Gold(III)-Catalysed Nucleophilic Substitution of Propargylic Alcohols

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Supporting Information

General information. Unless otherwise stated all commercial materials were used without further purification. Reactions were carried out in round bottom flasks equipped with a magnetic stirring bar and capped with a septum. Dichloromethane was distilled over CaH_2 and run over neutral alumina to remove any residual ethanol. TLC analysis of all reactions was performed on Merck silica gel 60 F₂₅₄ TLC plates. Chromatography was carried out on Merck 60 silica gel (40-63 μm). FT-IR spectra were recorded with a Perkin Elmer Spectrum BX spectrometer. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance-300 and Avance-500 spectrometers and referenced to CDCl_3 unless otherwise noted. Mass spectra, elemental and chiral HPLC analyses were obtained from the mass spectrometry, elemental analysis and HPLC facilities operated by the Institut de Chimie des Substances Naturelles.

General procedure for gold-catalysed nucleophilic substitutions of propargylic alcohols.

To a solution of propargylic alcohol (1 eq.) in dichloromethane (0,2 M) was added the nucleophile (1.5 eq. – 5 eq.) followed by the catalyst (5 mol%). The reaction mixture was stirred at room temperature and monitored periodically by TLC. Upon completion, the mixture was concentrated *in vacuo* and loaded on to a silica gel column and chromatographed with an appropriate mixture of pentane and diethyl ether to give the substitution products described below.

oct-1-en-5-yn-4-ylbenzene (**2a**)

82 %. Prepared with 1.5 eq. of allyltrimethylsilane and isolated as a clear oil. R_f = 0.75 (Heptane/EtOAc 8/2). IR (film) cm^{-1} : 2955, 2929, 2357. ^1H NMR (CDCl_3 , 300MHz) δ (ppm): 0.92 (t, J = 7Hz, 3H), 1.38 (m, 4H), 1.55 (m, 2H), 2.23 (td, J = 2.2Hz, J = 7Hz, 2H), 2.47 (t, J = 7Hz, 2H), 3.68 (tt, J = 2.2Hz, J = 7Hz, 1H), 5.04 (d, J = 10.5Hz, 1H), 5.05 (d, J = 16.8Hz, 1H), 5.87 (ddt, J = 7Hz, J = 10.4Hz, J = 16.9Hz, 1H), 7.20-7.39 (m, 5H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.2, 19.0, 22.4, 28.9, 31.2, 38.2, 43.2, 81.2, 84.0, 116.8, 126.7, 127.6, 128.5, 136.0, 142.3. MS (EI) : 185 (34), 91 (100), 77 (73), 41 (39). Anal. calcd. for $\text{C}_{17}\text{H}_{22}$: C, 90.20, H, 9.80. Found : C, 90.31, H, 10.15.

2-(oct-1-en-5-yn-4-yl)naphthalene (**2b**)

83 %. Prepared with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. R_f = 0.20 (pentane). IR (film) cm^{-1} : 3055, 2929. ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.93 (t, J = 7Hz, 3H), 1.41 (m, 4H), 1.56 (m, 2H), 2.27 (td, J = 2.2Hz, J = 7Hz, 2H), 2.60 (t, J = 7Hz, 2H), 3.85 (m, 1H), 5.05 (d, J = 10Hz, 1H), 5.06 (d, J = 17Hz, 1H), 5.90 (m, 1H), 7.47 (m, 3H), 7.8 (m, 4H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.0, 18.9, 22.2, 28.8, 31.1, 38.2, 42.9, 81.1, 84.1, 116.8, 125.5, 125.9, 126.0, 126.0, 127.6, 127.8, 128.0, 132.4, 133.5, 135.8, 139.6. Anal. calcd. for $\text{C}_{21}\text{H}_{24}$: C, 91.25, H, 8.75. Found : C, 91.17, H, 8.57.

