

Mechanism of regioselective ring-opening reactions of 1,2-epoxyoctane catalyzed by tris(pentafluorophenyl)borane: a combined experimental, DFT, and microkinetic study

Ying Yu,^a Youlong Zhu,^b Mihir N. Bhagat,^a Arjun Raghuraman^c, Kurt F. Hirsekorn^c, Justin M.

Notestein,^{a,} SonBinh T. Nguyen,^{b,*} Linda J. Broadbelt^{a,*}*

^aDepartment of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA. ^bDepartment of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA. ^cThe Dow Chemical Company, Lake Jackson, TX 77566, USA.

* Email: j-notestein@northwestern.edu; stn@northwestern.edu; broadbelt@northwestern.edu

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Section S1. General information.

^1H and ^{13}C NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer and Agilent DD2 500 spectrometer (^1H = 500 MHz, ^{13}C = 125 MHz) and processed using MestReNova software V8.14 (Mestrelab Research S.L, Santiago de Compostela, Spain).

GC-FID analysis were carried out on an Agilent Technologies HP 6890 GC system (Agilent, Santa Clara, CA, USA) equipped with an FID detector and a Restek Stabilwax (Restek, Bellefonte, PA, USA) GC capillary column (60 m $\times$ 0.25 mm $\times$ 0.5 μm film thickness). Analysis parameters were as follows: initial temperature = 80 $^\circ\text{C}$, initial time = 0 minutes, ramp = 10 $^\circ\text{C}/\text{min}$, final temperature = 200 $^\circ\text{C}$, final time = 8 minutes, flow rate = 1.4 mL/min. Peak areas for each of the components and the internal standard (o-xylene) were obtained using the Agilent ChemStation software version B.04.02 and calibration curves (molar ratio vs. area ratio against the internal standard) were constructed for 1,2-epoxyoctane and 2-isopropoxyoctan-1-ol (P1) using the pure compounds. Identical response factors are used for P1 and P2.

Karl Fischer (KF) titration was carried out on a C20X Coulometric Karl Fischer Titrator (Mettler-Toledo, Inc., Columbus, OH, USA) filled with Aquastar Coulomat A (EMD Chemicals, Gibbstown, NJ, USA) reagent with two injections being made for each sample.

Section S2. Materials.

Tris(pentafluorophenyl)borane (95%), o-Xylene (98%), 1,2-Epoxyoctane (97%) and 2-Propanol (99.5%) were purchased from the Aldrich Chemical Company (Milwaukee, WI, USA). Tetrahydrofuran (Stabilized, Certified ACS) was purchased from Fisher Scientific (Hampton, NH, USA).

Classical Lewis acid catalysis gives $\sim 1:1$ ratios of primary and secondary alcohol products in epoxide ring opening, so this method was chosen to synthesize and isolate P1 (2-isopropoxyoctan-1-ol) and P2 (1-isopropoxyoctan-2-ol) using $\text{Sc}(\text{OTf})_3$ as the catalyst. In a 250 mL round bottom flask charged with 2-propanol (10.0 g, 0.17 mol) and 1,2-epoxyoctane (5.0 g, 39 mmol), $\text{Sc}(\text{OTf})_3$ (0.20 g, 0.41 mmol) was added as the catalyst. The resulting mixture was heated to reflux, approx. 80 $^\circ\text{C}$, for 1 hour and cooled to room temperature. 100 mL ethyl ether was added to the mixture and washed with saturated bicarbonate solution and water; the aqueous layer was further extracted by ethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4 , and the solvent was removed under reduced pressure on a rotary evaporator to yield a mixture of P1 and P2 as a colorless oil. P1 and P2 were separated by normal silica flash column chromatography with 5%-10% ethyl acetate in hexanes as the eluent. ^1H NMR and ^{13}C NMR were consistent with the expected structure. See Figures S1-S8.

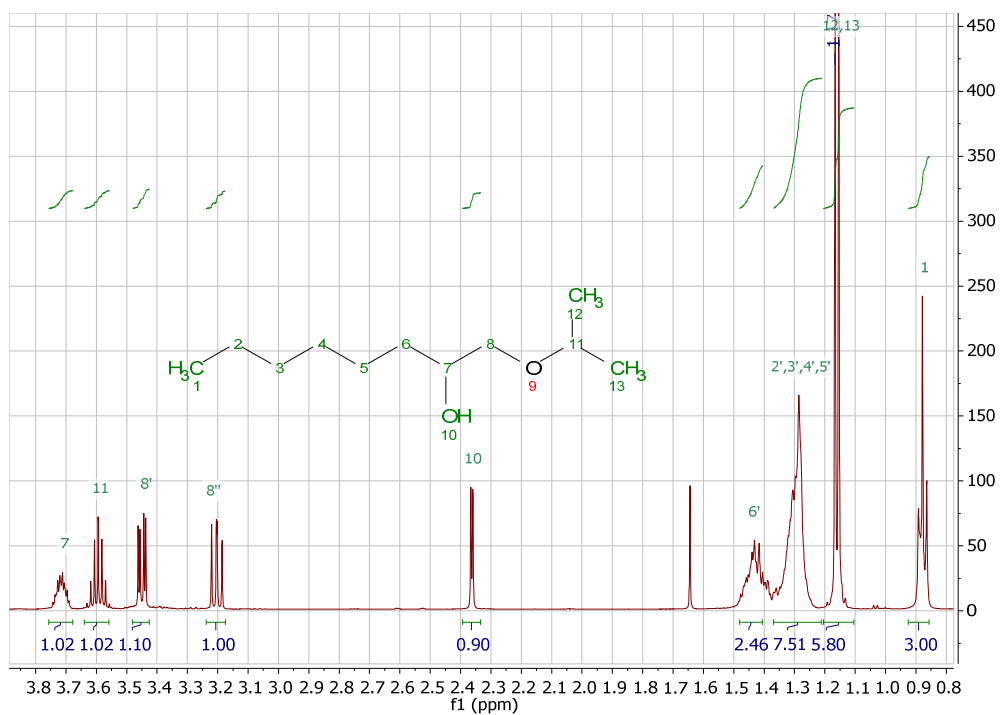


Figure S1. ^1H NMR of 1-isopropoxyoctan-2-ol (P2)

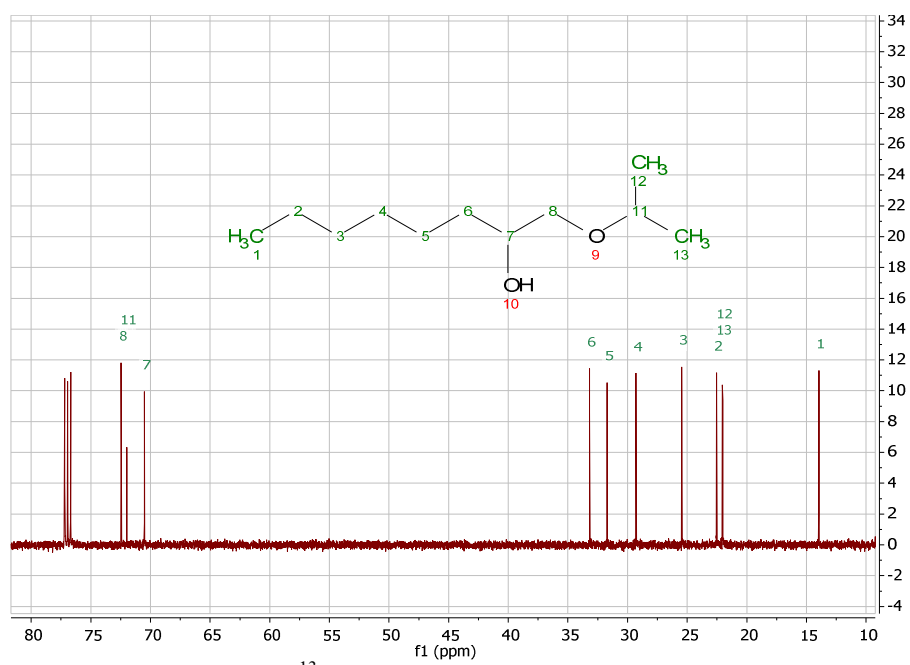


Figure S2. ^{13}C NMR of 1-isopropoxyoctan-2-ol (P2)

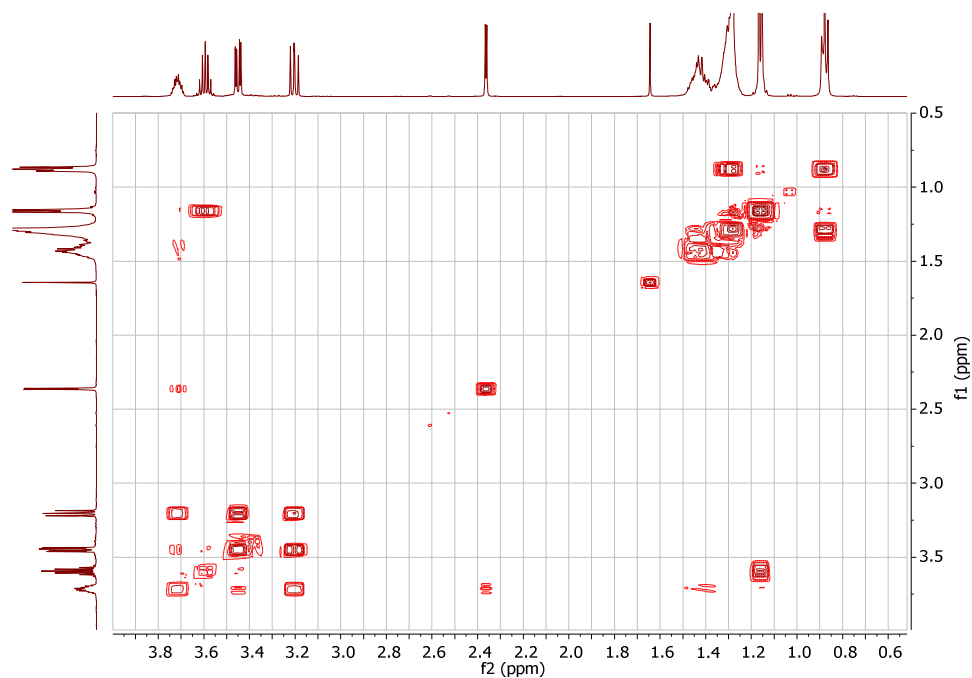


Figure S3. 2D HH COSY of 1-isopropoxyoctan-2-ol (P2)

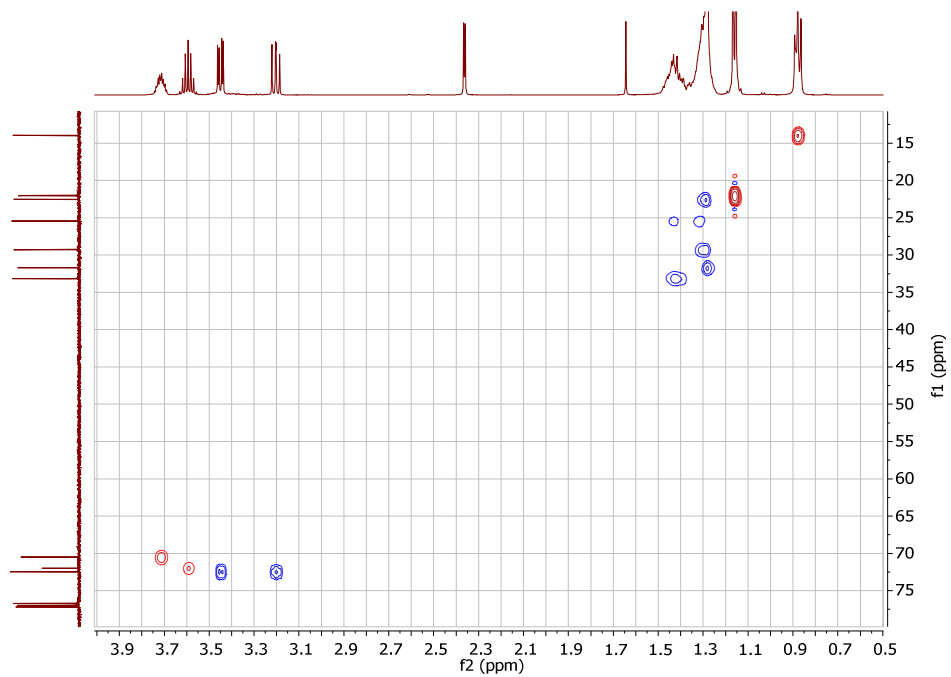


Figure S4. 2D CH HSQC of 1-isopropoxyoctan-2-ol (P2)

