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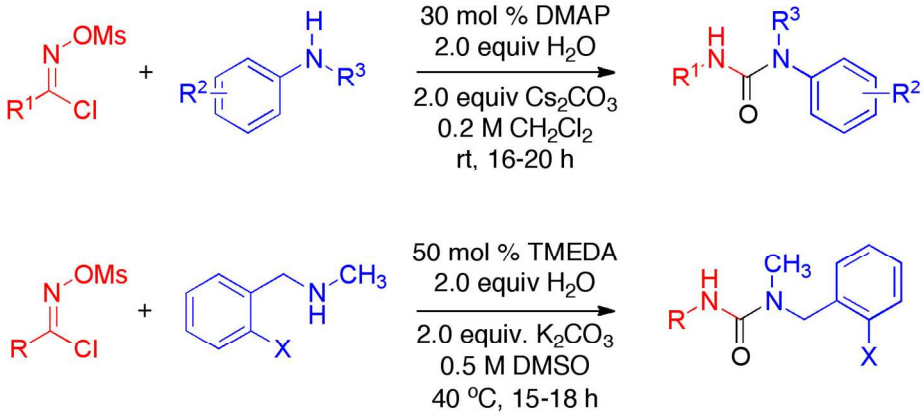

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Journal Name

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One-Pot Synthesis of Trisubstituted Ureas from α-Chloroaldoxime O-methanesulfonates and Secondary Amines

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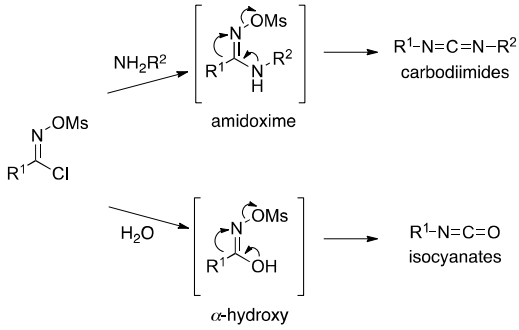
Trisubstituted ureas can be synthesized in one-pot fashion from bench-stable α-chloroaldoxime *O*-methanesulfonates and secondary amines under mild reaction conditions. Two practical protocols have been developed to achieve various urea syntheses from both secondary aromatic amines and aliphatic amines.

Introduction

Trisubstituted and disubstituted urea moieties comprise one of the most important groups in organic molecules due to their biological activities and important components in drug candidates.[1] Furthermore, ureas have been used as organic catalysts[2] and have many applications in material sciences.[3] Typically, urea derivatives have been efficiently synthesized via the condensation of amines with the corresponding isocyanates or from the reaction of amines and phosgene.[4] Due to the limited number of commercially available isocyanates and the toxicities of the phosgene, alternative environmental friendly methodologies to construct the urea core structures have been explored. One of the most attractive methods in symmetrical and asymmetrical urea synthesis was the reaction of carbamic acid derivatives,[5] which are particularly stable under a variety of reaction conditions and inert toward nucleophilic reagents such as, amines. Furthermore, several methodologies have been developed to obtain a variety of isocyanates[6] for asymmetric urea syntheses: the Curtius rearrangement,[7] Hoffmann rearrangement[8] and Lossen rearrangement.[9] However, some of those methodologies required the use of strong bases and metals. Alternatively, we have been inspired by the work of Yamamoto and co-workers in the chemistry of α-chloroaldoxime *O*-methanesulfonates[10] in which this molecule could undergo Tiemann rearrangement[11] to provide versatile carbodiimide intermediates[12] in the presence of primary amines (Scheme 1). Furthermore, this compound was found to be stable and stored at ambient temperature without any precautions. We envisioned that α-chloroaldoxime *O*-methanesulfonates could alternatively generate isocyanates via the rearrangement in the presence of water, allowing us to introduce other amines to achieve asymmetrical ureas. Herein, we reported a straightforward approach in the synthesis of trisubstituted ureas from α-chloroaldoxime *O*-methanesulfonates and secondary amines via one-pot reaction involving *in situ* generation of the postulated isocyanates under mild reaction condition.

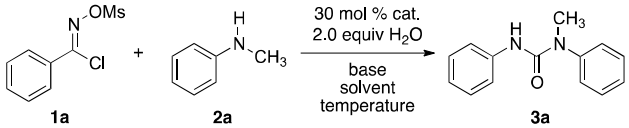
Scheme 1. Rearrangement of α-chloroaldoxime *O*-methanesulfonates



Results and discussion

Our investigation initially began with the optimization of the reaction conditions. The reaction of α-chloroaldoxime *O*-methanesulfonate **1a** and *N*-methylaniline was selected as a model study (Table 1).

