CHAPTER-3

tert-Butyl Nitrite Mediated Nitrogen Transfer Reactions: Synthesis of Benzotriazoles and Azides at Room Temperature

3.1 Introduction

Benzotriazoles belong to a family of nitrogen-containing heterocyclic compounds which play pivotal roles in synthetic organic chemistry as well as in medicinal chemistry [1]. In organic synthesis, benzotriazoles have been explored as synthetic auxiliaries, intermediates, protecting groups, activating groups and ligands [1-2, 5]. In addition, benzotriazoles have been employed in the preparation of various functional materials, polymers, dyes, corrosion inhibitors, pharmaceuticals, agrochemicals, etc. [6-10]. On the other hand, benzotriazole derivatives have been clinically used as dopamine antagonists (Alizapride), sunscreen agents (Bisoctrizole), antineoplastic agents (Vorozole), etc. (Fig. 3.1). Nevertheless, several other benzotriazole derivatives exhibit anticancer, anti-malarial, anti-bacterial, antiviral, antifungal and anti-HIV activities [3-4, 11-12].

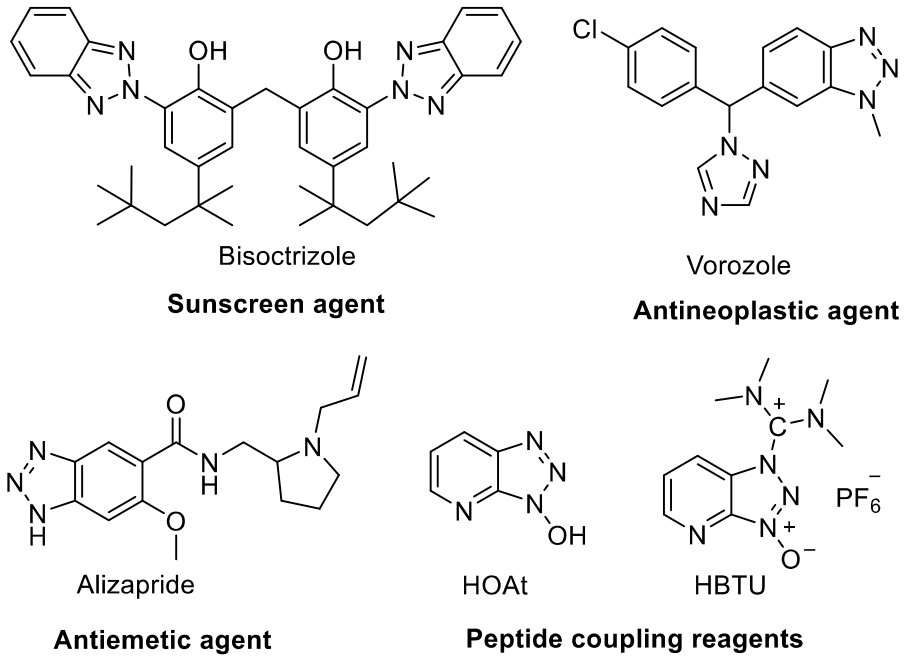
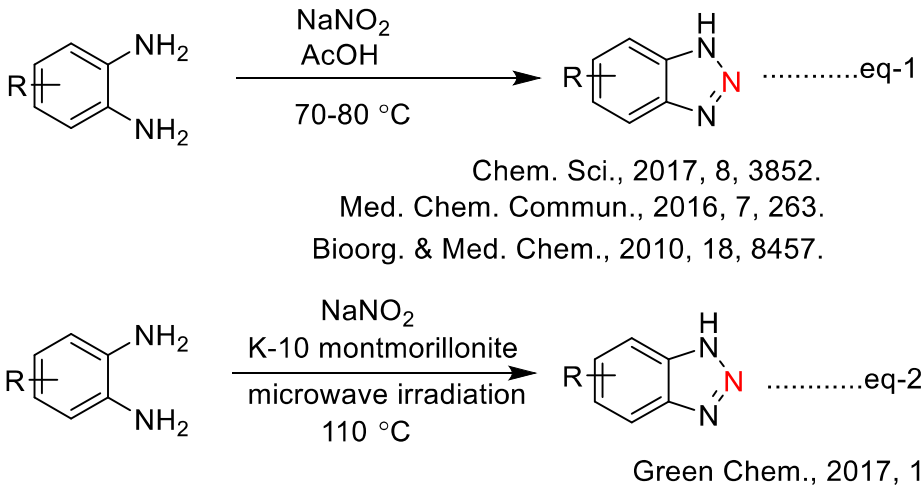
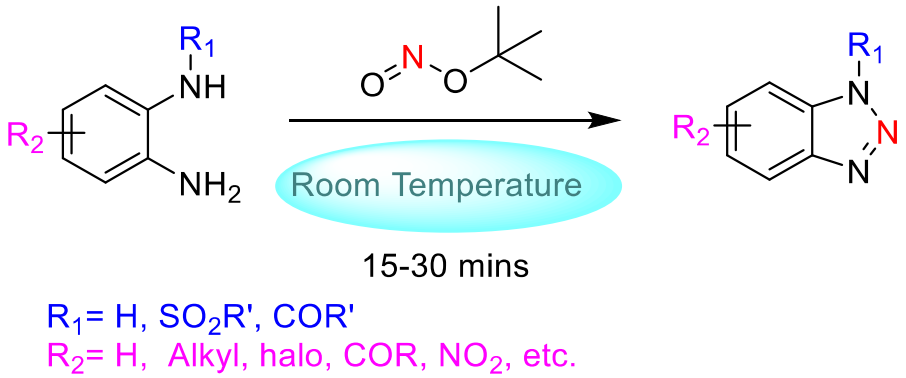


Figure 3.1 Benzotriazole based drugs and coupling agents

Synthesis of benzotriazoles has been achieved through a few methods including diazotization of *o*-phenylenediamine [11-12], [3 + 2] cycloaddition of azides to benzynes [13], palladium catalyzed cyclization of triazenes [14] and reaction of *ortho*-chloronitrobenzene with hydrazine followed by reduction [15]. Among them, the simplest approach is diazotization of *o*-phenylenediamines which is typically achieved using aqueous sodium nitrite in AcOH at 70–80 °C (Scheme 3.1, eq. (1)) [5,11-12]. Recently, Török *et al.* reported a microwave-assisted diazotization of *o*-phenylenediamines into benzotriazoles with sodium nitrite and K-10 montmorillonite at 110 °C (Scheme 3.1, eq (2)) [16]. However, use of acidic medium and requirement of higher reaction temperatures make these methods less attractive from the synthetic perspective. In this context, our interest was to develop/identify a suitable acid free reagent which can be used for the efficient conversion of *o*-phenylenediamines into benzotriazoles at room temperature.



Scheme 3.1. Sodium nitrite mediated diazotization of *o*-phenylenediamines



Scheme 3.2. *tert*-Butyl nitrite (TBN) mediated diazotization of *o*-phenylenediamines

tert-Butyl nitrite (TBN) is a highly useful synthetic reagent that has been explored in many organic transformations [17]. In this context, an efficient conversion of anilines to aryl azides in the presence of TBN and TMS-N_3 has been demonstrated by Moses *et al.* [18]. Subsequently, TBN has been explored for the nitration of phenols [19], alkenes [20], alkynes [21], sulfonanilides [22] and acetanilides [23]. Recently, Bhanage *et al*. have demonstrated *N*-nitrosation of amides using *tert*-butyl nitrite under mild conditions [24]. TBN is also employed as a source of nitrogen in many organic reactions [25-27]. *tert*-Butanol is the only by-product resulting from *tert*-butyl nitrite; hence TBN can be regarded as a green reagent. It is an acid-free reagent which is cheap and commercially available. Our research group is focused on the chemistry of *N*-nitrosamines [28-31] and we have recently demonstrated the applications of *tert*-butyl nitrite in *N*-nitrosation of secondary amines [28] and oxidative dimerization of thioamides to 1,2,4-thiadiazoles under mild conditions [31]. In continuation of these studies, here we report *tert*-butyl nitrite mediated conversion of *o*-phenylenediamines into benzotriazoles at room temperature (Scheme 3.2).

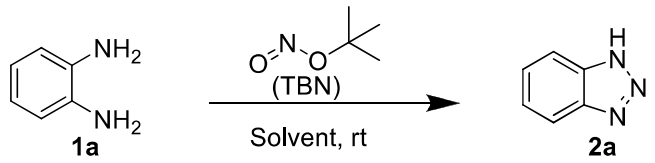
3.2 Results and discussion

3.2.1 Optimization for synthesis of benzotriazoles under different reaction conditions

To establish the optimized conditions, *o*-phenylenediamine (1a) was chosen as a model substrate and subjected to diazotization with one equiv. of *tert*-butyl nitrite in various solvents at room temperature. Aprotic solvents such as THF, toluene, benzene, dichloromethane, dichloroethane and acetonitrile gave a benzotriazole (2a) in 21–65% yield after 1 h (Table 3.1, entries 1–6). Among them, acetonitrile gave the desired product 2a in a high yield (i.e. 65% yield) when compared with other solvents (Table 3.1, entries 1–5).

On the other hand, protic solvents such as methanol, ethanol and water gave the desired product in 20–45% yields (Table 3.1, entries 7–9). The reaction was also attempted under solvent free conditions, which gave the desired product only in 37% yield (Table 3.1, entry 10). Furthermore, the reaction was investigated with 2.0 and 3.0 equiv. of *tert*-butyl nitrite in acetonitrile (Table 3.1, entries 11 and 12). To our delight, a quantitative conversion of *o*-phenylenediamine into benzotriazole was achieved with 2.0 equiv. of TBN in acetonitrile within 15 min at room temperature (Table 3.1, entry 11).

Table 3.1 Optimization for synthesis of benzotriazoles under various solvents



S.No.	Solvent	TBN (equiv.)	Time (min)	Yield (%)[b]
1	THF	1	60	25
2	Toluene	1	60	30
3	Benzene	1	60	21
4	DCM	1	60	32
5	DCE	1	60	41
6	CH_3CN	1	60	65
7	CH_3OH	1	60	45
8	C_2H_5OH	1	60	38
9	H_2O	1	60	20
10	Solvent- free	1	60	37
11	**CH_3CN**	**2**	**15**	**95**
12	CH_3CN	3	15	96

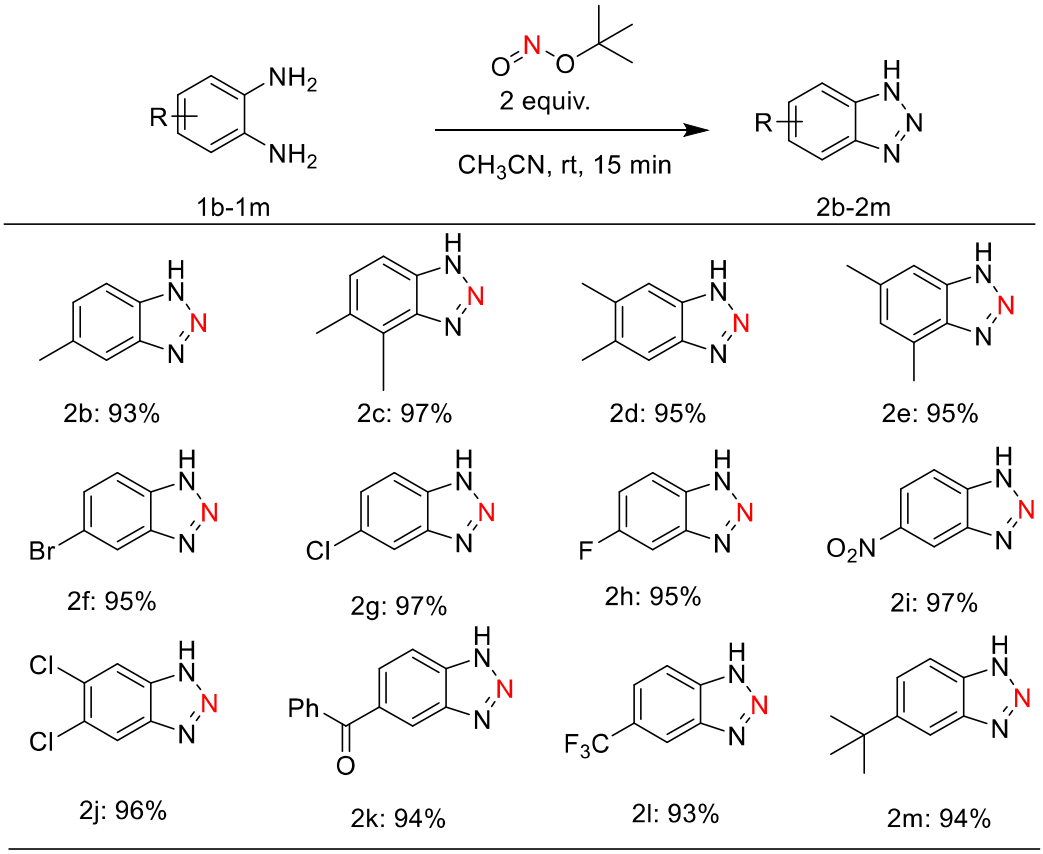
[a]Reaction conditions: Substrate (1 mmol) and TBN was stirred in the appropriate solvents (5 mL) at room temperature. [b]Isolated yields.

3.2.2 Substrate scope

With optimized conditions in hand, the transformation of various substituted *o*-phenylenediamines into corresponding benzotriazoles was investigated (Table 3.2). To our delight, *o*-phenylenediamines bearing electron donating groups (e.g.methyl and *tert*-butyl) and withdrawing groups (e.g. halogens, nitro group, trifluoromethane, etc.) underwent diazotization smoothly. These reactions provided the corresponding benzotriazoles in quantitative yields within 15 minutes at room temperature (Table 3.2,

2b–2m). It is noteworthy that the substituents present on the aryl ring (i.e. EDG or EWG) did not influence the reaction yield and time.

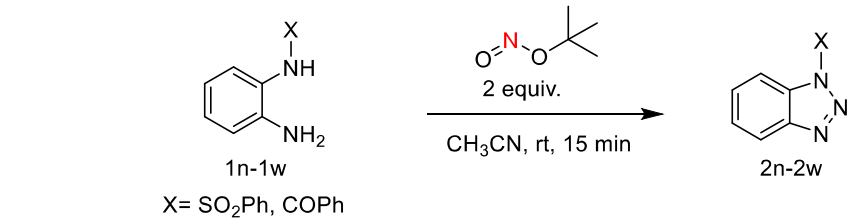
Table 3.2 Synthesis of benzotriazoles using *tert*-butyl nitrite in acetonitrile

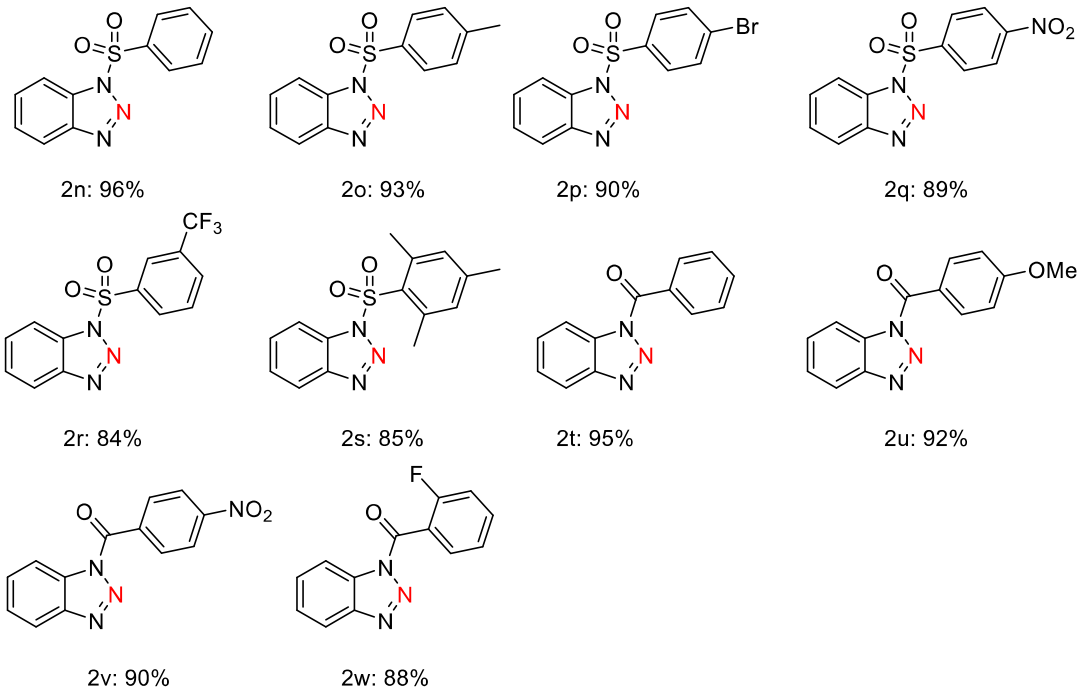


[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields.

Encouraged by this, we further investigated the conversion of various mono-*N*-sulfonyl and *N*-acyl *o*-phenylenediamines into corresponding benzotriazoles using *tert*-butyl nitrite under optimized conditions. To our delight, all these substrates underwent triazolation smoothly and gave the corresponding *N*-sulfonyl and *N*-acyl benzotriazoles in 84–96% yields within 15 min at room temperature (Table 3.3, 2n–2w).

Table 3.3 Synthesis of *N*-sulfonyl and *N*-acyl benzotriazoles



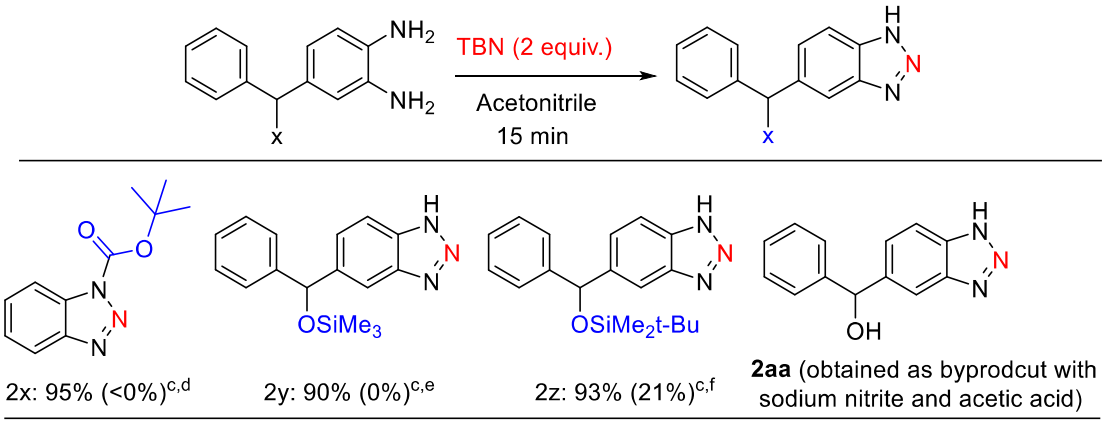


[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields.

