The [3 + 2] Cycloaddition Route to 5-Carbomethoxy-4*H*-1,2,3-triazolo[1,5-*a*][1]benzazepines from Baylis-Hillman Acetates of 2-Azidobenzaldehydes

Young Seok Song and Kee-Jung Lee*

Organic Synthesis Laboratory, Department of Chemical Engineering
Hanyang University, Seoul 133-791, Korea
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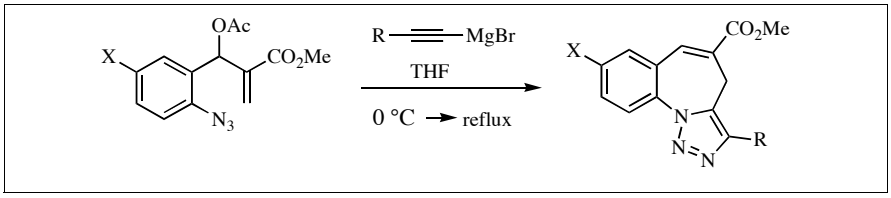

A new, simple synthesis of 5-carbomethoxy-4*H*-1,2,3-triazolo[1,5-*a*][1]benzazepines from the reaction of several Baylis-Hillman acetates of 2-azidobenzaldehydes with alkynide Grignard reagents such as phenylethynyl-, 1-propynyl- and ethynylmagnesium bromides followed by cycloaddition reaction has been described.

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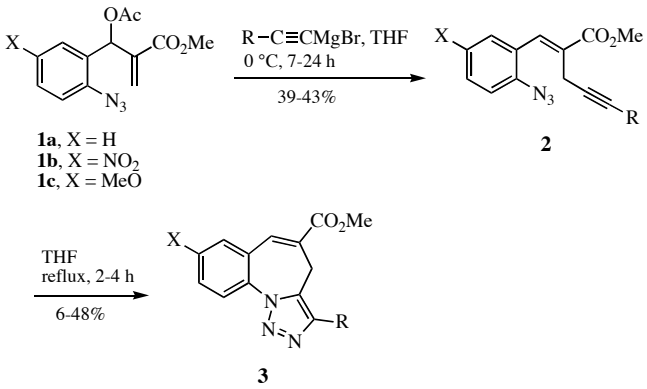
1,2,3-Triazoles and 1,2,3-triazole containing heterocycles are known to exhibit a wide range of biological activities such as anti-HIV activity [1], antimicrobial activity [2], selective ß$_3$ adrenergic receptor angonism [3], and antianxiety activity [4]. Also, the pharmacological value of benzazepines such as anticonvulsant, antiarrhythmic, antiinflammartory and analgesic activity has been noted [5]. Therefore, it is important to develop new and more efficient synthetic pathways to a diverse array of 1,2,3-triazole pharmacophores. The main synthetic route involves a 1,3-dipolar cycloaddition of an azide with an alkyne [6] or an alkyne equivalent such as a vinyl acetate, an enamine or an enol ether [7], although there are several other synthetic methods available.

The Baylis-Hillman (BH) reaction has been the subject of recent reviews [8] and continues to elicit attention. Among them, the BH adducts have been applied to provide convenient access to benzannulated or other heterocyclic systems [9]. Recently, we described facile syntheses of 4*H*-tetrazolo[1,5-*a*][1]benzazepines [10], 5*H*-1,2,3-triazolo[4,3-*a*][2]benzazepines [11] and naphtho[2,1-*c*]isoxazoles [12] from the BH adducts of 2-azidobenzaldehydes and 2-alkynylbenzaldehydes using an intramolecular 1,3-dipolar cycloaddition reaction. While it has been reported that the S_N2' reaction of the BH acetates with phenylethynylmagnesium bromide or 1-propynylmagnesium bromide afford the corresponding 2-carbomethoxypent-1-en-4-ynes [13]. At this stage it occurred to us that a one-pot procedure for obtaining a novel 1,2,3-triazole derivatives from the BH acetates of 2-azidobenzaldehydes should be possible. We herein report a simple synthesis of 5-carbomethoxy-4*H*-1,2,3-triazolo[1,5-*a*][1]-benzazepines by the tandem nucleophilic substitution of alkynides and an intramolecular 1,3-dipolar cycloaddition reaction of the BH acetates of 2-azidobenzaldehydes.

