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Manganese-catalyzed cyclopropanation of allylic alcohols with sulfones

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Cyclopropanes are among the most important structural units in natural products, pharmaceuticals, and agrochemicals. Herein, we report a manganese-catalyzed cyclopropanation of allylic alcohols with sulfones as carbene alternative precursors via a borrowing hydrogen strategy under mild conditions. Various allylic alcohols and arylmethyl trifluoromethyl sulfones work efficiently in this borrowing hydrogen transformation and thereby deliver the corresponding cyclopropylmethanol products in 58% to 99% yields. Importantly, a major benefit of this transformation is that the versatile free alcohol moiety is retained in the resultant products, which can undergo a wide range of downstream transformations to provide access to a series of functional molecules. Mechanistic studies support a sequential reaction mechanism that involves catalytic dehydrogenation, Michael addition, cyclization, and catalytic hydrogenation.

Cyclopropanes are ubiquitous structural units that exist widely in natural products, pharmaceuticals, and agrochemicals. The incorporation of cyclopropanes into biologically active molecules can allow fine-tuning of metabolic stability, enhancement of their potency, and reduction of off-target effects (Fig. 1a)[1–3]. Moreover, cyclopropyl fragments are also commonly used as versatile building blocks in organic synthesis and as radical clocks in mechanistic investigations[3–6].

Traditional methodologies for the synthesis of cyclopropanes from olefins mainly rely on carbene-based strategies[7–12], including Simmons-Smith reaction[13,14] and catalytic diazo-derived carbenoid transformation[15–17], Kulinkovich reaction[18] and Corey-Chaykovsky reaction (Fig. 1b)[19]. The typical Simmons-Smith protocol requires a stoichiometric amount of highly reactive zinc reagents to form zinc carbenoids from often difficulty-available 1,1- and 1,2-dihaloalkanes. The metal-catalyzed diazo-derived carbenoids procedure is powerful and straightforward as well. Unfortunately, the highly energetic diazo compounds are potentially explosive, and low yields were furnished with allylic alcohols due to undesired O–H insertion. In addition, the Kulinkovich reaction typically occurs with alkyl Grignard reagents and stoichiometric titanium alkoxide, and the noncarbenoid approach Corey-Chaykovsky reaction is limited to electron-deficient alkenes.

To this end, the development of readily available and bench-stable cyclopropanation reagents for the practical and broadly applicable cyclopropanation of olefins remains exceedingly required and scientifically interesting. In particular, the cyclopropanation of allylic alcohols for synthesizing cyclopropylmethanol[20–24], as these compounds would readily undergo downstream transformation to a series of valuable synthons and complex molecules by the utilization of the free hydroxide group.

On the other hand, sulfone is one of the most important building blocks in organic synthesis. For example, Julia-type olefination is a well-known method starting from α-H-containing sulfones for synthesizing alkenes, in which sulfonyl moiety is applied as the leaving group[25–27]. We envisioned that such sulfones could also be employed as carbene alternative precursors[28–30] for the cyclopropanation of allylic alcohols in the presence of a transition metal catalyst. Our hypothesis is that α, β-unsaturated carbonyl compounds could be formed by dehydrogenation of allylic alcohols under transition metal catalysis, and then undergo Michael addition with α-H-containing sulfones, followed by the intramolecular nucleophilic substitution to afford cyclopropane carboxaldehyde[31–36]. Finally, the borrowed hydrogen returns to the carbonyl group to provide the cyclopropylmethanol product.

Based on our continuous research interest[37–39] in pincer ligand-based manganese-catalyzed borrowing hydrogen (BH) transformation[40–44] and inspired by the recent advancements in the transition metal-catalyzed functionalization of allylic alcohols via

