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Palladium(0)-Catalyzed Substitution of Allylic Substrates in an Aqueous-Organic Medium

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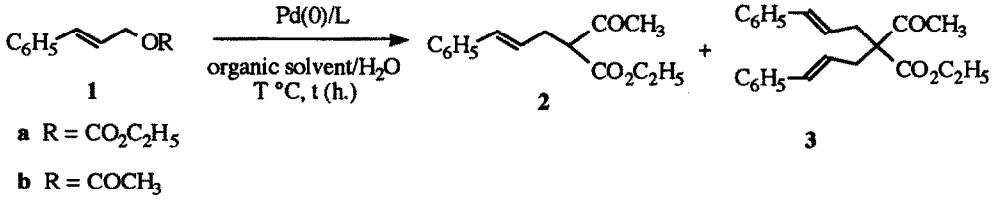
Abstract: A palladium(0)-water soluble catalyst prepared *in situ* from palladium acetate and the sulfonated triphenyl phosphine $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$ (or tppts) is an efficient catalyst for allylic substitution with various carbon and heteronucleophiles in an aqueous-organic medium, allowing a very easy separation of the product(s) and the recycling of the catalyst.

INTRODUCTION

Palladium promoted organic reactions are powerful tools in organic synthesis. Reactions induced by palladium, including allylic substitutions, coupling reactions, oligomerisations, telomerisations, oxidations, etc., provide mild and selective routes to a variety of valuable chemicals from basic organic precursors.[1] However, one of the greatest drawbacks of homogeneous metal catalysis is the separation of the organic products from the active catalyst, which is sometimes toxic and costly. A very elegant solution to this problem consists in using water soluble ligands which are poorly soluble in organic media; the catalysis could be carried out in a two-phase system and decantation of the two phases would allow an easy separation and recovery of the catalyst. The organic product is thus very easily separated from the catalyst and it is very often pure enough for subsequent transformations.[2] Several catalytic reactions have been achieved in such biphasic system: hydroformylation of olefins,[2] hydrogenation of olefins even in an enantioselective manner in the presence of chiral water-soluble ligands,[3] hydrogenation of saturated and unsaturated aldehydes,[4] addition of active methylene compounds to dienes,[5] carbonylation reactions [6] and telomerisation.[7] Our continuing interest in the area of palladium [8,9] was spured by the idea that aqueous soluble palladium catalysts may be used in such reactions under very mild conditions. It was recently shown that the cross-coupling reaction [10] and the allylic nucleophilic substitution reaction [10c,11] were catalyzed by palladium complexes associated with sulfonated phosphines in a two-phase system. In the present paper we report more details on the allylic nucleophilic substitution reaction catalyzed by palladium associated with the trisodium salt of the tri(*m*-sulfophenyl) phosphine $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$ (or tppts).

RESULTS AND DISCUSSION

The first aim in using Pd(0)/tppts as the catalyst in nucleophilic substitution of allylic substrates was the recycling of the water-soluble palladium catalyst. The choice of the best conditions for this purpose was done using the allylic nucleophilic substitution of (*E*)-cinnamyl ethyl carbonate **1a** by ethyl acetoacetate as shown in Scheme 1.



Scheme 1

As shown in Table 1, allylic substitution of **1a** occurred using THF or *i*-Pr_2O as the co-solvent of water; however we observed in these cases a rapid decomposition of the catalyst with a deposit of metallic palladium. More interesting was the use of nitriles as a co-solvent; the reaction occurred in acetonitrile, butyronitrile or benzonitrile, the conversion being quantitative when the reaction was monitored at 50 °C, and with a very high degree of selectivity in the product of monoalkylation **2**; the deposit of palladium was never observed in these cases. $Pd(dba)_2$, $Pd_2(dba)_3$ or $Pd(OAc)_2$ could be used as the precursors of Pd(0); however $Pd(OAc)_2$ seemed the more convenient, since it is soluble in water.

