Reaction of *N*-Nonaflylbenzotriazole with Silyl Enol Ethers

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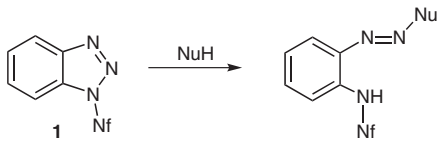
Abstract: *N*-Nonaflylbenzotriazole reacts with trimethylsilyl enol ethers in tetrahydrofuran at room temperature under tetrabutylammonium fluoride catalysis to afford *o*-(nonafluorobutylsulfonamido)phenylhydrazones in 19–82% yield. *N*-Nonaflylbenzotriazole reacts twice with the less sterically demanding silyl enol ethers to afford the corresponding *o*-(nonafluorobutylsulfonamido)phenylazo enols in 41–75% yield.

Key words: benzotriazole, hydrazones, ring opening, silyl enol ether

Benzotriazole has gained wide applications in organic synthesis as an activating auxiliary for numerous reactions.[1–6] Benzotriazole is a stable, inexpensive, and biologically innocuous compound that is usually stable under a wide variety of reaction conditions. Under more drastic conditions, namely pyrolysis and photolysis, however, benzotriazoles decompose via extrusion of nitrogen giving complex reaction mixtures. Nevertheless, some useful synthetic applications, such deazotations and dediazotations, of benzotriazoles are known. For example, in the classical Graebe–Ullmann reaction, 1-phenylbenzotriazole affords carbazole upon pyrolysis[7,8] or photolysis.[9,10] Other ring-cleavage reactions of benzotriazoles are known to occur upon treatment of benzotriazoles with Grignard reagents affording phenylenediamines in low to medium yield.[11–13] Katritzky also described domino reactions of some benzotriazole derivatives that proceeded via a ring-opening–ring-closure sequence to afford 1,2,4-triazolo[1,5-*a*]quinoxaline[14] and benzo[*c*]tetrazolo[1,5-*e*]triazepine.[15]



Nf = $SO_2C_4F_9$ NuH = carbon nucleophile

Scheme 1

Recently, we found a rather surprising ring-opening reaction of the triazole moiety upon reaction of soft nucleophiles with 1-(nonafluorobutylsulfonyl)-1*H*-benzotriazole (Nf-Bt, **1**) affording high yields of azo compounds (Scheme 1). For example, treatment of **1** with phenolates and naphtholates gave regioselectively 2-(2- and 4-hydroxyphenylazo)- and 2-(2- and 4-hydroxy-1-naphthylazo)anilines in high yields.[16–19] Likewise, a monotriazole-fused phthalocyaninato–zinc complex gave the corresponding 2-hydroxy-1-naphthylazo-substituted phthalocyaninato zinc–complex with strong solvatochromic properties.[20] This novel ring-opening reaction of **1** has been further extended to a new variation of the Japp–Klingemann reaction by treatment of **1** with CH-acidic compounds affording hydrazones in high yield.[21] Similarly, Wittig reagents react with **1** to afford triphenyl[(phenylazo)methylene]phosphoranes and [bis(phenylazo)methylene]triphenylphosphoranes.[22] Furthermore, we could recently show that **1** and 1-cyanobenzotriazole also react smoothly with enamines to give {[*o*-(nonafluorobutylsulfonamido)phenyl]azo}-substituted enamines, 4*H*-pyridazines, and imidazo[1,2-*b*][1,2,4]triazines.[23,24] Recently, Katritzky observed a similar 1,2,3-triazole ring-opening reaction when treating 1,1′-sulfonylbis(benzotriazole) with secondary amines.[25] Scheme 2 gives an overview of the ring-opening reactions of benzotriazoles observed so far. Here, we now report on the reaction of **1** with trimethylsilyl enol ethers.