Scheme I



2, 3	a	b	c	d	e	f	g	h	i
X	H	NO_2	MeO	H	NO_2	MeO	H	NO_2	MeO
R	Ph	Ph	Ph	Me	Me	Me	H	H	H

The readily available *ortho*-azido BH acetates **1a**-**c**, whose preparation has been previously described [10,14], provided a convenient starting point for the synthesis of this ring system, as shown in Scheme I. Treatment of the BH acetates **1a**-**c** with 1.5 molar equivalents of phenylethynylmagnesium bromide in tetrahydrofuran at 0 °C for 7-24 hours and reflux for 3 hours afforded 4*H*-1,2,3-triazolo[1,5-*a*][1]benzazepines **3a**-**c** in 45-48% yields, directly. Similar reaction of **1a**-**c** with 1.2 molar equivalents of 1-propynylmagnesium bromide in tetrahydrofuran at 0 °C for 7-24 hours and reflux for 4 hours gave the corresponding 4*H*-1,2,3-triazolo[1,5-*a*][1]benzazepines **3d**-**f** in 35-40% yields. But, reaction of **1a**-**c** with ethynylmagnesium bromide afforded very disappointing

yields of **3g-i** (6-14%). Also, several attempts were made to isolate the intermediate, 2-methoxycarbonylpent-1-en-4-ynes **2a,b,e** (39-43%) and then transformed into the triazolobenzazepines **3a,b,e** in excellent yields (90-94%) in refluxing tetrahydrofuran, respectively. The infrared spectra of **2a,b,e** showed very strong absorption of 2124-2131 cm^{-1} for the azide bond and no absorptions were observed for the carbon-carbon triple bond. In the ^1H nmr spectra of **2a,b,e**, the chemical shift of the methine proton of C1 were found at δ = 7.69-7.83 as a singlet, and two methylene protons of C3 were observed at δ = 3.51-3.52 as a singlet for **2a,b** and at δ = 3.23 (J = 2.4 Hz) as a quartet for **2e**. The infrared spectra of **3a,b,e** showed the disappearance of absorption of azide bonds. In the ^1H nmr spectra of **3a-i**, the characteristic chemical shift of the methine proton of C6 were found at δ = 7.65-7.90 as a singlet, and two methylen protons of C4 were observed at δ = 3.67-4.00 as a singlet.

In summary, we developed the first synthetic method of 5-carbomethoxy-4*H*-1,2,3-triazolo[1,5-*a*][1]benzazepine derivatives applying the one-pot reaction of the Baylis-Hillman acetates of 2-azidobenzaldehydes with alkynide Grignard reagents.

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 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. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The ^1H and ^{13}C nmr spectra were measured on a Gemini 300 spectrometer using deuteriochloroform. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane.

Methyl 3-acetoxy-3-(2-azidophenyl)-2-methylenepropanoate (**1a**) [10], methyl 3-acetoxy-3-(2-azido-5-nitrophenyl)-2-methylenepropanoate (**1b**) [14] and methyl 3-acetoxy-3-(2-azido-5-methoxyphenyl)-2-methylenepropanoate (**1c**) [14] were prepared following the literature procedures. The phenylethynyl–, 1-propynyl- and ethynylmagnesium bromides were purchased from Aldrich.

