Microwave-Assisted Solvent-Free Synthesis of Enol Carbamates

Julio A. Seijas,* M. Pilar Vázquez-Tato,* José Crecente-Campo

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Santiago de Compostela, Aptdo 280, 27080 Lugo, Spain
Fax +34(982)285872; E-mail: qoseijas@lugo.usc.es; E-mail: pilarvt@lugo.usc.es

Received 20 June 2007

Abstract: An efficient and simple method for the synthesis of enol carbamates by irradiation with microwaves under solvent-free conditions has been developed. The method has been applied to substituted acetophenones, cyclic aryl ketones and α-aryl ketones. Its main advantages are short reaction times, good conversions except for nitro acetophenones, and the environmentally friendly nature of the process. For α-aryl ketones the reaction shows regioselectivity to afford conjugated products.

Key words: solvent-free, microwave, enol carbamates

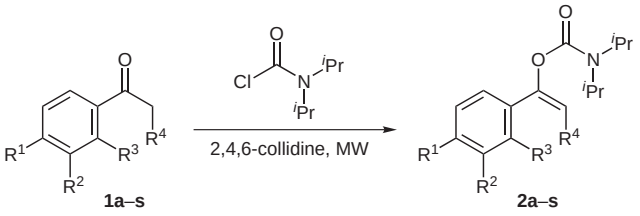
Carbamates are derivatives of carbamic acid and find diverse applications in agriculture. Vinyl carbamates are useful as agricultural pesticides, herbicides, insecticides and related products,[1] and are intermediates in the preparation of pharmaceutical products, or, after polymerization they yield interesting materials.[2] Enol carbamates are also valuable as umpoled synthons[3] due to the electrophilic character of their β-position[4] and the stabilization of anions at the γ-carbon.[5] 1-Aryl enol carbamate has proven to be a useful group for carbolithiations on the enolic double bond,[4] for 1,2-Wittig rearrangements,[6] and to direct stereoselective metallations in conjunction with the chiral base sparteine,[7–11] or to obtain enantiomerically enriched alcohols by asymmetric hydrogenation.[12,13] Until now, very few methods for their preparation have been described; some of them require the use of ruthenium[14] or palladium[15] complexes, or α-metallation.[16] Other methods based on enolization–acylation involve the deprotonation of the ketone with lithium 2,2,6,6-tetramethylpiperidide (LTMP) followed by acylation with a chloroformate using HMPA[17] (1-phenylvinyl *N*,*N*-diisopropylcarbamate was obtained by this procedure[13] in moderate yield of 49%), the heating of aromatic ketones and carbamoyl chlorides at 160 °C in the absence of a solvent (26% yield for 3,4-dihydronaphthalen-1-yl dimethyl carbamate),[18] or the addition of pyridine as a base and solvent at 90 °C.[4] This last procedure presents the inconvenience of very long reaction times (6–9 days) and it has been described for only a few examples. In fact, when we tried to apply these reaction conditions to convert 4-methoxyacetophenone into the corresponding *N*,*N*-diisopropylcarbamate, it failed completely.[19] This led us to start searching for an alternative method to get those compounds in a rapid and easy way.

SYNLETT 2007, No. 15, pp 2420–2424
Advanced online publication: 23.08.2007
DOI: 10.1055/s-2007-985607; Art ID: D18907ST

Microwave-assisted organic synthesis (MAOS) has shown to be a valuable tool for reducing reaction times, getting cleaner reactions, improving yields, simplifying work-up and designing energy-saving protocols. The increasing demand for clean and efficient 'eco-friendly' chemical syntheses has focused general interest on solvent-free reactions which, when combined with microwave irradiation, have advantages from both economic and environmental standpoints.[20–23] Our previous experience in MAOS[24–30] led us to consider to assist the formation of 1-phenylenol carbamates from ketones and *N*,*N*-diisopropylcarbamoyl chloride by microwave irradiation.

On the basis of these facts, for this study acetophenone was used as model compound. Therefore, acetophenone and *N*,*N*-diisopropylcarbamoyl chloride were irradiated without catalyst,[18] but low yields were obtained. Microwave irradiation with acid catalysis ($ZnCl_2$ or TsOH) in conditions similar to those used for the formation of enol acetates in steroid nucleus[31] was also disappointing. Therefore, basic catalysis was tried in order to favor the enolate formation. Thus, bases such as DABCO, DBU and Hünig's base, after 20 minutes of irradiation (150 °C) under solvent-free conditions[32] afforded the enol carbamate **2a** in 53%, 37% and 54% conversions, respectively. Pyridine, the base used in the conventional method, gave yields below 30% for different reaction times (20–45 min) and temperatures (125–180 °C). Pyridine derivatives were also studied; DMAP and 2,6-dimethylpyridine rendered 20% and 49% yields of enol carbamate, while 2,4,6-collidine raised the yield to 55% after 20 minutes of irradiation. This last reaction was very clean and allowed for longer reaction times. In this way the conversion was increased to 68% after one hour of irradiation at 150 °C in an open vessel;[32] thus, it was quantitative when the recovered starting material was considered. This result is a considerable improvement compared with the previous synthetic method (144-fold reduction in reaction time and better yield).[19] The same time and temperature conditions and the use of a heating mantle afforded just 34% conversion. Longer reaction times increased this yield slightly but it also caused the appearance of by-products.

