

Supporting Information

An unprecedented chelation-controlled Yb(OTf)₃ catalyzed aminolysis and azidolysis of cyclitol epoxides

Pedro Serrano,^{a,b} Amadeu Llebaria,^b and Antonio Delgado^{a,b*}

a Universitat de Barcelona, Facultat de Farmàcia, Unitat de Química Farmacèutica (Unidad Asociada al CSIC), Avgda. Joan XXIII, s/n, 08028 Barcelona, Spain.

*Corresponding author; email: adelgado@far.ub.es

fax: int+34-932045904

b RUBAM, Departament de Química Orgànica Biològica, Institut d'Investigacions Químiques i Ambientals de Barcelona (IIQAB-CSIC)
Jordi Girona 18-26, 08034 Barcelona, Spain.

General experimental methods, spectral data and copies of ¹³C NMR spectra for compounds **1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1j, 2b, 6, 8, 10, 11a and 12b**.

General methods: Solvents were distilled prior to use and dried by standard methods.¹ Melting points are uncorrected. FT-IR spectra are reported in cm⁻¹. ¹H and ¹³C NMR spectra were obtained in CDCl₃ solutions at 300 MHz (for ¹H) and 75 MHz (for ¹³C), respectively, unless otherwise indicated. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the singlet at 7.24 ppm of CDCl₃ for ¹H and in ppm relative to the center line of a triplet at 77.0 ppm of CDCl₃ for ¹³C. Electrospray mass spectra in negative mode were obtained by HPLC-MS, using a mixture of 10 mM ammonium formate/acetonitrile (25/75) at 0.5 mL/min as mobile phase. Samples were analyzed by FIA (flow inject analysis).

1a (single isomer): IR (film): 3350 (br), 2109. ¹H NMR (200 MHz): 2.78 (br, 1H), 3.46 (m, 5H), 3.67-3.99 (m, 6H), 7.20-7.35 (m, 15H); ¹³CNMR (50 MHz, C₆D₆): 53.5, 65.9, 73.0, 75.7, 82.4, 82.9, 127.8-128.7, 138.1.

1b (single isomer): IR (film): 2920, 1499, 1451. ¹³C NMR: 13.9, 20.3, 32.7, 44.5, 61.4, 71.3, 75.4, 75.7, 82.8, 84.3, 127.7, 127.8, 128.0, 128.4, 128.5, 138.5; ¹HNMR: 0.90 (t, J=J'= 7.5 Hz, 3H), 1.26-1.47 (m, 4H), 2.41 (t, 2H, J=9.4 Hz), 2.69 (t, 2H, J=6.9 Hz), 3.40-3.59 (m, 4H), 4.81-4.94 (m, 6H), 7.25-7.38 (m, 15H). MS, 506 (M+1).

1c (major isomer): IR (film): 2960, 2910, 1454, 1361. ¹³C NMR: 23.8, 40.1, 59.5, 74.0, 75.4, 75.7, 82.9, 84.2, 127.5, 127.7, 127.8, 127.9, 128.4, 128.5, 138.5.

¹HNMR: 1.1 (m, 6H), 2.42 (t, 1H, J=10.1 Hz), 3.25-3.34 (m, 3H), 3.41-3.59 (m, 3H), 3.40-3.59 (m, 4H), 4.80-4.94 (m, 6H), 7.25-7.38 (m, 15H). MS, 492 (M+1).

1d (major isomer): IR (film): 2960, 2920, 1453, 1362. ¹³C NMR 30.9, 50.9, 56.9, 73.9, 75.3, 75.5, 83.1, 84.2, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4, 138.5. ¹HNMR: 1.75 (s, 9H), 2.48 (t, 1H, J=10 Hz), 3.16 (t, 2H, J=9.5 Hz), 3.46 (t, 2H, J=9.1 Hz), 3.59 (t, 1H, J= 9 Hz), 4.83-4.94 (m, 6H), 7.23-7.39 (m, 15H). MS, 506 (M+1).

¹ Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Third Edition; Pergamon Press: Oxford, 1988

1e (major isomer): IR (film): 3400, 2923, 1496, 1454. ^{13}C NMR: 36.9, 46.1, 61.4, 71.5, 75.3, 75.7, 82.8, 84.2, 126.1, 127.8, 127.9, 128.2, 128.4, 128.4, 138.3, 138.5, 139.7. ^1H NMR: 2.41 (m, 1H), 2.75-2.80 (m, 3H), 2.99 (t, 2H, $J=7.2$ Hz), 3.40-3.43 (m, 4H), 4.79-4.94 (m, 6H), 7.20-7.39 (m, 20H). MS, 554 (M+1).

1f (single isomer): IR (film): 3437, 2927, 1453. ^{13}C NMR: 24.9, 34.7, 54.6, 59.4, 73.8, 75.4, 75.8, 82.9, 84.3, 127.7, 127.8, 127.9, 128.4, 128.5, 138.5. ^1H NMR: 1.01-1.29 (m, 6H), 1.56-1.62 (m, 1H), 1.67-1.75 (m, 2H), 1.85-1.91 (m, 2H), 2.46 (t, 1H, $J=10$ Hz), 2.76-2.85 (m, 1H), 3.30 (t, 2H, $J=9$ Hz), 3.44 (t, 2H, $J=9.1$ Hz), 3.55 (t, 1H, $J=9$ Hz), 4.81-4.94 (m, 6H), 7.25-7.38 (m, 15H). MS, 532 (M+1).

1g (major isomer): IR (film): 3390, 2922, 1602, 1498. ^{13}C NMR: 60.8, 74.2, 75.5, 75.7, 82.6, 83.6, 115.2, 119.4, 127.8, 127.9, 128.4, 128.5, 129.2, 138.3, 148.0. ^1H NMR: 3.28 (t, 1H, $J=9.6$ Hz), 3.43-3.59 (m, 5H), 4.82-4.96 (m, 6H), 6.79-6.95 (m, 3H), 7.18-7.39 (m, 17H). MS, 526 (M+1).

1h (single isomer): IR(film): 3418, 1605, 1492. ^{13}C NMR: 15.1, 63.8, 70.37, 75.3, 75.5, 82.8, 84.5, 127.6, 127.7, 127.9, 128.3, 138.4, 138.5. ^1H NMR: 1.09 (t, $J=J'=7.5$ Hz, 6H), 2.57 (t, 1H, $J=J'=9.2$ Hz), 2.76 (m, 4H), 3.48 (m, 5H), 4.83-4.98 (m, 10H), 7.24-7.40 (m, 25H). MS, 506 (M+1).

1j (major isomer): IR (film): 3390, 2912, 2873, 1454, 1355. ^{13}C NMR: 23.6, 48.1, 62.4, 70.4, 75.3, 75.7, 82.8, 84.6, 127.6, 127.7, 127.9, 128.4, 128.5, 138.5. ^1H NMR: 1.74-1.79 (m, 4H), 2.66 (t, 1H, $J=10.2$ Hz), 2.87-2.92 (m, 5H), 3.42-3.61 (m, 4H), 4.82-4.94 (m, 6H), 7.25-7.38 (m, 15H). MS, 504 (M+1).

2b: IR (film): 3418, 3062, 3028, 1669, 1492. ^{13}C NMR: 13.9, 20.3, 32.8, 45.9, 61.6, 71.7, 75.1, 75.7, 75.8, 80.3, 83.0, 84.0, 85.0, 85.5, 125.6-128.5, 138.1-138.3. ^1H NMR: 0.89 (t, $J=J'=8.5$ Hz, 3H), 1.21-1.42 (m, 4H), 2.4-2.8 (m, 3H), 3.20-3.45 (m, 5H), 4.80-5.02 (m, 8H), 7.26-7.34 (m, 20H). Ms, 596 (M+1). $[\alpha]_D +7.4$ (c , 1.5, CHCl_3).

Epoxide 6: IR(film): 3041, 3028, 1512, 1457. ^{13}C NMR: 53.9, 55.2, 73.1, 73.3, 75.5, 75.9, 79.0, 79.2, 79.3, 83.4, 127.6-128.5, 137.6-138.5. ^1H NMR: 3.21 (d, $J=3.8$ Hz, 1H), 3.33 (m, 1H), 3.47 (A

of an AB, J=10.4 Hz, J'=7.6 Hz, 1H), 3.63 (B of an AB, J=10.4 Hz, J'=8.4 Hz), 3.85-3.93 (m, 2H), 4.68-4.86 (m, 10H). $[\alpha]_D + 31.5$ (c 2.8, CDCl_3)

