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# DESIGN AN EFFICIENT METHOD FOR THE SYNTHESIS OF 2-(1,3-DIPHENYL-1*H*-PYRAZOL-4-YL)BENZO[D]THIAZOLE AND ITS BIOLOGICAL EVALUATION

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**ABSTRACT:**
Twenty new 2-(1,3-diphenyl-1*H*-pyrazol-4-yl)benzo[d]thiazole derivatives were synthesized with usingGadolinium(III) trifluoromethanesulfonateas a catalyst in ethanol solvent by optimized and it is highly efficient and environmentally friendly one potreaction method. Moreover, these new compound were an evaluation for their antimicrobial activity. Among these twenty compounds some derivatives were showed excellent antimicrobial activity on both Gram-positive and gram-negative bacterial strains.All these new products structures are confirmed by spectral analysis. By this one-pot synthetic method, we achieved pyrazolo benzo thiazole derivatives with more operational simplicity, short reaction time and good yields (up to 93%).

**KEYWORDS:**Anti-microbial, Gadolinium (III), Benzothiazoles, pyrazoles, one pot reactions

## INTRODUCTION

Benzothiazoles are important heterocyclic compounds and it has in their usage as a core construction for diversified valuableapplications[I] in the area of drug discovery and pharmaceutical chemistry such as including antimicrobial[II-IV] and antifungal,[V]cytotoxic,[VI] and antidiabetic[VII] applications and also substituted benzo thiazole have been designed and synthesized for biological evaluations[VIII]. Pyrazoles are the privileged compounds for the pharmaceutical and agricultural research[IX-XIV], such as Celebrex, Viagra, Zometapine, Cyenopyrafen,Fenpyroximate and Tebufenpyrad and pyrazole containing compounds in the field of medicinal chemistry such as anticancer[XV], and antimicrobial activities[XVI-XXII]

## EXPERIMENTAL SECTION

Chemical reagents were purchased from Sigma–Aldrich and were used without further purification. Solvents for extraction and column chromatography were distilled prior to use. TLC analysis were performed with silica gel plates (0.25 mm, E. Merck, 60 F254) using ninhydrine, *p*-anisaldehyde, $KMnO_4$, iodine, and UV lamp for visualization. $^1H$ and $^{13}C$ NMR experiments were performed on 300 or 500 and 75 or 125 MHz respectively, on a Bruker Avance. Chemical shifts are reported in parts per million (ppm) downstream from the internal tetramethylsilane standard. Spin multiplicities are described as s (singlet), bs (broad singlet), d (doublet), dd (double doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants are reported in Hertz (Hz).

## RESULTS AND DISCUSSIONS

The reaction optimization conditions was developed for the synthesis of 2-(1,3-diphenyl-1H-pyrazol-4-yl) benzo[d]thiazole derivatives by using Gadolinium (III) trifluoromethanesulfonate catalyst. By the condensation of benzo-thiazole and synthesized aldehydes in the simple reaction condition, in the presence of ethanol reflux for 6h offered the final required compound in excellent yield 93%, and then it was purified by the column chromatography.

