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Gold *versus* silver-catalyzed amination of allylic alcohols

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Dedicated to Professor Maria Teresa Chicote on occasion of his 60th birthday

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ABSTRACT

Direct substitution of the hydroxy group in allylic alcohols by different nitrogenated nucleophiles is performed using low loadings of cationic gold(I) or silver salts as catalysts. Sulfonamides, carbamates and aromatic amines can be used as nucleophiles. Comparative studies between the best catalysts, cationic (triphenylphosphite)gold(I) complex and silver triflate, demonstrate that the former catalyst shows, in general, better performance than silver, working at lower loadings, in shorter reaction times and at lower temperatures. Representative allylic alcohols are used giving good γ-regioselectivity, specially in the case of penta-1,4-dien-3-ol and (*E*)-1-phenylbut-2-en-1-ol affording the corresponding allylic sulfonamides with total regio and stereoselectivity by a hydroamination mechanism. In the case of crotyl alcohol and (*E*)-4-phenylbut-3-en-2-ol mainly and exclusively α-substituted sulfonamides were obtained, respectively, by a cationic mechanism.

1. Introduction

Direct nucleophilic substitutions using allylic alcohols as electrophilic substrates and nitrogenated compounds as nucleophiles constitute a straightforward access to allylic amines. This strategy is a green atom economy process, which use ready available starting materials and generates water as by-product [1]. In order to activate the hydroxy function as leaving group Brønsted acids such as sulfonic acids [2] and Lewis acids such as iodine [3], transition metal complexes or salts from Pd(0) [4], Pt(II) [5], Mo(VI) [6], Bi(III) [7], Au(III) [8], and Au(I) [8,9] have been used as catalysts. Inter and intramolecular gold-catalyzed reactions have been performed with *p*-toluenesulfonamide and different anilines as nucleophiles [8] as well as with 1-methylimidazolidin-2-one and related nucleophiles [9]. However, the nucleophilic substitution of allylic alcohols with nitrogenated nucleophiles using silver salts as catalysts has not been described. We recently reported that cationic (triphenylphosphite) gold(I) complexes [10] and silver triflate [11] are good catalysts for the challenging intermolecular hydroamination of alkenes and dienes. In this paper we describe comparative studies about the intermolecular amination of allylic alcohols with different nitrogenated compounds using gold and silver catalysts.

2. Results and discussion

The reaction between (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) with *p*-toluenesulfonamide (**2a**) as a model reaction was studied using different cationic gold(I) complexes and silver salts at room temperature during 1 h (Table 1). The first experiment was carried out with 0.5 mol% of (Ph_3P) AuCl/AgOTf as catalyst in dioxane giving the expected product **3aa** in 75% yield (Table 1, entry 1). The same experiment described by Liu et al. [8a] in THF afforded product **3aa** in 76% yield but after 12 h and with 5 mol% catalyst loading. Using dioxane as solvent the complex $[(PhO)_3P]$ AuCl/AgOTf (0.5 mol%) gave higher 93% yield than the former one (Table 1, compare entry 1 and 2). Again, triphenyl phosphite formed a more cationic gold(I) complex than triphenylphosphine [10]. When AgOTf was used as catalyst even with 2 mol% loading only 45% crude yield was obtained (Table 1, entry 3). Both reactions were performed with $[(PhO)_3P]$ AuCl/$AgSbF_6$ and $AgSbF_6$, respectively, instead of AgOTf giving better yield only in the last case (Table 1, entries 4 and 5). Comparison studies with other solvents such as acetonitrile or nitromethane using either $[(PhO)_3P]$ AuCl/AgOTf or AgOTf, lower yields were obtained with the cationic gold complex. However, in the case of employing AgOTf in acetonitrile a better 78% yield than in dioxane was obtained (Table 1, entries 6–9). In general, cationic gold complexes and specially the triphenylphosphite derivative showed better catalytic performance than silver salts, which needed higher loading under the same reaction conditions.