To evaluate the merits of the current methodology, triazolation of acid labile (i.e. *tert*-butoxycarbonyl (Boc), trimethylsilyl (TMS) and *tert*-butyldimethylsilyl (TBS)) group protected *o*-phenylenediamines was attempted. To our delight, all these substrates gave the desired products 2x, 2y and 2z in quantitative yields with *tert*-butyl nitrite. In fact, no deprotection was observed even after prolonged stirring at room temperature with TBN. In this context, the traditional method i.e. $NaNO_2$/ AcOH was found to be inferior. For instance, Boc and TMS groups were completely deprotected during the

process of triazole formation. These reactions provided 2a and 2aa, respectively, as the sole product. In the case of the TBS protected substrate, only 21% of the desired product was obtained along with 2aa in 69% yield (Table 3.4).

Table 3.4 Synthesis of acid labile functional group benzotriazoles using TBN

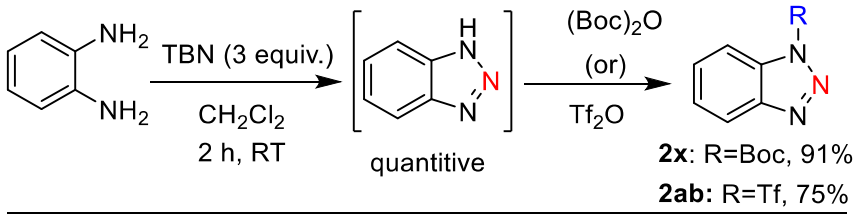


2x: 95% (<0%)[c,d] | 2y: 90% (0%)[c,e] | 2z: 93% (21%)[c,f] | **2aa** (obtained as byprodcut with sodium nitrite and acetic acid)

[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields, [c] Reaction was performed using $NaNO_2$/AcOH as described in the literature procedure (Ref 5). [d]Triazole (**2a**) was obtained in 91% yield. [e]**2aa** was obtained in 94%. [f]**2aa** was obtained in 69% yield.

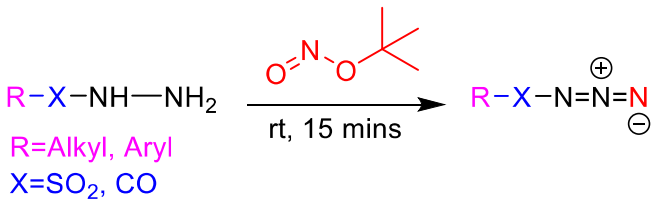
In order to explore further advantages of the developed protocol, one-pot synthesis of *N*-protected benzotriazoles was investigated. *o*-phenylenediamine 1a was quantitatively converted into benzotriazole using three equiv. of TBN in dichloromethane which was subsequently treated with acid anhydrides. This one-pot procedure gave the desired products i.e. *N*-Boc and *N*-Tf protected benzotriazoles (2x and 2ab, respectively) in 75–91% yields (Scheme 3.3). In contrast, the onepot procedure failed while attempting the preparation of *N*-Boc and *N*-Tf protected benzotriazoles (2x and 2ab) with the sodium nitrite–acetic acid system. This observation clearly indicates the merits of using TBN over the traditional method.

Scheme 3.3 One-pot synthesis of *N*-protected benzotriazoles



[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields.

Similar to benzotriazoles, sulfonyl and acyl azides have found wide applications in organic synthesis [32-33] For instance, sulfonyl azides were employed in diazo and azido transfer reactions [34-37], click chemistry [38-39], coupling reactions [40-41], aziridation [42-43] and radical amination reactions [44] etc. Likewise, acyl azides were utilized in peptide synthesis [45], cycloaddition reactions [46] and also in the preparation of isocyanates (i.e. Curtius rearrangement), amides, urethanes, ureas, etc. [32, 46].



Scheme 3.4 Synthesis of sulfonyl and acyl azides

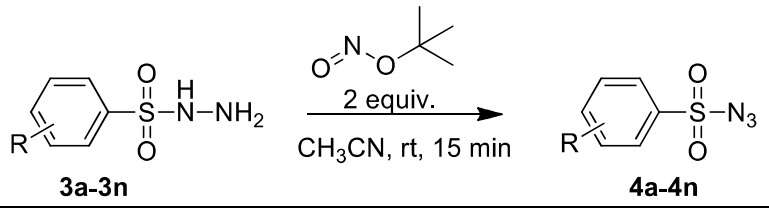
Sulfonyl and acyl azides were typically prepared from corresponding acid chlorides in the presence of sodium azide [33, 46]. Alternatively, they were obtained from corresponding hydrazines (or hydrazides) in the presence of nitrosating reagents. The advantages of using the latter method is that sulfonyl and acyl hydrazines usually exist in the solid form and are noncorrosive, odorless and compatible with water and

moisture [47–48]. It is also worth mentioning that the conversion of acyl hydrazines into corresponding azides is the most frequently used transformation in peptide synthesis [45, 49].

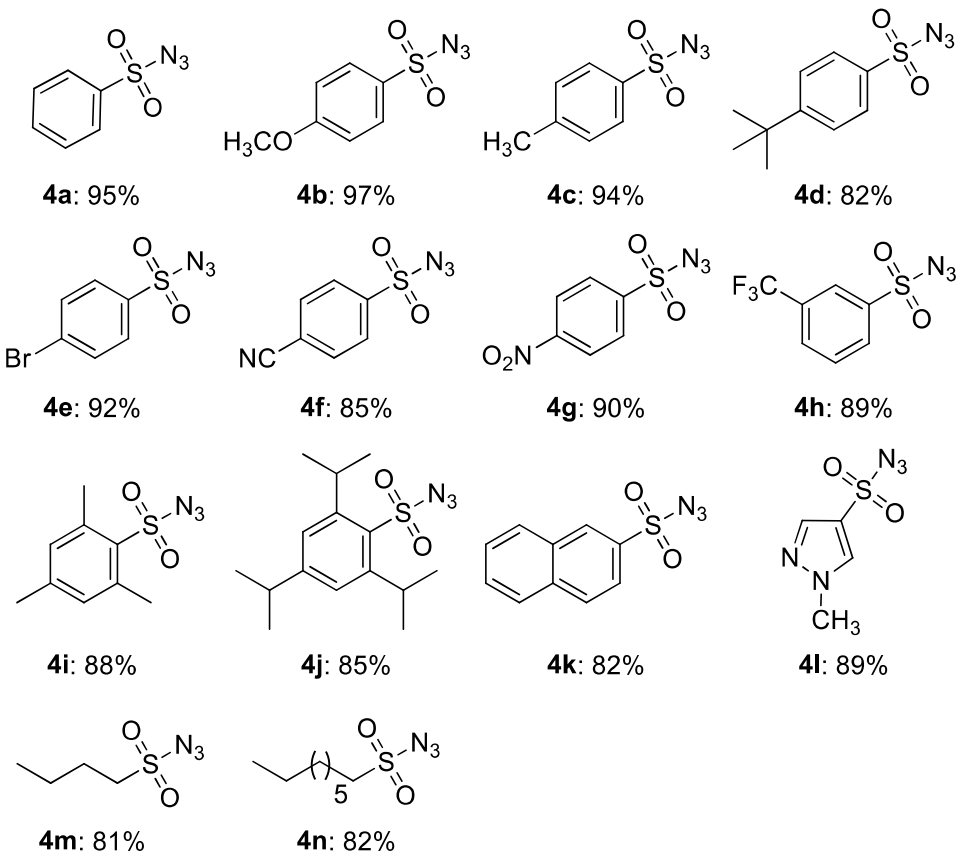
Conversion of sulfonyl and acyl hydrazines into corresponding azides was previously reported with $NaNO_2$/HCl [49, 50] dinitrogen tetroxide [51], nitrosyl tetrafluoroborate [52] and Ph_3P/ Br_2/*n*-Bu_4NNO_2 [53]. The major limitations of the existing methods are the use of acidic medium and harmful (or unstable) reagents. To the best of our knowledge, *tert*-butyl nitrite has not been explored for these transformations. Therefore, the conversion of various sulfonyl and acyl hydrazides into corresponding azides was attempted using *tert*-butyl nitrite (Scheme 3.4) and the results are summarised in Tables 3.5 and 3.6.

Initially, the reaction was investigated with benzenesulfonyl hydrazide in the presence of 2.0 equiv. *tert*-butyl nitrite in acetonitrile at room temperature. To our delight, the desired product, i.e. benzenesulfonyl azide, was achieved in a quantitative yield within 15 minutes (Table 3.5, 4a). Encouraged by this, we further investigated the reaction with different arylsulfonyl hydrazides bearing electron-donating groups (e.g. methoxy, methyl and *tert*-butyl) as well as withdrawing groups (e.g. bromo, cyano, nitro and trifluoromethane). Irrespective of their electronic nature, all these substrates were smoothly converted into the desired products with excellent yields (Table 3.5, 4b–4h).

Table 3.5 Conversion of sulfonyl hydrazines into sulfonyl azides using TBN



3a-3n **4a-4n**

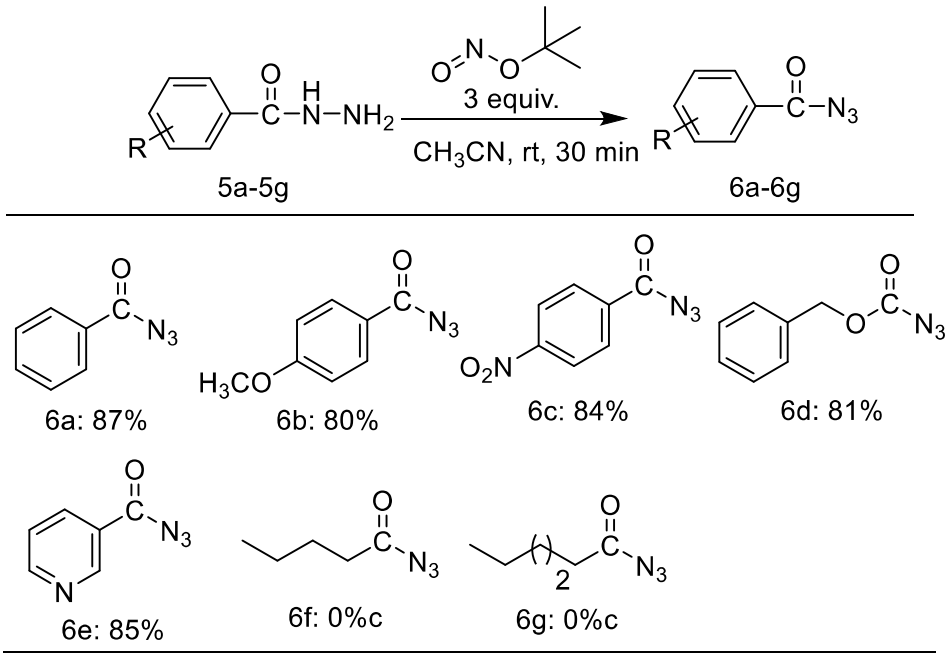


[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields.

It is worth mentioning that the sterically hindered substrates (i.e. 2,4,6-trimethylbenzene sulfonyl hydrazide and 2,4,6-triisopropylbenzene sulfonyl hydrazide) also gave the desired azides (4i and 4j) in >85% yields. Likewise, 2-naphthalenesulfonyl azide 4k was obtained in 82% yield from the corresponding hydrazide. To our surprise, this protocol works very well with heteroaromatic

substrates, for instance, 1-methyl-1H-pyrazole-4-sulfonyl hydrazide was successfully converted into the corresponding azide (4l) in 89% yield within 15 min. Similar to aryl substrates, alkyl sulfonyl hydrazides were also smoothly transformed into corresponding azides in good yields (Table 3.5, 4m and 4n).

Table 3.6 Conversion of acyl hydrazines using *tert*-butyl nitrite in acetonitrile

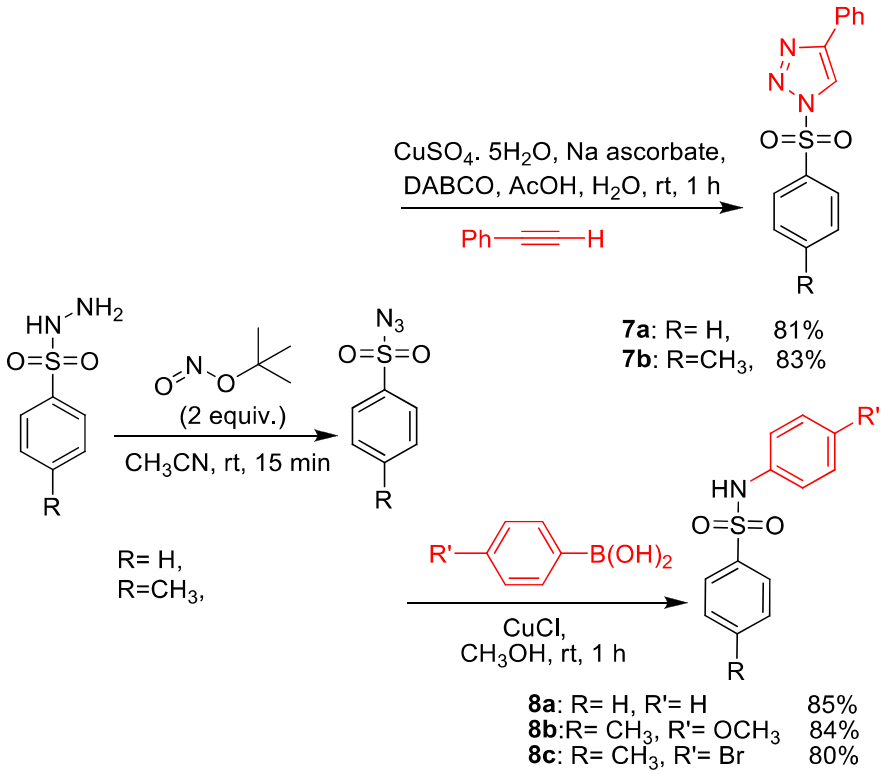


Reaction conditions: Substrate (1 mmol), TBN (3 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields. [c]Alkyl carboxylic azides were found extremely unstable and could not be isolated, hence, yields were given as 0%. See the reference [54].

Having studied the reaction of sulfonyl hydrazides with *tert*-butyl nitrite, we extended our investigation with acyl hydrazines (Table 3.6). To our delight, unsubstituted as well as electron donating or withdrawing group (e.g. methoxy and nitro) substituted benzoyl hydrazines were successfully converted into corresponding azides in 80–87% yields with 3.0 equiv. of *tert*-butyl nitrite (Table 3.6, 6a–6c). Moreover, conversion of carbonate hydrazides, heterocyclic hydrazides and alkyl

carboxylic hydrazides into their respective azides was achieved in 80–94% yields (Table 3.6, 6d–6g) [54], which illustrate the broad scope of the methodology.

3.3 Applications of current methodology to click reaction and coupling reaction



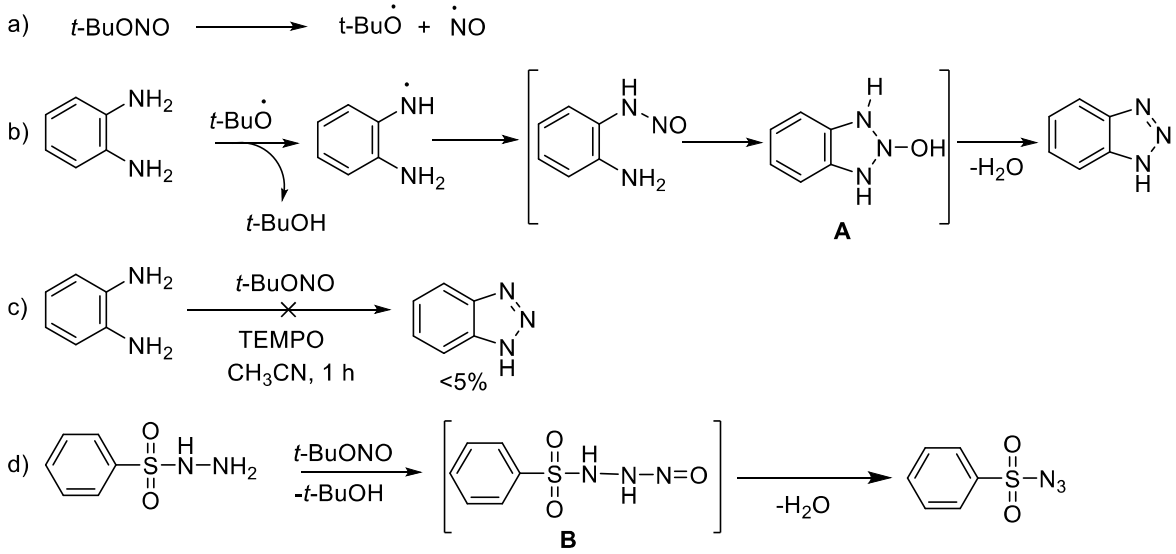
Scheme 3.5 Applications of sulfonyl azides in one-pot synthesis

Having established a simple and efficient method for the conversion of hydrazides into azides, we attempted a one-pot click reaction with alkynes. For this study, sulfonyl hydrazides 4a and 4c were converted into corresponding azides in situ and subsequently reacted with phenylacetylene in the presence of copper sulphate [38]. To our delight, the desired triazole product was obtained in 81–83% yields (Scheme 3.5, 7a and 7b). Furthermore, we performed a coupling reaction between in situ generated sulfonyl azides and boronic acids in the presence of copper chloride [40],

which gave the corresponding sulfonamides in excellent yields as illustrated in Scheme (3.5, 8a–8c).

3.4 Plausible mechanism

A proposed mechanism for the TBN prompted nitrogen transfer reactions is shown in Scheme 3.6. Initially, *tert*-butyl nitrite undergoes homolytic cleavage and forms *tert*-butoxy and nitroso radicals (Scheme 3.6, a) [17-27]. For benzotriazole formation: *o*-phenylenediamine undergoes radical mono-*N*-nitrosation to form the intermediate A, which gives the desired product upon releasing a water molecule (Scheme 3.6, b). To confirm the radical path, diazotization of *o*-phenylenediamine was performed with radical scavenger TEMPO (Scheme 3.6, c).



