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Copper-Catalyzed Coupling of Amines with Carbazates: An Approach to Carbamates

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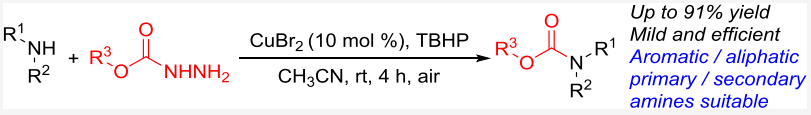

ABSTRACT: A new approach for the preparation of carbamates *via* the copper-catalyzed cross-coupling reaction of amines with alkoxycarbonyl radicals generated from carbazates is described. This environmentally friendly protocol takes place under mild conditions and is compatible with a wide range of amines, including aromatic/aliphatic and primary/secondary substrates.

INTRODUCTION

The carbamate moiety plays an important role in organic synthesis and modern drug discovery.[1−3] In addition to being a common feature in a number of approved drugs and prodrugs, it is widely employed in industries such as agrochemicals and polymers (Figure 1).[4−6] Structurally, carbamates are like a hybrid of amide and ester, and in general, exhibit very good chemical stability. Hence, they are commonly employed as protecting groups for amines[7] as well as amino acids in peptide chemistry.[8,9] Owing to the enormous importance of the carbamate motif, there is strong interest in the development of sustainable preparatory methods.

Over the years, carbamates have been traditionally prepared *via* the rearrangement of amides[10−12] or acyl azides,[13,14] the reaction of phosgene or its derivative with amines,[15−17] the reductive carbonylation of nitroaromatics,[18,19] the oxidative carbonylation of amines,[20−24] the carboxylation of amines,[25−27] and the reaction of alcohols with isocyanates[28] (Scheme 1). In recent times, significant efforts have been devoted to the development of modified reagents toward optimizing the traditional procedures.[29−34] Nevertheless, the operational complexity, hazardous by-products, and the use of toxic and/or specialized reagents are major limitations. In recent times, oxidative carbonylation reactions utilizing carbazates as a source of alkoxycarbonyl radicals have emerged as a powerful means of synthesizing value-added products.[35−40] For instance, Taniguchi et al.[35] disclosed an iron-catalyzed oxidative addition of alkoxycarbonyl radicals generated from methyl carbazates, to alkenes to furnish β-hydroxyesters. Furthermore, the radical alkoxycarbonylation of 2-isocyanobiphenyls with carbazates has been studied by other groups toward the preparation of phenanthridine derivatives.[37,38] However, these examples have largely focused on the addition of multiple bonds. In recent times, our group has been active in the development of novel oxidative coupling processes for the construction of carbon−heteroatom bonds.[41−44] We envisioned that alkoxycarbonyl radicals generated from carbazates under suitable conditions could oxidatively couple with amines to directly afford carbamates. Such a strategy would eliminate the synthetic limitations, as well as toxicity issues commonly encountered with traditional methods.

RESULTS AND DISCUSSION

Our initial investigations began by examining the oxidative coupling reaction of aniline **1a** and methyl carbazate **2** in MeCN at 80 °C (Table 1). In the presence of an Fe(II)-catalyst and *tert*-butyl hydroperoxide (TBHP), the reaction could only afford trace amounts of the desired product **3a** (entry 1). Desirably, the use of $CuCl_2$ *in lieu* of $FeCl_2$ furnished product **3a** in 70% yield (entry 2). As a result of the efficacy exhibited by $CuCl_2$, a variety of copper salts were tested, and $CuBr_2$ was determined to be the most effective, affording product **3a** in 82% yield (entries 2−9). Notably, the reaction efficiency was still maintained at ambient temperature (entries 4, 10, and 11). Finally, after a systematic screening of the ideal amount of methyl carbazate, $CuBr_2$ catalyst, and TBHP (entries 12−22), the optimized conditions were determined to be: aniline **1a** (1 mmol), methyl carbazate **2** (5 equiv), $CuBr_2$ (10 mol %), and TBHP (7.5 equiv) in CH_3CN at room temperature (rt) for 4 h to furnish 86% yield of **3a** (entry 14).

With the optimized reaction conditions in hand, the scope of the reaction with respect to amines was examined. As illustrated in Table 2, the reaction was amenable to a variety of amines, including aromatic and aliphatic substrates. In the case of anilines bearing meta- or para-electron-donating groups

