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Ruthenium Catalyzed Rearrangement of Ene-cyclopropenes. Divergent Reaction Pathways

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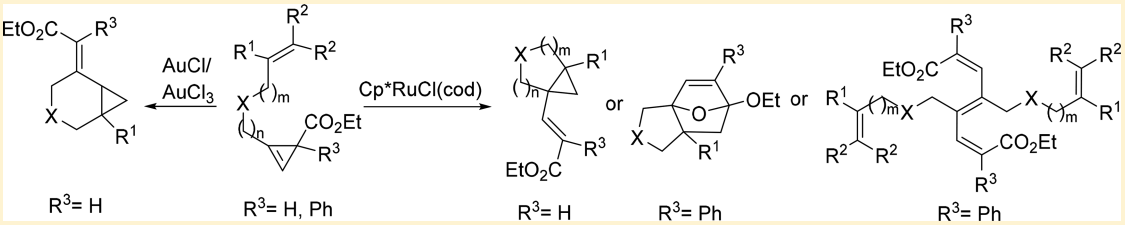
Supporting Information



ABSTRACT: The reaction of ene-cyclopropenes with Cp*RuCl(cod) leads to alkenyl bicyclo[3.1.0]hexanes, bicyclo[4.1.0]-heptanes, and bicyclo[5.1.0]octanes. This reaction involves a reverse regioselectivity in the cyclopropene opening than with gold chlorides. With *gem*-disubstituted cyclopropenes, a novel cycloisomerization based on ring-opening nucleophilic attack and rearrangement is observed. Alternatively, some *gem*-disubstituted cyclopropenes give dimerizations of the intermediate carbene.

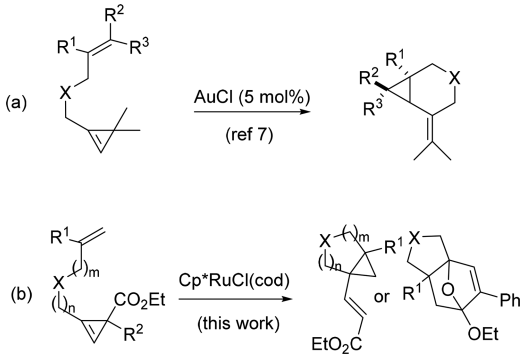
INTRODUCTION

Cyclopropenes are highly strained compounds and therefore are reactive molecules that undergo a wide variety of interesting transformations.[1] They behave in some cases as typical olefins, but in many ways, they share characteristics of alkynes. Thus, the C−H bonds of the vinylic carbons are similar to those of terminal alkynes. This increased π-density of its double bond facilitates the coordination with π-philic transition metals including those with high alkynophilicity. This paves the way for the development of different types of rearrangements,[2] additions,[3] and cycloaddition reactions.[4]

After coordination of various metal complexes, ring-opening of cyclopropenes can occur to generate organometallic species, which are resonance hybrids of metal-stabilized allyl cations and vinyl-metal carbenoids. The ring-opening can occur with two possible regiochemistries. Allyl gold carbocations arising from the ring-opening of cyclopropenes have shown to open mainly to generate the terminal carbene.[5] It has been previously published that these carbenes can cyclopropanate an alkene either inter-[6] or intramolecularly (Scheme 1a).[7] The latter was disclosed by Cossy et al. starting from ene-cyclopropenes where the cycloisomerization proceeded with regioselective ring-opening of the cyclopropene. The reaction gave access to 3-oxa- or 3-azabicyclo[4.1.0]heptanes. The starting isopropenes invariably had a dimethyl substitution, giving isopropylidene containing products.

Herein we show the reactivity of ene-cyclopropenes with different substitution patterns both at the ring and at the olefinic part using ruthenium catalysts. In the presence of Cp*RuCl(cod),[8] we show that the cyclopropene is opened with the reverse regioselectivity with regard to gold catalysts and gives alkenylbicyclo[*n*.1.0]alkanes (Scheme 1b). These

Scheme 1. Regioselectivity in Ene-cyclopropene Rearrangements



products were previously described by Dixneuf et al. from enynes where a mechanism based on metathesis was proposed and supported by DFT calculations.[9] The intermediate carbene formed upon the cyclopropene opening gives the *E*-alkenyl configuration and allows the extension of the method to the synthesis of seven-membered rings. *gem*-Disubstituted cyclopropenes produce novel polycyclic products or dimerization of the intermediate carbene.

RESULTS AND DISCUSSION

Despite their high reactivity, cyclopropenes are readily available and stable. The most general approach for the synthesis of cyclopropenes involves the reaction of alkynes

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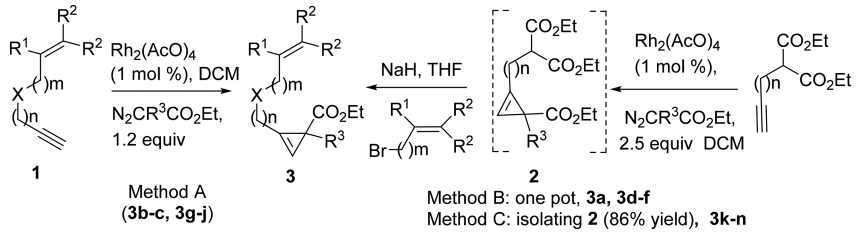
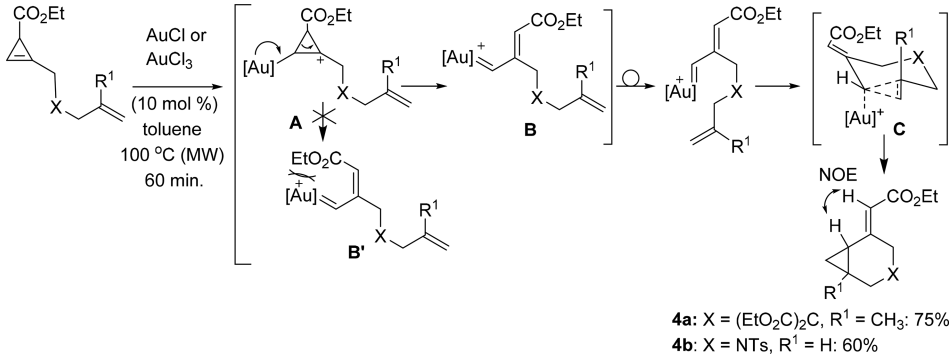
Table 1. Synthesis of Ene-cyclopropenes 3



prod·	X	R^1	R^2	R^3	*n*	*m*	method	yield[a] (%)
3a	$C(CO_2Et)_2$	Me	H	H	1	1	B	73
3b	$C(CO_2Et)_2$	H	H	H	1	1	A	84
3c	$C(CO_2Et)_2$	H	Me	H	1	1	A	71
3d	$C(CO_2Et)_2$	H	H	H	2	1	B	67
3e	$C(CO_2Et)_2$	H	H	H	1	2	B	61
3f	$C(CO_2Et)_2$	H	H	H	1	3	B	48
3g	NTs	H	H	H	1	1	A	64
3h	NTs	Me	H	H	1	1	A	71
3i	NTs	H	H	H	1	2	A	66
3j	NTs	H	H	H	1	3	A	52
3k	$C(CO_2Et)_2$	H	H	Ph	1	1	C	67
3l	$C(CO_2Et)_2$	Me	H	Ph	1	1	C	89
3m	$C(CO_2Et)_2$	H	Me	Ph	1	1	C	81
3n	$C(CO_2Et)_2$	H	H	Ph	1	3	C	41

[a]In pure product.

Scheme 2. Gold Catalyzed Synthesis of 4a–b with Reaction Pathway



with metal carbenoids generated from diazocompounds.[10] We prepared some ene-cyclopropenes by cyclopropenation of either enynes **1** or of alkynes which were further alkenylated (Table 1). This latter procedure was used when the reaction of the diazocompound with the enyne gave mixtures of cyclopropene and cyclopropane products. For the synthesis of products **3k–n**, propargylmalonate was cyclopropenated, and the resulting intermediate **2** was treated with different alkenyl bromides. Overall, the yields were generally good except with 4-pentenyl-containing substrates that gave products **3f**, **3j**, and **3n** in moderate yields.

Using ene-cyclopropenes **3a** and **3g**, we tested their reactivity with three different catalytic systems. Both gold(I) and (III) chlorides gave readily the reorganized bicyclo[4.1.0] derivatives **4a–b** in good yields (Scheme 2). This process involves the coordination of gold with the cyclopropane double bond, producing a carbocationic intermediate **A** which evolves to the gold carbene **B**. The situation of the positive charge in **A** at the most substituted carbon would explain the preference of this metal to form the less substituted carbene **B**.[11] Further intramolecular cyclopropanation yields the final products **4**. This process was described by Cossy et al.,[7] but in their case, dimethyl substituted cyclopropene rings were always used. Thus, we show that our ethoxycarbonylcyclopropene systems give this transformation with total selectivity, as an only isomer of the exocyclic olefin was isolated in good yields. We used either AuCl or $AuCl_3$ for this reaction under MW heating at 100 °C for 60 min. The stereoselective outcome would be a consequence of steric hindrance as in **B′**, which is not present in **B** (Scheme 2). The cyclopropanation follows through the chairlike transition state **C**. **4a–b** were assigned with NOESY experiments.

When using Cp*RuCl(cod), the process gave alkenylbicyclo[3.1.0]hexanes **5** with *E*-configuration. We optimized the conditions for this transformation using substrate **3a** as model (Table 2). Initially, the reaction was tested at room temperature, achieving poor conversions in long reaction times (entries 1 and 2). Under refluxing toluene, it reached total conversion but not good yields (entries 3 and 4). Thus, we used microwave heating, and after tuning up the temperature and reaction times (entries 5–10), we selected as the best conditions for this rearrangement 100 °C in MW

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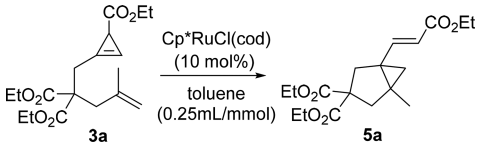
Table 2. Reaction Conditions for the Transformation of 3a into 5a



entry	temp (°C)	time (min)	conv[a]	yield (%)
1	RT	90	20	18
2	RT	300	20	14
3	Δ	90	70	42
4	Δ	300	100	45
5	45 (MW)	20	70	58
6	45 (MW)	90	99	69
7	80 (MW)	60	100	72
8	80 (MW)	10	87	59
9	100 (MW)	10	100	75
10	100 (MW)	5	100	78
11[b]	100 (MW)	10	85	62

[a]By NMR. [b]5 mol % of catalyst was used.

for 5 min, reaching total conversion and a 78% yield. Catalyst loading was kept at 10 mol % as when using 5 mol % (entry 11) results were clearly lower.

