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One Pot Sequential Synthesis of *N*-(2-(Phenylsulfinyl)phenyl)acetamides: A Ring Opening Rearrangement Functionalization (RORF)

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Abstract: A Cu(II) catalyzed one-pot sequential synthesis of *N*-(2-(phenylthio)phenyl)acetamides from benzo[*d*]thiazol-2-amines, iodoarenes and carboxylic acids (RCOOH) has been accomplished via ring opening rearrangement functionalization (RORF). Here, the ring opening is associated with the loss of carbon and nitrogen atoms with concurrent *S*-arylation and *N*-acylation leading to *ortho*-bifunctionalized products. A further sequential addition of *tert*-butyl hydroperoxide (TBHP) results in the formation of a sulfur oxidized product, *N*-(2-(phenylsulfinyl)phenyl)acetamide. A plausible mechanism has been proposed for this unprecedented ring opening rearrangement functionalization (RORF).

Keywords: Carboxylic acids; Cross-coupling; Isotopic labeling; Oxidation; Ring opening rearrangement functionalization (RORF).

Introduction

The transition-metal catalyzed concurrent construction of C–S and C–N bonds leading to functionally diverse structural motifs are in great demand.[1] Recently the C–N bond formations have attracted much attention and become one of the most promising strategy in organic reactions.[2] Similarly, owing to the importance of organo-sulfur compounds in biological, pharmaceutical and material chemistry, the C–S bond forming process has also gained considerable attention in organic synthesis.[3] On the other hand one-pot sequential strategies are effective as several bond-forming process can be carried out in a single-pot, circumventing purification at each step, thereby creating high diversity per step. A further appealing aspects of this strategy is to produce large molecular diversity and complexity in a single transformation.[4]

Due to the associated ring strains in three and four membered carbo- and heterocycles, they often undergo ring opening in the presence of appropriate nucleophiles.[5] Although five membered heterocycles such as thiazole, imidazole,oxazole and some of their benzo fused heterocycles *viz.* benzothiazole, benzoimidazole, benzoxazole and benzoisothiazole are more stable in terms of ring strain but are susceptible to ring opening.[6-8] The ring opening reactions are not only restricted to simple benzothiazoles and 1,3-azoles but also observed in 2-aminobenzothiazoles. In a coupling reaction between 2-aminobenzothiazole and terminal alkyne resulted in the formation of benzo[*b*][1,4]thiazine-4-carbonitrile.[9a] Here, the ring opening is followed by an oxidative coupling with an alkyne and finally the reaction terminates *via* an intermolecular cyclization process. In yet another method, the synthesis of 2-(phenylthio)phenylcyanamide from 2-halothiourea and iodobenzene in the presence of CuI/ligand or $CuSO_4.5H_2O$ has been established by our group and Punniyamurthy group via the intermediacy of 2-aminobenzothiazole.[9b,c] In 2015, a non-enzymatic decomposition of guanidine derivatives into anilides with the loss of a –CN moiety has been developed by Shi group [Scheme1, (i)]. Here, a combination of catalyst $Pd(OAc)_2$, an equivalent of $Cu(OAc)_2$ and CO were utilized for the transformation of 1,3-diarylguanidines to acetanilides *via* the cleavage of C–N bond.[10] Very recently, our group has developed another -CN sacrificial arylthio-arylamination of quinoline/isoquinoline *N*-oxides where, 2-(arylthio)arylcyanamides serves as efficient arylaminating agents [Scheme1, (ii)].[11] The later proceeds via the attack of a nucleophilic *N*-oxide onto electrophilic cyano (-CN) group of the 2-(arylthio)arylcyanamide followed by a rearrangement to provide an auto-reduced C2-arylaminated quinoline/isoquinoline. In both these examples the -CN bearing moiety *viz.* 2-(arylthio)arylcyanamides and guanidines, loses their cyano group in the presence of respective nucleophiles *viz.* quinoline *N*-oxides and acetate anions.

Inspired by the recent advances in transition-metal catalyzed one-pot sequential reactions,[12] ring opening processes[5-8] and N–CN bond activation strategies,[13] we envisaged a telescopic protocol for the synthesis of *N*-(2-(phenylthio)phenyl)acetamides (**1aa´**) (Scheme 1). 2-(Phenylthio)phenylcyanamide (**A**) can be obtained from 2-aminobenzothiazole (**1**) and iodobenzene (**a**) in the presence of $CuSO_4.5H_2O$ via a ring opening intermolecular C–S cross coupling reaction (Scheme 1).[9c] We anticipated that the *in situ* generated cyanamide (**X**) possesses an electrophilic carbon,[14] and a fragile N–CN bond which may undergo a similar cyano

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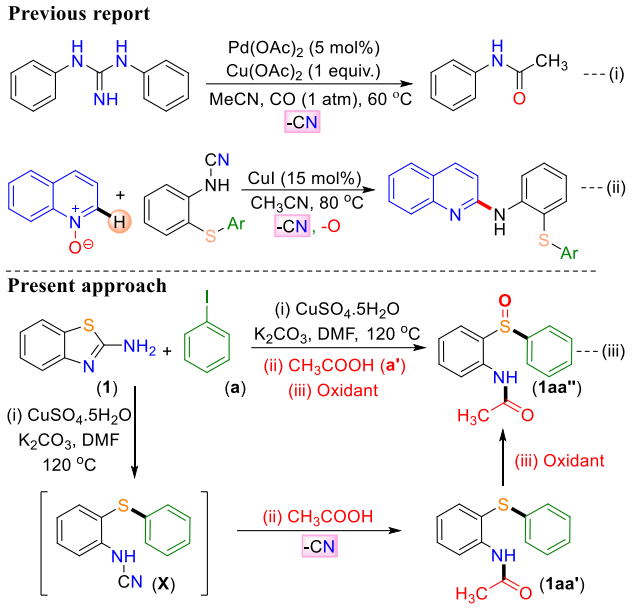
sacrificial acetolysis to that of 1,3-diarylguanidine to generate an acetamide (**1aa´**) (Scheme 1). The *N*-(2-(phenylthio)phenyl)acetamide (**1aa´**) having a diarylsulfide moiety can be further oxidized to its sulfoxide (**1aa´´**) analogue in the presence of a suitable oxidant [Scheme 1, (iii)].



Scheme 1. Cyano sacrificial functionalization strategies.

Results and Discussion

An initial experiment was carried out using 2-aminobenzothiazole (**1**) and iodobenzene (**a**) in the presence of $CuSO_4.5H_2O$ and Cs_2CO_3. The exclusive formation of cyanamide (**X**) was observed after 4 h, which is consistent with the previous literature reports.[9b,c] To check whether the envisioned cyano sacrificial acetolysis could be accomplished in one pot, AcOH (5 equiv.) was added to the same reaction mixture after the initial formation of cyanamide (**X**) and heating was continued further. To our delight, the expected *N*-acetylated product 2-(phenylthio)phenylacetamide (**1aa´**, 29%) was obtained via the loss of a cyano (-CN) group. The structure of the product (**1aa´**) was further confirmed by X-ray crystallographic analysis (Figure 1). Thus, herein, we report a one pot sequential ring opening rearrangement functionalization (RORF) using 2-aminobenzothiazole (**1**), iodobenzene (**a**) and acetic acid (**a´**). The notable features of this transformation is the sequential formation of two new C–heteroatom bonds such as C–S and C–N *ortho* to each other providing a 1,2-bifunctionalized product *N*-(2-(phenylthio)phenyl)acetamide (**1aa´**).

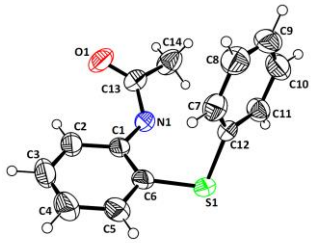
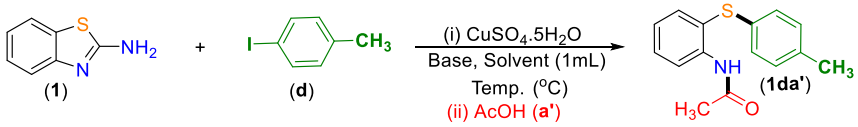


Figure 1. ORTEP diagram of *N*-(2-(phenylthio)phenyl)acetamide (**1aa´**) with 40% ellipsoid contour probability.[15]

Inspired by this positive outcome, various reaction parameters were again scrutinized to achieve an improved yield of the 1,2-bifunctionalized product (**1da´**). The investigation was commenced by using benzo[*d*]thiazol-2-amine (**1**) and 4-methyliodobenzene (**d**) as the reacting partners (Table 1, entry 1). As most of the N–CN bond cleaving reactions proceeds in the presence of a metal catalyst,[10,13] the quantity of $CuSO_4.5H_2O$ was first optimized. An increase in the catalyst ($CuSO_4.5H_2O$) loading to 10 mol% improve the yield to 47 % (Table 1, entry 3). However, the yield (48%) remained virtually unchanged even using 15 mol% of the catalyst loading (Table 1, entry 4). The use of base K_2CO_3 (2 equiv.) is found to be equally effective to that of Cs_2CO_3 (1.5 equiv.) for the ring opening leading to the formation of intermediate cyanamide (**X**) in DMSO (Table 1, entry 5). Use of solvent DMF (58%) (Table 1, entry 6) was found to be marginally superior to DMSO (53%). Keeping all other parameters constant, the addition of 10 and 20 equivalents of AcOH improved the yield of the final product (**1da´**) to 63% and 69% respectively (Table 1, entry 7 and 8). The yield of the product improved progressively when the reaction was carried out at 100 °C (76%), 110 °C (79%) and 120 °C (84%) (Table 1 entries 9-11). Finally, a two-step optimized process was developed for the ring opening rearrangement functionalization (RORF) strategy. In the first step the combination of $CuSO_4.5H_2O$ (10 mol%), K_2CO_3 (2 equiv.) and DMF (1 mL) at 120 °C for 4 h and in the second step addition of AcOH (20 equiv, 0.6 mL) at 120 °C for 5 h was found to be the best optimal condition for this telescopic synthesis (Table 1, entry 11).

