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Article

Highly Selective and Catalytic C−N Bond Cleavage of Tertiary Sulfonamides: Scope and Mechanistic Insight

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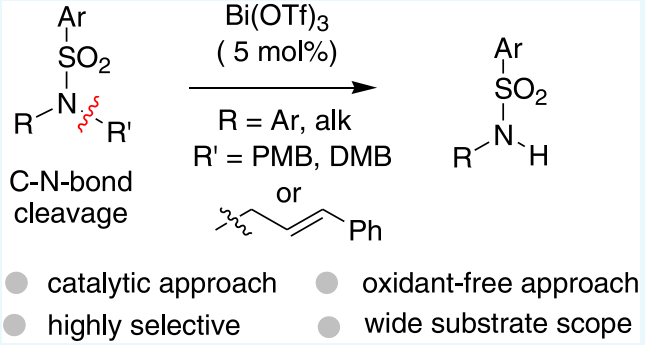
ABSTRACT: A highly chemoselective C−N bond cleavage reaction of *p*-methoxybenzyl- (PMB), 3,4-dimethoxybenzyl- (DMB), or cinnamyl-substituted tertiary sulfonamides in the presence of catalytic $Bi(OTf)_3$ is presented. A wide range of sulfonamide substrates smoothly furnished the corresponding C−N bond cleavage products in good to excellent yields. Great efforts have been made to obtain insights into the reaction mechanism based on a series of control experiments and mass spectroscopy.



INTRODUCTION

The cleavage of the C−N bond of amines or amides with activated groups, such as 4-methoxybenzyl- (PMB) or dimethoxybenzyl- (DMB) including prenyl- or cinnamyl-substituents, is frequently used in organic synthesis.[1] The common use of such activated groups over the other unactivated groups (alkyl- or benzyl-) was mostly privileged due to its high proclivity to undergo cleavage under mild acidic conditions. The stability of the in situ-generated carbocation and, in sequel, the use of a suitable nucleophilic scavenger in a stoichiometric amount are keys to success (Scheme 1).[2] Great progress has been made in developing milder *N*-debenzylation conditions with substrates like PMB- or DMB-protected amines and amides.[3] Nucleophilic scavengers, for example, anisole or thioanisole, and the use of excess acid are often used to increase the yield of the cleavage product. The other well-accepted methods are either Pd-C-mediated hydrogenolysis[4] or oxidative cleavage mediated by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[5] or ceric ammonium nitrate (CAN).[6]

In our recent intriguing study on Friedel−Crafts reactions,[7] we unexpectedly isolated a C−N bond cleavage product **3a** during the attempted Friedel−Crafts-type alkylation of tertiary sulfonamide **1d** in the presence of bismuth(III)-triflate as a catalyst (Scheme 2). While the substrates **1a−b** (X = CH_2) underwent smoothly Friedel−Crafts-type hydroarylation and afforded the desired tetracyclic compounds **2a−b** in excellent yields, under the same catalytic condition, the substrate **1d** (X = NTs) gave only the C−N bond cleavage product **3a** in a good yield (84%). We envisaged that this catalytic procedure might constitute a new method for the selective C−N bond cleavage of tertiary sulfonamides under the catalytic acid condition.

In prior works on C−N bond cleavage of N-alkyl sulfonamides or *N*,*N*-dialkyl sulfonamides, reagent systems with more than stoichiometric amounts such as $PhI(OAc)_2$-I_2,[8] excess acid H_5IO_6-$Cr_3(OAc)_7(OH)_2$,[9] and KBr-oxone[10] including the organic electron donor[11] were employed. There was half-stoichiometric use of $Cu^{II}(CH_3CN)_4PF_6$ (0.5 equiv)−K_3PO_4 (8.0 equiv) reagent systems for N-dealkylation/N-arylation of secondary sulfonamides in the presence of air.[12] Solely, a single catalytic method, $Ag^{I}SbF_6$-mediated deprenylation of allylsulfonamides, has been reported at a very high temperature and under microwave-irradiated conditions.[13] Furthermore, a ruthenium-catalyzed C−N bond cleavage of *N*-propargyl sulfonamides and amides has also been reported.[14] Recently, an electrochemical method for C−N bond cleavage of secondary and tertiary *N*-alkyl sulfonamides has been developed.[15]

Nevertheless, the C−N bond cleavage of *N*-alkyl sulfonamides needing harsh conditions and the use of toxic metals and excess oxidants still make many of these methods inappropriate in the current scenario. Recently, Javorskis and Orentas described a highly chemoselective detosylation (N−S bond cleavage) process of *N*-aryl sulfonamides in the presence of

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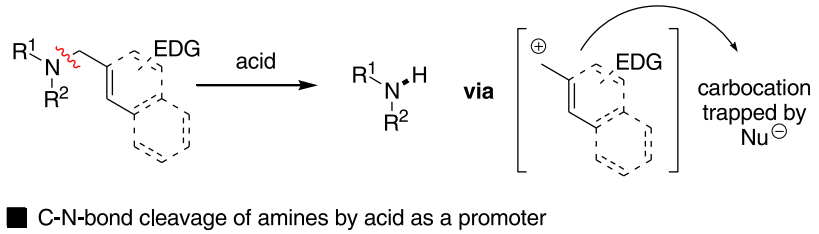
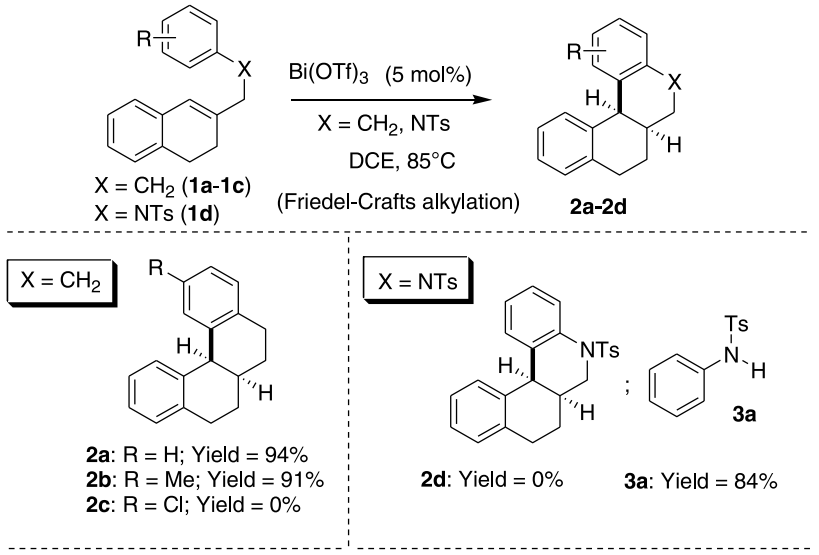
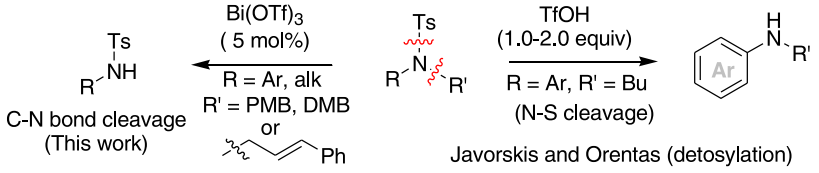
Scheme 1. General Approaches for C−N Bond Cleavage of Amine/Amides with π-Activated Protecting Groups



Scheme 2. Initial Observation of C−N Bond Cleavage of Tertiary Sulfonamide in the Presence of Catalytic $Bi(OTf)_3$



Scheme 3. C−N Bond Cleavage vs N−S Bond Cleavage of Tertiary Sulfonamide



either nearly or more than a stoichiometric amount of triflic acid.[16] In this perspective (N−S vs C−N bond cleavage) and in view of the mechanistic standpoint (stoichiometric vs catalytic), the observation of C−N bond cleavage of tertiary N-aryl or alkyl sulfonamide using $Bi(OTf)_3$ in a catalytic amount is still significant and needs to be further studied (Scheme 3).

RESULTS AND DISCUSSION

To establish the reaction condition, *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** was chosen as a model substrate. The substrate **4a** was reacted under various metal triflate-/halide-based Lewis acids in 1,2-dicholoroethane ($ClCH_2CH_2Cl$) at 85 °C. The key results are summarized in Table 1. Lewis acids such as $Bi(OTf)_3$, $Fe(OTf)_3$, $Sc(OTf)_3$, and $Al(OTf)_3$ afforded the desired C−N bond cleavage product **3a** in good to excellent yields (78−95%; entries 1−4). Halide-based Lewis acids such as $FeCl_3$ and $AlCl_3$ were also tested using this catalytic method, albeit slightly lower yields were observed (entries 5 and 6). Among these Lewis acids, $Bi(OTf)_3$ in 5 mol % was found to be the best in terms of yield (95%) and clean reaction (entry 1). However, other Bi(III)-Lewis acids with variation of counterions such as $Bi(NO_3)_3$ and $BiCl_3$ were not found suitable for the cleavage reaction (entries 7 and 8). This observation suggests that the triflate counteranion might have played an important role in enhancing the chemical yield of the cleavage product. While the reaction was conducted at room temperature (25 °C), no C−N bond cleavage product was observed, even after 24 h. Other solvents such as 1,4-dioxane, acetonitrile, toluene, and ethanol were also studied; however, none of the solvents gave the desired product **3a** as high as 1,2-dichloroethane (entries 9−12). It is noteworthy that the reaction was studied in the presence of air or N_2 (balloon), and under both conditions, the cleavage product **3a** was obtained in comparable yields, 95 and 92%, respectively (entries 1 and 13). Thus, the optimum conditions for this C−N bond cleavage reaction were **4a** (1.0 equiv) and $Bi(OTf)_3$ (0.05 equiv) in 1,2-dichloroethane heated at 85 °C in an open air atmosphere for 2 h, which afforded the desired cleavage product 4-methyl-*N*-phenyl-benzenesulfonamide **3a** in a 95% yield.

To explore the scope of the C−N bond cleavage reactions, various DMB- or PMB-protected *N*-aryl sulfonamides **4** were studied under the optimized conditions. The results are summarized in Scheme 4. With the variation of the aryl moiety

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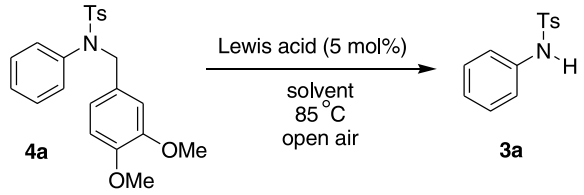
Table 1. Reaction Optimization[a]



entry	Lewis acid	solvent[b]	time (h)	yield of 3a (%)[c]
1	$Bi(OTf)_3$	DCE	2	95
2	$Fe(OTf)_3$	DCE	2	84
3	$Sc(OTf)_3$	DCE	3	81
4	$Al(OTf)_3$	DCE	3	78
5	$FeCl_3$	DCE	2	71
6	$AlCl_3$	DCE	2	61
7	$Bi(NO_3)_3$	DCE	12	22
8	$BiCl_3$	DCE	12	18
9	$Bi(OTf)_3$	1,4-dioxane	3	86
10	$Bi(OTf)_3$	acetonitrile	1.5	71
11	$Bi(OTf)_3$	toluene	2	81
12	$Bi(OTf)_3$	ethanol	2	43
13[d]	$Bi(OTf)_3$	DCE	2	92

[a]Reaction conditions: **4a** (1.0 equiv, 0.25 mmol) and Lewis acid (0.05 equiv, 0.0125 mmol) were mixed together in 2 mL of solvent and heated at 85 °C. [b]Solvent used in the reaction without any further purification protocol. [c]Isolated (column purified) yield was reported. [d]The reaction was conducted under a N_2-balloon and a degasified solvent was used (DCE = 1,2-dichloroethane).

