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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.5b02755 • Publication Date (Web): 11 Mar 2016

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Sulfonyl Azides as Precursors in Ligand-free Palladium-Catalyzed Synthesis of Sulfonyl Carbamates and Sulfonyl Ureas and Synthesis of Sulfonamides

*Shiao Y. Chow,[a] Marc Y. Stevens,[a] Luke R. Odell[a]**

Organic Pharmaceutical Chemistry, Department of Medicinal Chemistry, Uppsala Biomedical Center, Uppsala University, P. O. Box 574, SE-751 23 Uppsala, Sweden

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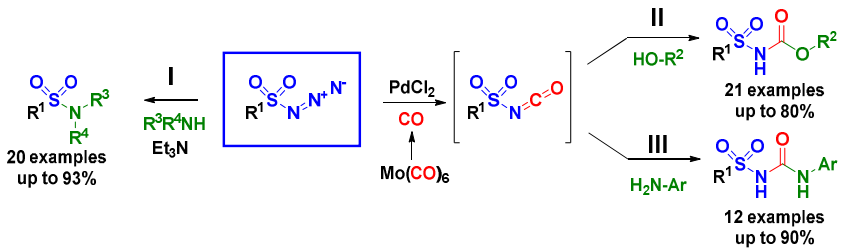
To whom correspondence should be addressed. Luke Odell, Phone: +46-18-4714297, Fax: +46-18-4714474. E-mail: luke.odell@orgfarm.uu.se

Graphical Abstract



Abstract

An efficient synthesis of sulfonyl carbamates and sulfonyl ureas from sulfonyl azides employing a palladium-catalyzed carbonylation protocol has been developed. Using a two-chamber system, sulfonyl azides, $PdCl_2$, and CO gas, released *ex situ* from $Mo(CO)_6$, were assembled to generate sulfonyl isocyanates *in situ* and alcohols and aryl amines were exploited as nucleophiles to afford a broad range of sulfonyl carbamates and sulfonyl ureas. A protocol for the direct formation of substituted sulfonamides from sulfonyl azides and amines *via* nucleophilic substitution was also developed.

Introduction

Sulfonyl-containing moieties (sulfonamides, sulfonyl carbamates, and sulfonyl ureas) are an important class of functional group, particularly in pharmaceuticals due to their hydrogen bonding capabilities, structural rigidity and potential role as non-cleavable amide surrogates (Figure 1).[1] Conventionally, sulfonyl carbamates (also useful N-nucleophiles for the Mitsunobu reaction)[2] are synthesized via *N*-acylation of a sulfonamide with a pre-activated carbonic acid derivative (chloroformate or anhydride) in the presence of a strong base, or in milder conditions using an acylating catalyst (i.e. DMAP).[3] Very recently, the preparation of sulfonyl carbamates from sulfamoyl inner salts and organometallic nucleophiles was reported.[4] Sulfonyl ureas are commonly synthesized from the condensation of aryl sulfonamides with phenoxycarbamates[5] or isocyanates[6] or alternatively by aminolysis of sulfonyl carbamates with alkyl[7] or (hetero)arylamines.[8]

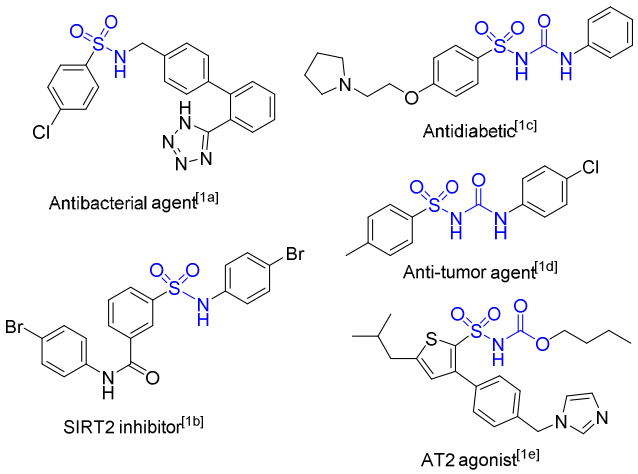
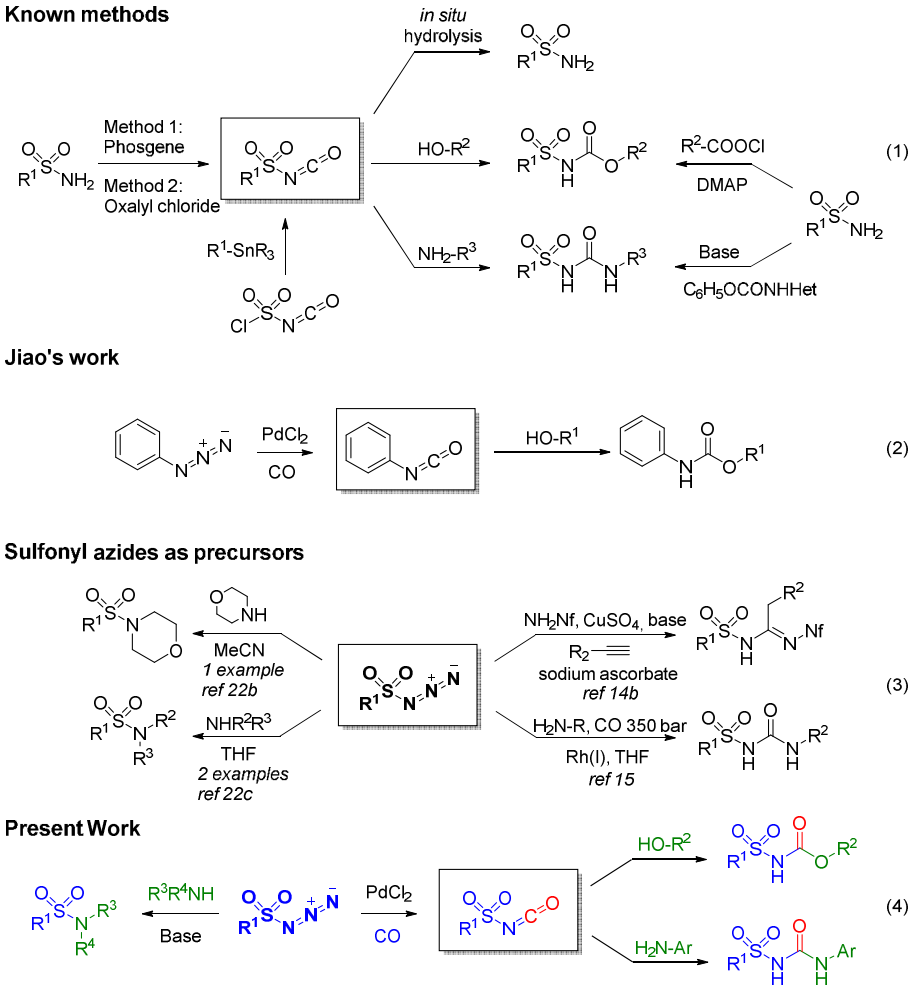


Figure 1. Biologically active sulfonyl group containing compounds

An alternate and arguably more divergent synthesis of sulfonamides, sulfonyl carbamates and sulfonyl ureas is *via* the reaction of a sulfonyl isocyanate intermediate with an appropriate nucleophile (Scheme 1).[9] Unfortunately, the utility of this synthetic manifold is currently hampered by the limited commercial availability of sulfonyl isocyanates and a paucity of simple, effective and environmentally friendly methods for their preparation. Sulfonyl isocyanates are typically prepared by reacting sulfonyl ureas or sulfonamides and alkyl isocyanates with phosgene[10] or oxalyl chloride followed by heating in *o*-dichlorobenzene [Eq. (1)].[9a] Recently, Jiao *et al.* reported a mild and facile palladium-

catalyzed synthesis of aryl carbamates *via* aryl isocyanate intermediates by assembling inexpensive aryl azides, carbon monoxide (CO), and alcohols without the use of costly and environmentally unfriendly reagents [Eq. (2)].[11] Accordingly, we proposed that sulfonyl isocyanates could also be generated *in situ* from sulfonyl azides and CO via palladium-catalyzed carbonylation[12] in a one-pot, cascade reaction with amines or alcohols to afford sulfonyl ureas and sulfonyl carbamates.



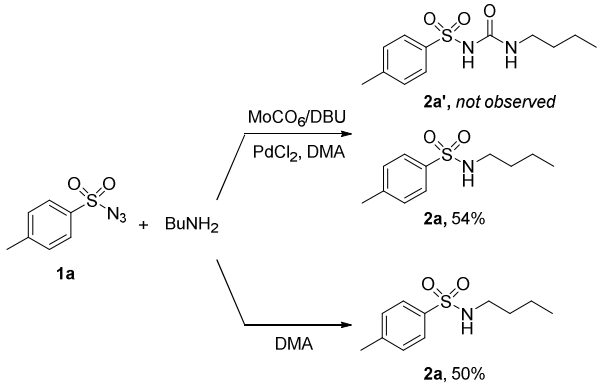
Scheme 1. Synthesis of sulfonamides, sulfonyl carbamates and sulfonyl ureas.

