Vinyl Sulfone Modified- Azidofuranoside Building-Blocks: 1,4-/1,5-Disubstituted-1,2,3-Triazole Linked Trisaccharides via an Aqueous / Ionic-Liquid Route and "Click" Chemistry

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Experimental Section

General methods: All reactions were conducted under nitrogen atmosphere. Melting points were determined in open-end capillary tubes and uncorrected. Carbohydrates and other fine chemicals were obtained from commercial suppliers and are used without purification. Solvents were dried and distilled following the standard procedures. TLC was carried out on pre-coated silica gel plates and the spots were visualized with UV light or by charring the plates dipped in 5% H_2SO4-MeOH solution or in 5% H_2SO4-vaniline-EtOH solution. Column chromatography was performed on silica gel (230-400 mesh). ^1H and ^{13}C NMR for compounds were recorded at 200/400 MHz instrument using $CDCl_3$ and D_2O as the solvent. DEPT experiments have been carried out to identify the methylene carbons. Optical rotations were recorded at 589nm. High Resolution Mass Spectra (HRMS) were recorded on an Electrospray-Ionisation Mass Spectrometer.

Compound 13: To a well stirred solution of the known epoxide **12**[1] (1.00 g, 3.90 mmol) in DMF (15 mL) was added sodium azide (0.76 g, 11.72 mmol) and ammonium chloride (0.10 g, 1.95 mmol). The mixture was heated at 90 °C with stirring under N_2. After 16 h the reaction mixture was cooled, poured into an aqueous saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 X 10 mL). The combined organic layer was dried over anhyd Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified over silica gel to afford the azido alcohol derivative **13** (1.05 g, 90 %). Eluent: EtOAc/petroleum ether (1:4). Yellow oil. $[\alpha]^{25.2}_D$ (+): 40.4 (*c* 0.72, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.40-1.68 (m, 10H), 3.38 (s, 3H), 3.75-3.82 (m, 2H), 3.92-4.03 (m, 1H), 4.12-4.21 (m, 2H), 4.30-4.39 (m, 1H), 4.88 (s, 1H). ^{13}C

NMR (50 MHz, $CDCl_3$): δ 23.5 (CH_2), 23.7 (CH_2), 24.9 (CH_2), 34.1 (CH_2), 35.8 (CH_2), 54.7, 66.2 (CH_2), 67.6, 75.4, 79.8, 83.1, 108.7, 110.6. HRMS [ES^+, $(M+Na)^+$]: for $C_{13}H_{21}N_3O_5Na$ found 322.1370, calcd 322.1379.

Compound 20a: Following the procedure described for the preparation of **10**, over 16 h compound **19**[1] (2.00 g, 7.81 mmol) was converted to **20a** (0.23 g, 10 %). Eluent: EtOAc/petroleum ether (1:4). Yellow oil. $[\alpha]^{25.2}_D$ (-): 119.2 (*c* 0.92, $CHCl_3$). ^1H NMR (200 MHz, CDCl3): δ 1.37-1.64 (m, 11H), 3.38 (s, 3H), 3.96-4.03 (m, 2H), 4.10-4.19 (m, 2H), 4.24-4.39 (m, 2H), 4.86 (s, 1H). ^{13}C NMR (50 MHz, CDCl3): δ 23.9 (CH_2), 24.1 (CH_2), 25.1 (CH_2), 34.8 (CH_2), 36.6 (CH_2), 55.6, 70.0 (CH_2), 70.4, 73.6, 74.9, 83.5, 107.1, 110.2. HRMS [ES+, (M+Na)+]: for $C_{13}H_{21}N_3O_5Na$ found 322.1382, calcd 322.1379.

Compound 20b: Following the procedure described for the preparation of **10**, over 16 h compound **19**[1] (2.00 g, 7.81 mmol) was converted to **20b** (1.86 g, 80 %). Eluent: EtOAc/petroleum ether (1:4). Yellow oil. $[\alpha]^{25.2}_D$ (-): 42.8 (*c* 0.82, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.58-1.67 (m, 10H), 3.42 (s, 3H), 3.66-3.76 (m, 1H), 3.87-4.06 (m, 5H), 4.09-4.16 (m, 1H), 4.76 (d, 1H, $J = 4.2$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.7 (CH_2), 23.8 (CH_2), 25.0 (CH_2), 34.6 (CH_2), 36.3 (CH_2), 55.0, 66.8 (CH_2), 68.6, 76.8, 77.3, 81.7, 101.9, 110.4. HRMS [ES^+, $(M+Na)^+$]: for $C_{13}H_{21}N_3O_5Na$ found 322.1398, calcd 322.1379.

Compound 14: To a well-stirred solution of the azido alcohol derivative **13** (1.00 g, 3.34 mmol) in DMF (20 mL) was added sodium hydride (0.21 g, 4.34 mmol) at 0 °C. After 30 minutes benzyl bromide (0.60 mL, 5.01 mmol) was added to the reaction mixture and the mixture was stirred at ambient temperature under N_2 for 6 h After completion of the reaction (TLC), the reaction mixture was poured into an aqueous saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 X 10 mL). The combined organic layer was dried over anhyd Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford the benzyl derivative **14** (1.17 g, 90 %). Eluent: EtOAc/petroleum ether (1:19). Yellow oil. $[\alpha]^{25.2}_D$ (+): 62.8 (*c* 0.82, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.40-1.67 (m, 10H), 3.34 (s, 3H), 3.84-3.97 (m, 4H), 4.08-4.15 (m, 2H), 4.53-4.66 (m, 2H), 4.90 (s, 1H), 7.27-7.38 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.8 (CH_2), 24.0 (CH_2), 25.2 (CH_2), 34.7 (CH_2), 36.4 (CH_2), 54.9, 67.0 (CH_2), 67.3, 72.2 (CH_2), 76.1, 82.6, 88.2, 107.0, 110.5, 127.9, 128.1, 128.6, 137.1. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{27}N_3O_5Na$ found 412.1841, calcd 412.1848.

Compound 21a: Following the procedure described for the preparation of **14**, over 6 h compound **20a** (0.20 g, 0.67 mmol) was converted to **21a** (0.23 g, 90 %). Eluent: EtOAc/petroleum ether (1:19). Yellowish oil. $[\alpha]^{25.2}_D$ (-): 112.7 (*c* 0.90, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.40-1.64 (m, 10H), 3.39 (s, 3H), 3.93-4.22 (m, 5H), 4.36-4.46 (m, 1H), 4.67 (s, 2H), 4.77 (d, 1H, *J* = 1.8 Hz), 7.26-7.40 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.8 (CH_2), 24.1 (CH_2), 25.2 (CH_2), 34.9 (CH_2), 36.4 (CH_2), 55.9, 66.7

(CH_2), 69.4, 72.6 (CH_2), 73.2, 81.2, 82.2, 107.3, 109.7, 127.9, 128.4, 137.4. HRMS [ES+, (M+Na)+]: for $C_{20}H_{27}N_3O_5Na$ found 412.1866, calcd 412.1848.

Compound 21b: Following the procedure described for the preparation of **14**, over 5 h compound **20b** (1.00 g, 3.34 mmol) was converted to **21b** (1.17 g, 90 %). Eluent: EtOAc/petroleum ether (1:19). Yellow oil. $[\alpha]^{25.2}_D$ (-): 58.8 (*c* 1.0, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.39-1.65 (m, 10H), 3.31 (s, 3H), 3.65-3.79 (m, 2H), 3.87-3.93 (m, 1H), 3.96-4.22 (m, 3H), 4.58-4.75 (m, 3H), 7.26-7.39 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.8 (CH_2), 23.9 (CH_2), 25.1 (CH_2), 34.6 (CH_2), 36.4 (CH_2), 54.9, 66.8, 67.0 (CH_2), 72.8 (CH_2), 77.3, 81.5, 82.6, 101.1, 110.4, 128.1 (2 X C), 128.5, 137.3. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{27}N_3O_5Na$ found 412.1866, calcd 412.1848.

