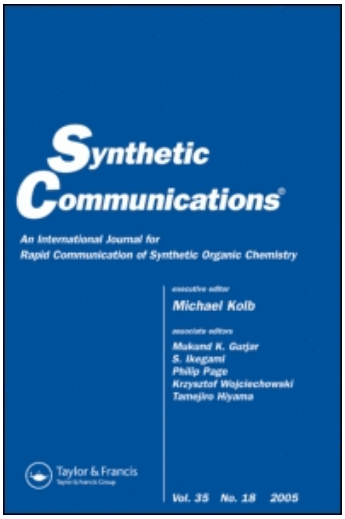

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GREEN AND PRACTICAL SYNTHESIS OF CARBAMATES FROM UREAS AND ORGANIC CARBONATES

Xiaoguang Guo,[1,2] Jianpeng Shang,[1,2] Jian Li,[1,2] Liguo Wang,[1,2] Yubo Ma,[1,2] Feng Shi,[1] and Youquan Deng[1]

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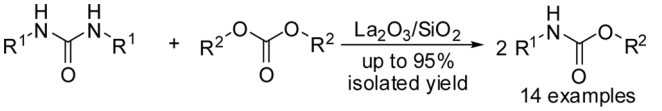
GRAPHICAL ABSTRACT



Abstract *A practical method for the synthesis of carbamates from ureas and organic carbonates was developed with 100% atom economy using La_2O_3/SiO_2 as catalyst without any additional solvent. The scope of the protocol is demonstrated in the synthesis of 14 carbamates with various functional groups in excellent yields (76–95%).*

Keywords Atom economy; carbamates; carbonates; clean synthesis; lanthana; urea derivatives

INTRODUCTION

The practical synthesis of carbamates has attracted much attention in the past few decades because of the extensive usage of carbamates in organic synthesis and pharmaceutical compound fabrication.[1] More important, carbamate derivatives are the key intermediates for the nonphosgene synthesis of isocyanates, which are the raw materials of polyutherates.[2] In 2005, up to 13.7 mtons of polyutherates were produced by phosgene technologies. Introduction of nonphosgene isocyanate synthesis hence can reduce the use of toxic and dangerous phosgene, as well as eliminate the by-product of hydrogen chloride. Unfortunately, the current industrial production of cabamates is still utilizing phosgene as intermediate.[3] Thus the development of an environmentally friendly and practical method for cabamate synthesis is the pivotal step to realize the "green" nonphosgene isocyanate process.[4]

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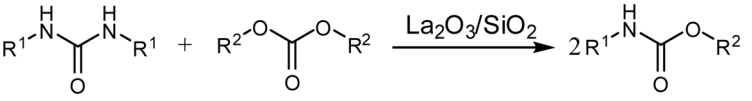


Scheme 1. Synthesis of carbamates from carbonate derivatives and ureas.

The metathesis reaction of substituted ureas and organic carbonates offers a good opportunity for the production of carbamates.[5] Both disubstituted ureas and organic carbonates are available using carbon dioxide as the carbonyl source.[6,7] Moreover, this methathesis reaction has 100% atom-efficiency. The combination of the processes presents an ideal route for the nonphosgene synthesis of carbamates from the greenhouse gas of carbon dioxide. In these reports, homogeneous catalysts were always employed,[5b,5c] and although good results were obtained over solid silica gel as catalyst, the reaction between aromatic ureas and aliphatic carbonate proceeded with difficulty.[5a]

With our continuous efforts to develop nonphosgene carbonylation processes,[8] herein we present our new results about the synthesis of carbamates from ureas and organic carbonates using La_2O_3/SiO_2 as catalyst (Scheme 1).

RESULTS AND DISCUSSION

First, the reaction of dicyclohexyl urea (DCU) and dimethyl carbonate (DMC) was used as a model reaction to optimize the reaction condition (Table 1). The control reaction was carried out in the absence of catalyst (entry 1). The conversion of DCU was <5%, and only <1% methyl cyclohexyl carbamate (MCC) formed. If SiO_2 was directly used as catalyst, the yield of MCC was 28% (entry 2). The results were greatly improved when La_2O_3/SiO_2 was applied. The molar ratio between DMC and DCU, reaction temperature, and reaction time were all screened (entries 3–7). Clearly, 150 °C and 6 h are the suitable conditions.

