Ruthenium-Catalyzed Transformations of Cyclopropylethynes[1]

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Abstract: The addition of various carboxylic acids to (*trans*-2-ethoxycyclopropyl)ethyne (**1**) by catalysis with $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ proceeds regioselectively in the Markovnikov sense with ring opening of the cyclopropyl group to furnish allenylacetaldehyde acyl ethyl acetals **3** in high yields (44–96%, 11 examples). The allenylacetaldehyde derivatives undergo palladium-catalyzed Heck-type cross coupling with iodobenzene and subsequent trapping of the π-allylpalladium intermediate with primary and secondary amines to yield labile [β-(1-aminomethyl)styryl]acetaldehyde acyl ethyl acetals **12** (24–83%, 4 examples). Anti-Markovnikov addition of carboxylic acids to the triple bond in (*trans*-2-ethoxycyclopropyl)ethyne (**1**) without ring opening can be brought about under $[Ru(CH_2CMeCH_2)_2(dppb)]$ catalysis to give 2-(*trans*-2-ethoxycyclopropyl)ethenyl esters **13** (69–92%, 3 examples). (1-Hydroxycyclopropyl)ethyne (**14**), under catalysis by $[Ru(O_2CH)(CO)_2(PPh_3)]_2$, reacts with carboxylic acids to yield 1-acetylcyclopropyl esters **15** (49–74%, 4 examples) by Markovnikov-sense addition and intramolecular transesterification. Anti-Markovnikov- and Markovnikov-sense addition of carboxylic acids to unsubstituted cyclopropylethyne can both be achieved regioselectively under catalysis with $[Ru(CH_2CMeCH_2)_2(dppb)]$ and $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ to furnish 2-cyclopropylethenyl esters **23** (68–98%, 6 examples) and 1-cyclopropylethenyl esters **24** (66–97%, 5 examples), respectively.

Key words: acetylenes, cyclopropanes, allenes, ruthenium catalysis, palladium catalysis

Modern 'acetylene chemistry' has much to do with transition-metal-mediated and -catalyzed transformations.[2] Among the various catalysts employed, relatively simple ruthenium complexes[3] play a pivotal role. Some of their reactions proceed via vinylideneruthenium intermediates[4] with oxidative coupling or cycloisomerization.[5] Particularly interesting reactions are those that take place with skeletal rearrangements accompanied by C–C bond breaking and forming, such as additions to disubstituted alkynes,[6] enyne metatheses,[7] or reorganizations.[8] Ethynylcyclopropane and its derivatives constitute versatile oligofunctional building blocks that have both enhanced reactivity across their triple bond as well as their three-membered ring.[9–11] In fact, activation of their triple bond and, as a result, their cyclopropyl group, with electrophilic metals has been found to be a versatile reaction principle.[11]

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Among the various ruthenium complexes that were found to catalyze additions of carboxylic acids to alkynes,[12] $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**) promotes the regioselective addition of carboxylic acids to terminal alkynes according to the Markovnikov rule.[12a–e] Treatment of the readily available (5 steps, up to 52% overall yield)[13] racemic (*trans*-2-ethoxycyclopropyl)ethyne (**1**) with an equimolar amount of acetic acid (**2b**) in the presence of 0.4 mol% of the ruthenium catalyst **A** gave, after three hours at 75 °C, 1-ethoxypenta-3,4-dienyl acetate (**3b**) in 96% isolated yield as the sole product (Table 1).[14]

Under similar conditions, the reactions of pentanoic acid (**2c**), undec-10-enoic acid (**2d**), and cyclopropanecarboxylic acid (**2e**) gave the corresponding allenylacetaldehyde acyl ethyl acetals **3c–e** in 84%, 92%, and 93% yields, respectively. The treatment of **1** with formic acid (**2a**) in benzene-d_6 (70 °C, 2 h) also led exclusively to the allene **3a**, as identified by its ^1H and ^{13}C NMR spectra, however, isolation of **3a** failed, mainly because of its low boiling point. The addition of succinic acid (**2f**) to **1** gave the bisallenyl bisacetal **3f** in moderate yield (44%), when carried out in dichloromethane.

Carboxylic acids with more sterically demanding groups such as pivalic acid (**2g**), benzoic acid (**2h**), 5-methylthiophene-2-carboxylic acid (**2i**), 2-iodobenzoic acid (**2j**), and 2-acetylbenzoic acid (**2k**) also reacted quantitatively with **1**, however, they each gave two products **3** and **4**. The main products were the allenes **3g–k** (50–68%, Table 1), which could be separated by chromatography on silica gel from the 1-(*trans*-2-ethoxycyclopropyl)ethenyl esters **4g–k** (10–29%) formed as side products.

As is evident from these examples, the conditions are compatible with the presence of aryl halide, alkenyl double bond, carbonyl, and thiophene moieties in the carboxylic acid. With cyanoacetic acid, however, decomposition occurred,[15] and with hydroxyacetic acid no reaction was observed.

The choice of solvent and concentration was critical. Generally, the reactions were performed in benzene in a 0.7 M solution. Under these conditions, acetic acid (**2b**) gave the allene **3b** in 96% isolated yield. When run at a concentration of 6.1 M, the same reaction gave the enol ester **4b** in 8% yield along with **3b** in 84% yield. When toluene was employed instead of benzene, the yields were slightly lower (4% and 11%, respectively), yet the product ratios,

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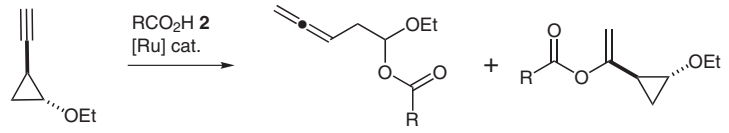
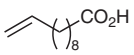
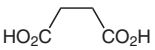
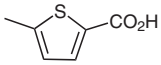
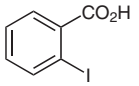
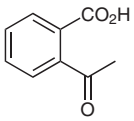
e.g. for **3h/4h**, remained virtually the same. For the reaction of succinic acid, the use of dichloromethane instead of benzene increased the yield from 10% to 44% due to better solubility.

In order to learn something about the mechanism of this reaction, some control experiments were performed. To rule out a simple acid catalysis, (*trans*-2-ethoxycyclopropyl)ethyne (**1**) was heated with pentanoic acid (**2c**) in the absence of the ruthenium complex. After 17 hours at 75 °C, only a trace of the product **3c** (<2%) could be observed by ^{1}H NMR. No reaction was observed when a solution of **1** and **2b** was treated with pyridinium *p*-toluenesulfonate (PPTS), or when the alkyne **1** was treated with the ruthenium complex without an added carboxylic acid. Silver(I) and mercury(II) salts are also known to catalyze the addition of nucleophilic reagents to triple bonds.[16] Indeed, addition of silver tetrafluoroborate to a solution of **1** and **2b** in benzene-d_6 resulted in complete conversion of the alkyne within 15 hours at 70 °C. However, only 30% of the allene **3b** was observed along with a complex mixture

Table 1 Ruthenium-Catalyzed Reaction of (*trans*-2-Ethoxycyclopropyl)ethyne (**1**) with Carboxylic Acids **2** To Yield 5-Acyloxy-5-ethoxypenta-1,2-dienes **3** and 1-(*trans*-2-Ethoxycyclopropyl)ethenyl Esters **4**[14]



1 **3** **4**

Carboxylic acid		Solvent	[Ru] cat.[a] (mol%)	Temp. (°C)	Time (h)	Yield[b] (%)	
2	RCO_2H					**3**	**4**
a	HCO_2H	C_6D_6	0.3	70	2	>95[c]	–
b	$MeCO_2H$	C_6H_6[d]	0.4	75	3	96	–
		C_6H_6[e]	1.0	70	12	84	8
c	$BuCO_2H$	C_6H_6	0.2	70	6	84	–
		toluene	1.4	80	14	80	–
		C_6D_6[f]	—	80	24	<2	–
d		C_6H_6	0.4	70	6	92	–
e	$cPrCO_2H$	C_6H_6	0.4	70	4	93	–
f		C_6H_6	0.4	70	15	10	–
		CH_2Cl_2	0.4	70	15	44	–
g	*t*-$BuCO_2H$	C_6H_6	0.4	70	6	62	29
h	$PhCO_2H$	C_6H_6	0.4	70	6	58	27
		toluene	1.0	80	18	50	24
i		C_6H_6	0.4	70	6	64	25
j		C_6H_6	0.4	70	6	68	18
k		C_6H_6	0.4	70	6	58	10

[a] [Ru] cat. = $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**).[12a]
[b] Isolated yield unless otherwise indicated.
[c] Yield according to ^{1}H NMR of the crude product.
[d] Concentration 0.73 molar.
[e] Concentration 6.1 molar.
[f] Control experiment without catalyst.

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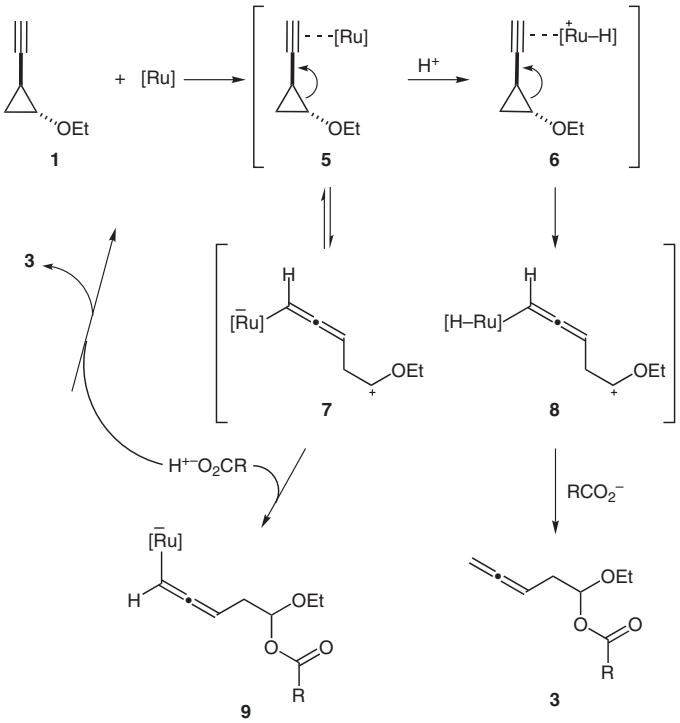
of decomposed material. Complete decomposition occurred under the influence of mercury(II) acetate.

The sequence of events that eventually leads to the allenes **3**, apparently starts with electrophilic attack of the ruthenium complex on the triple bond of **1** (Scheme 1). As a result of the complexation, the electron-withdrawing ability of the ethynyl group in the η^2-complex **5** is increased, and this may initiate ring opening of the donor-substituted cyclopropyl group leading to the zwitterionic σ-allenylruthenate intermediate **7**, the positive end of which is stabilized by the ethoxy group. Nucleophilic attack of a carboxylate ion on the electrophilic carbon furnishes the σ-allenylruthenium complex **9**, from which the allene **3** is formed by protiodemetalation. Alternatively, the ruthenium center in **5** can be protonated first to give the cationic η^2-alkyneruthenium complex **6**. Subsequent ring opening, followed by nucleophilic attack and reductive elimination would also form the allene **3**. The enol esters **4b**,**g**–**k** must be formed by direct nucleophilic attack of the respective carboxylate ion on the activated triple bond in **5** or **6**. Alternatively, the coordination of the triple bond is expected to increase the electrophilicity of the ethoxy-substituted cyclopropyl carbon atom in **5** and **6** and favor direct nucleophilic addition of the carboxylate to give **9** and **3**.

Allenes are known to be versatile starting materials for a wide range of applications.[17] The particular allenes **3** obtained by transformation of **1** with carboxylic acids contain a protected aldehyde functionality and thus have additional reactivity that should make them valuable building blocks for organic synthesis. To demonstrate just one type of further transformation, the allene **3b** was employed in a Heck-type coupling with iodobenzene (Table 2). Since allenes usually undergo carbopalladations regioselectively to yield π-allylpalladium intermediates that are trapped by added nucleophiles,[18] the palladium-catalyzed coupling of **3b** with iodobenzene was carried out in the presence of a primary or a secondary amine **11**. The employed catalyst system [$Pd(OAc)_2$, TFP, amine **11**] performed well with bulky *tert*-butylamine (**11a**) and dibenzylamine (**11d**) to furnish the 2-phenylallylamines **12ba** and **12bd** in 82% and 83% yield, respectively, but with cyclohexylamine (**11b**), and isobutylamine (**11c**) the yields of **12bb** and **12bc** were only 46% and 24%, respectively. Whereas all three primary amines selectively gave the *Z*-isomers of the highly functionalized styrene derivatives **12**, *N*,*N*-dibenzylallylamine **12bd** was a 1:1 mixture of the *E*- and *Z*-isomers. These allylamines cannot be stored for long periods, but must be rapidly transformed to more stable products.

