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FULL PAPER

# A novel C-N Migration Rearrangement Based on N-F Compounds for the Synthesis of N-alkyl Diaryl Ureas

Yi-Xiao Zhao, [a] Tian Xie, [c] San-Ke Yang, *[c] and Xian-Jin Yang *[a] [b]

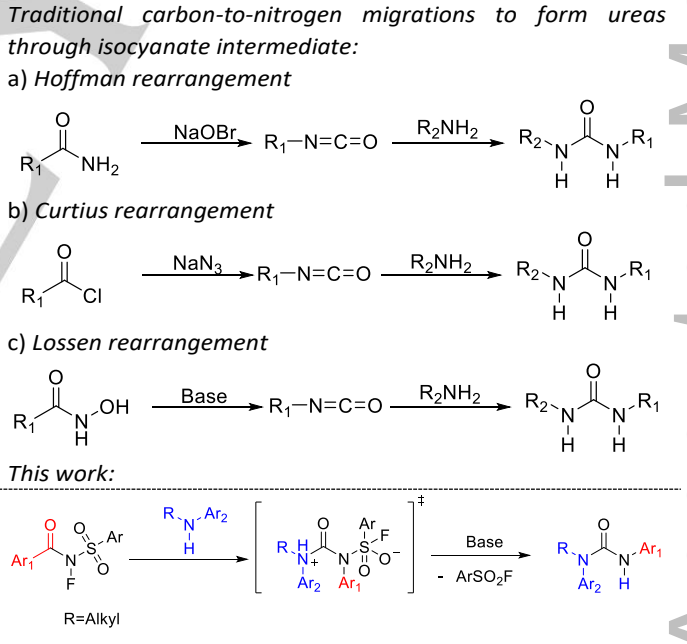
Dedication ((optional))

**Abstract:** A novel rearrangement reaction based on the structure of *N*-fluoro-*N*-(phenylsulfonyl) Benzamides (FPSBA) was developed. In the presence of base, unsymmetrical *N*-alkyl diaryl ureas were obtained in good yields which were accomplished through secondary alkyl phenyl amines initiated 1,2-phenyl-shift migration rearrangement of *N*-fluoro-*N*-(phenylsulfonyl) benzamides. The proceed was carried out without using traditional, highly toxic reagents and noble metal. Whereas without rearrangement occurrence for primary phenyl amines and aliphatic amines, normal amides and *N*-(phenylsulfonyl) benzamides were afforded respectively. Nitrene and phenyl isocyanate included process were denied and a secondary alkyl phenyl amine initiated vicinal $S_N2'$ mechanism was supposed. This rearrangement reaction features an interesting reaction mechanism, mild reaction conditions, simple operation, and useful products.

## Introduction

Currently, urea derivatives have found significant interest in applications in biological studies,[1] polymer science, and agrochemicals.[2] The traditional routes for the synthesis of urea were the reaction of an amine with phosgene or its analogues, [3] and an amine with isocyanate intermediate. Another grouping of techniques for urea generation is transition metal-catalyzed synthesis. The Buchwald group described a Pd-catalyzed synthesis of unsymmetrical diaryl urea via a one-pot arylation and deprotection protocol.[4] In another approach, CO or $CO_2$ has been reacted with amines via metal catalysis to synthesize a urea derivative. Stephan and co-workers developed a method for the preparation of urea derivatives, which used the conversion of In-catalyzed silamine to the corresponding urea through $CO_2$ insertion into the In-N bond.[5] Besides this, a series of Pd-,[6] W-,[7] Co/Rh-,[8] Cu-,[9] and Au-[10] catalyzed oxidations and subsequent carbonylations of amines to urea have also been reported. However, all of these procedures either use highly toxic reagents or expensive metal catalysts.

The classical C-N migration rearrangement reaction is an important method in organic synthesis for preparing urea derivates. Conventional *Hoffman rearrangement*, *Curtius rearrangement*, and *Lossen rearrangement* all generate an isocyanate intermediate through a C-N migration rearrangement reaction while subsequently reacted with an amine or an alcohol to afford urea or carbamate compounds.[11] Unlike previous studies, we have newly developed a series of FPSBA compounds that can undergo a C-N migration rearrangement reaction under secondary alkyl phenyl amine initiation to obtain *N*-alkyl diaryl ureas (scheme 1). And the reaction was proceeded without the generation of isocyanate and could effectively avoid some side reactions caused by isocyanate.




**Scheme 1** The formation of ureas from carbon-to-nitrogen migrations.

## Results and Discussion

Our group are interested in some N-F compounds and their transformation.[12] *N*-fluoro-*N*-(phenylsulfonyl) benzamide (**1a**) could be conveniently prepared by the reaction of benzoyl chloride with commercially available *N*-fluorobenzenesulfonamide in the presence of Py in DCM. Then

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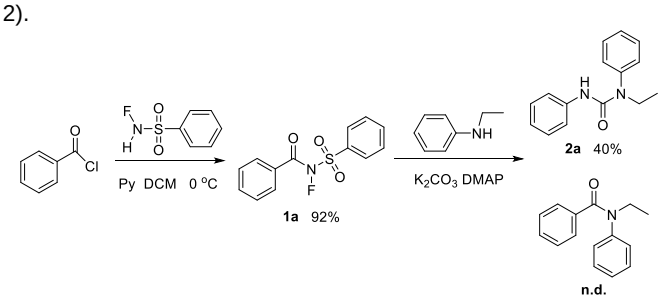
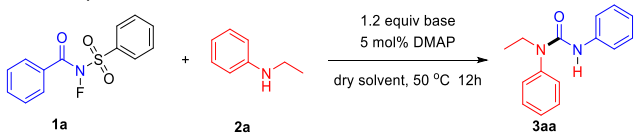
compound **1a** was reacted with N-ethylaniline **2a** with the intent of obtaining an amide. However, 1-ethyl-1,3-diphenylurea **3aa** was obtained in 40% yield when pyridine (Py) and 4-dimethyl amino pyridine (DMAP) were tested as the base and additive (Scheme 2).




**Scheme 2** The generation of **1a** and its reaction with **2a**.

**Table 1** Optimization of the reaction conditions of 1a with 2a[a]

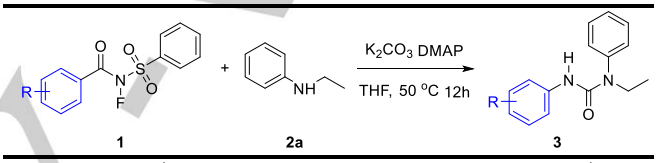


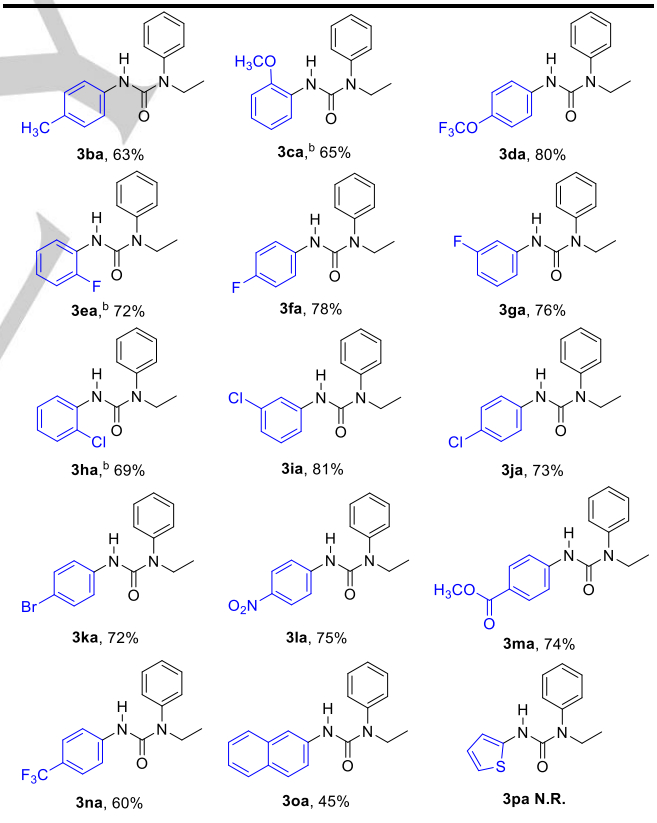

| Entry | Solvent | Base | Additive | Temp | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | $CH_3CN$ | Py | DMAP | 50 | trace |
| 2 | $CCl_4$ | Py | DMAP | 50 | trace |
| 3 | EA | Py | DMAP | 50 | 42 |
| 4 | Dioxane | Py | DMAP | 50 | 30 |
| 5 | Acetone | Py | DMAP | 50 | 37 |
| 6 | THF | Py | DMAP | 50 | 52 |
| 7 | Toluene | Py | DMAP | 50 | 47 |
| 8 | DCE | Py | DMAP | 50 | 45 |
| 9 | THF | DABCO | | 50 | 75 |
| 10 | THF | DBU | | 50 | trace |
| 11 | THF | $NEt_3$ | | 50 | <5 |
| 12 | THF | NaOH | DMAP | 50 | 56 |
| **13** | **THF** | **$K_2CO_3$** | **DMAP** | **50** | **84** |
| 14[c] | THF | $K_2CO_3$ | DMAP | 50 | 80 |
| 15 | THF | No base | DMAP | 50 | 0 |
| 16 | THF | $K_2CO_3$ | | 50 | 72 |
| 17[d] | THF | $K_2CO_3$ | DMAP | 90 | 60 |
| 18 | THF | $K_2CO_3$ | DMAP | 0 | trace |

