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Cobalt(II)-Catalyzed Isocyanide Insertion Reaction with Sulfonyl Azides in Alcohols: Synthesis of Sulfonyl Isoureas

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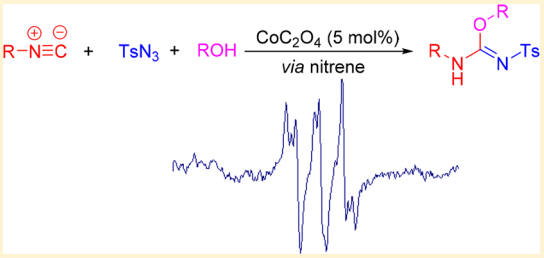
Supporting Information

ABSTRACT: A Co(II)-catalyzed isocyanide insertion reaction with sulfonyl azides in alcohols to form sulfonyl isoureas via nitrene intermediate has been developed. This protocol provides a new, environmentally friendly, and simple strategy for the synthesis of sulfonyl isourea derivatives by employing a range of substrates under mild conditions.



INTRODUCTION

Isourea moiety is present in various agrochemicals, pharmacologically active substances, and starting material for the synthesis of other important molecules.[1−4] For example, Isourea salt **I** is an important starting material for the synthesis of fluorouracil antitumor drugs, imidazole and herbicides.[1] Trimeturon **II** is useful against hard-to-kill weeds developed by Bayer.[2] Isoureas **III** and **IV** are the intermediates for the synthesis of herbicide dinotefuran and natural product (+)-batzelladine B, respectively.[3] Isoureas **V** are useful polymerization initiators (Figure 1).[4] The main

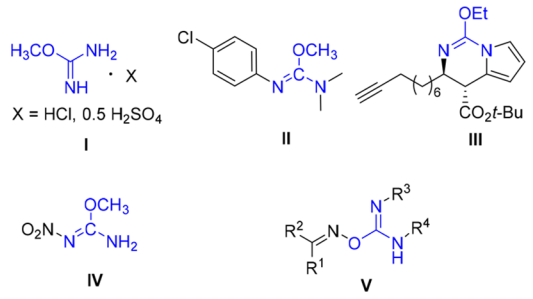
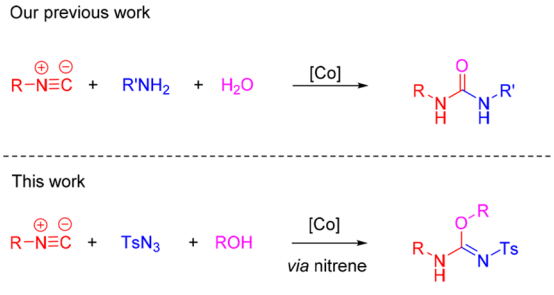


Figure 1. Isourea-based bioactive molecules.

strategy to isourea compounds is based on the reaction of carbodiimide with alcohols with limited reaction scope.[5] However, only few symmetrical carbodiimides are commercial available. The reported methods suffer from limited substrates, longer reaction time, toxic reagents, poor atom economy, and expensive catalysts, which limit their further applications. Therefore, the development of an efficient protocol to construct isoureas directly under transition metal-free and mild conditions is more desirable.

Recently, organic azides have been widely used for the C−N bond formation[6] catalyzed by Rh,[7] Ru,[8] Fe,[9] Ir,[10] etc. During the past decades, Prof. Zhang's group made a great contributions to cobalt-catalyzed nitrene chemistry utilizing porphyrin as ligands.[11] However, to the best of our knowledge, there is no report about the cobalt-catalyzed reactions of organic azides with isocyanides and alcohols via nitrene intermediate. As important and powerful C1 synthons, isocyanide-based multicomponent reactions (IMCRs) have attracted sustainable attention for the synthesis of guanidines, thiourea derivatives and other *N*-heterocycles.[12] Recently, we developed a Co-catalyzed isocyanide insertion reaction with amines and water to construct ureas (Scheme 1).[13] As a continuation on isocyanide-based multicomponent reactions (IMCRs),[14] herein, we reported a novel cobalt-catalyzed isocyanide insertion reaction with organic azides in alcohols to form sulfonyl isoureas via nitrene intermediate under mild conditions.

Scheme 1. Cobalt-Catalyzed Isocyanide Insertion To Construct Ureas and Isoureas



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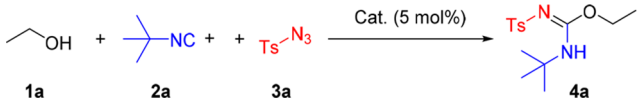
RESULTS AND DISCUSSION

Initially, we tried the reaction of *t*-BuNC (**2a**) and tosyl azide (**3a**) in ethanol (**1a**) catalyzed by CoC_2O_4 (5 mol%) at 80 °C for 8 h. To our delight, the desired product (**4a**) could be isolated in 90% yield. (Table 1, entry 1). Next, we

