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Article

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Specific *Z*-Selectivity in the Oxidative Isomerization of Allyl Ethers to Generate Geometrically Defined *Z*-Enol Ethers using a Cobalt(II)(salen) Complex Catalyst

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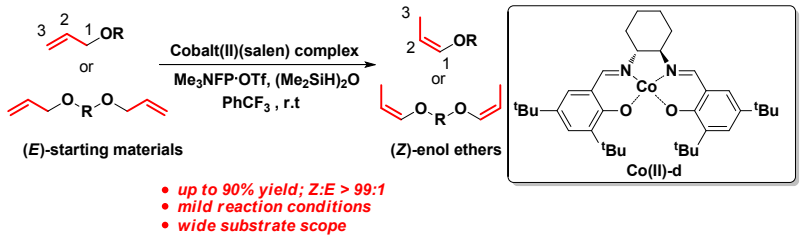
Supporting Information Placeholder



ABSTRACT: Enol ether structural motifs exist in many highly oxygenated biologically active natural products and pharmaceuticals. The synthesis of the geometrically less stable *Z*-enol ethers is challenging. An efficient *Z*-selective oxidative isomerization of allyl ethers catalyzed by a cobalt(II)(salen) complex using N-fluoro-2,4,6-trimethylpyridinium trifluoromethanesulfonate (Me_3NFPY•OTf) as an oxidant has been developed. Thermodynamically less stable *Z*-enol ethers were prepared in excellent yields with high geometric control. This methodology also demonstrates the effectiveness in controlling the *Z*-selective isomerization reaction of diallyl ethers at room temperature. This catalytic system provides an alternative pathway to extend the traditional reductive isomerization of allyl ethers.

Introduction

Enol ethers are stable, electron-rich π-bonds that are excellent substrates for the incorporation of oxygen functionalities. They are commonly employed in a large number of valuable synthetic transformations, such as the Claisen rearrangement,[1] isoxazoline synthesis,[2] cycloaddition,[3] Diels-Alder reaction,[4] Nazarov cyclization,[5] and cross aldol reaction.[6] In addition, enol ethers are important pharmacophores in a variety of bioactive natural products, which display antidiarrheal, antibiotic, antihypertensive, hypoglycemic and antalgic properties.[7–9] (Figure 1). Structure–activity relationship studies have demonstrated the necessity of the enol ether group and a specific enol ether geometry. Both *E*- and thermodynamically disfavored *Z*-enol ethers are widely found in pharmaceutically active molecular scaffolds in drug discovery. A large number of strategies for the construction of enol ether substructures have been developed to identify an efficient synthetic route to prepare these compounds, including the Wittig olefination of lactones,[10] Julia olefination with alkoxysulfones,[11] and the elimination of *β*-halo ethers,[12] *β*- hydroxy ethers,[13] and *β*-halo acetals.[14] However, these methods exhibit poor *Z*/*E* selectivity unless the steric demand of the substituents are substantially different. In general, the copper (I or II)-catalyzed carbon–oxygen Ullmann coupling of *sp*2-hybridized halides with oxygen-centered nucleophiles is perceived as a possible solution to circumvent the poor stereoselectivity observed in the aforementioned methods. The use of inexpensive copper salts as the catalyst make the Ullmann coupling strategy an attractive alternative to synthesize *E*-enol ethers with high stereospecificity.[15] However, the drawback to this protocol is the need to heat the reaction, which could be problematic for sensitive substrates or some functional groups.

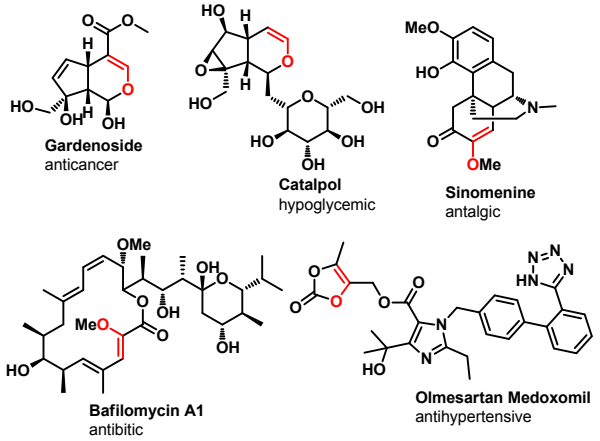
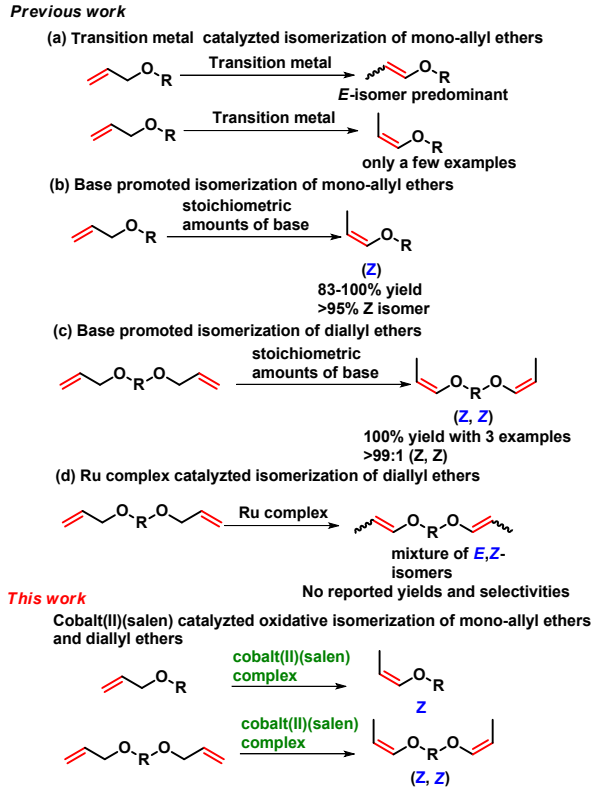


Figure 1. Natural products and pharmaceuticals containing enol ether scaffolds

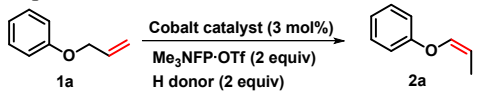
The catalytic isomerization of an allyl ether is a simple and atom-economical process, which is very important in the synthesis of enol ethers using transition-metal catalysts in both the research laboratory and large-scale industrial applications. However, this catalytic isomerization reaction is thermodynamically favorable and gives an *E*/*Z* mixture of the enol ether isomer with the *E*-isomer formed as the predominant thermodynamic product (Scheme 1a).[16] High *Z* -selective isomerization of allyl ethers in the presence of stoichiometric amounts of strong bases have been reported (Scheme 1b).[17]



Scheme 1. Challenges in the isomerization of mono-allyl ethers and diallyl ethers.

