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Solvent-Free Preparation of Primary Carbamates

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Herein, we describe a simple and efficient method for the conversion of compounds containing a hydroxyl group to primary carbamates at room temperature with excellent yield and purity, and without any epimerization, in the absence of solvent.

Key Words: Solvent-free, N-unsubstituted carbamates, isocyanic acid, compounds containing hydroxyl group.

Introduction

Carbamates (urethanes) are of particular interest due to their usefulness in various industries[1−3], such as agrochemicals[1,2,4,5], where they are used as herbicides, fungicides, and pesticides, in the pharmaceuticals industry[1,2,6] as drug intermediates, and the polymer industry[1,2,7] in the synthesis of polyurethane, as well as in peptide synthesis. In addition to these, among the various amine-protecting groups, carbamates are commonly used due to their chemical stability towards acids, bases, and hydrogenation[8]. The most widely utilized method for the synthesis of carbamates uses highly toxic phosgene as a reagent in organic solvents, which is also toxic and flammable[1−3]. Therefore, the conventional method involves environmental and safety problems. Owing to the above-mentioned, considerable effort has been directed toward alternative routes of preparation of urethanes using carbon dioxide as a phosgene replacement. Carbon dioxide is well known to react rapidly with amines to form carbamic acid ammonium salts. However, as the nucleophilicity of the carbamate anion is lower than that of the amine formed in the equilibrium of the salt formation reaction, the reaction of the carbamate salts with alkyl halides does not selectively afford carbamates. Furthermore, this method cannot produce N-unsubstituted carbamates. Synthesis of N-unsubstituted carbamates **1** from alcohols has also been accomplished by several-pot reaction methods such as trichloroacetyl isocyanate[9,10], chloroformates (starting from toxic phosgene)[11], chlorosulfonyl isocyanate[12], and cyanogen chloride[13].

Loev and coworkers reported the synthesis of N-unsubstituted carbamates from alcohols by treatment with sodium cyanate and trifluoroacetic acid in certain organic solvents such as benzene, methylene chloride, and tetrachloride carbon, without any spectral data such as IR and NMR[14]. These solvents are toxic and are

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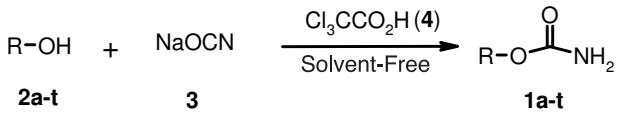
not eco-friendly. In addition, trifluoroacetic acid is very expensive. From the standpoint of 'green chemistry', significant efforts have been made to find an alternative to organic solvents. A very attractive substitute for the use of these solvents is a solvent–free reaction.

In attempts to the synthesize tetrazoles and imidoyl azides from alcohols[15,16], we shifted our interest to developing methods for the synthesis of carbamates under solvent–free conditions (industrially important due to reduced pollution, low cost, and simplicity in processing and handling)[17−22]. Furthermore, in the past decade, the development of new technologies has been expedited in the strive to eliminate the need for chromatographic separation of mixtures, especially impurities, and this itself has led to the development of new technologies in synthetic organic chemistry[23]. In this paper, a simple and efficient solvent-free methodology was performed to prepare primary carbamates **1** in high yield and purity from compounds **2**, sodium cyanate, and trichloroacetic acid, Scheme 1.

Results and Discussion

In a typical procedure, a mixture of ROH (1 mmol) and trichloroacetic acid (2 mmol) was thoroughly ground in an agate mortar for a few minutes. Then sodium cyanate (2 mmol) was placed in the mortar and ground thoroughly for 30 min. The reaction mixture was allowed to stand for 12 h at room temperature. The product was precipitated by the addition of a small amount of water and pure carbamates **1** were filtered (see Table, Scheme 1).



