# Synthesis of 3-substituted 1-aryl-4,6-dinitro-1*H*-indazoles based on picrylacetaldehyde and their behavior in nucleophilic substitution reactions

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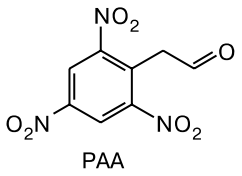
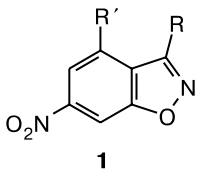
A method for the synthesis of 1-aryl-3-formyl-4,6-dinitro-1*H*-indazoles by the reaction of picrylacetaldehyde with aryldiazonium salts followed by intramolecular cyclization of the resulting picrylglyoxal monoarylhydrazones was developed. Various 4,6-dinitro-1-phenyl-1*H*-indazoles substituted in position 3 were prepared *via* transformations involving the formyl group of 3-formyl-4,6-dinitro-1-phenyl-1*H*-indazole. 3-R-4,6-Dinitro-1-phenyl-1*H*-indazoles (R = CHO, CN, 1,3-dioxolan-2-yl) react regiospecifically with anionic O-, S-, and N-nucleophiles, in particular, with replacement of only the 4-$NO_2$ group. Thus previously unknown 3-R-4-Nu-6-nitro-1-phenyl-1*H*-indazoles were synthesized (Nu is a nucleophile residue).

**Key words:** picrylacetaldehyde, 1*H*-indazoles, formyl group, nitro group, nucleophilic substitution, condensations, cyclizations.

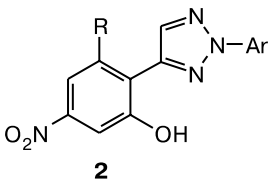
Previously,[1] we reported on the development of a method for the preparation of picrylacetaldehyde (PAA) from 2,4,6-trinitrotoluene. Within the framework of our research dealing with PAA as a multipurpose synthon, we found that this compound can serve as a precursor for the synthesis of diverse heterocyclic products with a new combination of functional substituents. In particular, we developed PAA-based syntheses of 6-nitrobenzo[*d*]isoxazoles **1** [2] and 2,4-disubstituted 1,2,3-triazoles of type **2**.[3]



PAA



**1**

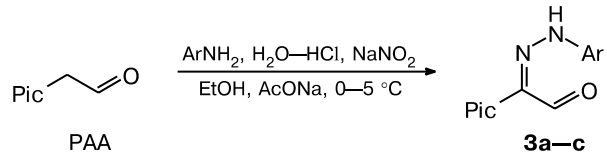


**2**

Here we developed a convenient method for the preparation of 1-aryl-3-formyl-4,6-dinitro-1*H*-indazoles from PAA (for preliminary communication, see Ref. 4) and used these products to obtain various 3,4-disubstituted 1-aryl-6-nitro-1*H*-indazoles.

To prepare 1-aryl-3-formyl-4,6-dinitro-1*H*-indazoles, PAA was first introduced in the reactions with aryldiazonium salts in a weakly acid medium; this gave azo coupling products, namely, monoarylhydrazones of picrylglyoxal **3a—c** (Scheme 1).

**Scheme 1**



Pic = 2,4,6-$(NO_2)_3C_6H_2$

| Compound | Ar | Yield (%) |
|---|---|---|
| **3a** | Ph | 79 |
| **3b** | 4-Cl-$C_6H_4$ | 66 |
| **3c** | 4-MeO-$C_6H_4$ | 71 |

It should be noted that the pH of the diazonium salt solution plays an important role in these reactions. The maximum product yields were attained at pH 5 when AcONa was used to neutralize excess acid. Compounds **3a—c** are relatively unstable and decompose during purification. Therefore, they were not fully characterized and were used in the subsequent reactions without additional purification.

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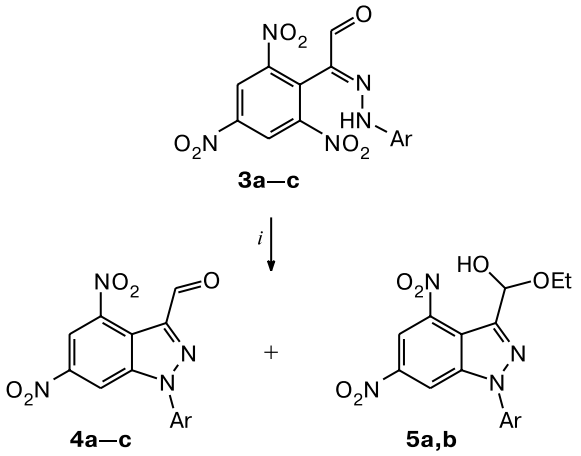
Previously unknown 1-aryl-3-formyl-4,6-dinitro-1*H*-indazoles (**4a—c**) (Scheme 2) were formed upon treatment of hydrazones **3a—c** with alkalis or alkali metal carbonates; the best results were attained with $K_2CO_3$ in EtOH at room temperature. Cyclization of hydrazones **3a—c** is due to intramolecular nucleophilic replacement of the nitro group (see Scheme 2).

**Scheme 2**




*i*. $K_2CO_3$, EtOH, 20 °C, 24 h.

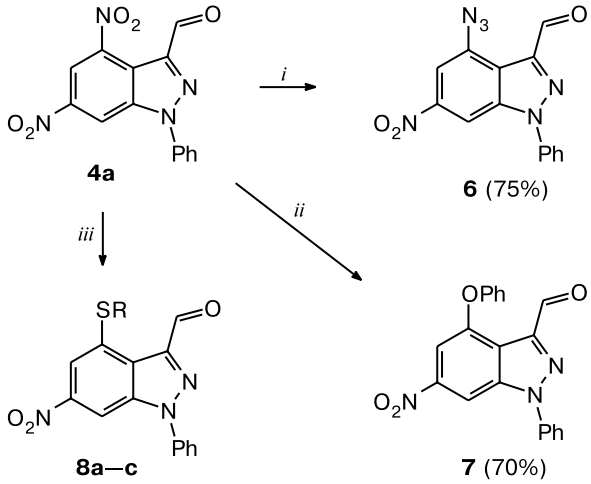
| Compound | Ar | Yield (%) |
|---|---|---|
| **4a** | Ph | 91 |
| **4b** | 4-Cl-$C_6H_4$ | 86 |
| **4c** | 4-MeO-$C_6H_4$ | 82 |

Dinitroformylindazoles **4** can also be obtained in satisfactory overall yields without isolation of intermediate hydrazones **3**.

A characteristic feature of formyldinitroindazoles **4**, containing no electron-donating groups in the *N*-aryl substituent, is transformation into stable hemiacetals **5a,b**, which occurs to some extent even during the synthesis of compounds **4** (see Scheme 2). Complete transformation into hemiacetals **5a,b** takes place on refluxing in EtOH for 30 min. On heating in air (80 °C, 8 h), crystalline hemiacetal **5a** splits off an ethanol molecule to recover formyldinitroindazole **4a**.

