Markovnikov Alcohols via Epoxide Hydroboration by Molecular Alkali Metal Catalysts

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SUMMARY

Synthesis of branched "Markovnikov" alcohols is crucial to various chemical industries. The catalytic reduction of substituted epoxides under mild conditions is a highly attractive method for preparing such alcohols. Classical methods based on heterogeneous or homogeneous transition metal-catalyzed hydrogenation, hydroboration or hydrosilylation usually suffer from poor selectivity, reverse regioselectivity, limited functional group compatibility, high cost and/or low availability of the catalysts. Here we report the discovery of highly regioselective hydroboration of nonsymmetrical epoxides catalyzed by ligated archetypal reductants in organic chemistry – alkali metal triethylborohydrides. The chemoselectivity and turnover efficiencies of the present catalytic approach are excellent. Thus, terminal and internal epoxides with ene, yne, aryl, and halo groups were selectively and quantitatively reduced under a substrate-to-catalyst ratio (S/C) of up to 1000. Mechanistic investigations point to a mechanism reminiscent of frustrated Lewis pair action on substrates in which a nucleophile and Lewis acid act cooperatively on the substrate.

INTRODUCTION

Markovnikov alcohols are important chemicals with myriad applications in bulk/fine agrochemicals, pharmaceuticals, and fragrance industries. Thus, their synthesis is continuously of great interest. Petroleum-derived olefins are currently the largest-volume building blocks to access alcohols. Mono- or polysubstituted olefins can give two regioisomeric alcohols in the general case (Yao et al., 2019; Dong et al., 2011; Jensen and Trogler, 1986). Markovnikov alcohols, in which the hydroxyl group is bound to the more substituted one of two adjacent carbons (Figure 1), can be obtained from such olefins by liquid or solid acid catalysed hydration or a two-step Wacker oxidation-reduction process. However, due to the frequent limitations of these transformations (isomerization, cyclization, poor catalyst performance, equilibria issues and/or harsh conditions employed, limited functional group tolerance, chemoselectivity), stoichiometric oxymercuration-demercuration (Brown and Geoghegan, 1967), catalytic Mukaiyama hydration (Shigeru and Teruaki, 1989) as well as enzymatic hydration (Demming et al., 2019) reactions emerged as more efficient methods (Figure 1).

The reduction of strained epoxides, easily obtainable from olefins via epoxidation, is an alternative method of preparing alcohols (Yao et al., 2019). The combination of appropriately regioselective and functional-group-tolerant reduction with the inexpensive and selective epoxidation of olefins will permit the two-step synthesis of functionalized alcohols. Conventional methods for the epoxide ring-opening are based on stoichiometric amounts of strong reducing agents such as $LiAlH_4$. Such methods usually suffer from poor regioselectivities by providing a mixture of both primary and secondary alcohols, poor functional group tolerance and the generation of enormous amounts of waste. Heterogeneous (Duval et al., 2021; Thiery et al., 2007; Nandi et al., 2017) and particularly homogeneous transition-metal catalysed hydrogenation (Yao et al., 2019; Liu et al., 2019), hydroboration (Patnaik and Sadow, 2019; Song et al., 2017; Desnoyer et al., 2017), and hydrosilylation (Zhang et al., 2018; Wenz et al., 2017; Zhang et al., 2017; Henriques et al., 2016; Gansäuer et al., 2012; Park and Brookhart, 2011; Nagashima et al., 2000) of epoxides as well as transition-metal-free approaches (Patnaik and Sadow, 2019; Zhang et al., 2018; Huang et al., 2022; Ton et al., 2021) were developed by several laboratories leading preferentially to *anti*-Markovnikov alcohols. Many fewer catalysts have been reported for the selective reduction of epoxides into Markovnikov alcohols. Examples include heterogeneous (Kwon et al., 2007) and homogeneous hydrogenation (Thiyagarajan and Gunanathan, 2019; Ito et al., 2003; Fujitsu et al., 1981) as well as transfer hydrogenation (Oshima et al., 1989) with precious metals (Ru, Rh, Pd), substrate limited hydrosilylation with Zn (Mimoun, 1999), and high-catalyst loading hydroboration with alkaline-earth Mg (Magre et al., 2022; Cao et al., 2020). Noyori-type molecular catalysts based on precious Ru (Thiyagarajan and Gunanathan, 2019; Ito et al., 2003) are particularly regio- and/or chemoselective methods, but are either limited to terminal epoxides (Thiyagarajan and Gunanathan, 2019; Ito et al., 2003) or monosubstituted epoxides (Ito et al., 2003), and/or are not tolerant to terminal C=C bonds (Thiyagarajan and Gunanathan, 2019). Selective reduction of unsymmetrical epoxides bearing terminal and internal double bonds leading to olefinic Markovnikov alcohols would be of particular value (Ibrahim et al., 2017).

Here we report an example of highly selective epoxide ring-opening catalysed by major rock-forming non-transition metal-based species, being some of the most abundant metals in the Earth's crust (M = Li, Na and K). *s*-Block metal catalysis is an active field of study (Magre et al., 2022). However, the potential of such catalysts is still underexplored relative to *d*-block catalysts. We found that readily available and inexpensive off-the-shelf alkali metal triethylborohydrides in the presence of a ligand catalyze highly regio- and chemoselective hydroboration of substituted epoxides producing secondary alcohols in excellent yields and with broad functional group tolerance.

RESULTS AND DISCUSSION

Inspired by the recently discovered catalytic activity of traditional reducing agent $LiAlH_4$ (Elsen et al., 2018), we attempted to reduce model substrate styrene oxide **8a** by pinacolborane (HBpin) with a catalytic amount of $LiAlH_4$ along with more common $NaBH_4$, KBH_4 and BH_3-THF reagents under neat conditions (Scheme S1). In all cases negligible (~20) turnovers were detected. The existence of catalytic activity for $NaBH_4$ supplements the previously reported data on anti-Markovnikov BH_3 addition (Brown and Yoon, 1968), although the regioselectivity was not measured due to the poor yield. Furthermore, similarly poor activity was found for corresponding saline MH (M = Li, Na, K) hydrides (Scheme S1). Promisingly, we found that stronger reducing agents such as $MHBEt_3$ (M = Li, Na, K; Et = ethyl) are one-order more efficient for the same reaction, leading to an appreciable ~500 turnovers (Scheme S1). Moreover, consistent with the stoichiometric reduction of epoxides with these reagents, the regioselectivity of ~9:1 was noted in favor of the Markovnikov product. Inspired by this notable activity and promising selectivity, we further tested the same reactions in the presence of 1 equiv. of various commercially available mono- and polydentate organic ligands (Scheme S2). Based on 102 tested reactions, a ligand was found to generally have a beneficial effect on both the catalytic efficiency and regioselectivity. For example, the reaction yield increased to ~ 99% from an average of 40%, whereas the regioselectivity reached up to a ~40:1 ratio in the best cases.

In the next step, by using two promising ligands for both efficiency and selectivity, namely 2,2′:6′,2″-terpyridine (**L17**) and 18-crown-6 (**L31**), we attempted to isolate active catalytic species and reaction intermediates. For M/**L17** (M = Li, Na and K) and M/**L31** (M = Na and K), isolable complexes **1–5** were obtained in moderate-to-appreciable yields and characterized by NMR spectroscopies and X-ray crystallography (Figure 2 and SI). The reaction of styrene oxide with isolated **2** and **5** afforded products **6** and **7**, respectively, the regioselectivity of which is consistent with the Markovnikov formulation.

Notably, all the isolable complexes **1–7** are active catalyst precursors for the hydroboration of styrene oxide (Scheme S3). Furthermore, complexes **1–7** feature even improved activity and/or selectivity relevant to the *in situ* 1:1 M[$HBEt_3$]/ligand reactivity (Scheme S2 and S3). We particularly noted 30:1 Markovnikov selectivity achieved with complexes **2** or **3** in the quantitative (>99%) hydroboration of styrene oxide under neat conditions (Scheme S3). Next, we compared the efficiency of **1–7** with various homogeneous catalysts from our laboratories, popular commercially available metal–ligand bifunctional catalysts, classical precious metal catalyst precursors, as well as $MgBu_2$ being the state-of-the-art catalyst for Markovnikov epoxide hydroboration (Magre et al., 2020) (Scheme S3). Under identical conditions employed, all the complexes based on transition metals screened were found to be very poor catalysts. Furthermore, all complexes **1–7** provide significantly higher activity and selectivity for this reaction relative to $MgBu_2$, placing them to the category of most-efficient catalysts reported to date for the reaction under study.

In the next step, after proper optimization of the reaction conditions as summarized in Table S2, we tested the scope for the hydroboration of various simple and functional epoxides **8** catalyzed by **2** under solvent-free conditions (Figure 3).

We found that epoxides **8** were quantitatively reduced in the presence of such reducible groups as terminal and internal ene, yne, aryl and halo by using only 0.1 mol% catalyst loading, and the corresponding secondary alcohols **9** were isolated in good to high yields after hydrolysis. We also noted that the regioselectivity remains on very high level (25:1 to 99:1) for all substrates tested except 4-fluorostyrene oxide that affords the Markovnikov alcohol with 12:1 regioselectivity. The potential application of our catalyst in industrial synthesis of Markovnikov alcohols was demonstrated on the example of **8f** hydroboration performed at 10 mmol scale (see Scheme S4). Thus 1.34 g of the corresponding product **9f** was isolated in 88% yield from the reaction where only 5.4 mg of catalyst **2** was used (S/C = 1000). Similarly to $MgBu_2$ (Magre et al., 2020), catalyst **2** also promoted the ring opening of less-reactive oxetane by hydroboration with good yield, yet it showed no activity toward the much more challenging oxolane from our preliminary catalytic test (Scheme S5). Limitations of our method have been noticed for several functionalized oxiranes that contain ester, sulfonate and N-heterocyclic groups (Scheme S6). In addition, the carbonyl-containing oxirane, 1,3-diphenyl-2,3-epoxy-1-propanone was found to be selectively hydroborated on the ketone over the oxirane with high yield (Figure S7). Pleasingly, when enantioenriched (*S*)-**8a** was employed for the hydroboration catalyzed by **2**, no detectable loss of enantiomeric excess was observed (Scheme S7).

Next, we performed a deuterium-labelling experiment, kinetics studies and computational analysis based on Density Functional Theory (DFT) aimed at building the mechanistic understanding of **2**-catalyzed hydroboration. Here, our goal was to decipher the role that the sodium cation, the anion and the **L17** ligand alone and altogether played in the catalytic reaction. A further goal was to identify the regioselectivity-determining step and probe the identity of the catalytic cycle. Full details are available in the SI, and here we would like to summarize the most important findings.