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a 4a

entry	catalyst (mol%)	solvent	time (h)	*T* (°C)	yield[b] (%)
1	CoC_2O_4 (5)	EtOH	8	80	90
2	$Co(acac)_2$ (5)	EtOH	8	80	72
3	$Cp^*Co(CO)I_2$ (5)	EtOH	8	80	trace
4	$Co(OAc)_2{\cdot}4H_2O$ (5)	EtOH	8	80	77
5	$CoCl_2{\cdot}6H_2O$ (5)	EtOH	8	80	78
6	$Pd(OAc)_2$ (5)	EtOH	8	80	trace
7	$Cu(OAc)_2$ (5)	EtOH	8	80	trace
8	$PdCl_2$ (5)	EtOH	8	80	trace
9	CoC_2O_4 (1)	EtOH	8	80	69
10	CoC_2O_4 (10)	EtOH	8	80	90
11	CoC_2O_4 (15)	EtOH	8	80	90
12	$CoC2O_4$ (20)	EtOH	8	80	90
13	CoC_2O_4 (5)	EtOH	8	20	trace
14	CoC_2O_4 (5)	EtOH	8	40	80 (80[d])
15	CoC_2O_4 (5)	EtOH	8	60	83 (83[d])
16	CoC_2O_4 (5)	EtOH	2	80	82
17	CoC_2O_4 (5)	EtOH	4	80	90
18	CoC_2O_4 (5)	EtOH	6	80	90
19[c]	CoC_2O_4 (5)	CH_3CN	4	80	50

[a]Reaction conditions: **1a** (2 mL), **2a** (0.6 mmol), **3a** (0.5 mmol), catalyst (5 mol%) under air atmosphere. [b]Isolated yield. [c]1.2 equiv of EtOH was used. [d]Reaction time: 12 h.

investigated the reaction utilizing different catalysts (Table 1, entry 1−12). The reaction failed to give the desired product **4a** when copper or palladium salts were employed (Table 1, entries 6−8). Comparing with the cobalt(III) salt, cobalt(II) catalysts showed unique activities for the transformation to form **4a** (Table 1, entries 1−5). Further screening of reaction time and temperature (Table 1, entries 13−18) showed that **4a** could be observed in the highest 90% yield just after 4 h at 80 °C (Table 1, entry 17). It should be noted that the reaction could also lead to **4a** in 50% yield when stoichiometric ethanol was used using acetonitrile as the solvent (Table 1, entry 19).

With the optimized reaction conditions in hand (Table 1, entry 17), we turned to investigate the scope of various isocyanides (Scheme 2). Most of the reactions proceeded smoothly to afford the desired isourea products in moderate to excellent yields. The reaction of tosyl azide **3a** with adamantanyl isocyanide and cyclohexyl isocyanide performed well under the optimal conditions and led to the desired product **4b** and **4c** in 93% and 97% yields, respectively. Unfortunately, only trace amount of product could be detected when *n*-butylisocyanide was applied in this reaction, perharps due to the decomposion of isocyanide under standard conditions. The reactions of tosyl azide **3a** and ethanol **1a** with substituted aryl isocyanides bearing electron-withdrawing groups, such as cyano, nitro, ester, and trifluoromethyl groups could furnish the desired products in 39−90% yields. Besides, the aryl isocyanides bearing electron-donating groups also gave the desired isoureas in moderate to excellent results (57−99% yield). In addition, when isocyanides with substituted halogens were employed, the desired products **4i** and **4m** could be isolated in 97% and 76% yields, respectively.

To further explore the diversity of products, we next investigated the scope of alcohols (Scheme 3). The reactions of **2a** with **3a** in methanol and propanol proceeded smoothly to furnish the desired isoureas **5a** and **5b** in 77% and 72% yields, respectively. Unfortunately, benzyl alcohol and bulky alcohols, such as isopropanol, 2-butyl alcohol, and isobutyl alcohol, failed to afford the desired isoureas, perhaps due to the steric hindrance. It should be noted that the reactions of **2a** with **3a** in ethylene glycol could lead to **5d** in 98% yield. We also tried the reaction of **2a** with **3a** in water, which could not led to the corresponding urea under the optimized conditions.

Then, we investigated the scope of organo azides **3** (Scheme 4). A variety of sulfonyl azides bearing different functional groups were tested. Various kinds of substituents, such as H, OMe, F, Cl, Br, and I, were well tolerated under the optimal conditions. The 4-acetamidobenzenesulfonyl azide and naphthalene-2-sulfonyl azide gave the products **6g** and **6h** in 95% and 94% yields, respectively. Besides, *n*-butylsulfonyl azide and 3-pyridinesulfonyl azide also exhibited good reactivities in this transformation, delivering the target products **6j** and **6i** in 57% and 99% yields, respectively.

To investigate the Co intermediate species in the reaction, several electron paramagnetic resonance (EPR) experiments were also carried out and the results are summarized in Figure 2. It was found that the mixture of CoC_2O_4 in EtOH, the mixture of CoC_2O_4 and *p*-toluenesulfonyl azide **3a** in EtOH and the mixture of CoC_2O_4 and isocyanide **2a** in EtOH all failed to give EPR signals. It should be noted that a triplet EPR signal was obtained (g = 1.8942) from the mixture of CoC_2O_4, isocyanide **2a** and *p*-toluenesulfonyl azide **3a** in EtOH. This result indicates that the in situ generated cobalt nitrene species from the mixture of CoC_2O_4, isocyanide and *p*-toluenesulfonyl azide in EtOH might be involved in the reaction.

Based on the above results and literature reports,[10] a plausible mechanism is described in Scheme 5. The fast ligand exchange of CoC_2O_4 with isocyanides gives cobalt complex **A**. Complex **A** reacts with sulfonyl azide in ethanol to give complex **B**. The dissociation of N_2 from **B** affords Co(III)−nitrene intermediate **C**. Following the coupling reaction of **C** with the coordinated isocyanide ligand to afford intermediate **E**. In the path a, the reaction of the intermediate **E** with isocyanide **2** affords the carbodiimide intermediate **F** and regenerates the Co catalyst **A**. Subsequently, the addition of ethanol to carbodiimide intermediate **F** to furnish isourea **4**. In the path b, the addition of EtOH to **E** leads to intermediate **G**. Then, the intermediate **G** reacts with **2** via ligand exchange to furnish isourea **4** and regenerates the Co-catalyst **A**.

