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Construction of Multifunctionalized Azopyrazoles by Silver-Catalyzed Cascade Reaction of Diazo Compounds

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Abstract: A variety of multisubstituted azopyrazoles were synthesized in good yield from an efficient one-pot silver trifluoromethanesulfonate (AgOTf)-catalyzed cascade reaction of α-diazo-β-keto esters with two arylhydrazines or two arylhydrazine hydrochlorides. This cascade reaction included pyrazolone formation, N–H insertion, and oxidation. For the synthesis of more diverse azopyrazoles bearing two different aromatic rings, the silver(I)-catalyzed cascade reaction of 4-diazopyrazol-3-one with arylhydrazine hydrochlorides was also developed. The advantages of these methodologies are easy handling, mild reaction conditions, and an effective and non-toxic catalyst usage.

Keywords: activation; coupling; ethers; multifunctionalized azopyrazoles; palladium; radicals

Introduction

Pyrazoles belong to one of the most important classes of heteroaromatic compounds and have been reported to possess a wide range of biological properties, such as anti-inflammatory,[1] antibacterial,[2] analgesic,[3] antifungal,[4] antipyretic,[5] plant growth regulating properties,[6] protein kinase inhibitors,[7] and antiviral[8] activities. They have been also used as an important building blocks and structural motifs in the synthesis of natural products, agrochemicals, and medicines.[9] Among these, rimonabant (**1**), celecoxib (**2**), and fipronil (**3**) have been commercialized as medicines or insecticides (Figure 1). Owing to their importance and usefulness, a number of methods for the preparation of pyrazoles have been developed.[10]

Pyrazoles bearing an azo group (azopyrazoles) are also found as the core structure in many food colorings,[11] dyestuffs,[12] and bioactive molecules (Figure 2).[13] They exhibited a broad spectrum of biological properties such as antibacterial,[14] antifungal[15] and HIV-1 inhibitory activities.[16] In addition to pyrazoles, several methods for the synthesis of azopyra-

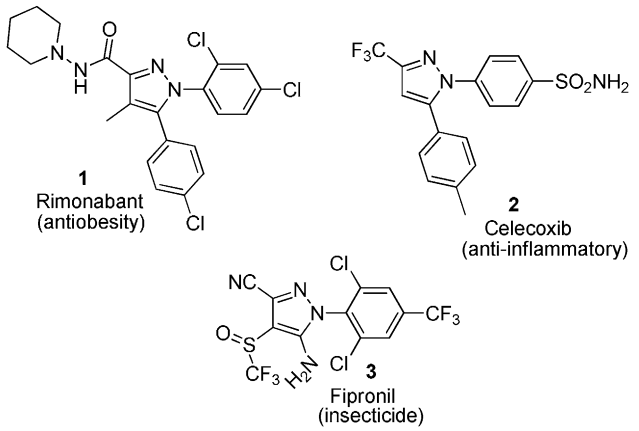


Figure 1. Selected examples of commercialized materials bearing a pyrazole scaffold.

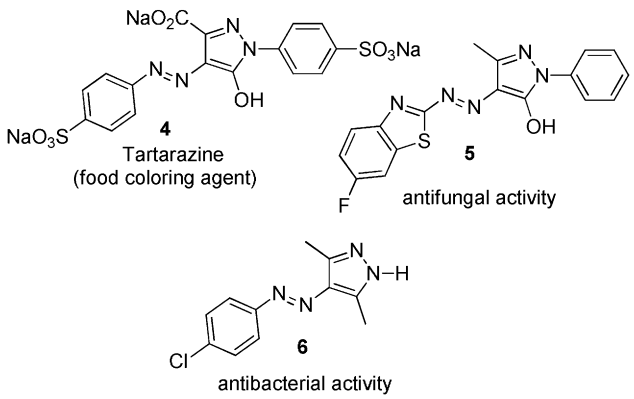
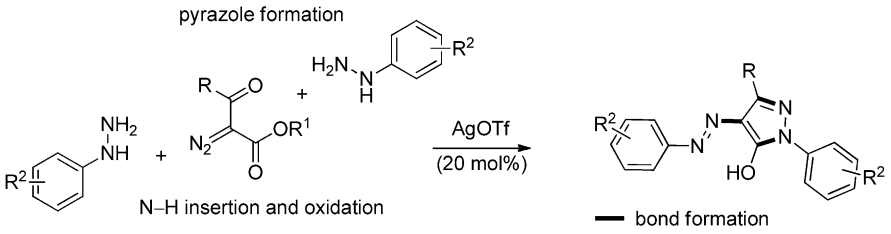


Figure 2. Examples of food coloring and bioactive materials bearing azopyrazole skeleton.



Scheme 1. Silver-catalyzed synthesis of diverse azopyrazoles.

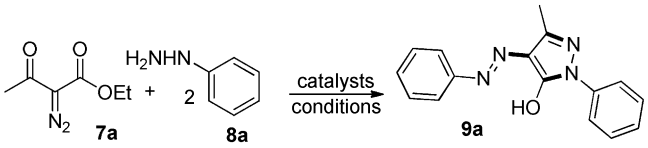
zoles have been reported.[17] Most of these methods involve harsh operations and multistep procedures through reactions of aryldiazonium salts with β-keto esters followed by pyrazole formation using hydrazines.[17]

Although several approaches to the synthesis of azopyrazoles have been reported, they are limited by harsh reaction conditions, low yields, raw material availability, and required multiple synthetic steps. Accordingly, there is a demand for a facile one-step approach for the synthesis of azopyrazoles. To the best of the authors' knowledge, there is a paucity of reports on one-step procedures for the synthesis of azopyrazole derivatives from readily available starting materials, which prompted us to develop a novel one-pot reaction relying on the characteristic reactivity of diazo compounds.[18] The present study has established the decomposition of diazo compounds as an effective means of synthesizing various heterocycles and new molecules.[19] As a part of an ongoing study in this area, this paper reports a silver(I)-catalyzed reaction for the synthesis of a variety of multifunctionalized azopyrazoles by pyrazole formation, N–H insertion, and oxidation through a cascade reaction from readily available diazodicarbonyl compounds and two arylhydrazines (Scheme 1).