Scheme 3.6 Proposed mechanism for the TBN prompted nitrogen transfer reactions

The desired product, i.e. benzotriazole was not observed even after 1 h at room temperature. This observation lends support to our assumption. Similarly, *tert*-butyl nitrite (TBN) reacts with sulfonyl hydrazide to form corresponding *N*-nitroso

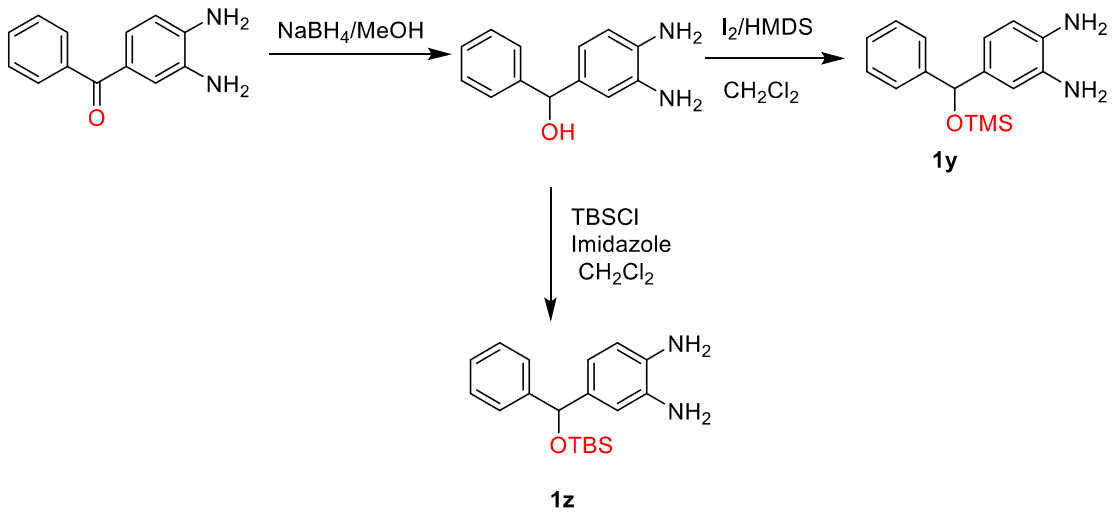
intermediate B, which leads to azide formation upon releasing a water molecule (Scheme 3.6, d).

3.5 Conclusion

In conclusion, mild and practical methods for the (i) transformation of *o*-phenylenediamines into benzotriazoles and (ii) conversion of sulfonyl and acyl hydrazines into corresponding sulfonyl and acyl azides were demonstrated with green reagent *tert*-butyl nitrite. All the reactions were carried out at room temperature to obtain the desired products in excellent yields. Moreover, this protocol does not require any catalyst, acidic medium or high temperature which clearly demonstrates the merits of the current methodology. Acid labile groups were found to be very stable during triazole formation with TBN. The developed methodology has been used as a key in one-pot synthesis of *N*-protected benzotriazoles, benzene sulfonyl triazoles and benzene sulphonamide.

3.6 Experimental section

3.6.1 Synthesis of TMS and TBS protected *o*-phenylenediamines



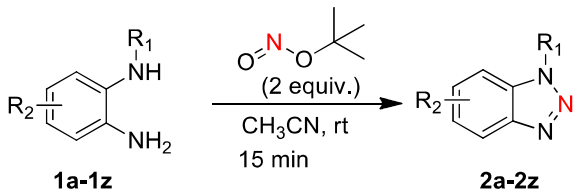
[A] Reduction of ketone: 2-Amino-4-benzoylaniline (10 mmol, 2.10 g) was stirred in methanol at room temperature and then cooled to 0 °C to which sodium borohydride (15 mmol, 567 mg) was added portion wise. Further the reaction was allowed to stir for 4 h at room temperature. Methanol was evaporated, diluted with water and extracted with ethyl acetate. Ethyl acetate layer was dried over sodium sulfate and evaporated to get the desired alcohol quantitatively.

[B] Synthesis of 1y: TMS protection was performed using literature procedure developed by B. Karimi and B. Golshani. The alcohol (2.33 mmol, 500 mg) and Iodine (0.233 mmol, 30 mg) was stirred in CH_2Cl_2 to which hexamethyldisilazane (HMDS) (1.86 mmol, 300 mg) in 5 mL of CH_2Cl_2 was added dropwise within 5 minutes. This reaction was allowed to stir for 30 min at room temperature after which finely powered $Na_2S_2O_3$ (approx. 500 mg) was added, the mixture was allowed to stirr for additional 30 minutes. Then, the reaction mixture was filtered, concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding protected diammine (**1y**). The title compound was obtained as yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.40; Yield 88% (586 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44–7.39 (m, 2H), 7.38–7.33 (m, 2H), 7.30–7.25 (m, 1H), 6.76–6.72 (m, 1H), 6.69 (d, J = 1.9 Hz, 1H), 6.64 (d, J = 7.9 Hz, 1H), 5.72 (s, 1H), 3.28 (s, 4H), 0.16 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.1, 136.8, 134.4, 133.6, 127.9, 126.6, 126.2, 118.5, 116.1, 115.0, 76.1, 0.09. HRMS: Calc. for $C_{19}H_{29}N_2OSi$ $[M+H]^+$: 287.1580, Obser.: 287.1571.

[C] Synthesis of 1z: TBS protection was performed using literature procedure described by Dahal *et al*. The alcohol (2.33 mmol, 500 mg) was stirred in CH_2Cl_2 to which *tert*-butyl dimethylsilyl chloride (TBSCl), (2.80 mmol, 350 mg) and Imidazole (2.30 mmol, 190 mg) was added simultaneously. This reaction was allowed to stir for 1 h at room temperature; the reaction mixture was diluted with brine solution and then extracted through ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding protected diammine (**1z**). The title compound was obtained as a viscous brown liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.33; Yield 78% (597 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37 (dd, J = 4.1, 3.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.23–7.20 (m, 1H), 6.73–6.71 (m, 1H), 6.67 (d, J = 1.9 Hz, 1H), 6.62 (d, J = 7.9 Hz, 1H), 5.66 (s, 1H), 3.19 (s, 4H), 0.95 (s, 9H), 0.01 (d, J = 6.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.7, 137.4, 134.4, 133.4, 127.9, 126.5, 126.1, 118.3, 116.2, 114.9, 76.3, 25.8, 18.2, −4.8, −4.7. HRMS: Calc. for $C_{19}H_{29}N_2OSi$ $[M+H]^+$: 329.2049, Obser.: 329.2040.

3.6.2 Synthesis of benzotriazoles:-

[A] Reactions using *tert*-butyl nitrite in acetonitrile



1a-1z 2a-2z

R_1= H, SO_2R', COR'
R_2= H, Alkyl, halo, COR, NO_2, etc.

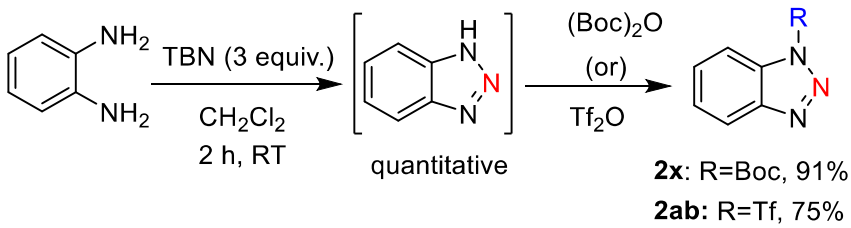
The substituted *o*-phenylenediamine (**1a-1z**) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of *tert*-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding benzotriazole (**2a-2z**).

[B] Reactions with sodium nitrite and acetic acid

For these reactions, procedure was adopted from previous report described by Wang *et al.*[5]: 1 mmol *o*-phenylenediamine (**1x** or **1y** or **1z**) was stirred in acetic acid (2 mL) and subsequently, aqueous solution of sodium nitrite (1M, 5 mL) was added and the mixture was stirred at 70–80 °C for 1 h. The reaction was monitored through thin layer chromatography (TLC) where the only the deprotected product (**2aa**) was observed instead of the desired protected benzotriazoles (**2x** or **2y** or **2z**).

[C] One-pot procedure for the synthesis of benzotriazoles

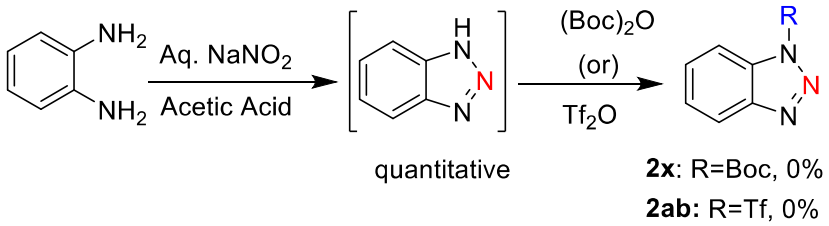
(i) Using *tert*-butyl nitrite in dichloromethane



The *o*-phenylenediamine (**1a**) (1 mmol) was stirred in dichloromethane (3 mL) at room temperature to which 3 equiv. of *tert*-butyl nitrite (TBN) was added. After the

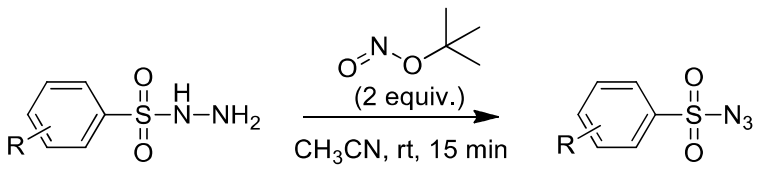
formation of benzotriazole, boc or triflic anhydride (5 equiv.) was added to it at room temperature. The progress of the reaction was monitored by TLC. After completion, dichloromethane was evaporated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding protected (Boc or Tf) benzotriazole (**2x or 2ab**).

(ii) Reactions with sodium nitrite and acetic acid



For these reactions, procedure was adopted from previous report described by Wang *et al.*[5]: 1 mmol *o*-phenylenediamine (**1a**) was stirred in acetic acid (2 mL) and subsequently, aqueous solution of sodium nitrite (1M, 5 mL) was added and the mixture was stirred at 70–80 °C for 1 h. After the formation of benzotriazole, it was allowed to cool down upto room temperature and then, boc or triflic anhydride (5 equiv.) was added to it. The reaction was monitored through thin layer chromatography (TLC) where the only the deprotected product (**2a**) was observed instead of the desired protected benzotriazoles (**2x** or **2ab**).

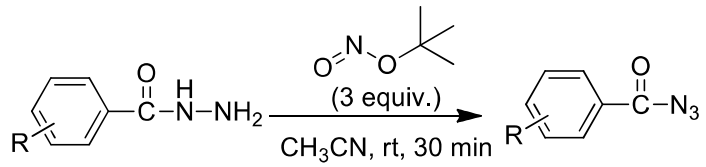
3.6.3 Conversion of sulfonyl hydrazines into sulfonyl azides using *tert*-butyl nitrite



3a-3n **4a-4n**

The substituted sulfonyl hydrazines (**3a-3n**) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of *tert*-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the desired products (**4a-4n**).

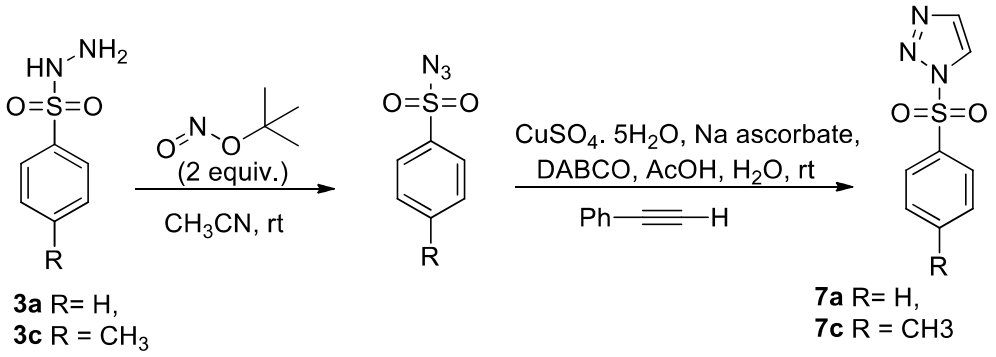
3.6.4 Conversion of benzene acyl hydrazines in to acyl azide using *tert*-butyl nitrite



5a-5g **6a-6g**

The substituted carbonyl hydrazines **(5a-5g)** (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 3 equiv. of *tert*-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After completion, acetonitrile was evaporated and then, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), concentrated and subjected for silica gel (60-120 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the desired products **(6a-6g).**

3.6.5 Experimental procedure for the triazole formation with the sulfonyl azides

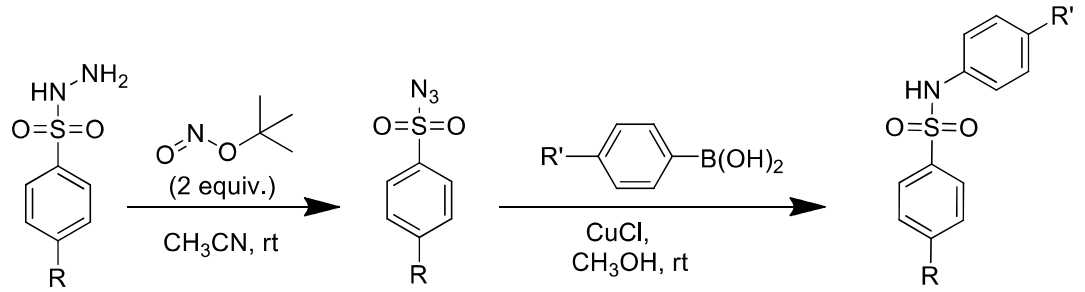


3a R= H,
3c R = CH_3

7a R= H,
7c R = CH3

The substituted sulfonyl hydrazines (benzene sulfonyl hydrazine and 4-methyl benzenesulfonyl hydrazine) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of *tert*-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. Along with it, a mixture of $CuSO_4.5H_2O$ (0.03 mmol, 7 mg), sodium ascorbate (0.12 mmol, 23 mg) and DABCO (0.06 mmol, 0.006 mg) in H_2O (2 mL) was stirred vigorously in round bottom flask and added to the formed respective sulfonyl azide followed by acetic acid (0.06 mmol) and phenyl acetylene (1 mmol, 102 mg). After consumption of the starting material, acetonitrile was evaporated further, diluted with ethyl acetate (10 mL) and aqueous ammonium chloride solution (5 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layer were dried over anhydrous Na_2SO_4, filtered and evaporated. The obtained crude product was subjected for silica gel (60-120 mesh) column chromatography purification (SiO2: ethyl acetate/hexane) to obtain the desired product (**7a** and **7b**).

3.6.6 Experimental procedure for the coupling of boronic acids with the sulfonyl azides

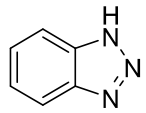


8a: R= H, R'= H
8b: R= CH_3, R'= OCH_3
8c: R= CH_3, R'= Br

The substituted sulfonyl hydrazines (benzene sulfonyl hydrazine and 4-methyl benzenesulfonyl hydrazine) (1 mmol) was stirred in acetonitrile (5 mL) at room temperature to which 2 equiv. of *tert*-butyl nitrite (TBN) was added. The progress of the reaction was monitored by TLC. After the formation of desired product, the substituted arylboronic acid (1.2 mmol) and CuCl (10 mol %) were dissolved in methanol (5 mL) and then added to the flask. The reaction mixture was stirred at room temperature in an open flask. After completion of the reaction, the solvent was evaporated and the obtained crude product was subjected for silica gel (60-120 mesh) column chromatography purification (SiO2: ethyl acetate/hexane) to obtain the desired product (**8a-8c**).

3.7 Analytical data of the benzotriazoles product

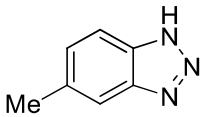
[3.7.1] 1,2,3-Benzo[d]triazole (2a)



2a

The title compound was obtained as a white solid. M.p. 97 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.65; Yield 96% (114 mg); IR (neat): 1726, 1376, 1190, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 13.60 (s, 1H), 7.99–7.90 (m, 2H), 7.40 (s, 2H). ^{13}C NMR (125 MHz, CDCl3) δ = 138.8, 126.0, 114.9. HRMS: Calc. for $C_6H_6N_3$ $[M+H]^+$: 120.0562, Obser.: 120.0558.

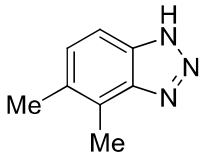
[3.7.2] 5-Methyl-1*H*-benzo[d][1,2,3]triazole (2b)



2b

The title compound was obtained as a white solid. M.p. 135 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.66; Yield 93% (123 mg); IR (neat): 2340, 1734, 1380, 1225, 1062 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ =14.23 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.62 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.6, 138.0, 136.7, 127.8, 115.2, 112.9, 21.6. HRMS: Calc. for $C_7H_8N_3$ $[M+H]^+$: 134.0718, Obser: 134.0703.

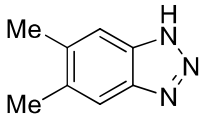
[3.7.3] 4,5-Dimethyl-1*H*-benzo[d][1,2,3]triazole (2c)



2c

The title compound was obtained as a pale yellow solid. M.p. 154 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.63; Yield 97% (142 mg); IR (neat): 2344, 1734, 1380, 1220, 1062 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$ & DMSO-d_6) δ = 7.50 (d, J = 31.6 Hz, 1H), 7.16 (d, J = 8.3 Hz, 1H), 2.57 (s, 3H), 2.30 (d, J = 44.5 Hz, 3H. ^{13}C NMR (125 MHz, CDCl3 & DMSO-d_6) δ = 132.05, 127.59, 111.70, 18.29, 13.39. HRMS: Calc. for $C_8H_{10}N_3$ $[M+H]^+$: 148.0875, Obser.: 148.0873.

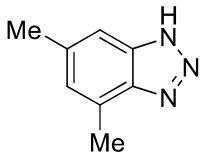
[3.7.4] 5,6-Dimethyl-1*H*-benzo[d][1,2,3]triazole (2d)



2d

The title compound was obtained as a brown solid. M.p. 156 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.62; Yield 95% (140 mg); IR (neat): 2340, 1734, 1376, 1222, 1062 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 15.41 (s, 1H), 7.60 (d, J = 99.7 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 143.4, 136.9, 132.8, 131.8, 117.6, 109.9, 20.0. HRMS: Calc. for $C_8H_{10}N_3$ $[M+H]^+$: 148.0875, Obser.: 148.0868.

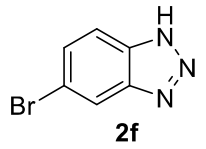
[3.7.5] 4,6-Dimethyl-1*H*-benzo[d][1,2,3]triazole (2e)



2e

The title compound was obtained as a brown solid. M.p. 158 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 95% (140 mg); IR (neat): 2344, 1740, 1390, 1225, 1062 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 15.50 (s, 1H), 7.40 (s, 1H), 6.96 (s, 1H), 2.58 (s, 3H), 2.39 (s, 3H).^{13}C NMR (125 MHz, DMSO-d_6) δ = 135.5, 126.4, 109.4, 21.1, 16.4. HRMS: Calc. for $C_8H_{10}N_3$ $[M+H]^+$: 148.0875, Obser.: 148.0872.

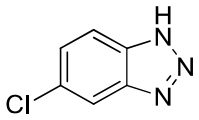
[3.7.6] 5-Bromo-1*H*-benzo[d][1,2,3]triazole (2f)



2f

The title compound was obtained as a brown solid. M.p. 154 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.67; Yield 94% (183 mg); IR (neat): 2334, 1730, 1380, 1225, 1062 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 15.90 (s, 1H), 8.15 (s, 1H), 7.86 (s, 1H), 7.50 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 138.6, 130.7, 128.8, 128.4, 118.1. HRMS: Calc. for $C_6H_5BrN_3$ $[M+H]^+$: 197.9667, Obser: 197.9668.

