Tetrahedron 66 (2010) 2181–2188

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Arylation of alkenylidenecyclopropanes via Heck reaction. A simple access to arylallylidenecyclopropanes

Yacoub Fall [a], Henri Doucet [b,*], Maurice Santelli [a,*]

[a] Laboratoire Chimie Provence, UMR 6264, Faculté des Sciences de St-Jérôme, Université d'Aix-Marseille, Avenue Escadrille Normandie-Niemen 13397 Marseille Cedex 20, France
[b] Institut Sciences Chimiques de Rennes, UMR 6226, Université de Rennes 1 "Catalyse et Organométalliques", Campus de Beaulieu 35042 Rennes, France

ARTICLE INFO

Article history:
Received 16 December 2009
Accepted 11 January 2010
Available online 25 January 2010

Keywords:
Alkenylidenecyclopropanes
Arylallylidenecyclopropanes
Heck reaction
Tetradentate ligand
Allenes

ABSTRACT

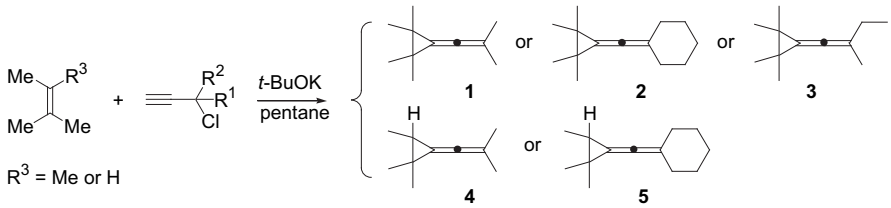
Five alkenylidenecyclopropanes have been arylated using a catalytic amount of $[Pd(C_3H_5)Cl]_2$ (0.004%) associated to the tetradentate ligand *cis*, *cis*, *cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane or Tedicyp as the catalyst. The carbo-palladation step occurs on the terminal double bond of the vinylidenecyclopropanes, without interaction with the internal one. The addition of the complex $PdArL_2$ corresponds to an electrophilic attack on the face of the double bond, *syn* to the best electron-donor cyclopropyl substituent.

1. Introduction

In the modern chemistry of the palladium-catalyzed reactions, the Heck–Mizoroki vinylation reaction is one of the most important carbon–carbon bonds forming process. From the seminal reports of Heck, which described the fascinating reactivity of organopalladium compounds prepared in situ by exchange reactions with corresponding organomercury derivatives,[1] and Mizoroki,[2] concerning the phenylation of ethylene, propene and styrene using a catalytic amount of palladium catalyst; an impressive number of applications have been described both at the laboratory and industrial scale.

Here, we wish to describe the Heck type coupling reaction of aryl bromides with alkenylidenecyclopropanes to give arylallylidenecyclopropanes in good yields.[3] To the best of our knowledge, alkenylidenecyclopropanes have not been employed in the Heck reactions.[4]

Vinylidenecyclopropanes are some of the most remarkable hydrocarbon compounds known. They have an allene moiety connected by a cyclopropane ring, and yet they are thermally stable and reactive substances. Alkenylidenecyclopropanes are readily available by the addition of Hatzler's carbene (alkenylidene carbene)[5] to alkenes (Scheme 1).[6] The synthetic availability of vinylidenecyclopropanes enhances their attractiveness as reactive building blocks.



Scheme 1. Preparation of alkenylidenecyclopropanes **1**–**5**.

These highly unsaturated small-ring compounds undergo thermal interconversions,[7] and present an unusual behavior in the course of electrophilic additions (acidic medium,[8] acetoxymercuration,[9] ozonolysis,[10] radical additions,[11] cycloadditions,[12] homoallenyl

* Corresponding authors. Fax: +33 4 91289112.
E-mail addresses: henri.doucet@univ-rennes1.fr (H. Doucet), m.santelli@univ-cezanne.fr (M. Santelli).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.01.052

participation,[13]). Carbolithiation reactions led to allenols or vinylcyclopropenes,[14] and BuLi-mediated carboxylation to corresponding carboxylic adducts.[15] The cycloaddition of vinylidenecyclopropanes with aldehydes gave rise to tetrahydrofuranes.[16] The reaction of Fischer chromiumcarbene complexes with alkenylidene-cyclopropanes afforded allylidenecyclopropanes in good yields.[17] Recently, palladium-catalyzed synthesis of 1,3-dienes from intramolecular[18] or intermolecular[19] Heck reactions of allenes with aryl halides have been described. Quite often, 1,3-dienes have been trapped in situ by a Diels–Alder reaction.[20] Recently, many π-allylpalladium complexes resulting from the addition of $[PdI(Ph)(PPh_3)]_2$ to allenes have been described.[21]

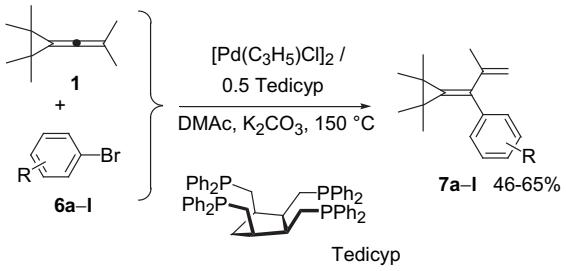
2. Results

We prepared the alkenylidenecyclopropanes **1**–**5** via the reaction of propargyl chlorides with alkenes in the presence of potassium *tert*-butoxide (Scheme 1).

Then, these compounds have been arylated using a catalytic amount (0.004%) of $[Pd(C_3H_5)Cl]_2$ associated to the tetradentate ligand, *cis*, *cis*, *cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane or Tedicyp as the catalyst.[22]

We have already reported several results concerning the efficiency of this tetraphosphine ligand for palladium-catalyzed cross-coupling reactions[23] and particularly for Heck vinylation.[24] The presence of the four diphenylphosphino groups on the same face of the cyclopentane ring seems to increase the stability and longevity of the catalyst.

We observed that using our catalyst $[Pd(C_3H_5)Cl]_2$/2 Tedicyp with *N*,*N*-dimethylacetamide as the solvent and potassium carbonate as the base, the aryl bromides **6a**–**l** cleanly react with **1** to give the 3-aryl-2-methyl-3-(2,2,3,3-tetramethylcyclopropylidene)propenes **7a**–**l** in 46–65% yields (Scheme 2). In the course of this reaction no formation of by-product was detected. Moreover, the reaction allows the use of a relatively high substrate/catalyst ratio of 250.



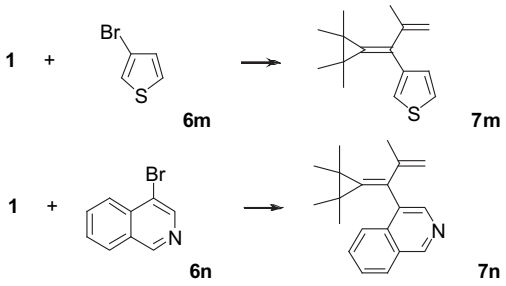
R: a, H; b, 3-Me; c, 4-*tert*-Bu; d, 4-HCO; e, 4-MeCO; f, 4-PhCO; g, 4-CO_2Me; h, 4-CN; i, 2-CN; j, 4-NO_2; k, 3-NO_2; l, 4-CF_3.

Scheme 2. Heck reaction of 1-(2-methylpropenylidene)-2,2,3,3-tetramethylcyclopropane **1** with aryl bromides **6a**–**l**.

The reactions using the heteroaryl bromides, 3-bromothiophene **6m** or 4-bromoisoquinoline **6n** also led to the corresponding arylallylidenecyclopropanes **7m** and **7n** in good yields (Scheme 3).

The structure of products **7a**–**n** was determined using ^1H and ^{13}C NMR spectroscopic data and the structure of **7f** has been confirmed by crystal X-ray analysis (Fig. 1 and Table 1).

Then, we explored the scope of this reaction using other alkenylidenecyclopropanes. A similar result was observed for the reaction of 1-cyclohexenylylidene-2,2,3,3-tetramethyl-cyclopropane **2** with 4-bromoacetophenone **6e**, which gave **8** in 62% yield (Scheme 4).



Scheme 3. Heck reaction of **1** with 3-bromothiophene **6m** or 4-bromoisoquinoline **6n**.

