



## Supporting Information

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## A Novel Tin-Free Procedure for Alkyl Radical Reactions

*Luisa Benati, Rino Leardini, Matteo Minozzi,\* Daniele Nanni,\* Rosanna Scialpi,  
Piero Spagnolo, Samantha Strazzari, and Giuseppe Zanardi*

Dipartimento di Chimica Organica "A. Mangini"

Università di Bologna

Viale Risorgimento 4, I-40136 Bologna (Italy)

Fax: +39 051 2093654

E-mail: nanni@ms.fci.unibo.it

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**General Procedures.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in deuteriochloroform on 200, 300, or 400 MHz instruments using tetramethylsilane as an internal standard. EI mass spectra and high-resolution mass spectra (HRMS) were obtained with 70 eV ionization. GC-MS analyses were run on a chromatograph fitted with a 25 m capillary column (5% phenyl methyl silicone) and a quadrupolar detector working at 70 eV. IR spectra were recorded neat or in chloroform solution. Column chromatography was carried out on ICN silica gel (70-230 mesh or 230-400 mesh) by gradual elution with mixtures of *n*-hexane and diethyl ether or dichloromethane and final elution with 100% diethyl ether or dichloromethane. Organic phases were dried over magnesium sulfate. Previously reported reaction products were identified by spectral comparison.

**Starting Materials.** 1-Bromoundecane, 2-bromodecane, 1,2:3,4-di-*O*-iso-propylidene-D-galactopyranose, 1-thio- $\beta$ -D-glucose tetraacetate (**4**), methyl thioglycolate (**7a**), 3-bromo-dihydro-2(3*H*)-furanone, *n*-butyl vinyl ether (**6A**), vinyl acetate (**6B**), (*iso*-propenyloxy)-(trimethyl)silane (**6C**), trimethoxy(vinyl)silane (**6D**), *tert*-butyl isonitrile, *n*-butyl isonitrile, potassium thioacetate, and 2,2'-azobis(*iso*-butyronitrile) (AIBN) were commercially available.

4-Chlorophenyl isonitrile,<sup>[1]</sup> 1-mercaptadamantane,<sup>[2]</sup> mercaptoacetonitrile (**7b**),<sup>[3]</sup> and 6-bromo-1,1-diphenyl-1-hexene<sup>[4]</sup> were prepared according to the literature.

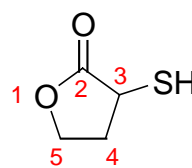
**1-Undecanethiol.** A solution of 1-bromoundecane (5 mmol) and potassium thioacetate (6 mmol) in acetone (30 mL) was kept overnight at r.t. under stirring. The solvent was then evaporated and the residue poured into water and extracted with dichloromethane. The organic phase was dried and the solvent was removed to give *S*-undecyl ethanethioate<sup>[5]</sup> (95%); <sup>1</sup>H NMR (200 MHz)  $\delta$  0.90 (3 H, t, *J* = 6.1 Hz), 1.20-1.40 (16 H, m), 1.48-1.63 (2 H, m), 2.35 (3 H, s), 2.85 (2 H, t, *J* = 7.2 Hz). The thioester was directly reduced to the title thiol. A 1 M LAH solution in THF (1 eq.) was added dropwise at 0 °C to a stirred solution of thioester in anhydrous THF (100 mL). The resulting solution was stirred at 0 °C for 30 minutes and then cautiously quenched with water. THF was evaporated and the remaining aqueous phase was extracted with dichloromethane. The organic phase was dried and the solvent was evaporated to give 1-undecanethiol<sup>[6]</sup> in practically quantitative yield; <sup>1</sup>H NMR (300 MHz)  $\delta$  0.90 (3 H, t, *J* = 6.1 Hz), 1.20-1.35 (16 H, m), 1.33 (1 H, t, *J* = 7.7 Hz), 1.60 (2 H, quint, *J* = 7.5 Hz), 2.52 (2 H, td, *J*<sub>t</sub> = *J*<sub>d</sub> = 7.6 Hz); <sup>13</sup>C NMR (75 MHz)  $\delta$  14.79, 23.37, 25.34, 29.07, 29.77, 30.02, 30.21, 30.28 (2 CH<sub>2</sub>), 32.59, 34.75.

**2-Decanethiol.** Following the procedure described above for 1-undecanethiol, 2-bromodecane and potassium thioacetate gave *S*-(1-methylnonyl) ethanethioate<sup>[7]</sup> (96%); <sup>1</sup>H NMR (400 MHz)  $\delta$  0.85 (3 H, t, *J* = 6.9 Hz), 1.23-1.31 (15 H, m), 1.50-1.57 (2 H, m), 2.30 (3 H, s), 3.54 (1 H, td, *J*<sub>t</sub> = *J*<sub>d</sub> = 6.9 Hz); <sup>13</sup>C NMR (100 MHz)  $\delta$  14.77, 22.03, 23.34, 27.67, 29.91, 30.06, 30.14, 31.44, 32.53, 37.09, 40.27, 196.78 (C); IR  $\nu_{\text{max}}$  1692.2, 2855.7, 2926.5, 2957.8 cm<sup>-1</sup>; GC-MS *m/z* 173 (M<sup>+</sup> – 43, 11), 140 (23), 111 (7), 97 (11), 85 (11), 71 (21), 57 (28), 43 (100). Following the procedure described above, the thioester was reduced with LAH to 2-decanethiol<sup>[8]</sup> (>98 %); <sup>1</sup>H NMR (400 MHz)  $\delta$  0.88 (3 H, t, *J* = 6.6 Hz), 1.22-1.59 (17 H, m), 1.32 (1 H, d, *J* = 6.9 Hz), 2.91 (1 H, sept, *J* = 6.6 Hz); GC-MS *m/z* (rel. inten.) 174 (M<sup>+</sup>, 16), 140 (41), 111 (23), 97 (46), 85 (50), 83 (46), 70 (70), 61 (73), 57 (80), 55 (84), 43 (100), 41 (93).