3-Formyl-4,6-dinitro-1-phenyl-1*H*-indazole (**4a**) was taken as an example to study the transformations of formyldinitroindazoles. This compound was found to have an interesting feature, namely, it reacts with anionic N-, O-, and S-nucleophiles (in DMF or *N*-methylpyrrolidone (NMP)) to replace only the nitro group in position 4 giving rise to previously unknown 4-substituted 3-formyl-6-nitro-1-phenyl-1*H*-indazoles **6—8** as the only products (Scheme 3). The nucleophiles used were phenol and thiols in the presence of solid $K_2CO_3$ (equimolar amount) as a deprotonating agent and $NaN_3$. The reaction proceeded up to complete conversion of the starting indazole **4a** and was carried out at ~20 °C in the case of $NaN_3$ and benzenethiol or at 80 °C in the case of phenol. In the case of alkanethiols, the reaction does proceed at 20 °C but conducting it at 60 °C is more convenient. It should be noted that the outcome does not depend on whether aldehyde **4a** or its hemiacetal **5a** is used as the starting compound.

**Scheme 3**



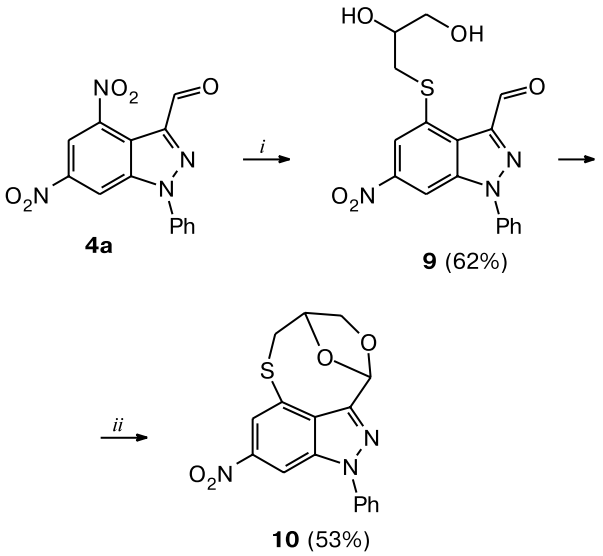

**Reagents and conditions:** *i*. $NaN_3$, DMF, 20 °C; *ii*. PhOH, $K_2CO_3$, NMP, 80 °C; *iii*. RSH, $K_2CO_3$, NMP, 20—60 °C.

| Compound | R | Yield (%) |
|---|---|---|
| **8a** | Ph | 95 |
| **8b** | $CH_2Ph$ | 90 |
| **8c** | *cyclo*-$C_6H_{11}$ | 89 |

The formation of only one of the two possible products of replacement of the nitro group was proved by $^1H$ NMR spectroscopy of the crude reaction product, both for this reaction and for other 3-substituted dinitroindazoles. The fact that the 4-$NO_2$ group is replaced was confirmed in the following way. For the starting 3-formyl-4,6-dinitro-1-phenyl-1*H*-indazole (**4a**), all the carbon and hydrogen signals observed in the $^1H$ and $^{13}C$ NMR spectra were assigned using 1D NOE and 2D $^1H$—$^{13}C$ techniques (HSQC, HMBC). In the case of formylmononitroindazoles **6—8**, formed upon replacement of the nitro group, the signal of the C(4) atom substantially shifts upfield compared to that in the spectrum of the initial formyldinitroindazole **4a**, while the chemical shift of C(6) remains virtually the same. An additional and independent piece of evidence for the replacement of the 4-$NO_2$ group is the fact that the NOESY spectrum of formylmononitroindazole **8a** reflects through-space interaction between the formyl group proton and the phenyl *ortho*-protons in the SPh substituent. The pattern of re-

placement of the nitro group was also demonstrated by a chemical procedure. The reaction of **4a** with thioglycerol gave glycol **9**, which was converted into intramolecular cyclic acetal **10** in the presence of *para*-toluenesulfonic acid as a catalyst (Scheme 4). This product could form only in the case of replacement of the nitro group located in the *peri*-position to the formyl group, *i.e.*, in position 4.

**Scheme 4**

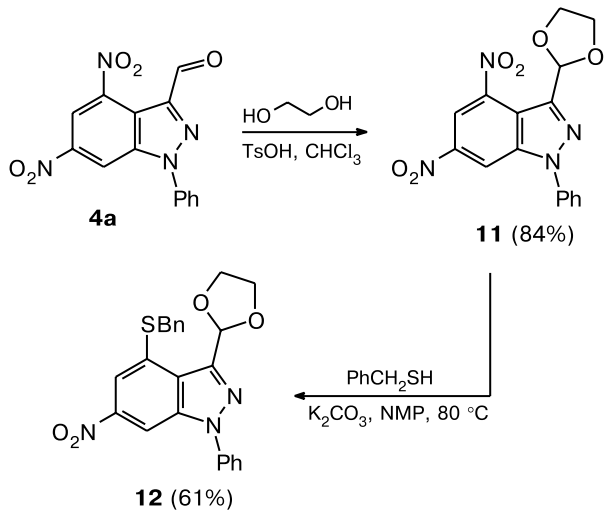



**Reagents and conditions:** *i.* $HSCH_2CH(OH)CH_2OH$, $K_2CO_3$, NMP, 20 °C; *ii.* TsOH, $C_6H_6$, 80 °C.

In order to prepare new 3-substituted 4,6-dinitro-1*H*-indazoles, we studied transformations of formyldinitroindazole **4a** involving the formyl group. On treatment with ethylene glycol in chloroform in the presence of catalytic amounts of TsOH, dinitroindazole **4a** is converted into cyclic acetal **11** in a good yield (Scheme 5).

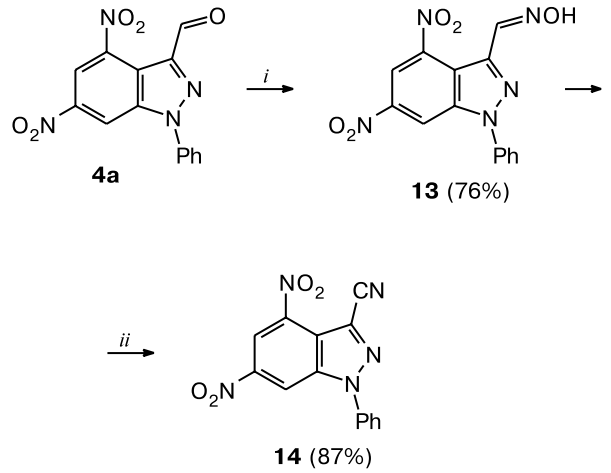
The reaction with phenylmethanethiol was used to demonstrate that the nitro group in dioxolane derivative **11** can also be substituted on treatment with a nucleophile but under more drastic conditions than that in 3-formyl-4,6-dinitroindazoles. The reaction with $PhCH_2SH$ proceeds only at 80 °C (in NMP in the presence of $K_2CO_3$, see Scheme 5), whereas in the case of **4a**, it can be carried out at ~20 °C. It should be noted that the process is regiospecific, *i.e.*, only the nitro group in position 4 is replaced. This is indicated by the substantial change in the chemical shift of the C(4) atom in product **12** compared to that in the starting dinitro derivative **11**, for which full assignment of the hydrogen and carbon signals was performed using NOE and $^1H—^{13}C$ 2D NMR techniques. The chemical shifts of the other carbon atoms in compound **12** remained virtually the same.

**Scheme 5**




The reaction of aldehyde **4a** with hydroxylamine hydrochloride in AcOH gave oxime **13** (Scheme 6), which splits off a water molecule on treatment with $Ac_2O$ to give previously unknown 3-cyano-4,6-dinitro-1-phenyl-1*H*-indazole (**14**).

