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REACTION OF *N*-NITRO-BENZOTRIAZOLE WITH NUCLEOPHILES

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N-*Nitro-benzotriazole* 1 *reacts with various C-nucleophiles* 2 *in tetrahydrofuran at room temperature to afford* o-*nitramidophenylazo-compounds* 3a–f *and* o-*nitramidophenyl hydrazones* 3g–l, *respectively. Reaction of* 1 *with sodium azide in aqueous acetonitrile gives a reactive 2-azidophenylnitramide intermediate* 4 *which is trapped by Cu-catalyzed 1,3-dipolar cycloadition with phenyl acetylene to afford 1-*o*-nitramidophenyl-4-phenyl-1,2,3-triazole* 5. *Reaction of* 1 *with trimethylsilylcyanide affords 3-amino-benzo[e][1,2,4]triazine* 6.

Keywords: Azo compounds; benzotriazole; hydrazones; ring opening; tetrazine

INTRODUCTION

Benzotriazole is a widely used activating auxiliary for numerous condensation reactions.[1–6] Benzotriazole is a stable, inexpensive, and biologically innocuous compound that is usually stable under a wide variety of reaction conditions. More drastic conditions, however, may result in the cleavage of the triazole ring in benzotriazole. 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 yields.[11–13] Katritzky et al. 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] Recently, we decribed a novel ring-opening reaction of 1-nonafluorobutanesulfonyl-1*H*-benzotriazole (Nf-Bt) upon reaction with soft nucleophiles, affording azo compounds. Specifically, treatment of Nf-Bt with phenolates and naphtholates gave *o*- and *p*-hydroxy-substituted phenylazo- and naphthylazo-anilines in excellent yields.[16–20] Likewise, CH-acidic compounds reacted with Nf-Bt to afford hydrazones in excellent yield in a new variant of the Japp–Klingemann reaction.[21] Similarly, Wittig reagents reacted with Nf-Bt to afford phenylazomethylene-triphenylphosphoranes and

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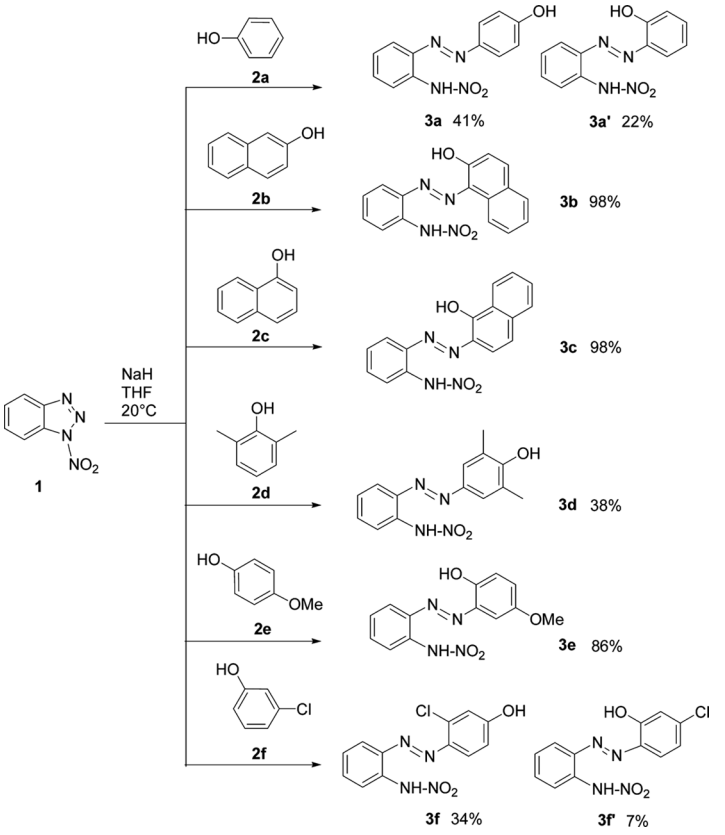
bis-phenylazomethylene-triphenylphosphoranes,[22] enamines reacted with Nf-Bt and 1-cyano-benzotriazole to give *o*-nonafluorobutanesulfonamido-phenylazo-enamines, 4H-pyridazines, and imidazo[1,2-b][1,2,4]triazines,[23,24] silylenolether reacted with Nf-Bt to afford hydrazones,[25] and secondary amines reacted with 1,1′-sulfonyl-bisbenzotriazole to give o-sulfamidotriazobenzenes.[26] Here, we report on the reaction of *N*-nitrobenzotriazole (**1**) with C-nucleophiles.

