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**Research Article**

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# One Pot Synthesis and Characterization of Some New 1,3,5-Trisubstituted Pyrazoline Derivatives

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## ABSTRACT

*1,3,5-trisubstituted pyrazoline derivatives containing both azo-linkages and benzyloxy moieties have been synthesized via one-pot three-component condensation reaction in high yields and short reaction process. The structures of the synthesized compounds were characterized by using FT-IR, $^{1}$H-NMR, $^{13}$C-NMR and $^{13}$C- DEPT 135 spectra.*

**Keywords:** One-pot synthesis; Benzylation; Diazotization; Chalcones; Pyrazolines

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## INTRODUCTION

Synthesis of newly chemical compounds via a one pot reaction technique is broadly considered to improve the competency of chemical reactions in synthetic organic chemistry, whereby a mixture of reactive materials (three or more components) interact in a single reactor are undergoing successive chemical reactions to produce the target product [1]. There are several terminologies to describe multi-step reactions that take place in one pot such as “domino reaction”, “cascade reaction” [2,3], and “tandem reaction” [4,5], but the concept of one pot synthesis is still the most common applicable term as it reflects much wider meaning. This protocol is a very useful tool for organic chemists in industrially and medicinal purposes due to its economic impact. It shortened considerably the reaction time by reducing the number of synthetic steps, avoiding a long purification process, minimizing the waste of solvents and the separation stages of the intermediate chemicals [6]. Besides, it increases the proportion of products output [7]. Although this approach has firstly been employed since 100 years ago when Robinson [8] has reported his one-pot synthesis of tropinone, but it still has not received much of interest. Later on, among many other classic examples, one-pot reactions have been elegantly utilized in the biomimetic syntheses of progesterone by Johnson [9] endiandric acid by Nicolaou, [10-12] and proto-daphniphylline by Heathcock [13]. Over last two decades with the introduction of high-throughput biological screening, the importance of one pot synthesis for drug discovery has been recognized and considerable efforts from both academic and industrial researchers have been focussed especially on the design and development of single-pot methodology for the generation of bio-active heterocyclic compounds. Recently, one pot synthesis technique considered as a good protocol for green chemistry approach and the environmentally friendly applications compared to the conventional methods.

Pyrazolines and azopyrazloine scaffold compounds are medicinally very important class of heterocyclic compounds due to their diverse of biological activities. They exhibited as anti-cancer [14], anti-fungal [15], Anti-convulsant [16] anti-inflammatory [17], analgesic [18], anti-leishmanial [19], anti-oxidant [20] and other anti-microbial activities [21-23]. Based on such facts we get prompted to design and synthesis of di-substituted pyrazoline compounds utilizing the one-pot synthesis strategy. In this work, nine target molecule of 1,3,5-trisubstited prazoline derivatives containing azo-linkages and benzyloxy moieties were synthesized along with spectroscopic characterization through a one-pot three-component condensation reaction.

## EXPERIMENTAL SECTION

Melting points were determined by a Stuart Scientific melting point apparatus (SMP3). FT-IR spectra were recorded on IR Affinity-1 Spectrophotometer, using KBr disc. $^{1}$H-NMR, $^{13}$C-NMR and $^{13}$C-DEPT-135 spectra were recorded on a Bruker (400MHz) with $CDCl_3$ as internal reference in Queen Mary University of London.

**Synthesis of 4-(4-hydroxy-3-chlorophenyl)azoacetophenone (1) and its benzyloxy product (2)**
Compounds (1& 2) have been prepared in three steps according to our published article [13].
**Compound (1):** $C_{14}H_{11}ClN_2O$, m.p. 174-175$^{o}$C, yield (95%), IR(cm$^{-1}$): 3201(*b.*), 1670, 1577, 1254. ($^{1}$H-NMR) (ppm): 2.69(s, 3H, $CH_3$), 6.0(s 1H, OH), 7.21(d, 1H, $H_{11}$), 7.28(d, 1H, $H_{12}$), 7.96- 8.03(*m* 5H Ar-H). $^{13}$C-NMR: 26.79($CH_3$), 111.87($C_{11}$), 117.5($C_{12}$), 120.21($C_{3,5}$), 121.03($C_9$), 125.36($C_8$) 129.12($C_{2,6}$), 138.32($C_1$), 147.06($C_7$), 154.31($C_{10}$), 155.73($C_4$), 199.8(C=O).

**Compound (2):** $C_{21}H_{17}ClN_2O$, m.p. 138-140$^{o}$C, yield (93%), IR(cm$^{-1}$): 1670, 1589, 1249. $^{1}$H-NMR (ppm): 2.68(s, 3H, $COCH_3$); 5.25(s, 2H, $OCH_2$ -$C_{13}$); 7.12-8.13(*m* 12H, Ar-H). $^{13}$C-NMR: 26.56($CH_3$), 71.16($C_{13}$), 113.46($C_{11}$), 122.86($C_{12}$), 123.79($C_{3,5}$), 124.46($C_9$), 125.40($C_8$), 127.25($C_{15,19}$), 128.58($C_{17}$), 128.96($C_{16,18}$), 129.27($C_{2,6}$), 135.92($C_{14}$), 138.54($C_1$), 146.90($C_7$), 155.03($C_{10}$), 157.07($C_4$), 197.8(C=O).

