

Rhenium(VII) Oxide Catalyzed Heteroacylative Ring-Opening **Dimerization of Tetrahydrofuran**

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Abstract: Re₂O₇, which is known primarily as a strong oxidant, was found to be a highly selective Lewis acid catalyst that affects the heteroacylative dimerization of THF at room temperature. This multicomponent reaction, which involves THF, trifluoroacetic anhydride (TFAA), and a carboxylic acid, produces a nonsymmetrical diester, RCO₂(CH₂)₄O(CH₂)₄OCOCF₃, in high yields. The reaction is quite general with respect to the carboxylic acid but is highly selective for unsubstituted THF in preference to other cyclic ethers. It is also highly selective for TFAA in preference to other anhydrides. Isotope labeling experiments indicate that two of the five oxygen atoms in the product originate from THF; one comes from rhenium oxide, and the two carbonyl oxygens originate from the carboxylic acid and from TFAA. The catalytic cycle, which is proposed on the basis of these experiments, involves a multistep sequence of nucleophilic attacks, starting with an attack of a rhenium oxo ligand on a coordinated THF, then attack of the resultant alkoxide ligand on a second coordinated THF, nucleophilic addition of the resultant alkoxide ligand to the coordinated carboxylic acid (an intramolecular metal-oxygen bond metathesis), and, finally, electrophilic cleavage of the other coordinated alkoxide by TFAA to produce the nonsymmetrical diester. This synthetically useful reaction highlights the unique, frequently avoided Lewis acidity of transition-metal oxides.

Introduction

High-oxidation-state transition metal oxides are attractive synthetic reagents and catalysts because they are strong oxidants and Lewis acids and can accommodate a high coordination number of ligands. The latter property allows for highly controlled synthetic transformations to occur intramolecularly within the metal coordination sphere. These advantages have been manifested by the many synthetic applications of rhenium-(VII) oxides in various oxidation reactions,¹ including the use of CH₃ReO₃ in olefin epoxidation reactions^{2,3} and of Re₂O₇ in oxidative cyclization of bis-homoallylic alcohols.⁴ The latter reaction has found useful applications in highly selective total syntheses of natural products containing THF and poly-THF fragments, such as the Annonaceous acetogenins.⁵ Surprisingly, the Lewis acid property of Re(VII) oxides has remained

unexplored, and this property has often been mentioned in the literature as a disadvantage. For example, pyridine has been employed in the CH₃ReO₃-catalyzed olefin-epoxidation reaction in order to diminish the Lewis acidity of the catalyst and prevent further ring opening of the epoxide product.³ This report reveals a new reaction, heteroacylative ring-opening dimerization of tetrahydrofurans, based on the unique Lewis acidity of Re(VII) oxides.

The reaction was discovered serendipitously while attempting to expand the substrate scope of the oxidative cyclization reaction to include not only bis-homoallylic alcohols but also other analogous compounds, including the γ , δ -unsaturated carboxylic acid, 1a. Unexpectedly, treatment of 1a with Re₂O₇ and trifluoroacetic anhydride (TFAA) in THF and CH₂Cl₂ did not produce the expected oxidative cyclization product, 2^6 (Scheme 1). Instead, the nonsymmetrical diester, 3a, was obtained in high yield and high purity.

Ring-opening reactions of cyclic ethers are important synthetic transformations because they provide an effective approach to difunctional intermediates and monomers.⁷ Tetrahydrofuran, in particular, has been the most studied cyclic ether in this regard because the resultant 4-carbon building block has many applications in organic synthesis and in polymer chemistry.7a,8 Several Lewis acids⁹ and transition metals^{8,10,11} have been

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Scheme 1



reported to catalyze the ring opening of THF. Nonetheless, most of the known examples have resulted in either monomeric products9,10b-e or complex mixtures of oligomers.8,11 The few reports on the dimerization of THF describe harsh reaction conditions (120-180 °C)^{10a,12} and stoichiometric amounts of the acidic reagent.¹³ Furthermore, no method has been described for nonsymmetric ring-opening dimerization reaction of THF to produce a product with two different end groups.

Here we report on the scope and characteristics of this newly discovered reaction and show that rhenium(VII) oxide can be used as a highly selective Lewis acid catalyst. We show that, in the presence of TFAA and a carboxylic acid at room temperature, Re₂O₇ catalyzes the ring-opening dimerization of THF to produce a nonsymmetrical diester at room temperature. Furthermore, we show that this reaction is highly selective for unsubstituted THF and propose a catalytic cycle on the basis of isotope labeling experiments.

Results and Discussion

Our first goal was to define the reaction conditions and the appropriate proportions of the various reactants in this multicomponent ring opening reaction. In our initial experiments with acid 1a, the choice of the rhenium(VII) reagent was based on our protocol for the oxidative cyclization reactions,^{4,5} where Re₂O₇ was premixed with TFAA and 2 equiv of THF in order to form either $(THF)_2 ReO_3(\eta^1 - O, O - CF_3 CO_2)$ or $(THF) ReO_3 - O_3 - O_3$ $(\eta^2 - O, O - CF_3CO_2)$ in situ.¹⁴ Obviously, the key question from both practical and mechanistic standpoints was whether rhenium(VII) oxide could be used in catalytic amounts. Assuming that other acids could be used instead of 1a, we employed benzoic acid, **1b**, in our exploratory reactions. Thus, using Re_2O_7 (1 equiv), THF (2 equiv), 1b (1 equiv), and TFAA (1.3 equiv) in CH₂Cl₂ at room temperature for 24 h afforded compound 3b in over 90% yield (based on 1b). By varying the amount of Re₂O₇ we found that with 10 mol % Re₂O₇ product 3b was

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- 1957. 348 (14) There are two steps in a typical Re₂O₇-mediated oxidative cyclization reaction. In the first step, (THF)ReO₃(η²-O,O-CF₃CO₂), **10**, was generated reaction for the first step (THF)ReO₃(η²-O,O-CF₃CO₂), **10**, was generated

quantitatively. See: Scheme 2 for details.

obtained in excellent yield (95%). Lower catalyst loadings at a

mmol scale could also be used, but the reaction progressed at slower rates. Interestingly, using THF as solvent rather than CH_2Cl_2 resulted in very low yields of **3b**.

