Supporting Information

For

Robust eco-friendly protocol for the preparation of γ-hydroxy-α,β-acetylenic esters by sequential one-pot elimination-addition of 2-bromoacrylates to aldehydes promoted by LTMP in 2-MeTHF

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Materials and Instrumentation.

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-500 MHz spectrometer at room temperature at 500 MHz and at 125 MHz respectively, from $CDCl_3$ solutions. Chemical shifts are reported in δ (ppm) downfield from TMS, the center of the solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H) and δ 77.0 ppm (^{13}C). Spin-spin coupling constants (*J*) are given in Hz. Whenever necessary, 2D NMR experiments such as HSQC (HMQC) and HMBC were carried out. Melting points were determined with a Büchi SMP-20 apparatus and are uncorrected. IR absorption spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotomer.

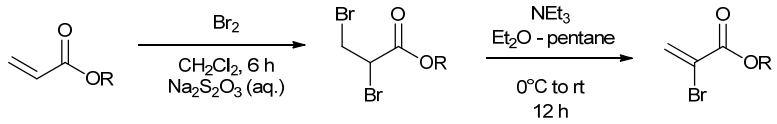
2-MeTHF was distilled under atmospheric pressure immediately before its use. All chemicals were purchased from Sigma-Aldrich, Acros, Alfa-Aesar or TCI and used as received, except 2,2,6,6-tetramethylpiperidine which was purified by bulb distillation prior to its use. Organolithiums were titrated immediately before their use according to standard procedures.[1] Methyl-2-chloroacrylate was prepared according to the literature.[2]

Elementary microanalyses were carried out using a Leco® CHNS 932 equipment. Column chromatography purifications were conducted on silica gel 60 (40-63 μm). TLC was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (Macherey-Nagel, Merk); the spots were visualized under UV light (λ=254 nm) and/or potassium permanganate basic solution was used as revealing system.

General procedure for the Preparation of LTMP solution in 2-MeTHF.

In a dry and argon flushed *Schlenk*-flask, 2,2,6,6-tetramethylpiperidine (1.0 equiv.) was dissolved in dry 2-MeTHF and cooled to 0ºC. MeLi (3% in 2-MeTHF, 0.98 equiv.) was added dropwise and the resulting mixture was stirred for 45 min. Then, the colorless solution was transferred *via* cannula dropwise into the appropriate flask containing the aldehyde and the α-haloacrylate as reported below.

General procedure for the preparation of α-bromoacrylate esters 1a-c.[3]

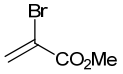


SI-0a-c **SI-1a-c** **1a-c**

a = Me
b = Et
c = ^{t}Bu

Bromine (3.0 M, 1.10 equiv.) in dichloromethane was added dropwise to the solution of the acrylate ester (1.0 equiv.) in the same solvent, cooled at -10°C over 30 min. The mixture was stirred, providing that the internal temperature did not exceed 5°C, for 5 hours at which stage an orange color persisted. Then a saturated solution of sodium thiosulfate was added until a persistent colorless solution was observed and the solution was extracted with dichloromethane. The organic phase was dried over sodium sulfate, filtered and after removal of the solvent *in vacuo* **SI-1a-c** were obtained and used for the next step without further purification. Dibrominated compounds **SI-1a-c** were dissolved in an 1:1 mixture (v/v) of diethyl ether and pentane and cooled at 0°C. Then a solution of triethylamine (2.5 equiv.) in diethyl ether was added dropwise, the mixture was allowed to reach rt and was stirred for 12 h at this temperature. The precipitate was filtered, washed with pentane and the combined organic solution were washed with water and dried over sodium sulfate. After removal of the solvent *in vacuo*, Kugelrohr distillation of the crudes afforded pure compounds **1a-c**. To avoid polymerizations of the so obtained haloacrylates, they were kept under nitrogen at -20°C.

Methyl 2-bromoacrylate (1a)[3]



By following the aforementioned procedure, starting from methyl acrylate (70 mmol, 1.0 equiv.) and bromine (77 mmol, 1.10 equiv.), compound **1a** was obtained in 88% yield (10.16 g) after Kugelrohr distillation.

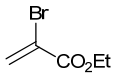
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.87 (s, 3H), 6.30 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 54.5, 122.1, 131.7, 163.0.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3131, 1739, 1625, 1438, 1303.

