LC-MS based quantification of 2′-ribosylated nucleosides Ar(p) and Gr(p) in tRNA

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Supplementary Figure

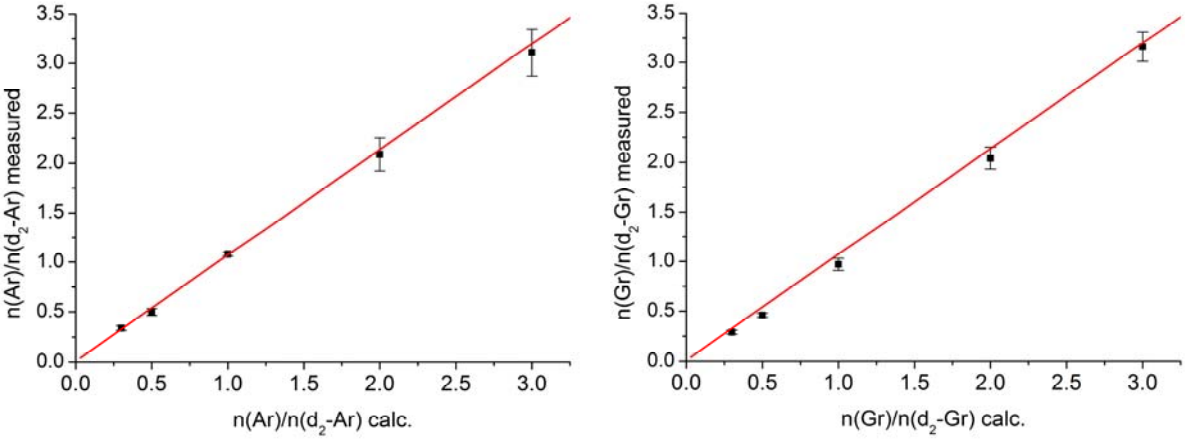

Fig. S1. Calibration curves for d_2-Ar and d_2-Gr compared to the respective natural nucleosides. Error bars represent +/- 1 s.d. from the mean value.

Experimental

Culture methods

S. scrofa liver samples and *E. coli* and HeLa cells were grown/obtained and extracted as described previously, and enzymatic digests and all LC-MS experiments were performed as previously resported.[1] 1L-cultures of *S. cerevisiae* (wild type, DMS No: 70449) and *C. albicans* (wild type, DMS No: 1386) were grown in rich medium (YPD, 2% glucose, 2% peptone, and 1% yeast extract) at 30 °C or 37 °C, respectively. Cells were grown to an OD_{600} of 0.6 - 0.7 then harvested. Mushroom (*C. nebularis* and *F. fomentarius*) samples (~5 g) were supplied by Prof. Wolfgang Steglich (LMU Munich). tRNA was extracted from yeast samples as described previously for E. coli, and from mushroom samples as described for porcine tissue.[1]

Synthetic methods

9-[2-*O*-(5,5-deutero-*β*-*D*-ribofuranosyl)-*β*-*D*-ribofuranosyl]-adenine 6: To compound **14** (35 mg, 0.041 mmol) was added a solution of NH_3 (7 N in MeOH, 2 mL) and the resulting solution was stirred for 5 days then concentrated. The residue was suspended in H_2O (2 mL) and washed with DCM (2 mL × 3) then concentrated. The crude product was purified by reverse-phase HPLC to give 7 mg of **6** as a white solid (43%): mp 120-123 ºC, ^{1}H NMR (400 MHz, D_2O) δ 8.36 (s, 1H), 8.25 (s, 1H), 6.17 (d, J = 6.43 Hz, 1H, NC*H*CH), 5.09 (s, 1H, OC*H*O), 4.85-4.81 (m, 1H, NCHC*H*), 4.61-4.57 (m, 1H, NCHCHC*H*), 4.33 (d, J = 2.50 Hz, 1H, C*H*CH_2), 4.17 (d, J = 4.55 Hz, 1H,

C*H*CHCHCD$_2$), 4.03 (dd, *J* = 7.27, 4.66 Hz, 1H, C*H*CHCD$_2$), 3.96 (d, *J* = 12.88 Hz, 1H, C*H*H), 3.92-3.82 (m, 2H, C*H*CD$_2$, CH*H*), ^{13}C NMR (101 MHz, D$_2$O) δ 155.7, 152.6, 148.3, 140.6, 119.0, 105.9, 86.9 (N*C*HCH), 86.4 (*C*HCH$_2$), 82.5 (*C*HCD$_2$), 78.1 (NCH*C*H), 74.3 (*C*HCHCHCD$_2$), 70.8 (*C*HCHCD$_2$), 68.9 (NCHCH*C*H), 61.4 (*C*H$_2$), *m*/*z* (ES) 402.1577, calcd for $C_{15}H_{20}D_2N_5O_8$ (MH^+) 402.1594.

9-[2-*O*-(5,5-deutero-*β*-*D*-ribofuranosyl)-*β*-*D*-ribofuranosyl]guanine 7: To **18** (76 mg, 0.073 mmol) was added TBAF (0.5 M in THF, 0.35 mL) and the resulting solution was stirred for 15 min then concentrated and co-evaporated twice with DCM. To the residue was added a solution of NH_3 (7N in MeOH, 6.5 mL) and the resulting solution was stirred for 3 days then concentrated. The residue was suspended in H_2O (2 mL) and washed with DCM (2 mL × 3) then concentrated. The crude product was purified by reverse-phase HPLC to give 9 mg of **7** as a white solid (30%). mp 120-123 ºC, ^{1}H NMR (600 MHz, D$_2$O) δ 8.00 (s, 1H, NC*H*N), 5.99 (d, *J* = 6.04 Hz, 1H, NC*H*CH), 5.09 (s, 1H, OC*H*O), 4.55-4.52 (m, 1H, C*H*CHCH$_2$), 4.24 (s, 1H, C*H*CH$_2$), 4.14 (d, *J* = 4.11 Hz, 1H, C*H*CHCHCD$_2$), 4.05 (dd, *J* = 6.91, 4.18 Hz, 1H, C*H*CHCD$_2$), 3.91-3.81 (m, 3H, C*H*$_2$ + C*H*CD$_2$), ^{13}C NMR (151 MHz, D2O) δ 158.9, 153.8, 151.1, 138.1 (N*C*HN), 116.6, 106.1 (O*C*HO), 86.4 (N*C*HCH), 86.0 (*C*HCH$_2$), 82.6 (*C*HCD$_2$), 77.8 (NCH*C*H), 74.3 (*C*HCHCHCD$_2$), 71.0 (*C*HCHCD$_2$), 68.8 (*C*HCHCH$_2$), 61.3 (*C*H$_2$), *m*/*z* (ES) 418.1536, calcd for $C_{15}H_{20}D_2N_5O_9$ (MH^+) 418.1543.

1,2,3-*O*-benzoyl-5,5-deutero-5-*O*-(4-methoxyphenyldiphenylmethyl)-*D*-ribofuranose 9: A solution of 5,5′-d$_2$-ribose **8** (1g, 6.6 mmol) and monomethoxytrityl chloride (2.4g, 7.8 mmol) in pyridine (13 mL) was stirred at r.t for 24 h, then cooled to 0ºC and a solution of benzyl chloride (3.5 mL, 4.2 g, 30 mmol) in 1,2-dichloroethane (10 mL) was added. The resulting solution was stirred for at r.t for 16 h, then cooled to 0ºC and EtOH (3.5 mL) was added. The solution was stirred at r.t for 20 min, then concentrated. The residue was redissolved in chloroform, washed with H_2O, dried over $NaSO_4$, concentrated, then coevaporated twice with toluene. The crude material was partially purified by flash chromatography, eluting with 1:4 EtOAc/isohexane to give **9** (4.8g) as a mixture of the α and β anomers that was used in the subsequent step without further purification.

1,2,3-*O*-benzoyl-5,5-deutero-*D*-ribofuranose 10: A mixture of **9** (3.7g, 5.0 mmol) and 80% AcOH in H_2O (100 mL) was stirred for 16 h, then concentrated and coevaporated twice with toluene. The crude material was purified twice by silica column chromatography, eluting with 1:39 EtOAc/DCM to give **10β** (480 mg, 20% over two steps) as a white foam: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.4, 1.4 Hz, 2H), 8.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.91 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.65-7.40 (m, 7H), 7.34 (t, *J* = 7.7 Hz, 2H), 6.67 (s, 1H, OC*H*O), 5.95-5.90 (m, 2H), 4.62-4.57 (m, 1H, C*H*CD$_2$), 2.18 (s, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 165.0, 164.7, 133.8, 133.6, 133.5, 130.0, 129.9, 129.7, 128.9, 128.9, 128.8, 128.6, 128.5, 128.4, 98.9 (OC*H*O), 83.1 (*C*HCD$_2$), 75.5, 70.9, *m*/*z* (ES) 499.1125, calcd for $C_{26}H_{20}D_2O_8$ (MCl^-) 499.1129, then eluting with 1:9 EtOAc/DCM to give **10α** (660 mg, 28% over two steps) as a white foam: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.41 Hz, 4H), 7.86 (dd, *J* = 8.33, 1.24 Hz, 2H), 7.57 (dd, *J* = 16.99, 7.59 Hz, 2H), 7.48 (t, *J* = 7.46 Hz, 1H), 7.34-7.15 (m, 6H), 6.95 (d, *J* = 4.38 Hz, 1H, OC*H*O), 5.84 (dd, *J* = 6.61, 2.28 Hz, 1H, (C*H*CHCD$_2$)), 5.65 (dd, *J* = 6.61, 4.40 Hz, 1H, C*H*CHCHCD$_2$), 4.65 (d, *J* = 2.28 Hz, 1H, C*H*CD$_2$), 2.53 (s, 1H, O*H*), ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 165.3, 165.0, 133.5, 133.4, 133.4, 129.9, 129.

8, 129.7, 129.6, 129.4, 128.7, 128.4, 128.3, 95.0 (O*C*HO), 85.5 (*C*HCD$_2$), 71.8 (*C*HCHCHCD$_2$), 71.0 (*C*HCHCD$_2$), *m*/*z* (ES) 482.1787, calcd for $C_{26}H_{24}D_2NO_8$ (M.NH$_4^+$) 482.1778.

