Synthesis of 5*H*-1,2,3-Triazolo[4,3-*a*][2]benzazepines from the Baylis-Hillman Adducts of 2-Alkynylbenzaldehydes

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The facile synthesis of 5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepines **5a-d** by the intramolecular 1,3-dipolar cycloaddition reaction of 2-alkynylphenylallyl azides **4a-d** is described. The latter were readily obtained from 2-alkynylbenzaldehydes **1a-d** through the Baylis-Hillman adducts **2a-d** followed by acetylation to compounds **3a-d** and nucleophilic substitution by azide to compounds **4a-d**.

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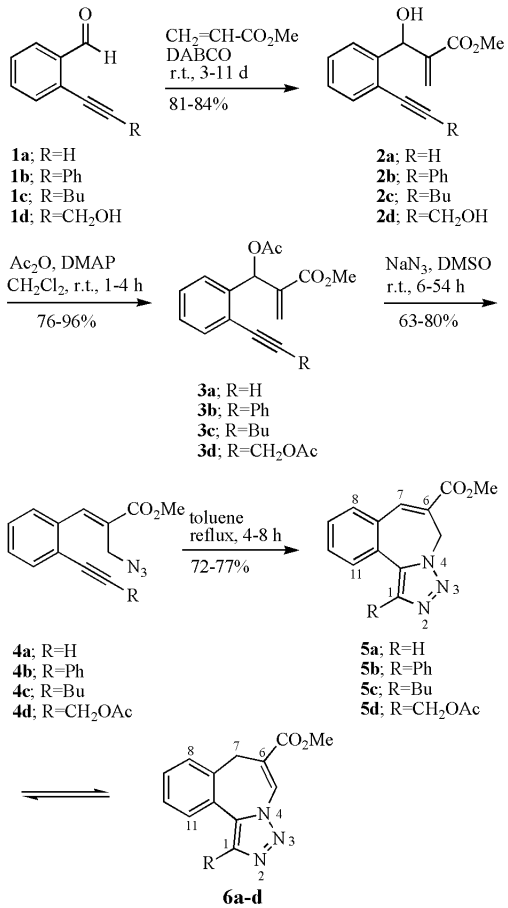
1,2,3-Triazoles and 1,2,3-triazole containing heterocycles are known to display a wide range of biological activities such as anti-HIV activity [1], antimicrobial activity against Gram positive bacteria [2], selective β_3 adrenergic receptor agonism [3], and antianxiety activity [4]. 1,2,3-Triazoles have also found wide use in industrial applications such as dyes, corrosion inhibition, photostabilizers, photographic materials, and agrochemicals [5]. Therefore, it is important to develop new and more efficient synthetic pathways to a diverse array of 1,2,3-triazole pharmacophores. Several different methods have been described for the synthesis of 1,2,3-triazoles, including the intramolecular cyclization of bishydrazones or mixed hydrazones, miscellaneous oxidations, as well as the most important 1,3-dipolar cycloaddition of azides to alkynes [5-10].

The Baylis-Hillman reaction has been the subject of recent reviews [11] and continues to elicit attention. We have demonstrated applications of this reaction in the synthesis of 3-oxo-2,3-dihydro-1*H*-isoindoles from 2-cyanobenzaldehyde [12] and 4*H*-tetrazolo[1,5-*a*][1]benzazepines from 2-azidobenzaldehyde using intramolecular 1,3-dipolar cycloaddition reaction [13]. Here we report a facile synthesis of 5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepines **5** *via* treatment of the Baylis-Hillman acetate adducts of 2-alkynylbenzaldehydes with azide followed by intramolecular 1,3-dipolar cycloaddition reaction.