The sulfonyl azide functional group has been the subject of intense research over the past decade and has been reported to undergo a wealth of diverse and unique transformations[13] (e.g cycloaddition, amidation, amination) to form sulfonyl-containing pharmacophores, such as 1,2,3-triazoles, amidates, amidines and amides.[13b,14] More importantly, they can be readily accessed from primary sulfonamides *via* a diazotransfer process or by treatment of sulfonyl chlorides with sodium azide.[13a] The conversion

of sulfonyl azides to sulfonyl ureas *via* a carbonylative process[15] has been reported by Långström *et al.,* but this method requires the use of expensive rhodium catalysts and specialized high pressure equipment, limiting its synthetic utility. In addition, the carbonylative synthesis of sulfonyl carbamates from sulfonyl azides has, to the best of our knowledge, not yet been reported. We report herein a practical, divergent and environmentally benign ligand-free palladium-catalyzed synthesis of sulfonyl carbamates and sulfonyl ureas from sulfonyl azides *via in situ* generation of sulfonyl isocyanates and subsequent nucleophilic attack by alcohols or aryl amines [Eq. (3)]. A modified two-chamber vial-system[16] originally disclosed by Skrydstrup *et al.*[17] was employed, using $Mo(CO)_6$ as an *ex situ* CO releasing source (Chamber A) for the carbonylative transformations (Chamber B). We also report an unexpected direct synthesis of substituted sulfonamides from sulfonyl azides and alkyl amine nucleophiles [Eq. (3)].

Results and Discussion

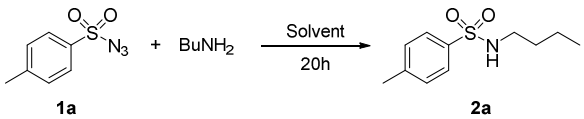
The initial study commenced with the treatment of *p*-tolyl sulfonyl azide (**1a**) with butylamine (2 equiv), 5 mol% $PdCl_2$, and $MoCO_6$ as the *ex situ* CO generating source. Formation of desired sulfonyl urea **2a'** was not observed (ESI-MS analysis), and unexpectedly, the substituted sulfonamide **2a** was obtained in 54% yield (Scheme 2). To delineate the mechanism of the unexpected reaction, **1a** and butylamine were subjected to a one-pot reaction in the absence of metal catalyst and carbon monoxide (Scheme 2, Table 1, Entry 1), furnishing **2a** in 50% yield. It was hypothesized that **2a** was the product of a direct nucleophilic attack on **1a** by butylamine, analogous to the formation of amides from acyl azides and aminea via *N*-acylation[18] employing a substitution mechanism similar to that observed for the reaction of sulfonyl chlorides.



Scheme 2. Unexpected formation of substituted sulfonamide **2a.**

The synthesis of substituted sulfonamides using sulfonyl azides as precursors has been previously reported by Chang and co-workers, however the preparation involved a multi-component copper-catalyzed hydrative reaction between sulfonyl azides, terminal alkynes and water in the presence of an amine base to afford the resulting sulfonamides.[19] Cyclic sulfonamides (benzosultams) have also been prepared *via* intramolecular nitrene insertion of C-H bonds with sulfonyl azides using cobalt (II) catalysts.[20] In previous reports, sulfonyl azides have also been used as diazotransfer agents in the presence of amines (and other CH-acid compounds such as activated esters, beta-ketoesters and ketosulfones), and formation of sulfonamides was not observed.[21] Indeed, amine-containing substrates led to decreased yields in diazotransfer reactions between sulfonamides and an imidazole-1-sulfonyl azide salt, possibly due to nitrogen interaction with the $S^{(VI)}$ center.[13a] The catalyst-free direct nucleophilic substitution reaction between sulfonyl azides and amines represents an attractive and simple preparation of substituted sulfonamides and there are only a few rare examples of this type of reaction reported in the literature.[22] Notably, this method has great potential for the selective late-stage functionalization of primary sulfonamide derivatives, which can be readily transformed into sulfonyl azides *via* diazotransfer.[13a,14b,22d] Subsequent optimization studies were then carried out (Table 1) and it was discovered that the reaction proceeded smoothly at ambient temperature, polar solvents (DMA > MeCN > THF > MeOH > toluene) were favored and the addition of TEA as base afforded a drastic improvement in efficiency and **2a** was isolated in 84% yield.

Table 1. Optimization of the direct synthesis of **2a**



1a **2a**

entry	solvent	temp (°C)	yield[a]
1	DMA	75	50%
2	DMA	rt	55%
3	THF	rt	35%
4	MeCN	rt	37%
5	MeOH	rt	31%
6	Toluene	rt	28%
7	-	rt	21%
8[b]	DMA	rt	84%

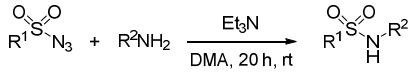
[a]Isolated yield. [b]1 equiv TEA was added.

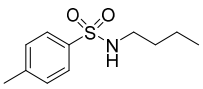
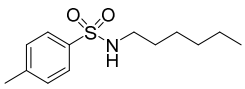
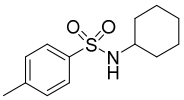
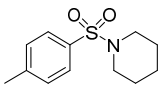
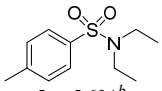
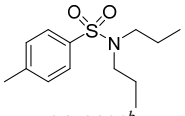
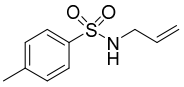
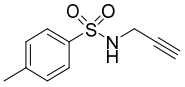
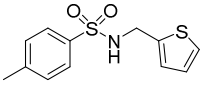
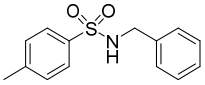
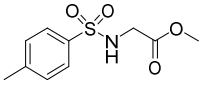
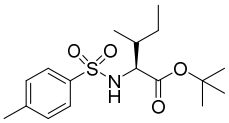
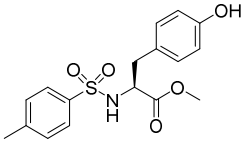
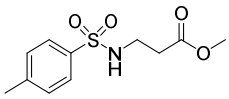
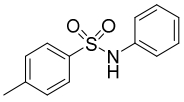
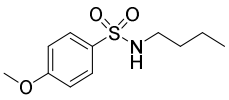
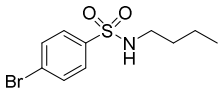
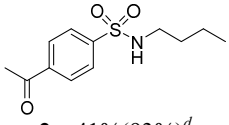
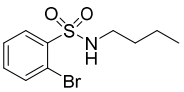
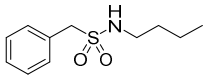
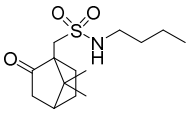
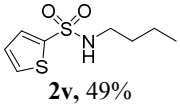
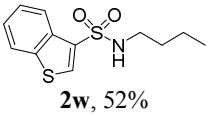
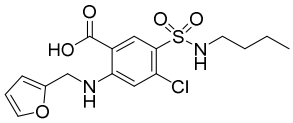
Using the optimized protocol, the substrate scope in respect to the amine component was investigated (Table 2). The reaction performed well with primary and unhindered secondary amines affording moderate to excellent yields of sulfonamides **2b**–**2d**. Hindered secondary amines were found to react less efficiently and returned decreased yields due to unfavorable steric effects resulting in the competing decomposition of the azide starting material (**2e**, **2f**, 33–36%). Notably, good chemoselectivity was observed with allylamine and propargylamine with no traces of side-products being observed by ESI-MS analysis (**2g**, **2h**). Heterocyclic and benzylic amines reacted smoothly to give the desired sulfonamide in moderate yields (**2i**, **2j**). However, amino acids performed poorly as substrates, with a low yield obtained for glycine methyl ester (**2k**) and only traces of product were observed for bulkier amino acids (**2l**, **2m**). This is most likely due to reduced nucleophilicity as a result of the electron-withdrawing character of the adjacent α-carboxyl group. However, this effect was offset by the addition of a methylene group, demonstrated by a substantial increase in isolated yield (61%) for the β-alanine-derivative **2n**. Additionally, no reaction was observed when employing poorly nucleophilic aniline as a substrate (**2o**).

Next, the reaction scope was extended to include different sulfonyl azides and substrates carrying electron-donating or electron-withdrawing groups in the *para*-position were found to be well-tolerated (**2p**–**2r**). The lower yield observed in **2r** was due to instability of the sulfonyl azide precursor, despite the reaction being carried out at room temperature. The presence of an *ortho* substituent was also

compatible with the reaction and 59% of desired product **2s** was obtained. Interestingly, no reaction was observed for alkyl sulfonyl azide substrates, indicating a requirement for an aryl group on the sulfur atom (**2t, 2u**). Electron-rich heterocyclic azides afforded moderate yields of the desired products (**2v, 2w**) and the diuretic furosemide was chemoselectively transformed into sulfonamide analogue **2x** in modest yield.

