Pergamon

Tetrahedron 54 (1998) 3255–3278

TETRAHEDRON

Stereoselective Peterson Olefinations of Silylated Benzyl Carbamates

L. Frances van Staden, Birgit Bartels-Rahm, John S. Field and Neville D. Emslie*

Department of Chemistry, University of Natal, Private Bag X01, Scottsville, 3209, South Africa

Received 24 November 1997; revised 20 January 1998; accepted 22 January 1998

Abstract: An investigation of the effects of solvent, temperature and the bulk of the silyl and carbamate functionalities on the stereoselective synthesis of substituted vinyl carbamates from α-silyl benzyl carbamates is described.

In celebration of the discovery of the Peterson olefination 30 years ago,[1] we report that this reaction affords trisubstituted vinyl carbamates in good yields and Z-selectivity from α-silyl benzyl carbamates.

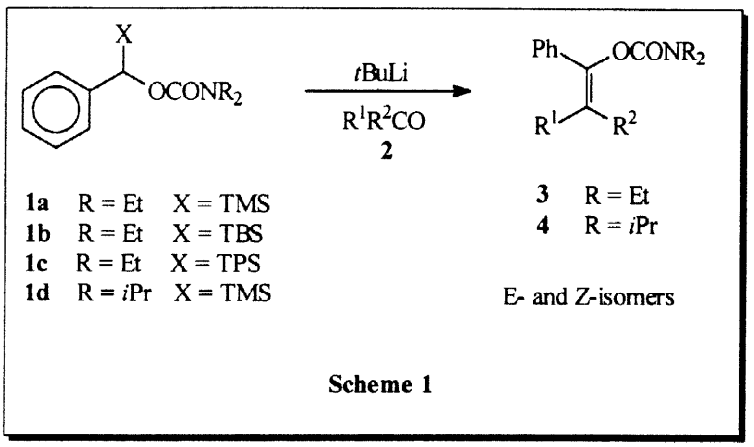
The Peterson olefination is considered to be the silicon variation of the Wittig reaction. One advantage of the Peterson olefination is that the β-hydroxysilyl intermediate can be treated with either acid or base to yield the desired olefin products. These conversions are stereoselective and either the E- or Z-isomer can be obtained from a single diastereomer; *e.g.* treatment of the erythro β-hydroxysilane with acid would favour the formation of the E-isomer, whereas the Z-isomer would be formed under basic conditions.[2] Furthermore elimination of the silanol affords disiloxanes as the by-products, which are volatile and readily removed in comparison with the triphenylphosphine oxide of the Wittig reaction.[3] It is believed that the stereoselective preparation of β-hydroxysilanes is pivotal in increasing the application of this reaction.[4] The good Z-selectivity obtained when α-silyl benzyl carbamates carbanions are reacted with carbonyl compounds enhances the scope of this reaction.

Our previous investigations of the Peterson olefination of ^{t}butyldimethylsilyl benzyl carbamates with aromatic carbonyl compounds provided a method for the preparation of aromatic vinyl carbamates with good Z-selectivity.[5] The olefin products were isolated directly when silylated benzyl carbamates are reacted with carbonyl compounds. This is not surprising, since it is believed that the β-hydroxysilanes are only isolated if there is no carbanion stabilising group present α to the silyl functionality.[6,7] The inherent stability of the benzylic anion, enhanced by the presence of the silyl functionality, therefore explains why the olefin products are isolated directly when silylated benzyl substrates are used in the Peterson olefination.[8]

The Peterson olefination of silylated benzyl carbamates was optimised using 1-^{t}butyldimethylsilyl-1-*N,N*-diethylcarbamoyloxy-1-phenylmethane **1b** and 3,4-methylenedioxybenzaldehyde **2a** as the model system (Scheme 1). It is evident from the results that ^{t}BuLi gives better yields than ^{n}BuLi and therefore we decided to use the stronger base (Table 1, entries 1 and 2). Diethyl ether was found to be the solvent of choice for enhanced Z-selectivity (Table 1, entries 2 and 3). The reaction time and temperature[8b, 8c] did not appear to have any significant effect on the E:Z ratio of this system (Table 1, entries 3, 4, 5 and 6). Extending the reaction time and allowing the reaction mixture to warm to room temperature after addition of the electrophile, did however, increase the yields of other systems (Table 2, entries 4-12), without adversely affecting the selectivity. The

0040-4020/98/$19.00
PII: S0040-4020(98)00070-2

increased number of by-products detected when 1.5 rather than 1.2 eq. of base (Table 1, entries 6 and 7) was used, was considered to be a disadvantage.



Scheme 1

	R1	R2
a	3,4-methylenedioxyphenyl	H
b	4-quinoline	H
c	propyl	H
d	cinnamyl	H
e	2-quinoline	H
f	2-pyridine	H
g	2-furanyl	H
h	2-thiophene	H
j	phenyl	H
k	4-pyridine	H
l	phenyl	phenyl

Table 1: Results of optimising the Peterson olefination of benzyl carbamates on the model system **3a**.

	Substrate	Product	Solvent	Base[a]	Time/hrs	Yield[b,9]/%	E:Z[10]
1	1b	**3a**	THF	nBuLi	3	73	38:62
2	1b	**3a**	THF	tBuLi	3	79	40:60
3	1b	**3a**	Et_2O	tBuLi	3	73	4:96
4	1b	**3a**	Et_2O	tBuLi	1	76	5:95
5	1b	**3a**	Et_2O	tBuLi	21	76[c]	9:91
6	1b	**3a**	Et_2O	tBuLi	5	76[b,c]	4:96
7	1b	**3a**	Et_2O	tBuLi[d]	5	75	6:94
8	1b	**3a**	HMPA/THF[e]	tBuLi	3	80	30:70
9	1b	**3a**	HMPA/Et_2O[e]	tBuLi	3	82	59:41
10	1b	**3a**	TMEDA	tBuLi	3	52	25:75
11	1b	**3a**	TMEDA/Et_2O[f]	tBuLi	3	33	24:76
12	1b	**3a**	TMEDA/THF[f]	tBuLi	3	trace	39:61

a 1.2 eq. base. **b** Reactions were stirred at -78°C. **c** Reactions warmed to room temperature following the addition of the electrophile. **d** 1.5 eq. of base. **e** 2 eq. HMPA.[11] **f** 1.4 eq. TMEDA.

The pioneering Peterson reactions were carried out in the polar solvents HMPA[2,8a-8d,11,12] or TMEDA.[1,13] Contrary to previous observations that the diastereomeric ratio of the Peterson olefination is insensitive to changes in temperature and variations in solvent (*e.g.* HMPA, 1:4 HMPA/THF, DMSO and DMF),[8b] we obtained better selectivity in diethyl ether. With a view to optimising the carbamate system fully, we investigated the effects of different solvents on both the yields and E/Z-selectivity. The addition of HMPA to both diethyl ether and THF increased the yields of the products (Table 1, entries 8 and 9). The Z-selectivity was, however, compromised with the additon of HMPA to diethyl ether. In THF the addition of HMPA increased the Z-selectivity by 10% (*cf.* entries 2 and 8), which was insignificant in comparison to the E:Z ratio obtained in diethyl ether (entry 3). When TMEDA was used as a solvent a decrease in yield was observed,

while the Z-selectivity was inferior to that obtained in diethyl ether (Table 1, entry 10). We observed a further decrease in the yield when TMEDA was used as a co-solvent (with preparation of the TMEDA-Li complex)[14] in diethyl ether, while only trace amounts of the olefins were isolated from the identical reaction in THF (Table 1, entries 11 and 12). The latter result could be attributed to the insolubility of the anion, which is predominantly ionic in a THF•TMEDA medium.[15] HMPA is considered to be a highly solvating,[11] powerful ionising solvent[8c] resulting in the formation of a free carbanion.[8b] Kende and co-workers[16] report that poor elimination of β-hydroxy phenyl sulfones is observed in the absence of HMPA.[17] We therefore conclude that the co-ordination of the TMEDA-Li complex[18] to the benzyl silyl carbamate anion generates a bulky intermediate hindering the approach of the electrophile resulting in the observed decrease in yield. In contrast we obtain increased yields with HMPA as co-solvent. This suggests that the HMPA is not co-ordinating to the anion through the nitrogen atoms, as this would result in the formation of a bulkier intermediate than the TMEDA complex with a resultant reduction in yield. We propose that co-ordination of HMPA occurs through the oxygen atom with a consequent reduction in the steric bulk at the carbanion relative to the TMEDA complex. Our results indicate that optimum yields and selectivity are obtained in the less polar weakly co-ordinating solvent, diethyl ether.

We have shown that good Z-selectivity is obtained when **1b** is reacted with aromatic carbonyl compounds in diethyl ether (Scheme 1, Table 2).[5] The only exceptions were **3b** and **3k** (Table 2, entry 1,2 and 11). No significant improvement in the selectivity and yield of **3b** was observed at room temperature (Table 2, entry 2). Contrary to our findings during optimisation (Table 1) we obtain good E-selectivity with electrophiles **2b** and **2k** in THF (Table 2, entries 3 and 11). Increasing the reaction time and temperature improved the yield of **3b** significantly (Table 2, entry 4).

Table 2: Results of the Peterson olefination with various aromatic electrophiles.

	Substrate	Product	Solvent	Base[a]	Time/hrs	Yield[b,9]/%	E:Z[19]
1	1b	**3b**	Et_2O	^{t}BuLi	5	45[c]	55:45
2	1b	**3b**	Et_2O	^{t}BuLi	5	61	65:35
3	1b	**3b**	THF	^{t}BuLi	5	42[c]	80:20
4	1b	**3b**	THF	^{t}BuLi	24	70	84:16
5	1b	**3b**	THF	^{t}BuLi	168	68	88:12
6	1b	**3e**	Et_2O	^{t}BuLi	5	80	20:80
7	1b	**3f**	Et_2O	^{t}BuLi [d]	5	65	23:77
8	1b	**3g**	Et_2O	^{t}BuLi	5	70	17:83
9	1b	**3h**	Et_2O	^{t}BuLi	5	78	11:89
10	1b	**3j**	Et_2O	^{t}BuLi	5	82	9:91
11	1b	**3k**	THF	^{t}BuLi	5	52	83:17
12	1b	**3l**	Et_2O	^{t}BuLi	5	82	n/a

a 1.2 eq. of base was used. **b** Reactions warmed to room temperature following the addition of the electrophile. **c** Reactions were stirred at -78°C. **d** 1.0 eq of base was used.

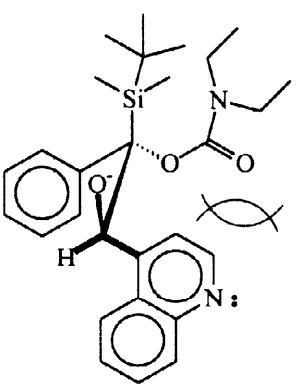
The unexpected E-selectivity (Table 2, entries 3-5) for **3b** is attributed to the fact that the Peterson olefination is kinetically (stereochemically) controlled (Table 3).[20] Theoretically, the thermodynamically stable product would be favoured if the reaction was allowed to equilibrate, *i.e.* proceed for a considerable length of

time. The continued E-selectivity, *i.e.* formation of the less stable isomer after stirring the reaction at room temperature for 168 hrs (Table 2, entry 5), confirmed the kinetic control of this reaction.[21] The E-isomer of **3b** was found to be thermodynamically less stable, rapidly converting to the thermodynamically stable Z-isomer (Table 3) on exposure to sunlight. On exposure of a product mixture of **3b** in $CDCl_3$ (E:Z = 87:13) to sunlight, the mixture had converted to an E:Z ratio of 52:48 after one week and 19:81 after four weeks. In an attempt to quantify these conversions we investigated the effect of ultraviolet irradiation and heating of the samples on the rate of conversion. Exposure of the samples to ultraviolet radiation (8W and 400W) led to decomposition of the products. Heating appears to be the more effective method for E/Z isomerisation. Direct heating of **3b** in an oven at 110°C also changed the initial E:Z ratio[22] of 71:29, to a final ratio of 6:94 after 192 hrs. Similarly **3k**, with an initial E:Z ratio of 83:17 was converted to 24:76 after 195 hrs. The controls which were maintained at ambient temperature in the dark did not show any isomerisation.

Table 3: Theoretical dipole moments and energies of the olefins investigated.

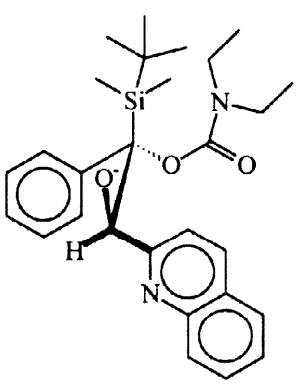
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3j**	**3k**
μ/D for E-isomer	3.73	3.28	3.87	3.77	2.36	4.14	4.58	4.96	3.80	3.54
μ/D for Z-isomer	3.50	3.95	3.54	3.80	3.21	3.42	3.07	2.49	3.44	3.92
E_R[23]/kcal.mol^{-1} for E-isomer	6.73	6.60	7.86	15.3	10.5	8.04	22.3	0	3.75	12.63
E_R[23]/kcal.mol^{-1} for Z-isomer	0	0	0	0	0	0	0	35.1	0	0

The steric and electronic repulsions between the quinoline and carbamate groups in the proposed reaction intermediate for the Z-isomer of **3b** (Figure 1), is a possible explanation for the kinetically controlled E-selectivity (Table 2, entries 1-5). If the steric bulk of the 4-quinoline **3b** and Z-selective 2-quinoline **3e** (Table 2, entry 6) moieties (Figures 1 and 2, respectively) are considered to be comparable, the only significant difference between these intermediates is the electronic repulsion of the 4-quinoline nitrogen and carbamate oxygen lone pairs in **3b**. A similar comparison can be drawn between **3k** and **3f**. Therefore, the poor Z-selectivity of **3b** and **3k** is attributed to electronic repulsions.