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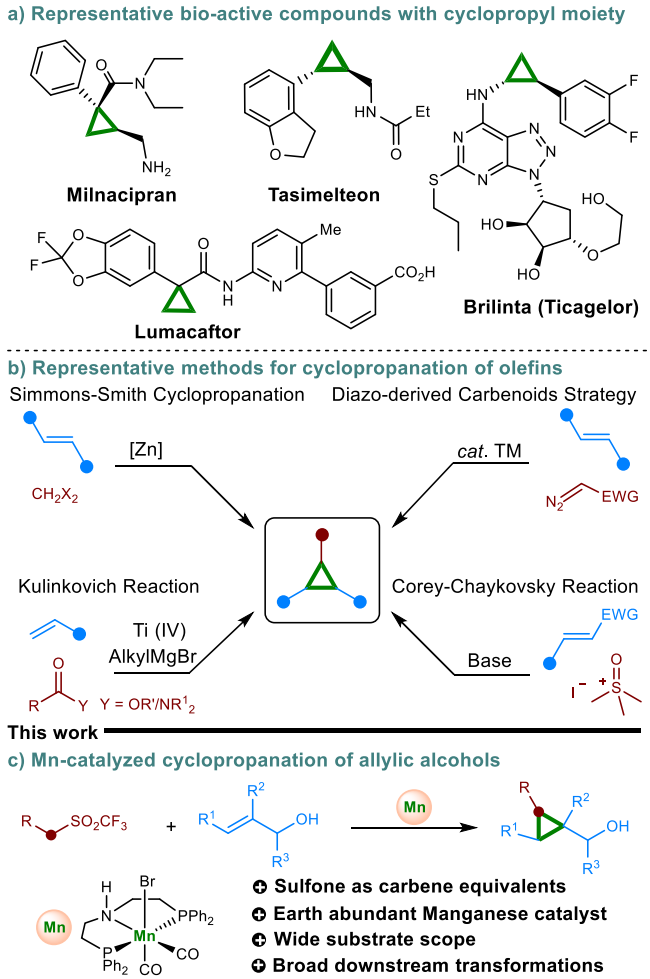

Fig. 1 | The importance of cyclopropane and its synthesis. a Biologically active compounds containing a cyclopropyl moiety. **b** Representative methods for cyclopropanation of olefins. **c** This work: manganese-catalyzed cyclopropanation of allylic alcohols.

borrowing hydrogen, including anti-Markovnikov hydroamination[45–50] and hydrocarbonation[51–54]. Herein, we report pincer ligand-based manganese-catalyzed[55–61] borrowing hydrogen cyclopropanation of allylic alcohols with sulfone as a carbene alternative precursor for the synthesis of valuable cyclopropylmethanol (Fig. 1c).

Results

We started our investigations by testing the cyclopropanation of allyl alcohol (**2a**) with sulfones containing different substituents in the presence of PNP-Mn catalyst (PNP-Mn = phosphine-nitrogen-phosphine tridentate manganese). To our delight, the desired cyclopropanation product was obtained in 23% yield using phenyl arylmethyl sulfone (**1a**) as the coupling partner (Table 1, entry 1). The hydrocarbonation product **3a** was isolated in a 64% yield and assigned as the major side product of the reaction. We then examined different substituted sulfonyl as the leaving group. When applying 4-trifluoromethylphenyl and *tert*-butyl sulfonyl as the leaving groups, comparable yields of **3** were obtained (Table 1, entries 2 and 4). When employing methyl arylmethyl sulfone (**1c**) as the cyclopropanation reagent, only a trace amount of cyclopropanation product was detected by GC-analysis (Table 1, entry 3). The yield of the desired product could be enhanced to 34% by using trifluoromethyl sulfonyl as the leaving group (Table 1, entry 5). Subsequently, different solvents, including THF, *t*AmOH, and 1,4-dioxane, were tested with **1e** as the cyclopropanation reagent, and *t*AmOH was found to be the optimal solvent (Table 1, entries 6–8). Other bases, such as NaO*t*Bu, KOMe, and KOH, either yielded **3** comparable or provided a lower yield (Table 1, entries 9–11). A slightly higher yield was obtained by increasing the loading amount of the base (Table 1, entry 12). We observed that the yield of the desired product could also be improved by decreasing the concentration of the reaction mixture, where 0.05 M concentration gave 88% isolated yield of **3** (Table 1, entries 13–15). The cyclopropanation process could not occur in the absence of a base or manganese catalyst, which demonstrated the critical role of the catalyst and base (Table 1, entries 16 and 17). Furthermore, we reexamined the substrates with different substituted sulfonyl as the leaving group (**1a**-**1e**) under the optimized conditions. The trifluoromethyl group again demonstrated the highest reactivity among the tested leaving groups (Supplementary Table 1). Additionally, the *i*Pr-MACHO (MACHO = bis[(2-phosphino)ethyl]amine) manganese complex exhibited reactivity comparable to the Ph-MACHO catalyst, and other scaffold PNP-Mn complexes afforded only a trace amount or lower yields of the desired product under the standard conditions (Supplementary Table 2).