**Scheme 6**

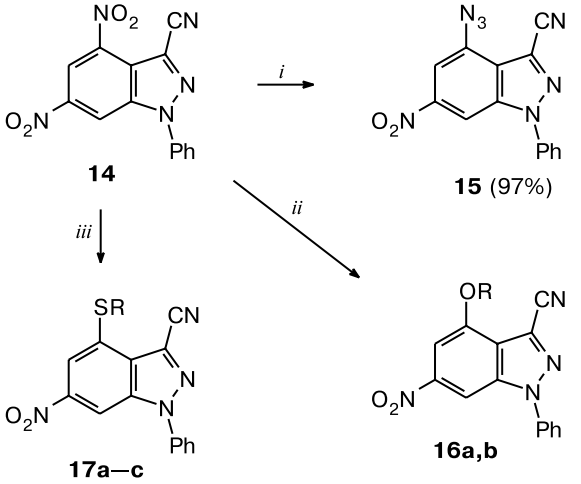



**Reagents and conditions:** *i.* $NH_2OH \cdot HCl$, AcOH; *ii.* $Ac_2O$, 140 °C.

We found that in the case of nitrile **14**, too, the nitro group in position 4 is highly reactive. In particular, only the 4-$NO_2$ group is replaced on treatment with anionic N-, O-, and S-nucleophiles (in NMP or DMF). This gives 4-substituted 3-cyano-6-nitro-1-phenyl-1*H*-indazoles **15—17** usually in high yields and under mild conditions (Scheme 7). The nucleophiles used included phenol, 2,2,3,3-tetrafluoropropan-1-ol, and thiols in the pres-

ence of $K_2CO_3$, and $NaN_3$ (see Scheme 7). In the case of $NaN_3$ and thiols, the reaction proceeds at ~20 °C and in the case of O-nucleophiles, at 80 °C.

**Scheme 7**




**Reagents and conditions:** *i*. $NaN_3$, DMF, 20 °C; *ii*. ROH, $K_2CO_3$, NMP, 80 °C; *iii*. RSH, $K_2CO_3$, NMP, 20 °C.

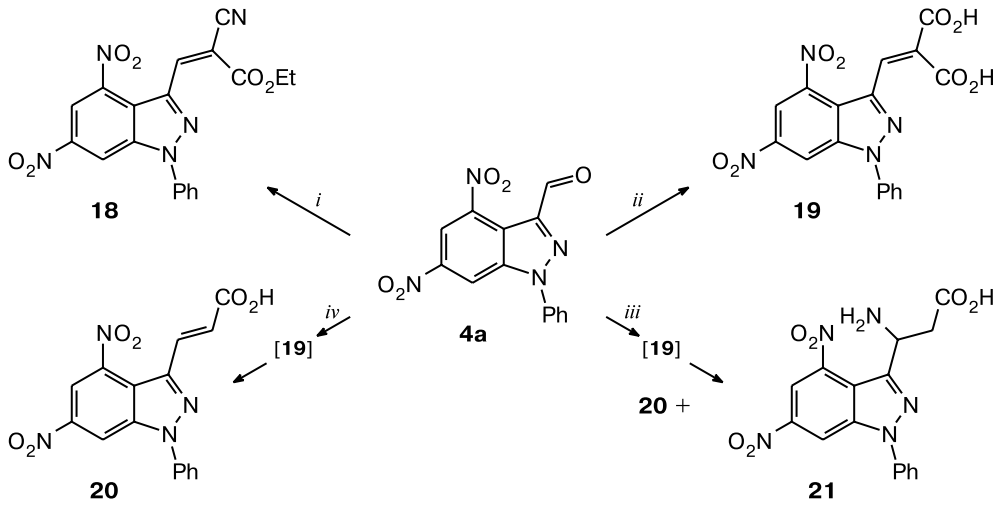
| Compound | R | Yield (%) |
|---|---|---|
| **16a** | Ph | 87 |
| **16b** | $CH_2CF_2CHF_2$ | 18 |
| **17a** | Ph | 98 |
| **17b** | $CH_2Ph$ | 98 |
| **17c** | $CH_2CO_2Me$ | 98 |

The regiospecificity of the nucleophilic substitution (replacement of only the 4-$NO_2$ group) was proved by NMR spectroscopy, as in the case of formyldinitroindazole **4a** (see above). Due to the low solubility of nitrile **14**, we were unable to record a satisfactory $^{13}C$ NMR spectrum for this compound. In the case of derivative **17c**, through-space interaction between the protons of the methylene fragment and H(5) was detected by $^1H$ NMR spectroscopy using the NOE procedure. In addition, interaction between H(7) and the phenyl *ortho*-protons was found in molecule **17c**. These facts provide the conclusion that the group replaced is the nitro group in position 4. We assigned all the carbon signals from derivative **17c** using a number of NMR techniques (NOE, HMBC) and found the chemical shifts for the C(4) (132.2 ppm) and C(6) (147.7 ppm) atoms. The $^{13}C$ NMR spectra of any of cyanomononitroindazoles **15—17**, formed upon replacement of the nitro group, exhibit signals in the region of δ 147—149 for C(6) and in the region of δ 132—135 for C(4). These results allowed us to conclude unambiguously that only the nitro group in position 4 was substituted under the action of any nucleophile. The rates of replacement of the nitro group in nitrile **14** and in 3-formylindazole **4a** do not probably differ much, as complete conversion of these compounds on treatment with the same nucleophile ($NaN_3$, $PhSH/K_2CO_3$) under identical conditions requires nearly equal time periods.

Thus, we developed a general method for the synthesis of 3-cyano-6-nitro-1-phenyl-1*H*-indazoles with various substituents in position 4.

The formation of stable hemiacetals **5a,b** from formyldinitroindazoles **4a,b** (see Scheme 2) attests to high electrophilicity of the formyl group in these molecules. This feature of formyldinitroindazoles **4** was used to study the reactions of dinitro derivative **4a** with compounds con-

**Scheme 8**

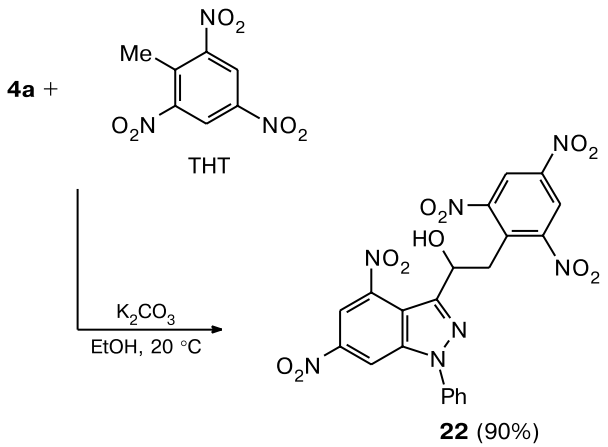



**Reagents and conditions:** *i*. $CH_2(CN)CO_2Et$ (1 equiv.), $NH_4OAc$ (10 mol. %), AcOH (10 mol. %), benzene, 80 °C, 6 h; *ii*. $CH_2(CO_2H)_2$, $NH_4OAc$ (2 equiv.), EtOH, 78 °C, 5 h; *iii*. $CH_2(CO_2H)_2$, $NH_4OAc$ (3 equiv.), AcOH, 118 °C, 10 h; *iv*. $CH_2(CO_2H)_2$, piperidine (10 mol. %), Py, 115 °C, 5 h.

taining an activated methylene fragment. Reactions of this type proceed very easily, for example, the reaction with ethyl cyanoacetate yields unsaturated compound **18** (Scheme 8). Of special note are the results of reaction of formyldinitroindazole **4a** with malonic acid. Different products can be formed depending on the conditions. The reaction carried out in EtOH in the presence of $NH_4OAc$ gave a methylenemalonic acid derivative **19**, while heating in pyridine in the presence of piperidine as the catalyst gave an acrylic acid derivative **20**, *i.e.*, under these conditions, dicarboxylic acid **19** is decarboxylated. If the reaction is carried out in the presence of excess $NH_4OAc$ but in acetic acid (Rodionov reaction conditions[5]), two products are formed in roughly the same amounts, namely, acrylic acid derivative **20** (yield 28%) and 3-aminopropionic acid derivative **21** (yield 20%). It was found that acid **20** does not add ammonia under the reaction conditions and amino acid **21** is not formed. Meanwhile, methylenemalonic acid **19** is converted under these conditions to give a mixture of acids **20** and **21** in 20 and 32% yields, respectively. Thus, one can conclude that the reaction of formyldinitroindazole **4a** with malonic acid in the presence of $NH_4OAc$ in acetic acid gives first dicarboxylic acid **19**. Under the reaction conditions, this product is either decarboxylated to give **20** or adds ammonia and is subsequently decarboxylated to give amino acid **21**, the rates of these reactions being similar.