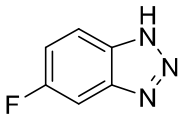
[3.7.7] 5-Chloro-1*H*-benzo[d][1,2,3]triazole (2g)



2g

The title compound was obtained as a white solid. M.p. 157 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.65; Yield 97% (148 mg); IR (neat): 2345, 1390, 1339, 1060, 885 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 15.89 (s, 1H), 8.01 (s, 2H), 7.45 (s, 1H).^{13}C NMR (125 MHz, DMSO-d_6) δ = 138.1, 130.2, 125.9, 116.8, 114.1, 79.1. HRMS: Calc. for $C_6H_5ClN_3$ $[M+H]^+$: 154.0172, Obser:154.0176.

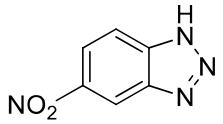
[3.7.8] 5-Fluoro-1*H*-benzo[d][1,2,3]triazole (2h)



2h

The title compound was obtained as a pale yellow solid. M.p. 148 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.66; Yield 95% (130 mg); IR (neat): 2336, 1732, 13076, 1220, 1062, 745 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 15.84 (s, 1H), 7.99 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.9 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 161.3, 159.4, 137.7, 117.7, 114.76 (d, J = 19.2 Hz), 99.0. HRMS: Calc. for $C_6H_5FN_3$ $[M+H]^+$: 138.0468, Obser: 138.0460.

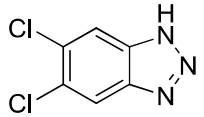
[3.7.9] 5-Nitro-1*H*-benzo[d][1,2,3]triazole (2i)



2i

The title compound was obtained as a yellow solid. M.p. 214 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.43; Yield 97% (159 mg); IR (neat): 2340, 1740, 1374, 1225, 1062 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 16.18 (s, 1H), 8.37 (s, 1H), 8.06 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 144.5, 140.4, 138.7, 120.9, 114.4, 114.0. HRMS: Calc. for $C_6H_5N_4O_2$ $[M+H]^+$: 165.0413, Obser.: 165.0416.

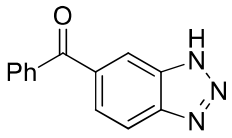
[3.7.10] 5,6-Dichloro-1*H*-benzo[d][1,2,3]triazole (2j)



2j

The title compound was obtained as a brown solid. M.p. 267 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.55; Yield 96% (178 mg); IR (neat): 2340, 1734, 1384, 1215, 1062 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 16.03 (s, 1H), 8.28 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 138.4, 128.4, 116.5. HRMS: Calc. for $C_6H_4Cl_2N_3$ $[M+H]^+$: 187.9782 Obser.: 187.9780.

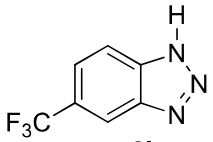
[3.7.11] (1*H*-Benzo[d][1,2,3]triazol-6-yl)(phenyl) methanone (2k)



2k

The title compound was obtained as a yellow solid. M.p. 115 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 94 % (209 mg); IR (neat): 2347, 1730, 1390, 1225, 1060 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 16.08 (s, 1H), 8.23 (s, 1H), 7.97 (d, J = 5.5 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 6.9 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 195.6, 137.6, 137.3, 134.0, 133.0, 130.1, 128.9, 127.1, 120.5, 114.0. HRMS: Calc. for $C_{13}H_{10}N_3O$ $[M+H]^+$: 224.0824, Obser.: 224.0820.

[3.7.12] 5-(Trifluoromethyl)-1*H*-benzo[d][1,2,3]triazole (2l)

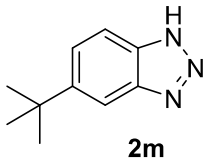


2l

The title compound was obtained as a brown solid. M.p. 130 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.65; Yield 93% (171 mg); IR (neat): 2340, 1730, 1378, 1222, 1062 cm^{-1}. ^1H NMR (500 MHz, DMSO-d6-d_6) δ = 16.15 (s, 1H), 8.37 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 139.8, 138.4, 127.5, 125.9, 125.7,

125.4, 125.2, 123.2, 122.1, 121.1, 115.3, 114.6. HRMS: Calc. for $C_7H_5F_3N_3$ $[M+H]^+$: 188.0436, Obser: 188.0430.

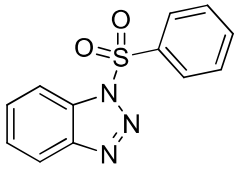
[3.7.13] 5-(*tert*-butyl)-1*H*-benzo[d][1,2,3]triazole (2m)



2m

The title compound was obtained as a pale yellow solid. M.p. 92 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.55; Yield 94% (165 mg); IR (neat): 2350, 1734, 1410, 1225, 1060 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 12.11 (s, 1H), 7.89–7.87 (m, 2H), 7.51 (d, J = 8.7 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 150.0, 138.3, 124.9, 114.8, 109.6, 35.1, 31.3. HRMS: Calc. for $C_9H_{11}N_3$ $[M+H]^+$: 161.0953 Obser: 161.0950.

[3.7.14] 1-(phenylsulfonyl)-1*H*-benzo[d][1,2,3]triazole (2n)

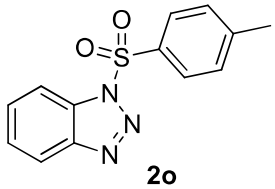


2n

The title compound was obtained as a white solid. M.p. 110 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.66; Yield 96% (248 mg); IR (neat): 3128, 2950, 2209, 1620, 1389, 1182, 956, 893, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.13 (dd, J = 20.3, 7.3 Hz, 4H), 7.68 (dd, J = 14.0, 6.9 Hz, 2H), 7.56 (t, J = 7.0 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.4, 137.1, 135.1, 131.6, 130.3, 129.6,

127.9, 125.8, 120.6, 112.0. HRMS: Calc. for $C_{12}H_{10}N_3O_2S$ $[M+H]^+$: 260.0494, Obser.: 260.0491.

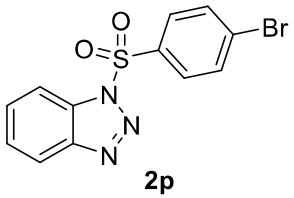
[3.7.15] 1-Tosyl-1*H*-benzo[d][1,2,3]triazole (2o)



2o

The title compound was obtained as a white solid. M.p. 132 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.65; Yield 93% (241 mg); IR (neat): 3143, 2958, 2217, 1623, 1377, 1179, 986, 903, 760 cm^{-1}. ^1H NMR (500 MHz, CDCl3) δ = 8.13 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ = 146.7, 145.4, 134.0, 131.6, 130.2, 130.1, 128.0, 125.7, 120.5, 112.0, 21.7. HRMS: Calc. for $C_{13}H_{12}N_3O_2S$ $[M+H]^+$: 274.0650, Obser.: 274.0643.

[3.7.16] 1-((4-Bromophenyl)sulfonyl)-1*H*-benzo[d][1,2,3]triazole (2p)

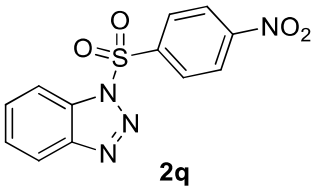


2p

The title compound was obtained as a white solid. M.p. 148 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.62; Yield 90% (302 mg); IR (neat): 3123, 2950, 2237, 1620, 1387, 1182, 946, 903, 737 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.09 (dd, *J* = 8.3, 2.6 Hz,

2H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.68 (t, *J* = 6.8 Hz, 3H), 7.50 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, CDCl3) δ = 145.4, 135.8, 133.0, 131.4, 130.8, 130.5, 129.2, 126.0, 120.7, 111.8. HRMS: Calc. for $C_{12}H_9BrN_3O_2S$ $[M+H]^+$: 337.9599, Obser.: 337.9591.

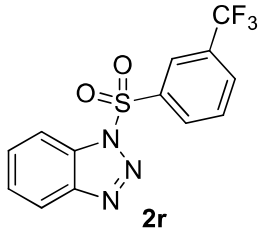
[3.7.17] 1-((4-Nitrophenyl)sulfonyl)-1*H*-benzo[d][1,2,3]triazole (2q)



2q

The title compound was obtained as a white solid. M.p. 180 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.60; Yield 89% (259 mg); IR (neat): 3160, 2872, 2360, 1525, 1391, 1225, 941, 739 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.37 (dd, *J* = 23.1, 8.6 Hz, 4H), 8.12 (d, *J* = 8.3 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 151.3, 145.4, 142.2, 131.4, 130.9, 129.3, 126.4, 124.8, 120.9, 111.7, HRMS: Calc. for $C_{12}H_9N_4O_4S$ $[M+H]^+$: 305.0345, Obser.: 305.0341.

[3.7.18] 1-((3-(Trifluoromethyl)phenyl)sulfonyl)-1*H*-benzo[d][1,2,3]triazole (2r)

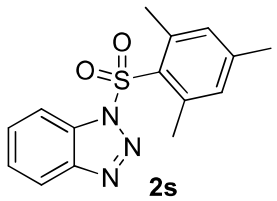


2r

The title compound was obtained as a white solid. M.p. 102 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.55; Yield 84% (275 mg); IR (neat): 3089,

2970, 2330, 1618, 1431, 1334, 1067, 970 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 8.19 (d, J = 7.8 Hz, 1H), 8.11 (dd, J = 6.5, 3.0 Hz, 2H), 7.70 (dd, J = 6.5, 2.9 Hz, 3H), 7.58 (t, J = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.3, 134.0, 131.1, 130.9, 130.5, 129.3, 127.6, 124.5, 123.1, 122.4, 114.0. HRMS: Calc. for $C_{13}H_9F_3N_3O_2S$ $[M+H]^+$: 328.0368, Obser.: 328.0359.

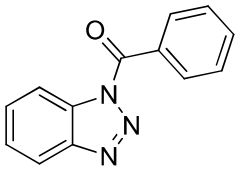
[3.7.19] 1-(Mesitylsulfonyl)-1*H*-benzo[d][1,2,3]triazole (2s)



2s

The title compound was obtained as a white solid. M.p. 121 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.64; Yield 85% (256 mg); IR (neat): 3130, 2852, 2320, 1575, 1391, 1080, 945, 770 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.10 (t, J = 7.3 Hz, 2H), 7.65 (t, J = 7.7 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.01 (s, 2H), 2.67 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.5, 144.7, 141.5, 132.4, 131.9, 131.4, 129.8, 125.4, 120.3, 112.2, 22.9, 21.0. HRMS: Calc. for $C_{15}H_{16}N_3O_2S$ $[M+H]^+$: 302.0963, Obser.: 302.0958.

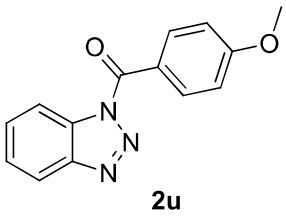
[3.7.20] (1*H*-Benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (2t)



2t

The title compound was obtained as a white solid. M.p. 112 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.66; Yield 95% (212 mg); IR (neat): 3164, 3050, 2940, 2345, 1730, 1060, 878 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.38 (d, J = 8.3 Hz, 1H), 8.21 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 8.3 Hz, 1H), 7.73–7.66 (m, 2H), 7.60–7.51 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.6, 145.6, 133.6, 132.2, 131.6, 131.4, 130.3, 128.3, 126.2, 120.1, 114.7. HRMS: Calc. for $C_{13}H_{10}N_3O$ $[M+H]^+$: 224.0824, Obser.: 224.0822.

[3.7.21] (1*H*-Benzo[d][1,2,3]triazol-1-yl)(4-methoxyphenyl)methanone (2u)

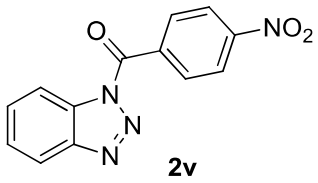


2u

The title compound was obtained as a white solid. M.p. 111 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.66; Yield 92% (233 mg); IR (neat): 3164, 2919, 2334, 1709, 1605, 1440, 1361, 1226, 980, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.39 (d, J = 8.3 Hz, 1H), 8.32 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.8 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ =

165.6, 164.1, 145.6, 134.3, 132.5, 130.1, 126.0, 123.4, 120.0, 114.8, 113.8, 55.5. HRMS: Calc. for $C_{14}H_{12}N_3O_2$ $[M+H]^+$: 254.0930, Obser.: 254.0928.

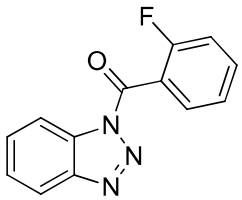
[3.7.22] (1*H*-Benzo[d][1,2,3]triazol-1-yl)(4-nitrophenyl)methanone (2v)



2v

The title compound was obtained as a white solid. M.p. 193 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.66; Yield 90% (241 mg); IR (neat): 3281, 2899, 2358, 1702, 1514, 1342, 1267, 1097, 773, 741 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.43 (d, J = 11.6 Hz, 5H), 8.23 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.0 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.9, 150.4, 145.8, 136.8, 132.6, 131.9, 131.0, 126.9, 123.4, 120.5, 114.7. HRMS: Calc. for $C_{13}H_9N_4O_3$ $[M+H]^+$: 269.0675, Obser.: 269.0674.

[3.7.23] (1*H*-Benzo[d][1,2,3]triazol-1-yl)(2-fluorophenyl)methanone (2w)

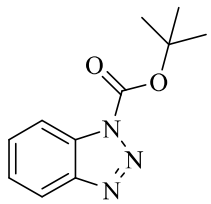


2w

The title compound was obtained as a white solid. M.p. 115 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.58; Yield 88% (212 mg); IR (neat): 3164, 3079, 2919, 2340, 1709, 1605, 1449, 1361, 1219, 940, 728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.41 (d, J =

8.2 Hz, 1H), 8.18 (d, J = 8.3 Hz, 1H), 7.81 (t, J = 7.1 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.67 (dd, J = 13.4, 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 18.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.0, 159.2, 146.0, 134.4, 131.3, 131.1, 130.4, 126.4, 124.1, 120.1, 116.4, 116.2, 114.2. HRMS: Calc. for $C_{13}H_9FN_3O$ $[M+H]^+$: 242.0730, Obser.: 242.0724.

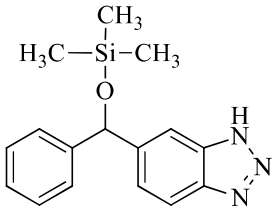
[3.7.24] *tert*-Butyl 1*H*-benzo[d][1,2,3]triazole-1-carboxylate (2x)



2x

The title compound was obtained as a yellow solid. M.p. 62 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.58; Yield 95% (208 mg); IR (neat): 3160, 3050, 2943, 2335, 1730, 1220, 1070, 840 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3) δ = 8.07 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.61–7.55 (m, 1H), 7.46–7.40 (m, 1H), 1.73 (s, 9H). ^{13}C NMR (125 MHz, CDCl3) δ = 147.1, 145.7, 131.5, 129.7, 125.3, 120.1, 113.4, 86.8, 27.9. HRMS: Calc. for $C_{11}H_{14}N_3O_2$ $[M+H]^+$: 220.1086, Obser.: 220.1083.

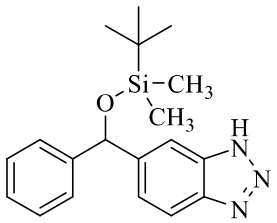
[3.7.25] 6-(Phenyl((trimethylsilyl)oxy)methyl)-1*H*-benzo[d][1,2,3]triazole (2y)



2y

The title compound was obtained as colorless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.38; Yield 90% (267 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.41–7.25 (m, 6H), 5.94 (s, 1H), 0.11 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.1, 143.7, 128.3, 127.4, 126.6, 125.4, 76.3, 0.09. HRMS: Calc. for $C_{16}H_{20}N_3OSi$ $[M+H]^+$: 298.1376, Obser.: 298.1372.

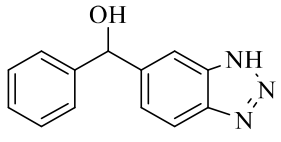
[3.7.26] 6-(*tert*-Butyldimethylsilyl)oxy)(phenyl)methyl)-1*H*- benzo[d][1,2,3]triazole (2z)



2z

The title compound was obtained as yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.40; Yield 93% (316 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.01 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 13.3, 8.0 Hz, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 5.92 (s, 1H), 0.92 (s, 9H), −0.01 (d, J = 1.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.5, 144.0, 139.2, 128.3, 127.2, 126.3, 125.2, 115.1, 76.5, 25.7, 18.2, −4.8 (d, J = 1.8 Hz). . HRMS: Calc. for $C_{19}H_{26}N_3OSi$ $[M+H]^+$: 340.1845, Obser.: 340.1840.

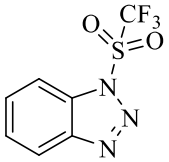
[3.7.27] (1*H*-Benzo[d][1,2,3]triazol-6-yl)(phenyl)methanol (2aa)



2aa

The title compound was obtained as a brown liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.58; Yield 69% (155 mg); IR (neat): 3140, 3040, 2860, 2400, 2347, 1630, 1390, 1225, 1060 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ = 15.66 (s, 1H), 8.32–7.47 (m, 3H), 7.44 (d, J = 7.4 Hz, 2H), 7.31 (dd, J = 10.6, 4.7 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.13 (s, 1H), 5.92 (d, J = 2.8 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 145.3, 143.5, 133.0, 128.8, 128.2, 126.9, 126.4, 123.0, 118.3, 115.3, 110.6, 107.4, 79.2, 74.1. . HRMS: Calc. for $C_{13}H_{12}N_3O$ $[M+H]^+$: 226.0980, Obser.: 226.0978.

[3.7.28] 1-(Trifluoromethyl)sulfonyl)-1*H*-benzo[d][1,2,3]triazole (2ab)



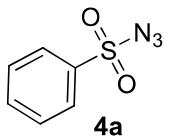
2ab

The title compound was obtained as a yellow solid. M.p. 62 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.62; Yield 75% (188 mg); IR (neat): 3080, 2968, 2332, 1618, 1401, 1334, 1070, 960 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.23 (dt, J = 8.3, 0.8 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.80–7.77 (m, 1H), 7.65–7.62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.4, 131.9,

127.2, 121.4, 120.4, 117.8, 111.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ = −74.6. HRMS: Calc. for $C_5H_5F_3N_3O_2$ $[M+H]^+$: 252.0055, Obser.: 252.0054.

[3.8.] Anitical data of azide products

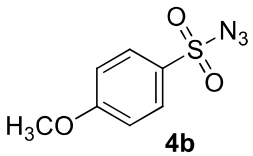
[3.8.1] Benzenesulfonyl azide (4a)



4a

The title compound was obtained as white solid. M.p. 153-155 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.59; Yield: 95% (173 mg); IR (neat): 3068, 2128, 1574, 1475, 1298, 1170, 1068, 1024, 1001 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, J = 8.0 Hz, 2H), 7.71 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.2, 134.7, 129.6, 127.3. HRMS: Calc. for $C_6H_6N_3O_2S$ $[M+H]^+$: 184.0181, Obser.: 184.0180.

[3.8.2] 4-Methoxy benzenesulfonyl azide (4b)

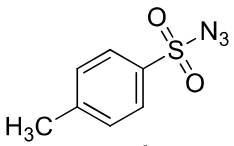


4b

The title compound was obtained as pale yellow solid. M.p. 55 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.60; Yield: 97% (206 mg); IR (neat): 2949, 2832, 2129, 1577, 1497, 1442, 1369, 1351, 1319, 1272, 1088, 1021 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ =

7.91 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.5, 129.8, 129.7, 114.7, 55.8. HRMS: Calc. for $C_7H_8N_3O_3S$ $[M+H]^+$: 214.0286, Obser.:214.0279.

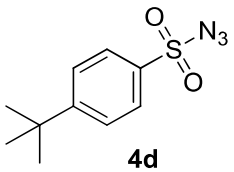
[3.8.3] 4-Methyl benzenesulfonyl azide (4c)



4c

The title compound was obtained as white solid. M.p. 22 °C. The esidue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.55; Yield: 94% (185 mg); IR (neat): 2943, 2829, 2123, 1565, 1489, 1349, 1309, 1261, 1078, 1019 cm^{-1}. 1H NMR (500 MHz, $CDCl_3$) δ = 7.79 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ = 146.1, 135.3, 130.2, 127.4, 21.6. HRMS: Calc. for $C_7H_8N_3O_2S$ $[M+H]^+$: 198.0337, Obser.:198.0335.

[3.8.4] 4-(*tert*-butyl)benzenesulfonyl azide (4d)

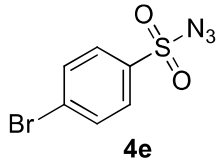


4d

The title compound was obtained as a pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.52; Yield 82% (196 mg); IR (neat): 3060, 2900, 2869, 2123, 1593, 1404, 1365, 1297, 1110, 1079, 1010 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3) δ = 7.90 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 1.39 (s, 4H). ^{13}C NMR (125 MHz,

$CDCl_3$) δ = 159.0, 135.4, 127.3, 126.6, 30.9. HRMS: Calc. for $C_{10}H_{14}N_3O_2S$ $[M+H]^+$: 240.0807, Obser.:240.0805.

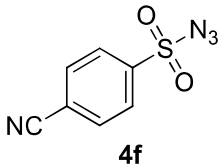
[3.8.5] 4-Bromobenzenesulfonyl azide (4e)



4e

The title compound was obtained as white solid. M.p. 53-53.5 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.52; Yield 92% (239 mg); IR (neat): 2832, 2821, 2120, 1562, 1480, 1355, 1342, 1300, 1069, 1011 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.84 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 137.3, 133.0, 130.2, 128.8. HRMS: Calc. for $C_6H_5BrN_3O_2S$ $[M+H]^+$: 261.9286, Obser.:261.9285.

[3.8.6] 4-Cyano benzenesulfonyl azide (4f)

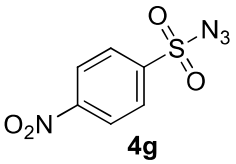


4f

The title compound was obtained as a white solid. M.p. 82 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.54; Yield 85% (177 mg); IR (neat): 2968, 2832, 2122, 1565, 1489, 1329, 1262, 1078, 1001 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.10 (d, J = 8.3 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 142.1, 133.4, 128.0, 118.4, 116.6. HRMS: Calc. for

$C_7H_5N_4O_2S$ $[M+H]^+$: 209.0133, Obser.:209.0131.

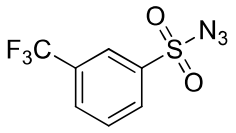
[3.8.7] 4-Nitro benzenesulfonyl azide (4g)



4g

The title compound was obtained as a white solid. M.p. 100-101 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.55; Yield 90% (205 mg); IR (neat): 3100, 2132, 1531, 1463, 1398, 1372, 1343, 1307, 1172, 1068, 1011 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.49 (d, J = 9.2 Hz, 2H), 8.19 (d, J = 9.2 Hz, 2H). (125 MHz, $CDCl_3$) δ = 151.2, 143.7, 128.8, 124.9. HRMS: Calc. For $C_6H_5N_4O_4S$ $[M+H]^+$: 229.0032, Obser.:229.0029.

[3.8.8] 3-(Trifluoromethyl)benzenesulfonyl azide (4h)

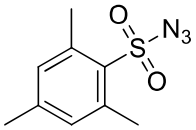


4h

The title compound was obtained as white solid. M.p. 30 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.56; Yield 89% (223 mg); IR (neat): 3100, 2850, 2129, 1531, 1463, 1398, 1362, 1323, 1307, 1172, 1068, 745 cm^{-1}. ^1H NMR (500 MHz, CDCl3) δ = 8.24 (s, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 139.6, 132.9, 132.6, 132.3, 132.1, 131.4, 131.4, 131.3, 131.3, 130.6, 130.6, 126.0, 124.6, 124.5, 124.5, 124.5, 123.8, 121.7,

119.5. HRMS: Calc. for $C_7H_5F_3N_3O_2S$ $[M+H]^+$: 252.0055, Obser.:252.0054.

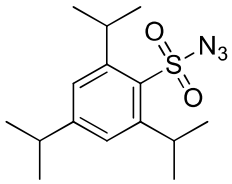
[3.8.9] 2,4,6-Trimethylbenzenesulfonyl azide (4i)



4i

The title compound was obtained as a yellow solid. M.p. 79-80 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (90:10), R_f = 0.60; Yield 88% (198 mg); IR (neat) 3273, 2982, 2933, 2352, 2123, 1451, 1400, 1352, 1117, 1101, 1156, 1042, 1031 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.04 (s, 2H), 2.68 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ = 144.5, 139.9, 133.1, 132.1, 22.7, 21.0. HRMS: Calc. for $C_9H_{12}N_3O_2S$ $[M+H]^+$: 226.0650, Obser.:226.0647.

[3.8.10] 2,4,6-Triisopropylbenzenesulfonyl azide (4j)

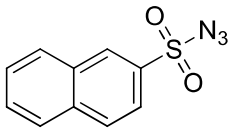


4j

The title compound was obtained as yellow oil. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.63; Yield 85% (262 mg); IR (neat) 2960, 2922, 2870 2120, 1569, 1420, 1370, 1362, 1350, 1256, 1167, 1100, 1032 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.25 (s, 2H), 4.08 (m, 2H), 3.03–2.87 (m, 1H), 1.30 (d, J = 10.2 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.2, 150.8, 132.0, 124.1, 34.3,

29.8, 24.7, 23.4. HRMS: Calc. for $C_{15}H_{24}N_3O_2S$ $[M+H]^+$: 310.1589, Obser.:310.1587.

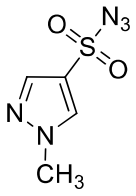
[3.7.2.11] Naphthalene-2-sulfonyl azide (4k)



4k

The title compound was obtained as yellow solid. M.p. 53 °C. The residue was purified by column chromatography in silica gel eluting with hexane:EtOAc (95:5), R_f = 0.60; Yield 82% (191 mg); IR (neat) 3053, 2132, 1589, 1450, 1368, 1232, 1160, 1130, 1071, 1011 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.59 (d, J = 8.6 Hz, 1H), 8.37 (d, J = 7.3 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 136.2, 134.2, 133.4, 130.0, 129.0, 128.0, 127.5, 124.3, 123.9. HRMS: Calc. for $C_{10}H_8N_3O_2S$ $[M+H]^+$: 234.0337, Obser.:234.0334.

[3.8.12] 1-Methyl-1H-pyrazole-4-sulfonyl azide (4l)

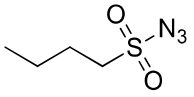


4l

The title compound was obtained as pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.65; Yield 89% (166 mg); IR (neat): 3053, 2132, 1589, 1450, 1368, 1262, 1140, 1071, 1011 cm^{-1}. ^1H NMR (500 MHz, CDCl3) δ = 7.99 (s, 1H), 7.92 (s, 1H), 4.02 (s, 3H). ^{13}C

NMR (125 MHz, CDCl3) δ = 139.0, 132.7, 120.3, 39.9. HRMS: Calc. for $C_6H_6N_5O_2S$ $[M+H]^+$: 188.0242, Obser.:188.0237.

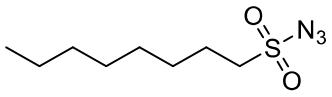
[3.8.13] Butane-1-sulfonyl azide (4m)



4m

The title compound was obtained as pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.60; Yield 81% (132 mg); ^{1}H NMR (500 MHz, CDCl3) δ = 3.32–3.29 (m, 2H), 1.90–1.87 (m, 2H), 1.49 (d, J = 7.3 Hz, 2H), 0.96 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ = 55.60, 25.17, 21.15, 13.30. HRMS: Calc. for $C_4H_{10}N_3O_2S$ $[M+H]^+$: 164.0494, Obser.:164.0492.

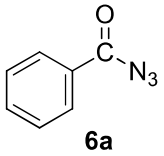
[3.8.14] Octane-1-sulfonyl azide (4n)



4n

The title compound was obtained as a yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.62; Yield 82% (180 mg); ^{1}1H NMR (500 MHz, CDCl3) δ = 3.30–3.27 (m, 2H), 1.88 (s, 2H), 1.43 (s, 2H), 1.27 (d, J = 12.1 Hz, 8H), 0.86 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ = 55.84, 31.54, 28.76, 27.82, 23.24, 22.46, 13.90. HRMS: Calc. for $C_8H_{18}N_3O_2S$ $[M+H]^+$: 220.1120, Obser.:220.1112.

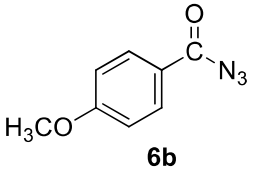
[3.8.15] Benzoyl azide (6a)



6a

The title compound was obtained as a white solid. M.p. 32 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.67; Yield 87% (128 mg); IR (neat): 3053, 2867, 2173, 2168, 2127, 1695, 1682, 1599, and 1453 cm^{-1}. ^1H NMR (500 MHz, CDCl3) δ = 8.03 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H). ^{13}C NMR (125 MHz, CDCl3) δ = 172.5, 134.3, 130.6, 129.4, 128.6. HRMS: Calc. for $C_7H_6N_3O$ $[M+H]^+$: 148.0511, Obser.:148.0510.

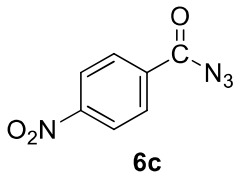
[3.8.16] 4-Methoxybenzoyl azide (6b)



6b

The title compound was obtained as a white solid. M.p. 69-70 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.66; Yield 80% (141 mg); IR (neat): 3011, 2983, 2179, 2143, 1677, 1584, 1500 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, CDCl3) δ = 171.8, 164.8, 131.9, 125.7, 123.4, 114.9, 114.1, 55.7. HRMS: Calc. for $C_8H_8N_3O_2$ $[M+H]^+$: 178.0617, Obser.:178.0615.

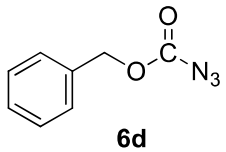
[3.8.17] 4-Nitrobenzoyl azide (6c)



6c

The title compound was obtained as a white solid. M.p. 71–72 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.66; Yield 84% (161 mg); IR (neat): 3108, 3091, 2181, 2180, 2123, 1746, 1678, 1687, 1545 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.30 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.8, 151.2, 135.6, 130.5, 123.7. HRMS: Calc. for $C_7H_5N_4O_3$ $[M+H]^+$: 193.0362, Obser.:193.0351.

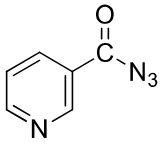
[3.8.18] Benzyl carbonazidate (6d)



6d

The title compound was obtained as a colorless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.66; Yield 81% (143 mg); IR (neat): 3100, 2970, 2181, 2170, 2123, 1746, 1678, 1587, 1080 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3) δ = 7.40 (s, 5H), 5.25 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 157.4, 134.3, 128.8, 128.7, 128.5, 70.0. HRMS: Calc. for $C_8H_8N_3O_2$ $[M+H]^+$: 178.0617 Obser.: 178.0615.

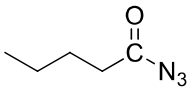
[3.8.19] Isonicotinoyl azide (6e)



6e

The title compound was obtained as an orange solid. M.p. 45–46 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.66; Yield 85% (125 mg); IR (neat): 2920, 2850, 2183, 2142, 1715, 1563, 1404, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.77 (d, J = 5.7 Hz, 1H), 7.78 (d, J = 5.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.4, 150.7, 137.3, 122.1. HRMS: Calc. for $C_6H_5N_4O$ $[M+H]^+$: 149.0463 Obser.:149.0458.

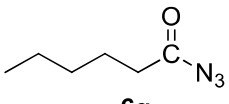
[3.8.20] Pentanoyl azide (6f)



6f

The title compound was obtained as yellow oil. Pentanoyl azide was found very unstable, hence could not be isolated. However, a complete conversion of pentanoyl hydrazide into pentanoyl azide was observed in TLC.

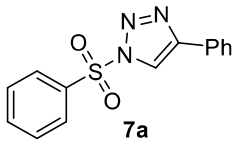
[3.8.21] Hexanoyl azide (6g)



6g

The title compound was obtained as yellow oil. Hexanoyl azide was found very unstable, hence could not be isolated. However, a complete conversion of hexanoyl hydrazide into hexanoyl azide was observed in TLC.

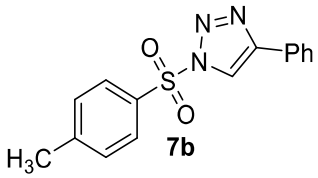
[3.8.22] 4-phenyl-1-(phenylsulfonyl)-1H-1,2,3-triazole (7a)



7a

The title compound was obtained as a white solid. M.p. 109 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.43; Yield 81% (230 mg); IR (neat): 2955, 1367, 1173, 1092. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.86 (d, J = 7.3 Hz, 2H), 7.59 (s, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.24 (t, J = 7.9 Hz, 2H), 7.16–7.09 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.8, 136.4, 132.9, 129.2, 128.9, 127.1, 125.2, 121.4. HRMS: Calc. for $C_{14}H_{12}N_3O_2S$ $[M+H]^+$: 286.0650, Obser.: 286.0648.

[3.8.23] 4-Phenyl-1-tosyl-1H-1,2,3-triazole (7b)

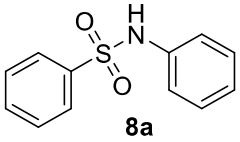


7b

The title compound was obtained as a white solid. M.p. 89 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.42; Yield 83% (248 mg); IR (neat): 3037, 1336, 1170, 1105. ^{1}H NMR (500 MHz, CDCl3) δ = 7.74 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.33–7.28 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.02–6.98 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.1, 135.7, 135.3, 132.2, 129.7, 127.1, 122.7, 118.2, 21.4. HRMS: Calc. for

$C_{15}H_{14}N_3O_2S$ $[M+H]^+$: 300.0807, Obser.: 300.0805.

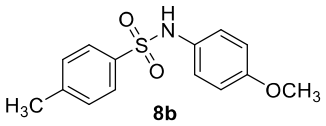
[3.8.24] *N*-Phenylbenzenesulfonamide (8a)



8a

The title compound was obtained as a white solid. M.p. 104 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.38; Yield 85% (198 mg); IR (neat): 3186, 1355, 1167. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.33–7.28 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.02–6.98 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.1, 135.7, 135.3, 132.2, 129.7, 127.1, 122.7, 118.2, 21.4. HRMS: Calc. for $C_{12}H_{12}NO_2S$ $[M+H]^+$: 234.0589, Obser.: 234.0584.

[3.8.25] 4-Methoxy-*N*-(*p*-tolyl)benzenesulfonamide (8b)

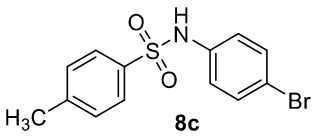


8b

The title compound was obtained as a white solid. M.p. 113–115 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.43; Yield 80% (221 mg); IR (neat): 3189, 1346, 1169. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.33–7.28 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.02–6.98 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.1, 135.7, 135.3, 132.2, 129.7, 127.1, 122.7, 118.2, 21.4. HRMS: Calc. for $C_{14}H_{16}NO_3S$

$[M+H]^+$: 278.0851, Obser.: 278.0848.

[3.8.26] 4-Bromo-*N*-(*p*-tolyl)benzenesulfonamide (8c)



8c

The title compound was obtained as a white solid. M.p. 147.5 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (95:5), R_f = 0.66; Yield 84% (272 mg); IR (neat): 3184, 1344, 1165. ^{1}H NMR (500 MHz, CDCl3) δ = 7.74 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.33–7.28 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.02–6.98 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.1, 135.7, 135.3, 132.2, 129.7, 127.1, 122.7, 118.2, 21.4. HRMS: Calc. for $C_{13}H_{13}BrNO_2S$ $[M+H]^+$: 325.9850, Obser.: 325.9847.

