Supporting Information:

Direct synthesis of anomeric tetrazolyl iminosugars from sugar-derived lactams

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Contents

1 Experimental

1.1 General remarks

The reagents were purchased from Sigma Aldrich, Alfa Aesar or TCI Chemicals and used without further purification. All reactions involving air- and moisture-sensitive materials were carried out under an argon atmosphere in flame-dried glassware with magnetic stirring. THF was distilled from Na and benzophenone. CH_2Cl_2 was distilled from CaH_2. Column chromatography was performed with Kieselgel (230-400 mesh). Analytical TLC was performed with Silica gel 60 F254 aluminum plates (Merck) with visualization by UV light and charring with Pancaldi reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O). NMR analyses were performed with Varian Mercury 400 MHz, Varian VNMRS 500 MHz and 600 MHz spectrometers. Chemical shifts (δ) are reported relative to tetramethylsilane (TMS). The residual signal of solvent was used as an internal secondary reference ($CDCl_3$: $\delta_{^1H} = 7.26$, $\delta_{^{13}C} = 77.0$). Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 spectrophotometer and are reported in frequency of absorption (cm^{-1}). HRMS spectra were recorded on an ESI-TOF Mariner spectrometer (Perspective Biosystem) and are given in m/z. Melting points were measured on a Melting Point Meter MPMH2 apparatus and are uncorrected.

1.2 Synthetic procedures and Characterization Data

1.2.1 Synthesis of sugar-derived lactams.

Sugar-derived lactams used in this work were prepared according to procedures published earlier.[S1]

1.2.2 Synthesis of glucose-derived α-tetrazolylamines (3).

General Procedure: To a solid mixture of lactam **1** (107.4 mg, 0.20 mmol) and Schwartz's reagent (82.5 mg, 0.36 mmol, 1.6 equiv.) 4 mL of dry THF was added at room temperature. The reaction mixture was stirred at RT until it cleared, typically for about 2 h. Then

isocyanide was added (0.22 mmol, 1.1 equiv., dissolved in 0.5 mL of dry THF if it wasn't liquid), followed by $TMSN_3$ (29.1 µL, 0.22 mmol, 1.1 equiv.). The reaction mixture was stirred overnight, if not stated otherwise. It was then evaporated using a rotary evaporator and purified by flash column chromatography in the appropriate solvent system to give a pure product.

(*2R,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-cyclohexyl-1*H*-tetrazol-5-yl)piperidine (**3a**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 26.7 µL (0.22 mmol) of cyclo|hexyl isocyanide. It was purified using AcOEt in hexanes in 25 % to 40 % gradient as eluent and exceptionally using Florisil® as stationary phase. It was recrystallized from diethyl ether/hexanes mixture for X-ray analysis. **yield** 73 % (white needles); **mp.** 166–167°C; **[**α_D^{23}**]** = 27.3 (c = 2.10, DCM); **^{1}H-NMR (500 MHz, $CDCl_3$):** δ (ppm) 7.58–6.95 (m, 20 H), 4.97–4.87 (m, 2 H), 4.90, 4.55 (ABq, J = 11.4 Hz, 2 H), 4.84, 4.58 (ABq, J = 12.1 Hz, 2 H), 4.67 (t, J = 9.1 Hz, 1 H), 4.39, 4.34 (ABq, J = 11.8 Hz, 2 H), 4.32 (d, J = 6.2 Hz, 1 H), 4.02–3.92 (m, 1 H), 3.84 (dd, J = 9.4, 6.2 Hz, 1 H), 3.61–3.54 (m, 1 H), 3.51 (t, J = 9.5 Hz, 1 H), 3.51–3.45 (m, 1 H), 3.43–3.34 (m, 1 H), 2.04–1.64 (m, 7 H), 1.31–1.10 (m, 3 H); **^{13}C-NMR (126 MHz, $CDCl_3$):** δ (ppm) 152.3, 138.7, 138.7, 138.3, 137.9, 128.5, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.8, 127.6, 127.6, 127.5, 83.2, 80.9, 80.4, 75.6, 74.6, 74.5, 73.2, 69.6, 57.6, 53.9, 49.8, 33.3, 32.5, 25.3, 25.3, 24.8; **IR (film)** 3334, 3087, 3062, 3030, 2934, 2861, 1953, 1874, 1811, 1604, 1586, 1496, 1453, 1362, 1292, 1247, 1209, 1095, 1068, 1028, 1002; **HRMS** (ESI-TOF) m/z calcd for $C_{41}H_{47}N_5O_4Na$: 696.3526 found: 696.3503

(*2S,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-cyclohexyl-1*H*-tetrazol-5-yl)piperidine (**2-epi-3a**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**), but with addition of 0.5 µL of dry MeOH before addition of 26.7 µL (0.22 mmol) of cyclo|hexyl isocyanide. It was purified using AcOEt in hexanes in 30 % to

40 % gradient as eluent. **yield** 37 % (white solid); **mp.** 153–154°C; **[α_D^{23}]** = 21.5 (c = 1.00, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.62–7.12 (m, 20 H), 4.83, 4.74 (ABq, J = 11.1 Hz, 2 H), 4.78, 4.68 (ABq, J = 11.1 Hz, 2 H), 4.76, 4.46 (ABq, J = 11.1 Hz, 2 H), 4.58, 4.44 (ABq, J = 12.1 Hz, 2 H), 4.05–4.00 (m, 1 H), 3.83–3.76 (m, 1 H), 3.70–3.59 (m, 3 H), 3.53–3.47 (m, 1 H), 3.44–3.37 (m, 1 H), 3.03–2.98 (m, 1 H), 1.85–1.75 (m, 2 H), 1.62–1.50 (m, 3 H), 1.37–1.27 (m, 3 H), 1.19–1.01 (m, 1 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 168.5, 137.3, 137.2, 137.1, 136.3, 127.5, 127.4, 127.3, 127.3, 127.2, 127.1, 127.0, 126.9, 126.9, 126.7, 126.7, 126.6, 81.7, 78.8, 78.6, 73.9, 73.6, 73.1, 71.9, 68.9, 55.1, 54.0, 46.6, 31.9, 24.5, 23.4; **IR (film)** 3340, 3087, 3062, 3030, 2928, 2854, 1951, 1874, 1809, 1666, 1529, 1496, 1453, 1363, 1311, 1252, 1208, 1070, 1028; **HRMS** (ESI-TOF) m/z calcd for $C_{41}H_{48}N_5O_4$: 674.3706 found: 674.3685

Ethyl (5-((*2R,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)piperidin-2-yl)-1*H*-tetrazol-1-yl)acetate (**3b**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 24.0 µL (0.22 mmol) of ethyl isocyanoacetate. It was purified using AcOEt in DCM in 3 % to 7 % gradient as eluent. **yield** 49 % (white solid); **mp.** 94–95°C; **[α_D^{23}]** = 23.0 (c = 1.00, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.35–7.03 (m, 20 H), 5.12, 4.61 (ABq, J = 17.7 Hz, 2 H), 4.85, 4.78 (ABq, J = 10.9 Hz, 2 H), 4.79, 4.45 (ABq, J = 11.2 Hz, 2 H), 4.71, 4.49 (ABq, J = 12.1 Hz, 2 H), 4.46–4.42 (m, 1 H), 4.33, 4.27 (ABq, J = 11.9 Hz, 2 H), 4.29 (d, J = 5.7 Hz, 1 H), 4.06 (q, J = 7.1 Hz, 2 H), 3.81 (dd, J = 8.9, 5.7 Hz, 1 H), 3.48 (dd, J = 9.4, 4.9 Hz, 1 H), 3.43 (dd, J = 9.7, 8.4 Hz, 1 H), 3.40 (dd, J = 9.4, 2.8 Hz, 1 H), 3.15 (ddd, J = 9.7, 4.9, 2.8 Hz, 1 H), 1.14 (t, J = 7.1 Hz, 3 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 164.8, 153.1, 137.6, 137.5, 137.2, 136.8, 127.6, 127.4, 127.3, 127.3, 127.0, 127.0, 127.0, 126.8, 126.7, 126.7, 126.6, 126.5, 81.5, 79.5, 78.7, 74.4, 73.5, 73.1, 72.1, 68.4, 61.5, 52.9, 48.9, 47.1, 13.0; **IR (film)** 3337, 3087, 3062, 3030, 2982, 2908, 2868, 1955, 1877, 1811, 1751, 1604, 1496, 1453, 1396, 1373, 1308, 1211, 1094, 1069, 1027; **HRMS** (ESI-TOF) m/z calcd for $C_{39}H_{43}N_5O_6$: 678.3292 found: 678.3286

(*2R,3S,4R,5R,6R*)- 3,4,5-tris(benzyloxy)-6-[(benzyloxy)methyl]-2-(1-benzyl-1*H*-tetrazol-5-yl)piperidine (**3c**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 26.8 µL (0.22 mmol) of benzyl isocyanide. It was purified using AcOEt in hexanes in 10 % to 40 % gradient as eluent. **yield** 18 % (white solid); **mp.** 160–161°C; **[**α_D^{23}**]** = 19.4 (c = 1.07, DCM); **^{1}H-NMR (600 MHz, CDCl$_3$):** δ (ppm) 7.30–6.89 (m, 25 H), 5.44, 5.06 (ABq, J = 15.6 Hz, 2 H), 4.86, 4.81 (ABq, J = 10.8 Hz, 2 H), 4.80, 4.44 (ABq, J = 11.3 Hz, 2 H), 4.61, 4.35 (ABq, J = 12.3 Hz, 2 H), 4.59 (t, J = 9.2 Hz, 1 H), 4.26, 4.21 (ABq, J = 11.8 Hz, 2 H), 4.18 (d, J = 6.1 Hz, 1 H), 3.70 (dd, J = 9.4, 6.1 Hz, 1 H), 3.36–3.29 (m, 3 H), 3.12 (ddd, J = 9.7, 5.1, 2.8 Hz, 1 H); **^{13}C-NMR (151 MHz, cdcl$_3$):** δ (ppm) 153.1, 138.7, 138.5, 138.3, 137.8, 133.7, 129.2, 128.7, 128.6, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.6, 127.5, 127.5, 127.1, 83.0, 80.6, 80.1, 75.7, 74.6, 73.9, 73.1, 69.6, 53.6, 50.7, 49.6; **IR (film)** 3334, 3087, 3062, 3031, 2923, 2858, 1954, 1875, 1811, 1731, 1680, 1604, 1496, 1453, 1361, 1313, 1259, 1208, 1069, 1028, 1002; **HRMS** (ESI-TOF) m/z calcd for $C_{42}H_{44}N_5O_4$: 682.3393 found: 682.3383

(*2R,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-(4-methoxyphenyl)-1*H*-tetrazol-5-yl)piperidine (**3d**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 26.8 µL (0.22 mmol) of benzyl isocyanide. It was purified using 25 % AcOEt in hexanes as eluent. **yield** 23 % (white solid); **mp.** 156–157°C; **[**α_D^{23}**]** = 54.5 (c = 0.99, DCM); **^{1}H-NMR (600 MHz, CDCl$_3$):** δ (ppm) 7.35–7.14 (m, 20 H), 7.03–6.99 (m, 2 H), 6.91–6.86 (m, 2 H), 4.94 (ABq, J = 11.1 Hz, 2 H), 4.92, 4.56 (ABq, J = 11.4 Hz, 2 H), 4.85–4.79 (m, 1 H), 4.69, 4.43 (ABq, J = 12.2 Hz, 2 H), 4.40, 4.34 (ABq, J = 11.7 Hz, 2 H), 4.37 (d, J = 6.3 Hz, 1 H), 3.85 (s, 3 H), 3.72 (dd, J = 9.5, 6.3 Hz, 1 H), 3.60–3.51 (m, 2 H), 3.47 (d, J = 5.6 Hz, 2 H); **^{13}C-NMR (151 MHz, CDCl$_3$):** δ (ppm) 160.9, 153.5, 138.8, 138.7, 138.0, 137.9, 128.4, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.5, 127.1, 126.3, 114.7, 83.2, 80.8, 80.4, 75.7, 74.7, 73.8, 73.2, 69.7, 55.7, 53.7, 49.2;

IR (film) 3652, 3329, 3062, 3030, 2909, 2867, 2053, 1955, 1879, 1813, 1607, 1589, 1517, 1454, 1362, 1306, 1255, 1209, 1098, 1068, 1027; **HRMS** (ESI-TOF) m/z calcd for $C_{42}H_{44}N_5O_5$: 698.3342 found: 698.3341

(*2S,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-(4-methoxyphenyl)-1*H*-tetrazol-5-yl)piperidine (**2-epi-3d**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 26.8 µL (0.22 mmol) of benzyl isocyanide. It was purified using 25 % AcOEt in hexanes as eluent. **yield** 6 % (yellow waxy oil); $[\alpha_D^{23}] = 8.7$ ($c = 0.27$, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.63–7.55 (m, 2 H), 7.49–7.28 (m, 20 H), 7.10–7.02 (m, 2 H), 4.88, 4.65 (ABq, $J = 11.4$ Hz, 2 H), 4.82 (s, 2 H), 4.80, 4.59 (ABq, $J = 12.1$ Hz, 2 H), 4.52–4.48 (m, 1 H), 4.43 (d, $J = 5.1$ Hz, 1 H), 4.41–4.36 (m, 1 H), 4.04 (t, $J = 7.3$ Hz, 1 H), 3.99 (s, 3 H), 3.81 (dd, $J = 9.3, 5.0$ Hz, 1 H), 3.57 (dd, $J = 9.3, 4.1$ Hz, 1 H), 3.05 (bs, 1 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 160.8, 153.8, 138.5, 138.5, 138.3, 138.1, 128.4, 128.4, 128.3, 127.9, 127.8, 127.8, 127.8, 127.6, 127.6, 127.6, 127.5, 126.7, 126.6, 114.6, 79.0, 76.7, 76.0, 73.8, 73.1, 73.0, 72.8, 69.0, 55.6, 55.4, 48.9; **IR (film)** 3330, 3061, 3029, 2924, 2854, 1952, 1878, 1728, 1607, 1517, 1497, 1454, 1364, 1306, 1256, 1208, 1174, 1096, 1027; **HRMS** (ESI-TOF) m/z calcd for $C_{42}H_{44}N_5O_5$: 698.3342 found: 698.3348

(*2R,3R,4R,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-(4-methoxybenzyl)-1*H*-tetrazol-5-yl)piperidine (**3e**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 32.4 mg (0.22 mmol) of 4-methoxybenzyl isocyanide dissolved in 0.5 mL of dry THF. It was purified using *tert*-butyl methyl ether in DCM in 0 % to 3 % gradient as eluent. **yield** 42 % (white needles); **mp.** 139–142°C; $[\alpha_D^{23}] = 22.1$ ($c = 1.00$, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.33–7.18 (m, 18 H), 7.13–7.09 (m, 2 H), 6.97–6.94 (m, 2 H), 6.75–6.72 (m, 2 H), 5.43, 5.09 (ABq, $J = 15.4$ Hz, 2 H), 4.92, 4.88 (ABq, $J = 10.8$ Hz, 2 H), 4.87, 4.51 (ABq, $J = 11.3$ Hz, 2 H), 4.68, 4.42 (ABq, $J = 12.3$ Hz, 2 H), 4.65 (t, $J = 9.2$ Hz, 1 H), 4.34, 4.30 (ABq, $J = 11.9$ Hz, 2 H), 4.29 (d, $J = 5.8$ Hz, 1 H), 3.81–

3.76 (m, 1 H), 3.70 (s, 3 H), 3.45–3.37 (m, 3 H), 3.24–3.18 (m, 1 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 159.8, 152.9, 138.8, 138.6, 138.3, 137.8, 128.8, 128.6, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.5, 114.6, 83.1, 80.7, 80.0, 75.7, 74.6, 73.9, 73.1, 69.5, 55.2, 53.7, 50.4, 49.6; **IR (film)** 3335, 3087, 3062, 3030, 2908, 2866, 1954, 1877, 1812, 1613, 1586, 1515, 1496, 1454, 1398, 1361, 1306, 1293, 1252, 1208, 1178, 1093, 1069, 1029, 1002; **HRMS** (ESI-TOF) m/z calcd for $C_{43}H_{46}N_5O_5$: 712.3499 found: 712.3484

(*2R,3R,4R,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-(*tert*-butyl)-1*H*-tetrazol-5-yl)piperidine (**3f**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 22.6 µL (0.22 mmol) of *tert*-butyl isocyanide. The reaction was stirred for 12 d. It was purified using AcOEt in hexanes in 10 % to 40 % gradient as eluent. **yield** 40 % (white solid); **mp.** 164–165°C; **[α_D^{23}]** = 37.1 (c = 0.54, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.32–6.96 (m, 20 H), 4.98 (t, J = 9.2 Hz, 1 H), 4.88, 4.87 (ABq, J = 10.8 Hz, 2 H), 4.85, 4.49 (ABq, J = 11.2 Hz, 2 H), 4.76, 4.53 (ABq, J = 12.0 Hz, 2 H), 4.68 (d, J = 6.4 Hz, 1 H), 4.30, 4.27 (ABq, J = 11.8 Hz, 2 H), 3.79 (dd, J = 9.5, 6.4 Hz, 1 H), 3.52–3.46 (m, 1 H), 3.43 (t, J = 9.5 Hz, 1 H), 3.40–3.37 (m, 1 H), 3.09 (ddd, J = 10.0, 4.7, 2.7 Hz, 1 H), 1.54 (s, 9 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 152.4, 138.9, 138.7, 138.2, 137.9, 128.4, 128.4, 128.4, 128.3, 128.1, 127.7, 127.7, 127.7, 127.7, 127.6, 127.5, 127.4, 83.5, 81.4, 80.6, 75.7, 74.6, 74.3, 73.1, 69.7, 61.2, 53.2, 50.5, 30.2; **IR (film)** 3328, 3087, 3061, 3030, 2984, 2915, 2866, 1954, 1875, 1812, 1728, 1604, 1496, 1453, 1400, 1363, 1334, 1285, 1238, 1211, 1094, 1069, 1028; **HRMS** (ESI-TOF) m/z calcd for $C_{39}H_{46}N_5O_4$: 648.3550 found: 648.3542

(*2R,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-(*tert*-octyl)-1*H*-tetrazol-5-yl)piperidine (**3g**)

The compound was synthesized according to the general procedure for glucose-derived α-tetrazoloamines (**3**) using 40.9 µL (0.22 mmol) of *tert*-octyl isocyanide. The reaction was stirred for 3 d. It was purified using 20 % AcOEt in hexanes as eluent. **yield** 48 % (yellow

oil); $[\alpha_D^{23}]$ = 24.2 (c = 0.83, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.34–7.01 (m, 20 H), 5.07 (t, J = 9.2 Hz, 1 H), 4.89, 4.87 (ABq, J = 10.8 Hz, 2 H), 4.85, 4.50 (d, J = 11.3 Hz, 2 H), 4.70 (d, J = 6.5 Hz, 1 H), 4.74, 4.54 (ABq, J = 12.1 Hz, 2 H), 4.27, 4.27 (ABq, J = 12.1 Hz, 2 H), 3.77 (dd, J = 9.5, 6.4 Hz, 1 H), 3.49 (dd, J = 9.1, 4.6 Hz, 1 H), 3.45 (dd, J = 10.1, 8.9 Hz, 1 H), 3.35 (dd, J = 9.1, 2.7 Hz, 1 H), 3.02 (ddd, J = 10.1, 4.6, 2.7 Hz, 1 H), 2.06 (s, 1 H), 1.99 (d, J = 15.2 Hz, 1 H), 1.74 (s, 3 H), 1.74 (d, J = 15.2 Hz, 1 H), 1.50 (s, 3 H), 0.62 (s, 9 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 152.2, 138.9, 138.8, 138.2, 137.9, 128.5, 128.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.0, 83.6, 81.5, 80.7, 75.7, 74.6, 74.1, 73.2, 69.5, 65.1, 53.7, 53.0, 50.7, 31.6, 30.8, 30.5, 30.0; **IR (film)** 3327, 3087, 3062, 3030, 2952, 2906, 2868, 1952, 1874, 1810, 1604, 1586, 1496, 1453, 1394, 1362, 1334, 1286, 1247, 1209, 1139, 1098, 1068, 1028, 1001; **HRMS** (ESI-TOF) m/z calcd for $C_{41}H_{55}N_5O_4Na$: 704.4152 found: 704.4152

1.2.3 Synthesis of galactose-derived α-tetrazolylamines (5).

General procedure: To a suspension of Schwartz's reagent (82.5 mg, 0.36 mmol, 1.6 equiv.) in dry THF (2 mL), a solution of lactam **4** (107.4 mg, 0.20 mmol) in 2 mL of dry THF was added at room temperature. The reaction mixture was stirred at RT until it cleared, typically for about 15 min. Then isocyanide was added (0.22 mmol, 1.1 equiv., dissolved in 0.5 mL of dry THF if it wasn't liquid), followed by $TMSN_3$ (29.1 µL, 0.22 mmol, 1.1 equiv.). The reaction mixture was stirred overnight, if not stated otherwise. It was then evaporated using a rotary evaporator and purified by flash column chromatography in the appropriate solvent system to give a pure product.

(*2R,3S,4R,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-cyclohexyl-1*H*-tetrazol-5-yl)piperidine (**5a**)

The compound was synthesized according to the general procedure for galactose-derived α-tetrazoloamines (**5**) using 26.7 µL (0.22 mmol) of cyclohexyl isocyanide. It was purified using a 2:28:70 mixture of Et_3N/AcOEt/hexanes as eluent. **yield** 33 % (white solid); **mp.**

158–159°C; $[\alpha_D^{23}]$ = 33.4 (c = 1.01, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.30–7.12 (m, 18 H), 6.97–6.91 (m, 2 H), 4.69, 4.33 (ABq, J = 10.8 Hz, 2 H), 4.60, 4.52 (ABq, J = 12.1 Hz, 2 H), 4.53–4.50 (m, 2 H), 4.42, 4.41 (ABq, J = 12.2 Hz, 2 H), 4.39 (t, J = 8.3 Hz, 1 H), 4.35–4.29 (m, 1 H), 4.12 (d, J = 8.5 Hz, 1 H), 3.88 (dd, J = 3.7, 2.9 Hz, 1 H), 3.84 (dd, J = 8.0, 2.6 Hz, 1 H), 3.56 (dd, J = 9.6, 5.1 Hz, 1 H), 3.50 (dd, J = 9.6, 5.6 Hz, 1 H), 3.20 (q, J = 5.0 Hz, 1 H), 1.94–1.49 (m, 7 H), 1.21–0.99 (m, 3 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 154.2, 138.6, 138.5, 138.4, 138.1, 128.8, 128.7, 128.7, 128.6, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 128.0, 127.7, 79.2, 75.2, 75.0, 73.8, 72.4, 72.2, 70.3, 58.1, 55.2, 51.8, 33.4, 32.8, 25.5, 25.5, 25.1; **IR (film)** 3328, 3087, 3062, 3030, 2933, 2860, 1952, 1872, 1811, 1670, 1604, 1496, 1453, 1365, 1261, 1207, 1097, 1027; **HRMS** (ESI-TOF) m/z calcd for $C_{41}H_{48}N_5O_4$: 674.3706 found: 674.3694

(*2R,3S,4R,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1-cyclohexyl-1*H*-tetrazol-5-yl)piperidine (**2-epi-5a**)

The compound was synthesized according to the general procedure for galactose-derived α-tetrazoloamines (**5**), but with addition of 0.5 µL of dry MeOH before addition of 26.7 µL (0.22 mmol) of cyclo|hexyl isocyanide. It was purified by preparative HPLC using 10 % acetone in toluene as eluent. **yield** 3 % (white waxy oil); $[\alpha_D^{23}]$ = 21.8 (c = 0.17, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.37–7.23 (m, 18 H), 7.16–7.12 (m, 2 H), 4.91, 4.56 (ABq, J = 11.3 Hz, 2 H), 4.79, 4.75 (ABq, J = 11.7 Hz, 2 H), 4.78, 4.59 (ABq, J = 11.7 Hz, 2 H), 4.46 (d, J = 6.2 Hz, 1 H), 4.43, 4.40 (ABq, J = 11.9 Hz, 1 H), 4.32–4.25 (m, 1 H), 4.17–4.07 (bs, 1 H), 4.09 (t, J = 2.4 Hz, 1 H), 3.72 (td, J = 6.8, 2.1 Hz, 1 H), 3.52–3.44 (m, 1 H), 3.43–3.35 (m, 1 H), 2.00–1.91 (m, 1 H), 1.91–1.86 (m, 1 H), 1.86–1.74 (m, 3 H), 1.72–1.63 (m, 1 H), 1.25–1.11 (m, 4 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 152.8, 138.8, 138.6, 138.3, 138.0, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 76.6, 75.3, 74.4, 74.2, 73.2, 72.9, 69.5, 57.8, 53.2, 49.9, 33.2, 32.5, 25.3, 25.2, 24.8; **IR (film)** 3316, 3061, 3031, 2923, 2855, 1952, 1876, 1811, 1733, 1668, 1604, 1496, 1453, 1365, 1266, 1208, 1097, 1027; **HRMS** (ESI-TOF) m/z calcd for $C_{41}H_{48}N_5O_4$: 674.3706 found: 674.3707

Ethyl (5-((*2R,3S,4R,5S,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)piperidin-2-yl)-1*H*-tetrazol-1-yl)acetate (**5b**)

The compound was synthesized according to the general procedure for galactose-derived α-tetrazoloamines (**5**) using 26.7 µL (0.22 mmol) of cyclohexyl isocyanide. It was purified using 30 % AcOEt in cyclohexane as eluent. **yield** 16 % (white solid); **mp.** 144–145°C; **[α_D^{23}]** = −48.9 (c = 0.43, DCM); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ (ppm) 7.38–7.13 (m, 20 H), 5.29, 5.26 (ABq, J = 17.3 Hz, 2 H), 4.74 (t, 1 H), 4.62 (s, 2 H), 4.53, 4.44 (ABq, J = 12.4 Hz, 2 H), 4.50, 4.46 (ABq, J = 12.1 Hz, 2 H), 4.40, 4.32 (ABq, J = 11.8 Hz, 2 H), 4.36–4.32 (m, 1 H), 4.14 (q, J = 7.1 Hz, 2 H), 3.91–3.85 (m, 2 H), 3.71 (dd, J = 9.3, 4.2 Hz, 1 H), 3.53 (dd, J = 9.3, 3.8 Hz, 1 H), 3.16–2.98 (m, 1 H), 2.41 (s, 1 H), 1.20 (t, J = 7.1 Hz, 3 H); **^{13}C-NMR (126 MHz, $CDCl_3$):** δ (ppm) 165.1, 153.8, 137.1, 136.9, 136.9, 136.8, 127.5, 127.4, 127.3, 127.3, 127.1, 126.9, 126.8, 126.8, 126.7, 126.6, 126.6, 126.5, 75.1, 72.4, 72.2, 72.1, 70.5, 70.1, 68.2, 61.1, 51.1, 50.5, 48.5, 13.1; **IR (film)** 3341, 3061, 3030, 2924, 2866, 1955, 1879, 1813, 1751, 1604, 1496, 1453, 1396, 1373, 1308, 1260, 1211, 1100, 1026; **HRMS** (ESI-TOF) m/z calcd for $C_{39}H_{43}N_5O_6$: 678.3292 found: 678.3298

