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Synthesis and spectroscopic characterization of some novel Schiff bases of benzylidene derivatives

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ABSTRACT

A novel series of N'-(substituted benzylidene)-2-(substituted phenyl)acetohydrazide (4a-n) Schiff bases have been synthesised by treatment of Methyl 2-(substituted phenyl)acetohydrazide (3a-d) with few benzaldehyde derivatives. Spectrocopic characterization viz: ^{1}H NMR, ^{13}C NMR, LCMS and elemental analysis of newly synthesised compounds were reported.

Keywords: Fischers esterification, acetohydrazide, Schiff bases, benzylidene derivatives

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INTRODUCTION

Schiff bases represent an important class of organic compounds, especially in the medicinal and pharmaceutical field. These are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine group. They are exhibit a broad range of biological activities. Antiviral [1] antibacterial [2,3], Antimicrobial activity [4,5] of Schiff bases well known in the literature. Anticancer [6], cytotoxic [7], properties of the Schiff bases have been studied by many researcher,

Many Schiff base are excellent chelating agents capable of coordination with metal ion such as cobalt (II), oxovanadium (IV), ruthenium (III), copper (II), zinc (II), chromium (II), cadmium (II), manganese (II), tin (VI) [8-16]. Metal complex of Schiff bases shows biological activities like urease inhibition[17], antioxidant[18], anticancer[19,20], antifungal [21] and antibacterial [22-23]. Few Schiff bases shows non-linear optical properties [24]. Multi-walled carbon nanotubes functionalized with a palladium(II)-Schiff base complex act as a recyclable and heterogeneous catalyst for the copper-, phosphorous-, and solvent free synthesis of ynones[25]. Atom transfer radical polymerization and ring opening metathesis polymerization will be done by using ruthenium complexes containing Schiff base ligand [26]. Some Schiff bases and its metal complex act as acid corrosion inhibitors for metal like copper, steel, aluminium [27-29].

Above mentioned considerations prompted us to explore a new series of substituted Schiff bases 4a-n with different benzylidene and phenyl rings. Complete report on the synthesis and spectroscopic characterization are reported herein.

MATERIALS AND METHODS

All reagents were used as received. All chemistry was performed under a nitrogen atmosphere using standard techniques. Progress of the reaction was monitored by TLC. Melting points were determined by Buchi B-545 apparatus. All the NMR spectra were measured using Bruker AMX 400 instrument with 5 mm PABBO BB-1H tubes. ^{1}H NMR spectra were measured for approximately 0.03 M solutions in d6-DMSO at 400 MHz with TMS as

internal reference. ^{13}C NMR spectra were measured for approximately 0.05 M solutions in d6-DMSO at 100 MHz with TMS as internal reference. LCMS were obtained using Agilent 1200 series LC and Micromass zQ spectrometer

Synthesis of methyl 2-(substituted phenyl)acetate derivatives (2a-d):
A solution of (substituted phenyl)acetic acid in methanol was refluxed in presence of catalytic amount of Conc. H_2SO_4 for 3 h. After the completion of the reaction, excess of methanol was removed under vacuum. Residue was dissolved in ethyl acetate and washed with aq.10% $NaHCO_3$ solution, Water, brine, dried over Na_2SO_4, filtered and concentrated under vacuum to afford the title compound 2a-d

Methyl 2-m-tolylacetate (2a):
Isolated yield 90%. Colourless oil. ^1H-NMR (400 MHz, DMSO-*d*6): δ 2.29 (s, 3H), 3.61 (s, 3H), 3.63 (s, 2H), 7.04-7.08 (m, 3H), 7.19-7.23 (m, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm):21.91, 52.65, 127.36, 128.44, 129.26, 130.90, 135.22, 138.46, 172.63; MS calcd. for $C_{10}H_{12}O_2$: 164.2. Found: 164.1, Anal. Calc. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37; O, 19.49. Found: C, 73.11; H, 7.32.

Methyl 2-p-tolylacetate (2b):
Isolated yield 92%. Pale yellow oil. ^1H-NMR (400 MHz, DMSO-*d*6): δ 2.26 (s, 3H), 3.60 (s, 3H), 3.63 (s, 2H), 7.05-7.15 (m, 4H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm):21.07, 52.05, 129.61, 131.74, 136.33, 172.17. MS calcd. for $C_{10}H_{12}O_2$: 164.2. Found: 164, Anal. Calc. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37; O, 19.49. Found: C, 73.13H, 7.34.