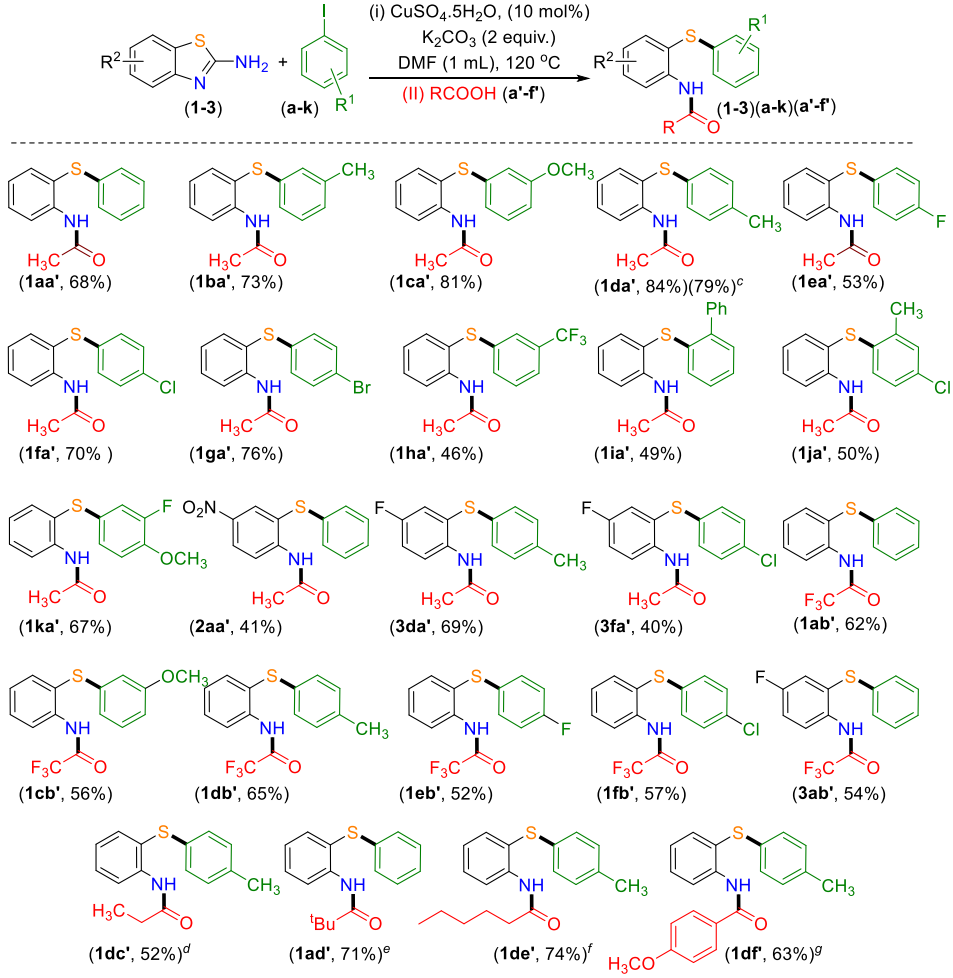
Table 1. Optimization for *N*-acetylation.[a,b]



Entry	Catalyst (mol %)	Base (equiv.)	Solvent	AcOH	Temp °C	Yield (%)
1	$CuSO_4.5H_2O$ (2.5)	Cs_2CO_3 (1.5)	DMSO	5 equiv.	90	37
2	$CuSO_4.5H_2O$ (5)	Cs_2CO_3 (1.5)	DMSO	5 equiv.	90	39
3	$CuSO_4.5H_2O$ (10)	Cs_2CO_3 (1.5)	DMSO	5 equiv.	90	47
4	$CuSO_4.5H_2O$ (15)	Cs_2CO_3 (1.5)	DMSO	5 equiv.	90	48
5	$CuSO_4.5H_2O$ (10)	K_2CO_3 (2)	DMSO	5 equiv.	90	53
6	$CuSO_4.5H_2O$ (10)	K_2CO_3 (2)	DMF	5 equiv.	90	58
7	$CuSO_4.5H_2O$ (10)	K_2CO_3 (2)	DMF	10 equiv.	90	63
8	$CuSO_4.5H_2O$ (10)	K_2CO_3 (2)	DMF	20 equiv.	90	69
9	$CuSO_4.5H_2O$ (10)	K_2CO_3 (2)	DMF	20 equiv.	100	76
10	$CuSO_4.5H_2O$ (10)	K_2CO_3 (2)	DMF	20 equiv.	110	79
11	**$CuSO_4.5H_2O$ (10)**	**K_2CO_3 (2)**	**DMF**	**20 equiv.**	**120**	**84**

[a] Reaction conditions: benzo[*d*]thiazol-2-amine (**1**) (0.5 mmol), 4-iodotoluene (**d**) (0.5 mmol), solvent (1 mL) for 4 h. (ii) acetic acid(a´) for 5 h was add. [b] Yields of isolated pure product.

With this stepwise optimal reaction conditions in hand, the generality and versatility of this one pot sequential 1,2-difunctionalization strategy was demonstrated using different benzo[*d*]thiazol-2-amines (**1-3**) with various aryl iodides (**a**-**k**) bearing electron-donating and electron-withdrawing groups in the presence of acetic acid (**a´**) (Scheme 2). Here, the iodoarenes having electron-neutral –H (**a**) and electron-donating substituents such as *m*-CH_3 (**b**) and *m*-OCH_3 (**c**), all yielded their desired ring opened *N*-acetylated products (**1aa´**, 68%), (**1ba´**, 73%) and (**1ca´**, 81%) in good yields (Scheme 2). Further, aryl iodides possessing moderately electron-withdrawing substituents such as *p*-F (**e**), *p*-Cl (**f**), *p*-Br (**g**) and strongly-electron-withdrawing substituent *m*-CF_3 (**h**) all furnished their respective 1,2-bifunctionalized *N*-acetylated products (**1ea´**, 53%), (**1fa´**, 70%), (**1ga´**, 76%) and (**1ha´**, 46%) (Scheme 2). A *o*-phenyl substituted iodobenzene (**i**) reacted with benzo[*d*]thiazol-2-amine (**1**) in the presence of acetic acid (**a´**) affording its corresponding bi-functionalized product (**1ia´**, 49%). In addition to these mono-substituted aryl iodides, the di-substituted aryl iodides, such as 2-CH_3-4-Cl (**j**) and 3-F-4-OCH_3 (**k**) all underwent efficient transformations with benzo[*d*]thiazol-2-amine (**1**) and acetic acid (**a´**) giving the desired *N*-acetylated products (**1ja´**, 50%) and (**1ka´**, 67%) respectively. Subsequently, presence of substituents on the 2-aminobenzothiazole was investigated. Benzothiazoles possessing 6-NO_2 (**2**) and 6-F (**3**), all experienced efficient RORF giving their respective 1,2-bifunctionalized products. The 6-nitrobenzo[*d*]thiazol-2-amine (**2**) reacted smoothly with iodobenzene (**a**) in presence of AcOH (**a´**), providing its *N*-acetylated product (**2aa**) in 41% yield. Further, the presence of a least deactivating substituent 6-F (**3**) in the benzothiazole ring underwent the *N*-acetylation with a variety of substituted iodoarenes. The electron-donating *p*-CH_3 (**d**) and electron-withdrawing *p*-Cl (**f**) iodoarenes, all endured the present one pot RORF strategy with 6-fluorobenzo[*d*]thiazol-2-amine (**3**) and acetic acid (**a´**) furnishing their bi-functionalized products (**3da´**, 69%) and (**3fa´**, 40%) respectively. From the trend in the yields obtained in Scheme 2, no appropriate correlation between the nature of substituents and their position of attachment with the actual yield obtained could be rationalized. To check the scalability of the present methodology, a reaction of benzo[*d*]thiazol-2-amine (**1**) (1 mmol), 4-methyliodobenzene (**d**) (1 mmol) and acetic acid (**a´**) (20 equiv.), under the standard optimized reaction condition provided a 79% yield of product (**1da´**) (Scheme 2).



Scheme 2. Demonstration of RORF using AcOH and other carboxylic acids. [a] Reaction conditions: (i) benzo[*d*]thiazol-2-amine (**1**) (0.5 mmol), aryl iodide (**a**–**k**) (0.5 mmol), $CuSO_4.5H_2O$ (10 mol%), K_2CO_3 (2 equiv.) and DMF (1 mL) for 4 h, (ii) AcOH (**a´**) (20 equiv.), (1 mmol scale)*c*, TFA (**b´**) (20 equiv.), propanoic acid (**c´**) (10 equiv.)*d*, pivalic acid (**d´**) (8 equiv.)*e* and hexanoic acid (**e´**) (10 equiv.)*f*, benzoic acids (**f´**) (6 equiv.)*g*, for another 5 h at 120 °C. [b] Yields of isolated pure products.

Now a query arises whether the acetic acid could be replaced with its halogen analogue such as trifluoroacetic acid to provide their corresponding *N*-trifluoroacylated products. With this objective, when acetic acid (**a´**) was substituted with trifluoroacetic acid (**b´**), using benzo[*d*]thiazol-2-amine (**1**) and iodobenzene (**a**) as the reacting partners under otherwise identical condition, the reaction furnished the anticipated *N*-trifluoroacetylated product (**1ab´**) in 62% yield. Inspired by the positive outcome, several other iodoarenes (**c**-**f**) bearing electron-donating and electron-withdrawing groups were

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examined with benzo[*d*]thiazol-2-amine (**1**) using TFA (**b´**) as the trifluoroacylation partner (Scheme 2). Initially, aryliodides bearing electron-donating substituents such as *m*-OCH_3 (**c**) and *p*-CH_3 (**d**) were employed with benzo[*d*]thiazol-2-amine (**1**) and TFA (**b´**) under the present reaction condition, all provided their corresponding products (**1cb´**, 56%) and (**1db´**, 65%) respectively. Similarly, iodoarenes bearing moderately electron-withdrawing substituents such as *p*-F (**e**) and *p*-Cl (**f**), all yielded their corresponding rearranged diaryl-sulfide products (**1eb´**) and (**1fb´**) in 52% and 57% yields respectively. Besides these substituted iodoarenes, 6-F-2-aminobenzothiazole (**3**) also successfully underwent the present transformation with iodobenzene (**a**) and TFA (**b´**) to result the corresponding trifluoroacetamide (**3ab´**) in 54% yield. Here, similar to acetic acid, no proper correlation between the nature of substituents and their position of attachment with the actual yield obtained could be ascertained. Besides AcOH and TFA this protocol is also applicable to other aliphatic acids such as propanoic acid (**c´**), pivalic acid (**d´**) and hexanoic acid (**e´**), all afforded their corresponding *ortho*-bifunctionalized products (**1dc´**), (**1ad´**) and (**1de´**) in 52%, 71% and 74% yields respectively (Scheme 2). An aromatic carboxylic acid such as *p*-methoxy benzoic acid (**f´**) also provided a decent yield of the bi-functionalized amidic product (**1df´**, 63%) (Scheme 2).

We believe that the bi-functionalized acetamides obtained after the addition of carboxylic acids, possessing a diarylsulfide moiety, can be further oxidized to their corresponding sulfoxide analogue in the same pot using a suitable oxidant. The *in situ* treatment of $K_2S_2O_8$ (3 equiv.) provided the sulfoxide product (**1da´´**) in a modest 21% yield after 17 h at 120 °C leaving behind substantial amount of unoxidized product (**1da´**) (Table 2, entry 1). Spectroscopic and HRMS analysis of the product confirmed its structure to be *N*-(2-(*p*-tolylsulfinyl)phenyl)acetamide (**1da´´**). This positive outcome is interesting because, sulfoxides exhibit a broad range of biological properties, including anticancer,[16a-d] anti-viral[16e] and anti-bacterial activities.[16f] They are also important structural motifs in marketed therapeutic drugs, such as Nexium for heartburn and esophagitis[17a] and Provigil for narcolepsy (Figure 2).[17b]

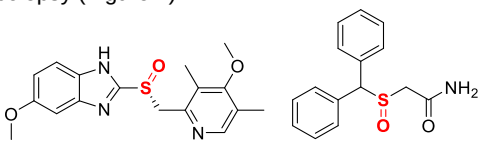
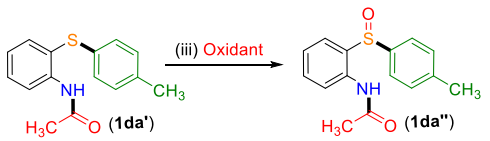


Figure 2. Representative sulfoxide containing therapeutics.

