Tetrahedron 64 (2008) 5150–5155

Contents lists available at ScienceDirect

Tetrahedron

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

Bismuth triflate-catalyzed rearrangement of acetates of the Baylis–Hillman adducts into (*E*)-trisubstituted alkenes

Thierry Ollevier *, Topwe M. Mwene-Mbeja

Département de chimie, Université Laval, Québec (Québec), Canada G1K 7P4

ARTICLE INFO

Article history:
Received 12 December 2007
Received in revised form 8 March 2008
Accepted 14 March 2008
Available online 21 March 2008

Keywords:
Bismuth
Lewis acids
Rearrangement
Claisen
Morita–Baylis–Hillman
Green chemistry

ABSTRACT

In the presence of a catalytic amount of bismuth triflate, methyl 3-acetoxy-3-aryl-2-methylenepropanoates and 3-acetoxy-3-aryl-2-methylenepropanitriles were smoothly converted into methyl (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enoates and (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enenitriles, respectively. A remarkable reversal in stereochemical directions from ester to nitrile was observed. 3-Aryl-3-hydroxy-2-methylenepropanoates and 3-aryl-3-hydroxy-2-methylenepropanitriles could be easily obtained as Baylis–Hillman adducts from methyl acrylate and acrylonitrile, respectively. The overall process is an efficient isomerization of the Baylis–Hillman adducts to the corresponding cinnamyl derivatives. The isomerization reaction proceeded rapidly and afforded smoothly the cinnamyl acetates in moderate to very good yields using catalytic amounts of $Bi(OTf)_3 \cdot 4H_2O$ (10 mol %).

1. Introduction

Morita–Baylis–Hillman reaction is a well-known carbon–carbon bond forming reaction.[1] The resultant α-methylene-β-hydroxy adducts are key intermediates as they can be further derivatized. The Morita–Baylis–Hillman adducts can be rearranged into the primary allylic alcohols.[2] The latter in the cinnamyl series are important because they constitute an important class of synthons for the synthesis of many bioactive molecules.[3] Esters of the rearranged allylic alcohols have been obtained by various methods.[4] The development of new methods for the isomerization of the acetates of these α-methylene-β-hydroxy adducts is an important area of synthetic efforts as allylic acetates are extremely important as key synthetic intermediates. [5] Among the variety of mediators so far reported for the isomerization of acetate derivatives are montmorillonite K10 clay or $FeCl_3$ used in stoichiometric quantities.[5,6] Catalytic rearrangement of the acetates has been reported in a few cases, e.g., with DABCO, TMSOTf, or $Pd(OAc)_2/Ph_3P$ as an efficient method to prepare the corresponding isomeric allylic acetates.[7]

Recently, some precedents have been disclosed regarding $Yb(OTf)_3$ as a catalyst for the rearrangement.[6c] High catalytic activity, low toxicity, and moisture and air tolerance make lanthanide triflates valuable catalysts.[8] However, the high cost of these catalysts restricts their use. Bismuth compounds provide a good alternative as they have recently attracted attention due to their low toxicity, low cost, and good stability.[9] Bismuth salts have been reported as catalysts for the Sakurai reaction,[10] opening of epoxides,[11] Mukaiyama-aldol reaction,[12] Mannich-type reactions,[13] formation or deprotection of acetals,[14] Friedel–Crafts reactions,[15] and Fries rearrangements.[16] $Bi(OTf)_3$ is particularly attractive because it is commercially available or can be easily prepared from readily available compounds.[17]

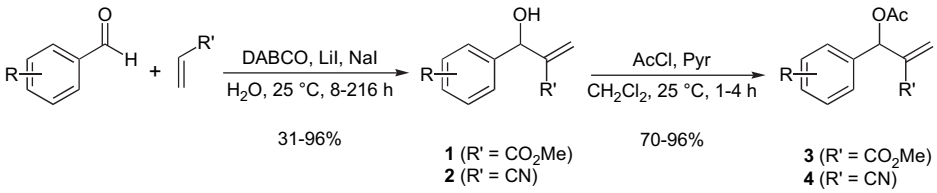
2. Results and discussion

As a part of our ongoing interest in bismuth(III)-catalyzed Claisen rearrangements,[18] we report herein our results in the bismuth(III)-catalyzed rearrangement of the acetates of 3-aryl-3-hydroxy-2-methylenepropanoates and 3-aryl-3-hydroxy-2-methylenepropanitriles easily obtained as the Baylis–Hillman adducts from methyl acrylate and acrylonitrile, respectively. The adducts **1** and **2** were prepared using various aromatic aldehydes, DABCO, and methyl acrylate or acrylonitrile,[19] and then converted to their corresponding acetates **3** and **4** (Scheme 1). Due to the importance of the cinnamyl series **5** and **6** (Tables 1 and 2) for the synthesis of many bioactive molecules,[3] only adducts **1** and **2** derived from aromatic aldehydes were prepared.