(Scheme 4A), the substrates bearing phenyl- (**4a**), *p*-tolyl- (**4b**), 2,4-dimethylphenyl- (**4c**), and *m*-chlorophenyl- (**4d**) substituted *p*-tolylsulfonamides provided the corresponding C−N bond cleavage products **3a**−**d** in good to excellent yields (90−95%). Interestingly, the substrate with electron-rich 3,4-dimethoxyphenyl-substituted sulfonamides (**4e**) afforded the C−N bond cleavage product in a moderate yield (60%). In this example, additional detosylated product **3e'** (23%) through N−S bond cleavage and the intermolecular *p*-tolylsulfonyl-group-migrated product **3e"** (12%) were formed. The in situ-generated triflic acid might be the plausible explanation for these observations.[16] Similarly, PMB-protected arylsulfonamides (**4f**−**i**) were also examined under the stated reaction conditions, and all of the substrates afforded C−N bond cleavage products **3a**, **3c**, **3d**, and **3f** in high yields (89−95%), respectively (Scheme 4A). However, *N*,*N*-4-methylbenzyl-phenyl-substituted *p*-tolylsulfonamide (**4j**) gave the cleavage product with a little low yield (89%). However, while a 4-bromobenzyl-substituted substrate (**4k**) was subjected to the optimized conditions, it was found completely inactive to this catalytic method (Scheme 4B). Furthermore, we also studied the substrates with the variation of different substituents at the aryl moiety on the sulfonyl part; the results are summarized in Scheme 4C. Likewise, *p*-tolyl-, *α*-naphthyl- (**4l**), *p*- and *o*-trifluoromethylphenyls- (**4m** and **4n**), and *p*-nitrophenyl- (**4o**) substitutions at the aryl moiety (Ar^3) were well tolerated and gave the cleavage products in high yields (80−90%).

Next, we turned our focus toward the cinnamyl- and (3,4-dihydro-naphthalen-2-ylmethyl)-substituted various *N*-aryl sulfonamides. Successfully, all of the substrates (**5a**−**e** and **1d**) well accepted this cleavage method and afforded the desired cleavage products in a range of good to high yields (Scheme 5). Likewise, electron-rich aryl-substituted sulfonamide substrates (**4e**) and the detosylation and tosyl-group-migrated products were also observed for the substrate **5e**. Further, the effect of electronic tuning on the dibenzyl moieties (chemoselectivity) in the sulfonamides (**6a**−**c**) was examined, and expectedly, the PMB group deprotected products (**3l** and **3n**) were obtained in good yields (Scheme 6). Interestingly, the substrate **6c** with di-PMB-substituted sulfonamide afforded the fully PMB-deprotected tosylamide product **3n** in 80% yield. Similarly, other *N*-alkyl sulfonamides (**7a** and **7b**) also responded well to this catalytic method and afforded the desired cleavage products **3o**−**p** in good yields (76%).

Several control experiments were conducted to obtain insights into the plausible reaction mechanism (Scheme 7). Irrespective of whether the Lewis acid $Bi(OTf)_3$ or the highly acidic in situ-generated hidden Brønsted acid (triflic acid)[17] plays the key role in this C−N bond cleavage reaction, we performed a reaction in anhydrous 1,2-dichoroethane in the presence of molecular sieves (MS 4A). A trace amount of the (<5%) cleavage product was formed (Scheme 7i). Another experiment, in DCE-H_2O (10:1 v/v), using catalytic $Bi(OTf)_3$ was conducted, which afforded the desired product in 93% yield (Scheme 7ii). It proves that the presence of water in the reaction system is essential for the C−N bond cleavage under optimized conditions. Further, a separate reaction using catalytic triflic acid (10 mol %) yielded **3a** almost in a similar yield (89%; Scheme 7iii). With these observations, we hypothesized that the cleavage reaction undergoes in the presence of hidden in situ-generated triflic acid. Moreover, the catalytic presence of triflic acid afforded the cleavage product with very high yields, deliberately, compelling us to examine further control experiments. Consequently, a reaction was conducted in the presence of the triflic acid scavenger DTBMP (2,6-di-tertiary-butyl-4-methylpyridine (Scheme 7iv).[18] The very low yield of the cleavage product obtained in this control experiment seemingly suggests that the true catalyst in the cleavage reaction could be triflic acid. The C−H oxidation at the benzylic position of the sulfonamides in the presence of oxygen (solvated oxygen/air) and followed by hemiaminal hydrolysis may give the desired product via a radical mechanism.[19] However, such a possibility is unlikely as the reaction under the N_2 gas atmosphere and using degasified solvent systems (DCE-H_2O) yielded the desired product in a similar yield (91%; Scheme 7v). Finally, under the dark condition and also in the presence of a radical scavenger BHT[20] (1.5 equiv), the same set of reaction provided the desired cleavage products **3a** in high yields (Scheme 7vi,vii). Thus, it can be unambiguously concluded that the cleavage method never follows the radical steps.

Arguably, triflic acid is the true active catalyst in this cleavage method, and with this validity, a plausible reaction mechanism is proposed, which is depicted in Scheme 8. The reaction mechanism presumably starts with the protonation event. There is a dual chance of the protonation taking place on both the nitrogen atom of sulfonamide or oxygen atoms of the sulfonyl group in the tertiary sulfonamide substrate.[21] To validate this, the substrates with *N*-aryl-*N*-3,4-dimethoxybenzylcarboxamides (**4p**−**q**) were reacted under the optimized conditions. These substrates completely failed to give the corresponding C−N bond cleavage products. The results from these unsuccessful substrates (with lack of a sulfonamide moiety) might be due to the higher electron-withdrawing capability of carboxamide (COR) rather than sulfonamide (SO_2R). On the basis of prior reports and experimental results, it can be concluded that the initial protonation most likely is

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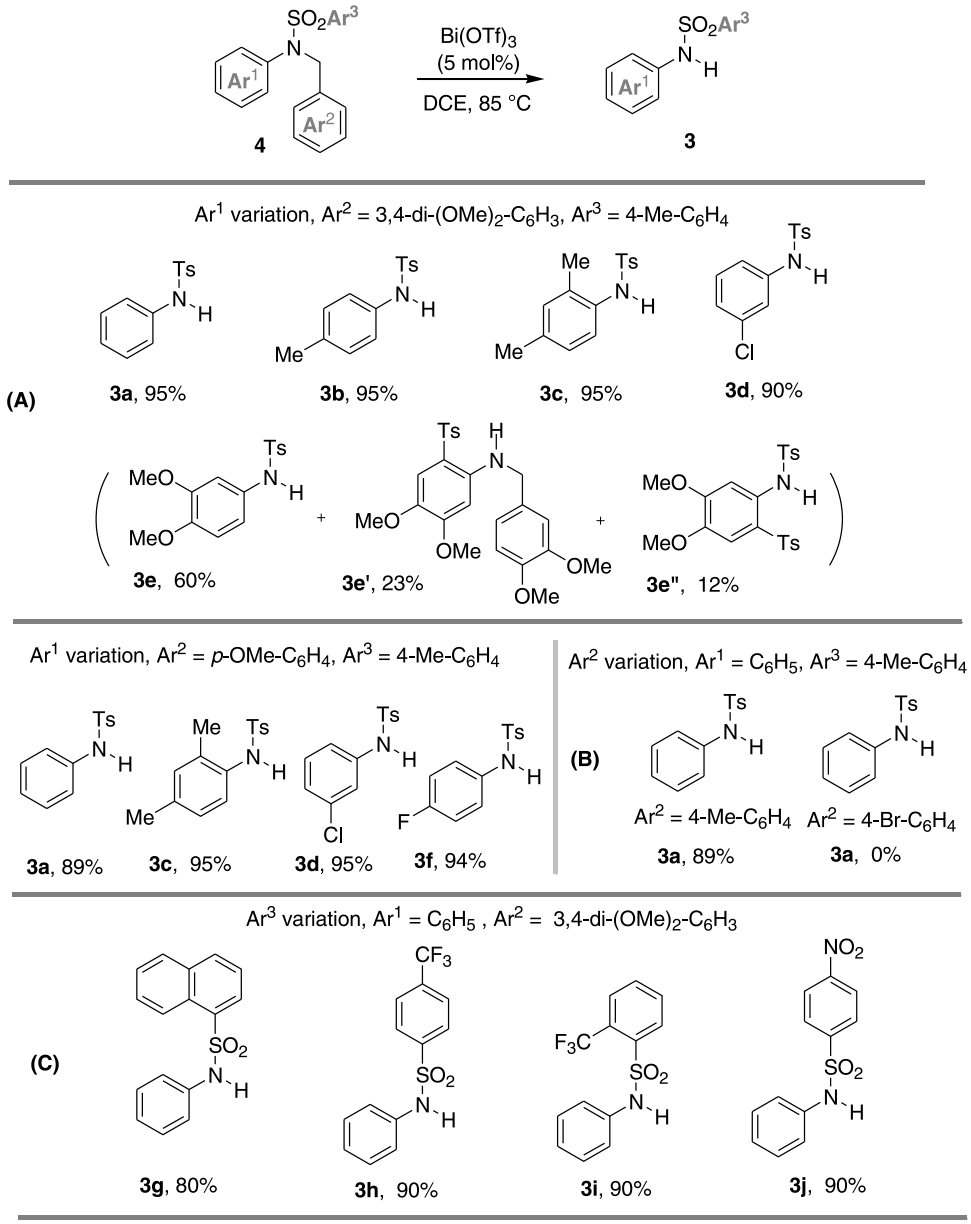
Scheme 4. C−N Bond Cleavage of *N*-Aryl Sulfonamides



taking place on the N atom of tertiary sulfonamide (Scheme 8).[21] Following the protonation, substrate **4** forms the intermediate **I**, which consequently releases a highly reactive benzyl carbocationic intermediate **II** or its resonance-stabilized intermediate **III**, affording the desired cleavage product **3a**. The in situ formation of highly reactive intermediate **II** or **III** is also further confirmed. The cleavage reaction was executed in the presence of the external nucleophile 1,2-dimethoxybenzene (2.0 equiv) under the optimized conditions. Pleasingly, we were able to isolate the Friedel−Craft alkylated products **8a** (45%) and **8b** (23%) in moderate yields alongside the desired cleavage product **3a** in 93% yield (Scheme 8i).

On the other hand, during the course of the reaction, the intermediate **II** or **III** might be trapped by water and the corresponding benzyl alcohol should be formed as a major byproduct as the reaction medium contains sufficient water. However, 3,4-dimethoxyphenylmethanol (R = OMe) was never isolated from the reaction system or traced by the TLC during the course of the reaction. Gratifyingly, a tribenzocyclononane (2,3,7,8,12,13-hexamethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononane) compound **10** was isolated in a 22% yield (based on sulfonamide substrate **4a**). To further probe, a separate reaction was conducted with 3,4-dimethoxyphenylmethanol in the presence of a catalytic amount of $Bi(OTf)_3$ (5 mol %) under the same optimized reaction conditions (Scheme 8ii). After 1 h, the alcohol was completely consumed, and as expected, tribenzocyclononane compound **10** was isolated in 76% yield (Scheme 8ii). The formation of compound **10** can be elucidated by acid-catalyzed trimerization reactions of 3,4,-dimethoxybenzylphenylmethanol under acidic conditions.[22] It is further verified using mass spectroscopic techniques. In the mass spectrum, the intense characteristic peak exhibited at 468.2575 m/z (M^+) can be attributed to compound **9**, which, in turn, can be easily cyclized to afford a tribenzocyclononane product **10**, which appeared at 451.2277 m/z ($M + H^+$). Based on these control experiments and observations, we conclude that this C−N bond cleavage protocol of tertiary sulfonamides (**4**, **5**, and **6**)