1.2.4 Synthesis of derived compounds (6, 7, 8 and 9).

(*8R,9R,10R,11S,11aR*)-9,10,11-tris(benzyloxy)-8-((benzyloxy)methyl)-9,10,11,11a-tetrahydro-8*H*-pyrido[1,6-a]tetrazolo[5,1-c]pyrazin-6(5*H*)-one (**6**)

The compound was synthesized by the following procedure: 70 mg (0.10 mmol) of compound **3b** and 14.7 mg (0.12 mmol, 1.2 equiv.) of benzoic acid was dissolved in 5.0 mL of toluene. The mixture was heated to 70 °C and stirred for 16 h. It was then let to cool to room temperature, quenched with 10 mL saturated $NaHCO_{3(aq)}$ and extracted with AcOEt (2 × 10 mL). Organic phase was washed with water, dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography using 40 % *tert*-butyl methyl ether in hexanes as eluent. **yield** 95 % (light yellow waxy oil); **[α_D^{23}]** = −10.8 (c = 1.00, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.37–7.13 (m, 18 H), 6.80–6.77 (m, 2 H), 5.36–5.33 (m, 1 H),

5.29–5.25 (m, 1 H), 5.01 (dd, $J = 17.3, 1.0$ Hz, 1 H), 4.83 (dd, $J = 17.3, 1.0$ Hz, 1 H), 4.69, 4.53 (ABq, $J = 11.5$ Hz, 2 H), 4.51, 4.48 (ABq, $J = 11.8$ Hz, 2 H), 4.48, 4.39 (ABq, $J = 12.1$ Hz, 2 H), 4.34, 4.01 (ABq, $J = 11.1$ Hz, 2 H), 3.98 (t, $J = 2.1$ Hz, 1 H), 3.82 (t, $J = 3.5$ Hz, 1 H), 3.81–3.78 (m, 2 H), 3.68 (dd, $J = 10.4, 5.7$ Hz, 1 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 161.6, 148.4, 137.6, 137.5, 136.9, 136.5, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 77.5, 74.9, 73.0, 73.0, 72.6, 72.3, 72.3, 66.2, 52.1, 49.5, 47.9; **IR (film)** 3087, 3062, 3031, 2923, 2868, 1956, 1879, 1813, 1725, 1671, 1604, 1585, 1567, 1496, 1454, 1421, 1393, 1367, 1347, 1256, 1207, 1177, 1092, 1028; **HRMS** (ESI-TOF) m/z calcd for $C_{37}H_{37}N_5O_5Na$: 654.2692 found: 654.2670

(*8R,9S,10R,11S,11aR*)-9,10,11-tris(benzyloxy)-8-((benzyloxy)methyl)-5,6,9,10,11,11a-hexahydro-8*H*-pyrido[1,6-a]tetrazolo[5,1-c]pyrazine (**7**)

The compound was synthesized by the following procedure: 10 mg (0.016 mmol) of compound **6** was dissolved in 0.3 mL of dry THF and added to 6.6 mg (0.026 mmol, 1.6 equiv.) of $Cp_2Zr(H)Cl$. The mixture was stirred at room temperature until it cleared (for about 4 h). 2.0 mg (0.048 mmol, 3.0 equiv.) of $NaBH_4$ was added and mixture was stirred at RT overnight. Then 0.048 mL 1.0 M solution of $BH_3 \cdot THF$ in THF (0.048 mmol, 3.0 equiv.) was added. After 3 d of stirring at RT the reaction was quenched by 2 mL of water, extracted with AcOEt (3×5 mL), dried with $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography using *tert*-butyl methyl ether in DCM in 10 % to 40 % gradient as eluent. **yield** 75 % (yellow oil); **[α_D^{23}]** = 3.8 ($c = 0.41$, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.34–7.24 (m, 12 H), 7.24–7.20 (m, 4 H), 7.18–7.14 (m, 2 H), 7.13–7.09 (m, 2 H), 4.58, 4.48 (ABq, $J = 12.4$ Hz, 2 H), 4.56 (d, $J = 2.8$ Hz, 1 H), 4.53 (ddd, $J = 12.7, 8.5, 4.5$ Hz, 1 H), 4.46–4.38 (m, 4 H), 4.40, 4.27 (ABq, $J = 11.7$ Hz, 2 H), 4.36 (dt, $J = 12.5, 4.3$ Hz, 1 H), 4.20–4.16 (m, 1 H), 3.80 (dd, $J = 10.1, 6.3$ Hz, 1 H), 3.67 (dt, $J = 12.9, 4.4$ Hz, 1 H), 3.61 (dt, $J = 7.5, 3.2$ Hz, 2 H), 3.58 (dd, $J = 10.1, 5.5$ Hz, 1 H), 3.41–3.37 (m, 1 H), 3.18 (dt, $J = 8.4, 4.4$ Hz, 1 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 150.8, 137.1, 136.8, 136.6, 136.4, 127.5, 127.5, 127.4, 127.4, 127.3, 126.9, 126.9, 126.8, 126.8,

126.7, 126.7, 126.6, 75.3, 73.0, 72.8, 72.6, 72.3, 71.5, 71.1, 66.1, 61.0, 50.6, 47.0, 44.2; **IR (film)** 3059, 3031, 2923, 2852, 1953, 1878, 1812, 1728, 1676, 1604, 1544, 1496, 1454, 1364, 1265, 1207, 1172, 1090, 1028; **HRMS** (ESI-TOF) m/z calcd for $C_{37}H_{39}N_5O_4Na$: 640.2900 found: 640.2892

(*2R,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(2-(4-methoxyphenyl)-2*H*-tetrazol-5-yl)piperidine (**8**)

The compound was synthesized by the following procedure: 20.0 mg (0.028 mmol) of compound **3e** was dissolved in 0.5 mL of TFA and was stirred at RT for 24 h. It was then evaporated, dissolved in 20 mL of DCM, washed with 20 mL of $NaHCO_{3(aq)}$ and 20 mL of brine and then dried with $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography using 5 % of AcOEt in DCM as eluent. **yield** 95 % (colourless oil); **[**α_D^{23}**]** = 49.6 (c = 0.87, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.32–7.12 (m, 22 H), 6.84–6.79 (m, 2 H), 5.68 (ABq, J = 14.5 Hz, 2 H), 4.91 (d, J = 5.9 Hz, 1 H), 4.88, 4.52 (ABq, J = 11.0 Hz, 2 H), 4.87, 4.77 (ABq, J = 10.8 Hz, 2 H), 4.66, 4.57 (ABq, J = 11.5 Hz, 2 H), 4.36 (ABq, J = 11.7 Hz, 2 H), 4.38–4.32 (m, 1 H), 3.90 (dd, J = 9.2, 6.5 Hz, 1 H), 3.74 (s, 3 H), 3.63–3.58 (m, 1 H), 3.49–3.41 (m, 3 H); **^{13}C-NMR (151 MHz, $CDCl_3$):** δ (ppm) 165.2, 159.8, 138.9, 138.4, 137.9, 137.8, 129.7, 128.3, 128.2, 128.2, 128.2, 127.9, 127.9, 127.8, 127.8, 127.6, 127.5, 127.5, 127.4, 125.4, 114.2, 82.9, 80.4, 80.0, 75.5, 74.9, 73.0, 72.2, 70.2, 56.2, 55.2, 53.9, 50.9; **IR (film)** 3341, 3087, 3062, 3030, 3005, 2925, 2864, 2056, 1954, 1877, 1812, 1613, 1586, 1515, 1496, 1454, 1394, 1362, 1330, 1305, 1251, 1208, 1178, 1088, 1070, 1029; **HRMS** (ESI-TOF) m/z calcd for $C_{43}H_{46}N_5O_5$: 712.3499 found: 712.3477

(*2R,3S,4R,5R,6R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-2-(1*H*-tetrazol-5-yl)piperidine (**9**)

The compound was synthesized by the following procedure: 44.3 mg (0.063 mmol) of compound **3g** was dissolved in 6.0 mL of 4.0 M solution of HCl in dioxane and the flask was closed tightly. The mixture was stirred at 90 °C for 24 h. It was then let to cool to room temperature, diluted with 10 mL of *tert*-butyl methyl ether and 10 mL of water. $NaHCO_3$

was slowly added while stirring until pH = 7 was reached, then the mixture was separated. Aqueous phase was extracted with *tert*-butyl methyl ether (2 × 5 mL). Combined organic phases were dried with $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography using $NH_{3(aq)}$/MeOH/DCM in 0:10:90 to 1:20:80 gradient as eluent. **yield** 75 % (light grey solid); **mp.** 180–183°C; $[\alpha_D^{23}]$ = 57.2 (c = 0.60, DCM); **^{1}H-NMR (600 MHz, $CDCl_3$):** δ (ppm) 7.34–7.10 (m, 20 H), 4.86, 4.71 (ABq, J = 11.2 Hz, 2 H), 4.81, 4.78 (ABq, J = 11.0 Hz, 2 H), 4.77, 4.46 (ABq, J = 11.0 Hz, 2 H), 4.69–4.66 (m, 1 H), 4.55, 4.41 (ABq, J = 11.9 Hz, 2 H), 4.03 (dd, J = 9.2, 5.7 Hz, 1 H), 3.64 (dd, J = 9.8, 2.7 Hz, 1 H), 3.54 (dd, J = 9.8, 6.0 Hz, 1 H), 3.51–3.42 (m, 2 H), 3.16–3.07 (m, 1 H); **^{13}C-NMR (126 MHz, $CDCl_3$):** δ (ppm) 154.8, 138.1, 137.8, 137.6, 136.8, 128.9, 128.7, 128.5, 128.4, 128.4, 128.2, 128.1, 127.9, 127.9, 127.8, 127.8, 127.8, 83.1, 79.6, 79.4, 75.7, 75.1, 74.8, 73.1, 69.1, 54.6, 51.0; **IR (film)** 3316, 3087, 3062, 3031, 2955, 2925, 2855, 1951, 1875, 1810, 1737, 1667, 1590, 1554, 1496, 1454, 1399, 1364, 1332, 1312, 1277, 1248, 1208, 1187, 1085, 1028; **HRMS** (ESI-TOF) m/z calcd for $C_{35}H_{38}N_5O_4$: 592.2924 found: 592.2925

2 Crystallographic data of compounds 3a and 3e

Colorless crystals suitable for X-ray structural analysis were obtained by slow evaporation of hexane–diethyl ether solution of **3a** and heptane-diethyl ether solution of **3e**. Crystal data were obtained on a Bruker APEX II CCD detector employing graphite monochromated Cu-Kα radiation ($\lambda = 1.541\,78$ Å) at 296(2) K and operating in the $\phi - \omega$ scan mode. The structure was solved by direct methods SHELXS-2014[S2] and refined with full-matrix least-squares calculations on F^2 using SHELX-2014.[S2] All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. Crystallographic data for **3a** and **3e** have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC 1878740). Copies of these data can be obtained free of charge *via* `www.ccdc.cam.ac.uk/conts/retrieving.html` or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK [fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk].

2.1 Crystal structure of compound 3a

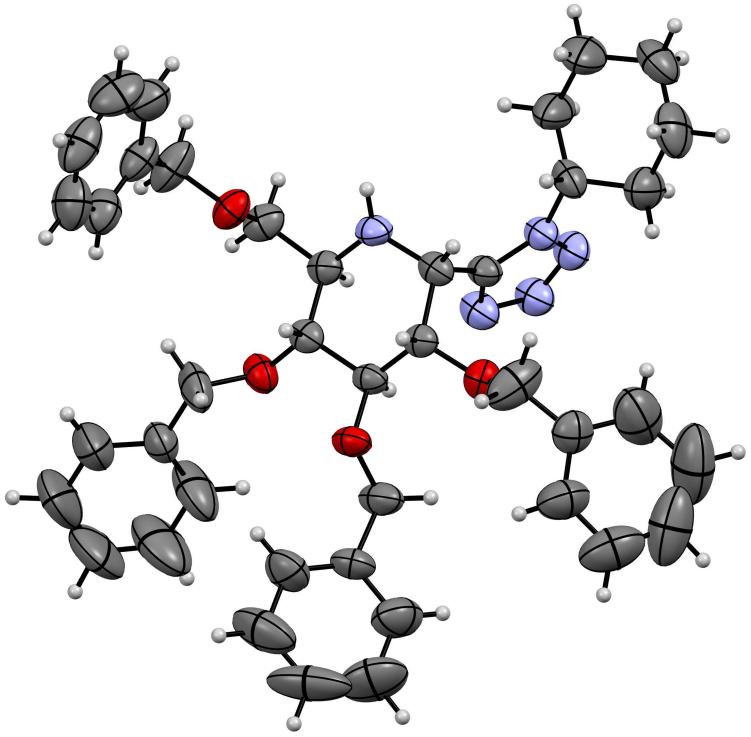


Figure S1: ORTEP plot of **3a**, represented by thermal ellipsoids shown at the 35 % probability level.

Table S1: Summary ofthe crystal parameters for **3e**

Chemical formula	$C_{41}H_{47}N_5O_4$
Formula weigh	673.83 g mol^{-1}
CCDC number	2001373
Crystal appearance	cubic, colourless
Crystal system	monoclinic
Space group	P 2_1
a	11.7353(5) Å
b	10.8296(4) Å
c	15.1159(6) Å
α	90°
β	93.981(3)°
γ	90°
volume	1916.42(13) Å^3
Z	2
R-factor	5.77 %

2.2 Crystal structure of compound 3e

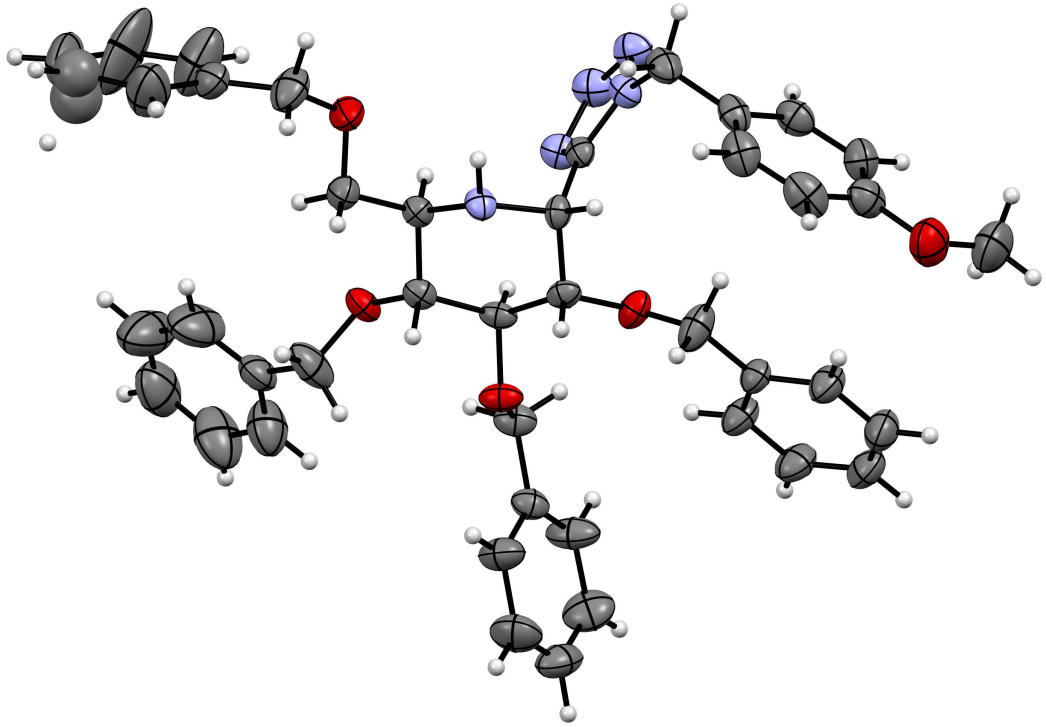


Figure S2: ORTEP plot of **3e**, represented by thermal ellipsoids shown at the 35 % probability level.

Table S2: Summary of the crystal parameters for **3a**

Chemical formula	$C_{43}H_{45}N_5O_5$
Formula weigh	711.84 g mol^{-1}
CCDC number	2001372
Crystal appearance	plate, yellow-colourless
Crystal system	monoclinic
Space group	P 2_1
a	5.8938(18) Å
b	19.634(6) Å
c	16.520(5) Å
α	90°
β	92.037(17)°
γ	90°
volume	1910.5(10) Å^3
Z	2
R-factor	4.01 %

3 Analysis of circular dichroism spectra of compounds 5a and 2-epi-5a

As stated in the main text, we recorded an ECD spectrum of compounds **5a** and **2-epi-5a** and compared it with the simulated spectra, generated for both possible diastereomers (2-(*R*) and 2-(*S*)) using computational chemistry software. The comparison of these results may be seen in Figure S3. The ECD spectra were acquired at room temperature in CH3CN (for UV-Spectroscopy, Fluka) on a Jasco J-815 spectropolarimeter and were collected with 0.2 nm/step and an integration time of 0.5 s over the range 195 nm to 400 nm. UV–Vis spectra were measured on a Jasco V-670 spectrophotometer in CH3CN. The conformational search for the calculations was made using CONFLEX software. Resulting sets of conformers were further optimized using Gaussian 09 software,[S3] using B3LYP functional and 6-31G** basis set. Optimized structures up to 3 kcal were used to calculate ECD spectra in Gaussian 16 software,[S4] using B3LYP functional and TZVP basis set, including PCM solvent model for acetonitrile. Simulated spectra were plotted with original Tesliper software,* using a gaussian function with 0.15 eV line width and hypsochromically shifted by 15 nm.

Unfortunately, the significant lability of the structures in question does not allow for accurate simulation in an acceptable time limit. This is particularly visible in the 180 nm to 200 nm range, with the strongest bands most likely coming from the −OBn groups. On the other hand, the bands in range 220 nm to 300 nm, shown in charts D, F, and H are not well developed and therefore hard to analyse. In conclusion, these experiments did not help to determine the absolute configuration of compounds **5a** and **2-epi-5a**, as there is no clear correspondence in simulated and experimental spectra.

*Source code available under an open software license at `https://github.com/Mishioo/tesliper`.

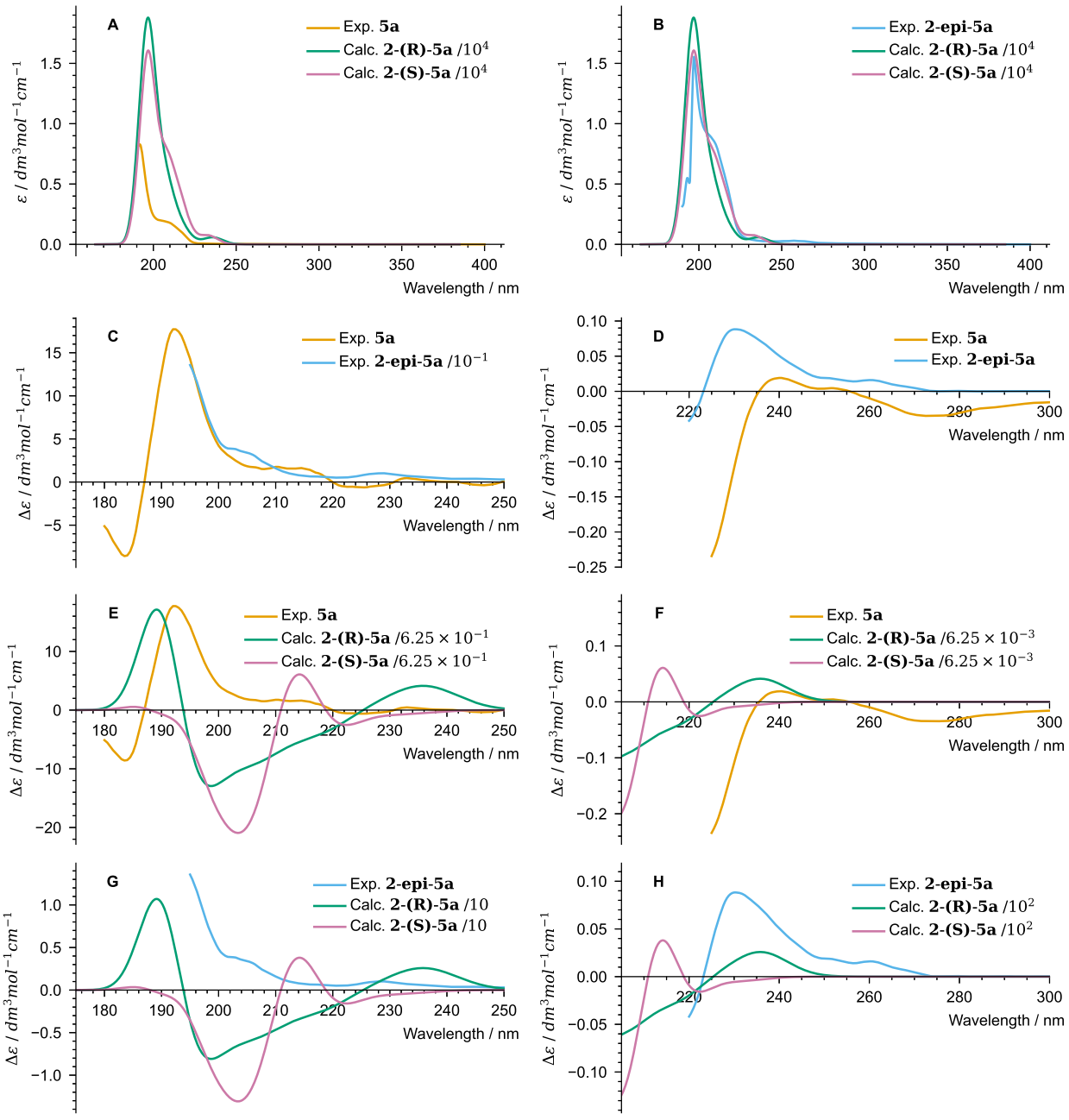
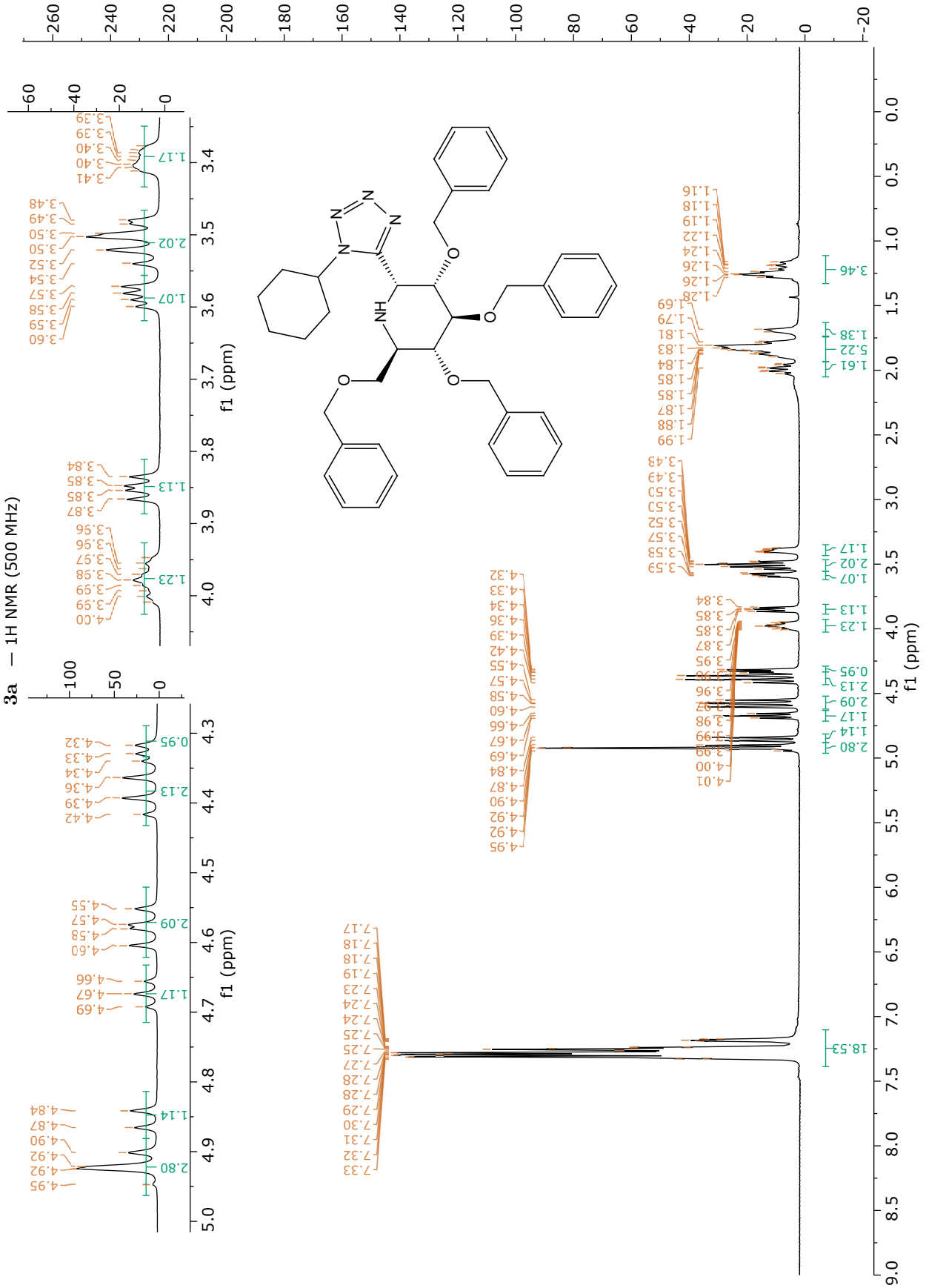
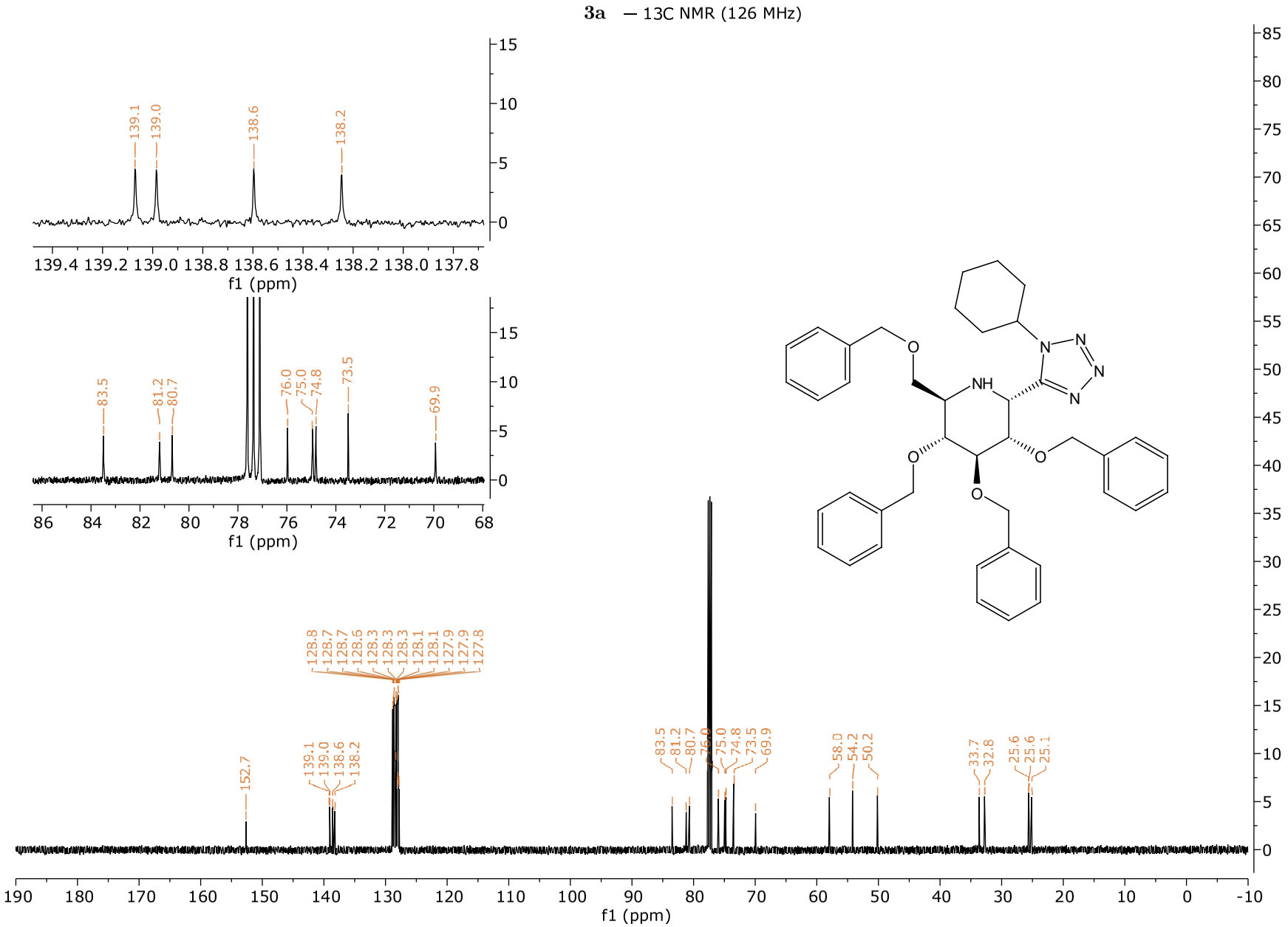
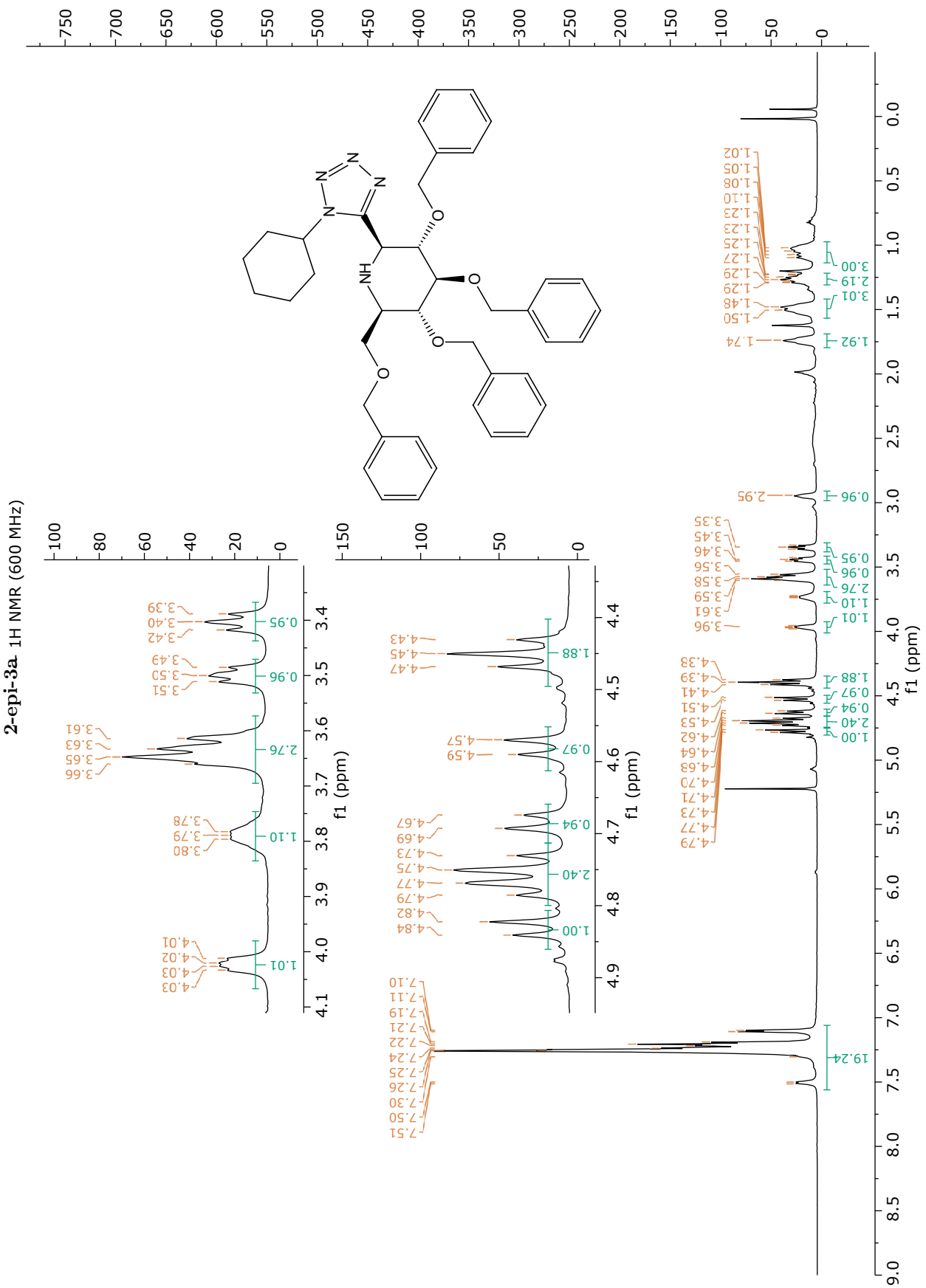