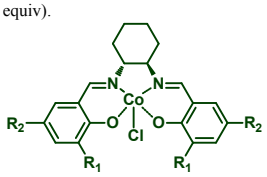
However, the transition metalcatalyzed *Z* -selective transformations of allyl ethers suffer from a poor *Z*/*E*-stereoisomer selectivity or a narrow substrate scope.[2,16b,16d,18] This is not surprising, as reports on the highly stereoselective transition metal-catalyzed isomerization of allyl ethers to give the thermodynamically less stable stereospecific *Z*-enol ether products are notably absent. There are only four reports describing the selective formation of the thermodynamically less stable *Z*-enol ether product (*Z*/*E* >99:1) using transition-metal catalysis.[16a, 16b] However, this is limited to only a few examples bearing little functionality. In addition, there are no reports on generating high order *Z*-dienol ethers with exceptional geometric control via the transition metal-catalyzed isomerization of allyl ethers.

Table 1. Optimization of the reaction conditions.[a]

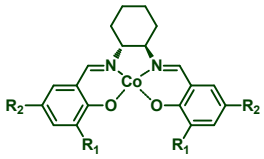


Entry	Catalyst	H donor	Solvent	Yield (%)[b]	Z/E[c]
1	**Co(III)-a**	$(Me_2SiH)_2O$	toluene	-	-
2	**Co(III)-b**	$(Me_2SiH)_2O$	toluene	-	-
3	**Co(III)-c**	$(Me_2SiH)_2O$	toluene	-	-
4	**Co(III)-a**	$(Me_2SiH)_2O$	THF	-	-
5	**Co(III)-a**	$(Me_2SiH)_2O$	acetone	-	-
6	**Co(III)-a**	$(Me_2SiH)_2O$	$PhCF_3$	-	-
7	**Co(II)-a**	$(Me_2SiH)_2O$	$PhCF_3$	25[d]	>99:1
8	**Co(II)-b**	$(Me_2SiH)_2O$	$PhCF_3$	33[e]	>99:1
9	**Co(II)-c**	$(Me_2SiH)_2O$	$PhCF_3$	31	>99:1
10	**Co(II)-d**	$(Me_2SiH)_2O$	$PhCF_3$	87(80)[f]	>99:1
11	**Co(II)-d**	$PhSiH_3$	$PhCF_3$	84	>99:1
12	**Co(II)-d**	Ph_2SiH_3	$PhCF_3$	67	>99:1
13	**Co(II)-d**	$PhSiH_2(OiPr)$	$PhCF_3$	22	>99:1
14[g]	**Co(II)-d**	$(Me_2SiH)_2O$	$PhCF_3$	40	>99:1
15[h]	**Co(II)-d**	$(Me_2SiH)_2O$	$PhCF_3$	37	>99:1

[a]Unless otherwise noted, all the reactions were carried out using **1a** (0.3 mmol), **Co(II)-d** (3 mol%), Me_3NFPY•OTf (2.0 equiv), and $(Me_2SiH)_2O$ (2.0 equiv) in $PhCF_3$ (3 mL) under a N_2 atmosphere at room temperature for 3 h. [b,c]The yield and *Z*/*E* selectivity were determined using **GC-MS**. [d]The reaction time was 5 h. [e]The reaction time was 7 h. [f]The isolated yield is provided in the parentheses. [g]Me_3NFPY•OTf (1.0 equiv). [h]$(Me_2SiH)_2O$ (1.0 equiv).

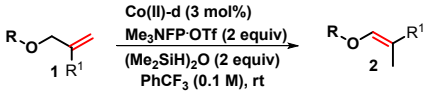


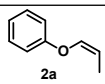
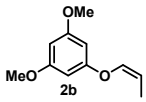
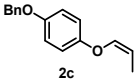
Co(III)-a: R_1=H, R_2=H
Co(III)-b: R_1=^{t}Bu, R_2=Me
Co(III)-c: R=^{t}Bu, R_2=^{t}Bu

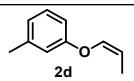
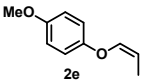
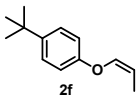
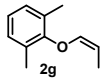
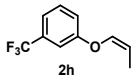
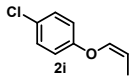
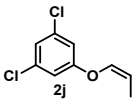
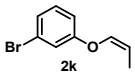
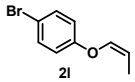
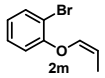
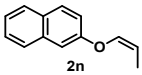
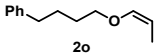
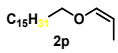
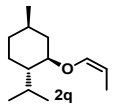
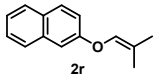


Co(II)-a: R_1=H, R_2=H
Co(II)-b: R_1=^{t}Bu, R_2=Me
Co(II)-c: R_1=Br, R_2=Br
Co(II)-d: R_1=^{t}Bu, R_2=^{t}Bu

Table 2. Substrate scope of the allyl ether used in the isomerization reaction.[a]



Entry	Product	Time (h)	Yield (%)[b]	Z/E[c]
1	 2a	3	80	>99:1
2	 2b	6	82	>99:1
3	 2c	5	84	>99:1

4	 2d	6	81	>99:1
5	 2e	5	79	>99:1
6	 2f	5	88	>99:1
7	 2g	35	72	>99:1
8	 2h	3	78	>99:1
9	 2i	5	75	>99:1
10	 2j	5	74	>99:1
11	 2k	5	79	>99:1
12	 2l	5	83	>99:1
13	 2m	5	74	>99:1
14	 2n	4	78	>99:1
15	 2o	7	53	>99:1
16	 2p	7	59	>99:1
17[d]	 2q	16	90	>99:1
18	 2r	8	81	-

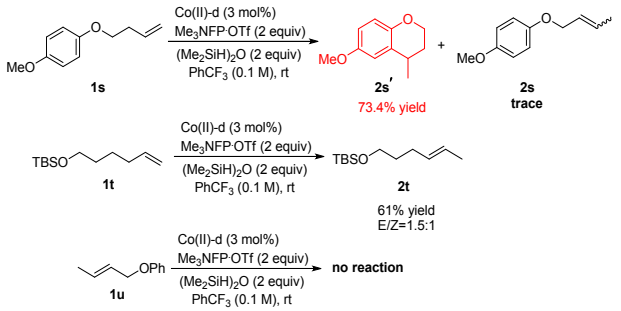
[a]Unless otherwise noted, all the reactions were carried out using **1** (0.3 mmol), **Co(II)-d** (3 mol%), Me_3NFPY•OTf (2.0 equiv), and $(Me_2SiH)_2O$ (2.0 equiv) in anhydrous $PhCF_3$ under a N_2 atmosphere at room temperature. [b]The isolated yield after column chromatography. [c]The *Z*/*E* selectivity was determined using **^{1}H NMR** spectroscopy. [d]The ee of **2q** was >99%.

