A new and efficient one-pot solid-supported synthesis of 1,2,4,6-tetraaryl-1,4-dihydropyridines

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Abstract: 1,2,4,6-Tetraaryl-1,4-dihydropyridines were obtained by the one-pot reaction of chalcones and substituted anilines on the surface of Bi(III)nitrate-Al_2O_3. The reaction seems to proceed via β-oxygenation of Bi(III) enolised chalcones followed by Michael addition and heteroannulation with simultaneous retro aldol disproportionation. The presence of the ring-activating groups at ortho and para positions in the aniline seems to be essential for the reaction.

Key words: 1,2,4,6-tetraryl-1,4-dihydropyridines, chalcones, substituted anilines, Bi(III) nitrate-alumina catalyst.

Résumé : On a réalisé la synthèse de 1,2,4,6-tétraaryl-1,4-dihydropyridines par le biais d'une réaction monotope de chalcones avec des anilines substituées à la surface d'un catalyseur de nitrate de Bi(III)-Al_2O_3. La réaction semble impliquer une β-oxygénation des sels de Bi(III) des chalcones énolisées, suivie d'une addition de Michael et d'une héteroannelation accompagnée d'une dismutation simultanée rétroaldolique. Il semble que la présence de groupes activants dans les positions ortho et para de l'aniline soit essentielle à la réalisation de la réaction.

Mots clés : 1,2,4,6-tétraaryl-1,4-dihydropyridines, chalcones, anilines substituées, catalyseur de nitrate de Bi(III)-alumine.

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Introduction

1,4-Dihydropyridine derivatives participate actively in biochemical oxidoreductase (1) and transaminase (2) reactions. They serve as key intermediates in the biogenesis of indole alkaloids (3) as well as the synthesis of several naturally occurring bioactive alkaloids (4) and substituted pyridines (5). These products are primarily potent calcium antagonists (6) and the activity is dictated by the stereochemistry at C-4 (7). The compounds also exhibit a wide range of other therapeutic properties such as antioxidant (8), antimutagenic (9), antidiabetic (10), hepatoprotective (11), antiaddictive (12), bronchodilating (13), herbicidal (14), and anticancer (15) activity. Therefore, the synthesis of 1,4-dihydropyridine derivatives continues to be a subject of fruitful research. These products, especially the calcium channel regulators, are synthesized chiefly by Hantzsch synthesis (14) or its modifications and by the reduction of pyridine derivatives or pyridinium salts. Several reviews (16) have exhaustively dealt with the synthesis, chemistry, pharmacology, and industrial utility of 1,4-dihydropyridine derivatives.

Our interest in the synthesis of 1,2,4,6-tetraaryl-1,4-dihydropyridines originated from the presumption that because of the planarity of the 1,4-dihydropyridine nucleus (17) these products may display the photodynamic activity akin to the symmetrical 2,4,6-triarylthiopyrylium, selenopyrylium, and telluropyrylium photosensitizers, which have been recommended for cell-specific cancer therapy (18). Moreover, since most of the known syntheses (16) of 1,4-dihydropyridine derivatives are multistage laborious processes and involve harsh or environmentally hazardous reaction conditions, together with the fact that the alkyl and the aryl primary amines have not gained popularity in their synthesis, we opined that a new and straightforward catalytic method, employing aryl primary amine as one of the substrates, was needed for the synthesis of 1,2,4,6-tetraaryl-1,4-dihydropyridines. Herein, we report a simple, convenient, and cost-effective one-pot solid-supported synthesis of these compounds from chalcones and substituted anilines using the hitherto unexplored Bi(III) nitrate-Al_2O_3 reagent.

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Results and discussion

Although Bi(III) nitrate is easily available in pure form and has negligible toxicity (19) and high stability in air and moisture, its catalytic efficacy has not been thoroughly explored. This led us to evaluate the possible catalytic utility of Bi(III) nitrate immobilized on neutral alumina in the synthesis of the title products. The catalyst was selected on the assumption that Bi(III) ions, being moderately acidic (20) in nature, could bind efficiently to the surface of neutral alumina, prevent its restructuring, synergise its catalytic activity (21), and initiate a reaction under mild conditions. The catalyst was prepared by adsorbing Bi(III) nitrate·$5H_2O$ (5% *w*/*w*) on neutral alumina and activation of the air-dried mixture in a hot air oven at 110 ± 5 °C, for six hours. The catalyst was reactivated each time before use.

The chalcone substrates **1a**–**1k** were prepared from the appropriate benzaldehyde and acetophenone by classical

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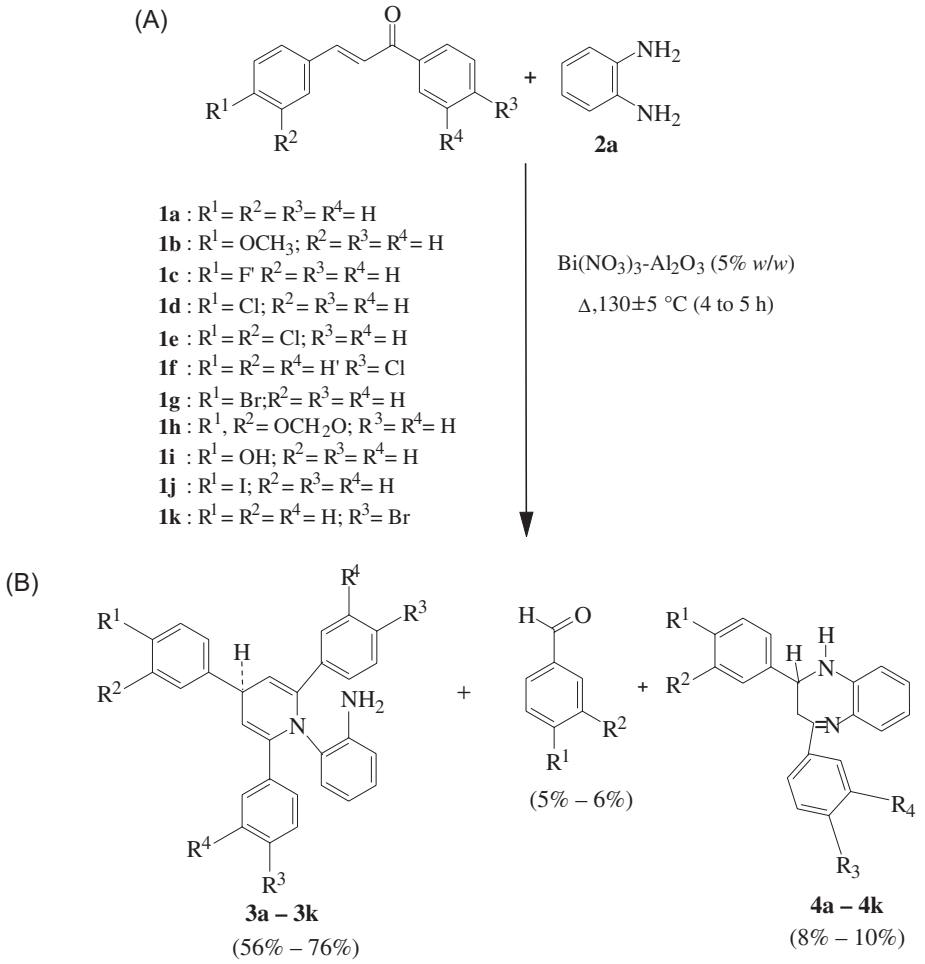
Scheme 1. 1,2,4,6-Tetraaryl-1,4-dihydropyridines from chalcones.