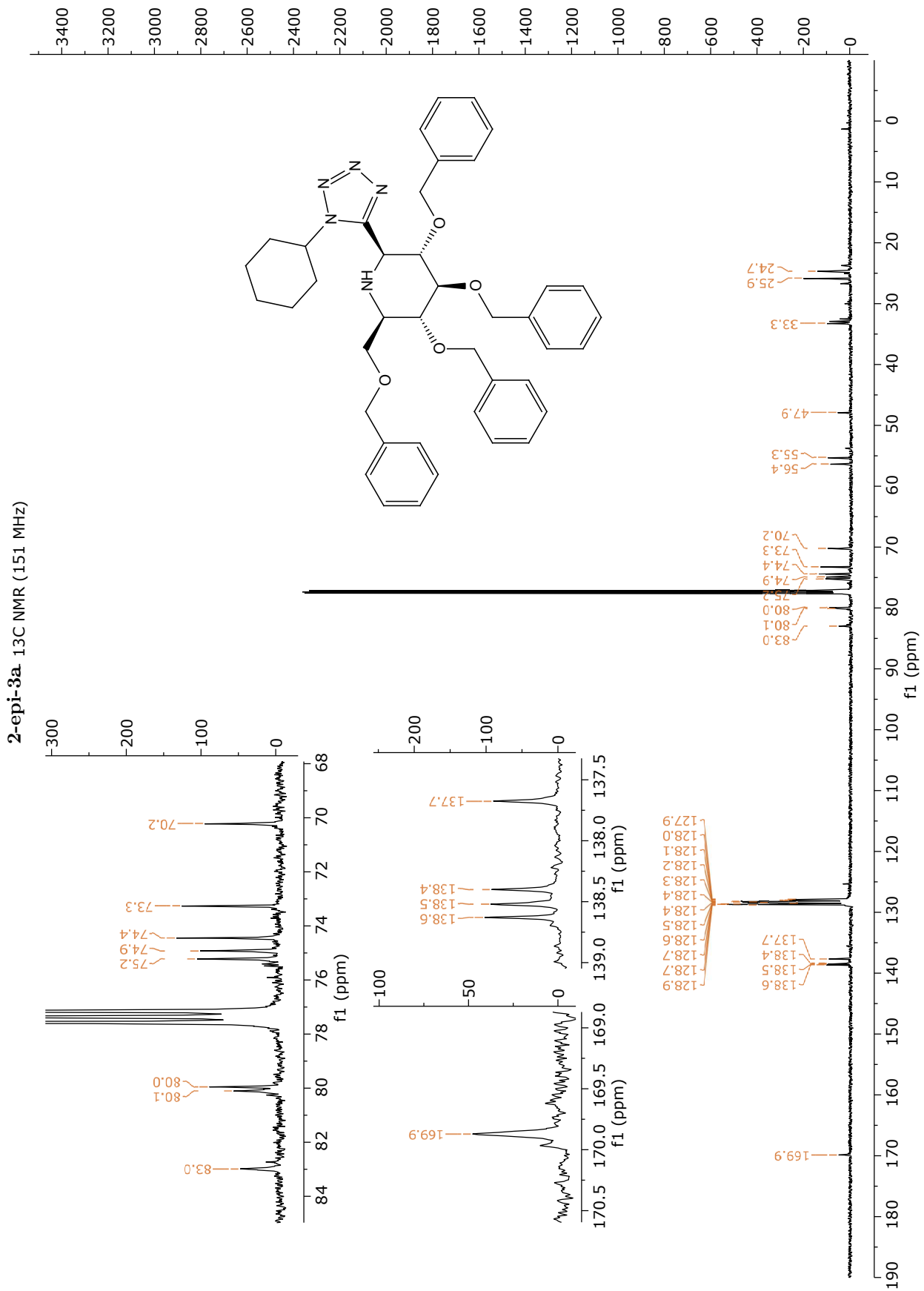
Figure S3: Comparison of experimental and simulated ECD spectra of **5a**. Intensity values were scaled for clarity by a factor given in the Figure.

4 NMR spectra


3a — 1H NMR (500 MHz)
f1 (ppm)


3a — 13C NMR (126 MHz)
139.1
139.0
138.6
138.2
f1 (ppm)
83.5
81.2
80.7
76.0
75.0
74.8
73.5
69.9
f1 (ppm)
NH
N
N
N
O
O
O
O
128.8
128.7
128.7
128.6
128.3
128.3
128.3
128.1
128.1
127.9
127.9
127.8
152.7
139.1
139.0
138.6
138.2
83.5
81.2
80.7
76.0
75.0
74.8
73.5
69.9
58.0
54.2
50.2
33.7
32.8
25.6
25.6
25.1
f1 (ppm)


2-epi-3a 1H NMR (600 MHz)
f1 (ppm)


2-epi-3a 13C NMR (151 MHz)
f1 (ppm)
83.0
80.1
80.0
75.2
74.9
74.4
73.3
70.2
56.4
55.3
47.9
33.3
25.9
24.7
169.9
138.6
138.5
138.4
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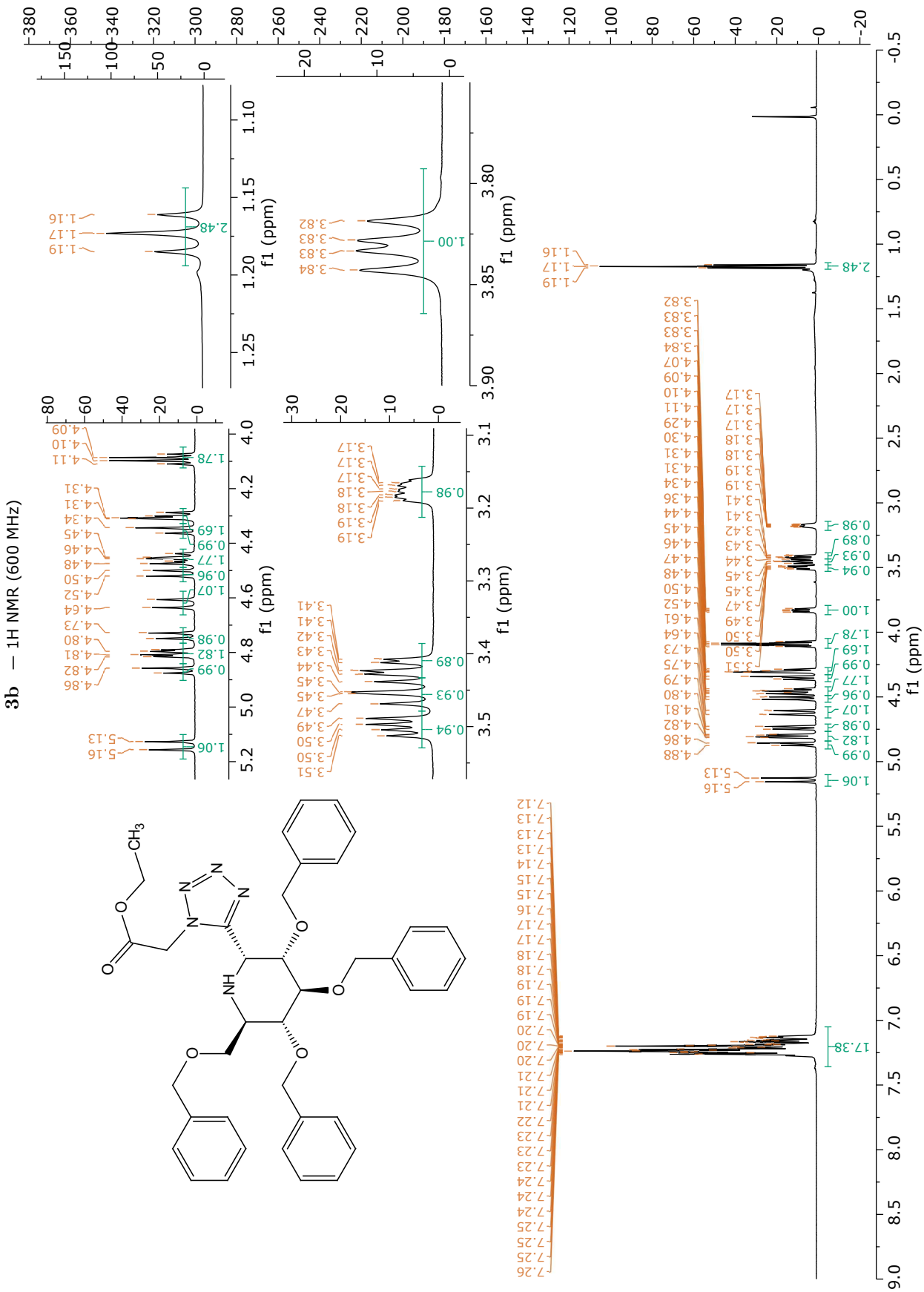
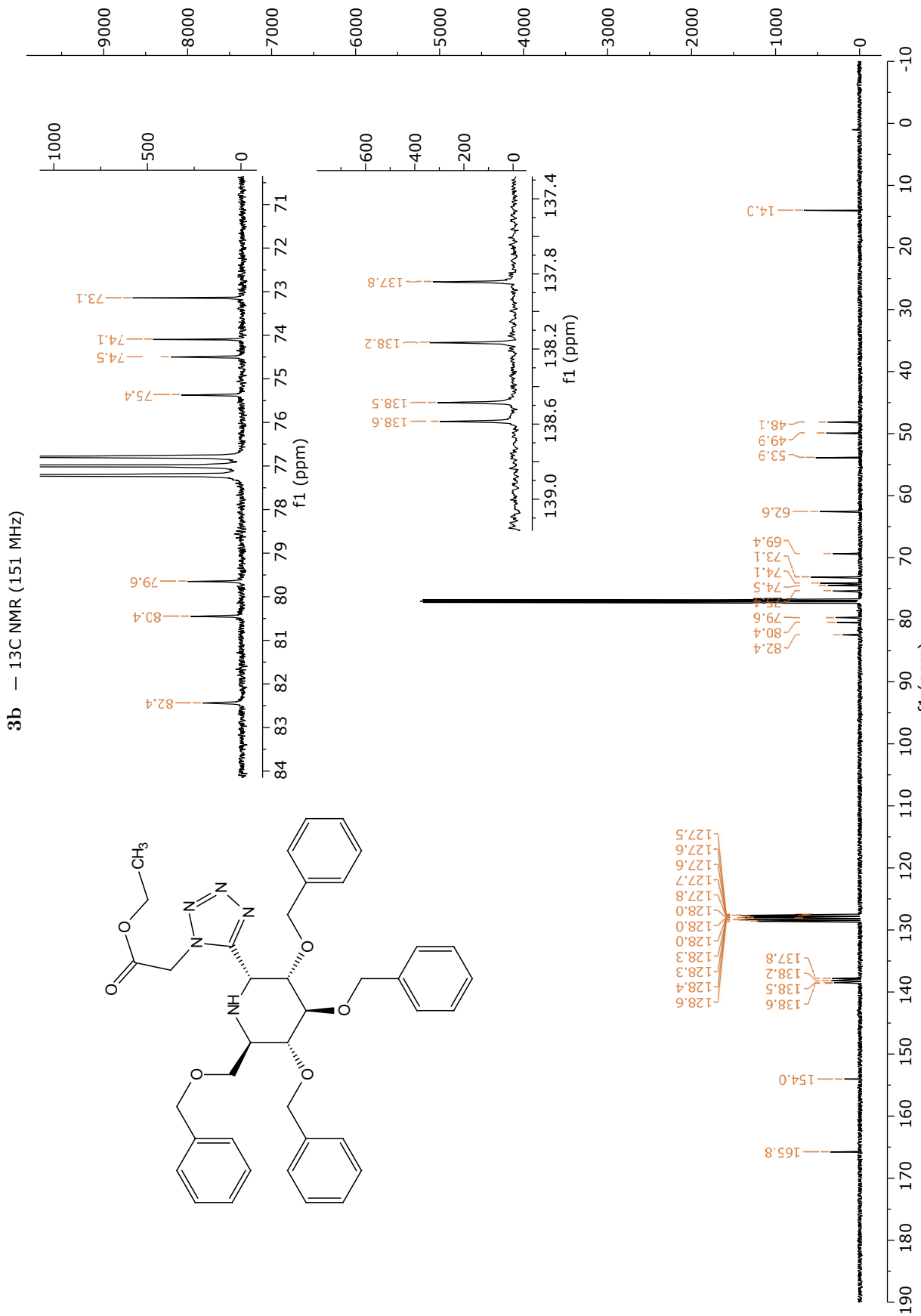
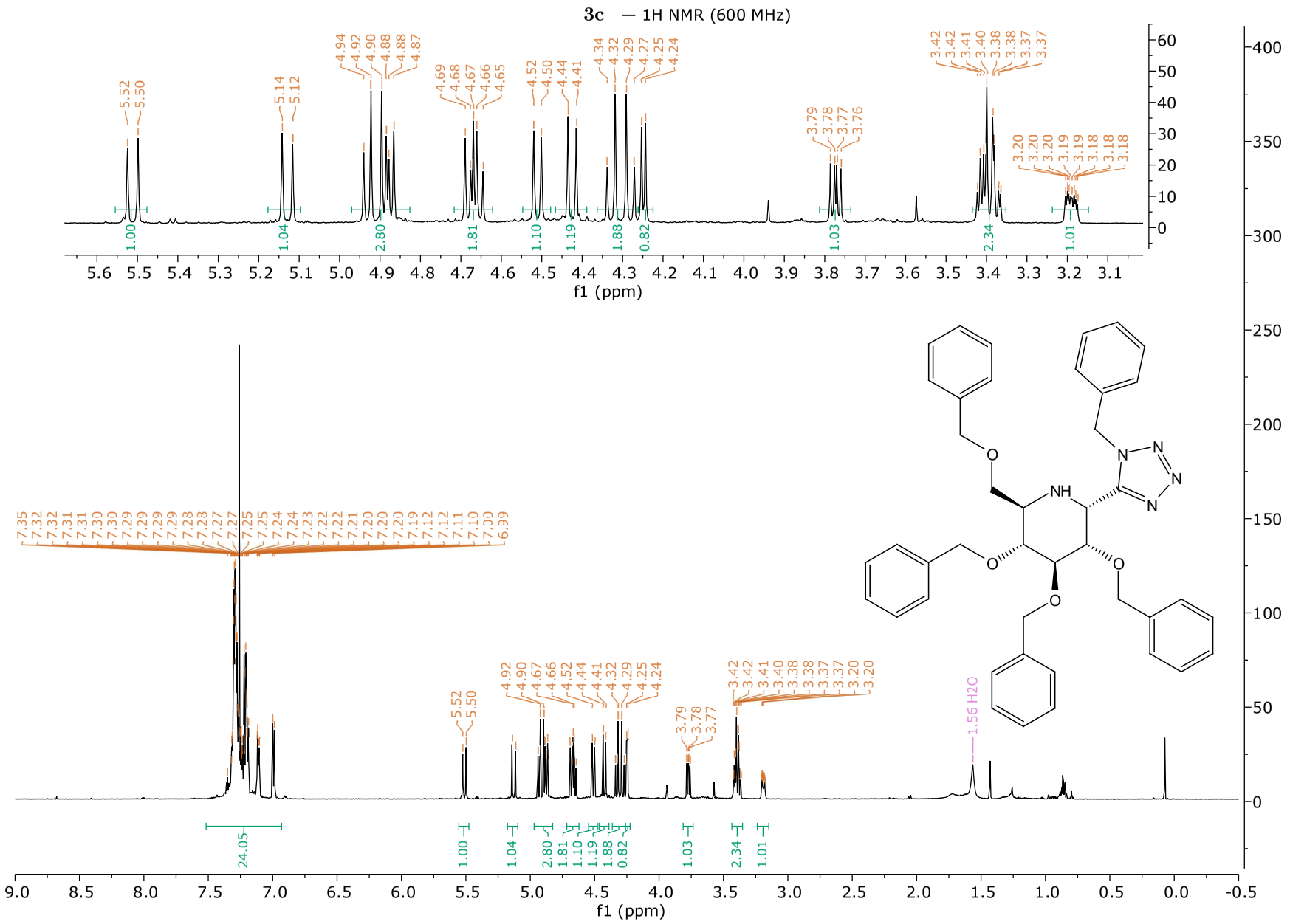
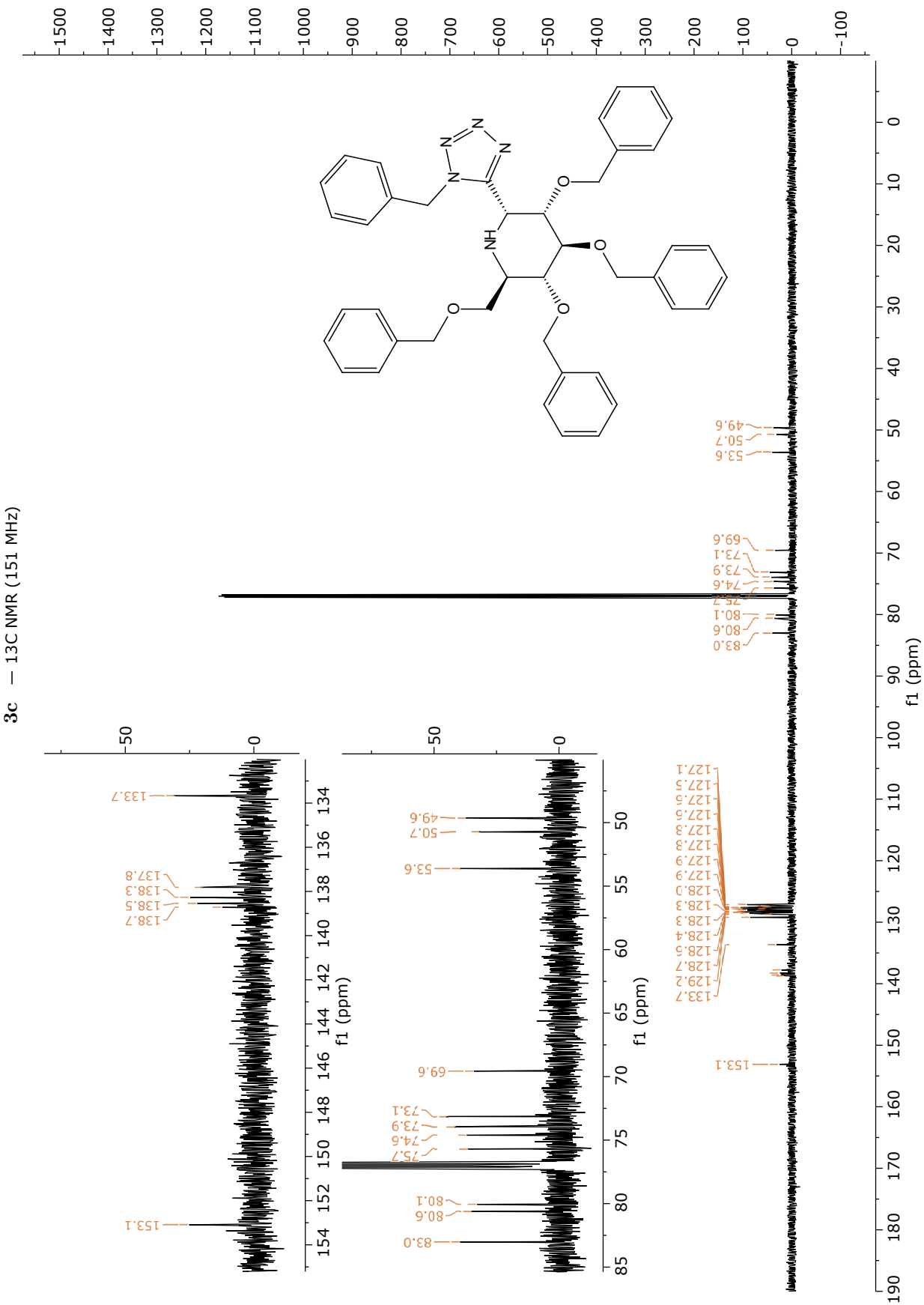
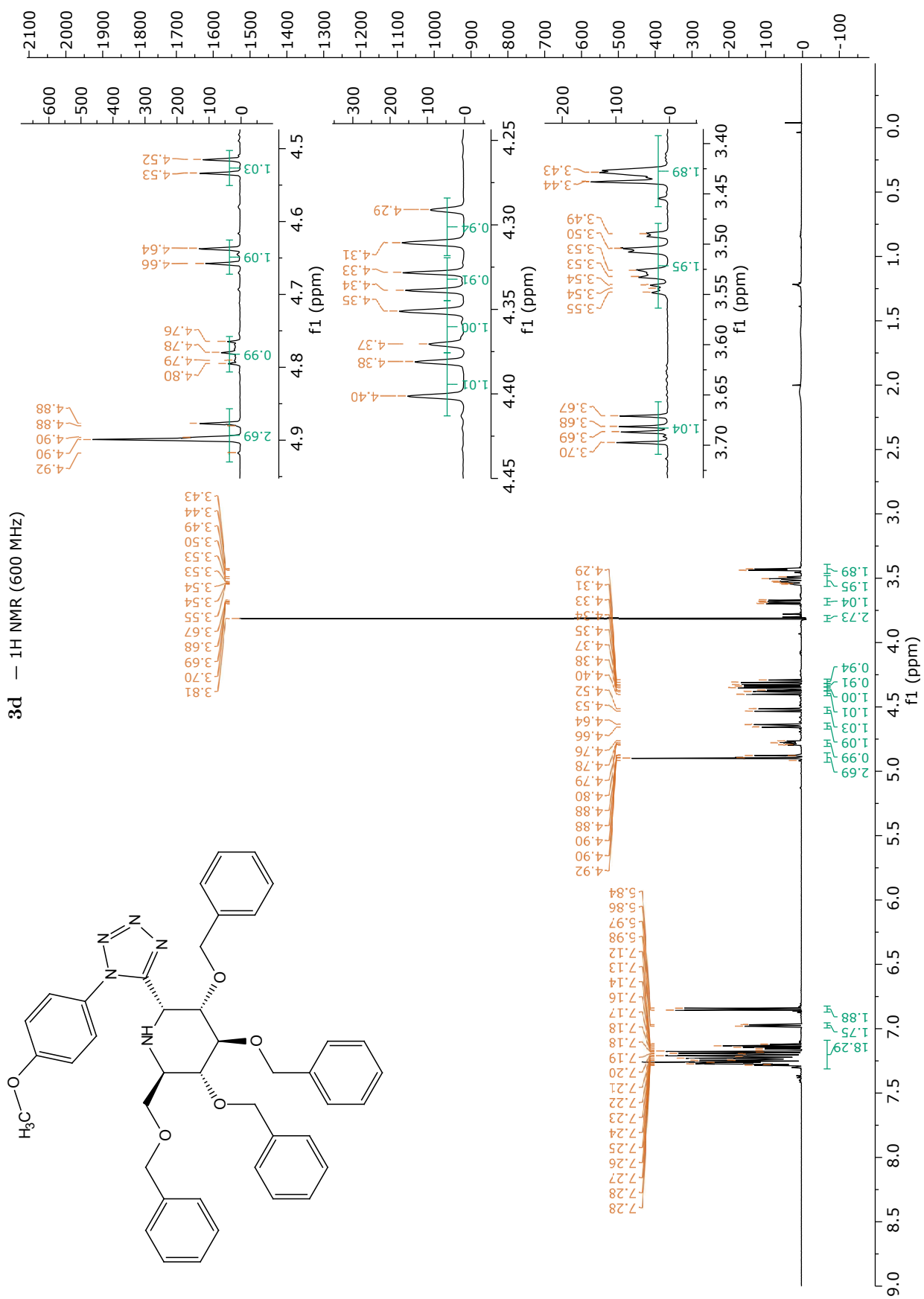
128.4
128.3
128.2
128.1
128.0
127.9

