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Efficient Synthesis and Characterization of Anthracene based 1,3,5-Trisubstituted Pyrazoline Derivatives

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A new series of anthracene scaffold containing 1,3,5-trisubstituted pyrazoline derivatives (**3a-p**) were synthesized and well characterized by ^{1}H NMR, ^{13}C NMR, FTIR, mass spectroscopic and elemental analysis methods. The reactions were carried out from anthracenyl pyrazolines (**1a-p**) and benzoyl chloride (**2**) in presence of anhydrous K_2CO_3 in acetone under reflux conditions for 2-7 h. The obtained yields were good to excellent (80-94%).

Keywords: Synthesis, Anthracenes, 1,3,5-Trisubstituted pyrazolines.

INTRODUCTION

Studies on functional substituents of pyrazole and its derivatives are known to occupy a leading position in medicinal and pesticide chemistry because of their varied biological activities. They are also used as building blocks in organic synthesis for scheming and designing various pharmaceutical and agrochemicals molecules and also as bifunctional ligands for metal catalysis. The pyrazole ring is present as the core in a variety of leading drugs and is reported to possess various biological activities such as antimicrobial [1-6], anticonvulsant [7,8], anti-inflammatory [9], antitubercular [10,11], cardiovascular [12] and as anticancer agents in different cellular lines including melanoma, liver, colon, lung, breast, alveolar adenocarcinoma, renal, neuroblastoma, ovarian, leukaemia human cancer cells [13-23], antiviral [24,25], type-2 diabetes, hyperlipidemia and obesity [26]. Apart from the significance of the pyrazole moiety, anthracenes are recognized to have substantial biological activities against L1210 *in vitro* tumor cells [27]. Pseudourea was the first examples of anthracene-based drugs tested in clinical trials [28] and anthracene itself was reported to be effective against specific skin ailments [29]. The planar, linear, three-ring system of the anthracene nucleus has potential for overlapping with the DNA base pairs [30]. Among the anthracene derivatives, anthraquinone is well known scaffold for the treatment of cancer which are classified as anthracycline drugs such as daunorubicin, doxorubicin, mitoxantrone and ametantrone that are widely used as chemotherapeutics [31]. Though the anthracyclines drugs are effective against a wide variety of cancer cells, their clinical use is reduced due to high cardiotoxicity [31].

In view of the above-mentioned findings and as the continuation of our efforts towards the synthesis of natural products based new organic scaffolds [32], herein a novel synthesis and characterization of anthracene-based 1,3,5-trisubstituted pyrazoline derivatives is reported.

EXPERIMENTAL

All the basic reagents and solvents were purchased from commercially sources and used without further purification. Anthracenyl pyrazolines (**1a-p**) were synthesized according to the reported procedures [32]. Progress of the reactions was monitored by thin layer chromatography (TLC) with silica gel plates (Merck) using ethyl acetate and *n*-hexane (3:7) as a solvent system and visualized under UV-light/iodine vapours. Melting points were recorded in open capillaries using IKON melting point apparatus and are uncorrected. ^{1}H & ^{13}C NMR spectra for the compounds were recorded using Bruker 300 MHz spectrometer in $CDCl_3$ as a solvent and TMS as an internal standard, values are given in parts per million (ppm). FTIR spectra of the compounds were recorded on Perkin-Elmer

spectrophotometer (Spectrum-Two) using KBr disk. Micro-analytical (CHN) data were obtained with a FLASH EA 1112 Series CHNS analyzer. Mass spectra for the compounds were recorded on Advion Expression-S CMS system.

