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Tandem $PtCl_2$ catalyzed–thermal [3,3] rearrangements of enyne acetates

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Abstract—1,6 Enyne systems flanked with an acetate group at the propargyl position undergo tandem $PtCl_2$-catalyzed–thermal [3,3] rearrangements leading to trienes. The scope of the transformation has been delineated by varying the nature of the alkynyl substituent R. For R=alkyl or phenyl, a direct 1,3-migration of the acetate group is proposed leading to an allenyl ester intermediate that undergoes a subsequent [3,3] rearrangement.

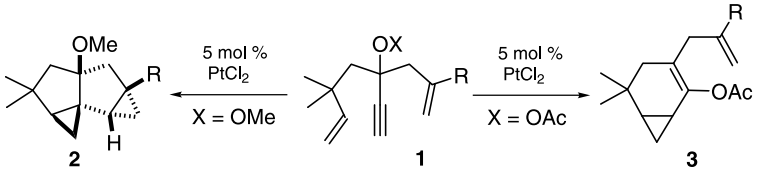
1. Introduction

The $PtCl_2$-catalyzed cycloisomerization of enyne systems is a recent addition to the palette of possible synthetic tools for the construction of cyclic derivatives.[1] The first report by Murai and Chatani established that this catalyst was ideal for promoting the formal metathesis of various enyne systems.[2] Applications of this process to the total synthesis of natural products,[3] as well as exploration of new partners[4] and mechanism rationalizations[5] have then followed rapidly. Most articles also show that the reactivity of this catalyst with enynes has largely extended beyond the simple metathesis process. Cyclopropanated hetero- and carbocycles resulting from carbenoid intermediates have been generated for instance.[5a,b] We have recently evidenced an interesting alteration of the reactivity of dienyne systems of type **1** by varying the nature of the protecting group of a hydroxy function at the propargylic position (Scheme 1).[6] Thus with a methoxy group, a domino process leads to diquinane **2** resulting from the formal transformation of the alkyne partner into a bis-carbene entity. However, with an acetate group, a 1,2-transposition step followed by an intramolecular cyclopropanation via a platinum carbene complex gives the bicyclic [4.1.0] derivative **3**. This reactivity could be extended to the preparation of cyclooctyl compounds.

The **1** to **3** transformation has incited further curiosity from us. First disclosed by Rautenstrauch on other ynol systems and catalyzed by $PdCl_2(MeCN)_2$ and in a minor extent by $PtCl_2(MeCN)_2$,[7] this reactivity has remained dormant for almost two decades until we initiated its renaissance,[6] soon accompanied by Uemura for the intermolecular version.[8] Several parameters have now been examined. Among all of them, we have notably concentrated on the substitution of the alkyne partner and, herein, we disclose the elements of reactivity of enynes of type **4**, which could by analogy with our previous findings give birth to bicyclic derivatives (Scheme 2).

2. Results and discussions

The general route to precursors is described on Scheme 3.



Scheme 1.

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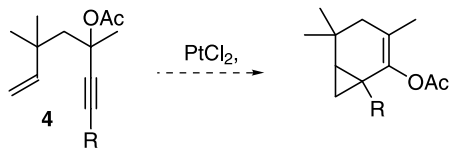


Scheme 2.

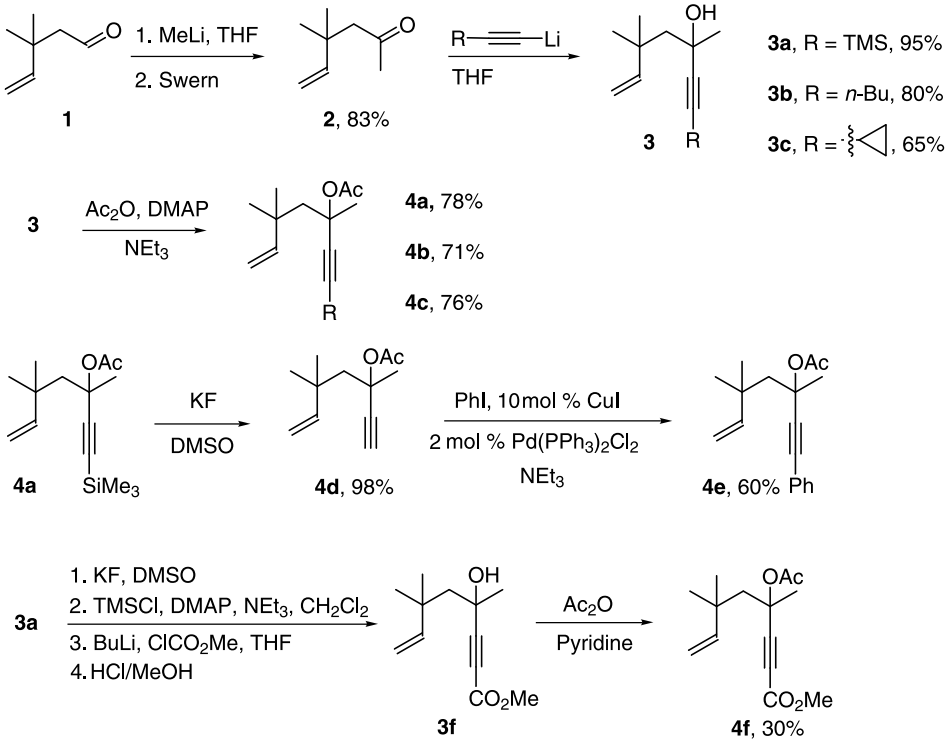
Known aldehyde **1**[9] was alkylated by methyllithium, and then oxidized to key building block, ketone **2**.[10]

Alkylation of this ketone by a series of lithium acetylides provided satisfactory yields of the corresponding alcohols **3a–c**, which were then acetylated to furnish **4a–c**. In the case of the cyclopropyl precursor, the lithium acetylide was generated from the cyclopropyldibromoolefin.[11] Phenyl substituted precursor **4e** was obtained through Sonagashira coupling, and precursor **4f** after methoxycarboxylation of a temporary *O*-silylated enynol substrate (Scheme 3).

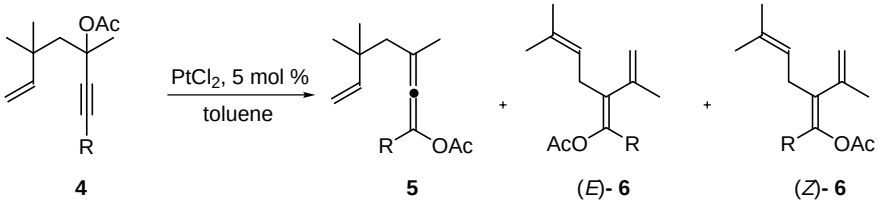
These precursors were then exposed to a catalytic amount of $PtCl_2$ (5 mol%) in toluene (0.025 M) under argon atmosphere at various temperatures (rt, 40 and 80 °C). Results of these reactions are given in Scheme 4. Thus, hexynyl substrate **4b** at 40 °C did not give any bicyclic adduct originating from the acetate 1,2-migration and carbene trapping. Instead, it underwent a smooth transformation in good yield to allenyl ester **5b** (entry 1), which results from a formal 1,3-migration of the acetate group and also corresponds to a [3,3] rearrangement of the propargyl acetate system. Interestingly, when this reaction was run at 80 °C, no allene **5b** was observed. A 9:1 mixture of two polyunsaturated, presumably isomeric products was isolated and careful spectroscopic analysis suggested trienic structures of type **6**. NOE analysis led to a *Z* relative configuration for the minor isomer of **6b** (Scheme 5).

Cyclopropyl precursor **4c** followed the same reactivity pattern: at 40 °C, no bicyclic adduct but allenyl ester **5c** (entry 3), and at 80 °C trienic adducts **6** in the same type of ratio and stereoselectivity (see also Scheme 5).

