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## Introduction

The selective introduction of a fluorine or fluoroalkyl moiety into molecules often results in improved physical, chemical, and biological properties.<sup>1</sup> In particular, the installation of a monofluoromethyl ( $\text{CH}_2\text{F}$ ) group as a bioisostere of various functional groups, such as methyl and hydroxymethyl, has been established as a robust and routine tactic in pharmaceutical chemistry and agrochemistry to tune the properties of bioactive compounds, including bioavailability and metabolic stability.<sup>2</sup> Typical drugs or inhibitors featuring a  $\text{CH}_2\text{F}$  unit are shown in Scheme 1a.<sup>3</sup> However, despite the significant progress made in selective fluoroalkylation,<sup>4</sup> the efficient incorporation of a  $\text{CH}_2\text{F}$  group in a highly enantioselective manner remains challenging and very much in demand.<sup>5</sup>

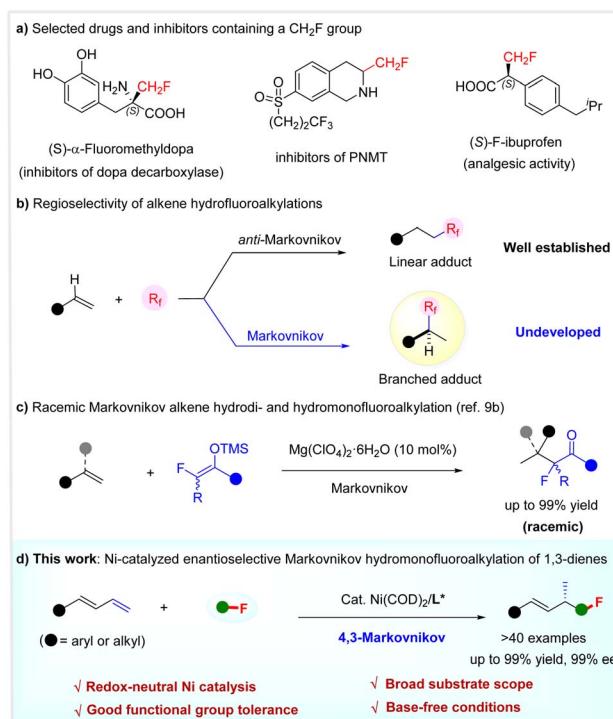
While the hydrofluoroalkylation of alkenes is a powerful strategy to introduce a fluoroalkyl group selectively,<sup>6</sup> the catalytic enantioselective incorporation of a monofluoroalkyl group is unexplored. Notably, most known alkene hydrofluoroalkylations are based on radical processes, affording linear adducts with anti-Markovnikov regioselectivity.<sup>6,7</sup> It is considered both interesting and urgent to develop the Markovnikov hydrofluoroalkylation of olefins. This not only offers the potential to

## Nickel-catalyzed regio- and enantio-selective Markovnikov hydromonofluoroalkylation of 1,3-dienes<sup>†</sup>

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A highly enantio- and regio-selective Markovnikov hydromonofluoro(methyl)alkylation of 1,3-dienes was developed using redox-neutral nickel catalysis. It provided a facile strategy to construct diverse monofluoromethyl- or monofluoroalkyl-containing chiral allylic molecules. Notably, this represents the first catalytic asymmetric Markovnikov hydrofluoroalkylation of olefins. The practicability of this methodology is further highlighted by its broad substrate scope, mild base-free conditions, excellent enantio- and regio-selectivity, and diversified product elaborations to access useful fluorinated building blocks.

develop catalytic enantioselective versions, but would afford branched adducts with a chemical space shape distinct from linear products, which are interesting targets for drug discovery because of the intimate relationship between the shape and their properties of organic molecules (Scheme 1b).<sup>8</sup> Following our interest in selective fluoroalkylation,<sup>9</sup> we recently developed the



Scheme 1 Regioselective hydrofluoroalkylation of alkenes.

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first Markovnikov hydrodi- and hydromonofluoroalkylation of simple alkenes using fluorinated enol silyl ethers, *via* an acid-catalyzed carbocationic process (Scheme 1c).<sup>9b</sup> Herein, we disclose a highly regio- and enantio-selective Markovnikov hydromonofluoro(methyl)alkylation reaction of 1,3-dienes by redox-neutral Ni catalysis (Scheme 1d).