[a]Reaction conditions: **1a** (0.60 mmol), **2a** (0.2 mmol), DMAP (5 mol%), 1.2 equiv. of base, in 3.0 mL solvent at 50 °C and 12 h. [b]Isolated yield. [c]$K_2CO_3$ (2 equiv.). [d]Reaction time: 24 h; DMAP = 4-dimethyl amino pyridine; DBU = 1,8-diazabicycloundec-7-ene; DABCO = 1,4-Diazabicyclo [2.2.2] octane.

Next, we began our investigation the unanticipated reaction with **1a** and **2a** as reaction partners. Utilizing Py and DMAP as base and additive, the desired product **3aa** was generated to a trace amount at 50 °C when the solvent was acetonitrile or $CCl_4$ (Table 1, entries 1-2). The desired product **3aa** can also be obtained by using other solvents such as ethyl acetate, 1,4- dioxane, acetone, THF, DCE and toluene (Table 1, entries 3-8). Entry 6 shows that **3aa** can be generated at 52% yield using THF as the solvent. A marked increase to 75%, in conversion was found when 1,4-diazabicyclo [2.2.2] octane (DABCO) was used as the base instead of Py (Table 1, entry 9). Switching to other bases, such as 1,8-diazabicycloundec-7-ene (DBU) and $NEt_3$, resulted in little or only a trace quantity of product formed (Table 1, entries 10-11). Next, further bases were tested to achieve higher yields, where 56% yield was noted using NaOH (Table 1, entry 12). Specifically, $K_2CO_3$ proved to be the most efficient base for this reaction, giving the desired product in 84% yield (Table 1, entry 13). Further optimization allowed us to increase the base loadings to two equivalents, but the product yield difference was insignificant (Table 1, entry 14). However, conversion to the desired product was not observed when the reaction was performed in the absence of any of these bases (Table 1, entry 15). Without use of DMAP, we can obtain the product in 72% yields (Table 1, entry 16). The effect of temperature was also examined, and a decrease in the yield of the product was observed when the reaction was carried out in THF at 90 °C for 24 hours (Table 1, entry 17), and no product was formed at 0 °C (Table 1, entry 18). After extensive screening of solvents, bases, temperatures, and reaction times, the optimal conditions for this reaction were identified to be: $K_2CO_3$ (1.2 equivalents), DMAP (5 mol%), THF as the solvent, temperature – 50 °C, reaction time – 12 h.

**Table 2** Substrate scope of FPSBA derivatives[a]

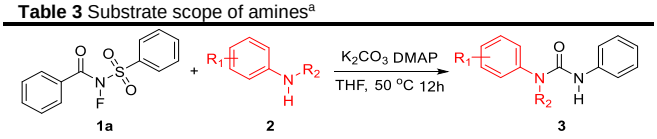


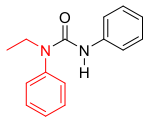

[a]Reaction conditions: **1** (0.6 mmol), **2a** (0.2 mmol), DMAP (5 mol %) and $K_2CO_3$ (1.2 equiv.) in dry THF (3 mL) at 50 °C, 12 h; Isolated yields. [b]Reaction time: 24 h.

Having established the optimal reaction conditions for the synthesis of **3aa**, the scope of the reaction with respect to FPSBA derivatives was explored (Table 2). As shown, the scope of the

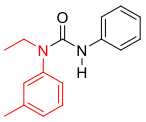
**Table 3** Substrate scope of amines[a]



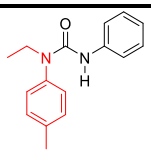

1a 2 3



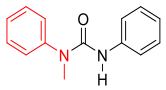
**3aa**, 84%



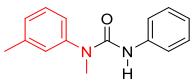
**3ab**, 75%



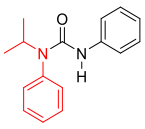
**3ac**, 68%



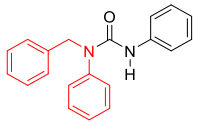
**3ad**, 80%



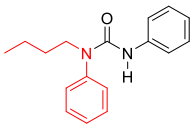
**3ae**, 66%



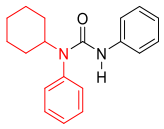
**3af**, 52%



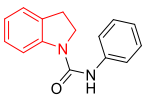
**3ag**, 58%



**3ah**, 56%



**3ai**, 52%



**3aj**, 58%

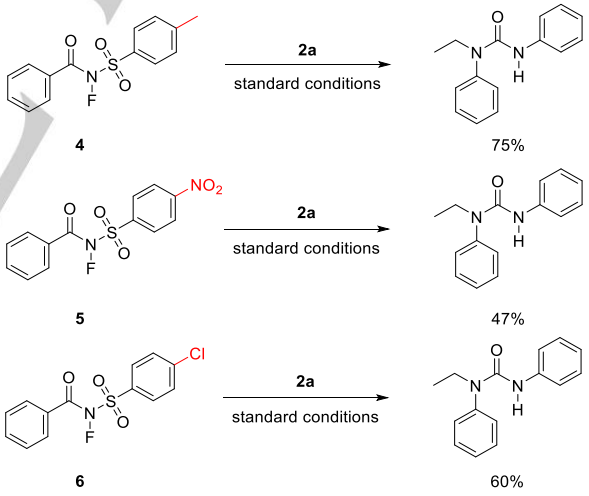
[a]Reaction conditions: **1a** (0.6 mmol), **2** (0.2 mmol), DMAP (5 mol %) and $K_2CO_3$ (1.2 equiv.) in dry THF (3 mL) at 50 °C, 12 h; Isolated yields.

reaction is very broad and tolerates electron-neutral, electron-withdrawing, and electron-rich substrates. FPSBA derivatives containing different substituents can be converted to unsymmetric ureas in 45-81% yields. Some electron-rich FPSBA derivatives, such as -$CH_3$, -$OCH_3$, -$OCF_3$, can obtain corresponding products in moderate yields (**3ba-3da**). Additionally, substrates containing halogen substituents (F, Cl, Br) were tolerated and gave adducts in synthetically useful yields (**3ea-3ka**). Moreover, *para*- *meta*- and *ortho*-substituted halogens on the FPSBA were also tolerated, as shown by the formation of the corresponding products. However, the substrates with an *ortho* group resulted in decreased yield of the desired product (**3ea, 3ha**) and required longer reaction time (24 h), which is likely related to steric hindrance. Notably, substrates with electron-withdrawing substituents, such as -$NO_2$ and -$CF_3$, were readily converted to the product with moderate yields (**3la, 3na**). It is worth mentioning that the reaction is chemoselective, and the use of substrate **1m** bearing an ester group provided **3ma** in 74% yield and without monitoring the product of ester amidation. As postulated, the substrate containing a naphthalene group was also able to react with compound **2a** yielding the target product **3oa**, albeit with a slightly lower yield (45%). But unfortunately, the product **3pa**, which should have been generated from the reaction of substrate containing thiophene **1p** with **2a**, was not detected. It is noteworthy that the influence of different electronic components used in the synthesis of unsymmetrical ureas is not obvious.