**One Pot Synthesis of 1,3,5-trisubstituted Pyrazolines (4a-i)**
A mixture of azo-benzyloxy-acetophenone (1 mmol), substituted benzaldehydes 3a-i (1 mmol), alcoholic sodium hydroxide 4% (4 mL) and phenylhydrazine (3 mmol) in ethanol (20 mL) was refluxed with stirring for 3-5 hrs until completed. The reaction was monitored by either through the change in the reaction color or by the formation of precipitate and testing it with $H_2SO_4$ to gives a green color. The precipitate was filtered under vacuum, washed with ethanol, dried and recrystallized from toluene as a suitable solvent [24].

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(2-chlorophenyl)-1-phenyl-2-pyrazoline** (**4a**):
$C_{34}H_{26}Cl_2N_4O$, m.p. 181-182, 75%, Time: 3h., FTIR/cm$^{-1}$: C=N:1595. $^{1}$H-NMR (ppm): 3.14 (dd 1H $CH_2$-$H_a$), 4.05 (dd 1H $CH_2$-$H_b$), 5.25 (s 2H -O-$CH_2$-$C_{13}$), 5.75 (dd 1H CH-$H_x$), 6.87-8.10 (*m* 21H Ar-H). $^{13}$C-NMR(ppm): 41.73:$CH_2$ of pyra., 61.43:CH of pyra., 71.02:O-$CH_2$-$C_{13}$, 113.32:$C_{21,25}$, 119.68: $C_{11}$, 123.17:$C_{23}$, 123.32:$C_{12}$, 124.30:$C_{3,5}$, 124.77:$C_9$, 126.38: $C_8$, 127.09: $C_{30}$, 127.31: $C_{15,19}$, 127.69: $C_{17}$, 128.20: $C_{29}$, 128.24: $C_{31}$, 128.92: $C_{28}$, 129.05: $C_{16,18}$, 129.11: $C_{2,6}$, 129.98: $C_{22,24.}$ 131.76: $C_{27}$, 134.98: $C_1$, 135.99: $C_{14}$,, 138.95: $C_{26}$, 143.95: $C_{20}$, 146.15:$C_7$, 147.11:C=N, 152.17: $C_4$, 156.34:$C_{10}$. $^{13}$C-DEPT NMR(ppm): -41.73: $CH_2$ of pyra., 61.43: CH of pyra., -71.02: O-$CH_2$-$C_{13}$, 113.32: $C_{21,25}$, 119.68: $C_{11}$, 123.17: $C_{23}$, 123.32: $C_{12}$, 124.30: $C_{3,5}$, 126.38: $C_8$, 127.09: $C_{30}$, 127.31: $C_{15,19}$, 127.69: $C_{17}$, 128.20: $C_{29}$, 128.24: $C_{31}$, 128.92: $C_{28}$, 129.05: $C_{16,18}$, 129.11: $C_{2,6}$, 129.98: $C_{22,24}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(4-chlorophenyl)-1-phenyl-2-pyrazoline** (**4b**):
$C_{34}H_{26}Cl_2N_4O$, m.p. 186-187, 79%, Time: 3h., FTIR/cm$^{-1}$: C=N:1595. $^{1}$H-NMR (ppm): 3.13 (dd 1H $CH_2$-$H_a$), 3.88 (dd 1H $CH_2$-$H_b$), 5.26 (s 2H -O-$CH_2$-$C_{13}$), 5.35 (dd 1H CH-$H_x$), 6.87-8.09 (*m* 21H Ar-H). $^{13}$C-NMR(ppm): 43.23:$CH_2$ of pyra., 64.01:CH of pyra., 71.01:O-$CH_2$-$C_{13}$, 113.31:$C_{21,25}$, 119.81:$C_{11}$, 123.21:$C_{23}$, 123.30:$C_{12}$, 124.29:$C_{3,5}$, 124.81:$C_9$, 126.35:$C_8$, 127.10:$C_{15,19}$, 127.31:$C_{17}$, 128.21:$C_{27,31}$, 128. 72:$C_{28,30}$, 128.93:$C_{16,18}$, 129.06: $C_{2,6}$, 129.44:$C_{22,24.}$ 133.50:$C_{29}$, 134.89:$C_1$, 135.98:$C_{14}$,, 140.79:$C_{26}$, 144.13:$C_{20}$, 145.76:$C_7$, 147.09:C=N, 152.16:$C_4$, 156.35:$C_{10}$. $^{13}$C-DEPT NMR(ppm): -43.23:$CH_2$ of pyra., 64.01:CH of pyra., -71.01:O-$CH_2$-$C_{13}$, 113.31:$C_{21,25}$, 119.81: $C_{11}$, 123.21:$C_{23}$, 123.30:$C_{12}$, 124.29:$C_{3,5}$, 126.35: $C_8$, 127.10:$C_{15,19}$, 127.31:$C_{17}$, 128.21:$C_{27,31}$, 128. 72:$C_{28,30}$, 128.93:$C_{16,18}$, 129.06: $C_{2,6}$, 129.44:$C_{22,24}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(4-bromophenyl)-1-phenyl-2-pyrazoline** (**4c**):
$C_{34}H_{26}Cl_2N_4O$, m.p. 196-197, 86%, Time: 3h., FTIR/cm$^{-1}$: C=N:1595. $^{1}$H-NMR (ppm): 3.13 (dd 1H $CH_2$-$H_a$), 3.90 (dd 1H $CH_2$-$H_b$), 5.26 (s 2H -O-$CH_2$-$C_{13}$), 5.35 (dd 1H CH-$H_x$), 6.85-8.10 (*m* 21H Ar-H). $^{13}$C-NMR(ppm): 43.18: $CH_2$ of pyra., 64.07: CH of pyra., 71.02: O-$CH_2$-$C_{13}$, 113.32: $C_{21,25}$, 119.82: $C_{11}$, 121.57: $C_{29}$, 123.20: $C_{23}$, 123.31: $C_{12}$, 124.29: $C_{3,5}$, 124.80: $C_9$, 126.35: $C_8$, 127.09:$C_{15,19}$, 127.65: $C_{17}$, 128.21: $C_{16,18}$, 128.72:$C_{27,31}$, 129.06: $C_{2,6}$, 129.42: $C_{22,24.}$ 132. 39:$C_{28,30}$, 134.87: $C_1$, 135.98: $C_{14}$,, 141.31: $C_{26}$, 144.11:$C_{20}$, 145.76:$C_7$, 147.10:C=N, 152.17: $C_4$, 156.35:$C_{10}$. $^{13}$C-DEPT NMR(ppm): -43.18: $CH_2$ of pyra., 64.07: CH of pyra., -71.02: O-$CH_2$-$C_{13}$, 113.32: $C_{21,25}$, 119.82: $C_{11}$, 121.57: $C_{29}$, 123.20: $C_{23}$, 123.31: $C_{12}$, 124.29: $C_{3,5}$, 126.35: $C_8$, 127.09:$C_{15,19}$, 127.65: $C_{17}$, 128.21: $C_{16,18}$, 128.72:$C_{27,31}$, 129.06: $C_{2,6}$, 129.42: $C_{22,24.}$ 132. 39:$C_{28,30}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(4-methylphenyl)-1-phenyl-2-pyrazoline** (**4d**):
$C_{35}H_{29}ClN_4O$, m.p. 191-193, 80%, Time: 3h., FTIR/cm$^{-1}$: C=N:1595. $^{1}$H-NMR (ppm): 2.31 (s 3H -Ar-$CH_3$), 3.15 (dd 1H $CH_2$-$H_a$), 3.84 (dd 1H $CH_2$-$H_b$), 5.26 (s 2H -O-$CH_2$-$C_{13}$), 5.35 (dd 1H CH-$H_x$), 6.85-8.11 (*m* 21H Ar-H). $^{13}$C-NMR(ppm): 21.12: $CH_3$ of Ar-$CH_3$, 43.37: $CH_2$ of pyra., 64.45: CH of pyra., 71.01: O-$CH_2$-$C_{13}$, 113.32: $C_{21,25}$, 119.49: $C_{11}$, 123.19: $C_{23}$, 123.30: $C_{12}$, 124.27: $C_{3,5}$, 124.76: $C_9$, 126.30: $C_8$, 127.10: $C_{27,31}$, 128.20:

$C_{15,19}$, 128.25: $C_{17}$, 128.72: $C_{28,30}$, 128.97: $C_{16,18}$, 129.06: $C_{2,6}$, 129.88: $C_{22,24.}$ 135.24: $C_1$, 136.01: $C_{14,}$, 137.39: $C_{26}$, 139.37: $C_{29}$, 144.38: $C_{20}$, 145.73:$C_7$, 147.13:C=N, 152.04: $C_4$, 156.30:$C_{10}$. $^{13}$C-DEPT NMR(ppm): 21.12: $CH_3$ of Ar-$CH_3$, -43.37: $CH_2$ of pyra., 64.45: CH of pyra.,- 71.01: O-$CH_2$-$C_{13}$, 113.32: $C_{21,25}$, 119.49: $C_{11}$, 123.19: $C_{23}$, 123.30: $C_{12}$, 124.27: $C_{3,5}$, 126.30: $C_8$, 127.10: $C_{27,31}$, 128.20: $C_{15,19}$, 128.25: $C_{17}$, 128.72: $C_{28,30}$, 128.97: $C_{16,18}$, 129.06: $C_{2,6}$, 129.88: $C_{22,24}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(4-methoxyphenyl)-1-phenyl-2-pyrazoline** (**4e**):
$C_{35}H_{29}ClN_4O_2$, m.p. 181-183, 82%, Time: 3h., FTIR/cm$^{-1}$: C=N:1595. $^1$H-NMR (ppm): 3.16 (dd 1H $CH_2$-$H_a$), 3.81 (s 3H -Ar-$OCH_3$),3.88 (dd 1H $CH_2$-$H_b$), 5.28 (s 2H -O-$CH_2$-$C_{13}$), 5.36 (dd 1H CH-$H_x$), 6.83-8.10 (*m* 21H Ar-H). $^{13}$C-NMR(ppm): 43.37:$CH_2$ of pyra., 55.29: $CH_3$ of Ar-$OCH_3$, 64.19:CH of pyra., 71.02:O-$CH_2$-$C_{13}$, 113.33:$C_{21,25}$, 114. 58:$C_{28,30}$, 119.51:$C_{11}$, 123.18:$C_{23}$, 123.30:$C_{12}$, 124.28:$C_{3,5}$, 124.75:$C_9$, 126.29:$C_8$, 127.04:$C_{15,19}$, 127.10:$C_{17}$, 128.20:$C_{27,31}$, 128.71:$C_{16,18}$, 128.95:$C_{2,6}$, 129.40:$C_{22,24.}$ 134.37:$C_1$, 135.25:$C_{14,}$, 136.00:$C_{26}$, 144.36:$C_{20}$, 145.72:$C_7$, 147.13:C=N, 152.05:$C_4$, 156.30:$C_{10}$ ,159.10:$C_{29}$. $^{13}$C-DEPT NMR (ppm): -43.37:$CH_2$ of pyra., 55.29: $CH_3$ of Ar-$OCH_3$, 64.19:CH of pyra., -71.02:O-$CH_2$-$C_{13}$, 113.33:$C_{21,25}$, 114. 58:$C_{28,30}$, 119.51:$C_{11}$, 123.18:$C_{23}$, 123.30:$C_{12}$, 124.28:$C_{3,5}$, 126.29:$C_8$, 127.04:$C_{15,19}$, 127.10:$C_{17}$, 128.20:$C_{27,31}$, 128.71:$C_{16,18}$, 128.95:$C_{2,6}$, 129.40:$C_{22,24}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(3-benzyloxyphenyl)-1-phenyl-2-pyrazoline** (**4f**):
$C_{41}H_{33}ClN_4O_2$, m.p. 161-163, 85%, Time: 4h., FTIR/cm$^{-1}$: C=N:1595. $^1$H-NMR (ppm): 3.15 (dd 1H $CH_2$-$H_a$), 3.85 (dd 1H $CH_2$-$H_b$), 5.09 (s 2H -O-$CH_2$-$C_{32}$), 5.29 (s 2H -O-$CH_2$-$C_{13}$), 5.35 (dd 1H CH-$H_x$), 6.82-8.13 (*m* 26H Ar-H). $^{13}$C-NMR(ppm): 43.29: $CH_2$ of pyra., 64.65: CH of pyra., 70.06: O-$CH_2$-$C_{32}$, 71.02: O-$CH_2$-$C_{13}$, 112.39: $C_{31}$, 113.33: $C_{21,25}$ , 114.00:$C_{29}$, 118.38:$C_{27}$, 119.60:$C_{11}$, 123.19:$C_{23}$, 123.31: $C_{12}$, 124.28:$C_{3,5}$, 124.78:$C_9$, 126.34:$C_8$, 127.10:$C_{34,38}$, 127.63:$C_{15,19}$, 128.01:$C_{17,36}$ ,128.21: $C_{35,37}$, 128.57: $C_{16,18}$, 128.72: $C_{2,6}$, 129.00: $C_{22,24.