Compound **1** was prepared from commercially available benzotriazole and nonafluorobutanesulfonyl fluoride as previously described.[16] Table 1 summarizes the results of the reaction of **1** with various silyl enol ethers **2**. Treatment of **1** with 1-(trimethylsiloxy)cyclohexene (**2a**) at room temperature in tetrahydrofuran did not result in a spontaneous reaction as was previously observed with the corresponding enamine derivative, i.e. pyrrolidinocyclohexene.[23] The failure of the reaction between **1** and **2a** while the corresponding enamines react smoothly with **1** can be explained by the fact that typical silyl enol ethers are seven-to-nine orders in magnitude less reactive than the analogously substituted enamines.[26,27] Accordingly, tetrabutylammonium fluoride was added to the reaction mixture in order to generate in situ a more nucleophilic enolate species from **2a**. However, when an equimolar amount of tetrabutylammonium fluoride was added in one portion to a solution of **1** and **2a** in tetrahydrofuran, extensive decomposition was detected by TLC and only benzotriazole could be isolated from the complex reaction mixture (details are not shown in the experimental part). Obviously, fluoride acted as a competitive nucleophile cleaving off the nonaflyl group in Nf-Bt **1**. Indeed, treatment of **1** alone with tetrabutylammonium fluoride in tetrahydrofuran gave benzotriazole in a fast reaction and in

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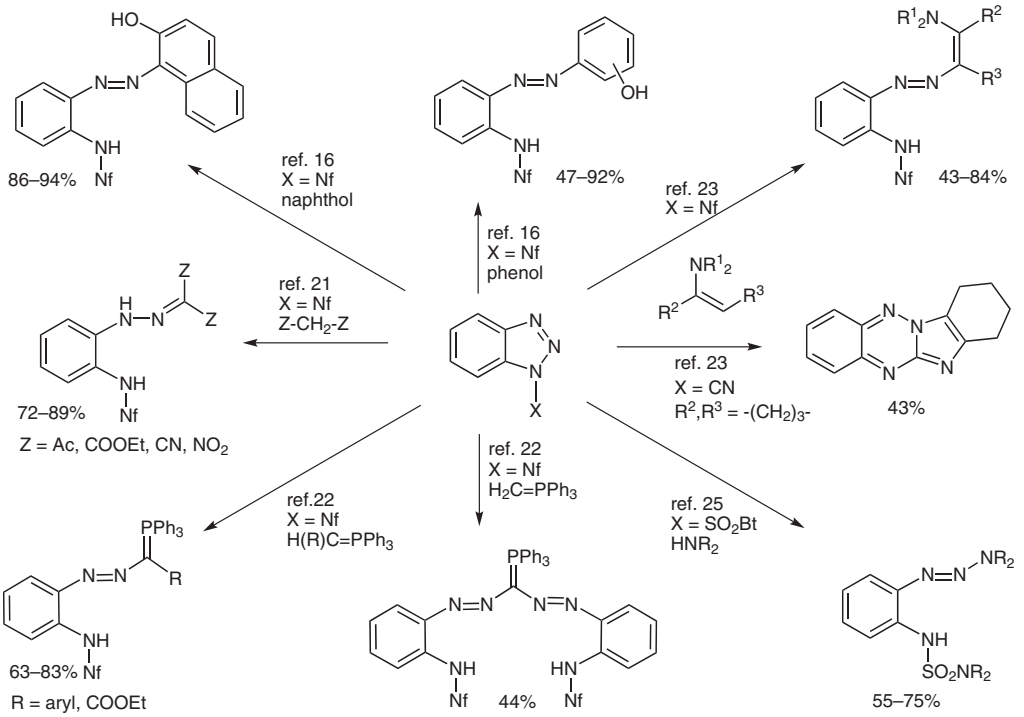