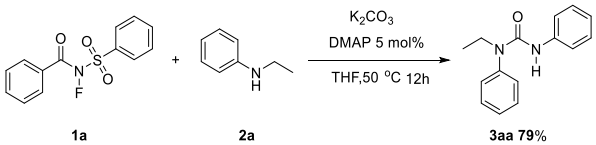
To further demonstrate the flexibility of the present approach for the synthesis of ureas, the substrate scope of aniline was investigated (Table 3). At first, the use of *para*- and *meta*-methyl substituted N-ethylaniline provided the desired product in good yields (**3ab, 3ac**). Then the substrates N-methylaniline **2d** and 3-methyl-*N*-methylaniline **2e** generated the products **3ad** and **3ae** in 80% and 66% yields, respectively. However, the steric effect became pronounced in the presence of isopropyl-, benzyl- and cyclohexyl- substituted substrates **2f**, **2g** and **2i**, where the substrates were able to form the desired products **3af, 3ag** and **3ai** at slightly lower yields. In addition, *N*-butylaniline **2h** was also a viable substrate, giving the product **3ah** in 56% yield. And the heterocyclic compound indoline **2j** can also be reacted with **1a** to gain the product **3aj** in 58% yield.

In addition, we also tested the effect of different substituted *N*-fluoro-*N*-phenylsulfonyl derivatives on the reaction (Scheme 3A). The result displayed that the reactions of *N*-fluoro-*N*-tosylbenzamide **4**, *N*-fluoro-*N*-((4-nitrophenyl) sulfonyl) benzamide **5** and *N*-((4-chlorophenyl) sulfonyl)-*N*-fluorobenzamide **6** with **2a** proceeded smoothly to obtain the product in moderate yields. And these results show that the electron-rich group is more advantageous in the reaction than the electron-deficient group. To further demonstrate the efficiency and practicality of this protocol for the synthesis of ureas, gram-scale synthesis of the product **3aa** was carried out (Scheme 3B). As expected, we can obtain the desired product in 79% yield.

A) The effect of different substituted *N*-fluoro-*N*-phenylsulfonyl derivatives



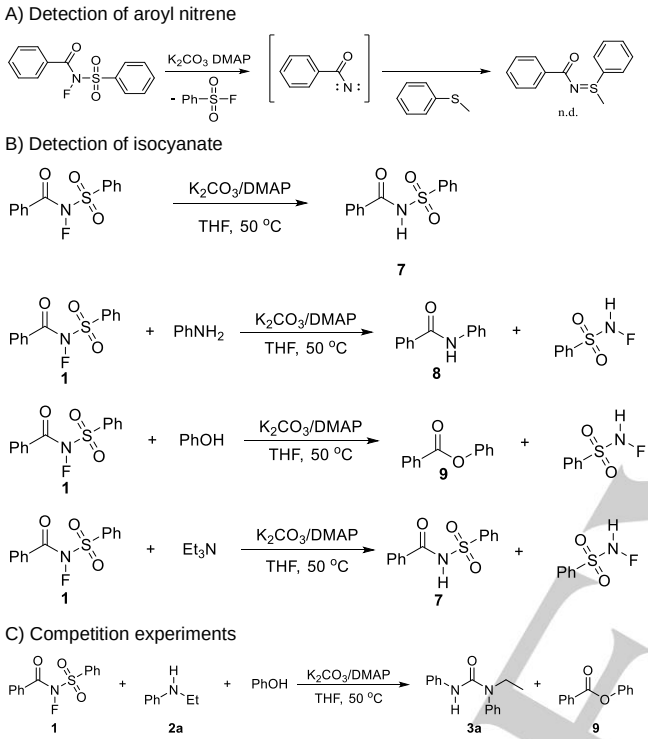

B) Gram-scale reaction




1a 2a **3aa 79%**

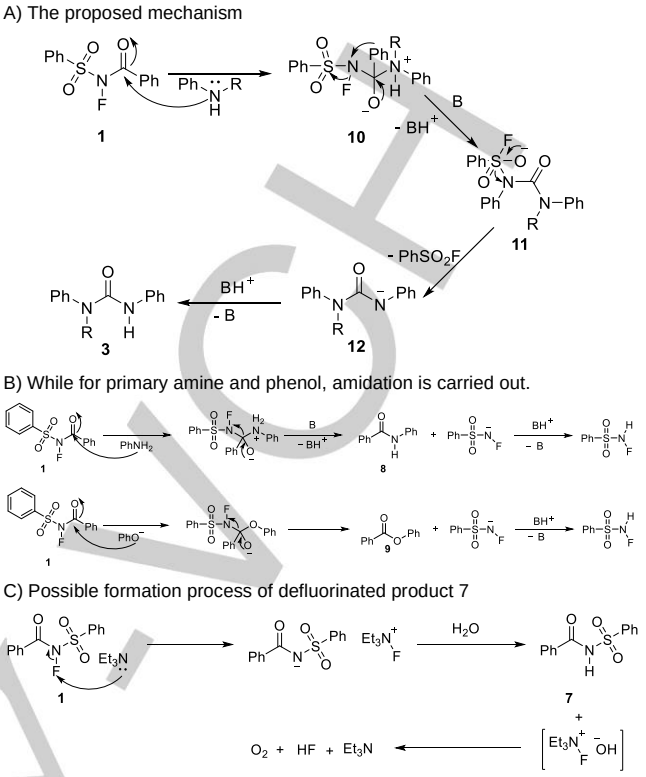
**Scheme 3**. Further study on the reaction

A series of experiments have been carried out with the aim of collecting mechanistic information. We can confirm the formation of benzenesulfonyl fluoride during the reaction by using $^{19}F$ NMR monitoring. Then we speculate that the aroyl nitrene may form after the departure of benzene-sulfonyl fluoride. Therefore, we attempted to use methyl phenyl sulfide to probe the intermediacy of the nitrene[13] (scheme 4A). But the desired product was not detected. Next, we suspect whether the reaction might form isocyanate intermediate. Hence, we tried to trap potential




**Scheme 4**. Mechanism study on the reaction

intermediate phenyl isocyanate. At first, we attempted to isolate phenyl isocyanate intermediate in the absence of **2a**, but we only obtain the compound **7** (Scheme 4B). Then we try to trap the phenyl isocyanate intermediate with phenol and aniline, and the phenyl benzamide **8** and phenyl benzoate **9** was formed but the desired product phenyl carbamate and diphenyl urea was not detected respectively (Scheme 4B). Aliphatic organic amines $Et_3N$, $Et_2NH$, etc., were also tried, defluorinated product **7** was afforded. Based on the above results, we speculate that the intermediate phenyl isocyanate was not formed. In addition, we conducted a competition experiment by adding **1a**, **2a** and phenol in one pot under the standard condition, the results showed that both **3aa** and **9** were produced. It shows that the reaction is closely related to the substrate's nucleophilicity and basicity (Scheme 4C).




**Scheme 5**. Possible mechanism

According to the results of the above experimental studies, a possible mechanism has been proposed as shown in scheme 5 A. The first step is nucleophilic reagent amine **2** to attack the carbonyl group in compound **1** to form intermediate **10**. Next, deprotonation occurred for intermediate **10** under alkaline conditions and the phenyl 1,2-shift migration promoted the left of fluoride ion from nitrogen and the fluoride ion nucleophilic attack benzenesulfonyl group to form the intermediate **11**. Finally, the product **3** is generated by the left of benzenesulfonyl fluoride and subsequent protonation.

From the above proposed mechanism, the rearrangement proceeded only for the secondary alkyl phenyl amine, might be contributed to its stronger nucleophilicity than primary phenyl amine and phenol, therefore promote the shift of phenyl from intermediate **10** to **11** in the mechanism process. And due to the stronger nucleophilicity, alkyl phenyl secondary amine might also facilly combine to the by-product benzenesulfonyl fluoride, which is beneficial to the accomplishment of the rearrangement process. And its great steric space hinders the alkyl phenyl amine **2** to approach fluorine atom of N-F bond in compound **1**, and naturally inhibit the defluorination side reaction.

## Conclusions

In conclusion, a novel aryl C-N shift rearrangement reaction to form alkyl diaryl ureas from facilely available *N*-fluoro-*N*-

(phenylsulfonyl) benzamides was developed. Proofs indicated the mechanism is different from *Hoffman*, *Curtius* and *Lossen* rearrangement, nitrene and isocyanate are not the intermediates. With the assistance of base, a continuous process including initial alkyl phenyl amine nucleophilic attack the carbonyl and the subsequent 1,2-aryl shift from carbon to nitrogen with the left of phenyl sulfonyl fluorine is more reasonable. This rearrangement reaction features an interesting reaction mechanism, mild reaction conditions, simple operation, and useful products. Further explorations of the scope and limitation of these reactions are underway in our lab.

