Synthesis of 3-cyano-4,6-dinitrobenzo[*d*]isoxazole and its reactions with anionic nucleophiles

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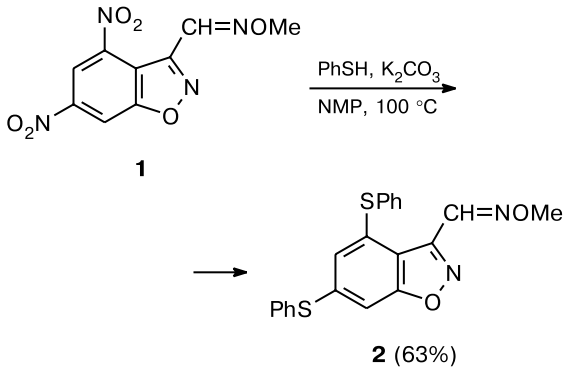
The action of various anionic O-, N-, and S-nucleophiles on 3-cyano-4,6-dinitrobenzo[*d*]isoxazole mostly resulted in regiospecific nucleophilic substitution for the nitro group in position 4. With an excess of an nucleophilic reagent, the nitro group in position 6 was also replaced.

Key words: nitro compounds, benzo[*d*]isoxazoles, nucleophilic substitution, the nitro group.

Earlier, we have reported regiospecific nucleophilic substitution for 4-NO_2 in various 4,6-dinitrobenzo-annulated heterocycles, including 3-R-4,6-dinitrobenzo[*d*]isoxazoles (R = CH=NOMe, CH=NNHAr, and 1,3-dioxolan-2-yl)[1] and 3-R-1-aryl-4,6-dinitro-1*H*-indazoles (R = H, CHO, and CN).[2,3] The nitro group in position 6 remains intact both with an excess of a nucleophile and under more drastic reaction conditions. The only exception is 6-nitrobenzo[*d*]isoxazole **1** (see Ref. 4): its treatment with excess PhSH in the presence of K_2CO_3 under comparatively drastic conditions (100 °C, *N*-methylpyrrolidone (NMP)) gave bissulfide **2** as the result of replacement of both the nitro groups (Scheme 1).

Scheme 1



Apparently, the heteroaromatic systems of most of the 4-R-6-nitro derivatives of the benzo[*d*]isoxazole and indazole series we have previously prepared are insufficiently electrophilic for replacement of the 6-NO_2 group. Introduction of an electron-withdrawing group (CHO, COOR, CN, *etc.*) in position 3 of the isoxazole ring could be expected to make the system much more electrophilic, which would facilitate the replacement of the 6-NO_2 group and affect the regioselectivities of the reactions of 4,6-dinitrobenzo[*d*]isoxazoles with nucleophiles.

Introduction of the formyl or carboxy group into the isoxazole ring seems to be inexpedient because 3-formyl- and 3-carboxybenzo[*d*]isoxazoles in basic media (in particular, under conditions for nucleophilic substitution of the nitro group) usually undergo deformylation and decarboxylation, respectively, with opening of the isoxazole ring;[5—9] the presence of the nitro groups in the benzo[*d*]isoxazole system facilitates this process still further. Benzo[*d*]isoxazole-3-carboxylates are easily hydrolyzed by bases[10—12] to give unstable salts of the corresponding acids. Indeed, we have failed to obtain 4,6-dinitrobenzo[*d*]isoxazoles with such substituents in position 3 because these compounds are very unstable.[1,13] That is why the cyano group seems to be most suitable for our purposes.

Recently,[14] we have developed a convenient and efficient single-step route to arylacetonitriles based on β-(*N*,*N*-dimethylamino)styrenes by treatment of starting enamines with $NH_2OH \cdot HCl$ in formic acid. Other aldehyde derivatives such as imines and acetals can also be transformed into nitriles under the conditions found.[14] Based on the data obtained, we chose a way of introducing the cyano group into 4,6-dinitrobenzo[*d*]isoxazole. For instance, a reaction of earlier[1] obtained cyclic acetal **3** with $NH_2OH \cdot HCl$ in boiling 95—98% HCO_2H gave previously unknown 3-cyano-4,6-dinitrobenzo[*d*]isoxazole **4** in good yield (Scheme 2).