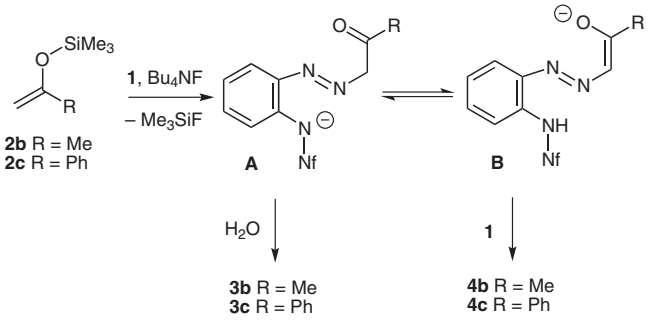
Scheme 2

virtually quantitative yield. The observation that fluoride does not induce ring opening of the triazole ring in **1** is most likely due to the fact that it is a hard nucleophile whereas attack at N2 of the triazole moiety occurs by soft nucleophiles like phenolates, mesomerically stabilized carbanions, and Wittig reagents only (see Scheme 2). A smooth reaction between **1** and various silyl enol ethers **2** was finally obtained by slow dropwise addition of a solution of an equimolar amount of tetrabutylammonium fluoride in tetrahydrofuran to a solution of **1** and **2**.

In this way, 1-(trimethylsiloxy)cyclohexene (**2a**) reacted with **1** to afford hydrazone **3a** in 82% yield (Table 1, entry 1). 2-(Trimethylsiloxy)propene (**2b**), however, afforded only 22% of the corresponding hydrazone **3b** while the bis-adduct **4b** was obtained in 75% yield (entry 2). Similarly, α-(trimethylsiloxy)styrene (**2c**) gave 30% of the hydrazone **3c** along with 41% of the bis-adduct **4c** (entry 3). The formation of the bis-adducts **4b** and **4c** can be interpreted in terms of a keto–enol equilibrium between the initially formed amide **A** and the corresponding enolate **B** (Scheme 3). The latter enolate **B** reacts as a strong nucleophile with a second molecule Nf-Bt **1** to give the bis-adducts **4**. The formation of the bis-adducts **4** resembles, to some extent, the formation of formazanes from β-diketones and diazonium salts under basic conditions,[28] although compounds **4** were isolated as bis(arylazo) tautomers. The bis(arylazo) tautomeric structures of compounds **4** were clearly evident from their NMR spectra which showed sharp singlets at δ = 5.10 and 4.56 for the hydroxy groups in **4b** and **4c**, respectively.

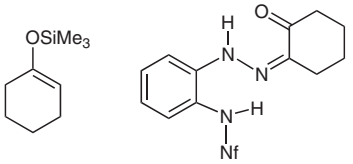
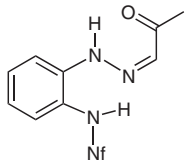
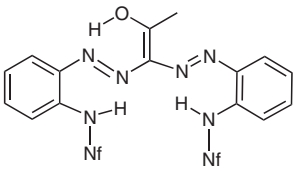
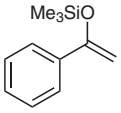
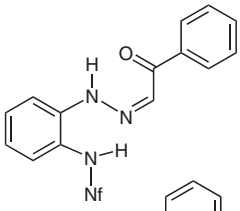
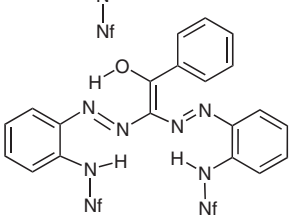
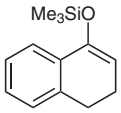
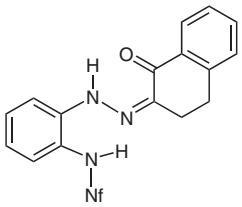
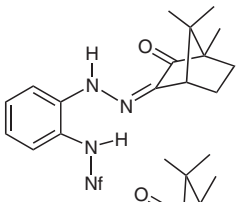
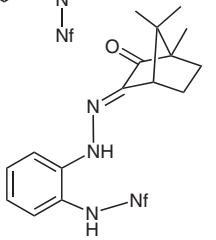
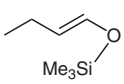
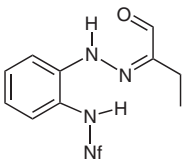
Silyl enol ethers **2d–f** gave solely the monohydrazones **3d–f**, respectively (entries 4–6). Whether monohydrazones **3** or bis(arylazo) derivatives **4** were formed was only dependent on sterical factors. Silyl enol ethers with an unsubstituted methylene group like **2b** and **2c** can attack Nf-Bt **1** twice to form bis(arylazo) adducts **4**, while all other silyl enol ethers cannot. Similar bis(arylazo) adducts were also obtained previously from sterically less demanding primary Wittig reagents[22] (see also Scheme 2). The hydrazone structure of compounds **3** and the bis(arylazo) structure of compounds **4** was also evident from the UV-Vis absorption spectra of those compounds. Typically, compounds **3** show absorption maxima of 323–376 nm, with the exception of **3d**, which shows a maximum at 424.8 nm. Bis(arylazo) compounds **4b** and **4c** have a maximum absorption of 438 and 453.7 nm, respectively.

