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Synthesis, structure, and synthetic potential of arenediazonium trifluoromethanesulfonates as stable and safe diazonium salts

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Abstract: Aromatic diazonium salts are valuable building blocks for organic synthesis; however, in the most cases, they are unstable, unsafe, poorly soluble, or expensive. Herein, we have shown that a variety of stable and safe arenediazonium triflates $ArN_2^+TfO^-$ can be obtained easily and in high yields by diazotization of anilines with *tert*-butyl nitrite in the presence of trifluoromethanesulfonic acid. Arenediazonium triflates are relatively shelf-stable in dry state and dissolve well in water, polar, and even non-polar organic solvents. Less than 800 J/g of energy is released during the thermal decomposition of these salts, indicating their explosion safety. Arenediazonium triflates have a high reactivity in the known reactions of diazonium chemistry and undergo an unusual metal-free chloro-dediazonization with chloroform and CCl_4.

Introduction

Aromatic diazonium salts are valuable building blocks used in fine organic synthesis and industry (see reviews [1]). They are also applied for preparation of modern macro- and nanoscale composite organic materials due to the ability to react with many metallic and non-metallic surfaces with the elimination of nitrogen and the formation of covalent bonds between aromatic radicals and the surface. [2]

Despite being broadly applied, the majority of diazonium salts have significant drawbacks such as poor storage stability and explosion hazard in dry state. Among the known compounds, arenediazonium tetrafluoroborates and hexafluorophosphates are relatively stable, however, they are often poorly soluble in water and organic solvents [1]. Recently obtained arenediazonium silica sulfates $ArN_2^+\ {}^-OSO_3\text{-}SiO_2$ are also insoluble, although shelf-stable at room temperature. [3] Benzenediazonium *o*-benzenedisulfonimides [4a,b] and diazonium salts with 1,1,2,3,3-pentacyanopropenide anion [4c] show both storage stability and solubility, but they are relatively expensive, as well as diazonium tetrachloroaurates $ArN_2^+AuCl_4^-$.[4d] Arenediazonium nitrates $ArN_2^+NO_3^-$ with electron-withdrawing substituents in the aromatic ring are also stable and can be stored at room temperature for 6 months, however they are explosive. [4e]

It has long been known that hydrochloric acid solutions of arenediazonium chlorides can be "stabilized" by additives of naphthalenesulfonic acid. Without any special evidence it was assumed that this stabilization occurs due to ion exchange and the formation of arenediazonium naphthylsulfonates or "charge transfer complexes" in solution. [1a] Earlier, for the first time, we have isolated arenediazonium tosylates $ArN_2^+TsO^-$ and shown that they are indeed fairly stable in a dry state and are readily soluble in both water and polar solvents. [5] At the same time, they are inexpensive, can be easily obtained from available raw materials, have high "diazonium" activity and are successfully used in the variety of reactions such as halide-dediazonization [5,6a-e] including the preparation of ^{18}F containing compounds [6f], the synthesis of aromatic azides [6g], azo-coupling reaction with ethyl α-methylacetoacetate [7a], substitution of diazonium group with triethoxysilyl moiety [7b], and Cu- and Pd-catalyzed arylation. [7c-e] In addition, arenediazonium tosylates proved to be convenient agents for covalent grafting of aromatic groups to the surfaces of carbonized metal nanoparticles [7f] and graphene. [7g]

The other diazonium salts with sulfonate anions – camphorsulfonates [8a] and 4-dodecylbenzenesulfonates [8b,c] have been prepared recently. They are also shelf-stable, well soluble and highly reactive.

Thus, all the known arenediazonium sulfonates are stable in the dry state, non-explosive, well soluble in water, polar and low-polar solvents, and highly reactive. These advantages make arenediazonium sulfonates promising candidates for "ideal" diazonium building block role. Importantly, the nature of the sulfonate counterion RSO_3^- influences the properties of the corresponding diazonium salts. For example, arenediazonium dodecylbenzenesulfonates showed lipophilicity unique to diazonium salts, the ability to dissolve in nonpolar solvents (C_6H_6, CCl_4) and exhibited properties unusual for traditional diazonium salts in these media. [8b,c]

It has also been reported that the diazotization of certain anilines in the presence of $MeSO_3H$ results in arenediazonium methanesulfonates, which have high *in situ* activity in the cross-coupling processes and the iododediazotization reaction. [8d, e] Additionally, arenediazonium tetrafluoroborates [8f] and arenediazonium o-benzenedisulfonimides [8g] form aryl methanesulfonates $ArOSO_2Me$ under the heating in

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methanesulfonic acid. Probably, in this case the reaction proceeds through intermediate arenediazonium methanesulfonates. However, these diazonium salts have not been isolated. According to our knowledge, their stability and spectral characteristics have not been described.

In our opinion, the preparation and study of arenediazonium trifluoromethanesulfonates (ADTf) are of fundamental interest, since trifluoromethanesulfonic acid is the strongest among the sulfonic acids. Thus, the diazonium salts with the TfO^- counterion must be the prominent members of the arenediazonium sulfonate series $ArN_2^+ RSO_3^-$. Several examples of such salts are already known. The $PhN_2^+ TfO^-$ **1a** salt was obtained by desilylation of $PhN(SiMe_3)_2$ by ONOTf. [9a] The synthesis of salts **1a-d** was carried out by the reaction of aryl triazenes $ArN{=}NNR_2$ with TfOH. [9b,c] 2-(Trifluoromethoxy)biphenylyl-2′-diazonium triflate was obtained by exchanging the tetrafluoroborate anion with TfONa. [9d] The salt **1b**, and also *m*- and *p*-fluorobenzenediazonium triflates are the only compounds obtained by the direct diazotization of the corresponding anilines by *iso*-amylnitrite and *tert*-butylnitrite with yields of 56 and 76%. [9e,f] Only few specific properties of such salts have been studied. [9] Their full spectral characteristics have not been given. The synthetic potential, stability, and safety of ADTf remain unknown.

Results and Discussion

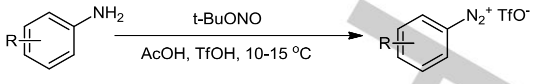
Synthesis and structure of arenediazonium triflates 1a-l

We have shown that aniline and its derivatives, both with electron-donating and electron-withdrawing substituents in the aromatic ring, when diazotized with *t*-BuONO in acetic acid solutions at 10-14 °C, form the corresponding ADTf **1a-l** in high yields (Table 1). Salts **1a-l** precipitated from acetic acid solution with the addition of Et_2O as colorless or slightly colored solids. The optimal molar ratio amine/*t*-BuONO/TfOH was 1.0:1.2:1.2. Diazotization of benzene-1,4-diamine under these conditions led to the formation of a mixture of products. However, on an increase of *t*-BuONO amount up to 2.4 equivalents only benzene-1,4-bis(diazonium) trifluoromethanesulfonate **1l** was isolated.

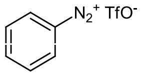
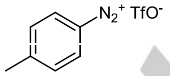
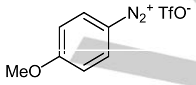
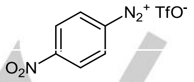
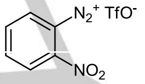
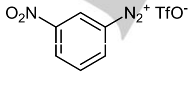
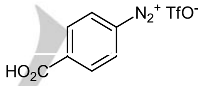
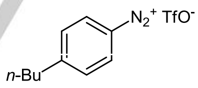
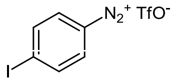
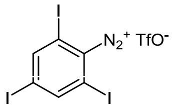
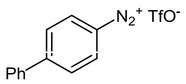
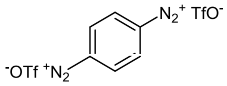
Importantly, the proposed method of arenediazonium triflates preparation is not suitable for the synthesis of pyridine- and quinolinediazonium triflates. Their diazotization in the presence of TsOH or TfOH produces pyridyl and quinolinyl tosylates and triflates instead of diazonium salts (see review [11]).

In the NMR and IR spectra of **1a-l** compounds all the characteristic features of diazonium salts were observed. The signals of the carbon atoms bound to the diazonium group in all cases were shifted upfield in the region of 103-122 ppm [5, 10]. Strong absorption band of the diazonium group at 2275- 2361 cm^{-1} was found in the IR spectra of all the salts **1a-l**.

Table 1. Preparation of arenediazonium triflates **1a-l**



1a-l

Product		Yield (%)	Mp (°C)
	**1a**	98 (85)[9a], (49)[9c]	88-89 (81)[9c]
	**1b**	80 (47)[9c], (56)[9e]	75-77 (82-83)[9e], (81)[9c]
	**1c**	85 (60)[9c]	94-97 (55)[9c]
	**1d**	95 (85)[9c]	104 (99)[9c]
	**1e**	94	110
	**1f**	98	108-109
	**1g**	99	118
	**1h**	63	93
	**1i**	90	122
	**1j**	55	142
	**1k**	92	124-126
	**1l**	86	135 (decomp.)

