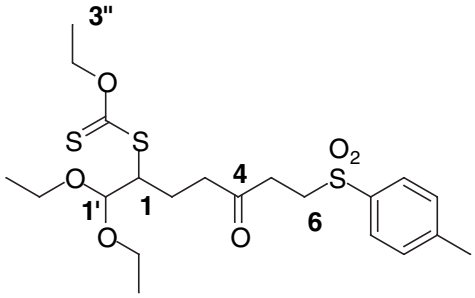
General procedure for the radical additions to olefins :

A solution of xanthate (1mmol) and olefin (1.5 - 2mmol) in 1,2-dichloroethane or cyclohexane (1ml) was heated to reflux for 15 min, then lauroyl peroxyde was added every 2 hrs (5 mol% *vs* xanthate, at the first time, followed by 2 mol% every 2 hrs) until complete consumption of the xanthate. The solvent was then removed under reduced pressure and the residue was purified by silicagel column chromatography .

Dithiocarbonic acid *S*-[1-diethoxymethyl-4-oxo-6-(toluene-4-sulfonyl)-hexyl] ester *O*-ethyl ester **1b**



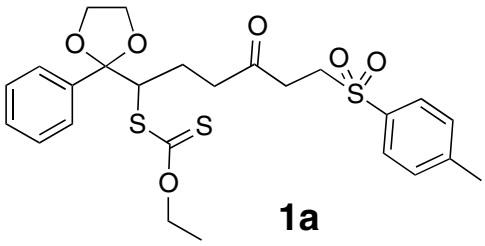
Solvent : 1,2-dichloroethane
The crude product was purified by flash chromatography on silica gel(Eluent: Heptane/Ethyl acetate : 8/2). 85% yield as a pale yellow oil

IR (cm^{-1}): 2977, 2929, 2896, 1718, 1597, 1444, 1406, 1316, 1219, 1148, 1111, 1053, 815.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.69 (d, 2H, H_{ar} , *J*=8.1Hz) ; 7.30 (d, 2H, H_{ar} , *J*=8.1Hz) ; 4.56 (q, 2H, $H_{2''}$, *J*=7.2Hz); 4.46 (d, 1H, $H_{1'}$, *J*=2.9Hz) ; 3.96(m, 1H, H_1) ; 3.58(m, 4H, $H_{2'}$) ; 3.32(dt, 2H, H_6) ; 2.82(dt, 2H, H_5) ; 2.60(dt, 2H, H_3)2.43(s, 3H, H_{Me}) ; 2.19(m, 1H, H_{2a}) ; 1.81(m, 1H, H_{2b}) ; 1.39(t, 3H, $H_{3''}$, *J*=7.2Hz) ; 1.17(m, 6H, H_{ethoxy})

^{13}C NMR (250MHz, $CDCl_3$): δ 214.2 $C_{C=S}$; 204.7 C_4 ; 144.3C_{ar} ; 135.5 C_{ar}; 129.5 C_{ar}; 127.5C_{ar} ; 103.4 $C_{1'}$; 69.8$C_{2''}$; 64.0 C_{ethoxy} ; 63.3 C_{ethoxy} ; 52.8; 50.1; 39.3 ; 34.8 ; 21.7 ; 21.1 ; ; 14.7 ; 13.3 .

Dithiocarbonic acid S-[6-benzensulfonyl-4-oxo-1-(2-phenyl-[1,3]dioxolan-2-yl)-hexyl] ester O-ethyl ester (**1a**)



1a

Compound **1a** was prepared following the general procedure for radical addition, starting from 4,43 g of xanthate. The reaction was complete after 6h (9 % DLP). The crude product was recristallized in ethanol to give 5,3 g of a cristal white (79% isolated yield).

IR (Nujol, cm^{-1}): 1048 ; 1111 ; 1144 ; 1223 ; 1298 ; 1376 ; 1461 ; 1721 ; 2854 ; 2924 ; 2954.

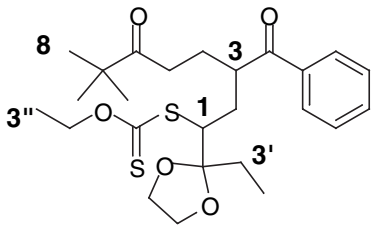
NMR ^{1}H ($CDCl_3$, 300 MHz) : δ=7.75 (d ; J=8.2 Hz ; 2H) ; δ=7.48 (d ; J=7.8 ; 2H) ; δ=7.35 (m, 5H); δ=4.59 (q, J= 7.5 Hz ; 2H) ; δ=4.38 (dd ; J_1=3.7 Hz ; J_2=10.3 ; 1H) ; δ=4.08 (t ; J=3.7 Hz ; 2H) ; δ=3.8 (m ; 2H) ; δ=(3.29 ; J=7.2 Hz ; 2H) ; δ=2.79 (m ; 2H) ; δ=2.55 (m ; 2H) ; δ=2.45 (s ; 3H) ; δ=2.05 (m ; 1H) ; δ=1.69 (m ; 1H) ; δ=1.40 (t ; J=7.1 Hz ; 3H).

NMR ^{13}C ($CDCl_3$, 300 MHz) : 205.14 ; 144.92 ; 139.95 ; 135.94 ; 130.00 ; 128.50 ; 128.15 ; 128.00 ; 126.32 ; 110.27 ; ($CDCl_3$: 77.45 ; 77.03 ; 76.60) ; 70.45 ; 65.55 ; 65.22 ; 58.85 ; 50.59 ; 39.88 ; 35.20 ; 23.76 ; 21.65 ; 13.78.