1,2-dimethoxy-3-(oct-1-en-5-yn-4-yl)benzene (**2c**)

85 %. Prepared with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. R_f = 0.18 (pentane). IR (film) cm^{-1} : 2929, 2359. ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.92 (t, J = 7Hz, 3H), 1.37 (m, 4H), 1.54 (m, 2H), 2.22 (td, J = 2.2Hz, J = 7Hz, 2H), 2.45 (m, 2H), 3.86 (s, 3H), 3.87 (s, 3H), 4.10 (m, 1H), 5.04 (d, J = 10Hz, 1H), 5.05 (d, J = 17Hz, 1H), 5.90 (m, 1H), 6.80 (d, J = 1.5Hz, J = 8Hz, 1H), 7.05 (t, J = 8Hz, 1H), 7.13 (dd, J = 1.6Hz, J = 7.8Hz, 1H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.0, 18.8, 22.2, 28.8, 31.1, 31.4, 41.8, 55.7, 60.8, 81.5, 82.8, 110.8, 116.4, 120.5, 123.8, 136.0, 136.2, 146.1, 152.5. Anal. calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68, H, 9.15. Found : C, 79.63, H, 9.28.

1-bromo-3-(oct-1-en-5-yn-4-yl)benzene (**2d**)

71 % Prepared with 1.5eq. of allyltrimethylsilane and isolated as a colorless oil. R_f = 0.20 (pentane). IR (film) cm^{-1} : 2928, 670. ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.92 (t, J = 7Hz, 3H), 1.37 (m, 4H), 1.50 (m, 2H), 2.23 (td, J = 2.2Hz, J = 7Hz, 2H), 2.46 (t, J = 7Hz, 2H), 3.64 (td, J = 2.1Hz, J = 7Hz, 2H), 5.04 (d, J = 10Hz, 1H), 5.05 (d, J = 17Hz, 1H), 5.84 (m, 1H), 7.23 (m, 1H), 7.37 (m, 2H), 7.52 (m, 1H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.1, 18.9, 22.3, 28.8, 31.2, 37.8, 43.0, 80.4, 84.6, 117.2, 122.5, 126.3, 129.8, 130.0, 130.8, 135.4, 144.6. Anal. calcd for $\text{C}_{17}\text{H}_{21}\text{Br}$: C, 66.89, H, 6.93. Found : C, 66.68, H, 7.17.

2f

66 %. Prepared with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. $R_f = 0.18$ (pentane). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : mixture of isomers (2/2/1) 0.90 (m, 15H), 1.34 (m, 20H), 1.53 (m, 10H), 2.25 (m, 8H), 2.37 (m, 4H), 2.49 (m, 8H), 3.28 (m, 1H), 3.39 (td, $J = 7\text{Hz}$, 2H), 4.04 (td, $J = 7\text{Hz}$, 2H), 4.96-5.15 (m, 10H), 5.47 (m, 4H), 5.71 (m, 4H), 5.90 (m, 3H), 6, 15 (dd, $J = 6,3\text{ Hz}$, $J = 15,7\text{ Hz}$, 1H), 6,20 (dd, $J = 7,6\text{ Hz}$, $J = 15,8\text{ Hz}$, 2H), 6.64 (dd, $J = 15,7\text{Hz}$, $J = 1,2\text{Hz}$, 1H), 7.16-7.39 (m, 25H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.0, 14.0, 18.8, 19.4, 19.6, 22.2, 22.3, 28.5, 28.5, 28.8, 31.1, 34.9, 39.7, 39.9, 40.4, 45.8, 48.9, 77.3, 78.9, 80.2, 84.3, 90.1, 95.2, 109.5, 110.3, 116.1, 116.5, 116.8, 126.3, 126.3, 126.5, 127.0, 127.2, 127.7, 128.5, 128.5, 130.1, 130.2, 135.7, 136.2, 136.3, 137.3, 142.9, 143.7, 144.6, 145.2.

trimethyl(3-phenylhex-5-en-1-ynyl)silane (**2g**)¹

71 %. Prepared with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. $R_f = 0.20$ (pentane). IR (film) cm^{-1} : 2958, 2173. ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.23 (s, 9H), 2.55 (t, $J = 7.1\text{Hz}$, 2H), 3.72 (t, $J = 7.1\text{Hz}$, 1H), 5.04 (d, $J = 11\text{Hz}$, 1H), 5.07 (d, $J = 15.5\text{Hz}$, 1H), 5.85 (m, 1H), 7.24 (m, 1H), 7.34 (m, 4H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 0.2, 38.8, 42.7, 87.7, 107.5, 116.8, 126.6, 127.4, 128.2, 135.1, 140.9.

Data are in accordance with previously reported results.¹

hex-5-en-1-yne-1,3-diyl dibenzene (**2h**)^{1,2}

97 %. with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. $R_f = 0.22$ (pentane). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 2.62 (t, $J = 7\text{Hz}$, 2H), 3.94 (t, $J = 7\text{Hz}$, 1H), 5.13 (m, 2H), 5.96 (ddt, $J = 7\text{Hz}$, $J = 10.1\text{Hz}$, $J = 17.1\text{Hz}$, 1H), 7.30-7.49 (m, 10H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 38.6, 42.8, 83.8, 90.9, 117.1, 123.7, 125.9, 126.3, 126.8, 127.3, 127.6, 127.8, 131.7, 131.9, 135.5, 141.4.

Data are in accordance with previously reported results.^{1,2}

Starting from enantiomerically enriched propargylic alcohol (96% ee), the enantiomeric purity was determined by chiral HPLC analysis, Chiralcel OD column, 100% hexane, 1 mL/min; t_R 10,73 min, 12,30 min, ee = 0.

(4-methyloct-1-en-5-yn-4-yl)benzene (**2j**)

33 %. Prepared with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. R_f = 0.24 (pentane). IR (film) cm^{-1} : 2928, 710. ^1H NMR (CDCl_3 , 300MHz) δ (ppm): 0.93 (t, J = 7Hz, 3H), 1.40 (m, 4H), 1.54 (s, 3H), 1.55 (m, 2H), 2.27 (t, J = 6.9Hz, 2H), 2.52 (m, 2H), 5.00 (d, J = 15.5Hz, 1H), 5.01 (d, J = 12Hz, 1H), 5.80 (m, 1H), 7.23 (m, 3H), 7.54 (d, J = 7.8Hz, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm): 14.0, 18.8, 22.2, 28.8, 29.5, 29.7, 31.1, 40.0, 48.9, 84.0, 84.9, 117.2, 126.2, 128.0, 135.2, 146.0. The compound decomposes rapidly at room temperature.

((3,3-dimethylhex-5-en-1-ynyl)benzene (**2k**)¹

59 %. Prepared with 1.5eq. of allyltrimethylsilane and isolated as a clear oil. R_f = 0.64 (pentane) ^1H NMR (CDCl_3 , 500MHz) δ (ppm): 1.31 (s, 6H), 2.29 (d, J = 7.2Hz, 2H), 5.14 (d, J = 8.8Hz, 1H), 5.14 (d, J = 16.8Hz, 1H), 6.04 (m, 1H), 7.29 (m, 3H), 7.42 (m, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm): 29.0, 31.5, 47.9, 80.7, 97.1, 117.5, 124.2, 127.5, 128.5, 131.8, 135.5.

Data are in accordance with previously reported results.¹

(1-butoxypent-2-ynyl)benzene (**2l**)

88 %. Prepared with 1.5 eq. of 1-butanol and isolated as a clear oil. R_f = 0.63 (Heptane/EtOAc 9/1). IR (film) cm^{-1} : 2956, 2930, 2223. ^1H NMR (CDCl_3 , 300MHz) δ (ppm): 0.91 (t, J = 7Hz, 3H), 0.92 (t, J = 7.3Hz, 3H), 1.37 (m, 6H), 1.59 (m, 4H), 2.28 (td, J = 2.2Hz, J = 7Hz, 2H), 3.48 (dt, J = 6.7Hz, J = 9Hz, 1H), 3.64 (dt, J = 6.7Hz, J = 8.9Hz, 1H), 5.15 (s, 1H), 7.34 (m, 3H), 7.52 (d, J = 7.2Hz, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm): 14.0, 14.1, 19.0, 19.5, 22.3, 28.5, 31.2, 31.9, 68.0, 71.8, 78.3, 88.3, 127.5, 128.2, 128.5, 139.8. MS

(EI) : 259 (9, MH^+), 258 (26, M^+), 192 (65), 160 (79), 118 (100), 91 (79). Anal. calcd. for $\text{C}_{18}\text{H}_{26}\text{O}$: C, 83.67, H, 10.14. Found : C, 83.84, H, 10.01.

(3-(but-3-enyloxy)-3-phenylprop-1-ynyl)trimethylsilane (**2m**)³

75 %. Prepared with 1.5eq. of 3-buten-1-ol and isolated as a clear oil. R_f = 0.57 (heptane/EtOAc 9/1). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.22 (s, 9H), 2.40 (q, J = 6.8Hz, 2H), 3.57 (dt, J = 7.1Hz, J = 8.5Hz, 1H), 3.71 (dt, J = 6.9Hz, J = 8.8Hz, 1H), 5.05 (d, J = 10.2Hz, 1H), 5.12 (d, J = 17.3Hz, 1H), 5.21 (s, 1H), 5.85 (ddt, J = 6.7Hz, J = 10.3Hz, J = 17Hz, 1H), 7.36 (m, 3H), 7.52 (d, J = 7.6Hz, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 0.06, 34.2, 67.6, 72.0, 92.7, 103.3, 116.5, 127.6, 128.4, 128.5, 135.4, 138.6. Data are in accordance with previously reported results.³

(3-(3-chloropropoxy)-3-methylbut-1-ynyl)benzene (**2n**)³

79 %. Prepared with 1.5eq. of 3-chloropropan-1-ol and isolated as a clear oil. R_f = 0.5 (heptane/ether 25/1). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 1.56 (s, 6H), 2.07 (~pent, J = 6.1Hz, 2H), 3.70 (t, J = 6.4Hz, 2H), 3.78 (t, J = 5.8Hz, 2H), 7.32 (m, 3H), 7.44 (m, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 28.6, 33.3, 42.2, 60.6, 70.5, 84.0, 91.6, 122.9, 128.2, 128.3, 131.7. Data are in accordance with previously reported results.³

(1-ethoxypent-2-ynyl)benzene (**2o**)

60 %. Prepared with 1.5 eq. of ethanol and isolated as a clear oil. R_f = 0.35 (Heptane/AcOEt 85/15). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.91 (t, J = 7Hz, 3H), 1.2 (t, J = 7Hz, 3H), 1.37 (m, 4H), 1.57 (m, 2H), 2.29 (td, J = 1.9Hz, J = 7Hz, 2H), 3.5 (m, 1H), 3.70 (m, 1H), 5.1 (s, 1H), 7.30-7.40 (m, 3H), 7.53 (m, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.1, 15.2, 18.8, 22.2, 28.3, 31.1, 63.5, 71.6, 78.2, 88.2, 127.4, 128.1, 128.4, 139.6.

(3-(2,4-dimethoxyphenyl)prop-1-yne-1,3-diyl)dibenzene (**2p**)⁴

75 %. Prepared with 5 eq. of 1,3-dimethoxybenzene and isolated as a white solid. $R_f = 0.45$ (Heptane/EtOAc 9/1). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 3.82 (s, 3H), 3.83 (s, 3H), 5.63 (s, 1H), 6.48 (d, $J = 2.4\text{Hz}$, 1H), 6.53 (dd, $J = 2.4\text{Hz}$, $J = 8.4\text{Hz}$, 1H), 7.22 (m, 1H), 7.31 (m, 5H), 7.49 (m, 4H), 7.52 (d, $J = 8.3\text{Hz}$, 1H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ (ppm) : 36.3, 55.6, 55.8, 83.6, 91.4, 98.8, 104.8, 123.1, 124.0, 126.6, 128.0, 128.4, 128.5, 129.7, 131.9, 142.3, 157.3, 160.1. Data are in accordance with previously reported results.⁴

(3-(4-methoxyphenyl)-3-phenylprop-1-ynyl)trimethylsilane (**2q**)⁵

65 %. Prepared with 1.1 eq. of anisole and isolated as a clear oil. $R_f = 0.20$ (pentane). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.27 (s, 9H), 2.96 (s, 3H), 5.00 (s, 1H), 6.86 (d, $J = 8.6\text{Hz}$, 2H), 7.20-7.33 (m, 5H), 7.38 (m, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 0.1, 43.3, 55.3, 88.9, 107.1, 114.1, 126.7, 127.8, 128.5, 128.8, 133.8, 141.9, 158.5. Data are in accordance with previously reported results.⁵

2-(1,3-diphenylprop-2-ynyl)furan (**2r**)⁴

46 %. Prepared with 1.5 eq. of furan and isolated as a yellow oil. $R_f = 0.48$ (Heptane/EtOAc 9/1). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 5.29 (s, 1H), 6.30 (d, $J = 3.2\text{ Hz}$, 1H), 6.34 (dd, $J = 1.9\text{Hz}$, $J = 3.2\text{Hz}$, 1H), 7.32 (m, 7H), 7.50 (m, 4H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 38.0, 84.1, 87.6, 106.8, 110.5, 123.3, 127.5, 128.0, 128.4, 128.8, 131.9, 139.0, 142.4, 153.9. Data are in accordance with previously reported results.⁴

Ethyl 2-(1-phenylpent-2-ynylthio)acetate (**2s**)

66 %. Prepared with 1.5eq. of ethylmercaptoacetate and isolated as a clear oil. $R_f = 0.70$ (Heptane/EtOAc 9/1). IR (film) cm^{-1} : 2930, 1731. ^1H NMR (CDCl_3 , 300MHz) δ (ppm): 0.92 (t, $J = 7\text{Hz}$, 3H), 1.24-1.44 (m, 4H), 1.30 (t, $J = 7\text{Hz}$, 3H), 1.60 (m, 2H), 2.30 (td, $J = 2.2\text{Hz}$, $J = 7\text{Hz}$, 2H), 3.23 (d, $J = 15\text{Hz}$, 1H), 3.50 (d, $J = 15\text{Hz}$, 1H), 4.19 (q, $J = 7\text{Hz}$, 2H), 5.01 (s, 1H), 7.30 (d, $J = 7.3\text{Hz}$, 1H), 7.52 (t, $J = 7.3\text{Hz}$, 2H), 7.53 (d, $J = 7.3\text{Hz}$, 2H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm): 14.1, 14.3, 19.0, 22.3, 28.6, 31.2, 33.8, 39.7, 61.5, 77.0, 87.6, 127.5, 128.2, 128.7, 138.2, 170.4. Anal. calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{S}$: C, 71.01, H, 7.95. Found: C, 71.01, H, 8.37.

(1,3-diphenylprop-2-ynyl)(phenyl)sulfane (**2t**)⁶

50 %.⁷ Prepared with 1.5eq. of thiophenol and isolated as a clear oil. $R_f = 0.52$ (Heptane/EtOAc 9/1). ^1H NMR (CDCl_3 , 300MHz) δ (ppm): 5.24 (s, 1H), 7.32 (m, 9H), 7.40 (m, 2H), 7.48 (m, 4H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm): 44.4, 87.0, 87.5, 123.1, 128.0, 128.2, 128.4, 128.4, 128.6, 128.6, 128.8, 131.8, 133.5, 134.6, 138.2. Data are in accordance with previously reported results.⁶

(2R)-ethyl 2-(*tert*-butoxycarbonylamino)-3-(1,3-diphenylprop-2-ynylthio)propanoate (**2u**)

35 %. Prepared with 1.5eq. of Boc(L)-Cys-OEt and isolated as a 1/1 mixture of 2 diastereoisomers (clear oil). $R_f = 0.47$ (Heptane/EtOAc 7/3). IR (film) cm^{-1} : 3358 (broad), 2976, 2928, 3258, 2339, 1736, 1711, 1697. ^1H NMR (CDCl_3 , 300MHz) δ (ppm): 1st diastereoisomer 1.25 (t, $J = 7.3\text{Hz}$, 3H), 1.46 (s, 9H), 2.93 (dd, $J = 7\text{Hz}$, $J = 13.9\text{Hz}$, 1H), 3.43 (dd, $J = 3.9\text{Hz}$, $J = 13.9\text{Hz}$, 1H), 4.23 (q, $J = 7.1\text{Hz}$, 2H), 4.65 (bs, 1H), 5.21 (s, 1H), 5.35 (t, $J = 7.7\text{Hz}$, 1H), 7.31-7.40 (m, 6H), 7.50-7.60 (m, 4H). 2nd diastereoisomer 1.27 (t, $J = 7.3\text{Hz}$, 3H), 1.45 (s, 9H), 3.07 (dd, $J = 7\text{Hz}$, $J = 13.9\text{Hz}$, 1H), 3.31 (dd, $J = 5.1\text{Hz}$, $J = 14\text{Hz}$, 1H),

