

Supplementary material for the communication entitled:

**Unexpected reactivity of acetylenic  $\omega$ -ketoesters towards TBAF and *t*-BuOK ; new cascade reactions affording allene and oxetane derivatives.**

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**General Procedure for the synthesis of allene derivatives :**

To a stirred solution of acetylenic  $\omega$ -ketoesters **6**, **7**, **8**, **17** or **18** (1 eq.; 0.4 mmol) in dry THF (5 mL) was added at room temperature a 1M solution of TBAF in THF (1 eq.; 0.4 mmol). The yellow solution was stirred at room temperature for 30 minutes, hydrolyzed with water (10 mL) and extracted with Et<sub>2</sub>O (2x10 mL). The organic layers were then washed with a saturated NaCl solution (10 mL), dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure (15 Torr, 25°C). The residue was chromatographed on a silica gel column (15g SiO<sub>2</sub>; ethyl acetate / hexane 10/90 then 20/80) to afford the corresponding allene derivatives **16**, **19**, **20**, **21** or **22**.

**Allene 16** [ (+) polar ] : colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) :  $\delta$  1.28 (t, *J* = 7.2 Hz, 3H); 1.38-1.45 (m, 1H); 1.61-2.09 (m, 10H), 2.13-2.21 (m, 1H); 4.18 (q, *J* = 7.2 Hz, 2H), 5.64 (dd, *J* = 3.0, 1.4 Hz, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) :  $\delta$  14.2, 20.0, 23.8, 27.6, 27.8, 28.1, 37.2, 47.5, 60.7, 79.4, 89.4, 111.7, 166.5, 207.6. IR (CCl<sub>4</sub>) : 3550, 3350, 1960, 1719 cm<sup>-1</sup>.

**Allene 16** [ (-) polar ] : colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) :  $\delta$  1.27 (t, *J* = 7.2 Hz, 3H); 1.48-1.85 (m, 1H); 1.88-2.02 (m, 10H), 2.06-2.13 (m, 1H); 2.21-2.28 (m, 1H); 2.39-2.45 (m, 1H); 4.15-4.29 (m, 2H), 5.66 (t, *J* = 2.0 Hz, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) :  $\delta$  14.2, 20.1, 23.9, 27.7, 27.9, 28.1, 37.3, 47.7, 60.7, 79.5, 89.6, 111.7, 166.4, 207.5. IR (CCl<sub>4</sub>) : 3550, 3350, 1960, 1716 cm<sup>-1</sup>.

**Allene 19** [mixture of the two isomers; isomer A (isomer B)] : colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz) :  $\delta$  1.00 (0.98) (s, 3H); 1.27 (1.25) (t, 3H,  $J = 7.1$  Hz); 1.29-2.00(m, 10H); 2.19-2.44 (m, 3H); 4.09-4.26 (m, 2H); 5.62-5.67 (m, 1H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz) :  $\delta$  14.2, 18.9 (18.7), 20.1 (19.8), 22.8 (22.6), 28.4 (28.9), 35.7 (34.9), 36.7 (35.9), 37.7 (36.1), 48.0 (46.8), 60.7, 81.8 (80.9), 90.0 (89.7), 113.0 (112.0), 166.8, 208.0 (207.0). IR ( $\text{CCl}_4$ ) : 1950, 1717  $\text{cm}^{-1}$ .

**Allene 20** [ (+) polar] : colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz) :  $\delta$  1.07 (s, 3H); 1.24 (t, 3H,  $J = 7.1$  Hz), 1.27-3.27 (m, 15H), 4.03-4.22 (m, 2H), 5.58-5.61(m, 1H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz) :  $\delta$  14.3, 21.1, 21.4, 22.4, 26.3, 28.3, 31.8, 33.2, 33.2, 33.9, 63.7, 74.4, 88.4, 111.9, 167.0, 207.2. IR ( $\text{CCl}_4$ ) : 3594, 3408, 1959, 1716  $\text{cm}^{-1}$ .

