(1)-C(7)	103.18(12)
O(1)-C(1)-O(3)	112.66(12)
O(1)-C(1)-C(2)	111.07(12)
O(1)-C(1)-C(7)	106.18(12)
C(2)-C(1)-C(7)	110.58(13)
H(4A)-C(4)-H(4B)	107.7
C(3)-C(4)-H(4A)	108.9
C(3)-C(4)-H(4B)	108.9
C(3)-C(4)-C(5)	113.29(12)
C(5)-C(4)-H(4A)	108.9
C(5)-C(4)-H(4B)	108.9
O(2)-C(3)-C(2)	107.27(12)
O(2)-C(3)-C(4)	113.10(13)
O(2)-C(3)-C(8)	106.89(12)
C(2)-C(3)-C(8)	109.68(13)
C(4)-C(3)-C(2)	110.28(12)
C(4)-C(3)-C(8)	109.51(12)
O(3)-C(5)-C(4)	112.05(12)
O(3)-C(5)-C(9)	102.32(12)
O(3)-C(5)-C(6)	111.66(12)
C(9)-C(5)-C(4)	107.29(12)
C(6)-C(5)-C(4)	114.20(12)

C(6)-C(5)-C(9)	108.46(13)
F(4)-C(8)-F(6)	107.32(13)
F(4)-C(8)-F(5)	107.16(13)
F(4)-C(8)-C(3)	111.53(12)
F(6)-C(8)-C(3)	110.79(13)
F(5)-C(8)-F(6)	107.40(12)
F(5)-C(8)-C(3)	112.39(13)
F(9)-C(9)-C(5)	112.34(13)
F(8)-C(9)-F(9)	107.39(13)
F(8)-C(9)-F(7)	107.36(14)
F(8)-C(9)-C(5)	109.98(13)
F(7)-C(9)-F(9)	106.47(13)
F(7)-C(9)-C(5)	113.00(13)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for (±)-1a. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	36(1)	17(1)	28(1)	-1(1)	4(1)	-2(1)
F(2)	27(1)	23(1)	31(1)	4(1)	2(1)	7(1)
F(3)	35(1)	25(1)	27(1)	6(1)	15(1)	2(1)
F(9)	20(1)	33(1)	41(1)	-1(1)	-1(1)	-7(1)
F(8)	20(1)	30(1)	46(1)	4(1)	2(1)	6(1)
F(4)	27(1)	27(1)	46(1)	-6(1)	-13(1)	0(1)
F(6)	36(1)	16(1)	42(1)	0(1)	-5(1)	-2(1)
F(7)	20(1)	45(1)	33(1)	4(1)	10(1)	1(1)
F(5)	47(1)	33(1)	26(1)	-10(1)	6(1)	-1(1)
O(3)	17(1)	16(1)	27(1)	2(1)	3(1)	-1(1)
O(1)	21(1)	24(1)	22(1)	-1(1)	10(1)	0(1)
O(2)	19(1)	31(1)	24(1)	4(1)	7(1)	-2(1)
C(2)	18(1)	18(1)	19(1)	1(1)	3(1)	2(1)
C(7)	24(1)	18(1)	21(1)	1(1)	4(1)	1(1)
C(1)	18(1)	18(1)	19(1)	0(1)	4(1)	0(1)
C(4)	18(1)	16(1)	23(1)	0(1)	3(1)	1(1)
C(3)	18(1)	17(1)	19(1)	0(1)	3(1)	-1(1)
C(5)	15(1)	19(1)	24(1)	1(1)	2(1)	1(1)
C(8)	25(1)	20(1)	26(1)	-1(1)	-1(1)	1(1)
C(9)	19(1)	26(1)	29(1)	2(1)	2(1)	0(1)
C(6)	22(1)	26(1)	22(1)	2(1)	1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for (±)-1a.

	x	y	z	U(eq)
H(2A)	3105	3856	5307	22
H(2B)	1325	3988	5679	22
H(4A)	5356	1978	5945	23
H(4B)	4935	1172	6736	23
H(6A)	6043	3957	8150	35
H(6B)	6102	2268	8075	35
H(6C)	4291	3081	7929	35
H(2)	2110(40)	1600(30)	7109(19)	88(11)
H(1)	2040(40)	4410(30)	7149(19)	90(12)

Figure S3: Compound (±)-3

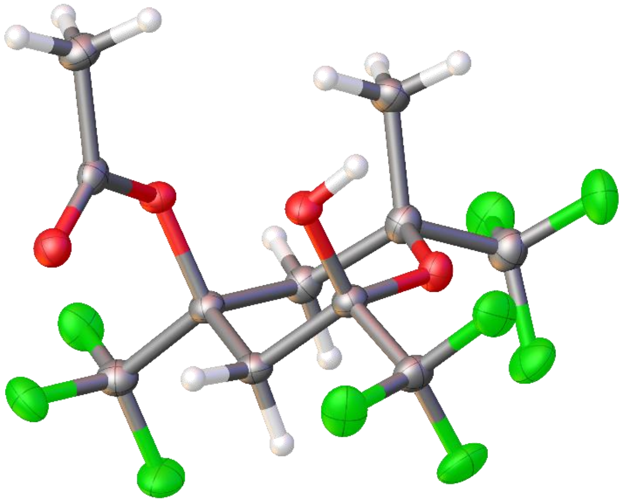


Table 1. Crystal data and structure refinement for (±)-3.