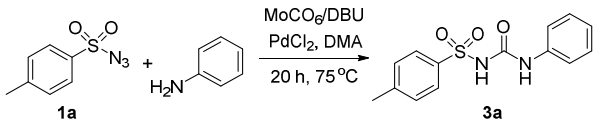
Table 2: Synthesis of various sulfonamides from different sulfonyl azides and amines[a]



 **2a,** 84%	 **2b,** 86%	 **2c,** 45%	 **2d,** 90%
 **2e,** 36%[b]	 **2f,** 33%[b]	 **2g,** 59%	 **2h,** 58%
 **2i,** 64%	 **2j,** 64%	 **2k,** 19%[c]	 **2l,** *trace*[c]
 **2m,** *trace*[c]	 **2n,** 61%	 **2o,** no reaction	 **2p,** 70%
 **2q,** 85%	 **2r,** 41%(93%)[d]	 **2s,** 59%	 **2t,** no reaction
 **2u,** no reaction	 **2v,** 49%	 **2w**, 52%	 **2x,** 23%

[a]Isolated yield. Reaction conditions: Sulfonyl azide (0.25 mmol, 1.0 equiv), amine (0.50 mmol, 2 equiv) and Et_3N (0.25 mmol, 1.0 equiv) in DMA (1 mL). [b]4 equiv amine, 6 equiv Et_3N for 5 days. [c]4 equiv amine, 6 equiv Et_3N for 4 days. [d]Reaction run without Et_3N.

Table 3. Optimization of the carbonylative synthesis of **3a**

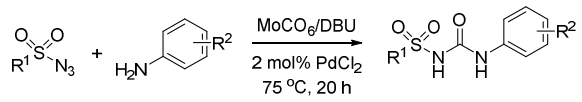


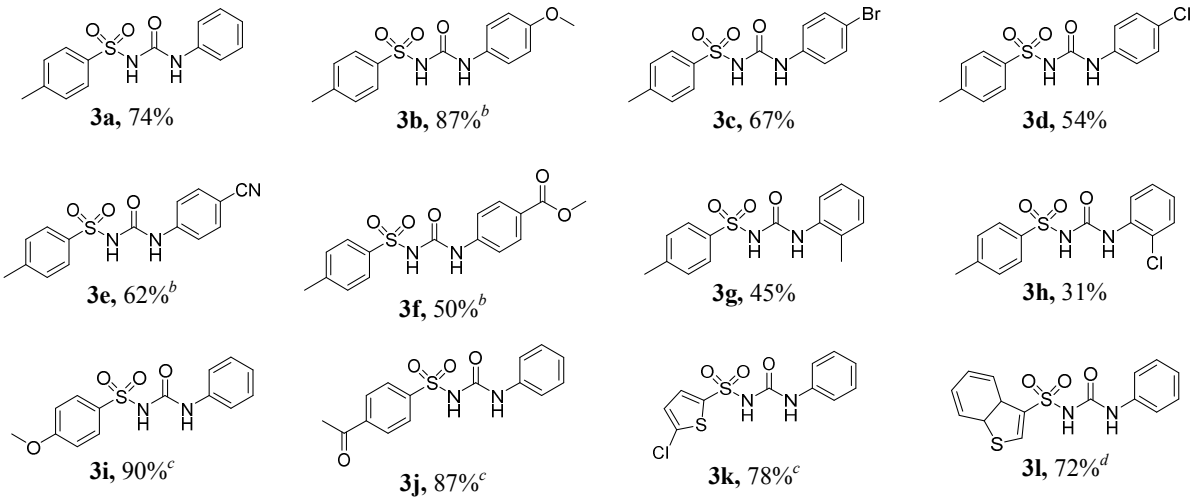
entry	$PdCl_2$ [mol%]	aniline [equiv]	yield[a]
1	5%	2	73%
2	5%	1	76%
3	2%	1	74%

[a]Isolated yield

Based on the lack of formation of sulfonamide **2o** from **1a** and aniline, we hypothesized that the palladium-catalyzed carbonylative transformation to corresponding sulfonyl urea **3a** would not be hampered by the competing nucleophilic substitution reaction. Accordingly, the synthesis of **3a** was explored using **1a**, excess aniline, 5 mol% $PdCl_2$, and $MoCO_6$ as the CO source (Table 3). Gratifyingly, the reaction afforded **3a** in an isolated yield of 73%. Significant formation of diphenylurea from aniline and CO was also observed and this was circumvented by using a stoichiometric amount of aniline. The amount of catalyst was also reduced to 2 mol% without concomitant reduction in yield. In addition, the product was purified as the TEA salt as sulfonyl ureas are prone to undergo acid- or self-catalyzed hydrolysis.[23] With these conditions in hand, we next studied the scope and limitations of the reaction (Table 4). *Para*- and *ortho*-substituted anilines carrying electron-donating or electron-withdrawing substituents gave the corresponding urea products in moderate to excellent yields (**3b**–**3h**). Notably, this methodology enables the isocyanate-free preparation of antitumor agent **3d**.[1d] Arylsulfonyl azides with electron-donating or electron-withdrawing p*ara*-substituents also performed well and returned excellent yields (**3i**, **3j**, 90% and 87%, respectively). Heteroarylsulfonyl azides underwent smooth conversion to the corresponding sulfonyl ureas, albeit in slightly decreased yields (**3k**–**3l**). Finally, due to the observed formation of primary sulfonamide side-products, resulting from thermal decomposition of arylsulfonyl azide substrates, the sulfonyl isocyanate intermediates or the sulfonyl urea products, lower reaction temperatures (30–50 °C) were employed in the preparation of sulfonyl ureas **3e**, **3f** and **3i**–**3l**.

Table 4: Synthesis of sulfonyl ureas from different sulfonyl azides and aryl amines[a]





[a]Isolated yield. Reaction conditions: **Chamber A**: $Mo(CO)_6$ (0.15 mmol, 0.6 equiv) and DBU (0.38 mmol, 1.5 equiv) in DMA (2 mL). **Chamber B**: Sulfonyl azide (0.25 mmol, 1.0 equiv), amine (0.25 mmol, 1.0 equiv), $PdCl_2$ (0.006 mmol, 0.02 equiv) in DMA (2 mL).[b]40 °C. [c]50 °C. [d]30 °C.

Encouraged by the above results, we next set about exploring the use of alcohols as nucleophiles to generate sulfonyl carbamates from sulfonyl azides. Our studies commenced with the reaction between **1a**, excess butanol, 5 mol% $PdCl_2$, and $MoCO_6$ at 75 °C for 20 h (Table 5). Rewardingly, the reaction proceeded smoothly to afford the desired sulfonyl carbamate **4a** in 82% isolated yield. The catalyst loading could again be reduced to 2 mol% without affecting the reaction outcome, although lowering the temperature to 50 °C led to a two-fold decrease in yield.

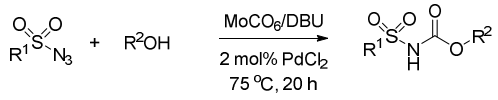
Table 5. Optimization of the carbonylative synthesis of **4a**

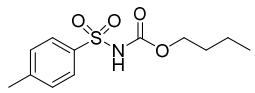
entry	$PdCl_2$ [mol%]	BuOH [equiv]	temp [°C]	yield[a]
1	5%	2	75	82%
2	5%	1	75	45%
3	2%	2	75	80%
4	2%	2	50	44%

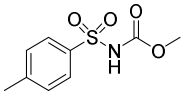
[a]Isolated yield

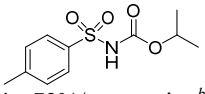
Using the optimized protocol, the alcohol substrate scope was then investigated. Primary, secondary and tertiary alcohols were all found to be compatible substrates, affording fair to good yields of the desired products (**4b**–**4e,** 52–76%). In the case of **4c**, a one-pot experiment was attempted, but no product could be detected. The presence of an electron-withdrawing trifluoromethyl substituent gave a reduction in yield, as did an sp or sp^2 carbon β to the alcohol moiety, presumably due to decreased nucleophilicity (**4f**–**4l**). Disappointingly, no traces of the desired product were observed when phenol was used as the nucleophile (**4m**) even with the addition of excess Et_3N. The substrate scope was also extended to include different sulfonyl azides. In line with the above results, *para*-substituted arylsulfonyl azides with electron-donating or electron-withdrawing substituents were well tolerated, giving moderate to good yields of the desired products (**4n**–**4p**, 45–78%). The presence of an *ortho* substituent led to a reduced yield due to steric effects (**4q**). The reaction was also found to be compatible with heteroarylsulfonyl azides and the corresponding sulfonyl carbamates were obtained in good yields (**4r**–**4t**). Finally, benzylsulfonyl azide reacted smoothly to give the desired sulfonyl carbamate in 80% isolated yield (**4u**). This is in contrast to the sulfonamide formation reaction, where the presence of a sp^2 center adjacent to the sulfur atom was found to be essential for the reaction to proceed.

