Supplementary Material (ESI) for Organic & Biomblecular Chemistry

Supplementary information

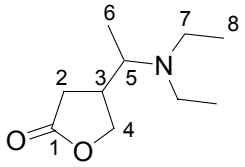
Thiocarbonyl compounds as regulating reagent in the radical addition of tertiary amines with alkenes using photoelectron transfer conditions

Dominique Harakat, Jens Pesch, Siniša Marinković and Norbert Hoffmann*

Laboratoire des Réactions Sélectives et Applications,
UMR CNRS et Université de Reims Champagne-Ardenne,
UFR Sciences, B.P. 1039,
F-51687 Reims, cedex 02, France.
Fax: +33 (0)3 26 91 31 66
Tel: +33 (0)3 26 91 31 96
*norbert.hoffmann@univ-reims.fr

NMR-Data

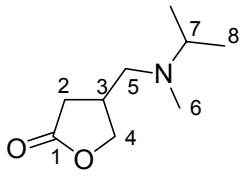
***rac*-3-(*R*/*S*)-[2-(*R*/*S*)-diethylaminoethyl]-butyrolactone:**



^{1}H-NMR (250 MHz, $CDCl_3$)**: δ = 4.27-4.36 (m, 2H, H-4), 4.04-4.11 (m, 1H, H-4), 3.84-3.90 (m, 1H, H-4), 2.37-2.62 (m, 10 H, H-5/2 × H-7), 2.03-2.28 (m, 6H, H-2/H-3), 0.93 (t, ^{3}J = 7.4 Hz, 12H, 4 × H-8), 0.85 (d, ^{3}J = 6.0 Hz, 3H, H-6), 0.82 (d, ^{3}J = 5.8 Hz, 3H, H-6) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$)*: δ = 177.6/177.3 (s, C-1), 71.5/73.0 (t, C-4), 57.0/57.9 (d, 2 × C-7), 43.1/43.0 (d, C-8'), 40.3/39.9 (d, C-8), 33.1/33.0 (d, C-2), 14.5/14.4 (q, 2 × C-8), 10.5/10.8 (q, C-6) ppm.

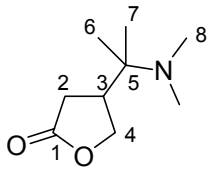
* = Diastereomer 1 + Diastereomer 2
** = Integrale calculated on two diastereoisomers

***rac*-3-(*R*/*S*)-[(isopropylmethylamino)-methylenyl]-butyrolactone:**



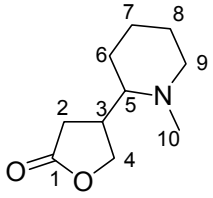
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 4.30-4.34 (m, 1H, H-4), 4.02-4.07 (m, 1H, H-4'), 2.48-2.77 (m, 3H, H-2 / H-5 / H-7), 2.17-2.42 (m, 3H, H-2' / H-5' / H-3), 2.12 (s, 3H, H-6), 0.90 (d, ^{3}J = 6.4 Hz, 3H, H-8), 0.91 (d, ^{3}J = 6.4 Hz, 3H, H-8) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 177.3 (s, C-1), 72.1 (t, C-4), 55.6 (t,C-5), 54.1 (d, C-7), 37.2 (q, C-6), 33.7 (d, C-3), 32.7 (t, C-2), 17.9 (q, C-8), 17.4 (q, C-8') ppm.

***rac*-3-(*R*/*S*)-[2-(2-dimethylamino)-propyl]-butyrolactone:**



^{1}H-NMR (250 MHz, $CDCl_3$): δ = 4.12-4.31 (m, 2H, H-4), 2.77-2.86 (m, 1H, H-3), 2.38-2.43 (m, 2H, H-4), 2.12-2.14 (m, 6H, H-8), 0.88 (d, ^{3}J = 6.5 Hz, 3H, H-6 / H-7), 0.87 (d, ^{3}J = 6.5 Hz, 3H, H-7 / H-6) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 177.4 (s, C-1), 69.8 (t, C-4), 56.8 (s,C-5), 41.6 (d, C-3), 38.2 (q, 2 × H-8), 30.3 (t, C-2), 18.3 (q, C-6/C-7), 17.8 (q, C-7/C-6) ppm.