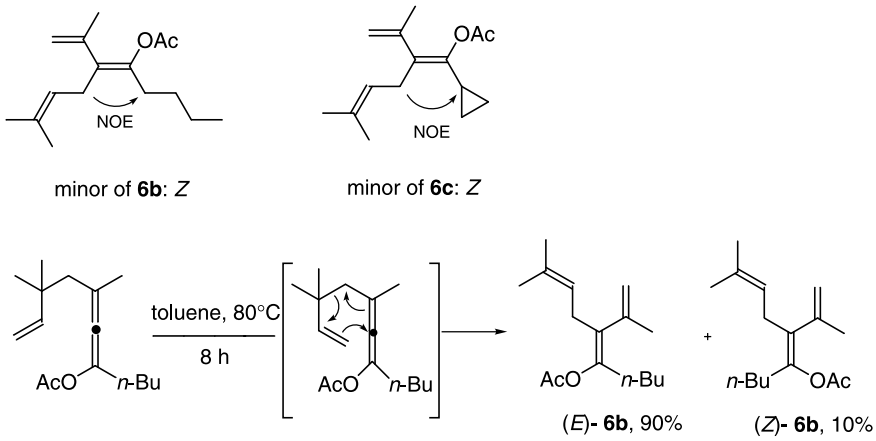
At that stage, it was interesting to have a better insight in the reactivity of these systems. Are allenes **5** intermediates between precursors **4** and trienes **6**? Then, would the transformation of **5** into **6** be platinum-catalyzed? We answered these questions by heating allenylester **5b** in toluene at 80 °C for a few hours, in the absence of $PtCl_2$. Very clean and complete conversion of **5b** to trienes **6b** was observed, suggesting that trienes **6** would originate from a



Scheme 3.



Scheme 4.



Scheme 5.

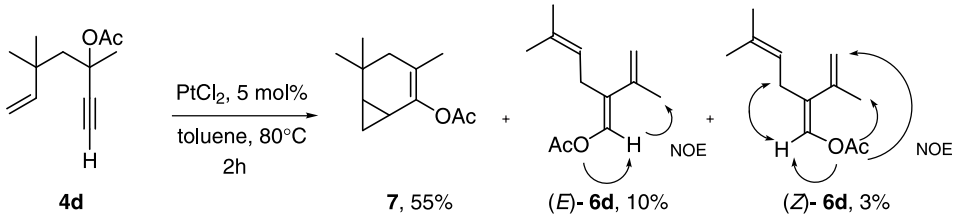
non metal catalyzed [3,3] (Cope type) rearrangement which involves an allene component[12] (Scheme 5).

Phenyl-substituted substrate **4d** proved more reactive since at rt a quasi equimolar mixture of allenyl ester **5d** and trienes **6d** was produced (Scheme 4, entry 5). Gentle heating to 40 °C is sufficient in that case (entry 6) to ensure complete formation of the trienes **6d**.[13] In sharp contrast, TMS precursor **4a** furnished very little amount of triene product **6a** among a complex mixture after 3 days in refluxing toluene.[14]

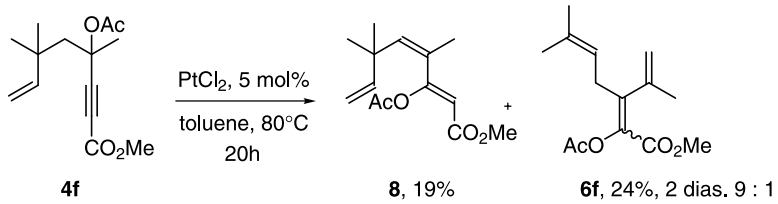
It was interesting to complete our study by examining the behavior of **4d** and **4f**. In the case of **4d** (Scheme 6), no reaction occurred at 40 °C after 4 h. However, at 80 °C, full consumption of the starting material was observed. As anticipated from our previous findings,[6] bicyclic adduct **7** was isolated in 55% yield, accompanied also by 13% of an inseparable mixture of triene derivatives **6d**, whose relative stereochemistries were attributed by NOE.

Reactivity of **4f** proved to be relatively sluggish. After prolonged reaction time (20 h) at 80 °C, starting material was consumed and an inseperable mixture of 3 products was isolated after chromatography in moderate overall yield (Scheme 7). Corresponding trienic derivatives **6f** were present in a 9:1 ratio with no determination of the relative stereochemistries. The second component of this mixture would correspond to another trienic derivative (**8**), whose structure is proposed after careful spectroscopic analysis and relative stereochemistry consistent with the following mechanism proposal (see below, Scheme 8).

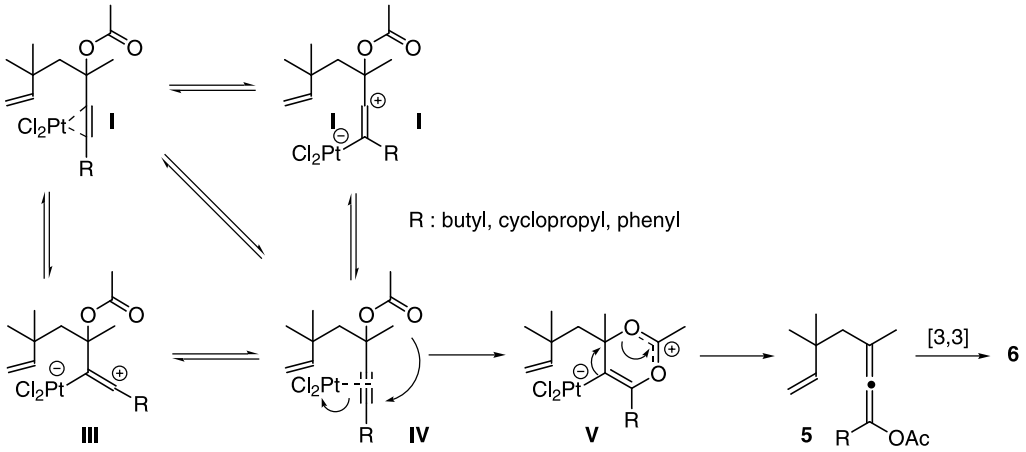
How to rationalize this new reactivity of the propargylic system and some of its divergent aspects? Clearly, substitution at the triple bond brings major alteration in the platinum-catalyzed step of the sequence, since no bicyclic adduct is formed. Allenyl esters are to a large extent the exclusively generated intermediates, which are formed in good yields and react further in a [3,3] rearrangement. π-Complexation of the alkyne moiety as in **I** can give birth to two σ-complexes **II** and **III**, whose potential intervention and relative contribution would be controlled by the nature of the R group. Thus, the presence of a R group that can stabilize a positively charged center will favor a species like **III** and this would take place through increasing donation from R=butyl, then cyclopropyl to phenyl.[15] Then, from **III**, anchimeric assistance from the best nucleophile, that is, the acetate group, would trigger the 1,3-migration of this group giving birth to the formal [3,3] product **5**.



Scheme 6.



Scheme 7.



Scheme 8.

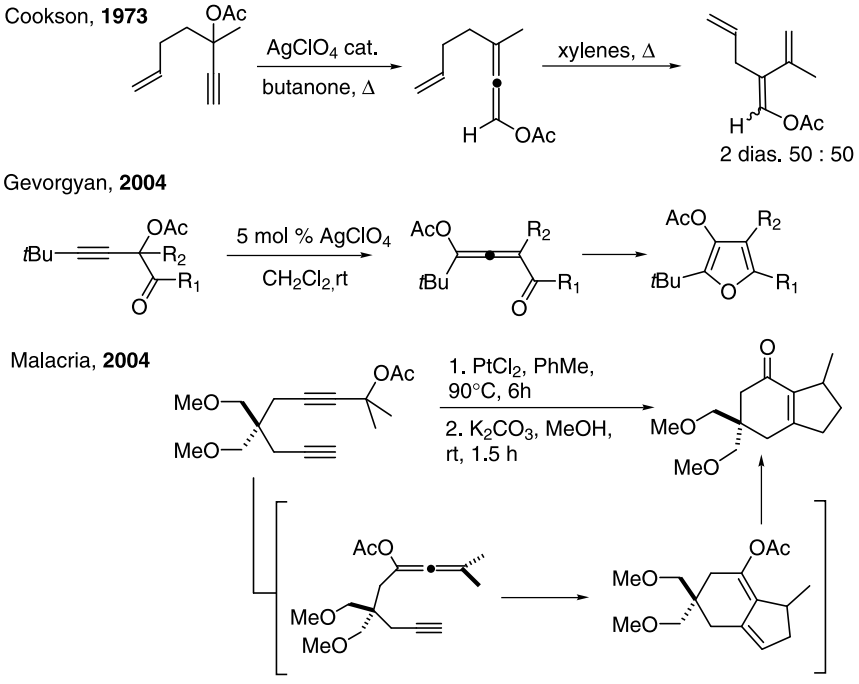
Interestingly, the observed order of reactivity correlates well with the R group stabilization ability.