Results and Discussion

Cobalt-catalyzed *Z*-selective alkene isomerization has been reported by Hilt et al.[19] Herein, we report a novel and general cobalt-catalyzed oxidative isomerization reaction for the synthesis of *Z*-enol ethers with excellent geometric selectivity. This methodology displays excellent functional group tolerance, uses a commercially available catalyst, and can be performed under mild reaction conditions. The catalytic system works well for not only the *Z*-selective isomerization of allyl ethers, but also the *Z*-selective isomerization of diallyl ethers.

We began our study on the isomerization of allyl ether **1a** using a series of Co(III)(R,R-salen)Cl catalysts with Me_3NFPY•OTf and $(Me_2SiH)_2O$ acting as the oxidant and hydrogen donor, respectively. Unfortunately, almost no reaction occurred at room temperature in a range of diverse solvents (Table 1, entry 1-6). Switching to a class of Co(II)(R,R-salen) catalysts was crucial to achieving the oxidative isomerization and surprisingly gave the thermodynamically less stable *Z*-enol ether **2a** using **Co(II)-a**-**Co(II)-c** with excellent geometric selectivity (*Z*/*E* >99:1) albeit in very poor yield (entries 7–9). To our delight, this oxidative isomerization gave the desired product **2a** in 87% yield and >99:1 *Z*-selectivity using the **Co(II)-d** catalyst (entry 10). Subsequently, different silanes were tested as the hydrogen donor in the reaction (entries 11–13). Isomerization of **1a** using $PhSiH_3$ and Ph_2SiH_2 was successful at room temperature and the reaction was completed within 3 h, resulting in *Z*-enol ether **2a** in 84% and 67% yield, respectively (entries 11 and 12). However, employing $PhSiH_2(OiPr)$ gave **2a** in 22% yield (entry 13). The selectivity observed for the conversion of **1a** to **2a** was always excellent (>99:1). Attempts to reduce the amount of oxidant and hydrogen donor used in the reaction caused a significant decrease in the product yield (entries 14, 15).

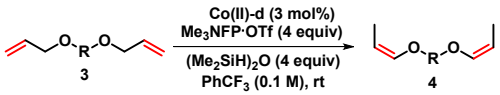
Having established the optimized reaction conditions, the scope of the isomerization reaction was examined. All the aromatic allyl ether derivatives studied were cleanly converted to the thermodynamically less stable *Z*-enol ether product in high yield (74–88%) with excellent stereospecificity (>99:1) (Table 2, entries 2–14). A steric bulky substituent, such as 2,6-dimethylphenyl allyl ether **1g** was used, the *Z*-product still be favoured with good yield and >99:1 *Z*/*E* but longer reaction time than other aromatic allyl ethers. The cobalt-catalyzed isomerization of aliphatic allyl ethers **1o** and **1p** was also investigated (entries 15 and 16). Remarkably, the double bond was selectively isomerized to afford the desired products (**2o** and **2p**) in 53% and 59% yield, respectively. Importantly, sterically hindered allyl ether **1q** bearing a menthol group required a longer reaction time to complete the isomerization reaction and gave **2q** in 90% with exclusive *Z*-selectivity (entry 17). The result reveals that steric hindrance has a significant effect on the rate of the isomerization reaction. Interestingly, double bond migration in **1q** (>99% ee) proceeded well without any loss of optical purity. 1,1-disubstituted allyl ether **1r** could still be convered to corresponding enol ether **2r** with excellent yield (entry 18). Excellent functional group tolerance was observed in **table 2** when different allyl ethers were subjected to the reaction conditions bearing methyl, trifluoromethyl, methyoxy, benzyloxy, tert-butyl, halides and so on.

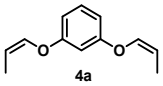
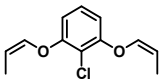
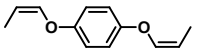
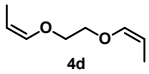
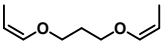
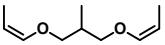
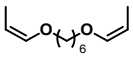
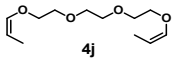


Scheme 2. Limitation of this method.

Nevertheless, our developed method also contains limitations (**Scheme 2**). When homoallyl ether **1s** was subjected to the standard reaction conditions, only trace amount of the isomerized product **2s** was observed. Instead, the bicyclic compound **2s'** was isolated as the major product. The isomerization of the higher alkenyl ether **1t** was also investigated, furnishing the isomerized product **2t** in 61% yield. The *E/Z* selectivity was rather poor, with the *E*-isomer being slightly favored. Finally, no isomerization reaction happened to compound **1u**, which contains a methyl group attaching to the terminal carbon of the double bond.

Table 3. Isomerization of diallyl ethers.[a]



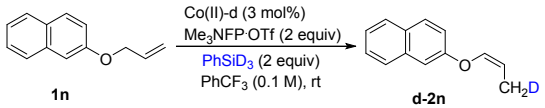
Entry	Product	Time (h)	Yield[b] (%)	Z/E[c]
1	 4a	9	83	>99:1
2	 4b	10	82	>99:1
3	 4c	9	78	>99:1
4	 4d	5	74	>99:1
5	 4e	4	75	>99:1
6	 4f	5	81	>99:1
7	 4g	6	77	>99:1
8	 4h	5	86	>99:1
9	 4i	6	86	>99:1
10	 4j	7	83	>99:1

[a]Unless otherwise noted, all the reactions were carried out using **3** (0.3 mmol), **Co-II-d** (3 mol%), Me_3NFPY•OTf (4.0 equiv), and $(Me_2SiH)_2O$ (4.0 equiv) in anhydrous $PhCF_3$ under a N_2 atmosphere at room temperature. [b]Isolated yield after column chromatography. [c]The *Z/E* selectivity was determined using **^{1}H NMR** spectroscopy.

