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# One-Pot Synthesis of 1-Arylmethyl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles via a Cross-Coupling/Click Reaction Sequence

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## 1 General information

NMR spectra were recorded on JEOL JNM-A-500 or JEOL JNM-ECA-600 spectrometers. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Coupling constants *J* are quoted in Hz. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer, and only the strongest/structurally most important absorption peaks are listed. Electrospray ionization (ESI) HRMS analyses were measured on a Thermo Scientific Exactive instrument. Melting points were determined on a Yamato MP-21 and are uncorrected. TLC analyses were carried out using aluminum sheets pre-coated with silica gel 60 $F_{254}$ purchased from Merck. Product purification was performed by column chromatography using silica gel 60 (Kanto Chemical, 63-210 μm). All reactions were carried out under an argon atmosphere. Unless otherwise noted, commercially available materials were used without any purification. Alk-1-yne, 2-methylbut-2-ene, and $Et_3N$ were used after distillation over $CaH_2$ under argon. THF was distilled from Na-benzophenone ketyl under argon before use. Borane dimethyl sulfide complex ($BH_3 \cdot SMe_2$) was purchased from Aldrich. (Trimethylsilyl)ethynyl bromide was

prepared according to the literature procedure.[1]

**2 General experimental procedure**

To a solution of $BH_3 \cdot SMe_2$ (1 mmol) in THF (3 mL) was added 2-methylbut-2-ene (0.14 g, 2 mmol) dropwise at – 15 ºC under argon, and the reaction mixture was stirred for 2 h at r.t. to form a solution of disiamylborane in THF.[2] To this solution was added alk-1-yne (1 mmol) dropwise at – 15 ºC, and the mixture was stirred for 2 h at 0 ºC. A solution of (*E*)-alk-1-enyldisiamylborane **1** (1 mmol) in THF, thus prepared, was cooled to – 15 ºC, and $Cu(acac)_2$ (0.013 g, 0.05 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.119 g, 0.67 mmol) and NaOMe (1M, 0.75 mL, 0.75 mmol). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. The solvents (THF and MeOH) were removed under reduced pressure, and acetone (2 mL) and water (1 mL) were added to the residue under argon. To the resulting mixture including (*E*)-alk-3-en-1-yne **2** were added successively (+)-sodium L-ascorbate (0.02 g, 0.1 mmol) and sodium azide (0.033 g, 0.5 mmol) under a flow of argon, followed by dropwise addition of benzyl bromide (0.086 g, 0.5 mmol). The resultant mixture was stirred at r.t. for 24 h and then treated with 3M NaOH (1 mL) and 30% $H_2O_2$ (0.5 mL) at 0 ºC for 1 h or by bubbling air through the solution with tube pump at r.t. for 2 h to oxidize the residual organoboron compound. The mixture was extracted with EtOAc (3 × 10 mL), washed with brine (10 mL), dried ($Na_2SO_4$), and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to give product **3**.

**References**

1. Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem. Int. Ed. Engl*. **1984**, *23*, 727.
2. Brown, H. C.; Mandal, A. K.; Kulkarni, S. U. *J. Org. Chem*. **1977**, *42*, 1392.

**2 Characterization data of the products**

**1-benzyl-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole** (**3aa**)

White solid. Eluent: hexane-EtOAc (7:3); mp 66–67 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3H), 1.23–1.35 (m, 6H), 1.38–1.47 (m, 2H), 2.14–2.19 (m, 2H), 5.46 (s, 2H), 6.32–6.40 (m, 2H), 7.23–7.26 (m, 2H), 7.31–7.37 (m, 3H), 7.35 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 13.9 ($CH_3$), 22.4 ($CH_2$), 28.6 ($CH_2$), 28.8 ($CH_2$), 31.5 ($CH_2$), 32.7($CH_2$), 53.8 ($CH_2$), 118.0 (=CH), 119.1 (=CH), 127.8 (2 × $CH_{arom}$), 128.4 ($CH_{arom}$), 128.8 (2 × $CH_{arom}$), 133.5 (=CH), 134.6 ($C_{arom}$), 146.7 (=C). IR (neat): 3033, 2923, 2854, 1454, 1222, 1049, 964, 761, 698 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{23}N_3Na$: 292.1790; found: 292.1787.

