

Indazole derivatives from substituted ylidene-*N*-phenylhydrazine-carbothioamides and benzo- as well as naphthoquinones

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Abstract

2-Substituted ylidene-*N*-phenylhydrazinecarbothioamides **1a-f** reacted with 2,3-dicyano-5,6-dichloro-1,4-benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, 2,3-dichloro-1,4-naphthoquinone, 2,3-dicyano-1,4-naphthoquinone and 3,4,5,6-tetrachloro-1,2-benzoquinone to form substituted *N*-phenylindazolecarbothioamides, substituted benzindazolecarbothioamides and substituted benzophthalazinediones. Rationales for the role of benzo- and naphthoquinones in heterocyclization of compounds **1a-f** are presented.

Keywords: 2-Substituted ylidene-*N*-phenylhydrazinecarbothioamides, benzo- and naphthoquinones, indazole derivatives

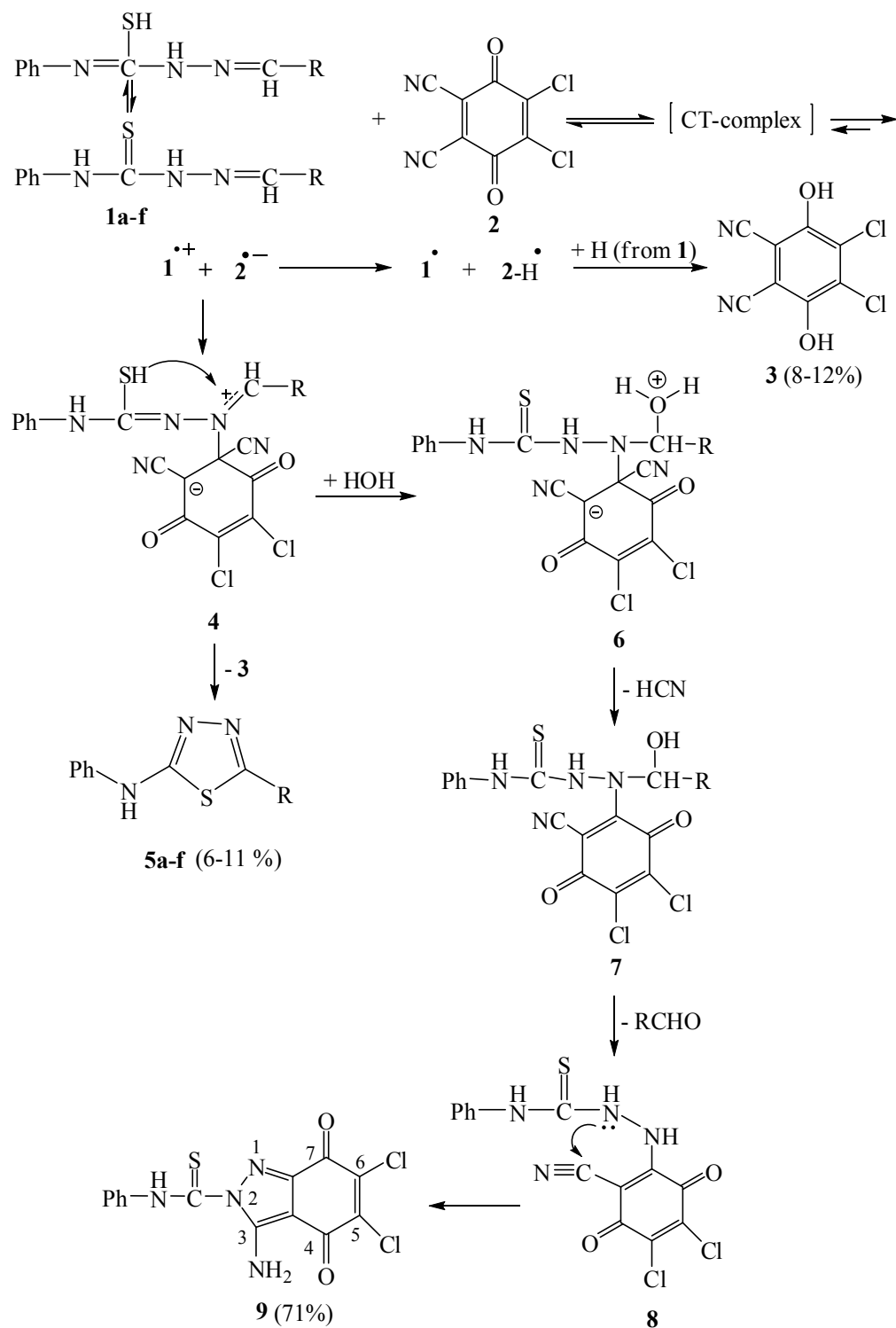
Introduction

Aldehyde thiosemicarbazones are appropriate substrates for the preparation of five- or six-membered heterocyclic rings that contains three heteroatoms by reacting them with oxidizing agents or other cyclization reagents.¹⁻⁶ Several oxidizing agents can be used for the cyclization of semi- and thiosemicarbazones and it has been investigated how the oxidant as well as the structure of the open chain molecules can affect regiochemistry and yield of the process.^{1,7-9} 2,3,5,6-Tetrachloro-1,4-benzoquinone (CHL-*p*, **10**) and 2,3-dichloro-1,4-naphthoquinone (**14**) undergo nucleophilic substitution of one or two chlorine atoms by thioacetamide,¹⁰⁻¹² thiourea,^{13,14} substituted thiourea,¹⁵ thiocarbazones,¹⁶ hydrazine-1,2-dicarbothioamides,¹⁷ thiosemicarbazides,¹⁸ and thiosemicarbazones.⁴ On the other hand, the synthesis of indazole derivatives from the reaction of diazoalkanes with some benzo- and naphthoquinones has been extensively investigated.¹⁹⁻²³ Much less attention has been given to the synthesis of indazole derivatives during the reaction of thiosemicarbazides with benzoquinones,^{4,18} therefore we undertook to prepare a series of indazole and benzindazole derivatives from the reaction of substituted ylidene-*N*-phenylhydrazinecarbothioamides **1a-f** with different benzo- and naphthoquinones.