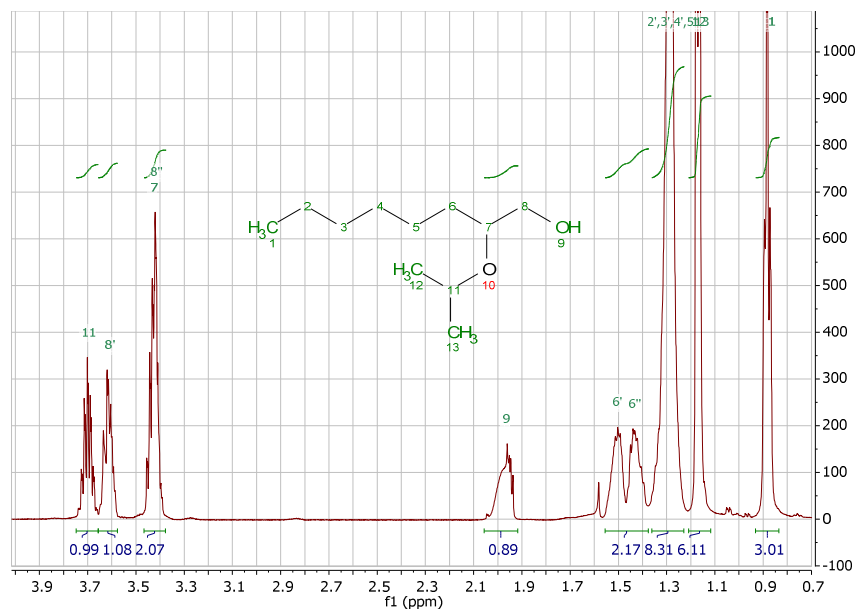


Figure S5. ¹H NMR of 2-isopropoxyoctan-1-ol (P1)

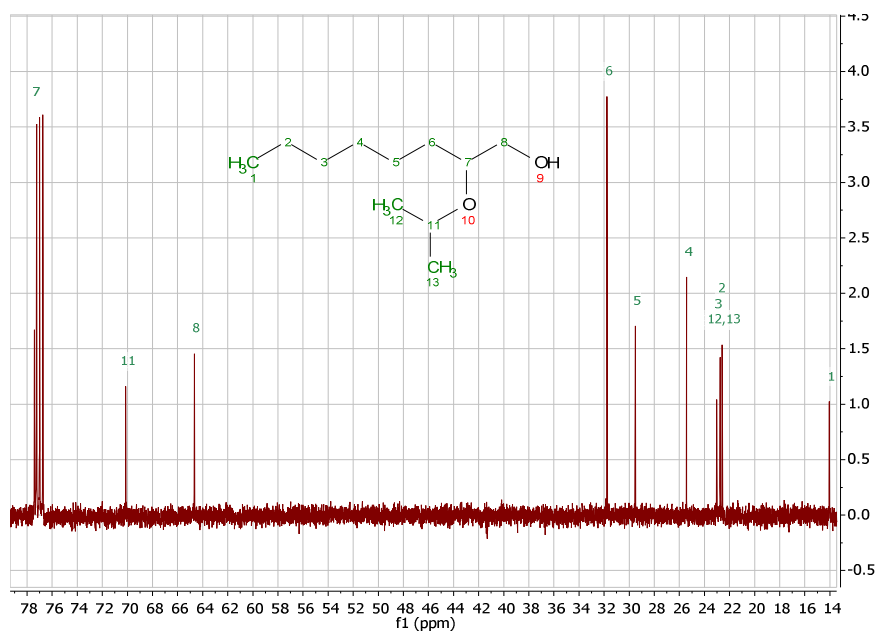


Figure S6. ¹³C NMR of 2-isopropoxyoctan-1-ol (P1)

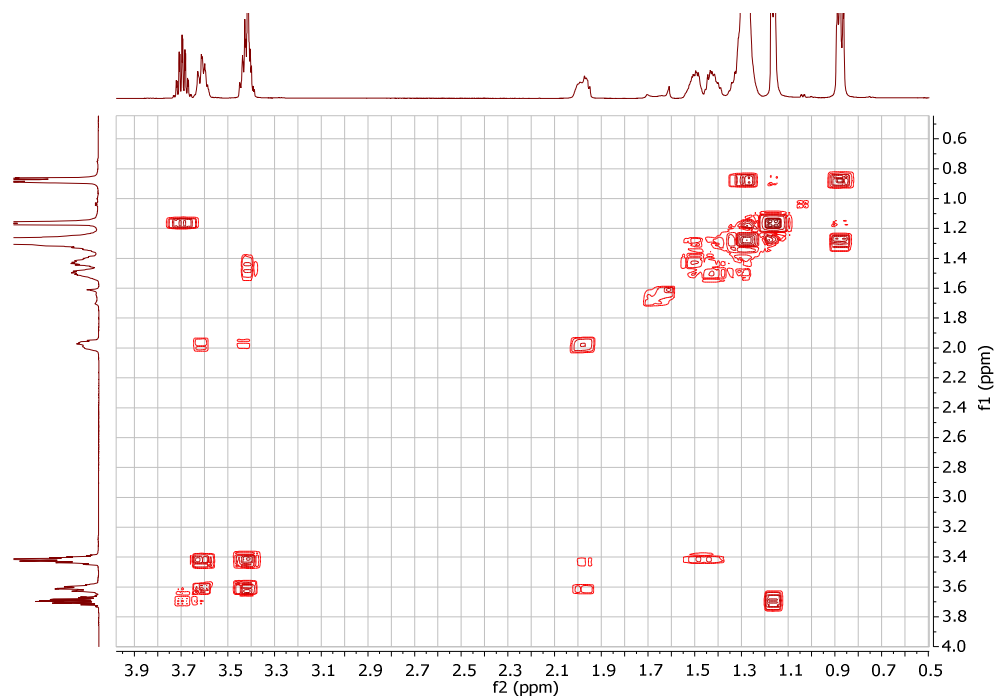


Figure S7. 2D HH COSY of 2-isopropoxyoctan-1-ol (P1)

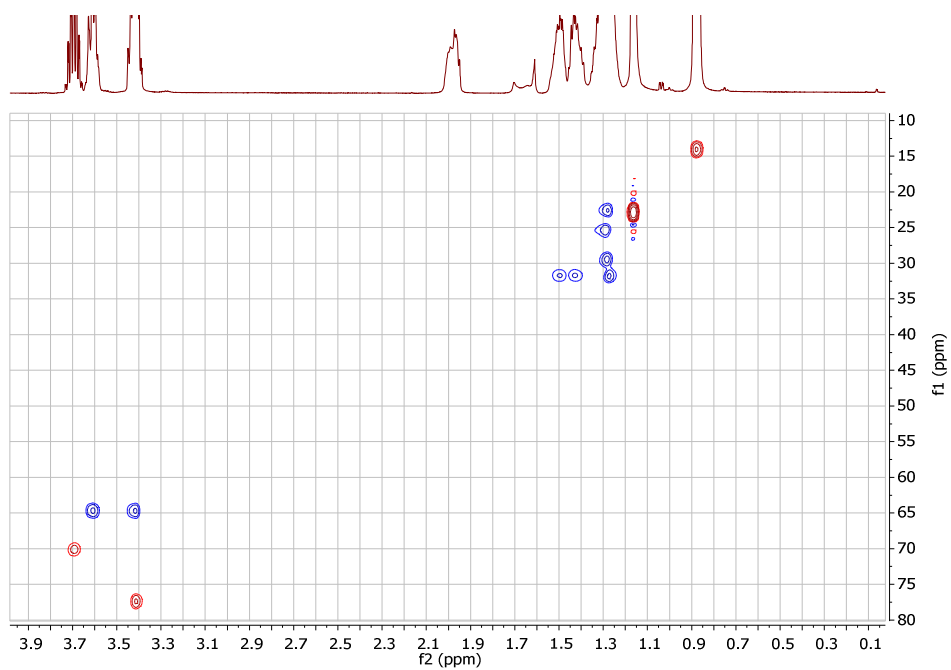


Figure S8. 2D CH HSQCAD of 2-isopropoxyoctan-1-ol (P2)

Section S3. Epoxide ring-opening reactions utilizing tris(pentafluorophenyl) borane.

For anhydrous conditions, solvents and reagents were pre-dried inside a N₂-filled glove box using activated 3A molecular sieves, which were heated at 250 °C under vacuum for 16 h and stored inside the glove box. In a typical drying preparation, the appropriate solvent/reagent bottle was taken into the glove box, combined with about 1/3 volume of the activated molecular sieves, left undisturbed for about 48 h. A sample was transferred into a 2-5 mL microwave vial (Biotage, LLC, Charlotte, NC, USA), crimp-capped, and then was removed from the glove box for KF titration. A syringe was used to withdraw an aliquot (~0.5 mL) of solvent or reagent and the whole syringe assembly was quickly weighed out on a TR104 scale (Denver Instrument Co., Denver, CO, USA). The sample was injected into a pre-equilibrated C20X Coulometric Karl Fischer Titrator and the syringe was then re-weighed prior to analysis. If the solvent was not dried completely to the level indicated in Table S1, more activated 3A molecular sieves were added and the drying process was continued for another 48 h before being reanalyzed. Dried reagents and solvents were kept over the molecular sieves and filtered through a 0.2 µm PTFE membrane Whatman syringe filter (GE Healthcare, Chicago, IL) before use.

Table S1. Water content in reagents or solvents measured by Karl Fischer water titration.

Reagent	H ₂ O content (ppm)
o-xylene ^a	10
2-propanol ^a	30
1,2-epoxyoctane	20

^aDried periodically in 20 mL batches.

For catalytic testing under strictly anhydrous conditions (residual water <200 ppm), all glassware was dried in the oven before use. In a typical ring-opening reaction, 2-propanol (1.20 g, 20.0 mmol) and 1,2-epoxyoctane (0.64 g, 5.0 mmol) was mixed in a 5 mL Biotage microwave vial with a magnetic stir bar inside the N₂ filled glovebox. Tris(pentafluorophenyl)borane (FAB) (2.6 mg, 5.0 µmol, 0.1 mol% with respect to 1,2-epoxyoctane) was mixed with o-xylene (0.69 g, as GC internal standard) in a second 5 mL Biotage microwave vial inside the N₂ filled glovebox. Both tubes were crimp sealed, removed from the glove box and transferred into a preheated oil bath. After stirring for 10 minutes to thermally equilibrate the vials, the catalyst solution was injected into the reagent solution to start the reaction.

For catalytic testing under moderate water content (200-500 ppm), solvents were pre-dried as above, but subsequent manipulation was carried out in a N₂-purged glove bag using oven-dried glassware. In a typical ring-opening reaction, 2-propanol (2 mL, 25.8 mmol) and 1,2-epoxyoctane (1 mL, 6.4 mmol) was mixed in a 20 mL scintillation vial and sealed with a PTFE septum cap. Water levels were adjusted by using mixtures of anhydrous and as-received 2-propanol. Tris(pentafluorophenyl)borane (FAB) (3.5 mg, 6.6 µmol, 0.1 mol% with respect to 1,2-epoxyoctane) was mixed with o-xylene (1 mL, as GC internal standard) in a second 20 mL scintillation vial and sealed with a PTFE septum cap. Both vials were placed on a Glas-Col shaker set at the desired temperature and a shaking speed of 500 RPM. After ~10 minutes to thermally equilibrate, the contents of the reagent vial were transferred to the catalyst solution vial via syringe to start the reaction. For catalytic testing at water levels exceeding 500 ppm, experiments were carried out in a fume hood with no special precautions against moisture. All procedures were followed as above, except that water levels were further adjusted by direct addition of water to the 2-propanol solution.

For all reactions, ~50 µL aliquots were taken periodically over 2 h, with increased sampling at the reaction start. The aliquots were quenched with ~1.5 mL THF and the samples were analyzed by GC-FID. Karl-Fisher titration was used to measure water levels of the residual reaction solution at the experiment conclusion. The inability to measure water content in real time is one source of uncertainty in these experiments.

