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Catalyst Free Synthesis of Thioamides from Pyrazole Aldehydes using DMSO as Solvent

S. HELEN PERCI*, K. GUNSUNDARI, P. MONISHA and S. JAYANTHI

Department of Chemistry, A.V.V.M. Sri Pushpam College (Autonomous) (Affiliated to Bharathidasan University, Tiruchirapalli), Poondi, Thanjavur-613503, India

*Corresponding author: E-mail: shelenperci9862@gmail.com

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A straightforward synthetic procedure for thioamides has been developed at 100 ºC using pyrazole aldehyde, a secondary amine, precipitated elemental sulphur and DMSO as solvent. The Willgerodt-Kindler reaction was successfully carried out by increasing the mole ratio of the precipitated sulphur and amine derivatives. The synthesized thioamides derivatives were characterized by ^{1}H and ^{13}C NMR, FT IR, HRMS spectrometric techniques. This method has various advantages, including high yields, a relatively rapid reaction time and the ability to operate in catalyst-free conditions.

Keywords: Pyrazolealdehydes, Sulphur Powder, Thioamide, Pyrrolidine.

INTRODUCTION

Recent reviews suggested the importance of one-pot multi-component strategy for many new organic reactions for novel drug-like compounds [1,2]. Multicomponent reactions (MCRs) have played an essential role in biologically relevant advances in the pharmaceutical, medical, agricultural and chemical industries [3]. Moreover, MCRs impart high-quantum yields, simple protocols, involving reactants of lower cost and incorporating green methodologies when compared with multi-step procedure. The key advantages of MCRs are faster reaction rates, more selectivity, a simple workup technique, atom economy, and the use of green solvents.

Thioamides have fascinated recognition of scientific society from an expert with its vast-range of pharmaceutical activities. For the treatment of tuberculosis, ethionamide and prothionamide are the excellent examples of thioamide drugs [4,5]. Thioamides are also an effective nucleophilic organocatalysts for activating the N-bromosuccinimide (NBS) in the aromatic electrophilic bromination reactions [6,7]. Moreover, in the presence of peroxides of acetic acids, thioamides have an excellent applications in the enhancement of fluorescent property [8]. Discrete heterocylic compounds like thiadazoles are generally synthesized by utilizing thioamides [9]. It undergoes the oxidative dimerization with variant oxidizing agents like hypervalent iodine, bromonitriles, *etc*. with the help of electrophilic reagent and DMSO [9]. The peptides having thioamides are used to increase pharmacokinetic properties and aqueous solubility for the synthesis of orthogonally protected thioamides [10].

Willgerodt reaction involves the formation of terminal amide by the oxidation/rearrangement of a ketone [11]. Kindler modified this procedure by reacting alkyl aryl ketone, sulfur, and amine to produce thioamide derivatives. In this work, the synthesis of novel thioamides is carried out, which involves a reaction between pyrazole aldehyde, precipitated sulfur and cyclic amine at 100 ºC in the presence of catalyst-free dimethyl sulfoxide as solvent.

EXPERIMENTAL

The chemicals and reagents which promote the reaction were procured from Sigma-Aldrich, USA. A 0.2 mm thickness-silica gel coated aluminium sheets were used in TLC technique (Germany-Merck, F-254) for monitoring the progress of the chemical reaction.

A JEOL spectrometer (600 MHz and 150 MHz) using $CDCl_3$ solvent was utilized to record ^{1}H NMR and ^{13}C NMR, respectively. A Perkin-Elmer spectrometer (4000-400 cm^{-1}) with KBR pellets were used to record FT-IR spectrum, whereas

the HR-MS spectrum was obtained with Q-T of mass spectrometer.

Synthesis: The reaction was carried out by mixing pyrazole aldehyde (2 mmol), precipitated sulphur (8 mmol), pyrrolidine (2 mmol) in the ratio of 1:4:1 using DMSO as solvent at 100 ºC without using catalyst in an oil bath with constant stirring. The progression of the reaction was observed by TLC. The whole mixture was poured into a ice water with continuous stirring after the completion of the reaction (**Scheme-I**). Then precipitated product was procured by normal filtration, washing with distilled water and dried.