**6-Thio-1,2:3,4-di-*O*-iso-propylidene-D-galactopyranose (2).** A pyridine (10 mL) solution of 1,2:3,4-di-*O*-iso-propylidene-D-galactopyranose (1.30 g, 5 mmol) and tosyl chloride (1.0 g, 5.25 mmol) was stirred at r.t. under nitrogen for 1 h and then kept overnight at 0-5 °C. The final mixture was filtered, the filtrate was poured into water and extracted with diethyl ether. The organic phase was washed with diluted hydrochloric acid and brine; it was finally dried and the solvent was evaporated to give quantitatively the *6*-tosylate of the starting sugar;<sup>[9]</sup> <sup>1</sup>H NMR (400 MHz)  $\delta$  1.28 (3 H, s), 1.31 (3 H, s), 1.34 (3 H, s), 1.50 (3 H, s), 2.44 (3 H, s), 4.04 (1 H, ddd,  $J_1 = 7.3$  Hz,  $J_2 = 5.7$  Hz,  $J_3 = 1.8$  Hz), 4.10 (1 H, dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.5$  Hz), 4.20 (1 H, dd,  $J_1 = 10.1$  Hz,  $J_2 = 5.5$  Hz), 4.20 (1 H, dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.9$  Hz), 4.29 (1 H, dd,  $J_1 = 5.0$  Hz,  $J_2 = 2.5$  Hz), 4.59 (1 H, dd,  $J_1 = 8.0$  Hz,  $J_2 = 2.5$  Hz), 5.45 (1 H, d,  $J = 5.0$  Hz), 7.33 (2 H, A part of AA'BB',  $J = 8.3$  Hz), 7.80 (2 H, B part of AA'BB',  $J = 8.3$  Hz); <sup>13</sup>C NMR (100 MHz)  $\delta$  22.18, 24.92, 25.48, 26.38, 26.54, 66.46, 68.80, 70.94, 70.99, 71.09, 96.70, 109.49 (C), 110.13 (C), 128.68, 130.33, 133.41 (C), 145.35 (C). The crude tosylate was treated with potassium thioacetate (1.1 eq) in DMF (25 mL) at 50 °C for 10 h. The final mixture was poured into water and extracted with dichloromethane; the organic phase was dried and the solvent evaporated to give the corresponding *6*-*S*-thioester in 85% yield;<sup>[10]</sup> IR  $\nu_{\max}$  1692.5 (O=C-S), 1354.9, 1130.6, 959.7 cm<sup>-1</sup>; GC-MS  $m/z$  (rel. inten.) 201 (14), 143 (2), 113 (2), 100 (2), 85 (7), 71 (2), 58 (23), 43 (100). The thioester was directly reduced to the title thiol **2**. A 1 M LAH solution in THF (1 eq.) was added dropwise at 0 °C to a stirred solution of thioester in anhydrous THF (100 mL). The resulting solution was stirred at 0 °C for 30 minutes and then cautiously quenched with water. THF was evaporated and the remaining aqueous phase was extracted with dichloromethane. The organic phase was dried and the solvent was evaporated to give thiol **2** in practically quantitative yield;<sup>[11]</sup> <sup>1</sup>H NMR (400 MHz)  $\delta$  1.34 (3 H, s), 1.35 (3 H, s), 1.44 (3 H, s), 1.55 (3 H, s), 1.62 (1 H, dd,  $J_1 = 9.7$  Hz,  $J_2 = 7.5$  Hz), 2.64-2.81 (2 H, m), 3.79 (1 H, td,  $J_t = 7.0$  Hz,  $J_d = 1.8$  Hz), 4.32 (1 H, dd,  $J_1 = 5.0$  Hz,  $J_2 = 2.5$  Hz), 4.35 (1 H, dd,  $J_1 = 7.9$  Hz,  $J_2 = 1.9$  Hz), 4.62 (1 H, dd,  $J_1 = 7.9$  Hz,  $J_2 = 2.5$  Hz), 5.53 (1 H, d,  $J = 4.8$  Hz); <sup>13</sup>C NMR (100 MHz)  $\delta$  25.08, 25.14, 25.60, 26.63, 26.71, 70.54, 71.22, 71.56, 71.95, 97.25, 109.34 (C), 110.00 (C); GC-MS  $m/z$  (rel. inten.) 261 ( $M^+ - 15$ , 27), 218 (5), 201 (11), 185 (5), 171 (7), 143 (23), 113 (36), 100 (39), 85 (50), 59 (57), 43 (100).

