Received: 24 December 2020 | Revised: 24 February 2021 | Accepted: 8 March 2021

DOI: 10.1002/aoc.6238

FULL PAPER

Applied Organometallic Chemistry WILEY

Boosting the catalytic performance of manganese (III)-porphyrin complex MnTSPP for facile one-pot green synthesis of 1,4-dihydropyridine derivatives under mild conditions

Mahmoud Abd El Aleem Ali Ali El-Remaily[1] | **Hesham A. Hamad**[2,3] | **Ahmed M. M. Soliman**[1] | **Omar M. Elhady**[1]

[1]Department of Chemistry, Faculty of Science, Sohag University, Sohag, Egypt

[2]Fabrication Technology Research Department, Advanced Technology and New Materials Research Institute (ATNMR), City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City, Alexandria, Egypt

[3]Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Warsaw, Poland

Correspondence

Mahmoud Abd El Aleem Ali Ali El-Remaily, Department of Chemistry, Faculty of Science, Sohag University-82524 Sohag, Egypt.
Email: msremaily@yahoo.com

Hesham A. Hamad, Fabrication Technology Research Department, Advanced Technology and New Materials Research Institute (ATNMR), City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City, Alexandria, Egypt.
Email: hhamad@srtacity.sci.eg

In this study, the metal complex (5,10,15,20-tetrakis-(4-sulfonatophenyl)-porphyrin manganese (III) chloride; denoted as MnTSPP) represents a promising efficient and reusable heterogeneous solid catalyst for facile and highly efficient one-pot synthesis of 1,4 dihydropyridine derivatives via three-component condensation reaction of aromatic aldehyde, ethyl acetoacetate, and ammonium acetate under green and mild reaction conditions. The simple operation, short reaction time (15 min), and the high efficiency (99%) are the special advantage of this protocol. Furthermore, the green aspects of this synthetic protocol were more studied by examination of the reusability of MnTSPP for four consecutive cycles without a significant loss of catalytic activity. Remarkably, the new synthesis presented advantages in terms of safety, commercially available catalyst, simplicity, stability, mild conditions, short reaction time, and excellent yields, using a mixture of H_2O and C_2H_5OH environmental-friendly solvent, operationally facile, wide tolerance of starting materials, and excellent recoverable of the catalyst.

KEYWORDS

1,4-dihydropyridines, benign protocol, manganese (III)-porphyrin complex, mild condensations; recoverable catalyst, three-component reaction

1 | INTRODUCTION

Metal-porphyrins have attracted more attention for broad applications in catalysis.[1] Among these reactions, metal-porphyrins have a significant catalytic activity towards the oxidative processes in organic synthesis. So the development of catalysts is claiming huge attention due to their wide applications of the produced organic compounds with high selectivity and productivity.

It is well known that the porous metal-porphyrin networks have demonstrated to be an excellent technology in the field of homogeneous and heterogeneous catalysis.[2] The strategy of immobilization of porous metal-porphyrin (Figure 1) has already been developed by organic amorphous polymers, amorphous inorganic matrices, or crystalline inorganic materials such as silica,[3] zeolites,[4] clay from the smectite group (montmorillonite),[5,6] layered double hydroxides,[7,8] tubular and fibrous matrices,[9] and silica matrix obtained by the sol–gel process. [10–16]

The search for broadly applicable metal catalysts operating in the aqueous phase is a subject of high interest.[17–19] Environmental applications of metal catalysis

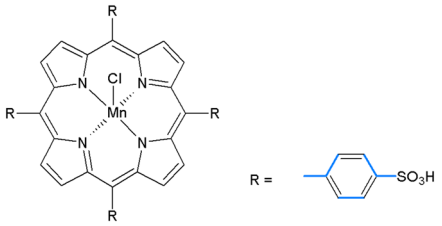


FIGURE 1 The structure of MnTSPP catalyst

in water are the treatment of aqueous waste effluents that result from chemical production streams (e.g., obtained from dyes production). The reactions of particular interest for such applications are catalytic oxidations, preferably promoted by the consumption of molecular oxygen or hydrogen peroxide as oxidizing agents. Until now, however, most metal-based catalytic applications have been related to organic media, as the sensitivity of complexes to moisture. Accordingly, the number of metal complexes suitable for catalysis in in aqueous media remains limited. The need for such catalysts has resulted in detailed studies with various metal complexes towards their suitability for such applications in aqueous media.

According to the green chemistry from both environmental and economic viewpoints, developments of efficient and environmentally benign heterogenous processes with green energies, and lowest-level waste, as well as stability in reaction media are the priorities. The performance with 5,10,15,20-tetrakis-(4-sulfonato-phenyl)-porphyrin manganese (III) chloride (MnTSPP; Figure 1) fulfills the prerequisites of water solubility,[20] low toxicity, commercially available catalyst, and high stability of the complexes, even in oxidation reaction.[21] In addition, this catalyst is commercially available from several suppliers up to gram scale. Further advantages are its high stability and its ability for prevention the aggregation in an aqueous solution.

Multicomponent reactions (MCRs) allow the creation of several bonds in one-step process in synthetic chemistry. MCRs also are attracting the interest as one of the most powerful emerging synthetic tools for the creation of molecular complexity and diversity due to their intrinsic atom economy, selectivity, simplicity, and energy efficiency.[22] Although MCRs have many advantages, it has still suffered from several drawbacks, such as harsh reaction conditions, requiring long reaction time, and usage of excessive number of reagents and toxic solvents. The most important one among them is the one-pot four-component synthesis of 1,4-dihydropyridines and hexahydroquinolines reported by Hantzsch in 1882. In the past few decades, much interest has been focused on the synthesis of 1,4-dihydropyridine compounds owing to their various pharmacological and therapeutic features. In particular, 1,4-dihydropyridine drugs are the most widely used in the treatment of cardiovascular disease,[23] have a broad range of pharmacological properties such as antitumor, antimutagenic, neuroprotective, geroprotective, heptaprotective, antimicrobial, anti-alzheimer, cytotoxic, and antidiabetic agents, [24–26] 1,4-Dihydropyridines have also proved to be very important synthetic intermediates, finding applications in the preparation of a large number of nitrogen alkaloids.[27] The remarkable drug activity of these compounds has not only attracted many chemists to synthesize this heterocyclic nucleus but has also become an active research area of continuing interest [28],[29].

Aromatization of Hantzsch esters compounds has been reported by several catalysts such as cellulose sulfuric acid[30], solid acid[31], silica supported 12-tungstophosphoric acid[32], Iron (III) trifluoroacetate,[33] ionic liquid [tbmim]Cl_2/$AlCl_3$,[34] organo catalyst,[35] cerric ammonium nitrate,[36] Ni nanoparticle,[37] aluminum phosphate,[38] bismuth nitrate,[39] gadolinium triflate,[40] TiO_2 nanoparticles,[41] FeF_3,[42] silica sulfuric acid,[43] MgO nanoparticles,[44] visible light[45], chitosan[46], sulfated polyborate,[47] and protic pyridinium ionic liquid[48] have been reported. The industrial and biological importance of 1,4-dihydropyridine derivatives is the reason to improve the several routes for synthesis of these compounds. Although these techniques suffer from several drawbacks drawbacks such as extended reaction times, unsatisfactory yields, elevated temperatures, tedious work-up, relatively expensive reagents, formation of numerous side products, and difficult recovery process of catalyst, the development, however, of simple, efficient, and environmental benign protocols of 1,4 dihydropyridine using reusable heterogenous solid acid catalyst is highly demanded.