Methyl 2-(4-ethoxyphenyl)acetate (2c):
Isolated yield 82%. Colorless oil. ^1H-NMR (400 MHz, DMSO-*d*6): δ 1.29 (t, J = 9.28 Hz, 3H), 3.57 (s, 3H), 3.58 (s, 2H), 3.96-3.98 (m, 2H), 6.84 (d, J = 11.60 Hz, 2H), 7.14 (d, J = 11.60 Hz, 2H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm):14.34, 15.10, 52.04, 63.37, 114.70. 126.55, 130.79, 157.89, 172.35. GCMS calcd. for $C_{11}H_{14}O_3$: 194.23. Found:194. Anal. Calc. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27; O, 24.71 Found: C, 68.01; H, 27.23.

Methyl 2-(2-nitrophenyl)acetate (2d)
Isolated yield 88%. Yellow liquid. ^1H-NMR (400 MHz, DMSO-*d*6): δ 3.62 (s, 3H), 4.07 (s, 2H), 7.54-7.59 (m, 2H), 7.69-7.74 (m, 1H), 8.09 (d, J = 12.00 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 38.98, 52.27, 0.00, 125.31, 129.32, 130.24, 134.20, 134.44, 148.86, 170.86. GCMS calcd. for $C_9H_9NO_4$: 194.23. Found:149 (-NO2), Anal. Calc. for $C_9H_9NO_4$: C, 55.39; H, 4.65; N, 7.18; O, 32.79 Found: C, 55.39; H, 4.65; N, 7.18; O, 32.79

Synthesis of (Substituted phenyl)acetohydrazide derivatives (3a-d):
To a solution of methyl 2-(substituted phenyl)acetates (2a-d) (0.010mmol) in methanol, hydrazine hydrate (0.015 mmol) was added and stirred at RT for 3h. After the completion of the reaction methanol was removed under vacuum. To the residue added water and filtered to afford the title compound 3a-d.

2-m-Tolylacetohydrazide (3a):
Isolated yield 81%. White solid. ^1H-NMR (400 MHz, DMSO-*d*6): : δ 2.28 (s, 3H), 3.30 (s, 2H), 4.21 (s, 2H), 7.02-7.03 (m, 3H), 7.17 (t, J = 7.48 Hz, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.42, 126.47, 127.41, 128.52, 129.99, 136.59, 137.61, 170.02. MS calcd. for $C_9H_{12}N_2O$ 164.2. Found: 165.2(M+1), Anal. Calc. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06; O, 9.74 Found: C, 65.79; H, 7.33; N, 17.02.

2-p-Tolylacetohydrazide (3b):
Isolated yield 79%, White solid. ^1H-NMR (400 MHz, DMSO-*d*6): δ 2.26 (s, 3H), 3.29 (s, 2H), 4.21 (s, 2H), 7.09 (d, J = 8.00 Hz, 2H), 7.14 (d, J = 8.00 Hz, 2H), 9.19 (s, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.09, 29.22, 133.65, 135.77, 170.17, MS calcd. for $C_9H_{12}N_2O$ 164.2. Found: 165.2(M+1), Anal. Calc. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06; O, 9.74 Found: C, 65.80; H, 7.31; N, 17.01.

2-(4-Ethoxyphenyl)acetohydrazide (3c):
Isolated yield 68%. Off white solid. ^1H-NMR (400 MHz, DMSO-*d*6): δ 1.31 (t, J = 6.96 Hz, 3H), 3.26 (s, 2H), 3.98 (q, J = 6.96 Hz, 2H), 0.19 (s, 2H), 6.83 (d, J = 8.48 Hz, 2H), 7.15 (d, J = 8.48 Hz, 2H), 9.16 (s, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 18.01, 63.34, 114.54, 128.50, 130.34, 157.59, 170.34 MS calcd. for $C_{10}H_{14}N_2O_2$ 194.23. Found: 195.2(M+1), Anal. Calc. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42; O, 16.47 Found: C, 61.81; H, 7.23; N, 14.40.