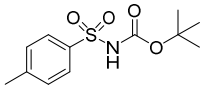
Table 6: Synthesis of sulfonyl carbamates from various sulfonyl azides and alcohols.[a]

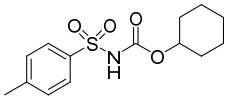


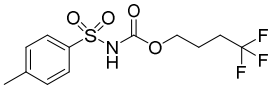

4a, 80%

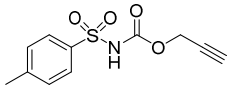

4b, 65%

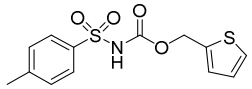

4c, 73%/no reaction[b]

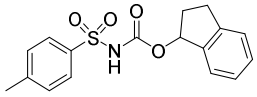

4d, 62%

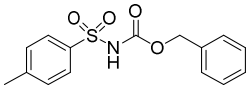

4e, 76%

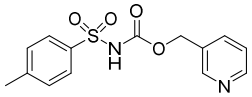

4f, 36%

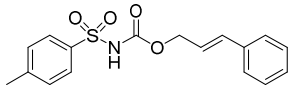

4g, 24%

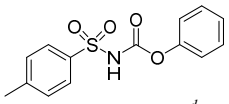

4h, 45%[c]

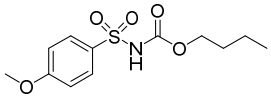

4i, 19%

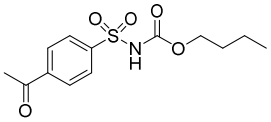

4j, 59%

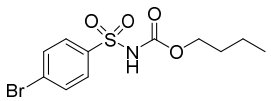

4k, 33%

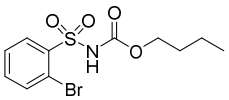

4l, 42%

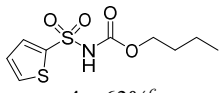

4m, no reaction[d]

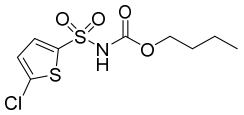

4n, 50%

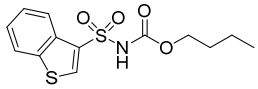

4o, 45%

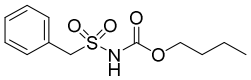

4p, 78%


4q, 37%


4r, 63%[c]


4s, 78%[c]

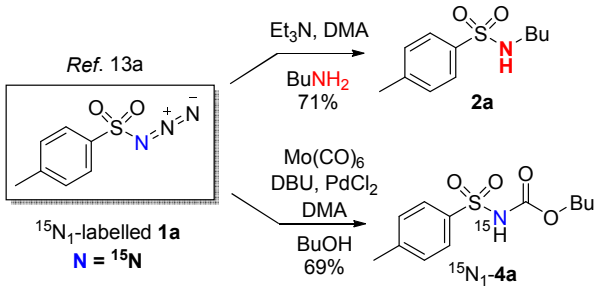

4t, 54%[c]


4u, 80%

[a]Isolated yield. Reaction conditions: **Chamber A**: $Mo(CO)_6$ (0.15 mmol, 0.6 equiv) and DBU (0.38 mmol, 1.5 equiv) in DMA (2 mL). **Chamber B**: Sulfonyl azide (0.25 mmol, 1.0 equiv), alcohol (0.50 mmol, 2.0 equiv), $PdCl_2$ (0.006 mmol, 0.02 equiv) in DMA (2 mL). [b]One-pot experiment. [c]50 °C. [d]2 equiv of Et_3N added.

To investigate the mechanism of the sulfonamide formation and carbonylation reactions, isotope labeling experiments were carried out using *p*-tolyl sulfonyl azide-1-^{15}N ($^{15}N_1$-**1a**).[13a] Thus, $^{15}N_1$-**1a** was treated with butylamine using the optimized conditions from Scheme 3. The resulting sulfonamide product **2a (**71% yield) lacked the characteristic M+1 ion expected upon incorporation of the ^{15}N atom. This suggests that the reaction proceeds *via* a direct nucleophilic substitution at the $S^{(VI)}$ center with the azide anion serving as the leaving group. Moreover, the isotopic ratio was similar to that obtained from the reaction in Table 2, indicating limited competition from potential azide exchange or tetrazine formation processes.[24] As mentioned above, the reaction of amines with

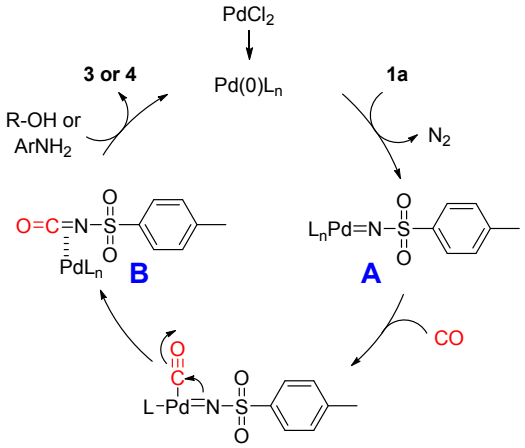
sulfonyl azides has previously been reported to result in diazotransfer to the amine and the development of a new and generally applicable deazidation substitution process is of significant importance. This opens up a potentially powerful alternative synthetic route to this valuable class of compounds from stable and readily available primary sulfonamides *via* selective late-stage diazotransfer[13a,14b] and subsequent functionalization of the sulfonyl azide intermediates.



Scheme 3. Mechanistic investigation using $^{15}N_1$-labeled **1a**

In contrast, the reaction of $^{15}N_1$-**1a** with butanol under the alkoxycarbonylation conditions in Table 6 resulted in the exclusive formation of the $^{15}N_1$-labeled sulfonyl carbamate $^{15}N_1$-**4a** in 69% yield. This is consistent with a reaction mechanism involving the extrusion of N_2 from the azide substrate. This suggests the reaction may proceed either *via* a Pd(0)/Pd(II) cycle similar to other alkoxy- or aminocarbonylation reactions,[25] or an oxidative Pd(II)/Pd(0) process analogous to that reported for the synthesis of carbamates and ureas from amines.[26] The latter reaction mode would require the addition of an external oxidant to facilitate palladium reoxidation and should also lead to product formation from a primary sulfonamide precursor. Considering that the carbonylation reaction does not require an external oxidant and no product was observed in a control reaction using tosyl amide we believe that the reaction operates within a Pd(0)/Pd(II) manifold. This is further supported by the successful use of the Pd(0) catalyst $Pd(PPh_3)_4$, which afforded **4a** in 59% yield using the conditions from Table 6. Based on these results, we suggest that the palladium-catalyzed carbonylation of sulfonyl azides occurs via the mechanism outlined in Scheme 4. Reduction of the pre-catalyst, by either CO or an alcohol or amine, to an active Pd(0) species followed by addition to the sulfonyl azide generates the

nitrene-palladium complex **A**.[27] Subsequent CO coordination and insertion gives an acyl palladium intermediate followed by reductive elimination to afford a sulfonyl isocyanate species (**B**), the identity of which was confirmed by EI-MS analysis. Finally, nucleophilic attack on the sulfonyl isocyanate by an alcohol or amine nucleophile gives the sulfonyl carbamate (**3**) or sulfonyl urea (**4**) products.



Scheme 4. Mechanistic proposal for the formation of **3** and **4**.

Conclusion

In conclusion, we have developed a facile synthesis of sulfonamides, sulfonyl carbamates and sulfonyl ureas using organic sulfonyl azides as versatile building blocks. We have successfully applied a ligand-free palladium-catalyzed carbonylation procedure to transform sulfonyl azides into sulfonyl isocyanate intermediates, in which further derivatizations with alcohol or aryl amine nucleophiles allow the robust generation of a broad range sulfonyl carbamates and sulfonyl ureas. In addition, a direct synthesis of substituted sulfonamides from aryl sulfonyl azides and a variety of amines was developed, providing a versatile synthetic platform for the preparation of substituted sulfonamides.

Experimental Section

General methods

All reagents were purchased at the highest commercial quality and used without further purification. Solvents used for extraction and silica gel chromatography (EtOAc, hexane, *n*-pentane, dichloromethane, methanol and Et_3N) were used without purification or removal of water. Yields are for isolated, homogenous and spectroscopically pure material. Silica gel chromatography was carried out using E. Merck silica gel (60 Å pore size, particle size 40-63 nm). ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra at 100 MHz and ^{15}N NMR spectra at 40 MHz. The chemical shifts for ^{1}H NMR and ^{13}C NMR were referenced to tetramethylsilane *via* residual solvent signals (^{1}H, $CDCl_3$ at 7.26 ppm; ^{13}C, $CDCl_3$ at 77.16 ppm; ^{1}H, DMSO-d_6 at 2.45 ppm; ^{13}C, DMSO-d_6 at 39.43 ppm, ^{1}H, CD_3OD at 3.31 ppm; ^{13}C, CD_3OD at 49.0 ppm). LC/MS was performed on an instrument equipped with a CP-Sil 8 CB capillary column (50 x 3.0 mm, particle size 2.6 μm, pore size 100 Å) running at an ionization potential of 70 eV with a CH_3CN/H_2O gradient (0.05% HCOOH). Accurate mass values were determined by electrospray ionization with a 7-T hybrid ion trap and a TOF detector running in positive or negative mode.

Preparation of sulfonyl azides. Sulfonyl azides were prepared either from the corresponding sulfonyl chloride[28] or the sulfonamide[13a] following the literature procedures. **Warning**! Sulfonyl azides are potentially explosive and all reactions should be carried out behind blast shields. The authors recommend the use of plastic spatulas for the handling of solid material.

6-(Trifluoromethyl)pyridine-3-sulfonyl azide (1j) for use in stability study (see Supporting Information). Prepared from the corresponding sulfonyl chloride. White solid (44 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29–9.22 (m, 1H), 8.51–8.39 (m, 1H), 7.96 (dd, J = 8.3, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (q, $^2J_{CF}$ = 35.9 Hz), 148.3, 138.0, 137.0, 121.3 (q, $^3J_{CF}$ = 2.6 Hz), 120.8 (q, $^1J_{CF}$ = 275.1 Hz); IR (neat) 2155 cm^{-1}; MS (ESI) calc'd for $C_6H_4F_3N_4O_2S$ ($[M+H]^+$) *m/z* 253.XXXX, found *m/z* 253.XXXX.

