Anionic [4 + 2] cycloaddition reactions of dihydropyrazolin-5-one dienolate with dienophiles: a novel approach for substituted and fused indazolones

Amrita Roy,[b] Kethiri R. Reddy,[b] Hiriyakkanavar Ila *[a] and Hiriyakkanavar Junjappa *[a]

[a] *Department of Chemistry, Indian Institute of Technology, Kanpur-208 016, U.P., India. E-mail: hila@iitk.ac.in*
[b] *Department of Chemistry, North-Eastern Hill University, Bijni Complex, Shillong-793 003, Meghalaya, India*

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Dihydropyrazolin-5-one dienolate **2** generated by deprotonation of 2,3-dimethyl-4-formyl-1-phenylpyrazolin-5-one (4-formylantipyrine) is shown to be an efficient anionic pyrazolone α-oxy-*o*-quinodimethane analog, which undergoes facile cycloaddition with a variety of dienophiles to give substituted indazolones in good yields after dehydration–dehydrogenation of cycloadducts.

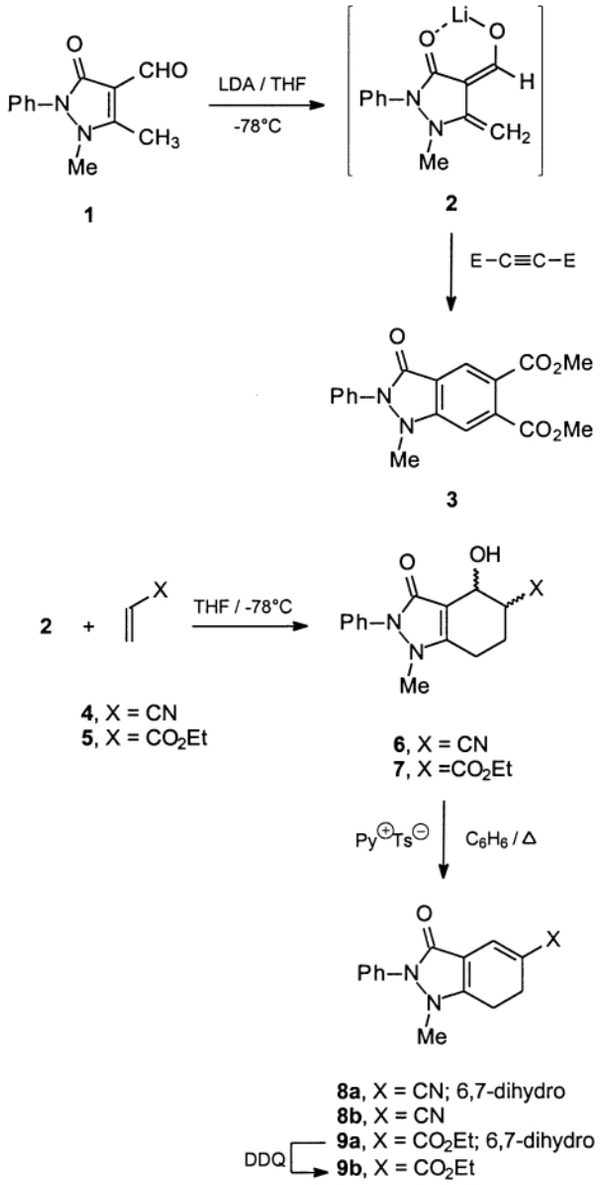
Introduction

The heterocyclic analogs of *o*-quinodimethane (OQDM, *o*-xylylene) are of considerable interest both from a theoretical point of view and for their potential in organic synthesis[1] as useful dienes. This has been elegantly demonstrated in the indole series[2] for the synthesis of several naturally occurring and biologically important indole[3] and carbazole[4] alkaloids. However, with the exception of indolo-2,3-quinodimethane, the synthetic potential of other heterocyclic analogs remain largely unexplored, although several studies involving their methods of generation and trapping have been published in recent years.[1] Most widely used routes to these heterocyclic *o*-quinodimethanes involve flash vacuum pyrolysis,[1,5] 1,4-elimination[1,6,7] of suitable precursors and thermal extrusion of sulfur dioxide from heteroaromatic fused 3-sulfolenes.[1,8,9] Flash pyrolytic 1,4-elimination requires very harsh reaction conditions resulting in formation of polymeric products, thus precluding trapping of *o*-quinodimethane intermediates except in the most stable cases. However, several heterocyclic *o*-quinodimethanes have been generated by 1,4-elimination in solution and are efficiently trapped by various dienophiles to afford the corresponding adducts in good yields.[1,6,7] Similarly, heterocyclic-fused 3-sulfolenes have also been shown to be useful precursors for generation and trapping of heterocyclic *o*-quinodimethanes (HQDM).[1,8,9] However, many of these precursors are not so easily accessible and do not lend themselves readily to structural elaboration, thus limiting the synthetic scope of these heterocyclic *o*-quinodimethanes, especially for regiocontrolled synthesis of substituted heteroaromatic compounds which have many proven applications.

