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Research Article

FACILE SYNTHESIS OF (4-PHENYL-1,2,4-TRIAZOL-5-YL- METHYL -1,2,3,4-TETRAZOL-2-YL)-2H-CHROMENES

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ABSTRACT

3-{1-[(3-Mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-1,2,3,4-tetrazol-2-yl}-2H-chromenes **(2a-e)** on alkylation with allyl bromide **(5)** in presence of K_2CO_3 in DMF give 3-{1 -{ [3-(allylsulfanyl)-4-phenyl-1,2,4-triazol-5-yl]methyl}-1,2,3,4-tetrazol-2-yl)-2H-chromenes **(6a-e)** in good yields.

Keywords: Allyl bromide, K_2CO_3, DMF, 3-{1-[(3-mercapto-4-phenyl-1,2,4-triazol-5-yl) methyl]- 1,2,3,4-tetrazol-2-yl}-2H-chromene

INTRODUCTION

Oxygen containing natural and synthetic hetrocycles are widely found in nature. The chromones (i.e., 4-Oxo-4H-chromenes) constitute one of the major classes of naturally occurring compounds. These compounds exhibits various biological activities include anticancer, neuroprotective, HIV-inhibitory, antimicrobial, antifungal, and antioxidant activity. Also, chromones with pyridyl, furyl, and quinoyl substitutents at 2-position have been tested for antitumor activity.[3] In addition, hetroannulated chromones exhibited significant biological activity including pharmacological, anti-inflammatory, and antiplatelet activities. On the other hand, flavones also constitute one of the major classes of oxygen containing natural products as well known to posses several biological activities. In addition, many flavonoids contains the basic skeleton of chromone motif have been found to posses diverse interesting biological activities.

MATERIAL AND METHODS

General: - Melting points were determined on a Polmon instrument (model no. MP-96).IR spectra were recorded on Perkin-Elmer 337 spectrometer, and ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) were recorded on a Varian Gemini 200 spectrometer using TMS as internal standard (chemical shifts values were described in ppm δ). UV spectra were obtained on a Shimadzu UV-visible spectrophotometer (model UV-1601). Mass spectra were recorded on a VG micromass LCMS 2010 instrument.

I. Synthesis of 3-{1-[(3-mercapto-4-phenyl-1,2,4-triazol-yl)methyl]-1,2,3,4-tetrazol-yl}-2H-chromenes (2a-e).

i) 3-{1-[(3-Mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-1,2,3,4-tetrazol-2-yl}-2H- chromene (2a)

A mixture of N-1-Phenyl-2-{2-[5-(2H-3-chromenyl)-2H-1,2,3,4-tetrazol-2-yl] acetyl}-1-hydrazinecarbothioamide **(1a)** (2.0g, 4.9mmol) and 5% Na_2CO_3 solution (30ml) was refluxed for 5 hours. The reaction mixture was cooled to room temperature and then adjusted to pH=6 with 10 % HCl to furnish a white precipitate, which was collected by filtration washed with water, dried, and purified by column chromatography eluted with pet.ether:ethyl acetate (9:2) to give **2a** (1.6gm, 84% yield), mp 210 °C.

IR (KBr): 3200 cm^{-1}(S-H).

^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.48-7.45 (m, H-3", H-4", H-5", H-4), 7.33 (d, J= 7.5Hz, H-5), 7.27-7.21 (m, H-2"', H-6"', H-7), 6.96 (dd, J=7.5Hz, J=7.3Hz, H-6), 6.87 (d, J=8.0Hz, H-8), 6.07 (s, N-CH_2), 5.07 (s, OCH_2).

^{13}C NMR (DMSO-d_6, 100.6MHz): δ 169.8 (C-3"), 162.1 (C-5'), 154.2 (C-8a), 145.8 (C-5"), 133.1 (C-l"'), 131.1 (C-7), 130.2 (C-4"'), 129.8 (C-3"', C-5"'), 128.6 (C-3), 128.2 (C-4), 125.4 (C-5), 122.3(C-2"',C-6"'), 121.5 (C-4a), 119.2(C-6), 116.0 (C-8), 64.8 (C-2), 47.9 (N-CH_2).

DIPMS: m/z 390 [M+H].

