ISSN 1070-4280, Russian Journal of Organic Chemistry, 2020, Vol. 56, No. 10, pp. 1815–1822. © Pleiades Publishing, Ltd., 2020.

Oxidative Cyclization of Chalcones in the Presence of Sulfamic Acid as Catalyst. Synthesis, Biological Activity, and Thermal Properties of 1,3,5-Trisubstituted Pyrazoles

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Received May 29, 2020; revised June 16, 2020; accepted June 30, 2020

Abstract—1-Aroyl-3,5-diaryl-1*H*-pyrazoles were synthesized by oxidative cyclization of chalcones with benzohydrazide and 4-nitrobenzohydrazide using sulfamic acid as a catalyst. The corresponding chalcones were prepared by condensation of aromatic aldehydes with acetophenones in PEG-400 in the presence of potassium hydroxide. Some representative features of the proposed procedure include exceptional regioselectivity, comparatively short reaction time, operational simplicity, and no need of external oxidant. The synthesized pyrazole derivatives were screened as antibacterial agents against *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and *Salmonella typhi* by the agar well diffusion method. Attempts were made to compute specific heat capacity of the synthesized pyrazole derivatives as a function of temperature using TGA–DSC in order to avail thermodynamic database for these biologically relevant heterocycles.

Keywords: sulfamic acid, pyrazoles, antibacterial activity, thermal analysis, specific heat capacity

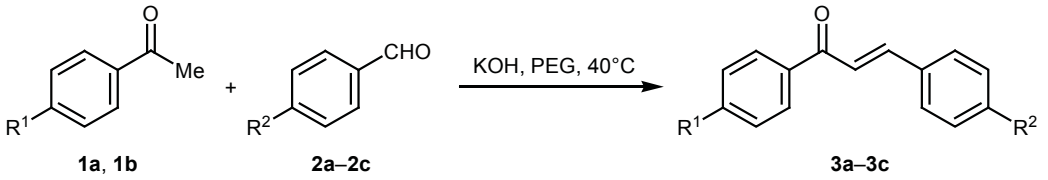
DOI: 10.1134/S1070428020100243

INTRODUCTION

Nowadays, even a superficial glimpse into the modern chemistry as well as biochemistry books unveils the significance of heterocyclic compounds and highlights their role in the life-governing processes [1–7]. Pyrazoles and their analogs are structural motifs with limited access in nature. However, these structural motifs have been extensively explored as pesticides in agriculture, and they have found applications as antibacterial, antidepressant, anticonvulsant, ulcerogenic, herbicidal, anticancer, insecticidal, antihyperglycemic, analgesic, anti-inflammatory, sedative, antipyretic, and antispasmodic agents [8–16]. Furthermore, these heterocycles are considered as versatile ligands in coordination chemistry and are utilized as optical brighteners, detergent additives, UV-stabilizers for polystyrene, and highly selective fluorescence sensors [17–24]. It is therefore of great interest for synthetic organic chemists to explore several prospects for the development of highly efficient synthetic strategies to access these privileged frameworks. In this context, the reaction of structurally diverse hydrazines with wide variety of α,β-unsaturated ketones gives rise to highly substituted pyrazole derivatives in the presence of various catalyst such as I_2 [25], (diacetoxy-λ^3-iodo)benzene [26], HBr/AcOH [27], zeolite [28], $Zn(OTF)_2$ [29], copper trifluoromethanesulfonate [14], SiO_2/H_2SO_4 [30], and Pd/C in acetic acid [31]. Mixed anhydride method has also been utilized for the synthesis of trisubstituted pyrazoles [8, 32]. The condensation between hydrazides and chalcones produces 1,3,5-trisubstituted pyrazoles via oxidative cyclization with high regioselectivity [26]. However, drawbacks associated with the use of expensive catalysts, unavoidable simultaneous formation of by-products while using organometallic catalysts, high catalyst loading because of strong coordination with the metal, low atom efficiency, and further purification of the product are also obvious [33–35].

Herein we report an efficient and environmentally benign protocol for the synthesis of biologically relevant 1,3,5-trisubstituted pyrazoles via oxidative cyclization of the corresponding chalcones with aromatic acid hydrazides using sulfamic acid as catalyst.

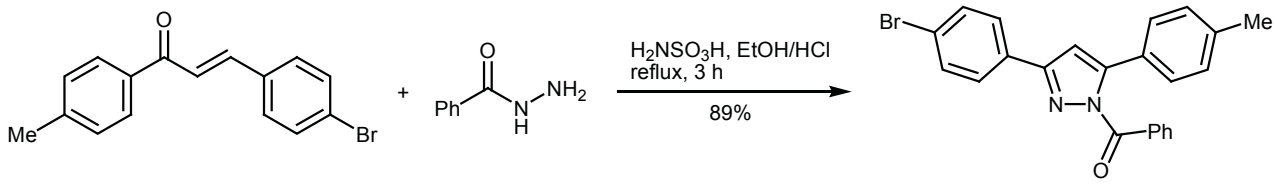
Scheme 1.



