One-pot direct conversion of 2,3-epoxy alcohols into enantiomerically pure 4-hydroxy-4,5-dihydroisoxazole 2-oxides

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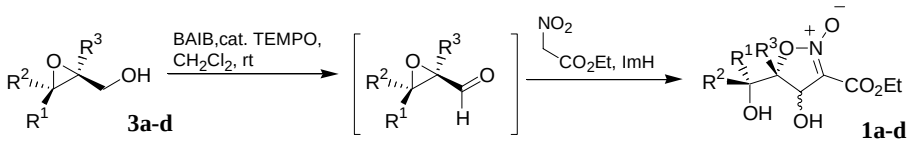
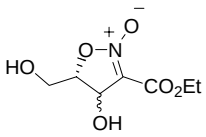
Supporting Information

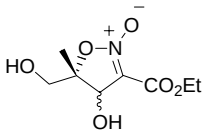
General: ^{1}H NMR spectra were recorded at 300.00 or 200.00 MHz at 20°C with either tetramethylsilane (δ 0.00), chloroform (δ 7.26), methanol (δ 3.30), dimethylsulfoxide (δ 2.49) or acetone (δ 2.20) as the internal standard. ^{13}C NMR spectra were recorded at 75.46 or 50.3 MHz at 20°C with either chloroform (δ 77.7) methanol (δ 49.3), dimethylsulfoxide (δ 39.0) or acetone (δ 29.8) as the internal standard. Signal multiplicities were established by DEPT experiments. Melting points were determined through a *Büchi* instrument and are uncorrected. Specific optical rotations were determined at the sodium D line through a *Perkin Elmer 341* polarimeter. Flash chromatographic separations were performed over Merck Silica gel 60 (230-400 mesh), TLC analyses were performed over Merck precoated TLC plates (Silica gel 60 GF_{254} 0.25 mm). Tetrahydrofuran was obtained anhydrous over sodium and benzophenone. Unless otherwise stated, other solvents and reagents were used as received.



General procedure for the one-pot consecutive transformation of 2,3-epoxy alcohols into 4-hydroxy-4,5-dihydroisoxazoles 2-oxides 1. To a stirred solution of 3-7 g of glycidol **3** in dichloromethane (1.1 ml/mmol of **3**), TEMPO (0.1 eq) and BAIB (1.1 eq.) were added at room temperature in a round bottomed flask equipped with a $CaCl_2$ tube. The reaction was monitored by TLC and after 4-5h the starting material was consumed. At this point, imidazole (3.3 eq.) and ethyl nitroacetate (1.1 eq.) were added in sequence. The course of the reaction was monitored by TLC and was complete after 18-24 h at room temperature. For water soluble products **1a** and **1b** the reaction mixture was concentrated in vacuo and purified by flash column chromatography. For products **1c** and **1d** the reaction mixture was diluted with dichloromethane, washed with a 10% w/w solution of sodium carbonate and with brine; each aqueous layer was back-extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate and concentrated in vacuo and the crude product was purified by flash column chromatography.

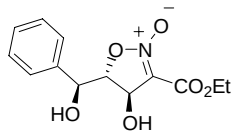


(4*R*,5*S*)- and (4*S*,5*S*)–3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-4,5-dihydroisoxazole 2-oxide (1a): flash chromatography (ethyl acetate/petroleum ether = 9/1) afforded 7.98 g of a mixture of the two dihydroisoxazoles (81% yield from 3.55 g of **3a**). See below for characterization of single isomers.

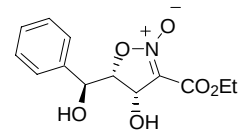


(4*R*,5*S*)- and (4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-5-methyl-4,5-dihydroisoxazole 2-Oxide (1b): flash chromatography (ethyl acetate/petroleum ether = 7/3) afforded 7.28 g of a mixture of the two dihydroisoxazoles (97% yield from 3.00 g of **3b**). See below for characterization of single isomers.

(4*R*,5*S*)- and (4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-[(*S*)-hydroxyphenylmethyl]-4,5-dihydroisoxazole 2-Oxide (1c): flash chromatography (ethyl acetate/petroleum ether = 1/1) afforded 6.52 g of 4,5-*cis*-**1c** and 2.79 g of 4,5-*trans*-**1c** (9.31 g combined, 71% yield from 7.00 g of **3c**)

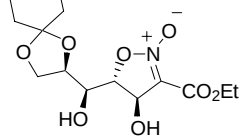


4,5-*trans*-**1c**: white solid; $[\alpha]_D^{24}$ –68.3 (*c* 0.912; $CHCl_3$); m.p. 118-120°C; IR (KBr): ν 3395, 3334, 1721, 1625, 1236 cm^{-1}; ^1H NMR (CD_3OD): δ 1.29 (t, 3H, J = 7.1 Hz, CH_3 (Et)), 4.27 (q, 2H, J = 7.1 Hz, CH_2 (Et)), 4.61 (dd, 1H, J = 1.8, 4.4 Hz, C^5H), 4.92 (d, 1H, J = 4.4 Hz, $C^{1'}H$), 5.37 (d, 1H, J = 1.8 Hz, C^4H); ^{13}C NMR (CD_3OD): δ 14.73 (CH_3), 62.95 (CH_2), 73.39 (CH), 74.13 (CH), 88.93 (CH), 112.80 (C), 127.80 (CH), 129.30 (CH), 129.80 (CH), 140.50 (C), 160.60 (C).



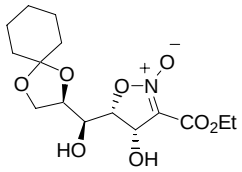
4,5-*cis*-**1c**: white solid; $[\alpha]_D^{26}$ +10.6 (*c* 0.995, $CHCl_3$); m.p. 171-173°C (decomposition); IR (KBr): ν 3515, 3446, 1713, 1599, 1242 cm^{-1}; ^1H NMR (CD_3OD): δ 1.33 (t, 3H, J = 7.1 Hz, CH_3 (Et)), 4.31 (q, 2H, J = 7.1 Hz, CH_2 (Et)), 6.61 (dd, 1H, J = 5.5, 9.2 Hz, C^5H), 5.08 (d, 1H, J = 9.2 Hz, $C^{1'}H$), 5.41(d, 1H, J = 5.5 Hz, C^4H), 7.30-7.46 (m, 5H, arom.);^{13}C NMR (CD_3OD): δ 14.75 (CH_3), 63.00 (CH_2), 70.04 (CH), 73.55 (CH), 84.29 (CH), 114.62 (C), 128.46 (CH), 129.48 (CH), 129.64(CH), 142.42 (C), 160.65 (C).

(4*R*,5*R*)- and (4*S*,5*R*)-5-{(*S*)-[(2*R*)-1,4-Dioxaspiro[4.5]dec-2-yl]hydroxymethyl}-3-ethoxycarbonyl-4-hydroxy-4,5-dihydroisoxazole 2-Oxide (1d): flash chromatography (ethyl acetate/petroleum ether = 4/6) afforded 2.72 g of 4,5-*cis*-**1d** and 2.26 g of 4,5-*trans*-**1d** (4.98 g combined, 62% yield from 4.98 g of **3d**).

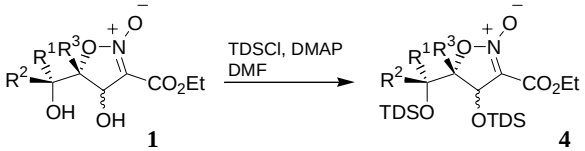


4,5-*trans*-**1d**: white solid; $[\alpha]_D^{27}$ –68.9 (*c* 1.374; CH_3OH); m.p. 142-145°C; IR (KBr): ν 3479, 3424, 1733, 1612, 1225 cm^{-1}; ^1H NMR (CD_3OD): δ 1.24 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.34, 1.52 (m, 10H; CH_2 (hexyl)), 3.53 (dd, 1H, J = 3.3, 6.6 Hz; $C^{1'}H$), 3.76 (dd, 1H, J = 7.4, 8.0 Hz; $C^{3''}H_a$), 3.88 (dd, 1H, J = 6.6, 8.0 Hz; $C^{3''}H_b$), 4.15 (m, 1H; $C^{2''}H$), 4.23 (dq, 2H, J

= 2.5, 7.1 Hz, CH_2 (Et)), 4.36 (dd, 1H, J = 1.6, 6.6 Hz; C^5H), 5.49 (d, 1H, J = 1.6 Hz; C^4H); ^{13}C NMR (CD_3OD): δ 15.30 (CH_3), 25.66 (CH_2), 25.80 (CH_2), 27.07 (CH_2), 37.47 (CH_2), 36.72 (CH_2), 63.56 (CH_2), 67.04 (CH_2), 70.55 (CH), 75.80 (CH), 77.41 (CH), 86.81 (CH), 112.07 (C), 112.97 (C), 161.17 (C).



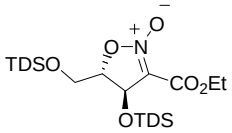
4,5-*cis*-**1d**: white solid; $[\alpha]_D^{25}$ –44.3 (*c* 1.453; CH_3OH); m.p. 120-122°C; IR (KBr): ν 3490, 3456, 1701, 1598, 1244 cm^{-1}; ^1H NMR (CD_3OD): δ 1.23 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.42, 1.68 (m, 10H; CH_2 (hexyl)), 3.90 (dd, 1H, J = 7.1, 7.7 Hz; $C^{3''}H_a$), 4.04 (dd, 1H, J = 3.0, 9.3 Hz; $C^{1'}H$), 4.05 (dd, 1H, J = 6.5, 7.7 Hz; $C^{3''}H_b$), 4.18 (dt, 1H, J = 3.0, 7.1; $C^{2''}H$), 4.32 (dq, 2H, J = 1.1, 7.1 Hz, CH_2 (Et)), 4.55 (dd, 1H, J = 5.5, 9.3 Hz; C^5H), 5.36 (d, 1H, J = 5.5 Hz; C^4H); ^{13}C NMR (CD_3OD): δ 15.30 (CH_3), 25.70 (CH_2), 25.85 (CH_2), 27.13 (CH_2), 36.67 (CH_2), 37.53 (CH_2), 63.60 (CH_2), 66.75 (CH_2), 67.50 (CH), 74.29 (CH), 77.88 (CH), 81.98 (CH), 111.92 (C), 114.75 (C), 161.19 (C).



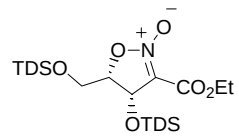
1 **4**

General procedure of protection of the 4-Hydroxy-4,5-dihydroisoxazole 2-Oxides 1a-b: To a stirred solution of the dihydroisoxazole **1** in dimethylformammide (DMF) (about 1.5 ml/mmol), 2.5 eq of 4-dimethylaminopyridine (DMAP) and 2.3 eq of *tert*-butyldimethylsilylchloride (TDSCl) were added at room temperature in a round-bottomed flask equipped of a calcium chloride tube. After 24 h the reaction was quenched with water (10 ml/mmol of starting material) and the mixture was extracted with ethyl acetate (4×5 ml/mmol of starting material). The organic layer was dried over sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography.

(4*R*,5*S*)- and (4*S*,5*S*)-4-*tert*-Butyldimethylsiloxy-5-*tert*-butyldimethylsiloxymethyl-3-ethoxycarbonyl-4,5-dihydro-isoxazole 2-Oxide (4a): 8.00 g (39.0 mmol) of starting material **1a** afforded 14.63 g of the bisprotected product **4a** (86% yield) and 0.75 g of *cis*-5-monoprotected dihydroisoxazole. Chromatographic conditions: diethyl ether/petroleum ether = 1/9, then 2/8, then 100% ethyl acetate.

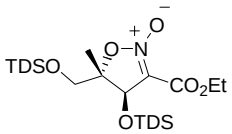


4,5-*trans*-**4a**: white solid; $[\alpha]_D^{23}$ –49.2 (*c* 1.037, $CHCl_3$); m.p. 53-55°C; IR (KBr): ν 1702, 1735, 1620, 1253 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.07 (s, 6H; CH_3Si), 0.14 (s, 3H; CH_3Si), 0.17 (s, 3H; CH_3Si), 0.87 (s, 9H; CH_3 (^{t}Bu)), 0.90 (s, 9H; CH_3 (^{t}Bu)), 1.35 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.70 (dd, 1H, J = 11.1, 5.5 Hz; $C^{1'}H_a$), 3.80 (dd, 1H, J = 11.1, 3.8 Hz; $C^{1'}H_b$), 4.26-4.42 (m, 3H; CH_2 (Et), C^5H), 5.40 (d, 1H, J = 1.2 Hz; C^4H); ^{13}C NMR ($CDCl_3$): δ -4.57 (CH_3), -3.84 (CH_3), -3.75 (CH_3), 15.32 (CH_3), 18.97 (C), 19.16 (C), 26.60 (CH_3), 26.72 (CH_3), 62.63 (CH_2), 62.84 (CH_2), 76.92 (CH), 85.04 (CH), 112.00 (C), 159.78 (C).

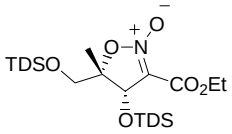


4,5-*cis*-**4a**: white solid; $[\alpha]_D^{17}$ –33.4 (*c* 1.036, $CHCl_3$); m.p. 104-107°C; IR (KBr): ν 1728, 1591, 1232 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.05 (s, 9H; CH_3Si), 0.15 (s, 3H; CH_3Si), 0.85-0.90 (s, 18H; CH_3 (^{t}Bu)), 1.35 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.92 (dd, 1H, J = 11.4, 6.8 Hz; $C^{1'}H_a$), 4.10 (dd, 1H, J = 11.4, 5.1 Hz; $C^{1'}H_b$), 4.24 (dq, 1H, J = 11.2, 7.2 Hz; CH_a (Et)), 4.28 (dq, 1H, J = 11.2, 7.2 Hz; CH_b (Et)), 4.54 (ddd, 1H, J = 6.8, 5.1, 5.2 Hz; C^5H), 5.34 (d, 1H, J = 5.2 Hz; C^4H); ^{13}C NMR ($CDCl_3$): δ –4.93 (CH_3), –4.88 (CH_3), –4.81 (CH_3), –4.72 (CH_3), 14.72 (CH_3), 18.74 (C), 26.18 (CH_3), 26.31 (CH_3), 59.84 (CH_2), 62.34 (CH_2), 73.83 (CH), 82.64 (CH), 112.90 (C), 159.26 (C).

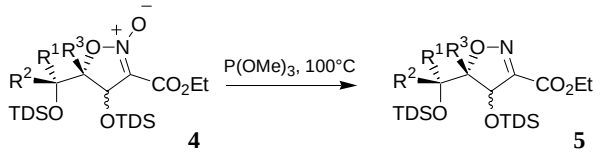
(4*R*,5*S*)- and (4*S*,5*S*)-4-*tert*-Butyldimethylsiloxy-5-*tert*-butyldimethylsiloxymethyl-3-etoxycarbonyl-5-methyl-4,5-dihydroisoxazole 2-Oxide (2b): 4.76 g (21.7 mmol) of starting material **1b** afforded 8.08 g of the dihydroisoxazoles **4b** (83% yield). Chromatographic conditions: diethyl ether/petroleum ether = 5/95, then 1/9.