3.9 Spectral data for few products

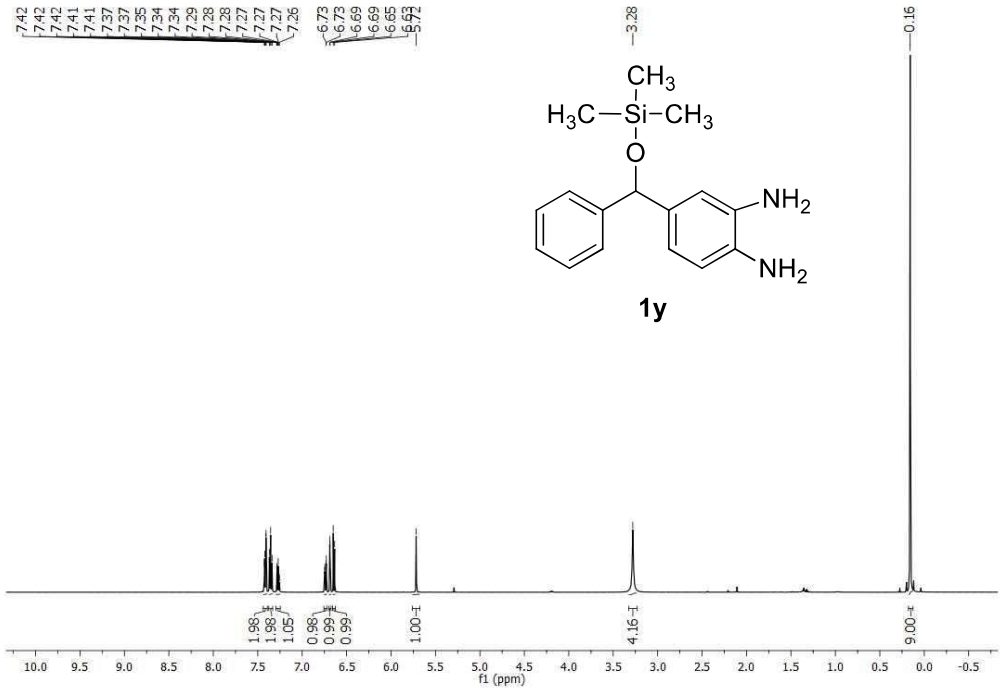


Figure 3.2 ^{1}H NMR of product **1y** in $CDCl_3$

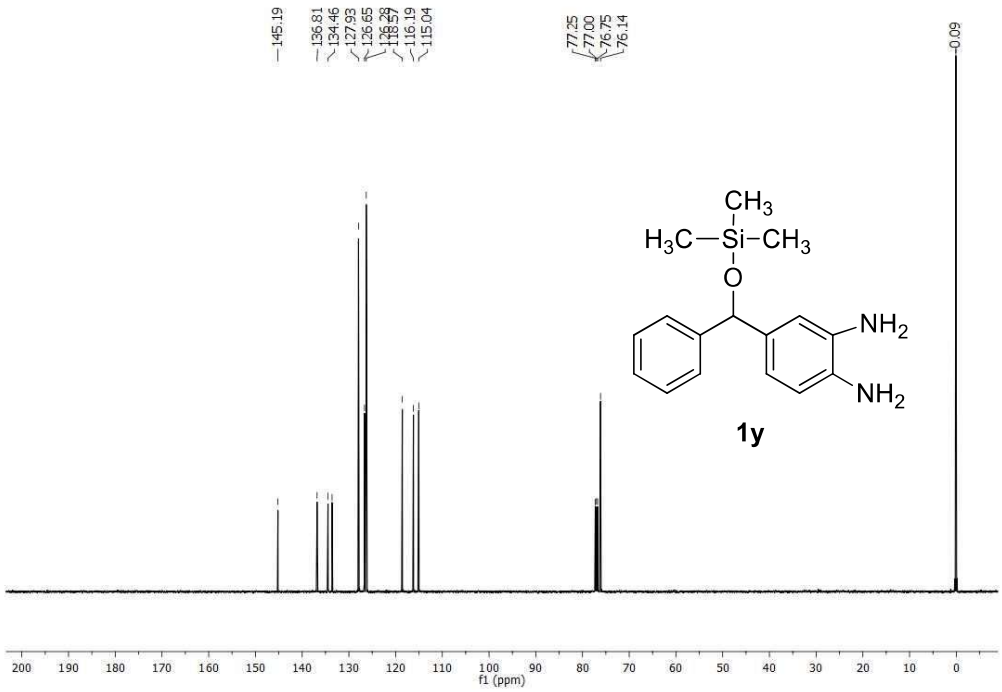


Figure 3.3 ^{13}C NMR of product **1y** in $CDCl_3$

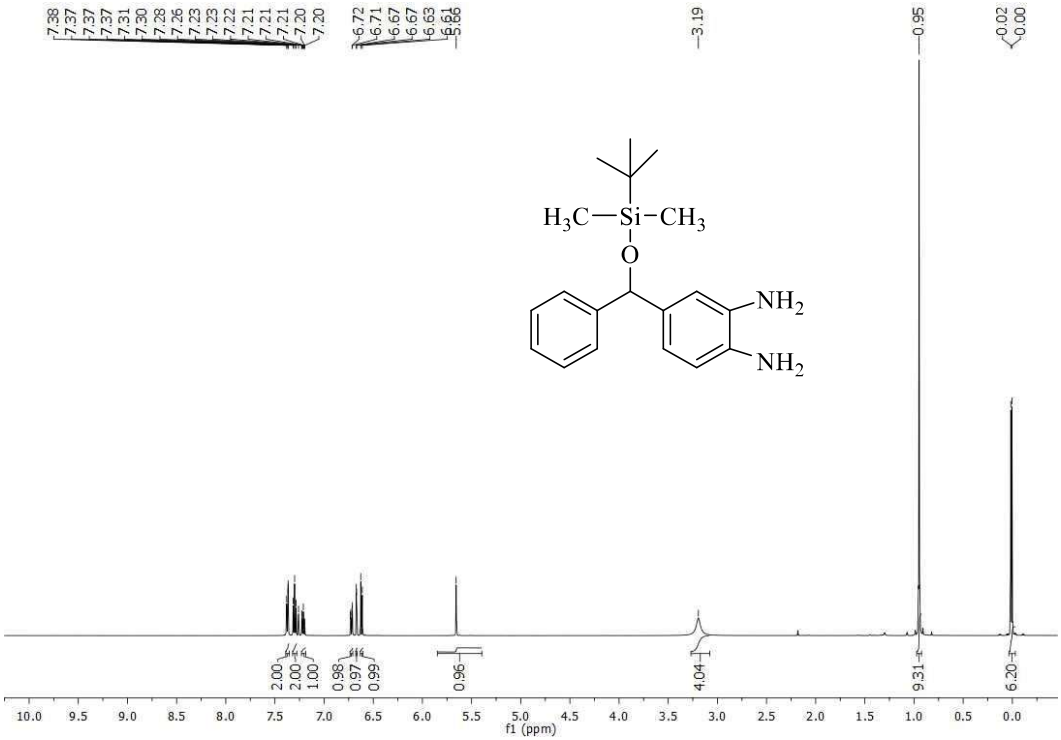


Figure 3.4 ^{1}H NMR of product **1z** in $CDCl_3$

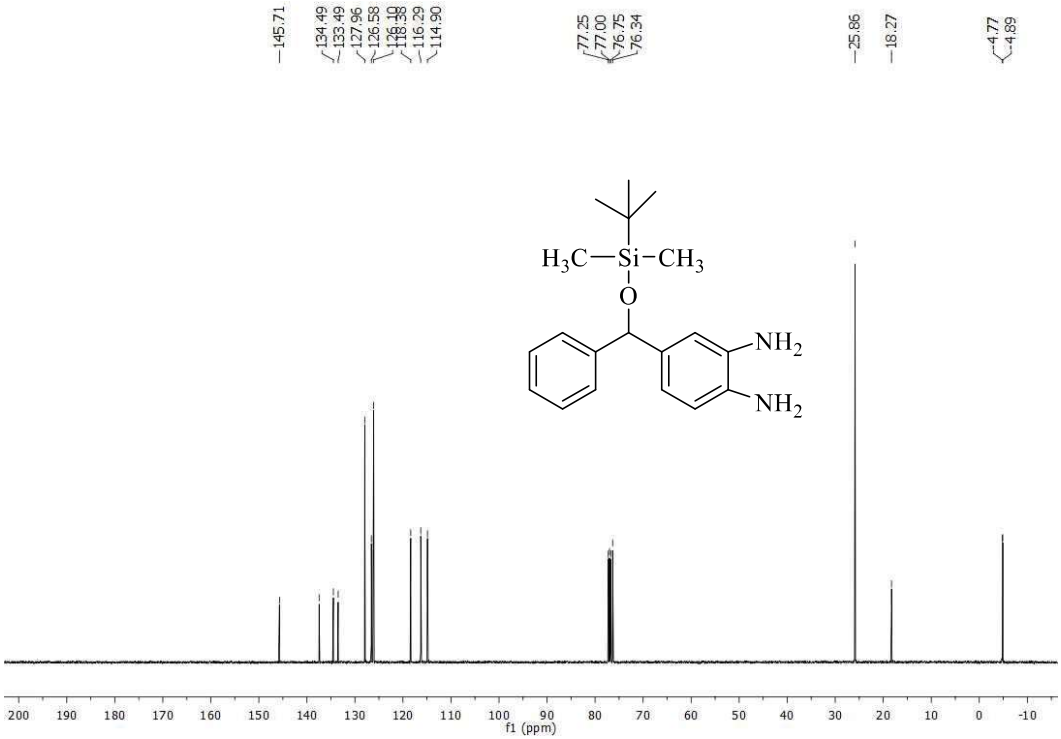


Figure 3.5 ^{13}C NMR of product **1z** in $CDCl_3$

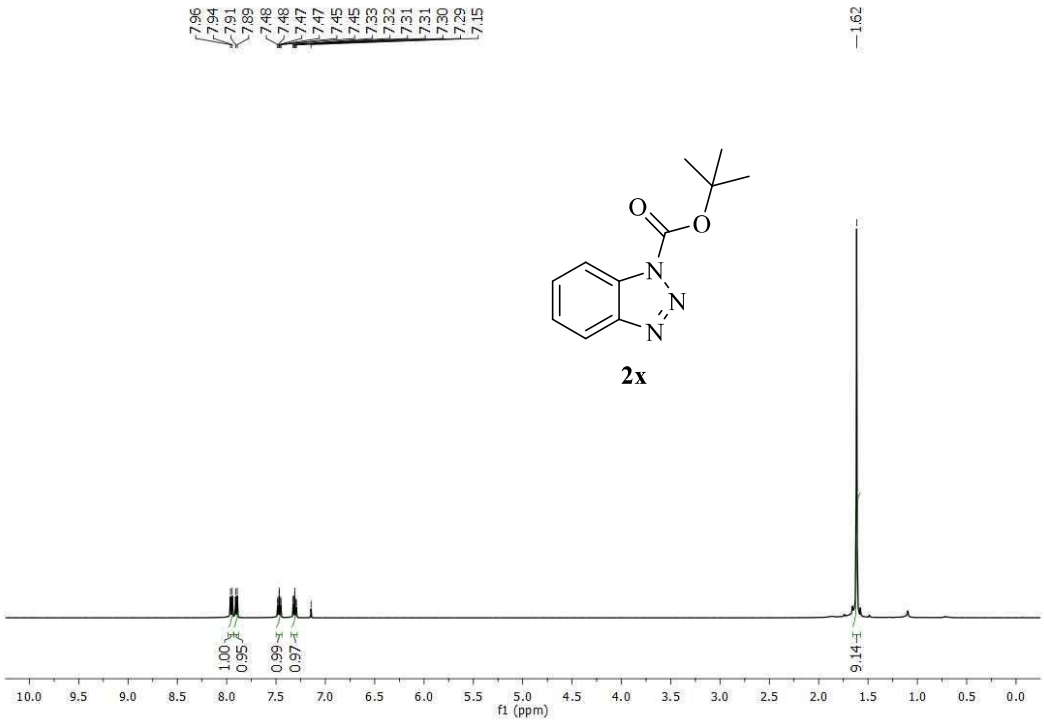


Figure 3.6 ^{1}H NMR of product **2x** in $CDCl_3$

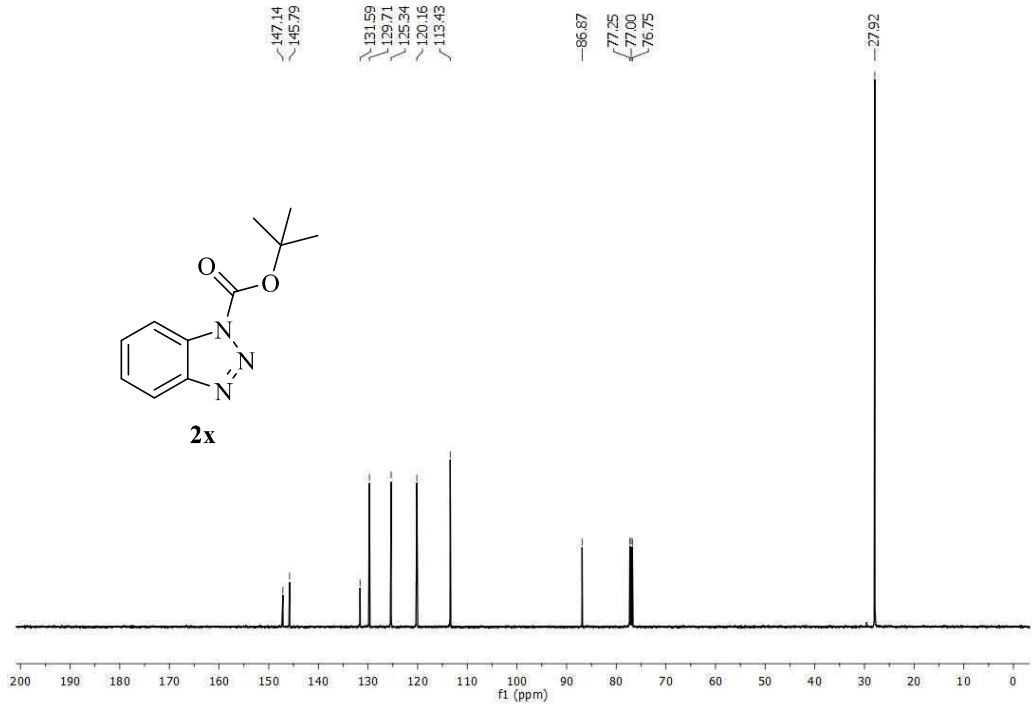


Figure 3.7 ^{13}C NMR of product **2x** in $CDCl_3$

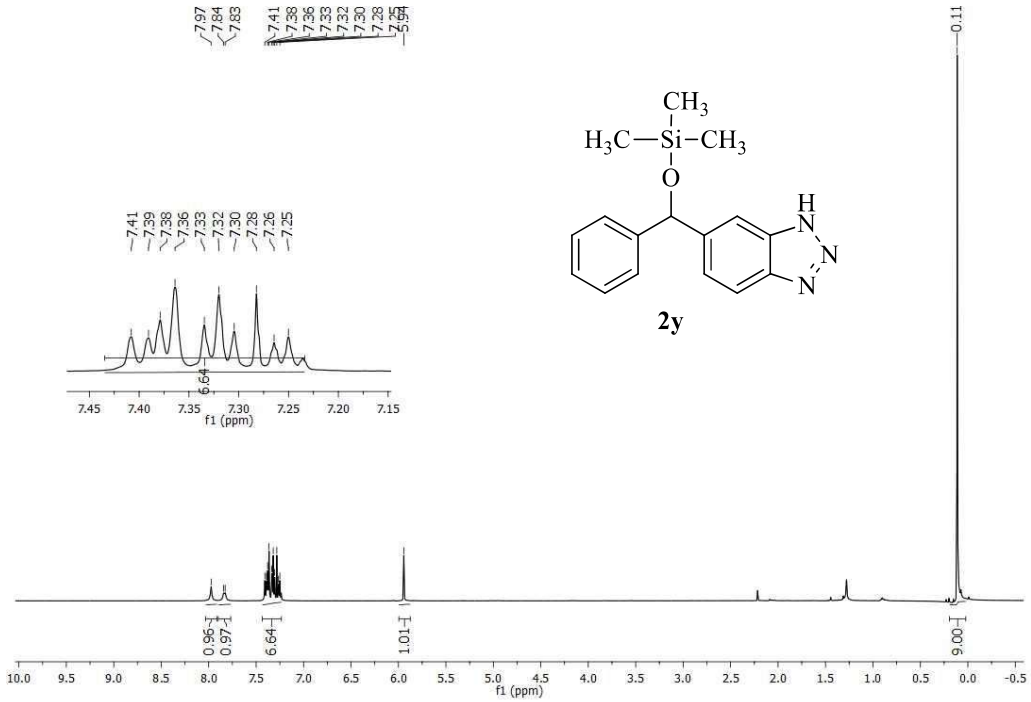


Figure 3.8 ^{1}H NMR of product **2y** in $CDCl_3$

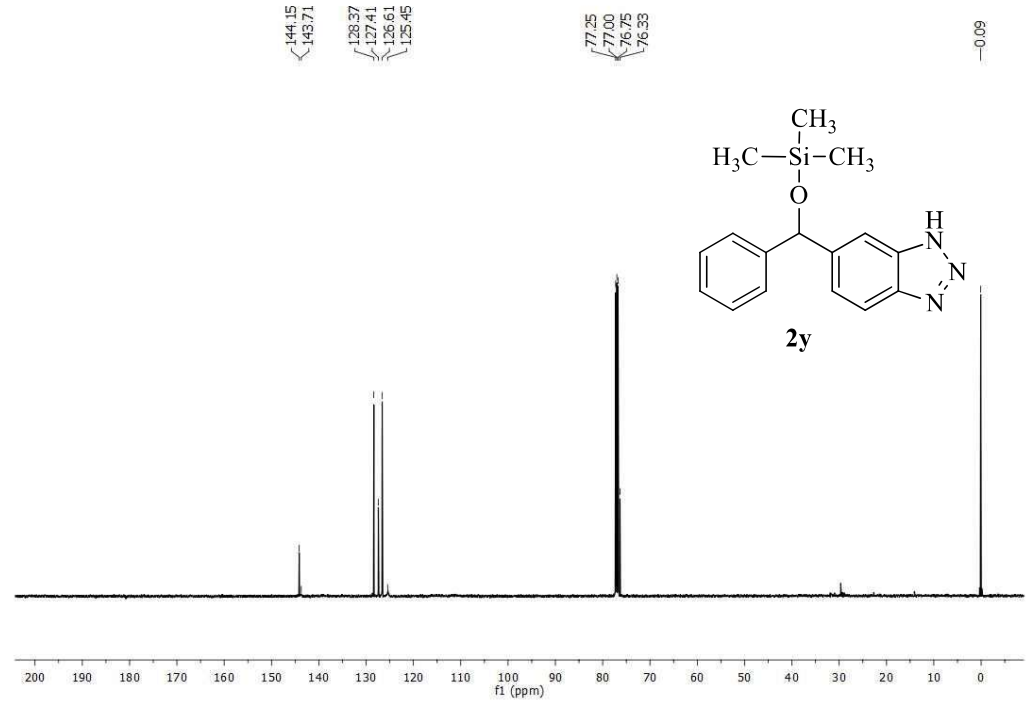


Figure 3.9 ^{13}C NMR of product **2y** in $CDCl_3$

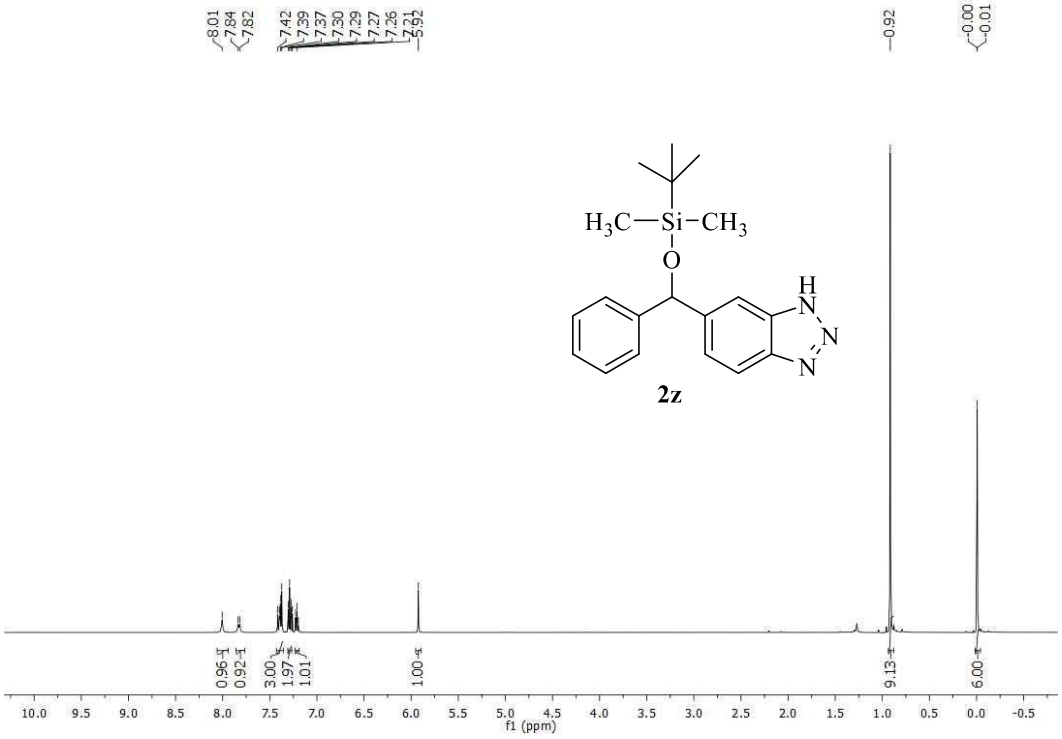


Figure 3.10 ^{1}H NMR of product **1z** in $CDCl_3$

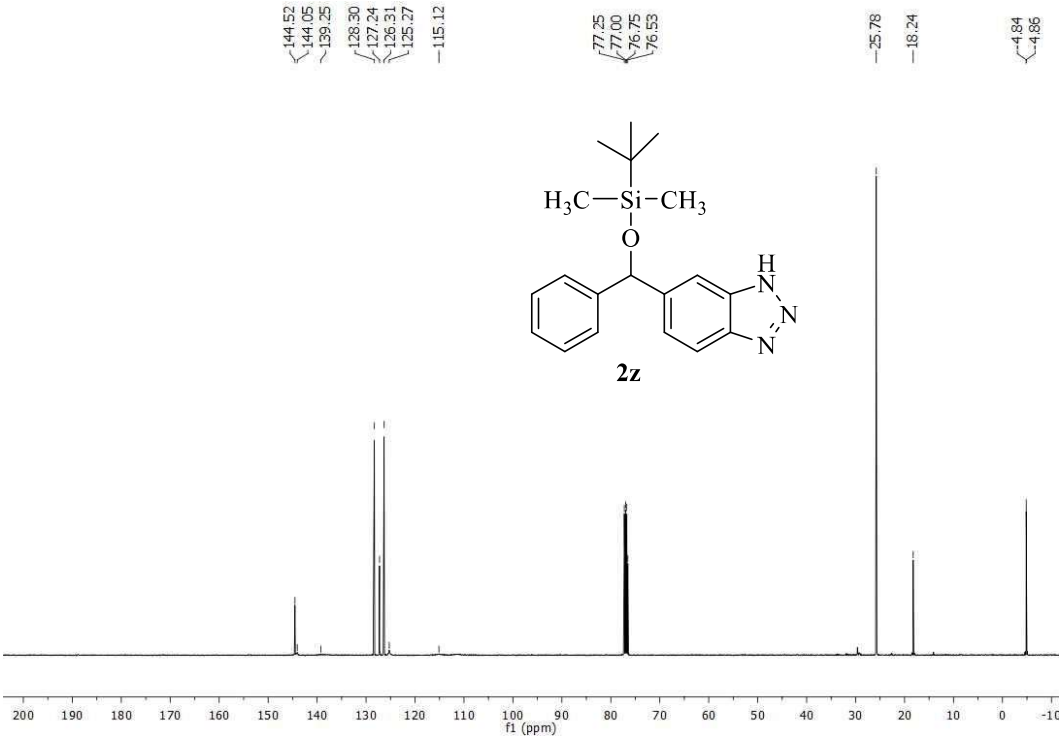


Figure 3.11 ^{13}C NMR of product **2z** in $CDCl_3$

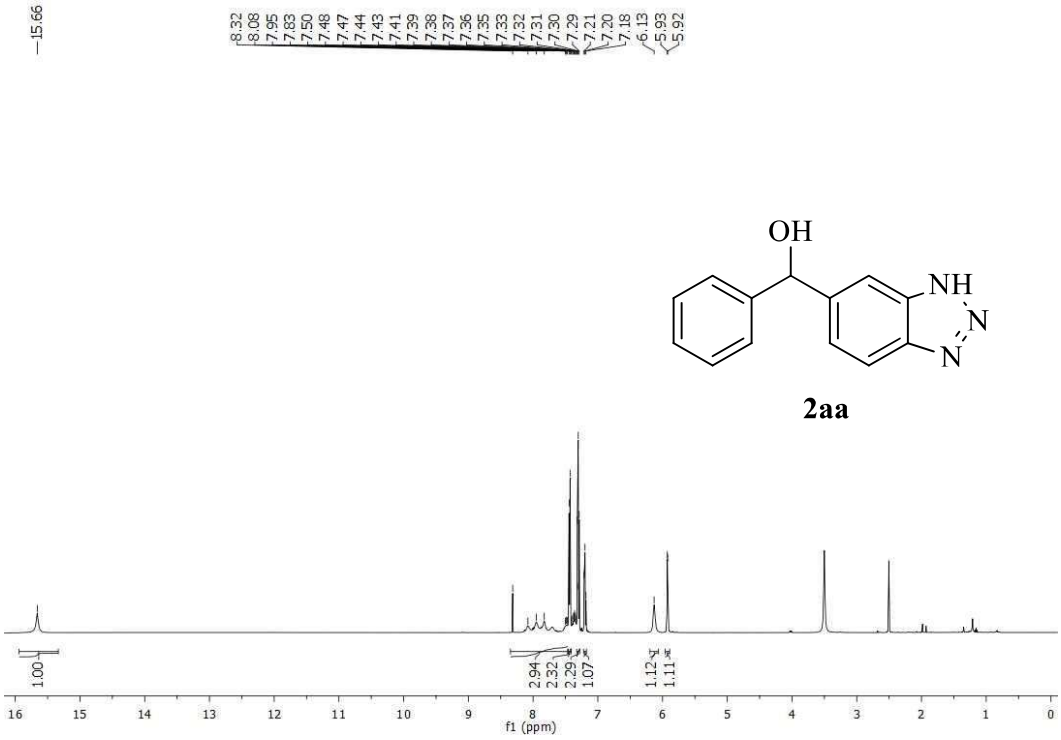


Figure 3.12 ^{1}H NMR of product **2aa** in DMSO-d_6

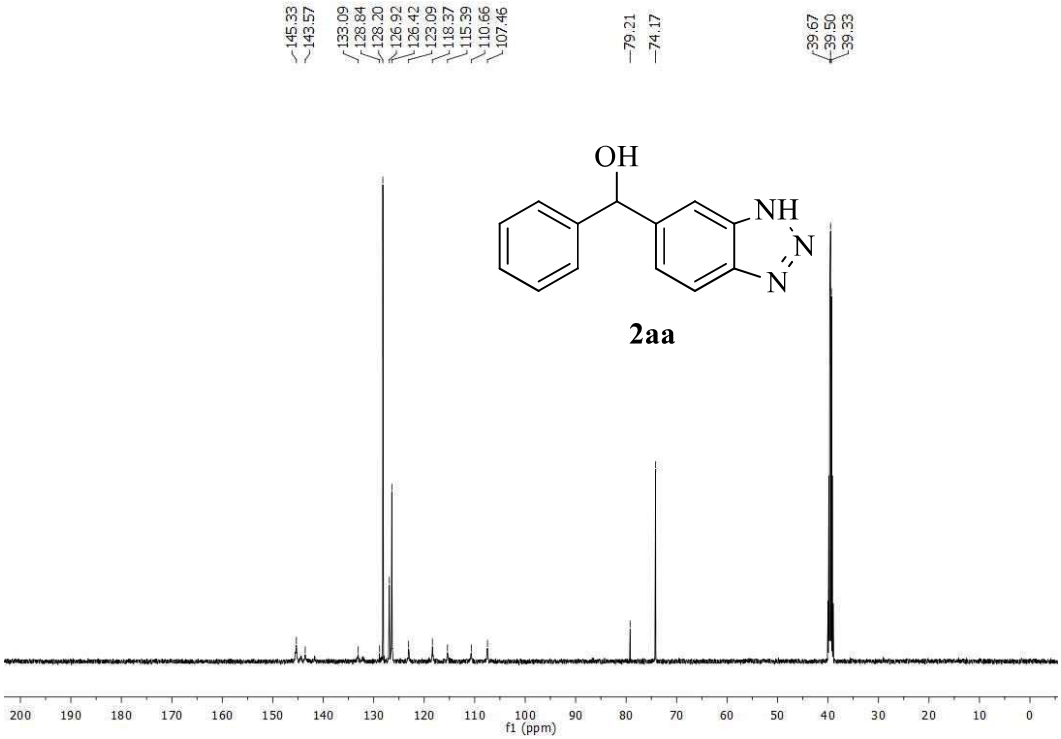


Figure 3.13 ^{13}C NMR of product **2aa** in DMSO-d_6

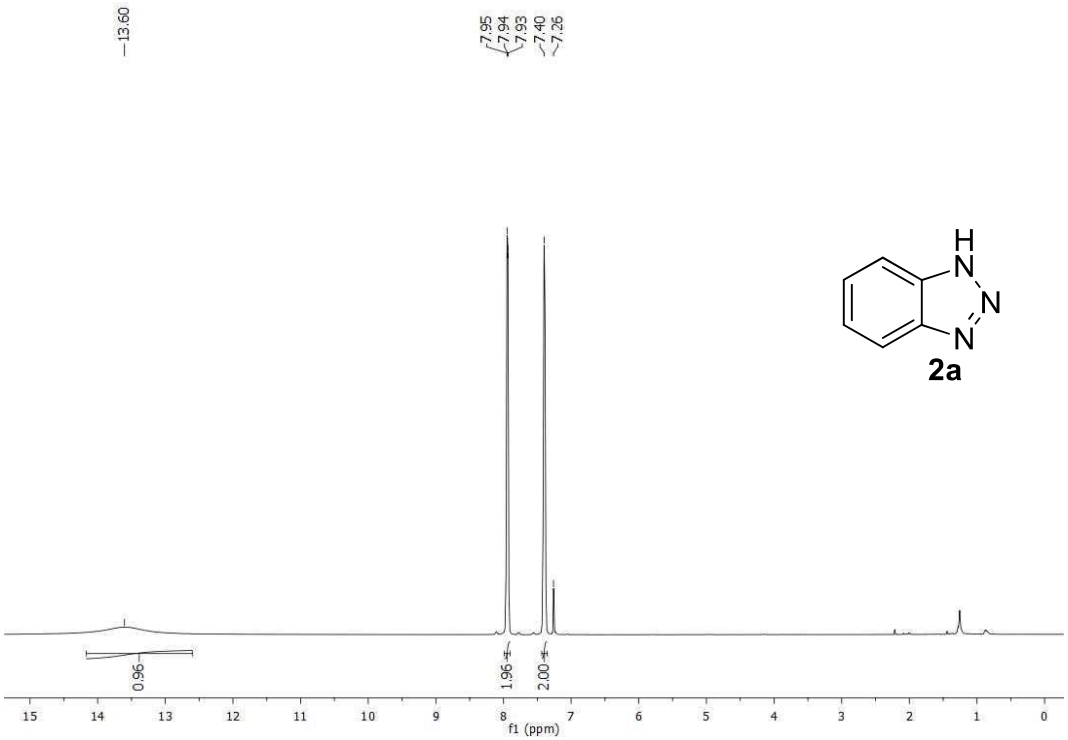


Figure 3.14 ^{1}H NMR of product **2a** in $CDCl_3$

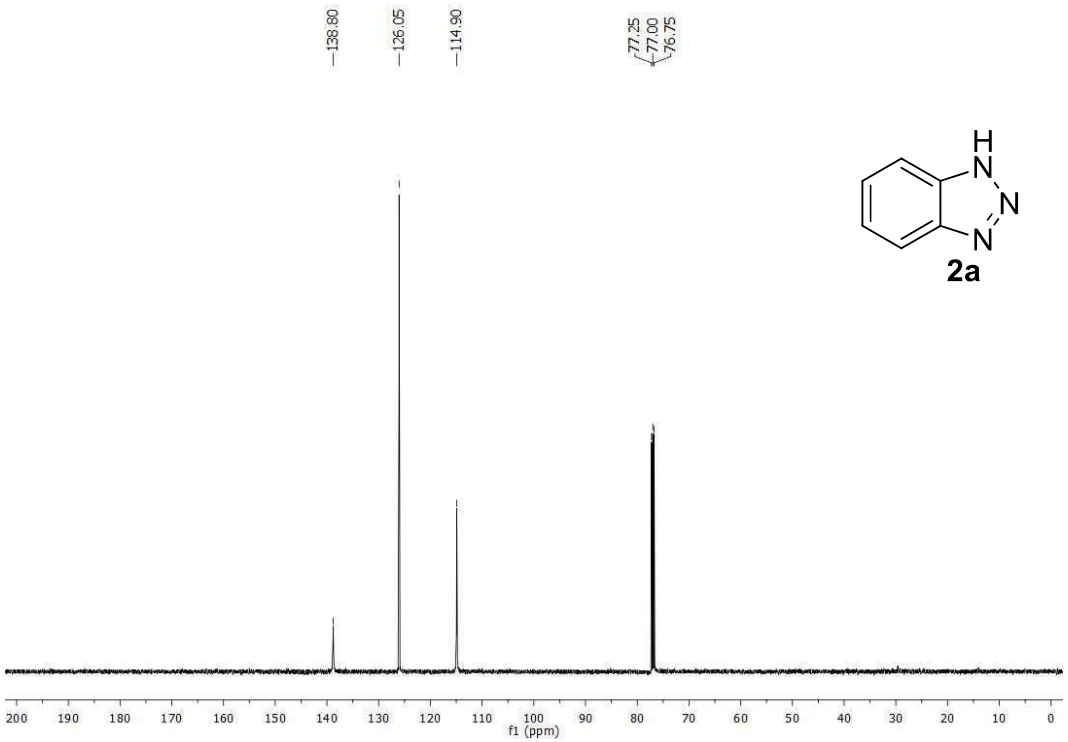


Figure 3.15 ^{13}C NMR of product **2a** in $CDCl_3$

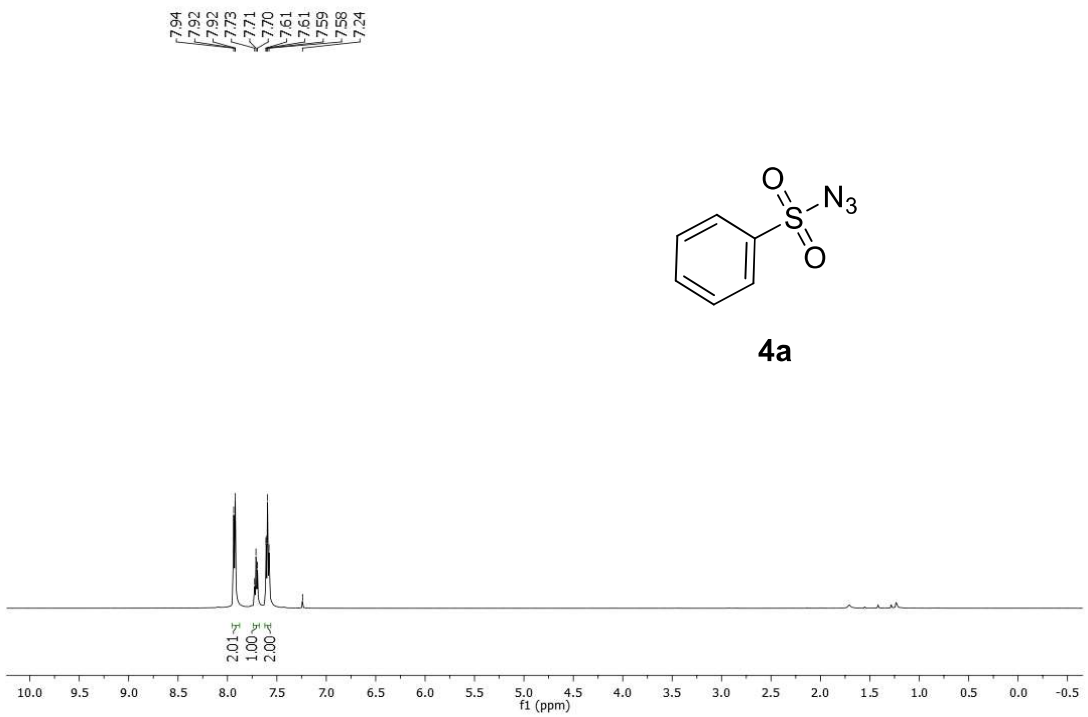


Figure 3.16 ^{1}H NMR of product **4a** in $CDCl_3$

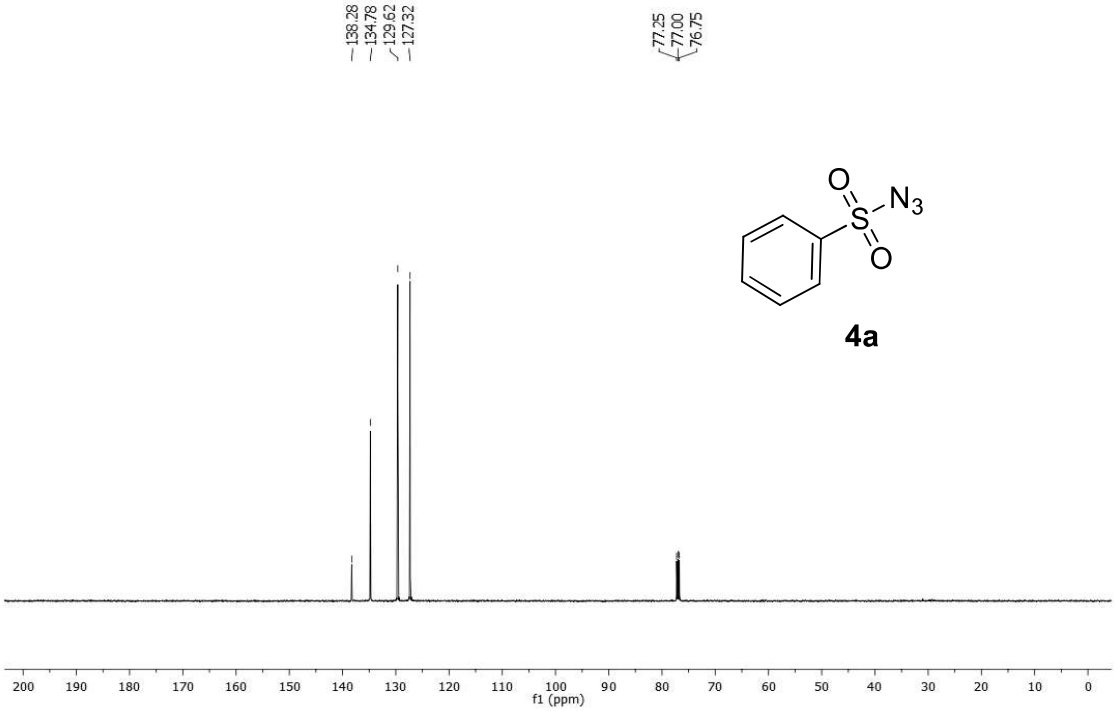


Figure 3.17 ^{13}C NMR of product **4a** in $CDCl_3$

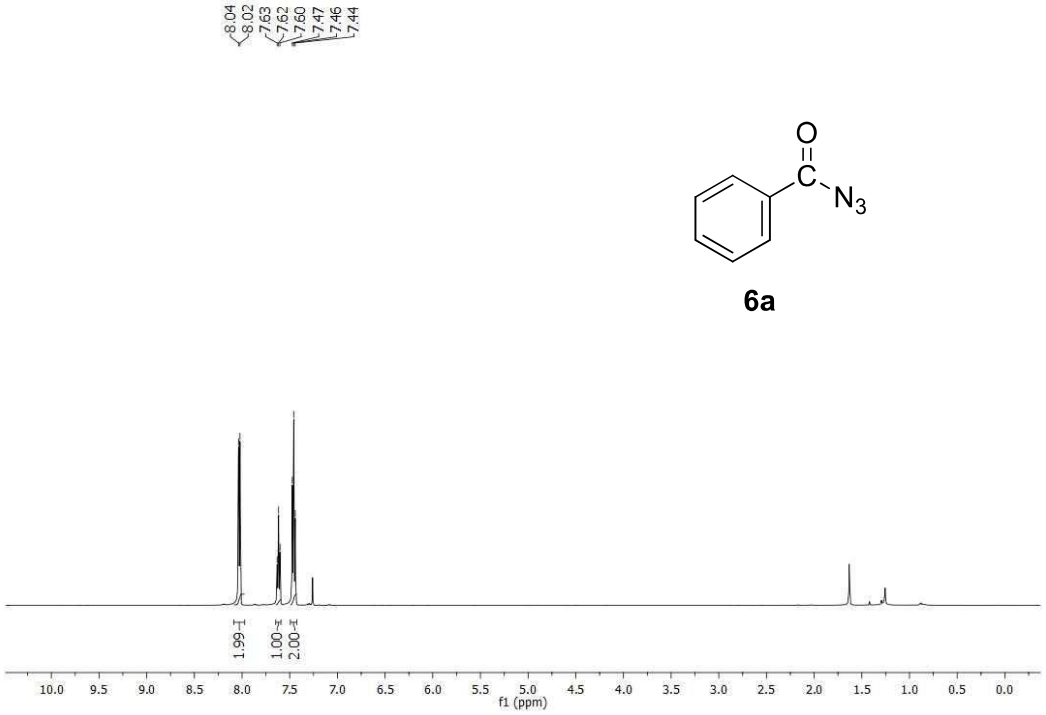


Figure 3.18 ^{1}H NMR of product **6a** in $CDCl_3$

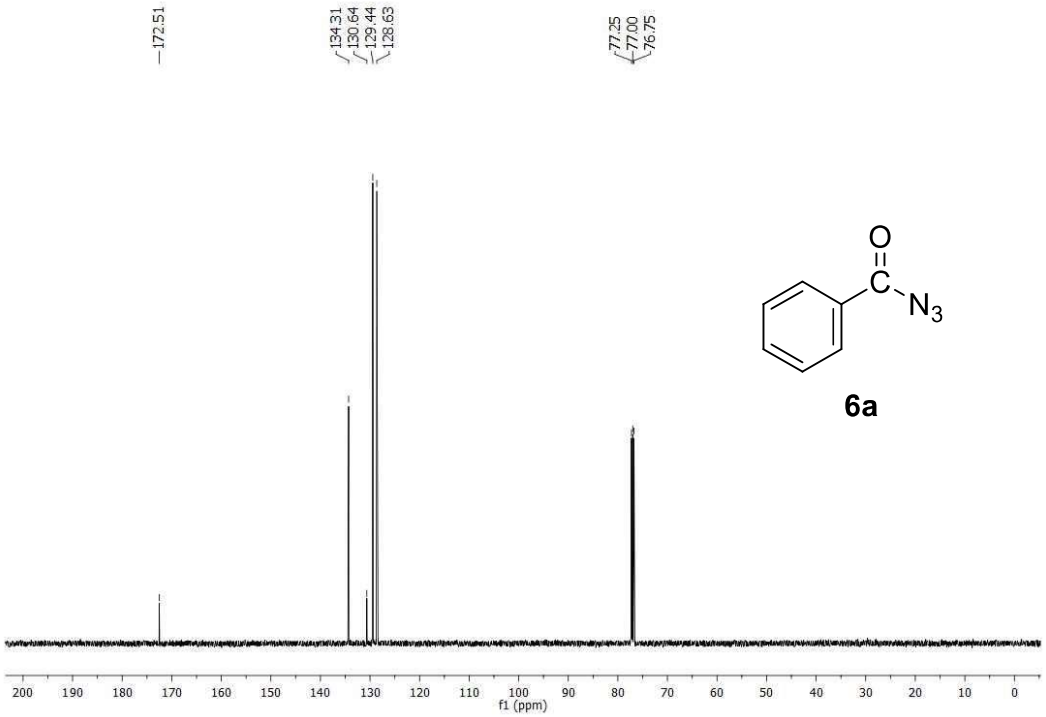


Figure 3.19 ^{13}C NMR of product **6a** in $CDCl_3$

3.10 References

[1] J.C.M. Monbaliu, The Chemistry of Benzotriazole Derivatives, Springer, 2016.

[2] A.R. Katritzky, S. Rachwal, "Synthesis of Heterocycles Mediated by Benzotriazole. 1. Monocyclic Systems," *Chemical Reviews*, **110**(2010) 1564–1610.

[3] I. Briguglio, S. Piras, P. Corona, E. Gavini, M. Nieddu, G. Boatto, A. Carta, "Benzotriazole: An Overview on its Versatile Biological Behaviour," *European Journal of Medicinal Chemistry,* **97**(2015) 612–648.

[4] Y. Ren, L. Zhang, C.H. Zhou, R.X. Geng, "Recent Development of Benzotriazole-Based Medicinal Drugs," *Medicinal Chemistry*, **4**(2014) 640–662.

[5] Y. Wang, Y. Wu, Y. Li, Y. Tang, "Denitrogenative Suzuki and Carbonylative Suzuki Coupling Reactions of Benzotriazoles with Boronic Acids," *Chemical Science*, **8**(2017) 3852–3857.

[6] H.J. Heller, H.R. Blattmann, "Some Aspects of Stabilization of Polymers Against Light," *Pure* and *Applied Chemistry*, **36**(1973) 141–161.

[7] J. Keck, G.J. Stüber, H.E. Kramer, "Deactivation Processes of Polymeric and Monomeric UV Absorbers of the Benzotriazole and Triazine Class," *Angewandte Chemie International Edition*, **252**(1997) 119–138.

[8] S. Yum, T.K. An, X. Wang, W. Lee, M.A. Uddin, Y.J. Kim, T.L. Nguyen, S. Xu, S. Hwang, C.E. Park, H.Y. Woo, "Benzotriazole-Containing Planar Conjugated Polymers with Noncovalent Conformational Locks for Thermally Stable and Efficient Polymer Field-Effect Transistors," *Chemistry of Materials*, **26**(2014) 2147–2154.

[9] M. Scalera, F.H. Adams, "Benzotriazole Analogs of Certain Naphthalene Dye Intermediates," *Journal of the American Chemical Society*, **75**(1953) 715–718.

[10] R. Walker, "Benzotriazole a Corrosion Inhibitor for Antique," *Journal of Chemical Education*, **57**(1980) 789–791.

[11] J. Fu, Y. Yang, X.W. Zhang, W.J. Mao, Z.M. Zhang, H.L. Zhu, "Discovery of 1*H*-Benzo[d][1,2,3]triazol-1-yl 3,4,5-trimethoxybenzoate as a Potential Antiproliferative Agent by Inhibiting Histone Deacetylase," *Bioorganic & Medicinal Chemistry*, **18**(2010) 8457–8462.

[12] Y. Luo, Z.J. Liu, G. Chen, J. Shi, J.R. Li, H.L. Zhu, "1,3,4-Oxadiazole Derivatives as Potential Antitumor Agents: Discovery, Optimization and Biological Activity Valuation," *MedChemComm*, **7**(2016) 263–271.