3b

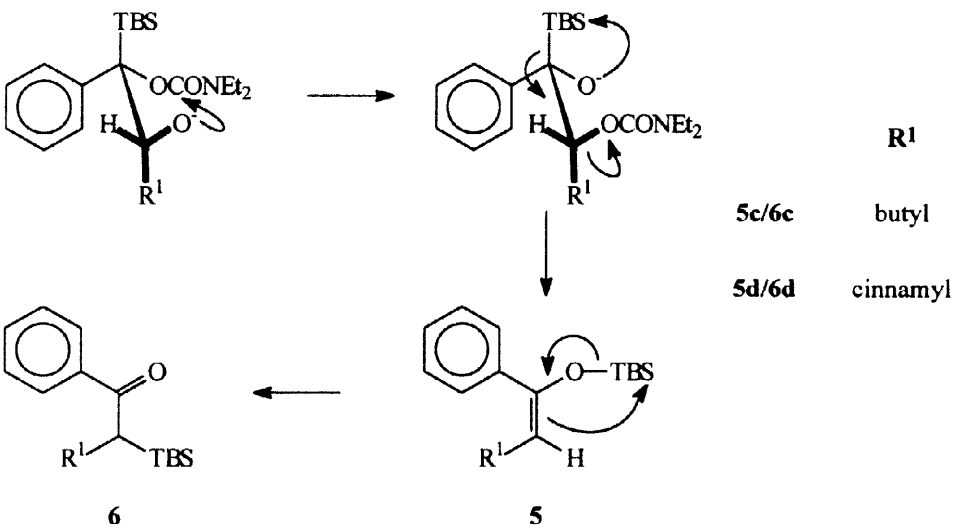
Figure 1



3e

Figure 2

The reaction of aliphatic aldehydes with 1-*t*butyldimethylsilyl-1-*N,N*-diethylcarbamoyloxy-1-phenylmethane **1b** gave good Z-selectivity in moderate yields (Scheme 1, Table 4). A possible explanation for the reduced yields observed with these aliphatic (relative to the aromatic) electrophiles could be that the silyl benzyl carbamate anion is acting as a base, abstracting the acidic proton α to the carbonyl in the aliphatic electrophiles, thereby quenching itself.[24] This would also explain why the ketones, 4-methylpent-2-one and octan-2-one did not yield any olefin products when reacted with **1b**, while citral gave a complex mixture of products. In addition to the olefin products, the silyl enol ethers **5** (Scheme 2), which rapidly rearrange to α-silylcarbonyl compounds **6**,[25] were isolated when **1b** was reacted with butanal **2c** or cinnamaldehyde **2d** (Table 4). Optimum yields of **5**, and ultimately **6**, were obtained when the reaction with **2c** was allowed to proceed at ambient temperature (Table 4, entry 1) or refluxed (entry 2). Lowering the reaction temperature adversely affected the yield of **5**, while significantly enhancing the Z-selectivity of the olefin product (Table 4, entry 3).



Scheme 2

Table 4: Peterson olefination results for aliphatic electrophiles.

	Substrate	Electrophile	Solvent	Base[a]	Time/hrs	Yield[9]/%		E:Z[19]
						3	5 and 6	of 3
1	1b	**2c**	Et_2O	*t*BuLi	5	33	13	20:80
2	1b	**2c**	Et_2O	*t*BuLi	5	41[c]	11[c]	12:88
3	1b	**2c**	Et_2O	*t*BuLi	5	31[b]	0[b]	<1:99
4	1b	**2d**	Et_2O	*t*BuLi	5	59	3	35:65

a 1.2 eq. of base was used. **b** Reaction allowed to proceed at -78°C. **c** Reaction was refluxed for the indicated time.

We propose that **5** and **6** are obtained in a competing reaction *via* a carbamate migration[26] onto the oxygen anion, followed by a Brook rearrangement[25] (Scheme 2). The formation of **5** is attributed to the increased stability of the β-hydroxysilyl intermediate when the benzyl carbamate is reacted with aliphatic aldehydes.[2,4] We propose that the rate of silyl migration and O-Si elimination is rapid in the aromatic systems, so that none of the products (**5** and **6**) derived from the competing carbamate migration is observed. These α-silylcarbonyl

compounds **6**, which are reportedly[11] difficult to prepare, have been converted to the olefins *via* α-hydroxysilanes using either Grignard reagents, organolithiums or DIBAH.[2,11]

Based on the results obtained by Bassindale and co-workers[8b] and our initial investigations of this olefination with **1a**, which showed capricious E-selectivity [27] compared with the good Z-selectivity obtained with **1b**; we investigated the effect of the bulk of the silyl functionality on the selectivity of the reaction (Scheme 1, Table 5). The difficulties experienced in preparing 1-*N,N*-diethylcarbamoyloxy-1-phenyl-1-trimethylsilylmethane **1a** did, however, preclude its use in further investigations.[24] Instead the use of 1-*N,N*-diisopropylcarbamoyloxy-1-phenyl-1-trimethylsilylmethane **1d** and 1-*N,N*-diethylcarbamoyloxy-1-phenyl-1-triphenyl-silylmethane **1c** was investigated with a view to obtaining improved E- and Z-selectivity, respectively. It was envisaged that the increased steric bulk of the *N,N*-diisopropyl functionality relative to the *N,N*-diethyl functionality, would further enhance the E-selectivity. Contrary to our expectations, variable E-selectivity was recorded with **1d** (Table 5, entries 1-6). These results are in agreement with previous results for trimethylsilyl benzyl substrates.[8]

Table 5: Results of the Peterson olefination on varying the bulk of the silyl group.

	Substrate	Product	Solvent	Base[a]	Time/hrs	Yield[b,9]/%	E:Z[19]
from Table 1	1b	**3a**	Et_2O	^{t}BuLi	3	73[c]	4:96
1	1d	**4a**	Et_2O	^{t}BuLi	5	76[d]	9:91
2	1d	**4a**	THF	^{t}BuLi	5	73[d]	66:34
3	1d	**4c**	Et_2O	^{t}BuLi	5	63[d]	52:48
4	1d	**4c**	THF	^{t}BuLi	5	65[d]	30:70
from Table 2	1b	**3e**	Et_2O	^{t}BuLi	5	80[e]	20:80
5	1d	**4e**	Et_2O	^{t}BuLi	5	43	43:66
6	1d	**4e**	THF	^{t}BuLi	5	35	42:58
from Table 2	1b	**3b**	THF	^{t}BuLi	24	70[e]	84:16
7	1c	**3b**	THF	^{t}BuLi	6	46	16:84
8	1c	**3b**	THF	^{t}BuLi	4	49[f]	13:87
9	1c	**3b**	THF	^{t}BuLi	4	63[g]	14:86
10	1c	**3b**	THF	^{n}BuLi	4	72[g]	13:87
from Table 2	1b	**3f**	Et_2O	^{t}BuLi	5	65[e]	23:77
11	1c	**3f**	THF	^{t}BuLi	5	43	9:91
12	1c	**3f**	THF	^{n}BuLi	4	65[g]	12:88
13	1c	**3g**	THF	^{n}BuLi	4	73[g]	13:86

a 1.2 eq. base. **b** Reactions warmed to room temperature following the addition of the electrophile at -78°C. **c** See Table 1 for details. **d** Corrected yields. **e** See Table 2 for details. **f** Reaction mixture was refluxed for the indicated time following the electrophile addition at -78°C, 45 min after formation of the anion at this temperature. **g** As in f, but anion was generated at 0°C.

As a consequence of the insolubility of **1c** in diethyl ether, the reactions of this substrate with selected electrophiles were carried out in THF. Using the optimum reaction conditions in THF, we observed good Z-selectivity, in moderate yield (Table 5, entry 7), when **1c** was reacted with **2b**. The yield of **3b** was improved

when the reaction mixture was refluxed, subsequent to generating the anion at 0°C rather than at -78°C (entries 8 and 9). A further improvement in yield was observed when the less bulky ^{n}BuLi was used as the base (entry 10). Similar effects were observed for **3f** and **3g** (entries 11-13).

We observed that with the use of **1c** the Z-selectivity was improved in the instances where unsatisfactory Z-selectivity or exclusive E-selectivity had been obtained previously. These results are in agreement with the results and proposed stepwise mechanistic model of Bassindale and co-workers.[8c,28] The observed Z-selectivity could also be explained by a "butterfly" transition state analogous to the model proposed for the Peterson olefination of silyl phosphonates,[7] with the carbamate group co-ordinating to the anion in a manner similar to that of the phosphonate. Both the stepwise and "butterfly" models propose that an increase in the steric bulk of the silyl functionality leads to a decrease in the E:Z ratio. For the TPS group this might be attributed to increased electronic interactions between this functionality and the electrophile in the E-transition state, favouring the Z-isomer.

These proposed stepwise mechanistic models do not make allowances for the observed variation in E/Z-selectivity in different solvents (Table 1). A further consideration might be the dipole moments of the respective isomers relative to the solvent. It has been proposed by Dimroth that,[29] for example, the more dipolar *cis*-aziridine would be the more stable isomer in polar solvents, while the reverse would be true for the less dipolar *trans*-aziridine. Similar effects have been reported for conformational equilibria. Larson and co-workers[13] report that the additions of various complexing agents, *e.g.* TMEDA, HMPA and 12-crown-4, result in increased Z-selectivity for the Peterson olefination of α-lithio-α-silyl esters. MM+ single point calculations[30] of the dipole moments of the E- and Z-isomers of ethyl 4-methylpent-2-enoate[13] showed that the respective dipole moments were 2.64 and 2.80 D. Considering the greater dipole moment of HMPA (5.5 D[31] or 2.33 D[30]) relative to that of TMEDA (1.10 D[32,30]), the increased Z-selectivity observed in HMPA[13] is not surprising. These solvent effects might explain some of the observed selectivities. The theoretical dipole moments for the E- and Z-isomers of **3a** are 3.73 and 3.50 D, respectively (Table 3).[30] Ignoring all other effects enhanced E-selectivity in the presence of HMPA (Table 1, entries 8 and 9) is not unexpected. A less marked effect is observed in THF than diethyl ether, which might be attributed to the co-ordination of THF. As reported by Larson and co-workers,[13] the selectivity towards the isomer with the greater dipole moment was not as marked when TMEDA was used as the co-solvent (Table 1, entries 10-12).

The theoretical dipole moments (Table 3) indicate that with the exception of **3b**, **3d**, **3e**, and **3k**, the E-isomers have greater dipole moments than the Z-isomers. If the dipole moments of diethyl ether (1.15 D[31] or 1.29 D[30]) and THF (1.75 D[31] or 1.32 D[30]) are considered, the Z-selectivity obtained in diethyl ether as opposed to THF (Table 1) could be attributed to solvent effects. Solvent effects do however not explain the increased E-selectivity of **3b** and **3k** in THF (Table 2, entries3-5 and 11). In these instances we believe that the electronic effects described earlier predominate. The dipole moments of the Z-isomers are of the same order of magnitude, therefore it is proposed that an even less polar solvent than diethyl ether would enhance the E-selectivity of **3e**. The poor selectivity observed for **3d** (Table 4, entry 4) is explained by the insignificant difference between the dipole moments of the isomers suggesting that the selectivity of this product would be insensitive to solvent effects.

The good E-selectivity of the Peterson olefination of α-methoxybenzyl silanes,[33] in contrast to the poor selectivity reported previously with trimethylsilyl benzyl substrates,[8] could be attributed to the solvent system which was used. The calculated dipole moments of the E- and Z-isomers of 1-methoxy-1-phenyl-2-(2″-

thiophene)ethene[33] are 2.49 and 2.65 D,[30] respectively. The relatively small dipole moment of TMEDA may be an explanation for the good E-selectivity observed with these vinyl ethers.

The E- and Z-isomers were separated by silica gel chromatography and fully characterised by NMR spectroscopy. The isomers were assigned based on nOe experiments. Saturating the vinyl proton gave a nOe with the phenyl ring α to the carbamate for the Z-isomers, which would clearly be absent in the E-isomer (Figure 3). The vinyl proton for the Z-isomer had a ^{1}H NMR shift *ca.* 0.2 ppm downfield from the E-isomer for the examples studied. These findings were in agreement with the relative predicted shifts for the E- and Z-isomers[34] and those reported for the analogous vinyl ethers.[33] The ^{13}C NMR shift for C-2 (β to the carbamate functionality) of the E-isomers was recorded *ca.* 2 ppm downfield from the corresponding signal for the Z-isomer in the examples studied. According to the predictions of Kimmelma and Toivo[35] for analogous CH ^{13}C NMR signals β to a heteroatom, these relative shifts indicate that the conjugation in the E-isomers is weaker than in the Z-isomers.

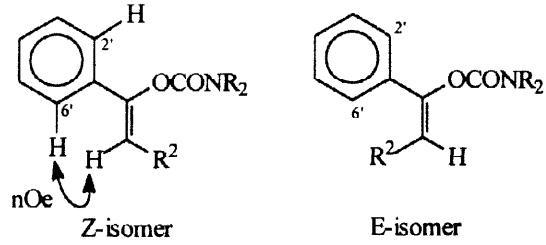


Figure 3

Crystal structures for the E- and Z-isomers (Figure 4 and 5, respectively) of **3a** show that for the E-isomer the phenyl ring α to the carbamate is out of the plane (less conjugated) with dihedral angles of 64.6° between the aromatic planes and 98.6° between the phenyl and olefin planes. In contrast, only a slight deviation from planarity is observed for the Z-isomer with an angle of 14.6° between the phenyl and 3,4-methylenedioxyphenyl planes and a 19.6° angle between the phenyl and olefin planes. Another interesting observation regarding the crystal structure of the Z-isomer of **3a** (Figure 5) is the distortions of the sp^2 bond angles. The angle[36] H1-C2-C3 is 95.7°, with the remaining two angles about C2 being of the order of 130° - a significant deviation from the idealised value of 120°. A similar deviation is observed for the C1-C2-C11 angle which is 130.1° in the Z-isomer of **3b** (Figure 6). These results suggest that in an attempt to have a fully conjugated, thermodynamically stable system, the Z-isomers (*e.g.* in **3a** and **3b**) have distorted sp^2 angles to avoid extreme deviations from planarity, which would diminish the extent of conjugation. The UV spectra of

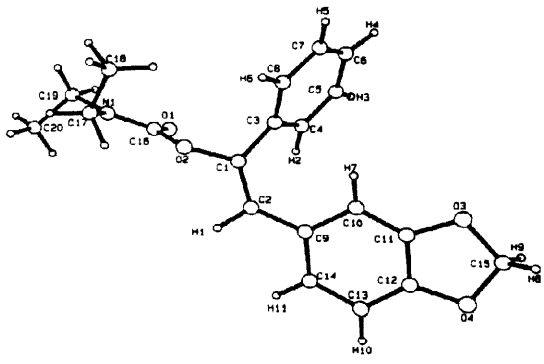


Figure 4

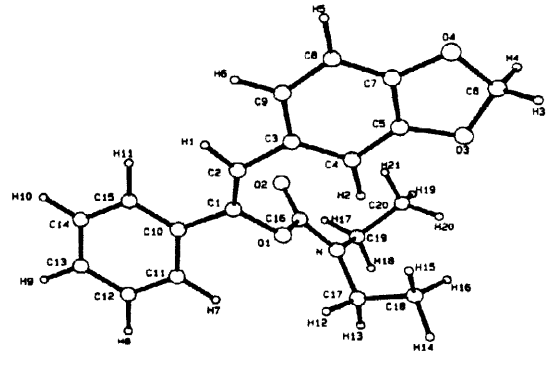


Figure 5

the E- and Z-isomers of **3a** indicate a bathochromic shift (20 nm) for the Z-isomer relative to the E-isomer in acetonitrile. The crystal structures of **3a** in combination with these UV spectra confirm that the conjugation in the E-isomer is weaker than in the Z-isomer which, based on the proposals of Kimmelma and Toivo,[35] is in agreement with our NMR observations for all the examples studied.

