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Nitrone Cycloadditions to Isolevoglucosenone: a Ready Access to a New Class of Directly Linked (1→3)-Imino-*C*-disaccharides

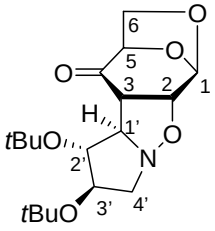
Org. Lett.

SUPPORTING INFORMATION

Experimental section

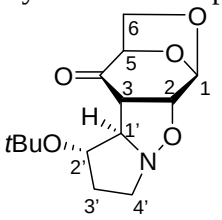
General Remarks: All operations were carried out under inert gas and with anhydrous solvents where required. R_f values refer to TLC on 0.25-mm silica gel plates (Merck F_{254}) with the same eluent used for separation of the compound by flash column chromatography. Melting points (m.p.) were measured with an RCH Kofler apparatus and are uncorrected. Optical rotation measurements were carried out with a Jasco DIP-370 polarimeter or a Perkin-Elmer 241 polarimeter. NMR spectra were recorded with Varian Gemini (^{1}H, 200 MHz) or Avance Bruker (^{1}H, 400 MHz, 500 MHz, 600 MHz) instruments, the NMR spectroscopic data are reported in δ (ppm) from TMS at 25 °C. IR spectra were recorded with a Perkin-Elmer 881 spectrophotometer. Mass spectra (EI, 70 eV) were recorded with a QMD 1000 Carlo Erba instrument by direct inlet. Elemental analyses were carried out with a Perkin-Elmer 2400 instrument.

Synthesis of compound **13**.



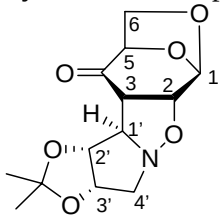
A solution of nitrone **11** (68.7 mg, 0.3 mmol) and isolevoglucosenone (**7**, 37.8 mg, 0.3 mmol) in toluene (0.6 mL) was stirred at room temperature for 1.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent petroluem ether/AcOEt, 4:1) gave **13** as a white solid (R_f = 0.33, 95 mg, 0.268 mmol, 89%). - m.p. 93-95 °C; $[\alpha]_D^{20}$ = -25.3 (c = 0.97, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 5.58 (s, 1 H, H-1), 4.61 (t, *J* = 3.4 Hz, 1 H, H-5), 4.36 (d, *J* = 7.6 Hz, 1 H, H-2), 4.02 (br s, 1 H, H-2'), 3.91-3.86 (m, 3 H, Ha-6, Hb-6, H-3'), 3.65 (dd, *J* = 12.2, 6.4 Hz, 1 H, Ha-4'), 3.63 (br d, *J* = 6.4 Hz, 1 H, H-1'), 3.41 (dd, *J* = 7.6, 7.3 Hz, 1 H, H-3), 2.67 (dd, *J* = 12.2, 4.9 Hz, 1 H, Hb-4'), 1.17 (s, 9 H, *t*Bu), 1.14 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 203.5 (s, C=O), 100.5 (d, C-1), 80.5 (d, C-2'), 78.5 (d, C-5), 77.7 (d, C-3'), 76.5 (d, C-2), 75.2 (d, C-1'), 74.6 (s, 1 C, $(CH_3)_3C$-O), 74.0 (s, 1 C, $(CH_3)_3C$-O), 66.2 (t, C-6), 61.9 (t, C-4'), 54.1 (d, C-3), 28.2 (q, 6 C, $(CH_3)_3$C-O). MS, m/z (%): 355 (M^+, 12), 298 (M^+ - *t*Bu, 19), 241 (13), 168 (29), 85 (53), 83 (99.6), 81 (39), 56 (100). IR (KBr): 2969, 2934, 2900, 1733, 1471, 1371 cm^{-1}. $C_{18}H_{29}NO_6$ (355.43): calcd. C 60.83, H 8.22, N 3.94; found C 61.05, H 8.30, N 3.78.

Synthesis of compound **14**.



A solution of nitrone **12** (25.1 mg, 0.16 mmol) and isolevoglucosenone (**7**, 20.2 mg, 0.16 mmol) in toluene (0.32 mL) was stirred at room temperature for 2.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent petroluem ether/AcOEt, 2:1) gave **14** as a white solid (R_f = 0.28, 40.2 mg, 0.142 mmol, 89%). - m.p. 103-105 °C; $[\alpha]_D^{25}$ = +18.4 (c = 0.67, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.62 (s, 1 H, H-1), 4.66 (dd, *J* = 3.7, 3.3 Hz, 1 H, H-5), 4.27 (d, *J* = 7.7 Hz, 1 H, H-2), 4.07 (dt, *J* = 7.3, 3.3 Hz, 1 H, H-2'), 3.95-3.86 (m, 2 H, Ha-6, Hb-6), 3.71 (dd, *J* = 4.0, 3.3 Hz, 1 H, H-1'), 3.36 (dt, *J* = 12.8, 7.7 Hz, 1 H, Ha-4'), 3.16 (dd, *J* = 7.7, 4.0 Hz, 1 H, H-3), 3.19-3.04 (m, 1 H, Hb-4'), 2.39-2.21 (m, 1 H, Ha-3'), 1.80-1.65 (m, 1 H, Hb-3'), 1.19 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 203.2 (s, C=O), 101.6 (d, C-1), 78.3 (d, C-5), 77.2 (d, C-1'), 76.6 (d, C-2), 75.8 (d, C-2'), 74.0 (s, 1 C, $(CH_3)_3C$-O), 66.5 (t, C-6), 55.2 (d, C-3), 54.7 (t, C-4'), 33.2, (t, C-3'), 28.4 (q, 3 C, $(CH_3)_3$C-O). MS, m/z (%): 284 (M^++1, 4), 227 (M^+-*t*Bu, 35), 184 (10), 152 (22), 84 (88), 57 (100). IR (KBr): 2983, 1726 cm^{-1}. $C_{14}H_{21}NO_5$ (283.32): calcd. C 59.35, H 7.47, N 4.94; found C 59.64, H 7.41, N 5.10.

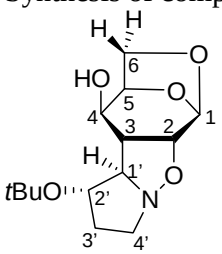
Synthesis of compound **16**.



A solution of nitrone **15** (53.4 mg, 0.34 mmol) and isolevoglucosenone (**7**, 21.4 mg, 0.17 mmol) in toluene (0.34 mL) was stirred at room temperature for 2.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography with an eluent of increasing polarity afforded **16** (R_f = 0.23, eluent pentane/AcOEt, 3:2, 31.1 mg, 0.11 mmol, 32%) and the recovered (-)-**15** (R_f = 0.29, eluent AcOEt/MeOH, 10:1, 27 mg, 0.172 mmol, 50%).

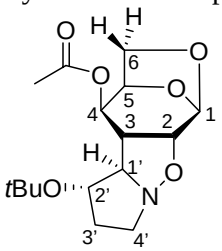
16: white solid. Crystals for X-ray crystal structure determination were obtained by slow evaporation from AcOEt. - m.p. 165-167 °C; $[\alpha]_D^{26}$ = +50.8 (c = 0.44, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 5.55 (s, 1 H, H-1), 4.87 (dd, *J* = 5.9, 5.5 Hz, 1 H, H-3'), 4.78 (d, *J* = 6.6 Hz, 1 H, H-2'), 4.67 (dd, *J* = 4.4, 2.2 Hz, 1 H, H-5), 4.33 (d, *J* = 8.4 Hz, 1 H, H-2), 3.91-3.87 (m, 3 H, Ha-6, Hb-6, H-1'), 3.51 (d, *J* = 12.5 Hz, 1 H, Ha-4'), 3.02 (dd, *J* = 8.4, 8.1 Hz, 1 H, H-3), 2.87 (dd, *J* = 12.5, 5.1 Hz, 1 H, Hb-4'), 1.50 (s, 3 H, Me), 1.30 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 202.9 (s, C=O), 112.2 (s, 1 C, $(CH_3)_2C$) 101.2 (d, C-1), 81.1 (d, C-2'), 78.5 (d, C-5), 78.3 (d, C-3'), 77.1 (d, C-2), 75.4 (d, C-1'), 66.9 (t, C-6), 59.5 (t, C-4'), 53.1 (d, C-3), 26.3 (q, 1 C, $(CH_3)_2$C), 24.8 (q, 1 C, $(CH_3)_2$C). MS, m/z (%): 283 (M^+, 5), 268 (M^+-Me, 2), 183 (3), 149 (5), 86 (69), 84 (100), 51 (44). IR (KBr): 2980, 2946, 2920, 1725 cm^{-1}. $C_{13}H_{17}NO_6$ (283.28): calcd. C 55.12, H 6.05, N 4.94; found C 55.11, H 5.98, N 4.72.

Synthesis of compound **17**.