(1,3-Diphenyl-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl)methanethione (4a): Sandal white solid, R_f: 0.45 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.72 (s, 4H), 2.65 (s, 4H), 7.40-7.87 (m, 10H), 8.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 56.0, 113.0, 119.9, 126.2, 128.7, 129.2, 129.3, 130.3, 133.0, 139.7, 150.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3433, 3066, 3032, 2922, 2853, 1954, 1889, 1811, 1733, 1597, 1544, 1483, 1440, 1329, 1265, 1153, 1061, 1031, 983, 917, 861, 760, 694, 521, 419; HRMS (ESI) $[M]^+$ *m/z*: 333.4; Anal. calcd. (found) % for $C_{20}H_{19}N_3S$: C, 72.04 (72.02); H, 5.74 (5.72); N, 12.60 (12.58); S, 9.62 (9.60).

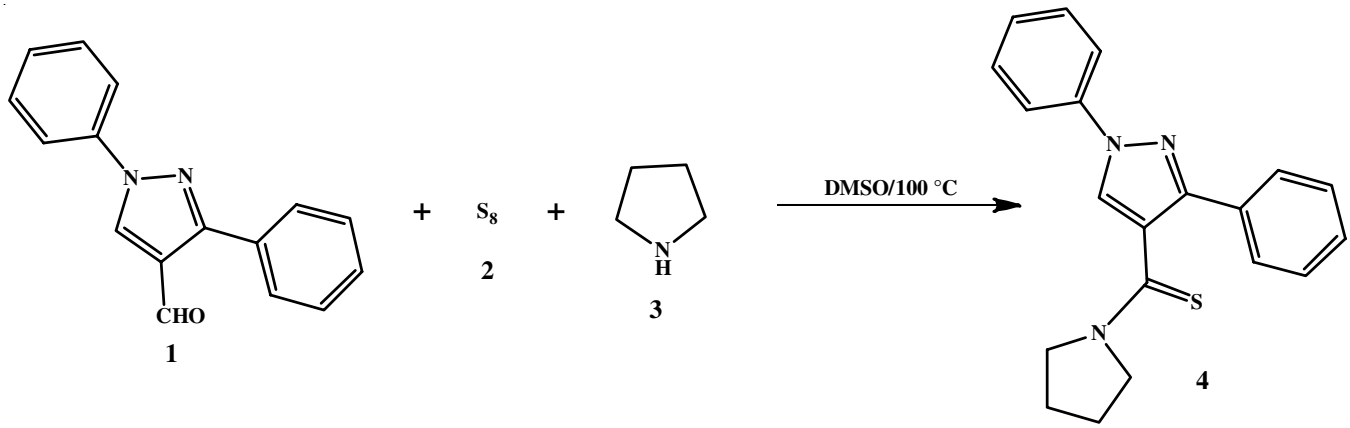
(3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-(pyrrolidin-1-yl)methanethione (4b): White solid, R_f: 0.45 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.70 (s, 4H), 2.63 (s, 4H), 7.45-7.98 (m, 9H), 8.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 56.0, 113.0, 119.9, 126.2, 128.9, 129.3, 130.3, 131.1, 134.3, 139.7, 150.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3430, 3060, 3030, 2920, 2851, 1954, 1889, 1810, 1731, 1595, 1543, 1480, 1440, 1325, 1261, 1151, 1060, 1030, 981, 914, 860, 762, 691, 520, 415; HRMS (ESI) $[M]^+$ *m/z*: 367.09; Anal. calcd. (found) % for $C_{20}H_{18}N_3SCl$: C, 65.29 (65.27); H, 4.93 (4.91); Cl, 9.64 (9.61); N, 11.42 (11.40); S, 8.72 (8.70).

(3-(4-Bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-(pyrrolidin-1-yl)methanethione (4c): Yellowish white solid, R_f: 0.50 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.70 (s, 4H), 2.63 (s, 4H), 7.45-7.78 (m, 9H), 8.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 56.0, 113.0, 119.9, 123.1, 126.2, 128.3, 129.3, 130.3, 132.0, 132.1, 134.3, 139.7, 150.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3429, 3058, 3028, 2918, 2849, 1952, 1885, 1808, 1728, 1591, 1540, 1478, 1438, 1321, 1261, 1148, 1058, 1028, 978, 911, 856, 760, 690, 518, 412; HRMS (ESI) $[M]^+$ *m/z*: 413.04; Anal. calcd. (found) % for $C_{20}H_{18}N_3SBr$: C, 58.26 (58.24); H, 4.40 (4.38); Br, 19.38 (19.36); N, 10.19 (10.17); S, 7.78 (7.76).