CONCLUSION

In summary, we have developed a Co(II)-catalyzed synthesis of sulfonyl isoureas by the reactions of sulfonyl azides with isocyanides in alcohols via nitrene intermediate. This protocol provides a new, environmentally friendly, and simple strategy for effective synthesis of sulfonyl isourea derivatives with a

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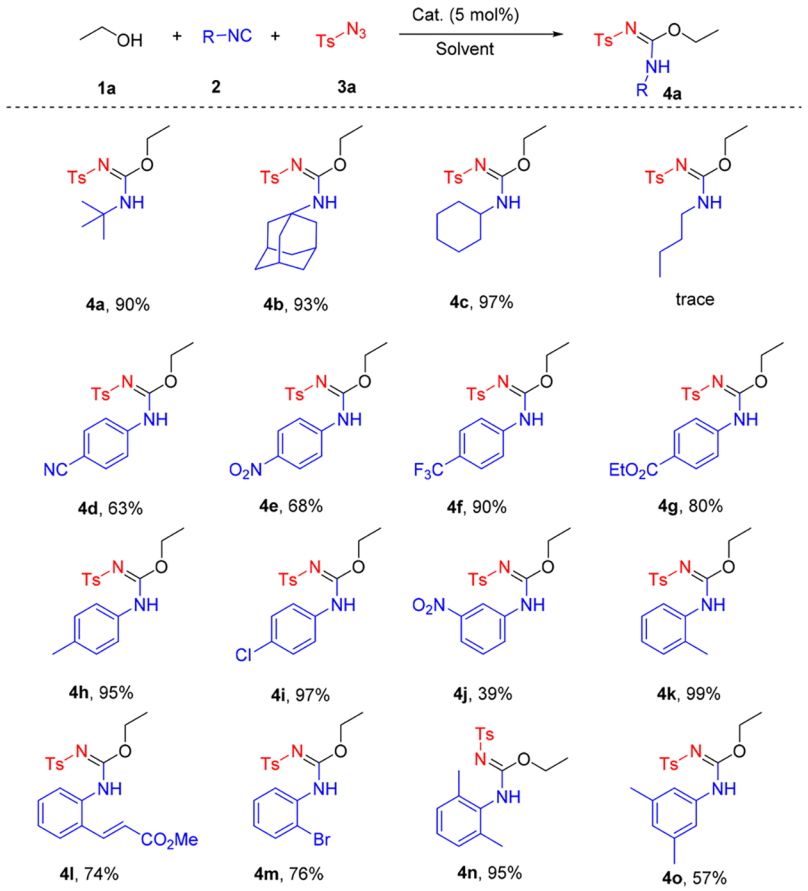
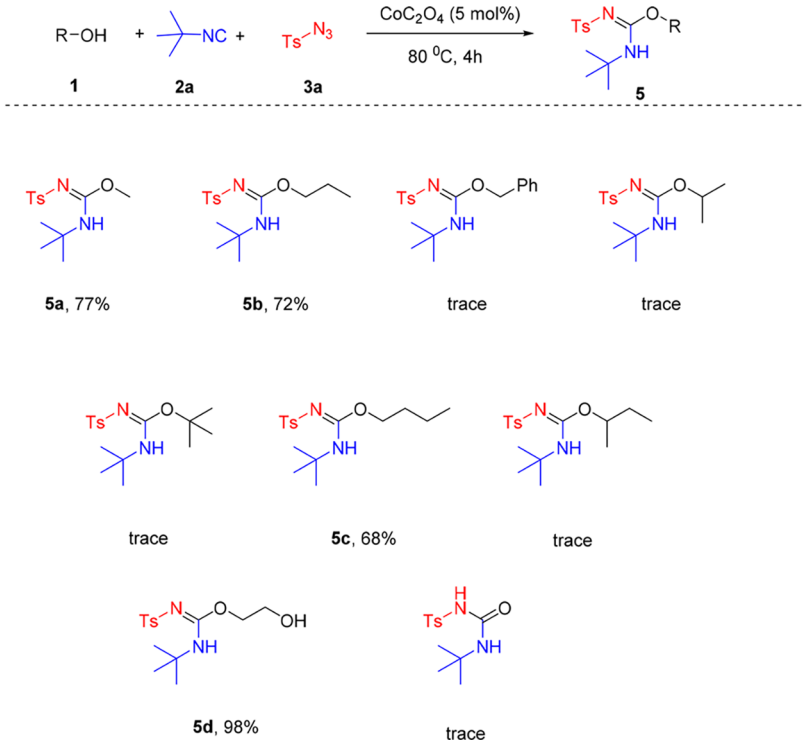
Scheme 2. Substrate Scope of Iscyanides 2[a,b]



[a]Reaction conditions: **1** (2 mL), **2** (0.6 mmol), **3a** (0.5 mmol), CoC_2O_4 (5 mol%), at 80 °C, 4 h under air atmosphere. [b]Isolated yield.

Scheme 3. Substrate Scope of the Alcohols 1 and Water[a,b]



[a]Reaction conditions: **1** (2 mL), **2a** (0.6 mmol), **3a** (0.5 mmol), CoC_2O_4 (5 mol%) at 80 °C, 4 h under air atmosphere. [b]Isolated yield.