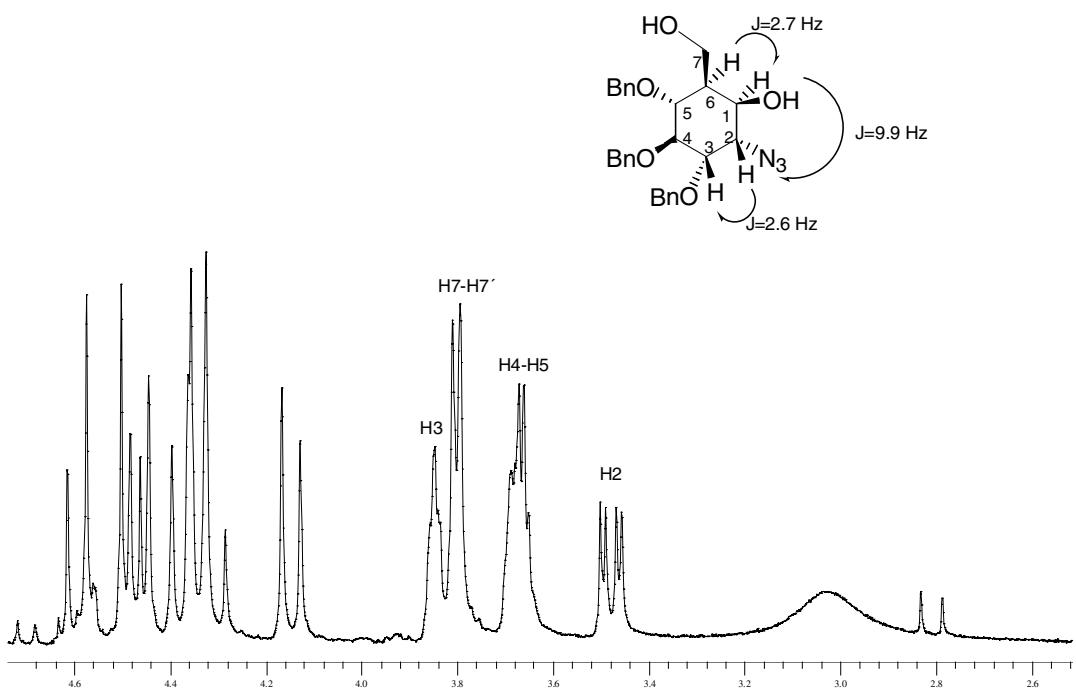
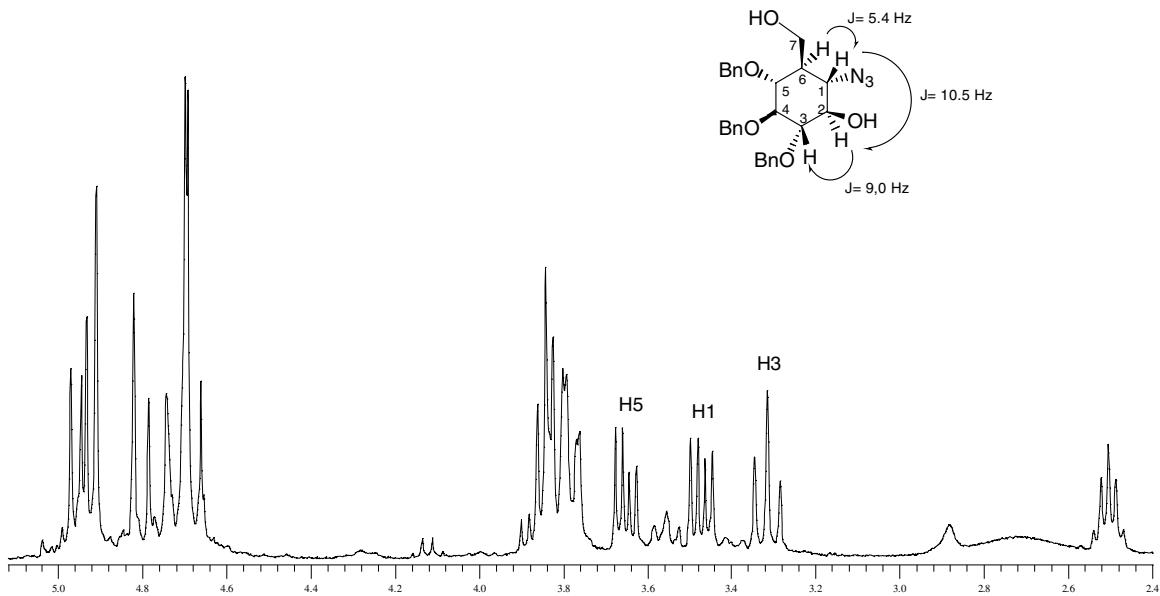
Epoxide 8: IR(film): 3034, 3003, 2910, 1496. ^{13}C NMR: 38.3, 53.9, 56.7, 67.3, 72.9, 73.9, 75.0, 75.9, 79.8, 80.7, 127-129, 138-149. ^1H NMR: 2.88 (m, 1H), 3.21(d, J= 5.4 Hz, 1H), 3.45(m, 1H), 3.65 (dd, J=8.1 Hz, J'=5.4 Hz, 1H), 3.73-3.90 (m, 4H), 4.55-4.88 (m, 8H), 7.2-7.4 (m, 15H). $[\alpha]_D + 31.5$ (c 2.8, CHCl_3).

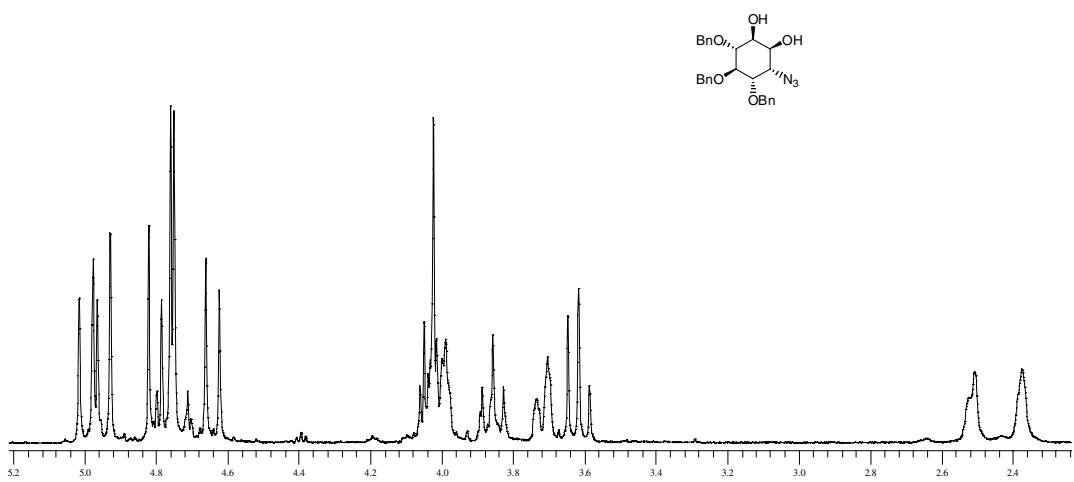
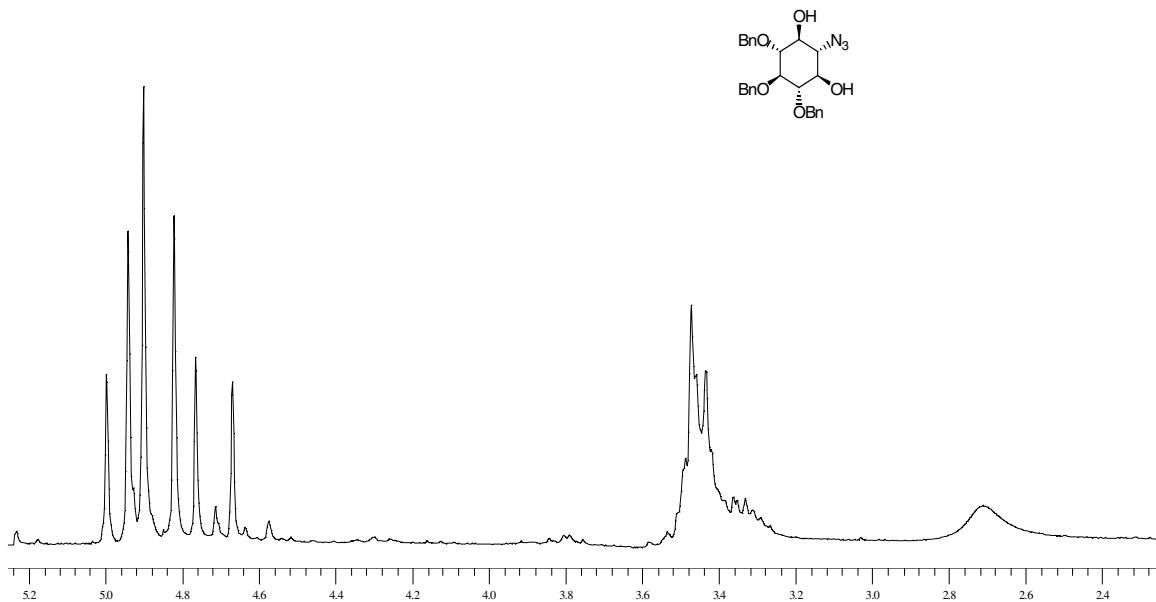
9: IR (film): 3590, 3323, 3033, 1942, 1872. ^{13}C NMR: 13.8, 30.9, 31.6, 36.85, 47.8, 60.5, 60.8, 70.6, 72.4, 75.5, 77.2, 80.3, 81.7, 83.7, 127.7-128.7, 137.8-138.3. ^1H NMR: 1.15-1.45 (m, 7H), 2.55-2.94 (m, 3H), 3.35 (t, 2H, J=J'= 9.2 Hz), 3.52-4.1 (m, 4H), 3.84 (t, 1H, J=J'=9.2 Hz), 3.96 (A of an AXY, 1H, J= 9.2 Hz, J'=3.2 Hz), 4.61-5.05 (m, 6H), 7.25-7.39 (m, 15H). $[\alpha]_D - 10.4$ (c, 1.35, CHCl_3).