Metal catalyzed [3,3] transposition of propargyl acetates have already been described with Ag(I)[16] and further exploited for an additional step. Thus, starting from a demethylated analog of **4d** and upon catalysis with $AgClO_4$, Cookson[17] observed a clean conversion to the corresponding allenyl ester intermediate, which was then further heated in boiling xylene to undergo an additional [3,3] rearrangement (Scheme 9).

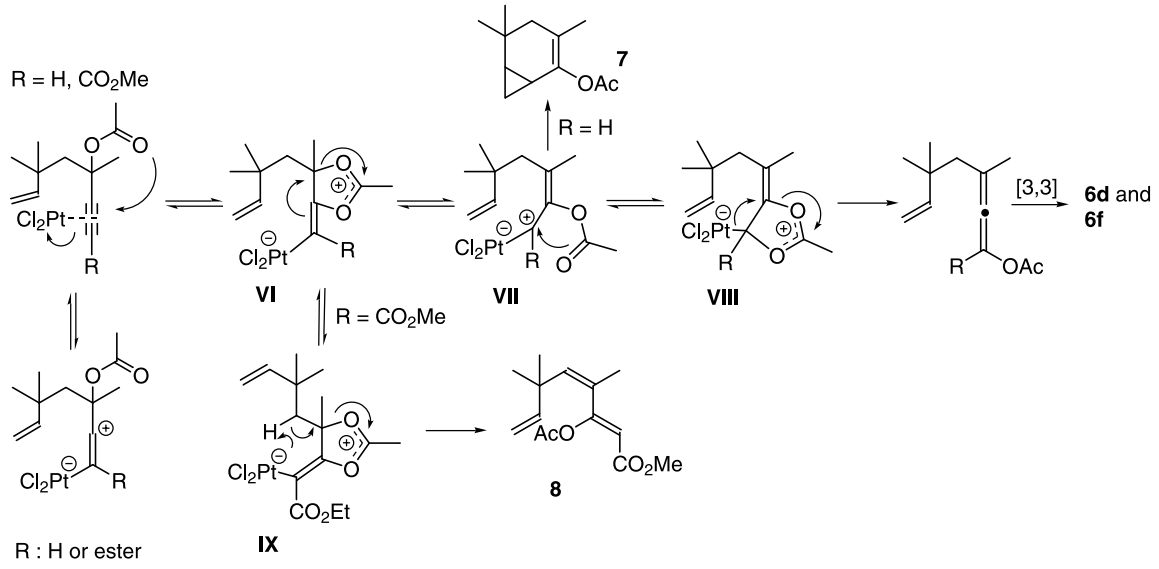
Very recently, Gevorgyan[18] has also used $AgClO_4$ for catalyzing a [3,3] rearrangement–1,2-migration–cycloisomerization cascade. We have also designed[4a] a $PtCl_2$-catalyzed [3,3] rearrangement–cycloisomerization tandem from a diyne acetate (Scheme 9). Thus, the formation of allenylesters from propargyl acetates has some precedent and can precede further interesting reactivity. In our case, the subsequent [3,3] rearrangement gives birth to a variety of trienes with a high diastereoselectivity that is not yet rationalized.

In the case of precursors **4d**, complex **III** (Scheme 8) is not stabilized and for **4f**, it is even destabilized. Presumably, 1,2-migration of the acetate takes place via **VI** (Scheme 10). A common path would consist of a second 1,2-migration of the acetate group (via **VII**) to give the allenyl ester. Then several paths are open. For R=H, cyclopropanation from carbenoid **VII** is the major pathway and provides **7** and for $R=CO_2Me$, platinum assisted elimination as in **IX** would yield to **8**.

Finally, this reactivity is not restricted to tertiary substrates. Secondary substrate **9** bearing an activating phenyl group on the triple bond could undergo the two consecutive [3,3]



Scheme 9.



Scheme 10.

transpositions to provide satisfactory yields of the trienic substrates **10** (Scheme 11), whose relative stereochemistries were also deduced from NOE analysis.

In conclusion, we have shown that enynes bearing an acetate group at the propargylic position and substitution on the triple bond can give birth to versatile transformations such as two consecutive [3,3] rearrangements, the first one being catalyzed by $PtCl_2$. The resulting trienes are formed stereoselectively. The scope of the transformation has been delineated by varying the nature of the alkynyl substituent R. For R=alkyl or phenyl, a direct 1,3-migration of the acetate group is proposed leading to an allenyl ester intermediate. Further applications of this valuable set of synthetic processes are underway, notably for the efficient preparation of relevant polyunsaturated building blocks.

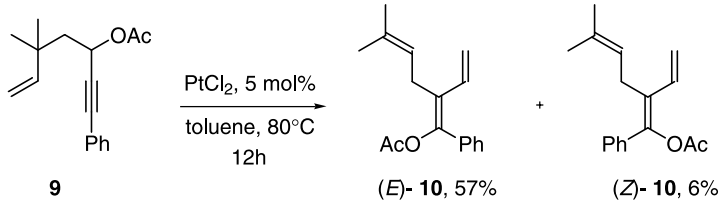
3. Experimental

3.1. General remarks

Reactions were carried out under an anhydrous atmosphere of Ar. Glassware was flame-dried under an argon gas flow prior to use. Anhydrous THF and Et_2O were obtained by distillation over sodium/benzophenone under nitrogen and used freshly distilled. Et_3N was dried then distilled from KOH; toluene and CH_2Cl_2 from CaH_2. *n*-Butyllithium was purchased as 2.5 M solutions in hexanes and titrated before use. Other reagents were commercially available and used without further purification unless otherwise indicated. NMR spectra (^1H, ^{13}C, DEPT, COSY ^1H–^1H and ^1H–^{13}C, NOE) were recorded on a 200 MHz ARX 200 or a 400 MHz AVANCE 400 Bruker spectrometers. ^1H NMR spectra are referenced at 7.26 ppm for $CDCl_3$ and 7.16 ppm for C_6D_6. ^{13}C NMR spectra are referenced at 77.23 ppm for $CDCl_3$ and 128.62 ppm for C_6D_6. Chemical shifts are given in ppm. IR spectra were recorded with a Tensor 27 (ATR diamond) Bruker spectrometer. IR is reported as characteristic bands (cm^{-1}) in their maximal intensity.

3.1.1. Synthesis of 2. Synthesis of 4,4-dimethyl-hex-5-en-2-ol: at −78 °C, MeLi (1.6 M in Et_2O, 18.4 mmol, 1.5 equiv) is added to a solution of aldehyde **1**[9] (1.4 g, 12.5 mmol, 1 equiv) in dry THF (15 mL). The mixture is allowed to heat up to rt, and then quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give the crude oil, which is engaged in the next step without further purification.

Synthesis of 4,4-dimethyl-hex-5-en-2-one **2**[10]: a 100 mL round bottom flask containing a solution of $(COCl)_2$ (1.4 mL, 16 mmol, 1.3 equiv) in CH_2Cl_2 (18 mL) is cooled at −78 °C, under an argon atmosphere. A solution of DMSO (2.2 mL, 31 mmol, 2.5 equiv) in CH_2Cl_2 (18 mL), is transferred, and after 5 min a solution of the crude alcohol (1.5 g, 12.5 mmol, 1 equiv) in CH_2Cl_2 (16 mL) is cannulated. After 15 min, Et_3N (9.6 mL, 69 mmol, 5.5 equiv) is added and after 15 min the mixture is allowed to warm up to rt. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and



Scheme 11.

evaporated to give crude **2**. The purification is done by simple filtration over silica gel and celite to give 1.3 g (10.4 mmol) of pure **2** (yield: 83% over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): 5.91 (dd, $J=17.7$, 10.3 Hz, 1H, =CH), 4.95 (m, 2H, $=CH_2$), 2.43 (s, 2H, CH_2), 2.10 (s, 3H, CH_3), 1.11 (s, 6H, 2 CH_3).

3.1.2. 3,5,5-Trimethyl-1-trimethylsilanyl-hept-6-en-1-yn-3-ol 3a. A 50 mL round bottom flask, containing 20 mL of dry THF, is cooled at −78 °C, under an argon atmosphere. First TMSA (1.7 mL, 12 mmol, 1.5 equiv) and then *n*-BuLi (2.3 M in hexanes, 4.1 mL, 9.5 mmol, 1.2 equiv), are added. After 40 min the ketone **2** (1.0 g, 8 mmol, 1 equiv), diluted in 20 mL of dry THF, is transferred. The mixture is kept 30 min at −78 °C and then is allowed to heat up to rt. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give 1.75 g (8 mmol) of crude **3a** (yield: 98%), that was engaged in the next step without further purification.

