

## Supplementary data

General experimental details and spectral data of all compounds associated with this article can be found as supplementary 10 informations.

(A) Typical Experimental Procedure

### Materials and Method:

All chemical were reagent grade purchased from Aldrich and Alfa Aesar and were used without purification. NMR spectra 15 were recorded on a BRUKER AVANCE II-400FT Spectrometer (400 for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR) using  $\text{CDCl}_3$  as solvent and TMS as an internal reference. Mass spectra were recorded on JEOL SX-102 (FAB) mass spectra at 70ev. All the reactions were monitored by TLC using pre coated sheets of 20 silica gel G/UV-254 of 0.25mm thickness (Merck 60F254). Melting points were determined by open glass capillary method and were uncorrected.

General Procedure-

**A general experimental procedure for the reaction of aldehyde (1), hydrazine (2) and alkyne (3) catalyzed by iodine is mentioned below**

To a 20ml round bottom flask, aldehyde 1a (1mmol), hydrazine 2a (1mmol), phenyl acetylene 3a (1mmol), water (5ml) and iodine (20mol %) were added successively. The reaction mixture 30 was stirred at  $60^\circ\text{C}$  and monitored periodically by TLC. Upon completion (normally 3-4 hr) water was removed under pressure and then the residue was purified by column chromatography(hexane/ethyl acetate) in silica gel to afford 1,3,5 trisubstituted pyrazoles.

**4 (a) 1,2,3-triphenylpyrazole:** pale yellow solid, mp  $136-140^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.97-7.92(\text{m}, 2\text{H}), 7.47-7.42(\text{m}, 2\text{H}), 7.39-7.28(\text{m}, 11\text{H}), 6.83(\text{s}, 1\text{H})$

ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta=152.1, 144.5, 140.3, 133.1, 130.6, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 127.5, 125.9, 125.4, 105.2$ , ppm; KBr, 40  $\text{IR}(\text{cm}^{-1})$  1680, 1640, 1620, 1530, 1490, 1420 MS:  $m/z=297[\text{M}+\text{H}^+]$

**4(b) 1-Phenyl-3-(4-nitrophenyl)-5-(4-methoxyphenyl)pyrazole:** yellow solid, mp 176-180 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=8.12-8.11$  (m, 2H), 7.91-7.90 (m, 2H) 7.45-7.29 (m, 2H), 7.24-7.19 (m, 2H), 7.11-7.08 (m, 3H), 6.73 (m, 2H), 6.65 (s, 1H), 3.66 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta=160.6, 148.9, 147.7, 145.1, 140.9, 139.2, 130.3, 128.9, 127.6, 125.8, 125.5, 124.3, 123.1, 114.6, 105.3, 54.3$  ppm; KBr, IR ( $\text{cm}^{-1}$ ) 2750, 1685, 1642, 1622, 1535, 1492, 1422, 1520, MS:  $m/z=372[\text{M}+\text{H}^+]$ .

**4 (c) 3-(4-Chlorophenyl)- 1,5-diphenyl pyrazole:** brown solid, 55 mp 144-145  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.87$  (d,  $J=8.4$  Hz, 2H), 7.39-7.28 (m, 12H), 6.81 (s, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta=151.0, 143.6, 139.8, 134.6, 131.8, 131.6, 130.1, 129.1, 128.8, 127.8, 127.2, 125.3, 122.1, 105.3$  ppm; KBr, IR ( $\text{cm}^{-1}$ ) 1682, 1643, 1628, 1534, 1495, 1426, 725 MS : $m/z=332[\text{M}+\text{H}^+]$ .

**4 (e) 3-(2-thienyl)-1, 5- Diphenyl -pyrazole:** yellow solid, mp 119-121 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.08-7.88$  (m, 13H), 6.86 (s, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta=150.6, 144.4, 140.2, 133.2, 130.6, 128.9, 128.7, 128.6, 128.5, 128.3, 127.4, 126.2, 125.8, 123.9, 108.2$ , ppm; KBr, IR ( $\text{cm}^{-1}$ ) 1684, 1639, 1624, 1538, 1485, 1423, 2210 MS:  $m/z=303[\text{M}+\text{H}^+]$ .

**4 (f) 1,2,3-triphenylpyrazole:** pale yellow solid, mp 138-140 $^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.96-7.91$  (m, 2H), 7.46-7.41 (m, 2H), 7.39-7.28 (m, 11H), 6.83 (s, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta=152.0, 144.4, 140.3, 133.1, 130.6, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 127.4, 125.9, 125.3, 105.2$ , ppm; KBr, IR ( $\text{cm}^{-1}$ ) 1679, 1647, 1621, 1533, 1489, 1421 MS:  $m/z=297[\text{M}+\text{H}^+]$

**4(g) 3-1,5- diphenyl –pyrazole (4- Methylphenyl):** white solid, mp 126-127 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ=8.26 (m, 2H), 7.4-7.29 (m, 6H), 7.06-6.95 (m, 6H), 6.85 (s, 1H), 2.26(s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):δ =151.8, 143.8, 140.6, 137.5, 131.3, 131.2, 131.0, 129.8, 128.9, 128.6, 128.3,127.6, 126.6, 126.3, 125.5, 105.6, 21.3 ppm; IR (cm<sup>-1</sup>) 2800, 1681, 1641, 1628, 1532, 1492, 1420 MS: m/z = 311 [M+H<sup>+</sup>].