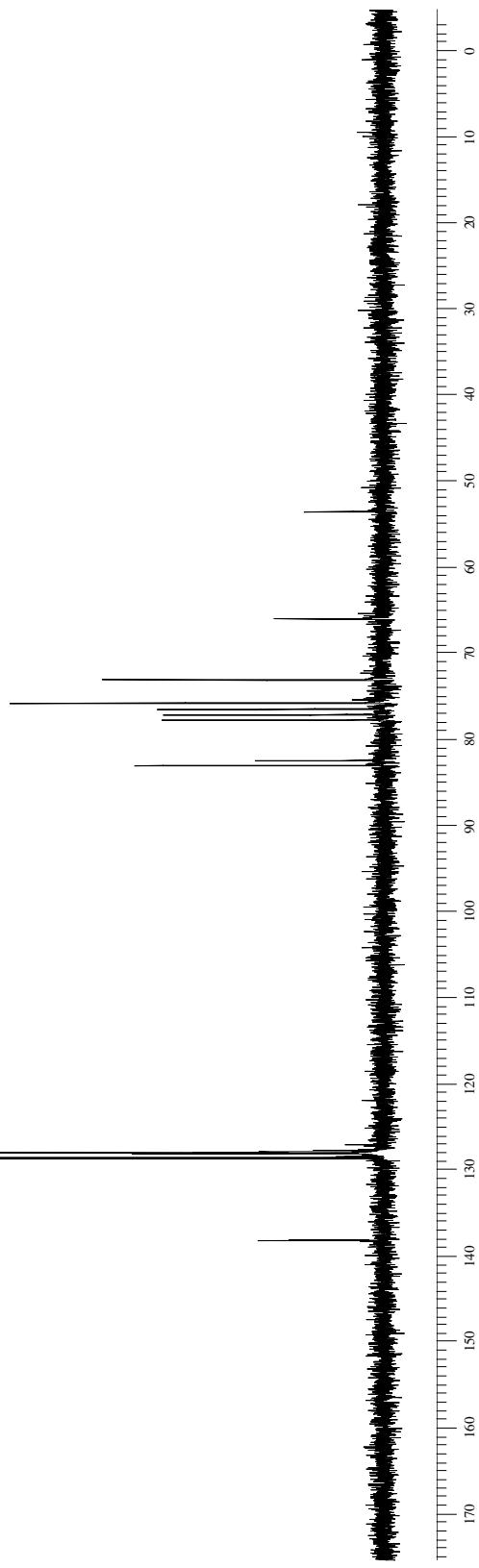
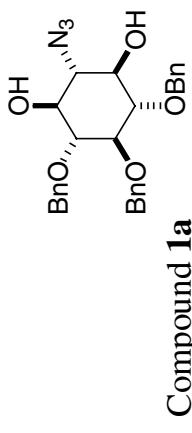
10: IR (film): 3444, 2910, 2106, 1878, 1813, 1732. ^{13}C NMR: 41.8, 58.4, 62.2, 73.3, 73.1, 75.4, 75.5, 80.2, 81.7, 83.7, 127-130, 137-139. ^1H NMR: 2.50 (m, 1H), 3.31(t, J=J'= 9Hz, 1H), 3.45 (dd, J=9 Hz, J'= 10.5 Hz, 1H), 3.65 (dd, J=9.9 Hz, J'=5.4 Hz, 1H), 3.75-3.90 (m, 4H), 4.6-5.0 (m, 6H), 7.2-7.4 (m, 15H).

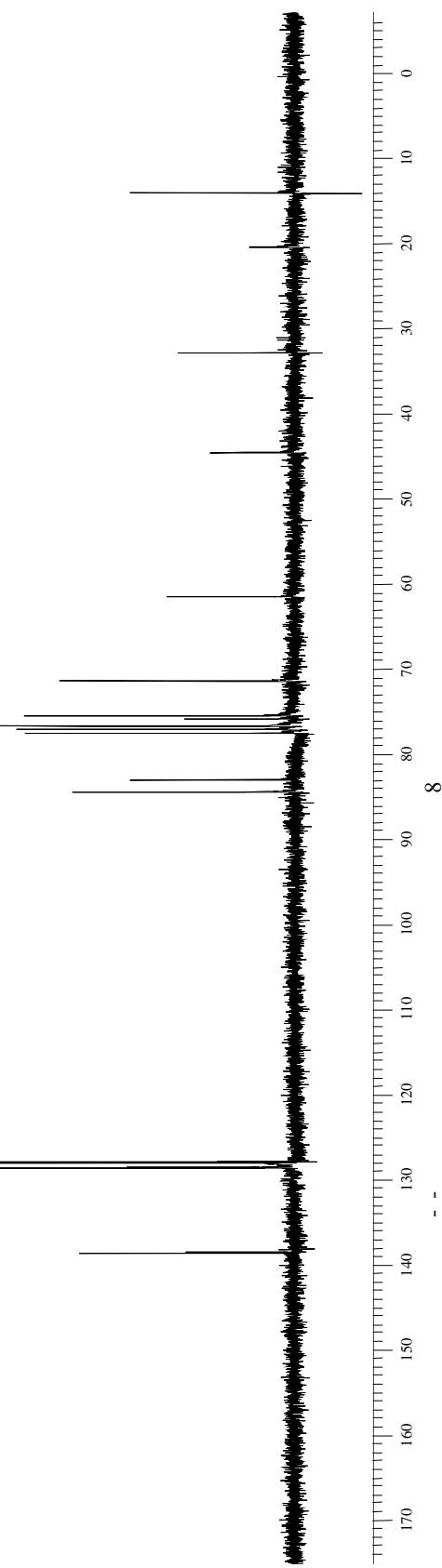
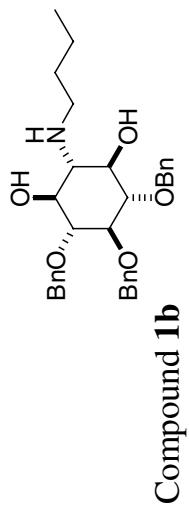
(±)-11a: ^{13}C NMR: 19.1, 21.5, 23.7, 37.0, 52.3, 53.6, 64.9. ^1H NMR: 1.05-1.45 (m, 3H), 1.45-1.52 (m, 1H), 1.75-1.85 (m, 2H), 1.95-2.10 (m, 1H), 3.17 (A of an ABXY, J=4.0 Hz, J'=J''=1,5 Hz, 1H), 3.22 (A of an ABX, J=4.0 Hz, J'= 2.4 Hz, 1H), 3.59 (A of an ABX, J=10.5 Hz, J'=6.0 Hz, 1H), 3.69 (B of an ABX, J=10.5 Hz, J'=7.5 Hz, 1H).