## Experimental Section

**General Information.**

All the starting chemicals were commercially available and used without further purification. Substrates were purchased from Energy chemical Co. Ltd. and Damas-beta Co. Ltd. N-fluorobenzenesulfonamide (NFH) and its derivatives were purchased from Aldrich or Shanghai Science Bio-pharmaceutical Co. Ltd. DCE was freshly distilled over $P_2O_5$, dry acetonitrile and DCM was obtained by refluxing with $CaH_2$, dry toluene and THF was obtained by refluxing with Na. Flash column chromatography was performed using silica gel (300-400 mesh). All $^1$H NMR spectra were recorded on a Bruker spectrometer at 400 MHz. The $^{13}$C NMR spectra were recorded on a Bruker spectrometer at 101 MHz or 151 MHz. The $^{19}$F NMR spectra were recorded on a Bruker spectrometer at 400 MHz. Chemical shifts (δ value) were reported in ppm down field from internal tetramethylsilane (TMS). IR spectrum (Film) were recorded on a Nicolet 6700 spectrophotometer in the range of 400~4000 cm$^{-1}$. HRMS (EI) and (ESI) Mass spectra were recorded on a Waters GCT Premier mass spectrometer with electron impact.

**General procedure A for the Preparation of *N*-fluoro-*N*-(phenylsulfonyl) benzamide (FPSBA) Derivatives** To a 100 mL round bottom flask equipped with a large magnetic stir bar, was added *N*-fluorobenzenesulfonamide (3.94 g, 0.023 mol, 1.5 equiv.), pyridine (2.53 g, 0.018 mol, 1.2 equiv.) and DCM (30 mL), the solution was stirred at 0 °C. Then benzoyl chloride (2.11 g, 0.015 mol, 1 equiv) dissolved in DCM (20 mL) was added dropwise to the solution (20 min). The solution was stirred at room temperature for 3 hours after the addition was complete. The mixture was quenched with hydrochloric acid (6 N) and then extracted with saturated sodium carbonate and brine. The combined organic layer was dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was further purified through recrystallization to afford FPSBA. (3.77 g, 90%, white solid). The procedure for the preparation FPSBA derivatives **4,5,6** were followed general procedure A.

**General Procedure B for the Preparation of Compound 3.** To a mixture of FPSBA (**1**, 0.6 mmol, 3.0 equiv), potassium carbonate (0.24 mmol, 1.2 equiv) and DMAP (0.010 mmol, 0.05 equiv) in THF (3.0 mL) were added N-ethylaniline (0.20 mmol, 1.0 equiv) with stirring at 50 °C overnight. The reaction was monitored by thin layer chromatography until completion. After the complete conversion of starting material, the reaction mixture was concentrated and directly purified by column chromatography on silica gel (eluent: PE:EA = 60:1).

***N*-fluoro-*N*-(phenylsulfonyl) benzamide** (**1a**) Following general procedure A, **1a** was obtained in 92% yield (257 mg, 1 mmol) as a white solid. M.p.: 68.9-69.8 °C. IR (KBr, cm$^{-1}$): v 3050, 2934, 1750, 1659, 1534, 1358, 1294, 1058. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.87 – 7.83 (m, 2H), 7.80 – 7.74 (m, 1H), 7.72 – 7.66 (m, 1H), 7.61 (t, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.9, 135.8, 135.0, 133.4, 130.9, 130.8, 129.64, 129.62, 128.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -50.12. HRMS-EI (m/z) calcd. for ($C_{13}H_{10}FNO_3S$) 279.0365, found 279.0366.

***N*-fluoro-4-methyl-*N*-(phenylsulfonyl) benzamide (1b)** Following general procedure A, **1b** was obtained in 96% yield (283 mg, 1 mmol) as a white solid. M.p.: 113.4-114.6 °C. IR (KBr, cm$^{-1}$): v 3262, 3090, 2925, 1777, 1726, 1605, 1579, 1505, 1472, 1389. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.80 (m, 3H), 7.80 - 7.73 (m, 2H), 7.64 - 7.56 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.7 (d, *J* = 4.9 Hz), 146.5, 133.3, 131.1, 131.0, 129.6, 129.4, 128.3, 128.2, 22.08. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -50.70. HRMS-EI (m/z) calcd. for ($C_{14}H_{12}FNO_3S$) 293.0522, found 293.0523.

***N*-fluoro-2-methoxy-*N*-(phenylsulfonyl) benzamide (1c)** Following general procedure A, **1c** was obtained in 91% yield (282 mg, 1 mmol) as a white solid. M.p.: 83.9-84.5 °C. IR (KBr, cm$^{-1}$): v 3083, 3027, 2985, 2952, 1740, 1598, 1580, 1544, 1490, 1389. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.79 – 7.73 (m, 1H), 7.63 – 7.58 (m, 2H), 7.54 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.46 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.04 – 6.95 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.7 (d, *J* = 5.2 Hz), 158.3, 135.6, 134.8, 134.3, 131.5, 131.4, 129.5, 121.2, 120.4, 111.8, 55.9. $^{19}$F NMR (376 MHz, CDCl3) δ -50.18. HRMS-EI (m/z) calcd. for ($C_{14}H_{12}FNO_4S$) 309.0471, found 309.0470.

***N*-fluoro-*N*-(phenylsulfonyl)-4-(trifluoromethoxy) bezamide (1d)** Following general procedure A, **1d** was obtained in 89% yield (320 mg, 1 mmol) as a white solid. M.p.: 58.5-59.6 °C. IR (KBr, cm$^{-1}$): v 3065, 1739, 1690, 1606, 1508, 1450, 1393. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.89 – 7.84 (m, 2H), 7.81 – 7.75 (m, 1H), 7.65 – 7.59 (m, 2H), 7.33 (dq, *J* = 8.1, 1.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.6 (d, *J* = 4.9 Hz), 154.0 (d, *J* = 1.9 Hz), 136.0, 133.2, 133.0, 133.0, 129.7, 129.6, 129.1 (d, *J* = 2.2 Hz), 120.2. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.73, -57.51. HRMS-EI (m/z) calcd. for ($C_{14}H_9F_4NO_4S$) 363.0188, found 363.0187.

**N,2-difluoro-*N*-(phenylsulfonyl) benzamide (1e)** Following general procedure A, **1e** was obtained in 97% yield (288 mg, 1 mmol) as a white solid. M.p.: 71.5-72.3 °C. IR (KBr, cm$^{-1}$): v 3080, 1723, 1611, 1581, 1509, 1486, 1452, 1396. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.82 – 7.76 (m, 1H), 7.69 – 7.60 (m, 4H), 7.31 – 7.25 (m, 1H), 7.20 (ddd, *J* = 9.7, 8.4, 1.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.8, 162.0, 159.4, 136.0, 133.7, 131.7, 129.8, 129.4, 124.4 (d, *J* = 3.7 Hz), 120.2 (dd, *J* = 12.3, 2.3 Hz), 116.8 (d, *J* = 21.2 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -50.14, -109.57. HRMS-EI (m/z) calcd. for ($C_{13}H_9F_2NO_3S$) 297.0271, found 297.0272.

**N,4-difluoro-*N*-(phenylsulfonyl) benzamide (1f)** Following general procedure A, **1f** was obtained in 98% yield (288.5 mg, 1 mmol) as a white solid. M.p.: 90.1-91.1 °C. IR (KBr, cm$^{-1}$): v 3084, 3033, 1728, 1598, 1505, 1475, 1449, 1396. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.87 – 7.82 (m, 2H), 7.81 – 7.75 (m, 1H), 7.64 – 7.58 (m, 2H), 7.23 – 7.16 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.2, 167.7 (d, *J* = 5.0 Hz), 165.7, 135.9, 133.8 (dd, *J* = 9.7, 2.5 Hz), 133.2, 129.7, 129.6, 116.1 (d, *J* = 22.4 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -50.03, -100.92. HRMS-EI (m/z) calcd. for ($C_{13}H_9F_2NO_3S$) 297.0271, found 297.0272.