Table 1. Synthesis of methyl cyclohexyl carbamate from DMC and DCU[a]

Entry	Catalyst	DMC/DCU (mol/mol)	Temp. (°C)	Time (h)	Con. (%)[b]	Sel. (%)[c]	Yield (%)[d]
1	None	15	150	6	<5%	—	—
2[e]	SiO_2	15	150	6	41	82	28
3	La_2O_3/SiO_2	12	150	6	95	92	84
4	La_2O_3/SiO_2	15	150	5	91	95	83
5	La_2O_3/SiO_2	15	130	6	83	96	75
6	La_2O_3/SiO_2	15	150	6	>99	94	90
7	La_2O_3/SiO_2	12	130	5	90	92	79
8[f]	La_2O_3/SiO_2	15	150	6	97	94	86

[a]5 mmol (1.12 g) DCU, 50 mg (0.3 mol La%) La_2O_3/SiO_2.
[b]Conversion of DCU determined by GC-FID.
[c]Chemoselectivity to MCC determined by GC-FID.
[d]Isolated yield.
[e]Commercial SiO_2 (200–300 mesh, BET surface area = 601.1 m^2/g, pore volume = 0.74 cm^3/g, average pore diameter = 4.93 nm). It was pretreated at 600 °C for 4 h and then cooled in a dryer before use.
[f]The 12th run of a recovered catalyst.

To understand the reaction well, it was traced by gas chromatography–mass spectrometry (GC-MS) during the reaction. The main side reactions were methylation. MS spectra of N-methyl cyclohexylamine, N,N'-dimethyl cyclohexylamine, and N-methyl methyl cyclohexyl carbamate are observed. This is in good agreement with the former reports about using dialkyl carbonate as alkylation compound.[9] Generally, in the presence of a nucleophile, DMC can react either as a methoxycarbonylating or as a methylating agent, and there is not always a clear cutoff between these two types of agents.[9c] Accordingly, when DMC reacted as a methylating agent, methanol and CO_2 were produced and the CO_2 was observed by Fourier transform–infrared (FT-IR). Subsequently, the alcoholysis reaction between DCU and methanol could be initiated, and these N-methylation by-products were formed in situ. At the same time, cyclohexyl isocyanate and methanol were also detected. They may be derived from the thermal decomposition of MCC during the reaction or inside the GC column.

This La_2O_3/SiO_2 catalyst can be reused more than 10 times without significant reduction of activity and selectivity. The La_2O_3/SiO_2 catalyst can be separated from the reaction mixture by centrifugation and filtration. It can be reused directly for the next run without further treatment. It has the advantage over the former reported method, in which the catalyst should be regenerated before use.[5b] The results of the reusability investigation are shown in Fig. 1 and Table 1, entry 8. An isolated yield of 86% was achieved when the catalyst was recycled at run 12. This result strongly suggests that our catalyst is promising for industrial applications.

The scope of this protocol was tested with various ureas and carbonate derivatives (Table 2). By using DCU as starting material, the industrially important carbonates, such as DMC, diethyl carbonate (DEC), and dibutyl carbonate (DBC), were evaluated. To our delight, excellent isolated yields, 80–90%, were obtained for the corresponding carbamates (Table 2, entries 1–3). This indicates that this technique covers carbonates with various steric bulkiness. This system was also tested using different aliphatic urea derivatives with DMC. Up to 95% yield was achieved (Table 2, entries 4–7).

Inspired by these results, we further applied the La_2O_3/SiO_2 catalyst in the reaction of aromatic ureas with DMC. The results are exciting and encouraging. All the aromatic carbamates were produced in 76–84% yield (Table 2, entries