As earlier work of Dixneuf et al. has shown,[12f–h] [$Ru(CH_2CMeCH_2)_2$(dppe)] (**B**) and [$Ru(CH_2CMeCH_2)_2$(dppb)] (**C**) catalyze the regioselective addition of carboxylic acids to terminal alkynes in the anti-Markovnikov sense to yield *Z*-configured alkenyl esters with high efficiency. Indeed, under similar conditions as used for the transformation to the allenes **3**, (*trans*-2-ethoxycyclopropyl)ethyne (**1**), in the presence of [$Ru(CH_2CMeCH_2)_2$(dppb)] (**C**) in benzene at 60 °C for 15 hours, reacted with pentanoic acid (**2c**) and benzoic acid (**2h**) to furnish (*Z*)-2-(*trans*-2-ethoxycyclopropyl)ethenyl esters **13c** and **13h** in 85% and 92% yield, respectively (Table 3). Thus, this ruthenium-catalyzed addition of the two acids occurred regio- as well as diastereoselectively



Scheme 1 Mechanistic rationalization of the formation 5-acyloxy-5-ethoxypenta-1,2-dienes **3a**–**k** from (*trans*-2-ethoxycyclopropyl)ethyne (**1**)

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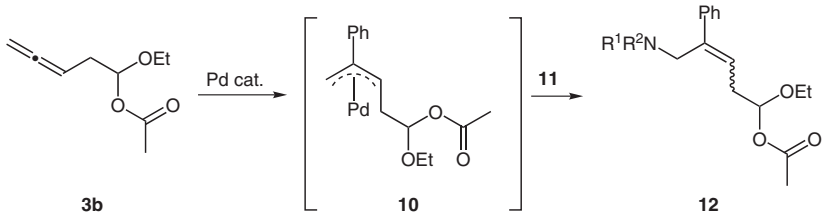
Table 2 Heck-Type Couplings of **3b** with Iodobenzene and Immediate Trapping of the Formed π-Allylpalladium Species by Primary and Secondary Amines **11**

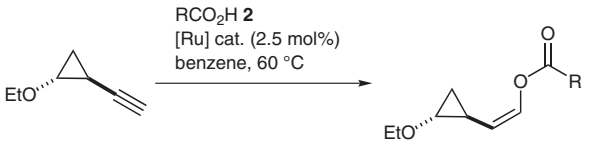


3b **10** **12**

Amine	NR^1R^2	Conditions[a]	Product	Yield (%)	Ratio *E*/*Z*
11a	NH*t*-Bu	55 °C, 45 min	**12ba**	82	>98:2
11b	NHCy	70 °C, 2 h	**12bb**	46	>98:2
11c	NH*i*-Bu	60 °C, 1 h	**12bc**	24	>98:2
11d	NBn_2	50 °C, 2 h then 75 °C, 1 h	**12bd**	83	1:1

[a] $Pd(OAc)_2$ (5 mol%), tri(2-furyl)phosphine (10 mol%), PhI (1 equiv), R^1R^2NH **11** (6–8 equiv), DMF.

Table 3 Anti-Markovnikov Addition of Carboxylic Acids **2** to (*trans*-2-Ethoxycyclopropyl)ethyne (**1**)



1 **13**

Carboxylic acid	R	Time (h)	Product	Yield (%)
2c	Bu	15	**13c**	85
2h	Ph	15	**13h**	92
2l	CH_2=CH	4.5	**13l**	69

[a] [Ru] cat. = $[Ru(CH_2CMeCH_2)_2(dppb)]$ (**C**).

without ring opening. Apparently, the activation of the ethynyl group by this ruthenium complex is such that the nucleophilic carboxylate can only attack at the alkyne terminus. The adduct **13l** of acrylic acid (**2l**) could also be obtained in 69% yield, but it decomposed within a few days even when stored at –15 °C.

The alkenyl esters **13** with their masked acetaldehyde functionality attached to a cyclopropyl ether moiety, represent multifunctional building blocks, which are potentially valuable for organic synthesis.[19] In view of these results it appeared to be worthwhile also to evaluate additions of carboxylic acids to 1-ethynylcyclopropanol (**14**), a differently substituted ethynylcyclopropane, which is also easily available in four steps from ethyl 3-chloropropanoate via cyclopropanone ethyl hemiacetal[20] and 1-(trimethylsilylethynyl)cyclopropanol in 54% overall yield.[21]

Upon reaction with several carboxylic acids (pentanoic, cyclopropanecarboxylic, benzoic, methoxyacetic, and salicylic acid) in the presence of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**), 1-ethynylcyclopropanol (**14**) gave 1-acetoxycyclopropyl esters **15c**,**e**,**h**,**m**,**n** in 28–74% yield (Table 4).

Just like the addition of carboxylic acids to **1** catalyzed by **A**, that of **14** occurs regioselectively according to Markovnikov's rule to yield an intermediate enol ester **17**, which experiences an intramolecular transesterification to give the cyclopropyl ester **18**.[22] The latter finally tautomerizes to the corresponding ketone **15** after reductive elimination.

This new access to 1-acetylcyclopropyl esters **15** is superior to the previously published synthesis by Conia et al.[23] A preparation of tetrahydropyranyl ethers of 1-acylcyclopropanols has been reported by Salaün et al.[24]

Since the dppe ligand in the ruthenium complex $[Ru(CH_2CMeCH_2)_2(dppe)]$ (**B**) has a smaller bite angle than the dppb ligand in complex **C** used above, it also usually shows different catalytic properties.[12f–i] When a mixture of (1-hydroxycyclopropyl)ethyne (**14**) and benzoic acid (**2h**) was treated with the ruthenium complex $[Ru(CH_2CMeCH_2)_2(dppe)]$ (**B**) (1.5 mol%), a mixture of two products **15h** and **19h** (ratio 1:2.6) was isolated in 36% yield. The main product **19h**, in this case, apparently is the result of the addition of benzoic acid to the triple bond of **14** in the anti-Markovnikov sense with subsequent or concomitant opening of the cyclopropyloxy to an ethyl ketone moiety. Such ring openings are known to occur easily under acid or base catalysis. The ring opening in this case might actually occur at the stage of the ruthenium-activated alkyne as depicted in **20** or **21** before the carboxylate ion attacks (Scheme 2).

Regioselective addition of carboxylic acids **2** to unsubstituted cyclopropylethyne (**22**)[25] in both the Markovnikov as well as the anti-Markovnikov sense without ring opening could be achieved by ruthenium catalysis. Thus treatment of **22** with pentanoic acid (**2c**) in the presence of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**) at 80 °C for seven hours gave the 1-cyclopropylethenyl ester **24c** in 66% yield. Cyclopropanecarboxylic acid (**2e**) and bulky pivalic acid (**2g**), after 15 hours at 80 °C, yielded the corresponding enol esters **24e** and **24g** (82% and 76%, respectively,

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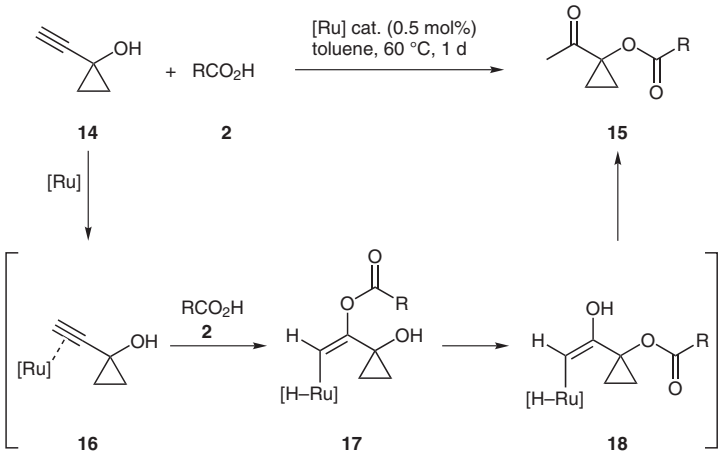
Table 4 Ruthenium-Catalyzed Additions of Various Carboxylic Acids **2** to 1-Ethynylcyclopropanol (**14**)[a]



Carboxylic acid	R	Time (h)	Product	Yield (%)
2c	Bu	18.5	**15c**	68
2e	cyclopropyl	18	**15e**	49
2h	Ph	16.5	**15h**	74
2m	$MeOCH_2$	17.5	**15m**	55
2n	2-HOC_6H_4	20	**15n**	28

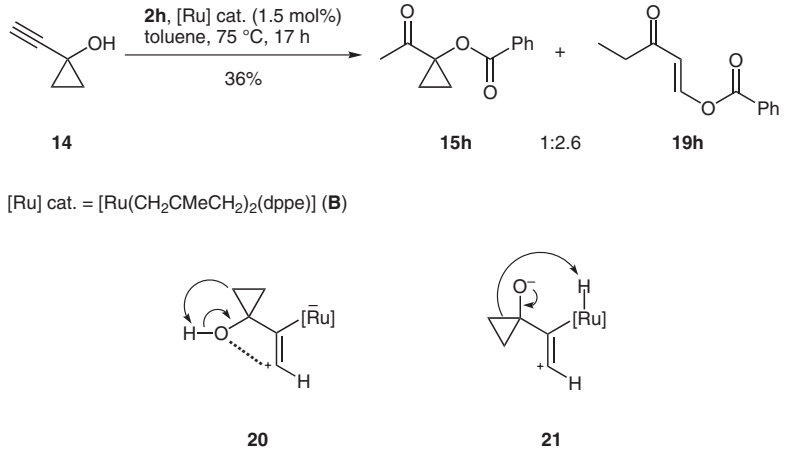
[a] [Ru] cat. = $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**).

Table 5, entries 2 and 3). For the addition of benzoic acid (**2h**) to occur quantitatively, the reaction mixture had to be heated to 80 °C for 40 hours (entries 4 and 5).

The addition of benzoic acid (**2h**) to **22** in the presence of the [1,4-bis(diphenylphosphino)butane]ruthenium complex **C** occurred in the anti-Markovnikov sense and gave the enol ester **23h** in 98% yield, when an equimolar solution of both substrates was heated at 70 °C for six hours; no reaction was observed at 20 °C for 15 hours (Table 5, entries 8 and 9). When both substrates are liquid, the reaction may be performed without solvent. Thus, treatment of **22** with pentanoic acid (**2c**) at 65 °C in the presence of **C** (1 mol%) for 15 hours gave the enol ester **23c** in almost quantitative yield (entry 7). The additions of the substituted benzoic acids **2o**,**p**,**q** were carried out in toluene solutions and provided the corresponding *cis*-2-substituted ethenyl esters in good to excellent yields (98%, 97%, and 68% respectively, entries 12–14).

Surprisingly, methoxyacetic acid (**2m**) reacted with **22** at 80 °C to yield a 2:1 mixture of **23m** and **24m**. At 55 °C, however, only **23m** was formed in 92% yield in four hours (entries 10 and 11). In contrast, acetic acid (**2b**) upon addition to **22** in the presence of the same catalyst **C** yielded exclusively the 1-cyclopropylethenyl acetate **24b** even at 50 °C (entry 6).[26]

With the (*p*-cymene)ruthenium complex **D**, which is known to favor the Markovnikov-sense addition,[12a–c,27]



Scheme 2

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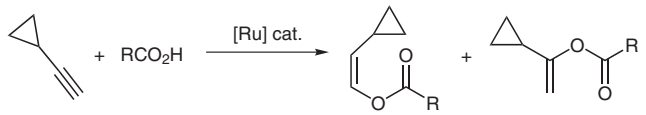
Table 5 Ruthenium-Catalyzed Additions of Carboxylic Acids **2** to Cyclopropylethyne **22**



22 **2** **23** **24**

Entry	**2**	R	[Ru] cat.[a] (mol%)	Temp. (°C)	Time (h)	Solvent	Yield (%)	
							23	**24**
1	**c**	Bu	**A** (0.5)	80	7	toluene	–	66
2	**e**	cyclopropyl	**A** (0.5)	80	15	toluene	–	82
3	**g**	*t*-Bu	**A** (0.5)	80	15	toluene	–	76
4	**h**	Ph	**A** (0.5)	80	7	toluene	–	61
5	**h**	Ph	**A** (0.5)	80	44	toluene	–	97
6	**b**	Me	**C** (0.3)	50	12	neat	–	94
7	**c**	Bu	**C** (1.0)	65	15	neat	97	–
8	**h**	Ph	**C** (1.0)	20	15	toluene	–	–
9	**h**	Ph	**C** (1.0)	70	6	toluene	98	–
10	**m**	CH_2OMe	**C** (1.0)	80	15	neat	(2)[b]	(1)[b]
11	**m**	CH_2OMe	**C** (1.0)	55	4	neat	92	–
12	**o**	2,6-$F_2C_6H_3$	**C** (1.0)	80	21	toluene	98	–
13	**p**	2,6-$(MeO)_2C_6H_3$	**C** (1.0)	80	18	toluene	97	–
14	**q**	4-$H_2NC_6H_4$	**C** (2.0)	80	21	toluene	68	–
15	**h**	Ph	**D** (10)	50	42	toluene	65 (1:7)	
16	**h**	Ph	**D** (10)	80	39	toluene	59 (1:6)	

[a] [Ru] cat: **A**: $[Ru(O_2CH)(CO)_2(PPh_3)]_2$. **C**: $[Ru(CH_2CMeCH_2)_2(dppb)]$. **D**: $[RuCl_2(p\text{-cymene})(PPh_3)]$.
[b] The yield was not determined, as the ^1H NMR spectrum indicated the formation of a mixture of the two products in the ratio of 2:1.

benzoic acid (**2h**) reacted with **22** to give inseparable mixtures of both regioisomers **23h** and **24h** in ratios ranging from 1:6 to 1:7 at 80 and 50 °C, respectively (entries 16 and 15).

Ruthenium-complex-catalyzed additions of carboxylic acids to cyclopropylethynes can be brought about in the Markovnikov as well as the anti-Markovnikov sense to give 1- and 2-cyclopropylethenyl esters, respectively, in high yields. (*trans*-2-Ethoxycyclopropyl)ethyne, in the presence of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ regioselectively adds carboxylic acids with ring opening to furnish allenylacetaldehyde acyl ethyl acetals.