Mp : 100.6 – 101.6 ^{0}C

M.S. (ESI) : 545.1 ($[M+Na]^+$. 100 %) ; 561.1 ($[M+K]^+$, 20 %).

Dithiocarbonic acid S-[3-benzoyl-1-(2-ethyl-[1,3]dioxolan-2-yl)-7,7-dimethyl-6-oxo-octyl]ester O-ethyl ester **1e**



Solvent : cyclohexane. DLP : 25% .
The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 95/5 to 9/1).
32% yield ; starting material recovered 35%

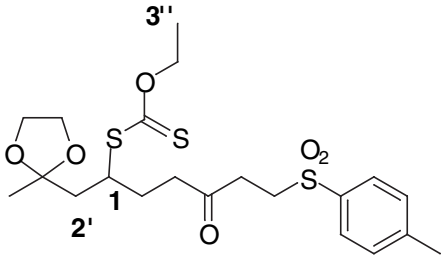
IR (cm^{-1}): 2963, 2928, 1704, 1679, 1632, 1597, 1581, 1477, 1448, 1366, 1189, 1162, 1112, 1083, 1045, 816.

^{1}H NMR ($CDCl_3$) : δ 7.95(m, 2H, H_{ar}) ; 7.56(m, 1H, H_{ar}) ; 7.46(m, 2H, H_{ar}) ; 5.06(t, *J*=7.0Hz) ; 4.97 (dd, J_1=11.0, Hz J_2=3.6Hz) 4.63 (m); 4.46 (m); 4.31 (m) ; 4.08-3.8 (m), 2.43 (m) ; 2.08-0.75 (m)

^{13}C NMR ($CDCl_3$): δ 214.6 ; 212.1 ; 203.0 ; 202.4 ; 136.7 ; 136.6 ; 133.2 ; 128.7 ; 128.5 ; 128.4 ; 112.2 ; 111.6 ; 70.5 ; 66.3 ; 66.0 ; 64.9 ; 56.0 ; 51.7 ; 51.0 ; 44.9 ; 44.2 ; 43.3 ; 42.8 ; 33.5 ; 32.9 ; 32.3 ; 29.8 ; 27.9 ; 27.126.4 ; 26.2 ; 25.7 ; 13.8 ; 13.4 ; 8.0 ; 7.2.

MS(CI):m/z=482($M+H^+$).

Dithiocarbonic acid O-ethyl ester S-[1-(2-methyl-[1,3]dioxolan-2-ylmethyl)-4-oxo-6-(toluène-4-sulfonyl)-hexyl] ester **1f**



Solvent : 1,2-dichloroethane ; 7% (DLP).
The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/AcOEt=9/1 to 7/3) (80% yield) pale yellow oil

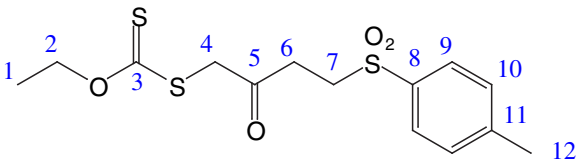
IR (cm^{-1}): 3423, 2982, 2935, 2889, 1718, 1597, 1446, 1412, 1377, 1316, 1303, 1289, 1270, 1219 , 1148, 1112, 1087, 949, 816, 735.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.76 (d, 2H, H_8, *J*= 8.1Hz) ; 7.36 (d, 2H, H_9, *J*= 8.1Hz) ; 4.61 (q, 2H, $H_{2''}$, *J*=7.1Hz) ; 3.93 (s, 4H, $H_{dioxolan}$) ; 3.85 (m, 1H, H_1) ; 3.36 (t, 2H, H_6) ; 2.85 (dt, 2H, H_5) ; 2.55 (t, 2H, H_3, *J*=7.3Hz) ; 2.44 (s, 3H, H_{11}) ; 2.01 (m, 4H, H_2 , $H_{2'}$) ; 1.40 (dt, 2H, $H_{3''}$, *J*= 7.1Hz) ; 1.35 (s, 3H, $H_{4'}$).

^{13}C NMR ($CDCl_3$): δ 213.9 $C_{c=s}$; 205.1 $C_{c=o}$; 144.8 C_{10} ; 135.8 C_7 ; 129.9 C_9, 127.9 C_8, 109.0 $C_{3'}$; 69.8 $C_{2''}$; 64.5$C_{dioxolan}$; 64.2 $C_{dioxolan}$; 50.4 C_6 ; 45.9 C_1 ; 42.8 $C_{2'}$; 39.6 C_3 ; 35.1 C_5 ; 28.1 C_2 ; 24.0 $C_{4'}$; 21.5 C_{11} ; 13.6 $C_{3''}$.

MS(ESI):m/z=497 (M+Na)

Compound 3



1) A solution of aluminum chloride (73.95g, 1.2eq) and chloroacetyl chloride (52.2g, 462.2mmol) in 350mL of dichloromethane (C=1.25mol/L) was degassed by bubbling argon and cooled to -10°C using an ethanol / dry ice bath. Ethylene was passed through the reaction mixture until the absorption stopped (5h). The temperature of the reaction mixture was strictly maintained between -5 and -10°C.
The remaining ethylene was eliminated by bubbling argon through the mixture for 0.1h. The reaction mixture was poured into an HCl / ice mixture and the aqueous phase was extracted with dichloromethane. The organic layer was washed with water, aqueous $NaHCO_3$, water and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum ; the product was used in the next step without further purification.
2) The resulting residue (65.17g, 462.2mmol) was dissolved in 460mL of acetone (C=1mol/L) and the mixture was cooled to –78°C using an ethanol / dry ice bath. Potassium xanthogenate (88.91g, 1.2eq) was added in portions over 30 minutes and the mixture was allowed to warm to room temperature. The reaction was completed after 2h as indicated by TLC monitoring.