Section S4. NMR experiments on binding energies

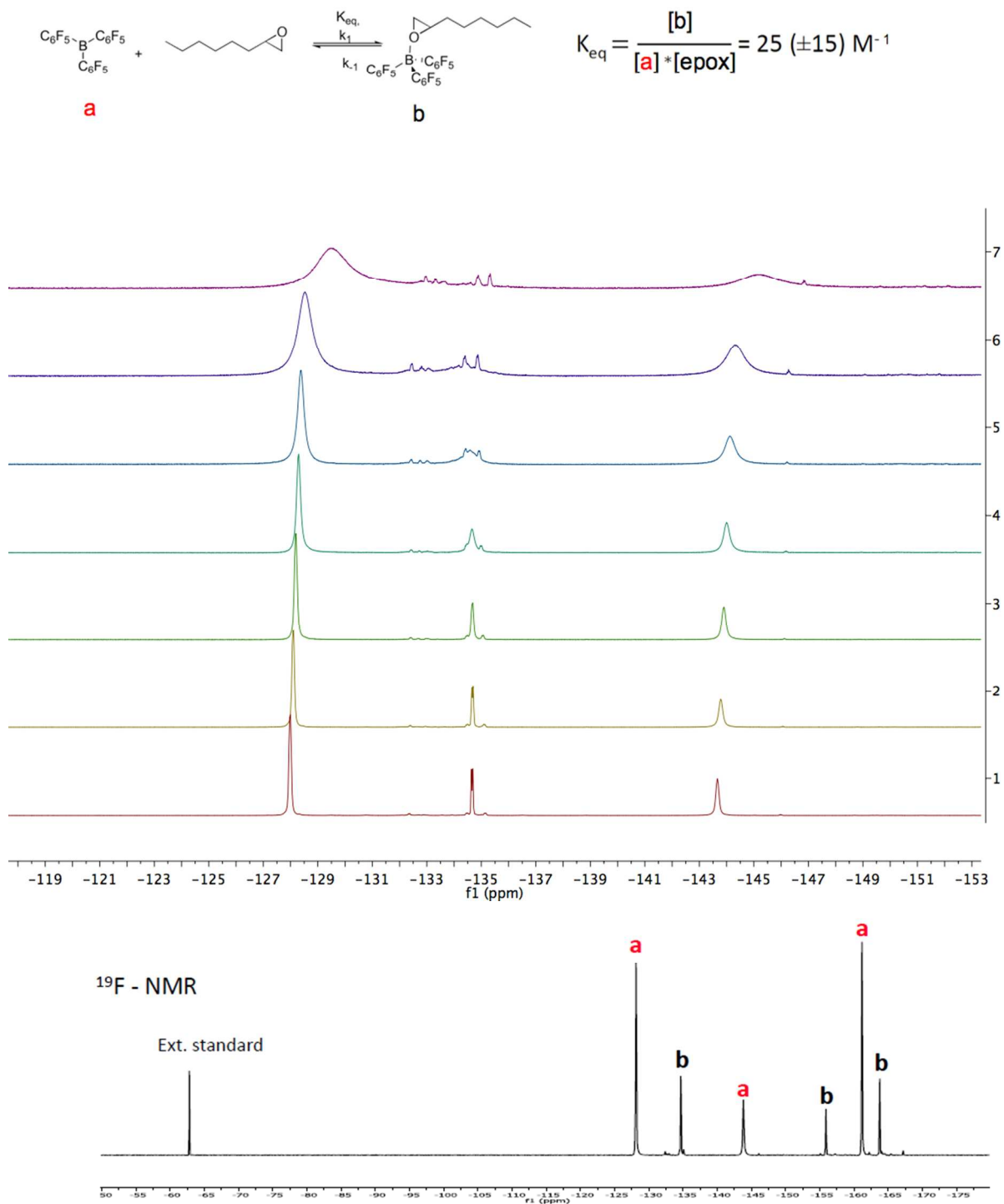


Figure S9. The full (bottom) and variable-temperature (middle) ^{19}F NMR spectra of a mixture of $(\text{C}_6\text{F}_5)_3\text{B}$ and 1,2-epoxyoctane (0.5 equiv) in anhydrous toluene. The estimated kinetic constant shown on the top panel is based on line-shape analysis of the ^{19}F NMR variable-temperature spectra.

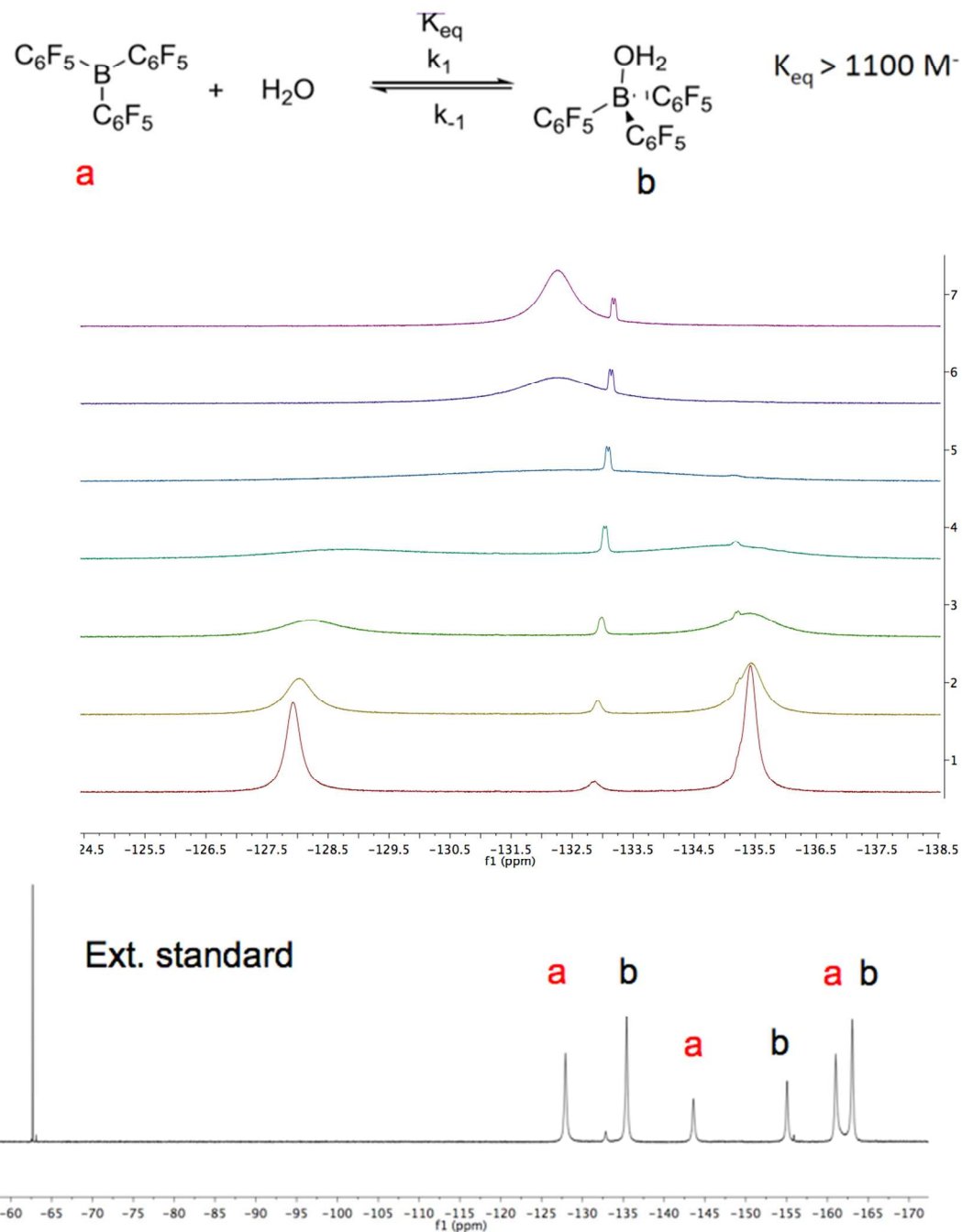


Figure S10. The full (bottom) and variable-temperature (top) ^{19}F NMR spectra of a mixture of $(\text{C}_6\text{F}_5)_3\text{B}$ and H_2O (0.5 equiv) in anhydrous toluene. The estimated kinetic constant shown on the top panel is based on line-shape analysis of the ^{19}F NMR variable-temperature spectra.

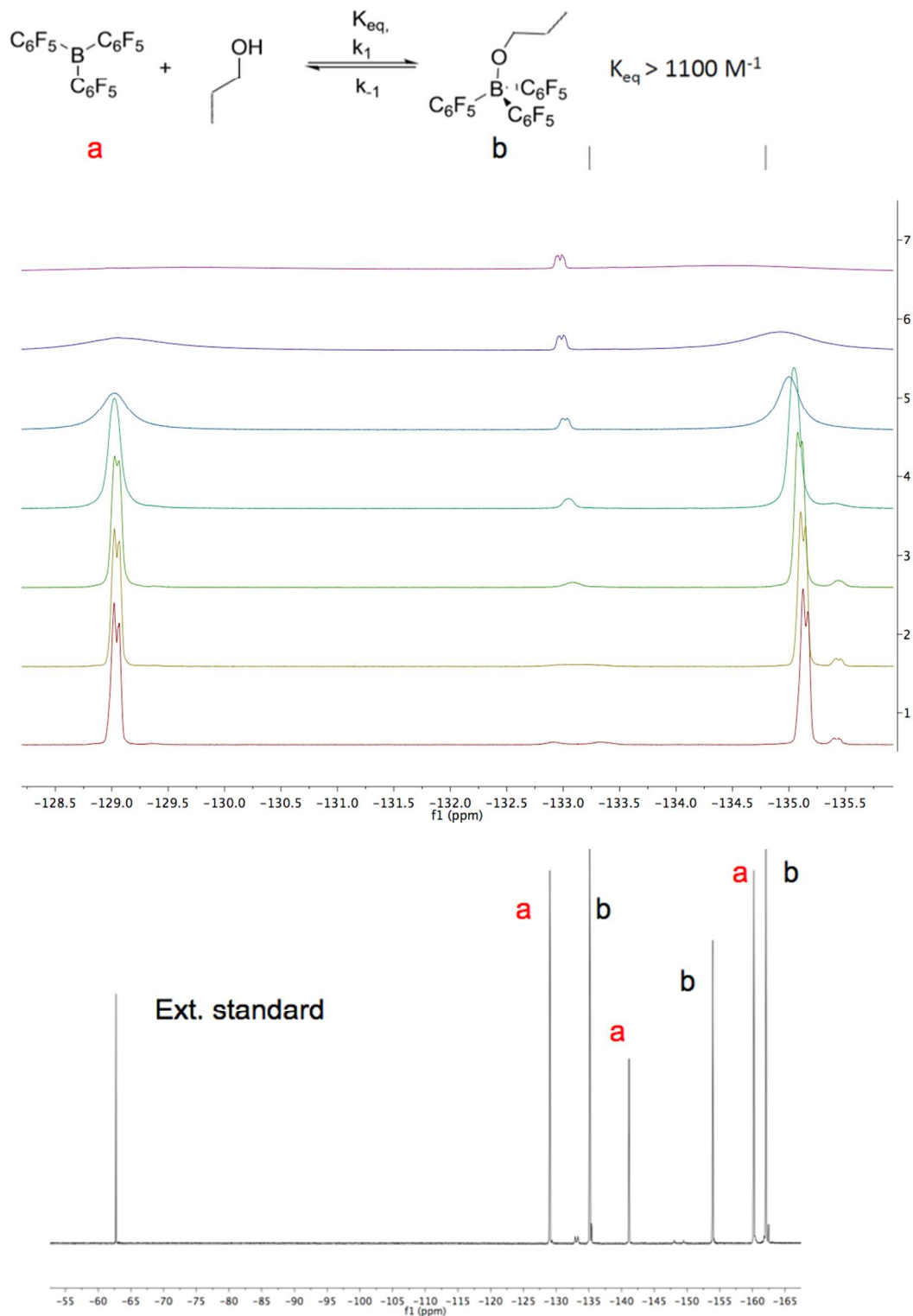


Figure S11. The full (bottom) and variable-temperature (top) ^{19}F NMR spectra of a mixture of $(\text{C}_6\text{F}_5)_3\text{B}$ and 1-propanol (0.5 equiv) in anhydrous toluene. The estimated kinetic constant shown on the top panel is based on line-shape analysis of the ^{19}F NMR variable-temperature spectra.