}$ 130.36: $C_{28}$, 135.31:$C_1$, 136.01:$C_{33}$, 136.73:$C_{14}$, 144.12: $C_{20}$, 144.40:$C_{26}$, 145.78:$C_7$, 147.13:C=N, 152.09:$C_4$, 156.32:$C_{10,}$ 159.52:$C_{30}$. $^{13}$C-DEPT NMR(ppm): -43.29: $CH_2$ of pyra., 64.65: CH of pyra., -70.06: O-$CH_2$-$C_{32}$, 71.02: O-$CH_2$-$C_{13}$, 112.39: $C_{31}$, 113.33: $C_{21,25}$ , 114.00:$C_{29}$, 118.38:$C_{27}$, 119.60:$C_{11}$, 123.19:$C_{23}$, 123.31: $C_{12}$, 124.28:$C_{3,5}$, 126.34:$C_8$, 127.10:$C_{34,38}$, 127.63:$C_{15,19}$, 128.01:$C_{17,36}$ ,128.21: $C_{35,37}$, 128.57: $C_{16,18}$, 128.72: $C_{2,6}$, 129.00: $C_{22,24.}$ 130.36: $C_{28}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(4-benzyloxyphenyl)-1-phenyl-2-pyrazoline** (**4g**):
$C_{41}H_{33}ClN_4O_2$, m.p. 174-176, 87%, Time: 4h., FTIR/cm$^{-1}$: C=N:1595. $^1$H-NMR (ppm): 3.12 (dd 1H $CH_2$-$H_a$), 3.88 (dd 1H $CH_2$-$H_b$), 5.04 (s 2H -O-$CH_2$-$C_{32}$), 5.22 (s 2H -O-$CH_2$-$C_{13}$), 5.31 (dd 1H CH-$H_x$), 6.82-8.13 (*m* 26H Ar-H). $^{13}$C-NMR(ppm): 43.12: $CH_2$ of pyra., 64.18: CH of pyra., 70.11: O-$CH_2$-$C_{32}$, 71.03: O-$CH_2$-$C_{13}$, 113.34: $C_{21,25}$, 115.51: $C_{28,30}$, 119.52: $C_{11}$, 123.19: $C_{23}$, 123.31: $C_{12}$, 124.30: $C_{3,5}$, 124.76: $C_9$, 126.30: $C_8$, 127.10: $C_{34,38}$, 127.50: $C_{15,19}$, 128.02: $C_{17,36}$ , 128.21: $C_{27,31}$, 128.61: $C_{35,37}$, 128.72: $C_{16,18}$, 128.96: $C_{2,6}$, 129.40: $C_{22,24.}$ 135.15: $C_1$, 136.0: $C_{14,33}$, 136.89: $C_{26}$, 144.32: $C_{20}$, 145.73: $C_7$, 147.23: C=N, 152.06: $C_4$, 156.32: $C_{10,}$ 159.27: $C_{29}$. $^{13}$C-DEPT NMR(ppm): -43.12: $CH_2$ of pyra., 64.18: CH of pyra., -70.11: O-$CH_2$-$C_{32}$, -71.03: O-$CH_2$-$C_{13}$, 113.34: $C_{21,25}$, 115.51: $C_{28,30}$, 119.52: $C_{11}$, 123.19: $C_{23}$, 123.31: $C_{12}$, 124.30: $C_{3,5}$, 126.30: $C_8$, 127.10: $C_{34,38}$, 127.50: $C_{15,19}$, 128.02: $C_{17,36}$ , 128.21: $C_{27,31}$, 128.61: $C_{35,37}$, 128.72: $C_{16,18}$, 128.96: $C_{2,6}$, 129.40: $C_{22,24}$.