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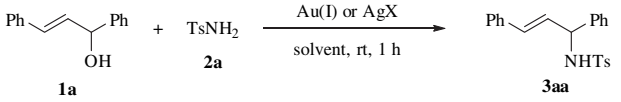
Table 1
Amination of 1,3-diphenylprop-2-en-1-ol (**1a**) with *p*-toluenesulfonamide catalyzed by Au(I) or AgX.[a]



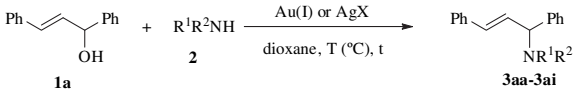
Entry	Cat (Mol %)	Solvent	Yield (%)[b]
1	$(Ph_3P)AuCl/AgOTf$ (0.5)	dioxane	75
2	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	dioxane	93
3	AgOTf (2)	dioxane	45
4	$[(PhO)_3P]AuCl/AgSbF_6$ (0.5)	dioxane	77
5	$AgSbF_6$ (2)	dioxane	63
6	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	CH_3CN	65
7	AgOTf (2)	CH_3CN	78
8	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	CH_3NO_2	74
9	AgOTf (2)	CH_3NO_2	70

[a] Reaction conditions: allyl alcohol **1a** (1 mmol), $TsNH_2$ **2a** (1.5 mmol), cat. (see column) and solvent (2 mL), 25 °C, 1 h.
[b] Isolated yield of the crude product (calculated from ^{1}H-NMR).

Next, different type of nucleophiles were essayed using 1,3-diphenylprop-2-en-1-ol (**1a**) as allylic substrate and either $[(PhO)_3P]$ AuCl/AgOTf or AgOTf as catalysts (Table 2). The reactions were performed with 2 eq. of sulfonamides, benzyl carbamate and anilines in dioxane, catalyst loading and reaction conditions being optimized for each nucleophile. Electron-rich sulfonamides **2a**–**2c** reacted at rt in the presence of either the gold (0.5 mol%) or the silver (2 mol%) catalyst (Table 2, entries 1–6). However *p*-nitrobenzenesulfonamide (**2d**) afforded **3ad** in very good yields using 2 mol% of catalyst loading during 1 d at 50 °C (Table 2, entries 7 and 8). Methanesulfonamide (**2e**) needed also the reaction to be heated at 50 °C and to increase the cationic gold complex to 2 mol% to provide **3ae** in good yields (Table 2, entries 9 and 10). In the case of benzyl carbamate (**2f**) the amination was carried out at 25 °C using 2 mol% of both catalysts affording product **3af** in 93% and 40% yield (Table 2, entries 11 and 12, respectively). Electron-poor anilines are appropriate reagents for this nucleophilic substitution, thus *p*-chloroaniline (**2g**) reacted at 50 °C to afford product **3ag** in good yields using 2 mol% of both catalysts (Table 2, entries 13 and 14). In the case of *p*-nitroaniline (**2h**) the substitution with gold as catalyst was performed at rt and with only 0.5 mol% loading (Table 2, entry 15). However, AgOTf needed 2 mol% loading and 50 °C to reach the same yield than the gold complex (Table 2, entry 16). In the case of the electron-rich *p*-toluidine (**2i**) high catalyst loadings, 2 and 5 mol % for gold and silver, respectively, 1 d reaction time and heating at 50 °C were necessary to afford moderate 45 and 44% yields (Table 2, entries 17 and 18).

Different representative allylic alcohols **1b-1f** were submitted to direct amination with *p*-toluenesulfonamide (**2a**) in dioxane and in the presence of either $[(PhO)_3P]AuCl/AgOTf$ or AgOTf as catalysts (Table 3). Aliphatic alcohols such as (*E*)-but-2-en-1-ol (**1b**) and penta-1,4-dien-3-ol (**1c**) needed higher temperatures and catalysts loading than (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**). Crotyl alcohol (**1b**) afforded a 1:2 mixture of the γ and α-substituted allylic sulfonamides **3ba** and **3'ba** in 50% overall yield using 1 mol% of the gold complex and 5 mol% of AgOTf under rather high temperature 85 and 110 °C, respectively (Table 3, entries 1 and 2). When penta-1,4-dien-3-ol (**1c**) was submitted to react with **2a** the γ-substituted product **3ca** was regio and stereoselectively obtained, although with moderate yields even working with 5 mol% of catalysts at 50 and 85 °C (Table 3, entries 3 and 4, respectively). Similar results were obtained when cyclohex-2-en-1-ol (**1d**) was allowed to react with *p*-toluenesulfonamide (**2a**) in the presence of the gold and the silver catalysts (Table 3, entries 5 and 6). Product **3da** was isolated in both cases in 67% yield using 1 and 2 mol% of each catalyst at 50 and 100 °C, respectively. In the case of the regioisomeric alcohols (*E*)-4-phenylbut-3-en-1-ol (**1e**) and (*E*)-1-phenylbut-2-en-1-ol (**1f**) the same product **3ea** was regio and stereoselectively obtained

