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ORIGINAL PAPER

Heterogeneous $AlPO_4(SO_3H)$ nanosheets: novel catalyst for the multi-component synthesis of quinazolinones and highly functionalized piperidines

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Abstract
Nanosheets $AlPO_4(SO_3H)$ as a highly active solid acid catalyst were prepared and characterized. The morphology of obtained catalyst exhibited nanosheets with ~ 25–35 nm thickness. The heterogeneous nanocatalyst was characterized by FT-IR, EDX, and FE-SEM analysis. The nanosulfonated-$AlPO_4$ were found useful for cyclization synthesis of highly functionalized piperidines and quinazolinones derivatives in good to excellent yields. Notable features include easy and quick isolation of products, ease of handling of the catalyst at low cost, no need to purify with column chromatography, and mild reaction conditions. In addition, according to the literature, another significant feature of our method for quinazolinone synthesis is that structurally diverse molecules were synthesized. Finally, the newly developed catalytic systems avoid the use of toxic metal catalysts and were reused up to 5 times without a noticeable their catalytic activity.

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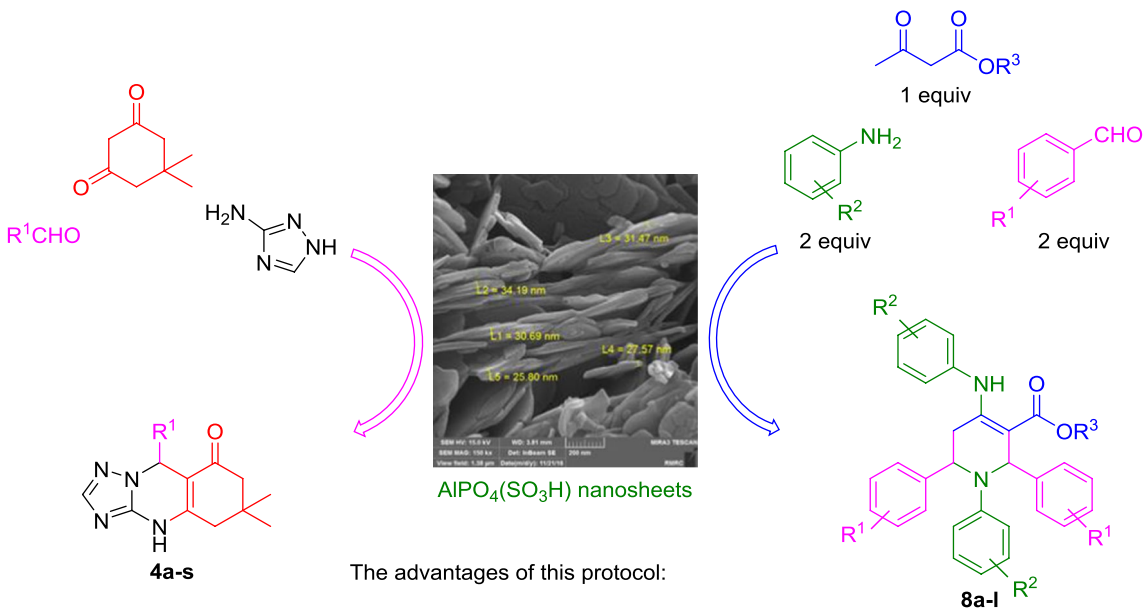
Graphical Abstract



Keywords Nanosheets $AlPO_4(SO_3H)$ · Heterogeneous catalysis · Multi-component reactions · Quinazolinone · Piperidine

Introduction

Homogeneous acids are the most frequently catalysts used in organic reactions. They are soluble in the reaction mixture which increases production costs. They cannot be completely washed out from the biodiesel, as well. Immobilization of homogeneous acid on solid materials is the best way to be easily separated from the reaction mixture. Recently, functionalized separable $AlPO_4$ nanocomposite materials have emerged as relatively new class and viable alternatives to conventional materials for organic transformations on account of their stability and large specific surface area [1]. Nonetheless, modification and functionalization of this support are less used and should be investigated more.

In recent decades, research interests have been devoted toward new methodologies in one-pot multi-component reactions (MCRs) for reasons of energy efficiency, atom economy, general environmental friendliness, and enabling straightforward access to large libraries of drug-like compounds [2–7]. Investigation on this topic is attractive in organic synthesis owing to their values in preparation of diverse heterocyclic molecules which may be efficient in drug discovery procedures.

Based on these contexts, the development of simple synthetic ways for *N*-heterocycles from ready substances is a critical task in organic reactions. Quinazolinone [8–10] and piperidine [11–14] ring systems are heterocyclic motif found in natural products and key units in pharmaceuticals. Some new methodologies have been investigated for their synthesis [8–19]. Based on our previous studies [20–24], which focus on the synthesis of new catalysts for multi-component reactions under mild conditions, herein, we wish to report $AlPO_4(SO_3H)$ nanosheets as a new, efficient, and reusable catalyst for

performing multi-component reaction toward quinazolinone and piperidine derivatives.

Experimental section

Instrumentation, analyses, and starting material

Chemical materials and solvents were purchased from Fluka, Sigma-Aldrich, and Merck Companies and used without further purification. NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ solvents on a Bruker Avance DPX-250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Characterization and surface morphology of the nanocatalyst were performed with a MIRA3 TESCAN SEM, operating at 20.0 kV. The energy-dispersive X-ray (EDX) analysis was done using SIRIUS SD EDX analyzer. By a Büchi-535 circulating oil melting point apparatus, melting points were obtained in open capillary tubes.

General procedure for the synthesis of 6,6-dimethyl-9-phenyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4a–s)

A mixture of aldehyde (1.0 mmol), dimedone (1.0 mmol), 1*H*-1,2,4-triazol-3-amine (1.0 mmol) and nano-$AlPO_4(SO_3H)$ (0.1 g) was stirred in the acetonitrile (4.0 mL) at 50 °C for an appropriate time. After the completion of the reaction as indicated by TLC, dichloromethane was added to the solidified mixture and the insoluble catalyst was separated by centrifugation. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol afforded the pure products in good to excellent yields.

General procedure for the synthesis of highly functionalized piperidines (8a–l)

A solution of aromatic amine (2.0 mmol) and alkyl acetoacetate (1.0 mmol) in EtOH (5.0 mL) stirred for 20 min in the presence of nano-$AlPO_4(SO_3H)$ (0.15 g) at room temperature. Next, the aromatic aldehyde (2.0 mmol) was added and the reaction mixture was stirred for the time indicated in Table 4. After the completion of the reaction, as indicated by TLC, the solid material was filtered off, dried, and then dissolved in CH_2Cl_2 (10 mL). The nano-$AlPO_4(SO_3H)$ was recovered by centrifuging, and the solvent was evaporated under vacuum. The obtained solid was washed with EtOH to give the pure product.

6,6-Dimethyl-9-phenyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4a) White solid; 95% yield; mp 248–250 °C; FT-IR (KBr cm^{-1}): 3224, 3085, 2965, 1651, 1573, 1365, 1257, 732; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.03, 1.09 (2s, 6H, $2CH_3$), 2.22 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 6.38 (s, 1H, CH), 7.15–7.26 (m, 5H, ArH), 7.60 (s, 1H, =CH), 11.76 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 27.6, 29.0, 32.8, 40.7, 50.4, 58.8, 107.4, 127.1, 128.3, 128.6, 140.6, 147.4, 148.5, 149.0, 193.8.