1,2,3-*O*-benzoyl-5,5-deutero-5-*O*-phenoxyacetyl-*β*-*D*-ribofuranose 11: To a solution of **10β** (450 mg, 0.97 mmol) in pyridine (1 mL) and 1,2-dichloroethane (4 mL) was added phenoxyacetic anhydride (360 mg, 1.3 mmol) and the resulting solution was stirred at r.t for 1 h, then MeOH (0.2 mL) was added. The solution was stirred for 30 min, then diluted with DCM, washed with brine, dried over $NaSO_4$ and concentrated. The crude material was purified by silica column chromatography, eluting with DCM to obtain **11** (350 mg, 60%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.23 Hz, 2H), 8.03 (d, *J* = 7.24 Hz, 2H), 7.90 (d, *J* = 7.26 Hz, 2H), 7.59 (t, *J* = 7.46 Hz, 2H), 7.52 (t, *J* = 7.47 Hz, 1H), 7.47-7.41 (m, 4H), 7.33 (t, *J* = 7.88 Hz, 2H), 7.25-7.20 (m, 2H), 6.95 (t, *J* = 7.38 Hz, 1H), 6.77 (d, *J* = 7.80 Hz, 2H), 6.64 (s, 1H, OC*H*O), 5.94-5.92 (m, 1H, C*H*CHCHCD$_2$), 5.89 (dd, *J* = 6.89, 4.88 Hz, 1H, C*H*CHCD$_2$), 4.74 (d, *J* = 6.89 Hz, 1H, C*H*CD$_2$), 4.51 (d, *J* = 16.04 Hz, 1H, C*H*H), 4.40 (d, *J* = 16.07 Hz, 1H, CH*H*), ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 165.4, 165.0, 164.5, 157.5, 133.8, 133.7, 133.7, 129.9, 129.9, 129.8, 129.5, 129.0, 128.8, 128.7, 128.6, 128.5, 121.7, 114.6, 99.0 (O*C*HO), 79.6 (*C*HCD$_2$), 75.0 (*C*HCHCHCD$_2$), 71.3 (*C*HCHCD$_2$), 64.9 (*C*H$_2$), *m*/*z* (ES) 616.2155, calcd for $C_{34}H_{30}D_2NO_{10}$ (M.NH$_4^+$) 616.2152.

***N*^{6}-benzoyl-9-[2-*O*-[2,3-*O*-benzoyl-5,5-deutero-5-*O*-phenoxyacetyl-*β*-*D*-ribofuranosyl]-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-*β*-*D*-ribofuranosyl]-adenine 13**: A solution of **11** (100 mg, 0.17 mmol) [note: reactants **11** and **12** were each dried under vacuum (<0.5 mmHg) at 45ºC for 4 h prior to reaction] in 1,2-dichloroethane (2 mL) was cooled to 0ºC and $SnCl_4$ (30 μL, 66 mg, 0.26 mmol) was added. The resultant solution was stirred at 0ºC for 10 min, then **12** (120 mg, 0.20 mmol) was added. The solution was stirred at 0ºC for 16 h, then DCM (2 mL) and sat. $NaHCO_3$ (2 mL) were added. The mixture was stirred for 20 min, then filtered through celite, washed with H_2O, dried over $NaSO_4$ and concentrated. The crude material was purified by silica column chromatography, eluting with 1:99 MeOH/DCM to give **13** (160 mg, 86%) as a white foam: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.04 (s, 1H, N*H*), 8.75 (s, 1H), 8.29 (s, 1H), 8.02 (dd, *J* = 8.35, 1.22 Hz, 2H), 7.98 (dd, *J* = 8.43, 1.30 Hz, 2H), 7.87 (dd, *J* = 8.41, 1.27 Hz, 2H), 7.62-7.57 (m, 2H), 7.54-7.50 (m, 3H), 7.43 (dd, *J* = 8.20, 7.52 Hz, 2H), 7.32 (dd, *J* = 8.25, 7.53 Hz, 2H), 7.21 (dd, *J* = 8.75, 7.37 Hz, 2H), 6.92 (t, *J* = 7.36 Hz, 1H), 6.85 (dd, *J* = 8.76, 0.99 Hz, 2H), 6.19 (s, 1H), 5.81 (dd, *J* = 4.98, 0.82 Hz, 1H), 5.80-5.77 (m, 2H), 4.97 (dd, *J* = 9.27, 4.64 Hz, 1H), 4.77 (d, *J* = 4.61 Hz, 1H), 4.66 (d, *J* = 16.16 Hz, 1H, OC*H*HCOO), 4.61 (d, *J* = 16.17 Hz, 1H, OCH*H*COO), 4.61 (d, *J* = 6.31 Hz, 1H), 4.21 (dd, *J* = 13.35, 1.43 Hz, 1H, CHC*H*H), 4.16 (td, *J* = 9.22, 2.18 Hz, 1H), 4.02 (dd, *J* = 13.30, 2.62 Hz, 1H, CHCH*H*), 1.11-0.94 (m, 28H, 4×CH(CH$_3$)$_2$), ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 165.3, 164.9, 164.5, 157.6, 152.7, 150.8, 149.4, 141.9, 133.8, 133.49, 133.48, 132.7, 129.7, 129.5, 129.0, 128.83, 128.78, 128.5, 128.4, 127.8, 123.5, 121.7, 114.6, 105.8, 88.8, 81.4, 79.6, 78.9, 75.5, 72.3, 69.8, 65.2 (O*C*H$_2$COO), 59.8 (CH*C*H$_2$), 17.4, 17.33, 17.28, 17.26, 17.2, 17.1, 16.9, 16.8, 13.3, 12.9, 12.8, 12.6, *m*/*z* (ES) 1090.4301, calcd for $C_{56}H_{64}D_2N_5O_{14}Si_2$ (MH$^+$) 1090.4270.

***N*^{6}-benzoyl-9-[2-*O*-[2,3-*O*-benzoyl-5,5-deutero-5-*O*-phenoxyacetyl-*β*-*D*-ribofuranosyl]-*β*-*D*-ribofuranosyl]-adenine 14**: To **13** (130 mg, 0.12 mmol) was added TBAF (0.5 M in THF, 1 mL) and the resulting solution was stirred for 15 min then

concentrated. The crude material was purified twice by silica column chromatography, eluting with 1:24 MeOH/DCM to give **14** (65 mg, 64%) as a white foam: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.80 (s, 1H), 8.21 (s, 1H), 8.01 (d, *J* = 7.17 Hz, 2H), 7.89-7.84 (m, 4H), 7.58 (t, *J* = 7.44 Hz, 1H), 7.54-7.50 (m, 2H), 7.49 (t, *J* = 7.78 Hz, 2H), 7.34 (dt, *J* = 8.27, 1.88 Hz, 4H), 7.26 (t, *J* = 8.05 Hz, 2H), 6.96 (t, *J* = 7.38 Hz, 1H), 6.92 (dd, *J* = 8.75, 0.93 Hz, 2H), 6.08 (d, *J* = 7.42 Hz, 1H, NC*H*CH), 6.02 (d, *J* = 11.06 Hz, 1H, CH_2OH), 5.58 (dd, *J* = 5.37, 2.13 Hz, 1H, C*H*CHCHCD$_2$), 5.55 (t, *J* = 5.28 Hz, 1H, C*H*CHCD$_2$), 5.19 (dd, *J* = 7.39, 4.70 Hz, 1H, NCHC*H*), 5.15 (d, *J* = 2.11 Hz, 1H, OC*H*O), 4.74 (d, *J* = 0.85 Hz, 2H, OCH_2COO), 4.63 (d, *J* = 4.70 Hz, 1H, C*H*CHCH$_2$), 4.34 (d, *J* = 5.23 Hz, 1H, C*H*CD$_2$), 4.30 (s, 1H, C*H*CH$_2$), 3.95 (d, *J* = 12.97 Hz, 1H, CHC*H*H), 3.73 (t, *J* = 11.85 Hz, 1H, CHCH*H*), 3.39 (s, 1H, CHO*H*), ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 165.4, 165.3, 164.53, 157.53, 152.2, 150.5, 150.3, 144.2, 133.8, 133.7, 133.5, 132.8, 129.8, 129.7, 129.6, 128.8, 128.5, 128.5, 128.5, 128.4, 127.9, 124.3, 121.9, 114.6, 106.7 (O*C*HO), 89.2 (N*C*HCH), 87.2 (*C*HCH$_2$), 81.1 (NCH*C*H), 79.9 (*C*HCD$_2$), 75.7 (*C*HCHCHCD$_2$), 71.7 (*C*HCHCH$_2$), 71.6 (*C*HCHCD$_2$), 65.3 (O*C*H$_2$COO), 63.2 (*C*HCH$_2$), *m*/*z* (ES) 848.2763, calcd for $C_{44}H_{38}D_2N_5O_{13}$ (MH^+) 848.2748.

1-*O*-methyl-2,3,5-*O*-benzoyl-5,5-deutero-β-*D*-ribofuranose 15: A solution of 5,5′-d_2-ribose **8** (200 mg, 1.3 mmol) in MeOH (4 mL) was cooled to 0ºC and Dowex 50 W-8 100 cation exchange resin (300 mg, vacuum dried) was added. The resulting mixture was kept at 4ºC for 24 h then filtered through celite and concentrated. The residue was dried by evaporation of pyridine (3 × 5 mL), then redissolved in DCM (1.1 mL) and pyridine (2.4 mL), cooled to 0ºC and BzCl (1 g, 7.1 mmol) was added. The resulting mixture was kept at 4ºC for 24 h, then H_2O (0ºC, 5 mL) was added and the organic layer was separated. The aqueous layer was washed with DCM (3 × 10 mL) then the organic layers were combined then co-evaporated with toluene (3 × 10 mL). The crude material was purified by column chromatography, eluting with 1:9 to 1:14 EtOAc/isohexane to give **15** (513 mg, 82%) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.41, 1.30 Hz, 2H), 8.02 (dd, *J* = 8.40, 1.30 Hz, 2H), 7.89 (dd, *J* = 8.42, 1.29 Hz, 2H), 7.59-7.49 (m, 3H), 7.44-7.38 (m, 4H), 7.32 (dd, *J* = 8.32, 7.51 Hz, 2H), 5.87 (ddd, *J* = 7.04, 4.86, 0.35 Hz, 1H), 5.68 (d, *J* = 4.87 Hz, 1H), 5.16 (s, 1H), 4.72 (d, *J* = 7.10 Hz, 1H), 3.42 (s, 3H, C*H*$_3$), ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 165.4, 165.2, 133.4, 133.3, 133.1, 129.8, 129.7, 129.7, 129.2, 128.9, 128.5, 128.3, 128.3, 106.4, 78.9, 75.4, 72.4, 55.4 (*C*H$_3$), *m*/*z* (ES) 496.1933, calcd for $C_{27}H_{26}D_2NO_8$ ($M.NH_4^+$) 496.1940.