(3-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-(pyrrolidin-1 yl)methanethione (4d): Dull white solid, R_f: 0.55 (15%E.A-P.E.); ^{1}H NMR (300- MHz, $CDCl_3$) δ, ppm: 1.70 (s, 4H), 2.63 (s, 4H), 3.83 (s, 3H), 7.05-7.62 (m, 9H), 8.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 55.8, 56.0, 113.0, 114.8, 119.9, 125.3, 126.2, 128.5, 129.3, 130.3, 139.7, 150.4, 160.6, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3427, 3056, 3026, 2916, 2847, 1950, 1883, 1806, 1726, 1589, 1538, 1476, 1436, 1319, 1259, 1146, 1056, 1026, 976, 909, 854, 758, 688, 516, 410; HRMS (ESI) $[M]^+$ *m/z*: 363.14; Anal. calcd. (found) % for $C_{21}H_{21}N_3O_2S$: C, 69.39 (69.37); H, 5.82 (5.80); N, 11.56 (11.54); O, 4.40 (4.38); S, 8.82 (8.80).

(3-(4-Ethoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-(pyrrolidin-1-yl)methanethione (4e): White solid, R_f: 0.50 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.32 (t, 3H), 1.70 (t, 4H), 2.63 (t, 4H), 4.09 (q, 2H), 7.05-7.62 (m, 9H), 8.40 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 14.8, 25.4, 56.0, 64.6, 113.0, 114.9, 119.9, 124.6, 126.2, 128.1, 129.3, 130.3, 132.0, 132.1, 134.3, 139.7, 150.4, 159.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3425, 3054, 3024, 2914, 2845, 1948, 1881, 1804, 1724, 1587, 1536, 1474, 1434, 1317, 1257, 1144, 1054, 1024, 974, 907, 852, 756, 686, 514, 408; HRMS (ESI) $[M]^+$ *m/z*: 377.16; Anal. calcd. (found) % for $C_{22}H_{23}N_3OS$: C, 70.00 (69.99); H, 6.14 (6.12); N, 11.13 (11.11); O, 4.24 (4.22); S, 8.49 (8.47).

(1-(2,4-dinitrophenyl)-3-phenyl-1*H*-pyrazol-4-yl)-(pyrrolidin-1-yl)methanethione (4f): Light white solid, R_f: 0.60 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.70 (t, 4H), 2.63 (t, 4H), 7.41-7.79 (m, 5H), 8.14 (s, 1H), 8.40 (s, 1H), 8.82 (d, 1H), 8.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 56.0, 113.0, 120.6, 124.7, 127.5, 127.6, 128.7, 129.2, 130.3, 133.0, 136.1, 142.1, 146.3, 150.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3423, 3052, 3022, 2912, 2843, 1946, 1879, 1802, 1722, 1585, 1534, 1472, 1432, 1315, 1255, 1142, 1052, 1022, 972, 905, 850, 754, 684, 512, 406; HRMS (ESI) $[M]^+$ *m/z*: 423.10; Anal. calcd. (found) % for $C_{20}H_{17}N_5O_4S$: C, 56.73 (56.71); H, 4.05 (4.03); N, 16.54 (16.52); O, 15.11 (15.10), S, 7.57 (7.55).



Scheme-I

(3-(4-Chlorophenyl)-1-(2,4-dinitrophenyl)-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl)methanethione (4g): White solid, R_f: 0.60 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.70 (t, 4H), 2.63 (t, 4H), 7.55-7.98 (m, 4H), 8.14 (s, 1H), 8.40 (s, 1H), 8.82 (d, 1H), 8.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 56.0, 113.0, 120.6, 124.7, 127.6, 128.9, 129.3, 130.3, 131.1, 134.3, 136.1, 142.1, 146.3, 150.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3421, 3050, 3020, 2910, 2841, 1944, 1877, 1800, 1720, 1585, 1532, 1470, 1430, 1313, 1253, 1140, 1050, 1020, 970, 903, 848, 752, 682, 510, 404; HRMS (ESI) $[M]^+$ *m/z*: 457.06; Anal. calcd. (found) % for $C_{20}H_{16}N_5O_4SCl$: C, 52.46 (52.44); H, 3.52 (3.50); Cl, 7.74 (7.72); N, 15.29 (15.27); O, 13.98 (13.96), S, 7.00 (6.99).