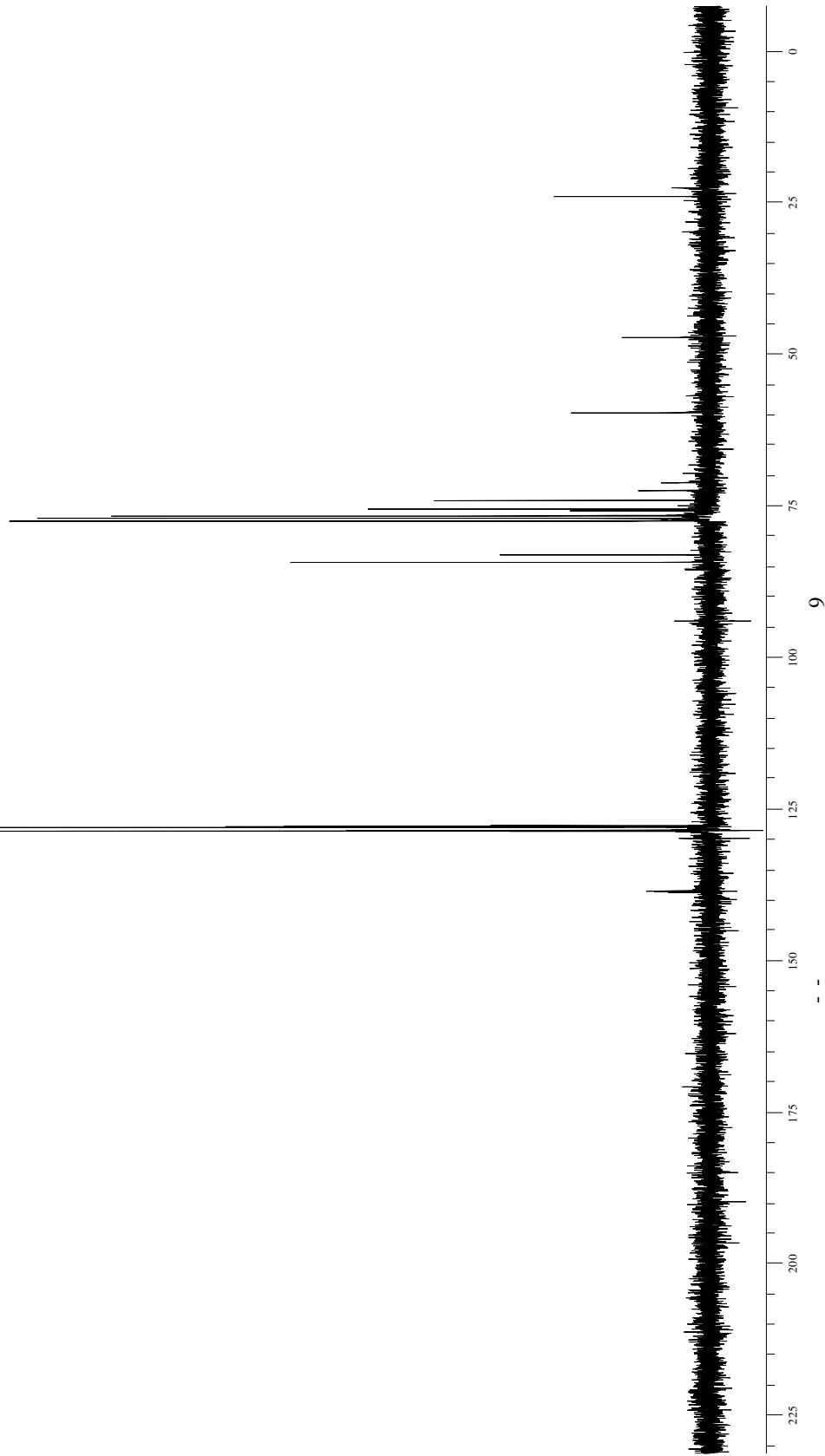
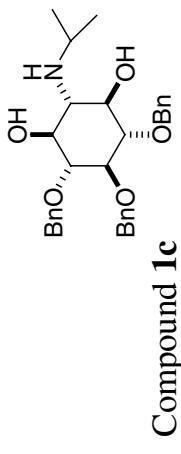
(±)-12b: ^{13}C NMR (50,3 MHz): 13.9, 20.1, 20.5, 25.6, 28.9, 32.6, 38.1, 46.9, 58.3, 71.1, 73.3, 74.3, 127.5, 127.6, 128.4. ^1H NMR (200 MHz): 0.95 (t, J=J'=8.5 Hz, 3H), 1.05-1.20 (m, 1H), 1.20-1.50 (m, 8H), 1.60-1.80 (m, 1H), 1.80-2.0 (m, 1H), 2.15-2.30 (m, 1H), 2.35-2.50 (m, 2H), 2.50-2.75 (m, 1H), 3.40-3.45 (m, 2H), 3.65 (m, 1H), 4.45 (s, 2H), 7.25 (m, 5H).

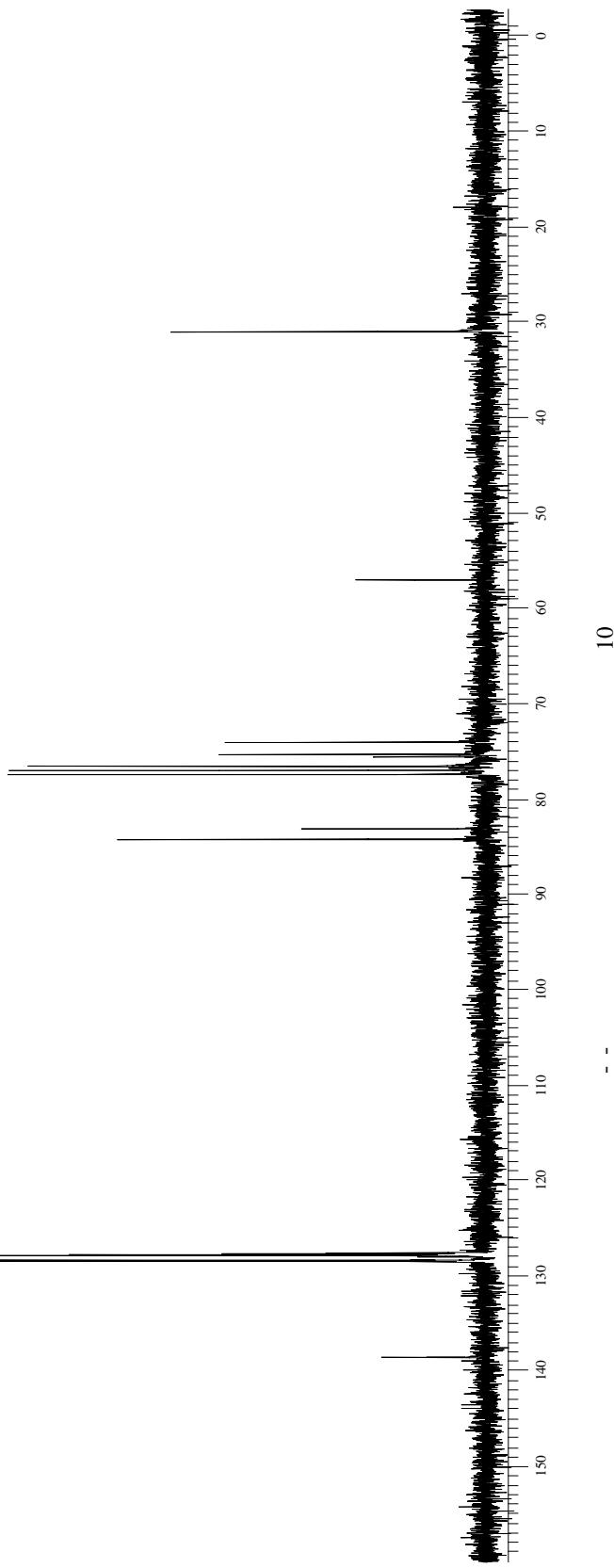
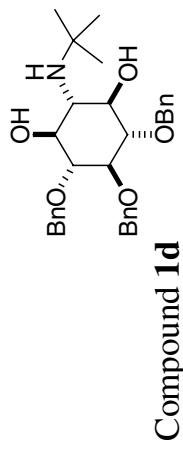


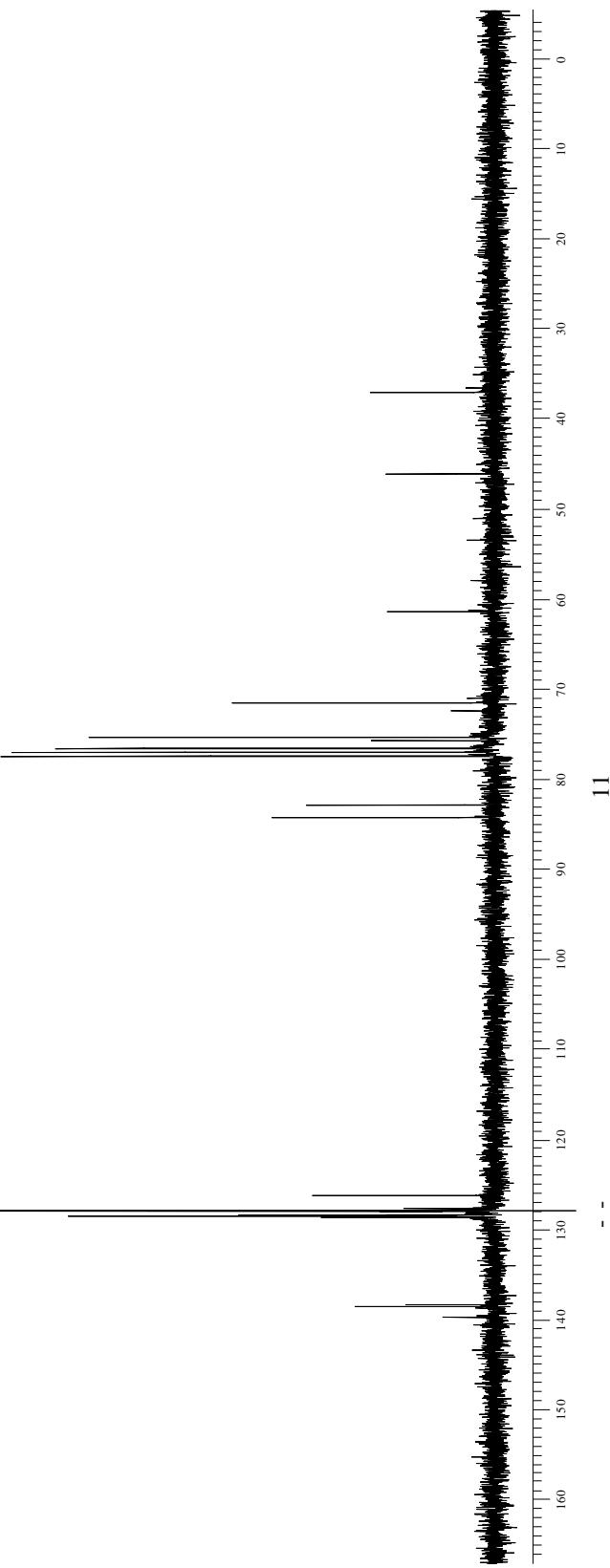
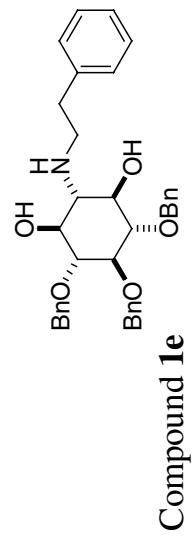