Initial investigations involved the Baylis–Hillman adducts derived from methyl acrylate (Scheme 2, Table 1). The benzaldehyde derived adduct **3a** was smoothly isomerized into methyl 2-(acetoxymethyl)-3-phenylprop-2-enoate **5a** with a good yield

* Corresponding author. Tel.: +1 418 656 5034; fax: +1 418 656 7916.
E-mail address: thierry.ollevier@chm.ulaval.ca (T. Ollevier).

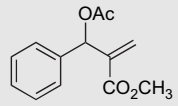
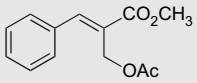
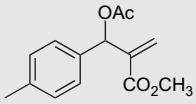
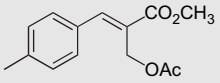
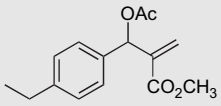
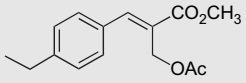
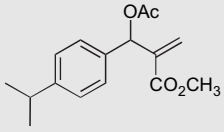
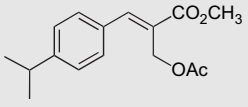
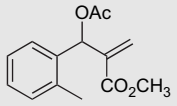
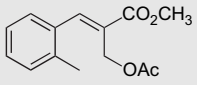
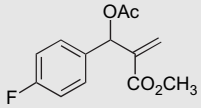
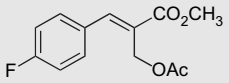
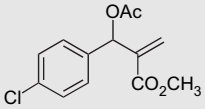
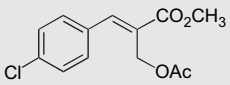
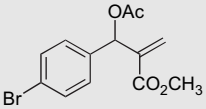
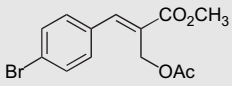
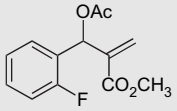
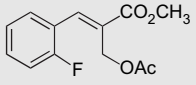
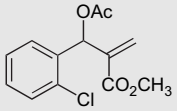
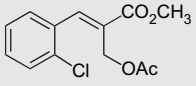
0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.03.053



Scheme 1.

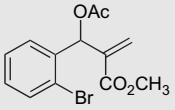
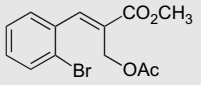
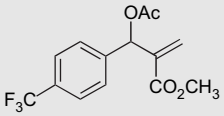
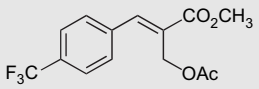
using 10 mol % of $Bi(OTf)_3 \cdot 4H_2O$ as the catalyst (Table 1, entry 1). The isomerized product was obtained as the major *E* isomer, (2*E*)-2-(acetoxymethyl)-3-phenylprop-2-enoate **5a** (*E*/*Z*=83:17). The stereochemistry of **5a** was unambiguously confirmed from the ^1H and ^{13}C NMR data.[7d] No rearrangement occurred when the reactant was submitted to the thermal conditions without catalyst (**3a**, MeCN, 82 °C, 28 h). Several examples of $Bi(OTf)_3 \cdot 4H_2O$-catalyzed isomerization of Baylis–Hillman adducts' acetates are summarized

Table 1
$Bi(OTf)_3$-catalyzed rearrangement of 3-acetoxy-3-aryl-2-methylenepropanoates **3**

Entry	Reactant **3**	Product (***E***)-**5**[a]	Time (h)	*E*/*Z* ratio[b]	Yield **5**[c] (%)
1			28	83:17 (**5a**)	77
2			17	82:18 (**5b**)	67
3			23	88:12 (**5c**)	73
4			25	88:12 (**5d**)	74
5			36	86:14 (**5e**)	62
6			26	75:25 (**5f**)	80
7			36	75:25 (**5g**)	80
8			36	81:19 (**5h**)	70
9			34	80:20 (**5i**)	60
10			28	92:8 (**5j**)	65

(*continued on next page*)