Employing the similar procedure as mentioned for **2a**, compounds **2b-e** was obtained from **1b-e** as solids.

ii) 3-{1-[(3-Mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl}-1,2,3,4-tetrazol-2-yl}-6,8-dimethyl-2H-chromene **(2b):**

White solid. mp 234 °C, yield 80%.

IR (KBr): 3180 cm^{-1} (S-H).

^{1}H NMR (DMSO-d_6, 400 MHz) : δ 7.36 (m, 3"', 4"', 5"', H-4), 7.15-7.10 (m, 2"',6"', H-7), 7.0 (m, H-5), 5.86 (s, N-CH_2), 5.0 (s, OCH_2), 2.21 (s, 6,8-CH_3).

^{13}C NMR (DMSO-d_6, 100.6MHz): δ 170.2 (C-3"), 161.9 (C-5'), 152.1 (C-8a), 144.3 (C-5"), 136.1 (C-l"'), 131.3 (C-6), 131.1 (C-7), 129.0 (C-4), 128.7 (C-4"'), 128.4 (C-3"', C-5"'), 125.2 (C-3), 125.1 (C-4a), 121.5 (C-2"', C-6"'), 119.1 (C-5), 115.7 (C-8), 64.9 (C-2), 48.8 (N-CH_2), 20.4 (2 x CH_3).

DIPMS: m/z 404 [M+H].

iii)3-{1-[(3-Mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-1,2,3,4-tetrazol-2-yl}-6,8-dichloro-2H-chromene (2c):

Light yellow solid. mp 237 °C, yield 77%.

IR (KBr): 3230 cm^{-1}(S-H).

^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.45-7.39 (m, H-4, H-3"', H-4"', H-5"'), 7.26-7.17 (m, H-5, H-7, H-2"', H-6"'), 5.92 (s,N-CH_2), 5.10(s, OCH_2).

^{13}C NMR (DMSO-d_6, 50.3MHz): δ 168. (C-3"), 160.9 (C-5'), 152.3 (C-8a), 144.5 (C-5"), 134.1 (C-l"'), 129.8 (C-7), 128.9 (C-4"'), 128.7 (C-4), 127.8 (C-3"', C-5"'), 127.3 (C-3), 125.3 (C-5), 123.4 (C-2"', C-6"'), 122.8 (C-4a), 120.2 (C-6), 117.2 (C-8), 64.4 (OCH_2), 48.6 (N-CH_2).

DIPMS: m/z 424[M+H], 426[M+H+2].

iv) 3-{1-[(3-Mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-1,2,3,4-tetrazol-2-yl}-6,8-dimethoxy-2H-chromene (2d):

White solid, mp 237 °C. yield 79%.

IR (KBr): 3210cm^{-1} (S-H).

^{1}H NMR (DMSO-d_6, 400 MHz) : δ 7.54-7.51 (m, H-3"', H-4"', H-5"'), 7.42 (s, H-4), 7.25-7.22 (m, H-2"', H-6"'), 6.90-6.88 (m, H-7, H-5), 5.90 (s, N-CH_2), 5.13 (s, OCH_2), 3.89 (s, 6,8-OCH_3).

^{13}C NMR (DMSO-d_6, 50.3 MHz) : δ 161.3 (C-3"), 153.9 (C-5'), 153.2 (C-6), 148.9 (C-5"), 147.3 (C-8a), 131.7 (C-l"'), 130.2 (C-4"'), 129.7 (C-3"', C-5"'), 126.8 (C-2"', C-6"'), 126.4 (C-4), 121.8 (C-3), 119.6(C-4a), 116.1 (C-7), 115.9 (C-5), 112.7 (C-8), 64.1 (C-2), 55.4 (6,8-OCH_3), 47.1 (N-CH_2).

DIPMS: m/z 420 [M+H].

v) 3-{1-[(3-mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-1,2,3,4-tetrazol-2-yl}-8-methyl-2H-chromene (2e):

Light yellow solid, mp 228 °C, yield 83%.

IR (KBr): 3160 cm^{-1} (S-H).

^{1}H NMR (DMSO-d_6, 400 MHz) : δ 7.46-7.42 (m, H-3"', H-4"', H-5"'), 7.41 (s, H-4), 7.24-7.21 (m, H-2"', H-6"'), 7.01-6.85 (m, H-7, H-6, H-5), 6.01 (s, N-CH_2), 5.17 (s, OCH_2), 4.17 (br, S-H), 2.35 (s, 8-CH_3).

