Change of the Reaction Pattern by Methodological Variations in a Multicomponent Assembly Promoted by Ni Complexes

Gabriel García-Gómez and Josep M. Moretó*[a]

Dedicated to Professor José Barluenga on the occasion of his 60th birthday

Abstract: The π-allylnickel complex formed by the addition of trimethylsilyl chloride (TMSCl) to a mixture of [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) and a vinyl ketone (Mackenzie complex) carbometalates an acetylene in a completely regioselective manner resulting in the formation of the corresponding vinyl nickel species. This intermediate is capable of controlled quenching in a variety of ways to give different types of compounds: under a CO atmosphere, an acylnickel species is formed that ensues from the carbometalation of the enol ether double bond to form cyclopentenone derivatives. Alternatively, if acetylene is present in excess and CO is absent, another acetylene moiety will replace the CO and cyclohexadienes will result instead. Finally, if only an excess of the vinyl ketone is used, the product from a slow double addition of the vinyl ketone across the triple bond is formed. The regioselectivities obtained by the present method are different from those obtained by the involvement of nickel acyclopentadienes as intermediates when the order of addition is reversed.

Keywords: allyl complexes · carbonylation · cyclization · nickel

Introduction

Reactions in which three or more *different* and *independent* components are assembled in a controlled single synthetic operation are rare, because of the high entropy barrier that is usually involved. However, they represent the highest chemical efficiency and atom economy for forming at least two new bonds in any designed path to a target molecule[1] (two or more simultaneous disconnections in a given retrosynthetic analysis). One of the ways to overcome the disorder parameter is to use metals. Alkaline ions, for instance, which are able to be solvated by reacting ligands, have been used to control the size of a crown ether that was obtained by dehydration, but these metals are not applicable to heterocomponents. Transition metals, on the other hand, are suitable orienting templates since they simultaneously allow different ligands to bond to their coordination sphere (heteroleptic complexes), the reactivities of which are usually altered by the bonding to the metal. Both ligand affinity and ligand activation have been found to be susceptible to modulation (ligand tailoring). Moreover, the preferred orientation in their coordination may be conveyed to the product that, in many cases, brings a high degree of selectivity to the reaction. Owing to this inherent feature, transition metals are almost exclusively the mediators for heterocomponent multibond formation (copolymerization, telomerization, etc.). However, it is hard to proceed further with the assembly of *three* different components through consecutive nonidentical reactions. To facilitate the formation of the necessary bonds and the selection of the desired substrates by the metal, very often one has to turn to intramolecularity as a major tool to obtain proficient yields (tandem processes).[2] Even the Pauson–Khand reaction, which can be considered as a three-component reaction, has been applied in the vast majority of cases in its intramolecular version.[3] Other efficient three-component metal-mediated reactions have been recently reported.[4] In this context, we have studied the interaction of Mackenzie's π-allylnickel complexes with CO and alkynes and report herein how the knowledge of the reacting species and the suspected mechanism that rules them allows a convenient manipulation of the mode of interaction, leading to a controlled formation of different types of compounds.

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Results and Discussion

Our initial purpose in this study was to extend the carbonylative cycloaddition of Mackenzie's π-allylnickel complexes of aldehydes with alkynes to form cyclopentenones[5] to those derived from ketones. As reported,[6] the formation of the π-

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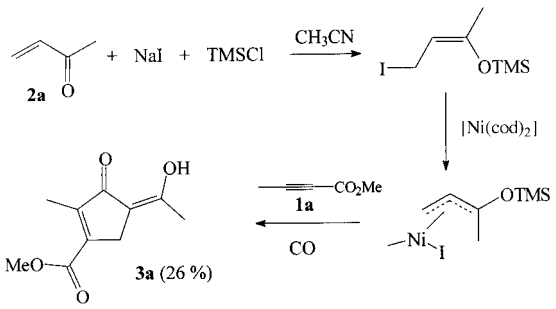
allylnickel complex from vinyl ketones was found to be more difficult and the reaction was more sluggish. We also observed no reaction of methyl vinyl ketone (**2a**) with either trimethylsilyl chloride (TMSCl) or bromide (TMSBr) in acetonitrile. However, the corresponding π-allylnickel iodide complex, which was generated in situ in a toluene-rich mixture (1:4 acetonitrile/toluene), reacted with a polarized alkyne, methyl 2-butynoate (**1a**), to give the corresponding cyclopentenone **3a** in 26% yield (Scheme 1). However, for

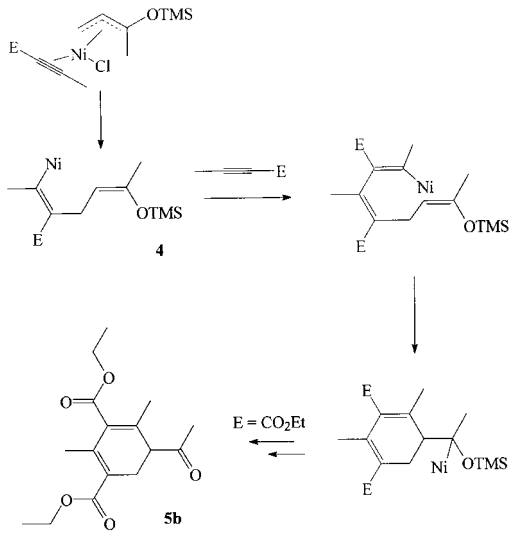


Scheme 1. Cyclopentenone formation from π-allylnickel iodide.

phenylacetylene (**1h**), there was no cyclopentenone formation and various phenylacetylene oligomers were obtained.