6,6-Dimethyl-9-(*p*-tolyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4b) Pale yellow solid; 93% yield; mp 265–267 °C; FT-IR (KBr cm^{-1}): 3240, 3085, 2923, 1651, 1581, 1365, 1249, 735; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.94, 1.02 (2s, 6H, $2CH_3$), 2.01–2.23 (m, 5H, CH_2 and CH_3), 2.44–2.59 (m, 2H, CH_2), 6.14 (s, 1H, CH), 7.05 (s, 4H, ArH), 7.65 (s, 1H, =CH), 11.07 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 20.56, 26.73, 28.47, 32.12, 49.75, 57.60, 105.67, 126.78, 128.72, 136.89, 138.73, 146.76, 149.90, 150.16, 192.85.

9-(4-Chlorophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4c) Pale yellow solid; 93% yield; mp 304–306 °C; FT-IR (KBr cm^{-1}): 3085, 2970, 1651, 1573, 1365, 1257, 763; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.70, 0.77 (2s, 6H, $2CH_3$), 1.89 (q, 2H, J = 17.5 Hz, CH_2), 2.26 (d, 2H, J = 10.0 Hz, CH_2), 5.97 (s, 1H, CH), 6.96 (d, 2H, J = 7.5 Hz, ArH), 7.08 (d, 2H, J = 7.5 Hz, ArH), 7.44 (s, 1H, =CH), 10.90 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.84, 28.33, 32.13, 49.70, 57.33, 99.48, 105.15, 128.20, 128.82, 132.24, 140.45, 146.74, 150.12, 150.49, 192.91.

9-(4-Methoxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4d) Pale yellow solid; 90% yield; mp 229–231 °C; FT-IR (KBr cm^{-1}): 3085, 2923, 1651, 1573, 1365, 1249; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.95, 1.02 (2s, 6H, $2CH_3$), 2.05 (d, 1H, J = 15.0 Hz), 2.20 (d, 1H, J = 15.0 Hz), 2.48–2.52 (m, 2H, CH_2), 3.67 (s, 3H, OCH_3), 6.14 (s, 1H, CH), 6.81 (d, 2H, J = 10.0 Hz, ArH), 7.09 (d, 2H, J = 10.0 Hz, ArH), 7.65 (s, 1H, =CH), 11.07 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.77, 28.47, 32.11, 49.76, 54.96, 57.29, 105.70, 113.51, 128.06, 133.80, 146.70, 149.88, 150.10, 158.63, 192.89.

9-(4-Isopropylphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4e) White solid; 93% yield; mp 283–284 °C; FT-IR (KBr cm^{-1}): 3247, 3085, 2962, 1651, 1581, 1365, 1249, 732; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.95, 1.01 (2s, 6H, $2CH_3$), 1.11 (d, 6H, J = 5 Hz, $2CH_3$), 2.05 (d, 1H, J = 17.5 Hz),

2.19 (d, 1H, J = 15.0 Hz), 2.51 (s, 2H, CH_2), 2.69–2.85 (m, 1H, CH), 6.14 (s, 1H, CH), 7.06–7.11 (m, 4H, ArH), 7.64 (s, 1H, =CH), 11.09 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 23.66, 23.73, 26.89, 28.39, 32.13, 32.99, 49.75, 57.59, 105.55, 126.10, 126.86, 139.03, 146.71, 147.70, 149.90, 150.28, 192.89.

6,6-Dimethyl-9-(4-nitrophenyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4f) Yellow solid; 94% yield; 290–291 °C; FT-IR (KBr cm^{-1}): 3085, 2947, 1643, 1573, 1350, 1249, 732; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.93, 1.02 (2s, 6H, $2CH_3$), 2.13 (q, 2H, J = 17.5 Hz, CH_2), 2.50 (d, 2H, J = 12.5 Hz, CH_2), 6.35 (s, 1H, CH), 7.46 (d, 2H, J = 7.5 Hz, ArH), 7.71 (s, 1H, =CH), 8.13 (d, 2H, J = 7.5 Hz, ArH), 11.30 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.90, 28.25, 32.18, 49.62, 57.48, 104.69, 123.51, 128.42, 146.78, 146.87, 148.35, 150.37, 150.94, 192.96.

9-(4-Fluorophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4g) Pale yellow solid; 90% yield; mp 258–260 °C; FT-IR (KBr cm^{-1}): 3132, 2954, 1651, 1581, 1365, 1218, 763; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.94, 1.02 (2s, 6H, $2CH_3$), 2.13 (q, 2H, J = 17.5 Hz, CH_2), 2.52 (s, 2H, CH_2), 6.21 (s, 1H, CH), 7.05–7.12 (m, 2H, ArH), 7.19–7.25 (m, 2H, ArH), 7.68 (s, 1H, =CH), 11.15 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.84, 28.35, 32.13, 49.71, 57.22, 105.34, 114.81, 115.15, 128.88, 129.01, 137.78, 137.82, 146.72, 150.07, 150.39, 159.49, 163.37, 192.92.

9-(4-(Dimethylamino)phenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4h) Pale yellow solid; 90% yield; mp 287–289 °C; FT-IR (KBr cm^{-1}): 3247, 3085, 2923, 1651, 1581, 1365, 1257, 732; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.96, 1.02 (2s, 6H, $2CH_3$), 2.04 (d, 1H, J = 15 Hz), 2.20 (d, 1H, J = 15.0 Hz), 2.55 (d, 2H, J = 15 Hz, CH_2), 2.80, 2.81 (2s, 6H, 2 N–CH_3), 6.07 (s, 1H, CH), 6.57 (d, 2H, J = 7.5 Hz, ArH), 6.97 (d, 2H, J = 7.5 Hz, ArH), 7.62 (s, 1H, =CH), 10.99 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.74, 28.59, 32.09, 40.00, 49.81, 57.34, 105.96, 111.83, 127.53, 129.33, 146.69, 149.71, 149.84, 192.88.

9-(2,3-Dimethoxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4i) White solid; 89% yield; mp 226–228 °C; FT-IR (KBr cm^{-1}): 3085, 2931, 1643, 1581, 1365, 1257, 748; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.96, 1.02 (2s, 6H, $2CH_3$), 2.09 (q, 2H, J = 17.5 Hz, CH_2), 2.48–2.57 (m, 2H, CH_2), 3.69, 3.74 (2s, 6H, $2OCH_3$), 6.43 (s, 1H, CH), 6.69–6.73 (m, 1H, ArH), 6.86–6.96 (m, 2H, ArH), 7.61 (s, 1H, =CH), 11.04 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 27.57, 29.02, 32.82, 50.53, 54.16, 56.18, 60.44, 106.08, 112.96, 120.95, 124.08, 135.18, 147.03, 147.51, 150.28, 151.16, 152.88, 193.41.

9-(3-Bromophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4j) Pale yellow solid; 90% yield; mp 281–283 °C; FT-IR (KBr cm^{-1}): 3209, 3070, 2935, 1643, 1573, 1365, 1257, 725; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 1.71, 1.78 (2s, 6H, $2CH_3$), 2.91 (q, 2H, J = 15.0, CH_2), 3.23–3.25 (m, 2H, CH_2), 6.97 (s, 1H, CH), 7.89 -8.03 (m, 2H, ArH), 8.16–8.19 (m, 2H, ArH), 8.46 (s, 1H, =CH), 11.96 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 25.71, 27.20, 31.08, 48.57, 56.30, 103.78, 120.27, 124.82, 128.79, 129.44, 142.88, 145.59, 149.09, 149.64, 191.86.

