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3,5-Disubstituted 6*H*-pyrrolo[1,2-*c*][1,2,3]triazoles from Morita–Baylis–Hillman adducts of propargyl aldehydes

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7,8-Dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]-indol-5(6*H*)-ones

ABSTRACT

A simple method for synthesizing several 6*H*-pyrrolo[1,2-*c*][1,2,3]triazole derivatives having a methoxy carbonyl or an acetyl group at C-5 position and 7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]indol-5(6*H*)-ones via an intramolecular 1,3-dipolar cycloaddition reaction of azido enynes, which were readily obtained from the Morita–Baylis–Hillman acetates of propargyl aldehydes with sodium azide, has been developed.

1. Introduction

1,2,3-Triazoles and 1,2,3-triazole-fused heterocycles are known to exhibit a wide range of biological activities such as *anti*-HIV activity,[1] antimicrobial activity against Gram positive bacteria,[2] selective β_3 adrenergic receptor agonism,[3] and antianxiety activity.[4] So it is important to develop new and more efficient synthetic methods to a diverse array of 1,2,3-triazole pharmacophores. The most important synthetic route involves a 1,3-dipolar cycloaddition reaction of an azide with an alkyne[5] or an alkyne equivalent, such as a vinyl acetate, an enamine or an enol ether.[6] Intramolecular applications of this reaction in more flexible systems have proven to be especially valuable for the synthesis of 1,2,3-triazole-fused heterocyles. For examples, 3-(*o*-azidophenoxy)propynes, 3-(*o*-azidothiophenoxy) propynes, and 1-(*o*-azidothiophenoxy)propynes cyclize upon heating to give triazolobenzoxazines,[7] triazolobenzthiazines,[8] and triazolobenzthiazoles,[8] respectively. The synthesis of 6*H*-pyrrolo[1,2-*c*][1,2,3]triazoles by the intramolecular 1,3-dipolar cycloaddtion reaction of 1-azido-2-penten-4-ynes has been reported by Bertrand et al.[9] and Dulcere et al.[10] Azido enynes were obtained by treatment of 1-chloro-2-penten-4-ynes[11] with sodium azide, which were prepared by the reaction of acrolein with ethynyl Grignard or lithium reagent followed by treatment with hydrochloric acid. This method has some drawbacks that the only simple alkyl substituted azido enynes were prepared and their thermal cyclization was studied limitedly.

The Morita–Bayis–Hillman reaction is a versatile carbon–carbon bond forming reaction which provides multi functionalized adducts, α-methylene-β-hydroxy carbonyl compounds.[12a–j] These adducts and their derivatives have widely been explored for the syntheses of a variety of useful heterocyclic compounds.[13,14]

Herein, we describe the synthesis of azido enynes from the Morita–Baylis–Hillman adducts of several acetylenic aldehydes and their conversion to the 6*H*-pyrrolo[1,2-*c*][1,2,3]triazoles and 7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]indol-5(6*H*)-ones involving an intramolecular 1,3-dipolar cycloaddition reaction of an azide to carbon–carbon triple bond.[15]

2. Results and discussion

The readily available Morita–Baylis–Hillman adducts **2**, whose preparation has been previously described,[16] provide a convenient starting point for the synthesis of key intermediate azido enynes **4**. Treatment of several acetylenic aldehydes **1** with methyl acrylate in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO) in dimethyl sulfoxide at room temperature produced the adducts **2a–f** in 47–64% yields. For methyl vinyl ketone, the corresponding adducts **2g–l** were obtained in 56–64% yields. The Morita–Baylis–Hillman reactions of phenylpropargyl aldehyde (**1a**) with cyclopent-2-enone and

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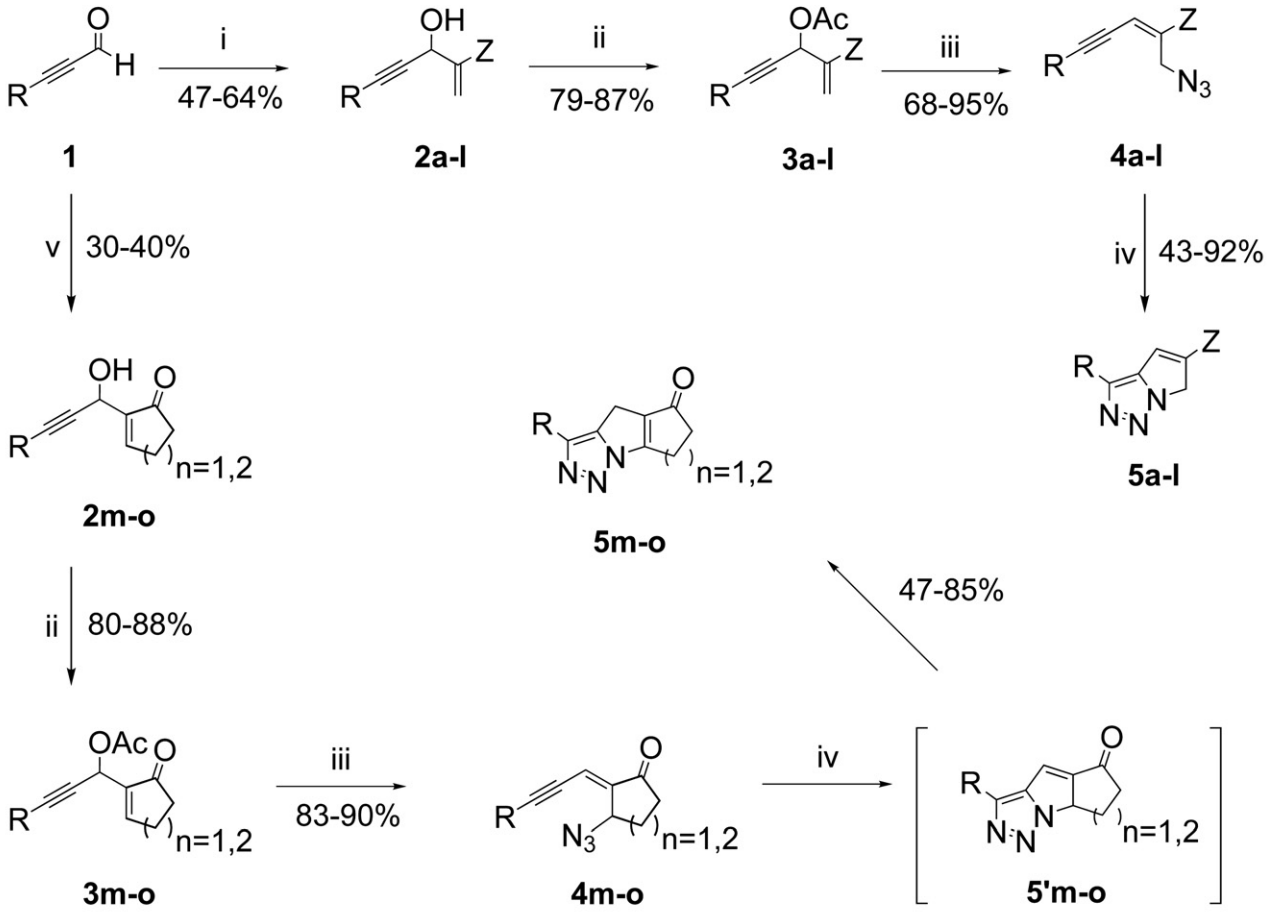
cyclohex-2-enone were performed in aqueous tetrahydrofuran using 20 mol % 4-(dimethylamino)pyridine (DMAP) as a catalyst, such that, **2m** and **2n** were produced in 35% and 40% yields, respectively. Similarly, the reaction of 2-octynal (**1f**) with cyclohex-2-enone the adduct **2o** was obtained in 30% yield. The reaction of adducts **2a**–**o** with acetic anhydride in the presence of catalytic amount of DMAP in dichloromethane at 0–5 °C gave the acetates of Morita–Baylis–Hillman adducts **3a**–**o** (79–88%), as shown in Scheme 1 and Table 1. The azidation reaction of the acetates **3a**–**o** with sodium azide[17] in methanol/water (9:1) at room temperature for 1 h afforded the



1	R	2,3,4,5		R	Z
a	phenyl	**a**		phenyl	CO_2CH_3
b	4-chlorophenyl	**b**		4-chlorophenyl	CO_2CH_3
c	4-fluorophenyl	**c**		4-fluorophenyl	CO_2CH_3
d	3-methoxyphenyl	**d**		3-methoxyphenyl	CO_2CH_3
e	2-thienyl	**e**		2-thienyl	CO_2CH_3
f	pentyl	**f**		pentyl	CO_2CH_3
		g		phenyl	$COCH_3$
		h		4-chlorophenyl	$COCH_3$
		i		4-fluorophenyl	$COCH_3$
		j		3-methoxyphenyl	$COCH_3$
		k		2-thienyl	$COCH_3$
		l		pentyl	$COCH_3$
		m	n=1	phenyl	
		n	n=2	phenyl	
		o	n=2	pentyl	

Scheme 1. Reagents and conditions: (i) methyl acrylate or methyl vinyl ketone, DABCO, DMSO, rt, 20 min to 4 h; (ii) Ac_2O, DMAP, CH_2Cl_2, 0–5 °C, 5–60 min; (iii) NaN_3, CH_3OH/H_2O (9:1), rt, 1 h; (iv) toluene, reflux, 1 h; (v) cyclopent-2-enone or cyclohex-2-enone, DMAP, THF/H_2O (1:1), rt, 1 h.

