

# <sup>t</sup>BuOLi-Promoted Hydroboration of Esters and Epoxides

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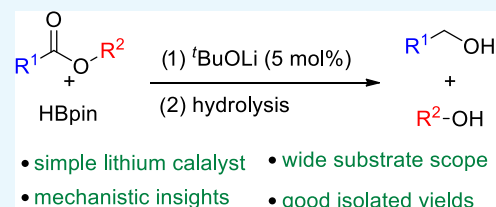
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**ABSTRACT:** Commercially available and inexpensive lithium *tert*-butoxide (<sup>t</sup>BuOLi) acts as a good precatalyst for the hydroboration of esters, lactones, and epoxides using pinacolborane as a borylation agent. Functional groups such as cyano-, nitro-, amino-, vinyl, and alkynyl are unaffected under the presented hydroboration process, representing high chemoselectivity. This transformation has also been effectively applied to the synthesis of key intermediates of Erlotinib and Cinacalcet. Preliminary investigations of the mechanism show that the hydroboration proceeds through the in situ formed BH<sub>3</sub> species.



## INTRODUCTION

The reduction of esters to alcohols is a fundamental transformation in organic chemistry for the production of a wide range of bulk and fine chemicals. The typical reduction reagents of esters include metal hydride compounds such as LiAlH<sub>4</sub>, NaBH<sub>4</sub>, NaH, and KH. However, major drawbacks include poor functional group tolerance, the formation of stoichiometric amounts of metallic waste, the need for laborious workup procedures for metal alkoxide intermediates, and the hazards involved in handling these highly reactive substances, which have hampered their development.<sup>1</sup> Catalytic hydrogenation of esters employing H<sub>2</sub> constitutes a completely atom-economic, waste-free, and environmentally benign transformation. However, it requires the use of flammable hydrogen gas under harsh reaction conditions such as high reaction temperature and pressure and/or costly dedicated catalysts.<sup>2</sup> The demanding conditions, along with frequent selectivity issues, strongly limit its synthetic applicability in the reduction of ester derivatives. Complementary to direct hydrogenation with molecular hydrogen, the transfer hydrogenation of esters using hydrogen donors such as alcohol is gaining a lot of attention because of its safety and operational simplicity. In this regard, several transition-metal-catalyzed transfer hydrogenations of esters have been reported.<sup>3</sup> The de Vries, Khaskin, Nikonov, and Clarke research groups independently developed transition-metal-catalyzed transfer hydrogenation of esters with cationic half-sandwich Ru complexes,<sup>3a</sup> Ru-SNS,<sup>3b</sup> Fe-PNP pincer complexes,<sup>3c</sup> and Mn-PNN pincer complexes.<sup>3d</sup> In addition, hydroelementation of unsaturated systems is becoming an issue of increasing importance to scientists.<sup>4</sup> Among them, catalytic hydrosilylation of esters has been extensively explored, with esters smoothly converted into the corresponding alcohol under catalysis with titanium,<sup>5</sup> iridium,<sup>6</sup> zinc,<sup>7</sup> ruthenium,<sup>8</sup> manganese,<sup>9</sup> and iron.<sup>10</sup> Although each approach has merits, many of these hydrosilylation methods are offset by the requirement of excessive high-cost and air-sensitive silanes such as PhSiH<sub>3</sub>, which has adversely affected the application of these strategies.

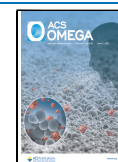
Compared with silanes, organoboranes are nontoxic; thus, they have become a preferable hydride choice. In contrast to the aforementioned ester hydrosilylation approaches, very limited examples regarding metal-catalyzed hydroboration of esters have been reported. Sadow et al. reported that the magnesium catalyst To<sup>M</sup>MgMe (To<sup>M</sup> = tris(4,4-dimethyl-2-oxazolinyl)-phenylborate) rapidly and efficiently catalyzed ester hydroboration via an ester cleavage zwitterionic reaction pathway.<sup>11</sup> Subsequently, Nembenna's group revealed the efficient hydroboration of esters using magnesium complexes bearing *N,N'*-chelated guanidinate and terminal amido ligands as a catalyst.<sup>12</sup> Next, homoleptic lanthanum complexes such as La[N-(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and La[C(SiHMe<sub>2</sub>)<sub>3</sub>]<sub>3</sub> were independently reported as efficient precatalysts for the hydroboration of a wide range of esters by the Marks, Sadow, and Xue groups.<sup>13</sup> Findlater found that the efficient hydroboration of esters could be realized using polynuclear lanthanide–diketonato clusters.<sup>14</sup> Recently, Eisen reported an efficient hydroboration of esters promoted by the thorium and uranium amide complexes U[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> and [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>An[κ<sup>2</sup>-(N,C)-CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>N(SiMe<sub>3</sub>)] (An = Th or U).<sup>15</sup> Owing to the complex nature of the reported ester hydroboration catalysts, these protocols have much room for improvement, particularly in terms of easily achieved simple catalysts and workup procedure.

Lithium compounds are frequently used in the dye, pigment, and pharmaceutical industries in preference to transition- or lanthanide-metal complexes.<sup>16</sup> Moreover, because most of the metal complexes are commonly prepared from the corresponding lithium reagents, direct use of lithium species in catalytic transformations would obviate the need for such additional

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synthesis of lithium reagents. The Sen group reported the efficient hydroboration of esters using two well-defined lithium complexes, 2,6-di-*tert*-butyl phenolate lithium and 1,1'-dilithioferrocene.<sup>17</sup> Recently, the Ding group reported the hydroboration of esters using a super hydride, LiHBEt<sub>3</sub>.<sup>18</sup> Apart from the aforementioned work, ester is the sole example of substrates that have been sporadically reported.<sup>19</sup> However, many of the reported lithium-catalyzed ester hydroboration protocols are marred by complexity and uncommercialized lithium catalysts. Recently, the hydroboration of unsaturated systems has been applied in synthetic solutions using main-group compounds as catalysts, as well as on catalyst-free approaches.<sup>20</sup> An's research group developed an efficient transition-metal-free protocol for the hydroboration of carbonyl and alkene functionalities.<sup>21a</sup> Hreczycho and co-workers reported that hydroboration of carbonyl compounds could be achieved in the presence of potassium fluoride.<sup>21b</sup> Zhao et al. showed that catalytic hydroboration of nonpolarized unsaturated compounds, such as alkenes, could be carried out in the presence of NaOH as a precatalyst.<sup>21c</sup> In this study, based on our previous hydroboration studies,<sup>22</sup> we herein present the results of our research on the catalytic hydroboration of esters and epoxides with simple <sup>t</sup>BuOLi and HBpin.