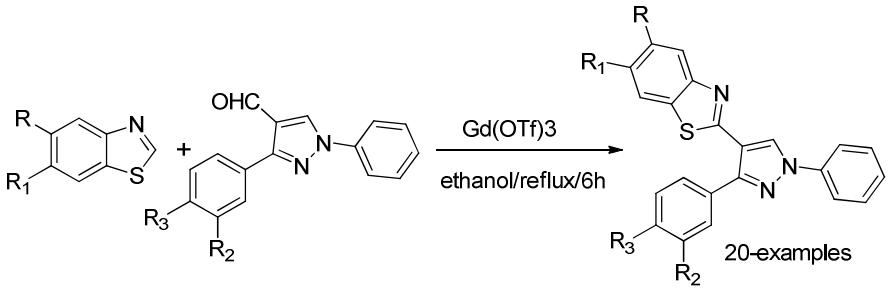


**Table 1:** Optimization of reaction conditions for the formation of required compound

| Entry | Solvent | Catalyst | Temperature (°C) | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|
| 1 | - | - | RT | 12 | - |
| 2 | $CH_3CN$ | - | RT | 12 | - |
| 3 | Methanol | - | Reflux | 10 | 28 |
| 4 | Ethanol | - | Reflux | 10 | 32 |
| 5 | -- | Gd(OTf)3 | 50 | 6 | 56 |
| 6 | $CH_3CN$ | $Cu(OTf)_3$ | Reflux | 6 | 53 |
| 7 | Methanol | Gd(OTf)3 | Reflux | 6 | 59 |
| 8 | Ethanol | $ZnCl_2$ | Reflux | 6 | 43 |
| 9 | Methanol | $Na_2S_2O_5$ | RT | 6 | 52 |
| 10 | Ethanol | HCl | Reflux | 6 | 71 |
| 11 | Methanol | Acetic acid | RT | 6 | 47 |
| **12** | **Ethanol** | **Gd(OTf)3** | **Reflux** | **6** | **93** |
| 13 | Methanol | CAN | Reflux | 6 | 81 |
| 14 | Ethanol | CAN | Reflux | 6 | 80 |

### General reaction procedure for the preparation of compounds

The reaction was performed using Benzothiazoles(1) and corresponding aldehydes (2) in various solvents at diverse conditions are revealed in Table-1. The reaction was approved in

the presence of gadolinium triflouoromethane sulfonate in ethanol reflux for 6h which provided good to excellent yields.

**Spectral data of the synthesised compounds**

**2-(1,3-diphenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3a):** light White solid, yield 93 %, Mp: 172-175 $^1$H NMR (300 MHz, DMSO-d6) d 8.57 (s, 1H), 7.80 & 7.71 (m, 4H), 7.54 (1 Hz, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.33 & 7.20 (m, 4H), 7.23 (d, 2H). $^{13}$C NMR (75 MHz, DMSO-d6) d 150.1, 146.3, 137.7, 136.3, 132.8, 129.8, 128.7, 127.1, 126.7, 125.3, 120.5,117.1, 115.2, 111.3. MS (ESI): m/z 353 [M+H]. HRMS (ESI) calcd for$C_{22}H_{15}N_3S$found: 353.10.Found, %: C, 74.66; H, 4.24; N, 11.84; S, 9.03. $C_{22}H_{14}FN_3S$. Calculated, %: C, 74.76; H, 4.28; N, 11.89; S, 9.07.ESI-HRMS: m/z $[M + H]^+$ = 353.04 (Calcd $M^+$ = 353.10)

**2-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3b):**Yield 77 %, brown Colour solid, mp 185-187$^0$C.$^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.53 (s, 1H), 7.70 (d, 2H), 7.69-7.70 (m, 2H), 7.60-7.49 (m, 6H), 7.27 (t, 2H), 7.03-6.93 (m, 1H). $^{13}$C NMR (75 MHz, DMSO-d6), δ, ppm: 160.1, 158.9, 151.7, 147.8, 138.3, 131.5, 131.3,128.4,128.9,127.1,126.8,125.9, 125.6,124.6, 124.4,118.2, 118.1,116.5,115.0,111.7. Found, %: C, 71.14; H, 3.80; F, 5.11; N, 11.31; S, 8.63. $C_{22}H_{14}FN_3S$. Calculated, %: C, 71.12; H, 3.81; F, 5.12; N, 11.30; S, 8.64.ESI-HRMS: m/z $[M + H]^+$ = 371.10 (Calcd $M^+$ = 371.09)

**2-(1-phenyl-3-(p-tolyl)-1H-pyrazol-4-yl)benzo[d]thiazole (3c):** Yield 73 %, light yellow solid, mp: 170-173$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz): 8.70 (s, 1H), 7.67 (d, J= 7.5 Hz, 2H), 7.59 (d, J = 3.1 Hz, 2H), 7.53-7.49 (m, 6H), 7.44 (d, J=7.3 Hz, 2H), 7.6 (d, 1H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-d6) δ, ppm:150.7, 146.8, 138.2, 133.8, 130.3, 131.6, 130.0, 129.8, 128.2, 127.4, 127.1, 126.5, 125.1, 120.3, 119.8, 117.8, 113.6, 23.6.; Found, %: C, 75.18; H, 4.66; N, 11.44; S, 8.73. $C_{23}H_{17}N_3S$. Calculated, %: C, 75.19; H, 4.65; N, 11.45; S, 8.72.ESI-HRMS: m/z $[M + H]^+$ = 367.07 (Calcd $M^+$ = 367.11)