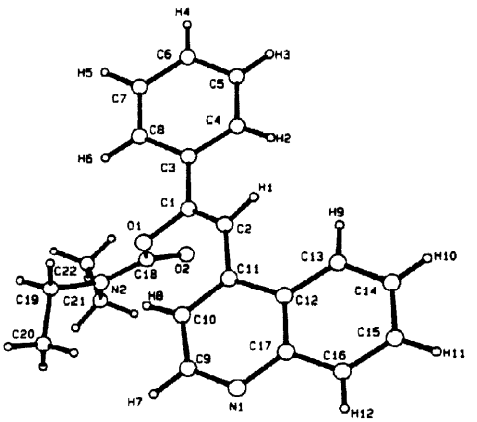


Figure 6

From the crystal structure and molecular modelling experiments for the Z-isomer of **3a**, it is evident that one ethyl group is in closer proximity to the aromatic substituent. Though we realise that the behaviour of the molecule in the solid state, a rigid medium, is not identical to its behaviour in solution, distinct signals are observed for the diethyl groups on the carbamate functionality[37] in the solution NMR spectra of the Z-isomers studied (the exception being **3b**). This is a further manifestation of the spatial arrangement of these Z-isomers resulting in restricted rotation of the *N,N*-diethyl group placing these ethyl groups in different magnetic environments. As a consequence of this restricted rotation about the amide bond of the carbamate, a *ca.* 0.2 ppm upfield shift for the *N*-Et protons shielded by the aromatic ring was observed. We therefore propose that the solution conformations of the compounds studied do not deviate substantially from their solid state and proposed gas phase conformations. Furthermore, the crystal structures of the E-isomer of **3a** and the Z-isomers of **3a** and **3b** confirm the nOe results for the assignments of the E- and Z-isomers (Figures 4 - 6).

The ^{1}H NMR spectra of these olefins are particularly interesting since the spectra obtained for the E- and Z-isomers are so distinct. The unusual ^{1}H spectrum obtained for the E-isomer of the 3,4-methylenedioxyphenyl system **3a**, led to some debate regarding the structure elucidation of this product. The ^{1}H NMR of the E-isomer of **3a** run in $CDCl_3$ did not show the expected *ortho* splitting between the H-5″ and H-6″ on the 3,4-methylenedioxyphenyl-ring, which was visible in the Z-isomer. The same effect, that is an absence of *ortho* splitting, was observed when a very concentrated sample of this isomer was run in C_6D_6. A diluted sample of the E-isomer of **3a** in C_6D_6 did, however, show the expected splitting pattern for the 3,4-methylenedioxy-system. Confirmation of the structure was obtained from the crystal structure (Figure 4). It therefore appears that in $CDCl_3$ the 3,4-methylenedioxyphenyl group shows degenerate signals for H-5″ and H-6″ in the ^{1}H NMR spectrum.[38] The ^{13}C NMR signal for C-2′,-6′ (of the phenyl ring α to the carbamate) is distinct at *ca.* 129 and 124 ppm in the E- and Z-isomers, respectively, of the examples studied.

We have reported an efficient preparation of Z-selective vinyl carbamates *via* the Peterson olefination. It is evident that solvent effects enhance the Z-selectivity of the 1-^{t}butyldimethylsilyl-1-*N,N*-diethylcarbamoyloxy-1-phenylmethane **1b** system. Optimum Z-selectivity is obtained when 1-*N,N*-diethylcarbamoyloxy-1-phenyl-1-triphenylsilylmethane **1c** is used. In the latter case the steric/electronic bulk of the triphenylsilyl-moiety appears to be the overriding factor promoting Z-selectivity.

Acknowledgements: The Authors wish to thank Prof. N. de Kimpe for useful discussions regarding the structural elucidation of **3a**, Miss N. Ramesar for assistance with the crystal structures, and P. H. Mason and O. Q. Munro for discussions regarding the molecular modelling. We also thank the University of Natal and the FRD for financial assistance.

Experimental

General: Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian Gemini-200 instrument. The NMR spectra were recorded as solutions in the specified solvents and are reported in parts per million (ppm, δ) downfield from internal tetramethylsilane (TMS). Mass spectra were recorded on a Hewlett-Packard gas chromatographic mass spectrometer (HP5988), using electron ionisation at 70eV. High resolution mass spectrometry (HRMS) was performed on a Kratos MS 9/50 instrument. Analytical GC analyses were performed on a Varian 3300 instruments fitted with a 15m DB-1 column. Elemental analyses were performed on a Perkin-Elmer 2400 CHN instrument. X-ray crystallography was carried out on an Enraf Nonius CAD-4 diffractometer and solved using ShelX 76 and 93.

THF and diethyl ether were twice distilled over sodium/potassium amalgam under a nitrogen atmosphere. All reagents were dried using standard techniques and distilled prior to use. The glassware was flame dried and all the reactions were carried out under a nitrogen atmosphere. Silica gel chromatography was performed by centrifugal thin layer chromatography on Merck silica gel 60 (230-400 mesh).

Molecular Mechanics Calculations: Energy-optimised geometries were obtained using the MM+ force field of Hyperchem[30] with a refinement termination criterion of 0.05 kcal.mol^{-1} (Polak-Ribiere conjugate gradient algorithm). Structural parameters and molecular dipole moments were obtained from single-point calculations on all minimum energy conformations.

General procedure A for the preparation of silylated benzyl carbamates :[39] To a solution of benzyl carbamate (1 eq.) and silyl chloride (1 eq.), in anhydrous THF, cooled to -78°C (acetone/CO_2) under an atmosphere of nitrogen, ^{n}BuLi (2.2 eq.) was added dropwise. After stirring at this temperature for 2 hrs the reaction was quenched with saturated NH_4Cl and allowed to warm to room temperature. The reaction mixture was extracted with diethyl ether, dried over anhydrous $MgSO_4$ and concentrated in *vacuo* to afford the crude products which were purified by distillation or chromatography.

1-*N,N*-Diethylcarbamoyloxy-1-phenyl-1-trimethylsilylmethane (1a)[40]

The above procedure was modified for the preparation of the title compound so that the formation of *bis*-silylated products[24] from benzyl *N,N*-diethylcarbamate[41] and trimethylsilyl chloride could be minimised. LDA (1.2 eq.) was added to a solution of the benzyl carbamate in anhydrous THF, cooled to -78°C (acetone/CO_2), followed by the rapid addition of trimethylsilyl chloride after 30 min. The reaction mixture was stirred at this temperature for a further 30 min before it was quenched with saturated NH_4Cl and allowed to warm to room temperature. The workup was as described previously. Purification by flash chromatography eluting with 10% Et_2O/hexane yielded the desired product as a colourless oil (34%); δ_H (200 MHz; $CDCl_3$) 0.02 [9H, s, -

Si(C$\underline{H}_3$)$_3$], 1.15 [6H, br, -OCON(CH$_2$C$\underline{H}_3$)$_2$], 3.49 (4H, br, -OCON(C$\underline{H}_2$CH$_3$)$_2$], 5.55 (1H, s, H-1), 7.13 (3H, c, H-3′, H-4′ and H-5′) and 7.25 (2H, c, H-2′ and H-6′); δ_C (50 MHz; $CDCl_3$) -3.80 [3 x CH_3, -Si($\underline{C}H_3$)$_3$], 13.58 [CH_3, -OCON(CH$_2$$\underline{C}H_3$)$_2$], 14.21 [$CH_3$, -OCON(CH$_2$$\underline{C}H_3$)$_2$], 41.45 [$CH_2$, -OCON($\underline{C}H_2CH_3$)$_2$], 42.01 [$CH_2$, -OCON($\underline{C}H_2CH_3$)$_2$], 71.96 (CH, C-1), 124.94 (2 x CH, C-3′ and C-5′), 125.79 (CH, C-4′), 128.13 (2 x CH, C-2′ and C-6′), 140.91 (q, C-1′) and 155.95 [C=O, -O$\underline{C}$ON(CH$_2$CH$_3$)$_2$]; *m/z* (EI) 279 (M^+, <1%), 187 (29), 144 (52), 135 (11), 105 (9), 100 (25), 91 (9), 77 (7), 73 (100) and 72 (35).

1-^{t}Butyldimethylsilyl-1-*N,N*-diethylcarbamoyloxy-1-phenylmethane (1b)[39]

The title compound was prepared by general procedure A, from benzyl *N,N*-diethylcarbamate and ^{t}butyldimethylsilyl chloride. Purification by flash chromatography eluting with 10% Et_2O/hexane yielded the desired product as a pale yellow oil (80%); δ_H (200 MHz; $CDCl_3$) -0.16 [3H, s, -Si(C$\underline{H}_3$)$_2$C(CH$_3$)$_3$], 0.08 [3H, s, -Si(C$\underline{H}_3$)$_2$C(CH$_3$)$_3$], 0.91 [9H, s, -Si(CH$_3$)$_2$C(C$\underline{H}_3$)$_3$], 1.40 [6H, br d, -OCON(CH$_2$C$\underline{H}_3$)$_2$], 3.35 [4H, br, -OCON(C$\underline{H}_2$CH$_3$)$_2$], 5.71 (1H, s, H-1), 7.20 (5H, c, Ar$\underline{H}$); δ_C (50 MHz; $CDCl_3$) -8.48 [CH_3, -Si($\underline{C}$H$_3$)$_2$C(CH$_3$)$_3$], -7.45 [CH_3, -Si($\underline{C}$H$_3$)$_2$C(CH$_3$)$_3$], 13.50 [CH_3, -OCON(CH$_2$$\underline{C}H_3$)$_2$], 14.29 [$CH_3$, -OCON(CH$_2$$\underline{C}H_3$)$_2$], 16.97 [q, -Si(CH$_3$)$_2$$\underline{C}$(CH$_3$)$_3$], 26.79 [3 × CH_3, -Si(CH$_3$)$_2$C($\underline{C}$H$_3$)$_3$], 41.41 [CH_2, -OCON($\underline{C}$H$_2$CH$_3$)$_2$], 41.85 [CH_2, -OCON($\underline{C}$H$_2$CH$_3$)$_2$], 70.00 (CH, C-1), 125.60 (2 x CH, C-3′ and C-5′), 125.95 (CH, C-4′), 128.13 (2 x CH, C-2′ and C-6′), 141.50 (q, Ar$\underline{C}$) and 155.75 [C=O, -O$\underline{C}$ON(CH$_2$CH$_3$)$_2$].

1-*N,N*-Diethylcarbamoyloxy-1-phenyl-1-triphenylsilylmethane (1c)

The title compound was prepared by general procedure A from benzyl *N,N*-diethylcarbamate and triphenylsilyl chloride. The crude product mixture afforded the desired product as colourless prisms after recrystallisation (50% yield); mp 120-122°C (from EtOAc/hexane); (Found: C, 77.2; H, 6.9; N, 2.9; $C_{30}H_{31}NO_2Si$ requires C, 77.4; H, 6.7; N, 3.0%); δ_H (200 MHz; $CDCl_3$) 0.96 [6H, br, -OCON(CH$_2$C$\underline{H}_3$)$_2$], 3.18 [4H, br m, -OCON(C$\underline{H}_2$CH$_3$)$_2$], 6.39 (1H, s, H-1), 6.93 (2H, c, H-2′ and H-6′), 7.10 (3H, c, H-3′, H-4′ and H-5′) and 7.39 [15H, m, -Si(C$_6$$\underline{H}_5$)$_3$]; δ_C (50 MHz; $CDCl_3$) 13.52 [CH_3, -OCON(CH$_2$$\underline{C}H_3$)$_2$], 13.84 [$CH_3$, -OCON(CH$_2$$\underline{C}H_3$)$_2$], 41.22 [$CH_2$, -OCON($\underline{C}H_2CH_3$)$_2$], 42.05 [$CH_2$, -OCON($\underline{C}H_2CH_3$)$_2$], 69.87 (CH, C-1), 126.47 (CH, C-4′), 127.21 (2 x CH, C-2′ and C-6′), 127.72 [6 x CH, -Si($\underline{C}_6$H$_5$)$_3$], 127.81 (2 x CH, C-3′ and C-5′), 129.81 [3 x CH, -Si($\underline{C}_6$H$_5$)$_3$], 132.09 [3 x q, -Si($\underline{C}_6$H$_5$)$_3$], 136.35 [6 x CH, -Si($\underline{C}_6$H$_5$)$_3$], 139.27 (q, C-1′) and 155.75 [C=O, -O$\underline{C}$ON(CH$_2$CH$_3$)$_2$]; *m/z* (EI) 277 (8%), 276 (30), 199 (100), 152 (19), 122 (30) and 77 (35).

