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Hypervalent Iodine Reagent-Promoted Hofmann-Type Rearrangement/Carboxylation of Primary Amides

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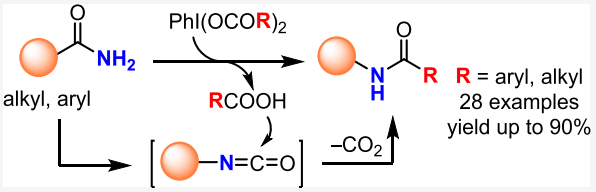
ABSTRACT: A novel transformation of primary amides to secondary amides promoted by hypervalent iodine reagents was developed. The hypervalent iodine reagent-mediated Hofmann-type rearrangement generated an isocyanate intermediate, which was subsequently trapped by an *in situ* generated carboxylic acid from the hypervalent iodine reagent to provide the corresponding secondary amides. This method provided a facile and efficient route for the synthesis of secondary amides from primary amides and also revealed novel reactivities of hypervalent iodine reagents.



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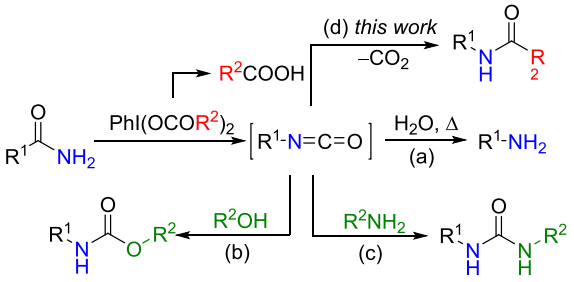
INTRODUCTION

As easily accessible, stable, efficient, and environmentally benign oxidants, hypervalent iodine reagents have been widely used in organic synthesis in recent years.[1] Among them, trivalent iodine compounds such as (diacyloxyiodo)arenes have been extensively studied and exhibited diverse reactivities beyond oxidation including ligand exchange, ligand coupling, reductive elimination, hemolytic cleavage, and single-electron transfer (SET).[1,2] Recently, it has also been revealed that these reagents were able to promote a number of rearrangement reactions.[3] The Hofmann rearrangement is an important process in organic synthesis, which can efficiently convert primary amides to the corresponding amines through an isocyanate intermediate.[4] Traditional Hofmann-type rearrangement required the use of halogen and a strong base that might limit their practical applications. In 1984, Loudon and coworkers first reported that the Hofmann rearrangement can be promoted by hypervalent iodine reagents.[5] Since then various iodine(III) reagents have been successfully used in different Hofmann-type rearrangements (Scheme 1a).[6] Some of them have even been applied in practical productions.[7]

Scheme 1. Reactions Based on Hypervalent Iodine Reagent-Promoted Hofmann Rearrangement



Methodologies based on hypervalent iodine reagent-promoted Hofmann rearrangement have also been developed for the synthesis of other useful compounds other than amines. Carbamates can be formed by nucleophilic addition of extra alcohols to the isocyanate intermediate (Scheme 1b).[8] Symmetrical ureas can be generated by addition of Hofmann-rearranged amines to isocyanates.[9] It can also be used for the synthesis of asymmetrical ureas with external amines (Scheme 1c).[10] However, in these methods, hypervalent iodine reagents only act as stoichiometric auxiliaries, which cannot be introduced to the products. On the other hand, it was reported that isocyanates can react with carboxylic acids to generate secondary amides.[11] In our continuing studies on hypervalent iodine chemistry,[12] we envisioned that trapping the isocyanate intermediate by an *in situ* generated carboxylic acid can form a carboxylation product. After intensive investigation, herein we reported the synthesis of secondary amides from primary amides through hypervalent iodine-promoted Hofmann-type rearrangement/carboxylation (Scheme 1d).

RESULTS AND DISCUSSION

The reaction of benzamide (**1a**) with $PhI(OAc)_2$ (PIDA) (**2a**) was carried out for the initial study and examination of the reaction parameters (Table 1). At first, it was found that the rearrangement/carboxylation product acetanilide (**3a**) was formed in 12% yield after reaction of **1a** and 1.5 equiv of

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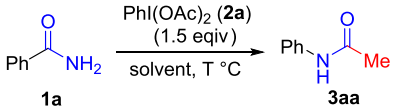
J. Org. Chem. 2021, 86, 2820–2826

Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	T (°C)	yield (%)
1	toluene	100	12
2	chlorobenzene	100	38
3	CH_3CN	100	<5
4	dimethylformamide (DMF)	100	<5
5	acetone	100	<5
6	tetrahydrofuran (THF)	100	<5
7	1,2-dimethoxyethane (DME)	100	NR
8	1,4-dioxane	100	NR
9	$CHCl_3$	100	60
10	dichloromethane (DCM)	100	46
11	DCE	100	83
12	DCE	80	45
13	DCE	120	80
14[b]	DCE	100	64
15[c]	DCE	100	50
16[d]	DCE	100	80