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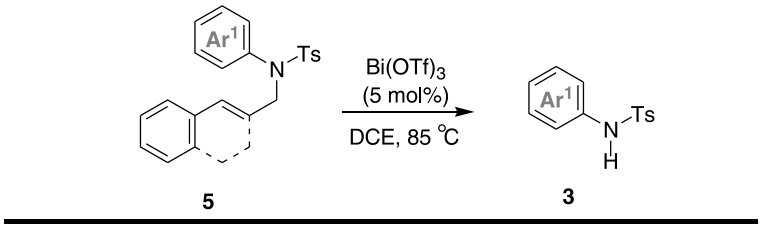
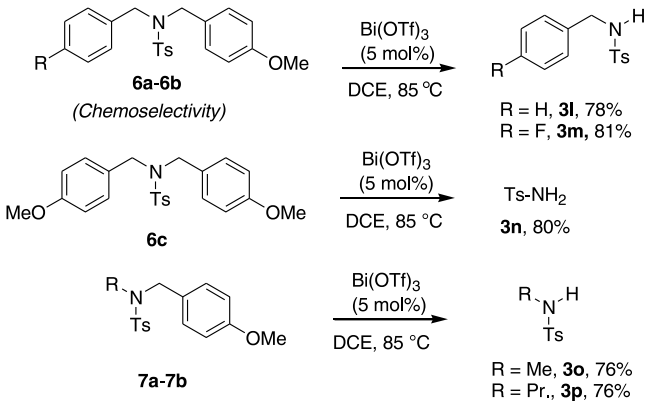
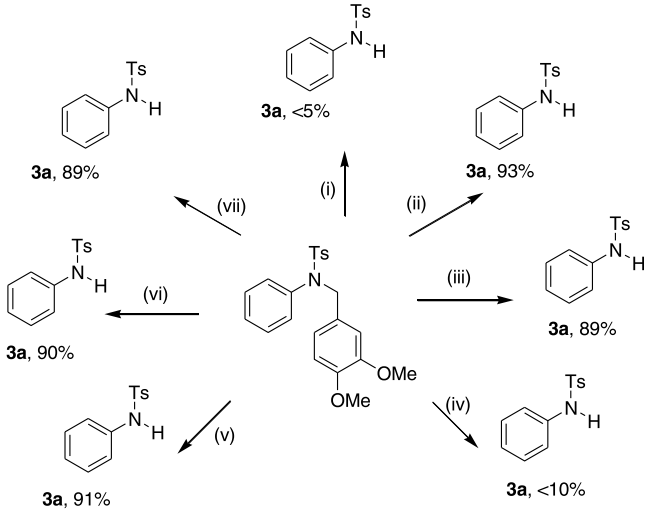
Scheme 5. C−N Bond Cleavage of *N*-Cinnamylsulfonamides



Scheme 6. C−N Bond Cleavage of PMB-Protected *N*-Alkyl Sulfonamides (Chemoselectivity)



Scheme 7. Control Experiments for Mechanistic Insight[a]



[a]Reagent and conditions: (i) $Bi(OTf)_3$ (5 mol %) ″dry DCE″, MS 4A, 85 °C; (ii) $Bi(OTf)_3$ (5 mol %), ″DCE-H_2O″ (10:1), 85 °C; (iii) ″TfOH″ (10 mol %), 85 °C; (iv) $Bi(OTf)_3$ (5 mol %), ″DCE-H_2O″ (10:1), DTBMP (1.5 equiv), 85 °C; (v) $Bi(OTf)_3$ (5 mol %), ″DCE-H_2O″ (10:1), ″N_2 balloon″, 85 °C; (vi) $Bi(OTf)_3$ (5 mol %), ″DCE-H_2O″ (10:1), ″dark condition″, 85 °C; (vii) $Bi(OTf)_3$ (5 mol %), ″DCE-H_2O″ (10:1), BHT (1.2 equiv), 85 °C.

proceeds via the protonation event, followed by the C−N bond cleavage step (step **I** to step **II**).

Finally, the methodology was applied to the gram scale for the one-pot synthesis of *N*-phenyl-*N*-tosylacetamide **11** from **4a** (Scheme 9).

CONCLUSIONS

In conclusion, we have developed a catalytic C−N bond cleavage protocol of tertiary PMB/DMB-protected sulfonamides under a mild acidic condition. Various DMB- or PMB-protected *N*-aryl/alkylsulfonamides underwent smoothly and afforded highly selective C−N bond cleavage products with high yields in most of the substrates. This catalytic protocol is applicable also to the cinnamyl-substituted *N*-aryl sulfonamides. However, both C−N and N−S bond cleavages including tosyl migration are observed in a parallel way while the electron-rich substituted *N*-aryl sulfonamides are used. On the basis of several control experiments and observations, the catalytic cleavage reaction most likely is proposed, which generally comprises protonation on the nitrogen atom of *N*-

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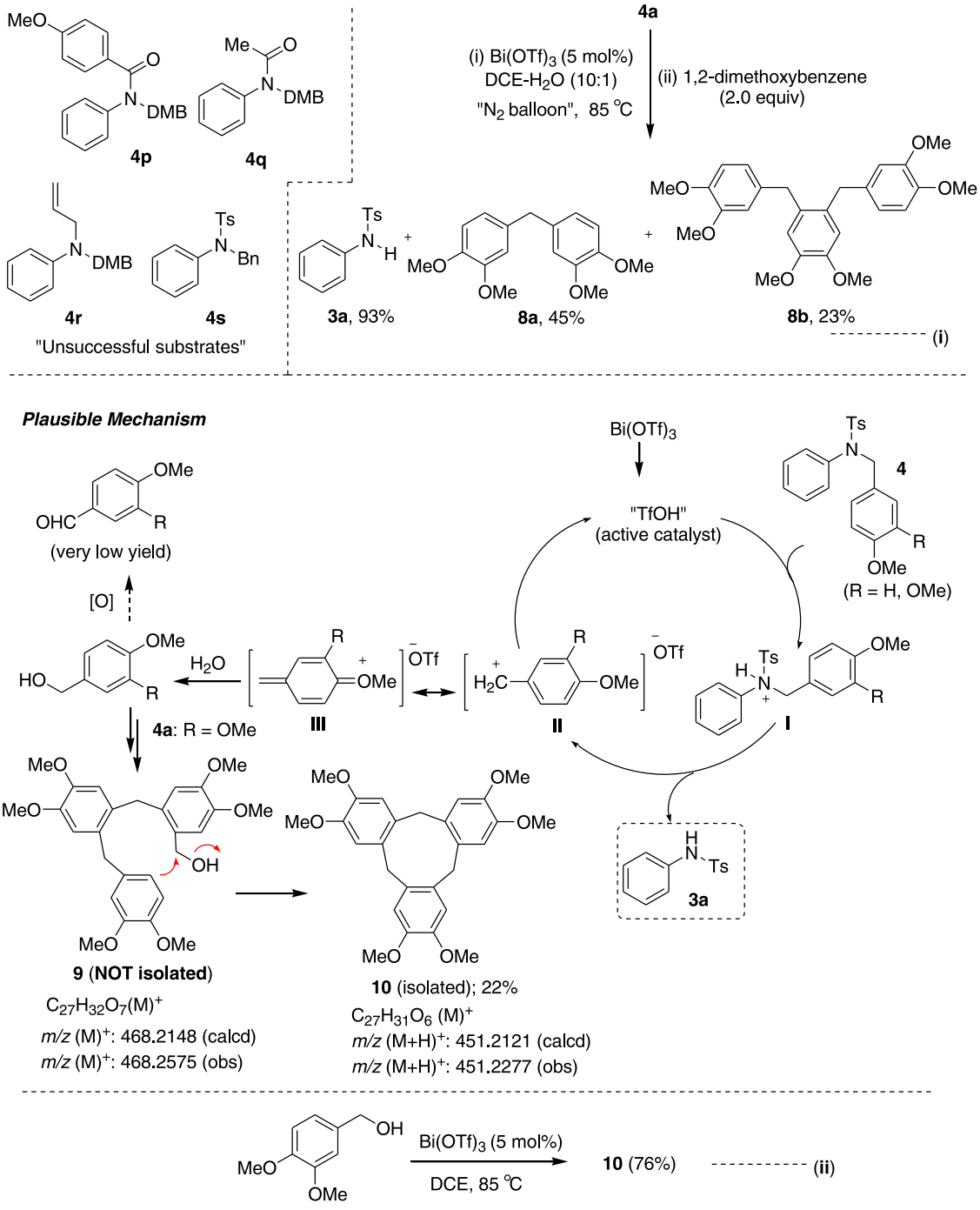
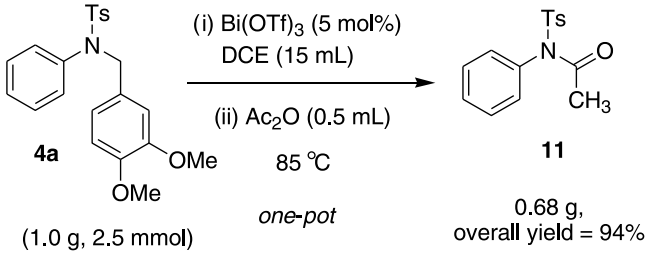
Scheme 8. Plausible Mechanism



Scheme 9. One-Pot Synthesis of *N*-Phenyl-*N*-tosylacetamide



aryl or *N*-alkyl tertiary sulfonamides, followed by C−N bond cleavage. The immediate stability of the in situ-generated benzylic carbocationic intermediate (**II**) is possibly the driving force for the highly selective C−N bond cleavage over the N−S bond cleavage (detosylation). Great efforts have been made regarding mechanism interrogation to realize a plausible reaction mechanism based on a series of control experiments and mass spectroscopy.

EXPERIMENTAL SECTION

All reactions were conducted using oven-dried glassware. Commercial AR-grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. However, all of the cleavage reactions were performed in DCE directly without any further purification

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(bottle-grade) purchased from CDH make in India. Flash column chromatography was performed in all cases using the indicated solvent system on silica gel (230−400 mesh). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed plates coated with silica gel 60 with an F_{254} indicator (Merck). The ^{1}H NMR spectra were measured with 400 MHz, and ^{13}C NMR spectra were recorded with 400 (100 MHz), using $CDCl_3$ as the solvent. ^{1}H NMR chemical shifts are expressed in parts per million (δ) downfield to $CHCl_3$ (δ = 7.26), and ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the central $CDCl_3$ resonance (δ = 77.0). Coupling constants in ^{1}H NMR are in Hz. The following abbreviations classify the multiplicity: s, singlet; d, doublet; t, triple; m, multiplet or unresolved; dd, doublet of doublets. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS.

All 1,2-dihydronaphthalene-based alkenes were synthesized according to the reported literature procedure.[23] *N*-Benzyl and *N*-cinnamyl amines were prepared by reaction between commercially available aniline and respective aldehydes using the following standard literature procedure.[24] 3,4-Dihydronaphthalen-2-ylmethyl)-aryl amines were prepared by reaction between commercially available anilines and the respective carbaldehyde using the following standard literature procedure.[23] All secondary amines were further protected by following standard protocols. All Lewis acids, Brønsted acids, and other solvents and reagents used in this study were purchased from commercial suppliers.

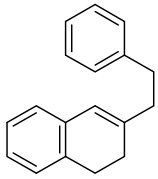
Preparation of Substrates. *General Procedure I: Synthesis of Secondary Amines.* In an oven-dried round-bottom flask, aniline derivative (1.0 equiv), aldehyde (1.0 equiv), and triethyl amine (1.5 equiv) were dissolved in MeOH, and the reaction mixture was stirred at room temperature until the starting material was completely consumed and imine was formed (checked by TLC). The reaction mixture was cooled to 0 °C, and $NaBH_4$ or $Zn(BH_4)_2$ (1.1 equiv) was added slowly and allowed to stir at room temperature until the intermediate imine was completely reduced to the corresponding amine. The reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vaccuo*, and the crude mixture was purified by flash column chromatography using petroleum ether and ethyl acetate as the eluent.

General Procedure II: Synthesis of Tertiary Sulfonamides (Protection of Secondary Amines). All sulfonyl protected tertiary *N*-aryl sulfonamides were prepared from the corresponding secondary amine and sulfonyl chloride (2.0 equiv) in the presence of Et_3N (3.0 equiv) and DMAP (10 mol %) in DCM at room temperature. *N*-Alkyl sulfonamides were synthesized via the *N*-alkylation reaction of monosubstituted sulfonamides with the corresponding alkyl halide following the standard literature procedure.[16]

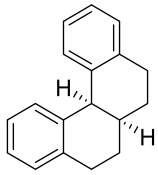
General Procedure III: Friedel−Crafts Alkylation of 1,2-Dihydronaphthalene-Based Alkenes. To a stirred solution of alkene **1** (0.43 mmol, 1.0 equiv) in dichloroethane (2 mL), $Bi(OTf)_3$ (0.05 equiv) was added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired Friedel−Crafts alkylated product **2**.

General Procedure IV: C−N Bond Cleavage of Tertiary Sulfonamides. To a stirred solution of tertiary sulfonamides [**4**−**6**] (0.25 mmol, 1 equiv) in 1,2-dichloroethane (2 mL), $Bi(OTf)_3$ (0.05 equiv) was added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product.