Transition-metal-catalyzed regio- and enantio-selective hydrofunctionalization of 1,3-dienes **1** offers an efficient and atom-economical method to access chiral functionalized allylic compounds from readily available starting materials.<sup>10</sup> Over the past few years, various highly enantioselective protocols have been used: hydroamination,<sup>11</sup> hydroalkylation,<sup>12</sup> hydroarylation,<sup>13</sup> and hydrosulfonylation,<sup>14</sup> among others.<sup>15</sup> Despite the advances made, these reactions mainly rely on using chiral precious metal Pd and Rh catalysts. Since the landmark work of the Zhou group in 2018,<sup>12c</sup> the use of earth-abundant and low-cost chiral Ni catalysts for developing the asymmetric hydrofunctionalization of acyclic 1,3-dienes has gained increasing attention.<sup>12c,e,f,13b,c</sup> Despite ongoing achievements, the catalytic enantio- and regio-selective Markovnikov hydromonofluoromethylation of 1,3-dienes to construct functionalized chiral allylic compounds with a  $\text{CH}_2\text{F}$  at the stereocenter is unexplored.

Inspired by these elegant advances, we speculated that the implementation of catalytic asymmetric 1,3-dienes hydromonofluoromethylation would provide a new direction for enantioselective monofluoromethylation and constitutes a new branch for the hydrofunctionalizations of 1,3-dienes. To reach this goal, the quest for a suitable monofluoromethyl reagent would be the key to success. Among various monofluoromethyl agents, fluorobis(phenyl-sulfonyl)methane (FBSM) **2a** proves to be a robust one in developing catalytic enantioselective monofluoromethylation reactions,<sup>5,16</sup> since the landmark work of Shibata.<sup>16a</sup> On this basis, we determined to use FBSM **2a** as a latent monofluoromethyl agent to explore the asymmetric Markovnikov hydromonofluoromethylation of 1,3-dienes **1** under the action of chiral nickel catalysis.

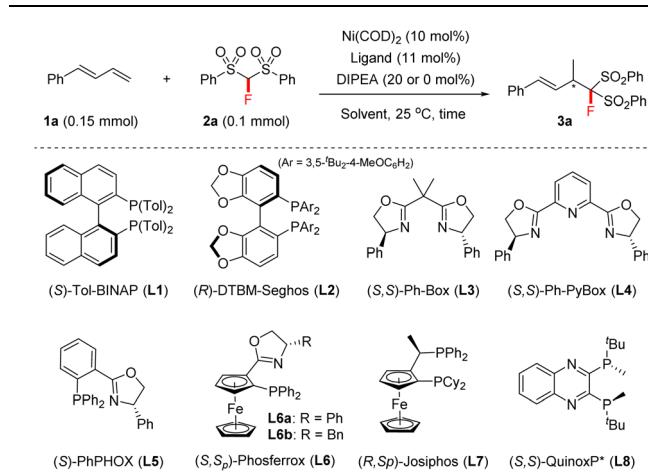
## Results and discussion

### Optimization of the reaction conditions

We commenced this study with 1-phenylbuta-1,3-diene **1a** and FBSM **2a** as the model substrates, in the presence of  $\text{Ni}(\text{COD})_2$  (10 mol%) and *N,N*-diisopropylethylamine (DIPEA) (20 mol%). As shown in Table 1, a series of axially chiral bisphosphine ligands were first investigated. The use of (*S*)-Tol-BINAP afforded the 4,3-Markovnikov adduct **3a** in 98% NMR yield with 37% ee within 14 h (entry 1), whilst the bulky (*R*)-DTBM-Segphos **L2** afforded product **3a** in only 9% NMR yield and 27% ee after 48 h (entry 2).