The reaction of **1** with the trimethylsilyl enol ether of (+)-camphene **2e** afforded the two isomeric hydrazones **3e** and **3e′** (entry 5). In general, all hydrazones described here, except hydrazone **3e′**, exhibit the *Z*-configuration at



Scheme 3

Table 1 Reaction of **1** with Various Silyl Enol Ethers **2**

Entry	Silyl enol ether	Product	**3**,**4** Yield
1	**2a**		**3a** 82%
			**3b** 22%
2	**2b**		**4b** 75%
			
3	**2c**		**3c** 30%
			**4c** 41%
			
4	**2d**		**3d** 70%
			
5	**2e**		**3e** 35%
			**3e′** 34%
			
6	**2f**		**3f** 74%
			

the C=N bond, although simple hydrazones of aldehydes and ketones usually form *E*-isomers.[29] Most likely, the preferred *Z*-configuration in the case of hydrazones **3** is due to a hydrogen bond between the NH group and the carbonyl group that stabilizes the *Z*-configuration. A similar observation, i.e. the stabilization of the *Z*-isomer through a hydrogen bond, has previously been observed for β-keto enamines and vinamidine.[30] As was also observed in these cases, the ^{1}H NMR spectra of compounds **3a–f** show the NH group resonating at lower field between δ = 12 and 14 while the proton of the NH group in *E*-isomer **3e′** is found at δ = 7.96. Therefore, **3e′** was assigned the *E*-configuration. It is noteworthy though, that **3e** and **3e′** could not be interconverted by heating. No reaction of silyl enol ethers **2** was observed with 1-cyano- and 1-nitrobenzotriazole.

All reagents were commercially obtained at highest commercial quality and used without further purification. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 45 °C. Reactions were carried out under anhydrous conditions using dry glassware within an argon atmosphere in dry, freshly distilled solvents, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H NMR, ^{13}C NMR) homogeneous and recrystallized materials. Analytical TLC was performed on glass plates precoated with a 0.25 mm thickness of Macherey & Nagel Polygram® SIL G/UV254. Silica gel 60 (particle size 0.040–0.063 mm) was used for flash chromatography. NMR spectra were recorded on a Bruker Advance 250 spectrometer (at 250 MHz for ^{1}H, and at 62.9 MHz for ^{13}C NMR spectra) and calibrated using the $CDCl_3$ as an internal reference. Melting points were determined on a Büchi B-540 and are uncorrected. Specific rotations were recorded with a Perkin Elmer polarimeter model 341 at 589 nm and 20 °C in a quartz cuvette of 10 cm length. Elemental analysis was performed on Hekatech GmbH Euro EA 3000 analyzer. FAB-MS were measured on a Finnigan MAT TSQ 70 spectrometer, MALDI-TOF-MS were measured on a Bruker Autoflex spectrometer, and HRMS were measured on a Bruker Apex II FT-ICR spectrometer.