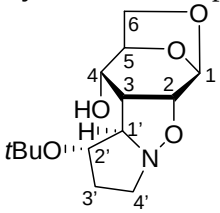
A 1.5 M solution of DIBAL-H in toluene (0.5 mL, 0.75 mmol), was added dropwise under nitrogen atmosphere to a solution of **14** (141.5 mg, 0.5 mmol) in dry CH_2Cl_2 (1 mL), cooled to –78°C. After stirring at –78 °C for 4 h, cooled MeOH (–78°C, 200 μL) was added and the cooling bath was removed. Once at 0°C, 1 M aq HCl (1 mL) was added. The mixture was extracted with CH_2Cl_2 (20 mL, 4 times). The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (5 mL), dried over Na_2SO_4, filtered and concentrated. Purification of the crude reaction mixture by flash column chromatography (eluent AcOEt/pentane, 4:1) gave **17** as a waxy solid (R_f = 0.31, 106 mg, 0.372 mmol, 74%). $[\alpha]_D^{26}$ = -21.9 (c = 0.51, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 5.43 (s, 1 H, H-1), 4.46-4.44 (m, 1 H, H-5), 4.09 (dd, *J* = 7.5, 0.7 Hz, 1 H, H_{endo}-6), 4.05 (dd, *J* = 8.1, 4.2 Hz, 1 H, H-4), 3.86 (dd, *J* = 5.9, 1.8 Hz, 1 H, H-2), 3.79 (dt, *J* = 7.0, 4.0 Hz, 1 H, H-2'), 3.73 (dd, *J* = 7.5, 5.9 Hz, 1 H, H_{exo}-6), 3.47-3.45 (m, 1 H, H-1'), 3.34-3.30 (m, 2 H, H-4'), 2.51 (dd, *J* = 8.1, 5.9 Hz, 1 H, H-3), 2.14-2.08 (m, 1 H, Ha-3'), 1.73-1.67 (m, 1 H, Hb-3'), 1.20 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 98.3 (d, C-1), 78.0 (d, 1 C), 76.6 (d, 1 C), 76.3 (d, 1 C), 75.1 (d, 1 C), 74.0 (s, 1 C, $(CH_3)_3C$-O), 68.3 (d, C-1'), 62.8 (t, C-6), 56.7 (t, C-4'), 50.5 (d, C-3), 34.7, (t, C-3'), 28.6 (q, 3 C, $(CH_3)_3$C-O). MS, m/z (%): 228 (M^+-*t*Bu, 38), 200 (5), 136 (25), 84 (69), 57 (100). IR ($CDCl_3$): 3612, 3379 (broad), 2977, 1365 cm^{-1}.

Synthesis of compound **18**.



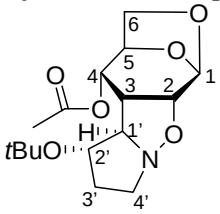
A mixture of **17** (51.3 mg, 0.18 mmol) in pyridine (0.3 mL) and acetic anhydride (0.2 mL) was stirred at room temperature for 5.5 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent AcOEt/pentane, 1:1) gave **18** as a white solid (R_f = 0.42, 44.1 mg, 0.135 mmol, 75%). - m.p. 177-178 °C; $[\alpha]_D^{26}$ = -43.7 (c = 0.81, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.45 (br s, 1 H, H-1), 5.12 (dd, *J* = 8.1, 4.4 Hz, 1 H, H-4), 4.60 (t, *J* = 4.8 Hz, 1 H, H-5), 4.00 (d, *J* = 7.7 Hz, 1 H, H_{endo}-6), 3.90 (br d, *J* = 5.9 Hz, 1 H, H-2), 3.79-3.70 (m, 2 H, H_{exo}-6, H-2'), 3.40 (d, *J* = 3.7 Hz, 1 H, H-1'), 3.34-3.26 (m, 2 H, H-4'), 2.65 (dd, *J* = 8.1, 6.2 Hz, 1 H, H-3), 2.18-2.00 (m, 1 H, Ha-3'), 2.05 (s, 3 H, Me), 1.76-1.60 (m, 1 H, Hb-3'), 1.16 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 169.6 (s, C=O), 98.6 (d, C-1), 78.2 (d, 1 C), 76.5 (d, 1 C), 76.1 (d, 1 C), 73.5 (s, 1 C, $(CH_3)_3C$-O), 71.9 (d, 1 C), 70.4 (d, 1 C), 63.2 (t, C-6), 56.6 (t, C-4'), 47.7 (d, C-3), 34.7 (t, C-3'), 28.9 (q, 3 C, $(CH_3)_3$C-O), 20.8 (q, 1 C, CH_3C=O). MS, m/z (%): 327 (M^+, 13), 270 (M^+-*t*Bu, 95), 210 (39), 136 (42), 58 (65), 55 (100). IR (KBr): 2973, 2935, 1728, 1367, 1243, 1231 cm^{-1}. $C_{16}H_{25}NO_6$ (327.37): calcd. C 58.70, H 7.70, N 4.28; found C 58.91, H 8.04, N 4.33.

Synthesis of compound **19**.



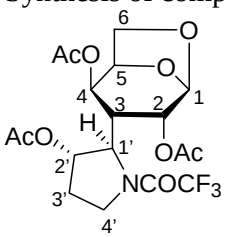
$NaBH_4$ (40 mg, 1.06 mmol), was slowly added to a solution of **14** (86.9 mg, 0.307 mmol) in ethanol (4 mL), cooled to 0°C. After 10 minutes the cooling bath was removed and the mixture was stirred at room temperature for 2.5 h. After concentration under reduced pressure, CH_2Cl_2 (10 mL) and water (10 mL) were added and the two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (5 mL, 3 times). The combined organic phases were dried over Na_2SO_4, filtered and concentrated, to give a 4:1 mixture of alcohols **19** and **17** (determined by 200 MHz ^{1}H NMR integration). Purification of the crude reaction mixture by flash column chromatography with an eluent of increasing polarity afforded **19** (R_f = 0.14, AcOEt /petroleum ether, 2:1, 61.8 mg, 0.217 mmol, 71%) and **17** (R_f = 0.25, eluent AcOEt/ petroleum ether, 3:1, 17.1 mg, 0.06 mmol, 19%).
19: viscous oil. $[\alpha]_D^{26}$ = -86.4 (c = 0.73, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 5.50 (br s, 1 H, H-1), 4.56 (dm, *J* = 5.9 Hz, 1 H, H-5), 3.84-3.80 (m, 2 H), 3.75 (dd, *J* = 7.9, 1.3 Hz, 1 H), 3.73 (dd, *J* = 5.1, 1.8 Hz, 1 H), 3.64-3.62 (m, 2 H), 3.39-3.29 (m, 2 H, H-4'), 2.83 (t, *J* = 5.9 Hz, 1 H, H-3), 2.16-2.10 (m, 1 H, Ha-3'), 1.73-1.67 (m, 1 H, Hb-3'), 1.18 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 98.0 (d, C-1), 77.4 (d, 1 C), 76.0 (d, 1 C), 74.8 (d, 1 C), 73.6 (s, 1 C, $(CH_3)_3C$-O), 73.4 (d, 1 C), 66.3 (d, C-1'), 64.1 (t, C-6), 56.3 (t, C-4'), 44.1 (d, C-3), 34.2 (t, C-3'), 28.5 (q, 3 C, $(CH_3)_3$C-O). MS, m/z (%): 285 (M^+, 6), 228 (M^+-*t*Bu, 100), 200 (9), 86 (61), 84 (99), 57 (61). IR ($CDCl_3$): 3547, 3381 (broad), 2977, 2899, 1364 cm^{-1}.

Synthesis of compound **20**.