Encouraged by these results, we then tested the performance of chiral bisoxazoline ligands and *P,N*-based PHOX (entries 3–6), and found that the use of (*S,Sp*)-Ph-Phosferrox **L6a** could improve the ee of product **3a** to 68% (entry 6). Interestingly, base DIPEA proved to be unnecessary in the current reaction. A comparable result was obtained in the absence of DIPEA (entries 6 vs. 7). The focus of further optimization was on chiral ferrocene-based chiral ligands, but there was no improvement

Table 1 Selected conditions for optimization<sup>a</sup>



Entry	Ligand	DIPEA (mol%)	Solvent	Time (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	<b>L1</b>	20	EtOH	14	98	37
2	<b>L2</b>	20	EtOH	48	9	27
3	<b>L3</b>	20	EtOH	24	4	22
4	<b>L4</b>	20	EtOH	24	nr <sup>d</sup>	—
5	<b>L5</b>	20	EtOH	14	79	22
6	<b>L6a</b>	20	EtOH	10	89	68
7	<b>L6a</b>	0	EtOH	10	90	67
8	<b>L6b</b>	0	EtOH	22	50	64
9	<b>L7</b>	0	EtOH	22	50	78
10	<b>L8</b>	0	EtOH	16	95	96
11	<b>L8</b>	0	Toluene	24	84	70
12	<b>L8</b>	0	THF	24	99	86
13	<b>L8</b>	0	$\text{CH}_2\text{Cl}_2$	24	Trace	—
14	<b>L8</b>	0	MeOH	24	Trace	—
15	<b>L8</b>	0	$\text{iPrOH}$	24	Trace	—
16 <sup>e</sup>	<b>L8</b>	0	EtOH	72	86	96

<sup>a</sup> Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol),  $\text{Ni}(\text{COD})_2$  (10 mol%), ligand (11 mol%), and DIPEA (20 or 0 mol%), run at 25 °C in the indicated solvent (1.0 mL), unless otherwise noted.

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as the internal standard. <sup>c</sup> Determined by chiral HPLC. <sup>d</sup> No reaction. <sup>e</sup> Run on a 0.25 mmol scale using  $\text{Ni}(\text{COD})_2$  (5 mol%) and **L8** (5.5 mol%).

in the ee values (entry 8, see the ESI† for details). Subsequently, we turned our attention to exploring *P*-chiral phosphine ligands because they usually exhibit distinct chirality-inducing ability.<sup>17</sup> To our delight, *P*-chiral (*S,S*)-QuinoxP\*<sup>18</sup> **L8**, never before used in hydrofunctionalizations of 1,3-dienes, proved to be efficient; it afforded **3a** in 95% NMR yield with 96% ee within 16 h (entry 10). An examination of the solvent effect revealed that EtOH was still the best solvent (entries 10 vs. 11–15), although the use of THF also afforded the desired product **3a** in 99% NMR yield, but with a slightly lower ee (entry 12). Moreover, the use of a 5 mol% Ni catalyst afforded the product **3a** in 86% isolated yield with 96% ee, albeit within 72 h (entry 16).

### Evaluation of substrate scope

With the optimized conditions in hand, we explored the generality of this Markovnikov hydromonofluoromethylation in



EtOH under the catalysis of a 5 mol% or 10 mol% *P*-chiral (*S,S*)-QuinoxP\* decorated Ni(COD)<sub>2</sub> complex (Table 2).

Various aromatic 1,3-dienes with different electron-donating and -withdrawing groups on the aryl ring were viable substrates, affording the corresponding 4,3-Markovnikov adducts **3b**–**3r** in 48–99% yields with 90–99% ee (entries 2–18). The increase in reaction temperature was necessary to ensure full conversion in the cases of *ortho*- or *meta*-substituted aromatic 1,3-dienes. Of note is that the current reaction tolerated various functional groups on the aryl ring of 1,3-dienes: amine (**3g**), non-conjugated