^{13}C NMR (DMSO-d_6, 50.3MHz) : δ 168.8 (C-3"), 161.4 (C-5'), 147.4 (C-8), 145.2 (C-8a), 142.5 (C-5"), 132.4 (C-l"'), 129.6 (C-4"'), 129.2 (C-3"', C-5"'), 127.7 (C-2"', C-6"'), 125.0 (C-4), 121.7 (C-3), 121.4 (C-4a), 119.9 (C-6), 118.7 (C-7), 114.0 (C-5), 64.1 (C-2), 55.6 (8-CH_3), 47.4 (N-CH_2).

DIPMS: m/z 420[M+H].

II. Synthesis of 3-(1-{[3-(methylsulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-5-yl)-2H-chromenes(4a-e)

i) 3-(1-{[3-(Methylsulfanyl)-4-phenyl-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-2H-chromene (4a):

A mixture of 3-{1-[(3-mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-2*H*-1,2,3,4-tetrazol-2-yl}-2H-chromene **(2a)** (0.3g, 0.8mmol) in DMF 20 ml, dimethylsulphate **(3)** (0.15ml, 1.5mmol) and anhyd K_2CO_3 (0.2g, l.5mmol) was stirred at room temperature for 6 hours. The reaction mixture was poured in to ice cold water. The precipitate obtained was collected by filtration, washed with water, dried; the crude product was purified by column chromatography eluted with pet.ether:ethyl acetate (9:2) to yield **4a** (0.2gm, 64 %), mp: 162°C.

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.52-7.48 (m, H-3"', H-4"', H-5"'), 7.42 (s, H-4), 7.18-7.12 (m, H-7, H-5, H-2"', H-6"'), 6.92 (m, H-6), 6.85 (d, J=8.0Hz, H-8), 5.86 (s, N-CH_2), 5.12 (s, OCH_2), 2.70 (s, S-CH_3).

^{13}C NMR (DMSO-d_6, 100.6MHz): δ 162.6 (C-3"), 154.8 (C-5'), 154.4 (C-8a), 148.3 (C-5"), 132.3 (C-1"'), 130.6 (C-7), 130.1 (C-4"'), 127.9 (C-3"', C-5"'), 127.0 (C-3), 126.9 (C-4), 125.8 (C-5), 121.7 (C-2"', C-6"'), 121.4 (C-4a), 119.0 (C-6), 115.9 (C-8), 64.9 (C-2), 47.0 (N-CH_2), 14.5 (S-CH_3).

DIPMS: m/z 404[M+H].

Employing the similar procedure as mentioned for **4a**, compounds **4b-e** were obtained **2b-e** from as solids.

ii) 3-(1-{[3-(Methylsulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-6,8-dimethyl-2H-chromene (4b):

white solid, mp 212 °C, yield 66%.

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.36 (m, 3"', 4"', 5"', H-4), 7.15-7.10 (m, 2"', 6"' - H), 7.0 (m, H-7, H-5), 5.86 (s, N-CH_2), 5.0 (s, OCH_2), 2.21 (s,6,8-CH_3), 2.58 (S-CH_3).

^{13}C NMR (DMSO-d_6, 100.6MHz): δ 170.2 (C-3"), 161.9 (C-5'), 152.1 (C-8a), 144.3 (C-5"), 136.1 (C-1"'), 131.3 (C-6), 131.1 (C-7), 129.0 (C-4), 128.7 (C-4"'), 128.4 (C-3"', C-5"'), 125.2 (C-3), 125.1 (C-4a), 121.5 (C-2"', C-6"'), 119.1 (C-5), 115.7 (C-8), 64.9 (C-2), 48.8 (N-CH_2), 20.4 (2x-CH_3).

DIPMS: m/z 418 [M+H].

***iii)3-(1-{[3-(Methylsulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-6,8-dichloro-2H-chromene* (4c) :**

Light yellow solid, mp 189 °C, yield 72%.

^{1}H NMR (DMSO-d_6, 200 MHz) : δ 7.56-7.48 (m, H-3"', H-4"', H-5"'), 7.46-7.41 (m, H-4, H-2"', H-6"'), 7.38 -7.21 (m, H-7, H-5), 6.1 (s, N-CH_2), 5.09 (s,OCH_2), 2.58(S-CH_3).

