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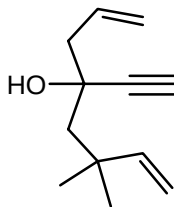
First Evidences of Hydroxy Protecting Group Effects in PtCl₂-Catalyzed Cyclization of Dienynes. A Novel, Efficient and Selective Synthesis of Various Carbocycles

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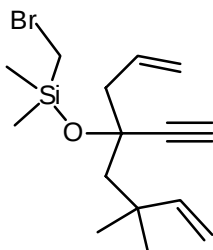
4-Ethynyl-6,6-dimethyl-octa-1,7-dien-4-ol 1a:



IR (neat) 3450, 3300, 3080, 2960, 2930, 2100, 1635 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 6.09 (dd, *J* = 17.2, 10.3 Hz, 1 H), 5.94 (ddt, *J* = 17.7, 10.8, 7.4 Hz, 1 H), 5.19-5.09 (m, 2 H), 5.08 (dd, *J* = 17.2, 1.5 Hz, 1 H), 5.01 (dd, *J* = 10.8, 1.5 Hz, 1 H), 2.66 (s, 1 H), 2.38 (m, 2 H), 1.76 (s, 2 H), 1.29 (s, 3 H), 1.09 (s, 3 H); ¹³C NMR (50 MHz, CDCl₃) δ 149.0, 133.1, 119.2, 111.3, 87.2, 74.0,

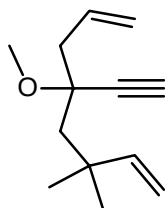
69.2, 52.4, 49.4, 37.0, 30.2, 26.7. Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85 ; H, 10.18. Found: C, 80.77 ; H, 10.23.

4-(Bromomethyldimethylsilanyloxy)-4-ethynyl-6,6-dimethyl-octa-1,7-diene 1b:



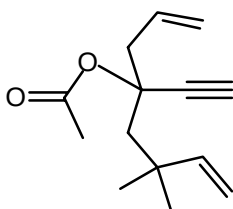
IR (neat) 3300, 3080, 2960, 2930, 2100, 1640 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.00 (dd, J = 17.6, 10.7 Hz, 1 H), 5.90 (m, 1 H), 5.20-5.05 (m, 2 H), 4.88 (m, 2 H), 2.60 (s, 2 H), 2.58 (s, 1 H), 2.47 (d, J = 6.6 Hz, 2 H), 1.75 (m_{AB} , 2 H), 1.18 (s, 3 H), 1.12 (s, 3 H), 0.38 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 133.7, 118.6, 109.4, 87.6, 75.4, 71.8, 53.0, 49.9, 37.0, 29.2, 28.0, 17.9, -0.8 (2C). Anal. Calcd. for $C_{15}H_{25}BrOSi$: C, 54.70; H, 7.65. Found: C, 54.68; H, 7.69.

4-Ethynyl-4-methoxy-6,6-dimethyl-octa-1,7-diene 1c:



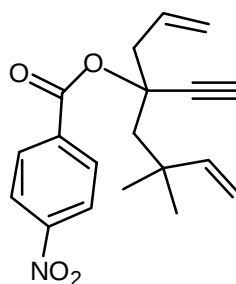
IR (neat) 3300, 3100, 2950, 2150, 1650, 1460, 1390 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$) δ 5.99 (dd, J = 17.7, 10.9 Hz, 1 H), 5.82 (m, 1 H), 5.12-4.80 (m, 4 H), 3.31 (s, 3 H), 2.53 (s, 1 H), 2.44 (d, J = 7.4 Hz, 2 H), 1.71 (s, 2 H), 1.18 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.3, 133.4, 118.3, 109.2, 84.1, 76.7, 75.3, 51.1, 49.6, 44.6, 36.7, 28.5, 28.2. Anal. Calcd. for $C_{13}H_{20}O$: C, 81.20 ; H, 10.48. Found: C, 80.91 ; H, 10.72.

Acetic acid 1-allyl-1-ethynyl-3,3-dimethyl-pent-4-enyl ester 1d:



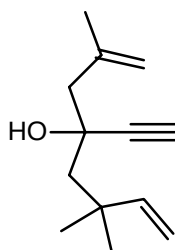
IR (neat) 3300, 3100, 2950, 2150, 1750, 1640, 1440, 1370 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.93 (dd, $J = 17.2, 10.3$ Hz, 1 H), 5.81 (m, 1 H), 5.13-5.04 (m, 2 H), 4.90 (dd, $J = 17.7, 1.5$ Hz, 1 H), 4.86 (dd, $J = 10.3, 1.5$ Hz, 1 H), 2.87 (dd, $J = 14.3, 7.4$ Hz, 1 H), 2.69 (dd, $J = 14.3, 7.4$ Hz, 1 H), 2.60 (s, 1 H), 2.15 (d, $J = 15.3$ Hz, 1 H), 1.95 (s, 3 H), 1.86 (d, $J = 15.3$ Hz, 1 H), 1.15 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 169.4, 148.7, 132.3, 119.1, 109.7, 83.5, 77.0, 75.9, 49.1, 44.6, 36.8, 28.9, 27.7, 22.2.

