Synthesis, Characterization, and Reactions of Selected Multichalcone Derivatives

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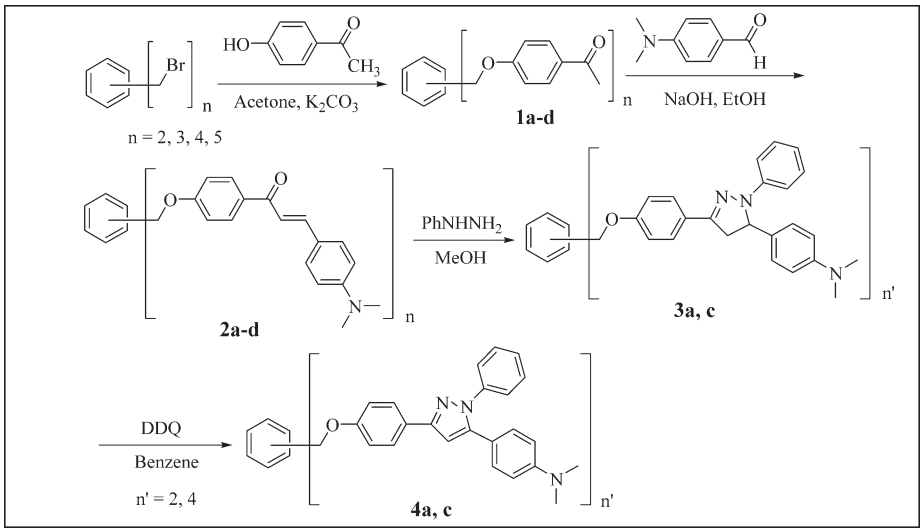

New multiarm aromatic chalcone derivatives **2a-d** were prepared through cross-aldol condensation reaction between multiarm aromatic ketones **1a-d** and 4-(dimethyl amino)benzaldehyde in basic medium. The multiarm aromatic chalcones **2a** and **2c** were able to undergo cyclization reactions when treated with hydrazine or any of it's derivatives to yield the corresponding pyrazolines **3a** and **3c** that were reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquenone in benzene to yield the aromatic pyrazoles **4a** and **4c**, respectively.

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INTRODUCTION

Heterocyclic chemistry is one of the most interesting and rapidly growing areas of chemical research. Heterocyclic components are found in many natural molecules, such as enzymes, vitamins, hormones, antibiotics and alkaloids, as well as pharmaceuticals, herbicides and dyes [1].

Chemically, chalcones consist of open-chain flavonoids in which the two aromatic rings are joined by a three carbon α,β-unsaturated carbonyl system. Chalcones can undergo many reactions to produce desirable products with desirable applications. They are precursors of flavonoids and isoflavonoids which are abundant in plants [2,3]. Chalcone derivatives have shown good physicochemical and biological activity, including antibacterial, antifungal, and anti-inflammatory [4]. Oxygenated chalcones serve as potential antimalarial agents [5], as antiplasmodial [6], as antiprotozoal, anti-HIV and antimicrobial and they also have an inhibitory effect on the proliferation of human leukemia cells [7]. Chalcones are also a class of anticancer agents, displaying promising therapeutic efficacy for the treatment of human cancers. For example, a chalcone derivative isolated from Chinese licorice root, has been associated with a wide variety of anticancer activity such as Licochalcone-A [8]. Chalcones have also found potential applications as artificial sweeteners, drugs, and agrochemicals [9]. The importance of this class of compounds is not only due to their biological activities but also due to their colors; they give yellow to orange colors in flowers. So, they are attractive to insects in such a way that they contribute to the flower's pollination [10]. Also they are part of some biological macromolecules and microenvironment in micelles [11]. Polymers that have pendent chalcone group become more photoconductive and photosensitive. Such polymers act as negative photo resist material [12]. Recently, the inhibitive action of chalcone derivatives on the corrosion of steel in hydrochloric acid and sulfuric acid solution was studied by Benkaddour and

coworkers [13]. In addition, chalcones were widely used for various optical applications including second harmonic generation materials in nonlinear optics [14], liquid crystal display [15], photorefractive polymers, holographic recording materials, and fluorescent probes for sensing of metal ions. As a result, the photophysical properties of chalcones containing alkylamino groups as electron donors have been studied by numerous researchers [16,17].