[13] F. Shi, J.P. Waldo, Y. Chen, R.C. Larock, "Benzyne Click Chemistry: Synthesis of Benzotriazoles from Benzynes and Azides," *Organic Letters*, **10**(2008) 2409–2412.

[14] J. Zhou, J. He, B. Wang, W. Yang, H. Ren, "1,7-Palladium Migration *via* C–H Activation, followed by Intramolecular Amination: Regioselective Synthesis of Benzotriazoles," *Journal of the American Chemical Society*, **133**(2011) 6868–6870.

[15] V. Gurram, H.K. Akula, R. Garlapati, N. Pottabathini, M.K. Lakshman, "Mild and General Access to Diverse 1*H*-Benzotriazoles *via* Diboron-Mediated N–OH Deoxygenation and Palladium Catalyzed C–C and C–N Bond Formation," *Advanced Synthesis and Catalysis*, **357**(2015) 451–462.

[16] A. Kokel, B. Török, "Microwave-Assisted Solid Phase Diazotation: a Method for the Environmentally Benign Synthesis of Benzotriazoles," *Green Chemistry*, **19**(2017) 2515–2519.

[17] P. Li, X. Jia, "*tert*-Butyl Nitrite (TBN) as a Versatile Reagent in Organic Synthesis," *Synthesis*, **50**(2018) 711–722.

[18] K. Barral, A.D. Moorhouse, J.E. Moses, "Efficient Conversion of Aromatic Amines into Azides: A One-pot Synthesis of Triazole Linkages," *Organic Letters*, **9**(2007) 1809–1811.

[19] D. Koley, O.C. Colón, S.N. Savinov, "Chemoselective Nitration of Phenols with *tert*-Butyl Nitrite in Solution and on Solid Support," *Organic Letters*, **11**(2009) 4172– 4175.

[20] S. Maity, T. Naveen, U. Sharma, D. Maiti, "Stereoselective Nitration of Olefins with *t*-BuONO and TEMPO: Direct Access to Nitroolefins under Metal-Free Conditions," *Organic Letters*, **15**(2013) 3384–3387.

[21] U. Dutta, S. Maity, R. Kancherla, D. Maiti, "Aerobic Oxynitration of Alkynes with *t*-BuONO and TEMPO," *Organic Letters*, **16**(2014) 6302–6305.

[22] B. Kilpatrick, M. Heller, S. Arns, "Chemoselective Nitration of Aromatic Sulfonamides with *tert*-Butyl Nitrite," *Chemical Communications*, **49**(2013) 514–516.

[23] Y. Ji, H. Yan, Q. Jiang, "Effective Nitration of Anilides and Acrylamides by *tert*-Butyl Nitrite," *European Journal of Organic Chemistry,* (2015) 2051–2060.

[24] S.L. Yedage, B.M. Bhanage, "*tert*-Butyl Nitrite Mediated Synthesis of *N*-Nitrosoamides, Carboxylic Acids, Benzocoumarins and Isocoumarins from Amides," *Journal of Organic Chemistry,* **82**(2017) 5769–5781.

[25] U. Dutta, D.W. Lupton, D. Maiti, "Aryl Nitriles from Alkynes using *tert*-Butyl Nitrite: Metal-Free Approach to C≡C Bond Cleavage," *Organic Letters*, **18**(2016) 860–863.

[26] X. Pang, L. Zhao, D. Zhou, P.Y. He, Z. An, J.X. Ni, R. Yan, "*tert*-Butyl Nitrite (TBN) as the *N*-Atom Source for the Synthesis of Substituted Cinnolines with 2-Vinylanilines and a Relevant Mechanism was Studied," *Organic and Biomolecular Chemistry*, **15**(2017) 6318–6322.

[27] F. Wang, B.L. Hu, L. Liu, H.Y. Tu, X.G. Zhang, "One-pot Synthesis of Quinoxalinones *via* Tandem Nitrosation/ Cyclization of *N*-Aryl Ayanoacetamides," *Journal of Organic Chemistry,* **82**(2017) 11247–11252.

[28] P. Chaudhary, S. Gupta, N. Muniyappan, S. Sabiah, J. Kandasamy, An Efficient Synthesis of *N*-Nitrosamines Under Solvent, Metal and Acid Free Conditions Using *tert*-Butyl Nitrite," *Green Chemistry*, **18**(2016) 2323–2330.

[29] P. Chaudhary, S. Gupta, P. Sureshbabu, S. Sabiah, J. Kandasamy, "A Metal Free Reduction of Aryl-*N*-Nitrosamines to the Corresponding Hydrazines Using

A Sustainable Reductant Thiourea Dioxide," *Green Chemistry*, **18**(2016) 6215–6221.

[30] P. Chaudhary, R. Korde, S. Gupta, P. Sureshbabu, S. Sabiah, J. Kandasamy, "An Efficient Metal-Free Method for the Denitrosation of Aryl *N*-Nitrosamines at Room Temperature," *Advanced Synthesis and Catalysis*, **360**(2018) 556–561.

[31] S. Chauhan, P. Chaudhary, A.K. Singh, P. Verma, V. Srivastava, J. Kandasamy, "*tert*-Butyl Nitrite Induced Radical Dimerization of Primary Thioamides and Selenoamides at Room Temperature," *Tetrahedron Letters,* **59**(2018) 272–276.

[32] S. Brase, K. Banert, "Organic Azides Syntheses and Applications," John Wiley & Sons, 2010.