General procedure for the synthesis of sulfonamides 2a–2x, exemplified by *N*-butyl-4-methylbenzenesulfonamide (CAS 1907-65-9) (2a).[29] To a stirred solution of **1a** (50 mg, 0.25 mmol) in DMA (2 mL) at ambient temperature were added butylamine (50 μL, 50 mmol) and triethylamine (35 μL, 0.25 mmol). The resulting mixture was stirred for 20 h, after which it was loaded on a silica column and eluted with 10% EtOAc in *n*-pentane to obtain the title compound as a colorless liquid (49 mg, 0.21 mmol, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.8, 0.8 Hz, 2H), 4.78 (s, 1H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.46–1.32 (m, 2H), 1.29–1.16 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.1, 129.8, 127.2, 43.0, 31.7, 21.6, 20.0, 13.6.

General procedure for the synthesis of sulfonyl ureas 3a–3m, exemplified by 4-methyl-*N*-(phenylcarbamoyl)benzenesulfonamide (CAS 13909-63-2) (3a).[30] Chamber A of an H-tube reactor[16] was charged with **1a** (100 mg, 0.51 mmol) and $PdCl_2$ (2 mg, 0.01 mmol). The chamber was capped and anhydrous DMA (1.5 mL) and aniline (47 mg, 0.51 mmol) were added through the septum. Chamber B was charged with $Mo(CO)_6$ (670 mg, 0.3 mmol) and capped.[16b] Anhydrous DMA (1.5 mL) and DBU (116 mg, 0.76 mmol) were added through the septum and the assembly was stirred for 20 h at 75 ºC, after which the contents of chamber A were loaded onto a silica gel column. The title compound was obtained as a colorless liquid (109 mg, 74%), eluting with 10% EtOAc in *n*-pentane with 1% Et_3N as a stabilizer (see below). Spectral data were in agreement with literature values. ^{1}H NMR (400 MHz, CD_3OD) δ 7.94–7.86 (m, 2H), 7.43–7.37 (m, 2H), 7.34–7.29 (m, 2H), 7.28–7.22 (m, 1H), 7.07–7.00 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 145.3, 136.6, 136.3, 130.2, 129.2, 126.9, 124.9, 120.3, 21.6.

General procedure for the synthesis of sulfonyl carbamates 4a–4u, exemplified by butyl tosylcarbamate (CAS 31224-37-0) (4a).[31] Chamber A of an H-tube reactor was charged with **1a** (50 mg, 0.25 mmol) and $PdCl_2$ (2 mg, 0.01 mmol). The chamber was capped and anhydrous DMA (1.5 mL) and *n*-butanol (38 mg, 0.51 mmol) were added through the septum. Chamber B was charged with

$Mo(CO)_6$ (40 mg, 0.15 mmol) and capped. Anhydrous DMA (1.5 mL) and DBU (58 mg, 0.38 mmol) were added through the septum and the assembly was stirred for 20 h at 75 ºC, after which the contents of chamber A loaded onto a silica gel column. The title compound was obtained as a colorless liquid (57 mg, 82%), eluting with 10% EtOAc in *n*-pentane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.95–7.76 (m, 2H), 7.23 (dd, *J* = 8.3, 2.1 Hz, 2H), 3.97 (td, *J* = 6.7, 2.3 Hz, 2H), 2.33 (s, 3H), 1.60–1.29 (m, 2H), 1.17 (m, 2H), 0.76 (td, *J* = 7.1, 2.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 144.2, 134.9, 128.8, 127.5, 66.1, 29.6, 20.9, 18.0, 12.8.

Stability issues with sulfonyl ureas (3a–3l) and sulfonyl carbamates (4l, 4n, 4o, 4r and 4s). These compounds were observed to degrade to the corresponding sulfonamide in acidic environments such as silica gel or $CDCl_3$. For this reason, the authors recommend the use of 1% Et_3N as a chromatography additive, enabling target compounds to be isolated as their triethylammonium salts. These are stable for up to a month at -21 °C.

***N*-Hexyl-4-methylbenzenesulfonamide (CAS 1143-01-7) (2b)**.[28,29a] Spectral data were in agreement with literature values. Colorless liquid (56 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.67 (m, 2H), 7.40–7.26 (m, 2H), 4.76–4.53 (m, 1H), 3.05–2.79 (m, 2H), 2.43 (s, 3H), 1.53–1.36 (m, 2H), 1.32–1.12 (m, 6H), 0.92–0.67 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.1, 129.8, 127.2, 43.3, 31.3, 29.6, 26.3, 22.6, 21.6, 14.1.

***N*-Cyclohexyl-4-methylbenzenesulfonamide (CAS 80-30-8) (2c)**.[29b,33] Spectral data were in agreement with literature values. Colorless liquid (29 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00–6.91 (m, 2H), 6.51–6.46 (m, 2H), 3.99–3.38 (m, 1H), 2.31 (td, *J* = 6.3, 3.0 Hz, 1H), 1.61 (s, 3H), 0.98–0.89 (m, 2H), 0.86–0.77 (m, 2H), 0.73–0.66 (m, 1H), 0.47–0.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.6, 129.7, 127.1, 52.7, 34.1, 25.3, 24.7, 21.6.

1-Tosylpiperidine (CAS 4703-22-4) (2d).[29b,34] Spectral data were in agreement with literature values. Colorless liquid (55 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.60 (m, 2H), 7.35–7.29

(m, 2H), 3.08–2.89 (m, 4H), 2.43 (s, 3H), 1.68–1.59 (m, 4H), 1.45–1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 133.4, 129.7, 127.9, 47.1, 25.3, 23.7, 21.7.

***N,N*-diethyl-4-methylbenzenesulfonamide (CAS 649-15-0) (2e).**[29b,35] Spectral data were in agreement with literature values. 4 equiv. diethylamine, 6 equiv. Et_3N, 120 h. Colorless liquid (21 mg, 36%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 8.0 Hz, 2H), 3.22 (q, J = 7.2 Hz, 4H), 2.41 (s, 3H), 1.12 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.4, 129.6, 127.0, 41.9, 21.5, 14.1.

***N,N*-dipropyl-4-methylbenzenesulfonamide (CAS 723-42-2) (2f)**.[29b,36] Spectral data were in agreement with literature values. 4 equiv. dipropylamine, 6 equiv. Et_3N, 120 h. Colorless liquid (21 mg, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 3.09–3.01 (m, 4H), 2.41 (s, 3H), 1.62–1.44 (m, 4H), 0.89–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.9, 129.3, 126.8, 49.8, 21.8, 21.3, 11.0.

***N*-Allyl-4-methylbenzenesulfonamide (CAS 50487-71-3) (2g)**.[37] Spectral data were in agreement with literature values. Colorless liquid (32 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.71 (m, 2H), 7.34–7.30 (m, 2H), 5.72 (ddt, J = 17.1, 10.2, 5.8 Hz, 1H), 5.21–5.14 (m, 1H), 5.10 (dd, J = 10.2, 1.3 Hz, 1H), 4.54 (s, 1H), 3.59 (tt, J = 6.2, 1.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.1, 133.1, 129.9, 127.3, 117.8, 45.9, 21.7.

4-Methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (CAS 55022-46-3) (2h).[38] Spectral data were in agreement with literature values. Colorless liquid (31 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.93 (m, 2H), 7.65–7.51 (m, 2H), 5.12–4.82 (m, 1H), 4.26–3.80 (m, 2H), 2.66 (s, 3H), 2.43–2.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.6, 129.8, 127.5, 78.1, 73.1, 33.0, 21.7.

4-Methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide (CAS 545358-50-7) (2i).[39] Spectral data were in agreement with literature values. Colorless liquid (43 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–7.95 (m, 2H), 7.61–7.55 (m, 2H), 7.45 (dd, J = 5.0, 1.2 Hz, 1H), 7.14 (dd, J = 5.0, 3.5 Hz, 1H),

7.12–7.10 (m, 1H), 5.07–4.92 (m, 1H), 4.59 (d, J = 6.1 Hz, 2H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.9, 136.8, 129.7, 127.2, 126.8, 126.5, 125.8, 42.1, 21.5.

***N*-Benzyl-4-methylbenzenesulfonamide (CAS 1576-37-0) (2j)**.[29b,40] Spectral data were in agreement with literature values. Colorless liquid (42 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.67 (m, 2H), 7.33–7.29 (m, 2H), 7.29–7.24 (m, 3H), 7.22–7.18 (m, 2H), 4.79 (t, J = 6.2 Hz, 1H), 4.12 (d, J = 6.2 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 137.0, 136.4, 129.8, 128.8, 128.13, 128.11, 127.3, 47.4, 21.7.

Methyl toluenesulfonylglycinate (CAS 2645-02-5) (2k).[41] Spectral data were in agreement with literature values. Colorless liquid (12 mg, 19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.69 (m, 2H), 7.39–7.27 (m, 2H), 5.00 (s, 1H), 3.78 (d, J = 5.3 Hz, 2H), 3.64 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 143.8, 136.1, 129.7, 127.2, 52.6, 44.0, 21.5.