6,6-Dimethyl-9-(3-nitrophenyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4k) Yellow solid; 94% yield; mp 266–268 °C; FT-IR (KBr cm^{-1}): 3075, 2930, 1643, 1527, 1350, 1257, 732; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.96, 1.03 (2s, 6H, $2CH_3$), 2.07 (d, 1H, J = 17.5 Hz), 2.07 (d, 1H, J = 17.5 Hz), 2.56 (s, 2H, CH_2), 6.40 (s, 1H, CH), 7.55–7.67 (m, 2H, ArH), 7.72 (s, 1H, =CH), 8.04–8.12 (m, 2H, ArH), 11.30 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.82, 28.30, 32.19, 49.62, 57.37, 104.56, 121.64, 122.76, 129.99, 133.67, 143.41, 146.72, 147.53, 150.38, 151.08, 193.04.

6,6-Dimethyl-9-(naphthalen-1-yl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4l) Light yellow solid; 85% yield; mp 299–300 °C; FT-IR (KBr cm^{-1}): 3078, 2923, 1643, 1573, 1365, 1249, 779; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 1.01, 1.05 (2s, 6H, $2CH_3$), 2.04 (d, 1H, J = 17.5 Hz), 2.20 (d, 1H, J = 17.5 Hz), 2.61 (s, 2H, CH_2), 7.09 (s, 1H, CH), 7.32–7.43 (m, 2H, ArH), 7.49–7.63 (m, 3H, ArH), 7.80 (d, 1H, J = 7.5, ArH), 7.90 (d, 1H, J = 7.5 Hz, ArH), 8.53 (s, 1H, =CH), 11.22 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 27.05, 28.42, 32.17, 49.78, 106.02, 123.80, 125.34, 125.67, 126.13, 128.25, 128.33, 130.70, 133.17, 138.27, 146.45, 149.72, 150.67, 193.03.

9-(2-Chlorophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4m) Pale yellow solid; 89% yield; mp 288–290 °C; FT-IR (KBr cm^{-1}): 3224, 3085, 2923, 1643, 1573, 1365, 1257, 748; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.97, 1.02 (2s, 6H, $2CH_3$), 2.04–2.05 (m, 1H), 2.19 (d, 1H, J = 17.5 Hz), 2.51–2.60 (m, 2H, CH_2), 6.55 (s, 1H, CH), 7.21–7.36 (m, 4H, ArH), 7.65 (s, 1H, =CH), 11.20 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 25.66, 27.38, 30.95, 48.62, 55.23, 103.38, 116.89, 125.99, 128.26, 128.43, 137.05, 145.72, 148.91, 149.90, 191.71.

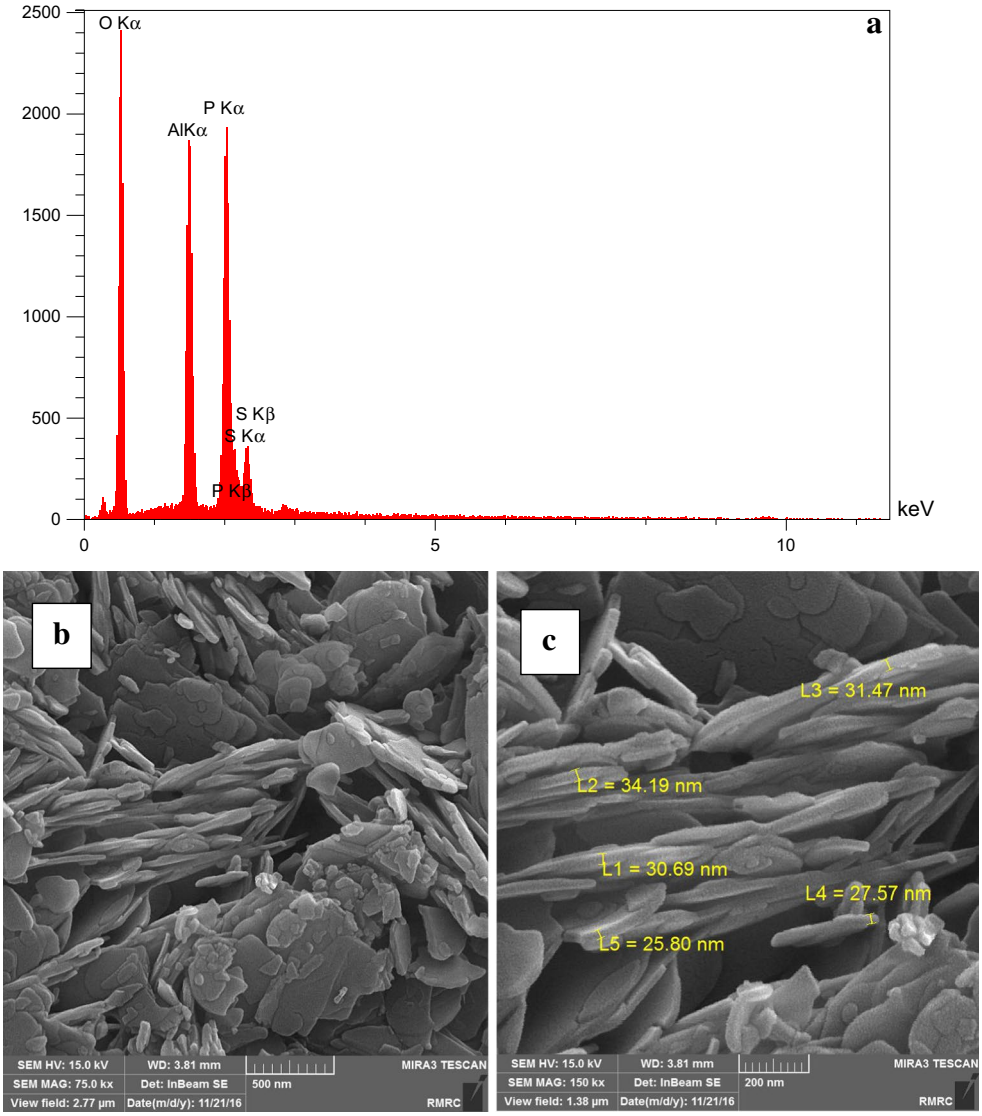


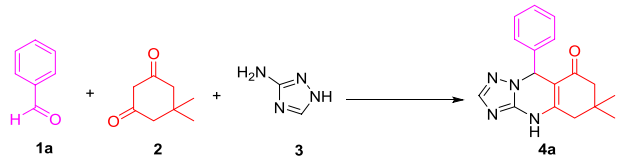
Fig. 1 **a** Energy-dispersive x-ray spectroscopy (EDX) of the $AlPO_4(SO_3H)$ nanosheets, **b** low magnification FE-SEM image of $AlPO_4(SO_3H)$ nanosheets, **c** high-magnification FE-SEM image of $AlPO_4(SO_3H)$ nanosheets

6,6-Dimethyl-9-(*o*-tolyl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4n) White solid; 93% yield; mp 299–300 °C; FT-IR (KBr cm^{-1}): 3085, 2925, 1643, 1581, 1365, 1257, 748; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.97, 1.03 (2s, 6H, $2CH_3$), 2.12 (q, 2H, J = 17.5 Hz, CH_2), 2.48–2.60 (m, 5H, CH_3 and CH_2), 6.42 (s, 1H, CH), 6.95–7.09 (m, 4H, ArH), 7.63 (s, 1H, =CH), 11.09 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 18.89, 26.83, 28.48, 32.18, 49.73, 54.12, 106.14, 126.18, 126.64, 127.43, 129.96, 135.56, 140.32, 146.55, 149.87, 150.42, 193.00.