RESULTS AND DISCUSSION

1-Nitro-1,2,3-benzotriazole **1** is a stable, crystalline, and nonexplosive compound that melts without decomposition at 74 °C. It can be easily prepared from 1-chloro-1,2,3-benzotriazole with trimethylphosphite–silver nitrate complex[27] or by simple nitration of benzotriazole with nitric acid in acetic acid.[28] The latter procedure affords **1** in 90% yield when fuming nitric acid is used. So far, 1-nitrobenzotriazole **1** has only been reacted with secondary amines to give triazenes[29] and with indolizines to give *o*-(nitroamino)phenylazo-indolizines.[30]

Scheme 1 summarizes the reactions of 1-nitrobenzotriazole **1** with phenolates and naphtholates **2a–f** to give azo compounds **3a–f**. All reactions were performed in



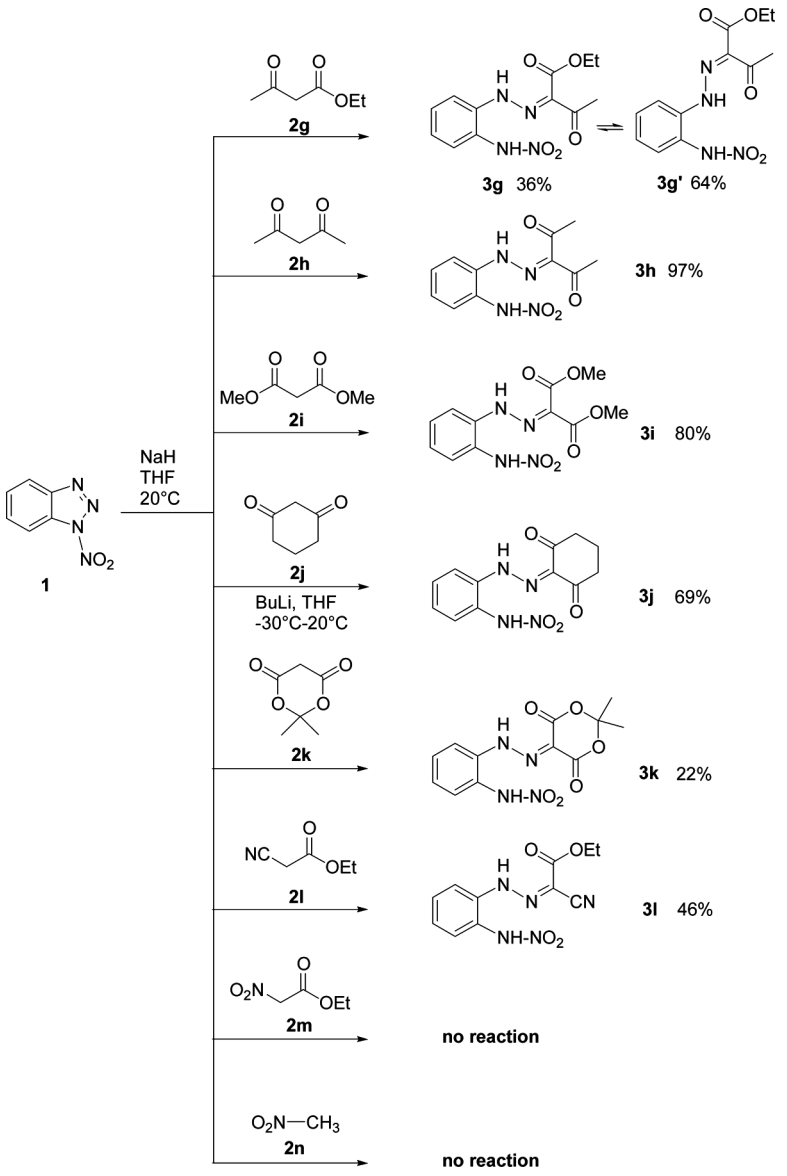
Scheme 1. Reaction of 1-nitrobenzotriazole with phenols and naphthols.

tetrahydrofuran (THF) as the solvent at room temperature. Compared to the corresponding reactions of phenolates and naphtholates with Nf-Bt,[16] 1-nitrobenzotriazole **1** reacts significantly more slowly (1–6 h versus 24 h). There is also no indication that **1** reacts through its possible 2-diazonitroimin form.[16,29] Similarly, the reaction of **1** with phenol **2a** affords a mixture of the *p*-azobenzene **3a** (41%) and the *o*-azobenzene **3a′** (22%), whereas Nf-Bt gave exclusively one isomer depending on the solvent.[16] Likewise, *m*-chlorophenol **2f** also results in a mixture of the corresponding *o*- and *p*-azobenzenes **3f** and **3f′**. The assignment of the *o*- and *p*-isomers **3a,a′** and **3f,f′** through their NMR spectra is unambiguous. In both *p*-isomers **3a** and **3f**, the protons of the aromatic OH groups resonate at 5.20 and 5.46 ppm, respectively, whereas the ones of the *o*-isomers resonate at 11.79 and 12.02 ppm, respectively. Similarly, the protons of the aromatic OH group of compound **3d** resonate at 5.07 ppm, and those of compounds **3b, 3c**, and **3e** resonate at 11.22–13.86 ppm, indicating that the downfield-shifted protons form strong hydrogen bonds with the azo groups. There is no indication in the NMR spectra for the presence of an azo-hydrazo-tautomeric equilibrium, as was observed for reactions products of **1** with secondary amines.[29]

