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Palladium(0)-catalyzed allylic substitution of optically active natural terpenic functionalized olefins

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Abstract

The palladium(0) *catalyzed* substitution reactions of allylic acetates, carbonates and chlorides derivatives from demanding natural terpenic olefins by diethyl malonate anion has been performed under mild conditions. The protocol uses a catalytic amount of $Pd(dba)_2/PPh_3$ as promoting agent, providing new allyl products in good yields. The reaction showed a highly regio- and stereoselectivity giving facile access to various products of great industrial potential. The analysis of the optical activity of the synthesized products has been discussed and gave some information on the intermediate complexes.

1. Introduction

The palladium-catalyzed allylic substitution reaction has become a mainstay methodology in organic synthesis [1-5]. Of great value is the allylic alkylation, since tremendous advances have been made in the development of new chiral catalysts for asymmetric allylic substitution [6-9]. The regiocontrol in these substitution reactions is of great significance. This is particulary relevant in asymmetric reactions as they often rely on a regiospecific addition to a pseudo meso Pd-allyl complex for enantioselectivity [10].

Recently, Mata et al. [11] have designed and synthesized a new family of readily available phosphate-phosphoramide ligands for Pd-catalyzed allylic alkylation. The ligands were derived from D-glucosamine and contain several substituents in the biphenyl moieties.

More recently, Marinho et al. [12] have reported a novel chiral P, O- ligands for the homogeneous Pd(0) catalyzes asymmetric allylic alkylation. A number of palladium pre-catalysts were used, but it was $[Pd(allyl)Cl]_2$ which gave the best results.

It has been reported that π-allylpalladium chloride reacts with carbonucleophiles such as malonates and acetoacetates offering a method for C-C bond formation [13-14]. Moreover, the allylic alkylation of alkyl substituted π-allylpalladium complexes requires enhancement of their electrophilicity by addition of ligands, phosphines and phosphates were preferred [15]. It is described by Fiaud et al. [16] that the allylic alkylation of allyl acetates using $Pd(dba)_2$/dpe catalytic system allowing good results, whereas the use of PPh_3 as ligand did not induce any reaction.

In the course of our studies on monoterpenes and their derivatives which are of much interest in perfumery, artificials flavouring and in the pharmaceutical industry [17-21], we recently reported that the allylic chlorination, amination, and allylic alkoxycarbonylation of allylic natural terpenic olefins offers a very good method for the preparation of new functionalized terpenic olefins [22-24].

With a view to extend the potential use of these naturally occurring alkenes, we focused our efforts on the allylic alkylation of those containing an allylic function. The present study is devoted to the investigation of Pd(0) allylic alkylation of cyclic and linear allyl carbonates, acetates and chlorides having limonene or myrcene skeletons obtained from the corresponding allylic alcohols, using diethyl malonate as nucleophile. The use of optically active monoterpenes as starting materials allowed preparing new asymmetric functionalized compounds derived from natural products.

2. Experimental details

2.1. *Apparatus*

The reaction mixtures were analyzed by gas chromatography equipped with FID using a Rtx-5 capillary column. Optical rotations were measured on a Perkin–Elmer 343 polarimeter. The NMR spectra were recorded on a Brucker AM 400 in $CDCl_3$ solution by using TMS as an internal standard (all chemical shifts assignments are given in ppm and were accomplished making use of one and two dimensional NMR techniques HMBC, HMQC, COSY and NOESY).

2.2. *Chemicals*

Allyl carbonates, allyl chlorides and allyl acetates were synthesized using procedures described below. Starting materials were purchased from Sigma-Aldrich chemical reagent grade and used as received. Catalysts and ligands were used without further purification. Solvents were commercial grade. THF and Ether were distilled from sodium benzophenone ketyl immediately and stored under nitrogen atmosphere. Reactions involving the use of palladium catalysts were run under a nitrogen atmosphere.

2.3. *Synthesis of allyl carbonates (**1**, **3**-**6**)*

To a coold (0°C) and stirred solution of the allylic alcohol (100 mmol) and dry pyridine (200 mmol) in dry ether (100 mmol) was added ethyl chloroformate (100 mmol) dropwise over 15 min. The mixture was stirred at room temperature for 3 h and then dilute hydrochloric acid was added. After extraction with ether, the organic layer was washed with water and dried over $MgSO_4$. Following the evaporation of the solvent, allyl carbonate was obtained in yields varying between 90 and 96% [25].