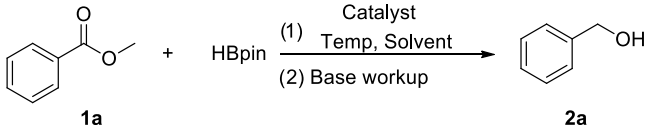
## RESULTS AND DISCUSSION

To optimize the reaction conditions for this <sup>t</sup>BuOLi-promoted ester hydroboration process, we selected methyl benzoate **1a** and pinacolborane as model reaction substrates. To our pleasure, the corresponding product **2a** was obtained in 32% yield after base workup when this reaction was conducted with Li<sub>2</sub>CO<sub>3</sub> (10 mol %) in 1,4-dioxane at 100 °C for 24 h (Table 1,

entry 1). Subsequently, the reaction conditions were optimized using different lithium catalysts, such as LiOCH<sub>3</sub>, <sup>t</sup>BuOLi, and lithium bis(trimethylsilyl)amide (LiHMDS), where <sup>t</sup>BuOLi and LiHMDS were found to give better results (Table 1, entries 2–4). Furthermore, NaHMDS and KHMDS were investigated, showing poor catalytic performance (Table 1, entries 5–6). The reaction could not work well when the catalyst was absent (Table 1, entry 7). When the catalyst loadings of <sup>t</sup>BuOLi and LiHMDS were reduced to 5 mol %, the yield of **2a** decreased to 83 and 80%, respectively (Table 1, entries 8–9). Next, the reaction conditions were optimized using different solvents, and THF was found to give the best result (Table 1, entries 10–13). We also studied the influence of the reaction temperature on this ester hydroboration process and found that 100 °C was the optimal reaction temperature (Table 1, entries 14–15). The yield of **2a** decreased to 82% when 2.2 equiv of HBpin was used (Table 1, entry 16). The yield of **2a** decreased to 79% while the reaction was performed in 18 h (Table 1, entry 17). Therefore, the optimal reaction conditions can be summarized as follows: 0.4 mmol of methyl benzoate and 1.0 mmol of HBpin in THF (1.0 mL) with <sup>t</sup>BuOLi catalyst (5 mol %), at 100 °C for 24 h.

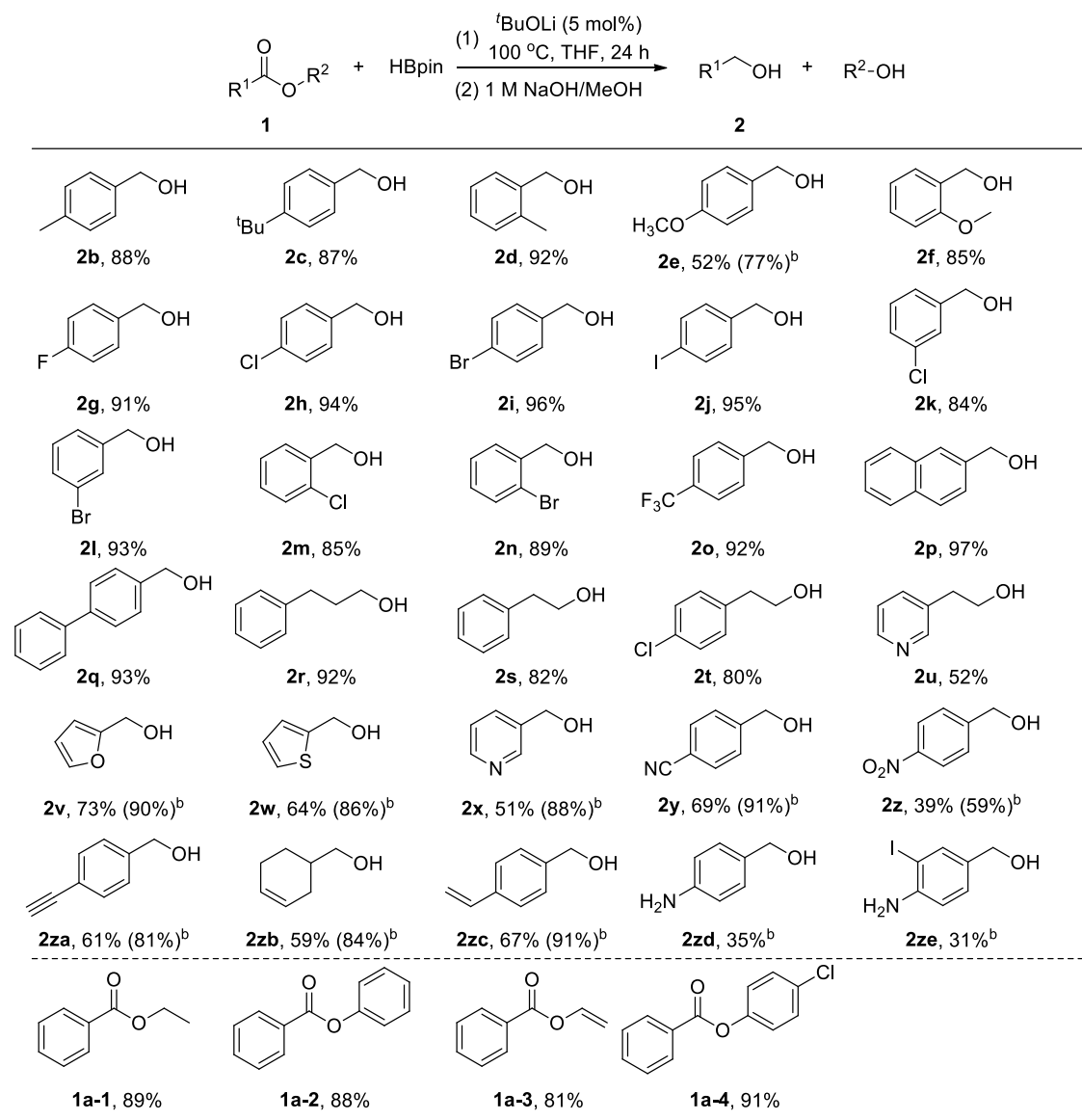
With the optimal conditions in hand, the substrate scope of the <sup>t</sup>BuOLi-promoted hydroboration of esters was explored. As shown in Scheme 1, a series of substituted methyl benzoates were tested and the reaction exhibited good functional group tolerance. The influence of substitutions on the aryl ring was investigated first. The electronic effect of the substituents affected the yields of this transformation to some extent. For example, when esters bearing an electron-donating methoxy group on the phenyl ring were examined, **2e** was obtained in a lower yield of 52% compared to those substrates with alkyl-containing groups attached to the aryl ring (**2b–2f**), respectively. Electron-withdrawing groups, such as fluoro, chloro, bromo, iodo, and trifluoromethyl on the phenyl ring, were well tolerated in this transformation, affording the desired alcohol products **2g–2o** in a higher yield, ranging from 84 to 96%. Functional groups, such as naphthyl and biphenyl, were also tolerated with observed yields of **2p** and **2q** in 97 and 93%, respectively. Next, aliphatic esters with alpha hydrogens (e.g., **1r–1u**) were also successfully transformed to target products **2r–2u** when subjected to the reaction conditions in moderate to good yield, ranging from 52 to 92%, with no Claisen condensation products formed, representing good chemoselectivity of the current catalytic system. To our delight, heteroaromatics such as furan, thiophene, and pyridine were found to be compatible, reaching 90% conversion with 10 mol % <sup>t</sup>BuOLi catalyst (**2v–2x**). It is worth noting that one of the major drawbacks of catalytic hydrogenations of esters is the low selectivity in the presence of additional unsaturated bonds. When we manage challenging substrates that might undergo additional hydroboration transformations, the additional cyano, nitro, C=C double bonds, and C≡C triple bonds remained intact, with only the ester group reacted (**2y–2zc**), representing high chemoselectivity of the <sup>t</sup>BuOLi catalytic system. To our delight, the catalytic system is effective for the transformation of amino-containing esters (**2zd–2ze**). In contrast, amino boranes can be easily formed via dehydrocoupling coupling reactions between the boranes and HBpin in the presence of alkaline-earth and alkali-metal catalysts,<sup>23</sup> and the amino group is usually incompatible in hydroboration reactions. Finally, when R<sup>2</sup> is equal with ethyl, phenyl, 4-chlorophenyl, and vinyl, these benzoates (**1a-1-1a-4**) were also well compatible in current