Table 1
Preparation of adducts **2**, acetates **3**, azido enynes **4**, and triazole derivatives **5**

Entry	**2** (Yield/time)	**3** (Yield/time)	**4** (Yield/time)	**5** (Yield/time)
1	**2a** (61%/2 h)	**3a** (87%/10 min)	**4a** (91%/1 h)	**5a** (81%/1 h)
2	**2b** (47%/4 h)	**3b** (80%/5 min)	**4b** (91%/1 h)	**5b** (91%/1 h)
3	**2c** (55%/3 h)	**3c** (79%/5 min)	**4c** (79%/1 h)	**5c** (88%/1 h)
4	**2d** (64%/2 h)	**3d** (87%/10 min)	**4d** (95%/1 h)	**5d** (91%/1 h)
5	**2e** (53%/30 min)	**3e** (82%/10 min)	**4e** (75%/1 h)	**5e** (86%/1 h)
6	**2f** (59%/1 h)	**3f** (82%/15 min)	**4f** (87%/1 h)	**5f** (43%/1 h)
7	**2g** (64%/2 h)	**3g** (80%/10 min)	**4g** (91%/1 h)	**5g** (62%/1 h)
8	**2h** (60%/2 h)	**3h** (79%/10 min)	**4h** (74%/1 h)	**5h** (81%/1 h)
9	**2i** (58%/3 h)	**3i** (82%/5 min)	**4i** (89%/1 h)	**5i** (75%/1 h)
10	**2j** (56%/2 h)	**3j** (83%/10 min)	**4j** (68%/1 h)	**5j** (92%/1 h)
11	**2k** (63%/20 min)	**3k** (81%/10 min)	**4k** (69%/1 h)	**5k** (80%/1 h)
12	**2l** (58%/1 h)	**3l** (80%/10 min)	**4l** (84%/1 h)	**5l** (—)
13	**2m** (35%/1 h)	**3m** (88%/1 h)	**4m** (90%/1 h)	**5m** (—)
14	**2n** (40%/1 h)	**3n** (80%/1 h)	**4n** (83%/1 h)	**5n** (85%/1 h)
15	**2o** (30%/1 h)	**3o** (82%/15 min)	**4o** (90%/1 h)	**5o** (47%/1 h)

required key intermediate methyl 2-(azidomethyl)pent-2-en-4-ynoates **4a–f** (75–95%), 3-(azidomethyl)hex-3-en-5-yn-2-ones **4g–l** (68–91%), 3-azido-2-(3-phenylprop-2-ynylidene)cyclopentanone **4m** (90%), 3-azido-2-(3-phenylprop-2-ynylidene)cyclohexanone **4n** (83%), and 3-azido-2-(oct-2-ynylidene)cyclohexanone **4o** (90%), respectively, solely with (*E*)-stereoselectivity. The stereochemistry of the azido enynes **4** was established by comparing ^{1}H NMR values of olefinic and methylene protons with literature values of similar compounds.[17,18] The olefinic proton of **4a–l** was observed at δ 6.94–7.11 and two methylene protons were resonated at δ 4.27–4.31 as each singlet, except **4f** and **4l**.[19] In the cases of **4m**, **4n**, and **4o** the vinyl proton was appeared at δ 6.89 as a doublet, δ 6.98 as a singlet and δ 6.76 as a triplet and the methine proton was observed at δ 5.04–5.07, δ 5.24–5.28, and δ 5.13–5.17 as each multiplet, respectively.

Finally, the intramolecular 1,3-dipolar cycloaddition reaction of **4a–o** between azide and alkyne groups in refluxing toluene for 1 h produced the corresponding 6*H*-pyrrolo[1,2-*c*][1,2,3]triazole **5a–k** (43–92%), 3-phenyl-7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]indol-5(6*H*)-one **5n** (85%), and 3-pentyl-7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]indol-5(6*H*)-one **5o** (47%) after isomerization of the expected 3-phenyl-6,7,8,8*a*-tetrahydro[1,2,3]triazolo[1,5-*a*]indol-5-one **5′n** and 3-pentyl-6,7,8,8*a*-tetrahydro[1,2,3]triazolo[1,5-*a*]indol-5-one **5′o**. In the cases of **4l** and **4m** very complex un-isolable decomposition products were produced. Exploration of different reaction conditions such as lower temperatures at 60, 80, and 90 °C in toluene and other solvent systems, such as tetrahydrofuran, acetonitrile at reflux temperature and dimethylformamide at 60 °C the desired triazoles **5l** and **5n** were not obtained. The IR spectra of **5** showed the disappearance of absorption of carbon–carbon triple bond and azide bands. In the ^{1}H NMR spectra of **5a–k**, the characteristic chemical shift of the methine proton of C-4 was found at δ 7.46–7.74 as a triplet, and two methylene protons of C-6 were observed at δ 5.06–5.17 as a doublet. In the ^{1}H NMR spectra of **5n** and **5o**, two methylene protons of C-4 were appeared at δ 3.82 and δ 3.57 as a doublet of doublet and ^{1}H–^{1}H 2D COSY spectra of **5n** and **5o** clearly showed long-range coupling of C-4 methylene protons and C-8 methylene protons. In DEPT ^{13}C NMR experiments **5n** exhibited four CH_2 absorption peaks (21.2, 22.2, 25.7, 37.3) and three CH peaks (125.6, 128.3, 129.0). Compound **5o** showed eight CH_2 absorption peaks (21.2, 22.2, 22.4, 24.4, 25.3, 28.1, 31.4, 37.3) and one CH_3 peak (14.0). No CH absorption peak observed. The molecular ion peaks of **5a–k** were not observed in the EI mass spectra, but we could observe $[M+Na]^+$ peaks in ESI-TOF mass spectra.

3. Conclusions

In summary, we have prepared several 6*H*-pyrrolo[1,2-*c*][1,2,3]triazoles and 7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]indol-5(6*H*)-ones via an intramolecular 1,3-dipolar cycloaddition reaction of the corresponding azido enynes, which were readily obtained from the Morita–Baylis–Hillman acetates of propargyl aldehydes with sodium azide.

4. Experimental

4.1. Synthesis general

The melting points were measured on an Electrothermal melting point apparatus and are uncorrected. TLC analyses were carried out on Merck silica gel 60 F_{254} and spots were visualized under UV light. Chromatography on silica gel was carried out on Merck silica (70–230 mesh ASTM). IR spectra were determined on a Nicolet Magna 550 FTIR spectrometer using KBr discs. ^{1}H NMR spectra were recorded on a Varian 300 spectrometer in $CDCl_3$ or DMSO-d_6 at 300 MHz. All chemical shifts are given in parts per million (ppm) using δ_H Me_4Si=0 ppm as reference and *J* values are given in hertz. The ^{13}C NMR spectra were run in the same instrument at 75.4 MHz using the solvent peak as internal reference. Low resolution mass spectra were recorded on a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. ESI-TOF mass spectra were recorded on a Micromass spectrometer (Model No. LCT). Elemental analyses were carried out on a Thermo Electron Corporation Flash EA 1112 instrument. Phenylpropargyl aldehyde (**1a**) and 2-octynal (**1f**) were obtained from Aldrich and used without further purification. The known propargyl aldehydes **1b–e** were prepared by the procedure for Sonogashira coupling of propargyl alcohol with the corresponding aryl iodide[20] followed by oxidation with manganese dioxide[21] according to the reported procedures.

4.2. General procedure for the synthesis of the Morita–Baylis–Hillman adducts 2a–l

A mixture of propargyl aldehyde **1** (20 mmol), methyl acrylate (2.07 g, 24 mmol) or methyl vinyl ketone (1.68 g, 24 mmol), and DABCO (1.12 g, 10 mmol) in 20 mL of dimethyl sulfoxide was stirred at room temperature for 20 min to 4 h. The reaction mixture was diluted with water (100 mL) and extracted with ethyl acetate (3×100 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (6:1 to 3:1) to produce **2** as an oil.