4,5-*trans*-**4b**: white solid; $[\alpha]_D^{20}$ –40.3 (*c* 0.417, $CHCl_3$); m.p. 42-44°C; IR (KBr): ν 1691, 1611, 1268 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.06 (s, 3H; CH_3Si), 0.07 (s, 3H; CH_3Si), 0.13 (s, 3H; CH_3Si), 0.15 (s, 3H; CH_3Si), 0.87 (s, 9H; CH_3 (^{t}Bu)), 0.89 (s, 9H; CH_3 (^{t}Bu)), 1.35 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.37 (s, 3H; CH_3C^5), 3.57 (d, 1H, J = 10.6 Hz; $C^{1'}H_a$), 3.63 (d, 1H, J = 10.6 Hz; $C^{1'}H_b$), 4.23 (dq, 1H, J = 10.9, 7.1 Hz; CH_a (Et)), 4.42 (dq, 1H, J = 10.9, 7.1 Hz; CH_b (Et)), 5.27 (s, 1H, C^4H); ^{13}C NMR ($CDCl_3$): δ –5.19 (CH_3), –4.33 (CH_3), –4.15 (CH_3), 14.77 (CH_3), 15.90 (CH_3), 18.53 (C), 18.74 (C), 25.23 (CH_3), 62.09 (CH_2), 66.89 (CH_2), 76.39 (CH), 86.51 (C), 112.90 (C), 159.30 (C).

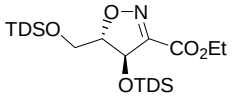


4,5-*cis*-**4b**: white solid; $[\alpha]_D^{26}$ +2.1 (*c* 0.858, $CHCl_3$); m.p. 82-83°C; IR (KBr): ν 1729, 1599, 1240 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.05 (s, 3H; CH_3Si), 0.06 (s, 3H; CH_3Si), 0.07 (s, 3H; CH_3Si), 0.12 (s, 3H; CH_3Si), 0.85 (s, 9H; CH_3 (^{t}Bu)), 0.88 (s, 9H; CH_3 (^{t}Bu)), 1.34 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.38 (s, 3H; CH_3C^5), 3.78 (d, 1H, J = 11.1 Hz; $C^{1'}H_a$), 3.92 (d, 1H, J = 11.1 Hz; $C^{1'}H_b$), 4.24 (dq, 1H, J = 3.9, 7.1 Hz; CH_a (Et)), 4.39 (dq, 1H, J = 3.9, 7.1 Hz; CH_b (Et)), 5.00 (s, 1H, C^4H); ^{13}C NMR ($CDCl_3$): δ –5.49 (CH_3), –5.12 (CH_3), –4.68 (CH_3), 14.20 (CH_3), 19.20 (C), 19.26 (C), 25.67 (CH_3), 61.73 (CH_2), 63.57 (CH_2), 78.70 (CH), 86.30 (C), 112.10 (C), 159.00 (C).

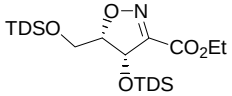


4 **5**

General procedure of deoxygenation of the dihydroisoxazoles 4a-b: The starting material was dissolved in 4 ml/mmol of trimethyl phosphite in a flask equipped with a condenser and a termometer. The mixture was stirred at 100°C for 5 h, then diethyl ether was added (25 ml/mmol of starting material) and the solution was washed with HCl 1*N* (3×10 ml/mmol of starting material), water (10 ml/mmol) and brine (5 ml/mmol). The organic layer was dried over sodium sulfate and concentrated in vacuo to give a crude product which could be used without further purification.

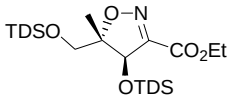


(4*R*,5*S*)-4-*tert*-Butyldimethylsiloxy-5-*tert*-butyldimethylsiloxymethyl-3-ethoxycarbonyl-4,5-dihydroisoxazole (4,5-*trans*-5a): 0.30 g (0.7 mmol) of the starting material *trans*-**4a** afforded 0.29 g of the product *trans*-**5a** (quantitative yield): colourless oil; $[\alpha]_D^{26}$ –72.1 (*c* 0.957, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.02 (s, 3H; CH_3Si), 0.03 (s, 3H; CH_3Si), 0.11 (s, 3H; CH_3Si), 0.13 (s, 3H; CH_3Si), 0.83 (s, 9H; CH_3 (^{t}Bu)), 0.84 (s, 9H; CH_3 (^{t}Bu)), 1.33 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.53 (dd, 1H, J = 11.0, 6.2 Hz; $C^{1'}H_a$), 3.76 (dd, 1H, J = 11.0, 4.0 Hz; $C^{1'}H_b$), 4.32 (q, 1H, J = 7.1 Hz; CH_a (Et)), 4.33 (q, 1H, J = 7.1 Hz; CH_b (Et)), 4.46 (ddd, 1H, J = 6.2, 4.0, 2.6 Hz; C^5H), 5.25 (d, 1H, J = 2.6 Hz; C^4H); ^{13}C NMR ($CDCl_3$): δ –5.49 (CH_3), –4.93 (CH_3), –4.82 (CH_3), 14.19 (CH_3), 17.97 (C), 18.22 (C), 25.70 (CH_3), 25.79 (CH_3), 61.44 (CH_2), 61.85 (CH_2), 77.36 (CH), 90.83 (CH), 152.71 (C), 160.21 (C).

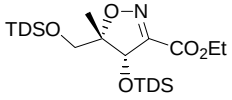


(4*S*,5*S*)-4-*tert*-Butyldimethylsiloxy-5-*tert*-butyldimethylsiloxymethyl-3-ethoxycarbonyl-4,5-dihydroisoxazole (4,5-*cis*-5a): 1.00 g (2.3 mmol) of the starting material *cis*-**4a** afforded 0.96 g of the product *cis*-**5a** (quantitative yield): colourless oil; $[\alpha]_D^{25}$ –59.5 (*c* 0.964, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.10-0.14 (s, 9H; CH_3Si), 0.15 (s, 3H; CH_3Si), 0.85 (s, 9H; CH_3 (^{t}Bu)), 0.90 (s, 9H; CH_3 (^{t}Bu)), 1.40 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.95 (dd, 1H, J = 11.3, 6.9 Hz; $C^{1'}H_a$), 4.06 (dd,

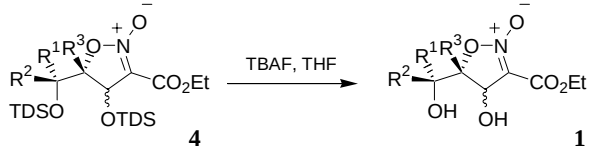
1H, J = 11.3, 5.2 Hz; $C^{1'}H_b$), 4.30-4.35 (m, 1H; C^5H), 4.31 (dq, 1H, J = 10.8, 7.1 Hz; CH_a (Et)), 4.41 (dq, 1H, J = 10.8, 7.1 Hz; CH_b (Et)), 5.21 (d, 1H, J = 6.7 Hz; C^4H); ^{13}C NMR ($CDCl_3$): δ –4.92 (CH_3), –4.30 (CH_3), –4.25 (CH_3), –4.13 (CH_3), 15.19 (CH_3), 19.24 (C), 19.40 (C), 26.69 (CH_3), 26.92 (CH_3), 60.36 (CH_2), 63.05 (CH_2), 75.17 (CH), 89.05 (CH), 154.87 (C), 161.41 (C).



(4*R*,5*S*)-4-*tert*-Butyldimethylsiloxy-5-*tert*-butyldimethylsiloxymethyl-3-ethoxycarbonyl-5-methyl-4,5-dihydro-isoxazole (*trans*-5b): 0.32 g (0.7 mmol) of the starting material *trans*-**4b** afforded 0.29 g of the product *trans*-**5b** (quantitative yield): colourless oil; $[\alpha]_D^{28}$ –48.1 (*c* 1.247, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.02 (s, 3H; CH_3Si), 0.03 (s, 3H; CH_3Si), 0.12 (s, 3H; CH_3Si), 0.13 (s, 3H; CH_3Si), 0.85 (s, 18H; CH_3 (^{t}Bu)), 1.34 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.35 (s, 3H; CH_3C^5), 3.34 (d, 1H, J = 10.2 Hz; $C^{1'}H_a$), 3.52 (d, 1H, J = 10.2 Hz; $C^{1'}H_b$), 4.27 (dq, 1H, J = 10.7, 7.1 Hz; CH_a (Et)), 4.37 (dq, 1H, J = 10.7, 7.1 Hz; CH_b (Et)), 5.10 (s,1H, C^4H); ^{13}C NMR ($CDCl_3$): δ –5.60 (CH_3), –5.50 (CH_3), –5.02 (CH_3), –4.66 (CH_3), 14.20 (CH_3), 15.34 (CH_3), 18.20 (C), 25.69 (CH_3), 25.77 (CH_3), 61.75 (CH_2), 65.86 (CH_2), 76.84 (CH), 92.39 (C), 153.10 (C), 160.70 (C).

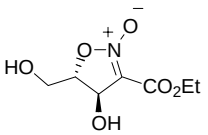


(4*S*,5*S*)-4-*tert*-Butyldimethylsiloxy-5-*tert*-butyldimethylsiloxymethyl-3-ethoxycarbonyl-5-methyl-4,5-dihydro-isoxazole (4,5-*cis*-5b): 1.43 g (3.2 mmol) of the starting material *cis*-**4b** afforded 1.35 g of product *cis*-**5b** (95% yield) after flash chromatography (diethyl ether/petroleum ether = 1/9): white solid; $[\alpha]_D^{27}$ –8.4 (*c* 0.834, $CHCl_3$); m.p. 58-60°C; IR (KBr): ν 1721, 1579 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.08 (s, 3H; CH_3Si), 0.10 (s, 3H; CH_3Si), 0.12 (s, 3H; CH_3Si), 0.14 (s, 3H; CH_3Si), 0.86 (s, 9H; CH_3 (^{t}Bu)), 0.92 (s, 9H; CH_3 (^{t}Bu)), 1.28 (s, 3H; CH_3C^5), 1.38 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.83 (d, 1H, J = 11.0 Hz; $C^{1'}H_a$), 3.88 (d, 1H, J = 11.0 Hz; $C^{1'}H_b$), 4.30 (dq, 1H, J = 10.7, 7.1 Hz; CH_a (Et)), 4.40 (dq, 1H, J = 10.7, 7.1 Hz; CH_b (Et)), 4.78 (s,1H, C^4H); ^{13}C NMR ($CDCl_3$): δ –4.29 (CH_3), –3.88 (CH_3), 15.20 (CH_3), 19.20 (C), 19.45 (C), 20.48 (CH_3), 26.70 (CH_3), 26.98 (CH_3), 62.94 (CH_2), 64.22 (CH_2), 81.06 (CH), 92.96 (C), 153.90 (C), 161.76 (C).

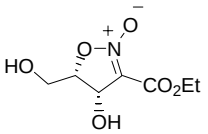


4 **1**

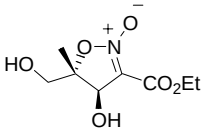
General procedure of desilylation: To a stirred solution of the dihydroisoxazole in anhydrous tetrahydrofuran (THF) (3 ml/mmol), 2.8 eq of tetrabutylammoniumfluoride (1M in THF) were added at room temperature in a round-bottomed flask equipped of a calcium chloride tube. After 5 minutes the TLC analisys (ethyl acetate) revealed that the starting material was consumed, ethanol was added (6 ml/mmol), the mixture was stirred for 1 h and concentrated in vacuo. The crude product was purified by flash chromatography.



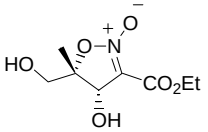
(4*R*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-4,5-dihydroisoxazole 2-Oxide (4,5-*trans*-1a): 0.350 g (0.71 mmol) of the starting material *trans*-**4a** afforded 0.115 g (78% yield) of the deprotected dihydroisoxazole *trans*-**1a**; chromatographic conditions: ethyl acetate/petroleum ether = 1/1 then 8/2: colourless oil; $[\alpha]_D^{24}$ –95.8° (*c* 0.711, EtOH); ^1H NMR ($(CD_3)_2CO$): δ 1.29 (t, 3H, J = 7.0 Hz; CH_3 (Et)), 3.80 (d, 2H, J = 4.4 Hz; $C^{1'}H_2$), 4.27 (q, 1H, J = 7.0 Hz; CH_a (Et)), 4.28 (q, 1H, J = 7.0 Hz; CH_b (Et)), 4.53 (dd, 1H, J = 4.4, 2.2 Hz; C^5H), 5.42 (d, 1H, J = 2.2 Hz; C^4H); ^{13}C NMR ($(CD_3)_2CO$): δ 14.82 (CH_3), 62.22 (CH_2), 75.34 (CH), 85.82 (CH), 112.19 (C), 159.79 (C).



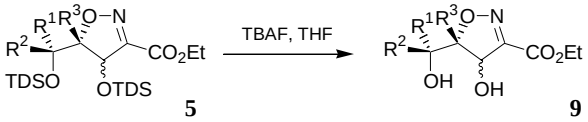
(4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-4,5-dihydroisoxazole 2-Oxide (4,5-*cis*-1a): 0.140 g (0.28 mmol) of the starting material *cis*-**4a** afforded 0.053 g (91% yield) of the deprotected dihydroisoxazole *cis*-**1a**; chromatographic conditions: ethyl acetate: clourless oil; $[\alpha]_D^{25}$ –42.6 (*c* 0.393, EtOH); ^{1}H NMR ($(CD_3)_2CO$): δ 1.29 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.98 (dd, 1H, J = 12.3, 6.6 Hz; $C^{1'}H_a$), 4.07 (dd, 1H, J = 12.3, 4.4 Hz; $C^{1'}H_b$), 4.27 (q, 1H, J = 7.1 Hz; CH_a (Et)), 4.28 (q, 1H, J = 7.1 Hz; CH_b (Et)), 4.78 (ddd, 1H, J = 6.6, 4.4, 6.1 Hz; C^5H), 5.50 (d, 1H, J = 6.1 Hz; C^4H); ^{13}C NMR ($(CD_3)_2CO$): δ 14.41 (CH_3), 59.33 (CH_2), 61.70 (CH_2), 73.39 (CH), 82.17 (CH), 112.71 (C), 159.28 (C).



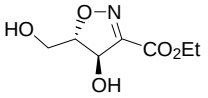
(4*R*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-5-methyl-4,5-dihydroisoxazole 2-Oxide (4,5-*trans*-1b): 0.340 g (0.70 mmol) of the starting material *trans*-**4b** afforded 0.130 g (88% yield) of the deprotected dihydroisoxazole *trans*-**1b**; chromatographic conditions: ethyl acetate/petroleum ether = 8/2: white solid; $[\alpha]_D^{27}$ –56.6° (*c* 1.085, EtOH); IR (KBr): ν 3433, 3333, 1728, 1616, 1249 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$): δ 1.29 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.41 (s, 3H; CH_3C^5), 3.62 (d, 1H, J = 11.8 Hz; $C^{1'}H_a$), 3.67 (d, 1H, J = 11.8 Hz; $C^{1'}H_b$), 4.26 (q, 2H, J = 7.1 Hz; CH_2 (Et)), 5.27 (s, 1H, C^4H); ^{13}C NMR ($(CD_3)_2CO$): δ 15.45 (CH_3), 15.96 (CH_3), 62.67 (CH_2), 67.38 (CH_2), 76.26 (CH), 87.92 (C), 113.88 (C), 160.59 (C).



