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Synthesis of *O*-Aroyl-*N*,*N*-dimethylhydroxylamines through Hypervalent Iodine-Mediated Amination of Carboxylic Acids with *N*,*N*-Dimethylformamide

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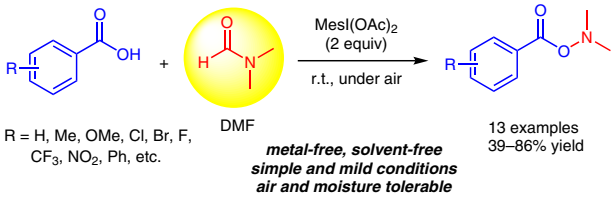

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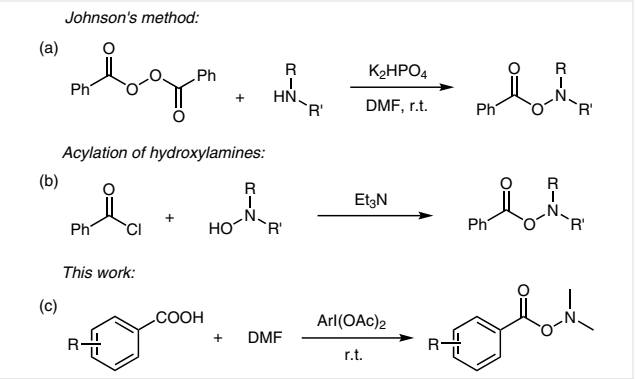
Abstract An efficient protocol for the synthesis of *O*-aroyl-*N*,*N*-dimethylhydroxylamines, which are important electrophilic amination reagents, is described. The reaction between carboxylic acids and *N*,*N*-dimethylformamide is mediated by hypervalent iodine and occurs under mild conditions at room temperature to give the desired products in good yields. The process shows good functional group compatibility and air and moisture tolerance.

Key words benzoyl hydroxylamine, hypervalent iodine, carboxylic acids, *N*,*N*-dimethylformamide, amination

Nitrogen-containing motifs are attractive functional groups because of their wide applications in biologically active compounds and functional materials, and due to their widespread occurrence in organic synthetic intermediates.[1] In recent years, many efforts have been expended on the development of procedures for C–N bond construction.[2] Among them, electrophilic amination has attracted significant attention, in which an electrophilic amination reagent was employed as the nitrogen source.[3] Some of the most widely used electrophilic amination reagents are the *O*-benzoyl hydroxylamines. Since Johnson and co-workers first reported a copper-catalyzed electrophilic amination of diorganozinc reagents with *O*-benzoyl hydroxylamines,[4] substantial efforts have been made toward the employment of such reagents for electrophilic aminations, especially in transition-metal-catalyzed C–N bond formation.[5]

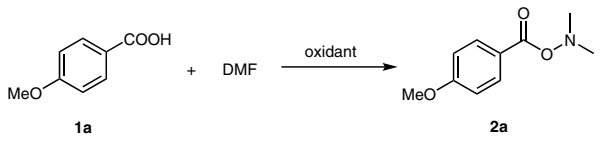
Therefore, the development of facile and efficient protocols for the synthesis of *O*-benzoyl hydroxylamines is also important. The most widely used method to prepare *O*-benzoyl hydroxylamines is via Johnson's method, in which amines are oxidized with benzoyl peroxide under basic conditions (Scheme 1, a).[6] This protocol allowed the preparation of a variety of *O*-benzoyl hydroxylamines from both primary and secondary amines, however, the employment of highly oxidative and explosive benzoyl peroxide has limited its practical application. An alternative route to *O*-benzoyl hydroxylamines involved acylation of hydroxylamine with benzoyl halides (Scheme 1, b).[4,7] However, most of the hydroxylamines and benzoyl halides were not readily available.



Scheme 1 Synthesis of *O*-aroyl hydroxylamines

In continuation of our recent studies on the development of efficient synthetic methodologies promoted by hypervalent iodine reagents,[8] herein we report the synthesis of *O*-aroyl-*N*,*N*-dimethylhydroxylamines through a hypervalent iodine-mediated reaction between cheap, stable and readily available carboxylic acids and *N*,*N*-dimethylformamide (DMF) (Scheme 1, c). The reaction proceeds under mild conditions at room temperature to give the desired products in good yields. It also shows good functional group compatibility and air and moisture tolerance.