**3-Sulfanyldihydro-2(3*H*)-furanone (7c).** According to a reported procedure,<sup>[12]</sup> *S*-(2-oxotetrahydro-3-furanyl) ethanethioate was prepared from 3-bromodihydro-2(3*H*)-furanone in nearly quantitative yield; <sup>1</sup>H NMR (400 MHz)  $\delta$  2.30 (1 H, m), 2.41 (3 H, s), 2.77 (1 H,

dddd,  $J_1 = 12.6$  Hz,  $J_2 = 9.3$  Hz,  $J_3 = 6.9$  Hz,  $J_4 = 3.5$  Hz), 4.25 (1 H, dd,  $J_1 = J_2 = 9.5$  Hz), 4.34 (1 H, ddd,  $J_1 = 9.1$  Hz,  $J_2 = 8.9$  Hz,  $J_3 = 6.9$  Hz), 4.47 (1 H, ddd,  $J_1 = J_2 = 8.9$  Hz,  $J_3 = 3.5$  Hz);  $^{13}\text{C}$  NMR  $\delta$  30.87, 30.94, 40.94, 67.32, 175.00 (C), 193.98 (C); GC-MS  $m/z$  160 ( $\text{M}^+$ , 4), 118 (77), 86 (5), 72 (11), 58 (7), 43 (100). A benzene (10 mL) solution of the thioester (30 mmol) and *p*-toluidine (30 mmol) was refluxed for 3 h. Light petroleum was added to the final mixture to precipitate the amide side-product. The mixture was filtered and the filtrate evaporated. The residue was poured into 5% hydrochloric acid and extracted with dichloromethane. The organic phase was dried, the solvent was evaporated, and the residue chromatographed (light petroleum/diethyl ether 95:5 v/v) to afford thiol **7c**<sup>[12]</sup> (40%);  $^1\text{H}$  NMR (400 MHz)  $\delta$  2.20 (1 H, dddd,  $J_1 = 13.5$  Hz,  $J_2 = 7.4$  Hz,  $J_3 = 6.9$  Hz,  $J_4 = 6.6$  Hz, **H4**), 2.36 (1 H d,  $J = 5.2$  Hz, **SH**), 2.73 (1 H, dddd,  $J_1 = 13.2$  Hz,  $J_2 = 8.5$  Hz,  $J_3 = 7.2$  Hz,  $J_4 = 5.7$  Hz, **H4**), 3.75 (1 H, ddd,  $J_1 = 8.3$  Hz,  $J_2 = 7.0$  Hz,  $J_3 = 5.1$  Hz, **H3**), 4.33 (1 H, ddd,  $J_1 = 9.1$  Hz,  $J_2 = 7.3$  Hz,  $J_3 = 6.6$  Hz, **H5**), 4.47 (1 H, ddd,  $J_1 = 9.1$  Hz,  $J_2 = 7.5$  Hz,  $J_3 = 5.7$  Hz, **H5**);  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  32.36 (**C4**), 35.18 (**C3**), 66.97 (**C5**), 177.09 (**C2**); IR  $\nu_{\text{max}}$  1023.5, 1163.7, 1207.1, 1374.1, 1450.6, 1769, 2361.0, 2557.0  $\text{cm}^{-1}$ ; GC-MS  $m/z$  (rel. inten.) 118 ( $\text{M}^+$ , 33), 41 (100).



**6,6-Diphenyl-5-hexene-1-thiol (14).** An ethanol (10 mL) solution of thiourea (0.38 g, 5 mmol) and 6-bromo-1,1-diphenyl-1-hexene (1.57 g, 5 mmol) was refluxed for 6 h. After cooling, the solvent was evaporated to give the solid isothiuronium salt, which was slowly added under stirring to an aqueous (10 mL) NaOH (0.30 g, 7.5 mmol) solution kept at 0 °C. The resulting mixture was stirred for 1 h at 0 °C, then slowly brought to acid pH with 5% hydrochloric acid, and finally extracted with dichloromethane. The organic phase was dried, the solvent evaporated, and the residue chromatographed (light petroleum/diethyl ether 95:5 v/v) to afford thiol **14** (70%);  $^1\text{H}$  NMR (300 MHz)  $\delta$  1.23 (1 H, t,  $J = 7.4$  Hz), 1.42-1.62 (4 H, m), 2.08 (2 H, q,  $J = 7.4$  Hz), 2.39 (2 H, q,  $J = 7.1$  Hz), 6.03 (1 H, t,  $J = 7.4$  Hz), 7.10-7.35 (10 H, m);  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  24.96, 29.12, 29.65, 34.07, 127.41, 127.48, 127.72, 128.30, 128.74, 129.87, 130.41, 140.68 (C), 142.56 (C), 143.17 (C); IR  $\nu_{\text{max}}$  (neat) 2848.4, 2820.2, 1492.9, 1422.3  $\text{cm}^{-1}$ ; MS  $m/z$  (rel. inten.) 268 ( $\text{M}^+$ , 12), 193 (36), 191 (19), 178 (36), 167 (33), 165 (39), 115 (72), 101 (100), 91 (55);  $\text{C}_{18}\text{H}_{20}\text{S}$  requires: C, 80.54; H, 7.51; found: C, 80.76; H, 7.53; HRMS calcd. for  $\text{C}_{18}\text{H}_{20}\text{S}$ : 268.1286, found: 268.1290.