*4.2.1. Methyl 3-hydroxy-2-methylene-5-phenylpent-4-ynoate (**2a**).* Reaction time: 2 h; yield: 61%; yellow oil; IR (neat) 3438, 2226, 1721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.19 (d, *J*=6.9 Hz, 1H, OH), 3.85 (s, 3H, CH_3), 5.46 (d, *J*=6.6 Hz, 1H, CH), 6.21 (s, 1H, CH), 6.38 (s, 1H, CH), 7.29–7.34 (m, 3H, aromatic), 7.44–7.47 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.2, 62.6, 86.5, 86.7, 122.2, 127.1, 128.3, 128.7, 131.7, 139.0, 166.3. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.03; H, 5.41.

*4.2.2. Methyl 5-(4-chlorophenyl)-3-hydroxy-2-methylenepent-4-ynoate (**2b**).* Reaction time: 4 h; yield: 47%; yellow oil; IR (neat) 3426, 2228, 1721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.21 (d, *J*=5.5 Hz, 1H, OH), 3.84 (s, 3H, CH_3), 5.43 (d, *J*=5.5 Hz, 1H, CH), 6.18 (s, 1H, CH), 6.37 (s, 1H, CH), 7.26–7.31 (m, 2H, aromatic), 7.36–7.39 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.3, 62.7, 85.5, 87.6, 120.1, 127.1, 128.6, 133.0, 134.8, 138.9, 166.3. Anal. Calcd for $C_{13}H_{11}ClO_3$: C, 62.29; H, 4.42. Found: C, 62.07; H, 4.26.

*4.2.3. Methyl 5-(4-fluorophenyl)-3-hydroxy-2-methylenepent-4-ynoate (**2c**).* Reaction time: 3 h; yield: 55%; yellow oil; IR (neat) 3444, 2225, 1721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.22 (d, *J*=6.9 Hz, 1H, OH), 3.84 (s, 3H, CH_3), 5.44 (d, *J*=6.6 Hz, 1H, CH), 6.19 (s, 1H, CH),

6.37 (s, 1H, CH), 6.98–7.04 (m, 2H, aromatic), 7.41–7.47 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.3, 62.6, 85.6, 86.3, 115.6 (d, J=22.0 Hz), 118.3, 127.1, 133.7 (d, J=8.6 Hz), 139.0, 162.7 (d, J=249.8 Hz), 166.3. Anal. Calcd for $C_{13}H_{11}FO_3$: C, 66.66; H, 4.73. Found: C, 66.81; H, 4.90.

*4.2.4. Methyl 3-hydroxy-5-(3-methoxyphenyl)-2-methylenepent-4-ynoate (**2d**).* Reaction time: 2 h; yield: 64%; yellow oil; IR (neat) 3440, 2235, 1722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.18 (d, J=6.6 Hz, 1H, OH), 3.80 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 5.46 (d, J=6.3 Hz, 1H, CH), 6.21 (s, 1H, CH), 6.38 (s, 1H, CH), 6.87–6.91 (m, 1H, aromatic), 6.98–6.99 (m, 1H, aromatic), 7.03–7.07 (m, 1H, aromatic), 7.19–7.26 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.3, 55.3, 62.7, 86.3, 86.7, 115.3, 116.6, 123.2, 124.3, 127.2, 129.4, 139.0 159.2, 166.3. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.53; H, 6.01.

*4.2.5. Methyl 3-hydroxy-2-methylene-5-(thiophen-2-yl)pent-4-ynoate (**2e**).* Reaction time: 30 min; yield: 52%; red oil; IR (neat) 3434, 2222, 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.20 (d, J=6.9 Hz, 1H, OH), 3.84 (s, 3H, CH_3), 5.46 (d, J=6.6 Hz, 1H, CH), 6.18(s, 1H, CH), 6.37 (s, 1H, CH), 6.97 (dd, J=5.2 and 3.6 Hz, 1H, aromatic), 7.24 (dd, J=3.6 and 1.1 Hz, 1H, aromatic), 7.27 (dd, J=5.2 and 1.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.3, 62.8, 80.0, 90.4, 122.0, 126.9, 127.3, 127.6, 132.6, 138.7, 166.2. Anal. Calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53. Found: C, 59.16; H, 4.31.

*4.2.6. Methyl 3-hydroxy-2-methylenedec-4-ynoate (**2f**).* Reaction time: 1 h; yield: 59%; yellow oil; IR (neat) 3425, 2227, 1726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=7.2 Hz, 3H, CH_3), 1.26–1.42 (m, 4H, two CH_2), 1.48–1.58 (m, 2H, CH_2), 2.24 (dt, J=7.2 and 2.2 Hz, 2H, CH_2), 3.00 (d, J=6.3 Hz, 1H, OH), 5.22 (dd, J=6.6 and 0.8 Hz, 1H, CH), 6.13 (s, 1H, CH), 6.30 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.7, 22.1, 28.2, 31.0, 52.1, 62.3, 77.7, 88.0, 126.6, 139.6, 166.5. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.32; H, 8.51.

*4.2.7. 4-Hydroxy-3-methylene-6-phenylhex-5-yn-2-one (**2g**)*[16a]. Reaction time: 2 h; yield: 64%; yellow oil; IR (neat) 3413, 2219, 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.32 (d, J=5.8 Hz, 1H, OH), 5.51 (d, J=5.8 Hz, 1H, CH), 6.25 (s, 1H, CH), 6.44 (s, 1H, CH), 7.30–7.34 (m, 3H, aromatic), 7.44–7.47 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.4, 62.3, 86.7, 86.8, 122.2, 127.6, 128.3, 128.6, 131.7, 146.6, 199.8. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.73; H, 6.12.

*4.2.8. 6-(4-Chlorophenyl)-4-hydroxy-3-methylenehex-5-yn-2-one (**2h**).* Reaction time: 2 h; yield: 60%; yellow oil; IR (neat) 3414, 2232, 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.33 (d, J=6.3 Hz, 1H, OH), 5.48 (d, J=6.1 Hz, 1H, CH), 6.25 (s, 1H, CH), 6.41 (s, 1H, CH), 7.27–7.31 (m, 2H, aromatic), 7.36–7.39 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.3, 62.4, 85.6, 87.8, 120.7, 127.7, 128.6, 133.0, 134.7, 146.4, 199.7. Anal. Calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.31; H, 4.52.

*4.2.9. 6-(4-Fluorophenyl)-4-hydroxy-3-methylenehex-5-yn-2-one (**2i**).* Reaction time: 3 h; yield: 58%; yellow oil; IR (neat) 3408, 2238, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.33 (d, J=6.1 Hz, 1H, OH), 5.48 (d, J=5.8 Hz, 1H, CH), 6.25 (s, 1H, CH), 6.42 (s, 1H, CH), 6.98–7.01 (m, 2H, aromatic), 7.41–7.46 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.3, 62.4, 85.7, 86.5, 115.6 (d, J=22.0 Hz), 118.3, 127.6, 133.7 (d, J=8.6 Hz), 146.5, 162.7 (d, J=250.1 Hz), 199.7. Anal. Calcd for $C_{13}H_{11}FO_2$: C, 71.55; H, 5.08. Found: C, 71.76; H, 4.84.

*4.2.10. 4-Hydroxy-6-(3-methoxyphenyl)-3-methylenehex-5-yn-2-one (**2j**).* Reaction time: 2 h; yield: 56%; yellow oil; IR (neat) 3426, 2225, 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.28 (d, J=5.5 Hz, 1H, OH), 3.79 (s, 3H, CH_3), 5.50 (d, 1H, J=4.4 Hz, CH), 6.25 (s, 1H, CH), 6.43 (s, 1H, CH), 6.89–6.90 (m, 1H, aromatic), 6.98–6.99 (m, 1H, aromatic), 7.03–7.06 (m, 1H, aromatic), 7.19–7.26 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.3, 55.3, 62.4, 86.6, 86.7, 115.3, 116.6, 123.3, 124.3, 127.6, 129.3, 146.6, 159.3, 199.7. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.77; H, 5.89.

*4.2.11. 4-Hydroxy-3-methylene-6-(thiophen-2-yl)hex-5-yn-2-one (**2k**).* Reaction time: 20 min; yield: 63%; red oil; IR (neat) 3414, 2221, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 3.31 (d, J=6.1 Hz, 1H, OH), 5.51 (d, J=5.8 Hz, 1H, CH), 6.26 (s, 1H, CH), 6.40 (s, 1H, CH), 6.97 (dd, J=5.2 and 3.6 Hz, 1H, aromatic), 7.24 (dd, J=3.6 and 1.1 Hz, 1H, aromatic), 7.27 (dd, J=5.2 and 1.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.3, 62.5, 80.1, 90.6, 122.1, 126.9, 127.5, 127.8, 132.6, 146.3, 199.7. Anal. Calcd for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89. Found: C, 63.85; H, 4.72.