1-*O*-acetyl-2,3,5-*O*-benzoyl-5,5-deutero-β-*D*-ribofuranose 16: A solution of **15** (350 mg, 0.73 mmol) in AcOH (1.6 mL) and Ac_2O (3.9 mL) was cooled to 0ºC and H_2SO_4 (98%, 0.55 mL) was added. The resulting solution was kept at 4ºC for 26 h, then H_2O (4ºC, 10 mL) was added and the organic layer was separated. The aqueous layer was washed with DCM (3 × 20 mL) then the organic layers were combined and concentrated. The crude material was purified by column chromatography, eluting with 1:4 EtOAc/ isohexane, then further purified by recrystallisation from isopropanol to give **16** (180 mg, 49%) as a white solid. m.p. 113-116ºC, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.40, 1.28 Hz, 2H), 8.00 (dd, *J* = 8.41, 1.28 Hz, 2H), 7.89 (dd, *J* = 8.42, 1.27 Hz, 2H), 7.60-7.51 (m, 3H), 7.45-7.39 (m, 4H), 7.33 (dd, *J* = 8.32, 7.51 Hz, 2H), 6.43 (s, 1H), 5.91 (dd, *J* = 7.12, 4.89 Hz, 1H), 5.79 (d, *J* = 4.89 Hz, 1H), 4.78 (d, *J* = 7.16 Hz, 1H), 2.00 (s, 3H, C*H*$_3$), ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 166.0, 165.3, 165.0, 133.6, 133.5, 133.2, 129.8, 129.7, 129.6, 128.8, 128.6, 128.5, 128.4, 128.4, 98.4, 79.8, 75.0, 71.3, 20.9, *m*/*z* (ES) 529.1436, calcd for $C_{28}H_{22}D_2NaO_9$ ($M.Na^+$) 519.1444.

***N*^{2}-isobutyryl-9-[2-*O*-[2,3,5-*O*-benzoyl-5,5-deutero-*β*-*D*-ribofuranosyl]-3,5-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-*β*-*D*-ribofuranosyl]guanine 18**: A solution of **16** (100 mg, 0.17 mmol) [note: reactants were dried under vacuum (<0.5 mmHg) at 45ºC for 4 h prior to reaction] in 1,2-dichloroethane (2 mL) was cooled to 0ºC and $SnCl_4$ (30 μL, 66 mg, 0.26 mmol) was added. The resultant solution was stirred at 0ºC for 10 min, then **17** (120 mg, 0.20 mmol) was added. The solution was stirred at 0ºC for 16 h, then sat. $NaHCO_3$ (1 mL) was added. The mixture was stirred for 10 min, then filtered through celite, washed with H_2O, dried over $NaSO_4$ and concentrated. The crude material was purified by silica column chromatography, eluting with 2:98 MeOH/DCM to give **18** (93 mg, 52%) as a white foam:
^{1}H NMR (600 MHz,$CDCl_3$) δ 8.16 (s, 1H, NC*H*N), 8.00-7.96 (m, 4H), 7.91 (dd, *J* = 8.31, 1.20 Hz, 2H), 7.59 (t, *J* = 7.45 Hz, 1H), 7.55 (t, *J* = 7.46 Hz, 2H), 7.43 (t, *J* = 7.88 Hz, 2H), 7.37-7.32 (m, 4H), 6.13 (t, *J* = 5.47 Hz, 1H), 5.89 (d, *J* = 5.52 Hz, 1H), 5.86 (s, 1H), 5.75 (s, 1H), 4.77 (d, *J* = 5.83 Hz, 1H), 4.57 (dd, *J* = 9.40, 3.81 Hz, 1H), 4.29 (d, *J* = 3.79 Hz, 1H), 4.27 (d, *J* = 13.59 Hz, 1H, CHC*H*H), 4.18 (dd, *J* = 9.42, 2.05 Hz, 1H), 4.01 (dd, *J* = 13.56, 2.60 Hz, 1H, CHCH*H*), 2.89 (sept., *J* = 6.88 Hz, 1H, COC*H*CH_3CH_3), 1.35 (d, *J* = 6.86 Hz, 3H, $COCHCH_3CH_3$), 1.25 (d, *J* = 6.83 Hz, 3H, $COCHCH_3CH_3$), 1.14-0.90 (m, 28H, 4×$CH(CH_3)_2$), ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 179.4, 167.9, 165.3, 165.0, 154.8, 148.6, 146.9, 135.7, 134.0, 133.6, 129.71, 129.68, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 120.5, 105.5, 87.5, 81.3, 79.3, 78.7, 75.8, 73.2, 69.3, 59.4 (CH_2), 36.1, 19.2 ($COCHCH_3CH_3$), 18.9 ($COCHCH_3CH_3$), 17.5, 17.4, 17.29, 17.27, 17.1, 17.0, 16.8, 16.7, 13.3, 13.0, 12.8, 12.6, *m*/*z* (ES) 1042.4273, calcd for $C_{52}H_{64}D_2N_5O_{14}Si_2$ (MH^+) 1042.4270.

NMR Spectra

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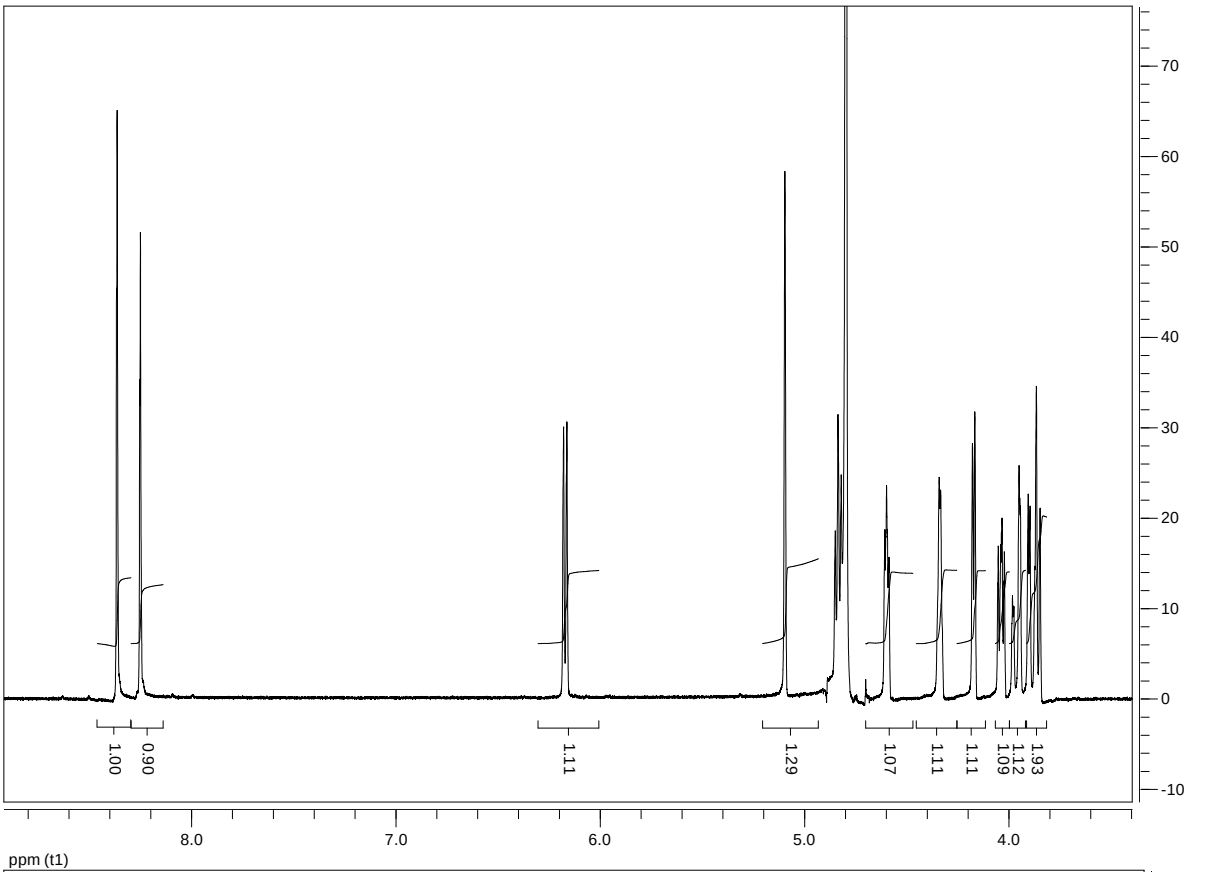

