Ruthenium-Catalyzed Transformations of Cyclopropylethylenes

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Dedicated to the late Professor Yoshihiko Ito for his outstanding contribution to synthetic organic chemistry and catalysis

Abstract: The addition of various carboxylic acids to (trans-2-ethoxycyclopropyl)ethyne (1) by catalysis with [Ru(O2CH)(CO)2(PPh3)]2 proceeds regioselectively in the Markovnikov sense with ring opening of the cyclopropyl group to furnish allenylacetalddehyde acyl ethyl acetals 3 in high yields (44–96%, 11 examples). The allenylacetalddehyde 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-aminoethyl)styryl]acetalddehyde acyl ethyl acetals 12 (24–83%, 4 examples). Anti-Markovnikov addition of carboxylic acids to the triple bond in (trans-2-ethoxycyclopropyl)ethylene (1) without ring opening can be brought about under [Ru(CH2CMeCH2)(dpbb)] catalysis to give 2-(trans-2-ethoxycyclopropyl)ethynyl esters 13 (69–92%, 3 examples). (1-Hydroxycyclopropyl)ethyne (14), under catalysis by [Ru(O2CH)(CO)2(PPh3)]2, reacts with carboxylic acids to yield 1-acycteyclpropyl esters 15 (49–74%, 4 examples) by Markovnikov-sense addition and intramolecular transesterification. Anti-Markovnikov- and Markovnikov-sense addition of carboxylic acids to unsubstituted cyclopropylethylene can both be achieved regioselectively under catalysis with [Ru(CH2CMeCH2)2(dpbb)] and [Ru(O2CH)CO2(PPh3)]2 to furnish 2-cyclopropylethynyl esters 23 (68–98%, 5 examples) and 1-cyclopropylethynyl 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. Among the various catalysts employed, relatively simple ruthenium complexes play a pivotal role. Some of their reactions proceed via vinylideneruthenium intermediates with oxidative coupling or cycloisomerization. Particularly interesting reactions are those that take place with skeletal rearrangements accompanied by C–C bond breaking and forming, such as additions to substituted alkynes, enyne metatheses, or reorganizations. Ethynylecyclopropane and its derivatives constitute versatile oligofunctional building blocks that have both enhanced reactivity across their triple bond as well as their three-membered ring. 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.

Among the various ruthenium complexes that were found to catalyze additions of carboxylic acids to alkynes, [Ru(O2CH)(CO)2(PPh3)]2 (A) promotes the regioselective addition of carboxylic acids to terminal alkynes according to the Markovnikov rule. Treatment of the readily available (5 steps, up to 52% overall yield) racemic (trans-2-ethoxycyclopropyl)ethyne (1) with an equimolar amount of acetic acid 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).

Under similar conditions, the reactions of pentanoic acid (2c), undec-10-enolic acid (2d), and cyclopropylenecarboxylic acid (2e) gave the corresponding allenylacetalddehyde acyl ethyl acetals 3c–e in 84%, 92%, and 93% yields, respectively. The treatment of 1 with formic acid (2a) in benzene-d6 (70 °C, 2 h) also led exclusively to the allene 3a, as identified by its 1H and 13C NMR spectra, however, isolation of 3a failed, mainly because of its low boiling point. The addition of succinic acid (2f) to 1 gave the bis-allyllic 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-acetylenbenzoic 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)ethynyl 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, alkynyl double bond, carbonyl, and thiophene moieties in the carboxylic acid. With cyanooacetic acid, however, decomposition occurred, 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 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 1H 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-d₆ 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-ethoxy-penta-1,2-dienes 3 and 1-(trans-2-Ethoxycyclopropyl)ethenyl Esters 4,

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Solvent</th>
<th>[Ru] cat. (mol%)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>a HCO₂H</td>
<td>C₆D₆</td>
<td>0.3</td>
<td>70</td>
<td>2</td>
<td>&gt;95</td>
</tr>
<tr>
<td>b MeCO₂H</td>
<td>C₆H₄</td>
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<td>75</td>
<td>3</td>
<td>96</td>
</tr>
<tr>
<td>c BuCO₂H</td>
<td>C₆H₆</td>
<td>0.2</td>
<td>70</td>
<td>6</td>
<td>84</td>
</tr>
<tr>
<td>d t-BuCO₂H</td>
<td>C₆D₆</td>
<td>1.4</td>
<td>80</td>
<td>24</td>
<td>&lt;2</td>
</tr>
<tr>
<td>e cPrCO₂H</td>
<td>C₆H₄</td>
<td>0.4</td>
<td>70</td>
<td>6</td>
<td>92</td>
</tr>
<tr>
<td>f PhCO₂H</td>
<td>C₆H₄</td>
<td>0.4</td>
<td>70</td>
<td>4</td>
<td>93</td>
</tr>
<tr>
<td>g t-BuCO₂H</td>
<td>C₆H₄</td>
<td>0.4</td>
<td>70</td>
<td>6</td>
<td>62</td>
</tr>
<tr>
<td>h PhCO₂H</td>
<td>C₆H₄</td>
<td>0.4</td>
<td>70</td>
<td>6</td>
<td>58</td>
</tr>
<tr>
<td>i</td>
<td>toluene</td>
<td>1.0</td>
<td>80</td>
<td>18</td>
<td>50</td>
</tr>
<tr>
<td>j</td>
<td>CH₂Cl₂</td>
<td>0.4</td>
<td>70</td>
<td>15</td>
<td>44</td>
</tr>
<tr>
<td>k</td>
<td>C₆H₆</td>
<td>0.4</td>
<td>70</td>
<td>6</td>
<td>64</td>
</tr>
<tr>
<td>l</td>
<td>C₆H₆</td>
<td>0.4</td>
<td>70</td>
<td>6</td>
<td>68</td>
</tr>
<tr>
<td>m</td>
<td>C₆H₆</td>
<td>0.4</td>
<td>70</td>
<td>6</td>
<td>58</td>
</tr>
</tbody>
</table>