Results and Discussion

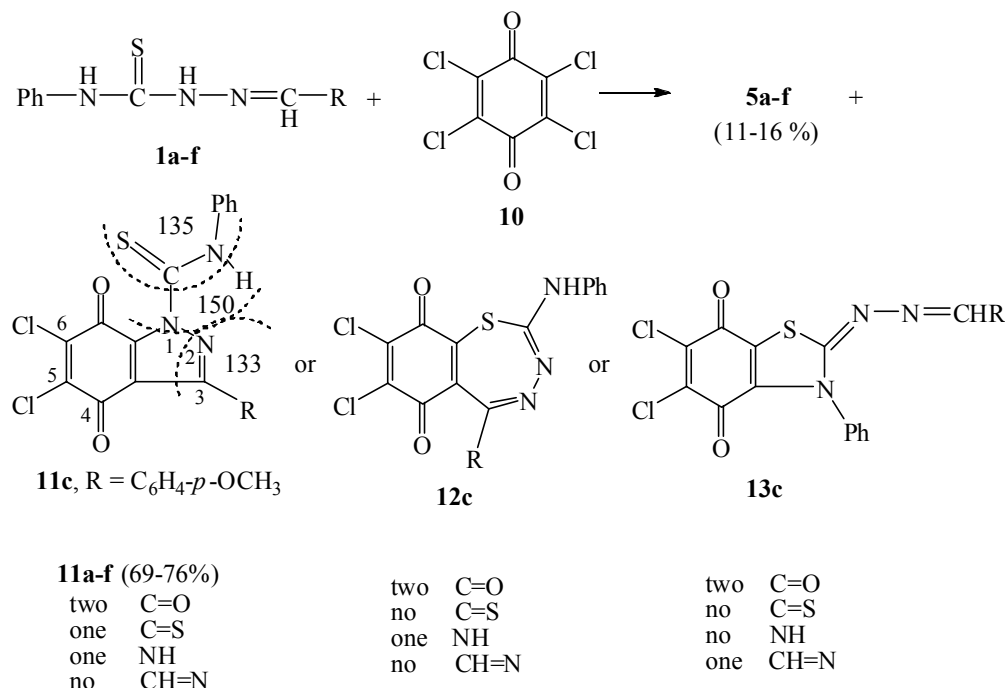
Addition of methylene chloride solutions of **1a-f** to solutions of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (**2**) in the same solvent resulted in the appearance of a green colour, which gradually changed into brown. After standing for 24 hours at room temperature, 2,3-dichloro-5,6-dicyanohydroquinone (**3**) was precipitated. From filtrate, 5-substituted-*N*-phenyl-1,3,4-thiadiazole-2-amines **5a-f** (6-11%), together with 3-amino-5,6-dichloro-4,7-dioxo-*N*-phenyl-4*H*-indazole-2(7*H*)-carbothioamide **9** (71%) were isolated by preparative thin layer chromatography. The structure assignment of **9** is based on the following data: The IR spectrum showed broad bands at 3410 and 3236 cm⁻¹ for NH₂ and NH groups, sharp band at 1680 (CO) and at 1575 cm⁻¹ due to (NH-deformation and C-N stretching) and intense band at 1352 as well as 980 cm⁻¹ assigned to sharply coupled vibrations between C=S and C-N.²⁴⁻²⁷ The ¹H-NMR spectrum of **9** showed two broad singlets with the ratio 2:1 centered at 6.95 and 10.03 ppm due to exocyclic-NH₂ and NH attached to the phenyl group, in addition to aromatic protons. In its ¹³C-NMR spectrum, the characteristic resonance signals of the carbonyl carbon atoms of chlorinated benzoquinone appeared at δ = 173.2 and 174.4 ppm.²⁸ The decoupled carbon spectrum of **9** showed signals at 93.2, 149.44 and 153.1 ppm, assigned to C-3a, C-7a and C-3, respectively. Also, the ¹³C-NMR spectrum of **9** showed thioxocarbonyl signal at 181.7 ppm, for carbothioamide function. The formation of **9** was further confirmed by EI-mass spectrometry. Besides the molecular ion at 366/370, *m/z* = 231 represents 3-amino-5,6-dichloro-4,7-dioxoindazole fragment, formed by release Ph-N=C=S from the molecular ion, since fragment ion with the mass of phenyl isothiocyanate is also formed. It is concluded that the positive charge may remain alternatively either with the ring or phenylisothiocyanate fragment.

The characteristic fragment ions pattern of the substituted dichloro compounds were also observed.²⁹ The formation of the products **3**, **5**, and **9** may be rationalized as in Scheme 1. Recombination of the ion pair **1**^{•+} and **2**^{•-} and formation the thiadiazole derivatives **5a-f** during intramolecular nucleophilic attacks by the SH of thiosemicarbazone on N=CH. After cyclization, **3** is released (Scheme 1). On the other hand, the salt **4** may be attacked by moist air with elimination of aldehydes followed by cyclization to give the indazole **9**. The participation of moist air in the formation of the above products, as illustrated in the proposed mechanism (Scheme 1), was confirmed by adding the methylene chloride solutions of **1a-f** to **2** under nitrogen and dry conditions. Only CT-complexes were formed which, in time, dissociate into the thiadiazole **5a-f** and DDQ-H₂ (**3**). Also, the cleavage of adduct **4** into the products **9** and different aldehydes supports our suggested mechanism. Thus, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**2**) may act either as a mediator or as a building block in heterocyclization of thiosemicarbazones **1a-f**.



1 and 5: **a**, R = C₆H₅; **b**, R = C₆H₄-*o*-OH; **c**, R = C₆H₄-*p*-OCH₃; **d**, R = C₆H₄-*p*-Cl;
e, R = 2-Thienyl; **f**, R = 2-Furyl

Scheme 1. Products formed during the reaction of **1a-f** with **2**.



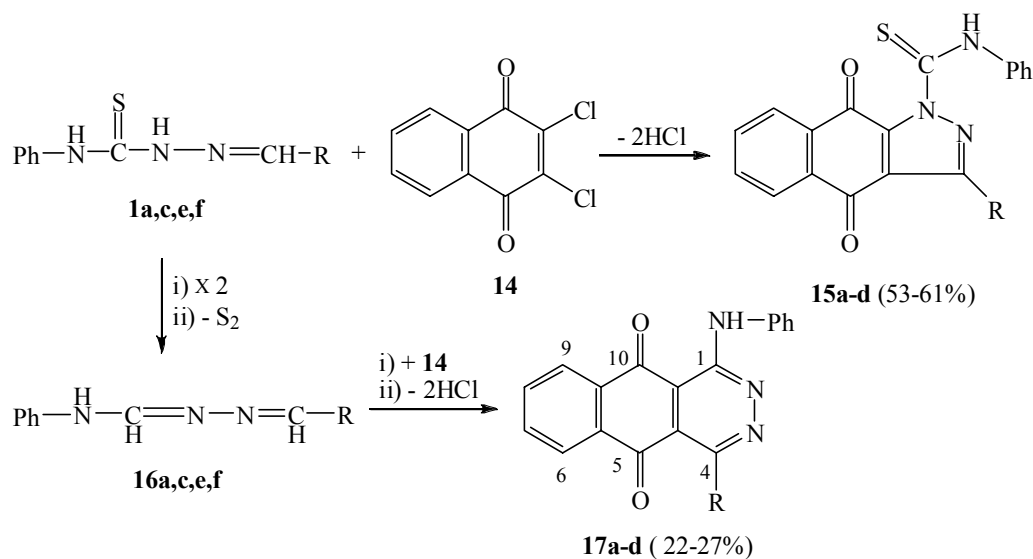
1, 5 and 11: a, R = C₆H₅; **b**, R = C₆H₄-*o*-OH; **c**, R = C₆H₄-*p*-OCH₃; **d**, R = C₆H₄-*p*-Cl
e, R = 2-Thienyl; **f**, R = 2-Furyl

Scheme 2. Products formed during the reaction of **1a-f** with **10**.

The addition of ethyl acetate solutions of **1a-f** to an equimolar quantity of another electron poor 2,3,5,6-tetrachloro-1,4-benzoquinone (**10**) in ethyl acetate gave, upon standing for 48 hours at room temperature, a green colour which gradually changed to brown. The separation of the reaction mixture by preparative layer chromatography yielded 3-substituted-5,6-dichlorodioxindazolecarbothioamides **11a-f** (69-75%) and thiadiazoles **5a-f** (11-16%).

The ¹H-NMR spectrum of **11c** revealed a broad singlet at 9.88 ppm for (Ph-NH) proton, singlet at 3.84 (OCH₃) and a multiplet at 7.05-7.69 ppm, which is characteristic of phenyl protons. The ¹³C-NMR spectrum showed the presence of two carbonyl groups at δ = 173.3 and 174.6 ppm, 143.8 (C-5, C-6), 149.2 (C-3) and 181.3 ppm (C=S). The analytical data of compound **11c** could also match for other isomers of products **12** and **13** (Scheme 2). The alternative structures **12** and **13** could also be ruled out on the basis of ¹H-NMR, ¹³C-NMR and fragment ions in the mass spectrum of **11c** at m/z 457/461, 422, 386, 251, 195, 150, 135, 133 and 93. As shown in scheme 2, structure **11c** fits best to all the spectroscopic data (see experimental section).

2,3-Dichloro-1,4-naphthoquinone (**14**) was chosen to compare its reactivity towards the thiosemicarbazones **1a,c,e,f** with chloranil (**10**).



1: **a**, R = C₆H₅; **c**, R = C₆H₄-*p*-OCH₃; **e**, R = 2-Thienyl; **f**, R = 2-Furyl

15 and 17: **a**, R = C₆H₅; **b**, R = C₆H₄-*p*-OCH₃; **c**, R = 2-Thienyl; **d**, R = 2-Furyl

Scheme 3. Products formed during the reaction of **1a, c, e, f** with **14**.