**2-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3d):** Yield 70 %, yellow solid, mp 189-190$^0$C, $^1$HNMR (400 MHz, DMSO-d6) δ, ppm (*J*, Hz): 8.57 (s, 1H), 7.80-7.75 (m, 2H), 7.70 (d,J = 5.8, Hz, 2H), 7.63-7.54 (m, 6H), 7.44 (t, J= 7.5 Hz, 2H),6.88 (d, J= 2.4 Hz, 1H), 3.73 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-d6)δ, ppm:157.5, 151.3, 146.6, 138.1, 133.2, 130.6, 129.8, 128.0, 127.7, 126.9,125.4, 125.9, 119.6, 119.3, 117.8, 115.9, 111.2, 56.8.; Found, %: C, 72.04; H, 4.47; N, 10.96; O, 4.17; S, 8.36. $C_{23}H_{17}N_3OS$. Calculated, %: C, 72.06; H, 4.46; N, 10.95; O, 4.16; S, 8.37.ESI-HRMS: m/z $[M + H]^+$ = 383.05 (Calcd $M^+$ = 383.11)

**6-chloro-2-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3e):** Yield 79%, yellow solid, mp188-190$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.37 (s, 1H), 7.72 (d,J= 7.64 Hz, 2H), 7.50-7.39 (m, 4H), 7.26-7.14 (m, 3H), 7.18 (d,J= 7.6 Hz, 1H), 6.56 (d, J = 8.5 Hz, 2H), 3.68 (s, 3H). $^{13}$C NMR(75 MHz, DMSO-d6) δ, ppm:161.1, 157.7, 146.0, 138.2, 131.5, 127.4, 127.1, 126.7,126.01, 124.3, 123.1, 118.4, 114.4, 112.5, 56.2; Found, %: C, 66.10; H, 3.86; Cl, 8.48; N, 10.05; O, 3.83; S, 7.67. $C_{23}H_{16}ClN_3OS$. Calculated, %: C, 66.11; H, 3.85; Cl, 8.46; N, 10.04; O, 3.81; S, 7.68.ESI-HRMS: m/z $[M + H]^+$ = 417.02 (Calcd $M^+$ = 417.07)

**6-fluoro-2-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3f):** Yield 70 %, brown solid, mp171-174$^0$C, $^1$H NMR (500 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.74 (s, 1H), 7.83 (d,J= 7.9 Hz, 2H), 7.73 (d, J= 8.44 Hz, 2H), 7.57-7.43 (m, 4H), 7.39 (t,J = 7.4 Hz, 1H), 7.02-6.85 (m, 3H), 3.90 (s, 3H); $^{13}$C NMR (125 MHz,DMSO-d6) δ, ppm:161.2, 160.9, 159.3, 151.7, 148.2, 140.3, 139.6, 129.7, 128.1,121.8, 120.6, 119.8, 117.9, 113.3, 118.6, 110.2, 54.1.;Found, %: C, 68.81; H, 4.02; F, 4.73; N, 10.47; O, 3.99; S, 7.99. $C_{23}H_{16}FN_3OS$. Calculated, %: C, 68.80; H, 4.02; F, 4.74; N, 10.48; O, 3.98; S, 7.99.ESI-HRMS: m/z $[M + H]^+$ = 401.05 (Calcd $M^+$ = 401.10)

**2-(1,3-diphenyl-1H-pyrazol-4-yl)-6-chlorobenzo[d]thiazole(3g):**Yield 80 %, brown Colour solid, mp 187-190$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz): 8.54 (s, 1H), 7.60 (d, 2H), 7.59-7.70 (m, 2H), 7.50-7.49 (m, 6H), 7.27 (t, 2H), 7.03-6.63 (m, 1H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm: 161.1, 159.9, 152.7, 148.8, 139.3, 132.3,129.4,128.9,128.1,126.8,125.6,124.4,119.1,118.5,116.0,112.7.; Found, %: C, 68.11; H, 3.65; Cl, 9.16; N, 10.82; S, 8.26. $C_{22}H_{14}ClN_3S$. Calculated, %: C, 68.12; H, 3.64; Cl, 9.14; N, 10.83; S, 8.27.ESI-HRMS: m/z $[M + H]^+$ = 387.02 (Calcd $M^+$ = 387.06)