IR (neat): 3550, 3080, 2960, 2930, 2170, 1640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 6.08 (dd, $J=17.5$, 10.7 Hz, 1H, =CH), 5.08 (dd, $J=17.5$, 1.3 Hz, 1H, =CH*H trans*), 5.02 (dd, $J=10.7$, 1.3 Hz, 1H, =C*H*H *cis*), 1.79 (s, 2H, CH_2), 1.44 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 0.15 (s, 9H, $Si(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 149.1 (=CH), 111.8 ($=CH_2$), 110.7 (C), 88.6 (C), 67.9 (C), 54.8 (C), 37.3 (C), 32.9 (CH_3), 30.6 (CH_3), 26.6 (CH_3), 0.0 ($Si(CH_3)_3$).

3.1.3. 3,3,5-Trimethyl-undec-1-en-6-yn-5-ol 3b. A 50 mL flask, containing 6 mL of dry THF, is cooled at −78 °C, under an argon atmosphere. First hex-1-yne (550 μL, 4.8 mmol, 1.5 equiv) and then *n*-BuLi (2.3 M in hexanes, 1.7 mL, 3.9 mmol, 1.2 equiv), are added. After 40 min the ketone **2** (400 mg, 3.2 mmol, 1 equiv), diluted in 4 mL of dry THF, is transferred. The mixture is kept 30 min at −78 °C and then is allowed to heat up to rt. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give crude **3b**, that was engaged in the next step without further purification.

IR (neat): 3500, 3080, 2960, 2870, 2240, 1640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 6.06 (dd, $J=17.5$, 10.7 Hz, 1H, =CH), 5.03 (dd, $J=17.5$, 1.0 Hz, 1H, =CH*H trans*), 4.98 (dd, $J=10.7$, 1.3 Hz, 1H, =C*H*H *cis*), 2.14 (t, $J=6.9$ Hz, 2H, CH_2), 1.78 (d, $J=14.4$ Hz, 1H, CH_2), 1.75 (d, $J=14.4$ Hz, 1H, CH_2), 1.41 (s, 3H, CH_3), 1.52–1.28 (m, 4H, CH_2, CH_2), 1.25 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.88 (t, $J=7.2$ Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 149.1 (=CH), 111.1 ($=CH_2$), 84.8, 84.5 (2C), 67.5 (C), 54.8 (C), 37.0 (C), 33.1 (CH_3), 30.6 (CH_2), 30.1 (CH_3), 26.6 (CH_3), 22.0 (CH_2), 18.4 (C), 13.6 (CH_3).

3.1.4. Acetic acid 1-cyclopropylethynyl-1,3,3-trimethyl-pent-4-enyl ester 3c. Synthesis of (2,2-dibromovinyl)-cyclopropane: to a solution of CBr_4 (6.64 g, 20 mmol, 1.4 equiv) in CH_2Cl_2 (15 mL), a solution of PPh_3 (10.48 g, 40 mmol, 2.8 equiv) in CH_2Cl_2 (15 mL) is added at 0 °C. After 30 min of stirring a solution of cyclopropylcarboxaldehyde (1 g, 14.3 mmol, 1 equiv) in CH_2Cl_2 (15 mL) is added. The mixture is allowed to heat up to rt, after 1 h the reaction is complete. The mixture is poured in 300 mL of pentane, filtered over celite and concentrated. The residue is diluted in 200 mL of pentane, filtered over celite and concentrated to give the crude dibromoalkene, which is engaged in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 5.77 (d, $J=9.3$ Hz, 1H, =CH), 1.55–1.70 (m, 1H, CH), 0.85 (m, 2H, CH_2), 0.53 (m, 2H, CH_2). Identical to those of the literature.[11a]

3.1.5. 1-Cyclopropyl-3,5,5-trimethyl-hept-6-en-1-yn-3-ol 3c. To a solution of crude dibromoalkene (1.81 g, 8 mmol, 1.25 equiv) in dry THF (10 mL) 6.8 mL of *n*-Buli (2.3 M in hexanes, 15.7 mmol, 2.4 equiv) are added at −78 °C. After 30 min, a solution of ketone **2** (815 mg, 6.5 mmol, 1 equiv) in dry THF (10 mL) is added. The mixture is then allowed to heat up to rt. After 45 min the reaction is complete. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give crude oil, that is purified by flash chromatography on silica gel (petroleum ether/Et_2O, 95:5) to give 850 mg (1.8 mmol, 73%) of **3c**.

^{1}H NMR (400 MHz, $CDCl_3$): 6.09 (dd, $J=17.6$, 10.7 Hz, 1H, =CH), 5.07 (dd, $J=17.5$, 1.3 Hz, 1H, =CH*H trans*), 5.03 (dd, $J=10.7$, 1.3 Hz, 1H, =C*H*H *cis*), 1.81 (d, $J=14.4$ Hz, 1H, CH_2), 1.76 (d, $J=14.4$ Hz, 1H, CH_2), 1.43 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.25 (m, 1H, CH), 1.10 (s, 3H, CH_3), 0.75 (m, 2H, CH_2), 0.67 (m, 2H, CH_2).

3.1.6. Acetic acid 1-(2,2-dimethyl-but-3-enyl)-1-methyl-hept-2-ynyl ester 4a. To a solution of crude **3a** (255 mg, 1.14 mmol, 1 equiv) in NEt_3 (3 mL), DMAP (28 mg, 0.23 mmol, 0.2 equiv) and Ac_2O (650 μL, 4.6 mmol, 4 equiv) are added and the mixture is stirred at rt overnight. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give the crude oil, which is purified by flash chromatography on silica gel (pentane/Et_2O, 95:5) to give 235 mg (0.89 mmol, 78%) of pure **4a**.

IR (neat): 3080, 2960, 2170, 1750, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 5.95 (dd, $J=17.4$, 10.8 Hz, 1H, =CH), 4.89 (dd, $J=17.4$, 1.3 Hz, 1H, =CH*H trans*), 4.83 (dd, $J=10.8$, 1.3 Hz, 1H, =C*H*H *cis*), 2.13 (d, $J=14.6$ Hz, 1H, CH_2), 1.95 (s, 3H, $COCH_3$), 1.88 (d, $J=14.6$ Hz, 1H, CH_2), 1.67 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 0.13 (s, 9H, $Si(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 169.0 (C=O), 148.8 (=CH), 109.5 ($=CH_2$), 106.3 (C), 90.3 (C), 75.2 (C), 51.8 (C), 36.8

(C), 28.9 (CH_3), 28.5 (CH_3), 27.9 (CH_3), 22.2 (CH_2), −0.3 ($Si(CH_3)_3$).

3.1.7. Acetic acid 1-(2,2-dimethyl-but-3-enyl)-1-methyl-hept-2-ynyl ester 4b. Compound **3b** (132 mg, 0.63 mmol, 1 equiv) is acylated using the same procedure as for alcohol **3a**, with 25 mg (0.2 mmol, 0.3 equiv) of DMAP, 250 μL of Ac_2O (2.6 mmol, 4.2 equiv) in 3 mL of NEt_3. After purification by flash chromatography on silica gel (pentane/Et_2O, 95:5), 112 mg (0.45 mmol, 71%) of pure **4b** were isolated.

IR (neat): 3080, 2960, 2930, 2250, 1740, 1640 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 5.95 (dd, $J=17.6$, 10.7 Hz, 1H, =CH), 4.88 (dd, $J=17.6$, 1.2 Hz, 1H, =CH*H trans*), 4.83 (dd, $J=10.7$, 1.2 Hz, 1H, =C*H*H *cis*), 2.16 (t, $J=7.1$ Hz, 2H, CH_2), 2.08 (d, $J=14.5$ Hz, 1H, CH_2), 1.94 (s, 3H, $COCH_3$), 1.86 (d, $J=14.5$ Hz, 1H, CH_2), 1.64 (s, 3H, CH_3), 1.53–1.30 (m, 4H, $2CH_2$), 1.12 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 0.87 (t, $J=7.2$ Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169.3 (C=O), 149.0 (=CH), 109.2 (=CH_2), 86.6 (C), 81.2 (C), 75.5 (C), 52.3 (C), 36.8 (C), 30.4 (CH_2), 29.4 (CH_3), 28.4 (CH_3), 28.0 (CH_3), 22.0 (CH_2), 18.5 (C), 13.6 (CH_3).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.26; H, 10.93.