Anal. Calcd. for $C_4H_5BrO_2$. Calcd.: C, 29.12; H, 3.05. Found: C, 29.40; H, 3.25.

Ethyl 2-bromoacrylate (1b)[2]



By following the aforementioned procedure, starting from ethyl acrylate (20 mmol, 1.0 equiv.) and bromine (22 mmol, 1.10 equiv.), compound **1b** was obtained in 83% yield (2.97 g) after Kugelrohr distillation.

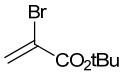
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.39 (t, *J* = 7.0 Hz, 3H), 4.33 (q, *J* = 6.8 Hz, 2H), 6.23 (d, *J* = 1.9 Hz, 1H), 7.01 (d, *J* = 1.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 14.1, 62.1, 121.2, 130.5, 161.9.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3133, 1731, 1621, 1492, 1435, 1298.

Anal. Calcd. for $C_5H_7BrO_2$. Calcd.: C, 33.55; H, 3.94. Found: C, 33.31; H, 4.12.

***tert*-Butyl 2-bromoacrylate (1c)**[4]



By following the aforementioned procedure, starting from *tert*-butyl acrylate (20 mmol, 1.0 equiv.) and bromine (22 mmol, 1.10 equiv.), compound **1b** was obtained in 93% yield (3.85 g) after Kugelrohr distillation.

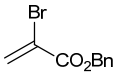
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.42 (s, 9H), 6.16 (d, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 1.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 28.1, 82.9, 123.2, 139.8, 161.5.

FT-IR (KBr) (νmax/cm^{-1}): 3135. 3021, 1736, 1628, 1493, 1463, 1101, 945, 852.

Anal. Calcd. for $C_7H_{11}BrO_2$. Calcd.: C, 40.60; H, 5.35. Found: C, 40.29; H, 5.62.

Benzyl 2-bromoacrylate (1d)[5]



To a solution of 2-bromoacrylic acid (10 mmol, 1.0 equiv.) in acetonitrile (50 mL) was added benzyl bromide (12 mmol, 1.2 equiv.) and anhydrous potassium carbonate (20 mmol, 2.0 equiv.) and, the resulting mixture was refluxed (83°C) for 6 hours. After cooling to rt, water (30 mL) and ethyl acetate (30 mL) were added. After extraction with ethyl acetate (2 x 30 mL) the organic phase was dried over sodium sulfate, filtered and the solvent was removed under

reduced pressure. The crude was immediately purified by Kugelrohr distillation, affording **1d** as a pale yellow oil (1.71 g, 73% yield). It is mandatory storing compound **1d** at -20°C under nitrogen to avoid any decomposition.

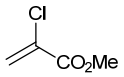
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.21 (s, 2H), 6.26 (d, *J* = 1.9 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 7.26-7.39 (m, 3H), 7.52-7.57 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 60.8, 123.9, 126.8, 127.7, 128.9, 138.8, 140.6, 162.1.

FT-IR (KBr) (νmax/cm^{-1}): 3131, 3082, 3020, 1726, 1608. 1496.

Anal. Calcd. for $C_{10}H_9BrO_2$. Calcd.: C, 49.82; H, 3.76. Found: C, 49.40; H, 3.42.

Methyl 2-chloroacrylate (1e)[2] Prepared according Ref. 2.



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.76 (s, 3H), 6.30 (d, *J* = 1.8 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.6, 126.9, 130.2, 161.5.

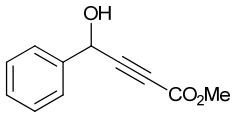
FT-IR (KBr) ($\nu_{ma)x}$/cm^{-1}):.

Anal. Calcd. for $C_4H_5ClO_2$. Calcd.: C, 39.86; H, 4.18. Found: C, 40.01; H, 4.02.

General procedure for the sequential one-pot elimination-addition of 2-bromoacrylates to aldehydes promoted by LTMP in 2-MeTHF.

To a solution of 2-bromoacrylate esters (**1a-d**, 3.00 mmol, 1.0 equiv.) in dry 2-MeTHF (10 mL) was added the aldehyde (3.00 mmol, 1.0 equiv.) dissolved in the same solvent (5 mL). The system was flushed with argon and cooled at -40°C. Then, the recently prepared solution of LTMP (see description above) was dropwise transferred *via cannula* and the resulting mixture was stirred for the appropriate time (see below) at -40°C. After completion of the reaction, a saturated aqueous ammonium chloride solution (10 mL) was added and the mixture was stirred until the system reached rt. The organic phase was simply extracted by adding further 2-MeTHF (2 x 10 mL) and after drying over sodium sulfate and filtering, the solvent was removed under reduced pressure. The acetylenic compounds (**2a-d**, **4a-k** and **6**) were obtained after purification by liquid chromatography as specified below.

Methyl 4-hydroxy-4-phenylbut-2-ynoate (2a)[6]



By following the afore mentioned procedure, starting from benzaldehyde (3.00 mmol, 318 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **2a** was obtained in 94% yield (536 mg) after LC (silica gel, petroleum ether / ethyl acetate 8 : 2) as a colorless oil.

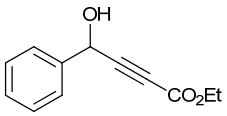
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.72 (d, *J*=6.1 Hz, 1H), 3.76 (s, 3H), 5.55 (d, *J*=6.1 Hz, 1H), 7.31-7.39 (m, 3H), 7.55 (d, *J* = 7.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.9, 64.1, 78.1, 87.1, 127.2, 129.5, 129.7, 138.6, 154.1.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3412, 3032, 2958, 2238, 1718, 1495, 1458, 1433.

Anal. Calcd. for $C_{11}H_{10}O_3$. Calcd.: C, 69.46; H, 5.30. Found: C, 69.35; H, 5.49.

Ethyl 4-hydroxy-4-phenylbut-2-ynoate (2b)[6]



By following the afore mentioned procedure, starting from benzaldehyde (3.00 mmol, 318 mg), ethyl 2-bromoacrylate **1b** (3.00 mmol, 537 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **2b** was obtained in 93% yield (570 mg) after LC (silica gel, petroleum ether / ethyl acetate 8 : 2) as a colorless oil.

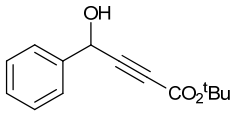
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.29 (d, *J* = 7.0 Hz, 3H), 2.53 (d, *J* = 5.8 Hz, 1H), 4.27 (q, *J* = 6.9 Hz, 2H), 5.54 (d, *J* = 5.5 Hz, 1H), 7.38-7.45 (m, 3H), 7.49 (d, *J* = 7.1 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 13.9, 63.1, 64.7, 77.9, 87.3, 127.2, 128.7, 128.9, 138.9, 153.6.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3413, 2956, 2237, 1717, 1496, 1453, 1430.

Anal. Calcd. for $C_{12}H_{12}O_3$. Calcd.: C, 70.57; H, 5.92. Found: C, 70.49; H, 5.79.

***tert*-butyl 4-hydroxy-4-phenylbut-2-ynoate (2c)**



By following the afore mentioned procedure, starting from benzaldehyde (3.00 mmol, 318 mg), *tert*-butyl 2-bromoacrylate **1c** (3.00 mmol, 621 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **2c** was obtained in 91% yield (634 mg) after LC (silica gel, petroleum ether / ethyl acetate 7 : 3) as a colorless oil.

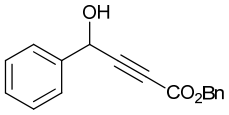
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.40 (s, 9H), 2.66 (d, *J* = 5.8 Hz, 1H), 5.50 (d, *J* = 5.1 Hz, 1H), 7.31-7.51 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 27.7, 63.3, 78.2, 81.4, 87.3, 127.2, 128.4, 128.9, 138.9, 156.9.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3414, 3030, 2958, 2238, 1719, 1496, 1455.

Anal. Calcd. for $C_{14}H_{16}O_3$. Calcd.: C, 72.39; H, 6.94. Found: C, 72.56; H, 7.11.

Benzyl 4-hydroxy-4-phenylbut-2-ynoate (2d)



By following the afore mentioned procedure, starting from benzaldehyde (3.00 mmol, 318 mg), benzyl 2-bromoacrylate **1b** (3.00 mmol, 723 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **2d** was obtained in 94% yield (750 mg) after LC (silica gel, petroleum ether / ethyl acetate 8 : 2) as a colorless oil.

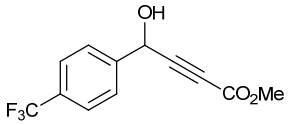
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.78 (d, *J* = 5.0 Hz, 1H), 5.29 (s, 2H), 5.61 (d, *J* = 5.2 Hz, 1H), 7.26-7.55 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 63.9, 66.8, 79.9, 86.8, 126.9, 127.2, 127.8, 128.0, 128.6, 128.9, 136.6, 139.1, 154.2.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3412, 3036, 2959, 2239, 1720, 1496, 1451, 1266.

Anal. Calcd. for $C_{17}H_{14}O_3$. Calcd.: C, 76.68; H, 5.30. Found: C, 76.91; H, 5.49.

Methyl 4-hydroxy-4-(4-(trifluoromethyl)phenyl)but-2-ynoate (4a)[7]



By following the afore mentioned procedure, starting from 4-trifluoromethylbenzaldehyde (3.00 mmol, 522 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4a** was obtained in 96% yield (743 mg) after LC (silica gel, petroleum ether / ethyl acetate 8 : 2) as a pale yellow oil.

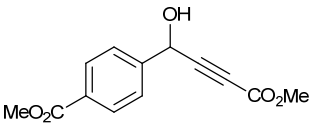
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.81 (s, 3H), 5.59 (d, *J* = 5.0 Hz, 1H), 7.55-7.66 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.0, 63.2, 77.4, 86.1, 123.8 (q, *J* = 270.6 Hz), 125.9 (q, *J* = 3.7 Hz), 126.9, 130.9 (q, *J* = 32.5 Hz), 142.6, 153.6

FT-IR (KBr) (ν_{max}/cm^{-1}): 3419, 3013, 2958, 2241, 1717, 1439, 1328, 1259, 1129.

Anal. Calcd. for $C_{12}H_9F_3O_3$. Calcd.: C, 55.82; H, 3.51. Found: C, 55.99; H, 3.68.

Methyl 4-(1-hydroxy-4-methoxy-4-oxobut-2-yn-1-yl)benzoate (4b)



By following the afore mentioned procedure, starting from methyl-4-formylbenzoate (3.00 mmol, 492 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4b** was obtained in 94% yield (702 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a yellow oil.

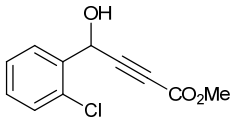
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.77 (s, 3H), 3.90 (s, 3H), 5.59 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 8.01 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 52.9, 63.0, 63.8, 78.0, 85.8, 126.4, 130.0, 130.4, 143.1, 153.5, 168.0.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3414, 3029, 2965, 2239, 1719, 1716, 1437, 1258.

Anal. Calcd. for $C_{13}H_{12}O_5$. Calcd.: C, 62.90; H, 4.87. Found: C, 63.14; H, 4.99.

Methyl 4-(2-chlorophenyl)-4-hydroxybut-2-ynoate (4c)[6]



By following the afore mentioned procedure, starting from 2-chlorobenzaldehyde (3.00 mmol, 422 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4c** was obtained in 87% yield (586 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a pale yellow oil.

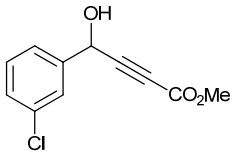
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.95 (d, *J* = 5.4Hz, 1H), 3.80 (s, 3H), 5.90 (d, *J* = 5.7 Hz, 1H), 7.25-7.34 (m, 2H), 7.41-7.45 (m, 1H), 7.68-7.72 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.9, 62.0, 77.7, 86.0, 128.1, 128.9, 130.6, 130.9, 133.2, 136.7, 154.7.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3420, 3014, 2960, 2239, 1715, 1438, 1131.

Anal. Calcd. for $C_{11}H_9ClO_3$. Calcd.: C, 58.81; H, 4.04. Found: C, 59.04; H, 4.17.

Methyl 4-(3-chlorophenyl)-4-hydroxybut-2-ynoate (4d)[6]



By following the afore mentioned procedure, starting from 3-chlorobenzaldehyde (3.00 mmol, 422 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4d** was obtained in 85% yield (572 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a pale yellow oil.

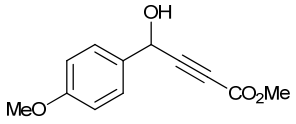
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.85 (d, *J* = 6,2Hz, 1H), 3.82 (s, 3H), 5.60 (d, *J* = 4.7 Hz, 1H), 7.32-7.34 (m, 2H), 7.41-7.45 (m, 1H), 7.55 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.9, 64.3, 78.7, 86.2, 125.1, 127.9, 129.7, 130.9, 135.3, 140.5, 154.6.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3417, 3023, 2956, 2241, 1717, 1435, 1263.

Anal. Calcd. for $C_{11}H_9ClO_3$. Calcd.: C, 58.81; H, 4.04. Found: C, 59.01; H, 3.95.

Methyl 4-hydroxy-4-(4-methoxyphenyl)but-2-ynoate (4e)[6]



By following the afore mentioned procedure, starting from 4-methoxybenzaldehyde (3.00 mmol, 408 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4e** was obtained in 88% yield (581 mg) after LC (silica gel, petroleum ether / ethyl acetate 7 : 3) as a pale yellow oil.

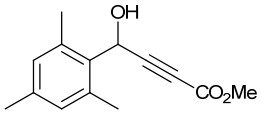
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.44 (br, 1H), 3.77 (s, 3H), 3.83 (s, 3H), 5.55 (s, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.8, 56.1, 64.7, 70.9, 87.1, 114.2, 128.8, 130.9, 154.7, 159.8.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3417, 2928, 2854, 2235, 1716, 1611, 1513, 1436, 1266, 750.

Anal. Calcd. for $C_{12}H_{12}O_4$. Calcd.: C, 65.45; H, 5.49. Found: C, 65.71; H, 5.61.

methyl 4-hydroxy-4-mesitylbut-2-ynoate (4f)



By following the afore mentioned procedure, starting from 2,4,6-trimethylbenzaldehyde (3.00 mmol, 445 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4f** was obtained in 84% yield (585 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a pale yellow oil.

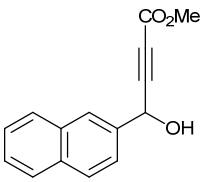
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.27 (s, 3H), 2.42 (s, 6H), 3.73 (s, 3H), 5.89 (d, *J* = 4.0 Hz, 1H), 6.88 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 19.6, 21.0, 56.2, 58.6, 77.1, 87.3, 130.0, 132.1, 137.0, 139.1, 154.1.

FT-IR (KBr) ($\nu_{ma)x}$/cm^{-1}): 3412, 2951, 2237, 1714, 1498, 1455, 1431, 756.

Anal. Calcd. for $C_{14}H_{16}O_3$. Calcd.: C, 72.39; H, 6.94. Found: C, 72.58; H, 7.13.

Methyl 4-hydroxy-4-(naphthalen-2-yl)but-2-ynoate (4g)[6]



By following the afore mentioned procedure, starting from 2-naphtaldehyde (3.00 mmol, 468 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4g** was obtained in 86% yield (620 mg) after LC (silica gel, petroleum ether / ethyl acetate 9.5 : 0.5) as a pale yellow oil.

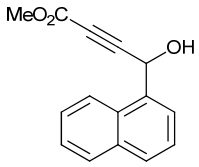
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.62 (d, *J* = 5,1 Hz, 1H), 3.77 (s, 3H), 5.77 (d, *J* = 3,3 Hz, 1H), 7.48-7.51 (m, 2H), 7.78 (d, *J* = 7.5Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.81-7.87 (m, 3H), 8.02 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 55.8, 64.2, 77.9, 86.9, 124.4, 125.9, 126.8, 127.2, 128.5, 128.9, 129.6, 133.1, 133.7, 136.5, 154.0.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3416, 3083, 3011, 2955, 2239, 1716, 1437, 1330, 1129.

Anal. Calcd. for $C_{15}H_{12}O_3$. Calcd.: C, 74.99; H, 5.03. Found: C, 74.77; H, 4.91.

Methyl 4-hydroxy-4-(naphthalen-4-yl)but-2-ynoate (4h)[6]



By following the afore mentioned procedure, starting from 1-naphtaldehyde (3.00 mmol, 468 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4h** was obtained in 91% yield (656 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a pale yellow oil.