The readily available acetylenic benzaldehydes **1a-d**, whose preparation has been previously described [14], provided a convenient starting point for the synthesis of this ring system, as shown in Scheme I. Treatment of 2-alkynylbenzaldehydes **1 a-d** with 3.0 molar equivalents of methyl acrylate in the presence of 1.0 molar equivalent of 1,4-diazabicyclo[2,2,2]octane (DABCO) in neat at room temperature afforded the adducts, methyl 3-(2-alkynylphenyl)-3-hydroxy-2-methylenepropanoates **2a-d** in good yields (81-84%). The reaction of adducts **2a-d** with acetic anhydride in the presence of catalytic amount of *N,N*-dimethylaminopyridine (DMAP) in dichloromethane at room temperature gave the Baylis-Hillman acetate adducts **3a-d** (76-96%). Nucleophilic substitution reaction of the acetates **3 a-d** with sodium azide in dimethyl sulfoxide at room temperature occurred in a S_N2' fashion to give the required key intermediates 2-alkynylphenylallyl azides **4a-d** (63-80%). The stereochemistry of the products was established by comparing NMR values of olefinic and methylene protons with literature values [15]. In all cases, the stereoselectivity was found to be 100% (*E*)-selectivity, as determined by ^{1}H nmr analysis. Finally, the intramolecular 1,3-dipolar cycloaddition reaction of azides with alkynes of **4a-d** in refluxing toluene produced good yields (72-77%) of the corresponding 5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepines

Scheme I



5 a-d. The infrared spectra of **5a-d** showed the disappearance of absorption of carbon-carbon triple bond and azide bands. In the ^{1}H nmr spectra, the charateristic chemical shift of the methine proton of C7 were found at δ = 7.92-8.03 as a singlet, and two methylene protons of C5 were observed at δ = 5.26-5.36 as a singlet. The possible tautomeric structure **6** was ruled out by two-dimensional NOESY experiment. In **5b**, correlation between C7 methine peak (s, δ = 8.03 ppm) and aromatic proton (m, δ = 7.55-7.57 ppm) was observed; a correlation between the C5 methylene protons (s, δ = 5.30 ppm) and any aromatic protons was not observed.

In summary, application of the Baylis-Hillman reaction to 2-alkynylbenzaldehydes provides convenient access to new substituted 5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepine derivatives by the intramolecular 1,3-dipolar cycloaddition of readily available 2-alkynylphenylallyl azides.

EXPERIMENTAL

All reagents and solvents were reagent grade or were purified by standard methods before use. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was performed on silica gel with fluorescent indicator coated on aluminium sheets. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. Mass spectra were obtained using a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The ^{1}H and ^{13}C nmr spectra were measured on a Gemini 300 spectrometer using deuteriochloroform. The NOESY spectrum was obtained on a 300 MHz Bruker spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane.

The 2-ethynylbenzaldehyde (**1a**) [14a], 2-(2-phenylethynyl)-benzaldehyde (**1b**) [14b], 2-(1-hexyn-1-yl)benzaldehyde (**1c**) [14c] and 2-(3-hydroxypropyn-1-yl)benzaldehyde (**1d**) [14d] were prepared following the literature procedure.

Methyl 3-(2-Ethynylphenyl)-3-hydroxy-2-methylenepropanoate (**2a**).

A solution of 2-ethynylbenzaldehyde **1a** (0.78 g, 6 mmoles), methyl acrylate (1.55 g, 18 mmoles) and DABCO (0.67 g, 6 mmoles) was stirred in a stoppered flask for four days at room temperature. The reaction mixture was diluted with water (20 ml) and extracted with dichloromethane (3 x 20 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/ethyl acetate (10:1) to afford 1.05 g (81%) of **2a** as an oil; ir (neat): 3435, 3280, 2104, 1715, 1629, 1435 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.30 (s, 1 H), 3.77 (s, 3 H), 3.79 (s, 1 H), 5.66 (s, 1 H), 6.07 (s, 1 H), 6.34 (s, 1 H), 7.20-7.57 (m, 4 H); ^{13}C nmr (deuteriochloroform): δ 52.02, 70.43, 81.27, 82.26, 120.68, 126.53, 126.83, 127.55, 129.16, 132.89, 140.97, 143.04, 166.96; ms: m/z (%) 216 (M$^+$, 16), 199 (14), 157 (33), 129 (36), 128 (100).

Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 69.93; H, 5.30.

Methyl 3-Hydroxy-2-methylene-3-(2-phenylethynyl)phenyl-propanoate (**2b**).