To the best of our knowledge, 1,4-dihydropyridine derivatives catalyzed by MnTSPP under mild reaction conditions have not been reported. In line with outlined strategies and continuation of our interest towards the development of new routes to the role of metal-porphyrin catalyst for synthesis bio-active heterocyclic compounds by MCRs.[49] With the merits of environment benign, readily accessibility, and cost-benefit, manganese (III)-porphyrin complex MnTSPP seems to be a promising reusable catalyst in the facile one-pot synthesis of hybrid molecules 1,4-dihydropyridine compounds **4a-o** through Hantzsch, a three-component coupling reaction of aromatic aldehyde, ethyl acetoacetate, and ammonium acetate under mild conditions. All products have been deposited in excellent yields in short reaction time.

2 | EXPERIMENTAL

All starting materials and solvents were used as received from Sigma Aldrich or Alfa Aesar. Thin-layer

chromatography was conducted using TLC silica gel $60F_{254}$ (Merck Co.), visualized with ultraviolet light. All melting points were recorded on Melt-Temp II melting point apparatus. IR spectra were measured as KBr pellets on a Shimadzu DR-8001 spectrometer. ^{1}H,^{13}C spectra were recorded on a Bruker DRX 400 MHz using TMS as an internal reference and $CDCl_3$ as a solvent. All compounds were checked for their purity on TLC plates.

2.1 | General procedure for the synthesis of 1,4-Dihydropyridine derivatives 4a–o

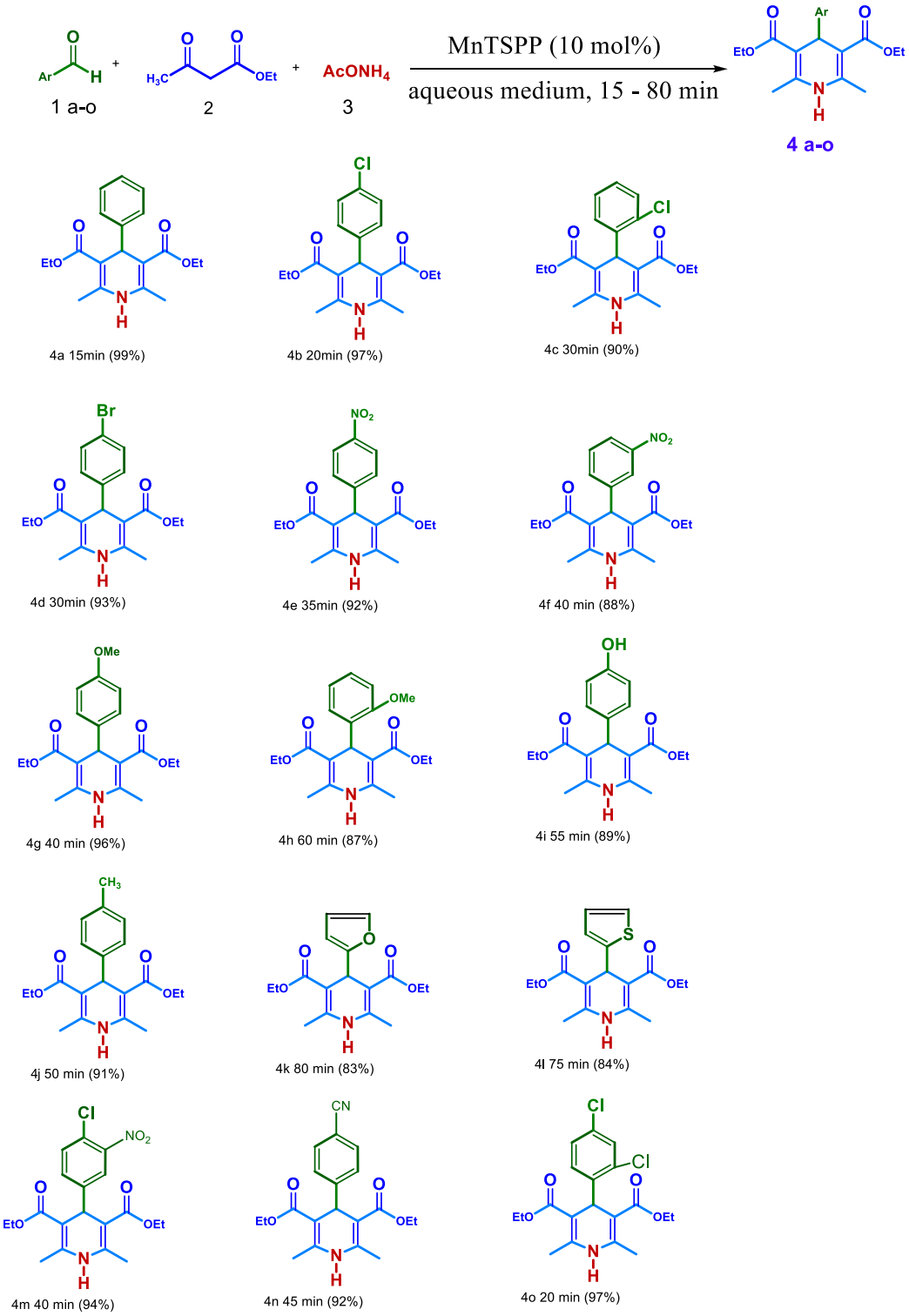
In a round bottom flask manganese (III)-porphyrin complex MnTSPP 10 mol % was dissolved in 30 ml H_2O at room temperature by magnetic stirrer. Then aromatic aldehyde $\mathbf{1_{a\text{-}o}}$ (1 mmol), ethyl acetoacetate **2** (2 mmol), and ammonium acetate **3** (2 mmol) were added. Due to the partial solubility of some aromatic aldehyde in water, we used to use a mixed solvent of H_2O and ethanol (v/v) (3/1). The reaction mixture was refluxed for the appropriate time see (Scheme 1). The reaction mixture was allowed to cool to room temperature. The organic material was extracted twice with ethyl acetate; the 1,4-dihydropyridine derivatives **4a–o** combined organic phases were washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure [30–43]. After completion of reaction as indicated by thin layer chromatography (TLC), the resulting solid product was filtered and recrystallized with 5 ml ethanol to give the pure product and characterized by their melting point, FT-IR. NMR spectra were recorded on a 400 MHz Bruker spectrometer using TMS as an internal reference and $CDCl_3$ as solvent (See Supporting Information).

2.2 | Catalyst recovery and reuse

The catalyst was recovered by adding drop wise (5 ml) of acetone to the aqueous layer while stirring at room temperature giving it a precipitated manganese-porphyrin catalyst which was cooled to 3°C. MnTSPP was recovered by filtration, dried, which could be reused without losing catalytic activity.