Table 1. The optimization reaction of α-chloroaldoxime *O*-methanesulfonate (**1a**) and *N*-methylaniline[a]



entry	cat.	bases	solvent	temp.	yield[b]
1	DMAP	Cs_2CO_3	CH_2Cl_2	rt	86

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† Electronic Supplementary Information (ESI) available: [This material includes ^1H and ^{13}C NMR spectra for all of new compounds]. See DOI: 10.1039/x0xx00000x

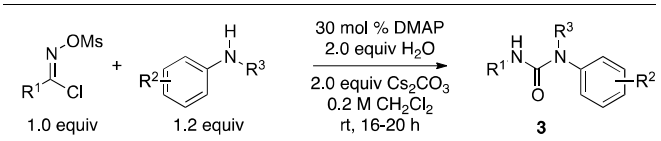
2	DABCO	Cs_2CO_3	CH_2Cl_2	rt	21
3	Imidazole	Cs_2CO_3	CH_2Cl_2	rt	trace[c]
4	-	Cs_2CO_3	CH_2Cl_2	rt	trace[c]
5	DMAP	K_2CO_3	CH_2Cl_2	rt	60
6	DMAP	K_3PO_4	CH_2Cl_2	rt	43
7	DMAP	NEt_3	CH_2Cl_2	rt	13
8	DMAP	-	CH_2Cl_2	rt	trace[c]
9	DMAP	Cs_2CO_3	THF	rt	47
10	DMAP	Cs_2CO_3	DMSO	rt	20
11	DMAP	Cs_2CO_3	CH_2Cl_2	40 °C	58

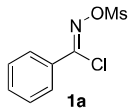
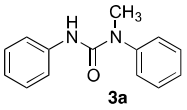
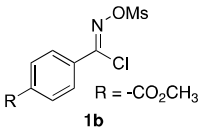
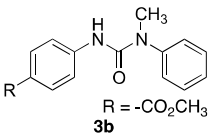
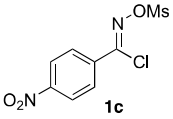
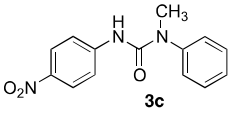
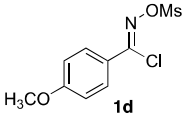
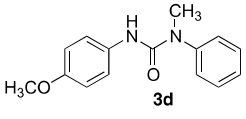
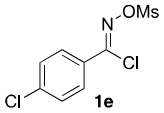
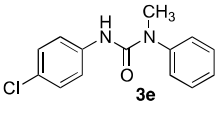
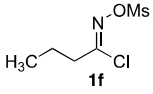
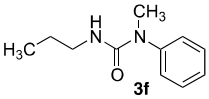
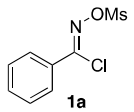
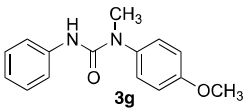
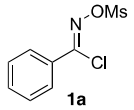
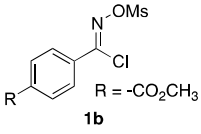
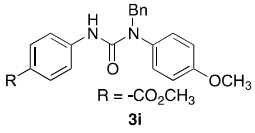
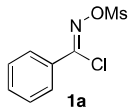
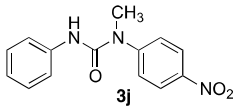
[a]Reaction conditions: all reactions were performed with 0.5 mmol of **1a**, 1.5 equiv. of **2a**, 2.0 equiv. of base and 2.5 mL of solvent, for 15–18 h. [b]Isolated yield. [c]From ^{1}H NMR spectrum of the crude reaction mixture.

The loading amount of DMAP also was investigated. The 30 mol % of DMAP was vital in our reaction to drive the reaction to completion, and the reaction gave 86% of desired urea. Other common nucleophilic catalysts such as DABCO and imidazole were subjected to the reaction conditions. The reaction with DABCO as the catalyst gave 21% yield (entry 2). On the other hand, imidazole gave only trace amount of urea product (entry 3). The control experiment with no catalyst was also performed. As we expected, with no catalyst the reaction gave trace amount of urea (entry 4). The reaction was carried out with a variety of bases. In this transformation Cs_2CO_3 gave the highest product yield (entries 1, 5 and 6). We initially believed that the solubility of the inorganic base in organic solvent played an important role in the reaction. But with amine base, the reaction also gave urea in low yield (entry 7). Note that, the presence of base was crucial in our reaction, the reaction without base gave trace amount of desired urea (entry 8). We then turned our attention to the effect of solvent polarity (entries 9 and 10). THF and DMSO were subjected to the optimization. Both gave lower product yields, especially DMSO, despite that **1a** was completely consumed. The result suggested that undesired side-reaction was pronounced in high polar solvent. Elevation of reaction temperature also triggered undesired reaction pathways, reaching 58% yield from 100% conversion of the reactant (entry 11).

After having established optimal reaction conditions, we next explored the scope of substrates in our urea formations. Unsubstituted aryl α-chloroaldoxime *O*-methanesulfonates gave good yield of urea with *N*-methyl anilines (entry 1). The aryl groups bearing electron-withdrawing substituents gave high yields (entries 2 and 3). In contrast, the aryl group bearing electron-donating substituent showed no reactivity in our urea transformation (entry 4). Based on these results we believed that the electrophilicity of chloroaldoxime motif played an important role in our reaction.