**4(h) 1-(4-Methoxyphenyl)-3-phenyl-5-(4-fluorophenyl)pyrazole :** pale brown solid, mp 132-135°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 8.26 (m, 2H), 7.45 (m, 2H), 7.29(m, 3H), 7.11(m, 2H), 6.76(s, 1H),6.75-6.66 (m, 4H), 90 3.76(s, 3H) ppm ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ= 162.7, 158.9, 151.8, 143.1, 133.9, 133.5, 130.7, 128.8, 126.7, 125.9, 124.4, 123.1, 115.4, 114.1, 105.3, 54.7, ppm ; KBr, IR (cm<sup>-1</sup>) 2700, 1679, 1639, 1621, 1531, 1496, 1421, 625; MS : m/z = 345 [ M+H<sup>+</sup>].

**4(i). 3-(4-Methoxyphenyl)-1,5-diphenyl-pyrazole :** brown solid, mp 130-132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) :δ = 7.87 (d, J = 8.9 Hz, 2H) 7.39- 7.31 (m, 10H), 6.98 (d, J = 8.9 Hz, 2H),6.77 (s, 1H), 3,86 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ=159.6, 100 151.8, 144.3, 139.8, 130.6, 128.9, 128.7, 128.5, 128.4, 127.3, 127.1, 125.8, 125.3, 113.9, 104.5, 55.2 ppm; KBr, IR (cm<sup>-1</sup>); 2820, 1680, 1640, 1620, 1530, 1490, 1420 MS: m/z =327 [M+H<sup>+</sup>].

**4(j). 3-(4-Nitrophenyl)-1,5-Diphenyl-pyrazole :** yellow solid, mp 161-163°C. <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>): δ=7.98-7.95(m, 2H), 7.78-7.74(m, 3H), 7.25-7.13(m, 4H), 7.05-6.91(m, 5H), 6.49(s,1H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>): δ=154.5, ,149.8, 147.5, 144.6, 140.8, 139.1, 132.6, 130.2, 128.9, 128.5, 127.6, 125.9, 110125.6, 124.3, 105.2 ppm; KBr, IR (cm<sup>-1</sup>) 1677, 1638, 1628, 1537, 1525, 1492, 1421 MS: m/z = 342 [M+H<sup>+</sup>]

**4(k) 5-(4-Methoxyphenyl)- 1, 3-diphenyl- pyrazole :** pale yellow solid, mp 77-79°C. <sup>1</sup> H NMR (400 MHz, CDCl<sub>3</sub>): δ= 7.83(d, J = 8.9 Hz, 2H), 7.35-7.29 (m, 4H), 7.24-7.09 (m, 6H), 6.84(d, J = 8.9 Hz, 2H),6.73 (s, 1H) 3.69 (s, 3H) ppm; <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>): δ=159.5,

151.8, 144.2, 140.2, 133.2, 129.9, 128.8, 128.5, 127.8, 127.6, 126.1, 125.4, 122.9, 113.9, 105.5, 55.5 ppm; KBr, IR (cm<sup>-1</sup>); 2700, 1678, 1638, 1619, 1532, 1491, 1419 MS: m/z = 327 [M+H<sup>+</sup>].

**4(l). 5-butyl- 1,3- diphenyl- pyrazole :** colourless solid, mp 51- 52<sup>0</sup>C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 7.78 (d, J = 7.7 Hz, 2H), 7.41- 7.38 (m, 4H) , 7.34-7.29 (m, 3H) , 7.23 (t, J = 7.3 Hz, 1H), 6.45(s, 1H), 2.58 (t, J = 7.6 Hz, 2H) , 1.51-1.57 (m, 2H), 1.25- 1.29 (m, 2H), 0.83(t, J = 7.5 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 151.3, 145.7, 139.8, 133.2, 129.1, 128.5, 127.9, 127.7, 125.7, 125.5, 102.7, 30.8, 25.9, 22.3, 13.7 ppm; KBr, IR (cm<sup>-1</sup>) 2900, 1681, 1644, 1622, 1531, 1489, 1422; MS: m/z = 277 [M+H<sup>+</sup>].

**4m. 5-(4- fluorophenyl)- 1,3-diphenyl- pyrazole:** pale yellow solid, mp 141-143<sup>0</sup>C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 8.27 (m, 2H), 7.39- 7.28 (m, 5H), 7.13- 6.98 (m, 5H), 6.73 (s, 1H), 6.71 (m, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 160.6, 151.2, 143.8, 140.2, 134.8, 130.7, 128.8, 128.6, 128.4, 127.5, 126.3, 125.2, 124.9, 115.6, 105.0 ppm; KBr, IR (cm<sup>-1</sup>) 1675, 1652, 1629, 1532, 1494, 1421, 630; MS = 315 [M+H<sup>+</sup>].

**4(n) 5-(4-bromoxyphenyl) - 1, 3- diphenyl- pyrazole :** pale yellow solid, mp 126-128<sup>0</sup>C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 7.87 (d, 2H, J=8.6 Hz), 7.34-7.21 (m, 12H), 6.76 (s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 151.9, 144.2, 140.2, 133.7, 131.7, 130.8, 129.2, 128.6, 128.3, 127.1, 126.3, 125.2, 124.9, 123.8, 105.3 ppm; KBr, IR (cm<sup>-1</sup>) 1686, 1641, 1627, 1533, 1494, 1425, 530 MS: m/z = 315[M+H<sup>+</sup>].

**4(o) 5-(4-Methylphenyl)-1,3-diphenyl-pyrazole:** white solid, mp 115-116<sup>0</sup>C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ= 7.93 (d, 2H, J=8.4 Hz), 7.38-7.33 (m, 12H), 6.78 (s, 1H), 2.37(s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 150.90, 142.99, 140.2, 135.6, 134.7, 132.8, 128.9, 127.6, 127.3, 126.1, 125.3, 125.7, 124.9, 124.8, 105.1, 20.5 ppm; KBr, IR (cm<sup>-1</sup>) 2840, 1677, 1638, 1621, 1538, 1497, 1423 MS: m/z = 311[M+H<sup>+</sup>].