Hydroboration of styrene oxide with DBpin shows >50:1 Markovnikov selectivity with deuterium atom incorporation at the less-substituted methylene group. The regioselectivity thus nearly doubled relative to HBpin, where a 30:1 ratio was observed. The corresponding product $PhCH(OH)CH_2D$ was isolated in 90% yield (Scheme S9). The initial rates method indicates that the catalytic reaction displays first-order dependence on both styrene oxide and HBpin concentrations and one-half order in **2** concentration leading to approximately the following rate equation in tetrahydrofuran: d[product]/dt ~ $k[\text{styrene oxide}]^1[\text{HBpin}]^1[\mathbf{2}]^{0.5}$ with $k \approx 0.39\ \text{min}^{-1}\ \text{M}^{-1.5}$ at 25 ºC, see SI. Kinetic studies thus indicate that both styrene oxide and HBpin enter the rate-determining zone of the catalytic cycle as well as corroborate the mononuclear reactivity of **2**, which therefore dissociates into two fragments under catalytic conditions.

To uncover the role that the sodium cation, the $[HBEt_3]^-$ anion and the **L17** ligand play in the regioselectivity-determining step, we have chosen the substrate **8f** that affords the product **9f** with the appreciably high regioselectivity of >99% in the computational analysis. Various transition states were manually sampled based on plausible bimolecular and trimolecular combinations (see SI). The optimized geometries of the most energetically accessible transition states are shown in Figure 4A.

Computations predict the highest regioselectivities for naked $[HBEt_3]^-$ based on a computed 5.5

kcal·mol^{-1} energy gap between the transition states leading to Markovnikov (**TS$_{\mathrm{A}}$**) and *anti*-Markovnikov (**TS$_{\mathrm{D}}$**) products. Addition of sodium to the model leads to a change of the molecularity (bimolecular → trimolecular) and a decrease of the energy gap to 2.6 kcal·mol^{-1} between the Markovnikov (**TS$_{\mathrm{H}}$**) and *anti*-Markovnikov (**TS$_{\mathrm{K}}$**) transition states. Thus, the presence of the cation in a non-covalent bonding position near the epoxide oxygen atom in the transition states decreases the Markovnikov regioselectivity. In the full reaction mixture, there are various states possible corresponding to tight $[HBEt_3]^-Na^+$, various solvent-shared/solvent-separated ion pairs, and free ions. Each of these species would ultimately contribute to the final regioselectivity, so the computed transition state energy gap for the reaction with $[HBEt_3]^-Na^+$ is therefore expected to lie between 2.6 and 5.5 kcal/mol. Because the experimental regioselectivity is small (12:1, which represents a relatively small 1.5 kcal/mol delta for the barrier at RT = 0.59 kcal/mol, see Scheme S8), the most populated species is likely to be a tight $[HBEt_3]^-Na^+$ ion pair. The discrepancy between the experimental 1.5 kcal/mol and the computed 2.6-5.5 kcal/mol range is possibly due to the limitations of the computational approach and/or experimental issues, e.g. potential background reactions that could lower selectivity. Nevertheless, the discrepancy is computationally small and these computational results provide a reasonable rationalization for the experimental observations with $[HBEt_3]^-Na^+$.

The experimental reaction of **8f** with precatalyst **2**, however, provides a better regioselectivity (99:1, which represents a 2.7 kcal/mol delta for the barrier). One might anticipate that the ligand **L17** either decreases the Lewis acidity of the cation and/or shifts the equilibrium in the ensemble towards free ions. Though full ion separation is the ideal case from a regioselectivity standpoint according to the calculations, this does not appear to be the case under the experimental catalytic conditions. Catalytic reactions of similar model compound **8a** with $[HBEt_3]^-Na^+$ in the presence of 0, 1 or 2 equiv. of **L17** all showed comparable regioselectivity (9:1, 10:1, and 9:1, respectively), although with varying yields (Schemes S1 and S2). Furthermore, precatalyst **1**, a six-coordinate bisligated monometal complex, shows comparable regioselectivity relative to monoligated catalyst precursors (Scheme S3), which suggests its transformation into the monoligated species under catalytic conditions.

The computational analysis of the transition states **TS$_{\mathrm{N}}$–TS$_{\mathrm{Q}}$** for $[HBEt_3]^-Na($**L17**$)^+$ (**int0**) (Figure 4A) does indeed reproduce the observed Markovnikov regioselectivity for the reaction of **8f** with **2**. However, the computed energy gap of 1.5 kcal·mol^{-1} is below the 2.6-5.5 kcal/mol range computed for $[HBEt_3]^-Na^+$ and $[HBEt_3]^-$ alone, despite the experimental reaction with **2** being more regioselective than that with $[HBEt_3]^-Na^+$. The computed gap is also slightly below the experimentally determined 2.7 kcal/mol. Most likely, this is a virtual result due to an incomplete conformational sampling achieved in our calculations, or due to the computational accuracy of the DFT method being ±3 kcal/mol, see SI. It is also possible that we have not properly identified the mechanism of regioselectivity and/or the catalytic reaction. However, the experimental and kinetics data do support the proposed rate-determining intermediate, and the computational analysis of this mechanism does support the Markovnikov regioselectivity overall. Thus, we conclude based on combined experimental observations, kinetics data, and computational data for $[HBEt_3]^-Na^+$ that the monoligated and monometal tight ion-pair complex $[HBEt_3]^-Na($**L17**$)^+$ (**int0**) is the likely catalytic species.

The full proposed computed catalytic cycle for the hydroboration of related test styrene oxide **8a** with **2** is displayed in Figure 4B (see SI for more details including further explanation of how we ruled out other possible reaction pathways). Here, species **int0** serves as the catalyst and selectivity-determining intermediate, and **TS$_{\mathrm{1}}$**, representing the concerted epoxide ring-opening by the $[HBEt_3]^-$ anion and HBpin, serves as the rate-determining transition state. The identity of these determining states is consistent with the experimental rate law, which is half-order in **2**, and first-order in both HBpin and **8a**. The computed energetic span of the overall reaction is 22.5 kcal/mol, a reasonable value for an S/C of 1000 and quantitative conversion under ambient conditions. Clearly, the monoligated alkali metal cation plays an important role within the catalytic cycle to establish a three-dimensional molecular assembly stabilized by non-covalent interactions.

CONCLUSIONS

In summary, we report a convenient catalytic protocol for the synthesis of Markovnikov alcohols via hydroboration of epoxides in the presence of old and cheap “stoichiometric” reagents $MHBEt_3$ (M = Li, Na, K) which become efficient catalysts upon coordination with various chelating ligands such as terpyridine or crown ethers. The method is tolerant to various functional and stereo groups, which further adds value to the present catalytic system. Computational analysis and kinetic studies indicate that both the $[HBEt_3]^-$ anion and alkali metal cation are equally important for the catalytic activity. The former determines catalytic efficiency, whereas the latter controls the reaction selectivity. Analysis of the catalytic cycle indicates that both the rate- and regioselectivity-determining transition state of this reaction is concerted HBpin-assisted epoxide ring-opening by the $[HBEt_3]^-$ anion. The ligated alkali metal cation plays an important role within the catalytic cycle to establish a three-dimensional molecular assembly stabilized by non-covalent interactions. This is somewhat reminiscent of the concept of Stephan’s frustrated Lewis pairs (Stephan, 2015).

Limitations of the study

This work reports a highly efficient and regioselective method for the preparation of Markovnikov alcohols via hydroboration of epoxides using well-defined alkali metal complexes of terpyridine or crown ethers. Although a good substrate scope of epoxides has been demonstrated, this method shows limitations on more challenging substrates such as oxolanes and complex oxiranes containing other reducible groups such as ketone, N-heterocycle, nitro and ester (Scheme S5 and S6, Figure S7). Further optimization of catalysts and reaction conditions is needed to expand the scope of substrates and improve the applicability of the method.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci. 2022.05.xxx.

ACKNOWLEDGMENTS

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AUTHOR CONTRIBUTIONS

G.Z., H.Z. and P.A.D. performed the experimental and mechanistic studies. M.C.N. conducted the X-ray crystallographic analysis. P.A.D. designed and performed the computational studies. G.Z., S.Z. and P.A.D. conceived and supervised the project. All authors analyzed the data and wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Main figure titles and legends

Figure 1. Current state-of-the-art in regioselective approaches to Markovnikov alcohols and the new method developed in this work. M = Li, Na, K.

Figure 2. Synthesis of complexes **1**-**7** including isolation of active catalytic species and possible reaction intermediates through stoichiometric reactions. X-ray structures are drawn with ellipsoids at 30% probability level. Non-critical H-atoms are omitted. The X-ray structure of **3** is isostructural to **2**. See also Figures S1-6 and Table S1.

Figure 3. The substrate scope for **2**-catalyzed hydroboration of epoxides. Conditions: epoxides (1.0 mmol), pinacolborane (1.1 mmol) and **2** (S/C = 1000), neat, rt, N_2, 2 h (to ensure completion of reactions). Complete conversion unless otherwise described. Isolated yields and ratios of two regioisomers determined by GC analysis using hexamethylbenzene as an internal standard.

[a] Reaction run in THF (1 mL) for 16 h, 75% conversion.

[b] NMR yield with hexamethylbenzene as an internal standard.

[c]Reaction run in THF (1 mL) at 80 °C for 16 h, 55% conversion.
See also Scheme S1-9, Figure S7 and Table S2.

Figure 4. Mechanistic studies. **A.** Geometries of optimized transition states determining Markovnikov vs *anti*-Markovnikov selectivities in the hydroboration of **8f** based on $[HBEt_3]^-$, $[HBEt_3]^-Na^+$ and $[HBEt_3]^-Na^+$(**L17**) species. **B.** Catalytic cycle for **8a** hydroboration catalysed by **2**, suggested by combined computational analysis and kinetics data. Non-critical H-atoms and all non-covalent interactions with Na are omitted for clarity for the optimized transition state structures, and dashed bonds represent transition vectors. All relative standard free energies are reported in kcal·mol^{-1}. See also Figures S8-13 and Table S3-6.

STAR METHODS

Detailed methods are provided in the online version of this paper and include the following:

KEY RESOUCES TABLE

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Guoqi Zhang (guzhang@jjay.cuny.edu).

Materials availability

All materials generated in this study are available within the article and the Supplemental Information or from the lead contact upon reasonable request.

Data and code availability

- All data reported in this article will be available from the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyse the data reported in this study is available from the lead contact upon request.