4'-Nitrobenzoic acid 1-allyl-1-ethynyl-3,3-dimethyl-pent-4-enyl ester 1e:



IR (neat) 3300, 3080, 2960, 2115, 1730, 1640, 1610, 1530, 1350 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.29 (d, $J = 9.0$ Hz, 2 H), 8.16 (d, $J = 9.0$ Hz, 2 H), 6.00 (dd, $J = 17.4, 10.6$ Hz, 1 H), 5.92 (m, 1 H), 5.18 (d, $J = 16.2$ Hz, 1 H), 5.16 (d, $J = 11.2$ Hz, 1 H), 4.95 (dd, $J = 17.4, 1.0$ Hz, 1 H), 4.84 (dd, $J = 10.6, 1.0$ Hz, 1 H), 3.07 (dd, $J = 14.0, 7.2$ Hz, 1 H), 2.90 (dd, $J = 14.0, 7.2$ Hz, 1 H), 2.76 (s, 1 H), 2.40 (d, $J = 15.0$ Hz, 1 H), 2.11 (d, $J = 15.0$ Hz, 1 H), 1.23 (s, 3 H), 1.20 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 163.0, 148.4, 136.5, 132.0, 130.8 (2C), 128.5, 123.6 (2C), 119.7, 110.4, 82.8, 79.1, 77.0, 49.2, 44.8, 36.9, 29.0, 28.0; EI GCMS m/z 286 (9, $\text{M}-\text{C}_3\text{H}_5$), 150 (100). Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: C, 69.71 ; H, 6.47 ; N, 4.28. Found: C, 69.65 ; H, 6.60 ; N, 4.18.

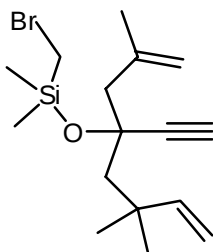
4-Ethynyl-2,6,6-trimethyl-octa-1,7-dien-4-ol 1f:



IR (neat) 3460, 3300, 3070, 2950, 2920, 2100, 1635 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.12 (dd, $J = 17.6, 10.7$ Hz, 1 H), 5.09 (dd, $J = 17.6, 1.3$ Hz, 1 H), 5.02 (dd, $J = 10.7, 1.3$ Hz, 1 H),

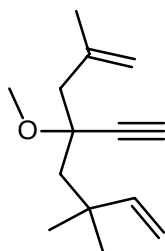
4.98 (m, 1 H), 4.85 (m, 1 H), 2.73 (s, 1 H), 2.40 (s, 2 H), 1.92 (s, 3 H), 1.82 (s, 2 H), 1.32 (s, 3 H), 1.15 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 149.0, 141.5, 115.7, 111.1, 88.2, 74.1, 68.9, 52.9, 52.3, 37.2, 30.0, 26.8, 24.5.

4-(Bromomethyldimethylsilanyloxy)-4-ethynyl-2,6,6-trimethyl-octa-1,7-diene 1g:

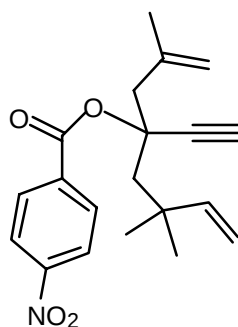


IR (neat) 3300, 3070, 2960, 2920, 2100, 1640 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.98 (dd, J = 17.6, 10.7 Hz, 1 H), 4.95-4.80 (m, 4 H), 2.60 (s, 2 H), 2.57 (s, 1 H), 2.41 (m_{AB} , 2 H), 1.82 (d, J = 14.7 Hz, 1 H), 1.81 (s, 3 H), 1.68 (d, J = 14.7 Hz, 1 H), 1.15 (s, 3 H), 1.10 (s, 3 H) 0.35 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 141.4, 115.9, 109.3, 88.1, 75.7, 71.9, 53.1, 53.0, 36.9, 29.2, 28.0, 24.6, 17.8, -0.9 (2C). Anal. Calcd. for $\text{C}_{16}\text{H}_{27}\text{BrOSi}$: C, 55.97 ; H, 7.93. Found: C, 56.20 ; H, 7.68.

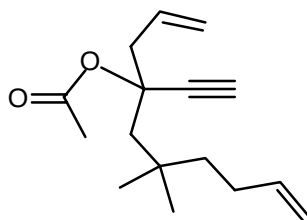
4-Ethynyl-4-methoxy-2,6,6-trimethyl-octa-1,7-diene 1h:



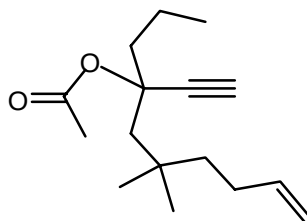
IR (neat) 3300, 3050, 2950, 2120, 1630, 1450, 1380 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.00 (dd, J = 17.7, 10.3 Hz, 1 H), 4.92-4.77 (m, 4 H), 3.31 (s, 3 H), 2.53 (s, 1 H), 2.39 (s, 2 H), 1.79 (s, 3 H), 1.73 (s, 2 H), 1.17 (s, 3 H), 1.12 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 149.5, 141.6, 115.3, 109.0, 84.4, 76.9, 75.4, 51.1, 49.7, 47.9, 36.6, 28.2 (2C), 24.1.