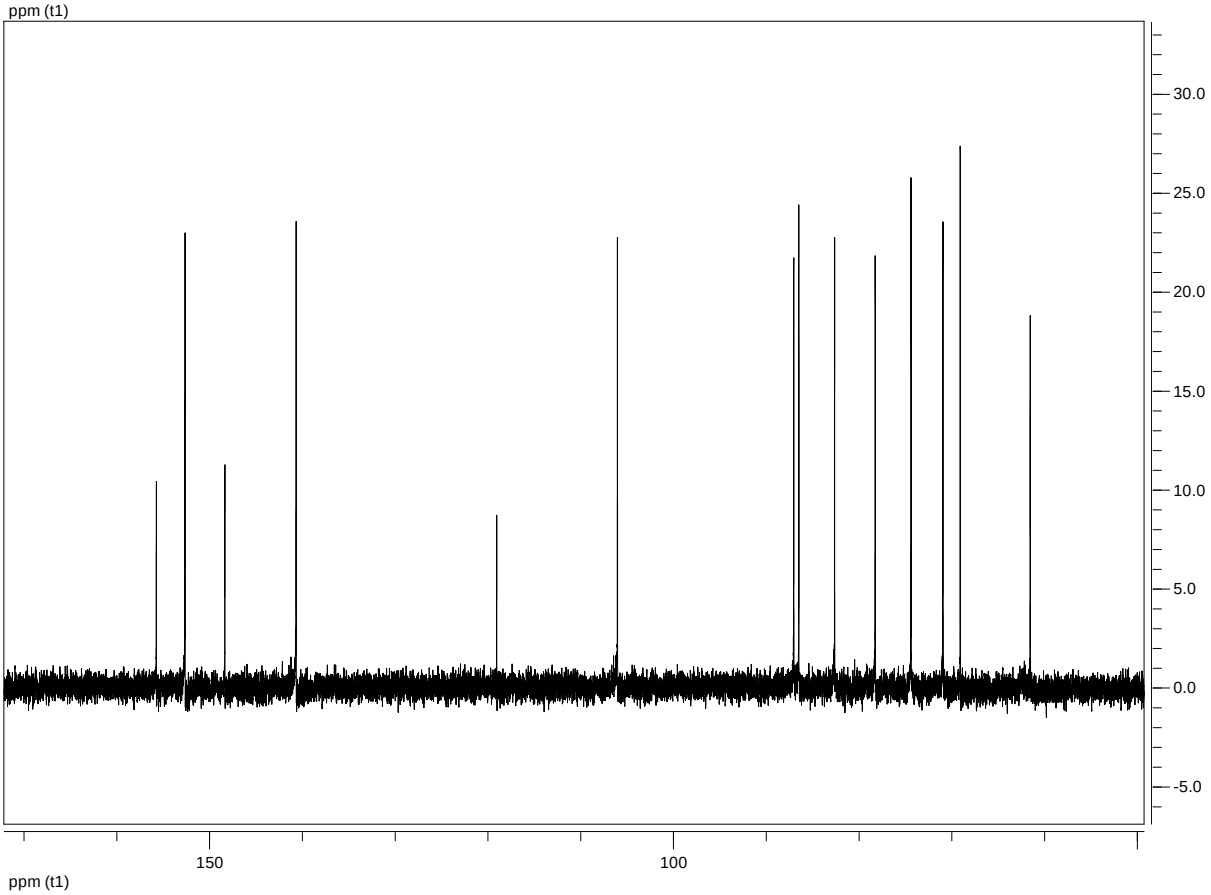

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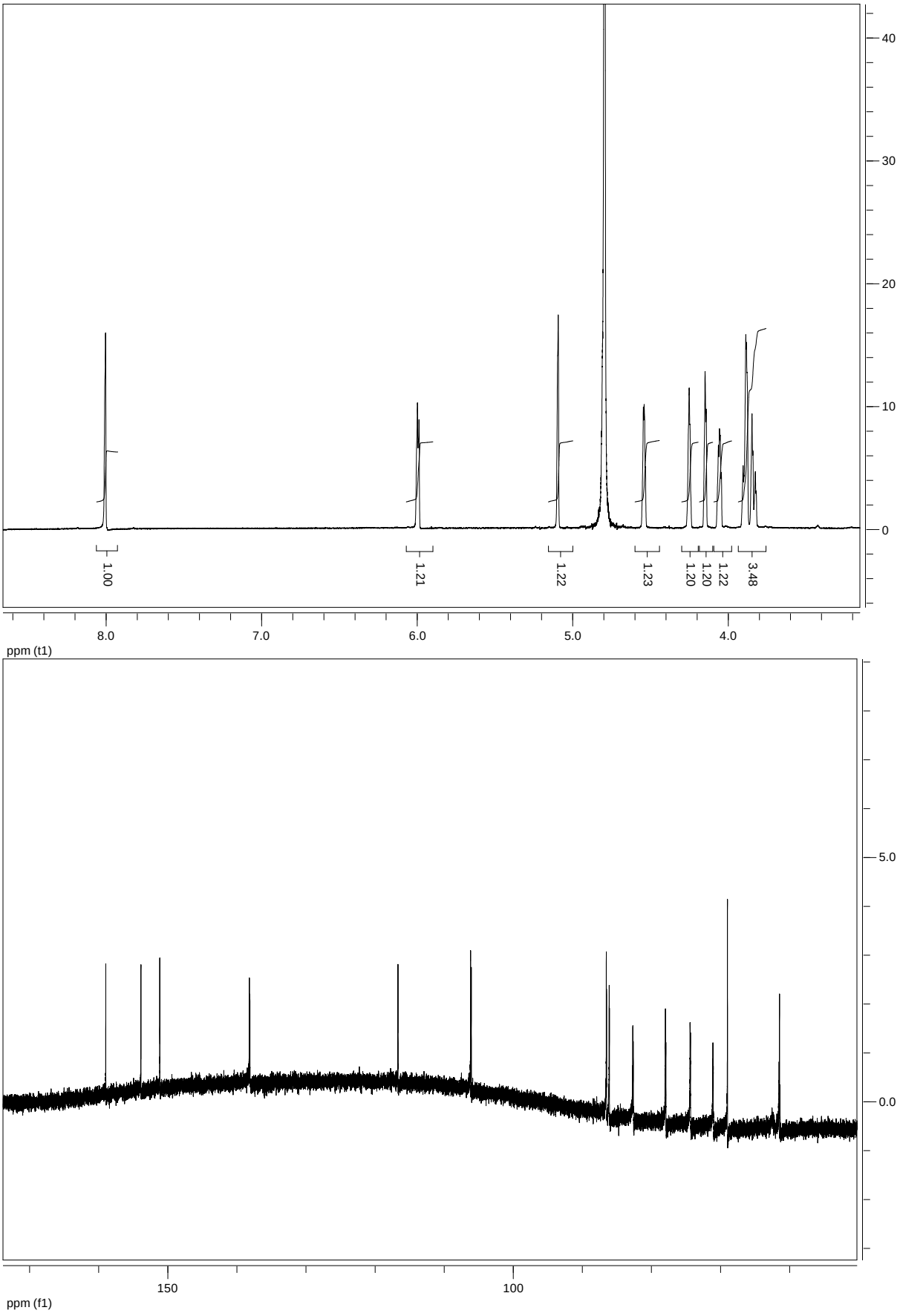
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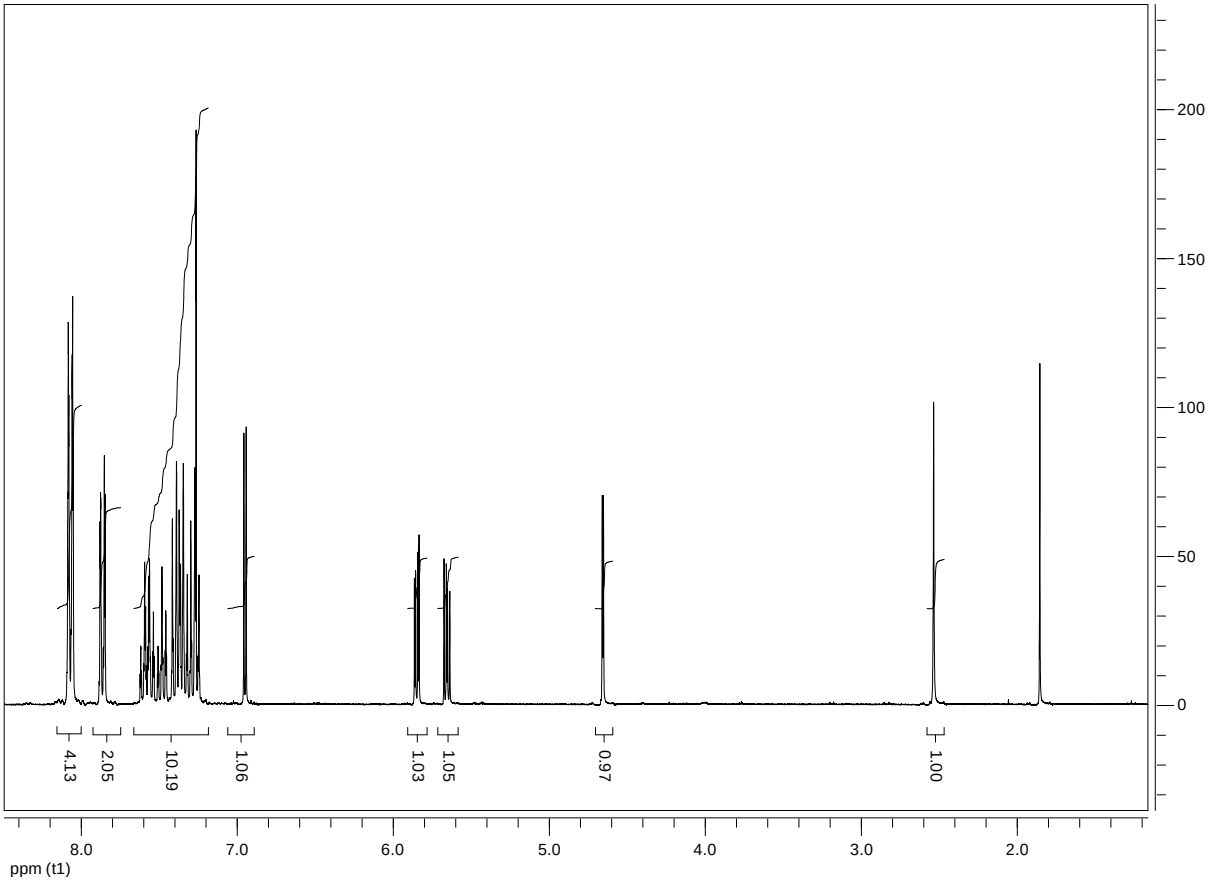
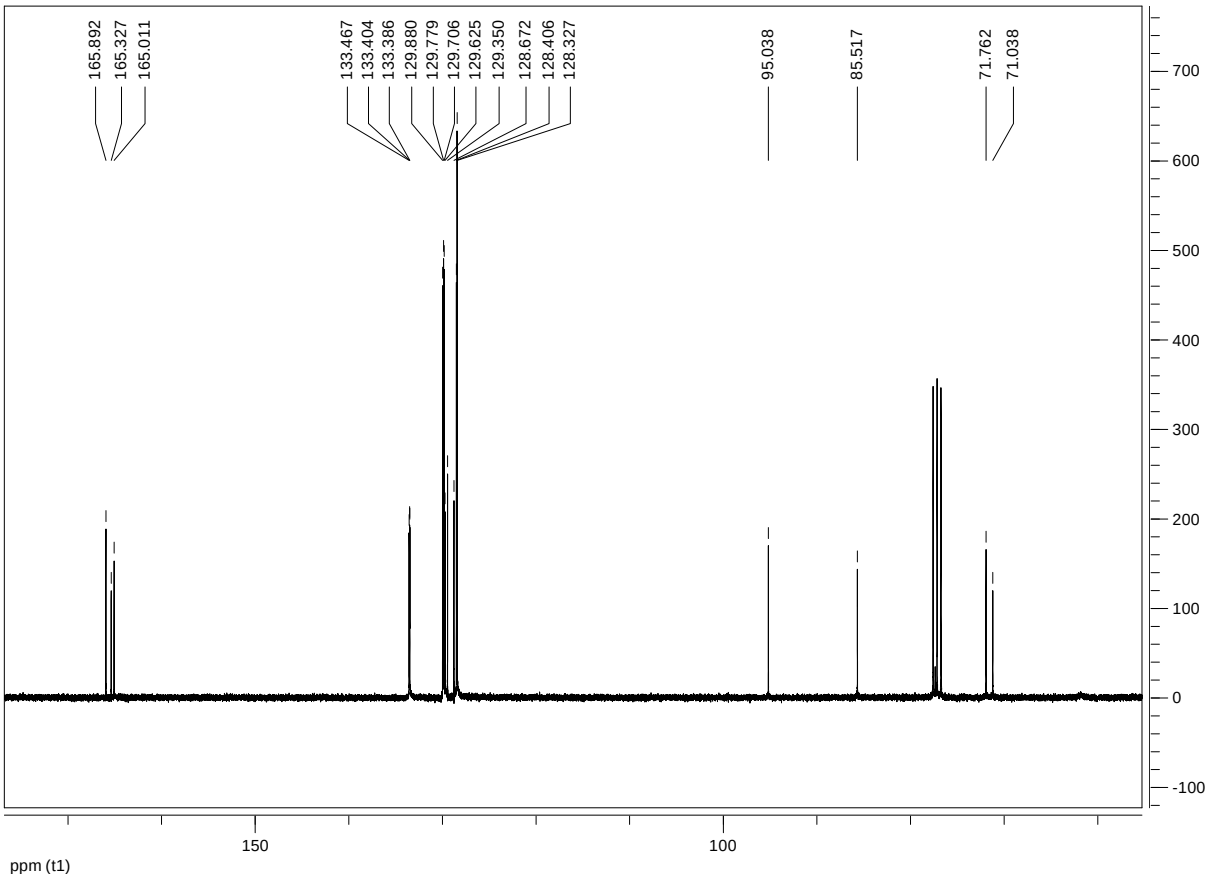
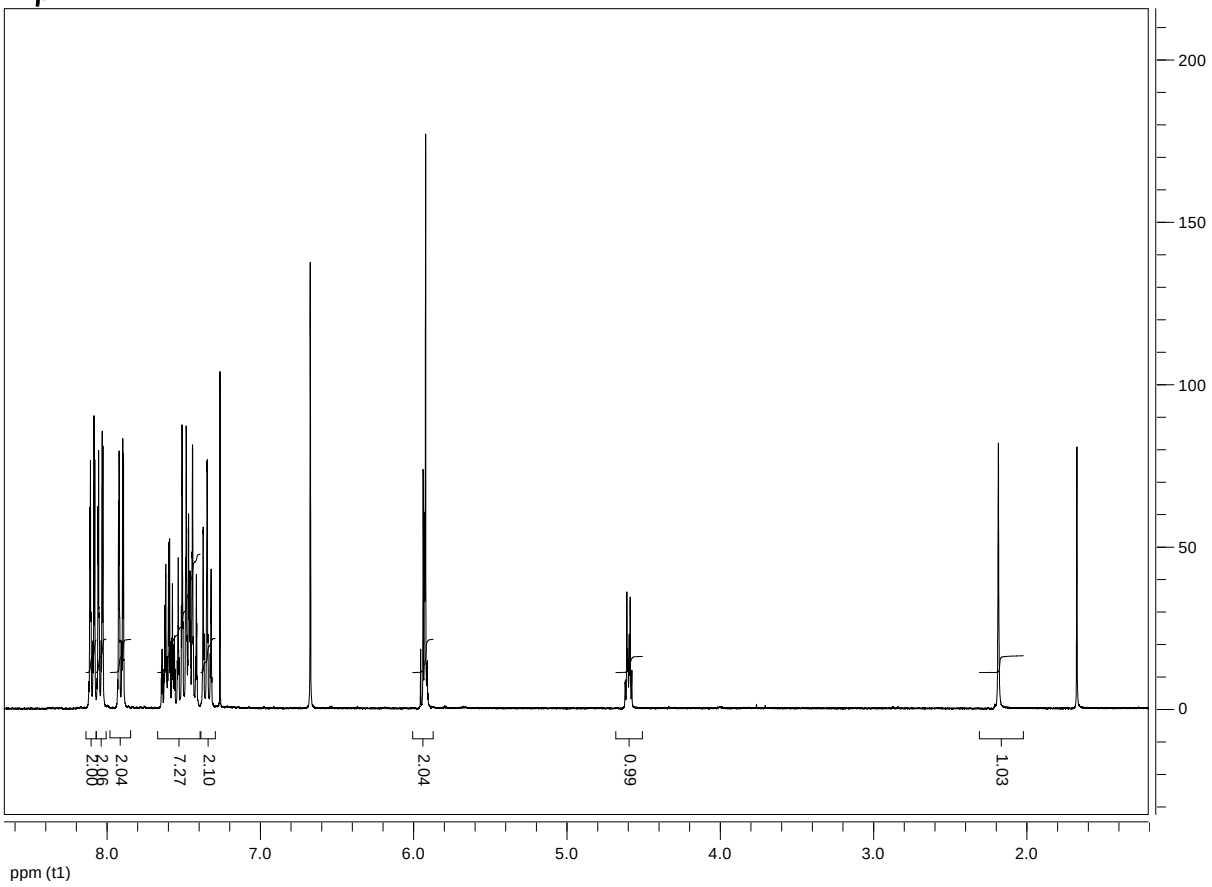
1.20
1.22
3.48
8.0
7.0
6.0
5.0
4.0
ppm (t1)
5.0
0.0
150
100
ppm (f1)