2.4. *Synthesis of allyl acetates (**11**-**14**)*

To a solution of the allylic alcohol (6.5 mmol) in 10 ml of $CHCl_3$ were added acetic anhydride (7.2 mmol) and trimethylamine (7.3 mmol). The reaction mixture was stirred at room temperature overnight. After that, a solution of $NaHCO_3$ was added and the mixture was extracted by $CHCl_3$. The organic phase was dried and the solvent removed leading to virtually pure allyl acetate in yields up to 90%.

2.5. *Synthesis of allyl chlorides*

2.5.1 *Synthesis of trans-carvyl chloride **16***

Trans-carvyl chloride was prepared according to the literature [26], by treatment of α-pinene (20 mmol) by dimethyl sulfoxide (80 mmol) and phosphorus oxychloride (20 mmol) in methylene chloride for 30 min over a temperature range of – 20 to 20°C. At the end of the reaction, a solution of $NaHCO_3$ was added, and the mixture was extracted by $CHCl_3$. The organic phase was washed with water, dried and the solvent removed leading to virtually pure trans-carvyl chloride in quantitative yield. The same procedure has been followed to prepare perillyl chloride **15** starting from β-pinene.

2.5.2 *Synthesis of geranyl chloride **17***

A dry 300 ml three-necked flask equipped with a magnetic stirring bar and reflux condenser was charged with 90 ml of carbon tetrachloride and 15.42 g of geraniol (0.10 mol). To this solution 34.09 g of triphenylphosphine (0.13 mol) were added, and the reaction mixture is stirred and heated to reflux for 1h. This mixture is allowed to cool to room temperature, dry pentane is added (100 ml), and stirring is continued for an additional 5 min. The precipitate of triphenylphosphine oxide is filtered and washed with 50 ml of pentane. The solvent is removed from the combined filtrate at the rotary evaporator under vacuum at room temperature. Distillation of the residue through a vigreux column provides 13-14 g (75-81 %) of geranyl chloride **17**, bp 47-49°C.

3. Results and Discussion

3.1. Alkylation of allyl terpenic carbonates

We first investigated the Pd-catalyzed allylic substitution of optically active perillyl carbonate **1** chosen as model substrate, with sodium diethyl malonate in THF using $Pd(dba)_2/PPh_3$ as catalytic system at room temperature (Figure 1). A conversion of 90% was observed, and the reaction leads smoothly after 24 hours under nitrogen atmosphere and mild conditions to the formation of optically active corresponding ester **2** in good yield (74%).

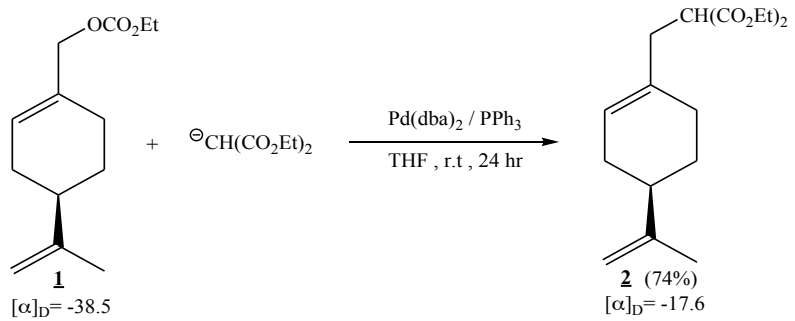


Figure 1: Allylic alkylation of allyl carbonate **1** (Reaction conditions : Allyl carbonate **1** (4.4 mmol) , $Pd(dba)_2$ (0.044 mmol) , PPh_3 (0.088 mmol) , diethyl-malonate (8.4 mmol) , NaH (5.1 mmol) , THF , under nitrogen atmosphere at r.t , 24 h, $[\alpha]_D$ determined at : c = 2, $CHCl_3$)

To evaluate the limitation of the system $Pd(dba)_2/PPh_3$, the reaction was performed by varying the molar ratios of ligand/catalyst and substrate/catalyst (Table 1). As observed in the table 1, the good result was obtained with 2 equivalent of ligand (entry 3). An increased of molar ratio substrate/catalyst, provided the same trends after 40 hours of reaction time (entry 6).