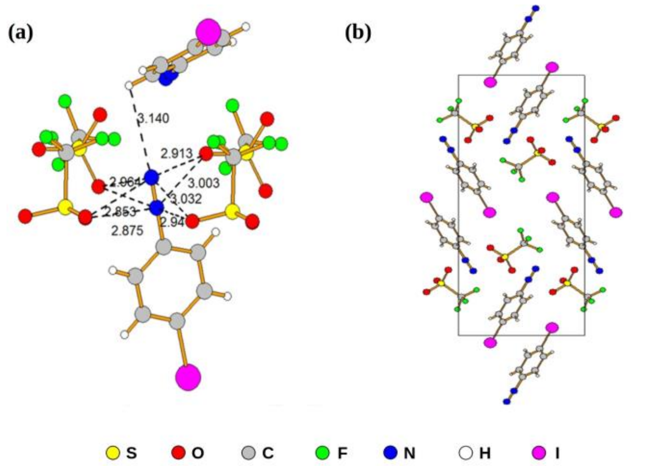


Figure 1. The molecular structure (a) and the crystal paking (b) of 4-iodobenzenediazonium trifluoromethanesulfonate **1i**. Displacement ellipsoids are drawn at the 25 % probability level, and H atoms are shown as small spheres of arbitrary radius. The ArN_2----O_3SCF_3 interactions are represented by dashed lines.

We have grown a single crystal of *p*-iodobenzenediazonium triflate **1i** from AcOH/Et_2O mixture and determined its crystallographic characteristics. The obtained X-ray data (Figure 1 and Supporting Information) show that 4-iodobenzenediazonium cation of salt **1i** has a structure typical for known diazonium-cations with a coplanar arrangement of the diazonium group and aromatic rings and C-N-N valence angle close to 180°. [1a] In the crystal lattice of the salt **1i**, 4-iodbenezenediazonium cation is surrounded by four counterions of triflic acid. Each of the counterions has one of the oxygen atoms located approximately at the same distance of ~ 2.8-3.0 Å from two nitrogen atoms of the diazonium group (Figure 1a, Table 2). For comparison, Table 2 also shows the key interatomic distances in 4-iodobenzenediazonium tosylate according to the paper. [5]

Table 2. Interatomic distances in 4-iodobenzenediazonium triflate **1i** and 4-iodobenzenediazonium tosylate, [5] Å.

Diazonium salt	L, C-N	L, N-N	S=O…..N
n-$IC_6H_4N_2^+$ OTf^- **1i**	1.405	1.089	2.853, 2.882, 2.913, 2.964, 3.003, 3.032
n-$IC_6H_4N_2^+$ OTs^- [5]	1.371 1.385	1.104 1.123	2.744, 2.892, 2.913, 2.916, 2.980, 3.004

Obviously, the multiple interactions between the sulfonic group of tosylate and triflate counterions RSO_3^- and diazonium N-N fragments can explain the relative stability of the arenediazonium tosylates and arenediazonium triflates **1a-l** in a dry solid state (see below). At the same time, it is noteworthy that the distance of the C-N bond in the diazonium triflate cation **1i** is significantly longer as compared to 4-iodobenzenediazonium tosylate (1.405 vs. 1.371 and 1.385 Å). This could indicate a lower strength of the C-N bonds in the arenediazonium triflates and, consequently, their higher reactivity in the N_2 cleavage reactions compared to the arenediazonium tosylates.

Thermal and storage stability of arenediazonium triflates 1a-l

The obtained salts **1a-l** are colorless or slightly colored solids with sharp melting points. They can be stored at room temperature in the dark or in daylight at least for several weeks without changes. In contrast to traditional diazonium salts, ADTf **1a-l** are readily soluble in water and organic solvents such as DMSO, MeOH, EtOH, AcOH, MeCN, and THF at room temperature, and also in CH_2Cl_2, $CHCl_3$, and even CCl_4 when heated. Under certain conditions, they react with such solvents as pyridine, CCl_4, and EtOH (see below).

To evaluate the explosion hazard of ADTf, thermal decomposition of salts **1a-l** was studied by the DSC/DTA/TGA method (Table 3).

Table 3. Temperatures (T decomp.) and energies (E decomp.) of decomposition of salts **1a-l**.

Salt	T decomp. (°C)	-E decomp. (J/g)
1a	84.5	136.1
1b	88.5	639.1
1c	136.6	328.9
1d	116.4	219.9
1e	143.3	753.4
1f	102.5	840.4
1g	102.0	445.0
1h	96.5	458.7
1i	104.8	246.5
1j	116.2	165.1
1k	114.9	277.8
1l	135.6	147.4

All the studied salts exothermically decomposed with the release of nitrogen in the temperature range of 85.3-143.3 °C. Their decomposition energy was below 800 J/g. Thus, according to the safety criteria of the United Nations Economic Commission for Europe (UNECE) [12], arenediazonium triflates **1a-l** belong to the group of compounds that are allowed to be transported safely.

Reactivity of arenediazonium triflates towards KI, NaN_3 and $B_2(OH)_4$

We investigated the chemical properties and synthetic potential of the obtained ADTf. In most cases we focused on salts **1c,d** as representatives of diazonium salts significantly different in reactivity.

Arenediazonium triflates **1c,d,e,g,k,l** reacted readily and rapidly with KI and NaN_3 in aqueous solution at room temperature, giving aryl iodides **2a-e** and aryl azides **3a-f** with high yields (Table 4).

The resulting iodides **2a-e** and azides **3a-f** precipitated during the reaction as sufficiently pure solids, which did not require further purification. The reactivity of the studied triflates **1c,d,e,g,k,l** was comparable to the corresponding arenediazonium tosylates. [6g] The effect of substituents in the aromatic ring on the reactivity of triflates **1c,d,e,g,k,l** was also similar to that in arenediazonium tosylates. In almost all cases, the electron-withdrawing groups NO_2, N_2^+, and CO_2H of triflates **1d,e,g,l** provided a higher conversion rate and higher yields of the target products **2b**, **3b-d,f** compared to triflate **1c** bearing OMe substituent.

Table 4. Preparation of aryl iodides and aryl azides from arenediazonium triflates [a].

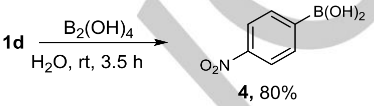
$$ArN_2^+\ TfO^- \xrightarrow[H_2O,\ rt]{MX} ArX$$

Substrate	MX	ArX	Time, min	Isolated yield, %
1c	KI	4-$MeOC_6H_5I$, **2a**	240	74
1d	KI	4-$NO_2C_6H_5I$, **2b**	5	98
1g	KI	4-$HO_2CC_6H_5I$, **2c**	240	64
1k	KI	4-PhC_6H_5I, **2d**	60	75
1l	KI	4-IC_6H_5I,[b] **2e**	20	77
1c	NaN_3	4-$MeOC_6H_5N_3$, **3a**	30	89
1d	NaN_3	4-$NO_2C_6H_5N_3$, **3b**	3	97
1e	NaN_3	2-$NO_2C_6H_5N_3$, **3c**	5	74
1g	NaN_3	4-$HO_2CC_6H_5N_3$, **3d**	10	95
1k	NaN_3	4-$PhC_6H_5N_3$, **3e**	5	84
1l	NaN_3	4-$N_3C_6H_5N_3$,[b] **3f**	3	76

[a] Reaction conditions: **1** (1 mmol), KI or NaN_3 (2 mmol). [b] Reaction conditions: **1** (1 mmol), KI or NaN_3 (4 mmol).

More recently, it was shown that arenediazonium tetrafluoroborates and chlorides are able to react with tetrahydroxydiborane or B_2pin_2, forming valuable for the organic synthesis aryl boronic acids and aryl-boronate esters with medium yields. [13] Using diazonium triflates **1c, d**, we have investigated the reactivity of ADTf towards tetrahydroxydiborane in aqueous solutions and showed that salt **1d** readily forms 4-nitrophenylboronic acid **4** in high yield (Scheme 1). Compound **4a** precipitated as pure crystalline solid during the reaction and did not require further purification. This method for the preparation of **4a** is quite simple and green. In contrast, known diazonium salts [13] give boronic acids in organic solvents (DMF, MeCN) with sorbitol additives. In this case, the use of column chromatography is necessary to purify the products.

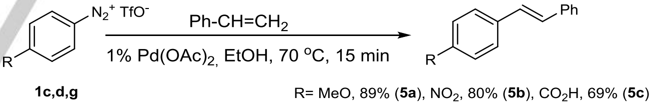
However, described conditions were inapplicable to triflate **1c**, which reacted with $B_2(OH)_4$ in water with the formation of desired 4-methoxyphenylboronic acid together with other resinous by-products and unidentified compounds. The reasons for such a different reactivity of triflates **1c** and **1d** require special investigation.



Scheme 1. Preparation of 4-nitrophenylboronic acid **4**.

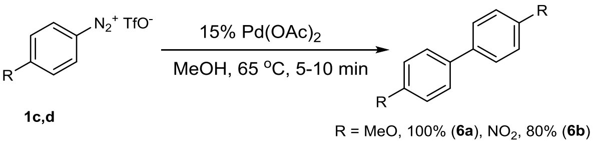
Reactivity of arenediazonium triflates in Pd-catalysed C-C-coupling

It is known that the diazonium group in certain diazonium salts is prone to substitution by C-nucleophiles in the presence of palladium catalysts, similarly to Heck and Suzuki coupling, carboxylation reactions, etc. [1] It was reported that the activity of diazonium salts in these reactions is higher than that of aryl iodides. We have found that the arenediazonium triflates **1c,d,g** could react easily with styrene in the presence of 1% $Pd(OAc)_2$ when heated in ethanol, providing high yields of stilbenes **5a-c** (Scheme 2).