These optimized conditions were applied to the whole array of substrates with the results shown in Figure 1. The procedure allows the formation of 5-, 6-, and 7-membered rings fused to the cyclopropane, and yields were generally good. The possibility of building seven-membered rings is interesting and shows this is a wide scope process. On the contrary, dimethyl substituted substrate **3c** did not react under any reaction conditions, not detecting the formation of the expected product **5c**. To our surprise, when using substrates **3k–l**, *gem*-disubstituted at the cyclopropene, we isolated products **6a–b**.

This reaction involves the opening of the cyclopropene ring with the reverse regioselectivity to give carbene **F**. Possibly the initial coordination of the ruthenium with both double bonds (**D**) explains the chemoselectivity as the bulky Cp* and Cl are situated in a less crowded area. Oxidative cycloaddition to the cyclopropane giving **E**, followed by cycloreversion, gives carbene **F**. A final intramolecular cyclopropanation through transition state **G** yields **5** (Scheme 3). Stereoselectivity of the emerging double bond is explained following Dixneuf et al.[9c] We understand that the intermediate **F** is common in the process described by this group. The stereochemistry of the double bond results from the electronic repulsion between the chlorine and the ester groups which favors the opening that lowers better the steric hindrance. This gives the alkenyl an *E*-configuration.

The reaction of **3k** gave, initially, a total decomposition of the starting material. Thus, we lowered the temperature to 50 °C, and we isolated **6a** as the only reaction product in 64% yield. We explain the formation of this structure in Scheme 3. The presence of the phenyl group allowed the formation of carbene **F′** which is preferred to **F** in order to situate this large group at a less hindered position. This arrangement allows the nucleophilic attack of the carbonyl oxygen atom of the ester group to deliver dioxacarbenium ion intermediate **H**. This type of intermediate was proposed by Meyer et al. for a rhodium catalyzed isomerization of cyclopropenylmethyl esters.[12] Rearrangement of **H** into final products **6** would go through transition state **I** and intermediate **J**. Only one isomer of **6** was isolated, and it was assigned using NOE experiments. With substrate **3l**, the reaction at 50 °C gave, on the contrary, the carbene dimer **7a**. However, this substrate allowed heating the process at 100 °C to give **6b** in 69% yield. The intermediate carbene dimerization was the only observed reaction with substrates **3m–n** under any reaction conditions, leading to products **7b–c** in high yields (Scheme 3).

CONCLUSIONS

In summary, we show a diverse reactivity of ene-cyclopropenes under gold and ruthenium catalysis. The transformation of compounds **3** into **5** is an interesting process, allowing the synthesis of 5-, 6-, and 7-membered rings fused to cyclopropanes. The formation of compounds **6** is a novel process, giving highly connected structures that we are currently studying with more substrates.

EXPERIMENTAL SECTION

General. All reactions promoted by microwaves were carried out in an Initiator+ microwave reactor. Reaction progress was monitored by ^{1}H NMR spectra or using analytical thin-layer chromatography (TLC) on silica gel 60 F-254 plate. Visualization was achieved by UV light (254 nm). NMR spectra were recorded on a 400 MHz for ^{1}H,

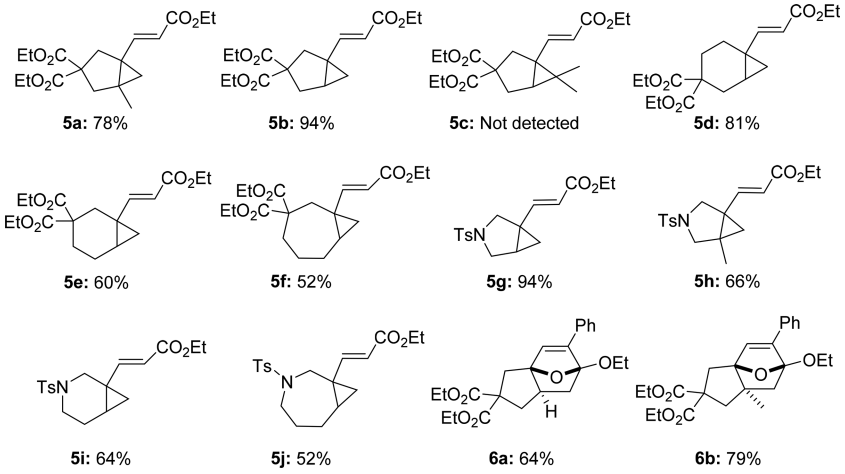


Figure 1. Structures and yields of compounds **5** and **6**.

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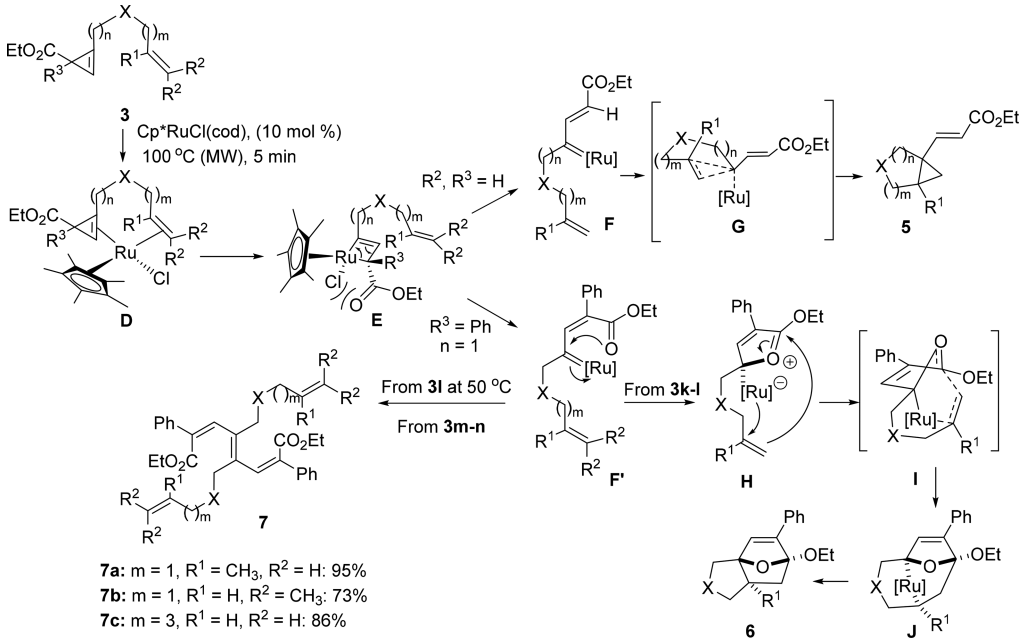
Scheme 3. Reaction Pathways Leading to Products 5, 6, and 7



and 101 MHz for ^{13}C spectrometer. Chemical shifts are reported in δ ppm referenced to chloroform-*d* (δ 7.26 for ^{1}H NMR and δ 77.16 for ^{13}C NMR). All the residues were purified by flash chromatography on silica gel.

Compounds diethyl 2-(prop-2-yn-1-yl)malonate,[13] diethyl 2-allyl-2-(prop-2-yn-1-yl)malonate,[14] **1b**, diethyl 2-(but-3-yn-1-yl)-malonate,[14] *N*-allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide,[15] **1g**, 4-methyl-*N*-(2-methylallyl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide,[16] **1h**, and *N*-(but-3-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide,[17] **1i**, were synthesized as described in the literature.

General Procedure for Alkylation Reactions. To a stirred solution of the starting material (1 equiv) in THF anh. (2.2 mL/mmol was added NaH (1.2 equiv) in portions at 0 °C. Once the addition was completed, the corresponding bromide (1.2 equiv) was added slowly. After the addition was completed, the mixture was allowed to warm up to room temperature and stirred until TLC showed the reaction to be completed. The reaction was then quenched with H_2O (2 mL/mmol), extracted with AcOEt (3 × 2.5 mL/mmol), and the combined organic phases were washed with brine (6 mL/mmol). The organic phase was then dried over $MgSO_4$, filtered, and concentrated under vacuum.

General Procedure for Cyclopropenation Reactions. To a stirred suspension of $Rh_2(AcO)_4$ (0.01 equiv) in DCM anh. (60 mL/mmol) was added a solution of the enyne **1** or the alkyne (1 equiv) in DCM anh. (0.6 mL/mmol) at reflux. After the addition was completed, a solution of the corresponding diazocompound (1.2 equiv. with enynes **1b−c**, **1g−i** (synthesis of **3b**, **3c**, **3g**, **3h**, **3i**, **3j**) or 2.5 equiv with diethyl 2-(prop-2-yn-1-yl)malonate or diethyl 2-(but-3-yn-1-yl)malonate (synthesis of **3a**, **3d**, **3e**, **3f**, and **2**) in DCM anh. (0.8 mL/mmol) was added slowly (5 mL/h). After the addition was completed, the mixture was stirred for another 30 min and then filtrated through a pad of Celite. The filtrate was concentrated under vacuum and purified by flash column chromatography.

Diethyl 2-(3-Methylbut-2-en-1-yl)-2-(prop-2-yn-1-yl)malonate, ***1c.*** It was obtained from diethyl 2-(prop-2-yn-1-yl)malonate (3 g, 15.15 mmol), NaH (436 mg, 18.18 mmol), and 1-bromo-3-methylbut-2-ene (1.67 mL, 16.67 mmol) following the general procedure for alkylation reactions. The spectroscopical data (3.31 g, 12.42 mmol, 82%) matched the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.94−4.87 (m, 1H, C*H*═C), 4.26−4.13 (m, 4H, 2xCH_2CH_3), 2.79−2.75 (m, 4H, CCH_2CH + CCH_2C), 1.99 (t, *J* = 2.7 Hz, 1H, C≡C*H*), 1.69 (s, 3H, CCH_3), 1.66 (s, 3H, CCH_3), 1.25 (t, *J* = 7.1 Hz, 6H, 2xCH_2CH_3).