Table 1: Effect of catalyst and ligand on the Pd-catalyzed alkylation of **1**

Entry[a]	Ratio Ligand/Catalyst	Ratio Substrate/Catalyst	Yield[b] (%)	Conv[d] (%)
1	1	100	57	74
2	1.5	100	66	80
3	2	100	74	88
4	3	100	70	86
5	2	50	70	84
6	2	200	76[c]	87

[a] Reaction conditions : Allyl carbonate **1** (4.4 mmol), $Pd(dba)_2$ (1 mol%, 0.044 mmol), PPh_3 (2 mol% , 0.088 mmol), diethyl-malonate (200 mol% , 8.4 mmol), NaH (116 mol% , 5.1 mmol), THF, under nitrogen atmosphere at r.t, 24 h.
[b] Isolated yield.
[c] Reaction time= 40h
[d] Conversions were determined by GC and based on the unreacted substrate.

Under the optimized conditions, the allylic alkylation of allylic carbonates (**3**-**6**) derived from the corresponding alcohols has been carried out (Table 2). The total conversion obtained for the carbonates (**3**, **4** and **6**) was slightly less than obtained with the carbonate **1**. However, carbonate **5** showed its limits since a maximum 20% conversion was obtained. The poor activity of carbonate **5** is probably due to the steric hindrance effect caused by the two cycles of pinene skeleton.
As shown in Table 2, it appeared that ester **8** obtained from optically active myrtenyl carbonate **4** has also an optical activity, in contrast the ester 7 derived from optically active cis-carvyl carbonate **3** was found optically inactive. Geranylcarbonate 6 was converted into alkylated product **10**, promoting a terminal compound.

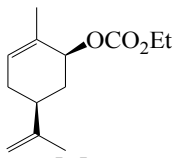
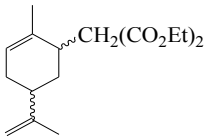
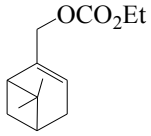
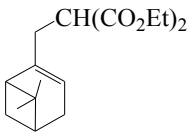
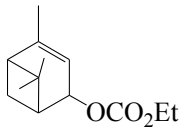
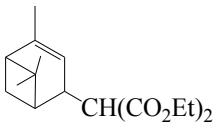
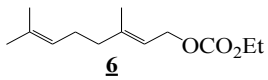
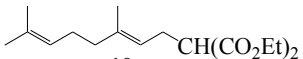
3.2. Alkylation of allyl terpenic acetates

These promising results prompted us to investigated the allylic substitution reaction using a much more demanding allyl acetate substrates. Monoterpenes derivatives (**11** – **14**) were chosen, and the results were collected in Table 3. The allyl acetates were less reactive than the allyl carbonates. The increase of the temperature to 55°C results in the decrease of the alkylated product's yield. In addition, cis-carvyl **13** lead mainly to the formation of the alkylated product **7** in the configuration cis.

3.3. Alkylation of allyl terpenic chlorides

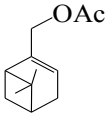
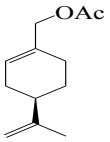
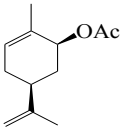
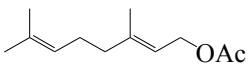
The scope and limitation of the catalytic system were examined by testing the allylic alkylation reaction of allyl chlorides with diethyl malonate. The results depicted in Table 4, demonstrate that allyl chlorides were found to be more reactive than allyl acetates. This can be explained by the fact, that chloride ions produced during the reaction course can stabilize the Pd(0) intermediate. It's noteworthy that the alkylation of trans-carvyl chloride **16** resulted in 74% conversion for which 62% yield of alkylated product **18** was obtained mainly in the trans configuration.

Table 2: Pd-catalyzed alkylation of terpenic allyl carbonates[a]

Allyl carbonate	Product	Yield[c] (%)	Conv[d] (%)
 **3** $[\alpha]_D^b$ = -16.7	 **7 (cis)** $[\alpha]_D^b$ = 0	72	86
 **4** $[\alpha]_D^b$ = -45.5	 **8** $[\alpha]_D^b$ = -4.8	60	70
 **5**	 **9**	8	20
 **6**	 **10**	62	74

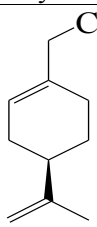
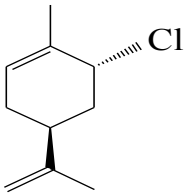
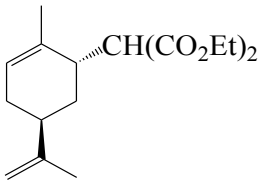
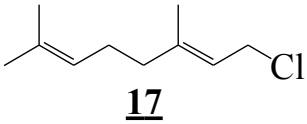
[a] Reaction Conditions : Allyl carbonate (4.4 mmol), $Pd(dba)_2$ (1 mol% , 0.044 mmol), PPh_3 (2 mol% , 0.088 mmol), diethyl-malonate (200 mol% , 8.4 mmol), NaH (116 mol% , 5.1 mmol), THF, under nitrogen atmosphere at r.t, 24 h.
[b] $[\alpha]_D$ determined at : c = 2, $CHCl_3$.
[c] Isolated yield.
[d] Conversions were determined by GC and based on the unreacted substrate.