Table 1. Optimization of Reaction Conditions<sup>a</sup>



entry	catalyst (x mol %)	solvent	T (°C)	yield (%)
1	Li <sub>2</sub> CO <sub>3</sub> (10 mol %)	1,4-dioxane	100	32
2	LiOCH <sub>3</sub> (10 mol %)	1,4-dioxane	100	81
3	<sup>t</sup> BuOLi (10 mol %)	1,4-dioxane	100	86
4	LiHMDS (10 mol %)	1,4-dioxane	100	85
5	KHMDS (10 mol %)	1,4-dioxane	100	14
6	NaHMDS (10 mol %)	1,4-dioxane	100	17
7		1,4-dioxane	100	trace
8	<sup>t</sup> BuOLi (5 mol %)	1,4-dioxane	100	83
9	LiHMDS (5 mol %)	1,4-dioxane	100	80
10	<sup>t</sup> BuOLi (5 mol %)	toluene	100	76
11	<sup>t</sup> BuOLi (5 mol %)	hexane	100	78
12	<sup>t</sup> BuOLi (5 mol %)	DCE	100	81
13	<sup>t</sup> BuOLi (5 mol %)	THF	100	90
14	<sup>t</sup> BuOLi (5 mol %)	THF	80	71
15	<sup>t</sup> BuOLi (5 mol %)	THF	60	46
16 <sup>b</sup>	<sup>t</sup> BuOLi (5 mol %)	THF	100	82
17 <sup>c</sup>	<sup>t</sup> BuOLi (5 mol %)	THF	100	79

<sup>a</sup>Reactions were conducted using **1a** (0.4 mmol), HBpin (1.0 mmol) in 1.0 mL of solvent under N<sub>2</sub> atmosphere for 24 h. The yield was determined by <sup>1</sup>H NMR spectroscopy of the crude product after base workup with 1,3,5-trimethoxybenzene as an external standard. <sup>b</sup>2.2 equiv of HBpin was used. <sup>c</sup>18 h.

Scheme 1. Scope of the <sup>t</sup>BuOLi-Promoted Hydroboration of Esters<sup>a,b</sup>

<sup>a</sup>All of the experiments were carried out with 1 (1.0 mmol), HBpin (2.5 mmol), <sup>t</sup>BuOLi (5 mol %), THF (1.0 mL), 100 °C, N<sub>2</sub>, 24 h, isolated yield after base workup. <sup>b</sup><sup>t</sup>BuOLi (10 mol %).

transformation, affording the desired product **2a** in 81–91% isolated yield.

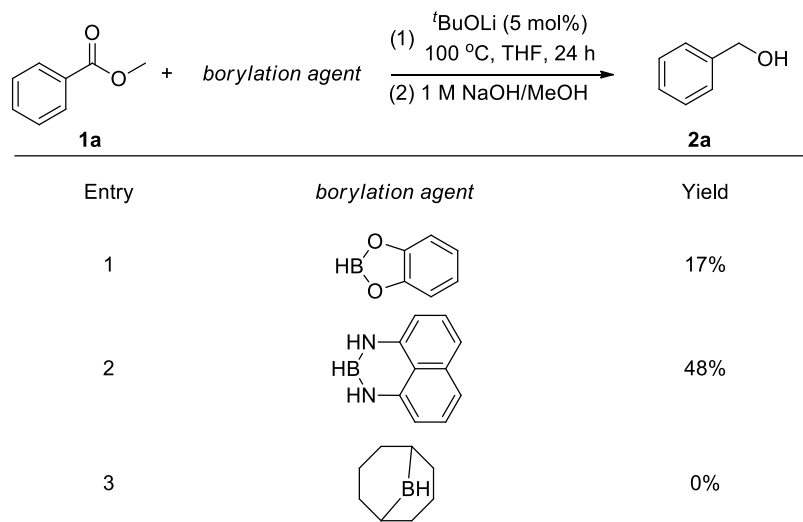
Other borylation agents such as catecholborane and 1,8-naphthalenediaminoborane instead of HBpin were also tested under the current reaction conditions, affording the desired product **2a** in 17–48% yield, respectively. The hydroboration of methyl benzoate failed when 9-borabicyclo[3.3.1]nonane was used as the borylation agent (Scheme 2).

We next focused our attention on the reduction of lactones. Selective formation of diols was achieved from lactones with HBpin, as shown in Scheme 3. The  $\delta$ -lactone 6-propyltetrahydro-2H-pyran-2-one (**1zf**) and  $\beta,\gamma$ -lactone 5-butyl-4-methyl-dihydrofuran-2(3H)-one (**1zg**) were fully converted into the corresponding nonane-1,5-diol (**2zf**) and 3-methyloctane-1,4-diol (**2zg**). Notably, isochroman-3-one (**1zh**) was converted selectively into 2-(2-(hydroxymethyl)phenyl)ethanol (**2zh**), which was isolated in 89% yield. Similarly, with isobenzofuran-

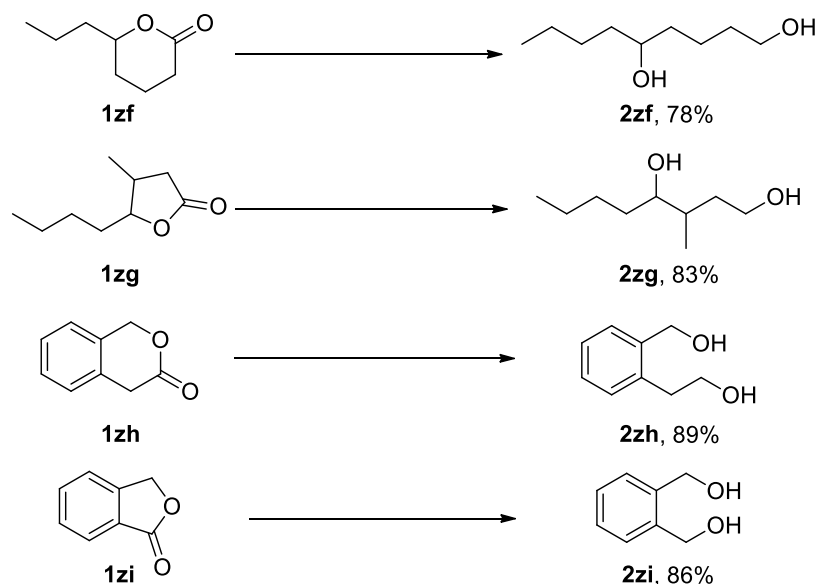
1(3H)-one (**1zi**) as the starting substrate, 1,2-phenylenedimethanol (**2zi**) was obtained in 86% yield.

On the basis of the high catalytic hydroboration reactivity of <sup>t</sup>BuOLi toward esters and lactones, we next investigated the ring-opening of epoxides to alcohols, which would also involve a C–O bond-cleavage step. As expected, <sup>t</sup>BuOLi is an active catalyst for this process, affording desired alcohol compounds **2zj**–**2zn** in high yields (Scheme 4).

