Synthesis of Some Novel Heterocyclic Xylidinyl Amines and Carboxamides

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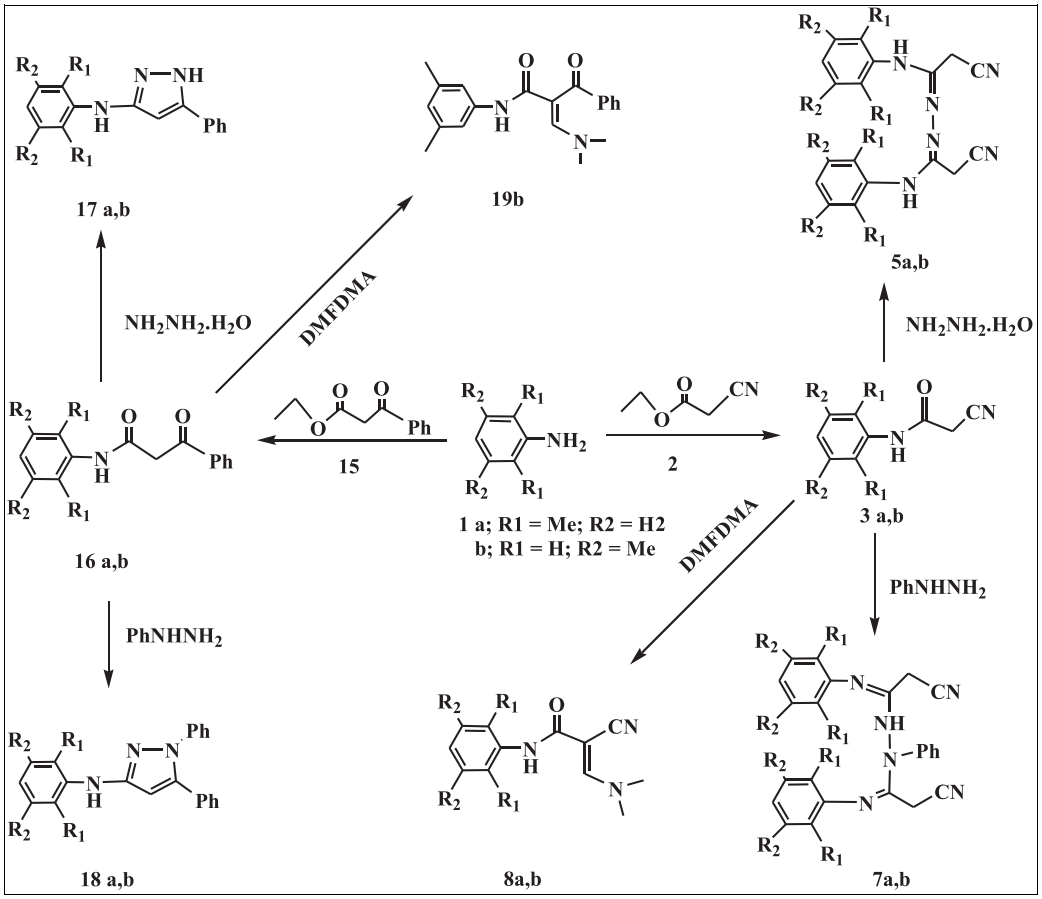


The xylidines **1a**,**b** undergo condensation with ethyl cyanoacetate **2** and ethyl benzoyl acetate **15** to afford the cyano acetanilides **3a**,**b** and the β-diketones **16a**,**b**, respectively. Compounds **3a**,**b** react with hydrazine and phenyl hydrazine to afford the azine-bis derivatives **5a**,**b** and **7a**,**b**, whereas **16a**,**b** react with the same reagents to afford the pyrazolyl amine derivatives **17a**,**b** and **18a**,**b**, respectively. Compounds **3a**,**b** react also with dimethylformamide dimethylacetal to afford the enaminonitriles **8a**,**b**, whereas **16a**,**b** react with the same reagent to afford only the enaminone **19b**. The enaminonitriles **8a**,**b** react with hydrazine and phenyl hydrazine to afford also the azine-bis derivatives **11a**,**b** and **14a**,**b**, respectively.