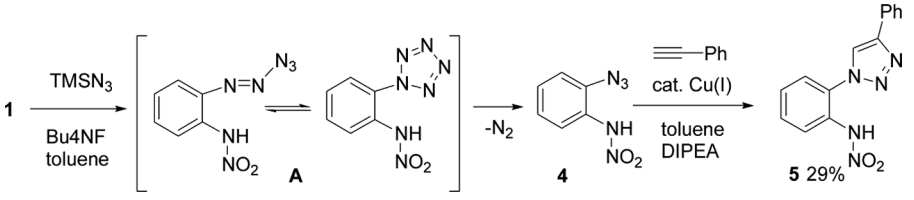
Scheme 2 summarizes the reactions of 1-nitrobenzotriazole **1** with various CH-acidic compounds **2g–n** under similar conditions (THF, 25 °C) to give hydrazones **3g–l**. Once again, **1** reacts with CH-acidic compounds significantly more slowly than Nf-Bt.[21] Ethyl nitroacetate **2 m** and nitromethane **2n** do not react with **1**. Likewise, enolethers and enamines do not react with **1** or result in complex reaction mixtures, showing the reduced reactivity of **1** compared to Nf-Bt. All hydrazones **3g–l** show ^{1}H NMR signals for the hydrazone NH group at 11–15 ppm, indicative that no azo-tautomer is present. The hydrazones formed from **1** and **2g** are obtained as an inseparable 64:36 E/Z-isomeric mixture of **3g′** and **3g** isolated in quantitative yield. All other hydrazones **3h–l** show the Z configuration, which is evident from the downfield shift of the NH-groups as a result of hydrogen bonds to the neighboring carbonyl group.

Treatment of **1** with trimethylsilylazide and tetrabutylammonium fluoride in toluene proceeds smoothly to afford *o*-azidonitraniline **4** after elimination of nitrogen (Scheme 3). The sodium salt of **4** was previously obtained by reacting **1** with NaN_3 in ethanol and is likely to proceed via pentazene and pentazole **A**.[31] Azide **4** is a very sensitive compound that could not be isolated in pure form without extensive decomposition. Therefore, crude **4** was directly converted into triazole **5** by a Cu(I)-catalyzed click reaction with phenylacetylene. The purification of **5** appeared to rather difficult, though, because many by-products were formed.

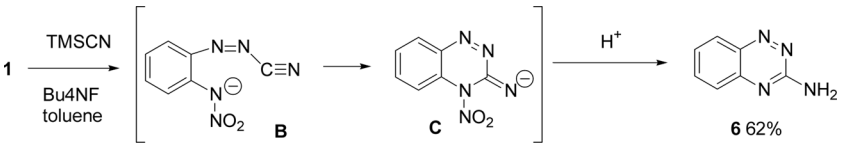
1-Nitrobenzotriazole **1** also reacts with trimethylsilylcyanide (TMSCN) and tetrabutylammonium fluoride in toluene to afford 3-amino-benzo[e][1,2,4]triazine **6** in 62% yield (Scheme 4). Although the mechanism for the formation of **6** remains enigmatic, it is likely that the sequence starts with a nucleophilic attack of cyanide on **1** followed by ring-closure of intermediate **B** to afford intermediate benzotriazine **C**. The latter is finally reduced to give **6**. Most likely, the hypervalent trimethyl cyanofluorosilicate which initially forms from TMSCN and tetrabutylammonium fluoride reduces intermediate **C** by cleaving off O_2N-CN, which in turn quickly decomposes to N_2 and CO.[32] This is supported by the fact that 2 mol equivalents of TMSCN are needed to drive the reaction to completion. An equimolar amount of TMSCN results in a turnover of only 50%.



Scheme 2. Reaction of 1-nitrobenzotriazole with CH-acidic compounds.



Scheme 3. Reaction of 1-nitrobenzotriazole with TMS-azide and phenyl acetylene.



Scheme 4. Reaction of 1-nitrobenzotriazole with TMS-cyanide.

EXPERIMENTAL

All reagents were commercially obtained at the best quality and used without further purification. Organic solutions were concentrated by rotary evaporation at less than 45 °C. Reactions were carried out under anhydrous conditions in dry, freshly distilled solvents. Yields refer to chromatographically and spectroscopically (^{1}H NMR,^{13}C NMR, mass, elemental analysis) homogeneous materials. Analytical thin-layer chromatography (TLC) was performed on glass plates precoated with 0.25-mm-thick Macherey & Nagel Polygram silica gel/UV254 with ultraviolet (UV) light as the visualizing agent. Silica gel 60 (particle size 0.040–0.063 mm) was used for flash chromatography. Mass spectra (MS) were recorded with a Bruker Apex II Fourier transform (FT)–ion cyclotron resonance (ICR) (fast atom bombardment, FAB) instrument. NMR spectra were recorded on a Bruker Advance 400 spectrometer (at 400 MHz for ^{1}H and at 100.2 MHz for ^{13}C NMR spectra) and on a Bruker 250 spectrometer (at 250 MHz for ^{1}H and at 62.9 MHz for ^{13}C NMR spectra), calibrated using $CDCl_3$ as an internal reference. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Pn, phenol; Ph, phenyl; and arom, aromatic protons or carbons. Melting points were determined on a Büchi B-540 instrument and are uncorrected. Elemental analysis was performed on Hekatech Euro EA 3000 analyzer.