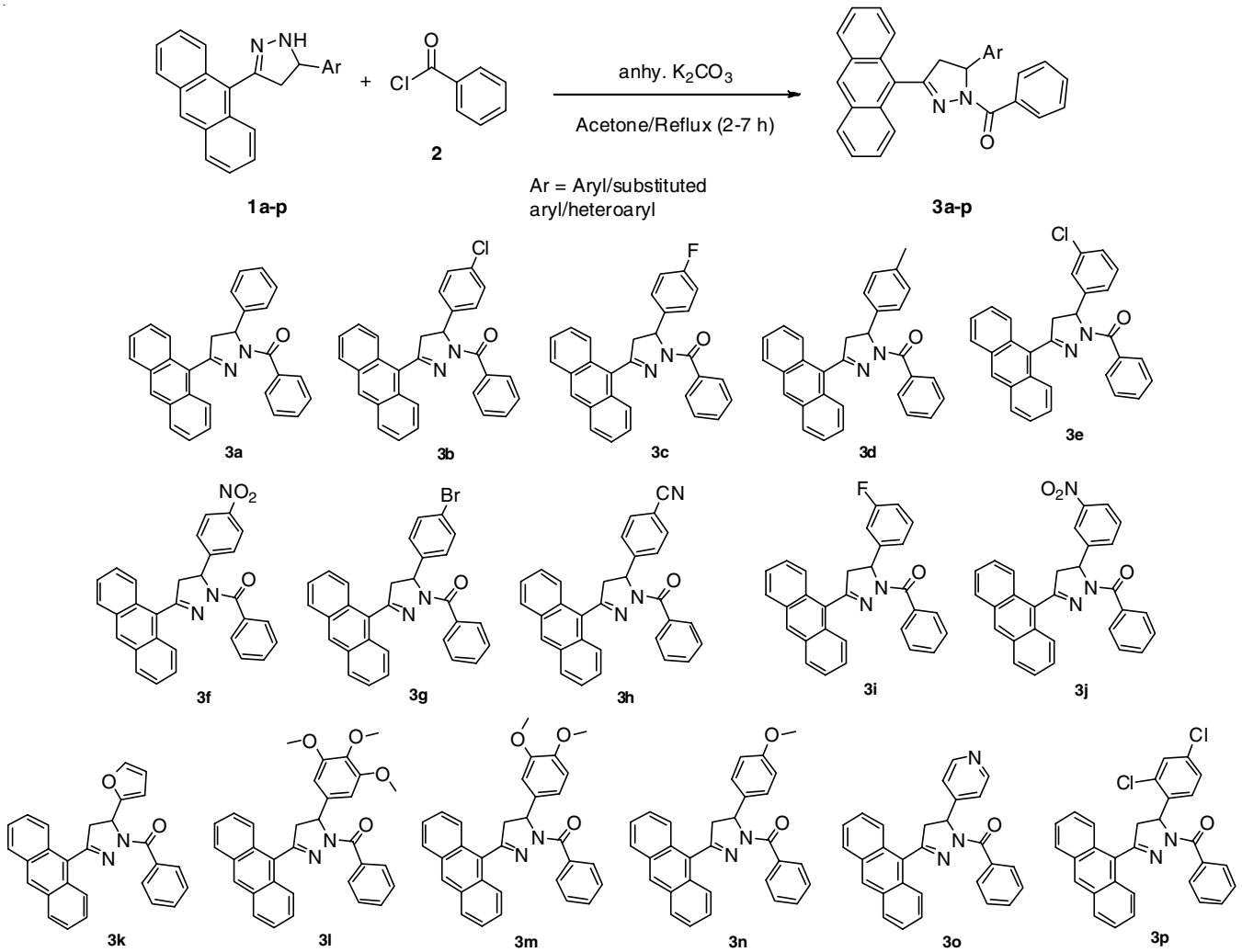
General procedure for the synthesis of new anthracene-based 1,3,5-trisubstituted pyrazolines (3a-p): To a stirred solution of corresponding anthracenyl pyrazoline (**1a-p**) (1 mmol), benzoyl chloride (**2**) (1 mmol) in acetone (10 mL) was added catalytic amount of anhydrous K_2CO_3. The reaction mixture was refluxed for 2-7 h with continuous stirring. After completion of the reaction monitored by TLC, the solvent was removed and added ice-cold water. The pure solid products of new anthracene-based 1,3,5-trisubstituted pyrazolines (**3a-p**) were collected by filtration methods, washed with water (3-4 time) and air dried at room temperature (**Scheme-I**).