**General Procedure for Radical Reactions of Thiols with *tert*-Butyl Isonitrile.** A toluene (10 mL) solution of thiol (1 mmol) and AIBN (0.1 mmol) was added by a syringe pump in 1 h under nitrogen to a stirred toluene (10 mL) solution of *tert*-butyl isonitrile (1.1 mmol) kept at 80 °C. For the addition reactions (thiols **7a-c**) the latter solution contained the alkene (10 mmol) as well. (Only for the reaction of thiol **7c** with alkene **6D** the solution of the thiol was added in 2 h.) The resulting mixture was stirred at 80 °C for an additional hour. The solvent was evaporated off in vacuo together with the side-product (*tert*-butyl isothiocyanate) and residual traces of isonitrile (and excess of alkene). The crude residue was quantified by <sup>1</sup>H NMR analysis and eventually chromatographed to further purify the product.<sup>[13]</sup> Acetaldehyde diethyl acetale was used as an internal standard for NMR quantification, except for product **8Cc**, for which 1,3,5-tribromobenzene was used. The defunctionalization reactions (alkanethiols and thiol-sugars **2** and **4**) were practically quantitative; the yields of the addition reactions are reported in Table 1.

The reactions at r.t. were carried out according to the same procedure, but replacing AIBN with triethylborane (0.1 mmol for alkanethiols, 5 mmol for **2** and **4**). With alkanethiols the reaction times and results were strictly comparable to those obtained at 80 °C. With thiols **2** and **4** the reagents required to be kept under stirring overnight; the yields were 95% and 80% for desulfurated sugars **3** and **5**, respectively. The characterization of all reaction products is reported below.

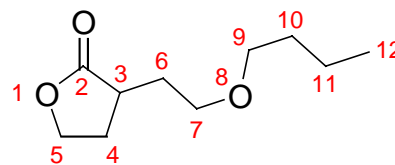
*6-Deoxy-1,2:3,4-di-O-iso-propylidene-D-galactopyranose (3).*<sup>[14]</sup> <sup>1</sup>H NMR (400 MHz) δ 1.26 (3 H, d, *J* = 6.6 Hz), 1.33 (3 H, s), 1.36 (3 H, s), 1.47 (3 H, s), 1.53 (3 H, s), 3.92 (1 H, qd, *J<sub>q</sub>* = 6.6 Hz, *J<sub>d</sub>* = 1.8 Hz), 4.08 (1 H, dd, *J<sub>1</sub>* = 7.8 Hz, *J<sub>2</sub>* = 2.0 Hz), 4.29 (1 H, dd, *J<sub>1</sub>* = 5.1 Hz, *J<sub>2</sub>* = 2.3 Hz), 4.59 (1 H, dd, *J<sub>1</sub>* = 7.8 Hz, *J<sub>2</sub>* = 2.3 Hz), 5.52 (1 H, d, *J* = 5.1 Hz); <sup>13</sup>C NMR (100 MHz) δ 15.88, 24.39, 24.87, 26.00 (2 Me), 63.43, 70.32, 70.91, 73.50, 96.52, 108.19 (C), 108.90 (C).

*1-Deoxy-β-D-glucose tetraacetate (5).*<sup>[15]</sup> <sup>1</sup>H NMR (400 MHz) δ 2.03 (3 H, s), 2.04 (6 H, br s), 2.09 (3 H, s), 3.31 (1 H, dd, *J<sub>1</sub>* = *J<sub>2</sub>* = 10.7 Hz), 3.60 (1 H, ddd, *J<sub>1</sub>* = 10.0 Hz, *J<sub>2</sub>* = 4.8 Hz, *J<sub>3</sub>* = 2.3 Hz), 4.11-4.24 (3 H, m), 4.97-5.07 (2 H, m), 5.20 (1 H, dd, *J<sub>1</sub>* = *J<sub>2</sub>* = 9.5 Hz); <sup>13</sup>C NMR (100 MHz) δ 20.57, 20.64 (2 Me), 20.69, 62.17 (CH<sub>2</sub>), 66.83 (CH<sub>2</sub>), 68.37, 68.91, 73.67, 76.41, 169.49 (C), 169.73 (C), 170.30 (C), 170.63 (C).

*Methyl 4-butoxybutanoate (8Aa)*.<sup>[16]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  0.85-0.92 (3 H, m), 1.29-1.59 (4 H, m), 2.39 (2 H, t,  $J$  = 7.0 Hz), 2.89 (2 H, m), 3.37 (2 H, t,  $J$  = 6.0 Hz), 3.42 (2 H, t,  $J$  = 6.8 Hz), 3.63 (3 H, s,); IR  $\nu_{\max}$  (neat) 1738.0 cm<sup>-1</sup>; GC-MS  $m/z$  (rel. inten.) 117 ( $M^+$  – 57, 28), 101 (42), 87 (60), 85 (69), 74 (98), 59 (97), 57 (100), 45 (50), 43 (25), 41 (47).

*4-Butoxybutanenitrile (8Ab)*.<sup>[17]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  0.92 (3 H, m), 1.24-1.63 (4 H, m), 1.90 (2 H, m), 2.47 (2 H, t,  $J$  = 7.0 Hz), 3.43 (2 H, t,  $J$  = 6.5 Hz), 3.51 (2 H, t,  $J$  = 5.8 Hz); <sup>13</sup>C NMR (50 MHz)  $\delta$  14.51, 14.77, 19.94, 26.47, 32.32, 68.60, 71.59, 120.20 (C); GC-MS  $m/z$  (rel. inten.) 99 ( $M^+$  – 42, 32), 98 (32), 68 (100), 57 (48), 41 (45); C<sub>8</sub>H<sub>15</sub>NO requires: C, 68.04; H, 10.71; N, 9.92; found: C, 68.24; H, 10.74; N, 9.89.

