Supporting Information

Tribromide ion immobilized on magnetic nanoparticle as new, efficient and reusable nanocatalyst in multicomponent reactions

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The synthesis of 2,3 dihydroquinazolin-4(1H)-ones derivatives and compounds characterization data

A stirred mixture of 4-chlorobenzaldehyde (1 mmol, 0.140 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.245 g (0.9496 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 95%.

![Structural formula of 2-(4-Chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one](image1)

2-(4-Chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 1, Table 2) (1a). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta_H$: 8.29 (s, 1H), 7.60–7.41 (m, 5H), 7.25–7.20 (t, $J = 7.5$, 1H), 7.12 (s, 1H), 6.75–6.63 (m, 2H), 5.75 (s, 1H) ppm.

A stirred mixture of 3,4-dimethoxybenzaldehyde (1 mmol, 0.166 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.281 g (0.9894 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 99%.

![Structural formula of 2-(3,4-Dimethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one](image2)

2-(3,4-Dimethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 2, Table 2) (1b). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta_H$: 8.21 (s, 1H), 7.64–7.41 (m, 5H), 7.25–7.20 (t, $J = 7.5$, 1H), 7.12 (s, 1H), 6.75–6.63 (m, 2H), 5.75 (s, 1H) ppm.
A stirred mixture of 4-methoxybenzaldehyde (1 mmol, 0.136 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.1778 g (0.7 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 70%.

![Chemical structure of 2-(4-Methoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 3, Table 2) (1c).](image)

**2-(4-Methoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 3, Table 2) (1c).** \(^1\)H NMR (400 MHz, DMSO-d\(_6\)):\(\delta\)H: 8.22 (s, 1H), 7.66–7.63 (m, 1H), 7.46–7.44 (d, J = 8.8, 2H), 7.29–7.24 (m, 1H), 7.04 (s, 1H), 6.99–6.69 (d, J=1.2, 2H), 6.78–6.76 (d, J = 8, 1H), 6.70–6.68 (t, J= 7.2, 1H), 5.74 (s, 1H), 3.77 (s, 3H) ppm.

A stirred mixture of 4-ethoxybenzaldehyde (1 mmol, 0.150 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.247 g (0.9216 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 92%.

![Chemical structure of 2-(4-Ethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 4, Table 2) (1d).](image)

**2-(4-Ethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 4, Table 2) (1d).** \(^1\)H NMR (400 MHz, DMSO-d\(_6\)):\(\delta\)H: 7.95–7.94 (b, 1H), 7.51–7.50 (m, 2H), 7.34 (s, 1H), 7.27 (s, 1H), 6.94–6.90 (m, 3H), 6.68–6.67 (m, 1H), 5.85 (s, 1H), 5.75 (s, 1H), 4.08–4.06 (q, J ¼ 4, 2H), 1.46– 1.44 (s, 3H) ppm.
A stirred mixture of 4-fluorobenzaldehyde (1 mmol, 0.124 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.23 g (0.95 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 95%.

2-(4-Fluorophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 5, Table 2) (1e). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta_H : 8.32\ (s, 1H), 7.65–7.63\ (m, 1H), 7.59–7.54\ (m, 2H), 7.30–7.23\ (m, 3H), 7.13\ (s, 1H), 6.79–6.77\ (d, J=0.8, 1H), 6.69-6.67\ (t, J=8, 1H) 5.80\ (s, 1H) ppm.

A stirred mixture of 4-bromobenzaldehyde (1 mmol, 0.185 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.248 g (0.8184 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 82%.

2-(4-Bromophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 6, Table 2) (1f). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta_H : 8.17–8.14\ (m, 1H), 7.79–7.77\ (m, 1H), 7.63–7.59\ (m, 3H), 7.48–7.45\ (m, 2H), 7.29–7.23\ (m, 1H), 6.77–6.72\ (d, J = 19.2, 1H), 6.70–6.67\ (m, 1H), 5.76\ (s, 1H) ppm.

A stirred mixture of 4-methylbenzaldehyde (1 mmol, 0.1202 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed
by evaporation. Finally, 0.2286 g (0.9596 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 96%.