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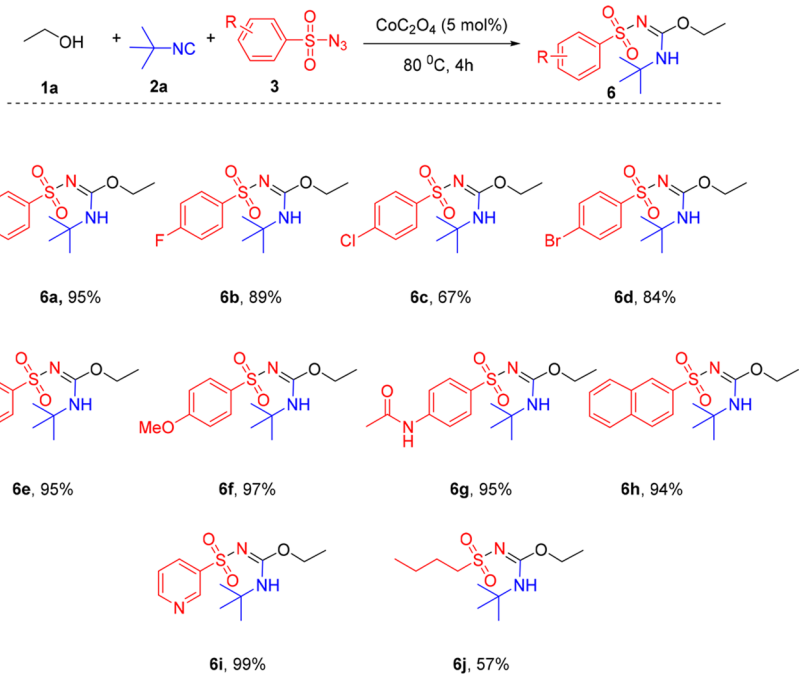
Scheme 4. Substrate Scope of the Sulfonyl Azides 3[a,b]



[a]Reaction Conditions: **1a** (2 mL), **2a** (0.6 mmol), **3** (0.5 mmol), CoC_2O_4 (5 mol%) at 80 °C, 4 h under air atmosphere. [b]Isolated yield.

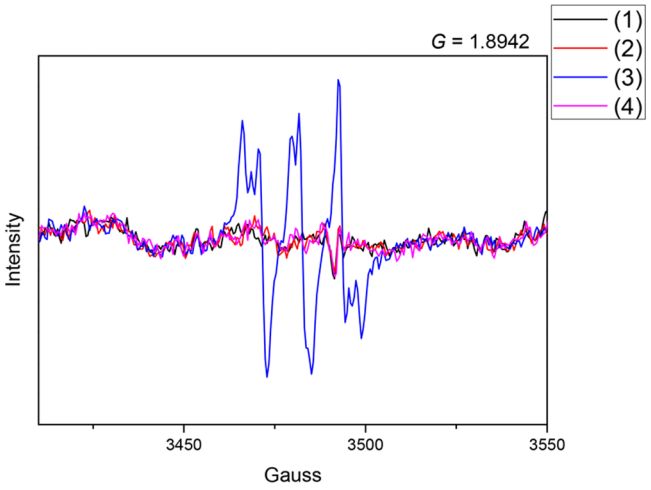


Figure 2. EPR spectrum studies: (1) CoC_2O_4 (0.5 mmol) in EtOH (2 mL) at 298 K. (2) Ts-N_3 **3a** (0.5 mmol), CoC_2O_4 (0.5 mmol) in EtOH (2 mL) at 298 K. (3) ^{t}Bu-NC 2a (0.5 mmol), Ts-N_3 **3a** (0.5 mmol), CoC_2O_4 (0.5 mmol) in EtOH (2 mL) at 298 K. (4) ^{t}Bu-NC **2a** (0.5 mmol), CoC_2O_4 (0.5 mmol) in EtOH (2 mL) at 298 K.

range of substrates. Further investigations of the Co(II)-catalyzed isocyanides insertion reactions involving nitrene intermediate are currently under study in our laboratory.

EXPERIMENTAL SECTION

General Experimental Information. Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 300−400 mesh silica gel was used. ^{1}H NMR and ^{13}C NMR were recorded on a BRUKER 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) or DMSO-d_6 residual peak (δ 2.50) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16) or DMSO-d_6 (δ 39.52). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Melting points were measured on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER micrOTOF-Q III instrument with ESI source.

General Procedure for the Construction of 4a. In a 15 mL reaction tube, *tert*-butyl isocyanide **2a** (0.6 mmol, 1.2 equiv) and tosyl azide **3a** (0.5 mmol, 1.0 equiv) were dissolved in 2.5 mL alcohol. The system was stirred in an oil bath at 80 °C under air. After 4 h, it was removed from the oil bath. The reaction mixture was charged with silica gel and concentrated. The residue was purified by silica gel column chromatography (eluent: PE/EtOAc = 4/1) to obtain the desired product **4a** as a pale white solid.

*Ethyl (E)-N-(tert-Butyl)-N′-tosylcarbamimidate (**4a**).* White solid (134 mg, 90%), m.p.: 85.3−86.9 °C. IR 3323, 2978, 1603, 1334, 1301, 1122, 1072 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (d, J = 8.3 Hz, 2H), 7.40 (s, 1H), 7.24 (d, J = 8.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.30 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-d) δ 157.3, 141.9, 139.7, 128.7, 125.5, 64.0, 52.1, 29.0, 21.0, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{22}N_2O_3SNa$, $[M+Na]^+$ 321.1249; found 321.1247.