*3-(2-Butoxyethyl)dihydro-2(3H)-furanone (8Ac)*. <sup>1</sup>H NMR (400 MHz)  $\delta$  0.85 (3 H, t,  $J$  = 7.3 Hz, **H12**), 1.23-1.36 (2 H, m, **H11**), 1.44-1.51 (2 H, m, **H10**), 1.62 (1 H, dddd,  $J_1$  = 14.0 Hz,  $J_2$  = 8.7 Hz,  $J_3$  = 6.4 Hz,  $J_4$  = 5.2 Hz, **H6**), 1.94 (1 H, dddd,  $J_1$  = 12.4 Hz,  $J_2$  =  $J_3$  = 10.4 Hz,  $J_4$  = 8.6 Hz, **H4**), 2.09 (1 H, dddd,  $J_1$  = 14.0 Hz,  $J_2$  = 7.0 Hz,  $J_3$  =  $J_4$  = 5.2 Hz, **H6**), 2.37 (1 H, dddd,  $J_1$  = 12.7 Hz,  $J_2$  = 9.0 Hz,  $J_3$  = 6.6 Hz,  $J_4$  = 2.6 Hz, **H4**), 2.62 (1 H, dddd,  $J_1$  = 10.3 Hz,  $J_2$  =  $J_3$  = 8.6 Hz,  $J_4$  = 4.9 Hz, **H3**), 3.35 (2 H, td,  $J_t$  = 6.6 Hz,  $J_d$  = 1.9 Hz, **H9**), 3.41-3.53 (2 H, m, **H7**), 4.12 (1 H, ddd,  $J_1$  = 9.9 Hz,  $J_2$  = 9.0 Hz,  $J_3$  = 6.6 Hz, **H5**), 4.28 (1 H, ddd,  $J_1$  =  $J_2$  = 8.8 Hz,  $J_3$  = 2.7 Hz, **H5**); <sup>13</sup>C NMR (100 MHz)  $\delta$  14.39 (**C12**), 19.85 (**C11**), 29.43 (**C4**), 30.87 (**C6**), 32.29 (**C10**), 37.31 (**C3**), 67.12 (**C5**), 68.67 (**C7**), 71.23 (**C9**), 180.07 (**C2**); GC-MS  $m/z$  (rel. inten.) 129 ( $M^+$  – 57, 14), 113 (41), 101 (57), 86 (100), 57 (68), 41 (61); C<sub>10</sub>H<sub>18</sub>O<sub>3</sub> requires: C, 64.49; H, 9.74; found: C, 64.70; H, 9.72.



*Methyl 4-(acetyloxy)butanoate (8Ba)*.<sup>[18]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  1.88-2.10 (2 H, m), 2.05 (3 H, s), 2.40 (2 H, t,  $J$  = 8.6 Hz), 3.68 (3 H, s), 4.10 (2 H, t,  $J$  = 6.5 Hz); IR  $\nu_{\max}$  (neat) 1739.3, 1240.7 cm<sup>-1</sup>; GC-MS  $m/z$  (rel. inten.) 129 ( $M^+$  – 31, 5), 117 (18), 100 (32), 87 (46), 85 (30), 43 (100).

*3-Cyanopropyl acetate (8Bb)*.<sup>[19]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  2.08 (3 H, s), 2.10 (2 H, m), 2.49 (2 H, t,  $J$  = 7.2 Hz), 4.18 (2 H, t,  $J$  = 5.8 Hz); <sup>13</sup>C NMR (50 MHz)  $\delta$  14.29, 20.86, 24.90, 62.29, 119.17 (C), 170.77 (C); GC-MS  $m/z$  (rel. inten.) 112 ( $M^+$  – 15, 2), 97 (7), 68 (6), 67 (13), 43 (100); C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> requires: C, 56.68; H, 7.13; N, 11.02; found: C, 56.75; H, 7.11; N, 11.06.



*2-(2-Oxotetrahydro-3-furanyl)ethyl acetate (8Bc)*.<sup>[20]</sup> <sup>1</sup>H NMR (400 MHz)  $\delta$  1.78 (1 H, dddd,  $J_1 = 14.6$  Hz,  $J_2 = 9.0$  Hz,  $J_3 = 6.3$  Hz,  $J_4 = 6.0$  Hz), 2.00 (1 H, dddd,  $J_1 = 10.8$  Hz,  $J_2 = 10.3$  Hz,  $J_3 = 2.4$  Hz,  $J_4 = 1.8$  Hz), 2.06 (3 H, s), 2.25 (1 H, dddd,  $J_1 = 13.0$  Hz,  $J_2 = 6.9$  Hz,  $J_3 = 6.8$  Hz,  $J_4 = 4.9$  Hz), 2.46 (1 H, dddd,  $J_1 = 12.6$  Hz,  $J_2 = 9.0$  Hz,  $J_3 = 6.5$  Hz,  $J_4 = 2.4$  Hz), 2.65 (1 H, dddd,  $J_1 = 10.8$  Hz,  $J_2 = J_3 = 8.9$  Hz,  $J_4 = 4.9$  Hz), 4.18-4.27 (3 H, m), 4.38 (1 H, ddd,  $J_1 = 8.9$  Hz,  $J_2 = J_3 = 2.4$  Hz); <sup>13</sup>C NMR (100 MHz)  $\delta$  21.56, 29.43 (CH<sub>2</sub>), 30.15 (CH<sub>2</sub>), 37.34, 62.71 (CH<sub>2</sub>), 67.20 (CH<sub>2</sub>), 171.63 (C), 179.43 (C); GC-MS  $m/z$  (rel. inten.) 129 ( $M^+ - 43$ , 18), 112 (18), 100 (30), 86 (100), 67 (43), 55 (21), 43 (93); C<sub>8</sub>H<sub>12</sub>O<sub>4</sub> requires: C, 55.81; H, 7.02; found: C, 55.95; H, 7.04.