Table 1. Influence of the Solvent on the Conversion of **1a**. [a]

Entry	Catalyst [b]	T °C	Solvent	Conversion of **1a** % [c] (**2**/**3** ratio %)
1	$Pd(OAc)_2$ + tppts	50	THF/H_2O	100 (100/0)
2	$Pd(dba)_2$ + tppts	50	*i*-Pr_2O/H_2O	80 (100/0)
3	$Pd(OAc)_2$ + tppts	25	CH_3CN/H_2O	100 (100/0)
4	$Pd(OAc)_2$ + tppts	50	CH_3CN/H_2O	100 (88/12)
5	$Pd(OAc)_2$ + tppts	25	C_6H_5CN/H_2O	30 (100/0)
6	$Pd(OAc)_2$ + tppts	50	C_6H_5CN/H_2O	94 (100/0)
7	$Pd(OAc)_2$ + dppets[d]	50	C_6H_5CN/H_2O	100 (97/3)
8	$Pd(dba)_2$ + dppbts[e]	50	C_6H_5CN/H_2O	100 (90/10)
9	$Pd(OAc)_2$ + tppts	50	*n*-C_3H_7CN/H_2O	100 (95/5)

[a] General conditions: 2.5 mmol of **1a** and 3.5 mmol of ethyl acetoacetate in 2.5 mL of organic solvent and 2.5 mL of water, 24 h. [b] 4 mol % of $Pd(OAc)_2$, 24 mmol % of tppts; 4 mol % of $Pd(dba)_2$, 16 mol % of tppts. [c] Determined by GC and ^1H NMR. [d] 4 mol % of $Pd(OAc)_2$, 12 mol % of dppets. [e] 4 mol % of $Pd(dba)_2$, 8 mol % of dppbts.

Table 2. Palladium(0)-tppts Catalyzed Reactions of Allylic Substrates with Various Carbon Nucleophiles.[a]

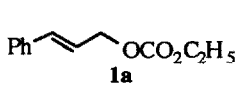
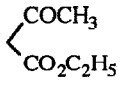
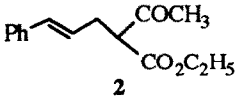
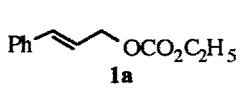
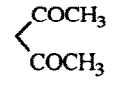
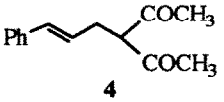
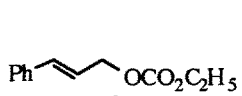
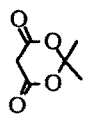
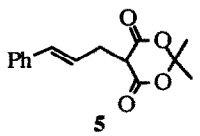
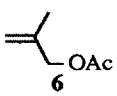
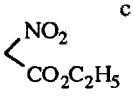
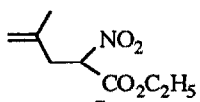
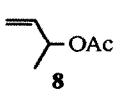
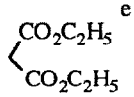
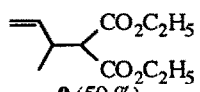
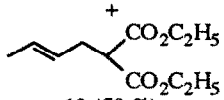
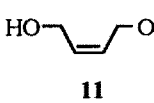
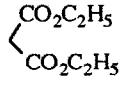
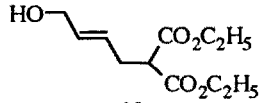
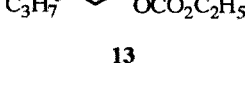
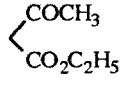
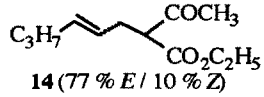
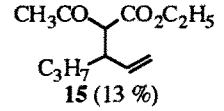
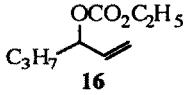
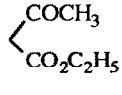
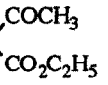
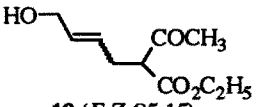
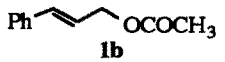
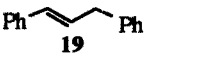
Entry	Substrate	Nucleophile	Solvent (ratio %)	T °C/h	Product(s)	Yield [b] %
1	 **1a**		C_3H_7CN/H_2O (1/1)	50/12	 **2**	84
2	 **1a**		$PhCN/H_2O$ (1/1)	50/12	 **4**	81
3	 **1a**		$PhCN/H_2O$ (1/1)	50/12	 **5**	58
4	 **6**	 [c]	CH_3CN/H_2O (15/1)	25/10	 **7**	88 [d]
5	 **8**	 [e]	CH_3CN/H_2O (15/1)	85/6	 **9** (50 %) +  **10** (50 %)	50
6	 **11**	 [e]	CH_3CN/H_2O (15/1)	85/6	 **12**	50
7	 **13**		CH_3CN/H_2O (1/1)	50/12	 **14** (77 % *E* / 10 % *Z*) +  **15** (13 %)	75
8	 **16**		CH_3CN/H_2O (1/1)	50/12	**14** (86 % *E* + 9 % *Z*) + **15** (5 %)	60