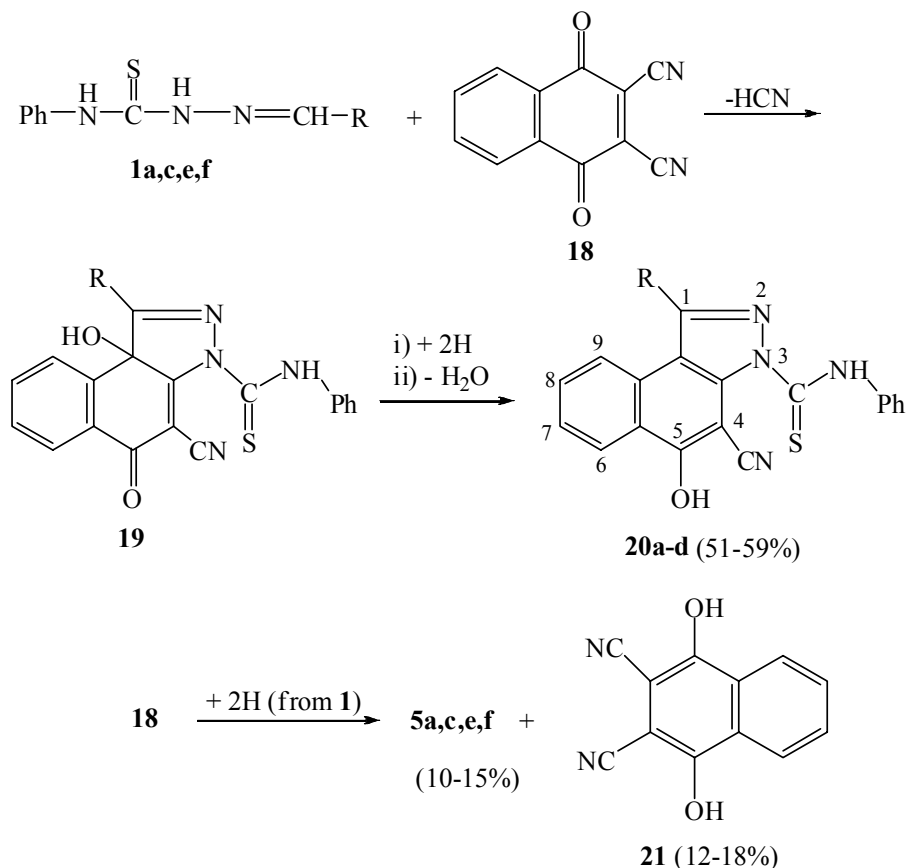
It has been described in the literature that **14** resembles **10** in most of its substitution reactions, especially with compounds containing nucleophilic nitrogen (amines, pyrazoles, imidazoles).³⁰⁻³³ From this point of view one might expect that thiosemicarbazones **1a,c,e,f** should react with **14** similarly like **10**. Mixing equimolar amounts of **1a,c,e,f** and **14** in ethyl acetate for 72 hours led to the formation of substituted benzindazole-4,9-diones **15a-d** as major products and substituted benzophthalazinediones **17a-d** as minor products (Scheme 3).

The gross formula of **15a** (C₂₄H₁₅N₃O₂S) represent a product from one molecule of **14** and one molecule of **1a** with loss of 2HCl. The structure of **15a-d** were supported by ¹H-NMR, ¹³C-NMR, mass spectroscopy and elemental analyses (see experimental).

The benzophthalazine derivatives **17a** exhibited two IR-absorption bands at ν_{max} 3290 (secondary amine) and 1690 cm⁻¹ (carbonyl group of naphthoquinone), respectively. The ¹³C-NMR spectrum showed absorption signals at 151.6 and 160.1 ppm, for (C-1 and C-4) as well as at 138.33 (C-4a, C-10a) and 178.2, 179.2 for ketonic carbon atoms (C-5, C-10), respectively. The phthalazines **17a-d** are fragmented alternatively by loss of mass 118 (which assigned to Ph-NH-CN) and 105 (which is assigned to the Ph-CO group).

Another type of benzindazoles, namely 4-cyano-5-hydroxy-*N*-substituted-1-phenylbenzo[e]indazole-3-carbothioamides **20a-d** was obtained in 51-59% yield from the reaction of thiosemicarbazones **1a,c,e,f** with 2,3-dicyano-1,4-naphthoquinone (Scheme 4). The benzindazoles **20a-d** exhibited three IR absorption at 3460-3450 (OH), 3330-3315 (NH) and 2220-2210 cm⁻¹ (CN), respectively. A sharp bands at 1575-1579 due to (NH-deformation and C-N stretching) and intense band in the range of 1360-1348 and 1010-995 cm⁻¹ assigned to strongly

coupled between C=S and C-N vibrations.³⁰⁻³³ The products **20a-d** show two broad signals are for Ph-NH at 9.96-9.89 ppm and the other at 9.76-9.71 due to OH, besides the nature of R as well as phenyl protons. In the ¹³C-NMR spectrum of **20a**, C-4 and C-5 resonate at 76.5 and 156.2 ppm, respectively, and are in accordance with the observed trends in the δ values for the C-atoms in push-pull alkenes.²⁸⁻³⁴ Further peaks at 117.8 (CN), 148.1 (C-1) and 181.6 (C=S), besides the aromatic carbons support the assigned structure. The formation of **20a-d** may be rationalized as follows (see Scheme 4).



1 and **5**: **a**, R = C₆H₅; **c**, R = C₆H₄-*p*-OCH₃; **e**, R = 2-Thienyl; **f**, R = 2-Furyl

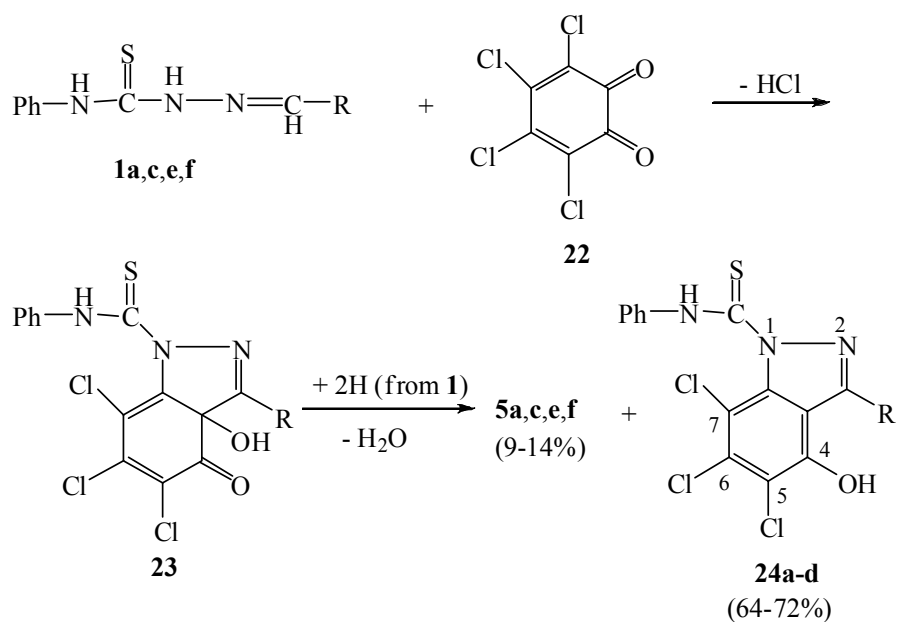
20: **a**, R = C₆H₅; **b**, R = C₆H₄-*p*-OCH₃; **c**, R = 2-Thienyl; **d**, R = 2-Furyl

Scheme 4. Products formed during the reaction of **1a, c, e, f** with **18**.

Replacement of one cyano group in the **18** by **1a,c,e,f** with intramolecular nucleophilic attack on carbonyl ketone afforded **19**. The intermediate **19** abstracts a molecule of hydrogen from **1a,c,e,f** followed by dehydration to give the products **20a-d**.