Results and Discussion

To approach azopyrazoles, our investigation first commenced with the reaction of ethyl 2-diazo-3-oxobutanoate[18j] (**7a**, 0.5 mmol) and phenylhydrazine (**8a**, 1.2 mmol) with different catalysts and solvents (Table 1). Treatment of **7a** with **8a** in the presence of 20 mol% of Ag_2O, $AgNO_3$, AgOAc or $AgSbF_6$, as catalysts at 70 °C for 24 h in acetonitrile provided the product **9a** in 17, 42, 45, and 52% yields, respectively (entries 1–4). Using 20 mol% of AgOTf at 70 °C for 24 h in acetonitrile, **9a** was produced in 72% yield (entry 5). Decreasing (10 mol%) or increasing (40 mol%) the AgOTf loading did not improve the yield (entries 6 and 7). With other non-polar and polar solvents, such as dichloroethane, toluene, dioxane, and ethanol, the yield of **9a** was not increased (entries 8–11).

Table 1. Reaction of diazodicarbonyl (**7a**) and phenylhydrazine (**8a**) under different metal catalysts and conditions.[a]



7a **8a** **9a**

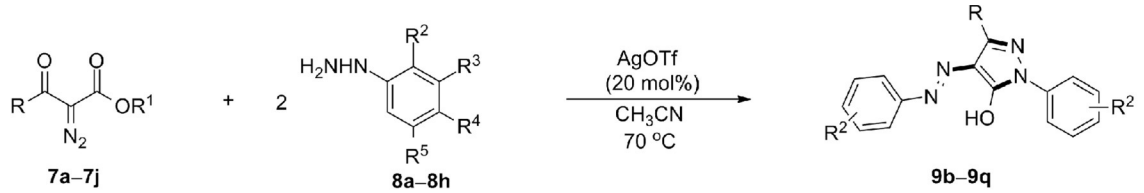
Entry	Catalyst	Conditions	Yield [%][b]
1	Ag_2O (20 mol %)	CH_3CN, 70 °C, 24 h	17
2	$AgNO_3$ (20 mol %)	CH_3CN, 70 °C, 24 h	42
3	AgOAc (20 mol %)	CH_3CN, 70 °C, 24 h	45
4	$AgSbF_6$ (20 mol %)	CH_3CN, 70 °C, 24 h	52
5	AgOTf (20 mol %)	CH_3CN, 70 °C, 24 h	72
6	AgOTf (10 mol %)	CH_3CN, 70 °C, 24 h	63
7	AgOTf (40 mol %)	CH_3CN, 70 °C, 24 h	60
8	AgOTf (20 mol %)	DCE, 70 °C, 24 h	37
9	AgOTf (20 mol %)	toluene, 70 °C, 24 h	50
10	AgOTf (20 mol %)	dioxane, 70 °C, 24 h	38
11	AgOTf (20 mol %)	EtOH, 70 °C, 24 h	25
12	$Cu(OTf)_2$ (20 mol %)	CH_3CN, 70 °C, 24 h	15
13	$Ru(PPh_3)_3Cl_2$ (5 mol %)	CH_3CN, 70 °C, 24 h	10
14	$Rh_2(OAc)_4$ (2 mol %)	CH_3CN, 70 °C, 24 h	48

[a] The reaction was carried out with **7a** (0.5 mmol) and **8a** (1.2 mmol).
[b] Isolated yields were calculated from **7a**.

With other catalysts, such as $Cu(OTf)_2$ (20 mol%), $Ru(PPh_3)_3Cl_2$ (5 mol%), and $Rh_2(OAc)_4$ (2 mol%), the yield of **9a** was not improved (entries 12–14). The structure of **9a** was determined by analysis of its spectral data. The ^{1}H NMR spectrum of **9a** showed a methyl signal on the pyrazole ring as a singlet at $\delta =$ 2.35 ppm and a hydroxy peak at 13.57 ppm as a singlet. The structure of **9a** was further confirmed by X-ray crystallographic analysis of the closely related compound **9m**[20] (see the Supporting Information for details).

Further reactions of α-diazo-β-keto esters **7b–7f** with alkyl substituents (R), such as ethyl, *n*-propyl, isopropyl, *n*-pentyl, and benzyl groups with phenylhydrazine (**8a**) for 24 h afforded the desired products **9b–9f** in 88–95% yield. In addition, reactions of α-diazo-β-keto esters **7g–7j** with phenyl or aryl rings containing electron-donating or electron-withdrawing groups afforded the desired products **9g–9j** in 85–93% yield. To demonstrate the versatility of this methodology, reactions with substituted phenylhydrazine hy-

Table 2. Formation of azopyrazoles **9b–9q** from diazo compounds **7a–7j** and arylhydrazines **8a–8h**.