The structure of compound **4** was confirmed by physicochemical methods (NMR and IR spectroscopy, mass spectrometry, and elemental analysis).

We studied reactions of benzo[*d*]isoxazole **4** with various anionic O-, N-, and S-nucleophiles. It turned out that NaN_3 and thiols in the presence of K_2CO_3 react with

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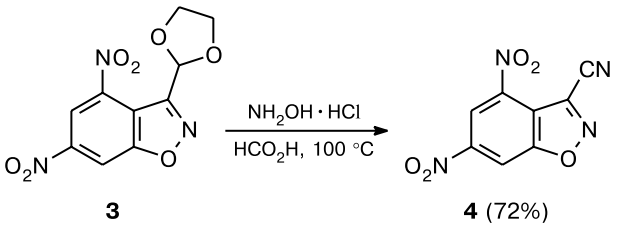
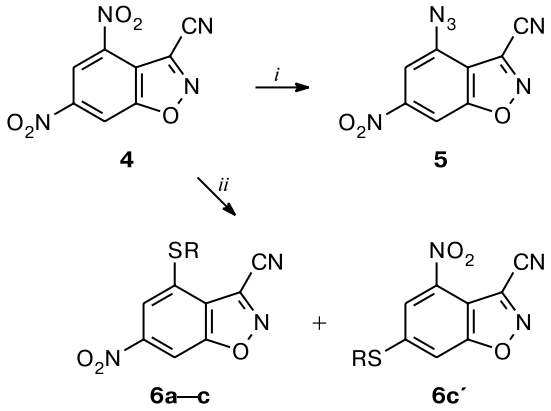
Scheme 2



3 **4** (72%)

compound **4** even at room temperature to give mononitro derivatives **5** and **6**, respectively (Scheme 3). The reactions were carried out in aprotic dipolar solvents (NMP and DMF); the starting dinitro compound **4** was fully converted in 1—2 h.

Scheme 3



4 **5** **6a—c** **6c´**

Reagents, conditions, and yields of the products: *i.* NaN_3, DMF, 20 °C; *ii.* RSH, K_2CO_3, NMP, 20 °C; the yields were 91 (**5**), 84 (**6a**), 80 (**6b**), and 64% (**6c** + **6c´**).

R = Ph (**6a**), CH_2CO_2Me (**6b**), CH_2Ph (**6c**,**c´**)

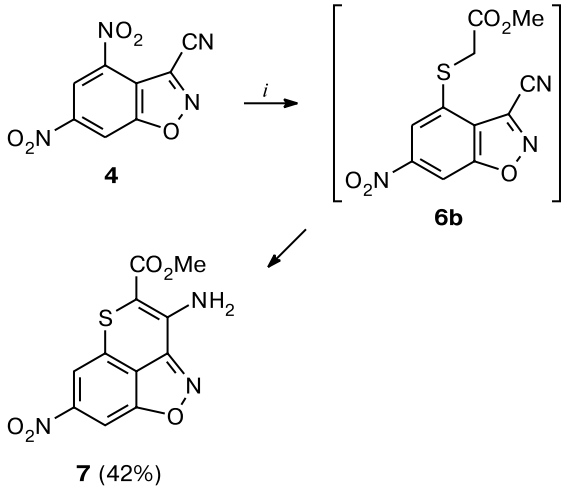
It should be noted that when dinitrobenzoisoxazole and a nucleophilic reagent were used in equimolar amounts, the nitro group in position 4 was regiospecifically replaced, while the 6-NO_2 group remained intact. The exception was $PhCH_2SH$: its reaction with compound **4** under the same conditions gave a mixture of products **6c** and **6c´**, in which the nitro groups are replaced in positions 4 and 6, respectively. The substitution product at position 4 (**6c**) was dominant (the ratio of the products was 4 : 1). Apparently, such an outcome can be associated with the highest reactivity of $PhCH_2SH$ in base-catalyzed nucleophilic substitution for the nitro group among other S-nucleophiles.