Table 2. The formation of ureas from α-chloroaldoxime *O*-methanesulfonates and aniline derivatives[a]



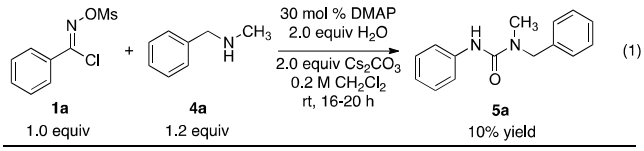
entry	chloroaldoximes	Ureas	yield[b]
1	 1a	 3a	86
2	 1b	 3b	95
3	 1c	 3c	92
4	 1d	 3d	NR[c]
5	 1e	 3e	74
6	 1f	 3f	47
7	 1a	 3g	72
8	 1a	 3h	61
9	 1b	 3i	72
10	 1a	 3j	NR[c]

[a]Reaction conditions: all reactions were performed with 0.5 mmol of α-chloroaldoxime *O*-methanesulfonates. [b]Isolated yield. [c]No reaction.

However, *para*-chloro phenyl group of α-chloroaldoxime *O*-methanesuldonate gave the corresponding urea product in

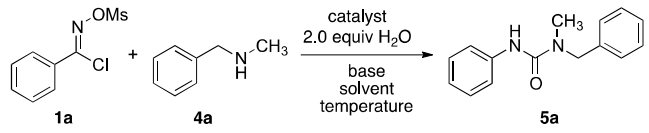
good yield (entry 5), suggesting that the electronic effect of halogen substituents was favourable in our reaction. Simple alkyl substituent of α-chloroaldoxime *O*-methanesulfonate was also applicable in our urea transformation with moderate yield (entry 6). While aniline group bearing electron-donating moiety gave good yield too (entry 7). *N*-benzyl aniline groups (entries 8 and 9) were applicable in our ureas formation with good yields. In addition, *N*-Methyl *para*-nitro aniline group gave no desired product (entry 10). This result suggested that the nucleophilicity of nitrogen atom of aniline was also crucial in our reaction.

In order to expand our substrate scopes, we next turned our attention to saturated alkyl secondary amines by investigating a reaction of **1a** and *N*-methyl benzylamine with our optimal conditions (1).



Surprisingly, the reaction gave the desired urea in very low yield albeit the amine being more nucleophilic than that of aniline derivatives. Moreover, ^{1}H NMR spectrum of the crude reaction mixture showed that **1a** was completely consumed. The result suggested that the higher nucleophilicity of amines might result in undesired reaction pathways and give unidentified side-products. According to the study of Yamamoto and co-workers, one of the possible ways was the formation of guanidine structures when more equivalence of amines was applied.[10b] We subsequently switched the ratio of the starting materials in which the amine was now used as a limiting reagent. As expected the product yield increased to 38%. The result gave us a clue that the reaction with saturated alkyl secondary amines can potentially be improved. Therefore, we further optimized reaction conditions by using the α-chloroaldoxime methanesulfonate **1a** and *N*-methylbenzylamine as a reaction model (Table 3).

Table 3. The optimization reaction of α-chloroaldoxime *O*-methanesuldonate (**1a**) and *N*-methybenzylamine[a]



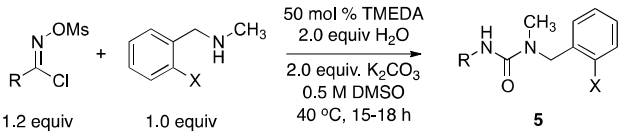
entry	cat.	bases	solvent	temp.	yield[b]
1	DMAP	Cs_2CO_3	0.2M CH_2Cl_2	rt	38
2	DMAP	K_2CO_3	0.2M CH_2Cl_2	rt	37
3	DMAP	K_2CO_3	0.5M CH_2Cl_2	rt	41
4	DMAP	K_2CO_3	0.5M THF	rt	40
5	DMAP	K_2CO_3	0.5M DMSO	rt	41
6	DMAP	K_2CO_3	0.5M DMSO	40 °C	69
7	DMAP	K_2CO_3	0.5M THF	40 °C	58
8	TMEDA	K_2CO_3	0.5M DMSO	40 °C	74
9	-	K_2CO_3	0.5M DMSO	40 °C	65

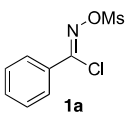
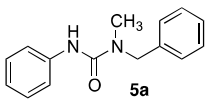
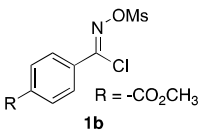
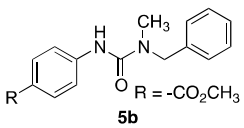
[a]Reaction conditions: all reactions were performed with 0.5 mmol of *N*-methylbenzylamine, 1.2 equiv. of 1, 2.0 equiv. of base and 50 mol % of catalyst for 15−18 h . [b]Isolated yield.