2.3 | Spectral data for the synthesized compounds

- **Compound 4a.**: M.P = 157–159°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10–7.31 (m, 5H, ArH), 5.59 (br, 1H, NH), 5.01 (s, 1H, CH), 4.10 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.34 (s, 6H, $2CH_3$), 1.24 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 148.2, 145.7, 132.3, 128.6, 126.1, 103.6, 59.9, 39.87, 19.1, 14.0. IR (KBr) cm^{-1} = 3342, 1701, 1650, 1483, 1210.
- **Compound 4b**: M.P = 150–152°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15–7.25 (dd, 4H, ArH), 5.68 (br, 1H, NH), 4.99 (s, 1H, CH), 4.09 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.32 (s, 6H, $2CH_3$), 1.23 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 147.0, 143.9, 131.3, 129.4, 128.1, 104.1, 60.0, 39.1, 19.6, 14.4. IR (KBr) cm^{-1} = 3344, 1698, 1650, 1489, 1212.
- **Compound 4c:** M.P = 130–132°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05–7.26 (m, 4H, ArH), 5.67 (s, 1H, NH), 5.30 (s, 1H, CH), 4.10 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.32 (s, 6H, $2CH_3$), 1.23 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 145.3, 143.9, 132.8, 130.4, 128.0, 127.1, 126.8, 103.5, 59.8, 37.1, 20.0, 14.1. IR (KBr)cm^{-1} = 3331, 1699, 1670, 1491, 1208.
- **Compound 4d:** M.P = 158–160°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12–7.31 (dd, 4H, ArH), 5.71 (s, 1H, NH)), 5.33 (s, 1H, CH), 4.11 (q, J = 7.1 Hz, 4 H, $2CH_2$), 2.35 (s, 6 H, $2CH_3$), 1.23 (t, J = 7.1 Hz, 6 H, $2CH_3$), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.7, 148.3, 142.3, 130.2, 131.0, 128.1, 104.0, 59.9, 39.3, 19.3, 14.2. IR (KBr)cm^{-1} = 3340, 1696, 1650, 1494, 1210.
- **Compound 4e:** M.P = 163–165°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02–7.32 (m, 4H, ArH), 5.74 (br, 1H, NH), 5.10 (s, 1H, CH), 4.10 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.33 (s, 6H, $2CH_3$), 1.24 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 149.9, 148.3, 144.9, 134.4, 129.0, 123.1, 121.2, 103.9, 59.8, 38.1, 19.3, 14.1. IR (KBr) cm^{-1} = 3342, 1701, 1645, 1487, 1212.
- **Compound 4f:** M.P = 129–131°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01–7.35 (m, 4H, ArH), 5.71 (br, 1H, NH), 5.07 (s, 1H, CH), 4.10 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.24 (s, 6H, $2CH_3$), 1.23 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 150.3, 146.7, 145.0, 126.3, 122.6, 103.6, 59.9, 38.7, 19.3, 14.2. IR (KBr) cm^{-1} = 3331, 1699, 1644, 1483, 1212.
- **Compound 4g**: M.P = 158–160°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18–6.81(dd, 4H, ArH), 5.71 (s, 1H, NH), 5.05 (s, 1H, CH), 4.09 (q, J = 7.1 Hz, 4H, $2CH_2$), 3.75 (s, 3H, CH_3), 2.32 (s, 6H, $2CH_3$), 1.22 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 158.0, 146.5, 136.3, 131.1, 113.6, 103.5, 59.8, 53.7, 39.3, 19.2, 14.3.
- IR (KBr) cm^{-1} = 3341, 1691, 1649, 1491, 1211.
- **Compound 4h**: M.P = 139–141°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–6.80 (m, 4H, ArH), 5.73 (s, 1H, NH), 5.11 (s, 1H, CH), 4.07 (q, J = 7.1 Hz, 4H, $2CH_2$), 3.90 (s, 3H, CH_3), 2.34 (s, 6H, $2CH_3$), 1.24 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.7, 158.3, 146.5, 131.2, 127.9, 122.1, 121.7, 112.7,



SCHEME 1 1,4-Dihydropyridine derivatives $\mathbf{4_{a\text{-}o}}$ time of reaction (min) and Yield(%)

103.9, 59.8, 54.3, 32.6, 19.3, 14.1. IR (KBr) cm^{-1} = 3334, 1698, 1650, 1491, 1210.

- **Compound 4i:** M.P = 230–232°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21–6.78 (dd, 4H, ArH), 5.64 (s, 1H, NH), 5.21 (s, 1H, OH), 5.02 (s, 1H, CH), 4.07 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.34 (s, 6H, $2CH_3$), 1.24 (t, J = 7.2 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, CDCl3) δ: 167.4, 155.3, 146.6, 135.7, 131.4, 115.4, 104.1, 59.9, 39.4, 19.5, 14.1. IR (KBr) cm^{-1} = 3342, 1689, 1641, 1491, 1221.
- **Compound 4j:** M.P = 137–139°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19–7.02 (m, 4H, ArH), 5.73 (s, 1H, NH), 5.02 (s, 1H, CH), 4.07 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.32

(s, 6H, $2CH_3$), 2.22 (s, 3H, CH_3), 1.21 (t, J = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 146.3, 143.9, 135.4, 128.3, 127.7, 104.1, 59.7, 39.4, 21.3, 19.5, 14.2. IR (KBr) cm^{-1} = 3348, 1699, 1650, 1487, 1212.

- **Compound 4 k:** M.P = 160–162°C, ^1H NMR (400 MHz, $CDCl_3$) δ: 7.23(s, 1H, CH), 6.34 (m, 1H, CH), 6.01 (d, J = 3.7 Hz, 1H, CH), 5.72 (s, 1H, NH), 5.00 (s, 1H, CH), 4.08 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.33 (s, 6H, $2CH_3$), 1.22 (t, J = 7.2 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 151.9, 146.3, 141.9, 110.2, 107.7, 103.4, 59.8, 29.6, 18.3, 14.1. IR (KBr) cm^{-1} = 3344, 1701, 1651, 1485, 1209.
- **Compound 4l:** M.P = 173–175°C, ^1H NMR (400 MHz, $CDCl_3$) δ: 7.19–7.08 (m, 1 H), 6.98–6.80 (m, 2 H), 5.81 (s, 1H, NH), 5.11 (s, 1H, CH), 4.11 (q, J = 7.1 Hz, 4 H, $2CH_2$), 2.33 (s, 6 H, $2CH_3$),1.28 (t, J = 7.1 Hz, 6 H, $2CH_3$), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.8, 151.3, 144.9, 143.3, 126.3, 123.1, 103.7, 59.7, 34.3, 19.3,14.1. IR (KBr) cm^{-1} = 3343, 1699, 1651, 1488, 1370, 1211.
- **Compound 4m:** M.P = 230–232°C, ^1H NMR (400 MHz, $CDCl_3$) δ: 7.79–7.26 (m, 3H, Ar), 5.88 (s, 1H, NH), 4.99 (s, 1H, CH), 4.13–4.08 (q, J = 7.1 Hz, 4H, $2CH_2$), 2.37 (s, 6H, $2CH_3$),1.25–1.22 (t, J = 7.1 Hz, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.8, 148.6, 147.5, 145.0, 133.3, 131.4, 131.3, 130.7, 102.9, 60.3, 39.6, 19.6, 14.1. IR (KBr) cm^{-1} = 32,462, 3101, 2979, 1680, 1530, 872.
- **Compound 4n:** M.P = 103–105°C, ^1H NMR (400 MHz, $CDCl_3$) δ: 7.71–7.40 (m, 4 H, ArH), 5.86 (s, 1H, NH), 5.14 (s, 1H, CH), 4.11–4.08 (q, *J* = 7.1 Hz, 4 H, CH_2), 2.39 (s, 6 H,CH_3), 1.11–1.08 (t, *J* = 7.1 Hz, 6 H, CH_3), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 156.23, 144.5, 141.4, 132.0, 129.1, 126.3, 118.6, 112.5, 61.7, 23.2, 14.0. IR (KBr) cm^{-1} = 3246, 2930, 2223, 1710, 1559, 1444, 868.
- **Compound 4o:** M.P = 148–150°C, ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.11 (m, 3 H, ArH), 5.71 (brs, 1H, NH), 5.29 (s, 1H, CH), 4.13–4.09 (q, *J* = 7.1 Hz, 4 H, CH_2), 2.33 (s, 6 H,CH_3), 1.19–1.16 (t, *J* = 7.1 Hz, 6 H, CH_3), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.2, 144.3, 143.9, 133.1, 132.7, 132.1, 129.0, 127.3, 103.6, 60.1, 37.3, 19.9, 14.1. IR (KBr) cm^{-1} = 3311, 1696, 1615, 1488, 1201, 861.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of various 1,4-dihydropyridine derivatives