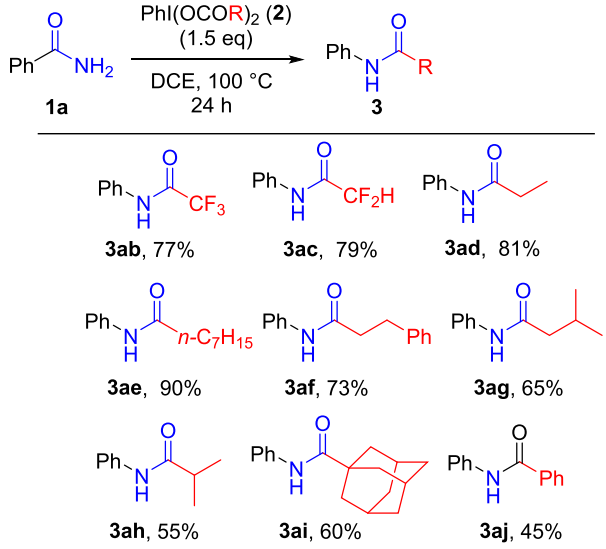
[a]Reaction conditions: benzamide (**1a**) (0.2 mmol) and PIDA (**2a**) (0.3 mmol) in the solvent (2.0 mL) stirred under air for 24 h. [b]Reaction for 20 h. [c]With 1 equiv of **2a**. [d]Reaction in the dark.

PIDA in toluene at 100 °C for 24 h (Table 1, entry 1). After investigating a variety of solvents (entries 2−11),[13] 1,2-dichloroethane (DCE) showed the best result in which the yield of the desired product was up to 83% (entry 11). The yield decreased to 45 and 80% when the temperature was reduced to 80 °C or elevated to 120 °C, respectively (entries 12 and 13). A lower yield (64%) was obtained within a shorter reaction time (20 h) (entry 14). Reducing the amount of PIDA to 1 equiv also led to a lower yield (entry 15). The reaction provided 80% yield even in the dark, which indicates that light has little effect on this reaction (entry 16). Thus, after screening the reaction conditions, those shown in entry 11 were chosen as the optimized conditions.

With the optimized conditions in hand, the reactions of benzamide (**1a**) with various (diacyloxyiodo)arenes (**2**) were examined and the results are showed in Scheme 2. All of the hypervalent iodine reagents were stable and easy to handle, which can be readily prepared from PIDA and the corresponding carboxylic acids. Trifluoromethylation and difluoromethylation both proceeded efficiently with iodobenzene trifluoroacetate (**2b**) and difluoroacetate (**2c**), which converted benzamide (**1a**) to trifluoroacetanilide (**3ab**) and difluoroacetanilide (**3ac**), respectively. The reactions of other (diacyloxyiodo)arenes also proceeded smoothly to give the corresponding rearrangement/carboxylation products in good yields (**3ad**−**3ag**). Even with a steric bulky alkyl group such as isopropyl or adamantyl, the desired products were formed in 55−60% yields (**3ah** and **3ai**). Iodobenzene dibenzoate (**3j**) was also applicable in this reaction; however, the corresponding product *N*-phenylbenzamide (**3aj**) was received in a lower yield.

Subsequently, a series of primary amides (**1**) were investigated in this reaction, as shown in Scheme 3. Various substituted benzamides (**1b**−**1k**) reacted with PIDA (**2a**) to give acetanilide derivatives in moderate to good yields (**3ba**−**3ka**). Good functional group tolerance was exhibited with

Scheme 2. Substrate Scope of Hypervalent Iodine Reagents (2)[a]



[a]Reaction conditions: benzamide (**1a**) (0.2 mmol) and (diacyloxyiodo)arenes (**2**) (0.3 mmol) in DCE (2.0 mL) stirred under air for 24 h at 100 °C.

benzamides. The substrates possessing an *ortho*-, *meta*-, or *para*-substituent afforded similar results without a significant steric hindrance effect (**3ba**−**3da**). But it showed an electronic effect as the benzamides with electron-donating substituents (**3ba**−**3fa**) provided higher yields than those with electron-withdrawing substituents (**3ha**−**3ka**). Naphthyl and heterocyclic amides were also applicable, which afforded the desired products in moderate yields (**3la**−**3na**). Aliphatic amides (**1o**−**1s**) were subsequently examined. Iodobenzene bis(3-phenylpropanoate) (**2f**) was used in these cases for easy monitoring and isolation. To our delight, all of the alkyl amides reacted smoothly in this method. The average yields were better than aryl amides (**3of**−**3sf**). Even the long-chain fatty amide stearamide (**3r**) and steric bulky cyclopropanecarboxamide (**3s**) showed good reactivity in this method, which provided the desired products in 71 and 73% yields, respectively. However, tertiary alkyl amides such as pivalamide did not give desired products in this reaction.

We also carried out several control experiments to clarify the reaction mechanism. At first, presynthesized isocyanate (**4a**) was tested in this reaction. The reaction of **4a** under standard conditions gave the desired product **3aa** in 76% yield (Scheme 4a). But no reaction occurred between **4a** and **2a** under room temperature (Scheme 4b). The reaction of **1a** and **2a** under room temperature did not give any product **3aa**, but isocyanate **4a** can be detected (Scheme 4c). These results proved the involvement of the isocyanate intermediate in this reaction. It can be easily generated from **1a** and **2a** in the presence of hypervalent iodine but heat was required for the formation of **3aa**.[13] Without the hypervalent iodine reagent, the reaction of **4a** with acetic acid did not give product **3aa** but only a symmetrical urea **5a** in 90% yield (Scheme 4d).[9] It showed that our conditions were essential for carboxylation and amide formation.