Spectral data

(3-(Anthracen-10-yl)-4,5-dihydro-5-phenylpyrazol-1-yl)(phenyl)methanone (3a): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3053.77 (arom. C-H), 2927.90 (aliph. C-H), 1709.77 (C=O) and 1641.75 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.51 (s, 1H, Ar-H), 8.06-8.01 (q, 4H, Ar-H), 7.93-7.90 (t, 2H, Ar-H), 7.80-7.77 (m, 8H, Ar-H), 7.38-7.33 (m, 4H, Ar-H), 6.10-6.04 (dd, 1H, -CH), 3.98-3.88 (dd, 1H, -CH), 3.32-3.24 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.09, 156.03, 141.75, 134.26, 131.34, 131.22, 130.22, 129.95, 129.35, 129.03, 128.97, 127.98, 127.89, 127.36, 126.95, 125.68, 125.60, 124.77, 61.50, 47.92. MS (*m/z*): 427.5 (M+1). Elemental anal. calcd. (found) % for $C_{30}H_{22}N_2O$: C, 84.48 (84.36); H, 5.20 (5.26); N, 6.57 (6.65).

(3-(Anthracen-10-yl)-5-(4-chlorophenyl)-4,5-dihydro-pyrazol-1-yl)(phenyl)methanone (3b): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3053.11 (arom. C-H), 1709 (C=O) and 1641.47 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.55-8.53 (d, *J* = 6.29 Hz,1H, Ar-H), 8.06-7.99 (t, 4H, Ar-H), 7.94-7.88 (t, 2H, Ar-H), 7.82-7.36 (m, 11H, Ar-H), 6.07-6.01 (dd, 1H, -CH), 3.99-3.3.79 (dd, 1H, -CH), 3.30-3.21 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.08, 155.98, 140.30, 134.25, 133.05, 131.77, 131.34, 130.23, 129.54, 129.10, 127.94, 127.15, 127.06, 126.67, 125.63, 125.41, 124.59, 60.89, 47.83. MS (*m/z*): 463.6 (M+2). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_2OCl$: C, 78.17 (78.25); H, 4.59 (4.52); N, 6.08 (6.15).

(3-(Anthracen-10-yl)-5-(4-fluorophenyl)-4,5-dihydro-pyrazol-1-yl)(phenyl)methanone (3c): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3053.76 (arom. C-H), 1708.40 (C=O) and 1640.78 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.52 (s, 1H, Ar-



Scheme-I: Synthesis of anthracene-based 1,3,5-trisubstituted pyrazolines derivatives (**3a-p**)

H), 8.03-7.78 (m, 7H, Ar-H), 7.50-7.37 (m, 8H, Ar-H), 7.16 (s, 1H, Ar-H), 6.06-6.04 (dd, 1H, -CH), 3.98-3.88 (dd, 1H, -CH), 3.28-3.21 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.52, 155.97, 137.52, 134.26, 131.77, 131.35, 130.23, 129.93, 129.09, 128.86, 127.93, 127.50, 127.39, 127.02, 125.63, 124.63, 116.40, 116.11, 111.25, 60.89, 47.83. MS (*m/z*): 446.6 (M+2). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_2OF$: C, 81.06 (80.92); H, 4.76 (4.81); N, 6.30 (6.25).

(3-(Anthracen-10-yl)-4,5-dihydro-5-*p*-tolylpyrazol-1-yl)(phenyl)methanone (3d): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3054.72 (arom. C-H), 1721.42 (C=O) and 1643.06 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.50 (s, 1H, Ar-H), 8.12-7.92 (m, 6H, Ar-H), 7.50-7.28 (m, 12H, Ar-H), 6.06-6.01 (dd, 1H, -CH), 3.96-3.86 (dd, 1H, -CH), 3.31-3.23 (dd, 1H, -CH), 2.38 (s, 3H, $-CH_3$) ppm.^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.08, 156.08, 138.84, 137.61, 134.34, 133.75, 131.34, 131.16, 130.21, 129.99, 129.95, 129.01, 128.93, 127.85, 126.92, 125.63, 125.58, 124.80, 61.33, 47.94, 21.31 ppm. MS (*m/z*): 441.6 (M+1). Elemental anal. calcd. (found) % for $C_{31}H_{24}N_2O$: C, 84.52 (84.45); H, 5.49 (5.53); N, 6.36 (6.29).