To avoid phenylacetylene self-interaction, we introduced methodological changes: 1 mol of TMSI and 1 mol of methyl vinyl ketone (instead of two) in toluene (instead of acetonitrile) were used to generate the π-allylnickel complex (in this case, there was no need to use a polar solvent for halide substitution), and CO was introduced before acetylene addition. Again, cyclopentenone was not produced. However, a considerable amount of the starting material was recovered as its Michael adduct, 4-iodo-2-butanone (52% yield), which led to the conclusion that although the presence of CO had prevented polyinsertion of phenylacetylene it had also precluded its insertion in the allyl ligand. Clearly, the metal selects the most suitable ligand. We then turned to a more polarized alkyne, ethyl 2-butynoate (**1b**). Using the same reaction procedure, this alkyne (2 mol) added prior to the introduction of CO yielded a new product, **5b**, in 48% yield (Scheme 2). From its structure, it is clear that CO had either not been coordinated during the process or its coordination had taken place once a second moiety of the alkyne had already been inserted. In other words, the second mole of alkyne replaced CO in the metal's coordination sphere, thus leading to a different type of product after its insertion.

Abstract in Catalan: *El complex π-al·lílic format per l'addició de clorur de trimetilsilil a una vinil cetona en presència de $Ni(cod)_2$ (complex de Mackenzie) carbometal·la regioselectivament un alquí per a donar una espècie vinil níquel. Aquest intermedi pot derivar cap a la formació de productes diversos segons la variant metodològica emprada. Així, s'obtenen ciclopentenones per tractament subsegüent amb CO; ciclohexadiens si un excès d'alquí hi es present en absència de CO o bé Z-olefines procedents d'una doble addició de la vinil cetona si aquesta es la que hi es present en excès.*



Scheme 2. Non-carbonylative cycloaddition of ethyl 2-butynoate.

Thus, the cyclohexenyl ketone structure derives from the interception of the *Z*-allylalkenyl nickel intermediate by excess alkyne. Now we could also check whether some of the "polyinserted" products obtained from phenylacetylene actually correspond to the cyclocodimer for this acetylene. In these introductory experiments, we found that there was a fine balance in the selection of ligands, which we could manipulate with the proper choice of the order of addition and the solvent. The formation of cycloadducts related to **5b** has been the subject of results recently reported by Ikeda et al.[7] As will be commented on further, they also obtained similar products through a three-component non-carbonylative intermolecular reaction, but, the methodology was essentially different—the components assemble in another manner and the regioselectivities obtained are completely different. Therefore, our results complement theirs according to the following general strategic motto: *When dealing with fairly stable intermediates, the experimentalist can, in principle, control the product formation on the coordination sphere of a metal by selecting the reagents (ligands) and their order of addition.* Since both types of products, **3a** and **5b**, arise from the common intermediate **4**, which, in turn, originates from insertion of the π-allylnickel complex to one moiety of acetylene, we decided to reference all results to the same reaction conditions, namely those that seemed more convenient from the bibliographic precedents[6, 7a,c, 8] for the formation of intermediate **4**. These conditions are: generation of the π-allylnickel complex with TMSCl in THF at 0°C. Under these conditions, we established three different protocols that lead to three compound types as depicted in Scheme 3.

Protocol 1: Addition of CO prior to the addition of the alkyne and with 2:1 ketone/alkyne stoichiometry: in this case, cyclopentenones (e.g. **3b**) are exclusively formed in high yield (See Table 1). Regioselectivity is complete when polarized acetylenes are used. The regiochemistry of the adducts is easily ascertained from the chemical shift of the

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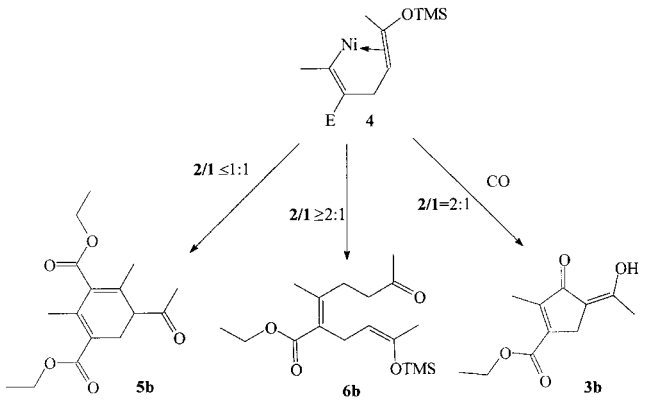
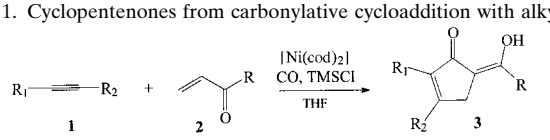


Scheme 3. Three different synthetic paths from a common intermediate.

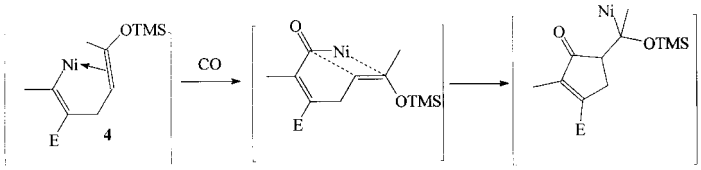
Table 1. Cyclopentenones from carbonylative cycloaddition with alkynes.



Entry	Acetylene	R^1	R^2	R	Products [%]
1	**1a**	Me	CO_2Me	Me (**2a**)[a]	**3a** (26)
2	**1b**	Me	CO_2Et	Me (**2a**)	**3b** (98)
5	**1b**	Me	CO_2Et	Et (**2b**)	**3bb** (95)
3	**1c**	Et	COMe	Me (**2a**)	**3c** (97)
4	**1d**	Ph	CO_2Me	Me (**2a**)	**3d** (98)
6	**1e**	Et	Et	Me (**2a**)	-
7	**1f**	TMS	H	Me (**2a**)	-

[a] As an exception, this reaction was performed in acetonitrile/toluene with addition of the alkyne prior to introduction of CO.

enone carbon atoms in the ^{13}C NMR spectrum, the chemical shift for the vinyl methyl protons in the ^1H NMR spectrum and, especially, the homoallyl coupling that is displayed by this methyl group when it is at the α-keto site.[9a] Nonpolarized acetylenes do not interact under these general conditions and they are recovered unchanged. These results match well with previous findings as does the reaction with (trimethylsilyl)-acetylene. We assume that the lack of reactivity is due to both electronic and steric effects.[9] The cyclopentenone ring arises from the insertion of a carbonyl ligand on the vinyl nickel bond followed by a *5-exo-trig* cyclization (Scheme 4).