*4.2.12. 4-Hydroxy-3-methyleneundec-5-yn-2-one (**2l**).* Reaction time: 1 h; yield: 58%: yellow oil; IR (neat) 3414, 2226, 1677 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=7.2 Hz, 3H, CH_3), 1.26–1.48 (m, 4H, two CH_2), 1.51–1.61 (m, 2H, CH_2), 2.24 (dt, J=7.2 and 2.2 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.12 (d, J=5.8 Hz, 1H, OH), 5.27–5.28 (m, 1H, CH), 6.18 (s, 1H, CH), 6.36 (d, J=1.1 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.7, 22.1, 26.4, 28.2, 31.0, 62.0, 77.8, 88.1, 127.2, 147.1, 199.9. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.37; H, 9.50.

*4.2.13. 2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)cyclopent-2-enone (**2m**).* A mixture of phenylpropargyl aldehyde **1a** (1.30 g, 10 mmol), cyclopent-2-enone (0.82 g, 10 mmol), and DMAP (0.24 g, 2 mmol) in 10 mL of aqueous tetrahydrofuran (1:1) was stirred at room temperature for 1 h. The reaction mixture was diluted with water (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (3:1) to produce **2m** (0.74 g, 35%) as a yellow oil; IR (neat) 3388, 2229, 1701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.53–2.56 (m, 2H, CH_2), 2.67–2.73 (m, 2H, CH_2), 3.30 (d, J=5.0 Hz, 1H, OH), 5.48 (br s, 1H, CH), 7.31–7.34 (m, 3H, aromatic), 7.46–7.48 (m, 2H, aromatic), 7.78 (td, J=2.8 and 1.1 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 26.6, 35.3, 58.4, 86.0, 86.4, 122.1, 128.3, 128.7, 131.8, 144.3, 160.4, 208.7. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.01; H, 5.58.

*4.2.14. 2-(1-Hydroxy-3-phenylprop-2-yn-1-yl)cyclohex-2-enone (**2n**).* A mixture of phenylpropargyl aldehyde **1a** (1.30 g, 10 mmol), cyclohex-2-enone (0.96 g, 10 mmol), and DMAP (0.24 g, 2 mmol) in 10 mL of aqueous tetrahydrofuran (1:1) was stirred at room temperature for 1 h. The work-up procedure was the same as above to produce **2n** (0.90 g, 40%) as a yellow oil; IR (neat) 3414, 2232, 1669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01–2.10 (m, 2H, CH_2), 2.46–2.54 (m, 4H, two CH_2), 3.50 (d, J=4.9 Hz, 1H, OH), 5.49 (br s, 1H, CH), 7.31–7.33 (m, 3H, aromatic), 7.37 (t, J=4.1 Hz, 1H, CH), 7.46–7.49 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 22.5, 25.7, 38.3, 61.9, 86.6, 87.0, 122.3, 128.2, 128.6, 131.8, 137.7, 148.3, 199.9. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.43; H, 6.02.

*4.2.15. 2-(1-Hydroxyoct-2-yn-1-yl)cyclohex-2-enone (**2o**).* A mixture of 2-octynal **1f** (1.24 g, 10 mmol), cyclohex-2-enone (0.96 g, 10 mmol), and DMAP (0.24 g, 2 mmol) in 10 mL of aqueous tetrahydrofuran (1:1) was stirred at room temperature for 1 h. The work-up procedure was the same as above to produce **2o** (0.66 g, 30%) as a yellow oil; IR (neat) 3443, 2240, 1672 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.86 (t, J=6.9 Hz, 3H, CH_3), 1.26–1.30 (m, 4H, two CH_2), 1.37–1.43 (m, 2H, CH_2), 1.84–1.92 (m, 2H, CH_2), 2.16 (td, J=6.9 and 1.9 Hz, 2H, CH_2), 2.32–2.42 (m, 4H, two CH_2), 5.07 (d, J=6.1 Hz, 1H, OH), 5.45 (d, J=6.1 Hz, 1H, CH), 7.18 (t, J=4.1 Hz, 1H, CH); ^{13}C NMR

(DMSO-d_6) δ 13.9, 18.0, 21.7, 22.4, 25.1, 27.9, 30.5, 37.9, 56.8, 81.2, 84.1, 139.4, 146.1, 196.7. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.14; H, 9.02.

4.3. General procedure for the synthesis of the Morita–Baylis–Hillman acetates 3a–o

To a stirred solution of the adduct **2** (10 mmol) in 20 mL of dichloromethane added acetic anhydride (1.53 g, 15 mmol) and DMAP (0.34 g, 3 mmol) at 0–5 °C. After stirring at the same temperature for 5 to 60 min the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane (3×20 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (6:1) to produce **3**.

*4.3.1. Methyl 3-acetoxy-2-methylene-5-phenylpent-4-ynoate (**3a**).* Reaction time: 10 min; yield: 87%; yellow oil; IR (neat) 2232, 1748, 1727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 6.34 (s, 1H, CH), 6.53 (s, 1H, CH), 6.54 (s, 1H, CH), 7.29–7.39 (m, 3H, aromatic), 7.45–7.48 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 52.3, 62.1, 83.7, 87.2, 121.8, 128.3, 128.9, 129.3, 131.9, 136.5, 164.9, 169.3. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.56; H, 5.53.

*4.3.2. Methyl 3-acetoxy-5-(4-chlorophenyl)-2-methylenepent-4-ynoate (**3b**).* Reaction time: 5 min; yield: 80%; yellow oil; IR (neat) 2234, 1749, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.30 (s, 1H, CH), 6.51 (s, 1H, CH), 5.62 (s, 1H, CH), 7.26–7.31 (m, 2H, aromatic), 7.37–7.41 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.8, 52.3, 62.0, 84.8, 86.0, 120.3, 128.7, 129.2, 133.2, 135.0, 136.4, 164.8, 169.3. Anal. Calcd for $C_{15}H_{13}ClO_4$: C, 61.55; H, 4.48. Found: C, 61.36; H, 4.27.

*4.3.3. Methyl 3-acetoxy-5-(4-fluorophenyl)-2-methylenepent-4-ynoate (**3c**).* Reaction time: 5 min; yield: 79%; yellow oil; IR (neat) 2234, 1747, 1729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.31 (s, 1H, CH), 6.51 (s, 1H, CH), 6.52 (s, 1H, CH), 6.97–7.05 (m, 2H, aromatic), 7.41–7.48 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 52.3, 62.1, 83.5, 86.1, 115.6 (d, J=22.2 Hz), 118.0, 129.1, 133.9 (d, J=8.6 Hz), 136.5, 162.9 (d, J=250.1 Hz), 164.9, 169.3. Anal. Calcd for $C_{15}H_{13}FO_4$: C, 65.21; H, 4.74. Found: C, 64.92; H, 4.57.

*4.3.4. Methyl 3-acetoxy-5-(3-methoxyphenyl)-2-methylenepent-4-ynoate (**3d**).* Reaction time: 10 min; yield: 87%; yellow oil; IR (neat) 2238, 1748, 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.33 (s, 1H, CH), 6.52 (s, 1H, CH), 6.53 (s, 1H, CH), 6.88–6.92 (m, 1H, aromatic), 6.98–6.99 (m, 1H, aromatic), 7.04–7.07 (m, 1H, aromatic), 7.19–7.26 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 52.3, 55.3, 62.1, 83.5, 87.1, 115.6, 116.7, 122.8, 124.5, 129.2, 129.4, 136.6, 159.3, 164.9, 169.3. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.54; H, 5.31.

*4.3.5. Methyl 3-acetoxy-2-methylene-5-(thiophen-2-yl)pent-4-ynoate (**3e**).* Reaction time: 10 min; yield: 82%; yellow oil; IR (neat) 2227, 1747, 1727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 6.30 (s, 1H, CH), 6.53 (s, 1H, CH), 6.54 (s, 1H, CH), 6.98 (dd, J=5.2 and 3.6 Hz, 1H, aromatic), 7.26 (dd, J=3.6 and 1.1 Hz, 1H, aromatic), 7.29 (dd, J=5.2 and 1.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) 20.9, 52.3, 62.1, 80.5, 87.6, 121.6, 127.0, 128.0, 129.3, 133.2, 136.3, 164.8, 169.3. Anal. Calcd for $C_{13}H_{12}O_4S$: C, 59.08; H, 4.58. Found: C, 58.87; H, 4.39.

*4.3.6. Methyl 3-acetoxy-2-methylenedec-4-ynoate (**3f**).* Reaction time: 15 min; yield: 82%; yellow oil; IR (neat) 2237, 1747, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=7.4 Hz, 1H, CH_3), 1.26–1.37 (m, 4H, two CH_2), 1.52–1.57 (m, 2H, CH_2), 2.24 (dt, J=7.4 and 2.2 Hz, 2H, CH_2), 2.86 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 6.24 (s, 1H, CH), 6.29 (dt, J=2.2 and 0.6 Hz, 1H, CH), 6.45 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.7, 20.9, 22.1, 28.0, 31.0, 52.1, 74.9, 88.7, 128.8, 137.0, 165.1, 169.4. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.43; H, 8.25.