Various heterocyclic systems can be obtained using chalcone as starting material. These derivatives have different applications. For example, pyrimidine is used as analgesic, antitumor, antifungal and antibacterial agent. Pyrazoles are used as ultraviolet stabilizer, anticancer, muscle relaxant, anti-inflammatory, antipyretic, antiarrhythmic, tranquilizing, anticonvulsant, hypotensive, monoamino oxidase inhibitor, antidiabetic and antibacterial agent [18–23]. Pyrazolines are used to produce photoconductive polymers [24], also used as scintillation solutes [25], as cytotoxic agent [26], they have also broad biological activities; such as psychoanaleptic, anticonvulsant, and antidepressant [27]. Thiazol derivatives have been reported to possess tuberculostatic, antibacterial, and antifungal activities [28].

Therefore, due to the wide application of chalcones and their heterocyclic derivatives, we have synthesized new compounds containing the benzene ring as a nucleus that is substituted with two, three, four or five-arm chalcone moieties. These multiarm chalcones were used for the synthesis of the corresponding heterocyclic compounds containing more than one pyrazoline or pyrazole rings.

RESULTS AND DISCUSSION

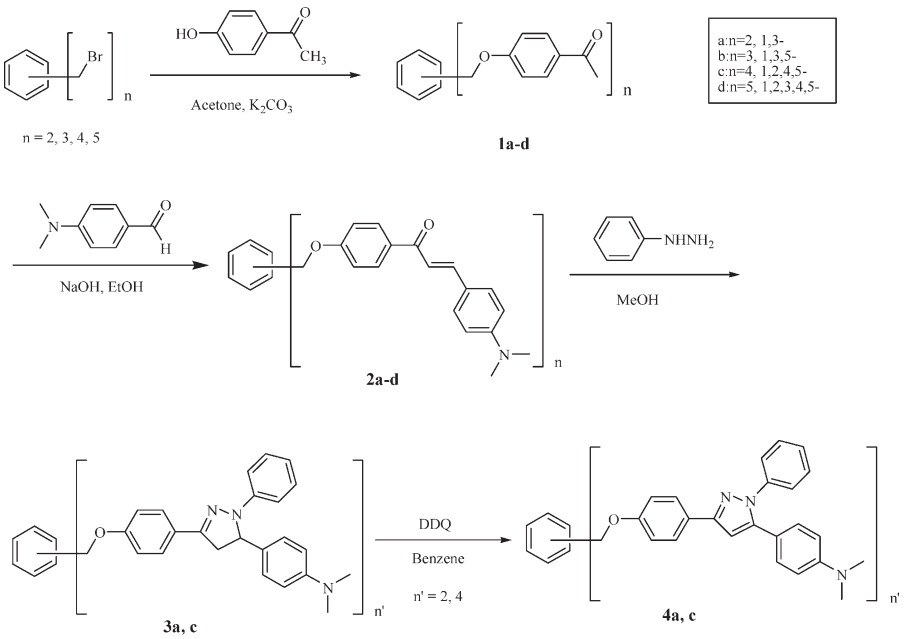
New heterocyclic five-membered ring compounds containing two, four pyrazolines **3a, c** and pyrazoles **4a, c** rings respectively were synthesized and characterized. The synthesis of the compounds **3a, c** and **4a, c** was carried out in a multistep procedure starting from cross-aldol condensation reaction between multiarm aromatic ketones **1a-d** and 4-(dimethylamino)benzaldehyde in basic medium to form the corresponding multiarm aromatic chalcones **2a-d**. We have already described the synthesis of the multiarm aromatic ketones **1b** and **1c** in previous work [29]. The ketones **1a** and **1d** are prepared by a similar procedure through nucleophilic substitution reaction between the corresponding 1,3-bis(bromomethyl)benzene and 1,2,3,4,5-pentakis(bromomethyl)-benzene with 4-hydroxyacetophenone respectively in the presence of potassium carbonate in refluxing dry acetone. The IR spectra of the chalcones **2a-d** showed characteristic bands in the range 1661–1679 for the carbonyl group, 1227–1261 cm^{-1} for the ether linkage and 1595–1599 cm^{-1} for the conjugated double bond. The ^1H NMR spectra of the chalcones **2a-d** showed characteristic singlet peak in the range 4.65–5.28 ppm for methylene protons (—CH_2O—), another singlet peak at 3.02–3.04 ppm for methyl protons on the nitrogen atom [—$N(CH_3)_2$] and appearance of new peaks at 7.47–7.66 ppm and 7.73–7.96 ppm for the protons of the conjugated double bond (—CH=CH—). The coupling constant value ($^3J_{-CH=CH-} = 16$ Hz) of the protons substituted on the double bond, showed that they are in the *trans* orientation relative to each other and thus the multiarm aromatic chalcones have *E*-configuration. The ^{13}C NMR spectra of the chalcones **2a-d** exhibit characteristic peaks at 66.7–69.9 ppm for the methylene carbon (—CH_2O—), at 40.0–40.2 ppm for the methyl carbons on the nitrogen atom [—$N(CH_3)_2$] and appearance of new peaks at 121.0–124.2 ppm and 143.0–145.2 ppm for the carbons of the double bond (—CH=CH—). The cyclization reaction of the chalcones **2a, c** was carried by treatment with phenylhydrazine in methanol at 0°C to yield the corresponding pyrazolines **3a, c** (**3a**: 63%, **3c**: 55%), which are nonaromatic. Aromatization of the pyrazolines **3a, c** was carried out through reacting them with 2,3-dichloro-5,6-dicyano-1,4-benzoquenone (DDQ) in boiling benzene to yield the aromatic pyrazoles **4a**, **c** in 75 and 43% yields, respectively.