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

To a stirred solution of **1a** (275 mg, 1 mmole) in tetrahydrofuran (5 ml) phenylethynylmagnesium bromide (1 *M* solution in tetrahydrofuran, 1.5 ml, 1.5 mmoles) was added dropwise at 0 °C. After stirring at 0 °C for 24 hours the reaction mixture was heated at reflux temperature for 3 hours. Then, water (20 ml) was added and the mixture was extracted with dichloromethane (3 × 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 (5:1) to afford 147 mg (46%) of **3a** as a white solid; mp 182 °C; ir (potassium bromide): 1703, 1633, 1493, 1439, 1293, 1241 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.91 (s, 3 H), 3.94 (s, 2 H) 7.41-7.64 (m, 6 H), 7.80 (s, 1 H), 7.89-7.92 (m, 2 H), 8.23 (d, J = 7.9 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 20.6, 52.7, 124.1, 126.4, 127.5, 128.0, 128.3, 128.9, 130.5, 130.7, 130.8, 131.6, 133.8, 135.4, 138.2, 142.7, 165.9.

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.67; H, 4.52; N, 13.02.

5-Carbomethoxy-8-nitro-3-phenyl-4*H*-1,2,3-triazolo[1,5-*α*][1]-benzazepine (**3b**).

To a stirred solution of **1b** (320 mg, 1 mmole) in tetrahydrofuran (5 ml) phenylethynylmagnesium bromide (1 *M* solution in tetrahydrofuran, 1.5 ml, 1.5 mmoles) was added dropwise at 0 °C. After stirring at 0 °C for 7 hours the reaction mixture was heated at reflux temperature for 3 hours. The work-up procedure was the same as described above to afford 163 mg (45%) of **3b** as a white solid; mp 175-176 °C; ir (potassium bromide): 1711, 1622, 1583, 1524, 1493, 1435, 1349, 1240 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.94 (s, 3 H), 4.00 (s, 2 H), 7.43-7.56 (m, 3 H), 7.83 (s, 1 H), 7.86-7.88 (m, 2 H), 8.42 (s, 3 H); ^{13}C nmr (deuteriochloroform): δ 20.6, 53.1, 125.2, 125.4, 127.0, 127.1, 127.5, 128.5, 129.0, 129.7, 133.0, 133.9, 136.2, 139.5, 143.5, 146.7, 165.3.

Anal. Calcd. for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.89; N, 15.46. Found: C, 62.71; H, 3.63; N, 15.22.

5-Carbomethoxy-8-methoxy-3-phenyl-4*H*-1,2,3-triazolo[1,5-*α*]-[1]benzazepine (**3c**).

To a stirred solution of **1c** (305 mg, 1 mmole) in tetrahydrofuran (5 ml) phenylethynylmagnesium bromide (1 *M* solution in tetrahydrofuran, 1.5 ml, 1.5 mmoles) was added dropwise at 0 °C. After stirring at 0 °C for 24 hours the reaction mixture was heated at reflux temperature for 3 hours. The work-up procedure was the same as described above to afford 166 mg (48%) of **3c** as a pale yellow solid; mp 207-208 °C; ir (potassium bromide): 1708, 1604, 1504, 1435, 1333, 1294, 1237 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.91 (s, 8 H), 6.99 (d, J = 2.7 Hz, 1 H), 7.15 (dd, J = 8.9 and 2.7 Hz, 1 H), 7.40-7.43 (m, 3 H), 7.75 (s, 1 H), 7.90 (d, J = 8.2, 2 H), 8.14 (d, J = 8.9, 1 H,); ^{13}C nmr (deuteriochloroform): δ 20.6, 52.7, 55.7, 115.1, 116.9, 125.5, 127.4, 127.6, 127.9, 128.8, 128.9, 130.6, 130.8, 133.3, 138.1, 142.5, 159.0, 165.9.

Anal. Calcd. for $C_{20}H_{17}N_3O_3$: C, 69.15; H, 4.93; N, 12.10. Found: C, 68.89; H, 4.71; N, 11.95.

5-Carbomethoxy-3-methyl-4*H*-1,2,3-triazolo[1,5-*α*][1]-benzazepine (**3d**).