1-*N,N*-Diisopropylcarbamoyloxy-1-phenyl-1-trimethylsilylmethane (1d)[39]

The title compound was prepared by general procedure A from benzyl *N,N*-diisopropylcarbamate and trimethylsilyl chloride. Purification by flash chromatography eluting with 10% Et_2O/hexane afforded the desired product as a pale yellow oil (70%); δ_H (200 MHz; $CDCl_3$) 0.01 [9H, s, -Si(C$\underline{H}_3$)$_3$], 1.23 {12H, br, -OCON[CH(C$\underline{H}_3$)$_2$]$_2$}, 3.93 {2H, br, -OCON[C$\underline{H}$(CH$_3$)$_2$]$_2$}, 5.58 (1H, s, H-1) and 7.19 (5H, c, Ar$\underline{H}$); δ_C (50 MHz; $CDCl_3$) -3.67 [3 x CH_3, -Si($\underline{C}$H$_3$)$_3$], 20.81 {4 × CH_3, -OCON[CH($\underline{C}$H$_3$)$_2$]$_2$}, 45.90 {2 x CH, -OCON[$\underline{C}$H(CH$_3$)$_2$]$_2$}, 71.92 (CH, C-1), 125.11 (2 x CH, Ar$\underline{C}$), 125.63 (CH, Ar$\underline{C}$), 128.01 (2 x CH, Ar$\underline{C}$), 140.90 (q, Ar$\underline{C}$) and 155.43 {C=O, -O$\underline{C}$ON[CH(CH$_3$)$_2$]$_2$}.

General procedure B for olefin preparation: A solution of 1-^{t}butyldimethylsilyl-1-*N,N*-diethylcarbamoyloxy-1-phenylmethane **1b** (1 mmol) in anhydrous Et_2O or THF (5 ml) was cooled to -78 °C (acetone / solid CO_2) under an atmosphere of nitrogen with stirring. ^{t}BuLi (1.2 eq.) was added slowly and the mixture stirred at this temperature for 45 minutes. A solution of the electrophile (2 eq.) in the selected solvent (3 ml) was added to the reaction mixture, *via* a cannula. The reaction mixture was maintained at this

temperature or warmed to room temperature as reported and stirred for a further 5 hours (unless stated otherwise) before is was quenched with a saturated aqueous NH_4Cl solution and extracted with Et_2O (3 × 10 ml). The combined ether extracts were dried over $MgSO_4$, filtered and the solvent evaporated to yield the crude reaction mixture, which was purified by centrifugal thin layer silica gel chromatography as indicated.

General procedure C for olefin preparation: A solution of 1-*N,N*-diethylcarbamoyloxy-1-phenyl-1-triphenylsilylmethane **1c** (1 mmol) in anhydrous THF (5 ml) was cooled to 0°C (ice / water) under an atmosphere of nitrogen with stirring. ^{n}BuLi (1.2 eq.) was added slowly and the mixture stirred at this temperature for 45 minutes. A solution of the electrophile (2 eq.) in anhydrous THF (3 ml) was added to the reaction mixture, *via* a cannula, which was subsequently refluxed under a nitrogen atmosphere for a further 4 hours (unless stated otherwise). The reaction mixture was allowed to cool to room temperature over an hour, prior to quenching with a saturated aqueous NH_4Cl solution and extracting with Et_2O (3 × 10 ml). The combined ethereal extracts were dried over $MgSO_4$, filtered and the solvent evaporated to yield the crude reaction mixture, which was purified by centrifugal thin layer silica gel chromatography as indicated.

General procedure D for olefin preparation: As for general procedure B, using 1-*N,N*-diisopropylcarbamoyloxy-1-phenyl-1-trimethylsilylmethane **1d** as the substrate.

(*E*)-1-*N,N*-Diethylcarbamoyloxy-2-(3'', 4''-methylenedioxyphenyl)-1-phenylethene (3a)

The title compound was prepared by general procedure B, using 3,4-methylenedioxybenzaldehyde as the electrophile. Optimum *E*-selectivity was obtained when the solvent used was THF. Purification by silica gel chromatography eluting with a 10-30% Et_2O/hexane gradient enabled the separation of the title compound as colourless needle-like crystals, from its geometric isomer (79% olefin yield, *E*:*Z* = 39:61); mp 74-75°C (from C_6H_6/ Et_2O/ hexane); (Found: C, 71.1; H, 6.4; N, 4.2; $C_{20}H_{21}NO_4$ requires C, 70.8; H, 6.2; N, 4.1%); δ_H (200 MHz; $CDCl_3$) 1.12 [3H, t, *J* 6.9, -OCON($CH_2C\underline{H}_3$)$_2$], 1.21 [3H, t, *J* 7.0, -OCON($CH_2C\underline{H}_3$)$_2$], 3.33 [4H, c, -OCON($C\underline{H}_2CH_3$)$_2$], 5.84 (2H, s, H_2-7''), 6.39 (1H, s, H-2), 6.54 (1H, dd, *J* 1.62 and 1.05, H-2''), 6.63 (2H, d, *J* 1.1, H-5'' and H-6''), 7.27 (3H, c, H-3', H-4' and H-5') and 7.38 (2H, c, H-2' and H-6'); nOe 6.39 ppm (interacts with H-2'' and H-6'') and 5.84 ppm (interacts with H-2'' and H-5''); δ_C (50 MHz; $CDCl_3$) 13.19 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.16 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.60 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 41.83 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 100.72 (CH_2, C_2-7''), 107.94 (CH, C-5''), 108.64 (C-2''), 119.04 (CH, C-2), 122.98 (CH, C-6''), 128.19 (2 × CH, C-3' and C-5'), 128.44 (CH, C-4'), 128.47 (q, C-1''), 128.62 (2 × CH, C-2' and C-6'), 135.02 (q, C-1'), 146.35 (q, C-4''), 146.95 (q, C-1), 147.16 (q, C-3'') and 153.99 [C=O, -O$\underline{C}$ON(CH_2CH_3)$_2$]; δ_H (200 MHz; C_6D_6) 0.89 [6H, br, -OCON($CH_2C\underline{H}_3$)$_2$], 3.06 [4H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 5.21 (2H, s, H_2-7''), 6.44 (1H, d, *J* 7.96, H-5''), 6.53 (1H, s, H-2), 6.60 (1H, ddd, *J* 8.0, 1.7 and 0.7, H-6''), 6.67 (1H, d, *J* 1.7, H-2''), 7.02 (3H, c, H-3', H-4' and H-5') and 7.58 (2H, c, H-2' and H-6'); nOe 6.53 ppm (interacts with H-2''); δ_C (50 MHz; C_6D_6) 14.00 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.97 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 42.33 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.63 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 101.39 (CH_2, C_2-7''), 108.91 (CH, C-5''), 109.65 (CH, C-2''), 120.46 (CH, C-2), 124.06 (CH, C-6''), 129.06 (2 x CH, C-3' and C-5'), 129.25 (CH, C-4'), 129.76 (q, C-1''), 129.97 (2 x CH, C-2' and C-6'), 136.65 (q, C-1'), 147.59 (q, C-1), 148.36 (q, C-4''), 148.52 (q, C-3'') and 154.46 [C=O, -O$\underline{C}$ON(CH_2CH_3)$_2$]; *m/z* (EI) 340 (M^++1, 6%), 339 (M^+, 28), 165 (3), 152 (4), 100 (100), 77 (3) and 72 (35); UV (CH_3CN) 210 nm (ε = 32107 $M^{-1}cm^{-1}$) and 302 nm (ε = 10529 $M^{-1}cm^{-1}$).

(*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-2-(3″, 4″-methylenedioxyphenyl)-1-phenylethene (3a)

The title compound was prepared by general procedure B, using 3,4-methylenedioxybenzaldehyde as the electrophile. Optimum *Z*-selectivity was obtained when the solvent used was Et_2O. Purification by silica gel chromatography eluting with a 10-30% Et_2O/hexane gradient enabled the separation of the title compound as pale yellow plate-like crystals, from its geometric isomer (76% olefin yield, *E*:*Z* = 7:93); mp 125-126 °C (from 20% Et_2O/hexane); (Found: C, 70.8; H, 6.3; N, 4.1; $C_{20}H_{21}NO_4$ requires C, 70.8; H, 6.2; N, 4.1%); δ_H (200 MHz; $CDCl_3$) 1.14 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 1.31 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 3.34 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 3.56 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 5.92 (2H, s, H_2-7″), 6.57 (1H, s, H-2), 6.76 (1H, d, *J* 8.1, H-5″), 6.94 (1H, ddd, *J* 8.1, 1.7 and 0.6, H-6″), 7.08 (1H, d, *J* 1.7, H-2″), 7.31 (3H, c, H-3′, H-4′ and H-5′) and 7.49 (2H, c, H-2′ and H-6′); nOe 6.57 ppm (interacts with H-2′, H-6′, H-2″ and H-6″) and 5.92 ppm (interacts with H-2″); δ_C (50 MHz; $CDCl_3$) 13.28 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.50 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.68 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 41.96 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 101.05 (CH_2, C_2-7″), 108.25 (CH, C-5″), 108.35 (CH, C-2″), 116.46 (CH, C-2), 123.34 (CH, C-6″), 124.56 (2 × CH, C-2′ and C-6′), 128.14 (CH, C-4′), 128.55 (2 × CH, C-3′ and C-5′), 128.84 (q, C-1″), 136.66 (q, C-1′), 145.71 (q, C-1), 146.83 (q, C-4″), 147.72 (q, C-3″) and 152.99 [C=O, -O$\underline{C}$ON(CH_2CH_3)$_2$]; *m/z* (EI) 340 (M^++1, 10%), 339 (M^+, 49), 152 (4), 100 (100), 77 (3) and 72 (32). ($\varepsilon = m^2.mol^{-1}$); UV ($CH_3CN$) 320 nm ($\varepsilon$ = 22243 $M^{-1}cm^{-1}$), 299 nm (ε = 19660 $M^{-1}cm^{-1}$) and 220 nm (ε = 15935 $M^{-1}cm^{-1}$).

(*E*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(4″-quinolyl)ethene (3b)

The title compound was prepared by general procedure B and C, using 4-quinolinecarboxaldehyde as the electrophile. Optimum *E*-selectivity was obtained with general procedure B in THF (24 hours). Purification by silica gel chromatography eluting with a 30-70% Et_2O/hexane gradient enabled the separation of the title compound as a yellow oil, from its geometric isomer (70% olefin yield, *E*:*Z* = 84:16); δ_H (200 MHz; $CDCl_3$) 1.18 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 1.30 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 3.37 [2H, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 3.50 [2H, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 6.89 (1H, d, *J* 1.1, H-2), 7.06 (1H, dd, *J* 4.5 and 1.1, H-3″), 7.21 (5H, m, Ar$\underline{H}$), 7.55 (1H, ddd, *J* 8.3, 6.9 and 1.3, H-6″), 7.72 (1H, ddd, *J* 8.4, 6.9 and 1.5, H-7″), 8.11 (1H, ddd, *J* 8.4, 1.3 and 0.6, H-8″), 8.20 (1H, ddd, *J* 8.3, 1.5 and 0.6, H-5″) and 8.66 (1H, d, *J* 4.5, H-2″); nOe 8.66 ppm (interacts with H-3″ and H-2), 6.89 ppm (interacts with H-3″ and H-5″), 8.11 ppm (no interaction) and 8.20 ppm (interacts with H-2); δ_C (50 MHz; $CDCl_3$) 13.28 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.32 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.79 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.07 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 114.70 (CH, C-2), 121.53 (CH, C-3″), 124.90 (CH, C-5″), 126.63 (CH, C-6″), 127.06 (q, C-4a″), 128.23 (4 × CH, C-2′, C-3′, C-5′ and C-6′), 128.95 (CH, C-4′), 129.49 (CH, C-7″), 129.64 (CH, C-8″), 134.04 (q, C-1′), 141.63 (q, C-4″), 148.22 (q, C-8a″), 149.81 (CH, C-2″), 151.04 (q, C-1) and 153.69 [C=O, -O$\underline{C}$ON(CH_2CH_3)$_2$]; *m/z* (EI) 347 (M^++1, <1%) 346 (M^+, 2), 114 (2), 101 (7), 100 (100), 77 (4) and 72 (48); HRMS Found: 346.1695, $C_{22}H_{22}N_2O_2$ requires 346.1681.

(*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(4″-quinolyl)ethene (3b)

The title compound was prepared by general procedures B and C, using 4-quinolinecarboxaldehyde as the electrophile. Optimum *Z*-selectivity was obtained using general procedure C. Purification by silica gel chromatography eluting with a 30-70% Et_2O/hexane gradient enabled the separation of the title compound as pale yellow needle-like crystals, from its geometric isomer (72% olefin yield, *E*:*Z* = 13:87); mp 105°C (from Et_2O, CH_2Cl_2 and hexane); (Found: C, 76.2; H, 6.4; N, 8.0; $C_{22}H_{22}N_2O_2$ requires C, 76.3; H, 6.4; N, 8.1%); δ_H

(200 MHz; $CDCl_3$) 1.01 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 1.03 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 3.22 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.28 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 7.15 (1H, s, H-2), 7.43 (3H, c, H-3′, H-4′ and H-5′), 7.53 (1H, dd, *J* 4.6 and 0.8, H-3″), 7.53 (1H, c, H-6″), 7.67 (3H, c, H-2′, H-6′ and H-7″), 8.09 (1H, dd, *J* 8.4 and 1.2, H-5″), 8.15 (1H, dd, *J* 8.4 and 0.8, H-8″) and 8.87 (1H, d, *J* 4.6, H-2″); nOe 8.87 ppm (interacts with H-3″) and 7.15 ppm (interacts with H-2′, H-6′ and H-5″); δ_C (50 MHz; $CDCl_3$) 13.13 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.19 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.69 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 41.99 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 111.54 (CH, C-2), 120.31 (CH, C-3″), 124.52 (CH, C-5″), 125.18 (2 × CH, C-2′ and C-6′), 126.53 (CH, C-6″), 126.80 (q, C-4a″), 128.73 (2 × CH, C-3′ and C-5′), 129.25 (CH, C-4′), 129.27 (CH, C-7″), 129.84 (CH, C-8″), 135.67 (q, C-1′), 140.35 (q, C-4″), 148.39 (q, C-8a″), 149.82 (CH, C-2″), 150.72 (q, C-1) and 152.83 [C=O, -O$\underline{C}$ON($CH_2CH_3)_2$]; *m/z* (EI) 347(M^++1, 2%) 346 (M^+, 7) 217 (3), 100 (100), 77 (5) and 72 (44); HRMS Found: 346.1691, $C_{22}H_{22}N_2O_2$ requires 346.1681. The structure of the title compound was confirmed by a crystal structure.

