Supporting Information

Addition of Hetero Allenyl Copper Reagents to Aldehydes: Scope and Behavior.

Emmanuel Vrancken*,^{1a} Nacira Alouane,^{1a} Hélène Gérard,^{1b} Pierre Mangeney*^{1a}

^{1a} Institut Fédératif de Recherche FR 2769, UMR 7611, Université Pierre et Marie Curie, 4 Place
Jussieu, F-75252, Paris Cedex, France.

^{1b} Laboratoire de Chimie Théorique, UMR CNRS 7616, Université Pierre et Marie Curie, 4 Place
Jussieu, F-75252, Paris Cedex, France.

vrانcken@ccr.jussieu.fr

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Computational details

Full geometry optimizations were carried out without symmetry constraints using the Gaussian 03 program within the framework of the DFT (B3LYP),¹ using the 6-31+G** basis set for all atoms. Analysis of the Electron Localisation Function was carried out using the TopMod Package.² The conventional color code is used for the representation of the basins: blue for protonated disynaptic basins, green for bonding pair disynaptic basins and red for lone pair monosynaptic basins.

General Considerations

Experiments were carried out under dry argon atmosphere. All glassware were dried at 120°C and assembled while hot under a stream of argon. All moisture-sensitive reactants are handled under an argon atmosphere. Low temperature experiments are carried out by cooling down a three-necked round bottom flask with an ether/acetone (-80/-90°C), bath, frozen with liquid nitrogen. The flask was equipped with an internal thermometer, a nitrogen inlet and a septum cap. Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Column chromatographies were performed over silica gel Si 0.040-0.063 mesh. Melting points are uncorrected. ¹H NMR spectra were recorded at 400 MHz, and ¹³C NMR spectra were recorded at 100 MHz, in CDCl₃ or C₆D₆ as solvent. Chemical shifts are reported in ppm (reference TMS for ¹H NMR and CDCl₃ or C₆D₆ for ¹³C NMR). Compounds **3**, **4**,³ **5**,⁴ **6**⁵ and *anti*-**11c-f**⁶ have already been described.

General procedure A for the addition of copper reagents derived from propargylic ethers **3, **4**, **5** and **6** to aldehydes.** A solution of propargylic ether (2 mmol) in THF (15 mL) cooled to -90°C was treated dropwise with *t*BuLi (1.5 M in hexane, 2.1 mmol), maintaining the internal temperature below -88°C. The mixture was stirred for 1 h at -90°C, during which an orange color developed. A solution of CuCN (270 mg, 3 mmol) and LiBr (521 mg, 6 mmol) in THF (10 mL) was then added dropwise, and the reaction was stirred an additional 30 min at -80°C. The reaction media turned yellow and a solution

of HMPA (2.8 mL, 16 mmol) in THF (5 mL) was added dropwise at -80°C , followed by the aldehyde (2.2 mmol). After 30 min at -90°C , the reaction was quenched by the addition of aqueous $\text{NH}_4\text{Cl}/\text{NH}_3$ (2/1) solution, and extracted with diethyl ether (3x20 mL). The combined organic layers were washed with water, brine, dried over magnesium sulfate and filtered off. The solvents were removed *in vacuo* and the product was then subjected to FC (flash chromatography) on SiO_2 .

General procedure B for the addition of copper reagent derived from propargylic ether 7 to aldehydes. A solution of propargylic ether **7** (256 mg, 2 mmol) in THF (15 mL) cooled to -90°C was treated dropwise with *t*BuLi (1.5 M in hexane, 2.1 mmol), maintaining the internal temperature below -88°C . The mixture was stirred for 1 h at -90°C , during which an orange color developed. A solution of CuCN (270 mg, 3 mmol) and LiBr (521 mg, 6 mmol) in THF (10 mL) was then added dropwise, and the reaction was stirred an additional 30 min at -80°C . The reaction media turned yellow and the aldehyde (2.2 mmol) was added dropwise. After 16h at -60°C , the reaction mixture was quenched by the addition of aqueous $\text{NH}_4\text{Cl}/\text{NH}_3$ (2/1) solution, and extracted with diethyl ether (3x20 mL). The combined organic layers were washed with water, brine, dried over magnesium sulfate and filtered off. The solvents were removed *in vacuo* and the product was then subjected to FC (flash chromatography) on SiO_2 .

General procedure C for the addition of copper reagents derived from propargylic ethers 8 and amines 17 to aldehydes. A solution of propargylic derivative (1 mmol) in THF (20 mL) cooled to -90°C was treated dropwise with *t*BuLi (1.5 M in hexane, 1.1 mmol), maintaining the internal temperature below -88°C . The mixture was stirred for 1 h at -90°C , during which an orange color developed. A solution of CuCN (135 mg, 1.5 mmol) and LiBr (261 mg, 3 mmol) in THF (5 mL) was then added dropwise, and the reaction was stirred an additional 30 min at -80°C . The reaction media turned yellow and the aldehyde (1.1 mmol) was added dropwise. After stirring 45 min at -60°C or -40°C , the reaction mixture was quenched by the addition of aqueous $\text{NH}_4\text{Cl}/\text{NH}_3$ (2/1) solution, and extracted with diethyl ether (3x20 mL). The combined organic layers were washed with water, brine,

dried over magnesium sulfate and filtered off. The solvents were removed *in vacuo* and the product was then subjected to FC (flash chromatography) on SiO₂.