1a, **1b** **2a–2c** **3a–3c**

1, R^1 = Br (**a**), F (**b**); **2**, R^2 = H (**a**), Me (**b**), Br (**c**); **3**, R^1 = Br, R^2 = H (**a**), Me (**b**), R^1 = F, R^2 = Br (**c**).

Scheme 2.



3b **4a** **5a**

The synthesized pyrazole derivatives were screened as antibacterial agents, and their thermal stability profiles were studied to determine specific heat capacity.

RESULTS AND DISCUSSION

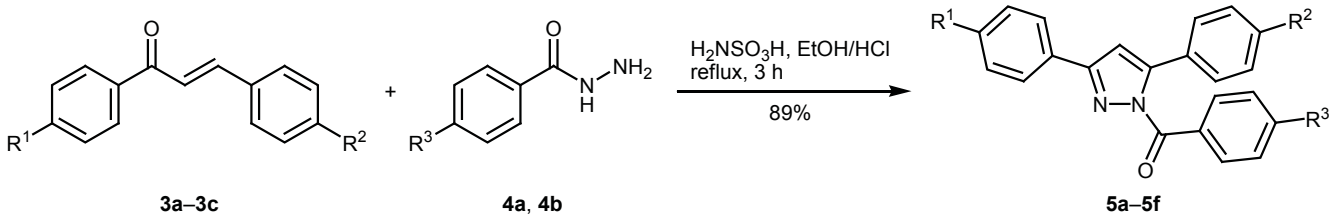
Numerous selective organic transformations catalyzed by sulfamic acid have already been reported in the literature [36–40]. Notably, an excellent catalytic potential with exceptional regio- and chemoselectivity was addressed by sulfamic acid in organic synthesis. Meanwhile, considering previous reports on the use of sulfamic acid as a catalyst, we decided to design oxidative cyclization of chalcones which were synthesized as shown in Scheme 1. Chalcones **3a**–**3c** were allowed to react with benzohydrazide (**4a**) in the presence of sulfamic acid. At the outset of our studies, sulfamic acid-catalyzed oxidative cyclization of (*E*)-3-(4-bromophenyl)-1-(4-methylphenyl)prop-2-en-1-one (**3b**) with benzohydrazide (**4a**) in ethanol was selected as a model system (Scheme 2). The reaction conditions were optimized by varying the catalyst loading, solvent, and temperature (Table 1). Initially, several model reactions were performed in different organic solvents, namely chloroform, acetonitrile, toluene, ethyl acetate, and acidified ethanol, and yields of 42, 49, 28, 20, and 89%, respectively, were obtained. Therefore, all further optimizations were carried out using acidified ethanol as solvent (Table 1, entry no. 1). The reaction temperature was found to significantly affect the formation of pyrazole **5a**. Continuous increase in the yield (57, 69, 89, and 89%) as a function of temperature (40, 60, 80, and 90°C, respectively) was observed (Table 1, entry nos. 1–4), so that the temperature 80°C was assumed to be optimal.

We then tried other commercially available catalysts such as montmorillonite K-10, Fuller's earth, Fe^{3+} montmorillonite, sulfamic acid, and $BF_3 \cdot Et_2O$, which afforded 28, 19, 30, 89, and 40% yield of **5a**, respec-

Table 1. Oxidative cyclization of (*E*)-3-(4-bromophenyl)-1-(4-methylphenyl)prop-2-en-1-one (**3b**) with benzohydrazide (**4a**) to pyrazole **5a** in EtOH/HCl in the presence of sulfamic acid

Entry no.	Catalyst concentration, mol %	Temperature, °C	Yield of **5a**, %
1	20	80	89
2	20	40	57
3	20	60	69
4	20	90	89
5	5	80	54
6	10	80	65
7	15	80	80
8	25	80	90
9	–	80	–

Scheme 3.



3a–3c **4a**, **4b** **5a–5f**

4, R^3 = H (**a**), NO_2 (**b**); **5**, R^1 = Br, R^2 = Me (**a**, **d**), R^1 = H, R^2 = Br (**b**, **e**), R^1 = Br, R^2 = F (**c**, **f**); R^3 = H (**a**–**c**), NO_2 (**d**–**f**).

tively. Thus, sulfamic acid was found to be superior to the other catalysts used. Next, the concentration of sulfamic acid was varied from 5 to 25 mol % (Table 1, entry nos. 5–9). Increase of the catalyst loading to 25 mol % did not improve the yield of **5a** to an appreciable extent, whereas significant decrease of the yield was observed when the amount of the catalyst was lowered. In the absence of sulfamic acid, the yield of **5a** did not exceed 10% (Table 1, entry no. 9).

