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Dual Activity of Grubbs-Type Catalyst in the Transvinylation of Carboxylic Acids and Ring-Closing Metathesis Reactions

Anna Brodzka,* Dominik Koszelewski, and Ryszard Ostaszewski*

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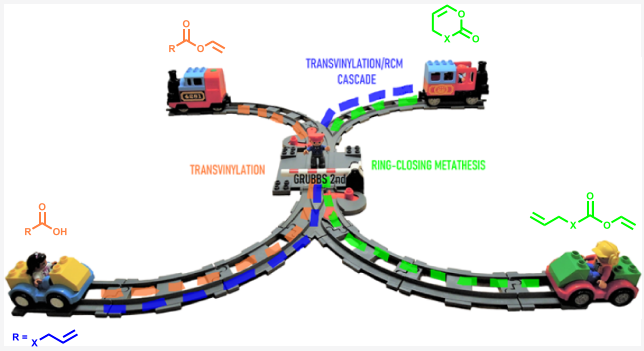
ABSTRACT: The development of a multifunctional catalyst, which mimics the promiscuity of enzymes, that would catalyze more than one chemical transformation in a single reaction vessel is one of the key points of modern sustainable chemistry. The results of our experiments indicated that Grubbs-type catalysts possess such multitask activity, catalyzing the transvinylation reaction of carboxylic acids without losing their original metathetic activity. This new activity of Grubbs catalysts was evidenced on several examples. It allows us to design a transvinylation/ring-closing metathesis (RCM) cascade reaction leading to the formation of endocyclic enol lactones from unsaturated carboxylic acids in an one-pot procedure. This unique ability of Grubbs catalyst to catalyze multiple mechanically distinct cascade reactions in a chemoselective way offers the new possibility for the synthesis of complex compounds from simple, easily accessible substrates.



INTRODUCTION

The design and synthesis of new catalysts is a tedious and time-consuming procedure. Usually, the catalyst can be applied only for a single reaction. One of the major challenges for organic chemists is to develop a multifunctional catalyst that may catalyze more than one reaction in a single vessel. Such a concept is also desired from the development of sustainable chemistry to solve the environmental issues.[1] Multiple processes performed in an one-reaction vessel, where the product of the first reaction is a substrate for the next transformation known as the sequential tandem catalysis, are of great importance for organic chemists.[2,3] The one-pot approach allows us to simplify the procedure and reduce costs and toxicity by minimizing the purification steps, which is economically and environmentally friendly.

Since the discovery of an air-stable ruthenium-based metathesis catalyst by Grubbs,[4] the metathesis reaction has become one of the most powerful tools for the formation of carbon−carbon double bond. However, the application of these mediators is limited mostly to metathesis reactions. To use such catalysts in other transformations, their structures have to be modified. For example, several ruthenium-based metathesis catalysts were found to be precatalysts for various side reactions[5,6] such as Kharasch addition,[7,8] hydrogenation,[9−11] oxidation,[12−14] isomerization,[15−17] cyclization,[18,19] and many others.[20−27] However, to promote nonmetathetic transformations, catalysts have to be converted to other Ru species, e.g., Grubbs catalyst transformed to [Ru-H] by a treatment with H_2 is an efficient catalyst for the olefin hydrogenation.[9−11] Such modifications of catalysts require special reaction conditions (such as the addition of ligands or other reagents, thermal decomposition, etc.), which seriously limits their applications.[28]

The majority of these nonmetathetic reactions were shown in tandem with olefin metathesis. However, usually, the metathesis is the first step of sequence, after which the catalyst structure is irreversibly changed (losing its original activity). Unfortunately, such modified catalysts are not active in metathesis reactions.

The examples of tandem protocols where nonmetathesis reaction is the first step of a cascade are very rare. Hodgson et al. described a nonmetathesis−metathesis sequence, where in the first step, the Grubbs second-generation Ru carbene complex catalyzes the homocoupling of diazoacetates, and in the next step, in the presence of an alkane, the metathesis occurs.[29−32] Thus, after the nonmetathetic transformation, the catalyst retained its original activity.

Recently, we have reported the ring-closing metathesis (RCM) of unsaturated carboxylic acids vinyl esters leading to valuable endocyclic enol lactones.[33] However, the syntheses of substrates are difficult and based on nonefficient, toxic protocols such as the transesterification of carboxylic acids

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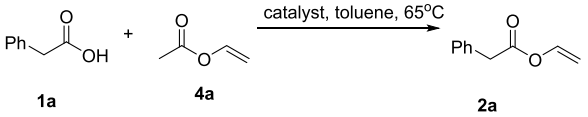
with vinyl acetate using $Hg(OAc)_2$.[34,35] Other approaches are based on Pd,[36] Ir,[37] Ag/Au,[38] or Rh[39] complexes as safer analogues of mercury. However, the usage of a large excess of vinyl acetate, which is a precursor of toxic acetaldehyde, makes those procedures less attractive. Recently, the application of ruthenium complexes as transvinylation catalysts has gained much attention[40] as they are less toxic and have a broad substrate scope and wide functional-group tolerability.

The versatility of Ru complexes encourages us to expand the scope of Grubbs catalyst activities. During our studies, we observed that the reaction of carboxylic acids with vinyl acetate in the presence of metathesis catalysts gave the corresponding carboxylic acid vinyl ester. This result led to the observation that these catalysts may promote the transvinylation of carboxylic acids. Herein, we present the details of our studies.

RESULTS AND DISCUSSION

In preliminary experiments, we have tested the reaction of phenylacetic acid (**1a**) with 2 equiv of vinyl acetate in the presence of several commonly used transvinylation catalysts as well as metathesis catalysts (Table 1). Usually, the transvinylation reaction requires the addition of strong acids or bases. However, in our studies, to make the process environmentally benign, the presence of these additives was excluded. All reactions were conducted in toluene at 65 °C.