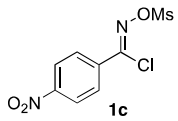
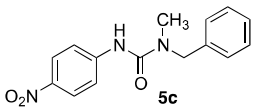
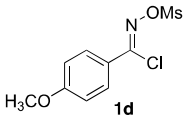
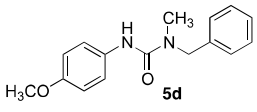
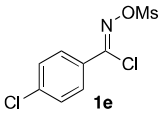
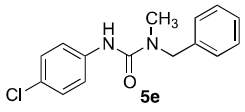
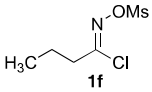
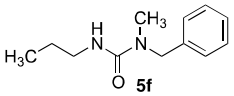
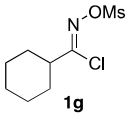
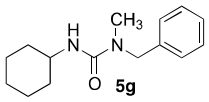
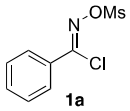
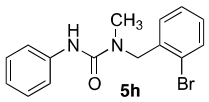
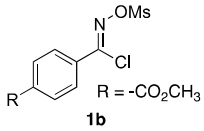
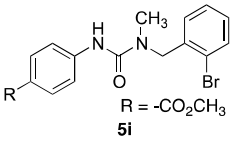
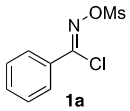
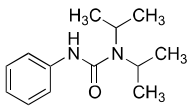
Catalyst loading was increased to 50 mol % in order to give the highest yield and achieve reaction completion. Using K_2CO_3 or Cs_2CO_3 as base, both reactions gave a comparable yield (entries 1 and 2). We therefore selected more common base as our optimal base which was K_2CO_3. By changing the concentration of reaction the yield slightly increased to 41% (entry 3). Higher polar solvents had no affect in the reaction (entries 4 and 5). However, the solvent with higher polarity would allow us to increase the temperature of the reaction. Switching solvent to DMSO or THF and increasing the temperature to 40 °C, the product yield satisfyingly increased to 69% and 58% respectively (entry 6 and 7). Note that, further increase in temperature did not afford greater product yield. Yamamoto and co-workers previously found that TMEDA may have acted as a nucleophilic catalyst and base.[10a] Based on their finding, we subsequently subjected TMEDA as a catalyst (50 mol %) in our reaction. Satisfyingly, the yield of urea was elevated to 74% (entry 8). The amount of TMEDA was also crucial in which the yield of urea was dropped to 48% yield when 20 mol % was employed. The product yield was slightly decreased to 63% yield when 1.0 equivalent was used in reaction. Interestingly, without any nucleophilic catalyst, the reaction also proceeded in good yield (entry 9). This result suggested that DMAP caused undesired reaction pathways in our urea synthesis from saturated amines. Although we could not clarify the role of TMEDA in our reaction, it provided an optimal condition for our urea synthesis based on the result with 50 mol% TMEDA.

Using the optimized reaction conditions, we then explored the feasibility of the reactions of α-chloroaldoxime *O*-methanesulfonates and saturated secondary amines (Table 4).

Table 4. The formation of ureas from α-chloroaldoxime *O*-methanesulfonates and *N*-methylbenzylamines[a]



entry	chloroaldoximes	ureas	yield[b]
1	 1a	 5a	74
2	 R = -CO_2CH_3 1b	 R = -CO_2CH_3 5b	86

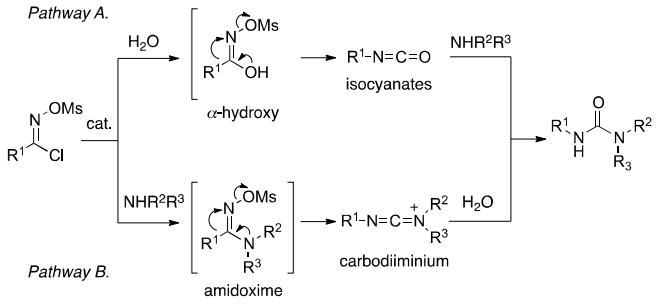
3	 1c	 5c	84
4	 1d	 5d	76
5	 1e	 5e	72
6	 1f	 5f	69
7	 1g	 5g	44
8	 1a	 5h	80
9	 1b	 5i	74
10	 1a	 5j	25

[a]Reaction conditions: all reactions were performed with 0.5 mmol of *N*-methylbenzylamines. [b]Isolated yield.

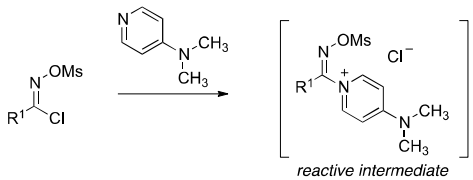
With aliphatic amines, a wide range of α-chloroaldoxime *O*-methanesulfonates was applicable. Aryl substitutes bearing both electron withdrawing and donating groups gave high yields (entries 1 − 5). Aliphatic pendent also gave high yield (entry 6). Similar to Yamamoto's report, we found that the yield diminished when more steric substituent was introduced (entry 7).[10b] In order to provide an alternative method for synthesizing six-membered ring cyclic ureas, we subjected *N*-methy-2-bromobenzylamine to our reaction, which gave corresponding ureas, good substrate for intramolecular Ullmann type coupling,[13] in high yields (entries 8 and 9). When the more sterically hindered amine (*N,N*-diisopropylamine) was subjected to the reaction, the product yield was dramatically decreased to 25% (entry 10). The result suggested that the steric of the nucleophile was also detrimental the yield of the ureas.