1-Nitro-1*H*-1,2,3-benzotriazole (1)

1*H*-Benzotriazole (5.0 g, 42.0 mmol) was dissolved in acetic acid (40 ml) and cooled to 0 °C, and fuming nitric acid (>99.5%, 2 ml) was added with stirring. After stirring the solution for 30 min, acetic anhydride (6 ml) was added, and stirring was continued for another 30 min. The clear solution was poured into ice water, and the precipitated crude **1** was collected by filtration. Chromatography of the crude **1** with toluene gave pure **1** (6.2 g, 90%). Mp 74 °C; lit.[28] mp 74 °C.

General Experimental Procedure for the Addition of Phenols and Naphthols

NaH (0.32 g of a 60% suspension in mineral oil, 7.9 mmol) was added under Ar with stirring at 20 °C to a solution of **1** (1.0 g, 6.1 mmol) and the respective phenol or naphthol **2a–f** or CH-acidic compound **2g–n** (7.3 mmol) in THF (50 ml). The resulting solution was stirred at 20 °C until TLC revealed completion (4–24 h). Ethyl acetate (100 ml), water (50 ml), and concentrated hydrochloric acid (2 ml) were added, and stirring was continued until the aqueous phase turned colorless. The

organic phase was separated, dried with Na_2SO_4, filtered, and concentrated. Chromatography of the residue with petroleum ether/ethyl acetate 4:1 + 1% acetic acid afforded azo compounds **3a–f** or hydrazones **3g–l**. Crystalline compounds were recrystallized.

(*E*)-*N*-(2-((4-Hydroxyphenyl)diazenyl)phenyl)nitramide (3a)

Phenol (**2a**) (0.69 g) gave **3a** (0.65 g, 41%), orange crystals, mp 140–141 °C (petroleum ether/Essigester 9:1); FAB-MS: $m/z = 259.1$ $[M+H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 357.9 (57965); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.20 (1H, s, OH), 6.91–6.95 (2H, m, H^{Pn}), 7.30–7.34 (1H, m, H^{arom}), 7.47–7.51 (1H, m, H^{arom}), 7.81–7.86 (3H, m, $H^{arom/Pn}$), 8.08–8.10 (1H, m, H^{arom}), 12.32 (1H, s, NH); ^{13}C NMR (62,9 MHz, $CDCl_3$): δ = 115.99 (2C, C^{Pn}), 125.27 (2C, C^{Pn}), 116.42, 128.11, 130.98 (3C, $C^{arom/Pn}$), 129.69, 132.73, 145.60, 146.58 (4C, C^{arom}), 161.54 (C-OH). Anal. calcd. for $C_{12}H_{10}N_4O_3$ (258.08): C, 55.81; H, 3.90; N, 21.70. Found: C, 56.03; H, 3.87; N, 21.89.

(*E*)-*N*-(2-((2-Hydroxyphenyl)diazenyl)phenyl)nitramide (3a′)

Phenol (**2a**) (0.69 g) gave **3a′** (0.35 g, 22%), orange crystals, mp 106–107 °C (petroleum ether/ethyl acetate 9:1); FAB-MS: $m/z = 259.1$ $[M+H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$) 324.05 (24655), 379.99 (13545); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99–7.07 (2H, m, H^{arom}), 7.34–7.43 (2H, m, H^{arom}), 7.49–7.53 (1H, m, H^{arom}), 7.81–7.84 (2H, m, H^{arom}), 8.04–8.06 (1H, d, H^{arom}), 11.79 (1H, s, OH), 12.89 (1H, s, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.54, 120.64, 123.65, 127.37, 127.61, 131.60, 131.94, 134.72 (8C, C^{arom}), 130.02, 136.80, 138.05 (3C, C^{arom}), 152.96 (C-OH). Anal. calcd. for $C_{12}H_{10}N_4O_3$ (258.08): C, 55.81; H, 3.90; N, 21.70. Found: C, 55.98; H, 3.95; N, 21.14.

(*E*)-*N*-(2-((2-Hydroxynaphthalene-1-yl)diazenyl)phenyl)nitramide (3b)

Freshly recrystallized β-naphthol (**2b**) (0.88 g) gave **3b** (1.85 g, 98%), deep red crystals, mp 148–150 °C (*n*-hexane/acetone 9:1); FAB-MS: $m/z = 309.1$ $[M+H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 306.46 (11100), 477.99 (19500); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.83–8.86 (1H, m, H^{arom}), 7.41–7.50 (3H, m, H^{arom}), 7.58–7.66 (2H, m, H^{arom}), 7.74–7.77 (1H, m, H^{arom}), 7.94–7.97 (1H, m, H^{arom}), 8.16–8.18 (1H, d, H^{arom}), 8.49–8.52 (1H, m, H^{arom}), 13.86 (1H, s, OH), 15.95 (1H, s, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 116.59, 121.56, 124.62, 126.52, 127.41, 127.96, 130.42, 130.83, 132.49, 141.53 (10C, C^{arom}), 125.72, 127.96, 129.09, 129.41, 140.80 (5C, C^{arom}), 172.78 (1C, C-OH). Anal. calcd. for $C_{16}H_{12}N_4O_3$ (308.09): C, 62.33; H, 3.92; N, 18.17. Found: C, 62.34; H, 3.98; N, 18.10.