(C)

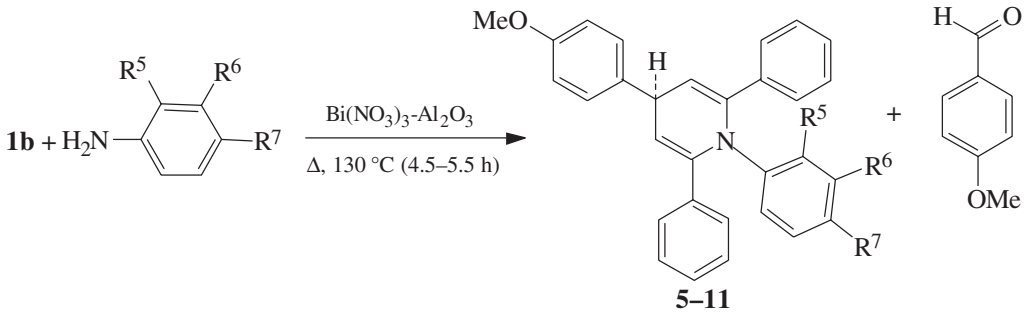
	3a/4a	3b/4b	3c/4c	3d/4d	3e/4e	3f/4f	3g/4g	3h/4h	3i/4i	3j/4j	3k/4k
R^1	H	OCH_3	F	Cl	Cl	H	Br	–O–	OH	I	H
R^2	H	H	H	H	Cl	H	H	CH_2	H	H	H
								–O–			
R^3	H	H	H	H	H	Cl	H	H	H	H	Br
R^4	H	H	H	H	H	H	H	H	H	H	H

Claisen–Schmidt condensation (22). Subsequent reactions of **1a**–**1k** with *o*-phenylenediamine, **2a**, (2:1 mol/L), and Bi(III) nitrate-Al_2O_3 (Scheme 1), in the proportion by weight of chalcones, were carried out in a thermostatically controlled hot air oven at 130 ± 5 °C, for 4 to 5 h. The resulting product mixtures were isolated with chloroform and separated by column chromatography to yield the major products **3a**–**3k** (56%–76%) (Table 1) and the minor products **4a**–**4k** (8%–10%). These reactions also afforded the aldehyde (5%–6%) from which **1a**–**1k** were prepared. The compounds **3a**–**3k** and **4a**–**4k** were analysed by spectral methods, HREI-MS, IR, ^{1}H NMR, ^{13}C NMR and DEPT 135°. The spectra established the structures of **3a**–**3k** as 1,2,4,6-tetraaryl-1,4-dihydropyridine derivatives (Scheme 1). The expanded peak segregated ^{1}H NMR spectra of the products showed a characteristic one proton triplet (J = 3.8 Hz) near δ 5.37 because of the α proton (5*a*, 23) at C-4, δ_C 54.7, coupled to the protons at C-3 and C-5, δ 6.80–7.1 (d, J = 3.9 Hz, 2H), δ_C 145.2, of the dihydropyridine nucleus. The IR absorption band at υ_{max} 3455 cm^{-1} and a broad singlet near δ 7.23 (2H) in the ^{1}H NMR spectra revealed the presence of a free amino group in the compounds. The ^{13}C NMR signals were assigned on the basis of DEPT 135 experiments. The mass spectra of **3a**–**3k** exhibited fragmentations typical of 1,4-dihydropyridines (24) and displayed abundant ion peaks corresponding to the loss of an aryl radical from the C-4 of the

Table 1. Yield of the products **3a**–**3k** and **4a**.

Compound	Oven yield (%)	MW yield (%)	Compound	Oven yield (%)	MW yield (%)	MW time (min)
3a	70.0	72.4	**4a**	8	6	20
3b	76.0	78.3	**4b**	8	7	22
3c	56.2	59.1	**4c**	10	12	20
3d	60.8	61.2	**4d**	10	10	23
3e	64.5	68.0	**4e**	9	12	22
3f	61.0	65.0	**4f**	10	12	23
3g	67.5	67.4	**4g**	8	14	19
3h	72.0	73.5	**4h**	8	6	23
3i	70.0	71.2	**4i**	9	9	25
3j	62.5	65.0	**4j**	9	10	25
3k	65.7	66.5	**4k**	7	9	26

Scheme 2. Reaction of **1b** with different substituted anilines.



5–11

2b : R^5= OH; R^6= R^7= H

2c : R^6= OH; R^5= R^7= H

2d : R^7= OH; R^5= R^6= H

2e : R^5= Br; R^6= R^7= H

2f : R^6= Br; R^5= R^7= H

2g : R^7= Br; R^5= R^6= H

2h : R^6= NO_2; R^5= R^7= H

2i : R^5= NO_2; R^6 = R^7= H (No reaction)

2j : R^7= NO_2; R^5= R^7= H (No reaction)

2k : R^5= R^6= R^7 = H (No reaction)

5: R^5= OH; R^6= R^7= H

6: R^6= OH; R^5= R^7= H

7: R^7= OH; R^5= R^6= H

8: R^5= Br; R^6= R^7= H

9: R^6= Br; R^5= R^7= H

10: R^7= Br; R^5= R^6= H

11: R^6= NO_2; R^5= R^7= H

molecular ion. The base peak fragment ion at *m/z* 246 resulted from the loss of the second aryl radical from the C-2 or C-6 position of the (M^+ – $Ar^·$) fragment ion. Except for compounds **3f** and **3k**, which possessed two monosubstituted aryl rings at positions 2 and 6 of the 1-(2-aminophenyl)-1,4-dihydropyridine nucleus, and compound **3a**, which possessed unsubstituted phenyl rings at positions 2,4, and 6 of the nucleus, all products had a lone substituted phenyl ring at position 4 of the nucleus.

The ^{1}H NMR spectra of the minor products **4a**–**4k** displayed resonance signals near δ 3.0 (dd, *J* = 8.2, 11.5 Hz, H_a-6), 3.20 (dd, *J* = 4.1, 11.5 Hz, H_b-6), 5.10 (dd, *J* = 4.1, 8.2 Hz, H-7), and 3.80–3.90 (s, br, 1H, NH) typical of benzo-1,4-diazepines. These compounds were known and their spectral data and melting points were consistent with the literature (25).

To generalize this reaction and assess the influence of the ring-activating and ring-deactivating substituents in anilines on the percentage yield of the products, chalcone **1b** was reacted separately but under identical conditions with *ortho*-, *meta*-, and *para*-hydroxyaniline **2b**–**2d**, bromoaniline **2e**–**2g**, nitroaniline **2h**–**2j**, and aniline **2k** (Scheme 2). Aniline, *o*-

Scheme 3. Probable mechanism for formation of 1,2,4,6-tetraaryl-1,4-dihydropyridine.