The procedure was the same as described in the preparation of **2a** with 2-(phenylethynyl)benzaldehyde **1b** (1.24 g, 6 mmoles) except reaction time (5 days). Yield: 1.47 g (84%); oil; ir (neat): 3431, 2217, 1711, 1633, 1493, 1439 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.28 (d, 1 H, J = 5.19 Hz), 3.75 (s, 3 H), 5.68 (s, 1 H), 6.15 (d, 1 H, J = 4.88 Hz), 6.34 (s, 1 H), 7.26-7.58 (m, 9 H); ^{13}C nmr (deuteriochloroform): δ 51.97, 70.71, 87.04, 94.57, 121.63, 122.96, 126.45, 126.72, 126.94, 127.63, 128.39, 128.80, 131.47, 132.25, 141.25, 142.56, 167.09; ms: m/z (%) 292 (M$^+$, 36), 260 (22), 232 (56), 231 (100), 203 (72), 202 (47), 178 (30).

Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.73; H, 5.27.

Methyl 3-[2-(1-Hexyn-1-yl)]phenyl-3-hydroxy-2-methylene-propanoate (**2c**).

The procedure was the same as described in the preparation of **2a** with 2-(1-hexyn-1-yl)benzaldehyde **1c** (1.12 g, 6 mmoles) except reaction time (11 days). Yield: 1.37 g (84%); oil; ir (neat): 3406, 2219, 1718, 1619, 1445 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.93 (t, 3 H, J = 7.17 Hz), 1.41-1.59 (two m, 4 H), 2.41 (t, 2 H, J = 7.02 Hz), 3.32 (d, 1 H, J = 4.88 Hz), 3.76 (s, 3 H), 5.60 (s, 1 H), 6.03 (d, 1 H, J = 4.88 Hz), 6.32 (s, 1 H), 7.19-7.48 (m, 4 H); ^{13}C nmr (deuteriochloroform): δ 13.56, 19.16, 21.95, 30.67, 51.92, 70.64, 78.21, 95.81, 122.50, 126.19, 126.52, 127.42, 127.81, 132.18, 141.19, 142.20, 167.08; ms: m/z (%) 272 (M$^+$, 12), 255 (17), 229 (41), 212 (38), 197 (37), 183 (56), 169 (62), 141 (89), 115 (100).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.83; H, 7.18.

Methyl 3-Hydroxy-3-[2-(3-hydroxypropyn-1-yl)]phenyl-2-methylenepropano-ate (**2d**).

The procedure was the same as described in the preparation of **2a** with 2-(3-hydroxypropyn-1-yl)benzaldehyde **1d** (0.96 g, 6 mmoles) except reaction time (3 days). Yield: 1.05g (81%); oil; ir (neat): 3473, 3411, 2140, 1723, 1695, 1634, 1429 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.51 (t, 1 H, J = 4.27 Hz), 3.37 (d, 1 H, J = 4.88 Hz), 3.75 (s, 3 H), 4.46 (d, 2 H, J = 4.27 Hz), 5.72 (s, 1 H), 6.08 (d, 1 H, J = 4.58 Hz), 6.33 (s, 1 H), 7.22-7.50 (m, 4 H); ^{13}C nmr (deuteriochloroform): δ 51.33, 52.08, 70.00, 83.17, 92.53, 121.32, 126.19, 126.66, 127.60, 128.73, 132.20, 141.32, 142.88, 167.20; ms: m/z (%) 228 (10), 200 (100), 168 (60), 129 (54), 115 (48).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.03; H, 5.50.

Methyl 3-Acetoxy-3-(2-ethynyl)phenyl-2-hydroxy-2-methylene-propanoate (**3a**).