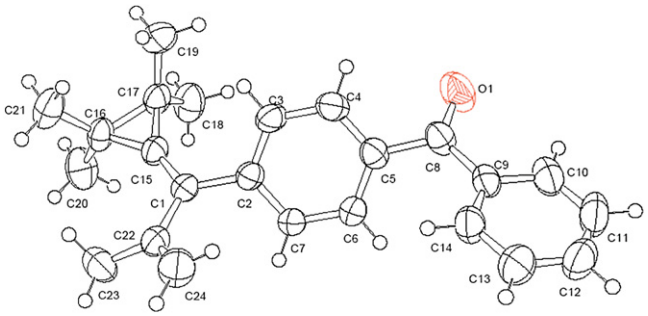
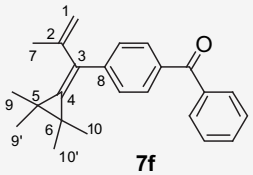
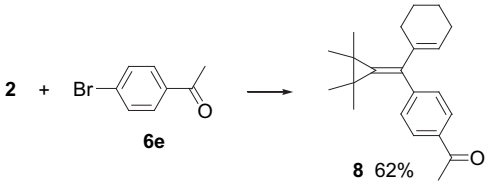


Figure 1. ORTEP diagram of compound **7f**.

Table 1
Selected bond lengths and angles of **7f**

Compound	Bond length (Å)	Angle (°)
	C1–C2:1.328	C2–C3–C8:119.1
	C2–C3:1.483	C5–C4–C6:63.4
	C3–C4:1.338	C4–C5–C6:58.2
	C4–C5:1.475	C4–C6–C5:58.4
	C4–C6:1.473	C9–C5–C9′:112.3
	C5–C6:1.549	C10–C6–C10′:112
	C2–C7:1.494	
	C3–C8:1.494	
	C5–C9:1.512	

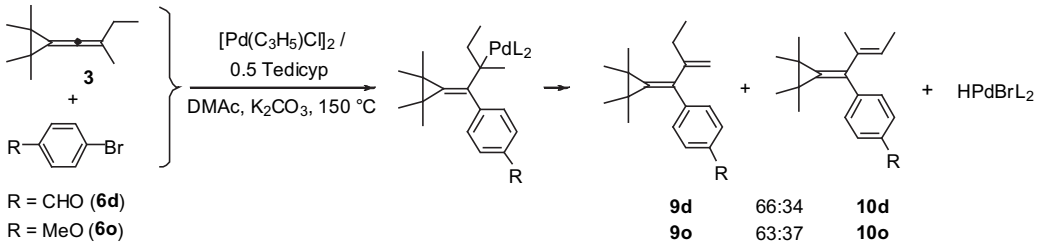
7f



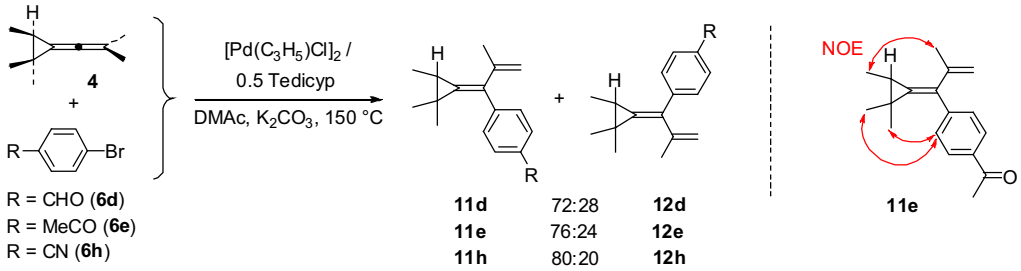
Scheme 4. Heck reaction of **2** with 4-bromoacetophenone **6e**.

Heck coupling reaction of vinylidenecyclopropane **3** with 4-bromobenzaldehyde or 4-bromoanisole led to a mixture of products **9d**/**10d** and **9o**/**10o**. With this vinylidenecyclopropane, the elimination of $PdHBrL_n$ at the end of the catalytic cycle can occur on both alkyl substituents (Scheme 5). The major products **9d** or **9o** arises from the elimination of the most acidic proton.

The Heck coupling reaction involving vinylidenecyclopropane **4** is also very interesting, as the choice of the face for the addition of $ArPdBrL_n$ to the allenic double bond will determine the geometry *cis*-*trans* of the products. The NOESY of the inseparable mixture of **11e** and **12e** is shown in the Scheme 6. It clearly indicates that the major isomer **11e** has a *Z*-configuration. Therefore, the addition of palladium seems to occur on the face containing the dimethyl group of the cyclopropane.

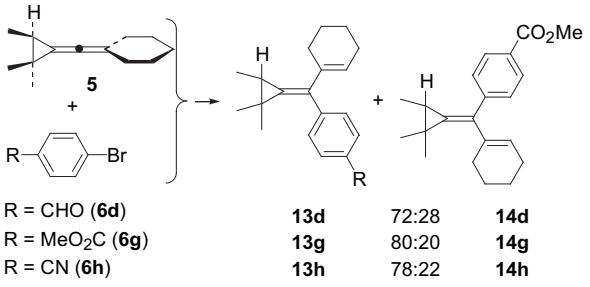


Scheme 5. Heck reaction of **3** with 4-bromobenzaldehyde (**6d**) or 4-bromoanisol (**6o**).

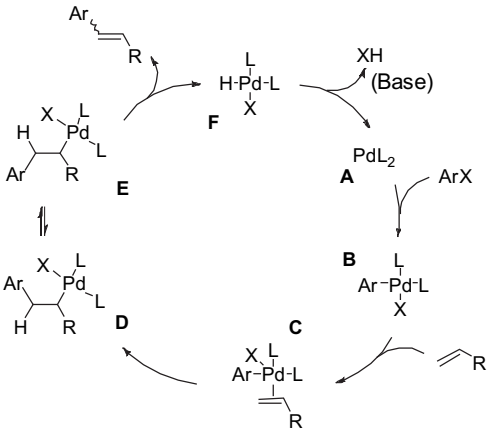


Scheme 6. Heck reaction of **4** with 4-bromobenzaldehyde (**6d**), 4-bromoacetophenone (**6e**) or 4-bromobenzonitrile (**6h**). NOE experiments for **11e**.

Similarly, the Heck reaction of the 1-cyclohexenylylidene-2,2,3-trimethylcyclopropane **5** with three aryl bromides led to mixtures of isomers (Scheme 7). Again, the *Z*-configuration was the major one in all cases.



Scheme 7. Heck reaction of **5** with 4-bromobenzaldehyde (**6d**), methyl 4-bromobenzoate (**6g**) or 4-bromobenzonitrile (**6h**).



Scheme 8. General mechanism of the Heck coupling reaction.

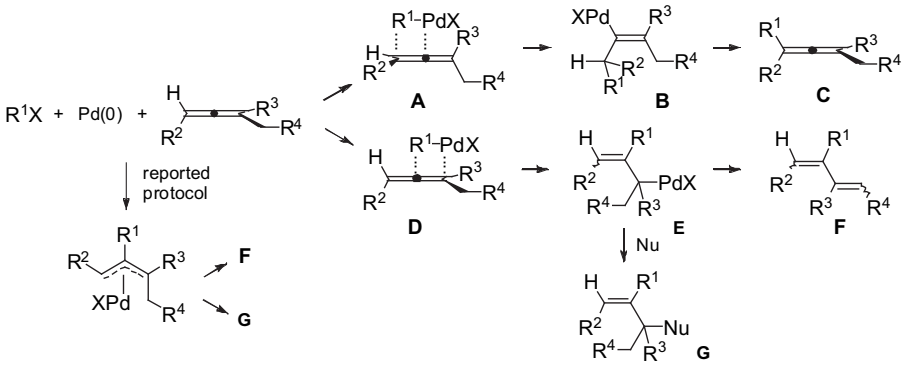
3. Discussion

The general mechanism for the Heck reaction involves the formation of a palladium(II) species **B** (oxidative addition) from the catalyst **A**, followed by the coordination of the alkene to give complex **C**. Then, the insertion of this alkene in the Ar–Pd bond gives **D**. Next, the change of the conformation gives **E** in order to allow a *syn*-elimination of the product, and the formation of the palladium hydride **F**. Finally, **F** undergoes a base assisted elimination which regenerates the active palladium(0) catalyst **A** (Scheme 8).[25]