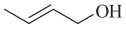
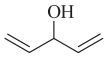
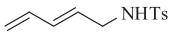
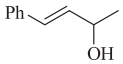
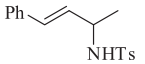
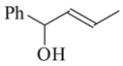
Table 2
Amination of (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) with different nucleophiles catalyzed by Au(I) or AgX.[a]



Entry	R^1R^2NH (No.)	Cat. (mol%)	T (°C)	Time	Product No.	Yield (%)[b]
1	p-$MeC_6H_4SO_2NH_2$ (**2a**)[c]	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	25	1 h	**3aa**	84 (93)
2	p-$MeC_6H_4SO_2NH_2$ (**2a**)[c]	AgOTf (2)[d]	25	1 h	**3aa**	78 (77)
3	p-$MeC_6H_4SO_2NHMe$(**2b**)	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	25	90 min	**3ab**	70 (95)
4	p-$MeC_6H_4SO_2NHMe$(**2b**)	AgOTf (5)	25	25 h	**3ab**	50 (58)
5	p-$MeOC_6H_4SO_2NH_2$(**2c**)	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	25	40 min	**3ac**	65 (87)
6	p-$MeOC_6H_4SO_2$ NH_2 (**2c**)	AgOTf (2)	25	24 h	**3ac**	(85)
7	p-$NO_2C_6H_4SO_2NH_2$ (**2d**)	$[(PhO)_3P]AuCl/AgOTf$ (2)	50	24 h	**3ad**	77 (80)
8	p-$NO_2C_6H_4SO_2NH_2$ (**2d**)	AgOTf (2)	50	24 h	**3ad**	96 (98)
9	$MeSO_2NH_2$ (**2e**)	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	50	4 h	**3ae**	82 (82)
10	$MeSO_2NH_2$ (**2e**)	AgOTf (2)	50	1 h	**3ae**	75 (85)
11	$BnCO_2NH_2$ (**2f**)	$[(PhO)_3P]AuCl/AgOTf$ (2)	25	1 h	**3af**	93 (95)
12	$BnCO_2NH_2$ (**2f**)	AgOTf (2)	25	8 h	**3af**	40 (75)
13	p-$ClC_6H_4NH_2$ (**2g**)	$[(PhO)_3P]AuCl/AgOTf$ (2)	50	24 h	**3ag**	90 (95)
14	p-$ClC_6H_4NH_2$ (**2g**)	AgOTf (2)	50	24 h	**3ag**	80 (84)
15	p-$NO_2C_6H_4NH_2$ (**2h**)	$[(PhO)_3P]AuCl/AgOTf$ (0.5)	25	7 h	**3ah**	90 (95)
16	p-$NO_2C_6H_4NH_2$ (**2h**)	AgOTf (2)	50	24 h	**3ah**	94 (95)
17	p-$CH_3C_6H_4NH_2$ (**2i**)	$[(PhO)_3P]AuCl/AgOTf$ (2)	50	24 h	**3ai**	45 (47)
18	p-$CH_3C_6H_4NH_2$ (**2i**)	AgOTf (5)	50	24 h	**3ai**	44 (45)

[a] Reaction conditions: allyl alcohol **1a** (1 mmol), R^1R^2NH **2** (2 mmol), cat. (see column) and dioxane (2 mL).
[b] Isolated yield after column chromatography. In parenthesis isolated crude yield determined by ^{1}H-NMR.
[c] 1.5 equiv of $TsNH_2$ were used.
[d] In acetonitrile.