alkene (**3h**), ester (**3j**), nitrile (**3k**), ketone (**3l**), and aldehyde (**3m**). Naphthyl-, 2-furyl-, and 2-thienyl-substituted 1,3-dienes all worked smoothly with **2a** to afford **3s**–**3v** in excellent yields and ee values (entries 19–22). A conjugated triene was also tolerated; it afforded product **3w** in 99% yield and with 97% ee (entry 23). Remarkably, the aliphatic 1,3-dienes, which are generally very challenging in terms of controlling both regio- and enantio-selectivity due to the small steric hindrance of the alkyl group,<sup>12c</sup> proved to be compatible in our reaction system. They afforded the adducts **3x**–**3z** with up to 81% yields and 94% ee at slightly elevated temperatures (entries 24–26). Notably, the ketone functionalities attached in aliphatic 1,3-diene were also compatible well (**3z**). The differently substituted FBSM **2b** and **2c** also reacted efficiently with 1-phenylbuta-1,3-diene **1a** at 50 °C to afford the targets **3aa** (94% yield and 97% ee) and **3ab** (99% yield and 95% ee). Furthermore, (*S*)-citronellal-derived alkyl 1,3-diene also reacted smoothly to afford adduct **3ac** in moderate yield and with 95% de. X-ray diffraction (XRD) analysis revealed that the absolute configuration of **3a** was (*S*). Subsequently, (*S*) was assigned to all other products **3** by analogy.

Unsurprisingly, the FBSM adduct **3a** could efficiently undergo a reductive desulfonylation to access chiral  $\alpha$ -monofluoromethyl ( $\text{CH}_2\text{F}$ ) allylic compound **4a** with 96% ee under the action of Mg/MeOH<sup>19</sup> (Scheme 2A). This result stimulated us to explore the assembly of deuterated monofluoromethyl ( $\text{CD}_2\text{F}$ )-containing chiral allylic molecules, given that the incorporation of a deuterium atom in the bioactive molecules is emerging as a promising tactic to modulate the bioactivity or pharmacological properties in drug discovery programs since the first deuterated drug, Austedo, was approved by FDA in 2017.<sup>20a</sup> However, while the development of efficient approaches for preparing deuterated compounds is of current interest, the selective introduction of a  $\text{CD}_2\text{F}$  group into the stereogenic center is still a challenging task and remains unexplored.<sup>21</sup> To

Table 2 Scope of hydromonofluoromethylation of dienes with **2**<sup>a</sup>

Entry	1: substituent (●)	2	Time (d)	3	Yield (%)	ee (%)
1	<b>1a</b> : $\text{C}_6\text{H}_5$	<b>2a</b>	3	<b>3a</b>	86	96
2	<b>1b</b> : 4-MeC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3b</b>	99	94
3	<b>1c</b> : 4-MeOC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3c</b>	97	97
4 <sup>b</sup>	<b>1d</b> : 3-MeOC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3d</b>	86	98
5 <sup>b</sup>	<b>1e</b> : 2-MeOC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3e</b>	93	98
6	<b>1f</b> : 3,5-Me <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>2a</b>	3	<b>3f</b>	98	99
7 <sup>b</sup>	<b>1g</b> : 4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3g</b>	48	93
8	<b>1h</b> : 4-CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3h</b>	68	95
9	<b>1i</b> : 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3i</b>	94	97
10	<b>1j</b> : 4-EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3j</b>	82	96
11	<b>1k</b> : 4-CNC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3k</b>	90	98
12	<b>1l</b> : 4-COMeC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3l</b>	90	98
13	<b>1m</b> : 4-CHOC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	3	<b>3m</b>	71	90
14	<b>1n</b> : 4-ClC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3n</b>	87	97
15	<b>1o</b> : 4-FC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3o</b>	74	99
16 <sup>c</sup>	<b>1p</b> : 3-FC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3p</b>	92	96
17 <sup>c</sup>	<b>1q</b> : 2-FC <sub>6</sub> H <sub>4</sub>	<b>2a</b>	4	<b>3q</b>	99	94
18	<b>1r</b> : 3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>2a</b>	3	<b>3r</b>	49	95
19	<b>1s</b> : 2-naphthyl	<b>2a</b>	3	<b>3s</b>	97	99
20 <sup>c</sup>	<b>1t</b> : 1-naphthyl	<b>2a</b>	3	<b>3t</b>	98	91
21 <sup>b</sup>	<b>1u</b> : 2-furyl	<b>2a</b>	3	<b>3u</b>	85	93
22 <sup>b</sup>	<b>1v</b> : 2-thienyl	<b>2a</b>	3	<b>3v</b>	98	98
23	<b>1w</b> : (E)-Ph-CH=CH	<b>2a</b>	5	<b>3w</b>	99	97
24 <sup>d</sup>	<b>1x</b> : <i>n</i> -C <sub>5</sub> H <sub>11</sub>	<b>2a</b>	3	<b>3x</b>	67	93
25 <sup>d</sup>	<b>1y</b> : PhCH <sub>2</sub> CH <sub>2</sub>	<b>2a</b>	5	<b>3y</b>	81	90
26 <sup>d</sup>	<b>1z</b> :	<b>2a</b>	4	<b>3z</b>	69	94
27 <sup>b</sup>	<b>1a</b> : C <sub>6</sub> H <sub>5</sub>	<b>2b</b>	5	<b>3aa</b>	94	97
28 <sup>b</sup>	<b>1a</b> : C <sub>6</sub> H <sub>5</sub>	<b>2c</b>	5	<b>3ab</b>	99	95
				5 d, 42%, 95% de <sup>b</sup>		