During the course of our continued interest in the synthesis of benzoheterocycles *via* heteroaromatic annelation,[10,11] we became interested in the generation and reactions of anionic heteroaromatic *o*-quinodimethanes which are shown to exhibit pronounced enophilic reactivity and high regiocontrol in cycloadditions as a result of an increased HOMO energy level (or net atomic charge) and charge controlled orientation of two reactive partners in the transition state.[12,13] It is pertinent to note that neutral HQDM usually affords a mixture of regioisomers on cycloaddition with unsymmetrical dienophiles which limits their synthetic scope for regiocontrolled construction of substituted benzoheterocycles.[1,6–9] We have recently reported that enolates derived from 1,2-dimethylindole-3-carbaldehyde are useful anionic α-oxyindolo-2,3-quinodimethane equivalents which undergo facile cycloaddition with a variety of dienophiles, affording a wide range of substituted carbazoles under mild conditions with efficient control of regioselectivity.[14] We have now demonstrated that dihydropyrazolinone dienolate **2** derived from 2,3-dimethyl-4-formyl-1-phenylpyrazolin-5-one is an efficient anionic pyrazolone *o*-quinodimethane equivalent which undergoes facile regioselective cycloaddition with electron deficient dienophiles to afford substituted indazolones in good yields. We report the results of these studies in this paper.

Results and discussion

In a typical experiment, the dienolate **2** was generated as a red colored solution by deprotonation of 4-formylantipyrine[15] (5 mmol) in THF with LDA (5 mmol) at −78 °C followed by addition of dimethyl acetylene dicarboxylate (DMAD) (5 mmol). The reaction mixture after overnight stirring at room temperature followed by work-up afforded the corresponding dimethyl oxodihydroindazole-5,6-dicarboxylate **3** in 72% yield (Scheme 1). The structure of **3** was established with the help of spectral and analytical data. The reaction of **2** with other electron deficient olefins was also investigated. Thus acrylonitrile and ethyl acrylate reacted with **2** to give the crude [1 : 1] adducts **6** and **7** in nearly quantitative yields. Attempted dehydration of **6** with pyridinium tosylate in refluxing benzene (1 h) gave a mixture of tetrahydroindazolone **8a** and 5-cyanodihydroindazolone **8b** in 52 and 40% yields respectively, whereas the acrylate adduct **7** yielded only oxotetrahydroindazolecarboxylate **9a** under similar conditions. The compound **9a** was dehydrogenated to **9b** by treatment with DDQ in refluxing dioxane (Scheme 1). Similarly, β-nitrostyrene (**10**) and chalcone (**11**) were reacted with **2** to give crude [1 : 1] adducts **12** and **13** which were converted to 5-nitro- (**14**) and 5-benzoyl- (**15**) 6-phenyldihydroindazolones in high yields by treatment with pyridinium tosylate under identical conditions (Scheme 2). The reaction of **2** with nitroketene *S*,*S*-acetal **16** was found to be very facile and yielded directly the corresponding 5-nitro-6-(methylthio)-dihydroindazolone **18** in 65% yield by *in situ* aromatization of the adduct **17** *via* dehydration and elimination of methanethiol (Scheme 2). Finally, the hitherto unknown indazole-fused naphthoquinone ring system **21** was obtained in 54% yield by reacting dienolate **2** with naphthoquinone **19** and subsequent dehydration of the resulting adduct **20** under the above described conditions (Scheme 3). Compound **21**, to our