Table 2. Optimization for sulfoxide formation.[a,b]



Entry	Oxidant (equiv.)	Temp (°C)	Yield (%)
1	$K_2S_2O_8$ (3)	120	21
2	$(NH_4)_2S_2O_8$ (3)	120	08
3	TBHP (3)	120	59[h]
4	aq. TBHP (3)	120	32
5	BPO (3)	120	00
6	TBPB (3)	120	18
7	DTBP (3)	120	26
8	H_2O_2 (3)	120	48
9	**TBHP (6)**	**120**	**67[h]**
10	TBHP (8)	120	68[g]

[a] Reaction conditions: (i) benzo[*d*]thiazol-2-amine (**1**) (0.5 mmol), 4-iodotoluene (**d**) (0.5 mmol), $CuSO_4.5H_2O$ (10 mol%), K_2CO_3 (2 equiv.) and DMF (1 mL) at 120 °C for 4 h, (ii) AcOH (**a**) (20 equiv.) for 5 h. [h]TBHP (5-6 M in decane). [b] Yields of isolated pure product.

Since the final yield (21%) of the oxidized product (**1da´´**) obtained was not promising, various other oxidants were then examined to achieve an improve yield of (**1da´´**) (Table 2). Among the oxidants such as $(NH_4)_2S_2O_8$ (08%), TBHP (5–6 M in decane) (59%), aq.TBHP (32%), benzoylperoxide (BPO) (00%), *tert*-butylperoxy benzoate (TBPB) (18%), di-*tert*-butyl peroxide (DTBP) (26%) and H_2O_2 (48%) tested (Table 2, entries 2–8), TBHP (5–6 M in decane) was found to be the most suitable oxidant for the conversion of sulfide (**1da´**) to sulfoxide (**1da´´**) analogue (Table 2, entry 3). Gratifyingly, using 6 equiv. of TBHP, an improved yield (67%) of product (**1da´´**) was observed (Table 2, entry 9). A further increase in the oxidant quantity to 8 equiv., gave no significant enhancement in the product (**1da´´**) yield (Table 1, entry 10). Thus, TBHP (5–6 M in decane) (6 equiv.) was used for the *in situ* oxidation of rest of the diarylsulfides in Scheme 3.

The above optimized oxidative condition was then implemented to explore the scope and generality of the developed RORF strategy via the *in situ* oxidation of sulfide to sulfoxide and the results are summarized in Scheme 3. Initially, the variation of both electron-donating and electron-withdrawing substituents on aryliodides (**a**–**i**) with unsubstituted benzo[*d*]thiazol-2-amine (**1**) using acetic acid (**a´**) was surveyed. Here again, the iodoarenes bearing electron neutral –H (**a**) and electron-donating substituents such as *m*-OCH_3 (**c**) provided their corresponding bifunctionalized sulfoxide products (**1aa´´**, 60%) and (**1ca´´**, 58%) respectively (Scheme 3). Further, the iodoarenes possessing moderately electron-withdrawing substituents such as *p*-F (**e**), *p*-Cl (**f**), *p*-Br (**g**) and strongly electron-withdrawing substituent *m*-CF_3 (**h**) all resulted their corresponding oxidized 1,2-disubstituted products (**1ea´´**, 52%), (**1fa´´**, 63%), (**1ga´´**, 65%) and (**1ha´´**, 27%) respectively (Scheme 3). Besides this, *o*-phenyl substituted iodobenzene (**i**) provided its corresponding sulfoxide product (**1ia´´**) in 36% yield. A fluoro substituted 2-aminobenzothiazole *viz.* 6-fluorobenzo[*d*]thiazol-2-amine (**3**) reacted smoothly with various substituted iodoarenes bearing electron neutral -H (**a**), electron donating *p*-CH_3 (**d**) and electron-withdrawing *p*-Cl (**f**) groups in the presence of AcOH (**a´**) and TBHP affording their *N*-acetylated sulfoxides (**3aa´´**), (**3da´´**) and (**3fa´´**) in 50%, 58% and 37% yields respectively.

Analogous to acetic acid, the one pot sequential RORF protocol was also performed in the presence of TFA (**b´**) under an identical reaction condition. Surprisingly, oxidation of the *in situ* generated sulfide (**1ab´**) to sulfoxide (**1ab´´**) failed completely. May be under a strongly acidic condition, the oxidant TBHP rapidly decomposes, thereby failed to oxidize the sulfide. However, the sulfoxide products (**1ab´´**) could be obtained in a decent yield (58%) by oxidizing the isolated sulfide analogue (**1ab´**) using TBHP as the oxidant in CH_3CN at room temperature for 24 h. The same strategy was applied for other diarylsulfides (**1cb´**-**1fb´** and **3ab´**). The yields of the sulfoxide products (**1cb´´**-**1fb´´** and **3ab´´**) reported in Scheme 3 are from the oxidation of their respective diarylsulfides. The structure of the product (**1ab´´**) was further reconfirmed by X-ray crystallographic analysis (Figure S1).[15] Other biaryl-sulfoxides (**1ac´´**, 50%), (**1ad´´**, 70%) (**1de´´**, 55%), (**1df´´**,47%) and (**1dg´´**, 42%) were also obtained via this one pot sequential RORF strategy using other aliphatic and aromatic acids such as propanoic (**c´**), pivalic (**d´**), hexanoic acid (**e´**), *p*-methoxy benzoic acid (**f´**) and *p*-chloro benzoic acid (**g´**) as shown in Scheme 3. It may be noted here, that the yields of the unoxidized products in Scheme 2 are generally superior to their corresponding oxidized products in Scheme 3.

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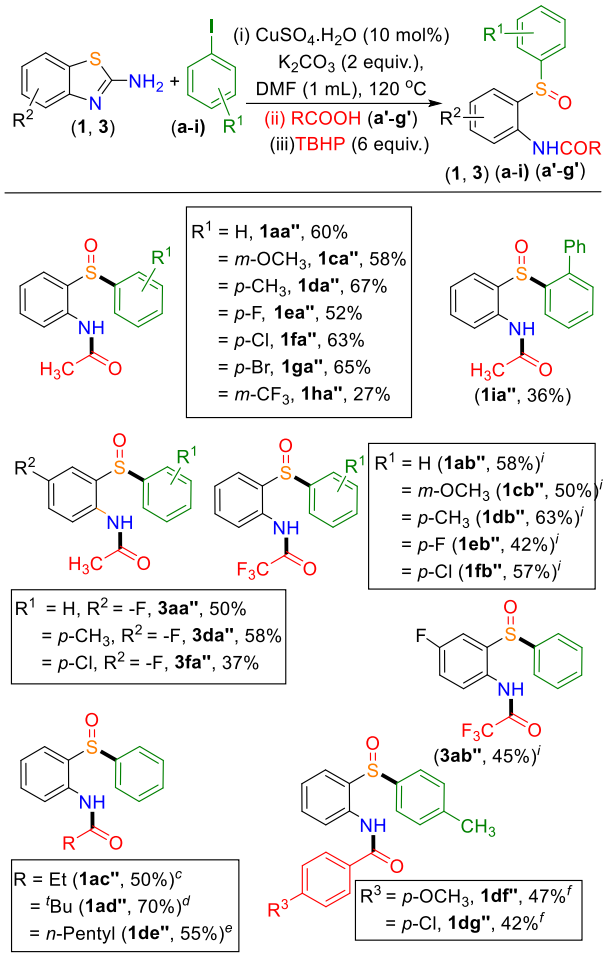
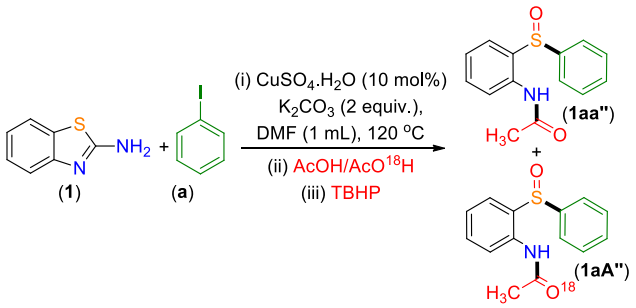


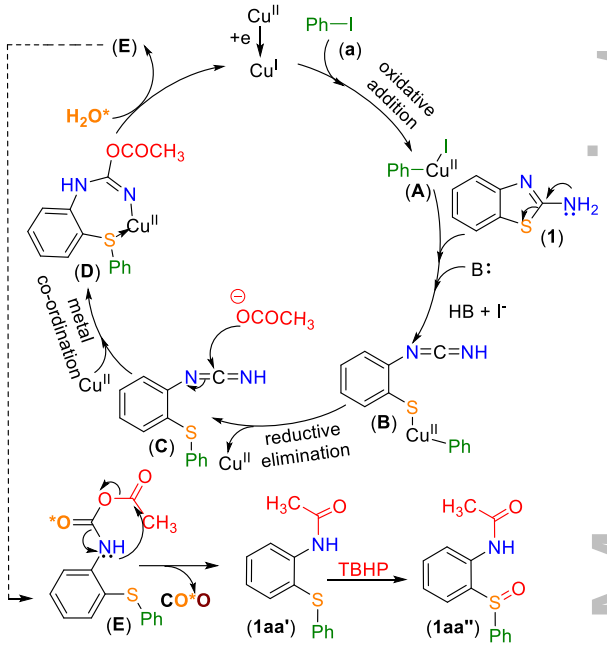
Scheme 3. Demonstration of RORF using AcOH and other carboxylic acids under oxidative condition.[a] Reaction conditions: (i) benzo[*d*]thiazol-2-amine (**1**) (0.5 mmol), aryl iodide (**a–n**) (0.5 mmol), $CuSO_4.5H_2O$ (10 mol%), K_2CO_3 (2 equiv.), DMF (1 mL) for 4 h, (ii) AcOH (**a´**) (20 equiv.), propanoic acid (**c´**) (10 equiv.)[d], pivalic acid (**d´**) (8 equiv.)[e], hexanoic acid (**e´**) (10 equiv.)[f] and benzoic acids (**f´** and **g´**) (6 equiv.)[g] for 5 h (iii) TBHP (5–6 M in decane) (6 equiv.) for 17 h at 120 °C. [f]Reaction conditions: *N*-trifluoroacetylated diarylsulfides (**1cb´-1fb´** and **3ab´**) (0.25 mmol), TBHP (5–6 M in decane) (6 equiv.), CH_3CN (1 mL), time (24 h) at room temp. [b] Yields of isolated pure product.

To illuminate the probable mechanism of this one pot sequential ring opening rearrangement functionalization (RORF), some control experiments were carried out. When the reaction was performed in the presence of ^{18}O labeled water no ^{18}O incorporated product was observed suggesting none of the oxygen in the product originates from water. However, when a reaction was carried out using ^{18}O labeled acetic acid, the product was found to have an ^{18}O labeled oxygen (Scheme 4). This result confirms carboxylic acids to be the acyl or aryl sources in this transformation.



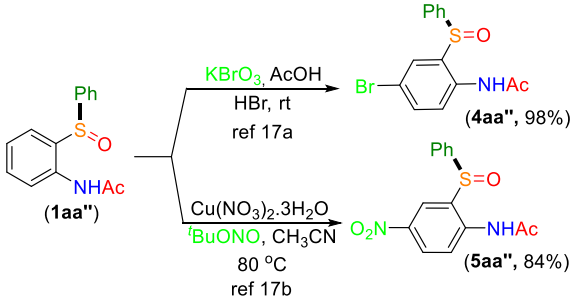
Scheme 4. Isotopic labelling experiment.