Scheme 1

As shown in the Table, several structurally varied substrates have been used for pure and clean synthesis of primary carbamates **1a-t** under this simple procedure. Primary, secondary, tertiary, allylic, benzylic alcohols, diols (**2n**, entry 14), phenols, and cyclohexyloxime (**2l**, entry 12) are all smoothly converted into the corresponding carbamates[14,24−30]. It is remarkable to note that in the case of (-)-menthol **2a,** the reaction produced the corresponding (-)-menthyl carbamate **1a** without any epimerization under this experimental condition[24,31]. In all cases, the crude product was actually quite pure and did not require additional purification or work-up. The conversions were improved using CF_3COOH; however, the best results were obtained by CCl_3COOH. Increasing the reaction temperature to 80 °C had no effect on the yield and/or purity, with the exception of **1t** (entry 20). In this case, the yield and purity was improved at 60-70 °C for 1 h. The steric hindrance of the *tert*-butyl group in comparison to the H and CH_3 groups could justify our finding. Phenols containing electron-withdrawing (CN, COOR, and CHO) failed to react under our experimental conditions. Most likely these functional groups decrease the nucleophilicity of phenol oxygen for effective attacking of intermediate **5** and/or **7**, Scheme 2. This may be the reason why compound **1s** (entry 19) was obtained in low yield (55%).

The products were identified by comparison of their IR, ^{1}H-NMR (80 MHz) spectral data, or by their physical properties with those of authentic samples[14,24,25]. In addition, they have also been characterized

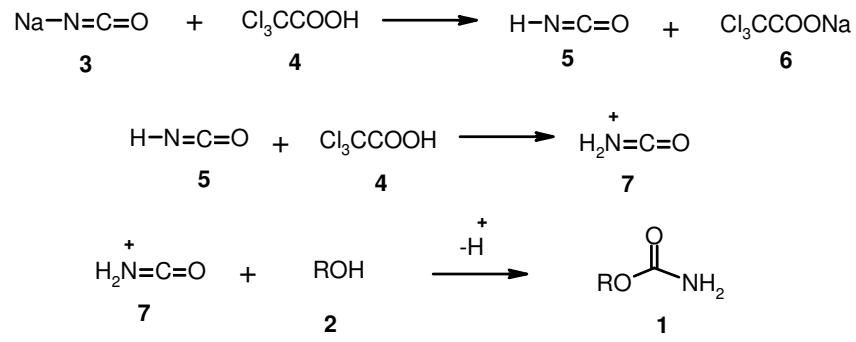
by ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz). ^{13}C-NMR spectral display signals for carbonyl carbons of aliphatic or aromatic carbamate were in the range of 147-157 ppm.

Table. Preparation of primary carbamates 1a-t.

Entry	Compound containing hydroxyl group	R	% Yield (#)	Mp (°C)
1	**2a**	(-)-menthyl	75 (**1a**)	166-168
2	**2b**	CH_3CH_2	60 (**1b**)	46-48
3	**2c**	$CH_3CH_2CH_2$	80 (**1c**)	58-59
4	**2d**	$(CH_3)_2CH$	80 (**1d**)	89-91
5	**2e**	$CH_3CH_2CH_2CH_2$	70 (**1e**)	53-55
6	**2f**	$CH_3CH_2(CH_3)CH$	70 (**1f**)	93-94
7	**2g**	$(CH_3)_2CHCH_2CH_2$	75 (**1g**)	64-66
8	**2h**	C_6H_{11}	80 (**1h**)	108-110
9	**2i**	$(CH_3)_3C$	70 (**1i**)	106-108
10	**2j**	$PhCH_2$	80 (**1j**)	87-89
11	**2k**	$(CH_3)_2CHOCH_2CH_2$	80 (**1k**)	57-59
12	**2l**	-$(CH_2)_5$-C=N	80 (**1l**)	94-96
13	**2m**	H_2C=$CHCH_2$	65 (**1m**)	19-21
14	**2n**	$(CH_2)_4$	65 (**1n**)	195-196
15	**2o**	C_6H_5	95 (**1o**)[a]	141-143
16	**2p**	2-$CH_3C_6H_4$	79 (**1p**)	132-135
17	**2q**	3-$CH_3C_6H_4$	83 (**1q**)	137-139
18	**2r**	4-$CH_3C_6H_4$	80 (**1r**)	134-136
19	**2s**	4-BrC_6H_4	55 (**1s**)	139-142
20	**2t**	2-$C(CH_3)_3$-4-$CH_3C_6H_3$	92 (**1t**)[b]	143-144

[a]By continuous extraction. [b] By heating at 60-70 °C for 1 h.

The possible reaction mechanism is depicted in Scheme 2. The first step could be the reaction of sodium cyanate **3** with an acid (trichloroacetic acid) to give isocyanic acid **5**[31,32]. In the second step, a proton of trichloroacetic acid **4** is added to isocyanic acid **5** to yield the intermediate **7**. Finally, formation of carbamate **1** may occur by a nucleophilic attack of alcohol **2** on the carbon of the intermediate **7** (Scheme 2).