Methyl 3-((4-methylphenyl)sulfonamido)propanoate (62456-75-1) (2n).[42] Spectral data were in agreement with literature values. Colorless liquid (42 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.62 (m, 2H), 7.36–7.26 (m, 2H), 5.31 (br s, 1H), 3.65 (s, 3H), 3.18 (t, J = 5.9 Hz, 2H), 2.68–2.48 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 143.2, 136.6, 129.4, 126.7, 51.6, 38.4, 33.6, 21.2.

***N*-butyl-4-methoxybenzenesulfonamide (CAS 35088-85-8) (2p)**.[43] Spectral data were in agreement with literature values. Colorless liquid (45 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) 8.17–7.64 (m, 2H), 7.20–6.90 (m, 2H), 4.50 (s, 1H), 3.97 (s, 3H), 3.15–2.91 (m, 2H), 1.62–1.46 (m, 2H), 1.45–1.30 (m, 2H), 1.08–0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 131.7, 129.3, 114.3, 55.7, 43.0, 31.7, 19.8, 13.7.

***N*-butyl-4-bromobenzenesulfonamide (CAS 1984-28-7) (2q)**.[43] Spectral data were in agreement with literature values. Colorless liquid (62 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.70 (m, 2H), 7.68–7.64 (m, 2H), 4.54 (br s, 1H), 3.17–2.84 (m, 2H), 1.51–1.39 (m, 2H), 1.37–1.19 (m, 2H),

0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 132.5, 128.7, 127.6, 43.1, 31.7, 19.8, 13.6.

4-acetyl-*N*-butylbenzenesulfonamide (CAS 733031-17-9) (2r). Colorless liquid (31 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.03 (m, 2H), 8.01–7.82 (m, 2H), 4.39 (s, 1H), 2.99 (d, J = 6.9 Hz, 2H), 2.66 (s, 3H), 1.50–1.39 (m, 2H), 1.32–1.25 (m, 4H), 0.91–0.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 144.2, 140.1, 129.1, 127.5, 43.2, 31.8, 27.0, 19.8, 13.6.

***N*-butyl-2-bromobenzenesulfonamide (CAS 951885-17-9) (2s)**.[44] Spectral data were in agreement with literature values. Colorless liquid (43 mg, 59%); ^{1}H NMR (400 MHz, CD_3OD) δ 8.22–7.92 (m, 1H), 7.96–7.72 (m, 1H), 7.57–7.51 (m, 1H), 7.48 (td, J = 7.6, 1.9 Hz, 1H), 2.90 (t, J = 7.0 Hz, 2H), 1.48–1.36 (m, 2H), 1.35–1.25 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 141.2, 136.5, 134.7, 132.3, 128.9, 120.9, 43.7, 32.8, 20.7, 13.9.

***N*-butylthiophene-2-sulfonamide (CAS 741728-91-6) (2v)**. Colorless liquid (26 mg, 49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.45 (m, 2H), 7.16–6.98 (m, 1H), 4.39 (s, 1H), 3.18–2.98 (m, 2H), 1.51–1.44 (m, 2H), 1.36–1.29 (m, 2H), 0.88 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 131.9, 127.5, 43.4, 31.6, 19.8, 13.8; MS (ESI) calc'd for $C_8H_{14}NO_2S_2$ ($[M+H]^+$) *m/z* 220.0466, found *m/z* 220.0469.

***N*-butylbenzo[b]thiophene-3-sulfonamide (2w)**. Colorless liquid (35 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.24–8.16 (m, 1H), 7.94 (dd, J = 7.9, 1.4 Hz, 1H), 7.57–7.48 (m, 2H), 4.63 (t, J = 6.2 Hz, 1H), 3.08–2.97 (m, 2H), 1.48–1.38 (m, 2H), 1.35–1.20 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2, 131.9, 127.5, 43.4, 31.6, 19.9, 13.7; MS (ESI) calc'd for $C_{12}H_{16}NO_2S_2$ ($[M+H]^+$) *m/z* 270,0622 found *m/z* 270.0633.

5-(*N*-butylsulfamoyl)-4-chloro-2-((furan-2-ylmethyl)amino)benzoic acid (CAS 207866-32-8) (2x).[45] Colorless liquid (12 mg, 23%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.54 (s, 1H), 7.57–7.35 (m, 1H), 7.03 (s, 1H), 6.45–6.19 (m, 2H), 4.57 (s, 2H), 2.84 (t, J = 7.0 Hz, 2H), 1.48–1.34 (m, 2H), 1.30–

1.21 (m, 2H), 0.77 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 169.3, 154.2, 152.3, 143.6, 138.2, 136.7, 124.5, 114.6, 111.4, 109.3, 108.6, 43.5, 40.4, 32.5, 20.5, 14.0; MS (ESI) calc'd for $C_{16}H_{20}ClN_2O_5S$ ($[M+H]^+$) *m/z* 387.0771, found *m/z* 387.0781.

Triethylammonium *N*-((4-methoxyphenyl)carbamoyl)-4-methylbenzenesulfonamide (CAS 92580-79-5, free urea) (3b).[46] Reaction run at 40 ºC on 0.25 mmol scale. Tan solid (93 mg, 87%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.66 (s, 1H), 8.00–7.64 (m, 2H), 7.58–7.35 (m, 2H), 7.26–7.08 (m, 2H), 6.86–6.61 (m, 2H), 3.65 (s, 3H), 3.01 (d, J = 7.2 Hz, 6H), 2.30 (s, 3H), 1.15 (t, J = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 158.0, 155.9, 155.9, 143.5, 142.3, 134.9, 129.9, 127.7, 121.2, 121.1, 114.7, 55.8, 46.9, 21.6, 9.8.

Triethylammonium *N*-((4-bromophenyl)carbamoyl)-4-methylbenzenesulfonamide (CAS 100716-09-4, free urea) (3c).[1d] 0.62 mmol scale. Colorless liquid (140 mg, 67%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.72 (s, 1H), 7.88–7.67 (m, 2H), 7.45–7.32 (m, 2H), 7.25–7.18 (m, 2H), 7.17–7.13 (m, 2H), 3.07 (q, J = 7.3 Hz, 7H), 2.25 (s, 3H), 1.14 (t, J = 7.3 Hz, 8H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 158.1, 143.34, 142.0, 141.2, 132.1, 129.6, 127.4, 120.9, 113.7, 46.7, 21.35, 9.2.

Triethylammonium *N*-((4-chlorophenyl)carbamoyl)-4-methylbenzenesulfonamide (CAS 3955-50-8, free urea) (3d).[15,47] 0.25 mmol scale. Colorless liquid (58 mg, 54%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.84 (s, 1H), 8.04–7.78 (m, 2H), 7.73–7.56 (m, 2H), 7.35–7.29 (m, 2H), 7.28–7.24 (m, 1H), 3.19 (t, J = 7.2 Hz, 6H), 1.32 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 159.5, 145.1, 143.4, 142.2, 131.1, 130.6, 128.9, 127.7, 122.0, 48.3, 22.8, 10.9.

Triethylammonium *N*-((4-cyanophenyl)carbamoyl)-4-methylbenzenesulfonamide (CAS 51594-96-8, free urea) (3e).[46a] Reaction run at 40 ºC on 0.25 mmol scale. Colorless liquid (65 mg, 62%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 9.01 (s, 1H), 7.93–7.81 (m, 2H), 7.76–7.65 (m, 2H), 7.60–7.42 (m, 2H), 7.36–7.15 (m, 2H), 3.27 (q, J = 7.3 Hz, 6H), 2.36 (s, 3H), 1.30 (t, J = 7.3 Hz, 9H); ^{13}C NMR

(100 MHz, $(CD_3)_2CO$) δ 157.6, 146.5, 146.4, 143.2, 143.1, 142.5, 142.5, 133.9, 129.9, 127.8, 127.8, 120.2, 119.2, 119.1, 104.7, 104.6, 47.2, 21.6, 9.3.

Triethylammonium methyl 4-(3-tosylureido)benzoate (CAS 404905-23-3, free urea) (3f).[48] Reaction run at 40 ºC on 0.62 mmol scale. Colorless liquid (141 mg, 50%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.91 (s, 1H), 7.89–7.73 (m, 4H), 7.73–7.45 (m, 2H), 7.39–7.09 (m, 2H), 3.81 (s, 3H), 3.20 (q, *J* = 7.4 Hz, 6H), 2.35 (s, 3H), 1.26 (d, *J* = 7.4 Hz, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 157.9, 146.5, 143.4, 141.9, 131.1, 129.6, 127.4, 123.4, 118.1, 51.8, 46.8, 21.3, 9.2.

Triethylammonium 4-methyl-*N*-(o-tolylcarbamoyl)benzenesulfonamide (CAS 53855-77-9, free urea) (3g).[1d] 0.62 mmol scale. Colorless liquid (115 mg, 45%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.64 (s, 1H), 8.11–7.74 (m, 3H), 7.42–7.34 (m, 2H), 7.21–7.17 (m, 1H), 7.17–7.13 (m, 1H), 7.01–6.95 (m, 1H), 3.37–3.13 (m, 4H), 2.45 (s, 3H), 2.29 (s, 6H), 1.44–1.26 (m, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 155.3, 142.8, 142.3, 138.7, 130.9, 129.9, 128.6, 127.5, 126.9, 123.7, 122.2, 46.4, 21.3, 18.2, 8.9.