To a stirred solution of **1a** (275 mg, 1 mmole) in tetrahydrofuran (5 ml) 1-propynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 2.4 ml, 1.2 mmoles) was added dropwise at 0 °C. After stirring at 0 °C for 23 hours the reaction mixture was heated at reflux temperature for 4 hours. Then, water (20 ml) was added and the mixture was extracted with dichloromethane (3 × 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 (2:1) to afford 89 mg (35%) of **3d** as a white solid; mp 160 °C; ir (potassium bromide): 1703, 1638, 1494, 1430, 1287, 1233 cm^{-1}; ^1H nmr (deuteriochloro-

form): δ 2.39 (s, 3 H), 3.69 (s, 2 H), 3.87 (s, 3 H), 7.47-7.60 (m, 3 H), 7.70 (s, 1 H), 8.14 (d, J = 7.9 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 9.8, 19.9, 52.6, 123.8, 126.2, 128.1, 130.7, 130.8, 131.7, 134.3, 135.6, 137.8, 138.7, 165.9.

Anal. Calcd. for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.68; H, 5.01; N, 16.27.

5-Carbomethoxy-3-methyl-8-nitro-4*H*-1,2,3-triazolo[1,5-*α*][1]-benzazepine (**3e**).

To a stirred solution of **1b** (320 mg, 1 mmole) in tetrahydrofuran (5 ml) 1-propynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 2.4 ml, 1.2 mmoles) was added dropwise at 0 ℃. After stirring at 0 ℃ for 7 hours the reaction mixture was heated at reflux temperature for 4 hours. The work-up procedure was the same as described above to afford 121 mg (40%) of **3e** as a white solid; mp 217 °C; ir (potassium bromide): 1715, 1614, 1579, 1520, 1493, 1349, 1291, 1271 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.41 (s, 3 H), 3.78 (s, 2 H), 3.91 (s, 3 H), 7.75 (s, 1 H), 8.37-8.41 (m, 3 H); ^{13}C nmr (deuteriochloroform): δ 9.7, 20.0, 53.0, 125.0, 125.1, 126.8, 127.1, 133.0, 134.5, 135.8, 139.7, 139.7, 146.6, 165.3.

Anal. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.83; H, 3.88; N, 18.42.

5-Carbomethoxy-8-methoxy-3-methyl-4*H*-1,2,3-triazolo[1,5-*α*]-[1]benzazepine (**3f**).

To a stirred solution of **1c** (305 mg, 1 mmole) in tetrahydrofuran (5 ml) 1-propynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 2.4 ml, 1.2 mmoles) was added dropwise at 0 °C. After stirring at 0 °C for 24 hours the reaction mixture was heated at reflux temperature for 4 hours. The work-up procedure was the same as described above to afford 100 mg (35%) of **3f** as a white solid; mp 189-190 °C; ir (potassium bromide): 1715, 1636, 1614, 1590, 1511, 1438, 1283, 1236 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.38 (s, 3 H), 3.67 (s, 2 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 6.94 (d, J = 2.7 Hz, 1 H), 7.10 (dd, J = 9.2 and 2.7 Hz, 1 H), 7.65 (s, 1 H), 8.05 (d, J = 9.2 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 9.8, 19.9, 52.7, 55.7, 115.3, 116.8, 125.2, 127.4, 129.2, 131.0, 133.8, 137.7, 138.5, 158.8, 165.9.

Anal. Calcd. for $C_{15}H_{15}N_3O_3$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.92; H, 5.08; N, 14.54.

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

To a stirred solution of **1a** (275 mg, 1 mmole) in tetrahydrofuran (5 ml) ethynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 3.0 ml, 1.5 mmoles) was added dropwise at 0 °C. After stirring at 0 °C for 24 hours the reaction mixture was heated at reflux temperature for 3 hours. Then, water (20 ml) was added and the mixture was extracted with dichloromethane (3 × 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 (2:1) to afford 31 mg (13%) of **3g** as a white solid; mp 118-119 °C; ir (potassium bromide): 1712, 1631, 1491, 1466, 1434, 1285, 1268 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.79 (s, 2 H), 3.88 (s, 3 H), 7.50-7.60 (m, 3 H), 7.56 (s, 1 H), 7.73 (s, 1 H), 8.18 (d, J = 7.9 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 20.4, 52.7, 123.9, 126.2, 128.3, 130.6, 130.7, 130.8, 131.7, 135.3, 137.5, 137.9, 165.8.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.47; H, 4.33; N, 17.08.