3.1.8. Acetic acid 1-cyclopropylethynyl-1,3,3-trimethyl-pent-4-enyl ester 4c. Compound **3c** (350 mg, 1.8 mmol, 1 equiv) is acylated using the same procedure as for alcohol **3a**, with 67 mg (0.55 mmol, 0.3 equiv) of DMAP, 0.5 mL of Ac_2O (5.25 mmol, 3 equiv) in 3 mL of NEt_3. After purification by flash chromatography on silica gel (pentane/Et_2O, 95:5), 321 mg (1.37 mmol, 76%) of pure **4c** were isolated.

IR (neat): 3290, 2970, 2880, 2120, 1750, 1650 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 5.98 (dd, $J=17.4$, 10.6 Hz, 1H, =CH), 4.90 (dd, $J=17.4$, 1.3 Hz, 1H, =CH*H trans*), 4.85 (dd, $J=10.6$, 1.3 Hz, 1H, =C*H*H *cis*), 2.08 (d, $J=14.7$ Hz, 1H, CH_2), 1.96 (s, 3H, $COCH_3$), 1.84 (d, $J=14.4$ Hz, 1H, CH_2), 1.63 (s, 3H, CH_3), 1.24 (m, 1H, CH), 1.12 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 0.73 (m, 2H, CH_2), 0.67 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 169.5 (C=O), 149.1 (=CH), 109.5 (=CH_2), 89.5 (C), 76.5 (C), 75.6 (C), 52.5 (C), 37.0 (C), 29.3 (CH_3), 28.5 (CH_3), 28.3 (CH_3), 22.8 (CH_3), 8.3 ($2CH_2$), 0.0 (CH).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.70; H, 9.63.

3.1.9. Acetic acid 1-ethynyl-1,3,3-trimethyl-pent-4-enyl ester 4d. Compound **4a** (280 mg, 1.05 mmol, 1 equiv) is diluted with 8 mL of DMSO. KF (100 mg, 1.7 mmol, 1.6 equiv) and a few drops of water are added. After 45 min the mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give 200 mg of **4d** (2.6 mmol, 98%), with no need of further purification.

IR (neat): 3290, 2970, 2880, 2140, 1750, 1650 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 5.95 (dd, $J=17.5$, 10.7 Hz, 1H, =CH), 4.93 (dd, $J=17.5$, 1.3 Hz, 1H, =CH*H trans*), 4.88 (dd, $J=10.7$, 1.3 Hz, 1H, =C*H*H *cis*), 2.58 (s, 1H, CH), 2.11 (d, $J=14.7$ Hz, 1H, CH_2), 1.99 (s, 3H, $COCH_3$), 1.95 (d, $J=14.7$ Hz, 1H, CH_2), 1.70 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.14 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169 (C=O), 149.1 (=CH), 110.1 (=CH_2), 85.2 (C), 74.9 (C), 74.7 (C), 52.3 (C), 37.3 (C), 29.1 ($2CH_3$), 28.2 (CH_3), 22.6 (CH_3).

3.1.10. Acetic acid 1,3,3-trimethyl-1-phenylethynyl-pent-4-enyl ester 4e. Compound **4d** (200 mg, 1.05 mmol, 1 equiv) is introduced under an argon atmosphere with PhI (120 μL, 1.08 mmol, 1.02 equiv). Dry NEt_3 (4 mL) is added and the solution is degassed with argon during 15 min. CuI (20 mg, 0.105 mmol, 0.1 equiv) and $PdPPh_3Cl_2$ (15 mg, 0.02 mmol, 0.02 equiv) are added, the mixture is heated at 70 °C. After 1 h the reaction is complete. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give the crude, which is purified by flash chromatography on silica gel (pentane/Et_2O, 95:5) to give 154 mg (0.57 mmol, 60%) of pure **4e**.

IR (neat): 3080, 2960, 2870, 2240, 1745, 1640 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 7.42 (m, 2H, H_{Ar}), 7.28 (m, 3H, H_{Ar}), 6.02 (dd, $J=17.5$, 10.7 Hz, 1H, =CH), 4.96 (dd, $J=17.5$, 1.1 Hz, 1H, =CH*H trans*), 4.91 (dd, $J=10.7$, 1.1 Hz, 1H, =C*H*H *cis*), 2.23 (d, $J=14.7$ Hz, 1H, CH_2), 2.01 (s, 3H, $COCH_3$), 2.00 (d, $J=14.7$ Hz, 1H, CH_2), 1.79 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.20 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169.3 (C=O), 148.9 (=CH), 131.6 (2 CH, Ar), 128.3 (CH, Ar), 128.0 (2 CH, Ar), 109.6 (=CH_2), 90.3 (C), 85.6 (C), 75.3 (C), 52.3 (C), 36.9 (C), 29.0 (CH_3), 28.4 (CH_3), 28.2 (CH_3), 22.3 (CH_3).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.46; H, 8.46.

3.1.11. 4-Acetoxy-4,6,6-trimethyl-oct-7-en-2-ynoic acid methyl ester 4f. Synthesis of 3,5,5-trimethyl-hept-6-en-1-yn-3-ol: crude alcohol **3a** (3.2 g, 14.3 mmol, 1 equiv) is diluted with 45 mL of DMSO. KF (1.34 g, 23 mmol, 1.6 equiv) and a few drops of water are added. After 45 min the reaction is complete. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give the crude, which is engaged in the next step without further purification.

^1H NMR (400 MHz, $CDCl_3$): 6.08 (dd, $J=17.5$, 10.7 Hz, 1H, =CH), 5.10 (dd, $J=17.5$, 1.3 Hz, 1H, =CH*H trans*), 5.02 (dd, $J=10.7$, 1.3 Hz, 1H, =C*H*H *cis*), 2.47 (s, 1H,

CH), 1.81 (s, 2H, CH_2), 1.48 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.09 (s, 3H, CH_3).

Synthesis of (1-ethynyl-1,3,3-trimethyl-pent-4-enyloxy)-trimethyl-silane: to a solution of the resulting alcohol (1.6 g, 10.5 mmol, 1 equiv) in CH_2Cl_2 (50 mL), 8.6 mL of NEt_3 (62 mmol, 6 equiv) and 380 mg of DMAP (3.1 mmol, 0.3 equiv) are added. The solution is cooled at 0 °C and the TMSCl (4 mL, 31.5 mmol, 3 equiv) is slowly added. The mixture is allowed to heat up to rt, the reaction is complete. The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried on $MgSO_4$ and evaporated to give crude silylether, which is engaged in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 6.02 (dd, $J=17.4$, 10.6 Hz, 1H, =CH), 4.90 (dd, $J=17.4$, 1.2 Hz, 1H, =CH*H trans*), 4.84 (dd, $J=10.6$, 1.2 Hz, 1H, =C*H*H *cis*), 2.45 (s, 1H, CH), 1.80 (d, $J=14.7$ Hz, 1H, CH_2), 1.76 (d, $J=14.5$ Hz, 1H, CH_2), 1.48 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 0.02 (s, 9H, $Si(CH_3)_3$).

4,6,6-Trimethyl-4-trimethylsilanyloxy-oct-7-en-2-ynoic acid methyl ester: to a solution of the crude resulting silylether (2.3 g, 10.5 mmol, 1 equiv) in dry THF (50 mL) 5 mL of a 2.3 M solution of *n*-BuLi (11.3 mmol, 1.1 equiv) is added at −78 °C. The $ClCO_2Me$ (2.4 mL, 31 mmol, 3 equiv) is added and the mixture is allowed to heat up to rt, the reaction is complete The mixture is quenched with saturated NH_4Cl solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give the crude methyl ethynate, which is engaged in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 6.00 (dd, $J=17.4$, 10.6 Hz, 1H, =CH), 4.92 (dd, $J=17.4$, 1.4 Hz, 1H, =CH*H trans*), 4.84 (dd, $J=10.6$, 1.4 Hz, 1H, =C*H*H *cis*), 3.77 (s, 3H, OCH_3), 1.80 (d, $J=14.7$ Hz, 1H, CH_2), 1.75 (d, $J=14.7$ Hz, 1H, CH_2), 1.50 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 0.02 (s, 9H, $Si(CH_3)_3$).

