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Osmium(0)-Catalyzed C−C Coupling of Ethylene and α-Olefins with Diols, Ketols, or Hydroxy Esters via Transfer Hydrogenation

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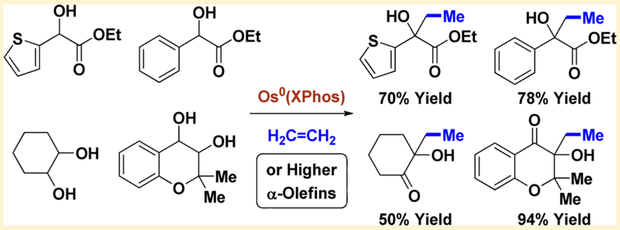
Ⓢ *Supporting Information*



ABSTRACT: Osmium(0) complexes derived from $Os_3(CO)_{12}$ and XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) catalyze the C−C coupling of α-hydroxy esters **1a**−**1i**, α-ketols **1j**−**1o**, or 1,2-diols *dihydro*-**1j**−**1o** with ethylene **2a** to form ethylated tertiary alcohols **3a**−**3o**. As illustrated in couplings of 1-octene **2b** with vicinally dioxygenated reactants **1a**, **1b**, **1i**, **1j**, **1k**, **1m**, higher α-olefins are converted to adducts **4a**, **4b**, **4i**, **4j**, **4k**, **4m** with complete levels of branched regioselectivity. Oxidation level independent C−C coupling is demonstrated by the reaction of 1-octene **2b** with diol *dihydro*-**1k**, α-ketol **1k**, and dione *dehydro*-**1k**. Functionalized olefins **2c**−**2f** react with ethyl mandelate **1a** to furnish adducts **5a**−**8a** as single regioisomers. The collective data, including deuterium labeling studies, are consistent with a catalytic mechanism involving olefin−dione oxidative coupling to form an oxa-osmacyclopentane, which upon reductive cleavage via hydrogen transfer from the secondary alcohol reactant releases the product of carbinol C-alkylation with regeneration of the ketone. Single-crystal X-ray diffraction data of the dinuclear complex $Os_2(CO)_4(O_2CR)_2(XPhos)_2$ and the trinuclear complex $Os_3(CO)_{11}(XPhos)$ are reported. These studies suggest increased π-backbonding at the stage of the metal−olefin π-complex plays a critical role in facilitating alkene−carbonyl oxidative coupling, as isostructural ruthenium(0) complexes, which are weaker π-donors, do not catalyze the transformations reported herein.

■ INTRODUCTION

α-Olefins are the most abundant petrochemical feedstock beyond alkanes.[1] Despite their ubiquity and low cost, the use of α-olefins in the commercial manufacture of commodity chemicals is largely restricted to polymerization,[2] hydroformylation,[3] and alkene metathesis.[4] The discovery of alternate classes of byproduct-free catalytic C−C couplings that convert α-olefins to value-added products remains an important yet elusive goal. For example, while intermolecular alkene hydroacylation is attractive, decarbonylation of acylmetal intermediates to form inactive metal carbonyl complexes mandates use of esoteric reactants with chelating groups.[5,6] Similarly, intermolecular Prins or carbonyl ene reactions do not extend to the coupling of α-olefins with unactivated aldehydes.[7a−c] Finally, whereas nickel(0) catalyzes the coupling of α-olefins with simple aldehydes, superstoichiometric quantities of TESOTf and Et_3N are required.[7d]

In connection with the development of C−C bond-forming hydrogenations and transfer hydrogenations beyond hydroformylation,[8] we recently found that zerovalent ruthenium complexes generated *in situ* from $Ru_3(CO)_{12}$ and various phosphine ligands catalyze the C−C coupling of vicinally dioxygenated hydrocarbons (1,2-diols, α-ketols, α-hydroxy esters) with diverse π-unsaturated reactants, including dienes,[9a−c] acrylates,[9d] and alkynes.[9f] As in related ruthenium(0)-catalyzed Pauson−Khand reactions of vicinal dicarbonyl compounds described by Chatani and Murai,[10] these processes are initiated through C=C/C=O oxidative coupling to furnish oxaruthenacycles. Catalytic turnover is achieved via transfer hydrogenolysis of the metalacycle by the alcohol reactant to release product and regenerate the carbonyl partner (Figure 1, top). On the basis of this mechanism, a ruthenium(0)-catalyzed coupling of α-olefins was developed (Figure 1, middle).[9e] This process, however, was restricted to the use of 3-hydroxy-2-oxindoles, which may be attributed to the exceptional reactivity of the transient isatins. In continuing efforts to broaden the scope of transfer hydrogenative α-olefin coupling, we now demonstrate that osmium(0) catalysts overcome this limitation, enabling the C−C coupling of ethylene[11] and higher α-olefins with diverse diols, α-ketols, and α-hydroxy esters (Figure 1, bottom).

■ RESEARCH DESIGN AND METHODS

The limitations evident in ruthenium(0)-catalyzed C−C couplings of α-olefins[9e] were believed to stem from a high energetic barrier to oxidative coupling. Guided by Hoffmann's theoretical analysis of the conversion of metal bisolefin complexes to metalacyclopentanes,[12] and a large body of experimental evidence,[13] the facility of oxidative coupling should be influenced by the degree of backbonding in the preceding metal−olefin π-complex.[14] Backbonding confers nucleophilic character to the bound olefin and, in the limiting case, may be viewed as an oxidative addition to the C=C π-

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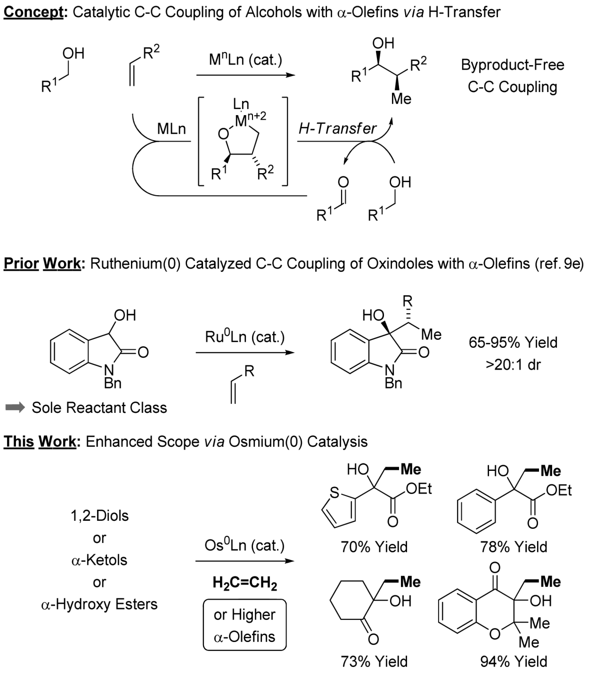
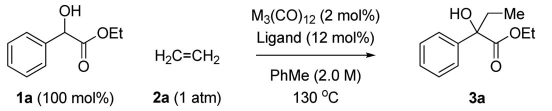


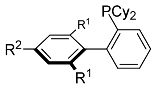
Figure 1. General mechanism for catalytic C−C coupling of alcohols with π-unsaturated reactants via hydrogen autotransfer and applications toward the coupling of α-olefins.

bond to form a metalacyclopropane. The Kulinkovich reaction,[15] wherein titanium(II)−olefin complexes behave as vicinal dianions, represents a dramatic illustration of this effect. Hence, it was posited that a more strongly reducing metal center should facilitate C═C/C═O oxidative coupling to broaden substrate scope in transfer hydrogenative C−C couplings of α-olefins.

As borne out by the carbonyl stretching frequencies of isostructural ruthenium and osmium complexes $HClM(CO)(PPh_3)_3$, M = Os, ν_{co} = 1906 cm^{-1}, M = Ru, ν_{co} = 1922 cm^{-1}, osmium is a stronger π-donor than ruthenium.[16] Indeed, osmium(0) catalysts are effective in couplings of activated secondary alcohols with vinyl acetates in cases where ruthenium(0) catalysts are not.[9g] For this reason, osmium(0) complexes were assayed in the coupling of racemic ethyl mandelate **1a** with ethylene **2a** with the goal of generating the ethylated tertiary alcohol **3a** (Scheme 1). It was found that monodentate or bidentate triaryl phosphine ligands were ineffective. However, the osmium(0) catalyst modified by PCy_3 (tricyclohexylphosphine) provided the desired adduct in 57% yield. Given this promising result, the osmium(0) complex modified by XPhos was eventually identified as the optimal catalyst, delivering the product of carbinol C−H ethylation **3a** in 78% yield. Notably, under all conditions evaluated, the corresponding ruthenium(0) catalysts were unable to promote formation of adduct **3a**.

Scheme 1. Selected Experiments in the Coupling of Ethyl Mandelate 1a with Ethylene 2a To Form Tertiary Alcohol 3a[a]





RuPhos, R^1 = O-^{i}Pr, R^2 = H
XPhos, R^1 = R^2 = ^{i}Pr
CyJohnPhos, R^1 = R^2 = H

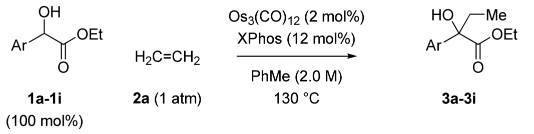
Metal	Ligand	Yield
Ru	PCy_3	---
Os	PCy_3	57
Ru	CyJohnPhos	---
Os	CyJohnPhos	31
Ru	RuPhos	---
Os	RuPhos	60
Ru	XPhos	---
⇨ **Os**	**XPhos**	**78**

[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details.