(*E*)- and (*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenylpentene (3c)

The title compounds were prepared by general procedure B in Et_2O, using butanal as the electrophile. The yield and *Z*-selectivity was optimum when the reaction was refluxed for 5 hours. Purification by silica gel chromatography eluting with a 0-15% Et_2O/hexane gradient enabled the separation of the title compounds as a colourless liquid, from the by-products (**5c/6c**) (41% olefin yield, *E*:*Z* = 12:88); (Found: C, 73.1; H, 9.4; N, 5.4; $C_{16}H_{23}NO_2$ requires C, 73.5; H, 9.1; N, 5.4%); δ_H (200 MHz; $CDCl_3$) 0.90 (3H-*min*, t, *J* 7.4, H_3-5), 0.96 (3H-*maj*, t, *J* 7.4, H_3-5), 1.15 [3H, t, *J* 7.0, -OCON($CH_2C\underline{H}_3)_2$], 1.27 [3H, t, *J* 7.0, -OCON($CH_2C\underline{H}_3)_2$], 1.49 (2H, sextet, *J* 7.4, H_2-4), 2.15 (2H, q, *J* 7.4, H_2-3), 3.34 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.46 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 5.47 (1H-*min*, t, *J* 7.7, H-2), 5.79 (1H-*maj*, t, *J* 7.4, H-2) and 7.31 (5H, m, Ar$\underline{H}$); nOe 5.47 ppm (no correlation) and 5.79 ppm (interacts with ArH); δ_C (50 MHz; $CDCl_3$) 13.22 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 14.25 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$],13.59 (CH_3-*min*, C_3-5), 13.77 (CH_3-*maj*, C_3-5), 22.12 (CH_2-*maj*, C_2-4), 23.00 (CH_2-*min*, C_2-4), 27.97 (CH_2-*maj*, C_2-3), 29.06 (CH_2-*min*, C_2-3), 41.62 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 41.89 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 117.72 (CH-*maj*, C-2), 119.59 (CH-*min*, C-2), 124.15 (2 × CH-*maj*, C-2′ and C-6′), 127.49 (CH-*maj*, C-4′), 127.74 (CH-*min*, C-4′), 127.82 (2 × CH-*min*, C-3′ and C-5′*), 127.91 (2 × CH-*min*, C-2′ and C-6′*), 128.15 (2 × CH-*maj*, C-3′ and C-5′), 134.91 (q-*min*, C-1′), 135.87 (q-*maj*, C-1′), 146.37 (q, C-1), 153.36 [C=O(*maj*), -O$\underline{C}$ON($CH_2CH_3)_2$] and 154.37 [C=O(*min*), -O$\underline{C}$ON($CH_2CH_3)_2$] ; *m/z* (EI) 262 (M^++1, 1%), 261 (M^+, 5), 145 (2), 128 (2), 105 (20), 100 (100), 91 (6), 77 (28) and 72 (54).

(1*E*, 3*E*)- and (1*Z*, 3*E*)-1-*N*,*N*-diethylcarbamoyloxy-1,4-diphenylbuta-1,3-diene (3d)

The title compounds were prepared by general procedure B in Et_2O, using cinnamaldehyde as the electrophile. Purification by silica gel chromatography eluting with a 5-25% Et_2O/hexane gradient enabled the separation of the title compounds from the by-products (**5d/6d**). Further chromatographic purification eluting with a 10-35% CH_2Cl_2/hexane gradient afforded the title compounds as a orange-yellow oil (59% olefin yield, 1*E*,3*E*:1*Z*,3*E* = 35:65); δ_H (200 MHz; $CDCl_3$) 1.14 [3H-*maj* and 6H-*min*, c, -OCON($CH_2C\underline{H}_3)_2$], 1.32 [3H-*maj*, t, *J* 7.0, -OCON($CH_2C\underline{H}_3)_2$], 3.33 [2H-*maj* and 4H *min*, c, -OCON($C\underline{H}_2CH_3)_2$], 3.51 [2H-*maj*, q, *J* 7.0, -OCON($C\underline{H}_2CH_3)_2$], 6.31 (1H-*min*, d, *J* 11.2, H-2), 6.59 (1H-*maj*, d, *J* 10.8, H-2), 6.62 (1H-*min*, d, *J* 15.6, H-4),

---

* Interchangeable assignment.

6.68 (1H-*maj*, d, *J* 15.7, H-4), 7.00 (1H-*maj*, dd, *J* 15.6 and 10.7, H-3), 7.01 (1H-*min*, ddd, *J* 15.6, 11.1 and 0.6, H-3), 7.28 (8H, m, H-3′, H-4′, H-5′ and Ar″*H*) and 7.49 (2H, m, H-2′ and H-6′); nOe 6.31 ppm [interacts with H-4 (*min*)]; δ_C (50 MHz; $CDCl_3$) 13.39 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.58 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.89 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.17 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 117.22 (CH-*maj*, C-2), 119.88 (CH-*min*, C-2), 122.31 (CH-*maj*, C-3), 123.71 (CH-*min*, C-3), 124.34 (2 × CH-*maj*, C-2′ and C-6′), 126.31 (2 × CH-*min*, C-2″ and C-6″), 126.42 (2 × CH-*maj*, C-2″ and C-6″), 127.67 (CH-*maj*, C-4″), 128.23 (CH-*maj*, C-4′*), 128.29 (2 × CH-*min*, Ar*C*), 128.33 (2 × CH-*min*, Ar*C*), 128.52 (2 × CH, Ar*C*), 128.58 (2 × CH, Ar*C*), 133.50 (CH-*min*, C-4), 133.53 (CH-*maj*, C-4), 135.17 (q-*min*, C-1″), 135.39 (q-*maj*, C-1″), 137.27 (q-*min*, C-1′), 137.31 (q-*maj*, C-1′), 147.00 (q-*maj*, C-1), 148.90 (q-*min*, C-1), 153.40 [C=O-*maj*, -O$\underline{C}$ON(CH_2CH_3)$_2$] and 154.05 [C=O-*min*, -O$\underline{C}$ON(CH_2CH_3)$_2$]; *m/z* (EI) 322 (M^++1, 2%), 321 (M^+, 7), 115 (6), 105 (8), 100 (100), 77 (8) and 72 (40); HRMS Found: 321.1737, $C_{21}H_{23}NO_2$ requires 321.1729.

(*E*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(2″-quinolyl)ethene (3e)

The title compound could not be isolated with a degree of purity allowing full characterisation.

(*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(2″-quinolyl)ethene (3e)

The title compound was prepared by general procedure B in Et_2O, using 2-quinolinecarboxaldehyde as the electrophile. Purification by silica gel chromatography eluting with a 50-80% Et_2O/hexane gradient enabled the separation of the title compound as orange-brown rectangular crystals, from its geometric isomer (80% olefin yield, *E*:*Z* = 20:80); mp 78-79°C (from Et_2O/benzene/hexane); (Found: C, 76.0; H, 6.4; N, 8.3; $C_{22}H_{22}N_2O_2$ requires C, 76.3; H, 6.4; N, 8.1%); δ_H (200 MHz; $CDCl_3$) 1.14 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 1.34 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 3.38 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 3.64 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 7.04 (1H, s, H-2), 7.41 (3H, c, H-3′, H-4′ and H-5′), 7.49 (1H, ddd, *J* 8.1, 6.9 and 1.2, H-6″), 7.67 (4H, c, H-2′, H-6′, H-3″ and H-7″), 7.76 (1H, dd, *J* 8.0 and 1.3, H-5″), 8.02 (1H, dd, *J* 8.6 and 1.2, H-8″) and 8.09(1H, dd, *J* 8.6 and 0.7, H-4″); nOe 7.04 ppm (interacts with H-2′, H-6′ and H-3″); δ_C (50 MHz; $CDCl_3$) 13.36 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.58 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.97 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.18 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 116.98 (CH, C-2), 121.79 (CH, C-3″), 125.26 (2 × CH, C-2′ and C-6′), 126.25 (CH, C-6″), 126.81 (q, C-4a″), 127.37 (CH, C-5″), 128.64 (2 × CH, C-3′ and C-5′),129.15 (CH, C-4′*), 129.18 (CH, C-8″*), 129.44 (CH, C-7″*), 135.88 (CH, C-4″), 136.08 (q, C-1′), 148.12 (q, C-8a″), 150.60 (q, C-1), 153.06 [C=O, -O$\underline{C}$ON(CH_2CH_3)$_2$] and 154.35 (q, C-2″); *m/z* (EI) 347 (M^++1, <1%) 346 (M^+, 2) 227 (10), 217 (4), 100 (100), 77 (5) and 72 (47); HRMS Found: 346.1695, $C_{22}H_{22}N_2O_2$ requires 346.1681.

(*E*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(2″-pyridyl)ethene (3f)

The title compound was prepared using general procedures B and C, using 2-pyridinecarboxaldehyde as the electrophile. Optimum *E*-selectivity was obtained with general procedure B in Et_2O. Purification by silica gel chromatography eluting with a 30-50% Et_2O/hexane gradient enabled the separation of the title compound as a yellow-brown oil, from its geometric isomer (65% olefin yield, *E*:*Z* = 24:76); δ_H (200 MHz; $CDCl_3$) 1.18 [6H, m, -OCON($CH_2C\underline{H}_3$)$_2$], 3.36 [4H, m, -OCON($C\underline{H}_2CH_3$)$_2$], 6.60 (1H, s, H-2), 6.96 (1H, d, *J* 8.0, H-3″), 7.03 (1H, ddd, *J* 7.5, 4.9 and 1.0, H-5″), 7.34 (6H, m, Ar*H* and H-4″) and 8.51 (1H, dd, *J* 4.4 and 1.6, H-6″); nOe 6.60 ppm (interacts with H-3″); δ_C (50 MHz; $CDCl_3$) 13.34 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.31 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.90 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.08 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 119.98 (CH, C-2), 121.47 (CH, C-3″), 123.74 (CH, C-5″), 128.34 (2 × CH, C-2′ and C-6′), 128.89 (2 × CH, C-3′ and C-5′), 129.05 (CH, C-4′), 134.88 (q, C-1′), 135.61 (CH, C-4″), 149.33 (CH, C-6″), 151.32 (q, C-1), 153.83 [C=O, -

O<u>C</u>ON(CH_2CH_3)$_2$] and 154.63 (q, C-2″); *m/z* (EI) 297 (M^++1, <1%), 296 (M^+, 5), 180 (3), 177 (8), 167 (5), 100 (100), 77 (3) and 72 (37); HRMS Found: 296.1527, $C_{18}H_{20}N_2O_2$ requires 296.1525.

(*Z*)-1-*N,N*-Diethylcarbamoyloxy-1-phenyl-2-(2″-pyridyl)ethene (3f)

The title compound was prepared using general procedures B and C, using 2-pyridinecarboxaldehyde as the electrophile. Optimum *Z*-selectivity was obtained using general procedure C. Purification by silica gel chromatography eluting with a 30-50% Et_2O/hexane gradient enabled the separation of the title compound as pale yellow needle-like crystals, from its geometric isomer (65% olefin yield, *E*:*Z* = 12:88); mp 66°C (from Et_2O/benzene/hexane); (Found: C, 73.0; H, 6.9; N, 9.4; $C_{18}H_{20}N_2O_2$ requires C, 72.95; H, 6.8; N, 9.45%); δ_H (200 MHz; $CDCl_3$) 1.17 [3H, t, *J* 7.0, -OCON($CH_2C\underline{H}_3$)$_2$], 1.32 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3$)$_2$], 3.37 [2H, q, *J* 7.0, -OCON($C\underline{H}_2CH_3$)$_2$], 3.58 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3$)$_2$], 6.86 (1H, s, H-2), 7.11 (1H, ddd, *J* 7.3, 4.8 and 1.4, H-5″), 7.38 (3H, c, H-3′, H-4′ and H-5′), 7.53 (1H, d, *J* 8.1, H-3″), 7.63 (3H, c, H-2′, H-6′ and H-4″) and 8.58 (1H, d, *J* 4.6, H-6″); nOe 6.86 ppm (interacts with H-2′, H-6′ and H-3″); δ_C (50 MHz; $CDCl_3$) 13.27 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.41 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.79 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.05 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 116.63 (CH, C-2), 121.64 (CH, C-5″), 123.52 (CH, C-3″), 125.15 (2 × CH, C-2′ and C-6′), 128.61 (2 × CH, C-3′ and C-5′), 128.94 (CH, C-4′), 136.02 (CH, C-4″), 136.16 (q, C-1′), 149.35 (CH, C-6″), 149.55 (q, C-1), 153.07 [C=O, -O<u>C</u>ON(CH_2CH_3)$_2$] and 154.07 (q, C-2″); *m/z* (EI) 297 (M^++1, <1%), 296 (M^+, 2), 167 (4), 100 (100), 77 (4) and 72 (39); HRMS Found: 296.1532, $C_{18}H_{20}N_2O_2$ requires 296.1525.

(*E*)-1-*N,N*-Diethylcarbamoyloxy-2-(2″-furanyl)-1-phenylethene (3g)

The title compound was prepared by general procedures B and C, using furfural as the electrophile. Optimum *E*-selectivity was obtained using general procedure B in Et_2O. Purification by silica gel chromatography eluting with 25% Et_2O/hexane enabled the separation of the title compound as a yellow oil, from its geometric isomer (70% olefin yield, *E*:*Z* = 17:83); (Found: C, 71.55; H, 7.0; N, 4.6; $C_{17}H_{19}NO_3$ requires C, 71.6; H, 6.7; N, 4.9%); δ_H (200 MHz; $CDCl_3$) 1.13 [6H, m, -OCON($CH_2C\underline{H}_3$)$_2$], 3.33 [4H, m, -OCON($C\underline{H}_2CH_3$)$_2$], 6.02 (1H, ddd, *J* 3.4, 0.7 and 0.7, H-3″), 6.26 (1H, ddd, *J* 3.4, 1.8 and 0.5, H-4″), 6.34 (1H, d, *J* 0.5, H-2), 7.24 (1H, dd, *J* 1.8 and 0.7, H-5″), 7.37 (3H, c, H-3′, H-4′ and H-5′) and 7.52 (2H, c, H-2′ and H-6′); nOe 6.34 ppm (no correlation); δ_C (50 MHz; $CDCl_3$) 13.29 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 14.28 [CH_3, -OCON($CH_2\underline{C}H_3$)$_2$], 41.78 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 42.03 [CH_2, -OCON($\underline{C}H_2CH_3$)$_2$], 108.86 (CH, C-3″), 109.24 (CH, C-2), 109.61 (CH, C-4″), 128.10 (2 × CH, C-3′ and C-5′), 128.64 (2 × CH, C-2′ and C-6′), 128.84 (CH, C-4′), 135.30 (q, C-1′), 141.59 (CH, C-5″), 147.05 (q, C-1), 149.53 (q, C-2″) and 153.97 [C=O, -O<u>C</u>ON(CH_2CH_3)$_2$]; *m/z* (EI) 286 (M^++1, 1%), 285 (M^+, 7), 157 (4), 128 (3), 115 (4), 100 (100), 77 (15) and 72 (69).