With the optimized conditions in hand, we explored the scope of trifluoromethyl sulfone-based substrates **1** in this manganese-catalyzed cyclopropanation reaction. As shown in Fig. 2, the desired cyclopropylmethanol products were furnished in 64% to 97% yields with over 20:1 diastereomeric selectivity. A series of electron-donating groups on the benzene ring of benzyl trifluoromethyl sulfone **1**, such as phenyl (**3**), methyl (**5, 21**, and **22**), *tert*-butyl (**6**), methoxy (**7, 17**, and **23**), benzyloxy (**8**), trifluoromethoxy (**9**), methylthio (**10**), and methylenedioxy (**24**), were well tolerated and furnished the desired cyclopropanation products in high efficiency. Substrates bearing labile halogen groups, including fluoro (**11, 14**, and **18**), chloro (**12, 15**, and **19**), and bromo (**13, 16** and **20**), irrespective of their location at the *para-*, *meta-* or *ortho-* position, exhibited high efficiency as well and afforded the corresponding cyclization products. The BH cyclopropanation process also proceeded smoothly with sulfone reagents containing π-extended aromatic substituents, such as 2- and 1-naphthalene (**25** and **26**) and 9-anthracene (**27**). Notably, amide, alkyne and olefin, which are normally sensitive to reduction, remained untouched in this manganese-catalyzed BH system (**28, 29**, and **30**). However, the reaction with alkyl trifluoromethyl sulfones, such as (2-(trifluoromethanesulfonyl)ethyl)benzene and (3-(trifluoromethanesulfonyl)propyl)benzene, afforded the corresponding cyclopropanation products in yields below 10%. Additionally, employing trifluoro(methylsulfonyl)methane as the substrate did not yield the desired cyclopropanation product, as confirmed by GC-MS analysis (Supplementary Fig. 1).

We then explored various substituted allylic alcohols **2** to demonstrate the generality of this transformation (Fig. 3). We found that in addition to allyl alcohol, a range of substituted allylic alcohols were also suitable substrates, affording the corresponding desired substituted cyclopropanes with high efficiency. For example, secondary allylic alcohols proceeded smoothly in the BH cyclopropanation reaction to furnish cyclopropyl-substituted secondary alcohols (**31**–**34**). Moreover, applying *β*- and *α*-substituted allylic alcohols as the substrates provided 1,2,3- and 1,1,2-trisubstituted cyclopropanes with yields between 74% and 99% (**35**–**42**). It should be noted that the cyclopropanation process selectively occurred on the allylic alcohol unit while the other alkenyl group in the substrate remained intact (**36**). Either *trans-* or *cis-* allylic alcohol underwent BH cyclopropanation smoothly to give the desired product in 87% and 88% yields, respectively. However, one pair of *dr* ratio is opposite, which indicated one pair of stereoselectivity of the cyclopropane comes from the configuration of internal allylic alcohol (**38**). Interestingly, 2-cyclohexenol was also suitable in the transformation to provide the bicyclic alcohol product with a good yield (**43**).

We were particularly delighted to find that this manganese-catalyzed cyclopropanation could also be applied to naturally

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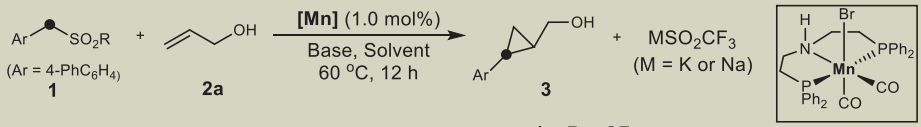
Table 1 | Optimization of manganese-catalyzed cyclopropanation of allyl alcohol 2a



1a: R = Ph **1b**: R = 4-CF_3-Ph **1c**: R = Me **1d**: R = *t*Bu **1e**: R = CF_3