The IR spectra of the pyrazolines **3a, c** and pyrazoles **4a, c** exhibited absorption bands at 1599–1601 cm^{-1} for the (C=N) bond, at 1340–1382 cm^{-1} for the (C—N) bond in pyrazoline and at 1669–1672 cm^{-1} for the (C=C) double bond in pyrazole. The ^1H NMR spectra of the pyrazolines **3a, c** showed characteristic doublet of doublet peaks in the range 4.12–5.04 ppm for the protons (—CH—N—) and two doublet of doublets at 3.07–3.76 ppm for the protons of the methylene group (—CH_2—) of the pyrazoline. However, a singlet peak at 6.68–7.09 ppm for the pyrazole aromatic proton was observed. The ^{13}C NMR spectra of the pyrazolines **3a, c** showed characteristic signals at 40–42 ppm for the carbon of the (—CH_2—) and another signal at 52–53 ppm for the carbon of the (—CH—N—) of the pyrazoline. In case of the pyrazole, the characteristic signals were observed at 105–106 ppm for the (—CH=C—N—) carbon bearing a proton and at 142–145 ppm for the (—C—N—) carbon of the pyrazole ring.

Since compounds **3a, c** and **4a, c** are solid, it was found that the melting point of the compound increases by increasing the number of the carbon atoms present. Also, it was found that the melting point of the pyrazoline derivatives is higher than that for the corresponding aromatic pyrazole derivatives.

The cytotoxicity and the biological activity of the chalcones **2a-d**, their pyrazoline and pyrazole

Scheme 1



derivatives will be studied in the near future (Scheme 1, Table 1).

EXPERIMENTAL

The melting points (mp) of all compounds were determined on an electrothermal digital melting point apparatus. Infrared (IR) spectra of the prepared compounds were recorded using a NICOLET 410 FTIR spectrometer (ν in cm^{-1}). The IR spectra of pure substances were measured as KBr-pellets. The ^1H and ^{13}C NMR spectra were recorded on Bruker AM400 and AC200 ultra shield spectrometers in deuterochloroform or dimethyl sulfoxide-d_6 with tetramethylsilane as an internal standard. The spectral data were reported in delta (δ) units relative to the tetramethylsilane reference line. Mass spectra were acquired using a MAT95 instrument of the Finnigan Company (FD: 5 kV Ionizing energy, field desorption) instruments. The signals were given as *m*/*z* with the relative intensity between brackets. Elemental analyses were performed in the analytical laboratory of the Institute of Organic Chemistry of the University of Mainz, Mainz, Germany. Analytical thin layer chromatography (TLC) was carried out using TLC-silica plates 60F254 (0.2 mm) of the Merck Company. The detection was followed by UV-lamp or through coloring with iodine. Chromatographic separation was carried out using Merck silica gel (60–230 mesh). The ratios of the solvents and mixed mobile phase were given in volume ratio.

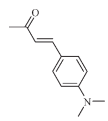
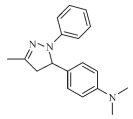
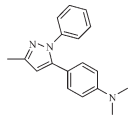
M-xylene, mesitylene, tetra- and penta-methylbenzene were obtained from Aldrich. 4-Hydroxyacetophenone, *N*-bromosuccinimide, 4-(dimethyl amino)benzaldhyde, 2,3-dichloro-5,6-dicyano-1,4-benzo-quenone were obtained from ACROS. These chemicals were used without further purification.