*4.3.7. 4-Acetoxy-3-methylene-6-phenylhex-5-yn-2-one (**3g**).* Reaction time: 10 min; yield: 80%; yellow oil; IR (neat) 2193, 1747, 1683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.35 (s, 1H, CH), 6.51 (s, 1H, CH), 6.58 (s, 1H, CH), 7.27–7.34 (m, 3H, aromatic), 7.36–7.50 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.2, 61.4, 84.2, 87.1, 121.9, 128.2, 128.6, 128.8, 131.9, 144.5, 169.2, 196.3. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.19; H, 5.73.

*4.3.8. 4-Acetoxy-6-(4-chlorophenyl)-3-methylenehex-5-yn-2-one (**3h**).* Reaction time: 10 min; yield: 79%; yellow solid; mp: 60–61 °C (hexane–EtOAc); IR (KBr) 2232, 1748, 1683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.35 (s, 1H, CH), 6.47 (s, 1H, CH), 6.56 (s, 1H, CH), 7.28–7.30 (m, 2H, aromatic), 7.37–7.39 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.8, 26.1, 61.3, 85.3, 85.8, 120.4, 128.5, 128.6, 1331, 135.0, 144.4, 169.2, 196.2. Anal. Calcd for: $C_{15}H_{13}ClO_3$: C, 65.11; H, 4.74. Found: C, 64.89; H, 4.61.

*4.3.9. 4-Acetoxy-6-(4-fluorophenyl)-3-methylenehex-5-yn-2-one (**3i**).* Reaction time: 5 min; yield: 82%; yellow oil; IR (neat) 2232, 1747, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.35 (s, 1H, CH), 6.48 (s, 1H, CH), 6.56 (s, 1H, CH), 6.98–7.03 (m, 2H, aromatic), 7.41–7.46 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.1, 61.3, 84.0, 85.9, 115.6 (d, J=22.2 Hz), 128.5, 133.9 (d, J=8.3 Hz), 144.4, 162.8, 162.8 (d, J=250.4 Hz), 169.3, 196.3. Anal. Calcd for: $C_{15}H_{13}FO_3$: C, 69.22; H, 5.03. Found: C, 68.97; H, 4.86.

*4.3.10. 4-Acetoxy-6-(3-methoxyphenyl)-3-methylenhex-5-yn-2-one (**3j**).* Reaction time: 10 min; yield: 83%; yellow oil; IR (neat) 2235, 1746, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.35 (s, 1H, CH), 6.51 (s, 1H, CH), 6.58 (s, 1H, CH), 6.87–6.91 (m, 1H, aromatic), 6.97–6.98 (m, 1H, aromatic), 7.04–7.06 (m, 1H, aromatic), 7.19–7.26 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.2, 55.3, 61.4, 84.0, 87.0, 115.6, 116.6, 122.8, 124.4, 128.6, 129.3, 144.4, 159.2, 169.3, 196.3. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.42; H, 5.77.

*4.3.11. 4-Acetoxy-3-methylene-6-(thiophen-2-yl)hex-5-yn-2-one (**3k**).* Reaction time: 10 min; yield: 81%; yellow oil; IR (neat) 2225, 1747, 1684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.36 (s, 1H, CH), 6.48 (s, 1H, CH), 6.59 (s, 1H, CH), 6.97 (dd, J=5.2 and 3.6 Hz, 1H, aromatic), 7.26 (dd, J=3.6 and 1.1 Hz, 1H, aromatic), 7.28 (dd, J=5.2 and 1.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.1, 61.4, 80.4, 88.1, 121.7, 126.9, 127.9, 128.7, 133.1, 144.2, 169.2, 196.2. Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.88; H, 4.87. Found: C, 62.66; H, 4.59.

*4.3.12. 4-Acetoxy-3-methyleneundec-5-yn-2-one (**3l**).* Reaction time: 10 min; yield: 80%; IR (neat) 2237, 1748, 1684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=7.2 Hz, 1H, CH_3), 1.30–1.39 (m, 4H, two CH_2), 1.47–1.54 (m, 2H, CH_2), 2.05 (s, 3H, CH_3), 2.23 (dt, J=7.2 and 2.2 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 6.27 (s, 1H, CH), 6.33 (dt, J=2.2 and 1.1 Hz, 1H, CH), 6.40 (d, J=1.1 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.7, 20.9, 22.1, 26.2, 28.0, 31.0, 61.4, 75.3, 88.5, 128.1, 145.0, 169.3, 196.5. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 69.94; H, 8.38.

*4.3.13. 2-(1-Acetoxy-3-phenylprop-2-yn-1-yl)cyclopent-2-enone (**3m**).* Reaction time: 1 h; yield; 88%; yellow oil; IR (neat) 2231, 1745, 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (s, 3H, CH_3), 2.51–2.54 (m, 2H, CH_2), 2.69–2.72 (m, 2H, CH_2), 6.38 (d, J=1.3 Hz, 1H, CH), 7.28–7.35 (m, 3H, aromatic), 7.45–7.49 (m, 2H, aromatic), 7.91

(td, J=2.7 and 1.1 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.6, 35.1, 58.0, 83.9, 86.2, 121.8, 128.3, 128.9, 131.9, 142.0, 162.5, 169.5, 205.6. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.35; H, 5.76.

*4.3.14. 2-(1-Acetoxy-3-phenylprop-2-yn-1-yl)cyclohex-2-enone (**3n**).* Reaction time: 1 h; yield: 80%; yellow solid; mp: 69–70 °C (hexane–EtOAc); IR (KBr) 2230, 1748, 1679 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02–2.06 (m, 2H, CH_2), 2.09 (s, 3H, CH_3), 2.48–2.53 (m, 4H, two CH_2), 6.56 (d, J=0.8 Hz, 1H, CH), 7.29–7.34 (m, 3H, aromatic), 7.45–7.48 (m, 2H, aromatic), 7.50 (t, J=4.1 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 20.9, 22.4, 26.0, 38.1, 60.6, 84.3, 87.1, 122.0, 128.2, 128.8, 131.9, 135.4, 150.0, 169.4, 196.2. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.85; H, 6.29.

*4.3.15. 2-(1-Acetoxyoct-2-yn-1-yl)cyclohex-2-enone (**3o**).* Reaction time: 15 min; yield: 82%; yellow oil; IR (neat) 2238, 1745, 1681 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=7.2 Hz, 3H, CH_3), 1.28–1.37 (m, 4H, two CH_2), 1.48–1.55 (m, 2H, CH_2), 2.02–2.09 (m, 2H, CH_2), 2.05 (s, 3H, CH_3), 2.23 (td, J=7.2 and 1.9 Hz, 2H, CH_2), 2.45–2.50 (m, 4H, two CH_2), 6.31 (d, J=0.8 Hz, 1H, CH), 7.40 (t, J=4.1 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.7, 21.0, 22.1, 22.5, 25.9, 28.1, 31.0, 38.1, 60.6, 75.3, 88.5, 135.8, 149.6, 169.5, 196.3. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 72.98; H, 8.32.

4.4. General procedure for the synthesis of azido enynes 4a–o

To a stirred solution of the acetate **3** (4 mmol) in 10 mL of aqueous methanol (MeOH/water: 9/1) was added sodium azide (0.39 g, 6 mmol) at room temperature. After stirring at the same temperature for 1 h the reaction mixture was diluted with water (10 mL) and extracted with dichloromethane (3×20 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuo. The mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (6:1) to produce **4**.

*4.4.1. (E)-Methyl 2-(azidomethyl)-5-phenylpent-2-en-4-ynoate (**4a**).* Yield: 91%; yellow solid; mp: 31–33 °C (hexane–EtOAc); IR (KBr) 2196, 2097, 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H, CH_3), 4.31 (s, 2H, CH_2), 7.11 (s, 1H, CH), 7.34–7.41 (m, 3H, aromatic), 7.48–7.52 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.1, 52.5, 84.5, 104.2, 121.8, 124.6, 128.5, 129.7, 132.0, 135.8, 165.9; EIMS: m/z (%) 213 (97), 182 (100), 154 (36), 127 (61). Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.60; H, 4.39; N, 17.21.

*4.4.2. (E)-Methyl 2-(azidomethyl)-5-(4-chlorophenyl)pent-2-en-4-ynoate (**4b**).* Yield: 91%; white solid; mp: 55–57 °C (hexane–EtOAc); IR (KBr) 2197, 2125, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H, CH_3), 4.30 (s, 2H, CH_2), 7.09 (s, 1H, CH), 7.33–7.37 (m, 2H, aromatic), 7.41–7.45 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.2, 52.6, 85.3, 102.7, 120.3, 124.2, 129.0, 133.2, 136.0, 136.2, 165.8; EIMS: m/z (%) 249 (34), 247 (100), 218 (31), 216 (92), 161 (34), 153 (14). Anal. Calcd for $C_{13}H_{10}ClN_3O_2$: C, 56.64; H, 3.66; N, 15.24. Found: C, 56.42; H, 3.46; N, 15.04.