Entry	1	Base	Solvent	3[a]
1	**1a**	KO*t*Bu (1.0 equiv)	PhMe (0.5 M)	23%
2	**1b**	KO*t*Bu (1.0 equiv)	PhMe (0.5 M)	21%
3	**1c**	KO*t*Bu (1.0 equiv)	PhMe (0.5 M)	<5%
4	**1d**	KO*t*Bu (1.0 equiv)	PhMe (0.5 M)	21%
5	**1e**	KO*t*Bu (1.0 equiv)	PhMe (0.5 M)	34%
6	**1e**	KO*t*Bu (1.0 equiv)	THF (0.5 M)	23%
7	**1e**	KO*t*Bu (1.0 equiv)	*t*AmOH (0.5 M)	46%
8	**1e**	KO*t*Bu (1.0 equiv)	1,4-dioxane (0.5 M)	14%
9	**1e**	NaO*t*Bu (1.0 equiv)	*t*AmOH (0.5 M)	45%
10	**1e**	KOMe (1.0 equiv)	*t*AmOH (0.5 M)	36%
11	**1e**	KOH (1.0 equiv)	*t*AmOH (0.5 M)	30%
12	**1e**	KO*t*Bu (1.25 equiv)	*t*AmOH (0.5 M)	50%
13	**1e**	KO*t*Bu (1.25 equiv)	*t*AmOH (0.17 M)	68%
14	**1e**	KO*t*Bu (1.25 equiv)	*t*AmOH (0.1 M)	72%
15	**1e**	KO*t*Bu (1.25 equiv)	*t*AmOH (0.05 M)	88%
16	**1e**	---	*t*AmOH (0.05 M)	---
17[b]	**1e**	KO*t*Bu (1.25 equiv)	*t*AmOH (0.05 M)	---

[a]Reaction conditions: **1** (0.25 mmol, 1.0 equiv), **2a** (0.3 mmol), base, solvent, and **[Mn]** (1.0 mol%), 60 °C, 12 h. Isolated yields are reported. Diastereomeric ratio (*d.r.*) of **3** was > 20:1 in all cases.
[b]Without catalyst.