**2-(1,3-diphenyl-1H-pyrazol-4-yl)-6-fluorobenzo[d]thiazole(3h):**Yield 72%, light White solid, mp 191-193$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.77 (s, 1H), 7.67 (d, J =7.5 Hz, 2H), 7.78 (d, J = 6.5, 3.0 Hz, 2H), 7.55-7.42 (m, 6H), 7.45 (t, J =7.4 Hz, 2H), 7.20 (d, J =7.4 Hz, 1H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm:151.1, 148.4, 139.2, 132.4, 129.8, 127.7, 127.1, 126.6, 126.31, 123.6, 116.1, 112.8,110.4; Found, %: C, 71.14; H, 3.80; F, 5.11; N, 11.31; S, 8.63. $C_{22}H_{14}FN_3S$. Calculated, %: C, 71.12; H, 3.81; F, 5.12; N, 11.30; S, 8.64.ESI-HRMS: m/z $[M + H]^+$ = 371.10 (Calcd $M^+$ = 371.09)

**6-chloro-2-(1-phenyl-3-(p-tolyl)-1H-pyrazol-4-yl)benzo[d]thiazole (3i):**Yield 72%, **b**rown solid, mp 180-183$^0$C, $^1$H NMR (500 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.45 (s, 1H),7.68-7.59 (m, 4H), 7.38 (d, J= 7.3 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H),7.30-7.32 (m, 2H), 7.06 (d, J = 8.0, Hz, 1H), 6.78 (t,2H), 2.54 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-d6) δ, ppm:162.1, 161.1, 148.2, 144.21, 138.1, 130.1, 129.4, 128.3, 127.5, 125.8, 124.4, 124.1, 123.2, 118.0, 116.9, 115.8, 113.7, 23.6; Found, %: C, 68.75; H, 4.01; Cl, 8.80; N, 10.47; S, 7.97. $C_{23}H_{16}ClN_3S$. Calculated, %: C, 68.73; H, 4.01; Cl, 8.82; N, 10.46; S, 7.98.ESI-HRMS: m/z $[M + H]^+$ = 401.3 (Calcd $M^+$ = 401.08)

**6-fluoro-2-(1-phenyl-3-(p-tolyl)-1H-pyrazol-4-yl)benzo[d]thiazole(3j):** yellow solid, yield 70 %, Mp: 173-176, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz): 8.58 (s, 1H), 7.73 (d, J= 7.6 Hz, 2H), 7.53 (d, J= 8.4 Hz, 2H), 7.40-7.32 (m, 7H), 7.18 (d, J = 8.22 Hz, 1H), 2.56 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm: 149.1, 146.1, 139.0, 133.6, 131.4, 130.0, 128.6, 128.1, 127.0, 125.7, 122.3, 116.5, 1112.9, 20.4; Found, %: C, 71.69; H, 4.17; F, 4.92; N, 10.91; S, 8.31. $C_{23}H_{16}FN_3S$. Calculated, %: C, 71.67; H, 4.18; F, 4.93; N, 10.90; S, 8.32.ESI-HRMS: m/z $[M + H]^+$ = 385.05 (Calcd $M^+$ = 385.10)

**5,6-dichloro-2-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole(3k):**Yield 69 %, light red solid, mp 206-209$^0$C, $^1$H NMR (500 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.63 (s, 1H), 7.85 (d, J =7.7 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.63 (s, 2H), 7.19 (d, J = 5.1 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.95-6.76 (m, 2H), 3.71 (s, 3H).$^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm:152.3, 151.3, 149.0, 137.8, 128.2, 129.1, 126.5, 123.7, 122.2, 118.2, 113.1, 111.8, 54.7.; Found, %: C, 61.09; H, 3.31; Cl, 15.66; N, 9.28; O, 3.55; S, 7.09. $C_{23}H_{15}Cl_2N_3OS$. Calculated, %: C, 61.07; H, 3.34; Cl, 15.67; N, 9.29; O, 3.54; S, 7.09.ESI-HRMS: m/z $[M + H]^+$ = 451.01 (Calcd $M^+$ = 451.03)