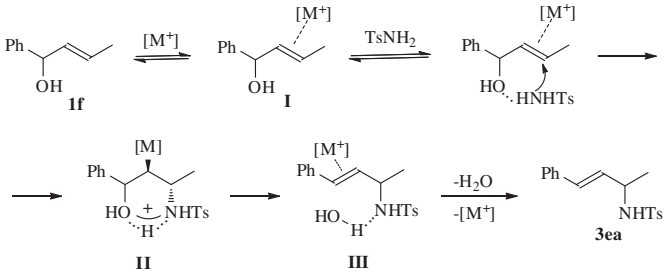
Table 3
Gold(I) *versus* Ag-catalyzed amination of allylic alcohols with *p*-toluenesulfonamide.[a]

Entry	Alcohol (**No.**)	Cat. (mol%)	T (°C)	Time (h)	Product (No.)	Yield (%)[b]
1	 (**1b**)	[(PhO)$_3$P]AuCl/AgOTf (1)	85	48	 (**3'ba**)  (**3ba**)	50[c] (54[c])
2	(**1b**)	AgOTf (5)	110	24	(**3ba**)	48[c] (50[c])
3	 (**1c**)	[(PhO)$_3$P]AuCl/AgOTf (5)	50	24	 (**3ca**)	36 (37)
4	(**1c**)	AgOTf (5)	85	24		40
5	 (**1d**)	[(PhO)$_3$P]AuCl/AgOTf (1)	50	8	 (**3da**)	67 (70)
6	(**1d**)	AgOTf (2)	100	8	(**3da**)	67
7	 (**1e**)	[(PhO)$_3$P]AuCl/AgOTf (2)	25	24	 (**3ea**)	84 (90)
8	(**1e**)	AgOTf (5)	50	24	(**3ea**)	90 (95)
9	 (**1f**)	[(PhO)$_3$P]AuCl/AgOTf (2)	25	24	(**3ea**)	84 (95)
10	(**1f**)	AgOTf (5)	50	24	(**3ea**)	94 (98)

[a] Reaction conditions: allyl alcohol **1** (1 mmol), *p*-toluenesulfonamide (**2a**) (342 mg, 2 mmol), cat. (see column) and dioxane (2 mL).
[b] Isolated yield after flash chromatography (hexane–EtOAc). In parenthesis isolated crude yield (calculated from ^{1}H-NMR).
[c] Combined yield of a 1:2 mixture of **3ba** and **3'ba**.

(Table 3, entries 7–10). Surprisingly, **1e** gave the α-substituted product and **1f** the γ-substituted, respectively under similar high yields and reaction conditions (Table 3, compare entry 7 and 9 with 8 and 10). The gold-catalyzed reactions needed 2 mol% loading and was performed at rt, whereas the silver-catalyzed amination a higher 5 mol% loading and heating at 50 °C must be used.

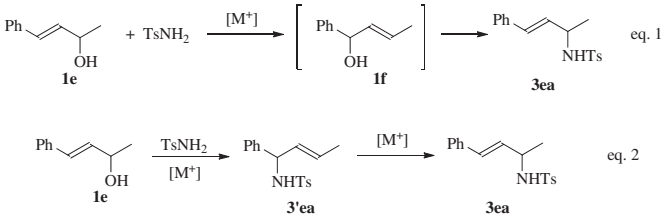
The regiochemical outcome of the gold- or silver-catalyzed amination of allylic alcohols can be explained using alcohols **1e** and **1f** as model substrates (Scheme 1). According to experimental studies performed by Mukherjee and Widenhoefer [9] in the gold (I)-catalyzed amination of allylic alcohols with cyclic ureas as nucleophiles two main possible mechanisms can be proposed. The first proposed mechanism is shown in Scheme 1 involving a hydroamination reaction of the C–C double bond instead of a concerted S_N2' substitution by σ-activation of the hydroxyl group. This pathway seems to be more plausible due to the low oxophilicity of gold(I) and silver against π-activation of the double bond.



Scheme 1. Proposed mechanism for the γ-substitution of allylic alcohol **1f**.