(3-(4-Bromophenyl)-1-(2,4-dinitrophenyl)-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl) methanethione (4h): Light white solid, R_f: 0.70 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.70 (t, 4H), 2.63 (t, 4H), 7.66-7.78 (m, 4H), 8.14 (s, 1H), 8.40 (s, 1H), 8.82 (d, 1H), 8.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 56.0, 113.0, 120.6, 123.1, 124.7, 127.6, 128.3, 130.3, 132.0, 132.1, 136.1, 142.1, 146.3, 150.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3419, 3048, 3018, 2908, 2839, 1942, 1875, 1798, 1718, 1583, 1530, 1468, 1428, 1311, 1251, 1138, 1048, 1018, 968, 901, 846, 750, 680, 508, 402; HRMS (ESI) $[M]^+$ *m/z*: 503.01; Anal. calcd. (found) % for $C_{20}H_{16}N_5O_4SBr$: C, 47.82 (47.80); H, 3.21 (3.19); Br, 15.91 (15.90); N, 13.94 (13.92); O, 12.74 (12.72); S, 6.38 (6.36).

(1-(2,4-Dinitrophenyl-(3-(4-methoxyphenyl)-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl) methanethione (4i): White solid, R_f: 0.65 (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.70 (t, 4H), 2.63 (t, 4H), 3.83 (s, 3H), 7.05-7.55 (m, 4H), 8.14 (s, 1H), 8.40 (s, 1H), 8.82 (d, 1H), 8.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 25.4, 55.8, 56.0, 113.0, 114.8, 120.6, 124.7, 125.3, 127.6, 128.5, 130.3, 136.1, 142.1, 146.3, 150.4, 160.6, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3417, 3046, 3016, 2906, 2837, 1940, 1873, 1796, 1716, 1581, 1528, 1466, 1426, 1309, 1249, 1136, 1046, 1016, 966, 898, 844, 748, 678, 506, 400; HRMS (ESI) $[M]^+$ *m/z*: 453.11; Anal. calcd. for $C_{21}H_{19}N_5O_5S$: C, 55.62; H, 4.22; N, 15.44; O, 17.64, S, 7.07; Found C, 55.60; H, 4.20; N, 15.42; O, 17.62, S, 7.05.

(1-(2,4-Dinitrophenyl (3-(4-ethoxyphenyl)-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl) methanethione (4j): Bright White solid, R_f: 0.70. (15%E.A-P.E.); ^{1}H NMR (300 MHz, $CDCl_3$) δ, ppm: 1.32 (t, 3H), 1.70 (t, 4H), 2.63 (t, 4H), 3.83 (s, 3H), 4.09 (q, 2H), 7.05-7.55 (m, 4H), 8.14 (s, 1H), 8.40 (s, 1H), 8.82 (d, 1H), 8.92 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, ppm: 14.8, 25.4, 56.0, 64.6, 113.0, 114.9, 120.6, 124.6, 124.7, 127.6, 128.1, 130.3, 136.1, 142.1, 146.3, 150.4, 159.4, 204.5; FT-IR (KBr, ν_{max}, cm^{-1}): 3415, 3044, 3014, 2904, 2835, 1938, 1871, 1794, 1714, 1579, 1526, 1464, 1424, 1307, 1247, 1134, 1044, 1014, 964, 896, 842, 746, 676, 504, 400; HRMS (ESI) $[M]^+$ *m/z*: 467.13; Anal. calcd. (found) % for $C_{22}H_{21}N_5O_5S$: C, 56.52 (56.50); H, 4.53 (4.51); N, 14.98 (14.96); O, 17.11 (17.10), S, 6.86 (6.84).