Obviously, the carboxylic acid, 1, plays a crucial role in this reaction because no reaction occurred in its absence. To verify the generality of the reaction with respect to this component, we carried out the reaction in the presence of various aliphatic and aromatic carboxylic acids, 1a-j, and found that in all cases the corresponding acylated THF dimers, 3a-j, were obtained in high yields (78-95%, Table 1). All aryl carboxylic acids examined, bearing either an electron-donating or an electronwithdrawing group, exhibited high reactivity. Likewise, various alkyl carboxylic acids were used successfully in this reaction. The only isolated side products were the corresponding monomeric and trimeric analogues of the main product. For example, in the reaction of **1b** the dimeric product, **3b** (95%), was accompanied by the monomeric, 4b (~4%), and trimeric, 5b(<1%), analogues. Interestingly, trifluoroacetic acid (entry 11) was found to be essentially inactive in this reaction with no reaction being observed even after 5 days at room temperature (<1%). These findings explain why we did not observe this reaction in our previous studies on the oxidative cyclization reactions.

Next, we examined the scope of the reaction with respect to the cyclic ether (Table 2). Interestingly, the reaction was found to be quite selective for unsubstituted THF. For example, unlike the reaction with THF (entry 1), the reactivity of either oxetane or THP (entries 2 and 3) under the same conditions was quite poor, and the expected products 6 and 7 were obtained in no more than 10% yields. In fact, in a competition experiment using acid 1b and a 1:1 mixture of THF and THP in the presence of TFAA and a catalytic amount (10%) of Re₂O₇, only the acylative dimerization of THF, 3b, was noticed by NMR. In the case of 2-methyl-THF (entry 4) only the two monomeric ring-opening products, 8a and 8b, were isolated (5:1, 62%). Similarly, the reaction with 2,5-dimethyl-THF resulted only in the monomeric product 9 in 59% yield (entry 5).

We have also examined the ring-opening reaction with respect to the anhydride partner and found that the reaction is quite selective for TFAA (entry 1, Table 3). When TFAA was replaced by either acetic anhydride (entries 2, 3) or pivalic anhydride (entries 4, 5), essentially no ring-opening products could be isolated in a reaction of THF with various acids even after 5 days. Even with benzoic anhydride, which is more electron deficient, yields did not exceed 5% after 48 h at 36 °C (entry 6).

Role of Re₂O₇. Several experiments were carried out in order to gain insight into the reaction mechanism and the origin of product selectivity. Re₂O₇ is known to react with TFAA in THF to produce the carboxylate complex 10 in high yields (Scheme 2),^{14,15} which can be readily converted to **11** via a carboxylate exchange reaction.^{15b} We prepared both complexes 10 and 11 and used each one of them in control experiments. When 10

Table 1. Re₂O₇-Catalyzed Heteroacylative Ring-Opening Dimerization of THF^a

	$R_{CO_2H} + \left(\begin{array}{c} R_2O_7 (10 \text{ mol}\%) \\ $							
	1 O TFA	A R O	3a-j					
Entry	RCO ₂ H, 1	Time (h)	Product (yield)					
1	C ₁₀ H ₂₁ 1a CO ₂ H	24	3a (R = $C_{10}H_{21}CHCHCH_2CH_2$, 80%)					
2	CO ₂ H 1b	24	3b (R = C ₆ H ₅ , 95%)					
3	H ₃ C 1c	24	3c (R = p -CH ₃ C ₆ H ₄ , 92%)					
4	H ₃ CO Td	24	3d (R = p -CH ₃ OC ₆ H ₄ , 91%)					
5	O ₂ N CO ₂ H	36	3e (R = p -NO ₂ C ₆ H ₄ , 86%)					
6	CO ₂ H	24	3f (R = p -(CH ₂ =CH)C ₆ H ₄ , 92%)					
7	CO ₂ H	24	$3g (R = C_6H_5CH_2, 92\%)$					
8	CO ₂ H	24	3h (R = C ₆ H ₅ CH=CH, 78%)					
9	CH₃CO₂H 1i	42	3i (R = CH ₃ , 87%)					
10	→co₂H 1j	42	3j (R = t-Bu, 82%)					
11	CF_3CO_2H 1k	120	3k (R = CF ₃ , < 1%)					

^{*a*} Yields of isolated products are based on substrate **1**. All reactions were carried out in CH₂Cl₂ at room temperature with molar ratio of Re₂O₇/1/THF/ TFAA = 1:10:25:15. Small amounts of monomeric products, **4** (<4%), and trimeric products, **5** (<1%), were also isolated in all cases.

was treated with **1b**, TFAA, and THF, compound **3b** was obtained in high yields. The same result was achieved when **11** was used for the same reaction in the absence of **1b**.^{15c} We conclude that Re_2O_7 is a catalyst precursor and that complexes **10** and **11** are probably the actual species that participate in the catalytic cycle.

Origin of the Oxygen Atoms in the Product. To reveal the origin of the three oxygen atoms in the saturated portion of **3b**, several isotope-labeling experiments were conducted. First, a stoichiometric amount of $\text{Re}_2^{18}O_7$ (>90 At%-¹⁸O)¹⁶ was used in the reaction with **1b**. In the high-resolution mass spectrum (HRMS, ESI-TOF) of the isolated product **3b**, a distinct peak

at m/z = 387.1288, consistent with incorporation of one ¹⁸O in [**3b** · Na⁺] ion, was observed along with a peak at m/z = 385.1239, consistent with its ¹⁶O-isotopomer.¹⁷ No indication for the incorporation of more than one ¹⁸O could be detected. These observations indicate that one Re=O bond is involved in the THF ring-opening step.