On the other hand, 3,4,5,6-tetrachloro-1,2-benzoquinone **22** reacted with an equimolar quantity of **1a,c,e,f** to give indazole derivatives **24a-d** and thiadiazole derivatives **5a,c,e,f** (Scheme 5). As an example, the structural assignment of **24a** was supported by the following

spectral data: In its ^{13}C -NMR spectrum the characteristic resonance signal of the two carbonyl C-atoms of *o*-chloranil **22**,²⁴ is replaced by signals at 133.2 and 152.2 ppm which are characteristic to indazole-C-3a and C-4.²⁸ In addition, indazole-C-7a was observed at 143.2. The IR spectrum showed two sharp bands at $\nu = 3460$ and 3295 cm^{-1} due to hydroxyl and NH groups, further bands were observed (see experimental section). ^1H -NMR spectrum of **24a** showed two broad signals at 9.88 and 9.56 ppm due to NH attached to phenyl ring and hydroxyl group, respectively. The formation of **24a** was further confirmed by mass spectrometry, at $m/z = 447/453$, the characteristic fragment ion patterns of substituted trichlororo compounds were observed.²⁹



1 and **5**: **a**, R = C₆H₅; **c**, R = C₆H₄-*p*-OCH₃; **e**, R = 2-Thienyl; **f**, R = 2-Furyl

24: **a**, R = C₆H₅; **b**, R = C₆H₄-*p*-OCH₃; **c**, R = 2-Thienyl; **d**, R = 2-Furyl

Scheme 5. Products formed during the reaction of **1a, c, e, f** with **22**.

Conclusions

The reactions and products presented here provide insight into the spontaneous reactions between the electron donating ylidenes-*N*-phenylhydrazinecarbothiamide derivatives **1a-f** and suitable electron acceptors, here **2, 10, 14, 18** and **22**. In a fairly complex and multisteps process two types of novel and interesting substituted indazoles (**9, 11, 15, 20** and **24**) as well as benzophthalazinediones **17** are formed from the interaction of electron rich **1a-f** and different benzo- and naphthoquinones. The ring forming reactions of **1a-f** with different quinones have

been observed: (i) Cyclization of **1a-f** by intramolecular nucleophilic attack, may be activated by quinones. (ii) On the other hand, the nucleophilic substitution reactions between **1a-f** and quinones followed by condensation. Thus, quinones may act either as a mediator or as a building block in heterocyclizations of thiosemicarbazones.

Experimental Section

General Procedures. The uncorrected melting points were determined using open glass capillaries in a Gallenkamp melting point apparatus. Elemental analyses have been determined by the Microanalytical Center, Cairo University, Egypt. The IR spectra were recorded with a Shimadzu 408 and on FT-IR 1650 (Perkin Elmer) instruments using potassium bromide pellets. 500MHz ^1H and 125 MHz ^{13}C -NMR spectra were recorded on a Bruker DRX 500 spectrometer. Chemical shifts are expressed as δ [ppm] with reference to tetramethylsilane as an internal standard, br = broad, s = singlet, and m = multiplet. ^{13}C assignments were made with the aid of DEPT 135/90 spectra. The mass spectra (70 eV, electron impact mode) were recorded on a Varian MAT 311 instrument. Preparative layer chromatography (plc) was made using 48 cm \times 20 cm glass plates covered with slurry applied and air dried 1mm thick layer of Merck silica gel Pf₂₅₄. Zones were detected by indicator fluorescence quenching upon 254 nm excitation, removed from plates and extracted with cold acetone.

Starting materials. All substituted ylidene-*N*-phenylhydrazinecarbothioamides **1a-f** were synthesized by reaction of 4-phenyl thiosemicarbazide and the proper aldehyde according to the published procedures, 2-benzylidene-*N*-phenylhydrazinecarbothioamide (**1a**),³⁵ 2-(2-hydroxybenzylidene)-*N*-phenylhydrazinecarbothioamide (**1b**),³⁶ 2-(4-methoxybenzylidene)-*N*-phenylhydrazinecarbothioamide (**1c**),³⁷ 2-(4-chlorobenzylidene)-*N*-phenylhydrazinecarbothioamide (**1d**),³⁸ *N*-phenyl-2-(thiophen-2-ylmethylene)hydrazinecarbothioamide (**1e**),³⁹ and 2-(furan-2-ylmethylene)-*N*-phenylhydrazinecarbothioamide (**1f**).⁴⁰ 2,3-Dicyano-5,6-dichloro-1,4-benzoquinone (DDQ, **2**), 2,3,5,6-tetra-chloro-1,4-benzoquinone (CHL-*p*, **10**), 3,4,5,6-tetrachloro-1,2-benzoquinone (CHL-*o*, **22**) and 2,3-dichloro-1,4-naphthoquinone (DCHNQ, **14**) (Aldrich) were used as received. 2,3-Dicyano-1,4-naphthoquinone (DCNQ, **18**) was prepared from 2,3-dichloro-1,4-naphthoquinone (**14**) according to Budni,⁴¹ and recrystallized from dichloromethane.

Reactions of thiosemicarbazones **1a-f** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**2**)

To a solution of 227 mg of DDQ (1.0 mmol) in 15 ml of dry methylene chloride, the thiosemicarbazones **1a-f** (1.0 mmol) in 20 ml of dry methylene chloride was added dropwise with stirring at room temperature. Therefore, the mixture was stirred for 3 hours and left standing for 24 hours at room temperature. Filtered and the precipitate washed with small amounts of cold methylene chloride which contains 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**3**). The filtrate was concentrated and the residue chromatographed on thin layer plates using toluene/ethyl acetate

(4:1) as eluent to give two zones. The fastest zone contained the disubstituted thiadiazoles **5a-f**, and the second zone contained the indazole derivatives **9**. The zones were extracted and recrystallised from the suitable solvent afforded pure compounds.

N,5-Diphenyl-1,3,4-thiadiazole-2-amine (5a). Yield (15 mg, 6%).^{42,43}

2-(5-(Phenylamino)-1,3,4-thiadiazol-2-yl)phenol (5b). Yield (24 mg, 10%).⁴⁴

5-(4-Methoxyphenyl)-N-phenyl-1,3,4-thiadiazole-2-amine (5c). Yield (20 mg, 7%).⁴³

5-(4-Chlorophenyl)-N-phenyl-1,3,4-thiadiazole-2-amine (5d). Yield (23 mg, 8%).⁴³

N-Phenyl-5-(thiophen-2-yl)-1,3,4-thiadiazole-2-amine (5e). Yield (23 mg, 9%).⁴⁵

5-(Furan-2-yl)-N-phenyl-1,3,4-thiadiazol-2-amine (5f). Yield (27 mg, 11%).⁴⁵

3-Amino-5,6-dichloro-4,7-dioxo-N-phenyl-4H-indazole-2(7H)-carbothioamide (9). Reddish brown crystals (ethanol) (260 mg, 71%), m.p. 236-238 °C; IR (KBr): ν_{\max} 3410, 3236 (NH₂, NH), 1685(CO), 1575 (NH-deformation and C-N stretching), 1352, 980 (C=S and C-N) cm⁻¹. ¹H-NMR (DMSO-d₆): δ 6.95 (br, 2H, NH₂), 7.27-7.71 (m, 5H, Ar-H), 10.03 (br, 1H, Ph-NH). ¹³C-NMR (DMSO-d₆): δ 93.2 (C-3a), 127.7, 128.5, 129.4 (Ar-CH), 138.1 (Ar-C), 143.2 (C-5, C-6), 149.8 (C-7a), 153.1 (C-3), 173.2, 174.4 (C-4, C-7), 181.7 (C=S). Ms; *m/z* (%): 366/370 (M⁺, 12) 231 (27), 160 (36), 135 (100), 132 (28), 77 (91), 65 (58). Anal. Calcd. For C₁₄H₈Cl₂N₄O₂S: C, 45.79; H, 2.20; Cl, 19.31; N, 15.26; S, 8.73. Found: C, 46.03; H, 2.31; Cl, 19.55; N, 15.08; S, 8.96.

Reaction of la-f with 2,3,5,6-tetrachloro-1,4-benzoquinone (10). To a stirred solution of 246 mg (1.0 mmol) of **10** in 20 ml of dry ethyl acetate, **la-f** (1.0 mmol) in 20 ml of dry ethyl acetate was added dropwise which caused a spontaneous change of colour from yellow to green and finally to brown. The mixture was stirred for 48 hours. After concentration, the residue was subjected to plc using toluene/ethyl acetate (3:1). The fastest moving zone contained compounds **5a-f**, while the slowest migrating zone contained compounds **11a-f**. Extraction of these zones with acetone and recrystallization from a suitable solvent afforded the pure compounds.