Table 2 (continued)

Entry	Substrate	Nucleophile	Solvent (ratio %)	T °C/h	Product(s)	Yield [b] %
9	 **17**		CH_3CN/H_2O (1/1)	50/12	 **18** (*E*:*Z* 85:15)	80
10	 **1b**	$NaBPh_4$	CH_3CN/H_2O (15/1)	25/1	 **19**	97

[a] General conditions: 2.5 mmol of allylic substrate and 3.5 mmol of carbon nucleophile in 5 mL of aqueous-organic solvent, 4 mol % $Pd(OAc)_2$, 8-20 mol % tppts. [b] Isolated yields. [c] NEt_3 (2.2 eq) was added. [d] Diallylated compound was obtained (12 %). [e] DBU (2.2 eq) was added.

The results concerning the palladium(0)-tppts catalyzed reaction of various allylic substrates with stabilized carbon nucleophiles are summarized in Table 2. As expected, allylic carbonates reacted with various active methylene compounds such as ethyl acetoacetate, acetylacetone or Meldrum's acid without the presence of a base. Cinnamyl ethyl carbonate **1a** gave a single regio- and stereoisomer with the *E* configuration (entries 1-3). The (*E*)-2-hexen-1-yl ethyl carbonate **13** and (2-vinyl)butyl ethyl carbonate **16** led to the formation of a mixture of monoalkylated products **14** and **15** (entries 7-8), the alkylation occurring predominantly at the less hindered side of the π-allyl system and the *E* isomer being the major product.

Alkylation of acetates needed the presence of a base such as triethylamine or better DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) (entries 4-6). Alkylation of the unsaturated hydroxy acetate **11** with diethyl malonate led regiospecifically to the formation of a single product **12** having the *E* configuration; the same regiospecificity was found in the reaction of ethyl acetoacetate on the 3,4-epoxy-1-butene **17** which gave the unsaturated hydroxy ester **18** as a mixture of *E* and *Z* isomers (85:15). Finally, sodium tetraphenyl borate reacted with (*E*)-cinnamyl acetate **1b** leading to a single product **19**.

The results concerning the reaction of various heteronucleophiles with allylic substrates catalyzed by palladium(0)-tppts in an aqueous-organic medium are summarized in Table 3. Secondary amines (morpholine, benzyl methylamine) and primary amines (*n*-butylamine, 2,2-diethylpropargylamine, cycloheptylamine, α-methylbenzylamine) reacted with (*E*)-cinnamyl acetate **1b** or 2-methyl allyl acetate **6** giving the product of monoalkylation in quite good yields (entries 1-6). Reaction of (*Z*)-4-acetoxy-2-buten-1-yl ethyl carbonate **28** with α-methylbenzylamine (entry 9) led to the compound **29** resulting from a double alkylation reaction, contaminated by some α-pyrrole ethylbenzene. The bis *N*,*O*-Boc protected hydroxylamine (entry 7) reacted with the formation of the *N*-allyl protected hydroxylamine in 80 % chemical yield, whereas hydroxylamine hydrochloride gave the hydroxylamine **27** resulting from a bis allylation reaction (entry 8). Finally, reaction of compounds **1a** or **1b** with sodium azide (entries 10-11) or *p*-toluene sulfinate (entry 12) which are soluble in water gave the corresponding allyl azide or sulfone in good yields using the biphasic system.