Based on the literature reports[9b,c] and experimental findings, a plausible reaction mechanism is depicted in Scheme 5. In this reaction, aryliodide undergoes an oxidative addition with Cu to form species (**A**). The 2-aminobenzothiazole opens up to a carbodiimide in the presence of a base which then reacts with the species (**A**) via the soft sulfur atom to generate intermediate (**B**). The intermediate (**B**) undergoes reductive elimination to form the diarylsulfide cyanamide intermediate (**C**). The resultant cyanamide intermediate (**C**) is attacked by the acetate ion which is assisted via the metal co-ordination to form a metal bound carbamimidic anhydride species (**D**). The intermediate (**D**) is hydrolyzed to a carbamic anhydride (**E**). The final acylated product (**1aa´**) is obtained via the loss of a CO_2 moiety. The acylated diarylsulfide (**1aa´**) is oxidized to sulfoxide (**1aa´´**) in the presence of an oxidant.



Scheme 5. Plausible Mechanism for one pot sequential RORF.

To further extend the functionalization, the isolated bifunctionalized product so obtained can be subsequently functionalized via aromatic electrophilic substitution reactions *viz.* bromination[18a] and nitration[18b] as demonstrated in Scheme 6.



Scheme 6. Further functionalization of the product (**1aa´**).

Conclusion

In conclusion, a one pot sequential synthesis of *N*-(2-(phenylthio)phenyl)acetamides has been developed using benzo[*d*]thiazol-2-amine, aryliodide and carboxylic acid via a copper catalyzed ring opening rearrangement functionalization (RORF). The sequential addition of TBHP leads to the formation of *N*-(2-(phenylsulfinyl)phenyl)acetamide. This RORF process is accompanied with the loss of C and N atoms with *S*-arylation followed by *N*-acylation leading to a bifunctionalized amidic product.

Experimental Section

General Information: All the reagents were of commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 GF_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$and DMSO with tetramethylsilane as the internal standard for ^1H NMR (400 MHz and 600 MHz) $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 MHz and 150 MHz) and. Mass spectra were recorded using ESI mode and APCI mode (Q-TOF MS analyzer). IR spectra were recorded in KBr or neat.

General Procedure for the Formation of *N*-(2-(phenylthio)phenyl)acetamide (1aa′): An oven-dried round bottom flask was charged with benzo[*d*]thiazol-2-amine (**1**) (75 mg, 0.5 mmol), iodobenzene (**a**) (102 mg, 0.5 mmol), $CuSO_4.5H_2O$ (10 mol%, 12.5 mg), K_2CO_3 (1 mmol, 138 mg) and DMF (1 mL). The flask was fitted with a condenser and the resultant reaction mixture was stirred in a pre-heated oil bath maintained at 120 °C. The reaction progress was monitored by TLC. The formation of *N*-(2-(phenylthio)phenyl)cyanamide (**X**) was observed with the consumption of benzo[*d*]thiazol-2-amine (**1**) and iodobenzene (**a**). After 4 h, AcOH (20 equiv., 0.6 mL) was added to the same reaction mixture. The heating of the reaction mixture was continued at 120 °C. The reaction progress was monitored by TLC. After 5 h, the reaction mixture was cooled to room temperature. Then the reaction mixture was admixed with ethyl acetate (35 mL) and washed successively with ice cold saturated $NaHCO_3$ solution (2 × 20 mL). The ethyl acetate layer was separated and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product so obtained was purified over a column of silica gel using hexane:EtOAc (89:11) as the eluents to afford the desired bi-functionalized product (**1aa′**) in an isolated yield of 68% (83 mg).

***N*-(2-(Phenylthio)phenyl)acetamide (1aa′):** Brownish solid; mp 75–77 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.04 (s, 3H), 7.08–7.13 (m, 3H), 7.17 (t, 1H, *J* = 7.2 Hz), 7.24 (d, 2H, *J* = 7.8 Hz), 7.44 (t, 1H, *J* = 7.8 Hz), 7.57 (d, 1H, *J* = 7.2 Hz), 8.20 (s, 1H), 8.43 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 120.0, 121.05, 124.6, 126.5, 127.3, 129.5, 131.2, 135.9, 136.6, 140.0, 168.6; IR (KBr) 3319, 2925, 2853, 1675, 1576, 1511, 1476, 1435, 1370, 1295, 1240, 1164, 1068, 1008, 944, 870, 757, 689, 672, 597, 543, 502 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{14}NOS$ $[M+H]^+$ 244.0791; found 244.0783.

***N*-(2-(*m*-Tolylthio)phenyl)acetamide (1ba′):** Brownish solid; mp 71–73 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.05 (s, 3H), 2.27 (s, 3H), 6.87 (d, 1H, *J* = 7.8 Hz), 6.92 (s, 1H), 6.98 (d, 1H, *J* = 7.8 Hz), 7.10–7.14 (m, 2H), 7.43 (t, 1H, *J* = 7.8 Hz), 7.56 (d, 1H, *J* = 7.2 Hz), 8.21 (s, 1H), 8.42 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.5, 25.0, 120.2, 121.0, 124.6, 127.5, 128.0, 129.4, 131.0, 135.5, 136.5, 139.5, 140.0, 168.6; IR (KBr): 3290, 3056, 2923, 1666, 1576, 1517, 1473, 1434, 1362, 1297, 1245, 1163, 1037, 1017, 964, 938, 876, 853, 781, 756, 685, 601, 548, 525, 470 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{16}NOS$ $[M+H]^+$ 258.0947; found 258.0939.

***N*-(2-((3-Methoxyphenyl)thio)phenyl)acetamide (1ca′):** Brownish gummy; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.04 (s, 3H), 3.69 (s, 3H), 6.60 (s, 1H), 6.64 (d, 1H, *J* = 7.8 Hz), 6.69 (d, 1H, *J* = 7.8 Hz), 7.09 (t, 1H, *J* = 7.2 Hz), 7.14 (t, 1H,*J* = 7.8 Hz), 7.41 (t, 1H, *J* = 7.8 Hz), 7.55 (d, 1H, *J* = 7.8 Hz), 8.20 (s, 1H), 8.41 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 55.4, 112.0, 112.8, 119.4, 119.8, 121.0, 124.6, 130.3, 131.2, 136.7, 137.2, 140.1, 160.3, 168.6; IR (KBr): 3549, 3292, 2934, 2835, 1700, 1588, 1520, 1477, 1426, 1367, 1299, 1230, 1182, 1160, 1096, 1069, 1038, 947, 858, 759, 652, 590, 546, 487 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896; found 274.0903.

***N*-(2-(*p*-Tolylthio)phenyl)acetamide (1da′):** Brownish solid; mp 74–76 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.06 (s, 3H), 2.29 (s, 3H), 7.01 (d, 2H, *J* = 8.4 Hz), 7.06–7.10 (m, 3H), 7.41 (t, 1H, *J* = 7.2 Hz), 7.54 (d, 1H, *J* = 7.2 Hz), 8.20 (s, 1H), 8.40 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.2, 25.0, 121.0, 124.5, 127.7, 128.0, 130.3, 130.8, 132.0, 136.2, 136.7, 139.7, 168.5; IR (KBr) 3306, 2918, 2861, 1670, 1577, 1525, 1460, 1435, 1367, 1301, 1244, 1164, 1103, 1036, 1017, 960, 835, 809, 753, 709, 669, 597, 544, 505, 450 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{16}NOS$ $[M+H]^+$ 258.0947; found 258.0958.

***N*-(2-((4-Fluorophenyl)thio)phenyl)acetamide (1ea′):** White solid; mp 93–95 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.08 (s, 3H), 6.96 (t, 2H, *J* = 8.4 Hz), 7.07–7.11 (m, 3H), 7.41 (t, 1H, *J* = 7.8 Hz), 7.52 (d, 1H, *J* = 7.2 Hz), 8.16 (s, 1H), 8.39 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 116.7 (d, *J* = 22.1 Hz), 120.8, 121.2, 124.7, 129.7 (d, *J* = 7.7 Hz), 130.7, 131.1, 136.2, 139.7, 160.6, 163.1, 168.5; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -118.4 (s); IR (KBr) 3291, 2924, 2853, 1893, 1662, 1584, 1525, 1487, 1436, 1395, 1370, 1270, 1223, 1156, 1036, 1014, 943, 867, 833, 814, 758, 676, 636, 599, 543, 515, 473 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}FNOS$ $[M+H]^+$ 262.0696; found 262.0722.

***N*-(2-((4-Chlorophenyl)thio)phenyl)acetamide (1fa′):** Light brownish solid; mp 78–80 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 6.98 (d, 2H, *J* = 8.4 Hz), 7.11 (t, 1H, *J* = 7.8 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 7.44 (t, 1H, *J* = 7.8 Hz), 7.54 (d, 1H, *J* = 7.2 Hz), 8.15 (s, 1H), 8.42 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 119.6, 121.2, 124.8, 128.4, 129.6, 131.4, 132.4, 134.5, 136.6, 140.0, 168.6; IR (KBr) 3447, 3827, 2924, 2853, 1663, 1577, 1520, 1473, 1433, 1369, 1298, 1251, 1092, 1013, 822, 760, 676, 601, 551, 504, 457 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}ClNOS$ $[M+H]^+$ 278.0401; found 278.0408.

***N*-(2-((4-Bromophenyl)thio)phenyl)acetamide (1ga′):** White solid; mp 121–123 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 6.91 (d, 2H, *J* = 8.4 Hz), 7.12 (t, 1H, *J* = 7.8 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 7.45 (t, 1H, *J* = 7.2 Hz), 7.54 (d, 1H, *J* = 7.8 Hz), 8.14 (s, 1H), 8.43 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 25.0, 119.4, 120.3, 121.3, 124.8, 128.7, 131.5, 132.6, 135.3, 136.7, 140.1, 168.5; IR (KBr) 3284, 2925, 2854, 1661, 1579, 1513, 1464, 1433, 1376, 1297, 1265, 1086, 1008, 815, 741, 589 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}BrNOS$ $[M+H]^+$ 321.9896; found 321.9892.

***N*-(2-((3-(Trifluoromethyl)phenyl)thio)phenyl)acetamide (1ha′):** Brownish solid; mp 81–83 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 7.10 (d, 1H, *J* = 7.8 Hz), 7.14 (t, 1H, *J* = 7.8 Hz), 7.33 (t, 1H, *J* = 7.8 Hz), 7.41 (d, 2H, *J* = 7.2 Hz), 7.48 (t, 1H, *J* = 7.8 Hz), 7.57 (d, 1H, *J* = 7.2 Hz), 8.16 (s, 1H), 8.46 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 118.5, 121.3, 123.1, 123.7, 124.9, 129.9 (d, *J* = 14.1 Hz), 131.9 (t, *J* = 13.3 Hz), 136.9, 137.7, 140.3, 168.5; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -66.1 (d, *J* = 0.9 Hz); IR (KBr): 3265, 2925, 2853, 1660, 1582, 1524, 1438, 1423, 1365, 1321, 1272, 1188, 1167, 1118, 1069, 1016, 971, 945, 905, 880, 854, 791, 763, 694, 649, 606, 550, 492 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}F_3NOS$ $[M+H]^+$ 312.0664; found 312.0649.