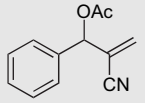
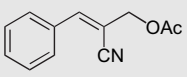
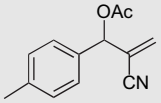
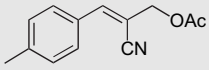
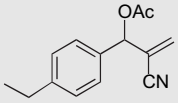
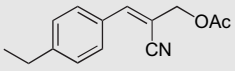
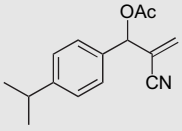
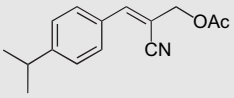
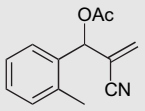
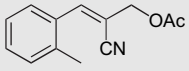
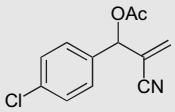
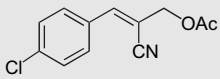
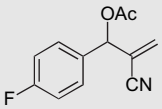
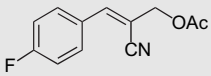
Table 1 (*continued*)

Entry	Reactant **3**	Product (***E***)-**5**[a]	Time (h)	*E*/*Z* ratio[b]	Yield **5**[c] (%)
11			35	98:2 (**5k**)	82
12			38	75:25 (**5l**)	83

[a] All compounds were characterized by ^{1}H NMR and ^{13}C NMR.
[b] Ratio determined by ^{1}H NMR. *E* and *Z* isomers could not be purified by silica gel chromatography.
[c] Isolated yield.

in Table 1. A variety of differently substituted aryl derivatives were reacted in acetonitrile in our optimized conditions. With both electron-poor, electron-rich and *o*-substituted benzaldehyde adducts **3**, the corresponding cinnamyl acetates **5** were obtained in moderate to good yields (Table 1, entries 1–12). *E*/*Z* ratios in all cases were greater than 75:25 (Table 1). *E* and *Z* isomers of **5** could never be separated by column chromatography. Chemical yields of the process are moderate to good (62–83% range, Table 1) due to incomplete conversion. No by-products were isolated and unreacted starting material could be observed. The stereochemistry of the products was assigned on the basis of the ^{1}H NMR chemical shifts values of the olefinic protons by comparison with the values reported in the literature.[7d,e] The yields and stereoselectivity of the $Bi(OTf)_3$-catalyzed process compares well with the ones obtained with montmorillonite K10 used as catalyst.[5,6b] However, our conditions are less efficient than the ones involving $Yb(OTf)_3$, TMSOTf or $Pd(OAc)_2/Ph_3P$ as a catalyst. When $Yb(OTf)_3$ was used as a catalyst, slight better chemical yields and *E*/*Z* ratios could be obtained.[6c] The two latest methods involving TMSOTf and $Pd(OAc)_2/Ph_3P$ appeared to be superior since they give the rearranged product in similar yields as in our conditions but affording the *E* isomer only, albeit longer reaction times were required with $Bi(OTf)_3$.[7c,e] Overall, no significant improvement could be obtained using $Bi(OTf)_3$ with the acetates of 3-aryl-3-hydroxy-2-methylenepropanoates as substrates.

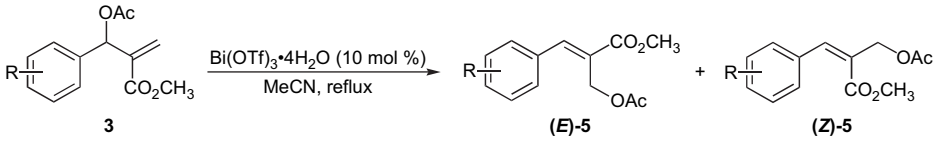
Table 2
$Bi(OTf)_3$-catalyzed rearrangement of 3-acetoxy-3-aryl-2-methylenepropanitriles **4**

Entry	Reactant **4**	Product (***E***)-**6**[a]	Time (h)	**6**	Yield **6**[b] (%)
1			24	**6a**	64
2			6	**6b**	63
3			36	**6c**	77
4			28	**6d**	81
5			45	**6e**	60
6			70	**6f**	59
7			19	**6g**	87

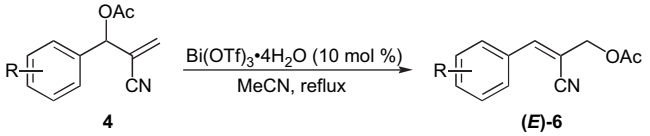
[a] All compounds were characterized by ^{1}H NMR and ^{13}C NMR.
[b] Isolated yield.