*Ethyl (E)-N-((3s,5s,7s)-Adamantan-1-yl)-N′-tosylcarbamimidate (**4b**).* White solid (175 mg, 93%), m.p.: 96.8−98.2 °C. IR 3309, 2905, 1605, 1508, 1486, 1385, 1332 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79−7.72 (m, 2H), 7.30 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.10−2.05 (m, 3H), 1.90 (d, J = 2.9 Hz, 6H), 1.65 (dd, J = 8.5, 4.5 Hz, 6H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 141.3, 128.2, 125.0, 63.3, 52.3, 41.0, 35.1, 28.4, 20.5, 13.2 ppm. HRMS (ESI) m/z calculated for $C_{20}H_{28}N_2O_3SNa$, $[M+Na]^+$ 399.1718; found 399.1722.

*Ethyl (E)-N-Cyclohexyl-N′-tosylcarbamimidate (**4c**).* White solid (157 mg, 97%), m.p.: 74.8−75.9 °C. IR 3316, 2910, 1592, 1472,

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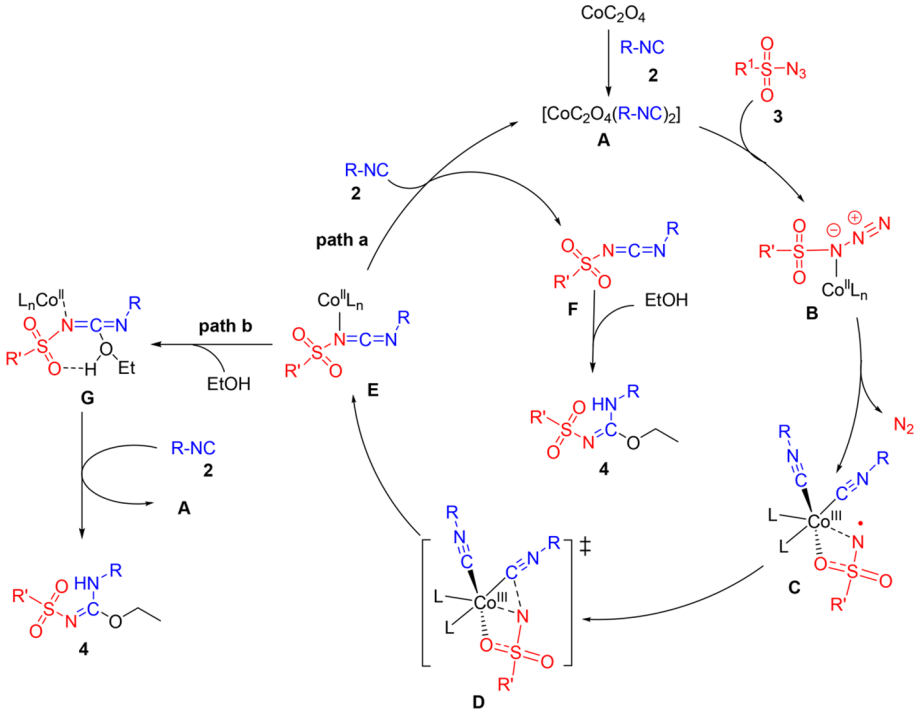
Scheme 5. Plausible Reaction Mechanism



1410, 1276, 1182, 1079, 1062 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.7 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.83 (d, J = 12.1 Hz, 2H), 1.73−1.67 (m, 2H), 1.56 (d, J = 12.1 Hz, 1H), 1.36−1.20 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 141.9, 128.7, 125.5, 64.0, 50.0, 32.4, 24.8, 23.9, 21.0, 13.8 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{24}N_2O_3SNa$, $[M+Na]^+$ 347.1405; found 347.1402.

Ethyl (E)-N-(4-Cyanophenyl)-N′-tosylcarbamimidate (***4d***). Yellow solid (113 mg, 63%), m.p.: 142.8−143.6. °C. IR 2988, 2225, 1624, 1600, 1376, 1099, 1018 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.66 (s, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.32 (dd, J = 18.2, 8.4 Hz, 4H), 4.39 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 142.9, 139.5, 132.8, 129.0, 125.7, 121.3, 117.9, 107.9, 65.6, 21.1, 13.6 ppm. HRMS (ESI) m/z calculated for $C_{17}H_{17}N_3O_3SNa$, $[M+Na]^+$ 366.0888; found 366.0880.

Ethyl (E)-N-(4-Nitrophenyl)-N′-tosylcarbamimidate (***4e***). Yellow solid (124 mg, 68%), m.p.: 134.0−134.6 °C. IR 2987, 1630, 1590, 1336, 1139, 1097 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.21 (d, J = 9.2 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 9.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.8, 143.0, 141.2, 129.1, 125.8, 124.6, 120.8, 65.7, 21.1, 13.6 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{17}N_3O_5SNa$, $[M+Na]^+$ 386.0787; found 386.0795.

Ethyl (E)-N′-Tosyl-N-(4-(trifluoromethyl)phenyl)carbamimidate (***4f***). Brown solid (175 mg, 90%), m.p.: 98.7−100.5 °C. IR 2987, 1613, 1351, 1138, 1099 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.57 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.32 (dd, J = 17.8, 8.3 Hz, 4H), 4.39 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 142.7, 138.9, 138.5, 129.0, 126.7, 125.9,125.7, 123.4, 121.4, 65.3, 21.0, 13.5 ppm. ^{19}F NMR (376 MHz, Chloroform-*d*) δ −62.3 ppm. HRMS (ESI) m/z calculated for $C_{17}H_{17}F_3N_2O_3SNa$, $[M+Na]^+$ 409.0810; found 409.0812.