**N,3-difluoro-*N*-(phenylsulfonyl) benzamide (1g)** Following general procedure A, **1g** was obtained in 99% yield (294 mg, 1 mmol) as a white solid. M.p.: 77.9-78.6 °C. IR (KBr, cm$^{-1}$): v 3072, 1733, 1607, 1585, 1523, 1479, 1393, 1259, 1195. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.82 – 7.76 (m, 1H), 7.70 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.58 – 7.47 (m, 2H), 7.39 (tdd, *J* = 8.3, 2.6, 1.1 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.8, 163.5, 161.1, 136.0, 133.2, 130.4 (d, *J* = 7.8 Hz), 129.7, 129.6, 126.8 (t, *J* = 2.9 Hz), 122.1 (d, *J* = 21.2 Hz), 117.5 (dd, *J* =

23.9, 2.6 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.47, -110.99. HRMS-EI (m/z) calcd. for ($C_{13}H_9F_2NO_3S$) 297.0271, found 297.0273.

**2-chloro-*N*-fluoro-*N*-(phenylsulfonyl) benzamide (1h)** Following general procedure A, **1h** was obtained in 89% yield (274.2 mg, 1 mmol) as a white solid. M.p.: 100.9-101.7 °C. IR (KBr, cm$^{-1}$): v 3082, 1739, 1588, 1523, 1452, 1434, 1366, 1299. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.82 – 7.75 (m, 1H), 7.67 – 7.57 (m, 3H), 7.54 – 7.45 (m, 2H), 7.38 (td, *J* = 7.4, 1.5 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 5.3 Hz), 136.0, 134.0, 133.7, 132.6 (d, *J* = 2.0 Hz), 131.6 (d, *J* = 1.9 Hz), 131.1 (d, *J* = 2.1 Hz), 130.8, 129.8, 129.6, 126.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.44. HRMS-EI (m/z) calcd. for ($C_{13}H_9FClNO_3S$) 312.9976, found 312.9978.

**3-chloro-*N*-fluoro-*N*-(phenylsulfonyl) benzamide (1i)** Following general procedure A, **1i** was obtained in 91% yield (283.4 mg, 1 mmol) as a white solid. M.p.: 91.3-92.0 °C. IR (KBr, cm$^{-1}$): v 3089, 1739, 1592, 1562, 1449, 1393, 1192. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.84 – 7.76 (m, 3H), 7.68 – 7.60 (m, 3H), 7.46 (t, *J* = 7.9 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.8 (d, *J* = 4.7 Hz), 136.0, 134.9, 133.2, 132.6 (d, *J* = 2.1 Hz), 130.43, 130.4, 130.0, 129.8, 129.6, 129.0 (d, *J* = 2.6 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.54. HRMS-EI (m/z) calcd. for ($C_{13}H_9FClNO_3S$) 312.9976, found 312.9973.

**4-chloro-*N*-fluoro-*N*-(phenylsulfonyl) benzamide (1j)** Following general procedure A, **1j** was obtained in 92% yield (289 mg, 1 mmol) as a white solid. M.p.: 95.6-96.1 °C. IR (KBr, cm$^{-1}$): v 3093, 3042, 2965, 1729, 1591, 1485, 1448, 1390, 1342. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 1.9 Hz, 4H), 7.81 – 7.75 (m, 1H), 7.61 (t, *J* = 7.9 Hz, 2H), 7.53 – 7.46 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.0 (d, *J* = 5.0 Hz), 141.8, 136.0, 133.2, 132.2 (d, *J* = 2.6 Hz), 129.7, 129.6, 129.4 (d, *J* = 2.1 Hz), 129.1. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.99. HRMS-EI (m/z) calcd. for ($C_{13}H_9FClNO_3S$) 312.9976, found 312.9978.

**4-bromo-*N*-fluoro-*N*-(phenylsulfonyl) benzamide (1k)** Following general procedure A, **1k** was obtained in 94% yield (337 mg, 1 mmol) as a white solid. M.p.: 93.1-93.5 °C. IR (KBr, cm$^{-1}$): v 3100, 1708, 1584, 1575, 1449, 1392, 1305. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.81 – 7.73 (m, 3H), 7.68 – 7.64 (m, 2H), 7.63 – 7.59 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.14 (d, *J* = 4.8 Hz), 135.97, 133.19, 132.19 (d, *J* = 2.5 Hz), 132.11, 130.61, 129.83 (d, *J* = 2.2 Hz), 129.72, 129.57. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.97. HRMS-EI (m/z) calcd. for ($C_{13}H_9FBrNO_3S$) 356.9471, found 356.9467.

***N*-fluoro-4-nitro-*N*-(phenylsulfonyl) benzamide (1l)** Following general procedure A, **1l** was obtained in 98% yield (316.2 mg, 1 mmol) as a yellow solid. M.p.: 130.5-131.2 °C. IR (KBr, cm$^{-1}$): v 3065, 2360, 1749, 1558, 1540, 1391, 1340. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.39 - 8.32 (m, 2H), 8.06 - 8.02 (m, 2H), 7.89 - 7.85 (m, 2H), 7.84 - 7.78 (m, 1H), 7.68 - 7.61 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.3 (d, *J* = 4.7 Hz), 151.3, 136.3, 133.1, 131.71, 131.69, 129.9, 129.5, 123.8. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.08. ESI - MS: calcd for ($C_{13}H_9N_2O_5S$ [M-F]$^-$) 305.0232; found 305.0233.

**methyl 4-(fluoro(phenylsulfonyl)carbamoyl) benzoate (1m)** Following general procedure A, **1m** was obtained in 99% yield (333.7mg, 1 mmol) as a white solid. M.p.: 128.1-129.7 °C. IR (KBr, cm$^{-1}$): v 3066, 3034, 2963, 1764, 1740, 1650, 1623,1592, 1460, 1385, 1190. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 2H), 7.97 – 7.90 (m, 2H), 7.85 (dd, *J* = 10.0, 3.8 Hz, 2H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.69 – 7.59 (m, 2H), 3.97 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.3 (d, *J* = 4.7 Hz), 165.9, 136.0, 135.5, 134.6 (d, *J* = 2.2 Hz), 133.3 130.7 (d, *J* = 2.3 Hz), 129.8, 129.5, 52.8. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.56. ESI - MS: calcd for ($C_{15}H_{12}FNO_5SNa$ [M+Na]$^+$) 360.0318; found 360.0320.

***N*-fluoro-*N*-(phenylsulfonyl)-4-(trifluoromethyl) benzamide (1n)** Following general procedure A, **1n** was obtained in 93% yield (320.4 mg, 1 mmol) as a white solid. M.p.: 72.8-73.2 °C. IR (KBr, cm$^{-1}$): v 3103, 1740, 1581, 1508, 1475, 1410, 1396, 1326. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.90 – 7.84 (m, 2H), 7.83 – 7.75 (m, 3H), 7.67 – 7.60 (m, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 167.9 (d, *J* = 5.4 Hz), 136.1, 134.2, 133.3, 131.1 (d, *J* = 3.4 Hz), 129.8, 129.6, 125.7 (q, *J* = 4.2 Hz), 124.3, 122.5. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.49, -63.35. HRMS-EI (m/z) calcd. for ($C_{14}H_9F_4NO_3S$) 347.0239, found 347.0240.

***N*-fluoro-*N*-(phenylsulfonyl)-2-naphthamide (1o)** Following general procedure A, **1o** was obtained in 99% yield (325.7 mg, 1 mmol) as a white solid. M.p.: 91.2-92.5 °C. IR (KBr, cm$^{-1}$): v 3058, 1728, 1625, 1450, 1388, 1196, 1175. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 1.6 Hz, 1H), 8.01 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.86 (ddd, *J* = 8.6, 5.1, 1.5 Hz, 3H), 7.81 – 7.75 (m, 1H), 7.67 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.61 (ddd, *J* = 8.8, 7.3, 1.6 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.0 (d, *J* = 4.9 Hz), 136.4, 135.8, 133.8, 133.8, 133.3, 132.1, 130.0, 129.7, 129.6, 128.6, 128.2, 128.1, 127.5, 125.2 (d, *J* = 2.4 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.92. HRMS-EI (m/z) calcd. for ($C_{17}H_{12}FNO_3S$) 329.0522, found 329.0520.