We then synthesized various (2*E*)-2-(acetoxymethyl)-3-arylprop-2-enenitriles **6** via the $Bi(OTf)_3 \cdot 4H_2O$-catalyzed isomerization of 3-acetoxy-3-aryl-2-methylenepropanitriles **4** (Scheme 3). Using our standard conditions, (2*E*)-2-(acetoxymethyl)-3-phenylprop-2-enenitrile **6a** could be obtained in moderate yield (Table 2, entry 1). Our results in the nitrile series are summarized in Table 2. With both electron-rich (Table 2, entries 2–5), electron-poor (Table 2, entries 6 and 7) and *o*-substituted benzaldehyde adducts **4** (Table 2, entry 5), the corresponding cinnamyl acetates **6** were obtained in moderate to very good yields (Table 2, entries 2–7). Exclusive formation of the (*E*)-isomer was observed in all cases (Table 2, entries 1–7). In this series, the cyano group was *cis* to the aryl group giving rise again to (*E*)-form due to inversion of priority of the substituents. The assignment of the (*E*)-stereochemistry of compounds **6** was based on the ^{1}H and ^{13}C NMR chemical shift values of the allylic methylene group in comparison with the published ones.[5,7d,e] We could not isolate the (*Z*)-isomer, which might be present in trace amounts in the reaction mixtures. Chemical yields were usually moderate, mostly due to incomplete conversion. The stereoselectivity of the present method appears to be as good as the one obtained using TMSOTf, except for the reaction time required, since 2 h is sufficient for the TMSOTf-catalyzed reaction to proceed.[7c] However, our method appears to be superior compared to other methods (e.g., montmorillonite K10 clay or $Pd(OAc)_2/Ph_3P$) leading to the formation of the product with *E*/*Z* ratio of 80:20–95:5 and 81:19–86:14, respectively.[5,6b,7e] *Z* isomer has never been detected using our method.

The remarkable reversal in stereochemical directions from ester to nitrile in these reactions is consistent with earlier work.[7d] This can possibly be explained through a Claisen-type rearrangement (Scheme 4).[7c] In the case of compounds **3**, there is a quasi-eclipsed 1,2-interaction between the Ar group and the pseudo-equatorial CO_2CH_3 group (transition state **TS I**). This interaction is likely to be stronger than the ones present in transition state **TS II**, where the ester group occupies a pseudo-axial position, leading to **(*E*)-5** as the major product. However, in the nitrile series, the corresponding



Scheme 2.



Scheme 3.

1,2-interaction (transition state **TS III**) may not result in such a strong steric bias. Product **(*E*)-6** is then produced exclusively.

3. Conclusions

As an improvement over other catalytic systems, $Bi(OTf)_3 \cdot 4H_2O$ is a versatile catalyst for the rearrangement of acetates of Morita–Baylis–Hillman adducts. The reaction affords moderate to good yields in isomeric acetates using 10 mol % of catalyst. This method offers several advantages including mild reaction conditions, catalytic process, and no formation of by-products. The conditions are suitable for a variety of aromatic aldehydes. Also, the practical use of $Bi(OTf)_3 \cdot 4H_2O$ is highly valuable as an environmentally benign Lewis acid. Because of its numerous benefits, this method for the synthesis of (*E*)-trisubstituted alkenes using $Bi(OTf)_3 \cdot 4H_2O$ catalysis should find utility in the synthesis of biologically active compounds. Whereas a good (*E*)-selectivity was obtained with the methyl acrylate derived series, the isomerization in the nitrile series occurred in complete (*E*)-stereoselectivity. Research is on its way to demonstrate other significant applications of this $Bi(OTf)_3 \cdot 4H_2O$-catalyzed rearrangement.

4. Experimental

4.1. General

^1H, ^{13}C, and ^{19}F spectra were recorded on a 400 MHz magnetic resonance spectrometer in $CDCl_3$. For ^1H NMR, tetramethylsilane (TMS) served as internal standard (δ=0) and data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, dd=doublet of doublet, dt=doublet of triplet, t=triplet, m=multiplet, and br=broad), coupling constant in hertz, integration, and assignment. For ^{13}C NMR, $CDCl_3$ was used as internal standard (δ=77.0) and spectra were obtained with complete proton decoupling. For ^{19}F NMR, $CFCl_3$ was used as internal standard (δ=0). Infrared spectra were recorded on a FT infrared spectrometer and are reported in reciprocal centimeters (cm^{-1}). Column chromatography was performed on silica gel (230–400 mesh) and analytical thin layer chromatography was carried out using 250 μm commercial silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance or aqueous potassium permanganate. Acetonitrile was distilled from calcium hydride. 3-Acetoxy-3-aryl-2-methyleneopropanoates **3** and 3-acetoxy-3-aryl-2-methylenepropanitriles **4** were synthesized according to known literature.[19]