Table 1 Optimization of the Reaction Conditions[a]



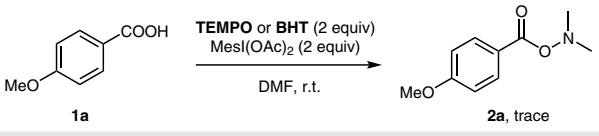
1a **2a**

Entry	Oxidant	T (°C)	Yield (%)[b]
1	PhIO	80	16
2	PhIO	60	16
3	PhIO	40	26
4	PhIO	25	39
5	I_2	25	NR
6	TBHP	25	NR
7	$NaIO_4$	25	NR
8	$K_2S_2O_8$	25	NR
9	$PhI(OAc)_2$	25	25
10	$PhI(OCOCF_3)_2$	25	5
11	$PhI(OPiv)_2$	25	48
12	*p*-Cl-C_6H_4-$I(OAc)_2$	25	26
13	*p*-Tol-$I(OAc)_2$	25	38
14	3,4-$(Me)_2$-C_6H_4-$I(OAc)_2$	25	38
15	*p*-MeO-C_6H_4-$I(OAc)_2$	25	5
16	$MesI(OAc)_2$	25	59
17[c]	**$MesI(OAc)_2$**	**25**	**70**

[a] Reaction conditions: **1a** (0.2 mmol), oxidant (2 equiv), DMF (2 mL), stirring under air, 24 h.
[b] Yield of isolated product. NR = no reaction.
[c] Reaction time = 48 h.

Our initial studies were focused on the amination of 4-methoxylbenzoic acid (**1a**) with DMF and the results are summarized in Table 1. The amination product **2a** was obtained in an isolated yield of 16% by employing two equivalents of iodosylbenzene as the oxidant at 80 °C (Table 1, entry 1). The product yield increased on reducing the reaction temperature and the best result was obtained at room temperature (25 °C) (Table 1, entries 2–4). The reaction demonstrated good air and moisture tolerance as it could be carried out under air with an undried solvent. Other oxidants were investigated, such as I_2, TBHP, $NaIO_4$ and $K_2S_2O_8$, which proved ineffective in this reaction (Table 1, entries 5–8). Subsequently, the effects of several other hypervalent iodine reagents, including $PhI(OAc)_2$, $PhI(OCOCF_3)_2$, $PhI(OPiv)_2$, 4-chlorophenyliodine diacetate, 4-methylphenyliodine diacetate, 3,4-dimethylphenyliodine diacetate, 4-methoxyphenyliodine diacetate, and mesityliodine diacetate were also examined (Table 1, entries 9–16). To our delight, the yield of isolated product **2a** was significantly increased to 59% when mesityliodine diacetate was used (Table 1, entry 16). The result was further improved by extending the reaction time to 48 hours, which provided the desired product in 70% yield (Table 1, entry 17). These conditions were therefore chosen as being optimum.[9]

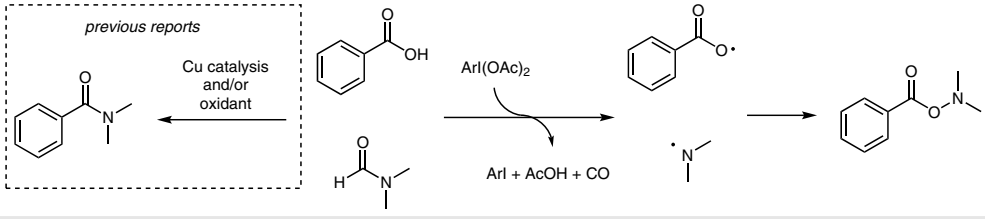
With optimized conditions in hand, the amination of an array of carboxylic acids was investigated as shown in Table 2. This method tolerated various functions groups such as OMe, F, Cl, Br, CF_3 and NO_2, giving the corresponding products in moderate to good yields. The electronic properties of the substituent did not show any significant effect on the product yields. Substrates possessing either electron-donating or electron-withdrawing groups provided high yields of the corresponding products (Table 2, entries 2–9). Among them, 4-chlorobenzoic acid gave the best result in this amination affording the desired product **2f** in 86% isolated yield (Table 2, entry 5). However, the reaction of 4-phenylbenzoic acid only gave a 39% yield of the desired product **2k** (Table 2, entry 10). Furthermore, this protocol was also applicable for heteroaryl and alkenyl substrates such as 2-thiophenic acid (**1l**) and cinnamic acid (**1m**). The corresponding products were obtained in 63% and 40% yields, respectively (Table 2, entries 11 and 12). However, the employment of alkyl carboxylic acids such as pivalic acid or phenylpropionic acid resulted in no reaction. In addition, a preliminary attempt applying other formamides was unsuccessful.