As expected, the use of a water-soluble palladium(0)-tppts catalyst not only allowed the easy separation of the catalyst from the reaction product(s), but also the recycling of the catalyst. Some examples are

Table 3. Palladium(0)-tppts Catalyzed Reactions of Allylic Substrates with Various Hetero Nucleophiles.[a]

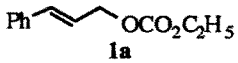
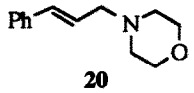
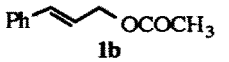
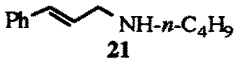
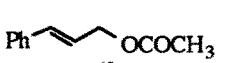
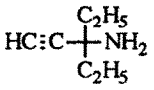
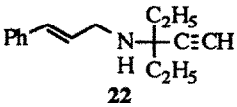
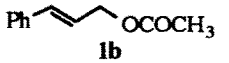
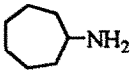
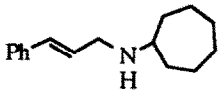
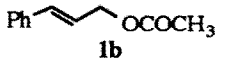
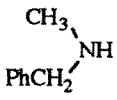
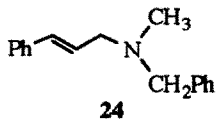
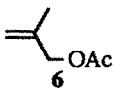
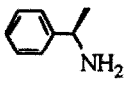
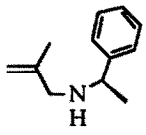
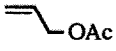
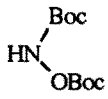
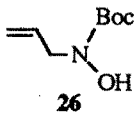
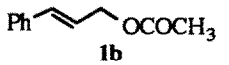
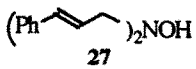
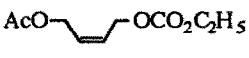
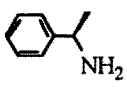
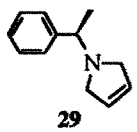
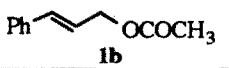
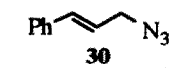
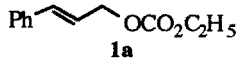
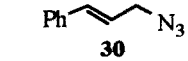
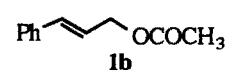
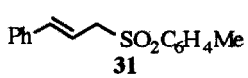
Entry	Substrate	Nucleophile	Solvent (ratio %)	T °C/h	Product(s)	Yield [b] %
1	 **1a**		C_3H_7CN/H_2O (1/1)	50/12	 **20**	86
2	 **1b**	n-$C_4H_9NH_2$	CH_3CN/H_2O (15/1)	40/2	 **21**	80 [c]
3	 **1b**		CH_3CN/H_2O (15/1)	40/0.5	 **22**	93
4	 **1b**		CH_3CN/H_2O (15/1)	40/4	 **23**	70
5	 **1b**		C_3H_7CN/H_2O (6/1)	40/0.5	 **24**	97
6	 **6**		CH_3CN/H_2O (15/1)	45/10	 **25**	92 [d]
7			CH_3CN/H_2O (15/1)	70/20	 **26**	81
8	 **1b**	NH_2OH,HCl	CH_3CN/H_2O (15/1)	25/48	 **27**	96
9	 **28**		CH_3CN/H_2O (15/1)	45/12	 **29**	50 [e]
10	 **1b**	NaN_3	C_3H_7CN/H_2O (1/1)	50/12	 **30**	92

Table 3 (continued)

Entry	Substrate	Nucleophile	Solvent (ratio %)	T °C/h	Product(s)	Yield [b] %
11	 **1a**	NaN_3	C_3H_7CN/H_2O (1/1)	50/12	 **30**	69
12	 **1b**	$MeC_6H_4SO_2Na$	C_3H_7CN/H_2O (1/1)	50/12	 **31**	95

[a] General conditions: 2.5 mmol of allylic substrate and 5 mmol of heteronucleophile in 5 mL of aqueous-organic solvent, 4 mol % $Pd(OAc)_2$, 8-20 mol % tppts. [b] Isolated yields. [c] Diallylated compound was obtained (11 %). [d] Diallylated compound was obtained (8 %). [e] Obtained as a 1/1 mixture of **29** and α-pyrrole ethylbenzene.

summarized in Table 4. All types of nucleophiles including carbon as well as heteronucleophiles allowed an easy recycling using benzonitrile or butyronitrile as the organic solvent, and this procedure is very interesting in the case of water-soluble nucleophiles, such as sodium azide or *p*-toluene sodium sulfinate. The reaction could also be run in acetonitrile which is easier to eliminate; however one of the limitations for the recycling using this solvent is its solubility in water, which required extraction whith an organic solvent such as ethyl acetate.

