Herrmann-Beller Phosphapalladacycle-Catalyzed Addition of Alkynes to Norbornadienes

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- **General:**

Reactions were carried out under an argon atmosphere. Commercial reagents were used without further purification. Ether was distilled prior to use from sodium/benzophenone. Petroleum ether (PE) and 1,2-dichloroethane (DCE) were distilled prior to use from calcium hydride. Alkynes not commercially available were prepared according literature procedures.¹ Methyl-prop-2-ynylcarbonate **3k**,² 4,4-Dimethyl-hept-6yn-2-one **3n**³ and prop-2-ynylsulfanylbenezene **3p**⁴ were prepared using methods as previously described. Analytical thin layer chromatography was performed on silica gel 60 F₂₅₄ plates (0.25 mm). Flash chromatography was performed on silica gel 60 (230-400 mesh). Melting points were taken on a capillary apparatus and are uncorrected. IR spectra were recorded as liquid films or KBr plates. ¹H and ¹³C NMR were referenced to CDCl₃ at δ 7.26 and 77.0 respectively. The different types of carbon in the structures have been identified by DEPT techniques.

- **Palladium-Catalyzed Alkynylation of Bicyclo[2.2.1]hepta-2,5-diene.**

- General Procedure.**

In a 10 mL flame-dried Schlenk tube, alkyne **3** (1 mmol) and norbornadiene **2** (184 mg, 2 mmol) in 6 mL of 1,2-dichloroethane (DCE) were added to a solution of palladacycle **1** (23.5 mg, 0.025 mmol) in 2 mL of DCE under argon. The reaction mixture was stirred under conditions reported in Table 1. The reaction mixture was evaporated *in vacuo*, and the residue was purified by chromatography on silica gel to give the enyne **4**.

***exo*-5-(2-phenylethynyl)bicyclo[2.2.1]hept-2-ene (**4a**)**

Chemical yield : 90%. Colorless oil. *R_f* (PE) 0.84; IR (neat) ν 3058, 2219, 1604, 1578 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.48 (*br* d, $J = 8.5$ Hz, 1H, $\text{H}_{7\text{anti}}$), 1.56 (ddd, $J = 2.3, 8.7, 11.5$ Hz, 1H, $\text{H}_{6\text{-en}}$), 1.68 (d, $J = 8.5$ Hz, 1H, $\text{H}_{7\text{syn}}$), 1.78 (dt, $J = 3.8, 11.5$ Hz, 1H, $\text{H}_{6\text{-ex}}$), 2.34 (ddd, $J = 0.9, 4.0, 8.7$ Hz, 1H, $\text{H}_{5\text{-en}}$), 2.95 (m, 1H, H_1), 3.01 (m, 1H, H_4), 6.07 (dd, $J = 2.9, 5.5$ Hz, 1H, H_3), 6.11 (dd, $J = 2.9, 5.5$ Hz, 1H, H_2), 7.25-7.29 (m, 3H), 7.39 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 29.5 (d), 34.8 (t), 41.9 (d), 46.8 (t), 49.3 (d), 80.3 (s), 95.0 (s), 124.1 (s), 127.4 (d), 128.1 (d), 131.5 (d), 135.3 (d), 137.4 (d). Anal. Calcd for $\text{C}_{15}\text{H}_{14}$: C, 92.74; H, 7.26. Found: C, 92.83; H, 7.14.

***exo*-6-Deuterio-*exo*-5-phenylethynyl-bicyclo[2.2.1]hept-2-ene **D**-(**4a**)**

D-(**4a**) was prepared in a similar manner as for **4a** (see above general procedure) but using norbornadiene **2** as solvent. The *exo* position of deuterium at C-6 was based on the disappearance of the signal of $\text{H}_{6\text{-ex}}$ as a dt at δ 1.78 and the resolution of signals for $\text{H}_{5\text{-en}}$ and $\text{H}_{6\text{-en}}$ as a d ($J = 8.7$ Hz) in comparison with data for **4a**.