Table 1. Transvinylation of Phenylacetic Acid[a]



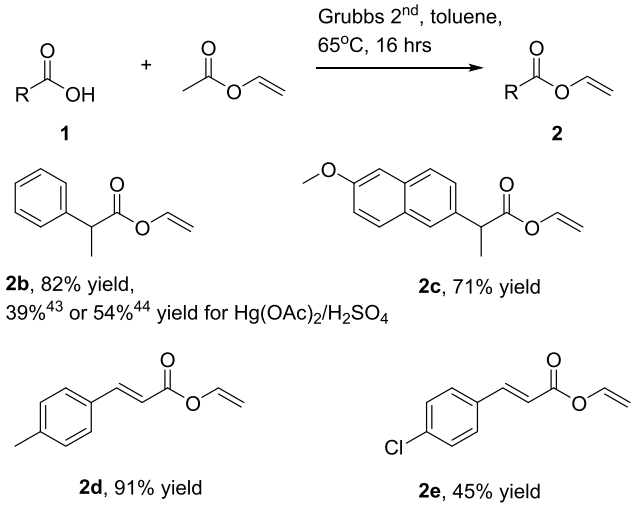
entry	catalyst	yield (%)[b]
1	$Hg(OAc)_2$	12
2	$Pd(OAc)_2$	35
3[c]	$Pd(OAc)_2$	38
4	$Ru_3(CO)_{12}$	28
5	$(Ph_3P)_3RuCl_2$	<1
6	$[Ru\text{-}(p\text{-cymene})Cl_2]_2$	<1
7	Grubbs first-generation	18
8	Grubbs–Hoveyda second-generation	41
9	Grubbs second-generation	86

[a]Conditions: **1a** (1 equiv), **4a** (2 equiv), catalyst (5 mol %), anhydrous toluene (c = 0.01), 16 h, inert atmosphere. [b]Yield of isolated product. [c]Literature data:[41] **1a** (1 equiv), **4a** (11 equiv), catalyst (1 mol %), tetrahydrofuran (THF), 60 °C, 16 h.

The reaction of **1a** with vinyl acetate catalyzed by commonly used transvinylation catalysts resulted in the formation of desired product **2a** in low yields (Table 1, entries 1–6). Surprisingly, both Grubbs first- and Grubbs–Hoveyda second-generation catalysts promoted the reaction; however, the yields of product **2a** were from low to moderate (Table 1, entries 7–8). The best result was received in the presence of Grubbs second-generation catalyst (86% yield) (Table 1, entry 9). In all cases, the metathesis catalysts did not manifest their metathetic activity as the formation of metathesis products (dimers) was not observed. The only obtained product was vinyl phenylacetate (**2a**). We have also performed similar reactions of methyl phenylacetate with vinyl acetate and palladium(II) acetate or Grubbs second-generation catalyst. However, the progress of reactions was not observed, which indicates that only carboxylic acids undergo the studied transvinylation.

In the next step, we explored the scope of transvinylation reaction using Grubbs second-generation catalyst (Scheme 1). In the studied cases, we used only such carboxylic acids, the structures of which prevent the RCM reaction.

Scheme 1. Transvinylation Reaction



In all cases, the appropriate vinyl esters **2b–e** were obtained in moderate to excellent yields. The application of biologically relevant 2-arylpropionic acids[42] provided the desired esters (as the only products) in high yields. The transvinylation of 4-methylcinnamic acid (**1d**) and 4-chlorocinnamic acid (**1e**) gave esters **2d** and **2e**, respectively.

Next, we tested if the transvinylation reaction of unsaturated carboxylic acids can be combined with subsequent RCM. Unlike the previous works concerning the tandem metathesis/nonmetathetic protocols,[5−27] we postulate that the first step of a cascade is a nonmetathetic reaction. Thus, the original metathetic activity of the catalyst should be retained after the transvinylation reaction.

As a model substrate, we choose 3-phenyl-4-pentenoic acid (**1f**). We have tested optimal cascade conditions (a catalyst, a transvinylation agent, and temperature) (Table 2).

All reactions catalyzed by Grubbs second-generation catalyst resulted in the formation of two products: vinyl ester (**2f**) and 4-phenyl-3,4-dihydro-2*H*-pyran-2-one (**3f**) (Table 2, entries 1–3). However, the best yield of tandem product was observed when vinyl propionate (**4b**) was used as a transvinylation agent at 80 °C (Table 2, entry 2). When vinylbenzoate (**4c**) was applied, the yield of **2f** was slightly lower, which can be explained by the difficulty with the purification procedure—the polarities of **4c** and **2f** are similar (Table 2, entry 3). We have also tested other catalysts that were efficient in the transvinylation reaction (Table 1, entries 2, 8) using donor **4b**. The reaction with $Pd(OAc)_2$ resulted only in the formation of product **2f** (Table 2, entry 4). The Grubbs–Hoveyda second-generation catalyst promoted both studied reactions leading to the formation of ester **2f** and lactone **3f** (Table 2, entry 5). However, the Grubbs second-generation catalyst proved to be the most efficient for a studied cascade (Table 2, entry 2). To demonstrate the practical utility of presented protocol, the cascade was performed on a larger scale (1.5 mmol), resulting in the formation of both desired products (Table 2, entry 6).

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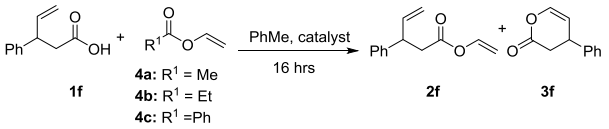
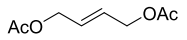
Table 2. Tandem Reaction Parameters[a]



Entry	Donor 4	Catalyst	Temp. [°C]	Yield of 2f [%][b]	Yield of 3f [%][b]
1	4a	Grubbs 2nd	65	40	18
2	4b	Grubbs 2nd	80	41	40
3	4c	Grubbs 2nd	80	35	41
4	4b	$Pd(OAc)_2$	80	38	0
5	4b	Grubbs-Hoveyda 2nd	80	52	25
6[c]	4b	Grubbs 2nd	80	52	33
7	**5** (allyl acetate)	Grubbs 2nd	80	 **6**	

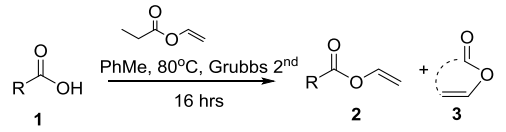
[a]Conditions: **1f** (1 equiv), **4** (2 equiv), catalyst (5 mol %), anhydrous toluene (c = 0.01), 16 h, inert atmosphere. [b]Yield of isolated product. [c]Reaction carried out on 1.5 mmol scale.

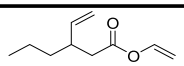
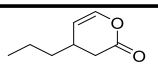
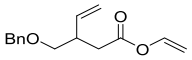
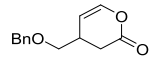
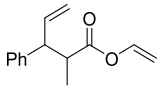
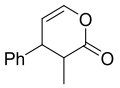
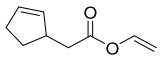
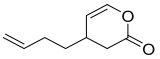
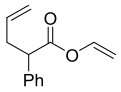
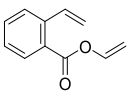
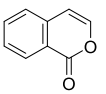
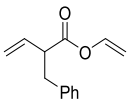
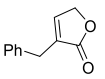
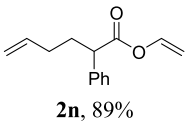
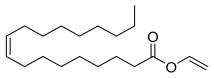
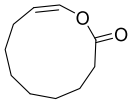
We have also examined the reaction of acid **1f** with allyl acetate (**5**). In this case 1,4-diacetoxybut-2-ene (**6**) (a product of cross-metathesis of **5**) was the only obtained product; acid **1f** was fully recovered from the reaction mixture (Table 2, entry 7).

