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SHORT COMMUNICATION

Direct synthesis of sulfonyl azides from sulfonic acids

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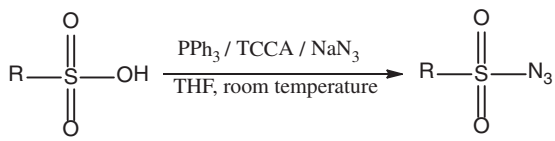
A one-pot process for the synthesis of various sulfonyl azides (RSO_2N_3) by treating sulfonic acids with triphenylphosphine/trichloroisocyanuric acid/sodium azide at room temperature is described. A wide range of arenesulfonyl and alkanesulfonyl azides was obtained in excellent yields under mild conditions.



Keywords: triphenylphosphine; trichloroisocyanuric acid; sulfonic acid; sulfonyl azide; sodium azide

1. Introduction

Sulfonyl azides are versatile reagents for a variety of chemical transformations which goes well beyond the commonly used diazo [1–3] and azide [4] transfer reactions. They have been used as valuable reagents for the preparation of α-diazocarbonyl reagents,[2, 3, 5, 6] the hydroazidation of olefins,[7] the aziridation of olefins,[8, 9] the radical amination,[4, 10, 11] and metal-catalyzed coupling reactions.[8] Owing to a wide range of applications, a general and convenient access to sulfonyl azides is highly desirable.

The reaction of sodium azide (NaN_3) with sulfonyl halides is the most direct synthetic approach to sulfonyl azides.[4, 16–21] The reaction requires the availability of sulfonyl halides which are electrophilic and hydrolytically unstable, and hence have limited functional group compatibility. Less common approaches include reactions of sulfonyl anhydrides, α-disulfonesand 1-sulfonyl benzothiazole with NaN_3.[22–25] Alternatively, diazotization of sulfonylhydrazides with NO^+ has also been employed,[26] these methods suffer from difficulty in preparing the starting materials. Therefore, a direct method for the synthesis of sulfonyl azides from sulfonic acids would be a welcome addition to the field.

To accomplish this transformation, and inspired by Jang and Kim,[27] we envisioned that trichloroisocyanuric acid (TCCA) as a sufficiently reactive N-halo reagent with triphenylphosphine (PPh_3) would favor the formation of sulfonyl azides from sulfonic acids.

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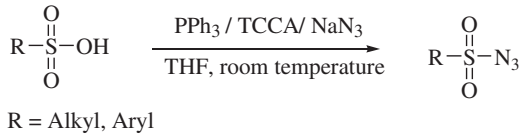
2. Results and discussion

As a part of our ongoing study on the application of PPh_3/TCCA mixed reagent in organic synthesis,[28] in this communication we wish to report on the direct synthesis of alkanesulfonyl and arenesulfonyl azides from sulfonic acids under mild reaction conditions (Scheme 1).



Scheme 1. Direct conversion of sulfonic acids to sulfonyl azides with $PPh_3/TCCA/NaN_3$ mixed reagent.