The scope of reaction was established for different substitution patterns in the aromatic ring, varying their nature, number and position (Scheme 1). Strong electron-donating groups such as methoxyl, isopropoxyl, benzyloxyl or hydroxyl groups were compatible affording the corresponding enolates in high grade of conversion (Table 1, entries 2–5). In the case of the hydroxyl group an additional reaction of acylation was observed to give an *O*-aryl



Scheme 1

N,*N*-diisopropylcarbamate in a quantitative yield. This reaction was very fast (5 min, 110 °C) and consumed one molar equivalent of carbamoyl chloride (CbCl).

These gratifying results allowed us to prepare **2b** which would have been unattainable using the conventional pyridine method.[4] Similar conversions were obtained when the electron-donating group was in the *ortho* position. For instance, enol carmabate **2k** was achieved in 65% conversion; however, *o*-hydroxyacetophenone gave **2l** in only 44% yield (Table 1, entries 11 and 12). This is in contrast with the previous case in which the hydroxyl group was located in position 4 (Table 1, entry 5). The decrease in the yield must have been caused by steric hindrance from the in situ formed carbamate in position 2. When an alkoxy substituent was in position 3 it gave somewhat lower yield as for 3-hydroxyacetophenone (Table 1, entries 8 and 9), probably due to the lack of conjugation between the enolate and the substituent in position 3.

The effect of electron-withdrawing groups was also studied. Nitro derivatives in *para* and *meta* positions (Table 1, entries 7 and 10) gave low yields; however, *p*-fluoroacetophenone (Table 1, entry 6) yielded the corresponding enol carbamate in a good conversion (70%). 3,4-Disubstituted acetophenones were also studied (Table 1, entries 13–15), giving the corresponding enol carbamates in slightly lower conversion than those with the activating groups in the *para* position. Condensed polycyclic aromatic methyl ketone **1p** was successfully transformed into the corresponding enol carbamate (Table 1, entry 16).

The scope of the reaction is not limited to acyclic ketones. Thus, cyclic ketones such as indanone, tetrahydronaphthalenone and chromanone gave high enol carbamate

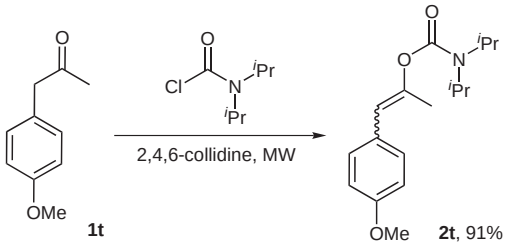
Table 1 Synthesis of Enol Carbamates

Entry	**1a**–**s**				Product	Molar ratio **1**/	Conversion (%)[b]
	R^1	R^2	R^3	R^4		CbCl/2,4,6-collidine	
1	H	H	H	H	**2a**[4]	2:3:3	68 [63][c]
2	OMe	H	H	H	**2b**	2:3:3	67
3	OBn	H	H	H	**2c**	2:3:3	70
4	O*i*-Pr	H	H	H	**2d**	2:3:3	66
5	OH	H	H	H	**2e** [R^1 = OCON(*i*-Pr)$_2$]	1:3:3	69
6	F	H	H	H	**2f**	2:3:3	70
7	NO_2	H	H	H	**2g**	2:3:3	25
8	H	OBn	H	H	**2h**	2:3:3	54
9	H	OH	H	H	**2i** [R^2 = OCON(*i*-Pr)$_2$]	1:3:3	53
10	H	NO_2	H	H	**2j**	2:3:3	35
11	H	H	OBn	H	**2k**	2:3:3	65
12	H	H	OH	H	**2l** [R^3 = OCON(*i*-Pr)$_2$]	1:3:3	44
13	OMe	OMe	H	H	**2m**	2:3:3	53
14	OBn	OMe	H	H	**2n**	2:3:3	60
15	OH	OMe	H	H	**2o** [R^1 = OCON(*i*-Pr)$_2$]	1:3:3	63
16	C_6H_4		H	H	**2p**	2:3:3	66
17	H	H	CH_2		**2q**[33]	2:3:3	93
18	H	H	CH_2CH_2		**2r**[4]	2:3:3	88
19	H	H	OCH_2		**2s**	2:3:3	84