The solvent was removed under vacuum at room temperature. Water was then added to the residue. Extraction with ether furnished a residue that was used in the next step without further purification.
3) To a solution of the above residue (104.80g, 462.2mmol) in 1.2L of ethanol (C=0.2mol/L) was added sodium p-toluenesulfinate (5% hydrate, 103.77g, 1.2eq). The reaction mixture was refluxed for 1.5h. It was rapidly filtered and the filtrate was allowed to cool to room temperature. The resulting crystals were collected, washed with water and ice-cold ethanol and recrystallized in ethanol to give 75.52g of a white solid (47% overall yield).

m.p.= 119.8-120.3°C (ethanol)

TLC : (eluent 6/4 heptane/ethyl acetate, UV and *p*-anisaldehyde)

Rf = 0.32 (pink)

^{1}H NMR : ($CDCl_3$)

1.42 (3H, t [J=7Hz], H-1), 2.47 (3H, s, H-12), 3.12 (2H, t [J=7.5Hz], H-6), 3.40 (2H, t [J=7.5Hz], H-7), 3.98 (2H, s, H-4), 4.63 (2H, q [J=7Hz], H-2), 7.38 (2H, d [J=8Hz], H-10), 7.80 (2H, d [J=8Hz], H-9)

^{13}C NMR : ($CDCl_3$)

13.70 (C-1), 21.64 (C-12), 34.64 (C-6), 45.05 (C-4), 50.63 (C-7), 71.10 (C-2), 127.97 (C-9), 130.03 (C-10), 136.00 (C-8), 145.09 (C-11), 199.43 (C-5), 212.96 (C-3)

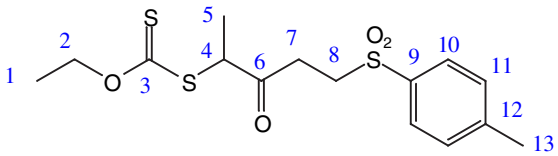
IR : (Nujol)

1048, 1114, 1142, 1239, 1319, 1460, 1725, 2854, 2924, 2953

MS : (ESI)

m/z = 396.2 (M+Na)

Compound



This compound was prepared following the same procedure as for compound **3**, starting with 70.63g of 2-chloropropionyl chloride (556.3mmol) to give 28.15g of a white solid (14% yield over the three steps). The reaction times were different from those of compound **3** : they were respectively of 7h, 4h and 3h for steps 1, 2 and 3.

m.p.= 69.6-70.2°C (ethanol)

TLC : (eluent 6/4 heptane/ethyl acetate, UV and *p*-anisaldehyde)

Rf = 0.38 (pink)

^{1}H NMR : ($CDCl_3$)

1.36 (3H, d [J=7Hz], H-5), 1.40 (3H, t [J=7Hz], H-1), 2.42 (3H, s, H-13), 3.11 (2H, t [J=7.5Hz], H-7), 3.33 (2H, t [J=7.5Hz], H-8), 4.41 (1H, q [J=7Hz], H-4), 4.58 (2H, q [J=7Hz], H-2), 7.33 (2H, d [J=8Hz], H-11), 7.75 (2H, d [J=8Hz], H-10)

^{13}C NMR : ($CDCl_3$)

13.67 (C-1), 15.31 (C-5), 21.61 (C-1), 33.02 (C-7), 50.72 (C-8), 53.13 (C-4), 70.89 (C-2), 128.00 (C-10), 130.00 (C-11), 135.82 (C-9), 144.25 (C-12), 202.99 (C-6), 212.10 (C-3)

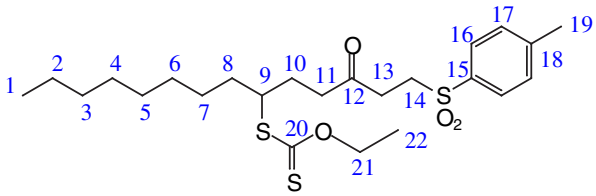
IR : (Nujol)

1046, 1116, 1155, 1232, 1311, 1454, 1729, 2854, 2925, 2955, 2983

MS : (ESI)

m/z = 383.2 (M+Na)

Compound 1c



Compound **1c** was prepared following the general procedure for radical additions, starting from 5g of xanthate (14.43mmol) to give 5.55g of a pale yellow oil (34% yield).
The reaction was complete after 4h (7%mol of DLP).

TLC : (eluent 6/4 heptane /ethyl acetate, UV and *p*-anisaldehyde)

Rf = 0.52 (orange)

^{1}H NMR : ($CDCl_3$)

0.85 (3H, t [J=7Hz], H-1), 1.23 (12H, m, C$\underline{H}_2$), 1.40 (3H, t J=7Hz, H-22), 1.59 (2H, m, H-8), 1.75 (1H, m, 1st H-10), 2.02 (1H, m, 2nd H-10), 2.44 (3H, s, H-19), 2.56 (2H, t [J=7Hz], H-14), 2.85 (2H, t [J=7.5Hz], H-11), 3.34 (2H, t [J=7.5Hz], H-13), 3.66 (1H, m, H-9), 4.61 (2H, q [J=7Hz], H-21), 7. 35 (2H, d [J=8Hz], H-17), 7.76 (2H, d [J=8Hz], H-16)