a [Ru] cat. = [Ru(O₂CH)(CO)₂(PPh₃)]₂(A).12a
b Isolated yield unless otherwise indicated.
c Yield according to 1H NMR of the crude product.
d Concentration 0.73 molar.
e Concentration 6.1 molar.
f Control experiment without catalyst.
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 \( \eta^2 \)-complex 5 is increased, and this may initiate ring opening of the donor-substituted cyclopropyl group leading to the zwitterionic \( \eta^2 \)-allenylruthenate intermediate 7, the positive end of which is stabilized by the ethoxy group. Nucleophilic attack of a carboxylate ion furnishes the \( \eta^2 \)-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 \( \eta^2 \)-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. 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 \( \pi \)-allylpalladium intermediates that are trapped by added nucleophiles, 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-butyamine (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, [Ru(CH$_2$CMeCH$_2$)$_2$(dppe)] (B) and [Ru(CH$_2$CMeCH$_2$)$_2$(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$_2$CMeCH$_2$)$_2$(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.
Table 2  Heck-Type Couplings of 3b with Iodobenzene and Immediate Trapping of the Formed π-Allylpalladium Species by Primary and Secondary Amines 11

<table>
<thead>
<tr>
<th>Amine</th>
<th>NR'R²</th>
<th>Conditions¹</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Ratio E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>NHr-Bu</td>
<td>55 °C, 45 min</td>
<td>12ba</td>
<td>82</td>
<td>&gt;98:2</td>
</tr>
<tr>
<td>11b</td>
<td>NH Cy</td>
<td>70 °C, 2 h</td>
<td>12bb</td>
<td>46</td>
<td>&gt;98:2</td>
</tr>
<tr>
<td>11c</td>
<td>NHr-Bu</td>
<td>60 °C, 1 h</td>
<td>12bc</td>
<td>24</td>
<td>&gt;98:2</td>
</tr>
<tr>
<td>11d</td>
<td>NBn₂</td>
<td>50 °C, 2 h then 75 °C, 1 h</td>
<td>12bd</td>
<td>83</td>
<td>1:1</td>
</tr>
</tbody>
</table>

¹Pd(OAc)₂ (5 mol%), tri(2-furyl)phosphine (10 mol%), PhI (1 equiv), R¹R²NH 11 (6–8 equiv), DMF.

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

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>R</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>Bu</td>
<td>15</td>
<td>13c</td>
<td>85</td>
</tr>
<tr>
<td>2h</td>
<td>Ph</td>
<td>15</td>
<td>13h</td>
<td>92</td>
</tr>
<tr>
<td>2l</td>
<td>CH₂=CH</td>
<td>4.5</td>
<td>13l</td>
<td>69</td>
</tr>
</tbody>
</table>

¹[Ru] cat. = [Ru(CH₂CMeCH₂)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 alkylene 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 alkynyl esters 13 with their masked acetaldehyde functionality attached to a cyclopropyl ether moiety, represent multifunctional building blocks, which are potentially valuable for organic synthesis. 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-chloropropionate via cyclopropanone ethyl hemiacetal and 1-(trimethylsilyl)ethynylcyclopropanol in 54% overall yield.²¹

Upon reaction with several carboxylic acids (pentanoic, cyclopropanecarboxylic, benzoic, methoxyacetic, and salicylic acid) in the presence of [Ru(O₂CH)(CO)₂(PPh₃)₂]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-acyclocyclopropyl esters 15 is superior to the previously published synthesis by Conia et al.²³ A preparation of tetrahydropyranyl ethers of 1-acyclocyclopropanols has been reported by Salatì et al.²⁴ Since the dppe ligand in the ruthenium complex [Ru(CH₂CMeCH₂)₂(dppe)] (B) has a smaller bite angle than the dppb ligand in complex C used above, it also usually shows different catalytic properties. When a mixture of (1-hydroxycyclopropyl)ethyne (14) and benzoic acid (2h) was treated with the ruthenium complex [Ru(CH₂CMeCH₂)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 cyclopropyloxyl 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 cyclopropylene (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(O₂CH)(CO)₂(PPh₃)₂]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 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](image-url)
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 cyclopropylethylenes 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(O2CH)(CO)2(PPh3)]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 CDCl3 are reported as δ values relative to CHCl3 (δ = 7.26) or benzene (δ = 7.20) as internal references. 13C NMR: Varian VXR-300 (75.5 MHz), Bruker AM 250 (62.9 MHz). Chemical shifts in CDCl3 are reported as δ values relative to CHCl3 (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 CH3 and CH groups, (–) for CH2 groups and (Cq) 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% H2O. TLC analyses were performed using Machery–Nagel pre-coated plates, 0.25 mm, Alugram Sil G/UV 254 (I) and Merck pre-coated silica gel 60 F 254 aluminum sheets (II). All reactions were carried out under an atmosphere of dry N2 or argon in oven- and/or flame-dried glassware. Unless otherwise specified, solns of NH4Cl, NaCl, Na2SO3, and NaHCO3 were sat. aq solns. Benzene, decalin, toluene, THF, and Et2O were distilled from Na/benzophenone. CH2Cl2 was distilled from CaH2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>[Ru] cat.a (mol%)</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>c Bu</td>
<td>A (0.5)</td>
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<td>7</td>
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<tr>
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<td>e cyclopropyl</td>
<td>A (0.5)</td>
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<td>toluene</td>
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<tr>
<td>3</td>
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<td>4</td>
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<td>92 –</td>
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<tr>
<td>12</td>
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<td>21</td>
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<td>98 –</td>
</tr>
<tr>
<td>13</td>
<td>p 2,6-(MeO)2C6H3</td>
<td>C (1.0)</td>
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<td>18</td>
<td>toluene</td>
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<td>14</td>
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</tr>
<tr>
<td>16</td>
<td>h Ph</td>
<td>D (10)</td>
<td>80</td>
<td>39</td>
<td>toluene</td>
<td>59 (1:6)</td>
</tr>
</tbody>
</table>