Report date	2016-06-17	
Identification code	dawson03	
Empirical formula	C11 H11 F9 O4	
Molecular formula	C11 H11 F9 O4	
Formula weight	378.20	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.2625(4) Å	α= 90°.
	b = 9.6405(4) Å	β= 90°.
	c = 17.8895(7) Å	γ = 90°.
Volume	1424.98(11) Å^3	
Z	4	
Density (calculated)	1.763 Mg/m^3	
Absorption coefficient	0.204 mm^{-1}	
F(000)	760	
Crystal size	0.24 x 0.12 x 0.12 mm^3	
Crystal color, habit	colorless block	
Theta range for data collection	2.277 to 26.748°.	
Index ranges	-10<=h<=10, -12<=k<=12, -19<=l<=22	
Reflections collected	17826	
Independent reflections	3022 [R(int) = 0.0544]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6466 and 0.5900	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3022 / 0 / 220	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0741	
R indices (all data)	R1 = 0.0352, wR2 = 0.0774	
Absolute structure parameter	0.2(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.217 and -0.223 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (±)-3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(8)	847(2)	3059(2)	7968(1)	29(1)
F(9)	-1153(2)	3267(2)	7216(1)	29(1)
F(6)	268(2)	5837(2)	4651(1)	33(1)
F(5)	2790(2)	6138(2)	4393(1)	31(1)
F(7)	3(2)	5093(2)	7651(1)	32(1)
F(1)	6213(2)	5338(2)	7355(1)	35(1)
F(4)	1671(2)	7301(2)	5286(1)	34(1)
F(2)	4837(2)	6974(2)	6834(1)	34(1)
F(3)	6752(2)	5971(2)	6224(1)	36(1)
O(3)	1830(2)	2420(2)	6540(1)	18(1)
O(2)	2227(2)	3642(2)	5116(1)	20(1)
O(1)	3688(2)	5322(2)	5773(1)	21(1)
O(4)	-467(2)	2014(2)	5887(1)	22(1)
C(10)	887(3)	1677(2)	6064(1)	19(1)
C(2)	879(3)	4768(2)	6110(1)	18(1)
C(9)	273(3)	3803(2)	7394(1)	22(1)
C(4)	3087(3)	4424(2)	7039(1)	20(1)
C(1)	2162(3)	4893(2)	5501(1)	18(1)
C(3)	1483(3)	3843(2)	6748(1)	18(1)
C(8)	1715(3)	6057(2)	4954(1)	23(1)
C(6)	5290(3)	3341(2)	6209(2)	23(1)
C(5)	4347(3)	4647(2)	6423(1)	21(1)
C(7)	5548(3)	5743(3)	6707(2)	27(1)
C(11)	1754(3)	407(2)	5812(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for (±)-3.

F(8)-C(9)	1.339(3)
F(9)-C(9)	1.325(3)
F(6)-C(8)	1.330(3)
F(5)-C(8)	1.342(3)
F(7)-C(9)	1.345(3)
F(1)-C(7)	1.341(3)
F(4)-C(8)	1.338(3)
F(2)-C(7)	1.344(3)
F(3)-C(7)	1.336(3)
O(3)-C(10)	1.359(3)
O(3)-C(3)	1.450(3)
O(2)-H(2)	0.8400
O(2)-C(1)	1.390(3)
O(1)-C(1)	1.413(3)
O(1)-C(5)	1.440(3)
O(4)-C(10)	1.207(3)
C(10)-C(11)	1.489(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(1)	1.525(3)
C(2)-C(3)	1.532(3)
C(9)-C(3)	1.528(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(3)	1.531(3)
C(4)-C(5)	1.531(4)
C(1)-C(8)	1.534(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(6)-C(5)	1.529(3)
C(5)-C(7)	1.537(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