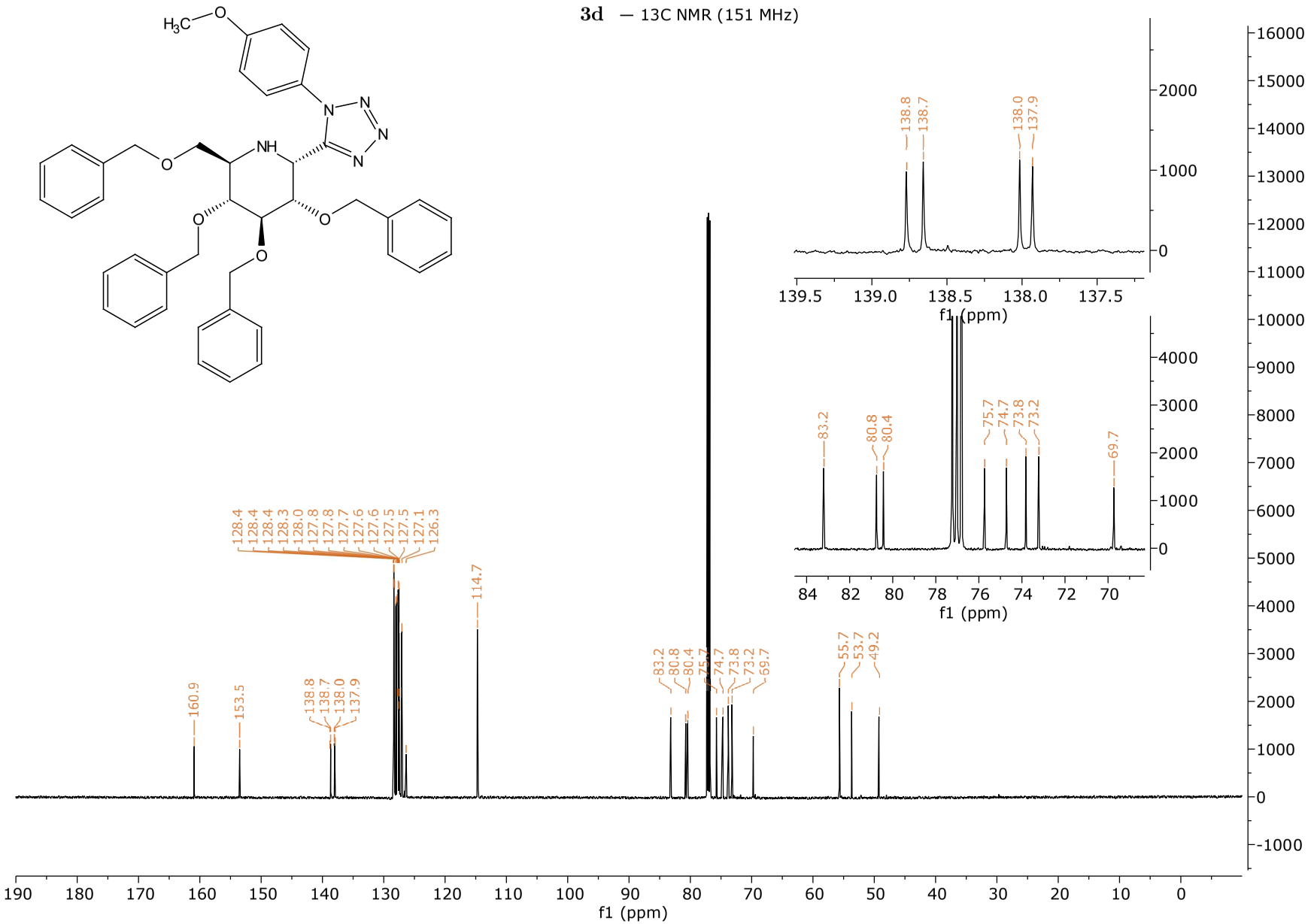

3b — 1H NMR (600 MHz)
f1 (ppm)

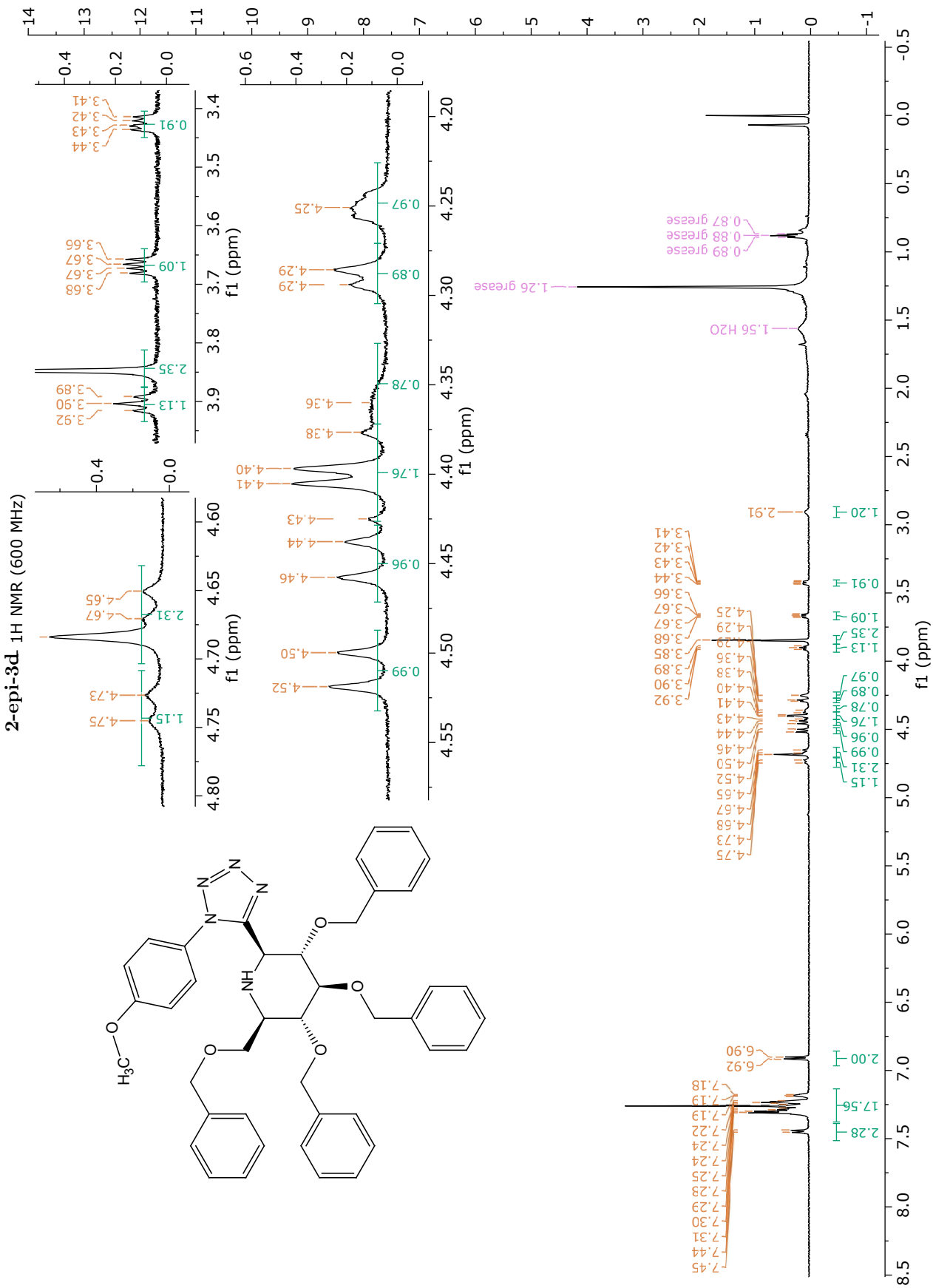

3b — 13C NMR (151 MHz)
f1 (ppm)
14.3
48.1
49.9
53.9
62.6
69.4
73.1
74.1
74.5
75.4
79.6
80.4
82.4
127.5
127.6
127.6
127.7
127.8
128.0
128.0
128.0
128.3
128.3
128.4
128.6
137.8
138.2
138.5
138.6
154.0
165.8
CH3
O
N
NH

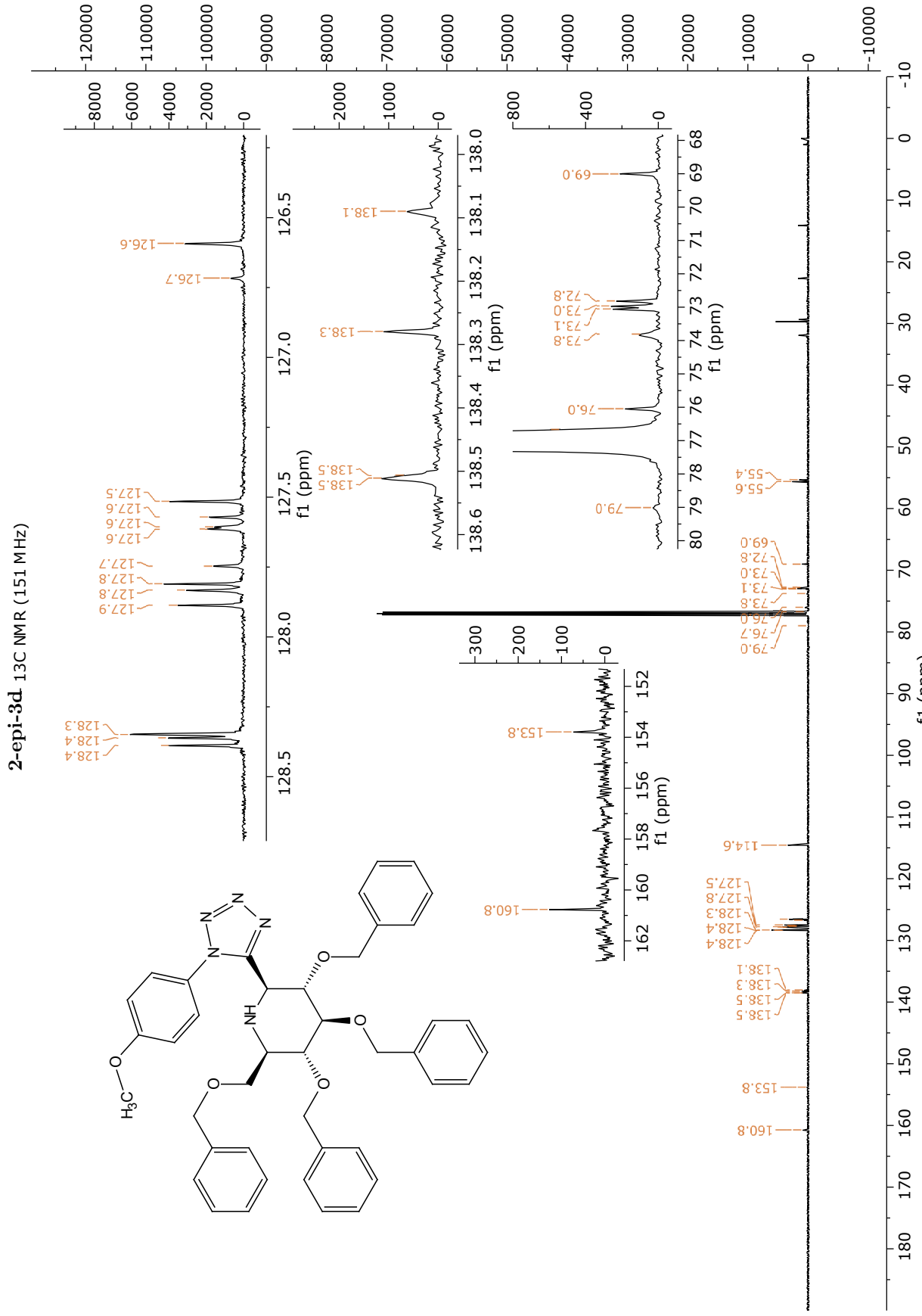

3c — 1H NMR (600 MHz)
f1 (ppm)
NH
O
N
1.56 H2O

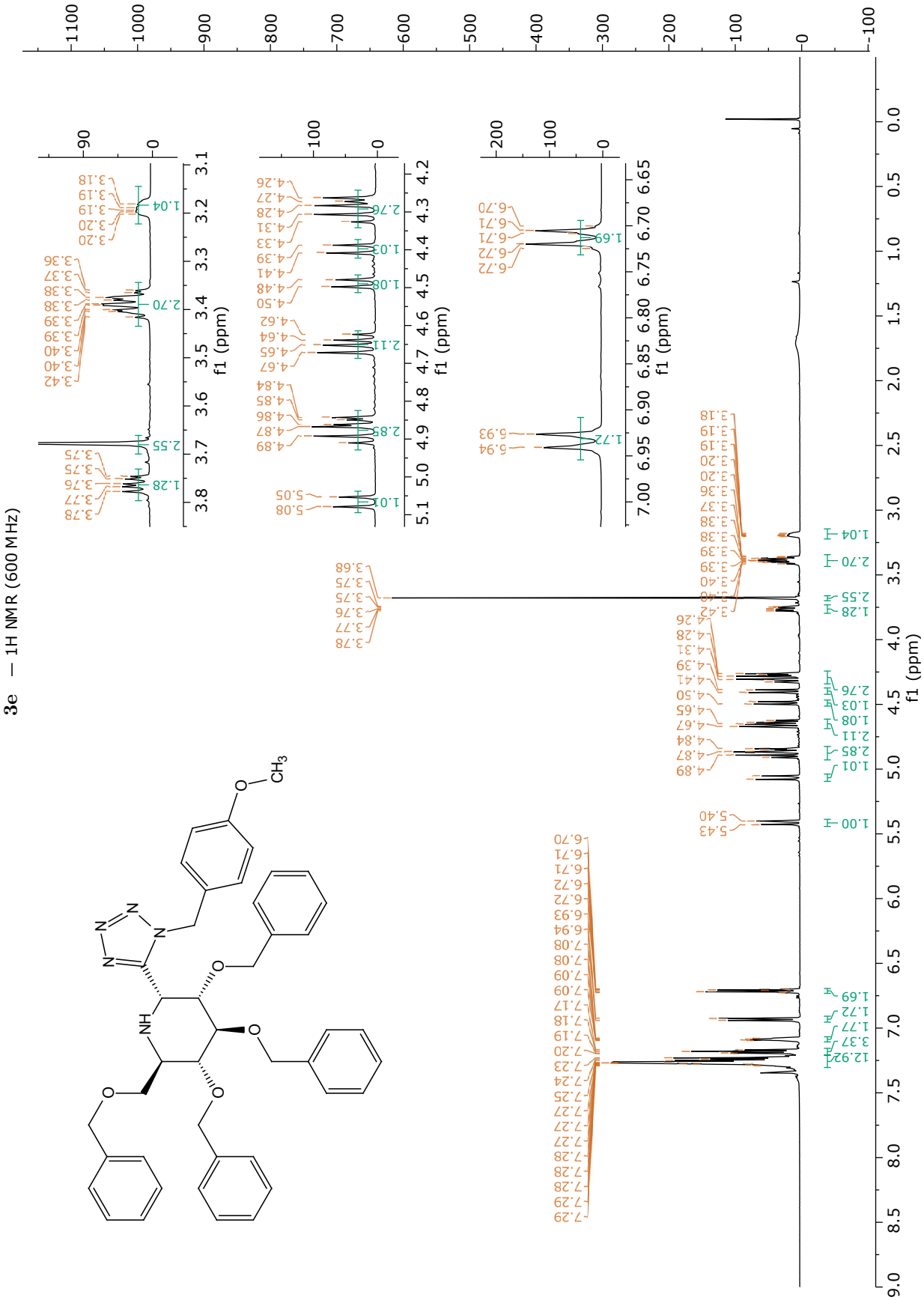

3c — 13C NMR (151 MHz)
f1 (ppm)
153.1
133.7
138.7
138.5
138.3
137.8
83.0
80.6
80.1
75.7
74.6
73.9
73.1
69.6
53.6
50.7
49.6
128.5
128.4
128.3
128.3
128.0
127.9
127.9
127.5
127.5
127.3
127.3
129.2
128.7

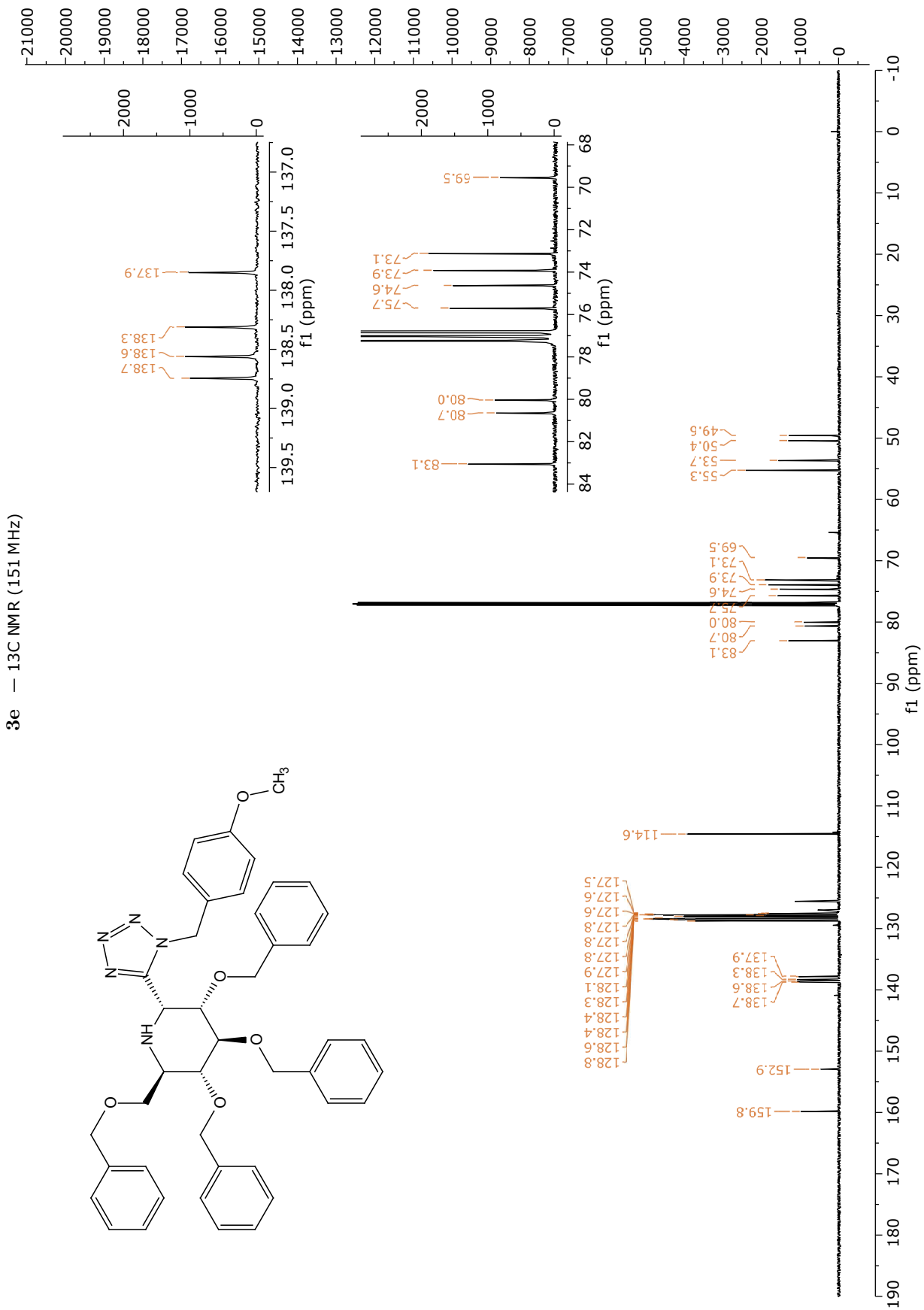

3d — 1H NMR (600 MHz)
f1 (ppm)

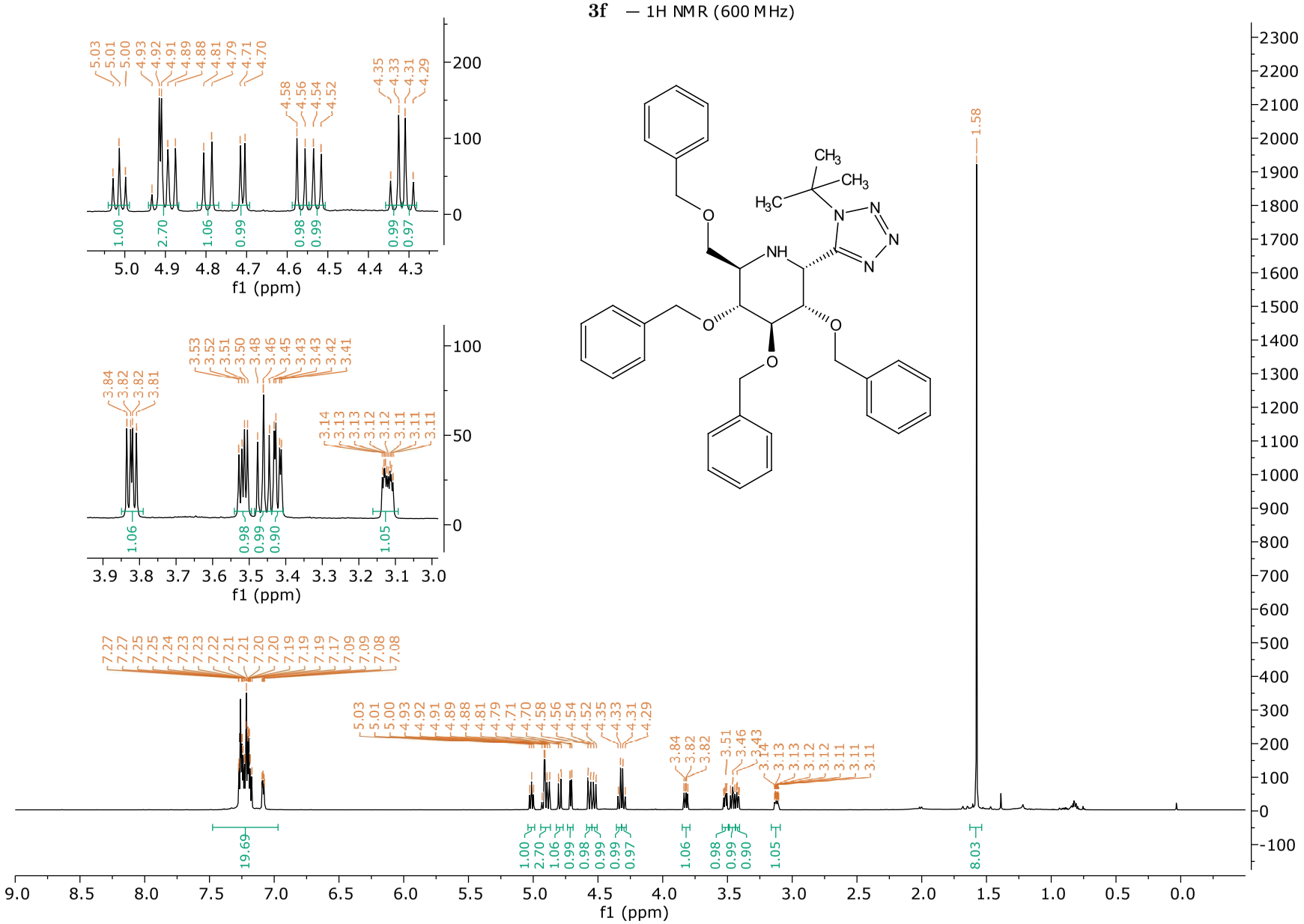

3d — 13C NMR (151 MHz)
H3C
O
N
N
N
N
NH
O
O
O
O
160.9
153.5
138.8
138.7
138.0
137.9
128.4
128.4
128.4
128.3
128.0
127.8
127.8
127.7
127.6
127.6
127.5
127.5
127.1
126.3
114.7
83.2
80.8
80.4
75.7
74.7
73.8
73.2
69.7
55.7
53.7
49.2
f1 (ppm)
138.8
138.7
138.0
137.9
f1 (ppm)
83.2
80.8
80.4
75.7
74.7
73.8
73.2
69.7
f1 (ppm)