**6-methyl-2-(3-(4-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3l):**Yield 70 %, brown solid, mp 184-185$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.45 (s, 1H), 7.68-7.59 (m, 4H), 7.40 (d, J =7.3 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 7.38-7.32 (m, 2H), 7.06 (d, J = 8.2,Hz, 1H), 6.88 (t, J = 8.49 Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm:165.1, 164.1, 148.8, 146.23, 139.3, 132.8, 130.1, 130.3, 128.5, 127.8, 127.4, 127.1, 124.4, 119.0, 115.4, 115.1, 112.8, 21.6.; Found, %: C, 66.97; H, 3.91; N, 13.58; O, 7.76; S, 7.77. $C_{23}H_{16}FN_4O_2S$. Calculated, %: C, 66.97; H, 3.91; N, 13.58; O, 7.76; S, 7.77.ESI-HRMS: m/z $[M + H]^+$ = 412 (Calcd $M^+$ = 412.10)

**6-chloro-2-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3m)**: Yield 75 %, white solid, mp 191-195$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.72 (s, 1H), 7.55 (d,J = 7.7 Hz, 2H), 7.69-7.52 (m, 2H), 7.44-7.45 (m, 3H), 7.38-7.31 (m,2H), 7.13e7.09 (m, 2H), 6.10 (t, J= 8.5 Hz, 1H); 13C NMR (75 MHz, DMSO-d6) δ, ppm: 161.5,

160.3 ,148.1, 145.4, 138.0, 137.8, 135.0, 129.4,128.2, 127.8, 126.7, 122.3, 118.0, 114.5, 113.2, 109.1; Found, %: C, 65.11; H, 3.22; Cl, 8.73; F, 4.68; N, 10.35; S, 7.90. $C_{22}H_{13}ClFN_3S$. Calculated, %: C, 65.10; H, 3.23; Cl, 8.73; F, 4.68; N, 10.35; S, 7.90.ESI-HRMS: m/z $[M + H]^+$ = 405 (Calcd $M^+$ = 405.05)

**2-(3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)-6-methylbenzo[d]thiazole(3n):**Yield 69 %, brown solid, mp 183-185$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.45 (s, 1H), 7.68-7.59 (m, 4H), 7.40 (d, J =7.3 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 7.38-7.32 (m, 2H), 7.06 (d, J = 8.2,Hz, 1H), 6.88 (t,J= 8.49 Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm:165.1, 164.1, 148.8, 146.23, 139.3, 132.8, 130.1, 130.3, 128.5, 127.8, 127.4, 127.1, 124.4, 119.0, 115.4, 115.1, 112.8, 21.9; Found, %: C, 71.67; H, 4.18; F, 4.93; N, 10.90; S, 8.32. $C_{23}H_{16}FN_3S$. Calculated, %: C, 71.69; H, 4.19; F, 4.91; N, 10.90; S, 8.31.ESI-HRMS: m/z $[M + H]^+$ = 385 (Calcd $M^+$ = 385.10)

**2-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)-6-methoxybenzo[d]thiazole (3o)**: Yield 71 %, Light yellow solid, mp 188-190$^0$C, 1H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.57 (s, 1H), 7.72 (d,J= 7.74 Hz, 2H), 7.50-7.49 (m, 4H), 7.24 (m, 3H), 7.18 (d, J = 7.6 Hz, 1H), 6.49 (d, J = 8.3 Hz, 2H), 3.75 (s, 3H). $^{13}$C NMR(75 MHz, DMSO-d6) δ, ppm:162.1, 157.7, 149.0, 139.2, 129.1, 129.2, 128.6, 127.1,126.1, 126.2, 123.5, 118.2, 112.2, 112.9, 55.9.Found, %: C, 66.10; H, 3.86; Cl, 8.48; N, 10.05; O, 3.83; S, 7.67. $C_{23}H_{16}ClN_3OS$. Calculated, %: C, 66.12; H, 3.85; Cl, 8.46; N, 10.06; O, 3.83; S, 7.67.ESI-HRMS: m/z $[M + H]^+$ = 417.01 (Calcd $M^+$ = 417.07)