Synthesis of 4-hydroxy-4,6,6-trimethyl-oct-7-en-2-ynoic acid methyl ester **3f**: a solution of crude silylated alcohol (3 g, 10.5 mmol), in methanol (50 mL), is cooled down to 0 °C. Then a few drops of concentrated HCl are added, the reaction is immediately complete. The mixture is quenched with saturated $NaHCO_3$ solution and extracted with diethylether. The combined organic layers are washed with brine, dried over $MgSO_4$ and evaporated to give crude **3f**, which is engaged in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): 6.07 (dd, $J=17.7$, 10.6 Hz, 1H, =CH), 5.13 (d, $J=17.7$ Hz, 1H, =CH*H trans*), 5.07 (d, $J=10.6$ Hz, 1H, =C*H*H *cis*), 3.77 (s, 3H, OCH_3), 1.86 (s, 2H, CH_2), 1.50 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.09 (s, 3H, CH_3).

Synthesis of 4-acetoxy-4,6,6-trimethyl-oct-7-en-2-ynoic acid methyl ester **4f**: compound **3f** (2.2 g, 10.5 mmol, 1 equiv) is acylated using the same procedure as for alcohol **3d**, with 29 mL of Ac_2O (305 mmol, 30 equiv) in 45 mL of pyridine. After purification by flash chromatography on silica gel (PE/Et_2O 9:1) 800 mg (3.1 mmol, 30%, 5 steps) of pure **3f** were isolated.

IR (neat): 3080, 2960, 2870, 2240, 1750, 1715 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 5.91 (dd, $J=17.4$, 10.6 Hz, 1H, =CH), 4.95 (dd, $J=17.4$, 1.4 Hz, 1H, =CH*H trans*), 4.89 (dd, $J=10.6$, 1.4 Hz, 1H, =C*H*H *cis*), 3.76 (s, 3H, OCH_3), 2.12 (d, $J=14.7$ Hz, 1H, CH_2), 2.01 (s, 3H, $COCH_3$), 1.97 (d, $J=14.7$ Hz, 1H, CH_2), 1.72 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.15 (s, 6H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169 (C=O), 149.1 (=CH), 110.1 (=CH_2), 85.2 (C), 74.9 (C), 74.7 (C), 52.3 (C), 37.3 (C), 29.1 ($2CH_3$), 28.2 (CH_3), 22.6 (CH_3).

3.2. Products from the $PtCl_2$-catalyzed reactions. General procedure for reactions involving $PtCl_2$

Reactions are carried out in anhydrous toluene. The enyne is introduced under an argon atmosphere. The solvent is then added and the solution ($c=0.025$ M) is submitted to argon bubbling during 15 min. The catalyst is then added, still under an argon atmosphere. The reaction requires stirring and heating. The reaction is monitored by TLC. When the reaction is complete, the solvent is evaporated and the crude is analyzed by ^{1}H NMR analysis before purification.

3.2.1. Acetic acid 1-trimethylsilyl-2-isopropenyl-5-methyl-hexa-1,4-dienyl esters *E*-6a. General procedure is applied to **4a** (146 mg, 0.55 mmol, 1 equiv), with 8.5 mg of $PtCl_2$ (0.032 mmol, 0.05 equiv), in 20 mL of toluene. The mixture is heated at reflux for 3d. After purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 8:2), 11 mg (8%) of **6a** are isolated.

IR (neat): 3085, 2960, 2860, 1740, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 4.96 (th, $J=7.0$, 1.4 Hz, 1H, =CH), 4.92 (m, 1H, =CH_2), 4.89 (m, 1H, =CH_2), 2.80 (d, $J=7.0$ Hz, 2H, CH_2), 2.12 (s, 3H, $COCH_3$), 1.81 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 0.12 (s, 9H, $Si(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$): 169.9 (C=O), 148.6 (C), 147.0 (C), 142.8 (C), 132.2 (C), 120.7 (=CH), 116.6 (=CH_2), 27.9 (CH_2), 25.6 (CH_3), 21.8 (CH_3), 20.7 (CH_3), 17.7 (CH_3), 0.0 ($Si(CH_3)_3$).

3.2.2. Acetic acid 1-butyl-3,5,5-trimethyl-hepta-1,2,6-trienyl ester 5b. General procedure is applied to **4b** (95 mg, 0.38 mmol, 1 equiv), with 5 mg of $PtCl_2$ (0.02 mmol, 0.05 equiv), in 18 mL of toluene. The mixture is heated at 40 °C during 2 h. After purification by simple filtration over silica gel 70 mg (0.28 mmol, 74%) of **5b** are isolated.

IR (neat): 3080, 2960, 2860, 1980, 1735, 1640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 5.87 (dd, $J=17.4$, 10.6 Hz, 1H, =CH), 4.94 (dd, $J=17.4$, 1.3 Hz, 1H, =CH*H trans*),

4.92 (dd, $J=10.6$, 1.3 Hz, 1H, =C*H*H *cis*), 2.20 (m, 2H, CH_2), 2.12 (s, 3H, $COCH_3$), 2.09 (s, 2H, CH_2), 1.81 (s, 3H, CH_3), 1.32–1.48 (m, 4H, CH_2), 1.06 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 0.92 (t, $J=7.2$ Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 194.0 (C), 169.3 (C=O), 148.6 (=CH), 121.9 (C), 110.7 (=CH), 109.5 (C), 48.5 (CH_2), 37.0 (C), 31.9 (CH_2), 28.9 (CH_2), 27.4 (CH_3), 27.2 (CH_3), 22.9 (CH_3), 21.5 (CH_3, 22.5 (CH_2), 14.3 (CH_3).

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.57; H, 10.61.

3.2.3. Acetic acid 1-butyl-2-isopropenyl-5-methyl-hexa-1,4-dienyl esters *E*-6b and *Z*-6b. General procedure is applied to **4b** (185 mg, 0.74 mmol, 1 equiv), with 10 mg of $PtCl_2$ (0.036 mmol, 0.05 equiv), in 30 mL of toluene. The mixture is heated at 80 °C during 15 h. After purification by flash chromatography on silica gel (pentane/Et_2O, 98:2), 110 mg (60%) of a mixture containing: *E*-**6b**/*Z*-**6b**, 9/1, are isolated.

IR (neat): 3080, 2960, 2860, 1750, 1640, 1610 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 5.01 (th, $J=7.1$, 1.5 Hz, 1H, =CH), 4.97 (m, 1H, =CH_2, *E*-**6b**), 4.95 (m, 1H, =CH_2, *Z*-**6b**), 4.77 (m, 1H, =CH_2, *E*-**6b**), 4.68 (m, 1H, =CH_2, *Z*-**6b**), 2.78 (d, $J=7.1$ Hz, 2H, CH_2, *Z*-**6b**), 2.70 (d, $J=7.1$ Hz, 2H, CH_2, *E*-**6b**), 2.3 (t, $J=7.5$ Hz, 2H, CH_2), 2.14 (s, 3H, $COCH_3$, *E*-**6b**), 2.03 (s, 3H, $COCH_3$, *Z*-**6b**) 1.79 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.24–1.40 (m, 4H, CH_2), 0.87 (t, $J=7.2$ Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169.1 (C=O), 144.1 (C), 142.9 (C), 132.0 (C), 129.8 (C), 121.4 (=CH), 114.7 (=CH_2), 30.3 (CH_2), 29.7 (CH_2), 28.0 (CH_2), 25.7 (CH_3), 22.6 (CH_3), 22.4 (CH_2), 20.9 (CH_3), 17.7 (CH_3), 13.9 (CH_3).

3.2.4. Acetic acid 1-cyclopropyl-3,5,5-trimethyl-hepta-1,2,6-trienyl ester 5c. General procedure is applied to **4c** (147 mg, 0.63 mmol, 1 equiv), with 8.5 mg of $PtCl_2$ (0.03 mmol, 0.05 equiv), in 25 mL of toluene. The mixture is heated at 40 °C during 1 h. After purification by simple filtration over silica gel 110 mg (0.47 mmol, 75%) of **5c** are isolated.