With the optimized conditions in hand, the scope of the reaction was further extended by reacting differently substituted chalcones **3a**–**3c** with hydrazides **4a** and **4b** (Scheme 3). The corresponding 1,3,5-trisubstituted pyrazole derivatives **5a**–**5f** were obtained in 72–92% yield.

Pyrazoles **5a**–**5f** were evaluated for their in vitro antimicrobial activity against *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 19429, *Salmonella typhi* ATCC 23564, and *Staphylococcus aureus* ATCC 29737 by the agar well diffusion method. The inhibition zone diameters are given in Table 2. Compounds **5a** and **5c** showed a noticeable antibacterial activity against *S. typhi*, and compound **5c** showed a good activity against *E. coli* at a level comparable to that of streptomycin. All compounds showed low activity against *P. aeruginosa* and *S. aureus.*

To our delight, the synthesized pyrazole derivatives can be regarded as effective antibacterial agents, and therefore we turned our attention to explore their thermal properties in order to calculate their specific heat capacities as a function of temperature. Thermal gravimetric analysis revealed that compounds **5a**–**5f** are thermally stable and are free from moisture (no appropriate inflection near 100°C was observed; Fig. 1a). The high thermal stability of these heterocyclic frameworks was attributed to thermally induced structural and isomorphic changes. On the other hand, DSC analysis (Figs. 1b) showed mesophase transitions below their melting temperature (~60°C). These mesophase transitions are very similar to the transitions observed for triglycerides [41]. It should also be noted that the push–pull effect exerted by electron-donating and electron-withdrawing substituents is quite strong, and the melting transition is clearly seen for compounds **5d**–**5f**, while the melting transition of **5a**–**5c** is difficult to visualize.

Heat capacity is a significant thermodynamic property which is of fundamental importance since it bridges quantum mechanics through enthalpy, entropy, and Gibbs energy functions [42–45]. In recent years, heat capacity data of biologically relevant molecules, including carbohydrates, amino acids, and proteins, have contributed much to the development of computational methods and molecular modeling [46]. Our results encouraged us to calculate specific heat capacities of the synthesized pyrazole derivatives. Figure 2 shows variation of the specific heat capacities of com-

Table 2. In vitro antimicrobial activity (inhibition zone diameter, mm) of compounds **5a**–**5f**

Compound no.	*Escherichia coli*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*	*Salmonella typhi*
5a	12	15	–	**23**
5b	–	11	12	17
5c	**21**	–	10	**24**
5d	–	14	12	–
5e	–	13	13	18
5f	13	12	14	14
Streptomycin	26	25	28	28
Ampicillin	24	–	27	–