2-(2-Nitrophenyl)acetohydrazide (3d):
Isolated yield 82%. Pale yellow solid. ^1H-NMR (400 MHz, DMSO-*d*6): δ 3.81 (s, 2H), 4.19 (d, J = 12.08 Hz, 2H), 7.48-7.50 (m, 2H), 7.65-7.65 (m, 1H), 7.99 (d, J = 8.12 Hz, 1H), 9.21 (s, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ

(ppm): 37.83, 124.91, 128.63, 131.01, 133.63, 133.73, 149.70, 168.62 MS calcd. for $C_8H_9N_3O_3$ 195.18. Found:196.2 (M^+), Anal. Calc. for $C_8H_9N_3O_3$: C, 49.23; H, 4.65; N, 21.53; O, 24.59 Found: C, 49.19; H, 4.62; N, 21.51.

Synthesis of (N'-(substituted benzylidene)-2-(substituted phenyl)acetohydrazide derivatives (4a-n):
To a solution of methyl 2-(substituted phenyl)acetohydrazide (3a-d) (0.010 mmol) in ethanol, substituted benzaldehyde (0.011) and catalytic amount of acetic acid was added. Reaction mixture was stirred at RT for 1h. Volume of the ethanol was reduced to ~20%, precipitated solid was filtered, washed with cold ethanol and dried under vacuum to afford Schiff base derivatives 4a-p.

(E)-N'-(4-Methoxybenzylidene)-2-p-tolylacetohydrazide (4a):
Isolated yield 83%. White solid. Melting point 153-155°C, ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.25 (s, 3H), 3.46 (s, 1H), 3.79 (s, 3H), 3.90 (s, 1H), 6.97-6.98 (m, 2H), 7.08-7.10 (m, 2H), 7.17-7.18 (m, 2H), 7.60-7.61 (m, 2H), 8.03 (d, J = 86.80 Hz, 1H), 11.33 (d, J = 84.40 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm):21.09, 41.32, 55.74,114.74, 127.29, 129.23, 133.20, 135.77, 143.11, 146.81, 161.01, 166.92, 172.65. MS calcd. for $C_{17}H_{18}N_2O_2$: 282.34. Found: 283.2 (M+1), Anal. Calc. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92; O, 11.33 Found: C, 72.28; H, 6.39; N, 9.88.

(E)-N'-(4-Cyanobenzylidene)-2-p-tolylacetohydrazide (4b):
Isolated yield 75%. White solid. Melting point: 202-205°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.25 (s, 3H), 3.52 (s, 1H), 3.95 (s, 1H), 7.09-7.11 (m, 2H), 7.18-7.20 (m, 2H), 7.86-7.89 (m, 4H), 8.14 (d, J = 95.12 Hz, 1H), 11.71 (d, J = 84.88 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.08, 41.26, 112.23, 119.11, 127.76, 129.36, 133.20, 136.14, 139.19, 141.32, 144.96, 167.5, 173.2. MS calcd. for $C_{17}H_{15}N_3O$: 277.32. Found: 278.2(M+1), Anal. Calc. for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15; O, 5.77 Found: C, 73.60; H, 5.42; N, 15.11.

(E)-N'-Benzylidene-2-p-tolylacetohydrazide (4c):
Isolated yield 71%. White solid. Melting point 160-162°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.24 (s, 3H), 3.48 (s, 1H), 3.92 (s, 1H), 7.08-7.10 (m, 2H), 7.18-7.18 (m, 2H), 7.38-7.38 (m, 3H), 7.65-7.66 (m, 2H), 8.09 (d, J = 89.28 Hz, 1H), 11.46 (d, J = 85.64 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.08, 41.29, 127.17, 129.23,130.17, 133.07, 134.73, 136.06, 143.21, 146.88, 167.16, 172.90. MS calcd. for $C_{16}H_{16}N_2O$: 252.31. Found: 253.2(M+1), Anal. Calc. for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10; O, 6.34 Found: C, 76.11; H, 6.32; N, 11.06