Table 4. Some Examples of Recycling in Palladium(0)-tppts Catalyzed Alkylation. [a]

Entry	Substrate	Nucleophile	Solvent (ratio %)	T °C/h	Product	Yield (%) [b]
1	**1a**	$CH_3COCH_2CO_2C_2H_5$	$PhCN/H_2O$ (1/1)	50/12	**2**	94
1a	"	"	$PhCN/H_2O$ (1/1)	50/12	**2**	93
1b	"	"	$PhCN/H_2O$ (1/1)	50/12	**2**	90
2	**1a**	$CH_3COCH_2CO_2C_2H_5$ [c]	$PhCN/H_2O$ (1/1)	50/12	**2**	90
2a	"	"	$PhCN/H_2O$ (1/1)	50/12	**2**	80
3	**1a**	$CH_3COCH_2CO_2C_2H_5$	C_3H_7CN/H_2O (1/1)	50/12	**2**	95
3a	"	"	C_3H_7CN/H_2O (1/1)	50/12	**2**	95
4	**1b**	$CH_3NHCH_2C_6H_5$	C_3H_7CN/H_2O (6/1)	40/0.5	**24**	97
4a	"	"	C_3H_7CN/H_2O (6/1)	40/2	**24**	95
4b	"	"	C_3H_7CN/H_2O (6/1)	40/4	**24**	95
5	**1b**	NaN_3	C_3H_7CN/H_2O (1/1)	50/12	**30**	69
5a	"	"	C_3H_7CN/H_2O (1/1)	50/12	**30**	53
6	**1b**	$CH_3COCH_2CO_2C_2H_5$	CH_3CN/H_2O (1/1)	50/12	**2**	80
6a	"	"	CH_3CN/H_2O (1/1)	50/12	**2**	87
7	**1b**	$CH_3C_6H_4SO_2Na$	C_3H_7CN/H_2O (1/1)	50/12	**31**	95
7a	"	"	C_3H_7CN/H_2O (1/1)	50/12	**31**	95

[a] a and b are the first and second recycling. [b] Isolated yields. [c] 2 mol % $Pd_2(dba)_3$ and 16 mol % of tppts.

CONCLUSION

In summary we have observed that a water-soluble palladium(0) species prepared from $Pd(OAc)_2$ and tppts is an excellent catalyst for allylic substitution in an organic-aqueous medium, the organic solvent used being a nitrile. These reaction conditions allowed the very easy separation of the catalyst from the reaction product(s) which could be used in most cases immediatly for the following sequence without purification. The catalyst could also be eventually recycle. These very mild reaction conditions should find considerable applications in organic synthesis.

EXPERIMENTAL SECTION

All reactions were carried out under nitrogen using Schlenk techniques. The solvents were distilled and stored under nitrogen. IR spectra were obtained on a Perkin-Elmer 681 spectrometer. ^1H NMR (200 and 300 MHz) and ^{13}C NMR (74.75 MHz) spectra were recorded on Brücker AM 200 and AM 300 spectrometers using $CDCl_3$ as solvent and Me_4Si as internal standard. Chromatography was carried out on silica gel, Merck, grade 60 (230-400 mesh, 60 Å). GLC analyses were recorded with a capillary gas chromatography GIRDEL DELSI 330 equipped with a capillary column OV 101 (25 x 0.32 mm). Starting materials and products **2**,[12] **4**,[13] **5**,[14] **7**,[15] **9**,[16] **10**,[16] **12**,[17] **18**,[17] **19**,[18] **20**,[19] **21**,[20] **30** [21] and **31**[22] were characterized by comparing their boiling or melting points, IR, ^1H and ^{13}C NMR and MS with literature data. $Pd(OAc)_2$, $Pd(dba)_2$, $Pd_2(dba)_3$, acetonitrile, butyronitrile, benzonitrile, cinnamyl acetate **1b**, 3,4-epoxy-1-butene **18** were from a commercial source. The other carbonates and acetates were prepared using known procedures. The sulfonated phosphine tppts was a gift of Rhône-Poulenc and the sodium salts of 1,2-bis[di(*m*-sulphophenyl)phosphino]ethane (dppets) and 1,4-bis[di(*m*-sulphophenyl)phosphino]butane (dppbts) were prepared as previously described.[3a]

General procedure for the palladium-catalyzed substitution of allylic esters. A mixture of $Pd(OAc)_2$ (4 mol %) and tppts (8-20 mol %) was stirred in H_2O (2.5 mL) for 1 h. The allylic compound (2.5 mmol) and the nucleophile (3.5 mmol) in 2.5 mL of nitrile was then added and the reaction mixture was stirred at the desired temperature. The solvent was evaporated and the residu was extracted with ether (3 x 50 mL). Evaporation of the solvent under reduced pressure followed by column chromatography on silica gel gave the pure compound.