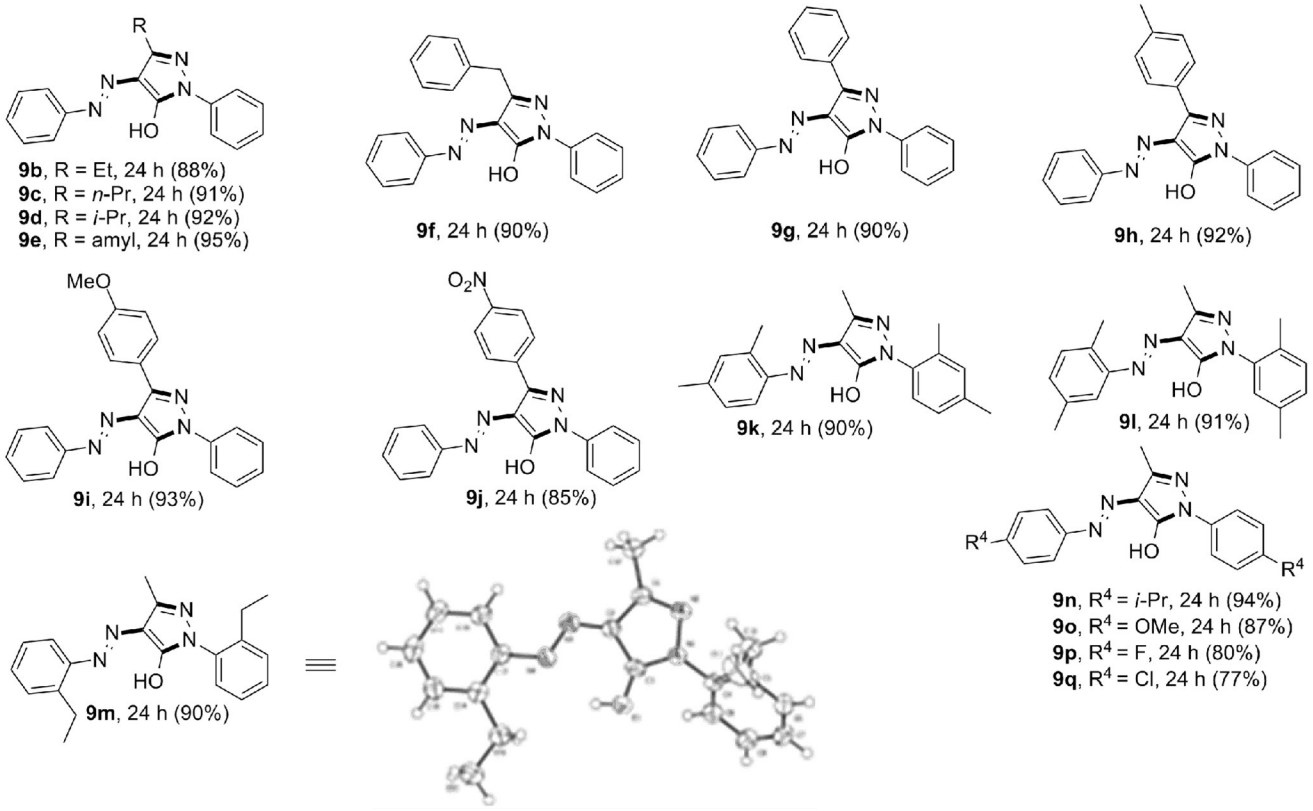
7a–7j

7a, R = Me, R^1 = Et
7b, R = R^1 = Et
7c, R = *n*-Pr, R^1 = Et
7d, R = *i*-Pr, R^1 = Me
7e, R = amyl, R^1 = Et
7f, R = Bn, R^1 = Me
7g, R = Ph, R^1 = Et
7h, R = 4-MeC_6H_4, R^1 = Me
7i, R = 4-$MeOC_6H_4$, R^1 = Me
7j, R = 4-$NO_2C_6H_4$, R^1 = Me

8a–8h

8a, R^2 = R^3 = R^4 = R^5 = H
8b, R^2 = Me, R^3 = H, R^4 = Me, R^5 = H, HCl
8c, R^2 = Me, R^3 = R^4 = H, R^5 = Me, HCl
8d, R^2 = Et, R^3 = R^4 = R^5 = H, HCl
8e, R^2 = R^3 = H, R^4 = *i*-Pr, R^5 = H, HCl
8f, R^2 = R^3 = H, R^4 = OMe, R^5 = H, HCl
8g, R^2 = R^3 = H, R^4 = F, R^5 = H, HCl
8h, R^2 = R^3 = H, R^4 = Cl, R^5 = H, HCl