Next, we prepared a doubly labeled benzoic acid (PhC¹⁸ O_2 H, > 92 At%-¹⁸O)¹⁸ and used it in a stoichiometric reaction with Re₂O₇. Unexpectedly, the HRMS of the isolated product revealed that only one out of the two ¹⁸O atoms in **1b** was incorporated into **3b** (ESI-TOF, m/z = 387.1282). The same result was obtained when **11**-(η^2 -O,O-¹⁸ O_2 CPh),¹⁹ which was prepared from **10** using PhC¹⁸ O_2 H, was employed instead of Re₂O₇ under the same conditions. The identity of ¹⁸O in the

^{(15) (}a) Edwards, P.; Wilkinson, G. J. Chem. Soc., Dalton Trans. 1984, 2695. (b) Complex 11 can be prepared by addition of 1b to a (THF)ReO₃(η²-O,O-RCO₂) complex, where R = CF₃, CH₃, or C(CH₃)₃. However, the carboxylate exchange with the trifluoroacetoxyl ligand would be the most kinetically favorable. These Re-carboxylate complexes are all moisturesensitive and thermally unstable.

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⁽¹⁷⁾ Theoretical mass: 387.1276 for ¹⁸O₁-[3b·Na⁺]; 385.1233 for ¹⁶O-[3b·Na⁺].

⁽¹⁸⁾ The ¹⁸O-labeled **1b** has been previously prepared; see: Wnuk, S. F.; Chowdhury, S. M.; Garcia, P. I., Jr.; Robins, M. J. J. Org. Chem. **2002**, 67, 1816 and references therein

⁽¹⁹⁾ The integrity of PhC¹⁸O₂-ligand was verified by ESI-TOF. In the CH₂Cl₂ extract of a hydrolyzed solution of $11-(\eta^2-O,O^{-18}O_2\text{-CPh})$, a distinct peak at m/z = 125.0376 attributed to PhC¹⁸O₂-anion was observed.



^a All reactions were carried out under the conditions mentioned in Table 1. Yields are based on benzoic acid, 1b.

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RCO ₂ H + (I 1	r'CO₂)O + ⟨	$\begin{array}{c} & & \\$	0. 3'	O O R'
THF ^a				

Table 3. Re₂O₇-Catalyzed Acylative Ring-Opening Dimerization of

entry	R	R′	time (h)	product (yield)
1	Ph	CF ₃	24	3b (95%)
2	CH ₃	CH ₃	120	3l (1%)
3	Ph	CH_3	72	
4	(CH ₃) ₃ C	(CH ₃) ₃ C	120	
5	Ph	$(CH_3)_3C$	72	
6	Ph	Ph	48 (at 36 °C)	3m (5%)

^{*a*} Yields of isolated products are based on substrate **1**. All reactions were carried out under the general conditions described in Table 1 with the appropriate changes of the carboxylic acid and anhydride.

Scheme 2

product was further determined by ¹³C{¹H} NMR experiments, taking advantage of the fact that¹⁸O-isotopes are known to induce an upfield-shift in ¹³C{¹H} NMR.²⁰ Thus, when a 1:1 mixture of **1b** and **1b**-¹⁸O₂ was used stoichiometrically, the resultant ¹³C{¹H} NMR spectrum confirmed that only the carbonyl oxygen in **3b** remained ¹⁸O-labeled ($\Delta \delta = \delta(C^{16}O) - \delta(C^{18}O) = 0.031$ ppm).²¹ Overall, two of the five oxygen atoms in **3b** originate from THF, one comes from thenium oxide, and the two carbonyl oxygens originate from **1b** and from TFAA. These findings represent the first example of oxygen incorporation from a transition-metal oxide into the ring-opening products of THF.

Proposed Mechanism. Our proposed catalytic cycle (Scheme 3) starts with **10**, which undergoes facile carboxylate exchange

to give 11 (Scheme 2).¹⁵ In solution the carboxylate ligand in both 10 and 11 is likely to undergo fast equilibrium between its η^1 and η^2 modes.^{15a,22} Complexation of the second carboxylate oxygen in 11 activates the trans oxo ligand to undergo nuclophilic attack on the adjacent THF ligand,^{23,24} resulting in a dioxometallacycle, A. This nucleophilic attack is reminiscent of the known reaction between CH₃ReO₃ and an epoxide.²⁵ Coordination of a second THF to give **B** followed by a nucleophilic attack of the alkoxide ligand on that THF leads to a second ring-opening step to produce C. Although complex C is analogous to A, the central oxygen in the diolate ligand in C can coordinate to Re and thereby shift the carboxylate η^2/η^1 equilibrium toward η^1 (C'/C") rather than η^2 (C). The η^1 carboxylate in C'/C", a 14e Re dioxide, would then undergo facile metal-oxygen bond metathesis with concomitant coordination of a THF molecule to give a 16e Re trioxide species, D. An analogous conversion of a 14e Re dioxide to a 16e Re trioxide has been recently reported.²⁶ Finally, electrophilic cleavage of the metal oxygen bond in **D** with TFAA leads to product **3b** which regenerates the catalyst, **10**.

This proposed catalytic cycle could also explain the observation that the main product, **3b**, is accompanied by small amounts of the monomeric analogue, **4b** (<4%), and trimeric one, **5b** (<1%).^{27a} Formation of **4b** could result from an η^1/η^2 equilibrium between **A** and **A'**, followed by metal–oxygen bond metathesis with concomitant coordination of a THF molecule to produce **E**, which then reacts with TFAA to produce **4b**, the

⁽²⁰⁾ Risley, J. M.; van Etten, R. L. In *NMR Basic Principles Progress*; Diehl, P., Fluck, E., Günther, E., Kosfeld, R., Seeling, J., Eds.; Springer: Berlin, 1990; Vol. 22.

^{(21) (}a) A difference of 0.031 ppm in ¹³C NMR is consistent with the average value for one ¹⁸O-incorporated isotopomers. The observed two ¹³C signals were not in equal intensity (~2:1), indicating a kinetic isotope effect may be involved. (b) The ¹³C resonance difference between PhCO₂H and PhC¹⁸O₂H is 0.046 ppm.