Scheme 2

Conclusion

This simple solvent-free method affords various primary carbamates at room temperature, with excellent yields and high purity, without involvement of toxic solvents, expensive starting materials, the formation of

any undesirable side products, or epimerization. Furthermore, this method does not require purification or separation techniques (column chromatography), nor heat. Further studies are in progress.

Experimental

General. ^{1}H-NMR and ^{13}C-NMR spectra were recorded by a Bruker Avanace DRX 500 (500 MHz) and a Varian EM 390 (80 MHz). The IR spectra were obtained on a Shimadzu-470. Melting points were recorded by an Electro Thermal 9100 and were uncorrected. Thin layer chromatography (TLC) was carried out using plastic sheets pre-coated with silica gel 60 F. The products were identified through comparison of their spectral data, IR, ^{1}H-NMR (80 MHz), and physical properties to those of authentic samples[14,24–30]. All starting materials and solvents were purified with the proper purification techniques before use[33,34].

General procedure. A mixture of (-)-menthol (0.156 g, 1 mmol) and trichloroacetic acid (0.34 g, 2 mmol) was thoroughly ground in an agate mortar for a few minutes. Then sodium cyanate (0.13 g, 2 mmol) was placed in the mortar and ground thoroughly for 30 min. The reaction mixture was allowed to stand for 12 h at room temperature. The product was precipitated by the addition of a small amount of water and pure carbamate **1a** was filtered[14,24].

In the cases that carbamates dissolved in water (such as **1b**, **1c**, **1d**, **1i**, **1m**, and **1o**), after the addition of a little HCl at pH∼3, the aqueous phase was constantly extracted with dichloromethane. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure to give the pure carbamates.

Menthyl Carbamate. The reaction afforded white crystals **1a** (75% yield), mp = 166-168 °C (lit.,[24] 156-157 °C), $[\alpha]_D^{17}$ = -125 °C (0.60, CHCl3) [24]. IR (KBr); 3415 (s), 3326 (w), 3285 (m), 3200 (w), 2950 (s), 2875 (w), 1675 (vs), 1610 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1455 (w), 1400 (s), 1370 (m), 1337 (w), 1319 (w), 1180 (w), 1100 (w), 1080 (w), 1060 (m), 1048 (s), 917 (w), 780 (w), 704 (w), 575 (m) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 0.80 (d, J = 6.9 Hz, 3H), 0.86 (dd, J = 12.1 Hz, J = 3.2 Hz, 1H), 0.90 (d, J = 2.7 Hz, 3H), 0.91 (d, J = 2.1 Hz, 3H), 0.97 (q, J = 12.0 Hz, 2H), 1.06 (qd, J = 13.1 Hz, J = 3.3 Hz, 1H), 1.30 (tt, J = 11.6 Hz, J = 2.9 Hz, 1H), 1.44-1.52 (m, 1H), 1.65 -1.69 (m, 2H), 1.94 (hd, J = 6.9 Hz, J = 2.5 Hz, 1H), 2.06 (dt, J = 11.8 Hz, J = 4.64 Hz, 1H), 4.54 (td, J = 10.9 Hz, J = 4.4 Hz, 1H), 4.85 (br, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 157.07, 74.93, 47.34, 41.29, 34.29, 31.36, 26.29, 23.57, 22.02, 20.75, 16.47.

Ethyl Carbamate. The reaction afforded white crystals **1b** (60% yield), mp = 46-48 °C (lit.,[25] 48-50 °C). IR (KBr); 3420 (s), 3322 (m), 3278 (m), 3200 (m), 2987 (m), 2900 (w), 1688 (s), 1615 (m), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1420 (m), 1380 (m), 1330 (m), 1075 (m) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 1.25 (t, J = 6.3 Hz, 3H), 4.16 (q, J = 6.3 Hz, 2H), 5.0 (br, 2H).

1-Propyl Carbamate. The reaction afforded white crystals **1c** (80% yield), mp = 58-59 °C (lit.,[25] 60 °C). IR (KBr); 3420 (s), 3326 (w), 3285 (m), 3200 (w), 2950 (m), 2890 (w), 1680 (vs), 1620 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1440 (w), 1425 (s), 1360 (s), 1300 (w), 1115 (w), 1060 (s), 917 (w) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 0.90 (t, J = 7.0 Hz, 3H), 1.6 (sextet, J = 7.0 Hz, 2H), 4.00 (t, J = 7.0 Hz, 2H), 4.90 (br, 2H).