a [Ru] cat: A: [Ru(O2CH)(CO)2(PPh3)]2, C: [RuCH2CMeCH2)(dppb)]. D: [RuCl2(–cymene)(PPh3)].
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.
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)ethene (1 equiv), carboxylic acid 2 (1 equiv), and [Ru(O2CH)(CO)(PPh3)]2 (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-Ethoxypenta-3,4-dienyl Formate (3a) (0.5 mL) in an NMR tube was heated at 70 °C for 2 h. The 1H 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.

1H NMR (250 MHz, CDCl3): δ = 0.95 (t, J = 7.0 Hz, 3 H, OCH2C¢), 1.69 (s, 3 H, CH3COO), 2.38 (mc, 2 H, H2), 3.31–3.38 (A part of an AB system, m, 1 H, OC=), 3.47 (mc, 2 H, OC), 4.55 (mc, 2 H, H5), 5.06 (mc, 1 H, H3), 5.88 (t, J = 5.4 Hz, 1 H, H1), 7.68 (s, 1 H, HCOO).

13C NMR (62.9 MHz, CDCl3): δ = 14.94 (+, OCH2C¢), 35.27, 53.00 (+, C2), 65.12 (–, OCH2C¢), 75.12 (–, C5), 84.28 (+, C3), 97.30 (+, C1), 160.37 (+, C=O), 209.98 (C¢, 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–Et2O, 20:1) gave 3b (119 mg, 96%) as a colorless oil; Rf = 0.42 (PE–Et2O, 9:1). Compound 4b was not observed.

Experiment II: Using 1 (4.0 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–Et2O, 20:1 to 5:1) gave 3b (5.22 g, 84%) and 4b (512 mg, 8%) as colorless oils.

3b

IR (neat): 1958 (C=C=C), 1735 (C=O), 995 (C=C), 911 cm–1.

IR (neat): (70 eV): m/z (%) = 170 (1) [M+], 188 (9) [M + H+].


MS (70 eV): m/z (%) = 212 (1) [M+], 183 (5) [M – CH2=C=CH2], 115 (53) [M – CH2=C=CH2], 85 (100) [C6H10O4], 57 (43) [C5H7].

RF: 0.81–0.91 (m, 2 H, H3¢), 1.09 (t, J = 7.0 Hz, 3 H, H1¢), 2.07 (s, 3 H, CH2COO), 3.28 (m, 1 H, H2¢), 3.44 (m, 2 H, OCH2CH3), 4.73–4.74 (m, 2 H, H2).

1H NMR (250 MHz, CD3CN): δ = 11.26 (–, C3‘), 14.78 (+, OCH2CH3), 20.13 (+, CH3COO), 20.82 (+, C1‘), 57.12 (+, C2‘), 66.11 (–, OCH2CH3), 101.72 (–, C2), 152.07 (C¢, C1), 168.84 (C¢, C=O).

MS (70 eV): m/z (%) = 170 (2) [M+], 128 (33) [M+ – CH2=CO], 81 (42), 43 (100) [CH2=CO*].

MS (DCI, NH3, 70 eV): m/z (%) = 171 (28) [M+ H+], 188 (100) [M + NH4+].

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–Et2O, 20:1) gave 3c (130 mg, 84%) as a colorless oil; Rf = 0.48 (PE–Et2O, 9:1).

IR (neat): 1959 (C=C=C), 1738 cm–1 (C=O).

IR (neat): (70 eV): m/z (%) = 294 (1) [M+], 265 (3) [M+ – CH2=CH2], 217 (30) [M+ – CH2=CH2], 167 (23) [C6H10O4], 149 (39), 128 (30), 111 (100) [M+ – CH2=CH2COO], 81 (44), 67 (31), 55 (69) [CH2=CH2CH2+], 41 (34) [CH2=CHCH2+].


Anal. Calcd for C18H30O3 (294.4): C, 73.43; H, 10.27. Found: C, 73.60; H, 10.39.

SPECIAL TOPIC
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–Et2O, 20:1) gave 3e (132 mg, 93%) as a colorless oil; Rf = 0.46 (PE–Et2O, 9:1).

IR (neat): 1732 cm–1 (C=O), 1660 cm–1 (C=C).

1H NMR (250 MHz, CD2Cl2): δ = 0.39–0.47 (m, 2 H, cPr-H), 0.84–1.05 (m, 5 H, cPr-H, OCH2CH3), 1.40 (m, 1 H, cPr-H), 2.41 (m, 2 H, H2), 3.32–3.42 (A part of an AB system, m, 1 H, OCH2CH3), 3.56–3.66 (B part of an AB system, m, 1 H, OCH2CH3), 4.55 (m, 2 H, H5), 5.08 (m, 1 H, H3), 9.73 (5 J = 5.4 Hz, 1 H, H1).