As far as we know, the less selective replacement of the 4-NO_2 group in nitrile **4** in a reaction with equimolar amounts of $PhCH_2SH$ and K_2CO_3 as a nucleophile is observed for the first time not only for 3-R-4,6-dinitrobenzo[*d*]isoxazoles but also for all the 4,6-dinitrobenzo-annulated five-membered aromatic heterocycles ever studied: indazoles,[2,3] various benzo[*b*]thiophenes,[15] and benzo[*d*]isothiazole.[16] One can assume that the lowered selectivity of the nucleophilic substitution is indirect evidence for the high electrophilicity of nitrile **4**, because a decreased selectivity is usually associated with an increased reactivity, all other factors being equal.

The replacement of just the 4-NO_2 group in compound **4** was evident from the ^{13}C NMR spectra of the starting dinitro compounds and reaction products. For the starting dinitro derivative **4**, we performed complete assignment of signals for the C atoms by analogy with earlier[1] obtained 4,6-dinitrobenzo[*d*]isoxazole derivatives with various substituents in position 3. For all the NO_2-replacement products obtained, the signal for the C(4) atom is considerably shifted upfield (from δ 140.5 in **4** to δ 133—136 in the mononitro derivative), while the signals for the C(6) atoms are virtually identical (δ 149—151). In addition, the ^1H NMR spectrum (NOE experiment) of compound **6b** revealed dipolar couplings between the H(5) atom and the methylene H atoms in the substituent SCH_2CO_2Me, which is absent between the CH_2 fragment and the H(7) atom; this also confirms the replacement of the nitro group in position 4.

Interestingly, with an increase in the reaction duration or when an excess of K_2CO_3 was used in a reaction of dinitro derivative **4** with methyl thioglycolate, intermediate product **6b** (resulting from replacement of the 4-NO_2 group) underwent cyclization due to addition of the active methylene fragment to the cyano group (Scheme 4). The resulting thiochromeno[4,5-*cd*]isoxazole (**7**) belongs

Scheme 4



4 **6b** **7** (42%)

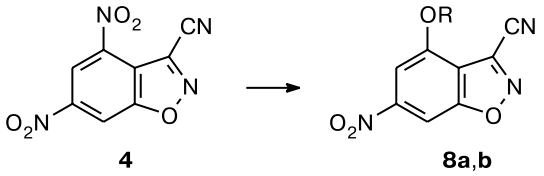
Reagents and conditions: *i.* $HSCH_2CO_2Me$, K_2CO_3, NMP, 20 °C.

to a novel aromatic *peri*-annulated heterocyclic system, which provides another piece of evidence for the replacement of the 4-NO_2 group.

Data on 14-π-electron *peri*-annulated heteroaromatic systems consisting of two six-membered and one five-membered rings are very scarce (*e.g.*, see Refs 17 and 18). As for the tricyclic system obtained in the present work, no synthesis of such compounds has been documented. Earlier,[19] using an analogous approach (regiospecific replacement of the nitro group followed by cyclization), we have synthesized for the first time some other *peri*-annulated tricyclic systems containing the indazole fragment.

We studied reactions of dinitrobenzoisoxazole **4** with such O-nucleophiles as phenol and acetophenone oxime (Scheme 5). The reactions were carried out in aprotic dipolar solvents in the presence of K_2CO_3. As with most other nucleophiles, the nitro group in position 4 was replaced regiospecifically to give mononitro derivative **8**.

Scheme 5



4 **8a**,**b**

R = Ph (**8a**), N=C(Me)Ph (**8b**)

Reagents, conditions, and yields of the products: ROH, K_2CO_3, NMP, 20 °C; the yields were 44 (**8a**) and 70% (**8b**).