4'-Nitrobenzoic acid 1-methallyl-1-ethynyl-3,3-dimethyl-pent-4-enyl ester 1i:

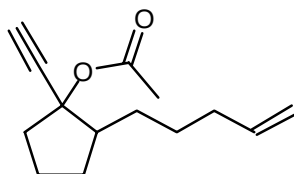
IR (neat) 3300, 3080, 2960, 2115, 1730, 1640, 1610, 1530, 1350 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.29 (d, $J = 9.2$ Hz, 2 H), 8.18 (d, $J = 9.2$ Hz, 2 H), 6.02 (dd, $J = 17.4, 10.6$ Hz, 1 H), 4.97 (dd, $J = 10.6, 1.0$ Hz, 1 H), 4.86 (d, $J = 1.2$ Hz, 2 H), 4.85 (dd, $J = 17.4, 1.0$ Hz, 1 H), 3.06 (d, $J = 14.4$ Hz, 1 H), 2.87 (d, $J = 14.4$ Hz, 1 H), 2.77 (s, 1 H), 2.42 (d, $J = 15.0$ Hz, 1 H), 2.11 (d, $J = 15.0$ Hz, 1 H), 1.82 (s, 3 H), 1.24 (s, 3 H), 1.20 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 163.1, 148.5, 140.2, 136.6, 130.8 (3C), 126.6 (2C), 116.7, 110.3, 83.1, 79.0, 77.5, 49.8, 48.2, 36.9, 29.2, 27.9, 24.1; EI GCMS m/z 286 (5, $\text{M}-\text{C}_4\text{H}_7$), 150 (100).

Acetic acid 1-allyl-1-ethynyl-3,3-dimethyl-hept-6-enyl ester 7:

IR (neat) 3300, 2950, 2150, 1750, 1640, 1450, 1370 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.88-5.79 (m, 2 H), 5.15 (d, $J = 10.0$ Hz, 1 H), 5.14 (d, $J = 18.8$ Hz, 1H), 5.02 (dd, $J = 17.2, 1.7$ Hz, 1 H), 4.93 (dd, $J = 10.2, 1$ Hz, 1 H), 2.93 (dd, $J = 13.8, 7.0$ Hz, 1 H), 2.82 (dd, $J = 13.8, 7.0$ Hz, 1 H), 2.67 (s, 1 H), 2.06 (d, $J = 15$ Hz, 1 H), 2.04 (m, 2 H), 2.03 (s, 3 H), 1.71 (d, $J = 15.0$ Hz, 1 H), 1.51 (m, 2 H), 1.09 (s, 3 H), 1.08 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 139.5, 132.3, 119.3, 113.9, 83.5, 76.9, 76.1, 47.6, 45.2, 42.7, 33.8, 28.6, 28.5, 28.4, 22.3. Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2$: C, 77.38 ; H, 9.74. Found: C, 77.26 ; H, 9.91.

Acetic acid 1-ethynyl-1-propyl-3,3-dimethyl-hept-6-enyl ester 12:

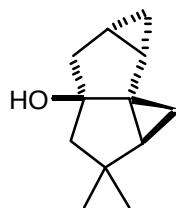
IR (neat) 3300, 2950, 2100, 1730, 1630, 1460, 1360 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.81 (ddt, $J = 16.7, 10.3, 6.4$ Hz, 1 H), 5.04-4.88 (m, 2 H), 2.61 (s, 1 H), 2.22-1.87 (m, 5 H), 2.01 (s, 3 H), 1.74 (d, $J = 15.3$ Hz, 1 H), 1.51-1.41 (m, 4 H), 1.06 (s, 3 H), 1.05 (s, 3 H), 0.92 (t, $J = 6.9$ Hz, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 169.4, 139.7, 114.0, 84.0, 78.4, 75.6, 47.8, 43.1, 43.0, 33.9, 28.7, 28.6, 28.5, 22.4, 17.6, 14.1.

Acetic acid 1-ethynyl-2-pent-4-enyl-cyclopentyl ester 15:

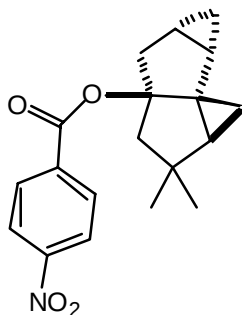
IR (neat) 3300, 3100, 2980, 2120, 1730, 1640, 1450 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.81 (ddt, $J = 16.7, 10.2, 6.6$ Hz, 1 H), 5.00 (dd, $J = 16.7, 1.5$ Hz, 1 H), 4.93 (dd, $J = 10.2, 1.5$ Hz, 1 H), 2.57 (s, 1 H), 2.49 (m, 1 H), 2.07 (m, 3 H), 2.05 (s, 3 H), 1.95 (m, 1 H), 1.89 (m, 1 H), 1.84-1.65 (m, 3 H), 1.55-1.28 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 138.8, 114.3, 83.1, 81.5, 75.2, 49.3, 39.2, 33.9, 30.5, 28.0, 27.4, 21.6, 21.0. Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2$: C, 76.33 ; H, 9.15. Found: C, 76.25 ; H, 9.32.

General procedure for the reaction :

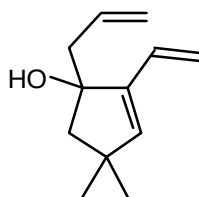
To a degassed solution of the corresponding precursor in dry toluene (0.025 M), under argon and at rt, PtCl_2 (0.05 equiv.) was added. The mixture was warmed to 80 $^\circ\text{C}$ and stirred until complete reaction (~ 2.5 h). Then the mixture was cooled to rt and the solvent was evaporated under vacuum. The residue was purified by flash chromatography.

Diquinane 3a:

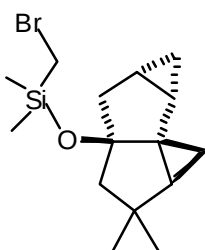
IR (neat) 3370, 2950, 1460, 1360 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.16 (dd, $J = 14.1, 6.6$ Hz, 1 H), 1.71 (m, 1 H), 1.67 (dd, $J = 14.1, 3.2$ Hz, 1 H), 1.60 (d, $J = 14.2$ Hz, 1 H), 1.36 (td, $J = 7.9, 4.0$ Hz, 1 H), 1.06 (s, 3 H), 1.03 (d, $J = 14.2$ Hz, 1 H), 0.92 (s, 3 H), 0.89 (td, $J = 7.9, 4.7$ Hz, 1 H), 0.85 (dd, $J = 8.4, 4.9$ Hz, 1 H), 0.78 (dd, $J = 8.4, 4.2$ Hz, 1 H), 0.69 (dd, $J = 4.9, 4.2$ Hz, 1 H), 0.50 (dt, $J = 4.7, 4.0$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 99.2, 47.2, 45.9, 44.4, 39.3, 35.4, 30.2, 28.1, 22.2, 20.5, 20.1, 11.5; EI GCMS m/z 178 (6, M), 145 (100). Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.85; H, 10.18. Found: C, 80.65; H, 9.98.

4-Nitrobenzoate ester of diquinane 3e:

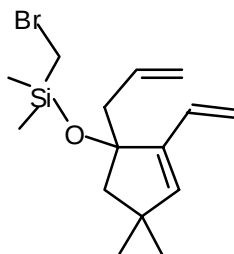
Solid, mp: 135°C; IR (in CH_3Cl solution) 3040, 2940, 1700, 1600, 1520, 1450 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.23 (m, 4 H), 2.74 (dd, $J = 15.7, 7.4$ Hz, 1 H), 2.26 (d, $J = 14.8$ Hz, 1 H), 1.83 (dd, $J = 15.7, 2.5$ Hz, 1 H), 1.64 (m, 1 H), 1.49 (td, $J = 7.4, 3.4$ Hz, 1 H), 1.16 (d, $J = 14.8$ Hz, 1 H), 1.14 (s, 3 H), 1.06 (m, 1 H), 0.93 (s, 3 H), 0.96-0.84 (m, 3 H), 0.58 (q, $J = 3.9$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 165.0, 150.7, 137.5, 131.0 (2C), 123.8 (2C), 109.9, 46.3, 45.2, 41.9, 40.2, 35.2, 30.7, 28.9, 22.7, 21.0 (2C), 12.9.

Diene 2a:

IR (neat) 3400, 2920, 1630, 1450 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.28 (dd, $J = 18.0, 11.4$ Hz, 1 H), 5.80 (m, 1 H), 5.69 (s, 1 H), 5.60 (dd, $J = 18.0, 2.0$ Hz, 1 H), 5.18-5.09 (m, 3 H), 2.63 (dd, $J = 13.7, 8.0$ Hz, 1 H), 2.41 (dd, $J = 13.8, 8.0$ Hz, 1 H), 2.13 (d, $J = 14.0$ Hz, 1 H), 1.74 (d, $J = 14.0$ Hz, 1 H), 1.35 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 142.2, 134.2, 130.4, 118.6, 116.0, 85.4, 53.5, 44.7, 42.0, 30.7, 28.8.

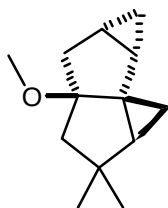
Diquinane 3b:

IR (neat) 3060, 2990, 2960, 2870, 1740, 1450, 1350 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 2.54 (s, 2 H), 2.21 (dd, $J = 15.0, 7.4$ Hz, 1 H), 1.70 (m, 1 H), 1.69 (d, $J = 9.4$ Hz, 1 H), 1.63 (d, $J = 14.0$ Hz, 1 H), 1.37 (td, $J = 7.4, 4.0$ Hz, 1 H), 1.11 (d, $J = 14.0$ Hz, 1 H), 1.07 (s, 3 H), 0.93 (s, 3 H), 0.90 (m, 2 H), 0.76 (m, 2 H), 0.49 (q, $J = 4.0$ Hz, 1 H), 0.32 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 102.7, 48.9, 45.9, 45.5, 38.9, 36.0, 30.3, 28.5, 22.5, 20.9 (2C), 18.3, 13.0, -0.7 (2C); EI GCMS m/z 330 (21, $\text{M}^{(81)\text{Br}}$), 328 (21, $\text{M}^{(79)\text{Br}}$), 145 (100). Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{BrOSi}$: C, 54.70 ; H, 7.65. Found: C, 55.00 ; H, 7.87.