(E)-N'-(4-Fluorobenzylidene)-2-p-tolylacetohydrazide (4d):
Isolated yield 78%. White solid. Melting point 162-164°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.24 (s, 3H), 3.47 (s, 1H), 3.91 (s, 1H), 7.12-7.17 (m, 2H), 7.24-7.25 (m, 2H), 7.27-7.28 (m, 2H), 7.71-7.71 (m, 2H), 8.09 (d, J = 92.12 Hz, 1H), 11.46 (d, J = 86.32 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.08, 41.27, 116.17, 129.24, 131.37, 133.06, 136.06, 142.07, 145.77, 162.10, 164.55, 167.16, 172.89. MS calcd. for $C_{16}H_{15}FN_2O$: 270.30. Found: 271.2(M+1), Anal. Calc. for $C_{16}H_{15}FN_2O$: C, 71.10; H, 5.59; F, 7.03; N, 10.36; O, 5.92 Found: C, 71.05; H, 5.54; N, 10.31.

(E)-N'-(4-Methoxybenzylidene)-2-(2-nitrophenyl)acetohydrazide (4e):
Isolated yield 69%. White solid. Melting point 199-202°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 3.78 (s, 3H), 4.00 (s, 1H), 4.42 (s, 1H), 6.97-6.98 (m, 2H), 7.52-7.52 (m, 2H), 7.66-7.67 (m, 2H), 7.69-7.70 (m, 1H), 8.04-8.05 (m, 1H), 8.06 (d, J = 64.92 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 38.25, 55.72, 114.73, 125.04, 127.22, 128.84, 131.63, 134.14,143.51, 146.54, 149.61, 161.08, 165.48, 170.97, MS calcd. for $C_{16}H_{15}N_3O_4$: 313.31. Found: 314.2(M+1), Anal. Calc. for $C_{16}H_{15}N_3O_4$: C, 61.34; H, 4.83; N, 13.41; O, 20.43 Found: C, 61.31; H, 4.80; N, 13.38.

(E)-N'-(4-Cyanobenzylidene)-2-(2-nitrophenyl)acetohydrazide (4f):
Isolated yield 75%. White solid. Melting point 236-238°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 4.04 (s, 1H), 4.46 (s, 1H), 7.58-7.58 (m, 2H), 7.69-7.69 (m, 1H), 7.86-7.87 (m, 4H), 8.05-8.06 (m, 1H), 8.17 (d, J = 65.68 Hz, 1H), 11.84 (d, J = 61.76 Hz, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 38.25, 112.11, 119.11, 125.08, 127.86, 128.84, 129.01, 130.61, 131.39, 133.17, 134.27, 139.09, 141.69, 144.69, 149.32, 166.2, 171.7, MS calcd. for $C_{16}H_{12}N_4O_3$: 308.29. Found: 309.2(M+1), Anal. Calc. for $C_{16}H_{12}N_4O_3$: C, 62.33; H, 3.92; N, 18.17; O, 15.57. Found: C, 62.27; H, 3.88; N, 18.13.

(E)-N'-Benzylidene-2-(2-nitrophenyl)acetohydrazide (4g):
Isolated yield 64%. White solid. Melting point 174-176°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 4.02 (s, 1H), 4.44 (s, 1H), 7.41-7.42 (m, 3H), 7.53-7.54 (m, 2H), 7.67-7.67 (m, 3H), 8.05-8.05 (m, 1H), 8.11 (d, J

= 66.04 Hz, 1H), 11.60 (d, J = 59.44 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 38.24,125.07, 0.00, 127.47, 128.93, 129.27, 130.43, 130.74, 131.54, 134.19, 134.62, 143.61, 146.62, 149.57, 165.75, 171.26, MS calcd. for $C_{15}H_{13}N_3O_3$: 283.28. Found:284,2(M+1), Anal. Calc. for $C_{15}H_{13}N_3O_{33}$: C, 63.60; H, 4.63; N, 14.83; O, 16.94 Found: C, 63.56; H, 4.60; N, 14.80.

(E)-N'-(4-Fluorobenzylidene)-2-(2-nitrophenyl)acetohydrazide (4h):
Isolated yield 88%. White solid. Melting point 176-178°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: 400 MHz, DMSO-d6: δ 4.01 (s, 1H), 4.43 (s, 1H), 7.24-7.24 (m, 2H), 7.53-7.53 (m, 2H), 7.68-7.69 (m, 3H), 8.04-8.04 (m, 1H), 8.11 (d, J = 69.00 Hz, 1H), 11.61 (d, J = 60.60 Hz, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 38.24, 116.19, 125.03, 128.75, 129.59, 130.74, 131.26, 134.02, 142.47, 145.52, 149.41, 162.18, 164.63, 165.78, 171.26, MS calcd. for $C_{15}H_{12}FN_3O_3$:301.2. Found:302.2(M+1), Anal. Calc. for $C_{15}H_{12}FN_3O_3$ C, 59.80; H, 4.01; F, 6.31; N, 13.95; O, 15.93 Found: C, 59.76; H, 4.00; N, 13.90.