To the best of our knowledge, the previously reported isomerization reactions of diallyl ethers form the dienol ether products as the (*Z, Z*)-isomer using stoichiometric amounts of strong bases (Scheme 1c)[17a, 17b] and as mixture of *E, Z*-isomers using Ru complex catalysts (Scheme 1d), respectively.[18g, 20] However transition meal-catalyzed exclusive (*Z, Z*)-selective translocation of various diallyl ethers has been rarely reported to date, which is especially noteworthy. Therefore, we turned our attention to investigating whether diallyl ethers could be selectively isomerized into the thermodynamically less stable (*Z, Z*)-isomer.

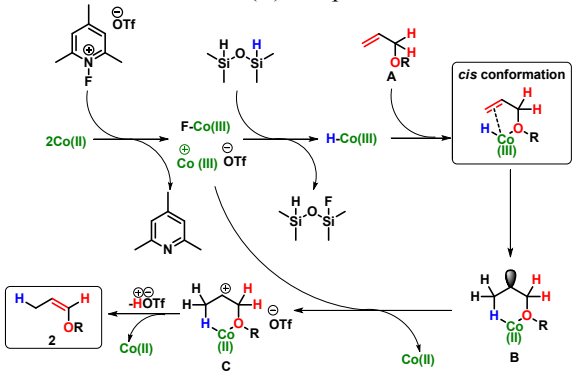
The results of the isomerization reactions are summarized in Table 3. We were pleased to find that these reactions worked well in the presence of **Co(II)-2d** (3 mol%) using 4 equiv of Me_3NFPY•OTf as the oxidant and 4 equiv of $(Me_2SiH)_2O$ as the hydrogen donor in $PhCF_3$ at room temperature. The isomerization reaction clearly shows high geometric selectivity in all cases to give the corresponding (*Z, Z*)-dienol ether products in good to excellent yield. It is noteworthy that aliphatic diallyl ethers (**4d-j**) (Table 3, entries 4–10) isomerized much faster than aromatic diallyl ethers (**4a-c**) (entries 1-3). As chiral catalyst were applied, we also investigated asymmetric desymmetrisation for **3f**, but no mono-isomerization product was found through GCMS and ^{1}H NMR under all the time-points. We speculate that the rate of isomerization is the same on both sides.

Deuterium labelling experiment has been done. We used $PhSiD_3$ (D=99.5%) as the H source to conduct the isomerization of **1n** under the standard reaction conditions, resulting in deuterium incorporation exclusively at the terminal carbon (**Scheme 3**).



Scheme 3. Mechanistic study.

Based on the above results, a plausible reaction pathway for the cobalt-catalyzed isomerization reaction is shown in Scheme 4. Initially, the catalytic cycle begins with the generation of a **Co(III)−F** complex and cationic **Co(III)OTf** complex in the presence of Me_3NFPY•OTf. Transformation of the **Co(III)−F** complex to the **Co(III)-H** complex occurs due to the strong F-Si bonding energy, which has been reported by Shigehisa[21] and Holland et al.[22] The **Co(III)-H** coordinates with the allyl ether to form a ***cis*-conformation**. Formation of similar ***cis*-conformation** via the coordination of Pt-H and Ru-H has been reported previously.[23] Subsequently, the key radical intermediate **B** generated via single electron transfer. **B** is subsequently oxidized by the cationic Co(III)OTf complex to form key carbocation intermediate **C** with the release of cobalt(II) complex . Finally, *trans*-coplanar elimination of the proton in **C** occurs to form the desired *Z*-vinyl ether **2** with the release of the second cobalt(II) complex.



Scheme 4. Proposed catalytic cycle for the oxidative isomerization reaction.

In summary, the oxidative isomerization of allyl ethers to *Z*-enol ethers has been developed based on carbon radicals and carbocation species as key intermediates using a cobalt(II)(salen) complex, $Me_3NFPY•OTf$, and $(Me_2SiH)_2O$. The reaction was found to tolerate a wide variety of functional groups and exhibited excellent yields and selectivity (*Z*/*E* >99:1). This methodology also works well for the *Z*-selective isomerization reaction of diallyl ethers at room temperature.

EXPERIMENTAL SECTION

General Information: Thin-layer chromatography (TLC) carried out on 0.25 mm silica gel platesvisualized with UV light and/or by staining with ethanolic phosphomolybdic acid (PMA) or iodine. Flash column chromatography was performed on silica gel (300-400 mesh). NMR spectraswere recorded on Bruker AM400 (400 MHz). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Optical rotations were taken on JASCO P1020. High-resolution mass spectra were recorded on Bruker ApeXIII 7.0 TESLA FTMS.

General Procedure for the Cobalt-catalyzed Allyl Ethers Isomerization: A Schlenk tube was charged with **Co(II)-d** (5.4 mg, 0.009 mmol, 3% equiv), $Me_3NFPY•OTf$ (173.5 mg, 0.6 mmol, 2 equiv), after being dried in vacuo for 3 mins, degassed trifluorotoluene (3 mL) was added. The solution was bubbled with N_2 for three times, after which **1a** (40.2 mg, 0.3 mmol, 1 equiv) and $(Me_2SiH)_2O$ (80.6 mg, 0.6 mmol, 2 equiv) was added under N_2. The resulting mixture was stirred at rt for 5 hours. After 1a was completely consumed as monitored by TLC, H_2O (5 mL) was added to quench the reaction. The resulted mixture was then extracted three times with diethyl ether (10 mL × 3). The combined organic layer was dried over Na_2SO_4. After evaporation of the volatile solvent under reduced pressure, the residue was purified by flash chromatography on silica gel to afford pure **2a** (32.2 mg, 0.25 mmol) as a colourless oil in a yield of 80%.

(Z)-(prop-1-en-1-yloxy)benzene (2a): purified by column chromatography (petroleum ether). Colorless oil; actual mass 32.2 mg, yield 80%. **(*Z*: *E* > 99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.38-7.34 (m, 2H), 7.10-7.05 (m, 3H), 6.44 (dd, *J*= 6.0, 1.5 Hz, 1H), 4.94 (m, 1H), 1.79 (dd, *J*= 6.9, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 157.6, 141.0, 129.6, 122.4, 116.2, 107.5, 9.4. (Only *Z* isomer is visible). This product is known.[17a]

(Z)-1,3-dimethoxy-5-(prop-1-en-1-yloxy)benzene (2b): purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 47.8 mg, yield 82%. **(*Z*: *E* > 99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.35 (dd, *J*= 5.9, 1.5 Hz, 1H), 6.18-6.17 (m, 3H), 4.88 (m, 1H), 3.77 (s, 6H), 1.71 (dd, *J*= 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 161.5, 159.4, 140.6, 107.9, 94.9, 55.4, 9.4. (Only *Z* isomer is visible).