This type of π-activation has been also proposed by Paton and Maseras for the gold(I)-catalyzed isomerisation of allylic ethers [12]. This mechanism can explain the γ-attack of the nucleophile **2a** to alcohol **1f** to afford product **3ea**. Metal-coordinate alcohol **1f**, complex **I**, can suffer *anti*-hydroamination to afford intermediate **II**, which after *anti*-elimination of H_2O and further decoordination of the catalyst afforded product **3ea**. This proposed pathway can also explain the formation of products **3ba** and **3ca**.

For the transformation of alcohol **1e** into the α-substituted product **3ea** two different isomerisation mechanisms have been proposed [9]. One possible explanation is the isomerisation of alcohol **1e** into **1f** mediated by the gold- or silver catalyst acting as Lewis acids involving carbocationic intermediates (Scheme 2, eq. (1)). This process has been observed in the case of 3-methylbut-2-en-1-ol, which isomerizes under the presence of a cationic gold(I) catalyst into 2-methylbut-3-en-2-ol [9]. The same authors found out isomerisation of the γ- to the α-aminated product. In the case of alcohol **1e**, it can be proposed that once the γ-substitution takes place to give product **3'ea** further gold- or silver-catalyzed isomerisation would form **3ea** (Scheme 2, eq. (2)). These processes can explain the formation of product **3'ba** as well.



Scheme 2. Proposed mechanisms for the α-substitution of allylic alcohol **1e**.

3. Conclusions

We can conclude that the intermolecular amination of allylic alcohols can be carried out not only in the presence of catalytic amounts of the cationic (triphenylphosphite) gold(I) complex but also with silver triflate. This process can be carried out using different nitrogenated compounds such as sulfonamides, benzyl carbamate and aromatic amines. Electron-deficient anilines and electron-rich sulfonamides are the best nucleophiles for these metal-based nucleophilic substitutions. In general AgOTf-catalyzed aminations needed higher loadings, temperatures, and longer reaction times than gold-catalyzed ones. The substitution seems to occur through a π-activation pathway of the double bond followed by hydroamination and elimination of H_2O and the cationic catalyst affording the γ-substituted product. Alternatively, the formation of α-substituted products can be explained by isomerisation of the initially formed γ-substituted product or by alcohol isomerisation, both processes being catalyzed by Au(I) or Ag(I) involving cationic intermediates.

4. Experimental

4.1. General

Unless otherwise noted all commercials reagents and dry solvents were used without further purification. All reactions were carried out in absence of light and under argon atmosphere. Melting points were determined with a Reichert Thermovar hot plate apparatus. IR spectra were recorded on a Nicolet 510 P-FT spectrophotometer. ^{1}H-NMR (300 or 400 MHz) and ^{13}C-NMR (75 or 100 MHz) spectra were obtained on a Bruker AC-300 and Bruker AC-400, respectively, using $CDCl_3$ as solvent and TMS as internal standard. Low-resolution electron impact (EI) mass spectra were obtained at 70 eV on an Agilent 5973 Network. Analytical TLC was performed on Merck aluminium sheets with silica gel 60 F_{254}. Silica gel 60, (0.04–0.06 mm) was employed for flash chromatography. Gas chromatographic analyses were performed on an Agilent 6890N instrument equipped with a WCOT HP–1 fused silica capillary column.

4.2. General procedure for the gold(I)- and silver(I)-amination of allylic alcohols

To a (1:1) mixture of gold catalyst or silver salt (see, Tables 1–3) and nucleophile (1.5–2 mmol, see Tables 1–3) in dry solvent (2 mL) was added the alcohol (1 mmol) with magnetic stirring under argon atmosphere in the dark. After the corresponding reaction time under the conditions indicated in Tables 1–3, water (2 mL) and brine (2 drops) were added to the reaction mixture. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). All organic phases were mixed, dried with $MgSO_4$ and evaporated (15 Torr). Pure products were obtained by flash chromatography.