IR (neat): 3080, 2960, 2870, 1940, 1750, 1640 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 5.85 (dd, $J=17.5$, 10.7 Hz, 1H, =CH), 4.93 (dd, $J=17.5$, 1.5 Hz, 1H, =CH*H trans*), 4.90 (dd, $J=10.7$, 1.5 Hz, 1H, =C*H*H *cis*), 2.12 (s, 3H, $COCH_3$), 2.07 (s, 2H, CH_2), 1.78 (s, 3H, CH_3), 1.45 (m, 1H, CH), 1.05 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 0.70 (m, 2H, CH_2), 0.50 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 193.2 (C), 168.9 (C=O), 148.1 (=CH), 123.4 (C), 110.5 (=CH_2), 110.0 (C), 48.0 (CH_2), 37.0 (C), 27.1 (CH_3), 26.8 (CH_3), 22.6 (CH_3), 21.1 (CH_3), 12.0 (CH), 6.0 (CH_2), 5.5 (CH_2).

3.2.5. Acetic acid 1-cyclopropyl-2-isopropenyl-5-methyl-hexa-1,4-dienyl esters *E*-6c and *Z*-6c. General procedure is applied to **4c** (93 mg, 0.4 mmol, 1 equiv), with 5.3 mg of $PtCl_2$ (0.02 mmol, 0.05 equiv), in 15 mL of toluene. The mixture is heated at 80 °C during 3 h. After purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 8:2), 71 mg (76%) of a mixture containing: *E*-**6c**/*Z*-**6c**, 9/1, are isolated.

IR (neat): 3080, 2960, 2860, 1750, 1640, 1610 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 5.09 (s, 1H, =CH_2), 5.00 (t, $J=7.1$ Hz, 1H, =CH), 4.91 (s, 1H, =CH_2), 3.00 (d, $J=6.6$ Hz, 2H, CH_2, *Z*-**6c**), 2.67 (d, $J=6.8$ Hz, 2H, CH_2, *E*-**6c**), 2.09 (s, 3H, $COCH_3$, *E*-**6c**), 2.00 (s, 3H, $COCH_3$, *Z*-**6c**), 1.84 (s, 3H, CH_3), 1.67 (s, 3H, CH_3, *Z*-**6c**), 1.65 (s, 3H, CH_3, *E*-**6c**), 1.62 (s, 3H, CH_3, *Z*-**6c**), 1.56 (s, 3H, CH_3, *E*-**6c**), 0.75 (m, 1H, CH_2), 0.57 (m, 2H, CH_2), 0.47 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 171.5 (C=O), 169.8 (C, *Z*-**6c**), 169.4 (C, *E*-**6c**), 143.3 (C), 132.6 (C), 130.1 (C), 121.9 (=CH, *Z*-**6c**), 121.6 (=CH, *E*-**6c**), 115.9 (=CH_2, *E*-**6c**), 114.1 (=CH_2, *Z*-**6c**), 29.1 (CH_2), 26.0 (CH_3), 22.8 (CH_3), 20.8 (CH_3), 18.1 (CH_3), 12.2 (CH), 5.5 ($2CH_2$).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.22; H, 9.85.

3.2.6. Acetic acid 3,5,5-trimethyl-bicyclo[4.1.0]hept-2-en-2-yl ester 7 and acetic acid 2-isopropenyl-5-methyl-hexa-1,4-dienyl esters *E*-6d and *Z*-6d. General procedure is applied to **4d** (154 mg, 0.78 mmol, 1 equiv), with 10.5 mg of $PtCl_2$ (0.04 mmol, 0.05 equiv), in 30 mL of toluene. The mixture is heated at 80 °C during 2 h. After purification by flash chromatography on silica gel (pentane/Et_2O, 95:5), 85 mg (55%) of **7** and 20 mg (13%) of a mixture containing: *E*-**6d**/*Z*-**6d**, 75/25, are isolated.

3.2.7. Acetic acid 3,5,5-trimethyl-bicyclo[4.1.0]hept-2-en-2-yl ester 7. IR (neat): 3075, 2950, 2870, 1750, 1450, 1610 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 2.22 (s, 3H, $COCH_3$), 1.82 (d, $J=16.5$ Hz, 1H, CH_2), 1.57 (dd, $J=16.5$, 2.0 Hz, 1H, CH_2), 1.50 (s, 3H, CH_3), 1.19–1.12 (m, 2H, CH_2), 1.12 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.85–0.64 (m, 2H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): 169.3 (C=O), 142.3 (C), 112.9 (C), 40.5 (CH_2), 29.5 (CH_3), 28.6 (CH_3), 28.0 (C), 26.4 (CH_3), 20.8 (CH_3), 16.5 (CH), 13.4 (CH), 9.7 (CH_2).

3.2.8. Acetic acid 2-isopropenyl-5-methyl-hexa-1,4-dienyl esters *E*-6d and *Z*-6d. IR (neat): 3080, 2960, 2860, 1750, 1640, 1610 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 7.41 (s, 1H, =CH, *E*-**6d**), 6.96 (s, 1H, =CH, *Z*-**6d**), 5.09 (m, 1H, CH, *Z*-**6d**), 5.07 (s, 1H, =CH_2), 5.05 (m, 1H, =CH, *E*-**6d**), 4.98 (s, 1H, =CH_2), 3.08 (d, $J=6.8$ Hz, 2H, CH_2, *E*-**6d**), 2.82 (d, $J=6.8$ Hz, 2H, CH_2, *Z*-**6d**), 2.20 (s, 3H, $COCH_3$, *E*-**6d**), 2.14 (s, 3H, $COCH_3$, *Z*-**6d**), 1.97 (s, 3H, CH_3, *Z*-**6d**), 1.92 (s, 3H, CH_3, *E*-**6d**), 1.74 (s, 3H, CH_3, *E*-**6d**), 1.72 (s, 3H, CH_3, *Z*-**6d**), 1.70 (s, 3H, CH_3, *E*-**6d**), 1.64 (s, 3H, CH_3, *Z*-**6d**).

^{13}C NMR (100 MHz, $CDCl_3$): 167.9 (C=O), 139.8 (C), 133.0 (=CH), 126.0 (C), 122.3 (=CH), 115.1 (C), 113.5

(CH_2), 25.7 (CH_3), 24.9 (CH_2), 20.9 (CH_3), 20.6 (CH_3), 17.8 (CH_3).

3.2.9. Acetic acid 3,5,5-trimethyl-1-phenyl-hepta-1,2,6-trienyl ester 5e and acetic acid 2-isopropenyl-5-methyl-1-phenyl-hexa-1,4-dienyl ester *E*-6e and *Z*-6e. General procedure is applied to **4e** (50 mg, 0.18 mmol, 1 equiv), with 2.5 mg of $PtCl_2$ (0.009 mmol, 0.05 equiv), in 8 mL of toluene. The mixture is stirred at rt during 60 h. After purification by flash chromatography on silica gel (pentane/Et_2O, 99:1), 35 mg (70%) of a mixture containing: **5e**/*E*-**6e**/*Z*-**6e**, 55/41/4, are isolated.

3.2.10. Acetic acid 3,5,5-trimethyl-1-phenyl-hepta-1,2,6-trienyl ester 5e. IR (neat): 3090, 3060, 2970, 2860, 1950, 1750, 1640, 1610 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 7.41 (m, 2H, H_{Ar}), 7.25 (m, 3H, H_{Ar}), 5.86 (dd, $J=17.4$, 10.6 Hz, 1H, =CH), 4.94 (dd, $J=17.4$, 1.5 Hz, 1H, =CH*H trans*), 4.89 (dd, $J=10.6$, 1.5 Hz, 1H, =C*H*H *cis*), 2.27 (s, 3H, $COCH_3$), 2.23 (s, 2H, CH_2), 1.94 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.07 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 195.3 (C), 168.8 (C=O), 147.9 (=CH), 132.2 (C), 128.3 ($2CH_{Ar}$), 127.8 ($2CH_{Ar}$), 124.5 (CH_{Ar}), 120.7 (C), 112.6 (C), 110.7 (CH_2), 48.0 (CH_2), 27.1 (CH_3), 26.9 (CH_3), 22.1 (CH_3), 21.0 (CH_3).