HRMS (EI-TOF): calcd. for $C_{11}H_{14}O_3$ (M^+) *m/z*: 194.0943, found: 194.0949.

(Z)-1-(benzyloxy)-4-(prop-1-en-1-yloxy)benzene (2c): purified by column chromatography (petroleum ether). Colorless oil; actual mass 60.6 mg, yield 84%. **(*Z*: *E* > 99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.45-7.31 (m, 5H), 6.93 (s, 4H), 6.31 (dd, *J*= 5.9, 1.5 Hz, 1H), 5.04 (s, 2H), 4.85-4.78 (m, 1H), 1.72 (dd, *J*= 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 154.3, 151.9, 141.9, 137.2, 128.6, 128.0, 127.5, 117.3, 115.8, 106.4, 70.7, 9.3. (Only *Z* isomer is visible).

HRMS (EI-TOF): calcd.for $C_{16}H_{16}O_2$ (M^+) *m/z*: 240.1150, found: 240.1155.

(Z)-1-methyl-3-(prop-1-en-1-yloxy)benzene (2d): purified by column chromatography (petroleum ether). Colorless oil; actual mass 36.0 mg, yield 81%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.24-7.20 (m, 1H), 6.89-6.83 (m, 3H), 6.40 (dd, *J*= 4.8, 1.5 Hz, 1H), 4.91-4.88 (m, 1H), 2.37 (s, 3H), 1.75 (dd, *J*= 6.8, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 157.6, 141.0, 139.7, 129.3, 123.2, 117.0, 113.2, 107.3, 21.5, 9.4. (Only *Z* isomer is visible).

HRMS (EI-TOF): calcd.for $C_{10}H_{12}O$ (M^+) *m/z*: 148.0888, found: 148.0887.

(Z)-1-methoxy-4-(prop-1-en-1-yloxy)benzene (2e): purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 38.9 mg, yield 79%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.98-6.96 (m, 2H), 6.88-6.86 (m, 2H), 6.34 (dd, *J*= 6.2, 1.9 Hz, 1H), 4.86-4.80 (m, 1H), 3.80 (s, 3H), 1.77 (dd, *J*= 6.8, 1.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 155.1, 151.8, 142.0, 117.4, 114.7, 106.2, 55.6, 9.4. (Only *Z* isomer is visible).

This product is known.[16b]

***(Z)-1-(tert-butyl)-4-(prop-1-en-1-yloxy)benzene (2f)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 50.2 mg, yield 88%. **(*Z*:*E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.44-7.42 (m, 2H), 7.05-7.03 (m, 2H), 6.47 (dd, *J*= 5.8, 1.4 Hz, 1H), 4.96-4.93 (m, 1H), 1.83 (dd, *J*= 6.9, 1.3 Hz, 3H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 155.5, 145.2, 141.3, 126.4, 115.8, 107.0, 34.3, 31.6, 9.5. (Only *Z* isomer is visible).

HRMS (EI-TOF): calcd.for $C_{13}H_{18}O$ (M^+) *m/z*: 190.1358, found: 190.1359.

(Z)-1,3-dimethyl-2-(prop-1-en-1-yloxy)benzene (2g): purified by column chromatography (petroleum ether). Colorless oil; actual mass 35.0 mg, yield 72%. **(*Z*:*E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.09-7.07 (m, 2H), 7.04-7.00 (m, 1H), 6.03 (dd, *J*= 6.0, 1.7 Hz, 1H), 4.69-4.62 (m, 1H), 2.32 (s, 6H), 1.85 (dd, *J*= 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 154.7, 144.6, 130.8, 128.8, 124.5, 102.3, 16.2, 9.2. (Only *Z* isomer is visible).

This product is known.[18d]

***(Z)-1-(prop-1-en-1-yloxy)-3-(trifluoromethyl)benzene (2h)* :** purified by column chromatography (petroleum ether). Colorless oil; actual mass 47.3 mg, yield 78%. **(*Z*: *E* >99:1)**.^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.44-7.40 (m, 1H), 7.30-7.28 (m, 1H), 7.24 (m, 1H), 7.18-7.16 (m, 1H), 6.38 (dd, *J*= 6.1, 1.7 Hz, 1H), 5.00 (m, 1H), 1.72 (dd, *J*= 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 157.6, 140.1, 130.1, 119.4, 119.0, 119.0, 118.9, 118.9, 113.0, 113.0, 113.0, 112.9, 109.3, 9.4.

HRMS (EI-TOF): calcd.for $C_{10}H_9F_3O$ (M^+) *m/z*: 202.0605, found: 202.0608.

***(Z)-1-chloro-4-(prop-1-en-1-yloxy)benzene (2i)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 37.9 mg, yield 75%. **(*Z*: *E* >99:1)**.^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.26-7.23 (m, 2H), 6.92-6.90 (m, 2H), 6.30 (dd, *J*= 6.0, 1.6 Hz, 1H), 4.91 (m, 1H), 1.71 (dd, *J*= 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 156.2, 140.6, 129.5, 127.3, 117.4, 108.3, 9.4. (**Only *Z* isomer is visible**).

This product is known.[16b]

***(Z)-1,3-dichloro-5-(prop-1-en-1-yloxy)benzene (2j)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 45.1 mg, yield 74%. **(*Z*: *E* >99:1)**.^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.55-6.46 (m, 3H), 6.30 (dd, *J*= 6.2, 1.7 Hz, 1H), 5.01 (m, 1H), 1.69 (dd, *J*= 6.9, 1.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 164.9 164.8, 162.5, 139.6, 110.1,

98.9, 99.8, 99.7, 99.6, 98.1, 97.8, 97.5, 9.4. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_9H_8Cl_2O$ (M^+) *m/z*: 201.9952, found: 201.9959.