<sup>a</sup> Conditions: **1** (0.375 mmol), **2** (0.25 mmol), and EtOH (2.5 mL), at rt, unless otherwise noted; yields of the isolated products are reported; the ee values were determined by chiral HPLC analysis. For **3a**, **3c**, **3o**, and **3s**: Ni(COD)<sub>2</sub> (5 mol%) and **L8** (5.5 mol%) were used; for the others: Ni(COD)<sub>2</sub> (10 mol%) and **L8** (11 mol%) were used. <sup>b</sup> At 50 °C. <sup>c</sup> At 60 °C. <sup>d</sup> At 70 °C.

**A) Reductive desulfonylation of **3a****

**B) Tandem synthesis of chiral  $\alpha$ -CH<sub>2</sub>F or  $\alpha$ -CD<sub>2</sub>F molecules **4** or **D-4****

**Scheme 2** Synthetic applications of hydromonofluoromethylation.

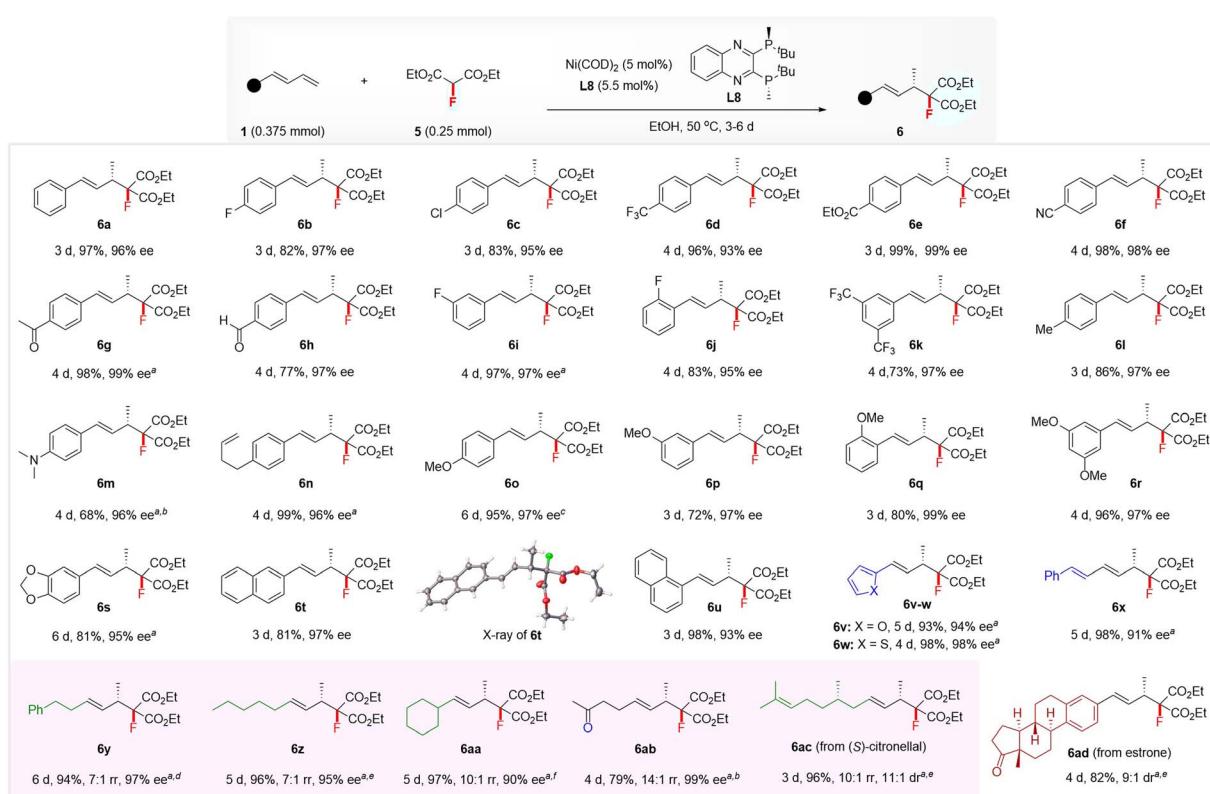


our delight, chiral deuterated allylic product **D-4a** featuring a  $\text{CD}_2\text{F}$  group at the stereocenter, difficult to access by other methods, could be obtained smoothly by using  $\text{CD}_3\text{OD}$  as the solvent in the desulfonylation step.

Furthermore, a tandem Ni-catalyzed asymmetric hydro-monofluoro bis(phenylsulfonyl)methylation/reductive desulfonylation sequence was developed for the direct access of  $\alpha\text{-CH}_2\text{F}$  