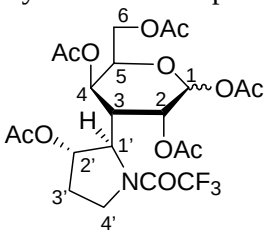
A mixture of **19** (19.1 mg, 0.067 mmol) in pyridine (0.3 mL) and acetic anhydride (0.15 mL) was stirred at room temperature for 16 h. After concentration under reduced pressure, purification of the crude reaction mixture by flash column chromatography (eluent AcOEt) gave **20** as a white solid (R_f = 0.17, 19.6 mg, 0.06 mmol, 90%). Crystals for X-ray crystal structure determination were obtained by slow evaporation from AcOEt. - m.p. 172-174 °C; $[\alpha]_D^{26}$ = -124.7 (c = 0.28, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 5.54 (s, 1 H, H-1), 4.87 (dd, *J* = 7.0, 1.8 Hz, 1 H, H-4), 4.61-4.59 (m, 1 H, H-5), 3.84-3.81 (m, 2 H, H-6), 3.81-3.76 (m, 2 H, H-2, H-2'), 3.41 dt (*J* = 12.4, 7.0 Hz, 1 H, Ha-4'), 3.39 (d, *J* = 4.4 Hz, 1 H, H-1'), 3.15 (dt, *J* = 12.4, 7.1 Hz, 1 H, Hb-4'), 2.82 (dd, *J* = 6.7, 6.1 Hz, 1 H, H-3), 2.20 (s, 3 H, Me), 2.04 (dq, *J* = 12.7, 6.5 Hz, 1 H, Ha-3'), 1.70-1.65 (m, 1 H, Hb-3'), 1.19 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 171.2 (s, C=O), 98.8 (d, C-1), 77.3 (d, 1 C), 74.6 (d, 1 C), 73.7 (s, 1 C, $(CH_3)_3C$-O), 73.3 (d, 1 C), 72.9 (d, 1 C), 67.6 (d, 1 C), 64.9 (t, C-6), 56.1 (t, C-4'), 44.1 (d, C-3), 33.5 (t, C-3'), 28.6 (q, 3 C, $(CH_3)_3$C-O), 21.3 (q, 1 C, CH_3C=O). MS, m/z (%): 327 (M^+, 13), 312 (M^+-Me, 0.3), 270 (M^+-*t*Bu, 100), 226 (8), 163 (18), 84 (52), 58 (49), 57 (26), 55 (98). IR ($CDCl_3$): 2977, 1735, 1374, 1238 cm^{-1}. $C_{16}H_{25}NO_6$ (327.37): calcd. C 58.70, H 7.70, N 4.28; found C 58.75, H 7.85, N 4.56.

Synthesis of compound **24**.



A mixture of alcohol **17** (42.8 mg, 0.15 mmol) and *p*-toluenesulfonic acid (51.6 mg, 0.3 mmol) in MeOH (1 mL) was heated at reflux for 3.5 h. Evaporation of the solvent afforded crude **21**, that was again dissolved in MeOH (10 mL) and stirred under H_2 atmosphere over $Pd(OH)_2/C$ (50 mg) at room temperature for 12 h. The catalyst was filtered off and the solvent evaporated under reduced pressure. Crude **22** was then dissolved in trifluoroacetic anhydride (2 mL) and trifluoroacetic acid (4 mL) and the mixture was stirred at room temperature overnight. The mixture was concentrated and the residue was dissolved in MeOH (6 mL). 6 Drops of 35% aqueous NH_3 were added, and after 10 minutes the solvent was evaporated under reduced pressure, affording crude **23**, that was dissolved in pyridine (1.2 mL) and acetic anhydride (0.4 mL). After stirring at room temperature overnight, the mixture was concentrated under reduced pressure and filtered over silica gel (eluent AcOEt), affording **24** as a white foam (R_f = 0.86, 20 mg, 0.044 mmol, 29% yield from **17**). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 5.59-5.56 (m, 1 H, H-2'), 5.41 (d, *J* = 2.2 Hz, 1 H, H-1), 5.15 (dd, *J* = 11.4, 4.4 Hz, 1 H, H-4), 4.90 (dd, *J* = 4.3, 2.2 Hz, 1 H, H-2), 4.59 (t, *J* = 4.4 Hz, 1 H, H-5), 4.35 (d, *J* = 4.8 Hz, 1 H, H-1'), 4.02 (d, *J* = 8.0 Hz, 1 H, H_{endo}-6), 3.87-3.59 (m, 2 H, H-4'), 3.69 (dd, *J* = 8.0, 5.1 Hz, 1 H, H_{exo}-6), 2.78 (ddd, *J* = 11.4, 4.8, 4.3 Hz, 1 H, H-3), 2.19-2.02 (m, 2 H, H-3'), 2.09 (s, 3 H, Me), 2.08 (s, 3 H, Me), 2.04 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz, detected signals) δ = 170.2 (s, C=O), 169.9 (s, C=O), 169.6 (s, C=O), 98.6 (d, C-1), 74.3 (d, 1 C), 71.7 (d, 1 C), 71.1 (d, 1 C), 68.6 (d, 1 C), 64.8 (d, 1 C), 64.1 (t, C-6), 44.2 (t, C-4'), 34.9 (d, C-3), 30.6 (t, C-3'), 20.9 (q, 1 C, *C*H_3C=O), 20.8 (q, 1 C, *C*H_3C=O), 20.7 (q, 1 C, *C*H_3C=O).

Synthesis of compounds **25**α**,** **25**β.



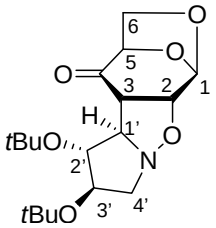
The triacetate **24** (20 mg, 0.0442 mmol) was dissolved in acetic anhydride (1.5 mL) and trifluoroacetic acid (1 mL) was added. After stirring at room temperature overnight, the mixture was diluted with ethyl acetate (20 mL) and washed with a 5% aqueous solution of $NaHCO_3$. The aqueous phase was again extracted with ethyl acetate (10 mL) and the combined organic phases dried over Na_2SO_4, filtered and concentrated to afford a 1.4:1 mixture (determined by 200 MHz ^{1}H NMR integration) of **25**β and **25**α. Purification of the crude reaction mixture by flash column chromatography (eluent petroleum ether/AcOEt, 3:2) gave **25**β (R_f = 0.32, 16.4 mg, 0.0295 mmol, 67%, impure of **25**α, ratio **25**β/**25**α = 5.5/1) and **25**α (R_f = 0.32, 6.4 mg, 0.0115 mmol, 26%), both as viscous oils that are inclined to retain solvents.

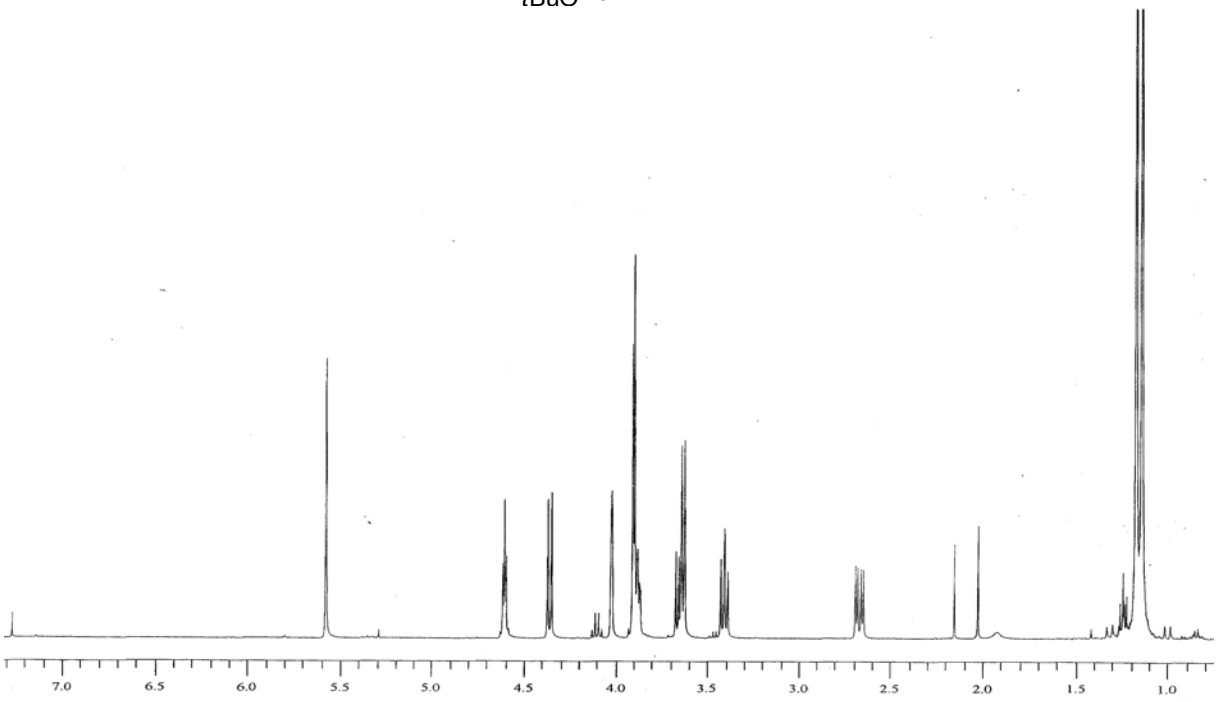
25β:$[\alpha]_D^{22}$ = -31.3 (c = 0.43, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.08 (d, *J* = 4.2 Hz, 1 H, H-1), 5.47 (d, *J* = 4.4 Hz, 1 H, H-2'), 5.41 (dd, *J* = 8.2, 4.4 Hz, 1 H, H-4), 5.00 (t, *J* = 3.9 Hz, 1 H, H-2), 4.52 (d, *J* = 8.2 Hz, 1 H, H-1'), 4.47 (td, *J* = 6.5, 4.5 Hz, 1 H, H-5), 4.24 (dd, *J* = 11.5, 6.7 Hz, 1 H, Ha-6), 4.18 (dd, *J* = 11.5, 6.4 Hz, 1 H, Hb-6), 3.95-3.88 (m, 1 H, Ha-4'), 3.66-3.61 (m, 1 H, Hb-4'), 2.66 (td, *J* = 8.2, 3.6 Hz, 1 H, H-3), 2.38-2.27 (m, 2 H, H-3'), 2.13 (s, 3 H, Me), 2.11 (s, 3 H,