Based on the above results and literature reports, a plausible mechanism for this reaction was depicted as shown in Scheme 5. At first, the primary amide (**1**) reacts with the hypervalent

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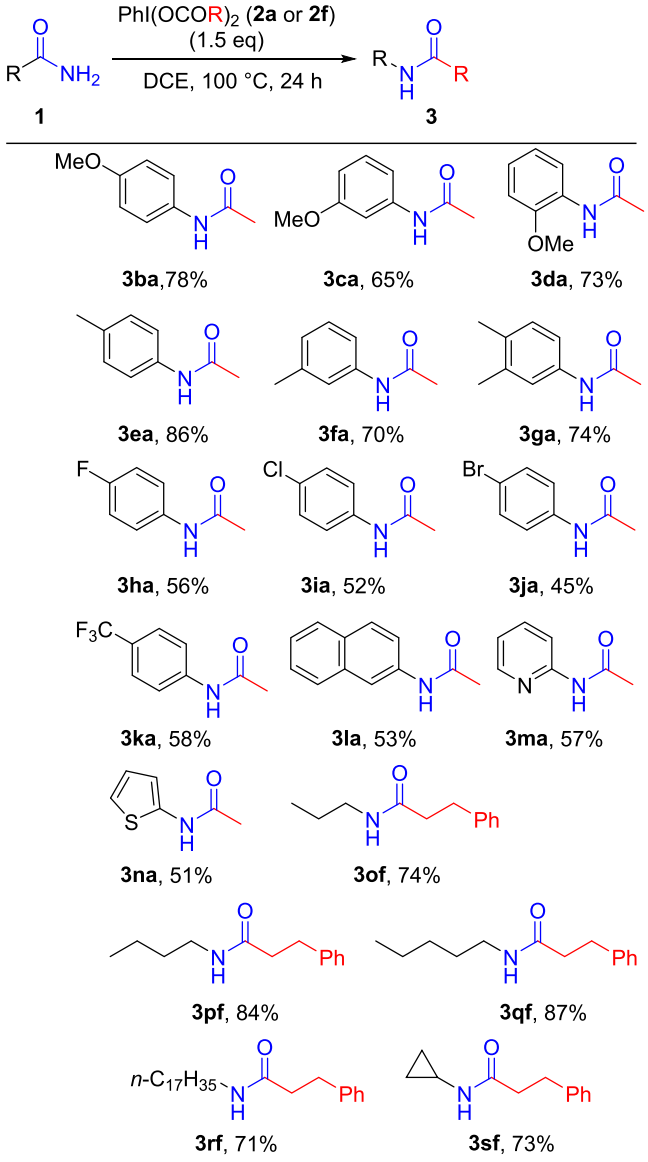
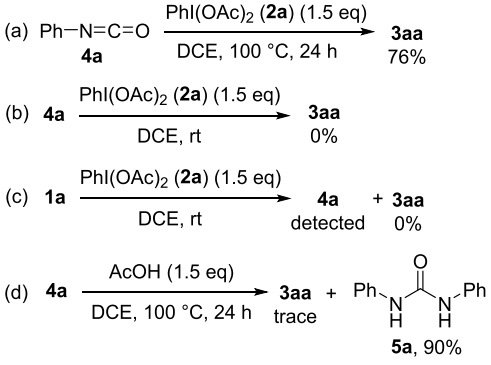
J. Org. Chem. 2021, 86, 2820−2826

Scheme 3. Substrate Scope of Amides (1)[a]



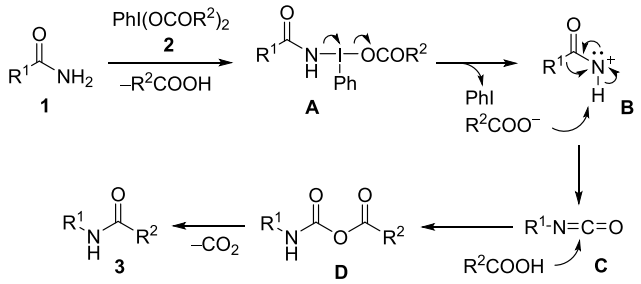
[a]Reaction conditions: amide (**1**) (0.2 mmol), **2a**, or **2f** (0.3 mmol) in DCE (2.0 mL) stirred under air for 24 h at 100 °C.

Scheme 4. Control Experiments



iodine reagent (**2**) to generate an amidoiodane intermediate **A**. Then, intermediate **A** undergoes reductive elimination to form a nitrenium cation **B** and releases iodobenzene and a carboxylate anion. Nitrenium **B** converts to isocyanate **C** through rearrangement with the assistance of the carboxylate anion.[6−8] Then, addition of the *in situ* generated carboxylic acid to isocyanate **C** generates carbamic anhydride **D**. Finally, decarboxylation of **D** converts to the final product **3** along with extrusion of CO_2.