2-Propyl Carbamate. The reaction afforded white crystals **1d** (80% yield), mp = 89-91 °C (lit.,[25]

92-94 °C). IR (KBr); 3420 (s), 3326 (w), 3285 (m), 3200 (w), 2989 (m), 1680 (s), 1615 (m), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1468 (w), 1409 (m), 1380 (w), 1319 (m), 1112 (m), 1047 (s), 790 (w), 600 (m) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 1.20 (d, J = 6.2 Hz, 6H), 4.85 (m, 3H).

1-Buthyl Carbamate. The reaction afforded white crystals **1e** (70% yield), mp = 53-55 °C (lit.,[25] 54 °C). IR (KBr); 3415 (s), 3320 (s), 3265 (m), 3200 (w), 2960 (s), 2870 (w), 1680 (vs), 1610 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1455 (w), 1415 (m), 1360 (m), 1334 (s), 1125 (w), 1075 (s), 915 (w), 885 (w), 785 (w), 735 (w), 680 (w) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 0.95 (t, J = 6.7 Hz, 3H), 1.23-1.80 (m, 4H), 4.12 (t, J = 6.7 Hz, 2H), 5.0 (br, 2H).

2-Buthyl Carbamate. The reaction afforded white crystals **1f** (70% yield), mp = 93-94 °C. IR (KBr); 3415 (s), 3326 (w), 3255 (m), 3200 (m), 2980 (m), 2915 (w), 2875 (w), 1677 (vs), 1651 (m), 1611 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1453 (m), 1405 (s), 1377 (w), 1325 (m), 1175 (w), 1115 (m), 1052 (s), 964 (w), 910 (w), 870 (w), 840 (w), 783 (w), 600 (m) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 0.81 (t, J = 7.5 Hz, 3H), 1.11 (d, J = 6.3 Hz, 3H), 1.42 [h (ddq), J = 13.9 Hz, J = 7.2 Hz, J = 6.8 Hz, 1H)], 1.50 [h (ddq), J = 13.9 Hz, J = 7.2 Hz, J = 7.1 Hz, 1H)], 4.60 [sex (ddq), J = 6.2 Hz, J = 6.2 Hz, J = 6.2 Hz, 1H)], 5.32 (br, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 157.63, 72.68, 28.81, 19.44, 9.42.

Isoamyl Carbamate. The reaction afforded white crystals **1g** (75% yield), mp = 64-66 °C (lit.,[25] 64 °C). IR (KBr); 3415 (s), 3320 (w), 3275 (w), 3200 (w), 2975 (m), 2870 (w), 1680 (vs), 1612 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1470 (w), 1455 (w), 1420 (m), 1370 (m), 1360 (m), 1089 (w), 790 (w), 560 (w) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 0.95 (d, J = 5.6 Hz, 6H), 1.3-1.6 (m, 3H), 4.15 (t, J = 7.0 Hz, 2H), 4.60 (br, 2H).

Cyclohexyl Carbamate [27]**.** The reaction afforded white crystals **1h** (80% yield), mp = 108-110 °C. IR (KBr); 3418 (s), 3317 (m), 3275 (m), 3200 (m), 2945 (m), 2880 (w), 1680 (s), 1615 (m), 1600 (m), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1460 (w), 1440 (m), 1400 (w), 1360 (m), 1340 (m), 1310 (w), 1100 (w), 1050 (s), 1020 (w), 910 (w), 790 (w), 560 (w) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm;1.21-1.89 (m, 10H), 4.6 (m, 1H), 4.95 (br, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 156.96, 73.33, 31.85, 25.30, 23.75.

***tert*-Buthyl Carbamate.** The reaction afforded white crystals **1i** (70% yield), mp = 106-108 °C (lit.,[14] 107-108 °C). IR (KBr); 3415 (s), 3330 (w), 3250 (w), 3200 (w), 2970 (m), 2920 (w), 1675 (vs), 1600 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1473 (w), 1382 (m), 1360 (m), 1250 (w), 1167 (m), 1055 (m), 1025 (w), 845 (w), 785 (w), 560 (w) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 1.34 (s, 9H), 4.40 (br, 2H).