INTRODUCTION

Pyrazole derivatives have received considerable attention in the last two decades because of their diverse biological activities [1,2]. This class of compounds is reported to show aldose-reductase inhibitory effect [3]. They are also used as antihistaminic, analgesic, anti-inflammatory [4], and cardiotonic agents with vasodilator activity [5]. In addition, these compounds were also reported to possess a good binding affinity toward α_1,α_2-adrenergic and 5-HT_{1A} serotoninergic receptors [6] and to show herbicidal and fungicidal [7,8] activities. In the last two decades, we have been involved in a program aiming at the synthesis of heterocyclic compounds of expected biological activity to be tested as biodegradable agrochemicals [9–12]. In the context of this program and because of the aforementioned stunning biological activities of pyrazole derivatives, we have reported several novel syntheses of some new pyrazole and fused-pyrazole derivatives [12–15]. Recently, some new

substituted heterocyclic derivatives incorporating xylidinyl residue were required for biological activity studies. Because there are enormous varieties of xylidines, we have chosen 2,6- and 3,5-xylidines as starting materials in the present work (Scheme 1). Condensation of these two xylidine derivatives with β-cyano ester and β-keto ester seemed suitable to fulfill this objective.

RESULTS AND DISCUSSION

The xylidines **1a**,**b** condense with ethyl cyanoacetate **2** to afford the *N*-aryl cyanoacetamide derivatives **3a**,**b** (Scheme 1). Compounds **3a**,**b** were reacted with hydrazine hydrate aiming to obtain the pyrazole derivatives **4a**,**b**; however, the mass spectral data of the products of this reaction showed a molecular ion peak at about double of the molecular weight of 3. The IR spectra of these products revealed the presence of cyano absorption and the absence of carbonyl absorption. Structures **5a**,**b** were thus assigned for these products. The ^{1}H NMR spectra were in complete agreement with these structures that revealed the methylene signal at ~3.9 ppm.

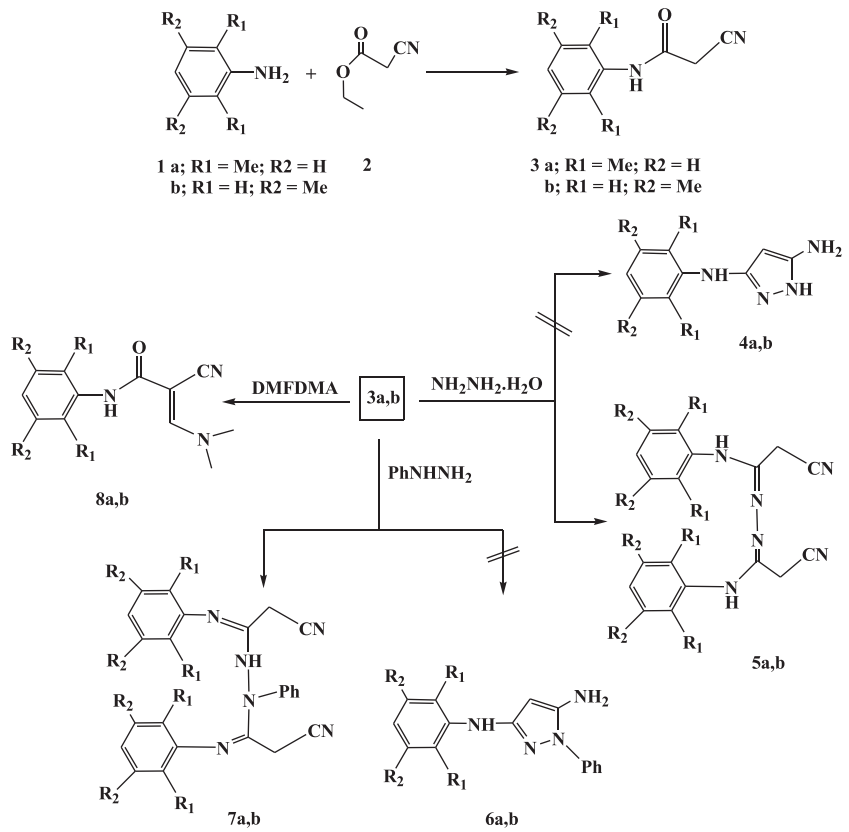
Likewise, the reaction of **3a**,**b** with phenyl hydrazine was expected to afford the pyrazole derivatives **6a**,**b**; however, all spectral and analytical data showed that the reaction followed the same pathway as with hydrazine and structures **7a**,**b** were assigned for these products.