Finally, we have examined the substrate scope for cascade reaction employing various unsaturated carboxylic acids and vinyl propionate (**4b**) in toluene at 80 °C (Table 3). The yields of lactones **3** obtained via RCM reactions starting from the corresponding vinyl esters **2** are given in parentheses.

First, we have tested 3-(alkyl or aryl)-4-pentenoic acids. In all cases, the desired transvinylation and cascade products were formed (Table 3, entries 1−3). When a diastereomeric mixture of 2-methyl-3-phenyl-4-pentenoic acid (**1i**) was subjected to the studied protocol, the corresponding vinyl ester **2i** was isolated in 1:1 diastereomeric ratio (dr) and its RCM product **3i**, in 82:18 dr as a main isomer trans (Table 3, entry 3). This phenomenon can be explained by the isomerization of the C═C bond by metathesis catalysts.[45,46] The stirring of a minor *cis*-**3i** isomer with Grubbs 2nd generation catalyst overnight resulted in its full conversion to isomer trans. The acid **1j** underwent the transvinylation reaction and subsequent domino ring-opening ring-closing metathesis reaction (ROM-RCM) as it was also observed in our previous study[33] (Table 3, entry 4). The studied protocol was also successfully applied for 2-phenyl-4-pentenoic acid (**1k**) and 2-vinylbenzoic acid (**1l**) (Table 3, entries 5 and 6). The reaction of 2-benzyl-3-butenoic acid (**1m**) results in the formation of ester **2m** and lactone **3m** (Table 3, entry 7). The structure of the obtained lactone **3m** differs from an expected RCM product of **2m** and is in its isomeric form.[33] The application of carboxylic acids with longer carbon chain than pentenoic results only in the formation of transvinylation product (Table 3, entries 8 and 9), which is in accordance with our previous research.[33] It is also worth mentioning that in all studied cases, only the transvinylation (**2**) and RCM (**3**) products were obtained. Moreover, the obtained results show that both reactions are catalyzed by the same catalyst, as after the transvinylation reaction, the same catalyst successfully mediates the metathesis

Table 3. Substrate Scope[a]



Entry	Transvinylation product yield [%][b]	Cascade product yield [%][b]
1	 **2g**, 10%	 **3g**, 83% (95%)[c]
2	 **2h**, 20%	 **3h**, 68% (98%)[c]
3	 **2i**, 35% (dr 1:1)	 **3i**, 44% (dr 82:18)
4	 **2j**, 50%	 **3j**, 35% (62%)[c]
5	 **2k**, 32%	 **3k**, 67% (97%)[c]
6	 **2l**, 15%	 **3l**, 78% (92%)[c]
7	 **2m**, 35%	 **3m**, 26% (36%)[c]
8	 **2n**, 89%	 **3n**, 0% (0%)[c]
9	 **2o**, 87%	 **3o**, 0% (0%)[c]

[a]Conditions: **1** (1 equiv), **4** (2 equiv), Grubbs second-generation catalyst (5 mol %), anhydrous toluene (c = 0.01), 16 h, 80 °C inert atmosphere. [b]Yield of isolated product. [c]The yields of products **3** obtained from RCM reaction starting from substrate **2** are given in parentheses.

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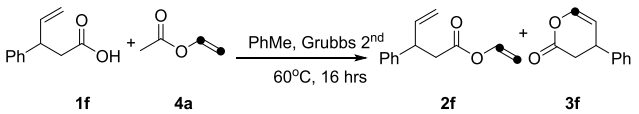
reaction. The promotion of nonmetathetic reaction does not result in the loss of metathetic activity of Grubbs catalyst.

We have also studied the mechanism of the newly developed cascade reaction. Thus, we performed the reaction between **1f** and vinyl-$^{13}C_2$ acetate in the presence of the Grubbs second-generation catalyst (Scheme 2). As a result, two ^{13}C-labeled

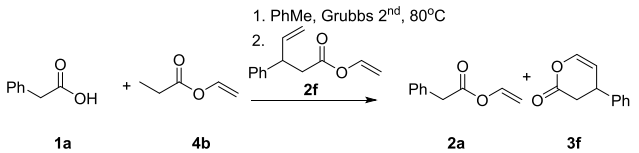
Scheme 2. Reaction of 1f with Vinyl-$^{13}C_2$ Acetate



products were obtained—vinyl-^{13}C2 3-phenyl 4-pentenoate **2f** and 4-phenyl(6-^{13}C)-3,4-dihydro-2*H*-pyran-2-one **3f**. The structures of products were confirmed by NMR analysis (Supporting Information).

Next, we have also performed additional experiments to test whether the metathesis activity of the Grubbs second-generation catalyst is retained after the transvinylation step. Thus, a set of experiments were designed (Table 4). First, the

Table 4. Studies on the Catalyst Activity



entry	reaction	V_{RCM} (mol/L·s)	time (h)	TON[e]
1	A[a]	1.5×10^{-7}	24	15
2	B[b]	1.9×10^{-7}	24	8.6[d]
3	C[c]	3.9×10^{-7}	2	20

[a]Conditions: **1a** (0.1 mmol), **4b** (0.2 mmol), Grubbs second-generation catalyst (5 mol %), anhydrous toluene (c = 0.01), 2 h, 80 °C inert atmosphere, then **2f** (0.1 mmol). [b]Conditions: **1a** (0.1 mmol), **4b** (0.2 mmol), Grubbs second-generation catalyst (5 mol %), anhydrous toluene (c = 0.01), 2 h, 80 °C inert atmosphere, then **2f** (0.1 mmol) and fresh Grubbs second-generation catalyst (5 mol %). [c]Conditions: **2f** (0.1 mmol), Grubbs second-generation catalyst (5 mol %), anhydrous toluene (c = 0.01), 2 h. [d]The amount of catalyst used was 2-fold. [e]Calculated from the equation: TON = $\frac{\text{yield} \times \frac{\text{no}}{\text{ncat}}}{100}$, where no = initial moles of **2f**; ncat = moles of catalyst used.

transvinylation reaction between phenylacetic acid **1a** and vinyl propionate **2a** was performed. Then, upon the completion of the transvinylation step, a cyclization precursor **2f** was added (reaction A). In the meantime, a similar reaction was carried out; however, in this case, after the transvinylation, a certain amount of fresh Grubbs second-generation catalyst was added to the reaction mixture (reaction B). The rates (V_{RCM}) as well as turnover number (TON) of both RCM reactions were measured and compared together with single RCM reaction starting from **2f** only (reaction C) (Table 4).