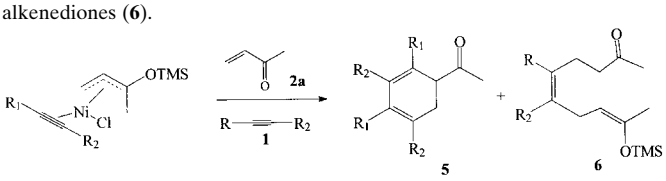


Scheme 4. *5-exo-trig* cyclization under carbonylative conditions.

Unlike similar cycloadditions using allyl halides,[9] there is no second carbonylation and the metal is removed by β-elimination. During work-up, the resulting enol ether is quantitatively hydrolyzed to the corresponding ketone. Since (trimethylsilyl)acetylene is active under non-carbonylative conditions, the inhibition of cyclopentenone formation in this case would result from the preferred coordination of a carbonyl ligand blocking that of the acetylene.

Protocol 2: In the absence of CO, the only species competing for insertion of the π-allyl ligand are the acrylic ketone and the alkyne. Of these, the alkyne is, by far, more reactive than the ketone and, if the molar ratio is 1:1 (or superior in alkyne), the vinyl nickel intermediate regiospecifically inserts a second alkyne which is followed by a second carbometalation of the enol ether double bond. Again, β-elimination (in either direction) restores the enol ether and allows isolation as the corresponding ketone **5** after work-up (Scheme 2 and 3; Table 2 entries 1, 2, 4, 8, 11, and 12). A strict regiocontrol

Table 2. Optional quenching of the vinyl nickel intermediate by alkynes or vinyl ketones that leads to cyclohexanediene adducts (**5**) or *Z*-disubstituted alkenediones (**6**).



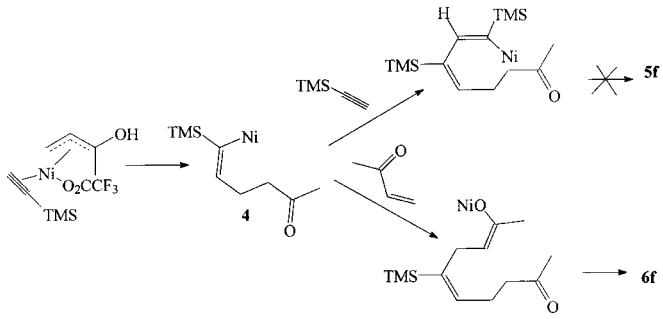
Entry	Acetylene	Ketone	ratio	**5** (yield [%])	**6** (yield [%])
1	**1b**	**2a**	1:1	**5b** (48)	–
2	**1b**	**2a**	2:1	**5b** (90)	–
3	**1b**	**2a**	1:2	–	**6b** (81)
4	**1f**	**2a**	2:1	**5f** (85)	–
5	**1f**	**2a**	1:2[a]	**5f** (40)	**6f** (20)
6	**1f**	**2a**	1:2	**5f** (17)	**6f** (56)
7[b]	**1f**	**2a**	1:2	traces	**6f** (40)[c]
8	**1g**	**2a**	2:1	**5g**(98)	–
9	**1g**	**2a**	1:2	–	**6g** (66)[c]
10	**1g**	**2a**	1:1[d]	**5g**(8)	**6g**(23),**7g**(27)
11	**1h**	**2a**	2:1	**5h** (60)	–
12	**1i**	**2a**	1:1	**5i** (37)[e]	**6i** (13)[c]
13	**1i**	**2a**	1:2		**6i** (63)[c]

[a] The acetylene was quickly added after π-allyl complex formation. [b] TMSCl was replaced by trifluoroacetic acid. [c] Product **6** was isolated as the corresponding diketone. [d] The π-allyl complex was prepared with a 1:1 ratio of vinyl ketone/*tert*-butyl acetylene and then methyl crotonate (2 mol) were added. [e] Product **5** underwent aromatization during chromatographic purification.

occurs in all cases and only one regioisomer is obtained. It is remarkable that in compounds **3a** and **5b**, the allyl compound inserts in the acetylene at the most negative end of the alkyne. This exceptional reactivity of the π-allylnickel complex as an electrophile has been previously reported by our group[9] and others.[10] Similar cyclohexadiene adducts have been prepared by Ikeda et al.[7] Although they also observed regioselectivity, it arose from the steric restrictions of the formation of a nickel acyclopentadiene intermediate and, therefore, the major isomers obtained were different from the ones reported herein for (trimethylsilyl)acetylene and *t*butylacetylene.

Protocol 3: Finally, the last variant of this reaction counts on the use of an excess of the vinyl ketone. In this case, intermediate **4** is the main product. The vinyl nickel bond in **4** has nucleophilic character and can react only with another vinyl ketone moiety.[11] Thus, products of type **6** are predom-

inantly formed by conjugate addition (see Scheme 3; Table 2, entries 3, 6, 9, and 13). Again, the regioselectivity is complete and electronically controlled (steric effects were synergic in some cases). However, in some cases, it was difficult to completely prevent the interaction of **4** (after its formation) with the acetylene. Thus, for (trimethylsilyl)acetylene, even though the vinyl ketone/acetylene ratio was 2:1, the major product was **5f** when the acetylene was quickly added after formation of the π-allyl complex (Table 2, entry 5). This result is due to the higher reactivity of the alkyne compared to that of the vinyl ketone. In contrast, when the acetylene addition took place slowly, up to 4 h (Table 2,entry 6), the product ratio was reversed. This result pointed to a high stability of intermediate **4** that we attribute to a coordinative assistance of the distal double bond to the metal.[12] A better chemoselectivity at the expense of lower yield could be attained for these products by using trifluoroacetic acid (TFA) instead of TMSCl (Scheme 5; Table 2, entry 7).