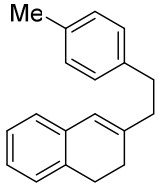
Characterization data for compounds **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **10**, and **11**



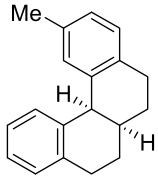
3-Phenethyl-1,2-dihydronaphthalene (**1a**): Prepared according to the reported literature procedure; 80% yield; viscous oil. All spectroscopic data are identical to those reported in the literature.[23]



5,6,6a,7,8,12b-Hexahydrobenzo[*c*]phenanthrene (**2a**): Prepared according to general procedure **III** using **1a** (100 mg, 0.43 mmol, 1.0 equiv); colorless oil (94 mg, 94% yield); R_f = 0.2 (2% EA/PE); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30−7.13 (m, 8H), 4.02 (d, J = 8.8 Hz, 1H), 2.90−2.83 (m, 4H), 2.51−2.40 (m, 1H), 2.06−1.97 (m, 2H), 1.67−1.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.9, 137.5, 129.8 (2C), 128.6 (2C), 128.3, 126.0 (2C), 125.3 (3C), 42.9, 32.4, 28.1 (2C), 27.3 (2C); HRMS (ESI)$^+$ calcd for $C_{18}H_{19}$, 235.1487 m/z (M + H)$^+$; found, 235.1488 m/z.



3-(4-Methylphenethyl)-1,2-dihydronaphthalene (**1b**): Prepared according to the reported literature procedure; 21% yield; colorless oil. All spectroscopic data are identical to those reported in the literature.[23]



2-Methyl-5,6,6*a*,7,8,12*b*-hexahydrobenzo[*c*]phenanthrene (**2b**): Prepared according to general procedure **III** using **1b** (100 mg, 0.40 mmol, 1.0 equiv); colorless oil (91 mg, 91% yield); R_f = 0.2 (2% EA/PE); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34−7.19 (m, 4H), 7.17−7.06 (m, 2H), 7.00 (s, 1H), 4.04 (d, J = 10.0 Hz, 1H), 3.01−2.84 (m, 4H), 2.49−2.44 (m, 1H), 2.39 (s, 3H), 2.14−1.96 (m, 2H), 1.72−1.52 (m, 2H); ^{13}C

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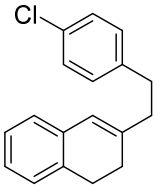
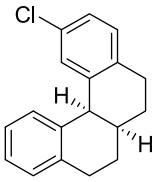
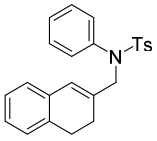
NMR ($CDCl_3$, 100 MHz): δ 139.0, 138.6, 137.5, 134.6, 134.3, 130.5, 129.8, 128.5 (2C), 126.8, 125.9, 125.3, 42.8, 32.4, 27.9, 27.6, 27.3, 27.2, 21.2; HRMS (ESI)$^+$ calcd for $C_{19}H_{21}$, 249.1643 m/z (M + H)$^+$; found, 249.1647 m/z.



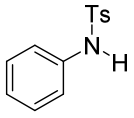
3-(4-Chlorophenethyl)-1,2-dihydronaphthalene (**1c**): Prepared according to the reported literature procedure;[1] 40% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46−7.24 (m, 3H), 7.19−7.12 (m, 4H), 7.06 (d, J = 12.4 Hz, 1H), 6.30 (s, 1H), 3.04−2.85 (m, 4H), 2.56 (t, J = 14.4 Hz, 2H), 2.35 (t, J = 16.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.0, 140.5, 134.9, 134.5, 131.7, 129.9 (2C), 128.6 (2C), 127.3, 126.6, 126.4, 125.6, 123.1, 39.3, 33.7, 28.3, 27.6; HRMS (ESI)$^+$ calcd for $C_{18}H_{18}Cl$, 269.1097 m/z (M + H)$^+$; found, 269.1099 m/z.



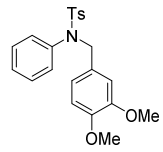
2-Chloro-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene (**2c**): The reaction was performed according to general procedure **III** using **1c** (100 mg, 0.37 mmol, 1.0 equiv). No cyclized product was obtained. Yield, 0%.



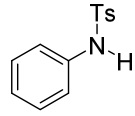
N-(3,4-Dihydronaphthalen-2-ylmethyl)-4-methyl-*N*-phenyl-benzenesulfonamide (**1d**). Prepared according to general procedure **II**; 89% yield; off-white solid; mp = 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, J = 8.0 Hz, 2H), 7.24−7.21 (m, 5H), 7.05−7.02 (m, 5H), 6.84−6.83 (m, 1H), 6.10 (s, 1H), 4.27 (s, 2H), 2.67 (t, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.35 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 138.2, 135.4, 135.3, 135.2, 133.8, 129.6 (2C), 128.9 (2C), 128.8 (2C), 127.9 (2C), 127.8, 127.4, 127.2, 127.0, 126.04, 126.0, 56.4, 27.9, 24.8, 21.7; HRMS (ESI)$^+$ calcd for $C_{24}H_{23}NNaO_2S$, 412.1347 m/z (M + Na)$^+$; found, 412.1348 m/z.



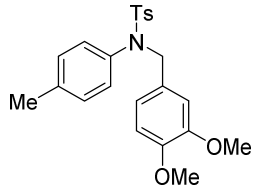
4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**):[25] Prepared according to general procedure **III** using **1d** (100 mg, 0.26 mmol, 1.0 equiv); white solid (54 mg, 84% yield). R_f = 0.25 (25% EA/PE); mp = 102−104 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 6.48, 2H), 7.44 (s, 1H), 7.25−7.22 (m, 4H), 7.15−7.08 (m, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 136.7, 136.1, 129.7 (2C), 129.3 (2C), 127.4 (2C), 125.2, 121.5 (2C), 21.6; HRMS (ESI)$^+$ calcd for $C_{13}H_{14}NO_2S$, 248.0745 m/z (M + H)$^+$; found, 248.0743 m/z.



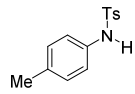
N-(3,4-Dimethoxy-benzyl)-4-methyl-*N*-phenyl-benzenesulfonamide (**4a**): Prepared according to general procedure **II**; 85% yield; off-white solid; mp = 158−160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.18−7.15 (m, 3H), 6.95−6.92 (m, 2H), 6.77 (s, 1H), 6.62−6.60 (m, 2H), 4.64 (s, 2H), 3.77 (s, 6H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.0, 148.9, 143.5, 139.0, 135.8, 129.6 (2C), 129.1 (2C), 128.9 (2C), 128.4, 127.9, 127.8 (2C), 121.1, 111.7, 110.7, 55.9, 55.8, 54.6, 21.6; HRMS (ESI)$^+$ calcd for $C_{22}H_{23}NNaO_4S$, 420.1245 m/z (M + Na)$^+$; found, 420.1245 m/z.



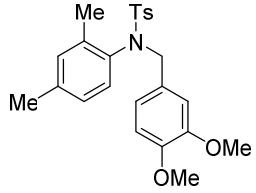
4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**):[25] Prepared according to general procedure **IV** using **4a** (100 mg, 0.25 mmol, 1.0 equiv); white solid (59 mg, 95% yield). All spectroscopic data are identical to **3a** obtained from **1d** and those reported in the literature.



N-(3,4-Dimethoxy-benzyl)-4-methyl-*N*-*p*-tolyl-benzenesulfonamide (**4b**): Prepared according to general procedure **II**; 83% yield; yellow solid; mp = 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.83−6.80 (m, 3H), 6.64 (s, 2H), 4.62 (s, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 2.42 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.9, 148.4, 143.4, 137.8, 136.3, 135.9, 129.54 (3C), 129.52 (2C), 128.8 (2C), 128.5, 127.8, 121.0, 111.6, 110.7, 55.9, 55.8, 54.6, 21.6, 21.1; HRMS (ESI)$^+$ calcd for $C_{23}H_{25}NNaO_4S$, 434.1402 m/z (M + Na)$^+$; found, 434.1401 m/z.



4-Methyl-*N*-*p*-tolyl-benzenesulfonamide (**3b**):[25] Prepared according to general procedure **IV** using **4b** (100 mg, 0.24 mmol, 1.0 equiv); white solid (60 mg, 95% yield); R_f = 0.2 (25% EA/PE); mp = 117−119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (d, J = 6.8 Hz, 2H), 7.29 (s, 1H), 7.20 (d, J = 6.4 Hz, 2H), 7.02−6.97 (m, 4H), 2.35 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 136.0, 135.2, 133.9, 129.9 (2C), 129.7 (2C), 127.4 (2C), 122.1 (2C), 21.6, 20.9; HRMS (ESI)$^+$ calcd for $C_{14}H_{16}NO_2S$, 262.0902 m/z (M + H)$^+$; found, 262.0903 m/z.



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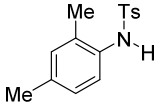
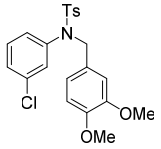
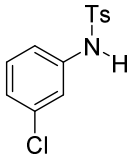
N-(3,4-Dimethoxy-benzyl)-*N*-(2,4-dimethyl-phenyl)-4-methyl-benzenesulfonamide (**4c**): Prepared according to general procedure **II**; 81% yield; yellow solid; mp = 108−110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.91 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 4.90 (d, J = 13.2 Hz, 1H), 4.14 (d, J = 13.2 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.44 (s, 3H), 2.23 (s, 3H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.7, 143.4, 140.0, 138.1, 136.5, 135.3, 132.1, 129.6 (2C), 128.2, 128.0 (3C), 127.9, 126.9, 121.9, 112.5, 110.6, 55.8 (2C), 55.7, 21.7, 21.1, 18.4; HRMS (ESI)$^+$ calcd for $C_{24}H_{27}NNaO_4S$, 448.1558 m/z (M + Na)$^+$; found, 448.1553 m/z.



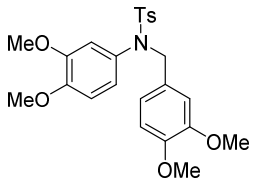
N-(2,4-Dimethyl-phenyl)-4-methyl-benzenesulfonamide (**3c**):[26] Prepared according to general procedure **IV** using **4c** (100 mg, 0.24 mmol, 1.0 equiv); white solid (62 mg, 95% yield); R_f = 0.25 (30% EA/PE); mp = 93−95 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.04 Hz, 1H), 6.93−6.88 (m, 2H), 6.50 (s, 1H), 2.38 (s, 3H), 2.25 (s, 3H), 1.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 136.9, 136.4, 132.2, 131.8, 131.6, 129.7 (2C), 127.6, 127.3 (2C), 125.3, 21.7, 21.0, 17.6; HRMS (ESI)$^+$ calcd for $C_{15}H_{18}NO_2S$, 276.1058 m/z (M + H)$^+$; found, 276.1061 m/z.



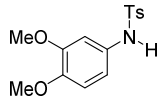
N-(3-Chloro-phenyl)-*N*-(3,4-dimethoxy-benzyl)-4-methyl-benzenesulfonamide (**4d**): Prepared according to general procedure **II**; 78% yield; white solid; mp = 156−158 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.15−7.11 (m, 2H), 6.96 (s, 1H), 6.86 (d, J = 7.6 Hz, 1H), 6.76 (s, 1H), 6.63 (d, J = 7.6 Hz, 2H), 4.61 (s, 2H), 3.78 (s, 6H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.0, 148.7, 143.9, 140.2, 135.3, 134.2, 129.8, 129.7 (2C), 129.1, 128.1, 127.8 (2C), 127.7, 127.3, 121.1, 111.6, 110.8, 55.9, 55.8, 54.4, 21.6; HRMS (ESI)$^+$ calcd for $C_{22}H_{22}ClNNaO_4S$, 454.0856 m/z (M + Na)$^+$; found, 454.0862 m/z.



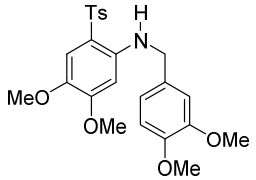
N-(3-Chloro-phenyl)-4-methyl-benzenesulfonamide (**3d**):[25] Prepared according to general procedure **IV** using **4d** (100 mg, 0.23 mmol, 1.0 equiv); white solid (59 mg, 90% yield); R_f = 0.25 (25% EA/PE); mp = 135−137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 8.04 Hz, 2H), 7.04 (d, J = 8.0 Hz, 1H), 7.00−6.97 (m, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 138.0, 135.6, 134.9, 130.4, 130.0 (2C), 127.4 (2C), 125.2, 120.8, 118.9, 21.7; HRMS (ESI)$^+$ calcd for $C_{13}H_{13}ClNO_2S$, 282.0356 m/z (M + H)$^+$; found, 282.0355 m/z.