(3-(Anthracen-10-yl)-5-(3-chlorophenyl)-4,5-dihydropyrazol-1-yl)(phenyl)methanone (3e): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3053.19 (arom. C-H), 1709.81 (C=O) and 1641.42 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53 (s, 1H, Ar-H), 8.06-8.02 (t, 4H, Ar-H), 7.92-7.89 (d, *J* = 7.97 Hz, 2H, Ar-H), 7.53-7.32 (m, 11H, Ar-H), 6.06-6.00 (dd, 1H, -CH), 3.98-3.88 (dd, 1H, -CH), 3.29-3.21 (dd, 1H, -CH) ppm. ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.11, 156.00, 143.81, 135.28, 134.26, 131.41, 131.34, 130.69, 130.26, 129.93, 129.09, 128.24, 127.96, 127.07, 126.05, 125.65, 124.63, 123.82, 61.06, 47.68. MS (*m/z*): 463.5 (M+2). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_2OCl$: C, 78.17 (78.32); H, 4.59 (4.52); N, 6.08 (6.15).

(3-(Anthracen-10-yl)-4,5-dihydro-5-(4-nitrophenyl)-pyrazol-1-yl)(phenyl)methanone (3f): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3055.43 (arom. C-H), 1714.57 (C=O) and 1639.97 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53 (s, 1H, Ar-H), 8.31 (s, 1H, Ar-H), 8.04-7.70 (m, 8H, Ar-H), 7.50-7.25 (m, 9H, Ar-H), 6.13-6.01 (dd, 1H, -CH), 3.97-3.91 (dd, 1H, -CH), 3.26-3.20 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.19, 156.02, 143.87, 147.72, 134.25, 133.45, 131.70, 131.31, 130.27, 129.18, 129.01, 128.04, 127.21, 126.68, 125.68, 124.76, 124.33, 121.24, 61.10, 47.32. MS (*m/z*): 472.5 (M+1). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_3O_3$: C, 76.42 (76.32); H, 4.49 (4.53); N, 8.91 (8.86).

(3-(Anthracen-10-yl)-5-(4-bromophenyl)-4,5-dihydropyrazol-1-yl)(phenyl)methanone (3g): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3061.57 (arom. C-H), 1721.87 (C=O) and 1599.39 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53 (s, 1H, Ar-H), 8.17-7.99 (m, 5H, Ar-H), 7.90-7.68 (m, 1H, Ar-H), 7.65-7.31 (m, 11H, Ar-H), 6.07-6.01 (dd, 1H, -CH), 3.99-3.89 (dd, 1H, -CH), 3.29-3.21 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 172.02, 162.52, 134.69, 133.92, 132.50, 132.20, 131.43, 130.72, 130.35, 129.45, 129.03, 128.63, 127.96, 127.50, 127.08, 125.65, 125.41, 124.59, 61.04, 47.64. MS (*m/z*): 507.4 (M+2). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_2OBr$: C, 71.29 (71.16); H, 4.19 (4.13); N, 5.54 (5.59).

3-(Anthracen-10-yl)-5-(4-cyanophenyl)-4,5-dihydropyrazol-1-yl)(phenyl)methanone (3h): Orange solid. IR (KBr, ν_{max}, cm^{-1}): 3055.20 (arom. C-H), 1714.17 (C=O) and 1641.46 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79-8.41 (m, 1H, Ar-H), 8.17-7.87 (m, 8H, Ar-H), 7.80-7.47 (m, 11H, Ar-H), 6.19-6.07 (dd, 1H, -CH), 4.00-3.91 (dd, 1H, -CH), 3.36-3.20 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 170.85, 167.22, 133.63, 133.28, 131.65, 131.32, 130.70, 130.27, 129.93, 129.10, 128.55, 127.99, 127.12, 126.57, 125.65, 125.46, 124.59, 124.38, 61.28, 47.64. MS (*m/z*): 452.5 (M+1). Elemental anal. calcd. (found) % for $C_{31}H_{21}N_3O$: C, 82.46 (82.35); H, 4.69 (4.62); N, 9.31 (9.38).

(3-(Anthracen-10-yl)-5-(3-fluorophenyl)-4,5-dihydropyrazol-1-yl)(phenyl)methanone (3i): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3054.62 (arom. C-H), 1712.07 (C=O) and 1641.16 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.51 (s, 1H, Ar-H), 8.07-8.00 (q, 4H, Ar-H), 7.91-7.88 (d, *J* = 7.64 Hz, 2H, Ar-H), 7.76-7.73 (d, *J* = 8.47 Hz, 2H, Ar-H), 7.50-7.31 (m, 9H, Ar-H), 7.08-7.03 (t, 1H, Ar-H), 6.08-6.02 (dd, 1H, -CH), 3.97-3.87 (dd, 1H, -CH), 3.29-3.21 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.14, 165.15, 161.88, 156.02, 144.28, 134.24, 133.96, 131.79, 131.39, 130.23, 129.07, 127.94, 127.04, 125.62, 124.60, 121.26, 115.11, 112.94, 61.04, 47.69. MS (*m/z*): 446.5 (M+2). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_2OF$: C, 81.06 (81.23); H, 4.76 (4.72); N, 6.30 (6.25).