METHOD DETAILS

General information

Unless specified otherwise, all reactions were carried out under a dry nitrogen atmosphere using standard glovebox. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Anhydrous grade solvents (stored over 4 Å molecular sieves), alkali metal reagents and dibutylmagnesium (**C-1**), epoxide substrates and organic ligands listed in Schemes S1-S3 and Fig. 3 (unless otherwise stated) were all purchased from Sigma-Aldrich, Strem, Fisher Scientific and TCI America. Pinacolborane was purchased from Acros or Alfa Aesar and redistilled under reduced pressure prior to use. Ligands L5 (Vasudevan et al., 2012), L12 (Dong et al., 2016), L13 (Dong et al., 2016), L14 (Crockett et al., 2020), L15 (Ebralidze et al., 2009), L16 (Kumar et al., 2001), and L22 (Castro et al., 2005) and complexes **C-2** (Zhang et al., 2016), **C-3** (Zhang et al., 2019) and **C-4** (Zhang et al., 2019) (Schemes S2 and S3) were prepared according to known procedures. Metal complexes **C5-11** (Scheme S3 and Star Method) were purchased from Strem, Fisher Scientific and TCI America. FT-IR spectra were recorded on a Shimadzu 8400S instrument with solid samples under N_2 using a Golden Gate ATR accessory. Elemental analyses were performed by Midwest Microlab LLC in Indianapolis. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature on a Bruker AV 500 or 600 MHz NMR spectrometer, with chemical shifts (δ) referenced to the residual solvent signal. GC-MS analysis was obtained using a Shimadzu GCMS-QP2010S gas chromatograph mass spectrometer.

Procedure for preparation of compound 1 (Figure 2)

In a glovebox under N_2, in a 20 mL scintillation vial, 2,2′;6′,2″-terpyridine (233 mg, 1.0 mmol) was dissolved in Et_2O (10 mL) upon rigorous stirring at room temperature. Lithium triethylborohydride (1.1 mL, 1.0 M in THF, 1.1 eq.) was added dropwise to the solution and a deep green solution developed immediately. The mixture was allowed to stir at room temperature for 4 h and then filtered. The filtrate was evaporated to ca. 3 mL and then placed in a -30 ºC refrigerator for 10 days. X-ray quality crystals were collected by filtration and washed with pentane (3 × 1 mL) to give green crystals. The filtrate was collected and further concentrated to ca. 2 mL and then kept at -30 ºC for 7 more days. Another portion of crystals was collected by filtration and washing. The combined product was dried under vacuum.

Procedure for preparation of compound 2 (Figure 2)

In a glovebox under N_2, in a 20 mL scintillation vial, 2,2′;6′,2″-terpyridine (233 mg, 1.0 mmol) was dissolved in Et_2O (10 mL) upon rigorous stirring at room temperature. Sodium triethylborohydride (1.1 mL, 1.0 M in THF, 1.1 eq.) was added dropwise to the solution and a dark green developed immediately. The mixture was allowed to stir at room temperature for 4 h and then filtered. The filtrate was evaporated to ca. 5 mL and then placed in a -30 ºC refrigerator for 3 days. X-ray quality crystals were collected by filtration and washed thoroughly with Et_2O (5 × 1 mL) and then pentane (3 × 1 mL) to give colorless crystals. The filtrate was collected and further concentrated to ca. 2 mL and then kept at -30 ºC for 7 more days. Another portion of crystals was collected by filtration and washing. The combined product was dried under vacuum.

Procedure for preparation of compound 3 (Figure 2)

The procedure was the same as that for synthesis of **1** except that potassium triethylborohydride (1.1 mL, 1.0 M in THF, 1.1 eq.) was used. Colorless large block-like crystals suitable for X-ray diffraction were collected and dried under vacuum.

Procedure for preparation of compound 4 (Figure 2)

In a glovebox under N_2, in a 20 mL scintillation vial, 18-crown-6 (264 mg, 1.0 mmol) was dissolved in Et_2O (10 mL) upon rigorous stirring at room temperature. Sodium triethylborohydride (1.1 mL, 1.0 M in THF, 1.1 eq.) was added dropwise to the solution and a clear colorless solution developed. The mixture was allowed to stir at room temperature for 2 h and then filtered. The filtrate was evaporated to ca. 5 mL and then placed in a -30 ºC refrigerator for 3 days. Colorless crystals were collected by filtration and washed with Et_2O (3 × 1 mL) and then pentane (3 × 1 mL). The product was dried under vacuum.

Procedure for preparation of compound 5 (Figure 2)

n a glovebox under N_2, in a 20 mL scintillation vial, 18-crown-6 (264 mg, 1.0 mmol) was dissolved in Et_2O (10 mL) at room temperature. Potassium triethylborohydride (1.1 mL, 1.0 M in THF, 1.1 eq.) was carefully added dropwise to the solution without stirring. Upon addition of $KHBEt_3$, fine colorless crystals appeared at the wall and the bottom. The solution was then allowed to stand at room temperature overnight, the crystals were filtered and washed with with Et_2O (3 × 1 mL) and then pentane (3 × 1 mL). The filtrate was collected and placed in a -30 ºC refrigerator for 7 days. X-ray quality, colorless block-like crystals were collected. The combined product was dried under vacuum.

Procedure for preparation of compound 6 (Figure 2)

In a glovebox under N_2, to a 3.8 mL vial, **2** (35.5 mg, 0.05 mmol) was added, followed by styrene oxide (30 mg, 0.25 mmol, 5 equiv.). The solid was dissolved in a minute, then toluene (1 mL) was added. The solution was mixed until a clear colorless (or greenish) solution developed. Pentane (ca. 2 mL) was carefully layered upon the solution and then sealed. The vial was allowed to stay at -30 ºC for 5 days. Colorless crystals suitable for X-ray diffraction were collected and washed with pentane (3 × 1 mL). The product was dried under vacuum.

Procedure for preparation of compound 7 (Figure 2)

In a glovebox under N_2, to a 3.8 mL vial, **5** (40.2 mg, 0.1 mmol) was added, followed by styrene oxide (30 mg, 0.25 mmol, 5 equiv.). The solid was dissolved in a minute, then toluene (1 mL) was added. The solution was mixed until a clear colorless solution developed. Pentane (ca. 2 mL) was carefully layered upon the solution and then sealed. The vial was allowed to stay at -30 ºC for 5 days. Colorless crystals suitable for X-ray diffraction were collected and washed with pentane (3 × 1 mL). The product was dried under vacuum.

X-ray crystallography

X-ray diffraction data were collected on a Bruker X8 Kappa Apex II diffractometer using Mo Kα radiation (**1-3**, **6**), a Bruker D8 VENTURE diffractometer using Mo Kα radiation (**5**), or a Bruker D8 VENTURE diffractometer using Cu Kα radiation (**7** and **11**). Crystal data, data collection and refinement parameters are summarized in Table S1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Sheldrick, 1981; Sheldrick, 2015). All hydrogen atoms bound to carbon were placed in calculated positions and refined with a riding model [$U_{iso}(H) = 1.2–1.5U_{eq}(C)$], while hydrogen atoms bound to boron were located on the difference map and freely refined. For **3**, some carbon-bound hydrogen atoms involved in sigma interactions with potassium were also located on the difference map and freely refined. CCDC Nos. 2159079-2159084 (**1-3** and **5-7**) and 2192622 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

General procedure for catalytic hydroboration of styrene oxide with various metal complexes.

In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 0.1 mol%) and epoxide (1 mmol) was added to 1.8 mL glass vial equipped with a stir bar. Pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) was then added and the reaction mixture was allowed to stir at room temperature for 2 h. After completion of the reaction, the reaction mixture was first analyzed by GC-MS to determine the regioselectivity of desired boronate esters. The results showing the comparison of the catalytic efficiency of 1–7 with various homogeneous catalysts from our laboratories (Zhang et al., 2016; Zhang et al., 2019), popular commercially available metal–ligand bifunctional catalysts (Dub et al., 2015; Blum et al., 1985; Kuriyama et al., 2012; Zhang et al., 2006), classical precious metal catalyst precursors, as well as $MgBu_2$ (Magre et al., 2020; Magre et al., 2022) being the state-of-the-art catalyst for Markovnikov epoxide hydroboration are illustrated in Scheme S3.

General procedure for 2-catalyzed hydroboration of epoxides
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 0.1 mol%) and epoxide (1 mmol) was added to 1.8 mL glass vial equipped with a stir bar. Pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) was then added and the reaction mixture was allowed to stir at room temperature for 2 h. After completion of the reaction, the reaction mixture was first analyzed by GC-MS to determine the regioselectivity of desired boronate esters. The reaction mixture was quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture then subject to a flash column chromatography on silica using ethyl acetate/hexane as an eluent. The pure products of alcohols were obtained and characterized by ^1H and ^{13}C NMR spectroscopies (Figure 3).

Procedure for synthesis of 2-((1-chloropropan-2-yl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9w, Figure 3)
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 1.0 μmol) was placed in a 1.5 mL glass vial equipped with a stir bar. 2-((Allyloxy)methyl)oxirane (92.5 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) were then added. Hexamethylbenzene (3.0 mg) was added as an internal standard. The reaction mixture was allowed to stir at room temperature for 2 h and then transferred to an NMR tube containing $CDCl_3$ for measurement.

Procedure for synthesis of 2,2'-(propane-1,2-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9x, Figure 3)
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 1.0 μmol) was placed in a 1.5 mL glass vial equipped with a stir bar. Glycidol (0.74 mg, 1.0 mmol) and pinacolborane (282 mg, 2.2 mmol, 2.2 eq.) were then added. Hexamethylbenzene (2.8 mg) was added as an internal standard. The reaction mixture was allowed to stir at room temperature for 2 h and then transferred to an NMR tube containing $CDCl_3$ for measurement.

Procedure for synthesis of 1,2-diphenylethan-1-ol (9y, Figure 3)
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 1.0 μmol) was placed in a Schlenk tube equipped with a stir bar. Trans-stilbene oxide (196 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) and THF (2 mL) were then added. The reaction mixture was allowed to stir at 80°C for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent.

Procedure for synthesis of 4,4,5,5-tetramethyl-2-propoxy-1,3,2-dioxaborolane (10, Figure 3)
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 1.0 μmol) was placed in a 1.5 mL glass vial equipped with a stir bar. Trimethylene oxide (58.0 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) were then added. Hexamethylbenzene (6 mg) was added as an internal standard. The reaction mixture was allowed to stir at room temperature for 1 h and then transferred to an NMR tube containing $CDCl_3$ for measurement.

Gram-scale experiment for 2-catalyzed hydroboration of 2-(phenoxymethyl)oxirane
In a glovebox under N_2 atmosphere, catalyst **2** (5.4 mg, 0.1 mol%) was placed in a 20 mL glass vial equipped with a tiny stir bar. 2-(Phenoxymethyl)oxirane (1.5 g, 10 mmol) and pinacolborane (1.41 g, 11 mmol, 1.1 eq) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS (92% GC yield) and then the product was isolated (1.34 g, 88%) by column chromatography (silica gel) using ethyl acetate/hexane (1:10, v/v) as an eluent. The product was characterized by ^1H and ^{13}C NMR spectroscopies (Scheme S4).