[a] Reactions were heated at 150 °C for 1 h.[34]
[b] Reaction conversion was determined by ^{1}H NMR analysis. The crude products were contaminated only by starting ketone.[35]
[c] Isolated yield with purification by distillation (160 °C, 1 mm Hg).

conversions (93%, 88% and 84%, respectively; Table 1, entries 17–19) that were not dependent on the size of the aliphatic ring or the presence of a heteroatom attached to the β-carbon of the keto group. In this case, our method also constitutes a great improvement on previously reported ones, not only for the good yields obtained but also for the very short reaction times (**2r** was synthesized in 1 h compared to 216 h using the previously described method).[4]

This procedure can also be applied to α-aryl ketones since 4-methoxyphenylacetone (**1t**) afforded regioselectively the conjugated enol carbamate **2t** (mixture of *E*- and *Z*-isomer) in 91% conversion (Scheme 2).[36]



Scheme 2

In summary, a fast, efficient and solvent-free procedure for the synthesis of enol carbamates from acetophenones or α-aryl ketones and *N*,*N*-diisopropylcarbamoyl chloride is presented. This method employs the pyridine derivative 2,4,6-collidine to favor enolate formation. The method is more competitive than previous ones, since it leads to better yields, requires noticeably shorter reaction times, is easy to handle, and is also valid for cyclic and acyclic ketones.

Acknowledgment

We are grateful to Xunta de Galicia for financial support (PGIDIT05PXIB26201PR, PR405 A 098/59-0). We would also like to thank USC for a predoctoral fellowship to J.C.C., and Dr. Jo Dee Anderson for her linguistic support.

References and Notes

(1) Khur, R. J.; Dorough, H. W. *Carbamate Insecticides: Chemistry, Biochemistry and Toxicology*; CRC Press: Cleveland, **1976**.
(2) Bambury, R. E.; Seelye, D. E. Eur. Patent, EP 0396364, **1990**; *Chem. Abstr*. **1991**, *114*, 254062.
(3) In *Umpoled Synthons*; Hase, T. A., Ed.; Wiley-Interscience: New York, **1987**, 87.
(4) Peters, J. G.; Seppi, M.; Fröhlich, R.; Wibbeling, B.; Hoppe, D. *Synthesis* **2002**, 381.
(5) Seppi, M.; Kalkofen, R.; Reupohl, J.; Fröhlich, R.; Hoppe, D. *Angew. Chem. Int. Ed.* **2004**, *43*, 1423.
(6) Superchi, S.; Sotomayor, N.; Miao, G.; Joseph, B.; Campbell, M. G.; Snieckus, V. *Tetrahedron Lett.* **1996**, *37*, 6061.
(7) Chedid, R. B.; Fröhlich, R.; Hoppe, D. *Org. Lett.* **2006**, *8*, 3061.
(8) Hoppe, D.; Kraemer, T.; Schwark, J. R.; Zschage, O. *Pure Appl. Chem.* **1990**, *62*, 1999.
(9) Hoppe, D.; Hintze, F.; Tebben, P.; Paetow, M.; Ahrens, H.; Schwerdtfeger, J.; Sommerfeld, P.; Haller, J.; Guarnieri, W.; Kolczewski, S.; Hense, T.; Hoppe, I. *Pure Appl. Chem.* **1994**, *66*, 1479.
(10) Hoppe, D.; Ahrens, H.; Guarnieri, W.; Helmke, H.; Kolczewski, S. *Pure Appl. Chem.* **1996**, *68*, 613.
(11) Hoppe, D.; Hense, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2282.
(12) Jiang, X.-B.; van den Berg, M.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G. *Tetrahedron: Asymmetry* **2004**, *15*, 2223.
(13) Panella, L.; Feringa, B. L.; de Vries, J. G.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 4177.
(14) Mahe, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518.
(15) Superchi, S.; Sotomayor, N.; Miao, G.; Joseph, B.; Snieckus, V. *Tetrahedron Lett.* **1996**, *37*, 6057.
(16) Sengupta, S.; Snieckus, V. *J. Org. Chem.* **1990**, *55*, 5680.
(17) Olofson, R. A.; Cuomo, J.; Bauman, B. A. *J. Org. Chem.* **1978**, *43*, 2073.
(18) Franko-Filipasic, B. R.; Patarcity, R. *Chem. Ind. (London)* **1969**, 166.
(19) It has been described that 1-phenylvinyl *N*,*N*-diisopropylcarbamate was obtained in 73% yield; however, we have never been able to get yields higher than 50%, even with longer reaction times or higher temperatures.
(20) Varma, R. S. *Green Chem.* **1999**, *1*, 43.
(21) Seijas, J. A.; Vázquez-Tato, M. P. *Chem. Today* **2007**, *25*, 20.
(22) Kidwai, M. *Pure Appl. Chem.* **2001**, *73*, 147.
(23) Varma, R. S. *Pure Appl. Chem.* **2001**, *73*, 193.
(24) Seijas, J. A.; Vázquez-Tato, M. P.; Carballido-Reboredo, M. R. *J. Org. Chem.* **2005**, *70*, 2855.
(25) Seijas, J. A.; Vázquez-Tato, M. P.; Martínez, M. M.; Rodríguez-Parga, J. *Green Chem.* **2002**, *4*, 390.
(26) Seijas, J. A.; Vázquez-Tato, M. P.; González-Bande, C.; Martínez, M. M.; López-Pacios, B. *Synthesis* **2001**, 999.
(27) Seijas, J. A.; Vázquez-Tato, M. P.; Martínez, M. M. *Synlett* **2001**, 875.
(28) Seijas, J. A.; Vázquez-Tato, M. P.; Martínez, M. M. *Tetrahedron Lett.* **2000**, *41*, 2215.
(29) Seijas, J. A.; Vázquez-Tato, M. P.; Martínez, M. M.; Núñez-Corredoira, G. *J. Chem. Res., Synop.* **1999**, 420.
(30) Vázquez-Tato, M. P. *Synlett* **1993**, 506.
(31) Marwah, P.; Marwah, A.; Lardy, H. A. *Tetrahedron* **2003**, *59*, 2273.
(32) Longer reaction times did not improve the yield significantly.
(33) Heinl, T.; Retzzow, S.; Hoppe, D.; Fraenkel, G.; Chow, A. *Chem. Eur. J.* **1999**, *5*, 3464.
(34) **General Procedure for the Synthesis of 1-Arylalkenyl *N*,*N*-Diisopropylcarbamates 2**; **Synthesis of 1-Phenylvinyl *N*,*N*-Diisopropylcarbamate (2a)**: A stirred mixture of acetophenone (**1a**) (120 mg, 1 mmol), *N*,*N*-diisopropylcarbamoyl chloride (163 mg, 1.5 mmol) and 2,4,6-collidine (121 mg, 1.5 mmol) was irradiated in an open vessel with microwaves in a monomode oven (Discover CEM, 50 W and temperature control set at 150 °C measured with an IR sensor) for 60 min. The crude was dissolved in CH_2Cl_2 (30 mL) and washed with 10% aq HCl (2 × 20 mL), dried (Na_2SO_4) and evaporated to give 1-phenylvinyl *N*,*N*-diisopropylcarbamate (**2a**). Further purification by distillation (160 °C, 1 mm Hg) gave 155 mg (63%) of **2a**; mp 61–63 °C (hexane), lit.[13] mp 60–62 °C.