Diene 2b:

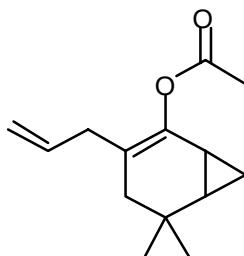
IR (neat) 3080, 2940, 1630, 1440, 1250 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.25 (dd, $J = 17.8$, 11.2 Hz, 1 H), 5.77 (m, 1 H), 5.61 (s, 1 H), 5.59 (dd, $J = 18.0$, 1.6 Hz, 1 H), 5.18-5.02 (m, 3 H), 2.66 (dd, $J = 13.4$, 7.0 Hz, 1 H), 2.49 (s, 2 H), 2.33 (dd, $J = 13.4$, 7.0 Hz, 1 H), 2.15 (d, $J = 13.0$ Hz, 1 H), 1.80 (d, $J = 13.0$ Hz, 1 H), 1.17 (s, 3 H), 1.06 (s, 3 H), 0.28 (s, 6 H); ^{13}C NMR (50 MHz, CDCl_3) δ 143.0, 140.7, 134.8, 130.6, 117.5, 115.9, 88.5, 52.5, 46.3, 41.7, 30.4, 28.5, 17.6, -0.9 (2C).

Diquinane 3c:



IR (neat) 2950, 1480, 1380 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 3.28 (s, 3 H), 2.36 (dd, $J = 14.3$, 7.0 Hz, 1 H), 1.61 (m, 1 H), 1.52 (dd, $J = 14.3$, 2.5 Hz, 1 H), 1.52 (d, $J = 14.3$ Hz, 1 H), 1.33 (td, $J = 7.4$, 3.4 Hz, 1 H), 1.08 (d, $J = 14.3$ Hz, 1 H), 1.06 (s, 3 H), 0.90 (s, 3 H), 0.89 (td, $J = 8.4$, 4.4 Hz, 1 H), 0.82-0.70 (m, 3 H), 0.47 (q, $J = 4.0$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 104.0, 51.9, 46.2, 43.8, 39.2 (2C), 35.8, 30.7, 28.3, 22.1, 21.7, 21.2, 12.2. Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}$: C, 81.20; H, 10.48. Found: C, 81.07; H, 10.59.

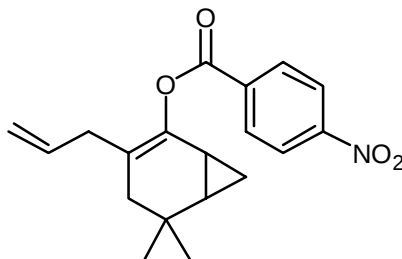
Acetic acid 3-allyl-5,5-dimethyl-bicyclo[4.1.0]hept-2-en-2-yl ester 4d:



IR (neat) 3090, 2950, 1750, 1690, 1640, 1450, 1360 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.56 (ddt, $J = 17.0$, 10.0, 7.0 Hz, 1 H), 4.95 (d, $J = 17.0$ Hz, 1 H), 4.93 (d, $J = 10.0$ Hz, 1 H), 2.63 (dd, $J = 14.8$, 6.4 Hz, 1 H), 2.50 (dd, $J = 14.8$, 6.4 Hz, 1 H), 2.13 (s, 3 H), 1.61 (m_{AB} , 2 H), 1.21 (m, 1 H), 1.05 (s, 3 H), 0.97 (s, 3 H), 0.96 (m, 1 H), 0.77 (m, 1 H), 0.66 (m, 1 H); ^{13}C NMR (50 MHz,

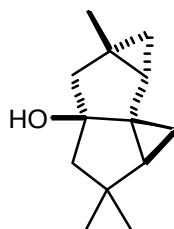
CDCl₃) δ 169.4, 143.4, 135.4, 115.8, 114.6, 37.9, 34.9, 29.5, 28.5, 28.0, 26.6, 20.8, 13.6, 9.8.
 Anal. Calcd. for C₁₄H₂₀O₂ : C, 76.33 ; H, 9.15. Found: C, 76.29 ; H, 9.28.

4'-Nitrobenzoic acid 3-allyl-5,5-dimethyl-bicyclo[4.1.0]hept-2-en-2-yl ester 4e:

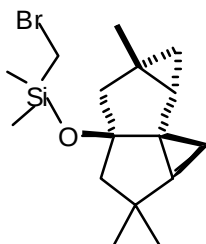


Solid, mp: 73-75°C; IR (KBr) 3115, 3000, 2950, 2850, 1725, 1610, 1530, 1350 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.33 (m, 4 H), 5.63 (m, 1 H), 4.99 (dd, $J = 17.2, 1.6$ Hz, 1 H), 4.98 (dd, $J = 11.0, 1.6$ Hz, 1 H), 2.72 (dd, $J = 14.6, 6.0$ Hz, 1 H), 2.60 (dd, $J = 14.6, 6.0$ Hz, 1 H), 1.82 (d, $J = 16.4$ Hz, 1 H), 1.68 (d, $J = 16.4$ Hz, 1 H), 1.37 (td, $J = 8.4, 4.2$ Hz, 1 H), 1.15 (s, 3 H), 1.09 (s, 3 H), 1.06-0.76 (m, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 163.3, 150.8, 143.6, 135.4, 135.0, 131.1 (2C), 123.8 (2C), 116.2, 115.6, 38.2, 35.0, 29.6, 28.5, 28.1, 26.9, 13.7, 10.2; EI GCMS m/z 327 (4, M), 150 (100). Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: C, 69.71 ; H, 6.47 ; N, 4.28. Found: C, 70.02 ; H, 6.65 ; N, 4.48.