Table 3: Pd-catalyzed alkylation of terpenic allyl acetates[a]

Allyl acetate	Product	Yield[c] (%)	Conv[d] (%)
 **11** $[\alpha]_D^b$ = -26.2	**8**	62	72
 **12** $[\alpha]_D^b$ = -85.3	**2**	45	54
 **13** $[\alpha]_D^b$ = -33.4	**7**	54	62
 **14**	**10**	64	74

[a] Reaction Conditions : Allyl acetate (4.4 mmol), $Pd(dba)_2$ (1 mol%, 0.044 mmol), PPh_3 (2 mol%, 0.088 mmol), diethyl-malonate (200 mol%, 8.4 mmol), NaH (116 mol%, 5.1 mmol), THF, under nitrogen atmosphere at r.t, 24 h.
[b] $[\alpha]_D$ determined at : c = 2, $CHCl_3$.
[c] Isolated yield.
[d] Conversions were determined by GC and based on the unreacted substrate.

Table 4: Pd-catalyzed alkylation of terpenic allyl chlorides[a]

Allyl chloride	Product	Yield[c] (%)	Conv[d] (%)
 **15** $[\alpha]_D^b = -56.5$	**2**	64	75
 **16** $[\alpha]_D^b = 0$	 **18** $[\alpha]_D^b = 0$	62	74
 **17**	**10**	54	70

[a] Reaction conditions : Allyl chloride (4.4 mmol), $Pd(dba)_2$ (1 mol% , 0.044 mmol), PPh_3 (2 mol%, 0.088 mmol), diethyl-malonate (200 mol%, 8.4 mmol), NaH (116 mol%, 5.1 mmol), THF, under nitrogen atmosphere at r.t, 24 h.
[b] $[\alpha]_D$ determined at : c = 2, $CHCl_3$.
[c] Isolated yield.
[d] Conversions were determined by GC and based on the unreacted substrate.

3.4. NMR analysis

The spectral data of all resulting products from the Pd-catalyzed alkylation are given in Table 5.

3.5. Mechanistic speculation

There are a number of the experimental investigations of the mechanism of the palladium-catalyzed allylic substitution [9, 27-28] and it was reported that generally the reaction proceed via a neutral or cationic π-allyl palladium complex. The first step in all of this reaction is oxidative addition of the allylic C-X system to palladium(0). This reaction results in an inversion of stereochemistry. Nucleophilic attack usually occurs from the face opposite to the metal and an overall retention of stereochemistry is achieved [4] more likely from a double inversion of configuration.
Recently, Tang et al. [29] have studied the mechanism of the enantioselective allylic alkylation catalyzed by chiral Pd-oxazolinylpyridine by means of the density functional theory (DFT). They have proved that the allylic alkylation was endothermic and goes mainly through association, oxidative addition, nucleophilic addition to the π-allyl cation complex, and dissociation of the Pd-oxazolinylpyridine-product complex to generate the product with regeneration of the catalyst. More recently, Xu et al. [30] have found that the Pd-catalyzed substitution of cyclic gem-difluorinated allylic carbonates proceeded via the symmetric Pd-π-allyl bonding.
From the mechanism point of view, we can predict that in our case, the intermediate of the Pd-catalyzed allylic substitution of terpenic olefins seemed to be a π-allyl palladium complex. By checking the optical rotation of products derivatives from carvyl skeletons, we can gain better insight into the reaction mechanism explaining that the reaction occurs via an symmetric π-allyl complex. Since the nucleophile attacks both allylic positions of (π-allyl)-palladium complex **19**, carvyl derivatives (cis or trans) would be obtained in racemic form (Figure 2) in good agreement with the results observed in our study.