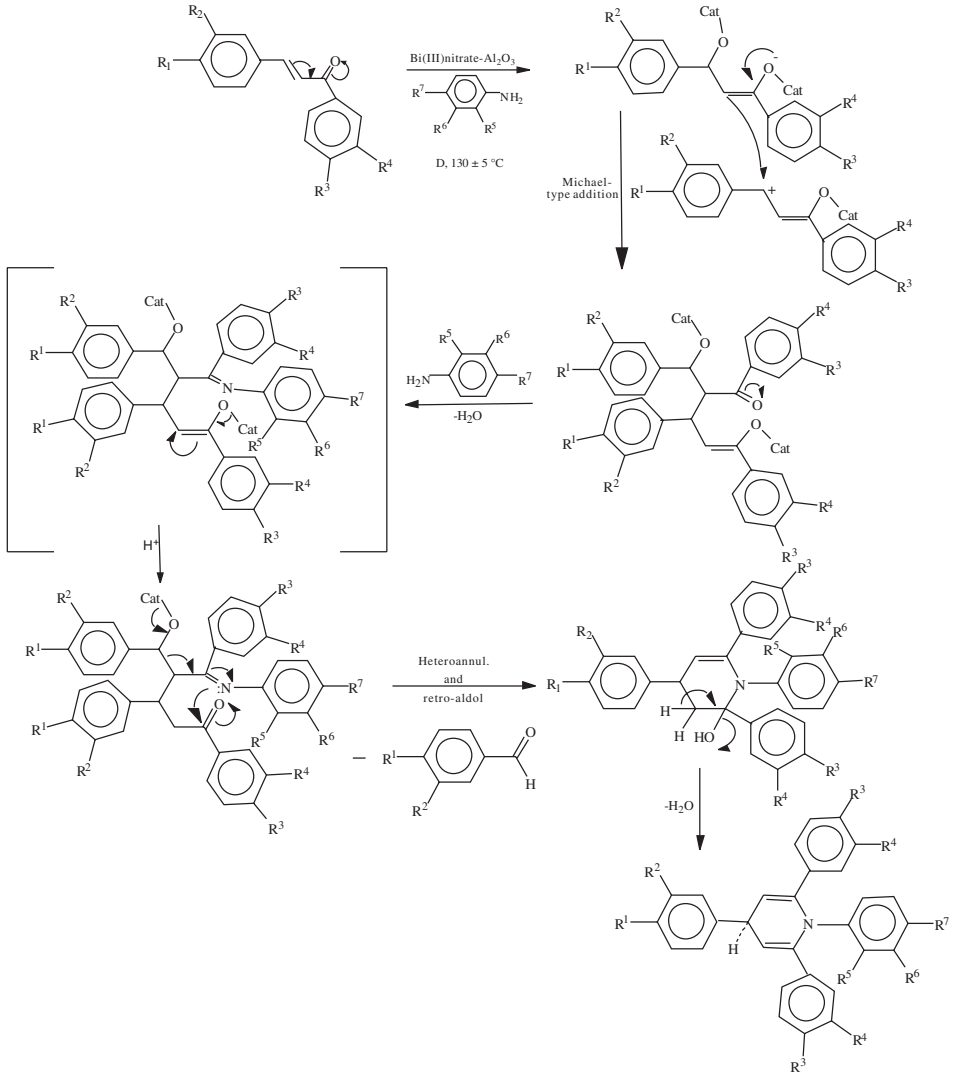


Table 2. Yield of the products of **1b** with different anilines **2b**–**2h**.

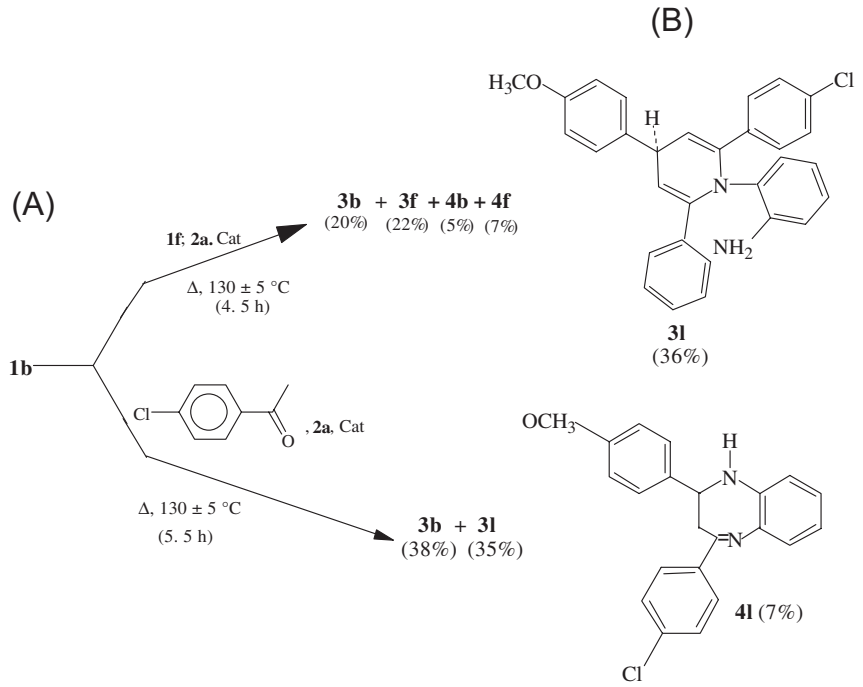
Product	Oven yield (%)	MW yield (%)	MW time (min)
5	65.6	68.2	20
6	22.5	26.0	26
7	72.0	74.3	25
8	73.4	75.4	18
9	19.5	19.8	25
10	76.5	78.5	20
11	32.5	33.0	20

nitroaniline, and *p*-nitroaniline failed to afford the desired 1,2,4,6-tetraaryl-1,4-dihydropyridines while *meta*- nitroaniline afforded the product **11**, albeit in low yield (Table 2). The ring-activating groups in anilines seem to favour the reaction and formed compounds **5**–**10** with the percentage yield in the expected order of para > ortho > meta substituted anilines (Table 2).

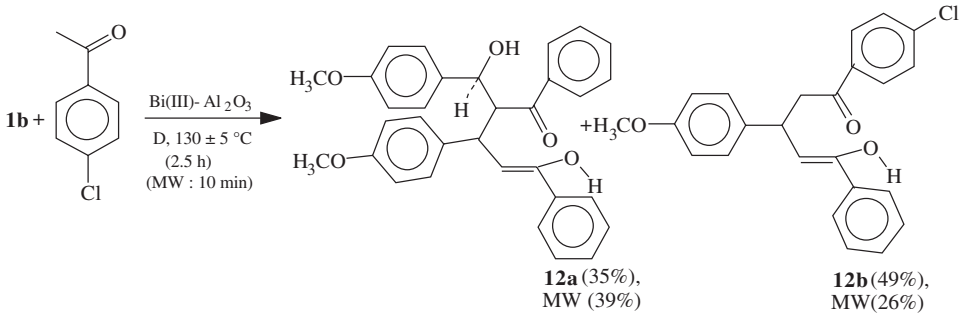
Since crystalline bismuth nitrate exists as $Bi(NO_3)_3{\cdot}5H_2O$ and alumina also chemisorbs water readily (25) and retains some of it even after activation at 110 ± 5 °C, the mechanism of the reaction may be rationalised as involving β-oxygenation of the Bi(III) nitrate activated chalcone enolate, which may then undergo a Michael addition to a second α,β-unsaturated ketone (Scheme 3) to form a 1,5-diketone enolate adduct. Subsequent heteroannulation with substituted anilines via condensation and retro-aldol disproportionation (26) may form 2-hydroxy-1,2,4,6-tetraaryl-1,2,3,4-tetrahydropyridine derivatives, which may undergo dehydration to yield 1,2,4,6-tetraaryl-1,4-dihydropyridines. This mechanism is supported by the fact that the products obtained from 4-substituted chalcones, like **3b**, possessed only one substituted phenyl group at position 4-4 of the 1-(2-aminophenyl)-1,4-dihydropyridines nucleus.

To substantiate the proposed mechanism, cross-reactions of chalcones **1b** and **1f** and also **1b** and *p*-chloroacetophenone (1:1 mol/L) with equimolar amounts of **2a** and 5% Bi(III) nitrate-Al_2O_3, in proportion by weight of the substrates, were carried out at 130 ± 5 °C (Scheme 4). The reaction of **1b**, **1f**, and **2a** yielded **3b** (20%), **3f** (22%), **3l** (36%),

Scheme 4. Cross reaction of **1b**.



Scheme 5. Reaction of **1b** and *p*-chloroacetophenone in the absence of aniline derivatives.