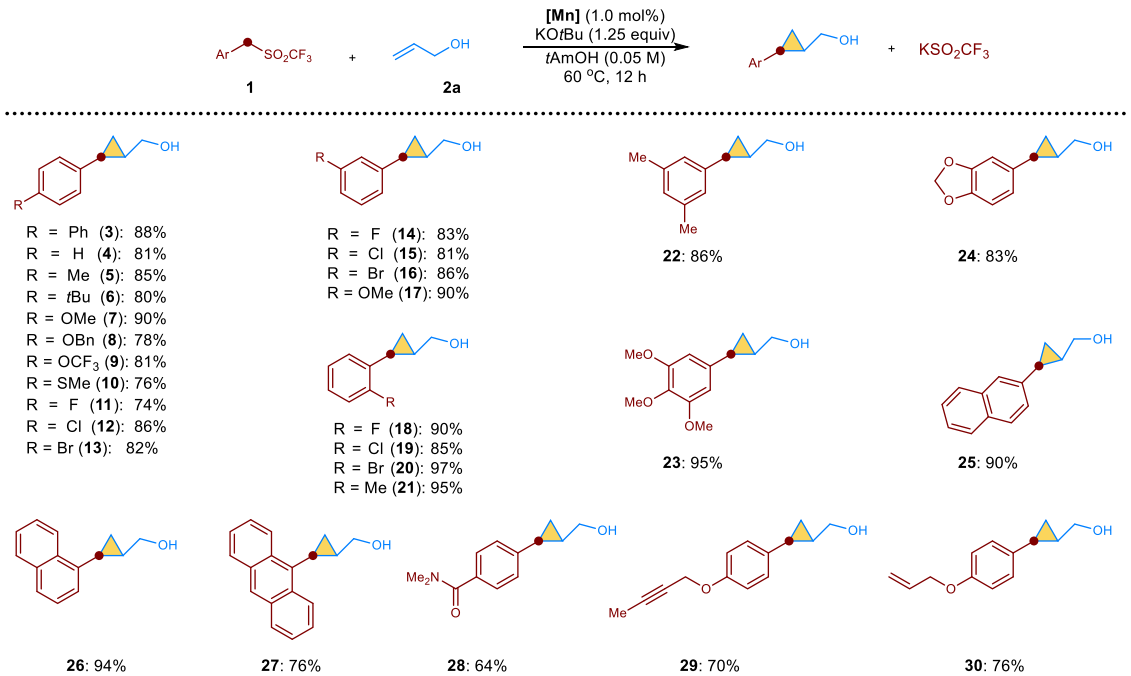


Fig. 2 | Manganese-catalyzed cyclopropanation of allyl alcohol with different arylmethyl trifluoromethyl sulfones. Reaction conditions: **1** (0.25 mmol, 1.0 equiv), **2a** (0.3 mmol), **[Mn]** (1.0 mol%). Isolated yields are reported. *d.r.* > 20:1 in all cases.

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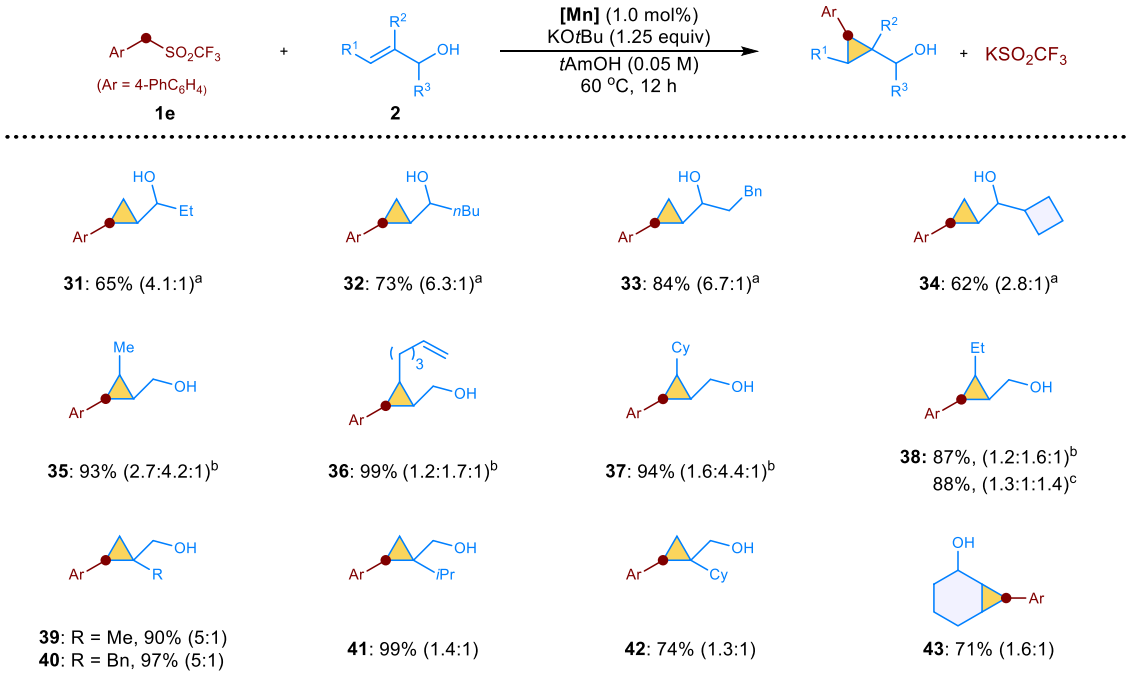

Fig. 3 | Manganese-catalyzed cyclopropanation of different allylic alcohols. Reaction conditions: **1e** (0.25 mmol, 1.0 equiv), **2** (0.3 mmol), **[Mn]** (1.0 mol%). Isolated yields are reported. *d.r.* was determined by ^{1}H NMR analysis. [a]KO*t*Bu (2.0 equiv), 20 h, *d.r.* was induced by the alcohol moiety. [b]*trans*-allylic alcohols were used as the substrates. [c]*cis*-allylic alcohol was used as the substrate.