Compounds **3a**,**b** react also with dimethylformamide dimethylacetal (DMFDMA) in refluxing xylene to afford the enaminonitrile derivatives **8a**,**b**, respectively. The ^{1}H NMR spectra of both products showed the disappearance of the methylene protons and the appearance of two extra methyl groups at lower field than those of original xylidine and a CH signal at ~7.8 ppm. The ^{13}C NMR of **8b** showed 10 signals, which is completely consistent with these structures (*cf*. Experimental).

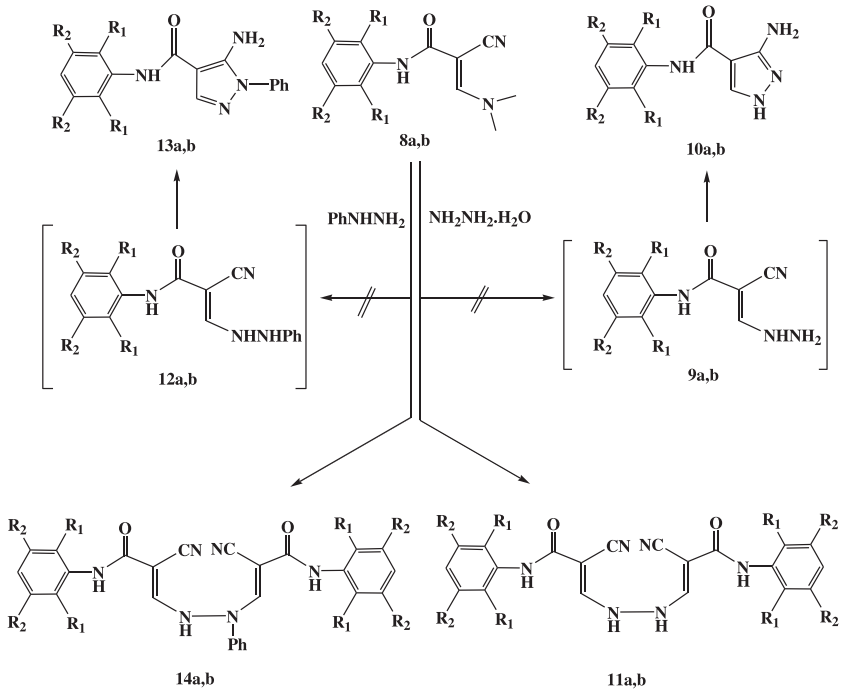
Reacting the enaminonitriles **8a**,**b** with hydrazine hydrate was expected to afford the pyrazole derivatives **10a**,**b** presumably via the intermediates **9a**,**b**; however, the IR spectra of the products revealed the presence of cyano absorption bands at (2258 and 2187 cm^{-1}) and carbonyl absorption bands at (1662 and 1671 cm^{-1}), respectively. The mass spectra showed $m/z = 428$ for both products. Thus, structures **11a**,**b** were assigned for these reaction products (*cf*. Scheme 2 and Experimental).

Similarly, the reaction of **8a**,**b** with phenyl hydrazine was expected to afford the pyrazole derivatives **13a**,**b** via the intermediates **12a**,**b**; however, all analytical and spectral data suggested structures **14a**,**b** to be assigned to these products.

Scheme 1. Synthesis of compounds 3, 5, 7 and 8.