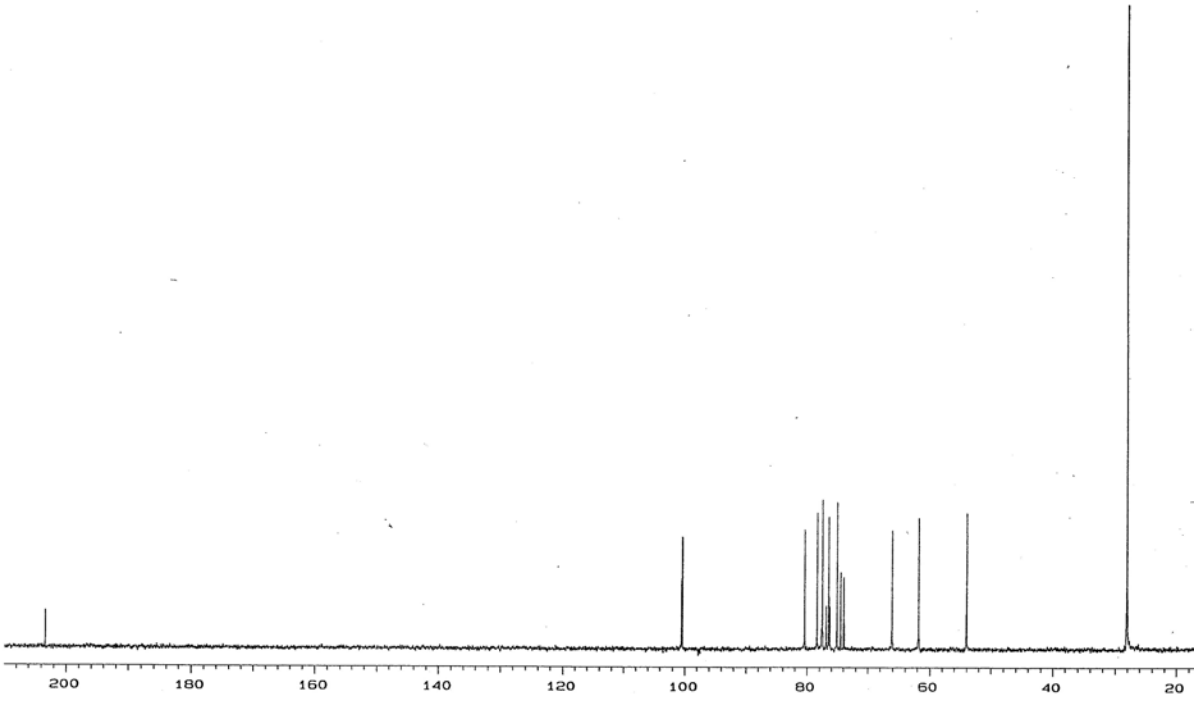
Me), 2.08 (s, 3 H, Me), 2.06 (s, 3 H, Me), 2.03 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz, detected signals) δ = 170.4 (s, C=O), 170.2 (s, C=O), 170.1 (s, C=O), 169.9 (s, C=O), 168.2 (s, C=O), 89.8 (d, C-1), 74.7 (d, 1 C), 69.9 (d, 1 C), 69.0 (d, 1 C), 68.2 (d, 1 C), 63.9 (d, 1 C), 62.4 (t, C-6), 44.3 (t, C-4'), 36.6 (d, C-3), 29.5 (t, C-3'), 21.1 (q, 1 C, *C*H_3C=O), 20.9 (q, 1 C, *C*H_3C=O), 20.8 (q, 2 C, *C*H_3C=O), 20.7 (q, 1 C, *C*H_3C=O). MS, m/z (%): 512 (M^+ - CH_3CO, 3), 496 (M^+ - CH_3COO, 25), 435 (10), 380 (10), 333 (26), 224 (100), 166 (58), 164 (96). IR ($CDCl_3$): 2963, 2928, 2855, 1747, 1697, 1447, 1372, 1231 cm^{-1}. $C_{22}H_{28}F_3NO_{12}$ (555.16): calcd. C 47.57, H 5.08, N 2.52; found C 47.94, H 5.18, N 2.60.

25α: $[\alpha]_D^{22}$ = +9.8 (c = 0.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.20 (d, *J* = 4.1 Hz, 1 H, H-1), 5.38-5.36 (m, 2 H, H-2', H-4), 5.33 (dd, *J* = 3.9, 3.8 Hz, 1 H, H-2), 4.75 (d, *J* = 7.4 Hz, 1 H, H-1'), 4.51 (td, *J* = 6.3, 3.1 Hz, 1 H, H-5), 4.18-4.10 (m, 2 H, H-6), 3.90-3.83 (m, 1 H, Ha-4'), 3.69-3.63 (m, 1 H, Hb-4'), 2.51-2.41 (m, 2 H, H-3, Ha-3'), 2.21-2.10 (m, 1 H, Hb-3'), 2.12 (s, 3 H, Me), 2.10 (s, 3 H, Me), 2.08 (s, 3 H, Me), 2.08 (s, 3 H, Me), 2.03 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$, 50 MHz, detected signals) δ = 170.5 (s, 2 C, C=O), 170.4 (s, C=O), 169.9 (s, C=O), 169.1 (s, C=O), 89.3 (d, C-1), 74.1 (d, 1 C), 69.4 (d, 1 C), 68.6 (d, 1 C), 66.6 (d, 1 C), 64.0 (d, 1 C), 61.5 (t, C-6), 43.9 (t, C-4'), 38.9 (d, C-3), 29.7 (t, C-3'), 20.9 (q, 1 C, *C*H_3C=O), 20.9 (q, 1 C, *C*H_3C=O), 20.8 (q, 2 C, *C*H_3C=O), 20.7 (q, 1 C, *C*H_3C=O). MS, m/z (%): 512 (M^+ - CH_3CO, 0.1), 496 (M^+ - CH_3COO, 2), 435 (2), 333 (10), 224 (70), 165 (100). IR ($CDCl_3$): 2961, 2928, 2849, 1748, 1697, 1447, 1373, 1231 cm^{-1}. $C_{22}H_{28}F_3NO_{12}$ (555.16): calcd. C 47.57, H 5.08, N 2.52; found C 47.69, H 4.99, N 2.63.

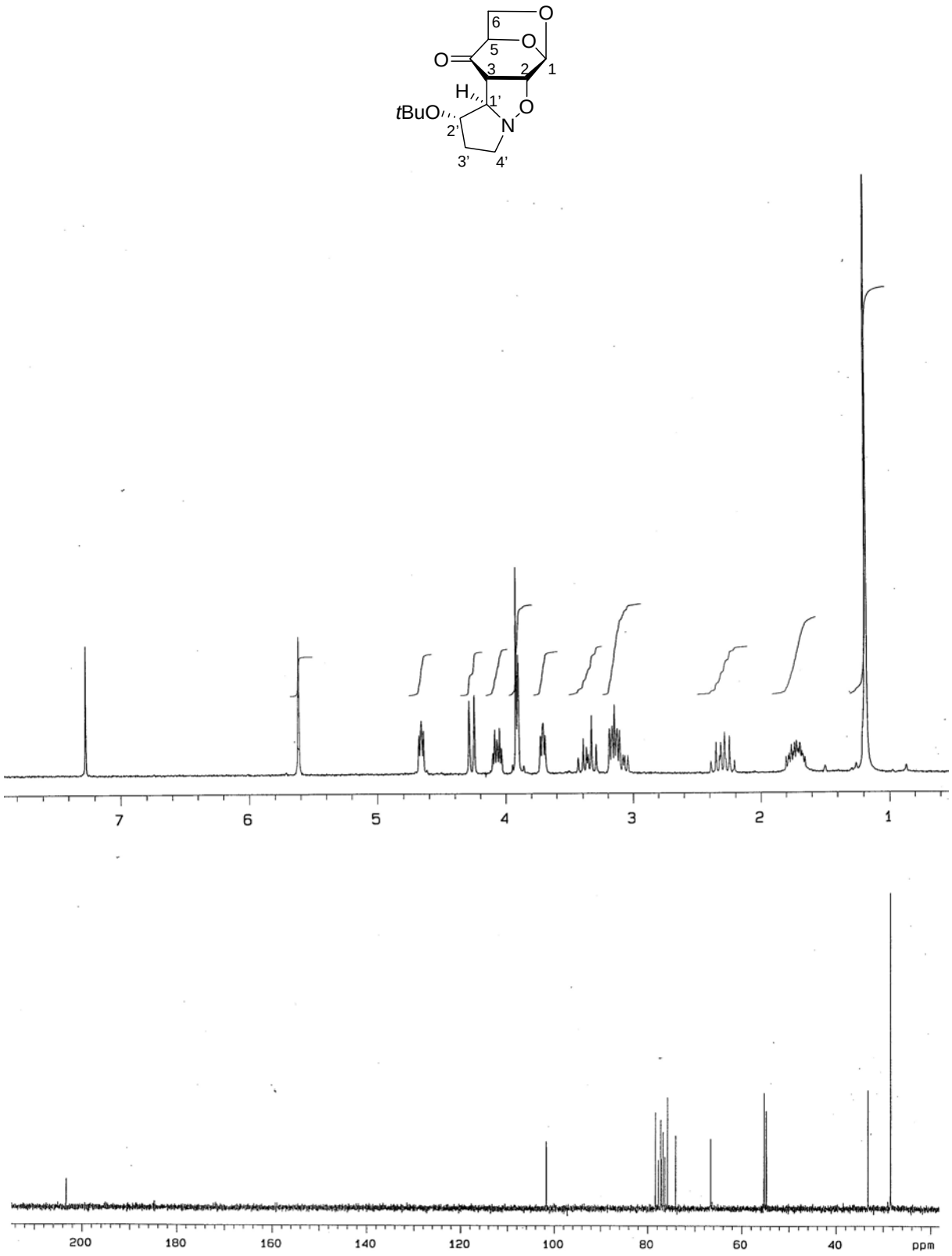
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **13**.