Benzyl Carbamate. The reaction afforded white crystals **1j** (80% yield), mp = 87-89 °C (lit.,[25] 91 °C). IR (KBr); 3420 (s), 3326 (m), 3285 (m), 3200 (w), 3020 (w), 2940 (w), 1675 (vs), 1615 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1470 (w), 1440 (m), 1400 (s), 1335 (s), 1120 (w), 1085 (m), 1070 (s), 1025 (w), 910 (m), 880 (w), 780 (w), 730 (s), 693 (m), 620 (w), 570 (w) cm^{-1}. ^{1}H-NMR (80 MHz, $CDCl_3$), δ ppm; 4.8 (br, 2H), 5.10 (s, 2H), 7.30 (quasi s, 5H).

Ethylene glycol monoisopropyl ether Carbamate. The reaction afforded white crystals **1k** (80% yield), mp = 57-59 °C (lit.,[26] 53 °C). IR (KBr); 3420 (vs), 3326 (s), 3285 (s), 3200 (s), 2970 (s), 2950 (m), 2900 (w), 2870 (w), 1718 (vs), 1612 (vs), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1467

(m), 1455 (m), 1400 (s), 1368 (w), 1320 (vs), 1279 (w), 1240 (w), 1179 (w), 1146 (w), 1124 (s), 1100 (m), 1065 (vs), 1005 (s), 964 (m), 885 (w), 850 (w), 790 (w), 780 (w), 733 (w), 670 (w), 580 (m), 535 (m), 505 (w) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 1.15 (d, J = 6.1Hz, 6H), 3.59 (h + t, 3H), 4.16 (t, J = 4.6 Hz, 2H), 5.19 (br, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 157.31, 71.98, 66.23, 64.58, 21.96.

Cyclohexyloxime Carbamate. The reaction afforded white crystals **1l** (80% yield), mp = 94-96 °C (lit.,[14] 94-96 °C). IR (KBr); 3450 (s), 3300 (m), 3295 (m), 3010 (m), 2998 (w), 2855 (w), 1718 (vs), 1676 (w), 1643 (w), 1578 (m), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1467 (w), 1430 (w), 1378 (vs), 1349 (m), 1340 (m), 1321 (w), 1253 (w), 1224 (w), 1136 (w), 1108 (w), 992 (s), 911 (s), 872 (s), 845 (w), 775 (m), 660 (w), 628 (s), 585 (m), 543 (m) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 1.58-1.72 (m, 6H), 2.25 (t, J = 6.3 Hz, 2H), 2.55 (t, J = 6.3 Hz, 2H), 6.08 (br, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 157.07, 166.08, 31.91, 26.71, 26.48, 25.57, 25.22.

Allyl Carbamate [30]**.** The reaction afforded white crystals **1m** (65% yield), mp = 19-21 °C. IR (KBr); 3475 (s), 3350 (s), 3195 (m), 3085 (w), 2945 (w), 1713 (vs), 1647 (w), 1601 (s), 1574 (w), 1558 (w), 1539 (w), 1518 (w), 1504 (w), 1486 (w), 1445 (w), 1397 (s), 1331 (s), 1286 (w), 1119 (m), 1062 (s), 995 (m), 931 (m), 783 (m) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 4.49 (d, J = 5.5 Hz, 2H), 5.15 (d, J = 10.4 Hz, 1H), 5.25 (dd, J = 17.2 Hz, J = 1.1 Hz, 1H), 5.38 (br, 2H), 5.85 [o (ddt), J = 17.2 Hz, J = 10.6 Hz, J = 5.4 Hz, 1H)]. ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 157.19, 132.46, 117.48, 65.39.

1,4-Butanediol dicarbamate [27]**.** The reaction afforded white crystals **1n** (65% yield), mp = 195-196 °C. IR (KBr), 3420 (s), 3320 (m), 3280 (m), 3200 (m), 2960 (m), 2900 (w), 2860 (w), 1680 (vs), 1620 (s), 1480 (w), 1460 (w), 1425 (s), 1360 (s), 1120 (w), 1085 (s), 1040 (w), 930 (w), 790 (w), 680 (w), 600 (m) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm, 1.55 (quasi s, 4H), 3.89 (quasi s, 4H), 6.42 (br, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 25.41, 62.99, 156.85, Analysis Calcd. For $C_6H_{12}N_2O_4$: C, 40.78; H, 6.85; N, 15.86; Found; C, 40.69; H, 7.49; N, 13.96% .