Formyldinitroindazole **4a** reacts with 2,4,6-trinitrotoluene (TNT) in an unusual way. Heating aromatic and heteroaromatic aldehydes with TNT in the presence of bases is known to give the corresponding stilbenes or their heteroaromatic analogs (see Ref. 6 and references cited therein). Indazole **4a** reacts with TNT even at room temperature (in the presence of $K_2CO_3$ in EtOH) to give alcohol **22** in a high yield (Scheme 9). No dehydration product of alcohol **22** was detected.

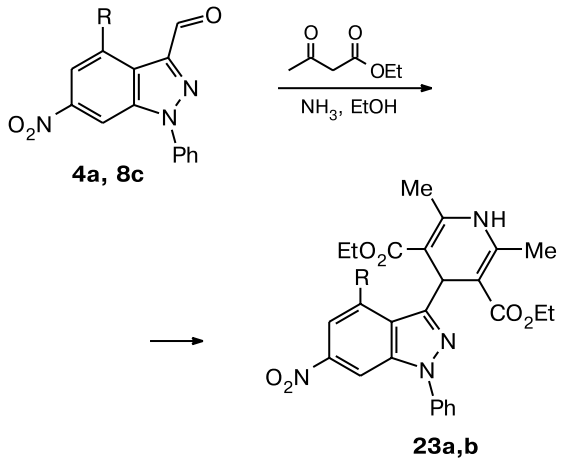
**Scheme 9**




In this respect, **4a** resembles aliphatic aldehydes ($CH_2O$, $X_3CCHO$, X = F, Cl), which also react with TNT to give alcohols, rather than aromatic aldehydes.[7] This fact confirms once again the high reactivity of the carbonyl group in 3-formylindazoles **4**.

3-Formylindazoles **4a** and **8c** react with ethyl acetoacetate under the Hantzsch reaction conditions[8] (refluxing in an alcohol solution of ammonia) to give 1,4-dihydropyridine derivatives **23a,b** (Scheme 10).

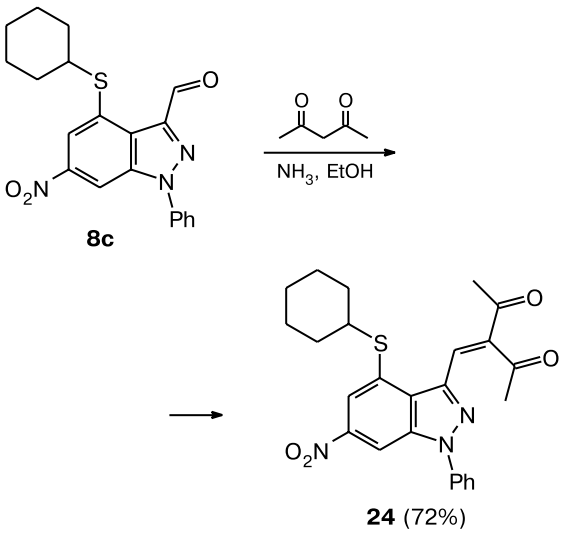
**Scheme 10**




**23a:** R = $NO_2$, yield 13%
**23b:** R = S-(*cyclo*)-$C_6H_{11}$, yield 70%

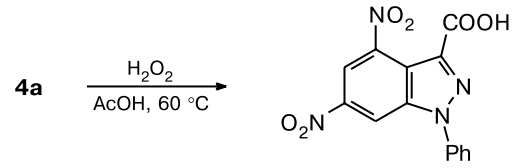
However, the reaction of mononitro-substituted formylindazole **8c** with acetylacetone under the same conditions follows a different route, giving rise to unsaturated compound **24** (Scheme 11).

**Scheme 11**



Formyldinitroindazole **4a** is smoothly oxidized by 30% hydrogen peroxide in acetic acid to give the corresponding acid, namely, 4,6-dinitro-1-phenyl-1*H*-indazole-3-carboxylic acid (**25**) (Scheme 12).

**Scheme 12**




**25** (73%)

The structures of the obtained compounds were proved by $^1$H and $^{13}$C NMR spectroscopy, mass spectrometry (a molecular ion was recorded in all cases), and IR spectroscopy ($\nu^{as}(NO_2)$ at 1540—1560 cm$^{-1}$, $\nu^{s}(NO_2)$ at 1340—1360 cm$^{-1}$, $\nu$(CN) at 2220—2240 cm$^{-1}$, and $\nu$(CHO) 1695—1715 cm$^{-1}$) and confirmed by elemental analysis.

Thus, as a result of this research, we developed convenient methods for the synthesis of previously unknown 3-substituted 1-aryl-4,6-dinitro-1*H*-indazoles, which were used to prepare a number of new 3-R-4-R´-6-nitro-1-phenyl-1*H*-indazoles.

## Experimental

$^1$H NMR spectra were recorded on a Bruker AC-200 spectrometer and $^{13}$C NMR spectra were run on a Bruker AM-300 instrument. The chemical shifts ($\delta$) are referred to tetramethylsilane. The spin-spin coupling constants are given in Hz. All the samples for NMR spectroscopy were prepared in a 1 : 1 DMSO-$d_6$—$CCl_4$ mixture. IR spectra were measured on a Specord M-80 instrument for KBr pellets. Mass spectra were run on a MS-30 Kratos mass spectrometer (always EI, 70 eV). The mass spectrum of compound **22** was obtained on a Finnigan LCQ instrument (electrospray ionization in the negative ion mode). The reactions were monitored and the purity of compounds was checked by TLC on Silufol UV-254 plates. The solvents were not specially dried.

**Preparation of picrylglyoxal monoarylhydrazones 3a—c (general procedure).** A solution of $NaNO_2$ (0.7 g, 10 mmol) was added dropwise at 0—5 °C to a solution of $ArNH_2 \cdot HCl$ (10 mmol) in a mixture of 3 mL of concentrated HCl and 3 mL of water. The mixture was stirred for 5 min and AcONa (2.8 g) was added portionwise at 0—5 °C (solution pH ~5). A suspension of finely ground* picrylacetaldehyde (2 g, 7.8 mmol) in 40 mL of EtOH was added to the resulting solution. The reaction mixture was stirred for 1 h at 0—5 °C and poured into 400 mL of water. The precipitate was filtered off, dried in air, and used without further purification.