4,4,5,5-Tetramethyl-2-(phenyl(3-phenyloxiran-2-yl)methoxy)-1,3,2-dioxaborolane (11)
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 1.0 μmol) was placed in a 3.8 mL glass vial equipped with a stir bar. 1,3-Diphenyl-2,3-epoxy-1-propanone (224 mg, 1.0 mmol), pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) and THF (1.5 mL) were then added were then added. The reaction mixture was allowed to stir at room temperature for 16 h to give white suspension. The solid was filtered and washed with Et_2O and then dried under vaccuum. White solid was isolated. Yield: 89 mg (92%). X-ray quality crystals were obtained by slow evaporation of a dichloromethane/THF solution (Figure S7).

Procedure for preparation of Mosher ester, (R)-1-phenylethyl (R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate
In a glovebox under N_2 atmosphere, catalyst **2** (0.71 mg, 1.0 μmol) was placed in a 1.5 mL glass vial equipped with a stir bar. (*S*)-(-)-Styrene oxide (120 mg, 1.0 mmol, 98% ee) and pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The organic phase was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil was isolated (92%). The product was subject to the reaction with (*R*)-(-)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride to give the desired Mosher ester for determination of enatiomeric excess by ^1H NMR (in comparison with the ^1H NMR of the diastereomeric mixture made from racemic 1-phenylethanol and (*R*)-(-)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride) (Scheme S7).

Deuterium-labeling experiment

1-Phenylethan-2-*d*-1-ol (**[D]-9a**): In a glovebox under N_2 atmosphere, $BD_3 \cdot THF$ (2 mL, 1 M in THF) was diluted with 1 mL THF. The solution was then added dropwise over 15 min to a 0 °C solution of pinacol (236 mg, 2 mmol) in 1 mL THF. After the completion of addition, the solution was warmed up to room temperature and then stirred for additional 2 h. To this solution, catalyst **2** (1.42 mg, 0.1 mol%) and styrene oxide (240 mg, 2 mmol) were then added and the solution was stirred for 1 h at room temperature. After GC analysis was conducted, the reaction was quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude product was purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **[D]-9a** was isolated. Yield: 221 mg (90%). ^1H NMR (400 MHz, Chloroform-*d*) δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 4.84 (t, $J = 6.1$ Hz, 1H), 2.20 (br, 1H), 1.48-1.43 (m, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 128.6, 127.5, 125.5, 70.4, 25.0 (t, $^1J_{C\text{-}D} = 19.5$ Hz) ppm. GC-MS (m/z): 123 (calc. 123). Note: In a separate control experiment, the reaction was carried out using the in-situ formed DBpin without the addition of catalyst **2**. Thus, styrene oxide (240 mg, 2 mmol) was directly added to the solution of DBpin formed in-situ and the mixture was stirred for 1 h at room temperature. Then, GC-MS analysis was conducted with hexamethylbenzene as an internal standard (Scheme S9).

Kinetics experiments

a. Initial rates versus concentration of styrene oxide 8a in THF

In a glovebox under N_2 atmosphere, a stock solution containing catalyst **2** (5.9 mg) and HBpin (460 mg) in THF (the total volume = 3.2 mL) was prepared. The solution was equally divided into 8 small vials equipped with stir bars. Various concentrations of styrene oxide as indicated were then added to each vial and then hexamethylbenzene (2.09 mg) as internal standard for GC analysis was added. The reaction mixture was allowed to stir at 25 °C. Aliquots for the GC analysis were withdrawn from each reaction mixture upon quenching of reactions by methanol after 5 minutes. The data are summarized in Table S3. The rate constant *k* was calculated as an average of *k* obtained in three experiments.

b. Initial rates versus concentration of HBpin in THF

In a glovebox under N_2 atmosphere, a stock solution containing catalyst **2** (12.5 mg) and styrene oxide (557 mg) in THF (the total volume = 5 mL) was prepared. The solution was equally divided into 10 small vials equipped with stir bars. Various concentrations of HBpin as indicated were then added to each vial and then hexamethylbenzene (0.95 mg) as internal standard for GC analysis was added. The reaction mixture was allowed to stir at 25 °C. Aliquots for the GC-MS analysis were withdrawn from each reaction mixture after 5 minutes. The data are summarized in Table S4.

c. Initial rates versus concentration of 2 in THF

In a glovebox under N_2 atmosphere, a stock solution containing styrene oxide (755 mg) and HBpin (556 mg) in THF (the total volume = 3.7 mL) was prepared. The solution was equally divided into 8 small vials equipped with stir bars. Various concentrations of **2** as indicated were then added to each vial and then hexamethylbenzene (2.8 mg) as internal standard for GC analysis was added. The reaction mixture was allowed to stir at 25 °C. Aliquots for the GC analysis were withdrawn from each reaction mixture after 5 minutes. The data are summarized in Table S5.

d. Rate law expression

Taking into account known accuracy limitations of initial rates method, the reaction can be approximately described by the following rate equation: $d[\text{product}]/dt \sim k[\text{styrene oxide}]^1[\text{HBpin}]^1[\mathbf{2}]^{0.5}$ with $k \approx 0.39\ \text{min}^{-1}\ \text{M}^{-1.5}$ at 25 °C. The rate consant *k* was calculated as an average of *k* obtained in three experiments.

Computational analysis

All calculations were performed with Gaussian 16 (rev. C01) software (Frisch et al., 2016). Hybrid ωB97X-D (Chai and Head-Gordon, 2008) (with 100 and 22% exchange at long and short ranges, respectively) functional implementing built-in D2 correction term (Grimme, 2006) was employed. To introduce non-specific solvent effects of THF in the geometry optimization steps, the Solvation Model based on Density (SMD) (Marenich et al., 2009), a popular version of a polarizable continuum model, was used. All the geometries were optimized with the def2-svp and further refined with the def2-qzvp basis, respectively. The standard reaction Gibbs energies (1M, 298K) were calculated by combining the single-point def2-svp//def2-qzvp energies with the thermal corrections from frequency calculations under def2-SVP level, adjusted by 0.00301 Hartree and converted to kcal·mol^{-1}. Various transition states were sampled with constrained potential energy surface scan and further optimized by using Berny algorithm. We report only the lowest energy located transition states for each scenario and/or relevant for discussion cases. Molecular graphics images were produced using the UCSF Chimera package (Pettersen et al., 2004). Table S6 contains information on energy data.

a. Origin of regioselectivity for 9f

Fig. S11 shows optimized transition states leading to Markovnikov and *anti*-Markovnikov products of **9f** with $[HBEt_3]^-$, $[HBEt_3]^-Na^+$ and $[HBEt_3]^-Na^+$(**L17**) catalysts alone or in the presence of 1 equiv of HBpin. For each catalyst, we considered a bimolecular catalyst–**9f** complex (e.g. transition state $\mathbf{TS_A}$, $\mathbf{TS_G}$, $\mathbf{TS_M}$, $\mathbf{TS_D}$, $\mathbf{TS_J}$ and $\mathbf{TS_P}$), or a trimolecular catalyst–**9f**–

HBpin complex (e.g. remaining transition states). In the latter case, HBpin can form a B–O bond as a result of a concerted trimolecular process (e.g. transition state $\mathbf{TS_B}$, $\mathbf{TS_E}$, $\mathbf{TS_H}$, $\mathbf{TS_K}$, $\mathbf{TS_N}$ and $\mathbf{TS_Q}$), or serve as a shuttle to deliver a hydride (e.g. transition state $\mathbf{TS_C}$, $\mathbf{TS_F}$, $\mathbf{TS_I}$, $\mathbf{TS_L}$, $\mathbf{TS_O}$ and $\mathbf{TS_R}$) via an $[(HBpin)HBEt_3]^-$ adduct, whose formation is endergonic but kinetically accesible (e.g. for example $\Delta G^o_{298K,\,r}$ = 5.7 kcal·mol^{-1} for $[(HBpin)HBEt_3]^-Na^+$ formation relative to HBpin and $[HBEt_3]^-Na^+$). The hydride transfer from HBpin via a shuttle to C-epoxide seems to be always energetically unfavorable (e.g. transition state $\mathbf{TS_C}$, $\mathbf{TS_F}$, $\mathbf{TS_I}$, $\mathbf{TS_L}$, $\mathbf{TS_O}$ and $\mathbf{TS_R}$) over HBpin-assisted hydride transfer from $[HBEt_3]^-$ (e.g. transition state $\mathbf{TS_B}$, $\mathbf{TS_E}$, $\mathbf{TS_H}$, $\mathbf{TS_K}$, $\mathbf{TS_N}$ and $\mathbf{TS_Q}$). Thus bimolecular catalyst–**9f** complexes (e.g. transition state $\mathbf{TS_A}$, $\mathbf{TS_G}$, $\mathbf{TS_M}$, $\mathbf{TS_D}$, $\mathbf{TS_J}$ and $\mathbf{TS_P}$) and/or trimolecular catalyst–**9f**–HBpin complexes (e.g. transition state $\mathbf{TS_B}$, $\mathbf{TS_E}$, $\mathbf{TS_H}$, $\mathbf{TS_K}$, $\mathbf{TS_N}$ and $\mathbf{TS_Q}$) are energetically possible. Of those, the most favorable ones are summarized in Figure 4.

We also note here that for the $[HBEt_3]^-Na^+$ catalyst, Na^+ can be placed anywhere in the initial guess for the geometry optimization. Located transition states $\mathbf{TS_G}$–$\mathbf{TS_L}$ represent the lowest energy pathways. Transition states that were sampled from the $[HBEt_3]^-Na^+$ contact ion pair were found to be uniformally less-stable on average by 3–4 kcal·mol^{-1}, i.e. the cases when Na^+ was always in close proximity to the hydride donor, consistent with the fact that Na^+ cannot establish any non-covalent interactions with the opposite site of the molecule within transition state structures.

b. Origin of regioselectivity for 9a. Catalytic cycle for 8a hydroboration

Fig. S12 provides additional information for optimized transition states leading to Markovnikov-product **9a** formation with the $[HBEt_3]^-Na^+$(**L17**) catalyst. Transition states $\mathbf{TS_1}$, $\mathbf{TS_3}$ and $\mathbf{TS_6}$ are structurally similar to $\mathbf{TS_N}$, $\mathbf{TS_M}$ and $\mathbf{TS_O}$, respectively. Here we also report an additional transition state, $\mathbf{TS_5}$, which is a spatial isomer of transition state $\mathbf{TS_1}$ for a trimolecular catalyst–**8a**–HBpin complex. As expected, the isomer $\mathbf{TS_1}$ is more energetically favorable, which is most likely the result of both cation-substrate//HBpin non-covalent ionic interaction and π-π catalyst-substrate stacking interaction. $\mathbf{TS_3}$ represents a bimolecular catalyst–**8a** complex, whereas in $\mathbf{TS_6}$ HBpin serves as a shuttle to deliver a hydride. Similar to **9f** (see discussion above), this hydride transfer from HBpin via a shuttle to C-epoxide seems to be energetivally unfavorable. Thus, in the catalytic cycle for **8a**, only two transition states $\mathbf{TS_1}$ and $\mathbf{TS_3}$ are energetically accesible. Taking into account the DFT accuracy, they are indistinguishable, which offers the possibility of two catalytic cycles connected with shared intermediates (branching points). Fig. S13 shows these catalytic cycles that are possible for **8a** hydroboration with **2** leading to Markovnikov-product **9a** based on the standard ~3 kcal·mol^{-1} accuracy of DFT (Dub and Gordon, 2017). Two pathways **A** and **B** are connected through **int0** and **int1a** branching points. Although both pathways are indistinguishable by computations, the pathways differ by the molecularity of the rate- and regioselectivity-determining transition states and thus predicted rate law expression. Only pathway **A** is consistent with the experimental rate law rate of ~ k[styrene oxide]^1[HBpin]^1[**2**]$^{0.5}$ (Kozuch et al., 2009). This pathway **A** is drawn in Figure 4B and represents the proposed catalytic cycle for the reaction under study.