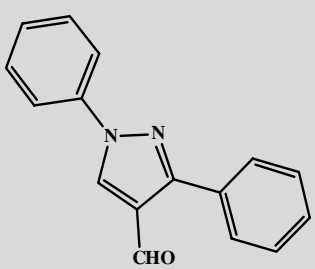
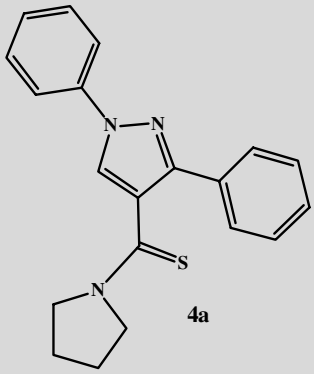
RESULTS AND DISCUSSION

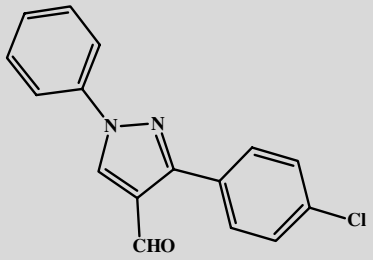
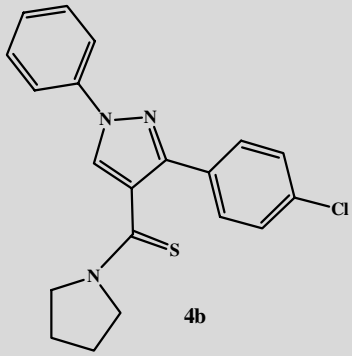
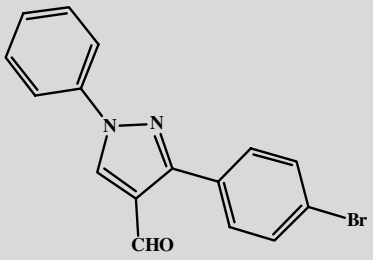
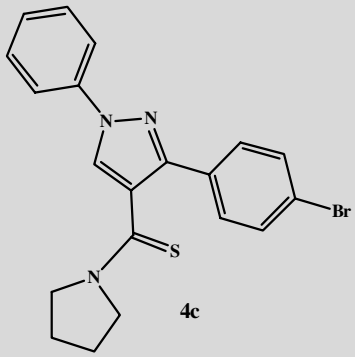
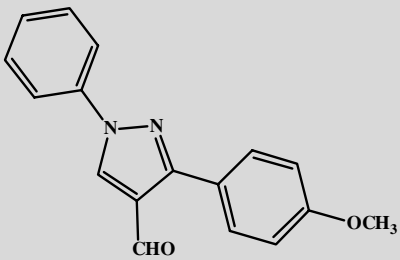
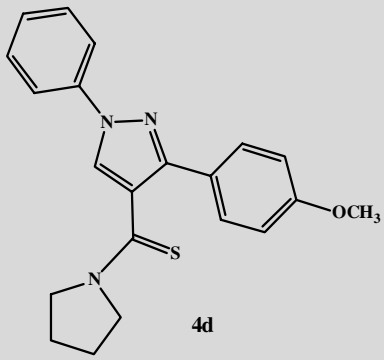
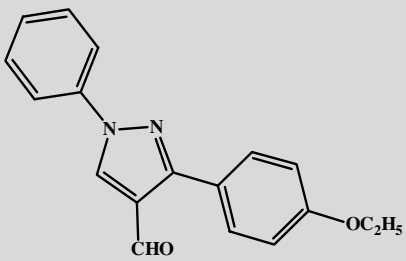
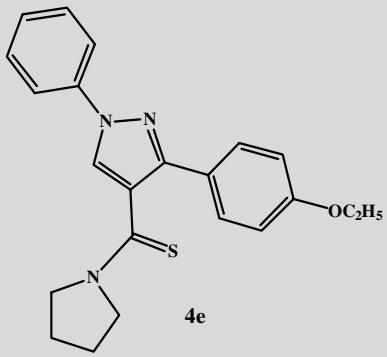
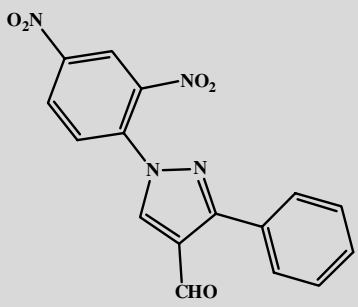
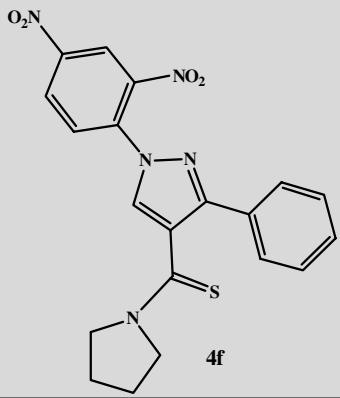
A cyclic secondary amine pyrrolidine was used in a Willgerodt-Kindler reaction with various pyrazole aldehyde, precipitated elemental sulphur and DMSO as solvent in a pre-heated oil bath at 100 ºC to synthesize (1,3-diphenyl-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl)methanethiones with excellent yields. In screening of the solvents mole ratio of the compounds have vital role in this reaction. DMSO is the specified solvent used in this reaction in the absence of the catalyst with very shorter reaction time (Table-1). The structure of the products was distinguished by different spectroscopic techniques like ^{1}H & ^{13}C NMR, FT-IR and HR-Mass spectroscopic techniques.