The compound (*E*)-*N*-(but-2-enyl)-4-methylbenzenesulfonamide (**3'ba**) is commercially available. The following compounds (*E*)-*N*-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (**3aa**) [7], (*E*)-*N*-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (**3ab**) [7], (*E*)-4-chloro-*N*-(1,3-diphenylallyl) benzenamine (**3ag**) [8a], (*E*)-*N*-(1,3-diphenylallyl)-4-nitroaniline (**3ah**) [2], (*E*)-*N*-(1,3-diphenylallyl)-4-methylaniline (**3ai**) [8a], (*E*)-*N*-(but-2-enyl)-4-methylbenzenesulfonamide (**3ba**) [13], (*E*)-4-methyl-*N*-(penta-2.4-dienyl)benzenesulfonamide (**3ca**) [13], *N*-(cyclohex-2-enyl)-4-methylbenzenesulfonamide (**3da**) [7], and (*E*)-4-methyl-*N*-(4-phenylbut-3-en-2-yl)benzenesulfonamide (**3ea**) [7] have been previously described. Physical and spectroscopic data of the other synthesized compounds follow.

4.2.1. (E)-N-(1,3-Diphenylallyl)-4-methoxybenzenesulfonamide (*3ac*)

White solid; m.p. 118 °C; R_f (hexane/ethyl acetate: 4/1) 0.28; ν (KBr) 3267, 3082, 3024, 2999, 2839, 1589, 1495, 1444, 1423, 1267, 1147, 1089, 1049, 825, 741, 687, 676 cm^{-1}; δ_H (300 MHz) 3.75 (s, 3H), 5.06–5.10 (m, 2H), 6.1 (dd, J = 15.7, 6.3 Hz, 1H), 6.4 (d, J = 15.7 Hz, 1H), 6.8 (d, J = 8.8 Hz, 2H), 7.20–7.23 (m, 10H), 7.7 (d, J = 8.8 Hz, 2H); δ_C (75 MHz) 55.5, 59.8, 113.9, 126.5, 127.0, 127.9, 128.2, 128.4, 128.7, 132.1, 132.2, 139.6, 162.7; *m/z*(EI): 379 [M$^+$, 2%], 209 (17), 208 (100), 207 (15), 204 (40), 192 (10), 115 (17), 104 (28), 91 (13), 77 (20).

4.2.2. (E)-N-(1,3-Diphenylallyl)-4-nitrobenzenesulfonamide (*3ad*)

Yellow solid; m.p. 160 °C; R_f (hexane/ethyl acetate: 4/1) 0.34; ν (KBr) 3278, 3100, 3057, 3021, 1607, 1524, 1415, 1339, 1310, 1154, 1086, 1024, 846 cm^{-1}; δ_H (400 MHz) 5.06–5.51 (m, 2H), 6.08 (dd, J = 15.8, 6.7 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 7.05–7.51 (m, 10H), 7.85 (d, J = 9.0 Hz, 2H), 8.10 (d, J = 9.0 Hz, 2H); δ_C (100 MHz) 29.7, 60.2, 123.9, 126.4, 127.1, 127.3, 128.3, 128.4, 128.6, 128.9, 133.0, 135.4, 138.7, 146.6, 149.6; *m/z* (EI) 394 [M$^+$, 4%], 209 (10), 208 (64), 207 (59), 206 (100), 193 (13), 192 (26), 181 (12), 178 (13), 165 (11), 130 (21), 122 (10), 115 (29), 105 (15), 104 (63), 103 (18), 91 (25), 77 (23).

4.2.3. (E)-N-(1,3-Diphenylallyl) methanesulfonamide (*3ae*)

White solid; m.p. 127 °C; R_f (hexane/ethyl acetate: 4/1) 0.30; ν (KBr) 3293, 3032, 3006, 2930, 1495, 1459, 1430, 1415, 1314, 1042, 966, 759, 745, 698 cm^{-1}; δ_H (300 MHz) 2.77 (s, 3H), 4.97 (d, J = 6.8 Hz, 1H), 5.30 (t, J = 6.8 Hz, 1H), 6.32 (dd, J = 15.7, 6.8 Hz, 1H), 6.62 (d, J = 15.7 Hz, 1H), 7.31–7.40 (m, 10H); δ_C (75 MHz) 42.2, 59.7, 126.6, 127.1, 128.2, 128.3, 128.4, 128.7, 129.0, 132.5, 135.8, 139.8; *m/z* (EI) 287 [M$^+$, 6%], 208 (47), 207 (48), 206 (100), 192 (27), 191 (12), 178 (11), 165 (10), 130 (17), 115 (22), 104 (43), 103 (13), 91 (14), 77 (15).