9b–9q

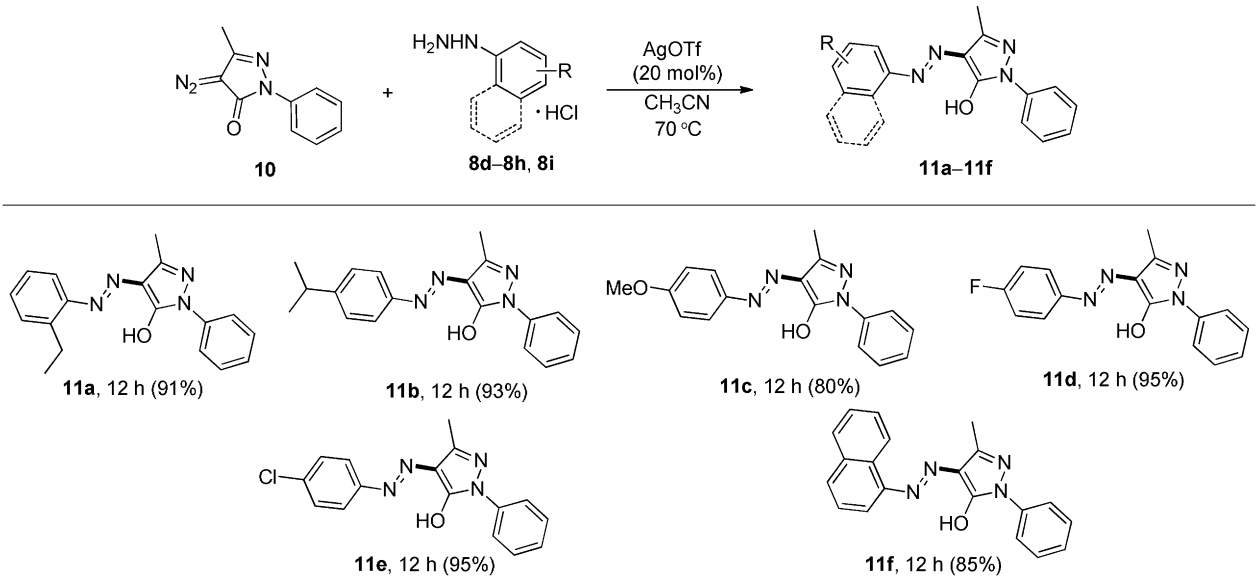


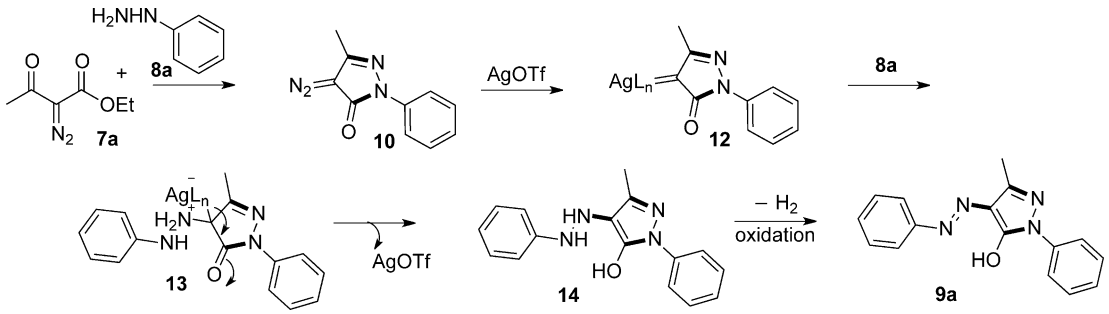
9b, R = Et, 24 h (88%)
9c, R = *n*-Pr, 24 h (91%)
9d, R = *i*-Pr, 24 h (92%)
9e, R = amyl, 24 h (95%)
9f, 24 h (90%)
9g, 24 h (90%)
9h, 24 h (92%)
9i, 24 h (93%)
9j, 24 h (85%)
9k, 24 h (90%)
9l, 24 h (91%)
9m, 24 h (90%)
9n, R^4 = *i*-Pr, 24 h (94%)
9o, R^4 = OMe, 24 h (87%)
9p, R^4 = F, 24 h (80%)
9q, R^4 = Cl, 24 h (77%)

drochlorides were examined further. For example, the reaction of **7a** with 2,4-dimethyl-, 2,5-dimethyl-, 2-ethyl-, 4-isopropyl-, or 4-methoxyphenylhydrazine hydrochloride bearing electron-donating groups on the benzene ring afforded the expected products **9k–9o** in 87–94% yield, and that with 4-fluoro- or 4-chlorophenylhydrazine hydrochloride bearing an electron-withdrawing group provided products **9p** (80%) and **9q** (77%) in slightly lower yields (Table 2).

Considering the general applicability of the reaction using α-diazo-β-keto esters **7a–7i** as starting materials, we examined the possibility of using 4-diazopyrazol-3-one as a starting material, which should lead to the formation of other azopyrazole derivatives bearing two different aromatic rings (Table 3). The reactions of **10** with 2-ethyl-, 4-isopropyl- or 4-methoxyphenylhydrazine hydrochloride bearing an electron-donating group on the benzene ring provided the expected products **11a–11c** in 91, 93, and 80% yield, respectively. A combination of **10** with 4-fluoro-, or 4-chlorophenylhydrazine hydrochloride bearing an electron-withdrawing group afforded products **11d** (95%) and **11e** (95%), whereas that with 1-naphthalenylhydrazine hydrochloride gave the desired product **11f** (85%).

Table 3. Formation of azopyrazoles (**11a**–**11 f**) from reaction of 4-diazopyrazol-3-one (**10**) and arylhydrazines (**8d**–**8i**).





Scheme 2. Proposed mechanism for the formation of **9a**.

The mechanism for the formation of the observed product **9a** can be explained, as shown Scheme 2. The diazo compound **7a** first reacts with phenylhydrazine (**8a**) to give 4-diazopyrazol-3-one **10**. To gain evidence of the formation of intermediate **10** in the absence of Ag(I) catalyst, we carried out the reaction of **7a** and **8a** in acetonitrile at 70 °C for 24 h without any catalyst. In this case, compound **10** was produced in 61% yield, together with recovery of the starting material **7a** (20%). The decomposition of diazo intermediate **10** is initiated by the Ag(I) catalyst to give a metal carbenoid **12** *via* the loss of N_2.[21] The nucleophilic attack of phenylhydrazine (**8a**) to an electrophic silver carbenoid **12** gives another ylide intermediate **13**, which undergoes the removal of a catalyst and proton transfer, leading to the formation of intermediate **14** as an N–H insertion product. The oxidation of **14** in the presence Ag(I) catalyst finally leads to **9a**.

Conclusions

In summary, diverse and multifunctionalized azopyrazole derivatives were synthesized in a one-pot procedure by the silver(I)-catalyzed reaction of α-diazo-β-keto esters with arylhydrazines or arylhydrazine hydrochlorides. This protocol includes cascade pyrazolone formation, N–H insertion, and oxidation. In addition, Ag(I)-catalyzed reactions of 4-diazopyrazol-3-one with arylhydrazine hydrochlorides for the synthesis of various other azopyrazoles bearing two different aromatic rings are described. This cascade reaction allows the synthesis of highly functionalized azopyrazole derivatives, which may find a wide range of applications in the synthesis of natural products, pharmaceuticals or coloring industry.

Experimental Section

General Remarks

All experiments were carried out under a nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VNS (300 and 75 MHz, respectively) spectrometer in $CDCl_3$ using $\delta = 7.24$ and 77.23 ppm as solvent chemical shifts. Multiplicities are abbreviated as follows; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and dd = doublet of doublets. IR spectra were recorded on an FT-IR (BIO-RAD), and HR-MS was carried out at the Korean Basic Science Institute. Structural measurements for the complexes were performed at Jeonju center of Korea Basic Science Institute.

General Experimental Procedure for the Synthesis of Azopyrazoles and Characterization Data for All New Compounds (9a–9q)

To a solution of α-diazo β-keto ester (0.5 mmol) and arylhydrazine or arylhydrazine hydrochloride (1.2 mmol) in acetonitrile (5.0 mL) was added AgOTf (26 mg, 20 mol%) and the mixture heated at 70 °C under a nitrogen atmosphere until completion of reaction as indicated by TLC. The volatiles were removed under vacuum and the residue was purified by silica gel column chromatography (hexane: ethyl acetate = 30:1) to give desired product as solid (see the Supporting Information for details).