4.2. Representative procedure for the bismuth triflate-catalyzed rearrangement of the acetates of Morita–Baylis–Hillman adducts

The benzylic acetate **3** or **4** (2.0 mmol) and $Bi(OTf)_3 \cdot 4H_2O$ (0.20 mmol) were mixed together in dry MeCN (4 mL) under argon atmosphere. The solution was then brought up to 82 °C (temperature of oil bath) for 6–70 h. The solvent was evaporated and the residue was quenched with water, extracted with ether (three times), dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude product. The crude was then purified by column chromatography (eluent: hexane/EtOAc 80:20). Spectral data accord exactly with those previously reported in the literature.[5,7c–e]

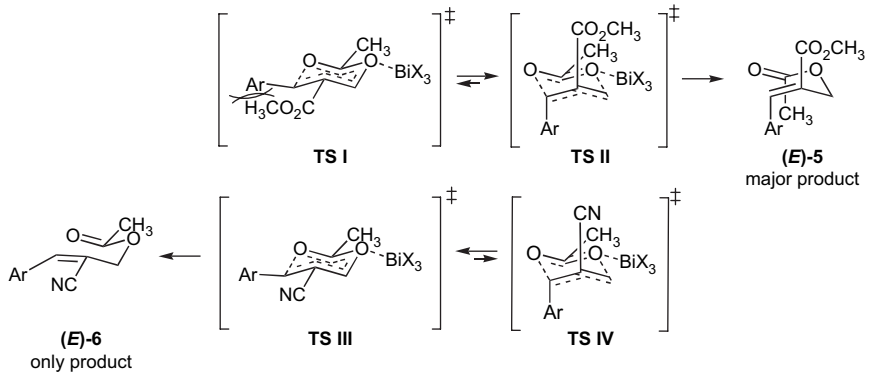
4.3. Spectroscopic data for cinnamyl acetates

*4.3.1. Methyl 2-(acetoxymethyl)-3-phenylacrylate (**5a**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.2. Methyl 2-(acetoxymethyl)-3-p-tolylacrylate (**5b**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.3. Methyl 2-(acetoxymethyl)-3-(4-ethylphenyl)acrylate (**5c**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.4. Methyl 2-(acetoxymethyl)-3-(4-isopropylphenyl)acrylate (**5d**)*
Spectral data were consistent with those previously reported.[7c]



Scheme 4.

*4.3.5. Methyl 2-(acetoxymethyl)-3-o-tolylacrylate (**5e**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.6. Methyl 2-(acetoxymethyl)-3-(4-fluorophenyl)acrylate (**5f**)*
^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39 (dd, J=8.8, 8.8 Hz, 2H), 7.11 (t, J=8.6 Hz, 2H), 4.94 (s, 2H, *E*), 4.89 (s, 2H, *Z*), 3.85 (s, 3H, *E*), 3.71 (s, 3H, *Z*), 2.11 (s, 3H, *E*), 2.10 (s, 3H, *Z*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=170.9, 170.7, 167.4, 163.6 (d, J_{C-F}=251.6 Hz), 144.5, 138.6, 131.7 (d, J_{C-F}=8.4 Hz), 130.7 (d, J_{C-F}=41.4 Hz), 130.5, 126.7, 116.1 (d, J_{C-F}=21.5 Hz), 115.4, 66.1, 59.4, 52.6, 52.1, 21.2; IR (film): 3074, 3000, 2954, 2907, 2848, 1747, 1718, 1637, 1601, 1509, 1437, 1236, 1118, 1026, 845 cm^{-1}; HRMS: calcd for $C_{13}H_{13}FO_4$ ($[M+NH_4]^+$): 270.1136, found: 270.1140.