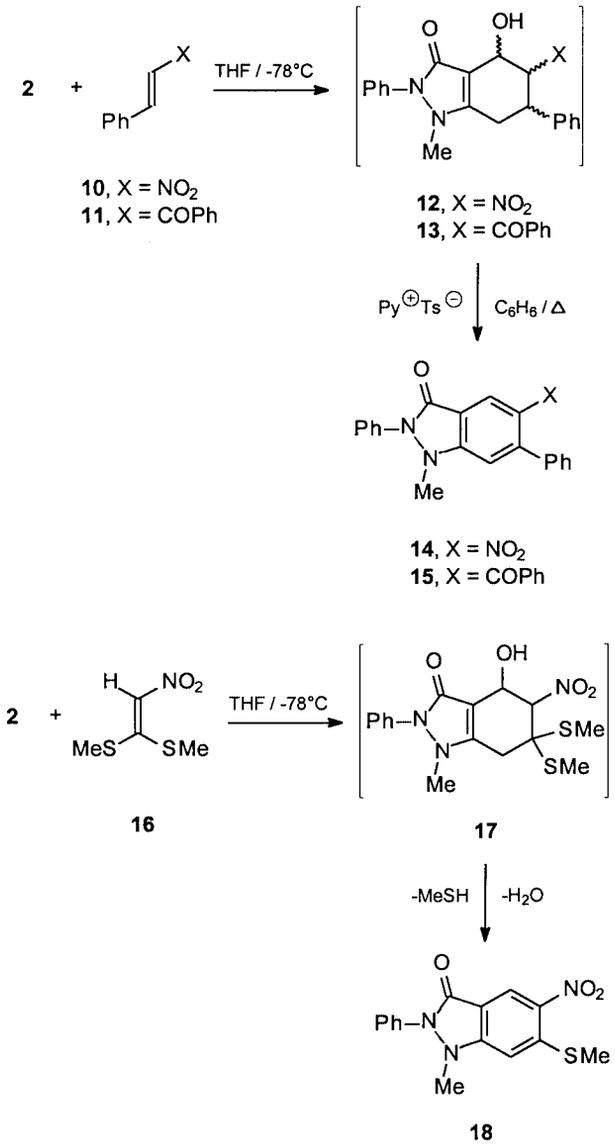


Scheme 1

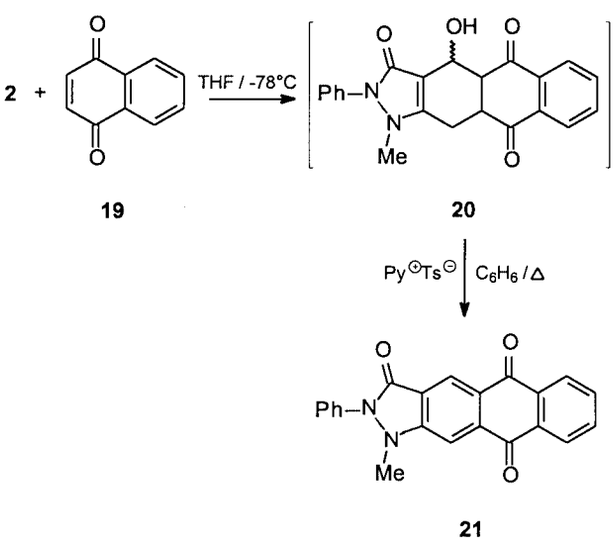
knowledge, is the first example of naphtho[2,3-*f*]indazole ring system.

In summary, the dihydropyrazolin-5-one dienolate **2** has been shown to be an efficient anionic α-oxy heteroaromatic *o*-quinodimethane undergoing facile cycloaddition with various dienophiles in a highly regiospecific fashion to afford substituted and fused indazolones in good yields. Neutral pyrazole *o*-quinodimethanes have been generated previously by dehalogenation of 4,5-bis(bromomethyl)pyrazole[7] or by thermolysis of pyrazole-fused 3-sulfolenes[8] followed their trapping with various dienophiles. However, the synthetic scope of these reactions has not been investigated extensively. Furthermore it should be noted that more recently the α-oxybenzo-*o*-quinodimethanes have been generated by base catalyzed ring opening of 2-hydroxycyclobutabenzene[16] instead of deprotonation of *o*-tolualdehyde so as to minimize the complication due to aldehyde–enolate condensation. However, the reactions described in this paper involving deprotonation of 3-methyl-4-formylpyrazolinone **1** to give dienolate **2** were found to be very clean and the formation of polymeric and open chain side products was not observed in the reaction mixture. This reactivity may be attributed to the stabilization of the dienolate arising from the chelated structure **2** formed by an intramolecular interaction between the OH and C-5 carbonyl group.