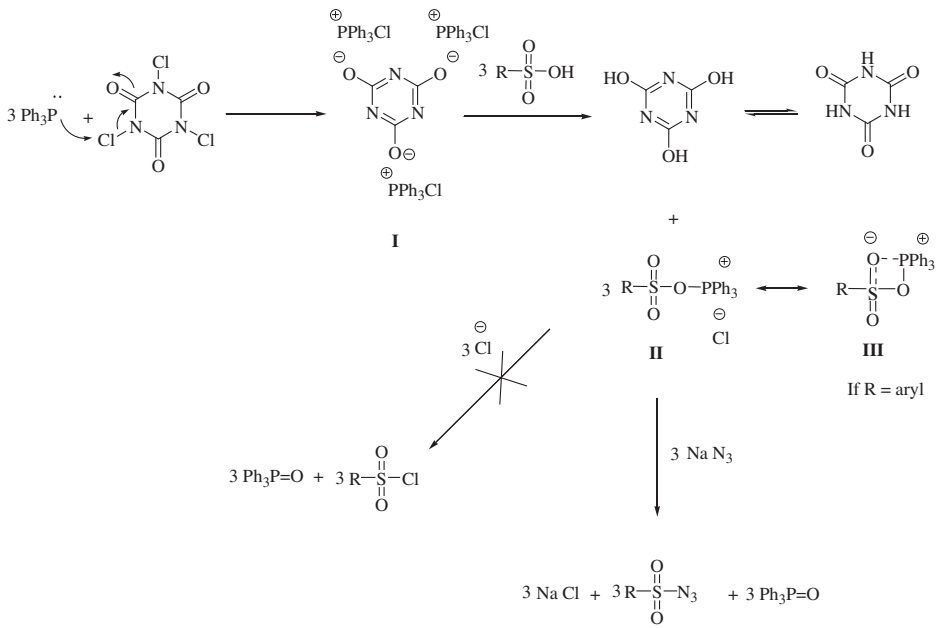
The reaction of *p*-toluenesulfonic acid with $PPh_3/TCCA/NaN_3$ served as the model experiment to achieve optimal reaction conditions. *p*-Toluenesulfonic acid was initially dehydrated by azeotropic distillation in benzene. In early trials with this mixed reagent, treating a solution of PPh_3 (1 equiv), TCCA (0.3 equiv) in CH_2Cl_2 at room temperature with different molar ratios of *p*-toluenesulfonic acid and NaN_3 afforded *p*-toluenesulfonyl azide in high yield over 40–90 min (Table 1, Entries 1–5). The order addition of the reactants is very important. When the mixture of TCCA and PPh_3 was prepared in solvent (formation of adduct **I** in proposed mechanism in Scheme 2), sulfonic acid was added to this mixture at 0–5°C. NaN_3 should be added to the reaction mixture after the formation of **II** which was formed by the reaction of sulfonic acid with **I** during 15 min. NaN_3 should never be mixed with acids directly, as formation of hydrazoic acid would immediately take place. Applying 1/0.3/0.5/1 molar ratio of PPh_3/TCCA/*p*-toluenesulfonic acid/NaN_3 in $CHCl_3$ and CH_3COCH_3 resulted *p*-toluenesulfonyl azide after 70 and 55 min, respectively (Table 1, Entries 6 and 7). As halogenated solvents, especially dichloromethane and chloroform should never be used in reactions involving NaN_3 as azidochloromethane and diazidomethane, both explosive, are easily formed, the reaction should be tested in other solvents. *p*-Toluenesulfonyl azide was obtained immediately when the reaction was performed in THF and

Table 1. Conversion of *p*-toluenesulfonic acid to *p*-toluenesulfonyl azide with the $PPh_3/TCCA/NaN_3$ system under different reaction conditions[a].

Entry	Molar ratio of(PPh_3/TCCA/ Sulfonic acid/NaN_3)	Solvent	Time (min)	Conversion (%)
1	1/0.3/0.5/3	CH_2Cl_2	40	100
2	1/0.3/0.5/2	CH_2Cl_2	60	100
3	1/0.3/0.5/1	CH_2Cl_2	65	100
4	1/0.3/0.5/0.5	CH_2Cl_2	70	100
5	1/0.3/1/2	CH_2Cl_2	90	100
6	1/0.3/0.5/1	$CHCl_3$	70	100
7	1/0.3/0.5/1	CH_3COCH_3	55	100
8	1/0.3/0.5/1	THF	Instantaneously	100
9	1/0.3/0.5/0.5	THF	Instantaneously	100
10	1/0.3/1/1	THF	55	100
11	1/0.3/0.5/1	1,4-dioxane	Instantaneously	100
12	1/0.3/0.5/0.5	1,4-dioxane	Instantaneously	100
13	1/0.3/0.5/1	CH_3CN	8	100

Notes: [a]Caution: The order addition of the reactants is very important. When the mixture of TCCA and PPh_3 was prepared in solvent, sulfonic acid was added to this mixture at 0-5°C. NaN_3 should be added after 15 min to the reaction mixture. NaN_3 should never be mixed with acids directly, as formation of hydrazoic acid would immediately take place.