3.2.11. Acetic acid 2-isopropenyl-5-methyl-1-phenyl-hexa-1,4-dienyl ester *E*-6e and *Z*-6e. ^1H NMR (400 MHz, $CDCl_3$): 7.41 (m, 2H, H_{Ar}), 7.25 (m, 3H, H_{Ar}), 5.10 (m, 1H, =CH), 4.90 (m, 1H, $=CH_2$), 4.79 (m, 1H, $=CH_2$), 2.93 (d, $J=7.0$ Hz, 2H, CH_2, *E*-**6e**), 2.90 (d, $J=7.0$ Hz, 2H, CH_2, *Z*-**6e**), 2.16 (s, 3H, $COCH_3$, *E*-**6e**), 2.08 (s, 3H, $COCH_3$, *Z*-**6e**), 1.74 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.66 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169.1 (C=O), 142.6 (C), 141.8 (C), 136.3 (C), 132.6 (C), 132.1 (C), 128.3 ($2CH_{Ar}$), 127.8 ($3CH_{Ar}$), 120.7 (=CH), 116.8 ($=CH_2$), 30.1 (CH_2), 25.7 (CH_3), 22.6 (CH_3), 20.9 (CH_3), 17.8 (CH_3).

3.2.12. 3-Acetoxy-4,6,6-trimethyl-octa-2,4,7-trienoic acid methyl ester 8 and 2-acetoxy-3-isopropenyl-6-methyl-hepta-2,5-dienoic acid methyl esters *E*-6f and *Z*-6f. General procedure is applied to **4f** (260 mg, 1.1 mmol, 1 equiv), with 14.5 mg of $PtCl_2$ (0.054 mmol, 0.05 equiv), in 40 mL of toluene. The mixture is heated at 80 °C during 20 h. After purification by flash chromatography on silica gel (pentane/Et_2O, 95:5), 115 mg (43%) a mixture containing: **8**/**6f**, 45/55, are isolated.

As we could not determine which isomer of **6f** was present in the mixture, we do not specify whether it is the *E* or the *Z* isomer.

Attribution between **8** and major dias. of **6f** was based on a H–C correlation NMR experiment.

^1H NMR (400 MHz, $CDCl_3$): 6.12 (s, 1H, =CH, **8**), 5.91 (dd, $J=17.4$, 10.6 Hz, 1H, =CH, **8**), 5.79 (s, 1H, =CH, **8**), 5.05 (dd, $J=17.4$, 1.4 Hz, 1H, =CH*H trans*, **8**), 5.00 (dd, $J=10.6$, 1.4 Hz, 1H, =C*H*H *cis*, **8**), 4.98 (s, 1H, $=CH_2$, **6f**), 4.92 (m, 1H, =CH, **6f**), 4.70 (s, 1H, $=CH_2$, **6f**), 3.71 (s, 3H, OCH_3, **6f**), 3.69 (s, 3H, OCH_3, **8**), 2.91 (d, $J=7.2$ Hz, 2H, CH_2, **6f**), 2.34 (s, 3H, $COCH_3$, **8**), 2.23 (s, 3H, $COCH_3$, **6f**), 1.94 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.70 (s, 3H, CH_3, **6f**), 1.64 (s, 3H, CH_3, **6f**), 1.22 (s, 6H, CH_3, **8**).

^{13}C NMR (50 MHz, $CDCl_3$): 169.6 (C=O), 168.6 (C=O), 165.5 (C=O), 160.5 (C=O), 146.3 (=CH, **8**), 144.7 (C), 143.4 (=CH, **8**), 143.0 (=CH), 134.5 (C), 130.3 (C), 128.9 (C), 128.7 (C), 129.3 (C), 119.2 (=CH, **6f**), 113.7 ($=CH_2$, **8**), 111.6 ($=CH_2$, **6f**), 104.6 (=CH, **8**), 52.2 (OCH_3), 51.7 (OCH_3), 39.0 (^3C, **8**), 30.9 (CH_2, **6f**), 29.2 (2 CH_3, **8**), 26.1 (CH_3, **6f**), 22.5 (CH_3), 21.3 (CH_3), 20.8 (CH_3), 15.7 (CH_3), 14.2 (CH_3).

3.2.13. Acetic acid 2-isopropenyl-1-phenyl-hexa-1,4-dienyl ester *E*-10 and *Z*-10. General procedure is applied to **9** (270 mg, 1.05 mmol, 1 equiv), with 14 mg of $PtCl_2$ (0.052 mmol, 0.05 equiv), in 40 mL of toluene. The mixture is heated at 80 °C during 15 h. After purification by flash chromatography on silica gel (pentane/CH_2Cl_2, 8:2), 170 mg (63%) of a mixture containing: *E*-**10**/*Z*-**10**, 9/1, were isolated.

IR (neat): 3090, 3020, 2970, 2860, 1760, 1640 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 7.28–7.41 (m, 5H, H_{Ar}), 6.48 (dd, $J=17.4$, 11.1 Hz, 1H, =CH), 5.32 (dd, $J=17.4$, 1.0 Hz, 1H, =CH*H*, *trans*), 5.10 (dd, $J=11.1$, 1.0 Hz, 1H, =C*H*H, *cis*), 5.09 (m, 1H, =CH), 3.04 (d, $J=6.6$ Hz, 2H, CH_2, *E*-**10**), 2.99 (d, $J=6.6$ Hz, 2H, CH_2, *Z*-**10**), 2.16 (s, 3H, $COCH_3$, *E*-**10**), 2.08 (s, 3H, $COCH_3$, *Z*-**10**), 1.73 (s, 3H, CH_3), 1.71 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): 169.8 (C=O), 146.4 (C), 135.2 (C), 133.6 (=CH), 131.8 (C), 129.5 ($2CH_{Ar}$), 128.5 (CH_{Ar}), 128.1 ($2CH_{Ar}$), 127.5 (C), 122.0 (=CH), 115.5 ($=CH_2$), 25.7 (CH_2), 25.7 (CH_3), 20.9 (CH_3), 17.9 (CH_3).

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References and notes

1. For reviews, see: (a) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813. (b) Méndez, M.; Mamane, V.; Fürstner, A. *Chemtracts-Org. Chem.* **2003**, *16*, 397. (c) Lloyd-Jones, G. C. *Org. Biomol. Chem.* **2003**, *1*, 215.
2. Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901.
3. (a) Trost, B. M.; Doherty, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 3801. (b) Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305.
4. (a) Allenynes: Cadran, N.; Cariou, K.; Hervé, G.; Aubert, C.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *J. Am.*

Chem. Soc. **2004**, *126*, 3408. (b) Ene-tosylynamides: Marion, F.; Coulomb, J.; Courillon, C.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2004**, *6*, 1509.

5. (a) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511. (b) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863. (c) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757. (d) Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 2627.
6. Mainetti, E.; Mouriès, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132.
7. Rautenstrauch, V. *J. Org. Chem.* **1984**, *49*, 950.
8. Miki, K.; Ohe, K.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 8505.
9. Ang, K. H.; Bräse, S.; Steinig, A. G.; Meuer, F. E.; Llebaria, A.; Voigt, K.; de Meijere, A. *Tetrahedron* **1996**, *52*, 11503–11528.
10. For another synthesis of ketone **2**, see: House, H. O.; Chu, C.-Y.; Phillips, W. V.; Sayer, T. S. B.; Yau, C.-C. *J. Org. Chem.* **1977**, *42*, 1709.
11. (a) Gajewski, J. J.; Olson, L. P.; Willcott, M. R. *J. Am. Chem. Soc*. **1996**, *118*, 299–306. (b) See also: Mainetti, E.; Fensterbank, L.; Malacria, M. *Synlett* **2002**, 923–926.
12. (a) Doutheau, A.; Balme, G.; Malacria, M.; Gore, J. *Tetrahedron* **1980**, *36*, 1953–1960 and references therein. (b) See also: Banert, K.; Fendel, W.; Schlott, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 3289–3292.
13. Relative stereochemistry of trienes **6d** was deduced by analogy with the previous cases.
14. It is relatively a general trend that TMS-substituted alkynes react sluggishly in the $PtCl_2$-catalyzed process.
15. This is consistent with calculations by Echavarren on the polarization by $PtCl_2$ of the bonded alkyne, cf. Ref. 5d.
16. (a) Saucy, G.; Marbet, R.; Lindlar, H.; Isler, O. *Helv. Chim. Acta* **1959**, *XLII*, 1945–1955. (b) Schlossarczyk, H.; Sieber, W.; Hesse, M.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 875. (c) Oelberg, D. G.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 1804. See also: (d) Cookson, R. C.; Cramp, M. C.; Parsons, P. *J. Chem. Commun.* **1980**, 197.
17. Bowden, B.; Cookson, R. C.; Davis, H. A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2634.
18. Sromek, A. W.; Kel'in, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 2280.