3-Methyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9a): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with phenylhydrazine **(8a**, 130 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 100 mg (72%); mp 130–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.57$ (1H, s, OH), 7.94 (2H, d, $J =$ 8.4 Hz), 7.45–7.38 (6H, m), 7.18 (2H, t, $J = 7.5$ Hz), 2.35 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.7$, 148.5, 141.1, 138.0, 129.6, 129.6, 129.0, 128.9, 125.7, 125.1, 121.7, 118.5, 118.5, 115.8, 115.8, 11.7; IR (KBr): $\nu = 1657$, 1555, 1493, 1342, 1263, 1157, 751 cm^{-1}; HR-MS (EI) $m/z = 278.1166$ (M^+), calcd. for $C_{16}H_{14}N_4O$: 278.1168.

3-Ethyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9b): Prepared from ethyl 2-diazo-3-oxopentanoate **7b** (85 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 128 mg (88%); mp 109–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.57$ (1H, s, OH), 7.95 (2H, d, $J = 7.8$ Hz), 7.43–7.40 (6H, m), 7.21–7.16 (2H, m), 2.76 (2H, q, $J =$ 7.5 Hz), 1.37 (3H, t, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.9$, 152.9, 141.1, 138.0, 129.6, 129.6, 128.8, 128.8, 127.9, 125.7, 125.1, 118.6, 118.6, 115.7, 115.7, 20.2, 11.7; IR (KBr): $\nu = 2967$, 1656, 1550, 1488, 1342, 1261, 1153, 1049, 747 cm^{-1}; HR-MS (EI): $m/z = 292.1322$ (M^+), calcd. for $C_{17}H_{16}N_4O$: 292.1324.

3-Propyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9c): Prepared from ethyl 2-diazo-3-oxohexanoate **7c** (92 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 139 mg (91%); mp 120–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.59$ (1H, s, OH), 7.95 (2H, d, $J =$ 8.1 Hz), 7.43–7.39 (6H, m), 7.21–7.16 (2H, m), 2.71 (2H, t, $J = 7.8$ Hz), 1.90–1.78 (2H, m), 1.05 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.8$, 151.9, 141.1, 138.0, 129.6, 129.6, 128.8, 128.8, 128.1, 125.7, 125.1, 118.6, 118.6, 115.7 115.7, 28.6, 20.9, 14.0; IR (KBr): $\nu = 2950$, 1656, 1551, 1490, 1152, 1260, 1154, 1056, 752 cm^{-1}; HR-MS (EI): $m/z =$ 306.1479 (M^+), calcd. for $C_{18}H_{18}N_4O$: 306.1481.

3-Isopropyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9d): Prepared from methyl 2-diazo-4-methyl-3-oxopentanoate **7d** (85 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 140 mg (92%); mp 145–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.61$ (1H, s, OH), 7.98 (2H, d, $J = 8.1$ Hz), 7.50–7.39 (6H, m), 7.21–7.14 (2H, m), 3.23–3.13 (1H, m), 1.43 (6H, d, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.9$, 155.9, 141.2, 138.1, 129.6, 129.6, 128.8, 128.8, 127.4, 125.5, 124.9, 118.5, 118.5, 115.6 115.6, 27.6, 20.7, 20.7; IR (KBr): $\nu = 2963$, 1656, 1548, 1486, 1344, 1259, 1150, 1009, 740 cm^{-1}; HR-MS (EI): $m/z = 306.1480$ (M^+), calcd. for $C_{18}H_{18}N_4O$: 306.1481.

3-Pentyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9e): Prepared from ethyl 2-diazo-3-oxooctanoate **7e** (106 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 158 mg (95%); mp 95–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.61$ (1H, s, OH), 7.95 (2H, d, $J =$ 8.1 Hz), 7.43–7.39 (6H, m), 7.21–7.16 (2H, m), 2.72 (2H, t, $J = 7.5$ Hz), 1.83–1.78 (2H, m), 1.41–1.36 (4H, m), 0.92 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.8$, 152.1, 141.1, 138.0, 129.6, 129.6, 128.8, 128.8, 128.1, 125.6, 125.0, 118.6, 118.6, 115.7 115.7, 31.5, 27.1, 26.6, 22.3, 13.9; IR (KBr): $\nu = 2927$, 1654, 1550, 1485, 1351, 1254, 1152, 1064, 745 cm^{-1}; HR-MS (EI): $m/z = 334.1792$ (M^+), calcd. for $C_{20}H_{22}N_4O$: 334.1794.

3-Benzyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9f): Prepared from methyl 2-diazo-3-oxo-4-phenylbutanoate **7f** (109 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 159 mg (90%); mp 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.44$ (1H, s, OH), 7.87 (2H, d, $J = 7.8$ Hz), 7.37–7.21 (10H, m), 7.14–7.07 (3H, m), 3.98 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 157.7$, 150.2, 141.0, 138.0, 137.0, 129.6, 129.6, 129.1, 129.1, 128.8, 128.8, 128.5, 128.5, 127.5, 126.7, 125.8, 125.1, 118.6, 118.6, 115.8, 115.8; 33.2 IR (KBr): $\nu = 3054$, 1661, 1546, 1494, 1339, 1260, 1143, 1055, 749 cm^{-1}; HR-MS (EI): $m/z = 354.1478$ (M^+), calcd. for $C_{22}H_{18}N_4O$: 354.1481.

3-Phenyl-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9g): Prepared from ethyl 2-diazo-3-oxo-3-phenylpropanoate **7g** (109 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as an orange red solid; yield: 153 mg (90%); mp 157–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.92$ (1H, s, OH), 8.16–8.13 (2H, m), 8.00–7.97 (2H, m), 7.43–7.31 (9H, m), 7.17–7.13 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.0$, 146.4, 141.1, 138.0, 130.3, 129.7, 129.7, 129.7, 128.9, 128.9, 128.5, 128.5, 127.4, 127.4, 127.2, 126.0, 125.4, 118.8, 118.8, 116.0, 116.0; IR (KBr): $\nu = 3051$, 1655, 1486, 1486, 1330, 1262, 1160, 955, 748 cm^{-1}; HR-MS (EI): $m/z = 340.1323$ (M^+), calcd. for $C_{21}H_{16}N_4O$: 340.1324.