^1H NMR: Varian VXR-300 (300 MHz), Bruker AM 250 (250 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to $CHCl_3$ (δ = 7.26) or benzene (δ = 7.20) as internal references. ^{13}C NMR Varian VXR-300 (75.5 MHz), Bruker AW 250 (62.9 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to $CHCl_3$ (δ = 77.0) or benzene (δ = 128); the multiplicities of the signals were determined by APT (Varian, Attached Proton Test) and DEPT (Bruker, Distortionless Enhancement of Polarization Transfer) techniques and are quoted as (+) for CH_3 and CH groups, (–) for CH_2 groups and (C_q) for quaternary carbon atoms. IR: Bruker IFS 66. LR-MS (EI): Finnigan MAT 95, ionizing voltage 70 eV. HRMS: Finnigan MAT 95; employing preselected ion peak matching, all HRMS results were satisfactory in comparison to the calculated accurate mass of the molecular ion (+/-2 ppm, R ~10000); for this reason, only calculated values are stated. Elemental analyses: Mikroanalytisches Labor des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen, Germany. Melting points are uncorrected. Solvents for extraction and chromatography were of technical grade and distilled before use. Flash chromatography (FC) was performed using Merck Kieselgel 60 (200–400 mesh). Alumina (ICN Alumina N, Super I) was obtained from ICN Biomedicals. Unless otherwise specified, alumina was deactivated with 5% H_2O. TLC analyses were performed using Machery–Nagel precoated plates, 0.25 mm, Alugram Sil G/UV_{254} (I) and Merck precoated silica gel 60 F_{254} aluminum sheets (II). All reactions were carried out under an atmosphere of dry N_2 or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solns of NH_4Cl, NaCl, Na_2SO_3, and $NaHCO_3$ were sat. aq solns. Benzene, decalin, toluene, THF, and Et_2O were distilled from Na/benzophenone. CH_2Cl_2 was distilled from CaH_2.

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Carboxylic Acid 1-Ethoxypenta-3,4-dienyl Esters 3a–k and 1-(2-Ethoxycyclopropyl)ethenyl Esters 4b,g–k; General Procedure

A small screw-capped Pyrex bottle was charged with (*trans*-2-ethoxycyclopropyl)ethyne (**1**, 1 equiv), carboxylic acid **2** (1 equiv), and $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**, 0.2–0.4 mol%, based on **1**) in degassed anhyd benzene (ca. 1 mL/mmol), and the sealed vessel was heated at 70–75 °C (3–15 h). After cooling to r.t., the solvent was evaporated under reduced pressure, and the products were separated by column chromatography (silica gel).

1-Ethoxypenta-3,4-dienyl Formate (3a)

A mixture of **1** (80.0 mg, 726 μmol), formic acid (**2a**, 33.4 mg, 726 μmol), and ruthenium catalyst **A** (2.0 mg, 0.3 mol%) in benzene-d_6 (0.5 mL) in an NMR tube was heated at 70 °C for 2 h. The ^{1}H NMR spectrum indicated quantitative conversion of **1** into **3a** with traces of impurities only. An attempted separation of **3a** from the benzene solvent failed due to the similar boiling points.

^{1}H NMR (250 MHz, C_6D_6): δ = 0.95 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.34 (m_c, 2 H, H2), 3.19–3.31 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.44–3.54 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.54 (m_c, 2 H, H5), 5.02 (m_c, 1 H, H3), 5.88 (t, ^3J = 5.4 Hz, 1 H, H1), 7.68 (s, 1 H, HCOO).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 14.94 (+, OCH_2CH_3), 34.26 (–, C2), 65.12 (–, OCH_2CH_3), 75.12 (–, C5), 84.28 (+, C3), 97.30 (+, C1), 160.37 (+, C=O), 209.98 (C_q, C4).

1-Ethoxypenta-3,4-dienyl Acetate (3b) and 1-(2-Ethoxycyclopropyl)ethenyl Acetate (4b)

Experiment I: Using **1** (80.0 mg, 726 μmol), AcOH (**2b**, 43.6 mg, 726 μmol), and **A** (2.6 mg, 0.4 mol%) in benzene (1 mL) and heating at 75 °C for 3 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **3b** (119 mg, 96%) as a colorless oil; R_f = 0.42 (PE–Et_2O, 9:1). Compound **4b** was not observed.

Experiment II: Using **1** (4.00 g, 36.3 mmol), AcOH (**2b**, 2.18 g, 36.3 mmol), and **A** (326 mg, 1 mol%) in benzene (6 mL) and heating at 70 °C for 12 h; chromatography (silica gel, PE–Et_2O, 20:1 to 5:1) gave **3b** (5.22 g, 84%) and **4b** (512 mg, 8%) as colorless oils.

3b

R_f = 0.65 (PE–Et_2O, 9:1).

IR (neat): 1959 (C=C=C), 1742 cm^{-1} (C=O).

^{1}H NMR (250 MHz, C_6D_6): δ = 0.99 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.69 (s, 3 H, CH_3COO), 2.38 (m_c, 2 H, H2), 3.31–3.38 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.53–3.62 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.55 (m_c, 2 H, H5), 5.06 (m_c, 1 H, H3), 5.92 (t, ^3J = 5.4 Hz, 1 H, H1).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.13 (+, OCH_2CH_3), 20.66 (+, CH_3COO), 34.43 (–, C2), 64.99 (–, OCH_2CH_3), 74.96 (–, C5), 84.63 (+, C3), 97.45 (+, C1), 170.08 (C_q, C=O), 209.98 (C_q, C4).

MS (70 eV): *m*/*z* (%) = 170 (2) [M$^+$], 141 (23) [M$^+$ – C_2H_5], 117 (30) [M$^+$ – CH_2=C=$CHCH_2$], 111 (29) [M$^+$ – CH_3COO], 83 (26), 81 (28), 53 (15) [CH_2=C=$CHCH_2^+$], 43 (100) [CH_3CO^+].

HRMS: calcd for $C_9H_{14}O_3$: 170.0942.

Anal. Calcd for $C_9H_{14}O_3$ (170.2): C, 63.51; H, 8.29. Found: C, 63.55; H, 8.15.

4b

(R_f = 0.20 in PE–Et_2O, 9:1).

IR (neat): 1759 (C=O), 1662 cm^{-1} (C=C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81–0.91 (m, 2 H, H3′), 1.09 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.45 (m_c, 1 H, H1′), 2.07 (s, 3 H, CH_3COO), 3.28 (m_c, 1 H, H2′), 3.44 (m_c, 2 H, OCH_2CH_3), 4.73–4.74 (m, 2 H, H2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 11.26 (–, C3′), 14.78 (+, OCH_2CH_3), 20.13 (+, CH_3COO), 20.82 (+, C–1′), 57.12 (+, C2′), 66.11 (–, OCH_2CH_3), 101.72 (–, C2), 152.07 (C_q, C1), 168.84 (C_q, C=O).

MS (70 eV): *m*/*z* (%) = 170 (2) [M$^+$], 128 (33) [M$^+$ – CH_3CO], 81 (42), 43 (100) [CH_3CO^+].

MS (DCI, NH_3, 70 eV): *m*/*z* (%) = 171 (28) [M + H$^+$], 188 (100) [M + NH_4^+].

1-Ethoxypenta-3,4-dienyl Pentanoate (3c)

Using **1** (80.0 mg, 726 μmol), pentanoic acid (**2c**, 74.2 mg, 726 μmol), and **A** (1.3 mg, 0.2 mol%) in benzene (0.5 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **3c** (130 mg, 84%) as a colorless oil; R_f = 0.48 (PE–Et_2O, 9:1).

IR (neat): 1959 (C=C=C), 1738 cm^{-1} (C=O).

^{1}H NMR (250 MHz, C_6D_6): δ = 0.75 (t, ^3J = 7.3 Hz, 3 H, H5), 1.02 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.16 (quint, ^3J = 7.3 Hz, 2 H, H4), 1.50 (quint, ^3J = 7.3 Hz, 2 H, H3), 2.12 (t, ^3J = 7.3 Hz, 2 H, H2), 2.45 (m_c, 2 H, H2′), 3.33–3.45 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.59–3.71 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.56 (m_c, 2 H, H5′), 5.12 (m_c, 1 H, H3′), 6.02 (t, ^3J = 5.4 Hz, 1 H, H1′).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 13.79 (+, C5), 15.17 (+, OCH_2CH_3), 22.44 (–, C4), 27.19 (–, C3), 34.25, 34.59 (–, C2, C2′), 65.00 (–, OCH_2CH_3), 74.97 (–, C5′), 84.71 (+, C3′), 97.32 (+, C1′), 172.92 (C_q, C1), 210.02 (C_q, C4′).

MS (70 eV): *m*/*z* (%) = 212 (1) [M$^+$], 183 (5) [M$^+$ – C_2H_5], 159 (6) [M$^+$ – CH_2=C=$CHCH_2$], 111 (53) [M$^+$ – C_4H_9COO], 85 (100) [$C_4H_9CO^+$], 57 (43) [$C_4H_9^+$].

HRMS: calcd for $C_{12}H_{20}O_3$: 212.1412.

Anal. Calcd for $C_{12}H_{20}O_3$ (212.3): C, 67.89; H, 9.50. Found: C, 68.11; H, 9.64.

1-Ethoxypenta-3,4-dienyl Undec-10-enoate (3d)

Using **1** (80.0 mg, 726 μmol), undec-10-enoic acid (**2d**, 134 mg, 726 μmol), and **A** (2.6 mg, 0.4 mol%) in benzene (2 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **3d** (197 mg, 92%) as a colorless oil; R_f = 0.56 (PE–Et_2O, 9:1).

IR (neat): 1958 (C=C=C), 1735 (C=O), 995 (C=C), 911 cm^{-1} (C=C).

^{1}H NMR (250 MHz, C_6D_6): δ = 1.03 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.05–1.40 (m, 10 H, H4, H5, H6, H7, H8), 1.55 (m_c, 2 H, H3), 1.96 (m_c, 2 H, H9), 2.15 (t, ^3J = 7.1 Hz, 2 H, H2), 2.44 (m_c, 2 H, H2′), 3.40–3.48 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.62–3.70 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.58 (m_c, 2 H, H5′), 5.06 (m_c, 3 H, 2 H11, H3′), 5.77 (m_c, 1 H, H10), 6.00 (t, ^3J = 5.4 Hz, 1 H, H1′).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.02 (+, OCH_2CH_3), 25.18, 29.23, 29.37 (2 C), 29.54, 29.63 (–, C3, C4, C5, C6, C7, C8), 34.15, 34.56, 34.59 (–, C2, C2′, C9), 65.00 (–, OCH_2CH_3), 74.98 (–, C5′), 84.71 (+, C3′), 97.33 (+, C1′), 114.50 (–, C11), 139.16 (+, C10), 172.93 (C_q, C1), 210.03 (C_q, C4′).

MS (70 eV): *m*/*z* (%) = 294 (1) [M$^+$], 265 (3) [M$^+$ – C_2H_5], 251 (2) [M$^+$ – C_2H_5 – CH_2], 167 (23) [$C_{10}H_{19}CO^+$], 149 (39), 128 (30), 111 (100) [M$^+$ – $C_{10}H_{19}COO$], 81 (44), 67 (31), 55 (69) [CH_2=$CHCH_2CH_2^+$], 41 (34) [CH_2=$CHCH_2^+$].

HRMS: calcd for $C_{18}H_{30}O_3$: 294.2194.

Anal. Calcd for $C_{18}H_{30}O_3$ (294.4): C, 73.43; H, 10.27. Found: C, 73.60; H, 10.39.

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1-Ethoxypenta-3,4-dienyl Cyclopropanecarboxylate (3e)

Using **1** (80.0 mg, 726 μmol), cyclopropanecarboxylic acid (**2e**, 62.5 mg, 726 μmol), and **A** (2.6 mg, 0.4 mol%) in benzene (0.5 mL) and heating at 70 °C for 4 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **3e** (132 mg, 93%) as a colorless oil; R_f = 0.46 (PE–Et_2O, 9:1).

IR (neat): 1959 (C=C=C), 1728 cm^{-1} (C=O).

^1H NMR (250 MHz, C_6D_6): δ = 0.39–0.47 (m, 2 H, cPr-H), 0.84–1.05 (m, 5 H, cPr-H, OCH_2CH_3), 1.40 (m_c, 1 H, cPr-H), 2.41 (m_c, 2 H, H2), 3.32–3.42 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.56–3.66 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.55 (m_c, 2 H, H5), 5.08 (m_c, 1 H, H3), 5.97 (t, ^3J = 5.4 Hz, 1 H, H1).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 8.38 (–, 2 C, cPr-C), 13.11 (+, cPr-C), 15.16 (+, OCH_2CH_3), 34.53 (–, C2), 64.99 (–, OCH_2CH_3), 74.96 (–, C5), 84.65 (+, C3), 97.45 (+, C1), 174.19 (C_q, C=O), 210.01 (C_q, C4).

MS (70 eV): *m*/*z* (%) = 196 (1) [M^+], 167 (3) [$M^+ - C_2H_5$], 111 (53) [$M^+ - C_3H_5COO$], 83 (51), 81 (43), 69 (100) [$C_3H_5CO^+$].

HRMS: calcd for $C_{11}H_{16}O_3$: 196.1099.

Anal. Calcd for $C_{11}H_{16}O_3$ (196.3): C, 67.32; H, 8.22. Found: C, 67.50; H, 8.48.

Bis(1-ethoxypenta-3,4-dienyl) Succinate (3f)

Using **1** (120 mg, 1.09 mmol), succinic acid (**2f**, 129 mg, 1.09 mmol), and **A** (3.9 mg, 0.4 mol%) in CH_2Cl_2 (20 mL) and heating at 70 °C for 15 h; chromatography (silica gel, PE–Et_2O, 4:1) gave **3f** (82 mg, 44%) as a colorless oil; R_f = 0.55 (PE–Et_2O, 4:1).

IR (neat): 1958 (C=C=C), 1735 cm^{-1} (C=O).