4b (5%), and **4f** (7%). The reaction involving **1b**, *p*-chloroacetophenone, and **2a** gave **3b** and **3l** in nearly equal proportions and **4l** (13%).

We attempted the reaction of equimolar quantities of **1b**, *p*-chloroacetophenone, and equal mass of Bi(III)nitrate-Al_2O_3 at 130 ± 5 °C (Scheme 5) in the absence of arylamines. The reaction afforded two products, **12a** and **12b**, which were separated by column chromatography and identified by spectral methods as 2-(4-methoxyphenyl)hydroxymethyl-3-(4-methoxy)phenyl-1,5-diphenylpentan-4-en-5-ol-1-one (**12a**) and 1-(4-chloro)phenyl-3-(4-methoxy)phenyl-5-phenylpentan-4-en-5-ol-1-one (**12b**) (Scheme 5). The ^{1}H NMR, ^{13}C NMR and DEPT 135 spectra for **12a** and **12b** showed the presence of a carbonyl group, δc 197.3, and an enol hydroxyl, δ 12.9 (s br, exch. D_2O, 1H). The spectra of **12a** revealed the absence of a methylene carbon whose presence in **12b** was evident from the resonance signals at δ 2.69 (d, J = 4.5 Hz, 2H) in its ^{1}H NMR spectrum and δ_C 25.3 in its ^{13}C NMR and DEPT 135 spectra. The spectra of **12a** showed the presence of a secondary hydroxyl displaying resonance signals at δ 2.80 (s br, exch. D_2O, 1H) and 5.01 (d, J = 3.6 Hz, 1H, -CH-OH), δ_C 83.2. These signals were absent in the spectra of **12b**. These observations were consistent with the proposed mechanism and indicated that the retro-aldol disproportionation is probably triggered by the heteroannulation of the Michael adduct with substituted anilines, especially the anilines having a ring-activating group at the ortho or para position.

The reaction is sensitive to temperature with the optimum temperature being 130 ± 5 °C. The reaction failed to proceed in solution or when neat Al_2O_3 or Bi(III) nitrate were used as the reagent. We repeated all the reactions in a domestic microwave (2450 MHz) using 60% power and followed the procedure of Mukhopadhyay et al. (27), which allows the temperature to remain at ca. 130 °C. The reactions were completed in 19–26 min without any appreciable improvement in the yield of the 1,2,4,6-tetraaryl-1,4-dihydropyridines (Tables 1 and 2).

Conclusion

In conclusion, we have devised a new one-pot environmentally benign and general solid-supported catalytic method for the synthesis of 1,2,4,6-tetraaryl–1,4-dihydropyridines

from the easily accessible chalcones and substituted anilines using Bi(III) nitrate immobilized on Al_2O_3 as a reagent. An advantage of this method is the low toxicity (19) and the antiulcerative (28) properties of bismuth compounds. Further studies on the scope and limitations of immoblized Bi(III) nitrate in organic transformations are under way.

Experimental

General

Melting points are uncorrected and were determined on Perfit melting point apparatus. IR, on KBr discs, were taken on a Brucker 4800 IR spectrometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) were recorded in DMSO or $CDCl_3$ using a Brucker Ac DPX-200 spectrometer; some spectra were recorded on Varian Gemini 300 MHz instrument. HREI-MS were recorded on JEOL D-300 mass spectrometer at 70 eV. TLC was performed on 0.5 mm thick plates using BDH silica gel-G adsorbent. Column chromatography was performed on silica gel (BDH, mesh size 60–120) using graded solvent systems of petroleum ether (40–60 °C), petroleum ether – $CHCl_3$ and $CHCl_3$–EtOAc. Microwave irradiations were carried out in a domestic microwave oven (LG Model No. MS-255R, No. 4140W1A347A) with frequency 2450 MHz and R_f output of 900W.

Preparation of catalyst

Bi(III) nitrate·$5H_2O$ (2.5 g) was dissolved in 50% MeOH (150 mL) and the solution was added to neutral alumina (50 g) and stirred for 12 h at room temperature. The mixture was air dried and then heated at 110 ± 5 °C in a thermostatic hot air oven for 6 h. The activated Bi(III) nitrate-Al_2O_3 mixture was cooled in a dessicator and preserved. The catalyst was reactivated at 110 ± 5 °C for 0.5 h each time before use.

Preparation of chalcones 1a–1k

Chalcones **1a**–**1k** were prepared from the appropriate benzaldehyde and acetophenone by the well known procedure for Claisen–Schmidt condensation (22). Chalcones were purified by CC on silica gel using petroleum ether – CH_2Cl_2 (9:1, 7:3, and 1:1 *v*/*v*, 40–60 °C) followed by crystallization from $CHCl_3$ –MeOH.

General procedure for the preparation of 3a–3k, 5–11 and cross-reactions of 1b

The solution of chalcone **1a**–**1k** (2×10^{-3} mol/L) and *o*-phenylenediamine **2a** (1×10^{-3} mol/L) in chloroform (10 mL) were adsorbed on a Bi(III) nitrate-Al_2O_3 mixture in proportion by weight of the chalcones. The solvent was evaporated in air and the air-dried solid mixture was charged into a stoppered flask. The flask was heated in a thermostatically controlled hot air oven and maintained at 130 ± 5 °C. Simultaneously, separate experiments were conducted to monitor the reaction by comparative TLC of the ethylacetate extracts of the aliquots drawn out from the reaction flask at 0.5 h intervals, using petroleum ether – CH_2Cl_2 (9:1, 7:3, and 3:7 *v*/*v*, 40–60 °C) as solvent systems. The plates were developed by spraying with Ce(IV) ions and heating at 110 ± 5 °C for 10 min when dark purple spots of the Ce(IV) complexes of 1,2,4,6-tetraaryl-1,4-dihydropyridines and yellow spots of the 1,4-benzodiazepines were observed against a white background. On completion of the reaction (4–5 h) the product mixtures were extracted with hot $CHCl_3$ in a soxhlet extractor, freed from the solvent, and separated by CC, using petroleum ether – CH_2Cl_2 (40–60 °C) graded solvent systems. Twenty milliliter fractions were collected and TLC identical fractions were pooled. The solvent was distilled and the residue was purified by crystallization from $CHCl_3$ – petroleum ether (40–60 °C) and $CHCl_3$–MeOH. This gave **3a**–**3k** as major product and **4a**–**4k** (25) as the minor product (Table 1). In addition to these compounds, minor quantities of aldehydes from which **1a**–**1k** were prepared were also obtained. Compounds **5**–**11** (Scheme 3) were prepared by reacting **1b** (2×10^{-3} mol/L) and 2-aminophenol (**2b**), 3-aminophenol (**2c**), 4-aminophenol (**2d**), 2-bromoaniline (**2e**), 3-bromoaniline (**2f**), 4-bromoaniline (**2g**), and 3-nitroaniline (**2h**) (1×10^{-3} mol/L), respectively, with Bi(III) nitrate-Al_2O_3 in proportion by weight of the substrates using the previously described procedure. The same procedure was adopted in the reaction of **1b** (1×10^{-3} mol/L), **1f** (1×10^{-3} mol/L), and Bi(III) nitrate-Al_2O_3 and a mixture of **3b**, **3f**, **3l**, **4b**, and **4f** were obtained (Scheme 4). The mixture was separated by CC as described earlier. A similar procedure was used in the reaction of **1b** (1×10^{-3} mol/L), *p*-chloroacetophenone (1×10^{-3} mol/L), and Bi(III) nitrate-Al_2O_3 (Scheme 4) when a mixture of **3b**, **3l**, and **4l** was recovered by adopting the previously described procedure for the isolation, separation, and purification of the compounds.