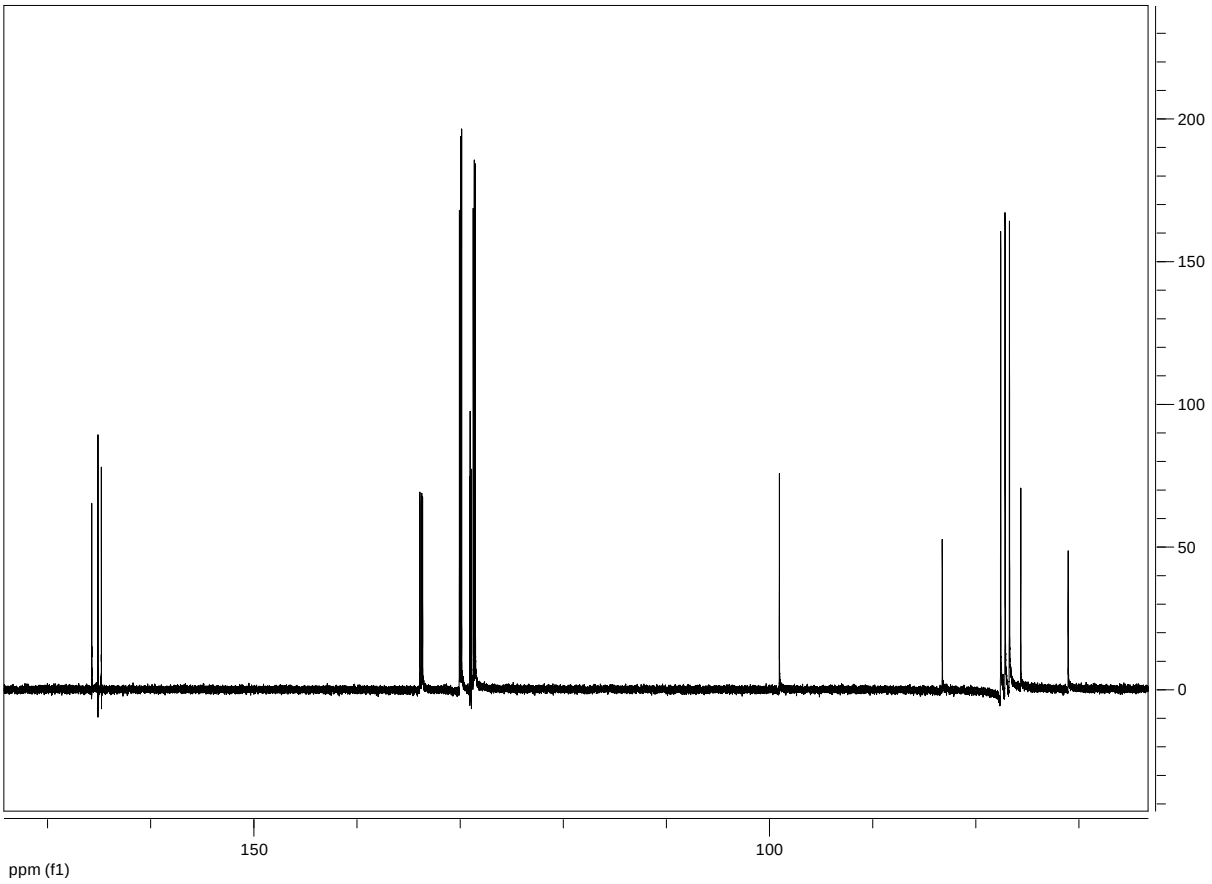
10α


4.13
2.05
10.19
1.06
1.03
1.05
0.97
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

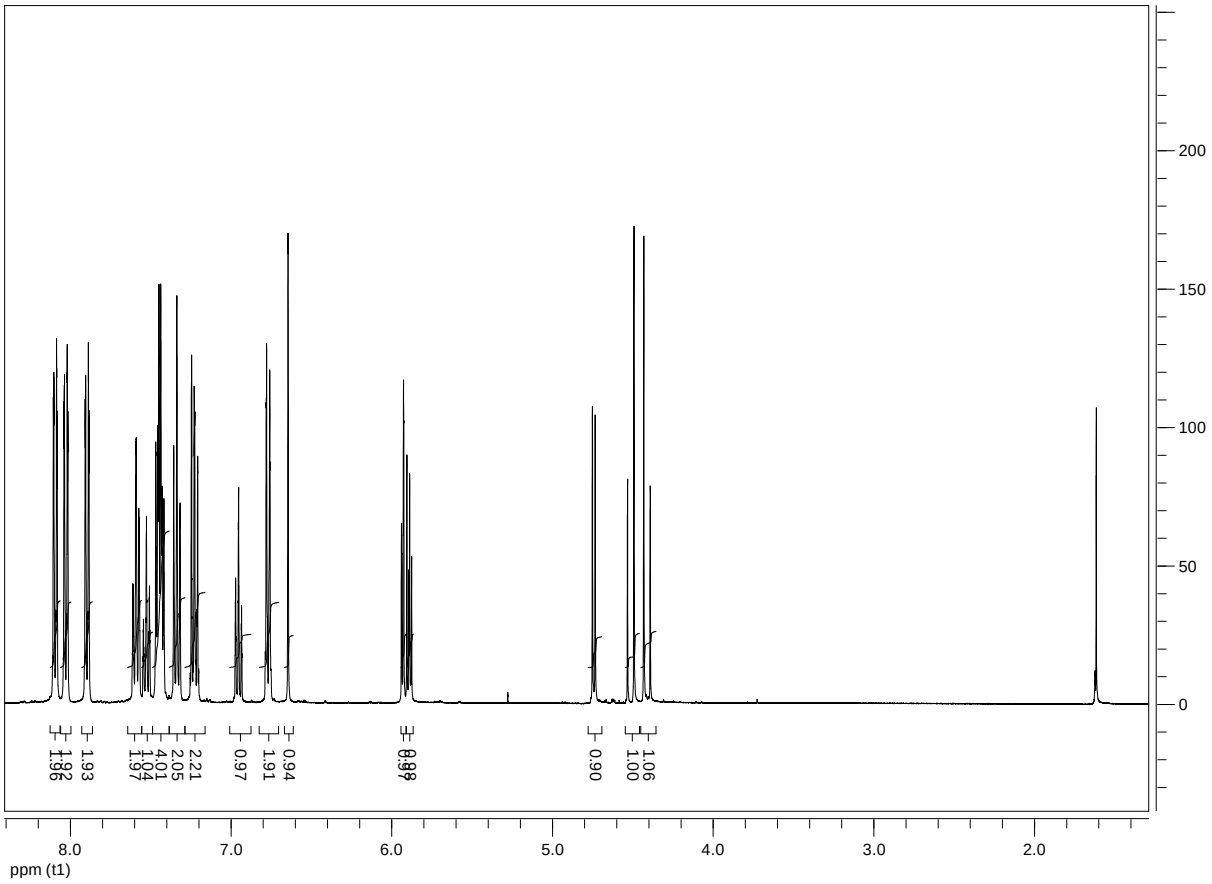

165.892
165.327
165.011
133.467
133.404
133.386
129.880
129.779
129.706
129.625
129.350
128.672
128.406
128.327
95.038
85.517
71.762
71.038
150
100
ppm (t1)