^1H NMR (250 MHz, C_6D_6): δ = 1.02 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 2.12–2.44 (m, 8 H, CH_2CH_2, H2), 3.56 (AB system, m_c, 4 H, OCH_2CH_3), 4.57 (dt, ^4J = 7.0 Hz, ^5J = 2.8 Hz, 4 H, H5), 5.11 (tt, ^3J = ^4J = 7.0 Hz, 2 H, H3), 6.00 (t, ^3J = 5.4 Hz, 2 H, H1).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.11 (+, 2 C, OCH_2CH_3), 29.08 (–, 2 C, CH_2CH_2), 34.46 (–, 2 C, C2), 65.06, 65.09 (–, OCH_2CH_3), 75.06 (–, 2 C, C5), 84.56 (+, 2 C, C3), 97.84, 97.87 (+, C1), 171.95 (C_q, 2 C, COO), 210.00 (C_q, 2 C, C4).

MS (70 eV): *m*/*z* (%) = 211 (1), 111 (100), 83 (42).

MS (DCI, NH_3, 70 eV): *m*/*z* (%) = 694 (18) [2 M + NH_4^+], 356 [M + NH_4^+].

1-Ethoxypenta-3,4-dienyl Pivalate (3g) and 1-(2-Ethoxycyclopropyl)ethenyl Pivalate (4g)

Using **1** (160 mg, 1.45 mmol), pivalic acid (**2g**, 148 mg, 1.45 mmol), and **A** (5.2 mg, 0.4 mol%) in benzene (1 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **3g** (192 mg, 62%) and **4g** (88.2 mg, 29%) as colorless oils.

3g

R_f = 0.48 (PE–Et_2O, 9:1).

IR (neat): 1959 (C=C=C), 1730 cm^{-1} (C=O).

^1H NMR (250 MHz, C_6D_6): δ = 1.00 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.14 [s, 9 H, $C(CH_3)_3$], 2.40 (m_c, 2 H, H2), 3.29–3.39 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.54–3.64 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.55 (m_c, 2 H, H5), 5.08 (m_c, 1 H, H3), 5.95 (t, ^3J = 5.3 Hz, 1 H, H1).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.19 (+, OCH_2CH_3), 27.11 [+, 3 C, $C(CH_3)_3$], 34.61 (–, C2), 38.95 [C_q, $C(CH_3)_3$], 64.84 (–, OCH_2CH_3), 74.89 (–, C5), 84.61 (+, C3), 97.40 (+, C1), 177.47 (C_q, C=O), 210.05 (C_q, C4).

MS (70 eV): *m*/*z* (%) = 212 (1) [M^+], 111 (35) [$M^+ - C_4H_9COO$], 85 (28) [$C_4H_9CO^+$], 57 (100) [$C_4H_9^+$].

HRMS: calcd for $C_{12}H_{20}O_3$: 212.1412.

Anal. Calcd for $C_{12}H_{20}O_3$ (212.3): C, 67.89; H, 9.50. Found: C, 67.96; H, 9.55.

4g

R_f = 0.20 (PE–Et_2O, 9:1).

IR (neat): 1748 cm^{-1} (C=O).

^1H NMR (250 MHz, C_6D_6): δ = 0.72 (dt, ^2J = ^3J = 6.3 Hz, 1 H, H3′), 0.96 (m_c, 1 H, H3′), 1.03 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.12 [s, 9 H, $C(CH_3)_3$], 1.68 (m_c, 1 H, H1′), 3.29 (m_c, 1 H, H2′), 3.37 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 4.44 (dd, ^2J = 1.5 Hz, ^4J = 0.8 Hz, 1 H, $H2_A$), 4.66 (d, ^2J = 1.5 Hz, 1 H, $H2_B$).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 13.18 (–, C3′), 15.21 (+, OCH_2CH_3), 22.26 (+, C1′), 27.10 [+, 3 C, $C(CH_3)_3$], 33.96 [C_q, $C(CH_3)_3$], 59.49 (+, C2′), 66.06 (–, OCH_2CH_3), 99.44 (–, C2), 155.53 (C_q, C1), 175.73 (C_q, C=O).

MS (70 eV): *m*/*z* (%) = 212 (1) [M^+], 167 (1) [$M^+ - OC_2H_5$], 111 (2) [$M^+ - C_4H_9COO$], 85 (13) [$C_4H_9CO^+$], 57 (100) [$C_4H_9^+$].

HRMS: calcd for $C_{12}H_{20}O_3$: 212.1412.

Anal. Calcd for $C_{12}H_{20}O_3$ (212.3): C, 67.89; H, 9.50. Found: C, 68.00; H, 9.50.

1-Ethoxypenta-3,4-dienyl Benzoate (3h) and 1-(2-Ethoxycyclopropyl)ethenyl Benzoate (4h)

Using **1** (80.0 mg, 726 μmol), benzoic acid (**2h**, 88.7 mg, 726 μmol), and **A** (2.6 mg, 0.4 mol%) in benzene (1 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **3h** (98.1 mg, 58%) and **4h** (45.7 mg, 27%) as colorless oils.

3h

R_f = 0.52 (PE–Et_2O, 9:1).

IR (neat): 1958 (C=C=C), 1718 cm^{-1} (C=O).

^1H NMR (250 MHz, C_6D_6): δ = 0.99 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.53 (m_c, 2 H, H2), 3.37–3.44 (A part of an AB system, m, 1 H, OCH_2CH_3), 3.61–3.68 (B part of an AB system, m, 1 H, OCH_2CH_3), 4.53 (m_c, 2 H, H5), 5.15 (m_c, 1 H, H3), 6.24 (t, ^3J = 5.3 Hz, 1 H, H1), 7.36–7.61 (m, 3 H, Ar-H), 7.96–8.11 (m, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.14 (+, OCH_2CH_3), 34.64 (–, C2), 65.18 (–, OCH_2CH_3), 75.04 (–, C5), 84.55 (+, C3), 98.39 (+, C1), 128.59 (+, 2 C, Ar-C), 130.05 (+, 2 C, Ar-C), 130.71 (C_q, Ar-C), 133.11 (+, Ar-C), 166.04 (C_q, C=O), 210.10 (C_q, C4).

MS (70 eV): *m*/*z* (%) = 232 (1) [M^+], 203 (1) [$M^+ - C_2H_5$], 111 (6) [M^+ – PhCOO], 105 (100) [$PhCO^+$], 77 (17) [Ph^+].

HRMS: calcd for $C_{14}H_{16}O_3$: 232.1099.

Anal. Calcd for $C_{14}H_{16}O_3$ (232.3): C, 72.39; H, 6.94. Found: C, 72.35; H, 6.96.

4h

R_f = 0.24 (PE–Et_2O, 9:1).

IR (neat): 1732 (C=O), 1660 (C=C), 1270 (C–O), 1232 cm^{-1} (C–O).

^1H NMR (250 MHz, C_6D_6): δ = 0.77 (dt, ^2J = ^3J = 6.4 Hz, 1 H, H3′), 0.96–1.03 (m, 4 H, H3′, OCH_2CH_3), 1.77–1.81 (m, 1 H, H1′), 3.31–3.40 (m, 3 H, H2′, OCH_2CH_3), 4.51 (d, ^2J = 1.8 Hz, 1 H, $H2_A$), 4.77 (d, ^2J = 1.8 Hz, 1 H, $H2_B$), 6.97–7.10 (m, 3 H, Ar-H), 8.07–8.11 (m, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 13.44 (–, C3′), 15.16 (+, OCH_2CH_3), 22.39 (+, C1′), 59.71 (+, C2′), 66.08 (–, OCH_2CH_3), 100.14 (–, C2), 128.65 (+, 2 C, Ar-C), 130.14 (+, 2 C, Ar-C), 130.35 (C_q, Ar-C), 133.24 (+, Ar-C), 155.62 (C_q, C1), 164.42 (C_q, C=O).

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MS (70 eV): *m/z* (%) = 233 (4) [M$^+$ + H], 232 (2) [M$^+$], 187 (1) [M$^+$ – OEt], 128 (28) [M$^+$ – PhCO], 105 (100) [PhCO$^+$], 85 (5) [$C_3H_4OEt^+$], 77 (23) [Ph$^+$].

HRMS: calcd for $C_{14}H_{16}O_3$: 232.1099.

Anal. Calcd for $C_{14}H_{16}O_3$ (232.3): C, 72.39; H, 6.94. Found: C, 72.55; H, 7.18.

1-Ethoxypenta-3,4-dienyl 5-Methylthiophene-2-carboxylate (3i) and 1-(2-Ethoxycyclopropyl)ethenyl 5-Methylthiophene-2-carboxylate (4i)

Using **1** (80.0 mg, 0.726 mmol), 5-methylthiophene-2-carboxylic acid (**2i**, 71.2 mg, 501 μmol), and **A** (2.6 mg, 0.4 mol%) in benzene (2 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 8:1) gave **3i** (80.8 mg, 64%) and **4i** (31.5 mg, 25%) as colorless oils.

3i

R_f = 0.60 (PE–Et_2O, 4:1).

IR (neat): 1958 (C=C=C), 1706 cm^{-1} (C=O).

^{1}H NMR (250 MHz, C_6D_6): δ = 0.99 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.91 (s, 3 H, H6), 2.51 (m$_c$, 2 H, H2′), 3.55 (AB system, m$_c$, 2 H, OCH_2CH_3), 4.54 (dt, ^4J = 7.0 Hz, ^5J = 2.9 Hz, 2 H, H5′), 5.14 (tt, ^3J = ^4J = 7.0 Hz, 1 H, H3′), 6.19 (t, ^3J = 5.3 Hz, 1 H, H1′), 6.30 (d, ^3J = 3.7 Hz, 1 H, H4), 7.65 (d, ^3J = 3.7 Hz, 1 H, H3).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.14, 15.19 (+, C6, OCH_2CH_3), 34.66 (–, C2′), 65.20 (–, OCH_2CH_3), 75.03 (–, C5′), 84.54 (+, C3′), 98.31 (+, C1′), 126.68 (+, C4), 131.82 (C$_q$, C2), 134.34 (+, C3), 148.33 (C$_q$, C5), 161.81 (C$_q$, C1), 210.10 (C$_q$, C4′).

MS (70 eV): *m/z* (%) = 252 (1) [M$^+$], 125 (100) [$C_5H_5SCO^+$].

Anal. Calcd for $C_{13}H_{16}O_3S$ (252.3): C, 61.88; H, 6.39. Found: C, 62.08; H, 6.30.

4i

R_f = 0.45 (PE–Et_2O, 4:1).

IR (neat): 1724 (C=O), 1661 (C=C), 1255 (C–O), 1233 cm^{-1} (C–O).

^{1}H NMR (250 MHz, C_6D_6): δ = 0.80 (q, ^3J = 6.4 Hz, 1 H, H3″), 0.98 (m$_c$, 2 H, H1′, H3″), 1.01 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.80 (m$_c$, 1 H, H2″), 1.86 (s, 3 H, H6), 3.34–3.42 (m, 2 H, OCH_2CH_3), 4.49 (d, ^2J = 2.1 Hz, 1 H, H2′), 4.82 (d, ^2J = 2.1 Hz, 1 H, H2′), 6.24 (d, ^3J = 3.7 Hz, 1 H, H4), 7.62 (d, ^3J = 3.7 Hz, 1 H, H3).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 13.38 (–, C3″), 15.14, 15.19 (+, C6, OCH_2CH_3), 22.45 (+, C1″), 59.61 (+, C2″), 66.10 (–, OCH_2CH_3), 100.21 (–, C2′), 126.79 (+, C4), 131.17 (C$_q$, C2), 134.83 (+, C3), 148.64 (C$_q$, C5), 155.19, (C$_q$, C1′), 159.69 (C$_q$, C1).

MS (70 eV): *m/z* (%) = 252 (1) [M$^+$], 125 (100) [$C_5H_5SCO^+$], 81 (19).

HRMS: calcd for $C_{13}H_{16}O_3S$: 252.0820.

Anal. Calcd for $C_{13}H_{16}O_3S$ (252.3): C, 61.88; H, 6.39. Found: C, 61.95; H, 6.18.

1-Ethoxypenta-3,4-dienyl 2-Iodobenzoate (3j) and 1-(2-Ethoxycyclopropyl)ethenyl 2-Iodobenzoate (4j)

Using **1** (400 mg, 3.63 mmol), 2-iodobenzoic acid (**2j**, 901 mg, 3.63 mmol), and **A** (13 mg, 0.4 mol%) in benzene (6 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 8:1) gave **3j** (881 mg, 68%) and **4j** (238 mg, 18%) as colorless oils.

3j

R_f = 0.65 (PE–Et_2O, 7:1).

IR (neat): 1958 (C=C=C), 1728 cm^{-1} (C=O).

^{1}H NMR (250 MHz, C_6D_6): δ = 1.01 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.51 (m$_c$, 2 H, H2), 3.55 (AB system, m$_c$, 2 H, OCH_2CH_3), 4.56 (dt, ^4J = 6.9 Hz, ^5J = 2.8 Hz, 2 H, H5), 5.13 (tt, ^3J = ^4J = 6.9 Hz, 1 H, H3), 6.15 (t, ^3J = 5.3 Hz, 1 H, H1), 6.59 (dt, ^3J = ^3J = 7.7 Hz, ^4J = 1.7 Hz, 1 H, Ar-H), 6.90 (dt, ^3J = ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1 H, Ar-H), 7.69 (m$_c$, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.22 (+, OCH_2CH_3), 34.44 (–, C2), 65.48 (–, OCH_2CH_3), 75.35 (–, C5), 84.57 (+, C3), 94.64 (C$_q$, CI), 99.06 (+, C1), 127.91 (+, Ar-C), 131.13 (+, Ar-C), 132.70 (+, Ar-C), 135.42 (C$_q$, Ar-C), 141.63 (+, Ar-C), 165.84 (C$_q$, COO), 209.97 (C$_q$, C4′).