From the results (Table 4), it can be seen that the rates of ring-closing metathesis of **2f**, where in the first step, the transvinylation of acid **1a** occurs, are similar (Table 4, entry 1 and 2). The addition of a certain amount of fresh metathesis catalyst did not significantly affect the reaction rate (reaction A vs B). The differences in the TON values are due to the amount of catalyst used; for the B reaction after the completion of first step (transvinylation), the same amount of catalyst was added (Table 4, entry 2). On the other hand, both discussed reactions (A and B) proceeded much slower than common RCM of **2f** (Table 4, entry 3). The differences in these values can be a result of complex reaction mixture. The formation of vinyl esters would be reversible (the formed propionic acid can undergo transvinylation); thus, a catalyst can be also still involved in transvinylation. Nevertheless, the obtained results indicate that the metathesis activity of Grubbs second-generation catalyst is retained after the transvinylation step.

Based on the obtained results and literature data,[47−49] we have proposed the plausible mechanism of transvinylation reaction mediated by Grubbs-type catalysts (Scheme 3).

In the first step, the Grubbs catalyst reacted with vinyl acetate leading to the formation of Fischer carbene complex **I**. As the decomposition of **I** in toluene proceeds slowly,[49] we assumed that in the next step, the transesterification with carboxylic acid **1** occurs, leading to the formation of complex **II**. Then, the complex **II** reacts with styrene molecule and the ester bond toward the ruthenium center is cleaved, resulting in the release of the vinyl ester **2** and catalyst, which can be used in the next cycle. If the structure of carboxylic acid **1** enables the RCM reaction, the formed ester **2** undergoes the subsequent ring-closing metathesis.

The previous studies[50−52] suggested that complex **I** is not involved in cross-metathesis; however, it can be applied for RCM. This statement is in accordance with our results that the only products of the proposed transformation are vinyl esters **2** and lactones **3**; formation of dimers is not observed.

To support our hypothesis, an additional experiment was performed. According to Johnson et al.[49] Fischer carbene complex **I** was prepared. The obtained compound **I** was added to the solution of phenylacetic acid (**1a**) in toluene and stirred at 80 °C. As a product, vinyl phenylacetate (**2a**) was obtained. The result of the presented experiment confirms that the transvinylation takes place through an acetoxycarbene **I**.

■ CONCLUSIONS

In conclusion, our studies show a new type of nonmetathetic activity of Grubbs-type catalyst in the transvinylation of carboxylic acids. In comparison to classical methods involving the application of toxic metal catalysts, the obtained protocol is more efficient, less toxic, and works well for a broad range of carboxylic acids under mild conditions. To the best of our knowledge, the transvinylation reaction catalyzed by Grubbs-type catalyst has no precedence in the literature. Since the proposed mechanism of studied reaction indicates that ruthenium catalyst did not lose its metathetic activity after transvinylation reaction, attempts were made to combine developed transvinylation protocol with subsequent metathesis reaction. For selected unsaturated carboxylic acids, RCM proceeds efficiently, leading to the formation of endocyclic enol lactones. It is worth mentioning that both cascade reactions are chemoselective, as the formation of side products was not observed. Moreover, this is a rare example of cascade protocol where a metathesis catalyst does not lose its metathetic activity in a nonmetathetic step (transvinylation). Vinyl esters of carboxylic acids as well as endocyclic enol lactones are important building blocks for the synthesis of biologically active compounds; thus, we expect that our newly

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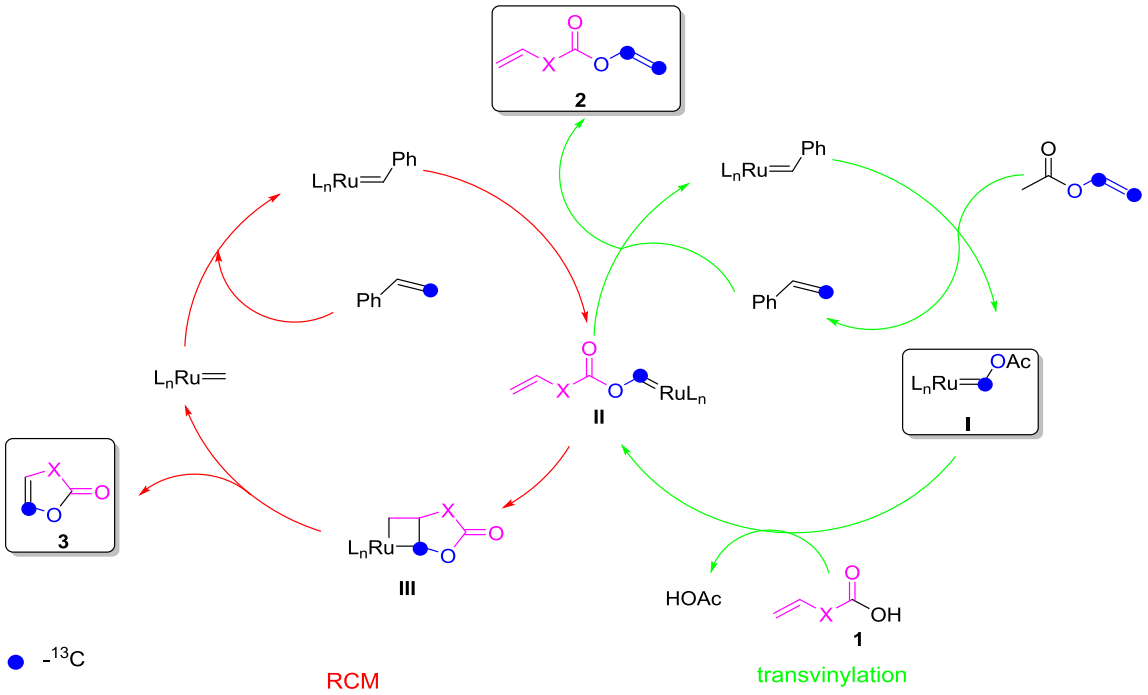
Scheme 3. Plausible Mechanism of the Studied Reaction



developed protocol will gain access for the synthesis of the pharmaceuticals and fine added-value chemicals.

EXPERIMENTAL SECTION

General. All of the chemicals were obtained from commercial sources. The solvents were of analytical grade. Phenylacetic acid, 4-chlorocinnamic acid, 4-methylcinnamic acid, 2-phenylpropionic acid, Naproxen, 2-cyclopent-1-acetic acid, 2-vinylbenzoic acid, and oleic acid were obtained from commercial source and used without further purification. All yields refer to isolated compounds. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard using Bruker 400 MHz spectrometers. The chemical shifts are reported in ppm (δ scale), and the coupling constants (J) are given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Synapt G2:SHD apparatus with QqTOF analyzer. All of the reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel Plates 60 F_{254}. Column chromatography was performed on Merck silica gel 60/230−400 mesh.