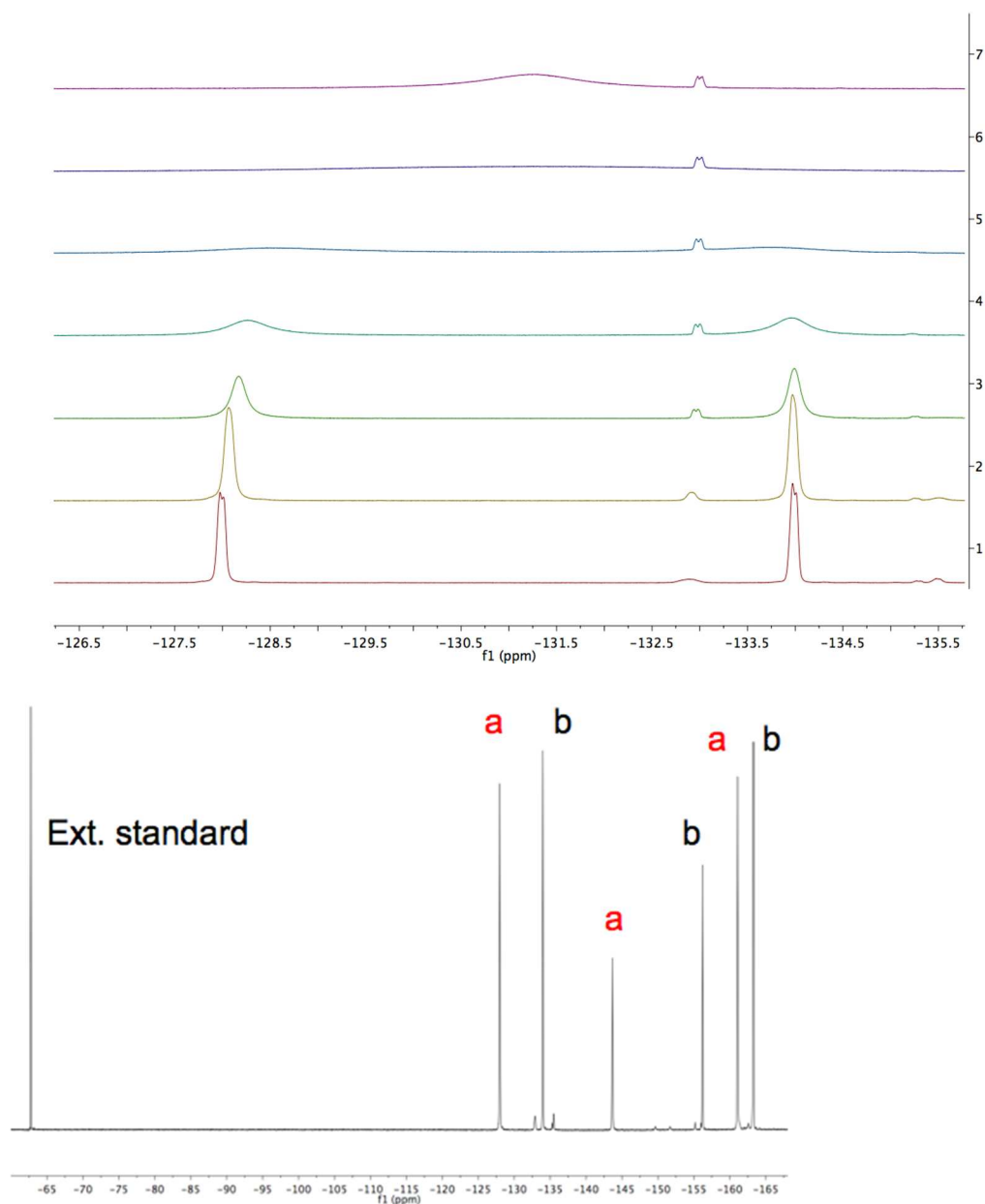
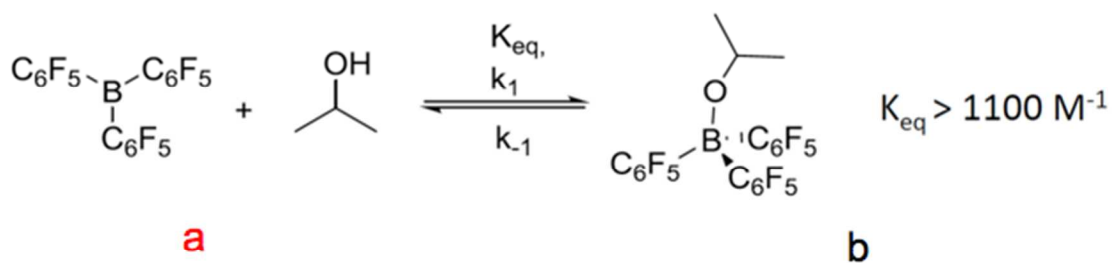


Figure S12. The full (top) and variable-temperature (bottom) ^{19}F NMR spectra of a mixture of $(\text{C}_6\text{F}_5)_3\text{B}$ and 2-propanol (0.5 equiv) in anhydrous toluene. The estimated kinetic constant shown on the top panel is based on line-shape analysis of the ^{19}F NMR variable-temperature spectra.

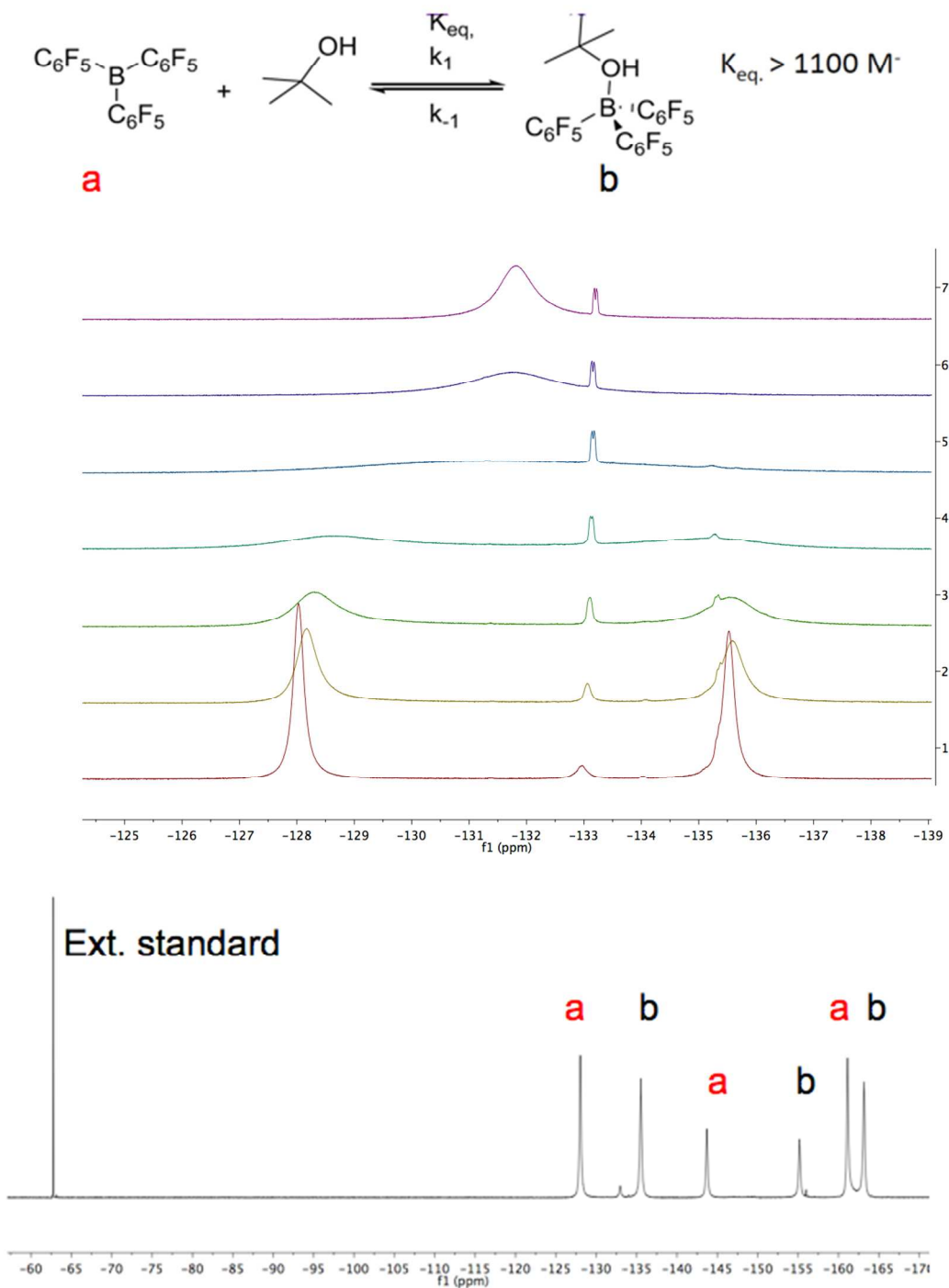


Figure S13. The full (top) and variable-temperature (bottom) ^{19}F NMR spectra of a mixture of $(\text{C}_6\text{F}_5)_3\text{B}$ and *tert*-butanol (0.5 equiv) in anhydrous toluene. The estimated kinetic constant shown on the top panel is based on line-shape analysis of the ^{19}F NMR variable-temperature spectra.

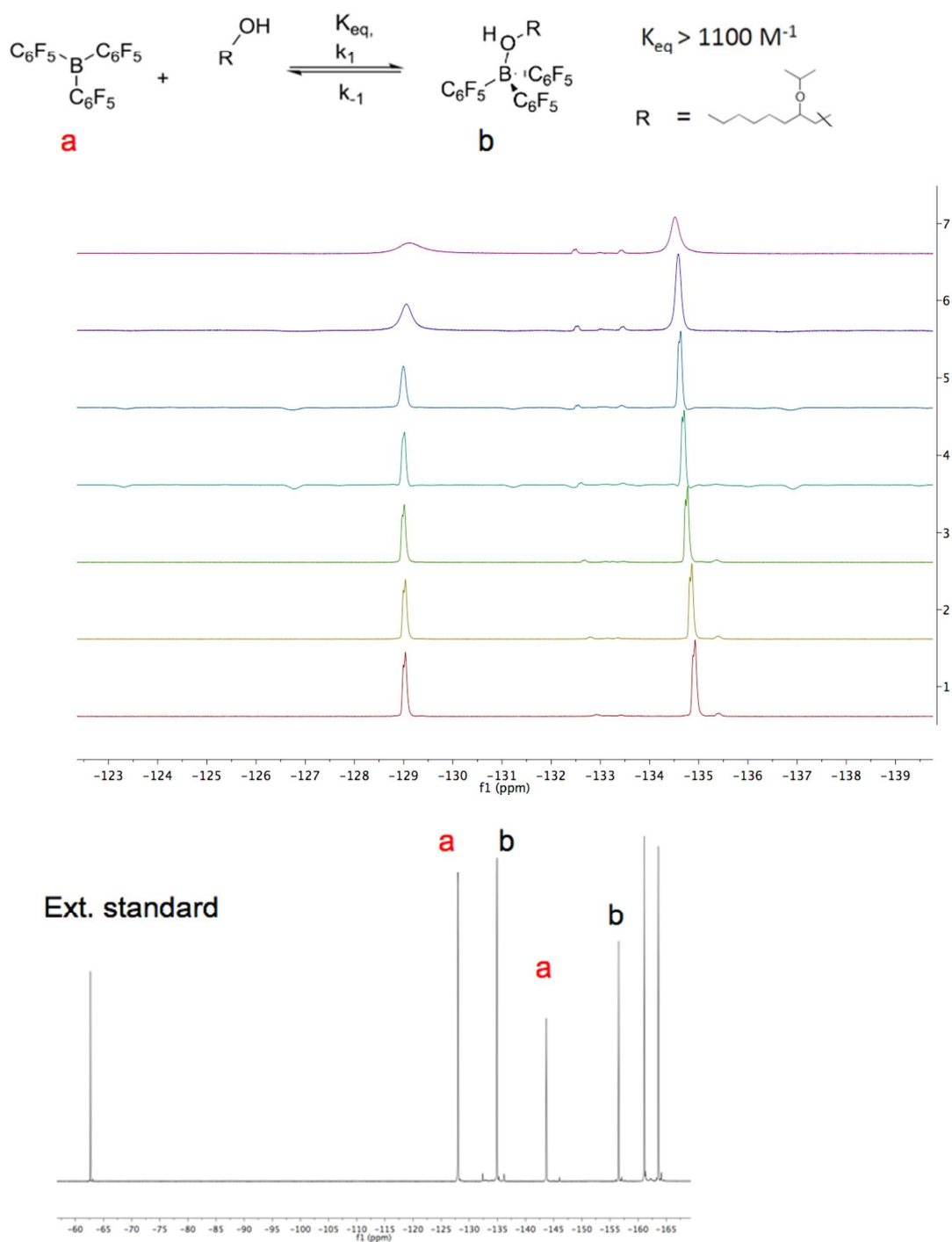


Figure S14. The full (top) and variable-temperature (bottom) ^{19}F NMR spectra of a mixture of $(\text{C}_6\text{F}_5)_3\text{B}$ and 2-isopropoxyoctan-1-ol (0.5 equiv) in anhydrous toluene. The estimated kinetic constant shown on the top panel is based on line-shape analysis of the ^{19}F NMR variable-temperature spectra.

