Efficient Demethylation of *N*,*N*-Dimethylanilines with Phenyl Chloroformate in Ionic Liquids

Satomi Imori,[a] Hideo Togo*[a,b]

[a] Graduate School of Science and Technology, Chiba University, Yayoi-cho 1-33, Inage-ku 263-8522, Japan

[b] Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inage-ku 263-8522, Japan
E-mail: togo@faculty.chiba-u.jp

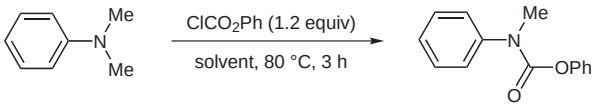
Received 24 July 2006

Abstract: Demethylation of *N*,*N*-dimethylanilines was carried out in various ionic liquids and acetonitrile as well as under solvent-free conditions. We have demonstrated that their reactivity dramatically depends on the ionic liquid employed; [bmim]Cl showed the best reactivity.

Key words: *N*,*N*-dimethylaniline, demethylation, phenyl chloroformate, ionic liquid, phenyl *N*-methyl-*N*-arylcarbamate

N-Dealkylation, especially N-demethylation, is important in organic synthesis as it can be applied to the demethylation of natural alkaloid products such as morphine to noromorphine or oxymorphone to noroxymorphone, respectively.[1] N-Dealkylation of aliphatic and acyclic tertiary amine to dialkylamines is well known.[1] Initially, tertiary amines were treated with cyanogen bromide (von Braun reaction) to form the corresponding N,N-disubstituted cyanamide and alkyl bromide. Phosgene has also been employed to effect N-dealkylation. Recently, these reagents, due to their high toxicity and poor selectivity, were replaced by chloroformates. In 1967, effective N-demethylation of tertiary amines with phenyl chloroformate was reported.[2] Generally, aliphatic tertiary amines react smoothly with phenyl chloroformate to provide the corresponding dealkylated *N*,*N*-dialkyl carbamates. Subsequently, many related reagents such as 2,2,2-trichloroethyl chloroformate,[3a] vinyl chloroformate,[3b] 1-chloroethyl chloroformate,[3c] chlorothionoformate,[3d] and acetic anhydride/boron trifluoride,[3e] were developed. Moreover, *N*-(2-acetoxyethyl) tertiary amines were converted to the corresponding secondary amine under photochemical conditions (350 nm) in the presence of 4,4′-dimethoxybenzophenone.[4] Once phenyl carbamates or methyl carbamates derived from the reaction of tertiary amines with phenyl chloroformate or methyl chloroformate are formed they can be smoothly converted to the corresponding free secondary amines under mild conditions, using $(CH_3)_3SiI$[5a] or TBAF/THF.[5b] However, the dealkylation of *N*,*N*-dialkylanilines using chloroformate esters to furnish the corresponding carbamate esters is extremely limited; long reaction times and drastic conditions are required compared with aliphatic and acyclic tertiary amines.[2] For example, *N*,*N*-dimethylaniline reacts with phenyl chloroformate at 100 °C to give the corresponding phenyl *N*-phenyl-*N*-methylcarbamate after 60 hours in 80% yield.[2]