General Procedure for the Transvinylation of Phenylacetic Acid (1a). To a solution of phenylacetic acid **1a** (0.4 mmol) and vinyl acetate (0.8 mmol) in an anhydrous toluene (40 mL) under argon atmosphere was added an appropriate catalyst (5 mol %). The reaction mixture was heated in an oil bath at 65 °C for 16 h. The reaction mixture was cooled to room temperature and filtered over a Celite pad. The excess of solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate).

*Vinyl Phenylacetate (**2a**).* The product was isolated as an yellow oil from a silica column eluted by EtOAc/hexanes (1:10) in 86% yield (56 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.21 (m, 5H), 7.18 (t, J = 3.2 Hz, 1H), 4.83 (dd, J = 13.9, 1.7 Hz, 1H), 4.52 (dd, J = 6.3, 1.7 Hz, 1H), 3.63 (s, 2H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 168.7, 141.3, 129.3, 128.7, 127.3, 98.0, 40.9. The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[53]

General Procedure for the Transvinylation of Carboxylic Acids (1b−e). To a solution of the corresponding carboxylic acid (**1b−e**) (0.4 mmol) and vinyl acetate (0.8 mmol) in an anhydrous toluene (40 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 65 °C for 16 h. The reaction mixture was cooled to room temperature and filtered over a Celite pad. The excess of solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate).

*Vinyl 2-Phenylpropionate (**2b**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 82% yield (57.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.21 (m, 4H), 7.21−7.14 (m, 2H), 4.78 (dd, J = 14.0, 1.6 Hz, 1H), 4.47 (dd, J = 6.3, 1.6 Hz, 1H), 3.70 (q, J = 7.2 Hz, 1H), 1.47 (d, J = 7.2 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 171.6, 141.4, 139.7, 128.7, 127.5, 127.3, 97.9, 45.3, 18.4. The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[43]

*Vinyl 2-(6-Methoxy-2-naphthyl)propionate (**2c**).* The product was isolated as white crystals from a silica column eluted by EtOAc/hexanes (15:85) in 71% yield (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.59 (m, 3H), 7.33 (dd, J = 8.5, 1.9 Hz, 1H), 7.22−7.15 (m, 1H), 7.09−7.03 (m, 2H), 4.77 (dd, J = 14.0, 1.6 Hz, 1H), 4.47 (dd, J = 6.3, 1.6 Hz, 1H), 3.84−3.81 (m, 4H), 1.54 (d, J = 7.1 Hz, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 171.7, 157.8, 141.4, 134.8, 133.8, 129.3, 128.9, 127.3, 126.1, 119.1, 105.6, 97.9, 55.3, 45.2, 18.4. The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[54]

*Vinyl 4-Methylcinnamate (**2d**).* The product was isolated as white crystals from a silica column eluted by EtOAc/hexanes (1:9) in 91% yield (68.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 15.9 Hz, 1H), 7.47−7.40 (m, 2H), 7.35 (dd, J = 14.0, 6.3 Hz, 1H), 6.88−6.81 (m, 2H), 6.25 (d, J = 16.0 Hz, 1H), 4.89 (dd, J = 14.0, 1.6 Hz, 1H), 4.54 (dd, J = 6.3, 1.6 Hz, 1H), 3.77 (s, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 164.2, 161.8, 146.3, 141.4, 130.0, 126.9, 114.4, 114.0, 97.4, 55.4; HRMS (EI+, m/z): calcd. for $C_{12}H_{12}O_2$ $[M]^+$: 188.0837, found 188 0840.

*Vinyl 4-Chlorocinnamate (**2e**).* The product was isolated as white crystals (mp 57 °C) from a silica column eluted by EtOAc/hexanes (1:9) in 45% yield (37.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 16.0 Hz, 1H), 7.44−7.38 (m, 2H), 7.37−7.28 (m, 3H), 6.36 (d, J = 16.0 Hz, 1H), 4.91 (dd, J = 14.0, 1.7 Hz, 1H), 4.57 (dd, J = 6.2, 1.7 Hz, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 163.7, 145.1, 141.3, 136.7, 132.6, 129.4, 129.3, 117.3, 97.9; HRMS (EI+, m/z): calcd. for $C_{11}H_9O_2Cl$ $[M]^+$: 208.0291, found 208,0298.

Synthesis of Carboxylic Acids. Carboxylic acids **1f**,[33,55] **1g**,[33] **1h**,[33] **1i**,[33,56] **1k**,[33,57] **1m**,[58] and **1n**[59] were synthesized and purified

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according to the literature procedure. The ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.

General Procedure for Tandem Transvinylation/RCM Reaction (2f−o, 3f−m). To a solution of an appropriate unsaturated carboxylic acid (**1f−o**) (0.4 mmol) and vinyl propionate (0.8 mmol) in an anhydrous toluene (40 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 80 °C for 16 h. The reaction mixture was cooled to room temperature and filtered over a Celite pad. The excess of solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate).

*Vinyl 3-Phenyl-4-pentenoate (**2f**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 41% yield (33 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.23 (m, 2H), 7.18−7.12 (m, 4H), 5.99−5.86 (m, 1H), 5.06−4.97 (m, 2H), 4.79 (dd, J = 14.0, 1.6 Hz, 1H), 4.48 (dd, J = 6.3, 1.6 Hz, 1H), 3.84 (q, J = 7.4 Hz, 1H), 2.82−2.69 (m, 2H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 168.9, 142.1, 141.1, 139.9, 128.7, 127.5, 126.9, 115.1, 97.8, 45.3, 39.9; HRMS (EI+, m/z): calcd. for $C_{13}H_{14}O_2$ $[M]^+$: 202.0994, found 202.0996.

*4-Phenyl-3,4-dihydro-2H-pyran-2-one (**3f**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 41% yield (28 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.20 (m, 3H), 7.17−7.12 (m, 2H), 6.61 (dd, J = 6.0, 1.8 Hz, 1H), 5.37 (dd, J = 6.0, 4.0 Hz, 1H), 3.79−3.69 (m, 1H), 2.91 (dd, J = 15.9, 6.5 Hz, 1H), 2.67 (dd, J = 16.0, 8.3 Hz, 1H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 167.3, 141.6, 141.2, 129.1, 127.5, 126.8, 109.4, 37.3, 36.7; HRMS (ESI+, m/z): calcd. for $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0759, found 175.0768.