(*E*)-*N*-(2-((1-Hydroxynaphthalene-2-yl)diazenyl)phenyl)nitramide (3c)

Freshly sublimated α-naphthol (**2c**) (1.05 g) gave **3c** (1.86 g, 98%), deep red crystals, mp 110.5–111.5 °C (ethyl acetate/petroleum ether 1:4); FAB-MS: $m/z = 309.0$ $[M+H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 288.86 (19264), 361.06 (10632),

495.60 (16647); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.22–7.25 (1H, d, H^{arom}), 7.32–7.34 (1H, d, H^{arom}), 7.41–7.45 (1H, m, H^{arom}), 7.49–7.63 (3H, m, H^{arom}), 7.70–7.78 (2H, m, H^{arom}), 8.06–8.08 (1H, d, H^{arom}), 8.32–8.34 (1H, d, H^{arom}), 13.84 (1H, s, OH), 14.78 (1H, s, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 116.42, 121.85, 124.44, 125.99, 126.84, 127.78, 128.04, 130.56, 132.44 (10C, C^{arom}), 126.74, 128.66, 133.63, 136.65, 141.20 (5C, C^{arom}), 170.52 (1C, C-OH). Anal. calcd. for $C_{16}H_{12}N_4O_3$ (308.09): C, 62.33; H, 3.92; N, 18,17. Found: C, 62.32; H, 3.76; N, 17.72.

(*E*)-*N*-(2-((4-Hydroxy-3,5-dimethylphenyl)diazenyl)phenyl)-nitramide (3d)

2,6-Dimethylphenol (**2d**) (0.89 g) gave **3d** (670 mg, 38%), yellow crystals, mp 129–129.5 °C (petroleum ether/ethyl acetate 9:1); FAB-MS: $m/z = 287.1$ $[M + H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 253.18 (28129), 367.60 (43028.5); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (6H, s, $2CH_3$), 5.07 (1H, s, OH), 7.29–7.33 (1H, m, H^{arom}), 7.44–7.48 (1H, m, H^{arom}), 7.56 (2H, s, H^{Pn}), 7.82–7.85 (1H, m, H^{arom}), 8.08–8.11 (1H, m, H^{arom}), 12.54 (1H, s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.92 (2C, CH_3), 122.01, 122.40, 124.00, 126.56, 131.27 (6C, C^{arom}), 123.94, 131.90, 139.07, 145.63 (5C, C^{arom}), 156.23 (1C, C-OH); FT-ICR-MS calcd. for $C_{14}H_{14}N_4O_3$: 309.09581 $[M + Na]^+$; found: 309.09582 $[M + Na]^+$ ($\Delta_m = 0.03$ ppm).

(*E*)-*N*-(2-((2-Hydroxy-5-methoxyphenyl)diazenyl)phenyl)nitramide (3e)

p-Methoxyphenol (**2e**) (0.91 g) gave **3e** (1.51 g, 86%), red crystals, mp 133.5–134.0 °C (petroleum ether/ethyl acetate 4:1); FAB-MS: $m/z = 287.1$ $[M - H]^-$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 255.67 (19402), 324.84 (27969), 438.50 (11595); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.82 (3H, s, CH_3), 6.93–7.02 (2H, m, H^{Pn}), 7.26–7.27 (1H, d, H^{Pn}), 7.38–7.42 (1H. m, H^{arom}), 7.48–7.53 (1H, m, H^{arom}), 7.79–7.82 (1H, m, H^{arom}), 8.02–8.04 (1H, m, H^{arom}), 11.22 (1H, s, OH), 12.65 (1H, s, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 55.40 (CH_3), 102.47, 116.96, 119.24, 122.28, 128.04, 129.76, 131.76 (7C, C^{arom}), 133.24, 138.89, 146.26, 150.49, 152.54 (5C, C^{arom}). Anal. calcd. for $C_{13}H_{12}N_4O_4$ (288.09): C, 54.17; H, 4.20; N, 19.44. Found: C, 54.37; H, 4.10; N, 19.40.

(*E*)-*N*-(2-((2-Chloro-4-hydroxyphenyl)diazenyl)phenyl)nitramide (3f)

3-Chlorophenol (**2f**) (0.94 g) gave **3f** (610 mg, 34%), yellow crystals, mp 152.0–152.5 °C (petroleum ether/ethyl acetate 9:1); FAB-MS: $m/z = 293.1$ $[M + H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 259.37 (14515), 362.21 (21039); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.46 (1H, s, OH), 6.77–6.81 (1H, m, H^{Pn}), 7.03–7.04 (1H, d, H^{Pn}), 7.31–7.38 (1H, m, H^{arom}), 7.45–7.52 (1H, m, H^{arom}), 7.71–7.74 (1H, d, H^{Pn}), 7.94–7.98 (1H, m, H^{arom}), 8.16–8.20 (1H, m, H^{arom}), 13.30 (1H, s, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 115.55, 116.46, 116.52, 118.94, 127.93, 129.68, 131.69 (7C, C^{arom}), 133.19, 137.10, 141.16, 146.39 (4C, C^{arom}), 162.10 (1C, C-OH). Anal. calcd. for $C_{12}H_9ClN_4O_3$ (292.04): C, 49.24; H, 3.10; N, 19.14. Found: C, 49.23; H, 3.00; N, 18.83.