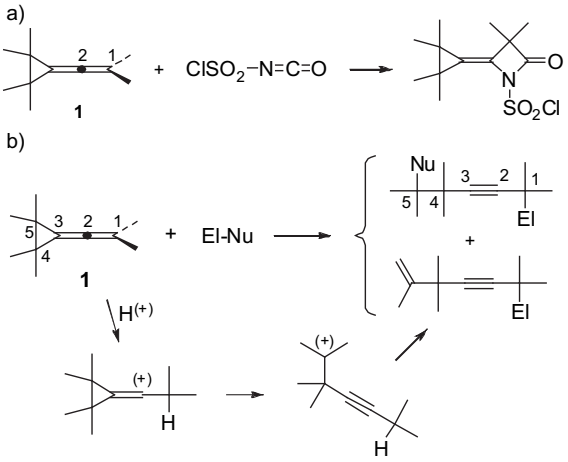
For the Heck reaction involving allenic compounds, previous studies concerning a wide range of aryl and heteroaryl iodides have demonstrated that these aryl halides undergo oxidative addition to Pd(0) followed by addition of the resulting RPdX species to the central carbon atom of the allene moiety. The formation of a π-allylpalladium(II) species was assumed. In the absence of a suitable nucleophile, this allylic species undergoes a slow β-hydride elimination, generating a substituted 1,3-diene. It should be mentioned that the η^3-coordination cannot be formed in the first step, due to the orthogonal orbitals of the allene.[26,28] The η^1-allyl precursor complexes **A** or **D** that lacks the conjugation to the remaining double bond are always formed first (Scheme 9).[27] According to the nature of the allene substituents, two major process can be involved. For example, with 1,2-allenyl sulfones, Ma demonstrated that the Heck reaction gave rise to polysubstituted 1,2-allenyl sulfones,[26] according to the reactive way **A**–**C**, resulting from the coordination of palladium to the central atom of the allene. In a few other examples, the palladium was linked to one of the terminal carbon atoms of the allene, and then, the mechanisms of the reactions involve intermediates **E**, **F** or **G**.[18,19]

In the case of the vinylidenecyclopropanes, the carbo-palladation step occurs on the terminal double bond. Many electrophilic additions and cycloadditions occurred in a similar manner. For example, the reported 2+2 addition of chlorosulfonyl isocyanate leading to a β-lactam derivative confirms this polarization (Scheme 10a).[8c,9,28] These results contrast with the polar addition reactions of electrophilic reagents to **1**. In most cases, an opening of the cyclopropane ring occurs with the formation of an acetylenic bond (Scheme 10b).[8c,29]

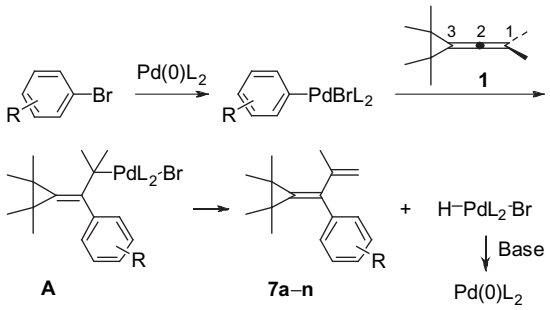
The Scheme 11 takes into account the general results. After the oxidative addition of the aryl bromide to palladium, and coordination of the alkenylidenecyclopropane **1**, the insertion of **1** in the Ar–Pd bond gives intermediate **A**. Then, the β-hydride elimination forms the products **7**. As the reaction of Fischer chromiumcarbene complexes,[17] the reaction described here is a formal ene reaction involving the Ar–Pd bond. The catalytically active Pd(0) species is regenerated by the base.



Scheme 9. General mechanisms for the Heck coupling reactions involving allene reagents.



Scheme 10. Previously reported electrophilic additions to alkenylidenecyclopropane **1**.



Scheme 11. Mechanism of the Heck coupling reaction involving alkenylidenecyclopropane **1**.

Very constraint compounds **7**, **9**–**14** have been obtained in similar yields both from electron-poor aryl bromides such as 4-bromobenzaldehyde, 4-bromoacetophenone, 4-bromobenzo-phenone, methyl 4-bromobenzoate, 4-nitrobromobenzene, 3-nitrobromobenzene, 4-bromobenzonitrile or 4-bromoisoquinoline and from electron-rich aryl bromides such as 3-bromotoluene, 4-*tert*-butylbromobenzene or 3-bromothiophene. This observation indicates that the rate-limiting step of the reaction is probably not the oxidative addition of the aryl bromide to the palladium complex, but more likely the insertion of the C(1)–C(2) double bond in the Ar–Pd bond. The reaction even occurs with the *ortho*-substituted aryl bromide, 2-bromobenzonitrile **6i**.

The structure of alkenylidenecyclopropane **1** has been calculated at the B3LYP/,[30] and MP2/,[31] levels using the 6.311G++(p,d) basis sets.[32] This structure was confirmed by X-ray crystal analysis (Fig. 2, and Table 2).

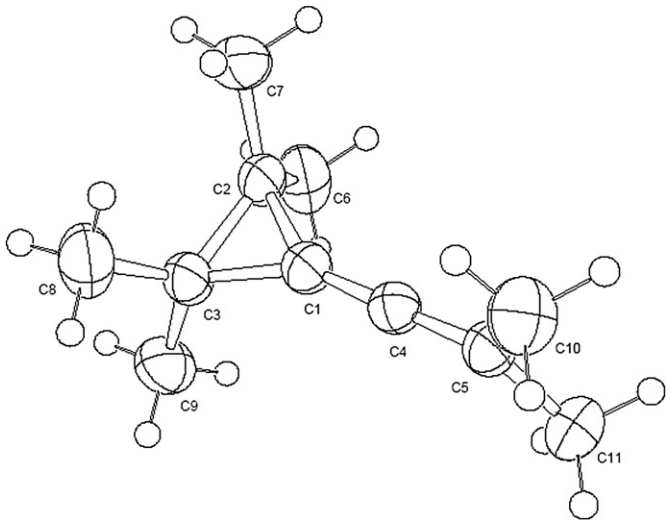


Figure 2. ORTEP diagram of alkenylidenecyclopropane **1**.

Table 2
Structure of alkenylidenecyclopropane **1**

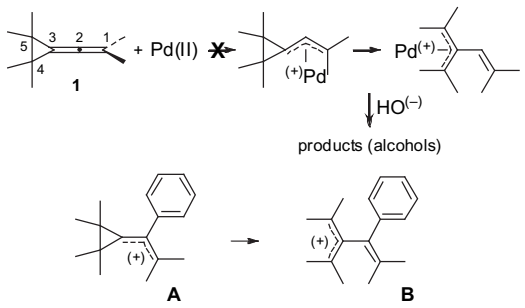
C(1)–C(2)bond	Bond length[a] (Å)	Bond length[b] (Å)	X-ray measured bond length (Å)
C(1)–C(2)	1.314	1.323	1.306
C(2)–C(3)	1.288	1.298	1.291
C(3)–C(4)	1.490	1.488	1.488
C(4)–C(4′)	1.552	1.545	1.546
C(4)–C(5)	1.524	1.519	1.512
C(1)–C(6)	1.524	1.511	1.497
Angle	**Calcd angle[a] (°)**	**Calcd angle[b] (°)**	**X-ray measured angle (°)**
C(6)–C(1)–C(6′)	118.6	116.6	116.0
C(4)–C(3)–C(4′)	62.8	62.6	62.6
C(3)–C(4)–C(4′)	58.6	58.7	58.7
C(5)–C(4)–C(5′)	111.9	112.4	112.1

[a] B3LYP/6.311G++(d,p).
[b] MP2/6.311G++(d,p).