9-(2-Bromophenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4o) White solid; 90% yield; mp 278–280 °C; FT-IR (KBr cm^{-1}): 3085, 29231648, 1573, 1365, 1257, 748; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.98, 1.03 (2s, 6H, $2CH_3$), 2.03 (m, 1H), 2.19 (d, 1H, J = 15.0 Hz), 2.49–2.60 (m, 2H, CH_2), 6.56 (s, 1H, CH), 7.10–7.16 (m, 1H, ArH), 7.25–7.30 (m, 2H, ArH), 7.52 (d, 1H, J = 7.5 Hz, ArH), 7.64 (s, 1H, =CH), 11.21 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 25.82, 27.32, 30.96, 48.63, 103.68, 116.88, 121.41, 126.64, 128.47, 131.66, 138.75, 145.61, 148.92, 149.86, 191.71.

9-(4-Hydroxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4p) Pale yellow solid; 89% yield; mp 305–307 °C; FT-IR (KBr cm^{-1}): 3209, 3085, 2931, 1635, 1573, 1365, 1257, 732; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.95, 1.01 (2s, 6H, $2CH_3$), 2.13 (q, 2H, J = 17.5 Hz, CH_2), 2.46 (d, 1H, 17.5 Hz), 2.54 (d, 1H,

Table 1 Optimization studies on one-pot three-component reaction of benzaldehyde (**1a**), dimedone (**2**), and 1*H*-1,2,4-triazol-3-amine (**3**) for synthesis of (**4a**) in the presence of $AlPO_4(SO_3H)$ nanosheets



Entry	Solvent	Temperature (°C)	Catalyst (g)	Time (min)	Yield (%)[a]
1	Acetonitrile	r.t.	$AlPO_4$ (0.3 g)	180	30
2	Acetonitrile	r.t.	Amino-functionalized $AlPO_4$ (0.3 g)	180	30
3	Acetonitrile	r.t.	$CuFe_2O_4$ (0.3 g)	180	24
4	Acetonitrile	r.t.	*p*-Dodecylbenzenesulfonic acid (0.3 g)	180	58
5	Acetonitrile	r.t.	Sulfonated $AlPO_4$ (0.3 g)	30	88
6	Ethanol	r.t.	Sulfonated $AlPO_4$ (0.3 g)	30	59
7	Methanol	r.t.	Sulfonated $AlPO_4$ (0.3 g)	30	48
8	–	r.t.	Sulfonated $AlPO_4$ (0.3 g)	180	5
9	Water	r.t.	Sulfonated $AlPO_4$ (0.3 g)	30	49
10	Acetonitrile	r.t.	Sulfonated $AlPO_4$ (0.2 g)	30	92
11	Acetonitrile	r.t.	Sulfonated $AlPO_4$ (0.1 g)	30	95
12	Acetonitrile	r.t.	Sulfonated $AlPO_4$ (0.05 g)	30	80
13	Acetonitrile	50	Sulfonated $AlPO_4$ (0.1 g)	10	95
14	Acetonitrile	Reflux	Sulfonated $AlPO_4$ (0.1 g)	10	95

All reactions were carried out using **1a** (1.0 mmol), **2** (1.0 mmol), **3** (1.0 mmol), and the catalyst (0.1 g) in solvent (4.0 mL) under air atmosphere

[a]Yield of the isolated product

17.5 Hz), 6.09 (s, 1H, CH), 6.63 (d, 2H, J = 7.5 Hz, ArH), 6.98 (d, 2H, J = 7.5 Hz, ArH), 7.65 (s, 1H, =CH), 9.39 (s, 1H, OH), 11.03 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 25.66, 27.40, 30.99, 48.69, 56.23, 104.75, 113.73, 126.95, 131.09, 145.58, 148.68, 148.88, 155.74, 191.78.

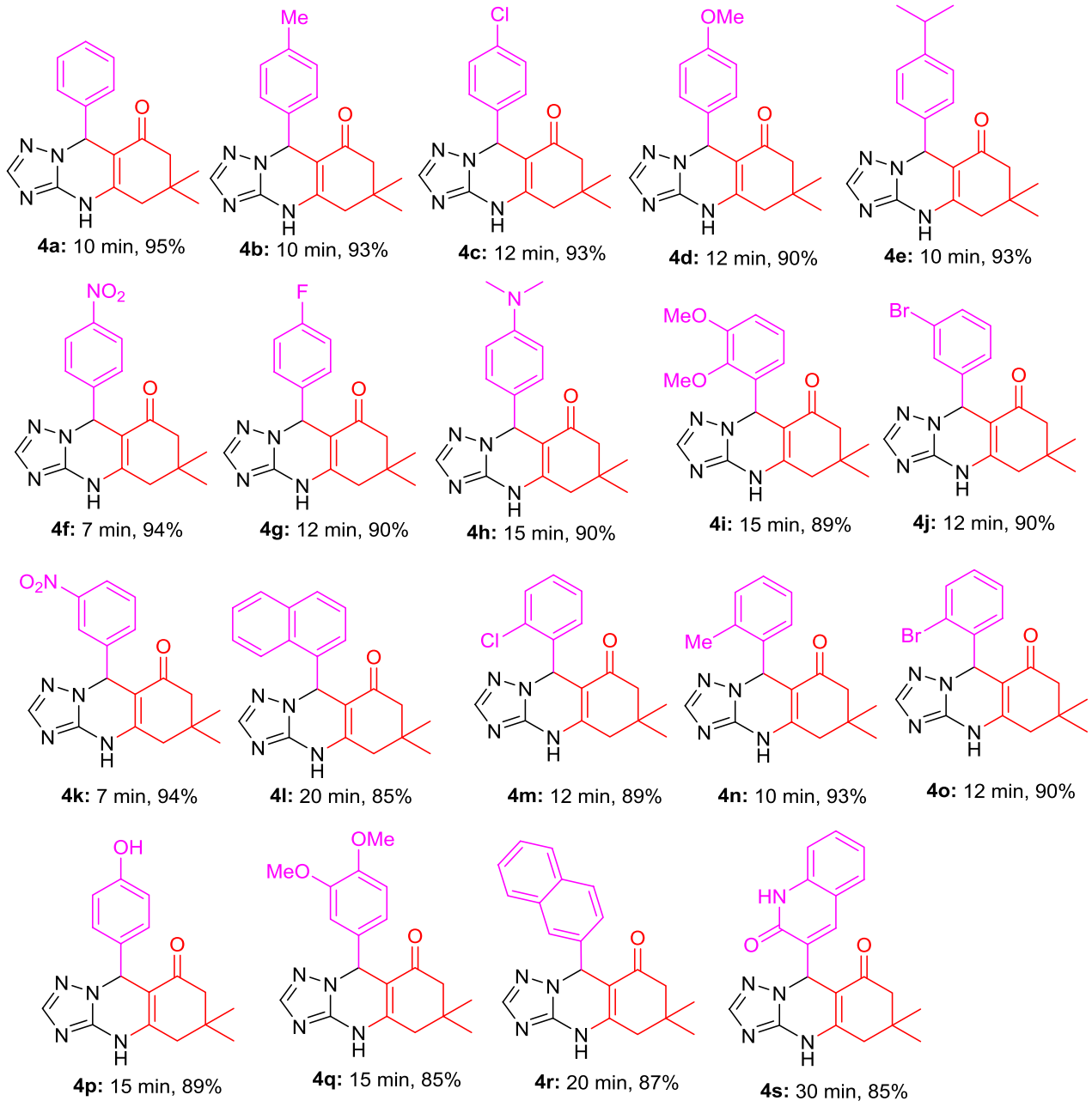
9-(3,4-Dimethoxyphenyl)-6,6-dimethyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4q) White solid; 85% yield; mp 219–220 °C; FT-IR (KBr cm^{-1}): 3078, 2931, 1651, 1581, 1365, 1257, 740; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.98, 1.02 (2s, 6H, $2CH_3$), 2.06 (d, 1H, J = 17.5 Hz), 2.21 (d, 1H, J = 17.5 Hz), 2.49–2.61 (m, 2H, CH_2), 3.67 (s, 6H, $2OCH_3$), 6.15 (s, 1H, CH), 6.64–6.69 (m, 1H, ArH), 6.80–6.84 (m, 2H, ArH), 7.67 (s, 1H, =CH), 11.05 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 25.52, 27.54, 31.00, 48.70, 54.29, 56.47, 104.54, 109.84, 110.38, 117.97, 133.05, 145.60, 147.22, 148.79, 149.17, 170.92, 191.88.