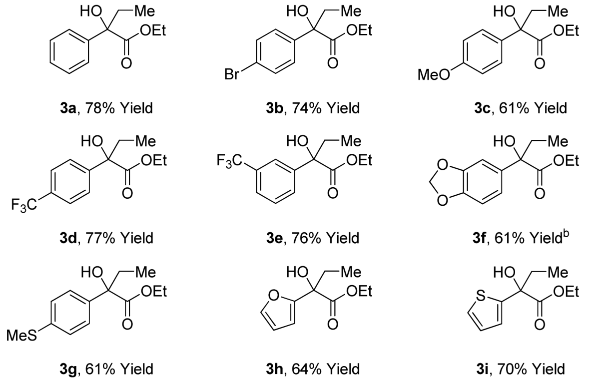
■ RESULTS AND DISCUSSION

Under these optimal conditions, aryl- and heteroaryl-substituted α-hydroxy esters **1a**−**1i** were coupled to ethylene **2a** to form products of carbinol C−H ethylation **3a**−**3i** (Table 1). As illustrated by the conversion of ethyl 4-bromomandelate **1b** to adduct **3b**, the osmium(0) catalyst is tolerant of aryl halide functional groups. The transformation of ethyl 4-methoxymandelate **1c** and ethyl 4-(trifluoromethyl)mandelate **1d** to adducts **3c** and **3d**, respectively, highlights tolerance of electron-rich and as well as electron-deficient aryl groups. Substituents at the *meta*-position of the aryl ring are tolerated, as shown in the formation of **3e** and **3f**, respectively. Finally, sulfur containing α-hydroxy ester **1g** and heteroaromatic α-hydroxy esters **1h** and **1i** groups are converted to adducts **3g**, **3h**, and **3i**, respectively. *ortho*-Substituted mandelates and alkyl-substituted α-hydroxy esters such as ethyl lactate were inefficient partners for C−C coupling under these conditions.

Table 1. Osmium(0)-Catalyzed Coupling of α-Hydroxy Esters 1a−1i with Ethylene 2a To Form Tertiary Alcohols 3a−3i[a]



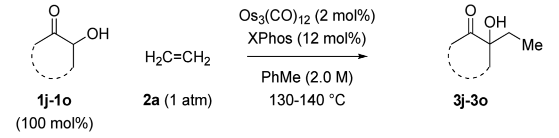
1a, Ar = Ph	**1b**, Ar = 4-Br-Ph	**1c**, Ar = 4-MeO-Ph
1d, Ar = 4-CF_3-Ph	**1e**, Ar = 3-CF_3-Ph	**1f**, Ar = 5-(benzodioxole)
1g, Ar = 4-MeS-Ph	**1h**, Ar = 2-furyl	**1i**, Ar = 2-thienyl



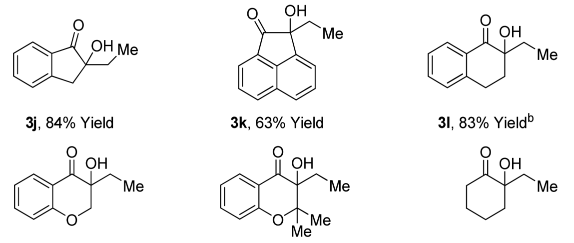
[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. [b] 140 °C.

α-Hydroxy esters **1a**−**1i** react by way of transient α-ketoesters for which the vicinal dicarbonyl moieties are electronically differentiated. In corresponding reactions of nonsymmetric α-ketols, the vicinal dicarbonyl intermediates are quite similar electronically, rendering the control of regioselectivity uncertain. In the event, application of optimal conditions to the coupling of ethylene **2a** with α-ketols **1j**−**1o**

Table 2. Osmium(0)-Catalyzed Coupling of α-Ketols 1j−1o with Ethylene 2a To Form Tertiary Alcohols 3j−3o[a]



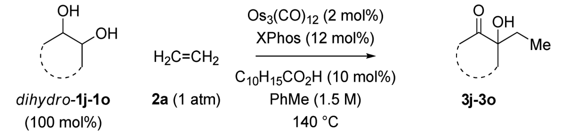
1j, 2-OH-indanone **1k**, 2-OH-acenaphthylene **1l**, 2-OH-tetralone
1m, 3-OH-chromanone **1n**, 3-OH-2,2-Me$_2$-chromanone **1o**, 2-OH-cyclohexanone



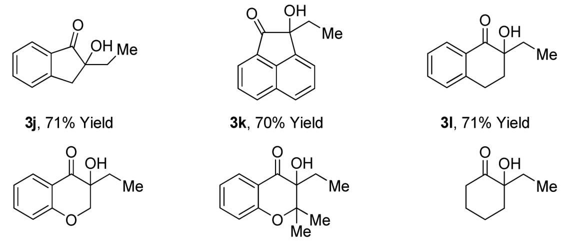
3j, 84% Yield **3k**, 63% Yield **3l**, 83% Yield[b]
3m, 86% Yield **3n**, 85% Yield **3o**, 73% Yield

[a]Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. [b]$C_{10}H_{15}CO_2H$ (10 mol%).

Table 3. Osmium(0)-Catalyzed Coupling of 1,2-Diols *dihydro*-1j−1o with Ethylene 2a To Form Tertiary Alcohols 3j−3o[a]



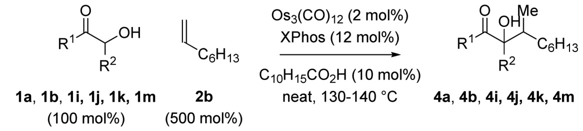
H$_2$-**1j**, indane diol H$_2$-**1k**, acenaphthylene diol H$_2$-**1l**, H$_4$-naphthalene diol
H$_2$-**1m**, chromane diol H$_2$-**1n**, 2,2-Me$_2$-chromane diol H$_2$-**1o**, cyclohexane diol

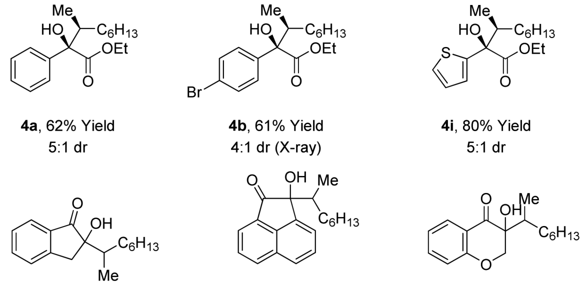


3j, 71% Yield **3k**, 70% Yield **3l**, 71% Yield
3m, 60% Yield **3n**, 94% Yield **3o**, 50% Yield[b]

[a]Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. [b]Reaction conducted in mesitylene at 150 °C using $Os_3(CO)_{12}$ (3 mol%), XPhos (18 mol%), and $C_{10}H_{15}CO_2H$ (15 mol%).

Table 4. Osmium(0)-Catalyzed Coupling of 1a, 1b, 1i, 1j, 1k, 1m with 1-Octene 2b To Form 4a, 4b, 4i, 4j, 4k, 4m[a]





4a, 62% Yield
5:1 dr
4b, 61% Yield
4:1 dr (X-ray)
4i, 80% Yield
5:1 dr
4j, 85% Yield
1:1 dr
4k, 95% Yield
2:1 dr
4m, 63% Yield
1:1 dr

[a]Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details.

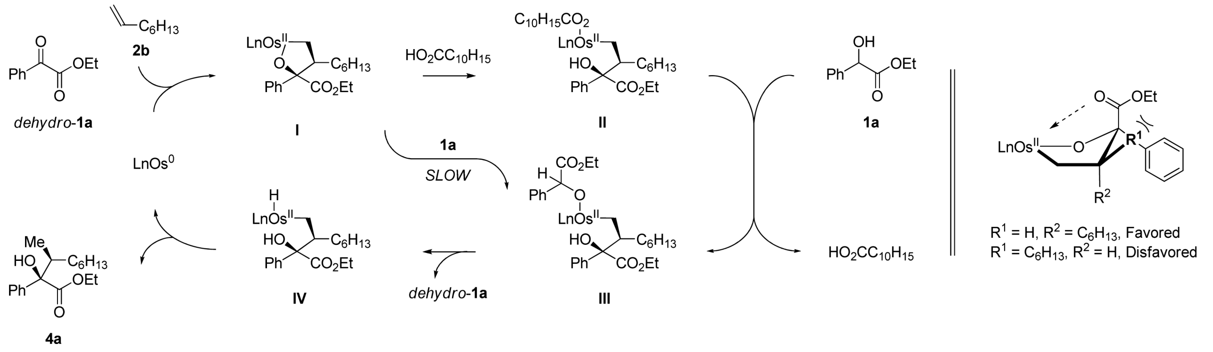
delivered the ethylated tertiary alcohols **3j**−**3o** in good to excellent yield (Table 2). Further, in the coupling of α-ketols **1j**, **1l**−**1n**, which proceeds by way of nonsymmetric diones, the adducts **3j**, **3l**−**3n** form as single regioisomers. In addition to the influence of electronic effects on the regioselectivity of oxidative coupling as described by Hoffman[12] and in prior work from our laboratory,[9d] steric effects also play an important role. That is, oxidative coupling will occur such that the osmium center is placed distal to the site of greatest steric demand. α-Ketol **1n** is an exception due to the electronic effect associated with the mesomeric effect of the *ortho*-oxygen atom.

The couplings of ethylene **2a** with α-hydroxy esters **1a**−**1i** or α-ketols **1j**−**1o** to form adducts **3a**−**3o** are redox-neutral transformations. In contrast, the reaction of ethylene **2a** with 1,2-diols *dihydro*-**1j**−**1o** represents oxidative processes in which 1 equiv of H_2 is evolved or transferred to an acceptor (Table 3). The feasibility of such an oxidative process finds precedent in the work of Shvo, who demonstrates that zerovalent ruthenium catalysts derived from $Ru_3(CO)_{12}$ promote oxidative esterifications in which tolane (diphenyl acetylene) serves as H_2-acceptor,[17] as well as work from our laboratory on oxidative diol-diene [4 + 2] cycloadditions.[9b] Initial attempts at the coupling of ethylene **2a** with 1,2-diols *dihydro*-**1j**−**1o** using the osmium(0)-catalyzed modified by XPhos led to only modest yields of adducts **3j**−**3o**. Given the ability of carboxylic acids to catalyze the hydrogenolysis[13] and transfer hydrogenolysis[9d] of oxa-metalacycles, these reactions were conducted in the presence of adamantane carboxylic acid (10 mol %). To our delight, the yields of adducts **3j**−**3o** improved considerably, and, as observed in couplings conducted from the α-ketol oxidative level, compounds **3j**, **3l**−**3n** were again generated as single regioisomers.

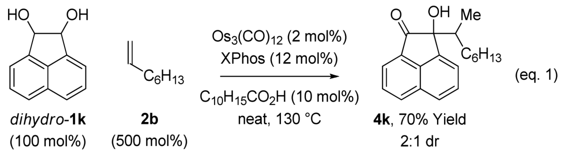
To evaluate the applicability of these conditions to higher α-olefins, the coupling of 1-octene **2b** with α-hydroxy esters **1a**, **1b**, and **1i** and α-ketols **1j**, **1k**, and **1m** was attempted (Table 4). Although corresponding reactions of ethylene **2a** proceed efficiently in the absence of a carboxylic acid cocatalyst, couplings of 1-octene **2b** required the presence of adamantane carboxylic acid (10 mol %) to increase conversion. Additionally, higher concentrations were beneficial, so the reactions were conducted neat. The α-hydroxy esters **1a**, **1b**, and **1i** were converted to adducts **4a**, **4b**, and **4i**, respectively, with complete levels of branched regioselectivity and good levels of diastereoselectivity. Relative stereochemistry for adducts **4a**, **4b**, and **4i** was determined by single-crystal X-ray diffraction analysis of a derivative of **4b**. A stereochemical model is provided (Scheme 2). α-Ketols **1j**, **1k**, and **1m** were converted to adducts **4j**, **4k**, and **4m** in a completely regioselective fashion, but with diminished levels of diastereoselectivity.

The present transfer hydrogenative couplings of α-olefins can be conducted in oxidative, redox-neutral, or reductive modes. While redox-neutral couplings are most efficient, oxidative and reductive transformations are preparatively useful. The following transformations illustrate this unique capability (eqs

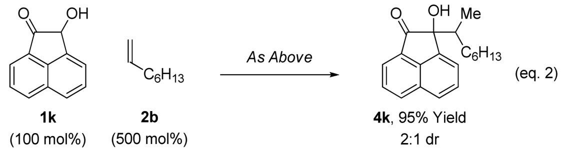
Scheme 2. General Mechanism As Illustrated in the Coupling of Ethyl Mandelate 1a with 1-Octene 2b and Stereochemical Model



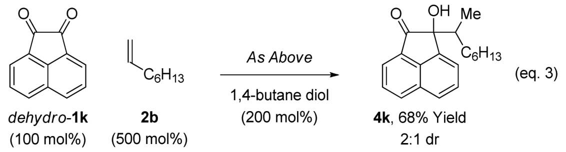
1−3). In the oxidative coupling of 1-octene **2b** with diol *dihydro*-**1k**, wherein 1-octene serves as hydrogen acceptor, adduct **4k** forms in 70% yield (eq 1). The redox-neutral coupling of 1-octene **2b** with α-ketol **1k** proceeds in 95% yield (eq 2). Finally, using 1,4-butanediol as terminal reductant,[18] the reductive coupling of 1-octene **2b** with the 1,2-dione *dehydro*-**1k** proceeds in 68% yield (eq 3). Such redox-economy allows one to bypass discrete manipulations otherwise required for the adjustment of oxidation level.[19]



(eq. 1)

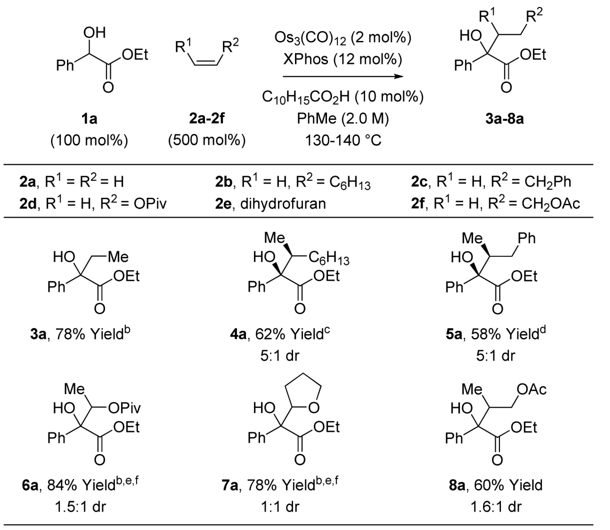


(eq. 2)



(eq. 3)

Table 5. Osmium(0)-Catalyzed Coupling of Ethyl Mandelate 1a with Functionalized Olefins 2a−2f[a]



[a] Yields are of material isolated by silica gel chromatography. See the Supporting Information for further experimental details. [b] $C_{10}H_{15}CO_2H$ was omitted. [c] Neat. [d] $C_{10}H_{15}CO_2H$ (30 mol%). [e] **2d** (300 mol%). [f] XPhos was omitted.

To determine the scope of the alkene partner, the coupling of olefins **2a**−**2f** with ethyl mandelate **1a** was explored (Table 5). Beyond the previously described couplings of ethylene **2a** and 1-octene **2b** to form adducts **3a** and **4a**, respectively, allyl benzene **2c** participates in C−C coupling to form tertiary alcohol **5a**. For carboxy- and alkoxy-substituted alkenes **2d** and **2e**, the indicated regioisomers **6a** and **7a** are formed exclusively. Here, omission of XPhos and adamantane carboxylic acid is required to suppress metalacycle fragmentation en route to products of vinyl transfer (not shown).[9g] Finally, allyl acetate **2f** participates in C−C coupling to form adduct **8a** with complete levels of branched regioselectivity. This result is remarkable in view of the fact that ionization of allyl acetate **2f** to form π-allyl species in the presence zerovalent osmium does not override the transfer hydrogenative C−C coupling pathway.

■ MECHANISM

With regard to the catalytic mechanism, a simple working model has been proposed as a basis for further refinement (Scheme 2). It is unclear whether the catalyst is mononuclear *versus* dimetallic or trimetallic. Upon heating toluene solutions of $Os_3(CO)_{12}$ with XPhos in the presence and absence of adamantane carboxylic acid (RCO_2H), crystals of the dinuclear complex $Os_2(CO)_4(O_2CR)_2(XPhos)_2$ and the trinuclear complex $Os_3(CO)_{11}(XPhos)$, respectively, were isolated and characterized by X-ray diffraction (Figure 2). Additionally, the reaction of $Os_3(CO)_{12}$ with 2-(dicyclohexylphosphino)-1-(2-methoxyphenyl)-imidazole, a monophosphine that is structurally related to XPhos, provides the trinuclear osmium complex, $Os_3(CO)_8L_2$.[20b] Alternatively, intervention of a mononuclear catalyst finds support in the reaction of $Ru_3(CO)_{12}$ with dppe, bis-(diphenylphosphino)ethane, to provide $Ru(CO)_3(dppe)$,[20a] and the reaction of $Ru_3(CO)_{12}$, 1-adamantanecarboxylic acid, and dppp, bis-(diphenylphosphino)propane, to form the catalytically active mononuclear complex Ru(CO) (dppp)-$(O_2CR)_2$.[9d] Oxidative coupling of the α-oxo-ester, *dehydro*-**1a**, with 1-octene **2b** mediated by zerovalent osmium delivers the oxa-osmacycle **I**.[9,10] Related ruthenium(0)-mediated carbonyl-diene oxidative couplings deliver isolable metalacycles that are catalytic active and have been shown to form in a reversible manner.[9c] The oxo-ester, *dehydro*-**1a**, required in the first turnover of the catalytic cycle may be generated via alcohol-olefin hydrogen transfer.[17] Direct protonation of oxa-osmacycle

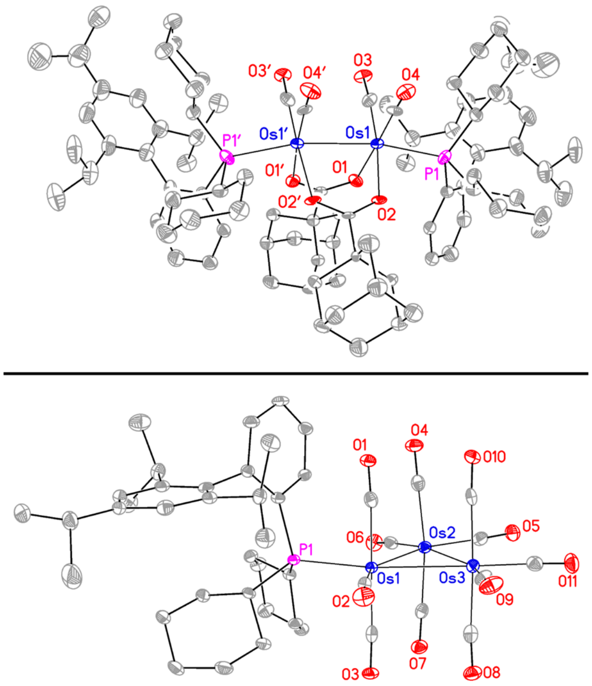
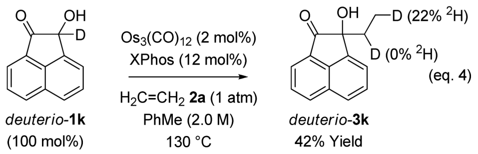


Figure 2. Structures of $Os_2(CO)_4(O_2CR)_2(XPhos)_2$ (top) and $Os_3(CO)_{11}(XPhos)$ (bottom) determined by single-crystal X-ray diffraction showing the atom labeling system. (Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been omitted for clarity.)

I by ethyl mandelate **1a** to form the osmium alkoxide **III** requires a 4-centered transition structure and is postulated to be slow compared to protonation of oxa-osmacycle **I** by 1-adamantanecarboxylic acid to form the osmium carboxylate **II**, which can proceed by way of a 6-centered transition structure.[13] Exchange of the carboxylate ligand with **1a** to form osmium alkoxide **III** also may proceed by way of a 6-centered transition structure.[13] β-Hydride elimination converts osmium alkoxide **III** to the osmium alkyl hydride complex **IV**, which upon C−H reductive elimination releases product **4a** and regenerates the osmium(0) catalyst. Beyond the aforesaid electronic effects,[9d,12] steric interactions between the *n*-hexyl side chain of 1-octene **2b** and the crowded osmium center contribute to branched regioselectivity.

To challenge the veracity of the proposed mechanism, the following isotopic labeling experiment was performed (eq 4). The deuterated acenaphthylene ketol *deuterio*-**1k** was exposed to ethylene under standard conditions. The pattern of deuterium incorporation in the adduct *deuterio*-**3k** was established by ^1H and ^2H NMR, as well as HRMS analysis. Deuterium incorporated occurs exclusively at the methyl group (22% ^2H). The transfer of deuterium from the carbinol position of *deuterio*-**1k** to the methyl group of *deuterio*-**3k** is consistent with the proposed mechanism (Scheme 2). The relatively low levels of deuterium incorporation may be attributed to exchange with adventitious water or with the hydroxylic proton *deuterio*-**1k**.[21]



CONCLUSIONS

In summary, the ability to transform abundant hydrocarbon feedstocks to value-added products in the absence of stoichiometric byproducts is a characteristic shared by nearly all large volume chemical processes. Hence, the discovery and development of byproduct-free transformations applicable to ethylene and α-olefins represents an important objective. Toward this end, we have shown that osmium(0) complexes derived from $Os_3(CO)_{12}$ and XPhos catalyze the transfer hydrogenative C−C coupling of ethylene and higher α-olefins with diverse vicinally dioxygenated hydrocarbons. Coupling may be conducted in a redox-neutral mode using α-ketols or α-hydroxy esters as reactants, or in oxidative or reductive modes using 1,2-diols or 1,2-diones as reactants, respectively. The collective data suggest increased π-backbonding at the stage of the osmium(0)-olefin π-complex plays a critical role in facilitating alkene−carbonyl oxidative coupling, as does the use of transient vicinal dicarbonyl partners, which have relatively low-lying LUMO energies. A challenge associated with the design of transfer hydrogenative coupling of α-olefins with simple primary alcohols will reside in the identification of metal catalysts that are sufficiently electron-rich so as to promote oxidative coupling, and whose low-valent forms are accessible through alcohol-mediated reduction of the high-valent ions. Indeed, intermolecular catalytic reductive couplings of α-olefins with unactivated carbonyl compounds remain an unmet challenge in chemical research.[22]

EXPERIMENTAL SECTION

General Information. All reactions were run under an atmosphere of argon. $Os_3(CO)_{12}$, XPhos, 1-adamantanecarboxylic acid, alkenes **2a**−**2f**, α-hydroxy ester **1a**, α-ketol **1o**, diol *dihydro*-**1o**, and dione *dehydro*-**1k** were purchased from commercial suppliers and used as received. α-Hydroxy esters **1b**−**1i**[23a] were prepared in accordance with the literature procedure. α-Ketols **1j**,[23b] **1k**,[23c] **1l**,[23b] **1m**,[23b] **1n**[23d] and diols *dihydro*-**1j**,[23e] *dihydro*-**1k**,[23f] *dihydro*-**1l**,[23b] **1m**,[23g] and *dihydro*-**1n**[23g] were prepared using the cited literature procedures. Pressure tubes were flame-dried followed by cooling in a desiccator. Toluene was dried over sodium metal-benzophenone and was distilled immediately prior to use. Anhydrous solvents were transferred by oven-dried syringes. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Infrared spectra were recorded on a PerkinElmer 1600 spectrometer. High-resolution mass spectra (HRMS) are reported as m/z (relative intensity) using time-of-flight (TOF) analyzers. Accurate masses are reported for the molecular ion (M+H, M+Na) or a suitable fragment ion. ^1H nuclear magnetic resonance spectra were recorded using a 400 MHz spectrometer. Coupling constants are reported in hertz (Hz) for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm). ^{13}C nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer for $CDCl_3$ solutions, and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.16 ppm).

General Procedure A. A resealable pressure tube (15 × 100 mm, 13 mL or 15 × 125 mm, 16 mL) was charged with $Os_3(CO)_{12}$ (5.5 mg, 0.006 mmol, 2 mol %), XPhos (17.1 mg, 0.036 mmol, 12 mol %), and the reactant alcohol (0.30 mmol, 100 mol %). The tube was sealed with a rubber septum and purged with ethylene. Toluene (0.15 mL, 2.0 M) was added, and the rubber septum was quickly replaced with a screw cap. The reaction was allowed to stir at the indicated temperature for the stated period of time. After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the indicated product.

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General Procedure B. A resealable pressure tube (13 × 100 mm, 9 mL) was charged with $Os_3(CO)_{12}$ (3.7 mg, 0.004 mmol, 2 mol %), XPhos (11.4 mg, 0.024 mmol, 12 mol %), $AdCO_2H$ (3.6 mg, 0.02 mmol, 10 mol %), and the reactant alcohol (0.20 mmol, 100 mol %). The tube was sealed with a rubber septum and purged with argon. 1-Octene (112.2 mg, 1.0 mmol, 500 mol %) was added via syringe, and the rubber septum was quickly replaced with a screw cap. The reaction was allowed to stir at the indicated temperature for the stated period of time. After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2) under the conditions noted to afford the indicated product.

*Ethyl 2-Hydroxy-2-(4-(methylthio)phenyl)acetate (**1g**).* To a flame-dried 50 mL round-bottom flask charged with ethyl 2-hydroxy-2-(4-(methylthio)phenyl)acetate (1.1 g, 4.9 mmol) was added ethanol (25 mL, 0.2 M). $NaBH_4$ (200 mg, 5.3 mmol) was added portionwise. The reaction mixture was allowed to stir at ambient temperature until the suspension became colorless. Distilled water was added, and the reaction mixture was allowed to stir until bubbling stopped. The mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with brine (1 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The residue was subjected to column chromatography (SiO_2: 20% ethyl acetate in hexanes) to give the title compound (0.93g, 4.1 mmol) in 84% yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 5.11 (d, J = 8.0 Hz 1H), 4.22 (m, 2H), 3.42 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 138.9, 135.2, 127.0, 126.5, 72.5, 62.3, 15.7, 14.0. HRMS (ESI-MS) calcd for $C_{11}H_{14}O_3S$ $[M + Na]^+$, 249.0556; found, 249.0557. FTIR (neat): 3438, 2979, 1726. MP: 91 °C.

*Ethyl 2-Hydroxy-2-phenylbutanoate (**3a**).*[24a] In accordance with general procedure A, **1a** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2−5% ether/hexanes) provided the title compound (48.7 mg, 0.23 mmol) as a yellow oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.59 (m, 2H), 7.37−7.32 (m, 2H), 7.30−7.26 (m, 1H), 4.32−4.16 (m, 2H), 3.78 (d, J = 0.4 Hz, 1H), 2.24 (dqd, J = 14.4, 7.2, 0.8 Hz, 1H), 2.07−1.98 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 142.0, 128.3, 127.7, 125.7, 78.7, 62.5, 32.8, 14.2, 8.2. HRMS (ESI) calcd for $C_{12}H_{16}O_3$, $[M + Na]^+$, 231.0992; found, 231.0998. FTIR (neat): 3504, 2980, 1721.

*Ethyl 2-(4-Bromophenyl)-2-hydroxybutanoate (**3b**).* In accordance with procedure A, **1b** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2−4% ether/hexanes) provided the title compound (63.7 mg, 0.22 mmol) as a yellow oil in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.44 (m, 4H), 4.32−4.15 (m, 2H), 3.80 (d, J = 0.5 Hz, 1H), 2.24−2.12 (m, 1H), 1.97 (dq, J = 14.7, 7.4 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 0.99 (dd, J = 9.5, 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 141.0, 131.4, 127.7, 121.9, 78.4, 62.8, 32.9, 14.2, 8.1. HRMS (ESI) calcd for $C_{12}H_{15}BrO_3$, $[M + Na]^+$, 309.0097, 311.0077; found, 309.0104, 311.0085. FTIR (neat): 3499, 2980, 1723.

*Ethyl 2-Hydroxy-2-(4-methoxyphenyl)butanoate (**3c**).* In accordance with procedure A, **1c** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 50−100% dichloromethane/hexanes to 5% ethyl acetate/hexanes) provided the title compound (43.6 mg, 0.18 mmol) as a yellow oil in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54−7.48 (m, 2H), 6.90−6.85 (m, 2H), 4.31−4.14 (m, 2H), 3.80 (s, 3H), 3.73 (s, 1H), 2.26−2.15 (m, 1H), 1.99 (dq, J = 14.6, 7.4 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 159.1, 134.2, 126.9, 113.6, 78.4, 62.5, 55.4, 32.8, 14.3, 8.2. HRMS (ESI) calcd for $C_{13}H_{18}O_4$, $[M + Na]^+$, 261.1097; found, 261.1099. FTIR (neat): 3511, 2970, 1721.

*Ethyl 2-Hydroxy-2-(4-(trifluoromethyl)phenyl)butanoate (**3d**).* In accordance with procedure A, **1d** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 1−5% ether/hexanes) provided the title compound (63.8 mg, 0.23 mmol) as a yellow oil in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.72 (m, 2H), 7.64−7.57 (m, 2H), 4.35−4.17 (m, 2H), 3.87 (s, 1H), 2.23 (dq, J = 14.5, 7.2 Hz, 1H), 2.01 (dq, J = 14.5, 7.4 Hz, 1H), 1.28 (t, J = 6.2 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 145.9, 130.0 (q, J = 32.0 Hz), 126.3, 125.2 (q, J = 4.0 Hz), 124.3 (q, J = 271.0 Hz), 78.6, 63.0, 33.1, 14.2, 8.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.6. HRMS (ESI) calcd for $C_{13}H_{15}F_3O_3$, $[M + Na]^+$, 299.0866; found, 299.0871. FTIR (neat): 3510, 2985, 1726.

*Ethyl 2-Hydroxy-2-(3-(trifluoromethyl)phenyl)butanoate (**3e**).* In accordance with procedure A, **1e** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2−5% ether/hexanes) provided the title compound (63.0 mg, 0.23 mmol) as a yellow oil in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.86−7.79 (m, 1H), 7.55 (dd, J = 7.7, 0.6 Hz, 1H), 7.46 (dd, J = 7.8, 7.8 Hz, 1H), 4.34−4.19 (m, 2H), 3.90 (d, J = 0.5 Hz, 1H), 2.29−2.18 (m, 1H), 2.01 (dq, J = 14.7, 7.4 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 143.1, 130.7 (q, J = 32.0 Hz), 129.3, 128.8, 124.6 (q, J = 3.7 Hz), 124.3 (q, J = 271.0 Hz), 122.9 (q, J = 4.0 Hz), 78.5, 63.0, 33.2, 14.2, 8.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.6. HRMS (ESI) calcd for $C_{13}H_{15}F_3O_3$, $[M + Na]^+$, 299.0866; found, 299.0873. FTIR (neat): 3513, 2985, 1725.

*Ethyl 2-(Benzo[d][1,3]dioxol-5-yl)-2-hydroxybutanoate (**3f**).* In accordance with procedure A, **1f** (0.2 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 290 mol %) in toluene (2.0 M) at 140 °C for a 40 h period. Flash column chromatography (SiO_2: 3−5% ether/hexanes) provided the title compound (30.8 mg, 0.12 mmol) as a colorless oil in 61% yield. Note: $Os_3(CO)_{12}$ (3.6 mg, 0.004 mmol, 2 mol %) and XPhos (11.4 mg, 0.024 mmol, 12 mol %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13−7.05 (m, 2H), 6.77 (dd, J = 7.5, 1.1 Hz, 1H), 6.01−5.92 (m, 2H), 4.33−4.14 (m, 2H), 3.75 (s, 1H), 2.16 (dq, J = 14.4, 7.2 Hz, 1H), 1.96 (dq, J = 14.7, 7.4 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 147.7, 147.1, 136.1, 119.1, 107.9, 106.7, 101.2, 78.5, 62.6, 32.9, 14.3, 8.1. HRMS (ESI) calcd for $C_{13}H_{16}O_5$, $[M + Na]^+$, 275.0890; found, 275.0899. FTIR (neat): 3507, 2971, 1722.

*Ethyl 2-Hydroxy-2-(4-(methylthio)phenyl)butanoate (**3g**).* In accordance with procedure A, **1g** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2−5% ether/hexanes) provided the title compound (30.8 mg, 0.18 mmol) as a yellow oil in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.48 (m, 2H), 7.26−7.20 (m, 2H), 4.37−4.10 (m, 2H), 3.76 (s, 1H), 2.48 (s, 3H), 2.25−2.15 (m, 1H), 2.04−1.95 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 138.7, 137.8, 126.2, 126.1 78.3, 62.4, 32.6, 15.7, 14.1, 7.9. HRMS (ESI) calcd for $C_{13}H_{18}O_3S$, $[M + Na]^+$, 277.0869; found, 277.0878. FTIR (neat): 3507, 2979, 1721.

*Ethyl 2-(Furan-2-yl)-2-hydroxybutanoate (**3h**).* In accordance with procedure A, **1h** (0.2 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 290 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 3−5% ether/hexanes) provided the title compound (25.0 mg, 0.13 mmol) as a yellow oil in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 1.1 Hz, 1H), 6.33 (s, 2H), 4.36−4.14 (m, 2H), 3.82 (s, 1H), 2.21−2.07 (m, 2H), 1.25 (t, J = 7.0 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 154.5, 142.5, 110.4, 106.8, 75.5, 62.8, 29.8, 14.3, 7.7. HRMS (ESI) calcd for $C_{10}H_{14}O_4$, $[M + Na]^+$, 221.0784; found, 221.0790. FTIR (neat): 3511, 2970, 1728.

*Ethyl 2-Hydroxy-2-(thiophen-2-yl)butanoate (**3i**).* In accordance with procedure A, **1i** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 30−50% dichloromethane/hexanes) provided the title compound (45.0 mg, 0.22 mmol) as a colorless oil in 70% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, J = 5.1, 1.2 Hz, 1H), 7.09 (dd, J = 3.6, 1.2 Hz, 1H), 6.97 (dd, J = 5.1, 3.6 Hz, 1H), 4.35−4.21 (m, 2H), 4.05 (d, J = 0.8 Hz, 1H), 2.26−2.16 (m, 1H), 2.06 (dq, J = 14.7, 7.4 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 147.1, 127.1, 124.9, 124.1, 77.7, 62.9, 34.4, 14.2, 8.1. HRMS (ESI) calcd for $C_{10}H_{14}O_3S$, $[M + Na]^+$, 237.0556; found, 237.0563. FTIR (neat): 3499, 2979, 1724.

2-Ethyl-2-hydroxy-2,3-dihydro-1H-inden-1-one ***(3j)***. (Using ketol) In accordance with procedure A, **1j** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 140 °C for a 40 h period. Flash column chromatography (SiO_2: 5−15% ethyl acetate/hexanes) provided the title compound (44.4 mg, 0.25 mmol) as a yellow oil in 84% yield. (Using diol) In accordance with procedure A, H_2-**1j** (0.15 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 390 mol %) in toluene (1.5 M) at 140 °C for a 48 h period. Flash column chromatography (SiO_2: 5−15% ethyl acetate/hexanes) provided the title compound (18.8 mg, 0.11 mmol) as a yellow oil in 71% yield. Note: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol %), XPhos (8.5 mg, 0.018 mmol, 12 mol %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77−7.72 (m, 1H), 7.61 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.45−7.41 (m, 1H), 7.40−7.34 (m, 1H), 3.27 (d, J = 17.0 Hz, 1H), 3.14 (d, J = 17.0 Hz, 1H), 2.89 (s, 1H), 1.81−1.64 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 151.7, 135.9, 134.4, 127.9, 126.7, 124.7, 80.3, 39.8, 31.6, 8.0. HRMS (ESI) calcd for $C_{11}H_{12}O_2$, $[M + Na]^+$, 199.0730; found, 199.0736. FTIR (neat): 3413, 2967, 1709.

2-Ethyl-2-hydroxyacenaphthylen-1(2H)-one ***(3k)***. (Using ketol) In accordance with procedure A, **1k** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 48 h period. Flash column chromatography (SiO_2: 5−15% ethyl acetate/hexanes) provided the title compound (40.1 mg, 0.18 mmol) as a yellow solid in 63% yield. (Using diol) In accordance with procedure A, H_2-**1k** (0.15 mmol, 100 mol %) was reacted with ethylene (15 × 125 mm pressure tube, 0.71 mmol, 480 mol %) in toluene (1.5 M) at 140 °C for a 48 h period. Flash column chromatography (SiO_2: 5−15% ethyl acetate/hexanes) provided the title compound (21.3 mg, 0.11 mmol) as a yellow solid in 70% yield. Note: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol %), XPhos (8.5 mg, 0.018 mmol, 12 mol %), and $AdCO_2H$ (2.7 mg, 0.015 mmol, 10 mol %). ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.0 Hz, 1H), 7.89 (dd, J = 7.9, 1.2 Hz, 1H), 7.74 (dd, J = 8.1, 7.1 Hz, 1H), 7.71−7.62 (m, 2H), 2.86 (s, 1H), 2.17−1.99 (m, 2H), 0.76 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 141.8, 139.5, 132.1, 131.2, 130.8, 128.9, 128.4, 125.4, 122.0, 120.5, 80.9, 31.6, 8.2. HRMS (ESI) calcd for $C_{14}H_{12}O_2$, $[M + Na]^+$, 235.0730; found, 235.0737. FTIR (neat): 3369, 2970, 2931, 1716. MP: 92.7−93.1 °C.

2-Ethyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one ***(3l)***.[24b] (Using ketol) In accordance with procedure A, **1l** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 140 °C for a 40 h period. Flash column chromatography (SiO_2: 5−7% ethyl acetate/hexanes) provided the title compound (47.4 mg, 0.25 mmol) as a brown oil in 83% yield. Note: $AdCO_2H$ (5.4 mg, 0.03 mmol, 10 mol %). (Using diol) In accordance with procedure A, H_2-**1l** (0.15 mmol, 100 mol %) was reacted with ethylene (15 × 125 mm pressure tube, 0.71 mmol, 480 mol %) in toluene (1.5 M) at 140 °C for a 48 h period. Flash column chromatography (SiO_2: 5−7% ethyl acetate/hexanes) provided the title compound (20.3 mg, 0.11 mmol) as a brown oil in 71% yield. Note: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol %), XPhos (8.5 mg, 0.018 mmol, 12 mol %), and $AdCO_2H$ (2.7 mg, 0.015 mmol, 10 mol %). ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, J = 7.8, 1.2 Hz, 1H), 7.51 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.33 (dd, J = 7.6, 7.6 Hz, 1H), 7.27−7.21 (m, 1H), 3.81 (s, 1H), 3.15−2.94 (m, 2H), 2.34 (ddd, J = 13.5, 5.1, 2.3 Hz, 1H), 2.21−2.10 (m, 1H), 1.78−1.60 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 143.6, 134.1, 130.4, 129.1, 128.0, 127.0, 75.9, 33.7, 28.5, 26.6, 7.3. HRMS (ESI) calcd for $C_{12}H_{14}O_2$, $[M + Na]^+$, 213.0886; found, 213.0892. FTIR (neat): 3488, 2931, 1681.

3-Ethyl-3-hydroxychroman-4-one ***(3m)***. (Using ketol) In accordance with procedure A, **1m** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 48 h period. Flash column chromatography (SiO_2: 2−4% ethyl acetate/hexanes) provided the title compound (49.6 mg, 0.26 mmol) as a yellow oil in 86% yield. (Using diol) In accordance with procedure A, H_2-**1m** (0.15 mmol, 100 mol %) was reacted with ethylene (15 × 125 mm pressure tube, 0.71 mmol, 480 mol %) in toluene (1.5 M) at 140 °C for a 48 h period. Flash column chromatography (SiO_2: 2−4% ethyl acetate/hexanes) provided the title compound (17.3 mg, 0.09 mmol) as a yellow oil in 60% yield. Note: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol %), XPhos (8.5 mg, 0.018 mmol, 12 mol %), and $AdCO_2H$ (2.7 mg, 0.015 mmol, 10 mol %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89−7.85 (m, 1H), 7.51 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 7.06 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 6.97 (dd, J = 8.4, 0.6 Hz, 1H), 4.39 (d, J = 11.3 Hz, 1H), 4.16 (d, J = 11.3 Hz, 1H), 3.62 (s, 1H), 1.80 (q, J = 7.5 Hz, 2H), 0.94 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 161.5, 136.7, 127.6, 121.9, 118.5, 118.0, 73.1, 72.9, 27.8, 7.0. HRMS (CI) calcd for $C_{11}H_{12}O_3$, $[M + Na]^+$, 215.0679; found, 215.0686. FTIR (neat): 3466, 2973, 2936, 1691, 1607.

3-Ethyl-3-hydroxy-2,2-dimethylchroman-4-one ***(3n)***. (Using ketol) In accordance with procedure A, **1n** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 140 °C for a 40 h period. Flash column chromatography (SiO_2: 2−4% ether/hexanes) provided the title compound (56.2 mg, 0.26 mmol) as a yellow oil in 85% yield. (Using diol) In accordance with procedure A, H_2-**1n** (0.15 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 390 mol %) in toluene (1.5 M) at 140 °C for a 48 h period. Flash column chromatography (SiO_2: 2−4% ethyl acetate/hexanes) provided the title compound (31.1 mg, 0.14 mmol) as a yellow oil in 94% yield. Note: $Os_3(CO)_{12}$ (2.7 mg, 0.003 mmol, 2 mol %), XPhos (8.5 mg, 0.018 mmol, 12 mol %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 7.8, 1.7 Hz, 1H), 7.48 (ddd, J = 8.6, 7.2, 1.8 Hz, 1H), 6.98 (dt, J = 12.0, 2.5 Hz, 1H), 6.89 (dd, J = 8.4, 0.5 Hz, 1H), 3.89 (s, 1H), 1.92−1.80 (m, 2H), 1.52 (s, 3H), 1.26 (s, 3H), 0.68 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 159.3, 136.7, 126.9, 121.1, 118.7, 118.3, 84.6, 78.7, 25.3, 22.2, 20.4, 7.3. HRMS (ESI) calcd for $C_{13}H_{16}O_3$, $[M + Na]^+$, 243.0992; found, 243.0993. FTIR (neat): 3484, 2976, 1690.

2-Ethyl-2-hydroxycyclohexan-1-one ***(3o)***.[24c] (Using ketol) In accordance with procedure A, **1o** (0.3 mmol, 100 mol %) was reacted with ethylene (15 × 100 mm pressure tube, 0.58 mmol, 190 mol %) in toluene (2.0 M) at 130 °C for a 48 h period. Flash column chromatography (SiO_2: 5−10% ether/hexanes) provided the title compound (31.1 mg, 0.22 mmol) as a colorless oil in 73% yield. (Using diol) In accordance with procedure A, H_2-**1o** (0.15 mmol, 100 mol %) was reacted with ethylene (15 × 125 mm pressure tube, 0.71 mmol, 480 mol %) in meistylene (2.0 M) at 150 °C for a 48 h period. Flash column chromatography (SiO_2: 5−10% ether/hexanes) provided the title compound (10.7 mg, 0.15 mmol) as a colorless oil in 50% yield. Note: $Os_3(CO)_{12}$ (4.1 mg, 0.0045 mmol, 3 mol %), XPhos (13.2 mg, 0.027 mmol, 18 mol %), and $AdCO_2H$ (4.1 mg, 0.023 mmol, 15 mol %). ^1H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 1H), 2.51−2.40 (m, 2H), 2.18 (ddd, J = 13.1, 5.8, 3.0 Hz, 1H), 2.14−2.03 (m, 1H), 1.91 (dq, J = 14.7, 7.4 Hz, 1H), 1.84−1.54 (m, 5H), 0.90−0.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.6, 79.4, 40.7, 38.2, 30.2, 28.0, 22.9, 7.0. HRMS (ESI) calcd for $C_8H_{14}O_2$, $[M + H]^+$, 143.1072; found, 143.1069. FTIR (neat): 3485, 2938, 1707.

Ethyl 2-Hydroxy-3-methyl-2-phenylnonanoate ***(4a)***. In accordance with procedure B, **1a** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2% ether/hexanes) provided the title compound (31.1 mg, 0.22 mmol, dr = 5:1) as a colorless oil in 62% yield. ^1H NMR (400 MHz, $CDCl_3$): δ (major) 7.67−7.62 (m, 2H), 7.37−7.30 (m, 2H), 7.29−7.24 (m, 1H), 4.33−4.13 (m, 2H), 3.68 (d, J = 0.6 Hz, 1H), 2.47−2.35 (m, 1H), 1.51−1.16 (m, 13H), 0.90 (dd, J = 8.9, 4.9 Hz, 3H), 0.68 (d, J = 6.8 Hz, 3H); (minor) 7.67−7.62 (m, 2H), 7.37−7.30 (m, 2H), 7.29−7.24 (m, 1H), 4.33−4.13 (m, 2H), 3.74 (d, J = 0.6 Hz, 1H), 2.47−2.35 (m, 1H), 1.51−1.16 (m, 13H), 0.97 (d, J = 6.6 Hz, 3H), 0.82 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 176.0, 141.5, 128.1, 127.5, 126.1, 81.7, 62.5, 40.8, 31.9, 31.8, 29.5, 27.7, 22.8, 14.3, 14.2, 12.8; (minor) 175.9, 141.3, 128.1, 127.5, 126.2, 81.6, 62.6, 40.6, 31.9, 29.6, 29.3, 27.6, 22.7, 14.2, 14.1, 12.8. HRMS (ESI) calcd for $C_{18}H_{28}O_3$, $[M + Na]^+$, 315.1931; found, 315.1940. FTIR (neat): 3514, 2928, 2857, 1721.

*Ethyl 2-(4-Bromophenyl)-2-hydroxy-3-methylnonanoate (**4b**).* In accordance with procedure B, **1b** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 20−35% dichloromethane/hexanes) provided the title compound (45.4 mg, 0.12 mmol, dr = 4:1) as a colorless oil in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.54−7.50 (m, 2H), 7.48−7.43 (m, 2H), 4.33−4.14 (m, 2H), 3.67 (s, 1H), 2.38−2.28 (m, 1H), 1.48−0.97 (m, 13H), 0.89 (d, J = 6.9 Hz, 3H), 0.66 (d, J = 6.8 Hz, 3H); (minor) 7.54−7.50 (m, 2H), 7.48−7.43 (m, 2H), 4.33−4.14 (m, 2H), 3.73 (s, 1H), 2.38−2.28 (m, 1H), 1.48−0.97 (m, 13H), 0.95 (d, J = 6.6 Hz, 3H), 0.83 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.5, 140.6, 131.3, 128.1, 121.7, 81.5, 62.8, 40.9, 31.9, 31.7, 29.5, 27.6, 22.8, 14.3, 14.2, 12.8; (minor) 175.4, 140.6, 131.3, 128.1, 121.7, 81.4, 62.9, 40.7, 31.9, 29.6, 29.3, 27.6, 22.7, 14.2, 14.1, 12.8. HRMS (ESI) calcd for $C_{18}H_{27}BrO_3$, $[M + Na]^+$, 393.1036; found, 393.1043. FTIR (neat): 3507, 2927, 2856, 1723.

*Ethyl 2-Hydroxy-3-methyl-2-(thiophen-2-yl)nonanoate (**4i**).* In accordance with procedure B, **1i** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 20−40% dichloromethane/hexanes) provided the title compound (47.8 mg, 0.16 mmol, dr = 5:1) as a colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.21 (dd, J = 5.2, 1.2 Hz, 1H), 7.09 (dd, J = 3.6, 1.2 Hz, 1H), 6.98 (dd, J = 5.2, 3.6 Hz, 1H), 4.38−4.19 (m, 2H), 3.95 (d, J = 0.5 Hz, 1H), 2.33−2.20 (m, 1H), 1.48−1.05 (m, 14H), 0.91−0.83 (m, 2H), 0.81 (d, J = 6.8 Hz, 3H); (minor) 7.22 (dd, J = 5.2, 1.2 Hz, 1H), 7.09 (dd, J = 3.6, 1.2 Hz, 1H), 6.99−6.97 (m, 1H), 4.38−4.19 (m, 2H), 4.00 (d, J = 0.5 Hz, 1H), 2.33−2.20 (m, 1H), 1.48−1.05 (m, 14H), 0.93 (d, J = 6.6 Hz, 3H), 0.91−0.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.0, 146.9, 127.1, 124.8, 124.3, 81.0, 62.8, 42.6, 31.9, 31.6, 29.5, 27.6, 22.8, 14.22, 14.15, 12.8; (minor) 174.9, 146.7, 127.1, 124.9, 124.4, 80.9, 62.9, 42.5, 31.9, 29.6, 29.4, 27.7, 22.7, 14.2, 14.0, 12.8. HRMS (ESI) calcd for $C_{16}H_{26}O_3S$, $[M + Na]^+$, 321.1495; found, 321.1502. FTIR (neat): 3502, 2929, 2857, 1725.

*2-Hydroxy-2-(octan-2-yl)-2,3-dihydro-1H-inden-1-one (**4j**).* In accordance with procedure B, **1j** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2−3% ether/hexanes) provided the title compound (44.3 mg, 0.17 mmol, dr = 1:1) as a colorless oil in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (A) 7.75 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 10.8, 4.1 Hz, 1H), 7.43 (d, J = 7.7 Hz, 1H), 7.37 (dd, J = 7.5, 7.5 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 2.98 (d, J = 17.4 Hz, 1H), 2.51 (s, 1H), 1.93−1.72 (m, 15H), 1.48−0.99 (m, 9.5H), 0.87 (t, J = 6.8 Hz, 3H), 0.67 (d, J = 6.9 Hz, 3H); (B) 7.75 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 10.8, 4.1 Hz, 1H), 7.43 (d, J = 7.7 Hz, 1H), 7.37 (dd, J = 7.5 Hz, 7.5 Hz, 1H), 3.28 (d, J = 17.4 Hz, 1H), 2.98 (d, J = 17.4 Hz, 1H), 2.53 (s, 1H), 1.93−1.72 (m, 1.5 H), 1.48−0.99 (m, 12.5H), 0.82 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (A) 209.1, 152.8, 135.8, 135.4, 127.8, 126.6, 124.5, 82.3, 40.6, 36.8, 32.0, 30.5, 29.6, 27.8, 22.8, 14.5, 13.5; (B) 209.0, 152.6, 135.8, 135.5, 127.8, 126.7, 124.5, 82.3, 40.6, 37.1, 31.9, 31.5, 29.4, 27.7, 22.7, 14.22, 14.16. HRMS (ESI) calcd for $C_{17}H_{24}O_2$, $[M + Na]^+$, 283.1669; found, 283.1679. FTIR (neat): 3447, 2926, 1709.

*2-Hydroxy-2-(octan-2-yl)acenaphthylen-1(2H)-one (**4k**).* (Using *dihydro*-**1k**) In accordance with procedure B, *dihydro*-**1k** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 5−7% ethyl acetate/hexanes) provided the title compound (41.5 mg, 0.14 mmol, dr = 2:1) as a light green solid in 70% yield. (Using **1k**) In accordance with procedure B, **1k** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 5−7% ethyl acetate/hexanes) provided the title compound (56.3 mg, 0.19 mmol, dr = 2:1) as a light green solid in 95% yield. (Using *dehydro*-**1k**) In accordance with procedure B, *dehydro*-**1k** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 5−7% ethyl acetate/hexanes) provided the title compound (40.3 mg, 0.14 mmol, dr = 2:1) as a light green solid in 68% yield. Note: The reaction was conducted in the presence of 1,3-butane diol (36.0 mg, 0.4 mmol, 200 mol %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 8.11 (dd, J = 8.1, 0.5 Hz, 1H), 7.92 (ddd, J = 4.0, 2.0, 2.0 Hz, 1H), 7.90−7.85 (m, 1H), 7.72 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H), 7.68−7.61 (m, 2H), 2.84 (d, J = 2.4 Hz, 1H), 2.27−1.94 (m, 1H), 1.49−0.96 (m, 10H), 0.91−0.83 (m, 3H), 0.58 (t, J = 6.2 Hz, 3H); (minor) 8.11 (dd, J = 8.1, 0.5 Hz, 1H), 7.92 (ddd, J = 4.0, 2.0, 2.0 Hz, 1H), 7.90−7.85 (m, 1H), 7.72 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H), 7.68−7.61 (m, 2H), 2.84 (d, J = 2.4 Hz, 1H), 2.27−1.94 (m, 1H), 1.49−0.96 (m, 13H), 0.79 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 207.2, 142.5, 138.4, 132.01, 131.99, 130.7, 128.7, 128.3, 125.4, 121.7, 121.6, 83.1, 41.6, 32.0, 30.2, 29.6, 27.9, 22.8, 14.4, 14.2; (minor) 207.2, 142.4, 138.7, 132.0, 131.9, 130.8, 128.7, 128.3, 125.4, 121.6, 121.4, 82.9, 41.4, 31.8, 31.3, 29.2, 27.5, 22.6, 14.1, 13.3. HRMS (ESI) calcd for $C_{20}H_{24}O_2$, $[M + Na]^+$, 319.1669; found, 319.1678. FTIR (neat): 3423, 2924, 1708. MP: 79.8−81.1 °C.

*3-Hydroxy-3-(octan-2-yl)chroman-4-one (**4m**).* In accordance with procedure B, **1m** (0.2 mmol, 100 mol %) was reacted with 1-octene (13 × 100 mm pressure tube, 0.15 mL, 1.0 mmol, 500 mol %) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 2−3% ether/hexanes) provided the title compound (34.8 mg, 0.13 mmol, dr = 1:1) as a pale yellow solid in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (A) 7.84 (dd, J = 7.8, 1.7 Hz, 1H), 7.56−7.47 (m, 1H), 7.05 (ddd, J = 8.2, 1.9, 1.0 Hz, 1H), 6.96 (ddd, J = 8.4, 3.0, 0.6 Hz, 1H), 4.60 (d, J = 11.7 Hz, 1H), 4.07 (d, J = 11.7 Hz, 1H), 3.56 (s, 1H), 1.97−1.87 (m, 1H), 1.76−1.64 (m, 0.5H), 1.49−0.94 (m, 12.5H), 0.88 (dd, J = 8.4, 5.0 Hz, 3H); (B) 7.84 (dd, J = 7.8, 1.7 Hz, 1H), 7.56−7.47 (m, 1H), 7.05 (ddd, J = 8.2, 1.9, 1.0 Hz, 1H), 6.96 (ddd, J = 8.4, 3.0, 0.6 Hz, 1H), 4.55 (d, J = 11.7 Hz, 1H), 4.04 (d, J = 11.7 Hz, 1H), 3.50 (s, 1H), 1.76−1.64 (m, 0.5H), 1.49−0.94 (m, 9.5H), 0.80 (t, J = 7.0 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (A) 209.1, 152.8, 135.8, 135.4, 127.8, 126.6, 124.5, 82.3, 40.6, 36.8, 32.0, 31.5, 29.6, 27.7, 22.8, 14.5, 14.2; (B) 209.1, 152.6, 135.8, 135.4, 127.8, 126.7, 124.5, 82.3, 40.6, 37.1, 31.9, 30.5, 29.4, 27.7, 22.7, 14.2, 13.5. HRMS (ESI) calcd for $C_{17}H_{24}O_3$, $[M + Na]^+$, 299.1618; found, 299.1623. FTIR (neat): 3453, 2927, 1684. MP: 67.8−68.0 °C.

*Ethyl 2-Hydroxy-3-methyl-2,4-diphenylbutanoate (**5a**).* In accordance with procedure B, **1a** (0.2 mmol, 100 mol %) was reacted with **2c** (13 × 100 mm pressure tube, 0.13 mL, 1.0 mmol, 500 mol %) in toluene (2.0 M) at 130 °C for a 40 h period. Flash column chromatography (SiO_2: 30−60% dichloromethane/hexanes) provided the title compound (34.6 mg, 0.11 mmol, dr = 5:1) as colorless oil in 58% yield. Note: $AdCO_2H$ (30 mol %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (major) 7.71−7.65 (m, 2H), 7.38−7.26 (m, 5H), 7.22 (d, J = 7.3 Hz, 3H), 4.33−4.15 (m, 2H), 3.84 (d, J = 0.5 Hz, 1H), 2.82−2.67 (m, 2H), 2.57 (dd, J = 13.4, 10.5 Hz 1H), 1.33 (t, J = 7.1 Hz, 3H), 0.62 (t, J = 6.8 Hz, 3H); (minor) 7.81−7.77 (m, 2H), 7.42 (dd, J = 10.5, 4.9 Hz, 2H), 7.38−7.26 (m, 2H), 7.18 (dd, J = 11.2, 4.3 Hz, 2H), 7.05 (d, J = 7.1 Hz, 2H), 4.33−4.15 (m, 2H), 3.87 (d, J = 0.6 Hz, 1H), 2.82−2.67 (m, 1H), 2.50 (d, J = 13.7 Hz, 1H), 2.21 (dd, J = 13.6 Hz, 11.6 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.8, 141.3, 141.0, 129.4, 128.4, 128.3, 127.6, 126.1, 126.0, 81.3, 62.8, 43.2, 38.6, 14.3, 12.7; (minor) 175.5, 141.4, 141.1, 129.2, 128.4, 128.3, 127.8, 126.2, 125.9, 81.2, 62.8, 43.4, 36.4, 14.2, 13.6. HRMS (ESI) calcd for $C_{19}H_{22}O_3$, $[M + Na]^+$, 321.1461; found, 321.1466. FTIR (neat): 3505, 2976, 2361, 2342, 1715.

*Ethyl 2-Hydroxy-2-phenyl-3-(pivaloyloxy)butanoate (**6a**).* In accordance with procedure B, **1a** (0.2 mmol, 100 mol %) was reacted with **2d** (13 × 100 mm pressure tube, 0.09 mL, 0.6 mmol, 300 mol %) in toluene (2.0 M) at 130 °C for a 24 h period. Flash column chromatography (SiO_2: 2−4% ethyl acetate/hexanes) provided the title compound (51.8 mg, 0.25 mmol, dr = 1.5:1) as a pale yellow oil in 84% yield. Note: XPhos and $AdCO_2H$ were omitted. ^1H NMR (400 MHz, $CDCl_3$): δ (major) 7.47−7.28 (m, 5H), 6.09 (q, J = 5.2 Hz, 1H), 5.19 (s, 1H), 4.25−4.06 (m, 2H), 1.53 (d, J = 5.2 Hz, 3H), 1.23−1.17 (m, 3H), 1.11 (s, 9H); (minor) 7.47−7.28 (m, 5H), 5.84 (q, J = 5.2 Hz, 1H), 5.14 (s, 1H), 4.25−4.06 (m, 2H), 1.44 (d, J = 5.3 Hz, 3H), 1.23−1.17 (m, 3H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 178.3, 170.6, 136.4, 128.7, 128.6, 127.3, 95.5, 79.0, 61.5, 38.9, 27.0, 20.9, 14.2; (minor) 178.3, 170.1, 136.0, 129.0, 128.8, 127.5, 95.0, 79.3, 61.4, 39.0, 27.1, 20.8, 14.1. HRMS (ESI) calcd for $C_{17}H_{24}O_5$, $[M + Na]^+$, 331.1516; found, 331.1520. FTIR (neat): 2979, 1789, 1174.

*Ethyl 2-Hydroxy-2-phenyl-2-(tetrahydrofuran-2-yl)acetate (**7a**).* In accordance with procedure B, **1a** (0.2 mmol, 100 mol %) was reacted with **2e** (13 × 100 mm pressure tube, 0.05 mL, 0.6 mmol, 300 mol %) in toluene (2.0 M) at 140 °C for a 24 h period. Flash column chromatography (SiO_2: 2−5% ethyl acetate/hexanes) provided the title compound (39.0 mg, 0.23 mmol, dr = 1:1) as a pale yellow oil in 78% yield. Note: XPhos and $AdCO_2H$ were omitted. ^1H NMR (400 MHz, $CDCl_3$): δ (A) 7.44 (ddd, J = 7.8, 7.8, 1.3 Hz, 2H), 7.39−7.27 (m, 3H), 5.36 (d, J = 3.6 Hz, 1H), 5.26 (s, 1H), 4.25−4.06 (m, 2H), 4.01−3.94 (m, 1H), 3.89−3.83 (m, 1H), 2.19−1.80 (m, 4H), 1.21 (t, J = 7.1 Hz, 3H); (B) 7.44 (ddd, J = 7.8, 7.8, 1.3 Hz, 2H), 7.39−7.27 (m, 3H), 5.17 (d, J = 4.4 Hz, 1H), 5.09 (s, 1H), 4.25−4.06 (m, 2H), 3.89−3.83 (m, 1H), 3.81−3.77 (m, 1H), 2.19−1.80 (m, 4H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (A) 171.4, 137.2, 128.5, 128.4, 127.2, 102.7, 75.8, 67.5, 61.3, 32.6, 23.3, 14.2; (B) 171.4, 136.6, 128.64, 128.56, 127.4, 103.2, 77.4, 67.7, 61.1, 32.5, 23.6, 14.2. HRMS (ESI) calcd for $C_{14}H_{18}O_4$, $[M + Na]^+$, 273.1097; found, 273.1108. FTIR (neat): 2981, 1747.

*Ethyl 4-Acetoxy-2-hydroxy-3-methyl-2-phenylbutanoate (**8a**).* In accordance with procedure B, **1a** (0.2 mmol, 100 mol %) was reacted with **2f** (13 × 100 mm pressure tube, 0.11 mL, 1.0 mmol, 500 mol %) in toluene (2.0 M) at 140 °C for a 40 h period. Flash column chromatography (SiO_2: 5−7% ethyl acetate/hexanes) provided the title compound (33.6 mg, 0.12 mmol, dr = 1.6:1) as a pale yellow oil in 60% yield. ^1H NMR (400 MHz, $CDCl_3$): δ (major) 7.62 (ddd, J = 3.4, 1.9, 1.9 Hz, 2H), 7.35 (ddd, J = 11.8, 4.6 Hz, 3H), 4.33−4.15 (m, 3H), 4.07 (dd, J = 11.0, 6.5 Hz, 1H), 3.80 (s, 1H), 2.96−2.86 (m, 1H), 2.04 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H), 0.70 (d, J = 6.9 Hz, 3H); (minor) 7.66 (ddd, J = 3.4, 1.9, 1.9 Hz, 2H), 7.31−7.25 (m, 3H), 4.33−4.20 (m, 2H), 3.90−3.81 (m, 2H), 3.80 (s, 1H), 2.96−2.86 (m, 1H), 1.81 (s, 3H), 1.29 (t, J = 7.0 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (major) 175.3, 170.8, 140.8, 128.3, 127.8, 126.0, 78.7, 66.0, 62.7, 40.0, 21.0, 14.1, 11.6; (minor) 174.7, 171.1, 140.2, 128.4, 127.9, 125.9, 79.6, 65.5, 62.9, 40.1, 20.8, 14.2, 12.6. HRMS (ESI) calcd for $C_{15}H_{20}O_5$, $[M + Na]^+$, 303.1203; found, 303.1215. FTIR (neat): 3494, 2981, 1727, 1231.

*2-(4-Bromophenyl)-2-hydroxy-3-methylnonyl 4-Bromo-benzenesulfonate (**4b** Derivative).* An ethereal solution (5 mL) of **4b** (1.39 g, 3.7 mmol) was added dropwise to a 100 mL round-bottom flask charged with an ethereal (30 mL, 0.12 M) suspension of LAH (709 mg, 18.7 mmol) at 0 °C. The reaction was removed from the ice-bath and was allowed to stir for a 1 h period. Distilled water (1 mL) was added slowly. Distilled water (3 mL) and 15% NaOH aqueous (1 mL) were added to the reaction mixture. To the vigorously stirred solution were added portions of $MgSO_4$ until the reaction mixture solidified. The reaction mixture was filtered through a fritted glass funnel with the aid of ether. The filtrate was evaporated under reduced pressure and was used in the next step without further purification. To the crude diol (1.16 g, 3.5 mmol) were added dichloromethane (30 mL, 1.1 M), 4-bromobenzenesulfonyl chloride (996 mg, 3.9 mmol), DMAP (42 mg, 0.35 mmol), and Et_3N (1 mL, 7.1 mmol). The reaction was allowed to stir at ambient temperature for a 1 h period. $NaHCO_3$ (10 mL) and distilled water (10 mL) were added to the reaction mixture. The mixture was transferred to a separatory funnel and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine (1 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude **4b** derivative residue was subjected to column chromatography (SiO_2: 20% ethyl acetate/hexanes) to give the title compound (1.7 g, 3.3 mmol) in 90% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.39. (d, J = 8.6, 2H), 7.12 (d, J = 8.6 Hz, 2H), 4.34 (s, 2H), 2.11 (s, 1H), 1.86−1.76 (m, 1H), 1.55−1.46 (m, 1H), 1.37−1.05 (m, 8H), 0.91−0.80 (m, 4H), 0.74 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 134.4, 132.6, 131.1, 129.2, 127.6, 74.7, 40.5, 31.8, 30.2, 29.4, 27.6, 22.6, 14.0, 13.8. HRMS (ESI−MS) calcd for $C_{22}H_{28}Br_2O_4S$ $[M + Na]^+$, 568.9967; found, 568.9983. FTIR (neat): 3610, 2927, 1727, 1577. MP: 98−100 °C.

*2-Hydroxyacenaphtylen-1(2H)-one-2-d (deuterio-**1k**).* To a flame-dried 50 mL round-bottom flask charged with 2*H*-spiro-[acenaphthylene-1,2′-[1,3]dioxolan]-2-one (891 mg, 3.9 mmol) was added ethanol (20 mL, 0.2 M). $NaBD_4$ (180 mg, 4.3 mmol) was added portionwise. The reaction mixture was allowed to stir at ambient temperature for 30 min. Distilled water was added, and the reaction mixture was allowed to stir until bubbling stopped. The mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with brine (1 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Without further purification, to the crude alcohol residue were added ethanol (20 mL) and 6.0 M HCl aqueous (15 mL). The reaction mixture was allowed to stir at ambient temperature for the stated time. Distilled water was added, and the mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with brine (1 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude solid was subjected to column chromatography (SiO_2: 15% ethyl acetate in hexanes) to give the title compound (0.69 g, 3.7 mmol) in 95% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.1 Hz, 1H), 7.92 (dd, J = 8.1, 1.1 Hz, 1H), 7.79−7.66 (m, 3H), 3.12 (s, 1H). ^2H NMR (77 MHz, $CHCl_3$): δ 5.37 (s, 1D). HRMS (ESI−MS) calcd for $C_{12}H_7DO_2$ $[M + Na]^+$, 208.0479; found, 208.0460. FTIR (neat): 3400, 3064, 1702. MP: 160−162 °C.

*2-(Ethyl-1,2-d2)-2-hydroxyacenaphthylen-1(2H)-one (deuterio-**3k**).* In accordance with procedure A, *deuterio*-**1k** (0.2 mmol, 100 mol %) was reacted with ethylene (15 × 125 mm pressure tube, 0.82 mmol, 410 mol %) in toluene (2.0 M) at 130 °C for a 48 h period. Flash column chromatography (SiO_2: 5−15% ethyl acetate/hexanes) provided the title compound (18.0 mg, 0.08 mmol) in 42% yield as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 7.0 Hz, 1H), 7.91 (dd, J = 7.9, 1.2 Hz, 1H), 7.79−7.64 (m, 3H), 2.72 (s, 1H), 2.19−2.01 (m, 2H), 0.78 (t, J = 7.5 Hz, 2.78H). ^2H NMR (77 MHz, $CHCl_3$): δ 0.77 (s, 0.22H). HRMS (ESI−MS) calcd for $C_{14}H_{11}DO_2$ $[M + Na]^+$, 236.0792; found, 236.0781. FTIR (neat): 3370, 2973, 2927, 1716. MP: 92−93 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01923.

X-ray data for $Os_3(CO)_{11}(XPhos)$ (CIF)

Spectroscopic data for all new compounds (^1H NMR, ^{13}C NMR, IR, HRMS), including images of NMR spectra (PDF)

X-ray data for a derivative of **4b** (CIF)

X-ray data for $Os_2(CO)_4(O_2CR)_2(XPhos)_2$ (CIF)

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Notes

The authors declare no competing financial interest.

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