MS (70 eV): *m/z* (%) = 358 (1) [M$^+$], 231 (100) [M$^+$ – I], 203 (7) [$C_6H_4I^+$], 127 (1) [I$^+$], 111 (15) [M$^+$ – C_6H_4ICOO].

HRMS: calcd for $C_{14}H_{15}IO_3$: 358.0065.

Anal. Calcd for $C_{14}H_{15}IO_3$ (358.2): C, 46.95; H, 4.22. Found: C, 46.96; H, 4.12.

4j

R_f = 0.25 (PE–Et_2O, 7:1).

IR (neat): 1741 (C=O), 1660 (C=C), 1287 (C–O), 1246 cm^{-1} (C–O).

^{1}H NMR (250 MHz, C_6D_6): δ = 0.65 (m$_c$, 1 H, H3′), 0.86 (m$_c$, 1 H, H3′), 1.04 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.47 (dt, ^3J = 6.5 Hz, ^3J = 9.6 Hz, 1 H, H1′), 3.02 (m$_c$, 1 H, H2′), 3.42 (m$_c$, 2 H, OCH_2CH_3), 4.83 (s, 1 H, H2), 4.99 (s, 1 H, H2), 6.57 (dt, ^3J = ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, Ar-H), 6.88 (dt, ^3J = ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1 H, Ar-H), 7.72 (m$_c$, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 12.14 (–, C3′), 15.35 (+, OCH_2CH_3), 20.79 (+, C1′), 57.84 (+, C2′), 66.43 (–, OCH_2CH_3), 94.72 (C$_q$, CI), 102.08 (–, C2), 127.95 (+, Ar-C), 131.36 (+, Ar-C), 132.77 (+, Ar-C), 135.31 (C$_q$, Ar-C), 141.60 (+, Ar-C), 153.19 (C$_q$, C1), 164.17 (C$_q$, COO).

MS (70 eV): *m/z* (%) = 358 (1) [M$^+$], 231 (100) [M$^+$ – I], 203 (11) [$C_6H_4I^+$].

Anal. Calcd for $C_{14}H_{15}IO_3$ (358.2): C, 46.95; H, 4.22. Found: C, 46.94; H, 4.16.

1-Ethoxypenta-3,4-dienyl 2-Acetylbenzoate (3k) and 1-(2-Ethoxycyclopropyl)ethenyl 2-Acetylbenzoate (4k)

Using **1** (80.0 mg, 726 μmol), 2-acetylbenzoic acid (**2k**, 119 mg, 726 μmol), and **A** (2.6 mg, 0.4 mol%) in benzene (2 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 4:1) gave **3k** (115 mg, 58%) and **4k** (20 mg, 10%) as colorless oils.

3k

R_f = 0.40 (PE–Et_2O, 4:1).

IR (neat): 1957 (C=C=C), 1773 (C=O), 1705 (C=O), 1266 cm^{-1} (C–O).

^{1}H NMR (250 MHz, C_6D_6): δ = 1.02 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.23 (s, 3 H, $COCH_3$), 2.54 (m$_c$, 2 H, H2), 3.60 (AB system, m$_c$, 2 H, OCH_2CH_3), 4.55 (dt, ^4J = 7.0 Hz, ^5J = 2.9 Hz, 2 H, H5), 5.16 (tt, ^3J = ^4J = 7.0 Hz, 1 H, H3), 6.18 (t, ^3J = 5.3 Hz, 1 H, H1), 6.94–6.99 (m, 3 H, Ar-H), 7.74 (m$_c$, 1 H, Ar-H).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.12 (+, OCH_2CH_3), 29.49 (+, $COCH_3$), 34.40 (–, C2), 65.49 (–, OCH_2CH_3), 75.11 (–, C5), 84.52 (+, C3), 99.15 (+, C1), 126.79 (+, Ar-C), 129.79 (+, Ar-C), 129.83 (+, Ar-C), 129.85 (C$_q$, Ar-C), 131.77 (+, Ar-C), 143.28 (C$_q$, Ar-C), 166.84 (C$_q$, COO), 200.97 (C$_q$, $COCH_3$), 210.04 (C$_q$, C4).

MS (70 eV): *m/z* (%) = 177 (1), 147 (100) [$C_8H_7OCO^+$], 111 (11) [M$^+$ – $C_8H_7OCO_2$].

MS (DCI, NH_3, 70 eV): *m/z* (%) = 292 [M + NH_4^+] (58), 566 [2 M + NH_4^+] (100).

Anal. Calcd for $C_{16}H_{18}O_4$ (274.3): C, 70.06; H, 6.61. Found: C, 69.93; H, 6.36.

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4k

R_f = 0.25 (PE–Et_2O, 4:1).

IR (neat): 1738 (C=O), 1703 (C=O), 1661 (C=C), 1266 (C–O), 1232 cm^{-1} (C–O).

^1H NMR (250 MHz, C_6D_6): δ = 0.81 (q, ^2J = ^3J = 6.3 Hz, 1 H, H3′), 0.99–1.03 (m, 2 H, H1′, H3′), 1.05 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.83 (m_c, 1 H, H2′), 2.16 (s, 3 H, $COCH_3$), 3.42 (m_c, 2 H, OCH_2CH_3), 4.49 (d, ^2J = 1.8 Hz, 1 H, H2), 4.86 (d, ^2J = 1.8 Hz, 1 H, H2); 6.89–6.92 (m, 3 H, Ar-H), 7.65 (m_c, 1 H, Ar-H).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 13.51 (–, C3′), 15.22 (+, OCH_2CH_3), 22.09 (+, C1′), 29.18 (+, $COCH_3$), 59.88 (+, C2′), 66.13 (–, OCH_2CH_3), 100.00 (–, C2), 126.96 (+, Ar-C), 127.87 (+, Ar-C), 129.87 (+, Ar-C), 129.96 (C_q, Ar-C), 131.73 (+, Ar-C), 142.96 (C_q, Ar-C), 155.72 (C_q, C1), 164.11 (C_q, COO), 200.38 (C_q, $COCH_3$).

MS (70 eV): *m*/*z* (%) = 147 (100) [$C_8H_7OCO^+$], 91 (12), 81 (17).

MS (DCI, NH_3, 70 eV): *m*/*z* (%) = 292 (100) [M + NH_4^+], 566 [2 M + NH_4^+] (42).

Anal. Calcd for $C_{16}H_{18}O_4$ (274.3): C, 70.06; H, 6.61. Found: C, 69.77; H, 6.39.

(*Z*)-5-(Alkylamino)-1-ethoxy-4-phenylpent-3-enyl Acetates 12; General Procedure

A screw-cap Pyrex bottle was charged with 1-ethoxypenta-3,4-dienyl acetate (**3b**, 1.18 mmol), amine (6–8 mmol), PhI (1.0 mmol), $Pd(OAc)_2$ (5 mol% based on PhI), tri(2-furyl)phosphine (TFP, 10 mol%, based on PhI) and degassed anhyd DMF (0.75 mL) under an inert atmosphere (N_2 or argon). The sealed bottle was heated for the stated time. After cooling to r.t., Et_2O (10 mL) was added, and the mixture was filtered through a short column [Celite (1 cm), activated carbon (1 cm), and silica gel (1 cm), Et_2O, 350 mL]. After evaporation of the solvent under reduced pressure the residue was subjected to column chromatography (silica gel).

(*Z*)-5-(*tert*-Butylamino)-1-ethoxy-4-phenylpent-3-enyl Acetate (12ba)

Using **3b** (201 mg, 1.18 mmol), *t*-$BuNH_2$ (439 mg, 6.00 mmol), PhI (204 mg, 1.00 mmol), $Pd(OAc)_2$ (11 mg, 5 mol%), and tri(2-furyl)phosphine (23 mg, 10 mol%) in DMF (0.75 mL) and heating at 55 °C for 45 min; chromatography (PE–Et_2O, 1:1) gave **12ba** (263 mg, 82%) as a colorless oil; R_f = 0.20 (PE–Et_2O, 1:1).

IR (neat): 1739 (C=O), 1239 cm^{-1} (C–O).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.13 [s, 9 H, $C(CH_3)_3$], 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.09 (s, 3 H, CH_3COO), 2.67 (dd, ^3J = 5.4 Hz, ^3J = 7.5 Hz, 2 H, H2), 3.59 (s, 2 H, H5), 3.64 (m_c, 2 H, OCH_2CH_3), 5.76 (t, ^3J = 7.5 Hz, 1 H, H1), 5.90 (t, ^3J = 5.4 Hz, 1 H, H3), 7.23–7.47 (m, 5 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.97 (+, OCH_2CH_3), 21.17 (+, CH_3COO), 28.80 [+, 3 C, $C(CH_3)_3$], 34.05 (–, C2), 41.20 (–, C5), 50.46 [C_q, $C(CH_3)_3$], 65.11 (–, OCH_2CH_3), 97.84 (+, C1), 123.11 (+, C3), 126.19 (+, 2 C, Ar-C), 127.01 (+, Ar-C), 128.26 (+, 2 C, Ar-C), 141.75 (C_q, 2 C, Ar-C, C4), 170.75 (C_q, COO).

MS (70 eV): *m*/*z* (%) = 319 (6) [M^+], 304 (5) [$M^+ - CH_3$], 290 (6) [$M^+ - C_2H_5$], 259 (41) [$M^+ - CH_3COOH$], 244 (24), 214 (32), 187 (100), 159 (23), 77 (6) [Ph^+], 59 (14) [CH_3COO^+], 43 (23) [CH_3CO^+].

HRMS: calcd for $C_{19}H_{29}NO_3$: 319.2147.

(*Z*)-5-(Cyclohexylamino)-1-ethoxy-4-phenylpent-3-enylAcetate (12bb)

Using **3b** (200 mg, 1.18 mmol), $CyNH_2$ (793 mg, 8.00 mmol), PhI (204 mg, 1.00 mmol), $Pd(OAc)_2$ (11 mg, 5 mol%), and tri(2-furyl)phosphine (23 mg, 10 mol%) in DMF (0.75 mL) and heating at 70 °C for 2 h; chromatography (PE–Et_2O, 1:1) gave **12bb** (160 mg, 46%) as a colorless oil; R_f = 0.25 (PE–Et_2O, 1:1).

IR (neat): 1738 cm^{-1} (C=O).

^1H NMR (250 MHz, $CDCl_3$): δ = 0.98–1.26 (m, 5 H, Cy-H), 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.57–1.82 (m, 5 H, Cy-H), 2.09 (s, 3 H, CH_3COO), 2.41 (m_c, 1 H, Cy-H), 2.66 (dd, ^3J = 7.5 Hz, ^3J = 5.4 Hz, 2 H, H2), 3.65 (m_c, 2 H, OCH_2CH_3), 3.65 (d, ^3J = 5.9 Hz, 2 H, H5), 5.75 (t, ^3J = 7.5 Hz, 1 H, H1), 5.89 (t, ^3J = 5.4 Hz, 1 H, H3), 7.21–7.43 (m, 5 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.96 (+, OCH_2CH_3), 21.17 (+, CH_3COO), 24.90 (–, 2 C, Cy-C), 26.06 (–, 2 C, Cy-C), 33.35 (–, Cy-C), 34.03 (–, C2), 45.14 (–, C5), 56.42 (+, Cy-C), 65.11 (–, OCH_2CH_3), 97.73 (+, C1), 123.23 (+, C3), 126.27 (+, 2 C, Ar-C), 127.04 (+, Ar-C), 128.31 (+, 2 C, Ar-C), 141.63, 141.74 (C_q, Ar-C, C4), 170.75 (C_q, COO).

MS (70 eV): *m*/*z* (%) = 345 (6) [M^+], 316 (23) [$M^+ - C_2H_5$], 285 (100) [$M^+ - CH_3COOH$], 256 (39), 240 (82), 211 (53), 187 (67), 155 (37), 138 (82), 112 (35), 99 (82) [$C_6H_{11}NH_2^+$], 84 (22), 56 (31).

HRMS: calcd for $C_{21}H_{31}NO_3$: 345.2303.

(*Z*)-1-Ethoxy-5-(isobutylamino)-4-phenylpent-4-enyl Acetate (12bc)

A mixture of **3b** (201 mg, 1.18 mmol), *i*-$BuNH_2$ (585 mg, 8.00 mmol), PhI (204 mg, 1.00 mmol), $Pd(OAc)_2$ (11 mg, 5 mol%), and tri(2-furyl)phosphine (23 mg, 10 mol%) in DMF (0.75 mL) was heated at 60 °C for 1 h. After cooling to r.t. the mixture was diluted with CH_2Cl_2 (70 mL), washed with H_2O (5 × 5 mL), and the organic phase dried ($MgSO_4$). After evaporation of the solvent under reduced pressure and chromatography of the residue (silica gel, PE–Et_2O, 1:1) **12bc** (76 mg, 24%) was isolated as a colorless oil; R_f = 0.25 (PE–Et_2O, 1:1).

IR (neat): 1739 (C=O), 1676 cm^{-1} (C=C).

^1H NMR (250 MHz, $CDCl_3$): δ = 0.81 [d, ^3J = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.20 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.64 [m_c, 1 H, $CH(CH_3)_2$], 2.08 (s, 3 H, CH_3COO), 2.32 [d, ^3J = 6.8 Hz, 2 H, $CH_2CH(CH_3)_2$], 2.66 (dd, ^3J = 7.5 Hz, ^3J = 5.4 Hz, 2 H, H2), 3.45–3.77 (m_c, 2 H, OCH_2CH_3), 3.62 (s, 2 H, H5), 5.75 (t, ^3J = 7.5 Hz, 1 H, H1), 5.89 (t, ^3J = 5.4 Hz, 1 H, H3), 7.23–7.41 (m, 5 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.95 (+, OCH_2CH_3), 20.57 [+, 2 C, $CH(CH_3)_2$], 21.15 (+, CH_3COO), 28.06 [+, $CH(CH_3)_2$], 33.95 (–, C2), 47.85 [–, $CH_2CH(CH_3)_2$], 57.23 (–, C5), 65.08 (–, OCH_2CH_3), 97.73 (+, C1), 123.36 (+, C3), 126.37 (+, 2 C, Ar-C), 127.06 (+, 2 C, Ar-C), 128.23 (+, Ar-C), 141.61 (C_q, 2 C, Ar-C, C4), 170.76 (C_q, COO).