6,6-Dimethyl-9-(naphthalen-2-yl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4r) White solid; 87% yield; mp 266–268 °C; FT-IR (KBr cm^{-1}): 3085, 2923, 1651, 1573, 1365, 1249, 756; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.95, 1.03 (2s, 6H, $2CH_3$), 2.13 (q, 2H, J = 17.5, CH_2), 2.56 (s, 2H, CH_2), 6.37 (s, 1H, CH), 7.25 (d, 1H, J = 10 Hz, ArH), 7.45–7.48 (m, 2H, ArH), 7.68 (s, 1H, =CH), 7.79–7.89 (m, 4H, ArH), 11.19 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.74, 28.45, 32.15, 49.76, 58.20, 105.39, 124.64, 126.05, 126.12, 126.28, 127.36, 127.87, 128.07, 132.39, 132.45, 138.80, 146.80, 150.08, 150.48, 171.96, 192.98.

6,6-Dimethyl-9-(2-oxo-1,2-dihydroquinolin-3-yl)-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-b]quinazolin-8(4*H*)-one (4s) White solid; 85% yield; mp > 300 °C; FT-IR (KBr cm^{-1}): 3278, 3085, 2930, 1658, 1620, 1566, 1357, 1257, 7565; ^{1}H NMR (250 MHz, DMSO-d_6) δ (ppm): 0.94, 1.02 (2s, 6H, $2CH_3$), 2.00 (d, 1H, J = 15.0 Hz), 2.20 (d, 1H, J = 15.0 Hz), 2.38 (d, 1H, J = 17.5 Hz), 2.57 (s, 1H), 6.20 (s, 1H, CH), 7.12–7.24 (m, 2H, ArH), 7.42–7.48 (m, 1H, ArH),7.62 (s, 1H, ArH), 7.70 (d, 1H, J = 7.5 Hz, ArH), 7.98 (s, 1H, =CH), 11.03 (s, 1H, NH), 11.57 (s, 1H, NH); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ (ppm): 26.28, 28.76, 32.09, 49.94, 56.32, 103.03, 114.60, 118.58, 121.77, 128.09, 130.24, 138.45, 149.49, 151.75, 160.00, 192.83.

Methyl (2R,6S)-1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate (8a) White solid; 94% yield; mp 220–221 °C; FT-IR (KBr cm^{-1}): 694, 748,

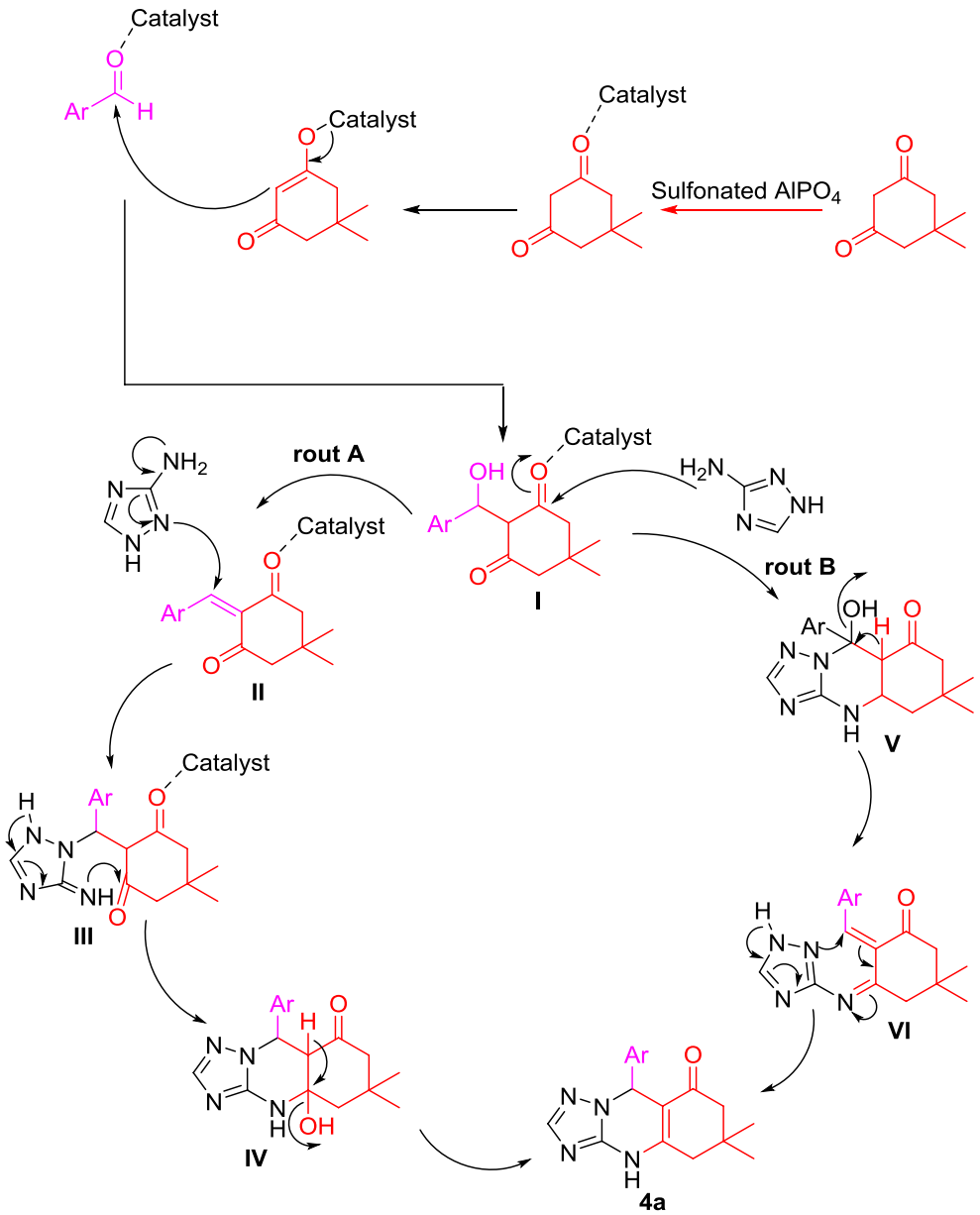
Table 2 Synthesis of quinazolinone derivatives