Ethyl (E)-4-((Ethoxy(tosylimino)methyl)amino)benzoate (***4g***). Brown solid (157 mg, 80%), m.p.: 83.5−85.0 °C. IR 2982, 1606, 1573, 1281, 1142, 1130, 1067 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.58 (s, 1H), 8.01 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.33−7.27 (m, 4H), 4.37 (p, J = 7.1 Hz, 4H), 2.41 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 142.7, 139.4, 130.3, 129.0, 126.6, 125.7, 120.7, 65.3, 60. 6, 21.1, 13.9, 13. Six ppm. HRMS (ESI) m/z calculated for $C_{19}H_{22}N_2O_5SNa$, $[M+Na]^+$ 413.1147; found 413.1142.

Ethyl (E)-N-(p-Tolyl)-N′-tosylcarbamimidate (***4h***). Yellow solid (158 mg, 95%), m.p.: 120.9−122.1 °C. IR 3308, 2992, 1578, 1518, 1393, 1309, 1235 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.14−7.04 (m, 3H), 4.25 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 2.14 (s, 6H), 1.12 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 142.3, 135.0, 132.5, 128.9, 127.7, 127.3, 125.8, 64.4, 21.0, 17.7, 13.8 ppm. HRMS (ESI) m/z calculated for $C_{17}H_{20}N_2O_3SNa$, $[M+Na]^+$ 355.1092; found 355.1090.

Ethyl (E)-N-(4-Chlorophenyl)-N′-tosylcarbamimidate (***4i***). Yellow solid (171 mg, 97%), m.p.: 119.6−122.5 °C. IR 3293, 1595, 1440, 1272, 1069 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.83 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 8.3 Hz, 4H), 7.15 (d, J = 8.2 Hz, 2H), 4.34 (q, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.27 (t, J = 6.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 1545.0, 142. 6, 139.1, 133.9, 129.0, 128.7, 125.7, 123.4, 65.0, 21.1, 13.6 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{17}ClN_2O_3SNa$, $[M+Na]^+$ 375.0546; found 375.0562.

Ethyl (E)-N-(3-Nitrophenyl)-N′-tosylcarbamimidate (***4j***). Yellow solid (71 mg, 39%), m.p.: 46.4−48.4 °C. IR 2988, 1528, 1340, 1300, 1237, 1100, 1067, 1021 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.62 (s, 1H), 8.20 (s, 1H), 8.02 (d, J = 6.6 Hz, 1H), 7.88−7.81 (m, 2H), 7.51 (d, J = 6.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 54.5, 148.2, 142.9, 138.7, 136.6, 129.5, 129.0, 127.2, 125.7, 119.5, 116.6, 65.6, 29.2, 21.1, 13.5 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{17}N_3O_5SNa$, $[M+Na]^+$ 386.0787; found 386.0784.

Ethyl (E)-N-(o-Tolyl)-N′-tosylcarbamimidate (***4k***). White solid (165 mg, 99%), m.p.: 75.0−77.2 °C. IR 3319, 1599, 1573, 1283, 1100, 1069, 1019 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 7.86 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.26−7.12 (m, 4H), 4.31 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 2.26 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 142.4, 139.4, 133.7, 131.6, 130.3, 128.9, 126.1, 126.1, 125.7,

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J. Org. Chem. 2017, 82, 7913−7919

124.6, 64.7, 21.0, 17.5, 13.6 ppm. HRMS (ESI) m/z calculated for $C_{17}H_{20}N_2O_3SNa$, $[M+Na]^+$ 355.1092; found 355.1090.

*Methyl (E)-3-(2-((((E)-Ethoxy(tosylimino)methyl)amino)phenyl)-acrylate (**4l**).* White solid (149 mg, 74%), m.p.: 113.6−115.0 °C. IR 3303, 2984, 1715, 1591, 1469, 1275, 1188, 1169, 1142, 1015, 1004 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.26 (s, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 16.0 Hz, 1H), 7.61 (dd, J = 7.8, 1.6 Hz, 1H), 7.42−7.28 (m, 5H), 6.43 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.45 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.2, 155.7, 142.5, 139.1, 138.7, 133.9, 130.1, 123.0, 129.0, 127.0, 126.8, 126.6, 125.8, 120.3, 64.8, 51.4, 21.1, 13.5 ppm. HRMS (ESI) m/z calculated for $C_{20}H_{22}N_2O_5SNa$, $[M+Na]^+$ 425.1147; found 425.1155.

*Ethyl (E)-N-(2-Bromophenyl)-N′-tosylcarbamimidate (**4m**).* Brown solid (152 mg, 76%), m.p.: 93.7−94.9 °C. IR 2987, 1943, 1565, 1507, 1474 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.57 (dd, J = 8.1, 1.5 Hz, 1H), 7.43 (dd, J = 8.2, 1.5 Hz, 1H), 7.28 (s, 1H), 7.05 (td, J = 7.7, 1.6 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.0, 142.5, 139.1, 134.0, 132.5, 128.9, 127.5, 126.7, 125.9, 125.2, 117.3, 65.0, 21.1, 13.6 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{17}BrN_2O_3SNa$, $[M+Na]^+$ 419.0041; found 419.0039.

*Ethyl (E)-N-(2,6-Dimethylphenyl)-N′-tosylcarbamimidate (**4n**).* White solid (171 mg, 99%), m.p.: 120.9−122.1 °C. IR 3302, 2988, 1699, 1172, 1087, 1066 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 7.88 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.14−7.04 (m, 3H), 4.25 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 2.14 (s, 6H), 1.12 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.6, 142.3, 135.0, 132.5, 128.9, 127.7, 127.3, 125.8, 64.4, 21.0, 17.7, 13.8 ppm. HRMS (ESI) m/z calculated for $C_{18}H_{22}N_2O_3SNa$, $[M+Na]^+$ 369.1249; found 369.1251.