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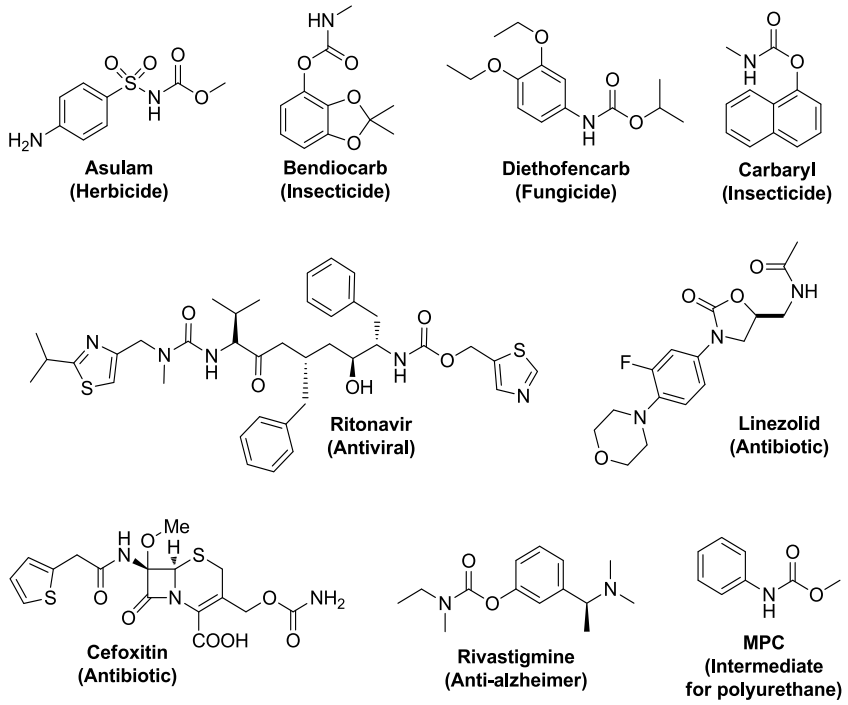
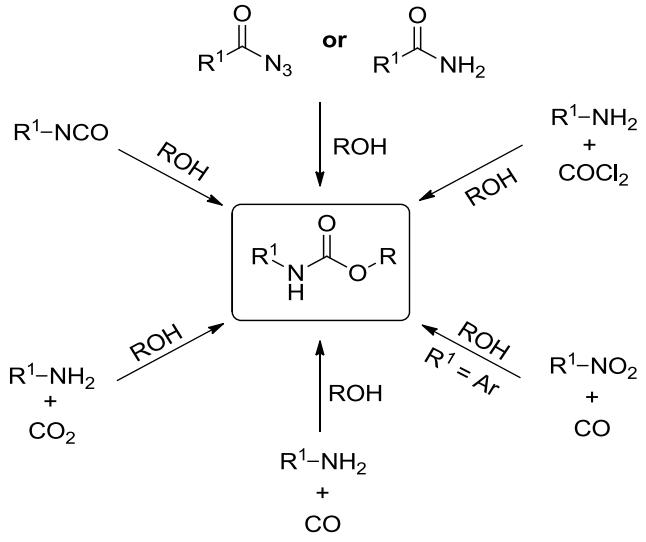


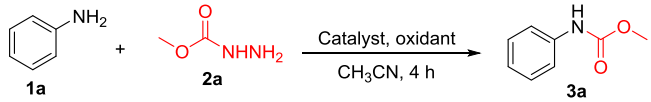
Figure 1. Examples of important carbamate-containing compounds.

Scheme 1. Traditional Methods for the Synthesis of Carbamates



such as methyl and methoxy, the reaction gave the corresponding carbamates in good yields (**3b**–**3e**). However, the yields of anilines bearing ortho-substituents were noticeably affected by steric hindrance as exemplified by products **3f** and **3g**. Moreover, this effect was more pronounced with the bulky 2-*tert*-butyl group (**3h**). In addition, the reactions of anilines bearing electron-withdrawing groups such as halogens (**3i**–**3l**), ethoxycarbonyl (**3m**), formyl (**3n**), and acetyl (**3o**) all afforded the desired carbamates in moderate to good yields. However, 4-nitroaniline could afford the corresponding product **3p** only in trace amounts, probably due to the greater electron-pulling effect of the $-NO_2$ group. Meanwhile, the reaction of 2-naphthylamine occurred smoothly to provide the desired product **3q** in 67% yield. Otherwise, the reaction took place readily with aliphatic amines: product **3r** was obtained in

Table 1. Optimization of the Reaction[a]



entry	1a/2	catalyst (10 mol %)	temp. (°C)	yield (%)[b]
1	1:4	$FeCl_2·4H_2O$	80	trace
2	1:4	$CuCl_2$	80	70
3	1:4	CuCl	80	58
4	1:4	$CuBr_2$	80	82
5	1:4	CuBr	80	57
6	1:4	CuI	80	58
7	1:4	CuO	80	15
8	1:4	$Cu(OAc)_2$	80	10
9	1:4	$CuSO_4·5H_2O$	80	30
10	1:4	$CuBr_2$	25	83
11	1:4	$CuBr_2$	0	82
12	1:1.5	$CuBr_2$	25	54
13	1:3	$CuBr_2$	25	78
14	1:5	$CuBr_2$	25	86
15	1:6	$CuBr_2$	25	82
16[c]	1:5	$CuBr_2$	25	51
17[d]	1:5	$CuBr_2$	25	64
18[e]	1:5	$CuBr_2$	25	75
19[f]	1:5	$CuBr_2$	25	86
20[g]	1:5	$CuBr_2$	25	52
21	1:5		25	0
22[h]	1:5	$CuBr_2$	25	82

[a]Reaction conditions: **1a** (1 mmol), **2a** (1–6 equiv), metal catalyst (10 mol %), and TBHP (70% in H_2O, 7.5 equiv) in CH_3CN (5 mL) under air. [b]Isolated yield. [c]TBHP (70% in H_2O, 3 equiv). [d]TBHP (70% in H_2O, 4.5 equiv). [e]TBHP (70% in H_2O, 6 equiv). [f]TBHP (70% in H_2O, 9 equiv). [g]5 mol % of $CuBr_2$ used. [h]15 mol % of $CuBr_2$ used.