(E)-N'-(4-Methoxybenzylidene)-2-m-tolylacetohydrazide (4i):
Isolated yield 91%. White solid. Melting point 129-131°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.26 (s, 3H), 3.46 (s, 1H), 3.78 (s, 3H), 3.90 (s, 1H), 6.97-6.98 (m, 6H), 7.60-7.60 (m, 2H), 8.04 (d, J = 88.28 Hz, 1H), 11.34 (d, J = 87.48 Hz, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.43, 41.67, 55.72, 114.72, 126.56, 127.25, 128.66, 129.04, 130.07, 130.52, 136.13, 137.63, 143.12, 146.83, 161.20, 166.78, 172.53. MS calcd. for $C_{17}H_{18}N_2O_2$: 283.28. Found: 283.2(M^+), Anal. Calc. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92; O, 11.33 Found: C, 72.28; H, 6.40; N, 9.89.

(E)-N'-(4-Cyanobenzylidene)-2-m-tolylacetohydrazide (4j)
Isolated yield 84%. White solid. Melting point 174-176°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.25 (s, 3H), 3.52 (s, 1H), 3.95 (s, 1H), 7.00-7.02 (m, 4H), 7.83-7.83 (m, 4H), 8.14 (d, J = 97.84 Hz, 1H), 11.71 (d, J = 87.36 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.42, 41.64, 112.24, 119.10, 126.60, 127.75, 128.59, 130.12, 130.52, 133.18, 135.76, 137.70, 139.19, 141.35, 145.02, 167.40, 173.13. MS calcd. for $C_{17}H_{15}N_3O$: 277.32. Found: 278.2 (M+1). Anal. Calc. for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15; O, 5.77 Found: C, 73.60; H, 5.41; N, 15.11.

(E)-N'-Benzylidene-2-m-tolylacetohydrazide (4k):
Isolated yield 66%. White solid. Melting point 112-113°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 2.25 (s, 3H), 3.50 (s, 1H), 3.93 (s, 1H), 7.01-7.02 (m, 4H), 7.40-7.40 (m, 3H), 7.66-7.66 (m, 2H), 8.11 (d, J = 97.04 Hz, 1H), 11.53 (d, J = 123.56 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 21.42, 41.64, 126.60, 126.86, 127.17, 127.45, 128.57, 129.22, 130.11, 130.41, 134.73, 136.05, 137.65, 143.26, 146.94, 167.07, 172.78, MS calcd. for $C_{16}H_{16}N_2O$: 252.31. Found:253.2(M+1), Anal. Calc. for $C_{16}H_{16}N_2O$: : C, 76.16; H, 6.39; N, 11.10; O, 6.34 Found: : C, 76.13; H, 6.33; N, 11.06.

(E)-N'-(4-Cyanobenzylidene)-2-(4-ethoxyphenyl)acetohydrazide (4l):
Isolated yield 89%. White solid. Melting point 172-174°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 1.29 (q, J = 6.28 Hz, 3H), 3.49 (s, 1H), 3.92 (s, 1H), 3.97 (t, J = 6.88 Hz, 2H), 6.85 (d, J = Hz, 2H), 7.21 (d, J = Hz, 2H), 7.86-7.89 (m, 4H), 8.15 (d, J = 94.88 Hz, 1H), 11.70 (d, J = 85.04 Hz, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 15.12, 38.42, 63.39, 112.01, 114.63, 119.17, 127.66, 130.55, 133.13, 139.22, 141.30, 144.95, 157.65, 167.73, 173.42. MS calcd. for $C_{18}H_{17}N_3O_2$: 307.35. Found: 308.2 (M^+), Anal. Calc. for $C_{18}H_{17}N_3O_2$: : C, 70.34; H, 5.58; N, 13.67; O, 10.41. Found: : C, 70.31; H, 5.54; N, 13.63.