Scheme 2. Phenylethenylation of arenediazonium triflates **1c,d,g**.

Arenediazonium triflates **1c,d** were also able to readily undergo homocoupling under the heating in MeOH solution in the presence of 15% $Pd(OAc)_2$ with the formation of symmetrical biphenyls **5a,b** (Scheme 3).



Scheme 3. Homocoupling of arenediazonium triflates **1c,d**.

No by-products were formed during the homocoupling of arenediazonium triflates, in contrast to the arenediazonium tetrafluoroborates. For the latter, the side reduction and substitution by methoxy group were observed. [14]

Solubility of arenediazonium triflates and their reactions with solvents

As mentioned above, the obtained ADTf **1a-k** dissolve in polar and non-polar solvents, such as $CHCl_3$, CCl_4, and THF. Table 5 shows solubility of salts **1c,d** in solvents of various nature and polarity. The salts were added to a solvent until a saturated solution was obtained. The solubility of arenediazonium triflates **1a,d-k** was qualitatively similar to solubility presented in Table 5. Whereas the solubility of salt **1l** differed significantly: it was insoluble in AcOH, non-polar solvents (benzene, toluene, hexane, CH_2Cl_2, $CHCl_3$, CCl_4) and EtOAc, poorly soluble in MeCN, BuOH, and iPrOH and reacted with water, MeOH, EtOH, acetone, and DMSO.

Unusually high solubility of arenediazonium triflates **1a-k** in nonpolar solvents is not typical for traditional diazonium salts. [1a] There are few examples, including complexes of diazonium salts with crown ethers [15] and recently obtained benzenediazonium 4-dodecylbenzenesulfonates, [8b,c] which are partially soluble in $CHCl_3$, CCl_4 and benzene.

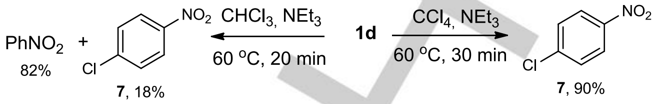
Table 5. Solubilities of arenediazonium triflates **1c,d** at 20 °C, mg/mL.

Solvent	**1c**	**1d**
H_2O	80	100
THF	35	100
1,4-Dioxane	100	100
DMSO	100	100
MeCN	100	100
EtOAc	50	100
CH_2Cl_2	16[a]	10
$CHCl_3$	16[a]	25[a]
CCl_4	16[a]	20[a]

[a] at 40 °C

In solvents listed in Table 5 salts **1a-k** can be stored without visible changes for at least several days at room temperature. However, when one equivalent of Et_3N was added to a solution of ADTf **1d** in $CHCl_3$ or CCl_4, a vigorous reaction with the release of N_2 was observed.

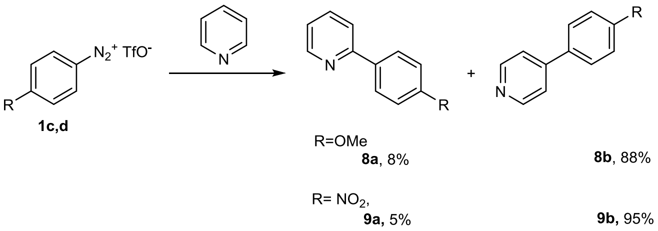
At 60 °C, complete conversion of salt **1d** was achieved in 20-30 min. As a result, chloro-dediazonization with the formation of 4-nitrochlorobenzene **7a** occurred in the CCl_4 solution. In $CHCl_3$, the main process was the reduction of **1d** with the formation of nitrobenzene, whereas product **7** was formed in minor amounts (GC-MS data) (Scheme 4).



Scheme 4. Chloro-dediazonization and hydro-dediazonization of arenediazonium triflate **1d**.

Such an easy substitution of the diazonium moiety in arenediazonium triflate **1d** by chlorine in CCl_4 in copper-free conditions is completely untypical for known diazonium salts. Usually, chloro-dediazonization (the Sandmeyer reaction) proceeds under the action of chloride ions in the presence of copper or its salts. [1a] We have previously shown that similar chloro-dediazonization occurs in reactions of benzenediazonium 4-dodecylbenzenesulfonates in CCl_4. [8b,c] Thus, it can be concluded that due to the good solubility of benzenediazonium 4-dodecylbenzenesulfonates and arenediazonium triflate **1d** in nonpolar CCl_4, new properties of diazonium salts have been discovered. In contrast to benzenediazonium 4-dodecylbenzenesulfonates, [8b,c] chloro-dediazonization of arenediazonium triflate **1d** is not accompanied by foaming and is more readily feasible on a preparative scale. Hence, this reaction has a practical interest.

We have also shown that upon contact of nitrobenzenediazonium triflate **1d** with pyridine at room temperature, a vigorous reaction occurred with instantaneous, complete conversion of salt **1d** and the formation of an inseparable mixture of two regioisomers of arylpyridines **8a,b** in 5:95 ratio (GC data) (Scheme 5).



Scheme 5. Arylation of pyridine by arenediazonium triflates **1c, d** (GC data).

Methoxybenzenediazonium triflate **1c** also arylated pyridine with the formation of regioisomers **9a, b**, but under more rigorous conditions – heating at 70 ° C for 1 h (Scheme 5). Importantly, arenediazonium triflates **1c, d** can arylate pyridine in the absence of any initiators, while such an arylation with known diazonium salts $ArN_2^+ X^-$ (X^-= Cl, BF_4), as a version of the Gomberg–Bachmann reaction, occurs under the action of bases [1a] or during the photochemical initiation in the presence of TiO_2. [16] In known methods of pyridine arylation by arenediazonium

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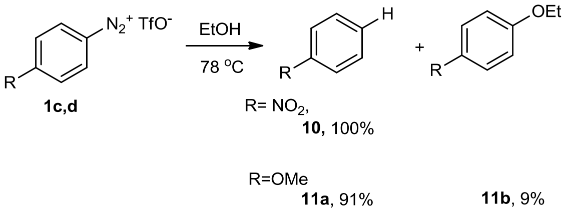
tetrafluoroborates, the reaction is catalysed by ferrocene [16b] or other free radical initiators in the presence of *t*-BuOK in DMSO. [16c] The high reactivity of the arenediazonium triflates **1c,d** towards pyridine in the absence of any initiators together with the good arylation regioselectivity makes them promising reagents for the synthesis of 4-arylpyridines.

Ethanol is another solvent, in which the transformations of the arenediazonium triflates were observed. Using arenediazonium triflates **1c, d**, we showed that their refluxing in ethanol led to a complete reduction of the salt **1d**. Whereas in the case of arenediazonium triflate **1c**, the reduction was non-selective and accompanied by ethoxy-dediazonization (Scheme 6).

The reactions of hydro-dediazonization (reduction) of diazonium salts by the action of various reagents are widely used in organic synthesis. [1a] Therefore, the demonstrated propensity of arenediazonium triflates to be easily reduced by ethanol has practical importance.



Scheme 6. The reaction of arenediazonium triflates **1c,d** with ethanol (GC data).

Conclusions

In summary, for the first time we have shown that arenediazonium triflates (ADTf) are easily obtained by diazotization of various anilines in the presence of trifluoromethanesulfonic acid as stable products, which can be stored in a dry solid state. With the use of DSC method, it was found that the energy of ADTf exothermic thermal decomposition is below 800 J/g. On several examples of ADTf, it was shown that they have high reactivity in known reactions of diazonium salts forming aromatic iodides, azides, and boronic acids. ADTf are also reactive in Pd-catalysed C-C coupling reactions. They are able to easily arylate pyridine and can be reduced by alcohols. ADTf are well soluble not only in polar, but also in nonpolar solvents, which is an unusual for the traditional diazonium salts. In CCl_4, an unexpected substitution of the diazonium group by chlorine occurs under the copper-free conditions. Due to the ease of preparation, storage stability, good solubility, and high reactivity, ADTf can be widely used in organic synthesis.

Experimental Section

General

All the reagents were ACS grade and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AVANCE III HD spectrometer at 400 MHz and 100.5 MHz, respectively unless otherwise indicated. IR spectra were recorded in ATR mode (ZnSe crystal) with Agilent Cary 630 FTIR (Agilent Technologies, USA) or in KBr disks with PerkinElmer BXII instrument. GC/MS analysis was performed using Agilent 7890/5975C system. Elemental analysis was conducted with a Vario MACRO cube CHNS instrument (Elementar Analysen systeme GmbH, Germany). Melting points (uncorrected) were measured using melting point system MP50 (Mettler, Toledo). DSC/TG/DTA studies were performed using DSC/TG/DTA analyzer (SDT Q600, TA Instruments, USA). with a heating rate of 10 °C/min.

Single crystal diffraction studies. Diffraction data for **1** were obtained by the standard technique using Bruker Apex2 Duo diffractometer equipped with CCD detector using MoKα radiation (graphite monochromator). Crystallographic data and details of the diffraction experiments are given in Table 1. Absorption corrections were applied empirically using SADABS program[13]. Both structures were solved by direct methods and refined with the full-matrix least-squares method on F^2 with SHELXTL programs set[14]. Hydrogen atoms of coordinated NH_3 molecules were refined in riding-on-pivot-atom model.