^{13}C NMR : ($CDCl_3$)

13.58 (C-1), 13.88 (C-22), 21.46 (C-19), 22.46 (C-2), 26.58, 27.76, 28.99, 29.17, 31.64 (C-3), 34.40 (C-13), 35.11, 39.70 (C-11), 50.40 (C-14), 50.80, 69.81 (C-21), 127.80 (C-16), 129.86 (C-17), 136.00 (C-15), 144.99 (C-18), 205.08 (C-12), 214.43 (C-20)

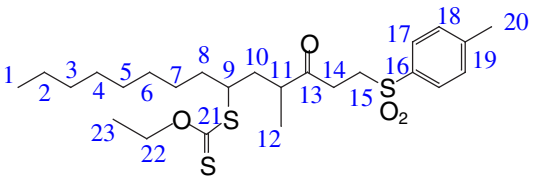
IR :

1050, 1087, 1112, 1150, 1215, 1317, 1453, 1719, 2855, 2926, 2954

MS : (ESI)

m/z = 509.2 (M+Na)

Compound 1d



Compound **1d** was prepared following the general procedure for radical additions, starting from 5g of xanthate (13.27mmol) to give 6.27g of a pale yellow oil (90% yield).
The reaction was complete after 8h (11%mol of DLP).

TLC : (eluent 6/4 heptane /ethyl acetate, UV and *p*-anisaldehyde)

Rf = 0.51 (orange)

^{1}H NMR : ($CDCl_3$)

0.85 (3H, t [J=7Hz], H-1), 1.09 (3H, t [J=6.5Hz], H-23), 1.30 (12H, m, C$\underline{H}_2$), 1.40 (3H, 2 d [J=7Hz], H-12), 1.61 (2H, m, H-8), 1.91 et 2.12 (2H, 2 ddd [J=5, 9 et 14Hz], H-10), 2.43 (3H, s, H-20), 2.64 to 3.05 (2H, m, H-14), 3.33 (2H, m, H-15), 3.57 and 3.70 (1H, 2 m, H-9), 4.57 (1H, dq [J=1, 7Hz], H-11), 4.62 (2H, q [J=6.5Hz], H-22), 7.34 (2H, d [J=8Hz], H-18), 7.76 (2H, d [J=8Hz], H-17)

^{13}C NMR : ($CDCl_3$)

13.67 (C-1), 13.96 (C-23), 17.55 (C-12), 21.51 (C-20), 22.49 (C-2), 26.55, 29.08, 31.72 (C-3), 33.37, 34.07 (C-14), 35.13, 43.66 (C-11), 44.19, 49.60, 50.54 (C-15), 69.95 (C-22), 127.88 (C-17), 129.88 (C-18), 136.06 (C-16), 144.70 (C-19), 208.98 (C-13), 214.22 (C-21)

IR :

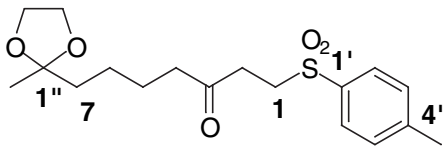
1050, 1088, 1112, 1150, 1216, 1317, 1458, 1715, 2855, 2927, 2954

MS : (ESI)

m/z = 523.2

Reduction with H_3PO_2/ NEt_3 : see note 15

7-(2-methyl-[1,3]dioxolan-2-yl)-1-(toluène-4-sulfonyl)-heptan-3-one **2f**



Solvent : 1,2-dichloroethane
The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/AcOEt=7/3) (75% yield) white cristal

IR (cm^{-1}): 3584, 3418, 2981, 2940, 2877, 1716, 1597, 1452, 1411, 1376, 1315, 1303, 1224, 1148, 1087, 1060, 948, 851, 817, 734.

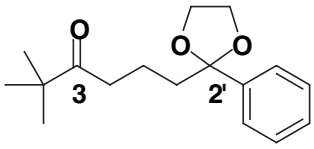
^{1}H NMR (300MHz, $CDCl_3$): δ 7.78 (d, 2H, $H_{2'}$, *J* =8.1Hz); 7.37 (d, 2H, $H_{3'}$, *J* =8.1Hz); 3.92(m, 4H, $H_{dioxolane}$) ; 3.36 (t, 2H, H_1, *J*=7.5Hz) ; 2.88 (t, 2H, H_2, *J*=7.5Hz) ; 2.46 (s, 3H, $H_{2''}$); 2.44 (t, 2H, H_4, *J*=7.4Hz); 1.57 (m, 4H, H_7 and H_5); 1.35 (m, 2H, H_6); 1.27 (s, 3H, $H_{5'}$).

^{13}C NMR (250MHz, $CDCl_3$): δ 206.0 C_3; 144.9 $C_{4'}$; 136.0 $C_{1'}$; 129.9 $C_{3'}$; 127.9 $C_{2'}$; 109.7 C_1 ; 64.5 $C_{dioxolane}$; 50.6 C_1; 42.7 C_7; 38.8 C_4; 35.0 C_2; 23.7 $C_{2''}$; 23.5 C_5; 21.6 $C_{5'}$.

