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RESEARCH ARTICLE

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A facile and sustainable protocol to the preparation of aryl iodides using stable arenediazonium bis(trifluoromethylsulfonyl) imide salts via the telescopic process

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Abstract
The preparation of aryl iodides in a telescopic reaction using *tert*-butyl nitrite as a diazotization reagent and a mixture of bis(trifluoromethane) sulfonamide and glacial acetic acid as a mild acidic agent in ethanol followed by iododediazoniation with tetraethylammonium iodide in water was investigated. The current method has other advantages such as minimized waste by avoiding solvent for the purification of products in diazotization step, simple experimental procedure, and good yield of the sterically hindered aryl amines, metal and strong acid-free waste and environmentally benign conditions. The noteworthy features of this study are the preparation of stable arenediazonium bis(trifluoromethylsulfonyl)imide salts that can be used with no significant loss activity after 1 week and bis(trifluoromethane)sulfonamide was recovered in high yields from reactions.

1 | INTRODUCTION

Arenediazonium salts play an important role in organic synthesis as intermediate and a wide variety of aromatic compounds have been prepared using them.[1,2] A serious drawback of arenediazonium salts is their instability in a dry state; therefore, they must be stored and handled carefully to avoid spontaneous explosion and other hazard events.[3-5] The nature of the counteranion of arenediazonium salts is of utmost important as it defines their stability; for example, the arenediazonium salts containing low nucleophilic counteranions such as BF_4^-, PF_6^-, *o*-benzenedisulfonimide, aryl sulfonates,[6] and bis(trifluoromethane)sulfonamide[7] can be isolated and stored for long periods of time. However, these arenediazonium salts have some drawbacks such as demanding for expensive, toxic, fatal reagents and very laborious steps for synthesis,[8] arduous separation and purification steps,[9] sensitivity to air, decomposing on heating, commercial unavailability of reagents. Use of metal nitrites as a diazotizing reagent is not promising in large scale; therefore, nitrite-exchange resin (Resin-NO_2^-) was investigated as a polymer-supported diazotizing reagent.[10,11] In this procedure, the filtered resin after preparation must be washed with water until the pH of the filtrate became neutral which generates large amounts of salt waste and greatly increases the risk of environmental pollution.[11,12] Considering the aforementioned drawbacks, the search continues for a better and more efficient method for preparation of stable arenediazonium salts in terms of operational simplicity, environmental acceptability, and metal free conditions.

Over the past decade, bis(trifluoromethane)sulfonamide (TFSI-H) and its salts have attracted much interest for their use as catalyst during the ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of hexamethyldisiloxane,[13] the synthesis of various non-reducing disaccharides via ketopyranosylation of 2,3,4,6-tetra-O-benzyl-1-C-methyl-D-hexopyranoses,[14] esterification carboxylic acid with alkyl halides,[15] reactant for preparing the *N*-fluorobis[(trifluoromethyl)sulfonyl]imide (TFSI-F) as an efficient fluorinating agent,[16,17] and as a component of solid polymer electrolytes.[18] Synthesis, properties, and reactions of TFSI-H were previously studied.[19] The salts of bis-trifluoromethane sulfonimide are widely used as non-aqueous electrolytes in electrochemical applications such as batteries,[20] fuel cells.[21,22] In this context, their conductivity and wide electrochemical window of bis(trifluoromethylsulfonyl)imide,

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where the negative charge is delocalized over larger volume as well as good thermal and hydrolytic stability are the most important physical properties.[23] Bis(trifluoromethylsulfonyl) imide (TFSI) as a non-coordinating anion is widely used in ionic liquids and highly efficient Lewis acid catalysts, as it is less toxic and more stable than BF_4^-, PF_6^-, $AlCl_4^-$, and halide anions.[24-26] Imidazolium-based ionic liquids with stable anions such as trifluoromethylsulfonate are the materials of choice for supercapacitors.[27]