13C NMR (62.9 MHz, CD2Cl2): δ = 8.38 (–, C2), 13.11 (+, C3), 15.16 (+, OCH2CH3), 34.53 (–, C2), 64.99 (–, OCH2CH3), 74.96 (–, C5), 84.65 (+, C3), 97.45 (+, C1), 133.11 (+, Ar-C), 166.04 (Cq, C=O), 210.00 (Cq, 2 C, C4).


MS (70 eV) Rf = 0.20 (PE–Et2O, 9:1).

IR (neat): 1732 cm–1 (C=O), 1660 cm–1 (C=C).

1H NMR (250 MHz, CD2Cl2): δ = 0.72 (dt, J = J = 6.3 Hz, 1 H, H3), 0.96 (m, 1 H, H3), 1.03 (t, J = 7.0 Hz, 3 H, OCH2CH3), 1.12 (s, 9 H, C(CH3)3), 1.68 (m, 1 H, H1'), 3.29 (m, 1 H, H2'), 3.37 (q, J = 7.0 Hz, 2 H, OCH2CH3), 4.44 (dd, J = 1.5 Hz, J = 0.8 Hz, 1 H, H2A), 4.66 (dd, J = 1.5 Hz, 1 H, H2B).

13C NMR (62.9 MHz, CD2Cl2): δ = 13.18 (–, C3'), 15.21 (+, OCH2CH3), 22.26 (+, C1'), 27.10 (+, 3 C, C(CH3)3), 33.96 [Cq, C(CH3)3], 59.49 (+, C2'), 66.06 (–, OCH2CH3), 99.44 (–, C2), 155.53 (Cq, C1), 175.73 (Cq, C=O).

MS (70 eV) Rf = 0.21 (1 M'), 167 (1) [M–OC2H5], 111 (2) [M–C(CH3)2CO], 85 (13) [C4H9CO+], 57 (100) [C4H9+].

HRMS: calculated for C14H17O2: 212.1412.


4g
Rf = 0.20 (PE–Et2O, 9:1).

1-Ethoxypenta-3,4-dienyl Benzoate (3f) and 1-(2-Ethoxycylopropyl)benzene (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–Et2O, 20:1) gave 3f (98.1 mg, 58%), and 4h (45.7 mg, 27%) as colorless oils.

1H NMR (250 MHz, CD2Cl2): δ = 0.99 (t, J = 7.0 Hz, 3 H, OCH2CH3), 2.53 (m, 2 H, H2), 3.37–3.44 (A part of an AB system, m, 1 H, OCH2CH3), 3.61–3.68 (B part of an AB system, m, 1 H, OCH2CH3), 4.53 (m, 2 H, H5), 5.15 (m, 1 H, H3), 6.24 (t, J = 5.3 Hz, 1 H, H1), 7.36–7.61 (m, 3 H, Ar-H), 7.96–8.11 (m, 2 H, Ar-H).

13C NMR (62.9 MHz, CD2Cl2): δ = 15.14 (+, OCH2CH3), 34.64 (–, C2), 65.18 (–, OCH2CH3), 75.06 (–, C5), 84.55 (+, C3), 97.84, 98.77 (+, C1), 171.95 (Cq, 2 C, COO), 210.00 (Cq, 2 C, C4).

MS (70 eV) Rf = 0.21 (1 M'), 111 (1) [M–OC2H5], 85 (13) [C4H9CO+], 57 (100) [C4H9+].

HRMS: calculated for C14H17O2: 212.1412.


1-Ethoxypenta-3,4-dienyl Benzoate (3h) and 1-(2-Ethoxy cyclopropyl)benzene (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–Et2O, 20:1) gave 3h (98.1 mg, 58%), and 4h (45.7 mg, 27%) as colorless oils.

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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) [C₆H₄OEt⁺], 77 (23) [Ph⁺].

HRMS: calc'd for C₁₄H₁₉NO₃: 232.1099.


1-Ethoxyenta-3,4-dienyl 5-Methylthiophene-2-carboxylate (3i)

Using 1 (80.0 mg, 0.726 mmol), 5-methylthiophene-2-carboxylic acid (2i, 71.2 mg, 501 μmol) and A (2.6 mg, 0.04 mol%) in benzene (2 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–EtO, 8:1) gave 3i (80.8 mg, 64%) and 4i (31.5 mg, 25%) as colorless oils.

3i

Rᵣ = 0.60 (PE–EtO, 4:1).

IR (neat): 1706 cm⁻¹ (C≡O).

1H NMR (250 MHz, C₆D₆): δ = 0.99 (t, J = 7.0 Hz, 3 H, OCH₃CH₃), 1.91 (s, 3 H, H₁), 2.51 (m, 2 H, H₂), 3.55 (AB system, m, 2 H, OCH₂CH₃), 4.54 (dt, J = 0.45 Hz, 1 H, H₃), 5.14 (tt, J = 7.0 Hz, J = 0.45 Hz, 1 H, H₃), 5.16 (dd, J = 7.3 Hz, 1 H, H₄), 6.95 (dt, J = 7.3 Hz, J = 0.45 Hz, 1 H, H₃), 7.69 (m, 2 H, Ar-H).

3k

Rᵣ = 0.45 (PE–EtO, 4:1).

IR (neat): 1724 (C≡C), 1601 (C≡C), 1233 cm⁻¹ (C≡O).