Preparation of 12a and 12b

To a mixture of **1b** (0.238 g, 1×10^{-3} mol/L) and *p*-chloroacetophenone (0.15 g, 1×10^{-3} mol/L) dissolved in $CHCl_3$ (10 mL) was added the reagent Bi(III)nitrate-Al_2O_3 (0.388 g). The mixture was dried in air and heated in a thermostatically controlled hot air oven at 130 ± 5 °C. A separate experiment was simultaneously conducted to monitor the reaction by TLC of the chloroform extract of the aliquots drawn from the reaction mixture at 0.5 h intervals. On completion of the reaction (2.5 h) the products were isolated with chloroform and filtered, and the filtrate was washed with water and dried over anhydr. $MgSO_4$. TLC (silica gel G, solvent C_6H_6) of the product mixture showed the presence of two products **12a** and **12b**, which were separated by CC (silica gel), using petroleum ether – benzene (1:1) and benzene and were crystalized from chloroform–methanol.

General procedure for microwave irradiation

The solid mixtures of chalcones, anilines, and Bi(III)nitrate- Al_2O_3 in the same proportions as were used during the reactions carried out in a thermostatically controlled hot air oven were heated in a domestic microwave (2450 MHz) using 60% power (540 W) using the procedure of Mukhopadhyay et al. (27), which permits the control of temperature at 130 °C. The reactions were monitored by TLC as described earlier. The reactions were completed within 18–26 min (Tables 1 and 2). The products were extracted and purified as before and were identified by co-TLC, mp, and mmp as **3a**–**3k**, **3l**, **4a**–**4k**, **4l**, **5**–**11**, **12a**, and **12b**.

1-(2-Aminophenyl)-2,4,6-triphenyl-1,4-dihydropyridine (3a)

Colourless crystals, mp 162 to163 °C. IR (cm^{-1}) υ_{max}: 3430, 3036, 3004, 2945–2669 (m), 1611, 1500, 1476, 1454,

1434, 1399, 1371, 1294, 1253, 1178, 1033, 965, 744. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.32 (t, *J* = 3.9 Hz, 1H), 7.02 (d, *J* = 3.9 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 4H), 7.25 (s br, 2H, NH_2), 7.49 (dd, *J* = 8.4, 3.2 Hz, 6H), 7.70 (m, 7H), 8.10 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 54.8, 114.5, 121.6, 122.3, 127.9, 128.4, 129.7, 131.5, 139.4, 151.1. HR EI-MS *m/z*: 400.1979 (M^+, 5) (calcd. for $C_{29}H_{24}N_2$: 400.1939), 323 ([$M^+ - C_6H_5$], 36), 246 (100), 154 (33), 101 (47), 88 (65). Anal. calcd. for $C_{29}H_{24}N_2$: C 86.95, H 6.05, N 6.99; found: C 87.38, H 5.98, N 6.72.

1-(2-Aminophenyl)-4(4-methoxyphenyl)-2,6-diphenyl-1,4-dihydropyridine (3b)

Colourless crystals, mp 183 °C. IR (cm^{-1}) υ_{max}: 3435, 3036, 3004, 2940–2673 (m), 1610, 1500, 1470, 1455, 1435, 1399, 1371, 1294, 1253, 1030, 967. ^{1}H NMR (DMSO-d_6) δ: 3.84 (s, 3H), 5.35 (t, *J* = 3.8 Hz, 1H), 7.15 (d, *J* = 3.8 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.33 (ddd, *J* = 6.9, 8.4, 3.9 Hz, 6H), 7.35 (s, br, 2H), 7.69 (d, *J* = 8.4 Hz, 6H), 7.80 (d, *J* = 6.9 Hz, 4H). ^{13}C NMR (DMSO-d_6) δ_C: 54.8, 55.3, 114.6, 116.5, 127.6, 127.7, 128.4, 128.6, 131.2, 143.0, 149.1, 158.6. HR EI-MS *m/z*: 430.2015 (20) (calcd. for $C_{30}H_{26}N_2O$: 430.2045), 416 (35), 353 (40), 246 (100), 154 (45), 101 (53), 88 (71). Anal. calcd. for $C_{30}H_{26}N_2O$: C 83.68, H 6.09, N 6.50; found: C 83.72, H 6.12, N 6.20.

1-(2-Aminophenyl)-4(4-fluoro)phenyl-2,6-diphenyl-1, 4-dihydropyridine (3c)

Colourless crystals, mp 102 °C. IR (cm^{-1}) υ_{max}: 3436, 3035, 3004, 2943–2675 (m), 1618, 1500, 1470, 1455, 1430, 1398, 1371, 1294, 1253, 1030, 967. ^{1}H NMR (DMSO-d_6) δ: 5.75 (d, *J* = 3.9 Hz, 1H), 7.09 (t, *J* = 3.9 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 3H), 7.18 (m, 10H), 7.35 (sbr, 2H), 7.49 (dd, J = 8.7, 3.9 Hz, 4H), 8.10 (d, *J* = 3.9 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ_C: 57.2, 114.3, 115.8, 121.7, 122.6, 124.6, 128.9, 129.8, 130.1, 134.9, 143.7, 151.2, 160.5. HR EI-MS *m/z*: 418.1846 (18) (calcd. for $C_{29}H_{23}FN_2$: 418.1851), 323 ([$M^+ - C_6H_4F$], 46), 246 ([$M^+ - C_6H_4F - C_6H_5$], 100), 92 (70), 77 (76). Anal. calcd for $C_{29}H_{23}FN_2$: C 83.22, H 5.55, N 6.69; found: C 83.35, H 5.42, N 6.20.

1-(2-Aminophenyl)-4(4-chloro)phenyl-2,6-diphenyl-1,4-dihydropyridine (3d)

Colourless crystals, mp 189 °C. IR (cm^{-1}) υ_{max}: 3437, 3010, 2945–2669 (m), 1620, 1480, 1456, 1434, 1399, 1370, 1295, 1253, 1178, 1033, 965, 745. ^{1}H NMR (DMSO-d_6) δ: 5.37 (d, *J* = 3.9 Hz, 1H), 7.09 (t, *J* = 3.9 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 4H), 7.46 (m, 13H), 7.37 (s br, 2H), 8.0 (d, *J* = 3.9 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ_C: 55.8, 111.2, 118.7, 121.5, 122.4, 126.3, 128.8, 129.7, 130.0, 134.9, 143.7, 151.1. HR EI-MS *m/z*: 436.1535, 434.1540 (M^+, 6) (calcd. for $C_{29}H_{23}ClN_2$: 436.1520, 334.1520), 222 ([$M^+ - C_6H_5Cl$], 30), 246 ([$M^+ - C_6H_5Cl - C_6H_5$], 100), 92 (73), 77 (67). Anal. calcd. for $C_{29}H_{23}ClN_2$: C 79.79, H 5.34, N 6.45; found: C 80.20, H 4.95, N 5.98.