Isolated yield

1072, 1188, 1257, 1319, 1373, 1442, 1504, 1589, 1658, 2862, 2947, 3016, 3232 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 2.35 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.79 (dd, J = 15.0, 2.5 Hz, 1H, H′-5), 2.91 (dd, J = 15.0, 5.0 Hz, 1H, H″-5), 3.95 (s, 3H, OCH_3), 5.13–5.16 (m, 1H, H-6), 6.31–6.35 (m, 2H, ArH), 6.44 (s, 1H, H-2), 6.56 (d, J = 7.5 Hz, 2H, ArH), 6.62 (t, J = 7.5 Hz, 1H, ArH), 7.06–7.13 (m, 11H, ArH), 7.24 (d, J = 10.0 Hz, 2H, ArH), 10.29 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 21.16, 21.24, 33.78, 51.09, 55.04, 58.03, 98.24, 113.01, 116.14, 125.73, 125.86, 126.43, 126.66, 128.92, 128.96, 129.06, 129.38, 135.86, 136.68, 138.03, 139.80, 141.06, 147.15, 156.36, 168.68.

Ethyl (2R,6S)-1-(4-chlorophenyl)-4-((4-chlorophenyl) amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (8g) Pale yellow solid; 89% yield; mp 201–203 °C; FT-IR (KBr cm^{-1}): ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.50 (t, J = 7.5 Hz, 3H, OCH_2CH_3), 2.72 (dd, J = 15.0,

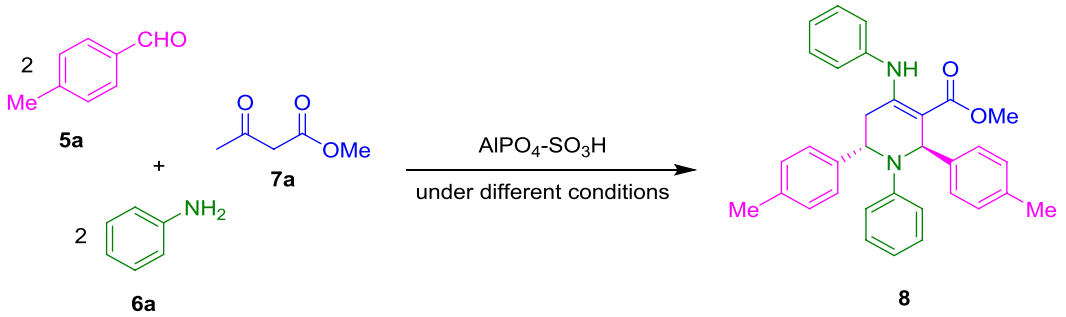


Scheme 1 Suggested mechanism for the synthesis of quinazolinone derivatives using nano-$AlPO_4(SO_3H)$

2.5 Hz, 1H, H′-5), 2.84–2.94 (m, 1H, H″-5), 4.34–4.41 (m, 1H, OCH_aH_b), 4.45–4.55 (m, 1H, OCH_aH_b), 5.13 (s, 1H, H-6), 6.17–6.22 (m, 2H, ArH), 6.44–6.49 (m, 3H, H-2 and ArH), 6.70–7.32 (m, 14H, ArH), 10.28 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 14.83, 33.51, 55.30, 58.34, 59.95, 98.76, 114.06, 121.24, 126.32, 126.52, 126.59, 127.02, 127.48, 128.41, 128.75, 128.83, 129.02, 131.34, 136.45, 142.28, 143.30, 145.53, 155.40, 168.14.

Methyl (2R,6S)-2,6-bis(4-methoxyphenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (8h) White solid; 90% yield; mp 185–187 °C; FT-IR (KBr cm^{-1}): 694, 756, 1033, 1072, 1180, 1249, 1373, 1450, 1504, 1596, 1651, 2839, 2954, 3232, 3448 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 2.78 (dd, J = 15.0, 2.5 Hz, 1H, H′-5), 2.89 (dd, J = 15.0, 5.0 Hz, 1H, H″-5), 3.80 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 5.10–5.13 (m, 1H, H-2), 6.36–6.41 (m, 5H, H-2 and ArH), 6.56 (d, J = 7.5 Hz, 2H, ArH), 6.63 (t, J = 7.5 Hz, 1H, ArH), 6.86 (d, J = 10.0 Hz, 4H, ArH), 7.06–7.15 (m, 7H, ArH), 7.23–7.27 (m, 2H, ArH), 10.31 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 33.83, 51.08, 54.65, 55.25, 55.32, 57.56, 98.23, 113.03, 113.68, 114.07, 116.17, 125.79, 127.53,

Table 3 Results of the reaction under different conditions



Entry	Solvent	Temperature (°C)	Catalyst (g)	Time (h)	Yield (%)[a]
1	Water	r.t.	Sulfonated $AlPO_4$ (0.05 g)	12	40
2	Acetonitrile	r.t.	Sulfonated $AlPO_4$ (0.05 g)	11	52
3	Methanol	r.t.	Sulfonated $AlPO_4$ (0.05 g)	10	60
4	Ethanol	r.t.	Sulfonated $AlPO_4$ (0.05 g)	7	72
5	–	r.t.	Sulfonated $AlPO_4$ (0.05 g)	12	36
6	Ethanol	65	Sulfonated $AlPO_4$ (0.05 g)	5	65
10	Ethanol	r.t.	Sulfonated $AlPO_4$ (0.1 g)	5	86
11	Ethanol	r.t.	Sulfonated $AlPO_4$ (0.15 g)	3.5	94
12	Ethanol	r.t.	Sulfonated $AlPO_4$ (0.2 g)	3.5	92
13	Ethanol	r.t.	–	24	–

All reactions were carried out using **5a** (2.0 mmol), **6a** (2.0 mmol), and **7a** (1.0 mmol) in the presence of the catalyst and solvent under air atmosphere