1H NMR (250 MHz, C₆D₆): δ = 0.70 (q, J = 6.4 Hz, 1 H, H₃), 0.98 (m, 2 H, H₁', H₃'), 1.01 (t, J = 7.0 Hz, 3 H, OCH₃CH₃), 1.86 (s, 3 H, H₆), 3.34–3.42 (m, 2 H, OCH₂CH₃), 4.49 (d, J = 2.1 Hz, 1 H, H₂'), 4.82 (d, J = 7.3 Hz, 1 H, H₂'), 6.24 (d, J = 3.7 Hz, 1 H, H₄), 7.62 (d, J = 3.7 Hz, 1 H, H₃).

HRMS: calc'd for C₁₄H₁₉NO₃: 252.0820.

Anal. Calc'd for C₁₄H₁₉NO₃: 252.3 (C₆H₄S₈O₃), 81.19.

1-Ethoxyenta-3,4-dienyl 2-Iodobenzoate (4j)

Using 1 (80.0 mg, 0.726 mmol), 2-iodobenzoic acid (2j, 901 mg, 3.63 mmol), and A (13 mg, 0.04 mol%) in benzene (6 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–EtO, 8:1) gave 3j (881 mg, 68%) and 4j (238 mg, 18%) as colorless oils.

3j

Rᵣ = 0.65 (PE–EtO, 7:1).

IR (neat): 1958 (C≡C), 1708 cm⁻¹ (C≡O).

1H NMR (250 MHz, C₆D₆): δ = 1.01 (t, J = 7.0 Hz, 3 H, OCH₃CH₃), 2.51 (m, 2 H, H₂), 3.55 (AB system, m, 2 H, OCH₂CH₃), 4.56 (dt, J₃ = 6.9 Hz, J₂ = 2.8 Hz, 2 H, H₅), 5.13 (tt, J₃ = 7.0 Hz, J₂ = 0.45 Hz, 1 H, H₃), 6.15 (t, J = 5.3 Hz, 1 H, H₁), 6.59 (dt, J = 7.0 Hz, J = 1.7 Hz, 1 H, Ar-H), 6.90 (dt, J = 7.0 Hz, J = 1.1 Hz, 1 H, Ar-H), 7.69 (m, 2 H, Ar-H).

13C NMR (62.9 MHz, C₆D₆): δ = 15.22 (+, OCH₃CH₃), 34.44 (–, C₂), 65.48 (–, OCH₂CH₃), 75.35 (–, C₅), 84.57 (+, C₃), 94.64 (C₆), 99.06 (+, C₁), 127.91 (+, Ar-C), 131.13 (+, Ar-C), 132.70 (+, Ar-C), 135.42 (C₆, Ar-C), 141.63 (+, Ar-C), 165.84 (C₆, COO), 209.97 (C₆, CO₂).

MS (70 eV): m/z (%) = 358 (1) [M⁺], 231 (100) [M⁺ – I], 203 (7) [C₆H₄I⁺], 127 (1) [I⁺], 111 (15) [M⁺ – CH₃COO].

HRMS: calc'd for C₁₄H₁₄I₂O: 358.0065.


1-Ethoxyenta-3,4-dienyl 2-Acetylbenezonate (3k)

Using 1 (80.0 mg, 726 μmol), 2-acetylbenzonic acid (2k, 119 mg, 726 μmol), and A (2.6 mg, 0.04 mol%) in benzene (2 mL) and heating at 70 °C for 6 h; chromatography (silica gel, PE–EtO, 8:1) gave 3k (115 mg, 58%) and 4k (20 mg, 10%) as colorless oils.

3k

Rᵣ = 0.40 (PE–EtO, 4:1).

IR (neat): 1757 (C≡C), 1773 (C≡C), 1705 (C≡O), 1266 cm⁻¹ (C≡O).

1H NMR (250 MHz, C₆D₆): δ = 1.02 (t, J = 7.1 Hz, 3 H, OCH₃CH₃), 2.23 (s, 3 H, COOH), 2.54 (m, 2 H, H₂), 3.60 (AB system, m, 2 H, OCH₂CH₃), 4.55 (dt, J = 7.0 Hz, J = 2.8 Hz, 2 H, H₅), 5.16 (tt, J = 7.0 Hz, J = 5.3 Hz, 1 H, H₃), 6.18 (t, J = 5.3 Hz, 1 H, H₁), 6.94–6.99 (m, 3 H, Ar-H), 7.74 (m, 1 H, Ar-H).

13C NMR (62.9 MHz, C₆D₆): δ = 15.12 (+, OCH₃CH₃), 29.49 (+, COOCH₃), 34.40 (–, C₂), 65.49 (–, OCH₂CH₃), 75.11 (–, C₅), 84.52 (+, C₃), 99.15 (+, C₁), 126.79 (+, Ar-C), 129.79 (+, Ar-C), 129.83 (+, Ar-C), 129.85 (C₆, Ar-C), 131.77 (+, Ar-C), 143.28 (C₆, Ar-C), 166.84 (C₆, COO), 200.97 (C₆, COOCH₃), 210.04 (C₆, CO₂).

MS (70 eV): m/z (%) = 177 (1), 147 (100) [C₆H₄O₃⁺], 111 (11) [M⁺ – C₆H₄O₃].

MS (DCI, NH₃, 70 eV): m/z (%) = 292 [M⁺ + NH₄⁺] (58), 566 [2 M + NH₄⁺] (100).