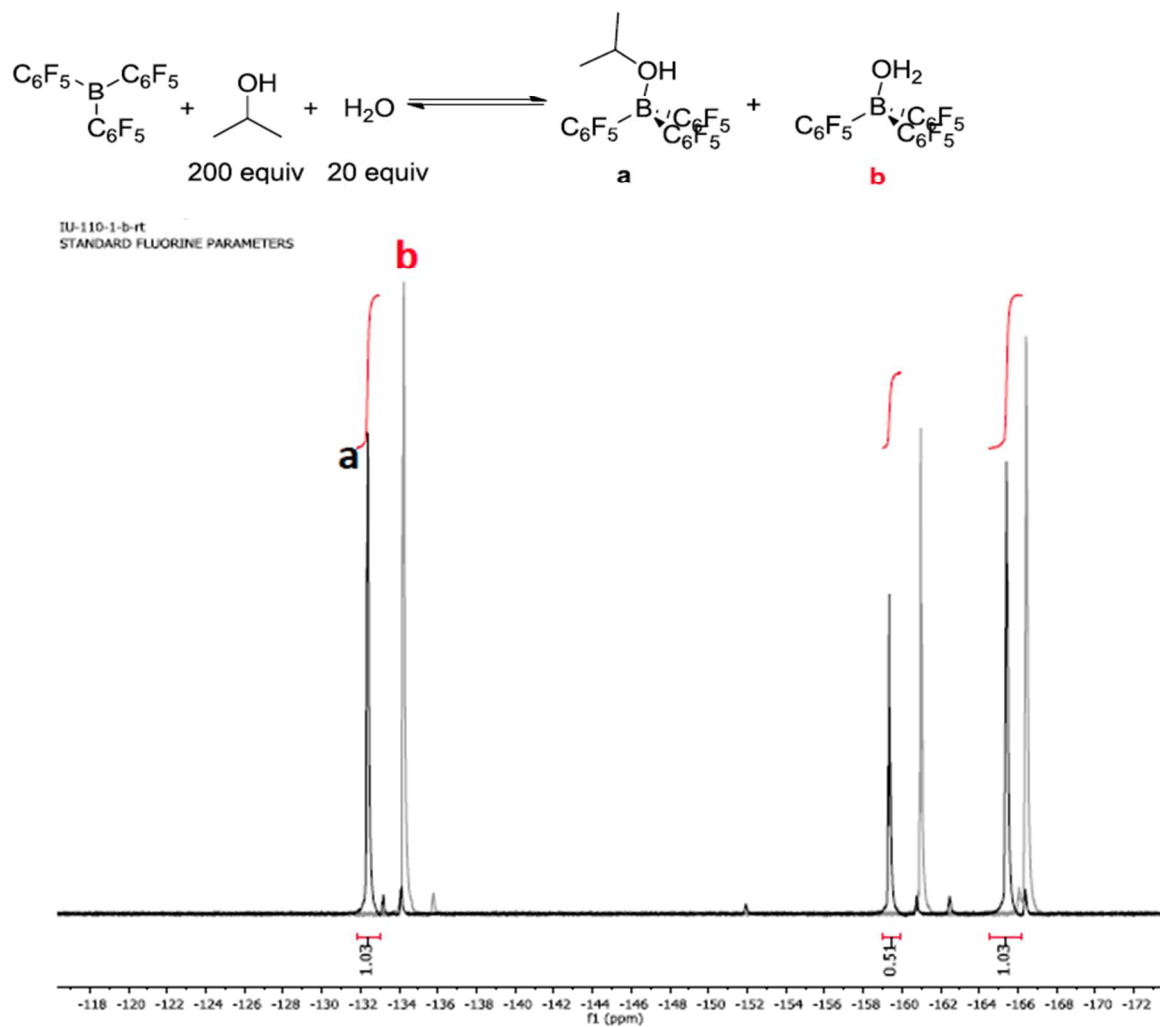


Figure S15. The ^{19}F NMR spectra of $(\text{C}_6\text{F}_5)_3\text{B}$ exposed to anhydrous 2-propanol NMR solvent (200 equiv, **a**, dark spectrum) which was then added H_2O (20 equiv, **b**, lighter spectrum). The 10:1 molar ratio of 2-propanol: H_2O clearly shows that H_2O outcompetes 2-propanol for binding to the B atom.

Section S5. Computational methods and results.

All quantum chemical calculations were carried out using the Gaussian 09 program.¹ For geometry optimization, we employed the B3LYP² functional with D3BJ dispersion correction,³ coupled with the 6-31+G(d,p) basis set. The implicit solvent effects were taken into account in all geometry optimizations and energy calculations by using the SMD model⁴ as implemented in Gaussian 09. The choice of computational method was made based on the benchmarking results (Figure S16) of calculated $-\Delta H_{\text{formation}}$ to experimental $\Delta H_{\text{dissociation}}^{\ddagger}$ of FAB·Lewis base (LB) adducts in toluene solvent. Vibrational frequencies based on the harmonic oscillator approximation were calculated. All species formed in competitive binding reactions were confirmed to be local minima with no imaginary frequencies, and are reported in Table S2. All competitive binding reactions are reported in Table S3, with calculated binding enthalpy, binding entropy, and binding free energy results at 298.15 K. Free energy at temperature T was calculated as $\Delta G(T) = \Delta H - T\Delta S$, whereas ΔH and ΔS were calculated at 298.15 K, and T ranged from 273.15 K to 333.15 K.

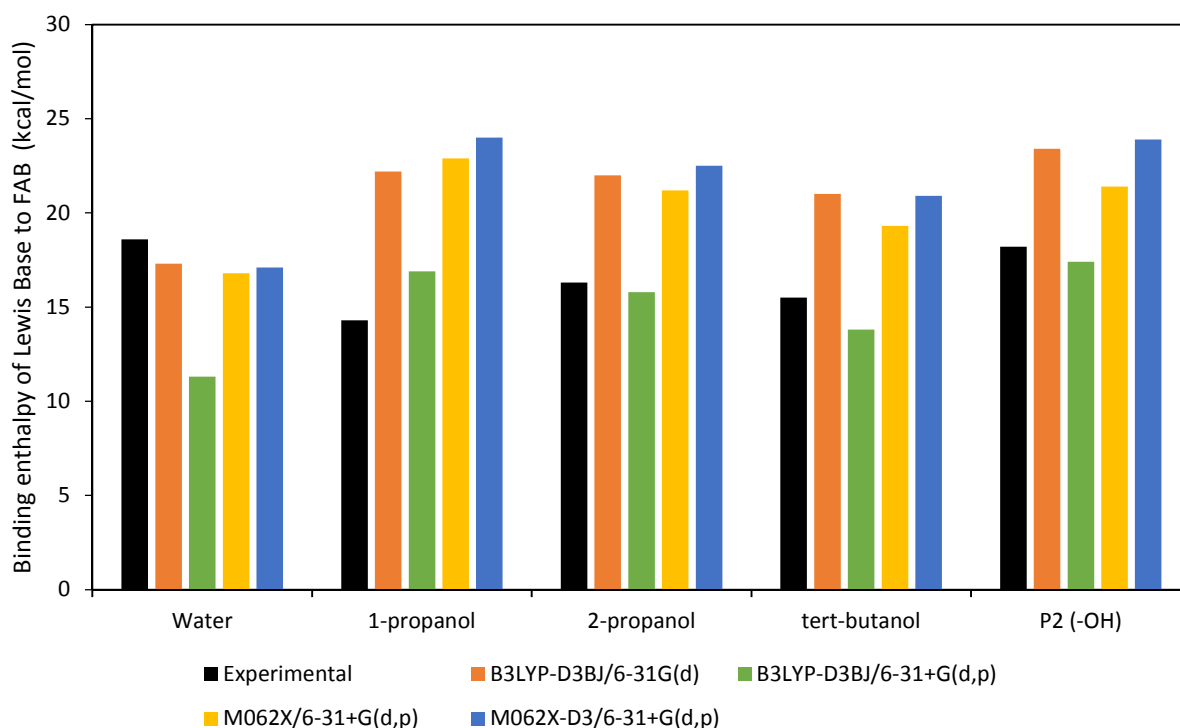


Figure S16. Benchmarking of calculated $-\Delta H_{\text{formation}}$ (colored bars) versus experimental $\Delta H_{\text{dissociation}}^{\ddagger}$ (black bars) of FAB·Lewis base (LB) adducts in toluene solvent. The FAB·LB adducts include: FAB·OH₂, FAB·1-propanol, FAB·2-propanol, FAB·*tert*-butanol, and FAB·P2 (-OH)^a, from left to right. The “-OH” notation indicates that the P2 forms a hydrogen bond with the FAB B center through the hydroxyl oxygen atom. It has been computationally confirmed that the total energy of the FAB·LB system increases monotonically during adduct dissociation and decreases monotonically during adduct formation. Thus $-\Delta H_{\text{formation}}$ can be a reasonable estimate of the $\Delta H_{\text{dissociation}}^{\ddagger}$ for the FAB·LB system, and vice versa. Overall, B3LYP-D3BJ/6-31+G(d,p) (green bars) was found to be the most promising level of theory in generating accurate estimates of $\Delta H_{\text{dissociation}}^{\ddagger}$ for the four FAB·alcohol adducts. However, it underestimated $\Delta H_{\text{dissociation}}^{\ddagger}$ for the FAB·OH₂ adduct by approximately 7.3 kcal/mol. This discrepancy would likely extend to our model system where 2-propanol is the effective solvent and will be addressed by parameter adjustment in microkinetic modeling.

Table S2. Enumerated species in a system initially consisting of FAB, 2-propanol, 1,2-epoxyoctane (abbr. EPX), H₂O, and ring-opened products. Ring-opened products are abbreviated as P1 (primary alcohol product: 2-isopropoxyoctan-1-ol) and P2 (secondary alcohol product: 1-isopropoxyoctan-2-ol). Names of adduct species indicate the binding structures. There are two main classes of binding structures: “first-shell” adducts and “second-shell” adducts. “First-shell” adducts are formed by direct binding between a Lewis base (LB) molecule and the FAB B center, with the general form of “FAB·LB”. “Second-shell” adducts are formed by hydrogen bonding between one or two H-bond acceptor (HBA) molecule(s) and a “first-shell” adduct whose Lewis base component is H₂O or 2-propanol, with the general form of [FAB·OH₂](HBA)_n (n = 1-2) or [(FAB·2-propanol)](HBA). For HBA molecules with more than one site that can form a hydrogen bond (i.e. oxygen atom, in this case), “-OH” and “-O-” notations are used to specify the site of hydrogen bonding to the “first-shell” adduct. “-OH & -O-” notation indicates that each site forms a hydrogen-bond with an H atom of H₂O in the FAB·OH₂ adduct.