^{13}C NMR (DMSO-d_6, 100.6MHz): δ 166.1 (C-3"), 160.2 (C-5'), 152.2 (C-8a), 151.9 (C-5"), 147.2 (c-1"'), 131.6 (C-7), 130.2 (C-4"'), 130.0 (C-4), 127.4 (C-3), 126.8 (C-3"', C-5"'), 127.2 (C-5), 125.6 (C-2"', C-6"'), 122.9 (C-4a), 120.6 (C-6), 117.0 (C-8), 64.6 (C-2), 47.7(N-CH_2), 15.6(S-CH_3).

DIPMS: m/z 438 [M+H], 440[M+H+2].

***iv)3-(1-{[3-(Methylsulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-6,8-dimethoxy-2H-chromene* (4d):**

White solid, mp 205 °C, yield 74%.

^{1}H NMR ($CDCl_3$+DMSO-d_6, 400 MHz) : δ7.52-7.50 (m, H-3"', H-4"', H-5"'), 7.40 (s, H-4), 7.25-7.22 (m, H-2"', H-6"'), 6.91-6.88 (m, H-7, H-5), 5.92 (s, N-CH_2), 5.13 (s, OCH_2), 3.87 (s, 2x-OCH_3), 2.67 (S-CH_3).

^{13}C NMR (DMSO-d_6, 50.3MHz): δ 161.3 (C-3"), 153.9 (C-5'), 153.2 (C-6), 148.9 (C-5"), 147.3 (C-8a), 131.7 (C-1"'), 130.2 (C-4"'), 129.7 (C-3"', C-5"'), 126.8 (C-2"', C-6"'), 126.4 (C-4), 121.8 (C-3), 119.6 (C-4a), 116.1 (C-7), 115.9 (C-5), 112.7 (C-8), 64.1 (C-2), 55.4 (2x-OCH_3), 47.1 (N-CH_2), 14.2(S-CH_3).

DIPMS:m/z434[M+H].

***v)3-(1-{[3-(Methylsulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-8-methyl-2H-chromene* (4e):**

White solid, mp 175°C, yield 70%.

^{1}H NMR (DMSO-d_6, 300 MHz) : δ 7.59-7.51 (m, H-3"', H-4"', H-5"'), 7.40 (s, H-4), 7.38-7.30 (m, H-2"', H-6"'), 6.96-6.85 (m, H-7, H-6, H-5), 6.03 (s, N-CH_2), 5.08 (s, OCH_2), 2.55 (s, 8-CH_3).

^{13}C NMR (DMSO-d_6, 100.6MHz) : δ 163.0 (C-3"), 155.5 (C-5'), 149.3 (C-8), 148.8 (C-8a), 142.3 (C-5"), 132.0 (C-l"'), 130.0 (C-4"'), 129.7 (C-3"', C-5"'), 126.7 (C-2"', C-6"'), 125.3 (C-4), 122.0 (C-3), 121.3 (C-4a), 120.1 (C-6), 118.8(C-7), 144.4 (C-5), 64.6 (C-2), 56.1 (8-CH_3), 46.8 (N-CH_2), 14.2 (S-CH_3).

DIPMS: m/z 434[M+H].

III. Synthesis of 3-(1-{[3-(allyl-sulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-5-yl)-2H-chromenes (6a-e)

***i) 3-(1-{[3-(Allyl-sulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-2H-chromene* (6a):**

A mixture of 3-{l-[(3-mercapto-4-phenyl-1,2,4-triazol-yl)methyl]-1,2,3,4-tetrazol-yl}-2H-chromene **(2a)** (0.3g, 0.8mmol) in DMF 20 ml, allylbromide **(5)** (0.07ml, 1.2mmol) and anhydrous potassium carbonate (0.2g, 1.5mmol) were added. The reaction mixture was stirred at room temperature for 6 hours. After completion of the reaction, the reaction mixture was poured in to ice cold water, the precipitate obtained was collected by filtration, washed with water, dried, the crude product purified by column chromatography eluted with pet.ether:ethyl acetate (9:2) to give **6a** (0.3gm, 90%), mp: 142°C.