MS (70 eV): *m*/*z* (%) = 319 (4) [M^+], 290 (10) [$M^+ - C_2H_5$], 259 (29) [$M^+ - CH_3COOH$], 216 (49), 187 (100), 170 (35), 159 (22), 141 (45), 86 (27), 57 (20) [$CH_2CH(CH_3)_2$], 43 (34) [$CH(CH_3)_2$].

HRMS: calcd for $C_{19}H_{29}NO_3$: 319.2147.

(*E*)-5-(Dibenzylamino)-1-ethoxy-4-phenylpent-3-enyl Acetate [(*E*)-12bd] and (*Z*)-5-(Dibenzylamino)-1-ethoxy-4-phenylpent-3-enyl Acetate [(*Z*)-12bd]

Using **3b** (201 mg, 1.18 mmol), Bn_2NH (1.18 g, 6.00 mmol), PhI (204 mg, 1.00 mmol), $Pd(OAc)_2$ (11 mg, 5 mol%), and tri(2-furyl)phosphine (23 mg, 10 mol%) in DMF (0.75 mL) and heating at 50 °C for 2 h then at 75 °C for1 h; chromatography (PE–Et_2O, 5:1), gave a mixture of (*E*)-**12bd** and (*Z*)-**12bd** (368 mg, 83%) as a colorless oil; ratio *E*/*Z*, 1:1; R_f = 0.40 (PE–Et_2O, 2:1).

IR (neat): 1737 cm^{-1} (C=O).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.27 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.07 (s, 3 H, CH_3COO), 2.13 (s, 3 H, CH_3COO), 2.56 (t, ^3J = 6.4 Hz, 2 H, H2),

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2.81 (t, ^3J = 6.4 Hz, 2 H, H2), 3.41–3.82 (m, 16 H, OCH_2CH$_3$, H5, CH_2C$_6$H$_5$), 5.84–6.02 (m, 4 H, H3, H1), 7.16–7.45 (m, 30 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.88 (+, OCH$_2$*C*H$_3$), 14.95 (+, OCH$_2$*C*H$_3$), 21.00 (+, *C*H$_3$COO), 21.09 (+, *C*H$_3$COO), 33.89 (–, C4), 34.13 (–, C2), 52.09 (–, C5), 57.46 (–, 2 C, *C*H$_2$C$_6$H$_5$), 57.90 (–, 2 C, *C*H$_2$C$_6$H$_5$), 61.11 (–, C5), 64.82 (–, O*C*H$_2$CH$_3$), 65.01 (–, O*C*H$_2$CH$_3$), 97.73 (+, C1), 97.54 (+, C1), 122.46 (+, C3), 124.87 (+, C3), 139.34, 139.46 (3 C), 139.51 (3 C), 141.17, 142.04 (C$_q$, 6 Ar-C, 2 C4), 170.60 (C$_q$, COO), 170.66 (C$_q$, COO).

MS (70 eV): *m*/*z* (%) = 443 (9) [M$^+$], 383 (21) [M$^+$ – CH$_3$COOH], 355 (15) [M$^+$ – CH$_3$COOEt], 210 (100) [Bzl$_2$NCH$_2^+$], 91 (81) [C$_7$H$_7^+$].

2-(*trans*-2-Ethoxycyclopropyl)ethenyl Esters 13; General Procedure

A screw-cap Pyrex bottle was charged with (*trans*-2-ethoxycyclopropyl)ethyne (**1**, 1 equiv), carboxylic acid (1 equiv), [Ru(CH$_2$CCH$_3$CH$_2$)$_2$(dppb)] (**C**, 2.5 mol%), and anhyd benzene, and the degassed mixture was heated in the sealed bottle at 60 °C for 4.5–15 h. After evaporation of the solvent under reduced pressure the residue was subjected to column chromatography (silica gel) or distilled in a Kugelrohr apparatus.

(*Z*)-(2-*trans*-2-Ethoxycyclopropyl)ethenyl Pentanoate (13c)

Using **1** (80.0 mg, 726 μmol), pentanoic acid (**2c**, 74 mg, 726 μmol), and **C**, (11.5 mg, 2.5 mol%) in benzene (1.5 mL) and heating for 15 h; chromatography (silica gel, PE–Et$_2$O, 20:1) gave **13c** (131 mg, 85%) as a colorless oil; R_f = 0.18 (PE–Et$_2$O, 9:1).

IR (neat): 1752 (C=O), 1669 cm^{-1} (C=C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (q, ^2J = ^3J = ^3J = 6.1 Hz, 1 H, H3″), 0.92 (t, ^3J = 7.3 Hz, 3 H, H4), 1.08 (m$_c$, 1 H, H3″), 1.18 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.37 (m$_c$, 2 H, H3), 1.64 (m$_c$, 2 H, H2), 1.88 (m$_c$, 1 H, H1″), 2.41 (t, ^3J = 7.5 Hz, 2 H, H1), 3.20 (m$_c$, 1 H, H2″), 3.54 (q, ^3J = 7.0 Hz, 2 H, OC*H*$_2$CH$_3$), 4.30 (dd, ^3J = 6.4 Hz, ^3J = 9.8 Hz, 1 H, H2′), 7.03 (dd, ^3J = 6.4 Hz, ^4J = 0.7 Hz, 1 H, H1′).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.64 (+, C4), 14.80 (–, C3″), 15.04, 15.71 (+, OCH$_2$*C*H$_3$, C1″), 22.16 (–, C3), 26.74 (–, C2), 33.72 (–, C1), 59.90 (+, C2″), 65.98 (–, O*C*H$_2$CH$_3$), 114.22 (+, C2′), 133.93 (+, C1′), 170.74 (C$_q$, COO).

MS (70 eV): *m*/*z* (%) = 212 (2) [M$^+$], 127 (49) [M$^+$ – C$_4$H$_9$CO], 99 (37), 85 (93) [C$_4$H$_9$CO$^+$], 57 (100) [C$_4$H$_9^+$], 43 (15) [C$_3$H$_7^+$].

Anal. Calcd for C$_{12}$H$_{20}$O$_3$ (212.3): C, 67.89; H, 9.50. Found: C, 68.05; H, 9.52.

(*Z*)-(2-*trans*-2-Ethoxycyclopropyl)ethenyl Benzoate (13h)

Using **1** (73.4 mg, 666 μmol), benzoic acid (**2h**, 81.3 mg, 666 μmol), and C, (10.6 mg, 2.5 mol%) in benzene (1.5 mL) and heating for 15 h; chromatography (silica gel, PE–Et$_2$O, 20:1) gave **13h** (142 mg, 92%) as a colorless oil; R_f = 0.25 (PE–Et$_2$O, 9:1).

IR (neat): 1732 (C=O), 1672 (C=C), 1111 cm^{-1} (C–O).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.72 (q, ^2J = ^3J = ^3J = 6.1 Hz, 1 H, H3″), 1.17 (m$_c$, 1 H, H3″), 1.20 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 2.04 (m$_c$, 1 H, H1″), 3.28 (m$_c$, 1 H, H2″), 3.59 (q, ^3J = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.46 (dd, ^3J = 6.3 Hz, ^3J = 9.8 Hz, 1 H, H2′), 7.28 (dd, ^3J = 6.3 Hz, ^4J = 0.8 Hz, 1 H, H1′), 7.43–7.49 (m, 2 H, Ar–H), 7.55–7.62 (m, 1 H, Ar-H), 8.10–8.14 (m, 2 H, Ar-H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.93 (–, C3″), 15.01, 15.92 (+, C1″, OCH$_2$*C*H$_3$), 59.97 (+, C2″), 66.00 (–, O*C*H$_2$CH$_3$), 114.97 (+, C2′), 128.43 (+, 2 C, C–Ar), 129.13 (C$_q$, Ar-C), 129.82 (+, 2 C, Ar-C), 133.39, 134.03 (+, C1′, Ar-C), 163.33 (C$_q$, COO).

MS (70 eV): *m*/*z* (%) = 232.2 (1) [M$^+$], 127 (18) [M$^+$ – PhCO], 105 (100) [PhCO$^+$], 89 (10) [PhC$^+$], 77 (22) [Ph$^+$].

Anal. Calcd for C$_{14}$H$_{16}$O$_3$ (232.3): C, 72.39; H, 6.94. Found: C, 72.31; H, 7.07.

(*Z*)-(2-*trans*-2-Ethoxycyclopropyl)ethenyl Acrylate (13l)

Using **1** (80.0 mg, 0.726 mmol), acrylic acid (**2l**, 52.3 mg, 0.726 mmol), and **C** (11.6 mg, 2.5 mol%) in benzene (0.5 mL) and heating for 4.5 h; Kugelrohr distillation gave **13l** (91.0 mg, 69%) as a colorless oil; bp 50 °C/0.1 mbar.

IR (neat): 1739 (C=O), 1635 cm^{-1} (C=C).

^{1}H NMR (250 MHz, C_6D_6): δ = 0.38 (q, ^2J = ^3J = ^3J = 6.0 Hz, 1 H, H3″), 1.04 (t, ^3J = ^3J = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 0.94–1.05 (m, 1 H, H3″), 2.01 (m$_c$, 1 H, H1″), 2.96 (m$_c$, 1 H, H2″), 3.34 (m$_c$, AB system, 2 H, OC*H*$_2$CH$_3$), 4.00 (dd, $^3J_{cis}$ = 6.4 Hz, $^3J_{allyl}$ = 9.8 Hz, 1 H, H2′), 5.20 (dd, $^2J_{gem}$ = 1.4 Hz, $^3J_{cis}$ = 10.4 Hz, 1 H, H$_B$), 5.83 (dd, $^3J_{cis}$ = 10.4 Hz, $^3J_{trans}$ = 17.3 Hz, 1 H, C*H*=CH$_2$), 6.23 (dd, $^2J_{gem}$ = 1.4 Hz, $^3J_{trans}$ = 17.3 Hz, 1 H, H$_A$), 7.28 (d, $^3J_{cis}$ = 6.4 Hz, 1 H, H1′).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 15.09 (–, C3″), 15.27, 16.16 (+, C1″, OCH$_2$*C*H$_3$), 60.26 (+, C2″), 65.92 (–, O*C*H$_2$CH$_3$), 115.03 (+, C2′), 127.52 (+, *C*H=CH$_2$), 131.73 (–, CH=CH$_2$), 133.99 (+, C1′), 162.70 (C$_q$, COO).

MS (70 eV): *m*/*z* (%) = 182 (3) [M$^+$], 127 (25) [M$^+$ – CH$_2$=CHCO], 111 (4) [M$^+$ – CH$_2$=CHCO$_2$], 84 (29), 71 (7) [CH$_2$=CHCO$_2^+$], 55 (100) [CH$_2$=CHCO$^+$].

HRMS: calcd for C$_{10}$H$_{14}$O$_3$: 182.0942.

1-Ethynylcyclopropanol (14)[28]

A previously published protocol of Salaün[29] was adjusted for the preparation of **14** in its terminally trimethylsilyl-protected form.

To a soln of 3 M MeMgCl in THF (160 mL, 0.480 mol) in anhyd THF (450 mL) was added dropwise with stirring at 0 °C a soln of cyclopropanone ethyl hemiacetal[20] in THF (200 mL), and the mixture was stirred at the same temperature for an additional 1 h.

To a soln of (trimethylsilyl)ethyne (51.86 g, 0.528 mol) in anhyd Et$_2$O (450 mL) was added at –78 °C 2.36 M BuLi in hexane (220 mL, 0.518 mol). The resulting soln of [(trimethylsilyl)ethynyl]lithium was added at 0 °C within 30 min to the soln of chloromagnesium 1-ethoxycyclopropanolate described above, and the mixture was stirred at 40 °C for 17 h. Then sat. NH$_4$Cl (600 mL) was added, the aqueous phase was extracted with Et$_2$O (2 × 100 mL), the combined organic phases were washed with H$_2$O (4 × 100 mL) and dried (MgSO$_4$). The solvents were distilled in vacuo to yield 1-[(trimethylsilyl)ethynyl]cyclopropanol (64.42 g, 87%); bp 81 °C/12 mbar.

To a soln of NH$_4$F (2.2 g, 60 mmol) in MeOH (30 mL) and H$_2$O (10 mL) was added 1-[(trimethylsilyl)ethynyl]cyclopropanol (4.0 g, 26 mmol) and the mixture was stirred at r.t. for 1.5 d, then poured into H$_2$O (50 mL). The mixture was carefully extracted with Et$_2$O (7 × 30 mL), the combined organic extracts were dried (MgSO$_4$) and concentrated by distilling the ether at ambient pressure. The residue was bulb-to-bulb distilled under reduced pressure to yield **14** (1.70 g, 80%); bp 48–50 °C/25 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.05 [AA′BB′ system, 4 H, H2(3)], 2.43 (s, 1 H, H2′), 2.69 (br s, 1 H, OH).

1-Acetylcyclopropyl Esters 15; General Procedure

In a sealed Schlenk tube were placed 1-ethynylcyclopropanol (**14**), the carboxylic acid, and the catalyst [Ru(O$_2$CH)(CO)$_2$(PPh$_3$)]$_2$ (**A**) in toluene, and the mixture was heated at 60 °C for the stated time. After cooling to r.t., the mixture was diluted with CH$_2$Cl$_2$ (50 mL), washed with 1 M NaOH (15 mL), dried (MgSO$_4$), and the solvent was evaporated under reduced pressure. The products were purified by Kugelrohr distillation in vacuo.