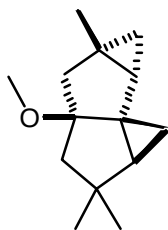
Diquinane 3f:



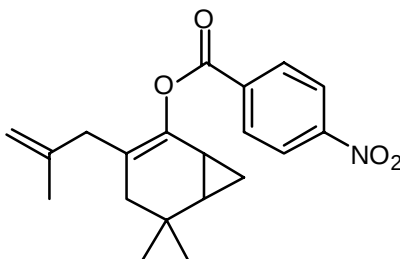
IR (neat) 3370, 3050, 2960, 2860, 1460, 1360 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.97 (d, J = 14.3 Hz, 1 H), 1.88 (d, J = 14.3 Hz, 1 H), 1.57 (d, J = 14.3 Hz, 1 H), 1.29 (s, 3 H), 1.07 (m, 1 H), 1.03 (s, 3 H), 0.99 (d, J = 14.3 Hz, 1 H), 0.89 (s, 3 H), 0.79-0.69 (m, 3 H), 0.66 (t, J = 2.9 Hz, 1 H), 0.60 (t, J = 3.5 Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 98.2, 50.6, 47.7, 46.6, 39.3, 35.4, 30.3, 29.0, 28.8, 28.2, 27.3, 24.0, 11.8; EI GCMS m/z 192 (33, M), 159 (100).

Diquinane 3g:

IR (neat) 3050, 2960, 2860, 1470, 1380 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 2.44 (s, 2 H), 1.97 (d, $J = 11.4$ Hz, 1 H), 1.85 (d, $J = 11.4$ Hz, 1 H), 1.53 (d, $J = 11.0$ Hz, 1 H), 1.23 (s, 3 H), 1.03 (d, $J = 11.0$ Hz, 1 H), 1.02 (m, 1 H), 0.98 (s, 3 H), 0.85 (s, 3 H), 0.81 (m, 1 H), 0.65 (m, 3 H), 0.51 (t, $J = 3.2$ Hz, 1 H), 0.23 (s, 3 H), 0.22 (s, 3 H); ^{13}C NMR (50 MHz, CDCl_3) δ 101.6, 51.9, 48.6, 46.9, 39.1, 35.4, 30.3, 29.0, 28.8, 28.5, 27.7, 23.9, 18.2, 12.9, -0.5, -0.6. Anal. Calcd. for $\text{C}_{16}\text{H}_{27}\text{BrOSi}$: C, 55.97 ; H, 7.93. Found: C, 55.79 ; H, 8.04.

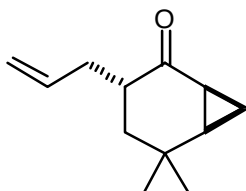
Diquinane 3h:

IR (neat) 3040, 2950, 1460 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 3.28 (s, 3 H), 2.19 (d, $J = 14.6$ Hz, 1 H), 1.72 (d, $J = 14.6$ Hz, 1 H), 1.53 (d, $J = 13.8$ Hz, 1 H), 1.30 (s, 3 H), 1.13 (d, $J = 13.8$ Hz, 1 H), 1.12 (m, 1 H), 1.09 (s, 3 H), 0.94 (s, 3 H), 0.91 (m, 1 H), 0.85-0.70 (m, 3 H), 0.64 (t, $J = 3.7$ Hz, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 103.2, 52.3, 46.5, 45.3, 45.2, 39.6, 36.0, 31.0, 30.0, 28.9 (2C), 28.6, 23.8, 12.8.

4'-Nitrobenzoic acid 3-methallyl-5,5-dimethyl-bicyclo[4.1.0]hept-2-en-2-yl ester 4i:

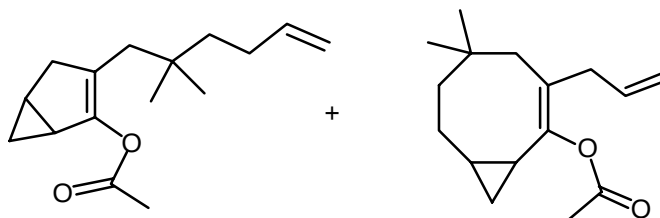
Solid, mp: 57-59°C; IR (KBr) 3110, 3070, 2960, 1730, 1610, 1525, 1350 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.31 (m, 4 H), 4.72, (s, 1 H), 4.67 (s, 1 H), 2.63 (s, 2 H), 1.71 (m_{AB} , 2 H), 1.63 (s, 3 H), 1.39 (td, J = 8.4, 4.4 Hz, 1 H), 1.13 (s, 3 H), 1.09 (s, 3 H), 1.12 (m, 1 H), 0.94-0.75 (m, 2 H); ^{13}C NMR (50 MHz, CDCl_3) δ 163.2, 150.8, 144.2, 142.5, 135.4, 131.1 (2C), 123.8 (2C), 115.3, 112.3, 39.1, 38.0, 29.6, 28.7, 28.0, 27.0, 22.0, 13.6, 10.2; EI GCMS m/z 341 (10, M), 150 (100). Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{NO}_4$: C, 70.36 ; H, 6.79 ; N, 4.10. Found: C, 70.65 ; H, 7.00 ; N, 4.40.