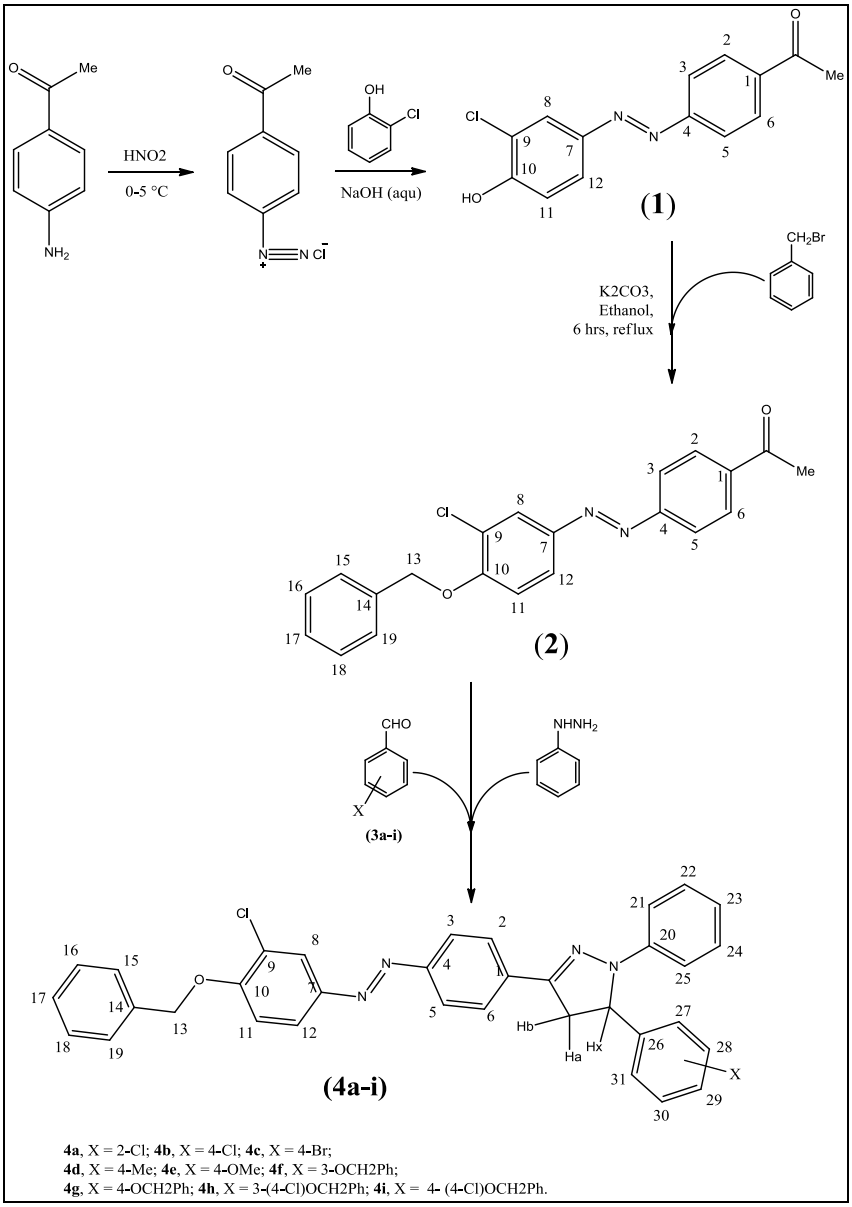
**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(3-(4-chlorobenzyloxy)phenyl)-1-phenyl-2-pyrazoline** (**4h**): $C_{41}H_{32}Cl_2N_4O_2$, m.p. 172-174, 89%, Time: 5h., FTIR/cm$^{-1}$: C=N: 1595. $^1$H-NMR (ppm): 3.18 (dd 1H $CH_2$-$H_a$), 3.87 (dd 1H $CH_2$-$H_b$), 4.98 (s 2H -O-$CH_2$-$C_{32}$), 5.28 (s 2H -O-$CH_2$-$C_{13}$), 5.34 (dd 1H CH-$H_x$), 6.92-8.16 (m 25H Ar-H). $^{13}$C-NMR(ppm): 43.28:$CH_2$ of pyra., 64.58: CH of pyra., 69.21: O-$CH_2$-$C_{32}$, 71.02: O-$CH_2$-$C_{13}$, 112.39: $C_{31}$, 113.32:$C_{3,5}$, 114.12:$C_{29}$, 118.62:$C_{27}$, 119.64:$C_{11}$, 123.20:$C_{23}$, 123.31: $C_{12}$, 124.29:$C_{3,5}$, 124.78:$C_9$, 126.33:$C_8$ 127.10:$C_{15,19}$, 127.58:$C_{17}$, 128.21:$C_{34,38}$, 128.72: $C_{16,18}$, 128.73:$C_{35,37}$, 128.88:$C_{2,6}$, 129.00:$C_{22,24.}$ 130.40:$C_{28}$, 133.79:$C_{36}$, 135.07:$C_1$, 135.23:$C_{33}$, 135.99:$C_{14}$, 144.16:$C_{20}$, 144.34:$C_{26}$, 145.79:$C_7$, 147.12: C=N, 152.11:$C_4$, 156.33:$C_{10,}$ 159.25:$C_{30}$. $^{13}$C-DEPT NMR(ppm): -43.28:$CH_2$ of pyra., 64.58: CH of pyra., -69.21: O-$CH_2$-$C_{32}$, -71.02: O-$CH_2$-$C_{13}$, 112.39: $C_{31}$, 113.32:$C_{3,5}$, 114.12:$C_{29}$, 118.62:$C_{27}$, 119.64:$C_{11}$, 123.20:$C_{23}$, 123.31: $C_{12}$, 124.29:$C_{3,5}$, 124.78:$C_9$, 126.33:$C_8$, 127.58:$C_{17}$, 128.21:$C_{34,38}$, 128.72: $C_{16,18}$, 128.73:$C_{35,37}$, 128.88:$C_{2,6}$, 129.00:$C_{22,24.}$ 130.40:$C_{28}$.