***N*-fluoro-*N*-(phenylsulfonyl) thiophene-2-carboxamide (1p)** Following general procedure A, **1p** was obtained in 99% yield (284 mg, 1 mmol) as a white solid. M.p.: 71.8-72.3 °C. IR (KBr, cm$^{-1}$): v 3070, 3012, 1680, 1612, 1360, 1265. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.93 (d, *J* = 1.5 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.79 – 7.73 (m, 1H), 7.65 – 7.57 (m, 2H), 7.20 (dd, *J* = 4.9, 3.9 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 162.5 (d, *J* = 6.2 Hz), 137.7 (d, *J* = 5.0 Hz), 136.9 (d, *J* = 2.5 Hz), 135.8, 133.4, 129.8, 129.6, 128.6, 126.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -48.05. HRMS-EI (m/z) calcd. for ($C_{11}H_8FNO_3S_2$) 284.9930, found 284.9928.

**1-ethyl-1,3-diphenylurea (3aa)[14]** Following general procedure B, **3aa** was obtained in 84% yield (40 mg, 0.2 mmol) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.34 – 7.30 (m, 2H), 7.27 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.22 (dd, *J* = 8.7, 7.0 Hz, 2H), 6.98 (tt, *J* = 7.0, 1.5 Hz, 1H), 6.08 (s, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.1, 141.2, 139.0, 130.4, 128.9, 128.9, 128.3, 122.9, 119.3, 44.4, 13.9. HRMS-EI (m/z) calcd. for ($C_{16}H_{18}N_2O_2$) 240.1263, found 240.1261.

**1-ethyl-1-phenyl-3-(p-tolyl) urea (3ba)** Following general procedure B, **3ba** was obtained in 63% yield (34 mg, 0.2 mmol) as a white solid. M.p.: 87.6-88.3 °C. IR (KBr, cm$^{-1}$): v 3271, 2968, 1656, 1649, 1593, 1513, 1493, 1296, 810. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.42 – 7.37 (m, 1H), 7.34 – 7.28 (m, 2H), 7.16 – 7.11 (m, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.01 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.3, 141.4, 136.5, 132.5, 130.4, 129.4, 128.9, 128.2, 119.6, 44.3, 20.8, 13.9. HRMS-EI (m/z) calcd. for ($C_{16}H_{18}N_2O$) 254.1419, found 254.1422.

**1-ethyl-3-(2-methoxyphenyl)-1-phenylurea (3ca)** Following general procedure B, **3ca** was obtained in 65% yield (34 mg, 0.2 mmol) as a white solid. M.p.: 65.4-66.5 °C. IR (KBr, cm$^{-1}$): v 3165, 2589, 1630, 1536, 1511, 1374, 1243. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.5, 2.2 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 7.35 – 7.30 (m, 2H), 6.97 – 6.85 (m, 2H), 6.72 (dd, *J* = 7.5, 1.9 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.2, 147.7, 141.4, 130.2, 129.2, 129.0, 128.1, 122.0, 121.3, 118.6, 109.9, 55.8, 44.1, 14.0. HRMS-EI (m/z) calcd. for ($C_{16}H_{18}N_2O_2$) 270.1368, found 270.1366.

**1-ethyl-1-phenyl-3-(4-(trifluoromethoxy) phenyl) urea (3da)** Following general procedure B, **3da** was obtained in 80% yield (52 mg, 0.2 mmol) as

a white solid. M.p.: 56.3-57.6 °C. IR (KBr, $cm^{-1}$): v 3325, 2770, 1653, 1595, 1512, 1494, 1378, 1243. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.45 – 7.39 (m, 1H), 7.32 (d, *J* = 1.5 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 2H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.11 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 153.9, 144.4, 141.0, 137.8, 130.5, 128.9, 128.5, 121.7, 120.3, 119.4, 44.5, 13.8. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -58.23. HRMS-EI (m/z) calcd. for ($C_{16}H_{15}F_3N_2O_2$) 324.1086, found 324.1085.

**1-ethyl-3-(2-fluorophenyl)-1-phenylurea (3ea)** Following general procedure B, **3ea** was obtained in 72% yield (38 mg, 0.2 mmol) as a yellow oily liquid. IR (KBr, $cm^{-1}$): v 3431, 3062, 2971, 2931, 1684, 1618, 1595, 1523, 1453, 1368, 1251. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.19 (td, *J* = 8.3, 1.6 Hz, 1H), 7.50 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.35 – 7.30 (m, 2H), 7.11 – 7.04 (m, 1H), 6.98 – 6.86 (m, 2H), 6.38 (s, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 153.62 (d, *J* = 10.5 Hz), 151.17, 140.80, 130.45, 128.78, 128.51, 127.62 (d, *J* = 9.6 Hz), 124.50 (d, *J* = 3.7 Hz), 122.63 (d, *J* = 7.6 Hz), 120.93, 114.48 (d, *J* = 19.3 Hz), 44.37, 13.83. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -133.32. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}FN_2O$) 258.1168, found 258.1166.

**1-ethyl-3-(4-fluorophenyl)-1-phenylurea (3fa)** Following general procedure B, **3fa** was obtained in 78% yield (40.2 mg, 0.2 mmol) as a white solid. M.p.: 78.6-79.1 °C. IR (KBr, $cm^{-1}$): v 3176, 2983, 1652, 1595, 1510, 1410, 1375, 1305, 1215. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.44 – 7.38 (m, 1H), 7.34 – 7.29 (m, 2H), 7.24 – 7.18 (m, 2H), 6.96 – 6.87 (m, 2H), 6.03 (s, 1H), 3.79 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 159.6, 158.0, 154.3, 141.2, 135.0 (d, *J* = 3.4 Hz), 130.5, 129.0, 128.4, 121.3 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 22.4 Hz), 44.4, 13.9. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -120.41. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}FN_2O$) 258.1168, found 258.1169.

**1-ethyl-3-(3-fluorophenyl)-1-phenylurea (3ga)** Following general procedure B, **3ga** was obtained in 76% yield (39 mg, 0.2 mmol) as a white solid. M.p.: 61.7-62.5 °C. IR (KBr, $cm^{-1}$): v 3310, 2899, 1659, 1602, 1530, 1492, 1439, 1375, 1243. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.46 – 7.38 (m, 1H), 7.34 – 7.29 (m, 2H), 7.13 (td, *J* = 8.2, 6.5 Hz, 1H), 6.83 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 6.66 (tdd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 6.13 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 164.5, 162.0, 153.7, 140.9, 130.6, 129.8 (d, *J* = 9.5 Hz), 128.9, 128.6, 114.4 (d, *J* = 2.9 Hz), 109.6, 106.7, 44.5, 13.9. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -112.10. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}FN_2O$) 258.1168, found 258.1169.

**3-(2-chlorophenyl)-1-ethyl-1-phenylurea (3ha)** Following general procedure B, **3ha** was obtained in 69% yield (39 mg, 0.2 mmol) as a white solid. M.p.: 51.6-52.2 °C. IR (KBr, $cm^{-1}$): v 3215, 3025, 2983, 1648, 1598, 1523, 1480, 1395, 1255. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.45 – 7.39 (m, 1H), 7.37 – 7.32 (m, 2H), 7.24 – 7.17 (m, 2H), 6.91 – 6.84 (m, 1H), 6.80 (s, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 153.6, 140.7, 136.0, 130.4, 129.0, 128.7, 128.6, 127.6, 122.9, 122.1, 120.3, 44.2, 13.8. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}ClN_2O$) 274.0873, found 274.0872.

**3-(3-chlorophenyl)-1-ethyl-1-phenylurea (3ia)** Following general procedure B, **3ia** was obtained in 80% yield (44 mg, 0.2 mmol) as a white solid. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.45 – 7.40 (m, 1H), 7.37 (q, *J* = 1.6 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.14 – 7.10 (m, 2H), 6.96 – 6.92 (m, 1H), 6.09 (s, 1H), 3.79 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 153.7, 140.9, 140.3, 134.6, 130.6, 129.9, 128.9, 128.6, 122.9, 119.2, 117.2, 44.5, 13.9. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}ClN_2O$) 274.0873, found 274.0871.

**3-(4-chlorophenyl)-1-ethyl-1-phenylurea(3ja)** Following general procedure B, **3ja** was obtained in 73% yield (40 mg, 0.2 mmol) as a white solid. M.p.: 108.3-109.6 °C. IR (KBr, $cm^{-1}$): v 3298, 3094, 2978, 2930, 1651, 1592, 1514, 1493, 1403, 1306, 1243. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.44 – 7.38 (m, 1H), 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.14 (m, 2H), 6.08 (s, 1H), 3.78 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 153.9, 141.0, 137.7, 130.5, 128.9, 128.8, 128.5, 127.8, 120.5, 44.4, 13.8. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}ClN_2O$) 274.0873, found 274.0872.