**Allene 21** [ (+) polar] : white crystals. M.p. 116-118°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) :  $\delta$  1.27 (t,  $J = 7.2$  Hz, 3H); 1.27-2.68 (m, 16H); 4.16 (m, 2H); 5.61 (d,  $J = 3.5$ , 1H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz) :  $\delta$  14.3, 21.6, 26.2, 26.4, 27.0, 28.0, 28.5, 37.1, 45.5, 60.8, 70.5, 88.6, 114.0, 167.0, 207.0. IR ( $\text{CCl}_4$ ) : 3500, 3350, 1959, 1717  $\text{cm}^{-1}$

**Allene 21** [ (-) polar] : colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) :  $\delta$  1.25 (t, 3H,  $J = 7.2$  Hz), 1.24-2.55 (m, 16H), 4.05-4.35 (m, 2H), 5.53 (d, 1H,  $J = 3.8$  Hz).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz) :  $\delta$  14.3, 21.5, 25.9, 26.5, 27.1, 28.1, 28.5, 36.8, 45.7, 60.5, 70.6, 88.6, 113.4, 166.3, 207.2. IR ( $\text{CCl}_4$ ) : 3500, 3350, 1959, 1717  $\text{cm}^{-1}$ .

**Allene 22** [ (+) polar] : colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz) :  $\delta$  1.23 (t, 3H,  $J = 7.2$  Hz), 1.25-1.27 (m, 15H), 2.36-2.62 (m, 3H), 4.04-4.30 (m, 2H), 5.54-5.58 (m, 1H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz) :  $\delta$  14.3, 21.0, 22.8, 26.4, 27.1, 27.6, 29.5, 30.0, 40.7, 49.0, 60.7, 75.0, 88.8, 113.2, 166.2, 208.1. IR ( $\text{CCl}_4$ ) : 3520, 2934, 1960, 1717  $\text{cm}^{-1}$ .

**Allene 22** [ (-) polar] : colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  1.26 (t, 3H,  $J = 7.2$  Hz), 1.23-1.95 (m, 15H), 2.20-2.50 (m, 3H), 4.06-4.24 (m, 2H), 5.51 (d, 1H,  $J = 3.7$  Hz).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz) :  $\delta$  14.3, 20.9, 26.6, 27.2, 27.4, 28.3, 29.8, 30.0, 41.0, 49.0, 60.5, 73.7, 88.4, 114.3, 166.4, 207.2. IR ( $\text{CCl}_4$ ) : 3530, 2940, 1960, 1717  $\text{cm}^{-1}$ .

## General Procedure for the synthesis of oxetane derivatives :

To a stirred solution of acetylenic  $\omega$ -ketoesters **7**, **8**, **17** or **18** (1 eq.; 0.4 mmol) in dry THF (3 mL) was added at room temperature potassium *tert*-butoxide (1 eq.; 0.4 mmol). The solution was stirred at room temperature for 30 minutes, hydrolyzed with water (10 mL) and extracted with Et<sub>2</sub>O (2x10 mL). The organic layers were then washed with a saturated NaCl solution (10 mL), dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure (15 Torr, 25°C). The residue was chromatographed on a silica gel column (15g SiO<sub>2</sub>; hexane, ethyl acetate / hexane 2/98) to afford the corresponding oxetane derivatives, **24**, **25**, **26** or **27**.