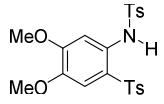
N-(3,4-Dimethoxy-benzyl)-*N*-(3,4-dimethoxy-phenyl)-4-methyl-benzenesulfonamide (**4e**): Prepared according to general procedure **II**; 90% yield; off-white solid; mp = 125−127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, J = 8.04 Hz, 2H), 7.25 (d, J = 8.04 Hz, 2H), 6.79 (s, 1H), 6.64−6.58 (m, 3H), 6.43−6.36 (m, 2H), 4.58 (s, 2H), 3.77 (s, 9H), 3.61 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.9, 148.7, 148.5, 148.3, 143.5, 135.9, 131.7, 129.5 (2C), 128.6, 127.9 (2C), 121.5, 121.3, 112.9, 111.8, 110.7, 110.6, 55.9 (4C), 55.1, 21.6; HRMS (ESI)$^+$ calcd for $C_{24}H_{27}NNaO_6S$, 480.1457 m/z (M + Na)$^+$; found, 480.1463 m/z.



N-(3,4-Dimethoxy-phenyl)-4-methyl-benzenesulfonamide (**3e**):[27] Prepared according to general procedure **IV** using **4e** (100 mg, 0.22 mmol, 1.0 equiv); white solid (40 mg, 60% yield); R_f = 0.25 (35% EA/PE); mp = 115−117 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.77 (s, 1H), 6.70−6.66 (m, 2H), 6.54−6.51 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.3, 147.4, 143.8, 136.0, 129.6 (2C), 129.5, 127.5 (2C), 115.7, 111.3, 107.9, 56.1, 56.0, 21.6; HRMS (ESI)$^+$ calcd for $C_{15}H_{18}NO_4S$, 308.0957 m/z (M + H)$^+$; found, 308.0958 m/z.



(3,4-Dimethoxy-benzyl)-[4,5-dimethoxy-2-(toluene-4-sulfonyl)-pheny]-amine (**3e′**): Obtained during the course of C−N bond cleavage of **4e** according to general procedure **IV**; white solid, (23 mg, 23% yield); R_f = 0.2 (35% EA/PE); mp = 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.85 (s, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.56 (s, 1H), 6.49 (d, J = 8.0 Hz, 1H), 6.44 (s, 1H), 6.10 (S, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 3.46 (s, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.4, 147.9, 147.8, 147.5, 143.8, 136.8, 131.6, 129.6 (2C), 127.7, 127.3, 127.2 (2C), 120.3, 113.4, 111.6, 111.5, 110.1, 56.1, 56.02, 56.01, 55.9, 37.0, 21.6; HRMS (ESI)$^+$ calcd for $C_{24}H_{28}NO_6S$, 458.1637 m/z (M + H)$^+$; found, 458.1634 m/z.



N-[4,5-Dimethoxy-2-(toluene-4-sulfonyl)-phenyl]-4-methyl-benzenesulfonamide (**3e″**): Obtained during the course of C−N bond cleavage of **4e** according to general procedure **IV**; white solid (13 mg, 12% yield); R_f = 0.22 (35% EA/PE); mp = 123−125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H), 7.31 (s, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 6.63 (d, J = 8.4 Hz,

https://doi.org/10.1021/acsomega.1c02276
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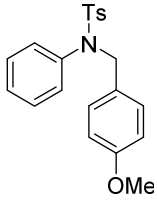
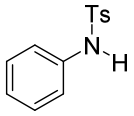
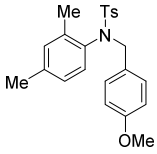
2H), 3.86 (s, 3H), 3.69 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.2, 146.4, 144.0, 136.0, 135.7, 133.5, 132.9, 130.0 (2C), 129.6 (2C), 127.4 (2C), 126.9 (2C), 118.6, 112.8, 104.8, 56.3, 56.2, 21.7, 21.1; HRMS (ESI)$^+$ calcd for $C_{22}H_{24}NO_6S_2$, 462.1045 m/z (M + H)$^+$; found, 462.1043 m/z.



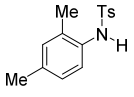
N-(4-Methoxy-benzyl)-4-methyl-*N*-phenyl-benzenesulfonamide (**4f**): Prepared according to general procedure **II**; 91% yield; off-white solid; mp = 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.18−7.17 (m, 3H), 7.09 (d, J = 8.0 Hz, 2H), 6.95−6.92 (m, 2H), 6.71 (d, J = 8.0 Hz, 2H), 4.64 (s, 2H), 3.71 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 143.5, 139.0, 135.9, 130.0 (2C), 129.6 (2C), 129.2 (2C), 128.9 (2C), 128.1, 127.8 (3C), 113.8 (2C), 55.3, 54.3, 21.7; HRMS (ESI)$^+$ calcd for $C_{21}H_{21}NNaO_3S$, 390.1140 m/z (M + Na)$^+$; found, 390.1142 m/z.



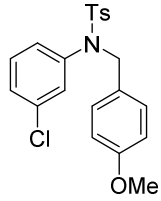
4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**):[25] Prepared according to general procedure **IV** using **4f** (100 mg, 0.27 mmol, 1.0 equiv); white solid (60 mg, 89% yield). All data are similar to the compound obtained from **4a**.



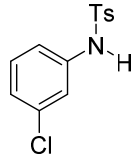
N-(2,4-Dimethyl-phenyl)-*N*-(4-methoxy-benzyl)-4-methyl-benzenesulfonamide (**4g**): Prepared according to general procedure **II**; 80% yield; off-white solid; mp = 110−112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.91 (s, 1H), 6.80 (d, J = 8.8 Hz, 1H), 6.71 (d, J = 8.8 Hz, 2H), 6.46 (d, J = 8.0 Hz, 1H), 4.92 (d, J = 13.6 Hz, 1H), 4.14 (d, J = 13.6 Hz, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 2.24 (s, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3, 143.4, 140.0, 138.1, 136.6, 135.3, 132.0, 130.8 (2C), 129.6 (2C), 128.1, 128.0 (2C), 127.9, 126.9, 113.6 (2C), 55.4, 55.3, 21.7, 21.2, 18.3; HRMS (ESI)$^+$ calcd for $C_{23}H_{25}NNaO_3S$, 418.1453 m/z (M + Na)$^+$; found, 418.1458 m/z.



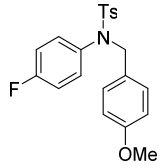
N-(2,4-Dimethyl-phenyl)-4-methyl-benzenesulfonamide (**3c**):[26] Prepared according to general procedure **IV** using **4g** (100 mg, 0.25 mmol, 1.0 equiv); white solid (66 mg, 95% yield). All data are similar to the compound obtained from **4c**.



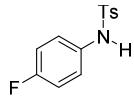
N-(3-Chloro-phenyl)-*N*-(4-methoxy-benzyl)-4-methyl-benzenesulfonamide (**4h**): Prepared according to general procedure **II**; 87% yield; white solid; mp = 138−140 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.17−7.09 (m, 4H), 6.98 (s, 1H), 6.86 (d, J = 7.6 Hz, 1H), 6.74 (d, J = 8.8 Hz, 2H), 4.62 (s, 2H), 3.72 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 143.9, 140.2, 135.1, 134.2, 129.9 (2C), 129.7 (3C), 129.1, 128.1, 127.7 (2C), 127.4, 127.2, 113.9 (2C), 55.2, 54.0, 21.7; HRMS (ESI)$^+$ calcd for $C_{21}H_{20}ClNNaO_3S$, 424.0750 m/z (M + Na)$^+$; found, 424.0753 m/z.



N-(3-Chloro-phenyl)-4-methyl-benzenesulfonamide (**3d**):[25] Prepared according to general procedure **IV** using **4h** (100 mg, 0.25 mmol, 1.0 equiv); white solid (67 mg, 95% yield). All data are similar to the compound obtained from **4d**.



N-(4-Fluoro-phenyl)-*N*-(4-methoxy-benzyl)-4-methyl-benzenesulfonamide (**4i**): Prepared according to general procedure **II**; 86% yield; white solid; mp = 142−144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.88−6.84 (m, 4H), 6.73 (d, J = 8.4 Hz, 2H), 4.61 (s, 2H), 3.71 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.7 (d, $J_{C\text{-}F}$ = 246.4 Hz), 159.1, 143.7, 135.4, 134.7 (d, $J_{C\text{-}F}$ = 3.04 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.7 Hz), 130.0 (2C), 129.7 (2C), 127.7 (3C), 127.6, 115.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 113.8 (3C), 55.2, 54.4, 21.6; HRMS (ESI)$^+$ calcd for $C_{21}H_{20}FNNaO_3S$, 408.1046 m/z (M + Na)$^+$; found, 408.1043 m/z.



N-(4-Fluoro-phenyl)-4-methyl-benzenesulfonamide (**3f**).[28] Prepared according to general procedure **IV** using **4i** (100 mg, 0.26 mmol, 1.0 equiv); white solid (65 mg, 94% yield); R_f = 0.25 (25% EA/PE); mp = 84−86 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, J = 8.0 Hz, 2H), 7.30 (s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.07−7.04 (m, 2H), 6.90 (t, J = 8.8 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.9, 159.6, 144.2, 135.7, 132.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 129.8 (3C), 127.4 (2C), 124.5 (d, $J_{C\text{-}F}$ = 8.3 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 21.7; HRMS (ESI)$^+$ calcd for $C_{13}H_{13}FNO_2S$, 266.0651 m/z (M + H)$^+$; found, 266.0649 m/z.

https://doi.org/10.1021/acsomega.1c02276
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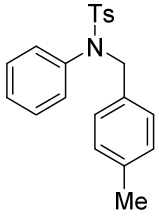
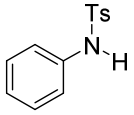
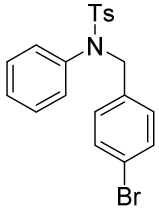


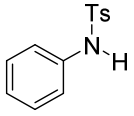
4-Methyl-*N*-(4-methyl-benzyl)-*N*-phenyl-benzenesulfonamide (**4j**): Prepared according to general procedure **II**; 82% yield; white solid; mp = 149−151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.18−7.16 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 7.00−6.94 (m, 4H), 4.66 (s, 2H), 2.41 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 139.1, 137.3, 135.8, 133.0, 129.6 (2C), 129.1 (2C), 129.0 (2C), 128.9 (2C), 128.6 (2C), 127.8 (3C), 54.5, 21.7, 21.2; HRMS (ESI)$^+$ calcd for $C_{21}H_{21}NNaO_2S$, 374.1191 m/z (M + Na)$^+$; found, 374.1195 m/z.



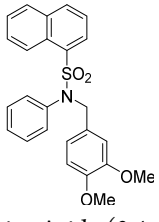
4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**):[25] Prepared according to general procedure **IV** using **4j** (100 mg, 0.28 mmol, 1.0 equiv); white solid (63 mg, 89% yield). All data are similar to the compound obtained from **4a**.



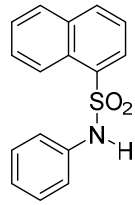
N-(4-Bromo-benzyl)-4-methyl-*N*-phenyl-benzenesulfonamide (**4k**): Prepared according to general procedure **II**; 80% yield; off-white solid; mp = 125−127 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.13−7.11 (m, 3H), 7.02 (d, J = 8.0 Hz, 2H), 6.88−6.87 (m, 2H), 4.58 (s, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 138.8, 135.4, 135.2, 131.6 (2C), 130.3 (2C), 129.6 (2C), 129.1 (2C), 128.9 (2C), 128.1, 127.8 (2C), 121.7, 54.2, 21.7; HRMS (ESI)$^+$ calcd for $C_{20}H_{18}BrNNaO_2S$, 440.0119 m/z (M + Na)$^+$; found, 440.0120 m/z.



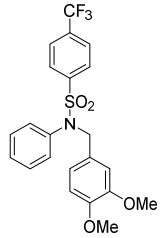
4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**): The reaction was performed according to general procedure **IV** using **4k** (100 mg, 0.24 mmol, 1.0 equiv). No product was obtained. Yield = 0%.