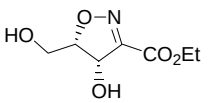
(4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-5-methyl-4,5-dihydroisoxazole 2-Oxide (4,5-cis-1b): 0.19 g (0.4 mmol) of the starting material *cis*-**4b** afforded 0.07 g (85% yield) of the deprotected dihydroisoxazole *cis*-**1b**; chromatographic conditions: ethyl acetate: colourless oil; $[\alpha]_D^{25}$ +18.5 (*c* 0.546, $CHCl_3$); ^{1}H NMR (CD_3OD): δ 1.33 (t, 3H, J = 7.1 Hz, CH_3 (Et)), 1.43 (s, 3H, CH_3), 3.81 (d, 1H, J = 12.1 Hz, $C^{1'}H_a$), 3.88 81 (d, 1H, J = 12.1 Hz, $C^{1'}H_b$),), 4.31 (q, 2H, J = 7.1 Hz, CH_2 (Et)), 5.06 (s, 1H, C^4H); ^{13}C NMR (CD_3OD): δ 14.71 (CH_3), 20.23 (CH_3), 62.94 (CH_2), 63.59 (CH_2), 79.04 (CH), 87.03 (C), 113.53 (C), 160.82 (C).



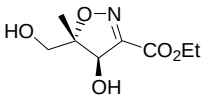
5 **9**



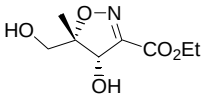
(4*R*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-4,5-dihydroisoxazole (4,5-*trans*-9a): 0.30 g (0.7 mmol) of the starting material *trans*-**5a** afforded 0.10 g (83% yield) of the free dihydroisoxazole 4,5-*trans*-**9a**; chromatographic conditions: ethyl acetate/petroleum ether = 8/2: colourless oil; $[\alpha]_D^{22}$ –112.3 (*c* 0.768, EtOH); ^{1}H NMR ($(CD_3)_2CO$): δ 1.32 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.67 (dd, 1H, J = 12.1, 4.9 Hz; $C^{1'}H_a$), 3.74 (dd, 1H, J = 12.1, 4.9 Hz; $C^{1'}H_b$), 4.31 (q, 1H, J = 7.1 Hz; CH_a (Et)), 4.32 (q, 1H, J = 7.1 Hz; CH_b (Et)), 4.54 (dt, 1H, J = 4.9, 3.6 Hz; C^5H), 5.31 (d, 1H, J = 3.6 Hz; C^4H); ^{13}C NMR ($(CD_3)_2CO$): δ 15.35 (CH_3), 62.64 (CH_2), 63.08 (CH_2), 77.93 (CH), 93.06 (CH), 155.24 (C), 161.98 (C).



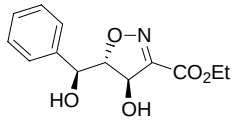
(4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-4,5-dihydroisoxazole (4,5-*cis*-9a): 0.25 g (0.6 mmol) of the starting material *cis*-**5a** afforded 0.07 g (70% yield) of the dihydroisoxazole *cis*-**9a**; chromatographic conditions: ethyl acetate/petroleum ether = 8/2: semisolid; $[\alpha]_D^{28}$ –107.2 (*c* 0.622, EtOH); IR (KBr): ν 3388, 1729, 1587 cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$): δ 1.82 (t, 3H, J = 7.0 Hz; CH_3 (Et)), 3.89-4.19 (m, 3H; $C^{1'}H_2$, $C^{1'}OH$), 4.31 (q, 2H, J = 7.0 Hz; CH_2 (Et)), 4.53 (m, 1H; C^5H), 5.17 (d, 1H, J = 6.0 Hz; C^4OH), 5.38 (dd, 1H, J = 6.0 Hz; C^4H); ^{13}C NMR ($(CD_3)_2CO$): δ 15.37 (CH_3), 60.11 (CH_2), 63.03 (CH_2), 75.72 (CH), 88.79 (CH), 155.95 (C), 161.95 (C).



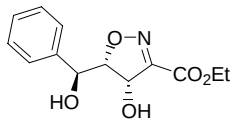
(4*R*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-5-methyl-4,5-dihydroisoxazole (4,5-*trans*-9b): 0.26 g (0.5 mmol) of the starting material *trans*-**5b** afforded 0.10 g (92% yield) of the dihydroisoxazole *trans*-**9b** chromatographic conditions: ethyl acetate/petroleum ether = 8/2: colourless oil; $[\alpha]_D^{28}$ –70.4 (*c* 1.034, EtOH); ^{1}H NMR ($(CD_3)_2CO$): δ 1.31 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 1.38 (s, 3H; CH_3C^5), 3.43 (d, 1H, J = 11.4 Hz; $C^{1'}H_a$), 3.55 (d, 1H, J = 11.4 Hz; $C^{1'}H_b$), 4.29 (q, 1H, J = 7.1 Hz; CH_a (Et)), 4.30 (q, 1H, J = 7.1 Hz; CH_b (Et)), 5.13 (s, 1H; C^4H); ^{13}C NMR ($(CD_3)_2CO$): δ 15.40 (CH_3), 15.79 (CH_3), 62.94 (CH_2), 67.12 (CH_2), 77.50 (CH), 94.09 (C), 155.35 (C), 162.26 (C).



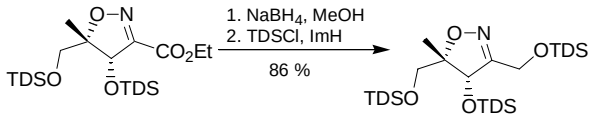
(4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-hydroxymethyl-5-methyl-4,5-dihydroisoxazole (4,5-*cis*-9b): 0.40 g (0.8 mmol) of the starting material *cis*-**5b** afforded 0.10 g (60% yield) of the dihydroisoxazole *cis*-**9b**; chromatographic conditions: ethyl acetate/diethyl ether = 1/9: colourless oil: $[\alpha]_D^{25}$ +4.1 (*c* 0.888, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.31 (s, 3H; CH_3C^5), 1.33 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.38 (bs, 1H; $C^{1'}OH$), 3.90 (bs, 2H; $C^{1'}H_2$), 4.32 (q, 2H, J = 7.1 Hz; CH_2 (Et)), 4.51 (d, 1H, J = 4.7 Hz; C^4OH), 5.00 (d, 1H, J = 4.7 Hz, C^4H); ^{13}C NMR ($CDCl_3$): δ 13.86 (CH_3), 20.58 (CH_3), 62.12 (CH_2), 63.77 (CH_2), 80.60 (CH), 90.56 (C), 152.56 (C), 160.46 (C).



(4*R*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-[(*S*)-hydroxyphenylmethyl]-4,5-dihydroisoxazole (4,5-*trans*-9c): 0.17 g (0.3 mmol) of the starting material *trans*-**5c** afforded 0.06 g (76% yield) of the dihydroisoxazole *trans*-**9c**; chromatographic conditions: diethyl ether/petroleum ether = 1/1: semisolid; $[\alpha]_D^{24}$ –112.9 (*c* 0.328, $CHCl_3$); IR (NaCl): ν 3419, 1717, 1590 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 0.84 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 3.84 (q, 2H, J = 7.1 Hz; CH_2 (Et)), 4.10 (dd, 1H, J = 5.2, 3.3 Hz; C^5H), 4.27 (bd, 1H; C^4H), 4.74 (bs, 1H; $C^{1'}H$), 5.45 (bs, 1H; $C^{1'}OH$), 5.70 (bd, 1H, C^4OH), 6.86-7.25 (m, 5H; arom.); ^{13}C NMR (DMSO-d_6): δ 13.96 (CH_3), 61.34 (CH_2), 70.76 (CH), 74.26 (CH), 93.95 (CH), 126.58 (CH), 127.38 (CH), 128.14 (CH), 140.74 (C), 153.38 (C), 159.86 (C).



(4*S*,5*S*)-3-Ethoxycarbonyl-4-hydroxy-5-[(*S*)-hydroxyphenylmethyl]-4,5-dihydroisoxazole (4,5-*cis*-9c): 0.08 g (0.15 mmol) of the starting material *cis*-**5c** afforded 0.05 g (quant. yield) of the dihydroisoxazole *cis*-**9c**; chromatographic conditions: ethyl acetate/petroleum ether = 1/1: white solid; $[\alpha]_D^{25}$ –44.5° (*c* 1.56, $CHCl_3$); m.p. 151-153°C; IR (KBr): ν 3521, 3431, 1727, 1589; ^{1}H NMR (DMSO-d_6): δ 1.30 (t, 3H, J = 7.1 Hz; CH_3 (Et)), 4.28 (q, 2H, J = 7.1 Hz; CH_2 (Et)), 4.29 (dd, 1H, J = 9.4, 6.8 Hz; C^5H), 4.90 (dd, 1H, J = 9.4, 4.7 Hz; $C^{1'}H$), 5.14 (dd, 1H, J = 7.5, 6.8 Hz; C^4H), 5.68 (d, 1H, J = 4.7 Hz; $C^{1'}OH$), 6.18 (d, 1H, J = 7.5 Hz; C^4OH), 7.20-7.50 (m, 5H; arom.); ^{13}C NMR (DMSO-d_6): δ 13.97 (CH_3), 61.30 (CH_2), 67.68 (CH), 72.54 (CH), 88.68 (CH), 127.26 (CH), 127.49 (CH), 127.96 (CH), 142.44 (C), 155.23 (C), 159.89 (C).

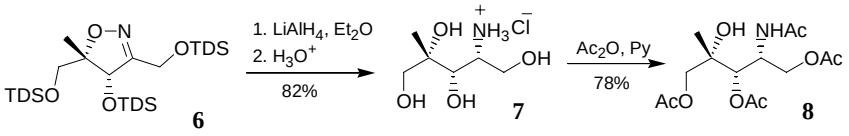


4,5-*cis*-**5b** **6**

(4*S*,5*S*)-4-*tert*-Butyldimethyldimethylsilyloxy-3,5-bis(*tert*-butyldimethylsilyloxymethyl)-5-methyl-4,5-dihydro-isoxazole (6). Sodium borohydride (660 mg, 17.4 mmol) was added to a flame-dried three-neck flask containing 4,5-*cis*-**5b** (5.00 g, 11.6 mmol) and EtOH (24 ml) at –10°C. The reaction mixture was allowed to reach room temperature and was stirred until TLC showed that there was no more starting material (ca.16 h). Excess borohydride was destroyed with 1 N hydrochloric acid and the mixture was diluted with water (50 ml). The aqueous layer was extracted with EtOAc (5 x 25

ml) and the combined organic layers were washed with brine (15 ml) and dried over magnesium sulphate. The solvent was removed by rotary evaporation to afford 4.30 g (95 % yield) of a colourless liquid which crystallized after ca.1 h and was used without further purification. ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 6H), 0.12 (s, 3H), 0.16 (s, 3H), 0.90 (s, 18H), 1.29 (s, 3H), 3.05 (bs, 1H), 3.72 (d, *J* =11.0 Hz, 1H), 3.78 (d, *J* =11.0 Hz, 1H), 4.28 (d, *J* =14.0 Hz, 1H), 4.46 (d, *J* =14.0 Hz, 1H), 4.80 (s, 1H); ^{13}C NMR ($CDCl_3$): δ -4.92; -4.86; -4.55; -4.35 (CH_3Si), 18.45; 18.91 (C), 20.60 (CH_3), 26.06; 26.43 (CH_3) 56.40 (CH_2), 64.18 (CH_2), 82.01 (CH), 88.33 (C), 159.81 (C); mp 44-46°C ; $[\alpha]_D^{22}$ +28.2 (c 1.02; CH_3Cl)

To a stirred solution of crude alcohol (4.3 g, 11.0 mmol) in DMF (20 ml) DMAP (4.3 mg, 35.2 mmol), and tert-butyldimethylsilyl chloride (2.58 g, 17.1 mmol) were added. The mixture was kept stirring at room temperature for 22 h, and then it was partitioned between water and ethyl acetate. The aqueous layer was extracted 3 times with EtOAc. The crude product was purified by column chromatography (petroleum ether- Et_2O, 9:1) to give **6** (4.90 g, 86% yield) as a white solid. mp 41-43°C; $[\alpha]_D^{22}$ -6.30 (c 1.007; CH_3Cl); ^{1}H NMR ($CDCl_3$): δ 0.07-0.16 (m, 18H), 0.90 (s, 27 H), 1.30 (s, 3H), 3.80(s, 2H), 4.35(d, *J* =12.7 Hz,1H), 4.40(d, *J* =12.7 Hz,1H), 4.72 (s, 1H);); ^{13}C NMR ($CDCl_3$): δ -4.35; -4.31; -4.27; -4.13; -4.06; -3.81 (CH_3Si), 19.10; 19.50 (C), 21.23 (CH_3); 26.70; 26.79; 27.04 (CH_3), 57.30 (CH_2),64.70(CH_2), 82.10 (CH), 88.45 (C), 160.00 (C).



(2*R*,3*S*,4*R*)-2-Acetamido-4-methyl-1,3,5-*tri*acetoxy-pentan-4-ol (8): 1.20 g (2.0 mmol) of **6** was dissolved in 2.5 ml of anhydrous diethyl ether, 5.3 ml (5.3 mmol) of a 1*M* solution of lithium aliuminum hydride in diethyl ether were added dropwise at –10°C. After 4h at 0°C the TLC analysis (petroleum ether/diethyl ether = 9/1) revealed that the starting material was consumed. 5.0 ml of HCl 6*N* were then added dropwise at –5°C and the mixture was extracted several times with ethyl acetate, the organic layer was washed with 30 ml of brine, dried with magnesium sulfate and concentrated *in vacuo*. The residual was dissolved in 4.0 ml of a 3 : 1 mixture of methanol/tetrahydrofuran, 2 ml of HCl 6*N* were added and the mixture was rifluxed for 3h. Concentration under reduced pressure afforded 560 mg (82% yield) of a brown oil constituted by the wished product which was characterized through the subsequent derivatization.

The crude product of the previous reaction was dissolved in 3 ml of dry pyridine under nitrogen. 0.92 ml (9.8 mmol) of acetic anhydride were added dropwise at room temperature. After 20 h the mixture was concentrated *in vacuo*, dissolved in 5 ml of chloroform and washed with 3 ml of a saturated solution of sodium carbonate, with 5 ml of a saturated solution of copper sulfate and with 10 ml of brine. Each aqueous layer was back-extracted with chloroform, the reunited organic layer was dried with magnesium sulfate and concentrated *in vacuo* to give 430 mg (78% yield, 64% overall) of a yellow oil constituted by the mixture (d.e. > 9:1 by ^{1}H NMR) of the two tetraacetilated isomers. $[\alpha]^{18}_D$ –25.2 (*c* 1.622, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 3H, CH_3), 1.94 (s, 3H, CH_3 (Ac)), 1.99 (s, 3H, CH_3 (Ac)), 2.01 (s, 3H, CH_3 (Ac)), 2.07 (s, 3H, CH_3 (Ac)), 3.50 (bs, 1H, OH), 3.92 (d, 1H, J = 11.4 Hz, C^5H_a), 4.04 (dd, 1H, J = 4.6, 11.3 Hz, C^1H_a), 4.08 (d, 1H, J = 11.4 Hz, C^5H_b), 4.10 (dd, 1H, J = 6.4, 11.3 Hz, C^1H_b), 4.65 (m, 1H, C^2H), 5.04 (d, 1H, J = 2.2, C^3H), 6.40 (d, 1H, J = 8.4 Hz, NH); ^{13}C NMR ($CDCl_3$): δ 21.13 (CH_3), 21.18 (CH_3), 21.26 (CH_3), 22.32 (CH_3), 23.53 (CH_3), 47.75 (CH), 64.27 (CH_2), 68.37 (CH_2), 73.30 (C), 73.44 (CH), 170.60 (C), 171.29 (C), 171.30 (C).