Table 1 Effects of Ionic liquids

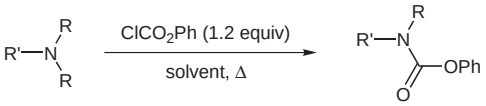


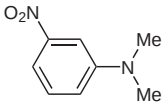
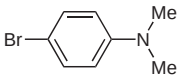
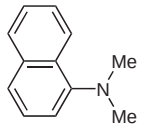
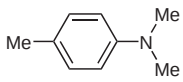
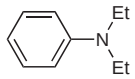
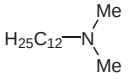
Entry	Solvent	Yield (%)
1	MeCN (1.5 mL)	24
2	Solvent-free	25
3	Solvent-free (NaCl, 3.0 equiv)	22
4	[bmim]$SO_3C_8H_{17}$ (2.0 mL)	4
5	[emim]OTs (2.0 mL)	15
6	[bmpy]NTf_2 (2.0 mL)	49
7	[bmpy]PF_6 (2.0 mL)	64
8	[bmim]PF_6 (2.0 mL)	70
9	[bmim]BF_4 (2.0 mL)	69
10	[bmim]Br (2.0 mL)	80
11	[bdmim]Cl (2.0 mL)	90
12	[bmim]Cl (2.0 mL)	95
13	[bmim]Cl (4.0 mL)	20
14	[bmim]Cl (1.0 mL)	95
15	[bmim]Cl (0.5 mL)	94
16	[bmim]Cl (0.2 mL)	95
17	[bmim]Cl (0.1 mL)	88
18	[bmim]Cl (0.04 mL)	79

Ionic liquids have become very popular as organic reaction media due to their ability to promote ionic reactions and also from an environmental point of view.[6] Thus, these solvents possess many advantages, such as negligible vapor pressure, non-flammability, high thermal stability, and easy reusability. As a result they have been successfully used in Friedel–Crafts reaction,[7] hydrogenation,[8] Diels–Alder reactions,[9] Heck, Suzuki, Sonogashira,

SYNLETT 2006, No. 16, pp 2629–2632
Advanced online publication: 22.09.2006
DOI: 10.1055/s-2006-951490; Art ID: U09106ST

Table 2 Dealkylation of *N*,*N*-Dimethyl- and *N*,*N*-Diethylanilines[20]

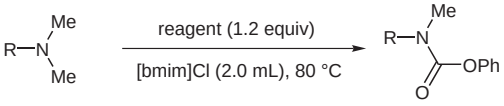


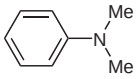
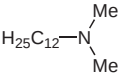
	Solvent (mL)	Temp (°C)	Time (h)	Yield (%)
	Solvent-free	100	72	6 (94)[a]
	[bmim]Cl (2.0)	100	72	99
	Solvent-free	80	18	24 (76)[a]
	MeCN (1.5)	80	18	25 (66)[a]
	[bmim]Cl (2.0)	80	18	94
	Solvent-free	80	12	19 (80)[a]
	MeCN (1.5)	80	12	32 (67)[a]
	[bmim]Cl (2.0)	80	12	91
	Solvent-free	80	6	66 (32)[a]
	MeCN (1.5)	80	6	79 (20)[a]
	[bmim]Cl (2.0)	80	6	85
	Solvent-free	100	24	63 (35)[a]
	[bmim]Cl (2.0)	100	24	99
	Solvent-free	80	2	66
	MeCN (1.5)	80	2	60
	[bmim]Cl (2.0)	80	2	94

[a] Starting amine was recovered.

and olefin metathesis reactions,[10] Michael additions,[11] oxidation,[12] condensation reaction,[13] formation of imines,[14] 1,2-rearrangement,[15] esterification of carboxylic acids and carboxylates,[16] Williamson ether synthesis,[17] and Grignard reaction.[18] Recently, we also reported the highly efficient esterification of carboxylic acids and phosphonic acids with trialkyl orthoacetate in an ionic liquid.[19] Here as a part of our study on the development of organic reactions with ionic liquids, we would like to report a dramatic rate acceleration by ionic liquids in the reaction of inert *N*,*N*-dimethylaniline with phenyl chloroformate; the reactivity is markedly dependent on the ionic liquid employed. All reactions proceeded under homogeneous conditions at 80 °C or 100 °C. The results for the reaction of *N*,*N*-dimethylaniline with phenyl chloroformate in MeCN, under solvent-free conditions, under solvent-free conditions with NaCl, and in various ionic liquids are shown in Table 1. Among them, [bmim]Cl showed the best reactivity, while [bdmim]Cl and [bmim]Br also showed high reactivity. However, [bmim]BF_4, [bmim]PF_6, [bmpy]PF_6, and [bmpy]NTf_2 showed moderate reactivity, and finally [emim]OTs and [bmim]$O_3SC_8H_{17}$ (1-butyl-3-methylimidazolium octanesulfonate) showed poorer reactivity than solvent-free or MeCN conditions. In all cases showing poor reactivity it was possible to recover the starting amines. Thus, the results indicate that the reactivity depends on the size of the anionic group in the ionic liquid; more specifically the reactivity is affected by ionic polarity or charge density. The amount of ionic liquid is also important; we found 0.2–2.0 mL was optimal for 1 mmol substrate (Table 1, entries 12–18).