5,6-Dichloro-4,7-dioxo-N,3-diphenyl-4,7-dihydro-1H-indazole-1-carbothioamide (11a). Brown crystals (acetone) (307 mg, 72%), m.p. 259-261 °C. IR (KBr): ν_{\max} 3325 (NH₂), 1690 (CO), 1620 (C=N), 1570 (NH def. and C-N str.), 1355, 1010 (C=S, C-N) cm⁻¹. ¹H-NMR (DMSO-d₆): δ 7.14-7.81 (m, 10H, Ar-H), 9.94 (br, 1H, NH). ¹³C-NMR (DMSO-d₆): δ 110.1 (C-3a), 126.9, 127.5, 128.4, 128.8, 129.2, 129.6 (Ar-CH), 133.6, 139.7 (Ar-C), 135.2 (C-7a), 143.7 (C-5, C-6), 149.3 (C-3), 173.8, 174.9 (C-4, C-7), 181.2 (C=S). MS; *m/z* (%) 427/431 (M⁺, 56), 392 (29), 356 (14), 221 (63), 193 (36), 150 (41), 135 (86), 102 (65), 77 (100), 65 (21). Anal. Calcd. For C₂₀H₁₁Cl₂N₃O₂S: C, 56.09; H, 2.59; Cl, 16.56; N, 9.81; S, 7.49. Found: C, 55.86; H, 2.37; Cl, 16.81; N, 10.07; S, 7.73.

5,6-Dichloro-3-(2-hydroxyphenyl)-4,7-dioxo-N-phenyl-4,7-dihydro-1H-indazole-1-carbothioamide (11b). Reddish brown crystals (methanol) (310 mg, 70 %), m.p. 280-282 °C. IR (KBr): ν_{\max} 3460 (OH), 3310 (NH), 1685 (CO), 1625 (C=N), 1565 (NH def. and C-N str.), 1348, 1015 (C=S, C-N) cm⁻¹. ¹H-NMR (DMSO-d₆): δ 7.16-7.78 (m, 9H, Ar-H), 9.28 (br, 1H, OH), 9.90 (br, 1H, Ph-NH). ¹³C-NMR (DMSO-d₆): δ 108.9 (C-3a), 126.9, 127.1, 127.84, 128.4, 128.6, 129.5, 129.7 (Ar-CH), 133.5, 139.2 (Ar-C), 135.1 (C-7a), 143.7 (C-5, C-6), 148.9 (C-3),

155.6 (Ar-C-OH), 173.8, 174.9 (C-4, C-7), 181.3 (C=S). MS; m/z (%) 443/447 (M^+ , 36), 408 (19), 372 (21), 237 (23), 150 (46), 135 (74), 119 (53), 93 (100), 77 (83), 65 (42). Anal. Calcd. For $C_{20}H_{11}Cl_2N_3O_3S$: C, 54.07; H, 2.50; Cl, 15.96; N, 9.46; S, 7.22. Found: C, 53.89; H, 2.69; Cl, 16.18; N, 9.31; S, 7.05.

5,6-Dichloro-3-(4-methoxyphenyl)-4,7-dioxo-*N*-phenyl-4,7-dihydro-1*H*-indazole-1-carbothioamide (11c). Reddish brown crystals (acetonitrile) (347 mg, 76%), m.p. 291-293 °C. IR (KBr): ν_{max} 3340 (NH), 1685 (CO), 1620 (C=N), 1575 (NH def. and C-N str.), 1350, 1005 (C=S, C-N) cm^{-1} . 1H -NMR (DMSO- d_6): δ 3.84 (s, 3H, OCH₃), 7.05-7.69 (m, 9H, Ar-H), 9.88 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 109.0 (C-3a), 126.7, 127.0, 128.5, 128.8, 129.5 (Ar-CH), 133.82, 138.9 (Ar-C), 135.2 (C-7a), 143.8 (C-5, C-6), 149.2 (C-3), 156.1 (Ar-C-O), 173.4, 174.6 (C-4, C-7), 181.3 (C=S). MS; m/z (%) 457/461 (M^+ , 29), 422 (9), 386 (11), 251 (38), 195 (22), 150 (39), 135 (69), 133 (72), 93 (81), 77 (100), 65 (46). Anal. Calcd. For $C_{21}H_{13}Cl_2N_3O_3S$: C, 55.03; H, 2.86; Cl, 15.47; N, 9.17; S, 7.00. Found: C, 54.86; H, 3.02; Cl, 15.65; N, 9.34; S, 6.83.

5,6-Dichloro-3-(4-chlorophenyl)-4,7-dioxo-*N*-phenyl-4,7-dihydro-1*H*-indazole-1-carbothioamide (11d). Brown crystals (ethanol) (318 mg, 69%), m.p. 303-305 °C. IR (KBr): ν_{max} 3330 (NH), 1690 (CO), 1620 (C=N), 1570 (NH def. and C-N str.) 1350, 995 (C=S, C-N) cm^{-1} . 1H -NMR (DMSO- d_6): δ 6.93-7.30, 7.53-7.88 (m, 9H, Ar-H), 9.86 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 111.0 (C-3a), 126.8, 128.5, 129.0, 129.2, 129.6 (Ar-CH), 134.4, 137.2, 151.2 (Ar-C), 134.8 (C-7a), 143.3 (C-5, C-6), 149.6 (C-3), 173.9, 174.7 (C-4, C-7), 181.6 (C=S). MS; m/z (%) 461/467 (M^+ , 34), 426 (19), 390 (7), 354 (16), 219 (33), 163 (41), 150 (51), 138 (30), 135 (96), 77 (100), 65 (51). Anal. Calcd. For $C_{20}H_{10}Cl_3N_3O_2S$: C, 51.91; H, 2.18; Cl, 22.98; N, 9.08; S, 6.93. Found: C, 52.14; H, 2.31; Cl, 23.16; N, 8.88; S, 7.12.

2,3-Dichloro-4,7-dioxo-*N*-phenyl-3-(thiophen-2-yl)-4,7-dihydro-1*H*-indazole-1-carbothioamide (11e). Brown crystals (acetonitrile) (316 mg, 73%), m.p. 268-270 °C. IR (KBr): ν_{max} 3310 (NH), 1690 (CO), 1625 (C=N), 1565 (NH def. and C-N str.), 1360, 980 (C=S, C-N) cm^{-1} . 1H -NMR (DMSO- d_6): δ 6.94-7.74 (m, 8H, Ar-H and thiophen-H), 9.85 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 109.3 (C-3a), 126.9, 127.7, 128.2, 128.7, 128.9, 129.5 (Ar-CH and thiophene-CH), 134.1 (C-7a), 138.4 (Ar-C), 140.2 (thiophene-C-2), 143.3 (C-5, C-6), 149, 8 (C-3), 173.4, 174.7 (C-4, C-7), 182.1 (C=S). MS; m/z (%) 433/437 (M^+ , 12), 398 (16) 362 (24), 227 (34), 171 (61), 135 (84), 109 (44), 83 (33), 77 (100), 65 (42). Anal. Calcd. For $C_{18}H_9Cl_2N_3O_2S_2$: C, 49.78; H, 2.09; Cl, 16.33; N, 9.67; S, 14.77. Found: C, 49.55; H, 2.24; Cl, 16.11; N, 9.91; S, 14.56.