**3-(4-(4-benzyloxy-3-chlorophenyldiazenyl) phenyl)-5-(4-(4-chlorobenzyloxy)phenyl)-1-phenyl-2-pyrazoline** (**4i**): $C_{41}H_{32}Cl_2N_4O_2$, m.p. 183-184, 94%, Time: 3h., FTIR/cm$^{-1}$: C=N: 1595. $^1$H-NMR(ppm): 3.17 (dd 1H $CH_2$-$H_a$), 3.85 (dd 1H $CH_2$-$H_b$), 5.03 (s 2H -O-$CH_2$-$C_{32}$), 5.27 (s 2H -O-$CH_2$-$C_{13}$), 5.34 (dd 1H CH-$H_x$), 6.81-8.10 (m 25H Ar-H). $^{13}$C-NMR(ppm): 43.35: $CH_2$ of pyra., 64.17: CH of pyra., 70.11: O-$CH_2$-$C_{32}$, 71.02: O-$CH_2$-$C_{13}$, 113.33: $C_{21,25}$, 115.51: $C_{28,30}$, 119.52: $C_{11}$, 123.19: $C_{23}$, 123.30: $C_{12}$, 124.28: $C_{3,5}$, 124.76: $C_9$, 126.30: $C_8$, 127.08: $C_{15,19}$, 127.10: $C_{17}$, 127.50: $C_{27,31}$, 128.02: $C_{34,38}$, 128.20: $C_{16,18}$, 128.61: $C_{35,37}$, 128.72: $C_{2,6}$, 128.97: $C_{22,24.}$ 134.66: $C_{36}$, 135.24: $C_1$, 135.52: $C_{33}$, 136.00: $C_{14,}$, 136.91: $C_{26}$, 144.36: $C_{20}$, 145.73:$C_7$, 147.14:C=N, 152.06: $C_4$, 156.30:$C_{10,}$ 158.36:$C_{29}$. $^{13}$C-DEPT NMR(ppm): -43.35: $CH_2$ of pyra., 64.17: CH of pyra., -70.11: O-$CH_2$-$C_{32}$, -