⁽²²⁾ In solid state, the carboxylate ligand exits in its η² mode. See: ref 15a.
(23) (a) Three resonance structures of a Re=O bond, Re⁺−O⁻, Re=O, and Re⁻≡O⁺ have been analyzed; see: Herrmann, W. A., et al. J. Am. Chem. Soc. **1991**, 113, 6527. (b) Upon complexation of a ligand, the increased electron density on the trans ligand could be attributable to a situation similar to a *trans influence* on the trans ligand; see: Cotton F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th ed.; John Wiley & Sons: New York, 1988; p 1300.

^{(24) (}a) The THF ligand is believed to undergo fast exchange. As **3** was not generated in reactions conducted in THF, this result could be attributable to the fact that the THF is constantly undergoing exchange rather than sticking to Re, resulting in no ring opening of THF. (b) The presence of TFAA and CF_3CO_2H , generated in situ, can slow down the THF exchange rate and thereby promote ring opening of a bound THF.

^{(25) (}a) Al-Ajlouni, A. M.; Espenson, J. H. J. Am. Chem. Soc. 1995, 117, 9243.
(b) Zhu, Z.; Al-Ajlouni, A. M.; Espenson, J. H. Inorg. Chem. 1996, 35, 1408.

⁽²⁶⁾ Herrmann, W. A.; Wojtczak, W. A.; Artus, G. R. J.; Kühn, F. E.; Mattner, M. R. Inorg. Chem. 1997, 36, 465. See: Scheme 2 on p 468.

Scheme 3. Proposed Catalytic Cycle



Scheme 4. Proposed Mechanism for the Formation of 4b and 5b



smaller analogue of **3b** (Scheme 4). Formation of **5b** reflects a minor route of THF coordination to **C**, leading to **F**, which could continue via **G**, **H**, then a metal alkoxide, **I**, and finally to **5b**. One possible mechanistic route to **3b** could involve a concerted ring-opening reaction in ReO₃(THF)₂(η^{1} -*O*-OCOPh), where two THF ligands are concurrently bound to the metal.^{27b} This model, however, cannot explain the formation of the trimeric products, **5b**, because a third THF ligand will bring the total electron count from 18 to 20. Therefore, it is more likely that the acylative dimerization reaction proceeds via a stepwise fashion with one coordinated THF at a time.

As some ring-opening reactions of THF have been reported to be governed by equilibrium control,^{8b,10a,28} we conducted a series of control experiments to examine this possibility. A CH_2Cl_2 solution of **5b** was treated with a catalytic amount (10 mol %) of Re_2O_7 , **10**, **11**, or CF_3CO_2H , separately, but no **3b** could be observed by TLC over a period of 24 h. Therefore, we exclude the equilibrium-control mechanism.

Apparently, TFAA plays an essential role in this reaction. On one hand, the coordinated trifluoroacetate in **10** is too electron-deficient to activate an oxo ligand for a nucleophilic attack on the coordinated THF (Table 1, entry 11). All other carboxylic acids examined, **1a**–**j**, seem to be sufficiently electron-rich to activate the oxo ligand (Table 1, entries 1–10). On the other hand, the low electrophilicity of other anhydrides examined (Table 3, entries 2–6) does not allow them to complete the last step of the catalytic cycle. Thus, the role of

^{(27) (}a) Compounds 4 and 5 are further characterized by partial hydrolysis. See: Supporting Information for details. (b) Such a model would be entropy disfavored.

⁽²⁸⁾ Delfs, P. B. 717, O.T.S., U.S. Department of Commerce.

TFAA is twofold, first, to form a labile carboxylate complex, **10**, and, second, to cleave the metal—oxygen bond in complex **D**, producing **3** and regenerating the actual catalyst, **10**.

Conclusions

An effective Re-catalyzed THF ring opening/dimerization was discovered with Re₂O₇ serving as a convenient catalyst precursor. This catalyst exhibits high selectivity for unsubstituted THF, providing the most effective method currently available for ring opening of THF. The methodology is of synthetic value, particularly for polymer chemistry. Since isotope-labeled Re₂¹⁷O₇ and Re₂¹⁸O₇ can be easily prepared, the transfer of one oxygen atom from Re to the product can be utilized as a useful tool for the synthesis of oxygen-labeled organic molecules. Overall, this study has not only expanded the scope of rhenium catalysis but also highlighted the unique, frequently avoided Lewis acidity of transition-metal oxides.

Experimental Section

General Methods. Unless otherwise stated, all NMR spectral data were acquired in CDCl3 at room temperature, in which ¹H and ¹³C NMR spectra were obtained on a Varian-Mercury 300 MHz (75.5 MHz for ¹³C) spectrometer, and ¹⁹F{¹H} NMR data were obtained on a Bruker-AMX 400 MHz spectrometer. The ¹H and ¹³C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to residual solvent resonances (¹H NMR: δ 7.24 for CDCl₃; ¹³C NMR: δ 77.00 for CDCl₃), where the ¹H NMR chemical shifts are given followed by multiplicity, coupling constants J in hertz, and integration in parentheses. For complex coupling patterns, e.g., δ (dt, J = 7.7, 4.8, 1H), the doublet (d) represents the larger coupling (7.7) Hz), and the triplet (t) indicates the smaller coupling (4.8 Hz). The ¹⁹F{¹H} NMR chemical shifts are referenced to an external perfluorobenzene solution. Assignments are provided for key moieties only. High-resolution mass spectra were obtained on an Agilent ESI-TOF mass spectrometer. For ¹⁸O-labeled starting materials, a technique of desorption/ionization on silicon (DIOS) was used with an Applied Biosystems Voyager-DE STR mass spectrometer, and the ¹⁸O-labeled percentage was calculated according to published methods. Chromatography was carried out on silica gel (230-400 mesh) from Merck, or with a Harrison Research Chromatotron, where silica gel plates were used under an argon atmosphere. Thin-layer chromatography (TLC) was performed on aluminum- or glass-backed silica gel 60-F254 sheets from Merck and was visualized under a UV lamp and by a cerium(IV) sulfate or cerium(IV) molybdate staining agent. All reactions were conducted under argon unless otherwise stated.