4-Methyl-N-(pent-4-en-1-yl)-N-(prop-2-yn-1-yl)benzenesulfonamide, ***1j.*** To a solution of 4-methyl-*N*-(prop-2-yn-1-yl)-benzenesulfonamide (1.20 g, 5.73 mmol) in acetone (12.12 mL) were added K_2CO_3 (960 mg, 6.88 mmol) and 5-bromo-1-pentene (0.82 mL, 6.88 mmol) at 0 °C. Then, the mixture was stirred at reflux overnight. Once TLC showed the completion of the reaction, it was quenched with water (15 mL) and extracted with AcOEt (3 × 15 mL). The combined organic phases were then washed with brine (40 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum. The titled compound was isolated as a colorless oil (1.38 g, 4.98 mmol, 73%) after filtration through a pad of silica plugged with Hexane/AcOEt (4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H, Ar), 7.29 (d, *J* = 8.0 Hz, 2H, Ar), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, C*H*═CH_2), 5.08−4.96 (m, 2H, CH═CH_2), 4.13 (d, *J* = 2.4 Hz, 2H, NCH_2C), 3.20 (t, *J* = 7.2 Hz, 2H, NCH_2CH_2), 2.42 (s, 3H, CCH_3), 2.14−2.06 (m, 2H, CH_2CH), 2.01 (t, *J* = 2.5 Hz, 1H, C≡C*H*), 1.68 (p, *J* = 7.5 Hz, 2H, $CH_2CH_2CH_2$); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 143.6 (C), 137.6 (CH), 136.1 (C), 129.6 (2xCH), 127.9 (2xCH), 115.5 (CH_2), 76.8 (C), 73.8 (CH), 46.0 (CH_2), 36.4 (CH_2), 30.8 (CH_2), 26.9 (CH_2), 21.7 (CH_3). IR: 2967, 2929, 1735, 1625 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_2S$ (277.11 g/mol): C, 64.95; H, 6.90%. Found: C, 65.00; H, 7.04%.

Diethyl 2-((3-(Ethoxycarbonyl)-3-phenylcycloprop-1-en-1-yl)-methyl)malonate, ***2a.*** It was obtained from diethyl 2-(prop-2-yn-1-yl)malonate (200 mg, 1.01 mmol) and ethyl 2-diazo-2-phenylacetate (480.25 mg, 2.23 mmol) following the general procedure for cyclopropenation reactions and purified by flash column chromatography (Hexane/AcOEt, 8:1). Colorless oil (314 mg, 0.87 mmol, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.22 (m, 4H, Ar), 7.22−7.16 (m, 1H, Ar), 6.79 (t, *J* = 1.4 Hz, 1H, C═C*H*), 4.22−4.06 (m, 6H, 3xCH_2CH_3), 3.67 (t, *J* = 7.5 Hz, 1H, C*H*CH_2), 3.17 (dd, *J* = 7.5, 1.4 Hz, 2H, CH_2C), 1.23 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.224 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.222 (t, *J* = 7.1 Hz, 3H, CH_2CH_3); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 174.8 (CO), 168.2 (CO), 168.1 (CO), 141.1 (C), 128.2 (2xCH), 128.1 (2xCH), 126.5 (CH), 117.9 (C), 99.9 (CH), 61.9 (2xCH_2), 61.0 (CH_2), 50.0 (CH), 33.5 (C), 24.2 (CH_2), 14.4 (CH_3), 14.1 (2xCH_3). IR (Neat): 2980, 2921, 2840, 1728 cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_6$ (360.16 g/mol): C, 66.65; H, 6.71%. Found: C, 66.83; H, 6.80%.

Diethyl 2-((3-(Ethoxycarbonyl)cycloprop-1-en-1-yl)methyl)-2-(2-methylallyl)malonate, ***3a.*** Diethyl 2-(prop-2-yn-1-yl)malonate (381

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mg, 1.92 mmol) was submitted to the general procedure for cyclopropenation reactions with ethyl diazoacetate (0.76 mL, 4.80 mmol). The crude mixture obtained was then submitted to the general procedure for alkylation reactions with NaH (55.3 mg, 2.30 mmol) and 3-bromo-2-methylprop-1-ene (0.24 mL, 2.30 mmol). The titled compound was purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (475 mg, 1.40 mmol, 73%, 2 steps); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (q, J = 1.5 Hz, 1H, C=C*H*), 4.91−4.87 (m, 1H, C=CH_2), 4.75−4.72 (m, 1H, C=CH_2), 4.25−4.13 (m, 4H, 2xCH_2CH$_3$), 4.11 (q, J = 7.1 Hz, 2H, CH_2CH$_3$), 3.22−3.09 (m, 2H, CH_2C=CH), 2.78 (q, J = 14.1 Hz, 2H, CH_2C=CH$_2$), 2.10 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 1.65 (s, 3H, CCH$_3$), 1.30−1.19 (m, 9H, 3xCH$_2$CH$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8 (CO), 170.6 (CO), 170.5 (CO), 140.1 (C), 116.6 (CH_2), 111.8 (C), 97.7 (CH), 61.8 (CH_2), 61.8 (CH_2), 60.4 (CH_2), 55.9 (C), 40.0 (CH_2), 28.2 (CH_2), 23.4 (CH_3), 19.8 (CH), 14.5 (CH_3), 14.1 (CH_3), 14.1 (CH_3). IR (Neat): 2987, 2928, 1730, 1642 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 63.73; H, 7.57%.

Diethyl 2-Allyl-2-((3-(ethoxycarbonyl)cycloprop-1-en-1-yl)-methyl)malonate, ***3b***. It was obtained from **1b** (2 g, 8.40 mmol) and ethyl diazoacetate (1.26 mL, 10.08 mmol) following the general procedure for cyclopropanation reactions and purified by flash column chromatography (Hexane/AcOEt, 12:1). Product **3b** was isolated with an 18% of diethyl maleate. Colorless oil (2.28 g, 7.06 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (q, J = 1.5 Hz, 1H, C=C*H*), 5.63 (ddt, J = 17.2, 9.6, 7.5 Hz, 1H, C*H*=CH$_2$), 5.16−5.08 (m, 2H, CH=CH_2), 4.25 (q, J = 7.2 Hz, 2H, CH_2CH$_3$), 4.20 (q, J = 7.1 Hz, 4H, 2xCH_2CH$_3$), 3.17−3.05 (m, 2H, CCH_2C), 2.81−2.67 (m, 2H, CCH_2CH=), 2.11 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 1.28−1.21 (m, 9H, 3xCH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.8 (CO), 170.2 (CO), 170.1 (CO), 131.9 (CH), 120.0 (CH_2), 111.5 (C), 97.7 (CH), 61.8 (CH_2), 61.81 (CH_2), 60.5 (CH_2), 56.3 (C), 36.9 (CH_2), 28.2 (CH_2), 19.8 (CH), 14.5 (CH_3), 14.2 (CH_3), 14.2 (CH_3). IR (Neat): 2983, 2929, 1731, 1643 cm^{-1}. A small sample was purified by semipreparative HPLC for microanalysis: Anal. Calcd for $C_{17}H_{24}O_6$ (324.16 g/mol): C, 62.95; H, 7.46%. Found: C, 63.01; H, 7.57%.

Diethyl 2-((3-(Ethoxycarbonyl)cycloprop-1-en-1-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate, ***3c***. It was obtained from **1c** (3.31 g, 11.8 mmol) and ethyl diazoacetate (1.77 mL, 14.16 mmol) following the general procedure for cyclopropenation reactions and purified by flash column chromatography (Hexane/AcOEt, 9:1). Product **3c** was isolated with an 11% of diethyl maleate. Colorless oil (2.93 g, 8.34 mmol, 71%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (q, J = 1.5 Hz, 1H, C=C*H*CH), 4.94 (t, J = 7.6 Hz, 1H, CH$_2$C*H*C), 4.25 (q, J = 7.1 Hz, 2H, CH_2CH$_3$), 4.21−4.14 (m, 4H, CH_2CH$_3$), 3.15−3.02 (m, 2H, CCH_2C), 2.77−2.60 (m, 2H, CH_2CH), 2.09 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 1.68 (s, 3H, CCH_3), 1.58 (s, 3H, CCH_3), 1.27−1.20 (m, 9H, 3xCH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.9 (CO), 170.5 (CO), 170.4 (CO), 136.6 (C), 117.3 (CH), 111.8 (C), 97.6 (CH), 61.7 (CH_2), 61.8 (CH_2), 60.4 (CH_2), 56.6 (C), 31.2 (CH_2), 28.2 (CH_2), 26.2 (CH_3), 19.8 (CH), 18.1 (CH_3), 14.5 (CH_3), 14.2 (CH_3), 14.1 (CH_3). IR (Neat): 2979, 2926, 1730, 1642 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_6$ (352.19 g/mol): C, 64.75; H, 8.01%. Found: C, 64.87; H, 7.85%.

Diethyl 2-Allyl-2-(2-(3-(ethoxycarbonyl)cycloprop-1-en-1-yl)-ethyl)malonate, ***3d***. Diethyl 2-(but-3-yn-1-yl)malonate (700 mg, 3.30 mmol) was submitted to the general procedure for cyclopropenation reactions with ethyl diazoacetate (1.30 mL, 8.25 mmol). The crude mixture obtained was then submitted to the general procedure for alkylation reactions with NaH (95 mg, 3.96 mmol) and allyl bromide (0.34 mL, 3.96 mmol). The titled compound was purified by flash column chromatography (Hexane/AcOEt, 8:1). Colorless oil (748 mg, 2.21 mmol, 67%, 2 steps); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (q, J = 1.5 Hz, 1H, C=C*H*), 5.64 (ddt, J = 17.5, 10.2, 7.4 Hz, 1H, C*H*=CH$_2$), 5.17−5.08 (m, 2H, CH=CH_2), 4.24−4.07 (m, 6H, 3xCH_2CH$_3$), 2.67 (d, J = 7.4 Hz, 2H, CH_2CH), 2.50−2.41 (m, 2H, CH_2C=CH), 2.17 (d, J = 8.2 Hz, 2H, CH_2CH$_2$C=CH), 2.14 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 1.25 (t, J = 7.0 Hz, 9H, 3xCH$_2$CH_3); ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 176.3 (CO), 170.9 (CO), 169.9 (CO), 132.2 (CH), 119.5 (CH_2), 114.9 (C), 95.1 (CH), 61.5 (2xCH$_2$), 60.4 (CH_2), 57.0 (C), 37.4 (CH_2), 29.6 (CH_2), 20.4 (CH_2), 20.0 (CH), 14.5 (CH_3), 14.2 (2xCH$_3$). IR (Neat): 2975, 2934, 1734, 1637 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 63.73; H, 7.87%.