1,4-dioxane but in CH_3CN, complete conversion was obtained after 8 min (Table 1, Entries 8, 11, and 13). A decrease in the amount of NaN_3 in THF and 1,4-dioxane had no effect on the time of the reaction (Table 1, Entries 9 and 12). According to the results shown in Table 1, the best results were obtained in THF and 1,4-dioxane. Because of economic consideration THF was chosen for further experiments. On the basis of this study, it seems that the effect of molar ratio of PPh_3 to *p*-toluenesulfonic acid is an important factor in preparation of *p*-toluenesulfonyl azide. An increase in the amount of *p*-toluenesulfonic acid relative to PPh_3 (applying molar ratio 1/0.3/1/1 of PPh_3/TCCA/sulfonic acid/NaN_3) made the required reaction time longer (Table 1, Entry 10).



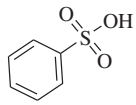
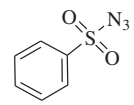
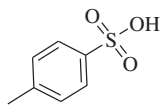
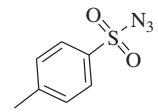
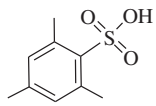
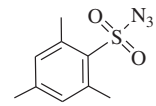
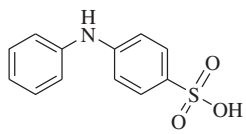
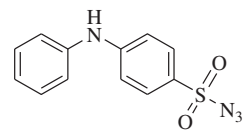
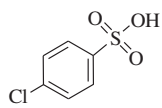
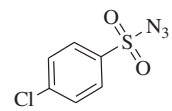
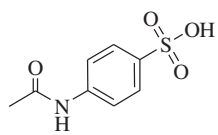
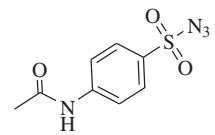
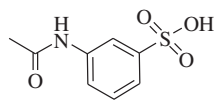
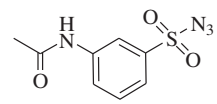
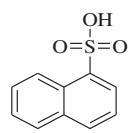
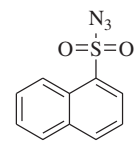
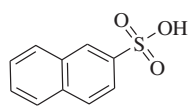
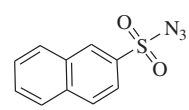
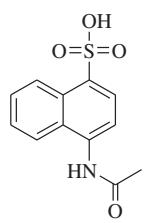
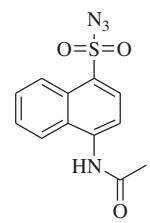
Scheme 2. The proposed mechanism of direct preparation of sulfonyl azides.

Encouraged by our initial studies, we tested the feasibility, generality, and versatility of the protocol using a series of structurally different sulfonic acids (commercially available) under these optimized conditions (Table 1, Entry 9). A combinatorial library of sulfonyl azides was smoothly prepared in high yields, and the results are summarized in Table 2.

Aryl sulfonic acids carrying either electron-donating or electron-withdrawing substituents and heteroaryl sulfonic acids reacted efficiently and the desired sulfonyl azides were obtained instantaneously, with equal efficiency (Table 2, Entries 1–10, 14, and 15). It means that aryl sulfonic acids appeared to be insensitive to substitution. 2,4,6-Trimethyl-benzenesulfonic acid which was dehydrated by azeotropic distillation in benzene reacts in 4 min with the PPh_3/TCCA/NaN_3 system. Difference in reactivity between 2,4,6-trimethyl-benzenesulfonic acid and the other aromatic sulfonic acids can be rationalized by the steric effects of two CH_3 groups in two and six positions of the aromatic ring (Table 2, Entry 3). On the basis of the results obtained from Table 2 and according to the proposed mechanism in Scheme 2, the formation of **II** is thought to be the determining step of the reaction. Conjugative electron donation by the aryl ring stabilizes the intermediate **II** which in turn facilitate the formation of the betaine form **III**.