Materials. Et₂O and THF were distilled over sodium benzophenone ketyl and potassium metal, respectively, and CH₂Cl₂ was distilled over CaH₂ under argon prior to use. Trifluoroacetic anhydride (TFAA) and liquid carboxylic acids were purified according to published procedures. Oxetane, tetrahydropyran, and substituted THF were distilled over potassium metal. Solid carboxylic acids were dried by azeotropic evaporation with CH₂Cl₂ repeatedly under a vacuum. Re₂O₇ was purchased from Strem. Labeled H₂¹⁸O (98.07 At%) was purchased from Rotem Industries, Israel. Labeled Re₂¹⁸O₇ was prepared according to modified literature methods, and the ¹⁸O-labeled percentage of Re₂O₇ was determined by the DIOS mass spectra obtained from ¹⁸O-labeled AgReO₄. Complexes **10** and **11** were prepared either in situ or in their isolated form prior to use.

PhC¹⁸*O*₂**H.** Benzoic acid (514 mg, 4.2 mmol) was dissolved in a mixture of $H_2^{18}O$ (98 At%, 1 mL) and a solution of HCl in Et₂O (2 mL, 1M) in a 25 mL reaction bomb. The reaction vessel was heated at 65 °C with vigorous stirring under a closed condition for 24 h. Volatile species was then removed, and the process was repeated once. The obtained residue was redissolved in Et₂O (20 mL), and the resulting

solution was concentrated to a volume of ca. 1.5 mL. The solution part was removed, and the obtained solid was further dried in vacuo over KOH to afford the title compound as a white crystalline solid (450 mg, 85%). The ¹⁸*O*-incorporation of the title compound is estimated to be >92%, as calculated from the obtained mass spectra according to literature methods. ESI-DIOS: m/z 125 (100, PhC¹⁸ O_2^-), 123 (9, PhC¹⁸ $O^{-6}O^-$), 121 (2, PhCO₂⁻).

 $\mathbf{Re_2}^{18}O_7$. The isotope-enriched $\mathrm{Re_2O_7}$ has been previously prepared (eqs 1–3).

$$\operatorname{Re}_{2}O_{7} + \operatorname{H}_{2}O \rightarrow [2 \operatorname{HReO}_{4}] \xrightarrow{2 \operatorname{AgNO}_{3}}{-2 \operatorname{HNO}_{3}} 2 \operatorname{AgReO}_{4}$$
(1)

$$AgReO_4 + (CH_3)_3SiCl \xrightarrow{-AgCl} (CH_3)_3SiOReO_3$$
(2)

$$2(CH_3)_3 SiOReO_3 + 2 THF \xrightarrow{-[(CH_3)_3Si]_2O} Re_2O_7(THF)_2$$
(3)

AgRe¹⁸ O_4 . To ensure high ¹⁸O-isotope incorporation into the rhenium oxide bonds, the procedure for the preparation of $AgRe^{18}O_4$ was modified. Re₂O₇ (485 mg, 1.0 mmol) was dissolved in 1 mL of H₂¹⁸O (98 At%), and the resulting solution was stirred at room temperature for 4 h. Volatile species was then removed under a vacuum, and the process was repeated twice. In a separate flask, AgNO3 (341 mg, 2.0 mmol) was dissolved in 1 mL of H218O (98 At%) in a 25 mL reaction bomb, and the resulting solution was heated at 65 °C with vigorous stirring under a closed condition for 24 h. Volatile species was removed under a vacuum, and the process was repeated once. The H218O-treated AgNO₃ salt was then added to the previous reaction flask containing ¹⁸O-labeled HRe¹⁸O₄, and 1 mL of H₂¹⁸O (98 At%) was added with stirring. A white precipitate was observable immediately. The resulting mixture was allowed to stir at room temperature for 1 h under subdued room light. The white precipitate was collected with a glass-fritted funnel and washed with Et₂O (2 \times 10 mL), and was further dried in vacuo over KOH to afford the title complex as a white powder (656 mg). The ¹⁸O-incorporation of the title compound is estimated to be >90%, as calculated from the obtained ESI-DIOS mass spectra and the computer-simulated isotope pattern.

Ring Opening/Dimerization Reactions of THF. Catalytic Reactions. (*Method a*) Using **1b** as an example. In a typical reaction, Re₂O₇ (130 mg, 0.268 mmol) was placed in a Schlenk flask under argon and the flask was capped with a septum. CH₂Cl₂ (8 mL) was added via syringe, followed by the addition of TFAA (570 μ L, 4.035 mmol) and THF (550 μ L, 6.780 mmol). Under positive argon pressure, **1b** (332 mg, 2.718 mmol) was added, and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was worked up with saturated NaHCO₃ aqueous solution (8 mL) and H₂O₂ (35 wt %, 2 mL) and was extracted with ether (3 × 25 mL). The ether extract was dried with MgSO₄ and concentrated under a vacuum and was purified by column chromatography (hexanes/EtOAc = 5:1) to afford **3b** (935 mg, 95%), **4b** (24 mg, 3%), and **5b** (11 mg, < 1%) as a colorless oil, respectively. The yield is based on **1b**.

(*Method b*) In a typical reaction, Re₂O₇ (130 mg, 0.268 mmol) was placed in a Schlenk flask under argon and the flask was capped with a septum. THF (550 μ L, 6.780 mmol) was added via syringe, and the solution was allowed to stir until Re₂O₇ was completely dissolved. CH₂-Cl₂ (8 mL) was added and a clear solution resulted. TFAA(570 μ L, 4.035 mmol) and **1b** (332 mg, 2.718 mmol) were then added, respectively, and the reaction mixture was allowed to stir under argon for 24 h. The result obtained was almost the same as that described in *method a*.

Stoichiometric Reactions. Similar to the procedure described in the catalytic reactions. In a typical reaction, the reaction was conducted in CH_2Cl_2 (8 mL) with the molar ratio of $Re_2O_7/TFAA/1b$: THF being equal to 1.15:3.45:2.0:6.90, in which 332 mg of 1b were used. The reaction mixture was allowed to stir at room temperature for 24 h, and the workup was carried out as stated in the catalytic reactions.