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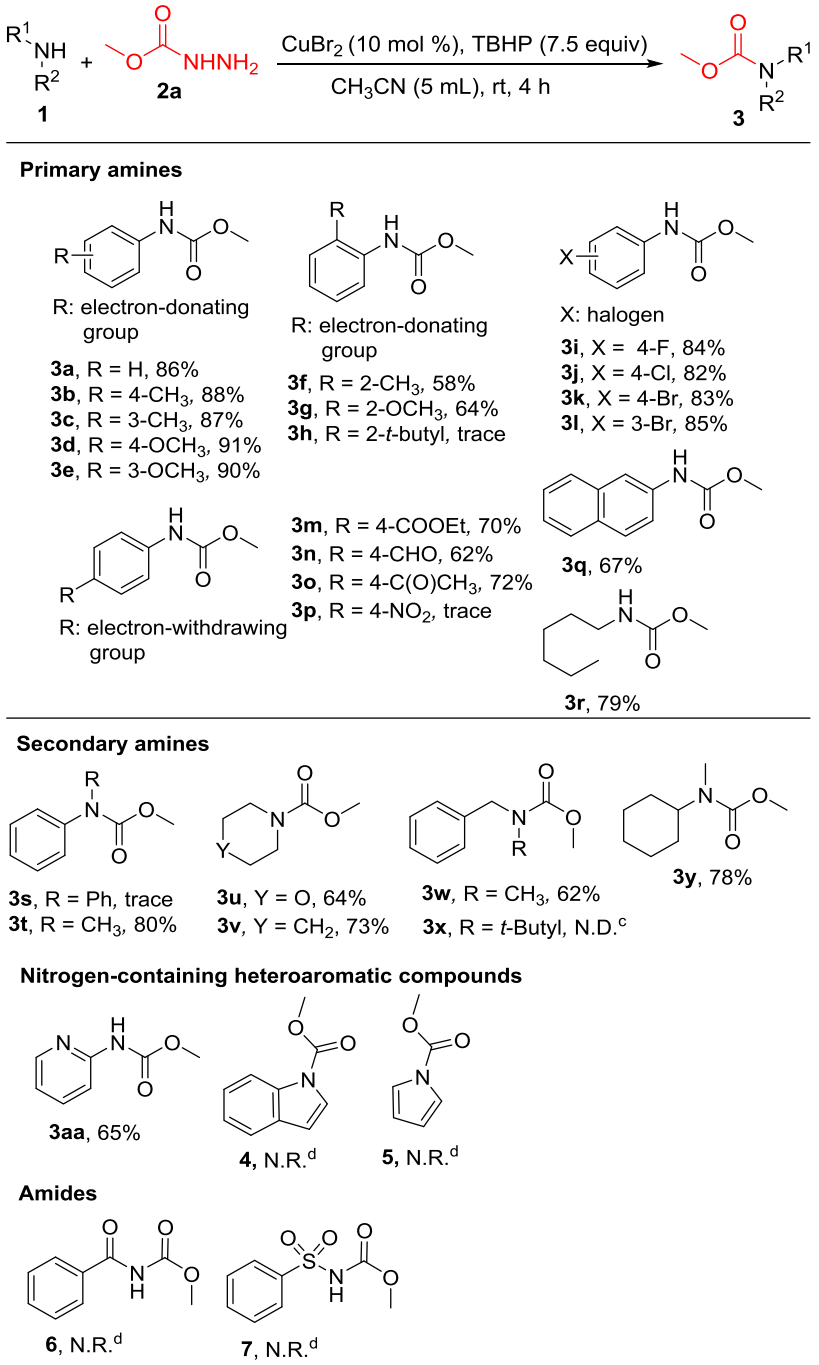
Table 2. Reaction Scope of Amines[a]



[a]Reactions were conducted using **1** (1 mmol), **2** (5 mmol), $CuBr_2$ (10 mol %), and TBHP (70% in water, 7.5 mmol) in CH_3CN (5 mL) at rt for 4 h. [b]Isolated yield. [c]N.D. = not detected. [d]N.R. = no reaction.