The present system was further examined for the synthesis of alkanesulfonyl azides (Table 2, Entries 11–13). Comparatively, aliphatic sulfonic acids undergo this reaction with equal efficiency

Table 2. Synthesis of various sulfonyl azides from sulfonic acids with the $PPh_3/TCCA/NaN_3$ system in THF at room temperature.

Entry	Substrate	Product	Time (min)	Isolated yield (%)
1			Instantaneously	97
2[a]			Instantaneously	98
3[a]			4	95
4			Instantaneously	93
5			Instantaneously	98
6			Instantaneously	94
7			Instantaneously	98
8[b]			Instantaneously	97
9			Instantaneously	95
10			Instantaneously	97

(*Continued*)

Table 2. Continued

Entry	Substrate	Product	Time (min)	Isolated yield (%)
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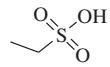
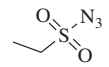
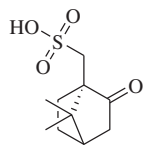
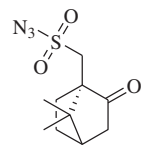
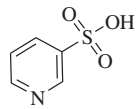
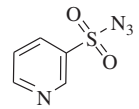
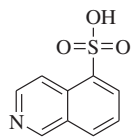
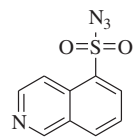
12			Instantaneously	96
13			10	98
14			Instantaneously	94
15			Instantaneously	92

Notes: [a]The acid was dehydrated by azeotropic distillation in benzene.
[b]The acid was dehydrated by azeotropic distillation in chloroform.

but in longer reaction times except for methane and ethane sulfonic acids which reacted immediately (Table 2, Entries 11 and 12). In aliphatic sulfonic acids, the formation of the betaine form **III** could not be facilitated by alkyl groups, but in the case of methanesulfonic acid ($pK_a = -1.9$) and ethane sulfonic acids ($pK_a = -1.7$), the acid strength plays an important role in the formation of **II**. More strong acid leads to the formation of **II** more quickly. In comparison (1S) – (+) 10-camphorsulfonic acid ($pK_a = 1.2$, Table 2, Entry 13) was converted to the corresponding sulfonyl azide in 10 min.

No side reactions/products (*e.g.* sulfonyl chloride) were observed during the course of the reaction; thus, we believe that the present methodology opens new possibilities for the synthetic organic chemistry and could be an important addition to the existing methodologies.

In our experiments, the completion of the reaction was confirmed by the disappearance of the sulfonic acid on TLC and the disappearance of hydroxy group (OH) stretching frequency at 3500–2400 cm^{-1} in FT-IR (Fourier transform infrared spectroscopy) spectra. Also, absorption band at 2141–2106 cm^{-1} due to azide group of sulfonyl azide in FT-IR spectra confirmed sulfonyl azide formation. The structure of all products was further confirmed by mass spectroscopy and elemental analysis CHN.

Various sulfonic acids were converted into the corresponding sulfonyl azides by the reaction of the $PPh_3/TCCA/NaN_3$ system. In general and where possible, yields and reaction times compared favorably with those reported in the literature.[27] The results presented in Table 2 clearly demonstrate the reliability of the $PPh_3/TCCA/NaN_3$ system to perform the reaction in excellent yield and short reaction times, with good functional group tolerance and a propensity in the conversion of a diverse range of sulfonic acids to sulfonyl azides.

3. Conclusions

In conclusion, a new method for the synthesis of a variety of alkanesulfonyl, arenesulfonyl, and heteroarenesulfonyl azides has been developed using the PPh_3/TCCA/NaN_3 system. This approach broadens the range of available sulfonyl azides, which are compounds of major synthetic importance. The elegance of this process lies in its mild reaction conditions, high yields, short reaction times, using low-priced reagents, and, crucially, direct formation of sulfonyl azides from sulfonic acids.