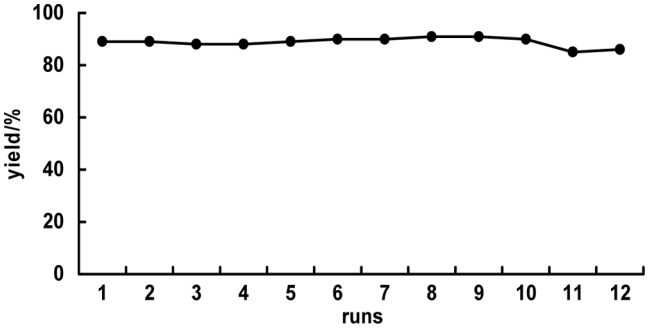
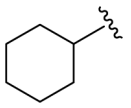
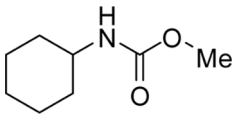
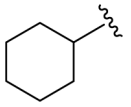
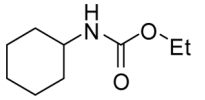
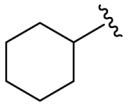
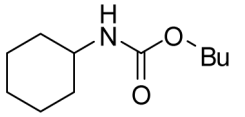
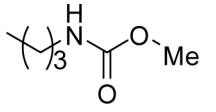
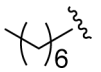
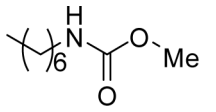
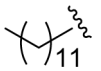
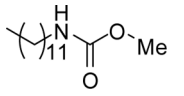
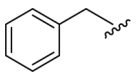
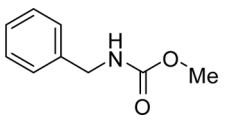
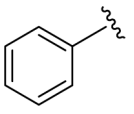
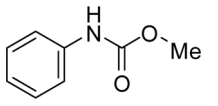
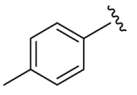
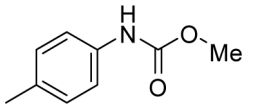
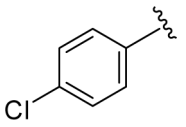
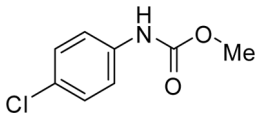
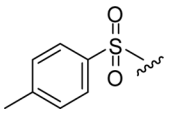
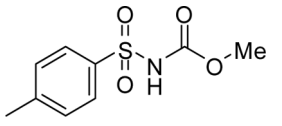


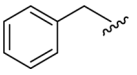
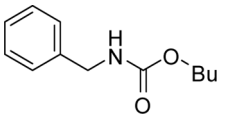
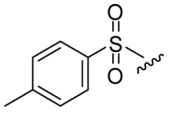
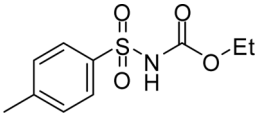
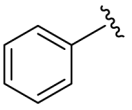
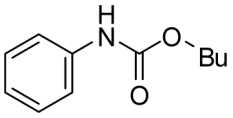
Figure 1. Reusability testing of 5 wt% La_2O_3/SiO_2.

Table 2. Scope and limitations[a]

Entry	R^1	R^2	Product	Reaction time (h)	Yield (%)[b]
1		Me		6	90
2		Et		6	81
3		Bu		6	80
4[c]		Me		5	84
5		Me		6	90
6		Me		8	95
7		Me		12	85
8		Me		12	84
9		Me		12	81
10		Me		12	76
11		Me		12	83

(*Continued*)

Table 2. Continued

Entry	R^1	R^2	Product	Reaction time (h)	Yield (%)[b]
12		Bu		12	87
13		Et		10	90
14		Bu		12	75

[a]5 mmol disubstituted ureas, 75 mmol carbonates, 50 mg (0.3 mol La%) La_2O_3/SiO_2, 150 °C.
[b]Isolated yield.
[c]120 °C.

8–12). DEC and DBC can also be reacted with N,N′-carbonyl-bis(4-methylbenzenesulfonamide) and diphenyl-urea to obtain the corresponding carbamates in 90% and 75% yields respectively (Table 2, entries 13 and 14).

In conclusion, a practical method for synthesis of carbamates from ureas and carbonate derivatives was developed using 5 wt% La_2O_3/SiO_2 as catalyst in 100% atom efficiency. The study of reaction mechanism of this reaction is now under way.

EXPERIMENTAL

Typical Procedure for the Catalyst Preparation (5 wt% La_2O_3/SiO_2)

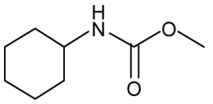
$La(NO_3)_3 \cdot 6H_2O$ was used as the precursor for the preparation of silica-gel-supported lanthana catalyst. The catalysts were prepared by the deposition–precipitation (DP) method. After being pretreated at 600 °C for 4 h, SiO_2 (5.0 g) was added into the solution containing suitable amounts of lanthanum nitrate (~0.66 g) and urea (~0.15 g) at room temperature under ultrasonic irradiation. The molar ratio of lanthanum to urea was ~1:1.7. The suspension was further magnetically stirred at 90 °C for 3 h, and the final pH value of the system was ~8. Then it was filtered and dried in air at 373 K (100 °C) for 4 h. It was further calcined at 873 K (600 °C) for 4 h and ~5.2 g 5 wt% La_2O_3/SiO_2 catalyst was obtained. The catalyst was characterized by X-ray diffraction (XRD), BET analysis, transmission electron microscopy (TEM), atomic emission spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS), and results showed the catalyst exhibits an amorphous phase [BET surface area = 447.3 m^2/g, pore volume = 0.59 cm^3/g, average pore diameter = 5.3 nm; particle size of lanthanum oxide ~5 nm; loading of the catalyst 5 wt%; and the lanthanum species of catalyst surface is La^{3+}].