(35) Enol carbamates and parent ketones show very similar R_f values, making it very difficult to separate them by chromatography. When purification by distillation is not possible, a very easy way to remove the starting material is to reduce it to the corresponding alcohol with sodium borohydride followed by column chromatography. This very method must also have been used in previously described literature procedures as we confirmed in our laboratory.

(36) Data of previously undescribed compounds:

1-(4-Methoxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2b): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28–1.32 [m, 12 H, 2 × CH(CH_3)$_2$], 3.80 (s, 3 H, OMe), 3.99–4.03 [m, 2 H, 2 × CH(CH$_3$)$_2$], 4.87 (d, J = 1.8 Hz, 1 H, C=CH$_2$), 5.28 (d, J = 1.8 Hz, 1 H, C=CH$_2$), 6.87 (d, J = 8.8 Hz, 2 H, ArH), 7.41 (d, J = 8.8 Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 46.4, 46.8, 55.5, 99.7, 114.0, 126.5, 128.4, 153.5, 153.7, 160.1. MS (EI): *m*/*z* (%) = 278 (9) [M$^+$ + 1], 277 (22) [M$^+$], 135 (45), 128 (100). IR (KBr, film): 1713, 1512, 1252, 1041, 837 cm^{-1}. Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 68.95; H, 8.76; N, 4.72.

1-(4-Benzyloxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2c): mp 94–95 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.33 [m, 12 H, 2 × CH(CH_3)$_2$], 4.02 [br s, 2 H, 2 × CH(CH$_3$)$_2$], 4.90 (d, J = 1.8 Hz, 1 H, C=CH$_2$), 5.07 (s, 2 H, OCH_2Ph), 5.30 (d, J = 1.8 Hz, 1 H, C=CH$_2$), 6.93 (d, J = 8.8 Hz, 2 H, ArH), 7.32–7.42 (m, 7 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 46.4, 46.9, 70.3, 99.8, 115.0, 126.6, 127.7, 128.2, 128.6, 128.8, 137.1, 153.5, 153.7, 159.4. MS (EI): *m*/*z* (%) = 353 (50) [M$^+$], 128 (100). IR (KBr, film): 1705, 1246, 1215, 1011, 841 cm^{-1}. Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 75.12; H, 8.07; N, 3.91.