MS: (ESI) : 377 (M+Na)

m.p (°C)= 60.4-60.8

2,2-Dimethyl-6-(2-phenyl--[1,3]dioxolan-2-yl)-hexan-3-one : **13**



Solvent : 1,2-dichloroethane
The crude product was purified by flash chromatography on silica gel (Eluent= Heptane/AcOEt=95/5) (43% yield) pale yellow oil

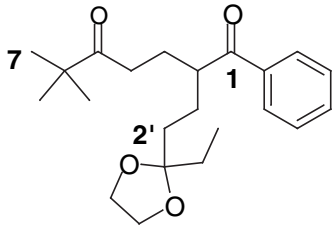
IR (cm^{-1}): 3060, 3029, 2966, 2887, 1704, 1477, 1448, 1408, 1394, 1366, 1306 , 1269, 1237, 1189, 1100, 1046, 995, 948, 918.

^{1}H NMR(200MHz, $CDCl_3$): δ 7.44 (d, 2H, H_{ar}, *J*=7.9Hz) ; 7.31 (m, 3H, H_{ar}) ; 4.01 (m, 2H, $H_{dioxolan}$) ; 3.75 (m, 2H, $H_{dioxolan}$) ; 2.48 (t, 2H, H_4, *J*=7.2Hz) ; 1.88 (m, 2H, H_6) ; 1.61 (m, 2H, H_5) ; 1.09 (s, 9H, H_1).

^{13}C NMR (200MHz, $CDCl_3$): δ 215.5 C_3, 142.5 C_{ar} ; 128.1 C_{ar}; 127.8 C_{ar} ; 125.7 C_{ar} ; 110.3 $C_{2'}$; 64.5 $C_{dioxolane}$; 43.9 C_2 ; 39.7 C_6, 36.2 C_4 ; 26.4 C_1, 18.1 C_5.

MS(C.I): 277($M+H^+$)

2-[2-(2-Ethyl-[1,3]dioxolan-2-yl)-ethyl]-6,6-dimethyl-1-phenyl-heptane-1,5-dione **2e**



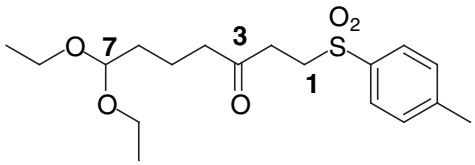
Solvent : 1,2-dichloroethane
(89% yield) without chromatography

IR (cm^{-1}) : 2968, 2936, 2880, 1704, 1678, 1596, 1580, 1478, 1464, 1448, 1366, 1189, 1071, 949, 908, 816, 702.

^{1}H NMR (300MHz, $CDCl_3$): 7.96 (d, 2H, H_{ar}); 7.56 (m, 1H, H_{ar}) ; 7.46 (m, 2H, H_{ar}); 3.88 (m, 4H, $H_{dioxolan}$) ; 3.54 (m, 1H, H_2) ; 2.46 (m) ; 2.01 (m) ; 1.84 (m) ; 1.59 (m) ; 1.05 (s, 9H, H_7) ; 0.85 (t, 3H, $H_{5'}$, *J*=7.4Hz)

^{13}C NMR (250MHz, $CDCl_3$): 215.5 ; 203.8 ; 137.2 ; 133.0 ; 128.6 ; 128.1 ; 111.6 ; 64.8 ; 44.5 ; 44.0 ; 33.8 ; 33.3 ; 30.2 ; 29.6 ; 26.3 ; 25.9 ; 7.9.

7,7-Diethoxy-1-(toluene-4-sulfonyl)-heptan-3-one **2b**



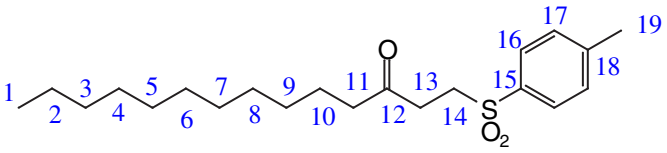
Solvent : 1,2-dichloroethane
The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 7/3).
68% yield.

IR (cm^{-1}): 2975, 2929, 2896, 1718, 1597, 1447, 1408, 1376, 1315, 1304, 1147, 1086, 1059, 815, 735.

^{1}H NMR (300MHz , $CDCl_3$): δ 7.78 (d, 2H, H_{ar} , *J*=8.1Hz) ; 7.36 (d, 2H , H_{ar} , *J* =8.1Hz) ; 4.44 (t, 1H, H_7 , *J*=5.2Hz) ; 3.54 (m, 4H, H_{ethoxy}) ; 3.35 (t, 2H, H_1 , *J*= 7.5Hz), 2.87 (t, 2H, H_2, *J*=7.5Hz) ; 2.45 (s+t, 5H, H_4 et H_{methyl}) ; 1.54 (m, 4H, H_5 et H_6) ; 1.18 (t, 6H, H_{ethoxy} , *J* = 7.0Hz).

^{13}C NMR (300MHz , $CDCl_3$): δ 205.8 ; 144.9 ; 136.0 ; 129.9 ; 127.9 ; 102.5 ; 61.1 ; 50.6 ; 42.4 ; 35.0 ; 32.8 ; 21.6 ; 18.8 ; 15.3.