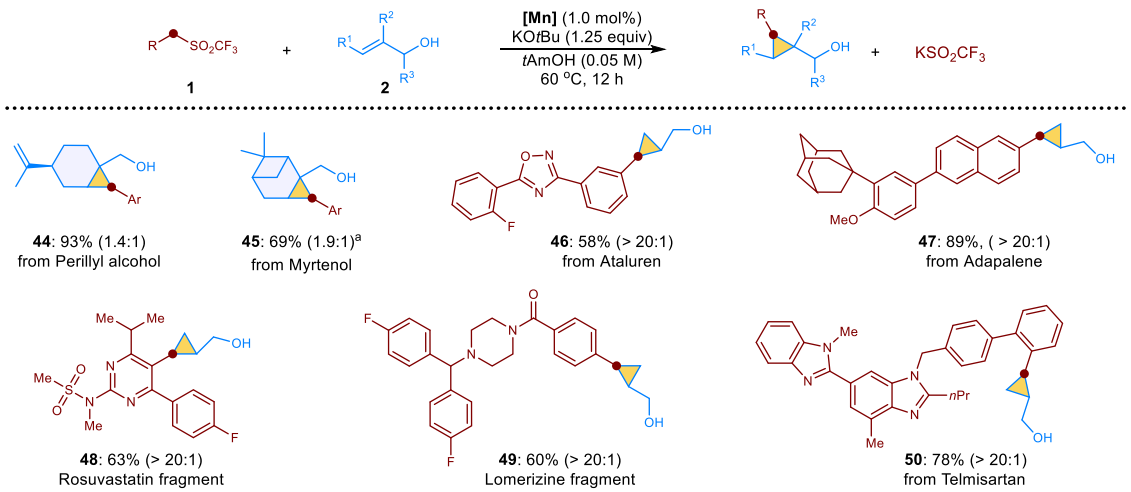

Fig. 4 | Manganese-catalyzed cyclopropanation with complex substrates. Reaction conditions: **1** (0.25 mmol, 1.0 equiv), **2** (0.3 mmol), **[Mn]** (1.0 mol%), KO*t*Bu (1.25 equiv), and *t*AmOH (5.0 mL), 60 °C, 12 h. Isolated yields are reported. *d.r.* was determined by ^{1}H NMR analyses. Ar = 4-Ph-C_6H_4. [a] KO*t*Bu (2.0 equiv), 20 h.

occurring allylic alcohols and sulfones derived from bio-active compounds, which reveal its broad applicability (Fig. 4). Specifically, perillyl alcohol and myrtenol, which are monoterpenes derived from the essential oils of botanicals, could successfully undergo cyclopropanation to furnish the corresponding cyclopropane products (**44** and **45**). As mentioned above, the cyclopropanation process selectively took place on the allylic alcohol unit while the other alkenyl group remains untouched in the case of perillyl alcohol (**44**). Delightfully, trifluoromethyl sulfones derived from bio-active Ataluren (**46**), Adapalene (**47**), Rosuvastatin (**48**), Lomerizine (**49**) fragment, and Telmisartan (**50**) were successfully applied as cyclopropanation reagents and furnished the desired corresponding products in 58% to 89% yields.

To demonstrate the synthetic utility of the cyclopropyl-methanol products, we investigated their late diversification (Fig. 5). Compound **3** could react with acetophenone and aniline through a manganese-catalyzed BH transformation to afford *β*-cyclopropyl ketone (**51**) and α-cyclopropyl aniline (**52**), respectively, which again highlighted the powerful ability of BH transformations with manganese catalysis. Furthermore, the hydroxy group could be easily converted to an aryl ether through a Mitsunobu reaction (**53**), an azide in two steps involving a nucleophilic substitution (**54**), and a nitrile-containing ether through a Michael addition reaction (**55**). In addition, cyclopropylmethanol (**3**) could be oxidized with PCC to deliver the corresponding aldehyde (**56**) in high yield, which could be further transformed to *β*-cyclopropyl acrylic acid (**57**) and vinylcyclopropane (**58**). Cyclopropanecarboxamide (**60**) could be successfully synthesized from **3** through oxidation and amide formation.