2-epi-3d 1H NMR (600 MHz)
f1 (ppm)
1.26 grease
1.56 H2O
H3C
O
NH
N

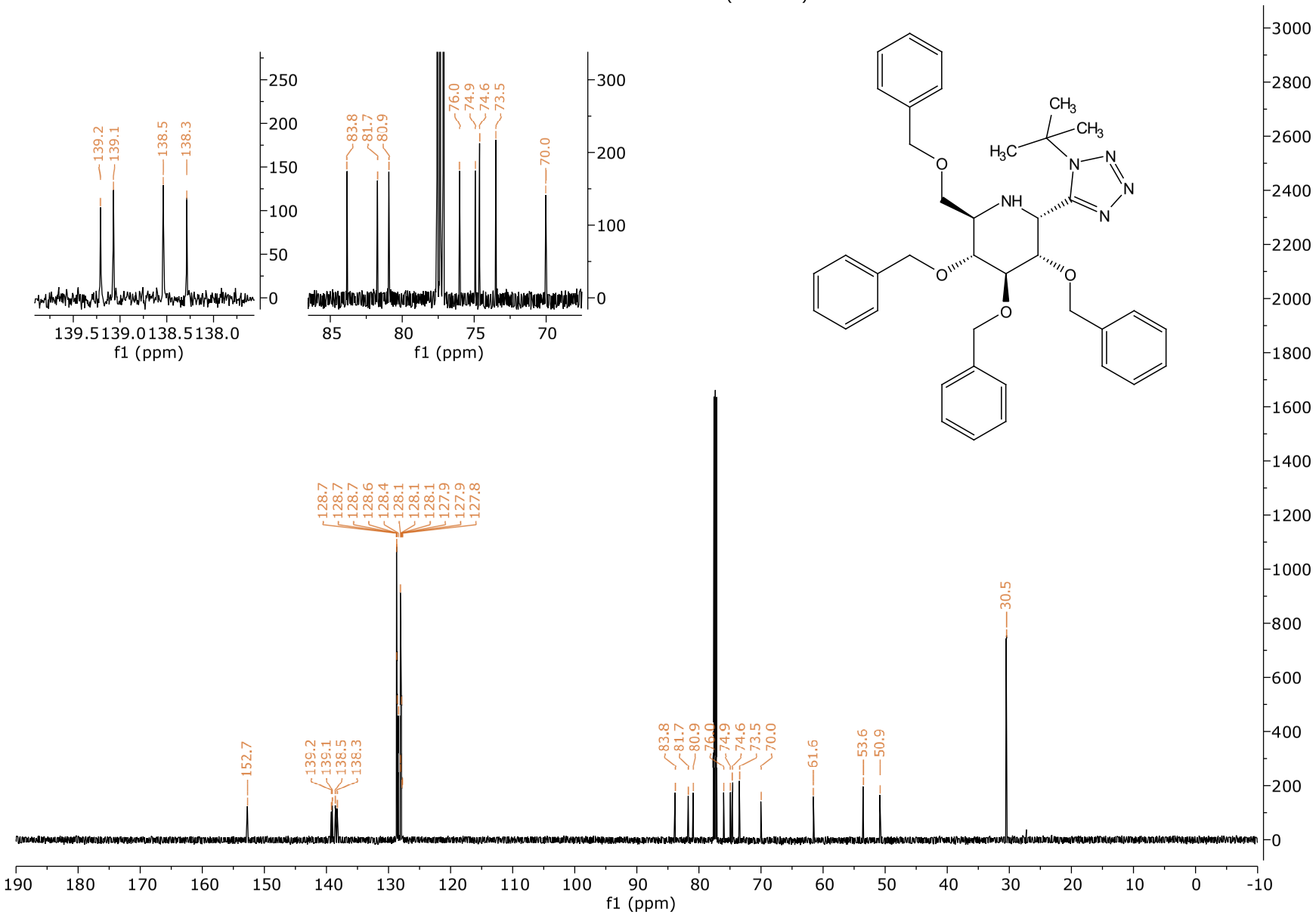

2-epi-3d 13C NMR (151 MHz)
f1 (ppm)

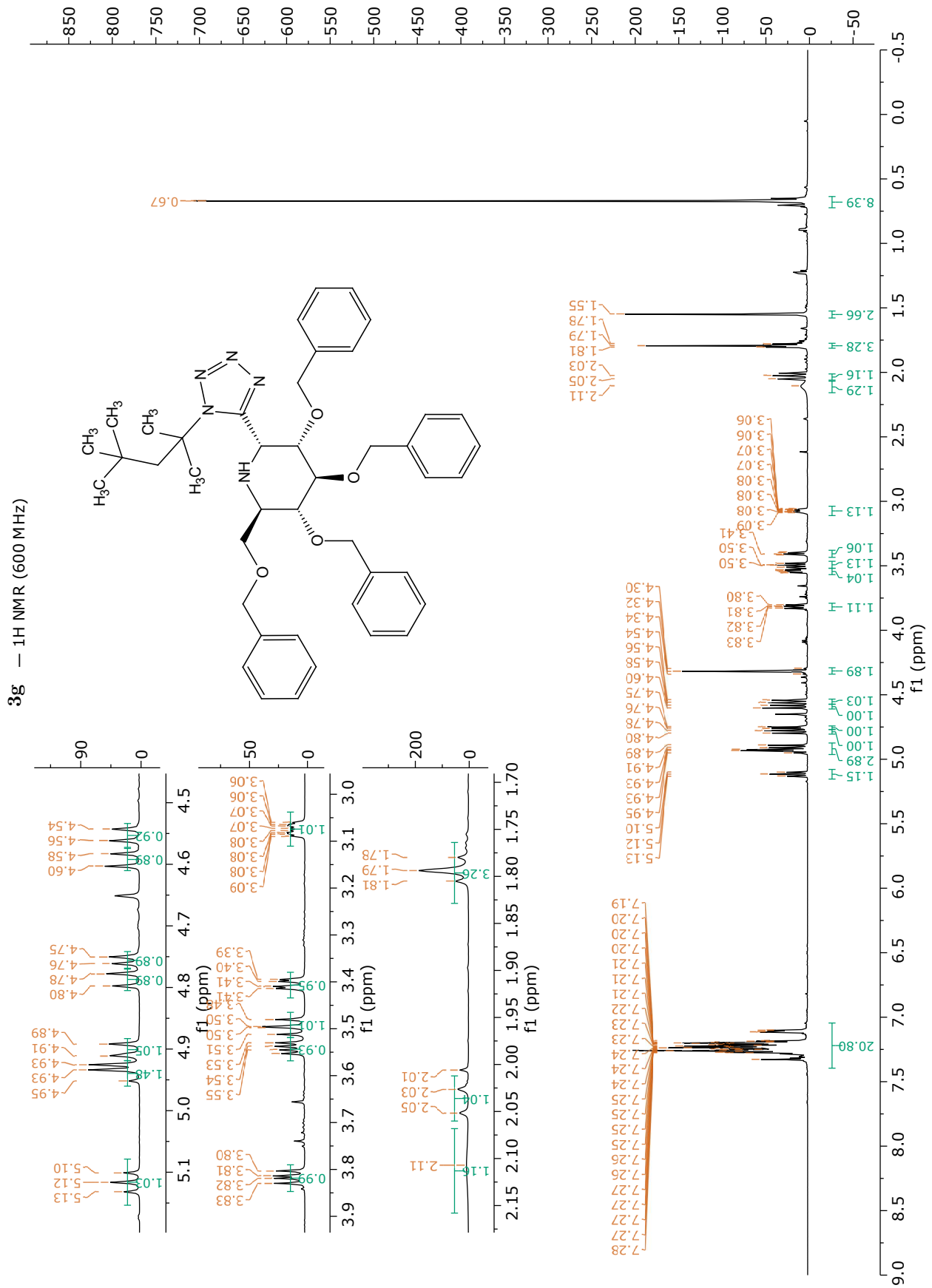

3e — 1H NMR (600 MHz)
f1 (ppm)
CH3
NH
N
O


3e — 13C NMR (151 MHz)
f1 (ppm)
114.6
127.5
127.6
127.6
127.8
127.8
127.8
127.9
128.1
128.3
128.4
128.4
128.6
128.8
137.9
138.3
138.6
138.7
152.9
159.8
49.6
50.4
53.7
55.3
69.5
73.1
73.9
74.6
75.7
80.0
80.7
83.1
CH3
O
NH
N

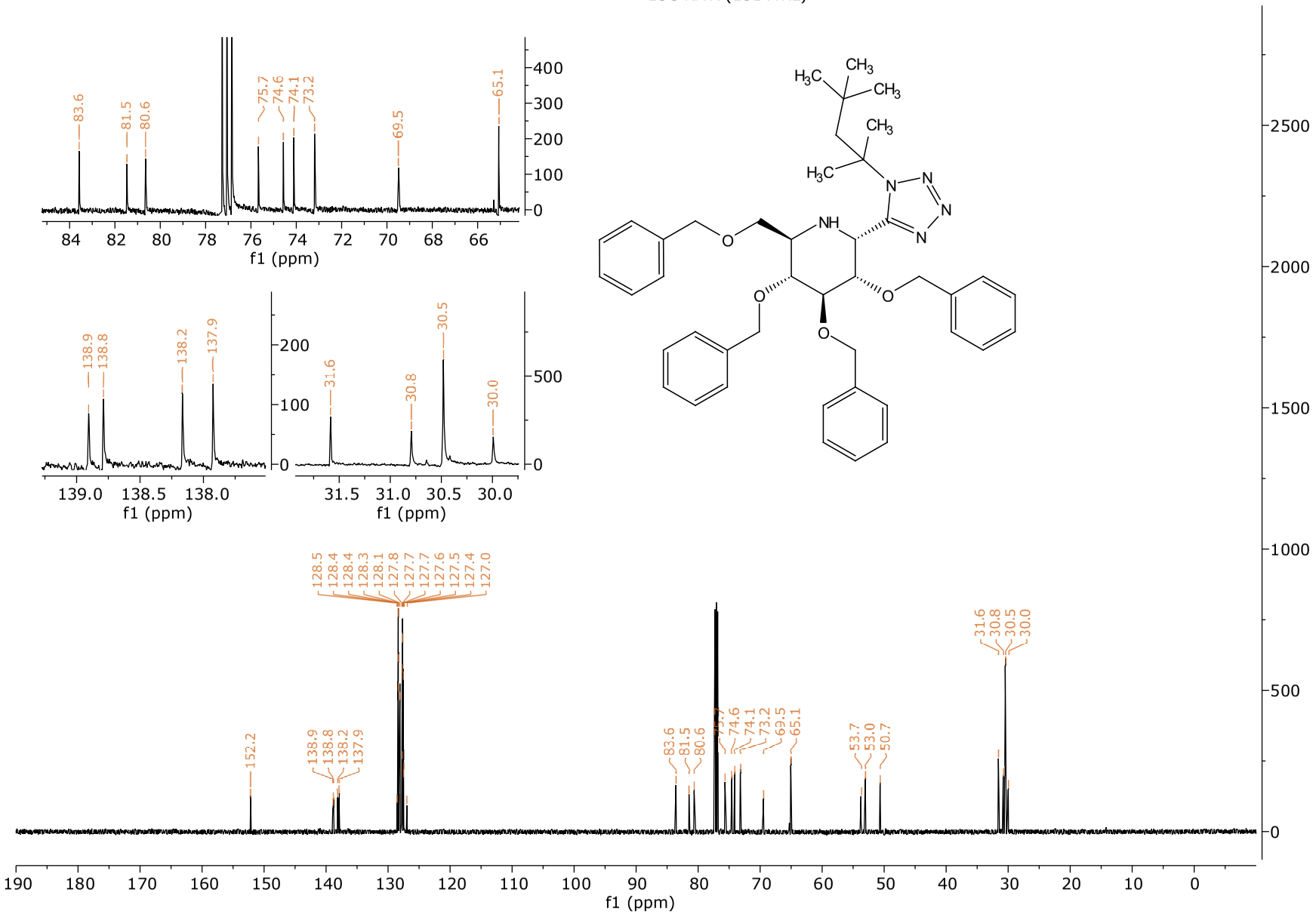

3f — 1H NMR (600 MHz)
f1 (ppm)

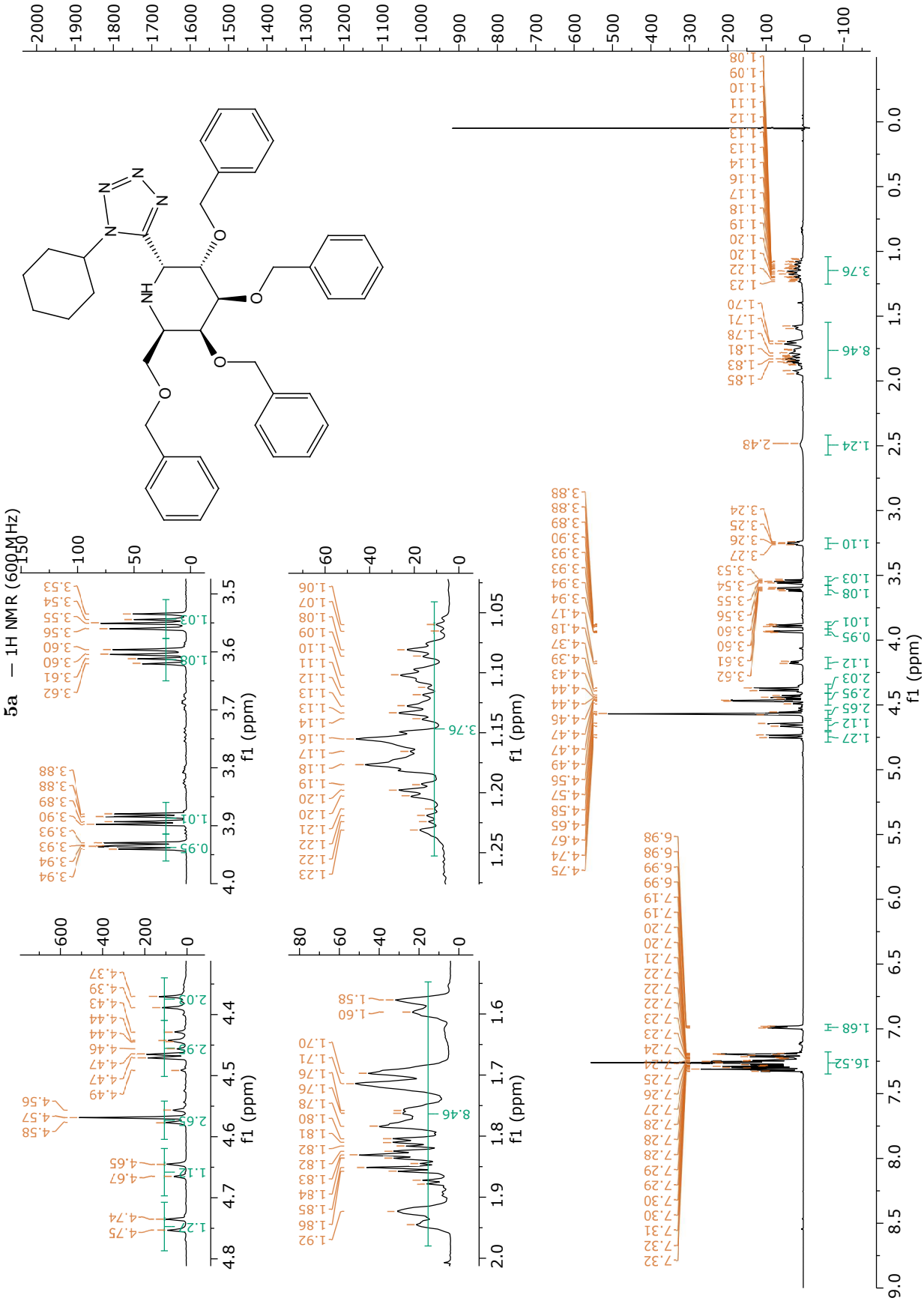
3f — 13C NMR (151 MHz)

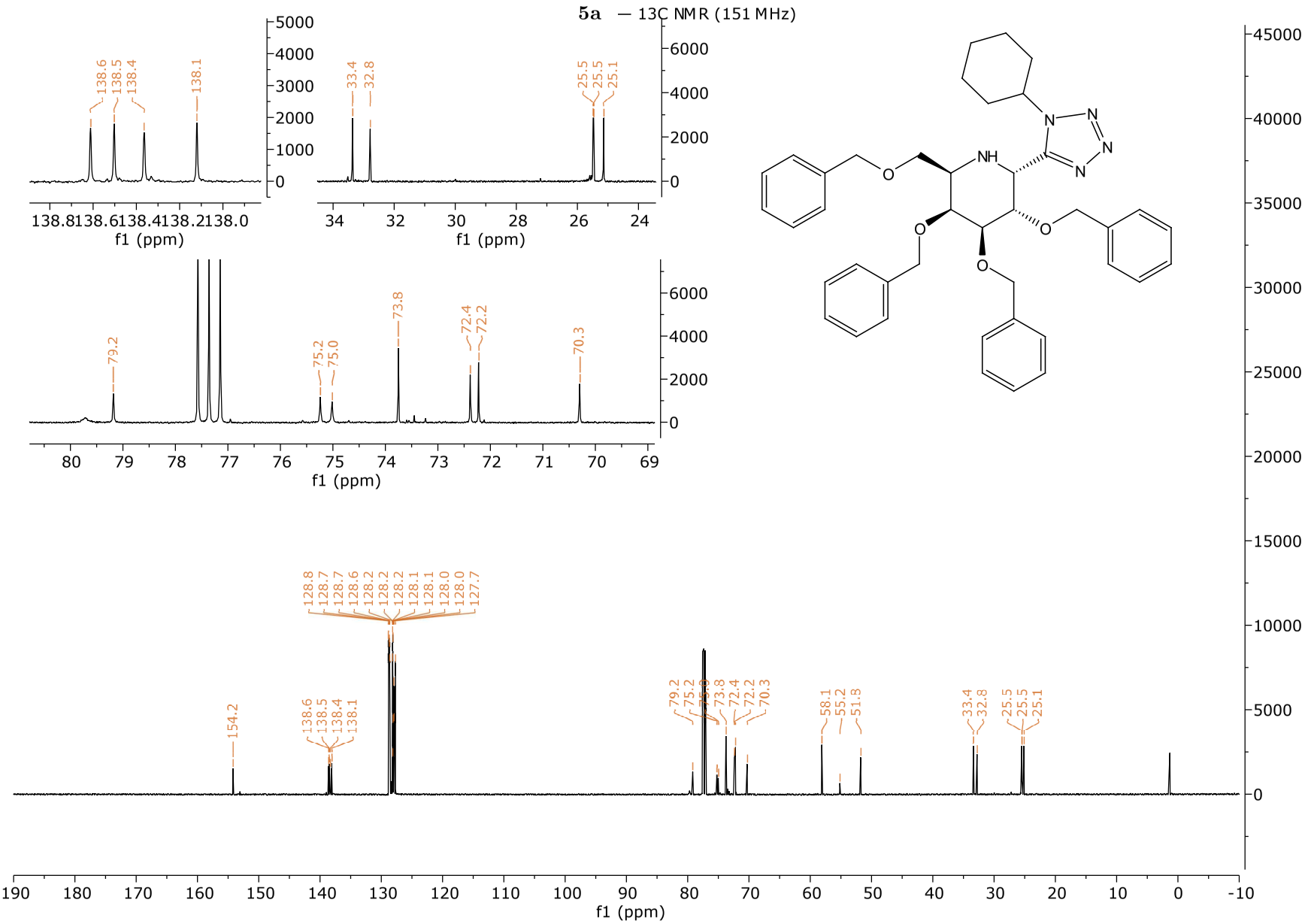


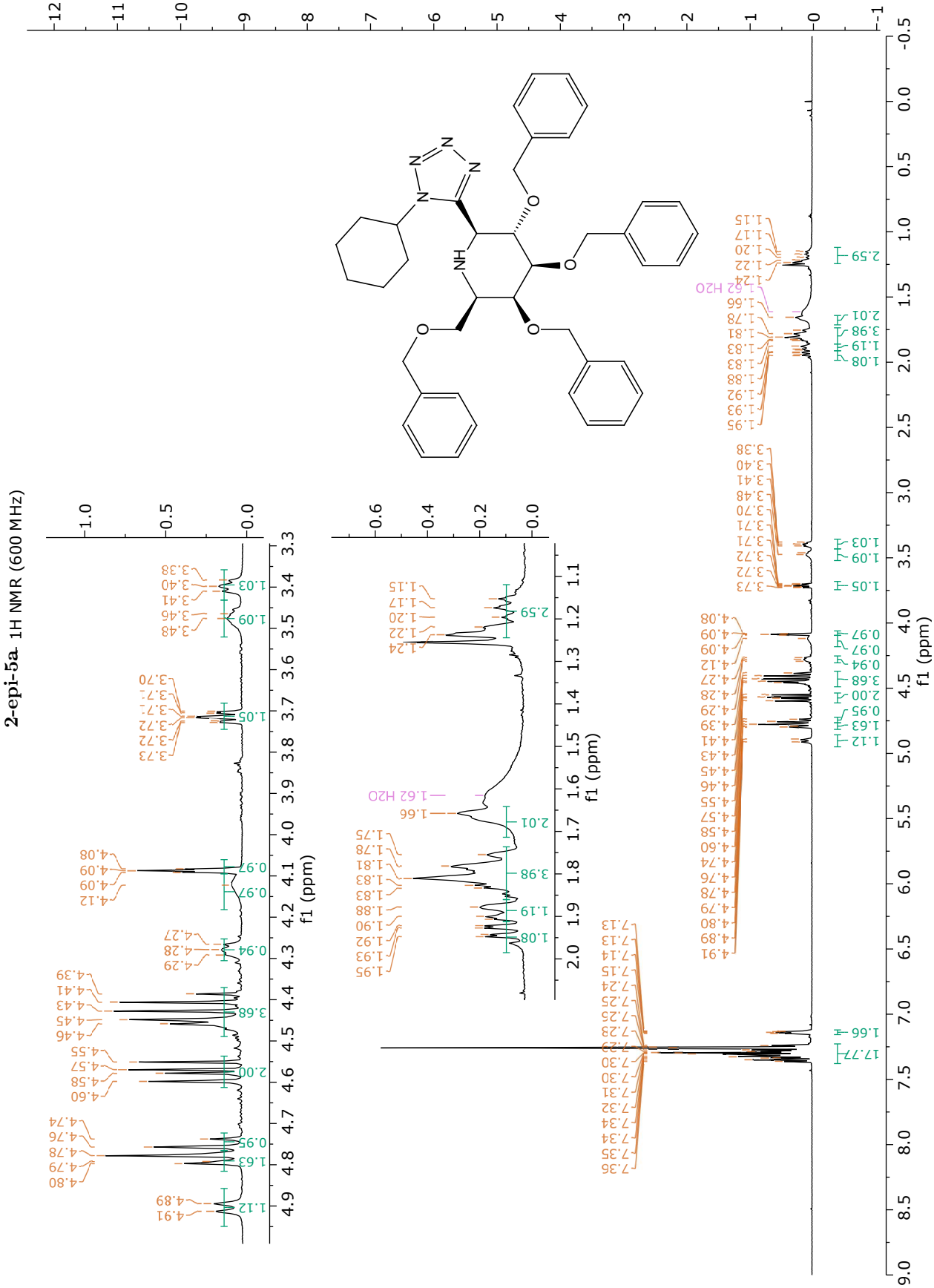

3g — 1H NMR (600 MHz)
f1 (ppm)