Aryl and heteroaryl halides have broad applications in some organic synthesis for carbon-carbon and carbon-heteroatom bond formation, such as palladium and copper-catalyzed cross-coupling,[28-32] Suzuki-Miyaura reaction (SMR),[33] and Ullmann coupling.[34] Aryl iodides have been also used in medicine as radioactivity label markers in radio-immunoassays or in nuclear magnetic imaging.[35,36] Sandmeyer reaction is one of the most commonly used methods for the selective introduction of iodine atoms into a specific position of the aromatic ring via the substitution of a diazonium group by iodine, while direct electrophilic iodination frequently offers a mixture of regioisomers. The alternatives to Sandmeyer reaction have been widely studied in the presence of alkyl nitriles, copper salts and the different sources of iodine under acidic and acid-free conditions in one or two steps.[28-34]

In continuation of our studies on simple, efficient and environmentally benign methods under mild reaction conditions;[37,38] very recently, the telescopic synthesis of azo compounds was reported via stable arenediazonium bis(trifluoromethylsulfonyl) imides using *tert*-butyl nitrite.[7] Herein, the potential of TFSI-H for preparation aryl iodides via diazotization-iodination of its stable salts $[ArN_2][TFSI]$ was investigated and found the aryl iodides can be efficiently prepared in the presence of TFSI-H (Scheme 1).

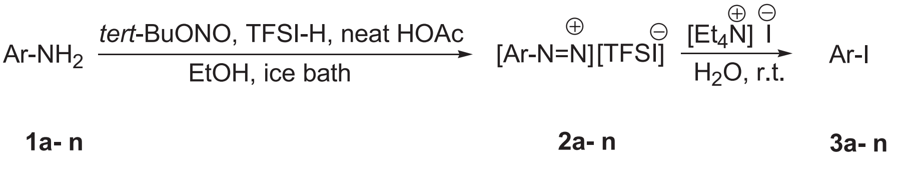
Arenediazonium salts were generated as the intermediates via an in situ strategy without being isolated; therefore, waste was minimized by avoiding solvent for the separation and purification of arenediazonium intermediates. In the present method, *tert*-butyl nitrite was employed as the diazotizing reagent due to its easy handling, commercial availability, and higher safety profile. Recently *tert*-butyl nitrite has developed as a mild, safe, easily handled and commercially available nitrating reagent.[39-47] Also tetraethylammonium iodide (TEAI) was used because it greatly lowers the risk of metal waste pollution. Also TEAI contains no components considered to be very persistent, bioaccumulative and toxic (PBT) at levels of 0.1% or higher according to Regulation (EC) No. 1272/2008 (MSDS, Sigma-Aldrich Chemie GmbH, Germany).

2 | RESULTS AND DISCUSSION

Diazotization of various primary aryl amines was carried out by slowly stirring a mixture of TFSI-H, glacial acetic acid, and *tert*-butyl nitrite in dry ethanol at low temperature in an ice bath. Then, a variety of aryl amines **1(a-l)** was added dropwise at the low temperature until the aryl amine disappeared. Next, an aqueous solution of TEAI was added in one portion to the intermediate of **2**(**a-l**) and the mixture was stirred vigorously at low temperature. After completion of the reaction, the crude residue was purified by flash chromatography to give the pure compound **3**(**a-l**). TFSI-H was recovered in 84% yield after the solvent was removed using rotary evaporation; also, the tetraethylammonium chloride (TEAC) was afforded in 68% yield according to tetraethylammonium cation. In a study relevant, the acidification of aqueous layer was done using hydriodic acid (≥57%) under same reaction conditions which afforded tetraethylammonium iodide (TEAI) in 62% yield. There are mainly cost-effective reasons which acidification was done using hydrochloric acid because hydriodic acid is generally more expensive than hydrochloric acid and TEAI is also relatively cheap.

In order to study the stability of intermediate, dry 4-methoxyphenyl diazonium bis(trifluoromethylsulfonyl) imide (**2l**) was separated in 80% yield on the simply evaporating under vacuum rotary. This solid salt was kept in refrigerator (4°C) for 1 week, and then the addition of this stored intermediate **2l** to the solution of TEAI in the deionized water gave 74% yield of 1-iodo-4-methoxybenzene (**3l**) in comparison to 80% yield in telescopic condition in the presence of freshly-prepared arenediazonium bis(trifluoromethylsulfonyl) imide.