*Vinyl 3-Propyl-4-pentenoate (**2g**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 10% yield (7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, J = 14.0, 6.3 Hz, 1H), 5.67−5.58 (m, 1H), 5.06−5.00 (m, 2H), 4.88 (dd, J = 14.0, 1.6 Hz, 1H), 4.54 (dd, J = 6.3, 1.4 Hz, 1H), 2.59−2.55 (m, 1H), 2.38 (ddd, J = 23.2, 15.0, 8.6 Hz, 2H), 1.35 (ddt, J = 20.4, 6.0, 5.4 Hz, 4H), 0.85 (t, J = 6.7 Hz, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 169.6, 141.2, 140.7, 115.3, 97.5, 39.9, 39.8, 36.6, 20.0, 13.9; HRMS (EI+, m/z): calcd. for $C_{10}H_{16}O_2$ $[M]^+$: 168.1150, found 168,1147.

*4-Propyl-3,4-dihydro-2H-pyran-2-one (**3g**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 83% yield (46.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (dd, J = 6.0, 1.6 Hz, 1H), 5.18 (dd, J = 5.9, 4.0 Hz, 1H), 2.69−2.59 (m, 1H), 2.51−2.42 (m, 1H), 2.34 (dd, J = 15.5, 8.0 Hz, 1H), 1.38−1.27 (m, 4H), 0.88−0.81 (m, 3H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 168.5, 140.6, 110.4, 36.8, 34.9, 30.2, 19.5, 13.9; HRMS (ESI+, m/z): calcd. for $C_8H_{12}O_2$ $[M + H]^+$: 140.0837, found 140.0849.

*Vinyl 3-(Benzyloxymethyl)-4-pentenoate (**2h**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 20% yield (20 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.21 (m, 6H), 5.82−5.73 (m, 1H), 5.19−5.09 (m, 2H), 4.86 (dd, J = 14.0, 1.5 Hz, 1H), 4.55 (dd, J = 6.3, 1.6 Hz, 1H), 4.51 (s, 2H), 3.54−3.50 (m, 1H), 3.42−3.38 (m, 1H), 2.96−2.94 (m, 1H), 2.71−2.64 (m, 1H), 2.48−2.42 (m, 1H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 169.5, 141.2, 138.2, 137.5, 128.4, 127.6, 127.5, 116.5, 97.6, 73.1, 72.6, 40.1, 36.3, HRMS (ESI+, m/z): calcd. for $C_{15}H_{18}O_3Na$ $[M + Na]^+$: 269.1154, found 269.1157.

*4-(Benzyloxymethyl)-3,4-dihydro-2H-pyran-2-one (**3h**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 68% yield (59 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.20 (m, 5H), 6.46 (dd, J = 6.0, 1.4 Hz, 1H), 5.16 (dd, J = 5.9, 4.2 Hz, 1H), 4.45 (s, 2H), 3.39−3.32 (m, 2H), 2.71−2.68 (m, 1H), 2.66−2.52 (m, 2H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 167.9, 141.9, 137.8, 128.4, 127.7, 127.5, 106.7, 73.3, 71.6, 32.2, 31.7; HRMS (ESI+, m/z): calcd. for $C_{13}H_{15}O_3$ $[M + H]^+$: 219.1021, found 219.1028.

*Vinyl 2-Methyl-3-phenyl-4-pentenoate (**2i**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 35% yield (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−6.89 (m, 6H), 5.98−5.82 (m, 1H), 5.11−4.92 (m, 2H), 4.75 (ddd, J = 68.9, 13.9, 1.6 Hz, 1H), 4.44 (ddd, J = 55.7, 6.3, 1.6 Hz, 1H), 3.50−3.39 (m, 1H), 2.84−2.79 (m, 1H), 1.18 (d, J = 7.0 Hz, 2H), 0.94 (d, J = 6.9 Hz, 1H). ^{13}C {H}NMR (100 MHz, $CDCl_3$): δ 172.6, 172.2, 141.8, 141.2, 141.1, 140.9, 139.3, 138.1, 128.7, 128.5, 128.0, 127.6, 126.8, 126.7, 117.0, 115.8, 97.8, 97.6, 53.5, 53.4, 45.1, 44.8, 15.6, 15.2., HRMS (ESI+, m/z): calcd. for $C_{14}H_{16}O_2Na$ $[M + Na]^+$: 239.1048, found 21739.1040.

*Trans-4-Phenyl-5-methyl-3,4-dihydro-2H-pyran-2-one (**3i**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 36% yield (27 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.10 (m, 5H), 6.53 (dd, J = 6.0, 2.4 Hz, 1H), 5.21 (dd, J = 6.0, 2.9 Hz, 1H), 3.35 (dt, J = 10.6, 2.7 Hz, 1H), 2.68 (dq, J = 10.6, 6.9 Hz, 1H), 1.11 (d, J = 6.9 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 170.7, 141.3, 140.6, 128.9, 127.5, 127.5, 109.9, 44.3, 41.5, 14.2; HRMS (EI+, m/z): calcd. for $C_{12}H_{12}O_2$ $[M]^+$: 188.0837, found 188.00843.

*cis-4-Phenyl-5-methyl-3,4-dihydro-2H-pyran-2-one (**3i**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (15:85) in 8% yield (6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.01 (m, 5H), 6.62 (d, J = 5.9 Hz, 1H), 5.45 (t, J = 5.9 Hz, 1H), 3.53−3.47 (m, 1H), 3.08−2.99 (m, 1H), 0.94 (d, J = 7.0 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 170.9, 141.2, 128.8, 128.1, 127.7, 109.9, 42.8, 39.4, 12.4. HRMS (EI+, m/z): calcd. for $C_{12}H_{12}O_2$ $[M]^+$: 188.0837, found 188.00843.

*Vinyl 2-Cyclopent-1-acetate (**2j**).* The product was obtained from commercially available 2-cyclopent-1-acetic acid, and it was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 50% yield (30 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, J = 14.0, 6.3 Hz, 1H), 5.72 (td, J = 4.3, 2.0 Hz, 1H), 5.61 (ddd, J = 5.8, 4.1, 2.0 Hz, 1H), 4.82 (dd, J = 14.0, 1.4 Hz, 1H), 4.50 (dd, J = 6.3, 1.4 Hz, 1H), 3.13−2.99 (m, 1H), 2.46−2.18 (m, 4H), 2.16−2.03 (m, 1H), 1.47−1.38 (m, 1H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 169.9, 141.1, 133.3, 131.8, 97.5, 41.8, 40.0, 31.8, 29.6; HRMS (ES+, m/z): calcd. for $C_9H_{12}O_2$ $[M]^+$: 152.0837, found 152.0842.

*4-(But-3-en-1-yl)-3,4-dihydro-2H-pyran-2-one (**3j**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 35% yield (21 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (dd, J = 6.0, 1.5 Hz, 1H), 5.75−5.66 (m, 1H), 5.20 (dd, J = 5.9, 4.1 Hz, 1H), 5.17−4.92 (m, 2H), 2.68−2.63 (m, 1H), 2.48−2.46 (m, 1H), 2.42−2.33 (m, 1H), 2.06−2.02 (m, 2H), 1.48−1.43 (m, 2H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 168.3, 140.8, 137.3, 115.5, 110.1, 34.8, 33.7, 30.5, 29.8; HRMS (ESI+, m/z): calcd. for $C_9H_{13}O_2$ $[M + H]^+$: 153.0916, found 153.0921.