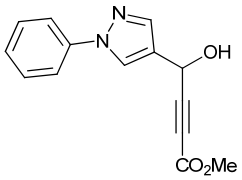
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.67 (d, *J* = 6,2Hz, 1H), 3.75 (s, 3H), 6,20 (d, *J* = 6,3 Hz, 1H), 7.44-7.58 (m, 3H), 7.78 (d, *J* = 7.5Hz, 1H), 7.85 (t, *J* = 8.3 Hz, 2H), 8.27 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 52.9, 63.2, 78.1, 86.8, 124.1, 125.2, 125.7, 126.8, 127.3, 129.5, 130.6, 131.0, 133.8, 134.2, 154.1.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3420, 3078, 3010, 2957, 2237, 1715, 1434, 1334, 1127, 756.

Anal. Calcd. for $C_{15}H_{12}O_3$. Calcd.: C, 74.99; H, 5.03. Found: C, 75.18; H, 5.14.

Methyl 4-hydroxy-4-(1-phenyl-1H-pyrazol-4-yl)but-2-ynoate (4i)



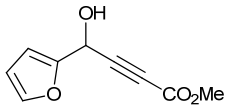
By following the afore mentioned procedure, starting from 1-phenyl-1H-pyrazole-4-carbaldehyde (3.00 mmol, 516 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4i** was obtained in 93% yield (715 mg) after LC (silica gel, petroleum ether / ethyl acetate 8 : 2) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.25 (d, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 5.63 (d, *J* = 6.3 Hz, 1H), 7.30 (m, 1H), 7.44 (m, 1H), 7.63 (m, 2H), 7.78 (s, 1H), 7.99 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.0, 56.5, 76.2, 86.1, 119.3, 122.4, 125.8, 127.0, 129.5, 139.4, 139.7, 153.7. **FT-IR** (KBr) ($\nu_{ma)x}$/cm^{-1}): 3411, 3081, 2933, 2857, 2237, 1715, 1613, 1511, 1434, 750.

Anal. Calcd. for $C_{14}H_{12}N_2O_3$. Calcd.: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.86; H, 4.91; N, 11.12.

Methyl 4-(furan-2-yl)-4-hydroxybut-2-ynoate (4j)[8]



By following the afore mentioned procedure, starting from furan-2-carbaldehyde (3.00 mmol, 288 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4j** was obtained in 82% yield (443 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a pale yellow oil.

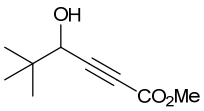
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.61 (d, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 5.61 (d, *J* = 6.5 Hz, 1H), 6.29 (d, *J* = 1.9 Hz, 1H), 6.43 (q, *J* = 3.8 Hz, 1H), 7.43 (d, *J* = 1.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.2, 58.1, 76.9, 83.9, 109.1, 110.5, 143.9, 150.9, 153.1.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3408, 3080, 3011, 2959, 2238, 1715, 1441, 1330, 1261.

Anal. Calcd. for $C_9H_8O_4$. Calcd.: C, 60.00; H, 4.48. Found: C, 59.89; H, 4.53.

Methyl 4-hydroxy-5,5-dimethylhex-2-ynoate (4k)[9]



By following the afore mentioned procedure, starting from pivaldehyde (3.00 mmol, 258 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), compound **4k** was obtained in 80% yield (408 mg) after LC (silica gel, petroleum ether / ethyl acetate 9.5 : 0.5) as a pale yellow oil.

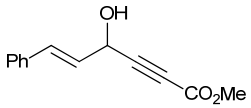
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.08 (s, 9H), 1.98-2.03 (m, 1H), 3.73 (s, 3H), 4.17 (d, *J* = 6.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 25.3, 36.2, 52.5, 70.7, 76.3, 87.5, 154.1.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3453, 2243, 1713.

Anal. Calcd. for $C_9H_{14}O_3$. Calcd.: C, 63.51; H, 8.29. Found: C, 63.39; H, 8.11.

Methyl 4-hydroxy-6-phenylhex-5-en-2-ynoate (4l)[8]



By following the afore mentioned procedure, starting from cinnamaldehyde (3.00 mmol, 396 mg), methyl 2-bromoacrylate **1a** (3.00 mmol, 495 mg) and LTMP solution (1 M) in 2-MeTHF (6.00 mmol, 6.0 mL), in the presence of lithium bromide (1.50 equiv., 4.50 mmol, 391 mg) compound **6** was obtained in 95% yield (616 mg) after LC (silica gel, petroleum ether / ethyl acetate 9 : 1) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.27 (d, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 5.22 (t, *J* = 5.4.5 Hz, 1H), 6.29 (dd, *J* = 7.1 Hz, 1H), 6.81 (d, *J* = 1.4 Hz, 1H), 7.29-7.37(m, 3H), 7.41 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 53.1, 62.2, 76.9, 84.9, 125.3, 127.0, 128.7, 129.0, 133.5, 135.8, 153.2.