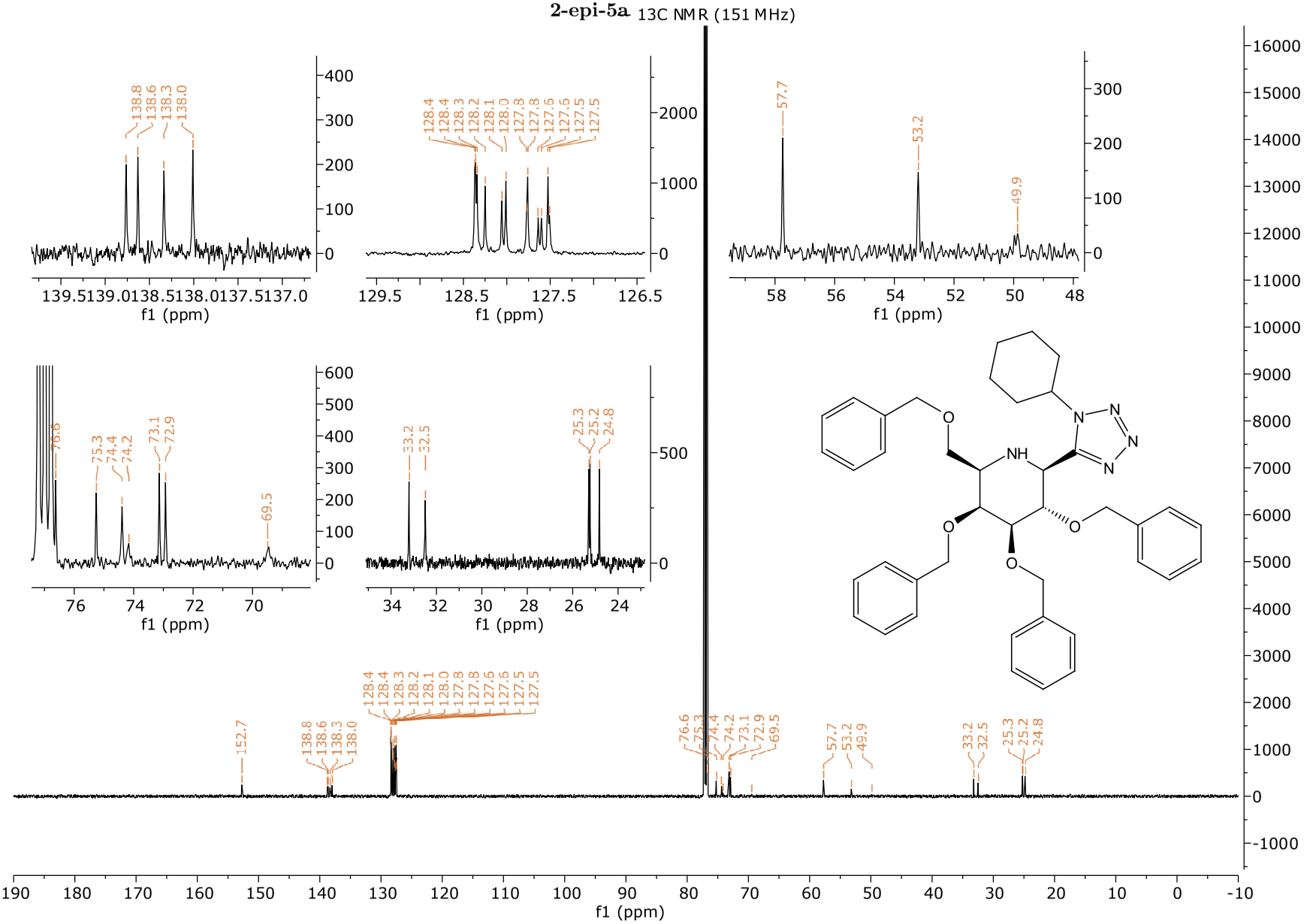
3g — 13C NMR (151 MHz)

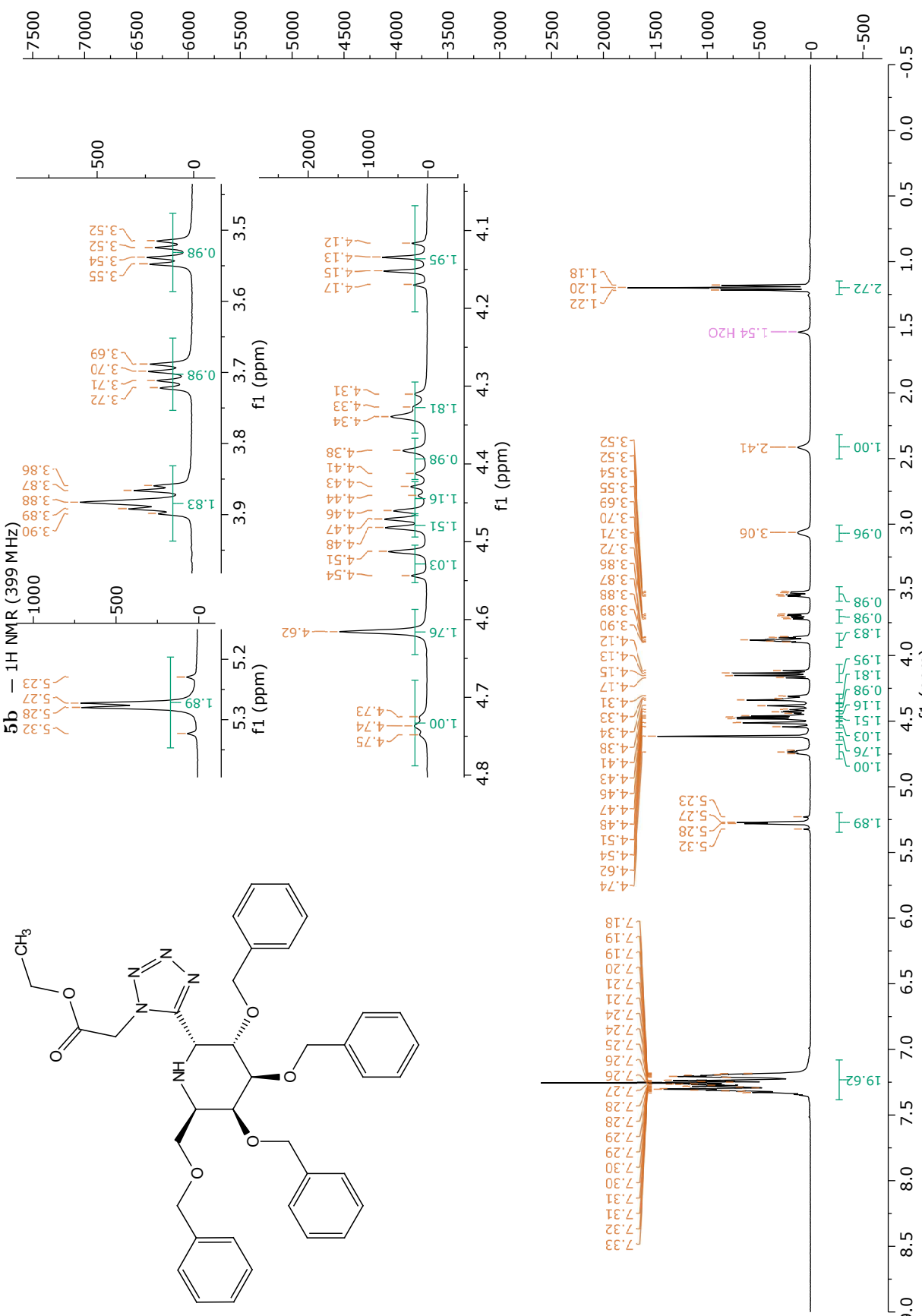


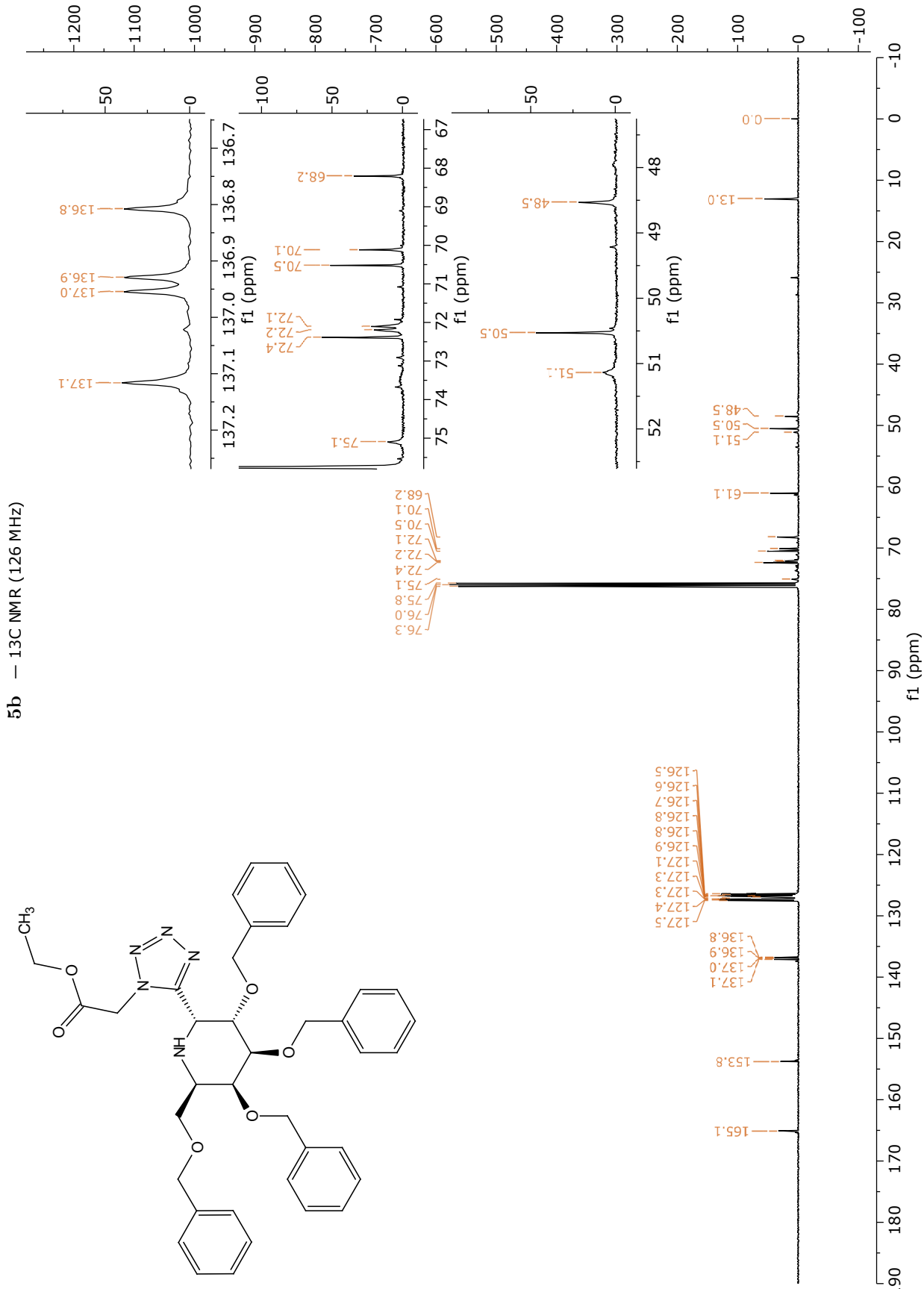

5a — 1H NMR (600 MHz)
f1 (ppm)

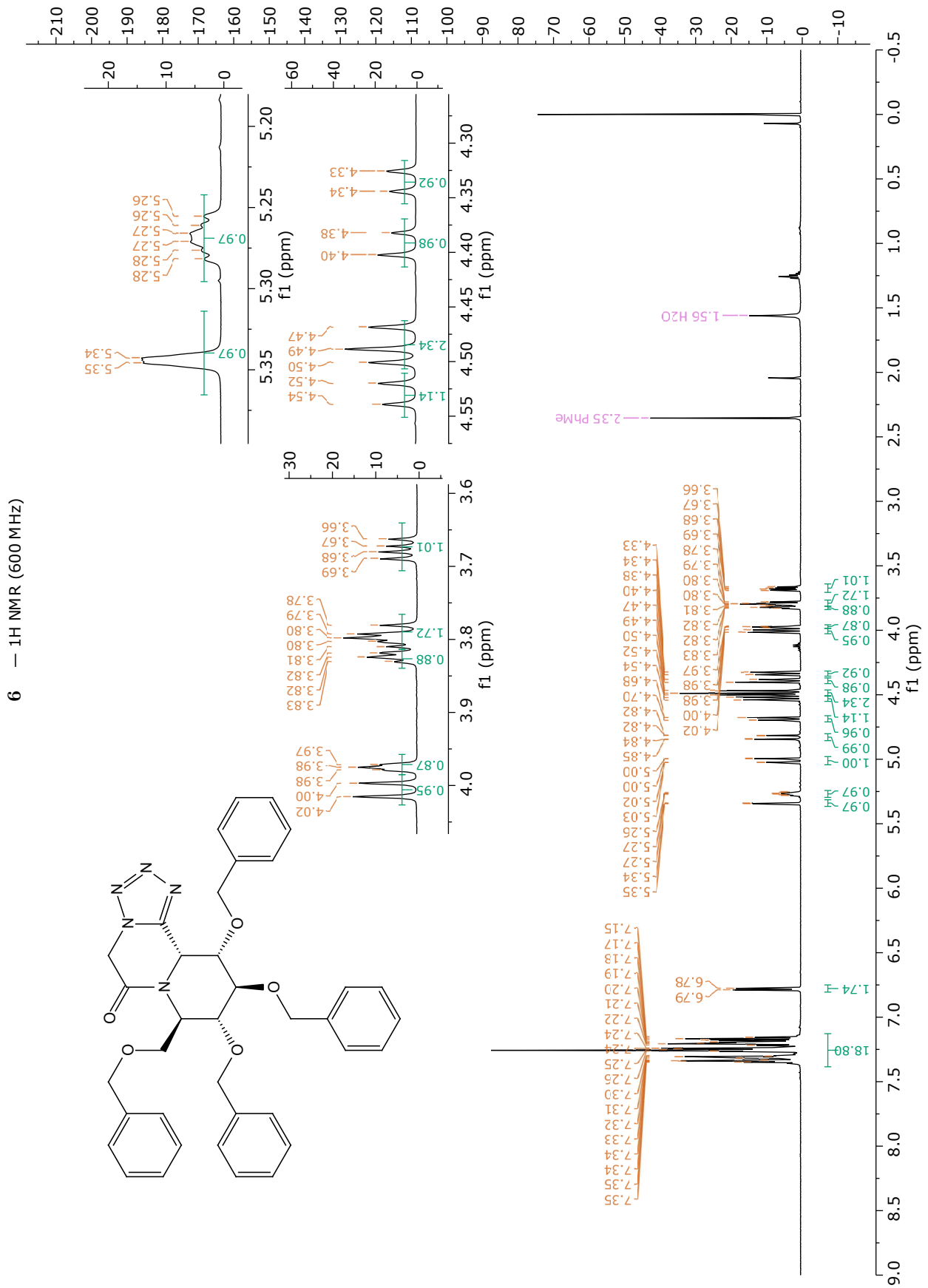

5a — 13C NMR (151 MHz)
138.6
138.5
138.4
138.1
33.4
32.8
25.5
25.5
25.1
79.2
75.2
75.0
73.8
72.4
72.2
70.3
NH
O
N
f1 (ppm)
128.8
128.7
128.7
128.6
128.2
128.2
128.2
128.1
128.1
128.0
128.0
127.7
154.2
79.2
75.2
73.8
72.4
72.2
70.3
58.1
55.2
51.8
33.4
32.8
25.5
25.5
25.1

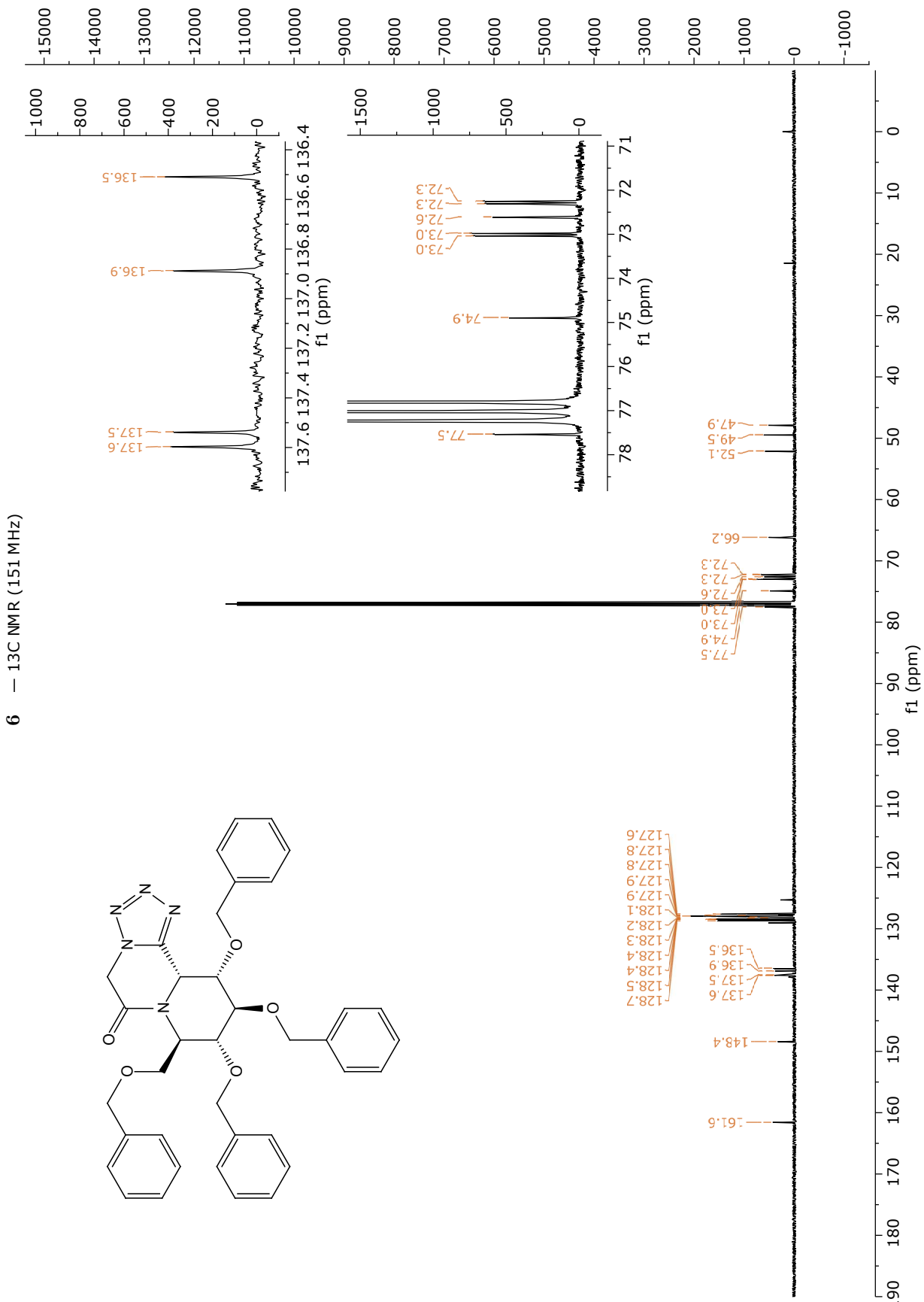

2-epi-5a 1H NMR (600 MHz)
f1 (ppm)

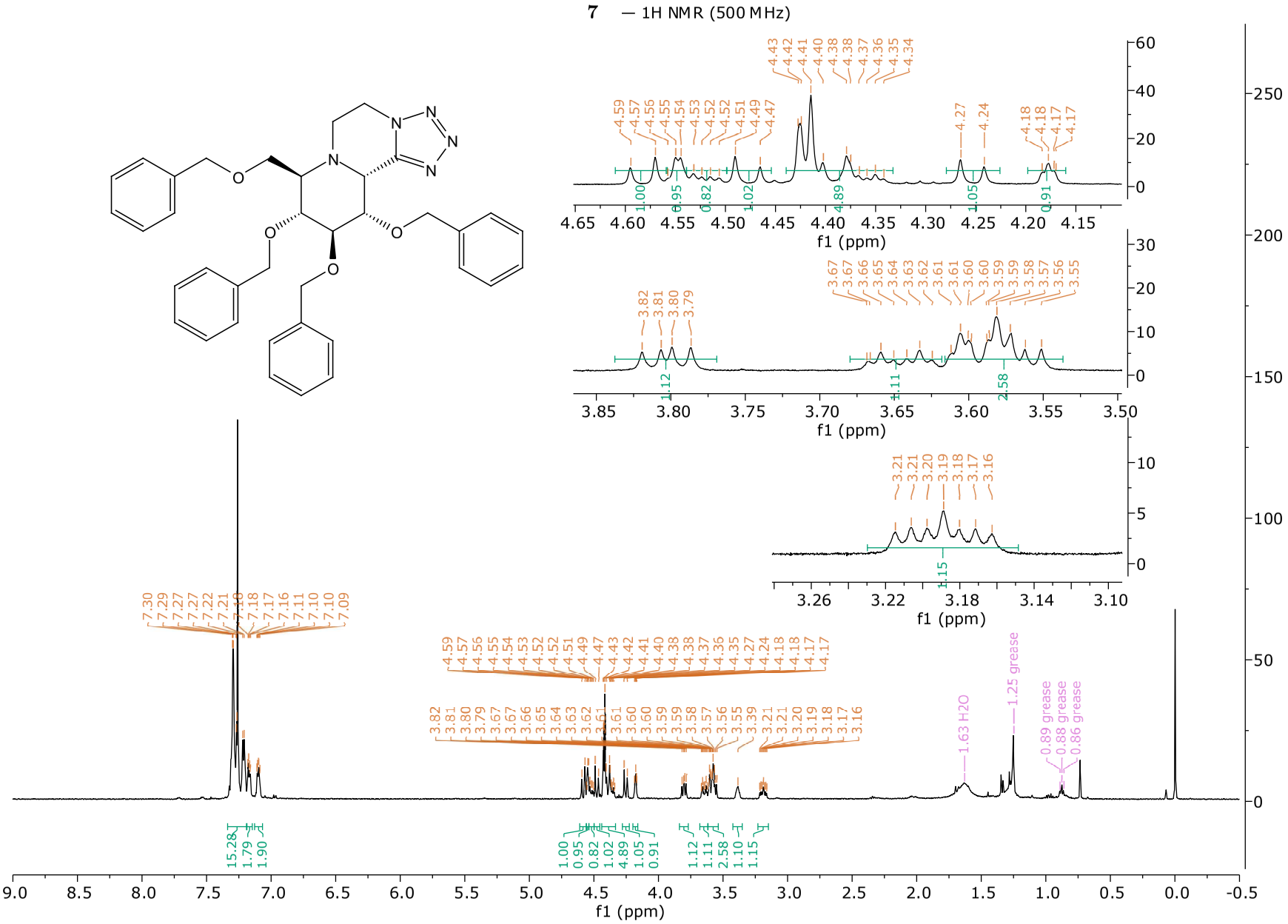

2-epi-5a 13C NMR (151 MHz)
f1 (ppm)

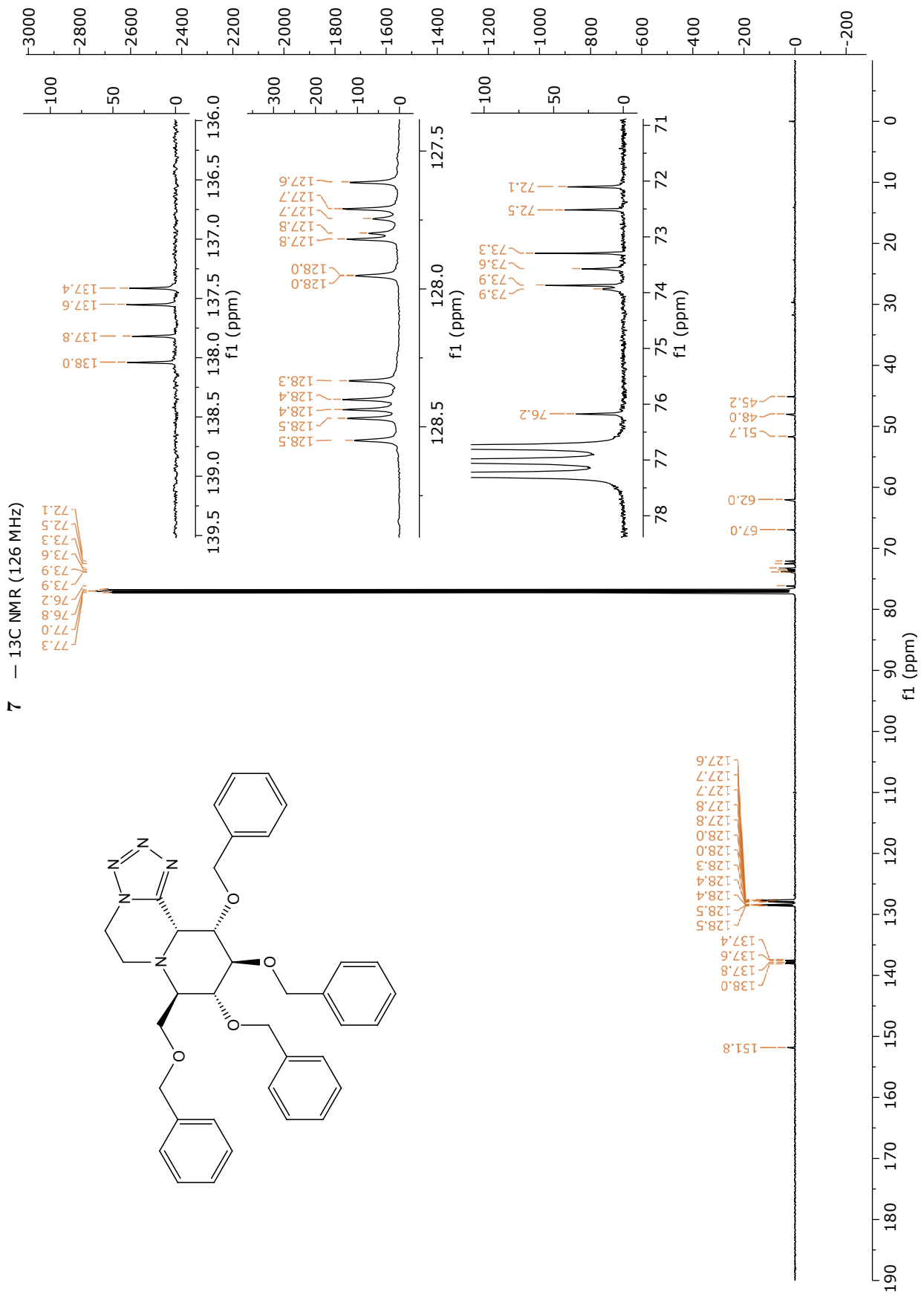

5b — 1H NMR (399 MHz)
f1 (ppm)