1-Phenyl-4-(phenyldiazenyl)-3-(*p*-tolyl)-1*H*-pyrazol-5-ol (9h): Prepared from methyl 2-diazo-3-oxo-3-(*p*-tolyl)propanoate **7h** (109 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as a red solid; yield: 177 mg (92%); mp 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.86 (1H, s, OH), 8.03 (2H, d, J = 8.1 Hz), 7.97 (2H, d, J = 7.8 Hz), 7.38–7.32 (6H, m), 7.20–7.11 (4H, m), 2.31 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0, 146.5, 141.1, 139.8, 138.0, 129.6, 129.6, 129.2, 129.2, 128.8, 128.8, 127.5, 127.4, 127.3, 127.3, 125.8, 125.2, 118.7, 118.7, 115.9, 115.9, 21.4; IR (KBr): ν = 3050, 1661, 1480, 1484, 1332, 1266, 1167, 957 cm^{-1}; HR-MS (EI): m/z = 354.1482 (M^+), calcd. for $C_{22}H_{18}N_4O$: 354.1481.

3-(4-Methoxyphenyl)-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9i): Prepared from methyl 2-diazo-3-(4-methoxyphenyl)-3-oxopropanoate **7i** (117 mg, 0.5 mmol) with phenylhydrazine **8a** (130 mg, 1.2 mmol) according to general procedure in 24 h as a red solid; yield: 172 mg (93%); mp 172–174 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 14.02 (1H, s, OH), 8.23 (2H, d, J = 8.4 Hz), 8.09 (2H, d, J = 8.1 Hz), 7.50–7.48 (6H, m), 7.28–7.24 (2H, m); 7.05 (2H, d, J = 8.4 Hz); 3.910 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 158.0, 146.3, 141.1, 138.0, 129.7, 129.7, 128.8, 128.8, 128.8, 128.8, 127.4, 125.9, 125.3, 122.9, 118.8, 118.8, 115.9, 115.9, 114.0, 114.0, 55.3; IR (KBr): ν = 3048,1654, 1544, 1485, 1336, 1253, 1161, 1027, 957, 744 cm^{-1}; HR-MS (EI): m/z = 370.1430 (M^+), calcd. for $C_{22}H_{18}N_4O_2$: 370.1430.

3-(4-Nitrophenyl)-1-phenyl-4-(phenyldiazenyl)-1*H*-pyrazol-5-ol (9j): Prepared from methyl 2-diazo-3-(4-nitrophenyl)-3-oxopropanoate **7j** (124 mg, 0.5 mmol) with phenylhydrazine **8a** (120 mg, 1.2 mmol) according to general procedure in 24 h as a yellow solid; yield: 163 mg (85%); mp 240–242 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 14.11 (1H, s, OH), 8.43 (2H, d, J = 9.0 Hz), 8.34 (2H, d, J = 8.7 Hz), 8.04 (2H, d, J = 7.8 Hz), 7.48–7.44 (6H, m), 7.28 (2H, d, J = 6.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.0, 148.1, 143.9, 140.7, 137.7, 136.4, 129.9, 129.9, 129.0, 129.0, 127.8, 127.8, 126.8, 126.6, 126.0, 123.8, 123.8, 119.0, 119.0, 116.3, 116.3; IR (KBr): ν = 3045,1652, 1545, 1487, 1335, 1250, 1160, 1022, 955, 741 cm^{-1}; HR-MS (EI): m/z = 385.1173 (M^+), calcd. for $C_{21}H_{15}N_5O_3$: 385.1175.

1-(2,4-Dimethylphenyl)-4-[(2,4-dimethylphenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9k): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 2,4-dimethylphenylhydrazine hydrochloride **8b** (206 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 150 mg (90%); mp 130–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.79 (1H, s, OH), 7.67 (1H, d, J = 8.4 Hz), 7.19 (1H, d, J = 7.8 Hz), 7.09–7.04 (3H, m), 6.99 (1H, s), 2.34 (3H, s), 2.32 (9H, s), 2.24 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 147.7, 138.3, 137.0, 135.3, 134.9, 133.0, 131.6, 131.6, 128.0, 128.0, 127.2, 126.6, 125.2, 114.4, 21.1, 20.9, 18.2, 16.6, 11.8; IR (KBr): ν = 2917, 1650, 1554, 1270, 1176, 1038, 797 cm^{-1}; HR-MS (EI): m/z = 334.1790 (M^+), calcd. for $C_{20}H_{22}N_4O$: 334.1794.

1-(2,5-Dimethylphenyl)-4-[(2,5-dimethylphenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9l): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 2,5-dimethylphenylhydrazine hydrochloride **8c** (206 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 151 mg (91%); mp 100–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.75 (1H, s, OH), 7.60 (1H, s), 7.18–7.14 (2H, m), 7.09–7.05 (2H, m), 6.90 (1H, d, J = 7.5 Hz), 2.37 (6H, s), 2.32 (6H, s), 2.25 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 147.9, 139.0, 137.3, 136.3, 135.3, 132.0, 130.8, 130.8, 129.3, 128.3, 127.1, 126.3, 122.3, 114.7, 21.2, 20.7, 17.9, 16.2, 11.8; IR (KBr): ν = 1646, 1565, 1451, 1270, 1139, 1048, 791 cm^{-1}; HR-MS (EI): m/z = 334.1792 (M^+), calcd. for $C_{20}H_{22}N_4O$: 334.1794.