General Procedure for the Preparation of Ketones (1a-d). Ketones **1b**, **c** were prepared from the corresponding bromomethylbenzene derivatives which were prepared from the corresponding methylbenzene derivatives and characterized as described in ref. 29. Whereas the new ketones **1a** and **1d** were prepared following the same procedure but using a mixture of 4-hydroxyacetophenone (1.36 g, 10.0 mmol) and (1.19 g, 4.5 mmol) of 1,3-bis(bromomethyl)benzene or (0.74 g, 1.4 mmol) of 1,2,3,4,5-pentakis(bromomethyl)benzene, respectively, potassium carbonate (1.38 g, 10.0 mmol) and the same equivalent amount of potassium iodide as the bromo compound in dry acetone (100 mL) were refluxed for 48–72 h. The reaction was followed up by TLC (20% chloroform:40% hexane:40% ethyl acetate) until completion. After cooling, the reaction mixture was diluted with water (50 mL) and extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over magnesium sulphate. The solvent was evaporated under vacuum and the residual solid was washed with diethyl ether. When necessary, a recrystalization from acetone or chloroform was performed.

1,1′-[1,3-Benzenediylbis(methyleneoxy-4,1-phenylene)]bisethanone (1a). This compound was obtained as colorless crystals (1.43 g, 85%)(acetone), mp 139–141°C; IR (potassium bromide): 2936, 1674, 1597, 1242, 1505, 831 cm^{-1}; ^1H NMR (deuteriochloroform): δ 2.55 (s, 6H, CH_3), 5.15 (s, 4H, 2xOCH_2), 6.98 (d, J = 7.4 Hz, 4H, Ph-H), 7.40 (m, 3H, central-Ph-H), 7.49 (s, 1H, central-Ph-H), 7.91 (d, J = 7.4 Hz, 4H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 26.31 (2C, CH_3), 69.87 (2C, 2 × OCH_2), 114.53 (4C, Ph-C), 126.39 (2C, Ph-C), 127.24 (2C, central-Ph-C), 129.10 (2C, central-Ph-C), 130.13 (1C, central-Ph-C), 130.63 (4C, Ph-C), 136.83 (1C, central-Ph-C), 162.48 (2C, Ph-C), 196.78 (2C, 2 × C=O); ms: (5 kV, fd) *m*/*z* (%) 374 (100). *Anal*. Calcd. for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.78; H, 5.81.

Table 1

Chemical percentage yield of the compounds (**1a**, **1d**, **2a-d**, **3a**, **3c** and **4a**, **4c**).

R	Cpd*	Yield (%)	Cpd*	Yield (%)	Cpd*	Yield (%)	Cpd*	Yield (%)
	**1a**	85					**1d**	87
	**2a**	85	**2b**	30	**2c**	75	**2d**	20
	**3a**	63			**3c**	55		
	**4a**	75			**4c**	43		

a:n = 2, 1,3-.
b:n = 3, 1,3,5-.
c:n = 4, 1,2,4,5-.
d:n = 5, 1,2,3,4,5-.
[Cpd*] is compound.

1,1′,1″,1‴,1⁗,1⁗′-[1,2,3,4,5-Benzenepentaylpentakis(methyleneoxy-4,1-phenylene)]pentakisethanone (1d). This compound was obtained as pale yellow powder (1.13 g, 87%), mp 234–235°C; IR (potassium bromide): 2932, 1674, 1598, 1575, 1505, 1241, 1171, 831 cm^{-1}. ^1H NMR (deuteriochloroform): δ 2.50 (s, 15H, CH_3), 5.10 (s, 10H, 5 × OCH_2), 6.99 (d, J = 7.4 Hz, 10H, Ph-H), 7.46 (s, 1H, central-Ph-H), 7.93 (d, J = 7.4 Hz, 10H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 26.35 (5C, CH_3), 63.57 (5C, 5 × OCH_2), 114.41 (10C, Ph-C), 126.39 (5C, Ph-C), 130.61 (10C, Ph-C), 130.50–131.18 (5C, central-Ph-C), 137.64 (1C, central-Ph-C), 161.83 (5C, Ph-C), 196.54 (5C, 5 × C=O); ms: (5 kV, fd) *m/z* (%) 818 (100). *Anal*. Calcd. for $C_{51}H_{46}O_{10}$: C, 74.80; H, 5.66. Found: C, 74.79; H, 5.56.