Compound 15: The compound **14** (1.50, 3.85 mmol) was treated with 80% aqueous acetic acid solution (20 mL) and the mixture was heated at 80 °C for 3 hrs. The solution was cooled and acid was co-evaporated with toluene under reduced pressure to get a residue. The residue was purified over silica gel column to afford the diol derivative **15** (0.89 g, 75%). Eluent: EtOAc/petroleum ether (2:3). Yellowish gum. $[\alpha]^{25.2}_D$ (+): 37.3 (*c* 0.72, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.90 (bs, 2H), 3.34 (s, 3H), 3.61-3.75 (m, 2H), 3.84-4.02 (m, 4H), 4.52-4.65 (m, 2H), 4.91 (s, 1H), 7.23-7.40 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 54.8, 65.1, 65.3 (CH_2), 69.8, 72.1 (CH_2), 81.5, 87.8, 106.7, 127.9, 128.1, 128.5, 136.8. HRMS [ES^+, $(M+Na)^+$]: for $C_{14}H_{19}N_3O_5Na$ found 332.1200, calcd 332.1222.

Compound 22a: Following the procedure described for the preparation of **15**, over 2.5 h compound **21a** (0.50 g, 1.28 mmol) was converted to **22a** (0.30 g, 75 %). Eluent: EtOAc/petroleum ether (2:3). Yellowish gum. $[\alpha]^{25.2}{}_D$ (-): 56.7 (*c* 0.82, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.33 (bs, 1H), 3.04 (bs, 1H), 3.40 (s, 3H), 3.65-3.87 (m, 2H), 3.98-4.18 (m, 4H), 4.56 (d, 1H, *J* = 11.6 Hz), 4.76 (d, 1H, *J* = 11.6 Hz), 4.82 (d, 1H, *J* = 2.0 Hz), 7.26-7.41 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.8, 63.8 (CH_2), 68.9, 70.4, 72.6 (CH_2), 79.5, 81.9, 107.2, 127.9, 128.2, 128.6, 136.7. HRMS [ES+, (M+Na)+]: for $C_{14}H_{19}N_3O_5Na$ found 332.1208, calcd 332.1222.

Compound 22b: Following the procedure described for the preparation of **15**, over 3 h compound **21b** (1.00 g, 2.57 mmol) was converted to **22b** (0.59 g, 75 %). Eluent: EtOAc/petroleum ether (2:3). Yellowish oil. $[\alpha]^{25.2}{}_D$ (-): 27.7 (*c* 0.85, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.34 (bs, 1H), 2.97 (bs, 1H), 3.36 (s, 3H), 3.65-3.88 (m, 5H), 4.23-4.31 (m, 1H), 4.60-4.75 (m, 3H), 7.26-7.38 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.7, 63.3 (CH_2), 65.1, 73.2 (CH_2), 73.3, 80.5, 83.1, 101.3, 128.4, 128.7, 137.2. HRMS [ES^+, $(M+Na)^+$]: for $C_{14}H_{19}N_3O_5Na$ found 332.1221, calcd 332.1222.

Compound 16: To a well-stirred solution of the diol **15** (1.00 g, 3.24 mmol) in dry pyridine and toluene (1:1, 20 mL), *p*-toluene sulfonyl chloride (0.74 g, 3.88 mmol) was added at 0 °C and the mixture was stirred for half an hour at the same temperature. Then the reaction mixture was stored at 4 °C for 72 h. After completion of the reaction (TLC), mixture was poured into aqueous saturated solution of $NaHCO_3$ and the product was extracted with EtOAc (3 X 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford the mono tosylated derivative **16** (1.27 g, 85%). Eluent: EtOAc/petroleum ether (1:4). Yellow gummy. $[\alpha]^{25.2}_{D}$ (+): 42.6 (*c* 0.92, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.45 (s, 3H), 2.53 (d, 1H, *J* = 4.4 Hz), 3.31 (s, 3H), 3.88-4.25 (m, 6H), 4.50-4.63 (m, 2H), 4.89 (s, 1H), 7.26-7.38 (m, 8H), 7.82 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.7, 55.0, 65.6, 70.0, 70.7 (CH_2), 72.2 (CH_2), 81.2, 87.7, 106.9, 128.0, 128.1, 128.3, 128.7, 130.1, 132.5, 136.9, 145.3. HRMS [ES^+, $(M+Na)^+$]: for $C_{21}H_{25}N_3O_7NaS$ found 486.1319, calcd 486.1311.

Compound 23a: Following the procedure described for the preparation of **16**, over 72 h compound **22a** (0.30 g, 0.97 mmol) was converted to **23a** (0.36 g, 80 %). Eluent: EtOAc/petroleum ether (3:7). Yellowish gum. $[\alpha]^{25.2}_{D}$ (+): 117.6 (*c* 0.82, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H), 2.89 (d, 1H, *J* = 3.6 Hz), 3.32 (s, 3H), 3.94 (t, 1H, *J* = 1.8 Hz), 4.05-4.32 (m, 5H), 4.53 (d, 1H, *J* = 11.6 Hz), 4.71 (d, 1H, *J* = 11.6 Hz), 4.76 (d, 1H, *J* = 1.8 Hz), 7.26-7.38 (m, 7H), 7.80 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.5, 55.9, 68.6, 68.8, 71.6 (CH_2), 72.7 (CH_2), 79.0, 81.9, 107.4, 128.0 (2 X C), 128.3, 128.7, 129.8, 132.6, 136.5, 144.8. HRMS [ES+, (M+Na)+]: for $C_{21}H_{25}N_3O_7NaS$ found 486.1320, calcd 486.1311.

Compound 23b: Following the procedure described for the preparation of **16**, over 72 h compound **22b** (1.00 g, 3.23 mmol) was converted to **23b** (1.27 g, 85 %). Eluent: EtOAc/petroleum ether (3:7). Yellowish gum. $[\alpha]^{25.2}_{D}$ (-): 34.6 (*c* 0.72, $CHCl_3$). ^1H NMR

(200 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.03 (bs, 1H), 3.26 (s, 3H), 3.63-3.70 (m, 1H), 3.76-3.82 (m, 2H), 3.98-4.06 (m, 1H), 4.14-4.25 (m, 2H), 4.54-4.71 (m, 3H), 7.26-7.35 (m, 7H), 7.79 (d, 2H, J = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.7, 55.6, 65.4, 71.1 (CH_2), 71.6, 73.1 (CH_2), 79.6, 82.9, 101.4, 128.1, 128.3, 128.6, 130.1, 132.4, 137.1, 145.3. HRMS [ES^+, $(M+Na)^+$]: for $C_{21}H_{25}N_3O_7NaS$ found 486.1316, calcd 486.1311.

Compound 17: To a well-stirred solution of the monotosylated compound **16** (1.00 g, 2.16 mmol) in DMF (15 mL) was added 4-chloro thiophenol (0.47 g, 3.24 mmol) and TMG (0.30 mL, 2.16 mmol). The mixture was heated at 90 °C with stirring under N_2. After 5 h the reaction mixture was cooled, poured into an aqueous saturated solution of $NaHCO_3$, and the product was extracted with EtOAc (3 X 10 mL). The combined organic layer was dried over anhyd Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified over silica gel column to afford the sulfide derivative **17** (0.84 g, 90 %). Eluent: EtOAc/petroleum ether (1:5). Yellowish oil. $[\alpha]^{25.2}_D$ (+): 40.6 (c 0.80, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.63 (d, 1H, J = 3.2 Hz), 2.93-3.04 (m, 1H), 3.20-3.29 (m, 1H), 3.33 (s, 3H), 3.83-3.95 (m, 4H), 4.51-4.65 (m, 2H), 4.91 (s, 1H), 7.24-7.36 (m, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 37.9 (CH_2), 54.8, 65.1, 69.7, 72.0 (CH_2), 83.0, 87.8, 106.8, 127.9, 128.1, 128.5, 129.2, 131.0, 132.5, 133.8, 136.8. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{22}N_3O_4NaSCl$ found 458.0916, calcd 458.0917.