We next turned our attention to the possible mechanism in our urea transformation. An attempt to monitor the reaction by ^{1}H NMR technique was failed because the intermediate signals were ambiguously identified from the ^{1}H NMR spectrum of the reaction mixture. However, a study by Truce and Naik showed that the α-chloroaldoxime *O*-methanesulfonates did not react with gaseous ammonia at room temperature but it did react with ammonium hydroxide in acetone. This study suggested that the nucleophilicity of amines affected the substitution reaction.[14] Rajagopalan and Talaty also showed that pyrrolidine could undergo substitution reaction with α-chloroaldoxime *O*-methanesulfonates to give amidoxime intermediate.[15] Based on these studies, including Yamamoto's finding[10a] and our results, we proposed two highly possible pathways. Firstly, α-hydroxy intermediates was generated from nucleophilic substitution of α-chloroaldoxime *O*-methanesulfonates with water, which could undergo a rearrangement to give isocyanate intermediates *in situ*, followed by the addition of corresponding secondary amine to give urea (Scheme 2, Pathway A.). On the other hand, we could not rule out the possibility of nucleophilic amines substituting α-chloroaldoxime *O*-methanesulfonates to generate amidoxime intermediates, followed by the Tiemann rearrangement to give carbodiiminium. Subsequently, carbodiiminium reacted with water to give a desire urea (Scheme 2, Pathway B.). The role of essential DMAP was possibly a nucleophilic catalyst to generate the reactive intermediate in the formation of trisubstituted ureas from secondary aromatic amines (Scheme 2, Plausible intermediate.).

Scheme 2. Possible reaction mechanisms



Plausible intermediate



Experimental

General procedure

Commercially available reagents and reaction solvents were used without further purification. Solvents for extraction and column chromatography were distilled at their boiling point ranges prior to use. Thin-layer chromatography (TLC) was

performed on silica gel 60 GF_{254} (Merck) and was visualized by fluorescene quenching under UV light. Column chromatography was performed on SilicaFlash® G60 (70-230 Mesh). ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a 300 MHz Bruker FTNMR Ultra Shield spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in parts per million (ppm) downfield from TMS (δ 0.00) and coupling constants are reported as Hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Infrared spectra (IR) were measured on Perkin Elmer Spectrum GX FT-IR system and recorded on wave number (cm^{-1})

General procedure for synthesis of *α*-chloroaldoxime *O*-methanesulfonates.

***N*-((Methylsulfonyl)oxy)benzimidoyl chloride (1a).** Prepared according to literature procedure.[10a] A dried round bottom flask was charge with 1.0 equiv of benzaldoxime in the mixture of 0.5 M of THF and $CHCl_3$ (1:1 ratio), followed by the portion addition of 1.5 equiv of *N*-chlorosuccinamide (NCS). After the addition was completed, the temperature of reaction was increased to 40 °C. After an hour, the reaction was quenched with water and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was dissolved in EtOAc. The resulting solution was cooled to 0 °C before the slow addition of 2.2 equiv of triethylamine. The reaction mixture was stirred for 10 min. Then, 1.1 equiv of chloromethanesulfonate was added dropwise at 0 °C. After completion of addition, the mixture was allowed to warm to room temperature and stirred for an hour, followed by filtration. The filtrate was washed with water. The organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under reduced pressure. The crude mixture was purified by column chromatography (2:1 hexanes:CH_2Cl_2) to afford **1a** as white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.61–7.56 (m, 1H), 7.51–7.46 (m, 2H), 3.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 132.7, 130.4, 128.8, 128.1, 37.0. Other data was identical to the literature values.[10a]

Methyl-4-(chloro(((methylsulfonyl)oxy)imino)methyl) benzoate (1b). Prepared according to the procedure described for **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 148.1, 134.2, 133.7, 129.9, 128.1, 52.6, 37.1. Other data was identical to the literature values.[16]

***N*-((Methylsulfonyl)oxy)-4-nitrobenzimidoyl chloride (1c).** Prepared according to the procedure described for **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7 Hz, 2H), 8.16 (d, *J* = 8.7 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 146.8, 136.0, 129.2, 123.9, 37.2. Other data was identical to the literature values.[17]

4-Methoxy-*N*-((methylsulfonyl)oxy)benzimidoyl chloride (1d). Prepared according to the procedure described for **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 148.8, 129.9, 122.5, 114.2, 55.6, 36.9; IR (thin film) ν 3422, 1607, 1510, 1372, 1261, 1148, 820, 522 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_9H_{10}ClNO_4S$ 285.9917, found 285.9917.