[33] S. Brase, C. Gil, K. Knepper, V. Zimmermann, "Organic Azides: An Exploding Diversity of Unique Class of Compounds," *Angewandte Chemie International Edition*, **44**(2005) 5188–5240.

[34] B. Charette, R.P. Wurz, T. Ollevier, "Trifluoromethanesulfonyl Azide: A Powerful Reagent for the Preparation of α-Nitro-α-Diazocarbonyl Derivatives," *Journal of Organic Chemistry*, **65**(2000) 9252–9254.

[35] E.D. Goddard-Borger, R.V. Stick, "An Efficient, Inexpensive, and Shelf-Stable Diazo Transfer Reagent: Imidazole-1-Sulfonyl Azide Hydrochloride," *Organic Letters*, **9**(2007) 3797–3800.

[36] C.J. Cavender, V.J. Shiner, "Trifluoromethanesulfonyl Azide. Its Reaction with Alkyl Amines to form Alkyl Azides," *Journal of Organic Chemistry,* **37**(1972) 3567–3569.

[37] Y. Berkov-Zrihen, I.M. Herzog, R.I. Benhamou, M. Feldman, K.B. Steinbuch, P. Shaul, S. Lerer, A. Eldar, M. Fridman, "Tobramycin And Nebramine as Pseudo-Oligosaccharide Scaffolds for the Development of Antimicrobial Cationic Amphiphiles," *Chemistry–A European Journal*, **21**(2015) 4340–4349.

[38] S.H. Kim, S.H. Park, J.H. Choi, S. Chang, "Sulfonyl and Phosphoryl Azides: Going Further Beyond the Click Realm of Alkyl and Aryl Azides," *Chemistry–An Asian Journal*, **6**(2011) 2618–2634.

[39] P.B. Sarode, S.P. Bahekar, H.S. Chandak, "Synthesis of Sulfonyl Azides *via* Lewis Base Activation of Sulfonyl Fluorides and Trimethylsilyl Azide," *Synlett*, **27**(2016) 2681–2684.

[40] S.Y. Moon, J. Nam, K. Rathwell, W.S. Kim, "Copper-Catalyzed Chan−Lam Coupling Between Sulfonyl Azides and Boronic Acids at Room Temperature," *Organic Letters*, **16**(2014) 338–341.

[41] M. Aswad, J. Chiba, T. Tomohiroa, Y. Hatanaka, "Coupling Reaction of Thioamides with Sulfonyl Azides: An Efficient Catalyst-Free Click-Type Ligation under Mild Conditions," *Chemical Communications*, **49**(2013) 10242–10244.

[42] J. Waser, H. Nambu, E.M. Carreira, "Cobalt-Catalyzed Hydroazidation of Olefins: Convenient Access to Alkyl Azides," *Journal of the American Chemical Society*, **127**(2005) 8294–8295.

[43] J.V. Ruppel, J.E. Jones, C.A. Huff, R.M. Kamble, Y. Chen, X.P. Zhang, "A Highly Effective Cobalt Catalyst for Olefin Aziridination with Azides: Hydrogen Bonding Guided Catalyst Design," *Organic Letters*, **10**(2008) 1995–1998.

[44] P. Panchaud, L. Chabaud, Y. Landais, C. Ollivier, P. Renaud, S. Zigmantas, "Radical Amination with Sulfonyl Azides: A Powerful Method for the Formation of C–N Bonds," *Chemistry–A European Jouranl*, **10**(2004) 3606–3614.

[45] C.A. Montalbetti, V. Falque, "Amide Bond Formation and Peptide Coupling," *Tetrahedron*, **61**(2005) 10827–10852.

[46] M. Balci, "Acyl Azides: Versatile Compounds in the Synthesis of Various Heterocycles," *Synthesis*, **50**(2018) 1373–1401.

[47] F.L. Yang, S.K. Tian, "Sulfonyl Hydrazides as Sulfonyl Sources in Organic Synthesis," *Tetrahedron Letters*, **58**(2017) 487–504.

[48] R. Braslau, M.O. Anderson, F. Rivera, A. Jimenez, T. Haddad, J.R. Axon, "Acyl Hydrazines as Precursors to Acyl Radicals," *Tetrahedron*, **58**(2002) 5513–5523.

[49] J.S. Zheng, S. Tang, Y.K. Qi, Z.P. Wang, L. Liu, "Chemical Synthesis of Proteins using Peptide Hydrazides as Thioester Surrogates," *Nature Protocols*, **8**(2013) 2483–2495.

[50] V. Bizet. C. Bolm, "Sulfur Imidations by Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions," *European Journal of Organic Chemistry*, **2015**(2015) 2854– 2860.

[51] Y.H. Kim, K. Kim, S.B. Shim, "Facile Synthesis of Azides: Conversion of Hydrazines Using Dinitrogen Tetroxide," *Tetrahedron Letters*, **27**(1986) 4749–4752.

[52] V. Pozsgay, H.J. Jennings, "Azide Synthesis with Stable Nitrosyl Salts," *Tetrahedron Letters*, **28**(1987) 5091–5092.

[53] N. Iranpoor, H. Firouzabadi, N. Nowrouzi, "$Ph_3P/Br_2/n$-Bu_4NNO_2 as an Efficient System for the Preparation of *N*-Nitrosamines and Azides," *Tetrahedron Letters*, **49**(2008) 4242–4244.

[54] D.S. Bose, A.V.N. Reddy, "Iodine (V) Reagents in Organic Synthesis. Dess–Martin Periodinane Mediated Efficient One-pot Oxidation of Aldehydes to Acyl Azides," *Tetrahedron Letters*, **44**(2003) 3543–3545.