*4.4.3. (E)-Methyl 2-(azidomethyl)-5-(4-fluorophenyl)pent-2-en-4-ynoate (**4c**).* Yield: 79%; white solid; mp: 42–44 °C (hexane–EtOAc); IR (KBr) 2197, 2099, 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 7.04–7.10 (m, 2H,aromatic), 7.09 (s, 1H, CH), 7.47–7.52 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.1, 52.5, 84.3, 103.0, 116.0 (d, J=22.2 Hz), 118.0, 124.4, 134.1 (d, J=8.6 Hz), 135.9, 163.3 (d, J=252.1 Hz), 165.9; EIMS: m/z (%) 231 (94), 200 (100), 172 (32), 145 (57). Anal. Calcd for $C_{13}H_{10}FN_3O_2$: C, 60.23; H, 3.89; N, 16.21. Found: C, 60.08; H, 3.91; N, 16.04.

*4.4.4. (E)-Methyl 2-(azidomethyl)-5-(3-methoxyphenyl)pent-2-en-4-ynoate (**4d**).* Yield: 95%; white solid; mp: 50–52 °C (hexane–EtOAc); IR (KBr) 2196, 2098, 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 4.31 (s, 2H, CH_2), 6.93–6.97 (m, 1H, aromatic), 7.01–7.02 (m, 1H, aromatic), 7.08–7.12 (m, 1H, aromatic), 7.10 (s, 1H, CH), 7.25–7.30 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.2, 52.5, 55.3, 84.2, 104.1, 116.4, 116.6, 122.7, 124.5 (two), 129.6, 135.9, 159.4, 165.9; EIMS: m/z (%) 243 (63), 242 (100), 214 (23), 213 (35), 212 (22). Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 62.21; H, 4.67; N, 15.24.

*4.4.5. (E)-Methyl 2-(azidomethyl)-5-(thiophen-2-yl)pent-2-en-4-ynoate (**4e**).* Yield: 75%; yellow solid; mp: 35–36 (hexane–EtOAc); IR (KBr) 2181, 2092, 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H, CH_3), 4.28 (s, 2H, CH_2), 7.05 (dd, J=4.9 and 3.1 Hz, 1H, aromatic), 7.11 (s, 1H, CH), 7.35 (d, J=3.1 Hz, 1H, aromatic), 7.42 (d, J=4.9 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.3, 52.5, 88.8, 97.5, 121.6, 124.1, 127.6, 129.8, 134.1, 135.2, 165.9; EIMS: m/z (%) 221 (100), 206 (14), 190 (22), 162 (88). Anal. Calcd for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99. Found: C, 53.29; H, 3.45; N, 17.15.

*4.4.6. (E)-Methyl 2-(azidomethyl)dec-2-en-4-ynoate (**4f**).* Yield: 87%; yellow oil; IR (neat) 2213, 2097, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J=7.2 Hz, CH_3), 1.33–1.44 (m, 4H, two CH_2), 1.57–1.64 (m, 2H, CH_2), 2.44 (dt, J=7.2 and 2.2 Hz, CH_2), 3.82 (s, 3H, CH_3), 4.20 (s, 2H, CH_2), 6.89 (t, 1H, J=2.2 Hz, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.0, 22.1, 27.9, 31.0, 47.9, 52.3, 76.3, 107.3, 125.8, 135.1, 166.2; EIMS: m/z (%) 235 (1) [M$^+$], 207 (42), 176 (15), 164 (100), 132 (49). Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.26; H, 7.28; N, 17.86. Found: C, 61.20; H, 7.10; N, 17.91.

*4.4.7. (E)-3-(Azidomethyl)-6-phenylhex-3-en-5-yn-2-one (**4g**).* Yield: 91%; yellow solid; mp: 32–34 °C (hexane–EtOAc); IR (KBr) 2193, 2099, 1668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 6.97 (s, 1H, CH), 7.36–7.43 (m, 3H, aromatic), 7.50–7.53 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 25.5, 46.9, 84.6, 106.0, 121.7, 124.5, 128.6, 129.9, 132.0, 143.7, 196.9; EIMS: m/z (%) 197 (64), 182 (100), 154 (38), 127 (55). Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.10; H, 4.70; N, 18.43.

*4.4.8. (E)-3-(Azidomethyl)-6-(4-chlorophenyl)hex-3-en-5-yn-2-one (**4h**).* Yield: 74%; white solid; mp: 64–65 °C (hexane–EtOAc); IR (KBr) 2193, 2095, 1661 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 4.27 (s, 2H, CH_2), 6.94 (s, 1H, CH), 7.35–7.38 (m, 2H, aromatic), 7.42–7.46 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 25.5, 47.0, 85.4, 104.5, 120.2, 124.0, 129.0, 133.2, 136.1, 144.1, 196.8; EIMS: m/z (%) 233 (20), 231 (61), 218 (32), 216 (100), 190 (9), 188 (26), 163 (11), 161 (57), 126 (20). Anal. Calcd for $C_{13}H_{10}ClN_3O$: C, 60.12; H, 3.88; N, 16.18. Found: C, 60.31; H, 3.72; N, 16.04.

*4.4.9. (E)-3-(Azidomethyl)-6-(4-fluorophenyl)hex-3-en-5-yn-2-one (**4i**).* Yield: 89%; white solid; mp: 40–42 °C (hexane–EtOAc); IR (KBr) 2196, 2095, 1669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 4.28 (s, 2H, CH_2), 6.95 (s, 1H, CH), 7.05–7.12 (m, 2H, aromatic), 7.48–7.54 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 25.5, 47.0, 84.4, 104.9, 116.1 (d, J=22.2 Hz), 117.9, 124.3, 134.1 (d, J=8.8 Hz), 143.8, 163.4 (d, J=252.7 Hz), 196.8; EIMS: m/z (%) 215 (20), 200 (100), 172 (39), 145 (62), 125 (17). Anal. Calcd for $C_{13}H_{10}FN_3O$: C, 64.19; H, 4.14; N, 17.28. Found: C, 63.92; H, 3.97; N, 17.13.

*4.4.10. (E)-3-(Azidomethyl)-6-(3-methoxyphenyl)hex-3-en-5-yn-2-one (**4j**).* Yield: 68%; white solid; mp: 46–48 °C (hexane–EtOAc); IR (KBr) 2193, 2095, 1668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.29 (s, 2H, CH_2), 6.96 (s, 1H, CH), 6.98–7.03 (m, 2H, aromatic), 7.10–7.12 (m, 1H, aromatic), 7.26–7.32 (m, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 25.5, 47.0, 55.3, 84.3, 105.9, 116.4, 116.6, 122.6, 124.4, 124.5, 129.7, 143.8, 159.4, 196.9; EIMS: m/z (%) 227 (90), 226 (100), 212 (30), 198 (22), 197 (34), 184 (20), 157 (25).

Anal. Calcd for: $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.68; H, 4.82; N, 16.37.

*4.4.11. (E)-3-(Azidomethyl)-6-(thiophen-2-yl)hex-3-en-5-yn-2-one (**4k**).* Yield: 69%; yellow oil; IR (neat) 2181, 2094, 1668 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (s, 3H, CH_3), 4.27 (s, 2H, CH_2), 6.97 (s, 1H, CH), 7.07 (dd, J=5.2 and 3.9 Hz, 1H, aromatic), 7.37 (dd, J=3.9 and 1.1 Hz, 1H, aromatic), 7.44 (dd, J=5.2 and 1.1 Hz, 1H, aromatic); ^{13}C NMR ($CDCl_3$) δ 25.5, 47.1, 88.9, 99.4, 121.5, 124.0, 127.7, 130.1, 134.2, 143.1, 196.8; EIMS: m/z (%) 205 (98), 190 (59), 162 (41), 106 (100). Anal. Calcd for $C_{11}H_9N_3OS$: C, 57.13; H, 3.92; N, 18.17. Found: C, 57.01; H, 4.06; N, 17.89.

*4.4.12. (E)-3-(Azidomethyl)undec-3-en-5-yn-2-one (**4l**).* Yield: 84%; yellow oil; IR (neat) 2211, 2095, 1671 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J=7.2 Hz, 3H, CH_3), 1.31–1.46 (m, 4H, two CH_2), 1.56–1.65 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 2.47 (dt, J=7.2 and 2.2 Hz, 2H, CH_2), 4.18 (s, 2H, CH_2), 6.75 (t, J=2.2 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.1, 22.1, 25.4, 27.9, 31.0, 46.7, 76.5, 109.3, 125.7, 143.4, 197.1; EIMS: m/z (%) 219 (1) [M^+], 191 (71), 176 (31), 148 (87), 106 (100). Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.73; H, 7.81; N, 19.16. Found: C, 65.59; H, 7.65; N, 19.01.