Chemical yield : 92%. Colorless oil. ^1H NMR (CDCl_3 , 500 MHz) δ 1.48 (d, $J = 8.5$ Hz, 1H, $\text{H}_{7\text{anti}}$), 1.54 (d, $J = 8.7$ Hz, 1H, $\text{H}_{6\text{-en}}$), 1.68 (d, $J = 8.5$ Hz, 1H, $\text{H}_{7\text{syn}}$), 2.34 (d, $J = 8.7$ Hz, 1H, $\text{H}_{5\text{-en}}$), 2.95 (m, 1H, H_1), 3.01 (m, 1H, H_4), 6.07 (dd, $J = 2.9, 5.5$ Hz, 1H, H_3), 6.11 (dd, $J = 2.9, 5.5$ Hz, 1H, H_2), 7.25-7.29 (m, 3H), 7.39 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 29.5 (d), [34.0, 34.4 and 34.8 (C-6)], 41.8 (d), 46.8 (t), 49.3 (d), 80.2 (s), 95.0 (s), 124.1 (s), 127.4 (d), 128.1 (d), 131.5 (d), 135.3 (d), 137.4 (d).

5-(hex-1-ynyl)bicyclo[2.2.1]hept-2-ene (4b)

4b

Chemical yield : 72%. Colorless oil. *R_f* (PE) 0.89; IR (neat) ν 3066, 2218, 1554 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 0.88 (t, J = 6.8 Hz, 3H), 1.43 (m, 8H), 2.10 (m, 3H), 2.82 (m, 2H), 6.00 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 13.6 (q), 18.8 (t), 21.9 (t), 28.9 (d), 31.3 (t), 34.9 (t), 41.8 (d), 46.6 (t), 49.3 (d), 79.8 (s), 85.0 (s), 135.3 (d), 137.0 (d). Anal. Calcd for $\text{C}_{13}\text{H}_{18}$: C, 89.59; H, 10.41. Found: C, 89.72; H, 10.28.

5-(2-cyclohexenylethynyl)bicyclo[2.2.1]hept-2-ene (4c)

4c

Chemical yield : 87%. Colorless oil. *R_f* (PE) 0.84; IR (neat) ν 3059, 2211, 1682, 1633 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.56 (m, 8H), 2.07 (m, 4H), 2.19 (m, 1H), 2.88 (m, 2H), 6.01 (m, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 21.6 (t), 22.4 (t), 25.5 (t), 29.3 (d), 29.6 (t), 34.9 (t), 41.8 (d), 46.7 (t), 49.3 (d), 81.9 (s), 92.0 (s), 121.1 (s), 133.0 (d), 135.3 (d), 137.2 (d). Anal. Calcd for $\text{C}_{15}\text{H}_{18}$: C, 90.85; H, 9.15. Found: C, 90.72; H, 9.01.

(2-(bicyclo[2.2.1]hept-5-en-2-yl)ethynyl)trimethylsilane (4d)

4d

Chemical yield : 93%. Colorless oil. *R_f* (PE) 0.94; IR (neat) ν 2964, 2172, 1604, 1254 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 0.12 (s, 9H), 1.41 (m, 2H), 1.54 (m, 1H), 1.67 (dt, J = 11.3, 3.6 Hz, 1H), 2.12 (m, 1H), 2.88 (m, 2H), 6.02 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 0.2 (q), 29.9 (d), 34.9 (t), 41.8 (d), 46.7 (t), 49.4 (d), 83.6 (s), 112.3 (s), 135.3 (d), 137.3 (d). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{Si}$: C, 75.72; H, 9.53. Found: C, 75.58; H, 9.37.

***exo*-5-(3-phenoxyprop-1-ynyl)bicyclo[2.2.1]hept-2-ene (4e)**

4e

Chemical yield : 80%. Colorless oil. *R*_f (PE/Et₂O, 95/5) 0.78; IR (neat) ν 3067, 2227, 1603, 1592 cm^{-1} ; ¹H NMR (CDCl₃, 200 MHz) δ 1.46 (m, 3H), 1.66 (dt, *J* = 3.6, 11.3 Hz, 1H), 2.15 (m, 1H), 2.89 (m, 2H), 4.69 (d, *J* = 2.1 Hz, 2H) 6.00 (dd, *J* = 3.1, 4.9 Hz, 1H), 6.06 (dd, *J* = 3.2, 4.8 Hz, 1H), 6.95 (m, 3H), 7.29 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 28.9 (d), 34.4 (t), 41.7 (d), 46.7 (t), 48.9 (d), 56.5 (t), 74.6 (s), 92.7 (s), 114.9 (d), 121.1 (d), 129.2 (d), 135.1 (d), 137.2 (d), 157.8 (s). Anal. Calcd for C₁₆H₁₆O: C, 85.68; H, 7.19. Found: C, 85.56; H, 7.12.

***exo*-5-(3-(benzyloxy)prop-1-ynyl)bicyclo[2.2.1]hept-2-ene (4f)**

4f

Chemical yield : 95%. Colorless oil. *R*_f (PE/Et₂O, 95/5) 0.60; IR (neat) ν 3059, 2219, 1704, 1667, 1610 cm^{-1} ; ¹H NMR (CDCl₃, 200 MHz) δ 1.55 (m, 3H), 1.65 (dt, *J* = 4.0, 11.6 Hz, 1H), 2.74 (m, 1H), 2.89 (m, 2H), 4.16 (d, *J* = 2.0 Hz, 2H), 4.57 (s, 2H), 6.02 (m, 2H), 7.33 (m, 5H); ¹³C NMR (CDCl₃, 50 MHz) δ 28.9 (d), 34.5 (t), 41.7 (d), 46.7 (t), 49.0 (d), 57.7 (t), 71.1 (t), 75.5 (s), 91.8 (s), 127.6 (d), 127.9 (d), 128.2 (d), 135.1 (d), 137.2 (d), 137.6 (s). Anal. Calcd for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.53; H, 7.72.

(3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyloxy)(tert-butyl)dimethylsilane (4g)

4g

Chemical yield : 95%. Colorless oil. *R*_f (PE) 0.15, *R*_f (PE/Et₂O, 98/2) 0.81; IR (neat) ν 2964, 2941, 2862, 2227, 1478, 1086, 843 cm^{-1} ; ¹H NMR (CDCl₃, 200 MHz) δ 0.1 (s, 6H), 0.89 (s, 9H), 1.47 (m, 3H), 1.64 (dt, *J* = 11.4, 3.8 Hz, 1H), 2.12 (ddd, *J* = 2.1, 4.2, 8.5 Hz, 1H), 2.87 (m, 2H), 4.30 (d, *J* = 2.1 Hz, 2H), 6.02 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ - 5.0 (q), 18.2 (s), 25.8 (q), 28.9 (t), 34.2 (d), 41.7 (d), 46.7 (t), 48.9 (d), 52.0 (t),

78.4 (s), 89.8 (s), 135.2 (d), 137.2 (d). Anal. Calcd for C₁₆H₂₆OSi: C, 85.68; H, 7.19. Found: C, 85.56; H, 7.32.

3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyl acetate (4h)

4h

Chemical yield : 67%. Colorless oil. *R_f* (PE/Et₂O, 95/5) 0.44; IR (neat) ν 3058, 2226, 1751 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.42 (m, 3H), 1.65 (dt, *J* = 11.5, 3.7 Hz, 1H), 2.04 (s, 3H), 2.14 (m, 1H), 2.88 (m, 2H), 4.65 (d, *J* = 2.1 Hz, 2H), 5.98 (dd, *J* = 3.3, 5.4 Hz, 1H), 6.04 (dd, *J* = 3.2, 5.5 Hz, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 20.8 (q), 28.9 (d), 34.4 (t), 41.8 (d), 46.7 (t), 49.0 (d), 52.9 (t), 73.5 (s), 92.1 (s), 135.1 (d), 137.3 (d), 170.3 (s). Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.58; H, 7.38.

4-(bicyclo[2.2.1]hept-5-en-2-yl)but-3-yn-2-yl acetate (4i)

4i

Chemical yield : 63%. Colorless oil. *R_f* (PE/Et₂O, 95/5) 0.47; IR (neat) ν 2976, 2227, 1744, 1237 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) 1.43 (d, *J* = 6.6 Hz, 3H), 1.47 (m, 3H), 1.64 (dt, *J* = 11.5, 4.0 Hz, 1H), 2.04 (s, 3H), 2.11 (m, 1H), 2.87 (pseudo dd, *J* = 1.6, 3.3 Hz, 2H), 5.43 (dq, *J* = 1.9, 6.6 Hz, 1H), 5.98 (ddd, *J* = 1.1, 3.5, 5.8 Hz, 1H), 6.04 (ddd, *J* = 1.2, 3.4, 5.7 Hz, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 21.0 (q), 21.7 (q), 28.6 (d), 34.4 (t), 41.6 (d), 46.5 (t), 48.9 (d), 60.7 (d), 78.1 (s), 89.8 (s), 135.0 (d), 137.1 (d), 169.6 (s). Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.38; H, 7.81.

4-(bicyclo[2.2.1]hept-5-en-2-yl)but-3-ynyl acetate (4j)

4j

Chemical yield : 91%. Colorless oil. *R_f* (PE/Et₂O, 95/5) 0.43; IR (neat) ν 3062, 2233, 1746, 1573 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.50 (m, 4H), 2.02 (m, 1H), 2.03 (s, 3H), 2.47 (dt, *J* = 2.0, 7.0 Hz, 2H), 2.83 (m, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 6.01 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 19.3 (t), 20.9 (q), 28.8 (d), 34.7 (t), 41.8 (d), 46.6 (t), 49.2

(d), 62.8 (t), 75.1 (s), 86.8 (s), 135.2 (d), 137.2 (d), 170.8 (s). Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.58; H, 7.78.

3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyl methyl carbonate (4k)

Chemical yield : 70%. Colorless oil. *R_f* (PE/Et₂O, 95/5) 0.46; IR (neat) ν 3066, 2234, 1756, 1263 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.49 (m, 3H), 1.65 (dt, *J* = 3.5, 11.3 Hz, 1H), 2.12 (m, 1H), 2.88 (m, 2H), 3.78 (s, 3H), 4.71 (d, *J* = 2.1 Hz, 2H), 6.01 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 28.9 (d), 34.4 (t), 41.8 (d), 46.7 (t), 48.9 (d), 55.0 (d), 56.4 (q), 73.0 (s), 93.0 (s), 135.1 (d), 137.4 (d), 154.6 (s). Anal. Calcd for C₁₂H₁₄O₃: C, 69.89; H, 6.84. Found: C, 69.68; H, 6.71.

dimethyl 2-(3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyl)propanedioate (4l)

Chemical yield : 92%. Colorless oil. *R_f* (PE/Et₂O, 80/20) 0.48; IR (neat) ν 2955, 2232, 1755, 1740, 1437, 1240 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.36-1.62 (m, 4H), 2.05 (m, 1H), 2.76 (dd, *J* = 2.2, 7.8 Hz, 2H), 2.81 (br, 1H), 2.86 (br, 1H), 3.57 (t, *J* = 7.8 Hz, 1H), 3.77 (s, 6H), 5.99 (dd, *J* = 2.7, 8.2 Hz, 1H), 6.04 (dd, *J* = 2.7, 8.3 Hz, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 18.9 (t), 28.6 (d), 34.5 (t), 41.6 (d), 46.4 (t), 49.1 (d), 51.5 (d), 52.4 (q), 75.0 (s), 87.4 (s), 135.0 (d), 137.1 (d), 168.4 (s). Anal. Calcd for C₁₅H₁₈O₄: C, 68.69; H, 6.92. Found: C, 68.47; H, 7.02.

diethyl (2-propenyl)(3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyl)propanedioate (4m)

Chemical yield : 82%. Colorless oil. *R_f* (PE/Et₂O, 95/5) 0.43; IR (neat) ν 2232, 1735, 1642, 709 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.23 (t, *J* = 7.1 Hz, 6H), 1.36-1.62 (m, 4H), 2.04 (m, 1H), 2.68-2.90 (m, 6H), 4.16 (q, *J* = 7.1 Hz, 4H), 5.01-5.20 (m, 2H), 5.62 (ddt, *J* = 17.2, 9.8, 7.4 Hz, 1H), 5.99 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 14.0 (q), 22.8 (t), 28.7 (d), 34.7 (t), 36.3 (t), 41.7 (d), 46.5 (t), 49.2 (d), 57.0 (s), 61.3 (t), 74.0 (s),

88.3 (s), 119.3 (t), 132.0 (d), 135.1 (d), 137.1 (d), 169.9 (s). Anal. Calcd for C₂₀H₂₆O₄: C, 72.70; H, 7.93. Found: C, 72.57; H, 7.78.

7-(bicyclo[2.2.1]hept-5-en-2-yl)-4,4-dimethylhept-6-yn-2-one (4n)

Chemical yield : 90%. Colorless oil. *R_f* (PE/Et₂O, 95/5) 0.38; IR (neat) ν 2226, 1718, 1364, 1158, 708 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.03 (s, 3H), 1.10 (m, 2H), 1.51 (m, 4H), 2.04-2.25 (m, 3H), 2.12 (s, 3H), 2.42 (s, 2H), 2.46 (m, 1H), 2.85 (m, 2H), 5.95-6.12 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 27.0 (q), 28.8 (d), 31.9 (t), 32.1 (q), 33.7 (s), 34.8 (t), 47.1 (d), 46.6 (t), 49.3 (d), 52.5 (t), 77.2 (s), 87.3 (s), 135.2 (d), 137.0 (d), 208.4 (s). Anal. Calcd for C₁₆H₂₂O: C, 83.43; H, 9.63. Found: C, 83.31; H, 9.49.

(3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyl)(phenyl)sulfane (4o) was obtained along with prop-2-ynylsulfanyl-benzene (**3o**) as an inseparable 1:1 mixture.

Chemical yield : 37%. *R_f* (PE) 0.55; ¹³C NMR (CDCl₃, 50 MHz) δ 23.2 (t), 28.8 (d), 34.4 (t), 41.7 (d), 46.5 (t), 49.0 (d), 75.1 (s), 88.9 (s), 126.4 (d), 128.6 (d), 129.9 (d), 135.0 (s + d), 137.1 (d).

5-exo-(3-(phenylsulfonyl)prop-1-ynyl)bicyclo[2.2.1]hept-2-ene (4p)

Chemical yield : 52%. Colorless oil. *R_f* (PE/AcOEt, 80/20) 0.61; IR (neat) ν 2974, 2237, 1593, 1455, 1326, 1136 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.37 (m, 3H), 1.52 (dt, *J* = 11.5, 3.9 Hz, 1H), 2.03 (m, 1H), 2.77 (m, 1H), 2.84 (m, 1H), 3.94 (d, *J* = 2.3 Hz, 2H), 5.95 (dd, *J* = 3.0, 5.6 Hz, 1H), 6.03 (dd, *J* = 2.9, 5.6 Hz, 1H), 7.61 (m, 3H), 7.94 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 28.8 (d), 34.1 (t), 41.7 (d), 46.6 (t), 48.8 (d), 49.1 (t), 67.2 (s), 93.3 (s), 128.8 (d), 128.9 (d), 134.0 (d), 134.9 (d), 137.4 (d), 137.7 (s). Anal. Calcd for C₁₆H₁₆SO₂: C, 70.56; H, 5.92. Found: C, 70.42; H, 5.81.

3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-yn-1-ol (4q)

4q

Chemical yield : 44%. Colorless oil. *R_f* (PE/AcOEt, 85/15) 0.37; IR (neat) ν 3350, 2225, 1342, 1132, 1023, 709 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.53 (m, 5H), 2.13 (m, 1H), 2.87 (m, 2H), 4.23 (dd, $J = 2.0, 5.8$ Hz, 2H), 6.01 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 28.8 (d), 34.5 (t), 41.8 (d), 46.6 (t), 49.0 (d), 51.3 (t), 78.0 (s), 91.0 (s), 135.1 (d), 137.3 (d). Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.04; H, 8.16. Found: C, 80.87; H, 8.02.

4-(bicyclo[2.2.1]hept-5-en-2-yl)but-3-yn-1-ol (4r)

4r

Chemical yield : 52%. Colorless oil. *R_f* (PE/AcOEt, 85/15) 0.33; IR (neat) ν 3340, 2977, 2232 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.44 (m, 3H), 1.60 (dd, $J = 11.2, 3.8$ Hz, 1H), 1.79 (m, 1H), 2.08 (m, 1H), 2.42 (dd, $J = 2.2, 6.2$ Hz, 2H), 2.83 (m, 2H), 3.62 (m, 2H), 6.01 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 23.3 (t), 28.8 (d), 34.8 (t), 41.8 (d), 46.6 (t), 49.3 (d), 61.4 (t), 75.9 (s), 87.5 (s), 135.3 (d), 137.2 (d). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.44; H, 8.70. Found: C, 81.28; H, 8.54.

1-(2-(bicyclo[2.2.1]hept-5-en-2-yl)ethynyl)cyclohexanol (4s)

4s

Chemical yield : 97%. White solid. Mp 59-60 $^{\circ}\text{C}$; *R_f* (PE/Et₂O 95/5) 0.20; IR (KBr) ν 3276, 3065, 2977, 2228, 1621 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 1.20 (m, 1H), 1.38-1.73 (m, 12H), 1.84 (m, 1H), 2.12 (m, 1H), 2.86 (m, 2H), 6.01 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 23.5 (t), 25.2 (t), 28.7 (d), 34.9 (t), 40.27 (t), 40.32 (t), 41.8 (d), 46.7

(d), 49.2 (d), 68.8 (s), 83.5 (s), 89.6 (s), 135.2 (d), 137.2 (d). Anal. Calcd for C₁₅H₂₀O: C, 83.29; H, 9.32. Found: C, 83.32; H, 9.25.

4-(3-(bicyclo[2.2.1]hept-5-en-2-yl)prop-2-ynyl)morpholine (4t)

Chemical yield : 69%. Colorless oil. *R_f* (Et₂O) 0.59; IR (neat) ν 2970, 2231, 1574, 1460, 1338, 1122 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.38-1.68 (m, 4H), 2.11 (m, 1H), 2.52 (pseudo t, *J* = 4.6 Hz, 4H), 2.86 (m, 2H), 3.24 (d, *J* = 2.0 Hz, 2H), 3.72 (pseudo t, *J* = 4.6 Hz, 4H), 6.02 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 28.8 (d), 34.7 (t), 41.8 (d), 46.7 (t), 47.7 (t), 49.2 (d), 52.2 (t), 66.8 (t), 74.0 (s), 90.6 (s), 135.2 (d), 137.1 (d). Anal. Calcd for C₁₄H₁₉NO: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.17; H, 8.65; N, 6.37.

(E)-hex-2-en-4-yne-1,6-diol (5)

Chemical yield : 43%. White solid. Mp 48-49 °C; *R_f* (PE/AcOEt, 40/60) 0.47; ¹H NMR (CD₃COCD₃/D₂O, 200 MHz) δ 3.35 (br s, 2H), 4.08 (d, *J* = 4.5 Hz, 2H), 4.23 (br s, 2H), 5.75 (dm, *J* = 15.9 Hz, 1H), 6.18 (dt, *J* = 15.9, 4.5 Hz, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 46.6 (t), 62.3 (t), 83.3 (s), 88.0 (s), 109.3 (d), 142.4 (d).

Trimethyl-(1,2,3,4-tetrahydro-1,4-methano-naphthalen-2-ylethynyl)-silane (8)

Chemical yield : 69%. Colorless oil that solidified on standing. Mp 25°C; *R_f* (PE) 0.53; IR (KBr) ν 3021, 2171, 1943, 1867, 1802 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 0.17 (s, 9H), 1.71 (m, 2H), 1.96 (m, 2H), 2.31 (dd, *J* = 8.7, 4.3 Hz, 1H), 3.37 (m, 1H), 3.42 (m, 1H), 7.12 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 0.2 (qx3), 31.9 (d), 37.2 (t), 43.7 (d), 47.5 (t), 50.9 (d), 84.5 (s), 111.6 (s), 120.7 (d), 121.1 (d), 125.7 (d), 126.2 (d), 146.6 (s), 147.9 (s). Anal. Calcd for C₁₆H₂₀Si: C, 79.93; H, 8.38. Found: C, 79.80; H, 8.27.

Trimethyl-(11-oxa-tricyclo[6.2.1.0^{2,7}]-undeca-2,4,6-trien-9-ylethynyl)-silane (9)

Chemical yield : 97%. White solid. Mp 99-101 °C; *R_f* (PE/EtOAc, 95/5) 0.65; IR (KBr) ν 3051, 2168, 1961, 1919, 1888, 1819 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 0.24 (s, 9H), 1.92 (dd, J = 11.5, 8.5 Hz, 1H), 2.24 (ddd, J = 11.5, 4.8, 4.4 Hz, 1H), 2.61 (dd, J = 8.5, 4.2 Hz, 1H), 5.45 (m, 1H), 5.55 (d, J = 4.9 Hz, 1H), 7.20-7.34 (m, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 0.1 (qx3), 32.5 (d), 36.6 (t), 79.0 (d), 84.2 (d), 85.1 (s), 108.8 (s), 118.9 (d), 119.1 (d), 126.7 (d), 127.0 (d), 144.3 (s), 145.1 (s). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{OSi}$: C, 74.33; H, 7.49. Found: C, 74.26; H, 7.42.