Entry #	Species Name	Entry #	Species Name
1	FAB	25	[FAB·OH ₂](H ₂ O)(EPX)
2	H ₂ O	26	[FAB·OH ₂](H ₂ O)(P1) (-OH)
3	2-propanol	27	[FAB·OH ₂](H ₂ O)(P1) (-O-)
4	EPX	28	[FAB·OH ₂](H ₂ O)(P2) (-OH)
5	P1	29	[FAB·OH ₂](H ₂ O)(P2) (-O-)
6	P2	30	[FAB·OH ₂](2-propanol) ₂
7	FAB·OH ₂	31	[FAB·OH ₂](2-propanol)(EPX)
8	FAB·2-propanol	32	[FAB·OH ₂](2-propanol)(P1) (-OH)
9	FAB·EPX	33	[FAB·OH ₂](2-propanol)(P1) (-O-)
10	FAB·P1 (-OH)	34	[FAB·OH ₂](2-propanol)(P2) (-OH)
11	FAB·P1 (-O-)	35	[FAB·OH ₂](2-propanol)(P2) (-O-)
12	FAB·P2 (-OH)	36	[FAB·OH ₂](EPX)(P1) (-OH)
13	FAB·P2 (-O-)	37	[FAB·OH ₂](EPX)(P1) (-O-)
14	[FAB·OH ₂](H ₂ O)	38	[FAB·OH ₂](EPX)(P2) (-OH)
15	[FAB·OH ₂](2-propanol)	39	[FAB·OH ₂](EPX)(P2) (-O-)
16	[FAB·OH ₂](EPX)	40	[FAB·2-propanol](H ₂ O)
17	[FAB·OH ₂](P1) (-OH)	41	[FAB·2-propanol](2-propanol)
18	[FAB·OH ₂](P1) (-O-)	42	[FAB·2-propanol](EPX)
19	[FAB·OH ₂](P1) (-OH & -O-)	43	[FAB·2-propanol](P1) (-OH)
20	[FAB·OH ₂](P2) (-OH)	44	[FAB·2-propanol](P1) (-O-)
21	[FAB·OH ₂](P2) (-O-)	45	[FAB·2-propanol](P2) (-OH)
22	[FAB·OH ₂](P2) (-OH & -O-)	46	[FAB·2-propanol](P2) (-O-)
23	[FAB·OH ₂](H ₂ O) ₂	47	PP1
24	[FAB·OH ₂](H ₂ O)(2-propanol)	48	PP2

Table S3. Calculated binding enthalpies, binding entropies and binding free energies at 298.15 K of enumerated competitive binding reactions in a system initially consisting of FAB, 2-propanol, 1,2-epoxyoctane (abbr. EPX), H₂O, and ring-opening products. Energies were calculated at the B3LYP-D3BJ/6-31+G(d,p) level of theory, with the implicit solvent effects of isopropanol accounted for using the SMD model.

Entry #	Binding Reaction	ΔH (kcal* mol^{-1})	ΔS (cal* mol^{-1} *K ⁻¹)	ΔG^a (kcal* mol^{-1})
1	FAB + EPX $\leftrightarrow$ FAB·EPX	-16.9	-48.5	-4.3
2	FAB + H ₂ O $\leftrightarrow$ FAB·OH ₂ ^b	-11.6	-39.3	-1.8
3	FAB + 2-propanol $\leftrightarrow$ FAB·2-propanol	-15.0	-45.1	-3.4
4	FAB + P1 $\leftrightarrow$ FAB·P1 (-OH)	-16.5	-49.9	-3.5
5	FAB + P1 $\leftrightarrow$ FAB·P1 (-O-)	-1.4	-59.5	14.4
6	FAB + P2 $\leftrightarrow$ FAB·P2 (-OH)	-17.5	-52.5	-3.8
7	FAB + P2 $\leftrightarrow$ FAB·P2 (-O-)	-1.4	-58.6	14.1
8	FAB·OH ₂ + H ₂ O $\leftrightarrow$ [FAB·OH ₂](H ₂ O)	-9.1	-35.4	-0.5
9	FAB·OH ₂ + 2-propanol $\leftrightarrow$ [FAB·OH ₂](2-propanol)	-12.9	-40.6	-2.7
10	FAB·OH ₂ + EPX $\leftrightarrow$ [FAB·OH ₂](EPX)	-14.2	-42.4	-3.4
11	FAB·OH ₂ + P1 $\leftrightarrow$ [FAB·OH ₂](P1) (-OH)	-12.8	-46.8	-0.8
12	FAB·OH ₂ + P1 $\leftrightarrow$ [FAB·OH ₂](P1) (-O-)	-12.1	-44.1	-0.9
13	FAB·OH ₂ + P1 $\leftrightarrow$ [FAB·OH ₂](P1) (-OH & -O-)	-13.9	-43.7	-2.8
14	FAB·OH ₂ + P2 $\leftrightarrow$ [FAB·OH ₂](P2) (-OH)	-15.1	-46.3	-3.2
15	FAB·OH ₂ + P2 $\leftrightarrow$ [FAB·OH ₂](P2) (-O-)	-14.5	-49.5	-1.6
16	FAB·OH ₂ + P2 $\leftrightarrow$ [FAB·OH ₂](P2) (-OH & -O-)	-20.1	-51.4	-6.7
17	FAB·2-propanol + H ₂ O $\leftrightarrow$ [FAB·2-propanol](H ₂ O)	-6.4	-31.1	1.0
18	FAB·2-propanol + 2-propanol $\leftrightarrow$ [FAB·2-propanol](2-propanol)	-10.0	-43.9	1.2
19	FAB·2-propanol + EPX $\leftrightarrow$ [FAB·2-propanol](EPX)	-11.6	-48.9	1.1
20	FAB·2-propanol + P1 $\leftrightarrow$ [FAB·2-propanol](P1) (-OH)	-9.5	-50.5	3.7
21	FAB·2-propanol + P1 $\leftrightarrow$ [FAB·2-propanol](P1) (-O-)	-6.9	-51.7	6.6
22	FAB·2-propanol + P2 $\leftrightarrow$ [FAB·2-propanol](P2) (-OH)	-12.4	-55.8	2.3
23	FAB·2-propanol + P2 $\leftrightarrow$ [FAB·2-propanol](P2) (-O-)	-5.5	-63.4	11.5
24	[FAB·OH ₂](H ₂ O) + H ₂ O $\leftrightarrow$ [FAB·OH ₂](H ₂ O) ₂	-7.1	-25.8	-1.3
25	[FAB·OH ₂](H ₂ O) + 2-propanol $\leftrightarrow$ [FAB·OH ₂](H ₂ O)(2-propanol)	-11.2	-38.1	-1.7
26	[FAB·OH ₂](H ₂ O) + EPX $\leftrightarrow$ [FAB·OH ₂](H ₂ O)(EPX)	-12.4	-41.7	-1.9
27	[FAB·OH ₂](2-propanol) + H ₂ O $\leftrightarrow$ [FAB·OH ₂](H ₂ O)(2-propanol)	-7.4	-32.9	0.5
28	[FAB·OH ₂](2-propanol) + 2-propanol $\leftrightarrow$ [FAB·OH ₂](2-propanol) ₂	-11.3	-38.3	-1.8
29	[FAB·OH ₂](2-propanol) + EPX $\leftrightarrow$ [FAB·OH ₂](2-propanol)(EPX)	-12.7	-38.0	-3.3
30	[FAB·OH ₂](EPX) + H ₂ O $\leftrightarrow$ [FAB·OH ₂](H ₂ O)(EPX)	-7.4	-34.7	1.1
31	[FAB·OH ₂](EPX) + 2-propanol $\leftrightarrow$ [FAB·OH ₂](2-propanol)(EPX)	-11.4	-36.1	-2.6
32	[FAB·OH ₂](EPX) + P1 $\leftrightarrow$ [FAB·OH ₂](EPX)(P1) (-OH)	-11.8	-43.3	-0.8
33	[FAB·OH ₂](EPX) + P1 $\leftrightarrow$ [FAB·OH ₂](EPX)(P1) (-O-)	-12.9	-45.6	-1.2
34	[FAB·OH ₂](EPX) + P2 $\leftrightarrow$ [FAB·OH ₂](EPX)(P2) (-OH)	-15.1	-44.1	-3.9
35	[FAB·OH ₂](EPX) + P2 $\leftrightarrow$ [FAB·OH ₂](EPX)(P2) (-O-)	-13.6	-45.2	-2.1
36	[FAB·OH ₂](H ₂ O)(P1) (-OH) + EPX $\leftrightarrow$ [FAB·OH ₂](EPX)(P1) (-OH)	-13.2	-38.9	-3.4

Entry #	Binding Reaction	ΔH (kcal* mol^{-1})	ΔS (cal* mol^{-1} * K^{-1})	ΔG^a (kcal* mol^{-1})
37	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P1}) (-\text{O}-) + \text{EPX} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{EPX})(\text{P1}) (-\text{O}-)$	-13.4	-43.9	-2.2
38	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P2}) (-\text{OH}) + \text{EPX} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{EPX})(\text{P2}) (-\text{OH})$	-14.2	-40.2	-4.1
39	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P2}) (-\text{O}-) + \text{EPX} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{EPX})(\text{P2}) (-\text{O}-)$	-13.3	-38.0	-3.9
40	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O}) + \text{P1} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P1}) (-\text{OH})$	-10.9	-41.8	-0.3
41	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O}) + \text{P1} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P1}) (-\text{O}-)$	-14.0	-45.9	-2.2
42	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O}) + \text{P2} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P2}) (-\text{OH})$	-16.4	-54.2	-2.2
43	$[\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O}) + \text{P2} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P2}) (-\text{O}-)$	-15.2	-51.0	-1.9
44	$[\text{FAB}\cdot\text{OH}_2](\text{P1}) (-\text{OH}) + \text{H}_2\text{O} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P1}) (-\text{OH})$	-7.2	-30.5	0.0
45	$[\text{FAB}\cdot\text{OH}_2](\text{P1}) (-\text{O}-) + \text{H}_2\text{O} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P1}) (-\text{O}-)$	-11.0	-37.3	-1.8
46	$[\text{FAB}\cdot\text{OH}_2](\text{P2}) (-\text{OH}) + \text{H}_2\text{O} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P2}) (-\text{OH})$	-10.5	-43.4	0.6
47	$[\text{FAB}\cdot\text{OH}_2](\text{P2}) (-\text{O}-) + \text{H}_2\text{O} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](\text{H}_2\text{O})(\text{P2}) (-\text{O}-)$	-9.9	-36.9	-0.8
48	$[\text{FAB}\cdot\text{OH}_2](2\text{-propanol}) + \text{P1} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P1}) (-\text{OH})$	-10.6	-39.6	-0.7
49	$[\text{FAB}\cdot\text{OH}_2](2\text{-propanol}) + \text{P1} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P1}) (-\text{O}-)$	-11.0	-40.5	-0.8
50	$[\text{FAB}\cdot\text{OH}_2](2\text{-propanol}) + \text{P2} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P2}) (-\text{OH})$	-16.0	-53.4	-2.0
51	$[\text{FAB}\cdot\text{OH}_2](2\text{-propanol}) + \text{P2} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P2}) (-\text{O}-)$	-15.5	-54.2	-1.2
52	$[\text{FAB}\cdot\text{OH}_2](\text{P1}) (-\text{OH}) + 2\text{-propanol} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P1}) (-\text{OH})$	-10.7	-33.4	-2.6
53	$[\text{FAB}\cdot\text{OH}_2](\text{P1}) (-\text{O}-) + 2\text{-propanol} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P1}) (-\text{O}-)$	-11.8	-37.0	-2.6
54	$[\text{FAB}\cdot\text{OH}_2](\text{P2}) (-\text{OH}) + 2\text{-propanol} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P2}) (-\text{OH})$	-13.8	-47.7	-1.5
55	$[\text{FAB}\cdot\text{OH}_2](\text{P2}) (-\text{O}-) + 2\text{-propanol} \leftrightarrow [\text{FAB}\cdot\text{OH}_2](2\text{-propanol})(\text{P2}) (-\text{O}-)$	-13.9	-45.3	-2.3

^aBinding free energies correspond to reference state: 298.15 K, 1 mol/L.