Compound 24a: Following the procedure described for the preparation of **17**, over 5 h compound **23a** (0.35 g, 0.77 mmol) was converted to **24a** (0.30 g, 90 %). Eluent: EtOAc/petroleum ether (1:4).Yellowish gum. $[\alpha]^{25.2}_D$ (-): 52.9 (c 1.2, $CHCl_3$). ^1H NMR

(200 MHz, $CDCl_3$): δ 3.01-3.05 (m, 2H), 3.34-3.41 (m, 4H), 3.96-3.99 (m, 1H), 4.08-4.15 (m, 3H), 4.54 (d, 1H, J = 11.6 Hz), 4.74 (d, 1H, J = 11.6 Hz), 4.80 (d, 1H, J = 2.0 Hz), 7.20-7.25 (m, 3H), 7.28-7.31 (m, 2H), 7.32-7.37 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.3 (CH_2), 55.9, 68.8, 69.2, 72.7 (CH_2), 81.4, 82.0, 107.2, 128.0, 128.4, 128.7, 128.9, 130.5, 131.8, 135.0, 136.4. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{22}N_3O_4NaSCl$ found 458.0912, calcd 458.0917.

Compound 24b: Following the procedure described for the preparation of **17**, over 5 h compound **23b** (1.00 g, 2.16 mmol) was converted to **24b** (0.89 g, 95 %). Eluent: EtOAc/petroleum ether (1:4). Yellowish oil. $[\alpha]^{25.2}_D$ (-): 87.4 (c 0.92, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 2.81-2.93 (m, 2H), 3.20 (s, 3H), 3.60-3.73 (m, 2H), 3.76-3.85 (m, 1H), 4.17-4.25 (m, 1H), 4.55-4.73 (m, 3H), 7.22-7.38 (m, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.7 (CH_2), 55.1, 65.0, 71.1, 72.7 (CH_2), 81.9, 82.6, 101.0, 128.0, 128.3, 129.0, 131.4, 132.5, 133.6, 136.9. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{22}N_3O_4NaSCl$ found 458.0912, calcd 458.0917.

Compound 18: To a well-stirred solution of sulfide **17** (0.80 g, 1.84 mmol) in dry MeOH (10 mL) was added magnesium bis-(monoperoxyphthalate) hexahydrate (MMPP) (1.82 g, 3.68 mmol), and the mixture was stirred at room temperature under N_2. After 12 h MeOH was evaporated to dryness under reduced pressure, and the residue was dissolved in aqueous saturated solution of $NaHCO_3$. The aqueous part was washed with EtOAc (3 X 10 mL). The combined organic layer was dried over anhyd Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford the sulfone derivative **18** (0.82 g, 95 %). Eluent: EtOAc/petroleum ether (3:7). Yellowish gum. $[\alpha]^{25.2}_{D}$ (+): 88.3 (*c* 0.86, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 3.24-3.28 (m, 1H), 3.30 (s, 3H), 3.36 (d, 1H, *J* = 2.4 Hz), 3.47 (dd, 1H, *J* = 1.4 Hz, 14.4 Hz), 3.82-3.92 (m, 3H), 4.24-4.28 (m, 1H), 4.51-4.59 (m, 2H), 4.85 (s, 1H), 7.26-7.39 (m, 5H), 7.54 (d, 2H, *J* = 8.4 Hz), 7.86 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.1, 59.2 (CH_2), 65.5, 66.9, 72.2 (CH_2), 83.1, 87.7, 107.0, 127.9, 128.2, 128.6, 129.6, 129.8, 136.8, 137.8, 140.8. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{22}N_3O_6NaSCl$ found 490.0814, calcd 490.0816.

Compound 25a: Following the procedure described for the preparation of **18**, over 12 h Compound **24a** (0.20 g, 0.46 mmol) was converted to **25a** (0.20 g, 95 %). Eluent: EtOAc/petroleum ether (1:2). Yellow gum. $[\alpha]^{25.2}_{D}$ (+): 40.6 (*c* 0.72, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 3.26-3.40 (m, 5H), 3.55-3.63 (m, 1H), 3.95-4.06 (m, 3H), 4.49 (d, 2H, *J* = 11.6 Hz), 4.67 (d, 1H, *J* = 11.6 Hz), 4.77 (d, 1H, *J* = 1.6 Hz), 7.23-7.28 (m, 2H), 7.34-7.42 (m, 3H), 7.47(d, 2H, *J* = 8.4 Hz), 7.82 (d, 2H, *J* = 8.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 56.2, 59.7 (CH_2), 66.4, 69.0, 72.9 (CH_2), 81.4, 81.8, 107.5, 128.2, 128.6, 128.9, 129.5, 129.7, 136.4, 138.5, 140.5. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{22}N_3O_6NaSCl$ found 490.0814, calcd 490.0816.

Compound 25b: Following the procedure described for the preparation of **18**, over 12 h compound **24b** (0.90 g, 2.07 mmol) was converted to **25b** (0.92 g, 95 %). Eluent: EtOAc/petroleum ether (1:2). Yellowish gum. $[\alpha]^{25.2}_{D}$ (-): 62.9 (*c* 0.88, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 3.00 (s, 3H), 3.14-3.20 (m, 1H), 3.46-3.65 (m, 4H), 3.73-3.80 (m, 1H), 3.96-4.05 (m, 1H), 4.13-4.20 (m, 1H), 4.49 (d, 1H, *J* = 4.2 Hz), 4.56-4.72 (m, 2H), 7.26-7.34 (m, 5H), 7.53-7.60 (m, 2H), 7.85-7.90 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.2, 59.5 (CH_2), 65.7, 68.6, 73.1 (CH_2), 81.5, 82.7, 101.4, 128.3, 128.6, 129.7, 129.9, 137.1, 137.4, 141.0. HRMS [ES^+, $(M+Na)^+$]: for $C_{20}H_{22}N_3O_6NaSCl$ found 490.0814, calcd 490.0816.

Compound 5: To a well-stirred solution of sulfone **18** (0.80 g, 1.71 mmol) in pyridine (10 mL) was added methanesulfonyl chloride (0.20 mL, 2.57 mmol) in pyridine (2 mL) dropwise at 0 °C under N_2. After completion of the addition, the reaction mixture was kept at 4 °C. After 24 h (TLC), the reaction mixture was poured into an aqueous saturated solution of $NaHCO_3$ and the product was extracted with EtOAc (3 X 10 mL). The combined organic layer was dried over anhyd Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was heated under reflux with pyridine. After 2 h (TLC) the reaction mixture poured into ice-cold water, and the aqueous layer was extracted with EtOAc (3 X 10 mL). The combined organic layers were dried over anhyd Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel to afford the vinylsulfone **5** (0.69 g, 90 %). Eluent: EtOAc/petroleum ether (1:4). Yellow gum. $[\alpha]^{25.2}_D$ (+): 118.1 (*c* 0.90, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.33 (s, 3H), 3.61-3.67 (m, 1H), 3.97-4.00 (m, 1H), 4.42-4.49 (m, 2H), 4.57 (s, 2H), 4.93 (s, 1H), 6.67 (dd, 1H, *J* = 1.5 Hz, 15.0 Hz), 7.03 (dd, 1H, *J* = 4.0 Hz, 15.0 Hz), 7.26-7.40 (m, 5H), 7.51 (d, 2H, *J* = 8.6 Hz), 7.82 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.3, 68.8, 72.5 (CH_2), 78.1, 88.1, 107.3, 127.9, 128.2, 128.6, 129.3, 129.7, 131.4, 136.7, 138.3, 140.3, 141.5. HRMS [ES$^+$, (M+Na)$^+$]: for $C_{20}H_{20}N_3O_5NaSCl$ found 472.0707, calcd 472.0710 (E).

Compound 6: Following the procedure described for the preparation of **5**, over 26 h compound **25a** (0.15 g, 0.32 mmol) was converted to **6** (0.12 g, 85 %). Eluent: EtOAc/petroleum ether (1:4). Brownish gum. $[\alpha]^{25.2}_D$ (+): 41.7 (*c* 0.97, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.40 (s, 3H), 3.87-3.91 (m, 2H), 4.04-4.10 (m, 1H), 4.51 (d, 1H, *J* = 12.0 Hz), 4.66 (d, 1H, *J* = 12.0 Hz), 4.75-4.82 (m, 2H), 6.60 (dd, 1H, *J* =1.6 Hz, 15.0 Hz), 7.04 (dd, 1H, *J* = 4.6 Hz, 15.0 Hz), 7.25-7.44 (m, 8H), 7.73-7.78 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 56.3, 68.7, 72.7 (CH_2), 78.4, 82.1, 107.1, 127.9, 128.2, 128.6, 129.1, 129.5, 131.6, 136.6, 138.6, 139.9, 143.0. HRMS [ES$^+$, (M+Na)$^+$]: for $C_{20}H_{20}N_3O_5NaSCl$ found 472.0707, calcd 472.0710 (E).