[a]Yield of the isolated product

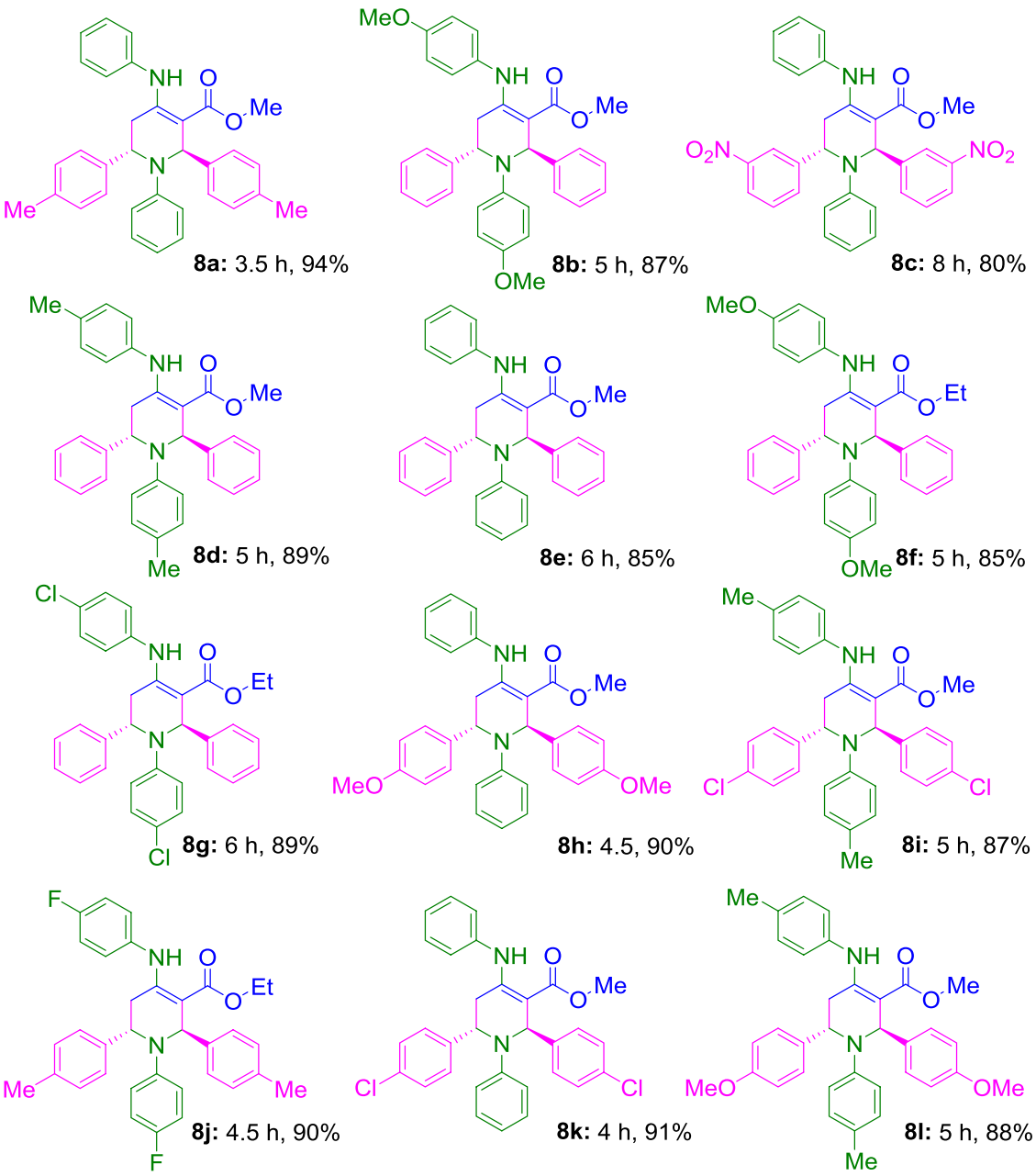
127.77, 128.97, 134.68, 135.92, 138.00, 147.08, 156.43, 158.18, 158.79, 168.64.

Methyl (2R,6S)-2,6-bis(4-chlorophenyl)-1-(*p*-tolyl)-4-(*p*-tolylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (8i) White solid; 87% yield; mp 213–215 °C; FT-IR (KBr cm^{-1}): 794, 979, 1010, 1072, 1180, 1257, 1512, 1581, 1650, 2862, 3016, 3255, 3442 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 2.19 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.72 (dd, $J_=$ 15.0, 2.5 Hz, 1H, H′-5), 2.81 (dd, $J_=$ 15.0, 5.0 Hz, 1H, H″-5), 3.93 (s, 3H, OCH_3), 5.06–5.09 (m, 1H, H-6), 6.30 (d, J = 10.0 Hz, 2H, ArH), 6.34 (s, 1H, H-2), 6.38 (d, J = 7.5 Hz, 2H, ArH), 6.90 (d, J = 7.5 Hz, 2H, ArH), 6.97 (d, J = 7.5 Hz, 2H, ArH), 7.08 (d, J = 10.0 Hz, 2H, ArH), 7.24–7.28 (m, 6H, ArH), 10.20 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 20.18, 20.96, 33.64, 51.12, 54.86, 57.36, 97.01, 112.96, 125.75, 125.89, 127.87, 128.12, 128.38, 128.77, 129.63, 132.06, 132.79, 134.96, 135.99, 141.23, 142.71, 144.35, 156.38, 168.36.

Ethyl (2R,6S)-1-(4-fluorophenyl)-4-((4-fluorophenyl)amino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate (8j) White solid; 90% yield; mp 183–185 °C; FT-IR (KBr cm^{-1}): ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.50 (t, J = 7.5 Hz, 3H, OCH_2CH_3), 2.36 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.66 (dd, J = 15.0, 2.5 Hz, 1H, H′-5), 2.88 (dd, J = 15.0, 5.0 Hz, 1H, H″-5), 4.30–4.40 (m, 1H, OCH_aH_b), 4.44–4.54 (m, 1H, OCH_aH_b), 5.07–5.09 (m, 1H, H-6), 6.23–6.30 (m, 2H, ArH), 6.36 (s, 1H, H-2), 6.43–6.50 (m, 2H, ArH), 6.75–6.85 (m, 4H, ArH), 7.10–7.26 (m, 8H, ArH), 10.24 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 14.81, 21.03, 21.13, 33.63, 55.41, 58.16, 59.72, 98.30, 113.58, 113.69, 115.06, 115.41, 115.78, 126.35, 126.57 127.90, 128.03, 128.98, 129.38, 133.94, 133.99, 135.93, 136.88, 139.74, 140.70, 143.58, 153.09, 156.03, 156.83, 158.75, 162.65, 168.26.

Methyl (2R,6S)-2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (8k) White solid; 91% yield; mp 226–228 °C; FT-IR (KBr cm^{-1}): 694, 748, 856, 979, 1072, 1188, 1265, 1326, 1372, 1404, 1504, 1596, 1651, 2869, 3039, 3240 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 2.78 (dd, J = 15.0, 2.5 Hz, 1H, H′-5), 2.88 (dd, J = 15.0, 5.0 Hz, 1H, H″-5), 3.96 (s, 3H, OCH_3), 5.13–5.16 (m, 1H, H-6), 6.42–6.52 (m, 5H, H-2 and ArH), 6.68 (t, J = 7.5 Hz, 1H, ArH), 7.08–7.28 (m, 13H, ArH), 10.31 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 33.77, 51.27, 54.80, 57.41, 97.61, 113.00, 116.84, 125.78, 126.11, 127.87, 128.15, 128.49, 128.85,

Table 4 Five-component synthesis of highly functionalized piperidines



Isolated yield

129.11, 129.15, 132.21, 132.93, 137.66, 141.00, 142.45, 146.52, 156.07, 168.34.