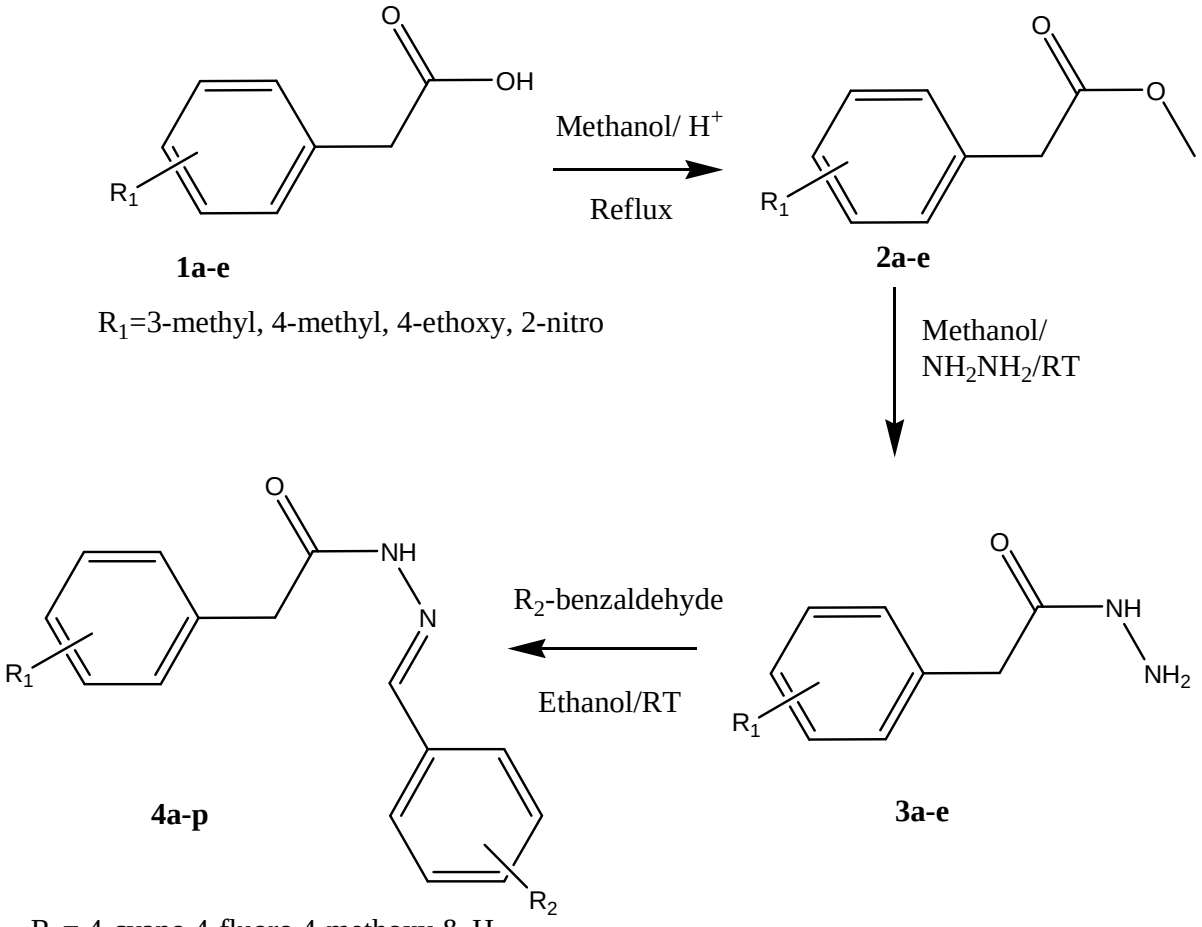
(E)-N'-Benzylidene-2-(4-ethoxyphenyl)acetohydrazide (4m):
Isolated yield 92%. White solid. Melting point 153-155°C ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 1.30 (t, J = 6.56 Hz, 3H), 3.46 (s, 1H), 3.90 (s, 1H), 3.97 (q, J = 6.80 Hz, 2H), 6.86 (t, J = 8.52 Hz, 2H), 7.21 (d, J = 8.08 Hz, 2H), 7.44 (d, J = 8.96 Hz, 3H), 7.69 (t, J = 8.48 Hz, 2H), 8.11 (d, J = 87.60 Hz, 1H), 11.46 (d, J = 85.20 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 15.13, 38.45, 63.37, 114.60, 127.18, 127.88, 129.23, 129.31, 130.18, 130.51, 130.81, 134.74, 143.19, 146.85, 157.60, 167.35, 173.07. MS calcd. for $C_{17}H_{18}N_2O_2$: 282.14. Found:283.2 (M^+). Anal. Calc. for $C_{17}H_{18}N_2O_2$: : C, 72.32; H, 6.43; N, 9.92; O, 11.33 Found: : C, 72.25; H, 6.39; N, 9.82