(*E*)-*N*-(2-((4-Chloro-2-hydroxyphenyl)diazenyl)phenyl)nitramide (3f′)

3-Chlorophenol (**2f**) (0.94 g) gave **3f′** (120 mg, 7%), yellow crystals, mp 132.5–133.5 °C (petroleum ether/ethyl acetate 9:1); FAB-MS: $m/z = 291.1$ $[M - H]^-$; ν_{max}, nm (ε, $mol^{-1}\,dm^3\,cm^{-1}$): 331.19 (15552.5), 373.86 (12302.5); ^1H NMR (250 MHz, $CDCl_3$): δ = 7.05–7.09 (2H, m, H^{arom}), 7.42–7.49 (1H, m, H^{arom}), 7.53–7.60 (1H, m, H^{arom}), 7.79–7.87 (2H, m, H^{arom}), 8.03–8.07 (1H, m, H^{arom}), 12.02 (1H, s, OH), 12.61 (1H, s, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 118.83, 121.50, 124.16, 127.29, 127.78, 132.37, 132.64 (7C, C^{arom}), 130.23, 135.71, 138.56, 140.67 (4C, C^{arom}), 153.74 (1C, C-OH). FT-ICR-MS calcd. for ($C_{12}^-H_9ClN_4O_3$): 315.02554 $[M + Na]^+$; found: 315.02541 $[M + Na]^+$ ($\Delta_m = 0.41$ ppm).

(*Z*)-Methyl 2-(2-(2-(Nitroamino)phenyl)hydrazono-3-oxobutanoate (3g) and (*E*)-Methyl 2-(2-(2-(Nitroamino)phenyl)hydrazono-3-oxobutanoate (3g′)

Methyl acetoacetate (**2g**) (0.85 g) gave a 64:36 mixture of **3g** and **3g′** (1.7 g, 100%), yellow crystals; FAB-MS: $m/z = 279.0$ $[M - H]^-$; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (1.9 H, s, CH_3 **3g′**), 2.51 (1.1 H, s, CH_3 **3g**), 3.80 (1.1 H, s, OCH_3 **3g**), 3.81 (1.9 H, s, OCH_3 **3g′**), 7.22–7.30 (1H, m, H^{arom}), 7.37–7.40 (1H, m, H^{arom}), 7.52–7.58 (1H, m, H^{arom}), 7.75–7.78 (1H, m, H^{arom}), 12.31 (0.64 H, s, $NH^{Hydrazon}$ **3g′**), 13.65 (1H, s, NH), 14.54 (0.36 H, s, $NH^{hydrazon}$ **3g**); ^{13}C NMR **3g** (100.6 MHz, $CDCl_3$): δ = 30.48 (1C, CH_3), 51.98 (1C, OCH_3), 115.80, 125.47, 127.85, 130.89 (4C, C^{arom}), 123.26, 127.51, 138.48 (3C, $2C^{arom}$, C=N), 164.36 (1C, *C*$OOCH_3$), 196.88 (1C, *C*OCH_3); ^{13}C NMR **3g′** (100.6 MHz, $CDCl_3$): δ = 26.47 (1C, CH_3), 52.17 (1C, OCH_3), 115.90, 124.55, 128.03, 130.78 (4C, C^{arom}), 122.89, 129.45, 138.45 (3C, $2C^{arom}$, C=N), 163.02 (1C, *C*$OOCH_3$), 193.40 (*C*OCH_3). Anal. calcd. for $C_{11}H_{12}N_4O_5$ (280.08): C, 47.14; H, 4.32; N, 19.99. Found: C, 47.43; H, 4.13; N, 20.24.

N-(2-(2-(2,4-Dioxopentane-3-yliden)hydrazinyl)phenyl)nitramide (3h)

Acetylacetone (**2h**) (0.73 g) gave **3h** (1.56 g, 97%), orange crystals, mp 147.0–147.5 °C (n-hexane/acetone 3:1); FAB-MS: $m/z = 263.1$ $[M - H]^-$; ν_{max}, nm (ε, $mol^{-1}\,dm^3\,cm^{-1}$): 359.57 (63805); ^1H NMR (400 MHz, DMSO-d_6): δ = 2.56–2.57 (6H, d, $2CH_3$), 7.34–7.38 (1H, m, H^{arom}), 7.45–7.48 (1H, m, H^{arom}), 7.62–7.66 (1H, m, H^{arom}), 7.94–7.98 (1H, m, H^{arom}), 13.77 (1H, s, NH), 14.47 (1H, s, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 26.49 (1C, CH_3), 31.22 (1C, CH_3), 115.91, 125.49, 127.85, 130.94 (4C, C^{arom}), 123.36, 134.47, 138.46 (3C, C^{arom}, C=N), 196.30 (1C, C=O), 197.55 (1C, C=O). Anal. calcd. for $C_{11}H_{12}N_4O_4$ (264.09): C, 50.00; H, 4.58; N, 21.20. Found: C, 49.95; H, 4.43; N, 21.21.