4. Experimental

4.1. *General*

The products were purified by column chromatography. Analytical TLC was performed on Merck DC precoated TLC plates with 0.25-mm Kieselgel 60 F_{254}. Visualization was performed with a 254-nm UV lamp. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 100 and 400 MHz instruments in $CDCl_3$ and DMSO. Elemental analyses were performed using a Thermofinnigan Flash EA 1112 Series instrument. Mass spectra were recorded with a Shimadzu GC-MS-QP5050 at 70 eV; in m/z (rel%). The known products were characterized by IR and ^{1}H NMR spectra and comparison of their melting points (or those of the derivatives) with authentic samples.

4.2. *Typical procedure for the preparation of p-toluenesulfonyl azide*

To a solution of TCCA (0.1548 g, 0.6 mmol) in tetrahydrofuran (3–5 mL), PPh_3 (0.5246 g, 2 mmol) was added at 0–5°C with stirring. A white suspension was formed to which *p*-toluenesulfonic acid (0.1720 g, 1 mmol) was added and stirring continued for 15 min. NaN_3 (0.065 g, 1 mmol) was added and the temperature was raised up to room temperature. Stirring was continued for 1 min at room temperature. After completion of the reaction (TLC), the reaction mixture was concentrated, washed with EtOAc (4–6 mL), and cold distilled water (5 mL). The organic layer was dried with anhydrous Na_2SO_4, passed through a short silica-gel column using *n*-hexane/ethyl acetate (10/1) as eluent. *p*-Toluenesulfonyl azide was obtained with 98% yield after removing the solvent under reduced pressure.

Caution: Azido compounds may represent an explosion hazard when being concentrated under vacuum or stored neat. A safety shield and appropriate handling procedures are recommended.

Benzenesulfonyl azide (Table 2, Entry 1). Colorless oil.[29] IR (neat, cm^{-1}) υ: 3096, 3068, 2385, 2352, 2129(N_3), 1588, 1482, 1449, 1373(SO_2), 1312, 1172(SO_2), 1087, 996, 752, 719, 685, 601, 564. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.71 (d, 2H, $J = 7.6$ Hz), 7.57 (t, 1H, $J = 7.4$ Hz), 7.49 (t, 2H, $J = 7.2$ Hz).

p-Toluenesulfonyl azide (Table 2, Entry 2). Colorless oil.[25] IR (neat, cm^{-1}) υ: 3056, 2917, 2856, 2128(N_3), 1593, 1372(SO_2), 1169(SO_2), 1086, 814, 748. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 7.85 (d, 2H, $J = 8.5$ Hz), 7.41 (d, 2H, $J = 8.0$ Hz), 2.48 (s, 3H).

Mesitylene-2-sulfonyl azide(Table 2, Entry 3). Oil.[30] IR (neat, cm^{-1}) υ: 2982, 2942, 2124(N_3), 1603, 1565, 1455, 1405, 1365(SO_2), 1191, 1167(SO_2), 1052, 1034, 854, 770, 744, 660. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 7.02 (s, 2H), 2.65 (s, 6H, $2CH_3$), 2.34 (s, 3H, CH_3).

4-(phenylamino)benzenesulfonyl azide (Table 2, Entry 4). m.p. 98–100°C, IR (KBr, cm^{-1}) υ: 3383, 3182, 3056, 3031, 2123(N_3), 1666, 1585, 1515, 1496, 1450, 1362(SO_2), 1160(SO_2), 1088, 829, 746, 700, 592, 557. ^{1}H NMR (400 MHz, DMSO, 25°C, ppm) δ: 9.23 (br, 1H, NH), 7.79 (d, 2H, $J = 8.8$ Hz), 7.39 (t, 2H, $J = 7.6$ Hz), 7.26 (d, 2H, $J = 8.0$ Hz), 7.17 (d, 2H, $J = 8.8$ Hz), 7.11 (t, 1H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, DMSO,25°C ppm) δ: 151.2, 140.5, 130.3, 129.9, 124.7, 123.9, 121.2, 114.4 cm^{-1}. EIMS: m/z 274 (M^+); 246 [M-N_2]$^+$, 230 (90) [M-N_2O]$^+$. Elemental analysis data: C%: 52.65 (calc. 52.54); H%: 3.88 (calc. 3.67); N%: 21.04 (calc. 20.43); S%11.07 (calc. 11.69).