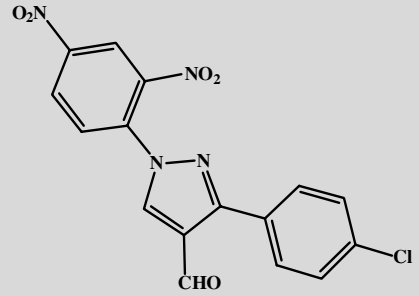
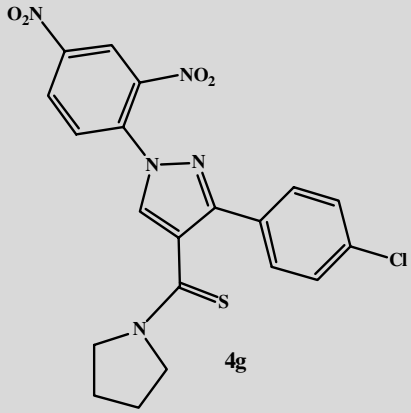
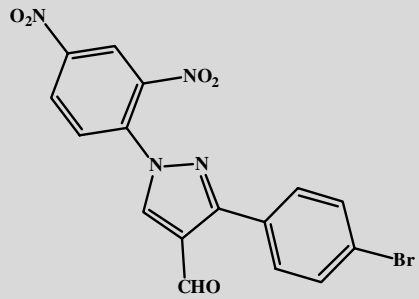
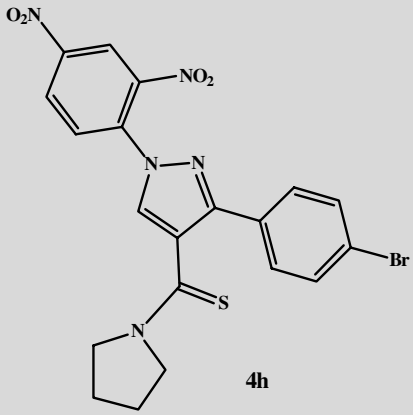
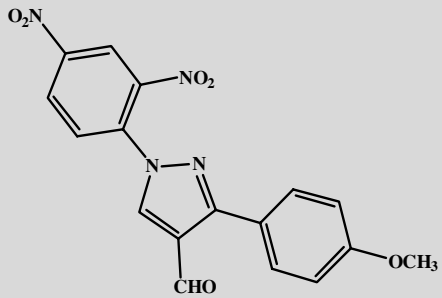
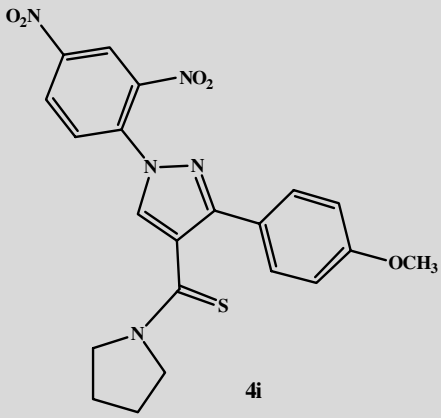
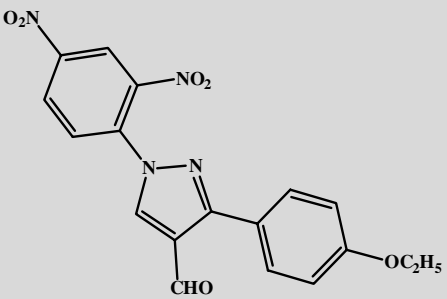
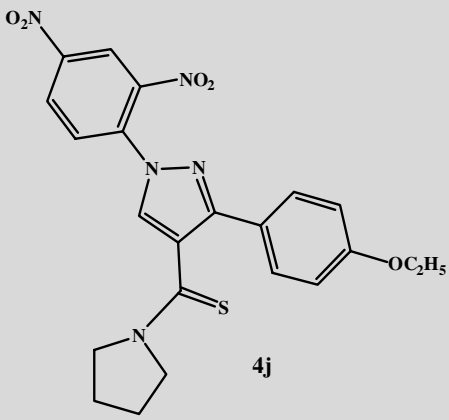
For maximization yield of the particular product in the synthesis of (1,3-diphenyl-1*H-p*yrazol-4-yl)(pyrrolidin-1-yl)-methanethione derivatives, various examination to increase the quality and quantity of the products were conducted. Nearly, different 10 solvents were used in the reaction but expected good amount of yield is not obtained (Table-2). But when DMSO was used, the rate and quantity of the product is improved and maximum amount of yield is also obtained in the overall different derivatives of thioamides. Various substituents of pyrazole aldehydes are involved in the reaction by using the specified solvent excellent yield of the product acquired.