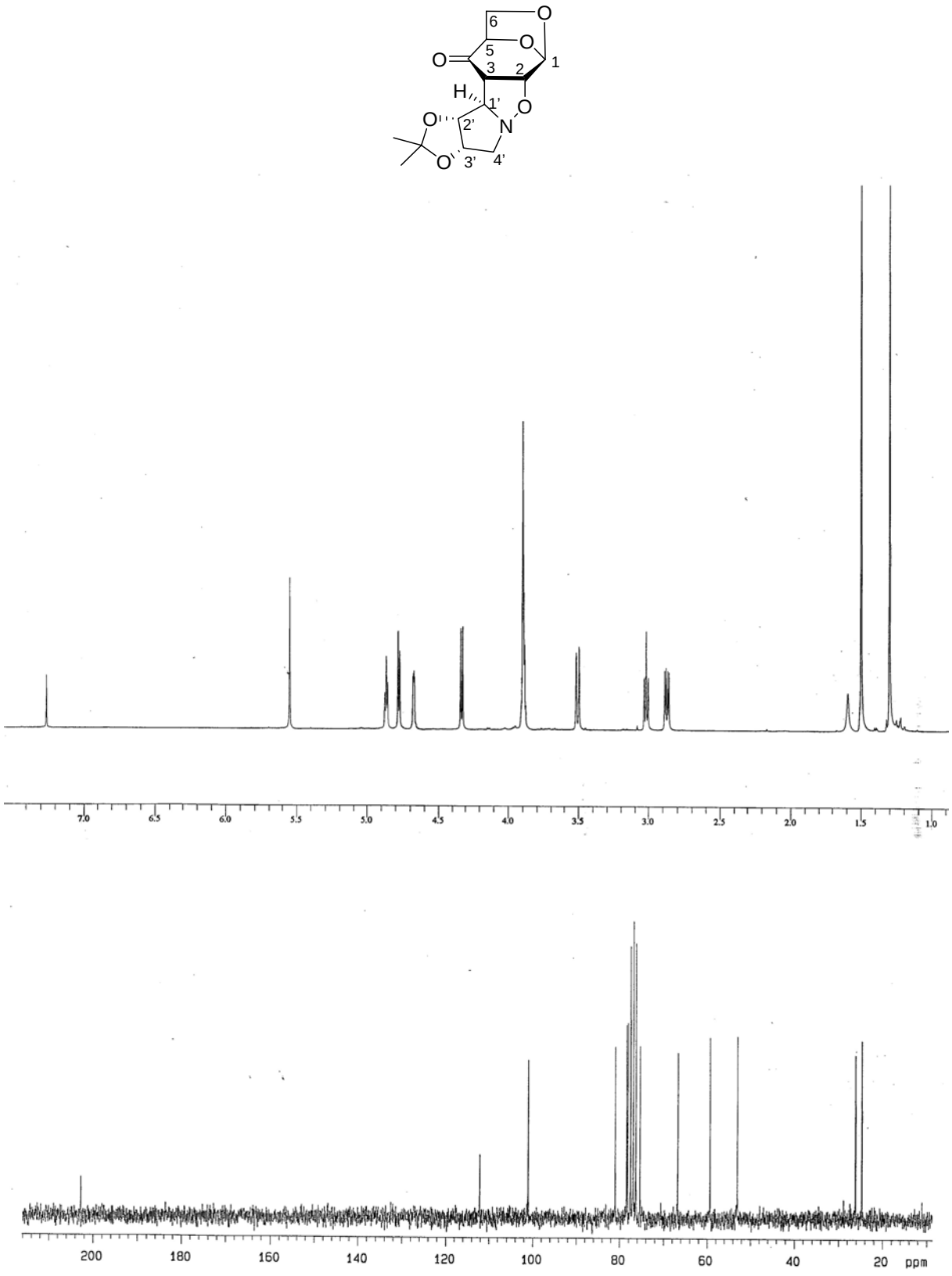




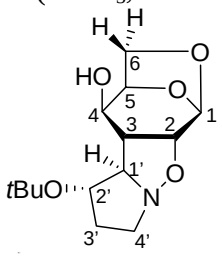
^{1}H NMR ($CDCl_3$, 200 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **14**.