The catalytic activity of MnTSPP catalyst was evaluated towards the Hantzsch synthesis of bioactive 1,4-dihydropyridines. In this context, the facile one-pot and three-component condensation reaction of aromatic aldehyde $\mathbf{1_{a-o}}$ (1 mmol), ethyl acetoacetate **2** (2 mmol), and ammonium acetate **3** (2 mmol) was designated as a model reaction. Through the present experiments, the growth of the condensation reaction was systemically studied the influence of catalyst dose, reaction-solvent, as well as the different Lewis acid catalysts on the catalytic activity. In the absence of catalyst, the product got at longer reaction time. In the presence of MnTSPP, it improves the yield of the products as clarified at Scheme 1. The series of aromatic aldehydes that undergo electrophilic substitutions reactions are successfully synthesized in excellent yields that illustrated in Scheme 1.

3.1.1 | Effect of catalyst loading

The relationship between catalyst dosages toward the product yields is shown in Table 1. In particular, the loading of the catalyst from 2 to 10 mol% was improved yield from 22% to 99% of the product (Table 1). The improvement of the yield by increasing the amount of MnTSPP can be rationalized to the possible increase in the number of available active sites, as well as increasing the amount of contact and collision chance between the surface of MnTSPP with the molecules of the starting materials. Note, that with a further increase of the loaded catalyst from 10 mol% to 11 mol%, the yields and reaction times did not change significantly (Table 1). Thus, 10 mol % of catalyst is the optimal catalyst loading.

TABLE 1 The amount of MnTSPP catalyst for the synthesis of 1,4-dihydropyridine derivative **4a**[a]

Entry	Cat. mol%	Yield %[b]	Entry	Cat. mol%	Yield %[b]
1	2	22	5	8	86
2	4	39	6	9	93
3	6	54	7	10	99
4	7	72	8	11	99

[a]Reaction conditions $\mathbf{1_a}$(1 mmol), **2** (2 mmol), **3** (2 mmol), and Catalyst (0.1 mmol) in mixture of water and ethanol (3:1 ratio) were refluxed 15 min.
[b]Isolated yields based on $\mathbf{4_a}$.

3.1.2 | Effect of solvents

To handle the procedure more easily, we then continued to optimize the model process mentioned above by detecting the efficiency of several classic solvents chosen as the medium for comparison (Table 2). The role of the solvents was evaluated with the model reaction **4a**. As indicated in Table 2, the polar protic solvents (MeOH, EtOH, AcOH, and H_2O) were much better than aprotic solvents (DCM, DMF, THF, CH_3CN, and $CHCl_3$). The results could be interpreted with much better solubility of the catalyst and the reagents in the polar solvents. From Table 2, it is evident that this reaction under mixture of solvents (water and ethanol (v/v) (3/1)) is obviously the best choice for the synthesis of 1,4-dihydropyridines **4a** proceeded rapidly with the highest yield. The authors preferred this mixture because it is green, safe, and cheap in comparison with organic solvents.

In the recent years, metal ions-polyphyrin complexes have received considerable attention as a mild Lewis acid catalyst for an array of organic transformation. The reaction of benzaldehyde **1a,** ethyl acetoacetate **2,** and ammonium acetate **3** in the absence of the catalyst at the same condition, trace product, was obtained (Table 3, entry 1). Various types of Lewis acids such as $AlCl_3$, $MgCl_2$, Mg

TABLE 2 Effect of solvent for the synthesis of 1,4-dihydropyridines **4a**

Solvent[a]	Time (min)	Yield (%)[b]
DCM	180	35
DMF	180	46
THF	180	49
CH_3CN	180	53
$CHCl_3$	180	50
MeOH	50	76
ACOH	60	69
EtOH	25	94
H_2O	20	84
H_2O/EtOH	15	99

Note: Effect of various Lewis acid catalysts.
[a]Reaction conditions $\mathbf{1}_a$ (1 mmol), **2** (2 mmol), **3** (2 mmol), and catalyst (0.1 mmol) in mixture of water and ethanol (3:1 ratio) were refluxed 15 min.
[b]Isolated yields based on $\mathbf{4}_a$.

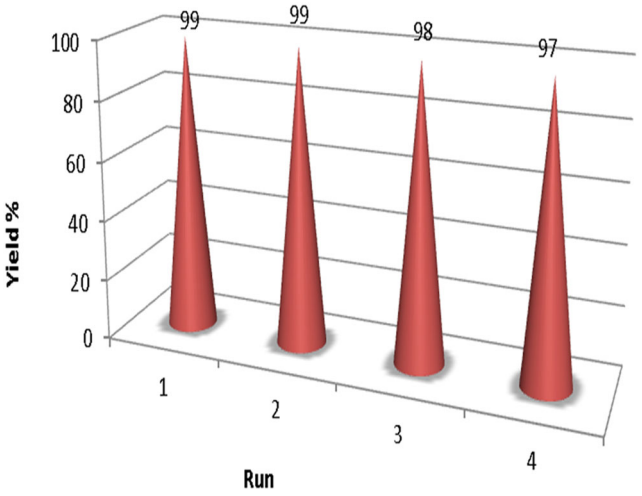


FIGURE 2 Recyclability of MnTSPP in the model reaction

TABLE 3 Use of different Lewis acid for the reaction **4a**[a]

Entry	Cat (mol%)	Conditions[a]	Yield (%)[b]
1	No catalyst	water/ethanol, 1 day	Trace
2	$AlCl_3$ (10)	water/ethanol, 15 min	58
3	$MgCl_2$ (10)	water/ethanol, 15 min	45
4	Mg $(OTf)_2$ (10)	water/ethanol, 15 min	34
5	$FeCl_3.6H_2O$ (10)	water/ethanol, 15 min	53
6	Fe $(OTf)_3$ (10)	water/ethanol, 15 min	61
7	$MnCl_2.4H_2O$ (10)	water/ethanol, 15 min	66
8	MnO_2 (10)	water/ethanol, 15 min	72
9	(10) $ZnBr_2$	water/ethanol, 15 min	54
10	Zn $(OTf)_2$ (10)	water/ethanol, 15 min	60
11	$CuCl_2$(10)	water/ethanol, 15 min	47
12	$TiCl_4$ (10)	water/ethanol, 15 min	60
13	*p*-TsOH (10)	water/ethanol, 15 min	63
14	**MnTSPP (10)**	water/ethanol, **15 min**	**99**

[a]Reaction conditions $\mathbf{1}_a$(1 mmol), **2** (2 mmol), **3** (2 mmol), and catalyst (0.1 mmol) in mixture of water and ethanol (3:1 ratio) were refluxed 15 min.
[b]Isolated yields based on $\mathbf{4}_a$.