Table 3 Reactivity of Chloroformates



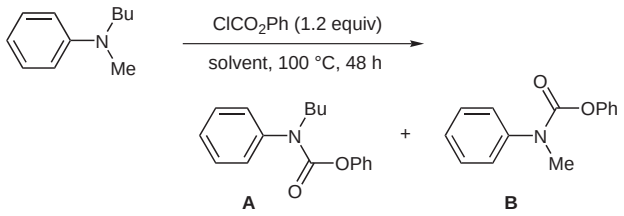
	Reagent	Time (h)	Yield (%)
	$ClCO_2Et$	3	1 (74)[a]
	$ClCO_2Ph$	3	95
	$ClCO_2Et$	2	8 (82)[a]
	$ClCO_2Ph$	2	94

[a] Starting amine was recovered.

Based on these results, various *N*,*N*-dimethylaniline derivatives were treated with phenyl chloroformate in [bmim]Cl and under solvent-free conditions. In every reaction, the [bmim]Cl matrix promotes the reaction efficiently, especially for dimethylanilines bearing electron-withdrawing groups, as shown in Table 2.

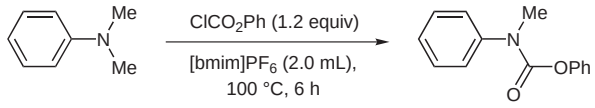
We also looked at the reactivity of phenyl chlorofomate versus ethyl chloroformate (Table 3) with phenyl chloroformate showing much higher reactivity in [bmim]Cl for both substrates tested (Table 3).

Table 4 Solution versus Solvent-Free Conditions



	A	B
[bmim]Cl (2.0 mL)	83%	16%
Solvent-free	46%	29%
MeCN (1.5 mL, reflux)	35%	7%

Table 5 Effect of Recycling [bmim]PF_6



Regeneration	Yield (%)
0	78
1	78
2	79
3	82
4	88

Next we looked at the selectivity of the reaction when two alkyl groups were present on the substrate. The selective demethylation of *N*-butyl-*N*-methylaniline with phenyl chloroformate in [bmim]Cl gave a higher reactivity and selectivity than the reaction performed under solvent-free conditions or in MeCN (Table 4).

Finally we tried to recycle the ionic liquid and to reuse it in further reactions. Unfortunately, [bmim]Cl cannot be conveniently extracted from the reaction mixture by standard procedures since it is soluble in water and cannot be washed with water after the extraction. However, the pure product can be obtained directly by distillation of the reaction mixture, and the remaining ionic liquid was reused for further demethylation reactions, maintaining the high yield of the carbamate ester. Fortunately, [bmim]PF_6 can be recovered by the standard extraction method since it is not soluble in water. Thus, after the extraction of the carbamate ester with ethyl acetate, the recovered [bmim]PF_6 was washed with water once and dried on a vacuum pump. It was then reused for the same demethylation reaction and the high yield of the carbamate ester was maintained (Table 5).

In summary, demethylation of *N*,*N*-dimethylanilines was carried out in various ionic liquids, under solvent-free conditions, and in acetonitrile. Their reactivity dramatically depends on the ionic liquid employed, with [bmim]Cl showing the best reactivity.

Acknowledgment

The present study was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Science, Education, Sports, and Culture of Japan.