**3-(4-bromophenyl)-1-ethyl-1-phenylurea (3ka)** Following general procedure B, **3ka** was obtained in 72% yield (45.4 mg, 0.2 mmol) as a white solid. M.p.: 63.9-65.0 °C. IR (KBr, $cm^{-1}$): v 3240, 3102, 2995, 1710, 1650, 1560, 1532, 1430, 1386. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.44 – 7.38 (m, 1H), 7.35 – 7.28 (m, 4H), 7.20 – 7.14 (m, 2H), 6.07 (s, 1H), 3.79 (q, *J* = 7.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 1H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 153.8, 141.0, 138.2, 131.8, 130.5, 128.9, 128.5, 120.8, 115.3, 44.5, 13.9. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}BrN_2O$) 318.0368, found 318.0366.

**1-ethyl-3-(4-nitrophenyl)-1-phenylurea (3la)** Following general procedure B, **3la** was obtained in 75% yield (42 mg, 0.2 mmol) as a claybank solid. M.p.: 59.8-60.3 °C. IR (KBr, $cm^{-1}$): v 3324, 3058, 2982, 2930, 1671, 1595, 1537, 1494, 1379, 1238. $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 7.56 – 7.49 (m, 2H), 7.47 – 7.44 (m, 1H), 7.44 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H) 6.46 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 153.0, 145.2, 142.4, 140.3, 130.7, 128.9, 128.8, 125.1, 118.0, 44.7, 13.7. HRMS-EI (m/z) calcd. for ($C_{15}H_{15}N_3O$) 285.1113, found 285.1111.

**methyl 4-(3-ethyl-3-phenylureido) benzoate (3ma)** Following general procedure B, **3ma** was obtained in 74% yield (42 mg, 0.2 mmol) as a white solid. M.p.: 86.7-87.9 °C. IR (KBr, $cm^{-1}$): v 3302, 2987, 2943, 1717, 1660, 1588, 1515, 1494, 1409, 1279. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.54 – 7.48 (m, 2H), 7.46 – 7.40 (m, 1H), 7.36 – 7.29 (m, 4H), 6.28 (s, 1H), 3.86 (s, 3H), 3.80 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 166.9, 153.4, 143.3, 140.8, 131.7, 130.8, 130.6, 128.8, 128.6, 124.1, 118.0, 113.9, 52.0, 44.5, 13.8. HRMS-EI (m/z) calcd. for ($C_{17}H_{18}N_2O_3$) 298.1317, found 298.1318.

**1-ethyl-1-phenyl-3-(4-(trifluoromethyl) phenyl) urea (3na)** Following general procedure B, **3na** was obtained in 60% yield (37 mg, 0.2 mmol) as a white solid. M.p.: 78.7-79.6 °C. IR (KBr, $cm^{-1}$): v 3325, 3092, 2995, 1735, 1620,1598, 1560, 1434, 1178. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.48 – 7.42 (m, 3H), 7.40 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 6.24 (s, 1H), 3.81 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 153.6, 142.2, 140.8, 130.6, 128.9, 128.7, 126.2 (q, *J* = 4.2 Hz), 118.5, 44.6, 13.8. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -61.88. HRMS-EI (m/z) calcd. for ($C_{16}H_{15}F_3N_2O$) 308.1136, found 308.1137.

**1-ethyl-3-(naphthalen-2-yl)-1-phenylurea (3oa)** Following general procedure B, **3oa** was obtained in 45% yield (24 mg, 0.2 mmol) as a white solid. M.p.: 75.5-76.1 °C. IR (KBr, $cm^{-1}$): v 3349, 3205, 3012, 2898, 1718, 1635, 1522, 1408, 1396, 1078. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.2 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.47 – 7.42 (m, 1H), 7.37 (d, *J* = 1.6 Hz, 2H), 7.35 (d, *J* = 1.1 Hz, 2H), 7.23 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.26 (s, 1H), 3.85 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (151 MHz, $CDCl_3$) δ 154.2, 141.2, 136.6, 134.2, 130.5, 130.1, 129.0, 128.6, 128.4, 127.6, 127.5, 126.4, 124.4, 120.1, 115.1, 44.5, 13.9. HRMS-EI (m/z) calcd. for ($C_{19}H_{18}N_2O$) 290.1419, found 290.1420.

**1-ethyl-3-phenyl-1-(m-tolyl) urea (3ab)** Following general procedure B, **3ab** was obtained in 75% yield (38 mg, 0.2 mmol) as a white solid. M.p.: 53.6-54.5 °C. IR (KBr, $cm^{-1}$): v 3313, 3021, 2975, 2926, 1655, 1597, 1533, 1487, 1363, 1261, 1242, 840. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 1H), 7.44 – 7.40 (m, 2H), 7.36 (td, *J* = 8.9, 8.0, 2.1 Hz, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.12 (tt, *J* = 7.2, 1.4 Hz, 1H), 6.25 (s, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.1, 141.1, 140.6, 139.1, 130.1, 129.4, 129.1, 128.9, 125.9, 122.8, 119.3, 44.3, 21.5, 13.9. HRMS-EI (m/z) calcd. for ($C_{16}H_{18}N_2O$) 254.1419, found 254.1421.

**1-ethyl-3-phenyl-1-(p-tolyl) urea (3ac)** Following general procedure B, **3ac** was obtained in 68% yield (35 mg, 0.2 mmol) as a white solid. M.p.: 62.9-63.5 °C. IR (KBr, $cm^{-1}$): v 3325, 3032, 2987, 2945,1682, 1602, 1545, 1434, 1396, 1259, 870. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 4H), 7.24 – 7.21 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.97 (tt, *J* = 7.2, 1.4 Hz, 1H), 6.10 (s, 1H), 3.77 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.3, 139.2, 138.5, 138.4, 131.0, 128.9, 128.8, 122.8, 119.3, 44.3, 21.3, 13.9. HRMS-EI (m/z) calcd. for ($C_{16}H_{18}N_2O$) 254.1419, found 254.1421.

**1-methyl-1,3-diphenylurea (3ad)[15]** Following general procedure B, **3ad** was obtained in 80% yield (36 mg, 0.2 mmol) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.42 – 7.37 (m, 1H), 7.34 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.23 (dd, *J* = 8.7, 7.0 Hz, 2H), 6.99 (tt, *J* = 7.1, 1.5 Hz, 1H), 6.23 (s, 1H), 3.35 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.6, 143.1, 139.0, 130.5, 129.0, 128.0, 127.6, 123.1, 119.4, 29.9. HRMS-EI (m/z) calcd. for ($C_{14}H_{14}N_2O$) 256.1106, found 256.1108.

**1-methyl-3-phenyl-1-(m-tolyl) urea (3ae)** Following general procedure B, **3ae** was obtained in 80% yield (36 mg, 0.2 mmol) as a white solid. M.p.: 78.7-79.5 °C. IR (KBr, $cm^{-1}$): v 3343, 3051, 2996, 2890, 1655, 1599, 1533, 1438, 1321, 1260. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.23 (dd, *J* = 8.8, 7.0 Hz, 2H), 7.18 (ddq, *J* = 7.5, 1.8, 0.9 Hz, 1H), 7.16 – 7.11 (m, 2H), 6.98 (tt, *J* = 6.9, 1.4 Hz, 1H), 6.26 (s, 1H), 3.32 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.6, 142.9, 140.7, 139.0, 130.2, 128.9, 128.8, 128.2, 124.5, 123.0, 119.4, 37.4, 21.5. HRMS-EI (m/z) calcd. for ($C_{15}H_{16}N_2O$) 240.1263, found 240.1262.

**1-isopropyl-1,3-diphenylurea (3af)** Following general procedure B, **3af** was obtained in 52% yield (27 mg, 0.2 mmol) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.26 (d, *J* = 1.4 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.04 – 6.96 (m, 1H), 5.87 (s, 1H), 4.99 (p, *J* = 6.8 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 6H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.2, 139.1, 137.5, 131.3, 130.0, 129.0, 128.9, 122.8, 119.4, 46.7, 21.6. HRMS-EI (m/z) calcd. for ($C_{16}H_{18}N_2O$) 254.1419, found 254.1420.