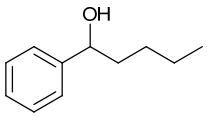
FT-IR (KBr) (ν_{max}/cm^{-1}): 3681, 3176, 3082, 3018, 2954, 2917, 2848, 2452, 2371, 2312, 1711, 1596, 1431, 1243, 1028.

Anal. Calcd. for $C_{13}H_{12}O_3$. Calcd.: C, 72.21; H, 5.59. Found: C, 72.45; H, 5.32.

Characterization of side-products obtained using lithium alkyl bases

The following compounds were obtained as side-products or main products accordingly to data and reaction conditions reported in Table 1 of the manuscript.

1-Phenylpentanol (3a)[10]



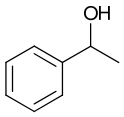
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.94 (t, *J* = 7.1 3H), 1.25-1.50 (m, 4H), 1.62-1.85 (m, 2H), 2.11 (bs, 1H), 4.61 (t, *J* = 7.0 Hz, 1H), 7.21-7.35 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 14.3, 22.8, 28.3, 39.2, 75.1, 126.4, 127.6, 128.9, 144.8.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3365, 2952, 1488, 1450, 1373, 1112, 1044, 1104, 1068, 1041, 1007, 906.

Anal. Calcd. for $C_{11}H_{16}O$. Calcd.: C, 80.44; H, 9.82. Found: C, 80.59; H, 10.01.

1-Phenylethanol (3b)[10]



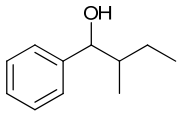
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.94 (t, *J* = 7.1 3H), 1.25-1.50 (m, 4H), 1.62-1.85 (m, 2H), 2.11 (bs, 1H), 4.61 (t, *J* = 7.0 Hz, 1H), 7.21-7.35 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 25.3, 71.0, 126.4, 127.6, 128.9, 144.8.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3362, 2950, 1491, 1450, 1370, 1108, 1070, 1051, 909.

Anal. Calcd. for $C_{11}H_{16}O$. Calcd.: C, 80.44; H, 9.82. Found: C, 80.59; H, 10.01.

2-Methyl-1-phenylbutan-1-ol (3c)[11]



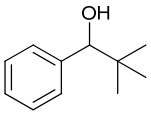
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.80 (d, *J* = 7.0 1.5H), 1.86 (d, *J* = 3.2 Hz, 1H), 0.92 (t, *J* = 7.8 Hz, 1.5H), 0.98 (d, *J* = 6.8 Hz, 1.5H), 0.99 (t, *J* = 7.3 Hz, 1.5H), 1.06-1.31 (m, 1H), 1.36-1.45 (m, 0.5H), 1.65-1.87 (m, 2.5H), 4.41 (d, *J* = 6.8Hz, 0.5H), 4.48 (d, *J* = 6.1 Hz, 0.5H), 7.25-7.41 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 12.1, 14.4, 25.8, 42.3, 79.5, 126.8, 127.7, 128.7, 143.9.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3358, 2951, 1487, 1448, 1372, 1074, 1051, 1026, 904.

Anal. Calcd. for $C_{11}H_{16}O$. Calcd.: C, 80.44; H, 9.82. Found: C, 80.63; H, 9.98.

***tert*- Butyl-phenylpropanol (3d)**[12]



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.92 (s, 9H), 1.86 (d, *J* = 3.2 Hz, 1H), 4.43 (d, *J* = 3.1 Hz, 1H), 7.21-7.27 (m, 1H), 7.33-7.38 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 25.7, 35.2, 82.1, 127.5, 127.8, 128.0, 142.6.

FT-IR (KBr) (ν_{max}/cm^{-1}): 3441, 3086, 1490, 1454, 1378, 1071, 1050, 1023, 906.

Anal. Calcd. for $C_{11}H_{16}O$. Calcd.: C, 80.44; H, 9.82. Found: C, 80.27; H, 9.69.

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