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1-Acetylcyclopropyl Pentanoate (15c)
Using **14** (246 mg, 3.00 mmol), pentanoic acid (**2c**, 308 mg, 3.02 mmol), and **A** (14 mg, 0.5 mol%) in degassed toluene (3 mL) and heating for 18.5 h; distillation gave **15c** (375 mg, 68%) as a colorless oil; bp 140 °C/0.2 mbar.

IR (neat): 1752 (C=O), 1709 cm^{-1} (C=O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.74 (t, ^3J = 7.2 Hz, 3 H, H4), 0.99 (AA′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.35 (BB′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.14–1.49 (m, 4 H, H3, H2), 1.95 (s, 3 H, $COCH_3$), 2.19 (t, ^3J = 7.2 Hz, 2 H, H1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.55 (+, C4), 17.25 (–, 2 C, cPr-C), 22.10 (–, C3), 25.16 (+, $CO\mathit{C}H_3$), 26.68 (–, C2), 33.59 (–, C1), 63.65 (C_q, cPr-C), 173.70 (C_q, COO), 204.53 (C_q, $\mathit{C}OCH_3$).

MS (70 eV): *m/z* (%) = 141 (56) [$M^+ - CH_3CO$], 85 (100) [$C_4H_9CO^+$], 57 (63) [$C_4H_9^+$], 43 (12) [CH_3CO^+].

MS (DCI, NH_3, 70 eV): *m/z* (%) = 386 (5) [2 M + NH_4^+], 219 (58) [M + NH_3 + NH_4^+], 202 (100) [M + NH_4^+], 185 (3) [MH^+].

1-Acetylcyclopropyl Cyclopropanecarboxylate (15e)
Using **14** (241 mg, 2.94 mmol), cyclopropanecarboxylic acid (**2e**, 258 mg, 3.00 mmol), and **A** (14 mg, 0.5 mol%) in toluene (3 mL) and heating for 18 h; distillation gave **15e** (243 mg, 49%) as a colorless oil; bp 130 °C/0.2 mbar.

IR (neat): 1744 (C=O), 1708 cm^{-1} (C=O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.77–0.92 (m, 4 H, cPr-H), 1.06 (AA′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.35 (BB′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.50–1.62 (m, 1 H, cPr-H), 2.01 (s, 3 H, CH_3).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 8.80 (–, 2 C, cPr-C), 12.64 (+, cPr-C), 17.49 (–, 2 C, cPr-C), 25.37 (+, CH_3), 63.84 (C_q, cPr-C), 174.96 (C_q, COO), 205.09 (C_q, $\mathit{C}OCH_3$).

MS (70 eV): *m/z* (%) = 125 (18) [$M^+ - CH_3CO$], 69 (100) [$C_3H_5CO^+$], 41 (41) [$C_3H_5^+$].

MS (DCI, NH_3, 70 eV): *m/z* (%) = 354 (2) [2 M + NH_4^+], 203 (29) [M + NH_3 + NH_4^+], 186 (100) [M + NH_4^+].

1-Acetylcyclopropyl Benzoate (15h)
Using **14** (281 mg, 3.42 mmol), benzoic acid (**2h**, 489 mg, 4.00 mmol), and **A** (16 mg, 0.5 mol%) in toluene (3.5 mL) and heating for 16.5 h; distillation gave **15h** (514 mg, 74%) as a colorless oil; bp 160 °C/0.2 mbar.

IR (neat): 1730 (C=O), 1707 (C=O), 1601 cm^{-1} (C=C).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (AA′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.56 (BB′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 2.11 (s, 3 H, CH_3), 7.33–7.51 (m, 3 H, Ar-H), 7.96–8.00 (m, 2 H, Ar-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.64 (–, 2 C, cPr-C), 25.50 (+, CH_3), 64.46 (C_q, cPr-C), 128.59 (+, 2 C, Ar-C), 129.17 (C_q, Ar-C), 129.82 (+, 2 C, Ar-C), 133.69 (+, Ar-C), 166.68 (C_q, COO), 204.76 (C_q, $\mathit{C}OCH_3$).

MS (70 eV): *m/z* (%) = 161 (16) [$M^+ - CH_3CO$], 105 (100) [$PhCO^+$], 77 (28) [Ph^+].

MS (DCI, NH_3, 70 eV): *m/z* (%) = 426 (4) [2 M + NH_4^+], 239 (100) [M + NH_3 + NH_4^+], 222 (72) [M + NH_4^+], 205 (4) [MH^+].

1-Acetylcyclopropyl Methoxyacetate (15m)
Using **14** (222 mg, 2.70 mmol), methoxyacetic acid (**2m**, 270 mg, 3.00 mmol), and **A** (28 mg, 1.1 mol%) in toluene (3 mL) and heating for 17.5 h; distillation gave **15m** (254 mg, 55%) as a colorless oil; bp 140 °C/0.2 mbar.

IR (neat): 1772 (C=O), 1706 (C=O), 1184 (C–O), 1126 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.12 (AA′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.44 (BB′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.99 [s, 3 H, $(C=O)CH_3$], 3.32 (s, 3 H, OCH_3), 3.96 (s, 2 H, OCH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.08 (–, 2 C, cPr-C), 24.99 [+, $(C=O)\mathit{C}H_3$], 59.32 (+, OCH_3), 64.20 (C_q, cPr-C), 69.42 (–, OCH_2), 170.31 (C_q, COO), 203.72 (C_q, COMe).

MS (70 eV): *m/z* (%) = 69 (8) [$C_4H_5O^+$], 45 (100) [CH_2OMe^+], 43 (79) [CH_3CO^+].

MS (DCI, NH_3, 70 eV): *m/z* (%) = 362 (2) [2 M + NH_4^+], 207 (27) [M + NH_3 + NH_4^+], 190 (100) [M + NH_4^+].

1-Acetylcyclopropyl Salicylate (15n)
Using **14** (239 mg, 2.91 mmol), salicylic acid (**2n**, 414 mg, 3.00 mmol), and **A** (13 mg, 0.5 mol%) in toluene (3 mL) and heating for 20 h; distillation gave **15n** (180 mg, 28%) as a colorless oil; bp 250 °C/0.2 mbar.

IR (neat): 3224 (O–H), 1711 (C=O), 1686 (C=O), 1615 (C=C), 1584 cm^{-1} (C=C).

^1H NMR (200 MHz, $CDCl_3$): δ = 1.33 (AA′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 1.64 (BB′ part of an AA′BB′ system, m_c, 2 H, cPr-H), 2.18 (s, 3 H, CH_3), 6.84–7.06 (m, 2 H, Ar-H), 7.43–7.52 (m, 1 H, Ar-H), 7.81–7.86 (m, 1 H, Ar-H), 10.46 (s, 1 H, OH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.59 (–, 2 C, cPr-C), 25.48 (+, CH_3), 64.90 (C_q, cPr-C), 116.72 (C_q, Ar-C), 117.87 (+, Ar-C), 119.47 (+, Ar-C), 130.05 (+, Ar-C), 136.60 (+, Ar-C), 162.04 (C_q, COH), 170.54 (C_q, COO), 204.18 (C_q, $\mathit{C}OCH_3$).

MS (DCI, NH_3, 70 eV): *m/z* (%) = 255 (100) [M + NH_3 + NH_4^+], 238 (62) [M + NH_4^+].

1-Cyclopropylethenylcarboxylates 24; General Procedure
In a sealed Schlenk tube were placed cyclopropylethyne (**22**), the carboxylic acid, and the catalyst $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ (**A**) in degassed toluene under an inert atmosphere and the mixture was heated at 50–80 °C for 7–44 h. After cooling to r.t., the mixture was diluted with Et_2O or CH_2Cl_2 (100 mL), washed with 1 M NaOH (15 mL), and dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The products were purified by Kugelrohr distillation in vacuo or by column chromatography (silica gel).

1-Cyclopropylethenyl Pentanoate (24c)
Using **22** (331 mg, 5.00 mmol), pentanoic acid (**2c**, 511 mg, 5.00 mmol), and **A** (23 mg, 0.5 mol%) in toluene (2.5 mL) and heating at 80 °C for 7 h; chromatography (silica gel, PE–Et_2O, 20:1) gave **24c** (553 mg, 66%) as a colorless oil; R_f = 0.50 (PE–Et_2O, 10:1).

IR (neat): 1757 (C=O), 1653 (C=C), 1150 (C–O), 1091 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.51–0.72 (m, 4 H, cPr-H), 0.91 (t, ^3J = 7.3 Hz, 3 H, H5), 1.26–1.70 (m, 5 H, H3, H4, cPr-H), 2.35 (t, ^3J = 7.1 Hz, 2 H, H2), 4.63 (d, ^2J = 1.7 Hz, 1 H, H_A), 4.75 (d, ^2J = 1.7 Hz, 1 H, H_B).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 5.39 (–, 2 C, cPr-C), 13.65, 13.74 (+, cPr-C, C5), 22.16 (–, C4), 26.96 (–, C3), 34.00 (–, C2), 99.55 (–, C2′), 156.60 (C_q, C1′), 171.95 (C_q, COO).

MS (70 eV): *m/z* (%) = 168 (3) [M^+], 153 (2) [$M^+ - CH_3$], 140 (4) [$M^+ - C_2H_4$], 126 (2) [$M^+ - C_3H_6$], 112 (1) [$M^+ - C_4H_8$], 85 (100) [$C_4H_9CO^+$], 69 (15) [$C_4H_9C^+$], 57 (62) [$C_4H_9^+$], 41 (18) [$C_3H_5^+$].

HRMS: calcd for $C_{10}H_{16}O_2$: 168.1150.

1-Cyclopropylethenyl Cyclopropanecarboxylate (24e)
Using **22** (291 mg, 4.40 mmol), cyclopropanecarboxylic acid (**2e**, 344 mg, 4.00 mmol), and **A** (19 mg, 0.5 mol%) in toluene (2 mL) and heating at 80 °C for 15 h; distillation gave **24e** (497 mg, 82%) as a colorless oil; bp 90 °C/0.2 mbar.

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IR (neat): 1746 (C=O), 1657 (C=C), 1263 (C–O), 1230 (C–O), 1148 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.50–0.64 (m, 4 H, cPr-H), 0.82–1.00 (m, 4 H, cPr-H), 1.46–1.75 (m, 2 H, cPr-H), 4.58 (s, 1 H, H_A), 4.69 (s, 1 H, H_B).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 5.44 (–, 2 C, cPr-C), 8.84 (–, 2 C, cPr-C), 12.87 (+, cPr-C), 13.83 (+, cPr-C), 99.53 (–, C2′), 156.61 (C_q, C1′), 173.03 (C_q, COO).

MS (70 eV): *m/z* (%) = 152 (3) [M^+], 69 (100) [$C_3H_5CO^+$], 41 (24) [$C_3H_5^+$].

HRMS: calcd for $C_9H_{12}O_2$: 152.0837.

Anal. Calcd for $C_9H_{12}O_2$ (152.2): C, 71.03; H, 7.95. Found: C, 71.24; H, 7.75.

1-Cyclopropylethenyl Pivalate (24g)

Using **22** (291 mg, 4.40 mmol), pivalic acid (**2g**, 409 mg, 4.00 mmol), and **A** (19 mg, 0.5 mol%) in toluene (2 mL) and heating at 80 °C for 15 h; distillation gave **24g** (512 mg, 76%) as a colorless oil; bp 100 °C/0.2 mbar.

IR (neat): 1749 (C=O), 1657 (C=C), 1285 (C–O), 1256 (C–O), 1131 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.47–0.60 (m, 4 H, cPr-H), 1.15 [s, 9 H, $C(CH_3)_3$], 1.45 (m_c, 1 H, cPr-H), 4.51 (d, ^3J = 1.6 Hz, 1 H, H_A), 4.65 (dd, ^2J = 1.6 Hz, ^4J = 0.47 Hz, 1 H, H_B).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 5.19 (–, 2 C, cPr-C), 13.81 (+, cPr-C), 27.03 [+, 3 C, $C(CH_3)_3$], 39.01 [C_q, $C(CH_3)_3$], 99.26 (–, C2′), 156.47 (C_q, C1′), 176.40 (C_q, COO).

MS (70 eV): *m/z* (%) = 168 (10) [M^+], 125 (10) [$M^+ - C_3H_7$], 85 (40) [$C_4H_9CO^+$], 69 (35) [$C_4H_9C^+$], 57 (100) [$C_4H_9^+$], 41 (20) [$C_3H_5^+$].

HRMS: calcd for $C_{10}H_{16}O_2$: 168.1150.

1-Cyclopropylethenyl Benzoate (24h)

Using **22** (331 mg, 5.00 mmol), benzoic acid (**2h**, 611 mg, 5.00 mmol), and **A** (45 mg, 1.0 mol%) in toluene (2.5 mL) and heating at 80 °C for 44 h; and chromatography (silica gel, PE–Et_2O, 20:1) gave **24h** (911 mg, 97%) as a colorless oil; R_f = 0.55 (PE–Et_2O, 10:1).

IR (neat): 1736 (C=O), 1658 (C=C), 1272 (C–O), 1235 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.60–0.77 (m, 4 H, cPr-H), 1.64 (m_c, 1 H, cPr-H), 4.79 (d, ^2J = 1.6 Hz, 1 H, H_A), 4.87 (dd, ^2J = 1.6 Hz, ^4J = 0.54 Hz, 1 H, H_B), 7.38–7.63 (m, 3 H, Ar-H), 7.95–8.11 (m, 2 H, Ar-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 5.47 (–, 2 C, cPr-C), 13.88 (+, cPr-C), 99.87 (–, C2′), 128.35 (+, 2 C, Ar-C), 129.56 (C_q, Ar-C), 129.79 (+, 2 C, Ar-C), 133.21 (+, Ar-C), 156.63 (C_q, C1′), 164.61 (C_q, COO).