Diethyl 2-(But-3-en-1-yl)-2-((3-(ethoxycarbonyl)cycloprop-1-en-1-yl)methyl)malonate, ***3e***. Diethyl 2-(prop-2-yn-1-yl)malonate (500 mg, 2.52 mmol) was submitted to the general procedure for cyclopropenation reactions with ethyl diazoacetate (1.00 mL, 6.30 mmol). The crude mixture obtained was then submitted to the general procedure for alkylation reactions with NaH (72.6 mg, 3.05 mmol) and 4-bromobut-1-ene (0.32 mL, 3.02 mmol). The titled compound was purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (520 mg, 1.54 mmol, 61%, 2 steps); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (q, J = 1.5 Hz, 1H, C=C*H*), 5.77 (ddt, J = 16.6, 10.1, 6.3 Hz, 1H, C*H*=CH$_2$), 5.03 (dq, J = 17.1, 1.5 Hz, 1H, CH=CH_2 (*trans*)), 4.97 (dq, J = 10.2, 1.3 Hz, 1H, CH=CH_2 (*cis*)), 4.31−4.03 (m, 6H, 3xCH_2CH$_3$), 3.2−3.09 (m, 2H, CH_2C=CH), 2.24−1.80 (m, 4H, 2xCH_2CH_2), 2.11 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 1.30−1.21 (m, 9H, 3xCH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.7 (CO), 170.6 (CO), 170.5 (CO), 137.4 (CH), 115.4 (CH_2), 111.5 (C), 97.7 (CH), 61.8 (CH_2), 61.7 (CH_2), 60.4 (CH_2), 56.3 (C), 31.7 (CH_2), 28.5 (CH_2), 28.5 (CH_2), 19.8 (CH), 14.5 (CH_3), 14.2 (CH_3), 14.1 (CH_3). IR (Neat): 2980, 2923, 1732, 1630 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 64.08; H, 7.90%.

Diethyl 2-((3-(Ethoxycarbonyl)cycloprop-1-en-1-yl)methyl)-2-(pent-4-en-1-yl)malonate, ***3f***. Diethyl 2-(prop-2-yn-1-yl)malonate (425 mg, 2.14 mmol) was submitted to the general procedure for cyclopropenation reactions with ethyl diazoacetate (0.85 mL, 5.35 mmol). The crude mixture obtained was then submitted to the general procedure for alkylation reactions with NaH (61.7 mg, 2.57 mmol) and 5-bromopent-1-ene (0.27 mL, 2.57 mmol). The titled compound was purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (361 mg, 1.03 mmol, 48%, 2 steps); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (q, J = 1.5 Hz, 1H, C=C*H*), 5.76 (ddt, J = 16.9, 10.1, 6.6 Hz, 1H, C*H*=CH$_2$), 5.00 (dq, J = 17.3, 1.8 Hz, 1H, CH=CH_2 (*trans*)), 4.96 (ddd, J = 10.2, 3.2, 1.3 Hz, 1H, CH=CH_2 (*cis*)), 4.27−4.04 (m, 6H, 3xCH_2CH$_3$), 3.24−3.06 (m, 2H, CH_2C=CH), 2.10 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 2.09−1.84 (m, 4H, CH_2CH_2CH_2), 1.35−1.16 (m, 2H of CH$_2$CH$_2$CH$_2$ + 9H of 3xCH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.8 (CO), 170.7 (CO), 170.6 (CO), 138.1 (CH), 115.2 (CH_2), 111.5 (C), 97.6 (CH), 61.7 (CH_2), 61.7 (CH_2), 60.4 (CH_2), 56.5 (C), 33.8 (CH_2), 31.9 (CH_2), 28.4 (CH_2), 23.5 (CH_2), 19.8 (CH), 14.5 (CH_3), 14.2 (CH_3), 14.1 (CH_3). IR (Neat): 2990, 2932, 1731, 1642 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_6$ (352.19 g/mol): C, 64.75; H, 8.01%. Found: C, 64.59; H, 7.88%.

Ethyl 2-(((N-Allyl-4-methylphenyl)sulfonamido)methyl)cycloprop-2-ene-1-carboxylate, ***3g***. It was obtained from **1g** (300 mg, 1.20 mmol) and ethyl diazoacetate (181 μL, 1.44 mmol) following the general procedure for cyclopropanation reactions and purified by flash column chromatography (Hexane/AcOEt, 8:1). Pale yellow oil (258 mg, 0.77 mmol, 64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H, Ar), 7.29 (d, J = 8.2 Hz, 2H, Ar), 6.18 (q, J = 1.5 Hz, 1H, C=C*H*), 5.71 (ddt, J = 17.3, 10.0, 6.4 Hz, 1H, C*H*=CH$_2$), 5.24−5.18 (m, 2H, CH=CH_2), 4.39 (d, J = 1.6 Hz, 2H, CH_2C), 4.14−4.03 (m, 2H, CH_2CH$_3$), 3.87 (d, J = 6.5 Hz, 2H, CH_2CH), 2.43 (s, 3H, CCH_3), 2.01 (d, J = 1.4 Hz, 1H, C*H*CO$_2$), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.2 (CO), 143.7 (C), 137.0 (C), 132.2 (CH), 129.8 (2xCH), 127.6 (2xCH), 120.1 (CH_2), 110.7 (C), 98.8 (CH), 60.6 (CH_2), 49.9 (CH_2), 42.0 (CH_2), 21.7 (CH_3), 20.5 (CH), 14.5 (CH_3). IR (Neat): 2985, 2923, 2849, 1725, 1640 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4S$ (335.12 g/mol): C, 60.88; H, 6.31%. Found: C, 60.72; H, 6.12%.

Ethyl 2-(((4-Methyl-N-(2-methylallyl)phenyl)sulfonamido)-methyl)cycloprop-2-ene-1-carboxylate, ***3h***. It was obtained from **1h** (724 mg, 2.75 mmol) and ethyl diazoacetate (0.42 mL, 3.34 mmol) following the general procedure for cyclopropanation reactions and purified by flash column chromatography (Hexane/

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AcOEt, 9:1). Pale yellow oil (679 mg, 1.95 mmol, 71%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H, Ar), 7.29 (d, J = 8.3 Hz, 2H, Ar), 6.05 (q, J = 1.6 Hz, 1H, C=C*H*), 4.94 (s, 1H, C=CH_2), 4.89 (s, 1H, C=CH_2), 4.42−4.28 (m, 2H, CH_2C=CH), 4.11−4.03 (m, J = 7.1, 3.6 Hz, 2H, CH_2CH$_3$), 3.79 (s, 2H, CH_2C=CH$_2$), 2.43 (s, 3H, Ar-CH_3), 1.93 (d, J = 1.4 Hz, 1H, C*H*CO$_2$), 1.74 (s, 3H, CH$_2$CCH_3), 1.23 (t, J = 7.2 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.2 (CO), 143.6 (C), 139.5 (C), 137.1 (C), 129.7 (2xCH), 127.7 (2xCH), 115.7 (CH$_2$), 110.4 (C), 98.6 (CH), 60.6 (CH$_2$), 53.3 (CH$_2$), 41.6 (CH$_2$), 21.7 (CH$_3$), 20.4 (CH), 19.8 (CH$_3$), 14.5 (CH$_3$). IR (Neat): 2988, 2925, 2848, 1723, 1646 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_4S$ (349.13 g/mol): C, 61.87; H, 6.63%. Found: C, 62.04; H, 6.82%.

Ethyl 2-(((N-(But-3-en-1-yl)-4-methylphenyl)sulfonamido)-methyl)cycloprop-2-ene-1-carboxylate, ***3i.*** It was obtained from **1i** (200 mg, 0.68 mmol) and ethyl diazoacetate (0.10 mL, 0.82 mmol) following the general procedure for cyclopropanation reactions and purified by flash column chromatography (Hexane/AcOEt, 8:1). Pale yellow oil (157 mg, 0.45 mmol, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H, Ar), 7.28 (d, J = 8.0 Hz, 2H, Ar), 6.18 (q, J = 1.6 Hz, 1H, C=C*H*), 5.73 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H, C*H*=CH$_2$), 5.12−5.02 (m, 2H, CH=CH$_2$), 4.51−4.35 (m, 2H, NCH_2C), 4.14−4.04 (m, 2H, CH_2CH$_3$), 3.30 (td, J = 7.1, 1.8 Hz, 2H, NCH_2CH$_2$), 2.43 (s, 3H, CCH_3), 2.37−2.29 (m, 2H, CH_2CH=CH$_2$), 2.03 (d, J = 1.5 Hz, 1H, C*H*CO$_2$), 1.24 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.2 (CO), 143.7 (C), 136.9 (C), 134.6 (CH), 129.8 (2xCH), 127.6 (2xCH), 117.5 (CH$_2$), 110.8 (C), 98.7 (CH), 60.6 (CH$_2$), 46.8 (CH$_2$), 43.0 (CH$_2$), 32.7 (CH$_2$), 21.7 (CH$_3$), 20.5 (CH), 14.5 (CH$_3$). IR (Neat): 2990, 2920, 2858, 1727, 1642 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_4S$ (349.13 g/mol): C, 61.87; H, 6.63%. Found: C, 61.70; H, 6.80%.

Ethyl 2-(((4-Methyl-N-(pent-4-en-1-yl)phenyl)sulfonamido)-methyl)cycloprop-2-ene-1-carboxylate, ***3j.*** It was obtained from **1j** (1.38 g, 4.98 mmol) and ethyl diazoacetate (787 μL, 6.29 mmol) following the general procedure for cyclopropanation reactions and purified by flash column chromatography (Hexane/AcOEt, 9:1). Pale yellow oil (945 mg, 2.60 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H, Ar), 7.28 (d, J = 8.0 Hz, 2H, Ar), 6.16 (q, J = 1.5 Hz, 1H, C*H*=C), 5.77 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H, C*H*=CH$_2$), 5.06−4.95 (m, 2H, CH=CH$_2$), 4.48−4.33 (m, 2H, NCH_2C), 4.14−4.03 (m, 2H, CH_2CH$_3$), 3.26−3.19 (m, 2H, NCH_2CH$_2$), 2.43 (s, 3H, CCH_3), 2.11−2.04 (m, 2H, CH$_2$CH_2CH$_2$), 2.02 (d, J = 1.4 Hz, 1H, C*H*CO$_2$), 1.71−1.61 (m, 2H, CH$_2$CH=CH$_2$), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (1 01 MHz, $CDCl_3$) δ 175.2 (CO), 143.6 (C), 137.5 (CH), 136.8 (C), 129.7 (2xCH), 127.6 (2xCH), 115.5 (CH$_2$), 110.8 (C), 98.6 (CH), 60.6 (CH$_2$), 47.0 (CH$_2$), 42.9 (CH$_2$), 30.7 (CH$_2$), 27.2 (CH$_2$), 21.7 (CH$_3$), 20.5 (CH), 14.5 (CH$_3$). IR (Neat): 2988, 2917, 2858, 1729, 1643 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_4S$ (363.15 g/mol): C, 62.79; H, 6.93%. Found: C, 62.90; H, 7.06%.