Due to the ability of the pincer ligand-based manganese catalyst for the BH cyclopropanation of allylic alcohols, we were interested in

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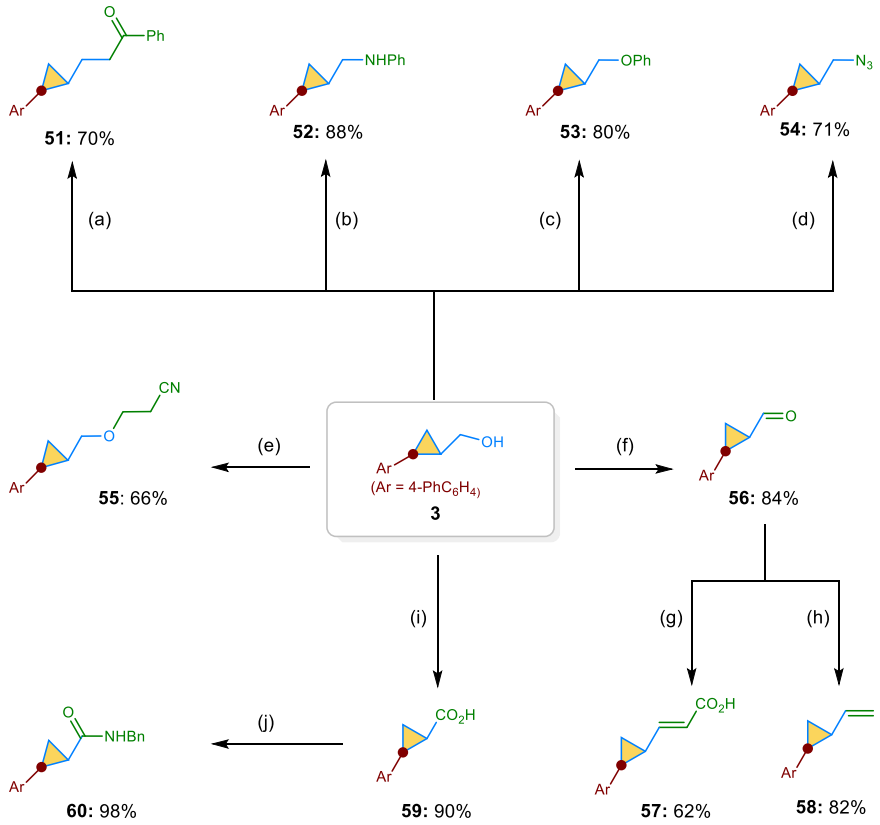

Fig. 5 | Diversification of product 3. Reagents: (a) PhCOMe, cat. **[Mn]**, Cs_2CO_3. (b) $PhNH_2$, cat. **[Mn]**, KO*t*Bu. (c) Phenol, DEAD, PPh_3. (d) TsCl, DMAP, Et_3N; then NaN_3. (e) acrylonitrile, KO*t*Bu. (f) PCC. (g) $HO_2CCH_2CO_2H$, piperidine. (h) Ph_3PCH_3Br, KO*t*Bu. (i) $RuCl_3$, $NaIO_4$. (j) $(COCl)_2$, cat. DMF; then $BnNH_2$, Et_3N. DEAD = diethyl azodicarboxylate, PCC = pyridinium chlorochromate.