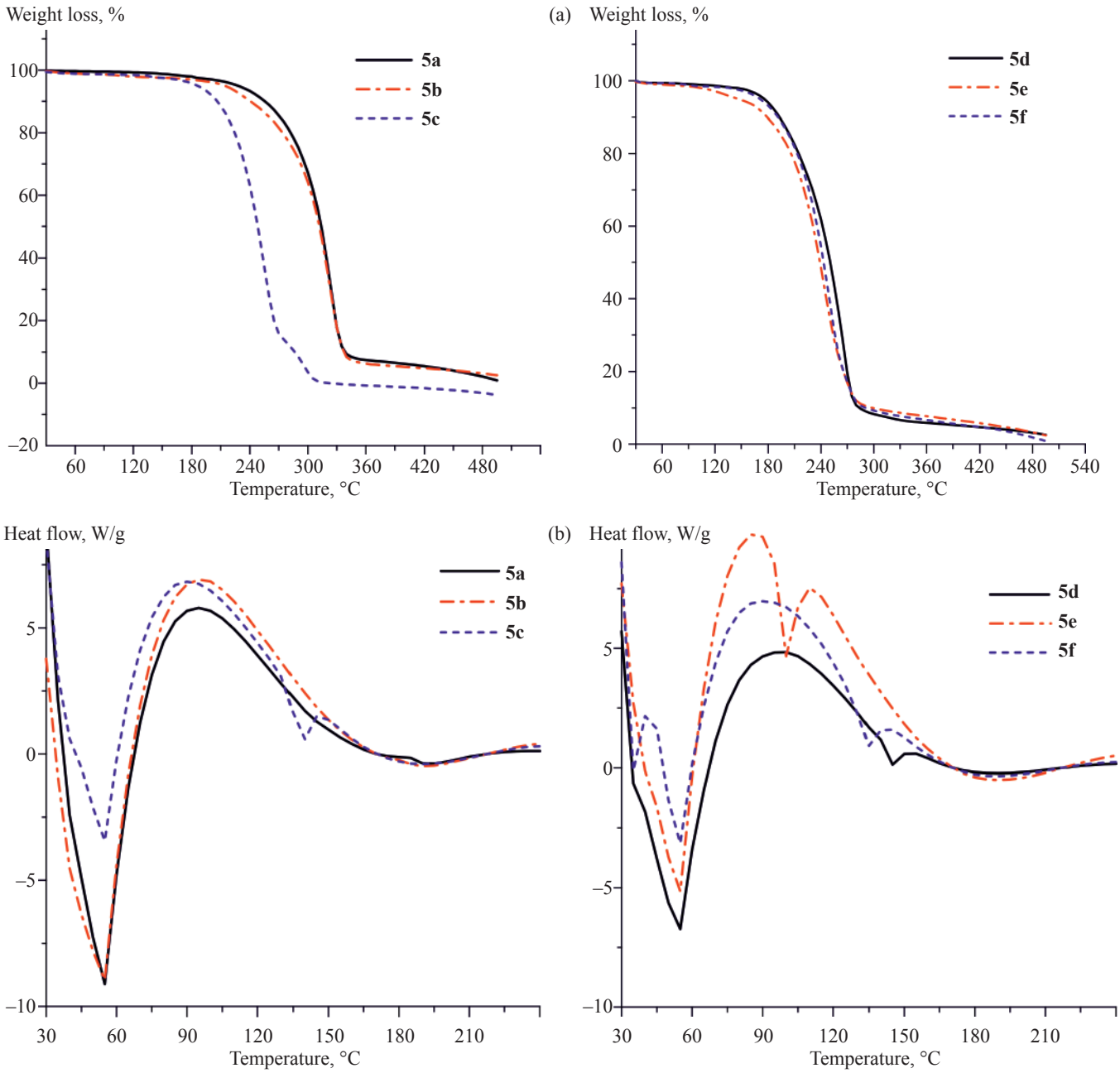


Fig. 1. (a) Thermogravimetry and (b) differential scanning calorimetry data for pyrazole derivatives **5a**–**5f**; heating rate 10 deg/min.

Table 3. Specific heat capacities (C_p, J K^{-1} g^{-1}) for pyrazole derivatives **5a**–**5f** at different temperatures

Temperature, °C	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**
75	1.35	1.17	0.70	0.94	0.90	0.73
85	1.28	1.10	0.75	0.88	0.98	0.80
95	1.31	1.13	0.83	0.90	1.21	0.89
105	1.38	1.20	0.92	0.94	1.40	0.97
115	1.46	1.30	1.02	1.01	1.39	1.08
125	1.56	1.41	1.12	1.10	1.55	1.22
135	1.66	1.52	1.30	1.21	1.70	1.43