**Z-(5-Alkylamino)-1-ethoxy-4-phenylpent-3-enyl Acetate 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), Pd (1.0 mmol), Pd(OAc)₂ (5 mol%) based on PhI, tri(2-furyl)phosphine (TFP, 10 mol%), and heated at 60 °C for 1 h. After cooling to r.t, the mixture was diluted with CH₂Cl₂ (70 mL), washed with H₂O (5 × 5 mL), and the organic phase dried (MgSO₄). 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-BuNH₂ (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 70 °C for 2 h; chromatography (PE–EtO, 1:1) gave 12bb (160 mg, 46%) as a colorless oil; Rf = 0.25 (PE–EtO, 1:1).

**Z-(5-Dibenzyloxymethyl)-1-ethoxy-4-phenylpent-3-enyl Acetate (12bd)**

Using 3b (200 mg, 1.18 mmol), CyNH₂ (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–EtO, 1:1) gave 12bd (160 mg, 46%) as a colorless oil; Rf = 0.25 (PE–EtO, 1:1).

**HRMS:** calcd for C₂₁H₃₁NO₃: 345.2303.

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**Special Topic**

Ruthenium-Catalyzed Transformations of Cyclopropylenes

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(Z)-2-(trans-2-Ethoxyacyclopropyl)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 cm\(^{-1}\) (C=O), 1635 cm\(^{-1}\) (C=C).

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 solution of cyclopropane ethyl hemiacetal\(^{29}\) in THF (200 mL), and the mixture was stirred at the same temperature for an additional 1 h.

A solution of (trimethylsilyl)ethynyl (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 solution of [trimethylsilyl]ethynyl]lithium was added at 0 °C within 30 min to the solution of chloromagnesium 1-ethoxyacyclopropanolate described above, and the mixture was stirred at 40 °C for 17 h. Then, the mixture was diluted with CH\(_2\)Cl\(_2\) (50 mL), and 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-l[(trimethylsilyl)ethynyl]cyclopropanol (64.42 g, 87%); bp 81 °C/12 mbar.

To a soln of NH\(_2\)F (2.2 g, 0.60 mol) in MeOH (30 mL) and H\(_2\)O (10 mL) was added 1-l[(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 (17.0 g, 80%); bp 48–50 °C/25 mbar.

1-Hexynylcyclopropanol (14)\(^{31}\) was obtained by the procedure described above, followed by the addition of a solution of trimethylsilyl chloride (5.0 g, 0.047 mol) in Et\(_2\)O (10 mL) and the mixture was stirred at r.t. for 1 h. Then, 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.

1-Acetylcyclopentadienyl Pentanoate (15e)

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 15e (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, CDCl₃): δ = 0.78 (t, J = 7.2 Hz, 3 H, H₃), 0.99 (AA' part of an ABB'B system, m, 2 H, cPr-H), 1.35 (BB' part of an ABB'B system, m, 2 H, cPr-H), 1.14–1.49 (m, 4 H, H3, H2), 1.95 (s, 3 H, CO₂CH₃), 2.19 (t, J = 7.2 Hz, 2 H, H).

13C NMR (50.3 MHz, CDCl₃): δ = 13.55 (+, C4), 17.25 (–, 2 C, cPr-C), 22.10 (–, C3), 25.16 (+, CO₂CH₃), 26.68 (–, C2), 33.59 (–, C1), 63.65 (C₉O, cPr-C), 173.70 (CO₂, CO), 204.53 (C₉O, COCH₃).

MS (70 eV): m/z % = 141 (56) [M⁺ – CH₂O⁺], 85 (100) [C₃H₅CO⁺], 57 (63) [C₄H₅⁺], 43 (12) [CH₂O⁺].

MS (DCI, NH₃, 70 eV): m/z % = 386 (5) [2 M + NH₄⁺], 219 (58) [M + NH₄⁺ + NH₄⁺], 202 (100) [M + NH₄⁺], 185 (3) [M⁺].

1-Acetylcyclopentadienyl Propylenecarboxylic Acid (15e)

Using 14 (241 mg, 2.94 mmol), propylenecarboxylic acid (2c, 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, CDCl₃): δ = 0.77–0.92 (m, 4 H, cPr-H), 1.06 (AA' part of an ABB'B system, m, 2 H, cPr-H), 1.35 (BB' part of an ABB'B system, m, 2 H, cPr-H), 1.50–1.62 (m, 1 H, cPr-H), 2.01 (s, 3 H, CH₃).

13C NMR (50.3 MHz, CDCl₃): δ = 8.80 (–, 2 C, cPr-C), 12.64 (+, cPr-C), 17.49 (–, 2 C, cPr-C), 25.37 (+, CH₂O), 63.84 (C₉O, cPr-C), 174.96 (CO₂, CO), 205.09 (C₉O, COCH₃).

MS (70 eV): m/z % = 125 (18) [M⁺ – CH₂O⁺], 69 (100) [C₄H₅CO⁺], 41 (41) [C₄H₅⁺].

MS (DCI, NH₃, 70 eV): m/z % = 354 (2) [2 M + NH₄⁺], 203 (29) [M + NH₄⁺ + NH₄⁺], 186 (100) [M + NH₄⁺].

1-Acetylcyclopentadienyl 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=O).

1H NMR (200 MHz, CDCl₃): δ = 1.21 (AA' part of an ABB'B system, m, 2 H, cPr-H), 1.56 (BB' part of an ABB'B system, m, 2 H, cPr-H), 2.11 (s, 3 H, CH₃), 7.33–7.51 (m, 3 H, Ar-H), 7.96–8.00 (m, 2 H, Ar-H).