***N*-(2-([1,1'-Biphenyl]-2-ylthio)phenyl)acetamide (1ia′):** Light brownish solid; mp 58–60 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.0 (s, 3H), 6.93 (d, 1H, *J* = 7.8 Hz), 7.10 (t, 1H, *J* = 7.2 Hz), 7.21 (t, 1H, *J* = 7.2 Hz), 7.28 (d, 1H, *J* = 7.8 Hz), 7.32 (d, 1H, *J* = 7.8 Hz), 7.42 (t, 1H, *J* = 7.8 Hz), 7.46 (d, 3H, *J* = 6.6 Hz), 7.49–7.53 (m, 3H), 7.95 (s, 1H), 8.39 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.0, 120.9, 124.5, 126.6,

128.1, 128.2, 128.5, 129.5, 130.7, 130.9, 134.4, 136.7, 139.9, 140.3, 141.6, 168.5; IR (KBr): 3363, 2925, 2853, 1700, 1579, 1511, 1460, 1430, 1368, 1298, 1235, 1160, 1073, 1036, 1007, 752, 702, 677, 652, 686, 548, 493, 455 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{18}NOS$ $[M+H]^+$ 320.1104; found 320.1101.

***N*-(2-((4-Chloro-2-methylphenyl)thio)phenyl)acetamide (1ja´):** Brownish solid; mp 97–99 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.08 (s, 3H), 2.40 (s, 3H), 6.61 (d, 1H, *J* = 8.4 Hz), 7.0 (d, 1H, *J* = 7.8 Hz), 7.11 (t, 1H, *J* = 7.2 Hz), 7.19 (s, 1H), 7.42–7.45 (m, 2H), 8.05 (s, 1H), 8.42 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 20.3, 25.0, 119.6, 121.3, 124.9, 127.2, 128.3, 130.5, 131.1, 132.2, 133.4, 136.1, 137.8, 139.9, 168.5; IR (KBr): 3239, 2924, 2853, 1681, 1654, 1577, 1528, 1466, 1437, 1367, 1297, 1257, 1199, 1158, 1098, 1050, 940, 870, 819, 749, 681, 599, 576, 548, 481, 457 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{15}ClNOS$ $[M+H]^+$ 292.0557; found 292.0551.

***N*-(2-((3-Fluoro-4-methoxyphenyl)thio)phenyl)acetamide (1ka´):** Dark brownish solid; mp 76–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.10 (s, 3H), 3.84 (s, 3H), 6.82–6.91 (m, 3H), 7.09 (t, 1H, *J* = 7.2 Hz), 7.40 (t, 1H, *J* = 7.6 Hz), 7.50 (d, 1H, *J* = 7.2 Hz), 8.16 (s, 1H), 8.38 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 25.0, 56.5, 114.4 (d, *J* = 2.2 Hz), 116.7 (d, *J* = 20.1 Hz), 121.2 (d, *J* = 11.1 Hz), 124.7 (d, *J* = 9.1 Hz), 126.9 (d, *J* = 6.0 Hz), 130.9, 135.9, 139.5, 147.0 (d, *J* = 10.5 Hz), 151.9, 153.5, 168.5; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -135.9 (s); IR (KBr): 3360, 2927, 2849, 1696, 1580, 1510, 1432, 1368, 1300, 1269, 1209, 1181, 1133, 1077, 1025, 894, 865, 808, 758, 687, 645, 593, 547, 477 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{15}FNO_2S$ $[M+H]^+$ 292.0802; found 292.0809.

***N*-(4-Nitro-2-(phenylthio)phenyl)acetamide (2aa´):** Brownish solid; mp 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.13 (s, 3H), 7.16 (d, 2H, *J* = 6.8 Hz), 7.28–7.33 (m, 3H), 8.27 (dd, 1H, *J* = 9.2, 2.8 Hz), 8.46 (d, 2H, *J* = 2.4 Hz), 8.68 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.1, 120.1, 126.4, 127.4, 127.5, 128.6, 129.6, 130.0, 131.4, 133.6, 145.1, 168.8; IR (KBr): 3447, 2924, 2854, 1621, 1577, 1499, 1337, 1262, 1092, 1022, 802, 742, 690 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}N_2O_3S$ $[M+H]^+$ 289.0641; found 289.0641.

***N*-(4-Fluoro-2-(*p*-tolylthio)phenyl)acetamide (3da´):** Brownish solid; mp 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 2.31 (s, 3H), 7.02–7.15 (m, 6H), 7.93 (s, 1H), 8.25 (dd, 1H, *J* = 9.2, 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.2, 24.6, 116.6 (d, *J* = 21.8 Hz), 120.9 (d, *J* = 23.3 Hz), 123.1 (d, *J* = 7.8 Hz), 125.0 (d, *J* = 7.8 Hz), 130.1 (d, *J* = 95.5 Hz), 135.0, 137.7, 157.6, 160.0, 168.4; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -120.3 (s); IR (KBr): 3232, 2924, 2854, 1647, 1544, 1474, 1392, 1302, 1239, 1190, 1018, 899, 853, 811, 738, 608, 504 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{15}FNOS$ $[M+H]^+$ 276.0856; found 276.0872.

***N*-(2-((4-Chlorophenyl)thio)-4-fluorophenyl)acetamide (3fa´):** Brownish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.07 (s, 3H), 7.06 (d, 2H, *J* = 8.4 Hz), 7.10–7.15 (m, 1H), 7.19–7.21 (m, 1H), 7.25–7.27 (m, 2H), 7.89 (s, 1H), 8.33 (dd, 1H, *J* = 8.8, 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.8, 117.7 (d, *J* = 21.7 Hz), 121.8 (d, *J* = 23.3 Hz), 122.9, 123.2 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 25.8 Hz), 133.3 (d, *J* = 18.6 Hz), 135.7, 157.6, 160.0, 168.4; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -119.9 (s); IR (KBr): 3437, 2963, 2856, 1646, 1526, 1475, 1392, 1261, 1094, 1021, 801, 700, 505 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{12}ClFNOS$ $[M+H]^+$ 296.0307; found 296.0337.

2,2,2-Trifluoro-*N*-(2-(phenylthio)phenyl)acetamide (1ab´): Light brownish solid; mp 53–55 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.12 (d, 2H, *J* = 7.2 Hz), 7.21 (t, 1H, *J* = 7.2 Hz), 7.25–7.28 (m, 3H), 7.51 (t, 1H, *J* = 8.4 Hz), 7.68 (d, 1H, *J* = 7.8 Hz), 8.40 (d, 1H, *J* = 7.8 Hz), 9.11 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 114.7, 116.7, 121.3, 122.5, 126.6, 127.2, 128.2, 129.7, 131.3, 132.0, 134.6, 136.8, 137.3, 154.8 (q, *J* = 37.3 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.2 (m); IR (KBr): 3451, 2926, 2855, 1637, 1534, 1443, 1154, 1024, 742, 690 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{11}F_3NOS$ $[M+H]^+$ 298.0508; found 298.0519.

2,2,2-Trifluoro-*N*-(2-((3-methoxyphenyl)thio)phenyl)acetamide (1cb´): Brownish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.73 (s, 3H), 6.64–6.75 (m, 3H), 7.17 (t, 1H, *J* = 8.0 Hz), 7.24–7.28 (m, 1H), 7.50 (t, 1H, *J* = 8.8 Hz), 7.68 (d, 1H, *J* = 8.0 Hz), 8.39 (d, 1H, *J* = 8.4 Hz), 9.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.5, 112.9, 113.8, 120.4, 121.4, 122.4, 126.6, 130.6, 131.4, 135.9, 136.9, 137.5, 160.6; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.2 (s); IR (KBr): 3329, 2924, 2854, 1720, 1587, 1540, 1444, 1413, 1148, 1095, 1025, 801, 690, 621 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}F_3NO_2S$ $[M+H]^+$ 328.0614; found 328.0632.

2,2,2-Trifluoro-*N*-(2-(*p*-tolylthio)phenyl)acetamide (1db´): Light brownish solid; mp 100–102 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 7.07 (q, 4H, *J* = 7.6 Hz), 7.23 (t, 1H, *J* = 7.8 Hz), 7.47 (t, 1H, *J* = 6.6 Hz), 7.64 (d, 1H, *J* = 7.8 Hz), 8.37 (d, 1H, *J* = 8.4 Hz), 9.13 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 21.2, 114.8, 116.7, 121.2, 123.5, 126.6, 129.0, 130.5, 130.8, 130.9, 136.4, 137.0, 137.6, 154.8 (q, *J* = 37.3 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.2 (s); IR (KBr): 3254, 2920, 1670, 1581, 1512, 1433, 1400, 1292, 1185, 1018, 803, 756, 535 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}F_3NOS$ $[M+H]^+$ 312.0464; found 312.0461.

2,2,2-Trifluoro-*N*-(2-((4-fluorophenyl)thio)phenyl)acetamide (1eb´): Light brownish solid; mp 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.98 (t, 2H, *J* = 8.4 Hz), 7.13–7.16 (m, 2H), 7.23–7.27 (m, 1H), 7.49 (t, 1H, *J* = 7.2 Hz), 7.63 (d, 1H, *J* = 7.6 Hz), 8.37 (d, 1H, *J* = 8.0 Hz), 9.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 114.4, 117.0 (d, *J* = 22.2 Hz), 117.2, 121.5, 123.3, 126.7, 129.6 (d, *J* = 3.3 Hz), 130.8 (d, *J* = 8.2 Hz), 131.3, 136.4, 137.0, 154.6, 155.0, 162.3 (d, *J* = 246.5 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -117.2 (s), -79.1 (s); IR (KBr): 3318, 2924, 1713, 1588, 1490, 1261, 1154, 1093, 1018, 800, 622, 515 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{10}F_4NOS$ $[M+H]^+$ 316.0414; found 316.0425.

***N*-(2-((4-Chlorophenyl)thio)phenyl)-2,2,2-trifluoroacetamide (1fb´):** Light brownish solid; mp 84–86 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.04 (d, 2H, J = 8.4 Hz), 7.23–7.29 (m, 3H), 7.52 (t, 1H, *J* = 8.4 Hz), 7.66 (d, 1H, *J* = 7.8 Hz), 8.40 (d, 1H, *J* = 8.4 Hz), 9.06 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 114.7, 116.7, 121.5, 122.1, 126.8, 129.4, 129.9, 131.6, 133.2, 133.3, 136.8, 137.3, 154.8 (q, *J* = 37.5 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.1 (s); IR (KBr): 3261, 2920, 1695, 1583, 1434, 1294, 1152, 1092, 1036, 815, 757, 535 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{10}ClF_3NOS$ $[M+H]^+$ 332.0118; found 332.0139.

2,2,2-Trifluoro-*N*-(4-fluoro-2-(phenylthio)phenyl)acetamide (3ab´): Brownish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.15–7.21 (m, 3H), 7.28–7.34 (m, 4H), 8.31 (dd, 1H, *J* = 9.2, 5.2 Hz), 8.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 117.2, 117.6 (d, *J* = 22.1 Hz), 122.4 (d, *J* = 23.4 Hz), 123.2 (d, *J* = 8.1 Hz), 125.9 (d, *J* = 8.0 Hz), 128.0, 129.4, 130.0, 132.9 (d, *J* = 3.2 Hz), 133.4, 154.7, 155.0, 159.9 (d, *J* = 248.2 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -117.0 (s), -79.1 (s); IR (KBr): 3314, 2923, 1708, 1584, 1485, 1253, 1150, 1089, 1015, 797, 618, 511 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{10}F_4NOS$ $[M+H]^+$ 316.0414; found 316.0418.