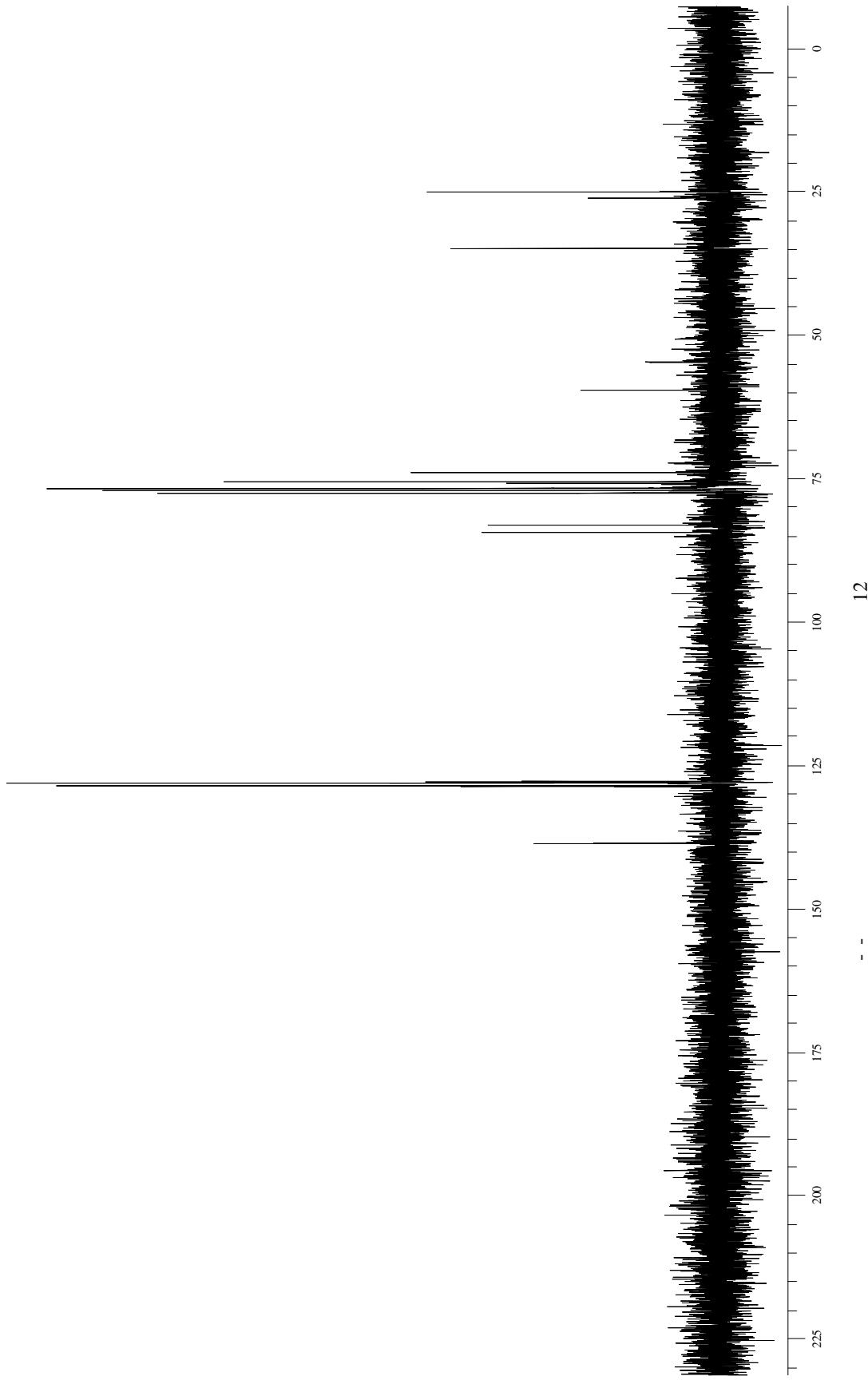
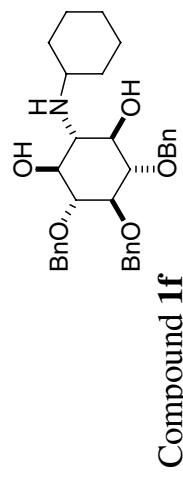


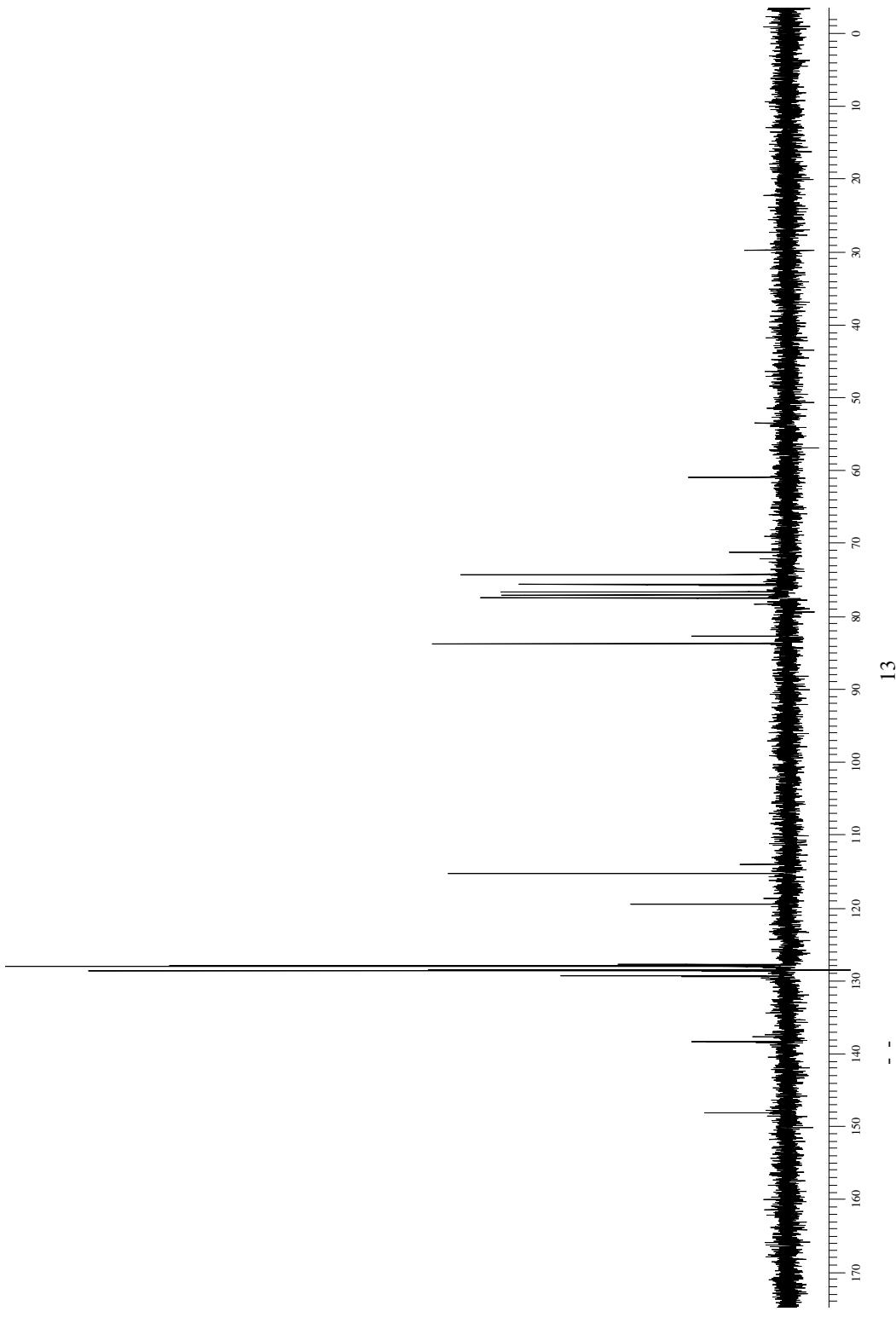
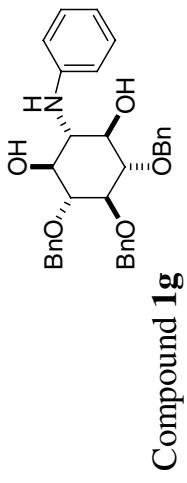