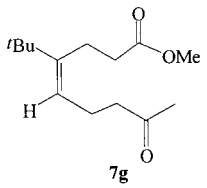


Scheme 5. Replacement of TMSCl by a protonic acid (TFA).

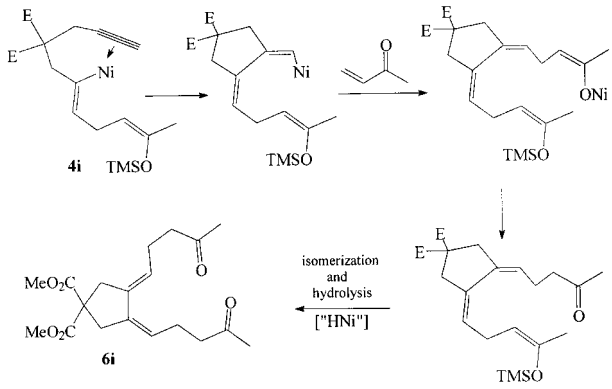
In this case, there is no stabilization of the vinyl Ni intermediate by the distal double bond and it therefore reacts with excess methyl vinyl ketone to afford adduct **6f**.

The corresponding open chain adduct (**6g**) could be obtained in good yield (Table 2, entry 9) from *tert*-butylacetylene (**1g**) in the presence of excess methyl vinyl ketone.

The *Z* stereochemistry of the double bond for product **6** was ascertained in **6f** and **6g** by the strong NOE effect between the equivalent trimethyl groups and the lone vinyl proton in close proximity. Although we failed to prepare π-allylnickel complexes of crotonic esters, we could use them as quenchers (Table 2, entry 10). However, even by using an excess of methyl crotonate, the interaction of the vinyl intermediate **4** with acetylene or vinyl ketone could not be completely prevented, and considerable amounts of adducts **5g** and **6g** were found together with the expected product **7g** in the final mixture.



With phenylacetylene (**1h**) in the absence of CO, we obtained a good yield of the cyclohexadiene adduct **5h** (Table 2, entry 11) and realized that this adduct was also present in a substantial amount in the crude reaction mixture from the reaction in the presence of CO (vide supra). Finally, we tried the intramolecular version with diacetylene methyl bis(2-propyne)malonate (**1i**) in both variants. In both cases, we obtained moderate yields of the expected adducts (Table 2, entries 12 and 13). Ikeda an co-workers and others have isolated products similar to **5i** by using the same stoichiometry (alkyne/vinyl ketone 1:2) as was used in the present methodology for the preparation of linear adduct **6i**.[13], [7b] This difference is clearly due to the different protocols applied and the involvement of the different intermediates. The stereochemistry of product **6i** should also be discussed. Mechanistically, the two ketone chains were expected to have *Z* configuration. However, one of the two chains was found to have *E* geometry. We think that there is significant strain between the two vinylic chains of the original di-*Z* isomer[14] and it rearranges to the more stable *E,Z* isomer by the known Ni-mediated H addition–elimination mechanism (Scheme 6).



Scheme 6. Formation of adduct **6i**.

Unlike what has been reported,[15] we found in all cases that, while the Mackenzie π-allyl complexes of vinyl ketones may not be of trivial preparation as are those of vinyl aldehydes, they are, however, very keen to insert the preferred ligand by the metal under the given conditions. Sometimes, the reactivity was so high that it was difficult to control the reaction and an undiscriminated amount of products were produced (similar to those reactions with phenylacetylene in the presence of carbon monoxide).

Conclusion

By careful analysis of the putative mechanism and variation of the reaction conditions, while considering the mutual reactivity of the reagents (ligands), we have been able to divert the regioselective reaction from formation of cyclopentenones towards that of 2,4-cyclohexadienes or 1,8-diketo-4-ethylene systems.

Experimental Section

General details: IR spectra were recorded with a Bomem MB-120 with Fourier transform instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions (unless otherwise indicated) with Varian Gemini 200 and Unity 300 machines, operating at 200 and 300 MHz for ^{1}H spectra and 50 and 75 MHz for ^{13}C spectra, respectively. Chemical shifts are reported in δ units, parts per million (ppm) downfield from Me_4Si, or in ppm relative to

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the singlet at $\delta = 7.26$ for $CDCl_3$ for ^1H, and in ppm relative to the center line of a triplet at $\delta = 77.0$ of $CDCl_3$ for ^{13}C. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad; *, apparent multiplicity. Elemental analyses were performed with a Carlo Erba apparatus (1106 and 1108 models). GC-MS was performed on a Fisons MD800 mass spectrometer coupled to a gas chromatograph equipped with a fused silica capillary column SPB-5 (30 m × 0.32 mm i.d.). High-resolution MS (EI) spectra (70 eV) were obtained on an Auto Spec-Q instrument. TLC was run on Merck 60 F_{254} silica gel plates. Flash chromatography was performed on 230–400 mesh Merck 60 silica gel. Commercial analytical-grade reagents were obtained from commercial suppliers and were used directly without further purification. Solvents were distilled under argon prior to use and dried by standard methods.