1-(methoxymethoxy)-pent-2-yne (7) and 1-(3-(methoxymethoxy)prop-1-ynyl)benzene (8): To a stirred solution of propargyl alcohol (11.7 mL, 200 mmol) in dimethoxymethane (200 mL), were added at room temperature lithium bromide (3.5g, 20 mmol) and toluenesulfonic acid (3.5g, 20 mmol). Stirring was continued for 24 hours. The mixture was treated with water and extracted with ether (2x20 mL). The organic layers were combined, dried over sodium sulphate, filtered off and concentrated *in vacuo*. Distillation of the residue (82-84 °C, 10 mmHg) gave 15g (75%) of methoxymethyl ether as a colourless liquid. A solution of methoxymethyl propargyl ether (15 g, 150 mmol) in THF (150 mL) cooled to -80°C was treated dropwise with *n*BuLi (2.3 M in hexane, 150 mmol), maintaining the internal temperature below -80°C. The mixture was stirred for 1 h at -80°C. EtI (13.5 mL, 165 mmol) was added dropwise at -80°C. The reaction mixture was then allowed to warm to room temperature and refluxed for 3 hours. The reaction was quenched using a saturated aqueous solution of ammonium chloride. The layers were separated, the aqueous phase was extracted with ether and the combined organic phases dried over magnesium sulphate and filtered off. The volatiles were removed under reduced pressure and the residue purified by fractionnal distillation under reduced pressure (10 mmHg, 77°C) to yield 17.1 g (85%) of **7** as a colourless oil. IR (neat) ν = 2938 (br), 2287, 2227, 2714, 1450, 1320, 1148, 1041, 990, 920 cm⁻¹; ¹H NMR (400 MHz) δ 4.45 (s, 2H), 3.95 (s, 2H), 3.13 (s, 3H), 2.03-1.99 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz) δ 94.6, 88.3, 74.7, 55.5, 54.7, 13.7, 12.4; Elem anal. Calcd for C₇H₁₂O₂: C, 65.60; H, 9.44; O, 24.97. Found: C, 65.52; H, 9.48.

The compound **8** was prepared as follow: A solution of methoxymethyl propargyl ether (5g, 50 mmol), 1-iodobenzene (5.6 mL, 50 mmol) and freshly distilled triethylamine (2 mL) in THF (20 mL) were added dropwise to a solution of CuI (560 mg) and Pd(PPh₃)₂Cl₂ (700mg) in THF (20 mL). The reaction was stirred for 12 hours, hydrolysed with NH₃/NH₄Cl (2/1) solution and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulphate, filtered

off and concentrated *in vacuo*. Purification by FC (pentane/Et₂O: 95/5) gave 7.6 g (86%) of **8** as a colourless oil. IR (neat) ν = 2850, 1489, 1148, 1099, 1041, 989, 919, 755, 690 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.48-7.32 (m, 5H), 4.80 (s, 2H), 4.47 (s, 2H), 3.44 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 131.8, 128.5, 128.3, 122.6, 94.8, 86.1, 84.6, 55.6, 54.8; Elem Anal. Calcd for C₁₁H₁₂O₂: C, 74.98; H, 6.86; O, 18.16. Found: C, 74.58; H, 6.69

***anti*-2-tert-Butoxy-1-cyclohexyl-4-trimethylsilanyl-but-3-yn-1-ol (*anti*-9):** This compound was prepared according to the general procedure A, using (3-tert-Butoxy-prop-1-ynyl)-trimethylsilane **3** (2 mmol, 368 mg) and cyclohexane carboxaldehyde (0.266 mL, 2.2 mmol). Purification by FC (pentane/Et₂O: 95/5) gave a mixture of homopropargylic alcohols *anti*-**9** and *syn*-**9** (383 mg, 65%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ¹H NMR to be 97:3. *anti*-**9**: IR (neat) ν = 3550 (br), 2972, 2924, 2852, 1450, 1391, 1366, 1249, 1190, 1057, 840, 759 cm⁻¹; ¹H NMR (400 MHz) δ 4.23 (d, *J* = 4.6 Hz, 1H), 3.32-3.28 (m, 1H), 2.40 (d, *J* = 3.5 Hz, 1H), 2.01-1.98 (m, 1H), 1.78-1.58 (m, 6H), 1.27 (s, 9H), 1.24-1.04 (m, 4H), 0.17 (s, 9H); ¹³C NMR (100 MHz) δ : 105.0, 90.9, 78.1, 75.7, 64.5, 39.8, 29.4, 28.4, 28.3, 26.6, 23.3, 26.0, 0.0; Elem anal. Calcd for C₁₇H₃₂O₂Si: C, 68.86; H, 10.88; O, 10.79. Found: C, 68.91; H, 10.72. *syn*-**9**: only the distinguishable ¹H NMR peaks are reported: ¹H NMR (400 MHz) δ 4.08 (d, *J* = 7.8 Hz, 1H), 3.39-3.34 (m, 1H), 2.53 (d, *J* = 2.3 Hz, 1H), 1.30 (s, 9H).