**6-chloro-2-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3p)** Yield 75 %, white solid, mp 191-195$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.72 (s, 1H), 7.55 (d,J = 7.7 Hz, 2H), 7.69-7.52 (m, 2H), 7.44-7.45 (m, 3H), 7.38-7.31 (m,2H), 7.13e7.09 (m, 2H), 6.10 (t, J= 8.5 Hz, 1H); 13C NMR (75 MHz, DMSO-d6) δ, ppm: 161.5, 160.3 ,148.1, 145.4, 138.0, 137.8, 135.0, 129.4,128.2, 127.8, 126.7, 122.3, 118.0, 114.5, 113.2, 109.1; Found, %: C, 62.59; H, 3.10; Cl, 16.78; N, 9.94; S, 7.59. $C_{22}H_{13}Cl_2N_3S$. Calculated, %: C, 62.57; H, 3.10; Cl, 16.79; N, 9.95; S, 7.59.ESI-HRMS: m/z $[M + H]^+$ = 421 (Calcd $M^+$ = 421.02)

**5,6-dichloro-2-(1,3-diphenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3q):**yield 68 %, light redsolid,Mp 213-215$^0$C, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz): 8.93 (s, 1H), 7.72 (m, 5H), 7.28 (s, 2H), 7.16 (t, J =7.8 Hz, 2H), 7.38 (m, 3H); $^{13}$C NMR (75 MHz,DMSO) δ, ppm: 151.1, 148.4, 139.4, 135.4, 129.8, 126.7, 125.7, 124.6, 123.3, 122.6, 119.1, 111.9.Found, %: C, 62.57; H, 3.10; Cl, 16.79; N, 9.95; S, 7.59. $C_{22}H_{13}Cl_2N_3S$. Calculated, %: C, 62.59; H, 3.10; Cl, 16.78; N, 9.94; S, 7.59.ESI-HRMS: m/z $[M + H]^+$ = 420.99 (Calcd $M^+$ = 421.02)

**5,6-dichloro-2-(1-phenyl-3-(p-tolyl)-1H-pyrazol-4-yl)benzo[d]thiazole (3r):**yellow solid, yield 74 %, Mp: 180-185, 1H NMR (500 MHz, CDCl3) 8.45 (s, 1H), 7.68-7.49 (m, 4H), 7.40 (d, J =7.4 Hz, 1H), 7.34 (t, J = 7.1Hz, 2H), 7.38 (m, 2H), 7.06 (d, J = 8.2,Hz, 1H), 6.88 (t, J = 8.39 Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (75 MHz, CDCl3) 165.1, 164.1, 147.8, 146.23, 139.3, 132.4, 130.1, 130.5, 128.5, 127.3, 127.4, 127.7, 124.4, 119.0, 115.4, 115.1, 112.2, 21.4.; Found, %: C, 63.31; H, 3.46; Cl, 16.25; N, 9.63; S, 7.35. $C_{23}H_{15}Cl_2N_3S$. Calculated, %: C, 63.31; H, 3.46; Cl, 16.25; N, 9.63; S, 7.35.ESI-HRMS: m/z $[M + H]^+$ = 435 (Calcd $M^+$ = 435.04)

**5,6-dichloro-2-(1,3-diphenyl-1H-pyrazol-4-yl)benzo[d]thiazole(3s):**Yield 74 %, yellow solid, mp 180-185$^0$C, 1H NMR (500 MHz, DMSO-d6) δ, ppm (*J*, Hz):8.45 (s, 1H), 7.68-7.49 (m, 4H), 7.40 (d, J =7.4 Hz, 1H), 7.34 (t, J = 7.1Hz, 2H), 7.38 (m, 2H), 7.06 (d, J = 8.2,Hz, 1H), 6.88 (t, J = 8.39 Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm:165.1, 164.1, 147.8, 146.23, 139.3, 132.4, 130.1, 130.5, 128.5, 127.3, 127.4, 127.7, 124.4, 119.0, 115.4, 115.1, 112.2, 21.4.; Found, %: C, 62.57; H, 3.10; Cl, 16.79; N, 9.95; S, 7.59.