The results show that the present developed process tolerates a wide variety of substituted aryl amines, and good yields have been offered in most of the cases. The reaction times and yields were apparently affected by electronic properties and steric demands of the substituents of aryl amines. The reaction with electron-withdrawing substituents proceeded smoothly and afforded the corresponding aryl iodides in good yields (Table 1, entries 6-10). Moreover, it was found that the yields were apparently affected by the steric hindrance of aryl amines and the steric hindrance effects seems be more effective than electronic properties in yields and



$$Ar\text{-}NH_2 \xrightarrow[\text{EtOH, ice bath}]{\textit{tert}\text{-BuONO, TFSI-H, neat HOAc}} \overset{\oplus}{[Ar\text{-}N{=}N]}\overset{\ominus}{[TFSI]} \xrightarrow[\text{H}_2\text{O, r.t.}]{\overset{\oplus}{[Et_4N]}\,\overset{\ominus}{I}} Ar\text{-}I$$

SCHEME 1 Telescopic synthesis of aryl iodides via the stable arenediazonium bis-trifluoromethane sulfonimide salts

TABLE 1 Telescopic diazotization-iodination reaction for a variety of aryl amines via the modified Knoevenagel's method[a]

					Melting point (°C)	
Entry	**Ar-NH$_2$** (1a-k)	**Product (3)**	**Total time (min)**	**Yield (%)**[b]	**Found**	**Reported (ref.)**[c]
1	C_6H_5-	a	90	81	Oil	Oil
2	4-CH_3-C_6H_4-	b	90	78	Oil	Oil
3	2,6-$(CH_3)_2$-C_6H_3-	c	120	67	Oil	-
4	2,6-$[(CH_3)_2CH]_2$-C_6H_3-	d	120	59	Oil	Oil
5	2,6-$(CH_3CH_2)_2$-C_6H_3-	e	120	47	Oil	-
6	4-Cl-C_6H_4-	f	90	80	55-56	53-54
7	2-Cl-C_6H_4-	g	110	78	Oil	Oil
8	4-Br-C_6H_4-	h	90	80	87-88	89-91
9	4-NO_2-C_6H_4-	i	90	88	170-172	170
10	2-NO_2-C_6H_4-	j	110	82	51-53	52
11	4-CH_3CO-C_6H_4-	k	90	81	81-83	82-84
12	4-CH_3O-C_6H_4-	l	95	80	52-54	53-55
13	3,4-(Methylenedioxy) aniline	m	95	81	Oil	Oil
14	4-Morpholinoaniline	n	90	73	159-161	158-163

[a] Reaction conditions: arylamine (**1**) (2.0 mmol), *tert*-butyl nitrile (0.30 mL, ~2.3 mmol), TFSI-H (0.56 g, 2.0 mmol) and glacial acetic acid (0.12 mL, 2.1 mmol) in ethanol/water mixed solvent (50:50% v/v, 5 mL); TEAI (0.52 g, 2 mmol).

[b] Isolated yield.