*Vinyl 2-Phenyl-4-pentenoate (**2k**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 32% yield (25.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.19 (m, 5H), 7.16 (dd, J = 12.3, 4.6 Hz, 1H), 5.71−5.61 (m, 1H), 5.04−4.96 (m, 2H), 4.79 (dd, J = 14.0, 1.6 Hz, 1H), 4.48 (dd, J = 6.3, 1.6 Hz, 1H), 3.62 (dd, J = 8.4, 7.1 Hz, 1H), 2.82−2.71 (m, 1H), 2.51−2.44 (m, 1H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 178.3, 142.2, 140.2, 128.9, 127.8, 127.1, 115.3, 45.5, 40.2; HRMS (EI+, m/z): calcd. for $C_{13}H_{14}O_2$ $[M]^+$: 202.0994, found 202.0998.

*5-Phenyl-3,4-dihydro-2H-pyran-2-one (**3k**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 67% yield (46.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.17 (m, 5H), 6.49 (ddd, J = 5.9, 2.0, 1.2 Hz, 1H), 5.31 (ddd, J = 5.8, 5.2, 3.6 Hz, 1H), 3.80−3.75 (m, 1H), 2.59−2.51 (m, 2H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 169.2, 141.6, 137.1, 128.7, 128.1, 127.7, 105.4, 45.3, 26.9; $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0759, found 175.0767.

*Vinyl 2-Vinylbenzoate (**2l**).* The product was obtained from commercially available 2-vinylbenzoic acid and isolated as a yellowish oil from a silica column eluted by EtOAc/hexanes (1:10) in 15% yield (10.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J = 7.9, 1.1 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.49−7.35 (m, 3H), 7.28 (td, J = 7.8, 1.2 Hz, 1H), 5.59 (dd, J = 17.4, 1.2 Hz, 1H), 5.31 (dd, J = 11.0, 1.2 Hz, 1H), 4.97 (dd, J = 14.0, 1.6 Hz, 1H), 4.63 (dd, J = 6.3, 1.6 Hz, 1H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 164.04, 141.38, 140.48,

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135.69, 132.79, 130.64, 127.50, 127.45, 127.08, 116.91, 98.24; HRMS (EI+, m/z): calcd. for $C_{11}H_{10}O_2$ $[M]^+$: 174.0681, found 174.0681.

*Isocumarin (**3l**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 78% yield (45.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 8.0 Hz, 1H), 7.70 (td, J = 7.7, 1.2 Hz, 1H), 7.56−7.49 (m, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 4.7 Hz, 1H), 6.48 (d, J = 5.6 Hz, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 162.3, 144.7, 136.3, 134.8, 129.7, 128.6, 125.5, 121.6, 106.9.; HRMS (ESI+, m/z): calcd. for $C_9H_7O_2$ $[M + H]^+$: 147.0446, found 147.0450.

*Vinyl 2-Benzyl-3-butenoate (**2m**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 35% yield (28 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.08 (m, 6H), 5.84−5.75 (m, 1H), 5.13−5.01 (m, 2H), 4.79 (dd, J = 14.0, 1.7 Hz, 1H), 4.49 (dd, J = 6.3, 1.7 Hz, 1H), 3.35−3.29 (m, 1H), 3.06 (dd, J = 13.7, 7.7 Hz, 1H), 2.81 (dd, J = 13.7, 7.3 Hz, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 170.4, 141.2, 138.2, 134.5, 129.1, 128.4, 126.6, 118.3, 98.1, 51.7, 38.2; HRMS (EI+, m/z): calcd. for $C_{13}H_{15}O_2$ $[M]^+$: 202.0994, found 202.0997.

*3-(Phenylmethyl)-2(5H)-furanone (**3m**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 26% yield (18 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.22 (m, 5H), 6.98−6.89 (m, 1H), 4.75 (dd, J = 4.0, 2.2 Hz, 2H), 3.60 (d, J = 1.8 Hz, 2H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 173.9, 145.4, 137.4, 134.4, 128.9, 128.8, 126.8, 70.2, 31.8; HRMS (ESI+, m/z): calcd. for $C_{11}H_{11}O_2$ $[M + H]^+$: 175.0759, found 175.0765.

*Vinyl 2-Phenyl-5-hexenoate (**2n**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 89% yield (80 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.18 (m, 5H), 7.16 (dd, J = 10.0, 3.9 Hz, 1H), 5.75−5.65 (m, 1H), 4.95-4.76 (m, 2H), 4.78 (dd, J = 14.0, 1.6 Hz, 1H), 4.47 (dd, J = 6.3, 1.6 Hz, 1H), 3.55 (t, J = 7.6 Hz, 1H), 2.18-2.09 (m, 1H), 1.96 (dd, J = 14.3, 6.9 Hz, 2H), 1.87−1.76 (m, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 171.0, 141.3, 138.1, 137.3, 128.7, 128.0, 127.5, 115.6, 97.9, 50.5, 32.3, 31.4; HRMS (EI+, m/z): calcd. for $C_{14}H_{16}O_2$ $[M]^+$: 216.1150, found 216.1157.

*Vinyl Oleate (**2o**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 87% yield (107 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, J = 13.9, 6.2 Hz, 1H), 5.31−5.22 (m, 2H), 4.80 (dd, J = 13.9, 1.6 Hz, 1H), 4.48 (dd, J = 6.3, 1.6 Hz, 1H), 2.31 (t, J = 7.5 Hz, 2H), 1.94 (q, J = 6.5 Hz, 4H), 1.59 (t, J = 7.2 Hz, 2H), 1.29−1.19 (m, 20H), 0.81 (t, J = 6.8 Hz, 3H).; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 170.8, 141.2, 130.0, 129.7, 97.4, 33.9, 31.9, 29.8, 29.7, 29.5, 29.3, 29.1, 29.1, 29.0, 27.2, 27.1, 24.6, 22.7, 14.1. ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[60]

*1,4-Diacetoxybut-2-ene (**6**).* The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 75% yield (51.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79 (dt, J = 3.0, 1.7 Hz, 2H), 4.56−4.45 (m, 4H), 2.01 (s, 6H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 170.6, 128.0, 63.8, 20.8. ^{1}H and ^{13}C NMR data were in accordance with those reported in the literature.[61]

Larger-Scale Tandem Transvinylation/RCM Reaction. To a solution of 3-phenyl-4-pentenoic acid (**1f**) (1.5 mmol) and vinyl propionate (3 mmol) in an anhydrous toluene (150 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 80 °C for 16 h. The reaction mixture was cooled to room temperature and filtered over a Celite pad. The excess of solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate): vinyl 3-phenyl-4-pentenoate (**2f**) was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 52% yield (157 mg); 4-phenyl-3,4-dihydro-2H-pyran-2-one (**3f**) was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 33% yield (86 mg).