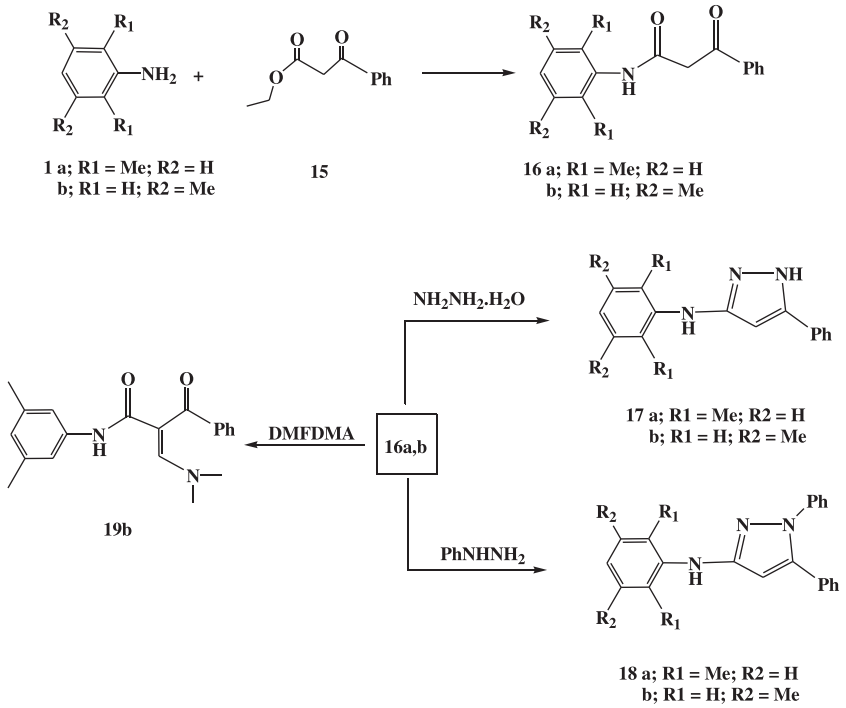
Scheme 2. Synthesis of compounds 11 and 14.



The xylidines **1a**,**b** were also condensed with ethyl benzoylacetate **15** to afford the 3-oxo-propionamide derivatives **16a**,**b**, respectively. Analytical and spectral data are in complete agreement with these structures (*cf*. Scheme 3 and Experimental).

Contrary to the behavior of **3a**,**b** towards hydrazine and phenyl hydrazine, compounds **16a**,**b** react with both reagents to afford the pyrazole derivatives **17a**,**b** and **18a**,**b**, respectively, as deduced from their analyses and spectra.

Scheme 3. Synthesis of compounds 16-19.



Compounds **16a**,**b** were also reacted with DMFDMA in refluxing xylene aiming to obtain the enaminones **19a**,**b**; however, only **19b** was obtained from **16b** as yellow crystalline solid mp 286–287°C, whereas **19a** could not be obtained even after reflux for 10 h. This may be attributed to steric factors due to the presence of the two methyl groups in the 2 and 6 positions. The IR showed two carbonyl absorptions at $\upsilon_{max} = 1718$ and 1681 cm^{-1} beside the NH absorption. The mass spectrum showed $m/z = 322$ [M^+]. The ^1H NMR revealed signals at $\delta = 2.29$ (s, 6H, $2CH_3$), 2.32 (s, 6H, $N(CH_3)_2$), 6.96–7.88 (m, 9H, Ar-H + CH), 8.18 (s, 1H, NH).

EXPERIMENTAL

Melting points were measured on a digital Electrothermal 9100 apparatus (Kleinfeld, Gehrden, Germany) and are uncorrected. FTIR spectra (KBr) were obtained on a Nicolet 205 spectrophotometer (Nicolet, Madison, WI, USA). The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer (Varian inc., Palo Alto, CA, USA) and ^{13}C NMR spectra were run at 75.46 MHz in DMSO-d_6 or $CDCl_3$ using TMS as reference. Chemical shifts are expressed in δ values. The mass spectra were recorded on a Shimadzu GCMS-QP-1000EX mass spectrometer (Shimadzu, Kyoto, Japan) at 70 ev. Elemental analysis were carried out at the Micro-analytical Center of Cairo University.

Synthesis of the acetamide derivatives 3a,**b**. A mixture of 2,6-dimethylaniline **1a**/3,5-dimethylaniline **1b** (10 mmol) and ethyl cyanoacetate **2** (10 mmol) in DMF (20 mL) was refluxed for 5 h and then left to cool to room temperature. The reaction mixture was then poured onto ice-cold water and the precipitated solid was filtered off and recrystallized from ethanol to afford compounds **3a** and **3b**, respectively.

2-Cyano-N-(2,6-dimethyl-phenyl)-acetamide 3a. White crystalline solid, yield 1.08 g (57.5%), mp 207–208°C. IR: $\upsilon_{max} = 3146$ (NH), 2258 (CN), and 1658 (CO) cm^{-1}. MS: $m/z = 187$ [$M^+ - 1$]; $\delta_H = 2.13$ (s, 6H, $2CH_3$), 3.91 (s, 2H, CH_2), 7.06–7.09 (m, 3H, Ar. H), 9.65 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{11}H_{12}N_2O$ (188.23): C 70.19; H 6.43; N 14.88. Found: C 70.15; H 6.40; N 14.98.