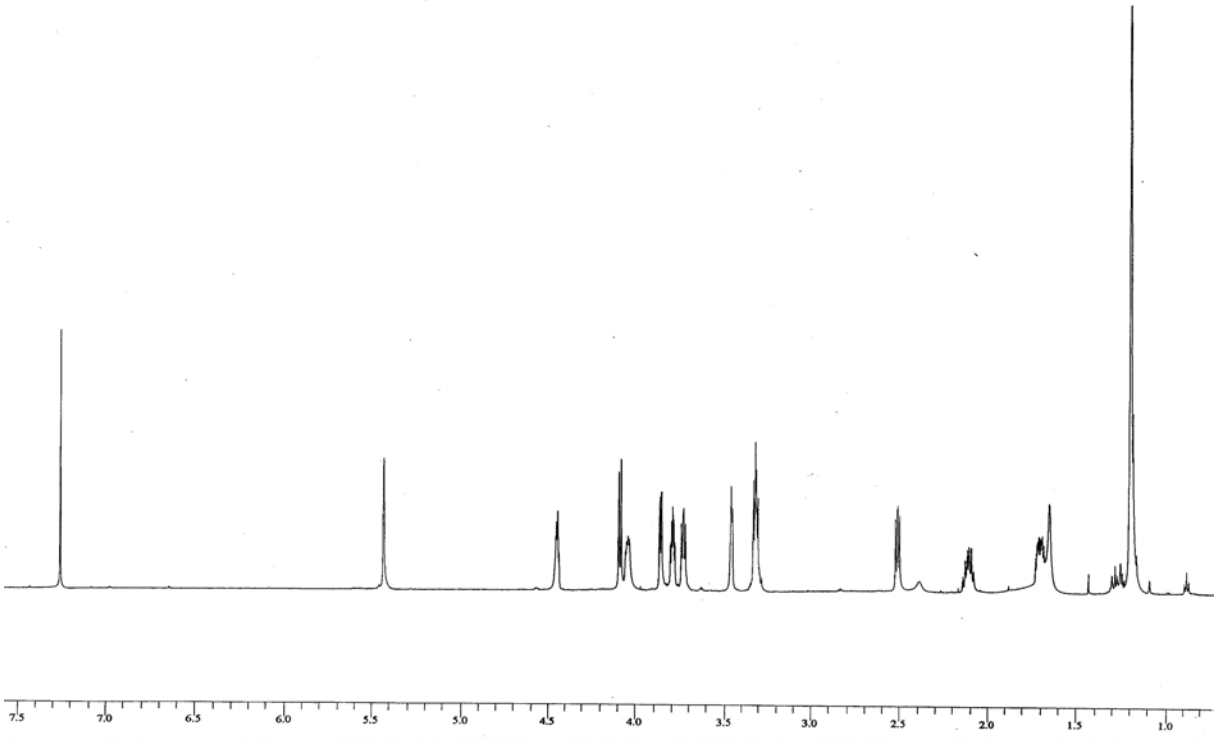


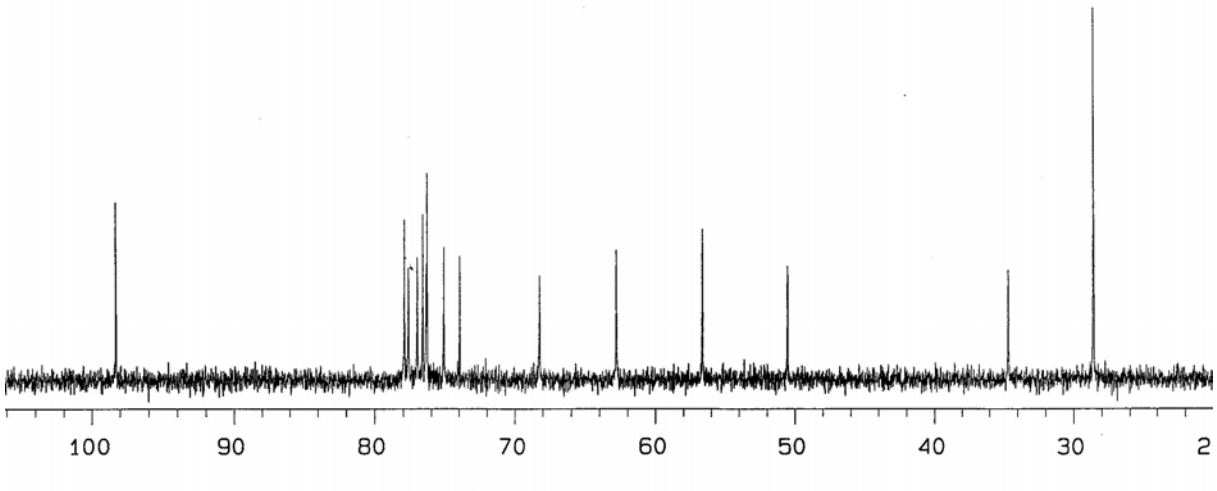
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **16**.



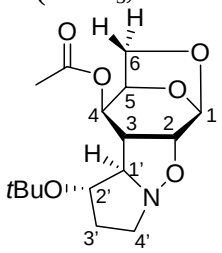
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **17**.