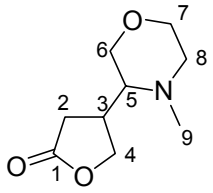
***rac*-3-(*R*/*S*)-[2-(*R*/*S*)-(1-methylpiperidyl)]-butyrolactone:**



^{1}H-NMR (250 MHz, $CDCl_3$)**: δ = 4.30-4.41 (m, 2H, H-4), 4.12 (m, 2H, H-4), 2.84-3.08 (m, 4H, H-2 / H-3), 2.00-2.67 (m, 6H, H-2 / 2 × H-9), 2.26 (s, 6H, H-10), 1.77-1.82 (m, 2H, 2 × H-5), 1.50-1.58 (m, 6H, H-6/H-7/H-8), 1.18-1.31 (m, 6H, H-6/H-7/H-8) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$)*: δ = 177.4/177.3 (s, C-1), 71.0/69.2 (t, C-4), 64.7/64.9 (d, C-5), 56.3/56.9 (t, C-9), 42.3/41.6 (q, C-10), 36.1/35.7 (d, C-3), 29.5/31.7 (d, C-2), 24.5/24.4 (t, C-8), 24.2/23.8 (t, C-6), 23.8/23.9 (q, C-7) ppm.

* = Diastereomer 1 + Diastereomer 2
** = Integrale calculated on two diastereoisomers

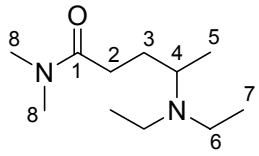
rac-3-(_R_/_S_)-[2-(_R_/_S_)-(1-methylmorpholyl)]-butyrolactone:



^{1}H-NMR (250 MHz, $CDCl_3$)**: δ = 4.37 (dd, ^{3}J = 9.4 Hz, ^{3}J = 7.9 Hz 1H, H-4), 4.12 (d, ^{3}J = 6.8 Hz, 2H, 2 × H-4'), 4.08 (dd, ^{3}J = 9.2 Hz, ^{3}J = 5.2 Hz, 1H, H-4), 3.47-3.79 (m, 4H, H-6 / H-7), 3.18-3.29 (m, 2H, H-7), 2.89-3.01 (m, 2H, H-6), 2.19-2.73 (m, 12H, H-2 / H-3, H-5 / H-8), 2.24/2.25 (s, 6H, 2 × H-9) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$)*: δ = 176.5 (s, 2 × C-1), 69.0/70.5 (t, C-4), 66.1/66.0 (d, C-6), 65.6/65.9 (t, C-7), 63.2/62.8 (d, C-5),54.5/54.0 (t,C-8), 42.6/42.3 (q, C-9), 33.6/34.0 (d, C-3), 31.1/29.6 (d, C-2) ppm.

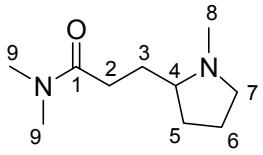
* = Diastereomer 1 + Diastereomer 2
** = Integrale calculated on two diastereoisomers

Dimethyl _rac_-4-(diethylamino)-pentanoic amide:



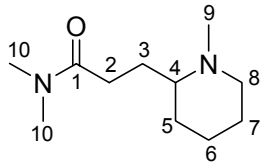
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.95 (s, 3H, H-8'), 2.86 (s, 3H, H-8), 2.62-2.74 (m, 1H, H-4), 2.46 (m, 2H, H-6'), 2.19-2.36 (m, 4H, H-2/H-6), 1.61-1.73 (m, 1H, H-3'), 1.47-1.58 (m, 1H, H-3), 0.92 (t, ^{3}J = 7.1 Hz, 6H, 2 × H-7), 0.85 (d, ^{3}J = 6.6 Hz, 3H, H-5) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 173.5 (s, C-1), 53.6 (d, C-4), 42.4 (t, 2 × C-6), 37.2 (q, C-8'), 35.3 (q, C-8), 30.4 (t, C-2), 29.3 (t, C-3), 14.3 (q, 2 × C-7), 13.7 (q, C-5) ppm.