*4.3.7. Methyl 2-(acetoxymethyl)-3-(4-chlorophenyl)acrylate (**5g**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.8. Methyl 2-(acetoxymethyl)-3-(4-bromophenyl)acrylate (**5h**)*
^{1}H NMR (400 MHz, $CDCl_3$): δ=7.86 (s, 1H, *E*), 7.52 (d, J=8.6 Hz, 2H, *E*), 7.42 (d, J=8.6 Hz, 2H, *Z*), 7.21 (d, J=8.2 Hz, 2H, *E*), 7.15 (d, J=8.2 Hz, 2H, *Z*), 4.87 (s, 2H, *E*), 4.85 (s, 2H, *Z*), 3.82 (s, 3H, *E*), 3.76 (3H, *Z*), 2.07 (s, 3H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=171.4, 170.9, 167.3, 144.4, 138.4, 138.3, 133.9, 133.2, 132.2, 131.6, 131.2, 130.5, 128.9, 127.5, 124.3, 123.2, 65.9, 65.8, 64.2, 59.4, 59.2, 52.7, 52.6, 52.2, 25.5, 21.2; IR (film): 3025, 2999, 2952, 2905, 2846, 1740, 1720, 1637, 1587, 1488, 1436, 1230 cm^{-1}; HRMS: calcd for $C_{13}H_{13}BrO_4$ ($[M+NH_4]^+$): 330.0336, found: 330.0334.

*4.3.9. Methyl 2-(acetoxymethyl)-3-(2-fluorophenyl)acrylate (**5i**)*
^{1}H NMR (400 MHz, $CDCl_3$): δ=8.0 (s, 1H), 7.29–7.41 (m, 3H), 7.09–7.20 (m, 3H), 4.92 (s, 2H, *Z*), 4.91 (s, 2H, *E*), 3.86 (s, 3H, *E*), 3.69 (s, 3H, *Z*), 2.12 (s, 3H, *Z*), 2.08 (s, 3H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=170.9, 170.7, 169.5, 166.9, 165.4, 160.7 (d, J_{C-F}=250.8 Hz), 160.2 (d, J_{C-F}=249.3 Hz), 138.3 (d, J_{C-F}=41.0 Hz), 132.6, 131.7, 131.6, 130.7, 130.6, 130.4, 129.1, 129.0, 127.1, 124.3, 123.9, 123.2, 122.4, 116.3, 116.1, 115.9, 115.7, 115.5, 65.6, 59.7, 52.6, 52.1, 21.1; IR (film): 3069, 3002, 2955, 2848, 1748, 1728, 1636, 1617, 1590, 1493, 1458, 1439, 1222, 761 cm^{-1}; HRMS: calcd for $C_{13}H_{13}FO_4$ ($[M+NH_4]^+$): 270.1136, found: 270.1140.

*4.3.10. Methyl 2-(acetoxymethyl)-3-(2-chlorophenyl)acrylate (**5j**)*
Spectral data were consistent with those previously reported.[7e]

*4.3.11. Methyl 2-(acetoxymethyl)-3-(2-bromophenyl)acrylate (**5k**)*
Spectral data were consistent with those previously reported.[7e]

*4.3.12. Methyl 2-(acetoxymethyl)-3-(4-(trifluoromethyl)phenyl)-acrylate (**5l**)*
^{1}H NMR (400 MHz, $CDCl_3$): δ=7.97 (s, 1H), 7.68 (d, J=8.2 Hz, 2H, *E*), 7.60 (d, J=8.2 Hz, 2H, *Z*), 7.50 (d, J=8.6 Hz, 2H, *E*), 7.41 (d, J=8.6 Hz, 2H, *Z*), 7.05 (s, 1H), 4.91 (s, 2H, *E*), 3.87 (s, 3H, *E*), 3.70 (s, 3H, *Z*), 2.12 (s, 3H, *Z*), 2.10 (s, 3H, *E*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=170.7, 167.0, 143.7, 137.9, 137.7, 131.4 (q, J_{C-F}=32.2 Hz), 130.4, 129.7, 129.1, 129.0, 125.9 (q, J_{C-F}=3.8 Hz), 125.3, 124.0 (q, J_{C-F}=271.5 Hz), 65.5, 59.1, 52.7, 52.2, 21.1; IR (film): 3002, 2954, 2915, 2852, 1723, 1630, 1572, 1435, 1246, 735 cm^{-1}; HRMS: calcd for $C_{14}H_{13}F_3O_4$ ($[M+NH_4]^+$): 320.1104, found: 320.1108.