Nonafluorobutane-1-sulfonamides 3; General Procedure

1-(Nonafluorobutylsulfonyl)-1*H*-benzotriazole[16] (**1**, 1.0 g, 2.5 mmol) and trimethylsilyl enol ether **2** (2.75 mmol) were dissolved under argon in abs THF (50 mL). A soln of TBAF·3 H_2O (0.59 g, 2.5 mmol) in THF (50 mL) was pre-dried with 3 Å molecular sieves and slowly added dropwise at r.t. to the stirred soln of **1** and **2** over the course of 30 min. The resulting soln was stirred at r.t. for an additional 15 min and diluted with EtOAc (100 mL). H_2O (50 mL) was added followed by concd aq HCl soln until the aqueous phase became colorless. The organic phase was separated, dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, *n*-hexane–EtOAc, 4:1) and recrystallization of the solids after evaporation of the eluent afforded compounds **3** and **4**.

(*Z*)-Nonafluoro-*N*-{2-[2-(2-oxocyclohexylidene)hydrazinyl]phenyl}butane-1-sulfonamide (3a)

Following the general procedure using 1-(trimethylsiloxy)cyclohexene[31] (**2a**, 0.47 g) gave **3a** (1.02 g, 82%) as light yellow crystals; mp 160–161 °C (EtOH).

^{1}H NMR ($CDCl_3$): δ = 1.77–1.83 (m, 4 H, 2 CH_2), 2.46–2.52 (m, 2 H, CH_2), 2.58–2.63 (m, 2 H, CH_2), 6.87–6.97 (m, 2 H, H_{arom}), 7.05–

7.12 (m, 1 H, H_{arom}), 7.51–7.55 (m, 1 H, H_{arom}), 10.74 (s, 1 H, SO_2NH), 13.73 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 22.4 (1 C, CH_2), 23.4 (1 C, CH_2), 32.2 (1 C, CH_2), 40.4 (1 C, CH_2), 117.7, 123.8, 132.6, 133.0, 123.5, 124.8, 127.2 (7 C, C_{arom}, C=N), 198.7 (1 C, C=O).

MS (FAB): *m*/*z* = 500.0 $[M + H]^+$, 217.2 $[M + H - Nf]^+$.

UV-Vis: λ_{max} (ε) = 356.7 nm (12,709 $dm^3\ mol^{-1}\ cm^{-1}$).

Anal. Calcd for $C_{16}H_{14}F_9N_3O_3S$ (499.06): C, 38.48; H, 2.83; N, 8.41. Found: C, 38.35; H, 2.85; N, 8.09.

(*Z*)-Nonafluoro-*N*-{2-[2-(2-oxopropylidene)hydrazinyl]phenyl}butane-1-sulfonamide (3b) and *N*,*N*′-[2,2′-(1*E*,1′*E*)-(2-Hydroxyprop-1-ene-1,1-diyl)bis(diazene-2,1-diyl)bis(2,1-phenylene)]bis(nonafluorobutane-1-sulfonamide) (4b)

Following the general procedure using 2-(trimethylsiloxy)propene[31] (**2b**, 0.36 g) gave first **3b** (0.25 g, 22%) as light yellow crystals and then **4b** (0.81 g, 75%) as deep red crystals.

Butane-1-sulfonamide 3b

Mp 104–105 °C (*n*-hexane–EtOAc, 9:1).

^1H NMR ($CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 6.95–7.02 (m, 1 H, H_{arom}), 7.19–7.22 (m, 1 H, H_{arom}), 7.29–7.36 (m, 1 H, H_{arom}), 7.59–7.59 (m, 2 H, H_{arom}, N=CH), 10.74 (s, 1 H, SO_2NH), 13.93 (s, 1 H, NNH).

^{13}C NMR ($CDCl_3$): δ = 21.0 (1 C, CH_3), 115.4, 121.6, 128.4, 129.0, 137.1, 120.6, 140.1 (7 C, C_{arom}, C=N), 171.9 (1 C, C=O).

MS (FAB): *m*/*z* = 460.0 $[M + H]^+$, 177.2 $[M + H - Nf]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{11}F_9N_3O_3S$: 460.03719; found: 460.03714.

UV-Vis: λ_{max} (ε) = 330.4 nm (27,974 $dm^3\ mol^{-1}\ cm^{-1}$).

Bis(butane-1-sulfonamide) 4b

Mp 190–191 °C (EtOH).