Diethyl 2-Allyl-2-((3-(ethoxycarbonyl)-3-phenylcycloprop-1-en-1-yl)methyl)malonate, ***3k.*** It was obtained from **2a** (240 mg, 0.85 mmol) and allyl bromide (0.89 mL, 1.02 mmol) following the general procedure for alkylation reactions with NaH (24.5 mg, 1.02 mmol) and purified by flash column chromatography (Hexane/AcOEt, 13:1). Colorless oil (228 mg, 0.57 mmol, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.16 (m, 5H, Ar), 6.78 (t, J = 1.6 Hz, 1H, C=C*H*), 5.59 (ddt, J = 17.6, 10.2, 7.5 Hz, 1H, C*H*=CH$_2$), 5.06 (ddt, J = 10.2, 1.9, 0.9 Hz, 1H, CH=CH$_2$ (*cis*)), 5.02 (dq, J = 16.9, 1.4 Hz, 1H, CH=CH$_2$ (*trans*)), 4.28−3.99 (m, 6H,3x CH_2CH$_3$), 3.24−3.04 (m, 2H, CCH_2C), 2.90−2.68 (m, 2H, CH_2CH), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.22 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.13 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.8 (CO), 170.1 (2xCO), 141.2 (C), 131.8 (CH), 128.3 (2xCH), 128.1 (2xCH), 126.5 (CH), 120.1 (CH$_2$), 116.9 (C), 100.3 (CH), 61.9 (CH$_2$), 61.8 (CH$_2$), 60.9 (CH$_2$), 56.3 (C), 36.7 (CH$_2$), 32.5 (C), 27.7 (CH$_2$), 14.4 (CH$_3$), 14.2 (CH$_3$), 14.1 (CH$_3$). IR (Neat): 2990, 2923, 2845, 1730 cm^{-1}. Anal. Calcd for $C_{23}H_{28}O_6$ (400.19 g/mol): C, 68.98; H, 7.05%. Found: C, 68.84; H, 7.21%.

Diethyl 2-((3-(Ethoxycarbonyl)-3-phenylcycloprop-1-en-1-yl)-methyl)-2-(2-methylallyl)malonate, ***3l.*** It was obtained from **2a** (250 mg, 0.70 mmol) and 3-bromo-2-methylprop-1-ene (84 μL, 0.84 mmol) following the general procedure for alkylation reactions with NaH (34 mg, 0.84 mmol) and purified by flash column chromatography (Hexane/AcOEt, 19:1). Colorless oil (256 mg, 0.62 mmol, 89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.15 (m, 5H, Ar), 6.79 (t, J = 1.7 Hz, 1H, C=C*H*), 4.84−4.81 (m, 1H, C=CH_2), 4.67−4.62 (m, 1H, C=CH_2), 4.24−3.98 (m, 6H, 3xCH_2CH$_3$), 3.28−3.09 (m, 2H, CH_2C=CH), 2.88−2.78 (m, 2H, CH_2C=CH$_2$), 1.61 (s, 3H, CCH_3), 1.24 (t, J = 7.2 Hz, 3H, CH$_2$CH_3), 1.21 (t, J = 7.2 Hz, 3H, CH$_2$CH_3), 1.09 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.8 (CO), 170.5 (CO), 170.4 (CO), 141.1 (C), 139.9 (C), 128.3 (2xCH), 128.1 (2xCH), 126.5 (CH), 117.3 (C), 116.6 (CH$_2$), 100.2 (CH), 61.9 (CH$_2$), 61.8 (CH$_2$), 60.9 (CH$_2$), 55.9 (C), 39.8 (CH$_2$), 32.5 (C), 27.6 (CH$_2$), 23.4 (CH$_3$), 14.4 (CH$_3$), 14.1 (CH$_3$), 14.0 (CH$_3$). IR (Neat): 2985, 2914, 2846, 1728 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_6$ (414.20 g/mol): C, 69.55; H, 7.30%. Found: C, 69.67; H, 7.49%.

Diethyl 2-((3-(Ethoxycarbonyl)-3-phenylcycloprop-1-en-1-yl)-methyl)-2-(3-methylbut-2-en-1-yl)malonate, ***3m.*** It was obtained from **2a** (250 mg, 0.70 mmol) and 1-bromo-3-methylbut-2-ene (97 μL, 0.84 mmol) following the general procedure for alkylation reactions with NaH (34 mg, 0.84 mmol) and purified by flash column chromatography (Hexane/AcOEt, 19:1). Colorless oil (246 mg, 0.57 mmol, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.16 (m, 5H, Ar), 6.77 (t, J = 1.7 Hz, 1H, CH$_2$C=C*H*), 4.90 (tt, J = 7.6, 1.4 Hz, 1H, CH$_2$C*H*C), 4.21−3.98 (m, 6H, 3xCH_2CH$_3$), 3.22−3.05 (m, 2H, CCH_2C), 2.75 (d, J = 7.6 Hz, 2H, CCH_2CH), 1.64 (s, 3H, CCH_3), 1.49 (s, 3H, CCH_3), 1.22 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.21 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.11 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.8 (CO), 170.4 (2xCO), 141.2 (C), 136.6 (C), 128.3 (2xCH), 128.1 (2xCH), 126.4 (CH), 117.2 (CH), 117.1 (C), 100.1 (CH), 61.7 (CH$_2$), 61.6 (CH$_2$), 60.9 (CH$_2$), 56.7 (C), 32.5 (C), 30.9 (CH$_2$), 27.7 (CH$_2$), 26.2 (CH$_3$), 18.0 (CH$_3$), 14.4 (CH$_3$), 14.1 (CH$_3$), 14.0 (CH$_3$). IR (Neat): 2988, 2920, 2853, 1729 cm^{-1}. Anal. Calcd for $C_{25}H_{32}O_6$ (428.22 g/mol): C, 70.07; H, 7.53%. Found: C, 70.21; H, 7.37%.

Diethyl 2-((3-(Ethoxycarbonyl)-3-phenylcycloprop-1-en-1-yl)-methyl)-2-(pent-4-en-1-yl)malonate, ***3n.*** It was obtained from **2a** (320 mg, 0.89 mmol) and 5-bromopent-1-ene (0.13 mL, 1.07 mmol) following the general procedure for alkylation reactions with NaH (40 mg, 0.98 mmol) and purified by flash column chromatography (Hexane/AcOEt, 13:1). Colorless oil (154 mg, 0.36 mmol, 41%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.16 (m, 5H, Ar), 6.74 (t, J = 1.6 Hz, 1H C=C*H*), 5.70 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H, C*H*=CH$_2$), 5.01−4.91 (m, 2H, CH=CH$_2$), 4.22−4.01 (m, 6H, 3xCH_2CH$_3$), 3.26−3.09 (m, 2H, CCH_2C), 2.08−1.92 (m, 4H, CH_2CH_2CH$_2$), 1.34−1.15 (m, 2H, CH_2CH_2CH$_2$), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.22 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.12 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7 (CO), 170.6 (CO), 170.5 (CO), 141.2 (C), 138.1 (CH), 128.2 (2xCH), 128.1 (2xCH), 126.5 (CH), 117.0 (C), 115.2 (CH$_2$), 99.9 (CH), 61.7 (CH$_2$), 61.6 (CH$_2$), 60.9 (CH$_2$), 56.5 (C), 33.8 (CH$_2$), 32.6 (C), 31.7 (CH$_2$), 27.8 (CH$_2$), 23.4 (CH$_2$), 14.5 (CH$_3$), 14.1 (CH$_3$), 14.0 (CH$_3$). IR (Neat): 2988, 2923, 2848, 1729 cm^{-1}. Anal. Calcd for $C_{25}H_{32}O_6$ (428.22 g/mol): C, 70.07; H, 7.53%. Found: C, 70.19; H, 7.60%.

General Procedure for Cycloisomerization Reactions with Gold Catalysts. To a stirred solution, in a microwave vessel, of the cyclopropenated compound (1 equiv) in toluene anh. (0.25/mmol) was added AuCl or $AuCl_3$ (0.1 equiv). Then, the vessel was sealed, and the mixture was heated up to 100 °C using microwave irradiation and stirred for 60 min. After this, the mixture was cooled down, concentrated under vacuum and purified by flash column chromatography.

Diethyl (E)-5-(2-Ethoxy-2-oxoethylidene)-1-methylbicyclo[4.1.0]-heptane-3,3-dicarboxylate, ***4a.*** It was obtained from **3a** (50 mg, 0.15 mmol) following the general procedure for cycloisomerization reactions with gold catalysts and purified by flash column chromatography (Hexane/AcOEt, 12:1). NOESY spectra showed

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strong cross-peak between olefinic proton and H6. Colorless oil (38 mg, 0.11 mmol, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 (d, J = 1.9 Hz, 1H, C=C*H*), 4.30 (dd, J = 15.4, 2.2 Hz, 1H, C*H*$_2$C=CH), 4.20−4.09 (m, 6H, 3xC*H*$_2$CH$_3$), 2.51 (dd, J = 14.2, 2.2 Hz, 1H, C*H*$_2$CCH$_3$), 2.17 (dd, J = 15.3, 2.1 Hz, 1H, C*H*$_2$C=CH), 1.90 (d, J = 14.1 Hz, 1H, C*H*$_2$CCH$_3$), 1.43 (dd, J = 9.3, 5.0 Hz, 1H, CC*H*C=), 1.25 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.24 (s, 3H, CC*H*$_3$), 1.22 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.17 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 0.88 (dd, J = 9.3, 4.6 Hz, 1H, C*H*$_2$CH), 0.72 (t, J = 4.8 Hz, 1H, C*H*$_2$CH); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4 (CO), 170.7 (CO), 165.8 (CO), 157.5 (C), 115.5 (CH), 61.7 (CH$_2$), 61.4 (CH$_2$), 59.6 (CH$_2$), 56.1 (C), 36.4 (CH$_2$), 29.7 (CH), 28.6 (CH$_2$), 27.0 (CH$_3$), 25.6 (CH$_2$), 21.6 (C), 14.5 (CH$_3$), 14.1 (CH$_3$), 14.0 (CH$_3$). IR (Neat): 2982, 2933, 2907, 1734, 1711, 1633 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 64.06; H, 7.61%.