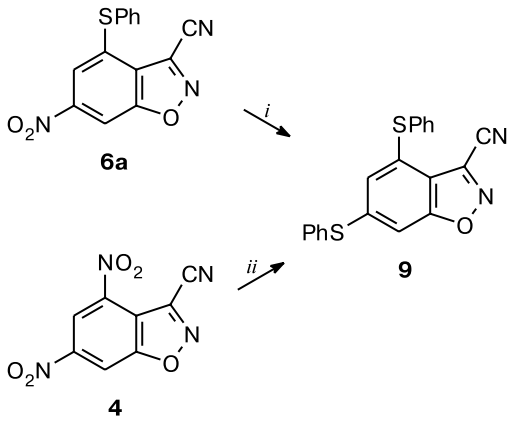
Interestingly, the reaction occurs at room temperature, while all the 3-R-4,6-dinitrobenzo[*d*]isoxazoles we studied earlier[1] react with phenol only on heating (80 °C). The position of the nitro group replaced was proven by ^{13}C NMR data as described above.

Further investigations showed that the 6-NO_2 group in mononitro compounds **5** and **6** can also be replaced by the nucleophiles used. For instance, the action of benzenethiol on mononitro derivative **6a** in NMP in the presence of K_2CO_3 at 20 °C resulted in replacement of the nitro group in position 6 (Scheme 6), yielding bissulfide **9**. However, this required more reaction time (24 h) than for replacement of the 4-NO_2 group in compound **4**.

In the reaction of dinitrobenzo[*d*]isoxazole **4** with two equivalents of PhSH under the same conditions, both the nitro groups were replaced to give compound **9** (see Scheme 6).

Azidonitrobenzo[*d*]isoxazole **5** reacted with NaN_3 (1 equiv.) to form a mixture of two products in the ratio 1 : 1. The reaction was carried out at 50 °C (since it did not occur at room temperature) in DMF; the starting

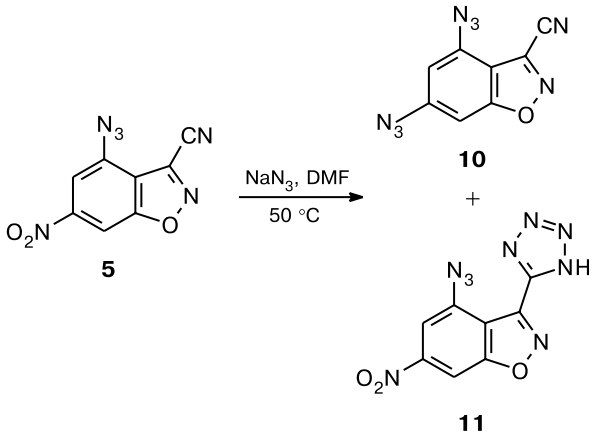
Scheme 6



Reagents, conditions, and yields of the products: *i*. PhSH, K_2CO_3, NMP, 20 °C; *ii*. PhSH (2 equiv.), K_2CO_3, NMP, 20 °C; the yields of compound **9** were 83 (from **6a**) and 97% (from **4**).

mononitro compound was completely converted in 4 h. According to ^1H NMR data, one of the reaction products is diazide **10** (the signals for the H(5) and H(7) atoms are shifted upfield compared to the signals for the starting compound (δ 7.28 and 7.59)). The second product seems to be tetrazole derivative **11** (Scheme 7).

Scheme 7

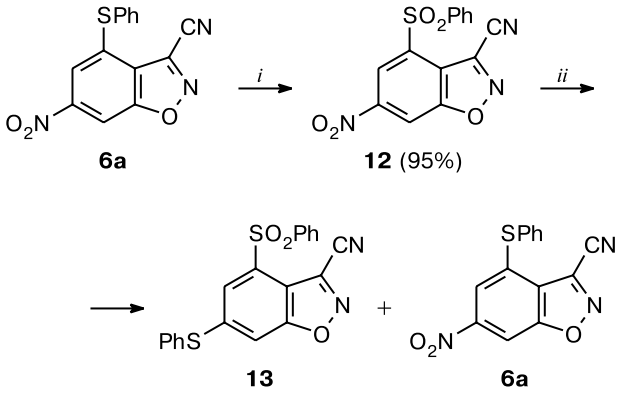


This assumption is supported by the presence of ^1H signals for the H(5) and H(7) atoms in the range characteristic of mononitrobenzo[*d*]isoxazoles (δ 8.12 and 8.67). In addition, the spectrum shows a broadened signal with the chemical shift varying with the recording conditions. Apparently, this signal corresponds to the mobile H atom of the tetrazole NH fragment. According to TLC data, the two reaction products strongly differ in polarity, which also confirms our assumption. We failed to separate and completely characterize these compounds because of their instabilities. It should be noted that an