***anti*-1-Cyclohexyl-2-methoxy-4-trimethylsilanyl-but-3-yn-1-ol (*anti*-10a):** This compound was prepared according to the general procedure A, using (3-methoxy-1-propynyl)-trimethylsilane **4** (2 mmol, 284 mg) and cyclohexane carboxaldehyde (0.266 mL, 2.2 mmol). Purification by FC (pentane/Et₂O: 85/15) gave pure homopropargylic alcohols *anti*-**10a** (350 mg, 69%) as a pale yellow oil. The diastereoselectivity of the reaction was determined to be 96:4. *anti*-**10a**: IR (neat) ν = 3452 (br), 2924, 2852, 2169, 1738, 1449, 1365, 1249, 1217, 1084, 1021, 840, 760 cm⁻¹; ¹H NMR (400 MHz) δ 4.05 (d, *J* = 4.3 Hz, 1H), 3.48-3.44 (m, 4H), 2.21 (d, *J* = 4.2 Hz, 1H), 2.02-1.99 (m, 1H), 1.78-1.59 (m,

5H), 1.31-1.04 (m, 5H), 0.21 (s, 9H); ^{13}C NMR (100 MHz) δ : 101.0, 93.3, 76.5, 56.9, 40.1, 29.1, 28.5, 26.5, 25.9, 0.0; Elem anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}$: C, 66.09; H, 10.30; O, 12.58. Found: C, 66.13; H, 10.46. *syn*-**10a**: only the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 3.93 (d, J = 7.3 Hz, 1H).

***anti*-1-Cyclohexyl-2-methoxymethoxy-4-trimethylsilanyl-but-3-yn-1-ol (*anti*-11a)**: This compound was prepared according to the general procedure A, using (3-(methoxymethoxy)-1-propynyl)-trimethylsilane **5** (2 mmol, 344 mg) and cyclohexane carboxaldehyde (0.266 mL, 2.2 mmol). Purification by FC (pentane/Et₂O: 85/15) gave pure homopropargylic alcohols *anti*-**11a** (426 mg, 75%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be 94:6. *anti*-**11a**: IR (neat) ν = 3490 (br), 2923, 2852, 2181, 1450, 1250, 1152, 1099, 840, 759 cm^{-1} ; ^1H NMR (400 MHz) δ 4.98 (d, J = 6.8 Hz, 1H), 4.66 (d, J = 6.8 Hz, 1H), 4.47 (d, J = 4.4 Hz, 1H), 3.47 (dt, J = 4.3, 7.1 Hz, 1H), 3.41 (s, 3H), 2.27 (d, J = 4.3 Hz, 1H), 2.05-2.02 (m, 1H), 1.80-1.66 (m, 5H), 1.30-1.06 (m, 5H), 0.20 (s, 9H); ^{13}C NMR (100 MHz) δ 100.7, 94.2, 93.2, 76.9, 68.6, 56.0, 40.2, 29.3, 28.4, 26.5, 26.3, 26.0, 0.0; Elem anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Si}$: C, 63.33; H, 9.92; O, 16.87. Found: C, 63.21; H, 9.99. *syn*-**11a**: only the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 4.98 (d, J = 6.8 Hz, 1H), 4.66 (d, J = 6.8 Hz, 1H), 4.35 (d, J = 6.32 Hz, 1H), 3.39 (s, 3H), 2.49 (d, J = 3.1 Hz, 1H), 0.19 (s, 9H).

***anti*-3-Methoxymethoxy-1-trimethylsilanyl-hept-1-yn-4-ol (*anti*-11b)**: This compound was prepared according to the general procedure A, using (3-(methoxymethoxy)-1-propynyl)-trimethylsilane **5** (2 mmol, 344 mg) and butyraldehyde (0.200 mL, 2.1 mmol). Purification by FC (pentane/Et₂O: 85/15) gave a mixture of homopropargylic alcohols *anti*-**11b** and *syn*-**11b** (386 mg, 79%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be 90:10. *anti*-**11b**: IR (neat) ν = 3467 (br), 2958, 2172, 1250, 1153, 1024, 840, 760 cm^{-1} ; ^1H NMR (400 MHz) δ 4.98 (d, J = 6.1 Hz, 1H), 4.68 (d, J = 6.1 Hz, 1H), 4.33 (d, J = 4.1 Hz, 1H), 3.77-3.71 (m, 1H), 3.42 (s, 3H), 2.25 (d, J = 5.6 Hz, 1H), 1.62-1.41 (m, 4H), 0.97 (t, J = 7.8 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz) δ 100.7, 94.5,

93.2, 72.8, 70.9, 56.0, 34.8, 19.0, 14.2, 0.0; Elem anal. Calcd for $C_{12}H_{24}O_3Si$: C, 58.97; H, 9.90; O, 19.64. Found: C, 58.57; H, 9.89. *syn-11b*: only the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 4.16 (d, J = 7.1 Hz, 1H).

anti-3-Methoxymethoxy-1-trimethylsilyl-undeca-1,5-diyn-4-ol (anti-11g): This compound was prepared according to the general procedure A, using (3-(methoxymethoxy)-1-propynyl)-trimethylsilane **5** (2 mmol, 344 mg) and 2-octynal (0.314 mL, 2.1 mmol). Purification by FC (pentane/Et₂O: 85/15) gave pure homopropargylic alcohol *anti-11g* (480 mg, 79%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be 96:4. *anti-11g*: IR (neat) ν = 3425 (br), 2932, 2237, 2175, 1249, 1151, 1101, 1026, 840, 760 cm^{-1} ; ^1H NMR (400 MHz) δ 4.94 (d, J = 6.8 Hz, 1H), 4.72 (d, J = 6.8 Hz, 1H), 4.50 (ddt, J = 2.0, 3.8, 8.1 Hz, 1H), 4.45 (d, J = 3.8 Hz, 1H), 3.44 (s, 3H), 2.75 (d, J = 8.1 Hz, 1H), 2.24 (dt, J = 2.0, 7.1 Hz, 2 H), 1.57-1.50 (m, 2H), 1.44-1.26 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz) δ 100.0, 95.0, 93.3, 87.3, 77.5, 71.4, 65.2, 56.1, 31.2, 28.4, 22.4, 19.0, 14.2, 0.0; Elem anal. Calcd for $C_{16}H_{28}O_3Si$: C, 64.82; H, 9.52; O, 16.19. Found: C, 64.49; H, 9.67. *syn-11g*: only the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 4.36 (d, J = 6.3 Hz, 1H).

anti-1-Cyclohexyl-2-(1-methoxy-1-methyl-ethoxy)-4-trimethylsilyl-but-3-yn-1-ol (anti-12a): This compound was prepared according to the general procedure A, using [3-(1-Methoxy-1-methyl-ethoxy)-prop-1-ynyl]-trimethyl-silane **6** (2 mmol, 400 mg) and cyclohexane carbaldehyde (0.266 mL, 2.2 mmol). Purification by FC (pentane/Et₂O: 90/10) gave a mixture of homopropargylic alcohols *anti-12a* and *syn-12a* (487 mg, 78%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be 95:5. *anti-12a*: IR (neat) ν = 3496 (br), 2990, 2923, 2852, 2172, 1450, 1374, 1310, 1250, 1210, 1184, 1072, 838, 758 cm^{-1} ; ^1H NMR (400 MHz) δ 4.50 (d, J = 3.5 Hz, 1H), 3.36 (dt, J = 4.0, 8.1 Hz, 1H), 3.25 (s, 3H), 2.31 (d, J = 4.3 Hz, 1H), 2.10-2.07 (m, 1H), 1.78-1.52 (m, 5H), 1.48 (s, 3H), 1.38 (s, 3H), 1.28-1.01 (m, 5H), 0.18 (s, 9H); ^{13}C NMR (C₆D₆, 100 MHz) δ 105.2, 101.9, 90.8, 78.1, 64.2, 49.3, 40.6, 29.4, 29.3, 27.0, 26.6, 26.4, 25.9, 24.8, 0.0; Elem anal. Calcd for

C₁₇H₃₂O₃Si: C, 65.33; H, 10.32; O, 15.36. Found: C, 65.53; H, 10.40. *syn*-**12a**: only the distinguishable ¹H NMR peaks are reported: ¹H NMR (400 MHz) δ 4.32 (d, *J* = 7.6 Hz, 1H), 3.42 (m, 1H), 3.29 (s, 3H), 1.49 (s, 3H), 1.41 (s, 3H).

***anti*-1-Cyclohexyl-2-methoxymethoxy-hex-3-yn-1-ol (*anti*-13a)**: This compound was prepared according to the general procedure B, using cyclohexane carboxaldehyde (0.266 mL, 2.2 mmol). Purification by FC (pentane/Et₂O: 85/15) gave a mixture of homopropargylic alcohols *anti*-**13a** and *syn*-**13a** (375 mg, 78%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ¹H NMR to be 97:3. *anti*-**13a**: IR (neat) ν = 3455 (br), 2922, 2851, 2231, 1450, 1151, 1096, 1021, 918 cm⁻¹; ¹H NMR (400 MHz) δ 4.97 (d, *J* = 6.7 Hz, 1H), 4.64 (d, *J* = 6.7 Hz, 1H), 4.64 (dt, *J* = 2.0, 3.8 Hz, 1H), 3.43 (ddd, *J* = 3.7, 4.0, 7.4 Hz, 1H), 3.38 (s, 3H), 2.31 (d, *J* = 4 Hz, 1H), 2.24 (dq, *J* = 4.0, 7.6 Hz, 2H), 2.06-2.02 (m, 1H), 1.71-1.48 (m, 5H), 1.33-1.29 (m, 3H), 1.16 (t, *J* = 7.4 Hz, 3H), 1.39-1.00 (m, 2H); ¹³C NMR (100 MHz) δ 12.5, 13.9, 25.8, 26.1, 26.4, 28.5, 29.1, 40.0, 55.7, 68.3, 74.0, 77.0, 90.1, 93.8; Elem anal. Calcd for C₁₄H₂₄O₃: C, 69.96; H, 10.07; O, 19.97. Found: C, 70.11; H, 9.99. *syn*-**13a**: only the distinguishable ¹H NMR peaks are reported: ¹H NMR (400 MHz) δ 4.98 (d, *J* = 6.8 Hz, 1H), 4.27 (dt, *J* = 2.0, 6.6 Hz, 1H).

***anti*-5-Methoxymethoxy-non-6-yn-4-ol (*anti*-13b)**: This compound was prepared according to the general procedure B, using butyraldehyde (0.200 mL, 2.1 mmol). Purification by FC (pentane/Et₂O: 80/20) gave pure homopropargylic alcohol *anti*-**13b** (296 mg, 74%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ¹H NMR to be 90:10. *anti*-**13b**: IR (neat) ν = 3457 (br), 2958, 2851, 2205, 1318, 1150, 1098, 1022, 919 cm⁻¹; ¹H NMR (400 MHz) δ 4.95 (d, *J* = 6.8 Hz, 1H), 4.65 (d, *J* = 6.8 Hz, 1H), 4.31 (dt, *J* = 1.8, 3.8 Hz, 1H), 3.74-3.68 (m, 1H), 3.39 (s, 3H), 2.33 (d, *J* = 5.0 Hz, 1H), 2.26 (dq, *J* = 2.0, 7.6 Hz, 2H), 1.64-1.32 (m, 4H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz) δ 94.0, 90.1, 74.1, 72.9, 70.5, 55.7, 34.7, 18.9, 14.0, 13.8, 12.4; Elem anal. Calcd for C₁₁H₂₀O₃: C, 65.97; H, 10.07; O, 23.97. Found: C, 65.75; H, 10.14. *syn*-**13b**: only

the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 4.98 (d, J = 6.8 Hz, 1H), 4.27 (dt, J = 2.0, 6.6 Hz, 1H).

***anti*-2-Methoxymethoxy-1-phenyl-hex-3-yn-1-ol (*anti*-13c):** This compound was prepared according to the general procedure B, using benzaldehyde (0.230 mL, 2.1 mmol). Purification by FC (pentane/Et₂O: 80/10) gave a mixture of homopropargylic alcohols *anti*-13c and *syn*-13c (375 mg, 78%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be 96:4. *anti*-13c: IR (neat) ν = 3449 (br), 2888, 2231, 1454, 1149, 1097, 1025, 916.7, 751, 699 cm⁻¹; ^1H NMR (400 MHz) δ 4.92 (d, J = 6.7 Hz, 1H), 4.82 (dd, J = 4.0, 4.4 Hz, 1H), 4.61 (d, J = 6.7 Hz, 1H), 4.64 (dt, J = 2.0, 5.0 Hz, 1H), 3.21 (s, 3H), 2.91 (d, J = 4.0 Hz, 1H), 2.24 (dq, J = 4.0, 7.6 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz) δ 139.6, 128.0, 126.9, 93.9, 90.8, 75.4, 74.1, 71.6, 55.6, 13.7, 12.5; Elem anal. Calcd for C₁₄H₁₈O₃: C, 71.77; H, 7.74; O, 20.49. Found: C, 71.36 H, 8.01. *syn*-13c: only the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 4.99 (d, J = 6.0 Hz, 1H), 4.76 (dd, J = 2.7, 7.2 Hz), 4.37 (dt, J = 1.8, 7.2 Hz, 1H), 3.33 (s, 3H), 2.16 (dq, J = 1.8, 7.3 Hz, 2H), 1.07 (t, J = 7.3 Hz, 3H).

***anti*-5-Methoxymethoxy-non-2-en-6-yn-4-ol (*anti*-13d):** This compound was prepared according to the general procedure B, using crotonaldehyde (0.180 mL, 2.1 mmol). Purification by FC (pentane/Et₂O: 75/25) gave pure homopropargylic alcohol *anti*-13d (299 mg, 76%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be >97:3. *anti*-13d: IR (neat) ν = 3449 (br), 2287, 2231, 1451, 1318, 1151, 1097, 1023, 964 cm⁻¹; ^1H NMR (400 MHz) δ 5.80 (dq, J = 6.6, 15.4 Hz, 1H), 5.60 (ddd, J = 1.8, 6.8, 15.4 Hz, 1H), 4.93 (d, J = 6.8 Hz, 1H), 4.66 (d, J = 6.8 Hz, 1H), 4.33 (dt, J = 2.0, 3.8 Hz, 1H), 4.17 (m, 1H), 3.38 (s, 3H), 2.55 (d, J = 5.8 Hz, 1H), 2.25 (dq, J = 2.0, 7.6 Hz, 2H), 1.74 (ddd, J = 0.8, 0.8, 6.8 Hz, 3H), 1.15 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz) δ : 129.4, 128.9, 94.2, 90.2, 74.2, 74.1, 70.7, 55.8, 17.9, 13.8, 12.5; Elem anal. Calcd for C₁₁H₁₈O₃: C, 66.64; H, 9.15; O, 24.21. Found: C, 66.97; H, 9.55.