Spectroscopic details

Compound 1 (Figure 2)

Yield: 73.5 mg (22%). FT-IR (solid, cm^{-1}): 2928s, 2890s, 2850s, 1590s, 1577s, 1469s, 1445s, 1402m, 1242m, 1153m, 1049m, 999m, 960m. ^{1}H NMR (600 MHz, THF-d_8) δ 8.68 – 8.63 (m, 4H), 8.63 – 8.57 (m, 4H), 8.50 (dd, J = 7.9, 1.9 Hz, 4H), 8.03 – 7.98 (m, 2H), 7.90 (ddd, J = 9.6, 5.8, 2.0 Hz, 4H), 7.36 (ddd, J = 7.4, 4.7, 1.3 Hz, 4H), 1.03 (dd, J = 7.4, 4.4 Hz, 4H), 0.90 (d, J = 9.3 Hz, 8H), 0.79 – 0.58 (m, 12H), 0.03 (dd, J = 7.6, 2.8 Hz, 6H) ppm. ^{13}C NMR (151 MHz, THF-d_8) δ 156.8, 156.3, 150.4, 150.2, 139.0, 137.9, 125.0, 121.8, 11.5, 11.1 ppm. Elemental analysis calc. (%) for $C_{42}H_{53}B_2LiN_6$: C 75.24, H 7.97, N 12.53; Found C 75.75, H 7.52, N 12.36.

Compound 2 (Figure 2)

Yield: 231 mg (65%). FT-IR (solid, cm^{-1}): 2927s, 2890s, 2838s, 1908s, 1590m, 1578m, 1445s, 1430s, 1307w, 1241w, 1153s, 1099w, 1046w, 998m, 931w. ^{1}H NMR (500 MHz, THF) δ 8.74 – 8.60 (m, 4H), 8.52 (d, J = 7.7 Hz, 2H), 7.96 (t, J = 7.9 Hz, 1H), 7.87 (t, J = 7.8 Hz, 2H), 7.34 (dd, J = 7.8, 4.5 Hz, 2H), 0.70 (t, J = 7.9 Hz, 9H), -0.02 (q, J = 7.9 Hz, 6H) ppm. ^{13}C NMR (126 MHz, THF) δ 157.2, 156.5, 150.2, 138.6, 137.6, 124.7, 121.8, 121.6, 15.9, 11.2 ppm. Elemental analysis calc. (%) for $C_{42}H_{54}B_2Na_2N_6$: C 71.00, H 7.66, N 11.83; Found C 70.82, H 7.18, N 11.96.

Compound 3 (Figure 2)

Yield: 267 mg (72%). FT-IR (solid, cm^{-1}): 2886s, 2839s, 2794s, 2027m, 1979m, 1587s, 1570s, 1475s, 1443s, 1428s, 1305w, 1239w, 1165m, 1152m, 1090s, 1051m, 997m, 936w. ^{1}H NMR (600 MHz, THF-d_8) δ 8.69 – 8.62 (m, overlapping, 8H), 8.52 (d, J = 7.7 Hz, 4H), 7.96 (t, J = 7.8 Hz, 2H), 7.87 (td, J = 7.7, 1.9 Hz, 4H), 7.33 (ddd, J = 74.5, 4.6, 1.3 Hz, 4H), 0.70 (dt, J = 44.3, 7.1 Hz, 18H), 0.07 – -0.06 (dq, J = 41.4, 7.5 Hz, 12H) ppm. ^{13}C NMR (151 MHz, THF-d_8) δ 157.2, 156.5, 150.2, 138.6, 137.6, 124.7, 121.8, 121.6, 14.2, 11.5 (d, J = 8 Hz) ppm. Elemental analysis calc. (%) for $C_{42}H_{54}B_2K_2N_6$: C 67.92, H 7.33, N 11.31; Found C 67.72, H 7.03, N 11.37.

Compound 4 (Figure 2)

Yield: 347 mg (90%). FT-IR (solid, cm^{-1}): 2887s, 2837s, 2788s, 2078w, 1471m, 1454m, 1285w, 1250s, 1106s, 965s. ^{1}H NMR (500 MHz, Tol- d_8) δ 3.14 (s, 24H), 1.50 (q, J = 6.2 Hz, 9H), 0.82 – 0.73 (m, 6H) ppm. ^{13}C NMR (126 MHz, THF) δ 71.7, 15.9, 15.1 ppm. Elemental analysis calc. (%) for $C_{18}H_{40}BNaO_6$: C 55.96, H 10.44; Found C 55.65, H 10.22.

Compound 5 (Figure 2)

Yield: 354 mg (88%). FT-IR (solid, cm^{-1}): 2886s, 2835s, 2787m, 2074w, 1979m, 1470m, 1455m, 1351s, 1285m, 1250m, 1103s, 961s. ^{1}H NMR (500 MHz, Tol-*d*$_8$) δ 3.14 (s, 24H), 1.55 – 1.43 (m, 9H), 0.82 – 0.73 (m, 6H) ppm. ^{13}C NMR (126 MHz, Tol-*d*$_8$) δ 70.5, 15.9, 15.1 ppm. Elemental analysis calc. (%) for $C_{18}H_{40}BKO_6$: C 53.72, H 10.02; Found C 53.37, H 9.88.

Compound 6 (Figure 2)
Yield: 267 mg (86%). FT-IR (solid, cm^{-1}): 2923m, 2890m, 2849s, 2793s, 1589s, 1579s, 1473s, 1444s, 1430s, 1400w, 1304w, 1240m, 1185w, 1155s, 1119m, 1262m, 998s, 947m. ^{1}H NMR (600 MHz, THF) δ 8.66 (dd, *J* = 7.2, 1.6 Hz, 4H), 8.52 (d, *J* = 8.0 Hz, 2H), 7.96 (t, *J* = 7.8 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.37 – 7.29 (m, 4H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.10 (m, 1H), 4.73 (t, *J* = 6.4 Hz, 1H), 1.35 (d, *J* = 6.4 Hz, 3H), 0.69 (p, *J* = 7.3 Hz, 9H), -0.05 (q, *J* = 7.7 Hz, 6H) ppm. ^{13}C NMR (151 MHz, THF) δ 157.2, 156.5, 150.2, 138.6, 137.6, 128.9, 127.4, 126.2, 124.7, 121.8, 121.6, 11.2 ppm. Elemental analysis calc. (%) for $C_{29}H_{35}BN_3NaO$: C 73.27, H 7.42, N 8.84; Found C 73.65, H 7.56, N 8.38.

Compound 7 (Figure 2)
Yield: 44.4 mg (85%). FT-IR (solid, cm^{-1}): 2886s, 2835s, 2787m, 2074w, 1979m, 1470m, 1455m, 1351s, 1285m, 1250m, 1103s, 961s. ^{1}H NMR (500 MHz, Tol-*d*$_8$) δ 7.77 – 7.69 (m, 2H), 7.30 – 7.22 (m, 2H), 7.15 – 7.11 (m, 1H), 5.26 (q, *J* = 6.5 Hz, 1H), 3.11 (s, 25H), 1.56 (d, *J* = 6.4 Hz, 3H), 1.34 (t, *J* = 7.7 Hz, 9H), 0.69 (dd, *J* = 7.7, 5.7 Hz, 6H) ppm. ^{13}C NMR (126 MHz, THF) δ 154.1, 127.0, 126.7, 69.3, 68.0, 28.3, 15.2, 12.0 ppm. Elemental analysis calc. (%) for $C_{26}H_{48}BKO_7$: C 59.76, H 9.26; Found C 59.32, H 9.12.

1-Phenylethanol (9a, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 116 mg (95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.09 (m, 5H), 4.72 (q, *J* = 6.5 Hz, 1H), 2.10 (s, 1H), 1.34 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 128.6, 127.5, 125.5, 70.4, 25.2 ppm.

1-(4-Fluorophenyl)ethanol (9b, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 119 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.17 (s, 1H), 1.45 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 161.0, 141.7, 141.6, 127.2, 127.1, 115.5, 115.2, 69.8, 25.4 ppm.

1-(4-Chlorophenyl)ethanol (9c, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. White solid was isolated. Yield: 146 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (q, *J* = 8.5 Hz, 4H), 4.79 (q, *J* = 6.5 Hz, 1H), 2.63 (s, 1H), 1.41 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 133.1, 128.6, 126.9, 69.7, 25.3 ppm.

2-Octanol (9d, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 109 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 – 3.71 (m, 1H), 1.74 (s, 1H), 1.51 – 1.25 (m, 10H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.93 – 0.83 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.2, 39.5, 31.9, 29.4, 25.9, 23.5, 22.7, 14.2 ppm.

2-Dodecanol (9e, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 160 mg (86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.83 – 3.72 (m, 1H), 1.77 (s, 1H), 1.49 – 1.23 (m, 18H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 68.2, 39.5, 32.0, 29.8, 29.8, 29.7, 29.5, 25.9, 23.5, 22.8, 14.2 ppm.

1-Phenoxypropan-2-ol (9f, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 143 mg (94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.96 (d, *J* = 1.2 Hz, 1H), 6.93 – 6.86 (m, 2H), 4.25 – 4.12 (m, 1H), 3.93 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.79 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.45 (s, 1H), 1.27 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 129.7, 121.3, 114.7, 73.4, 66.4, 18.9 ppm.

1-(2-Methylphenoxy)propan-2-ol (9g, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. White solid was isolated. Yield: 147 mg (92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.08 (m, 2H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.83 – 6.74 (m, 1H), 4.20 (dt, *J* = 6.7, 3.4 Hz, 1H), 3.92 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.80 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.42 (s, 1H), 2.24 (s, 3H), 1.29 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 130.9, 127.0, 126.9, 121.0, 111.4, 73.5, 66.6, 19.0, 16.3 ppm.