Ethyl (Z)-2-(3-Tosyl-3-azabicyclo[4.1.0]heptan-5-ylidene)-acetate, ***4b****.* It was obtained from **3g** (50 mg, 0.15 mmol) following the general procedure for cycloisomerization reactions with gold catalysts and purified by flash column chromatography (Hexane/AcOEt, 6:1). NOESY spectra showed strong cross-peak between olefinic proton and H6. Colorless oil (30 mg, 0.09 mmol, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.2 Hz, 2H, Ar), 7.32 (d, J = 8.0 Hz, 2H, Ar), 5.77 (t, J = 2.4 Hz, 1H, C=C*H*), 5.00 (d, J = 18.4 Hz, 1H, NC*H*$_2$C=), 4.16−4.08 (m, 2H, C*H*$_2$CH$_3$), 4.05−3.96 (m, 1H, NC*H*$_2$CH), 3.36 (dd, J = 18.4, 2.6 Hz, 1H, NC*H*$_2$C=CH), 2.67 (dd, J = 11.6, 2.2 Hz, 1H, NC*H*$_2$CH), 2.42 (s, 3H, CC*H*$_3$), 1.75−1.65 (m, 1H, CHC*H*$_2$CH), 1.60−1.50 (m, 1H, CH$_2$C*H*CH$_2$), 1.33 (q, J = 4.9 Hz, 1H, =CC*H*CH$_2$), 1.27 (t, J = 7.8 Hz, 3H, CH$_2$C*H*$_3$), 0.99 (ddd, J = 9.4, 7.7, 4.8 Hz, 1H, CHC*H*$_2$CH); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6 (CO), 154.7 (C), 143.8 (C), 133.3 (C), 130.0 (2xCH), 127.7 (2xCH), 115.2 (CH), 59.9 (CH$_2$), 47.3 (CH$_2$), 43.2 (CH$_2$), 21.7 (CH$_3$), 18.5 (CH$_2$), 14.5 (CH$_3$), 14.3 (CH), 10.5 (CH). IR (Neat): 2986, 2925, 2863, 1730, 1642 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4S$ (335.12 g/mol): C, 60.88; H, 6.31%. Found: C, 60.71; H, 6.40%.

General Procedure for Cycloisomerization Reactions with Cp*RuCl(cod). To a solution, of the cyclopropenated compound (1 equiv) in toluene anh. (0.25 mL/mmol) placed into a microwave vessel was added Cp*RuCl(cod) (10 mol %). Then, the vessel was sealed and the mixture was heated up to 100 °C (50 °C for compound **7a**) using microwave irradiation and stirred for 5 min. After this, the mixture was cooled down, concentrated under vacuum, and purified by flash column chromatography.

Diethyl (E)-1-(3-Ethoxy-3-oxoprop-1-en-1-yl)-5-methylbicyclo-[3.1.0]hexane-3,3-dicarboxylate, ***5a****.* It was obtained from **3a** (60 mg, 0.18 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (478 mg, 0.13 mmol, 78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, J = 15.7 Hz, 1H, C*H*=CHCO$_2$), 5.83 (d, J = 15.6 Hz, 1H, CH=C*H*CO$_2$), 4.23−4.12 (m, 6H, 3xC*H*$_2$CH$_3$), 2.76−2.59 (m, 3H, COCC*H*$_2$CCH= + COCCH*H*CCH$_3$), 2.32 (dd, J = 13.8, 1.5 Hz, 1H, COCCH*H*CCH$_3$), 1.28 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.25 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.24 (s, 3H, C*H*$_3$), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 0.89 (d, J = 6.0 Hz, 1H, CH$_2$ cyclopropane), 0.76 (dt, J = 6.0, 1.5 Hz, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5 (CO), 171.6 (CO), 166.8 (CO), 151.3 (CH), 118.7 (CH), 62.1 (CH$_2$), 61.9 (CH$_2$), 60.3 (CH$_2$), 57.8 (C), 42.2 (CH$_2$), 37.9 (CH$_2$), 34.9 (C), 34.7 (C), 25.2 (CH$_2$), 18.7 (CH$_3$), 14.5 (CH$_3$), 14.2 (CH$_3$), 14.1 (CH$_3$). IR (Neat): 2985, 2930, 1734, 1640 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 64.08; H, 7.90%.

Diethyl (E)-1-(3-Ethoxy-3-oxoprop-1-en-1-yl)bicyclo[3.1.0]-hexane-3,3-dicarboxylate, ***5b****.* It was obtained from **3b** (50 mg, 0.15 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod). The spectroscopical data of the product (47 mg, 0.14 mmol, 94%) matched those described in the literature.[9c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 (d, J = 15.6 Hz, 1H, C*H*=CHCO$_2$), 5.80 (d, J = 15.6 Hz, 1H, CH=C*H*CO$_2$), 4.20−4.11 (m, 6H, 3xC*H*$_2$CH$_3$), 2.65−2.57 (m, 3H, COCC*H*$_2$CCH= + COCCH*H*CCH), 2.48 (dd, J = 13.8, 5.1 Hz, 1H, COCCH*H*CCH), 1.64 (m, 1H, CH cyclopropane), 1.26 (t, J = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 1.24 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.21 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 0.92 (t, J = 7.8 Hz, 1H, CH$_2$ cyclopropane), 0.79 (t, J = 5.6, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.5 (CO), 171.4 (CO), 166.9 (CO), 153.1 (CH), 117.4 (CH), 62.1 (CH$_2$), 62.0 (CH$_2$), 60.3 (CH$_2$), 59.5 (C), 36.4 (CH$_2$), 35.4 (CH$_2$), 31.7 (C), 28.6 (CH), 19.6 (CH$_2$), 14.4 (CH$_3$), 14.1 (CH$_3$), 14.0 (CH$_3$).

Diethyl (E)-6-(3-Ethoxy-3-oxoprop-1-en-1-yl)bicyclo[4.1.0]-heptane-3,3-dicarboxylate, ***5d****.* It was obtained from **3d** (70 mg, 0.21 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (57 mg, 0.17 mmol, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (d, J = 15.7 Hz, 1H, C*H*=CHCO$_2$), 5.67 (d, J = 15.7 Hz, 1H, CH=C*H*CO$_2$), 4.26−4.07 (m, 6H, 3xC*H*$_2$CH$_3$), 2.81 (ddd, J = 14.2, 8.9, 2.2 Hz, 1H, CC*H*$_2$CH), 2.22−2.13 (m, 1H, CH$_2$C*H*$_2$), 1.96−1.88 (m, 1H, CH$_2$C*H*$_2$), 1.81 (td, J = 13.6, 5.0 Hz, 1H, CH$_2$C*H*$_2$), 1.68−1.57 (m, 2H, CH$_2$C*H*$_2$ + CC*H*$_2$CH), 1.38−1.28 (m, 1H, CH$_2$C*H*), 1.27 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.24 (t, J = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 1.22 (t, J = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 0.99 (dd, J = 9.2, 5.0 Hz, 1H, CH$_2$ cyclopropane), 0.71 (t, J = 5.6 Hz, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3 (CO), 170.8 (CO), 167.1 (CO), 157.4 (CH), 116.4 (CH), 61.6 (CH$_2$), 61.5 (CH$_2$), 60.3 (CH$_2$), 52.6 (C), 30.0 (CH$_2$), 25.5 (CH$_2$), 21.7 (CH$_2$), 21.6 (C), 21.1 (CH$_2$), 20.1 (CH), 14.5 (CH$_3$), 14.3 (CH$_3$), 14.2 (CH$_3$). IR (Neat): 2982, 2923, 2872, 1730, 1643 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 63.79; H, 7.59%.

Diethyl (E)-1-(3-Ethoxy-3-oxoprop-1-en-1-yl)bicyclo[4.1.0]-heptane-3,3-dicarboxylate, ***5e****.* It was obtained from **3e** following the general procedure for cycloisomerization reactions with Cp*RuCl-(cod) and purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (30 mg, 0.10 mmol, 60%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.61 (d, J = 15.7 Hz, 1H, C*H*=CHCO$_2$), 5.87 (d, J = 15.6 Hz, 1H, CH=C*H*CO$_2$), 4.21−4.13 (m, 6H, 3xC*H*$_2$CH$_3$), 2.93 (dd, J = 14.7, 1.6 Hz, 1H, CC*H*$_2$C), 2.11−2.06 (m, 1H, CH$_2$C*H*$_2$), 2.02−1.69 (m, 2H, CH$_2$C*H*$_2$), 1.73 (d, J = 14.6 Hz, 1H, CC*H*$_2$C), 1.60 (dd, J = 13.5, 5.3 Hz, 1H, CH$_2$C*H*$_2$), 1.31−1.20 (m, 10H, CH$_2$C*H* + 3xCH$_2$C*H*$_3$), 1.05 (dd, J = 9.4, 4.9 Hz, 1H, CH$_2$ cyclopropane), 0.72 (dd, J = 6.3, 4.6 Hz, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2 (CO), 170.9 (CO), 167.3 (CO), 157.5 (CH), 116.2 (CH), 61.6 (CH$_2$), 61.5 (CH$_2$), 60.2 (CH$_2$), 52.7 (C), 32.3 (CH$_2$), 24.9 (CH$_2$), 23.1 (CH), 22.4 (CH$_2$), 20.4 (C), 19.5 (CH$_2$), 14.5 (CH$_3$), 14.2 (CH$_3$), 14.2 (CH$_3$). IR (Neat): 2980, 2924, 2875, 1730, 1641 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_6$ (338.17 g/mol): C, 63.89; H, 7.74%. Found: C, 64.05; H, 7.57%.