C(10)-O(3)-C(3)	123.09(18)
C(1)-O(2)-H(2)	109.5
C(1)-O(1)-C(5)	118.80(18)
O(3)-C(10)-C(11)	110.3(2)
O(4)-C(10)-O(3)	123.7(2)
O(4)-C(10)-C(11)	126.0(2)
H(2A)-C(2)-H(2B)	108.1
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
C(1)-C(2)-C(3)	110.62(18)
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
F(8)-C(9)-F(7)	106.99(19)
F(8)-C(9)-C(3)	111.2(2)
F(9)-C(9)-F(8)	106.86(19)
F(9)-C(9)-F(7)	107.18(19)
F(9)-C(9)-C(3)	114.2(2)
F(7)-C(9)-C(3)	110.10(19)
H(4A)-C(4)-H(4B)	107.7
C(3)-C(4)-H(4A)	108.9
C(3)-C(4)-H(4B)	108.9
C(3)-C(4)-C(5)	113.3(2)
C(5)-C(4)-H(4A)	108.9
C(5)-C(4)-H(4B)	108.9
O(2)-C(1)-O(1)	112.96(19)
O(2)-C(1)-C(2)	108.23(18)
O(2)-C(1)-C(8)	109.11(19)
O(1)-C(1)-C(2)	113.45(19)
O(1)-C(1)-C(8)	102.67(18)
C(2)-C(1)-C(8)	110.27(19)
O(3)-C(3)-C(2)	115.10(18)
O(3)-C(3)-C(9)	107.42(18)
O(3)-C(3)-C(4)	105.23(18)
C(9)-C(3)-C(2)	111.43(19)
C(9)-C(3)-C(4)	108.54(19)
C(4)-C(3)-C(2)	108.79(19)
F(6)-C(8)-F(5)	107.4(2)
F(6)-C(8)-F(4)	107.4(2)
F(6)-C(8)-C(1)	111.09(19)
F(5)-C(8)-C(1)	111.1(2)
F(4)-C(8)-F(5)	107.3(2)
F(4)-C(8)-C(1)	112.3(2)
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
O(1)-C(5)-C(4)	112.9(2)
O(1)-C(5)-C(6)	111.2(2)
O(1)-C(5)-C(7)	101.50(18)
C(4)-C(5)-C(7)	107.3(2)
C(6)-C(5)-C(4)	114.3(2)
C(6)-C(5)-C(7)	108.6(2)
F(1)-C(7)-F(2)	106.8(2)
F(1)-C(7)-C(5)	110.5(2)
F(2)-C(7)-C(5)	112.4(2)
F(3)-C(7)-F(1)	107.6(2)
F(3)-C(7)-F(2)	106.9(2)
F(3)-C(7)-C(5)	112.4(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for (±)-3. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(8)	32(1)	39(1)	17(1)	4(1)	2(1)	1(1)
F(9)	22(1)	39(1)	26(1)	-5(1)	4(1)	-2(1)
F(6)	30(1)	36(1)	34(1)	10(1)	-10(1)	0(1)
F(5)	37(1)	30(1)	27(1)	10(1)	4(1)	2(1)
F(7)	42(1)	27(1)	28(1)	-9(1)	12(1)	2(1)
F(1)	32(1)	39(1)	33(1)	-3(1)	-14(1)	-6(1)
F(4)	50(1)	16(1)	37(1)	2(1)	0(1)	6(1)
F(2)	39(1)	22(1)	41(1)	-7(1)	-6(1)	-4(1)
F(3)	29(1)	38(1)	41(1)	1(1)	1(1)	-13(1)
O(3)	20(1)	17(1)	16(1)	-2(1)	0(1)	2(1)
O(2)	24(1)	18(1)	18(1)	-4(1)	4(1)	0(1)
O(1)	22(1)	21(1)	20(1)	2(1)	-3(1)	-3(1)
O(4)	23(1)	22(1)	22(1)	-2(1)	0(1)	-2(1)
C(10)	24(1)	18(1)	15(1)	1(1)	3(1)	-4(1)
C(2)	20(1)	17(1)	19(1)	-2(1)	-1(1)	3(1)
C(9)	26(1)	22(1)	20(1)	-4(1)	-1(1)	2(1)
C(4)	23(1)	20(1)	18(1)	-1(1)	-4(1)	0(1)
C(1)	21(1)	17(1)	18(1)	-2(1)	0(1)	1(1)
C(3)	20(1)	15(1)	18(1)	-4(1)	-1(1)	0(1)
C(8)	27(1)	20(1)	23(1)	2(1)	0(1)	2(1)
C(6)	19(1)	23(1)	28(1)	0(1)	-2(1)	3(1)
C(5)	23(1)	21(1)	19(1)	0(1)	-3(1)	-2(1)
C(7)	26(1)	25(1)	29(1)	-1(1)	-3(1)	-3(1)
C(11)	30(1)	20(1)	25(1)	-4(1)	0(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for (±)-3.

	x	y	z	U(eq)
H(2)	2984	3668	4803	30
H(2A)	-122	4368	5896	22
H(2B)	619	5701	6308	22
H(4A)	3535	3777	7416	24
H(4B)	2879	5321	7292	24
H(6A)	4542	2647	6006	35
H(6B)	5828	2964	6653	35
H(6C)	6103	3574	5831	35
H(11A)	2572	659	5439	38
H(11B)	979	-243	5590	38
H(11C)	2283	-33	6241	38