Compound 7: Following the procedure described for the preparation of **5**, over 26 h compound **25b** (0.90 g, 1.93 mmol) was converted to **7** (0.78 g, 90 %). Eluent: EtOAc/petroleum ether (1:4). Yellow gum. $[\alpha]^{25.2}_D$ (-): 117.8 (*c* 0.80, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.31 (s, 3H), 3.89 (dd, 1H, *J* = 4.0 Hz, 8.8 Hz), 4.02 (t, 1H, *J* = 8.3 Hz), 4.19-4.26 (m, 1H), 4.59-4.72 (m, 3H), 6.55 (dd, 1H, *J* = 1.6 Hz, 15.0 Hz), 6.98 (dd, 1H, *J* = 4.6 Hz, 15.0 Hz), 7.26-7.38 (m, 5H), 7.48-7.54 (m, 2H), 7.78-7.83 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 55.3, 66.3, 72.7 (CH_2), 76.8, 82.2, 101.0, 127.9, 128.0, 128.3, 129.0, 129.5, 130.9, 136.7, 138.2, 140.0, 143.7. HRMS [ES$^+$, (M+Na)$^+$]: for $C_{20}H_{20}N_3O_5NaSCl$ found 472.0705, calcd 472.0710 (E).

General procedure for the synthesis of Ionic Liquids (ILs): A mixture of N, N-dimethyl ethanol amine (0.50 g, 5.6 mmol) and HCOOH (0.2 mL, 5.6 mmol), CH_3COOH (0.32mL, 5.6 mmol) or HCl (0.2 mL, 5.6 mmol) were stirred at room temperature for 24 h to afford the corresponding ILs, N,N-dimethyl ethanol ammonium formate (DAF), N,N-dimethyl ethanol ammonium acetate (DAA) and N,N-dimethyl ethanol ammonium chloride (DAC) which were directly used for the triazolylation reaction without further purification.

Ionic liquid DAF*:* Following the general procedure, over 24 h **DEA** (0.50 g, 5.6 mmol) was converted to the ionic liquid **DAF** (0.72 g, 95 %). Colourless viscous oil. ^1H NMR (200 MHz, D_2O): δ 2.97 (s, 6H), 3.33-3.36 (m, 2H), 3.92-3.95 (m, 2H), 8.50 (s, 1H). ^{13}C NMR (50 MHz, D_2O): δ 42.8, 55.2 (CH_2), 58.8 (CH_2), 170.7. HRMS [ES^+, $(M+H)^+$]: for $C_5H_{14}NO_3$ found 136.0906, calcd 136.0901.

Ionic liquid DAA*:* Following the general procedure, over 24 h **DEA** (0.50 g, 5.6 mmol) was converted to the ionic liquid **DAA** (0.82 g, 98 %). Colourless viscous oil. ^1H NMR (200 MHz, D_2O): δ 1.97 (s, 3H), 2.97 (s, 6H), 3.31-3.36 (m, 2H), 3.92-3.97 (m, 2H). ^{13}C NMR (50 MHz, D_2O): δ 23.1, 42.8, 55.2 (CH_2), 58.8 (CH_2), 180.9. HRMS [ES^+, $(M+H)^+$]: for $C_6H_{16}NO_3$ found 150.1055, calcd 150.1057.

Ionic liquid DAC*:* Following the general procedure, over 24 h **DEA** (0.50 g, 5.6 mmol) was converted to the ionic liquid **DAC** (0.67 g, 95 %). Colourless viscous oil. ^1H NMR (200 MHz, D_2O): δ 2.83(s, 3H), 2.84 (s, 3H), 3.15-3.21 (m, 2H), 3.90-3.95 (m, 2H). ^{13}C

NMR (50 MHz, D_2O): δ 43.2, 56.1 (CH_2), 59.0 (CH_2). HRMS [ES^+, $(M+Na)^+$]: for $C_4H_{12}ClNONa$ found 148.0615, calcd 148.0613.

General procedure for the synthesis of 1,5-Disubstituted 1,2,3-triazole linked disaccharides 27-31. A mixture of vinyl sulfone modified carbohydrate (1 equiv) and azidosugar (1.5 equiv) in water (10 mL/mmol) was heated under refluxing condition using ILs (DAF, DAA and DAC) (1:1 H_2O/IL) for 24-30 h to afford 1,5-disubstituted 1,2,3-triazole linked disaccharides. The 1,2-*O*-isopropyledene groups of the vinyl sulfone and azidosugars **8** and **9** were unstable due to the elemination of sulfinic acid, and hence $NaHCO_3$ (1.5 equiv) was added to the reaction mixture.

Compound 27[2]**:** Following the general procedure, over 24-30 h compound **26**[3] (0.25 g, 0.55 mmol) was converted to **27** in 76-80% yield. Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27}_{D}$ (-): 65.2 (*c* 0.9, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 3H), 1.35 (s, 3H), 1.38 (s, 3H), 1.51 (s, 3H), 4.00-4.04 (m, 2H), 4.22-4.36 (m, 2H), 4.45-4.68 (m, 8H), 5.46 (d, 1H, *J* = 2.8 Hz), 5.87-5.91 (m, 2H), 6.96-6.99 (m, 2H), 7.23-7.35 (m, 9H), 7.67 (s, 1H).

Compound 28: Following the general procedure, over 24 h compound **5** (0.30 g, 0.67 mmol) was converted to **28** (0.30 g, 78 %). Eluent: EtOAc/petroleum ether (1:4). Yellowish gum. $[\alpha]^{27.6}_{D}$ (-): 41.8 (*c* 0.76, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.29 (s, 3H), 1.41 (s, 3H), 3.44 (s, 3H), 4.02-4.13 (m, 3H), 4.33-4.45 (m, 3H), 4.53 (d, 2H, *J* = 5.0 Hz), 4.59-4.71 (m, 4H), 4.86 (d, 1H, *J* = 3.2 Hz), 5.47 (d, 1H, *J* = 6.0 Hz), 5.94 (d, 1H, J = 3.6 Hz), 7.08-7.13 (m, 2H), 7.26-7.34 (m, 8H), 7.78 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.3, 26.8, 47.6 (CH_2), 56.7, 69.3, 72.1 (CH_2), 72.8 (CH_2), 73.1, 79.3, 81.2, 81.9, 82.1, 105.2, 107.6, 112.1, 127.9, 128.3 (2 X C), 128.7, 134.1, 134.7, 136.5, 137.1. HRMS [ES$^+$, (M+H)$^+$]: for $C_{29}H_{35}N_6O_7$ found 579.2541, calcd 579.2567.

Compound 29: Following the general procedure, over 30 h compound **5** (0.30 g, 0.67 mmol) was converted to **29** (0.37 g, 80 %). Eluent: EtOAc/petroleum ether (1:5). Yellowish gum. $[\alpha]^{27.6}_D$ (-): 39.8 (*c* 0.85, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.48 (s, 3H), 3.40 (s, 3H), 4.03-4.12 (m, 3H), 4.22 (s, 2H), 4.27-4.49 (m, 5H), 4.62-4.83 (m, 4H), 5.48 (d, 1H, J = 5.0 Hz), 5.92 (d, 1H, J = 3.8 Hz), 7.05-7.12 (m, 5H), 7.21-7.28 (m, 11H), 7.82 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.4, 26.9, 50.6 (CH_2), 56.5, 69.4, 71.9 (CH_2), 72.7 (CH_2), 73.1, 73.3 (CH_2), 75.7, 80.1, 81.0, 81.5, 81.6, 105.2, 107.4, 112.1, 127.9 (2 X C), 128.0 (2 X C), 128.2, 128.3, 128.4, 128.7, 129.3, 134.1, 135.3, 136.5, 137.1, 137.5. HRMS [ES$^+$, (M+H)$^+$]: for $C_{37}H_{43}N_6O_8$ found 699.3124, calcd 699.3142.