***anti*-5-Methoxymethoxy-trideca-3,7-diyn-6-ol (*anti*-13e):** This compound was prepared according to the general procedure B, using 2-octynal (0.314 mL, 2.1 mmol). Purification by FC (pentane/Et₂O: 80/20) gave a mixture of homopropargylic alcohols *anti*-13e and *syn*-13e (408 mg, 76%) as a pale yellow oil. The diastereoselectivity of the reaction was determined by ¹H NMR to be 96:4. *anti*-13e: IR (neat) ν = 3432 (br), 2932, 2235, 1318, 1149, 1100, 1025, 919 cm⁻¹; ¹H NMR (400 MHz) δ 4.94 (d, *J* = 6.8 Hz, 1H), 4.70 (d, *J* = 6.8 Hz, 1H), 4.48-4.42 (m, 2H), 3.42 (s, 3H), 2.82 (d, *J* = 7.6 Hz, 1H), 2.29-2.21 (m, 4H), 1.56-1.48 (m, 2H), 1.41-1.28 (m, 4H), 1.16 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz) δ : 94.5, 90.2, 86.9, 77.30, 73.8, 71.0, 65.3, 55.8, 30.9, 28.2, 22.2, 18.7, 13.9, 13.7, 12.5; Elem anal. Calcd for C₁₅H₂₄O₃: C, 71.39; H, 9.59; O, 19.02. Found: C, 70.99; H, 9.58. *syn*-13e: only the distinguishable ¹H NMR peaks are reported: ¹H NMR (400 MHz) δ 4.36 (dt, *J* = 2.0, 6.0 Hz, 1H).

Structure determination of *anti*-13a: preparation of 14. *anti*-13a (165 mg, 0.69 mmol) and anhydrous PPTS (1.73g, 6.9 mmol) in *t*-BuOH (5 mL) were boiled under argon during 24 hours. Water was added to the cooled solution and the aqueous layer was extracted with ether. The ether layer was washed with water, dried and evaporated. The crude product was then transformed into the corresponding oxazolidinone **14** according to reference 18. IR (neat) ν = 2926 (br), 2854, 2359, 2340, 2243, 1802, 1450, 1350, 1143, 1083, 1000, 769, 726 cm⁻¹; ¹H NMR (400 MHz) δ 5.27 (td, *J* = 2.0, 4.3, 7.1 Hz, 1H), 4.29 (dd, *J* = 7.1, 8.8 Hz 1H), 2.29 (dq, *J* = 2.0, 7.3, 9.6 Hz, 2H), 2.07-1.68 (m, 10H), 1.18 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz) δ 154.2, 93.9, 82.9, 70.7, 70.4, 38.8, 28.6, 28.1, 25.9, 25.3, 25.1, 13.3, 12.5; Elem anal. Calcd for C₁₇H₂₆O₃: C, 73.34; H, 9.41; O, 17.24. Found: C, 73.45; H, 9.40.

***anti*-1-cyclohexyl-2-(methoxymeyhoxy)-4-phenylbut-3-yn-1-ol (*anti*-15a):** This compound was prepared according to the general procedure C, using cyclohexane carboxaldehyde (0.13 mL, 1.1 mmol). Purification by FC (pentane/Et₂O: 80/20) gave pure homopropargylic alcohol *anti*-15a (268 mg, 93%) as a yellow oil. The diastereoselectivity of the reaction was determined by ¹H NMR to be

>97:3. **anti-15a**: IR (neat) ν = 3475 (br), 2922, 2850, 1357, 1150, 1097, 1022, 917 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.49-7.28 (m, 5H), 5.07 (d, 1H, J = 6.8 Hz), 4.72 (dd, 2H, J = 6.8, 4.0 Hz), 3.62-3.44 (m, 1H), 3.44 (s, 3H), 2.47 (d, 1H, J = 4.0 Hz), 2.11 (d, 1H, J = 12.9 Hz), 1.80-1.73 (m, 5H), 1.29-1.09 (m, 5H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 131.9, 128.6, 128.3, 122.4, 94.2, 87.7, 84.2, 76.8, 68.6, 55.9, 40.1, 29.1, 28.6, 26.4, 26.1, 25.9; Elem anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3$: C, 74.97; H, 8.39; O, 16.64. Found: C, 74.61; H, 8.41.

anti-(1S,2R)-2-(methoxymethoxy)-1,4-diphenylbut-3-yn-1-ol (anti-15b): This compound was prepared according to the general procedure C, using benzaldehyde (0.12 mL, 1.1 mmol). Purification by FC (pentane/ Et_2O : 70/30) gave pure homopropargylic alcohol **anti-15b** (231 mg, 82%) as a yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be >97:3. **anti-15b**: IR (neat) ν = 3449 (br), 2890, 2360, 1490, 1453, 1149, 1099, 917 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.54-7.28 (m, 5H), 5.02 (d, 1H, J = 6.8 Hz), 4.98 (t, 1H, J = 8.6 Hz), 4.77 (d, 1H, J = 4.8 Hz), 4.71 (d, 1H, J = 6.8 Hz), 3.29 (s, 3H), 3.02 (d, 1H, J = 3.5 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 139.4, 131.9, 128.7, 128.3, 128.2, 128.1, 126.9, 122.2, 94.3, 88.3, 84.0, 75.5, 71.9, 55.8; Elem anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.57; H, 6.43; O, 17.00. Found: C, 76.33; H, 6.81.

anti-(E)-3-(methoxymethoxy)-1-phenylhept-5-en-1-yn-4-ol (anti-15c): This compound was prepared according to the general procedure C, using crotonaldehyde (0.09 mL, 1.1 mmol). Purification by FC (pentane/ Et_2O : 80/20) gave a mixture of homopropargylic alcohol **anti-15c** and **syn-15c** (230 mg, 95%) as a yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be 95:5. IR (neat) ν = 3422 (br), 2887, 1489, 1442, 1350, 1210, 1150, 1097, 917 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.45-7.28 (m, 5H), 5.87 (dq, 1H, J = 8.8, 16.4 Hz), 5.71 (dq, 1H, J = 1.5, 8.8, 16.4 Hz), 5.03 (d, 1H, J = 6.8 Hz), 4.74 (d, 1H, J = 6.8 Hz), 4.60 (d, 1H, J = 3.8 Hz), 4.33 (q, 1H, J = 5.6, 10.4 Hz), 3.45 (s, 3H), 2.73 (d, 1H, J = 5.6 Hz), 1.78 (d, 3H, J = 5.6 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 131.9, 129.7, 128.7, 128.6, 128.3, 122.3, 94.5, 87.7, 84.3, 74.2, 70.9, 55.9, 17.9; Elem anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C, 73.15;

H, 7.37; O, 19.49. Found: C, 73.08; H, 7.38. **syn-15c**: only the distinguishable ^1H NMR peaks are reported: ^1H NMR (400 MHz) δ 4.43 (q, 1H, J = 7.1 Hz, 1H).

***N,N*-Dibenzyl-3-phenylprop-2-yn-1-amine (17)**: A solution of *N,N*-Dibenzyl-prop-2-yn-1-amine (5g, 21 mmol), 1-iodobenzene (2.4 mL, 21 mmol) and freshly distilled triethylamine (0.8 mL) in THF (10 mL) were added dropwise to a solution of CuI (238 mg) and Pd(PPh₃)₂Cl₂ (322mg) in THF (10 mL). When the reaction was completed, the mixture was hydrolysed with an aqueous NH₃/NH₄Cl (1/3) solution and diluted with ether. The combined organic layers were washed with brine and dried over anhydrous magnesium sulphate and filtered off. The solvent was evaporated *in vacuo* and the product was isolated by chromatography (pentane/Et₂O: 95/5) to yield 5.7 g (88%) of **17** as a yellow solid (mp 62 °C). IR (neat) ν = 2824, 1488, 1454, 1351, 1310, 755, 738 cm⁻¹; ^1H NMR (CDCl₃, 400 MHz) δ 7.78-7.50 (m, 15H), 4.03 (s, 4H), 3.74 (s, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ 139.2, 132.1, 129.4, 128.6, 128.3, 127.4, 86.2, 84.7, 57.9, 42.3; Elem Anal. Calcd for C₂₃H₂₁N: C, 88.71; H, 6.80; N, 4.50. Found: C, 88.71; H, 6.72; N, 4.49.

***anti*-1-cyclohexyl-2-(dibenzylamino)-4-phenylbut-3-yn-1-ol (*anti*-18a)**: This compound was prepared according to the general procedure C, using cyclohexane carboxaldehyde (0.13 mL, 1.1 mmol). Purification by FC (pentane/Et₂O: 90/10) gave pure homopropargylic alcohol ***anti*-18a** (385 mg, 91%) as a yellow oil. The diastereoselectivity of the reaction was determined by ^1H NMR to be >97:3. ***anti*-18a**: IR (neat) ν = 3448 (br), 2923, 2360, 1489, 1449, 1070, 745 cm⁻¹; ^1H NMR (CDCl₃, 400 MHz) δ 7.61-7.28 (m, 15H), 3.82 (d, 2H, J = 13.6 Hz), 3.80 (d, 1H, J = 7.8 Hz), 3.79-3.66 (m, 1H), 3.58 (d, 2H, J = 13.6 Hz), 2.01 (d, 1H, J = 4.6 Hz), 1.89-0.94 (m, 11H); ^{13}C NMR (CDCl₃, 100 MHz) δ 139.4, 132.1, 129.2, 128.5, 128.4, 127.2, 122.9, 87.9, 85.3, 75.9, 56.1, 56.0, 39.2, 30.7, 26.9, 26.5, 26.3, 24.8; Elem anal. Calcd for C₃₀H₃₃NO: C, 85.06; H, 7.85; N, 3.31; O, 3.78. Found: C, 84.76; H, 7.75; N, 3.29.

***anti*-(2-dibenzylamino)-1,4-diphenylbut-3-yn-1-ol (*anti*-18b).** This compound was prepared according to the general procedure C, using benzaldehyde (0.12 mL, 1.1 mmol). Purification by FC (pentane/Et₂O: 90/10) gave pure homopropargylic alcohol *anti*-18b (356 mg, 86%) as a yellow oil. The diastereoselectivity of the reaction was determined by ¹H NMR to be >97:3. *anti*-18b: IR (neat) ν = 3398 (br), 3027, 2974, 1490, 1453, 1026, 975 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.71-7.24 (m, 20H), 4.97 (d, 1H, *J* = 7.8 Hz), 4.09 (d, 1H, *J* = 8.1 Hz), 4.00 (d, 2H, *J* = 13.6 Hz), 3.64 (d, 2H, *J* = 13.6 Hz), 2.96 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.2, 138.9, 132.2, 128.9, 128.6, 128.5, 128.4, 128.2, 128.1, 127.5, 127.2, 122.9, 88.3, 84.9, 74.7, 59.9, 55.9; Elem anal. Calcd for C₃₀H₂₇NO: C, 86.30; H, 6.52; N, 3.35; O, 3.83. Found: C, 86.28; H, 6.59; N, 3.41.

***anti*-(*E*)-3-(dibenzylamino)-phenylhept-en-1-yn-4-ol (*anti*-18c):** This compound was prepared according to the general procedure C, using crotonaldehyde (0.09 mL, 1.1 mmol). Purification by FC (pentane/Et₂O: 80/20) gave pure homopropargylic alcohol *anti*-18c (304 mg, 80%) and *syn*-18c (10 mg, 2.6%) as yellow oils. The diastereoselectivity of the reaction was determined by ¹H NMR to be 95:5. *anti*-18c: IR (neat) ν = 3419 (br), 3060, 2913, 1489, 1452, 1070, 961 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.62-7.28 (m, 15H), 5.89-5.83 (m, 1H), 5.64 (dq, 1H, *J* = 1.5, *J* = 6.6, 15.2 Hz), 4.34-4.31 (m, 1H), 3.99 (d, 2H, *J* = 13.6 Hz), 3.77 (d, 1H, *J* = 7.6 Hz), 3.57 (d, 2H, *J* = 13.6 Hz), 2.55 (s, 1H), 1.83 (d, 3H, *J* = 6.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 139.3, 132.1, 131.3, 129.0, 128.4, 128.3, 127.2, 122.9, 87.8, 84.7, 72.9, 58.2, 56.0, 17.9; Elem anal. Calcd for C₂₇H₂₇NO: C, 85.00; H, 7.13; N, 3.67; O, 4.19. Found: C, 85.08; H, 7.14; N, 3.73.

syn-18c: IR (neat) ν = 3429 (br), 3027, 2920, 1489, 1452, 1070, 963 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.52-7.28 (m, 15H), 5.86 (dq, 1H, *J* = 6.6, 3.6 Hz), 5.41 (dq, 1H, *J* = 1.8, 6.6, 13.6 Hz), 4.16 (dd, 1H, ¹*J* = 6.8, 9.6 Hz), 4.03 (s, 1H), 3.98 (d, 2H, *J* = 13.4 Hz), 3.55 (d, 2H, *J* = 13.4 Hz), 3.47 (d, 1H, *J* = 9.9 Hz), 1.72 (dd, 3H, *J* = 1.5, 6.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 138.2, 131.8, 129.8, 129.2, 128.6, 128.4, 127.5, 122.9, 87.7, 83.6, 71.1, 58.6, 55.1, 17.9.

1-Methoxymethoxy-penta-1,2-diene (20) and (3-methoxymethoxy-propa-1,2-dienyl)-benzene (21): These compounds were obtained by hydrolysis of the corresponding copper derivatives and were analyzed without further purification. **20:** ^1H NMR (400 MHz) δ 6.58 (dt, 1H, $J = 2.5, 5.8$ Hz), 5.88 (q, 1H, $J = 5.8$ Hz), 4.80 (s, 2H), 3.42 (s, 3H), 2.17-2.04 (m, 2H), 1.03 (t, 3H, $J = 7.3$ Hz). **21:** ^1H NMR (400 MHz) δ 7.49-7.28 (m, 5H), 7.03 (d, 1H $J = 5.8$ Hz), 6.79 (d, 1H, $J = 5.8$ Hz), 4.91 (s, 2H), 3.50 (s, 3H).

1-cyclohexyl-4-trimethylsilanyl-but-3-yne-1,2-diol (22): *anti*-**12a** was dissolved in CDCl_3 and stirred at room temperature overnight to give pure diol **22** without further purification. IR (neat) $\nu = 3378$ (br), 2922, 2852, 2171, 1449, 1405, 1248, 1035, 962, 839, 758 cm^{-1} ; ^1H NMR (400 MHz) δ 4.42 (d, $J = 3.5$ Hz, 1H), 3.34 (dd, $J = 3.8, 10.8$ Hz, 1H), 2.03 (d, 1H, $J = 12.9$ Hz), 1.76-0.98 (m, 11H), 0.17 (s, 9H); ^{13}C NMR (100 MHz) δ : 51.9, 90.2, 40.3, 26.8, 26.2, 25.9, 25.6, 13.5; Elem anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$: C, 64.95; H, 10.06; O, 13.31; Si, 11.68. Found: C, 64.65; H, 10.46.

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