Space group $P2_1/c$ (14), a = 5.860 (2) Å, b = 22.379 (6) Å, c = 8.960 (2) Å, β= 95.443 (1), V = 1169.7 (6) Å ^{3}, Z = 4, T = 296 K, λ = 0.71073 Å, d_{calc} = 2.398 г/см^3, 11559 measured, 3579 independent data, R_1 = 0.0233, wR_2 =0.0556, R_1 = 0.0250, wR_2 = 0.0568 (all data), GOF = 1.080.

CCDC-1846942 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General synthetic procedure for preparation of arenediazonium triflates (1a-k)

A precooled solution of *t*-BuONO (1.2 mmol, 0.143 mL) and an aromatic amine (1 mmol) in 4 mL of glacial acetic acid was added drop-wise to a precooled solution (10-15 °C) of triflic acid (1.2 mmol, 0.106 mL) in 6 mL of glacial acetic acid. Reaction mixture was stirred for 10-20 min at 10-15 °C. The progress of the reaction was monitored by the consumption of the starting amine using TLC (eluent - ethylacetate/hexane=2/3). After the reaction was completed, 100-150 mL of diethyl ether was added to a reaction mixture. The precipitated diazonium salt **1a-k** was filtered and dried under vacuum.

Synthesis of benzene-1,4-bis(diazonium) trifluoromethanesulfonate (1l)

A precooled solution of *t*-BuONO (2.4 mmol, 0.143 mL) and 1,4-diaminobenzene (1 mmol) in 4 mL of glacial acetic acid was added drop-wise to a precooled solution (10-15 °C) of triflic acid (2.4 mmol, 0.212 mL) in 6 mL of glacial acetic acid. Reaction mixture was stirred for 10-20 min at 10-15 °C. The progress of the reaction was monitored by the consumption of the starting amine using TLC (eluent - ethylacetate/hexane=2/3). The diazonium salt **1l** precipitated during the reaction and after the completion of the reaction, was filtered from the reaction mixture, thoroughly washed with hexane and dried under vacuum.

Benzenediazonium trifluoromethanesulfonate (1a): Light beige solid; yield 246 mg (97%); m.p. 88-89 (lit. m.p. 81 ^{o}C [9c]). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.66 (d, *J* = 8.1 Hz, 2H, CH$_{Ar}$), 8.25-8.20 (m, 1H, CH$_{Ar}$), 7.98-7.93 (m, 2H, CH$_{Ar}$), ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 141.2 (CH$_{Ar}$), 132.9 (CH$_{Ar}$), 131.5 (CH$_{Ar}$), 120.9 (q, *J* = 319.6 Hz, CF$_3$), 116.1 (C$_{Ar}$-N$_2^+$) ppm. IR (KBr): 2297 cm^{-1} (lit. 2260 cm^{-1} [9c]).

4-Methylbenzenediazonium trifluoromethanesulfonate (1b): Light beige solid; yield 214 mg (80%); m.p. 83-84 ^{o}C (lit. m.p. 82-83 ^{o}C [9e]). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.55 (d, *J* = 8.4 Hz, 2H, CH$_{Ar}$), 7.79 (d, 2H, *J* = 7.8 Hz, 2H, CH$_{Ar}$), 2.57 (s, 3H, CH$_3$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 153.9 (C$_{Ar}$-CH$_3$), 132.7 (CH$_{Ar}$), 131.8 (CH$_{Ar}$), 120.6 (q, *J* = 320.0 Hz, CF$_3$), 111.9 (C$_{Ar}$-N$_2^+$), 22.4 (CH$_3$) ppm. IR (KBr): 2274 cm^{-1}.

4-Methoxybenzenediazonium trifluoromethanesulfonate (1c): Light beige solid; yield 241 mg (85%); m.p. 94-97 ^{o}C (lit. 55 ^{o}C [9c]). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.55 (d, *J* = 9.0 Hz, 2H, CH$_{Ar}$), 7.47 (d, *J* = 9.0 Hz, 2H, CH$_{Ar}$), 4.04 (s, 3H, OCH$_3$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 168.9 (C$_{Ar}$-OCH$_3$), 136.2 (CH$_{Ar}$), 120.7 (q, *J* = 320.0 Hz, CF$_3$), 118.6 (CH$_{Ar}$), 103.3 (C$_{Ar}$-N$_2^+$), (OCH$_3$) ppm. IR (KBr): 2249 cm^{-1}.

4-Nitrobenzenediazonium trifluoromethanesulfonate (1d): White solid; yield 284 mg (95%), m.p. 104 ^{o}C (lit. m.p. 99 ^{o}C [9c]). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 8.93 (d, *J* = 9.2 Hz, 2H, CH$_{Ar}$), 8.71 (d, *J* = 9.7 Hz, 2H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 153.2 (C$_{Ar}$-NO$_2$), 136.2 (CH$_{Ar}$), 134.5 (CH$_{Ar}$), 126.0 (CH$_{Ar}$), 120.0 (q, *J* = 320.0 Hz, CF$_3$), 121.8 (C$_{Ar}$-N$_2^+$) ppm. IR (KBr): 2303 cm^{-1}.

2-Nitrobenzenediazonium trifluoromethanesulfonate (1e): White solid; yield 281 mg (94%), m.p. 110 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 9.12 (d, *J* = 8.1 Hz, 1H, CH$_{Ar}$), 8.79 (d, *J* = 8.1 Hz, 1H, CH$_{Ar}$), 8.56-8.51 (m, 1H, CH$_{Ar}$), 8.39-8.44 (m, 1H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 144.5 (C$_{Ar}$-NO$_2$), 136.6 (CH$_{Ar}$), 128.1 (CH$_{Ar}$), 122.8 (CH$_{Ar}$), 120.6 (q, *J* = 320.0 Hz, CF$_3$), 118.5 (CH$_{Ar}$), 111.1 (C$_{Ar}$-N$_2^+$) ppm. IR (KBr): 2359 cm^{-1}. CHNS-analysis: calc. for $C_7H_4F_3N_3O_5S$: C, 28.10; H, 1.35; N, 14.04; S, 10.72; F, 19.05. Found C, 28.09; H, 1.32; N, 13.89; S, 10.85; F, 19.40.

3-Nitrobenzenediazonium trifluoromethanesulfonate (1f): White solid; yield 293 mg (98%), m.p. 108-109 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 9.60 (s, 1H, CH$_{Ar}$), 9.03-8.99 (m, 2H, CH$_{Ar}$), 8.27-8.23 (m, 1H, CH$_{Ar}$) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 148.1 (C$_{Ar}$-NO$_2$), 138.3 (CH$_{Ar}$), 135.5 (CH$_{Ar}$), 132.2 (CH$_{Ar}$), 128.5 (CH$_{Ar}$), 121.1 (q, *J* = 245.0 Hz, CF$_3$), 118.7 (C$_{Ar}$-N$_2^+$) ppm. IR (KBr): 2294 cm^{-1}. CHNS-analysis: calc. for $C_7H_4F_3N_3O_5S$: C, 28.10; H, 1.35; N, 14.04; S, 10.72. Found C, 28.29; H, 1.57; N, 14.16; S, 10.58.

4-Carboxybenzenediazonium trifluoromethanesulfonate (1g): White solid; yield 295 mg (99%), m.p. 118 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.77 (d, *J* = 8.4 Hz, 2H, CH$_{Ar}$), 8.41 (d, *J* = 8.4 Hz, 2H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 164.9 (CO$_2$H), 140.8 (C$_{Ar}$-CO$_2$H), 133.2 (CH$_{Ar}$), 131.4 (CH$_{Ar}$), 120.7 (q, *J* = 245.0 Hz, CF$_3$), 119.7 (C$_{Ar}$-N$_2^+$) ppm. IR (ATR): 2297 cm^{-1}. CHNS-analysis: calc. for $C_8H_5F_3N_2O_5S$: C, 32.22; H, 1.69; N, 9.39; S, 10.75. Found C, 32.26; H, 1.77; N, 9.42; S, 10.81.

4-Butylbenzenediazonium trifluoromethanesulfonate (1h): White solid; yield 195 mg (63%), m.p. 93 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.57 (d, *J* = 7.8 Hz, 2H, CH$_{Ar}$), 7.83 (d, *J* = 7.8 Hz, 2H, CH$_{Ar}$), 2.84 (d, *J* = 7.5 Hz, 2H, CH$_2$), 1.60 (m, 2H, CH$_2$), 1.30 (m, 2H, CH$_2$), 0.91 (d, *J* = 7.5 Hz, 3H, CH$_3$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 158.1 (C$_{Ar}$-C$_4$H$_9$), 132.8 (CH$_{Ar}$), 133.2 (CH$_{Ar}$), 131.1 (CH$_{Ar}$), 116.7 (q, *J* = 266.0 Hz, CF$_3$), 112.1 (C$_{Ar}$-N$_2^+$), 35.5 (CH$_{2Ar}$), 32.1 (CH$_2$), 21.6 (CH$_2$), 13.6 (CH$_3$) ppm. CHNS-analysis: calc. for $C_{11}H_{13}F_3N_2O_3S$: C, 42.58; H, 4.22; N, 9.03; S, 10.33. Found C, 42.40; H, 4.18; N, 9.01; S, 10.23.