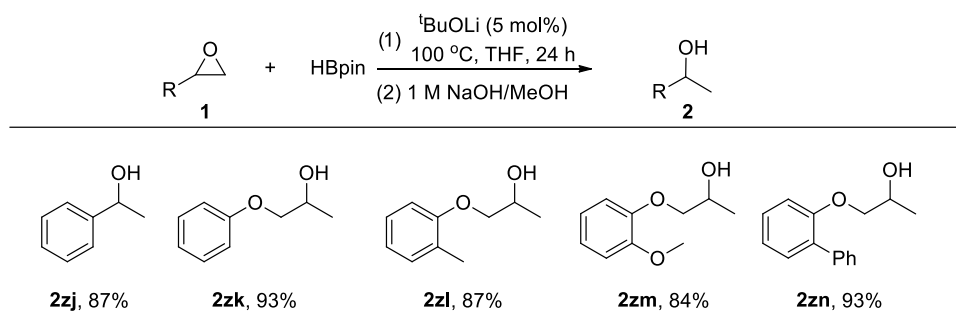
To show the scalability of this protocol, methyl 4-chlorobenzoate (**1h**) and HBpin were used at the gram scale (Scheme 5a). Pure (4-chlorophenyl)methanol **2h** was isolated in 91% yield (1.292 g). To demonstrate further the utility of our developed methodology in drug synthesis, some extended work was conducted. First, the key intermediate of tyrosine kinase inhibitor Erlotinib **2zo-1** was synthesized from the corresponding ester **1zo** through a two-step process in 50% overall yield (Scheme 5b). Furthermore, the utility of the current methodology was applied to the synthesis of 3-(3-(trifluoromethyl)-

Scheme 2. Scope of the Borylation Agent<sup>a</sup>

<sup>a</sup>All of the experiments were carried out with **1** (1.0 mmol), borylation agent (2.5 mmol), <sup>t</sup>BuOLi (5 mol %), THF (1.0 mL), 100 °C, N<sub>2</sub>, 24 h, isolated yield after base workup.

Scheme 3. Scope of the <sup>t</sup>BuOLi-Promoted Hydroboration of Lactones<sup>a</sup>

<sup>a</sup>All of the experiments were carried out with lactones (1.0 mmol), HBpin (2.5 mmol), <sup>t</sup>BuOLi (10 mol %), THF (1.0 mL), 100 °C, N<sub>2</sub>, 24 h, isolated yield after base workup.

Scheme 4. Scope of the <sup>t</sup>BuOLi-Promoted Hydroboration of Epoxides<sup>a</sup>

<sup>a</sup>All of the experiments were carried out with epoxide (1.0 mmol), HBpin (2.5 mmol), <sup>t</sup>BuOLi (5 mol %), THF (1.0 mL), 100 °C, N<sub>2</sub>, 24 h, isolated yield.

## Scheme 5. Gram-Scale Transformation and Applications of the Developed Method for Biologically Active Molecules Synthesis

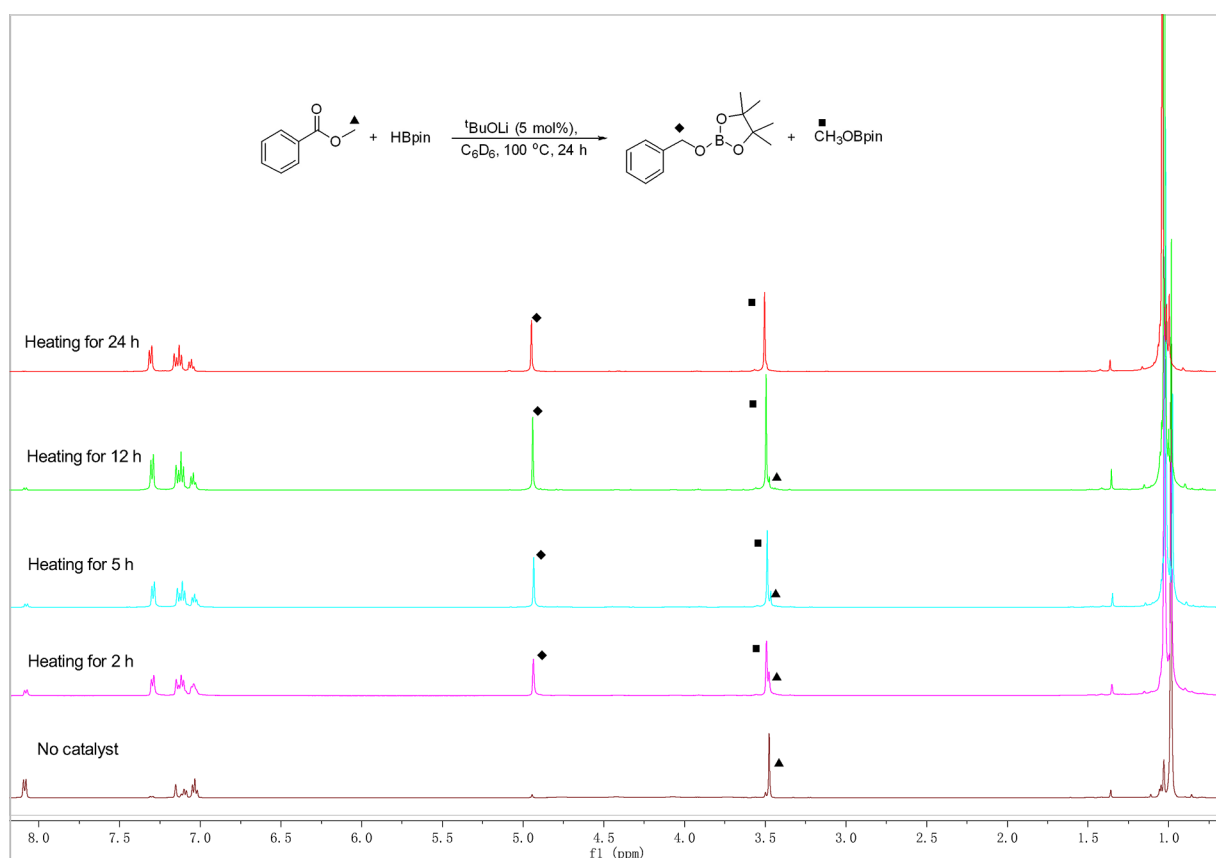
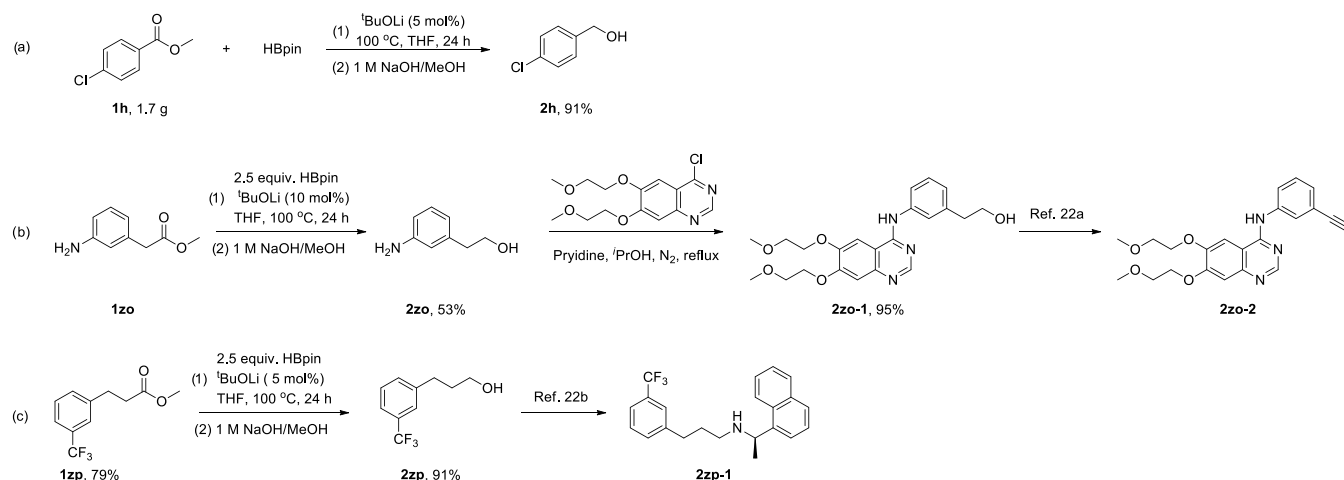