1-(2-Methoxyphenoxy)propan-2-ol (9h, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Yellowish solid was isolated. Yield: 171 mg (94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 – 6.92 (m, 2H), 6.90 (ddd, *J* = 8.0, 3.9, 2.3 Hz, 2H), 4.22 – 4.13 (m, 1H), 4.00 (dd, *J* = 9.7, 3.0 Hz, 1H), 3.85 (s, 3H), 3.79 (dd, *J* = 9.7, 8.3 Hz, 1H), 3.09 (s, 1H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 148.4, 122.4, 121.2, 115.8, 112.2, 66.1, 56.0, 18.5 ppm.

1-(4-Methoxyphenoxy)propan-2-ol (9i, Figure 3) (Thiyagarajan and Gunanathan, 2019)

The general procedure was followed. Yellowish solid was isolated. Yield: 173 mg (95%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.83 (d, *J* = 9.1 Hz, 2H), 6.81 (d, *J* = 9.5 Hz, 2H), 4.14 (tq, *J* = 6.6, 3.3 Hz, 1H), 3.86 (dd, *J* = 9.2, 3.4 Hz, 1H), 3.75 (s, 3H), 3.73 (d, *J* = 9.3 Hz, 1H), 2.67 (s, 1H), 1.24 (s, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 154.2, 152.9, 115.7, 114.8, 74.2, 66.3, 55.8, 18.9 ppm.

1-(2,4-Dibromophenoxy)propan-2-ol (9j, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Yellowish solid was isolated. Yield: 285 mg (92%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.66 (d, *J* = 2.4 Hz, 1H), 7.36 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 4.23 (dt, *J* = 6.9, 3.5 Hz, 1H), 3.98 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.81 (dd, *J* = 9.1, 7.4 Hz, 1H), 2.49 (d, *J* = 3.5 Hz, 1H), 1.30 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 154.4, 135.7, 131.5, 115.0, 113.7, 113.5, 66.2, 18.8 ppm.

1-(Benzyloxy)propan-2-ol (9k, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 150 mg (90%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.21 (m, 5H), 4.53 (s, 2H), 4.07 – 3.87 (m, 1H), 3.43 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.27 (dd, *J* = 9.4, 8.0 Hz, 1H), 2.72 (s, 1H), 1.13 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.0, 128.5, 127.8, 127.8, 75.9, 73.3, 66.5, 18.8 ppm.

1-([1,1'-Biphenyl]-2-yloxy)propan-2-ol (9l, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. White solid was isolated. Yield: 210 mg (92%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 – 7.46 (m, 2H), 7.39 (td, *J* = 7.1, 6.2, 1.2 Hz, 2H), 7.35 – 7.26 (m, 3H), 7.05 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.09 – 3.97 (m, 1H), 3.93 (dd, *J* = 9.2, 3.3 Hz, 1H), 3.73 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.17 (s, 1H), 1.16 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 155.5, 138.5, 131.5, 131.0, 129.5, 128.8, 128.2, 127.2, 121.7, 113.4, 74.3, 66.3, 18.7 ppm.

1-(4-Chlorophenyl)-3,4,4-trimethylpentan-3-ol (9m, Figure 3)
The general procedure was followed. Colorless oil was isolated. Yield: 197 mg (82%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 2.69 (ddd, *J* = 13.5, 12.1, 4.7 Hz, 1H), 2.56 (ddd, *J* = 13.5, 12.2, 5.4 Hz, 1H), 1.73 (dddd, *J* = 13.9, 12.2, 4.7, 0.8 Hz, 1H), 1.63 (ddd, *J* = 13.8, 12.2, 5.4 Hz, 1H), 1.14 (d, *J* = 0.9 Hz, 3H), 0.88 (s, 9H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 141.8, 131.5, 129.9, 128.6, 38.5 38.3, 30.1, 25.4, 21.1, 21.1 ppm. Anal. Calc. for $C_{14}H_{21}ClO$, C 69.84, H 8.79%; Found C 70.22, H 8.96%.

1-(3-(Triethoxysilyl)propoxy)propan-2-ol (9n, Figure 3)
The general procedure was followed. Colorless oil was isolated. Yield: 257 mg (92%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 3.90 (ddt, *J* = 8.1, 4.9, 1.7 Hz, 1H), 3.78 (q, *J* = 7.0 Hz, 6H), 3.45 – 3.34 (m, 3H), 3.17 (dd, *J* = 9.5, 8.1 Hz, 1H), 2.45 (br., 1H), 1.66 (ddt, *J* = 9.9, 8.3, 6.6 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 9H), 1.09 (d, *J* = 6.4 Hz, 3H), 0.65 – 0.58 (m, 2H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 76.4, 73.5, 66.4, 58.5, 24.9, 24.7, 23.1, 18.7, 18.4, 6.7 ppm. Elemental analysis calc. (%) for $C_{12}H_{28}O_5Si$: C 51.40, H 10.06; Found C 51.75, H 10.17.

Cyclohexanol (9o, Figure 3) (Magre et al., 2020)
The general procedure was followed. Colorless oil was isolated. Yield: 80 mg (80%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.60 (dt, *J* = 9.3, 4.9 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.94 – 1.84 (m, 2H), 1.79 – 1.68 (m, 2H), 1.60 – 1.50 (m, 1H), 1.31 – 1.21 (m, 4H), 1.18 (ddd, *J* = 11.8, 8.6, 5.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 70.4, 35.6, 25.6, 24.3 ppm.

1-(2,2,3,3-Tetrafluoropropoxy)propan-2-ol (9p, Figure 3)
The general procedure was followed. Colorless oil was isolated. Yield: 161 mg (85%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.92 (tt, *J* = 53.2, 4.7 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.89 (tt, *J* = 12.7, 1.7 Hz, 2H), 3.57 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.41 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.22 (s, 1H), 1.16 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 111.1 (t, *J* = 35.3 HZ), 109.4 (t, *J* = 35.3 HZ), 78.3, 68.4 (t, *J* = 28.1 HZ), 66.6 (d, *J* = 5.8 Hz), 18.7 ppm. Elemental analysis calc. (%) for $C_6H_{10}F_4O_2$: C 37.90, H 5.30; Found C 38.25, H 5.58.

1-(Furan-2-methoxy)propan-2-ol (9q, Figure 3) (Molander and McKie, 1992)
The general procedure was followed. Colorless oil was isolated. Yield: 142 mg (91%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (d, *J* = 1.9 Hz, 1H), 6.38 – 6.27 (m, 2H), 4.52 – 4.44 (m, 2H), 3.94 (ddd, *J* = 8.1, 6.4, 3.1 Hz, 1H), 3.45 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.27 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.54 (s, 1H), 1.12 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 151.7, 142.9, 110.4, 109.5, 75.7, 66.4, 65.1, 18.7 ppm.

Dec-9-en-2-ol (9r, Figure 3) (Thiyagarajan and Gunanathan, 2019)
The general procedure was followed. Colorless oil was isolated. Yield: 136 mg (87%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.01 – 4.95 (m, 1H), 4.92 (dq, *J* = 10.1, 1.5 Hz, 1H), 3.77 (q, *J* = 6.1 Hz, 1H), 2.07 – 2.00 (m, 2H), 1.88 (s, 1H), 1.49 – 1.26 (m, 10H), 1.17 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 139.2, 114.2, 68.1, 39.4, 33.8, 29.6, 29.2, 28.9, 25.8, 23.5 ppm.

1-(Allyloxy)propan-2-ol (9s, Figure 3) (Magre et al., 2020)
The general procedure was followed. Colorless oil was isolated. Yield: 95 mg (82%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.92 (ddt, *J* = 17.0, 10.2, 5.7 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.25 – 5.15 (m, 1H), 4.03 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.98 (td, *J* =

6.3, 3.0 Hz, 1H), 3.44 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.25 (dd, *J* = 9.5, 8.2 Hz, 1H), 2.55 (d, *J* = 2.7 Hz, 1H), 1.15 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 134.7, 117.3, 75.9, 72.3, 66.6, 18.8 ppm.

1-Methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (9t, Figure 3)
The general procedure was followed. Colorless oil was isolated. Yield: 96 mg (62%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.72 – 4.67 (m, 2H), 1.86 – 1.79 (m, 1H), 1.73 (s, 3H), 1.71 – 1.67 (m, 2H), 1.61 – 1.51 (m, 4H), 1.46 – 1.39 (m, 2H), 1.23 (s, 3H), 1.19 (s, 1H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 150.5, 108.5, 69.0, 44.9, 39.0, 31.6, 27.2, 21.1 ppm. Elemental analysis calc. (%) for $C_{10}H_{18}O$: C 77.87, H 11.76; Found C 77.53, H 11.35.

3-Vinylcyclohexanol (9u, Figure 3) and 4-vinylcyclohexanol (9u´, Figure 3) (9u : 9u´ = 10:7) (Molander and McKie, 1992)
The general procedure was followed. Colorless oil was isolated. Yield: 116 mg (92%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.87 – 5.73 (m, overlapping, 1H), 5.04 – 4.90 (m, overlapping, 2H), 4.08 (br, 1H, **9u**), 3.95 (br, 1H, **9u´**), 2.46 (br, 1H, **9u**), 2.09 – 2.03 (m, 1H, **9u´**), 1.95 (s, overlapping, 1H), 1.78 – 1.49 (m, overlapping, 7H), 1.47 – 1.41 (m, 1H), 1.22 – 1.13 (m, 1H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 143.8, 143.7, 112.6, 112.5, 66.9, 66.5, 40.0, 39.0, 35.6, 33.2, 32.1, 31.6, 26.7, 19.9 ppm.

1-(Prop-2-yn-1-yloxy)propan-2-ol (9v, Figure 3) (Steiniger and Lambert, 2021)
The general procedure was followed. Colorless oil was isolated. Yield: 73 mg (64%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.25 – 4.14 (m, 2H), 3.99 (ddt, *J* = 10.1, 6.2, 3.2 Hz, 1H), 3.54 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.34 (dd, *J* = 9.5, 7.9 Hz, 1H), 2.55 (s, 1H), 2.47 (t, *J* = 2.5 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 79.6, 75.6, 74.8, 66.4, 58.5, 18.8 ppm.

2-((1-Chloropropan-2-yl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9w, Figure 3)
NMR yield: 99%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.36 (td, *J* = 6.3, 5.3 Hz, 1H), 3.51 – 3.43 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.26 (s, 12H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 83.1, 70.7, 49.1, 24.7, 20.3 ppm. GC-MS: 220 (calc. 220).