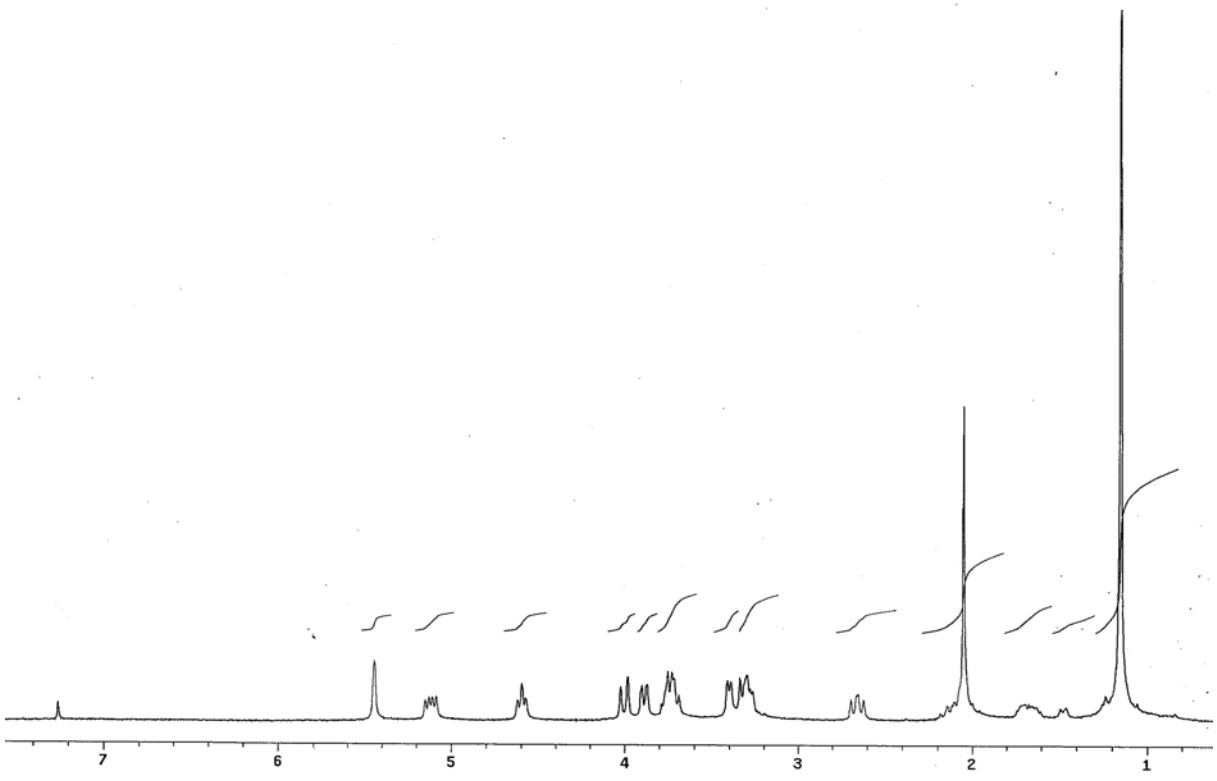


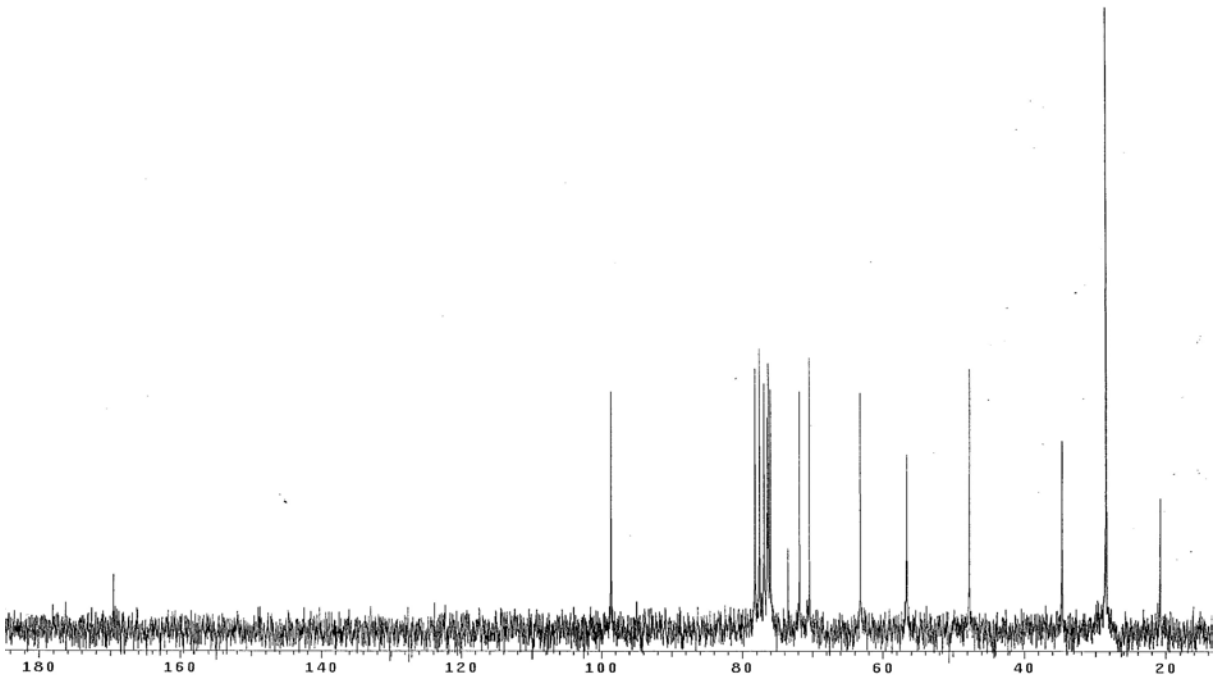




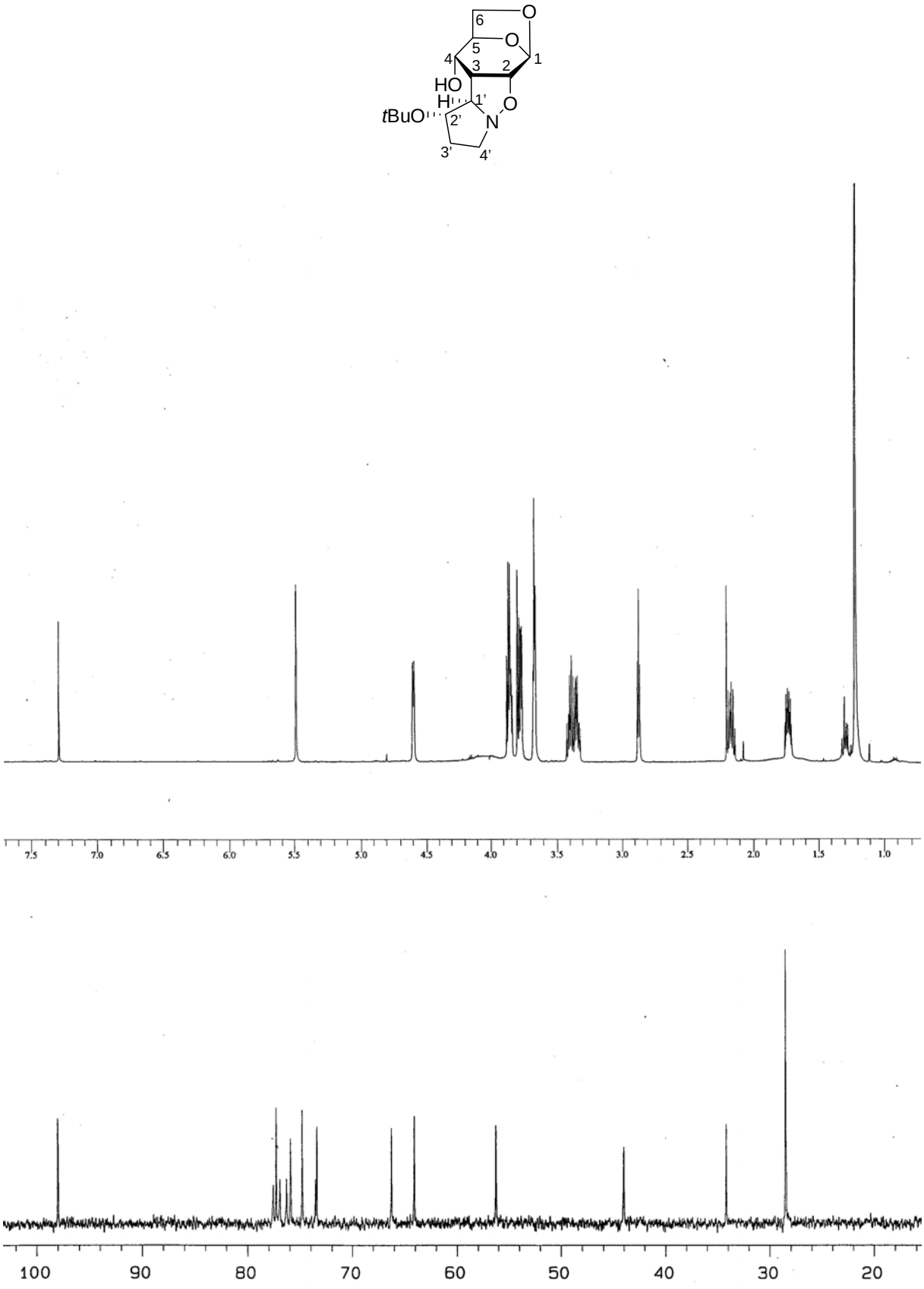
^{1}H NMR ($CDCl_3$, 200 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **18**.



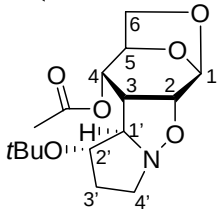


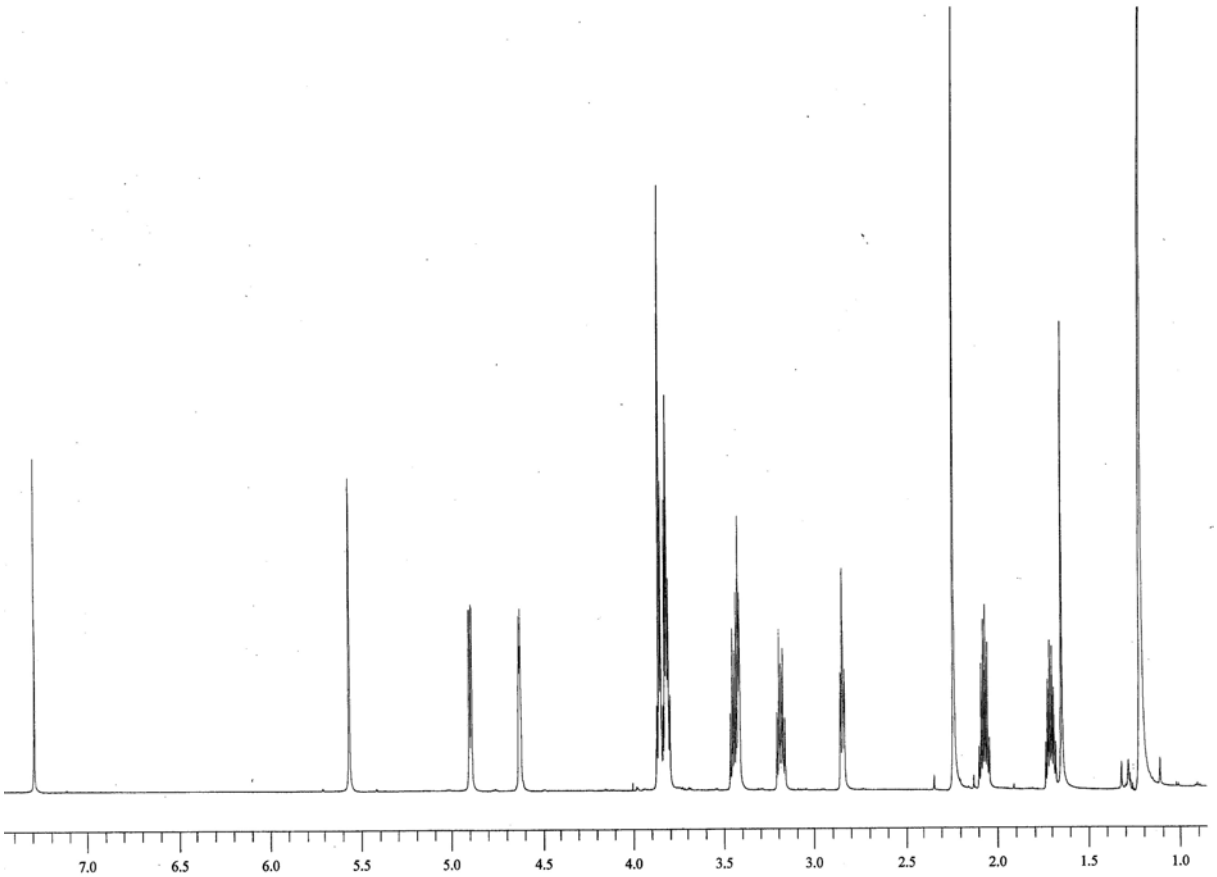


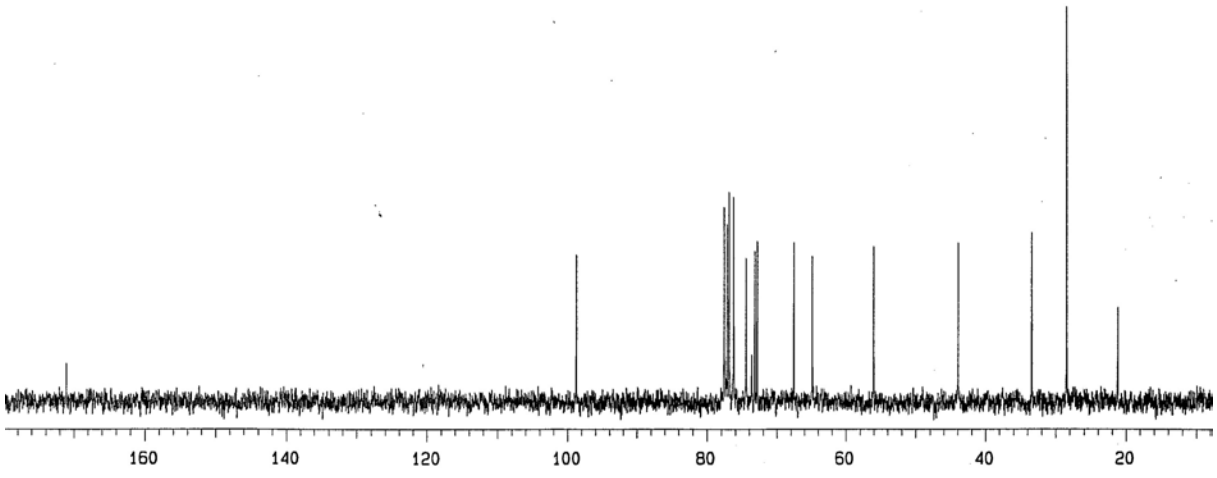
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **19**.