79% yield from 1-hexylamine. Next, we examined the coupling reaction of secondary amines with methyl carbazate. With the exception of diphenylamine (**3s**), the coupling products corresponding to *N*-methylaniline (**3t**), morpholine (**3u**), piperidine (**3v**), *N*-methylbenzylamine (**3w**), and *N*-methylcyclohexylamine (**3y**) were obtained in satisfactory yields. Unfortunately, other than the reaction of 2-aminopyridine with methyl carbazate that gave the expected product **3aa** in 65% yield, substrates both heteroaromatic amines like indole and pyrrole, and in which the amine nitrogen atom is electron-deficient such as benzamide and benzenesulfonamide were completely inert under standard conditions (Table 2, **4**–**7**).

Next, the scope of the reaction with respect to carbazates was also examined under optimized reaction conditions. As illustrated in Table 3, the reactions of carbazates like ethyl carbazate, *tert*-butyl carbazate, phenyl carbazate, and benzyl carbazate have been carried out, and the results indicated that all of the reactions gave the expected products in satisfactory yields (52–79%, see Table 3, **3ab**–**3ae**).

To gain an insight into the reaction mechanism, some control experiments were carried out (Scheme 2). First, well-

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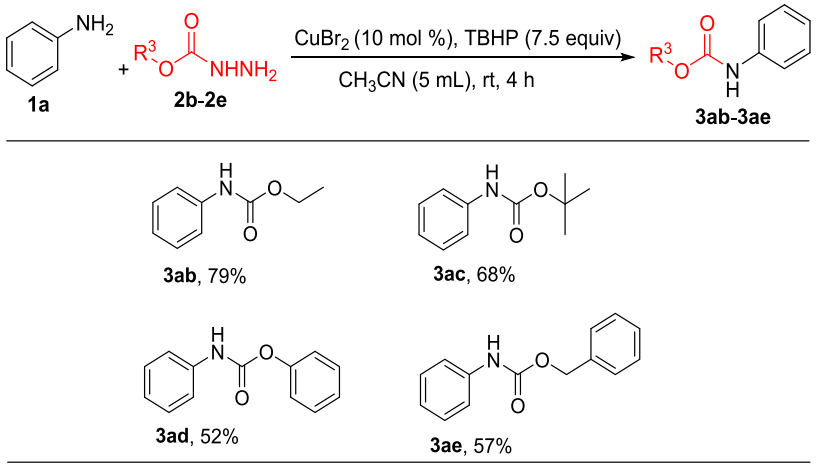
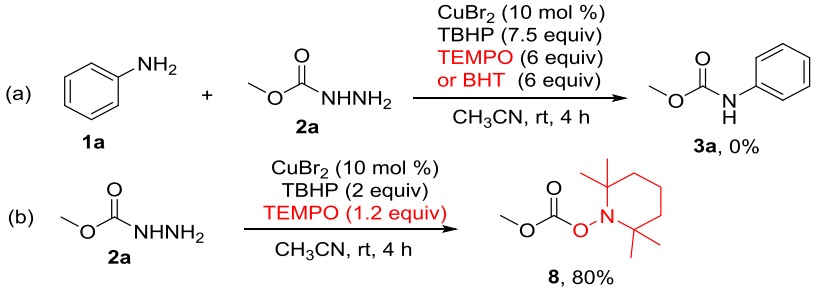
Table 3. Reaction Scope of Carbazates[a]

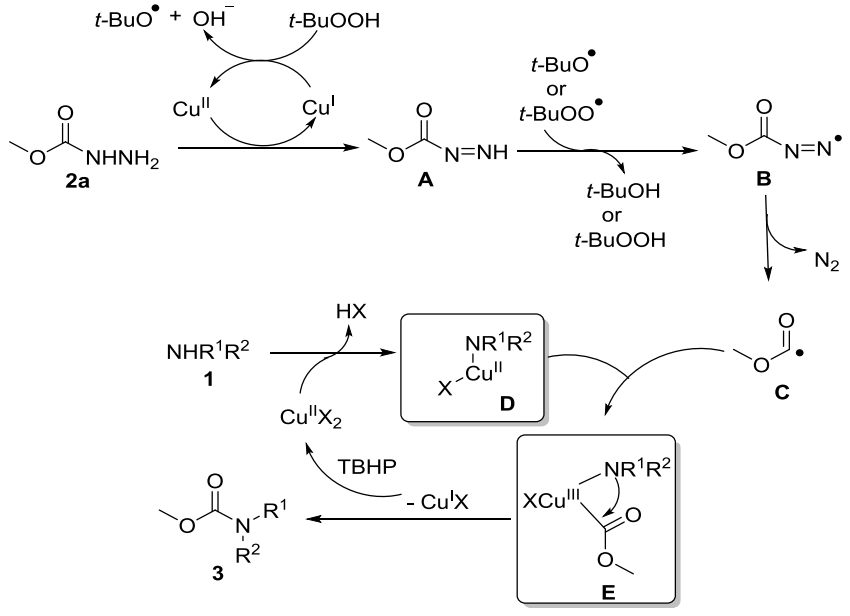


[a]Reactions were conducted using **1a** (1 mmol), **2** (5 mmol), $CuBr_2$ (10 mol %), and TBHP (70% in water, 7.5 mmol) in CH_3CN (5 mL) at rt for 4 h.