*4.4.13. (E)-3-Azido-2-(3-phenylprop-2-ynylidene)cyclopentanone (**4m**).* Yield: 90%; yellow oil; IR (neat) 2189, 2100, 1716, 1613 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08–2.17 (m, 2H, CH_2), 2.34–2.44 (m, 1H, CH_2), 2.52–2.65 (m, 1H, CH_2), 5.04–5.07 (m, 1H, CH), 6.89 (d, J=1.7 Hz, 1H, CH), 7.35–7.42 (m, 3H, aromatic), 7.53–7.56 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 27.1, 35.7, 60.4, 86.0, 104.0, 117.8, 121.8, 128.6, 129.9, 132.3, 144.3, 202.8; EIMS: m/z (%) 209 (100), 181 (59), 180 (75), 155 (23). Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.93; H, 4.86; N, 17.52.

*4.4.14. (E)-3-Azido-2-(3-phenylprop-2-ynylidene)cyclohexanone (**4n**).* Yield: 83%; yellow oil; IR (neat) 2193, 2095, 1683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84–1.90 (m, 2H, CH_2), 2.04–2.09 (m, 2H, CH_2), 2.27–2.39 (m, 1H, CH_2), 2.61–2.70 (m, 1H, CH_2), 5.24–5.28 (m, 1H, CH), 6.98 (s, 1H, CH), 7.35–7.41 (m, 3H, aromatic), 7.51–7.54 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 18.1, 28.9, 39.3, 58.7, 85.3, 104.6, 121.4, 121.9, 128.5, 129.7, 132.0, 142.0, 197.5; EIMS: m/z (%) 223 (90), 195 (100), 194 (27), 167 (38), 139 (10). Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.57; H, 5.19; N, 16.48.

*4.4.15. (E)-3-azido-2-(oct-2-ynylidene)cyclohexanone (**4o**).* Yield: 90%; yellow oil; IR (neat) 2207, 2096, 1687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J=7.2 Hz, 3H, CH_3), 1.33–1.43 (m, 4H, two CH_2), 1.55–1.62 (m, 2H, CH_2), 1.73–1.90 (m, 2H, CH_2), 1.96–2.11 (m, 2H, CH_2), 2.22–2.35 (m, 1H, CH_2), 2.45 (td, J=7.2 and 2.2 Hz, 2H, CH_2), 2.57–2.66 (m, 1H, CH_2), 5.13–5.17 (m, 1H, CH), 6.76 (t, J=2.2 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$)[22] δ 13.9, 18.1, 20.1, 22.1, 27.9, 28.8, 31.0, 39.3, 58.5, 107.9, 122.7, 141.4, 197.8; ^{13}C NMR (DMSO-d_6) δ 13.9, 17.9, 19.3, 21.6, 27.4, 28.1, 30.5, 58.8, 77.0, 107.4, 121.2, 142.1, 197.4; EIMS: m/z (%) 217 (73), 174 (100), 161 (22), 146 (22), 132 (11), 118 (19). Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.26; H, 7.69; N, 17.01.

4.5. General procedure for the synthesis of 3,5-disubstituted 6*H*-pyrrolo[1,2-*c*][1,2,3]triazoles 5a–k and 7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-*a*]indol-5(6*H*)-ones 5n, 5o

A stirred solution of the azido enyne **4** (2 mmol) in 6 mL of toluene was heated at reflux temperature for 1 h and the solvent was evaporated in vacuo. The mixture was chromatographed on silica gel eluting with hexane and ethyl acetate (3:1) to produce **5** as a solid.

*4.5.1. Methyl 3-phenyl-6H-pyrrolo[1,2-c][1,2,3]triazole-5-carboxylate (**5a**).* Yield: 81%; white solid; mp: 154–156 °C (hexane–EtOAc); IR (KBr) 1713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.92 (s, 3H, CH_3), 5.17 (d, J=2.2 Hz, 2H, CH_2), 7.36–7.50 (m, 3H, aromatic), 7.74 (t, J=2.2 Hz, 1H, CH), 7.88–7.91 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.1, 52.5, 125.9, 127.4, 128.6, 129.1, 130.1, 137.7, 139.4, 139.9, 162.2; EIMS: m/z (%) 215 (100), 200 (13), 184 (52), 156 (83), 138 (29), 106 (33); HRMS (FAB$^+$): m/z $C_{13}H_{11}N_3O_2Na$ [M+Na]$^+$ calcd 264.0750, obsd 264.0747. Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.57; H, 4.50; N, 17.28.

*4.5.2. Methyl 3-(4-chlorophenyl)-6H-pyrrolo[1,2-c][1,2,3]triazole-5-carboxylate (**5b**).* Yield: 91%; white solid; mp: 190–192 °C (hexane–EtOAc); IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H, CH_3), 5.16 (d, J=2.2 Hz, 2H, CH_2), 7.41–7.46 (m, 2H, aromatic), 7.69 (t, J=2.2 Hz, 1H, CH), 7.79–7.83 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.2, 52.5, 126.8, 127.0, 127.1, 128.7, 129.3, 134.4, 138.1, 139.4, 162.1; EIMS: m/z (%) 251 (33), 249 (100), 220 (21), 218 (66), 192 (25), 190 (78), 154 (28), 138 (36), 106 (56); HRMS (FAB$^+$): m/z $C_{13}H_{10}ClN_3O_2Na$ [M+Na]$^+$ calcd 298.0361, obsd 298.0360. Anal. Calcd for $C_{13}H_{10}ClN_3O_2$: C, 56.64; H, 3.66; N, 15.24. Found: C, 56.49; H, 3.78; N, 15.03.

*4.5.3. Methyl 3-(4-fluorophenyl)-6H-pyrrolo[1,2-c][1,2,3]triazole-5-carboxylate (**5c**).* Yield: 88%; white solid; mp: 196–197 °C (hexane–EtOAc); IR (KBr) 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H, CH_3), 5.16 (d, J=1.9 Hz, 2H, CH_2), 7.13–7.20 (m, 2H, aromatic), 7.69 (t, J=1.9 Hz, 1H, CH), 7.85–7.89 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 52.1, 52.5, 116.1 (d, J=21.7 Hz), 126.4, 127.1, 127.6 (d, J=8.3 Hz), 137.9, 138.9, 139.1, 162.1, 162.8 (d, J=248.7 Hz); EIMS: m/z (%) 233 (100), 218 (13), 202 (53), 174 (76), 138 (24), 106 (42); HRMS (FAB$^+$): m/z $C_{13}H_{10}FN_3O_2Na$ [M+Na]$^+$ calcd 282.0656, obsd 282.0656. Calcd for: $C_{13}H_{10}FN_3O_2$: C, 60.23; H, 3.89; N, 16.21. Found: C, 60.02; H, 3.69; N, 16.03.

*4.5.4. Methyl 3-(3-methoxyphenyl)-6H-pyrrolo[1,2-c][1,2,3]triazole-5-carboxylate (**5d**).* Yield: 91%; white solid; mp: 150–152 °C (hexane–EtOAc); IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.89 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 5.15 (d, J=2.2 Hz, 2H, CH_2), 6.90–6.94 (m, 1H, aromatic), 7.34–7.41 (m, 2H, aromatic), 7.49–7.50 (m, 1H, aromatic), 7.71 (t, J=2.2 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.1, 52.4, 55.4, 111.0, 114.7, 118.3, 127.3, 130.1, 131.5, 137.8, 139.5, 139.7, 160.2, 162.2; EIMS: m/z (%) 245 (100), 230 (13), 214 (50), 186 (77), 138 (37), 106 (29); HRMS (FAB$^+$): m/z $C_{14}H_{13}N_3O_3Na$ [M+Na]$^+$ calcd 294.0856, obsd 294.0854. Anal. Calcd for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.72; H, 4.76; N, 15.34.

*4.5.5. Methyl 3-(thiophen-2-yl)-6H-pyrrolo[1,2-c][1,2,3]triazole-5-carboxylate (**5e**).* Yield: 86%; white solid; mp: 195–197 °C (hexane–EtOAc); IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.91 (s, 3H, CH_3), 5.16 (d, J=1.9 Hz, 2H, CH_2), 7.13 (dd, J=5.2 and 3.0 Hz, 1H, aromatic), 7.38 (d, J=5.2 Hz, 1H, aromatic), 7.46 (d, J=3.0 Hz, 1H, aromatic), 7.67 (t, J=1,9 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 52.3, 52.5, 124.4, 124.7, 125.9, 126.7, 127.9, 132.4, 137.5, 138.6, 162.1; EIMS: m/z (%) 221 (100), 206 (15), 190 (23), 162 (88), 138 (10), 106 (42); HRMS (FAB$^+$): m/z $C_{11}H_9N_3O_2SNa$ [M+Na]$^+$ calcd 270.0315, obsd 270.0316. Anal. Calcd for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99. Found: C, 53.21; H, 3.54; N, 17.24.