Methyl (4*Z*)-4-(1-hydroxyethylidene)-2-methyl-3-oxocyclopent-1-ene-1-carboxylate (3a): (As an exception to the general procedure, this reaction was carried out in 20:5 toluene/acetonitrile). $[Ni(cod)_2]$ (0.53 g, 1.93 mmol) and anhydrous toluene (20 mL) were introduced in a 100 mL Schlenk flask. In another 25 mL flask under Ar, **2a** (0.27 g, 3.85 mmol), NaI (0.63 g, 4.24 mmol), and TMSCl (0.46 g, 4.24 mmol) in anhydrous acetonitrile (5 mL) were mixed. After the mixture had been stirred for 5 min at room temperature, the contents of the second flask were transferred by cannula to the first flask that contained the $[Ni(cod)_2]$ suspension at $-10\,^\circ C$. A deep red color developed quickly, which indicated formation of the π-allyl complex. The temperature was kept at $-10\,^\circ C$ for about 1 h, at which point the temperature was lowered to $-78\,^\circ C$ and acetylene **1a** (0.19 g, 1.93 mmol) was added. The Ar atmosphere was immediately replaced by CO by bubbling CO through the solution for approximately 10 min. The system was allowed to evolve until the bath temperature had reached room temperature, at which point methanol (2 mL) was added. Stirring at room temperature was continued overnight. The crude reaction mixture was evaporated to dryness[16] in vacuo and the residue was treated with brine and the solution was extracted with diethyl ether (3 × 15 mL). The organic extracts were combined and the resulting residue was purified by flash chromatography (Hexane/EtOAc 6:1) to obtain **3a** as a white solid (96 mg). Yield: 26%; m.p. 61 °C; IR (film): $\tilde{\nu} = 1720, 1668, 1616, 1436\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.86$ (s, 3H), 3.35 (q, $J = 2.4$ Hz, 2H), 2.23 (t, $J = 2.4$ Hz, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 189.8$, 180.2, 165.2, 149.2, 141.4, 110.4, 51.8, 32.4, 21.7, 10.3; MS (40 eV, EI): *m/z* (%): 196 (33) $[M]^+$, 154 (100), 121 (70), 94 (70); elemental analysis calcd (%) for $C_{10}H_{12}O_4$ (196.20): C 61.22, H 6.12; found: C 61.18, H 6.35.

General procedure for cyclization reactions: To a 100 mL Schlenk flask initially filled with Ar, $[Ni(cod)_2]$ (0.64 g, 2.33 mmol) and anhydrous THF (10 mL) were added and kept at 0 °C, while **2a** (0.326 g, 4.65 mmol) was added dropwise. This led to a red solution. After 20 min Me_3SiCl (0.303 g, 2.79 mmol) was added dropwise. After one hour, the oxidative addition was over. At this point, Ar was replaced by CO by bubbling CO under atmospheric pressure into the flask. The color faded considerably. Then, **1** (2.33 mmol) was added dropwise. The reaction was allowed to proceed for an additional 4 h. The solvent was removed completely in vacuo.[16] The residue was treated with brine, and the resulting mixture was extracted several times with diethyl ether. The combined organic phases were dried over Na_2SO_4 and evaporated to dryness in vacuo. The crude oil was either crystallized from diethyl ether/methanol or purified by flash chromatography (hexane/EtOAc).

Ethyl (4*Z*)-4-(1-hydroxyethylidene)-2-methyl-3-oxocyclopent-1-ene-1-carboxylate (3b): As per the general procedure above, **2a** (0.27 g, 3.85 mmol), $[Ni(cod)_2]$ (0.53 g, 1.93 mmol), TMSCl (0.25 g, 2.31 mmol), and **1b** (0.2 g, 1.93 mmol) were allowed to react. After crystallization (diethyl ether/MeOH 10:1), **3b** was isolated as a white solid (0.397 g). Yield: 98%; m.p. 52 °C; IR (film): $\tilde{\nu} = 1714, 1660, 1614, 1371\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.30$ (q, $J = 7.2$ Hz, 2H), 3.33 (q, $J = 2.4$ Hz, 2H), 2.21 (t, $J = 2.4$ Hz, 3H), 2.15 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 190.2$, 179.8, 164.8, 148.9, 142.0, 110.3, 60.8, 32.3, 21.7, 14.2, 10.3; elemental analysis calcd (%) for $C_{11}H_{14}O_4$ (210.22): C 62.86, H 6.67; found: C 62.86, H 6.76.

Ethyl (4*Z*)-4-(1-hydroxypropylidene)-2-methyl-3-oxocyclopent-1-ene-1-carboxylate (3bb):
As per the general procedure above, **2b** (0.45 g, 5.38 mmol), $[Ni(cod)_2]$ (0.74 g, 2.69 mmol), **1b** (0.30 g, 2.69 mmol), and TMSCl (0.35 g, 3.20 mmol) were alllowed to react. After crystallization (diethyl ether/MeOH 10:1), **3bb** was obtained as a white solid (0.573 g). Yield: 95%; m.p. 47 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.30$ (q, $J = 7.2$ Hz, 2H), 3.34 (q, $J = 2.4$ Hz, 2H), 2.45 (q, $J = 7.5$ Hz, 2H), 2.23 (t, $J = 2.4$ Hz, 3H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 188.7$, 185.6, 164.8, 148.8, 141.1, 109.7, 60.8, 32.3, 28.9, 14.2, 10.3, 9.4; elemental analysis calcd (%) for $C_{12}H_{16}O_4$ (224.22): C 64.28, H 7.14; found: C 64.01, H 7.36.