**Oxetane 24** [ (+) polar ] : colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) :  $\delta$  1.03 (s, 3H), 1.24 (t, 3H,  $J = 7.1$  Hz), 1.40-1.70 (m, 8H), 1.76 (tt, 1H,  $J = 14.2, 4.5$  Hz), 1.95 (dt, 1H,  $J = 12.5, 6.1$  Hz), 2.15-2.20 (m, 2H), 3.54 (ddd, 1H,  $J = 8.9, 3.5, 1.9$  Hz), 4.09, 4.12 (ABX<sub>3</sub>, 2H,  $J_{AB} = 14.4$  Hz,  $J = 7.1$ Hz), 5.09 (d, 1H,  $J = 1.9$  Hz). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  14.5, 18.7, 20.7, 24.3, 25.5, 37.4, 40.2, 41.9, 42.0, 47.4, 59.3, 89.6, 98.1, 167.8, 181.7. IR (CCl<sub>4</sub>) : 1709, 1660, 1462 cm<sup>-1</sup>

**Oxetane 25** [ (+) polar ] : colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) :  $\delta$  0.95 (s, 3H); 1.11-1.20 (m, 2H); 1.25 (t,  $J = 7.1$  Hz, 3H); 1.33-1.79 (m, 11H); 2.02 (td,  $J = 12.8, 4.3$  Hz, 1H); 3.05 (td,  $J = 5.7, 1.6$  Hz, 1H);  $\delta_A = 4.08$ ,  $\delta_B = 4.15$  (ABX<sub>3</sub>, 2H  $J_{AB} = 16.5$  Hz;  $J = 7.1$  Hz); 4.72 (d,  $J = 1.5$  Hz, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz) :  $\delta$  14.5, 15.0, 20.0, 20.8, 21.0, 23.5, 30.5, 34.1, 35.6, 36.3, 45.5, 59.1, 87.3, 93.6, 165.7, 178.5. IR (CCl<sub>4</sub>) : 1714, 1670, 1447 cm<sup>-1</sup>.

**Oxetane 25** [ (-) polar ] : colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) :  $\delta$  1.00 (s, 3H); 1.18-1.28 (m, 2H); 1.23 (t,  $J = 7.1$  Hz, 3H); 1.38-1.93 (m, 10H), 1.99 (td,  $J = 12.3, 3.7$  Hz, 1H); 2.32-2.39 (m, 1H); 3.40 (td,  $J = 6.2, 1.9$  Hz, 1H);  $\delta_A = 4.11$ ,  $\delta_B = 4.13$  (ABX<sub>3</sub>,  $J_{AB} = 10.2$  Hz;  $J = 7.1$  Hz); 5.18 (d,  $J = 1.9$  Hz, 1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz) :  $\delta$  14.5, 16.0, 19.3, 21.0, 21.1, 23.7, 31.3, 34.0, 36.1, 36.3, 46.9, 59.2, 90.8, 93.7, 167.8, 181.5. IR (CCl<sub>4</sub>) : 1709, 1657, 1470 cm<sup>-1</sup>.

**Oxetane 26** (only one isomer observed): colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) :  $\delta$  1.26 (t, 3H,  $J = 7.1$  Hz); 1.28-2.20 (m, 15H), 3.34 (td, 1H,  $J = 6.0, 1.5$  Hz), 4.12 (m, 2H), 5.18 (d, 1H,

$J = 1.5\text{Hz}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  14.5, 16.2, 20.1, 22.5, 23.1, 23.8, 30.8, 36.7, 37.0, 46.6, 59.3, 91.1, 92.1, 167.8, 181.3. IR ( $\text{CCl}_4$ ) : 1716, 1652, 1447  $\text{cm}^{-1}$ .

**Oxetane 27** (only one isomer observed) : colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz) :  $\delta$  1.25 (t, 3H,  $J = 7.2\text{Hz}$ ); 1.22-2.33 (m, 17H), 3.37 (ddd,  $J = 7.4, 3.5, 2.0\text{ Hz}$ ), 4.10 (m, 2H), 5.10 (d, 1H,  $J = 2.0\text{Hz}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  14.5, 19.4, 22.7, 23.4, 22.7, 23.4, 27.5, 29.0, 30.2, 32.9, 39.1, 43.7, 49.4, 59.2, 90.4, 95.3, 167.9, 181.7. IR ( $\text{CCl}_4$ ) : 1714, 1652, 1448  $\text{cm}^{-1}$ .