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Nano-Fe₃O₄@Silica sulphuric acid as a reusable and magnetically separable potent solid acid catalyst in Biginelli type reaction for the one-pot multi-component synthesis of fused dihydropyrimidine derivatives: A greener “NOSE” and “SFRC” approach.

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GENERAL REMARKS:-

All the chemicals were bought from Sigma-Aldrich, Alfa-Aesar and Merck and were used in reaction without further purification. FT-IR spectra were recorded by Perkin Elmer ($\nu_{\max}$ in cm^{-1}) on KBr disks. Melting points were determined in open capillaries and are uncorrected ^1H NMR and ^{13}C NMR (400 MHz and 100 MHz respectively) spectra were recorded on Bruker -400, Bruker Advance II-400 spectrometer in CDCl_3 and DMSO-d_6 (with TMS as internal standard). Waters ZQ-4000 was used for recording Mass spectra while CHN were recorded on CHN-OS analyser (Perkin Elmer 2400, Series II). Transmission Electron Microscope (TEM) was recorded by JEOL JSM 100CX, scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL). EDX was recorded by using INCA Penta FET x-ray instrument. TGA was done by using ZEN3690 instrument and VSM analysis was done by using Lakeshore 7410 series. Silica gel G (E-mark, India) was used for TLC.

EXPERIMENTAL PROCEDURE:-

Preparation of pyrimidine derivatives:-

Firstly, active methylene compounds (**4,5, or 6**) (1 mmol) and aldehydes (1 mmol) were mixed together with 0.006 g nano Fe_3O_4 @Silica sulphuric acid followed by addition of 2-aminobenzimidazole (**2**) or 2-aminothiazole (**3**) which is then magnetically stirred at 60°C for 1.5-3 h leading to the formation of desired product. After completion of the reaction (monitored by TLC), reaction mixture was extracted with ethylacetate or chloroform and nano- Fe_3O_4 @Silica sulphuric acid was removed from the reaction mixture by using an external magnet. In order to reactivate the catalyst, magnetic bit (to which catalyst is

attached) was washed with acetone several times to remove residual products (if any) and dried inside oven. This reactivated catalyst was then used in subsequent reactions. Combined organic extract was washed with water (3 x 10 ml), brine and dried with anhydrous Na_2SO_4 . Organic extract was then removed under vacuum and the crude reaction mixture was purified by column chromatography using ethyl acetate and hexane as eluent.

CHARACTERIZATION OF CATALYST:-

Comparative FT-IR of nano- Fe_3O_4 , nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ is shown in Fig S1. The strong absorption peaks at 599 cm^{-1} and 616 cm^{-1} in the spectra of nano- Fe_3O_4 and, nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2$ are because of Fe-O stretching vibration which shifts to 628 cm^{-1} in case of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ because of quantum confinement¹ and the peaks above 3000 cm^{-1} are because of -OH stretching vibration. Peaks in the region of $1638\text{--}1628\text{ cm}^{-1}$ which are present in all the three spectra are because of -OH deformed vibration. Important features which are observed in the FT-IR spectrum of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2$ are, the appearance of peaks at 474 , 803 and 1099 cm^{-1} which are due to the presence of asymmetric stretching, symmetric stretching and bending vibration of Si-O-Si group respectively. These peaks are also present in FT-IR spectra of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ at 471 , 795 and 1082 cm^{-1} respectively. Finally peaks at 1208 and 1140 cm^{-1} in the spectrum of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ confirmed the presence of sulphonyl group. SEM (Scanning electron microscopy) images revealed that nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ were spherical in shape (Fig S2). The Electron dispersive X-ray spectrum (EDX) (Fig SI 3) showed the presence of Fe, O, Si and S thereby confirming the successful surface modification of magnetic ferrite nanoparticles with SiO_2 and SO_3H . The weight % of Fe, O, Si and S are found to be 43.37%, 39.71%, 13.98% and 2.98% and their atomic % are 20.18%, 64.50%, 12.93 % and 2.38% respectively.