5,6-Dichloro-3-(furan-2-yl)-4,7-dioxo-*N*-phenyl-4,7-dihydro-1*H*-indazole-1-carbothioamide (11f). Brown crystals (ethanol) (296 mg, 71%), m.p. 251-253 °C. IR (KBr): ν_{max} 3330 (NH), 1680 (CO), 1620 (C=N), 1570 (NH def. and C-N str.), 1355, 1010 (C=S, C-N), 1090 (C-O-C) cm^{-1} . 1H -NMR (DMSO- d_6) δ 6.90-7.84 (m, 8H, Ar-H and furan-H), 9.93 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 109.0 (C-3a), 112.2, 115.3, (furan-C-3, C-4), 126.9, 128.8, 129.6 (Ar-CH), 134.1 (C-7a), 138.2 (Ar-C), 143.2, 143.3 (C-5, C-6 and furan-C-5), 148.8 (C-3), 158,3 (furan-C-2), 173.6, 174.6 (C-4, C-7), 181.6 (C=S). MS; m/z (%) 417/421 (M^+ , 28), 382 (16), 346 (22), 211 (31), 144 (46), 135 (76), 93 (63), 77 (100), 67 (42), 65 (56). Anal. Calcd. For $C_{18}H_9Cl_2N_3O_3S$: C,

51.69; H, 2.17; Cl, 16.95; N, 10.05; S, 7.67. Found: C, 51.91; H, 2.33; Cl, 17.19; N, 9.86; S, 7.86.

Reactions of 1a,c,e,f with 2,3-dichloro-1,4-naphthoquinone (14). A solution of 1a,c,e,f (1.0 mmol) in 20 ml of dry ethyl acetate was added dropwise with stirring to a solution of 2,3-dichloro-1,4-naphthoquinone (14) (1.0 mmol) in 15 ml of dry ethyl acetate. The reaction mixture was stirring for 72 hours, during which time it turned from faint orange into reddish brown colour. The reaction mixture was concentrated in vacuo and the residue separated by (plc) using toluene/ethyl acetate (4:1) into two zones. The fastest zone contained benzophthalazinediones 17a-d and the slowest migrating zone contained benzindazole derivatives 15a-d.

4,9-Dioxo-N,3-diphenyl-4,9-dihydro-1H-benzo[f]indazole-1-carbothioamide(15a). Reddish brown crystals (acetonitrile) (225 mg, 55%), m.p. 275-277 °C. IR (KBr): ν_{\max} 3310 (NH), 1690 (CO), 1625 (C=N), 1565 (NH def. and C-N str.), 1360, 980 (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 6.93-7.27, 7.41-8.12 (m, 14H, Ar-H), 9.88 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 106.7 (C-3a), 126.9, 127.0, 127.6, 128.5, 129.0, 129.4, 129.6, 130.2 (Ar-CH), 133.2, 134.4, 137.4 (Ar-C), 135.2 (C-9a), 149.1 (C-3), 178.1, 179.3 (C-4, C-9), 181.5 (C=S). MS; m/z (%) 409 (M^+ , 42), 274 (32), 259 (27), 156 (24), 150 (46), 135 (76), 104 (83), 77 (100), 65 (56). Anal. Calcd. For $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$: C, 70.40; H, 3.69; N, 10.26; S, 7.83. Found: C, 70.18; H, 3.52; N, 10.44; S, 8.02.

3-(4-Methoxyphenyl)-4,9-dioxo-N-phenyl-4,9-dihydro-1H-benzo[f]indazole-1-carbothioamide (15b). Reddish brown crystals (acetonitrile) (268 mg, 61%), m.p. 299-301 °C. IR (KBr): ν_{\max} 3335 (NH), 1695 (CO), 1620 (C=N), 1570 (NH def. and C-N str.), 1355, 995 (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 3.86 (s, 3H, OCH_3), 6.96-8.19 (m, 13H, Ar-H), 9.92 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 55.6 (OCH_3), 109.1 (C-3a) 126.8, 127.0, 127.9, 128.6, 128.8, 129.6, 130.2 (Ar-CH), 132.9, 134.2, 137.2 (Ar-C), 135.4 (C-9a), 149.7 (C-3), 178.3, 179.2 (C-4, C-9) 181.6 (C=S). MS; m/z (%) 439 (M^+ , 27), 408 (26), 273 (29), 258 (16), 135 (100), 92 (84) 77 (76), 65 (49). Anal. Calcd. For $\text{C}_{25}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$: C, 68.32; H, 3.90; N, 9.56; S, 7.30. Found: C, 68.56; H, 4.11; N, 9.35; S, 7.51.

4,9-Dioxo-N-phenyl-3-(thiophen-2-yl)-4,9-dihydro-1H-benzo[f]indazol-1-carbothioamide (15c). Brown crystals (ethanol) (241 mg, 58%), m.p. 281-283 °C. IR (KBr): ν_{\max} 3315 (NH), 1690 (CO), 1625 (C=N), 1575 (NH def. and C-N str.), 1350, 1010 (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 7.02- 8.17 (m, 12H, Ar-H and thiophen-H), 9.87 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 110.2 (C-3a), 126.8, 127.0, 127.7, 128.3, 128.7, 128.9, 129.6, 130.1 (Ar-CH and thiophene-CH), 134.6, 137.6 (Ar-C), 135.0 (C-9a), 140.3 (thiophene-C-2), 149.3 (C-3), 178.1, 179.1 (C-4, C-9) 181.7 (C= S). MS; m/z (%) 415 (M^+ , 46), 280 (35), 265 (21), 181 (26), 150 (37), 135 (84), 109 (26), 104 (69), 77 (100), 65 (38). Anal. Calcd. For $\text{C}_{22}\text{H}_{13}\text{N}_3\text{O}_2\text{S}_2$: C, 63.60; H, 3.15; N, 10.11; S, 15.43. Found: C, 63.84; H, 3.26; N, 9.89; S, 15.25.

3-(Furan-2-yl)-4,9-dioxo-N-phenyl-4,9-dihydro-1H-benzo[f]indazole-1-carbothioamide (15d). Brown crystals (ethanol) (209 mg, 53%), m.p. 265-267 °C. IR (KBr): ν_{\max} 3325 (NH), 1690 (CO), 1625 (C=N), 1575 (NH def. and C-N str.), 1360, 995 (C=S, C-N), 1085 (C-O-C) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 6.98-8.17 (m, 12H, Ar-H and furan-H), 9.90 (br, 1H, Ph-NH). ^{13}C -

NMR (DMSO- d_6): δ 109.18, 110.16, 124.24 (C-3a, furan-C-3, C-4), 126.88, 126.93, 128.45, 129.2, 130.0 (Ar-CH), 134.3, 137.3 (Ar-C), 135.2 (C-9a), 143.2 (furan-C-5), 149.2 (C-3), 158.2 (furan-C-2), 178.1, 179.3 (C-4, C-9), 181.5 (C=S). MS; m/z (%) 399 (M^+ , 21), 264 (19), 249 (8), 156 (16), 150 (36), 135 (84), 104 (71), 93 (51), 77 (100), 65 (56). Anal. Calcd. For $C_{22}H_{13}N_3O_3S$: C, 66.15; H, 3.28; N, 10.52; S, 8.03. Found: C, 65.91; H, 3.39; N, 10.74; S, 7.82.

1-Phenyl-4-(phenylamino)benzo[g]phthalazine-5,10-dione (17a). Reddish brown crystals (acetonitrile) (94 mg, 25%), m.p. 262-264 °C. IR (KBr): ν_{max} 3290 (NH), 1690 (CO), 1625 (C=N), 1600 (Ar-C=C) cm^{-1} . 1H -NMR (DMSO- d_6): δ 7.22-8.16 (m, 14H, Ar-H), 10.22 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 126.8, 127.0, 127.3, 127.8, 128.4, 128.8, 128.9, 129.8 (Ar-CH), 132.2, 133.5, 141.2 (Ar-C), 138.3 (C-4a, C-10a), 151.6 (C-1), 160.1 (C-4), 178.2, 179.2 (C-5, C-10). MS; m/z (%) 377 (M^+ , 26), 259 (21), 156 (44), 104 (71), 92 (86), 77 (100), 65 (62). Anal. Calcd. For $C_{24}H_{15}N_3O_2$: C, 76.38; H, 4.01; N, 11.13. Found: C, 76.61; H, 3.86; N, 11.34.