Results and discussion

The $AlPO_4(SO_3H)$ nanosheets morphology was produced by adding chlorosulfuric acid to commercially available $AlPO_4$ in CH_2Cl_2 solvent at room temperature [25]. It was characterized by FT-IR (Fourier-transform infrared spectroscopy), EDX analysis (energy-dispersive X-ray spectroscopy), and FE-SEM (field emission scanning electron microscopy). Since the position of the acidic peaks ($–SO_3H$) is covered by $AlPO_4$ in FT-IR spectroscopy, the new catalyst was identified by EDX and FE-SEM. The EDX analysis of the newly synthesized catalyst showed peaks for O, Al, P, and S elements that confirms the major constituents of nanosulfonated $AlPO_4$ (Fig. 1a).

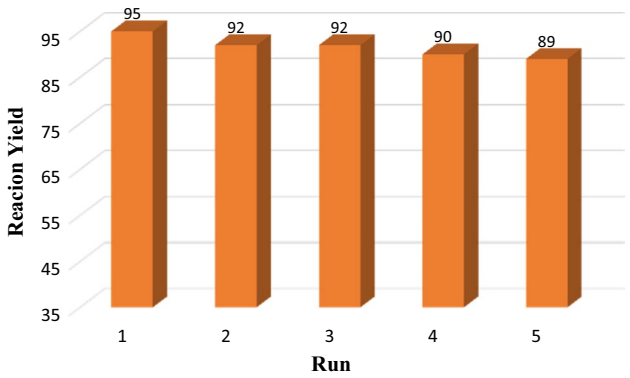


Fig. 2 Catalytic activity of the $AlPO_4(SO_3H)$ nanosheets in 5 cycles

Finally, FE-SEM images indicated sheet-like nanostructures of the catalyst. The size and thickness of the nanosheets measured to be 25–35 nm (Fig. 1b, c).

To find out the suitable condition for the reaction, a series of experiments were performed with the standard reaction of benzaldehyde (**1a**), dimedone (**2**), and 1*H*-1,2,4-triazol-3-amine (**3**) to form 6,6-dimethyl-9-phenyl-5,6,7,9-tetrahydro-[1,2,4]triazolo[5,1-*b*]quinazolin-8(4*H*)-one (**4a**). The results are depicted in Table 1. A variety of solvents such as acetonitrile, ethanol, methanol, and water were tested to find out the best solvent for this transformation. Among various solvents, acetonitrile was found to give the best result. When the reaction was carried out under solvent-free conditions (Table 1, entry 8), the product was obtained 5%, probably due to the absence of strong interactions between the various reactants. To show the efficiency of the nano-$AlPO_4(SO_3H)$ in comparison with other catalysts, $AlPO_4$, amino-functionalized $AlPO_4$, $CuFe_2O_4$, and *p*-dodecylbenzenesulfonic acid were also applied and these results showed that nano-$AlPO_4(SO_3H)$ catalyst is better in viewpoint of reactivity and experimental conditions for this reaction (Table 1, entries 1–4). After this, we studied the effect of various amounts of nano-$AlPO_4(SO_3H)$ catalyst for the synthesis of **4a**. In order to evaluate the appropriate catalyst loading, a model reaction was carried out using 0.3, 0.2, 0.1 and 0. 05 g of nano-$AlPO_4(SO_3H)$ in CH_3CN (Table 1, entries 5, 10–12). We also screened the effect of different temperature in the model reaction (Table 1, entries 11, 13–14). The lower amounts of catalyst gave a low yield, and a larger loading amount of the catalyst (0.3 g) neither increases the yield nor shortens the conversion time. So, 0.1 g of catalyst in CH_3CN at 50 °C was found to be the optimal quantity and sufficient to push the reaction forward (Table 1, entry 13).

After optimization of the reaction conditions, the catalytic activity of nano-$AlPO_4(SO_3H)$ was tested by different aromatic aldehydes bearing Me, Cl, isopropyl, OMe, NO_2, F, dimethyl amine, and Br substitutes at ortho, meta, and para. In all cases, the reaction proceeded to obtain [1,2,4] triazolo[5,1-*b*]quinazolin-8(4*H*)-one derivatives through a variety of electron-rich and electron-poor aromatic aldehydes. We are pleased to disclose that good to excellent yields (Table 2).

Considering the literature focusing on the catalytic activity of Lewis acids [16, 26, 27], we suggested a mechanism for this multi-component *N*-heterocycle synthesis, in this two plausible mechanisms can be proposed. Generally, these processes (route **A** and route **B**) can be started via Knoevenagel condensation for the formation of α, β-unsaturated carbonyl intermediate (intermediate **I**). Then, upon the loss of water molecule and nucleophilic attack of nitrogen in the ring gave intermediate **II** in route **A**. In the next step, intermediate **IV** was probably formed by intramolecular nucleophilic attack. Finally, the intermediate may undergo dehydration to give desired product. The second route (as shown in Scheme 1) was started by attacking NH_2 to carbonyl group of intermediate **I** and loss of two water molecules, resulting intermediate **VI.** Finally, this intermediate produced the desired product (**4a**) via intramolecular cyclization.

Motivated from the efficient catalytic activity of nano-$AlPO_4(SO_3H)$ for the synthesis of quinazolinones, we explored its catalytic activity for the synthesis of highly functionalized piperidines via one-pot, five-component reaction of aromatic aldehydes, aromatic amines, and methyl or ethyl acetoacetate in EtOH at room temperature.

In the first step, we optimized the conditions for the five-component reaction using aniline (2.0 mmol), 4-methyl benzaldehyde (2.0 mmol), and methyl acetoacetate (1.0 mmol) as model reaction in various solvents, temperatures, and in the presence of various amounts of catalyst loading (Table 3). As evident from Table 3, the best result was observed in ethanol at room temperature in the presence of 0.15 g of the catalyst (Table 3, entry 11).

To establish the generality and applicability of this method in five-component synthesis of piperidine derivatives, a variety of substituted aromatic aldehydes and amines (containing electron-withdrawing or electron-donating groups) were subjected to the same reaction conditions to furnish the corresponding piperidine derivatives. In all cases, the reaction proceeded to obtain piperidines in good yields (Table 4).

The reusability of the catalyst is an important factor from an economical and environmental point of views and has attracted much attention in recent years. Thus, the reusability of nano-$AlPO_4(SO_3H)$ was examined in the synthesis of **4a**. After each run, the catalyst was centrifugation, washed with dichloromethane, dried under atmosphere, and utilized directly in the next cycle. As shown in Fig. 2, the yield and time of the model reaction for five runs were almost the same as the first run (Fig. 2).

Conclusion

In summary, new $AlPO_4(SO_3H)$ nanosheets were prepared and the heterogeneous nanocatalysts were characterized by FE-SEM, EDX, and FT-IR analysis. The nanocatalyst was used for the synthesis of a series of [1,2,4]triazolo quinazolinone and piperidine derivatives. The conditions are mild, and a wide range of functional groups can be tolerated. Using $AlPO_4(SO_3H)$ nanosheets as heterogeneous catalyst offers some advantages including easy work-up, short reaction time, good to excellent yields, and no need to purify with column chromatography. Moreover, the catalyst could be successfully recovered and recycled by a simple centrifugation for at least five times without a noticeable their catalytic activity.

Acknowledgements We gratefully acknowledge the financial support of this work by the Shiraz University Research Council.

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