MS (70 eV): *m/z* (%) = 188 (1) [M^+], 160 (4) [$M^+ - C_2H_4$], 105 (100) [$PhCO^+$], 77 (36) [Ph^+], 41 (2) [$C_3H_5^+$].

HRMS: calcd for $C_{12}H_{12}O_2$: 188.0837.

Anal. Calcd for $C_{12}H_{12}O_2$ (188.2): C, 76.57; H, 6.43. Found: C, 76.75; H, 6.56.

1-Cyclopropylethenyl Acetate (24b)

A mixture of **22** (2.64 g, 40.0 mmol), AcOH (**2b**, 1.80 g, 30.0 mmol), and [$Ru(CH_2C(CH_3)CH_2)_2$(dppb)] (**C**) (50 mg, 0.33 mol%) without solvent was heated at 50 °C for 12 h. After cooling to r.t., the crude product was taken up in Et_2O (100 mL), the soln was then washed with 1 M NaOH (15 mL) and dried ($MgSO_4$). After evaporation of the solvent under reduced pressure and distillation of the residue, **24b** (3.56 g, 94%) was obtained as a colorless oil; bp 87–89 °C.

IR (neat): 1761 (C=O), 1658 (C=C), 1230 (C–O), 1196 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.51–0.76 (m, 4 H, cPr-H), 1.52 (m_c, 1 H, cPr-H), 2.11 (s, 3 H, CH_3), 4.63 (d, ^2J = 1.6 Hz, 1 H, C2′), 4.74 (d, ^2J = 1.6 Hz, 1 H, C2′).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 5.34 (–, 2 C, cPr-C), 13.65 (+, cPr-C), 20.75 (+, CH_3), 99.55 (–, C2′), 156.63 (C_q, C1′), 168.88 (C_q, C=O).

MS (70 eV): *m/z* (%) = 126 (8) [M^+], 98 (10) [$M^+ - C_2H_4$], 84 (100), 69 (71), 43 (98) [CH_3CO^+], 41 (19) [$C_3H_5^+$].

HRMS: calcd for $C_7H_{10}O_2$: 126.0680.

(*Z*)-2-Cyclopropylethenyl Carboxylates 23; General Procedure

In a sealed Schlenk tube cyclopropylethyne (**22**), the carboxylic acid, and the catalyst [$Ru(CH_2C(CH_3)CH_2)_2$(dppb)] (**C**) were dissolved in degassed toluene under an inert atmosphere and the mixture was heated at 55–80 °C for 4–21 h. After cooling to r.t. the mixture was diluted with Et_2O or CH_2Cl_2 (100 mL), the soln was washed with 1 M NaOH (15 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The products were purified by Kugelrohr distillation in vacuo or by column chromatography (silica gel).

(*Z*)-2-Cyclopropylethenyl Pentanoate (23c)

Using **22** (331 mg, 5.00 mmol), pentanoic acid (**2c**, 511 mg, 5.00 mmol), and **C** (32 mg, 1.0 mol%) and heating without solvent at 65 °C for 15 h; chromatography (silica gel, PE–Et_2O, 30:1) gave **23c** (814 mg, 97%) as a colorless oil; R_f = 0.50 (PE–Et_2O, 5:1).

IR (neat): 1744 (C=O), 1654 cm^{-1} (C=C).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.36 (m_c, 2 H, cPr-H), 0.75 (m_c, 2 H, cPr-H), 0.90 (t, ^3J = 7.3 Hz, 3 H, H4), 1.27–1.47 (m, 2 H, H3), 1.54–1.82 (m, 3 H, H2, cPr-H), 2.40 (t, ^3J = 7.3 Hz, 2 H, H1), 4.28 (dd, ^3J = 6.4 Hz, ^3J = 9.8 Hz, 1 H, H2′), 7.02 (d, ^3J = 6.4 Hz, 1 H, H1′).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 6.79 (–, 2 C, cPr-C), 7.35 (+, cPr-C), 13.68 (+, C4), 22.20 (–, C3), 26.79 (–, C2), 33.79 (–, C1), 118.21 (+, C2′), 133.59 (+, C1′), 170.95 (C_q, COO).

(*Z*)-2-Cyclopropylethenyl Benzoate (23h)

Using **22** (331 mg, 5.00 mmol), benzoic acid (**2h**, 611 mg, 5.00 mmol), and **C** (32 mg, 1.0 mol%) in toluene (5 mL) with heating at 70 °C for 6 h; chromatography (silica gel, PE–Et_2O, 10:1) gave **23h** (921 mg, 98%) as a colorless oil; R_f = 0.50 (PE–Et_2O, 5:1).

IR (neat): 1729 (C=O), 1669 (C=C), 1268 cm^{-1} (C–O).

^1H NMR (200 MHz, $CDCl_3$): δ = 0.45 (m_c, 2 H, cPr-H), 0.81 (m_c, 2 H, cPr-H), 1.90 (m_c, 1 H, cPr-H), 4.43 (dd, ^3J = 6.4 Hz, ^3J = 9.9 Hz, 1 H, H2′), 7.38 (d, ^3J = 6.4 Hz, 1 H, H1′), 7.42–7.59 (m, 3 H, Ar-H), 8.08–8.15 (m, 2 H, Ar-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 6.96 (–, 2 C, cPr-C), 7.63 (+, cPr-C), 119.00 (+, C2′), 128.44 (+, 2 C, Ar-C), 129.32 (C_q, Ar-C), 129.84 (+, 2 C, Ar-C), 133.34, 133.66 (+, Ar-C, C1′), 163.55 (C_q, COO).

MS (70 eV): *m/z* (%) = 188 (5) [M^+], 105 (100) [$PhCO^+$], 77 [Ph^+], 83 (2) [M^+ – PhCO].

HRMS: calcd for $C_{12}H_{12}O_2$: 188.0837.

Anal. Calcd for $C_{12}H_{12}O_2$ (188.2): C, 76.57; H, 6.43. Found: C, 76.88; H, 6.69.

(*Z*)-2-Cyclopropylethenyl Methoxyacetate (23m)

Using **22** (291 mg, 4.40 mmol), methoxyacetic acid (**2m**, 360 mg, 4.00 mmol), and **C** (26 mg, 1.0 mol%) and heating without solvent

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at 55 °C for 4 h; Kugelrohr distillation gave **23m** (573 mg, 92%) as a colorless oil; bp 80 °C/0.2 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (m_c, 2 H, cPr-H), 0.74 (m_c, 2 H, cPr-H), 1.69 (m_c, 1 H, cPr-H), 3.44 (s, 3 H, OCH_3), 4.11 (s, 2 H, C*H*$_2$OMe), 4.33 (dd, ^3J = 10.0 Hz, ^3J = 6.3 Hz, 1 H, H2′), 7.03 (d, ^3J = 6.3 Hz, 1 H, H1′).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 6.91 (–, 2 C, cPr-C), 7.41 (+, cPr-C), 59.50 (+, OCH_3), 69.45 (–, *C*H$_2$OMe), 119.35 (+, C2′), 132.98 (+, C1′), 167.58 (C_q, COO).

MS (70 eV): *m*/*z* (%) = 156 (10) [M$^+$], 83 (8) [M$^+$ – MeOCH$_2$CO], 67 (5) [M$^+$ – MeOCH$_2$COO], 45 (100) [CH$_2$OMe].

HRMS: calcd for $C_8H_{12}O_3$: 156.0786.

(*Z*)-2-Cyclopropylethenyl 2,6-Difluorobenzoate (23o)

Using **22** (291 mg, 4.40 mmol), 2,6-difluorobenzoic acid (**2o**, 632 mg, 4.00 mmol), and **C** (26 mg, 1.0 mol%) in toluene (4 mL) and heating at 80 °C for 21 h, Kugelrohr distillation gave **23o** (875 mg, 98%) as a colorless oil; bp 220 °C/0.2 mbar.

IR (neat): 1740 (C=O), 1625 (C=C), 1289 (C–O), 1260 cm^{-1} (C–O).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.38 (m_c, 2 H, cPr-H), 0.76 (m_c, 2 H, cPr-H), 1.82 (m_c, 1 H, cPr-H), 4.44 (dd, ^3J = 10.0 Hz, ^3J = 6.2 Hz, 1 H, H2′), 6.90–7.42 (m, 4 H, H1′, H3, H4, H5).

MS (70 eV): *m*/*z* (%) = 224 (3) [M$^+$], 141 (100) [$C_6H_3F_2CO^+$], 113 (11) [$C_6H_3F_2^+$], 83 (4) [M$^+$ – $C_6H_3F_2CO$], 67 (2) [M$^+$ – $C_6H_3F_2CO_2$].

HRMS: calcd for $C_{12}H_{10}F_2O_2$: 224.0648.

(*Z*)-2-Cyclopropylethenyl 2,6-Dimethoxybenzoate (23p)

Using **22** (291 mg, 4.40 mmol), 2,6-dimethoxybenzoic acid (**2p**, 729 mg, 4.00 mmol), and **B** (26 mg, 1.0 mol%) in toluene (4 mL) and heating at 80 °C for 18 h; chromatography (silica gel, PE–Et_2O, 3:1) followed by Kugelrohr distillation gave **23p** (964 mg, (97%) as a colorless oil; bp 230 °C/0.2 mbar; R_f = 0.40 (PE–Et_2O, 3:1).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.37 (m_c, 2 H, cPr-H), 0.72 (m_c, 2 H, cPr-H), 1.83 (m_c, 1 H, cPr-H), 3.80 (s, 6 H, OCH_3), 4.41 (dd, ^3J = 9.8 Hz, ^3J = 6.3 Hz, 1 H, H2′), 6.55 (d, ^3J = 8.5 Hz, 2 H, H3, H5), 7.16–7.33 (m, 2 H, H1′, H4).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 6.92 (–, 2 C, cPr-C), 7.58 (+, cPr-C), 56.02 (+, 2 C, OCH_3), 103.97 (+, 2 C, C3, C5), 112.19 (C_q, C1), 119.35 (+, C2′), 131.62, 134.15 (+, C4, C1′), 157.76 (C_q, 2 C, C2, C5), 163.79 (C_q, COO).

MS (70 eV): *m*/*z* (%) = 248 (1) [M$^+$], 165 (100) [$C_6H_3(OMe)_2CO^+$], 84 (20).

HRMS: calcd for $C_{14}H_{16}O_4$: 248.1048.

(*Z*)-2-Cyclopropylethenyl 4-Aminobenzoate (23q)

Using **22** (291 mg, 4.40 mmol), 4-aminobenzoic acid (**2q**, 549 mg, 4.00 mmol), and **C** (52 mg, 2.0 mol%) in toluene (20 mL) and heating at 80 °C for 21 h and Kugelrohr distillation gave **23q** (553 mg, 68%) as a colorless oil; bp 220 °C/0.2 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.40 (m_c, 2 H, cPr-H), 0.79 (m_c, 2 H, cPr-H), 1.86 (m_c, 1 H, cPr-H), 4.32–4.40 (m, 3 H, H2′, NH_2), 6.60 (d, ^3J = 8.5 Hz, 2 H, H3, H5), 7.22 (d, ^3J = 6.3 Hz, 1 H, H1′), 7.88 (d, ^3J = 8.5 Hz, 2 H, H2, H6).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 7.05 (–, 2 C, cPr-C), 7.75 (+, cPr-C), 113.88 (+, 2 C, C3, C5), 118.23 (+, C2′), 132.10 (+, 2 C, C2, C6), 132.40 (C_q, C1), 133.92 (+, C1′), 151.80 (C_q, C4), 163.95 (C_q, COO).

MS (70 eV): *m*/*z* (%) = 203 (3) [M$^+$], 120 (100) [$NH_2C_6H_4CO^+$], 92 (28) [$C_6H_4NH_2^+$], 65 (28).

HRMS: calcd for $C_{12}H_{13}NO_2$: 203.0946.

3-Oxopent-1-enyl Benzoate (19h) and 1-Acetylcyclopropyl Benzoate (15h)

In a sealed Schlenk tube 1-ethynylcyclopropanol (**14**, 411 mg, 5.00 mmol), benzoic acid (**2h**, 611 mg, 5.00 mmol), and [Ru(CH$_2$C(CH$_3$)CH$_2$)$_2$(dppe)] **B** (46 mg, 1.5 mol%) were dissolved in toluene (5 mL) and the mixture was heated at 75 °C for 17 h. After cooling to r.t., the mixture was diluted with CH_2Cl_2 (100 mL), washed with 1 M NaOH (15 mL), and dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Column chromatography of the crude product (silica gel, PE–Et_2O, 4:1) gave a mixture of **19h** and **15h** (374 mg, 36%) as a colorless oil; ratio **19h/15h** 2.6:1; R_f = 0.30 (PE–Et_2O, 4:1).

19h

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.3 Hz, 3 H, H5), 2.54 (q, ^3J = 7.3 Hz, 2 H, H4), 6.12 (d, ^3J = 12.8 Hz, 1 H, H2), 7.34–7.96 (m, 5 H, Ar-H), 8.42 (d, ^3J = 12.8 Hz, 1 H, H1).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 8.00 (+, C5), 34.01 (–, C4), 124.23 (+, C2), 128.76 (+, Ar-C), 128.86 (C_q, Ar-C), 130.26 (+, Ar-C), 134.40 (+, Ar-C), 148.56 (+, C1), 162.70 (C_q, COO), 199.93 (C_q, CO).

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