Scheme 2. Control Experiments



Scheme 3. Proposed Mechanism



known radical trapping agents such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and butylated hydroxytoluene (BHT) were added to the coupling reaction of aniline **1a** and methyl carbazate **2**; and as expected, the formation of **3a** was significantly inhibited (Scheme 2a). Moreover, in the absence of aniline **1a**, compound **8** presumably formed from the capture of the alkoxycarbonyl radical by TEMPO was isolated in 80% yield (Scheme 2b). This result suggests the generation of alkoxycarbonyl radicals in the reaction medium under the standard conditions.

On the basis of results obtained above and previous literature reports,[35,37−40,58−62] a plausible mechanism is

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proposed as depicted in Scheme 3. Initially, methyl carbazate **2a** was oxidized by the Cu^{II}/TBHP system to form a diazene intermediate **A**. Further, the proton abstraction step generates the diazenyl radical **B**, from which the alkoxycarbonyl radical **C** is formed, alongside the release of molecular nitrogen.[35,37−40] Radical **C** can be trapped by complex **D** formed *in situ* from Cu^{II} species and amine **1** to produce complex **E**, followed by reductive elimination to afford product **3** and release of Cu^{I} species to participate in the next cycle reaction.[58−62]

CONCLUSIONS

In summary, we have developed a new approach for the synthesis of carbamates *via* the copper-catalyzed cross-coupling reaction of primary and secondary amines with alkoxycarbonyl radicals generated from carbazates. Notably, the reaction proceeds with high efficiency utilizing inexpensive and easy-to-handle reagents. The benign protocol was shown to be compatible with a wide range of amines including aromatic/aliphatic and primary/secondary substrates.

EXPERIMENTAL SECTION

General Remarks. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian-Inova 300 or 400 MHz spectrometer. Spectra were referenced to residual chloroform (δ = 7.26 ppm, ^1H; 77.16 ppm, ^{13}C). Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) (δ). Multiplicities were indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet), and coupling constants J were reported in hertz (Hz). High-resolution mass spectra were recorded on a MicroMass-TOF machine (ESI). Column chromatography purifications were performed using 300−400 mesh silica gel.

Starting Materials. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification.

General Procedure A: Preparation of Carbamates 3. To a Schlenk tube equipped with a rubber septum was successively added amine **1** (1.0 mmol, 1.0 equiv), methyl carbazate **2a** (450 mg, 5.0 mmol, 5.0 equiv), $CuBr_2$ (22.3 mg, 0.1 mmol, 10 mol %), and acetonitrile (5 mL). The tube was capped and TBHP (70% in H_2O) (0.7 mL, 7.5 mmol, 7.5 equiv) was added dropwise. Then, the mixture was stirred for 4 h at room temperature. After the completion of the reaction (indicated by thin-layer chromatography (TLC)), the reaction mixture was concentrated under reduced pressure and the crude mixture was purified by column chromatography using petroleum ether/ethyl acetate 20:1 (v/v) as the eluent to obtain the pure products **3**.

Procedure for the Trapping of the Alkoxycarbonyl Radical. To a Schlenk tube equipped with a rubber septum was successively added methyl carbazate **2a** (90 mg, 1.0 mmol, 1.0 equiv), $CuBr_2$ (22.3 mg, 0.1 mmol, 10 mol %), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 187 mg, 1.2 mmol, 1.2 equiv), and acetonitrile (5 mL). The tube was capped and TBHP (70% in H_2O) (0.2 mL, 2.0 mmol, 2.0 equiv) was added dropwise. Then, the mixture was stirred for 4 h at room temperature. Afterward, the reaction mixture was concentrated under reduced pressure and the crude mixture was purified by column chromatography using petroleum ether/ethyl acetate 20:1 (v/v) as the eluent to obtain the pure compound **8**.

*Methyl Phenylcarbamate (**3a**).*[45] According to the general procedure A, compound **3a** was obtained from aniline (93 mg, 1 mmol) as a yellow solid (127 mg, 86%), mp = 42.3−43.8 °C. IR: ν 3342, 2950, 1707, 1599, 1543, 1490, 1435 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.37 (m, 2H), 7.34−7.27 (m, 2H), 7.10−7.02 (m, 1H), 6.91 (s, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.7, 137.5, 128.5, 123.0, 118.3, 51.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_8H_9NO_2Na$ 174.0531, found 174.0524.

*Methyl (4-Methylphenyl)carbamate (**3b**).*[46] According to the general procedure A, compound **3b** was obtained from the reaction of 4-methylaniline (107 mg, 1 mmol) as a white solid (145 mg, 88%), mp = 99.9−100.4 °C. IR: ν 3345, 2953, 1707, 1616, 1555, 1493, 1438 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29−7.22 (m, 2H), 7.14−7.08 (m, 2H), 6.55 (s, 1H), 3.77 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.8, 134.8, 132.6, 129.0, 118.4, 51.8, 20.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{11}NO_2Na$ 188.0687, found 188.0693.