General procedure for the preparation of multi arm Chalcones (2a-d). A mixture of 4-(dimethylamino)benzaldhyde (1.49 g, 10.0 mmol) and (1.50 g, 4.0 mmol) of ketone **1a**, or (1.41 g, 2.7 mmol) of ketone **1b**, or (1.27 g, 1.9 mmol) of ketone **1c**, or (0.98 g, 1.2 mmol) of ketone **1d**, respectively, was prepared by dissolving the ketone in dry and warm ethanol (25 mL) at 50°C. A second solution of equivalent amount of sodium hydroxide was dissolved in dry ethanol (20 mL) and was added very slowly to the first solution with stirring at 50°C until completion. The mixture was left stirring for 2–5 days. The reaction progress was followed by TLC with different ratio of mobile phase (hexane:ethyl acetate) for each compound until completion. The solvent was evaporated under vacuum and the residual solid was purified by Column chromatography using different ratio of eluants (hexane:ethyl acetate) for each compound.

(2E,2′E)-1,1′-[1,3-Benzenediylbis(methyleneoxy-4,1-phenylene)]bis{3-[4-(dimethylamino)phenyl]-2-propen-1-one} (2a). This compound was obtained as pale-yellow powder (1.46 g, 85%), mp 130°C (decomposition); IR (potassium bromide): 1672, 1598, 1254, 1227, 981, 811 cm^{-1}; ^1H NMR (deuteriochloroform): δ 3.02 (s, 12H, CH_3), 5.15 (s, 4H, 2 × OCH_2), 7.02 (d, 4H, Ph-H), 7.46 (m, 3H, central-Ph-H), 7.05 (s, 1H, central-Ph-H), 7.92 (d, 4H, Ph-H), 7.54 (d, 2H, $^3J_{11-12}$ = 16 Hz, Ph-H), 7.94 (d, 2H, Ph-H), 6.99 (d, 4H, Ph-H), 6.86 (d, 4H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 40.18 (4C, CH_3), 69.90 (2C, 2 × OCH_2), 111.29 (4C, Ph-C), 130.26 (2C, Ph-C), 127.14 (2C, central-Ph-C), 128.90 (2C, central-Ph-C), 130.28 (1C, central-Ph-C), 130.30 (4C, Ph-C), 142.03 (1C, central-Ph-C), 163.04 (2C, Ph-C), 121.21 (2C, Ph-C), 145.11 (2C, Ph-C), 121.69 (2C, Ph-C), 114.55 (4C, Ph-C), 127.36 (4C, Ph-C), 142.19 (2C, Ph-C), 188.67 (2C, 2 × C=O); ms: (5 kV, fd) *m/z* (%) 637 (100). *Anal*. Calcd. for $C_{42}H_{40}N_2O_4$: C, 79.22; H, 6.33; N, 4.40. Found: C, 79.34; H, 6.49; N, 4.33.

(2E,2′E,2″E)-1,1′,1″-[1,3,5-Benzenetriyltris(methyleneoxy-4,1-phenylene)]tris{3-[4-(dimethylamino)phenyl]-2-propen-1-one} (2b). This compound was obtained as orange solid (0.74 g, 30%), mp 180°C (decomposition); IR (potassium bromide): 1679, 1595, 1261, 1096, 799 cm^{-1}; ^1H NMR (deuteriochloroform): δ 3.02 (s, 18H, CH_3), 4.65 (s, 6H, 3 × OCH_2), 6.96 (d, 6H, Ph-H), 7.48 (s, 3H, central-Ph-H), 7.99 (d, 6H, Ph-H), 7.47 (d, 3H, $^3J_{11-12}$ = 16 Hz, Ph-H), 7.96 (d, 3H, Ph-H), 6.99 (d, 6H, Ph-H), 6.86 (d, 6H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 40.20 (6C, CH_3), 69.78 (3C, 3 × OCH_2), 115.51 (6C, Ph-C), 131.29 (3C, Ph-C), 128.94 (3C, central-Ph-C), 130.32

(3C, central-Ph-C), 130.95 (6C, Ph-C), 161.90 (3C, Ph-C), 122.70 (3C, Ph-C), 143.70 (3C, Ph-C), 122.74 (3C, Ph-C), 114.55 (6C, Ph-C), 127.30 (6C, Ph-C), 142.10 (3C, Ph-C), 189.50 (3C, 3 × C=O); ms: (5 kV, fd) *m/z* (%) 916 (100). *Anal*. Calcd. for $C_{60}H_{57}N_3O_6$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.43; H, 6.39; N, 4.45.