$C_{22}H_{13}Cl_2N_3S$. Calculated, %: C, 62.58; H, 3.11; Cl, 16.77; N, 9.96; S, 7.57.ESI-HRMS: m/z $[M + H]^+$ = 421.01 (Calcd $M^+$ = 421.02)

**5,6-dichloro-2-(3-(4-chlorophenyl)-1-phenyl-1H-pyrazol-4-yl)benzo[d]thiazole (3t):** yellow solid, yield 76 %, mp: 192-190, $^1$H NMR (300 MHz, DMSO-d6) δ, ppm (*J*, Hz): 8.59 (s, 1H), 7.92 (m,4H), 7.63 (s, 1H), 7.32 (t, J = 7.74 Hz, 2H) 7.32 (m, 4H). $^{13}$C NMR (75 MHz, DMSO-d6) δ, ppm:165.1, 164.1, 147.8, 146.23, 139.3, 134.4, 132.4, 130.1, 130.5, 127.3, 127.4, 127.7, 124.4, 119.0, 115.4, 115.1, 112.2, 21.4. Found, %: C, 57.85; H, 2.65; Cl, 23.28; N, 9.20; S, 7.02. $C_{22}H_{12}Cl_3N_3S$. Calculated, %: C, 57.87; H, 2.64; Cl, 23.27; N, 9.21; S, 7.01.ESI-HRMS: m/z $[M + H]^+$ = 456.93 (Calcd $M^+$ = 456.98)

**Table 2:Antimicrobial activity of the compounds against microbial strains**

| **Compound** | Minimum Inhibitory Concentration (MIC, µg/ml) | | |
|---|---|---|---|
| | *M.l* | *K.p* | *C.a* |
| **3a** | 3.2 | 3.8 | 7.8 |
| **3b** | 3.2 | 1.6 | 3.6 |
| **3c** | 3.2 | 1.6 | 1.8 |
| **3d** | 1.8 | 1.8 | 0.9 |
| **3e** | 3.8 | 3.8 | 3.8 |
| **3f** | 1.8 | 1.8 | 0.9 |
| **3g** | 3.2 | 3.2 | 7.8 |
| **3h** | 3.2 | 3.2 | 0.9 |
| **3i** | 3.2 | 3.2 | 3.8 |
| **3j** | 3.2 | 3.2 | 3.2 |
| **3k** | 3.2 | 3.2 | 6.5 |
| **3l** | 1.8 | 1.8 | 1.8 |
| **3m** | 1.8 | 7.8 | 3.6 |
| **3n** | 3.2 | 3.6 | 1.8 |
| **3o** | 7.8 | 1.8 | 0.9 |
| **3p** | 3.6 | 6.5 | 3.8 |
| **3q** | 1.8 | 3.8 | 7.8 |
| **3r** | 6.5 | 7.8 | 7.8 |
| **3s** | 1.8 | 1.8 | 3.6 |
| **3t** | 1.8 | 1.8 | 1.8 |
| Ampicillin | 1.8 | 1.8 | - |
| Miconazole | 1.2 | 1.2 | 0.9 |

Micrococcus luteus, MTCC 2470, KlebsiellaplanticolaMTCC 530, Candida albicansMTCC 3017.

## BIOLOGICAL STUDIES

### Antimicrobial activity,

All the synthesized 2-(1,3-diphenyl-1H-pyrazol-4-yl)benzo[d]thiazolederivatives were evaluated for their antibacterial activity using well diffusion methodagainst both Gram-positive bacterial strains all the compounds were evaluated for their antifungal potential against the fungal strain *Candida albicans*MTCC 3017 in comparison with Miconazole as standard drug. In this case, the compounds **3d, 3f, 3h** and **3o** showed potent antimicrobial activity with MIC values 1.8 µg/mL.

## CONCLUSION

In conclusion, a simple, efficient and eco-friendly method for the synthesis of 2-(1,3-diphenyl-1H-pyrazol-4-yl)benzo[d]thiazole was developed by gadolinium triflouoromethane sulfonate as a catalyst in ethanol at reflux condition. By using the method we prepared twenty compounds and evaluation for their antimicrobial activity among these twenty compounds some derivatives were showed excellent antimicrobial activity on both Gram-positive and Gram-negative bacterial strains. The compounds 3d, 3f, 3h, 3s and 3t showed potent antimicrobial activity with MIC values 1.8 µg/mL.

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