(E)-2-(4-Ethoxyphenyl)-N'-(4-fluorobenzylidene)acetohydrazide (4n):
Isolated yield 78%. White solid. Melting point 157-159°C. ^{1}H-NMR (400 MHz, DMSO-*d*6): 400 MHz, DMSO-d6: δ 1.28-1.30 (m, 3H), 3.46 (s, 1H), 3.90 (s, 1H), 3.94-3.96 (m, 2H), 6.83-6.85 (m, 2H), 7.21-7.22 (m, 4H), 7.72-7.73 (m, 2H), 8.10 (d, J = 90.84 Hz, 1H), 11.46 (d, J = 86.00 Hz, 1H), ^{13}C-NMR (400 MHz, DMSO-*d*6) δ (ppm): 15.12, 38.43, 63.32, 114.59, 116.24, 127.86, 129.35, 129.64, 130.50, 131.36, 142.05, 145.75, 157.60, 162.11, 164.56, 167.37, 173.07. MS calcd. for $C_{17}H_{17}FN_2O_2$: 300.33. Found: 301.2(M^+), Anal. Calc. for $C_{17}H_{17}FN_2O_2$: : C, 67.99; H, 5.71; F, 6.33; N, 9.33; O, 10.65 Found: : C, 67.95; H, 5.68; N, 9.29.

RESULTS AND DICUSSION

Methyl 2-(substituted phenyl)acetates (2a-d) was synthesized from substituted phenyl acetic acid(1a-d) by Fischers esterification in 82-92% yield. Methyl protons of ester appears as singlet at region δ3.60-3.63 ppm, Singlet at δ 3.58-3.63 ppm corresponding to R–CH_2- in ^{1}H NMR. Carbonyl peak of ester was appeared at 172 ppm in ^{13}C NMR. Methyl 2-(substituted phenyl)acetohydrazide (3a-d) was synthesised from methyl 2-(substituted phenyl)acetates (2a-d) in 95-98% yield. Benzylic methylene proton signal appears at the region of 3.26-4.21ppm. Signal for carbonyl carbon of acetohydrazide was appeared at the region of 168.62 – 170.34 ppm. We reported Single crystal structure of acetohydrazide 3b[30], and 3d[31].

N'-(substituted benzylidene)-2-(substituted phenyl)acetohydrazide (4a-n) has been synthesised by treatment of (substituted phenyl)acetohydrazide (3a-d) with substituted benzaldehyde in ethanol in good yield. The 1H-NMR spectrum (DMSO-d6) of compounds 4a-p showed benzylic –CH2- as two singlet. –N=CH- and –NH-N-proton appears as doublet. The signals for other aromatic and aliphatic protons were observed at expected regions In 13 C NMR , carbonyl peak appears in the region of 167-172 ppm. All the other signals in the spectra were accounted for the all equivalent and non-equivalent carbons present in the molecule.



Scheme:1 Synthesis of Schiff bases

CONCLUSION

Methyl phenyl acetate(2a-d) were synthesised from substituted phenyl acetic acid(1a-d) by Fischers eaterification. Esters (2a-d) was treated with hydrazine hydrate to obtain accetohydrazide derivatives(3a-d). A novel series of Schiff bases has been synthesised from substituted benzaldehyde and 2-(substituted phenyl)acetohydrazide(3a-d). The newly synthesised compounds were characterised with spectroscopic techniques such as 1H NMR, 13 C NMR, LC-MS and elemental analysis. The spectra of the synthesised compounds were in agreement with the theoretical values.

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