2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 7, Table 2) (1g). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$: 8.21 (s, 1H), 7.63–7.60 (d, $J = 7.5$, 1H), 7.38–7.35 (d, $J = 7.5$, 2H), 7.25–7.13 (m, 3H), 7.03 (s, 1H), 6.74–6.63 (m, 2H), 5.71 (s, 1H), 2.49–2.42 (s, 3H) ppm.

A stirred mixture of 2-nitrobenzaldehyde (1 mmol, 0.151 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.215 g (0.7992 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 80%.

2-(2-Nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 8, Table 2) (1h). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$: 8.25 (s, 1H), 8.10–8.08 (d, $J = 8$, 1H), 7.90–7.87 (d, $J = 8$, 1H), 7.83–7.79 (t, $J = 0.8$, 1H), 7.69–7.63 (m, 2H), 7.30–7.26 (m, 1H), 7.04 (s, 1H), 6.81 (d, $J = 1.2$, 1H), 6.77–6.72 (m, 1H), 6.36 (m, 1H) ppm.

A stirred mixture of 3-nitrobenzaldehyde (1 mmol, 0.151 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.266 g (0.9888 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 99%.
2-(3-Nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 9, Table 2) (1i). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$H: 8.57 (s, 1H), 8.40–8.39 (t, J=1.6, 1H), 8.24–8.21 (m, 2H), 7.98–7.96 (d, J=7.6, 1H), 7.74–7.70 (t, J=8, 1H), 7.66-7.64 (m, 1H), 7.38 (s, 1H), 7.32-7.28 (m, 1H), 6.83-6.81 (d, J=8, 1H), 6.74-6.70 (m, 1H), 5.98 (s, 1H) ppm.

The synthesis of polyhydroquinoline derivatives and compounds characterization data

A mixture of 4-chlorobenzaldehyde (1 mmol, 0.140 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.343 g (0.9183 mmol) pure product was obtained in yield of 92%.

Ethyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 1, Table 4) (2a). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$H: 9.13 (s, 1H), 7.25–7.28 (m, 2H), 7.17–7.19 (m, 2H), 4.86 (s, 1H), 4.01–3.96 (q, J = 7.2, 2H), 2.46–2.41 (d, J = 16.8, 1H), 2.31–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.01–1.97 (d, J = 16, 1H), 1.15–1.12 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.
A mixture of 4-bromobenzaldehyde (1 mmol, 0.185 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.372 g (0.8899 mmol) pure product was obtained in yield of 89%.

![Chemical Structure](image)

**Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, Table 4) (2b).** $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$H: 9.14 (s, 1H), 7.41–7.39 (d, J = 8.4, 2H), 7.13–7.11 (d, J = 8.4, 2H), 4.84 (s, 1H), 4.01–3.95 (q, J = 6.8, 2H), 2.52–2.46 (d, J = 26.4, 1H), 2.31–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.01–1.97 (d, J = 16, 1H), 1.15–1.11 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.84 (s, 3H) ppm.

A mixture of 4-methylbenzaldehyde (1 mmol, 0.1202 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.3037 g (0.8598 mmol) pure product was obtained in yield of 86%.
Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 3, Table 4) (2c). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$: 9.04 (s, 1H), 7.05–7.03 (d, $J = 8$, 2H), 7.00–6.97 (d, $J = 8$, 2H), 4.81 (s, 1H), 4.01–3.95 (q, $J = 6.8$, 2H), 2.44–2.40 (d, $J = 16$, 1H), 2.30–2.26 (m, 4H), 2.21–2.15 (m, 4H), 2.10–1.96 (d, $J = 16$, 1H), 1.17–1.13 (t, $J = 6.8$, 3H), 1.02 (s, 3H), 0.86 (s, 3H) ppm.

A mixture of 4-methoxybenzaldehyde (1 mmol, 0.136 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.303 g (0.8211 mmol) pure product was obtained in yield of 82%.

Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, Table 4) (2d). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta_H$: 9.04 (s, 1H), 7.08–7.06 (d, $J = 8.4$, 2H), 6.77–6.75 (d, $J = 8.4$, 2H), 4.81 (s, 1H), 4.01–3.96 (q, $J = 7.2$, 2H), 3.68 (s,
3H), 2.45–2.41 (d, J = 29.2, 1H), 2.31–2.29 (m, 4H), 2.20–2.16 (d, J = 16, 1H), 2.01–1.97 (d, J = 16.4, 1H), 1.17–1.14 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.