Compound 2c



Compound **2c** was prepared following the general procedure for radical reduction, starting from 1g of xanthate (2.05mmol) to give 0.471g of a white solid (63% yield) for the propanol procedure.
For the dioxane procedure starting from 0.5g of xanthate (1.03mmol) to give 298mg of a white solid (79% yield).

m.p. = 67.6-68.4°C (crude)

TLC : (eluent toluene/ethyle acetate 95/5, UV et *p*-anisaldehyde)

Rf = 0.43 (blue-grey)

^{1}H NMR : ($CDCl_3$)

0.88 (3H, t [J=7Hz], H-1), 1.25 (16H, m, C<u>H</u>$_2$), 1.55 (2H, m, H-10), 2.41 (2H, t [J=7.5Hz], H-11), 2.46 (3H, s, H-19), 2.89 (2H, t [J=7.5Hz], H-13), 3.36 (2H, t [J=7.5Hz], H-14), 7.37 (2H, d [J=8Hz], H-17), 7.78 (2H, d [J=8Hz], H-16)

^{13}C NMR : ($CDCl_3$)

14.06 (C-1), 21.58 (C-19), 22.64 (C-2), 23.41, 23.64 (C-10), 29.05, 29.29, 29.40, 29.60, 31.88 (C-3), 34.99 (C-13), 42.87 (C-11), 50.64 (C-14), 127.98 (C-16), 129.98 (C-17), 136.03 (C-15), 144.91 (C-18), 206.32 (C-12)

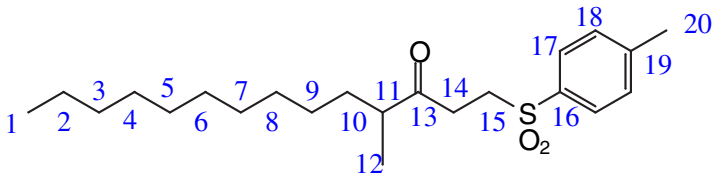
IR :

1087, 1138, 1158, 1242, 1286, 1296, 1378, 1415, 1469, 1599, 1709, 2850, 2918, 2954

MS : (ESI)

m/z = 389.4 (M+Na)

Compound 2d



Experimental

Compound **2d** was prepared following the general procedure for radical reduction, starting from 5.90g of xanthate (11.78mmol) to give 2.182g of a white solid (49% yield) for the propanol procedure.
For the dioxane procedure starting with 100mg of xanthate (0.20mmol) to give 57mg of a white solid (75% yield).

m.p.= 50.6-51.1°C (ethanol)

TLC : (eluent toluene/ethyl acetate 95/5)

Rf = 0.33 (blue-grey)

^{1}H NMR : ($CDCl_3$)

0.81 (3H, t [J=7Hz], H-1), 1.01 (3H, d [J=7Hz], H-12), 1.21 (16H, m, C$\underline{H}_2$), 1.50 (2H, m, H-10), 2.41 (3H, s, H-20), 2.49 (1H, dq [J=1 et 7Hz], H-11), 2.89 (2H, 2 t [J=7.5Hz], H-14), 3.31 (2H, t [J=7.5Hz], H-15), 7.32 (2H, d [J=8Hz], H-18), 7.75 (2H, d [J=8Hz], H-17)

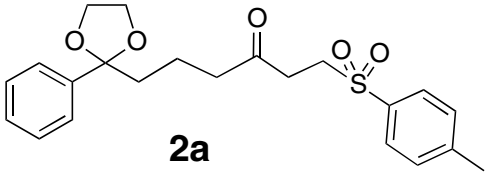
^{13}C NMR : ($CDCl_3$)

14.09 (C-1), 16.09 (C-12), 21.62 (C-20), 22.62 (C-2), 27.15 (C-10), 29.20, 29.27, 29.56, 31.85 (C-3), 32.85, 33.32 (C-14), 46.50 (C-11), 50.62 (C-15), 127.90 (C-17), 129.95 (C-18), 136.13 (C-16), 144.83 (C-19), 210.06 (C-13)

IR :

1086, 1141, 1240, 1260, 1307, 1378, 1409, 1465, 1597, 1710, 2850, 2916, 2951

***6-(2-Phenyl -[1,3]dioxolan-2-yl)-1-(toluene-4-sulfonyl)-hexan-3-one* (2a)**



2a

Compound **2a** was prepared following the general procedure for radical reduction of the xanthate.. The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 8/2).

For the reduction procedure with diethylphosphite/DLP : (see footnote 17) 66% isolated yield

For the reduction procedure with H_3PO_2/NEt_3/AIBN : (see footnote 15) 69% isolated yield

For the addition-reduction with diethylphosphite/DLP : (see footnote 17) : 58% isolated yield

IR (Nujol, cm^{-1}): 2924 ; 2854 ; 1719 ; 1462 ; 1377 ; 1145 ; 1042 ; 699.

NMR ^{1}H ($CDCl_3$, 300 MHz) : δ=7.76 (d ; J = 8.1 ; 2H) ; δ=7.34 (m ; 7H) ; δ=3.99 (t ; J=6.9 ; 2H) ; δ=3.75 (t ; J=6.9 ; 2H) ; δ=3.33 (t ; J=7.5 ; 2H) ; δ=2.84 (t ; J=7.0 ; 2H) ; δ=2.45 (s ; 3H) ; δ=2.42 (t ; J=7.4 ; 2H) ; δ=1.85 (t ; J=7.7 ; 2H) ; δ=1.61 (m, 2H).

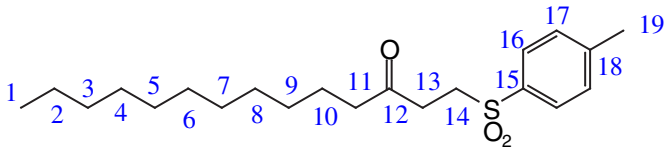
NMR ^{13}C ($CDCl_3$, 300 MHz) : δ=205.92 ; 144.93 ; 142.27 ; 136.04 ; 139.00 ; 128.16 ; 128.00 ; 127.93 ; 125.64 ; 110.07 ; ($CDCl_3$: 77.45 ; 77.02 ; 76.60) ; 64.47 ; 50.61 ; 42.55 ; 39.37 ; 35.02 ; 21.64 ; 17.85.