*Methyl (3-Methylphenyl)carbamate (**3c**).*[45] According to the general procedure A, compound **3c** was obtained from the reaction of 3-methylaniline (107 mg, 1 mmol) as a yellow solid (139 mg, 87%), mp = 70.5−72.8 °C. IR: ν 3345, 2952, 1707, 1616, 1555, 1492, 1438 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.24−7.13 (m, 3H), 6.91−6.85 (m, 1H), 6.63 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 154.1, 139.0, 137.8, 128.9, 124.3, 119.5, 116.0, 52.3, 21.5. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{11}NO_2Na$ 188.0687, found 188.0685.

*Methyl (4-Methoxyphenyl)carbamate (**3d**).*[46] According to the general procedure A, compound **3d** was obtained from the reaction of 4-methoxyaniline (123 mg, 1 mmol) as a white solid (165 mg, 91%), mp = 108.1−108.9 °C. IR: ν 3323, 2953, 2938, 1714, 1610, 1598, 1541, 1497, 1438 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36−7.22 (m, 2H), 6.95−6.77 (m, 2H), 6.56 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.0, 154.5, 130.9, 120.7, 114.3, 55.5, 52.3. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{11}NO_3Na$ 204.0637, found 204.0632.

*Methyl (3-Methoxyphenyl)carbamate (**3e**).*[45] According to the general procedure A, compound **3e** was obtained from the reaction of 3-methoxyaniline (123 mg, 1 mmol) as a yellow liquid (163 mg, 90%). IR: ν 3324, 2953, 2939, 1714, 1609, 1598, 1541, 1497, 1457 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.18 (t, J = 8.2 Hz, 1H), 7.12 (s, 1H), 6.89−6.85 (m, 1H), 6.77 (s, 1H), 6.64−6.59 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 159.8, 153.5, 138.7, 129.3, 110.4, 108.7, 103.9, 54.8, 51.8. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{11}NO_3Na$ 204.0637, found 204.0640.

*Methyl (2-Methylphenyl)carbamate (**3f**).*[50] According to the general procedure A, compound **3f** was obtained from the reaction of 2-methylaniline (107 mg, 1 mmol) as a yellow liquid (96 mg, 58%). IR: ν 3344, 2955, 1707, 1616, 1554, 1493, 1438 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.86−7.61 (m, 1H), 7.24−7.18 (m, 1H), 7.18−7.13 (m, 1H), 7.07−7.00 (m, 1H), 6.42 (s, 1H), 3.78 (s, 3H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.9, 135.3, 132.5, 129.9, 129.3, 126.4, 123.8, 51.9, 17.2. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{11}NO_2Na$ 188.0687, found 188.0684.

*Methyl (2-Methoxyphenyl)carbamate (**3g**).*[48] According to the general procedure A, compound **3g** was obtained from the reaction of 2-methoxyaniline (123 mg, 1 mmol) as a yellow liquid (156 mg, 64%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16−8.04 (m, 1H), 7.34−7.23 (m, 1H), 7.02−6.93 (m, 2H), 6.86−6.81 (m, 1H), 3.93 (s, 3H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.5, 147.1, 127.1, 122.3, 120.6, 117.7, 109.5, 55.1, 51.7. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_9H_{11}NO_3Na$ 204.0637, found 204.0634.

*Methyl (4-Fluorophenyl)carbamate (**3i**).*[47] According to the general procedure A, compound **3i** was obtained from the reaction of 4-fluoroaniline (111 mg, 1 mmol) as a white solid (142 mg, 84%), mp = 91.1−92.5 °C. IR: ν 3317, 2937, 1713, 1598, 1534, 1491, 1443 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.29 (m, 2H), 7.07−6.91 (m, 2H), 6.67 (s, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.5 (d, J = 242.1 Hz), 153.8, 133.3, 120.0, 115.2 (d, J = 22.6 Hz), 51.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ −119.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_8H_9FNO_2$ 170.0617, found 170.0625.

*Methyl (4-Chlorophenyl)carbamate (**3j**).*[45] According to the general procedure A, compound **3j** was obtained from the reaction of 4-chloroaniline (127 mg, 1 mmol) as a yellow solid (152 mg, 82%), mp = 126.1−126.9 °C. IR: ν 3341, 2971, 2892, 1698, 1599, 1542, 1489, 1435 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.30 (m, 2H), 7.28−7.22 (m, 2H), 6.72 (s, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.5, 136.0, 128.6, 128.0, 119.4, 52.0. HRMS

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(ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_8H_8ClNO_2Na$ 208.0141, found 208.0147.

*Methyl (4-Bromophenyl)carbamate (**3k**).*[45] According to the general procedure A, compound **3k** was obtained from the reaction of 4-bromoaniline (172 mg, 1 mmol) as a yellow solid (191 mg, 83%), mp = 135.1−136.2 °C. IR: ν 3341, 2972, 1699, 1599, 1543, 1490, 1435 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.38 (m, 2H), 7.32−7.25 (m, 2H), 6.69 (s, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.4, 136.5, 131.5, 119.8, 115.5, 52.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_8H_8BrNO_2Na$ 251.9636, found 251.9640.