The ^{1}H NMR *s*pectrum for compound **4a** includes four protons triplet at δ 1.72 ppm was assigned to methylene protons of pyrrolidine ring. A triplet at δ 2.65 ppm attributes to methylene protons of the pyrrolidine ring. The peaks from δ 7.40-7.87 ppm were attributed due to the aromatic protons. A singlet at

TABLE-1
SYNTHESIS OF (1,3-DIPHENYL-1*H*-PYRAZOL-4-YL)(PYRROLIDIN-1-YL)METHANETHIONE DERIVATIVES

Pyrazole Aldehyde (**1a-j**)	Product[a] (**4a-j**)	Time (h)	Yield (%)
 **1a**	 **4a**	5.0	95

 **1b**	 **4b**	4.0	85
 **1c**	 **4c**	4.5	88
 **1d**	 **4d**	5.0	84
 **1e**	 **4e**	5.0	87
 **1f**	 **4f**	5.5	90

 **1g**	 **4g**	6.0	85
 **1h**	 **4h**	5.5	90
 **1i**	 **4i**	6.0	88
 **1j**	 **4j**	6.0	90

[a]All the refined products were defined by ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy; [b]Deserted products.

TABLE-2
SCREENING OF SOLVENTS AND THE MOLE RATIO OF THE REACTANTS

Solvent	Mole ratio 1:4:1	Time (h)	Yield (%)
Acetonitrile	1:4:1	14	20
THF	1:4:1	24	No product
DCM	1:4:1	18	10
Ethyl acetate	1:4:1	24	Trace
Ethanol	1:4:1	20	No product
Acetone	1:4:1	20	40
DMF	1:4:1	24	65
1,4-Dioxane	1:4:1	24	No product
Toluene	1:4:1	24	Trace
DMSO	1:4:1	5	95

δ 8.44 ppm was allocated to pyrazole ring proton. In ^{13}C NMR spectrum, the peaks at 24.6, 25.1 ppm and 56.0, 56.5 ppm were due to the pyrrolidine carbons. The peaks extended at 113.0-150.3 ppm were attributed to pyrazole and aromatic carbons. The mass spectrum proclaimed the molecular ion peak (M+) *m/z* = 333.4. The confirmation of the product was further substantiated by elemental analysis.

Conclusion

An efficient method has been initiated through Willgerodt-Kindler reaction for the synthesis of thioamides using various derivatives of pyrazole aldehyde, cyclic amine pyrrolidine and precipitated sulphur at 100 ºC in the presence of DMSO as solvent without any catalyst. Solvent screening with a known mole fraction of the reactants yielded better results. Our study has as its ultimate goal to establish of a highly efficient and economically viable ecofriendly approach. The present work involves easily available reagents, less wastes and enhanced the reaction rate.

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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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