Dimethyl _rac_-3-(_N_-methylpyrrolidin-2-yl)-propanoic amide:



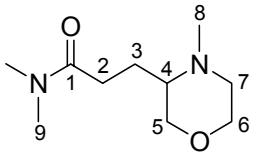
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.91-2.99 (m, 1H, H-4), 2.95 (s, 3H, H-9'), 2.88 (s, 3H, H-9), 2.26 (s, 3H, H-8), 1.32-2.40 (m, 10H, H-2/H-3/H-5/H-6/H-7) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 172.9 (s, C-1), 65.5 (d, C-4), 57.3 (t, C-7), 40.4 (q, C-8), 37.3 (q, C-9), 35.4 (t, C-9'), 30.2 (t, C-5), 29.8 (q, C-2), 28.5 (q, C-3), 21.8 (q, C-6) ppm.

Dimethyl *rac*-3-(*N*-methylpiperidin-2-yl)-propane acide dimethyl amide:



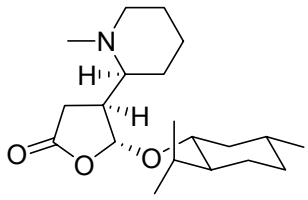
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 2.95 (s, 3H, H-10), 2.88 (s, 3H, H-10'), 2.75-2.80 (m, 1H, H-4), 2.22-2.38 (m, 2H, H-8), 2.20 (s, 3H, H-9), 1.63-2.07 (m, 5H, H-2/H-3/H-5), 1.18-1.54 (m, 5H, H-5/H-6/H-7) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 173.1 (s, C-1), 62.8 (d, C-4), 57.1 (t, C-8), 42.7 (q, C-9), 37.1 (q, C-10), 35.3 (q, C-10'), 30.3 (t, C-5), 28.1 (t, C-3), 27.8 (t, C-2), 25.6 (d, C-7), 24.3 (t, C-6) ppm.

***rac*-3-(*N*-methylmorpholin-2-yl)-propane acide dimethyl amide:**



^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.51-3.74 (m, 4H, H-5/H-6), 3.20-3.28 (m, 1H, H-5), 2.94 (s, 3H, H-9), 2.88 (s, 3H, H-9'), 2.24 (s, 3H, H-8), 1.53-2.34 (m, 4H, H-2/H-3) ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 172.3 (s, C-1), 70.4 (t, C-5), 67.0 (t, C-6), 61.7 (d, C-4), 55.4 (t, C-7), 42.7 (q, C-8), 37.1 (q, C-9), 35.5 (q, C-9'), 28.4 (t, C-2), 23.5 (t, C-3) ppm.

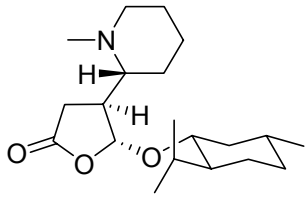
3-(*R*)-[1-methyl-2-(*S*)-piperidinyl]-5-menthyloxy-2,3,4,5-tetrahydro-furan-2-one :



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.43 (d, ^{3}J = 0;8 Hz, 1H, H-5), 3.51 (td, ^{3}J = 10.7 Hz, ^{3}J = 4.2 Hz, 1H, H-1'), 2.88 (d, ^{3}J = 11.7 Hz, 1H, H-6"b), 2.71-2.77 (m, 1H, H-4), 2.64 (dd, ^{3}J = 18.2 Hz, ^{3}J = 9.0 Hz, 1H, H-3b), 2.56 (dd, ^{3}J = 18.2 Hz, ^{3}J = 9.0 Hz, 1H, H-3a), 2.22 (s, 3H, H-7"), 2.17 (td, ^{3}J = 3.3 Hz, ^{3}J = 11.7 Hz, 1H, H-6"a), 2.06 (dsep, ^{3}J = 2.4 Hz, ^{3}J = 6.9 Hz, 1H, H-7'), 2.01-2.28 (m, 2H, H-6'eq/H-2"), 1.74-1.81 (m, 1H, H-4"b), 1.61-1.73 (m, 2H, H-3'eq/H-4'eq), 1.33-1.60 (m, 4H, H-5'/H-3"b/H-5"), 1.10-1.32 (m, 3H, H-2'/H-3"a/H-4"a), 0.74-1.07 (m, 3H, H-3'ax/H-4'ax/H-6'ax), 0.94 (d, ^{3}J = 6.5 Hz, 3H, H-10'), 0.88 (d, ^{3}J = 6.9 Hz, 3H, H-8',9'), 0.78 (d, ^{3}J = 6.9 Hz, 3H, H-8',9') ppm.
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 177.0 (s, C-2), 102.3 (d, C-5), 76.4 (d, C-1'), 63.3 (d, C-2"), 56.9 (t, C-6"), 47.8 (d, C-2'), 42.7 (q, C-7"), 42.3 (d, C-4), 39.8 (t, C-6'), 34.3 (t, C-4'),