Compound 30: Following the general procedure, over 24 h compound **7** (0.30 g, 0.67 mmol) was converted to **30** (0.30 g, 77 %). Eluent: EtOAc/petroleum ether (1:3). Yellowis gum. $[\alpha]^{27.6}_D$ (-): 92.3 (*c* 0.88, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28 (s, 3H), 1.41 (s, 3H), 3.31 (s, 3H), 3.87-3.94 (m, 1H), 4.02 (s, 1H), 4.38 (t, 1H, J = 8.7 Hz), 4.51-4.87 (m, 11H), 5.93 (d, 1H, J = 3.8 Hz), 7.26-7.39 (m, 10H), 7.62 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 26.3, 26.8, 47.0 (CH_2), 55.7, 67.6, 70.8, 72.1 (CH_2), 73.3 (CH_2), 79.2, 81.7, 82.1, 82.5, 101.1, 105.2, 112.1, 127.9, 128.3, 128.4, 128.5, 128.7, 128.8, 132.3, 136.9, 137.2, 137.4. HRMS [ES$^+$, (M+H)$^+$]: for $C_{29}H_{35}N_6O_7$ found 579.2546, calcd 579.2567.

Compound 31: Following the general procedure, over 30 h compound **7** (0.30 g, 0.67 mmol) was converted to **31** (0.35 g, 75 %). Eluent: EtOAc/petroleum ether (1:3). Yellow gum. $[\alpha]^{27.6}_D$ (+): 57.8 (*c* 0.86, CHCl$_3$). ^{1}H NMR (200 MHz, CDCl$_3$): δ 1.31 (s, 3H), 1.48 (s, 3H), 3.30 (s, 3H), 3.85-3.92 (m, 1H), 4.04-4.18 (m, 4H), 4.24-4.43 (m, 4H), 4.53-4.70 (m, 6H), 4.80-4.89 (m, 2H), 5.94 (d, 1H, *J* = 3.8 Hz), 7.00-7.05 (m, 2H), 7.18-7.38 (m, 13H), 7.66 (s, 1H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 26.4, 26.8, 50.6 (CH$_2$), 55.6, 68.1, 70.8, 71.7 (CH$_2$), 73.1 (CH$_2$), 73.4 (CH$_2$), 75.7, 80.3, 81.5, 81.7, 82.4, 101.0, 105.2, 112.0, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.6, 128.7, 132.5, 136.9, 137.1, 137.5, 137.9. HRMS [ES$^+$, (M+H)$^+$]: for $C_{37}H_{43}N_6O_8$ found 699.3129, calcd 699.3142.

Procedure for the synthesis of 1,5-Disubstituted 1,2,3-triazole linked trisaccharide 32. A mixture of 1,5-DT linked disaccharide **30** (1 equiv, 0.15 g, 0.26 mmol) having one unreacted azido group and another vinyl sulfone modified carbohydrate **10** (1.2 equiv) in water (10 mL/mmol) was heated under refluxing condition using DAF (1:1 H$_2$O/DAF) for 48 h. The 1,2-*O*-isopropyledene groups of the 1,5-DT **30** and vinyl sulfone modified carbohydrate **10** were unstable due to the elemination of sulfinic acid, and hence NaHCO$_3$ (1.5 equiv) was added to the reaction mixture. After completion of reaction, extracted with EtOAc (3 X 10 mL) and the organic layer was dried over anhyd. Na$_2$SO$_4$, filtered and filtrate was concentrated under reduced pressure to get a residue. The residue was purified by silica-gel column chromatography to afford 1,5-disubstituted 1,2,3-triazole linked trisaccharide **32** (0.04 g, 20 %). Eluent: EtOAc/petroleum ether (2:3).

Yellowish gum. $[\alpha]^{28}_{D}$ (+): 87.6 (*c* 0.68, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 6H), 1.34 (s, 3H), 1.38 (s, 3H), 3.39 (s, 3H), 3.85-4.10 (m, 1H), 4.12-4.58 (m, 9H), 4.65 (d, 1H, *J* = 3.8 Hz), 4.87-4.92 (m, 2H), 5.12 (d, 1H, *J* = 3.6 Hz), 5.46 (d, 1H, *J* = 3.0 Hz), 5.55-5.64 (m, 2H), 5.94 (d, 1H, *J* = 3.6 Hz), 6.22 (d, 1H, *J* = 3.6 Hz), 6.91-6.96 (m, 2H), 7.14-7.41 (m, 13H), 7.68 (s, 1H), 7.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.4, 26.5, 27.1, 27.2, 51.1 (CH_2), 57.4 (CH_2), 62.4 (CH_2), 72.1, 72.5, 72.8, 74.8, 74.9, 79.0, 82.3, 82.6, 83.1, 83.8, 104.9, 105.3, 108.9, 112.4, 112.9, 125.2, 128.1, 128.3, 128.4, 128.8, 128.9, 132.8, 133.2, 133.7, 134.5, 135.4, 136.5, 136.8. HRMS [ES^+, $(M+H)^+$]: for $C_{45}H_{53}N_6O_{11}$ found 852.3699, calcd 852.3694..

General procedure for the synthesis of 1,2,3-triazole linked trisaccharides 33-36. To a well-stirred solution of the 1,5-disubstituted 1,2,3-triazole linked disaccharides **28-31** (1 equiv) and a known alkyne **11**[4] (1 equiv) in $^tBuOH/H_2O$ (1:1) was added $CuSO_4$ (0.5 equiv) and sodium ascorbate (1 equiv). The reaction mixture was stirred at room temperature for 30-36 h. After completion of the reaction (TLC), the reaction mixture was poured into aqueous saturated solution of $NaHCO_3$ and extracted with EtOAc (3 X 10 mL). The organic phase was dried over anhyd. Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to afford the 1,2,3-triazole linked trisaccharides **33-36**.

Compound 33: Following the general procedure, over 36 h compound **28** (0.35 g, 0.60 mmol) was converted to **33** (0.52 g, 90 %). Eluent: EtOAc/petroleum ether (1:1). Yellowish gum. $[\alpha]^{27.6}_{D}$ (+): 55.8 (*c* 0.88, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.30

(s, 3H), 1.41 (s, 3H), 1.98 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.42 (s, 3H), 3.71-3.77 (m, 1H), 4.04 (d, 1H, *J* = 3.2 Hz), 4.19-4.25 (m, 2H), 4.31 (s, 2H), 4.42-4.51 (m, 2H), 4.61-4.71 (m, 5H), 4.77-5.24 (m, 9H), 5.76 (d, 1H, *J* = 6.2 Hz), 5.95 (d, 1H, *J* = 3.8 Hz), 6.91-6.96 (m, 2H), 7.18-7.31 (m, 10H), 7.44 (s, 1H), 7.87 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.5, 20.7, 26.1, 26.6, 47.7 (CH_2), 56.6, 61.7 (CH_2), 62.8 (CH_2), 68.2, 69.9, 71.2, 71.9 (C + CH_2), 72.7, 73.1 (C + CH_2), 79.2, 81.5, 81.8, 81.9, 100.0, 105.1, 106.9, 111.9, 123.8, 127.7, 127.8, 128.1, 128.2, 128.5, 134.0, 134.5, 136.1, 137.0, 144.6, 169.3, 169.4, 170.1, 170.5. HRMS [ES$^+$, (M+H)$^+$]: for $C_{46}H_{57}N_6O_{17}$ found 965.3760, calcd 965.3780.