1-(2-Aminophenyl)-4-(3,4-dichlorophenyl)-2,6-diphenyl-1,4-dihydropyridine (3e)

Colourless crystals, mp 235 °C. IR (cm^{-1}) υ_{max}: 3435, 3050, 2945–2669 (m), 1605, 1550, 1497, 1387, 1350, 1148, 1090, 1018, 970, 730. ^{1}H NMR (DMSO-d_6) δ: 5.38 (t, *J* = 3.9 Hz, 1H), 7.17 (d, *J* = 3.9 Hz, 1H), 7.38 (m, 8H), 7.50 (ddd, *J* = 8.3, 7.9, 2.9 Hz, 2H), 7.55 (s br, 2H), 7.57 (ddd, *J* = 8.3, 7.9, 2.9 Hz, 3H), 7.64 (ddd, *J* = 8.3, 7.9, 2.2 Hz, 2H), 7.89 (d, *J* = 8.3Hz, 1H), 8.02 (dd, *J* = 8.2, 2.2 Hz, 2H). ^{13}C NMR(DMSO-d_6) δ_C: 54.3, 108.9, 111.7, 121.9, 123.0, 123.8, 126.4, 125.3, 128.0, 128.9, 129.8, 130.7, 133.5, 135.6, 143.9,151.1. HR EI-MS *m/z*: 470, 468.1109 (M^+, 13) (calc. for $C_{29}H_{22}Cl_2N_2$, 468.1120), 323 ([$M^+ - C_6H_3Cl_2$], 30), 246 ([$M^+ - C_6H_3Cl_2 - C_6H_5$], 100), 169 (56), 155 (41), 77 (70). Anal. calcd. for $C_{29}H_{22}Cl_2N_2$: C 74.34, H 4.74, N 5.98; found: C 75.01, H 4.68, N 6.30.

1-(2-Aminophenyl)-2,6-di(4-chloro)phenyl-4-phenyl-1,4-dihydropyridine (3f)

Colourless crystals, mp 202 °C. IR (cm^{-1}) υ_{max}: 3456, 3030, 2669–2945 (m), 1610, 1475, 1496, 1387, 1350, 1140, 1090, 1072, 926. ^{1}H NMR (DMSO-d_6) δ: 5.35 (t, *J* = 3.9 Hz, 1H), 7.06 (d, *J* = 3.9 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 4H), 7.45 (m, 5H), 7.55 (s br, 2H), 7.63 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.64 (dd, *J* = 8.2, 2.2 Hz, 4H), 8.02 (dd, *J* = 8.2, 1.6 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ: 54.1, 111.3, 118.7, 121.6, 122.5, 126.4, 128.9, 129.8, 130.1, 135.0, 143.7, 151.2. HR EI-MS *m/z* (rel. int): 468.1110 (10) (calcd. for $C_{29}H_{22}Cl_2N_2$: 468.1101), 391 [M^+- Ph], 280 (100), 188 (57), 169 (46), 77 (62). Anal. calcd. for CHN: not found.

1-(2-Aminophenyl)-4-(4-bromo)phenyl-2,6-diphenyl-1,4-dihydropyridine (3g)

Colourless crystals, mp 178 °C. IR (cm^{-1}) υ_{max}: 3435, 3050, 1605, 1545, 1490, 1387, 1350, 1150, 1095, 920, 760. ^{1}H NMR ($CDCl_3$) δ: 5.37 (t, *J* = 3.9 Hz, 6H), 7.16 (d, *J* = 3.9 Hz, 2H), 7.26 (m, 4H), 7.36 (s br, 2H), 7.39 (dd, *J* = 8.7, 3.9 Hz, 2H), 7.51 (s, br, 2H), 7.58 (ddd, *J* = 8.3, 2.4, 8.3 Hz, 4H), 7.72 (d, *J* = 8.7 Hz, 2H), 8.28 (ddd, *J* = 8.3, 2.4, 8.3 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ_C: 55.9, 111.6, 118.9, 122.3, 125.6, 128.3, 129.7, 130.1, 131.9, 143.9, 151.1, 160.3. HR EI-MS *m/z*: 480.1018(13), 478.1030 (M^+, 10) (calcd. for $C_{29}H_{23}BrN_2$: 478.1025), 323 ([$M^+ - C_6H_5Br$], 40), 246 (100), 169 (58), 144 (67), 77 (70). Anal. calcd. for $C_{29}H_{23}BrN_2$: C 72.79, H 4.8, N 5.8; found: C 73.01, H 5.23, N 4.26.

1-(2-Aminophenyl)-4(3,4-dioxymethylene)phenyl-2,6-diphenyl-1,4-dihydropyridine (3h)

Colourless crystals, mp 173 °C. IR (cm^{-1}) υ_{max}: 3439, 3165, 3047, 2964–2531 (m), 1590, 1494, 1385, 1350, 1260, 1140, 1096, 920 760. ^{1}H NMR ($CDCl_3$) δ: 5.45 (t, *J* = 3.9 Hz, 1H), 6.02 (s, 2H), 7.10 (d, *J* = 3.9 Hz, 1H), 7.23 (s br, 2H, NH_2), 7.26 (dd, *J* = 8.5, 3.9 Hz, 4H), 7.35 (ddd, *J* = 8.1, 2.2, 8.3 Hz, 6H), 7.50 (ddd, *J* = 8.3, 2.4, 8.3 Hz, 5H), 7.53 (d, *J* = 8.3 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ_C: 55.3, 101.2, 114.5, 118.6, 122.8, 126.7, 128.3, 129.5, 135.5, 135.8, 147.3, 147.9, 149.3, 153.3. HR EI-MS *m/z* (rel.int): 444.1830 (M^+, 7) (calcd. for $C_{30}H_{24}N_2O_2$: 444.1839), 414 ([M^+ – HCHO], 20), 323 (15), 293 (21), 246 (100), 169 (52), 144 (56), 77 (70). Anal. calcd. C 81.04, H 5.44, N 6.30; found: C 82.10, H 5.70, N 5.85.

1-(2-Aminophenyl)-4(4-hydroxy)phenyl-2,6-diphenyl-1,4-dihydropyridine (3i)

Colourless crystals, mp 235 °C. IR (cm^{-1}) υ_{max}: 3560, 3430, 3265, 3050, 2964–2531 (m), 1605, 1550, 1485, 1380, 1345, 1280, 1140, 1096, 920, 750. ^{1}H NMR (DMSO-d_6) δ:

2.40 (s br, 1H), 5.10 (t, *J* = 3.8 Hz, 1H), 6.77 (dd, *J* = 8.3, 3.8 Hz, 4H), 7.26 (s br, 2H), 7.35 (ddd, *J* = 8.3, 5.6, 3.9 Hz, 6H), 7.50 (ddd, *J* = 8.6, 5.6 Hz, 6H), 7.56 (ddd, *J* = 8.3, 5.6, 8.5 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ_C: 54.8, 116.1, 122.6, 127.1, 127.2, 128.6, 128.8, 135.1, 135.7, 139.9, 151.8, 160.5. HR EI-MS *m/z* (rel. int.): 416.1896 (13) (calc. for $C_{29}H_{24}N_2O$: 416.1889), 323 (30), 246 (100), 169 (55), 144 (43), 77 (60). Anal. calcd. for CHN: not found.

1-(2-Aminophenyl)-4(4-iodo)phenyl-2,6-diphenyl-1, 4-dihydropyridine (3j)

Colourless crystals, mp 182 °C. IR (cm^{-1}) υ_{max}: 3453, 3052, 1605, 1549, 1490, 1382, 1357, 1148, 1090, 1018, 927, 730. ^{1}H NMR (DMSO-d_6) δ: 5.09 (t, *J* = 3.7 Hz, 1H), 6.80 (dd, *J* = 8.5, 3.7Hz, 4H), 7.20 (s br, 2H), 7.36 (ddd, *J* = 8.5, 2.4, 8.3 Hz, 4H), 7.52 (ddd, *J* = 8.6, 2.4, 8.3 Hz, 2H), 7.69 (dd, *J* = 8.6, 2.4 Hz, 6H), 7.86 (dd, *J* = 8.3, 8.5 Hz, 2H), 8.17 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ: 53.9, 111.10, 116.3, 116.5, 122.8, 127.2, 128.3, 131.1, 135.5, 139.3, 143.2, 152.1. HR EI-MS *m/z* (rel. int.): 526.1870 (5) (calcd. for $C_{29}H_{23}IN_2$: 526.1861), 323 (34), 246 (100), 165 (45), 144 (36), 77 (68). Anal. calcd. for CHN: not found.