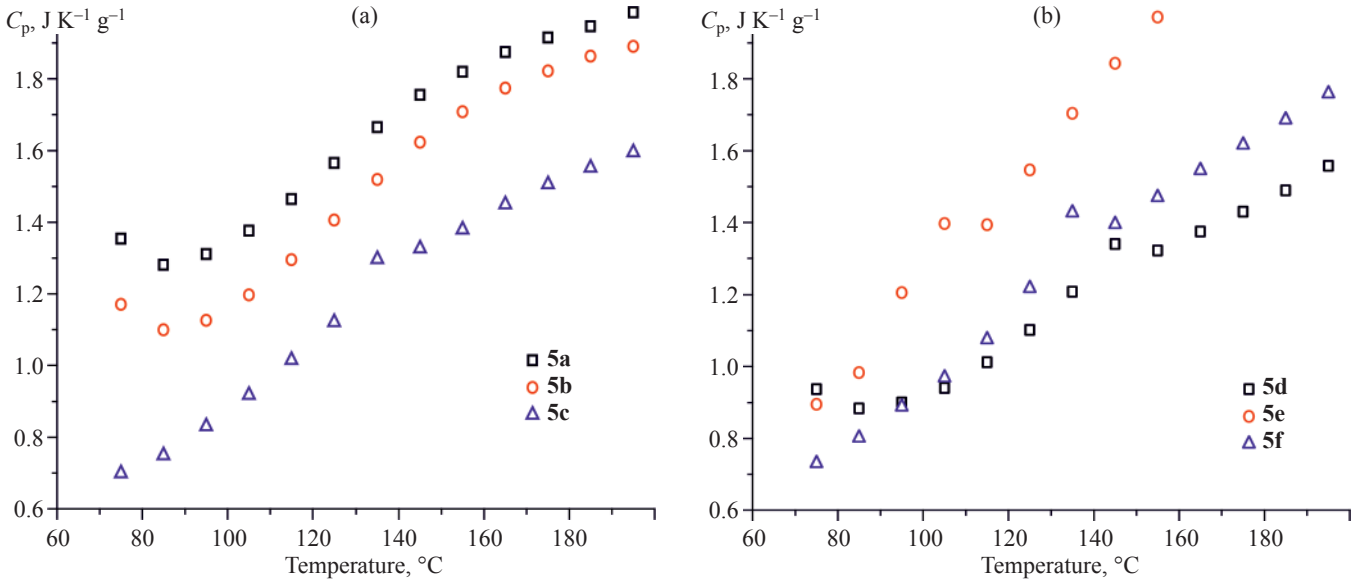


Fig. 2. Specific heat capacities of compounds (a) **5a**–**5c** and (b) **5d**–**5f** as a function of temperature.

pounds **5a**–**5f** versus temperature (see also Table 3). A closer scrutiny of Figs. 2a and 2b revealed smooth temperature increments in the heat capacities of compounds **5a**–**5c**, whereas thermal kinks are observed for compound **5d**–**5f**.

EXPERIMENTAL

Initial aldehydes, acetophenones, and hydrazides, as well as sulfamic acid, were purchased from S.D. Fine PVT. Ltd. (Mumbai). All solvents, including water, were distilled before use. The IR spectra were recorded in KBr on a Shimadzu Affinity FTIR spectrometer; the instrument was calibrated against a polystyrene film. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ using a Bruker Avance II 400 spectrometer at 400 and 100 MHz, respectively. The mass spectra were run on a Waters Q-TOF Micromass LC/MS instrument. The melting points were determined from the DSC data.

The TGA-DSC analyses were carried out on a TA Instruments SDT Q 600 V20.9 thermal analyzer with an accuracy of ±0.5 K under a nitrogen atmosphere, which was placed in an air-conditioned lab with a humidity of 5–10%. Samples with a weight of 4 to 10 mg were used for the measurements. Heat flow measurements were performed in the temperature range of 313.15–1073.15 K (heating rate 5 deg/min) at a nitrogen flow rate of 50 mL/min. The instrument was calibrated using an empty pan, sapphire, and zinc. The DSC data were obtained over the temperature range 298.15–773.15 K. The details regarding the calculation of specific heat capacities were reported previously [48–51].

Chalcones 3a–3c (*general procedure*). An equimolar mixture of acetophenone **1a** or **1b** and aldehyde **2a**–**2c** in PEG-400 (15 mL) containing 2 mmol of potassium hydroxide was stirred at 40°C for 1 h. The progress of the reaction was monitored by TLC (hexane–ethyl acetate, 95:5). After completion of the reaction, the mixture was poured into ice water (100 mL) [47], and the crystalline solid was filtered off and recrystallized from ethanol.

1,3,5-Trisubstituted pyrazoles 5a–5f (*general procedure*). A 50-mL round-bottom flask was charged with chalcone **3a**–**3c** (5 mmol), benzohydrazide (**4a**) or 4-nitrobenzohydrazide (**4b**) (5 mmol), and 20 mol % of sulfamic acid in acidified ethanol (15 mL). The mixture was refluxed with stirring until the reaction was complete (TLC, chloroform–diethyl ether, 80:20), cooled, and poured into ice water, and the solid product was filtered off and recrystallized from ethanol.

[5-(4-Bromophenyl)-3-(4-methylphenyl)-1*H*-pyrazol-1-yl](phenyl)methanone (5a). Yield 0.370 g (89%), pale yellow solid, mp 176–180 (open capillary), 178°C (DSC). IR spectrum, ν, cm^{-1}: 1485 (C=C), 1598 (C=N), 1654 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.03 d (2H, J = 8.2 Hz); 7.88 d (4H), 7.78 d.d (3H), 7.70 s (1H, 4-H), 7.63 d.d (2H), 7.34 d (2H, J = 8 Hz), 2.42 s (3H, CH_3). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 188.3 (C=O), 143.4 (C^3), 142.1

(C^5), 134.8, 133.8, 131.7, 130.4, 128.5, 123.8, 122.6 (C^4), 21.2 (CH_3). Mass spectrum: *m*/*z* 416/418 $[M]^+$.

[3-(4-Bromophenyl)-5-phenyl-1*H*-pyrazol-1-yl]-phenylmethanone (5b). Yield 0.349 g (87%), yellowish white solid, mp 178–182 (open capillary), 184°C (DSC). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.75 d (2H), 7.18–7.82 m (6H),7.14 d (2H), 7.07 s (1H, 4-H), 6.90 d.d (2H), 6.81 d.d (2H). Mass spectrum: *m*/*z* 402/404 $[M]^+$.