2-Cyano-N-(3,5-dimethyl-phenyl)-acetamide 3b. White crystalline solid, yield 1.1 g (58.5%), mp 190–192°C. IR: $\upsilon_{max} = 3154$ (NH), 2254 (CN), and 1683 (CO) cm^{-1}. MS: $m/z = 188$ [M^+]; $\delta_H = 2.23$ (s, 6H, $2CH_3$), 3.86 (s, 2H, CH_2), 6.73 (s, 1H, Ar-H), 7.15 (s, 2H, Ar-H), 10.15 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{11}H_{12}N_2O$ (188.23): C 70.19; H 6.43; N 14.88. Found: C 70.22; H 6.50; N 14.85.

Reaction of 3a,b with hydrazine hydrate and phenyl hydrazine. To a solution of compounds **3a** or **3b** (10 mmol) in 15 mL pyridine was added hydrazine hydrate or phenyl hydrazine (10 mmol) and the reaction mixture was refluxed for 2 h with stirring and then left to cool to room temperature. The reaction mixture was then poured onto ice cold water followed by few drops of conc. HCl. The precipitated solid that appeared was filtered off and recrystallized from ethanol to afford compounds **5a** or **5b** and **7a** or **7b**, respectively.

3,4-Diaza-2,5-bis[(2,6-dimethylphenyl)amino]hexa-2,4-diene-1,6-dicarbonitrile 5a. Faint rose crystalline solid, yield 2.00 g (53.8%), mp 211–212°C. IR: $\upsilon_{max} = 1\,3253$ (br. NH), 2258 (CN) cm^{-1}. MS: $m/z = 372$ [M^+]; $\delta_H = 2.16$ (s, 12H, $4CH_3$), 3.91 (s, 4H, $2CH_2$), 7.08–7.10 (m, 6H, Ar-H), 9.63 (s, 2H D_2O exch., 2NH). $\delta_C = 21.4$, 24.64, 114.59, 119.35, 124.28, 127.24, 146.03, 163.19. *Anal*. Calcd for $C_{22}H_{24}N_6$ (372.47): C 70.94; H 6.49; N 22.56. Found: C 70.95; H 6.45; N 22.60.

3,4-Diaza-2,5-bis[(3,5-dimethylphenyl)-amino]hexa-2,4-diene-1,6-dicarbonitrile 5b. White crystalline solid, yield 2.0 g (55%), mp 185–186°C. IR: $\upsilon_{max} = 3255$ (NH), 2254 (CN) cm^{-1}. MS: $m/z = 371$ [$M^+ - 1$]; $\delta_H = 2.32$ (s, 12H, $4CH_3$), 3.53 (s, 4H, $2CH_2$), 6.84 (s, 2H, Ar-H), 7.13 (s, 4H, Ar-H), 7.63 (s, 2H D_2O exch., 2NH). *Anal*. Calcd for $C_{22}H_{24}N_6$ (372.47): C 70.94; H 6.49; N 22.56. Found: C 71.00; H 6.55; N 22.50.

4,5-Diaza-4-phenyl-3,6-bis[(2,6-dimethylphenyl)imino]octane-1,8-dicarbonitrile 7a. Brown crystalline solid, yield 2.9 g (64.7%), mp 208–209°C. IR: $\upsilon_{max} = 3137$ (NH), 2258 (CN) cm^{-1}. MS: $m/z = 448$ [M^+]; $\delta_H = 2.29$ (s, 12H, $4CH_3$), 3.54 (s, 4H, $2CH_2$), 6.84–7.13 (m, 11H, Ar-H), 7.74 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{28}H_{28}N_6$ (448.56): C 74.97; H 6.29; N 18.74. Found: C 75.07; H 6.38; N 18.95.

4,5-Diaza-4-phenyl-3,6-bis[(3,5-dimethylphenyl)imino]octane-1,8-dicarbonitrile 7b. Yellow crystalline solid, yield 3.0 g (66.9%), mp 180–181°C. IR: $\upsilon_{max} = 3171$ (NH), 2255 (CN) cm^{-1}. MS: $m/z = 448$ [M^+]; $\delta_H = 2.26$ (s, 12H, $4CH_3$), 3.58 (s, 4H, $2CH_2$), 7.09–7.19 (m, 11H, Ar-H), 7.43 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{28}H_{28}N_6$ (448.56): C 74.97; H 6.29; N 18.74. Found: C 75.12; H 6.40; N 18.85.