4-Chloro-*N*-((methylsulfonyl)oxy)benzimidoyl chloride (1e). Prepared according to the procedure described for **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 3.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 139.2, 129.3, 129.2, 37.1. Other data was identical to the literature values.[18]

***N*-((Methylsulfonyl)oxy)butyrimidoyl chloride (1f).** Prepared according to the procedure described for **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.16 (s, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 1.69–1.77 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 38.6, 36.7, 19.5, 12.9. Other data was identical to the literature values.[10a]

***N*-((Methylsulfonyl)oxy)cyclohexanecarbimidoyl chloride (1g).** Prepared according to the procedure described for **1a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.17 (s, 3H), 2.66–2.59 (m, 1H), 2.03–1.69 (m, 5H), 1.56–1.34 (m, 2H), 1.29–1.19 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 45.7, 30.0, 25.4, 25.3. Other data was identical to the literature values.[10a]

Synthesis of Trisubstituted Ureas

General Procedure for One-Pot Synthesis of Trisubstituted Ureas from *α*-Chloroaldoxime *O*-Methanesulfonates and Secondary Amines

General Procedure A: For the Reaction of Aniline Derivatives

The reaction of *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) and *N*-methylaniline is representative: A dried 10 mL round bottom flask equipped with a magnetic stirring bar was charged with *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) (0.5 mmol), *N*-methylaniline (0.75 mmol), *N,N*-dimethylaminopyridine (DMAP) (0.15 mmol), water (1.0 mmol) and Cs_2CO_3 (1.0 mmol) in CH_2Cl_2 (2.5 mL). The reaction mixture was stirred at room temperature for 15-20 h. After completion of reaction, the reaction mixture was quenched with sat. NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude mixture was purified by column chromatography (5:1 hexanes:EtOAc) to afford **3a** in 97.29 mg (86% yield).

1-Methyl-1,3-diphenylurea (3a). Yield 97.29 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.34–7.21 (m, 5H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.30 (brs, 1H), 3.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 143.0, 138.9, 130.3, 128.8, 127.8, 127.4, 122.9, 119.3, 37.3. Other data was identical to the literature values.[19]

Methyl-4-(3-methyl-3-phenylureido)benzoate (3b). Prepared according to general procedure A from methyl-4-(chloro(((methylsulfonyl)oxy)imino)methyl)benzoate **(1b)** and *N*-methylaniline. Yield 135.04 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.7 Hz, 2H), 7.45–7.40 (m, 2H), 7.34–7.25 (m, 5H), 6.56 (brs, 1H), 3.78 (s, 3H), 3.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 153.8, 143.4, 142.4, 130.6, 130.4, 128.1, 127.3, 124.0, 117.9, 51.8, 37.4; IR (thin film) ν 3332, 2962, 2950, 1713, 1677, 1594, 1519, 1456, 1247, 1175, 1111, 767, 698 cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd. for $C_{16}H_{16}N_2O_3$ 285.1239, found 285.1241.

1-Methyl-3-(4-nitrophenyl)-1-phenylurea (3c). Prepared according to general procedure A from *N*-((methylsulfonyl)oxy)-4-nitrobenzimidoyl chloride **(1c)** and *N*-methylaniline. Yield 124.78 mg (92%). ^{1}H NMR (300 MHz,

$CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.55–7.40 (m, 5H), 7.35 (d, *J* = 7.8 Hz, 2H), 6.67 (brs, 1H), 3.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 145.0, 142.4, 142.1, 130.1, 128.5, 127.4, 125.0, 118.0, 37.5. Other data was identical to the literature values.[20]

3-(4-Chlorophenyl)-1-methyl-1-phenylurea (3e). Prepared according to general procedure A from 4-chloro-*N*-((methylsulfonyl)oxy)benzimidoyl chloride **(1e)** and *N*-methylaniline. Yield 96.47 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.39–7.29 (m, 3H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.34 (brs, 1H), 3.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 142.6, 137.6, 130.4, 128.7, 128.0, 127.4, 120.5, 37.3. Other data was identical to the literature values.[21]

1-Methyl-1-phenyl-3-propylurea (3f). Prepared according to general procedure A from *N*-((methylsulfonyl)oxy)butyrimidoyl chloride **(1f)** and *N*-methylaniline. Yield 45.20 mg (47%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.33–7.24 (m, 3H), 4.27 (brs, 1H), 3.27 (s, 3H), 3.14 (q, *J* = 6.9 Hz, 2H), 1.49–1.36 (m, 2H), 0.83 (t, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 143.5, 130.0, 127.3, 127.2, 42.4, 37.1, 23.3, 11.2; IR (thin film) ν 3354, 2962, 1655, 1569, 1495, 1339, 760, 700 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{11}H_{16}N_2O$ 215.1160, found 215.1160.