(2E,2′E,2″E,2‴E)-1,1′,1″,1‴-[1,2,4,5-Benzenetetrayltetrakis (methyleneoxy-4,1-phenylene)]tetrakis{3-[4-(dimethylamino) phenyl]-2-propen-1-one} (2c). This compound was obtained as pale-yellow powder (1.70 g, 75%), mp 240°C (decomposition); IR (potassium bromide): 1671, 1599, 1575, 1258, 1274, 827 cm^{-1}; ^1H NMR (deuteriochloroform): δ 3.03 (s, 24H, CH_3), 5.25 (s, 8H, 4 × OCH_2), 6.99 (d, 8H, Ph-H), 7.42 (s, 2H, central-Ph-H), 7.92 (d, 8H, Ph-H), 7.57 (d, 4H, $^3J_{11-12}$ = 16 Hz, Ph-H), 7.94 (d, 4H, Ph-H), 7.00 (d, 8H, Ph-H), 6.71 (d, 8H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 40.00 (8C, CH_3), 67.65 (4C, 4 × OCH_2), 114.39 (8C, Ph-C), 130.90 (4C, Ph-C), 114.12 (2C, central-Ph-C), 129.82 (4C, central-Ph-C), 130.67 (8C, Ph-C), 162.00 (4C, Ph-C), 124.20 (4C, Ph-C), 145.70 (4C, Ph-C), 124.20 (4C, Ph-C), 114.10 (8C, Ph-C), 127.10 (8C, Ph-C), 139.20 (4C, Ph-C), 189.01 (4C, 4 × C=O); ms: (5 kV, fd) *m/z* (%) 1195 (100). *Anal*. Calcd. for $C_{78}H_{74}N_4O_8$: C, 78.37; H, 6.24; N, 4.69. Found: C, 78.23; H, 6.12; N, 4.54.

(2E,2′E,2″E,2‴E,2⁗E)-1,1′,1″,1‴,1⁗-[1,2,3,4,5-Benzene-pentaylpentakis(methyleneoxy-4,1-phenylene)]pentakis{3-[4-(dimethylamino)phenyl]-2-propen-1-one} (2d). This compound was obtained as red solid (0.35 g, 20%), mp 205°C (decomposition); IR (potassium bromide): 1661, 1598, 1505, 1371, 1231, 1165, 824 cm^{-1}; ^1H NMR (deuteriochloroform): δ 3.04 (s, 30H, CH_3), 5.19 (s, 10H, 5 × OCH_2), 6.87 (d, 10H, Ph-H), 7.40 (s, 1H, central-Ph-H), 7.83 (d, 10H, Ph-H), 7.66 (d, 5H, $^3J_{11-12}$ = 16 Hz, Ph-H), 7.72 (d, 5H, Ph-H), 6.82 (d, 10H, Ph-H), 6.67 (d, 10H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 40.00 (10C, CH_3), 66.70 (5C, 5 × OCH_2), 114.41 (10C, Ph-C), 132.00 (5C, Ph-C), 114.19 (1C, central-Ph-C), 122.40–125.14 (5C, central-Ph-C), 130.79 (10C, Ph-C), 161.70 (5C, Ph-C), 122.30 (5C, Ph-C), 143.00 (5C, Ph-C), 121.20 (5C, Ph-C), 114.10 (10C, Ph-C), 128.60 (10C, Ph-C), 143.00 (5C, Ph-C), 190.76 (5C, 5 × C=O); ms: (5 kV, fd) *m/z* (%) 1475 (100). *Anal*. Calcd. for $C_{96}H_{91}N_5O_{10}$: C, 78.18; H, 6.22; N, 4.75. Found: C, 78.06; H, 6.15; N, 4.68.