References and Notes

(1) Review: Cooley, J. H.; Evain, E. J. *Synthesis* **1989**, 1; and references cited therein.
(2) Hobson, J. D.; McCluskey, J. G. *J. Chem. Soc. C* **1967**, 2015.
(3) (a) Montzka, T. A.; Matiskella, J. D.; Partyka, R. A. *Tetrahedron Lett.* **1974**, 1325. (b) Olofson, R. A.; Schnur, R. C.; Bunes, L.; Pepe, J. P. *Tetrahedron Lett.* **1977**, 1567. (c) Olefson, R. A.; Martz, J. T.; Senet, J. P.; Piteau, M.; Malfroot, T. *J. Org. Chem.* **1984**, *49*, 2081. (d) Millan, D. S.; Prager, R. F. *Tetrahedron Lett.* **1998**, *39*, 4387. (e) Dave, P. R. *J. Org. Chem.* **1996**, *61*, 5453.
(4) Cossy, J.; Rakotoarisoa, H. *Tetrahedron Lett.* **2000**, *41*, 2097.
(5) (a) Laurent, P.; Braekman, J.-C.; Daloze, D. *Eur. J. Org. Chem.* **2000**, 2057. (b) Jacquemard, U.; Beneteau, V.; Lofoix, M.; Routier, S.; Merour, Y.; Coudert, G. *Tetrahedron* **2004**, *60*, 10039.
(6) Reviews: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772. (c) Sheldon, R. *Chem. Commun.* **2001**, 2399. (d) Sheldon, R. A. *Pure Appl. Chem.* **2002**, *72*, 1233. (e) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391. (f) Zhao, H.; Malhotra, S. V. *Aldrichimica Acta* **2002**, *35*, 75. (g) Lee, S. *Chem. Commun.* **2006**, 1049. (h) Macfarlane, D. R.; Pringle, J. M.; Johansson, K. M.; Forsyth, S. A.; Forsyth, M. *Chem. Commun.* **2006**, 1905.
(7) (a) Surette, J. K. D.; Green, L.; Singer, R. D. *Chem. Commun.* **1996**, 2753. (b) Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. *Chem. Commun.* **1998**, 2097. (c) Jorapur, Y. R.; Lee, C.-H.; Chi, D. Y. *Org. Lett.* **2005**, *7*, 1231.
(8) (a) Monteiro, A. L.; Zinn, F. K.; De Souza, R. F.; Dupont, J. *Tetrahedron: Asymmetry* **1997**, *8*, 177. (b) Dyson, P. J.; Ellis, D. L.; Parker, D. G.; Welton, T. *Chem. Commun.* **1999**, 25. (c) Adams, C. J.; Earle, M. J.; Seddon, K. R. *Chem. Commun.* **1999**, 1043.
(9) (a) Howarth, J.; Hanlon, K.; Fayne, D.; McCormac, P. *Tetrahedron Lett.* **1997**, *38*, 3097. (b) Huddleston, J. G.; Rogers, R. D. *Chem. Commun.* **1998**, 1765. (c) Lee, C. W. *Tetrahedron Lett.* **1999**, *40*, 2461.
(10) (a) Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Org. Lett.* **1999**, *1*, 997. (b) Calo, V.; Nacci, A.; Lopez, L.; Mannarini, N. *Tetrahedron Lett.* **2000**, *41*, 8973. (c) Mathews, C. J.; Smith, P. J.; Welton, T. *Chem. Commun.* **2000**, 1249. (d) Fukuyama, T.; Shinmen, M.; Nishitani, S.; Sato, M.; Ryu, I. *Org. Lett.* **2002**, *4*, 1691. (e) Mayo, K. G.; Nearhoof, E. H.; Kiddle, J. J. *Org. Lett.* **2002**, *4*, 1567.
(11) Calo, V.; Nacci, A.; Lopez, L.; Lerario, V. L. *Tetrahedron Lett.* **2000**, *41*, 8977.