Dimethyl 2-(2-(2-(Nitroamino)phenyl)hydrazono)malonate (3i)

Diethyl malonate (**2i**) (0.96 g) gave **3i** (1.45 g, 80%), yellow crystals, mp 129–130 °C (ethyl acetate/*n*-hexane 1:4); FAB-MS: $m/z = 297.0$ $[M + H]^+$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 279.28 (19564), 416.32 (26750); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.12 (3H, s, CH_3), 3.13 (3H, s, CH_3), 6.41–6.46 (1H, m, H^{arom}),

6.56–6.63 (2H, m, H^{arom}), 6.85–6.87 (1H, m, H^{arom}), 10.84 (1H, s, NH), 12.17 (1H, s, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 52.51$ (1C, CH_3), 52.53 (1C, CH_3), 117.67, 124.97, 126.95, 129.18 (4C, C^{arom}), 119.56, 124.14, 134.01 (3C, C^{arom}, C=N), 162.55 (1C, C=O), 163.39 (1C, C=O). Anal. calcd. for $C_{11}H_{12}N_4O_6$ (296.08): C, 44.6; H, 4.08; N, 18.91. Found: C, 44.78; H, 4.08; N, 18.45.

N-(2-(2-(2,6-Dioxocyclohexylidene)hydrazinyl)phenyl)nitramide (3j)

1,3-Cyclohexandione (**2j**) (0.82 g) gave **3j** (1.15 g, 69%), orange crystals, mp (decomp.) 157–158 °C (ethyl acetate/petroleum ether 1:9); FAB-MS: $m/z = 274.9$ $[M-H]^-$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 381.77 (29700); ^1H NMR (400 MHz, DMSO-d_6): $\delta = 1.94$–2.01 (2H, m, CH_2), 2.60–2.63 (2H, t, CH_2), 2.69–2.72 (2H, t, CH_2), 7.32–7.36 (1H, m, H^{arom}), 7.41–7.43 (1H, m, H^{arom}), 7.57–7.61 (1H, m, H^{arom}), 7.84–7.86 (1H, m, H^{arom}), 13.74 (1H, s, NH), 15.06 (1H, s, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): $\delta = 17.61$ (1C, CH_2), 38.51 (1C, CH_2), 38.58 (1C, CH_2), 116.13, 126.36, 127.81, 131.03 (4C, C^{arom}), 123.97, 132.82, 138.48 (3C, C^{arom}, C=N), 193.16 (1C, C=O), 198.73 (1C, C=O). Anal. calcd. for $C_{12}H_{12}N_4O_4$ (276.09): C, 52.17; H, 4.38; N, 20.28. Found: C, 52.40; H, 4.49; N, 20.39.

N-(2-(2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazinyl)phenylnitramide (3k)

Butyllithium (1.46 ml of a 2.5 M solution in *n*-hexane, 3.7 mmol) was added slowly under Ar with stirring at −30 °C to a solution of Meldrum's acid (**2k**) (0.53 g, 3.7 mmol) in THF (50 ml). Stirring was continued for 30 min, and a solution of **1** (0.5 g, 3.0 mmol) in THF (10 ml) was slowly added. The solution was warmed to 20 °C and stirred until TLC revealed completion (**4 h**). Ethyl acetate (50 ml), water (25 ml), and concentrated hydrochloric acid (2 ml) were added, and stirring was continued until the aqueous phase turned colorless. The organic phase was separated, dried with Na_2SO_4, filtered, and concentrated. Chromatography of the residue with chloroform/methanol 30:1 + 1% acetic acid afforded **3k** (210 mg, 0.68, 22%), yellow crystals, mp 136.0–136.5 °C (petroleum ether/ethyl acetate 4:1); FAB-MS: $m/z = 307.1$ $[M-H]^-$; ν_{max}, nm (ε, $mol^{-1}\,dm^3\,cm^{-1}$): 366.94 (22165.5); ^1H NMR (250 MHz, DMSO-d_6): $\delta = 1.76$ (6H, s, $2CH_3$), 7.36–7.49 (2H, m, H^{arom}), 7.57–7.64 (1H, m, H^{arom}), 7.79–7.83 (1H, m, H^{arom}), 13.40 (1H, s, NH); ^{13}C NMR 62.9 MHz, DMSO-d_6): $\delta = 27.08$ (2C, CH_3), 116.66, 126.95, 127.89, 130.93 (4C, C^{arom}), 105.90, 115.02, 124.35, 137.46 [4C, C^{arom}, C=N, $C(CH_3)_2$], 158.25 (1C, C=O), 159.97 (1C, C=O). FT-ICR-MS calcd. for ($C_{12}H_{12}N_4O_6$): 331.06491 [M +Na]$^+$; found: 331.06489 [M +Na]$^+$ ($\Delta_m = 0.06$ ppm).

(*Z*)-Ethyl 2-Cyano-2-(2-(2-(Nitroamino)phenyl)hydrazono)acetate (3l)

Ethyl cyanoacetate (**2l**) (0.83 g) gave **3l** (0.77 g, 46%), yellow crystals, mp 153.5–154 °C (EtOH); FAB-MS: $m/z = 276.1$ $[M-H]^-$; ν_{max}, nm (ε, $mol^{-1}\,cm^3\,cm^{-1}$): 275.05 (10235), 351.80 (21383); ^1H NMR (400 MHz, DMSO-d_6): $\delta = 1.29$–1.32 (3H, t, CH_3), 4.30–4.35 (2H, q, CH_2), 7.29–7.33 (1H, m, H^{arom}), 7.40–7.42 (1H, m, H^{arom}), 7.53–7.57 (1H, m, H^{arom}), 7.69–7.71 (1H, m, H^{arom}),

13.04 (1H, s, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6): $\delta = 13.82$ (1C, CH_3), 62.45 (1C, CH_2), 115.86, 125.82, 127.9, 130.96 (4C, C^{arom}), 107.25, 115.27, 123.25, 137.61 (4C, C^{arom}, C=N, CN), 161.21 (C=O). Anal. calcd. for $C_{11}H_{11}N_5O_4$ (277.08): C, 47.66; H, 4.00; N, 25.26. Found: C, 47.67; H, 3.98; N, 24.49.