The present sequence thus represents an efficient route for



Scheme 2



Scheme 3

assembling the indazolone ring system from pyrazole precursors. Indazoles are shown to have interesting chemistry and are effective pharmacophores in medicinal chemistry, thus making them attractive targets for synthetic organic chemists.[17]

Most reported methods for the synthesis of indazoles involve construction of the pyrazole moiety on preconstructed benzenoid derivatives[18] while the methods based on more easily accessible pyrazole precursors are scantily described in the literature.[11,19]

Experimental

Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 983 spectrophotometer. NMR spectra were recorded on Bruker ACF-300 and Varian EM 390 spectrometers. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane. Mass spectra were obtained on a JEOL D-300 mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyzer. All reactions were conducted in oven-dried (120 °C) glassware under a dry argon or nitrogen atmosphere. THF was distilled over sodium benzophenone ketyl prior to use. *n*-BuLi was purchased from Aldrich. 2,3-Dimethyl-4-formyl-1-phenyl-3-pyrazolin-5-one **1** was prepared according to the reported procedure;[12] colorless crystals (chloroform–hexane); mp 162 °C (lit.[12] mp 162 °C) IR (KBr): ν_{max} 1640, 1509 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.56 (s, 3H, CH_3), 3.30 (s, 3H, NCH_3), 7.25–7.65 (m, 5H, ArH), 9.90 (s, 1H, CHO).

General procedure for generation of lithium (1-methyl-3-methylene-5-oxo-2-phenylpyrazolin-4-ylidene)methanolate 2 and its cycloaddition with dienophiles: synthesis of indazolones

To a solution of diisopropylamine (2 mL, 14 mmol) in dry tetrahydrofuran (10 mL) under a nitrogen atmosphere, was added *n*-BuLi (6.25 mL, 10 mmol, 1.6 M) at 0 °C and the reaction mixture was stirred for 20 min. To the resulting solution of lithium diisopropylamide (LDA) at −78 °C, a solution of **1** (1.08 g, 5 mmol) in dry THF (30 mL) was added followed by further stirring for 45 min. To the resulting red colored solution of dienolate **2**, appropriate dienophile (5 mmol) dissolved in dry THF (15 mL) was added while maintaining the temperature at −78 °C. The reaction mixture was then brought to room temperature during 45 min and left overnight with stirring. It was then poured into saturated ammonium chloride solution (150 mL) and extracted with chloroform (3 × 50 ml). The combined organic extracts were washed with water, dried (Na_2SO_4) and then concentrated to give the crude methanol adduct which was dissolved in dry benzene (50 mL) followed by addition of pyridinium tosylate (1.5 g, 6 mmol) and further refluxing for 1 h. The reaction mixture was poured into water (100 mL) and extracted with chloroform (3 × 50 mL), the combined organic layer was washed with water, dried over sodium sulfate and concentrated. The crude product thus obtained was purified by column chromatography over silica gel using ethyl acetate–hexane (19 : 1) as eluent.

Attempted purification of methanol adducts (**6**, **7**, **12**, **13** and **20**) by silica gel column chromatography was not successful and gave either dihydro (**8a**, **9a**) or fully aromatized (**14**, **15** and **21**) indazolones along with a mixture of several products.

1,2-Dihydro-5,6-bis(methoxycarbonyl)-1-methyl-2-phenyl-3*H*-indazol-3-one (3). Colorless crystals; mp 180–181 °C (chloroform–hexane); yield 72%; IR (KBr): ν_{max} 3043, 2948, 1728, 1705, 1678, 1621, 1309 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.26 (s, 3H, NCH_3), 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.33–7.38 (m, 1H, ArH), 7.47 (s, 1H, ArH), 7.51–7.53 (m, 4H, ArH), 8.47 (s, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.6, 52.7, 53.1, 112.2, 119.3, 124.2, 124.4, 127.3, 127.5, 129.4, 134.2, 138.2, 151.6, 160.7, 166.2, 168.5; MS (*m*/*z*, %): 340 (M^+, 100), 325 (37.5). Anal. calc. for $C_{18}H_{16}N_2O_5$ (340.33): C, 63.53; H, 4.74; N, 8.23%. Found: C, 63.81; H, 4.78; N, 8.30%.