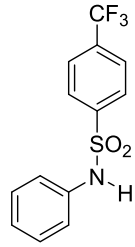
Naphthalene-1-sulfonic Acid (3,4-dimethoxy-benzyl)-phenyl-amide (**4l**): Prepared according to general procedure **II**; 80% yield; off-white solid; mp = 160−162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.58−7.45 (m, 3H), 7.14−7.12 (m, 3H), 6.94−6.92 (m, 2H), 6.62−6.60 (m, 2H), 6.56−6.54 (m, 1H), 4.73 (s, 2H), 3.78 (s, 3H), 3.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.7, 148.5, 138.6, 134.5 134.4, 134.3, 131.1, 129.7 (2C), 128.9 (4C), 128.5, 128.0 (2C), 126.9, 125.6, 124.2, 121.3, 111.7, 110.6, 55.9, 55.7, 55.0; HRMS (ESI)$^+$ calcd for $C_{25}H_{23}NNaO_4S$, 456.1245 m/z (M + Na)$^+$; found, 456.1243 m/z.



Naphthalene-1-sulfonic Acid Phenylamide (**3g**):[29] Prepared according to general procedure **IV** using **4l** (100 mg, 0.23 mmol, 1.0 equiv); white solid (52 mg, 80% yield); R_f = 0.25 (25% EA/PE); mp = 150−152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.77 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.65−7.63 (m, 1H), 7.60−7.58 (m, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.11 (t, J = 8.0 Hz, 2H), 7.02−6.96 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 134.8, 134.3, 134.1, 130.5, 129.4, 129.3 (3C), 128.7, 128.2, 127.0, 125.3, 124.3, 124.2, 121.5; HRMS (ESI)$^+$ calcd for $C_{16}H_{14}NO_2S$, 284.0745 m/z (M + H)$^+$; found, 284.0739 m/z.



N-(3,4-Dimethoxy-benzyl)-*N*-phenyl-4-trifluoromethyl-benzenesulfonamide (**4m**): Prepared according to general procedure **II**; 88% yield; off-white solid; mp = 140−142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79−7.37 (m, 4H), 7.24−7.22 (m, 3H), 6.94−6.92 (m, 2H), 6.77 (s, 1H), 6.67−6.64 (m, 2H), 4.68 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.6, 148.7, 142.5, 138.4, 129.2 (3C), 129.1 (2C), 128.4, 128.2 (3C), 127.8, 126.2, 126.1, 121.3, 111.7, 110.8, 55.9 (2C), 55.0; HRMS (ESI)$^+$ calcd for $C_{22}H_{20}F_3NNaO_4S$, 474.0963 m/z (M + Na)$^+$; found, 474.0961 m/z.



N-Phenyl-4-trifluoromethyl-benzenesulfonamide (**3h**):[30] Prepared according to general procedure **IV** using **4m** (100 mg, 0.22 mmol, 1.0 equiv); pale-yellow solid (60 mg, 90% yield), R_f = 0.25 (25% EA/PE); mp = 122−125 °C; ^{1}H NMR

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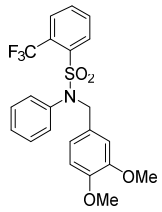
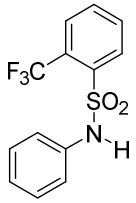
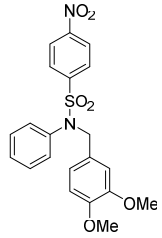
($CDCl_3$, 400 MHz): δ 7.89 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.26−7.22 (m, 3H), 7.15−7.07 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5, 135.8, 134.8 (J_{C-F} = 33.0 Hz), 129.7 (2C), 127.9 (2C), 126.4 (J_{C-F} = 7.0, 4.0 Hz, 2C), 126.2, 123.2 (J_{C-F} = 271.0 Hz), 122.1 (2C); HRMS (ESI)$^+$ calcd for $C_{13}H_{11}F_3NO_2S$, 302.0463 m/z (M + H)$^+$; found, 302.0462 m/z.



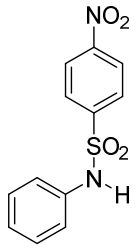
N-(3,4-Dimethoxybenzyl)-*N*-phenyl-2-trifluoromethyl-benzenesulfonamide (**4n**): Prepared according to general procedure **II**; 88% yield; off-white solid; mp = 141−143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.16−7.13 (m, 3H), 6.94−6.92 (m, 2H), 6.79 (s, 1H), 6.68−6.62 (m, 2H), 4.82 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.7 (d, J_{C-F} = 30.1 Hz), 138.2, 137.9, 133.0 (2C), 132.7, 131.9, 129.9 (3C), 129.1 (3C), 128.6, 128.2 (2C), 121.4 (2C), 111.8, 110.6, 55.8 (2C); HRMS (ESI)$^+$ calcd for $C_{22}H_{20}F_3NNaO_4S$, 474.0963 m/z (M + Na)$^+$; found, 474.0958 m/z.



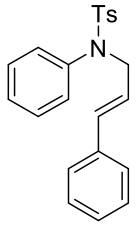
N-Phenyl-2-trifluoromethyl-benzenesulfonamide (**3i**):[31] Prepared according to general procedure **IV** using **4n** (100 mg, 0.22 mmol, 1.0 equiv); pale-yellow solid (60 mg, 90% yield); R_f = 0.25 (25% EA/PE); mp = 96−98 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.0 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.24−7.20 (m, 2H), 7.13−7.06 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.7, 133.2, 132.6, 132.3, 129.5 (4C), 128.6 (J_{C-F} = 7.0 Hz), 126.1, 122.3 (3C); HRMS (ESI)$^+$ calcd for $C_{13}H_{11}F_3NO_2S$, 302.0463 m/z (M + H)$^+$; found, 302.0460 m/z.



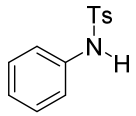
N-(3,4-Dimethoxy-benzyl)-4-nitro-*N*-phenyl-benzenesulfonamide (**4o**): Prepared according to general procedure **II**; 88% yield; pale-yellow solid; mp = 193−195 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 8.8 Hz, 2H), 7.26−7.23 (m, 3H), 6.93−6.91 (m, 2H), 6.77 (s, 1H), 6.69−6.63 (m, 2H), 4.70 (s, 2H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.1, 149.0, 148.8, 144.6, 138.0, 129.4 (2C), 129.1 (2C), 128.9 (2C), 128.6, 127.6, 124.3 (2C), 121.3, 111.6, 110.7, 55.9 (2C), 55.3; HRMS (ESI)$^+$ calcd for $C_{21}H_{20}N_2NaO_6S$, 451.0940 m/z (M + Na)$^+$; found, 451.0940 m/z.



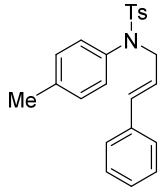
4-Nitro-*N*-phenyl-benzenesulfonamide (**3j**):[29] Prepared according to general procedure **IV** using **4o** (100 mg, 0.23 mmol, 1.0 equiv); pale-yellow solid (58 mg, 90% yield); R_f = 0.25 (30% EA/PE); mp = 168−170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.30−7.26 (m, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.08 (d, J = 7.2 Hz, 2H), 6.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.4, 144.7, 135.4, 129.8 (2C), 128.6 (2C), 126.5, 124.4 (2C), 122.6 (2C); HRMS (ESI)$^+$ calcd for $C_{12}H_{11}N_2O_4S$, 279.0440 m/z (M + H)$^+$; found, 279.0437 m/z.



4-Methyl-*N*-phenyl-*N*-(3-phenyl-allyl)-benzenesulfonamide (**5a**):[32] Prepared according to general procedure **II**; 80% yield; white solid; mp = 143−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, J = 8.4 Hz, 2H), 7.28−7.18 (m, 10H), 7.08−7.05 (m, 2H), 6.35 (d, J = 16.0 Hz, 1H), 6.12−6.04 (dt, J = 15.8, 6.5 Hz, 1H), 4.32 (dd, J = 6.8, 1.2 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 139.4, 136.5, 135.8, 133.8, 129.6 (2C), 129.1 (2C), 129.0 (2C), 128.6 (2C), 128.0, 127.9, 127.8 (2C), 126.6 (2C), 124.2, 53.4, 21.7; HRMS (ESI)$^+$ calcd for $C_{22}H_{21}NNaO_2S$, 386.1191 m/z (M + Na)$^+$; found, 386.1185 m/z.



4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**):[25] Prepared according to general procedure **IV** using **5a** (100 mg, 0.28 mmol, 1.0 equiv); white solid (55 mg, 81% yield). All data are similar to the compound obtained from **4a**.



4-Methyl-*N*-(3-phenyl-allyl)-*N*-*p*-tolyl-benzenesulfonamide (**5b**):[32] Prepared according to general procedure **II**; 80% yield; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.0 Hz, 2H), 7.26−7.20 (m, 7H), 7.06 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.1 Hz, 1H), 4.30 (dd, J = 6.1 Hz, 0.8 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 137.9, 136.6, 136.5, 135.9, 133.7, 129.7, 129.5, 128.8, 128.6, 127.9, 126.5,

https://doi.org/10.1021/acsomega.1c02276
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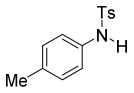
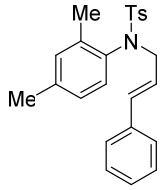
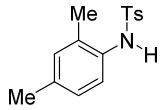
124.4, 53.5, 21.7, 21.2; HRMS (ESI)$^+$ calcd for $C_{23}H_{23}NNaO_2S$, 400.1347 m/z (M + Na)$^+$; found, 400.1349 m/z.



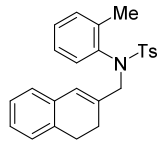
4-Methyl-*N*-*p*-tolyl-benzenesulfonamide (**3b**):[25] Prepared according to general procedure **IV** using **5b** (100 mg, 0.26 mmol, 1.0 equiv); white solid (53 mg, 78% yield). All data are similar to the compound obtained from **4b**.



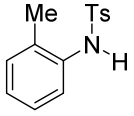
N-(2,4-Dimethyl-phenyl)-4-methyl-*N*-(3-phenyl-allyl)-benzenesulfonamide (**5c**): Prepared according to general procedure **II**; 82% yield; off-white solid; mp = 105−107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, J = 8.4 Hz, 2H), 7.28−7.20 (m, 7H), 7.04 (s, 1H), 6.84−6.82 (m, 1H), 6.52 (d, J = 7.2 Hz, 1H), 6.28 (d, J = 15.6 Hz, 1H), 6.13−6.05 (m, 1H), 4.44 (dd, J = 16.0 Hz, 5.6 Hz, 1H), 4.03 (dd, J = 14 Hz, 7.6 Hz, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 139.6, 138.3, 136.6, 136.5, 135.5, 134.0, 132.1, 129.5 (2C), 128.6 (2C), 128.3, 128.0 (2C), 127.9, 127.0, 126.5 (2C), 123.9, 54.4, 21.6, 21.1, 18.6; HRMS (ESI)$^+$ calcd for $C_{24}H_{25}NNaO_2S$, 414.1504 m/z (M + Na)$^+$; found, 414.1503 m/z.



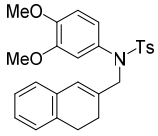
N-(2,4-Dimethyl-phenyl)-4-methyl-benzenesulfonamide (**3c**):[26] Prepared according to general procedure **IV** using **5c** (100 mg, 0.26 mmol, 1.0 equiv); white solid (53 mg, 76% yield). All data are similar to the compound obtained from **4c**.



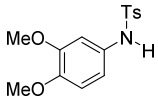
N-(3,4-Dihydro-naphthalen-2-ylmethyl)-4-methyl-*N*-*o*-tolyl-benzenesulfonamide (**5d**): Prepared according to general procedure **II**; 89% yield; off-white solid; mp = 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 3H), 7.28−7.17 (m, 2H), 7.09−7.07 (m, 3H), 6.86−6.85 (m, 1H), 6.64−6.63 (m, 1H), 6.03 (s, 1H), 4.47 (d, J = 13.0 Hz, 1H), 3.93 (d, J = 13.0 Hz, 1H), 2.78−2.72 (m, 2H), 2.70 (s, 3H), 2.47 (s, 3H), 2.40−2.38 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 139.8, 138.0, 135.0, 134.0, 132.5, 131.4, 129.4 (3C), 128.0 (3C), 127.4, 127.3, 127.1, 126.3, 126.0 (2C), 125.9, 57.3, 27.8, 25.2, 21.6, 18.6; HRMS (ESI)$^+$ calcd for $C_{25}H_{26}NO_2S$, 404.1684 m/z (M + H)$^+$; found, 404.1678 m/z.