$(OTf)_2$, $FeCl_3.6H_2O$, Fe $(OTf)_3$, $MnCl_2.4H_2O$, MnO_2, $ZnBr_2$, Zn $(OTf)_2$, $CuCl_2$, $TiCl_4$, and *p*-TsOH are tested in the selected reaction conditions. It was confirmed that the iron soluble porphyrin catalyst was much better in comparison with all the other Lewis acids stable in water (Table 3, entries 2–13). MnTSPP was found to be the most effective catalyst and afforded the desired product **4a** in 99% yield (Table 3, entry 14).

3.1.3 | Recycling of MnTSPP catalyst

The green and economic aspect of this synthetic protocol was further studied by examining the possibility of MnTSPP catalyst for reusing at the next runs of the Hantzsch condensation reaction. To do this, progress of the model reaction (aromatic aldehyde, ethyl acetoacetate, and ammonium acetate, water/ethanol (3:1 ratio), refluxed 15 min.) in the presence of MnTSPP was studied four times for the synthesis of compound **4a** and there was an inevitable loss of catalyst during the recovery process. The summarized results in Figure 2 show that the MnTSPP was reused for four consecutive cycles without the significant loss of catalytic activity, when we tried the next runs (five to seven) that gave low catalytic activity under the similar conditions.

The Hantzsch 1,4 dihydropyridine mechanism has been Studied with NMR (Katritzky et al.).[50] The

TABLE 4 The comparison of the catalytic activity of MnTSPP with formerly reported catalysts

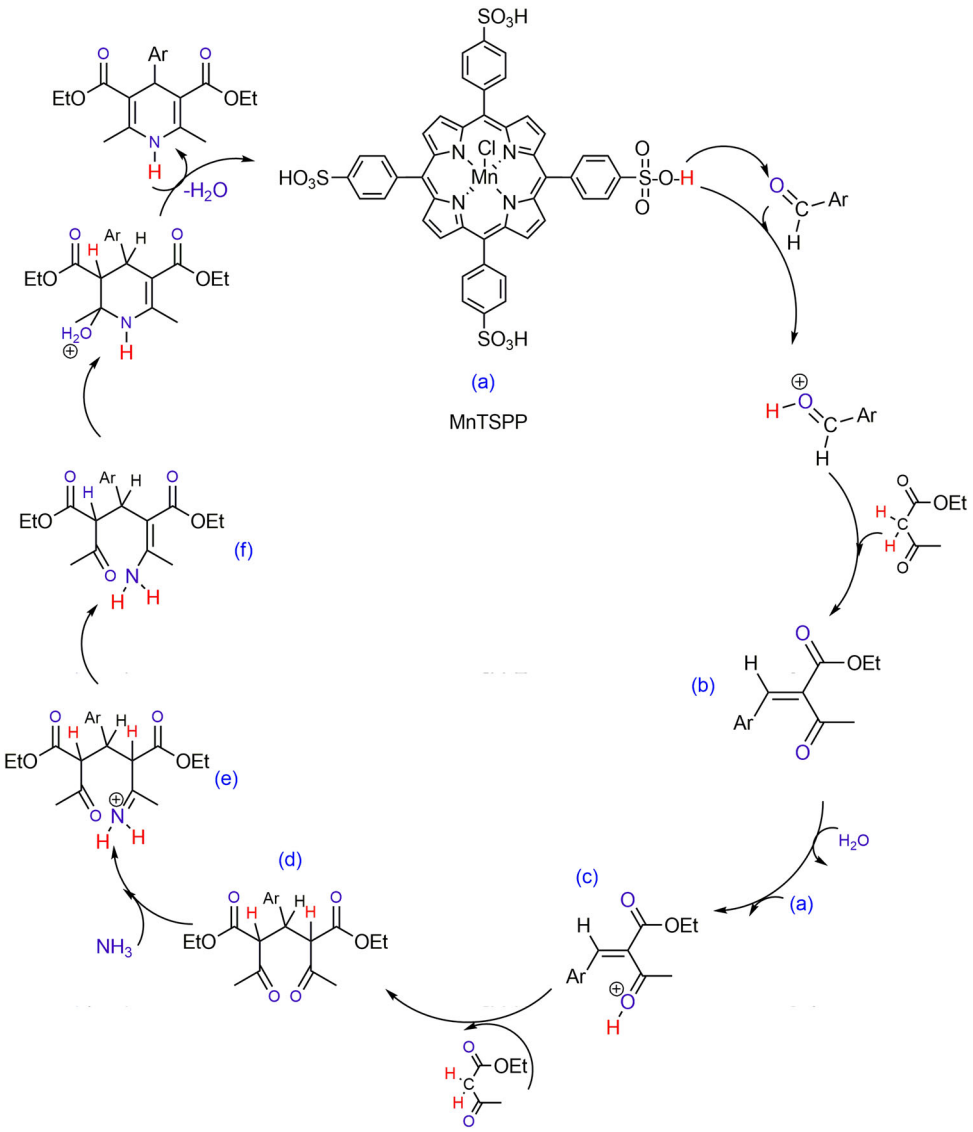
Entry catalyst	Time (min.)	Catalyst amount	Solvent	Temperature	Yield (%)	Ref.
$Yb(OTf)_3$	300	5 mol.%	EtOH	r.t	90	51
$Gd(OTf)_3$	300	5 mol.%	EtOH	Reflux	91	26
$H_5BW_{12}O_{40}$	45	10 mol.%	EtOH	Reflux	94	52
PdRuNi nanoparticles furnished with graphene oxide (PdRuNi@ GO NPs)	45	6 mg	DMF	70°C	93	53
Alumina sulfuric acid (ASA)	120	0.2 g	MeOH	70°C	92	54
Hafnium (IV) bis (perfluorooctanesulfonyl)imide Hf $(NPf_2)_4$	180	1 mol.%	perfluorodecalin	60°C	95	55
Tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$	20	7 mmol%	Solvent free	110°C	95	56
PPh_3	120	20 mol.%	EtOH	Reflux	94	57
$[PS\text{-}IM\ (CH_2)_4SO_3H][HSO_4]$	140	-	EtOH	Reflux	90	58
CeO_2	60	50 mg	EtOH	80°C	92	59
Cellulose sulfuric acid	300	15 mol.%	Solvent free	100°C	81	60
Chitosan-$CuSO_4$	24	20 mg	CH_3CN	Reflux	45	61
Montmorillonite K10	20	20 wt.%	EtOH	80	95	62
TiO_2 NPs	105	-	EtOH	80	90	63
MgO NPs	160	0.04 g	EtOH	Reflux	90	64
Hydrotalcite	120	20 mg	Water	60°C	93	65
$AlCl_3.\ 6H_2O$	120	10 mol.%	Solvent free	60°C	78	66
Alginic acid	40	20 mol.%	EtOH	Reflux	98	67
$NiFe_2O_4@SiO_2@SO_3H$	20	20 mg	H_2O	70°C	95	68
LiBr	180–360	10 mol.%	CH_3CN	Reflux	93	69
Zr-ZSM-5	30	40 mg	EtOH	40°C	94	70
Magnetic dextrin	15	3.5 wt.%	EtOH	Reflux	95	71
La_2O_3	60	10 mol.%	TFE	Reflux	95	72
$BiBr_3$	120	2 mol.%	EtOH	Reflux	85	73
magnetite/chitosan	70	0.04 gm	EtOH	r.t	90	74
MnTSPP	15	10 mol.%	H_2O/EtOH	Reflux	99	Present work