Isotope Labeling Experiments. The procedure described in the stoichiometric reactions was followed, and PhC¹⁸O₂H and Re₂¹⁸O₇ were used in separate reactions, respectively. According to the ESI-TOF mass spectra of the isolated products, isopotomers with one ¹⁸O-incorporation were observed along with peaks associated with their ¹⁶O-analogues. Isotopomers with two or more ¹⁸O-incorporation were not observed. The same result was obtained from **3b**, **4b**, and **5b**. HRMS m/z 385.1237 (**3b**·Na⁺ = 385.1233), 387.1280 (**3b**·Na⁺-¹⁸O₁ = 387.1276); 313.0677 (**4b**·Na⁺ = 313.0658), 315.0713 (**4b**·Na⁺-¹⁸O₁ = 315.0701); 457.1816 (**5b**·Na⁺ = 457.1808), 459.1858 (**5b**·Na⁺-¹⁸O₁ = 459.1851).

Compound 1a: Homoallylic carboxylic acid **1a** was obtained by hydrolysis of its corresponding ethyl ester, which was prepared from undecanal (Aldrich) according to conventional methods described for the syntheses of homoallylic alcohols.^{5b} ¹H NMR δ 11.25 (br s, 1H), 5.50–5.30 (m, 2H), 2.42–2.36 (m, 2H), 2.32–2.27 (m, 2H), 1.96–1.93 (m, 2H), 1.40–1.20 (m, 16H), 0.88–0.83 (m, 3H).

Compound 3a: ¹H NMR (600 MHz) δ 5.45–5.35 (m, 2H), 4.37 (t, J = 6.6, 2H, $CH_2OC(O)CF_3$), 4.07 (t, J = 6.5, 2H, $CH_2OC(O)CH_2-CH_2-$), 3.43 (t, J = 6.0, 2H), 3.41 (t, J = 6.0, 2H), 2.35–2.32 (m, 2H, HC=CH–CH₂CH₂CO₂–), 2.30–2.27 (m, 2H, HC=CH–CH₂CH₂CO₂–), 1.95–1.93 (m, 2H, HC=CH–CH₂CgH₁₉), 1.84–1.82 (m, 2H, CH₂CH₂OC(O)CF₃), 1.69–1.59 (m, 6H), 1.32–1.23 (m, 16H), 0.86 (vt, J = 5.9, 3H); ¹³C NMR (150.9 MHz) δ 173.32, 157.51 (q, J = 41.3, COCF₃), 131.85 (HC=CHC₁₀H₂₁), 127.84 (HC=CHC₁₀H₂₁), 114.45 (q, J = 285.8, CF₃), 70.35, 69.88, 68.06 (CH₂OC(O)CF₃), 64.06 (CH₂OC(O)CH₂CH₂–), 34.39, 32.49, 31.89, 29.62 (for 2 C), 29.49, 29.43, 29.33, 29.13, 27.93, 26.19, 25.81, 25.50, 25.22, 22.66, 14.09 (CH₃). The assignment is based on COSY, HMBC, and APT spectra.

Compound 3b: ¹H NMR δ 8.02 (app d, J = 7.8, 2H), 7.53 (app t, J = 7.2, 1H), 7.41 (app t, J = 7.6, 2H), 4.35 (t, J = 6.3, 2H, CH₂-OCOCF₃), 4.32 (t, J = 6.6, 2H, CH₂OCOPh), 3.45 (t, J = 6.0, 2H), 3.43 (t, J = 6.0, 2H), 1.85–1.60 (m, 8H); ¹³C NMR δ 166.56, 157.46 (q, J = 42.1, COCF₃), 132.82, 130.34, 129.49, 128.28, 114.49 (q, J = 285.8, CF₃), 70.34, 69.87, 68.06, 64.70 (CH₂OCOPh), 26.28, 25.79, 25.59, 25.20; ¹⁹F NMR δ –74.83. HRMS m/z 385.1219 385.1236 (MNa⁺ = 385.1233).

Compound 3c: ¹H NMR δ 7.90 (d, J = 8.0, 2H), 7.21 (d, J = 8.0, 2H), 4.36 (t, J = 6.6, 2H), 4.30 (t, J = 6.6, 2H), 3.45 (t, J = 5.4, 2H), 3.43 (t, J = 6.0, 2H), 2.38, (s, 3H), 1.85–1.60 (m, 8H); ¹³C NMR δ 166.69, 157.49 (q, $J = 41.2, COCF_3$), 143.49, 129.52, 129.00, 127.58, 114.49 (q, $J = 258.8, CF_3$), 70.37, 69.88, 68.07, 64.53, 26.28, 25.79, 25.59, 25.20, 21.60 (CH₃).

Compound 3d: ¹H NMR δ 7.96 (d, J = 8.7, 2H), 6.88 (d, J = 8.7, 2H), 4.35 (t, J = 6.5, 2H), 4.28 (t, J = 6.3, 2H), 3.44 (t, J = 6.0, 2H), 3.42 (t, J = 6.0, 2H), 1.85–1.60 (m, 8H); ¹³C NMR δ 166.33, 163.24, 157.45 (q, $J = 42.1, COCF_3$), 131.49, 122.74, 114.47 (q, $J = 285.8, CF_3$), 113.50, 70.35, 69.85, 68.06, 64.38, 55.34 (OCH₃), 26.28, 25.77, 25.61, 25.19.

Compound 3e: ¹H NMR δ 8.26 (AB pattern d, J = 8.7, 2H), 8.19 (AB pattern d, J = 8.7, 2H), 4.38 (t, J = 6.3, 2H), 4.37 (t, J = 6.6, 2H), 3.46 (t, J = 6.3, 2H), 3.44 (t, J = 6.0, 2H), 1.90–1.60 (m, 8H); ¹³C NMR δ 164.71, 157.52 (q, J = 42.1, COCF₃), 150.48, 135.72, 130.66, 123.52, 114.50 (q, J = 285.8, CF₃), 70.27, 70.02, 68.06, 65.77, 26.24, 25.79, 25.58, 25.25.