1-(2-Ethylphenyl)-4-[(2-ethylphenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9m): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 2-ethylphenylhydrazine hydrochloride **8d** (206 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 150 mg (90%); mp 90–92 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.79 (1H, s, OH), 7.73 (1H, d, J = 8.0 Hz), 7.26–7.12 (6H, m), 7.08–7.03 (1H, m), 2.69–2.55 (4H, m), 2.28 (3H, s), 1.21 (3H, t, J = 7.5 Hz), 1.10 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 147.9, 141.3, 138.6, 134.9, 131.2, 129.2, 129.0, 128.9, 128.3, 127.3, 127.3, 126.5, 125.6, 114.5, 24.6, 23.5, 14.3, 13.7, 11.7; IR (KBr): ν = 2966, 1648, 1548, 1454, 1339,1255, 1162, 1047, 751 cm^{-1}; HR-MS (EI): m/z = 334.1791 (M^+), calcd. for $C_{20}H_{22}N_4O$: 334.1794.

1-(4-Isopropylphenyl)-4-[(4-isopropylphenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9n): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 4-isopropylphenylhydrazine hydrochloride **8e** (223 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 170 mg (94%); mp 80–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.52 (1H, s, OH), 7.75 (2H, d, J = 8.7 Hz), 7.26–7.14 (6H, m), 2.86–2.77 (2H, m), 2.23 (3H, s), 1.17 (6H, d, J = 6.9 Hz), 1.15 (6H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.5, 148.1, 146.7, 145.6, 139.0, 135.8, 127.9, 127.5, 127.5, 126.7, 126.7, 118.6, 118.6, 115.7, 115.7, 33.6, 33.6, 23.9, 23.9, 23.8, 23.8, 11.6; IR (KBr): ν = 2951, 1650, 1538, 1345, 1265, 1152, 1046, 816 cm^{-1}; HR-MS (EI): m/z = 362.2107 (M^+), calcd. for $C_{22}H_{26}N_4O$: 362.2107.

1-(4-Methoxyphenyl)-4-[(4-methoxyphenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9o): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 4-methoxyphenylhydrazine hydrochloride **8f** (208 mg, 1.2 mmol) according to general procedure in 24 h as an orange red solid; yield: 147 mg (87%); mp 127–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.69 (1H, s, OH), 7.80 (2H, d, J = 9.0 Hz), 7.35 (2H, d, J = 9.0 Hz), 6.94–6.90 (4H, m), 3.80 (6H, s), 2.32 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 157.4, 157.0, 148.0, 134.7, 131.5, 127.5, 120.3, 120.3, 117.1, 117.1, 114.9, 114.9, 114.0, 114.0, 55.5, 55.4, 11.7; IR (KBr): ν = 2950, 1545, 1490, 1101, 1030, 811, 525 cm^{-1}; HR-MS (EI): m/z = 338.1376 (M^+), calcd. for $C_{18}H_{18}N_4O_3$: 338.1379.

1-(4-Fluorophenyl)-4-[(4-fluorophenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9p): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 4-fluorophenylhydrazine hydrochloride **8g** (194 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 125 mg (80%); mp 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.53 (1H, s, OH), 7.89–7.86 (2H, m), 7.37–7.34 (2H, m), 7.16–7.04 (4H, m), 2.31 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.2, 161.6, 158.9, 157.4, 148.4, 137.3, 128.3, 120.2, 120.1, 117.2, 117.1, 116.7, 116.4, 115.7, 115.4, 11.7; IR (KBr): ν = 1654, 1554, 1498, 1278, 1216, 1154, 820 cm^{-1}; HR-MS (EI): m/z = 314.0977 (M^+), calcd. for $C_{16}H_{12}F_2N_4O$: 314.0979.

1-(4-Chlorophenyl)-4-[(4-chlorophenyl)diazenyl]-3-methyl-1*H*-pyrazol-5-ol (9q): Prepared from ethyl 2-diazo-3-oxobutanoate **7a** (78 mg, 0.5 mmol) with 4-chlorophenylhydrazine hydrochloride **8h** (213 mg, 1.2 mmol) according to general procedure in 24 h as an orange solid; yield: 233 mg (77%); mp 217–219 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.48 (1H, s, OH), 7.89 (2H, d, J = 9.0 Hz), 7.37–7.35 (6H, m), 2.33 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$ + DMSO-d_6): δ = 157.4, 148.6, 139.5, 136.4, 130.9, 130.1, 129.6, 129.6, 128.8, 128.8, 128.5, 119.4, 119.4, 116.8, 116.8, 11.6; IR (KBr): ν = 1650, 1555, 1490, 1275, 1214, 1157, 825 cm^{-1}; HR-MS (EI): m/z = 346.0391 (M^+), calcd. for $C_{16}H_{12}Cl_2N_4O$: 346.0388.

General Experimental Procedure for the Synthesis of Azopyrazoles and Characterization Data for New Compounds (11a–11f)

To a solution of 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (100 mg, 0.5 mmol) and arylhydrazine hydrochloride (0.6 mmol) in acetonitrile (5.0 mL) was added AgOTf (26 mg, 20 mol%) and the mixture heated at 70 °C under a nitrogen atmosphere until completion of reaction as indicated by TLC. The volatiles were removed under vacuum and the residue was purified by silica gel column chromatography (hexane: ethylacetate = 30:1) to give desired products as solid.

4-[(2-Ethylphenyl)diazenyl]-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (11a): Prepared from 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (100 mg, 0.5 mmol) with 2-ethylphenylhydrazine hydrochloride **8d** (103 mg, 0.6 mmol) according to general procedure in 12 h as an orange solid; yield: 139 mg (91%); mp 107–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.77 (1H, s, OH), 7.87 (2H, d, J = 7.8 Hz), 7.72 (1H, d, J = 8.4 Hz), 7.34 (2H, t, J = 7.5 Hz), 7.22 (1H, d, J = 7.2 Hz), 7.17–7.05 (3H, m), 2.70 (2H, q, J = 7.2 Hz), 2.30 (3H, s), 1.27 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 148.4, 138.6, 137.9, 131.3, 129.1, 129.0, 128.9, 128.9, 127.3, 125.8, 125.1, 118.7, 118.7, 114.7, 23.6, 13.7, 11.7; IR (KBr): ν = 1653, 1546, 1484, 1328, 1249, 1152, 749 cm^{-1}; HR-MS (EI): m/z = 306.1478 (M^+). calcd. for $C_{18}H_{18}N_4O$: 306.1481.