***N*-(2-(*p*-Tolylthio)phenyl)propionamide (1dc´):** Yellowish gummy; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 1.11 (t, 3H, *J* = 7.8 Hz), 2.27–2.30 (m, 5H), 7.00 (d, 2H, *J* = 8.4 Hz), 7.06 (d, 2H, *J*

= 7.8 Hz), 7.09 (t, 1H, *J* = 7.8 Hz), 7.41 (t, 1H, *J* = 7.8 Hz), 7.55 (d, 1H, *J* = 7.8 Hz), 8.25 (s, 1H), 8.45 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 9.6, 21.1, 31.2, 120.8, 120.9, 124.4, 127.8, 130.3, 130.9, 132.0, 136.3, 136.6, 139.8, 172.2; IR (KBr) 3367, 2975, 2921, 1695, 1579, 1410, 1433, 1294, 1182, 1083, 1016, 805, 756 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{18}NOS$ $[M+H]^+$ 272.1104; found 272.1091.

***N*-(2-(Phenylthio)phenyl)pivalamide (1ad′):** Yellowish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.10 (s, 9H), 7.03 (d, 2H, *J* = 7.2 Hz), 7.09–7.15 (m, 2H), 7.22 (t, 2H, *J* = 7.2 Hz), 7.44–7.49 (m, 1H), 7.61 (d, 1H, *J* = 8.0 Hz), 8.52 (d, 1H, *J* = 8.4 Hz), 8.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.4, 40.2, 119.6, 120.8, 124.3, 126.3, 126.6, 129.5, 130.3, 131.4, 135.7, 136.1, 136.9, 140.3, 176.9; IR (KBr) 3384, 2926, 1690, 1580, 1511, 1478, 1421, 1301, 1175, 1025, 741, 691 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{20}NOS$ $[M+H]^+$ 286.1260; found 286.1238.

***N*-(2-(*p*-Tolylthio)phenyl)hexanamide (1de′):** Brownish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84–0.89 (m, 3H), 1.22–1.26 (m, 4H), 1.51–1.58 (m, 2H), 2.24 (t, 2H, *J* = 7.6 Hz), 2.29 (s, 3H), 6.99–7.11 (m, 5H), 7.42 (t, 1H, *J* = 8.4 Hz), 7.56 (d, 1H, *J* = 7.6 Hz), 8.22 (s, 1H), 8.46 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 19.4, 21.1, 22.5, 25.3, 31.4, 115.5, 118.9, 127.3, 130.0, 130.3, 130.9, 131.0, 133.2, 135.7, 137.7, 148.8; IR (KBr) 3368, 2924, 2855, 1699, 1510, 1459, 1262, 1092, 1021, 803, 702, 501 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{24}NOS$ $[M+H]^+$ 314.1573; found 314.1590.

4-Methoxy-*N*-(2-(*p*-tolylthio)phenyl)benzamide (1df′): Brownish solid; mp 115–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.27 (s, 3H), 3.85 (s, 3H), 6.90 (d, 2H, *J* = 8.8 Hz), 7.05 (s, 4H), 7.12 (t, 1H, *J* = 7.2 Hz), 7.47 (t, 1H, *J* = 8.0 Hz), 7.61 (d, 1H, *J* = 7.6 Hz), 7.65 (d, 2H, *J* = 8.8 Hz), 8.66 (d, 1H, *J* = 8.0 Hz), 9.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.1, 55.6, 114.1, 120.6, 120.9, 124.4, 127.2, 127.8, 129.1, 130.3, 131.1, 132.0, 136.5, 136.7, 140.2, 162.7, 165.0; IR (KBr) 3366, 2927, 2839, 1677, 1606, 1575, 1502, 1432, 1303, 1251, 1177, 1100, 1030, 837, 843, 806, 760, 692, 579, 507 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{20}NO_2S$ $[M+H]^+$ 350.1209; found 350.1202.

General Procedure for the Formation of *N*-(2-(phenylsulfinyl)phenyl)acetamide (1aa″): An oven-dried round bottom flask was charged with benzo[*d*]thiazol-2-amine (**1**) (75 mg, 0.5 mmol), iodobenzene (**a**) (102 mg, 0.5 mmol), $CuSO_4.5H_2O$ (10 mol%, 12.5 mg), K_2CO_3 (1 mmol, 138 mg) and DMF (1 mL). The flask was fitted with a condenser and the resultant reaction mixture was stirred in a pre-heated oil bath maintained at 120 °C. The reaction progress was monitored by TLC. The formation of *N*-(2-(phenylthio)phenyl)cyanamide (**X**) was observed with the consumption of benzo[*d*]thiazol-2-amine (**1**) and iodobenzene (**a**). After 4 h, AcOH (20 equiv., 0.6 mL) was added to the same reaction mixture. The heating of the reaction mixture was continued at 120 °C. The reaction progress was monitored by TLC. After 5 h, the consumption of the *in situ* generated cyanamide was observed with the formation of *N*-(2-(phenylthio)phenyl)acetamide **(1aa′)**. To the same reaction, TBHP (5-6 M in decane) (6 equiv.) was added. Again the reaction was heated at 120 °C. The formation of the sulfoxide was observed from the TLC. After 17 h, the reaction mixture was cooled to room temperature. Then the reaction mixture was admixed with ethyl acetate (35 mL) and the organic layer was washed successively with ice cold saturated $NaHCO_3$ solution (2 × 20 mL). The ethyl acetate layer was separated and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product so obtained was purified over a column of silica gel using hexane:EtOAc (60:40) as the eluents to afford the desired sulfoxide product (**1aa″**) in an isolated yield of 60% (78 mg).

***N*-(2-(Phenylsulfinyl)phenyl)acetamide (1aa″):** Dark brownish gummy; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.04 (s, 3H), 7.17 (t, 1H, *J* = 7.2 Hz), 7.43–7.47 (m, 3H), 7.47–7.50 (m, 3H), 7.57 (d, 1H, *J* = 7.2 Hz), 8.31 (d, 1H, *J* = 8.4 Hz), 10.04 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 123.4, 123.5, 124.4, 128.2, 129.4, 131.0, 133.4, 140.2, 142.9, 159.3, 168.7; IR (KBr): 3270, 2925, 2856, 1694, 1586, 1527, 1473, 1439, 1371, 1303, 1252, 1159, 1082, 1019, 925, 754, 692, 599, 553, 490, 486, 457 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{14}NO_2S$ $[M+H]^+$ 260.0740; found 260.0741.

***N*-(2-((3-Methoxyphenyl)sulfinyl)phenyl)acetamide (1ca″):** Dark brownish solid; mp 121–123 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.05 (s, 3H), 3.78 (s, 3H), 6.93 (d, 1H, *J* = 8.4 Hz), 6.98 (d, 1H, *J* = 7.8 Hz), 7.08 (s, 1H), 7.16 (t, 1H, *J* = 7.2 Hz), 7.33 (t, 1H, *J* = 7.8 Hz), 7.48 (t, 1H, *J* = 7.8 Hz), 7.54 (d, 1H, *J* = 7.8 Hz), 8.31 (d, 1H, *J* = 8.4 Hz), 10.04 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 55.7, 109.8, 116.5, 116.6, 123.3, 123.5, 128.09, 128.1, 130.5, 133.3, 140.2, 144.3, 160.4, 168.6; IR (KBr) 3242, 3050, 2926, 2852, 1693, 1592, 1539, 1471, 1428, 1365, 1307, 1285, 1230, 1184, 1164, 1072, 1040, 1020, 956, 915, 841, 772, 688, 600, 568, 515, 493, 468 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{16}NO_3S$ $[M+H]^+$ 290.0845; found 290.0848.

***N*-(2-(*p*-Tolylsulfinyl)phenyl)acetamide (1da″):** Dark brownish solid; mp 85–87 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.05 (s, 3H), 2.36 (s, 3H), 7.16 (t, 1H, *J* = 7.2 Hz), 7.25 (d, 2H, *J* = 8.4 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.46–7.49 (m, 1H), 7.53 (d, 1H, *J* = 7.2 Hz), 8.32 (d, 1H, *J* = 8.4 Hz), 10.11 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 21.5, 24.9, 120.0, 123.2, 123.5, 124.4, 127.9, 128.3, 130.2, 133.2, 139.7, 140.2, 141.6, 168.7; IR (KBr): 3451, 3259, 2925, 2853, 1700, 1589, 1532, 1467, 1435, 1370, 1302, 1249, 1161, 1082, 1021, 894, 811, 760, 705, 619, 597, 549, 533, 494, 468 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896; found 274.0907.

***N*-(2-((4-Fluorophenyl)sulfinyl)phenyl)acetamide (1ea″):** Dark brownish solid; mp 99–101 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.05 (s, 3H), 7.14–7.19 (m, 3H), 7.47–7.51 (m, 3H), 7.53 (d, 1H, *J* = 7.8 Hz), 8.31 (d, 1H, *J* = 7.8 Hz), 10.0 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 116.8 (d, *J* = 22.6 Hz), 123.6 (d, *J* = 21.1 Hz), 126.7 (d, *J* = 8.8 Hz), 128.0, 133.5, 138.5 (d, *J* = 3.0 Hz), 140.2, 163.5, 165.1, 168.6; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): **δ** -111.9 (s); IR (KBr) 3441, 2925, 2853, 1697, 1589, 1532, 1492, 1466, 1436, 1372, 1032, 1230, 1156, 1082, 1021, 837, 813, 761, 673, 650, 594, 533, 474 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}FNO_2S$ $[M+H]^+$ 278.0646; found 278.0658.

***N*-(2-((4-Chlorophenyl)sulfinyl)phenyl)acetamide (1fa″):** Dark brownish solid; mp 106–108 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.04 (s, 3H), 7.17 (t, 1H, *J* = 7.8 Hz), 7.42 (s, 4H), 7.48–7.51 (m, 1H), 7.54 (d, 1H, *J* = 7.8 Hz), 8.30 (d, 1H, *J* = 5.4 Hz), 9.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 119.9, 123.5, 123.7, 125.8, 128.0, 129.7, 133.6, 137.4, 140.2, 141.5, 168.6; IR (KBr) 3443, 2925, 2853, 1661, 1587, 1525, 1473, 1434, 1371, 1302, 1250, 1169, 1090, 1034, 1009, 825, 762, 741, 703, 650, 600, 559, 526, 507, 464 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}ClNO_2S$ $[M+H]^+$ 294.0350; found 294.0363.

***N*-(2-((4-Bromophenyl)sulfinyl)phenyl)acetamide (1ga″):** Brownish solid; mp 95–97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.05 (s, 3H), 7.18 (t, 1H, *J* = 7.2 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 7.50 (t, 1H, *J* = 7.8 Hz), 7.55 (d, 1H, *J* = 7.2 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 8.32 (d, 1H, *J* = 7.8 Hz), 9.95 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 123.5, 123.6, 125.7, 125.9, 127.7, 128.0, 132.6, 133.6, 140.2, 142.1, 168.6; IR (KBr): 3477, 3278, 2924, 2852, 1697, 1659, 1587, 1521, 1470, 1434, 1370, 1301, 1248, 1172, 1127, 1064, 1036, 1005, 820, 762, 723, 650, 598, 555, 502 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}BrNO_2S$ $[M+H]^+$ 337.9845; found 337.9850.