analogous mixture of products was also obtained by a reaction of dinitrobenzo[*d*]isoxazole **4** with two equivalents of NaN_3 under the same conditions. It is known[20,21] that closure of the tetrazole ring *via* addition of N_3^- to the triple CN bond requires heating (also in DMF); *i.e.*, this reaction occurs under the conditions of replacement of the nitro group.

Oxidation of phenylthiobenzo[*d*]isoxazole **6a** with aqueous 30% H_2O_2 in CF_3COOH at room temperature gave sulfone **12** (Scheme 8). We studied nucleophilic substitution pathways in its reaction with benzenethiol.

Scheme 8

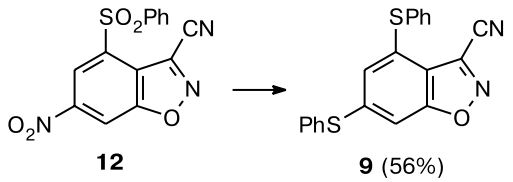


6a **12** (95%) **13** **6a**

Reagents and conditions: *i.* H_2O_2, CF_3CO_2H, 20 °C; *ii.* PhSH (1 equiv.), K_2CO_3, NMP, 20 °C.

The reactions yielded two products with close polarities (TLC), which hindered their separation and identification. ^{1}H NMR data allowed us to identify phenylthio derivative **6a** obtained in the present work (see above) and propose a structure for the other product (**13**). Thus, products **13** and **6a** in the ratio ~1 : 1 were obtained as the result of replacement of both the nitro and sulfonyl groups. A reaction of nitro sulfone **12** with an excess of PhSH (2 equiv.) at room temperature gave the sole product, bissulfide **9**, in high yield (Scheme 9).

Scheme 9



12 **9** (56%)

Reagents and conditions: PhSH (2 equiv.), K_2CO_3, NMP, 20 °C.

The results obtained suggest that the replacement rates of the sulfonyl and NO_2 groups in compound **12** under the action of PhSH are virtually equal. Earlier,[4] we have demonstrated with a number of examples that nucleophilic substitution in reactions of 3-substituted 4-(R-sulfonyl)-6-nitrobenzo[*d*]isoxazoles (R = CH=NOMe) and -indazoles (R = CN) with thiols is regiospecific and does not obey the known order of replacement of nitro and sulfonyl groups *meta*-arranged to each other: only RSO_2 is replaced, while the nitro group remains intact. Presumably, the high electrophilicity of the heteroaromatic system of compound **12** substantially facilitates the replacement of the 6-NO_2 group as well.

Thus, we obtained for the first time 3-cyano-4,6-dinitrobenzo[*d*]isoxazole, developed the convenient route to novel 4-R-3-cyano-6-nitrobenzo[*d*]isoxazoles *via* regiospecific nucleophilic substitution for the 4-NO_2 group, and showed that the nitro group in position 6 of these compounds can also be replaced by various anionic nucleophiles, which opens up a route to not easily accessible 4-R-6-R´-3-cyanobenzo[*d*]isoxazoles.

The whole of the data obtained (replacement of one or both nitro groups that are *meta* to each other in nitrile **4** under very mild conditions and the lowered selectivity of their replacement compared to other 4,6-dinitrobenzo-annulated five-membered aromatic heterocycles) suggests the high electrophilicity of nitrile **4**.

Experimental

^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on Bruker AC-200 and Bruker AM-300 instruments, respectively. Chemical shifts δ are referenced to $SiMe_4$. IR spectra were recorded on a Specord M-80 instrument (KBr pellets). Mass spectra were recorded on a Kratos MS-30 instrument (EI, 70 eV). The course of the reactions was monitored and the purity of the compounds was checked by TLC on Silufol UV-254 plates. Dry DMF was used for reactions; the other solvents were not additionally dried.