(*Z*)-1-*N,N*-Diethylcarbamoyloxy-2-(2″-furanyl)-1-phenylethene (3g)

The title compound was prepared by general procedures B and C, using furfural as the electrophile. Optimum *Z*-selectivity was obtained using general procedure C. Purification by silica gel chromatography eluting with 25% Et_2O/hexane enabled the separation of the title compound as fine colourless needle-like crystals from its geometric isomer (73†% olefin yield, *E*:*Z* = 14:86); mp 103-106°C (from 25% Et_2O / hexane); (Found: C, 71.5; H, 6.8; N, 5.0; $C_{17}H_{19}NO_3$ requires C, 71.6; H, 6.7; N, 4.9%); δ_H (200 MHz; $CDCl_3$) 1.17 [3H,

† Corrected yield - a small amount of the 1-*N,N*-diethylcarbamoyloxy-1-phenyl-1-triphenylsilyl methane substrate was detected by NMR and the yield corrected accordingly.

t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 1.33 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 3.37 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.57 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 6.40 (1H, ddd, *J* 3.4, 1.8 and 0.5, H-4″), 6.45 (1H, dd, *J* 3.4 and 0.6, H-3″), 6.69 (1H, s, H-2), 7.32 (3H, c, H-3′, H-4′ and H-5′), 7.35 (1H, dd, *J* 1.8 and 0.7, H-5″) and 7.50 (2H, dd, *J* 8.3 and 1.8, H-2′ and H-6′); nOe 6.69 ppm (interacts with H-3″, H-2′ and H-6′); δ_C (50 MHz; $CDCl_3$) 13.10 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.23 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.63 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 41.90 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 105.85 (CH, C-2), 109.74 (CH, C-3″), 111.50 (CH, C-4″), 124.21 (2 × CH, C-2′ and C-6′), 128.17 (CH, C-4′), 128.42 (2 × CH, C-3′ and C-5′), 135.45 (q, C-1′), 141.75 (CH, C-5″), 144.79 (q, C-1), 150.17 (q, C-2″) and 152.88 [C=O, -O$\underline{C}$ON($CH_2CH_3)_2$]; *m/z* (EI) 286 (M^++1, 2%), 285 (M^+, 8), 157 (4), 128 (3), 105 (7), 100 (100), 77 (14) and 72 (53).

(*E*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(2″-thiophene)ethene (3h)

The title compound was prepared using general procedure B in Et_2O when 2-thiophenecarboxaldehyde was used as the electrophile. Purification by silica gel chromatography eluting with a 15-35% Et_2O/hexane gradient enabled the separation of the title compound as a pale yellow oil (rapidly turns black), from its geometric isomer (78% olefin yield, *E*:*Z* = 11:89); (Found: C, 68.2; H, 6.4; N, 4.4; $C_{17}H_{19}NO_2S$ requires C, 67.7; H, 6.35; N, 4.65%); δ_H (200 MHz; $CDCl_3$) 0.98 [6H, br t, -OCON($CH_2C\underline{H}_3)_2$], 3.00 [4H, br, -OCON($C\underline{H}_2CH_3)_2$], 6.55 (1H, dd, *J* 5.2 and 3.4, H-4″), 6.62 (1H, dd, *J* 5.1 and 1.4, H-5″), 6.70 (1H, dd, *J* 3.4 and 1.2, H-3″), 6.72 (1H, s, H-2), 7.11 (3H, c, H-3′, H-4′ and H-5′) and 7.68 (2H, c, H-2′ and H-6′); δ_C (50 MHz; C_6D_6) 13.44 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.38 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.84 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 42.15 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 114.51 (CH, C-2), 125.27 (CH, C-5″), 126.67 (CH, C-4″), 127.95 (CH, C-3″), 128.80 (2 x CH, C-3′ and C-5′), 129.37 (CH, C-4′), 130.25 (2 x CH, C-2′ and C-6′), 135.68 (q, C-1′), 137.87 (q, C-2″), 148.06 (q, C-1) and 153.75 [C=O, -O$\underline{C}$ON($CH_2CH_3)_2$]; *m/z* (EI) 303 (M^++2, <1%), 302 (M^++1, 2), 301 (M^+, 12), 184 (7), 100 (100), 77 (20) and 72 (80).

(*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(2″-thiophene)ethene (3h)

The title compound was prepared using general procedure B in Et_2O, using 2-thiophenecarboxaldehyde as the electrophile. Purification by silica gel chromatography eluting with a 15-35% Et_2O/hexane gradient enabled the separation of the title compound as colourless needle-like crystals from its geometric isomer (78% olefin yield, *E*:*Z* = 11:89); mp 120 °C (from 25% Et_2O/hexane); (Found: C, 67.8; H, 6.4; N, 4.7; $C_{17}H_{19}NO_2S$ requires C, 67.7; H, 6.35; N, 4.65%); δ_H (200 MHz; C_6D_6) 0.94 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 1.10 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 3.11 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.35 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 6.77 (1H, dd, *J* 5.0 and 3.7, H-4″), 6.83 (1H, br s, H-2), 6.91 (2H, c, H-3″ and H-5″), 7.12 (3H, c, H-3′, H-4′ and H-5′) and 7.49 (2H, c, H-2′ and H-6′); nOe 6.83 ppm (interacts with H-3″, H-2′ and H-6′); δ_C (50 MHz; C_6D_6) 13.39 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.69 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.95 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 42.27 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 111.69 (CH, C-2), 125.08 (2 × CH, C-2′ and C-6′), 126.22 (CH, C-5″), 126.76 (CH, C-4″), 128.28 (CH, C-4′), 128.34 (CH, C-3″), 128.73 (2 × CH, C-3′ and C-5′), 136.66 (q, C-1′), 138.03 (q, C-2″), 145.86 (q, C-1) and 152.40 [C=O, -O$\underline{C}$ON($CH_2CH_3)_2$]; *m/z* (EI) 303 (M^++2, <1%), 302 (M^++1, 2), 301 (M^+, 9), 176 (4), 129 (4), 115 (2), 105 (6), 100 (100), 77 (18), 72 (79).

(*E*)- and (*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-1,2-diphenylethene (3j)

The title compounds were prepared by general procedure B in Et_2O, using benzaldehyde as the electrophile. Purification by silica gel chromatography eluting with a 5-15% Et_2O/hexane yielded a mixture of isomers (82% olefin yield, *E*:*Z* = 9:91). Recrystallization of the mixture of isomers yielded the *Z*-isomer as

colourless needle-like crystals; mp 86°C (from EtOAc/hexane); (Found: C, 77.4; H, 7.35; N, 4.8; $C_{19}H_{21}NO_2$ requires C, 77.3; H, 7.2; N, 4.7%); δ_H (200 MHz; $CDCl_3$) 1.09 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 1.24 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 3.30 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.47 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 6.48 [0.1H, s, H-2 (*E*)], 6.64 [0.9H, s, H-2 (*Z*)], 7.23 (6H, m, H-3′, H-4′, H-5′, H-3″, H-4″ and H-5″) and 7.51 (4H, m, H-2′, H-6′, H-2″ and H-6″); nOe 6.64 ppm (interacts with H-2′, H-6′, H-2″ and H-6″) and 6.48 ppm (no correlation); δ_C (50 MHz; $CDCl_3$) 13.06 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.25 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.48 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 41.74 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 116.53 [CH, C-2 (*Z*)], 119.22 [CH, C-2 (*E*)], 124.51 [2 × CH, C-2′ and C-6′[#] (*Z*)], 127.11 [CH, C-4″ (*Z*)], 128.12 [CH, C-1′ (*Z*)], 128.14 [2 × CH, C-2″ and C-6″ (*Z*)], 128.34 [2 × CH, PhC (*Z*)], 128.47 [2 × CH, PhC (*Z*)], 134.46 [q, C-1″ (*Z*)], 136.40 [q, C-1′ (*Z*)], 146.77 [q, C-1 (*Z*)] and 152.82 [C=O (*Z*), -O$\underline{C}$ON($CH_2CH_3)_2$]; *m/z* (EI) 296 (M^++1, 1%), 295 (M^+, 5), 177 (7), 166 (8), 151 (10), 100 (100), 77 (14) and 72 (67).

(*E*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(4″-pyridyl)ethene (3k)

The title compound was prepared by general procedure B, with 4-pyridinecarboxaldehyde as the electrophile. Optimum *E*-selectivity was obtained with general procedure B in THF. Purification by silica gel chromatography eluting with a 50-70% Et_2O/hexane gradient enabled the separation of the title compound as a pale yellow oil, from its geometric isomer (52% olefin yield, *E*:*Z* = 83:17); (Found: C, 72.55; H, 7.1, N 9.1; $C_{18}H_{20}N_2O_2$ requires C, 72.95; H, 6.8, N 9.45%); δ_H (200 MHz; $CDCl_3$) 1.13 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 1.23 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 3.30 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.41 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 6.40 (1H, s, H-2), 6.95 (2H, ddd, *J* 4.7, 1.5 and 0.5, H-3″ and H-5″), 7.34 (5H, m, Ar$\underline{H}$) and 8.37 (2H, d, *J* 6.0, H-2″ and H-6″); nOe 6.40 ppm (interacts with H-3″ and H-5″); δ_C (50 MHz; $CDCl_3$) 13.27 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.31 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.87 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 42.12 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 116.92 (CH, C-2), 123.45 (2 x CH, C-3″ and C-5″), 128.60 (2 x CH, C-2′ and C-6′), 128.76 (2 x CH, C-3′ and C-5′), 129.43 (CH, C-4′), 134.30 (q, C-1′), 142.95 (q, C-4″), 149.56 (2 x CH, C-2″ and C-6″), 151.58 (q, C-1) and 153.55 [C=O, -O$\underline{C}$ON($CH_2CH_3)_2$]; *m/z* (EI) 297 (M^++1, 1%), 296 (M^+, 6), 167 (2), 100 (100), 77 (4) and 72 (52); HRMS Found: 296.1537, $C_{18}H_{20}N_2O_2$ requires 296.1525.

(*Z*)-1-*N*,*N*-Diethylcarbamoyloxy-1-phenyl-2-(4″-pyridyl)ethene (3k)

The title compound was prepared by general procedure B, with 4-pyridinecarboxaldehyde as the electrophile. Purification by silica gel chromatography eluting with a 50-70% Et_2O/hexane gradient enabled the separation of the title compound as a crystalline solid, from its geometric isomer (52% olefin yield, *E*:*Z* = 83:17); mp 73-74°C (from EtOAc/hexane); (Found: C, 72.9; H, 6.8; N, 9.4; $C_{18}H_{20}N_2O_2$ requires C, 72.95; H, 6.8; N, 9.45%); δ_H (200 MHz; $CDCl_3$) 1.14 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 1.32 [3H, t, *J* 7.1, -OCON($CH_2C\underline{H}_3)_2$], 3.35 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 3.56 [2H, q, *J* 7.1, -OCON($C\underline{H}_2CH_3)_2$], 6.57 (1H, s, H-2), 7.38 (5H, m, H-3′, H-4′ and H-5′, H-3″ and H-5″), 7.54 (2H, m, H-2′ and H-6′) and 8.58 (2H, br s, H-2″ and H-6″); nOe 6.57 ppm (interacts with H-2′ and H-6′); δ_C (50 MHz; $CDCl_3$) 13.26 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 14.55 [CH_3, -OCON($CH_2\underline{C}H_3)_2$], 41.85 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 42.13 [CH_2, -OCON($\underline{C}H_2CH_3)_2$], 114.36 (CH, C-2), *ca.* 123[ς] (2 x CH, C-3″ and C-5″), 125.13 (2 x CH, C-2′ and C-6′), 128.75 (2 x CH, C-3′ and C-5′), 129.31 (CH, C-4′), 135.75 (q, C-1′), 142.32 (q, C-4″), 149.77 (2 x CH, C-2″ and C-6″), 150.85 (q, C-1) and

---

[#] Assignment based on observed trends for C-2′ and C-6′ shifts when the isomers were separated.

ς Signal was very broad and weak, but a correlation was detected in the ^1H-^{13}C HETCOR plot.

152.49 [C=O, -O<u>C</u>ON$(CH_2CH_3)_2$]; *m/z* (EI) 297 (M^++1, <1%), 296 (M^+, 3), 167 (2), 100 (100), 77 (4) and 72 (45); HRMS Found: 296.1529, $C_{18}H_{20}N_2O_2$ requires 296.1525.