71.02: O-$CH_2$-$C_{13}$, 113.33: $C_{21,25}$, 115.51: $C_{28,30}$, 119.52: $C_{11}$, 123.19: $C_{23}$, 123.30: $C_{12}$, 124.28: $C_{3,5}$, 126.30: $C_8$, 127.08: $C_{15,19}$, 127.10: $C_{17}$, 127.50: $C_{27,31}$, 128.02: $C_{34,38}$, 128.20: $C_{16,18}$, 128.61: $C_{35,37}$, 128.72: $C_{2,6}$, 128.97: $C_{22,24}$.

## RESULTS AND DISCUSSION

Following to our interest in developing the construction of azo-pyrazoline scaffold compounds using one pot multi component synthesis technique, we herein report the synthesize and characterization of a series of new 1,3,5-trisubstituted pyrazoline compounds containing azo-linkages and benzyloxy moieties in high yields and shorten reaction times without isolation and recrystallization process of the intermediate α,β-unsaturated aromatic ketones using a one-pot synthesis protocol. Initially the starting material 4-[4`-benzyloxy-3-chlorophenyl]azoacetophenone (2) has previously been prepared and characterized spectrally [25]. Treating of (2) as a main component with phenylhydarzine and the corresponded substituted benzaldehydes (3a-i) in a single rector afforded the corresponding desired products azo-pyrazolines (4a-i) respectively as shown in Scheme 1.




**Scheme 1**

The structure of the target molecules were confirmed by using FT-IR, $^1$H-NMR, $^{13}$C-NMR and $^{13}$C-DEPT-135 spectral analyses. The IR spectra (Figure 1) of the target molecule azo-pyrazoline are very informative and furnished good evidence for the formation of the expected structures. The disappearance of carbonyl group band for both reactants and appearance of two new bands around 1595 and 1545 cm$^{-1}$ for aromatic C=C and imine

system are good evidences for the cyclization reaction giving 2-pyrazoline compounds. Further supports were obtained from $^{1}$H- NMR and $^{13}$C-NMR which provide diagnostic tools for positional elucidation of the proton and carbons. The $^{1}$H-NMR spectra (Figure 2) of pyrazoline ring shows three clear peakss as doublet to doublet (dd) signals for the protons $H_a$, $H_b$ and $H_c$ in the 2-pyrazoline as an (ABX) spin system at δ 3.2, 3.85, 5.25 ppm respectively for two geminal and one vicinal protons confirm the 2-pyrazoline ring formation [26]. On the other hand the $^{13}$C- NMR spectrum (Figure 3) shows two additional distinct picks for two carbons bearing ($H_{a,b}$ and $H_c$) at 43 and 64ppm for the pyrazoline ring structure [27]. Further support was came from a downward signal of $^{13}$C- DEPT spectrum (Figure 4) at (-43 ppm) for $CH_2$ group of the ring along with benzyloxy ($OCH_2$) group band at (-71 ppm).