Diethyl (E)-1-(3-Ethoxy-3-oxoprop-1-en-1-yl)bicyclo[5.1.0]-octane-3,3-dicarboxylate, ***5f****.* It was obtained from **3f** (80 mg, 0.23 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 12:1). Colorless oil (42 mg, 0.12 mmol, 52%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, J = 15.8 Hz, 1H, C*H*=CHCO$_2$), 5.50 (d, J = 15.8 Hz, 1H, CH=C*H*CO$_2$), 4.30−4.01 (m, 6H, 3xC*H*$_2$CH$_3$), 2.90 (d, J = 15.9 Hz, 1H, CC*H*$_2$C), 2.30 (ddd, J = 13.5, 9.0, 3.9 Hz, 1H, CC*H*$_2$CH$_2$), 2.25−2.17 (m, 1H, CH$_2$C*H*$_2$CH), 2.11 (d, J = 15.9 Hz, 1H, CC*H*$_2$C), 2.01−1.86 (m, 1H, CH$_2$C*H*$_2$CH$_2$), 1.76−1.66 (m, 1H, CC*H*$_2$CH$_2$), 1.64−1.54 (m, 1H, CH$_2$C*H*$_2$CH$_2$), 1.37−1.28 (m, 1H, CH$_2$C*H*CH$_2$), 1.30−1.23 (m, 6H, 2xCH$_2$C*H*$_3$), 1.23 (t, J = 7.1 Hz, 3H, CH$_2$C*H*$_3$), 1.12−1.03 (m, 1H, CH$_2$C*H*$_2$CH), 0.98−0.92 (m, 1H, CH$_2$ cyclopropane), 0.75 (dd, J = 5.8, 4.4 Hz, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3 (CO), 172.0 (CO), 167.1 (CO), 156.2 (CH), 116.0 (CH), 61.6 (CH$_2$), 61.4, (CH$_2$), 60.2, (CH$_2$), 56.8 (C), 36.6 (CH$_2$), 33.4 (CH$_2$), 28.9 (CH$_2$), 28.7 (CH$_2$), 26.2 (CH), 23.9 (CH$_2$), 23.4 (C), 14.4 (CH$_3$), 14.2 (CH$_3$), 14.0 (CH$_3$). IR (Neat): 2982, 2924, 2853, 1731 cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_6$ (352.19 g/mol): C, 64.75; H, 8.01%. Found: C, 64.94; H, 7.87%.

Ethyl (E)-3-(3-Tosyl-3-azabicyclo[3.1.0]hexan-1-yl)acrylate, ***5g****.* It was obtained from **3g** (50 mg, 0.15 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and

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purified by flash column chromatography (Hexane/AcOEt, 4:1). The spectroscopical data of the product (47 mg, 0.14 mmol, 94%) matched those described in the literature;[9c,e] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.34 (d, J = 8.0 Hz, 2H, Ar), 6.62 (d, J = 15.8 Hz, 1H, C*H*CHCO$_2$), 5.68 (d, J = 15.8 Hz, 1H, CHC*H*CO$_2$), 4.15 (q, J = 7.1 Hz, 2H, CH_2CH$_3$), 3.60 (d, J = 9.0 Hz, 1H, NCH_2C), 3.59 (d, J = 9.3 Hz, 1H, NCH_2CH), 3.11 (d, J = 9.0 Hz, 1H, NCH_2C), 3.07 (dd, J = 9.3, 3.8 Hz, 1H, NCH_2CH), 2.44 (s, 3H, CCH_3), 1.70−1.67 (m, 1H, CH$_2$C*H*), 1.26 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.21 (t, J = 5.2 Hz, 1H, CH$_2$ cyclopropane), 1.06 (dd, J = 8.1, 5.3 Hz, 1H, CH$_2$ cyclopropane). ^{13}C{^{1}H}(101 MHz, $CDCl_3$) δ 166.3 (CO), 148.9 (CH), 144.0 (C), 132.9 (C), 129.9 (CH), 127.7 (CH), 118.5 (CH), 60.5 (CH$_2$), 50.1 (CH$_2$), 49.4 (CH$_2$), 29.9 (C), 26.6 (CH), 21.7 (CH$_3$), 17.2 (CH$_2$), 14.3 (CH$_3$). IR (Neat): 2982, 2924, 2853, 1731 cm^{-1}. Anal. Calcd for $C_{17}H_{21}NO_4S$ (335.12 g/mol): C, 60.88; H, 6.31%. Found: C, 60.99; H, 6.45%.

Ethyl (E)-3-(5-Methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)-acrylate, ***5h***. It was obtained from **3h** (70 mg, 0.20 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl-(cod) and purified by flash column chromatography (Hexane/AcOEt, 8:1). The spectroscopical data of the product (46 mg, 0.13 mmol, 66%) matched those described in the literature;[9c,e] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.3 Hz, 2H, Ar), 7.34 (d, J = 8.0 Hz, 2H, Ar), 6.66 (d, J = 15.8 Hz, 1H, C*H*CHCO$_2$), 5.68 (d, J = 15.8 Hz, 1H, CHC*H*CO$_2$), 4.16 (q, J = 7.0 Hz, 2H, CH_2CH$_3$), 3.60 (d, J = 9.1 Hz, 2H, NCH_2CCH$_3$ + NCH_2CCH═), 3.10 (d, J = 9.0 Hz, 1H, NCH_2CCH═), 2.81 (d, J = 9.1 Hz, 1H, NCH_2CCH$_3$), 2.44 (s, 3H, Ar-CH_3), 1.31−1.23 (m, 4H, CH$_2$CH_3 + CH$_2$ cyclopropane), 1.16 (s, 3H, CH$_2$CCH_3), 0.89 (d, J = 5.2 Hz, 1H, CH$_2$ cyclopropane). ^{3}C{^{1}H}(101 MHz, $CDCl_3$) δ 166.2 (CO), 146.9 (CH), 143.9 (C), 133.1 (C), 129.9 (CH), 127.8 (CH), 119.8 (CH), 60.5 (CH$_2$), 54.7 (CH$_2$), 51.4 (CH$_2$), 33.1 (C), 33.0 (CH), 22.9 (CH$_2$), 21.7 (CH$_3$), 15.4 (CH$_3$), 14.4 (CH$_3$). IR (Neat): 2982, 2924, 2853, 1731 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_4S$ (349.13 g/mol): C, 61.87; H, 6.63%. Found: C, 62.03; H, 6.71%

Ethyl (E)-3-(3-Tosyl-3-azabicyclo[4.1.0]heptan-1-yl)acrylate, ***5i***. It was obtained from **3i** (42 mg, 0.12 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 8:1). Colorless oil (26 mg, 0.08 mmol, 64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.3 Hz, 2H, Ar), 7.30 (d, J = 7.9 Hz, 2H, Ar), 6.14 (d, J = 11.4 Hz, 1H, C*H*═CHCO$_2$), 5.81 (d, J = 11.5 Hz, 1H, CH═C*H*CO$_2$), 4.18−4.08 (m, 2H, CH_2CH$_3$), 3.80 (dd, J = 11.2, 1.5 Hz, 1H, NCH_2C), 3.36−3.28 (m, 1H, CCH_2CH$_2$), 2.87 (d, J = 11.2 Hz, 1H, NCH_2C), 2.62 (ddd, J = 11.8, 10.3, 5.6 Hz, 1H, CCH_2CH$_2$), 2.42 (s, 3H, CCH_3), 2.13−2.02 (m, 1H, CCH$_2$CH_2), 1.92−1.82 (m, 1H, CCH$_2$CH_2), 1.25 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.14−1.05 (m, 1H, CH$_2$C*H*), 0.91 (dd, J = 6.0, 4.9 Hz, 1H, CH$_2$ cyclopropane), 0.78 (dd, J = 9.4, 4.9 Hz, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5 (CO), 148.8 (CH), 143.4 (C), 134.4 (C), 129.8 (2xCH), 127.6 (2xCH), 123.6 (CH), 60.4 (CH$_2$), 47.9 (CH$_2$), 42.8 (CH$_2$), 23.5 (CH$_2$), 21.7 (CH$_3$), 21.0 (C), 18.8 (CH), 18.3 (CH$_2$), 14.3 (CH$_3$). IR (Neat): 2988, 2923, 2852, 1721, 1637 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_4S$ (349.13 g/mol): C, 61.87; H, 6.63%. Found: C, 61.74; H, 6.76%.

Ethyl (E)-3-(3-Tosyl-3-azabicyclo[5.1.0]octan-1-yl)acrylate, ***5j***. It was obtained from **3j** (60 mg, 0.17 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 9:1). Pale yellow oil (35 mg, 0.10 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H, Ar), 7.31 (d, J = 8.0 Hz, 2H, Ar), 6.70 (d, J = 15.9 Hz, 1H, C*H*═CHCO$_2$), 6.03 (d, J = 15.9 Hz, 1H, CH═C*H*CO$_2$), 4.23−4.15 (m, 1H, NCH_2C), 4.18 (q, J = 7.0 Hz, 2H, CH_2CH$_3$), 3.59−3.48 (m, 1H, NCH_2CH$_2$), 2.72−2.61 (m, 1H, NCH_2CH$_2$), 2.55 (d, J = 14.3 Hz, 1H, NCH_2C), 2.43 (s, 3H, CCH_3), 2.29−2.19 (m, 1H, CH_2CH), 1.79−1.65 (m, 2H, CH$_2$CH_2CH$_2$), 1.31−1.23 (m, 1H, C*H*CH$_2$), 1.29 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.15−1.09 (m, 1H, CH_2CH), 1.13 (dd, J = 8.6, 5.1 Hz, 1H, CH$_2$ cyclopropane), 0.93 (t, J = 5.7 Hz, 1H, CH$_2$ cyclopropane); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.3 (CO), 154.0 (CH), 143.6 (C), 135.2 (C), 129.9 (2xCH), 127.5 (2xCH), 117.2 (CH), 60.3 (CH$_2$), 52.8 (CH$_2$), 51.9 (CH$_2$), 29.2 (CH$_2$), 28.6 (CH$_2$), 28.2 (CH), 26.8 (C), 24.3 (CH$_2$), 21.7 (CH$_3$), 14.5 (CH$_3$). IR (Neat): 2987, 2920, 2862, 1727, 1643 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_4S$ (363.15 g/mol): C, 62.79; H, 6.93%. Found: C, 62.92; H, 7.09%.

Diethyl (3aR,6S*,7aR*)-6-Ethoxy-5-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyindene-2,2(3H)-dicarboxylate,* ***6a***. It was obtained from **3k** (50 mg, 0.13 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 13:1). NOESY spectra showed cross-peak between the CH$_2$C*H*CH$_2$ and the olefinic proton. Thus, the titled compound was assigned as (3a*R**,6*S**,7a*R**). Colorless oil (34 mg, 0.08, 64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.48 (m, 2H, Ar), 7.38−7.30 (m, 2H, Ar), 7.29−7.23 (m, 1H, Ar), 6.60 (s, 1H, C = C*H*), 4.24−4.16 (m, 4H, 2xCH_2CH$_3$), 3.79 (dq, J = 9.4, 7.0 Hz, 1H, CH_2CH$_3$), 3.49 (dq, J = 9.3, 7.0 Hz, 1H, CH_2CH$_3$), 2.90 (d, J = 15.3 Hz, 1H, CCH_2C), 2.63 (d, J = 15.4 Hz, 1H, CCH_2C), 2.58 (dd, J = 12.9, 7.1 Hz, 1H, (EtO$_2$C)$_2$CCH_2CH), 2.28 (dd, J = 12.9, 11.3 Hz, 1H, (EtO$_2$C)$_2$CCH_2CH), 2.14 (dtd, J = 10.9, 7.2, 3.4 Hz, 1H, CH$_2$C*H*CH$_2$), 1.88 (dd, J = 11.4, 7.4 Hz, 1H, CHCH_2COEt), 1.81 (dd, J = 11.4, 3.4 Hz, 1H, CHCH_2COEt), 1.26 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.25 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.15 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.6 (CO), 171.1 (CO), 146.8 (C), 133.9 (CH), 133.2 (C), 128.8 (2xCH), 127.9 (CH), 124.8 (2xCH), 114.8 (C), 91.1 (C), 62.9 (C), 62.6 (CH$_2$), 61.9 (CH$_2$), 61.7 (CH$_2$), 49.0 (CH), 39.8 (CH$_2$), 37.2 (CH$_2$), 36.4 (CH$_2$), 15.4 (CH$_3$), 14.2 (CH$_3$), 14.2 (CH$_3$). IR (Neat): 2985, 2917, 2849, 1730 cm^{-1}. Anal. Calcd for $C_{23}H_{28}O_6$ (400.19 g/mol): C, 68.98; H, 7.05%. Found: C, 69.11; H, 7.23%.