3-Methoxycarbonyloxymethyl-bicyclo[2.2.1]hepta-2,5-dien-2-ylmethyl, methyl carbonate (10)

Methyl chloroformate (0.39 mL, 5.1 mmol) was added dropwise to an ice cooled solution of (3-hydroxymethyl-bicyclo[2.2.1]hepta-2,5-dien-2-yl)-methanol⁵ (190 mg, 1.27 mmol), pyridine (0.8 g, 0.82 mL, 10.1 mmol) and DMAP (10.0 mg, 0.08 mmol) in CH_2Cl_2 (7 mL). The resulting mixture was stirred at 0 °C for 15 min, then at room temperature for 12 h. The reaction mixture was concentrated in vacuo and diluted by addition of water (1 mL) and ether (5 mL). The organic layer was washed with a saturated aqueous solution of CuSO_4 (3x1 mL), brine (2 mL) and dried over Na_2SO_4 . After evaporation of the solvent, the crude product was purified by column chromatography (PE/Et₂O 1/9) to afford 300 mg (88%) of **10** as a pale yellow oil.

R_f (PE/Et₂O 1/1) 0.58. IR (neat) ν 2961, 2869, 1746, 1445, 1374, 1254, 939 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ 1.94 (dm, J = 6.2 Hz, 1H), 2.04 (dm, J = 5.8 Hz, 1H), 3.57 (m, 2H), 3.78 (s, 6H), 4.72 (d, J = 12.4 Hz, 2H), 4.87 (d, J = 13.2 Hz, 2H), 6.78 (*app* t, J = 1.9 Hz, 2H,). ^{13}C NMR (50 MHz, CDCl_3) δ 52.4 (q), 54.7 (d), 63.5 (t), 71.8 (t), 142.3 (d), 148.2 (s), 155.6 (s). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_6$: C, 58.20; H, 6.01. Found: C, 58.04; H, 5.93.

Cyclopropane **12**

Biscarbonate **10** (134.1 mg, 0.5 mmol) was added to a solution of palladium tetrakis(triphenylphosphine) (28 mg, 0.025 mmol) and methyl malonate **11** (66 mg, 0.55 mmol) in THF (2.5 mL) and the mixture was stirred at 50°C for 18 h. After removal of the solvent under vacuum, the diastereomeric ratio **12a/12b** (87/13) was determined by NMR analysis. The crude material was purified by silica gel chromatography (elution with Et₂O/PE 1/9) to afford 95.5 mg (77%) of **12** as a colorless oil. Spectroscopic data are in agreement with those reported in ref. 6.

3-Methoxycarbonyloxymethyl-6-phenylethynyl-bicyclo[2.2.1]hept-2-en-2-ylmethyl, methyl carbonate (**13**)

As reported for the general procedure, the reaction of an equimolar mixture of biscarbonate **10**, phenylethyne (**3a**) and methyl malonate **11** in the presence of phosphapalladacycle **1** (2.5 mol%) in DCE for 1 h at 50°C afforded after column chromatography (elution with PE/Et₂O 4/1) enyne **13** as a colorless oil in 88% yield.

R_f (PE/Et₂O, 70/30) 0.34; IR (neat) ν 2961, 2222, 1748, 1442, 1263, 788 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.60 (dt, *J* = 1.9, 8.7 Hz, 1H), 1.65 (dt, *J* = 2.2, 11.5 Hz, 1H), 1.73 (d, *J* = 8.9 Hz, 1H), 1.89 (dt, *J* = 3.8, 11.7 Hz, 1H), 2.47 (ddd, *J* = 1.0, 4.7, 8.7 Hz, 1H), 3.03 (m, 1H), 3.10 (m, 1H), 3.79 (s, 3H), 3.80 (s, 3H), 4.72 (*app* dd, *J* = 7.6, 13.0 Hz, 2H), 4.82 (*app* d, *J* = 13.0 Hz, 2H), 7.24-7.30 (m, 3H), 7.35-7.40 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 30.1 (d), 35.2 (t), 44.4 (d), 45.4 (t), 51.8 (d), 54.7 (q), 62.2 (t), 62.3 (t), 80.5 (s), 93.8 (s), 123.7 (s), 127.4 (d), 128.0 (d), 131.3 (d), 139.8 (s), 142.3 (s), 155.5 (s). Anal. Calcd for C₂₁H₂₂O₆: C, 68.10; H, 5.99. Found: C, 67.86; H, 5.81.