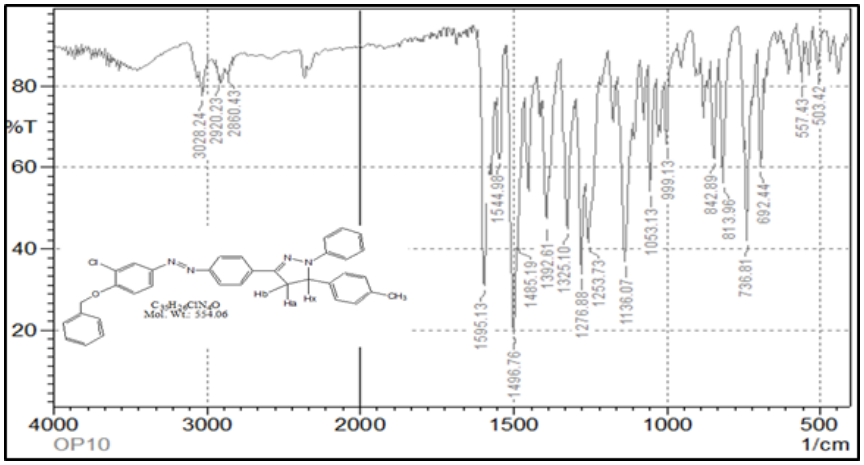



**Figure 1: IR spectrum of compound (4d)**

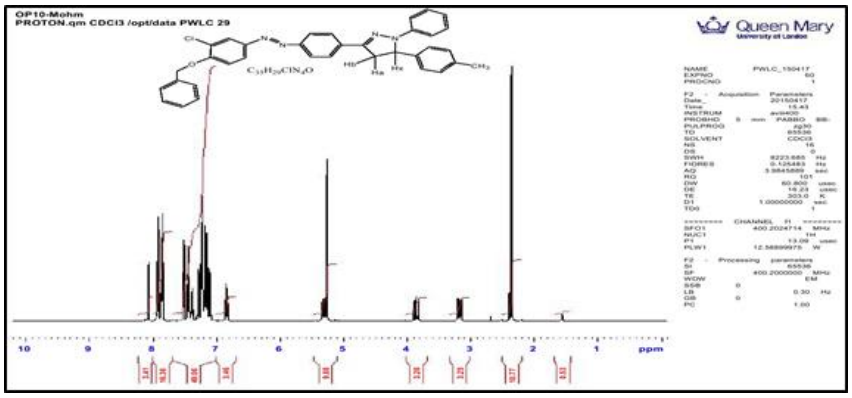



**Figure 2: $^{1}$H-NMR spectrum of compound (4d)**

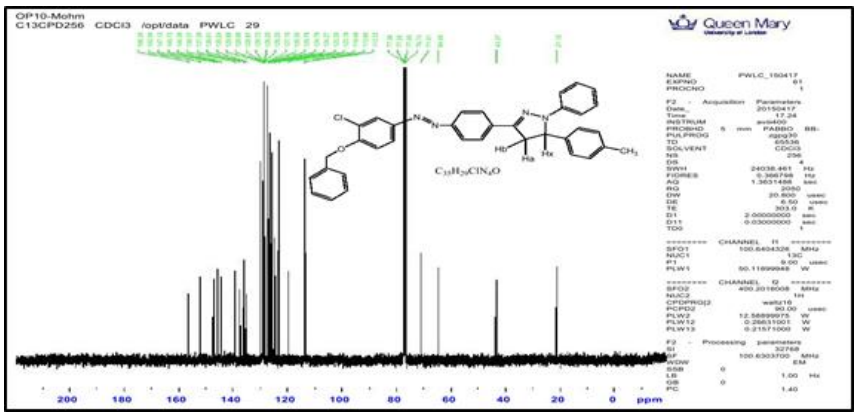



**Figure 3: $^{13}$C-NMR spectrum of compound (4d)**

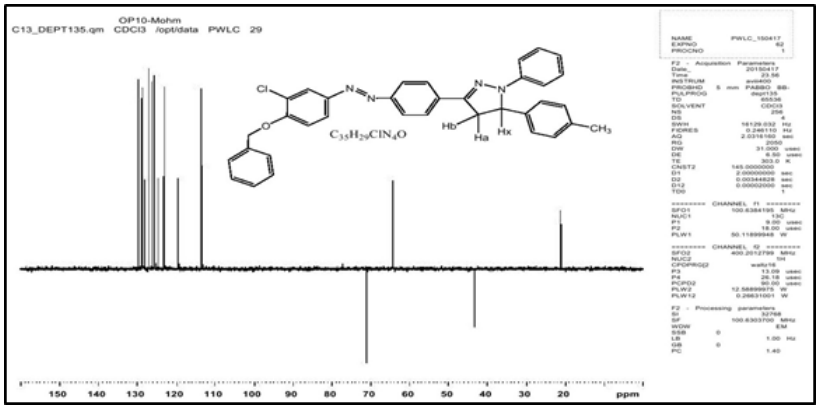



**Figure 4: $^{13}$C-DEPTNMR spectrum of compound (4d)**

## CONCLUSION

1,3,5-triisubstited prazoline derivatives containing azo-linkages and benzyloxy moieties were synthesized in excellent yields and short reaction times by using a one-pot synthesis strategy. It was observed that this technique is efficient, economic, fast, high yield, and reducing of some reactants, solvents and avoiding a long isolation and purification processes of chemical intermediates thereby preventing pollution and pay the way to green chemistry approach.

## ACKNOWLEDGEMENTS

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