4-Iodobenzenediazonium trifluoromethanesulfonate (1i): White solid; yield 342 mg (90%), m.p. 122 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.43 (d, *J* = 8.4 Hz, 2H, CH$_{Ar}$), 8.35 (d, *J* = 8.4 Hz, 2H, CH$_{Ar}$) ppm. ^{13}C NMR (75 MHz, DMSO-d$_6$): δ = 140.3 (CH$_{Ar}$), 132.9 (CH$_{Ar}$), 120.6 (q, *J* = 320.0 Hz, CF$_3$), 115.1 (C$_{Ar}$-N$_2^+$), 113.7 (C$_{Ar}$-I) ppm. IR (ATR): 2298 cm^{-1}. CHNS-analysis: calculated for $C_7H_4F_3IN_2O_3S$: C, 22.12; H, 1.06; N, 7.37; S, 8.44; I, 33.39. Found: C, 22.04; H, 1.09; N, 7.42; S, 8.55; I, 33.15.

2,4,6-triiodobenzenediazonium trifluoromethanesulfonate (1j): Light green solid; yield 265 mg (55%); m.p. 142 °C. ^{1}H NMR (400 MHz, DMSO -*d6*): δ = 8.89 (s, 2H, CH$_{Ar}$) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 148.7 (CH$_{Ar}$), 147.1 (CH$_{Ar}$), 146.3 (CH$_{Ar}$), 145.6 (CH$_{Ar}$), 134.1 (CH$_{Ar}$), 116.8 (q, *J* = 323.6 Hz, CF$_3$), 103.9 (C$_{Ar}$-N$_2^+$) ppm. IR (ATR): 2239 cm^{-1}.

[1,1'-biphenyl]-4-diazonium trifluoromethanesulfonate (1k): Beige solid; yield 304 mg (92%); m.p. 124-126 °C. ^{1}H NMR (400 MHz, DMSO - *d6*): δ = 8.74 (d, *J* = 8.0 Hz, 2H, CH$_{Ar}$), 8.33 (d, *J* = 8.0 Hz, 2H, CH$_{Ar}$), 7.92 (d, *J* = 8.0 Hz, 2H, CH$_{Ar}$), 7.55-7.65 (m, 3H, CH$_{Ar}$) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 151.9 (CH$_{Ar}$), 136.8 (CH$_{Ar}$), 133.9 (CH$_{Ar}$), 131.2 (CH$_{Ar}$), 130.0 (CH$_{Ar}$), 129.4 (CH$_{Ar}$), 128.4 (CH$_{Ar}$), 121.1 (q, *J* = 319.6 Hz, CF$_3$), 119.5 (C$_{Ar}$-N$_2^+$) ppm. IR (ATR): 2267 cm^{-1}.

Benzene-1,4-bis(diazonium) trifluoromethanesulfonate (1l): Beige solid; yield 370 mg (86%); m.p. 135 °C (dec.). ^{1}H NMR (400 MHz, DMSO -*d6*): δ = 9.13 (s, 4H, CH$_{Ar}$) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 137.0 (CH$_{Ar}$), 121.7 (q, *J* = 312.5 Hz, CF$_3$), 100.8 (C$_{Ar}$-N$_2^+$) ppm. IR (ATR): 2325 cm^{-1}.

Synthesis of aryliodides 2a-e from arenediazonium trifluoromethanesulfonates 1c,d,g,k,l: KI (2 mmol, 332 mg) was added to an aqueous solution of the arenediazonium trifluoromethanesulfonate **1c,d,g,k,l** (1 mmol in 6 ml H$_2$O) under the stirring. The reaction mixture was stirred at room temperature for the time indicated in Table 4. The progress of the reaction was monitored by the consumption of diazonium salt using 2-naphthol as indicator. The precipitated iodides **2a-d** were filtered off, washed with water and dried in vacuo. In the case of the salt **1l**, 4 mmol (664 mg) of KI was used.

1-Iodo-4-methoxybenzene (2a): Compound **2a** was prepared according to general procedure using salt **1c** (1 mmol, 284 mg). Light solid; yield 150 mg 64%; m.p. 50-51 ^{o}C (lit. m.p. 51-52 ^{o}C [6a]). GC-MS (EI, 70 eV), T retention 9.048 min: m/z (%) = 234 (100) [M$^+$], 219 (33), 191 (4), 165 (1), 141 (1), 127 (5), 107 (5), 92 (23), 77 (15), 63 (13), 49 (8).

1-Iodo-4-nitrobenzene (2b): Compound **2b** was prepared according to general procedure using salt **1d** (1 mmol, 300 mg). Light solid; yield 244 mg 98%; m.p. 171-172 ^{o}C (lit. m.p. 172-173 ^{o}C [6a]). GC-MS (EI, 70 eV), T retention 14.697 min: m/z (%) = 249 (100) [M$^+$], 220 (26), 203 (43), 176 (4), 152 (4), 127 (9), 93 (2), 76 (21), 50 (30).

4-Iodobenzoic acid (2c): Compound **2c** was prepared according to general procedure using salt **1g** (1 mmol, 298 mg). Light solid; yield 191 mg 77%; m.p. 269 ^{o}C (lit. m.p. 266-268 ^{o}C [6e]). GC-MS (EI, 70 eV), T retention 15.746 min: m/z (%) = 248 (100) [M$^+$], 231 (33), 203 (17), 176 (3), 152 (4), 127 (13), 121 (12), 104 (3), 75 (17), 65 (25), 39 (3).

4-iodo-1,1'-biphenyl (2d): Compound **2d** was prepared according to general procedure using salt **1k** (1 mmol, 330 mg). Beige solid; yield 209 mg 75%; m.p. 110 ^{o}C (lit. m.p. 110-111 °C[17a]). GC-MS (EI, 70 eV), T retention 13.227 min: m/z (%) = 280 (100) [M$^+$], 152 (70), 140 (6), 127 (7), 102 (2), 87 (1.5), 76 (14), 63 (5), 51 (4).

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1,4-diiodobenzene (2e): Compound **2e** was prepared according to general procedure using salt **1l** (1 mmol, 430 mg). Brown solid; yield 254 mg 77%; m.p. 126-127 ^{o}C (lit. m.p. 127-128 °C [17b]). GC-MS (EI, 70 eV), T retention 10.206 min: m/z (%) = 330 (100) [M^{+}], 203 (30), 165 (3), 127 (11), 76 (25), 50 (18), 49 (2).

Synthesis of azidoarenes 3a-f from arenediazonium trifluoromethanesulfonates 1c-e,g-l:

NaN_3 (2 mmol, 130 mg) was added to an aqueous solution of the arenediazonium trifluoromethanesulfonate **1c-e,g,k** (1 mmol in 10 ml H_2O) under the stirring at room temperature. During the reaction the release of nitrogen was observed. The reaction mixture was stirred for the time indicated in Table 4. The progress of the reaction was monitored by the consumption of diazonium salt using 2-naphthol as indicator. The precipitated azidoarenes **3a-f** were filtered off, washed with water (50 ml), dried in vacuo and recrystallized from ethanol. In the case of the salt **1l**, 4 mmol (260 mg) of NaN_3 was used.

1-Azido-4-methoxybenzene (3a): Compound **3a** was prepared according to general procedure using salt **1c** (1 mmol, 284 mg). White solid; yield 133 mg (89%), oil. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 7.05 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 6.98 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 3.74 (s, 3H, OCH_3) ppm. ^{13}C NMR (100.5 MHz, DMSO-d6): δ = 157.3 (C_{Ar}-OCH_3), 131.7 (C_{Ar}-N_3), 120.6 (CH_{Ar}), 115.6 (CH_{Ar}), 55.9 (OCH_3) ppm.

1-Azido-4-nitrobenzene (3b): Compound **3b** was prepared according to general procedure using salt **1d** (1 mmol, 300 mg). White solid; yield 159 mg (97%); m.p. 72 °C (lit. m.p. 71-72 °C [6g]). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 8.26 (d, *J* = 12.0 Hz, 2H, CH_{Ar}), 7.36 (d, *J* = 12 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 147.1 (C_{Ar}-N_3), 144.5 (C_{Ar}-NO_2), 126.0 (CH_{Ar}), 120.4 (CH_{Ar}) ppm.

1-Azido-2-nitrobenzene (3c): Compound **3b** was prepared according to general procedure using salt **1e** (1 mmol, 300 mg). White solid; yield 121 mg (74%); m.p. 51-52 °C (lit. m.p. 51-52 °C [6g]). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 7.99 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.73-7.75 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.35-7.39 (m, 1H, CH_{Ar}) ppm. ^{13}C NMR (100.5 MHz, DMSO-d6): δ = 140.8 (C_{Ar}-NO_2), 134.8 (CH_{Ar}), 134.1 (CH_{Ar}), 125.9 (CH_{Ar}), 125.8 (CH_{Ar}), 122.2 (C_{Ar}-N_3) ppm.

4-Azidobenzoic acid (3d): Compound **3d** was prepared according to general procedure using salt **1g** (1 mmol, 298 mg). White solid; yield 155 mg (95%); m.p 180 ^{o}C (lit. m.p. 180°C [6g]). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 13.16 (s, 1H, CO_2H), 7.96 (d, *J* = 12.0 Hz, 2H, CH_{Ar}), 7.22 (d, *J* = 12.0 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 167.3 (CO_2H), 144.7 (C_{Ar}-N_3), 131.5 (C_{Ar}-CO_2H), 127.7 (CH_{Ar}), 119.6 (CH_{Ar}) ppm.