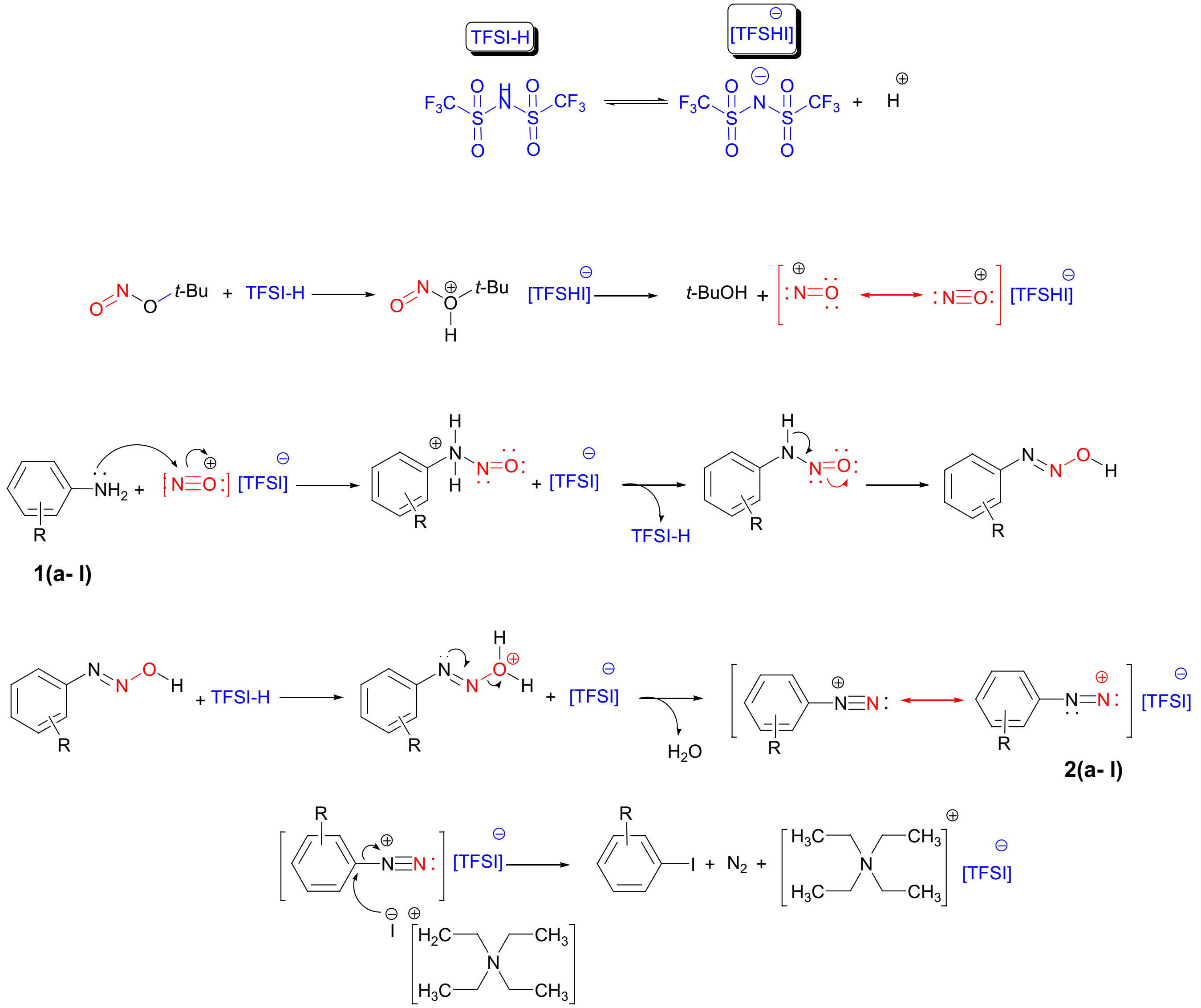
[c] All known products were identical in respects of melting point, FTIR, and NMR spectra to those previously reported.[8,10,12,48-51]

reaction times. The yields of the *ortho*-substituted aryl amines were lower within longer time than that of *para*-substituted aryl amines (Table 1, entries 6, 7, 9 and 10). The sterically hindered aryl amines showed lower reactivity; however, 1,3-dimethyl-2-iodobenzene (**3c**), 1,3-diethyl-2-iodobenzene (**3d**), and 1,3-diisopropyl-2-iodobenzene (**3e**) were obtained with 67%, 59%, and 47% yields, respectively (Table 1, entries 3-5). All known products were identical in respects of melting point, FTIR, and NMR spectra to those previously reported.[8,10,12,48-51]

The macro scale scope of this protocol was studied for 20 mmol of 4-nitroaniline (**1i**) under aforementioned conditions and 4-nitro-iodobenzene in 80% isolated yield was obtained. Owing to its broad substrate scope and mild nature, the present method is expected to find applications in academic and industrial processes.