1a **2a**, trace

Scheme 2 Control experiments

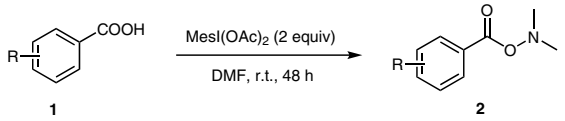
To investigate the reaction mechanism, several control experiments were carried out. The hypervalent iodine-mediated amination of **1a** with DMF in the presence of a radi-



Scheme 3 A plausible reaction mechanism

cal scavenger such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT) only generated a trace amount of the desired product (Scheme 2). It can be implied that the reaction probably proceeded through a radical mechanism. On the other hand, DMF is also known as an efficient building block in organic synthesis for providing various units including a dimethylamine group.[10] It can generate a dimethylamino radical under various oxidation conditions.[11]

Table 2 The Amination of Carboxylic Acids with DMF[a]



1 2

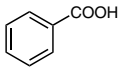
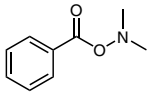
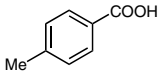
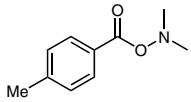
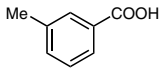
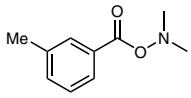
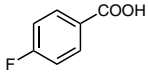
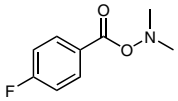
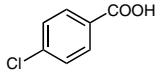
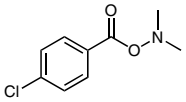
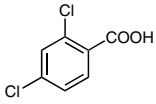
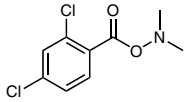
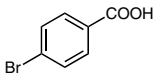
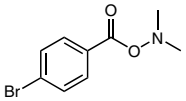
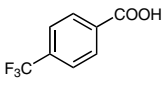
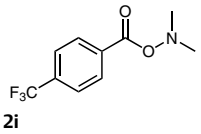
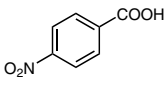
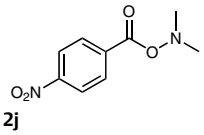
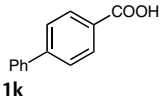
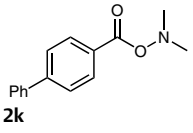
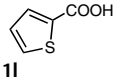
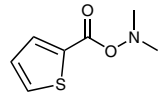
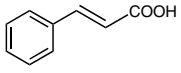
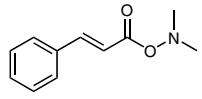
Entry	Carboxylic acid	Product	Yield (%)[b]
1	 **1b**	 **2b**	75
2	 **1c**	 **2c**	60
3	 **1d**	 **2d**	72
4	 **1e**	 **2e**	69
5	 **1f**	 **2f**	86
6	 **1g**	 **2g**	54
7	 **1h**	 **2h**	53

Table 2 (continued)

Entry	Carboxylic acid	Product	Yield (%)[b]
8	 **1i**	 **2i**	70
9	 **1j**	 **2j**	61
10	 **1k**	 **2k**	39
11	 **1l**	 **2l**	63
12	 **1m**	 **2m**	40

[a] Reaction conditions: **1** (0.2 mmol), $MesI(OAc)_2$ (2 equiv), DMF (2 mL), 25 °C, 48 h.
[b] Yield of isolated product.

Based on these results, a plausible mechanism is proposed in Scheme 3. First, a benzoyloxyl radical was generated by reaction of the oxidant $ArI(OAc)_2$ with benzoic acid.[12] Meanwhile, a dimethylamino radical was also generated accompanied with the elimination of CO. Finally, the benzoyloxyl radical coupled with the dimethylamino radical to provide the *O*-benzoyl-*N*,*N*-dimethylhydroxylamine product. Interestingly, it has also been reported that the reaction between carboxylic acids and DMF using copper catalysts and/or different oxidants could generate *N*,*N*-dimethylamides.[13] However, a different product was formed from identical substrates using our method.