4-azido-1,1'-biphenyl (3e): Compound **3e** was prepared according to general procedure using salt **1k** (1 mmol, 330 mg). Beige solid; yield 164 mg (84%); m.p 64-66 ^{o}C (lit. m.p. 62-64°C [17c]). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 7.73 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.66 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.45-7.49 (m, 3H, CH_{Ar}), 7.35-7.38 (m, 1H, CH_{Ar}), 7.22 (d, *J* = 8.0 Hz, 2H, CH_{Ar}) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 139.6 (CH_{Ar}), 139.1 (CH_{Ar}), 137.5 (CH_{Ar}), 129.5 (CH_{Ar}), 128.7 (CH_{Ar}), 128 (CH_{Ar}), 127 (CH_{Ar}), 120 (C_{Ar}-N_3) ppm.

1,4-diazidobenzene (3f): Compound **3f** was prepared according to general procedure using salt **1l** (1 mmol, 430 mg). Brown solid; yield 122 mg (76%); m.p 78-80 ^{o}C (lit. m.p. 81.2-82.2°C [17d]). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 7.17 (s, 4H, CH_{Ar}) ppm. ^{13}C NMR (100.5 MHz, DMSO-d$_6$): δ = 136.6 (CH_{Ar}), 121.5 (C_{Ar}-N_3) ppm.

(4-Nitrophenyl)boronic acid (4): Hypodiboric acid (2.5 mmol, 225 mg) was added to a stirred solution of 4-nitrobenzenediazonium trifluoromethanesulfonate **1e** (1 mmol, 300 mg) in water (4 ml). The reaction mixture was stirred at room temperature for 3.5 h. The precipitated solid was filtered off, washed with water (3-4 ml) and dried in vacuo. Light brown solid; yield 163 mg (98%); m.p. 285 °C (lit. m.p. 282 °C (decomp.) [17e]). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 8.18 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 8.01 (d, *J* = 7.8 Hz, 2H, CH_{Ar}) ppm.

Synthesis of 1,2-diarylethenes 5a-c from arenediazonium trifluoromethanesulfonates 1c,d,g and styrene: To a stirred solution of arenediazonium trifluoromethanesulfonate (1 mmol) in ethanol (10 ml), styrene (1.2 mmol, 125 mg) and $Pd(OAc)_2$ (1 mol %, 0.01 mmol, 2.4 mg) were added. The reaction mixture was stirred at 70 ^{o}C for 15-20 min until the full conversion of diazonium salt (the consumption of diazonium salt was monitored using 2-naphthol as indicator). The reaction mixture was then filtered through a silica gel pad and filtrate was cooled to 10 ^{o}C. The precipitated solid was filtered off, washed with ethanol and dried in vacuo.

(E)-1-methoxy-4-styrylbenzene (5a): Compound **5a** was prepared according to general procedure using salt **1c** (1 mmol, 284 mg). White solid; yield 187 mg (89%); m.p. 138 ^{o}C (lit 140 ^{o}C [7f]). ^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 7.57- 7.53 (m, 4H, CH_{Ar}), 7.38-7.33 (m, 2H, CH_{Ar}), 7.26-7.23 (m, 1H, CH_{Ar}), 7.19 (d, *J* = 16.5 Hz, 1H, CH=), 7.08 (d, 1H, *J* = 16.5 Hz, CH=), 6.95 (d, 2H, *J* = 8.7 Hz, CH_{Ar}), 3.77 (s, 3H, OCH_3) ppm. ^{13}C NMR (75 MHz, DMSO-d6): δ = 158.9 (C_{Ar}-OCH_3), 137.3 (C_{Ar}-CH=), 129.6 (CH_{Ar}), 128.6 (CH_{Ar}-CH=), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 127.1 (CH=), 126.1 (CH=), 114.1 (CH_{Ar}), 55.2 (OCH_3) ppm.

(E)-1-nitro-4-styrylbenzene (5b): Compound **5b** was prepared according to general procedure using salt **1d** (1 mmol, 300 mg). White solid; yield 180 mg (80%); m.p. 155-156 ^{o}C (lit. 154-157 ^{o}C [5]). ^{1}HNMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.64 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.56 (d, *J* = 7.5 Hz, 2H, CH_{Ar}), 7.35-7.45 (m, 3H, CH_{Ar}), 7.26 (d, *J* = 16.5 Hz, 1H, CH_2), 7.13 (d, *J* = 16.5 Hz, 1H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8 (C_{Ar}-NO_2), 143.9 (C_{Ar}-CH=), 136.2 (C_{Ar}-CH=), 133.4 (CH_{Ar}), 128.9 (CH_{Ar}), 127.1 (CH_{Ar}), 126.9 (CH=), 126.4 (CH=), 124.2 (CH_{Ar}) ppm.

(E)-4-styrylbenzoic acid (5c): Compound **5c** was prepared according to general procedure using salt **1g** (1 mmol, 298 mg). White solid; yield 154 mg (69%); m.p. 154 ^{o}C (lit. 153-155 ^{o}C [5]). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.70 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.63 (m, 2H, CH_{Ar}), 7.39-7.44 (m, 1H, CH_{Ar}), 7.35 (d, *J* = 16.5 Hz, 1H), 7.30 (d, *J* = 16.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.0 (CO_2H), 141.3 (C_{Ar}-CH=), 136.5 (C_{Ar}-CH=), 131.0 (C_{Ar}-CO_2H), 129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 128.8 (CH_{Ar}), 128.2 (CH_{Ar}), 127.4 (CH_{Ar}), 126.8 (CH=), 126.5 (CH=) ppm.

Synthesis of biaryls 6a,b from arenediazonium trifluoromethanesulfonates 1c,d:

The solution of arenediazonium trifluoromethanesulfonate (0.5 mmol) in methanol (1ml) was heated under the stirring with $Pd(OAc)_2$ (15 mol %, 0.075 mmol, 18 mg) at 65 ^{o}C for 10-15 min (the consumption of diazonium salt was monitored using 2-naphthol as indicator). The reaction mixture was then cooled to a room temperature and 30 ml of ethyl acetate was added. The mixture was filtered through cellulose. The organic layer was washed with 10% $NaHCO_3$ and dried over Na_2SO_4. The solvent was removed under reduced pressure. The obtained products did not require further purification.

4,4'-Dimethoxy-1,1'-biphenyl (6a): Compound **6a** was prepared according to general procedure using salt **1c** (0.5 mmol, 107 mg). White solid; yield 214 mg, 100%. m.p. 178-179 ^{o}C (lit. 178-180 ^{o}C [17f]). GC-MS (EI), T retention 19.953 min: m/z (%) = 214 (100) [M$^+$], 199 (92), 171 (30), 156 (12), 128 (20), 102 (8), 78 (1), 63 (4), 39 (16).

4,4'-Dinitro-1,1'-biphenyl (6b): Compound **6b** was prepared according to general procedure using salt **1d** (0.5 mmol, 150 mg). White solid; yield 195 mg (80%). m.p. 235 ^{o}C (lit. m.p. 234-236 ^{o}C [17g]). GC-MS (EI), T retention 23.622 min: m/z (%) = 244 (100) [M$^+$], 228 (7), 214 (19), 198 (5), 181 (9), 152 (70), 139 (25), 126 (10), 102 (5), 87 (4), 63 (9), 44 (21).

Chloro-dediazonization of 4-nitrobenzenediazonium trifluoromethanesulfonate 1d by CCl_4: Triethylamine (2 mmol, 0.14 mL) was added with stirring to a solution of diazonium salt **1d** (2 mmol, 600 mg) in CCl_4 (10 ml) heated to 60 ^{o}C. A rapid release of nitrogen was observed. The reaction mixture was stirred at 60 ^{o}C for 30 min. Then anhydrous Al_2O_3 (0.9 g) was added, the reaction mixture was stirred for 15 min and filtered. The Al_2O_3 was washed with 20 ml of CCl_4. The combined solutions were passed through a column filled with Al_2O_3. CCl_4 was removed under reduced pressure, yield **7** 283 mg (90%).

1-Chloro-4-nitrobenzene 7: Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.60 (d, *J* = 8.5 Hz, 2H, CH_{Ar}) ppm. GC-MS (EI), T retention 11.108 min: m/z (%) = 157 (70) [M$^+$]), 141 (4), 127 (52), 111 (91), 99 (39), 87 (13), 75 (100), 63 (10), 50 (35), 38 (10).

Hydro-dediazonization of 4-nitrobenzenediazonium trifluoromethanesulfonate 1d by $CHCl_3$: The reaction of diazonium salt **1d** with $CHCl_3$ was conducted according to procedure described for CCl_4. GC and GC-MS data showed the presence of two products: 1-chloro-4-nitrobenzene **7** (18%) and nitrobenzene (82%).

Nitrobenzene: GC-MS (EI), T retention 8.299 min: m\z (%) = 123 (58) [M$^+$]), 107 (4), 93 (15), 77 (100), 64 (14), 51 (46), 38 (6).

Arylation of pyridine by 4-methoxybenzenediazonium trifluoromethanesulfonate (1c): 4-methoxybenzenediazonium trifluoromethanesulfonate **1c** (284 mg, 1 mmol) was added with stirring to pyridine (2 ml). The reaction mixture was heated at 70 ^{o}C for 1 h until the full conversion of diazonium salt **1c** (the consumption of diazonium salt was monitored using 2-naphthol as indicator). Then reaction mixture was poured into water (50 ml) and treated with 10% $NaHCO_3$ until pH reached 8-9. The products were extracted by ethylacetate (3×15 ml). Organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. Total yield was 185 mg (100%). Purification by column chromatography using hexane over silica gel gave two fractions: (i) first fraction, yield 163 mg (88%), (ii) second fraction, yield 22 mg (8%).