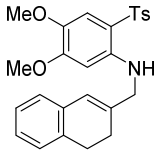
4-Methyl-*N*-*o*-tolyl-benzenesulfonamide (**3k**):[33] Prepared according to general procedure **IV** using **5d** (100 mg, 0.25 mmol, 1.0 equiv); white solid (55 mg, 84% yield); R_f = 0.25 (25% EA/PE); mp = 95−97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, J = 7.2 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 2H), 7.15−7.09 (m, 3H), 6.57 (s, 1H), 2.40 (s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7, 136.7, 134.5, 131.4, 130.7, 129.5 (2C), 127.1 (2C), 126.8, 126.1, 124.3, 21.5, 17.5; HRMS (ESI)$^+$ calcd for $C_{14}H_{16}NO_2S$, 262.0902 m/z (M + H)$^+$; found, 262.0899 m/z.



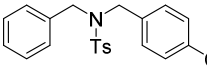
N-(3,4-Dihydro-naphthalen-2-ylmethyl-*N*-(3,4-dimethoxy-phenyl)-4-methyl-benzenesulfonamide (**5e**). Prepared according to general procedure **II**; 89% yield; off-white solid; mp = 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.05−7.01 (m, 3H), 6.83−6.82 (m, 1H), 6.66 (d, J = 8.4 Hz, 1H), 6.53−6.50 (m, 2H), 6.08 (s, 1H), 4.21 (s, 2H), 3.79 (s, 3H), 3.68 (s, 3H), 2.69 (t, J = 8.0 Hz, 2H), 2.41 (s, 3H), 2.36 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 148.6, 143.5, 135.4 (2C), 131.6, 129.5 (3C), 128.0 (3C), 127.4, 127.2, 127.0, 126.4, 126.0, 121.2, 112.6, 110.7, 56.8, 56.0, 55.9, 28.0, 24.8, 21.6; HRMS (ESI)$^+$ calcd for $C_{26}H_{28}NO_4S$, 450.1739 m/z (M + H)$^+$; found, 450.1742 m/z.



N-(3,4-Dimethoxy-phenyl)-4-methyl-benzenesulfonamide (**3e**):[27] Prepared according to general procedure **IV** using **5e** (100 mg, 0.22 mmol, 1.0 equiv); white solid (37 mg, 55% yield). All data are similar to the compound obtained from **4e**.



3,4-Dihydro-naphthalen-2-ylmethyl)-[4,5-dimethoxy-2-(toluene-4-sulfonyl)-phenyl amine (Detosylated product) (**5e'**): Obtained during the course of the C−N bond cleavage of **5e** according to general procedure **IV**; white solid (13 mg, 12% yield); R_f = 0.22 (35% EA/PE); mp = 123−125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.4 Hz, 2H), 7.08−6.98 (m, 6H), 6.85 (s, 1H), 6.50 (s, 1H), 6.35 (s, 1H), 5.89 (s, 1H), 3.72 (s, 6H), 2.95 (s, 2H), 2.62 (t, J = 8.0 Hz, 2H), 2.26 (s, 3H), 1.89 (t, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.0, 147.5, 143.9, 139.3, 136.7, 134.3, 134.1, 129.7 (3C), 127.6, 127.3 (3C), 126.9, 126.7, 126.0, 124.2, 113.2, 109.8, 56.1, 56.0, 39.2, 28.0, 27.1, 21.6; HRMS (ESI)$^+$ calcd for $C_{26}H_{28}NO_4S$, 450.1739 m/z (M + H)$^+$; found, 450.1737 m/z.



N-Benzyl-*N*-(4-methoxy-benzyl)-4-methyl-benzenesulfonamide (**6a**): Prepared according to general procedure **II**; 89% yield; off-white solid; mp = 110−112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.23−7.22 (m, 3H), 7.08−7.07 (m, 2H), 6.98−6.95 (m, 2H), 6.75 (d, J = 8.0 Hz, 2H), 4.29 (s, 2H), 4.26 (s, 2H), 3.76 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 143.3, 137.8, 135.9, 130.1 (3C), 129.8, 128.6 (3C), 128.6

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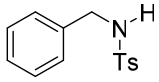
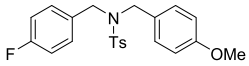
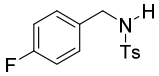
(2C), 127.6, 127.3 (3C), 113.8, 55.3, 50.3, 49.9, 21.6; HRMS (ESI)$^+$ calcd for $C_{22}H_{24}NO_3S$, 382.1477 m/z (M + H)$^+$; found, 382.1473 m/z.



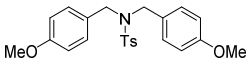
N-Benzyl-4-methyl-benzenesulfonamide (**3l**):[34] Prepared according to general procedure **IV** using **6a** (100 mg, 0.26 mmol, 1.0 equiv); white solid (53 mg, 78% yield); R_f = 0.25 (25% EA/PE); mp = 113−115 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 8.4 Hz, 2H), 7.29−7.23 (m, 5H), 7.19−7.17 (m, 2H), 4.97−4.95 (m, 1H), 4.09 (d, J = 6.00 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 136.9, 136.4, 129.8 (2C), 128.7 (2C), 128.0 (3C), 127.3 (2C), 47.3, 21.6; HRMS (ESI)$^+$ calcd for $C_{14}H_{16}NO_2S$, 262.0902 m/z (M + H)$^+$; found, 262.0898 m/z.



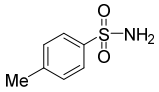
N-(4-Fluoro-benzyl)-*N*-(4-methoxy-benzyl)-4-methyl-benzenesulfonamide (**6b**): Prepared according to general procedure **II**; 87% yield; off-white solid; mp = 105−107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.04−7.01 (m, 2H), 6.94−6.86 (m, 4H), 6.73 (d, J = 8.8 Hz, 2H), 4.23 (s, 2H), 4.22 (s, 2H), 3.75 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.2 (d, $J_{C\text{-}F}$ = 244.5 Hz), 159.2, 143.4, 137.5, 131.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.1, 2C), 130.0 (2C), 129.8 (2C), 127.4, 127.2 (2C), 115.2 (d, $J_{C\text{-}F}$ = 21.3, 2C), 113.8 (2C), 55.3, 50.3, 49.7, 21.6; HRMS (ESI)$^+$ calcd for $C_{22}H_{23}FNO_3S$, 400.1383 m/z (M + H)$^+$; found, 400.1379 m/z.



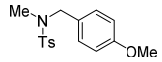
N-(4-Fluoro-benzyl)-4-methyl-benzenesulfonamide (**3m**):[34] Prepared according to general procedure **IV** using **6b** (100 mg, 0.25 mmol, 1.0 equiv); white solid (57 mg, 81% yield); R_f = 0.25 (35% EA/PE); mp = 92−94 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.17−7.15 (m, 2H), 6.95−6.90 (m, 2H), 5.05−5.02 (m, 1H), 4.07 (d, J = 6.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.4 (d, $J_{C\text{-}F}$ = 244.8 Hz), 143.8, 136.9, 132.2, 129.9 (2C), 129.7 (d, $J_{C\text{-}F}$ = 8.2 Hz, 2C), 127.2 (2C), 115.6 (d, $J_{C\text{-}F}$ = 21.4, 2C), 46.6, 21.6; HRMS (ESI)$^+$ calcd for $C_{14}H_{15}FNO_2S$, 280.0808 m/z (M + H)$^+$; found, 280.0809 m/z.



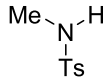
N,*N*-Bis-(4-methoxy-benzyl)-4-methyl-benzenesulfonamide (**6c**): Prepared according to general procedure **II**; 89% yield; off-white solid; mp = 105−107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.4 Hz, 4H), 6.75 (d, J = 8.8 Hz, 4H), 4.22 (s, 4H), 3.78 (s, 6H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 143.3, 138.0, 130.0 (5C), 129.8 (2C), 127.8, 127.3 (2C), 113.8 (5C), 55.4 (2C), 49.6 (2C), 21.7; HRMS (ESI)$^+$ calcd for $C_{23}H_{26}NO_4S$, 412.1583 m/z (M + H)$^+$; found, 412.1583 m/z.



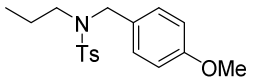
4-Methyl-benzenesulfonamide (**3n**): Prepared according to general procedure **IV** using **6c** (100 mg, 0.24 mmol, 1.0 equiv); white solid (33 mg, 80% yield); R_f = 0.25 (35% EA/PE); mp = 132−134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.95 (s, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 139.2, 129.9 (2C), 126.6 (2C), 21.7; HRMS (ESI)$^+$ calcd for $C_7H_{10}NO_2S$, 172.0432 m/z (M + H)$^+$; found, 172.0426 m/z.



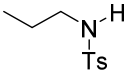
N-(4-Methoxy-benzyl)-4,*N*-dimethyl-benzenesulfonamide (**7a**): Prepared according to general procedure **II**; 87% yield; white solid; mp = 69−71 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.04 (s, 2H), 3.79 (s, 3H), 2.54 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 143.5, 134.3, 129.8 (3C), 127.6 (3C), 114.1 (3C), 55.4, 53.7, 34.2, 21.7; HRMS (ESI)$^+$ calcd for $C_{16}H_{20}NO_3S$, 306.1164 m/z (M + H)$^+$; found, 306.1167 m/z.



4,*N*-Dimethyl-benzenesulfonamide (**3o**):[35] Prepared according to general procedure **IV** using **7a** (100 mg, 0.3 mmol, 1.0 equiv); white solid (49 mg, 76% yield); R_f = 0.2 (20% EA/PE); mp = 70−72 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.75−4.70 (m, 1H), 2.62 (d, J = 5.6 Hz, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 135.8, 129.8 (2C), 127.4 (2C), 29.4, 21.6; HRMS (ESI)$^+$ calcd for $C_8H_{12}NO_2S$, 186.0589 m/z (M + H)$^+$; found, 186.0586 m/z.



N-(4-Methoxy-benzyl)-4-methyl-*N*-propyl-benzenesulfonamide (**7b**): Prepared according to general procedure **II**; 87% yield; off-white solid; mp = 79−81 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 4.23 (s, 2H), 3.76 (s, 3H), 3.02−2.99 (m, 2H), 2.41 (s, 3H), 1.34−1.28 (m, 2H), 0.67 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 143.1, 137.1, 129.7 (2C), 129.6 (2C), 128.5, 127.1 (2C), 113.8 (2C), 55.2, 51.3, 49.6, 21.5, 21.4, 11.2; HRMS (ESI)$^+$ calcd for $C_{18}H_{24}NO_3S$, 334.1477 m/z (M + H)$^+$; found, 334.1475 m/z.



4-Methyl-*N*-propyl-benzenesulfonamide (**3p**):[35] Prepared according to general procedure IV using **7b** (100 mg, 0.3 mmol, 1.0 equiv); white solid (49 mg, 76% yield); R_f = 0.2 (20% EA/PE); mp = 90−92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.86 (s, 1H), 2.90−2.84 (m, 2H), 2.41 (s, 3H), 1.49−1.43 (m, 2H), 0.84 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 137.0, 129.8 (2C), 127.2 (2C), 45.0, 23.0, 21.6, 11.2; HRMS (ESI)$^+$ calcd for $C_{10}H_{16}NO_2S$, 214.0902 m/z (M + H)$^+$; found, 214.0898 m/z.

Procedure for Control Experiments (Scheme 7). Scheme 7i. To a stirred solution of *N*-(3,4-dimethoxy-benzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in superdry dichloroethane (2 mL), Bi(OTf)$_3$ (8 mg, 0.0125 mmol, 0.05 equiv) was added along with 4Å

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molecular sieves, and the resultant mixture was refluxed at 85 °C for 2 h. A trace amount of the cleavage product was formed.

Scheme 7ii. To a stirred solution of *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in dry dichloroethane (2 mL), water (0.2 mL) and $Bi(OTf)_3$ (8 mg, 0.0125 mmol, 0.05 equiv) were added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product **3a** in 93% yield.

Scheme 7iii. To a stirred solution of *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in dichloroethane (2 mL), TfOH (2.2 μL, 0.025 mmol, 0.1 equiv) was added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product **3a** in 89% yield.

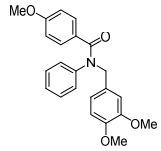
Scheme 7iv. To a stirred solution of *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in dichloroethane (2 mL), TfOH (2.2 μL, 0.025 mmol, 0.1 equiv) and the acid scavenger DTBMP (77 mg, 0.375 mmol, 1.5 equiv) were added, and the resultant mixture was refluxed at 85 °C for 2 h. A trace amount of the cleavage product was formed.