4,5-*trans*-1a

Acquisition Time (sec)	2.7304	***Comment***				***Date***	1-08-00	***Frequency (MHz)***	199.98
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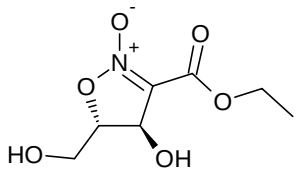
Sweep Width (Hz)	3000.30			***Temperature (grad C)***	20.000				



4,5-*trans*-1a

Acquisition Time (sec)	0.5464	***Comment***					
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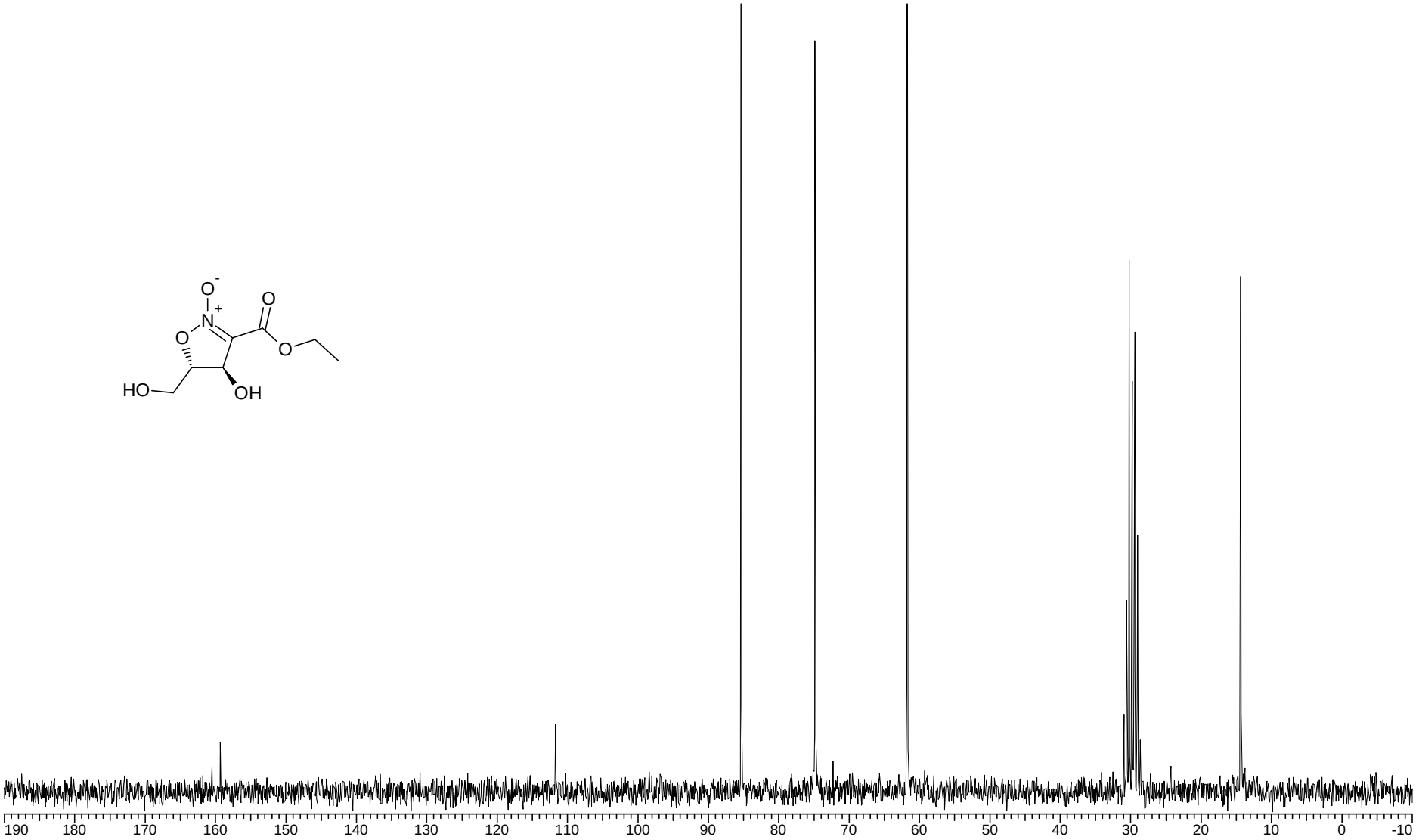
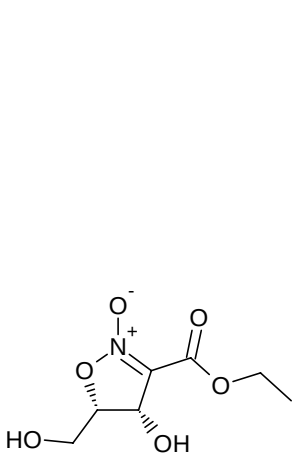


4,5-*cis*-1a

Acquisition Time (sec)	3.6405	***Comment***	LM85B			***Date***	1-15-00		
Frequency (MHz)	300.08	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	12000	***Points Count***	16384
Solvent	acetone	***Sweep Width (Hz)***	4500.45			***Temperature (grad C)***	20.000		



4,5-*cis*-1a

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-15-00	***Frequency (MHz)***	75.46	***Nucleus***	13C
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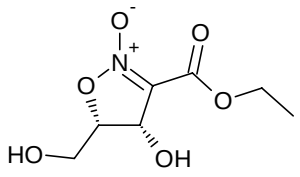
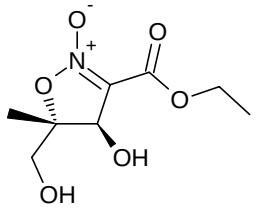


4,5-*trans*-1b

Acquisition Time (sec)	3.6405	***Comment***			***Date***	1-07-00	***Frequency (MHz)***	300.08	***Nucleus***	1H
Number of Transients	16	***Original Points Count***	12000	***Points Count*** 16384	***Solvent***	acetone	***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000



4,5-*trans*-1b

Acquisition Time (sec)	0.8192	***Comment***			***Date***	1-03-00	***Frequency (MHz)***	75.46
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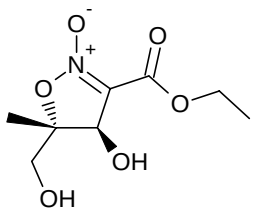
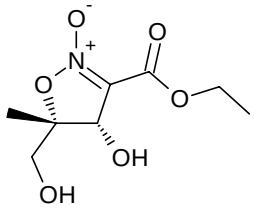
Temperature (grad C)	20.000							



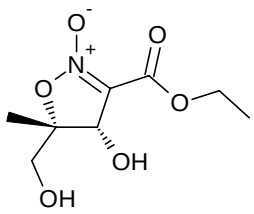
4,5-*cis*-1b

Acquisition Time (sec)	3.6405			***Comment***	RC34	***Date***	2-12-00	***Frequency (MHz)***	300.08
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	12000	***Points Count***	16384		
Solvent	cd3od			***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000		



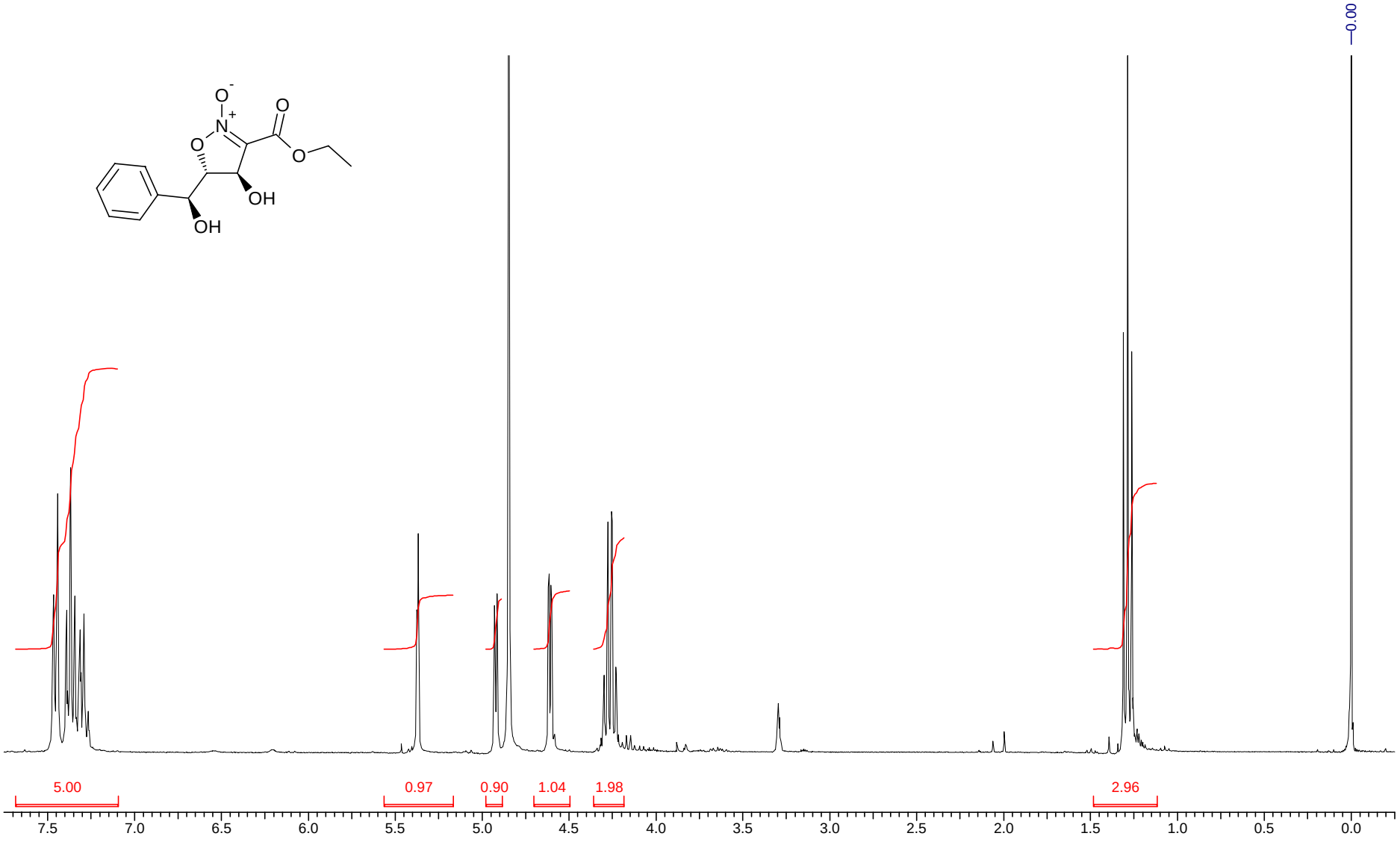
4,5-*cis*-1b

Acquisition Time (sec)	0.8192	***Comment***			***Date***	2-12-00	***Frequency (MHz)***	75.46
Nucleus	13C	***Original Points Count***	12000	***Points Count*** 16384	***Solvent***	cd3od	***Sweep Width (Hz)***	20000.00
Temperature (grad C)	20.000							



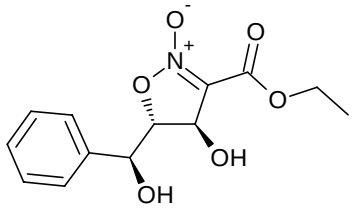
4,5-*trans*-1c

Acquisition Time (sec)	3.6405	***Comment***			***Date***	2-12-00	***Frequency (MHz)***	300.08
Nucleus	1H	***Number of Transients***	16	***Original Points Count*** 12000	***Points Count***	16384	***Solvent***	cd3od
Sweep Width (Hz)	4500.45	***Temperature (grad C)***	20.000					



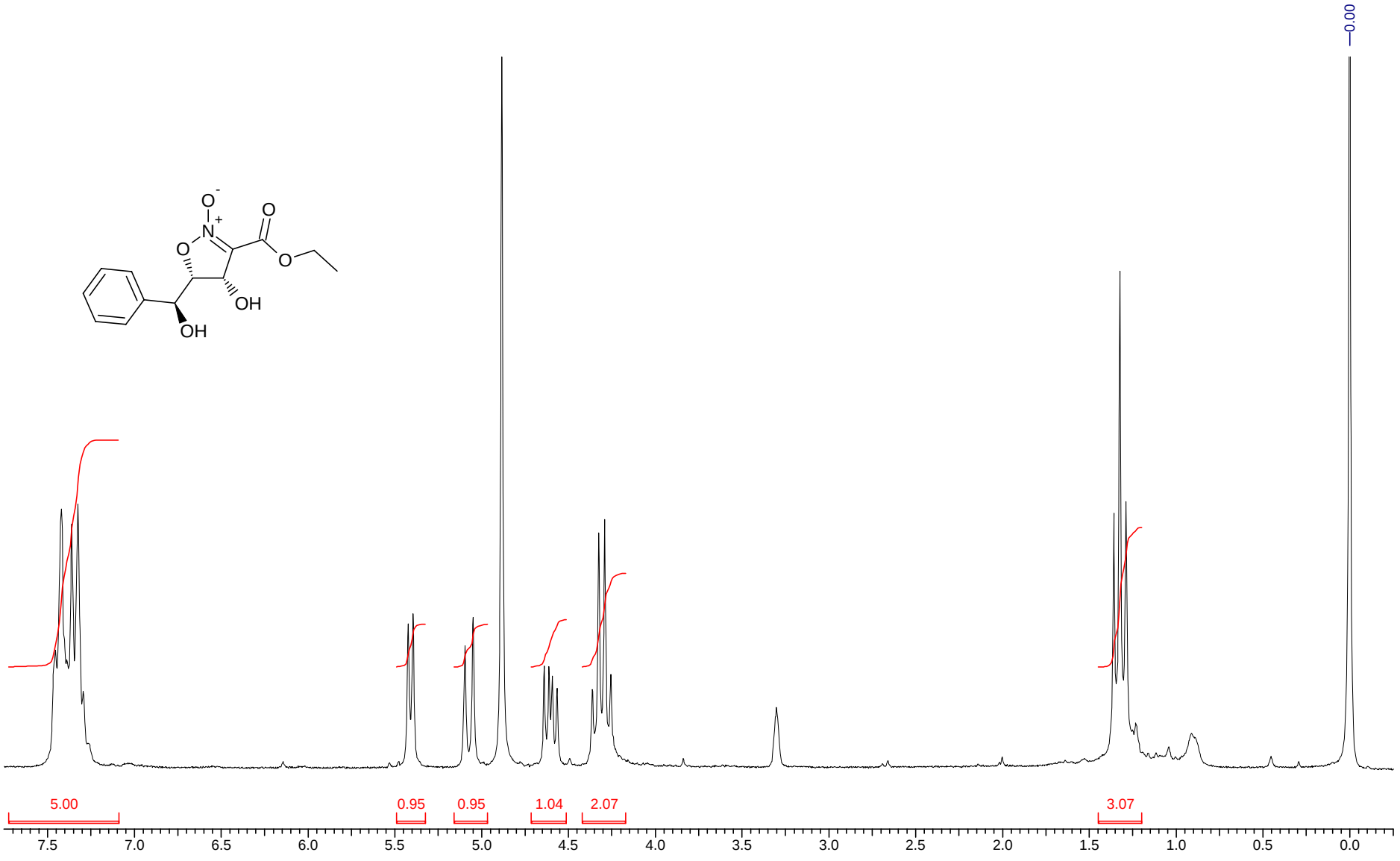
4,5-*trans*-1c

Acquisition Time (sec)	0.8192	***Comment***			***Date***	2-12-00	***Frequency (MHz)***	75.46
Nucleus	13C	***Original Points Count***	12000	***Points Count*** 16384	***Solvent***	cd3od	***Sweep Width (Hz)***	20000.00
Temperature (grad C)	20.000							