In order to acquire information regarding the size and crystalline behavior of the synthesized catalyst TEM (Transmission electron microscopy) images were taken. TEM images of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ (Fig SI 4b and SI 4c) shows that the nanoparticle is well dispersed, spherical in shape with size ranging between 10-40 nm and there is a uniform coating of $\text{SiO}_2\text{-SO}_3\text{H}$ of 5 nm around the nanoparticles. SAED pattern of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ shows that the catalyst is crystalline in behavior (Fig SI 4a). TEM images of recycled catalyst were also examined (Fig SI 4d and SI 4e) and it confirms that the catalyst retained its size, morphology and crystalline behavior even after five consecutive runs. To study the catalytic behavior of a catalyst, thermal stability is an important parameter needed to be determined. So we carried out thermo gravimetric analysis (TGA) of the synthesized nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$. In the TGA curve (Fig. SI 5) there are three important regions which can be rationalized as follows (1) Below 250 $^{\circ}\text{C}$, there is a mass loss which attributes to the loss of trapped water or adsorbed solvent from the catalyst. (2) Between 300-550 $^{\circ}\text{C}$ there is a large weight reduction which may be attributed to evaporation and subsequent decomposition of $\text{-SO}_3\text{H}$ groups. (3) At higher temperature above 550 $^{\circ}\text{C}$ there are further mass losses which are attributed to the decomposition of silica shell.² So, it is clear from this observation that the catalyst is stable till 250 $^{\circ}\text{C}$ and can be safely used in organic reactions below 250 $^{\circ}\text{C}$. The magnetic property of the catalyst was studied by using vibrating sample magnetometer. The magnetization curve of nano- $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SO}_3\text{H}$ is shown in Fig SI 6. Saturation magnetization value (Ms) was found to be 6.19 emu/g which is lower than bare MNPs² due to coated shell.

Fig SI 1: Comparative FT-IR spectra of (top) nano-Fe₃O₄@SiO₂, (middle) nano-Fe₃O₄ and (bottom) nano-Fe₃O₄@SiO₂@SO₃H.

(a)

(b)

(c)

Fig. SI 2: SEM images of (a) nano-Fe₃O₄, (b) nano-Fe₃O₄@SiO₂ and (c) nano-Fe₃O₄@SiO₂@SO₃H.

Fig. SI 3: EDX spectra of (a) nano-Fe₃O₄, (b) nano-Fe₃O₄@SiO₂ and (c) nano-Fe₃O₄@SiO₂@SO₃H.

Fig. SI 4: SAED pattern of nano-Fe₃O₄@SiO₂@SO₃H before use (a), after use (d) and TEM images of nano-Fe₃O₄@SiO₂@SO₃H before use (b-c), after use (e).

Fig. SI 5: TGA of nano-Fe₃O₄@SiO₂@SO₃H. Fig. SI 6: VSM of nano-Fe₃O₄@SiO₂@SO₃H

1= Chloroform, 2= EtOH, 3= Water, 4= DMF, 5= SFRC

Fig. SI 7: Solvent standardization

Fig. SI 8: Temperature variation

Fig. SI 9: Catalyst concentration variation

Fig.SI 10: Reusability of nano-Fe₃O₄@SiO₂@SO₃H

Analytical Data:

1. 7(a)

Yellow solid. Mp: 288-291 °C,³ IR (KBr): 3236, 2928, 1697 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.46 (d, *J* = 4.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 1H), 7.16 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.05-6.98 (m, 3H), 6.36 (s, 1H), 4.11 (q, *J* = 8.0 Hz, 2H), 2.68 (s, 3H), 1.23 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 165.8, 146.5, 146.4, 141.2, 140.0, 133.8, 131.4, 128.77, 128.75, 122.7, 121.1, 116.4, 109.7, 98.8, 60.2, 56.4, 19.6, 14.3. ESI- MS: *m/z* 368, 370 [M + H]⁺. Anal. Calcd for C₂₀H₁₈ClN₃O₂: C, 65.31; H, 4.93; N, 11.42; Found: C, 65.25; H, 4.98; N, 11.38.

2. 7(b)

Reddish Yellow solid. Mp: 278-280 °C,³ IR (KBr): 3235, 2926, 2228, 1698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.51 (d, *J* = 6.4 Hz, 2H), 7.46 (m, 3H), 7.14 (t, *J* = 5.2 Hz, 1H), 7.02-6.98 (m, 3H), 6.42 (s, 1H), 4.11-4.07 (m, 2H), 2.67 (s, 3H), 1.22 (t, *J* = 5.7 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 165.6, 146.8, 146.3, 141.0, 132.5, 131.1, 128.1, 123.0, 121.5, 118.4, 116.6, 112.0, 109.5, 98.2, 60.4, 56.6, 19.7, 14.3. ESI- MS: *m/z* 359 [M + H]⁺. Anal. Calcd for C₂₁H₁₈N₄O₂: C, 70.38; H, 5.06; N, 15.63; Found: C, 70.25; H, 4.93; N, 15.57.