1-(4-Isopropoxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2d): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29–1.33 [m, 18 H, 3 × CH(CH_3)$_2$], 4.01 [sept, J = 6.8 Hz, 2 H, 2 × CH(CH$_3$)$_2$], 4.54 [sept, J = 6.0 Hz, 1 H, CH(CH$_3$)$_2$], 4.86 (d, J = 2.2 Hz, 1 H, C=CH$_2$), 5.27 (d, J = 1.8 Hz, 1 H, C=CH$_2$), 6.8 (d, J = 8.8 Hz, 2 H, ArH), 7.39 (d, J = 8.8 Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 22.2, 46.3, 46.8, 70.1, 99.5, 115.7, 115.9, 126.5, 153.6, 153.7, 158.5. MS (EI): *m*/*z* (%) = 305 (8) [M$^+$], 128 (100), 86 (36). IR (KBr, film): 2975, 1712, 1509, 1248 cm^{-1}. Anal. Calcd for $C_{18}H_{27}NO_3$: C, 70.79; H, 8.91; N, 4.59. Found: C, 71.07; H, 8.94; N, 4.76.

1-(4-{[(Diisopropylamino)carbonyl]oxy}phenyl)vinyl *N*,*N*-Diisopropylcarbamate (2e): mp 59–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 [m, 24 H, 4 × CH(CH_3)$_2$], 4.00 [hept, J = 6.6 Hz, 4 H, 4 × CH(CH$_3$)$_2$], 4.95 (d, J = 2.2 Hz, 1 H, CH=CH_2), 5.33 (d, J = 2.2 Hz, 1 H, CH=CH_2), 7.10 (d, J = 8.8 Hz, 2 H, ArH), 7.46 (d, J = 8.8 Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.6, 21.8, 46.4, 46.8, 101.2, 121.9, 126.2, 132.6, 151.9, 153.2, 153.5, 153.8. MS (EI): *m*/*z* (%) = 390 (4) [M$^+$], 128 (100), 86 (44). IR (KBr, film): 1715, 1315, 1258, 1214, 1154 cm^{-1}. Anal. Calcd for $C_{22}H_{34}N_2O_4$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.36; H, 8.89; N, 7.05.

1-(4-Fluorophenyl)vinyl *N*,*N*-Diisopropylcarbamate (2f): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.33 [m, 12 H, 2 × CH(CH_3)$_2$], 4.00 [sept, J = 6.6 Hz, 2 H, 2 × CH(CH$_3$)$_2$], 4.96 (d, J = 2.2 Hz, 1 H, C=CH_2), 5.33 (d, J = 2.2 Hz, 1 H, C=CH_2), 7.02 (t, J = 8.8 Hz, 2 H, ArH), 7.44 (dd, J = 5.3, 9.0 Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 47.0, 101.4, 115.6 (d, $^2J_{CF}$ = 22 Hz), 127.0, 131.9, 152.9, 153.5, 163.1 (d, $^1J_{CF}$ = 248 Hz). MS (EI): *m*/*z* (%) = 265 (5) [M$^+$], 128 (68), 86 (100). IR (KBr, film): 2968, 1712, 1510, 1259, 1214, 1043 cm^{-1}. Anal. Calcd for $C_{15}H_{20}FNO_2$: C, 67.90; H, 7.60; N, 5.28. Found: C, 68.07; H, 7.47; N, 5.19.

1-(4-Nitrophenyl)vinyl *N*,*N*-Diisopropylcarbamate (2g): mp 83–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.35 [m, 12 H, 2 × CH(CH_3)$_2$], 4.01 [sept, J = 6.6 Hz, 2 H, 2 × CH(CH$_3$)$_2$], 5.19 (d, J = 2.2 Hz, 1 H, C=CH$_2$), 5.56 (d, J = 2.2 Hz, 1 H, C=CH$_2$), 7.60 (d, J = 9.2 Hz, 2 H, ArH), 8.20 (d, J = 8.8 Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 21.8, 46.6, 47.1, 105.5, 124.1, 125.9, 142.0, 147.9, 151.9, 153.1. MS (EI): *m*/*z* (%) = 292 (1) [M$^+$], 165 (28), 128 (94), 86 (100). IR (KBr, film): 2971, 1709, 1519, 1345, 1262 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.34; H, 6.41; N, 9.62.