Based on a schematic mechanism, diazotization-iodination reaction proceeds in two steps (Scheme 2). Initially, TFSI-H and *tert*-butyl nitrite reacted to form a mild electrophile nitroso ($^{+}N{=}O \leftrightarrow N{\equiv}O^{+}$), followed by the formation of arenediazonium bis(trifluoromethylsulfonyl) imide through the reaction of nitrogen atom of aryl amine with the mild electrophile nitroso ($^{+}N{=}O \leftrightarrow N{\equiv}O^{+}$) in Lewis acid/base fashion. In the second step, iodide anion reacted with $[ArN_2^{+}][TFSI^{-}]$ salt as a relatively weak electrophile and the corresponding aryl iodides were thus obtained. Owing to extensive delocalization of the charge over the SO_2-N-SO_2 framework, counteranion $[TFSI^{-}]$ and its salt $[ArN_2^{+}][TFSI^{-}]$ could be highly resonance-stabilized.

The diazotization-iodination of some aryl amines by other reported methods in literature are compared with the present method in Table 2. Each of these methods have their own advantages, but they often suffer from some drawbacks including the use of metal nitrites (entries 2,3,6-9), low yield (entry 4), long reaction time (entries 3,5,6,11), enhance waste in two step reactions due to use of the solvents for the purification of products in diazotization step (1,4), generates large quantities of salts in the preparation of Resin-NO_2^{-} that significantly increases the risk of pollution (4,11), cumbersome separation and purification of product from reagent and solvent (7), and demands for toxic and fatal reagents (1). It should be noted that performing a single-step diazotization-iodination reaction of aryl amines with Resin-NO_2^{-} and *p*-TsOH in the presence of KI in water leads to incomplete conversions of the starting amines and the formation of iodine and gaseous products (4,11). The present method is safer, cheaper, and more convenient than the previous diazotization-iodination reactions. In general, this process is applicable for various aryl amines with electron-donating and electron-withdrawing substituents as well as for the sterically hindered aryl amines.



SCHEME 2 The diazotization-iodination process of aryl amines in the presence of TFSI-H and *tert*-butyl nitrite

3 | EXPERIMENT

3.1 | Materials

Unless specified, all chemicals were analytical grade and purchased from Merck, Sigma-Aldrich, and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and FTIR, NMR and elemental analysis. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

3.2 | Instrumentation

The purity determination of the products was accomplished by GC-MS on an Agilent 6890GC/5973MSD analysis instrument under 70 eV conditions. The FTIR spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat for liquid samples in the range of 4,000-400 cm^{-1}. In all the cases the ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded with Bruker Avance 300 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS and $CFCl_3$ (positive for downfield shifts) as internal standards. Microanalyses were performed on a Perkin- Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

3.3 | Typical procedures for the telescopic diazotization-iodination of aniline

Bis(trifluoromethane) sulfonimide (TFSI-H) (0.57 g, 2.0 mmol), glacial acetic acid (0.12 mL, 2.1 mmol) and *tert*-butyl nitrite (0.30 mL, ~ 2.3 mmol) were stirred in dry ethanol (50:50% v/v, 5 mL) for 5 minutes at low temperature in the ice bath.

TABLE 2 Comparison of the present procedure with results reported by other methods for the diazotization-iodination of 2-NO_2-$C_6H_4NH_2$