p-Chlorobenzenesulfonyl azide (Table 2, Entry 5). m.p. 36–38°C, Lit. [26]: 37–38°C. IR (KBr, cm^{-1}) υ: 3088, 2345, 2130(N_3), 1585, 1478, 1397, 1375(SO_2), 1282, 1172(SO_2), 1091, 1014, 830, 795, 739, 619, 586. ^{1}H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 7.9 (d, 2H, $J = 8.4$ Hz), 7.57 (d, 2H, $J = 8.4$ Hz).

p-Acethamidobenzenesulfonyl azide (Table 2, Entry 6). m.p. 107–109°C, Lit. [31]: 108–110°C. IR (KBr, cm^{-1}) υ: 3374, 3322, 3277, 3187, 3109, 3056, 2921, 2856, 2128(N_3), 1684, 1590, 1532, 1404, 1371, 1318(SO_2), 1265, 1167(SO_2), 1088, 837, 754, 635. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 7.93 (d, 2H, $J = 8.0$ Hz,), 7.82 (d, 2H, $J = 8.0$ Hz), 7.63 (br, 1H, NH), 2.28 (s, 3H, CH_3).

3-Acethamidobenzenesulfonyl azide (Table 2, Entry 7). m.p. 98–100°C. IR (KBr, cm^{-1}) υ: 3293, 3252, 3187, 3134, 3089, 2957, 2925, 2852, 2135(N_3), 1669, 1597, 1552, 1483, 1372, 1320, 1307(SO_2), 1163, 1102(SO_2), 984, 874, 755, 678. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 8.07 (s, 1H, ArH), 8.04 (d, 1H, $J = 8.4$ Hz), 7.29 (br, 1H, NH), 2.29 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 191.7, 139.3, 139.0, 130.5, 125.7, 122.7, 117.9, 24.6 cm^{-1}. EIMS: m/z 240 (M^+); 238 [M-2H]$^+$, 197 (95) [M-$COCH_3$]$^+$, 155 (75) [M-$COCH_3$ N_3]$^+$. Elemental analysis data: C%: 40.69 (calc. 40.00); H%: 4.12 (calc. 3.36); N%: 23.08 (calc. 23.32); S%11.07 (calc. 13.29).

1-Naphthalenesulfonyl azide (Table 2, Entry 8). m.p. 51–53°C, Lit. [32]: 53°C. IR (KBr, cm^{-1}) υ: 3276, 3062, 2345, 2128(N_3), 1625, 1592, 1560, 1506, 1366(SO_2), 1267, 1173(SO_2), 1072, 1021, 975, 858, 831, 804, 770, 678, 655. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 8.60 (dd, 1H $J = 8.8$ Hz, $J = 0.8$ Hz), 8.39 (dd, 1H, $J = 7.6$ Hz, $J = 1.2$ Hz), 8.22 (d, 1H, $J = 8.0$ Hz), 8.02 (d, 1H, $J = 8.0$ Hz), 7.78 (t, 1H, $J = 8.4$ Hz), 7.70 (t, 1H, $J = 8.0$ Hz), 7.63 (t, 1H, $J =$ 8.0 Hz). EIMS: m/z 233 (M^+); 231 (75) [M-2H]$^+$, 190 (96) [M-HN_3]$^+$, 126 (100) [M-HSO_2 N_3]$^+$. Elemental analysis data: C%: 52.11 (calc. 51.49); H%: 3.11 (calc. 3.02); N%: 18.54 (calc. 18.02); S%13.23 (calc. 13.75).