3. 7(c)

Yellow solid. Mp: 230-232 °C,⁴ IR (KBr): 3235, 2928, 1697 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 12.24 (brs, 1H), 7.54 (d, J = 6.04 Hz, 1H), 7.42 (d, J = 7.12 Hz, 2H), 7.27 (d, J = 6.06 Hz, 2H), 7.20 (t, J = 6.32 Hz, 1H), 7.10-7.05 (m, 2H), 6.41 (s, 1H), 4.17-4.14 (m, 2H), 2.75 (s, 3H), 1.29 (t, J = 5.76 Hz, 3H). ESI- MS: m/z 412, 414 [M + H]⁺. Anal. Calcd for C₂₀H₁₈BrN₃O₂: C, 58.26; H, 4.40; N, 10.19; Found: C, 58.17; H, 4.42; N, 10.32.

4. 7 (d)

Yellow solid. Mp: 270-273 °C,³ IR (KBr): 3392, 2928, 1698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.43 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 12.0 Hz, 2H), 7.12-6.98 (m, 4H), 6.73 (d, J = 8.0 Hz, 2H), 6.34 (s, 1H), 4.12-4.04 (m, 2H), 3.67 (s, 3H), 2.64 (s, 3H), 1.22 (t, J = 6.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.0, 159.1, 146.6, 145.7, 141.1, 133.8, 131.5, 128.5, 122.5, 120.9, 116.3, 113.8, 109.8, 99.5, 60.0, 56.4, 55.2, 19.5, 14.3. ESI- MS: m/z 364 [M + H]⁺. Anal. Calcd for C₂₁H₂₁N₃O₃: C, 69.41; H, 5.82; N, 11.56; Found: C, 69.64; H, 5.60; N, 11.58.

5. 7 (e)

Yellow solid. Mp: 264-266 °C,³ IR (KBr): 3317, 2926, 1703 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 12.30 (brs, 1H), 7.41 (d, *J* = 6.6 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 2H), 7.08-7.06 (m, 2H), 6.99-6.95 (m, 3H), 6.34 (s, 1H), 4.08-4.05 (m, 2H), 2.66 (s, 3H), 2.18 (s, 3H), 1.21 (t, *J* = 5.78 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.0, 146.8, 146.0, 141.3, 138.6, 137.7, 131.6, 129.1, 127.2, 122.4, 120.9, 116.3, 109.8, 99.3, 60.0, 56.7, 21.1, 19.5, 14.3. ESI- MS: *m/z* 348 [M + H]⁺. Anal. Calcd for C₂₁H₂₁N₃O₂: C, 72.60; H, 6.09; N, 12.10; Found: C, 72.55; H, 6.06; N, 12.28.

6. 7(f)

White solid. Mp: 208-210 °C, IR (KBr): 3378, 2926, 1674 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.43 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.19-7.02 (m, 5H), 6.60 (d, *J* = 8.0 Hz, 2H), 6.37 (s, 1H), 4.17-4.15 (m, 2H), 2.88 (s, 6H), 2.71 (s, 3H), 1.31 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.2, 150.0, 146.7, 131.6, 129.3, 128.1, 122.2, 120.7, 116.3, 112.0, 109.8, 59.9, 56.4, 40.3, 19.5, 14.3. ESI- MS: *m/z* 377 [M + H]⁺. Anal. Calcd for C₂₂H₂₄N₄O₂: C, 70.19; H, 6.43; N, 14.88; Found: C, 70.01; H, 6.72; N, 15.01.

7. 7(g)

Yellow solid. Mp: 110-112 °C, IR (KBr): 3259, 2767, 1678, cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 8.20 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 4.0 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 6.30 (s, 1H), 3.65 (s, 3H), 2.44 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.2, 165.4, 157.0, 149.3, 147.7, 127.7, 126.2, 124.1, 106.4,

98.7, 60.0, 59.7, 14.2. ESI- MS: m/z 332 $[M + H]^+$. Anal. Calcd for $C_{15}H_{13}N_3O_4S$: C, 54.37; H, 3.95; N, 12.68; Found: C, 54.44; H, 3.86; N, 12.47.