Compound 3f: ¹H NMR δ 7.97 (d, J = 8.4, 2H), 7.43 (d, J = 8.4, 2H), 6.72 (dd, J = 17.7, 10.8, 1H, CH=CH₂), 5.84 (d, J = 17.7, 1H), 5.35 (d, J = 10.8, 1H), 4.36 (t, J = 6.6, 2H), 4.32 (t, J = 6.3, 2H), 3.45 (t, J = 6.0, 2H), 3.43 (t, J = 5.7, 2H), 1.87–1.59 (m, 8H); ¹³C NMR δ 166.37, 157.47 (q, J = 42.1, COCF₃), 141.84, 135.95 (CH=CH₂), 129.81, 129.42, 126.03, 116.41 (CH=CH₂), 114.49 (q, J = 285.6, CF₃), 70.35, 69.89, 68.06, 64.70, 26.26, 25.77, 25.58, 25.19.

Compound 3g: ¹H NMR δ 7.40–7.20 (m, 5H), 4.35 (t, J = 6.6, 2H), 4.09 (t, J = 6.3, 2H), 3.60 (s, 2H), 3.39 (t, J = 6.3, 2H), 3.37 (t, J = 6.3, 2H), 1.86–1.76 (m, 2H), 1.73–1.52 (m, 6H); ¹³C NMR δ 171.54, 157.42 (q, J = 42.1, COCF₃), 134.06, 129.16, 128.45, 126.95,

114.47 (q, J = 285.8, CF_3), 70.19, 69.76, 68.03, 64.58, 41.33 (CH_2 -Ph), 26.02, 25.73, 25.38, 25.16.

Compound 3h: ¹H NMR δ 7.66 (d, J = 15.9, 1H), 7.52–7.49 (m, 2H), 7.37–7.35 (m, 3H), 6.42 (d, J = 15.9, 1H), 4.37 (t, J = 6.6, 2H), 4. 21 (t, J = 6.3, 2H), 3.44 (t, J = 6.2, 4H), 1.86–1.60 (m, 8H); ¹³C NMR δ 167.03, 157.51 (q, J = 42.1, COCF₃), 144.67, 134.37, 130.24, 128.86, 128.03, 118.10, 114.50 (q, J = 285.8, CF₃), 70.36, 69.89, 68.08, 64.31, 26.23, 25.82, 25.59, 25.22.

Compound 3i: ¹H NMR δ 4.36 (t, J = 6.5, 2H), 4.06 (t, J = 6.5, 2H), 3.42 (t, J = 6.0, 2H), 3.40 (t, J = 5.4, 2H), 2.03 (s, 3H), 1.85–1.76 (m, 2H), 1.73–1.50 (m, 6H); ¹³C NMR δ 170.99, 157.32 (q, J = 41.2, COCF₃), 114.41 (q, J = 285.8, CF₃), 70.17, 69.74, 67.96, 64.10, 26.03, 25.67, 25.34, 25.10, 20.72 (CH₃); HRMS m/z 323.1074 (MNa⁺ = 323.1082).

Compound 3j: ¹H NMR δ 4.37 (t, J = 6.5, 2H), 4.05 (t, J = 6.2, 2H), 3.42 (t, J = 6.3, 2H), 3.41 (t, J = 5.4, 2H), 1.86–1.75 (m, 2H), 1.70–1.55 (M, 6H), 1.17 (s, 9H); ¹³C NMR δ 178.58, 157.48 (q, J = 42.1, COCF₃), 114.49 (q, J = 285.8, CF₃), 70.37, 69.85, 68.06, 64.09, 38.69 (CMe₃), 27.14 (CH₃), 26.18, 25.79, 25.48, 25.22.

Compound 3k: ¹H NMR δ 4.36 (t, J = 6.6, 4H), 3.43 (t, J = 6.0, 4H), 1.86–1.78 (m, 4H), 1.69–1.60 (m, 4H); ¹⁹F NMR δ –74.85. HRMS m/z 377.0803 (MNa⁺ = 377.0794).

Compound 31: ¹H NMR δ 4.06 (t, J = 6.3, 4H), 3.41 (t, J = 6.2, 4H), 2.03 (s, 6H), 1.72–1.58 (m, 8H). HRMS m/z 269.1357 (MNa⁺ = 269.1359).

Compound 3m: ¹H NMR δ 8.02 (app d, J = 7.8, 4H), 7.53 (app t, J = 7.2, 2H), 7.41 (app t, J = 7.6, 4H), 4.33 (t, J = 6.6, 4H, CH₂-OC(O)Ph), 3.47 (t, J = 6.0, 4H), 1.90–1.68 (m, 8H); ¹³C NMR δ 166.62, 132.84, 130.37, 129.53, 128.31, 70.33, 64.79, 26.35, 25.63. HRMS m/z 393.1677 (MNa⁺ = 393.1672).

Compound 4b: ¹H NMR δ 8.02 (app d, J = 7.8, 2H), 7.56 (app t, J = 7.2, 1H), 7.43 (app t, J = 7.7, 2H), 4.42 (t, J = 6.0, 2H), 4.36 (t, J = 6.0, 2H), 1.92–1.87 (m, 4H); ¹⁹F NMR δ –74.77.

Compound 5b: ¹H NMR δ 8.02 (app d, J = 8.1, 2H), 7.54 (app t, J = 7.2, 1H), 7.42 (app t, J = 7.7, 2H), 4.36 (t, J = 6.6, 2H), 4.33 (t, J = 6.6, 2H), 3.48–3.38 (m, 8H), 1.90–1.58 (m, 12H); ¹³C NMR, partial spectrum (carbon signals for *COCF*₃ are not provided) δ 166.63, 132.84, 130.38, 129.52, 128.31, 70.75, 70.68, 70.22, 69.80, 68.11, 64.80, 26.47 (with high intensity, two ¹³C signals overlapping), 26.35, 25.83, 25.62, 25.42; ¹⁹F NMR δ –74.85. HRMS m/z 457.1806 (MNa⁺ = 457.1808).