4,5-*cis*-1c

Acquisition Time (sec)	2.7304	***Comment***			***Date***	1-09-00	***Frequency (MHz)***	199.98	***Nucleus***	1H
Number of Transients	16	***Original Points Count***	8000	***Points Count*** 8192	***Solvent***	cd3od	***Sweep Width (Hz)***	3000.30	***Temperature (grad C)***	20.000



4,5-*cis*-1c

Acquisition Time (sec)	0.8192	***Comment***				***Date***	2-12-00	***Frequency (MHz)***	75.46
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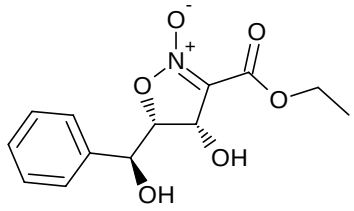
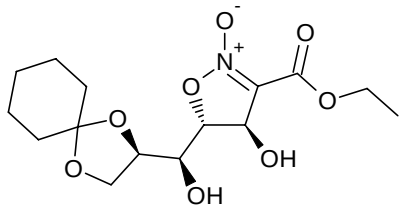
Temperature (grad C)	20.000								



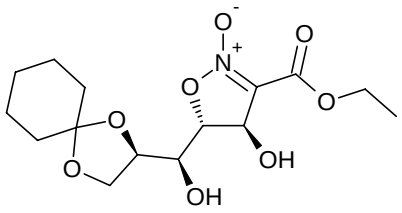
4,5-*trans*-1d

Acquisition Time (sec)	3.6405			***Comment***		***Date***	1-09-00	***Frequency (MHz)***	300.08
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	12000	***Points Count***	16384		
Solvent	cd3od			***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000		



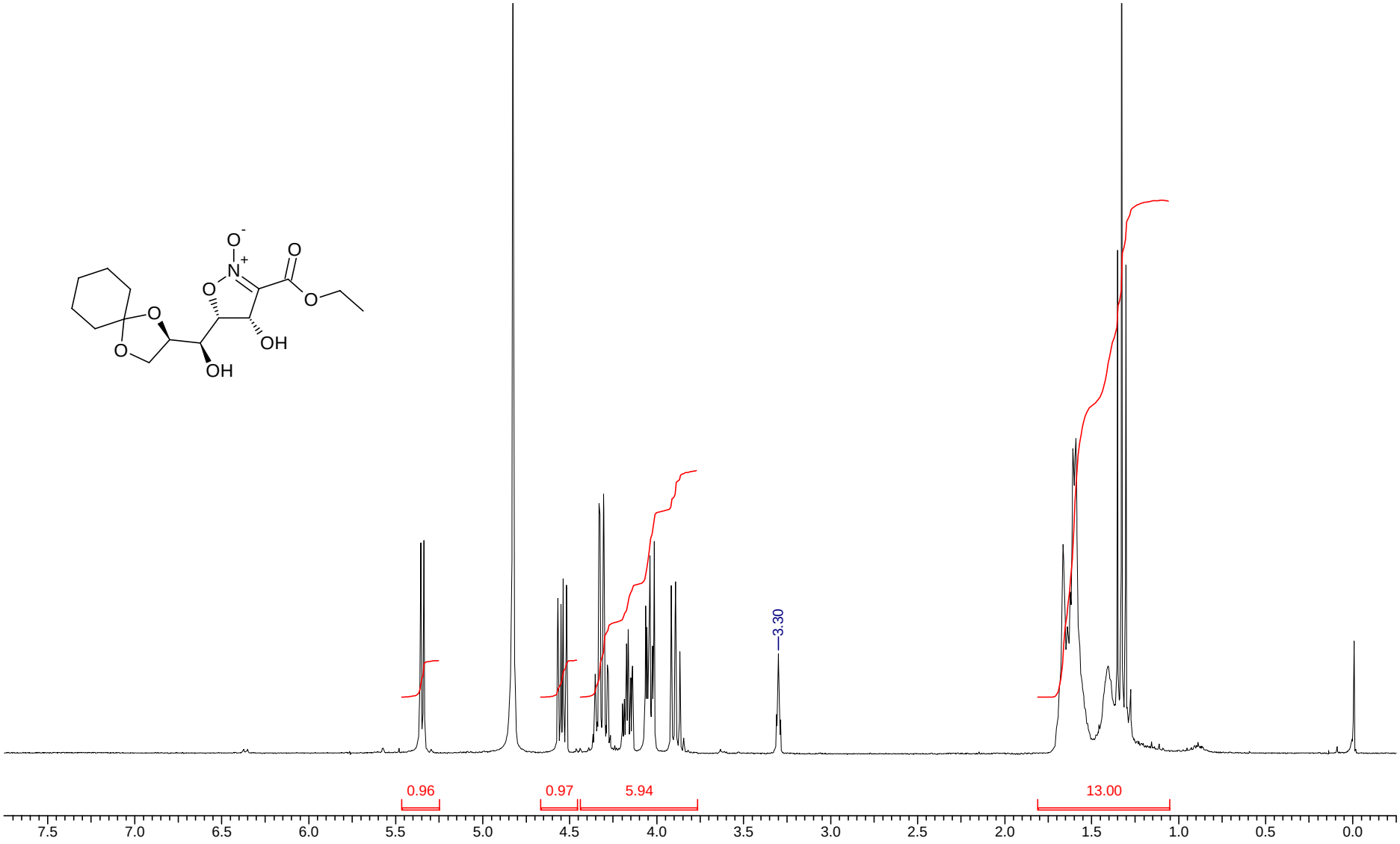
4,5-*trans*-1d

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-09-00
Frequency (MHz)	75.46	***Nucleus***	13C	***Original Points Count***	12000	***Points Count***	16384	***Solvent***	cd3od
Sweep Width (Hz)	20000.00	***Temperature (grad C)***	20.000						



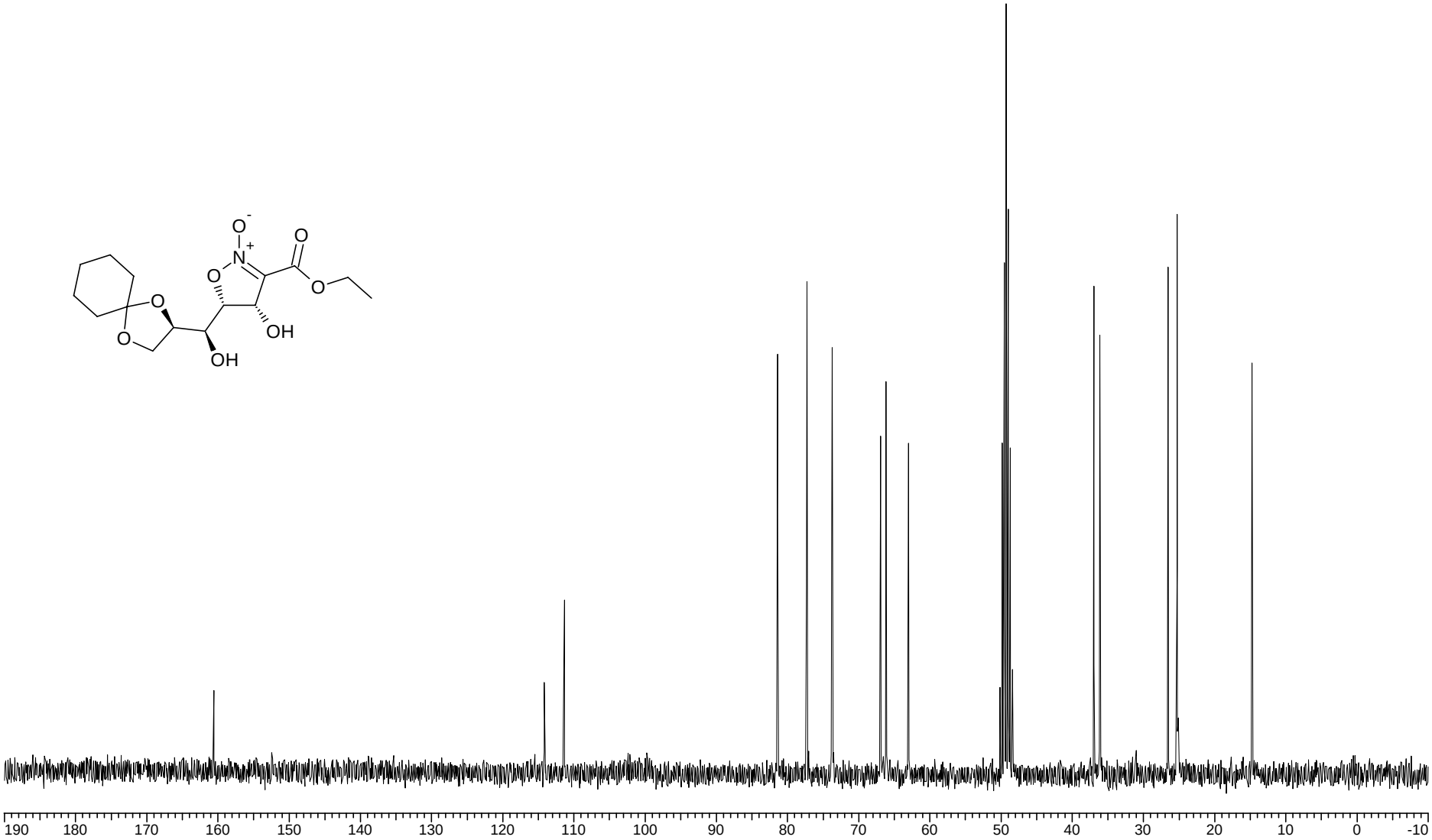
4,5-*cis*-1d

Acquisition Time (sec)	3.6405	***Comment***				***Date***	1-09-00
Frequency (MHz)	300.08	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count*** 12000	***Points Count*** 16384
Solvent	cd3od	***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000		



4,5-*cis*-1d

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-09-00
Frequency (MHz)	75.46	***Nucleus***	13C	***Original Points Count***	12000	***Points Count***	16384	***Solvent***	cd3od
Sweep Width (Hz)	20000.00	***Temperature (grad C)***	20.000						



4,5-*trans*-4a

Acquisition Time (sec)	3.6405	***Comment***			***Date***	1-01-00	***Frequency (MHz)***	300.08
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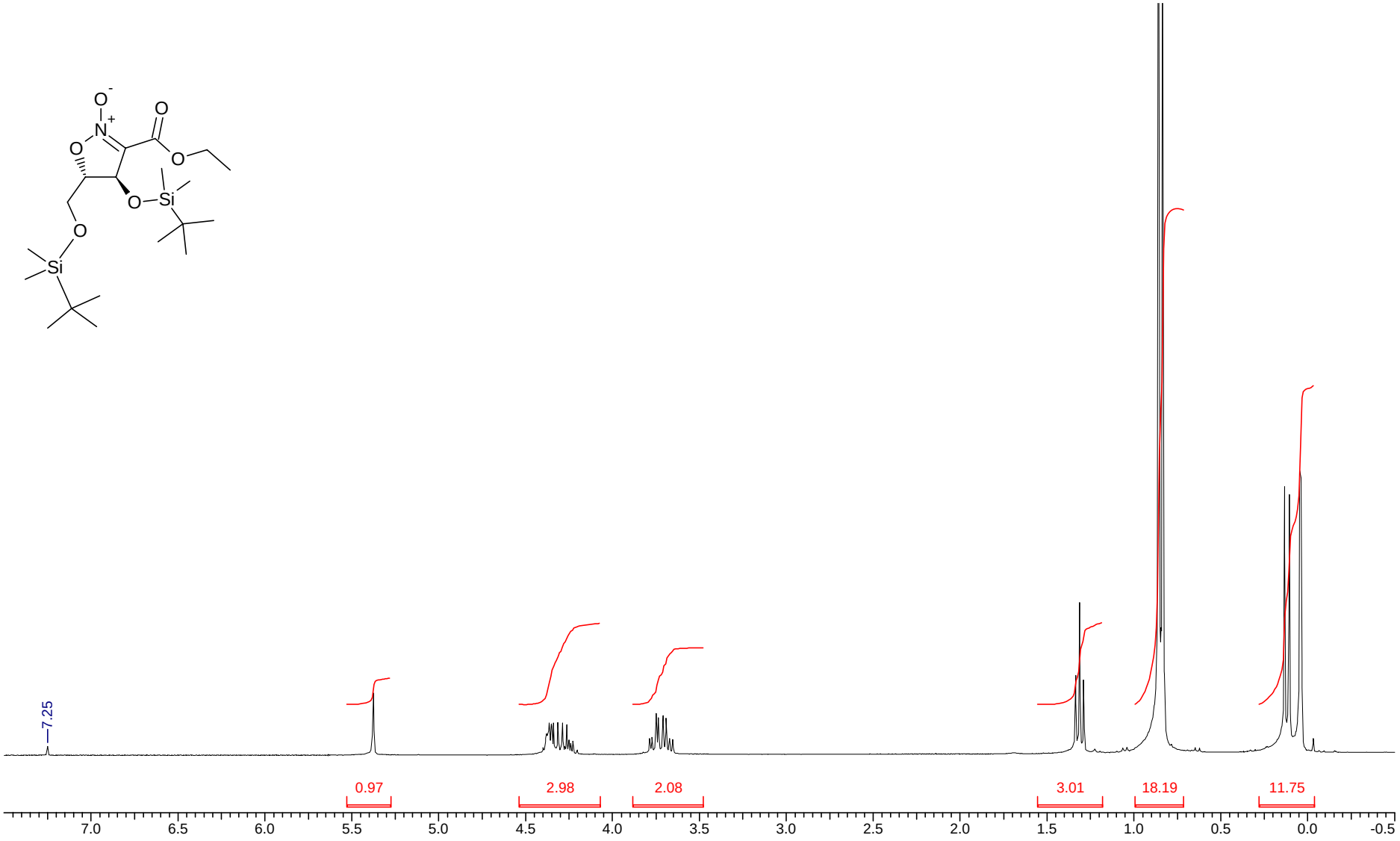
Sweep Width (Hz)	4500.45	***Temperature (grad C)***	20.000					



4,5-trans-4a

Acquisition Time (sec)	0.8192	***Comment***		***Date***	1-01-00	***Frequency (MHz)***	75.46
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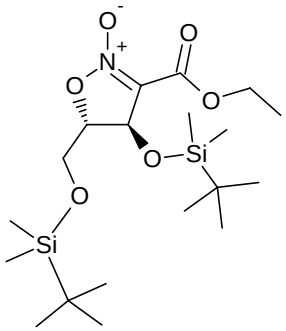
Temperature (grad C)	20.000						