(12) (a) Owens, G. S.; Abu-Omar, M. M. *Chem. Commun.* **2000**, 1165. (b) Howarth, J. *Tetrahedron Lett.* **2000**, *41*, 6627. (c) Ansari, I. A.; Gree, R. *Org. Lett.* **2002**, *4*, 1507. (d) Yanada, R.; Takemoto, Y. *Tetrahedron Lett.* **2002**, *43*, 6849. (e) Liu, Z.; Chen, Z.-C.; Zheng, Q.-G. *Org. Lett.* **2003**, *5*, 3321. (f) Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Narsaiah, A. V. *Tetrahedron* **2004**, *60*, 2131. (g) Chhikara, B. S.; Tehlan, S.; Kumar, A. *Synlett* **2005**, 63. (h) Wu, X.-E.; Ma, L.; Ding, M.- X.; Gao, L.-X. *Chem. Lett.* **2005**, *34*, 312. (i) Wu, X.-E.; Ma, L.; Ding, M.-X.; Gao, L.-X. *Synlett* **2005**, 607.

(13) (a) Morrison, D. W.; Forbes, D. C.; Davis, J. H. Jr. *Tetrahedron Lett.* **2001**, *42*, 6053. (b) Xie, Y.-Y.; Chen, Z.-C.; Zheng, Q.-G. *Synthesis* **2002**, 1505. (c) Su, C.; Chen, Z.-C.; Zheng, Q.-G. *Synthesis* **2003**, 555. (d) Kitaoka, S.; Nobuoka, K.; Ishikawa, Y. *Chem. Commun.* **2004**, 1902. (e) Sato, A.; Nakamura, Y.; Maki, T.; Ishihara, K.; Yamamoto, A. *Adv. Synth. Catal.* **2005**, *347*, 1337.

(14) Andrade, C. K. Z.; Takeda, S. C. S.; Alves, L. M.; Rodrigues, J. P.; Suarez, P. A. Z.; Brandao, R. F.; Soares, V. C. D. *Synlett* **2004**, 2135.

(15) Ren, R. X.; Zueva, L. D.; Ou, W. *Tetrahedron Lett.* **2001**, *42*, 8441.

(16) (a) Deng, Y.; Shi, F.; Beng, J.; Quio, K. *J. Mol. Catal. A: Chem.* **2001**, *165*, 33. (b) Fraga-Dubreuil, J.; Bourahla, K.; Rahmouni, M.; Bazureau, J. P.; Hamelin, J. *Catal. Commun.* **2002**, *3*, 185. (c) Brinchi, L.; Germani, R.; Savelli, G. *Tetrahedron Lett.* **2003**, *44*, 2027. (d) McNulty, J.; Cheekoori, S.; Nair, J. J.; Larichev, V.; Capretta, A.; Robertson, A. J. *Tetrahedron Lett.* **2005**, *46*, 3641.

(17) (a) Kim, D. W.; Song, C. E.; Chi, D. Y. *J. Am. Chem. Soc.* **2002**, *124*, 10278. (b) Chiappe, C.; Pieraccini, D.; Saullo, P. *J. Org. Chem.* **2003**, *68*, 6710. (c) Brinchi, L.; Germani, R.; Savelli, G. *Tetrahedron Lett.* **2003**, *44*, 6583. (d) Brinchi, L.; Germani, R.; Savelli, G. *Tetrahedron Lett.* **2003**, *44*, 2027. (e) Mohile, S. S.; Potdar, M. K.; Salunkhe, M. M. *Tetrahedron Lett.* **2003**, *44*, 1255. (f) Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Venkat Narsaiah, A. *Tetrahedron Lett.* **2003**, *44*, 2217. (g) Kotti, S. R. S. S.; Xu, X.; Li, G.; Headly, A. D. *Tetrahedron Lett.* **2004**, *45*, 1427.

(18) (a) Handy, S. T. *J. Org. Chem.* **2006**, *71*, 4659. (b) Law, M. C.; Wong, K.; Chen, T. H. *Chem. Commun.* **2006**, 2457.