Typical Procedure for the Reaction of Urea and Carbonate Derivatives

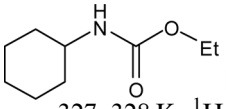
All the reactions were conducted in a 90-mL stainless-steel autoclave with a glass tube inside equipped with magnetic stirrer. In each reaction, ureas (5 mmol, 1.12 g), carbonates (75 mmol, 6.3 mL), and 5 wt% La_2O_3/SiO_2 catalyst (50 mg) were charged successively into the autoclave. After being flushed with N_2, it was heated up to 423 K (150 °C) and reacted for 6–14 h. Then, the autoclave was cooled to room temperature and opened to air. The catalyst was separated by centrifugation and filtration and directly reused for the next run without further treatment. The product was qualitatively and quantitatively analyzed with GC-MS (HP 6890/5973), GC-FID (Agilent 6820, biphenyl was chosen as an internal standard), ^{1}H NMR (Bruker AMX FT, 400 MHz), and ^{13}C NMR (Bruker AMX FT, 100 MHz).

The pure compounds were obtained with different procedures. For compounds in Table 2, entries 1 and 11, the DMC was removed by vacuum distillation (50 °C, 100 mmHg), and the pure product could be obtained after the solid was further washed by hexane and vacuum dried. For compounds in Table 2, entries 2 and 13, the DEC was removed by vacuum distillation (90 °C, 100 mmHg), and pure products could be obtained after the solids were further washed by hexane and vacuum dried. For compounds in Table 2, entries 3, 12, and 14, the DBC was removed by vacuum distillation (120 °C, 50 mmHg), and the carbamates could be achieved after the solid was further washed by hexane and vacuum dried. For compounds in Table 2, entries 4–10, the products were purified by column chromatography (silica gel, petroleum ether/methylene dichloride 75:25).

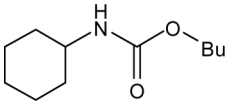
Analytical Data



Methyl cyclohexylcarbamate. White solid (GC-MS purity 98%); mp 343–344 K.^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.59$ (1H, s), 3.65 (3H, s), 3.49–3.47 (1H, s), 1.73–1.67 (4H, m, $J = 4.3$ Hz), 1.39–1.29 (4H, m), 1.20–1.07 (2H, m).^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.2$, 51.8, 49.8, 30.9, 25.4, 24.8. GC-MS (EI, 70 eV), m/z (rel. int.): 156 (M^+, 5), 140 (1), 128 (100), 115 (6), 102 (9), 90 (14), 83 (5), 67 (3), 55 (8), 42 (14), 27 (2).

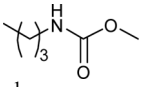


Ethyl cyclohexylcarbamate. White solid (GC-MS purity 98%); mp 327–328 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.55$ (1H, s), 4.15–4.10 (2H, m, $J = 6.5$ Hz), 3.47 (1H, s), 2.05–1.81 (4H, m), 1.80–1.49 (2H, m), 1.50–1.01 (7H, m).^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.8$, 60.5, 49.6, 33.5, 25.5, 24.8, 14.7. GC-MS (EI, 70 eV), m/z (rel. int.): 171 (M^+, 13), 142 (30), 128 (100), 115 (3), 100 (5), 90 (31), 82 (14), 67 (11), 56 (77), 41 (33), 27 (57).

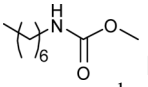


Butyl cyclohexylcarbamate. White solid (GC-MS purity 98%); mp 326–327 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.53$ (1H, s),

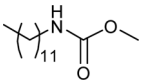
4.05–4.02 (2H, t, $J = 6.2$ Hz), 3.47 (1H, s), 1.94–1.92 (2H, m), 1.73–1.67 (2H, m), 1.64–1.57 (4H, m), 1.42–1.26 (4H, m), 1.21–1.07 (2H, m), 0.95–0.91 (3H, t, $J = 7.4$ Hz).^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.9$, 64.3, 49.6, 33.4, 31.1, 25.5, 24.7, 19.1, 13.7. GC-MS (EI, 70 eV), m/z (rel. int.): 199 (M^+, 19), 156 (100), 144 (16), 142 (43), 118 (13), 100 (19), 83 (14), 62 (23), 57 (19), 56 (46), 55 (14), 41 (20).