*4.3.13. (E)-2-Cyano-3-phenylallyl acetate (**6a**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.14. (E)-2-Cyano-3-p-tolylallyl acetate (**6b**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.15. (E)-2-Cyano-3-(4-ethylphenyl)allyl acetate (**6c**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.16. (E)-2-Cyano-3-(4-isopropylphenyl)allyl acetate (**6d**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.17. (E)-2-Cyano-3-(o-tolyl)allyl acetate (**6e**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.18. (E)-2-Cyano-3-(4-chlorophenyl)allyl acetate (**6f**)*
Spectral data were consistent with those previously reported.[7c]

*4.3.19. Methyl 2-(acetoxymethyl)-3-(4-fluorophenyl)acrylate (**6g**)*
^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (dd, J=7.1, 7.1 Hz, 2H), 7.19 (s, 1H), 7.14 (t, J=8.7 Hz, 2H), 4.81 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=170.5, 164.3 (d, J_{C-F}=253.9 Hz), 146.3, 131.6 (d, J_{C-F}=9.2 Hz), 129.0, 117.4, 116.4 (d, J_{C-F}=21.5 Hz), 105.7, 65.4, 21.0; IR (film): 3109, 3076, 3045, 2958, 2892, 2217, 1743, 1600, 1509, 1444, 1419, 1224, 732 cm^{-1}; HRMS: calcd for $C_{12}H_{10}FNO_2$ ($[M+NH_4]^+$): 237.1034, found: 237.1035.

Acknowledgements

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds Québécois de la Recherche sur la Nature et les Technologies (FQRNT, Québec, Canada), the Canada Foundation for Innovation (CFI), and Université Laval. We thank Rhodia (Lyon, France) and Sidech s.a. (Tilly, Belgium) for generous gift of chemicals.

References and notes

1. Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811–891.
2. Kim, H. S.; Kim, T. Y.; Lee, K. Y.; Chung, Y. M.; Lee, H. J.; Kim, J. N. *Tetrahedron Lett.* **2000**, *41*, 2613–2616.
3. Mohapatra, D. K.; Datta, A. *J. Org. Chem.* **1998**, *63*, 642–646.
4. Charette, A. B.; Côté, B.; Monroc, S.; Prescott, S. *J. Org. Chem.* **1995**, *60*, 6888–6894.
5. Shanmugam, P.; Rajasingh, P. *Tetrahedron* **2004**, *60*, 9283–9295.
6. (a) Kabalka, G. W.; Venkataiah, B.; Dong, G. *Tetrahedron Lett.* **2003**, *44*, 4673–4675; (b) Shanmugam, P.; Singh, P. R. *Synlett* **2001**, 1314–1316; (c) Krishna, P. R.; Kannan, V.; Sharma, G. V. M. *Synth. Commun.* **2004**, *34*, 55–64.
7. (a) Mason, P. H.; Emslie, N. D. *Tetrahedron* **1994**, *50*, 12001–12008; (b) Foucaud, A.; El Guemmout, F. *Bull. Soc. Chim. Fr.* **1989**, 403–408; (c) Basavaiah, D.; Muthukumaran, K.; Sreenivasulu, B. *Synthesis* **2000**, 545–548; (d) Basavaiah, D.; Padmaja, K.; Satyanarayana, T. *Synthesis* **2000**, 1662–1664; (e) Park, J. B.; Ko, S. H.; Kim, B. G.; Hong, W. P.; Lee, K.-J. *Bull. Korean Chem. Soc.* **2004**, *25*, 27–28.
8. Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227–2302.
9. (a) Suzuki, H.; Matano, Y. *Organobismuth Chemistry*; Elsevier: Amsterdam, 2001; (b) Gaspard-lloughmane, H.; Le Roux, C. *Eur. J. Org. Chem.* **2004**, 2517–2532; (c) Leonard, N. M.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58*, 8373–8397.
10. (a) Anzalone, P. W.; Baru, A. R.; Danielson, E. M.; Hayes, P. D.; Nguyen, M. P.; Panico, A. F.; Smith, R. C.; Mohan, R. S. *J. Org. Chem.* **2005**, *70*, 2091–2096; (b) Choudary, B. M.; Chidara, S.; Raja Sekhar, C. V. *Synlett* **2002**, 1694–1696; (c) Ollevier, T.; Li, Z. *Org. Biomol. Chem.* **2006**, *4*, 4440–4443; (d) Ollevier, T.; Ba, T. *Tetrahedron Lett.* **2003**, *44*, 9003–9005; (e) Ollevier, T.; Li, Z. *Eur. J. Org. Chem.* **2007**, 5665–5668.
11. (a) Ogawa, C.; Azoulay, S.; Kobayashi, S. *Heterocycles* **2005**, *66*, 201–206; (b) Ollevier, T.; Lavie-Compin, G. *Tetrahedron Lett.* **2004**, *45*, 49–52; (c) Ollevier, T.; Lavie-Compin, G. *Tetrahedron Lett.* **2002**, *43*, 7891–7893; (d) Ollevier, T.; Nadeau, E. *Tetrahedron Lett.* **2008**, *49*, 1546–1550.
12. (a) Le Roux, C.; Ciliberti, L.; Laurent-Robert, H.; Laporterie, A.; Dubac, J. *Synlett* **1998**, 1249–1251; (b) Kobayashi, S.; Ogino, T.; Shimizu, H.; Ishikawa, S.; Hamada, T.; Manabe, K. *Org. Lett.* **2005**, *7*, 4729–4731; (c) Ollevier, T.; Desyroy, V.; Debailleul, B.; Vaur, S. *Eur. J. Org. Chem.* **2005**, 4971–4973; (d) Ollevier, T.; Desyroy, V.; Catrinescu, C.; Wischert, R. *Tetrahedron Lett.* **2006**, *47*, 9089–9092; (e) Ollevier, T.; Desyroy, V.; Nadeau, E. *ARKIVOC (Gainesville, FL, U.S.)* **2007**, *x*, 10–20; (f) Ollevier, T.; Bouchard, J.-E.; Desyroy, V. *J. Org. Chem.* **2008**, *73*, 331–334.
13. (a) Ollevier, T.; Nadeau, E. *J. Org. Chem.* **2004**, *69*, 9292–9295; (b) Ollevier, T.; Nadeau, E.; Eguillon, J.-C. *Adv. Synth. Catal.* **2006**, *348*, 2080–2084; (c) Ollevier, T.; Nadeau, E. *Synlett* **2006**, 219–222; (d) Ollevier, T.; Nadeau, E.; Guay-Bégin, A.-A. *Tetrahedron Lett.* **2006**, *47*, 8351–8354; (e) Ollevier, T.; Nadeau, E. *Org. Biomol. Chem.* **2007**, *5*, 3126–3134.
14. (a) Leonard, N. M.; Oswald, M. C.; Freiberg, D. A.; Nattier, B. A.; Smith, R. C.; Mohan, R. S. *J. Org. Chem.* **2002**, *67*, 5202–5207; (b) Carrigan, M. D.; Sarapa, D.; Smith, R. C.; Wieland, L. C.; Mohan, R. S. *J. Org. Chem.* **2002**, *67*, 1027–1030.