5-Carbomethoxy-8-nitro-4*H*-1,2,3-triazolo[1,5-*α*][1]benzazepine (**3h**).

To a stirred solution of **1b** (320 mg, 1 mmole) in tetrahydrofuran (5 ml) ethynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 3.0 ml, 1.5 mmoles) was added dropwise at 0 ℃. After stirring at 0 ℃ for 10 hours the reaction mixture was heated at reflux temperature for 3 hours. The work-up procedure was the same as described above to afford 18 mg (6%) of **3h** as a yellow solid; mp 220-221 °C; ir (potassium bromide): 1708, 1613, 1578, 1523, 1493, 1428, 1347, 1241 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.88 (s, 2 H), 3.91 (s, 3 H), 7.61 (s, 1 H), 7.78 (s, 1 H), 8.42-8.44 (m, 3 H); ^{13}C nmr (deuteriochloroform): δ 20.5, 53.1, 125.2, 125.3, 127.0, 127.1, 131.5, 132.9, 135.9, 137.8, 139.4, 146.7, 165.1.

Anal. Calcd. for $C_{13}H_{10}N_4O_4$: C, 54.55; H, 3.52; N, 19.57. Found: C, 54.29; H, 3.36; N, 19.26.

5-Carbomethoxy-8-methoxy-4*H*-1,2,3-triazolo[1,5-*α*][1]benzazepine (**3i**).

To a stirred solution of **1c** (305 mg, 1 mmole) in tetrahydrofuran (5 ml) ethynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 3.0 ml, 1.5 mmoles) was added dropwise at 0 ℃. After stirring at 0 ℃ for 24 hours the reaction mixture was heated at reflux temperature for 3 hours. The work-up procedure was the same as described above to afford 38 mg (14%) of **3i** as a white solid; mp 168-169 °C; ir (potassium bromide): 1715, 1636, 1605, 1584, 1508, 1438, 1279, 1257 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.76 (s, 2 H), 3.87 (s, 3 H), 3.90 (s, 3 H), 6.96 (d, J = 2.7 Hz, 1 H), 7.12 (dd, J = 8.9 and 2.7 Hz, 1 H), 7.54 (s, 1 H), 7.67 (s, 1 H), 8.08 (d, J = 8.9 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 20.5, 52.7, 55.7, 115.4, 116.8, 125.3, 127.5, 128.8, 130.6, 130.9, 136.8, 137.8, 159.0, 165.8.

Anal. Calcd. for $C_{13}H_{10}N_4O_4$: C, 61.99; H, 4.83; N, 15.49. Found: C, 61.73; H, 4.59; N, 15.22.

(*E*)-1-(2-Azidophenyl)-2-carbomethoxy-5-phenylpent-1-en-4-yne (**2a**).

To a stirred solution of **1a** (550 mg, 2 mmole) in tetrahydrofuran (10 ml) phenylethynylmagnesium bromide (1 *M* solution in tetrahydrofuran, 3 ml, 3 mmoles) was added dropwise at 0 ℃. After stirring at 0 ℃ for 24 hours the reaction mixture was poured into water (20 ml) and was extracted with dichloromethane (3 × 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 247 mg (39%) of **2a** as a white solid; mp 69-70 °C; ir (potassium bromide): 2124, 2092, 1703, 1598, 1575, 1481 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 3.51 (s, 2 H), 3.88 (s, 3 H), 7.20-7.45 (m, 8 H), 7.66-7.69 (m, 1 H), 7.83 (s, 1 H) ; ^{13}C nmr (deuteriochloroform): δ 18.9, 52.4, 81.1, 87.0, 118.3, 123.5, 124.8, 126.6, 127.8, 128.1, 129.0, 130.3, 130.5, 131.7, 135.9, 139.1, 167.2.