2,2'-(Propane-1,2-diylbis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9x, Figure 3) (Kobylarski et al., 2022)
NMR yield: 94%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 4.28 (q, *J* = 6.1 Hz, 1H), 3.75 (d, *J* = 5.6 Hz, 2H), 1.25 (s, 24H), 1.17 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$) δ 82.9, 82.7, 70.5, 69.3, 24.7, 18.7 ppm.

1,2-Diphenylethan-1-ol (9y, Figure 3) (Magre et al., 2020)
White solid was isolated. Yield: 89 mg (45%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 – 7.10 (m, 10H), 4.91 (ddd, *J* = 8.2, 4.8, 2.8 Hz, 1H), 3.08 – 2.97 (m, 2H), 1.94 (d, *J* = 3.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.0, 138.2, 129.7, 128.7, 128.6, 127.8, 126.8, 126.0, 46.3 ppm.

4,4,5,5-Tetramethyl-2-propoxy-1,3,2-dioxaborolane (10, Scheme S5) (Hadlington et al., 2014)
NMR yield: 99%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.75 (t, *J* = 6.6 Hz, 2H), 1.54 (dtd, *J* = 14.0, 7.4, 6.6 Hz, 2H), 1.21 (s, 12H), 0.87 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 82.5, 66.5, 24.5, 16.7, 10.0 ppm. GC-MS: 186 (calc. 186).

4,4,5,5-Tetramethyl-2-(phenyl(3-phenyloxiran-2-yl)methoxy)-1,3,2-dioxaborolane (11, Figure S7) (Zhang et al., 2022)
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.45 (m, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (dd, *J* = 7.2, 4.9 Hz, 3H), 7.31 – 7.25 (m, 3H), 5.30 (d, *J* = 3.6 Hz, 1H), 4.17 (d, *J* = 2.0 Hz, 1H), 3.23 (dd, *J* = 3.7, 2.0 Hz, 1H), 1.30 (d, *J* = 18.3 Hz, 13H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 139.0, 137.0, 128.5, 128.4, 128.18, 128.15, 126.4, 125.8, 83.3, 74.1, 64.6, 55.4, 24.7, 24.5 ppm.

(R)-1-phenylethyl (R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (Hudlicky et al., 1991)
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.23 (ddd, *J* = 17.5, 7.7, 5.6 Hz, 5H), 7.17 (dd, *J* = 7.4, 2.3 Hz, 2H), 6.02 (q, *J* = 6.6 Hz, 1H), 3.52 – 3.44 (m, 3H), 1.56 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.6, 140.2, 132.3, 129.5, 128.5, 128.3, 128.3, 127.3, 126.2, 124.5, 122.2, 84.6 (q, *J* = 27.7 Hz), 75.0, 55.49, 22.2 ppm.

REFERENCES

Yao, C., Dahmen, T., Gansäuer, A., and Norton, J. (2019). Anti-Markovnikov alcohols via epoxide hydrogenation through cooperative catalysis. Science *364*, 764-767. https://doi/10.1126/science.aaw3913.

Dong, G., Teo, P., Wickens, Z. K., and Grubbs, R. H. (2011). Primary Alcohols from Terminal Olefins: Formal Anti-Markovnikov Hydration via Triple Relay Catalysis. Science *333*, 1609-1612. https://doi/10.1126/science.aaw3913.

Jensen, C. M., and Trogler, W. C. (1986). Catalytic Hydration of Terminal Alkenes to Primary Alcohols. Science *233*, 1069-1071. https://doi/10.1126/science.233.4768.1069.

Brown, H. C., and Geoghegan, P. (1967). The Oxymercuration-Demercuration of Representative Olefins. A Convenient, Mild Procedure for the Markovnikov Hydration of the Carbon-Carbon Double Bond. J. Am. Chem. Soc. *89*, 1522-1524. https://doi/10.1021/ja00982a043.

Shigeru, I., and Teruaki, M. (1989). A New Method for Preparation of Alcohols from Olefins with Molecular Oxygen and Phenylsilane by the Use of Bis(acetylacetonato)cobalt(II). Chem. Lett. *18*, 1071-1074. https://doi/10.1246/cl.1989.1071.

Demming, R. M., Hammer, S. C., Nestl, B. M., Gergel, S., Fademrecht, S., Pleiss, J., and Hauer, B. (2019). Asymmetric Enzymatic Hydration of Unactivated, Aliphatic Alkenes. Angew. Chem. Int. Ed. *58*, 173-177. https://doi/full/10.1002/anie.201810005.

Duval, M., Deboos, V., Hallonet, A., Sagorin, G., Denicourt-Nowicki, A., and Roucoux, A. (2021). Selective palladium nanoparticles-catalyzed hydrogenolysis of industrially targeted epoxides in water. J. Catal. *396*, 261-268. https://doi.org/10.1016/j.jcat.2021.02.027.

Thiery, E., Le Bras, J., and Muzart, J. (2007). Palladium nanoparticles-catalyzed regio- and chemoselective hydrogenolysis of benzylic epoxides in water. Green Chem. *9*, 326-327. https://doi.org/10.1039/B616486B.

Nandi, S., Patel, P., Jakhar, A., Khan, N. H., Biradar, A. V., Kureshy, R. I., and Bajaj, H. C. (2017) Cucurbit[6]uril-Stabilized Palladium Nanoparticles as a Highly Active Catalyst for Chemoselective Hydrogenation of Various Reducible Groups in Aqueous Media. ChemistrySelect. *2*, 9911-9919. https://doi.org/10.1002/slct.201702196.

Liu, W., Li, W., Spannenberg, A., Junge, K., and Beller, M. (2019). Iron-catalysed regioselective hydrogenation of terminal epoxides to alcohols under mild conditions. Nat. Catal. *2*, 523-528. https://doi.org/10.1038/s41929-019-0286-7.

Patnaik, S., and Sadow, A. D. (2019). Interconverting Lanthanum Hydride and Borohydride Catalysts for C=O Reduction and C−O Bond Cleavage. Angew. Chem. Int. Ed. *58*, 2505-2509. https://doi/full/10.1002/anie.201813305.

Song, H., Ye, K., Geng, P., Han, X., Liao, R., Tung, C.-H., and Wang, W. (2017). Activation of Epoxides by a Cooperative Iron–Thiolate Catalyst: Intermediacy of Ferrous Alkoxides in Catalytic Hydroboration. ACS Catal. *7*, 7709-7717. https://doi/full/10.1021/acscatal.7b02527.

Desnoyer, A. N., Geng, J., Drover, M. W, Patrick, B. O., and Love, J. A. (2017). Catalytic Functionalization of Styrenyl Epoxides via 2-Nickela(II)oxetanes. Chem. Eur. J. *23,* 11509-11512. https://doi/full/10.1002/chem.201702824.

Zhang, J., Park, S., and Chang, S. (2018). Piers' borane-mediated hydrosilylation of epoxides and cyclic ethers. Chem. Commun. *54*, 7243-7246. https://doi.org/10.1039/C8CC03741H.

Wenz, J., Wadepohl, H., and , L. H. (2017). Regioselective hydrosilylation of epoxides catalysed by nickel(ii) hydrido complexes. Chem. Commun. *53*, 4308-4311. https://doi.org/10.1039/C7CC01655G.

Zhang, Y.-Q., Poppel, C., Panfilova, A., Bohle, F., Grimme, S., and Gansäuer, A. (2017). SN_2 Reactions at Tertiary Carbon Centers in Epoxides. Angew. Chem. Int. Ed. *56*, 9719-9722. https://doi.org/10.1002/anie.201702882.

Henriques, D. S. G., Zimmer, K., Klare, S., Meyer, A., Rojo-Wiechel, E., Bauer, M., Sure, R., Grimme, S., Schiemann, O., Flowers II, R. A., and Gansäuer, A. (2016). Highly Active Titanocene Catalysts for Epoxide Hydrosilylation:

Synthesis, Theory, Kinetics, EPR Spectroscopy. Angew. Chem. Int. Ed. *55*, 7671-7675. https://doi.org/10.1002/anie.201601242.

Gansäuer, A., Klatte, M., Brändle, G. M., and Friedrich, J. (2012). Catalytic Hydrogen Atom Transfer (HAT) for Sustainable and Diastereoselective Radical Reduction. Angew. Chem. Int. Ed. *51*, 8891-8894. https://doi/full/10.1002/anie.201202818.

Park, S., and Brookhart, M. (2011). Hydrosilylation of epoxides catalyzed by a cationic η^1-silane iridium(iii) complex. Chem. Commun. *47*, 3643-3645. https://doi.org/10.1039/C0CC05714B.

Nagashima, H., Suzuki, A., Iura, T., Ryu, K., and Matsubara, K. (2000). Stoichiometric and Catalytic Activation of Si−H Bonds by a Triruthenium Carbonyl Cluster, (μ^3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$: Isolation of the Oxidative Adducts, Catalytic Hydrosilylation of Aldehydes, Ketones, and Acetals, and Catalytic Polymerization of Cyclic Ethers. Organometallics *19*, 3579-3590. https://doi/full/10.1021/om0003887.

Huang, C., Ma, W., Zheng, X., Xu, M., Qi, X., and Lu, Q. (2022). Epoxide Electroreduction. J. Am. Chem. Soc. *144*, 1389-1395. https://doi/full/10.1021/jacs.1c11791.

Ton, N. N. H., Mai, B. K., and Nguyen, T. V. (2021). Tropylium-Promoted Hydroboration Reactions: Mechanistic Insights Via Experimental and Computational Studies. J. Org. Chem. *86*, 9117-9133. https://doi/full/10.1021/acs.joc.1c01208.

Kwon, M. S., Park, I. S., Jang, J. S., Lee, J. S., and Park, J. (2007). Magnetically Separable Pd Catalyst for Highly Selective Epoxide Hydrogenolysis under Mild Conditions. Org. Lett. *9*, 3417-3419. https://doi/10.1021/ol701456w.

Thiyagarajan, S., and Gunanathan, C. (2019). Ruthenium-Catalyzed Selective Hydrogenation of Epoxides to Secondary Alcohols. Org. Lett. *21*, 9774-9778. https://doi/10.1021/acs.orglett.9b03995.

Ito, M., Hirakawa, M., Osaku, A., and Ikariya, T. (2003). Highly Efficient Chemoselective Hydrogenolysis of Epoxides Catalyzed by a (η^5-$C_5(CH_3)_5$)Ru Complex Bearing a 2-(Diphenylphosphino)ethylamine Ligand. Organometallics *22*, 4190-4192. https://doi/10.1021/om034006j.

Fujitsu, H., Shirahama, S., Matsumura, E., Takeshita, K., and Mochida, I. (1981). Catalytic hydrogenation of styrene oxide with cationic rhodium complexes. J. Org. Chem. *46*, 2287-2290. https://doi/abs/10.1021/jo00324a016.