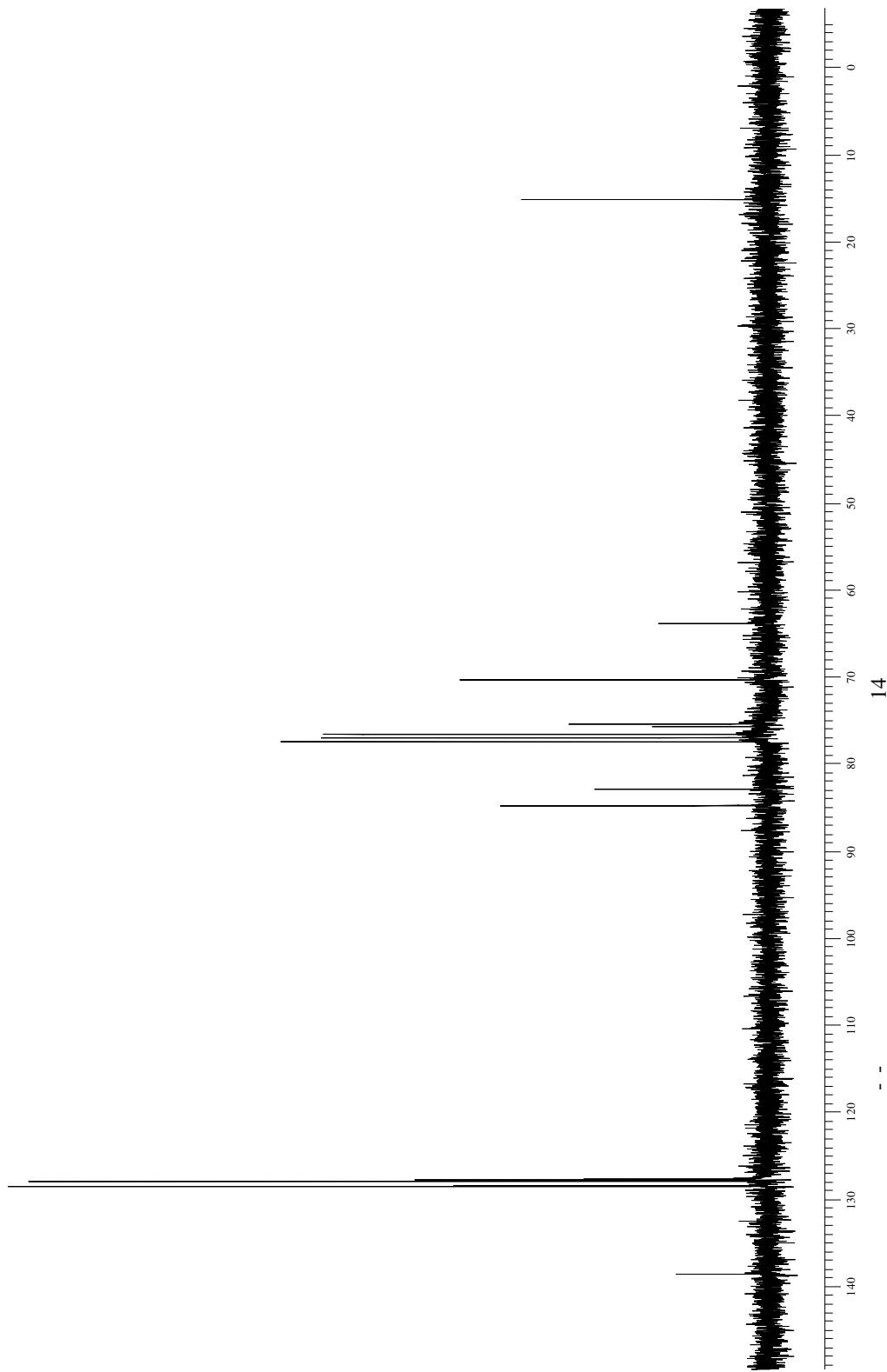
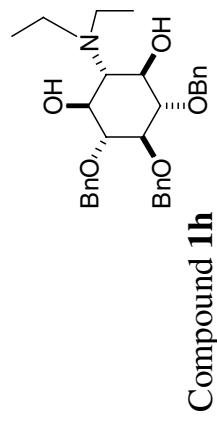


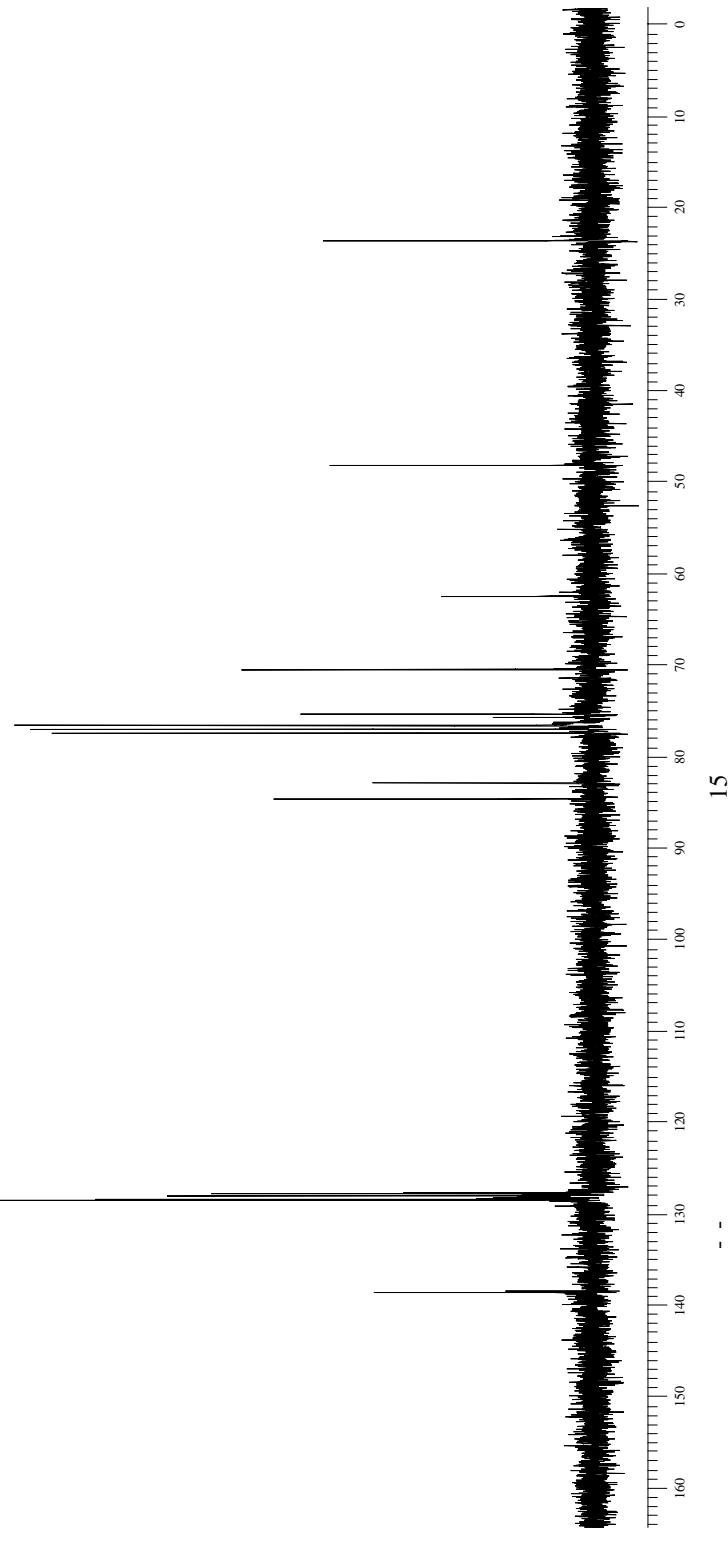
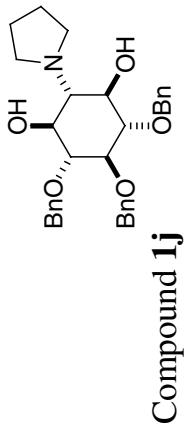


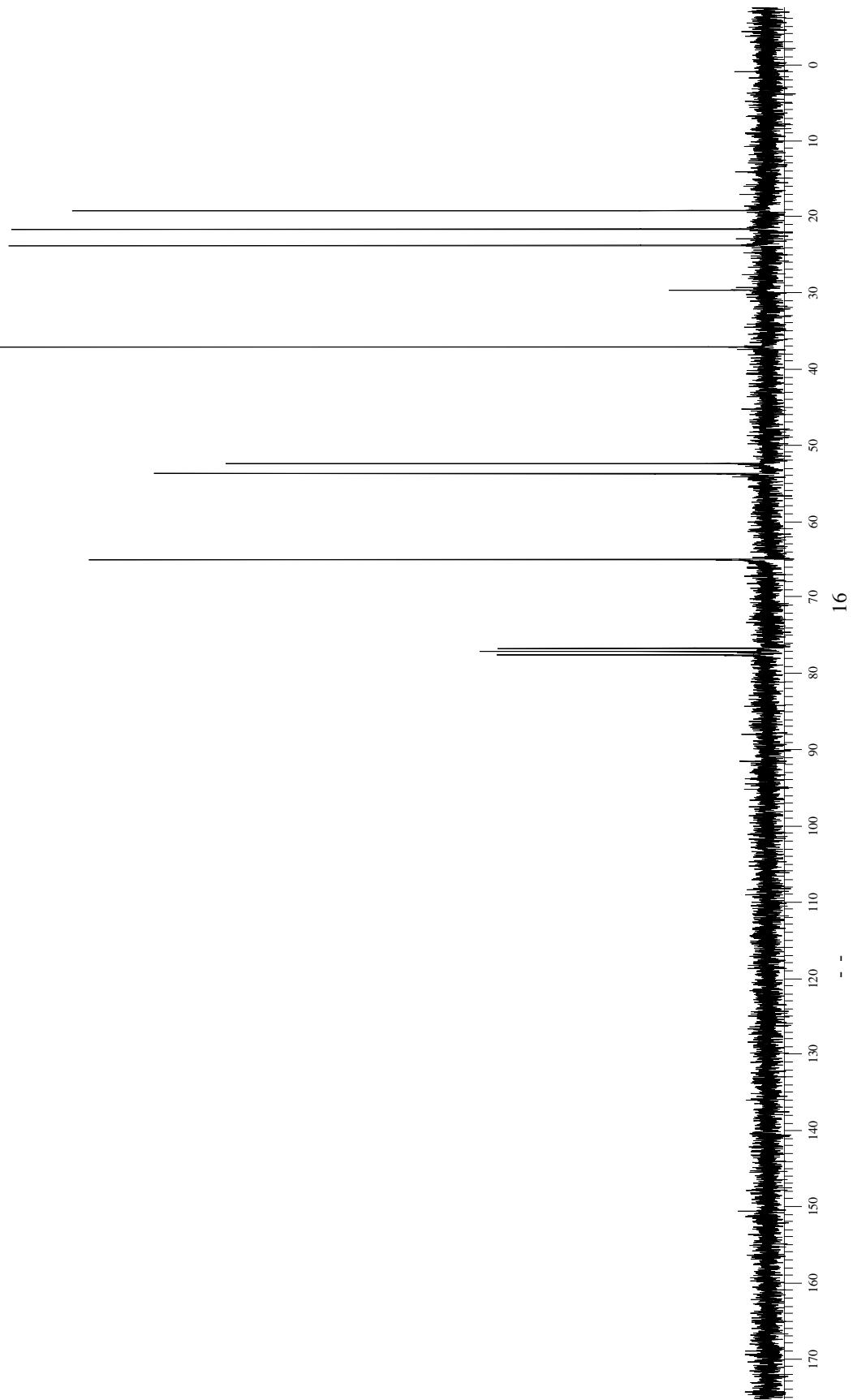
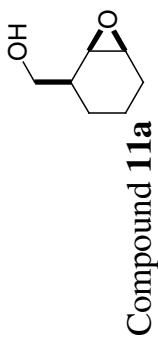