known mechanism for this reaction consists of three reaction paths: the MnTCPP catalyzed between benzaldehyde with an ethyl acetoacetate yields an arylidene compound by Knoevenagel condensation; the MnTSPP catalyzed condensation between NH_4 and an ethyl acetoacetate to give the α-amino α,β-unsaturated carbonyl compound; and the condensation products between arylidene compound and α-amino α,β-unsaturated carbonyl compound formation of 1,4-dihydropyridine derivatives.

As can be seen in Table 4, the catalytic activity of MnTSPP was compared with diverse catalysts such as which have been previously employed as catalysts in our model reaction. In terms of reaction times and the yield of the products, the present work exhibited the perfect efficiency than the other promoters.

3.1.4 | Plausible mechanism for the synthesis of 1,4-dihydropyridines derivatives

We propose that the possible following mechanism for the synthetic protocol (Scheme 2) could be outlined for the role of MnTSPP catalyzing the synthesis of 1,4-dihydropyridines derivatives. (4-sulfonatophenyl)-porphyrin manganese (III) chloride (a) primarily activates the carbonyl moiety of aromatic aldehyde that acts as appropriate electrophile using protonation of carbonyl group and then one molecule of ethyl acetoacetate condenses with activated aldehyde to form Knoevenagel intermediate (aldol condensation) (b). At the next, through the catalyst activation of intermediate (c) with the second molecule of ethyl acetoacetate material (Michael addition), intermediate (d) is



SCHEME 2 Suggested mechanism for synthesis of 1,4-dihydropyridines derivatives and the catalytic role of MnTSPP

produced. Nucleophilic attack of the NH_2 group of ammonia to carbonyl group leads to achieve intermediate (e). Finally, the ring closing of intermediate (f), then removal of one molecule of H_2O, owing to the driving force of conjugation of double bonds with carbonyl groups, the derivatives of 1,4-dihydropyridines will be produced.[75] This proposed mechanism was confirmed with the literature.[68]

4 | CONCLUSION

In conclusion, we successfully developed a facile and efficient method for synthesis a variety of 1,4-dihydropyridine derivatives from the reaction of aromatic aldehyde **1,** ethyl acetoacetate **2** and ammonium acetate in the presence of MnTSPP catalyst in mild conditions. The catalytic activity of Hantzsch three-component reaction approach for the synthesis of aromatization of 1,4-dihydropyridine derivatives using MnTSPP catalyst is remarkable, and the use of environmentally benign, and commercially available. We have investigated the advantages of MnTSPP to form precipitates in a multicomponent system in water for the enhancement of the Aromatization of 1,4-dihydropyridines. The higher catalytic activity of MnTSPP is ascribed to its high acidity and water tolerance. Also, the superiority of use MnTSPP towards the synthesis of 1,4-dihydropyridine is compared with other Lewis acids; the mildness of the conversion, compatibility with various functional groups, makes this procedure attractive to synthesize variety of these derivatives. All reactions were carried out in mixture of H_2O and C_2H_5OH within 15–80 min. to afford the products from high to excellent yields. The current protocol offers several significant advantages, in terms of the avoidance of discharging harmful organic solvents, experimental simplicity, the high yield of products, commercially available catalyst, short reaction times, easy workup procedures, low cost and nontoxicity of the catalyst, wide tolerance of starting materials, benefits of green and economic solvents, as well as excellent reusability of the catalyst. The simple, economical, and green procedure may be applied to the industry in the future.

ACKNOWLEDGMENTS

The authors are deeply grateful, and thanks to Sohag University in Egypt for supporting and facilitating for this study.

AUTHOR CONTRIBUTIONS

hesham hamad: Supervision. **Ahmed M. M. Soliman**: Supervision. **omar elhady:** Supervision.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

FUNDING INFORMATION

No funding.

ORCID

Mahmoud Abd El Aleem Ali Ali El-Remaily https://orcid.org/0000-0002-3591-0077
Hesham A. Hamad https://orcid.org/0000-0002-2434-8904
Ahmed M. M. Soliman https://orcid.org/0000-0003-2541-638X
Omar M. Elhady https://orcid.org/0000-0003-1702-2495

REFERENCES

[1] S. Nakagaki, K. A. D. F. Castro, G. S. Machado, M. Halma, S. M. Drechsel, F. Wypych, *J. Braz. Chem. Soc.* **2006**, *17*, 1672.
[2] K. S. Suslick, P. Bhyrappa, J. H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry, S. R. Wilson, *Acc. Chem. Res.* **2005**, *38*, 283.
[3] F. L. Benedito, S. Nakagaki, A. A. Saczk, P. G. Peralta-Zamora, M. C. M. Costa, *Appl. Catal. A* **2003**, *250*, 1.
[4] S. Nakagaki, C. R. Xavier, A. J. Wosniak, A. S. Mangrich, F. Wypych, M. P. Cantão, I. Denicoló, L. T. Kubota, *Colloids Surf. A* **2000**, *168*, 261.
[5] A. M. Machado, F. Wypych, S. M. Drechsel, S. Nakagaki, *J. Colloid Interface Sci.* **2002**, *254*, 158.
[6] A. L. Faria, T. O. C. M. Leod, V. P. Barros, M. D. Assis, *J. Braz. Chem. Soc.* **2009**, *20*, 895.
[7] S. Nakagaki, M. Halma, A. Bail, G. G. C. Arízaga, F. Wypych, *J. Colloid Interface Sci.* **2005**, *281*, 417.
[8] F. Wypych, A. Bail, M. Halma, S. Nakagaki, *J. Catal.* **2005**, *234*, 431.
[9] S. Nakagaki, F. Wypych, *J. Colloid Interface Sci.* **2007**, *315*, 145.
[10] E. A. Vidoto, M. S. M. Moreira, F. S. Vinhado, K. J. Ciuffi, O. R. Nascimento, Y. Iamamoto, *J. Non-Cryst. Solids* **2002**, *304*, 151.
[11] H. C. Sacco, K. J. Ciuffi, J. C. Biazzotto, M. R. Zucchi, C. A. M. Leite, O. R. Nascimento, O. A. Serra, Y. Iamamoto, *J. Non-Cryst. Solids* **2000**, *273*, 150.
[12] D. C. Oliveira, H. C. Sacco, O. R. Nascimento, Y. Iamamoto, K. J. Ciuffi, *J. Non-Cryst. Solids* **2001**, *284*, 28.
[13] A. T. Papacídero, L. A. Rocha, B. L. Caetano, E. Molina, H. C. Sacco, E. J. Nassar, Y. Martinelli, C. Mello, S. Nakagaki, K. J. Ciuffi, *Colloids Surf. A* **2006**, *275*, 27.
[14] H. Podbielska, A. Ulatowska-Jarza, G. Müller, I. Holowacz, J. Bauer, U. Bindig, *Biomol. Eng.* **2007**, *24*, 425.
[15] H. Tanaka, T. Yamada, S. Sugiyama, H. Shiratori, R. Hino, *J. Colloid Interface Sci.* **2005**, *286*, 812.
[16] a) I. Dror, D. Baram, B. Berkowitz, *Environ. Sci. Technol.* **2005**, *39*, 1283; b) H. Wang, Y. Song, Z. Wang, C. J. Medforth, J. E. Miller, L. Evans, P. Li, J. A. Shelnutt, *Chem. Mat.* **2008**, *20*, 7434.