^{1}H NMR (DMSO-d_6) 400 MHz) : δ 7.54-7.52 (m, H-3"', 4"', 5"'), 7.46 (s, H-4), 7.28-7.16 (m, H-2"', 6"', H-5,H-7), 6.96 (m, H-6), 6.88 (d, J=7.6Hz, H-8), 5.98-5.93 (m, CH=CH_2), 5.87 (s, N-CH_2), 5.30 (d, J= 16.8Hz, CH_2=CH), 5.18-5.15 (m,OCH_2, CH_2=CH), 3.90 (br, S-CH_2).

^{13}C NMR (DMSO-d_6, 100.6MHz) : δ 162.5 (C-3"), 154.4 (C-5'), 153.4 (C-8a), 148.3 (C-5"), 132.4 (C-1"'), 132.2 (C-7), 130.5 (C-4"'), 129.9 (CH=CH_2), 127.8 (C-3), 127.0 (C-3"', C-5"'), 125.8 (C-4), 125.7 (C-5), 121.7 (C-2"', C-6"'),121.4(C-4a), 118.9 (C-6, CH=CH_2), 115.8 (C-8), 64.8 (C-2), 47.0 (N-CH_2), 35.3 (S-CH_2-).

DIPMS: m/z 430 [M+H].

Employing the similar procedure as mentioned for **6a**, compounds **6b-e** were obtained from **2b-e** as solids.

***ii) 3-(l-{[3-(Allyl-sulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-6,8-dimethyl-2H-chromene* (6b):**

White solid, mp 89 °C, yield 82%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.46 (m, H-3"', H-4"', H-5"'), 7.40 (s, H-4), 7.18-7.07- (m, H-7, H-5, H-2"', H-6"'), 5.92-5.85 (m, CH=CH_2,

N-CH_2), 5.24-5.20 (d, J=16.0Hz, CH_2=CH), 5.10-5.07 (d, J=9.6Hz, CH_2=CH), 5.02 (s, O-CH_2), 3.80 (d, J=6.8Hz, S-CH_2), 2.25 (s,2x-CH_3).

^{13}C NMR ($CDCl_3$, 100.6 MHz) : δ 162.9 (C-3"), 153.3 (C-5'), 149.4 (C-8a), 148.4 (C-5"), 134.1 (C-1"), 132.3 (C-6), 130.5 (C-7), 129.9 (C-4), 128.5 (CH=CH_2), 128.2 (C-4"'), 127.4 (C-3"', C-5"'), 127.0 (C-3), 126.2 (C-4a), 125.8 (C-2"', C-6"'), 121.2 (C-5), 118.9 (CH=CH_2), 116.5 (C-8), 64.8 (C-2), 47.0 (N-CH_2), 35.4 (S-CH_2), 20.3 (6,-CH_3), 15.5 (8-CH_3).

DIPMS: m/z 444 [M+H].

iii) 3-(1-{[3-(Allyl-sulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-6,8-dichloro-2H-chromene (6c):

White solid, mp 118 °C, yield 85%.

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.56-7.45 (m, H-3"', H-4"', H-5"'), 7.43 (s, H-4), 7.20-7.07-7.07 (m, H-7, H-5, H-2"', H-6"'), 5.96-5.88 (m, CH=CH_2), 5.85 (s, N-CH_2), 5.27 (dd, J=17.2Hz, J=1.2Hz, CH_2=CH), 5.15 (d, J=l0.2Hz, CH_2=CH), 5.12 (s, OCH_2), 3.87 (d, J=6.8Hz, S-CH_2-).

^{13}C NMR (DMSO-d_6, 100.6MHz) : δ 167.2 (C-3"), 161.4 (C-5'), 153.4 (C-8a), 152.9 (C-5"), 148.1 (C-1"'), 132.4 (C-7), 130.4 (C-4"'), 130.0 (C-4), 129.9 (CH=CH_2), 127.2 (C-3), 127.0 (C-3"', C-5"'), 126.6 (C-5), 124.5 (C-2"', C-6"'), 122.7 (C-4a), 120.3 (C-6), 118.7 (CH=CH_2), 117.1 (C-8), 65.0 (C-2), 47.2 (N-CH_2), 35.6 (S-CH_2).

DIPMS: m/z 464[M+H], 466[M+H+2].