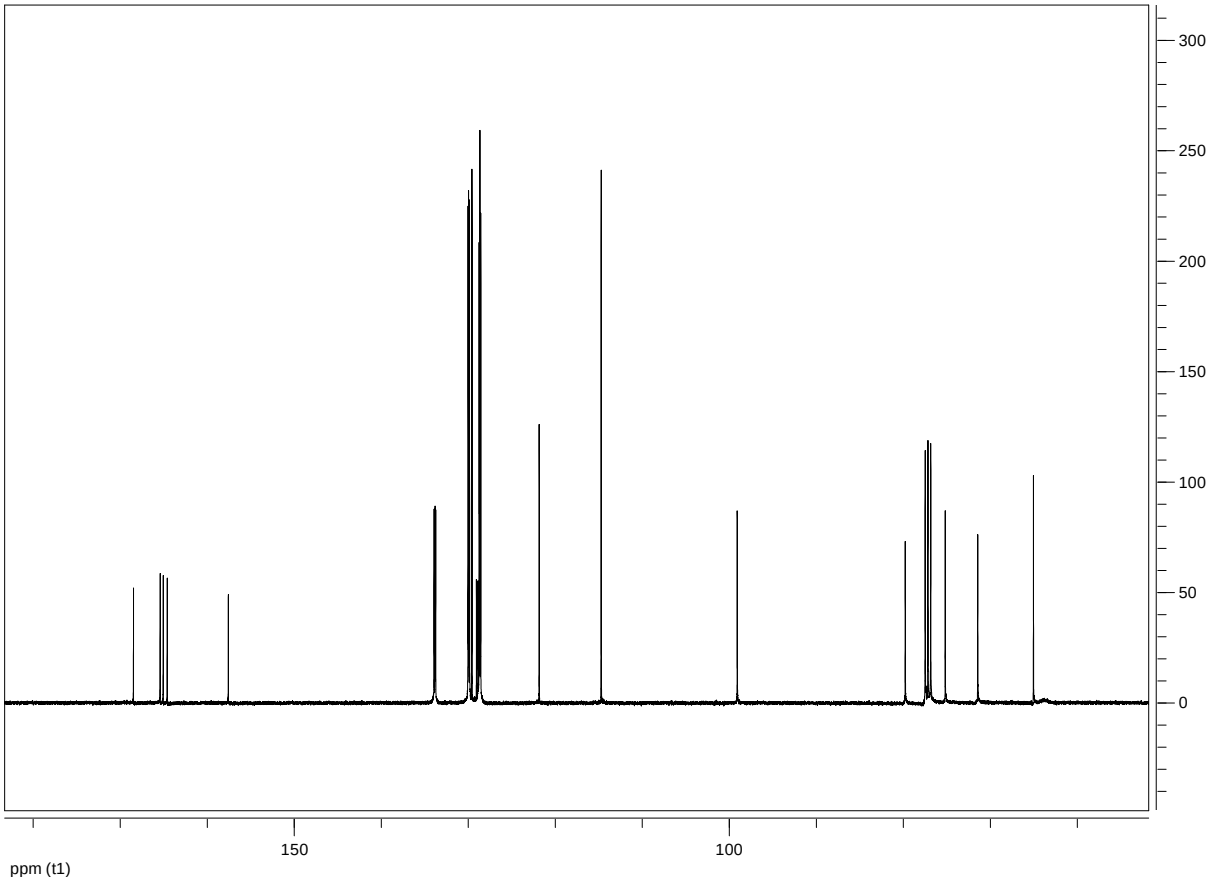
10β


200
150
100
50
0
2.06
2.06
2.04
7.27
2.10
2.04
0.99
1.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

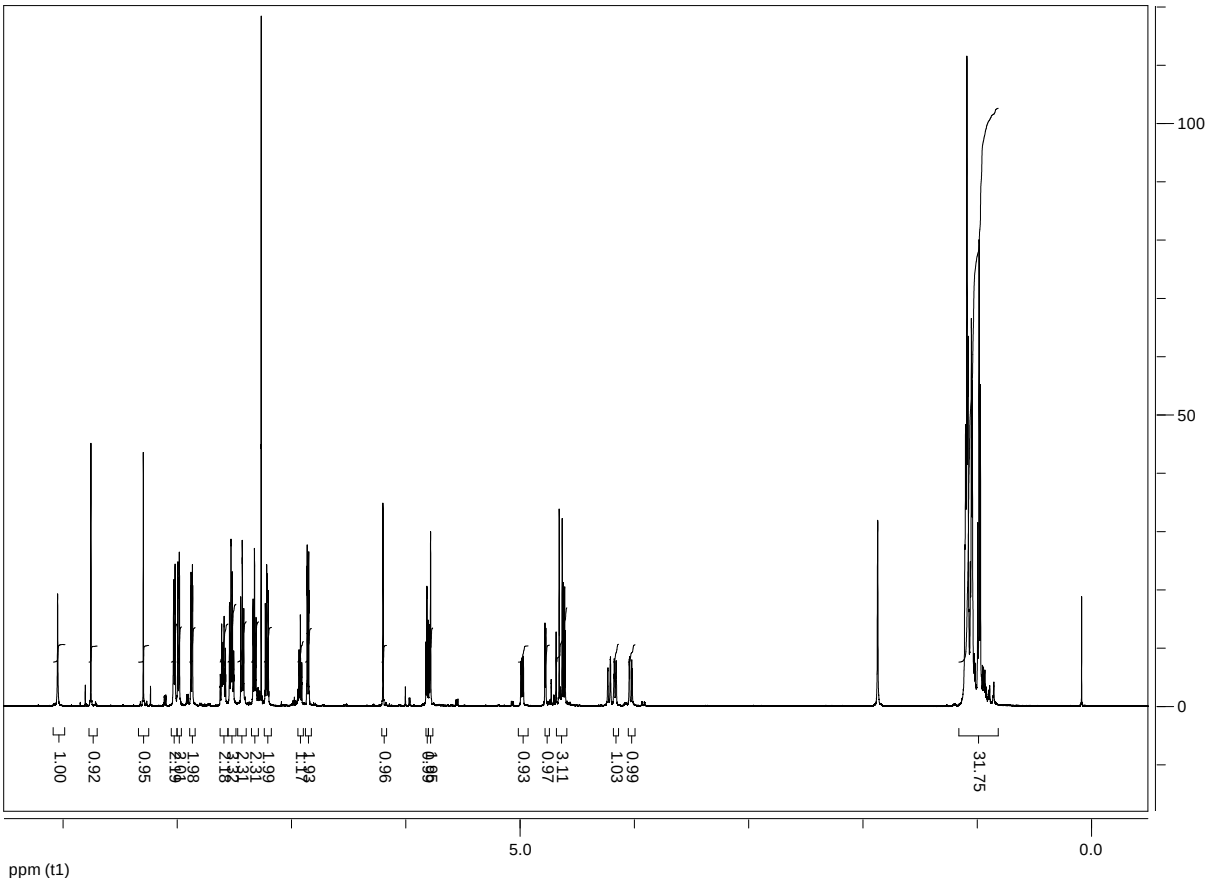

200
150
100
50
0
150
100
ppm (f1)

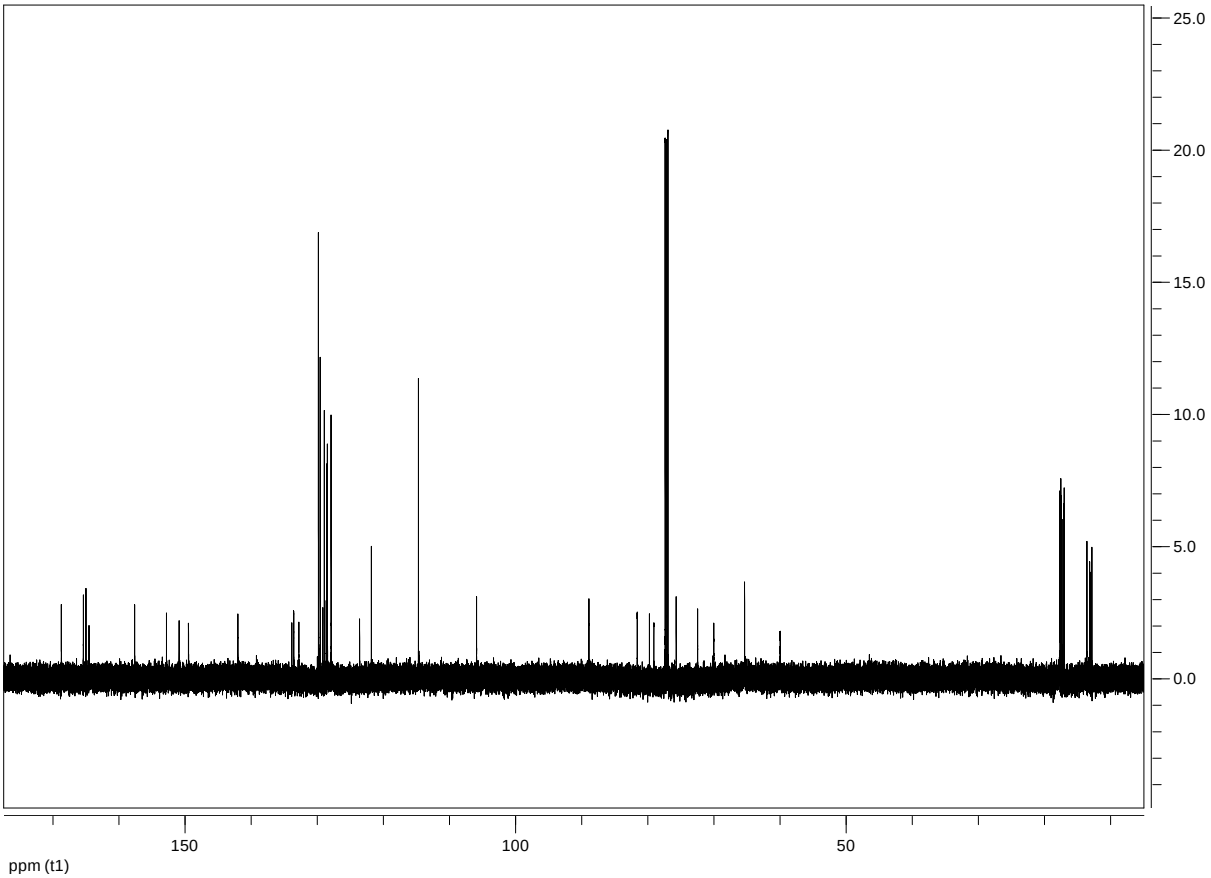
11


200
150
100
50
0
1.96
1.92
1.93
1.97
1.04
4.01
2.05
2.21
0.97
1.91
0.94
0.90
1.06
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