[17] For reviews about metal catalysis in water, see: a) W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524–1544; Angew. Chem 1993, *105*, 1588–1609; b) P. Dixneuf, V. Cadierno (Eds), *Metal-Catalyzed Reactions in Water*, Wiley-VCH, Weinheim **2013**.

[18] a) C. J. Li, *Acc. Chem. Res* **2002**, *35*, 533.

[19] P. Dixneuf, V. Cadierno (Eds), *Metal-Catalyzed Reactions in Water*, Wiley-VCH, Weinheim **2013**.

[20] L. Stefan, H.-J. Xu, C. P. Gros, F. Denat, D. Monchaud, *Chem. Eur. J*. **2011**, *17*, 10857.

[21] E. Rose, B. Andreoletti, S. Zrig, M. Quelquejeu-Etheve, *Chem. Soc. Rev*. **2005**, *34*, 573.

[22] S. Beigly, S. Ghiaee, S. A. Ebrahimi, M. Mahmoudian, *Acta Physiologica Hungarica* **2004**, *91*, 111.

[23] M. Faizi, M. Janahmadi, M. Mahmoudian, *Acta Physiolo Gica Hungarica* **2003**, *90*, 243.

[24] a) S. Sheik Mansoor, K. Aswin, K. Logaiya, S. P. N. Sudhan, *Arab. J. Chem* **2017**, *10*, S546. https://doi.org/10.1016/j.arabjc.2012.10.017 b) V. K. Sharma, S. K. Singh, *RSC Adv.* **2017**, *7*, 2682; c) M. George, L. Joseph, C. Joseph, *Pharm. Innov.* **2017**, *6*, 165.

[25] a) G. W. Zamponi, *Nat. Rev. Drug Discov* **2016**, *15*, 19; b) P. A. Datar, P. B. Auti, *J. Saudi Chem. Soc* **2016**, *20*, 510; c) S. A. Khedkar, P. B. Auti, *Mini-Rev. Med. Chem* **2014**, *14*, 282; d) R. S. Kumar, A. Idhayadulla, A. J. A. Nasser, J. Selvin, *J. Serb. Chem. Soc.* **2011**, *76*, 1.

[26] a) R. S. Kumar, A. Idhayadulla, A. J. A. Nasser, K. Murali, *Indian J. Chem*. **2011**, *50B*, 1140; b) G. Swarnalatha, G. Prasanthi, N. Sirisha, C. Madhusudhana Chetty, *Int. J. ChemTech. Res.* **2011**, *3*, 75.

[27] D. L. Comins, S. O'Connor, *Advances in Heterocyclic Chemistry* **1988**, *44*, 199. https://doi.org/10.1016/S0065-2725(08)60263-9

[28] R. Kumar, R. Chandra, *Advances in Heterocyclic Chemistry* **2001**, *78*, 269. https://doi.org/10.1016/S0065-2725(01)78005-1

[29] R. Lavilla, *J. Chem. Soc., Perkin Transactions* **2002**, *1*, 1141. https://doi.org/10.1039/B101371H

[30] J. Safari, S. H. Banitaba, S. D. Khalili, *J. Mol. Catal. A: Chem*. **2011**, *335*, 46.

[31] A. Bamoniri, S. Fouladgar, *RSC Adv.* **2015**, *5*, 78483.

[32] E. Rafiee, S. Eavani, S. Rashidzadeh, M. Joshaghani, *Inorg. Chim. Acta* **2009**, *362*, 3555.

[33] H. Adibi, H. A. Samimi, M. Beygzadeh, *Catal. Commun* **2007**, *8*, 2119.

[34] B. P. Reddy, K. Rajesh, V. Vijayakumar, *Arab. J. Chem*. **2011**, *11*. https://doi.org/10.1016/j.arabjc.2011.01.027

[35] S. M. Baghbanian, S. Khaksar, S. M. Vahdat, M. Farhang, M. Tajbakhsh, *Chin. Chem. Lett* **2010**, *22*, 563.

[36] C. S. Reddy, M. Raghu, *Chin. Chem. Lett* **2008**, *19*, 775.

[37] L. Saikia, D. Dutta, D. K. Dutta, *Catal. Commun*. **2012**, *19*, 1.

[38] K. Purandhar, V. Jyothi, P. P. Reddy, M. A. Chari, K. Mukkantid, *J. Heterocycl. Chem.* **2012**, *49*, 232.

[39] D. Bandyopadhyay, S. Maldonado, B. K. Banik, *Molecules* **2012**, *17*, 2643.

[40] S. S. Mansoor, S. S. Shafi, S. Z. Ahmed, *Arab. J. Chem*. **2011**. https://doi.org/10.1016/j.arabjc.2011.09.018

[41] M. Tajbakhsh, E. Alaee, H. Alinezhad, M. Khanian, F. Jahani, S. Khaksar, *Chin. J. Catal. 33*, 1517.

[42] R. Surasani, D. Kalita, A. V. D. Rao, K. Yarbagi, K. B. Chandrasekha, *J. Fluo. Chem.* **2012**, *135*, 91.

[43] E. Kolvari, M. A. Zulfigol, N. Koukabi, B. Shirmardi-Shaghasemi, *Chem. Pap*. **2011**, *65*(6), 898.

[44] H. Mirzaei, A. Davoodnia, *Chin. J. Catal* **2012**, *33*, 1502.

[45] S. Ghosh, F. Saikh, J. Das, A. K. Pramanik, *Tetrahedron Lett.* **2013**, *54*, 58.

[46] J. Safari, F. Azizi, M. Sadeghi, *New J. Chem.* **2015**, *39*, 1905.

[47] a) D. S. Rekunge, C. K. Khatri, G. U. Chaturbhuj, *Tetrahedron Lett* **2017**, *58*, 1240; b) S. Mondal, B. C. Patra, A. Bhaumik, *Chem. Cat. Chem.* **2017**, *9*, 1469.