1-*N,N*-Diethylcarbamoyloxy-1,2,2-triphenylethene (3l)

The title compound was prepared by general procedure B in Et_2O, when benzophenone was used as the electrophile. Purification by silica gel chromatography eluting with 15% Et_2O/hexane enabled the separation of the title compound as colourless prisms (82% yield); mp 121°C (from EtOAc and hexane); (Found: C, 80.9; H, 6.9; N, 3.85; $C_{25}H_{25}NO_2$ requires C, 80.8; H, 6.8; N, 3.8%); δ_H (200 MHz; $CDCl_3$) 0.89 [3H, t, *J* 7.1, -OCON$(CH_2C\underline{H}_3)_2$], 1.01 [3H, t, *J* 7.1, -OCON$(CH_2C\underline{H}_3)_2$], 3.26 [4H, c, -OCON$(C\underline{H}_2CH_3)_2$], 7.13 (8H, m, Ar<u>H</u>) and 7.25 (7H, m, Ar<u>H</u>); δ_C (50 MHz; $CDCl_3$) 13.22 [CH_3, -OCON$(CH_2\underline{C}H_3)_2$], 13.96 [CH_3, -OCON$(CH_2\underline{C}H_3)_2$], 41.61 [CH_2, -OCON$(\underline{C}H_2CH_3)_2$], 41.92 [CH_2, -OCON$(\underline{C}H_2CH_3)_2$], 126.89 (CH, Ar<u>C</u>), 127.01 (CH, Ar<u>C</u>), 127.78 (CH, Ar<u>C</u>), 127.83 (2 × CH, Ar<u>C</u>), 127.92 (2 × CH, Ar<u>C</u>), 127.99 (2 × CH, Ar<u>C</u>), 128.92 (2 × CH, Ar<u>C</u>), 129.32 (2 × CH, Ar<u>C</u>), 130.91 (2 × CH, Ar<u>C</u>), 131.51 (q, C-2), 136.49 (q, C-1′[#]), 140.14 (q, C-1‴[*]), 140.54 (q, C-1″[*]), 144.26 (q, C-1) and 154.12 [C=O, -O<u>C</u>ON$(CH_2CH_3)_2$]; *m/z* (EI) 372 (M^++1, <1%), 371 (M^+, <1), 165 (5), 100 (100), 77 (4) and 72 (39).

(*E*)-1-*N,N*-Diisopropylcarbamoyloxy-2-(3″, 4″-methylenedioxyphenyl)-1-phenylethene (4a)

The title compound was prepared by general procedure D, using 3,4-methylenedioxybenzaldehyde as the electrophile. Optimum *E*-selectivity was obtained when THF was used as the solvent. Purification by silica gel chromatography eluting with a 1-20% EtOAc/hexane gradient afforded a mixture of isomers. Further chromatography eluting with 70% hexane/CH_2Cl_2 enabled the separation of the title compound as a yellow oil, from its geometric isomer (73% olefin yield, *E*:*Z* = 66:34); (Found: C, 71.75: H, 6.9; N, 3.6; $C_{22}H_{25}NO_4$ requires C, 71.9; H, 6.9; N, 3.8%); δ_H (200 MHz; $CDCl_3$) 1.29 {12H, br d, *J* 7.0, -OCON[CH$(C\underline{H}_3)_2]_2$}, 3.96 {2H, br, -OCON[C<u>H</u>$(CH_3)_2]_2$}, 5.83 (2H, s, H_2-7″), 6.38 (1H, s, H-2), 6.55 (1H, br s, H-2″), 6.63 (2H, br s, H-5″ and H-6″), 7.26 (3H, m, H-3′, H-4′ and H-5′) and 7.38 (2H, m, H-2′ and H-6′); nOe 6.38 ppm (interacts with H-2″ and H-6″); δ_C (50 MHz; $CDCl_3$) 20.52 {2 × CH_3, -OCON[CH$(\underline{C}H_3)_2]_2$}, 21.45 {2 × CH_3, -OCON[CH$(\underline{C}H_3)_2]_2$}, 46.04 {CH, -OCON[<u>C</u>H$(CH_3)_2]_2$}, 46.09 {CH, -OCON[<u>C</u>H$(CH_3)_2]_2$}, 100.85 (CH_2, C_2-7″), 108.09 (CH, C-5″), 108.85 (CH, C-2″), 119.02 (CH, C-2), 123.14 (CH, C-6″), 128.30 (2 × CH, C-3′ and C-5′), 128.48 (CH, C-4′), 128.76 (2 × CH, C-2′ and C-6′), 135.33 (q, C-1′), 146.45 (q, C-4‴[*]), 147.10 (q, C-1[*]), 147.29 (q, C-3″) and 153.65 {C=O, -O<u>C</u>ON[CH$(CH_3)_2]_2$}; *m/z* (EI) 240 (12%), 128 (64) and 86 (100).

(*Z*)-1-*N,N*-Diisopropylcarbamoyloxy-2-(3″, 4″-methylenedioxyphenyl)-1-phenylethene (4a)

The title compound was prepared by general procedure D, using 3,4-methylenedioxybenzaldehyde as the electrophile. Optimum *Z*-selectivity was obtained when Et_2O was used as the solvent. Purification by silica gel chromatography eluting with a 1-20% EtOAc/hexane gradient yielded a mixture of the isomers. Further chromatography eluting with 70% hexane/CH_2Cl_2 enabled the separation of the title compound as pale yellow rhombohedral crystals, from its geometric isomer (76%[†] olefin yield, *E*:*Z* = 9:91); mp 108-109°C (from hexane/EtOAc); (Found: C, 71.9; H, 6.8; N, 3.8; $C_{22}H_{25}NO_4$ requires C, 71.9; H, 6.9; N, 3.8%); δ_H (200 MHz; $CDCl_3$) 1.28 {6H, d, *J* 7.3, -OCON[CH$(C\underline{H}_3)_2]_2$}, 1.31 {6H, d, *J* 7.4, -OCON[CH$(C\underline{H}_3)_2]_2$}, 3.76 {1H, m, *J* 6.8, -OCON[C<u>H</u>$(CH_3)_2]_2$}, 4.37 {1H, m, *J* 6.8, -OCON[C<u>H</u>$(CH_3)_2]_2$}, 5.87 (2H, s, H_2-7″), 6.58 (1H, s, H-2), 6.74

[#] This assignment is based on previous assignments of C-1′ which is usually observed at 135 ± 1 ppm.

[*] Interchangeable assignments.

(1H, d, *J* 8.1, H-5″), 6.91 (1H, dd, *J* 8.1 and 1.7, H-6″), 7.08 (1H, d, *J* 1.7, H-2″), 7.31 (3H, c, H-3′, H-4′ and H-5′) and 7.49 (2H, c, H-2′ and H-6′); nOe 6.58 ppm (interacts with H-2′, H-6′, H-2″ and H-6″); δ_C (50 MHz; $CDCl_3$) 20.50 {2 × CH_3, -OCON[CH(CH_3)$_2$]$_2$}, 21.40 {2 × CH_3, -OCON[CH(CH_3)$_2$]$_2$}, 46.05 {CH, -OCON[CH(CH$_3$)$_2$]$_2$}, 47.23 {CH, -OCON[CH(CH$_3$)$_2$]$_2$}, 101.02 (CH_2, C_2-7″), 108.11 (CH, C-5″), 108.30 (CH, C-2″), 116.41 (CH, C-2), 123.36 (CH, C-6″), 124.50 (2 × CH, C-2′ and C-6′), 128.02 (CH, C-4′), 128.50 (2 × CH, C-3′ and C-5′), 128.91 (q, C-1″), 136.80 (q, C-1′), 145.56 (q, C-1), 146.80 (q, C-4″), 147.69 (q, C-3″) and 151.80 {C=O, -OCON[CH(CH$_3$)$_2$]$_2$}; *m/z* (EI) 368 (M^++1, 1%), 367 (M^+, 5), 240 (14), 165 (6), 152 (12), 135 (14), 128 (84), 105 (15), 86 (100) and 77 (13).

(*E*)- and (*Z*)-1-*N,N*-Diisopropylcarbamoyloxy-1-phenylpentene (4c)

The title compounds were prepared by general procedure D, using butanal as the electrophile. Optimum *E*-selectivity was obtained when Et_2O was used as the solvent. Purification by centrifugal thin layer silica gel chromatography eluting with a 1-10% Et_2O/hexane gradient enabled the separation of the title compounds as a colourless oil (63%† olefin yield, *E:Z = 30:70*); (Found: C, 74.5; H, 9.6; N, 4.55; $C_{18}H_{27}NO_2$ requires C, 74.7; H, 9.4; N, 4.8%); δ_H (200 MHz; $CDCl_3$) 0.91 (3H-*min*, t, *J* 7.3, H-5), 0.95 (3H-*maj*, t, H_3-5), 1.25 {12H-*maj*, d, *J* 6.5, -OCON[CH(CH_3)$_2$]$_2$}, 1.36 {12H-*min*, d, *J* 6.7, -OCON[CH(CH_3)$_2$]$_2$}, 1.47 (2H, m, H_2-4), 2.15 (2H-*maj*, q, *J* 7.4, H_2-3), 2.18 (2H-*min*, q, *J* 7.7, H_2-3), 4.01 {2H, br m, -OCON[CH(CH$_3$)$_2$]$_2$}, 5.45 (1H-*min*, t, *J* 7.7, H-2), 5.80 (1H-*maj*, t, *J* 7.4, H-2), 7.27 (3H, m, H-3′, H-4′ and H-5′) and 7.40 (2H, c, H-2′ and H-6′); δ_C (50 MHz; $CDCl_3$) 13.82 (CH_3-*min*, C_3-5), 13.99 (CH_3-*maj*, C_3-5), 20.52 {2 × CH_3, -OCON[CH(CH_3)$_2$]$_2$}, 21.68 {2 × CH_3, -OCON[CH(CH_3)$_2$]$_2$}, 23.24 (CH_2-*min*, C_2-4), 22.37 (CH_2-*maj*, C_2-4), 28.32 (CH2-*maj*, C_2-3), 29.30 (CH_2-*min*, C_2-3), 46.11 {CH, -OCON[CH(CH$_3$)$_2$]$_2$}, 46.62 {CH, -OCON[CH(CH$_3$)$_2$]$_2$}, 117.80 (CH-*maj*, C-2), 119.60 (CH-*min*, C-2), 124.39 (2 x CH-*maj*, C-2′ and C-6′), 127.60 (CH-*maj*, C-4′), 127.84 (CH-*min*, C-4′), 128.01 (2 x CH-*min*, C-3′ and C-5′*), 128.08 (2 x CH-*min*, C-2′ and C-6′*), 128.33 (2 x CH-*maj*, C-3′ and C-5′), 135.54 (q-*min*, C-1′), 136.28 (q-*maj*, C-1′), 146.50 (q-*min*, C-1), 146.56 (q-*maj*, C-1), 153.00 {C=O-*maj*, -OCON[CH(CH$_3$)$_2$]$_2$} and 154.06 {C=O-*min*, -OCON[CH(CH$_3$)$_2$]$_2$}; *m/z* (EI) 290 (M^++1, <1%), 289 (M^+, 3), 133 (35), 128 (78), 105 (14), 86 (100) and 77(18).

(*E*)- and (*Z*)-1-*N,N*-Diisopropylcarbamoyloxy-1-phenyl-2-(2″-quinolyl)ethene (4e)

The title compounds were prepared by general procedure D, using 2-quinolinecarboxaldehyde as the electrophile. Optimum *E*-selectivity was obtained when THF was used as the solvent. Purification by silica gel chromatography eluting with a 20-70% Et_2O/hexane gradient afforded the title compounds as a viscous yellow oil (35% olefin yield, *E:Z* = 42:58); (Found: C, 76.6; H, 7.1; N, 7.5; $C_{24}H_{26}N_2O_2$ requires C, 77.0; H, 7.0; N, 7.5%); δ_H (200 MHz; $CDCl_3$) 1.29 {12H, t, *J* 7.2, -OCON[CH(CH_3)$_2$]$_2$}, 3.79 {1H-*maj*, m, -OCON[CH(CH$_3$)$_2$]$_2$}, 3.96 {2H-*min*, m, -OCON[CH(CH$_3$)$_2$]$_2$}, 4.33 {1H-*maj*, m, -OCON[CH(CH$_3$)$_2$]$_2$}, 6.82 (1H-*min*, s, H-2), 7.02 (1H-*min*, d, *J* 8.6, H-3″), 7.09 (1H-*maj*, s, H-2), 7.37 (5H, c, ArH), 7.65 (4H, c, ArH), 8.00 (1H, c, H-8″) and 8.06 (1H-*maj*, c, H-4″); nOe 6.82 ppm (interacts with H-3″ and H-8″ of the *minor* isomer) and 7.09 ppm (interacts with H-4″, H-2′ and H-6′ of the *major* isomer); δ_C (50 MHz; $CDCl_3$) 20.17 {2 × CH_3, -OCON[CH(CH_3)$_2$]$_2$}, 21.14 {2 × CH_3, -OCON[CH(CH_3)$_2$]$_2$}, 45.81 {CH, -OCON[CH(CH$_3$)$_2$]$_2$}, 46.94 {CH, -OCON[CH(CH$_3$)$_2$]$_2$}, 117.34 (CH-*maj*, C-2), 120.11 (CH-*min*, C-2), 121.18 (CH-*maj*, C-3″), 121.57

† Corrected yield

* Interchangeable assignments

(CH-*min*, C-3″), 124.83 (2 x CH-*maj*, C-2′ and C-6′), 125.90 (CH-*maj*, C-6″), 126.26 (q-*min*, C-4a″), 126.47 (q-*maj*, C-4a″), 127.00 (CH-*maj*, C-4′), 127.06 (CH-*min*, C-5″), 127.98 (CH-*maj*, C-5″), 128.27 (2 x CH-*maj*, C-3′ and C-5′), 128.63 (CH-*min*, C-6″), 128.70 (4 x CH-*min*, C-2′, C-3′, C-5′ and C-6′), 128.83 (CH-*maj*, C-8″), 128.92 (CH-*min*, C-8″), 129.08 (CH, C-7″), 134.67 (q-*min*, C-1′), 134.85 (CH-*min*, C-4″), 135.35 (CH-*maj*, C-4″), 135.91 (q-*maj*, C-1′), 147.66 (q-*min*, C-8a″), 147.77 (q-*maj*, C-8a″), 150.18 (q-*maj*, C-1), 151.32 (q-*min*, C-1), 152.25 {C=O-*maj*, -O<u>C</u>ON[CH(CH_3)$_2$]$_2$}, 152.87 {C=O-*min*, -O<u>C</u>ON[CH(CH_3)$_2$]$_2$}, 154.15 (q-*maj*, C-2″) and 154.89 (q-*min*, C-2″); *m/z* (EI) 375 (M^++1, <1%), 374 (M^+, 3), 246(14), 170 (8), 128 (68), 86 (100) and 77(6).