13C NMR (50.3 MHz, CDCl₃): δ = 16.49 (–, 2 C, cPr-C), 25.50 (+, CH₂O), 44.05 (C₈O, cPr-C), 128.59 (+, 2 C, Ar-C), 129.71 (C₈O, cPr-C), 129.82 (+, 2 C, Ar-C), 133.69 (+, Ar-C), 166.68 (C₈O, CO), 204.76 (C₈O, COCH₃).

MS (70 eV): m/z % = 161 (16) [M⁺ – CH₂O⁺], 105 (100) [PhCO⁺], 77 (28) [Ph⁺].

MS (DCI, NH₃, 70 eV): m/z % = 462 (4) [2 M + NH₄⁺], 239 (100) [M + NH₄⁺ + NH₄⁺], 222 (72) [M + NH₄⁺], 205 (4) [M⁺].

1-Acetylcyclopentadienyl Methoxymethacetae (15m)

Using 14 (222 mg, 2.70 mmol), methoxymethacetic 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), 1760 (C=O), 1184 (C=O), 1126 cm⁻¹ (C=O).
IR (neat): 1746 (C=O), 1657 (C=C), 1263 (C=O), 1230 (C=O), 1148 cm⁻¹ (C-O).

1H NMR (200 MHz, CDCl₃): 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, H₃), 4.69 (s, 1 H, H₄).

13C NMR (50.3 MHz, CDCl₃): δ = 5.44 (2 C, C₃H₅), 8.84 (2 C, cPr-C), 12.87 (2 C, cPr-C), 13.83 (2 C, cPr-C), 99.53 (Cq, C₂), 156.61 (Cq, C’), 173.03 (COOC), 128.44 (2 C, C₃H₅), 129.32 (Cq, C’), 156.63 (Cq, C’), 163.55 (Cq, C’), 128.44 (2 C, C₃H₅), 133.34 (2 C, C₃H₅), 133.66 (2 C, C₃H₅), 163.55 (Cq, COOC).

MS (70 eV): m/z (%) = 152 (3) [M⁺], 69 (100) [C₆H₄O⁺], 41 (24) [C₃H₅].

IR (neat): 1761 (C=O), 1658 (C=C), 1230 (C=O), 1196 cm⁻¹ (C-O).

1H NMR (200 MHz, CDCl₃): δ = 0.51–0.76 (m, 4 H, cPr-H), 1.52 (m, 1 H, cPr-H), 2.11 (s, 3 H, CH₃), 4.63 (d, Jₚ = 1.6 Hz, 1 H, C’), 4.74 (d, Jₚ = 1.6 Hz, 1 H, C’).

13C NMR (50.3 MHz, CDCl₃): δ = 5.34 (2 C, cPr-C), 13.65 (2 C, cPr-C), 20.75 (2 C, CH₃), 99.55 (Cq, C₂), 156.63 (Cq, C’), 168.88 (Cq, C’).

MS (70 eV): m/z (%) = 126 (8) [M⁺], 98 (10) [M⁺ – C₆H₄], 84 (100), 69 (71), 43 (98) [CH₃CO⁺], 41 (19) [CH₃⁺].

HRMS: calcd for C₉H₁₂O₂: 188.0837.


(Z)-2-Cyclopropylethenyl Pentanoates 23 (Special Topic) In a sealed Schlenk tube cyclopropylethane (22), the carbolic acid, and the catalyst [Ru(η₅-C₅H₅)₂(η₆-C₆H₆)][(dpbb)] (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 Et₂O or CH₂Cl₂ (100 mL), the soln was washed with 1 M NaOH (15 mL) and dried (MgSO₄), 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), pentaenoic 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–Et₂O, 30:1) gave 23c (814 mg, 97%) as a colorless oil; Rf = 0.50 (PE–Et₂O, 5:1).

IR (neat): 1744 (C=O), 1654 cm⁻¹ (C=C).

1H NMR (200 MHz, CDCl₃): δ = 0.36 (m, 2 H, cPr-H), 0.75 (m, 2 H, cPr-H), 0.90 (t, Jₚ = 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, Jₚ = 7.3 Hz, 2 H, H₁), 4.28 (dd, Jₚ = 6.4 Hz, Jₚ = 9.8 Hz, 1 H, H₂), 7.02 (d, Jₚ = 6.4 Hz, 1 H, H’).

13C NMR (50.3 MHz, CDCl₃): δ = 6.79 (2 C, cPr-C), 3.75 (2 C, cPr-C), 13.68 (2 C, cPr-C), 22.20 (2 C, cPr-C), 26.79 (2 C, cPr-C), 33.79 (2 C, cPr-C), 118.21 (2 C, cPr-C), 133.59 (2 C, cPr-C), 170.95 (Cq, COOC).

(Z)-2-Cyclopropylethenyl Benzoates 23b 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–Et₂O, 10:1) gave 23b (921 mg, 98%) as a colorless oil; Rf = 0.50 (PE–Et₂O, 5:1).

IR (neat): 1729 (C=O), 1669 (C=C), 1268 cm⁻¹ (C-O).

1H NMR (200 MHz, CDCl₃): δ = 0.45 (m, 2 H, cPr-H), 0.81 (m, 2 H, cPr-H), 1.19 (m, 1 H, cPr-H), 4.43 (dd, Jₚ = 6.4 Hz, Jₚ = 9.9 Hz, 1 H, H₂), 7.38 (d, Jₚ = 6.4 Hz, 1 H, H’), 7.42–7.59 (m, 3 H, Ar-H), 8.08–8.15 (m, 2 H, Ar-H).