*Methyl 4-[(trimethylsilyl)oxy]pentanoate (8Ca)*.<sup>[21]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  0.10 (9 H, s), 1.16 (3 H, d,  $J = 6.3$  Hz), 1.65-1.80 (2 H, m), 2.38 (2 H, td,  $J_t = 7.2$  Hz,  $J_d = 2.4$  Hz), 3.67 (3 H, s), 3.83 (1 H, qt,  $J_q = 6.3$  Hz,  $J_t = 1.5$  Hz); <sup>13</sup>C NMR (50 MHz)  $\delta$  0.82, 24.47, 31.05, 34.86, 52.17, 68.07, 162.14 (C); IR  $\nu_{\max}$  (neat) 2961.5, 1741.8, 1260.9, 1091.5, 1017.3, 840.7 cm<sup>-1</sup>; GC-MS  $m/z$  (rel. inten.) 189 ( $M^+ - 15$ , 21), 157 (28), 117 (46), 89 (68), 75 (35), 73 (100), 59 (11); ca. 20% of the product was recovered after column chromatography and was subjected to elemental analysis; C<sub>9</sub>H<sub>20</sub>O<sub>3</sub>Si requires: C, 52.90; H, 9.87; found: C, 53.12; H, 9.84.

*4-[(Trimethylsilyl)oxy]pentanenitrile (8Cb)*.<sup>[22]</sup> <sup>1</sup>H NMR (300 MHz)  $\delta$  0.08 (9 H, s), 1.12 (3 H, d,  $J = 6.2$  Hz), 1.56-1.74 (2 H, m), 2.33 (2 H, t,  $J = 7.2$  Hz), 3.8-3.9 (1 H, m); GC-MS  $m/z$  (rel. inten.) 156 ( $M^+ - 15$ , 89), 117 (28), 75 (100), 73 (79).

*3-{2-[(Trimethylsilyl)oxy]propyl}dihydro-2(3H)-furanone (8Cc)*. This compound was obtained as a 55:45 mixture of diastereoisomers; <sup>1</sup>H NMR (400 MHz)  $\delta$  0.12 (9 H, s, minor isomer), 0.13 (9 H, s, major isomer), 1.18 (3 H, d,  $J = 6.1$  Hz, major isomer), 1.20 (3 H, d,  $J = 6.1$  Hz, minor isomer), 1.46-1.59 (2 H, m, both isomers), 1.92-2.10 (4 H, m, both isomers), 2.38-2.50 (2 H, m, both isomers), 2.56-2.76 (2 H, m, both isomers), 3.89-3.97 (1 H, m, minor isomer), 4.09-4.17 (1 H, m, major isomer), 4.17-4.23 (2 H, m, both isomers), 4.30-4.38 (2 H, m, both isomers); <sup>13</sup>C NMR (100 MHz)  $\delta$  0.91 (6 Me), 24.47, 24.75, 29.84, 30.60, 36.64, 37.20, 40.58, 40.90, 66.65, 67.10, 67.15, 67.55, 180.30 (C), 180.48 (C); GC-MS  $m/z$  (rel. inten., both isomers) 201 ( $M^+ - 15$ , 57) 117 (64), 75 (73), 73 (100); the peaks of the two isomers were separated by 15 sec ( $T_i = 80$  °C,  $T_f = 260$  °C, rate: 15 °C/min); the product decomposed completely by column chromatography: a HRM determination was performed on the ( $M^+ - 15$ ) ion peak; HRMS calcd. for C<sub>9</sub>H<sub>17</sub>O<sub>3</sub>Si: 201.0947; found: 201.0946.

*Methyl 4-(trimethoxysilyl)butanoate (8Da)*.<sup>[23]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  0.69 (2 H, t,  $J$  = 8.2 Hz), 1.73 (2 H, m), 2.37 (2 H, t,  $J$  = 7.4 Hz), 3.57 (9 H, s), 3.68 (3 H, s); <sup>13</sup>C NMR (50 MHz)  $\delta$  9.35, 18.98, 37.37, 51.07, 51.96, 174.32 (C); IR  $\nu_{\text{max}}$  (neat) 1739.3 cm<sup>-1</sup>; GC-MS  $m/z$  (rel. inten.) 191 ( $M^+$  – 31, 17), 190 (24), 121 (100), 92 (5), 91 (58), 90 (11), 59 (17); C<sub>8</sub>H<sub>18</sub>O<sub>5</sub>Si requires: C, 43.22; H, 8.16; found: C, 43.31; H, 8.19.

*4-(Trimethoxysilyl)butanenitrile (8Db)*.<sup>[17]</sup> <sup>1</sup>H NMR (200 MHz)  $\delta$  0.79 (2 H, t,  $J$  = 8.0 Hz), 1.80 (2 H, m), 2.40 (2 H, t,  $J$  = 6.6 Hz), 3.58 (9 H, s); <sup>13</sup>C NMR (50 MHz)  $\delta$  9.20, 20.03, 20.45, 51.17, 120.15 (C); C<sub>7</sub>H<sub>15</sub>NO<sub>3</sub>Si requires: C, 44.42; H, 7.99; N, 7.40; found: C, 44.63; H, 8.02; N, 7.38.