3-Allyl-5,5-dimethyl-bicyclo[4.1.0]heptan-2-one 6:



IR (neat) 3080, 2950, 1680, 1470, 1360 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.60 (m, 1 H), 4.99-4.93 (m, 2 H), 2.35 (m, 1 H), 2.23-2.01 (m, 2 H), 1.72 (m, 1 H), 1.37-1.14 (m, 3 H), 1.06 (s, 3 H), 1.03 (s, 3 H), 1.07-0.89 (m, 2 H); ^{13}C NMR (50 MHz, CDCl_3) δ 210.3, 135.7, 117.1, 42.3, 36.0, 35.8, 30.2 (2C), 29.0, 27.7, 26.5, 9.7. Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.84 ; H, 10.18. Found: C, 80.72 ; H, 10.26.

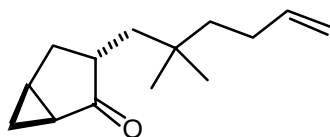
Acetic acid 3-(2',2'-dimethyl-hex-5'-enyl)-bicyclo[3.1.0]hex-2-en-2-yl ester 8 and Acetic acid 3-allyl-5,5-dimethyl-bicyclo[6.1.0]non-2-en-2-yl ester 9:



IR (mixture of the two isomeres) (neat) 2940, 1750, 1670, 1450, 1370 cm^{-1} ; cyclopentene : ^1H NMR (400 MHz, CDCl_3) δ 5.82 (ddt, J = 16.8, 10.2, 6.6 Hz, 1 H), 5.01 (dd, J = 16.8 Hz, 1.5 Hz, 1 H), 4.93 (dd, J = 10.2, 1.5 Hz, 1 H), 2.66 (dd, J = 16.8, 7.1 Hz, 1 H), 2.31 (dd, J = 16.8, 3.1 Hz, 1 H), 2.18 (s, 3 H), 2.00 (m, 2 H), 1.94 (m, 1 H), 1.86 (d, J = 13.2 Hz, 1 H), 1.79 (d, J = 13.2 Hz, 1 H), 1.50 (m, 1 H), 1.25 (m, 2 H), 0.86 (m, 1 H), 0.85 (s, 6 H), 0.27 (q, J = 4.1 Hz, 1 H); ^{13}C

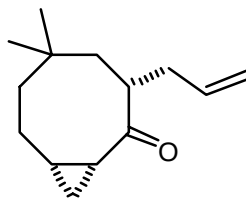
NMR (100 MHz, CDCl_3) δ 168.9, 139.6, 126.9, 120.6, 113.9, 41.7, 38.5, 36.8, 34.7, 28.7, 27.6 (2C), 27.5, 20.9, 15.7, 12.7. cyclooctene : ^1H NMR (400 MHz, CDCl_3) δ 5.65 (dddd, $J = 17.3$, 9.7, 7.1, 5.6 Hz, 1 H), 5.01 (dd, $J = 17.3$, 2.0 Hz, 1 H), 4.98 (dd, $J = 9.7$, 2.0 Hz, 1 H), 3.11 (dd, $J = 14.7$, 5.6 Hz, 1 H), 2.65 (d, $J = 13.7$ Hz, 1 H), 2.40 (dd, $J = 14.7$, 7.1 Hz, 1 H), 2.13 (s, 3 H), 1.95-1.88 (m, 2 H), 1.74 (d, $J = 13.7$ Hz, 1 H), 1.58 (m, 2 H), 1.13 (m, 1 H), 0.97 (s, 3 H), 0.94 (s, 3 H), 0.86 (m, 1 H), 0.60 (m, 1 H), 0.12 (q, $J = 5.1$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 150.4, 145.0, 135.8, 115.4, 46.2, 41.2, 37.4, 35.4, 34.6, 25.6, 25.1, 23.0, 20.9, 17.6, 7.7. Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2$ (mixture of the two isomeres) : C, 77.38 ; H, 9.74. Found: C, 77.34 ; H, 9.69.

3-(2',2'-Dimethyl-hex-5'-enyl)-bicyclo[3.1.0]hexan-2-one 10:



IR (neat) 2900, 1710, 1630, 1450, 1360 cm^{-1} ; ^1H NMR (400 MHz, C_6D_6) δ 5.75 (ddt, $J = 16.8$, 10.2, 6.6 Hz, 1 H), 5.02 (dd, $J = 16.8$, 2.0 Hz, 1 H), 4.97 (dd, $J = 10.2$, 2.0 Hz, 1 H), 2.16 (dd, $J = 14.2$, 2.0 Hz, 1 H), 2.02-1.85 (m, 2 H), 1.94 (dd, $J = 12.2$, 8.6 Hz, 1 H), 1.66 (q, $J = 9.2$ Hz, 1 H), 1.52 (ddd, $J = 8.1$, 4.6, 3.0 Hz, 1 H), 1.33-1.25 (m, 2 H), 1.17 (dd, $J = 6.1$, 4.0 Hz, 1 H), 1.14 (dd, $J = 6.1$, 4.0 Hz, 1 H), 0.79 (dd, $J = 14.2$, 9.2 Hz, 1 H), 0.70 (s, 6 H), 0.51 (m, 1 H), 0.38 (q, $J = 4.6$ Hz, 1 H); ^{13}C NMR (100 MHz, C_6D_6) δ 213.0, 139.7, 114.1, 42.6, 41.8, 36.8, 33.5, 32.7, 28.9, 27.6, 27.4, 26.7, 19.2, 13.7. Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$: C, 81.50 ; H, 10.75. Found: C, 81.36 ; H, 10.94.