(19) Yoshino, T.; Imori, S.; Togo, H. *Tetrahedron* **2006**, *62*, 1309.

(20) **Phenyl *N*-Methyl-*N*-phenylcarbamate; Typical Procedure**: A flask containing [bmim]Cl (2.0 mL) was dried under reduced pressure by a vacuum pump for 2 h at 80 °C. Then, *N*,*N*-dimethylaniline (1.0 mmol) and phenyl chloroformate (1.2 equiv) were added to the flask. The resulting mixture was stirred and heated at 80 °C for 3 h. Then H_2O (3 mL) was added and the reaction mixture was extracted with EtOAc (20 × 5 mL). The combined extract was condensed to give a residue; the purity of the product was about 50% due to the presence of phenyl chloroformate and a little ionic liquid. The residue was purified by preparative TLC (hexane–EtOAc, 7:1) to give pure phenyl *N*-methyl-*N*-phenylcarbamate in 95% yield; colorless oil; bp 155 °C (1 mmHg). IR (neat): 1730, 1600, 1205, 740, 695 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.39–7.09 (10 H, m), 3.39 (3 H, s). The following abbreviations are used in ^{13}C spectral data: p, s, t, q, for primary, secondary, tertiary, and quarternary carbon, respectively. ^{13}C NMR ($CDCl_3$, TMS): δ = 153.9 (q), 151.2 (q), 142.8 (q), 129.1 (2 t), 128.9 (2 t), 126.5 (t), 125.8 (t), 125.3 (2 t), 121.5 (2 t), 38.1 (p). HRMS (FAB): *m*/*z* calcd for $C_{14}H_{14}NO_2$ (M + H): 228.1025; found: 228.1012.

Phenyl *N*-Methyl-*N*-phenylcarbamate; Distillation Method: A flask containing [bmim]Cl (4.0 mL) was dried under reduced pressure by a vacuum pump for 2 h at 80 °C. Then, *N*,*N*-dimethylaniline (20.0 mmol)and phenyl chloroformate (1.2 equiv) were added to the flask. The resulting mixture was stirred and heated at 80 °C for 3 h. Then the reaction mixture was distilled to give pure phenyl *N*-methyl-*N*-phenylcarbamate in 90% yield; bp 155 °C (1 mmHg).

Phenyl *N*-Methyl-*N*-*p*-bromophenylcarbamate: Colorless oil; bp 210 °C (1 mmHg). IR (neat): 1720, 1590, 1200, 830, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.49–7.45 (2 H, m), 7.34–7.09 (7 H, m), 3.38 (3 H, s). ^{13}C NMR ($CDCl_3$, TMS): δ = 153.5 (q), 151.0 (q), 141.8 (q), 131.9 (2 t), 129.1 (2 t), 127.2 (t), 125.3 (2 t), 121.4 (2 t), 121.4 (q), 38.1 (p). HRMS (FAB): *m*/*z* calcd for $C_{14}H_{13}BrNO_2$ (M + H): 306.0130; found: 306.0137.

Phenyl *N*-Methyl-*N*-*p*-methylphenylcarbamate: Colorless oil; bp 170 °C (1 mmHg). IR (neat): 1720, 1595, 1205, 820, 740, 690 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.33–7.08 (9 H, m), 3.38 (3 H, s), 2.34 (3 H, s). ^{13}C NMR ($CDCl_3$, TMS): δ = 154.0 (q), 151.3 (q), 140.3 (q), 136.4 (q), 129.6 (2 t), 129.1 (2 t), 125.7 (t), 125.2 (2 t), 121.6 (2 t), 38.2 (p), 20.9 (p). HRMS (FAB): *m*/*z* calcd for $C_{15}H_{16}NO_2$ (M + H): 242.1181; found: 242.1190.