15. (a) Le Roux, C.; Dubac, J. *Synlett* **2002**, 181–200; (b) Desmurs, J. R.; Labrouillère, M.; Le Roux, C.; Gaspard, H.; Laporterie, A.; Dubac, J. *Tetrahedron Lett.* **1997**, *38*, 8871–8874; (c) Répichet, S.; Le Roux, C.; Dubac, J.; Desmurs, J. R. *Eur. J. Org. Chem.* **1998**, 2743–2746.
16. Ollevier, T.; Desyroy, V.; Asim, M.; Brochu, M.-C. *Synlett* **2004**, 2794–2796.
17. (a) Répichet, S.; Zwick, A.; Vendier, L.; Le Roux, C.; Dubac, J. *Tetrahedron Lett.* **2002**, *43*, 993–995; (b) Labrouillère, M.; Le Roux, C.; Gaspard, H.; Laporterie, A.; Dubac, J.; Desmurs, J. R. *Tetrahedron Lett.* **1999**, *40*, 285–286; (c) Peyronneau, M.; Arrondo, C.; Vendier, L.; Roques, N.; Le Roux, C. *J. Mol. Catal. A: Chem.* **2004**, *211*, 89–91. $Bi(OTf)_3 \cdot 4H_2O$ has been prepared from Bi_2O_3 according to Ref. 17a.
18. (a) Ollevier, T.; Mwene-Mbeja, T. M. *Synthesis* **2006**, 3963–3966; (b) Ollevier, T.; Mwene-Mbeja, T. M. *Tetrahedron Lett.* **2006**, *47*, 4051–4055; (c) Ollevier, T.; Mwene-Mbeja, T. M. *Can. J. Chem.* **2008**, *86*, 209–212.
19. (a) Rafel, S.; Leahy, J. W. *J. Org. Chem.* **1997**, *62*, 1521–1522; (b) Augé, J.; Lubin, N.; Lubineau, A. *Tetrahedron Lett.* **1994**, *35*, 7947–7948.