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Synthesis of ethyl 2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*H*/2*H*-chromene-3-carboxylates by cycloaddition of ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylates with alkynes

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The cycloaddition reaction of ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylates with phenylacetylene/ 4-fluorophenylacetylene have provided a mixture of 2*H*- and 4*H*-triazolylchromene-3-carboxylates. 4-Methoxyphenylacetylene, 3-methylphenylacetylene and acetylenedicarboxylates have provided exclusively 2*H*-triazolylchromene-3-carboxylates. Interestingly, prop-2-yn-1-ol and ethyl propiolate have provided exclusively 4*H*-triazolylchromene-3-carboxylates.

Keywords: 2*H*-/4*H*-Chromene-1,2,3-triazoles, 4*H*-chromene-3-carboxylates, click reaction, 2*H*-chromenes

Chromene is an important scaffold have been used for the synthesis of natural products and heterocyclic compounds[1-6]. 4*H*-Chromenes were displayed variety of biological properties[7-9] and chromenotriazolopyrimidines were reported as MDM2-p53 protein-protein inhibitors[10]. Due to the importance of 4*H*-chromenes, few useful heterocyclic compounds were reported. Dihydro-8*H*-indeno[1,2-*d*]oxazoles and 2-aryl 2*H*-chromenes were reported by the chemical modification of 4*H*-chromenes[11]. Pyrolysis of 4*H*-chromene was provided mixture of compounds such as benzofuran, 1-indanone and styrene[12]. Lithiation (Li, DTBB) of 4*H*-chromene followed by hydrolysis provided the useful chemicals such as 3-phenylpropanal and 2-allyl phenol[13].

In the course of our research programme on synthesis and biological activities of heterocyclic compounds, we reported 2*H*-chromene-3-carboxylates by the reaction of salicylaldehydes with ethyl 4-chloro-3-oxobutanoate[14]. The 2*H*-chromene-3-carboxylates were successfully converted to ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylates with $(C_2H_5)_3$-SiH in presence of $BF_3.O(C_2H_5)_2$[15]. The chemical modifications of ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylates were provided chromenopyrrolones and triazolyl-chromenopyrrolones[15]. The ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylate is a useful intermediate with important functional groups such as chloromethyl at C-2 position and carboxylic ester at C-3 position. To the best of our knowledge, the conversion of ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylate to ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylate and click reaction of ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylate with alkynes are not reported in the literature. Herein, we report the preparation of 4*H*/2*H*-triazolylchromene-3-carboxylates by the reaction of ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylates with various alkynes such as phenylacetylenes, prop-2-yn-1-ol, ethyl propiolate and acetylenedicarboxylates. The obtained results were depicted below.

Results and Discussion

Scheme I describes the preparation of ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylates **5a-b**. 2*H*-Chromene-3-carboxylates **3a-b** were prepared by reacting salicylaldehydes **1a-b** with ethyl 4-chloro-3-oxobutanoate **2** in presence of piperidine[14] and treatment of **3a-b** with $(C_2H_5)_3$-SiH in presence of $BF_3.O(C_2H_5)_2$ provided ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylates **4a-b**[15]. The chloromethyl compounds **4a-b** were treated with NaN_3 in presence of NaI provided the corresponding azides **5a-b**. The compounds **3a-b**, **4a-b** are known and compared with the reported data[15]. The compounds **5a-b** are new and characterized by spectral data (see Supporting Information).

Thus obtained azide compounds **5a-b** were subjected for cycloaddition[16-18] with alkynes to

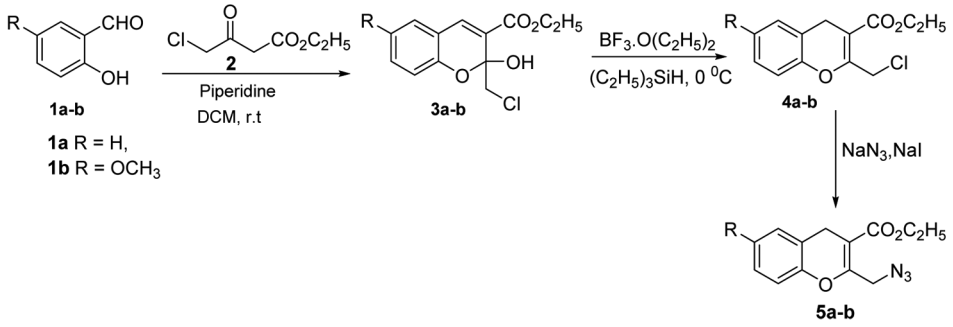
prepare triazoles as depicted in Scheme II. In an initial reaction, compound **5a** (1.0 equiv) was reacted with phenylacetylene **6a** (1.0 equiv) in the presence of copper sulphate and sodium L-ascorbate in aqueous *tert*-butanol at RT. The reaction was provided two compounds after column chromatography (colorless solid, 45% and pale yellow color solid, 46% yield). Based on spectral data, the compounds were identified as ethyl 2-((4-phenyl-1*H*-1,2,3-triazol-1-*yl*)methyl)-4*H*-chromene-3-carboxylate **7a** and ethyl 2-hydroxy-2-((4-phenyl-1*H*-1,2,3-triazol-1-*yl*)methyl)-2*H*-chromene-3-carboxylate **8a**. Under similar conditions, when **5a** was reacted with 4-fluorophenylacetylene **6b** provided two compounds, 4*H*/2*H*-triazolylchromene-3-carboxylates **7b** and **8b**. Interestingly, 4-methoxyphenylacetylene **6c** and 3-methylphenyl-acetylene **6d** were provided exclusively 2*H*-triazolylchromene-3-carboxylates **8c-d**. The 4*H*-triazolylchromene-3-carboxylates **7e-f** were exclusively formed when azide **5a** was reacted with prop-2-yn-1-ol **6e** and ethyl propiolate **6f**.

It is interesting to note that, the phenylacetylene **6a** and 4-fluorophenylacetylene **6b** were provided mixture of compounds such as 4*H*-triazolylchromene-3-carboxylates **7a-b** and 2*H*-triazolylchromene-3-carboxylates **8a-b**. The electron donating groups present on phenylacetylene **6c-d** were provided exclusively 2*H*-triazolylchromene-3-carboxylates **8c-d**. 4*H*-Triazolylchromene-3-carboxylates **7e-f** were exclusively formed when **5a** was reacted with prop-2-yn-1-ol **6e** and ethyl propiolate **6f** (Scheme II). Under similar reaction conditions, compound 4*H*-triazolylchromene-3-carboxylate **7g** was formed exclusively when ethyl 2-(azidomethyl)-7-methoxy-4*H*-chromene-3-carboxylate **5b** reacted with phenylacetylene **6a**.

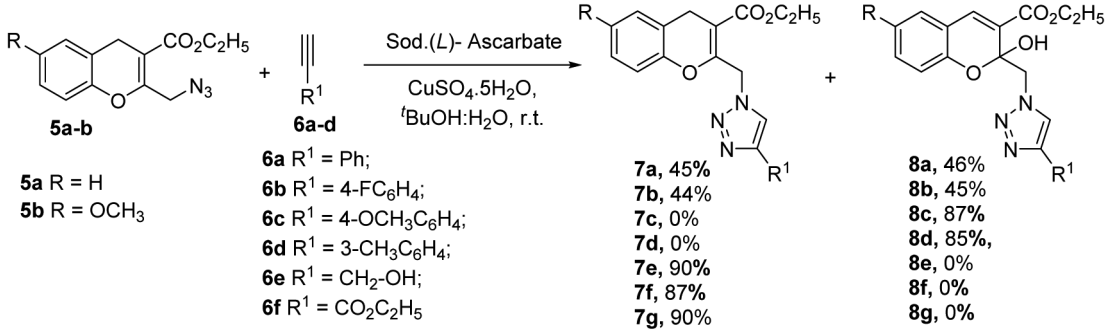
Next, compound **5a** was reacted with activated alkynes such as acetylenedicarboxylates **6g-h** under established reaction conditions (Scheme III). This reaction was exclusively provided 2*H*-triazolylchromene-3-carboxylic acids **8h-i**. Similarly, when ethyl 2-(azidomethyl)-7-methoxy-4*H*-chromene-3-carboxylate **5b** was reacted with **6h** provided two compounds such as 4*H*-triazolylchromene-3-carboxylate **7j** and 2*H*-triazolylchromene-3-carboxylic acid **8j** (Scheme III). The newly prepared compounds **7a-b**, **7e-g**, **7j**, **8a-d** and **8h-j** are characterized by spectral data and documented in supporting information.

Experimental Section

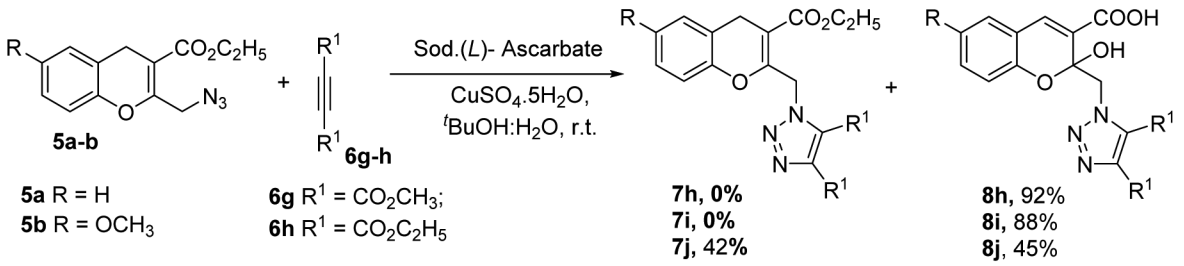
Salicylaldehydes, ethyl 4-chloro-3-oxobutanoate, triethylsilane and $BF_3.O(C_2H_5)_2$ were procured from



Scheme I



Scheme II



Scheme III

Sigma-Aldrich. Sodium azide, Sodium iodide, copper sulphate, Sodium L-ascarbate, piperidine and solvents were obtained from local suppliers. Chromenyl azides and triazoles were prepared in the laboratory as per standard procedures. Reactions were monitored by thin layer chromatography (TLC) on pre-coated silica gel 60 F_{254} (mesh); spots were visualized under UV light. Column chromatographic separations were carried out on silica gel (60-120 mesh). Melting points were determined on a Mettler-Temp apparatus and are uncorrected. IR spectra were recorded with a Thermo Nicolet Nexus 670 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Gemini 200 MHz, Bruker Avance 300 MHz spectrometers. Chemical shifts (δ) are quoted in parts per million and are referenced to tetramethylsilane (TMS) as internal standard. EI-MS were obtained on 7070H spectrometer operating at 70 eV using a direct inlet system; HRMS were carried out on Agilent 6510 Q-TOF LC/MS instrument.

Procedure for the preparation of 2*H*-chromenes, 3a-b

Ethyl 4-chloro-3-oxobutanoate (1.0 mmol) was added slowly to a stirred solution of salicylaldehyde (1.0 mmol) and piperidine (30 mol%) in CH_2Cl_2 (4 mL) at RT over a period of 15 min. The contents were stirred for another 8 h at the same temperature. After completion of the reaction (TLC), the crude product was subjected to column chromatographic purification over silica gel (60-120) with hexane/ethyl acetate (95:5) as eluent to give ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate **3a**. Yield: 60%. Colorless solid. m.p. 113-115°C (lit. 112-114°C)[14]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (t, 3H, CH_3), 4.04 (d, 1H, *J* = 11.8 Hz, CHCl), 4.28 (d, 1H, *J* = 11.8 Hz, CHCl), 4.32 (q, 2H, OCH_2), 6.94-7.02 (m, 2H, aromatic), 7.20-7.28 (m, 2H, aromatic), 7.68 (s, 1H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.37, 49.39, 61.70, 98.26, 116.80, 118.22, 121.93, 122.37, 129.19, 133.12, 136.89, 152.52, 165.32; IR (KBr): 3410, 3049, 2980, 1690, 1630, 1570, 1374, 1341, 1297, 1218, 1056, 1017 cm^{-1}; ESI-MS: *m/z* 251[M-OH]$^+$, 291[M+Na]$^+$; HRMS-ESI: *m/z* Calcd for $C_{13}H_{14}ClO_4$ [M+H]$^+$: 269.0502. Found: 269.0507.

Ethyl 2-(chloromethyl)-2-hydroxy-6-methoxy-2*H*-chromene-3-carboxylate, 3b: Yield: 42%. Yellow color liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (t, 3H, CH_3), 3.70 (s, 3H, OCH_3), 3.98 (d, 1H, *J* = 11.14 Hz, CHCl), 4.18 (d, 1H, *J* = 11.14 Hz, CHCl), 4.28 (q, 2H, OCH_2), 6.68 (d, 1H, *J* = 6.68 Hz, aromatic), 6.82-6.88 (m, 2H, aromatic), 7.56 (s, 1H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.02, 49.04, 55.62, 61.56, 98.03, 112.46, 117.82, 118.20, 119.12, 122.46, 136.82, 146.26, 154.58, 165.20; IR (KBr): 3433, 2922, 2852, 1707, 1633, 1495, 1219, 1041 cm^{-1}; ESI-MS: *m/z* 281 [M-OH]$^+$, 321 [M+Na]$^+$.

Procedure for the preparation of ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylates, 4a-b

$BF_3.O(C_2H_5)_2$ (0.25 mL, 2.2 mmol) was added drop wise to a stirred solution of ethyl 2-(chloromethyl)-2-hydroxy-2*H*-chromene-3-carboxylate **3a** (268 mg, 1.0 mmol) in dry DCM at -78°C under nitrogen atmosphere. The contents were stirred for 30 min at the same temperature and triethylsilane (0.24 mL, 1.5 mmol) was added drop wise over a period of 15 min. After completion of the reaction (TLC), the reaction was quenched with water and diluted with $CHCl_3$. The organic layer was separated, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography (hexane/ethyl acetate 98:2) afforded ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylate **4a** (202 mg, 80% yield) as pale yellow solid. m.p. 48-50°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (t, 3H, *J* = 7.2 Hz, CH_3), 3.66 (s, 2H, CH_2), 4.27 (q, 2H, *J* = 7.2 Hz, OCH_2), 4.72 (s, 2H, CH_2), 6.97 (dd, 1H, *J* = 1.1, 8.2 Hz, aromatic), 7.05 (dd, 1H, *J* = 1.2, 7.2 Hz, aromatic), 7.09 (dd, 1H, *J* = 1.5, 7.5 Hz, aromatic),

7.14-7.18 (m, 1H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.18, 25.10, 40.15, 60.88, 104.60, 116.19, 119.52, 124.56, 127.81, 128.67, 149.92, 156.97, 166.03; IR (KBr): 2983, 2930, 1709, 1656, 1608, 1489, 1457, 1289, 1220, 1185, 1055 cm^{-1}; ESI-MS: *m/z* 253 $[M+H]^+$.

Ethyl 2-(chloromethyl)-6-methoxy-4*H*-chromene-3-carboxylate, 4b: Yield: 82%. Yellow color solid. m.p. 46-48°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (t, 3H, *J* = 7.2 Hz, CH_3), 3.64 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 4.26 (q, 2H, *J* = 7.2 Hz, OCH_2), 4.71 (s, 2H, CH_2), 6.60 (d, 1H, *J* = 2.6 Hz, aromatic), 6.70 (dd, 1H, *J* = 2.4, 8.2 Hz, aromatic), 6.91 (d, 1H, *J* = 8.2 Hz, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.01, 25.35, 40.15, 55.84, 60.74, 103.34, 112.76, 113.33, 116.94, 120.20, 143.73, 156.16, 157.06, 166.05; IR (KBr): 2981, 2838, 1708, 1496, 1465, 1281, 1215, 1153, 1034 cm^{-1}; ESI-MS: *m/z* 283 $[M+H]^+$.

Procedure for the preparation of ethyl 2-(azido methyl)-4*H*-chromene-3-carboxylates, 5a-b

NaN_3 (1.2 mmol) and NaI (0.12 mmol) were added to the stirred solution of ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylate (**4a**, 1.0 mmol) in acetone (4 mL) at RT. These contents were stirred under reflux condition for 5 h. After completion of the reaction (TLC), solvent was removed under reduced pressure, and the reaction mixture was quenched with water, and then the crude product was extracted with diethyl ether (3×10 mL), layers were separated, the organic layer was dried over Na_2SO_4. Solvent was removed under reduced pressure; the crude product was purified by column chromatography by using silica gel (hexane) gave ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylate **5a**. Yield: 92%. Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (t, 3H, *J* = 7.17 Hz, CH_3), 3.67 (s, 2H, CH_2), 4.25 (q, 2H, *J* = 7.17 Hz, OCH_2), 4.45 (s, 2H, NCH_2), 6.96 (d, 1H, *J* = 8.09 Hz, aromatic), 7.03-7.11 (m, 2H, aromatic), 7.16 (t, 1H, *J* = 7.78 Hz, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.18, 24.86, 49.49, 60.86, 104.57, 116.24, 119.60, 124.61, 127.80, 128.73, 149.67, 156.46, 166.27; IR (KBr): 2982, 2924, 2103, 1710, 1653, 1490, 1292, 1223, 1189, 1057, 973, 759, 597 cm^{-1}; ESI-MS: *m/z* 258 $[M-H]^+$; HRMS (ESI): *m/z* Calcd for $C_{13}H_{12}O_3N_3$ $[M-H]^+$: 258.0873. Found: 258.0881.

Ethyl 2-(azidomethyl)-6-methoxy-4*H*-chromene-3-carboxylate 5b: Yield: 90%. Brownish liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (t, 3H, *J* = 7.17 Hz, CH_3), 3.66 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 4.25 (q, 2H, *J* = 7.17 Hz, OCH_2), 4.45 (s, 2H, NCH_2), 6.62 (d, 1H, *J* = 2.90 Hz, aromatic), 6.71 (dd, 1H, *J* =8.85, 2.90 Hz, aromatic), 6.91 (d, 1H, *J* = 8.85 Hz, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.23, 25.33, 49.62, 55.58, 60.83, 103.51, 112.96, 113.46, 117.14, 120.47, 143.73, 156.34, 156.70, 166.44; IR (KBr): 2926, 2854, 2103, 1709, 1646, 1495, 1371, 1285, 1208, 110, 1034, 901, 767 cm^{-1}; ESI-MS: *m/z* 312 $[M+Na]^+$.

Procedure for the preparation of 2*H* and 4*H*-chromenyltriazoles 7a-g and 8a-g

Sodium L-Ascarbate (0.05 mmol), $CuSO_4.5H_2O$ (0.1 mmol) were added to the stirred solution of ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylate (**5a**, 1.0 mmol), 1-ethynyl-benzene (**6a**, 1.0 mmol) in 1:1 ^{t}BuOH, H_2O (3 mL) at RT. After completion of the reaction (12h, TLC), the solvent was removed under reduced pressure and the reaction mixture was diluted with diethyl ether (3×10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography by using silica gel (hexane/ethyl acetate 95:5) gave ethyl 2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*H*-chromene-3-carboxylate **7a**. Similarly, compounds **7b-g** and **8a-g** were prepared as per the above procedure.

Ethyl 2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-4*H*-chromene-3-carboxylate, 7a: Yield: 45%. Colorless solid. m.p. 118-120°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (t, 3H, *J* = 7.17 Hz, CH_3), 3.70 (s, 2H, CH_2), 4.32 (q, 2H, *J* = 7.17 Hz, OCH_2), 5.76 (s, 2H, NCH_2), 6.88 (d, 1H, *J* = 8.12 Hz, aromatic), 7.00-7.16 (m, 3H, aromatic), 7.31 (t, 1H, *J* = 7.17 Hz, aromatic), 7.40 (t, 2H, *J* = 7.17 Hz, aromatic), 7.84 (d, 2H, *J* = 7.17 Hz, aromatic), 8.02 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.25, 24.90, 49.53, 61.19, 105.39, 116.39, 119.27, 120.26, 124.86, 125.61, 125.71, 127.95, 128.03, 128.72, 130.57, 147.77, 149.52, 154.60, 166.42; IR (KBr): 3124, 2926, 2851, 1711, 1653, 1488, 1305, 1224, 1191, 1100, 1053, 840, 764 cm^{-1}; ESI-MS: *m/z* 362 $[M+H]^+$, 384 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{21}H_{20}O_3N_3$ $[M+H]^+$: 362.1489. Found: 362.1499.

Ethyl 2-((4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-*yl*)methyl)-4*H*-chromene-3-carboxylate, 7b: Yield: 44%. Light green color solid. m.p. 106-108°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (t, 3H, *J* = 6.88

Hz, CH_3), 3.71 (s, 2H, CH_2), 4.32 (q, 2H, J = 6.88 Hz, OCH_2), 5.76 (s, 2H, NCH_2), 6.89 (d, 1H, J = 7.15 Hz, aromatic), 7.02-7.17 (m, 5H, aromatic), 7.81 (t, 2H, J = 7.15 Hz, aromatic), 7.98 (s, 1H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.27, 24.91, 49.57, 61.23, 105.49, 115.61, 115.82, 116.41, 119.28, 119.99, 124.91, 126.88, 127.49, 127.99, 128.71, 146.96, 149.55, 154.60, 161.37, 163.83, 166.45; IR (KBr): 3089, 2983, 1713, 1654, 1612, 1495, 1368, 1229, 1190, 1102, 1054, 837, 760 cm^{-1}; ESI-MS: *m/z* 380 $[M+H]^+$, 402 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{21}H_{19}O_3N_3F$ $[M+H]^+$: 380.1391. Found: 380.1405.

Ethyl 2-((4-(hydroxymethyl)-1*H*-1,2,3-triazol-1-*yl*)methyl)-4*H*-chromene-3-carboxylate, 7e: Yield: 90%. Light orange color solid. m.p. 148-150°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, 3H, J = 7.09 Hz, CH_3), 3.69 (s, 2H, CH_2), 4.30 (q, 2H, J = 7.09 Hz, OCH_2), 4.79 (s, 2H, OCH_2), 5.72 (s, 2H, NCH_2), 6.88 (d, 1H, J = 8.07 Hz, aromatic), 7.02-7.10 (m, 2H, aromatic), 7.13 (t, 1H, J = 8.07 Hz, aromatic), 7.83 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.25, 24.88, 49.48, 56.63, 61.21, 105.49, 116.39, 119.26, 122.36, 124.02, 124.90, 127.98, 128.71, 149.51, 154.48, 166.36; IR (KBr): 3287, 3054, 2986, 2872, 1705, 1656, 1583, 1493, 1369, 1270, 1188, 947, 704 cm^{-1}; ESI-MS: *m/z* 316 $[M+H]^+$; HRMS (ESI): *m/z* Calcd for $C_{16}H_{18}O_4N_3$ $[M+H]^+$: 316.1292. Found: 316.1302.

Ethyl 1-((3-(ethoxycarbonyl)-4*H*-chromen-2-*yl*)methyl)-1*H*-1,2,3-triazole-4-carboxylate, 7f: Yield: 87%. Pale yellow solid. m.p. 118-120°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (t, 3H, J = 7.01 Hz, CH_3), 1.40 (t, 3H, J = 7.17 Hz, CH_3), 3.70 (s, 2H, CH_2), 4.31 (q, 2H, J = 7.01 Hz, OCH_2), 4.42 (q, 2H, J = 7.17 Hz, OCH_2), 5.78 (s, 2H, NCH_2), 6.86 (d, 1H, J = 8.24 Hz, aromatic), 7.03-7.10 (m, 2H, aromatic), 7.14 (t, 1H, J = 8.24 Hz, aromatic), 8.33 (s, 1H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.20, 14.27, 24.81, 49.73, 61.25, 61.29, 105.89, 116.34, 119.17, 125.00, 128.02, 128.11, 128.71, 140.29, 149.39, 153.84, 160.76, 166.24; IR (KBr): 3111, 2983, 2930, 1720, 1645, 1458, 1375, 1218, 1103, 1050, 887, 760, 667 cm^{-1}; ESI-MS: *m/z* 358 $[M+H]^+$, 380 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{18}H_{20}N_3O_5$ $[M+H]^+$: 358.1385. Found: 358.1397.

Ethyl 6-methoxy-2-((4-phenyl-1*H*-1,2,3-triazol-1-*yl*)methyl)-4*H*-chromene-3-carboxylate, 7g: Yield: 90%. Pale yellow solid. m.p. 124-126°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, 3H, J = 7.09 Hz, CH_3), 3.68 (s, 2H, CH_2), 3.75 (s, 3H, CH_3), 4.31 (q, 2H, J = 7.17 Hz, OCH_2), 5.75 (s, 2H, NCH_2), 6.59 (d, 1H, J = 2.69 Hz, aromatic), 6.66 (dd, 1H, J = 8.80, 2.69 Hz, aromatic), 6.82 (d, 1H, J = 8.80 Hz, aromatic), 7.31 (t, 1H, J = 7.33 Hz, aromatic), 7.41 (t, 2H, J = 7.33 Hz, aromatic), 7.84 (d, 2H, J = 7.21 Hz, aromatic), 8.01 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.10, 24.63, 49.40, 55.68, 61.21, 105.50, 116.18, 119.14, 120.10, 124.58, 125.55, 125.75, 127.87, 128.14, 128.58, 130.75, 147.59, 149.64, 154.48, 166.18; IR (KBr): 2975, 2934, 1704, 1649, 1501, 1431, 1207, 1113, 1071,1036, 808, 761, 696 cm^{-1}; ESI-MS: *m/z* 392 $[M+H]^+$, 414 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{22}H_{22}O_4N_3$ $[M+H]^+$: 392.1605. Found: 392.1622.

Diethyl 1-((3-(ethoxycarbonyl)-6-methoxy-4*H*-chromen-2-yl)methy*l*)-1*H*-1,2,3-triazole-4,5-dicarboxylate, 7j: Yield: 42%. Colorless solid. m.p. 102-104°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (tt, 6H, J = 7.17, 2.74 Hz, CH_3), 1.42 (t, 3H, J = 7.17 Hz, CH_3), 3.64 (s, 2H, CH_2), 3.74 (s, 3H, OCH_3), 4.29 (q, 2H, J = 7.17 Hz, OCH_2), 4.42 (q, 2H, J = 7.17 Hz, OCH_2), 4.45 (q, 2H, J = 7.17 Hz, OCH_2), 6.09 (s, 2H, NCH_2), 6.58 (s, 1H, aromatic), 6.62 (d, 2H, J = 1.68 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.86, 14.15, 14.26, 25.10, 49.59, 55.56, 60.97, 61.81, 62.85, 102.77, 112.90, 113.42, 117.02, 120.20, 131.76, 139.68, 143.26, 153.28, 156.52, 158.52, 160.05, 166.31; IR (KBr): 2986, 1725, 1701, 1647, 1550, 1499, 1321, 1279, 1158, 1067, 864, 766, 648 cm^{-1}; ESI-MS: *m/z* 460 $[M+H]^+$, 482 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{22}H_{26}O_8N_3$ $[M+H]^+$: 460.1714. Found: 460.1734.

Ethyl 2-hydroxy-2-((4-phenyl-1*H*-1,2,3-triazol-1-*yl*)methyl)-2*H*-chromene-3-carboxylate, 8a: Yield: 46%. Pale yellow color solid. m.p. 108-110°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (t, 3H, J = 7.17 Hz, CH_3), 4.33 (q, 2H, J = 7.17 Hz, OCH_2), 5.04 (d, 1H, J = 14.03 Hz, NCH), 5.21 (d, 1H, J = 14.03 Hz, *N*CH), 6.93-7.00 (m, 2H, aromatic), 7.20 (d, 1H, J = 7.78 Hz, aromatic), 7.29-7.34 (m, 2H, aromatic), 7.39 (t, 2H, J = 7.78 Hz, aromatic), 7.64 (s, 1H, aromatic), 7.77 (d, 2H, J = 7.32 Hz, aromatic), 7.86 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.17, 56.59, 61.67, 97.16, 116.55, 118.06, 121.52, 121.56, 122.43, 125.69, 128.08, 128.73, 129.09, 130.37, 132.93, 136.52, 147.47, 151.77, 165.17; IR (KBr): 3411, 2925, 2854, 1706, 1631, 1607, 1460, 1370, 1294, 1215, 1194, 1055, 764 cm^{-1}; ESI-MS: *m/z*

378 $[M+H]^+$, 400 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{21}H_{20}O_4N_3$ $[M+H]^+$: 378.1448. Found: 378.1441.

Ethyl 2-((4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-*yl*)methyl)-2-hydroxy-2*H*-chromene-3-carboxylate 8b: Yield: 45%. Pale yellow solid. m.p. 100-102°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (t, 3H, *J* = 7.17 Hz, CH_3), 4.34 (q, 2H, *J* = 7.17 Hz, OCH_2), 5.03 (d, 1H, *J* = 14.04 Hz, NCH), 5.19 (d, 1H, *J* = 14.04 Hz, *N*CH), 6.95 (d, 1H, *J* = 8.24 Hz, aromatic), 6.99 (t, 1H, *J* = 8.24 Hz, aromatic), 7.09 (t, 2H, *J* = 8.69 Hz, aromatic), 7.22 (d, 1H, *J* = 7.47 Hz, aromatic), 7.33 (t, 1H, *J* = 7.47 Hz, aromatic), 7.64 (s, 1H, *J* = 7.47 Hz, aromatic), 7.72-7.76 (m, 2H, aromatic), 7.83 (s, 1H, aromatic);^{13}C NMR (125 MHz, $CDCl_3$): δ 14.18, 56.63, 61.72, 97.17, 115.64, 115.81, 116.56, 118.08, 121.31, 121.48, 122.52, 126.66, 127.48, 129.14, 133.01, 136.51, 146.67, 151.78, 161.62, 163.59, 165.23; IR (KBr): 3404, 2925, 2855, 1708, 1630, 1609, 1497, 1293, 1217, 1055, 920, 840, 770 cm^{-1}; ESI-MS: *m/z* 396 $[M+H]^+$, 418 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{21}H_{19}N_3O_4F$ $[M+H]^+$: 396.1341. Found: 396.1354.

Ethyl 2-hydroxy-2-((4-*m*-tolyl-1*H*-1,2,3-triazol-1-*yl*)methyl)-2*H*-chromene-3-carboxylate 8c: Yield: 87%. Light green color solid. m.p. 110-112°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (t, 3H, *J* = 6.87 Hz, CH_3), 2.38 (s, 3H, CH_3), 4.33 (q, 2H, *J* = 6.87 Hz, OCH_2), 5.04 (d, 1H, *J* = 14.04 Hz, *N*-CH), 5.19 (d, 1H, *J* = 14.04 Hz, *N*-CH), 6.93-7.01 (m, 2H, aromatic), 7.12 (d, 1H, *J* = 7.02 Hz, aromatic), 7.21 (d, 1H, *J* = 7.02 Hz, aromatic), 7.27-7.36 (m, 2H, aromatic), 7.50 (d, 1H, *J* = 7.02 Hz, aromatic), 7.63 (s, 1H, aromatic), 7.71-7.76 (m, 1H, aromatic), 7.84 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.19, 21.39, 56.66, 61.71, 97.17, 116.60, 118.10, 121.54, 122.50, 122.82, 126.42, 128.64, 128.87, 129.13, 130.32, 130.75, 132.99, 136.46, 138.45, 147.67, 151.79, 165.26; IR (KBr): 3382, 3136, 2960, 1709, 1631, 1456, 1293, 1216, 1186, 1023, 921, 758, 696 cm^{-1}; ESI-MS: *m/z* 392 $[M+H]^+$, 414 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{22}H_{22}N_3O_4$ $[M+H]^+$: 392.1589. Found: 392.1604.

Ethyl 2-hydroxy-2-((4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-*yl*)methyl)-2*H*-chromene-3-carboxylate 8d: Yield: 85%. Colorless solid. m.p. 122-124°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 3H, *J* = 7.21 Hz, CH_3), 3.83 (s, 3H, OCH_3), 4.33 (q, 2H, *J* = 7.21 Hz, OCH_2), 5.04 (d, 1H, *J* = 14.06 Hz, *N*CH), 5.18 (d, 1H, *J* = 14.06 Hz, NCH), 6.92-7.00 (m, 4H, aromatic), 7.20 (d, 1H, *J* = 7.21 Hz, aromatic), 7.32 (t, 1H, *J* = 7.21 Hz, aromatic), 7.63 (s, 1H, aromatic), 7.69 (d, 2H, *J* = 8.80 Hz, aromatic), 7.77 (m, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.15, 50.32, 56.63, 61.49, 97.56, 116.15, 118.26, 121.12, 121.26, 122.13, 125.29, 128.38, 128.83, 129.29, 130.85, 132.53, 136.35, 147.13, 151.47, 164.87; IR (KBr): 3401, 2956, 1710, 1609, 1562, 1458, 1369, 1216, 1181, 1057, 975, 837, 764 cm^{-1}; ESI-MS: *m/z* 408 $[M+H]^+$, 430 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{22}H_{22}N_3O_5$ $[M+H]^+$: 408.1542. Found: 408.1695.

Dimethyl 1-((3-(ethoxycarbonyl)-2-hydroxy-2*H*-chromen-2-*yl*)methyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate 8h: Yield: 92%. Colorless solid. m.p. 116-118°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (t, 3H, *J* = 6.87 Hz, CH_3), 3.94 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.35 (q, 2H, *J* = 6.87 Hz, OCH_2), 4.77 (broad, 1H, OH), 5.31-5.48 (m, 2H, *N*CH_2), 6.84 (d, 1H, *J* = 7.97 Hz, aromatic), 7.01 (t, 1H, *J* = 7.15 Hz, aromatic), 7.23 (d, 1H, *J* = 6.60 Hz, aromatic), 7.32 (t, 1H, *J* = 7.15 Hz, aromatic), 7.64 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.14, 52.56, 53.39, 55.13, 61.68, 96.77, 116.64, 117.87, 121.35, 122.62, 129.04, 132.52, 132.97, 136.47, 139.07, 151.25, 159.27, 160.15, 164.94; IR (KBr): 3357, 2957, 1752, 1711, 1609, 1466, 1287, 1220, 1131, 1062, 840, 758, 638 cm^{-1}; ESI-MS: *m/z* 418 $[M+H]^+$, 440 $[M+Na]^+$; HRMS (ESI): *m/z* Calcd for $C_{19}H_{20}O_8N_3$ $[M+H]^+$: 418.1245. Found: 418.1228.

2-((4,5-bis(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-*yl*)methyl)-2-Hydroxy-2*H*-chromene-3-carboxylic acid 8i: Yield: 88%. Colorless solid. m.p. 132-134°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, 3H, *J* = 7.17 Hz, CH_3), 1.44 (t, 3H, *J* = 7.17 Hz, CH_3), 4.37 (q, 2H, *J* = 7.17 Hz, OCH_2), 4.47 (q, 2H, *J* = 7.17 Hz, OCH_2), 6.25 (s, 2H, *N*CH_2), 7.39-7.46 (m, 2H, aromatic), 7.71-7.77 (m, 2H, aromatic), 8.69 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$):δ 13.79, 14.13, 59.61, 61.86, 62.65, 116.89, 117.92, 121.13, 125.47, 129.95, 130.77, 135.68, 140.49, 150.03, 155.46, 158.21, 159.20, 160.10, 187.50; IR (KBr): 3446, 3398, 2993, 1728, 1606, 1559, 1373, 1296, 1213, 1152, 1011, 979, 705 cm^{-1}; ESI-MS: *m/z* 400 $[M-OH]^+$; HRMS (ESI): *m/z* Calcd for $C_{19}H_{20}N_3O_8$ $[M+H]^+$: 418.1630. Found: 418.1865.

2-((4,5-bis(ethoxycarbonyl)-1*H*-1,2,3-triazol-1-*yl*)methyl)-2-Hydroxy-6-methoxy-2*H*-chromene-3-carboxylic acid 8j: Yield: 45%. Colorless solid. m.p. 138-140°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (t, 3H, *J* = 7.02 Hz, CH_3), 1.44 (t, 3H, *J* = 7.02 Hz, CH_3), 3.88

(s, 3H, OCH_3), 4.37 (q, 2H, J = 7.02 Hz, OCH_2), 4.47 (q, 2H, J = 7.02 Hz, OCH_2), 6.25 (s, 2H, NCH_2), 7.08 (s, 1H, aromatic), 7.30-7.39 (m, 2H, aromatic), 8.63 (s, 1H, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.85, 14.17, 55.95, 59.69, 61.91, 62.67, 111.25, 118.07, 118.28, 121.29, 124.47, 130.03, 140.54, 149.81, 150.23, 156.68, 158.26, 159.40, 160.15, 187.63; IR (KBr): 3426, 3386, 2956, 1727, 1621, 1569, 1466, 1316, 1237, 1165, 844, 767, 613 cm^{-1}; ESI-MS: *m/z* 430 $[M - OH]^+$; HRMS (ESI): *m/z* Calcd for $C_{20}H_{20}O_8N_3$ $[M - OH]^+$: 430.1245. Found: 430.1244.

Conclusion

In conclusion, series of 2*H*-/4*H*-triazolylchromene-3-carboxylates were prepared by reacting ethyl 2-(azidomethyl)-4*H*-chromene-3-carboxylates with alkynes. Electron donating groups present on phenylacetylenes provided exclusively 2*H*-triazolylchromene-3-carboxylates, whereas electron withdrawing groups provided mixture of 2*H*-/4*H*-triazolylchromene-3-carboxylates. Interestingly, prop-2-yn-1-ol and ethyl propiolate have provided exclusively 4*H*-triazolylchromene-3-carboxylates. The prepared compounds are new heterocycles and being reported for the first time. Presently, we are working on ethyl 2-(chloromethyl)-4*H*-chromene-3-carboxylates to prepare biologically important heterocyclic compounds which will be reported in due course.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/ 123456789/58776.

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