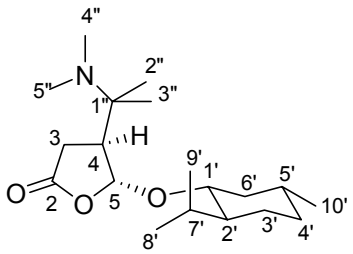
31.3 (d, C-5'), 28.2 (t, C-3), 25.4 (d, C-7'), 24.9 (t, C-5"), 24.7 (t, C-3"), 24.1 (t, C-4"), 23.0 (t, C-3'), 22.2 (q, C-10'), 20.9 (q, C-8',9'), 15.5 (q, C-8',9') ppm.

3-(*R*)-[1-methyl-2-(*R*)-piperidinyl]-5-menthyloxy-2,3,4,5-tetrahydro-furan-2-one :



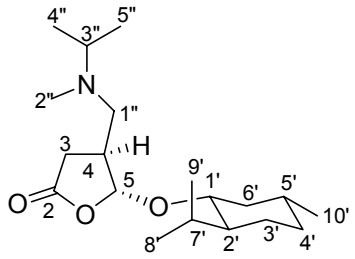
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.72 (s, 1H, H-5), 3.48 (td, ^{3}J = 10.6 Hz, ^{3}J = 4.2 Hz, 1H, H-1'), 2.86 (d, ^{3}J = 11.5 Hz, 1H, H-6"b), 2.75-2.84 (m, 2H, H-3b/H-4), 2.25 (s, 3H, H-7"), 2.21 (d, ^{3}J = 15.9 Hz, 1H, H-3a), 2.13-2.17 (m, 1H, H-6'eq), 2.11 (dd, ^{3}J = 3.9 Hz, ^{3}J = 11.5 Hz, 1H, H-6"a), 2.04 (dsep, ^{3}J = 2.3 Hz, ^{3}J = 6.9 Hz, 1H, H-7'), 1.86-1.93 (m, 1H, H-2"), 1.74-1.82 (m, 1H, H-4"b), 1.60-1.70 (m, 2H, H-3'eq/H-4'eq), 1.44-1.59 (m, 3H, H-3"b/H-5"), 1.33-1.43 (m, 1H, H-5'), 1.08-1.28 (m, 3H, H-2'/H-3"a/H-4"a), 0.74-1.05 (m, 3H, H-3'ax/H-4'ax/H-6'ax), 0.94 (d, ^{3}J = 6.5 Hz, 3H, H-10'), 0.87 (d, ^{3}J = 7.0 Hz, 3H, H-8',9'), 0.77 (d, ^{3}J = 7.0 Hz, 3H, H-8',9') ppm.
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 177.2 (s, C-2), 101.4 (d, C-5), 76.8 (d, C-1'), 64.7 (d, C-2"), 57.5 (t, C-6"), 47.8 (d, C-2'), 42.7 (q, C-7"), 41.8 (d, C-4), 39.9 (t, C-6'), 34.4 (t, C-4'), 31.3 (d, C-5'), 30.7 (t, C-3), 25.4 (d, C-7'), 25.2 (t, 2×, C-3"/C-5"), 24.1 (t, C-4"), 23.0 (t, C-3'), 22.2 (q, C-10'), 20.9 (q, C-8',9'), 15.5 (q, C-8',9') ppm.