**2-(2-Phenylhydrazono)-2-(2,4,6-trinitrophenyl)acetaldehyde (3a).** $^1$H NMR: 7.05 (m, 1 H, Ph); 7.30 (m, 4 H, Ph); 9.21 (s, 2 H, Pic); 9.53 (s, 1 H, CHO); 11.11 (s, 1 H, NH).

**2-[2-(4-Chlorophenyl)hydrazono]-2-(2,4,6-trinitrophenyl)acetaldehyde (3b).** $^1$H NMR: 7.32 (m, 4 H, *p*-$ClC_6H_4$); 9.21 (s, 2 H, Pic); 9.56 (s, 1 H, CHO); 11.12 (s, 1 H, NH).

**2-[2-(4-Methoxyphenyl)hydrazono]-2-(2,4,6-trinitrophenyl)acetaldehyde (3c).** $^1$H NMR: 3.79 (s, 3 H, $CH_3$); 6.90, 7.25 (both d, each 2 H, *p*-$MeOC_6H_4$); 9.20 (s, 2 H, Pic); 9.47 (s, 1 H, CHO); 11.10 (s, 1 H, NH).

**Preparation of 1-aryl-3-formyl-4,6-dinitro-1*H*-indazoles (4a—c) (general procedure).** Potassium carbonate (2.76 g, 20 mmol) was added to a solution of picrylglyoxal monoarylhydrazone (20 mmol) in 220 mL of EtOH. The mixture was stirred for 24 h and the precipitate was filtered off, washed with water, recrystallized from EtOH, and dried at 80 °C (drying in air at 20 °C results in hemiacetals **5a** and **5b**).

**3-Formyl-4,6-dinitro-1-phenyl-1*H*-indazole (4a).** M.p. 190 °C (EtOH). Found (%): C, 53.44; H, 2.76. $C_{14}H_8N_4O_5$. Calculated (%): C, 53.85; H, 2.58. $^1$H NMR: 7.60—7.80 (m, 3 H, Ph); 7.90 (m, 2 H, Ph); 8.75 (s, 1 H, H(5)); 8.85 (s, 1 H, H(7)); 10.35 (s, 1 H, CHO). $^{13}$C NMR: 113.2 (C(7)), 114.8 (C(5)), 115.9 (C(3a)), 124.5 (*o*-Ph), 129.9 (*p*-Ph), 130.2 (*m*-Ph), 137.2 (*ipso*-Ph), 140.7 (C(7a)), 141.7 (C(4)), 142.0 (C(3)), 146.0 (C(6)), 185.4 (CHO).

**1-(4-Chlorophenyl)-3-formyl-4,6-dinitro-1*H*-indazole (4b).** M.p. 218—220 °C (EtOH). Found (%): C, 48.21; H, 2.43. $C_{14}H_7ClN_4O_5$. Calculated (%): C, 48.50; H, 2.04. $^1$H: 7.70, 7.90 (both d, each 2 H, $^4J$ = 8.8); 8.60 (s, 1 H, H(5)); 8.80 (s, 1 H, H(7)); 10.40 (s, 1 H, CHO).

**3-Formyl-1-(4-methoxyphenyl)-4,6-dinitro-1*H*-indazole (4c).** M.p. 210—212 °C (EtOH). Found (%): C, 52.81; H, 3.23. $C_{15}H_{10}N_4O_6$. Calculated (%): C, 52.64; H, 2.94. $^1$H NMR: 3.92 (s, 3 H, $OCH_3$); 7.22, 7.75 (both d, each 2 H, $^3J$ = 8.85 Hz); 8.76 (s, 2 H, H(5) and H(7)); 10.32 (s, 1 H, CHO).

Hemiacetals **5a,b** were not obtained in an analytically pure state. Their melting points were not determined either, as during heating, they lose an EtOH molecule before melting.

**(4,6-Dinitro-1-phenyl-1*H*-indazol-3-yl)(ethoxy)methanol (5a).** $^1$H NMR: 1.14 (t, 3 H, Me, $^3J$ = 6.96 Hz); 3.54, 3.87 (both m, each 1 H, $CH_2$); 5.95, 6.69 (both d, each 1 H, OCH and OH, $^3J_{H,H}$ = 9.11 Hz); 7.50—7.90 (m, 5 H, Ph); 8.53, 8.77 (both d, each 1 H, H(5) and H(7), $^4J$ = 1.60 Hz).

**[1-(4-Chlorophenyl)-4,6-dinitro-1*H*-indazol-3-yl](ethoxy)methanol (5b).** $^1$H NMR: 1.13 (t, 3 H, Me, $^3J$ = 6.99 Hz); 3.50, 3.82 (both m, each 1 H, $CH_2$); 5.89, 6.83 (both d, each 1 H, OCH and OH, $^3J$ = 9.32 Hz); 7.68, 7.89 (both d, each 2 H, *p*-$ClC_6\underline{H}_4$, $^3J$ = 8.85 Hz); 8.53, 8.80 (both s, each 1 H, H(5) and H(7)).

**Preparation of 4-azido-6-nitro-1-phenylindazoles 6 and 15 (general procedure).** A mixture of compound **4a** or **14** (1 mmol), $NaN_3$ (0.07 g, 1 mmol), and 5 mL of DMF was stirred for 24 h at 20 °C. The reaction mixture was poured in water and acidified to pH 2. The precipitate was filtered off and recrystallized from EtOH.

**4-Azido-3-formyl-6-nitro-1-phenyl-1*H*-indazole (6).** M.p. 194—195 °C (EtOH). Found (%): C, 54.81; H, 2.38. $C_{14}H_8N_6O_3$. Calculated (%): C, 54.55; H, 2.62. $^1$H NMR: 7.60—7.90 (m,

* **Caution!** Picrylacetaldehyde is a potentially explosive substance. Grinding should be carried out with caution. For example, this can be done in an agate mortar with an agate pestle.

5 H, Ph); 8.02 (s, 1 H, H(5)); 8.35 (s, 1 H, H(7)); 10.50 (s, 1 H, CHO).

**4-Azido-3-cyano-6-nitro-1-phenyl-1*H*-indazole (15).** M.p. 170—172 °C (EtOH). Found (%): C, 55.01; H, 2.49. $C_{14}H_7N_7O_2$. Calculated (%): C, 55.09; H, 2.31. $^1$H NMR: 7.50—7.90 (m, 5 H, Ph); 8.05 (s, 1 H, H(5)); 8.35 (s, 1 H, H(7)). $^{13}$C NMR: 105.1, 107.9, 112.7, 118.7, 120.6, 124.3, 130.1, 130.7, 135.3, 137.9, 139.5, 148.9.

**Preparation of 6-nitro-1-phenyl-4-phenyloxy-1*H*-indazoles 7 and 16a (general procedure).** A mixture of compound **4a** or **14** (1 mmol), phenol (0.094 g, 1 mmol), $K_2CO_3$ (0.14 g, 1 mmol), and NMP (5 mL) was stirred for 8 h at 80 °C. After completion of the reaction, the mixture was poured in water and acidified to pH 2. The precipitate was filtered off and recrystallized from EtOH.

**3-Formyl-6-nitro-1-phenyl-4-phenyloxy-1*H*-indazole (7).** M.p. 192—194 °C (EtOH). Found (%): C, 66.70; H, 3.72. $C_{20}H_{13}N_3O_4$. Calculated (%): C, 66.85; H, 3.65. $^1$H NMR: 7.20—7.40 (m, 4 H, Ph); 7.50—7.80 (m, 5 H, H(5), Ph); 7.91 (m, 2 H, Ph); 8.32 (s, 1 H, H(7)); 10.53 (s, 1 H, CHO).