2-Naphthalenesulfonyl azide (Table 2, Entry 9). m.p. 44–46°C, Lit. [33]: 44.2–46°C. IR (KBr, cm^{-1}) υ: 3276, 3064, 2124(N_3), 1626, 1589, 1515, 1446, 1369, 1352(SO_2), 1196, 1170, 1130(SO_2), 1071, 966, 857, 816, 753, 660, 634, 581, 540. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 8.58 (d, 1H, $J = 1.2$ Hz), 8.08 (d, 1H, $J = 9.2$ Hz), 8.06 (d, 1H, $J = 9.2$ Hz), 8.00 (d, 1H, $J = 8.4$ Hz), 7.93 (dd, 1H, $J = 8.8$ Hz, $J = 2$ Hz), 7.78–7.74 (ddd, 1H, $J = 8.20$ Hz, $J = 7.00$ Hz, $J = 1.20$ Hz), 7.73–7.69 (ddd, 1H, $J = 8.10$ Hz, $J = 6.90$ Hz, $J = 1.20$ Hz).

p-Acethamidobenzenesulfonyl azide (Table 2, Entry 10). m.p. 153–155°C, Lit. [34]: 154–156°C. IR (KBr, cm^{-1}) υ: 3284, 3084, 3064, 2132(N_3), 1613, 1520, 1437, 1361(SO_2), 1296, 1164, 1137, 1114(SO_2), 947, 756, 722.

Methanesulfonyl azide (Table 2, Entry 11). Colorless oil.[27] IR (neat, cm^{-1}) υ: 2938, 2141(N_3), 1450, 1413, 1363(SO_2), 1199, 1168(SO_2), 967, 780. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 3.25 (*s*, 3 H, CH_3).

Ethanesulfonyl azide (Table 2, Entry 12). Colorless oil.[29] IR (neat, cm^{-1}) υ: 2987, 2942, 2884, 2138(N_3), 1454, 1360(SO_2), 1270, 1200, 1159(SO_2), 1049, 782,746, 612, 585. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 3.35 (q, 2H, $J = 7.3$ Hz), 1.51 (t, 3H, $J = 7.3$ Hz).

(1*S*) − (+) *10-Camphorsulfonyl azide (Table 2, Entry 13).* Oil.[27] IR (neat, cm^{-1}) υ: 3056, 2965, 2888, 2136(N_3), 1747, 1413, 1367(SO_2), 1267, 1164(SO_2), 1052, 972, 902, 795, 736, 704, 613, 573. ^1H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 3.83 (d, 1H, $J = 14.8$ Hz), 3.24 (d, 1H, $J = 14.8$ Hz), 2.45–2.33 (m, 2H), 2.18 (t, 1H, $J = 4.2$ Hz), 2.13–2.06 (m, 1H), 2.00 (d, 1H, $J = 18.8$ Hz), 1.84–1.77 (m, 1H), 1.54–1.48 (m, 1H), 1.12 (s, 3H), 0.92 (s, 3H).

3-Pyridinesulfonyl azide (Table 2, Entry 14). Pale yellow oil.[25] IR (neat, cm^{-1}) υ: 3060, 2921, 2847, 2340, 2135(N_3), 1573, 1475, 1422, 1374, 1328(SO_2), 1174, 1107(SO_2), 1012, 804, 763, 694, 622, 607, 569. ^1H NMR (400 MHz, $CDCl_3$, 25°C, ppm) δ: 9.20 (d, 1H, $J = 2.0$ Hz), 8.97 (dd, 1H, $J = 4.8$ Hz, $J = 1.6$ Hz), 8.26 (dt 1H, $J = 8.0$ Hz, $J = 2.0$ Hz), 7.61 (dd, 1H, $J = 8.2$ Hz, $J = 5$ Hz).

5-Isoquinolinesulfonyl azide (Table 2, Entry 15). Oil.[35] IR (neat, cm^{-1}) υ: 3096, 3068, 2106(N_3), 1687, 1659, 1587, 1368(SO_2), 1246, 1129(SO_2), 1052, 748. ^1H NMR (100 MHz, $CDCl_3$, 25°C, ppm) δ: 9.65 (s, 1H), 8.91 (d, 1H, $J = 7.5$ Hz), 8.7–8.4 (m, 3H), 7.99 (t, 1H, $J = 7.5$ Hz).

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