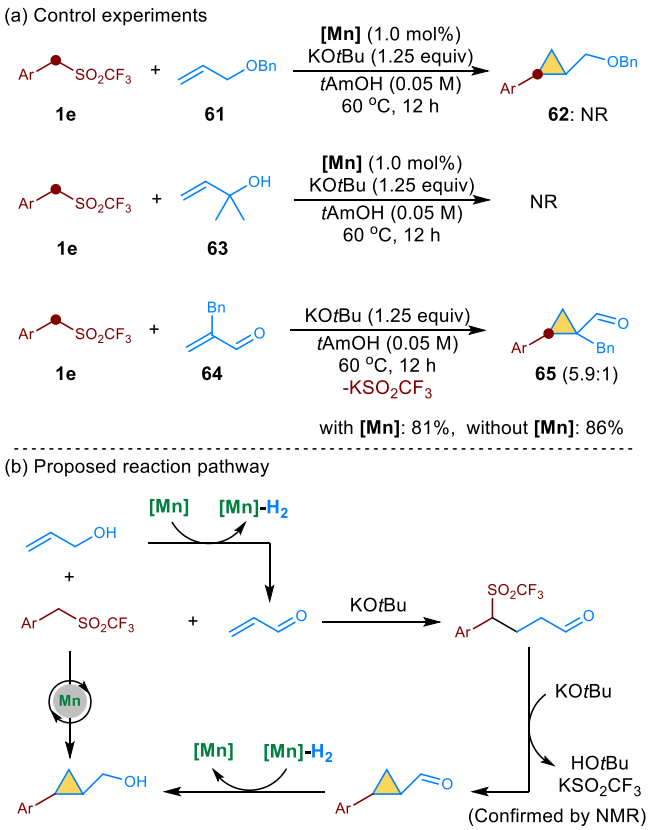

Fig. 6 | Selected mechanistic studies and proposed pathway. a Control experiments. **b** Proposed reaction pathway.

exploring the mechanism of this transformation. Firstly, we conducted the experiment with benzyl-protected allylic alcohol (**61**) and tertiary allyl alcohol (**63**) to replace **2a** as the substrates, and no cyclopropanation product was observed. From these results, it was clearly demonstrated that the reaction proceeds via BH catalysis. Control experiments applying *α*, *β*-unsaturated aldehyde (**64**) as the substrate delivered the corresponding cyclopropane carbaldehyde (**65**) in comparable high yields both with or without the manganese catalyst (Fig. 6a). These results supported that the *α*, *β*-unsaturated carbonyl compound might be a reaction intermediate, and the addition step does not require the manganese catalyst. On the basis of the above observations, a plausible reaction pathway is proposed for this manganese-catalyzed BH cyclopropanation of allylic alcohols. First, an *α*, *β*-unsaturated carbonyl compound was generated from allylic alcohol through manganese-catalyzed dehydrogenation[62–70]. Then, base-promoted addition between the *α*, *β*-unsaturated carbonyl compound and an *α*-H containing sulfone, followed by intramolecular nucleophilic substitution, afforded cyclopropane carbaldehyde[31–36], simultaneously generating KSO_2CF_3, which was confirmed by ^{19}F NMR. Finally, the borrowed hydrogen returns to the carbonyl group to provide the desired cyclopropanation product (Fig. 6b).

Discussion

In summary, a manganese-catalyzed cyclopropanation of allylic alcohols using sulfone as carbene equivalents via a borrowing hydrogen strategy for the synthesis of cyclopropylmethanol is demonstrated. Various substituted allylic alcohols and functionalized arylmethyl trifluoromethyl sulfones are suitable in this borrowing hydrogen transformation, which allows access to a range of cyclopropylmethanol products in 58% to 99% yields. Importantly, the free alcohol groups in the products allow further derivatization to a series of functional

molecules, which include ketone, aniline, ether, azide, aldehyde, alkene, carboxylic acid and amide. Mechanistic studies suggest the reaction proceeds sequentially, consisting of catalytic dehydrogenation, Michael addition, cyclization and catalytic hydrogenation.

Methods

Representative procedure for the synthesis of compound 3

In a nitrogen-filled glove box, an oven-dried Schlenk pressure tube (25 mL) containing a stirring bar was charged with **[Mn]** (1.0 mol%), KO*t*Bu (125 mol%) and degassed *t*AmOH (1.0 mL), and stirred at room temperature for 5 min. Then trifluoromethyl sulfones **1e** (0.25 mmol), allyl alcohol **2a** (0.3 mmol) and *t*AmOH (4.0 mL) were added in sequential. The tube was brought out of the glove box and stirred vigorously at 60 °C for 12 h. After completion, the reaction mixture was concentrated under reduced pressure. The residue was then filtered through Celite and washed with dichloromethane. Finally, it was purified by silica gel column chromatography using ethyl acetate/petroleum ether as eluent to afford the desired products **3** (49 mg, 88%).

Data availability

The data reported in this paper are available within the article and its Supplementary Information files. All data are also available from the corresponding author upon request.

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Author contributions

W. Liu. and K. Yu conceived and designed the experiments. K. Yu and Q. Nie performed the experiments and analyzed the data. Q. Chen participated in the discussions. W. Liu supervised the research and wrote the manuscript with the assistance of other authors.

Competing interests

The authors declare no competing interests.

Additional information

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