2-(4-Methoxyphenyl)pyridine (8a): Light yellow oil; yield 22 mg (8%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 5.0 Hz, 1H, CH_{Py}), 8.20 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.60 (m, 1H, CH_{Py}), 7.15-7.11 (m, 3H, CH_{Py}, CH_{Ar}), 7.17 (d, *J* = 5.0 Hz, CH_{Py}), 7.10 (t, *J* = 5.0 Hz, 1H, CH_{Py}), 3.81 (s, 3H, OCH_3) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.8 (C_{Ar}-OCH_3), 157.0 (C_{Py}-Ar), 149.3 (CH_{Py}), 134.9 (CH_{Py}), 132.0 (C_{Ar}-Py), 128.6 (CH_{Ar}), 122.0 (CH_{Py}), 121.1 (CH_{Py}), 115.7 (CH_{Ar}), 55.0 (OCH_3) ppm. GC-MS (EI), T retention 18.046 min: m/z (%) = 185 (100) [M$^+$], 170 (18), 154 (3), 142 (36), 115 (22), 89 (9), 63 (9), 51 (5), 39 (5).

4-(4-Methoxyphenyl)pyridine (8b): Light yellow oil; yield 163 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 7.9 Hz, 2H, CH_{Py}), 8.98 (d, *J* = 7.9 Hz, 2H, CH_{Py}), 7.71 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 6.98 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 3.84 (OCH_3) ppm. GC-MS (EI), T retention 17.913 min: m/z (%) = 185 (100) [M$^+$], 170 (39), 154 (5), 142 (43), 127 (4), 115 (19), 89 (9), 75 (4), 63 (9), 51 (7), 39 (5).

Arylation of pyridine by 4-nitrobenzenediazonium trifluoromethanesulfonate (1d): 4-nitrobenzenediazonium trifluoromethanesulfonate **1d** (300 mg, 1 mmol) was added with stirring to pyridine (2 ml). The reaction occurred immediately upon the reagents contact and accompanied with rapid release of nitrogen. After the 20 min the reaction mixture was treated as described above. Total yield was 200 mg (100%). TLC of the light oily crude showed the presence of two products; however, they were inseparable by chromatography. NMR, GC and GC-MS data showed the presence of two isomers - 2-(4-nitrophenyl)pyridine 9a (5%) and 4-(4-nitrophenyl)pyridine 9b (95%). The chemical shifts of isomer **9a** were overlapped by more intense chemical shifts of isomer **9b**.

2-(4-Nitrophenyl)pyridine (9a): Light yellow oil; yield 10 mg (5%). GC-MS (EI), T retention 19.628 min: m/z (%) = 200 (29) [M$^+$], 184 (7), 170 (100), 152 (21), 142 (14), 127 (25), 118 (9), 107 (3), 89 (7), 64 (7), 45 (5).

4-(4-Nitrophenyl)pyridine (9b): Light yellow oil; yield 190 mg (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 5.0 Hz, 1H, CH_{Py}), 8.30 (d, *J* = 8.0 Hz, 2H, CHAr), 8.02-7.91 (m, 4H, CH_{Py}, CH_{Ar}) ppm. GC-MS (EI), T retention 19.628 min: m/z (%) = 200 (100) [M$^+$], 170 (31), 152 (29), 142 (20), 127 (46), 118 (7), 101 (7), 77 (12), 63 (8), 51 (10).

Reduction of arenediazonium trifluoromethanesulfonates 1c,d by ethanol: Arenediazonium trifluoromethanesulfonates **1c,d** (1 mmol) were dissolved in ethanol (5 ml) and heated at 70 ^{o}C for 20 min until the full conversion of diazonium salt (the consumption of diazonium salt was monitored using 2-naphthol as indicator). The reaction mixture was poured into water (50 ml), neutralized by NaOH until pH 7-8 and extracted with ethylacetate. Organic layer was dried over Na_2SO_4. GC and GC-MS data showed the presence of two products for the salt **1c** (91% anisole and 9% 1-ethoxy-4-methoxybenzene) and only single product (nitrobenzene) for salt **1d**. The results of GC-MS:

Anisole: GC-MS (EI): m/z (%) = 108 (100) [M$^+$], 93 (16), 78 (60), 65 (56), 51 (12), 39 (20).

1-Ethoxy-4-methoxybenzene: GC-MS (EI): m/z (%) = 152 (70) [M$^+$], 137 (3), 124 (70), 109 (100), 95 (17), 81 (17), 65 (9), 53 (9), 41 (5).

Nitrobenzene: GC-MS (EI): m/z (%) = 123 (58) [M$^+$]), 107 (4), 93 (15), 77 (100), 64 (14), 51 (46), 38 (6).

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Keywords: safe diazo compounds • diazonium triflates • structure • diazonium reactivity

[1] (a) H. Zollinger, *Diazo Chemistry I: Aromatic and Heteroaromatic Compounds*; VCH, Weinheim, **1994,** pp. 221-288. (b) A. Roglands, A. Pla-Quintana, M. Moreno-Manas, *Chem. Rev*. **2006**, *106*, 4622-4643.

(c) H. Bonin, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal*. **2011**, *353*, 3063-3084. (d) F. Mo, G. Dong, Y. Zhang, J. Wang, *Org. Biomol. Chem*. **2013**, *11*, 1582-1593. (e) D. K. Kölmel, N. Jung, S. Bräse, *Aust. J. Chem*. **2014**, *67*, 328-336. (f) B. J. Deadman, S. G. Collins, A. Maguire, R. *Chem. Eur. J.* **2015**, *21*, 2298-2308. (g) N. Oger, E. Le Grognec, F.-X. Felpin, *Org. Chem. Frontiers* **2015**, *2*, 590-614. (h) T. Hu, I. R. Baxendale, M. Baumann, *Molecules* **2016**, *21*, 918-931.(i) S. Kindt, M. R. Heinrich, *Synthesis* **2016**, *48*, 1597-1606. (j) G. Micheletti, C. Boga, *Synthesis* **2017**, *49*, 3347-3356.

[2] S. Mahouche-Chergui, S. Gam-Derouich, C. Manganey, M. M. Chehimi, *Chem. Soc. Rev.* **2011**, *40*, 4143-4166.

[3] (a) A. Zarei, A. R. Hajipour, L. Khazdooz, B. F. Mirjalili, A. Najafichermahini, *Dyes & Pigments* **2009**, *81*, 240-244. (b) A. Zarei, A. R. Hajipour, L. Khazdooz, Synthesis **2009**, *6*, 941-944. (c) H. Valizadeh, M. Amiri, F. Hosseinzadeh, *Dyes & Pigments* **2012**, *92*, 1308-1313.

[4] (a) M. Barbero, M. Crisma, I. Degani, R. Fochi, P. Perracino, *Synthesis* **1998**, 1171-1175. (b) M. Barbero, I. Degani, S. Dughero, R. Fochi, *J. Org. Chem*. **1999**, *64*, 3448-3453. (c) A. V. Kachanov, O. Yu. Slabko, V. A. Kaminski, *Tetrahedron Lett*. **2012**, *53*, 5807-5808. (d) S. N. Neal, S. A. Orefuwa, A. T. Overton, R. J. Staples, A. A. Mohamed, *Inorganics* **2013**, *1*, 70-84. (e) Z. Zhang, Q. Zhang, S. Zhang, X. Liu, G. Zhao, *Synth. Commun*. **2001**, *31*, 329-334.

[5] V. D. Filimonov, M. E. Trusova, P. S. Postnikov, E. A. Krasnokutskaya, Y. M. Lee, *Org. Lett.*, **2008**, *10*, 3961-3964.

[6] (a) E. A. Krasnokutskaya, N. I. Semenischeva, V. D. Filimonov, P. Knochel, *Synthesis*, **2007**, *1*, 81-84. (b) D. A. Gorlushko, V. D. Filimonov, E. A. Krasnokutskaya, N. I. Semenischeva, B. S. Go, H. Y. Hwang, K-W. Chi, *Tetrahedron Lett.*, **2008**, *49*, 1080-1082. (c) M. E. Moon, Y. Choi, Y. M. Lee, V. Vajpayee, M. E. Trusova, V. D. Filimonov, K.-W. Chi, *Tetrahedron Lett.*, **2010**, *51*, 6769-6771. (d) Y. M. Lee, M. E. Moon, V. Vajpayee, V. D. Filimonov, K.-W. Chi *Tetrahedron*, **2010**, *66*, 7418-7422. (e) M. E. Trusova, E. A. Krasnokutskaya, P. S. Postnikov, Y. Choi, K-W. Chi, V.D. Filimonov, *Synthesis*, **2011**, 2154-2158. (f) P. J. Riss, S. Kuschel, F. I. Aigbirhio, *Tetrahedron Lett*. **2012**, *53*, 1717-1719. (g) K.V. Kutonova, M.E. Trusova, P.S. Postnikov, V.D. Filimonov, J. Parello, *Synthesis*. **2013**, *45*, 2706-2710.