Reaction of 3a,b with dimethylformamide dimethylacetal. A mixture of **3a** or **3b** (10 mmol) and DMFDMA (10 mmol) in 20 mL dry xylene was refluxed for 7 h and then left to cool to room temperature over night. The precipitated solid was filtered off and recrystallized from ethanol to afford compounds **8a** or **8b**.

2-Cyano-3-dimethylamino-N-(2,6-dimethyl-phenyl)-acrylamide 8a. White crystalline solid, yield 1.6 g (65.8%), mp 151–152°C. IR: $\upsilon_{max} = 3246$ (NH), 2180 (CN), 1666 (CO) cm^{-1}. MS: $m/z = 243$ [M^+]; $\delta_H = 2.12$ (s, 6H, $2CH_3$), 3.18 (s, 3H, CH_3), 3.28 (s, 3H, CH_3), 7.05 (m, 3H, Ar-H), 7.79 (s, 1H, CH), 8.53 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{14}H_{17}N_3O$ (243.30): C 69.11; H 7.04; N 17.27. Found: C 69.15; H 7.14; N 17.20.

2-Cyano-3-dimethylamino-N-(3,5-dimethyl-phenyl)-acrylamide 8b. Yellow crystalline solid, yield 1.75 g (72%), mp 198–199°C. IR: $\upsilon_{max} = 3247$ (NH), 2186 (CN), 1665 (CO) cm^{-1}. MS: $m/z = 243$ [M^+]; $\delta_H = 2.22$ (s, 6H, $2CH_3$), 3.19 (S, 3H, CH_3), 3.26 (s, 3H, CH_3), 6.65 (s, 1H, Ar-H), 7.22 (s, 2H, Ar-H), 7.80 (s, 1H, CH), 8.83 (s, 1H D_2O exch., NH). $\delta_C = 21.02$, 46.84, 70.97, 117.89, 119.21, 124.38, 137.20, 139.03, 156.19, 163.48. *Anal*. Calcd for $C_{14}H_{17}N_3O$ (243.30): C 69.11; H 7.04; N 17.27. Found: C 69.20; H 7.18; N 17.05.

Reaction of 8a,b with hydrazine hydrate and phenyl hydrazine: synthesis of 11a,b and 14a,b. A mixture of compound **8a** or **8b** (10 mmol) and hydrazine hydrate or phenyl hydrazine (10 mmol) in pyridine (15 mL) was refluxed for 4 h with stirring and then left to cool to room temperature. The reaction mixture was then poured onto ice cold water (few drops of HCl were added if no precipitate appeared), and the precipitated solid was then filtered off and recrystallized from ethanol to afford compounds **11a/11b** and **14a/14b**, respectively.

2-Cyano-3-{N′-[2-cyano-2-(2,6-dimethyl-phenylcarbamoyl)-vinyl]-hydrazino}-N-(2,6-dimethyl-phenyl)-acrylamide 11a. White crystalline solid, yield 2.70 g (63%), mp 193–194°C. IR: $\upsilon_{max} = 3254$ (NH), 2258 (CN), 1662 (CO) cm^{-1}. MS: $m/z = 428$ [M^+]; $\delta_H = 2.26$ (s, 12H, $4CH_3$), 3.58 (s, 2H D_2O exch., 2NH), 7.09–7.27 (m, 8H, Ar-H + 2 = CH), 7.40 (s, 2H D_2O exch., 2NH). *Anal*. Calcd for

$C_{24}H_{24}N_6O_2$ (428.49): C 67.27; H 5.65; N 19.61. Found: C 67.27; H 5.65; N 19.61.

2-Cyano-3-{N′-[2-cyano-2-(3,5-dimethyl-phenylcarbamoyl)-vinyl]-hydrazino}-N-(3,5-dimethyl-phenyl)-acrylamide 11b. Yellow crystalline solid, yield 2.78 g (65%), mp 191–192°C. IR: υ_{max} = 3246 (NH), 2187 (CN), 1671 (CO) cm^{-1}. MS: *m/z* = 428 [M^+]; δ_H = 2.30 (s, 12H, $4CH_3$), 3.52 (s, 2H D_2O exch., 2NH), 6.83 (s, 2H, Ar-H), 7.15 (s, 4H, Ar-H), 7.55 (s, 2H, 2 CH), 7.87 (s, 2H D_2O exch., 2NH). *Anal*. Calcd for $C_{24}H_{24}N_6O_2$ (428.49): C 67.27; H 5.65; N 19.61. Found: C 67.27; H 5.65; N 19.61.