*Ethyl (E)-N-(3,5-Dimethylphenyl)-N′-tosylcarbamimidate (**4o**).* Yellow solid (99 mg, 57%), m.p.: 120.9−122.1 °C. IR 3295, 2989, 1625, 1589, 1143, 1077, 1036 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.25 (s, 1H), 7.84 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 6.84 (s, 3H), 4.34 (q, J = 7.0, 6.4 Hz, 2H), 2.42 (s, 3H), 2.30 (s, 6H), 1.28 (t, J = 6.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.4, 139.4, 138.3, 135.1, 128.9, 126.9, 125.7, 119.9, 64.8, 21.0, 20.8, 13.6 ppm. HRMS (ESI) m/z calculated for $C_{18}H_{22}N_2O_3SNa$, $[M+Na]^+$ 369.1249; found 369.1251.

*Methyl (E)-N-(tert-Butyl)-N′-tosylcarbamimidate (**5a**).* White solid (109 mg, 77%), m.p.: 71.9−73.1 °C. IR 3323, 2969, 1604, 1490, 1364, 1278, 1141, 1116, 1076 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78−7.70 (m, 2H), 7.39 (s, 1H), 7.25−7.20 (m, 2H), 3.77 (s, 3H), 2.36 (s, 3H), 1.27 (s, 9H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 142.0, 139.6, 128.7, 125.5, 54.6, 52.2, 28.9, 21.0 ppm. HRMS (ESI) m/z calculated for $C_{13}H_{20}N_2O_3SNa$, $[M+Na]^+$ 307.1092; found 307.1094.

*Propyl (E)-N-(tert-Butyl)-N′-tosylcarbamimidate (**5b**).* White solid (112 mg, 72%), m.p.: 56.2−57.3 °C. IR 3330, 2970, 1600, 1333, 1268, 1122, 1075 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77−7.72 (m, 2H), 7.40 (s, 1H), 7.25−7.21 (m, 2H), 4.15 (t, J = 6.6 Hz, 2H), 2.37 (s, 3H), 1.69−1.61 (m, 2H), 1.30 (s, 9H), 0.92 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 141.9, 139.7, 128.7, 125.5, 69.7, 52.1, 29.0, 21.4, 21.0, 10.1 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{24}N_2O_3SNa$, $[M+Na]^+$ 335.1405; found 335.1404.

*Butyl (E)-N-(tert-Butyl)-N′-tosylcarbamimidate (**5c**).* White solid (145 mg, 88%), m.p.: 129.6−131.3 °C. IR 3513, 3336, 2972, 1598, 1335, 1073 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.2 Hz, 2H), 7.42 (s, 1H), 7.25 (d, J = 7.6 Hz, 2H), 4.21 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H), 1.65−1.59 (m, 2H), 1.39−1.33 (m, 2H), 1.31 (s, 9H), 0.90 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 141.9, 139.8, 128.7, 125.5, 67.9, 52.1, 30.1, 29.0, 21.0, 18.7, 13.2 ppm. HRMS (ESI) m/z calculated for $C_{16}H_{26}N_2O_3SNa$, $[M+Na]^+$ 349.1562; found 349.1559.

*2-Hydroxyethyl (E)-N-(tert-Butyl)-N′-tosylcarbamimidate (**5d**).* White solid (154 mg, 98%), m.p.: 72.3−74.2 °C. IR 3340, 2965, 1594, 1240, 1135, 1076 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78−7.73 (m, 2H), 7.47 (s, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 4.37−4.33 (m, 2H), 3.83−3.79 (m, 2H), 2.40 (d, J = 2.0 Hz, 3H), 1.36−1.33 (m, 9H), 1.31 (d, J = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 142.2, 139.3, 128.8, 125.5, 69.3, 60.7, 52.5, 29.0, 21.0 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{22}N_2O_4SNa$, $[M+Na]^+$ 337.1198; found 337.1197.

*Ethyl (E)-N-(tert-Butyl)-N′-(phenylsulfonyl)carbamimidate (**6a**).* Yellow oil (135 mg, 95%). IR 3345, 2987, 1596, 1280, 1208, 1106, 1021 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, J = 6.9 Hz, 2H), 7.43 (td, J = 14.9, 14.3, 7.3 Hz, 4H), 4.24 (dd, J = 7.1, 2.1 Hz, 2H), 1.29−1.26 (m, 9H), 1.24−1.18 (m, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 142.5, 131.4, 128.1, 125.4, 64.0, 52.2, 28.9, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{13}H_{20}N_2O_3SNa$, $[M+Na]^+$ 307.1092; found 307.1097.

*Ethyl (E)-N-(tert-Butyl)-N′-((4-fluorophenyl)sulfonyl)-carbamimidate (**6b**).* White solid (135 mg, 89%), m.p.: 46.4−48.4 °C. IR 3315, 2979, 1598, 1491, 1338, 1278, 1138, 1070 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92−7.81 (m, 2H), 7.36 (s, 1H), 7.10 (t, J = 8.6 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 1.32−1.27 (m, 9H), 1.23 (d, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 157.3, 138.8, 128.1, 115.2, 64.1, 52.3, 28.9, 13.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.1 ppm. HRMS (ESI) m/z calculated for $C_{13}H_{19}FN_2O_3SNa$, $[M+Na]^+$ 325.0998; found 325.1006.