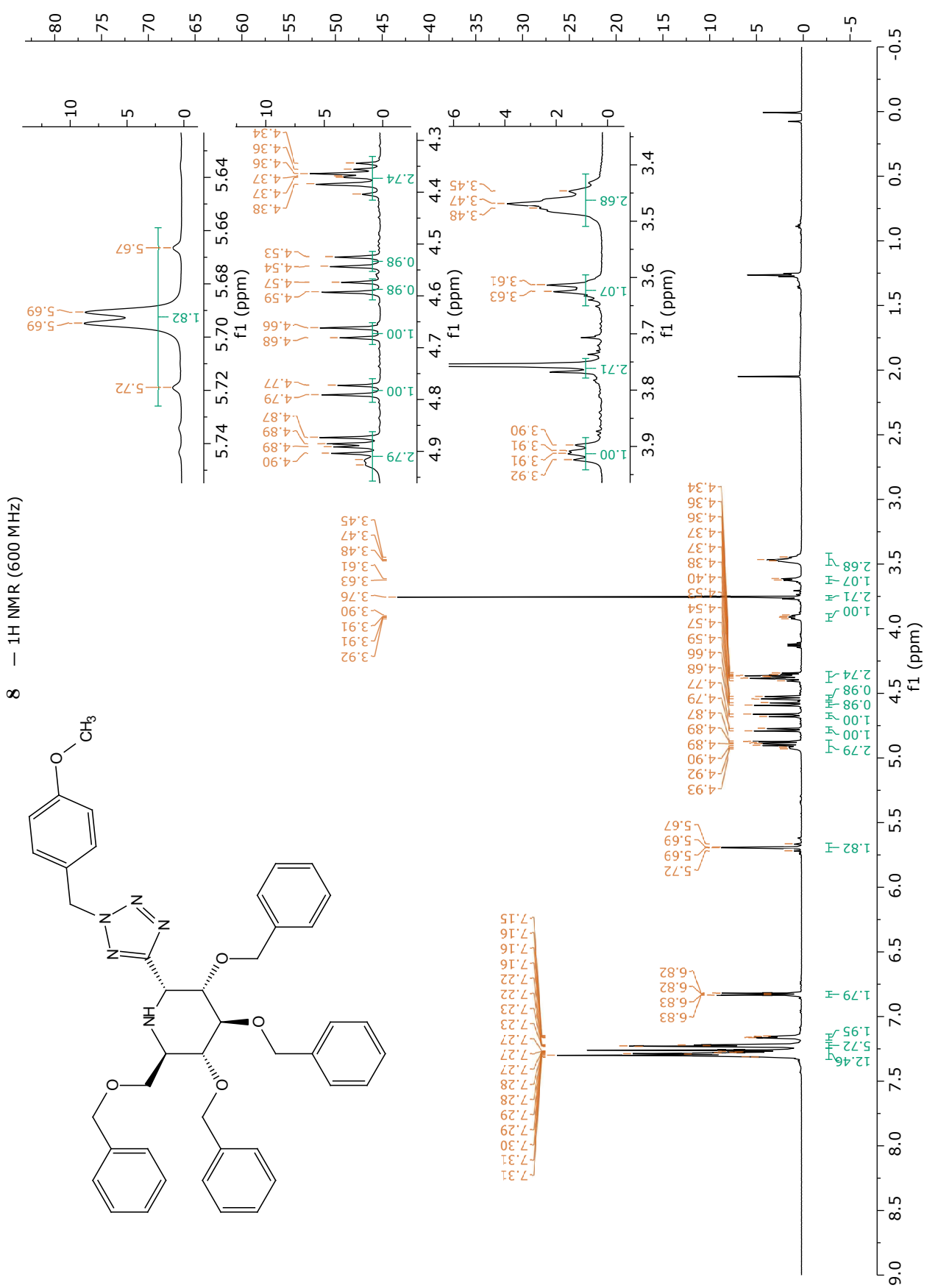

5b — 13C NMR (126 MHz)
f1 (ppm)

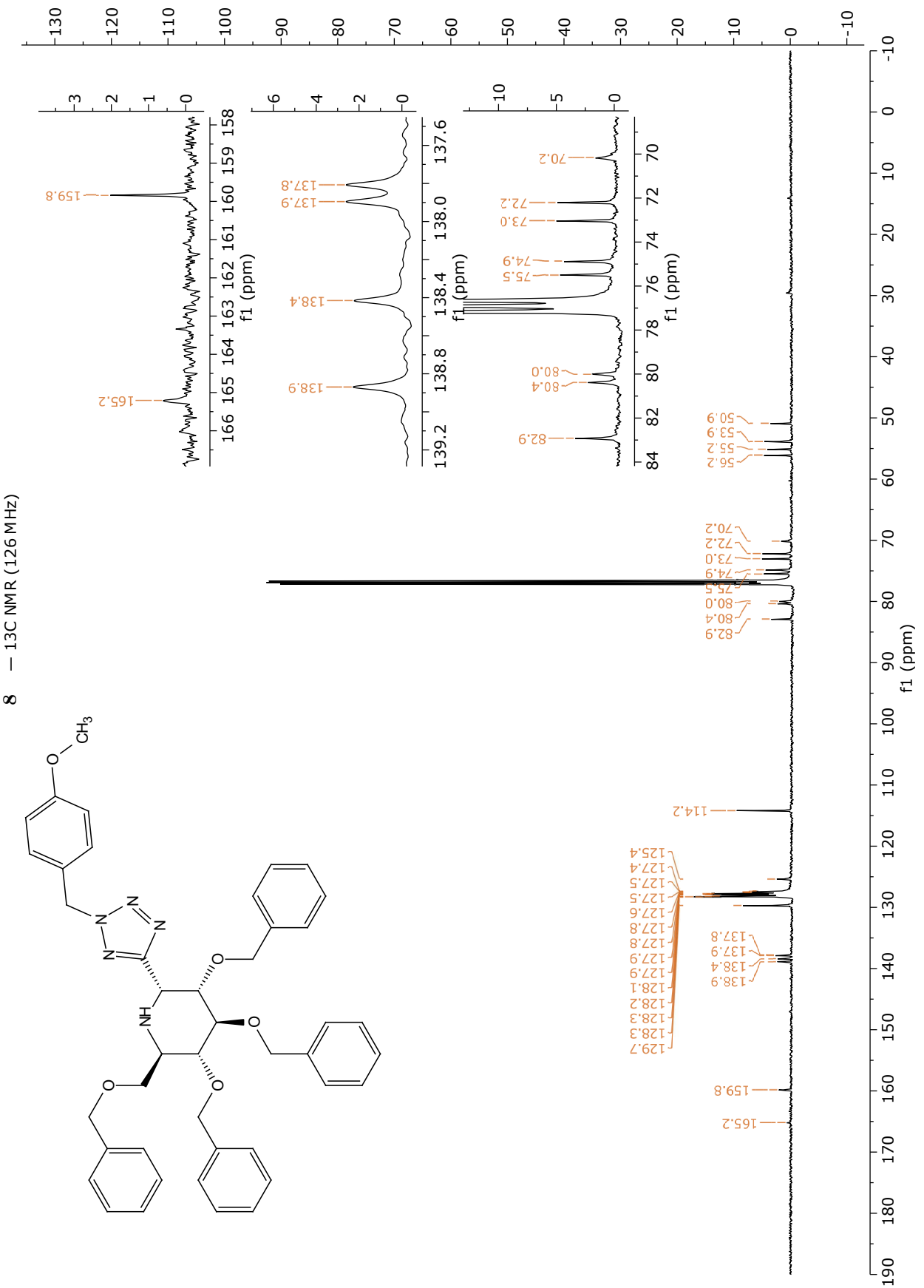

6 — 1H NMR (600 MHz)
f1 (ppm)
1.55 H2O
2.35 PhMe

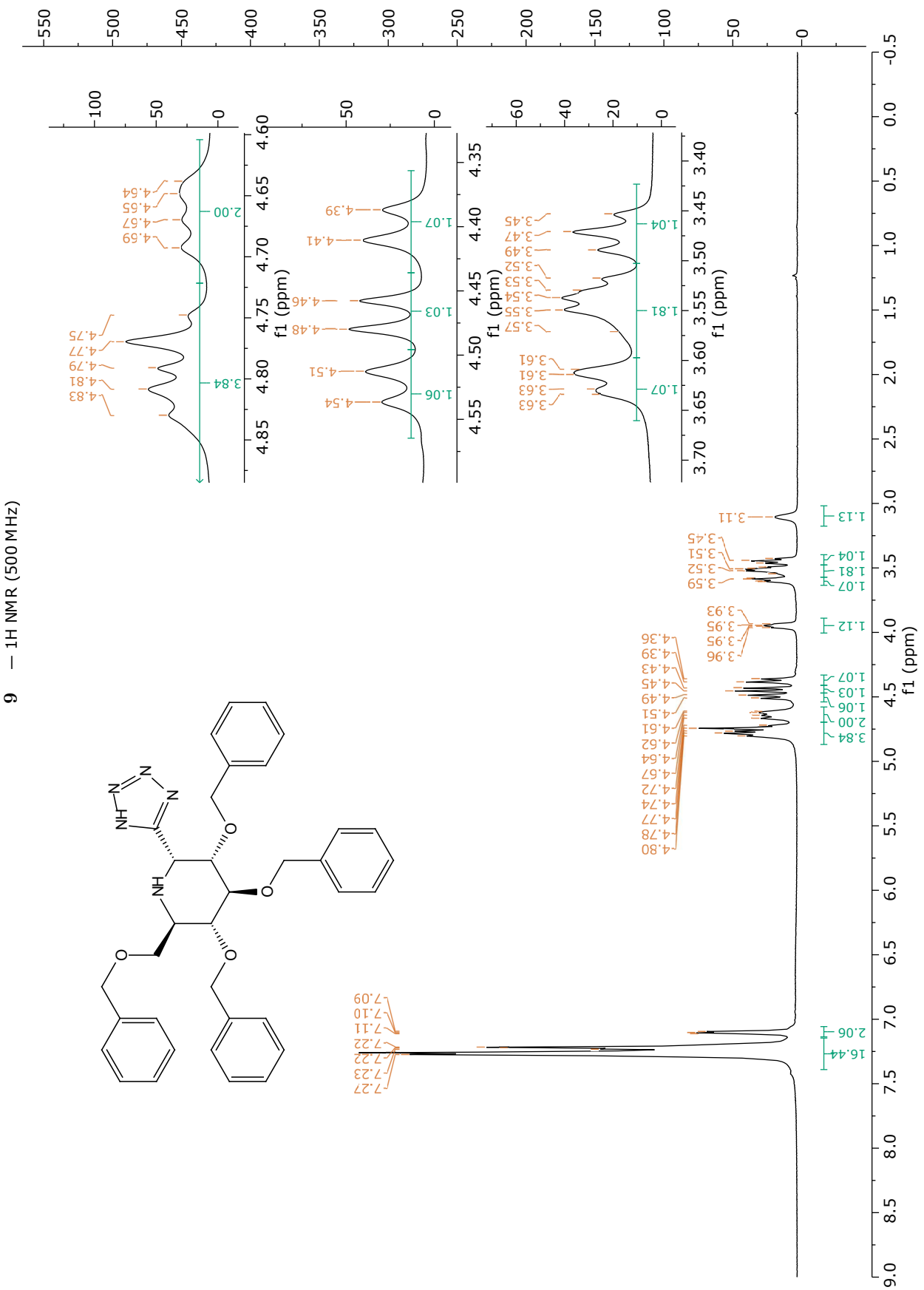

6 — 13C NMR (151 MHz)
f1 (ppm)
161.6
148.4
137.6
137.5
136.9
136.5
128.7
128.5
128.4
128.4
128.3
128.4
128.2
128.1
127.9
127.9
127.9
127.8
127.8
127.6
77.5
74.9
73.0
73.0
72.6
72.3
72.3
66.2
52.1
49.5
47.9

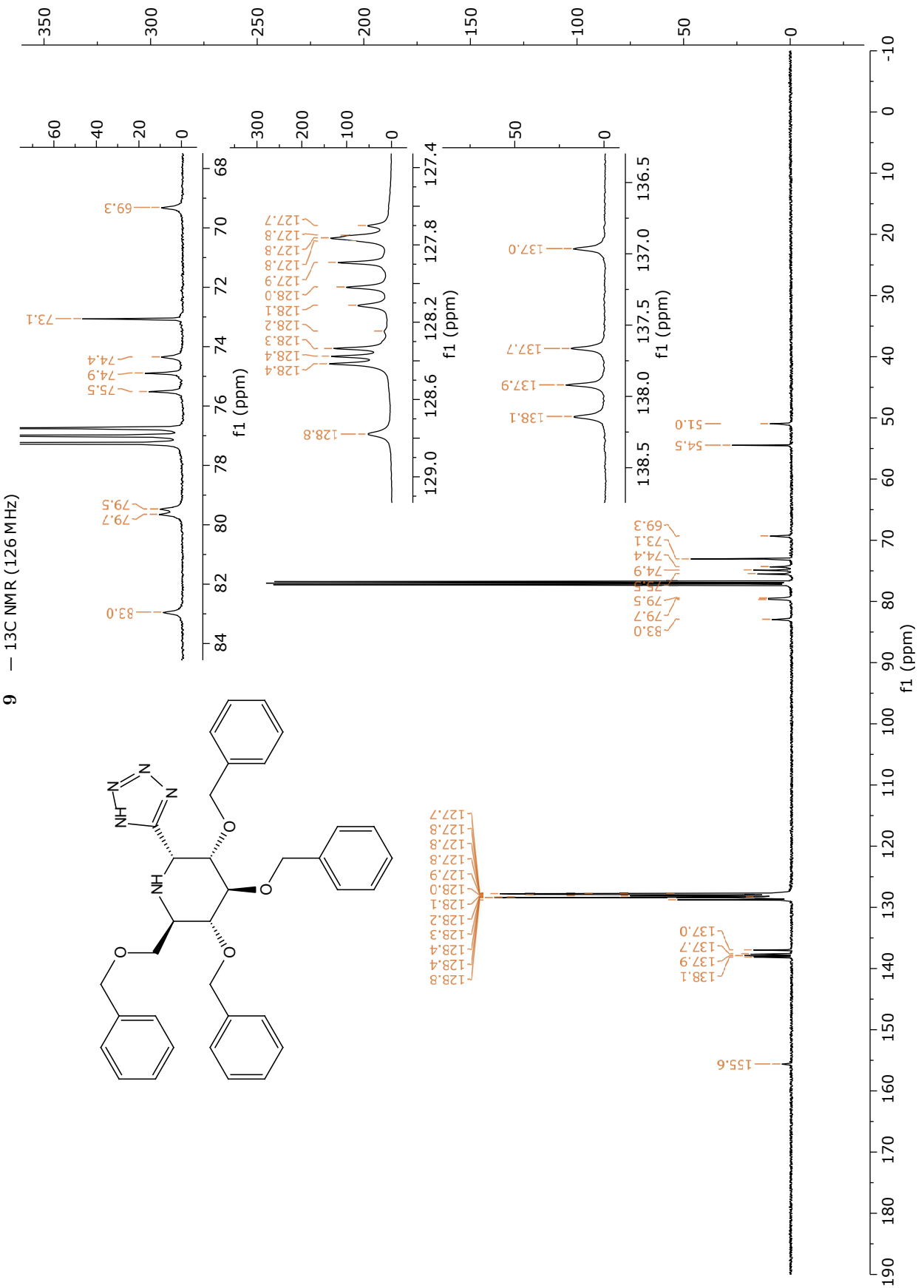

7 — 1H NMR (500 MHz)
f1 (ppm)
1.63 H2O
1.25 grease
0.89 grease
0.88 grease
0.86 grease


7 — 13C NMR (126 MHz)
f1 (ppm)


8 — 1H NMR (600 MHz)
f1 (ppm)


8 — 13C NMR (126 MHz)
f1 (ppm)
159.8
165.2
137.8
137.9
138.4
138.9
70.2
72.2
73.0
74.9
75.5
80.4
80.0
82.9
50.9
53.9
55.2
56.2
114.2
125.4
127.4
127.5
127.5
127.6
127.8
127.8
127.9
127.9
128.1
128.2
128.3
128.3
129.7
137.8
137.9
138.4
138.9


9 — 1H NMR (500 MHz)
f1 (ppm)


9 — 13C NMR (126 MHz)
f1 (ppm)

5 Computational data

INT-1-A

No. of imaginary frequencies = 0

Total energy = −1221.110 627

Zr	0.862 482	0.046 202	0.022 516
C	2.583 919	1.903 839	−0.484 495
C	1.621 470	1.915 929	−1.539 769
C	1.931 623	2.299 435	0.702 776
H	3.623 985	1.623 999	−0.578 842
C	0.391 038	2.374 474	−1.000 918
H	1.811 008	1.672 891	−2.576 977
C	0.568 450	2.580 438	0.384 228
H	2.370 998	2.351 202	1.689 495
H	−0.543 978	2.452 788	−1.537 490
H	−0.195 658	2.874 241	1.090 366
C	2.238 446	−2.047 904	0.683 332
C	1.090 444	−2.522 086	−0.008 376
C	3.028 340	−1.311 146	−0.227 472
H	2.440 609	−2.184 665	1.735 816
C	1.187 202	−2.100 877	−1.357 941
H	0.285 325	−3.099 885	0.424 899
C	2.371 562	−1.333 052	−1.495 146
H	3.968 277	−0.824 955	−0.005 147
H	0.458 068	−2.285 582	−2.135 361
H	2.731 525	−0.874 143	−2.405 971
Cl	0.368 070	−0.098 738	2.451 081
N	−2.671 263	−1.140 836	0.789 191
O	−0.986 748	−0.168 607	−0.588 613
C	−3.124 541	−0.669 205	−1.568 711
H	−3.885 108	−1.456 974	−1.628 441
H	−2.634 019	−0.598 577	−2.545 275
C	−3.776 033	0.664 523	−1.178 548
H	−4.563 061	0.928 199	−1.894 269
H	−3.017 577	1.456 110	−1.224 855
C	−4.337 416	0.582 546	0.248 750
H	−4.747 047	1.550 069	0.561 601
H	−5.156 750	−0.147 357	0.278 717
C	−3.244 095	0.142 808	1.226 296
H	−3.658 139	−0.000 139	2.229 700
H	−2.474 344	0.928 218	1.297 727
C	−2.084 064	−1.092 613	−0.526 848
H	−1.695 697	−2.094 291	−0.760 787
H	−1.960 158	−1.428 627	1.457 689

TS-1-A

No. of imaginary frequencies = 1 (−108.168)

Total energy = −1221.074 579

Zr	0.941 712	−0.017 547	−0.120 112
C	2.417 408	2.122 020	0.415 284
C	1.880 074	2.266 232	−0.899 263
C	1.351 952	2.171 633	1.330 677
H	3.457 306	1.949 454	0.655 178
C	0.483 081	2.486 769	−0.774 970
H	2.445 121	2.274 617	−1.822 381
C	0.147 809	2.388 795	0.591 042
H	1.416 085	2.036 575	2.401 789
H	−0.204 666	2.612 038	−1.599 991
H	−0.841 261	2.457 777	1.022 763
C	2.281 246	−2.017 631	0.973 605
C	1.777 492	−2.477 812	−0.277 165
C	3.250 326	−1.024 841	0.718 951
H	1.944 685	−2.344 110	1.947 469
C	2.441 690	−1.770 063	−1.304 369
H	1.005 788	−3.223 278	−0.413 240
C	3.331 629	−0.846 149	−0.691 908
H	3.795 253	−0.462 765	1.465 151
H	2.258 682	−1.867 514	−2.365 547
H	3.985 807	−0.156 730	−1.209 600
Cl	−0.625 619	−0.650 862	1.816 800
N	−2.808 643	−1.135 752	−1.115 556
O	−0.227 560	−0.351 160	−1.515 510
C	−3.247 708	1.235 833	−0.738 759
H	−4.051 441	1.629 400	−1.380 379
H	−2.490 758	2.025 882	−0.692 309
C	−3.764 954	0.848 579	0.653 546
H	−4.436 383	1.625 555	1.029 679
H	−2.913 954	0.771 462	1.337 218
C	−4.480 983	−0.507 473	0.588 013
H	−4.849 663	−0.801 256	1.574 830
H	−5.350 661	−0.445 142	−0.079 397
C	−3.523 492	−1.590 324	0.090 371
H	−4.053 520	−2.510 397	−0.173 432
H	−2.758 460	−1.815 476	0.840 392
C	−2.630 733	0.097 023	−1.470 378
H	−2.028 495	0.265 349	−2.351 993
H	−2.170 465	−1.790 921	−1.562 384

INT-2-A

No. of imaginary frequencies = 0

Total energy = −1221.106 694

Zr	1.058 567	−0.017 639	−0.065 847
C	1.984 236	2.313 115	0.544 170
C	1.522 364	2.374 637	−0.803 606
C	0.865 434	2.115 661	1.380 538
H	3.015 710	2.374 125	0.862 805
C	0.105 019	2.272 533	−0.782 105
H	2.135 994	2.519 248	−1.682 952
C	−0.299 578	2.088 345	0.557 003
H	0.881 033	1.980 718	2.453 285
H	−0.537 800	2.264 220	−1.650 815
H	−1.307 566	1.917 951	0.905 435
C	2.669 713	−1.817 100	0.862 632
C	2.309 289	−2.240 479	−0.444 891
C	3.419 093	−0.621 514	0.747 449
H	2.376 731	−2.296 283	1.785 707
C	2.853 651	−1.318 083	−1.371 430
H	1.692 452	−3.094 137	−0.688 714
C	3.527 813	−0.306 875	−0.639 397
H	3.831 186	−0.047 670	1.566 753
H	2.716 051	−1.344 122	−2.443 380
H	4.051 600	0.541 363	−1.059 365
Cl	−0.361 015	−0.987 252	1.743 086
N	−2.669 742	−0.056 998	−1.388 137
O	0.017 023	−0.603 510	−1.626 459
C	−4.242 172	0.994 596	0.241 014
H	−5.231 586	1.228 558	−0.180 143
H	−3.995 953	1.835 528	0.902 138
C	−4.267 507	−0.337 617	1.000 057
H	−5.141 984	−0.389 134	1.656 648
H	−3.374 168	−0.412 993	1.631 721
C	−4.259 048	−1.484 266	−0.017 040
H	−4.291 508	−2.458 015	0.483 082
H	−5.152 471	−1.418 001	−0.652 949
C	−2.996 895	−1.398 507	−0.881 176
H	−3.068 741	−2.055 440	−1.755 153
H	−2.119 676	−1.729 811	−0.313 105
C	−3.239 544	0.968 049	−0.889 492
H	−2.954 387	1.938 303	−1.309 469
H	−0.889 554	−0.253 482	−1.803 824

INT-1-B

No. of imaginary frequencies = 0

Total energy = −1221.106 03

Zr	−0.953 677	−0.009 751	−0.040 892

C	−2.482 332	1.087 275	1.678 081
C	−1.823 204	2.175 717	1.048 854
C	−3.363 852	0.497 629	0.721 031
H	−2.377 536	0.792 353	2.713 912
C	−2.239 760	2.221 170	−0.298 855
H	−1.061 195	2.797 802	1.496 661
C	−3.203 619	1.188 318	−0.498 686
H	−4.019 003	−0.344 874	0.895 091
H	−1.874 549	2.897 429	−1.059 080
H	−3.692 224	0.956 373	−1.434 733
C	−0.577 582	−2.508 894	−0.566 277
C	0.466 690	−2.125 870	0.306 263
C	−1.808 357	−2.417 917	0.139 420
H	−0.466 604	−2.767 224	−1.609 159
C	−0.114 395	−1.804 259	1.564 548
H	1.504 241	−1.999 674	0.030 200
C	−1.516 012	−2.003 114	1.466 580
H	−2.789 130	−2.642 859	−0.258 344
H	0.418 079	−1.462 770	2.442 489
H	−2.235 750	−1.852 044	2.259 173
Cl	−0.878 505	0.013 057	−2.523 870
N	2.530 761	0.054 799	−0.945 534
O	0.731 299	0.980 921	0.237 445
C	2.837 831	0.654 288	1.400 527
H	2.501 218	−0.341 910	1.709 557
H	2.531 883	1.367 480	2.173 468
C	4.361 172	0.662 403	1.199 179
H	4.870 244	0.354 458	2.119 338
H	4.690 418	1.689 339	0.986 629
C	4.758 859	−0.245 215	0.024 740
H	5.833 961	−0.169 521	−0.174 887
H	4.542 825	−1.290 953	0.277 332
C	3.966 433	0.130 685	−1.232 170
H	4.191 736	−0.558 501	−2.052 622
H	4.277 756	1.141 875	−1.560 461
C	2.120 621	1.002 672	0.092 550
H	2.396 208	2.041 830	−0.187 402
H	1.978 406	0.239 179	−1.781 230

TS-1-B

No. of imaginary frequencies = 1 (−386.7343)

Total energy = −1221.010 227

Zr	1.044 381	−0.070 195	0.090 005
C	2.068 187	1.688 861	−1.421 622
C	0.738 693	2.118 224	−1.146 342

C	2.806 283	1.744 485	−0.212 307
H	2.450 054	1.390 509	−2.387 541
C	0.671 508	2.466 170	0.228 866
H	−0.069 259	2.190 109	−1.860 794
C	1.938 460	2.222 911	0.808 778
H	3.840 252	1.455 847	−0.078 716
H	−0.210 283	2.799 416	0.757 508
H	2.195 673	2.337 241	1.852 354
C	0.546 574	−2.535 085	−0.299 828
C	−0.451 798	−1.826 616	−1.017 083
C	1.804 173	−2.292 817	−0.920 274
H	0.382 909	−3.148 978	0.575 795
C	0.195 231	−1.098 778	−2.047 904
H	−1.494 731	−1.747 567	−0.711 931
C	1.592 997	−1.399 138	−1.996 417
H	2.757 124	−2.687 238	−0.595 697
H	−0.287 121	−0.454 348	−2.771 069
H	2.350 514	−1.036 728	−2.677 493
Cl	2.469 868	−0.838 489	1.919 693
N	−2.745 238	−0.789 069	1.032 825
O	−0.774 843	0.097 773	1.162 264
C	−2.510 668	1.170 026	−0.453 755
H	−2.065 014	0.570 921	−1.255 358
H	−2.120 563	2.194 008	−0.519 603
C	−4.051 762	1.180 293	−0.594 015
H	−4.334 004	1.608 233	−1.562 770
H	−4.465 764	1.850 521	0.174 226
C	−4.654 692	−0.223 507	−0.408 057
H	−5.750 729	−0.164 477	−0.448 550
H	−4.326 470	−0.871 254	−1.231 764
C	−4.180 998	−0.842 712	0.928 847
H	−4.514 622	−1.885 088	0.995 957
H	−4.698 893	−0.296 521	1.751 441
C	−2.228 843	0.505 407	0.893 824
H	−2.442 075	1.240 720	1.705 785
H	−1.244 637	−0.808 246	1.469 096

INT-2-B

No. of imaginary frequencies = 0

Total energy = −1221.009 687

Zr	−1.047 397	−0.073 710	−0.079 296
C	−2.064 530	1.678 207	1.440 723
C	−0.751 631	2.130 877	1.127 174
C	−2.834 975	1.707 769	0.250 041
H	−2.415 812	1.383 080	2.419 173

C	−0.726 585	2.465 407	−0.253 104
H	0.072 939	2.226 204	1.819 563
C	−2.003 437	2.193 282	−0.797 365
H	−3.866 840	1.399 553	0.146 671
H	0.134 685	2.809 332	−0.808 104
H	−2.289 377	2.292 355	−1.834 983
C	−0.513 667	−2.527 251	0.296 962
C	0.507 585	−1.806 886	0.969 545
C	−1.747 724	−2.293 861	0.966 282
H	−0.380 538	−3.143 360	−0.582 324
C	−0.104 815	−1.082 631	2.024 740
H	1.536 289	−1.713 707	0.613 145
C	−1.500 576	−1.394 440	2.030 831
H	−2.709 293	−2.699 709	0.683 334
H	0.400 077	−0.432 395	2.727 052
H	−2.232 682	−1.036 998	2.741 725
Cl	−2.475 977	−0.880 604	−1.888 693
N	2.770 828	−0.804 426	−1.061 316
O	0.746 447	0.123 467	−1.239 108
C	2.475 958	1.197 638	0.367 308
H	2.005 104	0.629 024	1.176 272
H	2.071 594	2.218 017	0.372 797
C	4.006 675	1.230 461	0.575 858
H	4.243 223	1.703 944	1.535 766
H	4.452 493	1.866 384	−0.203 840
C	4.612 554	−0.178 505	0.476 399
H	5.705 847	−0.123 654	0.566 553
H	4.241 835	−0.793 830	1.307 403
C	4.199 238	−0.838 225	−0.860 493
H	4.542 177	−1.879 892	−0.881 600
H	4.761 232	−0.313 233	−1.668 886
C	2.250 847	0.473 847	−0.965 286
H	2.457 169	1.193 362	−1.795 336
H	1.060 529	−0.756 704	−1.610 368

INT-3

No. of imaginary frequencies = 0

Total energy = −250.661 194

N	−0.658 652	−1.359 350	0.054 364
C	1.464 563	−0.034 345	−0.102 710
H	1.856 358	0.069 693	−1.125 794
H	2.343 894	−0.184 323	0.536 337
C	0.676 313	1.216 567	0.304 853
H	1.211 381	2.125 269	0.009 733
H	0.577 340	1.245 415	1.397 762

C	−0.718 663	1.155 476	−0.326 346
H	−1.315 251	2.036 668	−0.064 664
H	−0.621 782	1.147 448	−1.420 272
C	−1.440 248	−0.120 130	0.128 555
H	−2.351 511	−0.278 278	−0.460 127
H	−1.772 555	−0.016 567	1.171 570
C	0.607 216	−1.283 458	−0.054 954
H	1.147 606	−2.234 534	−0.121 486

TS-3

No. of imaginary frequencies = 1 (−127.6484)

Total energy = −824.174 398

N	1.358 231	0.092 438	−0.020 950
C	3.592 771	1.168 797	0.097 266
H	3.889 659	1.483 052	1.109 728
H	3.921 573	1.981 721	−0.561 833
C	4.230 909	−0.174 740	−0.274 407
H	5.271 086	−0.203 047	0.060 712
H	4.242 032	−0.287 434	−1.364 973
C	3.413 121	−1.310 276	0.347 424
H	3.836 119	−2.287 932	0.098 534
H	3.421 627	−1.223 684	1.441 091
C	1.973 328	−1.253 547	−0.155 573
H	1.332 657	−1.950 431	0.388 675
H	1.912 864	−1.521 509	−1.215 990
C	2.096 067	1.140 586	0.086 431
H	1.574 116	2.089 548	0.192 052
Si	−0.608 231	0.142 496	−0.021 822
C	−0.903 235	−0.780 644	−1.620 371
H	−0.662 707	−1.845 425	−1.540 606
H	−1.977 571	−0.680 281	−1.803 455
H	−0.339 643	−0.352 140	−2.456 672
C	−0.954 797	1.976 519	−0.051 055
H	−0.528 142	2.484 057	−0.922 870
H	−2.049 319	2.022 113	−0.108 728
H	−0.634 433	2.491 878	0.860 874
C	−0.913 548	−0.728 627	1.605 819
H	−1.966 928	−0.535 622	1.829 564
H	−0.780 187	−1.812 759	1.536 320
H	−0.279 160	−0.344 780	2.412 408
N	−3.437 698	0.189 643	−0.050 020
N	−4.599 428	−0.120 112	0.015 316
N	−5.731 978	−0.409 209	0.075 293

INT-4

No. of imaginary frequencies = 0
Total energy = −659.784 677

N	0.262 727	0.080 794	−0.023 668
C	2.408 659	1.317 561	0.058 409
H	2.681 144	1.685 616	1.060 623
H	2.663 555	2.143 929	−0.617 489
C	3.147 411	0.019 793	−0.288 646
H	4.181 528	0.076 673	0.057 995
H	3.181 428	−0.104 985	−1.376 733
C	2.416 556	−1.166 938	0.345 650
H	2.908 604	−2.112 190	0.101 356
H	2.419 382	−1.075 131	1.438 375
C	0.977 126	−1.228 143	−0.155 872
H	0.392 540	−1.966 618	0.397 428
H	0.933 283	−1.500 022	−1.215 986
C	0.924 928	1.184 887	0.068 570
H	0.339 995	2.097 363	0.174 664
Si	−1.631 766	0.003 862	−0.003 191
C	−2.046 618	−1.000 119	−1.522 724
H	−1.651 638	−2.019 038	−1.472 080
H	−3.135 568	−1.079 054	−1.614 391
H	−1.674 377	−0.527 522	−2.437 196
C	−2.224 718	1.773 652	−0.089 406
H	−1.869 899	2.298 852	−0.981 915
H	−3.319 438	1.759 009	−0.143 956
H	−1.962 565	2.359 608	0.797 300
C	−2.041 976	−0.838 026	1.613 962
H	−3.131 307	−0.879 641	1.726 639
H	−1.674 216	−1.867 122	1.664 859
H	−1.645 016	−0.285 343	2.471 196

TS-4

No. of imaginary frequencies = 1 (−290.9038)
Total energy = −1098.809 155

N	2.670 223	0.096 093	−0.065 723
C	3.368 167	−2.013 629	0.956 328
H	3.184 435	−2.603 069	1.857 127
H	4.412 814	−1.680 468	0.992 607
C	3.109 135	−2.836 257	−0.325 981
H	2.327 582	−3.576 494	−0.129 244
H	4.015 040	−3.394 543	−0.576 050
C	2.682 090	−1.933 659	−1.506 638
H	3.052 901	−2.329 757	−2.455 873
H	1.589 395	−1.903 717	−1.587 812
C	3.184 803	−0.498 676	−1.325 762

H	2.864 120	0.127 711	−2.161 847
H	4.281 882	−0.473 693	−1.306 928
C	2.544 580	−0.745 128	0.994 985
H	2.495 784	−0.248 950	1.963 132
Si	2.093 426	1.818 687	−0.085 469
C	3.522 810	2.850 209	−0.718 167
H	3.836 080	2.543 156	−1.721 129
H	3.232 925	3.904 898	−0.775 538
H	4.390 798	2.777 145	−0.055 483
C	1.608 928	2.247 443	1.676 848
H	2.449 869	2.173 592	2.374 053
H	1.258 854	3.284 914	1.705 971
H	0.790 216	1.623 281	2.050 144
C	0.611 358	1.894 575	−1.239 882
H	0.261 908	2.929 170	−1.327 875
H	0.857 245	1.550 686	−2.249 793
H	−0.225 474	1.293 911	−0.870 684
C	0.792 771	−1.333 330	1.072 627
N	−0.320 172	−1.039 586	0.866 791
C	−1.636 372	−0.710 500	0.622 866
C	−2.179 628	−0.934 168	−0.649 901
C	−2.412 510	−0.143 499	1.651 954
C	−3.500 146	−0.589 349	−0.904 499
H	−1.567 559	−1.377 265	−1.427 940
C	−3.724 355	0.198 564	1.394 595
H	−1.978 601	0.016 329	2.632 839
C	−4.284 008	−0.019 906	0.117 383
H	−3.912 082	−0.766 759	−1.889 264
H	−4.351 893	0.635 784	2.162 536
O	−5.566 405	0.348 390	−0.017 670
C	−6.229 113	0.152 706	−1.272 690
H	−7.244 343	0.518 751	−1.126 859
H	−5.742 919	0.727 767	−2.068 619
H	−6.257 111	−0.909 037	−1.541 423

INT-5

No. of imaginary frequencies = 0

Total energy = −1098.814 285

N	2.553 350	0.264 493	0.163 642
C	2.390 463	2.506 079	−0.977 665
H	1.561 887	3.066 866	−1.425 230
H	3.257 271	2.649 489	−1.627 191
C	2.684 546	3.004 333	0.448 495
H	2.540 820	4.087 223	0.495 141
H	3.732 488	2.808 458	0.698 012

C	1.784 049	2.280 453	1.450 830
H	1.893 449	2.693 397	2.457 363
H	0.731 159	2.428 845	1.175 152
C	2.133 097	0.781 002	1.488 029
H	1.281 406	0.208 608	1.888 606
H	2.972 581	0.625 556	2.171 902
C	2.050 740	0.980 725	−0.974 912
H	2.432 868	0.530 061	−1.895 629
Si	3.071 631	−1.446 488	0.013 957
C	4.127 819	−1.826 912	1.514 688
H	3.554 261	−1.803 219	2.446 320
H	4.553 456	−2.831 624	1.420 232
H	4.959 990	−1.121 696	1.606 627
C	4.037 443	−1.605 576	−1.590 715
H	4.846 761	−0.870 671	−1.647 851
H	4.494 203	−2.600 310	−1.637 064
H	3.416 251	−1.505 972	−2.487 424
C	1.536 058	−2.547 532	−0.029 042
H	1.811 803	−3.607 307	−0.043 798
H	0.907 963	−2.384 644	0.854 342
H	0.931 641	−2.359 436	−0.924 398
C	0.557 235	0.770 358	−1.027 307
N	−0.548 015	0.523 415	−0.769 663
C	−1.856 732	0.198 033	−0.487 242
C	−2.841 207	1.195 335	−0.525 444
C	−2.176 421	−1.134 774	−0.160 075
C	−4.156 799	0.866 880	−0.233 110
H	−2.572 734	2.214 204	−0.782 541
C	−3.486 282	−1.454 742	0.128 628
H	−1.398 774	−1.889 913	−0.136 911
C	−4.490 774	−0.462 136	0.096 063
H	−4.913 354	1.639 815	−0.263 944
H	−3.773 583	−2.468 022	0.384 302
O	−5.724 807	−0.887 388	0.392 685
C	−6.817 788	0.041 192	0.382 417
H	−7.697 423	−0.542 172	0.649 937
H	−6.664 856	0.835 213	1.121 367
H	−6.953 940	0.475 513	−0.613 893

TS-5

No. of imaginary frequencies = 1 (−79.4602)

Total energy = −1263.213 899

N	−2.708 886	0.385 474	−0.323 278
C	−2.640 076	−1.243 076	−2.226 403
H	−3.422 152	−0.737 031	−2.805 301

H	−1.928 793	−1.674 689	−2.940 032
C	−3.265 681	−2.309 026	−1.324 283
H	−3.809 304	−3.034 627	−1.938 814
H	−2.482 807	−2.844 542	−0.775 200
C	−4.199 687	−1.628 640	−0.317 329
H	−4.636 576	−2.370 949	0.358 159
H	−5.022 540	−1.126 922	−0.844 802
C	−3.418 336	−0.612 907	0.516 691
H	−4.101 547	−0.055 197	1.166 187
H	−2.715 992	−1.161 526	1.154 559
C	−1.937 630	−0.138 043	−1.413 541
H	−1.689 104	0.683 272	−2.101 071
C	−0.539 652	−0.549 900	−0.983 019
N	0.564 487	−0.485 412	−0.622 341
N	−1.241 012	−2.964 350	1.339 336
C	1.930 600	−0.270 738	−0.515 333
C	2.644 893	−0.711 568	0.601 005
C	2.566 582	0.408 818	−1.573 554
C	4.012 579	−0.463 771	0.664 908
H	2.083 557	−1.205 299	1.398 248
C	3.924 940	0.647 396	−1.500 924
H	1.991 162	0.739 526	−2.432 084
C	4.660 176	0.211 579	−0.380 586
H	4.560 661	−0.801 676	1.535 174
H	4.448 876	1.168 234	−2.294 232
C	6.798 463	0.088 563	0.682 360
H	7.808 842	0.417 654	0.438 837
H	6.789 698	−1.001 090	0.805 011
H	6.475 982	0.562 677	1.617 048
O	5.983 273	0.494 824	−0.415 057
N	−0.479 036	−2.176 599	1.785 553
N	0.277 545	−1.373 414	2.230 608
Si	−2.293 798	1.924 747	0.479 301
C	−1.042 813	2.825 157	−0.616 923
C	−1.577 072	1.586 962	2.180 442
C	−3.874 111	2.943 765	0.601 339
H	−1.416 625	2.996 255	−1.632 678
H	−0.082 423	2.302 767	−0.681 755
H	−0.839 552	3.809 398	−0.180 829
H	−0.838 751	0.773 792	2.163 469
H	−2.363 295	1.287 043	2.881 848
H	−1.100 562	2.486 247	2.587 773
H	−4.657 486	2.401 661	1.141 328
H	−4.263 620	3.193 351	−0.390 914
H	−3.691 401	3.879 306	1.142 075

INT-6

No. of imaginary frequencies = 0

Total energy = −1263.270 157

N	−1.961 257	0.868 176	−0.429 019
C	−1.705 319	−0.863 558	−2.216 482
H	−1.479 046	−0.147 585	−3.016 541
H	−1.164 010	−1.788 535	−2.448 021
C	−3.219 047	−1.105 615	−2.186 849
H	−3.557 193	−1.437 947	−3.175 170
H	−3.458 668	−1.905 586	−1.477 803
C	−3.938 984	0.181 857	−1.771 165
H	−5.021 607	0.019 308	−1.709 558
H	−3.764 229	0.960 145	−2.525 857
C	−3.420 651	0.676 042	−0.417 037
H	−3.885 252	1.637 698	−0.181 213
H	−3.732 205	−0.032 689	0.364 124
C	−1.148 655	−0.256 791	−0.908 181
H	−0.163 212	0.145 386	−1.147 949
C	−0.887 900	−1.297 173	0.187 310
N	0.224 861	−1.625 538	0.729 517
N	−2.085 731	−1.866 191	0.702 546
C	1.469 000	−1.157 475	0.274 654
C	2.355 994	−0.615 152	1.213 464
C	1.901 044	−1.269 512	−1.061 130
C	3.609 678	−0.135 191	0.833 606
H	2.042 604	−0.555 477	2.250 666
C	3.154 293	−0.811 639	−1.444 416
H	1.249 424	−1.735 633	−1.793 527
C	4.014 694	−0.228 257	−0.504 098
H	4.258 525	0.296 960	1.585 591
H	3.492 552	−0.896 495	−2.471 696
C	6.130 589	0.796 286	−0.079 172
H	7.008 867	1.067 508	−0.666 926
H	6.429 697	0.097 227	0.713 277
H	5.712 577	1.701 024	0.382 316
O	5.218 023	0.201 094	−0.988 251
N	−1.941 656	−2.655 306	1.655 491
N	−1.943 174	−3.393 274	2.517 219
Si	−1.207 406	2.076 283	0.612 126
C	0.491 602	2.500 363	−0.090 912
C	−1.009 530	1.456 127	2.388 611
C	−2.292 027	3.621 677	0.613 285
H	0.426 773	2.763 450	−1.152 007
H	1.213 724	1.685 864	0.016 593
H	0.898 549	3.366 911	0.442 950

H	−0.385 664	0.556 940	2.419 246
H	−1.980 800	1.201 554	2.827 363
H	−0.541 882	2.213 198	3.028 657
H	−3.231 189	3.480 632	1.157 713
H	−2.533 882	3.939 409	−0.406 257
H	−1.754 930	4.443 017	1.101 053

TS-6

No. of imaginary frequencies = 1 (−256.4598)

Total energy = −1263.250 449

N	−2.082 501	0.765 156	−0.410 877
C	−1.916 418	−1.080 222	−2.086 134
H	−1.774 525	−0.412 884	−2.945 722
H	−1.361 350	−2.002 268	−2.296 481
C	−3.413 594	−1.363 817	−1.918 091
H	−3.818 339	−1.764 520	−2.854 740
H	−3.562 633	−2.123 231	−1.144 267
C	−4.141 977	−0.074 940	−1.520 036
H	−5.207 911	−0.268 875	−1.351 773
H	−4.064 286	0.659 536	−2.332 866
C	−3.527 394	0.521 310	−0.249 788
H	−4.008 007	1.478 694	−0.028 866
H	−3.726 995	−0.150 669	0.596 044
C	−1.283 691	−0.367 579	−0.870 776
H	−0.323 010	0.031 634	−1.203 475
C	−0.923 439	−1.339 946	0.270 134
N	0.241 811	−1.547 455	0.753 377
N	−2.039 296	−1.966 215	0.887 316
C	1.473 837	−1.090 490	0.283 232
C	2.358 050	−0.485 156	1.184 690
C	1.880 755	−1.252 018	−1.055 553
C	3.594 078	0.002 095	0.762 011
H	2.057 648	−0.386 797	2.222 440
C	3.112 893	−0.776 622	−1.480 600
H	1.224 808	−1.762 909	−1.753 238
C	3.976 153	−0.136 752	−0.579 187
H	4.246 525	0.479 655	1.482 526
H	3.434 372	−0.892 677	−2.510 053
C	6.075 201	0.952 302	−0.236 719
H	6.934 709	1.218 106	−0.853 647
H	6.405 392	0.292 397	0.576 360
H	5.645 212	1.865 543	0.195 526
O	5.157 968	0.299 972	−1.102 423
N	−1.555 690	−2.630 879	1.885 646
N	−0.553 516	−2.893 389	2.402 421

Si	−1.295 564	2.056 797	0.499 145
C	0.350 317	2.460 729	−0.331 294
C	−0.988 562	1.563 904	2.299 274
C	−2.410 781	3.579 062	0.453 033
H	0.217 593	2.649 758	−1.401 811
H	1.096 072	1.669 588	−0.213 153
H	0.767 801	3.369 302	0.117 750
H	−0.345 034	0.680 319	2.358 415
H	−1.929 602	1.320 905	2.804 960
H	−0.505 696	2.372 160	2.860 601
H	−3.313 239	3.461 893	1.061 256
H	−2.718 795	3.814 563	−0.570 915
H	−1.864 780	4.444 157	0.846 112

INT-7

No. of imaginary frequencies = 0

Total energy = −1263.293 985

N	−2.118 930	0.766 701	−0.362 750
C	−2.218 800	−1.101 189	−2.002 970
H	−2.186 230	−0.419 499	−2.861 770
H	−1.714 640	−2.029 309	−2.298 690
C	−3.679 250	−1.366 728	−1.618 480
H	−4.222 530	−1.765 908	−2.482 640
H	−3.717 670	−2.123 418	−0.827 660
C	−4.330 070	−0.070 858	−1.118 280
H	−5.356 420	−0.260 098	−0.782 550
H	−4.378 430	0.659 992	−1.936 480
C	−3.518 290	0.528 052	0.035 410
H	−3.956 020	1.484 892	0.334 710
H	−3.574 700	−0.146 298	0.902 710
C	−1.422 690	−0.422 929	−0.866 620
H	−0.475 320	−0.084 679	−1.291 630
C	−1.076 580	−1.393 529	0.248 210
N	0.179 500	−1.640 139	0.713 370
N	0.080 920	−2.458 049	1.802 420
N	−1.177 251	−2.690 839	1.965 140
N	−1.923 810	−2.055 379	1.022 510
C	1.443 740	−1.159 659	0.271 070
C	2.301 420	−0.547 889	1.182 760
C	1.817 530	−1.288 309	−1.071 640
C	3.528 210	−0.039 570	0.757 780
H	2.004 910	−0.471 209	2.222 420
C	3.028 940	−0.768 249	−1.502 930
H	1.160 690	−1.798 409	−1.768 370
C	3.891 920	−0.137 050	−0.592 850

H	4.180 650	0.433 890	1.480 280
H	3.338 330	−0.848 369	−2.538 900
C	5.973 120	0.988 260	−0.252 260
H	6.815 170	1.284 180	−0.878 750
H	6.329 110	0.314 790	0.537 700
H	5.531 550	1.882 150	0.206 490
O	5.052 080	0.336 990	−1.118 980
Si	−1.203 130	2.059 911	0.406 890
C	0.380 360	2.344 981	−0.581 780
H	0.163 080	2.475 691	−1.647 190
H	1.107 570	1.534 981	−0.477 900
H	0.865 150	3.261 921	−0.227 630
C	−2.249 629	3.629 701	0.373 760
H	−1.644 509	4.484 171	0.697 450
H	−3.115 289	3.574 982	1.041 280
H	−2.613 599	3.838 852	−0.637 310
C	−0.764 530	1.647 271	2.200 800
H	−0.200 020	2.458 121	2.675 610
H	−0.159 900	0.737 001	2.262 930
H	−1.669 150	1.476 991	2.794 580

INT-8

No. of imaginary frequencies = 0

Total energy = −854.609 153

N	2.344 906	−0.775 454	−1.061 963
C	1.787 277	−0.867 611	1.345 301
H	0.719 970	−1.009 527	1.153 713
H	1.883 162	−0.314 115	2.285 457
C	2.477 063	−2.235 508	1.440 141
H	1.993 197	−2.847 819	2.208 746
H	3.520 641	−2.096 541	1.755 378
C	2.450 905	−2.946 824	0.080 266
H	2.994 678	−3.896 772	0.128 445
H	1.414 186	−3.172 668	−0.198 567
C	3.069 473	−2.052 196	−0.996 504
H	3.005 959	−2.528 617	−1.980 297
H	4.142 597	−1.908 281	−0.767 763
C	2.409 484	−0.031 697	0.210 311
H	3.454 712	0.184 661	0.491 845
H	2.744 854	−0.194 365	−1.795 439
C	1.785 261	1.324 667	0.049 893
N	0.473 948	1.662 041	−0.097 611
N	0.405 541	3.021 788	−0.189 321
N	1.615 432	3.461 954	−0.102 046
N	2.496 479	2.440 689	0.042 052

C	−0.735 181	0.900 354	−0.137 754
C	−1.848 756	1.378 238	0.551 078
C	−0.813 886	−0.283 659	−0.880 517
C	−3.051 906	0.674 343	0.509 756
H	−1.773 868	2.303 411	1.110 550
C	−2.006 095	−0.992 560	−0.907 167
H	0.069 702	−0.647 644	−1.395 307
C	−3.134 138	−0.519 830	−0.218 740
H	−3.906 557	1.062 064	1.049 581
H	−2.093 483	−1.916 403	−1.468 543
C	−5.432 882	−0.859 484	0.341 792
H	−6.191 718	−1.611 511	0.122 194
H	−5.288 593	−0.798 792	1.428 328
H	−5.771 838	0.115 647	−0.031 014
O	−4.251 433	−1.291 157	−0.320 277

Benzyl isocyanide

No. of imaginary frequencies = 0

Total energy = −439.038 58

C	0.733 872	−1.158 835	−0.000 074
C	−0.652 348	−1.010 897	−0.000 139
C	−1.215 554	0.272 401	−0.000 125
C	−0.378 741	1.400 558	−0.000 014
C	0.998 515	1.251 987	0.000 103
C	1.562 787	−0.034 034	0.000 082
H	1.179 452	−2.147 524	−0.000 128
H	−1.275 995	−1.895 917	−0.000 157
H	−0.837 284	2.383 183	0.000 064
H	1.649 878	2.118 929	0.000 256
N	2.938 731	−0.185 625	0.000 048
C	4.113 129	−0.312 269	0.000 008
C	−3.455 248	−0.563 298	0.000 289
H	−4.454 877	−0.127 321	0.000 395
H	−3.333 258	−1.187 660	−0.894 113
H	−3.332 822	−1.187 149	0.895 035
O	−2.550 584	0.533 644	−0.000 309

$Cp_2Zr(OH)Cl$

No. of imaginary frequencies = 0

Total energy = −970.431 956

Zr	−0.005 933	0.095 094	0.229 621
C	−1.703 633	−0.748 660	−1.485 564
C	−1.601 067	−1.759 486	−0.484 567
C	−2.312 212	0.386 103	−0.894 842
H	−1.384 306	−0.834 977	−2.515 630

C	−2.143 658	−1.240 047	0.717 673
H	−1.196 479	−2.752 724	−0.624 392
C	−2.568 234	0.090 021	0.469 133
H	−2.495 160	1.332 942	−1.381 760
H	−2.173 742	−1.743 804	1.673 779
H	−2.978 475	0.771 333	1.201 397
C	2.093 002	0.034 639	−1.261 280
C	2.564 866	0.278 949	0.061 667
C	1.541 278	−1.264 457	−1.296 064
H	2.123 112	0.740 705	−2.079 248
C	2.314 860	−0.877 909	0.833 847
H	3.014 993	1.199 158	0.407 370
C	1.650 569	−1.825 265	0.011 274
H	1.098 298	−1.746 343	−2.156 756
H	2.545 542	−1.010 277	1.882 331
H	1.327 950	−2.812 957	0.311 955
Cl	0.090 544	2.486 362	−0.378 871
O	−0.108 827	0.237 475	2.220 219
H	0.672 339	0.441 921	2.747 500

$TMSN_3$

No. of imaginary frequencies = 0

Total energy = −573.536 386

Si	0.663 505	−0.000 109	0.020 109
C	1.999 183	0.002 318	−1.293 089
H	1.920 871	−0.882 848	−1.931 929
H	1.917 474	0.887 309	−1.931 748
H	2.994 893	0.004 178	−0.836 627
C	0.718 297	1.544 763	1.093 397
H	0.670 082	2.452 012	0.482 976
H	−0.120 603	1.567 660	1.797 502
H	1.643 786	1.580 032	1.679 287
C	0.717 288	−1.549 392	1.087 067
H	−0.120 311	−1.573 321	1.792 696
H	0.665 990	−2.454 102	0.473 143
H	1.643 813	−1.588 912	1.671 035
N	−0.863 419	0.002 298	−0.904 471
N	−1.970 500	0.001 011	−0.379 029
N	−3.039 463	0.000 032	0.026 056

N_3^-

No. of imaginary frequencies = 0

Total energy = −164.379 062

N	1.169 683	−0.205 645	0.000 000
N	0.000 000	0.000 621	0.000 000

N	−1.169 683	0.205 024	0.000 000

H_2O
No. of imaginary frequencies = 0
Total energy = −76.448 012

O	0.000 000	0.000 000	0.119 179
H	0.000 000	−0.759 328	−0.476 717
H	0.000 000	0.759 328	−0.476 717

Me_3SiOH
No. of imaginary frequencies = 0
Total energy = −485.149 91

Si	−0.005 225	0.000 000	0.038 191
C	−1.765 508	−0.000 005	−0.610 009
H	−2.309 233	−0.884 665	−0.263 483
H	−2.309 260	0.884 608	−0.263 405
H	−1.784 374	0.000 043	−1.705 431
C	0.918 670	−1.538 012	−0.543 009
H	0.988 149	−1.560 671	−1.636 806
H	1.941 606	−1.574 560	−0.150 906
H	0.404 342	−2.449 723	−0.221 422
C	0.918 663	1.538 015	−0.543 011
H	0.404 322	2.449 724	−0.221 442
H	1.941 590	1.574 575	−0.150 887
H	0.988 166	1.560 666	−1.636 807
O	−0.160 471	0.000 004	1.709 862
H	0.660 666	−0.000 016	2.213 185

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