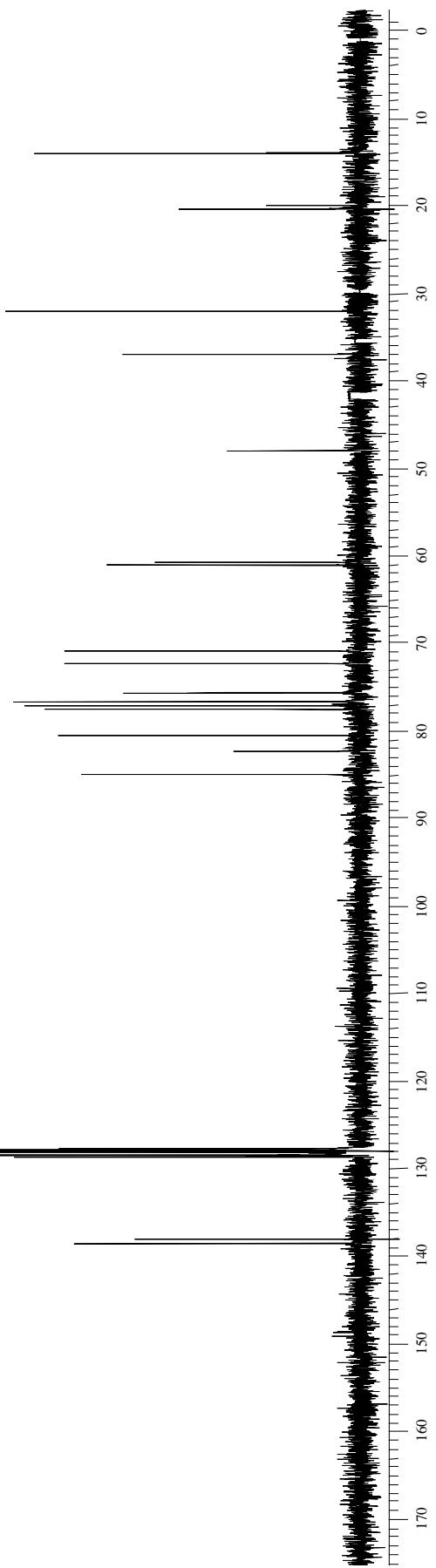
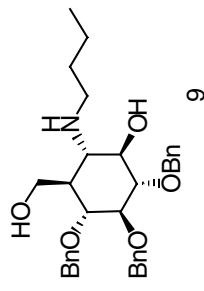




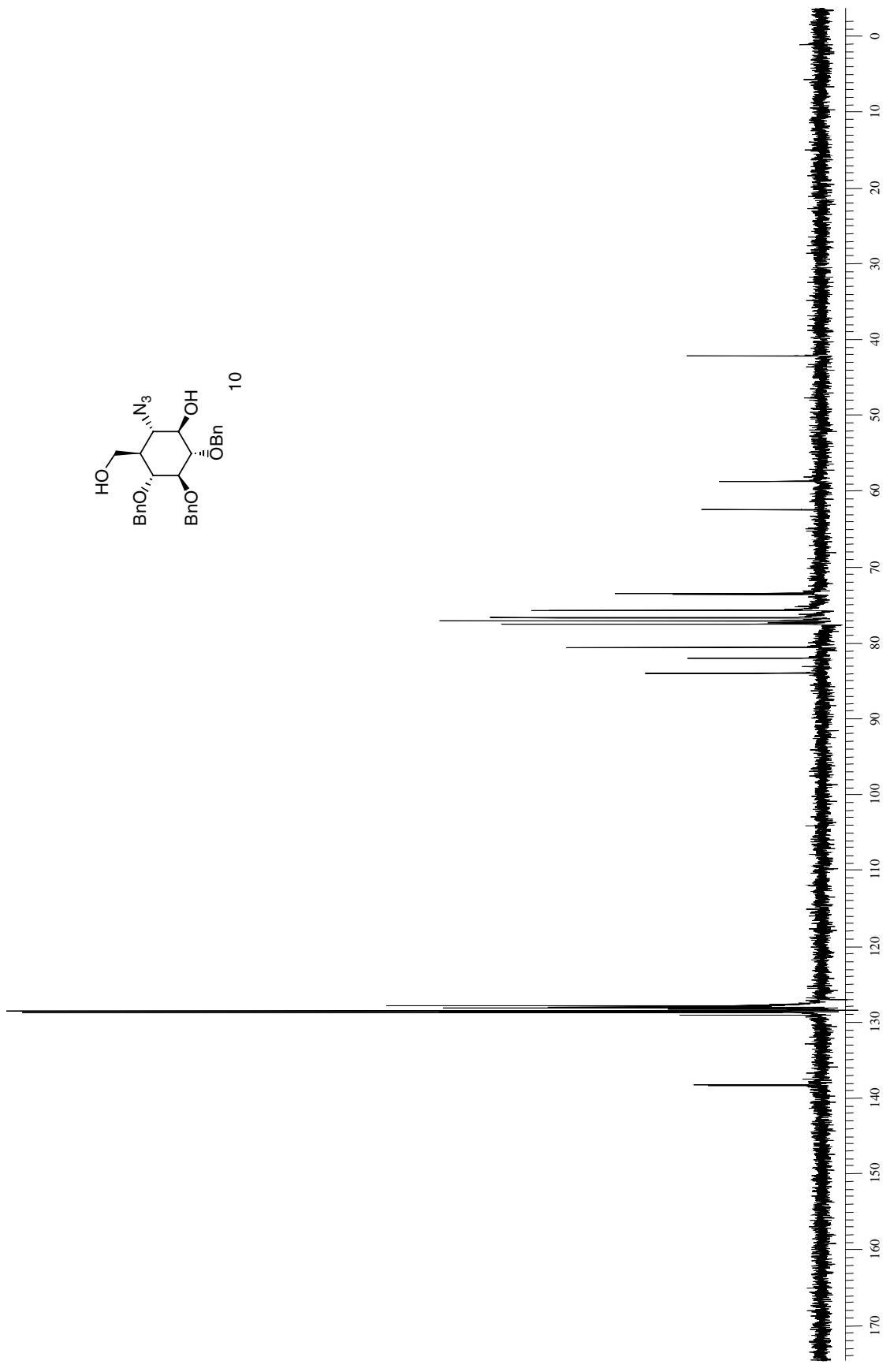
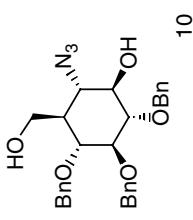