8. 7 (h)

Yellow solid. Mp: 108-110 $^{\circ}C$, IR (KBr): 3433, 2964, 1686 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ = 7.49 (d, J = 4.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 4.0 Hz, 1H), 6.33 (d, J = 4.0 Hz, 1H), 6.15 (s, 1H), 3.64 (s, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.0, 165.2, 156.8, 144.9, 131.7, 130.5, 129.8, 126.3, 125.5, 123.0, 106.0, 98.8, 60.0, 51.0, 23.9. ESI- MS: m/z 365, 367 $[M + H]^+$. Anal. Calcd for $C_{15}H_{13}BrN_2O_2S$: C, 49.33; H, 3.59; N, 7.67; Found: C, 49.47; H, 3.33; N, 7.78.

9. 7 (i)

Brown solid. Mp: 113-115 $^{\circ}C$, IR (KBr): 3436, 2926, 1679 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ = 7.77 (s, 1H), 7.44 (s, 2H), 6.51 (d, J = 4.0 Hz, 1H), 6.35 (d, J = 4.0 Hz, 1H), 6.20 (s, 1H), 4.06-4.00 (m, 2H), 2.37 (s, 3H), 1.18 (t, J = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.1, 142.9, 131.4, 125.9, 123.6, 106.9, 98.6, 60.2, 59.4, 23.8, 14.3. ESI- MS: m/z 380, 382 $[M + H]^+$. Anal. Calcd for $C_{16}H_{14}ClN_3O_4S$: C, 50.60; H, 3.72; N, 11.06; Found: C, 50.87; H, 3.63; N, 10.87.

10. 7 (j)

Brown solid. Mp: 158-160 °C, IR (KBr): 3110, 2977, 1686 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 6.79 (s, 2H), 6.54 (s, 1H), 6.43 (s, 1H), 6.15 (s, 1H), 3.97-3.95 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.71 (s, 3H), 2.43 (s, 3H), 1.06 (t, J = 6.0 Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 166.6, 164.9, 157.0, 149.9, 143.7, 127.0, 122.9, 112.4, 104.8, 97.9, 97.3, 59.4, 56.7, 56.5, 56.0, 53.0, 23.6, 14.2. ESI- MS: m/z 391 $[\text{M} + \text{H}]^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$: C, 58.45; H, 5.68; N, 7.17; Found: C, 58.37; H, 5.43; N, 6.98.

11. 7 (k)

Brown solid. Mp: 115-117 °C, IR (KBr): 3109, 2987, 1676 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ = 7.30 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 4.4 Hz, 1H), 6.40 (s, 1H), 6.17 (s, 1H), 4.13-4.05 (m, 2H), 3.79 (s, 3H), 2.49 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 166.6, 165.0, 159.5, 155.8, 135.6, 128.1, 126.7, 114.0, 105.4, 99.7, 60.0, 59.6, 55.2, 23.7, 14.2. ESI- MS: m/z 331 $[\text{M} + \text{H}]^+$. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: C, 61.80; H, 5.49; N, 8.48; Found: C, 61.88; H, 5.23; N, 8.19.

12. 7 (l)

White solid. Mp: 190-192 °C, ³ IR (KBr): 3405, 2951, 1699 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 12.06 (s, 1H), 7.54 (d, *J* = 6.04 Hz, 1H), 7.35 (d, *J* = 6.6 Hz, 1H), 7.26-7.17 (m, 2H), 5.66 (t, *J* = 3.3 Hz, 1H), 4.29-4.25 (m, 2H), 2.68 (s, 3H), 2.03-1.97 (m, 1H), 1.80-1.75 (m, 1H), 1.38 (t, *J* = 5.78 Hz, 3H), 0.99-0.93 (m, 2H), 0.79 (t, *J* = 6.04 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.4, 148.1, 148.0, 141.4, 131.5, 122.2, 120.7, 116.4, 109.2, 97.2, 59.9, 52.3, 36.8, 19.4, 17.0, 14.5, 13.9. ESI- MS: *m/z* 300 [M + H]⁺. Anal. Calcd for C₁₇H₂₁N₃O₂: C, 68.20; H, 7.07; N, 14.04; Found: C, 68.32; H, 6.89; N, 13.93.

13. 7(m)

White solid. Mp: 178-180 °C, IR (KBr): 3407, 2929, 1706 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 7.50 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.16-7.10 (m, 3H), 5.58 (s, 1H), 3.74 (s, 3H), 2.59 (s, 3H), 1.97- 1.90 (m, 2H), 1.73-1.66 (m, 2H) 0.72 (t, *J* = 6.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.7, 148.3, 147.7, 141.3, 122.3, 120.8, 116.6, 109.2, 97.1, 52.3, 51.2, 36.8, 19.4, 16.9, 13.8. ESI- MS: *m/z* 286 [M + H]⁺. Anal. Calcd for C₁₆H₁₉N₃O₂: C, 67.35; H, 6.71; N, 14.73; Found: C, 67.27; H, 6.89; N, 14.99.