3-Cyano-4,6-dinitrobenzo[*d*]isoxazole (4). A solution of compound **3** (0.56 g, 2 mmol) (see Ref. 1) and $NH_2OH \cdot HCl$ (0.20 g, 2.8 mmol) in 95—98% formic acid (15 mL) was refluxed for 15 h, cooled, and poured into water (60 mL). The precipitate that formed was filtered off and dried in air to give compound **4** (0.34 g, 72%), m.p. 147—149 °C. Found (%): C, 41.02; H, 0.82. $C_8H_2N_4O_5$. Calculated (%): C, 41.04; H, 0.86. ^{1}H NMR, δ: 9.02 (s, 1 H, H(5)); 9.50 (s, 1 H, H(7)). ^{13}C NMR, δ: 109.2 (CN), 113.8 (C(7)), 117.2 (C(5), C(3a)), 136.4 (C(3)), 140.5 (C(4)), 149.0 (C(6)), 163.5 (C(7a)). IR, ν/cm^{-1}: 3100, 3080, 2264, 1608, 1560, 1544, 1356, 1340, 1248, 1068, 1016, 964, 932, 800, 744, 742, 692, 640.

4-Azido-3-cyano-6-nitrobenzo[*d*]isoxazole (5). Sodium azide (0.13 g, 2 mmol) was added to a solution of compound **4** (0.47 g, 2 mmol) in DMF (5 mL). The reaction mixture was stirred at ~20 °C for 1 h and poured into water with ice (50 mL). The precipitate that formed was filtered off and dried in air to give compound **5** (0.42 g, 91%), m.p. 121—122 °C. Found (%): C, 41.53; H, 0.87; N, 35.96. $C_8H_2N_6O_3$. Calculated (%) C, 41.75; H, 0.88; N, 36.52. ^{1}H NMR, δ: 8.24 (s, 1 H, H(5)); 8.76 (s, 1 H, H(7)). ^{13}C NMR, δ: 103.3, 109.1, 110.5, 116.2,

136.2, 146.1, 150.8, 163.5. IR, ν/cm^{-1}: 3112, 3060, 2220, 2152, 2132, 1620, 1608, 1540, 1488, 1372, 1348, 1316, 1216, 1200, 1064, 932, 920, 876, 788, 740. MS, *m*/*z*: 230 (M^+).

Synthesis of sulfides 6 (general procedure). Potassium carbonate (0.28 g, 2 mmol) and an appropriate thiol (2 mmol) were added to a solution of compound **4** (0.47 g, 2 mmol) in NMP (5 mL). The reaction mixture was stirred at ~20 °C for 1 h, poured into water with ice (50 mL), and acidified with conc. HCl to pH 3. The precipitate that formed was filtered off and dried in air.

3-Cyano-6-nitro-4-phenylthiobenzo[*d*]isoxazole (6a). The yield was 0.50 g (84%), m.p. 122—123 °C. Found (%): C, 41.53; H, 0.87; N, 35.96. $C_{14}H_7N_3O_3S$. Calculated (%): C, 41.75; H, 0.88; N, 36.52. ^{1}H NMR, δ: 7.58 (m, 3 H, Ph); 7.64 (m, 2 H, Ph); 7.68 (s, 1 H, H(5)); 8.84 (s, 1 H, H(7)). ^{13}C NMR, δ: 105.0, 109.5, 119.0, 122.4, 129.0, 130.0, 130.5, 133.6, 134.6, 135.6, 150.0, 162.9. IR, ν/cm^{-1}: 3104, 3060, 2132, 1592, 1576, 1540, 1444, 1352, 1332, 1216, 1196, 1024, 1000, 984, 940, 876, 852, 752.