[48] a) M. Tajbakhsh, H. Alinezhad, M. Norouzi, S. Baghery, M. Akbari, *J. Mol. Liq.* **2013**, *177*, 44; b) S. K. Das, S. Mondal, S. Chatterjee, *A. Bhaumik, Chem. Cat. Chem*. **2018**, *10*, 2488.

[49] a) M. A. A. El-Remaily, M. Elhady, *Appl.Organometal.Chem.* **2019**, *33*, 4989; b) M. A. A. El-Remaily, O. M. Elhady, *Tetrahedron Lett.* **2016**, *57*, 435; c) M. A. A. El-Remaily, H. A. Hamad, *J. Mol. Catal. A: Chem.* **2015**, *404*, 148; d) M. A. A. El-Remaily, A. M. Abu-Dief, *Tetrahedron* **2015**, *71*, 2579; e) M. A. A. El-Remaily, *Tetrahedron* **2014**, *70*, 2971; f) M. A. A. El-Remaily, *Chin. J. Catal.* **2015**, *36*, 1124; g) A. M. M. Soliman, S. K. Mohamed, M. A. A. El-Remaily, H. Abdel-Ghany, *Eur. J. Med. Chem.* **2012**, *47*, 138; h) M. A. A. El-Remaily, S. K. Mohamed, *Tetrahedron* **2014**, *70*, 270; i) M. A. A. El-Remaily, A. M. Abu-Dief, O. M. Elhady, *Appl. Organometal. Chem.* **2019**, *33*, 5005; j) M. A. A. El-Remaily, A. M. Abu-Dief, M. Rafat, *El-Khatib. Appl. Organometal. Chem.* **2016**, *30*, 1022; k) M. A. A. El-Remaily, A. M. M. Soliman, O. M. Elhady, *ACS Omega* **2020**, *5*, 6194; l) A. M. Abu-Dief, N. M. El-Metwaly, S. O. Alzahrani, F. Alkhatib, M. M. Abualnaja, T. El-Dabea, M. A. A. El-Remaily, *J. Mol. Liq.* **2021**, *326*, 115277; m) M. A. A. El-Remaily, O. M. Elhady, *Chemistry Select* **2020**, *5*(39), 12098; n) E. A. Ahmed, A. M. M. Soliman, A. M. Ali, M. A. A. El-Remaily, *Appl. Organometal. Chem.* **2021**, *35*, e6197. https://doi.org/10.1002/aoc.6197

[50] A. R. Katritzky, D. L. Ostercamp, T. I. Yousaf, *Tetrahedron* **1986**, *42*, 5729.

[51] L.-M. Wang, J. Sheng, L. Zhang, J.-W. Han, Z.-Y. Fan, H. Tiana, C.-T. Qian, *Tetrahedron* **2005**, *61*, 1539.

[52] T. Momeni, M. M. Heravi, T. Hosseinnejad, M. Mirzaei, V. Zadsirjan, *J. Mol. Strut.* **2020**, *1199*. 127011

[53] T. Demirci, B. Çelik, Y. Yıldız, S. Eris, M. Arslan, F. Sen, B. Kilbas, *RSC Adv.* **2016**, *6*, 76948.

[54] M. M. Heravi, V. Zadsirjan, B. Fattahi, N. Nazari, *Curr. Org. Chem.* **2016**, *20*, 1676.

[55] M. Hong, C. Cai, W.-B. Yi, *Hafnium J. Fluorine Chem* **2010**, *131*, 111.

[56] A. Davoodnia, M. Khashi, N. Tavakoli-Hoseini, *Chin. J. Catal.* **2013**, *34*, 1173.

[57] A. Debache, W. Ghalem, R. Boulcina, A. Belfaitah, S. Rhouati, B. Carboni, *Tetrahedron Lett.* **2009**, *50*, 5248.

[58] B. Jahanbin, A. Davoodnia, H. Behmadi, N. Tavakoli-Hoseini, *Bull. Korean Chem. Soc.* **2012**, *33*, 2140.

[59] O. D'alessandro, Á. G. Sathicq, J. E. Sambeth, H. J. Thomas, G. P. Romanelli, *Catal. Commun*. **2015**, *60*, 65.

[60] Y. L. N. Murthy, A. Rajack, M. T. Ramji, J. J. Babu, C. Praveen, K. A. Lakshmi, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 6016.

[61] M. G. Dekamin, E. Kazemi, Z. Karimi, M. Mohammadalipoor, M. R. Naimi-Jamal, *Int. J. Biol. Macromol.* **2016**, *93*, 767.

[62] G. Song, B. Wang, X. Wu, Y. Kang, L. Yang, *Synth. Commun.* **2005**, *35*, 2875.
[63] M. Tajbakhsh, E. Alaee, H. Alinezhad, M. Khanian, F. Jahani, S. Khaksar, P. Rezaee, M. Tajbakhsh, *Chin. J. Catal.* **2012**, *33*, 1517.
[64] H. Mirzaei, A. Davoodnia, *Chin. J. Catal.* **2012**, *33*, 1502.
[65] P. Ramakanth, S. Maddila, V. D. B. C. Dasireddy, S. B. Jonnalagadda, *Catal. Commun.* **2014**, *45*, 148.
[66] S. D. Sharma, P. Hazarika, D. Konwar, *Catal. Commun.* **2008**, *9*, 709.
[67] M. G. Dekamin, S. Ilkhanizadeh, Z. Latifidoost, H. Daemi, Z. Karimi, M. Barikani, *RSC Adv.* **2014**, *4*, 56658.
[68] B. Zeynizadeh, S. Rahmani, E. Eghbali, *Polyhedron.* **2019**, *168*, 57.
[69] D. K. Yadav, R. Patel, V. P. Srivastava, G. Watal, L. D. S. Yadav, *Chin. J. Chem.* **2011**, *29*, 118.
[70] U. Kusampally, N. Dhachapally, R. Kola, C. R. Kamatal, *Mater. Chem. Phys.* **2020**, *242*, 122497.
[71] A. Maleki, F. Hassanzadeh-Afruzi, Z. Varzi, M. S. Esmaeili, *Mater. Sci. Eng. C* **2020**, *109*, 110502.
[72] S. U. Tekale, V. P. Pagore, S. S. Kauthale, R. P. Pawar, *Chin. Chem. Lett.* **2014**, *25*(8), 1149. https://doi.org/10.1016/j.cclet.2014.03.037
[73] J. S. Yoo, T. J. Laughlin, J. J. Krob, R. S. Mohan, *Tetrahedron Lett.* **2015**, *56*(27), 4060. https://doi.org/10.1016/j.tetlet.2015.04.121
[74] A. Maleki, M. Kamalzare, M. Aghaei, *J. Nanostruct. Chem.* **2015**, *5*(1), 95. https://doi.org/10.1007/s40097-014-0140-z
[75] S. M. Vahdat, M. A. Zolfigol, S. Baghery, *Appl. Organometal. Chem.* **2016**, *30*, 311.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Ali El-Remaily Mahmoud Abd El Aleem Ali, Hamad HA, Soliman AMM, Elhady OM. Boosting the catalytic performance of manganese (III)-porphyrin complex MnTSPP for facile one-pot green synthesis of 1,4-dihydropyridine derivatives under mild conditions. *Appl Organomet Chem*. 2021;e6238. https://doi.org/10.1002/aoc.6238