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***N*-(2-((3-(Trifluoromethyl)phenyl)sulfinyl)phenyl)acetamide (1ha˝):** Dark brownish solid; mp 86–88 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.03 (s, 3H), 7.20 (t, 1H, *J* = 7.2 Hz), 7.48–7.52 (m, 2H), 7.54 (t, 1H, *J* = 7.8 Hz), 7.61 (dd, 1H, *J* = 7.8, 1.3 Hz), 7.69 (d, 1H, *J* = 7.8 Hz), 7.96 (s, 1H), 8.27 (d, 1H, *J* = 8.4 Hz), 9.86 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.5, 121.2 (q, *J* = 3.7 Hz), 122.6, 123.7 (d, *J* = 29.2 Hz), 124.4, 127.7 (t, *J* = 3.3 Hz), 127.9, 128.1, 131.9 (q, *J* = 33.0 Hz), 133.9, 140.1, 144.5, 168.6; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -66.0 (s); IR (KBr) 3487, 3255, 2924, 2852, 1664, 1585, 1523, 1467, 1433, 1375, 1327, 1304, 1280, 1173, 1129, 1098, 1069, 1035, 913, 806, 761, 695, 648, 626, 600, 578, 509, 476 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}F_3NO_2S$ $[M+H]^+$ 328.0614; found 328.0621.

***N*-(2-([1,1'-Biphenyl]-2-ylsulfinyl)phenyl)acetamide (1ia˝):** Dark brownish solid; mp 73–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.09 (s, 3H), 6.17 (d, 1H, *J* = 7.6 Hz), 6.59 (t, 1H, *J* = 7.6 Hz), 7.09 (d, 2H, *J* = 7.2 Hz), 7.22 (t, 2H, *J* = 7.6 Hz), 7.32–7.42 (m, 3H), 7.49 (t, 1H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.6 Hz), 8.09 (d, 1H, *J* = 8.0 Hz), 8.16 (d, 1H, *J* = 7.6 Hz), 9.67 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 122.8, 122.84, 123.9, 126.7, 127.7, 128.4, 128.5, 128.8, 129.5, 131.2, 131.5, 132.3, 138.1, 139.4, 139.9, 140.9, 168.3; IR (KBr) 3261, 2925, 1700, 1587, 1530, 1434, 1368, 1301, 1245, 1159, 1072, 1007, 756, 702, 552, 519, 489 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{18}NO_2S$ $[M+H]^+$ 336.1053; found 336.1068.

***N*-(4-Fluoro-2-(phenylsulfinyl)phenyl)acetamide (3aa˝):** Yellowish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.05 (s, 3H), 7.17–7.22 (m, 1H), 7.28–7.30 (m, 1H), 7.47–7.54 (m, 5H), 8.30 (dd, 1H, *J* = 9.2, 4.8 Hz), 9.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.7, 114.8 (d, *J* = 24.3 Hz), 119.9 (d, *J* = 21.6 Hz), 124.4, 125.0 (d, *J* = 4.4 Hz), 125.4 (d, *J* = 6.9 Hz), 129.3 (d, *J* = 4.4 Hz), 129.7, 129.9 (d, *J* = 5.4 Hz), 131.3 (d, *J* = 5.8 Hz), 131.5, 136.4 (d, *J* = 2.9 Hz), 142.3, 156.8, 159.2, 168.6; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -119.8 (s); IR (KBr) 3258, 2926, 2856, 1690, 1602, 1485, 1396, 1301, 1244, 1193, 1124, 1080, 1025, 896, 812, 750, 689, 584, 545, 499 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}FNO_2S$ $[M+H]^+$ 278.0646; found 278.0647.

***N*-(4-Fluoro-2-(*p*-tolylsulfinyl)phenyl)acetamide (3da˝):** Light brownish solid; mp 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.03 (s, 3H), 2.35 (s, 3H), 7.12–7.17 (m, 1H), 7.20–7.26 (m, 3H), 7.37 (d, 2H, *J* = 8.0 Hz), 8.27 (dd, 1H, *J* = 8.8, 4.8 Hz), 9.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.5, 24.8, 114.6 (d, *J* = 24.2 Hz), 119.6 (d, *J* = 21.6 Hz), 124.5, 125.2 (d, *J* = 6.9 Hz), 130.1 (d, *J* = 4.9 Hz), 130.4, 136.3 (d, *J* = 3.0 Hz), 139.1, 142.1, 156.7, 159.2, 168.6; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -120.0 (s); IR (KBr) 3434, 3272, 2925, 2856, 1663, 1598, 1517, 1471, 1391, 1265, 1242, 1181, 1117, 1057, 1024, 888, 841, 815, 680, 632, 584, 506, 451 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{15}FNO_2S$ $[M+H]^+$ 292.0802; found 292.0802.

***N*-(2-((4-Chlorophenyl)sulfinyl)-4-fluorophenyl)acetamide (3fa˝):** Light brownish solid; mp 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.06 (s, 3H), 7.18–7.23 (m, 1H), 7.26–7.29 (m, 1H), 7.46 (s, 4H), 8.29 (dd, 1H, *J* = 9.2, 4.8 Hz), 9.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.7, 114.7 (d, *J* = 24.3 Hz), 120.2 (d, *J* = 21.5 Hz), 125.6 (d, *J* = 7.0 Hz), 125.8, 129.7 (d, *J* = 5.0 Hz), 129.9, 136.3, 137.9, 140.8, 156.8, 159.3, 168.5; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -119.4 (s); IR (KBr) 3423, 3273, 2926, 2855, 1661, 1598, 1515, 1476, 1391, 1373, 1245, 1184, 1089, 1058, 1015, 888, 825, 740, 679, 587, 506, 477 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{12}ClFNO_2S$ $[M+H]^+$ 312.0256; found 312.0354.

2,2,2-Trifluoro-*N*-(2-(phenylsulfinyl)phenyl)acetamide (1ab˝): Brownish solid; mp 92–94 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.25 (t, 1H, *J* = 7.2 Hz), 7.40 (q, 3H, *J* = 6.3 Hz), 7.45 (d, 2H, *J* = 7.2 Hz), 7.48 (t, 1H, *J* = 7.2 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 8.28 (d, 1H, *J* = 8.4 Hz), 11.51 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 114.8, 116.7, 123.1, 126.4, 127.3, 129.5, 129.9, 130.2, 134.4, 135.6, 140.5, 155.0 (q, *J* = 37.8 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.1 (s); IR (KBr): 3441, 2924, 2854, 1728, 1614, 1554, 1462, 1441, 1280, 1186, 1160, 1138, 1018, 897, 800, 758, 738, 682, 549, 530, 494 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{11}F_3NO_2S$ $[M+H]^+$ 314.0457; found 314.0461.

2,2,2-Trifluoro-*N*-(2-((3-methoxyphenyl)sulfinyl)phenyl)acetamide (1cb˝): Brownish solid; mp 95–97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 3.81 (s, 3H), 6.95–6.99 (m, 2H), 7.14 (s, 1H), 7.30–7.33 (m, 1H), 7.35 (t, 1H, *J* = 7.8 Hz), 7.54–7.57 (m, 1H), 7.62 (dd, 1H, *J* = 7.8, 1.3 Hz), 8.36 (d, 1H, *J* = 8.4 Hz), 11.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 55.7, 108.9, 116.4, 117.5, 123.4, 125.6, 128.0, 129.3, 130.7, 133.3, 138.1, 143.4, 155.1 (d, *J* = 37.8 Hz), 160.6; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.1 (s); IR (KBr): 3434, 2923, 2852, 1734, 1595, 1467, 1440, 1282, 1248, 1158, 1037, 896, 762, 683, 613, 593, 513, 464 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}F_3NO_3S$ $[M+H]^+$ 344.0563; found 344.0558.

2,2,2-Trifluoro-*N*-(2-(*p*-tolylsulfinyl)phenyl)acetamide (1db˝): Brownish solid; mp 80–82 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 2.37 (s, 3H), 7.27 (d, 2H, *J* = 8.4 Hz), 7.30 (t, 1H, *J* = 7.8 Hz), 7.40 (d, 2H, *J* = 7.8 Hz), 7.53–7.55 (m, 1H), 7.58–7.59 (m, 1H), 8.36 (d, 1H, *J* = 8.4 Hz), 11.68 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 21.6, 114.8, 116.7, 121.4, 123.5, 124.4, 125.6, 127.9, 129.5, 129.6, 132.2, 133.2, 138.0, 140.0, 141.8, 155.1 (q, *J* = 37.7 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.1 (s); IR (KBr): 3441, 2926, 1733, 1604, 1547, 1444, 1281, 1199, 1158, 1080, 1012, 900, 808, 761, 619, 549, 530, 492 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}F_3NO_2S$ $[M+H]^+$ 328.0614; found 328.0617.

2,2,2-Trifluoro-*N*-(2-((4-fluorophenyl)sulfinyl)phenyl)acetamide (1eb˝): Dark brownish solid; mp 99–101 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.18 (t, 2H, *J* = 8.4 Hz), 7.33 (t, 1H, *J* = 7.2 Hz), 7.50–7.52 (m, 2H), 7.56–7.59 (m, 1H), 7.61–7.62 (m, 1H), 8.37 (d, 1H, *J* = 8.4 Hz), 11.52 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 114.8, 116.7, 117.1 (d, *J* = 22.6 Hz), 123.7, 125.7, 126.6 (d, *J* 9.0 Hz), 127.8, 129.2, 133.5, 137.6 (d, *J* = 3.0 Hz), 138.1, 155.2 (q, *J* = 37.8 Hz), 163.7, 165.4; ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -111.2 (s), -79.1 (s); IR (KBr): 3441, 3061, 2924, 1729, 1613, 1553, 1489, 1438, 1281, 1234, 1192, 1162, 1069, 899, 831, 758, 734, 531, 475 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{10}F_4NO_2S$ $[M+H]^+$ 332.0363; found 332.0372.

***N*-(2-((4-Chlorophenyl)sulfinyl)phenyl)-2,2,2-trifluoroacetamide (1fb˝):** Brownish solid; mp 100–102 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33 (t, 1H, *J* = 7.2 Hz), 7.45 (s, 4H), 7.57 (t, 1H, *J* = 9.0 Hz), 7.61–7.63 (m, 1H), 8.36 (d, 1H, *J* = 8.4 Hz), 11.48 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 118.0, 118.2, 123.6, 125.6, 125.7, 127.9, 128.5, 129.0, 129.5, 130.0, 133.6, 137.9, 138.1, 140.6, 155.1 (q, *J* = 37.8 Hz); ^{19}F NMR ($CDCl_3$ + hexafluorobenzene): δ -79.1 (s); IR (KBr): 3459, 2925, 2855, 1717, 1615, 1551, 1474, 1446, 1391, 1281, 1243, 1200, 1161, 1090, 1024, 1009, 901, 823, 758, 741, 617, 578, 556, 523, 485, 455 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{10}ClF_3NO_2S$ $[M+H]^+$ 348.0067; found 348.0065.