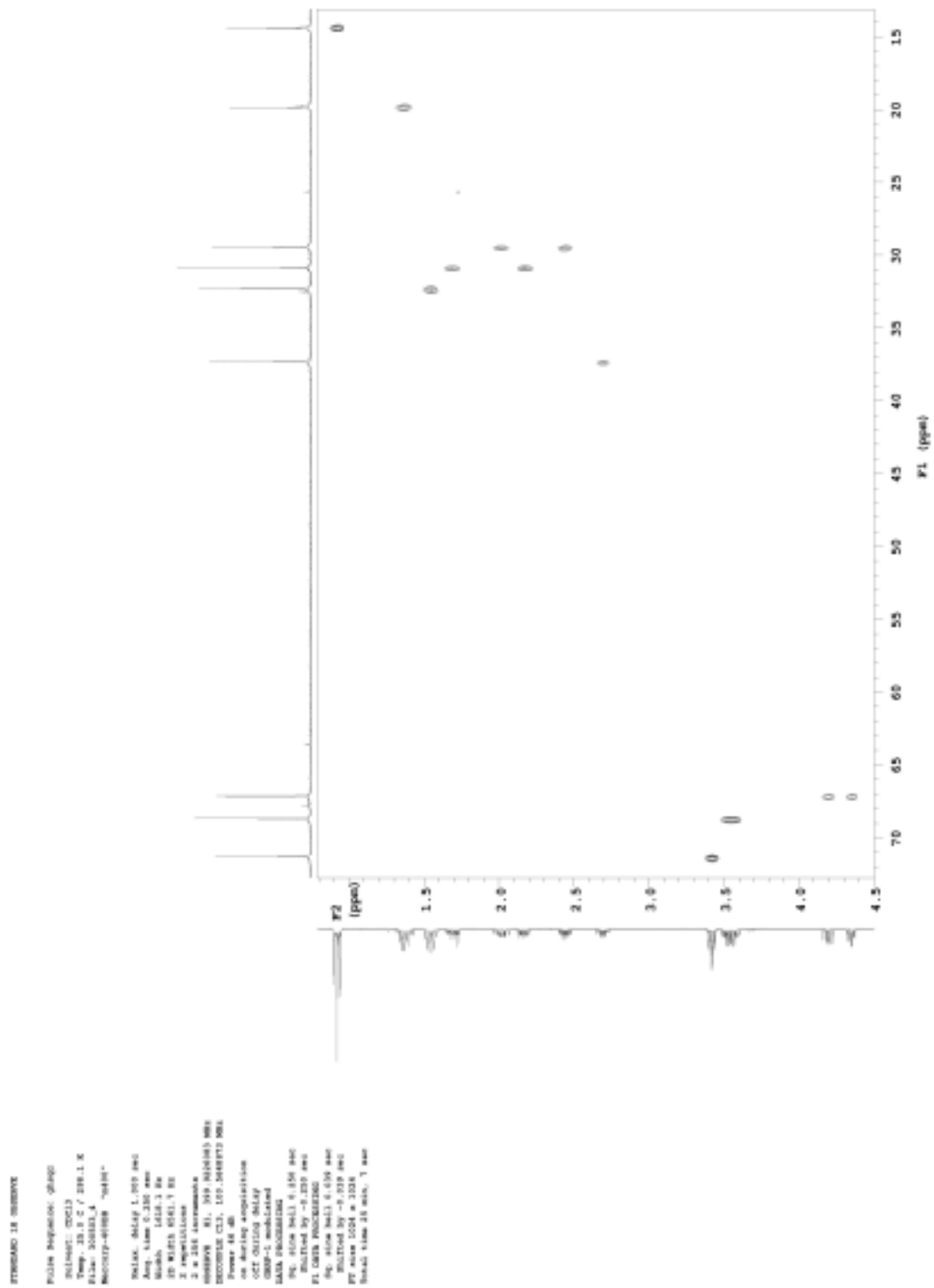
*3-[2-(Trimethoxysilyl)ethyl]dihydro-2(3H)-furanone (8Dc)*. <sup>1</sup>H NMR (400 MHz)  $\delta$  0.67 (2 H, ddd,  $J_1$  = 10.6 Hz,  $J_2$  = 7.8 Hz,  $J_3$  = 6.0 Hz), 1.49-1.59 (1 H, m), 1.83-1.94 (2 H, m), 2.34 (1 H, dddd,  $J_1$  = 12.4 Hz,  $J_2$  = 8.8 Hz,  $J_3$  = 6.8 Hz,  $J_4$  = 3.0 Hz), 2.49 (1 H, dddd,  $J_1$  = 9.9 Hz,  $J_2$  =  $J_3$  = 8.6 Hz,  $J_4$  = 5.2 Hz), 3.51 (9 H, s), 4.12 (1 H, ddd,  $J_1$  =  $J_2$  = 9.3 Hz,  $J_3$  = 6.8 Hz), 4.26 (1 H, ddd,  $J_1$  =  $J_2$  = 8.7 Hz,  $J_3$  = 3.1 Hz); <sup>13</sup>C NMR (100 MHz)  $\delta$  7.24 (CH<sub>2</sub>), 24.12 (CH<sub>2</sub>), 28.61 (CH<sub>2</sub>), 41.77, 51.09, 66.95 (CH<sub>2</sub>), 179.64 (C); GC-MS  $m/z$  (rel. inten.) 206 ( $M^+$  – 28, 46), 202 ( $M^+$  – 32, 42), 174 (9), 121 (100), 91 (43); the product partially decomposed by column chromatography: elemental analysis was however performed on a small sample; C<sub>9</sub>H<sub>18</sub>O<sub>5</sub>Si requires: C, 46.13; H, 7.74; found: C, 46.20; H, 7.72.