and  $\alpha\text{-CD}_2\text{F}$  substituted chiral allylic compounds **4** and **D-4** (Scheme 2B). Both aryl- and alkyl-substituted 1,3-dienes were suitable partners for this tandem sequence, as exemplified by the preparation of **4a-4d** and **D-4a-4d** with excellent ee values. It is worth mentioning that the facile synthesis of chiral allylic compounds bearing a  $\text{CD}_2\text{F}$ -substituted stereocenter justified the use of FBSM as the monofluoromethylation reagent and further highlighted the value of our method.

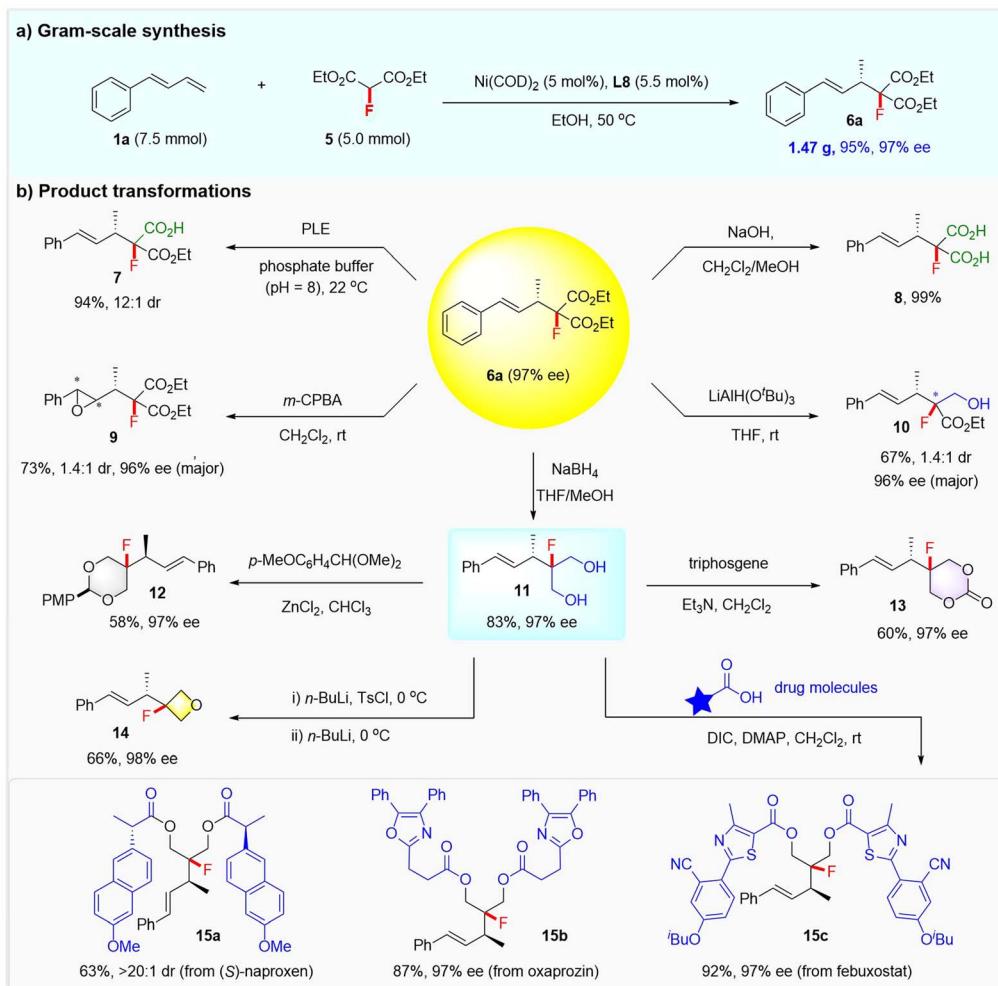
The excellent regio- and enantio-selectivity of the above hydromonofluoromethylation inspired us to explore the realization of enantioselective hydromonofluoroalkylation with diethyl fluoromalonate<sup>4p,16d</sup> **5** because of its ability to simultaneously incorporate a fluorine atom and two convertible ester groups,<sup>22</sup> which allows the construction of functionalized chiral monofluorinated molecules with high structural complexity. After optimization of the reaction conditions (see the ESI† for details), the combination of  $\text{Ni}(\text{COD})_2$  and  $(S,S)\text{-QuinoxP}^*$  **L8** still proved