***iv)3-(1-{[3-(Allyl-sulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methyl}-2H-1,2,3,4-tetrazol-2-yl)-6,8-dimethoxy-2H-chromene* (6d):**

White solid, mp 149 °C, yield 77%.

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.51-7.49 (m, 3"', 4"', 5"' – H), 7.42 (s, H-4), 7.16-7.14 (m, 2"',6"'-H), 6.89-6.87 (m, H-7, H-5), 5.95-5.89 (m, CH=CH_2), 5.86 (s, N-CH_2), 5.27 (d, J=16.4Hz, CH_2=CH), 5.17 (s, OCH_2), 5.13 (d, J=10.0Hz, CH_2=CH), 3.89-3.85 (br, 6,8-OCH_3, S-CH_2).

^{13}C NMR (DMSO, 100.6MHz) : δ 162.5 (C-3"), 153.4 (C-5', C-6), 148.2 (C-5"), 148.0 (C-8a), 132.3 (C-1"'), 130.5 (C-4''), 129.9 (CH=CH_2), 127.0 (C-3"', 5"'), 125.7 (C-2"', C-6"'), 122.3 (C-4), 121.4 (C-3), 120.3 (CH=CH_2), 119.0 (C-4a), 118.9 (C-7), 114.3 (C-8, C-5), 65.0 (C-2), 56.4 (6-OCH_3), 55.4 (8-OCH_3), 47.0 (N-CH_2), 35.3 (S-CH_2).

DIPMS: m/z 460[M+H].

v)3-(1-{[3-(Allyl-sulfanyl)-4-phenyl-4H-1,2,4-triazol-5-yl]methy}-2H-1,2,3,4-tetrazol-2-yl)-8-methyl-2H-chromene (6e):

Light yellow solid, mp 128 °C, yield 78%.

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.56-7.50 (m, H-3"', H-4"', H-5"'), 7.41 (s, H-4), 7.34 -7.30 (m, H-2"', H-6"'), 6.94-6.83 (m, H-7, H-6, H-5), 5.96-5.90 (CH=CH_2), 5.87 (s, N-CH_2), 5.25 (d, J=16.4Hz,CH_2=CH), 5.13 (d, J=10.0Hz,CH_2=CH), 5.08 (s, OCH_2), 3.84 (br, 8-CH_3, S-CH_2).

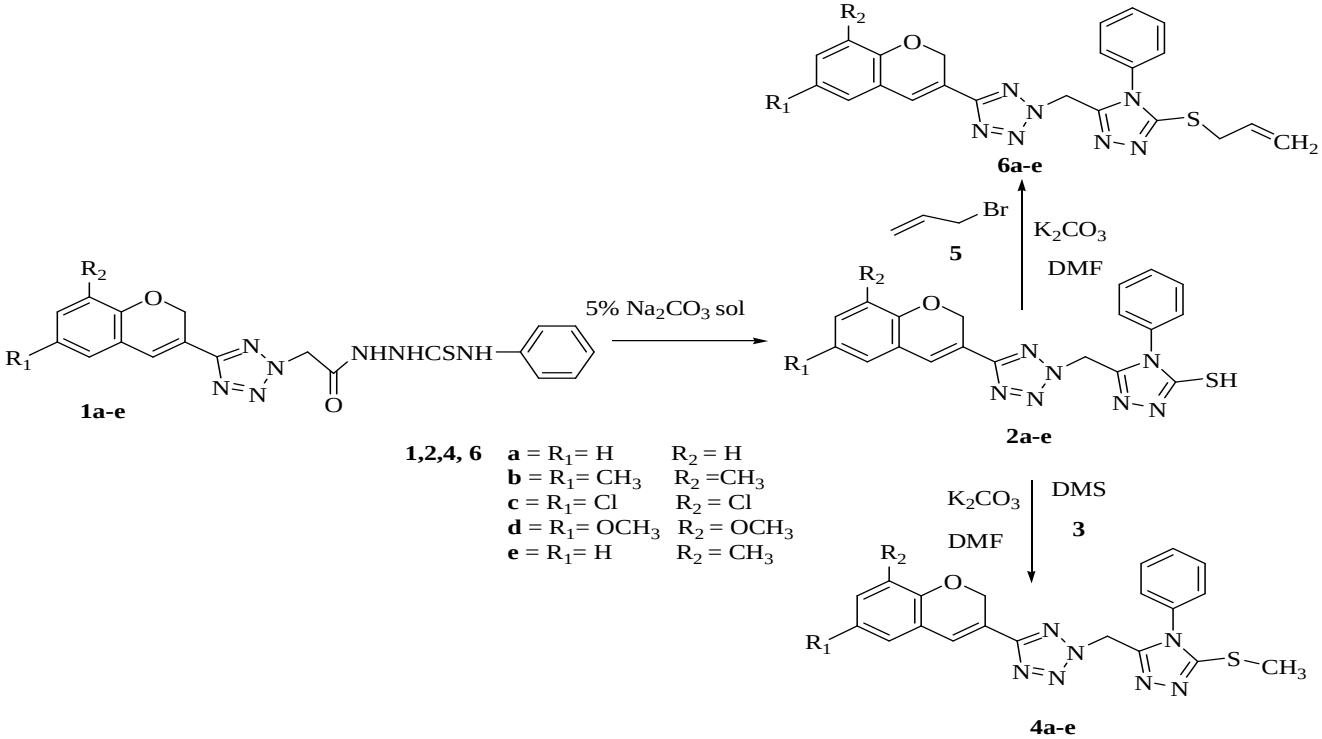
^{13}C NMR (DMSO, 100.6MHz) : δ 162.0 (C-3"), 152.3 (C-5'), 149.5 (C-8), 148.1 (C-8a), 143.3 (C-5"), 133.3 (C-1"'), 132.4 (C-4"'), 130.7 (CH=CH_2), 130.2 (C-3"', C-5"'), 127.5 (C-2"', C-6"'), 125.4 (C-4), 122.4 (C-3), 122.0 (C-4a), 120.6 (C-6), 119.4 (C-7), 119.0 (CH=CH_2)t 115.3 (C-5), 64.6 (C-2), 15.6 (8-CH_3), 47.6 (N-CH_2), 35.4 (S-CH_2).