General procedure for the preparation of Multi arm pyrazolines (3a, c) and pyrazoles (4a, c). Phenylhydrazine (0.43 g, 4 mmol) in methanol (1.0 mL) was added dropwise at 0°C under nitrogen atmosphere to a solution of (0.31 g, 0.50 mmol) enone 2a or (0.30, 0.25 mmol) enone 2c respectively in dry methanol (20 mL). The addition was completed within 5 h after which the mixture was left stirring for about 30 h. The reaction was followed by TLC in (40% toluene:60% ethyl acetate) until completion. The solvent was evaporated under vacuum and the residual solid was purified by column chromatography using (40% toluene:60% ethyl acetate) as eluant to yield the pyrazolines 3a, c which already contains some autoxidation product of pyrazoles 4a, c. The regular oxidation of pyrazolines 3a, c to the corresponding pyrazoles 4a, c was achieved by evaporating methanol and dissolving the residual solid in boiling benzene (3.0 mL) then (0.09 g, 0.4 mmol) 2,3-dichloro-5,6-dicyano-1,4-benzoquenone was added slowly with stirring. After 1–2 h, the products were purified by column chromatography using (50% toluene:50% ethyl acetate) as the eluant for the compounds.

3,3′-[1,3-Benzenediylbis(methyleneoxy-4,1-phenylene)]bis {4,5-dihydro-5-[4-(dimethylamino)phenyl]-1-phenylpyrazol-3-yl} (3a). This compound was obtained as orange solid (0.25 g, 63%), mp 172–174°C; IR (potassium bromide): 1601, 1455, 1382, 1219, 1076, 792 cm^{-1}; ^1H NMR (deuteriochloroform): δ 3.10 (s, 12H, CH3), 5.26 (s, 4H, 2 × OCH_2), 7.09 (d, 4H, Ph-H), 7.76 (m, 3H, central-Ph-H), 7.55 (s, 1H, central-Ph-H), 7.76 (d, 4H, Ph-H), 2.07 (dd, 4H, —CH_2—), 4.12 (m, 2H, —CH—), 6.70 (d, 4H, Ph-H), 6.99 (d, 4H, Ph-H), 7.10 (m, 10H, Phen-H); ^{13}C NMR (deuteriochloroform): δ 40.23 (4C, CH_3), 67.78 (2C, 5 × OCH_2), 111.86 (4C, Ph-C), 125.09 (2C, Ph-C), 140.48 (2C, central-Ph-C), 128.90 (2C, central-Ph-C), 130.14 (1C, central-Ph-C), 130.67 (4C, Ph-C), 128.35 (1C, central-Ph-C), 162.09 (2C, Ph-C), 152.02 (2C, Ph-C), 40.23 (2C, —CH_2—), 53.29 (2C, —CH—), 121.06 (2C, Ph-C), 114.40 (4C, Ph-C), 128.35 (4C, Ph-C), 143.52 (2C, Ph-C), 135.12 (2C, Ph-C), 113.57, 130.42, 132.08 (10C, Ph-C); ms: (5 kV, fd) m/z (%) 817 (100). *Anal*. Calcd. For $C_{54}H_{52}N_6O_2$: C, 79.38; H, 6.42; N, 10.29. Found: C, 79.23; H, 6.29; N, 10.21.

3,3′,3″,3‴-[1,2,4,5-Benzenetetrayltetrakis(methyleneoxy-4,1-phenylene)]pentakis{4,5-dihydro-5-[4-(dimethylamino)phenyl]-1-phenylpyrazol-3-yl} (3c). This compound was obtained as brown solid (0.21 g, 55%), mp 106°C (decomposition); IR (potassium bromide): 1648, 1599, 1340, 1255, 1164, 812 cm^{-1}; ^1H NMR (deuteriodimethylsulfoxide-d_6): δ 2.89 (s, 24H, CH_3), 5.02 (s, 8H, 4 × OCH_2), 6.84 (d, 8H, Ph-H), 7.34 (s, 2H, central-Ph-H), 7.40 (d, 8H, Ph-H), 3.69 (dd, 8H, —CH_2—), 5.04 (m, 4H, —CH—), 7.01 (d, 8H, Ph-H), 6.71 (d, 8H, Ph-H), 6.92 (m, 20H, Ph-H); ^{13}C NMR (deuteriodimethylsulfoxide-d_6): δ 40.99 (8C, CH_3), 69.10 (4C, 4 × OCH_2), 112.90 (8C, Ph-C), 125.67 (4C, Ph-C), 114.12 (2C, central-Ph-C), 129.09 (4C, central-Ph-C), 130.63 (8C, Ph-C), 164.12 (4C, Ph-C), 152.29 (4C, Ph-C), 42.28 (4C, —CH_2—), 52.29 (4C, —CH—), 124.84 (4C, Ph-C), 114.40 (8C, Ph-C), 128.79 (8C, Ph-C), 139.74 (4C, Ph-C), 136.73 (4C, Ph-C), 113.60, 130.63, 130.84 (20C, Ph-C); ms: (5 kV, fd) *m/z* (%) 1556 (100). *Anal*. Calcd. For $C_{102}H_{98}N_{12}O_4$: C, 78.74; H, 6.35; N, 10.80. Found: C, 78.66; H, 6.28; N, 10.69.