4.20 (q, $J = 7.1\text{Hz}$, 2H), 4.60 (bs, 1H), 5.21 (s, 1H), 5.35 (t, $J = 7.7\text{Hz}$, 1H), 7.31-7.40 (m, 6H), 7.50-7.60 (m, 4H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 1st diastereoisomer 14.3, 28.5, 34.8, 39.6, 53.1, 61.9, 80.2, 86.7, 86.9, 122.7, 128.1, 128.1, 128.4, 128.5, 128.8, 131.9, 137.8, 155.3, 171.1. 2nd diastereoisomer 14.3, 28.5, 34.5, 39.9, 53.2, 61.9, 80.2, 86.5, 86.6, 122.8, 128.1, 128.2, 128.4, 128.6, 128.8, 131.9, 137.9, 155.4, 171.2. Anal. calcd. for $\text{C}_{25}\text{H}_{29}\text{NO}_4\text{S}$: C, 68.31, H, 6.65. Found : C, 68.62, H, 6.88.

1-pentyl-3-phenylbicyclo[3.1.0]hex-2-ene (**3a**)

10 %. Prepared with 1.5eq. of allyltrimethylsilane, 0.05 eq. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and isolated as a colorless oil. $R_f = 0.75$ (Heptane/AcOEt 85/15). ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 0.26 (t, $J = 3.8\text{Hz}$, 1H), 0.8 (dd, $J = 3.7\text{Hz}$, $J = 8\text{Hz}$, 1H), 0.91 (t, $J = 7\text{Hz}$, 3H), 1.32 (m, 4H), 1.46 (m, 3H), 1.67 (m, 1H), 2.70 (d, $J = 17\text{Hz}$, 1H), 3.05 (ddd, $J = 1.6\text{Hz}$, $J = 7\text{Hz}$, $J = 17\text{Hz}$, 1H), 6.32 (s, 1H), 7.26-7.39 (m, 5H). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 14.1, 21.3, 22.7, 23.19, 28.2, 32.0, 33.4, 36.6, 36.9, 125.1, 126.6, 128.3, 132.3, 136.8, 138.6. The compound decomposes rapidly at room temperature.

Synthesis of (R)-1,3-diphenyl-2-propyn-1-ol ((R)-1h).

A 100 mL oven dried round bottom flask was cooled under an argon purge and charged with (R)-Alpine-Borane[®] solution (4.3 mL, 2.15 mmol, 0.5 M in THF).⁸ The solution was concentrated *in vacuo* to afford a pale yellow oil. The flask was backfilled with argon and the resulting oil was cooled to 0 °C. 1,3-diphenylprop-2-yn-1-one (0.4g, 1.94 mmol) was added dropwise *via* syringe and the resulting yellow mixture was warmed to room temperature and left to stir for 4 days. Acetaldehyde (0.5mL, 8.95 mmol) was then added dropwise and the mixture was left to stir at room temperature for 1 h. The reaction mixture was diluted with THF (1 mL), 15% NaOH solution (1.3 mL), and 30% H_2O_2 solution (1.3 mL) were added. The flask was opened to air, equipped with a reflux condenser, and heated at 40 °C for 4 h. The resulting mixture was cooled to room temperature and extracted with Et_2O . The combined extracts were washed with brine, dried over MgSO_4 , filtered, and concentrated. The crude residue was purified by flash column chromatography (95:5 heptane:EtOAc eluent) to afford the desired alcohol (0.231 g, 57% yield).

$R_f = 0.14$ (Heptane/EtOAc 85/15). IR (film) cm^{-1} : 3323, 2228. ^1H NMR (CDCl_3 , 300MHz) δ (ppm) : 2.3 (d, 1H, OH, $J = 6\text{Hz}$), 5.72 (d, 1H, $J = 5.9\text{Hz}$), 7.30-7.50 (m, 8H), 7.64 (d, 2H, $J = 8.4\text{Hz}$). ^{13}C NMR (CDCl_3 , 75MHz) δ (ppm) : 65.1, 86.7, 88.7, 122.4, 126.8, 128.3, 128.46, 128.6, 128.7, 131.8, 140.7.

Enantiomeric purity was determined by chiral HPLC analysis, Chiralcel OD column, 90:10 hexanes/isopropanol, 1 mL/min; t_R 11.5 min (major), 19.39 min (minor): 96% ee.⁹

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