1-(3-Benzyloxyphenyl)vinyl Diisopropylcarbamate (2h): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29–1.34 [m, 12 H, 2 × CH(CH_3)$_2$], 4.03 [sept, J = 6.8 Hz, 2 H, 2 × CH(CH$_3$)$_2$], 5.00 (d, J = 1.8 Hz, 1 H, C=CH_2), 5.07 (s, 2 H, OCH_2Ph), 5.40 (d, J = 1.8 Hz, 1 H, C=CH_2), 6.93 (br d, J = 7.9 Hz, 1 H, ArH), 7.10 (m, 2 H, ArH), 7.26 (t, J = 7.9 Hz, 1 H, ArH), 7.30–7.45 (m, 5 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 46.5, 46.9, 70.3, 101.9, 111.8, 115.5, 118.0, 127.7, 128.2, 128.8, 129.7, 137.1, 137.2, 153.5, 159.1. MS (EI): *m*/*z* (%) = 353 (2) [M$^+$], 128 (100), 91 (30). IR (KBr, film): 2969, 1712, 1431, 1264, 1042 cm^{-1}. Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.38; H, 7.24; N, 3.38.

1-(3-{[(Diisopropylamino)carbonyl]oxy}phenyl)vinyl *N*,*N*-Diisopropylcarbamate (2i): mp 74–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 [m, 24 H, 4 × CH(CH_3)$_2$], 4.00 [br s, 4 H, 4 × CH(CH$_3$)$_2$], 5.00 (d, J = 1.8 Hz, 1 H, CH=CH_2), 5.41 (d, J = 2.2 Hz, 1 H, CH=CH_2), 7.08 (dt, J = 2.2, 7.0 Hz, 1 H, ArH), 7.20 (m, 1 H, ArH), 7.28–7.34 (m, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.7, 46.6, 102.2, 118.7, 121.7, 122.3, 129.4, 137.1, 151.7, 153.0. MS (EI): *m*/*z* (%) = 390 (18) [M$^+$], 128 (100). IR (KBr, film): 1712, 1427, 1257, 1198, 1153 cm^{-1}. Anal. Calcd for $C_{22}H_{34}N_2O_4$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.57; H, 8.42; N, 7.68.

1-(3-Nitrophenyl)vinyl *N*,*N*-Diisopropylcarbamate (2j): mp 85–89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27–1.39 [m, 12 H, 2 × CH(CH_3)$_2$], 4.02 [br s, 2 H, 2 × CH(CH$_3$)$_2$], 5.17 (d, J = 2.6 Hz, 1 H, C=CH$_2$), 5.54 (d, J = 2.2 Hz, 1 H, C=CH$_2$), 7.52 (t, J = 8.1 Hz, 1 H, ArH), 7.81 (ddd, J = 0.8, 1.7, 7.9 Hz, 1 H, ArH), 8.16 (ddd, J = 1.4, 2.2, 8.2 Hz, 1 H, ArH), 8.30 (t, J = 2.0 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 21.7, 46.7, 47.1, 104.1, 120.0, 123.4, 129.7, 130.9, 137.6, 148.7, 151.6, 153.1. MS (EI): *m*/*z* (%) = 292 (2) [M$^+$], 165 (40), 128 (100), 86 (32). IR (KBr, film): 2975, 1713, 1532, 1350, 1255, 1042 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.36; H, 7.15; N, 9.34.

1-(2-Benzyloxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2k): mp 38–40 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 [d, J = 6.6 Hz, 12 H, 2 × CH(CH_3)$_2$], 3.97 [sept, J = 6.6 Hz, 2 H, 2 × CH(CH$_3$)$_2$], 5.16 (m, 3 H, C=CH_2, OCH_2Ph), 5.60 (d, J = 0.9 Hz, 1 H, C=CH_2), 6.93–6.98 (m, 2 H, ArH), 7.20–7.46 (m, 7 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.7, 46.3, 46.7, 70.7, 106.5, 113.2, 121.0, 125.2, 127.5, 128.0, 128.7, 129.6, 137.2, 150.5, 153.8, 156.4. MS (EI): *m*/*z* (%) = 353 (40) [M$^+$], 128 (100) [Cb], 91 (23). IR (KBr, film): 2969, 1710 (C=O), 1446, 1289, 1240 (CO), 1043, 754 cm^{-1}. Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.76; H, 7.43; N, 3.87.