Phenyl Carbamate. Reaction afforded white crystals **1o** (95% yield), mp = 141-143 °C (lit.,[14] 145-148 °C). IR (KBr); 3400 (m), 3300 (m), 3250 (m), 2950 (w), 1700 (vs), 1590 (w), 1490 (w), 1470 (vw), 1380 (m), 1300 (m), 1200 (m), 970 (w), 820 (w), 760 (w), 740 (w), 700 (w), 580 (vw), 500 (vw) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 5.06 (br, s, 2H), 7.16 (d, J = 8.2 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H).

2-Methylphenyl Carbamate [28]**.** The reaction afforded white crystals **1p** (79% yield), mp = 132-135 °C. IR (KBr); 3400 (m), 3350 (w), 3300 (w), 2800 (vw), 1700 (s), 1610 (w), 1490 (w), 1360 (m), 1225 (m), 1180 (m), 1110 (m), 1040 (w), 970 (m), 780 (w), 750 (w), 720 (w), 600 (w) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 2.24 (s, 3H), 5.11 (br, s, 2H), 7.07 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.4 Hz, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 6.3 Hz, 1H), ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 16.01, 122.11, 125.98, 126.90, 130.64, 131.11, 149.22, 155.00.

3-Methylphenyl Carbamate. The reaction afforded white crystals **1q** (83% yield), mp = 137-139 °C (lit.,[35] 139 °C). IR (KBr); 3400 (m), 3310 (m), 3250 (m), 3180 (w), 1700 (s), 1600 (w), 1580 (w), 1480 (w), 1350 (m), 1240 (m), 1150 (m), 1080 (w), 1010 (w), 1000 (w), 970 (w), 910 (w), 800 (w), 750 (w), 700 (w), 680 (w), 550 (w) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 2.38 (s, 3H), 5.12 (br, s, 2H), 6.96 (d, J = 8.1 Hz, 1H), 6.98 (s, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), ^{13}C-NMR (125 MHz, $CDCl_3$),

δ ppm; 21.30, 118.59, 122.26, 126.49, 129.10, 139.57, 150.68, 155.22.

4-Methylphenyl Carbamate [28]**.** The reaction afforded white crystals **1r** (80% yield), mp = 134-136 °C. IR (KBr); 3410 (m), 3405 (m), 3200 (vw), 3265 (w), 2915 (w), 1700 (vs), 1613 (m), 1505 (m), 1361 (s), 1382 (s), 1217 (s), 1205 (s), 1163 (w), 1016 (w), 975 (w), 853 (w), 810 (w), 549 (w), 501 (w) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 2.36 (s, 3H), 5.23 (br, s, 2H), 7.04 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 20.86, 121.40, 129.92, 135.34, 148.56, 155.63.

4-Bromophenyl Carbamate [29]**.** The reaction afforded white crystals **1s** (55% yield), mp = 139-142 °C. IR (KBr); 3400 (m), 3300 (m), 3250 (w), 3200 (w), 1700 (s), 1650 (w), 1610 (w), 1580 (w), 1560 (w), 1540 (w), 1480 (m), 1460 (w), 1380 (m), 1200 (m), 1060 (w), 1010 (w), 980 (w), 800 (w), 722 (w), 500 (m) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 5.05 (br, s, 2H), 7.06 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 118.70, 123.43, 132.40, 149.80, 154.46.

2-*tert*-Butyl-4-Methylphenyl Carbamate. After heating the reaction in 60-70 °C for 1 h, the resultant mixture was put aside for the appropriate period of 12 h. The reaction afforded white crystals **1t** (92% yield), mp = 143-144 °C. IR (KBr); 3450 (m), 3250 (m), 2950 (m), 1720 (vs), 1610 (m), 1570 (w), 1490 (m), 1480 (w), 1450 (m), 1360 (s), 1280 (w), 1200 (s), 980 (m), 840 (w), 790 (w), 770 (w), 730 (w), 670 (w), 590 (w) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$), δ ppm; 1.39 (s, 9H), 2.36 (s, 3H), 5.30 (br, 2H), 6.97 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.19 (s, 1H), ^{13}C-NMR (125 MHz, $CDCl_3$), δ ppm; 21.22, 30.31,34.46, 123.93, 127.44, 127.82, 135.07, 141.02, 147.04, 155.76.

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