Scheme 5. Plausible Mechanism



CONCLUSIONS

In summary, we have reported a novel transformation of primary amides to secondary amides promoted by hypervalent iodine reagents. A mechanistic study suggested that the reaction was initiated by the hypervalent iodine reagent-mediated Hofmann-type rearrangement to generate an isocyanate intermediate. It was subsequently trapped by the carboxylic acid, which was *in situ* generated from the hypervalent iodine to provide the corresponding secondary amides. The reaction proceeded using hypervalent iodine reagents as both rearrangement auxiliaries and carboxylation reagents without any metal, acid/base, or additives. It also showed broad substrate scope and good functional group compatibility, affording the corresponding secondary amides in moderate to good yields. It provided a facile and efficient route for the synthesis of secondary amides from primary amides and also revealed novel reactivities of hypervalent iodine reagents.

EXPERIMENTAL SECTION

General Experimental Methods. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Melting points were measured by an SGW X-4A microscopic apparatus. High-resolution mass spectrometry-electrospray ionization (HRMS-ESI) was measured by a Q Exactive Hybrid Quadrupole-Orbitrap LC/MS spectrometer.

Ethyl acetate and hexane were used for column chromatography without further purification. All solvents and chemicals were obtained from commercial sources and used as received unless otherwise noted. Hypervalent iodine reagents **2a** and **2b** were obtained from commercial sources and the others were prepared according to known methods.[14]

General Procedure for Preparation of Hypervalent Iodine Reagents (2c−2j). A mixture of $PhI(OAc)_2$ (**2a**) (3.22 g, 10 mmol, 1.0 equiv) and corresponding carboxylic acid (20 mmol, 2.0 equiv) were added into a round-bottom flask containing a stirring bar. Then, xylene (50 mL, 0.2 M) was introduced. The resulting mixture was stirred at 65 °C in an oil bath for 4 h. After the reaction was complete, xylene was removed under reduced pressure. Petroleum ether was used to wash the residuals three times and the white solid was filtered and dried in vacuum. The product can be used in the next reaction without further purification.

*Phenyl-λ^3-iodanediyl bis(2,2-difluoroacetate) (**2c**).* White solid, mp 99−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91−5.71 (m, 2H), 7.56−7.51 (m, 2H), 7.68−7.65 (m, 1H), 8.16 (d, J = 5.32 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 105.5 (t, J = 166.84 Hz), 122.4,

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131.7, 135.1, 133.1, 166.9 (t, J = 18.18 Hz). HRMS-ESI (m/z): calcd for $C_{10}H_8F_4IO_4$ $[M + H]^+$: 394.9398, found 394.9401.

*Phenyl-λ^3-iodanediyl dipropionate (**2d**).* White solid, mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (t, J = 7.56 Hz, 6H), 2.27 (dd, J_1 = 7.56 Hz, J_2 = 7.52 Hz, 4H), 7.47−7.52 (m, 2H), 7.57−7.60 (m, 1H), 8.07−8.10 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.9, 27.3, 121.7, 130.9, 131.6, 134.8, 179.6. HRMS-ESI (m/z): calcd for $C_{12}H_{16}IO_4$ $[M + H]^+$: 351.0088, found 351.0091.

*Phenyl-λ^3-iodanediyl dioctanoate (**2e**).* White oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80−0.83 (m, 6H), 1.19 (s, 16H), 1.48−1.50 (m, 4H), 2.19−2.22 (m, 4H), 7.44 (t, J = 5.08 Hz, 2H), 7.53 (t, J = 4.88 Hz, 1H), 8.03 (d, J = 5.32 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.5, 25.6, 28.8, 29.1, 31.6, 34.0, 121.8, 130.7, 131.5, 134.8, 178.9. HRMS-ESI (m/z): calcd for $C_{22}H_{36}IO_4$ $[M + H]^+$: 492.1653, found 492.1655.

*Phenyl-λ^3-iodanediyl bis(3-phenylpropanoate) (**2f**).* White oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.73−2.76 (m, 4H), 3.01−3.03 (m, 4H), 7.13−7.16 (m, 1H), 7.27 (d, J = 4.92 Hz, 6H), 7.35−7.37 (m, 4H), 7.51 (t, J = 5.04 Hz, 1H), 7.76 (d, J = 5.08 Hz, 1H), 10.06 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 30.6, 35.7, 126.4, 128.3, 128.6, 130.2, 130.3, 133.9, 137.5, 140.2, 179.4. HRMS-ESI (m/z): calcd for $C_{24}H_{24}IO_4$ $[M + H]^+$: 503.0714, found 503.0716.

*Phenyl-λ^3-iodanediyl bis(3-methylbutanoate) (**2g**).* White solid, mp 85−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (d, J = 4.52 Hz, 12H), 1.94−1.99 (m, 2H), 2.11 (d, J = 4.8 Hz, 4H), 7.44−7.46 (m, 2H), 7.53−7.56 (m, 1H), 8.05 (d, J = 5.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 22.4, 26.1, 43.1, 121.8, 130.8, 131.5, 134.8, 178.2. HRMS-ESI (m/z): calcd for $C_{16}H_{24}IO_4$ $[M + H]^+$: 407.0714, found 407.0716.