1-Nitro-(2-azido-phenyl)amide (4)

A solution of tetrabutylammonium fluoride trihydrate (1.92 g, 6.1 mmol) in toluene (50 ml) was dried over molecular sieves (3 Å) and slowly added over 30 min at 20 °C under Ar to a stirred solution of trimethylsilyl azide (0.84 g, 7.32 mmol) and **1** (0.84 g, 7.32 mmol) in toluene (50 ml). Stirring was continued until TLC revealed completion of the reaction (15 min). Toluene (100 ml), water (50 ml), and conc. hydrochloric acid (2 ml) were added with stirring. The organic phase was separated, dried with Na_2SO_4, filtered, and concentrated to give **4** in approximately 150 ml of toluene. This solution was directly used for the next step. An analytical sample was concentrated further for measuring the NMR spectra. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 6.89$–6.94 (2H, m, H^{arom}), 7.0–7.04 (1H, m, H^{arom}), 7.35–7.37 (1H, m, H^{arom}); ^{13}C NMR (100.6 MHz, DMSO-d_6): $\delta = 119.82$, 123.11, 124.55, 124.69 (4C, C^{arom}), 131.60, 142.04 (2C, C^{arom}).

1-Nitro-[2-(4-phenyl-[1,2,3]triazole-1-yl)-phenyl]amide (5)

Phenylacetylene (0.62 g, 6.1 mmol), diisopropyl ethyl amine (3.1 ml, 18.3 mmol), and $(EtO)_3$P-CuI (0.22 g, 0.61 mmol) were added at 20 °C to the described solution of **4** in toluene, and the solution was stirred for 16 h. Concentration of the solution and chromatography (petroleum ether/ethyl acetate 1:1 containing 1% acetic acid) of the residue gave **5** (500 mg, 29%), mp 160–161 °C (*n*-hexane/ethyl acetate 9:1); FAB-MS: $m/z = 280.0$ $[M-H]^-$; ν_{max}, nm (ε, mol^{-1} dm^3 cm^{-1}): 253.97 (31656); ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 7.35$–7.42 (1H, m, H^{arom}), 7.47–7.53 (2H, m, H^{arom}), 7.66–7.73 (3H, m, h^{arom}), 7.79–7.84 (1H, m, H^{arom}), 7.93–7.97 (2H, m, H^{arom}), 8.99 (1H, s, $CH^{triazol}$), 13.79 (1H, s, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6): $\delta = 122.26$ (1C, $CH^{triazol}$), 125.33, 129.00 (2C, C^{Ph}), 125.83, 128.23, 129.52, 130.27, 130.30 (5C, $C^{Ph/arom}$), 128.79, 130.13, 133.10 (3C, $C^{Ph/arom}$), 146.59 (1C, $C^{triazol}$). FT-ICR-MS calcd. for ($C_{14}H_{11}N_5O_2$): 304.08050 $[M+Na]^+$; found: 304.080315 $[M+Na]^+$ ($\Delta_m = 0.6$ ppm).

3-Amino-1,2,4-benzo[e]triazine (6)

A solution of tetrabutylammonium fluoride trihydrate (1.92 g, 6.1 mmol) in MeCN (50 ml) was dried over molecular sieves (3 Å) and slowly added over 30 min at 20 °C under Ar to a stirred solution of trimethylsilyl cyanide (0.61 g, 6.1 mmol) and **1** (0.50 g, 3.05 mmol) in MeCN (50 ml). Stirring was continued until TLC revealed completion of the reaction (15 min). Ethyl acetate (100 ml), water (50 ml), and conc. hydrochloric acid (2 ml) were added with stirring. The organic phase was separated, dried with Na_2SO_4, filtered, and concentrated. Chromatography (petroleum ether/ethyl acetate 1:1 containing 1% acetic acid) of the residue gave **6** (280 mg, 62%), yellow crystals, mp 205–206 °C ($CHCl_3$), lit.[33] 205–208 °C;

FAB-MS: $m/z = 147.0$ $[M + H]^+$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.00$ (2H, s, NH_2), 7.47–7.51 (1H, m, H^{arom}), 7.59–7.61 (1H, d, H^{arom}), 7.76–7.80 (1H, m, H^{arom}), 8.28–8.31 (1H, m, H^{arom}); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 126.07$, 126.14, 130.005, 136.22 (4C, C^{arom}), 142.02, 143.52 (2C, C^{arom}), 159.69 (1C, C-NH_2). Anal. calcd. for $C_7H_6N_4$ (146.06): C, 57.38; H, 4.21; N, 38.26. Found: C, 57.53; H, 4.14; N, 38.34.

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