1-(4-Methoxyphenyl)-1-methyl-3-phenylurea (3g). Prepared according to general procedure A from *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) and 4-methoxy-*N*-methylaniline. Yield 92.27 mg (72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.16 (m, 6H), 7.00–6.96 (m, 3H), 6.26 (brs, 1H), 3.85 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 154.8, 139.0, 135.3, 128.9, 128.8, 122.8, 119.2, 115.5, 55.6, 37.4. Other data was identical to the literature values.[21]

1-Benzyl-1-(4-methoxyphenyl)-3-phenylurea (3h). Prepared according to general procedure A from *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) and *N*-benzyl-4-methoxyaniline. Yield 101.38 mg (61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.7.22 (m, 10H), 7.06 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.25 (brs, 1H), 4.90 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 154.7, 139.0, 138.4, 133.4, 130.1, 128.8, 128.7, 128.4, 127.3, 122.9, 119.3, 115.3, 55.5, 53.3; IR (thin film) ν 2928, 2420, 1672, 1511, 1441, 1248, 752, 693, 556 cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd. for $C_{21}H_{20}N_2O_2$ 333.1603, found 333.1602.

Methyl 4-(3-benzyl-3-(4-methoxyphenyl)ureido)benzoate (3i). Prepared according to general procedure A from methyl-4-(chloro(((methylsulfonyl)oxy)imino)methyl)benzoate **(1b)** and *N*-benzyl-4-methoxyaniline. Yield 140.55 mg (72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.30–7.28 (m, 5H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.44 (brs, 1H), 4.90 (s, 2H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.5, 154.1, 143.3, 137.9, 132.9, 130.7, 130.0, 128.7, 128.4, 127.4, 124.1, 117.9, 115.4, 55.5, 53.4, 51.8; IR (thin film) ν 3346, 2950, 1713, 1674, 1511, 1279, 1247, 1175, 769, 699, 561cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd. for $C_{23}H_{22}N_2O_4$ 391.1658, found 391.1654.

General Procedure B: For the Reaction of *N*-Benzylamine Derivatives

The reaction of *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) and *N*-methylbenzylamine is representative: A dried 10 mL round bottom flask equipped with a magnetic stirring bar was charged with *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) (0.75 mmol), *N*-methylbenzylaniline (0.50 mmol), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (0.25 mmol), water (1.0 mmol) and K_2CO_3 (1.0 mmol) in DMSO (1.5 mL). The reaction mixture was warmed to 40 °C and stirred for 15-18 h. After completion of reaction, the reaction mixture was quenched with sat. NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude mixture was purified by column chromatography (5:5:1 hexanes:CH_2Cl_2:EtOAc) to afford **5a** in 88.91 mg (74% yield).

1-Benzyl-1-methyl-3-phenylurea (5a). Yield 88.91 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.15 (m, 8H), 7.06–7.02 (m, 2H), 6.64 (brs, 1H), 4.59 (s, 2H), 3.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 139.1, 137.5, 128.9, 128.8, 128.7, 127.6, 127.3, 123.1, 122.3, 120.2, 119.2, 52.3, 34.8. Other data was identical to the literature values.[22]

Methyl 4-(3-benzyl-3-methylureido)benzoate (5b). Prepared according to general procedure B from methyl-4-(chloro(((methylsulfonyl)oxy)imino)methyl)benzoate **(1b)** and *N*-methylbenzylamine. Yield 128.29 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.33–7.22 (m, 5H), 7.77 (brs, 1H), 4.54 (s, 2H), 3.84 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 155.3, 143.9, 137.1, 130.6, 128.9, 127.6, 127.3, 124.0, 118.7, 52.3, 51.9, 34.8; IR (thin film) ν 3334, 2950, 1716, 1650, 1525, 1411, 1280, 1247, 1175, 1111, 770, 700; HRMS (ESI) $[M+H]^+$ calcd. for $C_{17}H_{18}N_2O_3$ 299.1395, found 299.1391.

1-Benzyl-1-methyl-3-(4-nitrophenyl)urea (5c). Prepared according to general procedure B from *N*-((methylsulfonyl)oxy)-4-nitrobenzimidoyl chloride **(1c)** and *N*-methylbenzylamine. Yield 119.83 mg (84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.41–7.28 (m, 5H), 6.98 (brs, 1H), 4.61 (s, 2H), 3.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 145.5, 142.4, 136.7, 127.9,127.2, 125.0, 118.5, 52.5, 35.0. Other data was identical to the literature values.[23]

1-Benzyl-3-(4-methoxyphenyl)-1-methylurea (5d). Prepared according to general procedure B from 4-methoxy-*N*-((methylsulfonyl)oxy)benzimidoyl chloride **(1d)** and *N*-methylbenzylamine. Yield 102.73 mg (76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.24 (m, 7H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.44 (brs, 1H), 4.57 (s, 2H), 3.78 (s, 3H), 2.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 155.8, 137.7, 132.2, 128.8, 127.5, 127.3, 127.2, 122.4, 114.0, 55.5, 52.3, 34.7; IR (thin film) ν 3330, 2934, 1651, 1538, 1413, 1379, 1296, 1238, 1034, 826, 753, 700, 568, 523; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{16}H_{18}N_2O_2$ 293.1266, found 293.1266.