The very high regioselectivity of the carbo-palladation step is certainly determined by electronic factors. Calculations have shown that the HOMO's of **1** and **4** are mainly localized on C(1)–C(2) double bond [**1**, Σatom. coef.(|2s|,|2p|), C(1)=0.193; C(2)=0.156] (the LUMO is not clearly localized). The difference of positive charges between C(1) and C(2) is important (**1**, q[C(1)]=0.446; q[C(2)]=0.244). The HOMO-1 is localized on C(2)–C(3) double bond. The palladium atom attacks the most charged carbon atom, which also bears the largest relative sizes of component atomic orbitals of the HOMO. The previously reported 2+2 addition of

chlorosulfonyl isocyanate leading to a β-lactam derivative is in accordance with this polarization of the HOMO.[8c,28]

The preservation of the alkenylidenecyclopropane moiety seems to reveal that a π-allylpalladium intermediate, where the carbon atom bears a positive charge leading to a nucleophilic attack from nucleophiles as hydroxyl anion or acetate anion, is not involved in the course of this reaction.[4d] To confirm the instability of the cyclopropylallylique cation, we have calculated at the B3LYP/6-311G(++)(d,p) level of theory, the total energies of the two cations **A** (E=−661.530658 hartrees, ZPE=0.348932 hartree, ΔG=−661.229640 hartrees) and **B** (E=−661.553526 hartrees, ZPE=0.348887 hartree, ΔG=−661.250907 hartrees). The isomerization is an exothermic process by 13.3 kcal/mol[33] (Scheme 12).



Scheme 12. Stability of the allylcyclopropane cations.

The Heck reaction of vinylidenecyclopropanes **4** and **5** mainly occurs on the most hindered face (face bearing the two methyl groups) (*syn*-face preference). In fact, for **4**, calculations at the B3LYP/6-311G(++)(d,p) level of theory, shown that the HOMO (38th OM) localized on C(1)–C(2) present an anisotropy. The orbital is expanding on the face bearing the dimethyl groups including the C(3)–C(4) bond (Fig. 3)(orbital distortions). In contrast, the LUMO (39th OM) was relocalized on several atoms including carbon atoms of the methyl. The complex $PdArL_2$ adds to **4** or **5** in accordance with the interaction of the LUMO of the Pd–Ar bond with the HOMO of allenic compounds. So, the addition occurred according to the π-facial selectivity of the electrophilic additions:[34] *it is observed that the preferred direction of attack by the complex $PdArL_2$ was syn to the best electron-donor bond among the vicinal substituents.*

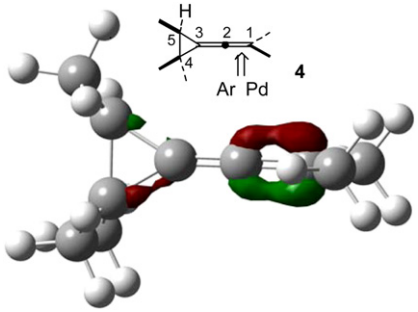
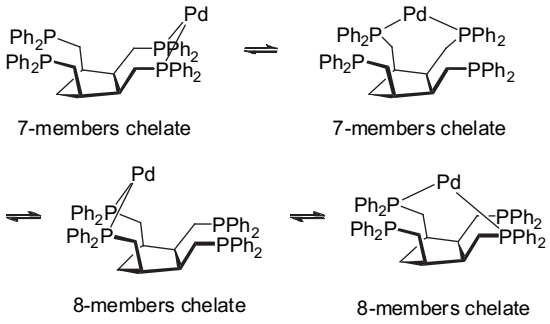


Figure 3. HOMO (38th OM) of the alkenylidenecyclopropane **4**.

The following step is the β-hydride elimination to give the 1,3-diene and the palladium hydride **F** $PdBrHL_2$ (Scheme 8). In the case of the vinylidenecyclopropane **3**, a mixture of the two 1,3-dienes **9** and **10** is obtained, but the major one correspond to the β-elimination of the most acidic proton according to the Hoffmann rule, affording the kinetic diene **9** at the detriment of the thermodynamic diene **10**.[35] The orientation of the double bond might result from the great size of the palladium complex.

This arylation reaction is catalyzed by a palladium associated to the tetraphosphine ligand, Tedicyp. It is accepted that some metal complexes containing chelating diphosphines, might be less robust than those containing monodentate phosphine ligands due to the inability of the phosphorus donors to adopt the thermodynamically more stable *trans*-geometry.[25f] More generally, small ring chelated palladium species, such as with dppm, seems to be poor catalysts for the Heck reaction.[25a] Concerning Tedicyp ligand, its complexation with Pd might led to 4 different rings types.[36] We believe that, according to the step of the catalytic cycle, the appropriate conformation of the Pd-Tedicyp complex will be formed to increase the efficiency of the catalyst and this might help to obtain high turnover numbers (Scheme 13).



Scheme 13. Chelation of palladium complex by Tedicyp.

4. Conclusion

In conclusion, we have developed a simple access to highly complex structures starting from simple molecules in four steps from propargyl alcohols, alkenes and aryl bromides. Many methylenecyclopropanes are interesting compounds, due to their biological properties.[37] Moreover, we have demonstrated that the Heck reaction occurred on the terminal double bond of the allene moiety without interaction with the internal one. Finally, the addition of the complex $PdArL_2$ corresponds to an electrophilic attack on the face of the double bond, *syn* to the best electron-donor cyclopropyl substituent.

4.1. X-ray crystallography

CCDC-751561 (for **1**) and CCDC-752203 (for **7f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk].

5. Experimental part

5.1. General information

All reactions were run under argon in oven-dried glassware. Reagents and solvents were obtained from commercial sources and used as received. Flash column chromatography (FC): Merck 230–400 Mesh silica gel; EtOAc, Et_2O and petroleum ether as eluents. Thin-layer chromatography (TLC): Macherey–Nagel silica gel UV_{254} analytical plates; detection either with UV, or using revealing solution. ^1H and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ solutions at 500 or 300, and 125 or 75 MHz, respectively, using a Bruker Advance DPX 500 or AC300 spectrometers. Chemical shift in parts per million relative to $CDCl_3$ (signals for residual $CHCl_3$ in the $CDCl_3$: 7.24 ppm for ^1H NMR and 77.16 ppm (central) for ^{13}C NMR). Carbon-proton couplings were determined by DEPT sequence experiments.

*5.1.1. 1-(2-Methylpropenylidene)-2,2,3,3-tetramethylcyclo-propane (**1**)*[5,7a]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 6H), 1.20 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.4 (s), 97.1 (s), 96.1 (s), 27.3 (s)(2C), 21.8 (q)(2C), 21.6 (q)(4C).

*5.1.2. 1-Cyclohexenylidene-2,2,3,3-tetramethylcyclopropane (**2**).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16–2.11 (m, 4H), 1.63–1.51 (m, 6H), 1.21 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.3 (s), 104.6 (s), 96.4 (s), 32.7 (t)(2C), 27.8 (t)(2C), 27.2 (s)(2C), 26.5 (t), 21.6 (q)(4C). $C_{14}H_{22}$ (190.2): C 88.35, H 11.65; found C 88.22, H 11.75.

*5.1.3. 1-(2-Methylbutenylidene)-2,2,3,3-tetramethylcyclo-propane (**3**).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (q, J=7.3 Hz, 2H), 1.74 (br s, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.4 (s), 103.9 (s), 98.4 (s), 27.7 (t), 27.2 (s), 21.5 (q)(4C), 20.5 (q), 12.5 (q). $C_{12}H_{20}$ (164.2): C 87.73, H 12.27; found C 87.82, H 12.05.

*5.1.4. 1-(2-Methylpropenylidene)-2,2,3-trimethylcyclopropane (**4**)*[5]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 6H), 1.20 (br s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7 (s), 97.3 (s), 92.4 (s), 24.1 (s), 21.7 (q*, d*), 21.5 (q*,d*), 18.9 (q), 13.2 (q).

*5.1.5. 1-Cyclohexenylidene-2,2,3-trimethylcyclopropane (**5**).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17–2.12 (m, 4H), 1.60–1.50 (m, 7H), 1.20 (s, 3H), 1.14 (d, J=4.9 Hz, 3H), 1.13 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.5 (s), 104.9 (s), 92.6 (s), 32.8 (t), 32.5 (t), 27.7 (t), 27.6 (t), 26.5 (q*), 26.5 (t), 26.3 (d*), 24.1 (s), 19.1 (q), 13.4 (q). $C_{13}H_{20}$ (176.3): C 88.57, H 11.43; found C 88.62, H 11.55.