[5-(4-Bromophenyl)-3-(4-fluorophenyl)-1*H*-pyrazol-1-yl]phenylmethanone (5c). Yield 0.302 g (72%), pale yellow solid, mp 142–144 (open capillary), 139°C (DSC). IR spectrum, ν, cm^{-1}: 1496 (C=C), 1600 (C=N), 1656 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.15 t (2H), 7.75 d (4H), 7.52 t.d (5H), 7.41 s (1H, 4-H), 7.22–7.39 m (2H). Mass spectrum: *m*/*z* 420/422 $[M]^+$.

[5-(4-Bromophenyl)-3-(4-methylphenyl)-1*H*-pyrazol-1-yl](4-nitrophenyl)methanone (5d). Yield 0.410 g (89%), yellow solid, mp 148–151 (open capillary), 145°C (DSC). IR spectrum, ν, cm^{-1}: 1508 (C=C), 1600 (C=N), 1656 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.91 d (2H, *J* = 8.1 Hz), 7.70 d (2H), 7.52 d.d (6H), 7.47 s (1H, 4-H), 7.25 t (2H), 2.42 s (3H, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 189.6 (C=O), 143.8 (C^3), 142.9 (C^5), 135.4, 133.8, 132.1, 129.7, 129.3, 128.6, 124.6, 122.5 (C^4), 21.69 (CH_3).

[3-(4-Bromophenyl)-5-phenyl-1*H*-pyrazol-1-yl]-(4-nitrophenyl)methanone (5e). Yield 0.375 g (84%), yellow solid, mp 200–202 (open capillary), 186°C (DSC). IR spectrum, ν, cm^{-1}: 1500 (C=C), 1598 (C=N), 1653 (C=O). Mass spectrum: *m*/*z* 447/449 $[M]^+$.

[5-(4-Bromophenyl)-3-(4-fluorophenyl)-1*H*-pyrazol-1-yl](4-nitrophenyl)methanone (5f). Yield 0.427 g (92%), yellow solid, mp 135–137 (open capillary), 135°C (DSC). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: :8.41 d (2H), 8.25–8.41 m (1H), 7.87 s (1H, 4-H), 7.57–7.63 m (2H), 7.37 d.d (2H), 7.23 t (2H). Mass spectrum: *m*/*z* 465/467 $[M]^+$.

Antibacterial study. The antibacterial activity of compounds **5a**–**5f** was evaluated by the agar well diffusion method [52]. The turbidity of bacterial culture was adjusted to a required value according to McFarland standards by using sterile saline. Muller Hinton agar medium (15 mL) was poured into preliminarily sterilized and labeled Petri dishes, and the medium was swabbed with 100 μL of bacterium inoculum and kept for 10–15 min for absorption. Wells were bored in the seeded agar plates using a sterile cork borer (6 mm in diameter), and 100 μL of a DMSO solution of **5a**–**5f** or reference drug with a concentration of 100 μg/mL was added into each well. The dishes were incubated for 24 h at 37°C under aerobic conditions, and the bacterial growth inhibition zone diameter (mm) was measured; pure DMSO was used as control.

ACKNOWLEDGMENTS

The authors are thankful to the central Instrumentation Laboratory, Moolji Jaitha College (Jalgaon) for recording the FT-IR spectra and evaluating biological activity. The authors are also grateful to Punjab University, Chandigarh, for providing the spectral data of the synthesized compounds and to Nagpur University for TGA/DSC analysis.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at https://doi.org/10.1134/S1070428020100243 and are accessible for authorized users.

REFERENCES

1. Gupta, G.R., Shah, J., Vadagaonkar, K.S., Lavekar, A.G., and Kapdi, A.R., *Org. Biomol. Chem*., 2019, vol. 17, p. 7596. https://doi.org/10.1039/C9OB01152H
2. Sainsbury, M., *Heterocyclic Chemistry*, Cambridge UK: Roy. Soc. Chem., 2001.
3. Gupta, G.R., Chaudhari, G.R., Tomar, P.A., Waghulade, G.P., and Patil, K.J., *Asian J. Chem*., 2012, vol. 24, p. 4675.
4. Gupta, G., Chaudhari, G., Tomar, P., Gaikwad, Y., Azad, R., Pandya, G., Waghulde, G., and Patil, K., *Eur. J. Chem*., 2012, vol. 3, p. 475. https://doi.org/10.5155/eurjchem.3.4.475-479.709
5. Oparin, A.I., *The Origin of Life*, New York, Dover Publications, 1965.
6. Bhirud, J.D., Mahulikar, P.P., and Narkhede, H.P., *Indian J. Chem., Sect. B*., 2018, vol. 57, p. 1208. http://nopr.niscair.res.in/handle/123456789/45042
7. Bhilare, S., Shah, J., Gaikwad, V., Gupta, G., Sanghvi, Y., Bhanage, B., and Kapdi, A.R., *Synthesis*, 2019, vol. 51, p. 4239. https://doi.org/10.1055/s-0039-1690190
8. Mishra, S.K., Majumdar, P., Behera, R.K., and Behera, A.K., *Synth. Commun*., 2014, vol. 44, p. 32. https://doi.org/10.1080/00397911.2013.765483