**1-benzyl-1,3-diphenylurea (3ag)[16]** Following general procedure B, **3ag** was obtained in 58% yield (35 mg, 0.2 mmol) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.34 – 7.30 (m, 2H), 7.30 – 7.26 (m, 5H), 7.24 (d, *J* = 1.5 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.00 (tt, *J* = 7.2, 1.3 Hz, 1H), 6.19 (s, 1H), 4.94 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.48, 141.30, 138.93, 138.34, 130.34, 128.96, 128.83, 128.66, 128.53, 128.38, 127.43, 123.12, 119.47, 53.59. HRMS-EI (m/z) calcd. for ($C_{20}H_{18}N_2O$) 302.1419, found 302.1421.

**1-butyl-1,3-diphenylurea (3ah)** Following general procedure B, **3ah** was obtained in 56% yield (30 mg, 0.2 mmol) as a white solid. M.p.: 64.9-65.6 °C. IR (KBr, $cm^{-1}$): v 3294, 3056, 2958, 2926, 2857, 1652, 1595, 1522, 1493, 1439, 1378, 1239. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.44 – 7.37 (m, 1H), 7.34 – 7.30 (m, 2H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 1.4 Hz, 1H), 7.22 (dd, *J* = 8.7, 6.9 Hz, 2H), 7.03 – 6.93 (m, 1H), 6.09 (s, 1H), 3.77 – 3.70 (m, 2H), 1.59 – 1.49 (m, 2H), 1.35 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.3, 141.6, 139.1, 130.4, 128.9, 128.9, 128.3, 122.9, 119.3, 49.4, 30.8, 20.2, 14.0. HRMS-EI (m/z) calcd. for ($C_{17}H_{20}N_2O$) 268.1576, found 268.1577.

**1-cyclohexyl-1,3-diphenylurea (3ai)** Following general procedure B, **3ai** was obtained in 52% yield (31 mg, 0.2 mmol) as a white solid. M.p.: 78.9-79.6 °C. IR (KBr, $cm^{-1}$): v 3305, 3028, 2995, 2946, 1612, 1572, 1530, 1462, 1393, 1195. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.41 (m, 3H), 7.27 – 7.23 (m, 3H), 7.23 – 7.17 (m, 3H), 6.95 (tt, *J* = 6.5, 2.0 Hz, 1H), 5.81 (s, 1H), 4.51 (tt, *J* = 12.1, 3.6 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.74 (dt, *J* = 14.1, 3.3 Hz, 2H), 1.41 (qt, *J* = 13.5, 3.6 Hz, 2H), 1.06 (qd, *J* = 12.4, 3.7 Hz, 2H), 0.97 – 0.81 (m, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 154.2, 139.2, 138.0, 131.3, 130.0, 129.0, 128.9, 122.8, 119.3, 54.7, 32.4, 26.1, 25.6. HRMS-EI (m/z) calcd. for ($C_{19}H_{22}N_2O$) 294.1732, found 294.1731.

***N*-phenylindoline-1-carboxamide (3aj)** Following general procedure B, **3aj** was obtained in 58% yield (27 mg, 0.2 mmol) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.30 (m, 2H), 7.20 (t, *J* = 7.9 Hz, 2H), 7.12 – 7.05 (m, 1H), 7.00 – 6.91 (m, 1H), 6.48 (s, 1H), 4.10 (t, *J* = 8.5 Hz, 2H), 3.25 (t, *J* = 8.5 Hz, 2H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 152.4, 143.3, 138.4, 130.8, 129.2, 127.9, 124.9, 123.8, 122.6, 120.3, 115.1, 47.7, 29.8, 28.1. HRMS-EI (m/z) calcd. for ($C_{15}H_{14}N_2O$) 238.1106, found 238.1107.

***N*-fluoro-*N*-tosylbenzamide (4)** Following general procedure B, compound **4** was obtained in 92% yield (269.5 mg, 1 mmol) as a white solid. M.p.: 94.5-95.8 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.76 – 7.71 (m, 2H), 7.68 – 7.63 (m, 1H), 7.57 – 7.47 (m, 2H), 7.42 – 7.36 (m, 2H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, *J* = 4.7 Hz), 147.4, 134.9, 131.2 (d, *J* = 2.1 Hz), 130.9 (d, *J* = 2.4 Hz), 130.3, 129.6, 128.6, 22.0. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -50.38. HRMS-EI (m/z) calcd. for ($C_{14}H_{12}FNO_3S$) 293.0522, found 293.0520.

***N*-fluoro-*N*-((4-nitrophenyl) sulfonyl) benzamide (5)** Following general procedure B, compound **5** was obtained in 85% yield (275.4 mg, 1 mmol) as a white solid. M.p.: 129.5-130.9 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.41 (m, 2H), 8.13 – 8.07 (m, 2H), 7.94 – 7.86 (m, 2H), 7.76 – 7.68 (m, 1H), 7.57 – 7.49 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.4, 151.9, 138.8, 135.6, 131.2, 131.0 (d, *J* = 2.9 Hz), 130.2 (d, *J* = 1.9 Hz), 128.9, 124.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -47.50. HRMS-EI (m/z) calcd. for ($C_{13}H_9FN_2O_5S$) 324.0216, found 324.0218.

***N*-((4-chlorophenyl) sulfonyl)-*N*-fluorobenzamide (6)** Following general procedure B, compound **6** was obtained in 90% yield (281 mg, 1 mmol) as a white solid. M.p.: 94.7-96.1 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.8 (d, *J* = 4.7 Hz), 142.9, 135.2, 131.7, 131.0, 131.0, 130.9 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 2.1 Hz), 130.1, 128.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -49.09. HRMS-EI (m/z) calcd. for ($C_{13}H_9ClFNO_3S$) 312.9976, found 312.9975.

***N*-(phenylsulfonyl) benzamide (7)[17]** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.89 – 7.84 (m, 2H), 7.68 – 7.62 (m, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 7.40 – 7.33 (m, 2H), 7.19 – 7.11 (m, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 165.9, 138.0, 135.1, 132.0, 129.2, 128.9, 127.2, 124.7, 120.4. HRMS-EI (m/z) calcd. for ($C_{13}H_{11}NO_3S$) 261.0460, found 261.0461.

***N*-phenylbenzamide (8)[18]** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.90 – 7.82 (m, 2H), 7.71 – 7.61 (m, 2H), 7.58 – 7.51 (m, 1H), 7.46 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.19 – 7.11 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.9, 138.1, 135.2, 132.0, 129.3, 129.0, 127.2, 124.7, 120.3. HRMS-EI (m/z) calcd. for ($C_{13}H_{11}NO$) 197.0841, found 197.0839.

**phenyl benzoate (9)**[19] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.3, 151.1, 133.7, 130.3, 129.7, 129.6, 128.7, 126.0, 121.9. HRMS-EI (m/z) calcd. for ($C_{13}H_{10}O_2$) 198.0681, found 198.0684.

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**Keywords:** C-N Aryl Migration • Rearrangement • Metal-free • N-F Compound • Alkyl Aryl Amine

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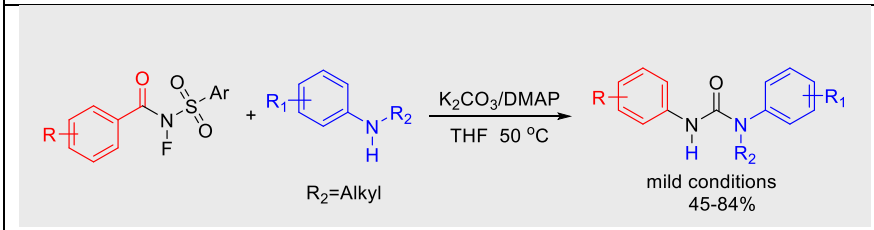


**Key Topic**: Rearrangement, C-N Aryl Migration, N-F Compound

A novel aryl C-N shift rearrangement reaction to form alkyl diaryl ureas from facilely available FPSBA derivates was developed. FPSBA selectively reacted with secondary alkyl phenyl amines to afford unsymmetrical alkyl diaryl ureas in good yields and the proceed undergo the vicinal $S_N2'$ mechanism rather than the traditional isocyanate intermediate pathway.

*Yi-Xiao Zhao, Tian Xie, San-Ke Yang, * and Xian-Jin Yang **

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**A novel C-N Migration Rearrangement Based on N-F Compounds for the Synthesis of N-alkyl Diaryl Ureas**