3-(*R*)-[2-(2-*N*,*N*-dimethylamino)-propanyl]-5-menthyloxy-2,3,4,5-tetra-hydrofuran-2-one:



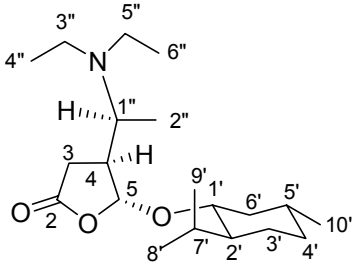
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.68 (s, 1H, H-5), 3.50 (dt, ^{3}J = 10.6 Hz, ^{3}J = 4.1 Hz, 1H, H-1'), 2.72 (dd, ^{3}J = 17.9 Hz, ^{3}J = 9.5 Hz, 1H, H-3b), 2.55 (d, ^{3}J = 9.8 Hz, 1H, H-4), 2.44 (d, ^{3}J = 17.9 Hz, H-3a), 2.20 (s, 6H, H-4"/H-5"), 1.89-2.24 (m, 2H, H-7'/H-6'eq), 1.57-1.73 (m, 2H, H-3'eq/H-4'eq), 1.12-1.46 (m, 2H, H-2'/H-5'), 0.76-1.11 (m, 3H, H-3'ax/H-4'ax/H-6'ax), 0.93 (m, 12H, H-10'/H-2",3"), 0.88 (m, 6H H-8',9'/H-2",3"), 0.78 (d, ^{3}J = 6.9 Hz, 3H, H-9',8') ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 177.4 (s, C-2), 102.3 (d, C-5), 76.8 (d, C-1'), 56.7 (s, C-1"), 48.2 (d, C-4), 47.8 (d, C-2'), 39.8 (t, C-6'), 38.2 (q, 2 × C-4"/C-5"), 34.3 (t, C-4'), 31.3 (d, C-5'), 29.8 (t, C-3), 25.4 (d, C-7'), 23.0 (t, C-3'), 22.2 (q, C-10'), 20.9 (q, C-9',8'), 18.5 (q, C-2",3"), 17.3 (q, C-2",3"), 15.5 (q, C-9',8') ppm.

3-(*R*)-(*N*-isopropyl-*N*-methylaminomethylene)-5-menthyl-oxy-2,3,4,5-tetra-hydrofuran-2-one:



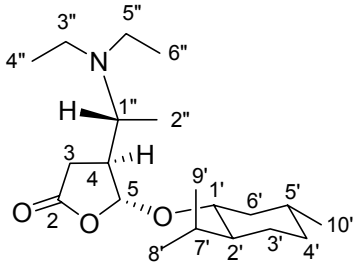
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.45 (s, 1H, H-5), 3.45 (dt, ^{3}J = 10.6 Hz, ^{3}J = 4.2 Hz, 1H, H-1'), 2.82 (sep, ^{3}J = 6.6 Hz H-3"), 2.77 (dd, ^{3}J = 18.0 Hz, ^{3}J = 8.8 Hz, 1H, H-3b), 2.14-2.51 (m, 4H, H-3a/H-4/H-1"a/H-1"b), 2.12 (s, 3H, H-2"), 1.89-2.11 (m, 2H, H-6'eq/H-7'), 1.51-1.68 (m, 2H, H-3'eq/H-4'eq), 1.10-1.44 (m, 2H, H-2'/H-5'), 0.75-1.10 (m, 3H, H-3'ax/H-4'ax/H-6'ax), 0.75-1.10 (m, 3H, H-3'ax/H-4'ax/H-6'ax), 0.99 (d, ^{3}J = 6.6Hz, 3H, H-4",5"), 0.97 (d, ^{3}J = 6.6Hz, 3H, H-4",5"), 0.93 (d, ^{3}J = 6.6Hz, 3H, H-10'), 0.88 (d, ^{3}J = 7.0 Hz, 3H, H-8',9'), 0.77 (d, ^{3}J = 6.9 Hz, 3H, H-9',8') ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 176.8 (s, C-2), 103.3 (d, C-5), 76.8 (d, C-1'), 54.3 (t, C-1"), 53.8 (d, C-3"), 47.7 (d, C-2'), 39.8 (t, C-6'), 39.7 (d, C-4), 36.5 (q, C-2"), 34.3 (t, C-4'), 31.8 (t, C-3), 31.3 (d, C-5'), 25.4 (d, C-7'), 23.0 (t, C-3'), 22.4 (q, C-10'), 20.9 (q, C-9',8'), 17.7 (q, C-4",5"), 17.3 (q, C-4",5"), 15.5 (q, C-9',8') ppm.

3-(*R*)-[1-(2-(*S*)-*N*,*N*-diethylamino)-ethyl]-5-menthyloxy-2,3,4,5-tetra-hydrofuran-2-one :



^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.92 (s, 1H, H-5), 3.50 (td, ^{3}J = 10.7 Hz, ^{3}J = 4.1 Hz, 1H, H-1'), 2.78 (dd, ^{3}J = 19 Hz, ^{3}J = 10 Hz, 1H, H-3b), 44-2.59 (m, 3H, H-1", H-3", H-5"), 2.22-2.34 (m, 3H, H-4, H-3", H-5") 2.22 (s, 3H, H-7"), 2.16 (dd, ^{3}J = 19 Hz, ^{3}J = <2 Hz, 1H, H-3a), 2.01-2.19 (m, 2H, H-6'eq, H-7'), 1.57-1.71 (m, 2H, H-4'eq, H-3'eq), 1.15-1.45 (m, 2H, H-2', H-5'), 0.76-1.05 (m, 3H, H-3'ax, H-4'ax, H-6'ax), 1.01 (t, ^{3}J = 7.4 Hz, H-4",6"), 0.97 (t, ^{3}J = 7.4 Hz, H-4",6"), 0.93 (d, 3H, ^{3}J = 6.6 Hz, H-10'), 0.90 (d, ^{3}J = 6.6 Hz, H2"), 0.84 (d, ^{3}J = 7.0 Hz, 3H, H-8',9'), 0.78 (d, ^{3}J = 7.0 Hz, 3H, H-8',9') ppm.
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 177.0 (s, C-2), 103.5 (d, C-5), 76.5 (d, C-1'), 55.0 (d, C-1"), 47.8 (d, C-2'), 45.4 (d, C-4), 43.1 (t, C-3"5"), 40.0 (t, C-6'), 34.3 (t, C-4'), 31.6 (t, C-3), 31.3 (d, C-5'), 25.4 (d, C-7'), 23.0 (t, C-3'), 22.3 (q, C-10'), 20.9 (q, C-8',9'), 15.5 (q, C-8',9'), 14.4 (q, C-4", C-6"), 10.2 (q, C-2") ppm.

3-(*R*)-[1-(2-(*R*)-*N*,*N*-diethylamino)-ethyl]-5-menthyloxy-2,3,4,5-tetra-hydrofuran-2-one :



^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.38 (d, ^{3}J = 1.5 Hz, 1H, H-5), 3.52 (td, ^{3}J = 10.8 Hz, ^{3}J = 4.1 Hz, 1H, H-1'), 2.87 (dd, ^{3}J = 19 Hz, ^{3}J = 4.3 Hz, 1H, H-3b), 2.63 (dd, 1H, ^{3}J = 19 Hz, ^{3}J = 9 Hz, H-3a), 2.44-2.59 (m, 3H, H-1", H-3", H-5"), 2.22-2.34 (m, 3H, H-4, H-3", H-5") 2.01-2.19 (m, 2H, H-6'eq, H-7'), 1.57-1.71 (m, 2H, H-4'eq, H-3'eq), 1.15-1.45 (m, 2H, H-2', H-5'), 0.76-1.05 (m, 3H, H-3'ax, H-4'ax, H-6'ax), 1.01 (t, ^{3}J = 7.4 Hz, H-4",6"), 0.99 (d, ^{3}J = 6.4 Hz, H2"), 0.97 (t, ^{3}J = 7.4 Hz, H-4",6"), 0.93 (d, 3H, ^{3}J = 6.6 Hz, H-10'), 0.88 (d, ^{3}J = 7.0 Hz, 3H, H-8',9'), 0.78 (d, ^{3}J = 7.0 Hz, 3H, H-8',9') ppm.