Energies of transition states (TS) of epoxide ring-opening reactions were calculated using the same computational method as above. The scale factor corresponding to the level of theory, B3LYP/6-31+G(d,p), was used, for ZPE (0.964).⁵ Activation free energies, $\Delta G^\ddagger$, were obtained to calculate rate constants, $k(T)$, based on transition state theory (TST) as shown in Eq S1.

$$k(T) = \kappa(T) \frac{k_B T}{h} (c^0)^{1-m} e^{(-\frac{\Delta G^\ddagger}{RT})} \quad (\text{S1})$$

where k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, R is the universal gas constant, c^0 is a pressure- and temperature-dependent concentration factor used to account for the standard state (1 mol/L in this study), m is the number of reactants, $\Delta G^\ddagger$ is the free-energy difference between the transition state and reactants for the forward reaction or between the transition state and products for the reverse reaction, and $\kappa(T)$ is the tunneling correction factor which accounts for quantum mechanical tunneling. One approach to quantify this factor is given by the second order Wigner correction to the reaction rate as shown in Eq S2,⁶ in which the correction factor depends on the magnitude, $|v|$, of the imaginary frequency along the reaction coordinate:

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{h|v|}{k_B T} \right)^2 \quad (\text{S2})$$

Rate constants, $k(T)$, were calculated under different temperatures from -10 °C to 60 °C, covering the range of representative experimental conditions. Linear regression was performed to obtain Arrhenius rate parameters: activation energies (E_a) and pre-exponential factors (A). As epoxide ring-opening reactions are irreversible,⁷ we only considered forward reactions in this study. All possible catalyzed ring-opening reactions are reported in Table S4, with the corresponding activation energies (E_a) and pre-exponential factors (A) from DFT calculations.

Table S4. Calculated activation energies (E_a) and pre-exponential factors (A) of the catalyzed ring-opening reactions of 1,2-epoxyoctane by the attack of the 2-propanol nucleophile on the coordinated epoxide in an FAB·EPX or [FAB·OH₂](EPX)(HBA)_n ($n = 0-1$) or [FAB·(2-propanol)](EPX) intermediate. Energies were calculated at B3LYP-D3BJ/6-31+G(d,p) level of theory, and the implicit solvent effects of isopropanol were accounted for using the SMD model.

Entry #	Catalyzed Ring Opening Reaction	E_a (kcal* mol^{-1})	A (L* mol^{-1} * s^{-1})
1	FAB·EPX + 2-propanol $\rightarrow$ P1 + FAB	3.1	5.32E+05
2	FAB·EPX + 2-propanol $\rightarrow$ P2 + FAB	4.6	1.74E+05
3	[FAB·2-propanol](EPX) + 2-propanol $\rightarrow$ P1 + FAB·2-propanol	10.5	3.73E+06
4	[FAB·2-propanol](EPX) + 2-propanol $\rightarrow$ P2 + FAB·2-propanol	11.3	1.01E+07
5	[FAB·OH ₂](EPX) + 2-propanol $\rightarrow$ P1 + FAB·OH ₂	8.1	4.27E+04
6	[FAB·OH ₂](EPX) + 2-propanol $\rightarrow$ P2 + FAB·OH ₂	9.6	5.41E+06
7	[FAB·OH ₂](H ₂ O)(EPX) + 2-propanol $\rightarrow$ P1 + [FAB·OH ₂](H ₂ O)	12.0	3.69E+06
8	[FAB·OH ₂](H ₂ O)(EPX) + 2-propanol $\rightarrow$ P2 + [FAB·OH ₂](H ₂ O)	12.3	5.16E+07
9	[FAB·OH ₂](2-propanol)(EPX) + 2-propanol $\rightarrow$ P1 + [FAB·OH ₂](2-propanol)	11.5	1.65E+05
10	[FAB·OH ₂](2-propanol)(EPX) + 2-propanol $\rightarrow$ P2 + [FAB·OH ₂](2-propanol)	11.5	1.96E+05
11	[FAB·OH ₂](EPX)(P1) (-OH) + 2-propanol $\rightarrow$ P1 + [FAB·OH ₂](P1) (-OH)	10.0	1.30E+06
12	[FAB·OH ₂](EPX)(P1) (-OH) + 2-propanol $\rightarrow$ P2 + [FAB·OH ₂](P1) (-OH)	7.3	1.24E+06
13	[FAB·OH ₂](EPX)(P1) (-O-) + 2-propanol $\rightarrow$ P1 + [FAB·OH ₂](P1) (- O-)	7.1	4.28E+05
14	[FAB·OH ₂](EPX)(P1) (-O-) + 2-propanol $\rightarrow$ P2 + [FAB·OH ₂](P1) (- O-)	8.1	1.99E+06
15	[FAB·OH ₂](EPX)(P2) (-OH) + 2-propanol $\rightarrow$ P1 + [FAB·OH ₂](P2) (-OH)	9.7	5.21E+06
16	[FAB·OH ₂](EPX)(P2) (-OH) + 2-propanol $\rightarrow$ P2 + [FAB·OH ₂](P2) (-OH)	10.8	6.07E+06
17	[FAB·OH ₂](EPX)(P2) (-O-) + 2-propanol $\rightarrow$ P1 + [FAB·OH ₂](P2) (- O-)	8.5	4.65E+04
18	[FAB·OH ₂](EPX)(P2) (-O-) + 2-propanol $\rightarrow$ P2 + [FAB·OH ₂](P2) (- O-)	10.2	1.70E+05

S6. Experimental data.

Experimental kinetic data are reported here, with run number corresponding to Table 1. Note that regioselectivity is reported as P1% of total yield, which does not include the amount of P1 or P2 that is initially added.

Run #1:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.46E+00	0.00E+00	0.00E+00	-
30	1.45E+00	4.09E-02	1.08E-02	79.1
120	1.39E+00	9.20E-02	2.42E-02	79.2
240	1.32E+00	1.38E-01	3.63E-02	79.1
360	1.25E+00	1.87E-01	4.93E-02	79.1
480	1.20E+00	2.20E-01	5.80E-02	79.2
600	1.15E+00	2.53E-01	6.66E-02	79.2
900	1.04E+00	3.20E-01	8.40E-02	79.2
1200	9.46E-01	3.72E-01	9.72E-02	79.3
2400	6.85E-01	5.03E-01	1.31E-01	79.4
3600	5.23E-01	5.82E-01	1.51E-01	79.4
7200	1.91E-01	7.16E-01	1.85E-01	79.5
10800	1.31E-01	7.42E-01	1.91E-01	79.5
68400	0.00E+00	8.00E-01	2.06E-01	79.5

Run #2:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.59E+00	0.00E+00	0.00E+00	-
120	1.49E+00	5.21E-02	1.49E-02	77.7
240	1.41E+00	1.20E-01	3.41E-02	77.9
360	1.31E+00	1.89E-01	5.25E-02	78.2
480	1.22E+00	2.69E-01	7.41E-02	78.4
600	1.15E+00	3.14E-01	8.63E-02	78.4
1200	7.67E-01	5.48E-01	1.50E-01	78.5
1800	4.93E-01	6.92E-01	1.89E-01	78.5
2400	3.03E-01	8.02E-01	2.19E-01	78.6
3000	1.84E-01	8.53E-01	2.33E-01	78.5
3600	1.15E-01	8.86E-01	2.42E-01	78.6
4200	7.26E-02	9.04E-01	2.46E-01	78.6
4800	0.00E+00	9.09E-01	2.48E-01	78.6

Run #3:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.50E+00	0.00E+00	0.00E+00	-
30	1.50E+00	7.44E-03	1.91E-03	79.6
120	1.50E+00	1.21E-02	3.27E-03	78.8
240	1.49E+00	2.01E-02	5.45E-03	78.7
360	1.47E+00	2.91E-02	8.18E-03	78.1
480	1.46E+00	3.90E-02	1.10E-02	78.1
600	1.45E+00	4.90E-02	1.39E-02	77.9
900	1.41E+00	7.58E-02	2.13E-02	78.1

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
1200	1.38E+00	1.02E-01	2.84E-02	78.2
2400	1.24E+00	2.01E-01	5.63E-02	78.1
3600	1.08E+00	2.90E-01	8.07E-02	78.2
7200	6.40E-01	5.57E-01	1.55E-01	78.3
10800	3.45E-01	7.14E-01	1.98E-01	78.3
68400	0.00E+00	8.62E-01	2.37E-01	78.5

Run #4:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.65E+00	0.00E+00	0.00E+00	-
30	1.65E+00	3.33E-03	1.38E-03	70.8
120	1.62E+00	2.89E-02	1.14E-02	71.7
240	1.61E+00	3.32E-02	1.27E-02	72.4
360	1.57E+00	5.64E-02	2.00E-02	73.8
480	1.55E+00	6.88E-02	2.39E-02	74.2
600	1.54E+00	8.41E-02	2.84E-02	74.7
1200	1.43E+00	1.55E-01	4.87E-02	76.1
1800	1.33E+00	2.18E-01	6.66E-02	76.6
3600	1.05E+00	3.79E-01	1.12E-01	77.2
7200	6.07E-01	6.11E-01	1.77E-01	77.5
10800	3.84E-01	7.24E-01	2.09E-01	77.6
60000	1.09E-03	8.84E-01	2.58E-01	77.4

Run #5:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.66E+00	0.00E+00	0.00E+00	-
30	1.65E+00	1.70E-03	1.02E-03	62.4
240	1.64E+00	1.60E-02	7.94E-03	66.8
360	1.62E+00	2.60E-02	1.22E-02	68.0
510	1.60E+00	3.62E-02	1.60E-02	69.4
600	1.59E+00	4.22E-02	1.80E-02	70.1
1200	1.54E+00	7.57E-02	2.82E-02	72.8
1800	1.49E+00	1.09E-01	3.83E-02	74.1
3600	1.34E+00	2.02E-01	6.59E-02	75.4
7200	1.06E+00	3.61E-01	1.13E-01	76.2
10800	8.90E-01	4.57E-01	1.41E-01	76.5
60000	8.36E-04	8.50E-01	2.60E-01	76.6

Run #6:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.66E+00	0.00E+00	0.00E+00	-
300	1.64E+00	1.79E-02	6.34E-03	73.9
600	1.61E+00	2.34E-02	8.21E-03	74.0
900	1.59E+00	4.14E-02	1.41E-02	74.6
1200	1.57E+00	5.77E-02	1.93E-02	74.9
1830	1.52E+00	9.00E-02	2.96E-02	75.2
3600	1.41E+00	1.59E-01	5.12E-02	75.7

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
7500	1.21E+00	2.83E-01	8.93E-02	76.0
9000	1.04E+00	3.73E-01	1.16E-01	76.2
68400	9.16E-02	8.39E-01	2.54E-01	76.8

Run #7:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.67E+00	0.00E+00	0.00E+00	-
300	1.66E+00	8.11E-03	2.86E-03	73.9
600	1.63E+00	2.68E-02	9.42E-03	74.0
900	1.62E+00	3.00E-02	1.04E-02	74.2
1200	1.60E+00	4.10E-02	1.42E-02	74.3
1800	1.57E+00	6.21E-02	2.13E-02	74.5
3570	1.48E+00	1.18E-01	3.97E-02	74.9
7500	1.30E+00	2.80E-01	8.96E-02	75.8
9000	1.20E+00	3.06E-01	9.84E-02	75.7
68400	1.53E-01	7.91E-01	2.44E-01	76.4

Run #8:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.58E+00	0.00E+00	0.00E+00	-
18	1.57E+00	2.02E-02	5.45E-03	78.7
120	1.57E+00	3.04E-02	8.27E-03	78.6
240	1.58E+00	2.53E-02	7.02E-03	78.3
360	1.58E+00	2.85E-02	8.05E-03	78.0
480	1.55E+00	3.14E-02	8.96E-03	77.8
600	1.55E+00	3.46E-02	9.94E-03	77.7
900	1.55E+00	4.22E-02	1.22E-02	77.6
1200	1.55E+00	5.05E-02	1.45E-02	77.6
2400	1.49E+00	8.49E-02	2.39E-02	78.0
3600	1.45E+00	1.20E-01	3.39E-02	78.0
7200	1.30E+00	2.20E-01	6.10E-02	78.3
10800	1.17E+00	3.14E-01	8.65E-02	78.4
14400	1.02E+00	3.91E-01	1.07E-01	78.5