^1H NMR (DMSO-d_6): δ = 2.61 (s, 3 H, CH_3), 5.10 (s, 1 H, OH), 7.25–7.38 (m, 4 H, H_{arom}), 7.56–7.60 (m, 2 H, H_{arom}), 7.92–7.95 (m, 2 H, H_{arom}).

^{13}C NMR (DMSO-d_6): δ = 27.1 (1 C, CH_3), 119.9, 125.1, 126.2, 130.2, 133.5, 140.5, 142.4 (7 C, C_{arom}, *C*=COH), 193.9 (1 C, COH).

MS (FAB): *m*/*z* = 861.0 $[M + H]^+$, 577.1 $[M - Nf]^+$.

MS (MALDI-TOF): *m*/*z* = 883.02 $[M + Na]^+$.

UV-Vis: λ_{max} (ε) = 438.0 nm (13,048 $dm^3\ mol^{-1}\ cm^{-1}$).

(*Z*)-Nonafluoro-*N*-{2-[2-(2-oxo-2-phenylethylidene)hydrazinyl]phenyl}butane-1-sulfonamide (3c) and *N*,*N*′-[2,2′-(1*E*,1′*E*)-(2-Hydroxy-2-phenylethene-1,1-diyl)bis(diazene-2,1-diyl)bis(2,1-phenylene)]bis(nonafluorobutane-1-sulfonamide) (4c)

Following the general procedure using α-(trimethylsiloxy)styrene[31] (**2c**, 0.53 g) gave first **3c** (0.39 g, 30%) as neon yellow crystals followed by **4c** (0.47 g, 41%) as deep red crystals.

Butane-1-sulfonamide 3c

Mp 191–192 °C ($CHCl_3$).

^1H NMR ($CDCl_3$): δ = 7.03–7.09 (m, 2 H, H_{arom}), 7.17–7.21 (m, 1 H, H_{arom}), 7.46–7.50 (m, 2 H, H_{arom}), 7.55–7.62 (m, 2 H, 2 H_{arom}), 7.69 (s, 1 H, N=CH), 7.94–7.96 (m, 2 H, H_{arom}), 10.21 (s, 1 H, SO_2NH), 14.53 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 113.0, 117.6, 119.2, 119.5, 119.6, 122.4, 123.3, 124.1, 127.8, 128.7, 131.8 (11 C, C_{arom}, C=N), 182.2 (1 C, C=O).

MS (FAB): *m*/*z* = 522.0 $[M + H]^+$, 239.1 $[M + H - Nf]^+$.

UV-Vis: λ_{max} (ε) = 375.9 nm (177,823 $dm^3\ mol^{-1}\ cm^{-1}$).

Anal. Calcd for $C_{18}H_{12}F_9N_3O_3S$ (521.05): C, 41.47; H, 2.32; N, 8.06. Found: C, 41.37; H, 2.42; N, 8.71.

Bis(butane-1-sulfonamide) 4c

Mp 164–165 °C (EtOH).

^1H NMR (DMSO-d_6): δ = 4.56 (s, 1 H, OH), 7.27–7.31 (m, 2 H, H_{Ph}), 7.34–7.38 (m, 2 H, $H_{Phenylene}$), 7.56–7.60 (m, 4 H, $H_{Phenylene}$), 7.66–7.70 (m, 1 H, H_{Ph}), 7.73–7.75 (m, 2 H, H_{Ph}), 7.94–7.96 (m, 2 H, $H_{Phenylene}$).

^{13}C NMR (DMSO-d_6): δ = 119.2, 126.6, 133.2 (3 C, C_{Ph}) 125.7, 128.96, 130.0, 130.72 (4 C, $C_{Phenylene}$), 115.8, 133.0, 138.4, 141.0, (4 C, $C_{Ph/Phenylene}$, *C*=COH), 189.3 (COH).

MS (FAB): *m*/*z* = 944.8 $[M + Na]^+$, 923.0 $[M + H]^+$.

MS (MALDI-TOF): *m*/*z* = 945.05 $[M + Na]^+$.