**1-Benzyl-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3ba)**

White solid. Eluent: hexane-EtOAc (7:3); mp 141–143 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 5.46 (s,

2H), 7.05 (d, *J* = 16.1 Hz, 1H), 7.21–7.36 (m, 9H), 7.42–7.46 (m, 2H), 7.51 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 53.9 ($CH_2$), 116.5 (=CH), 126.2 (2 × $CH_{arom}$), 127.7 ($CH_{arom}$), 127.8 (2 × $CH_{arom}$), 128.5 (2 × $CH_{arom}$), 128.6 ($CH_{arom}$), 128.9 (2 × $CH_{arom}$), 130.4 (=CH), 134.4 ($C_{arom}$), 136.5 ($C_{arom}$). IR (KBr): 1494, 1454, 1434, 1355, 1218, 1045, 970, 796, 758, 705, 692, 650 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{17}H_{15}N_3Na$: 284.1164; found: 284.1160.

**1-Benzyl-4-[(*E*)-5-chloropent-1-enyl]-1*H*-1,2,3-triazole (3ca)**

White solid. Eluent: hexane-EtOAc (7:3); mp 43–45 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.87–1.95 (m, 2H), 2.30–2.38 (m, 2H), 3.55 (t, *J* = 6.3 Hz, 2H), 5.48 (s, 2H), 6.30–6.47 (m, 2H), 7.23–7.28 (m, 2H), 7.32–7.39 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 29.8 ($CH_2$), 31.6 ($CH_2$), 44.2 ($CH_2$), 54.0 ($CH_2$), 119.5 (=CH), 119.6 (=CH), 127.9 (2 × $CH_{arom}$), 128.6 ($CH_{arom}$), 129.0 (2 × $CH_{arom}$), 131.2 (=CH), 134.7 ($C_{arom}$), 146.3 (=C). IR (KBr): 3120, 3035, 2952, 1496, 1454, 1311, 1218, 1047, 968, 754, 711, 650 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{14}H_{16}ClN_3Na$: 284.0930; found: 284.0928.

**1-Benzyl-4-[(*E*)-2-(cyclohex-1-enyl)ethenyl]-1*H*-1,2,3-triazole (3da)**

Yellowish white solid. Eluent: hexane-EtOAc (7:3); mp 70–72 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.57–1.72 (m, 4H), 2.12–2.22 (m, 4H), 5.48 (s, 2H), 5.85 (br s, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 6.87 (d, *J* = 16.1 Hz, 1H), 7.23–7.27 (m, 2H), 7.32–7.37 (m, 3H), 7.40 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 22.2 ($CH_2$), 22.3 ($CH_2$), 24.0 ($CH_2$), 25.9 ($CH_2$), 53.8 ($CH_2$), 112.8 (=CH), 119.4 (=CH), 127.8 (2 × $CH_{arom}$), 128.5 ($CH_{arom}$), 128.9 (2 × $CH_{arom}$), 131.3 (=CH), 134.4(=CH), 134.6 ($C_{arom}$), 135.2 (=C), 147.1 (=C). IR (KBr): 3134, 3039, 2929, 2858, 1496, 1454, 1434, 1353, 1226, 1049, 960, 794, 761, 719, 692 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{17}H_{19}N_3Na$: 288.1477; found: 288.1475.

**1-(2-Methylbenzyl)-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3ab)**

Light-brown solid. Eluent: hexane-EtOAc (7:3); mp 68–69 ºC.$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3H), 1.22–1.35 (m, 6H), 1.38–1.47 (m, 2H), 2.13–2.19 (m, 2H), 2.27 (s, 3H), 5.49 (s, 2H), 6.30–6.40 (m, 2H), 7.12–7.16 (m, 1H), 7.19–7.30 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 13.9 ($CH_3$), 18.8 ($CH_3$), 22.4 ($CH_2$), 28.7 ($CH_2$), 28.8 ($CH_2$), 31.5 ($CH_2$), 32.7 ($CH_2$), 52.1 ($CH_2$), 118.1 (=CH), 126.4 ($CH_{arom}$), 128.9 ($CH_{arom}$), 129.1 ($CH_{arom}$), 130.8 ($CH_{arom}$), 132.5 ($C_{arom}$), 133.5 ($C_{arom}$), 136.7 (=CH). IR (KBr): 3116, 3053, 2929, 2854, 1460, 1211, 1041, 974, 786, 761 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{25}N_3Na$: 306.1946; found: 306.1942.