To a stirred solution of **2a** (0.87 g, 4 mmoles) in dichloromethane (20 ml) was added acetic anhydride (0.57 ml, 6 mmoles) and *N,N*-dimethylaminopyridine (98 mg, 0.8 mmoles) at room temperature. After stirring at the same temperature for 1 hour the reaction mixture was diluted with water (10 ml) and extracted with dichlorormethane (3 x 10 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/ethyl acetate (10:1) to afford 0.99 g (96%) of **3a** as an oil; ir (neat): 3276, 2108, 1738, 1719, 1633, 1439 cm^{-1}; ^{1}H nmr (deuteriochloro-

form): δ 2.23 (s, 3 H), 3.33 (s, 1 H), 3.74 (s, 3 H), 5.69 (s, 1 H), 6.47 (s, 1 H), 7.11 (s, 1 H), 7.29-7.55 (m, 4 H); ^{13}C nmr (deuteriochloroform): δ 20.58, 52.08, 71.15, 82.33, 82.69, 121.79, 126.81, 127.32, 128.13, 128.84, 133.08, 138.52, 139.76, 165.36, 169.23; ms: m/z (%) 258 (M^+, 93), 215 (31), 199 (86), 161 (72), 128 (100).

Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.55; H, 5.19.

Methyl 3-Acetoxy-2-methylene-3-(2-phenylethynyl)phenylpropanoate (**3b**).

The procedure was the same as described in the preparation of **3a** with **2b** (1.17 g, 4 mmoles) except reaction time (4 hours). Yield: 1.18 g (88%); oil; ir (neat): 2217, 1742, 1719, 1633, 1493 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.12 (s, 3 H), 3.70 (s, 3 H), 5.74 (s, 1 H), 6.49 (s, 1 H), 7.23 (s, 1 H), 7.31-7.58 (m, 9 H); ^{13}C nmr (deuteriochloroform): δ 20.91, 52.01, 71.28, 86.37, 86.60, 94.77, 122.91, 126.80, 127.32, 127.56, 128.34, 131.48, 131.62, 132.29, 132.49, 138.66, 139.13, 165.48, 169.31; ms: m/z (%) 334 (M^+, 2), 292 (17), 259 (40), 231 (71), 215 (100), 203 (54), 187 (18).

Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.14; H, 5.23.

Methyl 3-Acetoxy-3-[2-(1-hexyn-1-yl)]phenyl-2-methylenepropanoate (**3c**).

The procedure was the same as described in the preparation of **3a** with **2c** (1.09 g, 4 mmoles) except reaction time (2 hours). Yield: 1.14 g (91%); oil; ir (neat): 2233, 1750, 1727, 1633, 1439 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.93 (t, 3 H, J = 7.17 Hz), 1.42-1.60 (two m, 4 H), 2.12 (s, 3 H), 2.42 (t, 2 H, J = 7.02 Hz), 3.73 (s, 3 H), 5.63 (s, 1 H), 6.45 (s, 1 H), 7.10 (s, 1 H), 7.23-7.43 (m, 4 H); ^{13}C nmr (deuteriochloroform): δ 13.53, 19.17, 20.87, 22.03, 30.58, 51.94, 71.35, 77.67, 96.17, 123.68, 126.45, 127.35, 127.51, 127.99, 132.33, 138.73, 138.92, 162.52, 169.23; ms: m/z (%) 314 (M^+, 24), 255 (100), 254 (81), 239 (46), 223 (50), 195 (79), 165 (98), 153 (59), 141(35).

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.38; H, 7.29.

Methyl 3-Acetoxy-3-[2-(3-acetoxypropyn-1-yl)]phenyl-2-methylenepropanoate (**3d**).

The procedure was the same as described in the preparation of **3a** with **2d** (0.97 g, 4 mmoles) except the amount of acetic anhydride (1.14 ml, 12 mmoles) and reaction time (3 hours). Yield: 1.01 g (76%); mp 61-62°; ir (potassium bromide): 1738, 1707, 1637 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.12 (s, 3 H), 2.13(s, 3 H), 3.73 (s, 3 H), 4.91 (s, 2 H), 5.71 (s, 1 H), 6.47 (s, 1 H), 7.03 (s, 1 H), 7.28-7.47 (m, 4 H); ^{13}C nmr (deuteriochloroform): δ 20.60, 20.72, 52.09, 52.47, 70.92, 83.42, 88.34, 121.67, 126.69, 127.33, 128.05, 128.72, 132.57, 138.34, 139.52, 165.22, 169.08, 170.05; ms: m/z (%) 330 (M^+, 7), 228 (53), 211 (68), 169 (100), 141 (75), 115 (36).

Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.45; H, 5.49. Found: C, 65.20; H, 5.26.

Methyl 2-Azidomethyl-3-(2-ethynylphenyl)-2-propenoate (**4a**).

To a stirred solution of **3a** (0.78 g, 3 mmoles) in dimethyl sulfoxide (15 ml) was added sodium azide (0.29 g, 4.5 mmoles) at room temperature. After stirring at the same temperature for 15 hours the reaction mixture was diluted with water (10 ml) and extracted with dichloromethane (3 x 20 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/ethyl acetate (7:1) to afford 0.45 g (68%) of **4a** as a solid after crystallization with hexane; mp 63-64°; ir (potassium bromide): 3252, 2116, 2100, 1715, 1625, 1431 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.39 (s, 1 H), 3.91 (s, 3 H), 4.13 (s, 2 H), 7.36-7.59 (m, 4 H), 8.23 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 47.18, 52.58, 81.08, 83.43, 122.60, 127.99, 128.95, 129.22, 133.14, 136.54, 142.66, 142.72, 167.23; ms: m/z (%) 241 (M^+, 18), 181 (14), 155 (100), 127 (55), 126 (26), 115 (11).

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.49; H, 4.38; N, 17.18.

Methyl 2-Azidomethyl-3-(2-phenylethynyl)phenyl-2-propenoate (**4b**).

The procedure was the same as described in the preparation of **4a** with **3b** (1.00 g, 3 mmoles) except reaction time (6 hours). Yield: 0.70 g (73%); mp 67-69°; ir (potassium bromide): 2104, 2073, 1715, 1622 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.92 (s, 3 H), 4.17 (s, 2 H), 7.36-7.56 (m, 9 H), 8.38 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 47.16, 52.47, 86.99, 95.93, 122.66, 123.91, 127.48, 128.11, 128.41, 128.66, 128.95, 131.25, 131.80, 135.87, 142.94, 143.22, 167.31; ms: m/z (%) 317 (M^+, 33), 288 (42), 274 (59), 230 (100), 203 (26), 155(75), 127(36).

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.68; H, 4.49; N, 12.91.

Methyl 2-Azidomethyl-3-[2-(1-hexyn-1-yl)]phenyl-2-propenoate (**4c**).

The procedure was the same as described in the preparation of **4a** with **3c** (0.94 g, 3 mmoles) except reaction time (54 hours). Yield: 0.71 g (80%); oil; ir (neat): 2225, 2100, 1712, 1633 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.95 (t, 3 H, J = 7.17 Hz), 1.45-1.63 (two m, 4 H), 2.46 (t, 2 H, J = 7.02 Hz), 3.90 (s, 3 H), 4.13 (s, 2 H), 7.31-7.47 (m, 4 H), 8.24 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 13.61, 19.15, 21.78, 30.52, 47.12, 52.16, 78.34, 97.25, 124.72, 127.01, 127.51, 128.81, 132.23, 135.75, 143.35, 143.53, 167.27; ms: m/z (%) 297 (M^+, 5), 268 (15), 255 (100), 194 (21), 180 (34), 168 (44), 155(45), 127 (24).

Anal. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.67; H, 6.44; N, 14.13. Found: C, 68.55; H, 6.20; N, 13.77.

Methyl 2-Azidomethyl-3-[2-(3-acetoxypropyn-1-yl)]phenyl-2-propenoate (**4d**).

The procedure was the same as described in the preparation of **4a** with **3d** (0.99 g, 3 mmoles) except reaction time (7 hours). Yield: 0.59 g (63%); oil; ir (neat): 2093, 1745, 1719, 1633 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.14 (s, 3 H), 3.91 (s, 3 H), 4.12 (s, 2 H), 4.93 (s, 2 H), 7.35-7.52 (m, 4 H), 8.17 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 20.70, 47.15, 52.56, 83.88, 89.13, 122.56, 127.97, 128.82, 129.03, 129.32, 132.74, 136.22, 142.44, 142.65, 167.13, 170.13; ms: m/z (%) 313 (M^+, 16), 270 (100), 182 (16), 154 (15).

Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.34; H, 4.83; N, 13.41. Found: C, 61.45; H, 4.70; N, 13.19.

6-Carbomethoxy-5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepine (**5a**).

A stirred solution of **4a** (0.24 g, 1 mmole) in toluene (3 ml) was heated at reflux temperature for 8 hours and the solvent was evaporated *in vacuo*. The residue was chromatographed on silica

gel eluting with hexane/ethyl acetate (5:1) to afford 0.18 g (73%) of **5a** as a solid; mp 122-123°; ir (potassium bromide): 1696, 1637, 1610 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.90 (s, 3 H), 5.36 (s, 2 H), 7.54-7.73 (m, 4 H), 7.92 (s, 1 H), 7.96 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 44.82, 52.83, 126.15, 127.76, 128.92, 129.40, 130.54, 131.32, 132.53, 136.29, 142.29, 142.37, 165.12; ms: m/z (%) 241 (M^+, 26), 181 (12), 155 (100), 127 (57), 126 (26), 115 (9).

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.53; H, 4.53; N, 17.28.

6-Carbomethoxy-1-phenyl-5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepine (**5b**).

The procedure was the same as described in the preparation of **5a** with **4b** (0.32 g, 1 mmole). Yield: 0.24 g (77%); mp 172-173°; ir (potassium bromide): 1704, 1631 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.92 (s, 3 H), 5.30 (s, 2 H), 7.34-7.57 (m, 9 H), 8.03 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 44.85, 52.80, 126.45, 128.00, 128.28, 128.63, 129.27, 129.75, 130.30, 130.97, 131.33, 131.68, 132.59, 142.50, 142.59, 145.18, 165.02; ms: m/z (%) 317 (M^+, 45), 288 (56), 274 (75), 230 (100), 202 (35), 155 (59), 127 (61).

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.78; H, 4.62; N, 13.02.

1-Butyl-6-carbomethoxy-5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepine (**5c**).

The procedure was the same as described in the preparation of **5a** with **4c** (0.30 g, 1 mmole). Yield: 0.23 g (75%); oil; ir (neat): 1707, 1629 cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.91 (t, 3 H, J = 7.32 Hz), 1.34-1.42 (m, 2 H), 1.69-1.73 (m, 2 H), 2.82 (t, 2 H, J = 7.78 Hz), 3.89 (s, 3 H), 5.26 (s, 2 H), 7.52-7.61 (m, 4 H), 7.93 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 13.73, 22.51, 25.53, 31.38, 44.77, 52.72, 126.91, 128.67, 129.02 129.98, 131.46, 131.91, 132.31, 142.26, 142.35, 145.83, 165.08; ms: m/z (%) 297 (M^+, 6), 268 (16), 255 (100), 194 (23), 180 (32), 168 (50), 167 (40), 166 (34), 155 (48), 115 (13).

Anal. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.67; H, 6.44; N, 14.13. Found: C, 68.32; H, 6.19; N, 13.87.

1-Acetoxymethyl-6-carbomethoxy-5*H*-1,2,3-triazolo[4,3-*a*]-[2]benzazepine (**5d**).

The procedure was the same as described in the preparation of **5a** with **4d** (0.31 g, 1 mmole) except reaction time (4 hours). Yield: 0.23 g (72%); mp 148-150°; ir (potassium bromide): 1742, 1711, 1631 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.12 (s, 3 H), 3.90 (s, 3 H), 5.26 (s, 2 H), 5.31 (s, 2 H), 7.56-7.72 (m, 4 H), 7.95 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 20.90, 44.89, 52.85, 57.69, 125.53, 128.88, 129.60, 130.47, 132.19, 132.34, 134.54, 139.70, 142.11, 142.20, 164.87, 170.64; ms: m/z (%) 31 (M^+, 17), 281 (26), 270 (100), 166 (18), 154 (20).

Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.34; H, 4.83; N, 13.41. Found: C, 61.16; H, 4.60; N, 13.22.

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