Substitution reaction of compounds 13 and 16 by ethyl acetoacetate. Compounds **14** ***Z*** and ***E*** and **15** were characterized in the mixture. ^1H NMR ($CDCl_3$) δ (as a mixture of **14** and **15**) 0.96 (t, 3H, CH_3), 1.23-1.36 (m, 5H, $-CH_2CH_3$), 1.89-1.99 (m, 2H, $-CH_2-CH=$), 2.22, 2.27 and 2.31 (3 x s, 3H, $-COCH_3$), 2.50-2.56 (dd, 2H, $=CH-CH_2-CH<$), 3.43-3.51 (m, 1H, -CH<), 4.13-4.25 (m, 2H, $-OCH_2-$), 5.28-5.55 (m, 2H, -CH=). ^{13}C NMR ($CDCl_3$) δ (determined on the mixture of **14** and **15**) **14** ***E*** 13.6 (C-8), 14.1 (CH_3), 22.4 (C-7), 29.1 ($COCH_3$), 31.3 (C-6), 34.6 (C-3), 59.9 (C-2), 61.3 (OCH_2), 125.6 (C-4), 133.7 (C-5), 169.4 (C-1), 202.8 (CO); **14** ***Z*** 13.8 (C-8), 14.3 (CH_3), 22.7 (C-7), 24.8 (C-6), 26.1 (C-3), 30.1 ($COCH_3$), 59.7 (C-2), 61.3 (OCH_2), 124.9 (C-4), 132.9 (C-5), 169.4 (C-1), 202.8 (CO); **15** 13.8 (C-6 and CH_2CH_3), 22.7 (C-5), 28.3 (C-4), 29.3 ($COCH_3$), 43.8 and 43.9 (C-3), 63.9 (OCH_2), 65.3 and 65.5 (C-2), 117.2 ($=CH_2$), 138.1 (-CH=), 167.1 (C-1), 202.8 (CO). MS (EI) **14** (***E*** + ***Z***) *m/z* 212 ($M^{+\cdot}$), 169, 167, 139, 131, 123, 95, 82, 43; **15** *m/z* 212 ($M^{+\cdot}$) 169, 167, 141, 139, 131, 127, 125, 123, 99, 85, 82, 81, 43.

***N*-(*E*)-Cinnamyl-1,1-diethylpropargylamine 22.** ^{1}H NMR ($CDCl_3$) δ 1.0 (t, J = 7.4 Hz, 6H, CH_3), 1.2 (s, 1H, NH), 1.65 (2q, 4H, -C*H*$_2$CH$_3$), 2.4 (s, 1H, ≡CH), 3.5 (dd, J = 6.2 Hz, J = 1.1 Hz, 2H, -CH_2N<), 6.4 (dt, J = 15.8 Hz, J = 6.2 Hz, 1H, =C*H*-CH_2-), 6.6 (d, J = 15.8 Hz, 1H, -CH=), 7.2-7.4 (m, 5H, C_6H_5). ^{13}C NMR δ ($CDCl_3$) 8.0 (CH_3), 30.5 (*C*H$_2$CH$_3$), 45.8 (CH_2N), 57.0 (C-3), 71.5 (C-1), 87.4 (C-2), 126.2, 127.2, 128.4 and 137.1 (C_6H_5), 128.6 (=*C*H-CH_2), 131.1 (-CH=). MS (EI) *m/z* 227 ($M^{+\cdot}$), 212, 198, 117; (CI, NH_3) *m/z* 245 ($MH^+ + NH_3$), 228 (MH^+). Anal. Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.45; H, 9.35; N, 6.23.

***N*-Cycloheptyl-(*E*)-cinnamylamine 23.** ^{1}H NMR ($CDCl_3$) δ 1.4-2.0 (m, 12H, -CH_2-), 2.3 (s, 1H, NH), 3.3 (dd, J = 6.4 Hz, J = 1.0 Hz, 2H, -CH_2N<), 6.3 (dt, J = 16.0 Hz, J = 6.4 Hz, 1H, =C*H*-CH_2-), 6.5 (d, J = 16.0 Hz, 1H, -CH=), 7.2-7.5 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ 25.8, 26.8, 27.9 and 30.1 (CH_2), 52.5 (CH_2N), 60.5 (-NCH<), 126.1, 127.1, 128.4 and 137.3 (C_6H_5), 129.4 (=*C*H-CH_2), 131.4 (-CH=). MS (EI) *m/z* 229 ($M^{+\cdot}$), 117.