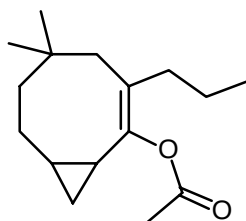
3-Allyl-5,5-dimethyl-bicyclo[6.1.0]nonan-2-one 11:



IR (neat) 2900, 1680, 1630, 1440, 1360 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.75 (ddt, $J = 17.3$, 10.2, 6.6 Hz, 1 H), 5.05 (d, $J = 17.3$ Hz, 1 H), 5.01 (d, $J = 10.2$ Hz, 1 H), 2.95 (tdd, $J = 8.6$, 6.1, 3.6 Hz, 1 H), 2.59 (dt, $J = 14.2$, 7.2 Hz, 1 H), 2.14 (dt, $J = 9.7$, 6.1 Hz, 1 H), 2.06 (dt, $J = 14.2$,

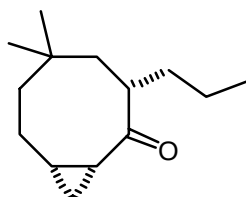
7.2 Hz, 1 H), 1.89 (m, 1 H), 1.68 (dd, $J = 14.8, 3.6$ Hz, 1 H), 1.51 (dd, $J = 14.8, 8.6$ Hz, 1 H), 1.36 (m, 2 H), 1.30 (m, 1 H), 1.17 (s, 3 H), 1.10 (q, $J = 5.1$ Hz, 1 H), 0.88 (s, 3 H), 0.81-0.69 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 213.1, 137.1, 116.4, 49.6, 44.0, 42.4, 36.6, 34.2, 33.3, 31.1, 30.0, 25.4, 21.8, 9.4. Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{O}$: C, 81.50 ; H, 10.75. Found: C, 81.46 ; H, 10.85.

Acetic acid 3-propyl-5,5-dimethyl-bicyclo[6.1.0]non-2-en-2-yl ester 13:



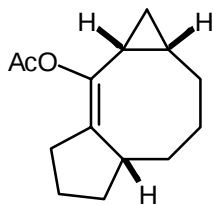
IR (neat) 2950, 1740, 1460, 1370 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.64 (d, $J = 13.7$ Hz, 1 H), 2.28 (m, 1 H), 2.14 (s, 3 H), 1.88 (m, 2 H), 1.72 (d, $J = 13.7$ Hz, 1 H), 1.62 (m, 1 H), 1.49 (m, 2 H), 1.44 (m, 1 H), 1.23 (m, 1 H), 1.11 (m, 1 H), 1.06 (m, 1 H), 0.97 (s, 3 H), 0.92 (s, 3 H), 0.88 (t, $J = 7.6$ Hz, 3 H), 0.57 (td, $J = 8.1, 4.1$ Hz, 1 H), 0.11 (q, $J = 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 144.1, 129.4, 46.3, 41.4, 35.4, 34.8, 34.7, 25.6, 25.1, 23.1, 21.4, 20.9, 17.7, 14.4, 7.7. Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2$: C, 76.75 ; H, 10.47. Found: C, 76.63 ; H, 10.60.

3-Propyl-5,5-dimethyl-bicyclo[6.1.0]nonan-2-one 14:



IR (neat) 2940, 1690, 1450, 1360 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.88 (tt, $J = 8.8, 4.5$ Hz, 1 H), 2.13 (ddd, $J = 10.0, 6.5, 5.7$ Hz, 1 H), 1.88 (m, 1 H), 1.85 (m, 1 H), 1.62 (dd, $J = 14.8, 3.5$ Hz, 1 H), 1.49 (dd, $J = 14.8, 8.8$ Hz, 1 H), 1.34 (m, 2 H), 1.30-1.15 (m, 4 H), 1.15 (s, 3 H), 1.08 (q, $J = 5.6$ Hz, 1 H), 0.90 (t, $J = 7.1$ Hz, 3 H), 0.85 (s, 3 H), 0.78-0.67 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 213.9, 49.8, 45.1, 42.2, 35.1, 34.2, 33.2, 31.1, 30.1, 25.2, 21.7, 21.5, 14.3, 9.4. Anal. Calcd. for $\text{C}_{14}\text{H}_{24}\text{O}$: C, 80.71 ; H, 11.61. Found: C, 80.56 ; H, 11.79.

5, 8, 3-Tricyclic derivative 16:



The reaction was run at rt for 24 hours.

IR (neat) 2940, 2900, 1750, 1690, 1440, 1360 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.82 (t, J = 8.0 Hz, 1 H), 2.25 (m, 1 H), 2.15 (m, 1 H), 2.10 (s, 3 H), 2.05 (m, 1 H), 1.88-1.69 (m, 3 H), 1.68-1.42 (m, 6 H), 1.08-0.95 (m, 2 H), 0.57 (m, 1 H), 0.13 (q, J = 5.0 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 139.2, 137.1, 42.3, 35.7, 35.6, 29.7, 29.1, 27.3, 23.0, 21.8, 20.7, 17.7, 8.0.