Entry	Reagents	conditions	Time (min)	Yield (%)	Ref.
1	Aryl amine (10 mmol)/*o*-benzenedisulfonimide (12 mmol)/glacial AcOH (60 mL)/*i*-pentyl-NO_2 (11 mmol)/TBAI (10 mmol)	Two steps: Step 1: 0-5°C; Step 2: CH_3CN/r.t. °C	45	92	[8]
2	Aryl amine (2 mmol)/ *p*-TsOH (6 mmol)/$NaNO_2$ (5 mmol)/KI (5 mmol)	Water-paste form	20-30	72	[9]
3	Aryl amine (2 mmol)/$NaNO_2$ (4 mmol)/sulfonated-resin (5 g)/KI (5 mmol)	H_2O (50 mL)/r.t.	90	71	[10]
4	Aryl amine (5.25 mmol)/ *p*-TsOH (5.25 mmol)/ glacial AcOH (8 mL)/resin-NO_2(5.25 mmol)/KI (13.125 mmol)	Two steps: Step 1: H_2O/r.t.; Step 2: H_2O/r.t.	30	34	[11]
5	Aryl amine (2 mmol)/Resin-NO_2 (6 mmol)/*p*-TsOH (6 mmol)/KI (5 mmol)	H_2O (5 mL)/r.t.	90	91	[12]
6	Aryl amine (3 mmol)/KI (7.5 mmol)/$NaNO_2$ (6 mmol)/*p*-TsOH (9 mmol)	MeCN (12 mL)/10-20°C	50	81	[48]
7	Aryl amine (10 mmol)/diiodomethane (10 mL)/*i*-pentyl-NO_2 (30 mmol)	80°C	240	65	[49]
8	Aryl amine (5 mmol)/HI (20 mmol)/KNO_2 (20 mmol)	DMSO (25 mL)/35°C	15	89	[52]
9	Aryl amine (1 mmol)/[H-NMP]HSO_4 (4 mmol)/ $NaNO_2$ (2.5 mmol)/NaI (2.5 mmol)	Solvent-free/r.t.	20-30	85	[53]
10	Aryl amine (2 mmol)/Wet CSA (1.5 g)/$NaNO_2$ (4 mmol)/KI (5 mmol)	Solvent-free/r.t.	12	82	[54]
11	Aryl amine (1 mmol)/[P4-VP]NO_2 (0.54 g)/H_2SO_4 (2 mmol)/KI (2.5 mmol)	Two steps: Step 1: 0-5°C; Step 2: r.t. or 60°C	100	74	[55]
12	Aryl amin (2 mmol)/TFSI-H (2 mmol)/ HOAc (2.1 mmol)/*tert*-$BuNO_2$ (2.3 mmol)/TEAI (2 mmol)	C_2H_5OH/0-10°C; H_2O/r.t.	30	82	This work

p-TsOH, *p*-toluenesulfonic acid; SSA, Silica sulfuric acid; CSA, Cellulose sulfuric acid; NMP, *N*-methyl-2-pyrrolidone; P4-VP, Poly(4-vinylpyridine); TBAI, Tetrabutyl ammonium iodide; TFSI-H, Bis(trifluoromethane) sulfonamide.

Then aniline (**1a**) (0.19 g, 2.0 mmol) was added dropwise over 2 minutes and stirring was gently continued at the low temperature until the aryl amine disappeared (monitored by TLC or color test of azo coupling with 2-naphthol). The solvent, by-product *tert*-BuOH and excess *tert*-BuONO were evaporated under reduced pressure. Then, an aqueous solution of TEAI (0.75 g, 2.0 mmol) in 5 mL deionized water was added in one portion to the arenediazonium intermediate of **2a** and the mixture was stirred vigorously at low temperature. After completion of reaction (confirmed by a negative test of azo coupling with 2-naphthol), 5 mL deionized water was added to the reaction mixture; then the aqueous layer was separated. The organic layer was washed with aq. 10% sodium sulfite (3 × 5 mL) until the remaining iodide ions could not be detected by an $AgNO_3$ solution. After it was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness on a rotary evaporator. The crude residue was purified by flash chromatography, eluting with *n*-hexane:EtOAc (9:1, v/v), to give the pure compound **3a**. The FTIR and ^{1}H NMR spectra of **3a** were identical to the authentic compound. The aqueous layer was acidified with HCl and evaporated under reduced pressure, then the residue was extracted with EtOAc (5 × 5 mL). The extracts were dried over anhydrous Na_2SO_4, filtered and TFSI-H was recovered in 84% yield after the solvent was removed using rotary evaporation. The resultant residue was tetraethylammonium chloride (TEAC) in 68% yield according to tetraethylammonium cation. The melting points and FTIR spectra of the recovered TFSI-H and the obtained TEAC were identical to authentic compound (Sigma-Aldrich ≥98%).