***(Z)-1-bromo-3-(prop-1-en-1-yloxy)benzene (2k)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 50.5 mg, yield 79%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.15 (m, 3H), 6.96-6.93 (m, 1H), 6.36-6.34 (dd, *J*= 6.1, 1.5 Hz, 1H), 5.00-4.93 (m, 1H), 1.73 (dd, *J*= 6.9, 1.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.2, 140.2, 130.7, 125.4, 122.9, 119.5, 114.9, 108.9, 9.4. (**Only *Z* isomer is visible**).This product is known.[16b]

***(Z)-1-bromo-4-(prop-1-en-1-yloxy)benzene (2l)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 53.1 mg, yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J*= 8.6 Hz, 2H), 6.88 (d, *J*= 8.7 Hz, 2H), 6.37 (dd, *J*= 6.4, 1.6 Hz, 1H), 4.95-4.90 (m, 1H), 1.73 (dd, *J*= 6.9, 1.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.7, 140.5, 132.4, 117.9, 114.7, 108.5, 9.4. (**Only *Z* isomer is visible**).This product is known.[16b]

***(Z)-1-bromo-2-(prop-1-en-1-yloxy)benzene (2m)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 47.3 mg, yield 74%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J*= 8.1, 1.5 Hz, 1H), 7.26 (td, *J*= 7.4, 1.5 Hz, 1H), 6.98 (dd, *J*= 8.2, 1.2 Hz, 1H), 6.92 (td, *J*= 7.9, 1.3 Hz, 1H), 6.35 (dd, *J*= 6.5, 1.6 Hz,, 1H), 5.00 (m, 1H), 1.77 (dd, *J*= 6.8, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.1, 140.5, 133.6, 128.5, 123.5, 115.9, 112.5, 109.1, 9.5. (**Only *Z* isomer is visible**). This product is known.[16b]

***(Z)-2-(prop-1-en-1-yloxy)naphthalene (2n)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 43.1 mg, yield 78%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*= 8.5 Hz, 2H), 7.74 (d, *J*= 8.2 Hz, 1H), 7.46 (t, *J*= 7.1 Hz, 1H), 7.37 (t, *J*= 7.3 Hz, 1H), 7.29-7.24 (m, 2H), 6.53-6.62 (m, 1H), 5.00-4.95 (m, 1H), 1.77 (dd, *J*= 6.9, 1.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 140.8, 134.3, 129.8, 129.7, 127.7, 127.0, 126.5, 124.2, 118.6, 110.1, 108.1, 9.5. (**Only Z isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{13}H_{12}O$ (M^+) *m/z*: 184.0888, found: 184.0884.

***(Z)-(4-(prop-1-en-1-yloxy)butyl)benzene (2o)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 30.3 mg, yield 53%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H), 7.27-7.23 (m, 3H), 6.00 (dd, *J*= 6.3, 1.7 Hz, 1H), 4.49-4.42 (m, 1H), 3.80 (t, *J*= 6.5 Hz, 2H), 2.72 (t, *J*= 7.5 Hz, 2H), 1.84-1.71 (m, 4H), 1.67 (dd, *J*= 7.0, 1.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.7, 142.4, 128.5, 128.4, 125.8, 100.9, 71.9, 35.7, 29.5, 27.8, 9.3. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{13}H_{18}O$ (M^+) *m/z*: 190.1358, found: 190.1362.

***(Z)-1-(prop-1-en-1-yloxy)hexadecane (2p)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 50.0 mg, yield 59%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (dd, *J*= 6.3, 1.5 Hz, 1H), 4.36 (m, 1H), 3.71 (t, *J*= 6.7 Hz, 2H), 1.64-1.62 (m, 2H), 1.58 (dd, *J*= 7.0, 1.4 Hz, 3H), 1.27 (m, 26H), 0.89 (t, *J*= 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.6, 100.7, 72.1, 32.0, 29.8, 29.8, 29.7, 29.6, 29.6, 29.4, 29.4, 25.9, 22.7, 14.1, 9.2. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{19}H_{38}O$ (M^+) *m/z*: 282.2923, found: 282.2929.

***(1S,2R,4R)-1-isopropyl-4-methyl-2-((Z)-prop-1-en-1-yloxy)cyclohexane (2q)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 53.0 mg, yield 90%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (dd, *J*= 6.2, 1.4 Hz, 1H), 4.36-4.30 (m, 1H), 3.34 (td, *J*= 10.5, 4.4 Hz, 1H), 2.20-2.12 (m, 1H), 2.00 (m, 1H), 1.67- 1.62 (m, 2H), 1.57 (dd, *J*= 6.7, 1.4 Hz, 3H), 1.39-1.32 (m, 2H), 1.01 (q, *J*= 12.0 Hz, 2H), 0.92-0.90 (m, 7H), 0.78 (d, *J*= 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.8, 100.2, 81.3, 47.9, 41.6, 34.4, 31.6, 25.9, 23.6, 22.2, 20.8, 16.4, 9.4. (**Only *Z* isomer is visible**).

This product is known.[17a]

***2-((2-methylprop-1-en-1-yl)oxy)naphthalene (2r)*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 48.2 mg, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.76 (m, 3H), 7.50-7.37 (m, 2H), 7.29-7.26 (m, 2H), 6.39 (s, 1H), 1.82 (s, 3H), 1.80 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.7, 135.1, 134.5, 129.6, 127.7, 126.9, 126.5, 124.0, 118.6, 118.3, 109.4, 19.6, 15.3. This product is known.[24]

***6-methoxy-4-methylchroman (2s')*:** purified by column chromatography (petroleum ether). Colorless oil; actual mass 39.2 mg, yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74-6.66 (m, 3H), 4.17-4.11 (m, 2H), 3.76 (s, 3H), 2.94-2.93 (m, 1H), 2.11-2.04 (m, 1H), 1.74-1.70 (m, 1H), 1.33 (d, 3H, *J* = 6.8 Hz). This product is known.[21a]

***tert-butyl(hept-5-en-1-yloxy)dimethylsilane (2t)*:** Colorless oil; actual mass 41.8 mg, yield 61%. (*E:Z* =1.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.43-5.40 (m, 2H), 3.63-3.58 (m, 2H), 2.10-2.02 (m, 2H), 1.64-1.55 (m, 5H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0 (*E*), 130.2 (*Z*), 125.0 (*E*), 124.2 (*Z*), 62.7, 32.7, 28.8 (*Z*), 26.0 (*E*), 23.1, 18.4 (*Z*), 17.9 (*E*), 12.7, -5.3. This product is known.[16h]

***1,3-bis((Z)-prop-1-en-1-yloxy)benzene (4a)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 47.4 mg, yield 83%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.22 (m, 1H), 6.71-6.68 (m, 3H), 6.39-6.38 (m, 2H), 4.95-4.89 (m, 2H), 1.73 (dd, *J*= 6.8, 1.3 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7, 140.6, 130.1, 110.0, 108.0, 104.4, 9.4. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{12}H_{14}O_2$ (M^+) *m/z*: 190.0994, found: 190.0989.