1-(2-{[(Diisopropylamino)carbonyl]oxy}phenyl)vinyl *N*,*N*-Diisopropylcarbamate (2l): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23–1.32 [m, 24 H, 4 × CH(CH_3)$_2$], 3.91 [br s, 3 H, 3 × CH(CH$_3$)$_2$], 4.18 [br s, 1 H, CH(CH$_3$)$_2$], 5.15 (s, 1 H, C=CH_2), 5.18 (s, 1 H, CH=CH_2), 7.09 (d, J = 7.9 Hz, 1 H, ArH), 7.16 (t, J = 7.5 Hz, 1 H, ArH), 7.29 (t, J = 7.7 Hz, 1 H,

ArH), 7.42 (d, *J* = 7.9 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.7, 46.7, 46.9, 105.4, 123.6, 125.1, 129.3, 129.4, 129.6, 149.0, 149.8, 153.4, 153.5. MS (EI): *m*/*z* (%) = 391 (5) [M^+ + 1], 390 (1) [M^+], 128 (100), 86 (81). IR (KBr, film): 2970, 1715, 1316, 1207, 1042 cm^{-1}. Anal. Calcd for $C_{22}H_{34}N_2O_4$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.22; H, 9.21; N, 6.95.

1-(3,4-Dimethoxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2m): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.32 [m, 12 H, 2 × CH(CH_3)$_2$], 3.86 (s, 6 H, 2 × OMe), 4.01 [sept, *J* = 6.6 Hz, 2 H, 2 × C*H*(CH$_3$)$_2$], 4.89 (d, *J* = 1.8 Hz, 1 H, C=CH_2), 5.28 (d, *J* = 1.8 Hz, 1 H, C=CH_2), 6.81 (d, *J* = 8.4 Hz, 1 H, ArH), 6.98 (d, *J* = 1.8 Hz, 1 H, ArH), 7.04 (dd, *J* = 2.2, 8.3 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 46.4, 46.8, 55.9, 56.1, 100.0, 108.4, 111.2, 118.0, 128.6, 148.9, 149.7, 153.4, 153.5. MS (EI): *m*/*z* (%) = 307 (7) [M^+], 180 (13), 128 (100), 86 (65). IR (KBr, film): 1712, 1516, 1265, 1221, 1143 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.41; H, 7.79; N, 4.63.

1-(4-Benzyloxy-3-methoxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2n): mp 75–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.33 [m, 12 H, 2 × CH(CH_3)$_2$], 3.89 (s, 3 H, OMe), 4.02 [m, 2 H, 2 × C*H*(CH$_3$)$_2$], 4.90 (d, *J* = 1.8 Hz, 1 H, C=CH_2), 5.16 (s, 2 H, OCH_2Ph), 5.30 (d, *J* = 2.2 Hz, 1 H, C=CH_2), 6.84 (d, *J* = 8.4 Hz, 1 H, ArH), 6.98–7.03 (m, 2 H, ArH), 7.25–7.44 (m, 5 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 21.8, 46.4, 46.9, 56.1, 71.2, 100.2, 109.0, 113.9, 117.9, 127.4, 128.1, 128.8, 129.1, 137.2, 148.9, 149.6, 153.4, 153.6. MS (EI): *m*/*z* (%) = 383 (5) [M^+], 128 (100), 91 (94), 86 (66). IR (KBr, film): 1712, 1520, 1272, 1222, 1147, 1020 cm^{-1}. Anal. Calcd for $C_{23}H_{29}NO_4$: C, 72.04; H, 7.62; N, 3.65. Found: C, 71.95; H, 7.93; N, 3.60.

1-(4-{[(Diisopropylamino)carbonyl]oxy}-3-methoxyphenyl)vinyl *N*,*N*-Diisopropylcarbamate (2o): Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 [m, 24 H, 4 × CH(CH_3)$_2$], 3.80 (s, 3 H, OMe), 4.00 [sept, *J* = 6.4 Hz, 4 H, 4 × C*H*(CH$_3$)$_2$], 4.96 (s, 1 H, CH=CH_2), 5.32 (s, 1 H, CH=CH_2), 7.03–7.05 (m, 3 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3, 20.7, 21.6, 46.8, 56.0, 101.3, 109.6, 117.8, 123.4, 133.8, 135.3, 141.3, 151.7, 153.3. MS (EI): *m*/*z* (%) = 420 (2) [M^+], 293 (1), 128 (100), 86 (44). IR (KBr, film): 1716, 1316, 1281, 1267, 1204, 1154, 1126 cm^{-1}. Anal. Calcd for $C_{23}H_{36}N_2O_5$: C, 65.69; H, 8.63; N, 6.66. Found: C, 65.63; H, 8.74; N, 6.54.