(3-(Anthracen-10-yl)-4,5-dihydro-5-(3-nitrophenyl)-pyrazol-1-yl)(phenyl)methanone (3j): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3054.06 (arom. C-H), 1708.59 (C=O) and 1639.00 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H, Ar-H), 8.25 (s, 1H, Ar-H), 8.03-7.74 (m, 7H, Ar-H), 7.53-7.30 (m, 11H, Ar-H), 5.99-5.94 (dd,1H, -CH), 3.92-3.82 (dd, 1H, -CH), 3.33-3.25 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.17, 156.52, 142.73, 139.17, 135.08, 134.14, 131.86, 131.30, 130.31, 129.94, 128.97, 127.90, 127.32, 125.63, 124.86, 121.26, 119.88, 117.85, 61.57, 47.86. MS (*m/z*): 472.5 (M+1). Elemental anal. calcd. (found) % for $C_{30}H_{21}N_3O_3$: C, 76.42 (76.32); H, 4.49 (4.53); N, 8.91 (8.85).

(3-(Anthracen-10-yl)-5-(furan-2-yl)-4,5-dihydropyrazol-1-yl)(phenyl)methanone (3k): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3053.62 (arom. C-H), 1697.66 (C=O) and 1639.75 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53-8.42 (t, 1H, Ar-H), 8.32-8.30 (t, 1H, Ar-H), 8.08-7.78 (m, 5H, Ar-H), 7.57-6.80 (m, 10H, Ar-H), 6.58-6.44 (m, 1H, Ar-H), 6.18-6.12 (dd, 1H, -CH), 3.79-3.72 (dd, 1H, -CH), 3.62-3.55 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.09, 156.03, 141.5, 134.26, 131.37, 131.20, 130.75, 130.23, 128.95, 128.91, 128.29, 127.83, 127.37, 126.93, 125.64, 125.47, 125.04, 124.38, 61.50, 47.92. MS (*m/z*): 417.4 (M+1). Elemental anal. calcd. (found) % for $C_{28}H_{20}N_2O_2$: C, 80.75 (80.65); H, 4.84 (4.79); N, 6.73 (6.81).

(3-(Anthracen-10-yl)-4,5-dihydro-5-(3,4,5-trimethoxyphenyl)pyrazol-1-yl)(phenyl)methanone (3l): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3054.36 (arom. C-H), 1710.13 (C=O) and 1641.57 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53 (s, 1H, Ar-H), 8.03 (m, 1H, Ar-H), 7.78 (s, 1H, Ar-H), 7.48-7.25 (m, 8H, Ar-H), 6.75 (s, 2H, Ar-H), 6.03-5.98 (dd, 1H, -CH), 3.92-3.69 (d, *J* = 11.23 Hz, 9H, Ar-OCH_3; dd, 1H, -CH),

3.34-3.27 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.00, 156.48, 154.06, 137.60, 134.25, 131.76, 131.33, 131.26, 130.05, 129.11, 127.97, 127.34, 126.93, 125.61, 125.44, 124.65, 103.85, 102.29, 61.55, 60.98, 56.40, 56.24, 47.87. MS (*m/z*): 517.5 (M+1). Elemental anal. calcd. (found) % for $C_{33}H_{28}N_2O_4$: C, 76.73 (76.65); H, 5.46 (5.42); N, 5.42 (5.48).