***N*-Benzyl-*N*-methyl-(*E*)-cinnamylamine 24.** ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3H, CH_3), 3.25 (d, J = 6.4 Hz, 2H, -CH_2N<), 3.6 (s, 2H, -CH_2N<), 6.4 (dt, J = 16.0 Hz, J = 6.4 Hz, 1H, =C*H*-CH_2-), 6.6 (d, J = 16.0 Hz, 1H, C_6H_5-C*H*=), 7.2-7.6 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ 42.2 (CH_3), 59.8 (CH_2N), 61.8 (CH_2N), 126.3, 126.5, 127.5, 128.2, 128.5, 129.0, 137.1 and 138.9 (C_6H_5), 127.3 (=*C*H-CH_2), 132.5 (-CH=).

***N*-(2-Methylprop-2-enyl)-1-methylbenzylamine 25.** ^{1}H NMR ($CDCl_3$) δ 1.40 (d, J = 6.6 Hz, 3H, CH_3), 1.45 (s, 1H, NH), 1.8 (s, 3H, CH_3), 3.0 (s, 2H, -CH_2-), 3.9 (q, 1H, -CH<), 4.9 (s, 1H, =CH-), 4.93 (s, 1H, =CH-), 7.2-7.5 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ 20.8 (CH_3), 24.4 (CH_3), 53.4 (CH_2), 57.3 (-CH<), 110.4 (=CH_2), 126.6, 126.8, 128.3 and 144.1 (C_6H_5), 145.7 (>C=). MS (EI) *m/z* 174 ($M^{+\cdot}$), 160, 143, 128, 118, 105; (CI, NH_3) 193 ($MH^+ + NH_3$), 176 (MH^+). Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.77; N, 7.99. Found: C, 81.95; H, 9.81; N, 8.02.

***N*-Prop-2-enyl-*N*-terbutyloxycarbonylhydroxylamine 26.** ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 9H, CH_3), 4.0 (d, J = 7.0 Hz, 2H, -CH_2-), 5.1 (dd, J = 10.0 Hz, J = 2.0 Hz, 1H, =CH_2), 5.2 (dd, J = 17.0 Hz, J = 7.0 Hz, 1H, =CH_2), 5.85 (ddt, 1H, =CH-), 7.8 (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ 28.2 (CH_3), 53.2 (CH_2), 82.0 (CMe_3), 117.6 (=CH_2), 132.2 (=CH-), 157.1(CO). MS (CI, NH3) *m/z* 191 ($MH^+ + NH_3$), 174 (MH^+), 135, 118. Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.55; H, 8.86; N, 7.90.

***N*,*N*-Di-(*E*)-cinnamyl hydroxylamine 27.** mp 75 °C. ^{1}H ($CDCl_3$) δ 2.0 (s, 1H, OH), 3.65 (d, J = 7.0 Hz, 4H, -CH_2-), 6.35 (dt, J = 16.0 Hz, J = 7.0 Hz, 2H, =C*H*CH_2-), 6.6 (d, 2H, C_6H_5C*H*=), 7.2-7.5 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$) δ 64.8 (CH_2), 123.2 (=*C*H-CH_2), 126.5, 127.9, 128.5 and 133.9 (C_6H_5), 136.2 (C_6H_5CH=). MS (EI) *m/z* 265 ($M^{+\cdot}$), 247; (CI, NH_3) *m/z* 283 ($MH^+ + NH_3$), 266 (MH^+).

***N*-(1-Methylbenzyl)-2,5-dihydropyrrole 29** [As a mixture 1/1 with *N*-(1-methylbenzyl)pyrrole]. ^{1}H NMR ($CDCl_3$) δ 1.4 (s, 3H, CH_3), 3.1 (s, 4H, -CH_2N<), 3.9 (m, 1H, -CH<), 5.6-5.9 (m, 2H, -CH=CH-), 7.2-7.5 (m, 5H, C_6H_5). MS (EI) *m/z* 173 ($M^{+\cdot}$), 158, 105.

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