2-Cyano-3-{N′-[2-cyano-2-(2,6-dimethyl-phenylcarbamoyl)-vinyl]-N′-phenyl-hydrazino}-N-(2,6-dimethyl-phenyl)-acrylamide 14a. Yellow crystalline solid, yield 2.50 g (50%), mp 174–175°C. IR: υ_{max} = 3226 (NH), 2184 (CN), 1650 (CO) cm^{-1}. MS: *m/z* = 504 [M^+]; δ_H = 2.34 (s, 12H, $4CH_3$), 3.25 (s, 1H D_2O exch., NH), 3.36 (s, 1H D_2O exch., NH), 6.65–7.92 (m, 13H, Ar-H + 2CH), 8.26 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{30}H_{28}N_6O_2$ (504.58): C 71.41; H 5.59; N 16.66. Found: C 71.55; H 5.50; N 16.60.

2-Cyano-3-{N′-[2-cyano-2-(3,5-dimethyl-phenylcarbamoyl)-vinyl]-N′-phenyl-hydrazino}-N-(3,5-dimethyl-phenyl)-acrylamide 14b. Yellow crystalline solid, yield 2.77 g (55%), mp 150–151°C. IR: υ_{max} = 3247 (NH), 2187 (CN), 1665 and 1645 (CO) cm^{-1}. MS: *m/z* = 504 [M^+]; δ_H = 2.33 (s, 12H, $4CH_3$), 3.23 (s, 1H D_2O exch., NH), 3.38 (s, 1H D_2O exch., NH), 6.75–7.87 (m, 13H, Ar-H + 2CH), 8.14 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{30}H_{28}N_6O_2$ (504.58): C 71.41; H 5.59; N 16.66. Found: C 71.62; H 5.55; N 16.50.

Condensation of the xylidines 1a,b with ethyl benzoylacetate 15. A mixture of 2,6-dimethylaniline **1a** or 3,5-dimethylaniline **1b** (10 mmol) and ethyl benzoylacetate **15** (10 mmol) in DMF (20 mL) was refluxed for 5 h and then left to cool to room temperature. The reaction mixture was then poured onto ice-cold water, and the precipitated solid was filtered off and recrystallized from ethanol to afford **16a**,**b**.

N-(2,6-Dimethylphenyl)-3-oxo-3-phenyl-propionamide 16a. Yellow crystalline solid, yield 1.85 g (59.1%); mp 145–146°C. IR: υ_{max} = 3239 (NH), 1693, 1631 (2CO) cm^{-1}. MS: *m/z* = 267 [M^+]; δ_H = 2.15 (s, 6H, $2CH_3$), 4.16 (s, 2H, CH_2), 7.05–8.06 (m, 8H, Ar. H), 9.55 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{17}H_{17}NO_2$ (267.32): C 76.38; H 6.41; N 5.24. Found: C 76.35; H 6.50; N 5.16.

N-(3,5-Dimethylphenyl)-3-oxo-3-phenyl-propionamide 16b. White crystalline solid; yield 1.6 g (51.1%), mp 95–96°C. IR: υ_{max} = 3230 (NH), 1693, 1656 (2CO) cm^{-1}. MS: *m/z* = 267 [M^+]; δ_H = 2.22 (s, 6H, $2CH_3$), 4.12 (s, 2H, CH_2), 6.70 (s, 1H, Ar-H), 7.20–8.02 (m, 7H, Ar. H), 10.08 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{17}H_{17}NO_2$ (267.32): C 76.38; H 6.41; N 5.24. Found: C 76.42; H 6.55; N 5.20.

Reaction of 16a,b with hydrazine hydrate and phenyl hydrazine. A mixture of compound **16a** or **16b** (10 mmol) and hydrazine hydrate or phenyl hydrazine (10 mmol) in pyridine (15 mL) was refluxed for 4 h with stirring and then left to cool to room temperature. The reaction mixture was then poured onto ice cold water (few drops of HCl were added if no precipitate appeared), and the precipitated solid was then filtered off and recrystallized from ethanol to afford compounds **17a**,**b** and **18a**,**b**.