1-(2-Aminophenyl)-2,6-di(4-bromo)phenyl-4-phenyl-1,4-dihydropyridine (3k)

Colourless crystals, mp 208 °C. IR (cm^{-1}) υ_{max}: 3443, 3050, 2967–2953 (m), 1605, 1545, 1487, 1360, 1350,1140, 1090, 1075, 930, 725. ^{1}H NMR (DMSO-d_6) δ: 5.74 (t, *J* = 3.8 Hz, 1H), 7.00 (d, *J* = 3.8 Hz, 2H), 7.26 (s br, 2H), 7.40 (5H), 7.52 (ddd, *J* = 8.8, 2.5, 8.3 Hz, 4H), 7.64 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.80 (s, 2H), 8.06 (dd, *J* = 8.7, 1.6 Hz, 2H), 8.25 (d, *J* = 3.9 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ_C: 55.4, 114.1, 116.3, 116.5, 126.8, 127.2, 128.3, 131.0, 139.1, 143.2, 149.7, 151.3, 160.5. HR EI-MS *m/z* (rel. int.): 556.1020 (5), 558.0123 (M$^+$) (calcd. for $C_{30}H_{22}N_2Br_2$: 556.0109, 558.0109) 481 (5), 479 (10) 222 (9), 323 (100), 218 (40), 126 (60), 77 (71). Anal. calcd. for $C_{30}H_{22}N_2Br_2$: C 62.36, H 3.9, N 5.01; found: C 63.06, H 4.32, N 4.91.

1-(2-Aminophenyl)-2(4-chloro)phenyl-4(4-methoxy)phenyl-6-phenyl-1,4-dihydropyridine (3l)

Colourless compound, mp 184 °C. IR (cm^{-1}) υ_{max}: 3430, 2966–2576 (m), 1610, 1605, 1540, 1490, 1385, 1350, 1140, 1080, 940. ^{1}H NMR (DMSO-d_6) δ: 3.82 (s, 3H), 5.32 (t, *J* = 3.9 Hz, 1H), 7.06 (dd, *J* = 8.70, 3.9 Hz, 4H), 7.23 (s br, 2H), 7.28 (d, *J* = 8.7 Hz, 4H), 7.41 (d, *J* = 6.5 Hz, 2H), 7.55 (ddd, *J* = 8.7, 3.7, 2.1 Hz, 2H), 7.75 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.82 (s, 1H), 8.08 (dd, *J* = 8.7, 1.6 Hz, 2H), 8.25 (d, *J* = 3.9 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ_C: 55.4, 58.5, 114.4, 116.8, 122.3, 125.6, 128.5, 128.9, 130.1, 139.9, 147.6, 157.8, 160.4. HR EI-MS *m/z* (rel. int.): 466.1640, 464.1634 (M$^+$, 15) (calcd. for $C_{30}H_{25}ClN_2O$: 466.1626, 464.1626) 357 (25), 246 (100), 169 (42), 144 (56), 77 (68). Anal. calcd. for $C_{30}H_{25}ClN_2O$: C 77.58, H 5.38, N 6.03; found: C 78.2, H 4.91, N 5.80.

1-(2-Hydoxyphenyl)-4(methoxyphenyl)-2,6-diphenyl-1,4-dihydropyridine (5)

Colourless needles, mp 276 °C. IR (cm^{-1}) υ_{max}: 3572, 3056, 3002, 1605, 1540, 1490, 1385, 1350, 1140, 1080, 940, 790. ^{1}H NMR (DMSO-d_6) δ: 3.80 (s, 3H), 5.57 (t, *J* = 3.8 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 6.80 (dd, *J*= 7.9 Hz, 2.9 Hz, 3H), 7.0 (d, *J* = 3.9 Hz, 2H), 7.20–7.29 (m, 6H), 7.30 (dd, *J* = 8.2, 2.9 Hz, 2H), 7.32 (dd, *J* = 8.2, 2.8 Hz, 2H), 8.20 (dd, *J* = 8.2, 2.8 Hz, 1H), 10.90 (s br, 1H). ^{13}C NMR (DMSO-d_6) δ_C: 55.6, 57.9, 113.7, 115.9, 122.5, 128.6, 130.1, 138.2, 138.7, 143.3, 143.7, 151.4. HR EI-MS *m/z* (rel. int.): 431.1892 (M$^+$, 7) (calcd. for $C_{30}H_{25}NO_2$: 431.1885), 416 (13), 323 (30), 246 (100), 180 (66), 164 (68), 90 (75). Anal. calcd. for CHN: not found.

1-(3-Hydroxyphenyl)-4(methoxyphenyl)-2,6-diphenyl-1,4-dihydropyridine (6)

Colourless needles, mp 230 °C. IR (cm^{-1}) υ_{max}: 3570, 3056, 3002, 1610, 1540, 1480, 1376, 1350, 1140, 1085, 945, 790. ^{1}H NMR (DMSO-d_6) δ: 3.81 (s, 3H), 5.37 (t, *J* = 3.8Hz, 1H), 6.78 (s br, 1H), 6.80 (dd, *J* = 8.0, 3.8 Hz, 3H), 6.92 (dd, *J* = 8.0, 2.8Hz, 2H), 7.12 (m, 8H), 7.30 (d, *J* = 3.8 Hz, 2H), 7.32 (dd, *J* = 8.2, 2.8 Hz, 3H), 8.00 (d, *J* = 8.2 Hz, 1H), 10.92 (s, 1H). ^{13}C NMR (DMSO-d_6) δ_C: 55.4, 58.1, 104.3, 110.2, 122.6, 131.2, 137.5, 138.2, 143.7, 151.4. HR EI-MS *m/z* (rel. int.): 431.1876 (M$^+$, 12) (calcd. for $C_{30}H_{25}NO_2$: 431.1885), 416 (24), 334 (36), 247 (100), 180 (57), 164 (68), 90 (75). Anal. calcd. for CHN: not found.

1-(4-Hydroxyphenyl)-4(methoxyphenyl)-2,6-diphenyl-1,4-dihydropyridine (7)

Colourless needles, mp 230 °C. IR (cm^{-1}) υ_{max}: 3554, 3050, 3005, 1610, 1540,1480, 1370, 1140, 1085, 940, 790. ^{1}H NMR (DMSO-d_6) δ: 3.85 (s, 3H), 5.56 (t, *J* = 3.9 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 4H), 7.00 (dd, *J* = 8.2, 3.9 Hz, 3H), 7.25 (m, 7H), 7.30 (dd, *J* = 3.9, 8.2 Hz, 2H), 7.32 (dd, *J* = 8.2, 2.9 Hz, 3H), 8.20 (dd, *J* = 8.5, 3.0 Hz, 1H), 10.76 (s, 1H). ^{13}C NMR (DMSO-d_6) δ_C: 55.6, 58.5, 104.6, 111.2, 116.5, 121.8, 122.6, 136.2, 137.1, 138.2, 143.1, 151.4, 156.5. HR EI-MS *m/z* (rel. int.): 441.1892 (M$^+$, 16) (calcd. for $C_{30}H_{25}NO_2$: 441.1885), 427 (13), 334 (26), 257 (100), 180 (45), 164 (52), 90 (61), 77 (63). Anal. calcd. for CHN: not done).