4,5-*cis*-4a

Acquisition Time (sec)	3.6405	***Comment***			***Date***	1-01-00	***Frequency (MHz)***	300.08
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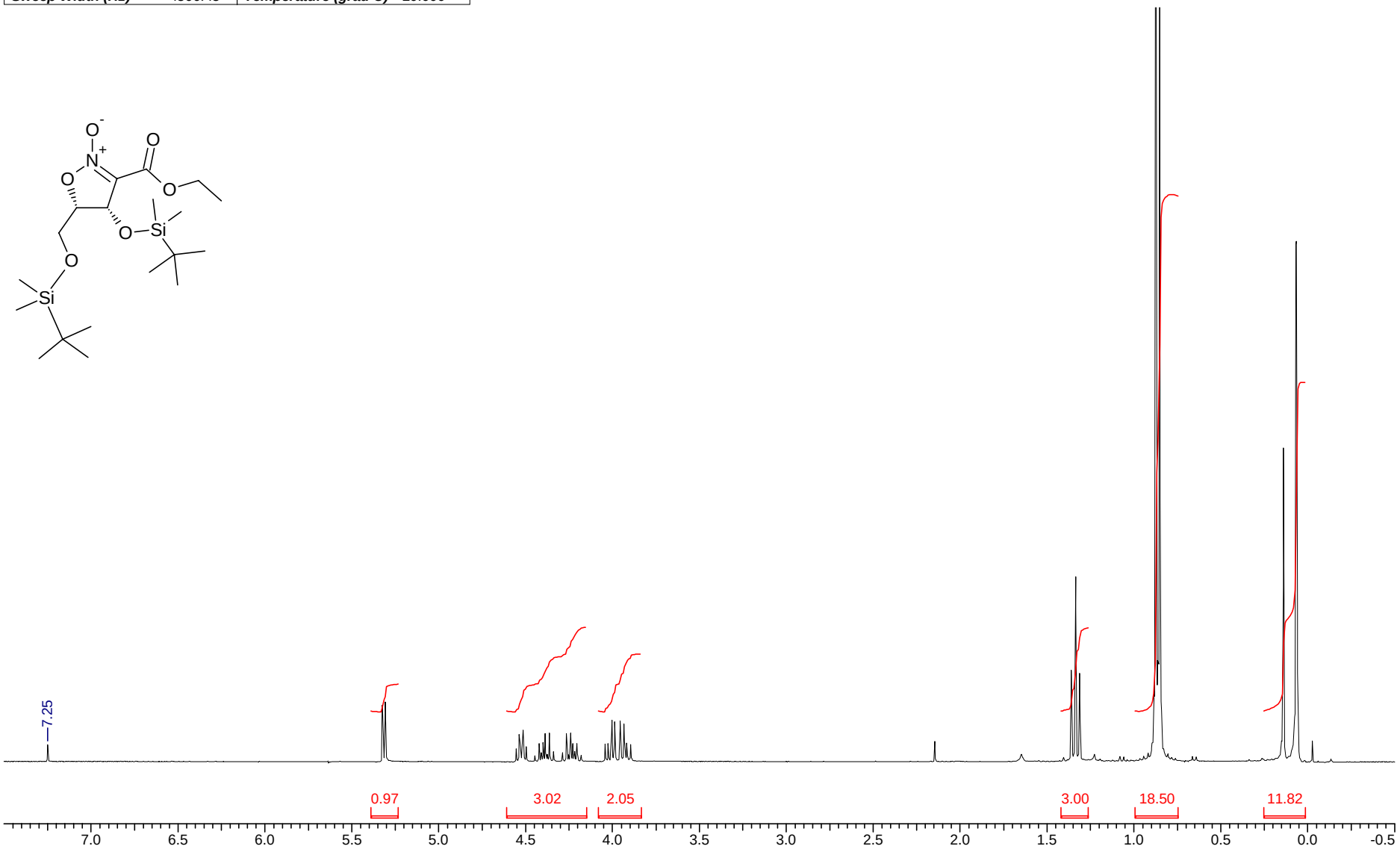
Sweep Width (Hz)	4500.45	***Temperature (grad C)***	20.000					



4,5-*cis*-4a

Acquisition Time (sec)	0.8192	***Comment***			***Date***	1-01-00	***Frequency (MHz)***	75.46
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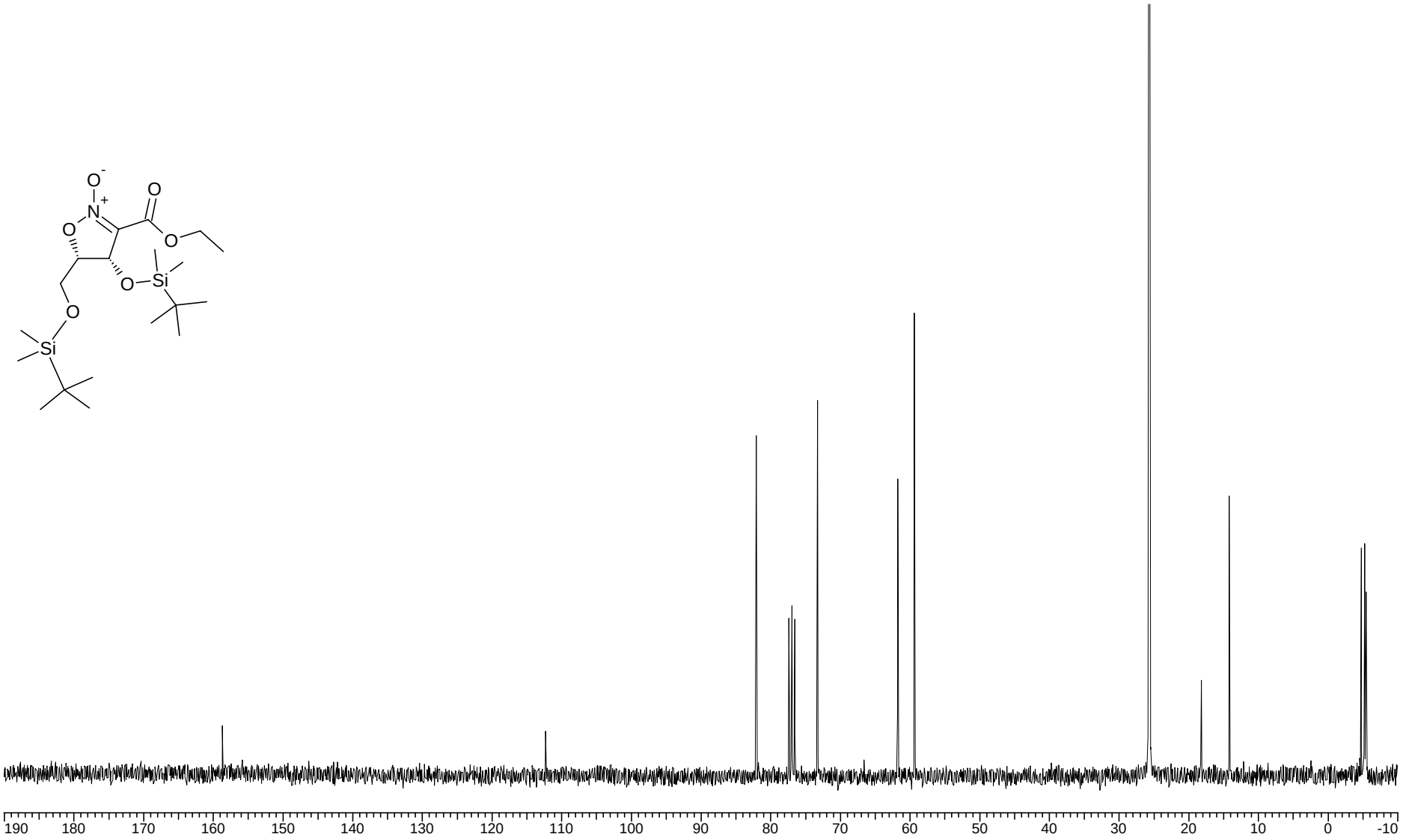
Temperature (grad C)	20.000							



4,5-*trans*-4b

Acquisition Time (sec)	3.6405	***Comment***				***Date***	1-04-00
Frequency (MHz)	300.08	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count*** 12000	***Points Count*** 16384
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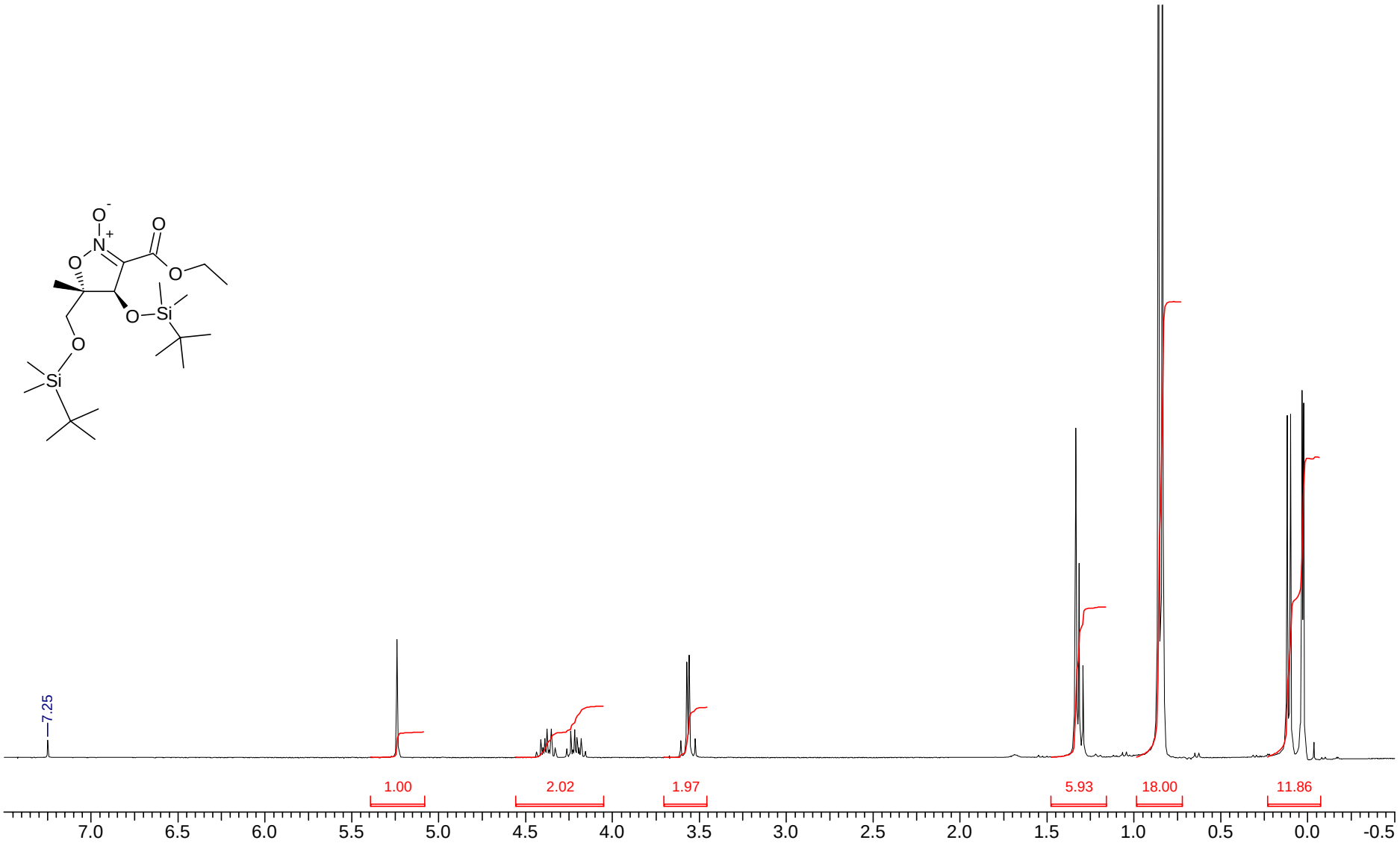

4,5-*trans*-4b

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-29-00	***Frequency (MHz)***	75.46	***Nucleus***	13C
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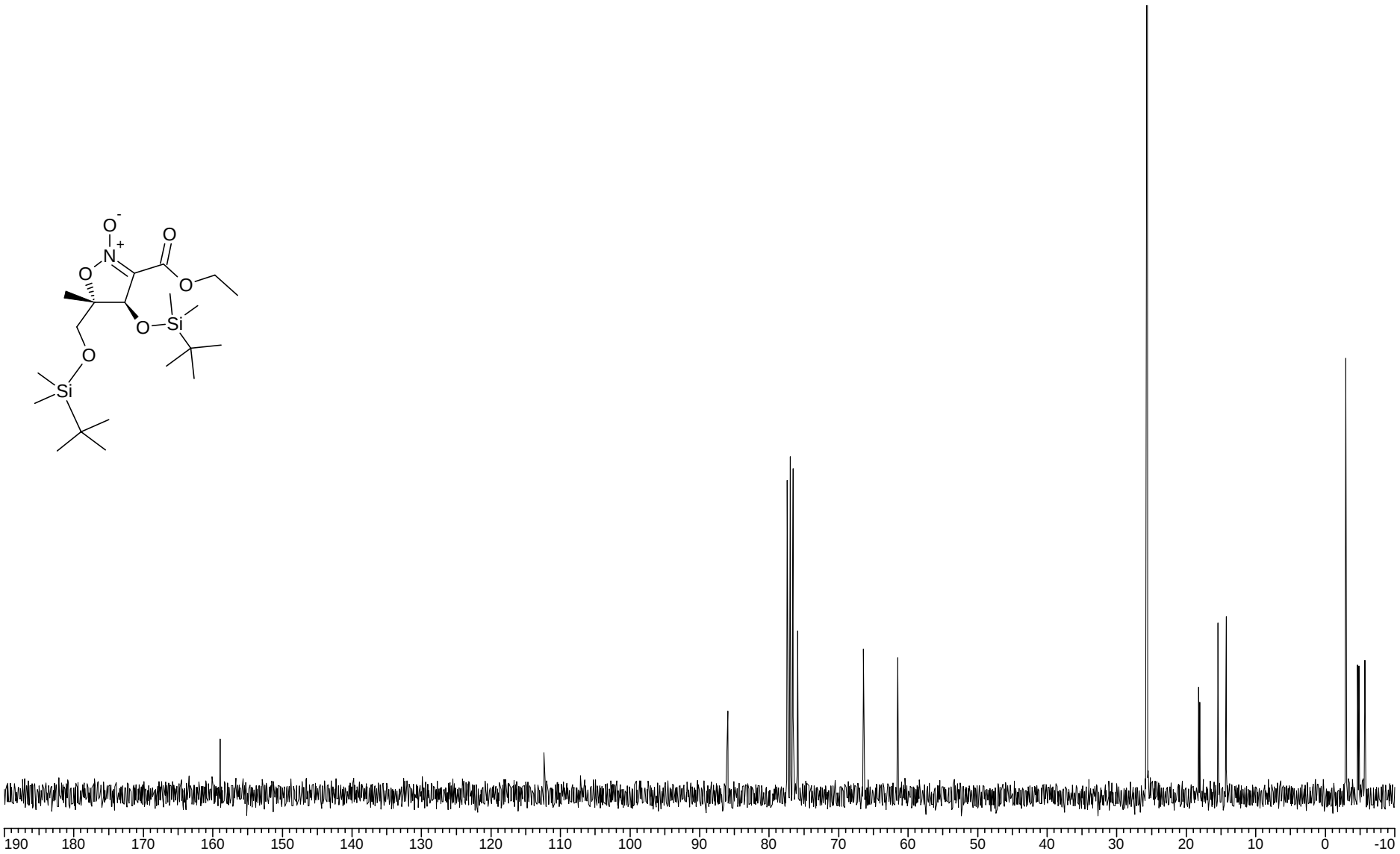
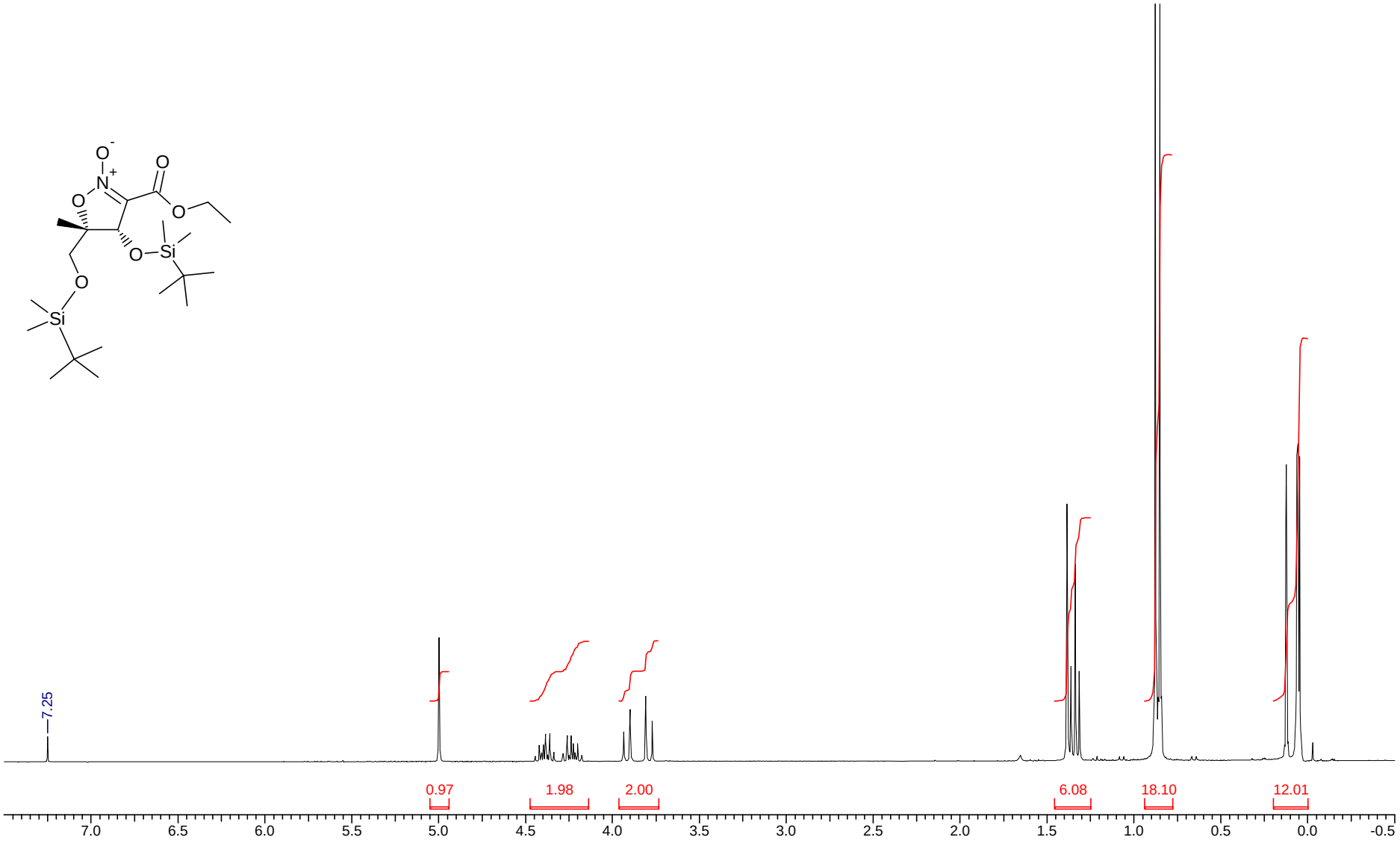