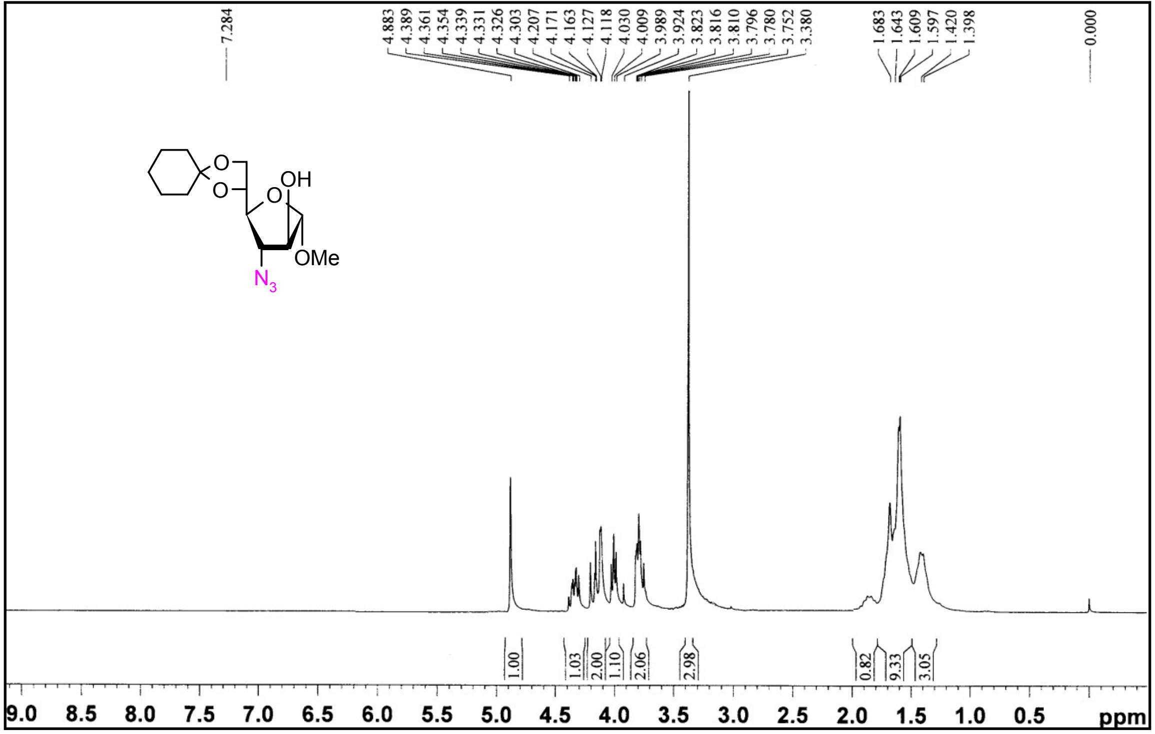
Compound 34: Following the general procedure, over 36 h compound **29** (0.40 g, 0.57 mmol) was converted to **34** (0.56 g, 90 %). Eluent: EtOAc/petroleum ether (1:1), Yellowish gum. $[\alpha]^{27.6}_D$ (-): 60.0 (*c* 0.93, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.33 (s, 3H), 1.49 (s, 3H), 1.97 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.37 (s, 3H), 3.71-3.78 (m, 1H), 4.05-4.45 (m, 11H), 4.62-4.70 (m, 3H), 4.76-4.88 (m, 6H), 4.94-5.21 (m, 5H), 5.75 (d, 1H, *J* = 5.6 Hz), 5.93 (d, 1H, *J* = 3.6 Hz), 6.92-6.97 (m, 3H), 7.06- 7.27 (m, 16H), 7.43 (s, 1H), 7.91 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.6, 20.7, 26.3, 26.8, 50.5 (CH_2), 56.5, 61.8 (CH_2), 62.7 (CH_2), 68.3, 70.0, 71.2, 71.8 (CH_2), 71.9, 72.8, 73.0 (CH_2), 73.2 (CH_2), 75.6, 79.9, 81.3, 81.5, 81.6, 100.0, 105.1, 106.8, 112.0, 123.9, 127.8 , 128.1, 128.2, 128.4, 128.6, 134.1, 135.1, 136.2, 137.0, 137.4, 144.5, 169.3, 169.4, 170.2, 170.6. HRMS [ES$^+$, (M+H)$^+$]: for $C_{54}H_{65}N_6O_{18}$ found 1085.4316, calcd 1085.4355.

Compound 35: Following the general procedure, over 30 h compound **30** (0.30 g, 0.52 mmol) was converted to **35** (0.46 g, 92 %). Eluent: EtOAc/petroleum ether (1:1).

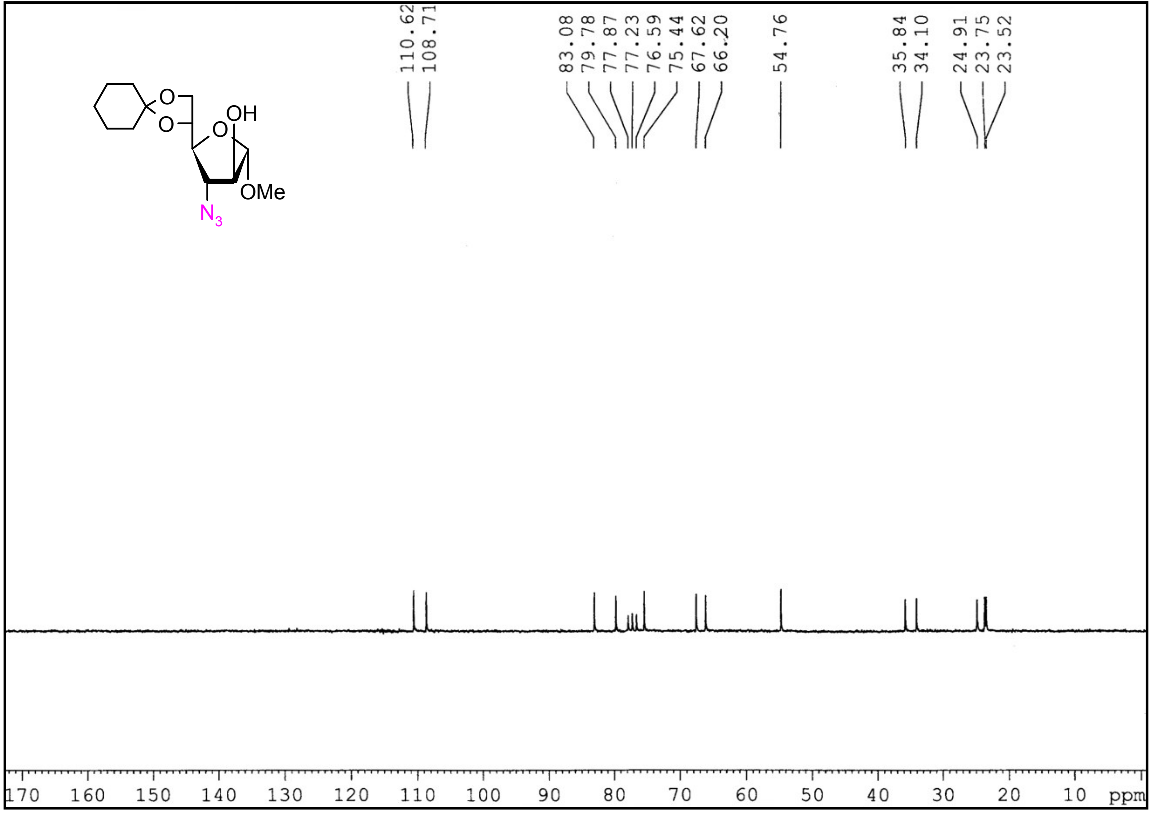
Yellowish gum. $[\alpha]^{27.6}_{D}$ (+): 70.4 (*c* 0.92, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.21 (s, 3H), 1.33 (s, 3H), 1.84 (s, 3H), 1.91 (s, 3H), 1.95 (s, 3H), 1.98 (s, 3H), 3.23 (s, 3H), 3.63-3.67 (m, 1H), 3.92 (d, 1H, *J* = 2.8 Hz), 4.05-4.37 (m, 2H), 4.39-4.66 (m, 11H), 4.72-4.77 (m, 3H), 4.83-5.18 (m, 3H), 5.27-5.36 (m, 1H), 5.71 (d, 1H, *J* = 8.6 Hz), 5.85 (d, 1H, *J* = 3.6 Hz), 7.13-7.24 (m, 10H), 7.47 (s, 1H), 7.59 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.6 (3 X C), 20.7, 26.2, 26.7, 47.0 (CH_2), 55.6, 61.7 (CH_2), 62.6 (CH_2), 67.2, 68.3, 70.2, 71.1, 71.8 (CH_2), 71.9, 72.7, 73.1 (CH_2), 79.2, 81.4, 81.5, 82.0, 100.0, 101.1, 105.0, 112.0, 124.1, 127.8, 128.0, 128.2, 128.5 (2 X C), 128.6, 132.6, 136.2, 136.5, 137.1, 144.4, 169.3, 169.4, 170.2, 170.6. HRMS [ES^+, $(M+H)^+$]: for $C_{46}H_{57}N_6O_{17}$ found 965.3745, calcd 965.3780.