3.4 | Physical and spectral data of 4-methoxybenzenediazonium bis(trifluoromethylsulfonyl) imide (2l)

Brown solid; m.p. 141-143°C; FTIR (KBr) $\nu_{max} = 3084$ ($\nu_{C\text{-}Harom}$), 2918, 2883 ($\nu_{C\text{-}H}$), 2303 ($\nu_{N\equiv N}$), 1681, 1658, 1557 ($\nu_{C=Carom}$), 1339 ($\nu_{asym\ SO2}$), 1320, 1250, 1173 ($\nu_{sym\ SO2}$), 1075, 821 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 3.81$ (s, 3H, OCH_3), 7.14 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.79 (d, $J = 7.6$ Hz, 2H, Ar-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) $\delta = 55.9$, 115.1, 120.4 ($J_{C\text{-}f} = 320.1$ Hz), 129.7, 139.1, 164.3 ppm; ^{19}F

NMR (282 MHz, $CFCl_3$) δ = − 80.492 ppm; Anal. Calcd. For $C_9H_7F_6N_3O_5S_2$: C, 26.03; H, 1.70; N, 10.12, S, 15.44; Found: C, 25.99; H, 1.65; N, 10.08, S, 15.40.

3.5 | Physical and spectral data of some aryl iodides

3.5.1 | 1,3-Dimethyl-2-iodobenzene (3c)

Colorless liquid; FTIR (KBr) ν_{max} = 3,067, 3,022, 2,917, 2,852, 1,579, 1,467, 1,378, 1,263, 1,164, 1,093, 1,033, 9,676, 920, 769, 483 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 6 H, CH_3), 6.92-7.23 (m, 3H, Ar-H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 123.7, 126.5, 126.8, 140.4 ppm; MS (EI) *m/z* 232 (M^+)

3.5.2 | 1,3-Diethyl-2-iodobenzene (3d)

Colorless liquid; FTIR (KBr) ν_{max} = 3,067, 3,022, 2,917, 2,852, 1,579, 1,467, 1,378, 1,263, 1,164, 1,093, 1,033, 9,676, 920, 769, 483 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.0 Hz, 6H, CH_3), 2.83 (q, *J* = 7.0 Hz, 4H, CH_2), 7.07 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.22 (t, *J* = 8.0 Hz, 1H, Ar-H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.7, 35.5, 107.2, 125.9, 128.1, 147.3 ppm; MS (EI) m/z 260 (M^+).

3.5.3 | 1,3-diisopropyl-2-iodobenzene (3e)

Colorless liquid; FTIR (KBr) ν_{max} = 3,054, 3,012, 2,908, 2,860, 1,581, 1,464, 1,379, 1,261, 1,158, 1,097, 1,041, 772, 488 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ = 1.24 (d, *J* = 7.0 Hz, 12H, $CH(C\underline{H}_3)_2$), 3.41 (sept, J = 7.0 Hz, 2H, $C\underline{H}(CH_3)_2$), 7.08 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.24 (t, *J* = 8.0 Hz, 1H, Ar-H) ppm; ^{13}C NMR (300 MHz, $CDCl_3$) δ = 23.4, 39.4, 109.2, 123.8, 128.3, 151.0 ppm; MS (EI) *m/z* 288 (M^+).

4 | CONCLUSION

In summary, an efficient telescopic catalyst-free synthesis of aryl iodides using *tert*-butyl nitrite and a mixture of bis(trifluoromethane) sulfonimide and glacial acetic acid in ethanol, followed by the reaction with tetraethylammonium iodide in water, was developed. The presence of heteroatoms such as fluorine, sulfur, and oxygen in bis(trifluoromethane)sulfonamide plays an essential structural role in stabilizing the intermediate arenediazonium bis(trifluoromethylsulfonyl)imide via resonance and inductive effects. The arenediazonium bis(trifluoromethylsulfonyl) imide salts can be stored for days and then used without significant loss in activity and ascertained threads. The current method has the advantages including minimization waste generated, use of commercially available reagents, reducing and eliminating the use and generation of toxic and hazardous reagents, simple and environmentally benign procedure, good yield of the relatively unreactive and sterically hindered aryl amines. Furthermore, bis(trifluoromethane) sulfonamide was easily recovered in high yield and also tetraethylammonium chloride (TEAC) was produced as a valuable by-product of the present procedure.

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