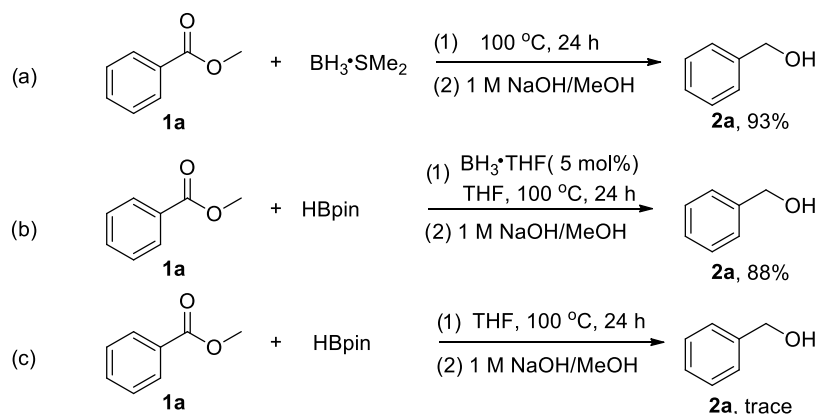
Figure 1.  $^1\text{H}$  NMR spectra for the progress of the reaction of **1a** and HBpin using  $^t\text{BuOLi}$  as a precatalyst in benzene- $d_6$  at  $100\text{ }^\circ\text{C}$ .

phenyl)propan-1-ol (**2zp**), which is the key intermediate of therapeutic agent Cinacalcet **2zp-1** (Scheme 5c).<sup>24</sup>

To gain insight into the mechanism of the reaction, some control experiments were performed. First,  $^1\text{H}$  NMR spectra for the progress of the model reaction were investigated and **1a** was cleanly converted into the corresponding hydroboration product benzylOBpin (Figure 1). According to the reported results, the hydroboration process is plagued by Trojan horse/hidden catalysis.<sup>25</sup> An's research group has shown that potassium carbonate acts as a catalyst in the hydroboration of carbonyl compounds reactions.<sup>21a</sup> Thomas and co-workers found that nucleophiles could promote the decomposition of

HBpin to release  $\text{BH}_3$ .<sup>26</sup> The reaction of HBpin with a catalytic amount of  $^t\text{BuOLi}$  together with  $\text{SMe}_2$  in benzene- $d_6$  at  $100\text{ }^\circ\text{C}$  for 30 min was performed to identify potential substrate-precatalyst complexes or catalyst intermediates with the aid of  $^{11}\text{B}$  NMR spectroscopy. The  $^{11}\text{B}$  NMR spectrum showed weak  $^{11}\text{B}$  signals at  $-13.50$ ,  $-20.67$ , and  $-39.83$  ppm (see Supporting Information Figure S1). The resonances at  $-13.50$  and  $-20.67$  ppm stem from  $\text{BH}_3$  and  $\text{BH}_3\text{-SMe}_2$ , respectively, whereas the  $-39.83$  ppm signal most likely arises from the  $\text{BH}_4^-$  anion.<sup>26a</sup> This result of  $^{11}\text{B}$  NMR spectroscopy shows that  $\text{BH}_3$  was formed in situ. The same control experiments were also carried out for the other borylation agents with  $^t\text{BuOLi}$  together with

## Scheme 6. Mechanistic Studies



$\text{SMe}_2$ , monitored by  $^{11}\text{B}$  NMR (see Supporting Information Figures S2–S4). No  $\text{BH}_3$  species were formed when 9-borabicyclo[3.3.1]nonane was used as the borylation agent. The  $\text{BH}_3$  was also found to be efficient reagent and catalyst for ester hydroboration (Scheme 6a,b). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) could form air- and moisture-stable mono- and bis-adducts with  $\text{BH}_3$ .<sup>26c</sup> To distinguish whether the in situ formed  $\text{BH}_3$  species acts as a real catalyst to drive the reaction, the  $^t\text{BuOLi}$ -promoted hydroboration reaction of methyl benzoate with TMEDA was further performed (Table 2). The addition of TMEDA significantly inhibited the

with its remarkable substrate tolerance, high chemoselectivity, and good yields, this method will be appealing for organic synthesis. Practical applications were demonstrated in a large-scale synthesis. This transformation has also been effectively applied to the synthesis of key intermediates of Erlotinib and Cinacalcet. Preliminary investigations of the mechanism show that the hydroboration proceeds through the in situ formed  $\text{BH}_3$  species. We believe this catalytic process to be very user-friendly, and we are investigating the use of this system in other reduction processes.

Table 2. Inhibition of Ester Hydroboration by TMEDA

entry	TMEDA: $^t\text{BuOLi}$	yield of 2a (%)
1 <sup>a</sup>	0:1	92
2 <sup>a</sup>	2:1	78
3 <sup>a</sup>	5:1	59
4 <sup>a</sup>	20:1	0
5 <sup>b</sup>	0:1	89
6 <sup>b</sup>	5:1	47
7 <sup>b</sup>	9:1	18

<sup>a</sup>Conditions: **1a** (1.0 mmol),  $^t\text{BuOLi}$  (0.05 mmol), HBpin (2.5 mmol), 100 °C, THF (1 mL), TMEDA,  $\text{N}_2$ , isolated yield.

<sup>b</sup>Conditions: **1a** (1.0 mmol),  $^t\text{BuOLi}$  (0.4 mmol), HBpin (2.5 mmol), room temperature, solvent-free, TMEDA,  $\text{N}_2$ , isolated yield.

hydroboration process, indicating that the in situ formed  $\text{BH}_3$  species was the key intermediate to drive the reaction. Finally, the ester hydroboration reaction failed to deliver the desired product **2a** when the  $^t\text{BuOLi}$  was absent (Scheme 6c), indicating that the  $^t\text{BuOLi}$  could promote the decomposition of HBpin to  $\text{BH}_3$  species.