A mixture of 3,4-dimethoxybenzaldehyde (1 mmol, 0.166 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.36 g (0.9022 mmol) pure product was obtained in yield of 90%.

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\text{Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, Table 4) (2e).} \]

\[\delta_H: 9.05 \text{ (s, 1H), 6.79–6.76 (m, 2H), 6.65–6.63 (d, J = 8, 1H), 4.81(s, 1H), 4.04–3.99 (q, J = 7.2, 2H), 3.69–3.68 (d, J = 4.4, 5H), 2.47–2.42 (d, J = 17.2, 2H), 2.35–2.29 (m, 4H), 2.22–2.18 (d, J = 16, 1H), 2.03–1.99 (d, J = 16, 1H), 1.20–1.16 (t, J = 7.2, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.} \]

A mixture of 4-hydroxybenzaldehyde (1 mmol, 0.1221 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.284 g (0.7997 mmol) pure product was obtained in yield of 80%.
Ethyl-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 7, Table 4) (2f). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$$_H$: 9.05 (s, 1H), 8.99 (s, 1H), 6.95–6.93 (d, $J$=8.8, 2H), 6.58–6.55 (m, 2H), 4.75 (s, 1H), 4.02–3.98 (m, 2H), 2.44–2.40 (d, $J$ = 16.8, 1H), 2.30–2.26 (m, 4H), 2.19–2.15 (d, $J$ = 16, 1H), 2.00–1.96 (d, $J$ = 16, 1H), 1.17–1.14 (t, $J$ = 7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.

A mixture of benzaldehyde (1 mmol, 0.106 g), dmedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.255 g (0.7522 mmol) pure product was obtained in yield of 75%.

Ethyl-4-(phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 8, Table 4) (2g). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$$_H$: 9.08 (s, 1H), 7.22–7.17 (m, 4H), 7.10–7.06 (m, 1H), 4.88 (s, 1H), 4.02–3.97 (q, $J$ = 7.2, 2H), 2.46–2.42(d, $J$ = 17.2 1H), 2.33–2.29 (t, $J$=8.8, 4H), 2.21–2.17 (d, $J$ = 16, 1H), 2.02–1.98 (d, $J$ = 16, 1H), 1.16–1.13 (t, $J$ = 7.2, 3H), 1.03 (s, 3H), 0.86 (s, 3H) ppm.
A mixture of 4-fluorobenzaldehyde (1 mmol, 0.124 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.31 g (0.8683 mmol) pure product was obtained in yield of 87%.

Ethyl-4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 9, Table 4) (2h). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta_H$ : 9.11 (s, 1H), 7.20–7.17 (m, 2H), 7.04–7.00 (t, J = 8.8, 2H), 4.87 (s, 1H), 4.02–3.96 (q, J = 7.2, 2H), 2.46–2.41 (d, J = 16.8, 1H), 2.32–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.15–1.12 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.

A mixture of 3-nitrobenzaldehyde (1 mmol, 0.151 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.33 g (0.8593 mmol) pure product was obtained in yield of 86%.
Ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 10, Table 4) (2i). $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$H : 9.25 (s, 1H), 8.12–8.10 (d, J = 8.4, 2H), 7.45–7.43 (d, J = 8.4, 2H), 4.99 (s, 1H), 4.01–3.95 (q, J = 7.2, 2H), 2.48–2.44 (d, J = 17.2, 1H), 2.34–2.30 (d, J = 16.8, 4H), 2.22–2.18 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.14–1.11 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.84 (s, 3H) ppm.

$^1$H NMR 1a
$^1$H NMR 1c
$^1$H NMR 1d
$^1$H NMR 1e
$^1$H NMR $1f$
$^1$H NMR 1g
$^1$H NMR 1h
\(^1\)H NMR
$^1$H NMR 2a
$^1$H NMR 2b
$^1$H NMR 2c
$^1$H NMR 2d
$^1$H NMR 2e
$^1$H NMR 2f
$^1$H NMR 2g
\(^1\text{H NMR 2h}\)
$^1$H NMR 2i