5.1.6. General procedure for the arylation of alkenylidenecyclo-propanes. As a typical experiment, 4-bromoacetophenone (200 mg, 1.0 mmol), **1** (300 mg, 2.0 mmol) and K_2CO_3 (276 mg, 2.0 mmol) in DMAc (10 mL) in the presence of catalyst[22] (0.004 mmol) are heated under argon for 20 h at 150 °C. Usual work-up gives rise to 161 mg of **7e** (60% yield).

*5.1.7. 3-Phenyl-2-methyl-3-(2,2,3,3-tetramethylcyclo-propylidene)-propene (**7a**).* Yield 46% . ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.18 (m, 5H), 4.97 (t, J=1.7 Hz, 1H), 4.66 (d, J=1.5 Hz, 1H), 2.00 (br s, 3H), 1.23 (s, 6H), 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1 (s), 144.3 (s), 141.4 (s), 132.0 (s), 129.0 (d)(2C), 127.7 (d)(2C), 126.2 (d), 114.3 (t), 22.1 (s), 22.1 (q), 21.9 (q)(2C), 21.1 (q)(2C), 20.3 (s). $C_{17}H_{22}$ (226.4): C 90.20, H 9.80; found C 89.88, H 9.75.

*5.1.8. 3-(3-Methylphenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7b**).* Yield 48%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (t, J=7.2 Hz, 1H), 7.01 (m, 3H), 4.96 (sept., J=1.2 Hz, 1H), 4.67 (t, J=1.1 Hz, 1H), 2.32 (s, 3H), 1.98 (s, 3H), 1.22 (s, 6H), 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7 (s), 144.3 (s), 141.2 (s), 137.1 (s), 132.0 (s), 129.7 (d), 127.6 (d), 126.9 (d), 126.0 (d), 114.2 (t), 22.1 (q), 22.1 (s), 21.9 (q)(2C), 21.6 (q), 21.1 (q)(2C), 20.3 (s). $C_{18}H_{24}$ (240.4): C 89.94, H 10.06; found C 89.96, H 10.12.

*5.1.9. 3-(4-tert-Butylphenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7c**).* Yield 48%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J=8.5 Hz, 2H), 7.14 (d, J=8.5 Hz, 2H), 4.98 (br s, 1H), 4.72 (br s, 1H), 1.98 (s, 3H), 1.32 (s, 9H); 1.21 (s, 6H), 1.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0 (s), 145.1 (s), 144.5 (s), 137.8 (s), 131.7 (s), 128.2 (d)(2C), 124.6 (d)(2C), 114.2 (t), 34.6 (s), 31.6 (q)(3C), 22.8 (s), 22.4 (q), 21.9 (q)(2C), 21.1 (q)(2C), 20.4 (s). $C_{21}H_{30}$ (282.5): C 89.29, H 10.71; found C 89.21, H 10.78.

*5.1.10. 3-(4-Formylphenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7d**).* Yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s), 7.81 (d, J=8.3 Hz, 2H), 7.36 (d, J=8.3 Hz, 2H), 5.00 (quint. J=1.48 Hz, 1H), 4.62 (br q, J=0.8 Hz, 1H), 2.00 (br q, J=0.6 Hz, 3H), 1.23 (s, 6H); 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3 (d), 148.2 (s), 143.6 (s), 134.7 (s), 131.3 (s), 129.7 (s), 129.5 (d)(4C), 114.8 (t), 22.3 (s), 22.1 (q), 21.8 (q)(2C), 21.0 (q)(2C), 20.5 (s). $C_{18}H_{22}O$ (254.4): C 84.99, H 8.72; found C 84.91, H 8.65.

*5.1.11. 3-(4-Acetylphenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7e**).* Yield 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J=8.3 Hz, 2H), 7.29 (d, J=8.3 Hz, 2H), 4.98 (br t, J=1.5 Hz, 1H), 4.62 (br s, 1H), 2.59 (s, 3H), 1.98 (s, 3H), 1.22 (s, 6H), 0.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1 (s), 147.7 (s), 146.7 (s), 143.7 (s), 135.3 (s), 131.3 (s), 129.1 (d)(2C), 128.1 (d)(2C), 114.7 (t), 26.7 (q), 22.3 (s), 22.1 (q), 21.8 (q)(2C), 21.0 (q)(2C), 20.5 (s). High resolution ESI-MS calcd for $[C_{19}H_{24}O+H]^+$: 269.1899. Found: 269.1896.

*5.1.12. 3-(4-Benzoylphenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7f**).* Yield 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J=8.5 Hz, 2H), 7.70 (d, J=8.5 Hz, 2H), 7.56 (t, J=7.4 Hz, 1H), 7.46 (t, J=7.4 Hz, 2H), 7.33 (d, J=8.2 Hz, 2H), 5.02 (br s, 1H), 4.70 (br s, 1H), 2.01 (s, 3H), 1.24 (s, 6H); 1.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6 (s), 147.6 (s), 146.0 (s), 143.7 (s), 138.0 (s), 135.4 (s), 132.2 (d), 131.4 (s), 130.0 (d)(2C), 129.9 (d)(2C), 128.7 (d)(2C), 128.3 (d)(2C), 114.7 (t), 22.2 (s), 22.1 (q), 21.8 (q)(2C), 21.0 (q)(2C), 20.5 (s). $C_{24}H_{26}O$ (330.5): C 87.23, H 7.93; found C 87.41, H 7.85.

*5.1.13. 3-(4-Methoxycarbonyl)phenyl-2-methyl-3-(2,2,3,3-tetrame-thylcyclopropylidene)-propene (**7g**).* Yield 52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J=8.3 Hz, 2H), 7.27 (d, J=8.3 Hz, 2H), 4.99 (br s, 1H), 4.63 (br s, 1H), 3.90 (s, 3H), 1.99 (s, 3H), 1.23 (s, 6H), 0.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (s), 147.5 (s), 146.5 (s), 143.7 (s), 131.4 (s), 129.2 (d)(2C), 128.9 (d)(2C), 128.1 (s), 114.6 (t), 52.1 (q), 22.3 (s), 22.0 (q), 21.8 (q)(2C), 21.0 (q)(2C), 20.4 (s). $C_{19}H_{24}O_2$ (284.4): C 80.24, H 8.51; found C 80.16, H 8.58.

*5.1.14. 3-(4-Cyanophenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7h**).* Yield 64%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J=8.3 Hz, 2H), 7.29 (d, J=8.3 Hz, 2H), 4.99 (br s, 1H), 4.57 (br s, 1H), 1.97 (s, 3H), 1.22 (s, 6H); 0.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5 (s), 146.4 (s), 143.4 (s), 131.8 (d)(2C), 130.9 (s), 129.6 (d)(2C), 119.4 (s), 114.9 (t), 110.0 (s), 22.4 (s), 22.0 (q), 21.8 (q)(2C), 21.0 (q)(2C), 20.5 (s). $C_{18}H_{21}N$ (251.4): C 86.01, H 8.42; found C 85.92, H 8.48.

*5.1.15. 3-(2-Cyanophenyl)-2-methyl-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7i**).* Yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, J=7.8, 0.8 Hz, 1H), 7.52 (td, J=7.7, 1.3 Hz, 1H), 7.34 (td, J=7.6, 1.3 Hz, 1H), 4.95 (t, J=1.3 Hz, 1H), 4.28 (br s, 1H), 2.15 (s, 3H), 1.27 (s, 6H), 0.91 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8 (s), 146.0 (s), 143.3 (s), 132.5 (d), 132.2 (d), 130.6 (d), 129.1 (s), 127.0 (d), 114.3 (t), 113.4 (s), 23.0 (s), 21.8 (q)(2C), 21.4 (q), 20.43 (s), 20.37 (q)(2C). $C_{18}H_{21}N$ (251.4): C 86.01, H 8.42; found C 86.12, H 8.40.

*5.1.16. 2-Methyl-3-(4-nitrophenyl)-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7j**).* Yield 59%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J=8.8 Hz, 2H), 7.36 (d, J=8.8 Hz, 2H), 5.02 (quint; J=1.45, 1H), 4.59 (br s, 1H), 1.99 (s, 3H), 1.23 (s, 6H); 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0 (s), 148.6 (s), 146.5 (s), 143.4 (s), 130.6 (s), 129.6 (d)(2C), 123.3 (d)(2C), 115.0 (t), 22.5 (s), 22.1 (q), 21.8 (q)(2C), 21.0 (q)(2C), 20.6 (s). $C_{17}H_{21}NO_2$ (271.4): C 75.25, H 7.80; found C 75.15, H 7.88.