## CONCLUSIONS

A general and practical  $^t\text{BuOLi}$ -promoted hydroboration of esters has been developed. Furthermore, lactones and epoxides underwent direct hydroboration with HBpin to give the desired alcohol products in synthetically useful yield after basic workup. Utilizing this low-toxicity, commercially available, and low-cost  $^t\text{BuOLi}$  as the initiator instead of environmentally unfriendly transition metals is the salient feature of this system. Coupled

## EXPERIMENTAL SECTION

**General Methods.** All hydroboration reactions were carried out under a moisture- and oxygen-free nitrogen atmosphere. 1,4-Dioxane, 1,2-dichloroethane (DCE), toluene, hexane, and tetrahydrofuran (THF) were taken from a solvent purification system (PS-400-5, Unilab Mbraun, Inc.). Glassware was predried in an oven at 100 °C for several hours and cooled prior to use.  $^t\text{BuOLi}$ , esters, lactones, and epoxides were obtained commercially from Energy Chemical, J&K, Acros Organics, Alfa Aesar, or TCI without further purification. Melting points are uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. Compounds **1zp**, **2zo-1**, and HBdan were synthesized according to ref 24. Deuterated solvents were obtained from Cambridge Isotope.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^{11}\text{B}$  NMR spectra were recorded on a JEOL ECA-500 NMR spectrometer (FT, 500 MHz for  $^1\text{H}$ ; 125 MHz for  $^{13}\text{C}$ ; 160 MHz for  $^{11}\text{B}$ ) at room temperature. All chemical shift values are quoted in ppm referenced to an internal tetramethylsilane at 0.00 ppm for  $^1\text{H}$  NMR and relative to residual  $\text{CHCl}_3$  at 77.16 ppm for  $^{13}\text{C}$  unless otherwise noted. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant (*J*) was reported in hertz. GC-MS analyses were measured on a Focus GC-ISQ MS instrument.

**General Procedure for  $^t\text{BuOLi}$ -Promoted Hydroboration of Esters.** In a nitrogen-filled glovebox, to a 10 mL Schlenk reaction tube equipped with a magnetic stirrer,  $^t\text{BuOLi}$  (4.0 mg, 5 mol %), THF (1.0 mL), HBpin (320.0 mg, 2.5 mmol), and the corresponding esters (1 mmol) were added in sequence. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 h. Thereafter, the reaction mixture was cooled down to room temperature and NaOH/MeOH (2 mL, 10% aq.) solution was added. The resulting mixture was stirred overnight for complete hydrolysis. Organic compounds were extracted from the mixture with  $\text{CH}_2\text{Cl}_2$  (3 × 12 mL). The

organic fraction was dried over  $\text{Na}_2\text{SO}_4$ , and all volatiles were removed using a rotary evaporator. The crude mixture was monitored by  $^1\text{H}$  NMR analysis using hexamethylbenzene or 1,3,5-trimethoxybenzene as the internal standard. The crude mixture was purified by flash column chromatography using PE/EtOAc (10/1) as the eluent to give the corresponding products.

**Benzyl Alcohol (2a).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (97.2 mg, 90%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37–7.36 (m, 4H), 7.32–7.28 (m, 1H), 4.67 (s, 2H), 2.01 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.0, 128.7, 127.8, 127.1, 65.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2d</sup>

**4-Methylbenzyl Alcohol (2b).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (107.4 mg, 88%), mp 61–62 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (d,  $J$  = 7.6 Hz, 2H), 7.16 (d,  $J$  = 7.7 Hz, 2H), 4.62 (s, 2H), 2.34 (s, 3H), 1.82 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 137.5, 129.4, 127.2, 65.4, 21.2. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3a</sup>

**4-tert-Butylbenzyl Alcohol (2c).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (142.7 mg, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J$  = 8.4 Hz, 2H), 7.31 (d,  $J$  = 8.5 Hz, 2H), 4.65 (s, 2H), 2.00 (brs, 1H), 1.34 (m, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 138.1, 127.0, 125.6, 65.2, 34.7, 31.5. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27a</sup>

**2-Methylbenzyl Alcohol (2d).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (112.2 mg, 92%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.34 (m, 1H), 7.23–7.19 (m, 3H), 4.67 (s, 2H), 2.35 (s, 3H), 2.08 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.8, 136.2, 130.4, 127.8, 127.6, 126.1, 63.5, 18.7. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>6a</sup>

**4-Methoxybenzyl Alcohol (2e).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (106.3 mg, 77%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J$  = 8.1 Hz, 2H), 6.87 (d,  $J$  = 7.7 Hz, 2H), 4.57 (s, 2H), 3.79–3.78 (m, 3H), 2.15 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 133.3, 128.7, 114.0, 64.9, 55.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2d</sup>

**2-Methoxybenzyl Alcohol (2f).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (117.3 mg, 85% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27–7.25 (m, 2H), 6.95–6.92 (m, 1H), 6.87 (d,  $J$  = 8.5 Hz, 1H), 4.66 (s, 2H), 3.83 (s, 3H), 2.58 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 129.2, 129.0, 128.8, 120.7, 110.3, 61.9, 55.3. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3d</sup>

**4-Fluorobenzyl Alcohol (2g).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (114.7 mg, 91%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.32 (m, 2H), 7.05–7.02 (m, 2H), 4.63 (s, 2H), 2.03 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 161.5, 136.8 (d,  $J$  = 3.1 Hz), 128.9 (d,  $J$  = 8.1 Hz), 115.5 (d,  $J$  = 21.4 Hz), 64.7. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3c</sup>

**4-Chlorobenzyl Alcohol (2h).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (133.5 mg, 94%), mp 74–75 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J$  = 8.4 Hz, 2H), 7.27 (d,  $J$  = 8.4 Hz, 2H), 4.63 (s, 2H), 2.11 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.4, 133.5, 128.8, 128.4, 64.6. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2d</sup>

**4-Bromobenzyl Alcohol (2i).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (178.6 mg, 96%), mp 76–77 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J$  = 8.2 Hz, 2H), 7.22 (d,  $J$  = 8.1 Hz, 2H), 4.62 (s, 2H), 2.03 (brs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 131.8, 128.7, 121.6, 64.6. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3d</sup>

**4-Iodobenzyl Alcohol (2j).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (222.3 mg, 95%), mp 71–72 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J$  = 8.1 Hz, 2H), 7.05 (d,  $J$  = 8.0 Hz, 2H), 4.56 (s, 2H), 2.60 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 137.6, 128.9, 93.0, 64.5. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3d</sup>

**3-Chlorobenzyl Alcohol (2k).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (119.3 mg, 84%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (s, 1H), 7.24–7.21 (m, 2H), 7.17 (d,  $J$  = 6.5 Hz, 1H), 4.59 (s, 2H), 2.60 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.9, 134.5, 129.9, 127.7, 127.0, 124.9, 64.5. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>9b</sup>

**3-Bromobenzyl Alcohol (2l).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (173.0 mg, 93%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (s, 1H), 7.40 (d,  $J$  = 7.6 Hz, 1H), 7.25–7.19 (m, 2H), 4.61 (s, 2H), 2.53 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.2, 130.7, 130.2, 130.0, 125.4, 122.7, 64.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27a</sup>

**2-Chlorobenzyl Alcohol (2m).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (120.7 mg, 85%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J$  = 7.3 Hz, 1H), 7.36–7.35 (m, 1H), 7.29–7.22 (m, 2H), 4.77 (s, 2H), 2.18 (brs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 132.9, 129.5, 129.0, 128.9, 127.1, 62.9. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>6a</sup>

**2-Bromobenzyl Alcohol (2n).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (165.5 mg, 89%), mp 78–79 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 8.0 Hz, 1H), 7.47 (d,  $J$  = 7.6 Hz, 1H), 7.34–7.31 (m, 1H), 7.17–7.14 (m, 1H), 4.73 (s, 2H), 2.33 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 132.7, 129.2, 129.0, 127.8, 122.7, 65.1. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2a</sup>