Compound 36: Following the general procedure, over 36 h compound **31** (0.40 g, 0.57 mmol) was converted to **36** (0.55 g, 89 %). Eluent: EtOAc/petroleum ether (9:11). Yellowish gum. $[\alpha]^{27.6}_{D}$ (+): 69.3 (*c* 0.88, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.49 (s, 3H), 1.90 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.10 (s, 3H), 3.31 (s, 3H), 3.71-3.76 (m, 1H), 4.04 (d, 1H, *J* = 3.0 Hz), 4.10-4.26 (m, 5H), 4.32-4.53 (m, 6H), 4.60-4.85 (m, 7H), 5.01-5.25 (m, 4H), 5.82 (d, 1H, *J* = 8.6 Hz), 5.91 (d, 1H, *J* = 3.6 Hz), 6.99-7.02 (m, 2H), 7.18-7.35 (m, 14H), 7.69 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.6 (3 X C), 20.7, 26.3, 26.7, 50.0 (CH_2), 55.6, 61.7 (CH_2), 62.5 (CH_2), 67.6, 68.2, 70.2, 71.1, 71.5 (CH_2), 71.9, 72.7, 73.0 (CH_2), 73.1 (CH_2), 80.2, 81.3, 81.4, 81.6, 100.0, 100.9, 105.0, 111.9, 123.8, 127.6 (2 X C), 127.7, 127.9, 128.2 (2 X C), 128.4, 128.5, 128.6, 132.7, 136.5, 136.6, 137.0, 137.6, 144.3, 169.3, 169.4, 170.1, 170.6. HRMS [ES^+, $(M+H)^+$]: for $C_{54}H_{65}N_6O_{18}$ found 1085.4346, calcd 1085.4355.