(S)-2,2,2-Trifluoro-*N*-(4-fluoro-2-(phenylsulfinyl)phenyl)acetamide (3ab˝): Brownish gummy; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.23–7.26 (m, 1H), 7.35 (dd, 1H, *J* = 6.9, 2.9 Hz), 7.49–7.52 (m, 3H), 7.53–7.55 (m, 2H), 8.35 (dd, 1H, *J* = 9.1, 4.6 Hz), 11.45 (s, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) 112.0 (d, *J* = 25.3 Hz), 114.8, 116.7, 119.5 (d, *J* = 22.8 Hz), 121.1, 129.7, 130.3 (d, *J* = 8.1 Hz), 132.0, 143.6, 143.8 (d, *J* = 5.7 Hz), 155.5, 155.7, 160.6, 162.2; ^{19}F NMR (DMSO-d_6 + hexafluorobenzene): δ -112.9 (s), -76.4 (s); IR (KBr): 3429, 1649, 1384, 1047, 1026, 997, 827, 766, 740, 640,

431 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{10}F_4NO_2S$ $[M+H]^+$ 332.0363; found 332.0566.

***N*-(2-(Phenylsulfinyl)phenyl)propionamide (1ac˝):** Dark brownish solid; mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.12 (t, 3H, *J* = 7.6 Hz), 2.20–2.35 (m, 2H), 7.17 (t, 1H, *J* = 7.6 Hz), 7.43–7.52 (m, 6H), 7.57 (d, 1H, *J* = 7.6 Hz), 8.38 (d, 1H, *J* = 8.4 Hz), 10.05 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 9.6, 31.2, 123.2, 123.3, 124.5, 124.9, 128.2, 129.4, 131.0, 133.4, 140.5, 143.0, 172.5; IR (KBr): 3403, 2924, 2852, 1695, 1586, 1531, 1466, 1439, 1380, 1297, 1261, 1188, 1155, 1086, 1019, 804, 753, 692, 542, 439 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896; found 274.0897.

***N*-(2-(Phenylsulfinyl)phenyl)pivalamide (1ad˝):** Dark brownish solid; mp 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.16 (s, 9H), 7.15–7.19 (m, 1H), 7.41–7.48 (m, 5H), 7.49–7.56 (m, 2H), 8.53 (d, 1H, *J* = 8.4 Hz), 10.3 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 27.5, 40.1, 123.07, 123.1, 125.0, 127.3, 128.4, 129.4, 131.0, 133.4, 141.0, 143.3, 177.7; IR (KBr): 3257, 2963, 2856, 1689, 1586, 1534, 1476, 1435, 1398, 1367, 1301, 1228, 1124, 1080, 1019, 919, 808, 754, 690, 592, 569, 532, 497 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{20}NO_2S$ $[M+H]^+$ 302.1209; found 302.1194.

***N*-(2-(Phenylsulfinyl)phenyl)hexanamide (1de˝):** Dark brownish gummy; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 0.88 (t, 3H, *J* = 7.2 Hz), 1.23–1.32 (m, 4H), 1.56–1.61 (m, 2H), 2.17–2.22 (m, 1H), 2.26–2.31 (m, 1H), 2.35 (s, 3H), 7.14 (t, 1H, *J* = 7.8 Hz), 7.23 (d, 2H, *J* = 8.4 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 7.47 (t, 1H, *J* = 7.8 Hz), 7.52 (d, 1H, *J* = 7.8 Hz), 8.39 (d, 1H, *J* = 8.4 Hz), 10.12 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 14.1, 21.4, 22.6, 25.1, 31.5, 38.1, 123.0, 123.2, 124.5, 127.8, 128.0, 130.1, 133.2, 139.7, 140.4, 141.5, 171.9; IR (KBr): 3358, 2927, 2857, 1706, 1588, 1526, 1465, 1440, 1378, 1315, 1225, 1148, 1092, 1041, 1019, 812, 734, 712, 653, 580, 554, 521 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{24}NO_2S$ $[M+H]^+$ 330.1522; found 330.9066.

4-Methoxy-*N*-(2-(*p*-tolylsulfinyl)phenyl)benzamide (1df˝): Yellowish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.27 (s, 3H), 3.87 (s, 3H), 6.99 (d, 2H, *J* = 8.8 Hz), 7.12 (d, 2H, *J* = 8.0 Hz), 7.17 (d, 1H, *J* = 7.4 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.49–7.55 (m, 2H), 7.98 (d, 2H, *J* = 8.8 Hz), 8.60 (d, 1H, *J* = 8.0 Hz), 11.1 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.4, 55.6, 114.1, 123.0, 123.2, 124.5, 126.4, 127.8, 127.9, 129.5, 130.1, 133.1, 139.6, 141.5, 141.6, 162.8, 164.8; IR (KBr) 3244, 2958, 2843, 1676, 1605, 1540, 1509, 1463, 1436, 1255, 1180, 1114, 1080, 1024, 896, 845, 810, 761, 735, 686, 624, 578, 543, 475 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{20}NO_3S$ $[M+H]^+$ 366.1158; found 366.1152.

4-Chloro-*N*-(2-(*p*-tolylsulfinyl)phenyl)benzamide (1dg˝): Yellowish gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.30 (s, 3H), 7.14 (d, 2H, *J* = 8.0 Hz), 7.20 (t, 1H, *J* = 7.2 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.47 (d, 2H, *J* = 8.8 Hz), 7.55 (d, 2H, *J* = 7.6 Hz), 7.94 (d, 2H, *J* = 8.4 Hz), 8.59 (d, 1H, *J* = 8.0 Hz), 11.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.4, 123.1, 123.7, 124.5, 127.9, 128.0, 129.0, 129.2, 130.2, 132.5, 133.2, 138.6, 139.6, 140.7, 141.7, 164.1; IR (KBr) 3430, 3243, 2923, 1682, 1598, 1540, 1489, 1436, 1315, 1256, 1103, 1012, 893, 848, 808, 756, 674, 620, 547, 524, 477 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{17}ClNO_2S$ $[M+H]^+$ 370.0663; found 370.0645.

General Procedure for the Bromination of *N*-(2-(Phenylsulfinyl)phenyl)acetamide (1aa˝): An oven-dried round bottom flask was charged with *N*-(2-(phenylsulfinyl)phenyl)acetamide (**1aa˝**) (52 mg, 0.2 mmol), $KBrO_3$ (0.06 mmol, 11 mg), AcOH (0.3 mL) and stirred at room temperature. Then 48% hydrobromic acid (0.04 mL) was added to the stirred reaction mixture. The reaction progress was monitored by TLC. After 30 min, the reaction mixture was admixed with ethyl acetate (20 mL) and the organic layer was washed with saturated $NaHCO_3$ solution. The ethyl acetate layer was separated and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure and the residue was purified by column chromatography with eluents hexane:EtOAc (60:40) to afford the desired product (**4aa˝**) in an isolated yield of 98% (66 mg).

***N*-(4-Bromo-2-(phenylsulfinyl)phenyl)acetamide (4aa˝):** White solid; mp 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.03 (s, 3H), 7.45–7.56 (m, 6H), 7.66 (s, 1H), 8.21 (d, 1H, *J* = 8.4 Hz), 10.0 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 24.8, 115.8, 124.4, 124.7, 129.6, 129.9, 130.2, 131.4, 135.9, 139.1, 142.2, 168.5; IR (KBr) 3433, 3253, 2926, 2854, 1664, 1577, 1505, 1468, 1375, 1286, 1244, 1140, 1080, 1036, 929, 828, 751, 694, 662, 592, 559, 498, 484, 427 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}BrNO_2S$ $[M+H]^+$ 337.9845; found 337.9827.

General Procedure for the Nitration of *N*-(2-(Phenylsulfinyl)phenyl)acetamide (1aa˝): *N*-(2-(Phenylsulfinyl)phenyl)acetamide (**1aa˝**) (52 mg, 0.2 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (4.8 mg,0.02 mmol), TBN (0.029 mL, 0.24 mmol) and CH_3CN (3.0 mL) were taken in an oven-dried round bottom flask. The resulting mixture was heated in an oil bath at 80 °C for 2 h, and the progress of the reaction was monitored by TLC. After cooling the mixture to room temperature, the volatiles were removed in vacuo, and the residue was purified by column chromatography with eluents hexane:EtOAc (53:47) to afford the desired product (**5aa˝**) in an isolated yield of 84% (51 mg).

***N*-(4-Nitro-2-(phenylsulfinyl)phenyl)acetamide (5aa˝):** Brownish solid; mp 120–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.16 (s, 3H), 7.51–7.57 (m, 5H), 8.31 (dd, 1H, *J* = 9.2, 2.5 Hz), 8.44 (d, 1H, *J* = 2.8 Hz), 8.65 (d, 1H, *J* = 9.2 Hz), 10.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 25.2, 122.4, 123.4, 124.4, 127.8, 128.4, 129.9, 131.9, 141.6, 142.3, 145.9, 169.1; IR (KBr) 3421, 3200, 2924, 2854, 1711, 1611, 1587, 1500, 1400, 1348, 1318, 1284, 1226, 1131, 1076, 1020, 908, 858, 749, 686, 603, 555, 533, 497, 448 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{13}N_2O_4S$ $[M+H]^+$ 305.0591; found 305.0577.

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[15] CCDC-1836285 for *N*-(2-(phenylthio)phenyl)acetamide (**1aa**′) and CCDC-1834795 for (R)-2,2,2-trifluoro-*N*-(2-(phenylsulfinyl)phenyl)acetamide (**1ab**″) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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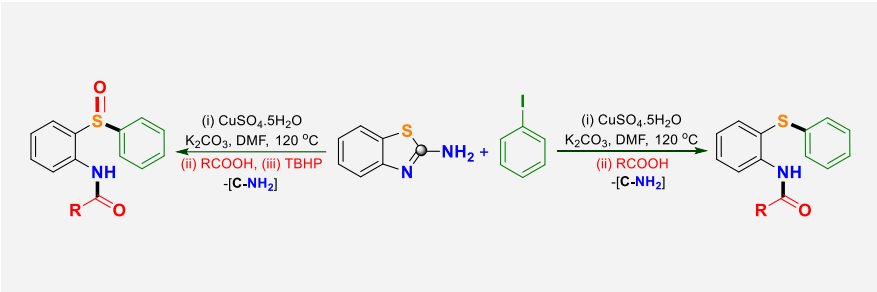
Graphical Abstract



A new telescopic synthesis of *N*-(2-(phenylthio)phenyl)acetamides has been established using benzo[*d*]thiazol-2-amine, aryliodide and carboxylic acid via a copper catalyzed ring opening rearrangement functionalization (RORF). The sequential addition of TBHP leads to the formation of *N*-(2-(phenylsulfinyl)phenyl)acetamide.

Ring opening rearrangement functionalization (RORF)

Ahalya Behera, Amitava Rakshit, Ashish K. Sahoo and Bhisma K. Patel*

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One Pot Sequential Synthesis of *N*-(2-(Phenylsulfinyl)phenyl)acetamides: A Ring Opening Rearrangement Functionalization (RORF)

Keywords: Carboxylic acids; Cross-coupling; Isotopic labeling; Oxidation; Ring opening rearrangement functionalization (RORF).