Partial Hydrolysis of 3b. Compound **3b** was further characterized by partial hydrolysis to remove the trifluoroacetyl group. Compound **3b** (20 mg) was dissolved in CH₂Cl₂ (5 mL), and a small amount of silica gel was added. The resulting mixture was allowed to stir overnight at room temperature. The solvent of the reaction mixture was evaporated, and the residue was purified by column chromatography (hexanes/EtOAc = 2.5 :1) to afford the partially hydrolyzed product, PhCO₂(CH₂)₄O(CH₂)₄OH, in quantitative yield. ¹H NMR δ 8.00 (app d, *J* = 8.0, 2H), 7.51 (app t, *J* = 7.5, 1H), 7.39 (app t, *J* = 7.6, 2H), 4.31 (t, *J* = 6.5, 2H), 3.60 (t, *J* = 6.2, 2H), 3.46 (t, *J* = 6.3, 2H), 3.43 (t, *J* = 5.7, 2H), 2.70 (br s, 1H, OH), 1.88–1.58 (m, 8H); ¹³C NMR δ 166.59, 132.80, 130.23, 129.45, 128.25, 70.85, 70.32, 64.67, 62.58 (CH₂OH), 30.10, 26.69, 26.16, 25.51.

Partial Hydrolysis of 5b. Compound **5b** (5 mg) was partially hydrolyzed, as described in the case of **3b**, to afford PhCO₂(CH₂)₄O-(CH₂)₄O(CH₂)₄O(CH₂)₄O(H in quantitative yield. ¹H NMR δ 8.02 (app d, *J* = 8.0, 2H), 7.54 (app t, *J* = 7.5, 1H), 7.42 (app t, *J* = 7.8, 2H), 4.32 (t, *J* = 6.3, 2H), 3.64–3.60 (m, 2H), 3.47–3.39 (m, 8H), 2.50 (br s, 1H, OH), 1.90–1.58 (m, 12H); ¹³C NMR δ 166.65, 132.84, 130.39, 129.53, 128.31, 70.88, 70.83, 70.63, 70.22, 64.83, 62.78 (CH₂OH), 30.44, 26.99, 26.43, 26.40, 26.36, 25.63.

Reactivity of Other Cyclic Ethers and Substituted THF. The procedure described in the catalytic reactions of THF was followed. See Tables 2 and 3 for yields.

Compound 6: ¹H NMR δ 8.06 (app d, J = 7.6, 2H), 7.58 (app t, J = 7.2, 1H), 7.43 (app t, J = 7.6, 2H), 4.37 (t, J = 6.2, 4H), 3.42 (t, J = 6.0, 4H), 1.96–1.88 (m 4H); ¹³C NMR δ 162.18, 157.27 (q, J = 42.1, COCF₃), 134.43, 130.43, 128.76, 120.07, 114.40 (q, J = 285.8, CF₃), 66.57 (with high intensity, two ¹³C signals overlapping), 65.23 (with high intensity, two ¹³C signals overlapping), 28.50 (with high intensity, two ¹³C signals overlapping).

Compound 7: ¹H NMR δ 8.02 (app d, J = 8.1, 2H), 7.53 (app t, J = 7.2, 1H), 7.41 (app t, J = 7.5, 2H), 4.33 (t, J = 6.6, 2H), 4.31 (t, J = 6.4, 2H), 3.42 (t, J = 6.5, 2H), 3.40 (t, J = 6.1, 2H), 1.84–1.70 (m, 4H), 1.67–1.40 (m, 8H); ¹³C NMR δ 166.36, 157.50 (q, J = 42.1, COCF₃), 132.65, 130.24, 129.34, 128.14, 114.39 (q, J = 285.8, CF₃), 70.70, 70.40, 68.15, 64.95, 29.49, 29.29, 28.70, 28.09, 22.93, 22.50.

Compound 8a: ¹H NMR δ 8.02 (app d, J = 8.2, 2H), 7.55 (app t, J = 7.2, 1H), 7.43 (app t, J = 7.8, 2H), 5.20–5.13 (m, 1H), 4.37–4.30 (m, 2H), 1.92–1.72 (m, 4H), 1.38 (d, J = 6.3, 3H); ¹³C NMR δ 166.39, 157.03 (q, J = 42.1, COCF₃), 132.94, 130.03, 129.45, 128.32, 114.49 (q, J = 285.8, CF₃), 75.89 (CHCH₃), 64.08 (CH₂OCOPh), 31.97, 24.41, 19.36 (CH₃). The characterization is based on APT and the ¹³C NMR data of the product isolated from the reaction with ¹³C-labeled **1b**.

Compound 8b: ¹H NMR δ 8.03 (app d, J = 7.5, 2H), 7.53 (app t, J = 7.2, 1H), 7.41 (app t, J = 7.8, 2H), 5.28–5.10 (m, 1H), 4.37–4.30 (m, 2H), 1.92–1.72 (m, 4H), 1.37 (d, J = 6.3, 3H); ¹³C NMR, partial spectrum, δ 166.04, 132.82, 132.76, 128.26, 71.03 (CHCH₃), 64.57 (CH₂OCOCF₃), 32.51, 24.80, 19.98 (CH₃).

Compound 9 (syn and anti): ¹H NMR, combined spectra, δ 8.02 (app d, J = 7.2, 2H), 7.55 (app t, J = 7.2, 1H), 7.43 (app t, J = 7.7, 2H), 5.23–5.05 (m, 2H), 1.90–1.60 (m, 4H), 1.35 (d, J = 6.3, 6H); ¹³C NMR, combined spectra, δ 166.05, 157.09 (q, J = 42.1, COCF₃), 132.91, 130.43, 129.49, 128.34, 114.52 (q, J = 286.2, CF₃), 76.21, 75.98, 70.96, 70.62, 31.58, 31.48, 31.42, 31.23, 20.04, 20.02, 19.46 (2 × C).

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