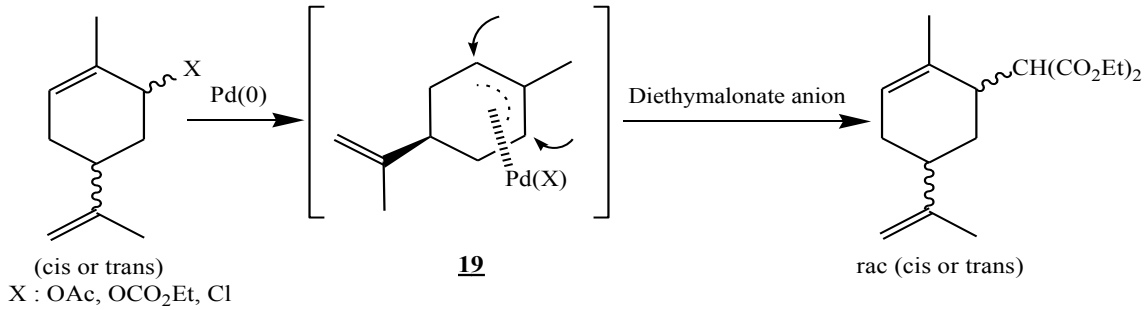


Figure 2: Proposed mechanism of Pd(0)-allylic substitution

Table 5: Spectral data of prepared compounds

Product	Spectral data
2	$[\alpha]_D^{20}$ = -17.6 (c = 2; $CHCl_3$). MS, m/z: 294 (M+), 251 (14.2), 220 (17.5), 203 (35.8), 159 (96.6), 134 (100), 119 (63.3), 91 (71.6), 79 (88.3), 67 (35.8), 55 (22.5). ^{13}C NMR: δ 169 (C=O); 149.9 (=C); 133 (=C); 123.3 (=CH); 108.7 (=CH_2); 61.4 (OCH_2CH_3); 50.7 (-CHCO); 40.9 (-CH); 36.5 (-CH_2); 30.7 (-CH_2); 28.5 (-CH_2); 27.4 (-CH_2); 20.8 (-OCH_2CH_3); 14.2 (-CH_3). ^{1}H NMR: δ 5.46 (1H, m); 4.68 (2H, m); 4.17 (2H, q, J= 7.13 Hz); 3.52 (1H, t, J= 7.9 Hz); 2.54 (2H, d, J= 7.9 Hz); 1.24 (3H, t, J= 7.13 Hz); 1.7 (3H, s).
7	$[\alpha]_D^{20}$ = 0. MS, m/z: 294 (M+), 279 (2), 251 (9), 159 (86), 134 (100), 105 (50), 119 (61.7), 93 (69). ^{13}C NMR: δ 168.19 (C=O); 168.5 (C=O); 149.59 (=C); 132.81 (=C); 125.29 (=CH); 108.89 (=CH_2); 61.41 (OCH_2CH_3); 61.03 (OCH_2CH_3); 53.4 (-CHCO); 41.6 (-CH); 40.7 (-CH); 30.9 (-CH_2); 30.8 (-CH_2); 21.25 (-CH_3); 20.6 (-CH_3); 14.15 (-CH_3); 14.1 (-CH_3). ^{1}H NMR: δ 5.5 (1H, m); 4.6 (2H, m); 4.25 (2H, q, J= 7.15 Hz); 4.2 (2H, q, J= 7.13 Hz); 3.7 (1H, d, J= 4.8 Hz); 2.9 (1H, m); 2.15 (1H, m); 1.7-2.05 (4H, m); 1.69 (3H, s); 1.64 (3H, s); 1.2 (3H, t, J= 7.13 Hz); 1.1 (3H, t, J= 7.15 Hz).
8	$[\alpha]_D^{20}$ = -4.8 (c = 2; $CHCl_3$). MS, m/z: 294 (M+), 251 (11.7), 233 (2.5), 176 (24.2), 159 (94.3), 134 (100), 105 (51.6), 91 (68.9). ^{13}C NMR: δ 168.33 (C=O)**;** 168.19 (C=O); 143.17 (=C); 117.78 (=CH); 60.51 (OCH_2CH_3); 60.29 (OCH_2CH_3); 49.33 (-CHCO); 44.63 (-CH); 39.64 (-CH); 36.97 (-C); 34.8 (-CH_2); 30.6 (-CH_2); 30.27 (-CH_2); 25.23 (-CH_3); 19.98 (-CH_3); 13.08 (-CH_3); 13.04 (-CH_3). ^{1}H NMR: δ 5.2 (1H, m); 4.1 (2H, q, J= 7.17 Hz); 4.05 (2H, q, J= 7.17 Hz); 3.38 (1H, t, J= 7.53 Hz); 2.5 (2H, dd, J= 7.53 Hz, J= 1.53 Hz); 2.25-2.35 (1H, m); 2.1-2.2 (2H, m); 1.8-2 (1H, m); 1.2 (3H, t, J= 7.17 Hz); 1.19 (3H, t, J= 7.17 Hz); 1.18 (3H, s); 1.05 (1H, d, J= 8.28 Hz); 0.72 (3H, s).