1-^{t}Butyldimethylsilyloxy-1-phenylpent-1-ene (5c)

The title compound was prepared by general procedure B in Et_2O, in addition to the Peterson olefination product when butanal was used as the electrophile. Purification by silica gel chromatography eluting with hexane enabled the separation of the title compound (which rearranged to the ketone *via* a 1,3-migration of the silicon from the oxygen to the carbon on standing at room temperature) as a colourless oil, from the olefin products (13% yield); δ_H (200 MHz; $CDCl_3$) –0.05 [6H, s, -OSi(C<u>H</u>$_3$)$_2$C(CH_3)$_3$], 0.91 (3H, t, *J* 7.6, H_3-5), 0.98 [9H, s, -OSi(CH_3)$_2$C(C<u>H</u>$_3$)$_3$], 1.46 (2H, m, H_2-4), 2.18 (2H, q, *J* 7.4, H_2-3), 5.11 (1H, t, *J* 7.2, H-2) 7.26 (3H, c, H-3′, H-4′ and H-5′) and 7.44 (2H, c, H-2′ and H-6′); δ_C (50 MHz; $CDCl_3$) –4.05 [2 × CH_3, -OSi(<u>C</u>H$_3$)$_2$C(CH_3)$_3$], 14.02 (CH_3, C_3-5), 18.33 [q, -OSi(CH_3)$_2$<u>C</u>(CH_3)$_3$], 22.92 (CH_2, C_2-4), 25.88 [3 × CH_3, -OSi(CH_3)$_2$C(<u>C</u>H$_3$)$_3$], 28.25 (CH_2, C_2-3), 111.88 (CH, C-2), 125.84 (2 × CH, C-2′ and C-6′), 127.26 (CH, C-4′), 127.84 (2 × CH, C-3′ and C-5′), 139.86 (q, C-1′) and 149.25 (q, C-1); *m/z* (EI) 277 (M^++1, 5%), 235 (100), 187 (78), 105 (7) and 73 (35); HRMS Found: 276.1915, $C_{17}H_{28}OSi$ requires 276.1909.

1-Phenyl-2-^{t}butyldimethylsilylpentanone (6c)

The title compound was obtained from 1-^{t}butyldimethylsilyloxy-1-phenylpent-1-ene, *via* a spontaneous 1,3-migration[25] of the silicon moiety from the oxygen to the carbon atom, as a colourless oil (>95% conversion); δ_H (200 MHz; $CDCl_3$) –0.03 [3H, s, -Si(C<u>H</u>$_3$)$_2$C(CH_3)$_3$], 0.05 [3H, s, -Si(C<u>H</u>$_3$)$_2$C(CH_3)$_3$], 0.88 [9H, s, -Si(CH_3)$_2$C(C<u>H</u>$_3$)$_3$], 0.93 (3H, t, *J* 7.4, H_3-5), 1.5 (2H, m, H_2-4), 1.77 (2H, m, H_2-3), 4.76 (1H, ddd, *J* 7.8, 5.3 and 0.7, H-2), 7.48 (3H, c, H-3′, H-4′ and H-5′) and 8.06 (2H, d, *J* 6.9, H-2′ and H-6′); δ_C (50 MHz; $CDCl_3$) –4.73 [CH_3, -Si(<u>C</u>H$_3$)$_2$C(CH_3)$_3$], –5.21 [CH_3, -Si(<u>C</u>H$_3$)$_2$C(CH_3)$_3$], 13.85 (CH_3, C_3-5), 18.25 [q, -Si(CH_3)$_2$<u>C</u>(CH_3)$_3$], 19.06 (CH_2, C_2-4), 25.75 [3 × CH_3, -Si(CH_3)$_2$C(<u>C</u>H$_3$)$_3$], 38.09 (CH_2, C_2-3), 77.87 (CH, C-2), 128.32 (2 × CH, C-3′ and C-5′), 129.22 (2 × CH, C-2′ and C-6′), 132.94 (CH, C-4′), 134.93 (q, C-1′) and 201.70 (C=O, C-1); *m/z* (EI) 278 (M^++2, 1%), 277 (M^++1, 5), 235 (100), 191 (10), 187 (78), 177 (5), 135 (5), 105 (7) and 73 (35); HRMS Found: 276.1915, $C_{17}H_{28}OSi$ requires 276.1909.

(1*E*,3*E*)-^{t}butyldimethylsilyloxy-1,4-diphenyl-buta-1,3-diene (5d) and (*E*)-2-^{t}Butyldimethylsilyl-1,4-diphenylbut-3-enone (6d)

The title compounds were prepared by general procedure B in Et_2O, in addition to the Peterson olefination products when cinnamaldehyde was used as the electrophile. Purification by silica gel chromatography eluting with a 5-25% Et_2O/hexane gradient enabled the separation of the title compound as a yellow oil, from the olefin products (3-6% yield, **5d**:**6d** = 10:90); δ_H (200 MHz; $CDCl_3$) –0.06 [3H, s, -Si(C<u>H</u>$_3$)$_2$C(CH_3)$_3$], 0.11 [3H, s, -Si(C<u>H</u>$_3$)$_2$C(CH_3)$_3$], 0.93 [9H-*maj*, s, -Si(CH_3)$_2$C(C<u>H</u>$_3$)$_3$], 0.96 [9H-*min*, s, -OSi(CH_3)$_2$C(C<u>H</u>$_3$)$_3$], 4.53 (1H-*maj*, d, *J* 10.0, H-2), 5.94 (1H-*min*, d, *J* 11.2, H-2), 6.42 (1H-*maj*, d, *J* 16.0, H-4), 6.46 (1H-*min*, d, *J* 15.5, H-4), 6.73 (1H, ddd, *J* 16.0, 10.0 and 0.7, H-3), 6.94 (1H-*min*, ddd, *J* 15.4, 11.1 and 0.7, H-3), 7.36 (8H, m, Ar<u>H</u>) and 7.95

(2H, dd, *J* 6.7 and 1.6, H-2′ and H-6′); nOe 4.53 ppm [interacts with H-3 (*maj*), H-4 (*maj*), H-2′ and H-6′ (*maj*)], 5.94 ppm [interacts with H-3 (*min*) and H-4 (*min*)] and 6.73 ppm [interacts with H-2 (*maj*), H-4 (*maj*), Ar$\underline{H}$ and -Si(C$\underline{H}_3$)$_2$C(CH$_3$)$_3$]; δ_C (50 MHz; $CDCl_3$) –6.58 [CH_3, -Si($\underline{C}H_3$)$_2$C(CH$_3$)$_3$], –5.61 [CH_3, -Si($\underline{C}H_3$)$_2$C(CH$_3$)$_3$], 18.54 [q, -Si(CH$_3$)$_2\underline{C}$(CH$_3$)$_3$], 27.02 [3 × CH_3, -Si(CH$_3$)$_2$C($\underline{C}H_3$)$_3$], 46.17 (CH-*maj*, C-2), 125.93 (2 × CH-*maj*, C-2″ and C-6″), 126.83 (CH-*maj*, C-4″), 127.70 (CH-*maj*, C-3), 128.21 (2 × CH-*maj*, C-2′ and C-6′), 128.49 (2 × CH-*maj*, C-3′ and C-5′*), 128.53 (2 × CH-*maj*, C-3″ and C-5″*), 128.66 (CH-*maj*, C-4), 132.68 (CH-*maj*, C-4′), 137.59 (q-*maj*, C-1″), 138.55 (q-*maj*, C-1′) and 199.99 (C=O-*maj*, C-1); *m/z* (EI) 337 (M^++1, 6%), 336 (M^+, 18), 279 (9), 202 (12), 115 (17), 105 (23), 91 (7), 77 (31), 75 (81), 73 (100) and 57 (61); HRMS Found: 336.1912, $C_{22}H_{28}OSi$ requires 336.1909.

References

1. Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780-784.
2. Ager, D. G. *Synthesis*, **1984**, 384-398.
3. Carruthers, W. *Some Modern Methods of Organic Synthesis 3rd ed.*; Cambridge University Press: Cambridge, 1986; pp. 135-7.
4. Ager, D. G. *Org Reactions*, **1990**, *38*, 1-224.
5. Van Staden, L. F.; Bartels-Rahm, B.; Emslie, N. D. *Tetrahedron Lett.* **1997**, *38*, 1851-1852.
6. Hudrlik, P. F.; Agwaramgbo, E. L. O.; Hudrlik, A. M. *J. Org. Chem.* **1989**, *54*, 5613-5618.
7. Waschbüsch, R.; Carran, J.; Savignac, P. *Tetrahedron*, **1996**, *52*, 14199-14216.
8. a) Chan, T. H.; Chang, E.; Vinokur, E. *Tetrahedron Lett.* **1970**, *14*, 1137-1140. (b) Bassindale, A. R.; Ellis, R. J.; Taylor, P. G. *Tetrahedron Lett.* **1984**, *25*, 2705-2708. (c) Bassindale, A. R.; Ellis, R. J.; Lau, J. C.-Y. *J. Chem. Soc., Perkin Trans. 2.* **1986**, 593-597. (d) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264-3268.
9. Average isolated yields determined from duplicate runs.
10. GC ratios in good agreement with ^{1}H and quantitative ^{13}C NMR ratios.
11. Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464-1468.
12. Kanemasa, S.; Tanaka, J.; Hideki, N.; Tsuge, O. *Chemistry Lett.* **1985**, 1223-1226.
13. Larson, G. L; Quiroz, F. Suárez, J. *Synth. Commun.* **1983**, 833-844.
14. a) Carstens, A.; Hoppe, D. *Tetrahedron* **1994**, *50*, 6097- 6108. (b) Hoppe, D.; Carstens, A.; Krämer, T. *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 1424- 1425.
15. Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 821-824.
16. Kende, A. S.; Mendoza, J. S. *Tetrahedron Lett.* **1990**, *31*, 7105-7108.
17. Marko, I. E.; Murphy, F.; Dolan, S. *Tetrahedron Lett.* **1996**, *37*, 2089.
18. Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry I;* Springer-Verlag: Berlin, 1987; p. 30.
19. E:Z ratios determined by quantitative ^{13}C NMR.
20. Larson, G. L.; Prieto, J. A.; Herenández, A. *Tetrahedron Lett.* **1981**, *22*, 1575-1578.
21. Dr D. Jaganji is thanked for useful discussions on the physical chemical aspects of these reactions.

---

* Interchangeable assignments.

22. GC ratios obtained prior to optimisation of the reaction conditions.
23. Relative theoretical energies for the isomers.
24. Mason, P. H.; Yoell, D. K.; Van Staden, L. F.; Emslie, N. D. *Synth. Commun.* **1995**, 3347-3350.
25. Colvin, E. *Silicon in Organic Synthesis;* Butterworths: London, 1981; p. 91 and 207-9.
26. Mahabir, S. *The Carbamate group Migrational and Leaving Properties: towards the Synthesis of Flavenes;* M. Sc. Thesis 1996: University of Natal, Pietermaritzburg.
27. These results were in agreement with the poor E-selectivity obtained previously when trimethylsilylbenzyl substrates were used for the Peterson olefination.[1, 8a-b]
28. There exists a discrepancy in the estimated bulk of the TPS moiety. Based on the steric influence of the silyl moiety on various reactions rates, the approximate size of the TMS and TPS groups are considered to be equal and smaller than the TES group for the alkaline hydrolysis of silyl ethers, while the TMS group is smaller than the TES group which is in turn smaller than the TBS group for determining the ratio of E/Z configuration. *in*: Hwu, J. R.; Wang, N. *Chem. Rev.* **1989**, *89*, 1599-1615, as opposed to Bassindale and co-workers.[8c]
29. a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry 2nd ed.*; VCH: New York, 1988; pp 110 and 117. (b) Sicher, J. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 200-214. (c) Schlosser, M.; Schub, B. *J. Am. Chem. Soc.* **1982**, *104*, 5821-5823.
30. Molecular mechanics program: Hyperchem Lite, Molecular modelling software; Hypercube, Inc.: 419 Phillip Street, Waterloo, Ontario.
31. Lowry, T. H. and Richardson, K. S. *Mechanisms and Theory in Organic Chemistry, 3rd ed.*; Harper and Row Publishers: NY; 1987.
32. No literature value for the dipole moment of this molecule could be found. The literature and theoretical values do however show the same trend: HMPA>THF>Et_2O>TMEDA. The fact that theoretical gas phase calculations do not take association effects into account is a possible explanation of the large discrepancy between the literature and theoretical values for HMPA. The theoretical dipole moment for water was found to be 1.36 D as opposed to a value of 1.84 D in the literature. This illustrates that hydrogen bonding effects are not taken into consideration in the theoretical gas phase calculations.
33. Kanemasa, S.; Tanaka, J.; Nagahama, H.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3385-3386.
34. a) Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Spectroscopy*; John Wiley and Sons: Chichester, 1988; pp. 18 and 200. (b) Pasual, C.; Meier, J.; Simon, W. *Helv. Chim Acta* **1966**, *49*, 164-168.
35. Kimmelma, R.; Toivo, A. *Acta Chem. Scandinavica* **1996**, *50*, 1064-1068.
36. Note: the numbering used in this discussion is not the usual convention, which was used for the NMR assignments (Figure 3), but the crystal structure numbering.
37. In the ^{1}H NMR spectra of the carbamate and α-silyl carbamate starting materials we observe broadening of the methylene and methyl signals, which is accentuated in the spectra of the E-isomers studied. This effect is attributed to the amide-like character of the carbamate system. Abraham, Fisher and Loftus[34a] explain that there is slow rotation about the amide bond due to its partial double bond character, which explains the distinct N-Et signals we observe. At increased temperatures where there is essentially free

rotation, these N-Et signals would therefore coalesce. The same phenomenon is observed in the ^{13}C NMR spectra of the compounds studied.

38. He, H.; Faulkner, D. J. *J. Org. Chem.* **1992**, *57*, 2176-2178.
39. Yoell, D. K. *The Reactions and Reactivity of Benzyl Carbamates*; Ph. D. Thesis 1996: University of Natal, Pietermaritzburg.
40. a) Hoppe, D.; Brönneke, A. *Synthesis* **1982**, 1045-1048. (b) Hoppe, D.; Hanko, R.; Brönneke, A.; Lichtenberg, F.; Van Hulsen, E. *Chem. Ber.* **1985**, *118*, 2822-2851.
41. Hoppe, D.; Hanko, R.; Brönneke, A.; Lichtenberg, F. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 1024 -1026.