[7] (a) A. V. Velikorodov, V. A. Ionova, S. I. Temirbulatova, M. A. Suvorova, *Rus. J. Org. Chem.* **2013**, *49*, 1004-1009. (b) Z. Y. Tang, Y. Zhang, T. Wang, W. Wang, *Synlett*. **2010**, 804-808. (c) G. U. Chaturbhuj, K. C. Akamanchi, *Tetrahedron Lett*. **2011**, *52*, 4950-4953. (d) V. Vajpayee, Y. H. Song, J. S. Ahn, K.-W. Chi, *Bull. Korean Chem. Soc*. **2011**, *32*, 2970-2972. (e) K. V. Kutonova, M. E. Trusova, A. V. Stankevich, P. S. Postnikov, V. D. Filimonov, *Beilstein J. Org. Chem.* **2015**, *11*, 358-362. (f) A. G. Pershina, A. E. Sazonov, V. D. Filimonov, *Rus.Chem.Rev.* **2014**, *83*, 299-322. (g) M. Min, S. Seo, J. Lee, S. M. Lee, E. Hwang, H. Lee, *Chem. Commun*. **2013**, *49*, 6289-6291.

[8] (a) V. Vajpayee, M. E. Moon, S. Lee, S. Ravikumar, H. Kim, B. Ahn, S. Choi, S. H. Hong, K-W. Chi, *Tetrahedron* **2013**, *69*, 3511-3517. (b) O. A. Guselnikova, K. V. Kutonova, M. E. Trusova, P. S. Postnikov, V.D. Filimonov *Izv. Akad. Nauk, ser. khim*. **2014**, 289-290. (c) K. V. Kutonova, M. E. Trusova, P. S. Postnikov, V. D. Filimonov, *Rus. Chem. Bull*. **2012**, *61*, 206-208. (d) S. Sengupta, S. K. Sadhukhan, S. Bhattacharyya, *Tetrahedron* **1997**, *53*, 2213-2218. (e) M. Teci, M. Tilley, M. A. McGuire, M. G. Organ, *Chem. Eur. J.* **2016**, *22*, 17407-17415. (f) M. I. Cuccovia, M. A. da Silva, H. M. C. Ferraz, J. R. Pliego, J. M. Riveros, H. Chaimovich, *J. Chem. Soc. Perkin 2* **2000**, 1896-1907. (g) M. Barbero, M. Degani, S. Dughera, R. Fochi, P. Perracino, *Synthesis* **1999**, 90-93.

[9] (a) R. Weiß, K.-G. Wagner, M. Hertel, *Chem. Ber*. **1984**, *117*, 1965-1972. (b) T. B. Patrick, R. P. Willaredt, D. J. DeGonia, *J. Org. Chem*. **1985**, *50*, 2232-2235. (c) C. Picherit, F. Wagner, D. Uguen, *Tetrahedron Lett*. **2004**, *45*, 2579-2583. (d) T. Umemoto, K. Adachi, S. Ishihara, *J. Org. Chem.* **2007**, *72*, 6905-6917. (e) A. Knöchel, O. Zwernemann, *J. Label. Comp. Radioparm*. **1986**, *38*, 325. (f) V. P. Nazaretyan, N. D. Volkov, N. I. Liptuga, *Rus. J. Org. Chem.* **2006**, *42*, 1188-1191.

[10] G.A. Olah, J.L.Grant, *J. Am. Chem. Soc.* **1975**, *97*, 1546-1548.

[11] A. I. Konovalov, I.S. Antipin, V.A. Burilov, T. I. Madzhidov, A. R. Kurbangalieva, A. V. Nemtarev, S. E. Solovieva, I. I. Stoikov, V. A. Mamedov, L. Y. Zakharova, E. L. Gavrilova, O. G. Sinyashin, I. A. Balova, A. V. Vasilyev, I. G. Zenkevich, M. Y. Krasavin, M. A. Kuznetsov, A. P. Molchanov, M. S. Novikov, V. A. Nikolaev, L. L. Rodina, A. F. Khlebnikov, I. P. Beletskaya, S. Z. Vatsadze, S. P. Gromov, N. V. Zyk, A. T. Lebedev, D.A. Lemenovskii, V. S. Petrosyan, V. G. Nenaidenko, V. V. Negrebetskii, Y. I. Baukov, T. A. Shmigol', A. A. Korlyukov, A. S., A. E. Shchekotikhin, V. F. Traven', L. G. Voskresenskii, F. I. Zubkov, O. A. Golubchikov, A. S. Semeikin, D. B. Berezin, P. A. Stuzhin, V. D. Filimonov, E. A. Krasnokutskaya, A. Y. Fedorov, A. V. Nyuchev, V. Y. Orlov, R. S. Begunov, A. I. Rusakov, A. V. Kolobov, E. R. Kofanov, O. V. Fedotova, A. Y. Egorova, V. N. Charushin, O. N. Chupakhin, Y. N. Klimochkin, V. A. Osyanin, A. N. Reznikov, A. S. Fisyuk, G. P. Sagitullina, A. V. Aksenov, N. A. Aksenov, M. K. Grachev, V. I. Maslennikova, M. P. Koroteev, A. K. Brel', S. V. Lisina, S. M. Medvedeva, K. S. Shikhaliev, G. A. Suboch, M. S. Tovbis, L. M. Mironovich, S. M. Ivanov, S. V. Kurbatov, M. E. Kletskii, O. N. Burov, K. I. Kobrakov, D. N. Kuznetsov, *Rus. J. Org. Chem*. **2018**, *54*, 157-371.

[12] http://www.unece.org/trans/danger/danger.html

[13] (a) L.D. Marciasini, N. Richy, M. Vaultier, M. Pucheault, *Adv. Synth. Catal*. **2013**, *355*, 1083-1088. (b) W. Erb, A. Hellal, M. Albini, J. Rouden, J. Blanchet, *Chem. Eur. J*. **2014**, *20*, 6608-6612. (c) S. Pietsch, E. C. Neeve, D. C. Apperley, R. Bertermann, F. Mo, D. Qiu, M.S. Cheung, L. Dang, J. Wang, U. Radius, Z. Lin, C. Kleeberg, T. B. Marder, *Chem. Eur. J.* **2015**, *21*, 7082-7098.

[14] M. K. Robinson, V. S. Kochurina, J. M. Hanna, *Tetrahedron Lett.* **2007**, *48*, 7687-7690.

[15] S. H. Korzeniowski, A. Leopold, J. R. Beadle, M. F. Ahern, W. A. Sheppard, R. K. Khanna, G. W. Gokel, *J.Org.Chem*. **1981**, *46*, 2153-2159.

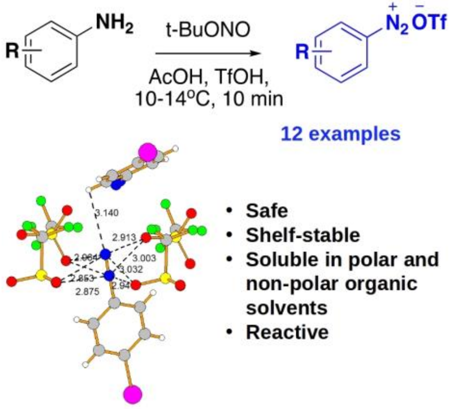
[16] (a) J. Zoller, D. C. Fabry, M. Rueping, *ACS Catal*. **2015**, *5*, 3900-3904. (b) S. Dixit, Q. T. Siddiqui, M. Muneer, N. Agarwal, *Tetrahedron Lett.* **2016**, *57*, 4228-4231. (c) K. Mandal, J. Ahmed, S. P. G.Vijaykumar, A. Jose, M. Raj, *Chem. Sci*. **2017**, *8*, 7798-7806.

[17] (a) M. Barbero, S. Cadamuro, S. Dughera, C. Giaveno, *Eur. J. Org. Chem.* **2006**, *21*, 4884-4890. b) E.B. Merkushev, N.D. Simakhina, G.M. Koveshnikova, *Synthesis* **1980**, *6*, 486-487. c) K. D. Grimes, A. Gupte, C. C. Aldrich, *Synthesis* **2010**, *9*, 1441–1448. d) D. L. Herring, *J. Org. Chem.* **1961**, *26*, 3998-3999. e) A. Granzhan, T. Riis- Johannessen, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2010**, 49, 5515-5518. f) Y. Moglie, E. Mascaró, F. Nador, C. Vitale, G. Radivoy, *Synth. Commun.* **2008**, *38*, 3861-3874. g) X. Chen, L. Wang, *Chin. J. Chem.* **2009**, *27*, 2037-2042.

Entry for the Table of Contents

FULL PAPER

A variety of stable, safe, and soluble arenediazonium triflates $ArN_2^+TfO^-$ were obtained easily by diazotization of anilines with *tert*-butyl nitrite in the presence of triflic acid. They have high reactivity forming aromatic iodides, azides, and boronic acids and also undergo an unusual metal-free chloro-dediazonization with chloroform and CCl_4.



Diazonium salts*

Victor D. Filimonov, Elena A. Krasnokutskaya, Assia Zh. Kassanova, Valentina A. Fedorova, Ksenia S. Stankevich, Nikolay G. Naumov, Alexander A. Bondarev, and Veronika A. Kataeva*

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Synthesis, structure, and synthetic potential of arenediazonium trifluoromethanesulfonates as stable and safe diazonium salts