*5.1.17. 2-Methyl-3-(3-nitrophenyl)-3-(2,2,3,3-tetramethyl-cyclo-propylidene)propene (**7k**).* Yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (br s, 1H), 7.55–7.36 (m, 3H), 5.02 (br s, 1H), 4.59 (br s, 1H), 2.00 (s, 3H), 1.24 (s, 6H), 1.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6 (s), 148.3 (s), 143.4 (s), 143.2 (s), 135.0 (d), 130.3 (s), 128.7 (d),

123.9 (d), 121.4 (d), 114.9 (t), 22.7 (s), 21.8 (q), 21.0 (q)(2C), 20.9 (q)(2C), 20.6 (s). $C_{17}H_{21}NO_2$ (271.4): C 75.25, H 7.80; found C 75.31, H 7.78.

*5.1.18. 3-(4-Trifluoromethylphenyl)-2-methyl-3-(2,2,3,3-tetramethylcyclopropylidene)-propene (**7l**).* Yield 57%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J=8.1 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H), 5.00 (br s, 1H), 4.60 (br s, 1H), 2.00 (s, 3H), 1.24 (s, 6H); 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6 (s), 145.2 (s, quadr. J(C–F)=1.1 Hz), 143.7 (s), 131.1 (s), 129.2 (d)(2C), 128.4 (s, quadr. J(C–F)=32.5 Hz), 124.8 (d, quadr. J(C–F)=3.8 Hz)(2C), 124.6 (s, quadr. J(C–F)=272.0 Hz), 114.7 (t), 22.4 (s), 22.0 (q), 21.9 (q)(2C), 21.0 (q)(2C), 20.4 (s). $C_{18}H_{21}F_3$ (294.3): C 73.45, H 7.19; found C 73.36, H 7.22.

*5.1.19. 2-Methyl-3-(2,2,3,3-tetramethylcyclopropylidene)-3-(3-thienyl)propene (**7m**).* Yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.20 (m, 1H), 7.04–7.00 (m, 2H), 4.98 (br s, 1H), 4.82 (br s, 1H), 2.00 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H), 1.08 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5 (s), 144.1 (s), 141.5 (s), 128.8 (d), 126.9 (s), 124.2 (d), 121.6 (d), 113.9 (t), 22.3 (q), 21.8 (q)(2C), 21.1 (q)(2C), 20.5 (s). $C_{15}H_{20}S$ (232.4): C 77.53, H 8.67; found C 77.46, H 8.62.

*5.1.20. 3-(4-Isoquinolin)-2-methyl-3-(2,2,3,3-tetramethyl-cyclopropylidene)propene (**7n**).* Yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.28 (s, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.69 (d, J=8.0 Hz, 1H), 7.60–7.50 (m, 2H), 4.87 (br s, 1H), 4.27 (br s, 1H), 2.14 (s, 3H), 1.31 (s, 6H), 0.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1 (d), 149.7 (s), 143.7 (d), 142.8 (s), 135.5 (s), 132.8 (s), 130.2 (d), 127.1 (d), 127.0 (s), 126.9 (d), 126.5 (s), 125.5 (d), 114.8 (t), 23.2 (s), 22.1 (q)(2C), 21.4 (q), 20.4 (q)(2C), 20.3 (s). $C_{20}H_{23}N$ (277.4): C 86.59, H 8.36; found C 86.54, H 8.28.

*5.1.21. 1-[(4-Acetylphenyl)(cyclohexen-1-yl)]methylene-2,2,3,3-tetramethylcyclopropane (**8**).* Yield 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J=8.1 Hz, 2H), 7.27 (d, J=8.1 Hz, 2H), 5.38 (br s, 1H), 2.58 (s, 3H), 2.35–2.0 (m, 2H), 1.85–1.55 (m, 4H), 1.20 (s, 6H), 1.09 (t, J=5.8 Hz, 2H), 0.97 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2 (s), 147.3 (s), 147.1 (s), 144.7 (s), 137.2 (s), 135.1 (s), 129.2 (d)(2C), 128.0 (d)(2C), 126.8 (d), 27.1 (t), 26.7 (q), 25.9 (t), 23.2 (t), 22.4 (t), 22.1 (s), 22.0 (q)(2C), 21.1 (q)(2C), 20.3 (s). $C_{22}H_{28}O$ (308.5): C 85.66, H 9.15; found C 85.72, H 9.18.

*5.1.22. 2-Ethyl-3-(4-formylphenyl)-3-(2,2,3,3-tetramethyl-cyclopropylidene)propene (**9d**) and 1-(4-formylphenyl)-2-methyl-1-(2,2,3,3-tetramethylcyclopropylidene)-2-butene (**10d**).* Overall yield 62%. **9d** (66%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.80 (d, J=8.3 Hz, 2H), 7.39 (d, J=8.3 Hz, 2H), 5.05 (q, J=1.1 Hz, 1H), 4.76 (s, 1H), 2.24 (q, J=7.5 Hz, 2H), 1.21 (br s, 12H), 1.05 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1 (d), 149.9 (s), 147.6 (s), 147.5 (s), 134.6 (s), 130.8 (s), 129.7 (d)(2C), 128.7 (d)(2C), 112.9 (t), 27.7 (t), 21.9 (s), 21.5 (q)(2C), 21.1 (q)(2C), 20.9 (s), 13.1 (q). **10d** (34%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.80 (d, J=8.3 Hz, 2H), 7.33 (d, J=8.3 Hz, 2H), 5.21 (qq, J=6.9, 1.3 Hz, 1H), 1.85 (s, 3H), 1.67 (d, J=6.9 Hz, 3H), 1.21 (br s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2 (d), 148.5 (s), 145.7 (s), 135.7 (s), 134.6 (s), 132.6 (s), 129.5 (d), 129.4 (d), 124.4 (d), 28.1 (q), 22.1 (s), 21.9 (d)(2C), 21.1 (d)(2C), 20.5 (s), 15.0 (q). $C_{19}H_{24}O$ (268.4): C 85.03, H 9.01; found C 84.82, H 9.08.

*5.1.23. 2-Ethyl-3-(4-methoxyphenyl)-3-(2,2,3,3-tetramethyl-cyclopropylidene)propene (**9o**) and 1-(4-methoxyphenyl)-2-methyl-1-(2,2,3,3-tetramethylcyclopropylidene)-2-butene (**10o**).* Overall yield 51%. **9o** (63%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J=8.4 Hz, 2H), 6.84 (d, J=8.4 Hz, 2H), 5.00 (d, J=1.4 Hz, 1H), 4.81 (d, J=1.0 Hz, 1H), 3.80 (s, 3H), 2.26 (q, J=7.3 Hz, 2H), 1.20 (s, 6H), 1.10 (s, 6H), 1.05 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2 (s), 151.0 (s), 143.5 (s), 136.5 (s), 133.4 (s), 129.9 (d)(2C), 129.3 (d)(2C), 113.3 (d), 112.0 (t), 55.3 (q), 27.7 (t), 21.69 (s), 21.66 (d)(2C), 21.2 (d)(2C), 20.5 (s), 13.2 (q). **10o** (37%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, J=8.4 Hz, 2H), 6.83 (d, J=8.4 Hz, 2H), 5.29 (q, J=6.8 Hz, 1H), 3.80 (s, 3H), 1.86 (s, 3H), 1.68 (d, J=7.0 Hz, 3H), 1.22 (s, 6H), 1.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (s), 151.0 (s), 142.7 (s), 134.1 (s), 132.7 (s), 130.8 (d), 129.3 (d)(2C), 123.5 (d), 113.1 (d), 55.28 (q), 22.0 (q), 21.98 (s), 21.2 (d)(2C), 20.2 (s), 14.9 (q), 14.0 (q). $C_{19}H_{26}O$ (270.4): C 84.39, H 9.69; found C 84.45, H 9.76.