1-Benzyl-3-(4-chlorophenyl)-1-methylurea (5e). Prepared according to general procedure B from 4-chloro-*N*-((methylsulfonyl)oxy)benzimidoyl chloride **(1e)** and *N*-methylbenzylamine. Yield 98.91 mg (72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.28 (m, 7H), 7.24–7.20 (m, 2H), 6.53 (brs, 1H), 4.58 (s, 2H), 3.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 137.8, 137.3, 128.9, 128.7, 128.0, 127.7, 127.3, 121.3, 52.4, 34.8. Other data was identical to the literature values.[10]

1-Benzyl-1-methyl-3-propylurea (5f). Prepared according to general procedure B from *N*-((methylsulfonyl)oxy)butyrimidoyl chloride **(1f)** and *N*-methylbenzylamine. Yield 71.17 mg (69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.28 (m, 3H), 7.24–7.19 (m, 2H), 4.61 (brs, 1H), 4.46 (s, 2H), 3.16 (q, *J* = 6.9 Hz, 2H), 2.84 (s, 3H), 1.51–1.41 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 138.0, 128.6, 127.2, 127.1, 52.1, 42.7, 34.3, 23.5, 11.3; IR (thin film) ν 3331, 2930, 1644, 1532, 1440, 1380, 1310, 1244, 1025, 751, 634 cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd. for $C_{12}H_{18}N_2O$ 207.1497, found 207.1586.

1-Benzyl-3-cyclohexyl-1-methylurea (5g). Prepared according to general procedure B from *N*-((methylsulfonyl)oxy)cyclohexanecarbimidoyl chloride **(1g)** and *N*-methylbenzylamine. Yield 54.20 mg (44%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 4.48 (s, 2H), 4.29 (brs, 1H), 3.69–3.64 (m, 1H), 2.86 (s, 3H), 1.94–1.90 (m, 2H), 1.69–1.57 (m, 4H), 1.41–1.26 (m, 2H), 1.18–1.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 138.1, 128.6, 127.3, 52.2, 49.4, 34.3, 34.1, 33.9, 25.6, 25.0. Other data was identical to the literature values.[23]

1-(2-Bromobenzyl)-1-methyl-3-phenylurea (5h). Prepared according to general procedure B from *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) and 1-(2-bromophenyl)-*N*-methylmethanamine. Yield 127.68 mg (80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 1H), 7.40–7.32 (m, 6H), 7.22-7.19 (m, 1H), 7.08–7.05 (m, 1H), 6.38 (brs, 1H), 4.70 (s, 2H), 3.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 138.9, 136.2, 133.1, 129.1, 128.9, 128.0, 123.2, 123.1, 120.0, 52.6, 35.1; IR (thin film) ν 3331, 2930, 1644, 1532, 1440, 1244, 1025, 751, 693 cm^{-1}; HRMS (ESI) $[M+Na]^+$ calcd. for $C_{15}H_{15}BrN_2O$ 341.0265, found 341.0265.

Methyl-4-(3-(2-bromobenzyl)-3-methylureido)benzoate (5i). Prepared according to general procedure B from methyl-4-(chloro(((methylsulfonyl)oxy)imino)methyl)benzoate **(1b)** and 1-(2-bromophenyl)-*N*-methylmethanamine. Yield 139.58 mg (74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.28–7.20 (m, 2H), 7.15–7.10 (m, 1H), 4.62 (s, 2H), 3.84 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 155.3, 143.7, 135.9, 133.1, 130.6, 129.1, 128.2, 127.9, 124.1, 123.1, 118.7, 52.6, 52.0, 35.1; IR (thin film) ν 3335, 2950, 1716, 1652, 1594, 1526, 1411, 1281, 1249, 1176, 1112, 1026, 751 cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd. for $C_{17}H_{17}BrN_2O_3$ 377.0501, found 377.0498.

1,1-Diisopropyl-3-phenylurea (5j). Prepared according to general procedure B from *N*-((methylsulfonyl)oxy)benzimidoyl chloride (**1a**) and diisopropylamine. Yield 27.54 mg (25%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.31–7.25 (m, 2H), 7.04–7.00 (m, 1H), 6.25 (brs, 1H), 4.04–3.95 (m, 2H), 1.33 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 139.3, 128.8, 128.7, 122.7, 119.8, 119.2, 45.8, 21.5. Other data was identical to the literature values.[24]

Conclusions

Mild and practical synthesis of trisubstituted ureas via one-pot reaction of the bench-stable α-chloroaldoxime *O*-methanesulfonates and secondary amines was accomplished. Two categories of secondary amines were carried out using two protocols, both of which were mild and operated under simple reaction conditions. The substrate scope was general for saturated secondary amines. For secondary aromatic amines, the electrophilicity of α-chloroaldoxime *O*-methanesulfonates and the nucleophilicity of amines played important role. Although we could not determine the mechanism of the urea transformation, this methodology enriched the chemistry of α-chloroaldoxime *O*-methanesulfonates. Further applications of reaction and a study of reaction mechanism are ongoing.

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