**3-Cyano-6-nitro-1-phenyl-4-phenyloxy-1*H*-indazole (16a).** M.p. 196—199 °C (EtOH). Found (%): C, 67.71; H, 3.14. $C_{20}H_{12}N_4O_3$. Calculated (%): C, 67.41; H, 3.39. $^1$H NMR: 7.20—7.50 (m, 4 H, Ph); 7.50—7.90 (m, 7 H, H(5), Ph); 8.33 (s, 1 H, H(7)). $^{13}$C NMR: 103.0, 103.5, 113.3, 119.0, 120.9, 121.3, 124.6, 127.0, 130.3, 131.0, 131.5, 138.3, 140.3, 149.5, 152.0, 154.6.

**Preparation of compounds 8a** and **17a—c (general procedure).** A mixture of compound **4a** or **14** (1 mmol), the corresponding thiol (1 mmol), $K_2CO_3$ (0.14 g, 1 mmol), and NMP (5 mL) was stirred for 24 h at 20 °C. After completion of the reaction, the mixture was poured in water and acidified to pH 2. The precipitate was filtered off and recrystallized from EtOH.

**3-Formyl-6-nitro-1-phenyl-4-phenylthio-1*H*-indazole (8a).** M.p. 199—200 °C (EtOH). Found (%): C, 63.71; H, 3.74; S, 8.40. $C_{20}H_{13}N_3O_3S$. Calculated (%): C, 63.99; H, 3.49; S, 8.54. $^1$H NMR: 7.59 (s, 1 H, H(5)); 7.50—7.90 (m, 10 H, 2 Ph); 8.25 (s, 1 H, H(7)); 10.42 (s, 1 H, CHO). $^{13}$C NMR: 103.9, 114.7, 120.2, 122.2, 123.8, 129.1, 129.6, 129.8, 130.2, 134.5, 136.5, 137.5, 139.8, 144.3, 147.1, 184.1.

**3-Cyano-6-nitro-1-phenyl-4-phenylthio-1*H*-indazole (17a).** M.p. 196—198 °C (EtOH). $^1$H NMR: 7.50—7.80 (m, 11 H, H(5), Ph); 8.42 (s, 1 H, H(7)).

**4-Benzylthio-3-cyano-6-nitro-1-phenyl-1*H*-indazole (17b).** M.p. 165—168 °C (EtOH). $^1$H NMR: 4.59 (s, 2 H, $CH_2$); 7.20—7.40 (m, 3 H, Ph); 7.50 (m, 2 H, Ph); 7.60—7.80 (m, 5 H, Ph); 8.07 (s, 1 H, H(5)); 8.35 (s, 1 H, H(7)).

**Methyl 2-[(3-cyano-6-nitro-1-phenyl-1*H*-indazol-4-yl)thio]acetic acid (17c).** M.p. 132—135 °C (EtOH). $^1$H NMR: 3.75 (s, 3 H, $CH_3$); 4.34 (s, 2 H, $CH_2$); 7.60—7.90 (m, 5 H, Ph); 8.10 (s, 1 H, H(5)); 8.38 (s, 1 H, H(7)). $^{13}$C NMR: 33.7 ($CH_2S$), 52.4 ($OCH_3$), 105.6 (C(7)), 112.9 (CN), 115.4 (C(5)), 118.7 (C(3)), 123.8 (*o*-Ph), 125.4 (C(3a)), 129.4 (*p*-Ph), 129.9 (*m*-Ph), 132.2 (C(4)), 137.2 (*ipso*-Ph), 137.8 (C(7a)), 147.7 (C(6)), 168.4 (C=O).

**Preparation of compounds 8b,c (general procedure).** A mixture of compound **4a** (2.6 g, 8.3 mmol), the corresponding thiol (8.3 mmol), $K_2CO_3$ (1.15 g, 8.3 mmol), and NMP (30 mL) was stirred for 24 h at 60 °C. After completion of the reaction, the mixture was poured in water and acidified to pH 2. The precipitate was filtered off and recrystallized from EtOH.

**4-Benzylthio-3-formyl-6-nitro-1-phenyl-1*H*-indazole (8b).** M.p. 152—153 °C (EtOH). $^1$H NMR: 4.52 (s, 2 H, $CH_2$); 7.29 (m, 2 H, Ph); 7.50—7.80 (m, 8 H, Ph); 8.03 (s, 1 H, H(5)); 8.25 (s, 1 H, H(7)); 10.42 (s, 1 H, CHO).

**4-Cyclohexylthio-3-formyl-6-nitro-1-phenyl-1*H*-indazole (8c).** M.p. 173—175 °C (EtOH). $^1$H NMR: 1.30—1.90, 2.00—2.20 (both m, 10 H, $(CH_2)_5$); 3.61 (m, 1 H, SCH); 7.50—7.90 (m, 5 H, Ph); 8.01, 8.30 (both d, each 1 H, H(5) and H(7), $^4J$ = 1.40 Hz); 10.58 (s, 1 H, CHO).

**4-(2,3-Dihydroxypropylthio)-6-nitro-1-phenyl-1*H*-indazole-3-carboxaldehyde (9).** A mixture of compound **4a** (0.312 g, 1 mmol), 1-thioglycerol (0.09 mL, 1.1 mmol), $K_2CO_3$ (0.14 g, 1 mmol), and NMP (4 mL) was stirred for 24 h at 20 °C. The reaction mixture was poured in water and acidified to pH 2. The resulting oil was separated and dried to give 0.24 g of compound **9**, which was used without further purification. $^1$H NMR: 3.10, 3.40 (both m, each 2 H); 3.80 (m, 1 H, CH); 4.50, 5.00 (both br.s, each 1 H, OH); 7.50—7.90 (m, 5 H, Ph); 8.07 (s, 1 H, H(5)); 8.21 (s, 1 H, H(7)); 10.51 (s, 1 H, CHO).

**10-Nitro-13-phenyl-3,16-dioxa-7-thia-13,14-diazatetracyclo[6.6.1.1$^{2,5}$.0$^{12,15}$]hexadeca-1(14),8(15),9,11-tetraene (10).** A mixture of compound **9** (0.23 g, 0.63 mmol) and TsOH (50 mg) in 20 mL of toluene was refluxed for 6 h. The solvent was evaporated and the residue was washed with water, dried in air, and recrystallized from an EtOH—benzene mixture (1 : 3) to give 0.1 g of compound **10**. M.p. 175—177 °C (EtOH—benzene, 1 : 3). $^1$H NMR: 3.20 (s, 2 H, $CH_2$); 4.05 (m, 1 H); 4.52 (d, 1 H, $J$ = 8.6 Hz); 4.81 (m, 1 H); 6.32 (s, 1 H); 7.50—7.80 (m, 5 H, Ph); 8.13 (s, 1 H, H(5)); 8.39 (s, 1 H, H(7)).