to be an optimal catalytic system.<sup>23</sup> As illustrated in Scheme 3, the substrate scope was examined by running the reaction in EtOH at 50 °C using 5 mol% of  $\text{Ni}(\text{COD})_2$ -ligated  $(S,S)\text{-QuinoxP}^*$  as the catalyst. Both (hetero)aromatic and aliphatic 1,3-dienes were suitable substrates, affording the 4,3-Markovnikov adducts **6** with excellent regio- and enantio-selectivity. Regardless of the nature and position of the substituent on the phenyl ring of aryl 1,3-dienes, all reacted well with **5** to afford the products **6a-6u** in 68–99% yields with 93–99% ee. The XRD analysis of **6t** confirmed its absolute configuration to be *(S)*, and that of other products was assigned by analogy. Various functional groups, such as ester (**6e**), nitrile (**6f**), ketone (**6g**), aldehyde (**6h**), amine (**6m**), and non-conjugated alkene (**6n**), on the aryl ring of aromatic 1,3-dienes were well-tolerated under this hydromonofluoroalkylation as well. Heteroaromatic 2-furyl- and 2-thienyl-substituted 1,3-dienes, as well as conjugated triene, also afforded the adducts **6v-6x** in 93–98% yields and 91–98% ee. Moreover, linear and branched alkyl-substituted 1,3-dienes were tolerated, affording 4,3-Markovnikov adducts **6y-6z** in 70–96% yields and 90–99% ee, with high to excellent regioselectivity, albeit with the generation of a small amount of 4,1-addition isomer in these cases.<sup>13c</sup> The use of a 10 mol% Ni catalyst was required to ensure excellent yields in the case of heteroaryl and alkyl 1,3-dienes. The protocol was also applied to the late-stage hydromonofluoroalkylation of *(S)*-