(2*R,3*S**,5*S**)-5-Phenylethynyl-bicyclo[2.2.1]heptane-2,3-diol**

Osmium tetroxide (*ca.* 5 mg, 2.10^{-2} mmol) was added to an ice-cooled mixture of *exo*-5-phenylethynyl-bicyclo[2.2.1]hept-2-ene (**4a**) (97 mg, 0.5 mmol) and NMO (67.5 mg, 0.5 mmol) in a (8/1) mixture of THF/water (2 mL). The mixture was stirred for 5.5 h at room temperature until complete consumption of the enyne monitored by TLC. The solution was treated by aqueous hydrochloric acid 2N (4 mL), aqueous sodium hydrogensulfite 15% (1.5 mL) and AcOEt (4 mL). The aqueous layer was extracted by AcOEt (3x4 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated under vacuo. The crude product was purified by silica gel chromatography (elution with 40-50% AcOEt in hexanes) to afford 72 mg (63 %) of pure diol as a white solid.

Mp 86-87°C; *R_f* (AcOEt/PE 1/1) 0.50; IR (KBr) ν 3432, 3387, 3240, 2966, 2950, 2877, 2225, 755 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 1.53-1.67 (m, 2H), 1.68 (dt, *J* = 4.9, 10.9 Hz, 1H), 1.85 (*br d*, *J* = 10.9 Hz, 1H), 2.25 (m, 1H), 2.35-2.42 (m, 2H), 2.64 (m, 1H, OH), 2.71 (m, 1H, OH), 3.72 (m, 2H), 7.25-7.29 (m, 3H), 7.34-7.39 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 29.1 (d), 30.1 (t), 34.3 (t), 42.8 (d), 50.0 (d), 73.5 (d), 73.9 (d), 80.7 (s), 93.6 (s), 123.7 (s), 127.6 (d), 128.1 (d), 131.4 (d). Anal. Calcd for C₁₅H₁₆O₂: C, 78.92; H, 7.06. Found: C, 78.69; H, 7.13.

(1*S,3*S**,4*S**)-4-Phenylethynyl-cyclopentane-1,3-dicarbaldehyde (**14**)**

Sodium metaperiodate (128 mg, 0.6 mmol) was added portionwise to a mixture of saturated aqueous NaHCO₃ (50 μ L) and a solution of the above diol (68.4 mg, 0.3 mmol) in CH₂Cl₂ (1 mL). The resulting mixture was vigorously stirred at room temperature for 1.5 h. The organic phase was removed and the residue was extracted

with CH₂Cl₂ (3x0.5 mL). The combined organic phases were dried over Na₂SO₄ and evaporated under vacuo to afford quantitatively the title compound as a colorless oil.

R_f (AcOEt/PE 1/1) 0.58; IR (neat) ν 3051, 2960, 2874, 2219, 1720 733 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.13 (ddd, J = 4.8, 7.9, 13.2 Hz, 1H), 2.25-2.42 (m, 3H), 3.03-3.18 (m, 2H), 3.23 (*app* q, J = 7.3 Hz, 1H), 7.28-7.32 (m, 3H), 7.38-7.42 (m, 2H), 9.70 (s, 1H), 9.76 (s, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 25.0 (t), 31.2 (d), 33.4 (t), 49.7 (d), 58.0 (d), 82.2 (s), 89.6 (s), 122.9 (s), 128.1 (d), 128.2 (d), 131.5 (d), 200.5 (s), 201.4 (s). Anal. Calcd for C₁₅H₁₄O₂: C, 79.62; H, 6.24. Found: C, 79.19; H, 6.40.

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- NMR Spectra of compounds (4a) and D-(4a)

RMN 1H CRYOPROBE CDCl3
 Laurent pdt deutere

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1.803
1.796
1.788
1.780
1.773
1.765

RMN 1H CRYOPROBE CDCl3
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