4-[(4-Isopropylphenyl)diazenyl]-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (11b): Prepared from 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (100 mg, 0.5 mmol) with 4-isopropylphenylhydrazine hydrochloride **8e** (112 mg, 0.6 mmol) according to general procedure in 12 h as an orange solid; yield: 148 mg (93%); mp 80–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.56 (1H, s, OH), 7.88 (2H, d, J = 7.8 Hz), 7.37–7.28 (4H, m), 7.21–7.10 (3H, m), 2.88-.2.81 (1H, m), 2.29 (3H, s), 1.19 (6H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8, 148.4, 146.9, 139.0, 128.8, 128.8, 127.6, 127.6, 127.0, 125.0, 122.7, 118.5, 118.5, 115.8, 115.8, 33.7, 23.9, 23.8, 11.7; IR (KBr): ν = 1656, 1546, 1495, 1266, 1154, 828 cm^{-1}; HR-MS (EI): m/z = 320.1638 (M^+), calcd. for $C_{19}H_{20}N_4O$: 320.1637.

4-[(4-Methoxyphenyl)diazenyl]-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (11c): Prepared from 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (200 mg, 1.0 mmol) with 4-methoxyphenylhydrazine hydrochloride **8f** (104 mg, 0.6 mmol) according to general procedure in 12 h as an orange red solid; yield: 123 mg (80%); mp 105–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.70 (1H, s, OH), 7.94 (2H, d, J = 8.1 Hz), 7.42–7.35 (4H, m), 7.17 (1H, t, J = 7.5 Hz), 6.93 (2H, d, J = 9.0 Hz), 3.81 (3H, s), 2.34 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0, 148.3, 138.2, 134.7, 128.8, 128.8, 126.1, 125.0, 118.5, 118.5 117.2, 115.2, 114.9, 114.8, 114.3, 55.5, 11.7; IR (KBr) 1545, 1491, 1236, 1153, 1031, 814, 530 cm^{-1}; HR-MS (EI): m/z = 308.1271 (M^+), calcd. for $C_{17}H_{16}N_4O_2$: 308.1273.

4-[(4-Fluorophenyl)diazenyl]-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (11d): Prepared from 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (100 mg, 0.5 mmol) with 4-fluorophenylhydrazine hydrochloride **8g** (97 mg, 0.6 mmol) according to general procedure in 12 h as an orange solid; yield: 140 mg (95%); mp 103–105 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.58 (1H, s, OH), 7.92 (2H, d, J = 8.4 Hz), 7.42–7.35 (4H, m), 7.20–7.06 (3H, m), 2.33 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 148.4, 138.0, 137.4, 128.8, 128.8, 128.8, 128.5, 125.1, 118.5, 118.5, 117.2, 117.1, 116.7, 116.4, 11.7; IR (KBr): ν = 3054, 1653, 1549, 1496, 1214, 1155, 828, 762, 516 cm^{-1}; HR-MS (EI): m/z = 296.1074 (M^+), calcd. for $C_{16}H_{13}FN_4O$: 296.1073.

4-[(4-Chlorophenyl)diazenyl]-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (11e): Prepared from 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (200 mg, 1.0 mmol) with 4-chlorophenylhydrazine hydrochloride **8h** (107 mg, 0.6 mmol) according to general procedure in 12 h as an orange solid; yield: 100 mg (95%); mp 132–134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.52 (1H, s, OH), 7.92 (2H, d, J = 8.1 Hz), 7.42–7.30 (6H, m), 7.18 (1H, t, J = 7.5 Hz), 2.32 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 148.4, 139.7, 137.9, 130.8, 129.7, 129.7, 129.0, 128.8, 128.8, 125.2, 118.4, 118.4, 116.8, 116.8, 11.7; IR (KBr): ν = 3062, 1654, 1553, 1490, 1263, 1089, 767 cm^{-1}; HR-MS (EI): m/z = 312.0776 (M^+), calcd. for $C_{16}H_{13}ClN_4O$: 312.0778.

3-Methyl-4-(naphthalen-1-yldiazenyl)-1-phenyl-1*H*-pyrazol-5-ol (11f): Prepared from 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **10** (100 mg, 1.0 mmol) with 1-naphthalenylhydrazine hydrochloride **8i** (116 mg, 0.6 mmol) according to general procedure in 12 h as an orange red solid; yield: 140 mg (85%); mp 198–200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 14.52 (1H, s, OH), 8.06 (1H, d, J = 8.1 Hz), 7.99–7.86 (4H, m), 7.70 (1H, d, J = 8.1 Hz), 7.65–7.41(5H, m), 7.24–7.18 (1H, m), 2.40 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0, 148.5, 138.0, 136.0, 134.0, 129.9, 128.9, 128.9, 128.8, 127.0, 126.5, 126.0, 125.9, 125.2, 123.1, 119.3, 118.8, 118.8, 111.3, 11.8; IR (KBr): ν = 3060, 1652, 1558, 1497, 1258, 1161, 775 cm^{-1}; HR-MS (EI): m/z = 328.1322 (M^+), calcd. for $C_{20}H_{16}N_4O$: 328.1324.

Crystal Refinement Data for Compound 9m

$C_{20}H_{22}N_4O$, M = 334.42, orthorhombic, space group *Pbca*, a = 7.2201(7) Å, b = 14.7712(13) Å, c = 33.119(3) Å, V = 3532.1(6) Å^3, Z = 8, T = 200 (2) K, $\rho_{calcd.}$ = 1.258 mg m^{-3}, 2θmax = 28.36, refinement of 230 parameters on 4409 independent reflections out of 24596 collected reflections (R_{int} = 0.0887) led to $R1$ = 0.0539 [I > 2σ(I)], $wR2$ = 0.1813 (all data) and S = 0.922 with the largest difference peak and hole of 0.543 and −0.424 e Å^{-3} respectively.

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