9. Brown, E.G., *Ring Nitrogen and Key Biomolecules. The Biochemistry of N-Heterocycles*, Dordrecht: Springer, 1998. https://doi.org/10.1007/978-94-011-4906-8
10. *Synthesis of Heterocycles in Contemporary Medicinal Chemistry*, Casar, Z., Ed., Switzerland: Springer, 2016. https://doi.org/10.1007/978-3-319-39917-1
11. Joule, J.A. and Mills, K., *Heterocyclic Chemistry*, Hoboken NJ: Wiley, 2009, 5th ed.
12. Joule, J.A. and Mills, K., *Heterocyclic Chemistry at a Glance*, Chichester: Wiley, 2012, 2nd ed.
13. Rauf, A. and Farshori, N.N., *Microwave-Induced Synthesis of Aromatic Heterocycles*, Dordrecht: Springer, 2012. https://doi.org/10.1007/978-94-007-1485-4
14. Rao, V.K., Tiwari, R., Chhikara, B.S., Shirazi, A.N., Parang, K., and Kumar, A., *RSC Adv*., 2013, vol. 3, p. 15396. https://doi.org/10.1039/C3RA41830H
15. Xian-Hai, L., Zi-Li, R., Ming-Jie, C., Peng, W., Xiang-Feng, M., Dong-Dong, L., and Hai, Q.C., *RSC Adv*., 2015, vol. 5, p. 55179. https://doi.org/10.1039/C5RA09286H
16. *Heterocyclic Chemistry in Drug Discovery*, Li, J.J., Ed., Hoboken NJ: Wiley, 2013.
17. Parameswaran, P.S., Naik, C.G., and Hegde, V.R., *J. Nat. Prod*., 1997, vol. 60, p. 802. https://doi.org/10.1021/np970134z
18. Motoba, K., Nishizawa, H., Suzuki, T., Hamaguchi, H., Uchida, M., and Funayama, S., *Pestic. Biochem. Physiol*., 2000, vol. 67, p. 73. https://doi.org/10.1006/pest.2000.2477
19. Orth, R.E., *J. Pharm. Sci*., 1968, vol. 57, p. 537. https://doi.org/10.1002/jps.2600570401
20. Ismail, M.A.H., Lehmann, J., Abou El Ella, D.A., Albohy, A., and Abouzid, K.A.M., *Med. Chem. Res*., 2009, vol. 18, p. 725. https://doi.org/10.1007/s00044-009-9163-2
21. Mukherjee, A. and Sarka, A., *Tetrahedron Lett*., 2004, vol. 45, p. 9525. https://doi.org/10.1016/j.tetlet.2004.11.016
22. Dorlars, A., Schellhammer, C.W., and Schroeder, J., *Angew. Chem., Int. Ed. Engl*., 1975, vol. 14, p. 665. https://doi.org/10.1002/anie.197506651
23. Catalan, J., Fabero, F., Claramunt, R.M., Santa Maria, M.D., Hernandez Cano, F., Martinez-Ripoll, M., Elguero, J., and Sastre, R., *J. Am. Chem. Soc*., 1992, vol. 114, p. 5039. https://doi.org/10.1021/ja00039a014
24. Yang, Z., Zhang, K., Gong, F., Li, S., Chen, J., Shi Ma, J., Sobenina, L.N., Mikhaleva, A.I., Trofimov, B.A., and Yang, G., *J. Photochem. Photobiol*., 2011, vol. 217, p. 29. https://doi.org/10.1016/j.jphotochem.2010.09.012
25. Zhang, X., Kang, J., Niu, P., Wu, J., Yu, W., and Chang, J., *J. Org. Chem*., 2014, vol. 79, p. 10170. https://doi.org/10.1021/jo501844x
26. Agarwal, R. and Kumar, R., *Synth. Commun*., 2009, vol. 39, p. 2169. https://doi.org/10.1080/00397910802640038
27. Chambers, W.L. and Willard, M.L., *J. Am. Chem. Soc*., 1960, vol. 82, p. 3373. https://doi.org/10.1021/ja01498a035
28. Sreekumar, R. and Padmakumar, R., *Synth. Commun*., 1998, vol. 28, p. 1661. https://doi.org/10.1080/00397919808006870
29. Alex, K., Tillack, A., Schwarz, N., and Beller, M., *Org. Lett*., 2008, vol. 10, p. 2377. https://doi.org/10.1021/ol800592s
30. Chen, X., She, J., Shang, Z., Wu, J., and Zhang, P., *Synth. Commun*., 2009, vol. 39, p. 947. https://doi.org/10.1080/00397910802441551
31. Nakamichi, N., Kawashita, Y., and Hayashi, M., *Org. Lett*., 2002, vol. 4, p. 3955. https://doi.org/10.1021/ol0268135
32. Kammoun, M., Turki, H., Ammar, H., and El Gharbi, R., *Synth. Commun*., 2012, vol. 42, p. 1677. https://doi.org/10.1080/00397911.2010.542863
33. Sharshira, E.M. and Hamada, N.M.M., *Molecules*, 2012, vol. 17, p. 4962. https://doi.org/10.3390/molecules17054962
34. Patel, A.R., Badmanaban, R., Sen, D.J., and Patel, C.N., *Am. J. Adv. Drug Delivery*, 2013, vol. 1, p. 113.
35. Deniβen, M., Nordmann, J., Dziambor, J., Mayer, B., Frank, W., and Müller, T.J.J., *RSC Adv*., 2015, vol. 5, p. 33838. https://doi.org/10.1039/c5ra03104d
36. Montes, M.G., Soares, R.M., Moura, R.R., and Granjao, V.F., *Fuel*, 2012, vol. 97, p. 884. https://doi.org/10.1016/j.fuel.2012.02.038
37. Heravi, M.M., Baghernejad, B., and Oskooie, H.A., *Curr. Org. Chem*., 2009, vol. 13, p. 1002. https://doi.org/10.2174/138527209788680790
38. Foroughifar, N., Mobinikhaledi, A., Bodaghi Fard, M.A., Moghanian, H., and Ebrahimi, S., *Synth. React. Inorg., Met.-Org., Nano-Met. Chem*., 2009, vol. 39, p. 161. https://doi.org/10.1080/15533170902785075
39. Sarkate, A.P., Sangshetti, J.N., Dharbale, N.B., Sarkate, A.P., and Shinde, D.B., *J. Chil. Chem. Soc*., 2015, vol. 60, p. 2832.
40. Brahmachari, G., Begam, S., and Nurjamal, K., *ChemistrySelect*, 2018, vol. 3, p. 3400. https://doi.org/10.1002/slct.201800488
41. Gupta, G., Shaikh, V., and Patil, K., *Curr. Phys. Chem*., 2018, vol. 8, p. 175. https://doi.org/10.2174/1877946808666181031113024