**1-(4-Methylbenzyl)-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3ac)**

Crystalline white solid. Eluent: hexane-EtOAc (7:3); mp 75–76 ºC.$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3H), 1.22–1.35 (m, 6H), 1.38–1.46 (m, 2H), 2.12–2.19 (m, 2H), 2.32 (s, 3H), 5.40 (s, 2H), 6.30–6.39 (m, 2H), 7.14 (s, 4H), 7.35 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 14.1 ($CH_3$),

21.1 ($CH_3$), 22.6 ($CH_2$), 28.8 ($CH_2$), 29.0 ($CH_2$), 31.7 ($CH_2$), 32.8 ($CH_2$), 53.7 ($CH_2$), 118.3 (=CH), 119.3 (=CH), 128.0 (2 × $CH_{arom}$), 129.6 (2 × $CH_{arom}$), 131.8 ($C_{arom}$), 133.5 (=CH), 138.4 ($C_{arom}$), 146.7 (=C). IR (KBr): 3105, 2952, 2850, 1454, 1218, 964, 796, 758 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{25}N_3Na$: 306.1946; found: 306.1945.

**1-[4-(Trifluoromethyl)benzyl]-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3ad)**

White solid. Eluent: hexane-EtOAc (7:3); mp 77–78 ºC. $^1H$ NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.22–1.49 (m, 8H), 2.14–2.23 (m, 2H), 5.56 (s, 2H), 6.37 (d, *J* = 16.1 Hz, 1H), 6.41 (dt, *J* = 16.1, 6.3 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.45 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 2H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 14.1 ($CH_3$), 22.6 ($CH_2$), 28.8 ($CH_2$), 28.9 ($CH_2$), 31.7 ($CH_2$), 32.9 ($CH_2$), 53.3 ($CH_2$), 117.9 (=CH), 119.6 (=CH), 123.3 ($CF_3$, q, *J* = 272.1 Hz), 126.0 (2 × $CH_{arom}$, q, *J* = 4.1 Hz), 128.1 (2 × $CH_{arom}$), 130.9 ($C_{arom}$, q, *J* = 32.1 Hz), 134.3 (=CH), 138.8 ($C_{arom}$), 147.1 (=C). IR (KBr): 3010, 2927, 2858, 1456, 1419, 1328, 1163, 1120, 1109, 1070, 964, 823 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{22}N_3F_3Na$: 360.1663; found: 360.1660.

**1-(4-Chlorobenzyl)-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3ae)**

Crystalline white solid. Eluent: hexane-EtOAc (7:3); mp 76–77 ºC. $^1H$ NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.22–1.36 (m, 6H), 1.39–1.47 (m, 2H), 2.14–2.21 (m, 2H), 5.45 (s, 2H), 6.35 (d, *J* = 16.1 Hz, 1H), 6.37 (dt, *J* = 16.1, 6.3 Hz, 1H), 7.17–7.21 (m, 2H), 7.30–7.34 (m, 2H), 7.36 (s, 1H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 14.1 ($CH_3$), 22.6 ($CH_2$), 28.8 ($CH_2$), 28.9 ($CH_2$), 31.7 ($CH_2$), 32.9 ($CH_2$), 53.2 ($CH_2$), 118.0 (=CH), 119.2 (=CH), 129.2 (2 × $CH_{arom}$), 129.3 (2 × $CH_{arom}$), 133.3 ($C_{arom}$), 134.0 (=CH), 134.6 ($C_{arom}$), 147.0 (=C). IR (KBr): 3103, 3051, 2952, 2929, 2850, 1494, 1454, 1218, 962, 796, 758 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{22}N_3ClNa$: 326.1400; found: 326.1399.