*Methyl (3-Bromophenyl)carbamate (**3l**).*[45] According to the general procedure A, compound **3l** was obtained from the reaction of 3-bromoaniline (172 mg, 1 mmol) as a yellow solid (195 mg, 85%), mp = 87.5−88.6 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 (s, 1H), 7.31−7.25 (m, 1H), 7.21−7.12 (m, 2H), 6.68 (s, 1H), 3.78 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.4, 138.7, 129.8, 125.9, 122.2, 121.1, 116.7, 52.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_8H_8BrNO_2Na$ 251.9636, found 251.9631.

*Ethyl 4-((Methoxycarbonyl)amino)benzoate (**3m**).*[48] According to the general procedure A, compound **3m** was obtained from the reaction of ethyl 4-aminobenzoate (165 mg, 1 mmol) as a yellow solid (156 mg, 70%), mp = 100.5−101.8 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06−7.94 (m, 2H), 7.50−7.42 (m, 2H), 6.87 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 166.2, 153.5, 142.0, 130.9, 125.2, 117.5, 80.8, 52.6, 14.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{11}H_{13}NO_4Na$ 246.0742, found 246.0738.

*Methyl (4-Formylphenyl)carbamate (**3n**).*[49] According to the general procedure A, compound **3n** was obtained from the reaction of 4-aminobenzaldehyde (149 mg, 1 mmol) as a yellow solid (111 mg, 62%), mp = 155.1−156.2 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.91 (s, 1H), 7.90−7.78 (m, 2H), 7.61−7.52 (m, 2H), 6.95 (s, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 190.5, 152.9, 143.1, 131.2, 130.8, 117.5, 52.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_9NO_3Na$ 202.0480, found 202.0474.

*Methyl (4-Acetylphenyl)carbamate (**3o**).*[48] According to the general procedure A, compound **3o** was obtained from the reaction of 4-acetylaniline (135 mg, 1 mmol) as a yellow solid (139 mg, 72%), mp = 165.1−166.5 °C. IR: ν 3264, 2914, 1732, 1667, 1588, 1539, 1438, 1414 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.13 (s, 1H), 3.79 (s, 3H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 196.5, 153.1, 142.0, 131.7, 129.4, 117.1, 52.1, 25.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_{11}NO_3Na$ 216.0637, found 216.0629.

*Methyl Naphthalen-2-ylcarbamate (**3q**).*[49] According to the general procedure A, compound **3q** was obtained from the reaction of naphthalen-2-amine (143 mg, 1 mmol) as a white solid (135 mg, 67%), mp = 112.5−113.8 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1H), 7.81−7.74 (m, 3H), 7.49−7.42 (m, 1H), 7.42−7.35 (m, 2H), 6.83 (s, 1H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.7, 134.8, 133.5, 129.7, 128.4, 127.1, 126.9, 126.1, 124.2, 118.7, 114.4, 52.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{11}NO_2Na$ 224.0687, found 224.0683.

*Methyl Hexylcarbamate (**3r**).*[51] According to the general procedure A, compound **3r** was obtained from the reaction of 1-hexylaniline (101 mg, 1 mmol) as a yellow liquid (126 mg, 79%). IR: ν 3348, 2959, 2932, 1700, 1557, 1457 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 4.75 (s, 1H), 3.63 (s, 3H), 3.14−2.98 (m, 2H), 1.51−1.33 (m, 2H), 1.30−1.11 (m, 6H), 0.88−0.70 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.6, 51.3, 40.5, 30.9, 29.4, 25.8, 22.0, 13.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_8H_{18}NO_2$ 160.1338, found 160.1344.

*Methyl N-Methyl(phenyl)carbamate (**3t**).*[45] According to the general procedure A, compound **3t** was obtained from the reaction of *N*-methylaniline (107 mg, 1 mmol) as a yellow liquid (132 mg, 80%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.39−7.31 (m, 2H), 7.28−7.14 (m, 3H), 3.70 (s, 3H), 3.30 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.1, 143.3, 128.9, 126.1, 125.8, 52.8, 37.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_{11}NO_2Na$ 188.0687, found 188.0689.

*Methyl Morpholine-4-carboxylate (**3u**).*[52] According to the general procedure A, compound **3u** was obtained from the reaction of morpholine (87 mg, 1 mmol) as a clear liquid (93 mg, 64%). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.70 (s, 3H), 3.68−3.61 (m, 4H), 3.49−3.41 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 155.9, 66.6, 52.7, 44.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_6H_{12}NO_3$ 146.0817, found 146.0809.

*Methyl 4-Methylpiperidine-1-carboxylate (**3v**).*[62] According to the general procedure A, compound **3v** was obtained from the reaction of piperidine (85 mg, 1 mmol) as a colorless liquid (104 mg, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.66 (s, 3H), 3.59−3.34 (m, 4H), 1.70−1.44 (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.0, 52.4, 44.8, 25.7, 24.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_7H_{14}NO_2$ 144.1025, found 144.1029.