Scheme 7v. To a stirred solution of *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in degassed dichloroethane (2 mL), water (0.2 mL) and $Bi(OTf)_3$ (0.05 equiv) were added, and the resultant mixture was refluxed at 85 °C for 2 h under a nitrogen atmosphere. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product **3a** in 91% yield.

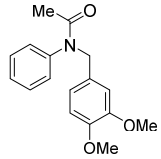
Scheme 7vi. To a stirred solution of *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in dry dichloroethane (2 mL), water (0.2 mL) and $Bi(OTf)_3$ (8 mg, 0.0125 mmol, 0.05 equiv) were added, and the resultant mixture was refluxed at 85 °C for 2 h under a dark condition. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product **3a** in 90% yield.

Scheme 7vii. To a stirred solution of *N*-(3,4-dimethoxybenzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in dry dichloroethane (2 mL), water (0.2 mL), $Bi(OTf)_3$ (8 mg, 0.0125 mmol, 0.05 equiv), and the radical scavenger BHT (66 mg, 0.3 mmol, 1.2 equiv) were added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product **3a** in 89% yield.

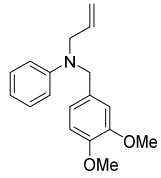
Preparation of Inactive Substrates 4p−4s.



N-(3,4-Dimethoxy-benzyl)-4-methoxy-*N*-phenyl-benzamide (**4p**). To a solution of *N*-(3,4-dimethoxybenzyl)aniline (200 mg, 0.82 mmol) in DMF, NaH (60% suspension, 30 mg, 1.23 mmol, 1.5 equiv) was added and stirred at room temperature for 1 h, followed by the addition of 4-methoxybenzoyl chloride (0.11 mL, 0.84 mmol, 1.02 equiv). The resultant mixture was stirred at 80 °C, and after the complete consumption of reactants (as monitored by TLC), the reaction was quenched with 1.0 M HCl aqueous solution, extracted with EtOAc, washed with brine, dried with Na_2SO_4, and evaporated *in vaccuo*. Purification of the crude product by flash column chromatography using an EtOAc and petroleum ether mixture (35% EA/PE) as the eluent afforded the desired titled compound **4p** (216 mg, 70%) as a colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (d, J = 8.8 Hz, 2H), 7.17−7.08 (m, 3H), 6.89 (d, J = 7.2 Hz, 2H), 6.84 (s, 1H), 6.81−6.73 (m, 2H), 6.64 (d, J = 8.8 Hz, 2H), 5.04 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.1, 160.7, 148.8, 148.3, 144.0, 131.0 (2C), 130.4, 129.1 (2C), 128.1, 127.8 (2C), 126.6, 121.0, 113.0 (2C), 111.8, 110.8, 55.9 (2C), 55.3, 53.8; HRMS (ESI)$^+$ calcd for $C_{23}H_{23}NNaO_4$, 400.1525 m/z (M + Na)$^+$; found, 400.1523 m/z.



N-(3,4-Dimethoxy-benzyl)-*N*-phenyl-acetamide (**4q**): To a solution of *N*-(3,4-dimethoxybenzyl)aniline (200 mg, 0.82 mmol) in acetic acid, Ac_2O (0.15 mL, 1.64 mmol, 2.0 equiv) was added, and the resultant mixture was heated to 100 °C, and after the complete consumption of reactants (as monitored by TLC), the reaction was quenched with saturated $NaHCO_3$ solution, extracted with EtOAc, washed with brine, dried with Na_2SO_4, and evaporated *in vaccuo*. Purification of the crude product by flash column chromatography using an EtOAc and petroleum ether mixture (35% EA/PE) as the eluent afforded the desired titled compound **4q** (198 mg, 85%) as a colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.29 (m, 3H), 6.97 (d, J = 7.2 Hz, 2H), 7.64 (s, 1H), 6.72 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.81 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 1.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 148.8, 148.4, 142.7, 130.1, 129.5, 128.9, 128.4, 128.0, 121.4, 119.9, 112.2, 110.8, 55.8 (2C), 52.5, 22.8; HRMS (ESI)$^+$ calcd for $C_{17}H_{19}NNaO_3$, 308.1263 m/z (M + Na)$^+$; found, 308.1263 m/z.



https://doi.org/10.1021/acsomega.1c02276
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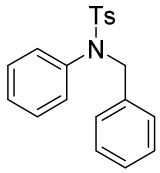
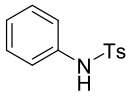
Allyl-(3,4-dimethoxy-benzyl)-phenyl-amine (**4r**): To a solution of *N*-(3,4-dimethoxybenzyl)aniline (200 mg, 0.82 mmol) in DMF, NaH (60% suspension, 30 mg, 1.23 mmol, 1.5 equiv) was added and stirred at room temperature for 1 h, followed by the addition of allyl bromide (0.072 mL, 0.84 mmol, 1.02 equiv). The resultant mixture was stirred at 80 °C, and after the complete consumption of reactants (as monitored by TLC), the reaction was quenched with 1.0 M HCl aqueous solution, extracted with EtOAc, washed with brine, dried with Na_2SO_4, and evaporated *in vaccuo*. Purification of the crude product by flash column chromatography using an EtOAc and petroleum ether mixture (20% EA/PE) as the eluent afforded the desired titled compound **4r** (192 mg, 83%) as a colorless thick oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (t, J = 8.0 Hz, 2H), 6.81−6.70 (m, 6H), 5.94−5.84 (m, 1H), 5.22−5.20 (m, 1H), 5.18 (s, 1H), 4.49 (s, 2H), 4.00 (d, J = 4.8 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2 (2C), 148.0, 133.8, 131.5, 129.2 (2C), 118.7, 116.7, 116.5, 112.7 (2C), 111.2, 109.8, 56.1, 55.9, 53.9, 52.8; HRMS (ESI)$^+$ calcd for $C_{18}H_{22}NO_2$, 284.1651 m/z (M + H)$^+$; found, 284.1648 m/z.

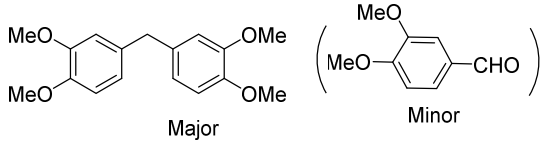


N-Benzyl-4-methyl-*N*-phenyl-benzenesulfonamide (**4s**):[15] Prepared according to general procedure **II**; 89% yield; white solid; mp = 118−120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.16−7.08 (m, 8H), 6.90−5.88 (m, 2H), 4.63 (s, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 140.0, 136.0, 135.5, 129.6 (2C), 129.0 (2C), 128.9 (2C), 128.6 (2C), 128.4 (2C), 127.9, 127.8 (2C), 127.6, 54.7, 21.7; HRMS (ESI)$^+$ calcd for $C_{20}H_{19}NNaO_2S$, 360.1034 m/z (M + Na)$^+$; found, 360.1031 m/z.

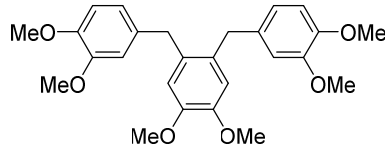
Experimental Procedure for the Preparation of Compounds 8a and 8b. To a stirred solution of *N*-(3,4-dimethoxy-benzyl)-4-methyl-*N*-phenyl-benzenesulfonamide **4a** (0.25 mmol, 1 equiv) in dichloroethane (2 mL), $Bi(OTf)_3$ (8 mg, 0.0125 mmol, 0.05 equiv) and 1,2-dimethoxybenzene (0.064 mL, 0.5 mmol, 2.0 equiv) were added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure completion. On completion, DCE was removed under reduced pressure and the crude mixture was directly subjected to purification by flash column chromatography using an EtOAc and petroleum ether mixture as the eluent, affording the desired cleavage product **3a** in 93% yield along with **8a** (45% yield) and **8b** (23% yield).



4-Methyl-*N*-phenyl-benzenesulfonamide (**3a**): Yield = 93%; all data are consistent with the molecule prepared according to general procedure **IV**.

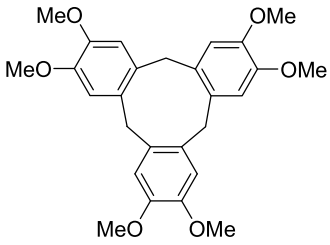


Bis(3,4-dimethoxy-phenyl)methane (**8a**):[36] 45% yield; brown thick oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.84 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.41(s, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 8H), 6.70 (d, J = 10.4 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.87 (s, 8H), 3.84 (s, 24H), 3.82 (s, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.0 (2C). 147.4 (2C), 134.0 (2C), 120.8 (2C), 112.2 (2C), 111.3 (2C), 56.0 (2C), 55.9 (2C), 41.1; HRMS (ESI)$^+$ calcd for $C_{17}H_{21}O_4$, 289.1440 m/z (M + H)$^+$; found, 289.1433 m/z. [bis(3,4-dimethoxyphenyl)methane and 3,4-dimethoxybenzaldehyde obtained in a 4:1 ratio]



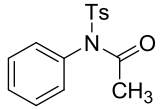
1-(2,3-Dimethoxybenzyl)-5-(3,4-dimethoxybenzyl)-2,3-dimethoxybenzene (**8b**): 23% yield; pale-yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.75 (d, J = 8.0 Hz, 2H), 6.65 (s, 2H), 6.60−6.57 (m, 4H), 3.84 (s, 10H), 3.80 (s, 6H), 3.76 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.0 (2C), 147.5 (2C), 147.4 (2C), 133.6 (2C), 131.3 (2C), 120.6 (2C), 113.9 (2C), 112.0 (2C), 111.2 (2C), 56.1 (2C), 56.0 (2C), 55.9 (2C), 38.2 (2C); HRMS (ESI)$^+$ calcd for $C_{26}H_{31}O_6$, 439.2121 m/z (M + H)$^+$; found, 439.2117 m/z.

Preparation of Tribenzocyclononane (2,3,7,8,12,13-Hexamethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononane) 10 (8ii).



2,3,7,8,12,13-Hexamethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]-cyclononane (**10**):[22] To a stirred solution of 3,4-dimethoxyphenylmethanol (0.1 g, 0.59 mmol) in dichloroethane (2 mL), $Bi(OTf)_3$ (0.05 equiv; 0.02 g) was added, and the resultant mixture was refluxed at 85 °C for 1 h. After the complete consumption of alcohol, the reaction mixture was cooled down and next evaporated *in vaccuo*. Purification of the crude product by flash column chromatography using an EtOAc and petroleum ether mixture (30% EA/PE) as the eluent afforded the desired titled compound **10** (68 mg, 76% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.83 (s, 6H), 4.77 (d, J = 13.6 Hz, 3H), 3.84 (s, 18H), 3.55 (d, J = 13.6 H, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.8, 131.9, 113.2, 56.1, 36.6; HRMS (ESI) calcd for $C_{27}H_{30}NaO_6$, 473.1940 m/z (M + Na)$^+$; found, 473.2135 m/z.

One-pot amide synthesis in a gram scale (Scheme 9)



N-Acetyl-4-methyl-*N*-phenyl-benzenesulfonamide (**11**): To a stirred solution of tertiary sulfonamide **4a** (1.0 g, 2.51 mmol, 1 equiv) in dichloroethane (15 mL), $Bi(OTf)_3$ (82 mg, 0. 125 mmol, 0.05 equiv) was added, and the resultant mixture was refluxed at 85 °C for 2 h. The reaction was monitored by TLC to ensure complete consumption of **4a**, and then, Ac_2O (0.50

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mL, 5.02 mmol, 2.0 equiv) was added to the same reaction pot. After the complete consumption of C−N bond cleavage product **3a** (confirmed by TLC), the reaction was quenched with saturated $NaHCO_3$ solution, extracted with EtOAc, washed with brine, dried with Na_2SO_4, and evaporated *in vaccuo*. Purification of the crude product by flash column chromatography using an EtOAc and petroleum ether mixture (20% EA/PE) as the eluent afforded the desired titled compound **11** (680 mg, 94% overall yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, J = 8.0 Hz, 2H), 7.49−7.47 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.28−7.25 (m, 2H), 2.44 (s, 3H), 1.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 145.1, 137.0, 136.1, 130.1 129.0 (4C), 129.5 (2C), 129.3 (2C), 25.2, 21.8; HRMS (ESI) calcd for $C_{15}H_{15}NNaO_3S$, 312.0670 m/z (M + Na)$^+$; found, 312.0670 m/z.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02276.

Copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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