*5.1.24. 3-(4-Formylphenyl)-2-methyl-3-(2,2,3-trimethylcyclo-propylidene)propene (Z: **11d**, 72%; E: **12d**, 28%).* Yield 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.81 (d, J=8.2 Hz, 2H), 7.38 (d, J=8.2 Hz, 2H), 5.02 (br s, 1H), 4.69 (br s, 1H, minor *iso.*), 4.66 (br, s, 1H, major *iso.*), 2.03 (s, 3H, major *iso.*), 1.99 (s, 3H, minor *iso.*), 1.41 (q, J=6.4 Hz, 1H), 1.19 (d, J=6.4 Hz, 3H), 1.06 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3 (d), 148.2 (s), 144.3 (s), 143.8 (s), 134.8 (s), 131.9 (s), 129.6 (d)(2C), 129.5 (d)(2C), 114.9 (t), 26.1 (d), 22.4 (d), 22.2 (d), 18.6 (d), 18.1 (s), 13.4 (q). $C_{17}H_{20}O$ (240.3): C 84.96, H 8.39; found C 84.92, H 8.45.

*5.1.25. 3-(4-Acetylphenyl)-2-methyl-3-(2,2,3-trimethylcyclo-propylidene)propene (Z: **11e**, 72%; E: **12e**, 28%).* Yield 59%. ^{1}H NMR (500 MHz, $CDCl_3$) δ major: 7.89 (d, J=8.3 Hz, 2H), 7.30 (d, J=8.3 Hz, 2H), 5.00 (br s, 1H), 4.66 (br s, 1H), 2.59 (s, 3H), 2.03 (s, 3H), 1.40 (q, J=6.2 Hz, 1H), 1.18 (d, J=6.4 Hz, 3H), 1.05 (s, 3H), 0.95 (s, 3H); minor: 7.89 (d, J=8.3 Hz, 2H), 7.36 (d, J=8.3 Hz, 2H), 5.01 (br s, 1H), 4.69 (br s, 1H), 2.58 (s, 3H), 1.99 (s, 3H), 1.40 (q, J=6.2 Hz, 1H), 1.19 (d, J=6.4 Hz, 3H), 1.05 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1 (s), 146.7 (s), 143.9 (s), 143.7 (s), 135.3 (s), 131.9 (s), 129.0 (d)(2C), 128.1 (d)(2C), 114.7 (t), 26.7, 26.1, 22.4, 22.1, 18.6, 18.0 (s), 13.4. $C_{18}H_{22}O$ (254.4): C 84.99, H 8.72; found C 85.06, H 8.75.

*5.1.26. 3-(4-Cyanophenyl)-2-methyl-3-(2,2,3-trimethyl-cyclopropylidene)propene (Z: **11h**, 80%; E: **12h**, 20%).* Yield 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J=8.2 Hz, 2H, major *iso.*), 7.37 (d, J=8.2 Hz, 2H, minor *iso.*), 7.31 (d, J=8.2 Hz, 2H), 5.01 (br s, 1H), 4.65 (br s. 1H, minor *iso.*), 4.61 (br s, 1H, major *iso.*), 2.01 (s, 3H, major *iso.*), 1.97 (s, 3H, minor *iso.*), 1.41 (q, J=6.4 Hz, 1H), 1.18 (d, J=6.4 Hz, 3H), 1.04 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4 (s), 144.5 (s), 143.6 (s), 131.8 (d)(2C), 131.5 (s, minor *iso.*), 129.5 (d)(2C), 119.4 (s), 114.9 (t), 110.1 (s), 26.6 (d,q, minor *iso.*), 26.1 (d,q), 22.4 (d,q), 22.1 (d,q), 18.5 (d,q), 18.1 (s), 13.3 (q). $C_{17}H_{20}N$ (237.3): C 86.03, H 8.07; found C 86.11, H 8.05.

*5.1.27. 1-[(Cyclohexen-1-yl)(4-formylphenyl)]methylene-2,2,3-trimethylcyclopropane (Z: **13d**, 72%; E: **14d**, 18%).* Yield 64%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (s, 1H, major *iso.*), 9.95 (s, 1H, minor *iso.*), 7.80 (d, J=8.2 Hz, 2H, major *iso.*), 7.75 (d, J=7.7 Hz, minor *iso.*), 7.35 (d, J=8.3 Hz, 2H), 5.46 (br s, 1H, minor *iso.*), 5.42 (br s, 1H, major *iso.*), 1.75–1.55 (m, 2H), 1.35–1.0 (m, 3H), 1.17 (d, J=6.6 Hz, 3H), 1.04 (s, 3H), 0.92 (s, 3H), 0.88–0.82 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3 (d), 148.6 (s), 141.3 (s), 137.3 (s), 134.6 (s), 132.3 (s), 129.54 (d)(2C), 129.49 (d)(2C), 127.05 (d, major *iso*), 126.98 (d, minor *iso.*), 31.1 (q*,d*), 27.4 (t), 26.2 (d*,q*), 25.9 (t), 23.2 (t), 22.4 (t), 19.6 (q), 17.7 (s), 13.6 (q). $C_{20}H_{24}O$ (280.4): C 85.67, H 8.63; found C 85.59, H 8.69.

*5.1.28. 1-[(Cyclohexen-1-yl)(4-methoxycarbonylphenyl)]-methylene-2,2,3-trimethylcyclopropane (Z: **13g**, 80%; E: **14g**, 18%).* Yield 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J=8.3 Hz, 2H, major *iso.*), 7.90 (minor *iso.*), 7.31 (minor *iso.*), 7.25 (d, J=8.3 Hz, 2H, major *iso.*), 5.45 (br, s, 1H, minor *iso.*), 5.41 (br, s, 1H, major *iso.*), 3.9 (s, 3H), 0.92–0.80 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (s), 146.9 (s), 140.5 (s), 137.4 (s), 132.4 (s), 129.2 (d)(2C), 129.0 (d)(2C), 128.0 (s), 126.85 (d, major *iso.*), 126.78 (d, minor *iso.*), 52.1 (q), 27.3 (t), 26.2 (d,q), 25.9

(t), 23.2 (t), 22.7 (d,q), 22.4 (t), 18.6 (d,q), 17.5 (s), 13.7 (q). $C_{21}H_{26}O$ (310.4): C 81.25, H 8.44; found C 81.52, H 8.49.

5.1.29. 1-[(4-Cyanophenyl)(cyclohexen-1-yl)]methylene-2,2,3-trimethylcyclopropane (Z: ***13h****, 78%; E:* ***14h****, 22%).* Yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J*=8.4 Hz, 2H, major *iso*.), 7.51 (d, *J*=8.4 Hz, 2H, minor *iso*.), 7.34 (d, *J*=8.4 Hz, 2H, minor *iso*.), 7.28 (d, *J*=8.4 Hz, 2H), 5.42 (br s, 1H, minor *iso*.), 5.38 (br s, 1H, major *iso*.), 2.40–2.00 (m, 3H), 1.75–1.50 (m, 4H), 1.16 (d, *J*=6.5 Hz, 3H), 1.02 (s, 3H), 0.91 (s, 3H), 0.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9 (s), 141.5 (s), 137.1 (s), 131.9 (s), 131.7 (d)(2C), 129.6 (d)(2C), 127.2 (d, major *iso*.), 127.09 (d, minor *iso*.), 119.5 (s), 109.8 (s), 27.3 (t), 26.2 (q*,d*), 25.9 (t), 23.1 (t), 22.35 (q*,d*), 22.33 (t), 18.6 (q), 17.7 (s), 13.6 (q). $C_{20}H_{23}N$ (277.4): C 86.59, H 8.36; found C 86.66, H 8.42.

Acknowledgements

Y.F. is grateful to the Mauritania Government for a grant. This work was supported by the CNRS and the Ministère de l'Education Nationale. We thank Dr. M. Giorgi (Spectropôle, Université d'Aix-Marseille) for the X-ray structure determinations and R. Rosas for NMR spectroscopic studies. We are indebted to Dr. B. Vacher (Pierre Fabre Médicaments, Castres, Fr) and Dr. N. Ferré for helpful comments and assistance.

References and notes

1. (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518–5542; (b) Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707–6714; (c) Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896–6901; (d) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320–2322; (e) Heck, R. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 201–224.
2. Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc.* **1971**, *44*, 581.
3. For preliminary results, see: Fall, Y.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2007**, *48*, 3579–3581.
4. (a) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679–1688; (b) Ma, S. *Chem. Rev.* **2005**, *105*, 2829–2871; (c) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067–3125; (d) Lu, J.-M.; Shi, M. *Tetrahedron* **2006**, *62*, 9115–9122; (e) Li, W.; Shi, M. *Eur. J. Org. Chem.* **2009**, 270–274.
5. Patrick, T. B.; Schmidt, D. J. *J. Org. Chem.* **1977**, *42*, 3354–3356.
6. Hartzler, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 4990–4996.
7. (a) Crandall, J. K.; Paulson, D. R. *J. Am. Chem. Soc.* **1966**, *88*, 4302–4303; (b) Paulson, D. R.; Crandall, J. K.; Bunnell, C. A. *J. Org. Chem.* **1970**, *35*, 3708–3714.
8. (a) Crandall, J. K.; Paulson, D. R.; Bunnell, C. A. *Tetrahedron Lett.* **1968**, 5063–5066; (b) Leandri, G.; Santelli-Rouvier, C. *Bull. Soc. Chim. Fr.* **1970**, 1515–1520; (c) Poutsma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 440–450.
9. Pasto, D. J.; Miles, M. F. *J. Org. Chem.* **1976**, *41*, 425–432.
10. Crandall, J. K.; Schuster, T. *J. Org. Chem.* **1990**, *55*, 1973–1975.
11. Pasto, D. J.; Miles, M. F. *J. Org. Chem.* **1976**, *41*, 2068–2070.
12. Sasaki, T.; Eguchi, S.; Ogawa, T. *J. Am. Chem. Soc.* **1975**, *97*, 4413–4414.
13. Santelli, M.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1973**, 2340–2343.
14. (a) Lu, J.-M.; Shi, M. *Org. Lett.* **2008**, *10*, 1943–1946; (b) Lu, J.-M.; Shi, M. *Chem.— Eur. J.* **2009**, *15*, 6065–6073.
15. Lu, B.-L.; Lu, J.-M.; Shi, M. *Tetrahedron* **2009**, *65*, 9328–9335.
16. Su, C.; Huang, X.; Liu, Q.; Huang, X. *J. Org. Chem.* **2009**, *74*, 8272–8279.
17. Hwu, C.-C.; Wang, F.-C.; Yeh, M.-C. P.; Sheu, J.-H. *J. Organomet. Chem.* **1994**, *474*, 123–128.
18. (a) Ma, S.; Negishi, E.-i *J. Am. Chem. Soc.* **1995**, *117*, 6345–6357; (b) Gardiner, M.; Grigg, R.; Sridharan, V.; Vicker, N. *Tetrahedron Lett.* **1998**, *39*, 435–438; (c) Knoke, M.; de Meijere, A. *Eur. J. Org. Chem.* **2005**, 2259–2268; (d) Ma, S. *Pure Appl. Chem.* **2006**, *78*, 197–208.
19. (a) Grigg, R.; Brown, S.; Sridharan, V.; Uttley, M. D. *Tetrahedron Lett.* **1998**, *39*, 3247–3250; (b) Chang, H.-M.; Cheng, C.-H. *J. Org. Chem.* **2000**, *65*, 1767–1773; (c) Brown, S.; Grigg, R.; Hinsley, J.; Koen, S.; Sridharan, V.; Uttley, M. D. *Tetrahedron* **2001**, *57*, 10347–10355; (d) Oh, C. H.; Jung, S. H.; Bang, S. Y.; Park, D. I. *Org. Lett.* **2002**, *4*, 3325–3327; (e) Fu, C.; Ma, S. *Org. Lett.* **2002**, *4*, 1707–1709.
20. (a) Brown, S.; Grigg, R.; Hinsley, J.; Korn, S.; Sridharan, V.; Uttley, M. D. *Tetrahedron* **2001**, *57*, 10347–10355.
21. Bai, T.; Xue, L.; Xue, P.; Zhu, J.; Sung, H. H.-Y.; Ma, S.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2008**, *27*, 2614–2626.
22. Laurenti, D.; Feuerstein, M.; Pèpe, G.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 1633–1637.
23. Doucet, H.; Santelli, M. *Synlett* **2006**, 2001–2015.
24. (a) Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923–5925; (b) Feuerstein, M.; Doucet, H.; Santelli, M. *Synlett* **2001**, 1980–1982; (c) Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2002**, *43*, 2191–2194; (d) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 1221–1225; (e) Berthiol, F.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2003**, 1091–1096; (f) Berthiol, F.; Doucet, H.; Santelli, M. *Synlett* **2003**, 841–844; (g) Kondolff, I.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 8487–8491; (h) Kondolff, I.; Doucet, H.; Santelli, M. *Synlett* **2004**, 1561–1564; (i) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2004**, *45*, 5633–5636; (j) Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2006**, *47*, 459–462; (k) Kondolff, I.; Doucet, H.; Santelli, M. *Eur. J. Org. Chem.* **2006**, 765–774; (l) Berthiol, F.; Doucet, H.; Santelli, M. *Synthesis* **2006**, 1518–1536; (m) Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *Synthesis* **2006**, 3495–3505; (n) Lemhadri, M.; Doucet, H.; Santelli, M. *Synlett* **2006**, 2935–2940; (o) Berthiol, F.; Doucet, H.; Santelli, M. *Tetrahedron* **2006**, *62*, 4372–4383.
25. (a) Knowles, J. P.; Whiting, A. *Org. Biomol. Chem.* **2007**, *5*, 21–44; (b) Alonso, F.; Beletskaya, I.; Yus, M. *Tetrahedron* **2005**, *61*, 11771–11835; (c) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553–1582; (d) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945–2963; (e) Littke, A.; Fu, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176–4211; (f) Withcombe, N.; Hii, K. K.; Gibson, S. *Tetrahedron* **2001**, *57*, 7449–7476; (g) Beletskaya, I.; Cheprakov, A. *Chem. Rev.* **2000**, *100*, 3009–3066; (h) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379–2411.
26. Fu, C.; Ma, S. *Org. Lett.* **2005**, *7*, 1605–1607.
27. The regioselectivity on catalyst dependence of condensation of phenylethyne and methyl 2,3-pentadienoate has been justified by a different Pd catalyst double bond coordination (η^1 precursor complexes as D (Scheme 9)), see: Trost, B. M.; Kottirsch, G. *J. Am. chem. Soc.* **1990**, *112*, 2816–2818.
28. Pasto, D. J.; Chen, A. F.-T.; Ciurdaru, G.; Paquette, L. A. *J. Org. Chem.* **1973**, *38*, 1015–1026.
29. Pasto, D. J.; Miles, M. F.; Chou, S.-K. *J. Org. Chem.* **1977**, *41*, 3098–3101.
30. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652; (b) Lee, C.; Yang, W.; Parr, R. G. *Physiol. Rev.* **1988**, *B37*, 785–789.
31. Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622.
32. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, revision E.01*; Gaussian: Pittsburgh, PA, 2004.
33. Vinylcyclopropyl tosylate underwent Pd(0) catalysed regioselective substitution at the terminal vinylic position with stabilized C-nucleophiles. An unsymmetric π-allyl palladium complex where the palladium would be positioned closer to the cyclopropyl carbon has been invoked. In fact, the opening of the cyclopropane to give 2-vinylallyl cation is weakly exothermic, $\delta\Delta G$=–2.06 kcal/mol (B3LYP/6-311G(++)(d, p)), see: Stolle, A.; Ollivier, J.; Piras, P. P.; Salaün, J.; de Meijere, A. *J. Am. Chem. Soc.* **1992**, *114*, 4051–4067.
34. (a) For reviews on diastereoselection, see a thematic issue: *Chem. Rev.* **1999**, *99*, 1069–1480; (b) Ohwada, T. *Chem. Rev.* **1999**, *99*, 1337–1375; (c) Mehta, G.; Singh, S. R.; Gagliardini, V.; Priyakumar, U. D.; Sastry, G. N. *Tetrahedron Lett.* **2001**, *42*, 8527–8530; (d) Moraleda, D.; Ollivier, C.; Santelli, M. *Tetrahedron Lett.* **2006**, *47*, 5471–5474.
35. Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 6th ed.; John Wiley & Sons: New York, NY, 2007; p 1497.
36. Reynaud, C.; Fall, Y.; Feuerstein, M.; Doucet, H.; Santelli, M. *Tetrahedron* **2009**, *65*, 7440–7448.
37. (a) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589–635; (b) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213–1269.