4,5-*cis*-4b

Acquisition Time (sec)	3.6405	***Comment***				***Date***	1-04-00
Frequency (MHz)	300.08	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count*** 12000	***Points Count*** 16384
Solvent	cdcl3	***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000		



4,5-*cis*-4b

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-29-00	***Frequency (MHz)***	75.46	***Nucleus***	13C
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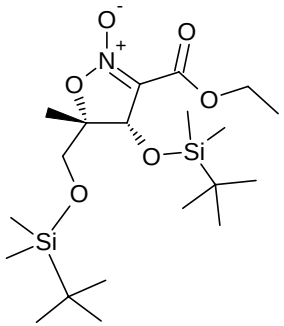

4,5-*trans*-5a

Acquisition Time (sec)	2.7304	***Comment***			***Date***	1-26-00		***Frequency (MHz)***	199.98
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Temperature (grad C)	20.000								

4,5-*trans*-5a

Acquisition Time (sec)	0.5464	***Comment***				***Date***	1-26-00	***Frequency (MHz)***	50.29	***Nucleus***	13C
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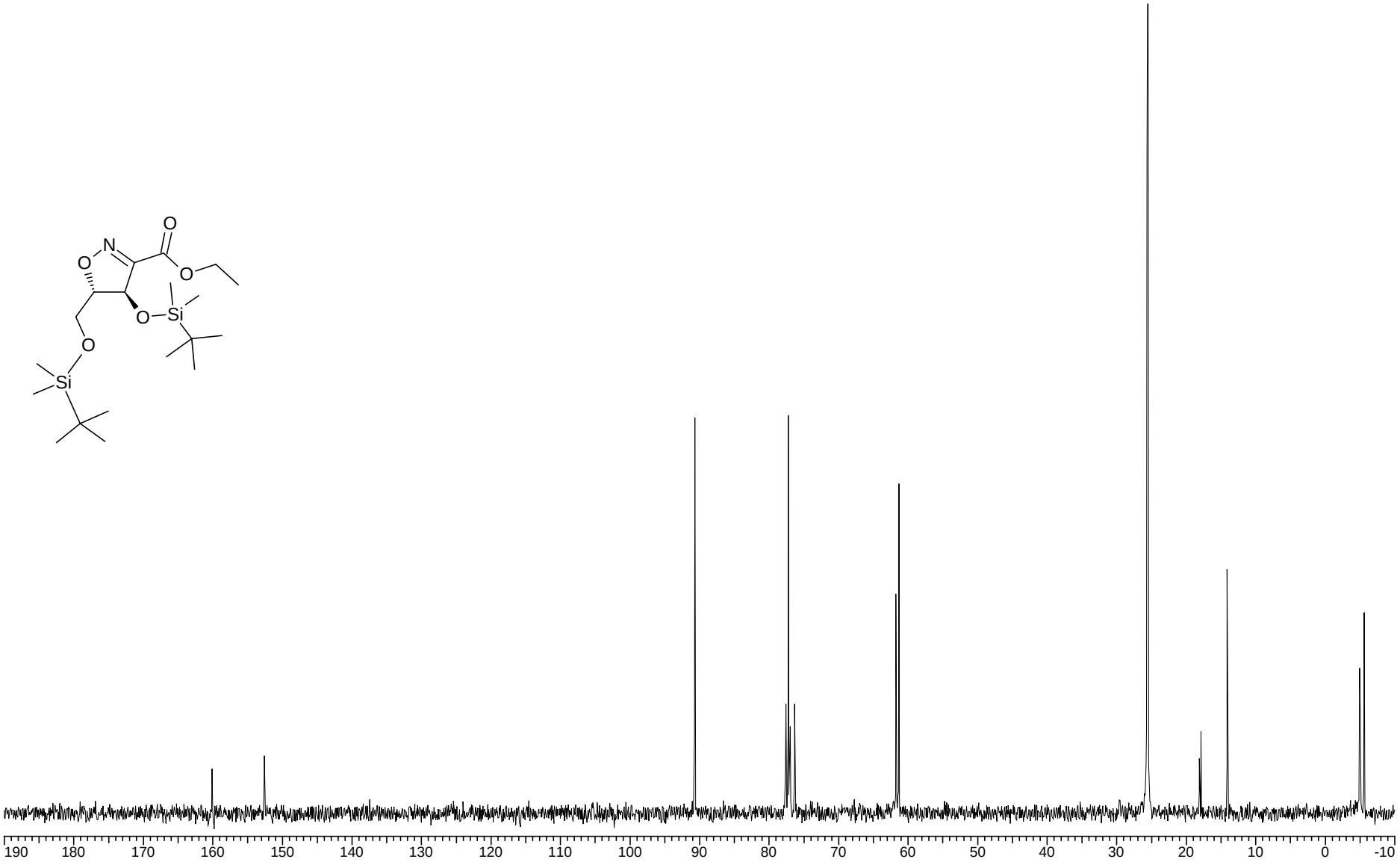

4,5-*cis*-5a

Acquisition Time (sec)	3.6405	***Comment***		***Date***	1-04-00	***Frequency (MHz)***	300.08
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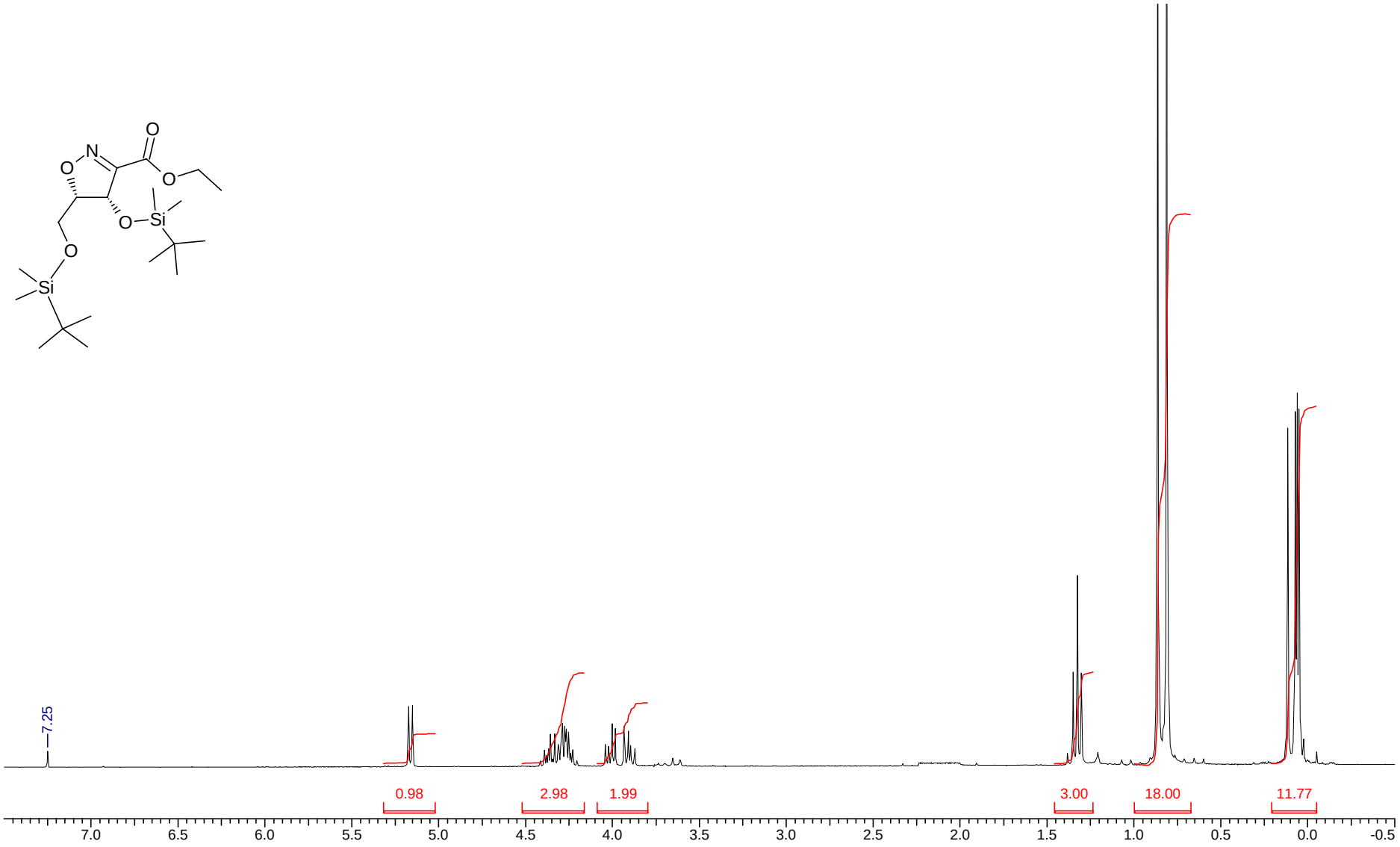
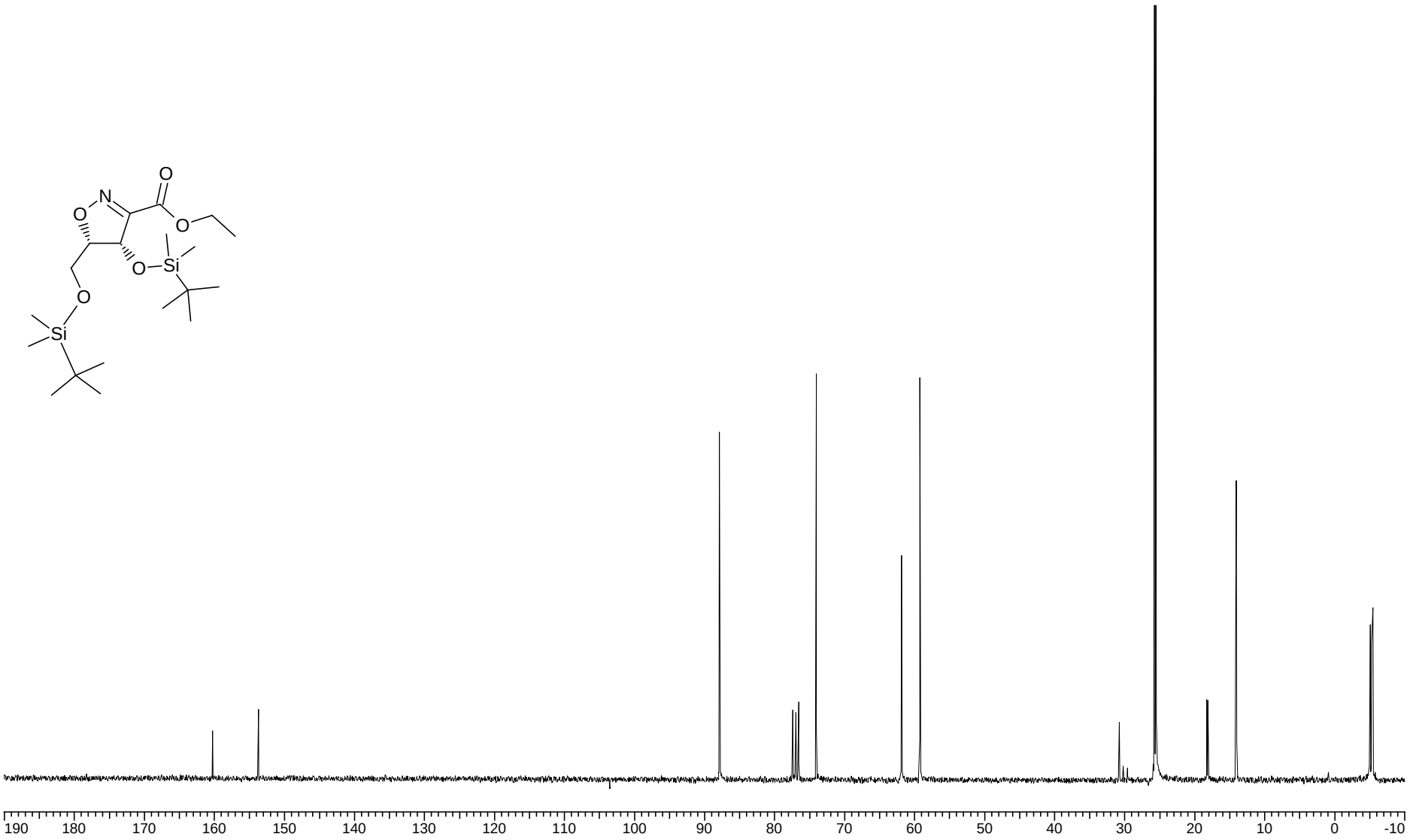
Sweep Width (Hz)	4500.45	***Temperature (grad C)***	20.000				