Oshima, M., Yamazaki, H., Shimizu, I., Nisar, M., and Tsuji, J. (1989). Palladium-catalyzed selective hydrogenolysis of alkenyloxiranes with formic acid. Stereoselectivity and synthetic utility. J. Am. Chem. Soc. *111*, 6280-6287. https://doi/10.1021/ja00198a045.

Mimoun, H. (1999). Selective Reduction of Carbonyl Compounds by Polymethylhydrosiloxane in the Presence of Metal Hydride Catalysts. J. Org. Chem. *64*, 2582-2589. https://doi/10.1021/jo982314z.

Magre, M., Paffenholz, E., Maity, B., Cavallo, L., and Rueping, M. (2020). Regiodivergent Hydroborative Ring Opening of Epoxides via Selective C–O Bond Activation. J. Am. Chem. Soc. *142*, 14286-14294. https://doi/full/10.1021/jacs.0c05917.

Cao, X., Li, J., Zhu, A., Su, F., Yao, W., Xue, F., and Ma, M. (2020). Syntheses of asymmetrical magnesium(i) complexes and their catalytic application in epoxide hydroboration. Org. Chem. Front. *7*, 3625-3632. https://doi.org/10.1039/D0QO00938E.

The opposite chemoselectivity, namely, the hydroboration of alknyl epoxides leading to saturated epoxides, has precedents, see for example: Ibrahim, A. D., Entsminger, S. W., and Fout, A. R. (2017). Insights into a Chemoselective Cobalt Catalyst for the Hydroboration of Alkenes and Nitriles. ACS Catal. *7*, 3730-3734. https://doi/full/10.1021/acscatal.7b00362.

Magre, M., Szewczyk, M., and Rueping, M. (2022). s-Block Metal Catalysts for the Hydroboration of Unsaturated Bonds. Chem. Rev. *122*, 8261-8312. https://doi/10.1021/acs.chemrev.1c00641.

Elsen, H., Färber, C., Ballmann, G., and Harder, S. (2018). $LiAlH_4$: From Stoichiometric Reduction to Imine

Hydrogenation Catalysis. Angew. Chem. Int. Ed. *57*, 7156-7160. https://doi.org/10.1002/anie.201803804.

Brown, H. C., and Yoon, N. M. (1968). The borohydride-catalyzed reaction of diborane with epoxides. The anti-Markovnikov opening of trisubstituted epoxides. J. Am. Chem. Soc. *90*, 2686-2688. https://doi/10.1021/ja01012a039.

Stephan, D. W. (2015). Frustrated Lewis pairs. J. Am. Chem. Soc. *137,* 10018-10032. https://doi/full/10.1021/jacs.5b06794.

Vasudevan, K.V., Scott, B.L., and Hanson, S.K. (2012). Alkene hydrogenation catalyzed by nickel hydride complexes of an aliphatic PNP pincer ligand. Eur. J. Inorg. Chem. *30*, 4898-4906. https://doi.org/10.1002/ejic.201200758.

Dong, Y.-W., Fan, R.-Q., Wang, X.-M; Wang, P., Zhang, H.-J., Wei, L.-G., Song, Y., Du, X., Chen, W., and Yang, Y.-L. (2016). Topological evolution in mercury(II) Schiff base complexes tuned through alkyl substitution – synthesis, solid-state structures, and aggregation-induced emission properties. Eur. J. Inorg. Chem. 3598-3610. https://doi.org/10.1002/ejic.201600231.

Crockett, M.P., Wong, A.S., Li, B., and Byers, J.A. (2020). Rational design of an iron-based catalyst for Suzuki–Miyaura cross-couplings involving heteroaromatic boronic esters and tertiary alkyl electrophiles. Angew. Chem. Int. Ed. *59*, 5392-5397. https://doi.org/10.1002/anie.201914315.

Ebralidze, I.I., Leitus, G., Shimon, L.J., Wang, Y., Shaik, S. and Neumann, R. (2009). Structural variability in manganese(II) complexes of N,N′-bis(2-pyridinylmethylene) ethane (and propane) diamine ligands. Inorg. Chim. Acta *362*, 4713-4720. https://doi.org/10.1016/j.ica.2009.06.037.

Kumar, R.N., Chauhan, N.K., Das, A.K.; Singh, S.K. (2001). Synthesis and characterization of Pd(II) and Pt(II) complexes of 2-pyridyl methyl ketazine. Asia. J. Chem. *13*, 752-754.

Castro, P.M., Lahtinen, P., Axenov, K., Viidanoja, J., Kotiaho, T., Leskelä, M., and Repo, T. (2005). Activation of 2,6-Bis(imino)pyridine Iron(II) Chloride Complexes by Methylaluminoxane: An Electrospray Ionization Tandem Mass Spectrometry Investigation. *Organometallics 24*, 3664-3670. https://doi.org/10.1021/om050351s.

Zhang, G., Zeng, H., Wu, J., Yin, Z., Zheng, S., and Fettinger, J.C. (2016). Highly selective hydroboration of alkenes, ketones and aldehydes catalyzed by a well-defined manganese complex. Angew. Chem. Int. Ed. *128*, 14581-14584. https://doi.org/10.1002/ange.201607579.

Zhang, G., Wu, J., Zheng, S., Neary, M.C., Mao, J., Flores, M., Trovitch, R.J., and Dub, P.A. (2019). Redox-noninnocent ligand-supported vanadium catalysts for the chemoselective reduction of C═X (X = O, N) functionalities. J. Am. Chem. Soc. *141*, 15230-15239. https://doi.org/10.1021/jacs.9b07062.

Zhang, G., Wu, J., Zeng, H., Neary, M.C., Devany, M., Zheng, S. and Dub, P.A. (2019). Dearomatization and functionalization of terpyridine ligands leading to unprecedented zwitterionic Meisenheimer aluminum complexes and their use in catalytic hydroboration. ACS Catal. *9*, 874-884. https://doi.org/10.1021/acscatal.8b04096.

Sheldrick, G. M. (1981). SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data; University of Göttingen, Göttingen, Federal Republic of Germany.

Sheldrick, G. M. (2015). SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.*, *A71*, 3-8. https://doi.org/10.1107/S2053273314026370.

Dub P. A., Scott, B. L., and Gordon, J. C. (2015). Air-stable NNS (ENENES) ligands and their well-defined ruthenium and iridium complexes for molecular catalysis. Organometallics *34*, 4464-4479. https://doi.org/10.1021/acs.organomet.5b00432.

Blum, Y., Czarkie, D., Rahamim, Y., and Shvo, Y. (1985). (Cyclopentadienone)ruthenium carbonyl complexes - a new class of homogeneous hydrogenation catalysts. Organometallics *4*, 1459-1461. https://doi.org/10.1021/om00127a027.

Kuriyama, W., Matsumoto, T., Ogata, O., Ino, Y., Aoki, K., Tanaka, S., Ishida, K., Kobayashi, T., Sayo, N., and Saito, T. (2012). Catalytic hydrogenation of esters. Development of an efficient catalyst and processes for synthesising (R)-1,2-propanediol and 2-(l-menthoxy)ethanol. Org. Process Res. Dev. *16*, 166-171. https://doi.org/10.1021/op200234j.

Zhang, J., Leitus, G., Ben-David, Y., and Milstein, D. (2006). Efficient homogeneous catalytic hydrogenation of esters to alcohols. Angew. Chem. Int. Ed. *45*, 1113-1115. https://doi.org/10.1002/anie.200503771.

Chai, J.-D., and Head-Gordon, M. (2008). Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. Phys. Chem. Chem. Phys. *10*, 6615-6620. https://doi.org/10.1039/B810189B.

Grimme, S. (2006). Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comp. Chem. *27*, 1787-1799. https://doi.org/10.1002/jcc.20495.

Marenich, A. V., Cramer, C. J., and Truhlar, D. G. (2009). Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. J. Phys. Chem. B *113*, 6378-6396. https://doi.org/10.1021/jp810292n.

Pettersen, E.F., Goddard, T.D., Huang, C.C., Couch, G.S., Greenblatt, D.M., Meng, E.C., and Ferrin, T.E. (2004). UCSF Chimera—A visualization system for exploratory research and analysis. J. Comp. Chem. 1605-1612. https://doi.org/10.1002/jcc.20084.

Dub, P. A., and Gordon, J. C. (2017). Metal–ligand bifunctional catalysis: the "accepted" mechanism, the issue of concertedness, and the function of the ligand in catalytic cycles involving hydrogen atoms. ACS Catal. *7*, 6635-6655. https://doi.org/10.1021/acscatal.7b01791.

Kozuch, S., Lee, S. E., and Shaik, S. (2009). Theoretical analysis of the catalytic cycle of a nickel cross-coupling process: application of the energetic span model. Organometallics *28*, 1303-1308. https://doi.org/10.1021/om800772g.

Thiyagarajan, S., and Gunanathan, C. (2019). Ruthenium-catalyzed selective hydrogenation of epoxides to secondary alcohols. Org. Lett. *21*, 9774-9778. https://doi.org/10.1021/acs.orglett.9b03995.

Molander, G. A., and McKie, J. A. (1992). Samarium(II) iodide-induced reductive cyclization of unactivated olefinic ketones. Sequential radical cyclization/intermolecular nucleophilic addition and substitution reactions. J. Org. Chem. *57*, 3132-3139. https://doi.org/10.1021/jo00037a033.

Steiniger, K.A., and Lambert, T.H. (2021). Primary alcohols via nickel pentacarboxycyclopentadienyl diamide catalyzed hydrosilylation of terminal epoxides. Org. Lett. *23*, 8013-8017. https://doi.org/10.1021/acs.orglett.1c03029.

Kobylarski, M., Berthet, J.C, and Cantat, T. (2022). Reductive depolymerization of polyesters and polycarbonates with hydroboranes by using a lanthanum(iii) tris(amide) catalyst. Chem. Commun. *58*, 2830-2833. https://doi.org/10.1039/D2CC00184E.

Hadlington, T.J., Hermann, K., Frenking, G., and Cameron, J. (2014). Low coordinate germanium(II) and tin(II) hydride complexes: efficient catalysts for the hydroboration of carbonyl compounds. J. Am. Chem. Soc. *136*, 3028-3031. https://doi.org/10.1021/ja5006477.

Zhang, G., Li, S., Zeng, H., Zheng, S., and Neary, M.C. (2022). Diplumbane-catalysed solvent- and additive-free hydroboration of ketones and aldehydes. RSC Adv. *12*, 19086-19090. https://doi.org/10.1039/D2RA03731A.

Hudlicky, T., Tsunoda, T., Gadamasettild, K.G., Murry, J.A., and Keck, G.E. (1991). Yeast-mediated resolution of β-keto esters of prochiral alcohols. J. Org. Chem. *56*, 3619-3623. https://doi.org/10.1021/jo00011a031.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A, and Nakatsuji, H. et al. (2016). Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT.