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Selective Direct Heterocoupling of Alkenes Catalyzed by *in Situ* Generated Ruthenium Complexes

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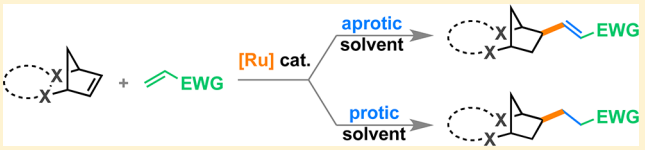
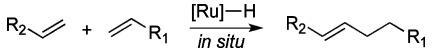
Supporting Information

ABSTRACT: We describe a ruthenium-based catalytic system that allows the codimerization of cyclic alkenes and Michael acceptors. High yields and excellent stereoselectivities toward the *exo*-(*E*) adducts are obtained on a wide range of substrates with various functional groups. In addition, running the reaction in protic media leads to the reduced product resulting from the tandem codimerization/reduction sequence.



Alkenes are key compounds in industrial organic chemistry, since they are generally easily available and cheap and can be transformed into a wide range of high value added products.[1] Among these transformations, the transition metal catalyzed heterodimerization of alkenes (also called codimerization of alkenes, Scheme 1) is a powerful methodology to convert readily accessible raw materials into valuable building blocks,[2] which also proceeds with atom economy.[3] However, the development of such a reaction is very challenging, requiring a fine control of the chemoselectivity, as both the substrates and the product include a reactive alkene functionality. Moreover, in order to meet the synthetic requirements, the reaction also needs to be highly regio- and stereoselective, tolerant toward a wide variety of functional groups, and of broad scope.

Scheme 1. Atom-Economical Heterocoupling of Alkenes



In this field, the hydrovinylation of alkenes, which consists of the addition of ethylene to an alkene, has been extensively studied, and many transition metal catalysts have been developed for the selective hydrovinylation of styrenes, dienes, or strained alkenes.[4] In addition, 1,3-dienes have also been used as efficient partners for the codimerization of alkenes using ruthenium,[5] cobalt,[6] or iron[7] complexes. Nevertheless, the heterodimerization of other classes of alkenes has only been scarcely explored so far. For example, Jamison[8] and Ogoshi[9] independently reported the nickel-catalyzed direct addition of various alkenes to enones, and Ho recently described the use of Ni/NHC hydride complexes for the coupling of aliphatic alkenes with styrenes.[10] Examples involving the ruthenium-catalyzed codimerization of acrylates were also developed by Mitsudo and Kondo.[11] However, the yields and selectivities obtained remain often moderate, and the substrate scope is limited. Hence, the development of an efficient catalytic system for the selective codimerization of alkenes is still challenging.[12]

We recently described a versatile, efficient, and easy to handle catalytic system for hydroarylation and hydroalkenylation reactions involving C−H bond activation.[13] This catalytic system consists of the in situ generation of a ruthenium(II) dihydride active catalyst from a stable and commercial ruthenium(II) or (III) source, sodium formate, and a phosphine ligand.[13c] We reasoned that, through an appropriate choice of the ligand, this *in situ* generated ruthenium hydride would provide a very efficient catalyst for the codimerization of alkenes.[14]

As reaction model, we investigated the reaction of norbornene **1a** and *n*-butylacrylate **2a**, the heterodimerization of which was expected to be particularly tricky since both of these substrates are known to oligomerize in the presence of ruthenium complexes.[15,16] These alkenes were mixed with the catalytic system composed of $[RuCl_2(p\text{-cymene})]_2$, sodium formate, and a ligand (Table 1).

We were pleased to find that the use of 10 mol % of triphenylphosphane (2 equiv/Ru) as the ligand in dioxane at 80 °C allowed the formation of the heterocoupling product **3aa** in a 51% yield (entry 1). Under these conditions, the *exo*-(*E*) adduct[17] was formed as the sole isomer and isolated with a yield of 50%. Decreasing the amount of ligand diminished the GC yield to 28% (entry 2), while the introduction of 3 or 4 equiv of ligand compared to ruthenium led to similar, though slightly lower, yields (entries 3 and 4). Other ligands were then investigated. The use of electron-rich or -deficient triarylphosphanes did not improve the yields (entries 5 and 6), whereas cyclohexyldiphenylphosphane allowed the formation of the heterocoupling product in 60% yield (entry 7). Moreover, better selectivities were observed in the heterodimerization of other substrates using this more hindered ligand. In contrast, diphosphane ligands were found to be less effective for this reaction (entries 8 and 9). The use of other solvents such as

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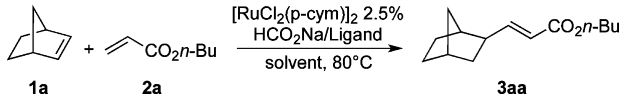
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

entry	ligand (mol %)	solvent	yield[b] [%]
1	PPh_3 (10)	1,4-dioxane	51 (50)
2	PPh_3 (5)	1,4-dioxane	28
3	PPh_3 (15)	1,4-dioxane	45
4	PPh_3 (20)	1,4-dioxane	48
5	$P(4\text{-}CF_3C_6H_5)_3$ (10)	1,4-dioxane	36
6	$P(4\text{-}MeOC_6H_5)_3$ (10)	1,4-dioxane	51
7	$PCyPh_2$ (10)	1,4-dioxane	60 (53)
8	dppf (10)	1,4-dioxane	17
9	dppe (10)	1,4-dioxane	43
10	$PCyPh_2$ (10)	toluene	31
11	$PCyPh_2$ (10)	cyclohexane	26

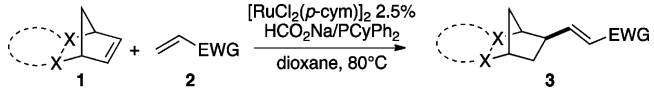
[a]Reaction conditions: **1a** (2 mmol), **2a** (1 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), $NaHCO_2$ (30 mol %), and ligand for 20 h at 80 °C. [b]Yields were determined by GC using an internal standard. Isolated yields are indicated in parentheses.

toluene (entry 10) or cyclohexane (entry 11) did not bring any improvement.

We next investigated the scope of these reaction conditions and found that various norbornene derivatives and Michael acceptors were reactive, allowing the formation of the heterodimerization product with high yields and excellent selectivities (Table 2).

1,4-Dihydro-1,4-methanonaphtalene reacts readily under the optimized conditions to afford adduct **3ba** with 89% yield and 99/1 *E*/*Z* selectivity. The bicyclic alkene **1c** leads to the heterodimerized product **3ca** with a good yield and a total stereoselectivity. The use of an excess of norbornene **1a** in the reaction with **2a** allows improving the yield of **3aa** to 62%,[18] though with a slight decrease in selectivity (from 100/0 to 98/2). Interestingly, the reaction of bicyclic hydrazines with **2a** occurs without any ring fragmentation, and the expected (*E*)-products **3da** and **3ea** are obtained as single stereoisomers with good to excellent yields. This transformation is all the more interesting since these structures are versatile building blocks for synthetic applications, for instance, in the synthesis of cyclopentanediamines.[19] Dienes can also be used as substrates, leading selectively to the monosubstituted adducts **3fa** and **3ga**. In the case of norbornene, 3% of the *endo*-(*E*) product was also isolated. This byproduct may be due to the ability of norbornadiene to behave as a bidentate ligand, which implies a complexation of the ruthenium to its *endo* face. The moderate

Table 2. Ruthenium-Catalyzed Heterodimerization of Alkenes[a]



1 2 3

Entry	Substrate **1**	Product	Yield[b] (*E*/*Z*)[c]
1	**1a**	**3aa**	62%[d] (98/2)
2	**1b**	**3ba**	89% (99/1)
3	**1c**	**3ca**	73% (100/0)
4	**1d**	**3da**	> 99% (100/0)
5	**1e**	**3ea**	69% (100/0)
6	**1f**	**3fa**	82% (100/0)
7	**1g**	**3ga**	50%[e] (100/0)
8	**1b**	**3bb**	51% (100/0)
9	**1f**	**3fb**	> 99% (100/0)
10	**1b**	**3bc**	78%[f,g] (98/2)
11	**1b**	**3bd**	69%[f] (55/45)

[a]Reaction conditions: alkene **1** (1 mmol), alkene **2** (2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), $NaHCO_2$ (30 mol %), and $PCyPh_2$ (10%) in dioxane for 20h at 80 °C. [b]Isolated yields. [c]Determined by ^1H NMR analysis. [d]Using 5 equiv of **1a**. [e]3% of *endo*-(*E*) adduct was also isolated. [f]Reaction conducted at 100 °C. [g]4% of *endo*-(*E*) adduct was also isolated.

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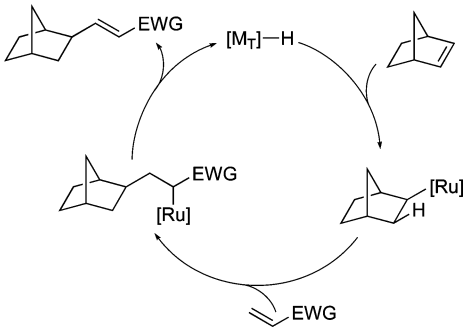
yield obtained with norbornadiene is likely to stem from the competitive ROMP reaction, as observed with norbornene.[18] Other Michael acceptors, such as enones or α,β-unsaturated amides, were also suited in this heterodimerization process. We were also pleased to find that disubstituted alkenes such as ethyl crotonate could be used as substrate, allowing the formation of product **3bd** with a good yield, despite a drop in the E/Z selectivity. However, the heterodimerization of Michael acceptors with less strained alkenes **1** led to a complex mixture of products, including homodimerization and oligomerization.

A plausible mechanism for this reaction is proposed in Scheme 2. The strained alkene first inserts into the Ru−H bond

Scheme 2. Proposed Reaction Mechanism

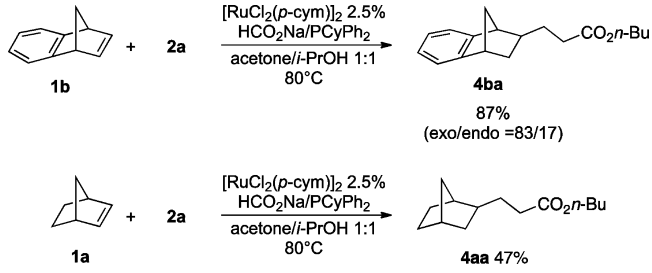


(on the less hindered *exo* face), leading to an alkylruthenium species that can then react with the Michael acceptor through a 1,4-addition to form the C−C bond. This step is followed by a β-hydride elimination that regenerates the ruthenium hydride complex and releases the product.[11a,d] The proceeding through a ruthenium-catalyzed C−H bond activation of the Michael acceptor, followed by the insertion of the norbornene derivative and a reductive elimination,[19] is unlikely because such a sequence is favored with electron-poor phosphanes, whereas electron-rich phosphanes are the most efficient in the current reaction (Table 1).[13d] Moreover, the expected configuration of the product with this mechanism is (Z), and the (E) selectivity obtained here would then originate from an isomerization, which is not conceivable since the E/Z product ratio is constant throughout the reaction. However, a mechanism involving a ruthenium(0)-catalyzed cyclometalation cannot be completely ruled out.

We wondered if it could be possible to obtain the reduced product, via a putative tandem heterodimerization/hydride transfer reduction, conducting the reaction in a protic solvent. Gratifyingly, the reaction of **1b** and **2a**, carried out in a 1:1 mixture of acetone/isopropanol, afforded the saturated ester **4ba** in a 87% yield (Scheme 3). In this case, the *endo* product is also formed with an *exo*/*endo* selectivity of 83/17. Under the same reaction conditions, **4aa** was obtained in a 47% yield from **1a**. A kinetic study of this reaction showed that, under these conditions, alkene **3ba** is quantitatively formed after 30 min and then slowly reduced into saturated adduct **4ba**, most likely via hydride transfer reduction by *in situ* generated ruthenium hydrides.

In conclusion, we have described quite general and efficient conditions for the heterocoupling of cyclic alkenes with Michael acceptors. These conditions are highly selective toward the *exo*-(E) product, which can be isolated with good yields. In addition, the reaction can be run in a protic solvent to obtain the product of the tandem heterocoupling/reduction reaction.

Scheme 3. Tandem Heterodimerization/Hydride Transfer Reduction



EXPERIMENTAL SECTION

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively; chemical shifts (δ) are reported in ppm relative to Me_4Si; coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. High resolution mass spectra were performed on a LTQ-Orbitrap apparatus. Thin layer chromatography was carried out on silica-gel plates, spots were detected with UV light and revealed with $KMnO_4$ solution. GC analyses were performed on an instrument equipped with a J&W Scientific DB-1701 capillary column (30 m, ϕ = 0.25 μm), using an ionization flame detector and the following temperature program: 70 °C for 1 min then 20 °C/min up to 210 °C. 1,4-Dioxane, toluene, and cyclohexane were distilled from $LiAlH_4$. 2-Propanol was freshly distilled from Na. Acetone extra dry was purchased from Acros Organics and used as received. Michael acceptors, norbornadiene, and norbornene were purchased and distilled prior to use. 1,4-Dihydro-1,4-methanonaphthalene,[20] 2,3-di(*tert*-butyloxycarbonyl)-2,3-diazabicyclo-[2.2.1]hept-5-ene,[21] 2,3-di(*tert*-butyloxycarbonyl)-2,3-diazabicyclo-[2.2.1]hept-5-ene,[21] 2,3-dicarboethoxynorbornadiene,[22] and 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one[23] were prepared according to the literature.

General Procedure for the Codimerization of Alkenes in Aprotic Solvent. A septum-capped vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 50 μmol, 5 mol % Ru), sodium formate (20.4 mg, 300 μmol, 30 mol %), and cyclohexyldiphenylphosphane (26.8 mg, 100 μmol, 10 mol %). The vial was placed under vacuum for 15 min and then under argon. Degassed dioxane (1 mL) was added, and then olefin (1 mmol) and Michael acceptor (2 mmol, 2 equiv) were added. The vial was placed in a preheated oil bath at 80 °C, and the mixture was stirred until completion of the reaction. After concentration under reduced pressure, the crude mixture was purified by silica gel chromatography.

***n*-Butyl (*E*)-*exo*-3-Bicyclo[2.2.1]hept-2-ylprop-2-enoate[11a] (3aa).** 138 mg (62% yield) of a light yellow oil was obtained from the reaction of norbornene (471 mg, 5 mmol) and *n*-butyl acrylate (145 μL, 1 mmol) according to the general procedure (E/Z = 98/2). R_f = 0.64 (cyclohexane/ethyl acetate 95:5). GC: t_R = 7.9 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.84 (1H, dd, J = 15.6 Hz and J = 8.2 Hz), 5.71 (1H, dd, J = 15.6 Hz and J = 0.7 Hz), 4.11 (2H, t, J = 6.7 Hz), 2.28 (1H, br s), 2.20−2.25 (1H, m), 2.15 (1H, br s), 1.12−1.68 (12H, m), 0.93 (3H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.3, 153.8, 118.8, 64.1, 44.7, 41.9, 37.0, 36.7, 35.9, 30.8, 29.7, 29.0, 19.3, 13.8.

***n*-Butyl (*E*)-*exo*-1,4-Dihydro-1,4-methanonaphthalen-2-yl-propenoate (3ba).** 112 mg (89% yield) of a light yellow oil was obtained from the reaction of 1,4-dihydro-1,4-methanonaphthalene (130 μL, 1 mmol) and *n*-butyl acrylate (290 μL, 2 mmol) according to the general procedure (E/Z = 99/1). R_f = 0.10 (cyclohexane/dichloromethane 9:1). GC: t_R = 12.0 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.06−7.21 (4H, m), 7.06 (1H, dd, J = 15.6 Hz and J = 8.7 Hz), 5.86 (1H, dd, J = 15.6 Hz and J = 1.1 Hz), 4.15 (2H, t, J = 6.7 Hz), 3.41 (1H, br s), 3.23 (1H, br s), 2.25−2.40 (1H, m), 1.37−1.82 (8H, m), 0.95 (3H, t, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 167.0, 152.9, 148.2, 147.4, 126.0, 125.8, 120.9, 120.7, 120.3, 64.2, 49.2, 46.4, 44.1, 43.1, 34.8, 30.8, 19.2, 13.7. HRMS (ESI): calculated for $C_{18}H_{22}O_2$ + Na 293.1512; found 293.1513.

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***n*-Butyl (*E*)-3-(2,4-Dimethyl-3-oxobicyclo[3.2.1]octan-6-yl)-acrylate (3ca).** 205 mg (73% yield) of a light yellow oil was obtained from the reaction of 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (155 μL, 1 mmol) and *n*-butyl acrylate (290 μL, 2 mmol) according to the general procedure (*E*/*Z* = 100/0). R_f = 0.17 (cyclohexane/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.86 (1H, dd, *J* = 15.5 Hz and *J* = 9.3 Hz), 5.76 (1H, dd, *J* = 15.5 Hz and *J* = 0.9 Hz), 4.56 (1H, dd, *J* = 7.1 Hz and *J* = 4.7 Hz), 4.26 (1H, d, *J* = 4.8 Hz), 4.13 (2H, t, *J* = 6.7 Hz), 2.79−2.86 (2H, m), 2.63−2.72 (1H, m), 2.01 (1H, dd, *J* = 13.2 Hz and *J* = 9.0 Hz), 1.58−1.77 (3H, m), 1.32−1.46 (2H, m), 0.99 (3H, d, *J* = 6.9 Hz), 0.96 (3H, d, *J* = 6.9 Hz), 0.94 (3H, t, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 208.2, 165.4, 149.3, 119.7, 84.8, 80.1, 63.3, 49.1 (2C), 40.3, 31.8, 29.7, 18.1, 12.7, 8.6, 8.3. HRMS (ESI): calculated for $C_{17}H_{26}O_3$ + Na 301.1780; found 301.1783.

***n*-Butyl (*E*)-*exo*-2,3-Di(*tert*-butyloxycarbonyl)-2,3-diazabicyclo[2.2.1]hept-5-ylpropenoate (3da).** 202 mg (>99% yield) of a light yellow oil was obtained from the reaction of 2,3-di(*tert*-butyloxycarbonyl)-2,3-diazabicyclo[2.2.1]hept-5-ene (296.4 mg, 1 mmol) and *n*-butyl acrylate (290 μL, 2 mmol) according to the general procedure (*E*/*Z* = 100/0). R_f = 0.19 (cyclohexane/diisopropyl ether 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.74 (1H, dd, *J* = 15.7 Hz and *J* = 7.5 Hz), 5.82 (1H, br d, *J* = 15.7 Hz), 4.2−4.7 (2H, m), 4.12 (2H, t, *J* = 6.7 Hz), 2.83 (1H, m), 2.10 (1H, m), 1.57−1.74 (5H, m), 1.31−1.57 (20H, m), 0.92 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 166.0, 156.0, 147.7, 121.4, 81.3, 64.1, 63.5, 59.8, 41.8, 35.1, 30.3, 29.9, 27.8, 18.8, 13.3. HRMS (ESI): calculated for $C_{22}H_{36}O_6N_2$ + Na 447.2466; found 447.2474.

***n*-Butyl (*E*)-2,3-Di(benzyloxycarbonyl)-2,3-diazabicyclo-[2.2.1]hept-5-ylpropenoate (3ea).** 340 mg (69% yield) of a light yellow oil was obtained from the reaction of 2,3-di-(benzyloxycarbonyl)-2,3-diazabicyclo[2.2.1]hept-5-ene (364 mg, 1 mmol) and *n*-butyl acrylate (290 μL, 2 mmol) according to the general procedure (69%, *E*/*Z* = 100/0). R_f = 0.15 (pentane/diisopropyl ether 1:3). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25−7.40 (10H, m), 7.67−7.75 (1H, m), 5.67−5.84 (1H, m), 5.18 (4H, s), 4.35−4.74 (2H, m), 4.12 (2H, t, *J* = 6.6 Hz), 2.71−2.88 (1H, m), 2.01−2.15 (1H, m), 1.69 (2H, sl), 1.57−1.68 (2H, m), 1.32−1.44 (2H, m), 0.93 (3H, t, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 166.1, 157.2, 147.4, 135.9, 128.5, 128.2, 128.0, 122.1, 68.0, 64.4, 63.9, 60.4, 42.1, 35.6, 34.5, 30.6, 19.1, 13.7. HRMS (ESI): calculated for $C_{28}H_{32}N_2O_6$ + Na 515.2158; found 515.2155.

Diethyl 5-(*exo*-(*E*)-3-Butoxy-3-oxoprop-1-en-1-yl)bicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate (3fa). 299 mg (82% yield) of a light yellow oil was obtained from the reaction of 2,3-dicarboethoxynorbornadiene (196 μL, 1 mmol) and *n*-butyl acrylate (290 μL, 2 mmol) according to the general procedure (*E*/*Z* = 100/0). R_f = 0.44 (cyclohexane/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.94 (1H, dd, *J* = 15.5 Hz and *J* = 8.4 Hz), 5.90 (1H, dd, *J* = 15.5 Hz and *J* = 1.1 Hz), 4.23 (4H, q, *J* = 7.1 Hz), 4.14 (2H, t, *J* = 6.7 Hz), 3.32 (1H, br s), 3.15 (1H, br s), 2.48−2.56 (1H, m), 1.61−1.72 (5H, m), 1.51−1.56 (1H, m), 1.35−1.44 (2H, m), 1.30 (6H, t, *J* = 7.1 Hz), 0.94 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 165.5, 163.6, 163.4, 150.1, 144.4, 142.6, 120.4, 63.2, 60.0, 49.8, 44.8, 43.6, 40.2, 31.5, 29.7, 29.1, 25.9, 18.1, 13.1, 12.7. HRMS (ESI): calculated for $C_{20}H_{28}O_6$ + Na 387.1784; found 387.1785.

Butyl (*E*)-3-(*exo*-Bicyclo[2.2.1]hept-5-en-2-yl)acrylate[24] (3ga). 110 mg (50% yield) of a light yellow oil was obtained from the reaction of norbornadiene (205 μL, 2 mmol) and *n*-butyl acrylate (145 μL, 1 mmol) according to the general procedure (*E*/*Z* = 100/0). R_f = 0.19 (cyclohexane/dichloromethane 7:3). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.96 (1H, dd, *J* = 15.5 Hz and *J* = 8.9 Hz), 6.10−6.13 (2H, m), 5.82 (1H, dd, *J* = 15.5 Hz and *J* = 1.1 Hz), 4.13 (2H, t, *J* = 6.7 Hz), 2.91(1H, br s), 2.71 (1H, br s), 2.12−2.21 (1H, m), 1.58−1.68 (3H, m), 1.35−1.44 (5H, m), 0.94 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 167.0, 153.9, 137.5, 136.0, 120.0, 64.1, 47.7, 45.5, 42.3, 41.4, 32.5, 30.7, 19.2, 13.7.

(*E*)-4-(*exo*-1,2,3,4-Tetrahydro-1,4-methanonaphthalen-2-yl)-but-3-en-2-one (3bb). 109 mg (51% yield) of a light yellow oil was obtained from the reaction of 1,4-dihydro-1,4-methanonaphthalene (130 μL, 1 mmol) and methylvinylketone (325 μL, 4 mmol) according the general procedure (*E*/*Z* = 100/0). R_f = 0.50 (cyclohexane/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.17−7.21 (2H, m), 7.08−7.11 (2H, m), 6.90 (1H, dd, *J* = 15.9 Hz and *J* = 8.4 Hz), 6.13 (1H, dd, *J* = 15.9 Hz and *J* = 0.9 Hz), 3.43 (1H, br s), 3.24 (1H, br s), 2.29−2.34 (1H, m), 2.28 (3H, s), 1.52−1.77 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 198.6, 151.9, 148.1, 147.3, 129.9, 126.1, 125.8, 120.9, 120.7, 49.3, 46.4, 44.1, 43.3, 35.0, 27.3. HRMS (ESI): calculated for $C_{15}H_{16}O$ + Na 235.1099; found 235.1098.

Benzyl (*E*)-*exo*-1,4-Dihydro-1,4-methanonaphthalen-2-yl-propenamide (3bc). 61 mg (78% yield) of a light brown solid was obtained from the reaction of 1,4-dihydro-1,4-methanonaphthalene (130 μL, 1 mmol) and benzyl acrylamide (322.4 mg, 2 mmol) according to the general procedure at 100 °C (7*E*/*Z* = 98/2). R_f = 0.12 (cyclohexane/ethyl acetate 4:1). MP = 79 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.27−7.39 (5H, m), 7.11−7.15 (2H, m), 7.05−7.11 (2H, m), 7.00 (1H, dd, *J* = 15.1 Hz and *J* = 8.9 Hz), 5.81 (1H, dd, *J* = 15.1 Hz and *J* = 1.0 Hz), 5.76 (1H, br s), 4.53 (2H, d, *J* = 5.8 Hz), 3.40 (1H, br s), 3.21 (1H, br s), 2.25−2.35 (1H, m), 1.69−1.87 (3H, m), 1.51−1.64 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 165.8, 149.1, 148.3, 147.6, 138.3, 128.7, 127.9, 127.6, 125.9, 125.7, 122.2, 120.9, 120.6, 49.4, 46.4, 44.1, 43.7, 44.1, 34.9. HRMS (ESI): calculated for $C_{21}H_{21}NO$ + Na 326.1515; found 326.1516.

Ethyl 3-(*exo*-1,2,3,4-Tetrahydro-1,4-methanonaphthalen-2-yl)but-2-enoate (3bd). The reaction of 1,4-dihydro-1,4-methanonaphthalene (130 μL, 1 mmol) and ethyl crotonate (260 μL, 2 mmol) was purified, and two fractions were obtained (overall yield 69%, *E*/*Z* = 55/45); 19 mg of a fraction containing the single (*Z*)-isomer was collected, along with 126 mg of another fraction containing a *E*/*Z* = 63/37 mixture.

(*Z*)-Isomer: R_f = 0.21 (cyclohexane/dichloromethane 7:3). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.15−7.22 (2H, m), 7.04−7.07 (2H, m), 5.70 (1H, br s), 4.07 (2H, q, *J* = 7.1 Hz), 3.51−3.57 (1H, m), 3.39 (1H, br s), 3.23 (1H, br s), 2.00 (3H, d, *J* = 1.4 Hz), 1.69−1.88 (4H, m), 1.21 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 166.0, 162.1, 149.1, 147.7, 125.7, 125.6, 121.0, 120.3, 117.4, 59.4, 48.8, 48.2, 43.8, 41.9, 34.1, 22.6, 14.3. HRMS (ESI): calculated for $C_{17}H_{20}O_2$ + Na 279.1361; found 279.1364.

(*E*)-Isomer: R_f = 0.20 (cyclohexane/dichloromethane 1:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.15−7.22 (2H, m), 7.04−7.07 (2H, m), 5.79 (1H, br s), 4.18 (2H, q, *J* = 7.1 Hz), 3.39 (2H, br s), 2.17−2.23 (1H, m), 2.20 (3H, d, *J* = 1.0 Hz), 1.61−1.82 (4H, m), 1.30 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 167.1, 162.7, 148.3, 148.2, 125.8, 125.7, 120.9, 120.5, 113.2, 59.6, 49.7, 46.7, 46.8, 44.0, 34.4, 19.5, 14.4.

***exo*-Diethyl 5-((*E*)-3-Oxobut-1-en-1-yl)bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (3fb).** 306 mg (>99% yield) of a light yellow oil was obtained from the reaction of 2,3-dicarboethoxynorbornadiene (196 μL, 1 mmol) and methylvinylketone (325 μL, 4 mmol) according the general procedure (*E*/*Z* = 100/0). R_f = 0.19 (cyclohexane/ethyl acetate 4:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.78 (1H, dd, *J* = 15.9 Hz and *J* = 8.4 Hz), 6.16 (1H, dd, *J* = 15.9 Hz and *J* = 0.9 Hz), 4.23 (4H, q, *J* = 6.9 Hz), 3.33 (1H, br s), 3.16 (1H, br s), 2.46−2.61 (1H, m), 2.26 (3H, s), 1.61−1.78 (4H, m), 1.30 (6H, t, *J* = 6(0.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 198.3, 164.7, 164.5, 150.0, 145.5, 143.5, 130.7, 61.1, 50.8, 45.9, 44.7, 41.4, 32.6, 27.5, 14.1. HRMS (ESI): calculated for $C_{17}H_{22}O_5$ + Na 329.1365; found 329.1361.

General Procedure for the Codimerization of Alkenes in Protic Solvent. A septum-capped vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (15.3 mg, 50 μmol, 5 mol % Ru), sodium formate (20.4 mg, 300 μmol, 30 mol %) and cyclohexyldiphenylphosphane (26.8 mg, 100 μmol, 10 mol %). The vial was placed under vacuum for 15 min and then under argon. Degassed isopropanol (0.5 mL) and acetone (0.5 mL) were added, and then olefin (1 mmol) and Michael acceptor (2 mmol, 2 equiv) were added. The vial was placed in a preheated oil bath at 80 °C, and the mixture was stirred until completion of the reaction. After concentration under reduced pressure, the crude mixture was purified by silica gel chromatography.

***n*-Butyl *exo*-3-Bicyclo[2.2.1]hept-2-ylpropanoate (4aa).** 105 mg (47% yield) of a light yellow oil was obtained from the reaction of norbornene (471 mg, 5 mmol) and *n*-butyl acrylate (145 μL, 1 mmol)

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according to the general procedure. R_f = 0.61 (pentane/diisopropyl ether 97:3). GC: t_R = 7.3 min. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.06 (2H, t, J = 6.7 Hz), 2.26 (2H, t, J = 7.6 Hz), 2.19 (1H, br s), 1.95 (1H, br s), 1.54−1.66 (4H, m), 1.24−1.52 (8H, m), 1.04−1.17 (3H, m), 0.93 (3H, t, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 174.2, 64.1, 41.8, 40.9, 37.9, 36.5, 35.2, 32.9, 31.9, 30.7, 30.0, 28.7, 19.1, 13.7. HRMS (ESI): calculated for $C_{14}H_{24}O_2$ + Na 247.1669; found 247.1669.

***n*-Butyl *exo*-1,4-Dihydro-1,4-methanonaphthalen-2-ylpropanoate (4ba).** 117 mg (87% yield) of a yellow oil was obtained from the reaction of 1,4-dihydro-1,4-methanonaphthalene (65 μL, 0.5 mmol) and *n*-butyl acrylate (73 μL, 0.5 mmol) according to the general procedure (*exo*/*endo* = 83/17). R_f = 0.08 (cyclohexane/dichloromethane 9:1). GC: t_R = 10.8 min (*exo*) and 10.3 min (*endo*). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.11−7.17 (2H, m), 7.01−7.09 (2H, m), 4.07 (2H, t, J = 6.6 Hz), 3.31 (1H, br s), 3.05 (1H, br s), 2.37 (2H, br t, J = 7.7 Hz), 1.31−1.98 (11H, m), 0.93 (3H, t, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 173.8, 148.7, 148.2, 125.5 (2C), 120.7, 120.3, 64.3, 48.2, 46.0, 43.9, 40.3, 35.0, 33.4, 31.6, 30.7, 19.1, 13.7. HRMS (ESI): calculated for $C_{18}H_{24}O_2$ + Na 295.1669; found 295.1668.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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