(5*Z*)-3-Acetyl-2-ethyl-5-(1-hydroxyethylidene)cyclopent-2-en-1-one (3c): As per the general procedure above, **2a** (0.18 g, 2.54 mmol), $[Ni(cod)_2]$ (0.35 g, 1.27 mmol), **1c** (0.12 g, 1.27 mmol), and TMSCl (0.16 g, 1.53 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 6:1), **3c** was obtained as a yellow oil (0.239 g). Yield: 97%; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.37$ (t, $J = 1.2$ Hz, 2H), 2.70 (qt, $J = 1.2$, 7.5 Hz, 2H), 2.45 (s, 3H), 2.17 (s, 3H), 1.14 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 187.8, 182.9, 152.2, 146.7, 110.7, 33.1 29.6, 22.5, 18.2, 12.9; MS (40 eV, EI): *m/z* (%): 194 (65) $[M]^+$, 151 (69), 137 (100), 109 (36); high-resolution MS for $C_{11}H_{14}O_3$, calcd: 194.094294; found: 194.093361.

Methyl (4*Z*)-4-(1-hydroxyethylidene)-3-oxo-2-phenylcyclopent-1-ene-1-carboxylate (3d): As per the general procedure, **2a** (0.17 g, 2.40 mmol), $[Ni(cod)_2]$ (0.33 g, 1.2 mmol), **1d** (0.19 g, 1.2 mmol), and TMSCl (0.16 g, 1.44 mmol) were reacted. After crystallization (diethyl ether/MeOH 10:1), **3d** was obtained as a white solid (0.303 g). Yield: 98%; m.p. 107 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$ (m, 5H), 3.74 (s, 3H), 3.54 (s, 2H), 2.20 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 188.9$, 180.2, 165.0, 148.7, 142.8, 130.3, 129.2, 128.9, 127.9, 127.8, 110.4, 52.0, 33.0, 21.8; elemental analysis calcd (%) for $C_{15}H_{14}O_4$ (258.27): C 69.77, H 5.42; found C 70.18, H 5.48.

Diethyl 5-acetyl-2,4-dimethylcyclohexa-1,3-diene-1,3-dicarboxylate (5b): As per the general procedure in the absence of CO, **2a** (0.102 g, 1.45 mmol), $[Ni(cod)_2]$ (0.40 g, 1.45 mmol), TMSCl (0.19 g, 1.74 mmol), and **1b** (0.32 g, 2.91 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 9:1), **5b** was obtained as a colorless oil (0.385 g). Yield: 90%; IR (film): $\tilde{\nu} = 1714\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.27$ (q, $J = 7.2$ Hz, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 3.04 (ddd, $J = 1.2$, 3.9, 17.1 Hz, 1H), 2.94 (dd, $J = 3.9$, 7.8 Hz, 1H), 2.63 (ddd, $J = 2.7$, 7.8, 17.1 Hz, 1H), 2.15 (s, 3H), 2.08 (dd, $J = 1.2$, 2.1 Hz, 3H), 1.96 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 207.2$, 168.2, 167.3, 139.7, 138.9, 133.3, 121.0, 61.0, 60.4, 52.7, 28.6, 26.8, 20.8, 17.2, 14.2, 14.1; MS (20 eV, EI): *m/z* (%): 295 (3) $[M+1]^+$, 253 (100), 238 (20), 224 (17), 107 (20).

Diethyl 5-acetyl-2,4-dimethylisophthalate (derived from **5b** by oxidation): ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.18$ (s, 1H), 4.42 (q, $J = 7.2$ Hz, 2H), 4.40 (q, $J = 7.2$ Hz, 2H), 2.59 (s, 3H), 2.53 (s, 3H), 2.44 (s, 3H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.39 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.7$, 169.2, 166.5, 139.2, 139.1, 137.8, 131.2, 128.4, 61.5, 61.3, 29.8, 18.2, 17.9, 14.2, 14.1; MS (40 eV, EI): *m/z* (%): 292 (60) $[M]^+$, 277 (100), 263 (42), 247 (96), 103 (26), 77 (20); high-resolution MS for $C_{16}H_{20}O_5$, calcd: 292.131074; found: 292.131693.

Ethyl (2*E*)-2-[(2*Z*)-3-trimethylsiloxybut-2-enyl]-3-methyl-6-oxohept-2-enoate (6b): As per the general procedure in the absence of CO, **2a** (0.38 g, 5.40 mmol), $[Ni(cod)_2]$ (0.75 g, 2.70 mmol), **1b** (0.302 g, 2.70 mmol), and TMSCl (0.35 g, 3.24 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 9:1), **6b** was obtained as a colorless oil (0.721 g). Yield: 81%; IR (film): $\tilde{\nu} = 1714, 1672\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.40$ (dt, $J = 1.2$, 6.9 Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.96 (d, $J = 6.9$ Hz, 2H), 2.50 (m, 2H), 2.40 (m, 2H), 2.16 (s, 3H), 1.90 (s, 3H), 1.75 (d, $J = 1.2$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 207.7$, 169.7, 146.8, 142.8, 128.5, 105.8, 60.1, 41.5, 29.8, 29.3, 25.9, 22.5, 20.6, 14.2, 0.62; elemental analysis calcd (%) for $C_{17}H_{30}O_4Si$ (326.50): C 62.48, H 9.19; found: C 62.30, H 9.44.

Ethyl (2*E*)-3-methyl-6-oxo-2-(3-oxobutyl)hept-2-enoate (from acid hydrolysis of **6b**): IR (film) $\tilde{\nu} = 1712\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.20$ (q, $J = 7.2$ Hz, 2H), 2.60 (m, 6H), 2.40 (m, 2H), 2.19 (s, 3H), 2.15 (s, 3H), 1.90 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.6$, 208.0, 169.4, 144.0, 127.5, 60.4, 42.8, 41.3, 29.9, 29.8, 28.9, 23.5, 20.5, 14.1; MS (40 eV, EI): *m/z* (%): 236 (2), 208 (98), 165 (98), 151 (100), 122 (79), 109 (71), 95 (99), 79 (63).