**3-(1,3-Dioxolan-2-yl)-4,6-dinitro-1-phenyl-1*H*-indazole (11).** A mixture of **4a** (1.2 g, 3.85 mmol), ethylene glycol (0.43 mL, 7.7 mmol), TsOH (50 mg), and 30 mL of chloroform was refluxed for 6 h with a water trap. The reaction mixture was cooled, the solvent was evaporated, and the residue was chromatographed on a column ($SiO_2$, elution with $CHCl_3$) to give 1.15 g of compound **11**. M.p. 192—194 °C. Found (%): C, 53.43; H, 3.14. $C_{16}H_{12}N_4O_6$. Calculated (%): C, 53.94; H, 3.39. $^1$H NMR: 4.02 (s, 4 H, $OCH_2CH_2O$); 6.48 (s, 1 H, OCHO); 7.57 (t, 1 H, Ph, $J$ = 7.5 Hz); 7.68 (m, 2 H, Ph); 7.80 (d, 2 H, Ph, $J$ = 7.5 Hz); 8.63 (s, 1 H, H(5)); 8.78 (s, 1 H, H(7)). $^{13}$C NMR: 64.3 ($OCH_2CH_2O$), 98.1 (OCHO), 112.1 (C(7)), 112.9 (C(5)), 115.9 (C(3a)), 123.7 (*o*-Ph), 128.6 (*p*-Ph), 129.7 (*m*-Ph), 137.4 (*ipso*-Ph), 140.1 (C(7a)), 141.9 (C(4)), 142.3 (C(3)), 145.3 (C(6)).

**4-Benzylthio-3-(1,3-dioxolan-2-yl)-6-nitro-1-phenyl-1*H*-indazole (12).** Potassium carbonate (0.125 g, 0.9 mmol) was added to a solution containing compound **11** (0.31 g, 0.87 mmol) and BnSH (0.1 mL, 0.9 mmol) in NMP (5 mL), and the mixture was stirred for 8 h at 80 °C. The reaction mixture was poured in water and acidified to pH 3. The precipitate was filtered off, washed with water, and recrystallized from EtOH to give 0.23 g of compound **12**. M.p. 145—147 °C (EtOH). $^1$H NMR: 4.00—4.30 (m, 4 H, $OCH_2CH_2O$); 4.47 (s, 2 H, $CH_2$); 6.62 (s, 1 H, OCHO); 7.20—7.80 (m, 10 H, Ph); 7.91 (s, 1 H, H(5)); 8.22 (s, 1 H, H(7)).

**4,6-Dinitro-1-phenyl-1*H*-indazole-3-carboxaldehyde oxime (13).** A mixture of **4a** (0.62 g, 2 mmol) and hydroxylamine hydrochloride (0.21 g, 3 mmol) in 10 mL of acetic acid was refluxed for 6 h. The solution was cooled, the precipitate was filtered off, washed with water, and dried in air to give 0.55 g of compound **13**. M.p. 218—220 °C. $^1$H: 7.60—7.90 (m, 5 H, Ph);

8.45 (s, 1 H, CH=N); 8.62 (s, 1 H, H(5)); 8.78 (s, 1 H, H(7)); 11.70 (s, 1 H, NOH).

**3-Cyano-4,6-dinitro-1-phenyl-1*H*-indazole (14).** A mixture of **13** (3 g, 9.2 mmol) and 75 mL of acetic anhydride was refluxed for 6 h. After cooling the solution, the precipitate was filtered off and washed with ethanol to give 2.46 g of compound **14**. M.p. 275—277 °C ($Ac_2O$). Found (%): C, 54.71; H, 2.14. $C_{14}H_7N_5O_4$. Calculated (%): C, 54.38; H, 2.28. $^1$H NMR: 7.60—7.90 (m, 5 H, Ph); 8.95 (s, 2 H, H(5) and H(7)). $^{13}$C NMR: 112.5, 115.1, 116.0, 124.5, 130.1, 136.7, 139.7, 146.1.

**3-Cyano-6-nitro-1-phenyl-4-(2,2,3,3-tetrafluoropropyloxy)-1*H*-indazole (16b).** A mixture of nitrile **14** (0.31 g, 1 mmol), 2,2,3,3-tetrafluoropropanol (0.09 mL, 1 mmol), and $K_2CO_3$ (0.14 g, 1 mmol) in 6 mL of NMP was stirred for 7 h at 80 °C. The reaction mixture was poured in water and acidified to pH 2, and the precipitate was filtered off and recrystallized from EtOH to give 0.07 g of compound **16b**. M.p. 198—200 °C (EtOH). Found (%): C, 51.77; H, 2.63. $C_{17}H_{10}F_4N_4O_3$. Calculated (%): C, 51.79; H, 2.56. $^1$H NMR: 5.05 (t, 2 H, $OCH_2$, $J$ = 18 Hz); 6.65 (tt, 1 H, $CHF_2$); 7.55—7.85 (m, 5 H, Ph); 7.91 (s, 1 H, H(5)); 8.28 (s, 1 H, H(7)).

**Ethyl 2-cyano-3-(4,6-dinitro-1-phenyl-1*H*-indazol-3-yl)acrylate (18).** A suspension of compound **4a** (1 g, 3.2 mmol), cyanoacetic ester (0.36 g, 3.2 mmol), AcOH (0.04 g), and $NH_4OAc$ (0.025 mg) in 20 mL benzene was refluxed for 5 h with a water trap. After cooling, the precipitate was filtered off, washed with benzene, and dried *in vacuo* to give 0.6 g (46%) of compound **18**, m.p. >300 °C (dec.). Found (%): C, 55.81; H, 3.13. $C_{19}H_{13}N_5O_6$. Calculated (%): C, 56.02; H, 3.22. $^1$H NMR: 1.41 (t, 3 H, $CH_3$, $^3J$ = 6.57 Hz); 4.40 (q, 2 H, $CH_2$, $^3J$ = 6.57 Hz); 7.60—7.80 (m, 3 H, Ph); 7.95 (m, 2 H, Ph); 8.92 (s, 1 H); 8.98 (s, 2 H).

**(4,6-Dinitro-1-phenyl-1*H*-indazol-3-ylmethylene)malonic acid (19).** A mixture of compound **4a** (1.25 g, 4 mmol), malonic acid (0.42 g, 4 mmol), $NH_4OAc$ (0.78 g, 10 mmol), and EtOH (40 mL) was refluxed for 5 h. The reaction mixture was cooled and the precipitate was filtered off, washed with EtOH and water, and dried in air to give 1.34 g (84%) of compound **19**. M.p. >300 °C (dec.). Found (%): C, 51.39; H, 2.44. $C_{17}H_{10}N_4O_8$. Calculated (%): C, 51.27; H, 2.53. $^1$H NMR: 7.00—7.50 (m, 5 H, Ph); 8.10 (s, 1 H, CH); 8.83 (s, 1 H, H(5)); 9.01 (s, 1 H, H(7)); 12.90 (br.s, 2 H, 2 OH). $^{13}$C NMR: 117.8, 114.5, 119.4, 124.6, 129.6, 130.8, 131.7, 134.0, 138.5, 140.4, 141.9, 143.3, 145.9, 167.6, 167.8. MS, *m/z*: 398 $[M]^+$.

**3-(4,6-Dinitro-1-phenyl-1*H*-indazol-3-yl)acrylic acid (20).** A solution of compound **4a** (1 g, 3.2 mmol), malonic acid (0.4 g, 3.8 mmol), and piperidine (0.03 mL, 0.32 mmol) in 5 mL of pyridine was stirred for 5 h at 80—90 °C. The mixture was cooled and the precipitate was filtered off, washed with pyridine, 5% HCl, and water, and dried *in vacuo* to give 0.5 g (44%) of compound **20**. M.p. >300 °C (dec.). Found (%): C, 54.31; H, 3.03. $C_{16}H_{10}N_4O_6$. Calculated (%): C, 54.24; H, 2.85. $^1$H NMR: 6.75 (d, 1 H, CH, $^3J_{H,H}$ = 15.26 Hz); 7.50—7.70 (m, 3 H, Ph); 7.90 (m, 1 H, Ph); 8.04 (d, 1 H, CH, $^3J_{H,H}$ = 15.26 Hz); 8.78 (s, 1 H, H(5)); 8.84 (s, 1 H, H(7)); 12.43 (br.s, 1 H, OH).