Phenyl *N*-Methyl-*N*-*m*-nitrophenylcarbamate: Colorless oil; bp 240 °C (1 mmHg). IR (neat): 1740, 1600, 1200, 810, 750, 695 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 8.27–8.26 (1 H, m), 8.07–8.05 (1 H, m), 7.75–7.73 (1 H, m), 7.54–7.50 (1 H, m), 7.37–7.33 (2 H, m), 7.20–7.13 (3 H, m), 3.48 (3 H, s). ^{13}C NMR ($CDCl_3$, TMS): δ = 153.3 (q), 150.6 (q), 148.3 (q), 143.8 (q), 131.3 (t), 129.5 (t), 129.2 (2 t), 125.6 (t), 121.3 (2 t), 120.7 (t), 120.1 (t), 37.5 (p). HRMS (FAB): *m*/*z* calcd for $C_{14}H_{13}N_2O_4$ (M + H): 273.0875; found: 273.0879.

Phenyl *N*-Methyl-*N*-naphthylcarbamate: White solid; mp 86–87 °C. IR (paraffin): 1720, 1595, 1200, 695 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 8.00–6.92 (12 H), 3.49–3.41 (3 H). ^{13}C NMR ($CDCl_3$, TMS): δ = 154.6 (q), 151.2 (q), 139.1 (q), 134.4 (q), 130.0 (q), 128.9 (2 t), 128.4 (t), 128.1 (t), 126.8 (t), 126.2 (t), 125.6 (t), 125.1 (t), 124.7 (t), 122.2 (t), 121.4 (2 t), 38.4 (p). HRMS (FAB): *m*/*z* calcd for $C_{18}H_{16}NO_2$ (M + H): 278.1181; found: 278.1165.

Phenyl *N*-Butyl-*N*-phenylcarbamate: Colorless oil; bp 150 °C (1 mmHg). IR (neat): 1720, 1595, 1200, 745, 690 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.42–7.09 (10 H, m), 3.78–3.74 (2 H, m), 1.66–1.59 (2 H, m), 1.40–1.31 (2 H, m), 0.93–0.89 (3 H, t, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$, TMS): δ = 153.8 (q), 151.3 (q), 141.5 (q), 129.1 (2 t), 129.0 (2 t), 127.3 (t), 126.9 (t), 125.1 (2 t), 121.5 (2 t), 50.6 (s), 30.2 (s), 19.8 (s), 13.7 (p). HRMS (FAB): *m*/*z* calcd for $C_{17}H_{20}NO_2$ (M + H): 270.1494; found: 270.1488.

Phenyl *N*-Ethyl-*N*-phenylcarbamate: Colorless oil; bp 160 °C (1 mmHg). IR (neat): 1720, 1595, 1200, 750, 690 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.42–7.08 (10 H, m), 3.83–3.79 (2 H, m), 1.24–1.21 (3 H, m). ^{13}C NMR ($CDCl_3$, TMS): δ = 153.6 (q), 151.3 (q), 142.8 (q), 129.1 (2 t), 129.0 (2 t), 127.3 (t), 126.9 (t), 125.1 (2 t), 121.5 (2 t), 45.8 (s), 13.8 (p). HRMS (FAB): *m*/*z* calcd for $C_{15}H_{16}NO_2$ (M + H): 242.1181; found: 242.1170.

Phenyl *N*-Methyl-*N*-dodecylcarbamate: Colorless oil; bp 180 °C (1 mmHg). IR (neat): 1730, 750, 690 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ = 7.36–7.37 (2 H, m), 7.20–7.09 (3 H, m), 3.43–3.31 (2 H), 3.06–2.98 (3 H), 1.63 (2 H), 1.32–1.26 (18 H, m), 0.91–0.86 (3 H, m). ^{13}C NMR ($CDCl_3$, TMS): δ = 153.6 (q), 151.3 (q), 142.8 (q), 129.1 (2 t), 129.0 (2 t), 127.3 (t), 126.9 (t), 125.1 (2 t), 121.5 (2 t), 45.8 (s), 13.8 (p). HRMS (FAB): *m*/*z* calcd for $C_{20}H_{34}NO_2$ (M + H): 320.2590; found: 320.2596.