**4-(Trifluoromethyl)benzyl Alcohol (2o).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (161.9 mg, 92%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J$  = 7.9 Hz, 2H), 7.45 (d,  $J$  = 7.9 Hz, 2H), 4.73 (s, 2H), 2.30 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 130.2 (q,  $J$  = 32.4 Hz), 127.0, 125.6 (q,  $J$  = 3.7

Hz), 123.2, 64.6. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2d</sup>

**2-Naphthalenemethanol (2p).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (153.3 mg, 97%), mp 79–80 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85–7.84 (m, 3H), 7.80 (s, 1H), 7.50–7.47 (m, 3H), 4.85 (s, 2H), 2.00 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 138.5, 133.5, 133.1, 128.5, 128.0, 127.8, 126.3, 126.0, 125.6, 125.3, 65.6. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3d</sup>

**[1,1'-Biphenyl]-4-ylmethanol (2q).** Purified by column chromatography using petroleum ether/EtOAc = 3:1 as eluent. Obtained as a white solid (171.1 mg, 93%), mp 99–100 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 7.4 Hz, 4H), 7.48–7.44 (m, 4H), 7.39–7.36 (m, 1H), 4.73 (s, 2H), 2.20 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 140.9, 140.7, 140.0, 128.9, 127.6, 127.4 (d, *J* = 4.2 Hz), 127.2, 65.1. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27b</sup>

**3-Phenyl-1-propanol (2r).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (125.1 mg, 92%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.26–7.23 (m, 2H), 7.17–7.16 (m, 3H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.82 (s, 1H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.87–1.81 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 141.9, 128.4, 128.4, 125.8, 62.0, 34.2, 32.1. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3c</sup>

**Phenethyl Alcohol (2s).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (100.3 mg, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.30–7.27 (m, 2H), 7.21–7.18 (m, 3H), 3.76 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 6.7 Hz, 2H), 2.35 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 138.6, 129.1, 128.5, 126.4, 63.6, 39.2. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>7</sup>

**4-Chlorophenethylalcohol (2t).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (124.8 mg, 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.26 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.78 (t, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.09 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 137.2, 132.2, 130.4, 128.7, 63.4, 38.5. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3c</sup>

**2-(Pyridin-3-yl)ethanol (2u).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (64 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 8.41–8.40 (m, 1H), 7.57–7.54 (m, 1H), 7.13–7.07 (m, 2H), 4.51 (s, 1H), 3.95 (t, *J* = 5.6 Hz, 2H), 2.96 (t, *J* = 5.6 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 160.4, 148.7, 136.7, 123.5, 121.5, 61.7, 39.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>6b</sup>

**2-Furanmethanol (2v).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a yellow oil (88.2 mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.37 (s, 1H), 6.32–6.31 (m, 1H), 6.26 (d, *J* = 2.9 Hz, 1H), 4.55 (s, 2H), 2.65 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 154.1, 142.6, 110.4, 107.8, 57.3. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3c</sup>

**2-Thiophenemethanol (2w).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent.

Obtained as a colorless oil (98.0 mg, 86%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.27–7.26 (m, 1H), 6.98–6.97 (m, 2H), 4.78 (s, 2H), 2.44 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 144.1, 127.0, 125.7, 125.6, 60.1. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>6a</sup>

**3-Pyridinemethanol (2x).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (95.9 mg, 88%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 8.44–8.43 (m, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.30–7.27 (m, 1H), 4.71 (s, 2H), 3.59 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 148.5, 148.2, 137.0, 135.3, 123.7, 62.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2a</sup>

**4-(Hydroxymethyl)benzonitrile (2y).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (121.0 mg, 91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 4.75 (s, 2H), 2.44 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 146.5, 132.4, 127.1, 119.0, 111.1, 64.2. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2a</sup>

**4-Nitrobenzyl Alcohol (2z).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a white solid (90.3 mg, 59%), mp 94–95 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 4.82 (s, 2H), 2.30 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 148.4, 147.3, 127.1, 123.8, 64.1. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>6a</sup>

**4-Ethynylbenzyl Alcohol (2za).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (106.9 mg, 81%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 4.62 (s, 2H), 3.08 (s, 1H), 2.54 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 141.7, 132.4, 126.8, 121.3, 83.6, 77.3, 64.7. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27b</sup>

**3-Cyclohexene-1-methanol (2zb).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (94.1 mg, 84%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.69–5.64 (m, 1H), 3.55–3.49 (m, 2H), 2.12–2.05 (m, 3H), 1.82–1.72 (m, 3H), 1.63 (s, 1H), 1.31–1.23 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 127.3, 126.0, 67.9, 36.4, 28.2, 25.3, 24.7. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>9a</sup>

**4-Vinylbenzyl Alcohol (2zc).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (121.9 mg, 91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37–7.34 (m, 2H), 7.27–7.25 (m, 2H), 6.73–6.65 (m, 1H), 5.75–5.69 (m, 1H), 5.24–5.20 (m, 1H), 4.59–4.58 (m, 2H), 2.44 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 140.5, 137.0, 136.6, 127.3, 126.4, 113.9, 64.9. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>17</sup>

**4-Aminobenzyl Alcohol (2zd).** Purified by column chromatography using petroleum ether/EtOAc = 1:1 as eluent. Obtained as a colorless oil (43.1 mg, 35%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.15 (d, *J* = 7.6 Hz, 2H), 6.67 (d, *J* = 7.4 Hz, 2H), 4.54 (s, 2H), 3.67 (brs, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) 146.1, 131.2, 128.9, 115.3, 65.3. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3d</sup>



**4-Amino-3-iodo-phenyl-methanol (2ze).** Purified by column chromatography using petroleum ether/EtOAc = 1:1 as eluent. Obtained as a colorless oil (77.2 mg, 31%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (s, 1H), 7.13 (d,  $J = 8.1$  Hz, 1H), 6.72 (d,  $J = 8.1$  Hz, 1H), 4.51 (s, 2H), 4.10 (brs, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 138.2, 132.7, 128.9, 114.7, 84.1, 64.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27c</sup>

**Nonane-1,5-diol (2zf).** Purified by column chromatography using petroleum ether/EtOAc = 2:1 as eluent. Obtained as a colorless oil (124.8 mg, 78%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.59–3.54 (m, 3H), 3.28 (brs, 1H), 2.93 (brs, 1H), 1.56–1.27 (m, 12H), 0.88–0.85 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  71.7, 62.4, 37.3, 36.9, 32.5, 28.0, 22.8, 21.9, 14.1. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>9b</sup>

**3-Methyl-1,4-octanediol (2zg).** Purified by column chromatography using petroleum ether/EtOAc = 2:1 as eluent. Obtained as a colorless oil (132.8 mg, 83%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.72–3.52 (m, 3H), 3.37–3.34 (m, 1H), 1.73–1.63 (m, 2H), 1.54–1.22 (m, 7H), 0.91–0.85 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  75.8, 75.0 (d,  $J = 3.3$  Hz), 60.5, 60.3, 36.5, 36.1, 36.1, 35.4, 34.2, 33.3, 28.8, 28.1, 22.9, 16.6, 14.2, 14.0. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>9b</sup>