Methyl [(3-cyano-6-nitrobenzo[*d*]isoxazol-4-yl)sulfanyl]acetate (6b). The yield was 0.47 g (80%), m.p. 77—78 °C. Found (%): C, 44.69; H, 2.38; N, 14.26. $C_{11}H_7N_3O_5S$. Calculated (%): C, 45.05; H, 2.41; N, 14.33. ^{1}H NMR, δ: 3.69 (s, 3 H, Me); 4.40 (s, 2 H, CH_2); 8.26 (s, 1 H, H(5)); 8.82 (s, 1 H, H(7)). ^{13}C NMR, δ: 34.3, 52.6, 104.7, 109.6, 118.7, 122.5, 133.7, 135.6, 150.0, 162.5, 168.8. IR, ν/cm^{-1}: 3092, 2976, 1736, 1608, 1544, 1440, 1352, 1316, 1292, 1232, 1200, 1152, 988, 944, 884, 748.

4-Benzylthio-3-cyano-6-nitrobenzo[*d*]isoxazole (6c) and 6-benzylthio-3-cyano-4-nitrobenzo[*d*]isoxazole (6c′). The yield of a mixture of compounds **6c** and **6c′** was 0.40 g (64%). Found (%): C, 57.69; H, 3.38; N, 13.26. $C_{15}H_9N_3O_3S$. Calculated (%):C, 57.87; H, 2.91; N, 13.50. **6c**: ^{1}H NMR, δ: 4.64 (s, 2 H, CH_2); 7.2—7.5 (m, 5 H, Ph); 8.22 (s, 1 H, H(5)); 8.75 (s, 1 H, H(7)). **6c′**: ^{1}H NMR, δ: 4.58 (s, 2 H, CH_2); 7.2—7.5 (m, 5 H, Ph); 8.32 (s, 1 H, H(5)); 8.44 (s, 1 H, H(7)).

Methyl 3-amino-7-nitrothiochromeno[4,5-*cd*]isoxazole-4-carboxylate (7). Potassium carbonate (0.56 g, 4 mmol) and methyl thioglycolate (0.18 mL, 2 mmol) were added to a solution of compound **4** (0.47 g, 2 mmol) in NMP (5 mL). The reaction mixture was stirred at ~20 °C for 24 h, poured into water with ice (50 mL), and acidified with conc. HCl to pH 3. The precipitate that formed was filtered off, washed with acetone (30 mL), and dried in air to give compound **7** (0.25 g, 42%), m.p. 249—251 °C. Found (%): C, 44.60; H, 2.43; N, 13.96. $C_{11}H_7N_3O_5S$. Calculated (%): C, 45.05; H, 2.41; N, 14.33. ^{1}H NMR, δ: 3.86 (s, 3 H, Me); 7.97 (s, 2 H, NH_2); 8.23 (s, 1 H, H(5)); 8.29 (s, 1 H, H(7)). ^{13}C NMR, δ: 52.6, 94.9, 100.3, 112.1, 131.5, 139.4, 150.8, 157.2, 161.5, 165.5. IR, ν/cm^{-1}: 3484, 3360, 3096, 2964, 1696, 1640, 1596, 1548, 1536, 1496, 1440, 1428, 1368, 1348, 1264, 1136, 1092, 1028, 988, 948, 904, 884, 856, 800, 764, 744. MS, *m*/*z*: 293 (M^+).

Synthesis of compounds 8a,b (general procedure). Potassium carbonate (0.28 g, 2 mmol) and an appropriate nucleophilic reagent (2 mmol) were added to a solution of compound **4** (0.47 g, 2 mmol) in NMP (5 mL). The reaction mixture was stirred at ~20 °C for 2 h, poured into water with ice (50 mL), and acidified with conc. HCl to pH 3. The product was extracted with ethyl acetate (3×30 mL), the extract was dried and concentrated, and the residue was recrystallized from EtOH.