***2-chloro-1,3-bis((Z)-prop-1-en-1-yloxy)benzene (4b)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 55.3 mg, yield 82%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (t, *J*= 8.3 Hz, 1H), 6.69 (d *J*= 8.2 Hz, 2H), 6.33 (dd, *J*= 5.8, 1.4 Hz, 2H), 5.00-4.95 (m, 2H), 1.74 (dd, *J*= 6.8, 1.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.5, 140.5, 127.0, 109.6, 109.3, 9.5. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{12}H_{13}ClO_2$ (M^+) *m/z*: 224.0604, found: 224.0598.

***1,4-bis((Z)-prop-1-en-1-yloxy)benzene (4c)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 44.5 mg, yield 78%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (m, 4H), 6.33 (dd, *J*= 6.2, 1.8 Hz, 2H), 4.88-4.82 (m, 2H), 1.74 (dd, *J*= 6.8, 1.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.0, 141.6, 117.3, 106.8, 9.4. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{12}H_{14}O_2$ (M^+) *m/z*: 190.0994, found: 190.0999.

***1,2-bis((Z)-prop-1-en-1-yloxy)ethane (4d)* :** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 31.6 mg, yield 74%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (dd, *J*= 6.1, 1.5

Hz, 2H), 4.45-4.38 (m, 2H), 3.89 (s, 4H), 1.58 (dd, *J*= 6.8, 1.6 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 145.5, 101.7, 70.9, 9.2. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_8H_{14}O_2$ (M^+) *m/z*: 142.0994, found: 142.0997.

***1,3-bis((Z)-prop-1-en-1-yloxy)propane (4e)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 35.1 mg, yield 75%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (dd, *J*= 6.1, 1.5 Hz, 2H), 4.45-4.38 (m, 2H), 3.85 (t, *J*= 6.2 Hz, 4H), 1.98-1.92 (m, 2H), 1.60 (dd, *J*= 6.8, 1.6 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 145.5, 101.2, 68.3, 30.3, 9.2. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{10}H_{18}O_2$ (M^+) *m/z*: 156.1150, found: 156.1151.

***(Z)-1-(2-methyl-3-((Z)-prop-1-en-1-yloxy)propoxy)prop-1-ene (4f)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 41.4 mg, yield 81%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96-5.94 (m, 2H), 4.41-4.36 (m, 2H), 3.74-3.70 (m, 2H), 3.67-3.63 (m, 2H), 2.15-2.08 (m, 1H), 1.60 (dd, *J*= 6.8, 1.6 Hz, 6H), 1.00 (d, *J*= 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 145.9, 100.9, 73.7, 34.7, 13.7, 9.2. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_9H_{16}O_2$ (M^+) *m/z*: 170.1307, found: 170.1311.

***(Z)-1-(2,2-dimethyl-3-((Z)-prop-1-en-1-yloxy)propoxy)prop-1-ene (4g)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 42.6 mg, yield 77%. **(Z: E >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (dd, *J*= 6.1, 1.4 Hz, 2H), 4.36-4.20 (m, 2H), 3.52 (s, 4H), 1.58 (dd, *J*= 6.8, 1.5 Hz, 6H), 0.96 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 146.5, 100.2, 77.5, 37.0, 21.7, 9.2. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{11}H_{20}O_2$ (M^+) *m/z*: 184.1463, found: 184.1460.

***1,1-bis(((Z)-prop-1-en-1-yloxy)methyl)cyclopropane (4h)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 47.0 mg, yield 86%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97 (dd, *J*= 6.1, 1.6 Hz, 2H), 4.38-4.35 (m, 2H), 3.66 (s, 4H), 1.59 (dd, *J*= 6.8, 1.6 Hz, 6H), 0.55 (s, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 146.0, 100.9, 74.9, 21.3, 9.2, 8.3. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{11}H_{18}O_2$ (M^+) *m/z*: 182.1307, found: 182.1311.

***1,6-bis((Z)-prop-1-en-1-yloxy)hexane (4i)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 47.4 mg, yield 86%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dd, *J*= 6.3, 1.6 Hz, 2H), 4.37-4.33 (m, 2H), 3.70 (t, *J*= 6.5 Hz, 4H), 1.64-1.60 (m, 4H), 1.56 (dd, *J*= 6.9, 1.4 Hz, 6H), 1.41-1.38 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 145.6, 100.8, 71.9, 29.7, 25.6, 9.2. (**Only *Z* isomer is visible**). This product is known.[17a]

***(2Z,14Z)-4,7,10,13-tetraoxahexadeca-2,14-diene (4j)*:** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 57.1 mg, yield 83%. **(*Z*: *E* >99:1)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95 (dd, *J*= 6.2, 1.6 Hz, 2H), 4.37-4.34 (m, 2H), 3.85 (t, *J*= 4.9 Hz, 4H), 3.67-3.64 (m, 8H), 1.54 (dd, *J*= 6.9, 1.4 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 145.6, 101.3, 71.3, 70.8, 70.4, 9.2. (**Only *Z* isomer is visible**).

HRMS (EI-TOF): calcd.for $C_{12}H_{22}O_4$ (M^+) *m/z*: 230.1518, found: 230.1522.

***1,3-bis(allyloxy)-2-chlorobenzene (3b)* : Method A:** Allyl bromide (7.86 mL, 90.89 mmol) was slowly added to a stirred solution of 2-chlorobenzene-1,3-diol (3.3 g, 22.73 mmol) and K_2CO_3 (9.4 g, 68.15 mmol) in dry DMF (22 mL) kept at room temperature under nitrogen with stirring. After 20 h the mixture was diluted with H_2O, until dissolution of the precipitate, and washed with ether (3 x 100 mL). The combined extracts were washed with H_2O (8 x 200 mL), brine (200 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressures to give **4b** (4.95 g, 97%) as a yellow oil without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (t, *J*= 8.4 Hz, 1H), 6.58 (d, *J*= 8.3 Hz, 2H), 6.11-6.02 (m, 2H), 5.46 (dd, *J*= 17.2, 1.5 Hz, 2H), 5.30 (dd, *J*= 10.5, 1.4 Hz, 2H), 4.61-4.60 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 155.4, 132.8, 126.9, 117.8, 106.4, 69.9.

HRMS (EI-TOF): calcd.for $C_{12}H_{13}ClO_2$ (M^+) *m/z*: 224.0604, found: 224.0609.