*Phenyl-λ^3-iodanediyl bis(2-methylpropanoate) (**2h**).* White solid, mp 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, J = 4.68 Hz, 12H), 2.45−2.49 (m, 2H), 7.44−7.46 (m, 2H), 7.54 (t, J = 5Hz, 1H), 8.02 (d, J = 5.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.5, 33.9, 121.9, 130.7, 131.4, 134.5, 182.1. HRMS-ESI (m/z): calcd for $C_{14}H_{20}IO_4$ $[M + H]^+$: 379.0401, found 379.0405.

*Phenyl-λ^3-iodanediyl bis(adamantane-1-carboxylate) (**2i**).* White solid, mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61−1.71 (m, 12H), 1.78 (s, 8H), 1.91 (d, J = 12.24 Hz, 8H), 2.01 (s, 2H), 7.45−7.47 (m, 2H), 7.52−7.54 (m, 1H), 7.99 (d, J = 5.48 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 27.8, 28.1, 36.4, 36.5, 38.6, 39.4, 121.9, 130.6, 131.1, 134.2, 182.6. HRMS-ESI (m/z): calcd for $C_{28}H_{36}IO_4$ $[M + H]^+$: 563.1653, found 563.1648.

*Phenyl-λ^3-iodanediyl dibenzoate (**2j**).* White solid, mp 152−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.37 (m, 4H), 7.47−7.49 (m, 2H), 7.51−7.55 (m, 2H), 7.60−7.62 (m, 1H), 7.93 (d, J = 5.44 Hz, 4H), 8.23(d, J = 5.52 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 128.2, 130.0, 131.0, 131.7, 132.5, 134.8, 171.3. HRMS-ESI (m/z): calcd for $C_{20}H_{16}IO_4$ $[M + H]^+$: 447.0088, found 447.0092.

General Procedure for the Hypervalent Iodine Reagent-Promoted Rearrangement/Carboxylation of Primary Amides. A mixture of amide (**1**) (0.2 mmol, 1.0 equiv) and (diacyloxyiodo)-arenes (**2**) (0.3 mmol, 1.5 equiv) was added into a vial containing a stirring bar. Then, DCE (2 mL) was introduced. The resulting mixture was stirred at 100 °C in an oil bath for 24 h. After the reaction, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After removal of the solvent in vacuo, the residue was purified by column chromatography (ethyl acetate/hexane = 1:5) to afford the pure product.

Gram Scale Experiment for the Synthesis of 3aa. A mixture of the benzamide (**1**) (1.21 g, 10 mmol), $PhI(OAc)_2$ (**2a**) (4.82 g, 15 mmol), and DCE (100 mL) was added into a round-bottom flask containing a stirring bar. The resulting mixture was stirred at 100 °C in an oil bath for 24 h. After the reaction, the mixture was added into 200 mL of H_2O. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (100 mL) three times. The combined organic layer was washed with H_2O and then dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residue was purified by column chromatography (ethyl acetate/hexane = 1:5) to afford **3aa** (1.14 g, 84%).

*Acetanilide (**3aa**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 107−109 °C, 83% yield (22.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 7.09 (t, J = 7.38 Hz, 1H), 7.27−7.31 (m, 2H), 7.50 (d, J = 7.84 Hz, 2H), 7.83 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3): δ 24.5, 120.0, 124.3, 128.9, 138.0, 168.8. HRMS-ESI (m/z): calcd for $C_8H_{10}NO$ $[M + H]^+$: 136.0757, found 136.0764.

*2,2,2-Trifluoro-N-phenylacetamide (**3ab**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), brown yellow solid, mp 78−80 °C, 77% yield (29.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.27 (m, 1H), 7.38−7.43 (m, 2H), 7.55−7.58 (m, 2H), 7.93 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 115.7 (q, J = 286.92 Hz), 120.6, 126.4, 129.4, 135.1, 154.9 (q, J = 37.04 Hz). HRMS-ESI (m/z): calcd for $C_8H_5F_3NO$ $[M - H]^-$: 188.0329, found 188.0327.

*2,2-Difluoro-N-phenylacetamide (**3ac**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 53−55 °C, 79% yield (27.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (t, J = 54.35 Hz, 1H), 7.21 (t, J = 7.44 Hz, 1H), 7.35−7.39 (m, 2H), 7.57 (d, J = 8.05 Hz, 2H), 7.99 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 108.5 (t, J = 252.39 Hz), 120.4, 125.9, 129.3, 135.6, 160.4 (t, J = 24.38 Hz). HRMS-ESI (m/z): calcd for $C_8H_6F_2NO$ $[M - H]^-$: 172.0423, found 172.0421.

*N-Phenylpropionamide (**3ad**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), white solid, mp 98−100 °C, 81% yield (24.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, J = 7.56 Hz, 3H), 2.37 (q, J = 15.12 Hz, J = 7.56 Hz, 2H), 7.08 (t, J = 7.38 Hz, 1H), 7.26−7.30 (m, 2H), 7.52 (d, J = 7.88 Hz, 2H), 7.87 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.8, 30.6, 120.1, 124.1, 128.9, 138.0, 172.6. HRMS-ESI (m/z): calcd for $C_9H_{12}NO$ $[M + H]^+$: 150.0913, found 150.0917.