1-(2,4-Bistrimethylsilylcyclohexa-2,4-dien-1-yl)ethanone (5f): As per the general procedure in the absence of CO, **2a** (0.17 g, 2.40 mmol), $[Ni(cod)_2]$ (0.66 g, 2.40 mmol), **1f** (0.47 g, 4.80 mmol), and TMSCl (0.31 g, 2.88 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 9:1), **5f** was obtained as a colorless oil (0.544 g. Yield: 85%; IR (film) $\tilde{\nu} = 1716$,

1455 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.48$ (s, 1H), 6.12 (dd, $J = 3.0$, 5.7 Hz, 1H), 3.04 (dd, $J = 3.0$, 9.0 Hz, 1H), 2.53 (ddd, $J = 3.0$, 5.7, 18.0 Hz, 1H), 2.37 (ddd, $J = 3.0$, 9.0, 18.0 Hz, 1H), 2.09 (s, 3H), 0.11 (s, 9H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 211.6$, 136.7, 136.2, 135.7, 134.7, 47.5, 28.0, 27.1, −1.6, −2.2; MS (20 eV, EI): *m/z* (%): 295 (3) $[M+1]^+$, 253 (100), 238 (20), 224 (17), 107 (20); elemental analysis calcd (%) for $C_{14}H_{26}OSi_2$ (266.53): C 63.03, H 9.75; found: C 62.59, H 9.95.

1-(2,4-Bistrimethylsilylphenyl)ethanone (aromatic product arising from the oxidation of cyclohexadiene derivative **5f** as per the method of Ikeda et al.[17]): Compound **5f** (1 mmol) was added to a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.3 mmol) in methanol. The mixture was stirred in air for approximately one day. The solution was concentrated in vacuo and diethyl ether (15 ml) was added, the mixture was then extracted with 1N HCl (10 ml) and then the organic phase was evaporated to dryness in vacuo. Yield: 93%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.91$ (dd, $J = 0.6$, 1.2 Hz, 1H), 7.86 (dd, $J = 0.6$, 7.5 Hz, 1H), 7.64 (dd, $J =$ 1.2, 7.5 Hz, 1H), 2.62 (s, 3H), 0.31 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.5$, 145.0, 142.7, 140.7, 140.3, 133.9, 128.5, 27.3, 0.27, −1.36; MS (20 eV, EI): *m/z* (%): 291 (2) $[M-1]^+$, 275 (28), 259 (30), 187 (50), 147 (70), 73 (100).

(5*E*, 8*Z*)-9-Trimethylsiloxy-5-trimethylsilyldeca-5,8-diene-2-one (6f): As per the general procedure in the absence of CO, **2a** (0.22 g, 3.13 mmol), $[Ni(cod)_2]$ (0.43 g, 1.56 mmol), **1f** (0.15 g, 1.56 mmol), and TMSCl (0.20 g, 1.88 mmol) (or alternatively, the corresponding amount of TFA for the experiment in entry 7 of Table 2) were allowed to react. After flash chromatography (9:1 hexane/EtOAc), **6f** was obtained as a colorless oil (0.274 g, 56%) together with **5f** (71 mg, 17%) (or **6f** (ca. 40%) in the alternative experiment). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.70$ (t, $J =$ 6.9 Hz, 1H), 4.41 (dt, $J = 1.2$, 7.2 Hz, 1H), 2.76 (ddd, $J = 1.2$, 6.9, 7.2 Hz, 2H), 2.39 (br. s, 4H), 2.14 (s, 3H), 1.78 (d, $J = 1.2$ Hz, 3H), 0.19 (s, 9H), 0.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.6$, 147.0, 140.0, 138.6, 106.5, 43.9, 29.8, 24.8, 23.3, 22.6, 0.6, −1.4; elemental analysis calcd (%) for $C_{16}H_{32}O_2Si_2$ (312.59): C 61.42, H 10.24; found: C 61.54, H 10.41; a part of the isolated product was found as the hydrolyzed product after chromatography.

(5*E*)-5-Trimethylsilyldec-5-ene-2,9-dione (6f hydrolyzed): ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.65$ (t, $J = 6.9$ Hz, 1H), 2.51 (m, 2H), 2.36 (m, 4H), 2.14 (s, 6H), 0.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.4$, 208.2, 140.7, 138.9, 43.7, 43.1, 29.9, 29.8, 23.3, 22.6, −1.4; MS (40 eV, EI): *m/z* (%): 225 (43), 182 (28), 167 (27), 143 (67), 130 (34), 115 (96), 73 (100).

1-(2,4-Di-*t*butylcyclohexa-2,4-dien-1-yl)ethanone (5g): As per the general procedure in the absence of CO, **2a** (81 mg, 1.16 mmol), $[Ni(cod)_2]$ (0.32 g, 1.16 mmol), **1g** (95 mg, 1.16 mmol), and TMSCl (0.15 g, 1.40 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 9:1), **5g** was obtained as a colorless oil (0.267 g). Yield: 98%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.14$ (d, $J = 1.2$ Hz, 1H), 5.37 (ddd, $J = 1.2$, 4.2, 4.8 Hz, 1H), 3.05 (dd, $J = 4.2$, 6.0 Hz, 1H), 2.45 (dd, $J = 4.8$, 6.0 Hz, 2H), 2.10 (s, 3H), 1.07 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 212.3$, 145.8, 145.6, 119.1, 112.5, 47.5, 36.1, 34.0, 29.1, 28.9, 28.8, 27.7; elemental analysis calcd (%) for $C_{16}H_{26}O$ (234.38): C 81.91, H 11.09; found: C 81.93, H 11.22.