*Methyl Benzyl(methyl)carbamate (**3w**).*[51] According to the general procedure A, compound **3w** was obtained from the reaction of *N*-methyl-1-phenylmethanamine (121 mg, 1 mmol) as a colorless liquid (111 mg, 62%). IR: ν 2957, 2887, 1706, 1598, 1541, 1498, 1448 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.32 (m, 2H), 7.31−7.16 (m, 3H), 4.60−4.40 (m, 2H), 3.77 (s, 3H), 3.00−2.70 (m, 3H),; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.4, 157.1, 137.5, 128.6, 127.8, 127.4, 127.2, 52.8, 52.6, 52.3, 34.4, 33.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{14}NO_2$ 180.1025, found 180.1021.

*Methyl Cyclohexyl(methyl)carbamate (**3y**).*[51] According to the general procedure A, compound **3y** was obtained from the reaction of *N*-methylcyclohexanamine (113 mg, 1 mmol) as a colorless liquid (133 mg, 78%). ^1H NMR ($CDCl_3$, 400 MHz): δ 4.01−3.71 (m, 1H), 3.63 (s, 3H), 2.70 (s, 3H), 1.77−1.55 (m, 5H), 1.39−1.22 (m, 4H), 1.08−0.96 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.8, 54.8, 52.4, 30.2, 28.1, 25.7, 25.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{18}NO_2$ 172.1338, found 172.1341.

*Methyl Pyridin-2-ylcarbamate (**3aa**).*[53] According to the general procedure A, compound **3aa** was obtained from the reaction of 2-aminopyridine (94 mg, 1 mmol) as a white solid (98 mg, 65%), mp = 129.8−130.2 °C. IR: ν 3260, 2979, 1731, 1657, 1588, 1540, 1438 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 10.55 (s, 1H), 8.34 (d, J = 4.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.02−6.92 (m, 1H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 154.2, 152.6, 147.5, 138.6, 118.4, 112.6, 52.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_7H_8N_2O_2Na$ 175.0483, found 175.0490.

*Ethyl Phenylcarbamate (**3ab**).*[54] According to the general procedure A, compound **3ab** was obtained from the reaction of ethyl carbazate (520 mg, 5 mmol) as a yellow liquid (130 mg, 79%). IR: ν 3317, 2987, 2968, 1716, 1599, 1540, 1489, 1444 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, J = 7.7 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.03 (t, J = 7.3 Hz, 1H), 6.93 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.9, 138.1, 129.0, 123.3, 118.8, 61.2, 14.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_{11}NO_2Na$ 188.0687, found 188.0692.

*tert-Butyl Phenylcarbamate (**3ac**).*[55] According to the general procedure A, compound **3ac** was obtained from the reaction of *tert*-butyl carbazate (660 mg, 5 mmol) as a white solid (130 mg, 68%), mp = 135.2−136.6 °C. IR: ν 3311, 2985, 2963, 1687, 1597, 1528, 1488, 1440 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.23 (m, 4H), 7.02 (t, J = 7.3 Hz, 1H), 6.56 (bs, 1H), 1.51 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 152.8, 138.4, 129.0, 123.0, 118.6, 80.5, 28.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{16}NO_2$ 194.1181, found 194.1189.

*Phenyl Phenylcarbamate (**3ad**).*[56] According to the general procedure A, compound **3ad** was obtained from the reaction of phenyl hydrazinecarboxylate (760 mg, 5 mmol) as a white solid (129 mg, 57%), mp = 77.2−78.5 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.48−7.37 (m, 4H), 7.36−7.29 (m, 2H), 7.28−7.17 (m, 3H), 7.16−7.00 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 151.7, 150.6, 137.4, 129.5, 129.2, 125.8, 123.9, 121.7, 118.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{13}H_{11}NO_2Na$ 236.0687, found 236.0686.

*Benzyl Phenylcarbamate (**3ae**).*[57] According to the general procedure A, compound **3ae** was obtained from the reaction of benzyl hydrazinecarboxylate (830 mg, 5 mmol) as a white solid (110

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mg, 52%), mp = 135.4−136.5 °C. IR: ν 3271, 2987, 2900, 1688, 1599, 1545, 1493, 1444 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.22 (m, 9H), 7.04 (t, J = 7.3 Hz, 1H), 6.82 (bs, 1H), 5.17 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.5, 137.9, 136.1, 129.1, 128.7, 128.4, 128.4, 123.6, 118.8, 67.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_2Na$ 250.0844, found 250.0847.

*Methyl (2,2,6,6-Tetramethylpiperidin-1-yl) Carbonate (**8**).*[35] According to the procedure described for the radical trapping experiment, compound **8** was obtained as a yellow liquid (172 mg, 80%). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.79 (s, 3H), 1.71−1.48 (m, 5H), 1.42−1.35 (m, 1H), 1.15 (s, 6H), 1.11 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.4, 60.5, 55.0, 39.2, 31.5, 20.3, 16.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{22}NO_3$ 216.1600, found 216.1605.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01031.

^1H and $^{13}C\{^1H\}$ NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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