(3-(Anthracen-10-yl)-4,5-dihydro-5-(3,4-dimethoxyphenyl)pyrazol-1-yl)(phenyl)methanone (3m): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3053.23 (arom. C-H), 1705.07 (C=O) and 1640.77 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.53 (s, 1H, Ar-H), 8.02-7.79 (m, 5H, Ar-H), 7.48-6.81 (m, 9H, Ar-H), 6.05-6.00 (dd, 1H, -CH), 3.95-3.67 (d, 6H, Ar-OCH_3; dd, 1H, -CH), 3.34-3.18 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.44, 156.44, 141.46, 134.26, 131.77, 131.18, 130.13, 129.08, 128.82, 127.91, 126.93, 125.61, 124.74, 119.62, 117.84, 111.89, 111.36, 108.82, 61.20, 56.16, 56.05, 47.86. MS (*m/z*): 487.5 (M+1). Elemental anal. calcd. (found) % for $C_{32}H_{26}N_2O_3$: C, 78.99 (78.89); H, 5.39 (5.34); N, 5.76 (5.81).

(3-(Anthracen-10-yl)-4,5-dihydro-5-(4-methoxyphenyl)pyrazol-1-yl)(phenyl)methanone (3n): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3055.93 (arom. C-H), 1721.60 (C=O) and 1644.22 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.51 (s, 1H, Ar-H), 8.17-7.95 (m, 5H, Ar-H), 7.94-7.92 (d, *J* = 7.67 Hz, 2H, Ar-H), 7.64-7.57 (q, 6H, Ar-H), 7.51-7.32 (m, 3H, Ar-H), 7.01-6.98 (d, *J* = 8.44 Hz, 2H, Ar-H), 6.06-6.01 (dd, 1H, -CH), 3.96-3.86 (dd, 1H, -CH), 3.83 (s, 3H, Ar-OCH_3), 3.31-3.23 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.12, 159.31, 156.08, 134.67, 134.34, 133.89, 131.35, 131.17, 130.20, 129.95, 129.03, 128.94, 127.86, 127.00, 126.94, 125.59, 124.78, 114.71, 61.01, 55.51, 47.93. MS (*m/z*): 457.5 (M+1). Elemental anal. calcd. (found) % for $C_{31}H_{24}N_2O_2$: C, 81.56 (81.45); H, 5.30 (5.36); N, 6.14 (6.21).

(3-(Anthracen-10-yl)-4,5-dihydro-5-(pyridin-4-yl)-pyrazol-1-yl)(phenyl)methanone (3o): Brown solid. IR (KBr, ν_{max}, cm^{-1}): 3052.5 (arom. C-H), 1713.19 (C=O) and 1641.78 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.72 (s, 1H, Ar-H), 8.56-8.54 (d, *J* = 8.50 Hz, 1H, Ar-H), 8.316 (s, 1H, Ar-H), 8.05-7.99 (m, 4H, Ar-H), 7.85-7.70 (q, 3H, Ar-H), 7.49-7.45 9 (m, 7H, Ar-H), 7.12-7.02 (m, 1H, Ar-H), 6.07-6.01 (dd, 1H, -CH), 4.01-3.91 (dd, 1H, -CH), 3.28-3.19 (dd, 1H, -CH) ppm. ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 167.89, 155.99, 150.60, 134.27, 131.81, 130.28, 129.15, 128.93, 128.10, 128.03, 127.18, 126.61, 125.69, 125.47, 125.25, 124.42, 120.77, 111.42, 60.58, 47.10. MS (*m/z*): 428.4 (M+1). Elemental anal. calcd. (found) % for $C_{29}H_{21}N_3O$: C, 81.48 (81.36); H, 4.95 (4.91); N, 9.83 (9.94).

(3-(Anthracen-10-yl)-5-(2,4-dichlorophenyl)-4,5-dihydropyrazol-1-yl)(phenyl)methanone (3p): Yellow solid. IR (KBr, ν_{max}, cm^{-1}): 3058.79 (arom. C-H), 1724.91 (C=O) and 1644.50 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.47 (s, 1H, Ar-H), 8.33-8.01 (m, 5H, Ar-H), 7.85-7.82 (q, 1H, Ar-H), 7.70-7.33 (m, 10H, Ar-H), 6.35-6.29 (dd, 1H, -CH), 4.08-3.98 (dd, 1H, -CH), 3.21-3.13 (dd, 1H, -CH). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 171.63, 162.51, 156.74, 137.31, 134.67, 133.86, 131.55, 131.30, 130.71, 130.32, 129.10, 129.01, 128.61, 128.01, 127.95, 127.06, 125.63, 124.51, 59.05, 46.49. MS (*m/z*): 497.1 (M+2). Elemental anal. calcd. (found) % for $C_{30}H_{20}N_2OCl_2$: C, 72.73 (72.65;); H, 4.07 (4.12); N, 5.65 (5.62).