In summary, we have developed an efficient method for the synthesis of *O*-aroyl *N*,*N*-dimethylhydroxylamines through a hypervalent iodine-mediated amination reaction. This protocol employed cheap, stable and readily available carboxylic acids and DMF as the substrates, showed good functional group tolerance, and gave the desired products in moderate to good yields. Notably, this synthetic procedure was carried out under metal-free conditions at room temperature, and showed good air and moisture tolerance. Furthermore, the procedure provides a novel and facile route to *O*-aroyl-*N*,*N*-dimethylhydroxylamines.

All carboxylic acids and other reagents were obtained from commercial sources and used as received. All the hypervalent iodine reagents are known compounds. All solvents were obtained from commercial sources and were typically used without further purification. Petroleum ether (PE) and EtOAc were used for column chromatography. TLC was performed using precoated silica gel GF254 (Qingdao Haiyang Chemcal Co. Ltd.) plates. Column chromatography was accomplished using silica gel (zcx-II, 200–300 mesh, Qingdao Haiyang Chemical Co. Ltd.). Melting points were measured using an SGW X-4A microscopic apparatus. IR spectra were recorded on a Nicolet IS50 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, respectively. ^{19}F NMR spectra were recorded at 376 MHz with $CDCl_3$ as the solvent and $CFCl_3$ as an internal standard. HRMS-ESI spectra were measured using a Q Exactive LC/HRMS spectrometer.

O-Aroyl-*N*,*N*-dimethylhydroxylamines 2; General Procedure

A mixture of $MesI(OAc)_2$ (145.6 mg, 0.4 mmol) and carboxylic acid **1** (0.2 mmol) was added to a vial containing DMF (2 mL). The resulting mixture was stirred at r.t. (25 °C) for 48 h. The progress of the reaction was monitored by TLC. Next, the mixture was extracted with EtOAc and washed with H_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc) to afford the pure product.

O-(4-Methoxybenzoyl)-*N*,*N*-dimethylhydroxylamine (2a)

Light yellow oil; yield: 27.2 mg (70%).

IR (KBr): 774, 844, 1684, 2853, 2922 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 6 H), 3.86 (s, 3 H), 6.92 (d, *J* = 8.84 Hz, 2 H), 7.97 (d, *J* = 8.88 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6, 55.5, 113.6, 121.6, 131.5, 163.4, 164.7.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{14}NO_3$: 196.0968; found: 196.0964.

O-Benzoyl-*N*,*N*-dimethylhydroxylamine (2b)[5n]

Light yellow oil; yield: 24.7 mg (75%).

IR (KBr): 717, 805, 1463, 2853, 2920 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (s, 6 H), 7.35–7.38 (m, 2 H), 7.47–7.51 (m, 1 H), 7.94 (d, *J* = 7.96 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.5, 126.2, 127.4, 128.4, 132.0, 163.9.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_9H_{12}NO_2$: 166.0863; found: 166.0859.

O-(4-Methylbenzoyl)-*N*,*N*-dimethylhydroxylamine (2c)

Light yellow oil; yield: 21.5 mg (60%).

IR (KBr): 750, 842, 1076, 1734, 2689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.89 (s, 6 H), 7.23 (d, *J* = 7.96 Hz, 2 H), 7.90 (d, *J* = 8.00 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 48.5, 126.5, 129.1, 129.5, 143.7, 165.1.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{14}NO_2$: 180.1019; found: 180.1014.

O-(3-Methylbenzoyl)-*N*,*N*-dimethylhydroxylamine (2d)

Light yellow oil; yield: 25.8 mg (72%).

IR (KBr): 742, 841, 1077, 1737, 2925 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 2.84 (s, 6 H), 7.19–7.25 (m, 1 H), 7.29–7.31 (m, 1 H), 7.72–7.75 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 47.5, 125.5, 127.3, 128.1, 128.9, 132.8, 137.2, 164.0.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{14}NO_2$: 180.1019; found: 180.1014.

O-(4-Fluorobenzoyl)-*N*,*N*-dimethylhydroxylamine (2e)

Light yellow oil; yield: 25.3 mg (69%).

IR (KBr): 612, 777, 853, 1665, 2925 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.91 (s, 6 H), 7.09–7.14 (m, 2 H), 8.01–8.05 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6, 115.6 (d, *J* = 21.87 Hz), 125.5 (d, *J* = 3.05 Hz), 132.0 (d, *J* = 9.23 Hz), 164.0, 165.8 (d, *J* = 252.7 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ = –105.34.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_9H_{11}FNO_2$: 184.0768; found: 184.0772.

O-(4-Chlorobenzoyl)-*N*,*N*-dimethylhydroxylamine (2f)

Light yellow oil; yield: 34.2 mg (86%).