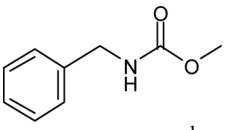
Methyl n-butylcarbamate. Colorless liquid (GC-MS purity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.65$ (1H, s), 4.03 (3H, s), 3.18–3.15 (2H, t, $J = 6.8$ Hz), 1.72–1.55 (2H, m), 1.39–1.32 (2H, m), 0.94–0.92 (3H, t). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.8$, 49.6, 40.6, 31.0, 18.9, 13.6. GC-MS (EI, 70 eV), m/z (rel. int.): 131 (M^+, 1), 117 (1), 103 (15), 90 (6), 77 (57), 70 (100), 55 (85), 41 (57), 29 (34).



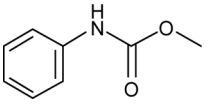
Methyl n-heptylcarbamate. White solid (GC-MS purity 98%); mp 301–302 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.71$ (1H, s), 3.68 (3H, s), 3.28–3.12 (2H, m, $J = 7.2$ Hz), 1.50–1.41 (2H, m), 1.36–1.28 (8H, m), 0.89–0.86 (3H, q). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.1$, 52.0, 41.1, 31.6, 30.3, 28.9, 26.9, 22.6, 14.1. GC-MS (EI, 70 eV), m/z (rel. int.): 174 (M^+, 3), 158 (3), 144 (2), 130 (3), 103 (2), 88 (100), 76 (14), 59 (11), 44 (37), 29 (10).



Methyl n-dodecylcarbamate. White solid (GC-MS purity 98%); mp 315–318 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.62$ (1H, s), 4.03 (3H, s), 3.17–3.14 (2H, q, $J = 6.6$ Hz), 1.62–1.55 (2H, m), 1.38–1.21 (18H, m), 0.90–0.86 (3H, t, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.8$, 49.7, 40.9, 31.9, 29.6, 29.5, 29.3 29.3 (4C), 26.7, 22.6, 14.0. GC-MS (EI, 70 eV), m/z (rel. int.): 243 (M^+, 3), 228 (3), 212 (2), 200 (1), 184 (5), 172 (1), 158 (3), 144 (6), 130 (6), 112 (8), 99 (16), 88 (100), 76 (20), 67 (9), 55 (20), 41 (27), 29 (13).

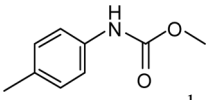


Methyl benzylcarbamate. White solid (GC-MS purity 98%); mp 323–325 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$–7.33 (2H, t, $J = 8.0$ Hz), 7.32–7.28 (2H, d), 7.27–7.25 (1H, t), 5.04 (1H, s), 4.38–4.36 (2H, d, $J = 8$ Hz), 3.75 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.1$, 138.6, 128.5, 127.6, 127.5, 52.2, 45.1. GC-MS (EI, 70 eV), m/z (rel. int.): 165 (M^+, 40), 150 (78), 133 (32), 121 (9), 106 (12), 91 (100), 79 (66), 65 (29), 59 (12), 51 (39), 44 (13), 29 (9).

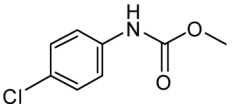


Methyl phenylcarbamate. White solid (GC-MS purity 98%); mp 313–315 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$–7.37 (2H, d, $J = 7.6$ Hz), 7.32–7.28 (2H, t, $J = 7.8$ Hz), 7.09–7.06 (1H, t), 6.69 (1H, s), 3.77 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.1$, 137.9, 129.2, 123.5, 118.7, 52.4. GC-MS

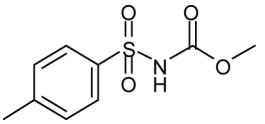
(EI, 70 eV), m/z (rel. int.): 151 (M^+, 100), 135 (4), 119 (75), 106 (97), 92 (48), 77 (30), 65 (81), 51 (18), 39 (40), 28 (8).