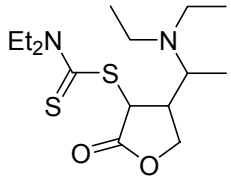
^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 176.8 (s, C-2), 103.3 (d, C-5), 76.7 (d, C-1'), 54.9 (d, C-1"), 47.8 (d, C-2'), 46.6 (d, C-4), 42.9 (t, C-3"5"), 49.7 (t, C-6'), 34.3 (t, C-4'), 31.5 (t, C-3), 31.3 (d, C-5'), 25.3 (d, C-7'), 23.0 (t, C-3'), 22.3 (q, C-10'), 20.9 (q, C-8',9'), 15.6 (q, C-8',9'), 14.3 (q, C-4", C-6"), 10.7 (q, C-2") ppm.

Electropspray mass spectroscopy of compounds 16 and 17

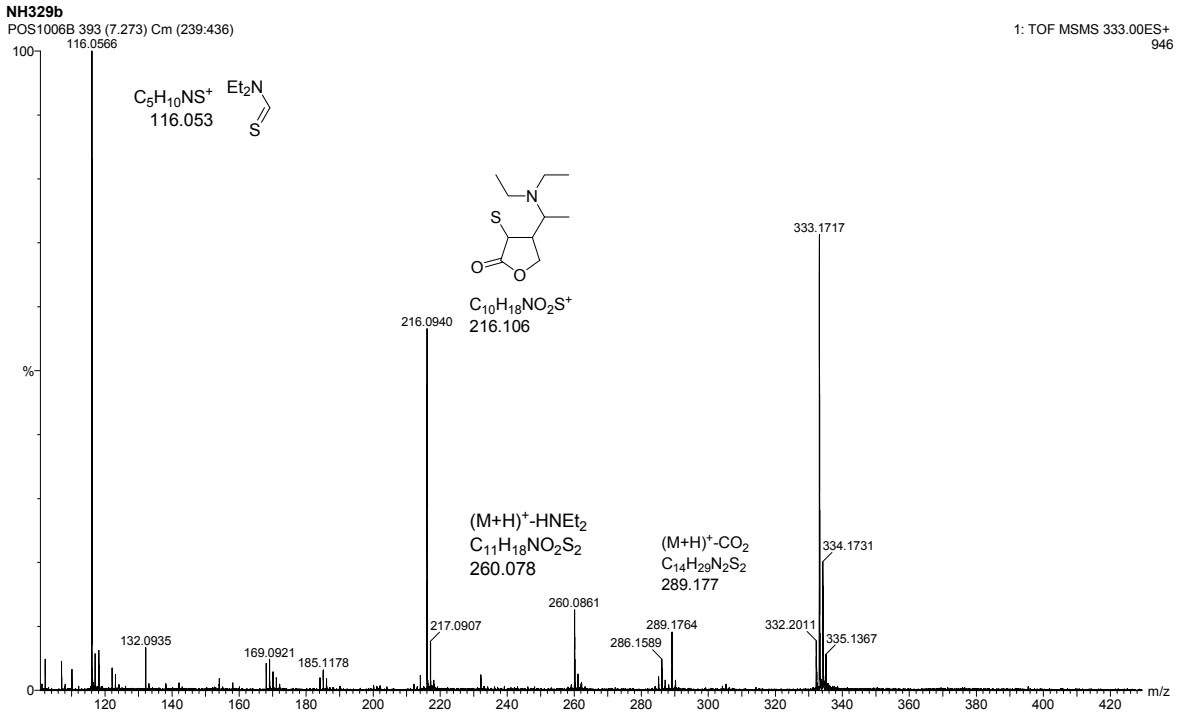
All measurements were performed in the positive mode.