(2,6-Dimethylphenyl)-(5-phenyl-1H-pyrazol-3-yl)-amine 17a. Yellowish crystalline solid, yield 1.8 g (68%), mp 225–226°C. IR: υ_{max} = 3258 (NH) cm^{-1}. MS: *m/z* = 263 [M^+]; δ_H = 2.2 (s, 6H, $2CH_3$), 4.34 (s, 1H, NH), 6.66–7.51 (m, 9H, Ar. H + ring CH), 8.2 (s, 1H D_2O exch., NH). *Anal*. Calcd for $C_{17}H_{17}N_3$ (263.34): C 77.54; H 6.51; N 15.96. Found: C 77.45; H 6.55; N 16.16.

(3,5-Dimethylphenyl)-(5-phenyl-1H-pyrazol-3-yl)-amine 17b. Yellowish crystalline solid, yield 2.0 g (76%), mp 243–245°C. IR: υ_{max} = 3120 (NH) cm^{-1}. MS: *m/z* = 263 [M^+]; δ_H = 2.24 (s, 6H, $2CH_3$), 3.2 (s, 1H, NH), 6.37–7.38 (m, 9H, Ar. H + ring CH), 8.64 (br. s, 1H D_2O exch., NH). *Anal.* Calcd for $C_{17}H_{17}N_3$ (263.34): C 77.54; H 6.51; N 15.96. Found: C 77.59; H 6.65; N 15.84.

(2,6-Dimethylphenyl)-(1,5-diphenyl-1H-pyrazol-3-yl)-amine 18a. Brown crystalline solid, yield 2.17 g (64%), mp 165–166°C. IR: υ_{max} = 3235 (NH) cm^{-1}. MS: *m/z* = 339 [M^+]; δ_H = 2.16 (s, 6H, $2CH_3$), 4.04 (s, 1H D_2O exch., NH), 6.79–8.04 (m, 14H, Ar. H + ring CH). *Anal*. Calcd for $C_{23}H_{21}N_3$ (339.43): C 81.38; H 6.24; N 12.38. Found: C 81.45; H 6.30; N 12.30.

(3,5-Dimethylphenyl)-(1,5-diphenyl-1H-pyrazol-3-yl)-amine 18b. Brown crystalline solid, yield 2.27 g (67%), mp 270–272°C. IR: υ_{max} = 3228 (NH) cm^{-1}. MS: *m/z* = 339 [M^+]; δ_H = 2.18 (s, 6H, $2CH_3$), 4.24 (s, 1H D_2O exch., NH), 6.65–8.14 (m, 14H, Ar. H + ring CH). *Anal*. Calcd for $C_{23}H_{21}N_3$ (339.43): C 81.38; H 6.24; N 12.38. Found: C 81.55; H 6.34; N 12.25.

Reaction of 16a,b with DMFDMA. A mixture of **16a** or **16b** (10 mmol) and DMFDMA (10 mmol) in 20 mL of dry xylene was refluxed for 7 h and then left to cool to room temperature over night. The precipitated solid was filtered off and recrystallized from ethanol. Compound **16a** was recovered unreacted, whereas compound **19b** was obtained.

2-Benzoyl-3-dimethylamino-N-(3,5-dimethylphenyl)-acrylamide 19b. Yellow crystalline solid, yield 2.1 g (65%), mp 286–287°C. IR: υ_{max} = 3230 (NH), 1718 and 1681 (2CO) cm^{-1}. MS: *m/z* = 322 [M^+]; δ_H = 2.29 (s, 6H, $2CH_3$), 2.32 (s, 6H, $N(CH_3)_2$), 6.96–7.88 (m, 9H, Ar-H + CH), 8.18 (s, 1H D_2O exch., NH). δ_C = 21.25, 45.8, 108.65, 118.6, 125.85, 128.9, 129.4, 136.85, 138.2, 138.6, 142.73, 158.5, 161.8, 185.2. *Anal.* Calcd for $C_{20}H_{22}N_2O_2$ (322.40): C 74.51; H 6.88; N 8.69. Found: C 74.55; H 6.85; N 8.55.

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