**Radical Reaction of Thiol 14 with *p*-Chlorophenyl Isonitrile.** A toluene (10 mL) solution of thiol (1 mmol) and AIBN (0.1 mmol) was added by a syringe pump in 1 h under nitrogen to a refluxing toluene (10 mL) solution of *p*-chlorophenyl isonitrile (1.1 mmol). The resulting mixture was refluxed for an additional hour. The solvent was evaporated and the residue chromatographed (*n*-hexane) to give (diphenylmethyl)cyclopentane **15**<sup>[24]</sup> in 80% yield; <sup>1</sup>H NMR (200 MHz)  $\delta$  1.48-1.75 (9 H, m), 3.56 (1 H, d,  $J$  = 11.0 Hz), 7.05-7.32 (10 H, m); <sup>13</sup>C NMR (50 MHz)  $\delta$  26.01, 32.87, 45.14, 59.30, 126.57, 128.61, 128.97, 146.12 (C); GC-MS  $m/z$  (rel. inten.) 236 ( $M^+$ , 6), 168 (24), 167 (100), 165 (34), 152 (29). Further elution gave 4-chlorophenyl isothiocyanate (>90%).

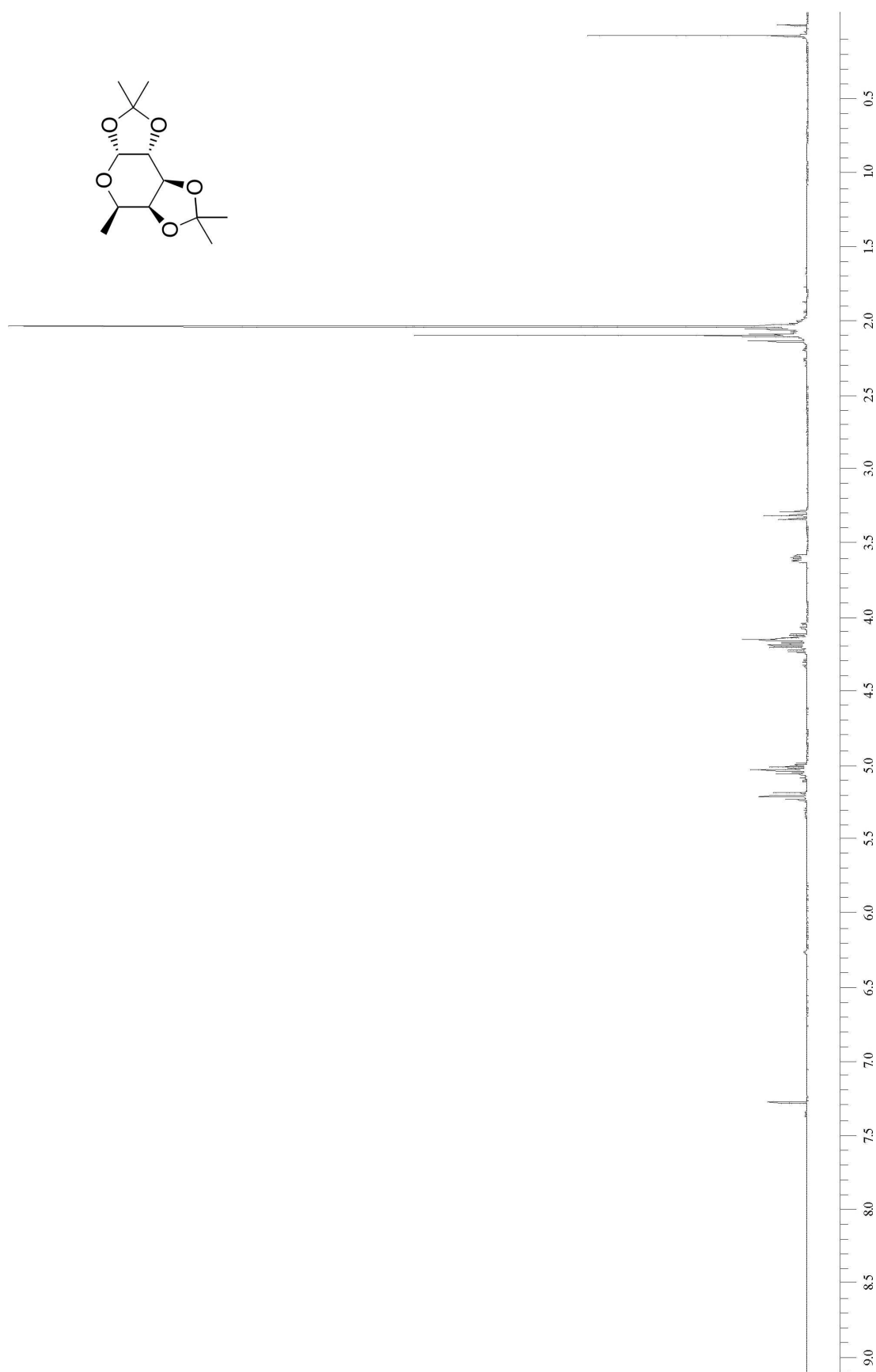






HSQC spectrum of adduct **8Ac**.

$^1\text{H}$  NMR spectrum of the reaction crude of desulfurated sugar **3**.



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