Compound 9

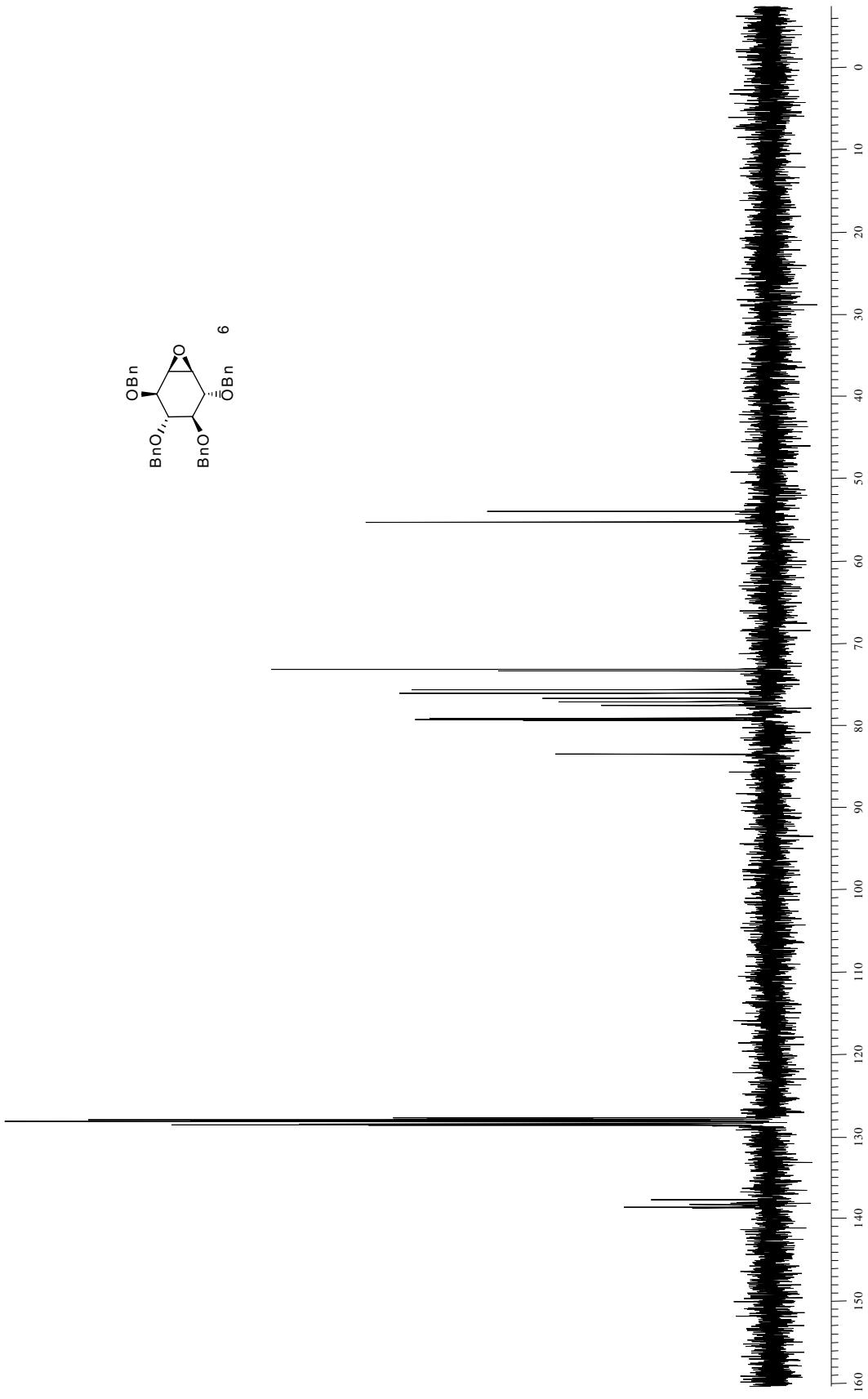
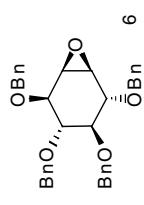


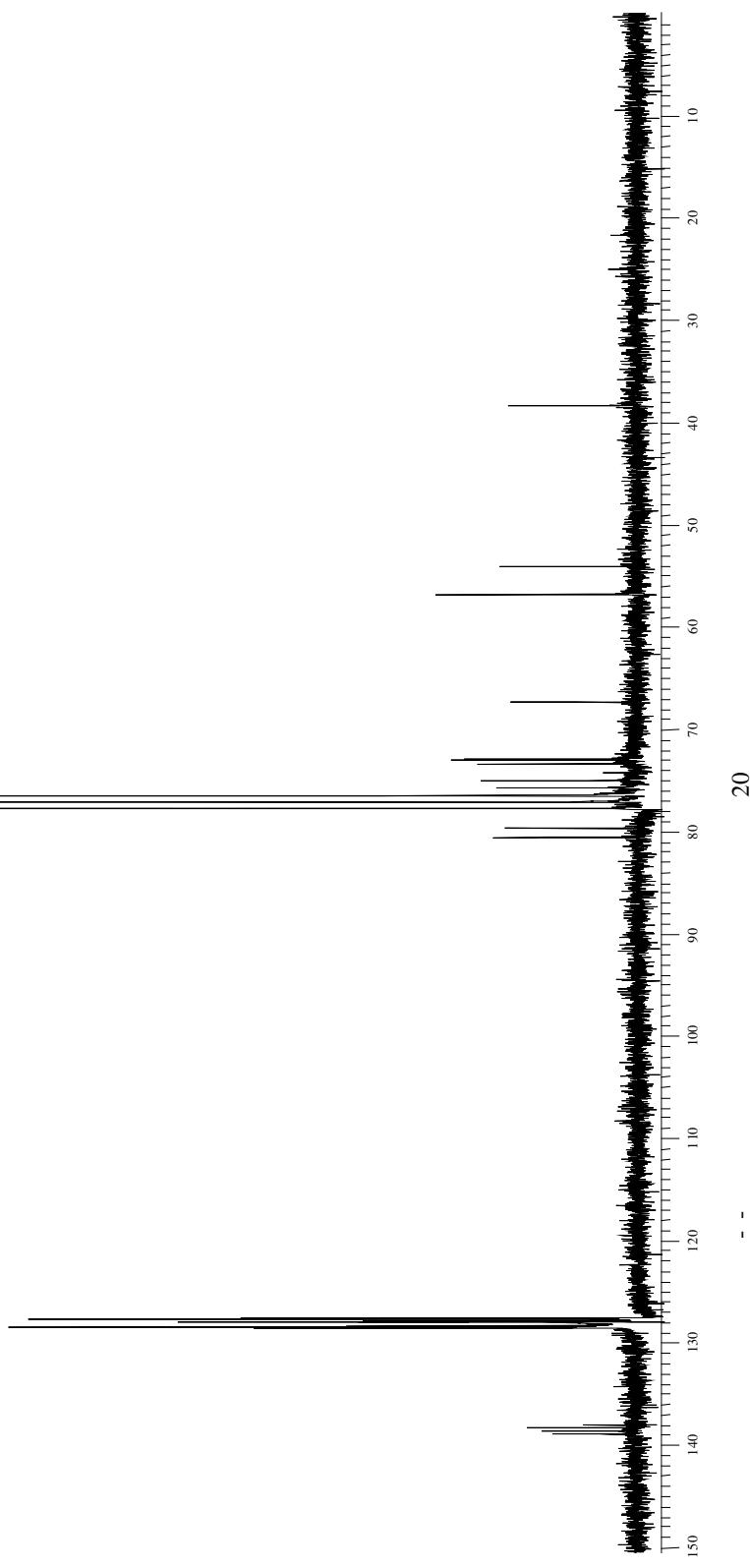
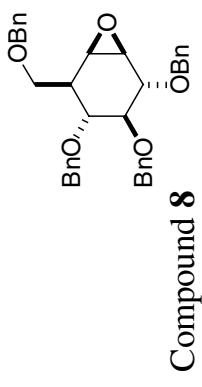
Compound 10



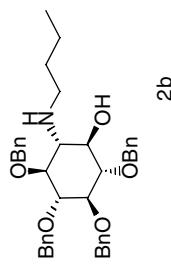
18

Compound 6

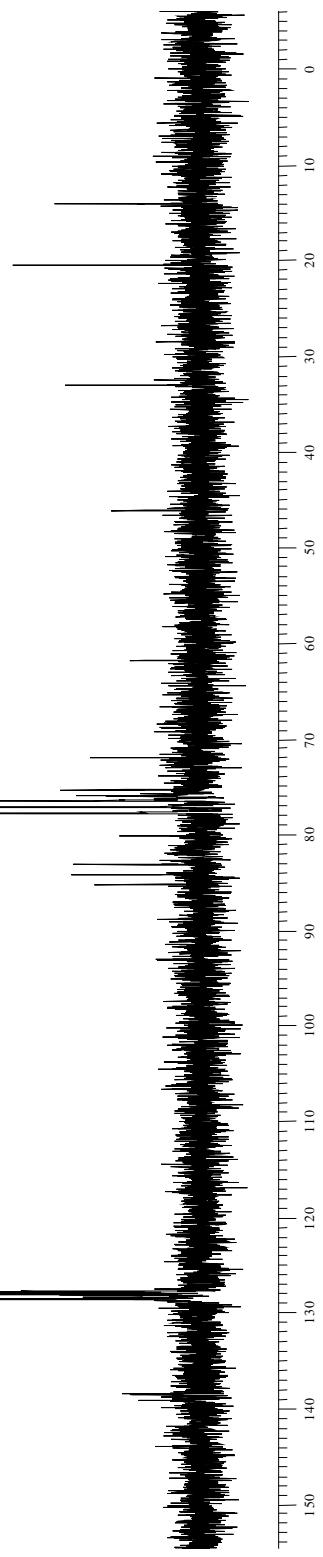


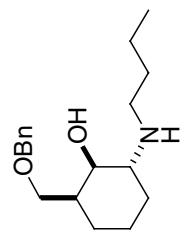


Compound 2b



2b





Compound 12b (\pm)-12b