**1-(4-Bromobenzyl)-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3af)**

White solid. Eluent: hexane-EtOAc (7:3); mp 73–74 ºC. $^1H$ NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.22–1.36 (m, 6H), 1.39–1.47 (m, 2H), 2.14–2.21 (m, 2H), 5.44 (s, 2H), 6.35 (d, *J* = 16.1 Hz, 1H), 6.38 (dt, *J* = 16.1, 6.3 Hz, 1H), 7.10–7.15 (m, 2H), 7.39 (s, 1H), 7.45–7.50 (m, 2H). $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 14.1 ($CH_3$), 22.6 ($CH_2$), 28.8 ($CH_2$), 28.9 ($CH_2$), 31.6 ($CH_2$), 32.9 ($CH_2$), 53.3 ($CH_2$), 117.9 (=CH), 119.3 (=CH), 122.7 ($C_{arom}$), 129.5 (2 × $CH_{arom}$), 132.1 (2 × $CH_{arom}$), 133.8 ($C_{arom}$), 134.2 (=CH), 146.9 (=C). IR (KBr): 3103, 2950, 2929, 2852, 1488, 1456, 1409, 1222, 1055, 1012, 962, 792 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{22}N_3BrNa$: 370.0895; found: 370.0894.

**1-(4-Cyanobenzyl)-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3ag)**

White solid. Eluent: hexane-EtOAc (7:3); mp 94–95 ºC. $^1H$ NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* =

6.8 Hz, 3H), 1.23–1.37 (m, 6H), 1.40–1.48 (m, 2H), 2.15–2.22 (m, 2H), 5.58 (s, 2H), 6.36 (d, $J$ = 16.1 Hz, 1H), 6.39 (dt, $J$ = 16.1, 6.8 Hz, 1H), 7.32–7.36 (m, 2H), 7.45 (s, 1H), 7.62–7.66 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 14.1 ($CH_3$), 22.5 ($CH_2$), 28.8 ($CH_2$), 28.9 ($CH_2$), 31.6 ($CH_2$), 32.9 ($CH_2$), 53.2 ($CH_2$), 112.5 (≡C), 117.8 (=CH), 118.2 ($C_{arom}$), 119.6 (=CH), 128.3 (2 × $CH_{arom}$), 132.8 (2 × $CH_{arom}$), 134.4 (=CH), 140.1 ($C_{arom}$), 147.2 (=C). IR (KBr): 3093, 3051, 2952, 2920, 2850, 2231, 1419, 1340, 1220, 1053, 1033, 968, 812, 761 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{22}N_4Na$: 317.1742; found: 317.1743.

**1-(4-Methoxycarbonylbenzyl)-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (3ah)**

Light-brown solid. Eluent: hexane-EtOAc (7:3); mp 105–107 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, $J$ = 6.9 Hz, 3H), 1.23–1.36 (m, 6H), 1.41–1.47 (m, 2H), 2.16–2.21 (m, 2H), 3.90 (s, 3H), 5.56 (s, 2H), 6.36 (d, $J$ = 16.5 Hz, 1H), 6.36–6.43 (m, 1H), 7.30 (d, $J$ = 8.2 Hz, 2H), 7.37 (s, 1H), 8.03 (d, $J$ = 8.2 Hz, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 14.1 ($CH_3$), 22.6 ($CH_2$), 28.8 ($CH_2$), 28.9 ($CH_2$), 31.7 ($CH_2$), 32.9 ($CH_2$), 52.2 ($CH_3$), 53.4 ($CH_2$), 118.0 (=CH), 119.6 (=CH), 127.7 (2 × $CH_{arom}$), 130.2 (2 × $CH_{arom}$), 130.3 ($C_{arom}$), 134.0 (=CH), 139.8 ($C_{arom}$), 147.0 (=C), 166.3 (O=C). IR (KBr): 2922, 2850, 1724, 1458, 1436, 1280, 1217, 1109, 1055, 960 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{19}H_{25}N_3O_2Na$: 350.1844; found: 350.1840.