Mp : 120.9 – 121.5 ^{0}C

M.S. (ESI) : 425.1 ($[M+Na]^+$, 100 %) ; 441.1 ($[M+K]^+$, 30 %)

Compound 2c:

Compound **2c** was prepared following the general procedure for radical addition-reduction of the xanthate to the olefin.. The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 95/5 then 9/1) to give an solide white : 71% isolated yield.



NMR ^{1}H : ($CDCl_3$)

0.88 (3H, t [J=7Hz], H-1), 1.25 (16H, m, C<u>H</u>$_2$), 1.55 (2H, m, H-10), 2.41 (2H, t [J=7.5Hz], H-11), 2.46 (3H, s, H-19), 2.89 (2H, t [J=7.5Hz], H-13), 3.36 (2H, t [J=7.5Hz], H-14), 7.37 (2H, d [J=8Hz], H-17), 7.78 (2H, d [J=8Hz], H-16)

NMR ^{13}C : ($CDCl_3$)

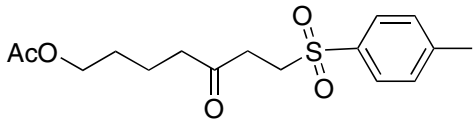
14.06 (C-1), 21.58 (C-19), 22.64 (C-2), 23.41, 23.64 (C-10), 29.05, 29.29, 29.40, 29.60, 31.88 (C-3), 34.99 (C-13), 42.87 (C-11), 50.64 (C-14), 127.98 (C-16), 129.98 (C-17), 136.03 (C-15), 144.91 (C-18), 206.32 (C-12)

IR (Nujol, cm^{-1}): 1087, 1138, 1158, 1242, 1286, 1296, 1378, 1415, 1469, 1599, 1709, 2850, 2918, 2954

MS : (ESI) 389.4 ([M+Na]+, 100 %).

Mp. = 67.6 - 68.4°C (crude)

***Acetic acid 5-oxo-7-(toluene-4-sulfonyl)-heptyl ester* (12)**



12

Compound 1**2** was prepared following the general procedure for radical addition-reduction of xanthates to olefins. The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 8/2 then 7/3) to give a white solid: 44% isolated yield.

IR (Nujol, cm^{-1}):2954 ; 1732 ; 1597 ; 1366 ; 1315 ; 1303 ; 1244 ; 1149 ; 1087 ; 1040 ; 817 ; 735.

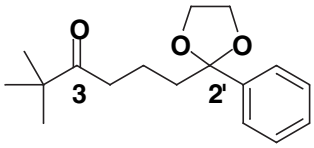
NMR ^1H ($CDCl_3$, 300 MHz) : δ = 7.76 (d, J = 8.3 Hz ; 2H) ; δ = 7.35 (d. J = 8.3 Hz ; 2H) ; δ = 4.01 (t, J = 6.0 Hz ; 2H) ; δ = 3.34 (t, J = 7.5 Hz ; 2H) ; δ = 2.86 (t, J = 7.5 Hz ; 2H) ; δ = 2.46 (t, 6.9; 2H). ; δ = 2.43 (s, 3H) ; δ = 2.02 (s, 2H) ; δ = 1.58 (m, 4H).

NMR ^{13}C ($CDCl_3$, 300 MHz) : δ = 205.57 ; 171.06 ; 144.93 ; 135.94 ; 129.96 ; 127.93 ; 128.41 ; 63.82 ; 50.53 ; 42.10 ; 35.00 ; 27.86 ; 21.61 ; 20.91 ; 19.93.

Mp : 44.7 – 45.7 ^0C

M.S. (ESI) :348.9 ($[M+Na]^+$, 100 %) ; 364.9 ($[M+K]^+$, 12 %)

2,2-Dimethyl-6-(2-phenyl--[1,3]dioxolan-2-yl)-hexan-3-one : 13



Compound **13** was prepared following the general procedure for radical addition-reduction of xanthates to olefins. The crude product was purified by flash chromatography on silica gel (Eluent= Heptane/AcOEt=95/5) (43% isolated yield) pale yellow oil

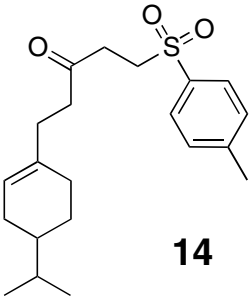
IR (cm^{-1}): 3060, 3029, 2966, 2887, 1704, 1477, 1448, 1408, 1394, 1366, 1306 , 1269, 1237, 1189, 1100, 1046, 995, 948, 918.

^1H NMR(200MHz, $CDCl_3$): δ 7.44 (d, 2H, H_{ar}, *J*=7.9Hz) ; 7.31 (m, 3H, H_{ar}) ; 4.01 (m, 2H, $H_{dioxolan}$) ; 3.75 (m, 2H, $H_{dioxolan}$) ; 2.48 (t, 2H, H_4, *J*=7.2Hz) ; 1.88 (m, 2H, H_6) ; 1.61 (m, 2H, H_5) ; 1.09 (s, 9H, H_1).

^{13}C NMR (200MHz, $CDCl_3$): δ 215.5 C_3, 142.5 C_{ar} ; 128.1 C_{ar}; 127.8 C_{ar} ; 125.7 C_{ar} ; 110.3 $C_{2'}$; 64.5 $C_{dioxolane}$; 43.9 C_2 ; 39.7 C_6, 36.2 C_4 ; 26.4 C_1, 18.1 C_5.