4.2.4. (E)-Benzyl 1,3-diphenylallylcarbamate (*3af*)

White solid; m.p. 110 °C; R_f (hexane/ethyl acetate: 4/1) 0.39; ν (KBr) 3412, 3318, 3263, 3191, 3086, 3057, 3031, 2948, 1959, 1694, 1604, 1528, 1448, 1342, 1288, 1234, 1064, 962, 727 cm^{-1}; δ_H (300 MHz) 5.15 (t, J = 7.1 Hz, 1H), 5.54 (s, 1H), 6.33 (dd, J = 15.9, 6.0 Hz, 1H), 6.56 (d, J = 16 Hz, 1H), 7.10–7.49 (m, 15H); δ_C (75 MHz) 66.9, 126.5, 127.0, 127.7, 128.1, 128.2, 128.5, 128.8, 129.0, 131.2, 135.2, 136.5, 140.9, 142.1, 156.7; *m/z* (EI): 343 [M$^+$, 2%], 253 (19), 252 (96), 235 (16), 209 (30), 208 (12), 206 (25), 193 (17), 192 (28), 191 (86), 181 (14), 178 (14), 165 (13), 130 (14), 115 (32), 108 (12), 105 (10), 104 (43), 103 (17), 91 (100), 79 (17), 77 (28), 65 (12).

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References

[1] For recent reviews, see: (a) J. Muzart, Tetrahedron 61 (2005) 4179; (b) Y. Tamaru, Eur. J. Org. Chem. (2005) 2647.
[2] R. Sanz, A. Martínez, D. Miguel, J.M. Alvarez-Gutiérrez, F. Rodríguez, Adv. Synth. Catal. 348 (2006) 1841.
[3] W. Wu, W. Rao, Y.Q. Er, J.K. Loh, C.Y. Poh, P.W.H. Chan, Tetrahedron Lett. 49 (2008) 2620.
[4] (a) J. Muzart, Eur. J. Org. Chem. (2007) 3077 and references cited therein; (b) T. Nishikata, B.H. Lipshutz, Org. Lett. 11 (2009) 2377.
[5] (a) T. Ohshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya, K. Mashima, J. Am. Chem. Soc. 131 (2009) 14317; (b) G. Mora, O. Piechaczyk, R. Houdard, N. Mezailles, X.F. Le Goff, P. Le Floch, Chem. Eur. J. 14 (2008) 10047; (c) M. Utsunomiya, Y. Miyamoto, J. Ipposhi, T. Ohshima, K. Mashima, Org. Lett. 9 (2007) 3371.

[6] (a) H. Yang, L. Fang, M. Zhang, C. Zhu, Eur. J. Org. Chem. (2009) 666;
(b) Y. Tao, Y. Zhou, J. Qu, M. Hidai, Tetrahedron Lett. 51 (2010) 1982.
[7] H.B. Qin, N. Yamagiwa, S. Matsunaga, M. Shibasaki, Angew. Chem. Int. Ed. 46 (2007) 409.
[8] (a) S. Guo, F. Song, Y. Liu, Syn. lett. (2007) 964;
(b) X.-Z. Shu, X.-Y. Liu, H.-Q. Xiao, K.-G. Ji, L.N. Guo, Y.M. Liang, Adv. Synth. Catal. 350 (2008) 243;
(c) Y. Lu, X. Fu, H. Chen, X. Du, X. Jia, Y. Liu, Adv. Synth. Catal. 351 (2009) 129;
(d) P. Kothandaraman, S.J. Foo, P.W.H. Chan, J. Org. Chem. 74 (2009) 5947.
[9] P. Mukherjee, R.A. Widenhoefer, Org. Lett. 12 (2010) 1184.
[10] X. Giner, C. Nájera, Org. Lett. 10 (2008) 2119.
[11] X. Giner, C. Nájera, Syn. Lett. (2009) 3211.
[12] R.S. Paton, F. Masera, Org. Lett. 11 (2009) 2237.
[13] D. Xing, D. Yang, Org. Lett. 12 (2010) 1068.