*Ethyl (E)-N-(tert-Butyl)-N′-((4-chlorophenyl)sulfonyl)-carbamimidate (**6c**).* White solid (106 mg, 67%), m.p.: 64.5−64.7 °C. IR 3690, 3320, 2978, 1597, 1368, 1335, 1072 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.84−7.79 (m, 2H), 7.45−7.41 (m, 2H), 7.40 (s, 1H), 4.26 (qd, J = 7.1, 1.6 Hz, 2H), 1.32 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.3, 141.1, 137.6, 128.4, 127.0, 64.2, 52.3, 28.9, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{13}H_{19}ClN_2O_3SNa$, $[M+Na]^+$ 341.0703; found 341.0704.

*Ethyl (E)-N′-((4-Bromophenyl)sulfonyl)-N-(tert-butyl)-carbamimidate (**6d**).* White solid (152 mg, 84%), m.p.: 92.7−94.5 °C. IR 3676, 3334, 2976, 1596, 1340, 1140, 1073 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71−7.66 (m, 2H), 7.56−7.51 (m, 2H), 7.34 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.26 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.3, 141.7, 131.4, 127.1, 126.0, 64.2, 52.3, 28.9, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{13}H_{20}BrN_2O_3S$, $[M+H]^+$ 363.0378; found 363.0386.

*Ethyl (E)-N-(tert-Butyl)-N′-((4-iodophenyl)sulfonyl)-carbamimidate (**6e**).* White solid (195 mg, 95%), m.p.: 112.6−114.5 °C. IR 3340, 2971, 1593, 1403, 1382, 1339, 1106 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.40 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.32 (s, 9H), 1.27 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.3, 142.3, 137.3, 127.1, 98.3, 64.2, 52.3, 29.0, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{13}H_{19}IN_2O_3SNa$, $[M+Na]^+$ 433.0059; found 433.0056.

*Ethyl (E)-N-(tert-Butyl)-N′-((4-methoxyphenyl)sulfonyl)-carbamimidate (**6f**).* White solid (153 mg, 97%), m.p.: 77.0−78.8 °C. IR 3312, 2976, 1595, 1344, 1258, 1113, 1094, 1021 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.9 Hz, 2H), 7.37 (s, 1H), 6.91 (d, J = 8.9 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 1.30 (s, 9H), 1.25 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.7, 157.2, 134.6, 127.5, 113.2, 63.9, 55.0, 52.1, 29.0, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{14}H_{23}N_2O_4S$, $[M+H]^+$ 315.1379; found 315.1381.

*Ethyl (E)-N′-((4-Acetamidophenyl)sulfonyl)-N-(tert-butyl)-carbamimidate (**6g**).* White solid (162 mg, 95%), m.p.: 146.8−148.2 °C. IR 3676, 3324, 2975, 1589, 1316, 1140, 1075 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.62 (s, 1H), 7.79 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.37 (s, 1H), 4.28 (q, J = 7.0 Hz, 2H), 2.20 (s, 3H), 1.33 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.9, 157.4, 141.4, 136.8, 126.4, 118.7, 64.2, 52.3, 28.9, 24.0, 13.7 ppm. HRMS (ESI) m/z calculated for $C_{15}H_{23}N_3O_4SNa$, $[M+Na]^+$ 364.1299; found 364.1307.

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*Ethyl (E)-N-(tert-Butyl)-N′-(naphthalen-2-ylsulfonyl)-carbamimidate (**6h**).* Yellow oil (157 mg, 94%). IR 3326, 2974, 1600, 1337, 1102, 1067 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.92−7.81 (m, 4H), 7.58−7.47 (m, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.28 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 139.4, 134.0, 131.5, 128.6, 128.5, 127.8, 127.3, 126.8, 125.9, 121.7, 64.1, 52.2, 29.1, 28.9, 13.7 ppm. HRMS (ESI) *m*/*z* calculated for $C_{17}H_{22}N_2O_3SNa$, $[M+Na]^+$ 357.1249; found 357.1240.

*Ethyl (E)-N-(tert-Butyl)-N′-(pyridin-3-ylsulfonyl)carbamimidate (**6i**).* Yellow oil (141 mg, 99%). IR 3332, 2978, 1599, 1403, 1337, 1288, 1082 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.01 (d, *J* = 2.2 Hz, 1H), 8.66 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 8.0, 4.9 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.25 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 151.9, 146.4, 138.9, 133.2, 122.9, 64.4, 52.4, 28.8, 13.6 ppm. HRMS (ESI) *m*/*z* calculated for $C_{12}H_{20}N_3O_3S$, $[M+H]^+$ 286.1225; found 286.1225.

*Ethyl (E)-N-(tert-Butyl)-N′-(butylsulfonyl)carbamimidate (**6j**).* Yellow oil (76 mg, 57%). IR 3309, 2965, 1610, 1338, 1267, 1091 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 (s, 1H), 4.25 (q, *J* = 6.7, 6.2 Hz, 2H), 3.00−2.94 (m, 2H), 1.76 (p, *J* = 7.5 Hz, 2H), 1.44−1.37 (m, 2H), 1.30 (s, 12H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.3, 63.7, 53.9, 52.0, 28.9, 25.2, 21.0, 13.7, 13.1 ppm. HRMS (ESI) *m*/*z* calculated for $C_{11}H_{24}N_2O_3SNa$, $[M+Na]^+$ 287.1405; found 287.1405.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01127.

The copies of ^1H and ^{13}C NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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