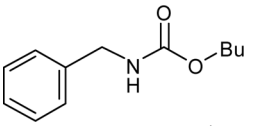
Methyl p-tolylcarbamate. White solid (GC-MS purity 98%); mp 368–370 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.27$–7.25 (2H, d, $J = 8.0$ Hz), 7.12–7.10 (2H, d), 6.62 (1H, s), 3.76 (3H, s), 2.30 (3H, S). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.1$, 135.2, 133.0, 129.5, 118.8, 52.3, 20.7. GC-MS (EI, 70 eV), m/z (rel. int.): 165 (M^+, 100), 150 (6), 133 (78), 120 (16), 106 (42), 91 (14), 77 (36), 51 (94), 29 (2).



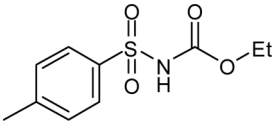
Methyl 4-chlorophenylcarbamate. White solid (GC-MS purity 98%); mp 355–356 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$–7.53 (2H, d, $J = 8.0$ Hz), 7.47–7.45 (2H, d), 6.69 (1H, s), 3.77 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.1$, 136.9, 134.5, 129.2, 123.5, 52.4. GC-MS (EI, 70 eV), m/z (rel. int.): 185 (M^+, 44), 153 (46), 140 (39), 128 (11), 112 (7), 99 (28), 90 (18), 73 (21), 62 (25), 49 (18), 32 (100).



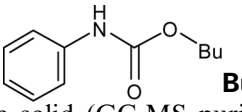
Methyl p-tosylcarbamate. White solid (GC-MS purity 98%); mp 382–383 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$–7.92 (2H, d, $J = 8.0$ Hz), 7.85 (1H, s), 7.36–7.34 (2H, d), 3.70 (3H, s), 2.45 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.0$, 145.2, 135.3, 129.6, 128.6, 53.6, 21.7. GC-MS (EI, 70 eV), m/z (rel. int.): 229 (M^+, 5), 214 (5), 199 (8), 183 (1), 170 (8), 155 (15), 139 (1), 107 (10), 91 (100), 77 (5), 73 (15), 65 (50), 28 (20).



Butyl benzylcarbamate. White solid (GC-MS purity 98%); mp 313–314 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$–7.24 (5H, m), 5.13 (1H, s), 4.35–4.34 (2H, d, $J = 5.6$ Hz), 4.09–4.05 (2H, t, $J = 6.6$ Hz), 1.62–1.56 (2H, m), 1.55–1.32 (2H, m), 0.94–0.90 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 156.8$, 138.9, 128.5, 127.4, 127.3, 64.89, 44.9, 30.9, 18.9, 13.6. GC-MS (EI, 70 eV), m/z (rel. int.): 207 (M^+, 16), 151 (17), 150 (100), 106 (42), 105 (11), 91 (43), 79 (18).



Ethyl p-tosylcarbamate. White solid (GC-MS purity 98%); mp 342–344 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$–7.92 (2H, d, $J = 8.0$ Hz), 7.65 (1H, s), 7.36–7.34 (2H, d), 4.17–4.11 (3H, s, $J = 6.7$ Hz), 2.45 (3H, s), 1.23–1.19 (3H, t). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.5$, 145.1, 135.5, 128.5, 122.2, 63.1, 21.7, 14.0. GC-MS (EI, 70 eV), m/z (rel. int.): 243 (M^+, 2), 229 (2), 170 (8), 155 (15), 139 (10), 107 (5), 90 (100), 74 (23), 29 (38).



Butyl n-phenylcarbamate (butyl phenylcarbamate). White solid (GC-MS purity 98%); mp 333–334 K. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$–7.37 (2H, d, $J = 7.6$ Hz), 7.32–7.28 (2H, t, $J = 7.8$ Hz), 7.07–7.04 (1H, t, $J = 7.2$ Hz), 6.60 (1H, s), 4.19–4.15 (2H, t, $J = 6.6$ Hz), 1.70–1.60 (2H, m), 1.47–1.39 (2H, m), 0.97–0.94 (3H, t, $J = 7.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.8$, 137.9, 128.9, 123.2, 118.6, 65.0, 30.9, 19.0, 13.7. GC-MS (EI, 70 eV), *m/z* (rel. int.): 193 (M+, 59), 137 (26), 120 (33), 93 (100), 92 (13), 77 (15), 65 (18), 57 (24), 41 (25), 29 (17).

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