42. Gupta, G.R., Patil, P.D., Shaikh, V.R., Kolhapurkar, R.R., Dagade, D.H., and Patil, K.J., *Curr. Sci*., 2018, vol. 114, p. 2525. https://doi.org/10.18520/CS/V114/I12/2525-2529
43. Patil, K.S., Zope, P.H., Patil, U.T., Patil, P., Dubey, R.S., and Gupta, G.R., *Bull. Mater. Sci*. 2019, vol. 42, p. 24. https://doi.org/10.1007/s12034-018-1705-0
44. *The Nature of Biological Systems as Revealed by Thermal Methods*, Lörinczy, D., Dordrecht: Kluwer Academic, 2004.
45. *Applied Plastics Engineering Handbook: Processing, Materials, and Applications*. Myer, K., Ed., Oxford UK: Elsevier, 2017, 2nd ed. https://doi.org/10.1016/C2014-0-04118-4
46. *Heat Capacities: Liquids, Solutions and Vapours*, Wilhelm, E. and Letcher, T.M., Eds., Cambridge: Roy. Soc. Chem., 2010.
47. Sreedhar, N.Y., Jayapal, M.R., Sreenivasa Prasad, K., and Reddy Prasad, P., *Res. J. Pharm. Biol. Chem. Sci*., 2010, vol. 1, p. 480.
48. Girase, T.R., Patil, K.J., Kapdi, A.R., and Gupta, G.R., *ChemistrySelect*, 2020, vol. 5, p. 4251. https://doi.org/10.1002/slct.201904837
49. Patil, K.S. and Gupta, G.R., *Int. J. Manage. Technol. Eng*., 2019, vol. 9, p. 1530. http://ijamtes.org/gallery/187-jan19.pdf
50. Sarode, C., Yeole, S., Chaudhari, G., Waghulde, G., and Gupta, G., *Curr. Phys. Chem*., 2020, vol. 10, in press. https://doi.org/10.2174/1877946810999200519102040
51. Gupta, G., Shaikh, V., Kalas, S., and Patil, K.J., *Curr. Phys. Chem*., 2020, vol. 10, in press. https://doi.org/10.2174/1573412916999200430092644
52. Vankatasatyanarayana, G., Lakshmana Rao, V., Laxminarayana, E., and Tirumala Chary, M., *Indian J. Chem., Sect. B*, 2016, vol. 55, p. 718.