*N-Phenyloctanamide (**3ae**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), yellow solid, mp 42−44 °C, 90% yield (39.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86−0.89 (m, 4H), 1.17−1.27 (m, 7H), 1.68−1.75 (m, 2H), 2.33−2.37 (m, 2H), 7.09 (t, J = 7.32 Hz, 1H), 7.28−7.32 (m, 2H), 7.48 (s, 1H), 7.52 (d, J = 7.88 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 25.7, 29.1, 29.2, 31.7, 37.8, 119.8, 124.1, 128.9, 138.0, 171.7. HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO$ $[M + H]^+$: 220.1696, found 220.1695.

*N,3-Diphenylpropanamide (**3af**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), brown yellow solid, mp 90−91 °C, 73% yield (32.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.61−2.65 (m, 2H), 3.01−3.04 (m, 2H), 7.08 (t, J = 7.36 Hz, 1H), 7.19−7.22 (m, 3H), 7.24−7.30 (m, 4H), 7.33 (s, 1H), 7.42 (d, J = 7.80 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 31.6, 39.4, 120.1, 124.3, 126.4, 128.4, 128.6, 128.9, 137.8, 140.6, 170.6. HRMS-ESI (m/z): calcd for $C_{15}H_{16}NO$ $[M + H]^+$: 226.1226, found 226.1229.

*3-Methyl-N-phenylbutanamide (**3ag**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), brown red solid, mp 89−92 °C, 65% yield (23.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (d, J = 5.48 Hz, 6H), 1.25 (s, 1H), 2.21 (s, 2H), 7.08−7.11 (m, 1H), 7.29−7.32 (m, 2H), 7.36−7.40 (m, 1H), 7.52 (d, J = 7.80 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 22.5, 26.3, 47.4, 119.9, 124.2, 129.0, 137.97, 171.0. HRMS-ESI (m/z): calcd for $C_{11}H_{16}NO$ $[M + H]^+$: 178.1226, found 178.1227.

*N-Phenylisobutyramide (**3ah**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), brown yellow solid, mp 77−79 °C, 55% yield (17.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (d, J = 6.88 Hz, 6H), 2.46−2.57 (m, 1H), 7.09 (t, J = 7.40 Hz, 1H), 7.28−7.32 (m, 2H), 7.43 (s, 1H), 7.53 (d, J = 7.80 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.6, 36.6, 119.9, 124.1, 128.9, 138.1, 175.5. HRMS-ESI (m/z): calcd for $C_{10}H_{14}NO$ $[M + H]^+$: 164.1070, found 164.1076.

*N-Phenyladamantane-1-carboxamide (**3ai**).* Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 154−156 °C, 60% yield (30.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72−1.80 (m, 6H), 1.91 (d, J = 2.76 Hz, 1H), 1.96 (d, J = 2.56 Hz, 5H), 2.09 (s, 3H), 7.08 (t, J = 7.40 Hz, 1H), 7.30 (t, J = 7.90 Hz, 2H), 7.38 (s, 1H), 7.54 (d, J = 7.63 Hz, 2H); $^{13}C\{^1H\}$ NMR (100

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J. Org. Chem. 2021, 86, 2820−2826

MHz, $CDCl_3$): δ 28.1, 36.4, 39.3, 41.5, 119.9, 124.1, 128.9, 138.0, 176.1. HRMS-ESI (*m*/*z*): calcd for $C_{17}H_{22}NO$ $[M + H]^+$: 256.1696, found 256.1700.

*N-Phenylbenzamide (**3aj**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), brown solid, mp 91−94 °C, 45% yield (17.7 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.42 Hz, 1H), 7.37 (t, *J* = 7.91 Hz, 2H), 7.47 (t, *J* = 7.45 Hz, 2H), 7.53−7.57 (m, 1H), 7.65 (d, *J* = 7.82 Hz, 2H), 7.85−7.87 (m, 2H), 7.91 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 120.3, 124.6, 127.0, 128.8, 129.1, 131.8, 135.0, 138.0, 165.8. HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{12}NO$ $[M + H]^+$: 198.0913, found 198.0907.

*N-(4-Methoxyphenyl)acetamide (**3ba**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 120−122 °C, 78% yield (25.7 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 3.78 (s, 3H), 6.83−6.87 (m, 2H), 7.27 (s, 1H), 7.37−7.41 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.3, 55.5, 114.1, 122.0, 131.0, 156.5, 168.3. HRMS-ESI (*m*/*z*): calcd for $C_9H_{12}NO_2$ $[M + H]^+$: 166.0863, found 166.0866.