1,2,6,7-Tetrahydro-5-cyano-1-methyl-2-phenyl-3*H*-indazol-3-one (8a). Colorless crystals; mp 204–205 °C (chloroform–hexane); yield 52%; IR (KBr): ν_{max} 2200, 1669, 1562, 1495 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.67–2.73 (m, 2H, CH_2), 2.80–2.86 (m, 2H, CH_2), 3.23 (s, 3H, NCH_3), 7.17 (s, 1H, H-4), 7.29–7.41 (m, 3H, ArH), 7.46–7.52 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.1, 24.3, 34.0, 98.3, 103.3, 120.1, 125.7, 128.2, 129.5, 133.8, 152.5, 161.2; MS (*m*/*z*, %): 251 (M^+, 100). Anal. calc. for $C_{15}H_{13}N_3O$ (251.29): C, 71.70; H, 5.21; N, 16.72%. Found: C, 71.94; H, 5.13; N, 16.80%.

1,2-Dihydro-5-cyano-1-methyl-2-phenyl-3*H*-indazol-3-one (8b). Colorless crystals; mp 196–197 °C (chloroform–hexane); yield 40%; IR (KBr): ν_{max} 2185, 1661, 1594, 1482 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.28 (s, 3H, NCH_3), 7.36 (d, 1H, J = 8.6 Hz, ArH), 7.49–7.53 (m, 5H, ArH), 7.82 (dd, 1H, J = 8.6, 1.6 Hz, ArH), 8.25 (d, 1H, J = 1.5 Hz, ArH); MS (*m*/*z*, %): 249 (M^+, 23.8). Anal. calc. for $C_{15}H_{11}N_3O$ (249.27): C, 72.28; H, 4.45; N, 16.86%. Found: C, 72.09; H, 4.52; N, 16.97%.

1,2,6,7-Tetrahydro-5-(ethoxycarbonyl)-1-methyl-2-phenyl-3*H*-indazol-3-one (9a). Colorless crystals; mp 197–198 °C (chloroform–hexane); yield 60%; IR (KBr): ν_{max} 1691, 1660, 1548, 1204 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (t, 3H, J = 7.1 Hz, CH_3), 2.78–2.83 (m, 4H, CH_2–CH_2), 3.22 (s, 3H, NCH_3), 4.22 (q, 2H, J = 7.1 Hz, OCH_2), 7.33–7.37 (m, 3H, ArH), 7.45–7.51 (m, 2H, ArH), 7.57 (s, 1H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 20.8, 22.0, 34.3, 60.4, 104.7, 119.9, 125.3, 127.6, 128.4, 129.4, 134.4, 155.1, 162.4, 167.1; MS (*m*/*z*, %): 298 (M^+, 100). Anal. calc. for $C_{17}H_{18}N_2O_3$ (298.34): C, 68.44; H, 6.08; N, 9.39%. Found: C, 68.73; H, 6.03; N, 9.48%.

1,2-Dihydro-5-(ethoxycarbonyl)-1-methyl-2-phenyl-3*H*-indazol-3-one (9b). A solution of **9a** (300 mg, 1 mmol) and DDQ (295 mg, 1.3 mmol) in dry dioxane (10 mL) was refluxed with stirring for 2 h. The reaction mixture was then cooled, diluted with chloroform (20 mL) and filtered. The filtrate was evaporated to dryness and the residue obtained was purified by passing it through a silica gel column using hexane–ethyl acetate (19 : 1) as eluent; colorless crystals; mp 125–126 °C (chloroform–hexane); yield 90%; IR (KBr): ν_{max} 1680 (br), 1626, 1368, 1295 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (t, 3H, J = 7.1 Hz, CH_3), 3.25 (s, 3H, NCH_3), 4.41 (q, 2H, J = 7.1 Hz, OCH_2), 7.29–7.37 (m, 2H, ArH), 7.48–7.58 (m, 4H, ArH), 8.31 (dd, 1H, J = 8.7, 1.5 Hz, ArH), 8.45 (d, 1H, J = 1.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 38.8, 61.2, 111.8, 118.5, 124.0, 125.3, 126.9, 127.2, 129.3, 134.0, 134.6, 153.4, 161.6, 165.9. Anal. calc. for $C_{17}H_{16}N_2O_3$ (296.32): C, 68.91; H, 5.44; N, 9.45%. Found: C, 69.14; H, 5.32; N, 9.61%.