**3-Amino-3-(4,6-dinitro-1-phenyl-1*H*-indazol-3-yl)propionic acid (21).** A mixture of compound **4a** (0.624 g, 2 mmol), malonic acid (0.26 g, 2.5 mmol), $NH_4OAc$ (0.48 g, 6.2 mmol), and AcOH (20 mL) was stirred for 6 h at 100 °C. After cooling the reaction mixture, the precipitate was filtered off, the filtrate was poured in water, and the acid precipitated was filtered off to give 0.14 g (19%) of compound **21**. M.p. 217—218 °C. Found (%): C, 52.21; H, 3.38. $C_{16}H_{13}N_5O_6$. Calculated (%): C, 51.76; H, 3.53. $^1$H NMR: 2.90—3.10 (m, 2 H, $CH_2$); 5.76 (m, 1 H, $\underline{H}CNH_2$); 7.50—7.90 (m, 6 H, $NH_2$, Ph); 8.30 (d, 1 H, $NH_2$); 8.61, 8.79 (both d, each 1 H, H(5) and H(7), $^4J_{H,H}$ = 1.40 Hz). $^{13}$C NMR: 22.84, 44.98, 112.90, 113.70, 117.46, 124.21, 129.17, 130.57, 138.42, 140.62, 143.30, 145.81, 146.16, 172.39. MS, *m/z*: 371 $[M]^+$.

**1-(4,6-Dinitro-1-phenyl-1*H*-indazol-3-yl)-2-(2,4,6-trinitrophenyl)ethanol (22).** Potassium carbonate (0.14 g, 1 mmol) was added to a suspension of TNT (0.23 g, 1 mmol) and **4a** (0.32 g, 1 mmol) in 10 mL of EtOH and the mixture was stirred for 24 h at 20 °C. The precipitate was filtered off, washed with water, dried in air, and recrystallized from benzene to give 0.49 g of compound **22**. M.p. 204—206 °C ($C_6H_6$). Found (%): C, 46.83; H, 2.38. $C_{21}H_{13}N_7O_{11}$. Calculated (%): C, 46.76; H, 2.43. $^1$H NMR: 3.85 (dd, 1 H, $CH_2$, $J$ = 14 Hz); 4.10 (dd, 1 H, $CH_2$, $J$ = 14 Hz); 5.40 (m, 1 H, CH); 5.90 (d, 1 H, OH, $J$ = 6.1 Hz); 7.50—7.80 (m, 3 H, Ph); 7.85 (d, 2 H, Ph, $J$ = 7.3 Hz); 8.60 (s, 1 H, H(5)); 8.80 (s, 1 H, H(7)); 9.00 (s, 2 H, Pic). MS, *m/z*: 538 $[M]^-$, 226 $[C_6H_2(NO_2)_3]^-$.

**Diethyl 2,6-dimethyl-4-(4,6-dinitro-1-phenyl-1*H*-indazol-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (23a).** A mixture of compound **4a** (1.05 g, 3.37 mmol), ethyl acetoacetate (0.93 mL, 6.75 mmol), conc. aqueous $NH_3$ (0.6 mL), and EtOH (15 mL) was refluxed for 6 h. After cooling the reaction mixture, the precipitate was filtered off and the filtrate was poured in water. The resulting precipitate was filtered off and dried in air to give 0.22 g of compound **23a**. M.p. 112—114 °C. $^1$H NMR: 1.05 (t, 6 H, 2 $CH_3$, $J$ = 6.7 Hz); 2.25 (s, 6 H, 2 $CH_3$); 3.95 (m, 4 H, 2 $CH_2$); 5.60 (s, 1 H, CH); 7.50—7.70 (m, 5 H, Ph); 8.61 (s, 1 H, NH); 8.69 (s, 2 H, H(5) and H(7)).

**Diethyl 2,6-dimethyl-4-[4-(cyclohexylthio)-6-nitro-1-phenyl-1*H*-indazol-3-yl]methylene-1,4-dihydropyridine-3,5-dicarboxylate (23b).** A mixture of compound **8c** (1.53 g, 4 mmol), ethyl acetoacetate (1.1 mL, 8 mmol), conc. aqueous $NH_3$ (0.5 mL), and EtOH (15 mL) was refluxed for 16 h. After cooling, the reaction mixture was poured in water and the precipitate was filtered off and dried in air to give 1.7 g of compound **23b**. M.p. 271—272 °C. Found (%): C, 63.31; H, 6.03; S, 5.57. $C_{32}H_{36}N_4O_6S$. Calculated (%): C, 63.56; H, 6.00; S, 5.30. $^1$H NMR: 0.95 (t, 6 H, 2 $CH_3$, $J$ = 6.9 Hz); 1.30—1.90 (m, *cyclo*-$C_6H_{11}$); 2.32 (s, 6 H, 2 $CH_3$); 3.60 (m, 1 H, CHS); 3.95 (m, 4 H, 2 $CH_2$); 5.88 (s, 1 H, CH); 7.41 (m, 1 H, Ph); 7.60—7.70 (m, 4 H, Ph); 7.80 (s, 1 H, H(5)); 8.22 (s, 1 H, H(7)); 8.63 (s, 1 H, NH).

**3-[4-(Cyclohexylthio)-6-nitro-1-phenyl-1*H*-indazol-3-yl]methylene-2,4-pentanedione (24).** A mixture of compound **4a** (1.15 g, 3 mmol), acetylacetone (0.62 mL, 6 mmol), conc. aqueous $NH_3$ (0.4 mL), and EtOH (15 mL) was refluxed for 5 h. After cooling the reaction mixture, the precipitate was filtered off and recrystallized from EtOH to give 1 g of compound **24**. M.p. 167—169 °C (EtOH). Found (%): C, 64.23; H, 5.46; S, 6.97. $C_{26}H_{25}N_3O_4S$. Calculated (%): C, 64.68; H, 5.44; S, 6.92. $^1$H NMR: 1.30—1.90 and 2.00—2.30 (both m, 10 H, $SC_6H_{11}$); 2.40 (s, 1 H, $CH_3$); 2.52 (s, 1 H, $CH_3$); 3.61 (m, 1 H, CHS); 7.50—7.80 (m, 5 H, Ph); 8.13 (s, 1 H, H(5)); 8.36 (s, 1 H, H(7)); 8.51 (s, 1 H, CH).

**4,6-Dinitro-1-phenyl-1*H*-indazole-3-carboxylic acid (25).** A 30% solution of $H_2O_2$ (3 mL) was added to a solution of compound **4a** (0.624 g, 2 mmol) in 20 mL of AcOH. The mix-

ture was stirred for 6 h at 60 °C. After cooling to 20 °C, the mixture was poured in water and the precipitate was filtered off and washed with $CHCl_3$ to give 0.48 g of compound **25**. M.p. 216—219 °C. Found (%): C, 51.31; H, 2.67. $C_{14}H_8N_4O_6$. Calculated (%): C, 51.23; H, 2.46. $^1$H NMR: 7.60—7.90 (m, 5 H, Ph); 8.65 (s, 1 H, H(5)); 8.82 (s, 1 H, H(7)). $^{13}$C NMR: 112.5, 113.6, 116.1, 124.0, 129.1, 129.9, 137.3, 139.8, 141.8, 145.7, 151.9, 162.0.

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