Triethylammonium *N*-((2-chlorophenyl)carbamoyl)-4-methylbenzenesulfonamide (CAS 53855-79-1. **free urea) (3h)**.[1d,49] 0.62 mmol scale. Colorless liquid (82 mg, 31%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.92 (s, 1H), 8.28 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.99–7.76 (m, 2H), 7.35 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.31–7.25 (m, 3H), 7.19 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 2H), 6.94 (td, *J* = 8.1, 7.3, 1.5 Hz, 1H), 3.26 (q, *J* = 7.2 Hz, 6H), 2.35 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 155.6, 142.7, 142.5, 137.7, 129.8, 129.7, 128.1, 127.4, 123.5, 122.7, 121.8, 46.4, 21.3, 8.8.

Triethylammonium 4-methoxy-*N*-(phenylcarbamoyl)benzenesulfonamide (CAS 51327-24-3, free urea) (3i).[50] Reaction run at 50 ºC on a 0.19 mmol scale. Colorless liquid (69 mg; 90%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.79 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.54 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.21 (m, *J* = 8.6, 7.3 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.94 – 6.89 (m, 1H), 3.86 (s, 4H), 3.04 (q, *J* = 7.2 Hz,

6H), 1.22 (t, J = 7.2 Hz, 9H). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 162.6, 157.4, 141.7, 138.0, 129.4, 129.3, 122.3, 119.3, 114.2, 55.8, 46.7, 9.9.

Triethylammonium 4-acetyl-*N*-(phenylcarbamoyl)benzenesulfonamide (CAS 51327-25-4, free urea) (3j).[51] Reaction run at 50 ºC on a 0.19 mmol scale. Colorless liquid, (68 mg, 87%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.37 (s, 1H), 8.07–8.01 (m, 2H), 8.01–7.96 (m, 2H), 7.52 (dd, J = 8.5, 1.3 Hz, 2H), 7.16 (dd, J = 8.5, 7.3 Hz, 2H), 6.85 (td, J = 7.3, 1.3 Hz, 1H), 3.00 (q, J = 7.3 Hz, 9H), 2.58 (s, 3H), 1.18 (t, J = 7.3 Hz, 12H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 197.4, 159.7, 151.3, 142.1, 139.2, 129.2, 128.9, 127.3, 121.9, 119.2, 46.8, 26.9, 10.0.

Triethylammonium 5-chloro-*N*-(phenylcarbamoyl)thiophene-2-sulfonamide (3k). Reaction run at 50 ºC on a 0.25 mmol scale. Colorless liquid (82 mg, 78%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.30 (s, 1H), 7.61–7.57 (m, 2H), 7.41 (d, J = 3.9 Hz, 1H), 7.36–7.12 (m, 2H), 6.96 (d, J = 4.0 Hz, 1H), 6.94–6.89 (m, 1H), 3.28 (q, J = 7.3 Hz, 6H), 1.33 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 158.8, 146.9, 140.8, 131.5, 128.2, 127.6, 125.7, 121.0, 118.2, 45.7, 7.9; MS (ESI) calc'd for $C_{11}H_{10}ClN_2O_3S_2$ ($[M+H]^+$) *m/z* 316.9821, found *m/z* 316.9835.

Triethylammonium *N*-(phenylcarbamoyl)benzo[b]thiophene-3-sulfonamide (3l). Reaction run at 30 ºC on a 0.25 mmol scale. Colorless liquid (78 mg, 72%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.54 (s, 1H), 8.51–8.47 (m, 1H), 8.33 (s, 1H), 8.02–7.92 (m, 1H), 7.63–7.51 (m, 2H), 7.50–7.40 (m, 2H), 7.18 (dd, J = 8.5, 7.3 Hz, 2H), 6.98–6.84 (m, 1H), 3.19 (q, J = 7.3 Hz, 6H), 1.25 (t, J = 7.3 Hz, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 159.1, 141.8, 141.2, 140.7, 136.0, 130.9, 129.2, 125.7, 125.5, 125.2, 123.4, 122.1, 119.3, 46.7, 9.1; MS (ESI) calc'd for $C_{15}H_{13}N_2O_3S_2$ ($[M+H]^+$) *m/z* 333.0372, found *m/z* 333.0377.

Methyl tosylcarbamate (CAS 14437-03-7) (4b).[52] Spectral data were in agreement with literature values. Colorless liquid (38 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.33–8.08 (m,

2H), 7.66–7.57 (m, 2H), 5.50–4.48 (m, 1H), 2.72 (s, 3H), 1.47 (d, J = 6.3 Hz, 6H);^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 145.3, 135.5, 129.8, 128.5, 53.7, 21.8.

Isopropyl tosylcarbamate (CAS 18303-02-1) (4c).[53] Colorless liquid (48 mg, 73%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 4.87 (hept, J = 6.3 Hz, 1H), 2.41 (s, 3H), 1.16 (d, J = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 144.9, 135.8, 129.5, 129.5, 128.4, 71.5, 21.7, 21.6.

***tert*-Butyl tosylcarbamate (CAS 18303-04-3) (4d)**.[54] Spectral data were in agreement with literature values. Colorless liquid (43 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.74 (m, 2H), 7.81 (s, 1H), 7.41–7.15 (m, 2H), 2.43 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 144.8, 136.1, 129.6, 128.3, 84.1, 27.9, 21.7.

Cyclohexyl tosylcarbamate (CAS 18303-08-7) (4e).[55] Colorless liquid (58 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.99–7.83 (m, 2H), 7.40–7.27 (m, 2H), 4.63 (tt, J = 9.0, 3.7 Hz, 1H), 2.42 (s, 3H), 1.80–1.71 (m, 2H), 1.69–1.57 (m, 2H), 1.50–1.43 (m, 1H), 1.41 – 1.17 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 144.9, 135.8, 129.6, 128.4, 76.2, 31.4, 25.2, 23.5, 21.7.

4,4,4-trifluorobutyl tosylcarbamate (4f). 0.50 mmol scale. Colorless liquid (59 mg, 36%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.94–7.87 (m, 2H), 7.39–7.33 (m, 2H), 4.14 (t, J = 6.2 Hz, 2H), 2.44 (s, 3H), 2.10–1.95 (m, 2H), 1.89–1.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.5, 135.5, 129.7, 128.4, 126.8 (q, $^1J_{CF}$ = 276.2 Hz), 65.3, 30.4 (q, $^2J_{CF}$ = 29.5 Hz), 21.8, 21.8 (q, $^3J_{CF}$ = 3.1 Hz); MS (ESI) calc'd for $C_{12}H_{13}F_3NO_4S$ ($[M-H]^-$) *m/z* 324.0517, found *m/z* 324.0513.

Prop-2-yn-1-yl tosylcarbamate (CAS 63924-66-3) (4g).[56] Colorless liquid (16 mg, 24%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.93 (m, 2H), 7.55–7.31 (m, 2H), 5.52 (s, 1H), 4.85–4.65 (m, 2H), 4.52 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 148.0, 136.7, 135.9, 131.7, 129.9, 92.5, 68.8, 31.4, 23.5.

Thiophen-2-ylmethyl tosylcarbamate (4h). Reaction run at 50 °C. Colorless liquid (36 mg, 45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.66 (m, 2H), 7.30–7.19 (m, 3H), 7.03–6.96 (m, 1H), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.19 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 145.0, 136.0, 135.3, 129.5, 129.0, 128.3, 127.4, 126.9, 62.5, 21.6; MS (ESI) calc'd for $C_{15}H_{16}N_2O_4S_2Na$ ($[M+MeCN+Na]^+$) *m/z* 375.0449, found *m/z* 375.0456.

2,3-Dihydro-1*H*-inden-1-yl tosylcarbamate (4i). Colorless liquid (16 mg, 19%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.72 (m, 2H), 7.61 (s, 1H), 7.32–7.20 (m, 5H), 7.18–7.11 (m, 1H), 6.06 (dd, *J* = 6.8, 3.1 Hz, 1H), 3.07–2.90 (m, 1H), 2.81 (ddd, *J* = 16.2, 8.6, 4.2 Hz, 1H), 2.41 (s, 3H), 2.45–2.31 (m, 1H), 2.05 (dddd, *J* = 14.3, 8.3, 4.2, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.0, 144.7, 139.6, 135.6, 129.6, 129.5, 128.5, 126.9, 125.8, 124.9, 81.6, 32.1, 30.2, 21.8; MS (ESI) calc'd for $C_{19}H_{20}N_2O_4SNa$ ($[M+MeCN+Na]^+$) *m/z* 395.1041, found *m/z* 395.1038.

Benzyl tosylcarbamate (CAS 18303-10-1) (4j).[52b] Spectral data were in agreement with literature values. Colorless liquid (46 mg, 59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.87–7.69 (m, 2H), 7.66–6.66 (m, 8H), 5.03 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 145.1, 135.5, 134.5, 129.7, 128.8, 128.7, 128.49, 128.48, 68.7, 21.8.

Pyridin-3-ylmethyl tosylcarbamate (4k). Colorless liquid (26 mg, 33%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.55–8.52 (m, 2H), 7.93–7.81 (m, 2H), 7.72–7.66 (m, 1H), 7.46–7.38 (m, 2H), 7.34 (ddd, *J* = 7.9, 4.8, 0.9 Hz, 1H), 5.14 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 150.94, 150.87, 146.0, 137.7, 137.4, 137.0, 132.5, 130.8, 129.3, 124.6, 66.4, 21.9; MS (ESI) calc'd for $C_{14}H_{13}N_2O_4S$ ($[M-H]^-$) *m/z* 305.0596, found *m/z* 305.0600.