UV-Vis: λ_{max} (ε) = 453.7 nm (15,165 $dm^3\ mol^{-1}\ cm^{-1}$).

(*Z*)-Nonafluoro-*N*-(2-{2-[1-oxo-3,4-dihydronaphthalen-2(1*H*)-ylidene]hydrazinyl}phenyl)butane-1-sulfonamide (3d)

Following the general procedure using 1-(trimethylsiloxy)-3,4-dihydronaphthalene[32] (**2d**, 0.60 g) gave **3d** (0.96 g, 70%) as orange crystals; mp 156–157 °C (EtOH).

^1H NMR ($CDCl_3$): δ = 2.88–2.91 (m, 2 H, CH_2), 3.03–3.06 (m, 2 H, CH_2), 6.94–7.01 (m, 2 H, $H_{Phenylene}$), 7.11–7.15 (m, 1 H, $H_{Phenylene}$), 7.24–7.26 (d, 1 H, $H_{Naphthyl}$), 7.30–7.34 (t, 1 H, $H_{Naphthyl}$), 7.46–7.50 (m, 1 H, $H_{Naphthyl}$), 7.55–7.58 (m, 1 H, $H_{Phenylene}$), 7.97–7.99 (m, 1 H, $H_{Naphthyl}$), 10.76 (s, 1 H, SO_2NH), 14.00 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 29.1 (1 C, CH_2), 31.6 (1 C, CH_2), 117.5, 123.6, 123.8, 127.4 (4 C, $C_{Phenylene}$), 127.7, 128.3, 128.8, 134.3 (4 C, $C_{Naphthyl}$), 124.4, 133.1, 133.2, 134.5, 143.0 (5 C, $C_{Phenylene/Naphthyl}$, C=N), 184.9 (1 C, C=O).

MS (FAB): *m*/*z* = 548 $[M + H]^+$, 265.1 $[M + H - Nf]^+$.

UV-Vis: λ_{max} (ε) = 424.8 nm (15,375 $dm^3\ mol^{-1}\ cm^{-1}$).

Anal. Calcd for $C_{20}H_{14}F_9N_3O_3S$ (547.06): C, 43.88; H, 2.58; N, 7.68. Found: C, 43.88; H, 2.32; N, 7.70.

(1*S*,4*R*)-(*Z*)-Nonafluoro-*N*-{2-[2-(4,7,7-trimethyl-3-oxobicyclo[2.2.1]heptan-2-ylidene)hydrazinyl]phenyl}butane-1-sulfonamide (3e) and (1*S*,4*R*)-(*E*)-Nonafluoro-*N*-{2-[2-(4,7,7-trimethyl-3-oxobicyclo[2.2.1]heptan-2-ylidene)hydrazinyl]phenyl}butane-1-sulfonamide (3e′)

Following the general procedure using (1*S*,4*R*)-1,7,7-trimethyl-2-(trimethylsiloxy)bicyclo[2.2.1]hepta-2-ene[33] (**2e**, 0.62 g) gave first **3e** (0.48 g, 35%) as yellow crystals followed by **3e′** (0.47 g, 34%) as light yellow crystals.

(*Z*)-Isomer 3e

Mp 97.5–98.5 °C (*n*-hexane–EtOAc, 9:1).

$[\alpha]_D^{20}$ +161.3 (*c* 1, $CHCl_3$).

^1H NMR ($CDCl_3$): δ = 0.89 (s, 3 H, CH_3), 0.99 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 1.47–1.62 (m, 2 H, CH_2), 1.77–1.90 (m, 1 H, CH*H*), 2.07–2.21 (m, 1 H, CH*H*), 2.62–2.64 (m, 1 H, CH), 6.90–7.00 (m, 2 H, H_{arom}), 7.13–7.20 (m, 1 H, H_{arom}), 7.55–7.59 (m, 1 H, H_{arom}), 11.9 (s, 1 H, NNH).