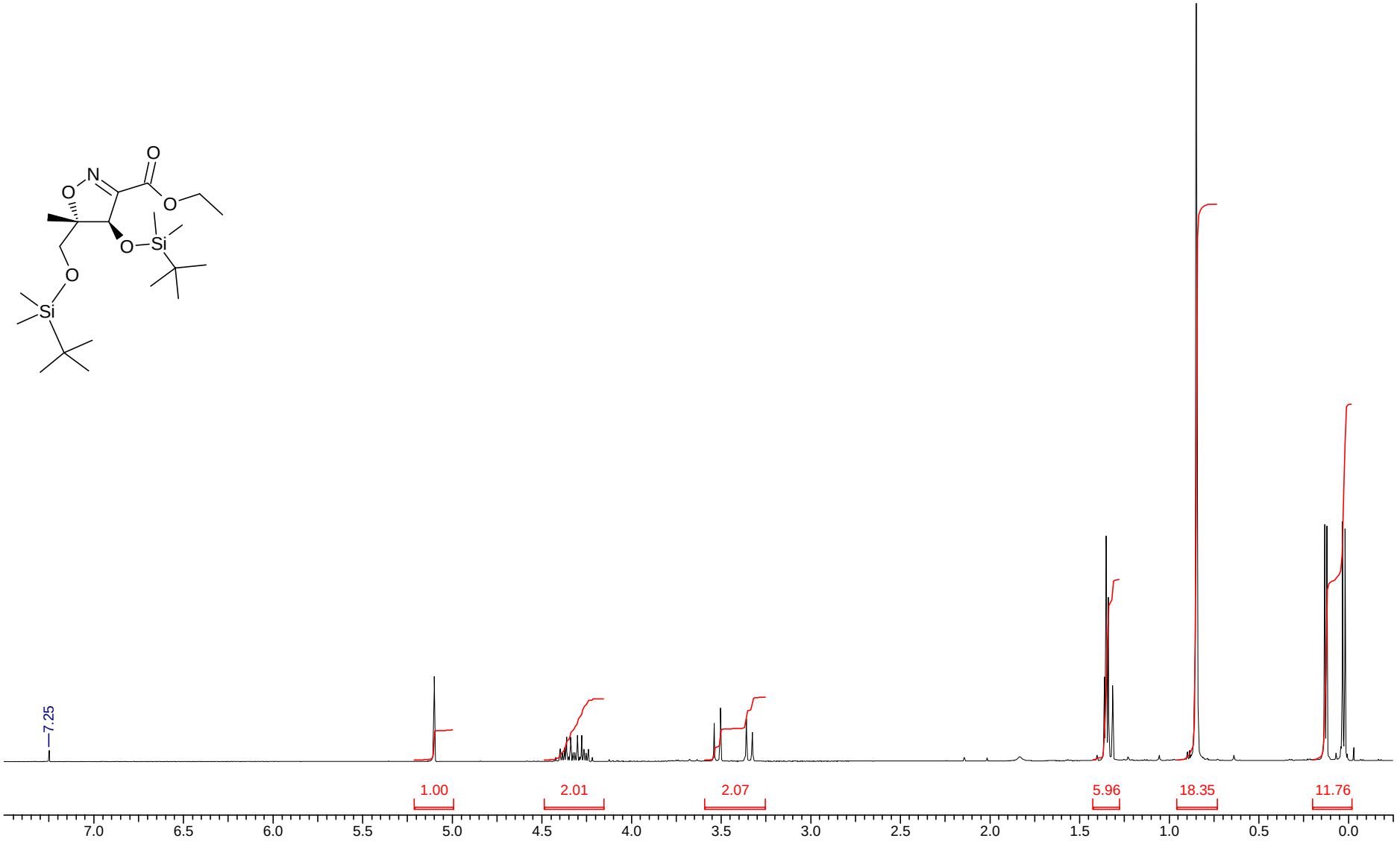
4,5-*cis*-5a

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-04-00
Frequency (MHz)	75.46	***Nucleus***	13C	***Original Points Count***	12000	***Points Count***	16384	***Solvent***	cdcl3
Sweep Width (Hz)	20000.00	***Temperature (grad C)***	20.000						



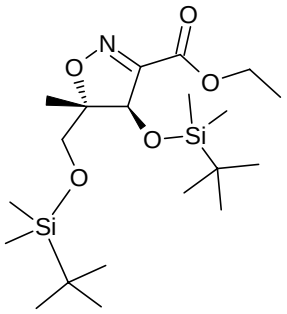
4,5-*trans*-5b

Acquisition Time (sec)	3.6405	***Comment***				***Date***	1-04-00
Frequency (MHz)	300.08	***Nucleus***	1H	***Number of Transients***	16	***Original Points Count*** 12000	***Points Count*** 16384
Solvent	cdcl3	***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000		



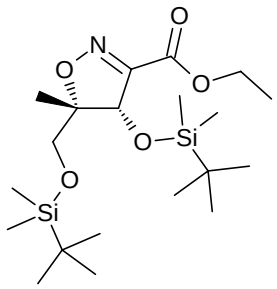
4,5-*trans*-5b

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-04-00
Frequency (MHz)	75.46	***Nucleus***	13C	***Original Points Count***	12000	***Points Count***	16384	***Solvent***	cdcl3
Sweep Width (Hz)	20000.00	***Temperature (grad C)***	20.000						



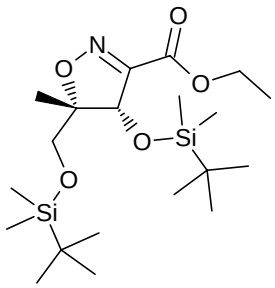
4,5-*cis*-5b

Acquisition Time (sec)	3.6405	***Comment***			***Date***	1-23-00	***Frequency (MHz)***	300.08	***Nucleus***	1H
Number of Transients	5	***Original Points Count***	12000	***Points Count*** 16384	***Solvent***	cdcl3	***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	29.000



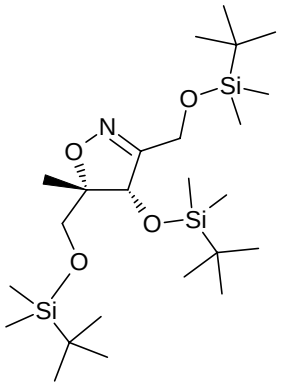
4,5-*cis*-5b

Acquisition Time (sec)	0.8192	***Comment***				***Date***	1-23-00	***Frequency (MHz)***	75.46	***Nucleus***	13C
Number of Transients	1000	***Original Points Count***	12000	***Points Count***	16384	***Solvent***	cdcl3	***Sweep Width (Hz)***	20000.00		
Temperature (grad C)	20.000										



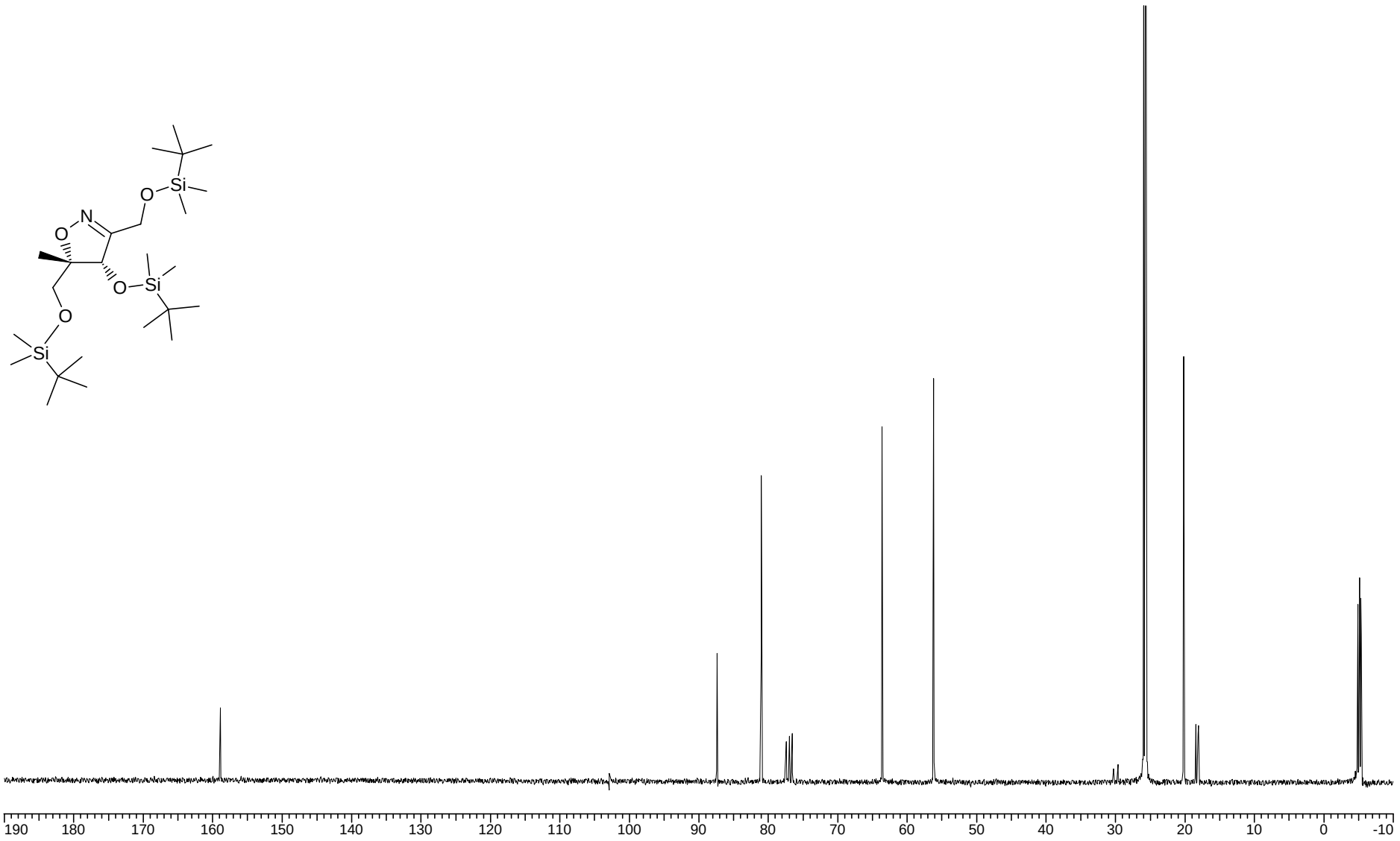
4,5-*cis*-6

Acquisition Time (sec)	3.6405	***Comment***			***Date***	1-04-00	***Frequency (MHz)***	300.08	***Nucleus***	1H
Number of Transients	16	***Original Points Count***	12000	***Points Count*** 16384	***Solvent***	cdcl3	***Sweep Width (Hz)***	4500.45	***Temperature (grad C)***	20.000



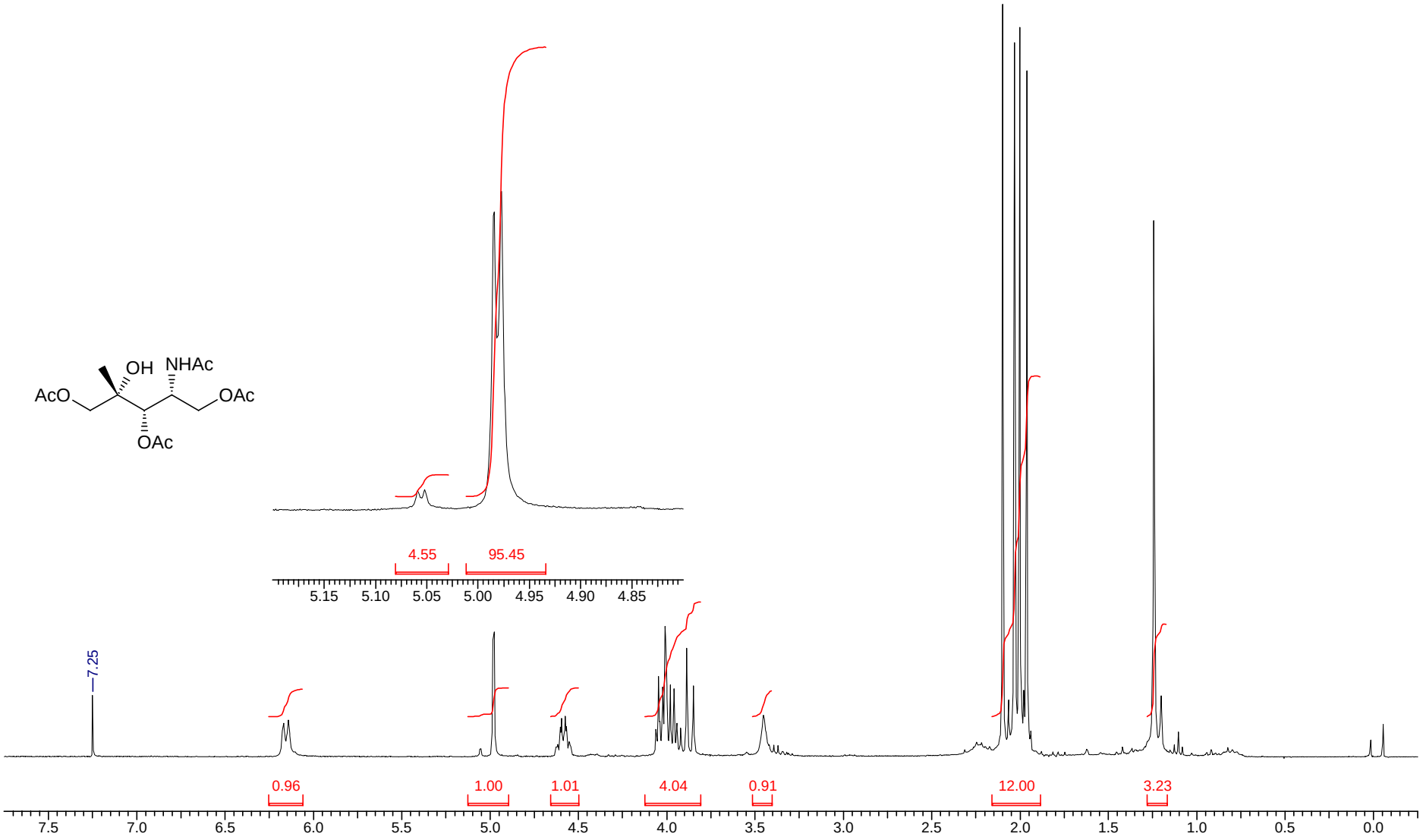
4,5-*cis*-6

Acquisition Time (sec)	0.8192	***Comment***			***Date***	1-04-00	***Frequency (MHz)***	75.46
Nucleus	13C	***Original Points Count***	12000	***Points Count*** 16384	***Solvent***	cdcl3	***Sweep Width (Hz)***	20000.00
Temperature (grad C)	20.000							



Tetraacetate 8

Acquisition Time (sec)	3.6405			***Comment***				***Date***	2-22-00
Frequency (MHz)	300.08			***Nucleus***	1H	***Number of Transients***	16	***Original Points Count***	12000	***Points Count***	16384
Solvent	cdcl3	***Sweep Width (Hz)***	4500.45			***Temperature (grad C)***	20.000		



Tetraacetate 8

Acquisition Time (sec)	0.8192			***Comment***				***Date***	2-22-00		
Frequency (MHz)	75.46	***Nucleus***	13C	***Number of Transients***	128	***Original Points Count***	12000	***Points Count***	16384	***Solvent***	cdcl3
Sweep Width (Hz)	20000.00			***Temperature (grad C)***	20.000