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.62; H, 4.55; N, 13.12.

(*E*)-1-(2-Azido-5-nitrophenyl)-2-carbomethoxy-5-phenylpent-1-en-4-yne (**2b**).

To a solution of **1b** (640 mg, 2 mmole) in tetrahydrofuran (10 ml) phenylethynylmagnesium bromide (1 *M* solution in tetrahydrofuran, 3 ml, 3 mmoles) was added dropwise at 0 °C and stirred at ambient temperature for 7 hours. The work-up procedure was the

same as described above to afford 315 mg (43%) of **2b** as a white solid; mp 104 °C; ir (potassium bromide): 2131, 2089, 1711, 1606, 1583, 1520, 1485, 1435, 1349 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.52 (s, 2 H), 3.91 (s, 3 H), 7.28-7.33 (m, 4 H), 7.45-7.49 (m , 2 H), 7.76 (s, 1 H), 8.29 (dd, J = 8.7 and 2.1 Hz, 1 H), 8.74 (d, J = 2.1 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 18.9, 52.7, 82.3, 85.7, 118.6, 123.1, 125.4, 126.2, 127.3, 128.1, 128.2, 131.3, 131.8, 133.6, 144.3, 145.4, 166.6.

Anal. Calcd. for $C_{19}H_{14}N_4O_4$: C, 62.98; H, 3.89; N, 15.46. Found: C, 62.71; H, 3.76; N, 15.21.

(*E*)-1-(2-Azido-5-nitrophenyl)-2-carbomethoxy-hex-1-en-4-yne (**2e**).

To a solution of **1b** (640 mg, 2 mmole) in tetrahydrofuran (10 ml) 1-propynylmagnesium bromide (0.5 *M* solution in tetrahydrofuran, 4.8 ml, 2.4 mmoles) was added dropwise at 0 °C and stirred at ambient temperature for 7 hours. The work-up procedure was the same as described above to afford 212 mg (43%) of **2e** as a white solid; mp 98 °C; ir (potassium bromide): 2131, 2089, 1707, 1606, 1575, 1520, 1474, 1435, 1353, 1287 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.84 (t, J = 2.4 Hz, 3 H), 3.22 (q, J = 2.4 Hz, 2 H), 3.89 (s, 3 H), 7.32 (d, J = 8.8 Hz, 1 H), 7.69 (s, 1 H), 8.28 (dd, J = 8.8 and 2.4 Hz, 1 H), 8.72 (d, J = 2.4 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 3.5, 18.2, 52.6, 75.3, 78.0, 118.5, 125.2, 126.3, 127.4, 132.0, 133.1, 144.3, 145.3, 166.7.

Anal. Calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.74; H, 3.86; N, 18.49.

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

Stepwise. A stirred solution of **2a** (317 mg, 1 mmole) in tetrahydrofuran (5 ml) was heated at reflux temperature for 3 hours and the resulting solution was concentrated to dryness. The residue was crystallized from ether/petroleum ether to afford 285 mg (90%) of **3a** as a white solid.

5-Carbomethoxy-8-nitro-3-phenyl-4*H*-1,2,3-triazolo[1,5-α][1]-benzazepine (**3b**).

Stepwise. A stirred solution of **2b** (362 mg, 1 mmole) in tetrahydrofuran (5 ml) was heated at reflux temperature for 3 hours. The work-up procedure was the same as described above to afford 329 mg (91%) of **3b** as a white solid.

5-Carbomethoxy-3-methyl-8-nitro-4*H*-1,2,3-triazolo[1,5-α][1]-benzazepine (**3e**).

Stepwise. A stirred solution of **2e** (300 mg, 1 mmole) in tetrahydrofuran (5 ml) was heated at reflux temperature for 2 hours. The work-up procedure was the same as described above to afford 282 mg (94%) of **3e** as a white solid.

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* Author to whom correspondence should be addressed.

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