1-(4-Methoxyphenyl)-4-(Phenylamino)benzo[g]phthalazine-5,10-dione (17b). Reddish brown crystals (methanol) (110 mg, 27%), m.p. 285-287 °C. IR (KBr): ν_{max} 3310 (NH), 1695 (CO), 1620 (C=N), 1595 (Ar-C=C) cm^{-1} . 1H -NMR (DMSO- d_6): δ 3.87 (s, 3H, OCH₃), 7.19-8.11 (m, 13H, Ar-H), 10.29 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 126.7, 126.9, 127.2, 127.5, 127.9, 128.4, 128.9, 129.1, 130.0 (Ar-CH) 131.7, 133.2, 141.3 (Ar-C), 151.5 (C-1), 138.4 (C-4a, C-10a), 160.2 (C-4), 178.3, 179.3 (C-5, C-10). MS; m/z (%) 407 (M^+ , 34), 376 (41), 258 (37), 155 (44), 104 (76), 93 (100), 77 (74), 65 (63). Anal. Calcd. For $C_{25}H_{17}N_3O_3$: C, 73.70; H, 4.21; N, 10.31. Found: C, 73.94; H, 4.06; N, 10.09.

4-(Phenylamino)-1-(thiophen-2-yl)benzo[g]phthalazine-5,10-dione (17c). Orange crystals (acetonitrile) (92 mg, 24 %), m.p. 276-278 °C. IR (KBr): ν_{max} 3295 (NH), 1690 (CO), 1630 (C=N), 1600 (Ar-C=C) cm^{-1} . 1H -NMR (DMSO- d_6): δ 7.12-8.16 (m, 12H, Ar-H and thiophene-H), 10.21 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 126.7, 126.9, 127.2, 127.7, 128.2, 128.7, 129.6, 130.0 (Ar-CH and thiophene-CH), 132.3, 141.3 (Ar-C), 139.7 (thiophene-C-2), 138.2 (C-4a, C-10a), 166.2 (C-4), 178.2, 179.3 (C-5, C-10). MS; m/z (%) 383 (M^+ , 24), 300 (19), 182 (33), 118 (46), 109 (39), 104 (76), 91(75), 77 (100), 65 (41). Anal. Calcd. For $C_{22}H_{13}N_3O_2S$: C, 68.91; H, 3.42; N, 10.96; S, 8.36. Found: C, 69.12; H, 3.26; N, 11.21; S, 8.57.

1-(Furan-2-yl)-4-(phenylamino)benzo[g]phthalazine-5,10-dione (17d). Orange crystals (ethanol) (81 mg, 22%), m.p. 255-257 °C. IR (KBr): ν_{max} 3310 (NH), 1685 (CO), 1625(C=N), 1590 (Ar-C=C) cm^{-1} . 1H -NMR (DMSO- d_6): δ 6.98-8.12 (m, 12H, Ar-H and furan-H), 10.27 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 108.1, 113.2 (furan-C-3, C-4), 126.8, 127.6, 128.7, 129.6, 130.1 (Ar-CH), 132.5, 141.2 (Ar-C), 143.1 (furan-C-5), 138.4 (C-4a, C-10a), 158.1 (furan-C-2), 151.1 (C-1), 160.3 (C-4), 178.3, 179.3 (C-5, C-10). MS; m/z (%) 367 (M^+ , 41), 300 (36), 182 (29), 104 (86), 93 (41), 91 (86), 77 (100), 65 (43). Anal. Calcd. For $C_{22}H_{13}N_3O_3$: C, 71.93; H, 3.57; N, 11.44. Found: C, 72.11; H, 3.41; N, 11.65.

Reactions of 1a,c,e,f with 2,3-dicyano-1,4-naphthoquinone (18). To a chilled solution of 416 mg (2.0 mmol) of **18** in 15 ml of dry ethyl acetate a pre-cooled solution of **1a,c,e,f** in 20 ml of dry ethyl acetate was added dropwise, which caused a spontaneous change of colour from yellow to dark green. The mixture was allowed to warm up to room temperature and stirred for 36 hours

after which time the reaction mixture changed to brown colour. The mixture was concentrated to a few ml and subjected to plc using toluene/ethyl acetate (3:1) to afford three zones. The fastest migrating fraction contained the disubstituted thiadiazoles **5a,c,e,f**, the second zone which was a reddish brown colour contained the cyanohydroxybenzindazoles **20a-d**. The slowest migrating zone contained dihydro-2,3-dicyanonaphthoquinone **21**.

4-Cyano-5-hydroxyl-N,1-diphenyl-3H-benzo[e]indazole-3-carbothiomide (20a). Reddish brown crystals (methanol) (239 mg, 57%), m.p. 287-289 °C. IR (KBr): ν_{\max} 3460 (OH), 3320 (NH), 2220 (CN), 1620 (C=N), 1575 (NH def. and C-N str.), 1360, 1010 (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 9.76 (br, 1H, OH), 9.93 (br, 1H, Ph-NH), 7.21-8.16 (m, 14H, Ar-H). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 76.5 (C-4), 117.8 (CN), 126.8, 127.0, 127.5, 128.4, 128.8, 129.3, 129.8, 129.9 (Ar-CH), 131.7, 133.8, 135.1, 137.4 (Ar-C), 126.2 (C-3b), 143.1 (C-3a), 148.1 (C-1), 156.2 (C-5), 181.6 (C=S). MS; m/z (%) 420 (M^+ , 29), 394 (17), 259 (32), 244 (23), 150 (37), 141 (22), 135 (86), 103 (53), 77 (100), 65 (56). Anal. Calcd. For $\text{C}_{25}\text{H}_{16}\text{N}_4\text{OS}$: C, 71.41; H, 3.84; N, 13.32; S, 7.63. Found: C, 71.65; H, 4.02; N, 13.11; S, 7.84.

4-Cyano-5-hydroxy-1-(4-methoxyphenyl)-N-phenyl-3H-benzo[e]indazole-3-carbothioamide (20b). Reddish brown crystals (acetonitrile) (266 mg, 59%), m.p. 312-314 °C. IR (KBr): ν_{\max} 3450 (OH), 3315 (NH), 2215 (CN), 1625 (C=N), 1570 (NH def. And C-N str.), 1348, 1005 (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 3.83 (s, 3H, OCH_3), 6.97-7.93 (m, 13H, Ar-H), 9.73 (br, 1H, OH), 9.89 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 53.9 (OCH_3), 77.1 (C-4), 118.1 (CN), 126.6, 126.9, 127.5, 127.9, 128.6, 129.1, 129.7 (Ar-CH), 132.1, 133.8, 135.2, 137.6 (Ar-C), 126.2 (C-3b), 143.0 (C-3a), 148.4 (C-1), 156.0 (C-5), 159.8 (C- OCH_3), 181.7 (C=S). MS; m/z (%) 450 (M^+ , 20), 419 (22), 394 (18), 258 (41), 243 (16), 135 (64), 92 (100), 77 (83), 65 (61). Anal. Calcd. For $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_2\text{S}$: C, 69.32; H, 4.03; N, 12.44; S, 7.12. Found: C, 69.54; H, 3.88; N, 12.63; S, 6.94.

4-Cyano-5-hydroxyl-N-phenyl-1-(thiophen-2-yl)-3H-benzo[e]indazole-3-carbothioamide (20c). Reddish brown crystals (ethanol) (230 mg, 54%), m.p. 296-298 °C. IR (KBr): ν_{\max} 3450 (OH), 3330 (NH), 2210 (CN), 1625 (C=N), 1570 (NH def. and C-N str.), 1348, 995, (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 7.21-8.19 (m, 12H, Ar-H and thiophene-H), 9.73 (br, 1H, OH), 9.96 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 76.7 (C-4), 118.1 (CN), 126.3 (C-3b), 126.6, 127.0, 127.6, 128.1, 128.6, 128.9, 129.1, 129.5, 129.9 (Ar-CH and thiophene-CH), 131.6, 133.8, 137.2 (Ar-C), 140.0 (thiophene-C-2), 143.4 (C-3a), 146.8 (C-1), 156.4 (C-5), 181.3 (C=S). MS; m/z (%) 426 (M^+ , 41), 400 (26), 317 (12), 182 (40), 167 (23), 150 (44), 135 (66), 77 (100), 65 (61). Anal. Calcd. For $\text{C}_{23}\text{H}_{14}\text{N}_4\text{OS}_2$: C, 64.77; H, 3.31; N, 13.14; S, 15.04. Found: C, 64.92; H, 3.22; N, 12.93; S, 14.82.