IR (KBr): 756, 855, 1737, 2923, 3453 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (s, 6 H), 7.35 (d, *J* = 8.36 Hz, 2 H), 7.87 (d, *J* = 8.36 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6, 127.8, 128.8, 130.8, 131.5, 164.1.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_9H_{11}ClNO_2$: 200.0473; found: 200.0468.

O-(2,4-Dichlorobenzoyl)-*N*,*N*-dimethylhydroxylamine (2g)

Light yellow oil; yield: 25.2 mg (54%).

IR (KBr): 781, 847, 1585, 2922, 3417 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85 (s, 6 H), 7.23 (d, *J* = 8.40 Hz, 1 H), 7.40 (s, 1 H), 7.60 (d, *J* = 8.36 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6, 127.1, 128.2, 130.8, 132.0, 134.3, 138.2, 163.8.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_9H_{10}Cl_2NO_2$: 234.0083; found: 234.0086.

O-(4-Bromobenzoyl)-*N*,*N*-dimethylhydroxylamine (2h)

Light yellow solid; yield: 25.8 mg (53%); mp 143–145 °C.

IR (KBr): 755, 848, 926, 1681, 2919, 3417 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90 (s, 6 H), 7.58 (d, *J* = 8.32 Hz, 2 H), 7.87 (d, *J* = 8.36 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6, 127.2, 128.2, 130.9, 131.8, 164.3.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_9H_{11}BrNO_2$: 243.9968; found: 243.9964.

O-(4-Trifluoromethylbenzoyl)-*N*,*N*-dimethylhydroxylamine (2i)

Light yellow oil; yield: 32.6 mg (70%).

IR (KBr): 704, 861, 1698, 2925 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.93 (s, 6 H), 7.71 (d, *J* = 8.16 Hz, 2 H), 8.13 (d, *J* = 8.20 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6, 125.4 (q, *J* = 3.74 Hz), 129.9, 130.1, 132.6, 134.7, 163.8.

^{19}F NMR (377 MHz, $CDCl_3$): δ = –63.06.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{11}F_3NO_2$: 234.0736; found: 234.0740.

***O*-(4-Nitrobenzoyl)-*N*,*N*-dimethylhydroxylamine (2j)**

Light yellow solid; yield: 25.6 mg (61%); mp 92–94 °C.

IR (KBr): 719, 806, 1345, 2920, 3416 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 6 H), 8.11 (d, *J* = 8.48 Hz, 2 H), 8.22 (d, *J* = 8.40 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.7, 122.5, 129.6, 133.7, 149.6, 162.1.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_9H_{11}N_2O_4$: 211.0713; found: 211.0708.

***O*-(1,1′-Biphenyl-4-carbonyl)-*N*,*N*-dimethylhydroxylamine (2k)**

Light yellow solid; yield: 18.8 mg (39%); mp 63–65 °C.

IR (KBr): 750, 864, 936, 1707, 2927 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85 (s, 6 H), 7.30–7.34 (m, 1 H), 7.38–7.41 m, 2 H), 7.53–7.60 (m, 4 H), 7.99–8.01 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.6, 126.0, 126.2, 127.0, 127.2, 127.9, 128.9, 138.9, 144.8, 163.8.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{16}NO_2$: 242.1176; found: 242.1171.

***O*-(Thiophene-2-carbonyl)-*N*,*N*-dimethylhydroxylamine (2l)**

Light yellow oil; yield: 21.5 mg (63%).

IR (KBr): 633, 730, 1735, 2853, 2921 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.82 (s, 6 H), 7.03–7.05 (m, 1 H), 7.50 (d, *J* = 4.92 Hz, 1 H), 7.75 (d, *J* = 3.68 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.7, 127.7, 132.1, 132.5, 133.6, 160.8.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_7H_{10}NO_2S$: 172.0427; found: 172.0425.

***O*-Cinnamoyl-*N*,*N*-dimethylhydroxylamine (2m)**

Light yellow oil; yield: 15.3 mg (40%).

IR (KBr): 867, 1194, 1708, 2859, 2925 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.78 (s, 6 H), 6.32 (d, *J* = 16.04 Hz, 1 H), 7.31–7.33 (m, 3 H), 7.44–7.46 (m, 2 H), 7.67 (d, *J* = 16.04 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.5, 115.1, 127.0, 129.3, 133.3, 144.2, 144.4, 164.6.

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{14}NO_2$: 192.1019; found: 192.1015.

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Supporting Information

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