13C NMR (50.3 MHz, CDCl₃): δ = 6.96 (2 C, cPr-C), 7.63 (2 C, cPr-C), 119.00 (2 C, cPr-C), 128.44 (2 C, Ar-C), 129.32 (2 C, Ar-C), 133.34 (2 C, Ar-C), 133.66 (2 C, Ar-C), 163.55 (Cq, COOC).

MS (70 eV): m/z (%) = 188 (5) [M⁺], 105 (100) [PhCO⁺], 77 (36) [Ph⁺], 41 (24) [C₃H₅]⁺.

HRMS: calcd for C₁₃H₁₃O₂: 188.0837.

Anal. Calcd for C₁₃H₁₃O₂: 188.232 (82.2); C, 76.57; H, 6.43. Found: C, 76.88; H, 6.69.

(Z)-2-Cyclopropylethenyl Methoxycetate 23m Using 22 (291 mg, 4.40 mmol), methoxycetic acid (2m, 360 mg, 4.00 mmol), and C (26 mg, 1.0 mol%) and heating without solvent
at 55 °C for 4 h; Kugelrohr distillation gave 23m (573 mg, 92%) as a colorless oil; bp 80 °C/0.2 mbar.

1H NMR (200 MHz, CDCl3): δ = 0.35 (m, 2 H, cPr-H), 0.74 (m, 2 H, cPr-H), 1.69 (m, 1 H, cPr-H), 3.44 (s, 3 H, OCH3), 4.11 (s, 2 H, CH2OMe), 4.33 (dd, J = 10.0 Hz, J = 3.3 Hz, 1 H, H2), 7.03 (d, J = 6.3 Hz, 1 H, H1').

13C NMR (50.3 MHz, CDCl3): δ = 6.91 (−, 2 C, cPr-C), 7.41 (+, cPr-C), 59.50 (+, OCH3), 69.45 (−, CH2OMe), 119.35 (+, C2'), 123.98 (+, C1'), 167.58 (Cq, COO).

MS (70 eV): m/z (%): 156 (10) [M]+, 83 (8) [M− − MeOCH3CO], 67 (5) [M− − MeOCH3CO]+, 45 (100) [CH2OMe].

HRMS: calcld for C14H16O4: 248.1048.

(Z)-2-Cyclopropylethyl 2,6-Difluoroanisole (23a)

Using and heating at 80 °C for 18 h; chromatography (silica gel, PE–Et2O, 68%) as a colorless oil; bp 220 °C/0.2 mbar.

Terada, M.; Yamamoto, Y.; Späth, T.; de Meijere, A. 'Cyclopropyl Building Blocks for Organic Synthesis'.


(Z)-2-Cyclopropylethyl 2,6-Dimethoxyanisole (23p)

Using and heating at 80 °C for 18 h; chromatography (silica gel, PE–Et2O, 3:1) followed by Kugelrohr distillation gave 23p (964 mg, 97%) as a colorless oil; bp 230 °C/0.2 mbar; Rf = 0.40 (PE–Et2O, 3:1).

1H NMR (200 MHz, CDCl3): δ = 0.37 (m, 2 H, cPr-H), 0.72 (m, 2 H, cPr-H), 1.83 (m, 1 H, cPr-H), 3.80 (s, 6 H, OCH3), 4.41 (dd, J = 8.9 Hz, J = 6.3 Hz, 1 H, H2'), 6.55 (d, J = 8.5 Hz, 2 H, H3, H5), 7.16–7.33 (m, 2 H, H1, H4).

13C NMR (50.3 MHz, CDCl3): δ = 6.92 (−, 2 C, cPr-C), 7.58 (+, cPr-C), 56.02 (+, 2 C, C3, C5), 103.97 (+, 2 C, C3, C5), 119.19 (+, C2'), 119.35 (+, C2'), 131.62, 134.15 (+, C4, C1'), 157.76 (C, C2, C2, C5), 163.79 (Cq, COO).

MS (70 eV): m/z (%) = 248 (1) [M]+, 165 (100) [CH2(OCH3)Me]+, 84 (20).


(Z)-2-Cyclopropylethyl 4-Aminobenzoate (23q)

Using and heating at 80 °C for 21 h and Kugelrohr distillation gave 23q (374 mg, 36%) as a colorless oil; ratio 19h:15h 2.6:1; Rf = 0.30 (PE–Et2O, 4:1).

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

In a sealed Schlenk tube 1-ethynylecloplopanol (14, 411 mg, 5.00 mmol), benzoic acid (2h, 611 mg, 5.00 mmol), and [Ru(CH2CH2CH2CH3)2(dpppe)] 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 CH2Cl2 (100 mL), washed with 1 M NaOH (15 mL), and dried (MgSO4) and the solvent was evaporated under reduced pressure. Column chromatography of the crude product (silica gel, PE–Et2O, 4:1) gave a mixture of 19h and 15h (374 mg, 36%) as a colorless oil; ratio 19h:15h 2.6:1.


References


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(14) Emme, I.; Bruneau, C.; de Meijere, A.; Dixneuf, P. H.

(10) Salaün, J. R. Y.


(13) The ring closure in this sequence is best performed with LiHMDS, not with LDA. Subsequent complete isomerization of the cis- to the trans-isomer in the initially obtained mixture is then achieved by treatment with LDA for 5 min.

(14) Emme, I.; Bruneau, C.; de Meijere, A.; Dixneuf, P. H. Synlett 2000, 1315.

(15) Possibly, the cyano group participates in the ruthenium-catalyzed reaction, see ref. 3a and original publications cited therein.