**1-(2-Methylbenzyl)-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3bb)**

White solid. Eluent: hexane-EtOAc (7:3); mp 120–121 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 5.47 (s, 2H), 7.02 (d, $J$ = 16.1 Hz, 1H), 7.11–7.13 (m, 1H), 7.18–7.32 (m, 7H), 7.36 (s, 1H), 7.41–7.45 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.9 ($CH_3$), 52.2 ($CH_2$), 116.7 (=CH), 120.2 (=CH), 126.4 (2 × $CH_{arom}$), 126.6 ($CH_{arom}$), 127.8 ($CH_{arom}$), 128.6 (2 × $CH_{arom}$), 129.0 ($CH_{arom}$),129.2 ($CH_{arom}$), 130.4 (=CH), 130.9 ($CH_{arom}$), 132.5 ($C_{arom}$), 136.6 ($C_{arom}$), 136.8 ($C_{arom}$), 146.2 (=C). IR (KBr): 3111, 3028, 1494, 1460, 1265, 1226, 1217, 1049, 960, 835, 773, 740, 731,705, 690 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{17}N_3Na$: 298.1320; found: 298.1316.

**1-(4-Methylbenzyl)-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3bc)**

White solid. Eluent: hexane-EtOAc (7:3); mp 137–138 ºC. $^1$H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 5.47 (s, 2H), 7.04 (d, $J$ = 16.6 Hz, 1H), 7.18 (s, 4H), 7.22–7.28 (m, 2H), 7.30–7.35 (m, 2H), 7.43–7.48 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.2 ($CH_3$), 53.9 ($CH_2$), 116.7 (=CH), 120.1 (=CH), 126.4 (2 × $CH_{arom}$), 127.8 ($CH_{arom}$), 128.1 (2 × $CH_{arom}$), 128.6 (2 × $CH_{arom}$), 129.7 (2 × $CH_{arom}$), 130.5 (=CH), 131.5 ($C_{arom}$), 136.7 ($C_{arom}$), 138.7 ($C_{arom}$), 146.5 (=C). IR (KBr): 1458, 1213, 962, 748, 705, 688 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{17}N_3Na$: 298.1320; found: 298.1321.

**1-[4-(Trifluoromethyl)benzyl]-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3bd)**

Crystalline colorless solid. Eluent: hexane-EtOAc (7:3); mp 150–151 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$): δ = 5.80 (s, 2H), 7.24–7.32 (m, 2H), 7.33–7.42 (m, 3H), 7.54–7.63 (m, 4H), 7.78–7.80 (m, 2H), 8.42 (s, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 52.3 ($CH_2$), 117.3 (=CH), 122.6 (=CH), 124.2 ($CF_3$, q, $J$ = 270.4 Hz), 125.7 (2 × $CH_{arom}$, q, $J$ = 4.1 Hz), 126.4 (2 × $CH_{arom}$), 127.8 ($CH_{arom}$), 128.6 (2 × $CH_{arom}$), 128.7 (2 × $CH_{arom}$), 128.8 ($C_{arom}$, q, $J$ = 32.9 Hz), 129.6 (=CH), 136.6 ($C_{arom}$), 140.7 ($C_{arom}$), 145.6 (=C). IR (KBr): 1419, 1334, 1218, 1170, 1124, 1070, 960, 860, 825, 788, 752, 704, 690 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{18}H_{14}N_3F_3Na$: 352.1037; found: 352.1035.

**1-(4-Chlorobenzyl)-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3be)**

White solid. Eluent: hexane-EtOAc (7:3); mp 151–152 ºC. $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 5.46 (s, 2H), 7.04 (d, $J$ = 16.6 Hz, 1H), 7.17–7.22 (m, 2H), 7.23–7.27 (m, 1H), 7.27 (d, $J$ = 16.6 Hz, 1H), 7.30–7.36 (m, 4H), 7.43–7.47 (m, 2H), 7.50 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 53.3 ($CH_2$), 116.4 (=CH), 120.2 (=CH), 126.4 (2 × $CH_{arom}$), 127.9 ($CH_{arom}$), 128.7 (2 × $CH_{arom}$), 129.2 (2 × $CH_{arom}$), 129.3 (2 × $CH_{arom}$), 130.8 (=CH), 133.1 ($C_{arom}$), 134.7 ($C_{arom}$), 136.5 ($C_{arom}$), 146.7 (=C). IR (KBr): 3095, 1488, 1442, 1218, 1055, 960, 785, 746, 705, 690 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{17}H_{14}N_3ClNa$: 318.0774; found: 318.0770.