1-(2-Bromophenyl)-4(4-methoxy)phenyl-2,6-diphenyl-1,4-dihydropyridine (8)

Colourless crystals, mp 162 °C. IR (cm^{-1}) υ_{max}: 3005, 2964–2538 (m), 1605, 1543, 1480, 1370, 1150, 1110, 1085, 940, 790. ^{1}H NMR (DMSO-d_6) δ_C: 3.86 (s, 3H), 5.37 (t, *J* = 3.9Hz, 1H), 7.20 (d, *J* = 3.9 Hz, 2H), 7.27 (m, 8H), 7.37 (dd, *J* = 8.2, 2.9 Hz, 5H), 7.57 (dd, *J* = 8.2, 2.9 Hz, 4H), 7.97 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ: 55.3, 58.2, 113.1, 116.2, 123.2, 123.5, 131.4, 136.9, 137.3, 138.1, 143.5, 151.8. HR EI-MS *m/z* (rel. int.): 495, (3), 493.1030 (M$^+$, 11) (calcd. for $C_{30}H_{24}BrNO$: 495.1021, 493.1021), 388 (9), 386 (27), 311 (41), 309 (100), 234 (27), 232 (20), 146 (15), 144 (56), 77 (56). Anal. calcd. for $C_{30}H_{24}BrNO$: C 73.02, H 4.86, N 2.8; found: C 74.1, H 3.9, N 3.01.

1-(3-Bromophenyl)-4(4-methoxy)phenyl-2,6-diphenyl-1, 4-dihydropyridine (9)

Colourless crystals, mp 127 °C. IR (cm^{-1}) υ_{max}: 3000, 2950–2623 (m), 1605, 1543, 1480, 1370, 1150, 1110, 1085, 940, 790. ^{1}H NMR (DMSO-d_6) δ: 3.81 (s, 3H), 5.35 (t, *J* = 3.9 Hz, 1H), 7.0 (d, *J* = 8.2 Hz, 2H), 7.16 (dd, *J* = 8.2, 3.9 Hz, 4H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.29 (m, 6H), 7.37 (d, *J* = 8.2 Hz, 3H), 7.57 (d, *J* = 8.2 Hz, 2H), 8.00 (s, 1H). ^{13}C

NMR (DMSO-d_6) δ_C: 58.1, 114.1, 116.3, 121.6, 123.2, 123.5, 132.2, 136.9, 137.3, 138.1, 143.5, 151.9. HR EI-MS *m/z* (rel. int.): 495 (7), 493.1010 (M^+, 21). (calcd. for $C_{30}H_{24}BrNO$: 493.1021), 388 (16), 386 (27), 311(20), 309 (100), 234 (48), 232 (20), 146 (15), 144 (36), 77 (66). Anal. calcd. for CHN: not found.

1-(4-Bromophenyl-4(4-methoxy)phenyl-2,6-diphenyl-1, 4-dihydropyridine (10)

Colourless crystals, mp 148 °C. IR (cm^{-1}) υ_{max}: 3010, 2952–2623 (m), 1605, 1543, 1480, 1370, 1150, 1110, 1085, 940, 790. ^1H NMR (DMSO-d_6) δ: 3.86 (s, 3H), 5.36 (t, *J* = 3.9 Hz, 1H), 7.0 (dd, *J* = 8.2, 3.9 Hz, 2H), 7.20 (m, 5H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 4H), 7.45 (dd, *J* = 8.2, 2.4 Hz, 6H), 8.02 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ: 58.7, 114.3, 116.5, 121.1, 123.7, 128.4, 130.9, 138.1, 143.2, 143.5, 151.3. HR EI-MS *m/z* (rel. int.): 495(10), 493.103 (M^+, 31) (calcd. for $C_{30}H_{24}BrNO$: 493.1021), 388 (27), 386 (36), 311 (10), 309 (100), 234 (29), 232 (15), 146 (15), 144 (67), 77 (63). Anal. calcd. for CHN: not found.

1-(3-Nitrophenyl-4(4-methoxy)phenyl-2,6-diphenyl-1,4-dihydropyridine (11)

Pale yellow crystals, mp 121 °C. IR (cm^{-1}) υ_{max}: 3020, 2695–2559 (m), 2215, 1605, 1600, 1485, 1415, 1375, 1360, 1150, 1090, 940, 790, 665. ^1H NMR ($CDCl_3$) δ: 3.57 (s, 3H), 5.10 (t, *J* = 3.9 Hz, 1H), 7.10 (dd, *J* = 8.1,3.9 Hz, 4H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.26 (m, 9H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.77 (dd, *J* = 8.1, 2.3 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ_C: 54.8, 55.6, 105.3, 118.6, 122.5, 124.2, 130.1, 131.2, 137.4, 139.1, 146.7, 153.2, 156.4. HR EI-MS *m/z* (rel. int.): 460.1792 (M^+, 10) (calcd. for $C_{30}H_{24}N_2O_3$: 460.1787), 393 (25), 316 (100), 239 (40), 194 (33), 77 (56). Anal calcd. for $C_{30}H_{24}N_2O_3$: C 78.26, H 5.21, N 6.08; found: C 78.31, H 4.85, N 5.91.

Hydroxymethyl-(4-methoxyphenyl-3-(4-methoxy)phenyl-1,5-diphenyl-pentan-4-en-5-ol-1-one, (12a)

Colourless crystals, mp 132 °C. IR (cm^{-1}) υ_{max}: 3590, 3423, 3010, 2810, 1700, 1640, 1580, 1410, 1245, 1090, 920, 750. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.70 (d, *J* = 3.3 Hz, 1H), 2.80 (s br, 1H, OH), 3.05 (dd, *J* = 3.0, 3.6 Hz, 1H), 3.86 (s, 6H), 5.01 (dd, *J* = 3.0 Hz, 1H), 6.9 (s, 1H), 7.10–7.20 (m, 10H), 7.23 (dd, *J* = 3.2, 8.9 Hz, 4H), 7.65 (dd, *J* = 3.2, 8.6 Hz, 4H), 12.9 (s br, 1H). ^{13}C NMR ($CDCl_3$) δ_C: 55.6, 64.6, 77.2, 83.2, 114.4, 116.5, 124.9, 127.0, 128.9, 131.2, 138.5, 139.6, 149.5, 159.4, 197.3. HR EI-MS *m/z* (rel. int.): 494.2071 (M^+, 30) (calcd. for $C_{32}H_{30}O_5$: 494.2085), 493 (29), 476 (42), 466 (31), 371 (45), 239 (66), 224 (27), 134 (76), 133 (58), 105 (100), 92 (91), 77 (70), 64 (87).

1-(4-Chloro)phenyl-3-(4-methoxy)phenyl-5-phenyl-pentan-4-en-5-ol-1-one, (12b)

Colourless compound, mp 135 °C. IR (cm^{-1}) υ_{max}: 3020, 2816, 1715, 1580, 1640, 1420, 1250, 1090, 1075, 925, 780. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.69 (d, *J* = 4.5 Hz, 2H), 3.08 (t, *J* = 4.5 Hz, 1H), 3.86 (s, 3H) 6.9 (s, 1H), 7.20 (m, 5H), 7.23 (dd, *J* = 3.2, 8.6 Hz, 2H), 7.41 (d, 2H, *J* = 6.5 Hz, 2H), 7.55 (d, *J* = 6.5 Hz, 2H), 7.66 (dd, *J* = 3.2, 8.6 Hz, 2H), 12.9 (s, 1H). ^{13}C NMR ($CDCl_3$) δ_C: 25.3, 42.6, 556, 114.4, 116.6, 116.8, 124.9, 127.0, 127.3, 128.6, 128.9, 130.1, 131.3, 138.5, 139.9, 149.5, 159.3, 160.4, 197.3. HR EI-MS *m/z* (rel. int.): 392.1172 (M^+, 28) (calc. for $C_{24}H_{21}O_3Cl$: 392.1165), 391 (25), 378 (48), 24 (26), 139 (68), 134 (56), 119 (62), 108 (38), 105 (100), 93 (76), 65 (80).

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