RESULTS AND DISCUSSION

Anthracene-based 1,3,5-trisubstituted pyrazoline derivatives (**3a-p**) were synthesized by carrying out by reacting anthracenyl pyrazolines (**1a-p**) [32] with benzoyl chloride (**2**) in presence of anhydrous K_2CO_3 in acetone solution under reflux conditions for 2-7 h (**Scheme-I**). The obtained yields are in good to excellent. When different anthracenyl pyrazoline derivatives were used for the reaction, it is observed that the time taken for each reaction to complete was different depending on the functional group present in the aromatic ring observed with time interval monitoring of the reaction by TLC. The obtained yields and time taken for each reaction to complete is listed in Table-1.

TABLE-1
SYNTHESIS AND PHYSICO-CHEMICAL FEATURES OF NEW ANTHRACENE-BASED 1,3,5-TRISUBSTITUTED PYRAZOLINE DERIVATIVES (**3a-p**)[a]

Ar	Product	Time (h)	Yield (%)	m.p. (°C)
-C_6H_5	**3a**	2	80	100-102
-4-ClC_6H_4	**3b**	3	93	84-86
-4-FC_6H_4	**3c**	4	92	85-87
-4-$CH_3C_6H_4$	**3d**	2	94	195-197
-3-ClC_6H_4	**3e**	4	86	86-88
-4-$NO_2C_6H_4$	**3f**	7	91	80-82
-4-BrC_6H_4	**3g**	5	93	92-94
-4-CNC_6H_4	**3h**	2	91	106-108
-3-FC_6H_4	**3i**	3	85	55-57
-3-$NO_2C_6H_4$	**3j**	5	92	102-104
-2-Furan	**3k**	4	83	84-86
-3,4,5-$(OCH_3)_3C_6H_2$	**3l**	3	90	68-70
-3,4-$(OCH_3)_2C_6H_3$	**3m**	3	85	65-67
-4-$(OCH_3)C_6H_4$	**3n**	3	94	151-153
-4-Pyridine	**3o**	2	90	84-86
-2,4-$(Cl)_2C_6H_3$	**3p**	2	92	60-62

[a]Reaction conditions: Anthracenyl pyrazolines (**1a-p**) (1 mmol), benzoyl chloride (**2**) (1 mmol), anhyd. K_2CO_3 in 10 mL acetone and reflux for 2-7 h.

In general, all the newly synthesized pyrazoline compounds revealed that the comparable characteristic spectral features. For example, the IR spectra of pyrazoline compound **3a** showed the characteristics bands for aromatic C-H at 3053.77 cm^{-1} and aliphatic C-H stretch at 2927.90 cm^{-1}, C=O at 1709.77 cm^{-1} and C=N stretching at 1641.75 cm^{-1}. The disappearance of the absorption band of NH of the anthracenyl pyrazoline [14] and appearance of strong C=O absorption band at 1709.77 cm^{-1} confirmed the formation of the synthesized product. The ^{1}H NMR spectrum displayed a pair of doublet of doublet signals of methylene protons at δ 3.98-3.88 ppm for -CH_B, δ 3.32-3.24 ppm for -CH_A and a double doublet peaks at δ 6.10-6.04 ppm for methine proton -CH_X because of the neighboring protons of the methylene (CH_2) group.

The ^{13}C NMR spectra, the distinctive chemical shift values of the pyrazoline ring carbons appears at δ 47.92 ppm (C, CH_2 pyrazoline), δ 61.50 ppm (C, CH pyrazoline), δ 156.03 ppm (C, C=N pyrazoline) and δ 167.09 ppm (C, C=O), which gives the characteristic features for the formation of the corresponding anthracene based 1,3,5-trisubstituted pyrazoline product **3a**.

Conclusion

In summary, a novel efficient synthesis of anthracene-based 1,3,5-trisubstituted pyrazolines derivatives (**3a-p**) is reported. All the synthesized compounds were also characterized by various spectroscopic methods. The present protocol is simple, easy workup procedure and obtained yields were good to excellent with a simple filtration method.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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