**1-(4-Bromobenzyl)-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3bf)**

White solid. Eluent: hexane-EtOAc (7:3); mp 163–164 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$): δ = 5.62 (s, 2H), 7.21 (d, $J$ = 16.1 Hz, 1H), 7.25–7.33 (m, 4H), 7.35–7.40 (m, 2H), 7.56–7.62 (m, 4H), 8.34 (s, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ = 52.0 ($CH_2$), 117.2 (=CH), 121.3 ($C_{arom}$), 122.2 (=CH), 126.2 (2 × $CH_{arom}$), 127.7 ($CH_{arom}$), 128.6 (2 × $CH_{arom}$), 129.4 (=CH), 130.1 (2 × $CH_{arom}$), 131.6 (2 × $CH_{arom}$), 135.3 ($C_{arom}$), 136.5 ($C_{arom}$), 145.4 (=C). IR (KBr): 3095, 1488, 1442, 1220, 1159, 1072, 1056, 1012, 958, 785, 744, 705, 690 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{17}H_{14}N_3BrNa$: 362.0269; found: 362.0267.

**1-(4-Cyanobenzyl)-4-[(*E*)-2-phenylethenyl]-1*H*-1,2,3-triazole (3bg)**

White solid. Eluent: hexane-EtOAc (7:3); mp 125–127 ºC. $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 5.58 (s, 2H), 7.05 (d, $J$ = 16.6 Hz, 1H), 7.24–7.37 (m, 6H), 7.43–7.48 (m, 2H), 7.61 (s, 1H), 7.61–7.65 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 53.3 ($CH_2$), 112.6 (≡C), 116.0 (=CH), 118.1 ($C_{arom}$), 120.7 (=CH), 126.5 (2 × $CH_{arom}$), 128.1 ($CH_{arom}$), 128.3 (2 × $CH_{arom}$), 128.7 (2 × $CH_{arom}$), 131.3 (=CH), 132.8 (2 × $CH_{arom}$), 136.3 ($C_{arom}$), 139.8 ($C_{arom}$), 146.7 (=C). IR (KBr): 3101, 3045, 2235, 1454, 1442, 1417, 1222, 1053, 1024, 962, 786, 750, 707, 690 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{18}H_{14}N_4Na$: 309.1116; found: 309.1118.

**1-(2-Methylbenzyl)-4-[(*E*)-5-chloropent-1-enyl]-1*H*-1,2,3-triazole (3cb)**

White solid. Eluent: hexane-EtOAc (7:3); mp 73–74 ºC. $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 1.91 (quin, *J* = 6.8 Hz, 2H), 2.28 (s, 3H), 2.32–2.38 (m, 2H), 3.53–3.58 (m, 2H), 5.51 (s, 2H), 6.32–6.42 (m, 2H), 7.14–7.17 (m, 1H), 7.20–7.25 (m, 2H), 7.24 (s, 1H), 7.27–7.32 (m, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 18.9 ($CH_3$), 29.8 ($CH_2$), 31.6 ($CH_2$), 44.2 ($CH_2$), 52.3 ($CH_2$), 119.3 (=CH), 119.5 (=CH), 126.6 ($CH_{arom}$), 129.1 ($CH_{arom}$), 129.3 ($CH_{arom}$), 131.0 ($CH_{arom}$), 131.5 (=CH), 132.4 ($C_{arom}$), 136.9 ($C_{arom}$), 145.9 (=C). IR (KBr): 3118, 3057, 1456, 1311, 1213, 1047, 974, 719 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{15}H_{18}N_3ClNa$: 298.1087; found: 298.1085.

**1-(4-Methylbenzyl)-4-[(*E*)-5-chloropent-1-enyl]-1*H*-1,2,3-triazole (3cc)**

White solid. Eluent: hexane-EtOAc (7:3); mp 67–68 ºC. $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 1.88–1.95 (m, 2H), 2.32–2.38 (m, 2H), 2.34 (s, 3H), 3.55 (t, *J* = 6.3 Hz, 2H), 5.44 (s, 2H), 6.34 (dt, *J* = 16.1, 6.3 Hz, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 7.14–7.19 (m, 4H), 7.32 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.1 ($CH_3$), 29.8 ($CH_2$), 31.6 ($CH_2$), 44.2 ($CH_2$), 53.8 ($CH_2$), 119.5 (=CH), 119.6 (=CH), 128.0 (2 × $CH_{arom}$), 129.7 (2 × $CH_{arom}$), 131.1 (=CH), 131.6 ($C_{arom}$), 138.6 ($C_{arom}$), 146.2 (=C). IR (KBr): 3112, 2952, 1456, 1434, 1217, 972, 792, 758, 667 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{15}H_{18}N_3ClNa$: 298.1087; found: 298.1086.