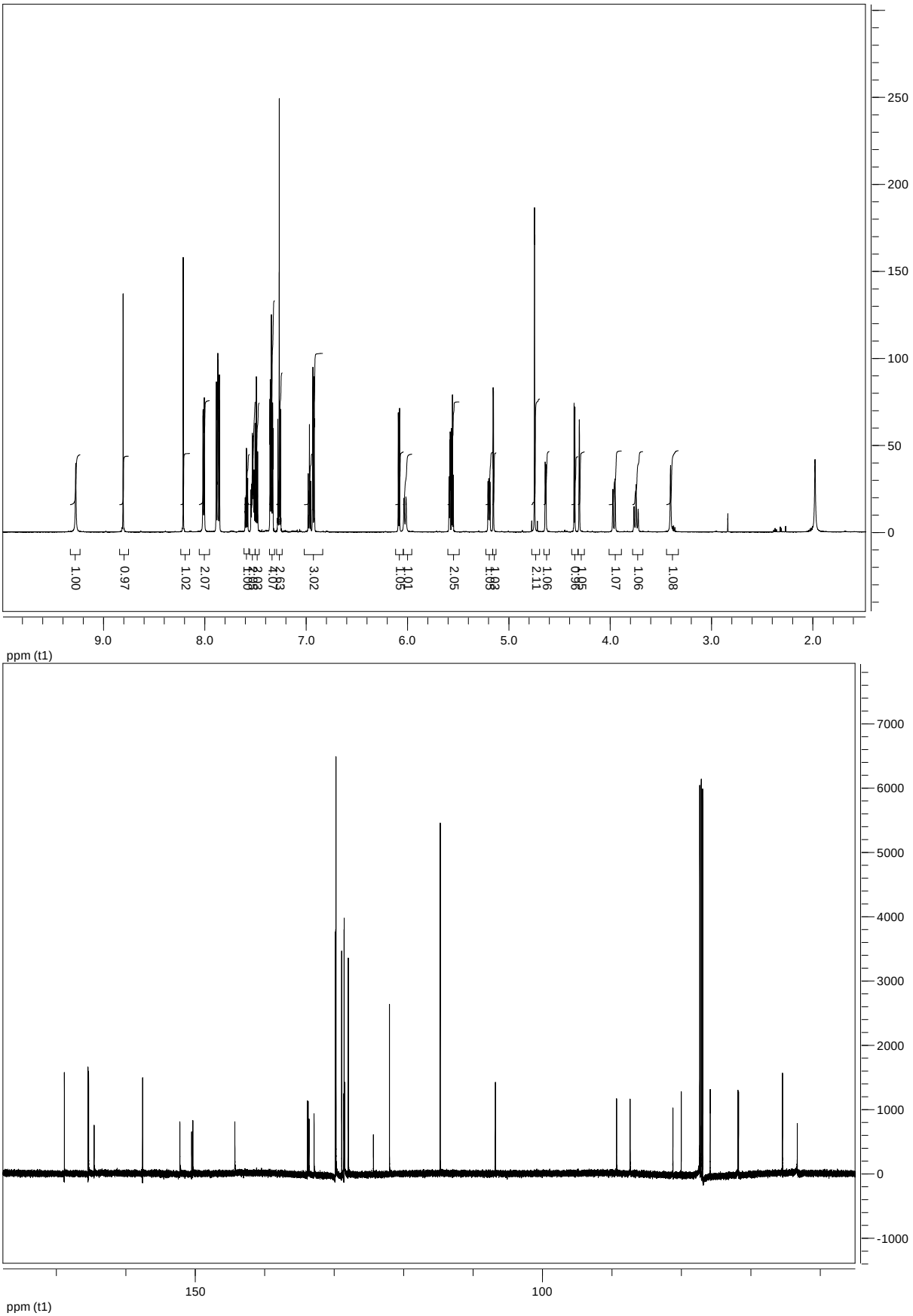

300
250
200
150
100
50
0
150
100
ppm (t1)

13

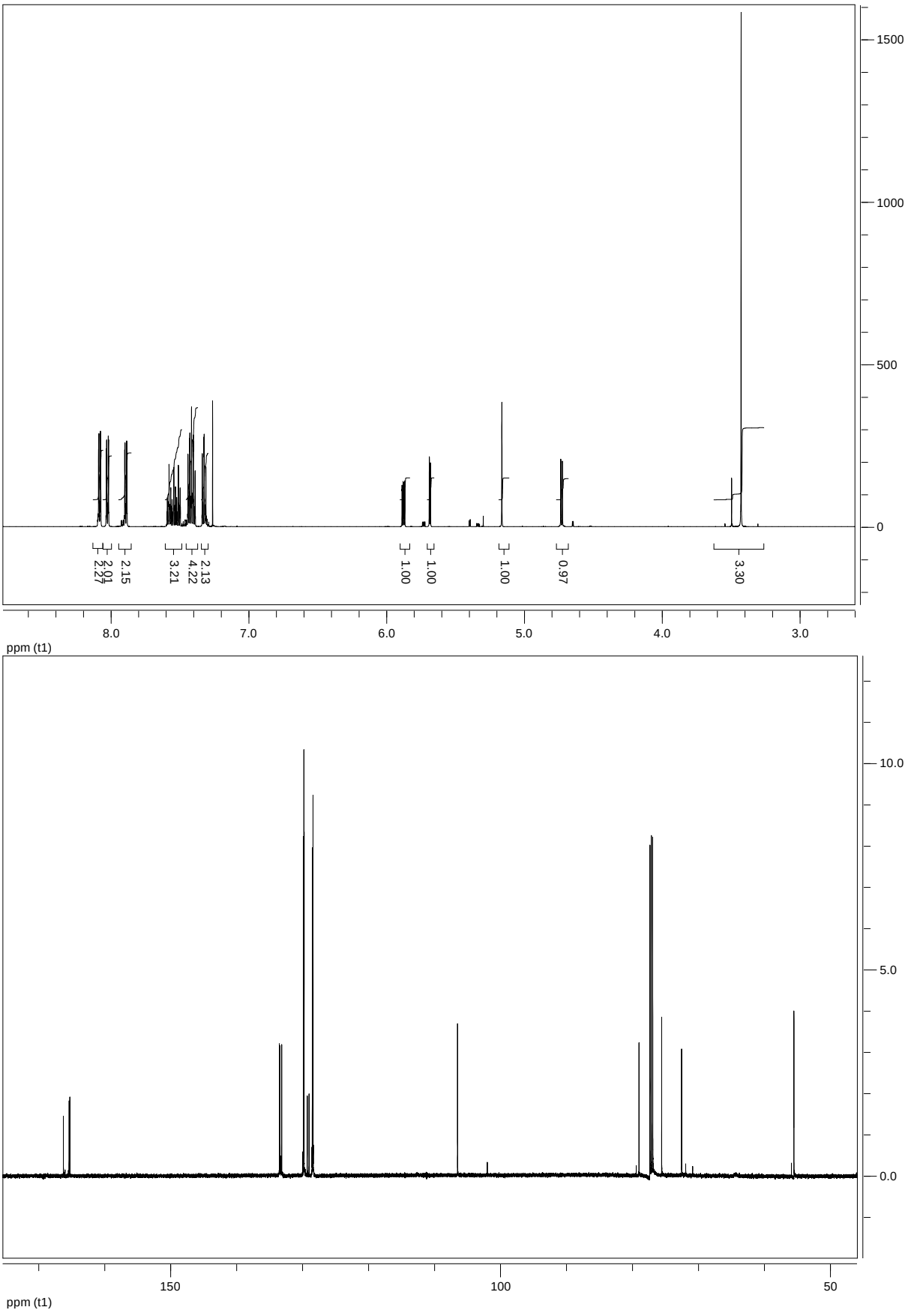

100
50
0
1.00
0.92
0.95
1.98
1.99
0.96
0.93
3.11
0.97
0.99
1.03
31.75
5.0
0.0
ppm (t1)


25.0
20.0
15.0
10.0
5.0
0.0
150
100
50
ppm (t1)