1,2-Dihydro-2,6-diphenyl-1-methyl-5-nitro-3*H*-indazol-3-one (14). Colorless crystals; mp 196–197 °C (chloroform–hexane); yield 58%; IR (KBr): ν_{max} 1675, 1623, 1522, 1344 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 3.32 (s, 3H, NCH_3), 7.31 (s, 1H, H-7), 7.40–7.75 (m, 10H, ArH), 8.66 (s, 1H, H-4); MS (*m*/*z*, %): 345 (M^+, 100). Anal. calc. for $C_{20}H_{15}N_3O_3$ (345.36): C, 69.56; H, 4.38; N, 12.17%. Found: C, 69.73; H, 4.47; N, 12.09%.

1,2-Dihydro-5-benzoyl-2,6-diphenyl-1-methyl-3*H*-indazol-3-one (15). Light yellow crystals; mp 58–59 °C (ether–hexane); yield 80%; IR (KBr): ν_{max} 1658 (br), 1616, 1491, 1315 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.27 (s, 3H, NCH_3), 7.25–7.37 (m, 9H, ArH), 7.45–7.63 (m, 5H, ArH), 7.69–7.74 (m, 2H, ArH), 8.09 (s, 1H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.1, 113.9, 116.9, 123.9, 126.2, 126.8, 128.0, 128.3, 128.5, 128.8, 129.3, 130.0, 133.0, 134.4, 134.7, 137.5, 139.9, 147.1, 152.0, 161.5, 196.9; MS: (*m*/*z*, %): 404 (M^+, 82.4), 389 (19). Anal. calc. for $C_{27}H_{20}N_2O_2$ (404.47): C, 80.18; H, 4.98; N, 6.93%. Found: C, 79.91; H, 5.06; N, 7.02%.

1,2-Dihydro-1-methyl-5-nitro-2-phenyl-6-methylthio-3*H*-indazol-3-one (18). Light yellow crystals; mp 200–201 °C (chloroform–hexane); yield 65%; IR (KBr): ν_{max} 1673, 1615, 1512, 1296 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.57 (s, 3H, SCH_3), 3.32 (s, 3H, NCH_3), 7.01 (s, 1H, H-7), 7.33–7.39 (m, 1H, ArH), 7.50–7.53 (m, 4H, ArH), 8.84 (s, 1H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.7, 38.4, 106.9, 114.4, 124.2, 124.3, 127.4, 129.5, 134.2, 141.2, 145.5, 152.0, 160.6; MS (*m*/*z*, %): 315 (M^+, 100), 236 (53). Anal. calc. for $C_{15}H_{13}N_3O_3S$ (315.35): C, 57.13; H, 4.15; N, 13.33%. Found: C, 57.43; H, 4.07; N, 13.50%.

1,2,5,10-Tetrahydro-1-methyl-2-phenyl-3*H*-naphtho[2,3-*f*]-indazole-3,5,10-trione (21). Red crystals; mp 240–241 °C chloroform–hexane); yield 50%; IR (KBr): ν_{max} 1694, 1669, 1589, 1325 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.41 (s, 3H, NCH_3), 7.39–7.42 (m, 1H, ArH), 7.52–7.59 (m, 4H, ArH), 7.83–7.87 (m, 2H, ArH), 8.21 (s, 1H, H-11), 8.37, 8.39 (two d, 2H, $J = 8$ Hz, H-6 and H-9), 8.96 (s, 1H, H-4); MS (*m*/*z*, %): 354 (M^+, 100). Anal. calc. for $C_{22}H_{14}N_2O_3$ (354.36): C, 74.57; H, 3.98; N, 7.91%. Found: C, 74.34; H, 4.11; N, 7.79%.

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