DIPMS: m/z 460 [M+H].

RESULTS AND DISCUSSION

Synthesis of of 3-(1-{[3-(allylsulfanyl)-4-phenyl-1,2,4-triazol-5-yl]]methyl}-1,2,3,4-tetrazol-2-yl)-2H-chromenes (6a-e)

3-{1-[(3-Mercapto-4-phenyl-1,2,4-triazol-5-yl)methyl]-1,2,3,4-tetrazol-2-yl}-2H-chromenes **(2a-e)** on alkylation with allyl bromide **(5)** in presence of K_2CO_3 in DMF gave 3-(1 -{ [3-(allylsulfanyl)-4-phenyl-1,2,4-triazol-5-yl]methyl}-1,2,3,4-tetrazol-2-yl)-2H-chromenes **(6a-e).** In the ^{1}H NMR (DMSO-d_6, 400MHz) of **6a,** the allyl protons S-CH_2 appeared as broad singlet at δ 3.90, CH=CH_2 at δ 5.98-5.93 (m), 5.30 (d, J=16.8Hz, CH_2=CH),), 5.18-5.15 (m, CH_2=CH), the other protons appeared as follows δ 5.87 (s, N-CH_2), the phenyl protons H-3"', H-4"', H-5"' at δ 7.54-7.52 (m), H-2"', H-6"' and H-7, H-5 at δ 7.28-7.16(m), 7.46 (s, H-4), H-6 at δ 6.96 (m), H-8 at δ 6.88 (d, J=7.6.Hz). In ^{13}C NMR (DMSO-d_6,100.6MHz) of **6a** the allyl moiety S-CH_2- appeared at δ 35.3, 129.9(CH=CH_2), 118.9 (C-6,CH=CH_2), N-CH_2 at δ 47.0, the 1,2,4-triazole carbons C-3", C-5" at δ 162.5, 148.3 respectively, tetrazole carbon C-5' at δ 154.4, and the phenyl carbons at δ 132.4 (C-l"'), δ 130.5 (C-4"'), δ 127.8 (C-3"', C-5"'), δ 121.7 (C-2"', C-6"'), the chromene carbons at δ 64.8 (OCH_2), 153.4 (C-8a), 132.2 (C-7), 127.0 (C-3), 125.8 (C-4), 125.7 (C-5), 121.4 (C-4a) and 115.8(C-8).



Scheme 1

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