3-Cyano-6-nitro-4-phenoxybenzo[*d*]isoxazole (8a). The yield was 0.23 g (40%), m.p. 149—151 °C (EtOH). Found (%): C, 60.33; H, 2.91; N, 14.90. $C_{14}H_7N_3O_4$. Calculated (%): C, 59.79; H, 2.51; N, 14.94. ^{1}H NMR, δ: 7.40 (m, 3 H, OPh); 7.42 (s, 1 H, H(5)); 7.60 (m, 2 H, OPh); 8.72 (s, 1 H, H(7)). ^{13}C NMR, δ: 101.5, 105.1, 109.3, 116.1, 120.6, 126.6, 130.9, 134.7, 151.1, 151.7, 153.6, 164.0. IR, ν/cm^{-1}: 3060, 1632, 1620, 1588, 1540, 1488, 1372, 1344, 1296, 1200, 1100, 1072, 1056, 952, 936, 872, 788, 744, 692.

6-Nitro-4-[(1-phenylethylidene)aminooxy]benzo[*d*]isoxazole-3-carbonitrile (8b). The yield was 0.45 g (70%), m.p. 210 °C (decomp.). Found (%): C, 59.14; H, 3.25; N, 16.90. $C_{16}H_{10}N_4O_4$. Calculated (%): C, 59.63; H, 3.13; N, 17.38. ^{1}H NMR, δ: 2.67 (s, 3 H, Me); 7.56 (m, 3 H, OPh); 7.91 (m, 2 H, OPh); 8.22 (s, 1 H, H(5)); 8.65 (s, 1 H, H(7)). ^{13}C NMR, δ: 14.1, 100.8, 103.2, 109.6, 127.1, 128.9, 131.2, 133.9, 151.5, 152.0, 163.4, 163.7. IR, ν/cm^{-1}: 3116, 2916, 2852, 1624, 1548, 1468, 1444, 1320, 1284, 1188, 1112, 1088, 1056, 984, 956, 928, 904, 880, 836, 768, 756, 744, 696.

3-Cyano-4,6-bis(phenylthio)benzo[*d*]isoxazole (9). Potassium carbonate (0.56 g, 4 mmol) and PhSH (0.4 mL, 4 mmol) were added to a solution of compound **4**, **6a**, or **12** (2 mmol) in NMP (5 mL). (In the case of compound **6a**, the following amounts were added: K_2CO_3 (0.28 g, 2 mmol) and PhSH (0.2 mL, 2 mmol).) The reaction mixture was stirred at ~20 °C for 24 h, poured into water with ice (50 mL), and acidified with conc. HCl to pH 3. The precipitate that formed was filtered off and dried in air. The yield of product **9** was 0.70 g (97%) from dinitro compound **4** and 0.60 g (83%) from mononitro sulfone **12**. M.p. 110—111 °C. Found (%): C, 66.55; H, 3.41; N, 7.92. $C_{20}H_{12}N_2OS_2$. Calculated (%): C, 66.64; H, 3.36; N, 7.77. ^{1}H NMR, δ: 6.58 (s, 1 H, H(5)); 7.42 (m, 10 H, 2 Ph); 7.57 (s, 1 H, H(7)). ^{13}C NMR, δ: 105.7, 110.0, 116.5, 123.5, 129.4, 129.6, 129.9, 130.3, 132.7, 133.1, 134.2, 134.5, 145.3, 164.2. IR, ν/cm^{-1}: 3068, 1592, 1572, 1476, 1456, 1440, 1368, 1352, 1332, 1224, 1100, 1056, 1028, 972, 924, 832, 780, 748, 708, 688.

3-Cyano-6-nitro-4-phenylsulfonylbenzo[*d*]isoxazole (12). Hydrogen peroxide (0.37 mL) was added to a solution of compound **6a** (0.33 g, 1.1 mmol) in CF_3COOH (5 mL). The reaction mixture was stirred at room temperature for 1 h and poured into water with ice (50 mL). The precipitate that formed was filtered off and dried in air to give compound **12** (0.36 g, 95%), m.p. 182—184 °C. Found (%): C, 51.33; H, 2.19; N, 12.31; $C_{14}H_7N_3O_5S$. Calculated (%):C, 51.06; H, 2.14; N, 12.76. ^{1}H NMR, δ: 7.69—7.80 (m, 3 H, *m*,*p*-Ph); 8.17 (d, 2 H, *o*-Ph, J = 7.8 Hz); 8.86 (s, 1 H, H(5)); 9.45 (s, 1 H, H(7)).

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