14. 7 (n)

Brown solid. Mp: 265-267 °C,³ IR (KBr): 3378, 2926, 1618 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ = 12.07 (s, 1H), 8.52 (s, 1H), 7.64-7.04 (m, 7H), 6.58 (s, 1H), 4.17-4.11 (m, 2H), 2.77 (s, 3H), 1.21 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ = 166.0, 159.7, 149.3, 147.7, 146.6, 141.2, 136.6, 131.8, 122.8, 122.4, 122.1, 120.8, 116.3, 110.2, 97.2, 59.9, 58.7, 19.6, 14.3. ESI- MS: *m/z* 335 [M + H]⁺. Anal. Calcd for C₁₉H₁₈N₄O₂: C, 68.25; H, 5.43; N, 16.76; Found: C, 67.97; H, 5.67; N, 16.78.

15. 7 (o)

White solid. Mp: 242-245 °C,³ IR (KBr): 3425, 3150, 1672 cm⁻¹. ¹H NMR (DMSO-*d*₆, 400 MHz) δ = 10.63 (brs, 1H), 7.22-7.14 (m, 3H), 6.86-6.82 (m, 2H), 6.35 (s, 1H), 6.24 (s, 1H), 6.10 (s, 1H), 3.86-3.82 (m, 2H), 2.28 (s, 3H), 0.93 (s, 3H). ¹³C NMR (DMSO-*d*₆, 100 MHz) δ = 165.0, 152.6, 147.7, 145.5, 142.5, 121.8, 120.2, 116.7, 110.3, 109.7, 107.6, 94.2, 59.2, 49.0, 18.6, 14.0. ESI- MS: *m/z* 324 [M + H]⁺. Anal. Calcd for C₁₈H₁₇N₃O₃: C, 66.86; H, 5.30; N, 13.00; Found: C, 66.89; H, 5.41; N, 13.28.

16. 8 (a)

Brown solid. Mp: 335-338 °C,⁵ IR (KBr): 3446, 2926, 1648 cm⁻¹. ¹H NMR (CDCl₃+DMSO-d₆, 400 MHz) δ = 8.17 (s, 1H), 7.31-6.92 (m, 8H), 6.37 (s, 1H), 2.23 (d, *J* = 16.0 Hz, 2H), 2.06 (d, *J* = 16.0 Hz, 2H), 1.05 (s, 3H), 0.92 (s, 3H). ESI- MS: *m/z* 378, 380 [M + H]⁺. Anal. Calcd for C₂₂H₂₀ClN₃O: C, 69.93; H, 5.33; N, 11.12; Found: C, 70.11; H, 5.41; N, 10.90.

17. 8 (b)

White solid. Mp: 315-318 °C,⁵ IR (KBr): 3456, 2961, 1644 cm⁻¹. ¹H NMR (CDCl₃+DMSO-d₆, 400 MHz) δ = 11.06 (brs, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 6.6 Hz, 3H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.35 (s, 1H), 3.64 (s, 3H), 2.26 (d, *J* = 16.0 Hz, 2H), 2.05 (d, *J* = 16.0 Hz, 2H), 1.04 (s, 3H), 0.93 (s, 3H). ¹³C NMR (CDCl₃+DMSO-d₆, 100 MHz) δ = 192.7, 158.3, 145.1, 133.2, 131.6, 127.8, 121.4, 120.2, 116.7, 113.2, 109.2, 106.5, 54.6, 53.7, 50.0, 32.1, 28.7, 26.7. ESI- MS: *m/z* 374 [M + H]⁺. Anal. Calcd for C₂₃H₂₃N₃O₂: C, 73.97; H, 6.21; N, 11.25; Found: C, 73.71; H, 6.22; N, 11.28.

Spectroscopic Data:

1. 7(f)

¹H NMR:

¹³C NMR :

2.7 (g)

¹H NMR:

¹³C NMR:

3. 7 (h)

¹H NMR:

¹³C NMR:

4. 7(i)

¹H NMR:

¹³C NMR:

5. 7 (j)

^1H NMR:

¹³C NMR :

6. 7 (k)

^1H NMR:

¹³C NMR:

7. 7(m)

¹H NMR:

^{13}C NMR:

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