Triethylammonium ((cinnamyloxy)carbonyl)(tosyl)amide (CAS 159259-78-6, free carbamate) (4l).[57] Colorless liquid (46 mg, 42%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68–7.61 (m, 2H), 7.43–7.35 (m, 2H), 7.35–7.27 (m, 2H), 7.28–7.23 (m, 1H), 7.23–7.17 (m, 2H), 6.55 – 6.45 (m, 1H), 6.25 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.42 (dd, *J* = 5.8, 1.5 Hz, 2H), 3.09 (q, *J* = 7.3 Hz, 6H), 2.32 (s, 3H), 1.17 (t, *J* = 7.3

Hz, 9H); ^{13}C NMR (100 MHz, CD_3OD 158.9, 143.2, 141.2, 137.8, 133.7, 129.7, 129.3, 128.6, 128.1, 127.3, 125.2, 66.2, 47.5, 21.2, 8.9.

Triethylammonium (butoxycarbonyl)((4-methoxyphenyl)sulfonyl)amide (CAS 100371-49-1, free carbamate) (4n).[58] Colorless liquid (49 mg, 50%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.00–7.92 (m, 2H), 7.15–7.04 (m, 2H), 3.99 (t, *J* = 6.7 Hz, 2H), 3.96 (s, 3H), 3.02 (q, *J* = 7.2 Hz, 5H), 1.64–1.52 (m, 2H), 1.42–1.34 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 9H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 163.4, 153.5, 131.9, 129.6, 113.6, 65.4, 54.9, 46.4, 30.4, 18.5, 12.5, 7.8.

Butyl ((4-acetylphenyl)sulfonyl)carbamate (2: 1 mixture with Et_3N) (4o). Colorless liquid (45 mg, 45%); ^{1}H NMR (400 MHz, CD_3OD) δ 8.15–8.09 (m, 2H), 8.07–8.01 (m, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.23 (q, *J* = 7.3 Hz, 3H), 2.65 (s, 3H), 1.58–1.45 (m, 2H), 1.42–1.21 (m, 7H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 CD_3OD) δ 199.2, 156.0, 139.5, 128.1, 127.5, 65.0, 46.4, 30.6, 25.6, 18.6, 12.6, 7.8; MS (ESI) calc'd for $C_{13}H_{16}NO_5S$ ($[M-H]^-$) *m/z* 298.0749, found *m/z* 298.0753.

Butyl ((4-bromophenyl)sulfonyl)carbamate (4p). Colorless liquid (66 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.02 (m, 2H), 6.92–6.81 (m, 2H), 3.30 (td, *J* = 6.7, 0.9 Hz, 2H), 0.86–0.64 (m, 2H), 0.57–0.39 (m, 2H), 0.08 (td, *J* = 7.4, 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 136.8, 131.7, 129.2, 128.6, 66.6, 29.8, 18.2, 12.9; MS (ESI) calc'd for $C_{11}H_{13}BrNO_4S$ ($[M-H]^-$) *m/z* 333.9749, found *m/z* 333.9753.

Butyl ((2-bromophenyl)sulfonyl)carbamate (4q). Colorless liquid (31 mg, 37%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 10.7 (s, 1H), 8.24 (ddd, *J* = 7.4, 1.9, 0.7 Hz, 1H), 7.87 (ddd, *J* = 7.0, 1.9, 0.7 Hz, 1H), 7.69–7.59 (m, 2H), 4.02 (td, *J* = 6.5, 0.7 Hz, 3H), 1.48 (ddt, *J* = 8.4, 7.0, 6.0 Hz, 2H), 1.30–1.18 (m, 3H), 0.84 (td, *J* = 7.4, 0.6 Hz, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 153.0, 140.9, 137.8, 137.3, 135.4, 130.3, 122.0, 68.4, 32.8, 21.0, 15.4; MS (ESI) calc'd for $C_{11}H_{13}BrNO_4S$ ($[M-H]^-$) *m/z* 333.9749, found *m/z* 333.9740.

Triethylammonium (butoxycarbonyl)(thiophen-2-ylsulfonyl)amide (CAS 14437-09-3, free carbamate) (4r).[59] Reaction run at 50 °C. Colorless liquid (57 mg, 63%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.75 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.68 (dd, *J* = 3.7, 1.4 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.97 (t, *J* = 6.7 Hz, 2H), 3.27 (q, *J* = 7.3, Hz, 6H), 1.59–1.47 (m, 2H), 1.41–1.25 (m, 10H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($(CD_3)_2CO$) δ 154.7, 131.8, 131.0, 126.6, 64.6, 45.1, 30.8, 18.8, 13.1, 7.7.

Butyl ((5-chlorothiophen-2-yl)sulfonyl)carbamate (4s). Reaction run at 50 ºC. Colorless liquid (54 mg, 73^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.42 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 4.0 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 3.28 (q, *J* = 7.4 Hz, 6H), 1.58–1.48 (m, 2H), 1.39–1.27 (m, 11H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$)) δ 157.9, 145.4, 133.9, 130.6, 126.9, 64.9, 46.1, 31.9, 19.8, 14.0, 8.6; MS (ESI) calc'd for $C_9H_{11}ClNO_4S_2$ ($[M-H]^-$) *m/z* 295.9823, found *m/z* 295.9824.

Butyl (benzo[*b*]thiophen-3-ylsulfonyl)carbamate (2:1 mixture with Et_3N) (4t). Reaction run at 50 °C. Colorless liquid (56 mg, 54%); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.48 (s, 1H), 8.44–8.20 (m, 1H), 8.19–7.90 (m, 1H), 7.71–7.25 (m, 2H), 3.92 (td, *J* = 6.6, 0.7 Hz, 2H), 3.33 (q, *J* = 7.3 Hz, 3H), 1.51–1.41 (m, 2H), 1.37 (t, *J* = 7.3 Hz, 4H), 1.29–1.15 (m, 2H), 0.90–0.74 (m, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$)) δ 156.4, 141.3, 137.9, 137.5, 136.7, 127.6, 127.5, 126.4, 126.3, 124.7, 124.1, 66.0, 47.6, 31.8, 19.9, 14.2, 9.0; MS (ESI) calc'd for $C_{13}H_{14}NO_4S_2$ ($[M-H]^-$) *m/z* 312.0369, found *m/z* 312.0368.

Butyl (benzylsulfonyl)carbamate (4u). Colorless liquid (55 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.32 (m, 5H), 7.02 (s, 1H), 4.63 (s, 2H), 4.23 (t, *J* = 6.6 Hz, 2H), 1.73–1.61 (m, 2H), 1.45–1.34 (m, 2H), 1.02–0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 130.8, 129.4, 129.1, 128.1, 67.4, 58.6, 30.7, 19.0, 13.7; MS (ESI) calc'd for $C_{12}H_{16}NO_4S$ ($[M-H]^-$) *m/z* 270.0800, found *m/z* 270.0791.

Isotopic labelling studies

Starting from ammonium-^{15}N chloride (CAS 39466-62-1), $^{15}N_1$-**1a** was prepared in 7% total yield following the literature procedure.[13a] Spectral data were in agreement with literature values.

Azide displacement study, ^{14}N-butyl-4-methylbenzenesulfonamide (2a). Following the general procedure (starting from 0.05 mmol $^{15}N_1$-**1a**), the title compound was obtained as a colorless liquid (11 mg, 71%). Mass spectrometry and ^{15}N NMR confirmed its identity as the title compound.

Butyl tosylcarbamate-^{15}N (^{15}N-4a). Following the general procedure (starting from 0.05 mmol $^{15}N_1$-**1a**), the title compound was isolated as a colorless liquid (8 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.53 (m, 2H), 7.34–7.27 (m, 2H), 4.55 (s, 1H), 3.03–2.79 (m, 2H), 2.42 (s, 3H), 1.43 (s, 2H), 1.35–1.22 (m, 2H), 0.84 (dd, J = 7.8, 6.8 Hz, 3H); ^{15}N NMR (40 MHz) δ -241.2. MS (ESI) calc'd for $C_{12}H_{18}{}^{15}NO_4S$ ($[M+H]^+$) *m/z* 273.0927, found *m/z* 273.0936.

Control reaction

Following the general procedure for formation of sulfonyl carbamates but with tosyl amide (43 mg, 0.25 mmol), no product could be observed. Using **1a** (50 mg, 0.25 mmol) and $Pd(PPh_3)_4$ (6 mg, 5 μmol), **4a** was isolated in 59% yield.

Acknowledgements

The authors thank Prof. Adolf Gogoll for assistance with ^{15}N NMR studies and Dr. Lisa Haigh for assistance with accurate mass determination. Financial support from the Knut and Alice Wallenberg foundation and the Carl Tryggers Stiftelse för Vetenskaplig Forskning (CTS) is gratefully acknowledged.

Associated Content

Supporting information

Two-chamber, experimental apparatus for carbonylation, stability studies, ^{1}H and ^{13}C spectra for all products and ^{15}N spectra for **^{15}N-4a**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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