**1-(4-Chlorobenzyl)-4-[(*E*)-5-chloropent-1-enyl]-1*H*-1,2,3-triazole (3ce)**

White solid. Eluent: hexane-EtOAc (7:3); mp 64–65 ºC. $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 1.92 (quin, *J* = 6.8 Hz, 2H), 2.32–2.38 (m, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 5.47 (s, 2H), 6.32–6.40 (m, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 7.18–7.22 (m, 2H), 7.32–7.36 (m, 2H), 7.35 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 29.8 ($CH_2$), 31.6 ($CH_2$), 44.2 ($CH_2$), 53.3 ($CH_2$), 119.4 (=CH), 119.5 (=CH), 129.2 (2 × $CH_{arom}$), 129.3 (2 × $CH_{arom}$), 131.4 (=CH), 133.2 ($C_{arom}$), 134.7 ($C_{arom}$), 146.5 (=C). IR (KBr): 3097, 3053, 1490, 1436, 1315, 1220, 1087, 1018, 968, 802, 725 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{14}H_{15}N_3Cl_2Na$: 318.0541; found: 318.0540.

**1-(4-Bromobenzyl)-4-[(*E*)-5-chloropent-1-enyl]-1*H*-1,2,3-triazole (3cf)**

White solid. Eluent: hexane-EtOAc (7:3); mp 76–78 ºC. $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 1.86–1.94 (m, 2H), 2.30–2.37 (m, 2H), 3.55 (t, *J* = 6.8 Hz, 2H), 5.44 (s, 2H), 6.31–6.39 (m, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.43–7.48 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 29.5 ($CH_2$), 31.3 ($CH_2$), 44.0 ($CH_2$), 52.9 ($CH_2$), 119.1 (=CH), 119.5 (=CH), 122.4 ($C_{arom}$), 129.3 (2 × $CH_{arom}$), 131.1 (=CH), 131.8 (2 × $CH_{arom}$), 133.5 ($C_{arom}$), 146.2 (=C). IR (KBr): 3116, 3043, 1488, 1454, 1409, 1352, 1220, 1053, 1010, 966, 798, 650 cm$^{-1}$. HRMS(ESI): *m/z* [M + Na]$^{+}$ calcd for $C_{14}H_{15}N_3ClBrNa$: 362.0036; found: 362.0033.

**1-(4-Methylbenzyl)-4-[(*E*)-2-(cyclohex-1-enyl)ethenyl]-1*H*-1,2,3-triazole (3dc)**

White solid. Eluent: hexane-EtOAc (7:3); mp 88 ºC (dec). $^{1}$H NMR (500 MHz, $CDCl_3$): δ = 1.57–1.75 (m, 4H), 2.12–2.23 (m, 4H), 2.34 (s, 3H), 5.44 (s, 2H), 5.83–5.88 (m, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.85 (d, *J* = 16.1 Hz, 1H), 7.11–7.21 (m, 4H), 7.36 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 21.2 ($CH_3$), 22.3 ($CH_2$), 22.4 ($CH_2$), 24.1 ($CH_2$), 26.0 ($CH_2$), 53.8 ($CH_2$), 113.0 (=CH), 119.3 (=CH), 128.0 (2 × $CH_{arom}$), 129.7 (2 × $CH_{arom}$), 131.4 (=CH), 131.7 ($C_{arom}$), 134.5 (=CH), 135.4 (=C), 138.6 ($C_{arom}$), 147.2 (=C). IR (KBr): 3116, 2931, 2860, 1515, 1454, 1434, 1348, 1220, 1051, 962, 804, 771, 756 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{21}N_3Na$: 302.1633; found: 302.1629.