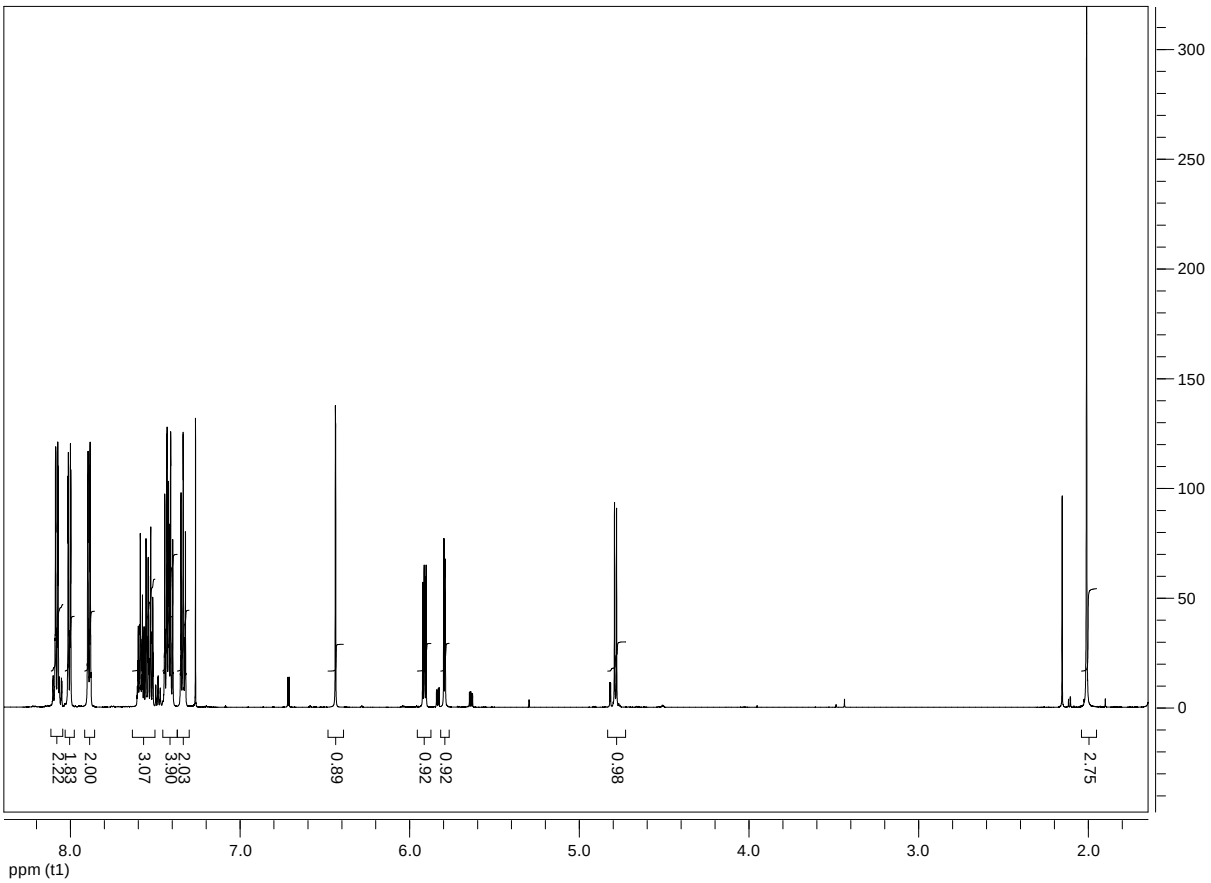
14

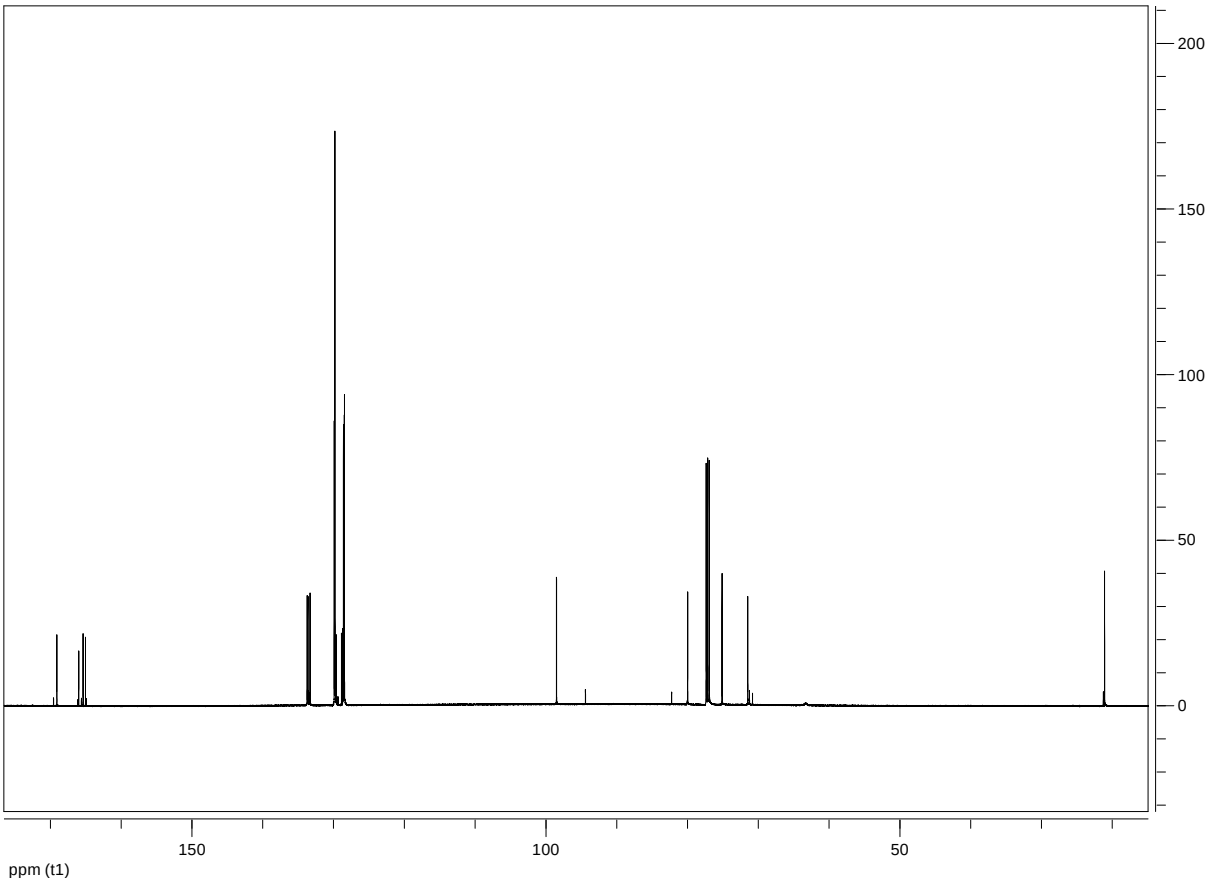

1.00
0.97
1.02
2.07
3.02
2.05
1.06
2.11
1.06
1.07
1.06
1.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
250
200
150
100
50
0
7000
6000
5000
4000
3000
2000
1000
0
-1000
150
100
ppm (t1)

15

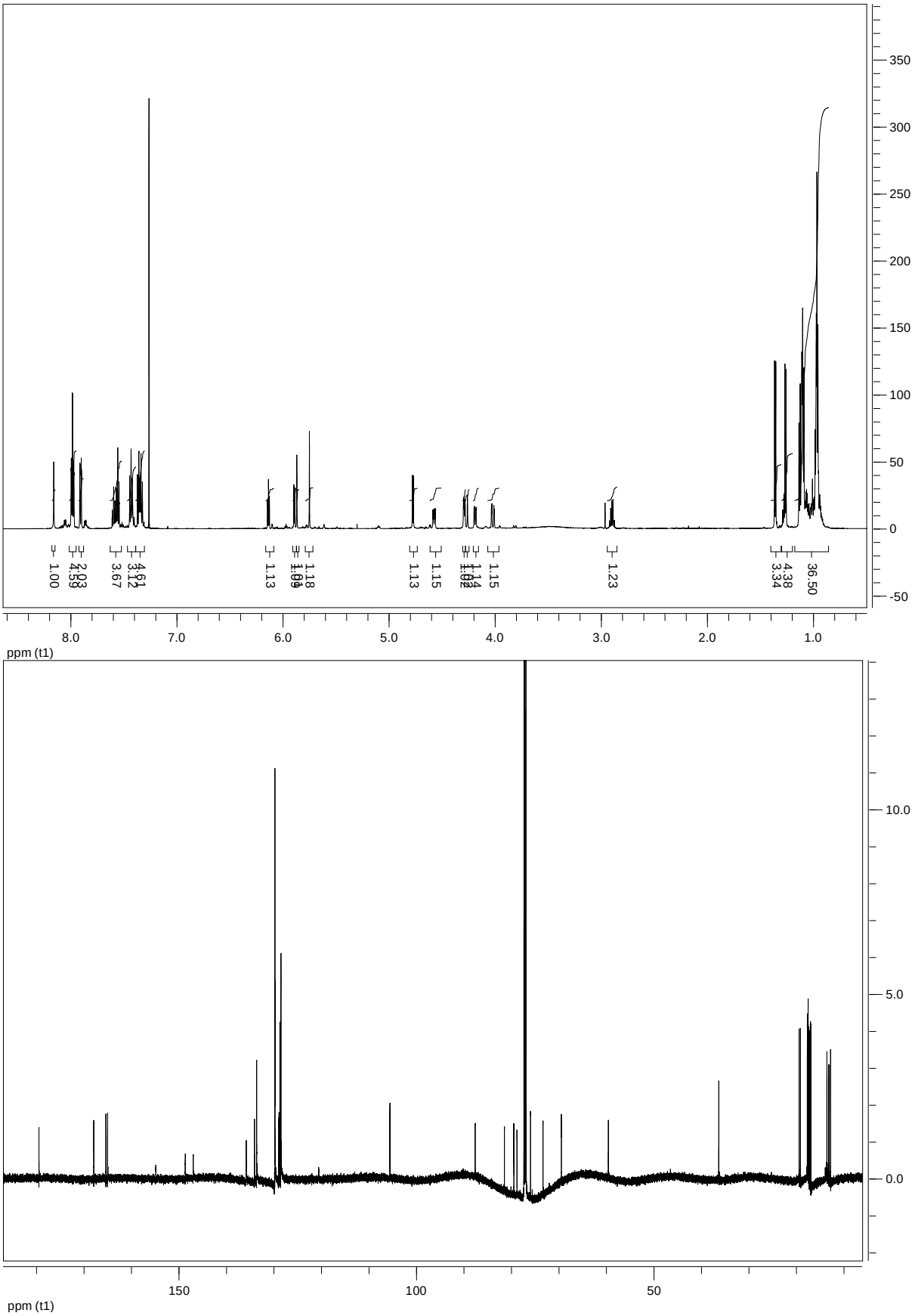

1500
1000
500
0
2.27
2.01
2.15
3.21
4.22
2.13
1.00
1.00
1.00
0.97
3.30
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)
10.0
5.0
0.0
150
100
50
ppm (t1)

16


2.22
1.83
2.00
3.07
2.03
3.90
0.89
0.92
0.92
0.98
2.75
300
250
200
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


200
150
100
50
0
150
100
50
ppm (t1)

18


1.00
2.03
4.59
3.67
3.12
4.61
1.13
1.18
1.00
1.13
1.15
1.14
1.02
1.15
1.23
3.34
4.38
36.50
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
350
300
250
200
150
100
50
0
-50
10.0
5.0
0.0
150
100
50
ppm (t1)

Reference

1. T. Brückl, D. Globisch, M. Wagner, M. Müller and T. Carell, *Angew. Chem. Int. Ed.*, 2009, **48**, 7932 –7934.