Diethyl (3aS,6S*,7aR*)-6-Ethoxy-7a-methyl-5-phenyl-1,6,7,7a-tetrahydro-3a,6-epoxyindene-2,2(3H)-dicarboxylate,* ***6b***. It was obtained from **3l** (42 mg, 0.10 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 19:1). NOESY spectra showed cross-peak between the CCH_3 and the olefinic proton. Thus, the titled compound was assigned as (3a*S**,6*S**,7a*R**). Colorless oil (33 mg, 0.08 mmol, 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.51 (m, 2H, Ar), 7.37−7.30 (m, 2H, Ar), 7.29−7.21 (m, 1H, Ar), 6.55 (s, 1H, C*H*═C), 4.25−4.20 (m, 4H, 2xCH_2CH$_3$), 3.75 (dq, J = 9.4, 7.1 Hz, 1H, CH_2CH$_3$), 3.44 (dq, J = 9.4, 7.0 Hz, 1H, CH_2CH$_3$), 2.95 (d, J = 15.2 Hz, 1H, CCH_2CCH), 2.85 (d, J = 13.8 Hz, 1H, CCH_2CCH$_3$), 2.79 (d, J = 15.2 Hz, 1H, (EtO$_2$C)$_2$CCH_2CCH), 2.36 (d, J = 13.8 Hz, 1H, (EtO$_2$C)$_2$CCH_2-CCH$_3$), 2.20 (d, J = 11.3 Hz, 1H, CH$_3$CCH_2COEt), 1.53 (d, J = 11.3 Hz, 1H, CH$_3$CCH_2COEt), 1.25 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 1.11 (t, J = 7.1 Hz, 3H, CH$_2$CH_3), 0.83 (s, 3H, CCH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.0 (CO), 171.6 (CO), 147.4 (C), 133.0 (C), 131.8 (CH), 128.7 (2xCH), 127.9 (CH), 125.0 (2xCH), 114.1 (C), 93.1 (C), 62.2 (CH$_2$), 62.0 (CH$_2$), 61.8 (CH$_2$), 60.8 (C), 55.6 (C), 47.1 (CH$_2$), 47.1 (CH$_2$), 35.0 (CH$_2$), 24.1 (CH$_3$), 15.4 (CH$_3$), 14.2 (2xCH$_3$). IR (Neat): 2982, 2915, 2849, 1730 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_6$ (414.20 g/mol): C, 69.55; H, 7.30%. Found: C, 69.47; H, 7.13%.

Tetraethyl (E)-6,7-Bis((Z)-3-ethoxy-3-oxo-2-phenylprop-1-en-1-yl)-2,11-dimethyldodeca-1,6,11-triene-4,4,9,9-tetracarboxylate, ***7a***. It was obtained from **3l** (41 mg, 0.10 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) at 50 °C and stirred overnight. The titled compound was purified by flash column chromatography (Hexane/AcOEt, 19:1). Colorless oil (39 mg, 0.05 mmol, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.52 (m, 4H, Ar), 7.32 (t, J = 7.8 Hz, 4H, Ar), 7.17−7.11 (m, 2H, Ar), 6.27 (s, 2H, 2xC═C*H*), 4.94 (t, J = 1.8 Hz, 2H, 2xC═CH_2), 4.85 (s, 2H, 2xC═CH_2), 4.24 (q, J = 7.2 Hz, 4H, 2xCH_2CH$_3$), 4.20 (q, J = 7.2 Hz, 8H, 4xCH_2CH$_3$), 3.26 (s, 4H, 2xC═CCH_2), 2.73 (s, 4H, 2xCH_2C═CH$_2$), 1.72 (s, 6H, 2xCCH_3), 1.39 (t, J = 7.1 Hz, 6H, 2xCH$_2$CH_3), 1.26 (t, J = 7.1 Hz, 12H, 4xCH$_2$CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.0 (4xCO), 154.6 (2xCO), 141.2 (2xC), 140.7 (2xC), 132.7 (2xC), 128.6 (4xCH), 125.6 (4xCH), 125.4 (2xCH), 116.2 (2xCH$_2$), 109.0 (2xCH), 100.5 (2xC), 68.1 (2xCH$_2$), 61.6 (4xCH$_2$), 57.0 (2xC), 39.8 (2xCH$_2$), 31.2 (2xCH$_2$), 23.7

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(2xCH$_3$), 15.4 (2xCH$_3$), 14.2 (4xCH$_3$). IR (Neat): 2978, 2940, 1734 cm^{-1}. Anal. Calcd for $C_{48}H_{60}O_{12}$ (828.41 g/mol): C, 69.55; H, 7.30%. Found: C, 69.39; H, 7.21%.

*Tetraethyl (E)-7,8-Bis((Z)-3-ethoxy-3-oxo-2-phenylprop-1-en-1-yl)-2,13-dimethyltetradeca-2,7,12-triene-5,5,10,10-tetracarboxylate, **7b**.* It was obtained from **3m** (41 mg, 0.10 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 19:1). Colorless oil (30 mg, 0.04 mmol, 73%); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.54 (d, J = 7.5 Hz, 4H, Ar), 7.32 (t, J = 7.7 Hz, 4H, Ar), 7.14 (t, J = 7.4 Hz, 2H, Ar), 6.25 (s, 2H, 2xC=C*H*C), 5.05 (t, J = 7.4 Hz, 2H, 2xC=C*H*CH$_2$), 4.27−4.16 (m, 12H, 6xC*H*$_2$CH$_3$), 3.20 (s, 4H, 2xCC*H*$_2$C), 2.62 (d, J = 7.4 Hz, 4H, 2xCC*H*$_2$CH), 1.72 (s, 6H, 2xCC*H*$_3$), 1.61 (s, 6H, 2xCC*H*$_3$), 1.38 (t, J = 7.1 Hz, 6H, 2xCH$_2$C*H*$_3$), 1.26 (t, J = 7.1 Hz, 12H, 4xCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 170.9 (4xCO), 154.6 (2xCO), 141.2 (2xC), 135.8 (2xC), 132.7 (2xC), 128.6 (4xCH), 125.6 (4xCH), 125.4 (2xCH), 117.7 (2xCH), 108.8 (2xCH), 100.6 (2xC), 68.1 (2xCH$_2$), 61.5 (4xCH$_2$), 57.6 (2xC), 31.1 (2xCH$_2$), 30.9 (2xCH$_2$), 26.3 (2xCH$_3$), 18.2 (2xCH$_3$), 15.3 (2xCH$_3$), 14.2 (4xCH$_3$). IR (Neat): 2980, 2940, 1733 cm^{-1}. Anal. Calcd for $C_{50}H_{64}O_{12}$ (856.44 g/mol): C, 70.07; H, 7.53%. Found: C, 70.25; H, 7.69%.

*Tetraethyl (E)-8,9-Bis((Z)-3-ethoxy-3-oxo-2-phenylprop-1-en-1-yl)hexadeca-1,8,15-triene-6,6,11,11-tetracarboxylate, **7c**.* It was obtained from **3n** (25 mg, 0.06 mmol) following the general procedure for cycloisomerization reactions with Cp*RuCl(cod) and purified by flash column chromatography (Hexane/AcOEt, 19:1). Colorless oil (22 mg, 0.03 mmol, 86%); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (d, J = 7.7 Hz, 4H, Ar), 7.32 (t, J = 7.6 Hz, 4H, Ar), 7.14 (t, J = 7.4 Hz, 2H, Ar), 6.25 (s, 2H, 2xC*H*=C), 5.78 (ddt, J = 16.9, 10.2, 6.6 Hz, 2H, 2xC*H*=CH$_2$), 5.01 (dd, J = 17.2, 1.8 Hz, 2H, 2xCH=C*H*H), 4.95 (dd, J = 10.3, 1.9 Hz, 2H. 2xCH=C*H*H), 4.27−4.17 (m, 12H, 6xC*H*$_2$CH$_3$), 3.22 (s, 4H, 2xCC*H*$_2$C), 2.06 (q, J = 7.1 Hz, 4H, 2xC*H*$_2$CH=CH$_2$), 1.92−1.84 (m, 4H, 2xCC*H*$_2$CH$_2$), 1.43−1.32 (m, 4H, 2xCH$_2$C*H*$_2$CH$_2$), 1.39 (t, J = 7.1 Hz, 6H, 2xCH$_2$C*H*$_3$), 1.27 (t, J = 7.1 Hz, 12H, 4xCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 171.1 (4xCO), 154.7 (2xCO), 141.1 (2xC), 138.2 (2xCH), 132.8 (2xC), 128.6 (4xCH), 125.6 (4xCH), 125.4 (2xCH), 115.1 (2xCH$_2$), 108.7 (2xCH), 100.7 (2xC), 68.1 (2xCH$_2$), 61.5 (4xCH$_2$), 57.7 (2xC), 34.0 (2xCH$_2$), 31.7 (2xCH$_2$), 31.3 (2xCH$_2$), 23.6 (2xCH$_2$), 15.4 (2xCH$_3$), 14.2 (4xCH$_3$). IR (Neat): 2980, 2942, 1732 cm^{-1}. Anal. Calcd for $C_{50}H_{64}O_{12}$ (856.44 g/mol): C, 70.07; H, 7.53%. Found: C, 69.96; H, 7.39%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02849.

Copies of ^{1}H, ^{13}C NMR spectra of all products and 2D spectra of new products (PDF)

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Notes

The authors declare no competing financial interest.

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