*N-(3-Methoxyphenyl)acetamide (**3ca**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), red oil, 65% yield (21.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 3.37 (s, 3H), 6.65 (dd, *J* = 8.20 Hz, *J* = 1.92 Hz, 1H), 6.98 (d, *J* = 7.40 Hz, 1H), 7.19 (t, *J* = 8.12 Hz, 1H), 7.27 (s, 1H), 7.71 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.6, 55.3, 105.8, 110.0, 112.1, 129.6, 139.2, 160.1, 168.7. HRMS-ESI (*m*/*z*): calcd for $C_9H_{12}NO_2$ $[M + H]^+$: 166.0863, found 166.0868.

*N-(2-Methoxyphenyl)acetamide (**3da**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), brown solid, 73% yield (24.1 mg), mp 75−77 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.87 (s, 3H), 6.87 (d, *J* = 7.92 Hz, 1H), 6.93−6.97 (m, 1H), 7.01−7.05 (m, 1H), 7.78 (s, 1H), 8.35 (d, *J* = 7.72 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.9, 55.6, 109.9, 119.8, 121.1, 123.6, 127.7, 147.7, 168.2. HRMS-ES (*m*/*z*): calcd for $C_9H_{12}NO_2$ $[M + H]^+$: 166.0863, found 166.0865.

*N-(p-Tolyl)acetamide (**3ea**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 131−133 °C, 86% yield (25.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.14 (s, 3H), 2.30 (s, 3H), 7.10 (d, *J* = 8.20 Hz, 2H), 7.37 (d, *J* = 8.48 Hz, 2H), 7.40−7.41 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 20.9, 24.5, 120.1, 129.5, 133.9, 135.4, 168.4. HRMS-ESI (*m*/*z*): calcd for $C_9H_{12}NO$ $[M + H]^+$: 150.0913, found 150.0918.

*N-(m-Tolyl)acetamide (**3fa**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), yellow oil, 70% yield (20.9 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 2.31 (s, 3H), 6.91 (d, *J* = 7.56 Hz, 1H), 7.16−7.20 (m, 1H), 7.26−7.35 (m, 2H), 7.55 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.5, 24.5, 117.1, 120.6, 125.1, 128.8, 137.9, 138.9, 168.6. HRMS-ESI (*m*/*z*): calcd for $C_9H_{12}NO$ $[M + H]^+$: 150.0913, found 150.0918.

*N-(3,4-Dimethylphenyl)acetamide (**3ga**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 84−86 °C, 74% yield (24.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.13 (s, 3H), 2.20 (d, *J* = 2.88 Hz, 6H), 7.04 (d, *J* = 8.04 Hz, 1H), 7.21 (d, *J* = 7.92 Hz, 1H), 7.27 (s, 1H), 7.59 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 19.2, 19.9, 24.4, 117.6, 121.5, 129.9, 132.6, 135.7, 137.1, 168.5. HRMS-ESI (*m*/*z*): calcd for $C_{10}H_{14}NO$ $[M + H]^+$: 164.1070, found 164.1076.

*N-(4-Fluorophenyl)acetamide (**3ha**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), brown red solid, mp 141−144 °C, 56% yield (17.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 6.97−7.01 (m, 2H), 7.45 (s, 2H), 7.59 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.4, 115.6 (d, *J* = 22.35 Hz), 121.8 (d, *J* = 7.82 Hz), 133.8 (d, *J* = 2.87 Hz), 159.4 (d, *J* = 241.96 Hz), 168.3. HRMS-ESI (*m*/*z*): calcd for C_8H_9FNO $[M + H]^+$: 154.0663, found 154.0665.

*N-(4-Chlorophenyl)acetamide (**3ia**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow solid, mp 156−157 °C, 52% yield (17.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H), 7.26−7.28 (m, 2H), 7.45 (d, *J* = 8.27 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.6, 121.1, 129.0, 129.3, 136.4, 168.4. HRMS-ESI (*m*/*z*): calcd for C_8H_9ClNO $[M + H]^+$: 170.0367, found 170.0372.

*N-(4-Bromophenyl)acetamide (**3ja**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), brown red solid, mp 147−150 °C, 45% yield (19.3 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H), 7.32 (s, 1H), 7.39−7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 116.9, 121.4, 132.0, 136.9, 168.3. HRMS-ESI (*m*/*z*): calcd for C_8H_7BrNO $[M - H]^-$: 211.9717, found 211.9715.

*N-(4-(Trifluoromethyl)phenyl)acetamide (**3ka**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), white solid, mp 147−149 °C, 58% yield (23.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3H), 7.56 (d, *J* = 8.56 Hz, 2H), 7.64 (d,*J* = 8.24 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.7, 119.4, 124.1 (q, *J* = 269.85 Hz), 125.9, 126.3 (q, *J* = 3.74 Hz), 140.9, 168.7. HRMS-ESI (*m*/*z*): calcd for $C_9H_9F_3NO$ $[M + H]^+$: 204.0631, found 204.0638.

*N-(Naphthalen-2-yl)acetamide (**3la**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), brown solid, mp 124−125 °C, 53% yield (19.6 mg); ^1H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 3H), 7.36−7.46 (m, 3H), 7.73−7.76 (m, 3H), 7.81 (s, 1H), 8.17 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.6, 116.7, 120.0, 125.0, 126.5, 127.5, 127.6, 128.7, 130.6, 133.8, 135.4, 168.8. HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{12}NO$ $[M + H]^+$: 186.0913, found 186.0907.