Sample preparation: Solutions containing 30 mg (0.44 mmol) of 2,4-dihydrofuran-2-one **1**, 9 mg (0.04 mmol) of 4,4'-dimethoxybenzophenone, 360 mg of the thiocarbamate **3** and either 90 mg (0.9 mmol, 6 10^{-2} mol/L), 356 mg (3. 52 mmol, 23.5 10^{-2} mol/L) or 20 mg (0.20 mmol, 1.33 10^{-2} mol/L) triethylamine in acetonitrile (15 ml) were irradiated (Rayonet reactor) for 10 min in pyrex tubes (Ø = 1 cm) at λ = 350 nm.

rac-Diethyl-dithiocarbamic acid 4-(1-diethylamino-ethyl)-2-oxo-tetrahydro-furan-3-yl ester 16

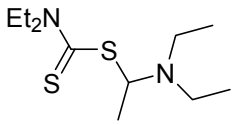


HMRS calculated for $C_{15}H_{29}N_2O_2S_2$ $(M+H)^+$: 333.1670, found: 333.1675

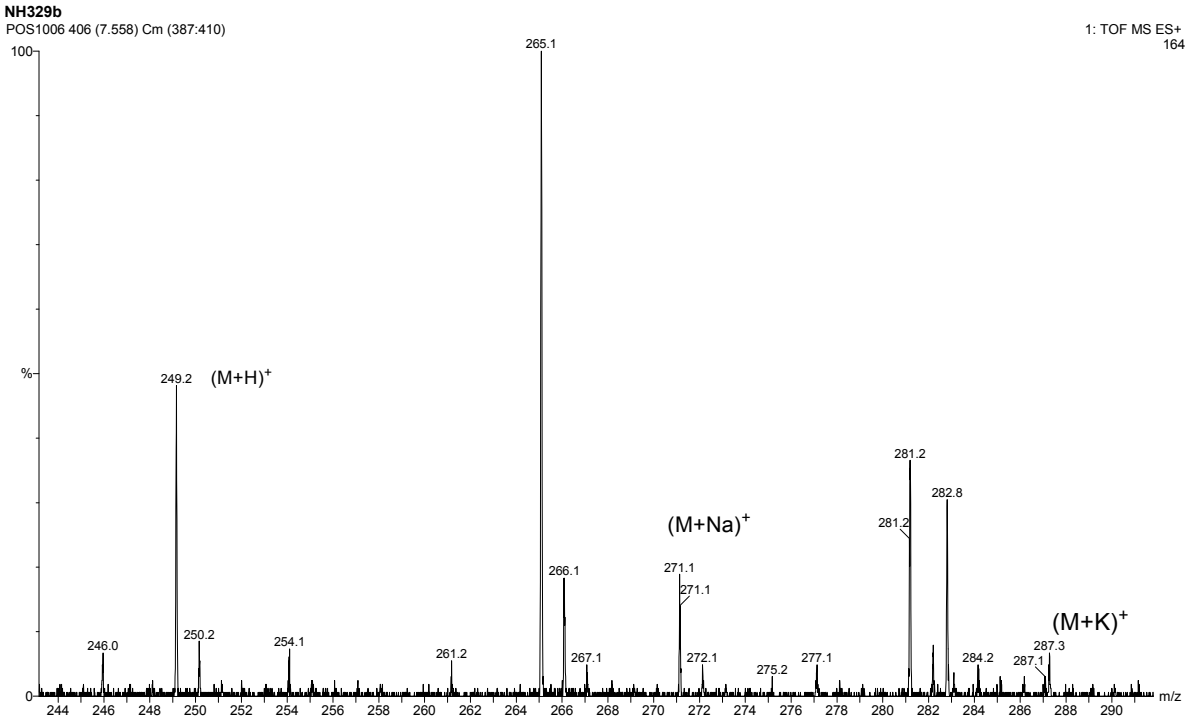


Fragmentation of (**16**+H)$^+$

rac-Diethyl-dithiocarbamic acid 1-dethylamino-ethyl ester 17



HMRS calculated for $C_{11}H_{24}N_2NaS_2$ $(M+Na)^+$: 271.1279, found: 271.1284



Electrospray mass spectrum of **17.**