*4.5.6. Methyl 3-pentyl-6H-pyrrolo[1,2-c][1,2,3]triazole-5-carboxylate (**5f**).* Yield: 43%; white solid; mp: 70–72 °C (hexane–EtOAc); IR (KBr) 1722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J=7.2 Hz, 3H, CH_3), 1.33–1.39 (m, 4H, two CH_2), 1.68–1.76 (m, 2H, CH_2), 2.79 (t, J=7.2 Hz, 2H, CH_2), 3.88 (s, 3H, CH_3), 5.06 (d, J=2.2 Hz, 2H, CH_2), 7.46 (t, J=2.2 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 25.7, 28.8, 31.4, 51.9, 52.3, 127.2, 136.2, 140.1, 141.2, 162.5; EIMS: m/z (%) 207 (43), 176 (15), 164 (100), 138 (9), 132 (48); HRMS (FAB$^+$): m/z $C_{12}H_{17}N_3O_2Na$ [M+Na]$^+$ calcd 258.1220, obsd 258.1218. Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.26; H, 7.28; N, 17.86. Found: C, 61.07; H, 7.04; N, 17.68.

*4.5.7. 5-Acetyl-3-phenyl-6H-pyrrolo[1,2-c][1,2,3]triazole (**5g**).* Yield: 62%; white solid; mp: 152–154 °C (hexane–EtOAc); IR (KBr) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.54 (s, 3H, CH_3), 5.14 (d, J=1.9 Hz, 2H,

CH_2), 7.37–7.51 (m, 3H, aromatic), 7.57 (t, J=1.9 Hz, 1H, CH), 7.87–7.90 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.1, 51.9, 125.9, 126.3, 128.7, 129.1, 130.1, 139.5, 140.8, 146.5, 192.9; EIMS: m/z (%) 199 (75), 184 (100), 156 (16), 106 (54); HRMS (FAB$^+$): m/z $C_{13}H_{11}N_3ONa$ [M+Na]$^+$ calcd 248.0801, obsd 248.0800. Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.13; H, 5.04; N, 18.49.

*4.5.8. 5-Acetyl-3-(4-chlorophenyl)-6H-pyrrolo[1,2-c][1,2,3]triazole (**5h**).* Yield: 81%; white solid; mp: 195–196 °C; IR (KBr) 1661 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3H, CH_3), 5.17 (d, J=1.9 Hz, 2H, CH_2), 7.44–7.48 (m, 2H, aromatic), 7.56 (t, J=1.9 Hz, 1H, CH), 7.81–7.85 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.2, 52.0, 125.9, 127.1, 128.7, 129.3, 134.6, 139.6, 139.8, 146.8, 192.8; EIMS: m/z (%) 235 (21), 233 (64), 220 (51), 218 (100), 192 (4), 190 (12), 106 (68); HRMS (FAB$^+$): m/z $C_{13}H_{10}ClN_3ONa$ [M+Na]$^+$ calcd 282.0412, obsd 282.0411. Anal. Calcd for $C_{13}H_{10}ClN_3O$: C, 60.12; H, 3.88; N, 16.18. Found: C, 59.92; H, 3.69; N, 15.89.

*4.5.9. 5-Acetyl-3-(4-fluorophenyl)-6H-pyrrolo[1,2-c][1,2,3]triazole (**5i**).* Yield: 75%; white solid; mp: 154–156 °C; (hexane–EtOAc); IR (KBr) 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H, CH_3), 5.16 (d, J=1.9 Hz, 2H, CH_2), 7.15–7.21 (m, 2H, aromatic), 7.55 (t, J=1.9 Hz, 1H, CH), 7.85–7.89 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.1, 52.0, 116.2 (d, J=22.0 Hz), 126.0, 126.5, 127.7 (d, J=8.6 Hz), 139.3, 140.0, 146.6, 162.9 (d, J=249.0 Hz), 192.8; EIMS: m/z (%) 217 (73), 202 (100), 174 (17), 146 (9), 106 (77); HRMS (FAB$^+$): m/z $C_{13}H_{10}FN_3ONa$ [M+Na]$^+$ calcd 266.0707, obsd 266.0705. Anal. Calcd for $C_{13}H_{10}FN_3O$: C, 64.19; H, 4.14; N, 17.28. Found: C, 64.26; H, 4.20; N, 17.01.

*4.5.10. 5-Acetyl-3-(3-methoxyphenyl)-6H-pyrrolo[1,2-c][1,2,3]triazole (**5j**).* Yield: 92%; white solid; mp: 165–157 (hexane–EtOAc); IR (KBr) 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 5.16 (d, J=1.9 Hz, 2H, CH_2), 6.93–6.97 (m, 1H, aromatic), 7.39–7.41 (m, 2H, aromatic), 7.50–7.51 (m, 1H, aromatic), 7.58 (t, J=1.9 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 26.2, 51.9, 55.4, 111.2, 114.5, 118.2, 126.3, 130.1, 131.4, 139.7, 140.7, 146.5, 160.1, 193.0; EIMS: m/z (%) 229 (70), 214 (100), 186 (20), 106 (42); HRMS (FAB$^+$): m/z $C_{14}H_{13}N_3O_2Na$ [M+Na]$^+$ calcd 278.0907, obsd 278.0905. Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.63; H, 5.06; N, 16.21.

*4.5.11. 5-Acetyl-3-(thiophen-2-yl)-6H-pyrrolo[1,2-c][1,2,3]triazole (**5k**).* Yield: 80%; white solid; mp: 157–158 °C (hexane–EtOAc); IR (KBr) 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H, CH_3), 5.15 (d, J=2.0 Hz, 2H, CH_2), 7.14 (dd, J=5.4 and 3.9 Hz, 1H, aromatic), 7.39 (dd, J=5.4 and 0.9 Hz, 1H, aromatic), 7.48 (dd, J=3.9 and 0.9 Hz, 1H, aromatic), 7.51 (t, J=2.0 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 26.1, 52.1, 124.8, 125.6, 126.0, 128.0, 132.3, 136.2, 138.8, 146.3, 192.9; EIMS: m/z (%) 205 (98), 190 (58), 162 (40), 106 (100); HRMS (FAB$^+$): m/z $C_{11}H_9N_3OSNa$ [M+Na]$^+$ calcd 254.0366, obsd 254.0365. Anal. Calcd for $C_{11}H_9N_3OS$: C, 57.13; H, 3.92; N, 18.17. Found: C, 56.88; H, 3.81; N, 18.02.

*4.5.12. 3-Phenyl-7,8-dihydro-4H-[1,2,3]triazolo[1,5-a]indol-5(6H)-one (**5n**).* Yield: 85%; light yellow solid; mp: 204–205 °C (hexane–EtOAc); IR (KBr) 1668, 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.32–2.40 (m, 2H. CH_2), 2.61–2.66 (m, 2H, CH_2), 3.16–3.22 (m, 2H, CH_2), 3.82 (dd, J=2.7 and 2.5 Hz, 2H, CH_2) 7.35–7.51 (m, 3H, aromatic), 7.85–7.88 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.2, 22.2, 25.7, 37.3, 125.6, 128.3, 129.0, 129.2, 129.9, 135.7, 140.6, 152.8, 195.0; EIMS: m/z (%) 251 (2) [M$^+$], 225 (89), 207 (31), 197 (34), 169 (100); HRMS (FAB$^+$): m/z $C_{15}H_{13}N_3ONa$ [M+Na]$^+$ calcd 274.0958, obsd 274.0953. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.56; H, 5.47; N, 16.50.

*4.5.13. 3-Pentyl-7,8-dihydro-4H-[1,2,3]triazolo[1,5-a]indol-5(6H)-one (**5o**).* Yield: 47%; yellow solid; mp: 49–50 °C (hexane–EtOAc); IR (KBr) 1670, 1634 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J=6.1 Hz, 3H, CH_3), 1.32–1.37 (m, 4H, two CH_2), 1.67–1.77 (m, 2H, CH_2), 2.29–2.37 (m, 2H, CH_2), 2.58–2.63 (m, 2H, CH_2), 2.80 (t, J=7.7 Hz, 2H, CH_2), 3.12–3.18 (m, 2H, CH_2), 3.57 (dd, J=2.7 and 2.5 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 14.0, 21.2, 22.2, 22.4, 24.4, 25.3, 28.1, 31.4, 37.3, 129.0, 136.6, 141.9, 152.9, 195.2; EIMS: m/z (%) 245 (2) [M$^+$], 217 (56), 174 (100), 146 (21), 132 (11), 118 (16); HRMS (FAB$^+$): m/z $C_{14}H_{19}N_3ONa$ [M+Na]$^+$ calcd 268.1428, obsd 268.1425. Anal. Calcd for $C_{14}H_{19}N_3O$: C, 68.54; H, 7.81; N, 17.13. Found: C, 68.25; H, 7.92; N, 16.95.

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