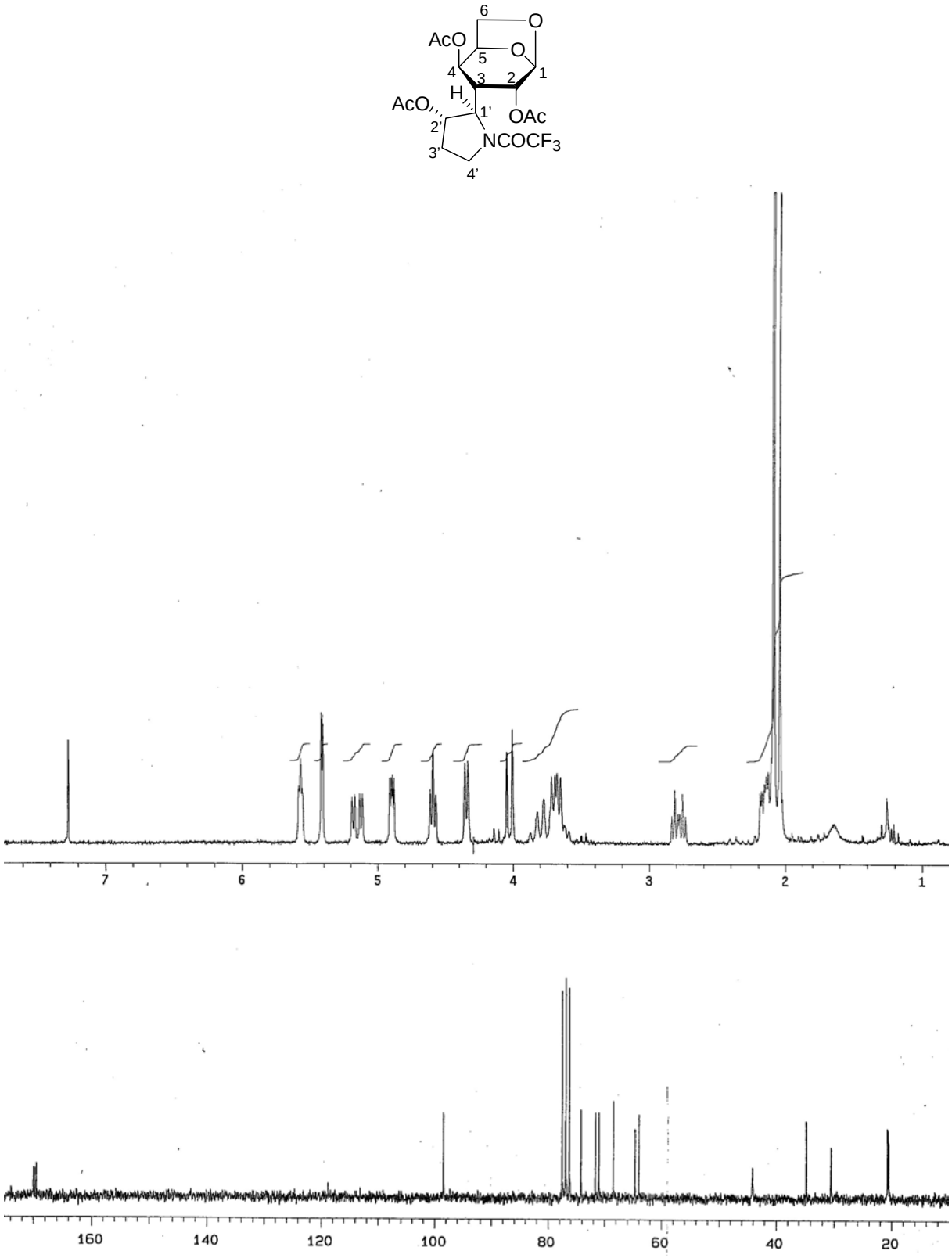
^{1}H NMR ($CDCl_3$, 600 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) of compound **20**.



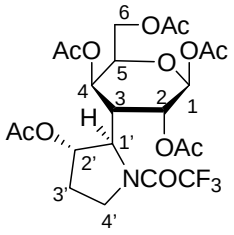


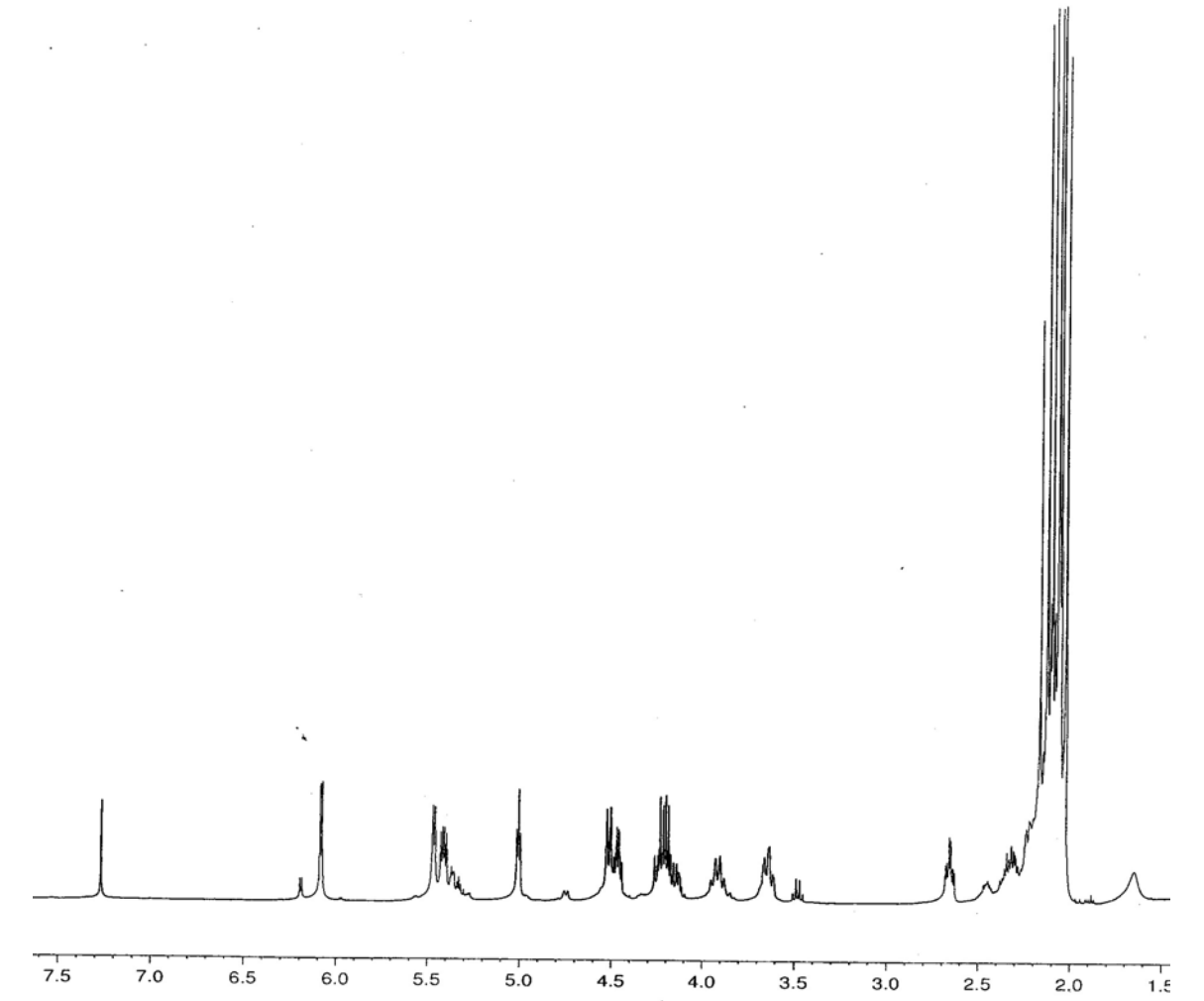


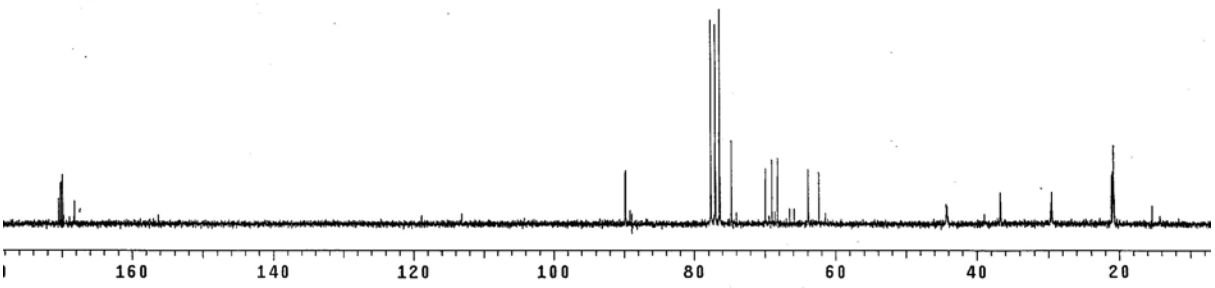
^{1}H NMR ($CDCl_3$, 200 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz, detected signals) of compound **24**.



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz, detected signals) of compound **25**β.







^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz, detected signals) of compound **25**α.