***3-(3-(allyloxy)-2-methylpropoxy)prop-1-ene (3f):* Method B:** The starting alcohol (1.8 g, 20 mmol) was dissolved in dry THF (50 ml) under an atmosphere of nitrogen at 0°C. To this solution was added sodium hydride (2.4 g, 60 mmol) and was allowed to stir for 10 minutes at 0°C. After adding allyl bromide (7.3 g, 60 mmol), the solution was then allowed to stir at room temperature for 30 minutes and reflux overnight. The reaction was quenched by the addition of saturated ammonium chloride solution. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over Na_2SO_4. After evaporation of the volatile solvent under reduced pressure, the residue was purified by flash chromatography(petroleum ether/ethyl acetate = 30/1) on silica gel to afford pure **3f** (2.59g, 76.0%,) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94-5.85 (m, 2H), 5.25 (d, *J*= 17.5 Hz, 2H), 5.14 (d, *J*= 10.9 Hz, 2H), 3.95 (d, *J*= 5.2 Hz, 4H), 3.42-3.86 (m, 2H), 3.32-3.28 (m, 2H), 2.07-1.99 (m, 1H), 0.95 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 135.1, 116.5, 72.8, 72.0, 34.3, 14.5.

HRMS (EI-TOF): calcd.for $C_{10}H_{18}O_2$ (M^+) *m/z*: 170.1307, found: 170.1311.

***1,1-bis((allyloxy)methyl)cyclopropane (3h)*: (Method B: the synthesis method is the same as *3f*):** purified by column chromatography (petroleum ether/ethyl acetate = 30/1). Colorless oil; actual mass 2.6 g, yield 71.1%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90-5.84 (m, 2H), 5.22 (dd, *J*= 17.1, 1.5 Hz, 2H), 5.11 (dd, *J*= 10.3, 1.1 Hz, 2H), 3.95 (d, *J*= 5.5 Hz, 4H), 3.33 (s, 4H), 0.46 (s, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 135.1, 116.6, 73.6, 71.8, 20.7, 8.5.

HRMS (EI-TOF): calcd.for $C_{10}H_{18}O_2$ (M^+) *m/z*: 182.1307, found: 170.1307.

***4,7,10,13-tetraoxahexadeca-1,15-diene (3j)*: (Method B: the synthesis method is the same as *3f*):** Colorless oil; actual mass 3.1 g, yield 67.4%. purified by column chromatography (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93-5.84 (m, 2H), 5.24 (d, *J*= 17.0, 2H), 5.14 (d, *J*= 10.3, 2H), 4.00 (d, *J*= 5.3, 4H), 3.64-3.62 (m, 8H), 3.58-3.56 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 134.7, 117.1, 72.2, 70.6, 69.4.

HRMS (EI-TOF): calcd.for $C_{12}H_{22}O_4$ (M^+) *m/z*: 230.1518, found: 230.1515.

Synthesis of $PhSiD_3$[25]: $LiAlD_4$ (1.2 g, 31.22 mmol) was mixed with dry Et_2O (100 ml) and cooled to 0 °C in an ice bath. Trichlorophenylsilane (2.5 ml, 15.61 mmol) was added slowly to the above suspension in a drop wise manner. After the addition the reaction mixture was brought to room

temperature and refluxed for 24 h. The solvent was evacuated and $PhSiD_3$ was distilled into a cold trap.

$PhSiD_3$: (D=99.5%) Colorless oil; actual mass1.25 g, yield 74.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.48-7.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.3, 130.3, 128.6.

Deuterium labelling experiment: A Schlenk tube was charged with **Co(II)-d** (5.4 mg, 0.009 mmol, 3% equiv), Me_3NFPY•OTf (173.5 mg, 0.6 mmol, 2 equiv), after being dried in vacuo for 3 mins, degassed trifluorotoluene (3 mL) was added. The solution was bubbled with N_2 for three times, after which **1n** (55.3 mg, 0.3 mmol, 1 equiv) and $PhSiD_3$ (66.7 mg, 0.6 mmol, 2 equiv) was added under N_2. The resulting mixture was stirred at rt for 4 hours. After **1n** was completely consumed as monitored by TLC, H_2O (5 mL) was added to quench the reaction. The resulted mixture was then extracted three times with diethyl ether (10 mL × 3). The combined organic layer was dried over Na_2SO_4. After evaporation of the volatile solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (petroleum ether) to afford pure **d-2n** (17.2 mg, 0.17 mmol) as a colourless oil in a yield of 31.0%.

(*d-2n*): Colorless oil; actual mass 17.2 mg, yield 31.0%. (*Z*: *E* >99:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*= 8.5 Hz, 2H), 7.74 (d, *J*= 8.2 Hz, 1H), 7.46 (t, *J*= 7.1 Hz, 1H), 7.37 (t, *J*= 7.3 Hz, 1H), 7.29-7.24 (m, 2H), 6.53-6.62 (m, 1H), 5.00-4.95 (m, 1H), 1.76-1.74 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 140.8, 134.3, 129.8, 129.7, 127.7, 127.0, 126.5, 124.2, 118.6, 110.1, 108.1, 9.2 (t, *J*= 19.5 Hz). (Only *Z* isomer is visible).

HRMS (EI-TOF): calcd.for $C_{13}H_{11}DO$ (M^+) m/z: 185.0951, found: 185.0951.

Gram scale experiment: A 150 mL Three-necked flask was charged with **Co(II)-d** (135.0 mg, 0.225 mmol, 3% equiv), Me_3NFPY•OTf (4.338 g, 15 mmol, 2 equiv), after being dried in vacuo for 3 mins, degassed trifluorotoluene (75 mL) was added. The solution was bubbled with N_2 for three times, after which **1a** (1.005 g, 7.5 mmol, 1 equiv) and $(Me_2SiH)_2O$ (2.015 g, 15 mmol, 2 equiv) was added under N_2. The resulting mixture was stirred at rt for 5 hours. After **1a** was completely consumed as monitored by TLC, H_2O (50 mL) was added to quench the reaction. The resulted mixture was then extracted three times with diethyl ether (100 mL × 3). The combined organic layer was dried over Na_2SO_4. After evaporation of the volatile solvent under reduced pressure, the residue was purified by flash chromatography on silica gel to afford pure **2a** (663.3 mg, 4.95 mmol) as a colourless oil in a yield of 66%, *Z*/*E* >99:1.

ASSOCIATED CONTENT

Supporting Information

General experimental conditions, NMR spectra, and HPLC analysis of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Any additional relevant notes should be placed here.

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