*N-(Pyridin-2-yl)acetamide (**3ma**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), yellow oil, 57% yield (15.5 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H), 7.03−7.06 (m, 1H), 7.70−7.74 (m, 1H), 8.23 (d, *J* = 8.44 Hz, 1H), 8.25−8.27 (m, 1H), 8.81 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.7, 114.2, 119.7, 138.6, 147.4, 151.6, 168.9. HRMS-ESI (*m*/*z*): calcd for $C_7H_9N_2O$ $[M + H]^+$: 137.0709, found 137.0707.

*N-(Thiophen-2-yl)acetamide (**3na**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), black solid, mp 133−135 °C, 51% yield (14.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 6.65 (dd, *J* = 3.68 Hz, *J* = 1.36 Hz, 1H), 6.82−6.85 (m, 1H), 6.88 (dd, *J* = 5.52 Hz, *J* = 1.00 Hz, 1H), 8.27 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 23.3, 111.9, 118.1, 123.9, 138.9, 166.8. HRMS-ESI (*m*/*z*): calcd for C_6H_8NOS $[M + H]^+$: 142.0321, found 142.0316.

*3-Phenyl-N-propylpropanamide (**3of**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow oil, 74% yield (28.3 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.42 Hz, 3H), 1.39−1.48 (m, 2H), 2.45−2.48 (m, 2H), 2.93−2.97 (m, 2H), 3.13−3.18 (m, 2H), 5.56 (s, 1H), 7.18−7.21 (m, 3H), 7.22−7.26 (m, 1H), 7.27−7.30 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 11.3, 22.7, 31.8, 38.5, 41.3, 126.2, 128.3, 128.5, 140.9, 172.4. HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{18}NO$ $[M + H]^+$: 192.1383, found 192.1391.

*N-Butyl-3-phenylpropanamide (**3pf**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow oil, 84% yield (34.4 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.28 Hz, 3H), 1.20−1.29 (m, 2H), 1.36−1.43 (m, 2H), 2.44−2.48 (m, 2H), 2.94−2.98 (m, 2H), 3.17−3.22 (m, 2H), 5.42 (s, 1H), 7.18−7.23 (m, 3H), 7.27−7.30 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.7, 20.0, 31.6, 31.8, 38.6, 39.3, 126.2, 128.4, 128.5, 140.9, 172.2. HRMS-ESI (*m*/*z*): calcd for $C_{13}H_{20}NO$ $[M + H]^+$: 206.1539, found 206.1544.

*N-Pentyl-3-phenylpropanamide (**3qf**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), light yellow oil, 87% yield (38.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.18 Hz, 3H), 1.17−1.24 (m, 2H), 1.26−1.31 (m, 2H), 1.37−1.45 (m, 2H), 2.44−2.48 (m, 2H), 2.94−2.98 (m, 2H), 3.16−3.21 (m, 2H), 5.40 (s, 1H), 7.18−7.21 (m, 3H), 7.27−7.30 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.3, 29.0, 19.2, 31.8, 38.6, 39.5, 126.3, 128.4, 128.5, 140.9, 172.1. HRMS-ESI (*m*/*z*): calcd for $C_{14}H_{22}NO$ $[M + H]^+$: 220.1696, found 220.1701.

*N-Heptadecyl-3-phenylpropanamide (**3rf**)*. Purification by column chromatography (ethyl acetate/hexane = 1:5), white solid, mp 56−58 °C, 71% yield (55.0 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 0.86−0.90 (m, 3H), 1.26−1.33 (m, 28H), 1.36−1.43 (m, 2H), 2.44−2.48 (m, 2H), 2.94−2.99 (m, 2H), 3.16−3.21 (m, 2H), 5.38 (s, 1H), 7.19−7.20 (m, 3H), 7.27−7.31 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz,

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J. Org. Chem. 2021, 86, 2820−2826

$CDCl_3$): δ 14.1, 22.7, 26.9, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 31.8, 31.9, 38.6, 39.6, 126.2, 128.4, 128.5, 140.9, 172.1. HRMS-ESI (*m*/*z*): calcd for $C_{26}H_{46}NO$ $[M + H]^+$: 388.3574, found 388.3557.

N-Cyclopropyl-3-phenylpropanamide (***3sf***). Purification by column chromatography (ethyl acetate/hexane = 1:5), white solid, mp 126−129 °C, 73% yield (27.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 0.37−0.41 (m, 2H), 0.69−0.73 (m, 2H), 2.40−2.43 (m, 2H), 2.62−2.67 (m, 1H), 2.94 (t, *J* = 7.66 Hz, 2H), 5.63 (s, 1H), 7.17−7.21 (m, 3H), 7.27−7.31 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 6.6, 22.5, 31.7, 38.3, 126.2, 128.4, 128.5, 140.9, 173.5. HRMS-ESI (*m*/*z*): calcd for $C_{12}H_{16}NO$ $[M + H]^+$: 190.1226, found 190.1232.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02767.

Optimization process data and copies of ^1H and $^{13}C\{^1H\}$ NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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