**2-[2-(Hydroxymethyl)phenyl]ethanol (2zh).** Purified by column chromatography using petroleum ether/EtOAc = 2:1 as eluent. Obtained as a colorless oil (135.3 mg, 89%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (d,  $J = 8.0$  Hz, 2H), 7.18–7.15 (m, 2H), 4.51 (s, 2H), 4.32 (brs, 1H), 3.73 (t,  $J = 6.0$  Hz, 2H), 2.83 (t,  $J = 5.9$  Hz, 2H), 2.40 (brs, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 138.3, 130.2, 129.8, 128.6, 126.8, 63.3, 63.0, 35.2. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27d</sup>

**1,2-Benzenedimethanol (2zi).** Purified by column chromatography using petroleum ether/EtOAc = 2:1 as eluent. Obtained as a colorless oil (118.7 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (s, 4H), 4.54 (s, 4H), 4.30 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 129.5, 128.4, 63.5. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>2b</sup>

**1-Phenylethan-1-ol (2zj).** Purified by column chromatography using petroleum ether/EtOAc = 3:1 as eluent. Obtained as a colorless oil (106.2 mg, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32–7.31 (m, 4H), 7.24 (m, 1H), 4.81 (q,  $J = 6.3$  Hz, 1H), 2.55 (s, 1H), 1.44 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 128.6, 127.6, 125.5, 70.5, 25.3. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>3a</sup>

**1-Phenoxypropan-2-ol (2zk).** Purified by column chromatography using petroleum ether/EtOAc = 3:1 as eluent. Obtained as a colorless oil (141.4 mg, 93%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.28 (m, 2H), 6.99–6.96 (m, 1H), 6.92 (d,  $J = 7.9$  Hz, 2H), 4.20 (s, 1H), 3.95 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 3.1$  Hz, 1H), 3.82–3.79 (m, 1H), 2.53 (s, 1H), 1.29 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 129.6, 121.2, 114.7, 73.4, 66.4, 18.9. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27e</sup>

**1-(*o*-Tolyloxy)propan-2-ol (2zl).** Purified by column chromatography using petroleum ether/EtOAc = 3:1 as eluent. Obtained as a colorless oil (144.4 mg, 87%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17–7.15 (m, 2H), 6.91–6.88 (m, 1H), 6.82

(d,  $J = 8.4$  Hz, 1H), 4.23 (s, 1H), 3.95 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 3.1$  Hz, 1H), 3.82 (t,  $J = 8.0$  Hz, 1H), 2.40 (s, 1H), 2.26 (s, 3H), 1.31 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 130.9, 127.0, 126.9, 121.0, 111.4, 73.4, 66.6, 19.0, 16.4. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27e</sup>

**1-(2-Methoxyphenoxy)propan-2-ol (2zm).** Purified by column chromatography using petroleum ether/EtOAc = 3:1 as eluent. Obtained as a colorless oil (152.9 mg, 84%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98–6.89 (m, 4H), 4.20–4.17 (m, 1H), 4.00 (dd,  $J_1 = 9.6$  Hz,  $J_2 = 2.6$  Hz, 1H), 3.86 (s, 3H), 3.79 (t,  $J = 9.0$  Hz, 1H), 3.24 (s, 1H), 1.24 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.1, 148.3, 122.3, 121.2, 115.5, 112.1, 76.0, 66.1, 55.9, 18.5. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27e</sup>

**1-([1,1'-Biphenyl]-2-yloxy)propan-2-ol (2zn).** Purified by column chromatography using petroleum ether/EtOAc = 3:1 as eluent. Obtained as a colorless oil (212.0 mg, 93%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 7.6$  Hz, 2H), 7.44–7.41 (m, 2H), 7.35–7.31 (m, 3H), 7.09–7.06 (m, 1H), 6.99 (d,  $J = 8.1$  Hz, 1H), 4.07–4.04 (m, 1H), 3.98 (dd,  $J_1 = 9.1$  Hz,  $J_2 = 2.8$  Hz, 1H), 3.75 (t,  $J = 8.5$  Hz, 1H), 2.05 (s, 1H), 1.19 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 138.5, 131.6, 131.0, 129.5, 128.8, 128.2, 127.2, 121.8, 113.5, 74.4, 66.3, 18.7. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>27e</sup>

**2-(3-Aminophenyl)ethan-1-ol (2zo).** Purified by column chromatography using petroleum ether/EtOAc = 1:1 as eluent. Obtained as a colorless oil (72.6 mg, 53%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11–7.08 (m, 1H), 6.62 (d,  $J = 7.5$  Hz, 1H), 6.56–6.55 (m, 2H), 3.81 (t,  $J = 6.5$  Hz, 2H), 2.90 (brs, 2H), 2.76 (t,  $J = 6.5$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 139.9, 129.6, 119.4, 115.9, 113.4, 63.6, 39.3. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>24a</sup>

**2-(3-((6,7-bis(2-Methoxyethoxy)quinazolin-4-yl)amino)phenyl)ethan-1-ol (2zo-1).** Purified by column chromatography using dichloromethane/methanol = 20:1 as eluent. Obtained as a light yellow solid (392.4 mg, 95%), mp 76–77 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (s, 1H), 8.15 (brs, 1H), 7.45 (d,  $J = 7.9$  Hz, 1H), 7.40 (s, 1H), 7.29 (s, 1H), 7.17–7.14 (m, 1H), 7.06 (s, 1H), 6.87 (d,  $J = 7.5$  Hz, 1H), 4.11–4.08 (m, 4H), 3.77–3.72 (m, 4H), 3.66 (m, 2H), 3.36 (s, 3H), 3.32 (s, 3H), 2.74 (t,  $J = 5.9$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.8, 154.3, 153.5, 148.6, 147.1, 139.9, 138.8, 129.0, 125.0, 123.1, 120.5, 109.4, 108.2, 102.9, 70.8, 70.4, 68.8, 68.2, 63.1, 59.2, 59.2, 39.2. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>24a</sup>

**3-(3-Trifluoromethylphenyl)propionic Acid Methyl Ester (1zp).** Purified by column chromatography using EtOAc as eluent. Obtained as a colorless oil (183.3 mg, 79%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.44 (m, 2H), 7.38–7.37 (m, 2H), 3.64 (s, 3H), 2.99 (t,  $J = 7.7$  Hz, 2H), 2.63 (t,  $J = 7.8$  Hz, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 141.5, 131.9, 130.8 (q,  $J = 32$  Hz), 129.0, 125.3, 125.1 (q,  $J = 3.6$  Hz), 123.2 (q,  $J = 3.7$  Hz), 51.6 (d,  $J = 5.1$  Hz), 35.3, 30.7. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>24b</sup>

**3-(3-Trifluoromethylphenyl)propan-1-ol (2zp).** Purified by column chromatography using petroleum ether/EtOAc = 10:1 as eluent. Obtained as a colorless oil (185.6 mg, 91%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46–7.44 (m, 2H), 7.41–7.38 (m, 2H),

3.67 (t,  $J = 6.4$  Hz, 2H), 2.76 (t,  $J = 7.6$  Hz, 2H), 1.95 (s, 1H), 1.93–1.87 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.9, 132.0, 130.8 (q,  $J = 32$  Hz), 128.9, 125.5, 125.2 (q,  $J = 3.7$  Hz), 123.3, 122.9 (q,  $J = 3.8$  Hz), 62.0, 34.0, 31.9. Spectroscopic data for the title compound were consistent with those reported in the literature.<sup>24b</sup>

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c01866>.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all products (PDF)

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### Notes

The authors declare no competing financial interest.

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