3,3′-[1,3-Benzenediylbis(methyleneoxy-4,1-phenyl-ene)]bis {5-[4-(dimethylamino)phenyl]-1-phenylpyrazol-3-yl} (4a). This compound was obtained as dark brown solid (0.30 g, 75%), mp 135–137°C; IR (potassium bromide): 1669, 1599, 1255, 1213, 811 cm^{-1}; ^1H NMR (deuteriochloroform): δ 2.92 (s, 12H, CH_3), 5.11 (s, 4H, 2 × OCH_2), 6.97 (d, 4H, 7-H), 7.40 (m, 3H, central-Ph-H), 7.27 (s, 1H, central-Ph-H), 7.54 (d, 4H, Ph-H), 7.09 (s, 2H, Pyrazol-H), 7.38 (d, 4H, Ph-H), 6.97 (d, 4H, Ph-H), 7.14 (m, 10H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 40.35 (4C, CH_3), 63.14 (2C, 2 × OCH_2), 114.98 (4C, Ph-C), 130.30 (2C, Ph-C), 142.16 (2C, central-Ph-C), 129.58 (2C, central-Ph-C), 130.37 (1C, central-Ph-C), 130.63 (4C, Ph-C), 127.10 (1C, central-Ph-C), 161.90 (2C, Ph-C), 159.40 (2C, Ph-C), 105.35 (2C, Pyrazol-C), 142.16 (2C, Pyrazol-C), 125.34 (2C, Ph-C), 114.56 (4C, Ph-C), 128.82 (4C, Ph-C), 140.90 (2C, Ph-C), 139.83 (2C, Ph-C), 113.30, 127.19, 129.89 (10C, Ph-C); ms: (5kV, fd) *m/z* (%) 813 (100). *Anal*. Calcd. For $C_{54}H_{48}N_6O_2$: C, 79.78; H, 5.95; N, 10.34. Found: C, 79.64; H, 5.88; N, 10.31.

3,3′,3″,3‴-[1,2,4,5-Benzenetetrayltetrakis(methyleneoxy-4,1-phenyl-ene)]pentakis{5-[4-(dimethylamino)phenyl]-1-phenyl-pyrazol-3-yl} (4c). This compound was obtained as dark brown solid (0.17 g, 43%), mp 190°C (decomposition); IR

(potassium bromide): 1672, 1597, 1356, 1124, 997 cm^{-1}; ^1H NMR (deuteriochloroform): δ 2.97 (s, 24H, CH_3), 5.17 (s, 8H, 4 × OCH_2), 6.90 (d, 8H, Ph-H), 7.44 (s, 2H, central-Ph-H), 7.59 (d, 8H, Ph-H), 7.19 (s, 4H, Pyrazol-H), 7.38 (d, 8H, Ph-H), 6.87 (d, 8H, Ph-H), 7.28 (m, 20H, Ph-H); ^{13}C NMR (deuteriochloroform): δ 40.17 (8C, CH_3), 64.17 (4C, 4 × OCH_2), 116.60 (8C, Ph-C), 130.63 (4C, Ph-C), 114.46 (2C, central-Ph-C), 129.23 (4C, central-Ph-C), 130.70 (8C, Ph-C), 161.62 (4C, Ph-C), 151.97 (4C, Ph-C), 106.60 (4C, Pyrazol-C), 145.34 (4C, Pyrazol-C), 122.81 (4C, Ph-C), 114.61 (8C, Ph-C), 127.23 (8C, Ph-C), 149.94 (4C, Ph-C), 145.34 (4C, Ph-C), 116.60, 130.64, 130.70 (20C, Ph-C); ms: (5kV, fd) *m/z* (%) 1548 (100). *Anal*. Calcd. For $C_{102}H_{90}N_{12}O_4$: C, 79.15; H, 5.86; N, 10.86. Found: C, 79.04; H, 5.78; N, 10.71.

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