9	^{13}C NMR: δ 170.31 (C=O); 170.19 (C=O); 144.23 (=C); 113.02 (=CH); 61.67 (OCH_2CH_3); 61.03 (OCH_2CH_3); 53.88 (-CHCO); 49.42 (-CH); 46.36 (-CH); 43.39 (-CH); 40.65 (-C); 34.86 (-CH_2); 26.36 (-CH_3); 23.4 (-CH_3); 21.82 (-CH_3); 14.29 (-CH_3); 14.23 (-CH_3). ^{1}H NMR: δ 5.35 (1H, m); 3.5 (2H, q, J= 7.16 Hz); 3.45 (2H, q, J= 7.16); 3.15 (1H, d, J= 4.4 Hz); 2.68 (1H, m); 2.1-2.3 (2H, m); 1.9-2 (1H, m); 1.43 (1H, d, J= 6.7 Hz); 1.7 (3H, m); 1.33 (3H, s); 1.2 (3H, t, J= 7.16 Hz); 1.1 (3H, t, J= 7.16 Hz); 0.85 (3H, s).
10	MS, m/z: 296 (M+), 281 (2), 253 (6), 159 (76.5), 136 (100). ^{13}C NMR: δ 168.64 (C=O); 168.24 (C=O); 137.41 (=C); 130.46 (=C); 123.05 (=CH); 118.65 (=CH); 60.45 (OCH_2CH_3); 60.23 (OCH_2CH_3); 51.29 (-CHCO); 38.68 (-CH_2); 26.48 (-CH_2); 25.58 (-CH_2); 24.62 (-CH_3); 16.64 (-CH_3); 15.08 (-CH_3); 14.82 (-CH_3); 13.07 (-CH_3). ^{1}H NMR: δ 4.95-5.1 (2H, m); 4.1 (2H, q, J= 7.17 Hz); 3.25 (1H, t, J= 7.53 Hz); 2.55 (2H, t, J= 7.53 Hz); 1.9-2 (4H, m); 1.59 (3H, s); 1.55 (3H, s); 1.52 (3H, s); 1.19 (3H, t, J= 7.17 Hz).
18	$[\alpha]_D^{20}$ = 0. ^{13}C NMR: δ 169.79 (C=O); 168.34 (C=O); 149.04 (=C); 133.07 (=C); 125.09 (=CH); 109.04 (=CH_2); 61.45 (OCH_2CH_3); 61.36 (OCH_2CH_3); 55.3 (-CHCO); 38.77 (-CH); 36.77 (-CH); 31.2 (-CH_2); 30.65 (-CH_2); 22.74 (-CH_3); 20.81 (-CH_3); 14.12 (-CH_3); 14.1 (-CH_3). ^{1}H NMR: δ 5.35 (1H, m); 4.69 (2H, m); 4.19 (2H, q, J= 7.14 Hz); 4.18 (2H, q, J= 7.17 Hz); 3.56 (1H, d, J= 7.48 Hz); 2.9 (1H, m); 2.22 (1H, m); 1.9 (1H, m); 1.77 (1H, td, J= 2.96 Hz, J= 0.99 Hz); 2.13 (1H, m); 1.81 (1H, td, J_{eq-ax}= 2.93 Hz, J_{eq-eq}= 1.01 Hz); 1.7 (3H, s); 1.64 (3H, s); 1.2 (3H, t, J= 7.14 Hz); 1.1 (3H, t, J= 7.17 Hz).

Conclusion

An efficient methodology for the preparation of new monoterpenic compounds from Pd(0)-catalyzed allylic alkylation has been investigated. The reaction has been successfully carried out under mild conditions and led to the terpenic esters in good to excellent yields. The reaction shows a high degree of efficiency and selectivity. Starting from optically active monoterpenes, the reaction proceeded in a stereo- and regioselective manner to afford optically active allylic esters.

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