**1-[4-(Trifluoromethyl)benzyl]-4-[(*E*)-2-(cyclohex-1-enyl)ethenyl]-1*H*-1,2,3-triazole (3dd)**

Light-brown solid. Eluent: hexane-EtOAc (7:3); mp 80–81 ºC. $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 1.59–1.74 (m, 4H), 2.14–2.23 (m, 4H), 5.57 (s, 2H), 5.87–5.91 (m, 1H), 6.40 (d, *J* = 16.5 Hz, 1H), 6.89 (d, *J* = 16.5 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 2H). $^{13}$C NMR (200 MHz, $CDCl_3$): δ = 23.3 ($CH_2$), 23.4 ($CH_2$), 24.1 ($CH_2$), 26.1 ($CH_2$), 53.3 ($CH_2$), 112.6 (=CH), 119.7 (=CH), 123.8 ($CF_3$, q, *J* = 271.7 Hz), 126.0 (2 × $CH_{arom}$, q, *J* = 4.3 Hz), 128.1 (2 × $CH_{arom}$), 130.9 ($C_{arom}$, q, *J* = 33.2 Hz), 131.9 (=CH), 135.0 (=CH), 135.3 (=C), 138.8 ($C_{arom}$), 147.6 (=C). IR (KBr): 2931, 1622, 1454, 1421, 1330, 1159, 1120, 1107, 1068, 1051, 1018, 958, 817 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{18}N_3F_3Na$: 356.1350; found: 356.1349.

**1-(4-Bromobenzyl)-4-[(*E*)-2-(cyclohex-1-enyl)ethenyl]-1*H*-1,2,3-triazole (3df)**

Light-brown solid. Eluent: hexane-EtOAc (7:3); mp 113 ºC (dec). $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 1.59–1.73 (m, 4H), 2.14–2.23 (m, 4H), 5.45 (s, 2H), 5.86–5.90 (m, 1H), 6.39 (d, *J* = 16.5 Hz, 1H), 6.87 (d, *J* = 16.5 Hz, 1H), 7.10–7.19 (m, 2H), 7.39 (s, 1H), 7.46–7.53 (m, 2H). $^{13}$C NMR (200 MHz, $CDCl_3$): δ = 22.3 ($CH_2$), 22.4 ($CH_2$), 24.1 ($CH_2$), 26.0 ($CH_2$), 53.3 ($CH_2$), 112.7 (=CH), 119.4 (=CH), 122.8 ($C_{arom}$), 129.5 (2 × $CH_{arom}$), 131.7 (=CH), 132.2 (2 × $CH_{arom}$), 133.8 ($C_{arom}$), 134.8 (=CH), 135.3 (=C), 147.4 (=C). IR (KBr): 2931, 1488, 1456, 1434, 1407, 1072, 1051, 1012, 958, 796 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{18}N_3BrNa$: 366.0582; found: 366.0579.

**1-(4-Methoxycarbonylbenzyl)-4-[(*E*)-2-(cyclohex-1-enyl)ethenyl]-1*H*-1,2,3-triazole (3dh)**

White solid. Eluent: hexane-EtOAc (7:3); mp 113–115 ºC. $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 1.58–1.73 (m, 4H), 2.13–2.23 (m, 4H), 3.91 (s, 3H), 5.56 (s, 2H), 5.86–5.89 (m, 1H), 6.40 (d, *J* = 16.5 Hz, 1H), 6.89 (d, *J* = 16.5 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H). $^{13}$C NMR (200 MHz, $CDCl_3$): δ = 22.3 ($CH_2$), 22.4 ($CH_2$), 24.1 ($CH_2$), 26.0 ($CH_2$), 52.2 ($CH_3$), 53.5 ($CH_2$), 112.6 (=CH), 119.6 (=CH), 127.7 (2 × $CH_{arom}$), 130.3 (2 × $CH_{arom}$), 130.4 ($C_{arom}$), 131.7 (=CH), 134.9 (=CH), 135.3 (=C), 139.6 ($C_{arom}$), 147.5 (=C), 166.4 (O=C). IR (KBr): 2933, 1724, 1434, 1280, 1110, 962, 729, 667 $cm^{-1}$. HRMS(ESI): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{21}N_3O_2Na$: 346.1531; found: 346.1528.