**Scheme 3** Scope of enantioselective hydromonofluoroalkylation of 1,3-dienes **1** with diethyl fluoromalonate **5**. Conditions: **1** (0.375 mmol), **2** (0.25 mmol),  $\text{Ni}(\text{COD})_2$  (5 mol%), and **L8** (5.5 mol%) at 50 °C in EtOH (1.5 mL), unless otherwise noted. Yields of isolated products were reported and ee was determined by chiral HPLC analysis. <sup>a</sup> Using  $\text{Ni}(\text{COD})_2$  (10 mol%) and **L8** (11 mol%). <sup>b</sup> At 70 °C. <sup>c</sup> At 50–70 °C. <sup>d</sup> At 60 °C. <sup>e</sup> At 80 °C. <sup>f</sup> At 75 °C. The rr indicates the regioselectivity ratio of 4,3-Markovnikov isomer with another isomer, which was determined by <sup>1</sup>H NMR analysis. The ee value of **6z** and **6aa** was determined by their derivatives; see the ESI† for details. The dr value of **6ac** and **6ad** was determined by <sup>19</sup>F NMR analysis.





Scheme 4 Synthetic utility.

citronellal and estrone derivatives, affording **6ac** in 96% yield with 11:1 dr and **6ad** in 82% yield with 9:1 dr.

### Synthetic utility

To further highlight the practicality of the reaction, a gram-scale synthesis of product **6a** and its synthetic elaborations toward structurally diversified fluorine-containing molecules was conducted. As shown in Scheme 4, starting from **1a** (7.5 mmol) and **5** (5 mmol), 1.47 g of **6a** could be readily generated in 95% yield and with 97% ee under the standard conditions. The two ester groups of **6a** could be selectively hydrolyzed to fluorinated carboxylic acid or dicarboxylic acid, as demonstrated by the synthesis of **7** (94% yield and 12:1 dr) *via* a porcine liver esterase (PLE) enabled hydrolytic desymmetrization, and **8** (99% yield) *via* NaOH-mediated hydrolysis. The treatment of **6a** with *m*-CPBA led to the epoxidation of the alkenyl and afforded chiral fluorinated epoxide **9** in 73% yield, albeit with modest dr. Compound **6a** could also be selectively reduced with LiAl(O<sup>t</sup>Bu)<sub>3</sub> or NaBH<sub>4</sub>, affording a fluorinated hydroxy ester **10** in 67% yield with 1.4:1 dr and 96% ee, or a fluorinated diol **11** in 83% yield with 97% ee, respectively.

Notably, diol **11** was readily converted into a synthetically useful fluorinated 1,3-dioxane **12** or 1,3-dioxan-2-one **13** (ref.<sup>24</sup>) under the action of 1-(dimethoxymethyl)-4-methoxybenzene or triphosgene. A fluorinated oxetane **14** was also obtained from diol **11** *via* a selective monotosylation and sequential cyclization process. The versatile diol **11** proved to be a very useful linker that can merge two drugs to form complex fluorine-containing molecules, as exemplified by the efficient installation of fluorinated compounds **15a–15c** from drugs (S)-naproxen, oxaprozin, and febuxostat.

### Conclusions

In summary, we have developed a highly enantioselective Markovnikov regioselective hydromonofluoroalkyl(methyl)ation of 1,3-dienes by using chiral Ni catalysis, allowing access to various functionalized chiral allylic compounds bearing a CH<sub>2</sub>F, CD<sub>2</sub>F or monofluoroalkyl group at the stereocenter. Remarkably, such a methodology provides a new direction for enantioselective monofluoroalkyl(methyl)ation, and it constitutes a new branch of asymmetric 1,3-diene hydrofunctionalizations. Moreover, this



represents the first enantio- and regio-selective Markovnikov hydrofluoroalkylation of olefins. The salient features include broad substrate scope for both aromatic and aliphatic 1,3-dienes, excellent enantio- and regio-selectivity, good functional group tolerance, mild base-free conditions, and diverse product transformations. Further studies in our laboratory will focus on elucidating the reaction mechanism<sup>25</sup> and developing other asymmetric Markovnikov regioselective hydrofluoroalkylation reactions.

## Data availability

All of the experimental data have been included in the ESI.† Crystallographic data can be obtained from the CCDC (2130032 and 2130034).

## Author contributions

L. Liao and Y. Zhang performed the experiments, and collected and analyzed the data; Z.-W. Wu, Z.-T. Ye, and X.-X. Zhang synthesized some of the 1,3-dienes. J.-S. Yu conceived the idea and directed the project; J.-S. Yu and G. Chen co-wrote the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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