(5*E*)-5-*tert*-Butyldec-5-ene-2,9-dione (6g): As per the general procedure in the absence of CO, **2a** (97 mg, 1.38 mmol), $[Ni(cod)_2]$ (0.19 g, 0.69 mmol), **1g** (57 mg, 0.69 mmol), and TMSCl (90 mg, 0.83 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 6:1), **6g** was obtained as a yellow oil (0.102 g). Yield: 66%; IR (film): $\tilde{\nu} =$ 1716, 1478 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.14$ (t, $J = 6.9$ Hz, 1H), 2.49 (m, 2H), 2.30 (m, 4H), 2.22 (m, 2H), 2.16 (s, 3H), 2.15 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.5$, 147.2, 120.9, 44.3, 43.7, 36.6, 30.3, 29.8, 29.1, 22.3, 21.5.

Methyl (4*E*)-5-*tert*-butyl-8-oxonon-4-enoate (7g): As per the general procedure in the absence of CO, **2a** (0.185 g, 2.65 mmol), $[Ni(cod)_2]$ (0.729 g, 2.65 mmol), **1g** (0.218 g, 2.65 mmol), TMSCl (0.345 g, 3.18 mmol), and methyl crotonate (0.48 g, 5.30 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 6:1), **7g** was obtained as a yellow oil (0.174 g). Yield: 27%, together with **5g** (52 mg, 8%) and **6g** (0.140 g, 23%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.17$ (t, $J = 6.9$ Hz, 1H), 3.68 (s, 3H), 2.49 (m, 2H), 2.37 (m, 4H), 2.25 (q*, $J = 7.2$ Hz, 2H), 2.15 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.3$, 173.7, 146.7, 121.5, 51.5, 43.7, 36.5, 34.6, 30.0, 29.5, 29.1, 23.0, 22.3.

1-(2,4-Diphenylcyclohexa-2,4-dien-1-yl)ethanone (5h): As per the general procedure in the absence of CO, **2a** (65 mg, 0.91 mmol), $[Ni(cod)_2]$ (0.25 g, 0.91 mmol), **1h** (0.18 g, 1.82 mmol) and TMSCl (0.12 g, 1.09 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 9:1), **5h** was obtained as a colorless oil (0.128 g). Yield: 60%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$ (m, 10H), 6.93 (s, 1H), 6.15 (ddd, $J = 1.2$, 3.3, 6.3 Hz, 1H), 3.60 (dd, $J = 2.7$, 9.0 Hz, 1H), 3.03 (ddd, $J = 2.7$, 6.3, 18.0 Hz, 1H), 2.80 (ddd, $J = 3.3$, 9.0, 18.0 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 209.8, 140.0, 139.8, 136.8, 136.2, 128.8, 128.5, 127.8, 127.3, 125.6, 125.5, 124.7, 121.8, 48.8, 28.2, 27.7; elemental analysis calcd (%) for $C_{16}H_{26}O$ (234.38): C 81.91, H 11.09; found: C 81.93, H 11.22.

Dimethyl 5-acetyl-1,3-dihydro-2H-indene-2,2-dicarboxylate (5i): (By passing through the chromatography column, the total amount of diene aromatized and, therefore, was characterized as the corresponding dehydro derivative). As per the general procedure, **2a** (0.06 g, 0.87 mmol), $[Ni(cod)_2]$ (0.24 g, 0.87 mmol), **1i** (0.18g, 0.87 mmol), and TMSCl (0.11g, 1.05 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 7:1), **5i** was obtained (89 mg, 37%) together with **6i** (40 mg, 13%); for **5i** (colorless oil): IR (film): $\tilde{\nu} = 3002$, 1735, 1681, 1434 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.80$ (m, 2H), 7.30 (d, $J = 8.1$ Hz, 1H), 3.77 (s, 6H), 3.64 (bs, 4H), 2.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$); $\delta = 197.8$, 171.7, 145.6, 140.5, 136.5, 127.7, 124.3, 124.1, 60.3, 53.1, 40.5, 40.2, 26.7; MS (40 eV, EI): *m/z* (%): 276 (23) $[M]^+$, 216 (65), 201 (100), 115 (42).

Dimethyl (3*Z*,4*E*)-3,4-bis(4-oxopentylidene)cyclopentane-1,1-dicarboxylate (6i): As per the general procedure in the absence of CO, **2a** (0.26 g, 3.70 mmol), $[Ni(cod)_2]$ (0.51 g, 1.85 mmol), **1i** (0.38 g, 1.85mmol), and TMSCl (0.22 g, 2.04 mmol) were allowed to react. After flash chromatography (hexane/EtOAc 7:1), **6i** was obtained as a yellow oil (0.409 g). Yield: 63%; IR (film): $\tilde{\nu} = 1735$, 1716, 1434 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.63$ (tt, $J = 2.1$, 7.5 Hz, 1H), 5.30 (t, $J = 6.0$ Hz, 1H), 3.76 (s, 6H), 3.01 (bs, 2H), 2.92 (d, $J = 2.1$ Hz, 2H), 2.54 (m, 6H), 2.35 (m, 2H), 2.15 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 208.3$, 207.9, 171.7, 136.8, 136.4, 125.8, 123.3, 57.1, 52.8, 43.5, 42.9, 42.7, 38.3, 29.9, 29.8, 24.2, 23.3; MS (40 eV, EI): *m/z* (%): 351 (38) $[M+1]^+$, 292 (26), 215 (55), 189 (95), 129 (100), 117 (54), 91 (59).

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[16] Care must be taken in this operation since the untransformed Ni may end up as the volatile and hazardous $Ni(CO)_4$. If white rubber septa have been used, an indication of nickel carbonyl formation is a black stain on its internal surface. As a cautionary measure, we recommend working in an efficient fume hood and a cold trap ($-80\,^{\circ}C$) should be inserted between the vacuum line and the evaporation flask. After the crude reaction mixture has reached dryness, the contents of the trap should be treated with iodine until the brown color remains.
[17] Despite what was reported by Ikeda (S. Ikeda, H. Kondo, N. Mori, *Chem. Comm.* **2000**, 815–816) we did not have any difficulties with this transformation.

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