Studies on Catalyst Activity: Reaction A. To a solution of phenylacetic acid (**1a**) (0.1 mmol) and vinyl propionate (0.2 mmol) in an anhydrous toluene (10 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 80 °C for 2 h (upon the completion of transvinylation step). Then, vinyl-3-phenyl-4-pentenoate (**2f**) (0.1 mmol) was added. The progress of the reaction was monitored on high-performance liquid chromatography (HPLC; Kromasil SI 60/5 μm column); hexane/isopropanol (98:2), λ = 216 nm; 0.5 mL/min, retention time (in min): t**2a** = 4.8, t**2f** = 5.1, t**3f** =11.3. Reaction B: To a solution of a phenylacetic acid (**1a**) (0.1 mmol) and vinyl propionate (0.2 mmol) in an anhydrous toluene (10 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 80 °C for 2 h (upon the completion of transvinylation step). Then, vinyl-3-phenyl-4-pentenoate (0.1 mmol) and a certain amount of Grubbs second-generation catalyst (5 mol %) were added. The progress of the reaction was monitored on HPLC (Kromasil SI 60/5 μm column); hexane/isopropanol (98:2), λ = 216 nm; 0.5 mL/min, retention time (in min): t**2a** = 4.8, t**2f** = 5.1, t**3f** =11.3. Reaction C: To a solution of vinyl 3-phenyl-4-pentenoate (0.1 mmol) in an anhydrous toluene (10 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 80 °C for 2 h. The progress of the reaction was monitored on HPLC (Kromasil SI 60/5 μm column); hexane/isopropanol (98:2), λ = 216 nm; 0.5 mL/min, retention time (in min): t**2f** = 5.1, t**3f** =11.3.

Mechanistic Studies on the Tandem Transvinylation/RCM Reaction. To a solution of 3-phenyl-4-pentenoic acid (**1f**) (0.15 mmol) and vinyl-$^{13}C_2$ acetate (0.3 mmol) in an anhydrous toluene (5 mL) under argon atmosphere was added Grubbs second-generation catalyst (5 mol %). The reaction mixture was heated in an oil bath at 60 °C for 16 h. The reaction mixture was cooled to room temperature and filtered over a Celite pad. The excess of solvent was removed under reduced pressure. The products were purified by column chromatography on silica gel (hexanes/ethyl acetate).

Vinyl-$^{13}C_2$ 3-phenyl-4-pentenoate. The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:10) in 40% yield (12 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (ddd, J = 14.0, 9.6, 6.3 Hz, 0.5H), 7.29−7.20 (m, 2H), 7.20−7.10 (m, 3H), 6.89 (ddd, J = 14.0, 9.6, 6.3 Hz, 0.5), 6.00−5.84 (m, 1H), 5.06−4.99 (m, 2H), 4.97 (ddd, J = 14.0, 8.2, 1.7 Hz, 0.5H), 4.67 (ddd, J = 7.8, 6.3, 1.6 Hz, 0.5H), 4.58 (ddd, J = 14.0, 8.2, 1.7 Hz, 0.5H), 4.26 (ddd, J = 7.8, 6.3, 1.6 Hz, 0.5H), 3.83 (q, J = 7.4 Hz, 1H), 2.83−2.66 (m, 2H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 168.9, 142.1, 141.5 (^{13}C-labeled, J = 82.2 Hz), 139.9, 128.7, 127.5, 126.8, 115.1, 97.8 (^{13}C-labeled, J = 82.2 Hz), 45.3, 39.9. HRMS (EI+, m/z): calcd. for $C_{11}{}^{13}C_2H_{14}O_2$ $[M]^+$: 204.1061, found 204.1059.

4-Phenyl(6-^{13}C)-3,4-dihydro-2H-pyran-2-one. The product was isolated as a colorless oil from a silica column eluted by EtOAc/hexanes (1:9) in 17% yield (5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.23 (m, 3H), 7.24−7.12 (m, 2H), 6.86 (dd, J = 6.0, 1.8 Hz, 0.5H) 6.36 (dd, J = 6.0, 1.8 Hz, 0.5H), 5.37 (ddd, J = 8.4, 6.0, 4.0 Hz, 1H), 3.80−3.69 (m, 1H), 2.91 (dd, J = 15.9, 6.5 Hz, 1H), 2.67 (dd, J = 16.0, 8.3 Hz, 1H).; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 167.3, 141.6 (^{13}C-labeled), 141.2, 129.1, 127.5, 126.8, 109.4, 37.1, 36.8. HRMS (EI+, m/z): calcd. for $C_{10}{}^{13}CH_{10}O_2$ $[M]^+$: 175.0714, found 175.0718.

Mechanistic Studies on the Transvinylation Reaction: Complex 1. Complex 1 was prepared according to the literature method.[49] To a stirred solution of Grubbs second-generation catalyst (0.05 mmol) in toluene (5 mL) was added excess vinyl acetate (1.02 mmol, 20.4 equiv). The solution was stirred for 1 h, over which time the color changed from purple to orange. Then, the excess of vinyl acetate was distilled off and a solution of phenylactetic acid **1a** (0.1 mmol) in toluene (5 mL) was added. The reaction mixture was heated in an oil bath at 80 °C for 2 h. The reaction mixture was cooled to room temperature and filtered over a Celite pad. The excess of solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate) to give vinyl 2-phenylacetate (2a) in 85% yield.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02135.

Studies on catalyst activity—conversion, reaction rate, and TON calculation; ^{1}H NMR and ^{13}C NMR spectra of all products; standard curves for compounds **2f** and **3f**; progress of reactions A, B, and C; calculation of initial rates of RCM reactions; and calculation of TON (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Anna Brodzka − *Institute of Organic Chemistry Polish Academy of Sciences, 01-224 Warszawa, Poland;* orcid.org/0000-0002-6659-0758; Email: anna.brodzka@icho.edu.pl

Ryszard Ostaszewski − *Institute of Organic Chemistry Polish Academy of Sciences, 01-224 Warszawa, Poland;* orcid.org/0000-0002-3032-196X; Email: ryszard.ostaszewski@icho.edu.pl

Author

Dominik Koszelewski − *Institute of Organic Chemistry Polish Academy of Sciences, 01-224 Warszawa, Poland*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c02135

Author Contributions

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Notes

The authors declare no competing financial interest.

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