MS(C.I): 277($M+H^+$)

***1-(4-Isopropyl-cyclohex-1-enyl)-5-(toluene-4-sulfonyl)-pentan-3-one* (14)**



14

Compound 1**2** was prepared following the general procedure for radical addition-reduction of xanthates to olefins. The crude product was purified by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 9/1 then 8/2) to give an solide white : 76% isolated yield.

IR (Nujol, cm^{-1}): 2953 ; 2923 ; 2854 ; 1713 ; 1598 ; 1462 ; 1376 ; 1312 ; 1284 ; 1147 ; 1086.

NMR ^{1}H ($CDCl_3$, 250 MHz) : δ = 7.76 (d, J = 8.1 Hz ; 2H) ; δ = 7.34 (d, J = 8.1 Hz ; 2H) ; δ = 5.3 (s, 1H) ; δ = 3.33 (t, J = 7.6 Hz ; 2H) ; δ = 2.86 (t, J = 7.6 Hz ; 2H) ; δ = 2.50 (t, J = 7.6 Hz ; 2H) ; δ = 2.43 (s ; 3H) ; δ = 2.15 (t, J = 7.5 Hz ; 2H) ; δ = 1.5 8 – 2.05 (4H) ; δ = 1.50 – 1.36 (m, 1H) ; δ = 1.11 – 1.24 (2H) ;δ = 0.86 (2d; 6H).

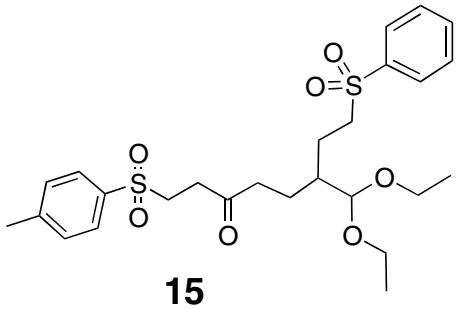
NMR ^{13}C ($CDCl_3$, 300 MHz) : 206.12 ; 144.94 ; 136.05 ; 135.69 ; 130.00 ; 128.01 ; 121.67 ; 50.66 ; 41.25 ; 40.01 ; 35.04 ; 32.23 ; 31.30 ; 29.09 ; 28.86 ; 26.31 ; 21.66 ; 19.96 ; 19.67.

Mp : 89.5 – 90.9 °C

$[\alpha]_D^{22°C}$ = 41.7° (c = 0.75, $CHCl_3$)

M.S. (ESI) : 385.0 ($[M+Na]^+$, 100 %) ; 401.1 ($[M+K]^+$, 10 %)

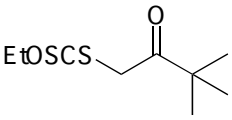
8-Benzenesulfonyl-6-diethoxymethyl-1-(toluene-4-sulfonyl)-octan-3-one **(15)**



15

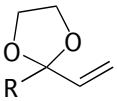
Compound **15** was obtained after purification by flash chromatography on silica gel (Eluent: Heptane/Ethyl acetate : 7/3) as a pale yellow oil (15% isolated yield)
IR (cm^{-1}): 2975 ; 2929 ; 2896 ; 1718 ; 1597 ; 1447 ; 1315 ; 1304 ; 1147 ; 1086 ;1059 ; 735 ; 690.
NMR ^{1}H ($CDCl_3$, 300 MHz) : δ = 7.88 (d, J = 7.4 Hz ; 2H) ; δ = 7.76 (d, J = 8.2 Hz ; 2H) ; δ = 7.63 (d, J = 7.2 Hz ; 1H) ; δ = 7.56 (d, J = 8.0 Hz ; 2H) ; δ = 7.35 (d, J = 8.1 Hz ; 2H) ; δ = 4.17 (d, J = 4.2 Hz ; 1H) ; δ = 3.53 – 3.64 (m, 2H) ; δ = 3.30 - 3.43 (m, 4H) ; δ = 3.15 - 3.21(2H) ; δ = 2.82 (t, J = 7.5 Hz ; 2H) ; δ = 2.48 (t, J = 7.2 Hz ; 2H) ; δ = 2.44 (s, 3H) ; δ = 1.55 - 1.82 (4H) ; δ = 1.36 – 1.49 (m, 1H) ; δ = 1.11 (m; 6H) ;
NMR ^{13}C ($CDCl_3$, 300 MHz) : δ = 205.70 ; 139.05 ; 135.87 ; 133.52 ; 129.95 ; 129.25 ; 129.16 ; 128.17 ; 127.91 ; 105.56 ; 63.37 ; 63.01 ; 54.03 ; 50.52 ; 40.02 ; 39.43 ; 35.07 ; 22.43 ; 23.04 ; 21.56 ; 15.22 ; 15.16.
M.S. (ESI) : 546.9 ($[M+Na]^+$, 100 %) ; 562.9 ($[M+K]^+$, 2 %)

Compound **4** is a known compound:



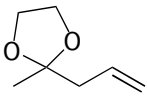
Brown, Michael D.; Gillon, David W.; Meakins, G. ; Denis; Whitham, Gordon H.; *J.Chem.Soc.Perkin Trans.1*; **1985**; 1623-1626.

Compound **5** is a known compound:



Gutzmann, Joern; Messinger, Paul; *Arch.Pharm.(Weinheim Ger.);* GE; *328*; 6; **1995**; 523-526

Compound **7** is a known compound:



B. Santiago and J.A. Sonderquist, *J.Org. Chem.* **1992**, *57*, 5844-5847.