^{13}C NMR ($CDCl_3$): δ = 8.7 (1 C, CH_3), 18.3 (1 C, CH_3), 20.5 (1 C, CH_3), 25.7 (1 C, CH_2), 30.2 (1 C, CH_2), 47.9 [1 C, $C(CH_3)_2$], 50.8 (1 C, CH), 59.8 (1 C, CCH_3), 116.2, 122.5, 125.0, 127.8, 122.6, 134.7, 143.6 (7 C, C_{arom}, C=N), 205.2 (1 C, C=O).

MS (FAB): *m*/*z* = 554.1 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{20}F_9N_3NaO_3S$: 576.09739; found: 576.09711.

UV-Vis: λ_{max} (ε) = 362.0 nm (10,500 dm^3 mol^{-1} cm^{-1}).

(*E*)-Isomer 3e′

Mp 161–162 °C (*n*-hexane–EtOAc, 9:1).

$[\alpha]_D^{20}$ +163.3 (*c* 1, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 0.90 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3), 1.45–1.65 (m, 2 H, CH_2), 1.78–1.89 (m, 1 H, CH*H*), 2.04–2.16 (m, 1 H, CH*H*), 2.91–2.93 (m, 1 H, CH), 6.95–7.01 (m, 1 H, H_{arom}), 7.22–7.25 (m, 2 H, H_{arom}), 7.40–7.43 (m, 1 H, H_{arom}), 7.96 (s, 1 H, NNH), 8.81 (s, 1 H, SO_2NH).

^{13}C NMR ($CDCl_3$): δ = 9.1 (1 C, CH_3), 18.1 (1 C, s, CH_3), 20.6 (1 C, CH_3), 23.8 (1 C, CH_2), 31.3 (1 C, CH_2), 45.7 (1 C, CH), 46.1 [1 C, $C(CH_3)_2$], 58.3 (1 C, CCH_3), 116.9, 122.7, 127.2, 129.0, 121.3, 137.3, 148.7 (7 C, C_{arom}, C=N), 203.6 (1 C, C=O).

MS (FAB): *m*/*z* = 554.1 $[M + H]^+$, 271.2 $[M + H – Nf]^+$.

UV-Vis: λ_{max} (ε) = 336.4 nm (26,703 dm^3 mol^{-1} cm^{-1}).

Anal. Calcd for $C_{20}H_{20}F_9N_3O_3S$ (553.11): C, 43.40; H, 3.67; N, 7.59. Found: C, 43.13; H, 2.70; N, 7.12.

(*Z*)-Nonafluoro-*N*-{2-[2-(1-formylpropylidene)hydrazinyl]phenyl}butane-1-sulfonamide (3f)

Following the general procedure using 1-(trimethylsiloxy)but-1-ene (**2f**, 0.39 g) gave **3f** (0.88 g, 74%) as yellow-orange crystals; mp 68.5–69.5 °C (*n*-hexane–EtOAc, 9:1).

^{1}H NMR (DMSO-d_6): δ = 1.03 (t, 3 H, CH_3), 2.48 (q, 2 H, CH_2), 7.00–7.04 (m, 1 H, H_{arom}), 7.29–7.35 (m, 2 H, H_{arom}), 7.55–7.57 (m, 1 H, H_{arom}), 9.09 (s, 1 H, SO_2NH), 9.32 (s, 1 H, O=CH), 13.58 (s, 1 H, NNH).

^{13}C NMR ($CDCl_3$): δ = 9.2 (1 C, CH_3), 15.1 (1 C, CH_2), 117.4, 123.9, 128.4, 130.1, 121.2, 138.3 (6 C, C_{arom}), 149.2 (1 C, C=N), 192.1 (1 C, C=O).

MS (FAB): *m*/*z* = 473.9 $[M + H]^+$, 191.1 $[M + H – Nf]^+$.

UV-Vis: λ_{max} (ε) = 323.3 nm (21,429 dm^3 mol^{-1} cm^{-1}).

Anal. Calcd for $C_{14}H_{12}F_9N_3O_3S$ (473.05): C, 35.53; H, 2.56; N, 8.88. Found: C, 35.39; H, 2.52; N, 8.25.

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