1-(2-Naphthyl)vinyl *N*,*N*-Diisopropylcarbamate (2p): mp 58–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.40 [m, 12 H, 2 × CH(CH_3)$_2$], 4.07 [m, 2 H, 2 × C*H*(CH$_3$)$_2$], 5.09 (d, *J* = 2.0 Hz, 1 H, C=CH_2), 5.55 (d, *J* = 2.0 Hz, 1 H, C=CH_2), 7.44–7.48 (m, 2 H, ArH), 7.63 (dd, *J* = 1.8, 8.8 Hz, 1 H, ArH), 7.79–7.82 (m, 3 H, ArH), 7.90 (d, *J* = 1.7 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 46.5, 46.9, 102.1, 123.2, 124.3, 126.5, 126.6, 127.8, 128.4, 128.7, 133.0, 133.4, 133.6, 153.6, 153.7. MS (EI): *m*/*z* (%) = 298 (11) [M^+ + 1], 297 (42) [M^+], 170 (39), 128 (90), 86 (100). IR (KBr, film): 2968, 1707 (C=O), 1645, 1429, 1323, 1265, 1041, 864, 760 cm^{-1}. Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 77.11; H, 7.47; N, 5.13.

1*H*-Inden-3-yl *N*,*N*-Diisopropylcarbamate (2q):[33] Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 [d, *J* = 7.0 Hz, 12 H, 2 × CH(CH_3)$_2$], 3.62 (s, 2 H, CH_2), 3.90 [br s, 1 H, C*H*(CH$_3$)$_2$], 4.11 [br s, 1 H, C*H*(CH$_3$)$_2$], 6.53 (s, 1 H, C*H*CH$_2$), 7.12 (td, *J* = 1.8, 7.0 Hz, 1 H, ArH), 7.20–7.29 (m, 2 H, ArH), 7.32 (d, *J* = 7.2, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.8, 38.3, 46.4, 47.1, 113.3, 120.7, 123.5, 124.0, 126.8, 137.6, 143.7, 152.8, 156.8. MS (EI): *m*/*z* (%) = 260 (2) [M^+ + 1], 132 (54), 128 (84), 86 (100). IR (KBr, film): 2970, 1711, 1606, 1272, 1132, 748, 715 cm^{-1}.

2*H*-Chromen-4-yl *N*,*N*-Diisopropylcarbamate (2s): mp 74.1–77.4 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30–1.32 [m, 12 H, 2 × CH(CH_3)$_2$], 4.02 [sept, *J* = 6.8 Hz, 2 H, 2 × C*H*(CH$_3$)$_2$], 4.96 (d, *J* = 3.5 Hz, 2 H, CH_2O), 5.49 (t, *J* = 3.7 Hz, 1 H, C=C*H*CH$_2$), 6.79 (dd, *J* = 0.9, 8.0 Hz, 1 H, ArH), 6.87 (td, *J* = 0.9, 7.5 Hz, 1 H, ArH), 7.06 (dd, *J* = 1.6, 7.7 Hz, 1 H, ArH), 7.13 (td, *J* = 1.6, 7.9 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.7, 46.7, 47.0, 65.7, 108.0, 116.1, 120.5, 121.3, 121.9, 130.0, 143.4, 152.9, 155.4. MS (EI): *m*/*z* (%) = 276 (4) [M^+ + 1], 275 (19) [M^+], 147 (69), 128 (83), 86 (100). IR (KBr, film): 2970, 1716 (C=O), 1306, 1207, 755 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.89; H, 8.05; N, 5.06.

1-(4-Methoxyphenyl)prop-1-en-2-yl *N*,*N*-Diisopropylcarbamate (2t); mixture of *E*- and *Z*-isomers (2:1): oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.26 [m, 12 H, 2 × CH(CH_3)$_2$], 2.04 (d, *J* = 0.9 Hz, 3 H, Me, *E*-isomer), 2.09 (d, *J* = 0.9 Hz, 3 H, Me, *Z*-isomer), 3.73 (s, 3 H, OMe, *E*-isomer), 3.75 (s, 3 H, OMe, *Z*-isomer), 3.85–4.00 [m, 2 H, 2 × C*H*(CH$_3$)$_2$], 5.83 (s, 1 H, C=CH, *E*-isomer), 6.19 (s, 1 H, C=CH, *Z*-isomer), 6.77 (d, *J* = 8.8 Hz, 2 H, ArH, *E*-isomer), 6.83 (d, *J* = 8.8 Hz, 2 H, ArH, *Z*-isomer), 7.18 (d, *J* = 8.4 Hz, 2 H, ArH, *Z*-isomer), 7.26 (d, *J* = 8.8 Hz, 2 H, ArH, *E*-isomer). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7, 20.8, 21.1, 21.7, 46.6, 55.3, 113.7, 113.9, 115.7, 117.7, 127.9, 128.2, 129.5, 130.1, 145.2, 147.2, 152.7, 154.1, 158.5. MS (EI): *m*/*z* (%) = 292 (6) [M^+ + 1], 291 (16) [M^+], 164 (27), 163 (23), 135 (29), 128 (90), 121 (43), 86 (100). IR (KBr, film): 2970, 1707, 1512, 1252, 1041, 837, 757 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 70.55; H, 8.74; N, 4.79.