4-Cyano-1-(furan-2-yl)-5-hydroxyl-N-phenyl-3H-benzo[e]indazole-3-carbothioamide (20d). Reddish brown crystals (acetonitrile) (209 mg, 51%), m.p. 279-281 °C. IR (KBr): ν_{\max} 3460 (OH), 3320 (NH), 2220 (CN), 1625 (C=N), 1570 (NH def. and C-N str.), 1355, 1000 (C=S, C-N), 1085 (C-O-C) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 6.98-7.92 (m, 12H, Ar-H and furan-H), 9.71 (br, 1H, OH), 9.92 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 77.1 (C-4), 108.1, 113.2 (furan-C-3, C-4), 118.0 (CN), 126.4 (C-3b), 126.7, 127.0, 128.3, 128.5, 129.5, 129.8 (Ar-CH), 131.1, 133.6,

137.5 (Ar-C), 142.8 (C-3a), 147.9 (C-1), 155.8 (C-5) 143.4 (furan-C-5), 158.7 (furan-C-2), 181.5 (C=S). MS; m/z (%) 410 (M^+ , 25), 374 (19), 307 (9), 172 (35), 150 (43), 135 (74), 77 (100), 67 (36), 65 (54). Anal. Calcd. For $C_{23}H_{14}N_4O_2S$: C, 67.30; H, 3.44; N, 13.65; S, 7.81. Found: C, 67.09; H, 3.56; N, 13.42; S, 8.06.

Reactions of 1a,c,e,f with 3,4,5,6-tetrachloro-1,2-benzoquinone (22). To a solution of 246 mg (1.0 mmol) of **22** in 40 ml of dry methylene chloride, a solution of **1a,c,e,f** (1.0 mmol) in 25 ml of dry methylene chloride was added and stirred at 20 °C for three days, during which time the reaction mixture colour first turned from reddish brown to green and then brown. A fine precipitate formed which was collected and recrystallised from acetonitrile to give needles of **24a-d**. The mother liquor was separated by plc using toluene/ethyl acetate (5:1) to give numerous zones, one of which with high intensity was removed and extracted which contained disubstituted thiadiazoles **5a-d**.

5,6,7-Trichloro-4-hydroxyl-*N*,3-phenyl-1*H*-indazole-1-carbothioamide (24a). Brown crystals (acetonitrile) (313 mg, 70%), m.p. 298-300 °C. IR (KBr): ν_{max} 3465 (OH), 3295 (NH), 1625 (C=N) 1575 (NH def. and C-N str.), 1350, 980 (C=S, C-N) cm^{-1} . 1H -NMR (DMSO- d_6): δ 7.05-7.82 (m, 10H, Ar-H), 9.56 (br, 1H, OH), 9.88 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 126.7, 127.6, 128.4, 128.8, 129.4, 129.8 (Ar-CH), 130.1, 131.3, 131.9, 133.2, 134.3, 139.2 (Ar-C), 143.2 (C-7a), 149.7 (C-3), 152.2 (Ar-C-4), 181.7 (C=S), MS; m/z (%) 447/453 (M^+ , 36), 413 (26), 377 (19), 339 (11), 204 (44), 189 (32), 150 (38), 135 (67), 103 (18), 77 (100), 65 (41). Anal. Calcd. For $C_{20}H_{12}Cl_3N_3OS$: C, 53.53; H, 2.70; Cl, 23.70; N, 9.36; S, 7.15. Found: C, 53.77; H, 2.58; Cl, 23.93; N, 9.59; S, 6.96.

5,6,7-Trichloro-4-hydroxyl-3-(4-methoxyphenyl)-*N*-phenyl-1*H*-indazole-1-carbothioamide (24b). Brown crystals (acetonitrile) (434 mg, 72%), m.p. 322-324 °C. IR (KBr): ν_{max} 3450 (OH), 3310 (NH), 1630 (C=N), 1565 (NH def. and C-N str.), 1355, 995 (C=S, C-N) cm^{-1} . 1H -NMR (DMSO- d_6): δ 3.85 (s, 3H, OCH₃), 6.94-7.61 (m, 9H, Ar-H), 9.61 (br, 1H, OH), 9.91 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 53.7 (OCH₃), 126.6, 126.8, 127.4, 128.6, 129.18 (Ar-CH), 130.0, 131.2, 131.7, 132.9, 133.9, 139.3 (Ar-C), 160.7 (C-OCH₃), 142.9 (C-7a), 150.1 (C-3), 152.6 (C-4), 181.5 (C=S). MS; m/z (%) 477/483 (M^+ , 27), 443 (25), 407 (18), 371 (9), 205 (26), 190 (12), 150 (37), 135 (49), 134 (27), 92 (100), 77 (83), 65 (53). Anal. Calcd. For $C_{21}H_{14}Cl_3N_3O_2S$: C, 52.68; H, 2.95; Cl, 22.21; N, 8.78; S, 6.70. Found: C, 52.44; H, 3.06; Cl, 22.47; N, 8.55; S, 6.46.

5,6,7-Trichloro-4-hydroxy-*N*-phenyl-3-(thiophen-2-yl)-1*H*-indazole-1-carbothioamide (24c). Brown crystals (acetonitrile) (299 mg, 66%), m.p. 309-311 °C. IR (KBr): ν_{max} 3465 (OH), 3290 (NH), 1620 (C=N), 1570 (NH def. and C-N str.), 1348, 990 (C=S, C-N) cm^{-1} . 1H -NMR (DMSO- d_6): δ 7.06-7.63 (m, 8H, Ar-H and thiophene-H), 9.68 (br, 1H, OH), 9.94 (br, 1H, Ph-NH). ^{13}C -NMR (DMSO- d_6): δ 126.7, 127.8, 128.1, 128.7, 128.9, 129.4 (Ar-CH and thiophene-CH), 130.1, 130.7, 130.9, 131.6, 139.2, 140.2 (Ar-C and thiophene-C-5), 143.5 (C-7a), 149.6 (C-3), 152.2 (Ar-C-4), 181.5 (C=S). MS; m/z (%) 453/459 (M^+ , 52), 419 (33), 383 (19), 347 (12), 212 (44), 150 (39), 135 (76), 83 (21), 77 (100), 65 (63). Anal. Calcd. From $C_{18}H_{10}Cl_3N_3OS_2$: C, 47.54; H, 2.22; Cl, 23.39; N, 9.24; S, 14.10. Found: C, 47.31; H, 2.36; Cl, 23.17; N, 9.48; S, 13.86.

5,6,7-Trichloro-4-hydroxy-N-phenyl-3-(furan-2-yl)-1H-indazole-1-carbothioamide (24d). Brown crystals (acetonitrile) (280 mg, 64%), m.p. 291-293 °C. IR (KBr): ν_{\max} 3450 (OH), 3310 (NH), 1625 (C=N), 1575 (NH def. and C-N str.), 1360, 1010 (C=S, C-N) cm^{-1} . $^1\text{H-NMR}$ (DMSO- d_6): δ 7.12-7.83 (m, 8H, Ar-H and furan-H), 9.58 (br, 1H, OH), 9.90 (br, 1H, Ph-NH). $^{13}\text{C-NMR}$ (DMSO- d_6): δ 108.4, 113.3, (furan-C-3, C-4), 126.9, 128.7, 129.7 (Ar-CH), 130.2, 130.5, 131.1, 131.7, 139.3 (Ar-C), 143.3 (C-7a), 145.1 (furan-C-5), 149.4 (C-3), 152.3 (Ar-C-4), 159.2 (furan-C-2), 182.1 (C=S). MS; m/z (%) 437/443 (M^+ , 37), 403 (28), 367 (26), 331 (9), 196 (32), 150 (39), 135 (100), 77 (89), 67 (76), 65 (41). Anal. Calcd. For $\text{C}_{18}\text{H}_{10}\text{Cl}_3\text{N}_3\text{O}_2\text{S}$: C, 49.28; H, 2.30; Cl, 24.24; N, 9.58; S, 7.31. Found: C, 49.52; H, 2.19; Cl, 24.02; N, 9.81; S, 7.54.

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