Run #9:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.54E+00	0.00E+00	0.00E+00	-
18	1.53E+00	4.69E-03	1.38E-03	77.2
120	1.52E+00	2.07E-02	6.27E-03	76.8
240	1.50E+00	3.03E-02	8.95E-03	77.2
360	1.48E+00	4.75E-02	1.39E-02	77.4
480	1.45E+00	6.49E-02	1.88E-02	77.5
600	1.43E+00	8.35E-02	2.40E-02	77.7
900	1.36E+00	1.33E-01	3.81E-02	77.7
1200	1.31E+00	1.81E-01	5.16E-02	77.8
2400	9.99E-01	3.74E-01	1.05E-01	78.0
3600	6.94E-01	5.61E-01	1.58E-01	78.1

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
7200	1.73E-01	8.24E-01	2.31E-01	78.1
10800	3.50E-02	8.94E-01	2.51E-01	78.1
14400	8.90E-03	8.98E-01	2.52E-01	78.1

Run #10:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.51E+00	0.00E+00	0.00E+00	-
30	1.50E+00	4.50E-03	1.20E-03	79.0
120	1.50E+00	6.99E-03	2.02E-03	77.6
240	1.52E+00	1.19E-02	3.44E-03	77.6
360	1.49E+00	1.61E-02	4.74E-03	77.3
480	1.49E+00	2.11E-02	6.16E-03	77.4
600	1.49E+00	2.62E-02	7.66E-03	77.4
900	1.45E+00	3.98E-02	1.16E-02	77.5
1200	1.44E+00	5.30E-02	1.55E-02	77.4
2400	1.37E+00	1.05E-01	3.04E-02	77.6
3600	1.30E+00	1.55E-01	4.47E-02	77.7
7200	1.07E+00	3.02E-01	8.61E-02	77.8
10800	8.49E-01	4.35E-01	1.24E-01	77.9
68400	0.00E+00	8.51E-01	2.40E-01	78.0

Run #11:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.55E+00	0.00E+00	0.00E+00	-
30	1.54E+00	3.32E-02	8.74E-03	79.2
120	1.47E+00	8.59E-02	2.26E-02	79.2
240	1.41E+00	1.31E-01	3.46E-02	79.2
360	1.36E+00	1.74E-01	4.57E-02	79.2
480	1.30E+00	2.09E-01	5.49E-02	79.1
600	1.25E+00	2.36E-01	6.21E-02	79.2
900	1.17E+00	2.89E-01	7.59E-02	79.2
1200	1.10E+00	3.32E-01	8.72E-02	79.2
2400	9.05E-01	4.41E-01	1.16E-01	79.2
3600	7.84E-01	5.05E-01	1.32E-01	79.3
7200	5.67E-01	6.04E-01	1.58E-01	79.3
10800	5.29E-01	6.26E-01	1.64E-01	79.3
68400	4.60E-02	8.29E-01	2.20E-01	79.1

Run #12:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.59E+00	0.00E+00	0.00E+00	-
120	1.58E+00	5.61E-03	2.05E-03	73.3
240	1.56E+00	1.17E-02	4.29E-03	73.1
360	1.56E+00	1.88E-02	6.94E-03	73.1
480	1.54E+00	2.50E-02	9.23E-03	73.0
600	1.53E+00	3.33E-02	1.20E-02	73.5
900	1.50E+00	5.01E-02	1.77E-02	73.9

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
1800	1.45E+00	1.02E-01	3.44E-02	74.8
2700	1.40E+00	1.53E-01	4.94E-02	75.6
3600	1.30E+00	1.98E-01	6.26E-02	76.0
4800	1.21E+00	2.59E-01	7.94E-02	76.5
7200	1.04E+00	3.71E-01	1.09E-01	77.3
9000	9.18E-01	4.49E-01	1.30E-01	77.6
10800	7.94E-01	5.25E-01	1.49E-01	77.9

Run #13:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.67E+00	0.00E+00	0.00E+00	-
30	1.65E+00	0.00E+00	0.00E+00	-
130	1.64E+00	1.64E-02	6.93E-03	70.3
240	1.60E+00	4.68E-02	1.71E-02	73.3
368	1.53E+00	9.10E-02	3.12E-02	74.5
480	1.49E+00	1.23E-01	4.12E-02	74.9
600	1.45E+00	1.53E-01	5.06E-02	75.1
1200	1.19E+00	3.25E-01	1.03E-01	75.9
1800	9.52E-01	4.68E-01	1.46E-01	76.3
3600	4.81E-01	7.26E-01	2.20E-01	76.7
7980	3.62E-01	7.30E-01	2.19E-01	76.9
12780	1.87E-01	8.58E-01	2.57E-01	76.9
21600	4.55E-02	9.25E-01	2.77E-01	77.0

Run #14:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.68E+00	0.00E+00	0.00E+00	-
26	1.66E+00	0.00E+00	0.00E+00	-
120	1.65E+00	9.56E-03	4.04E-03	70.3
240	1.62E+00	3.14E-02	1.14E-02	73.4
360	1.58E+00	5.71E-02	1.99E-02	74.2
480	1.54E+00	8.96E-02	3.03E-02	74.7
600	1.51E+00	1.07E-01	3.59E-02	74.9
1200	1.38E+00	2.04E-01	6.56E-02	75.7
1800	1.19E+00	3.20E-01	9.99E-02	76.2
3570	8.68E-01	5.20E-01	1.57E-01	76.8
7920	4.63E-01	7.19E-01	2.14E-01	77.1
12720	1.39E-01	8.80E-01	2.60E-01	77.2
21600	1.18E-01	9.01E-01	2.66E-01	77.2

Run #15:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.53E+00	0.00E+00	0.00E+00	-
35	1.52E+00	0.00E+00	0.00E+00	-
120	1.52E+00	0.00E+00	0.00E+00	-
310	1.51E+00	1.34E-02	5.21E-03	72.0
600	1.49E+00	2.97E-02	1.08E-02	73.4

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
900	1.47E+00	4.54E-02	1.58E-02	74.1
1200	1.44E+00	6.51E-02	2.21E-02	74.7
1800	1.40E+00	9.88E-02	3.25E-02	75.3
3000	1.31E+00	1.56E-01	4.98E-02	75.8
4710	1.19E+00	2.41E-01	7.48E-02	76.3
7200	9.37E-01	4.13E-01	1.25E-01	76.7
12060	6.71E-01	5.76E-01	1.71E-01	77.1
21000	4.20E-01	7.03E-01	2.07E-01	77.2

Run #16:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.66E+00	0.00E+00	0.00E+00	-
30	1.66E+00	0.00E+00	0.00E+00	-
120	1.65E+00	0.00E+00	0.00E+00	-
300	1.65E+00	7.94E-03	0.00E+00	-
600	1.64E+00	1.85E-02	7.10E-03	72.2
900	1.62E+00	2.92E-02	1.07E-02	73.2
1200	1.61E+00	3.94E-02	1.41E-02	73.7
1800	1.58E+00	5.81E-02	2.01E-02	74.3
3000	1.53E+00	9.60E-02	3.19E-02	75.1
4680	1.46E+00	1.44E-01	4.68E-02	75.5
7200	1.37E+00	2.07E-01	6.60E-02	75.9
12060	1.12E+00	3.46E-01	1.07E-01	76.4
21000	5.72E-01	6.68E-01	2.00E-01	77.0

Run #17:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.61E+00	0.00E+00	0.00E+00	-
120	1.58E+00	1.76E-02	7.17E-03	71.1
240	1.56E+00	3.29E-02	1.26E-02	72.3
360	1.54E+00	4.99E-02	1.84E-02	73.1
484	1.52E+00	6.62E-02	2.37E-02	73.7
600	1.49E+00	8.61E-02	2.99E-02	74.2
900	1.43E+00	1.31E-01	4.34E-02	75.2
1800	1.24E+00	2.58E-01	7.92E-02	76.5
2700	1.00E+00	4.03E-01	1.19E-01	77.2
3600	8.24E-01	5.12E-01	1.50E-01	77.4
4800	6.17E-01	6.25E-01	1.81E-01	77.5
6000	4.91E-01	6.90E-01	1.99E-01	77.6
7200	3.68E-01	7.50E-01	2.16E-01	77.7

Run #18:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.84E+00	2.95E-01	0.00E+00	-
30	1.83E+00	2.98E-01	9.27E-04	79.3
79.8	1.83E+00	3.05E-01	3.54E-03	73.8
120	1.82E+00	3.12E-01	6.02E-03	73.8

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
180	1.81E+00	3.16E-01	9.14E-03	69.8
240	1.80E+00	3.26E-01	1.23E-02	71.8
300	1.79E+00	3.32E-01	1.52E-02	71.1
600	1.74E+00	3.67E-01	2.78E-02	72.2
1200	1.63E+00	4.28E-01	4.73E-02	73.7
2100	1.48E+00	5.10E-01	7.34E-02	74.6
3000	1.34E+00	5.87E-01	9.69E-02	75.1
6600	8.73E-01	8.09E-01	1.66E-01	75.6
59400	1.06E-03	1.15E+00	2.73E-01	75.7

Run #19:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.65E+00	0.00E+00	3.01E-01	-
120	1.61E+00	1.61E-02	3.06E-01	77.4
243	1.59E+00	3.80E-02	3.16E-01	71.8
360	1.56E+00	5.63E-02	3.21E-01	74.6
600	1.49E+00	8.81E-02	3.30E-01	75.7
739.8	1.46E+00	1.04E-01	3.35E-01	75.5
900	1.43E+00	1.25E-01	3.39E-01	77.0
1200	1.36E+00	1.58E-01	3.44E-01	78.6
1800	1.25E+00	2.23E-01	3.58E-01	79.8
3600	9.48E-01	4.01E-01	3.92E-01	81.5
10800	3.31E-01	7.05E-01	4.49E-01	82.6

Run #20:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.58E+00	0.00E+00	2.99E-01	-
155	1.55E+00	1.59E-02	3.03E-01	82.9
240	1.55E+00	2.08E-02	3.06E-01	76.0
360	1.53E+00	3.09E-02	3.09E-01	76.8
480	1.51E+00	4.76E-02	3.13E-01	77.5
600	1.49E+00	6.10E-02	3.17E-01	78.0
900	1.44E+00	9.26E-02	3.23E-01	79.9
1800	1.28E+00	1.84E-01	3.37E-01	82.9
2700	1.15E+00	2.68E-01	3.53E-01	83.3
3600	1.01E+00	3.43E-01	3.66E-01	83.8
4200	9.45E-01	3.79E-01	3.72E-01	83.9
5400	8.20E-01	4.54E-01	3.90E-01	83.3
8400	5.87E-01	5.70E-01	4.09E-01	83.8

Run #21:

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
0	1.57E+00	3.36E-01	0.00E+00	-
120	1.54E+00	3.44E-01	0.00E+00	-
240	1.55E+00	3.51E-01	5.96E-03	72.1
364	1.54E+00	3.61E-01	8.32E-03	74.8
480	1.52E+00	3.70E-01	1.17E-02	74.2

Time (s)	Epoxide concentration (mol/L)	P1 concentration (mol/L)	P2 concentration (mol/L)	Regioselectivity (P1%)
610	1.51E+00	3.76E-01	1.40E-02	74.0
900	1.49E+00	3.86E-01	1.73E-02	74.2
1140	1.45E+00	4.07E-01	2.41E-02	74.5
1800	1.40E+00	4.39E-01	3.37E-02	75.3
2400	1.34E+00	4.69E-01	4.35E-02	75.4
3000	1.27E+00	5.02E-01	5.44E-02	75.3
3600	1.24E+00	5.22E-01	6.04E-02	75.5
4500	1.17E+00	5.63E-01	7.28E-02	75.7

S7. Author contributions.

Y.Y. carried out the computational study, including DFT calculations and microkinetic modeling. Y.Z. and M.N.B. carried out the experimental evaluation of the catalytic reactions and characterized all the reaction products. J.M.N., S.T.N., and L.J.B. supervised the research. Y.Y. and L.J.B. wrote and edited the manuscript with input from all coauthors.

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