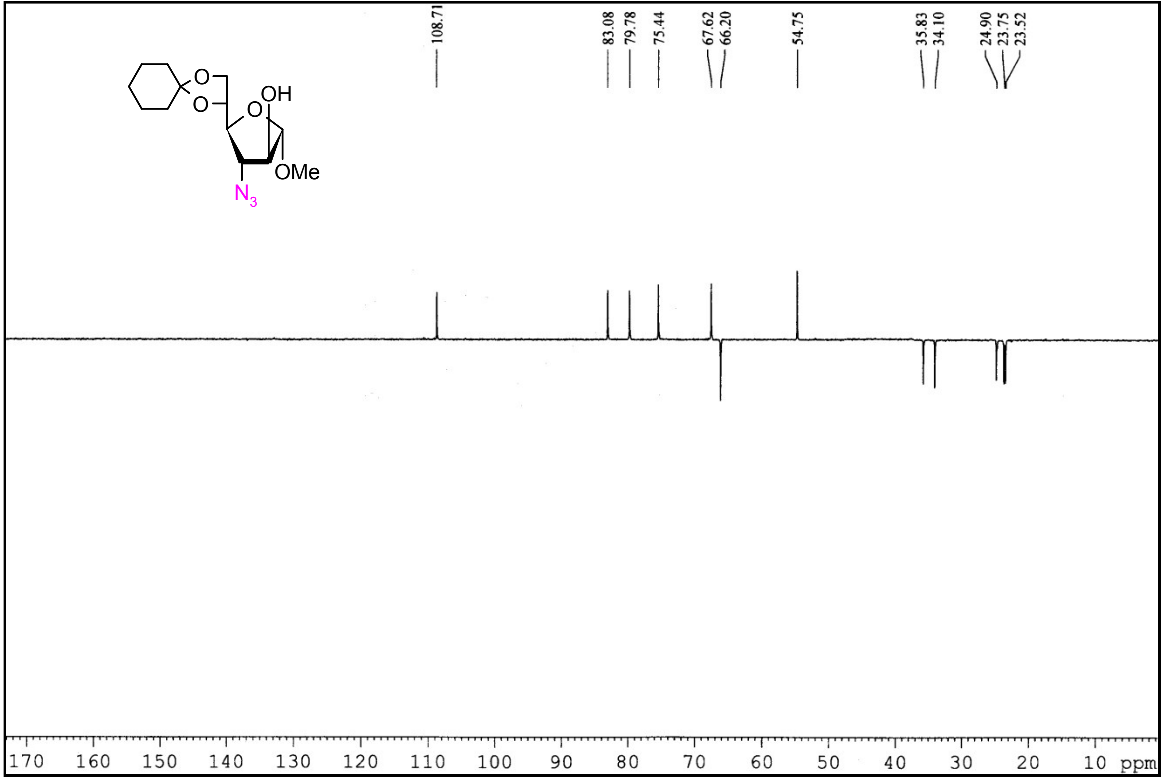
^{1}H NMR spectrum of 13



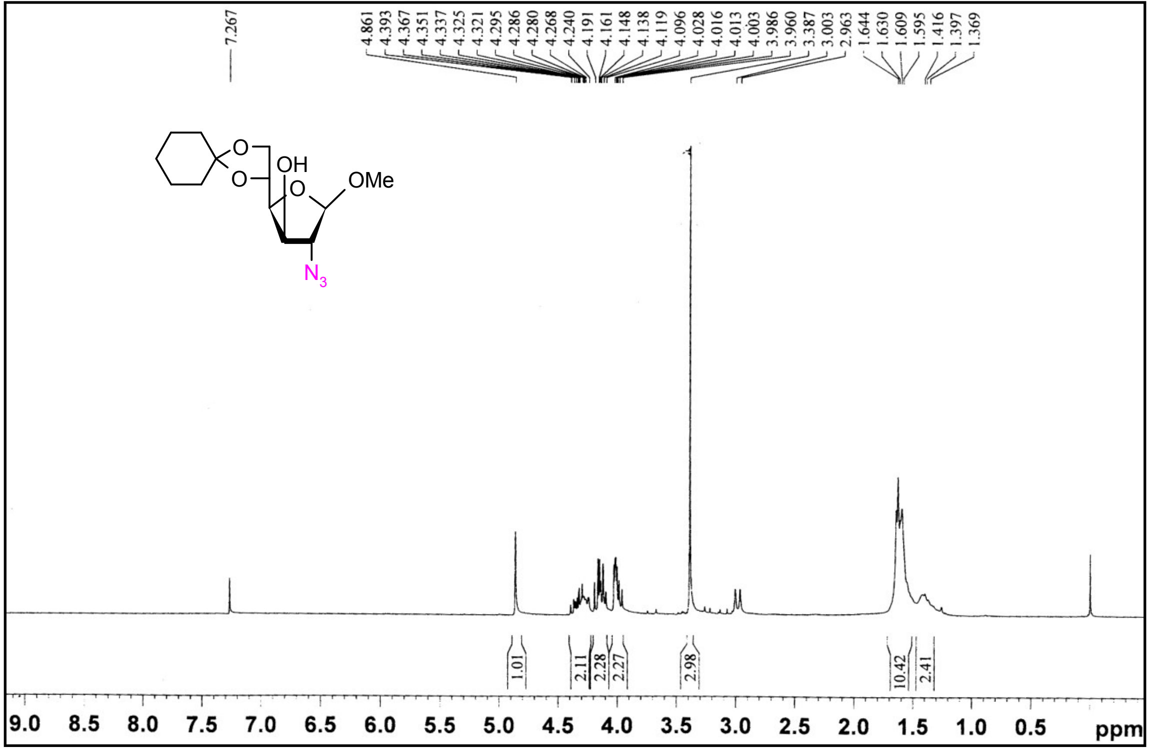
^{13}C NMR spectrum of 13



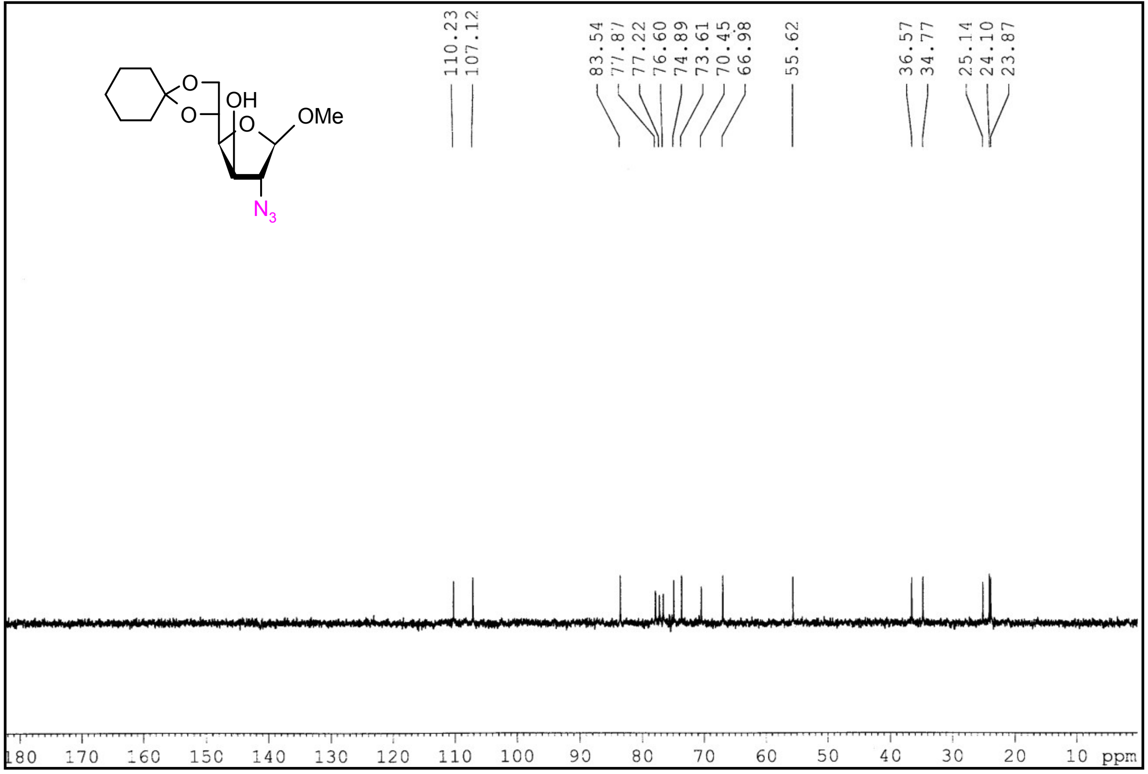
DEPT spectrum of 13



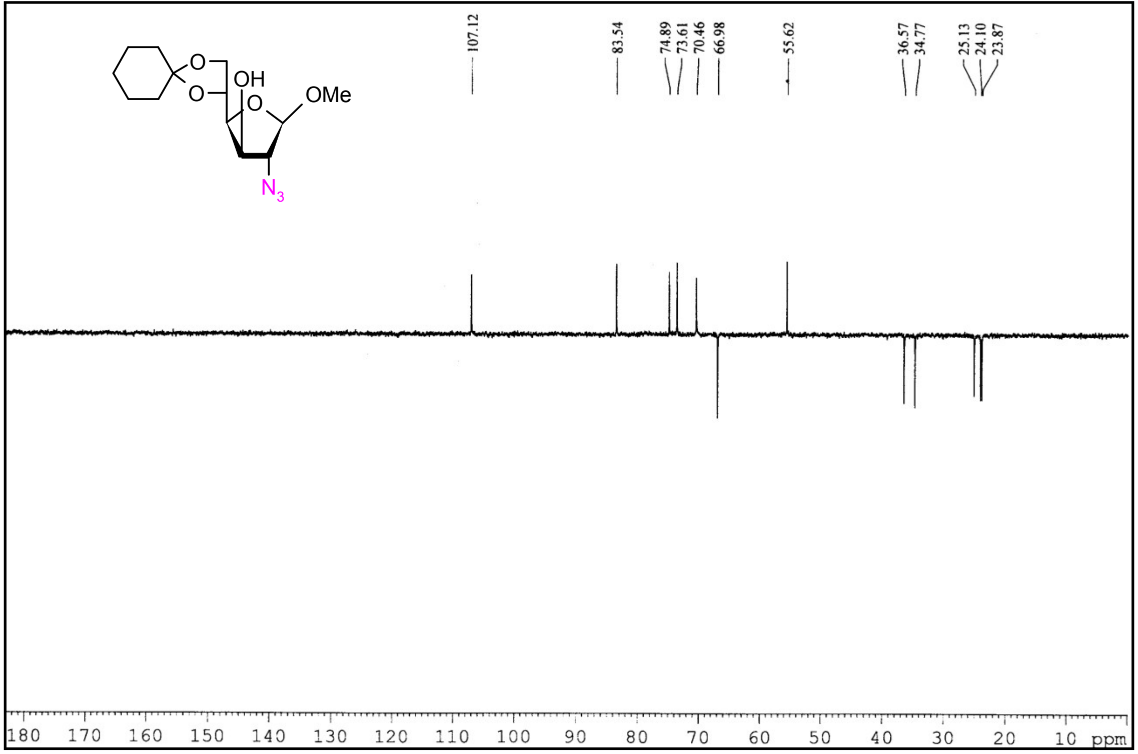
^{1}H NMR spectrum of 20a



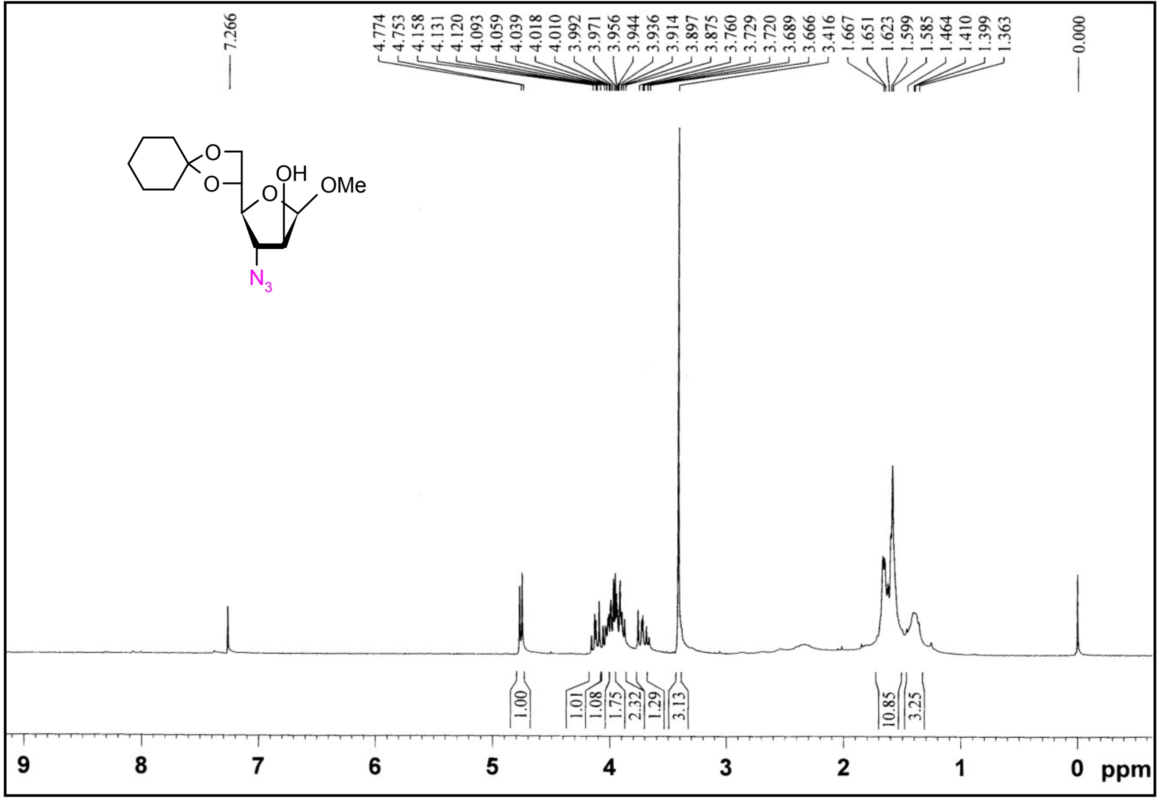
^{13}C NMR spectrum of 20a



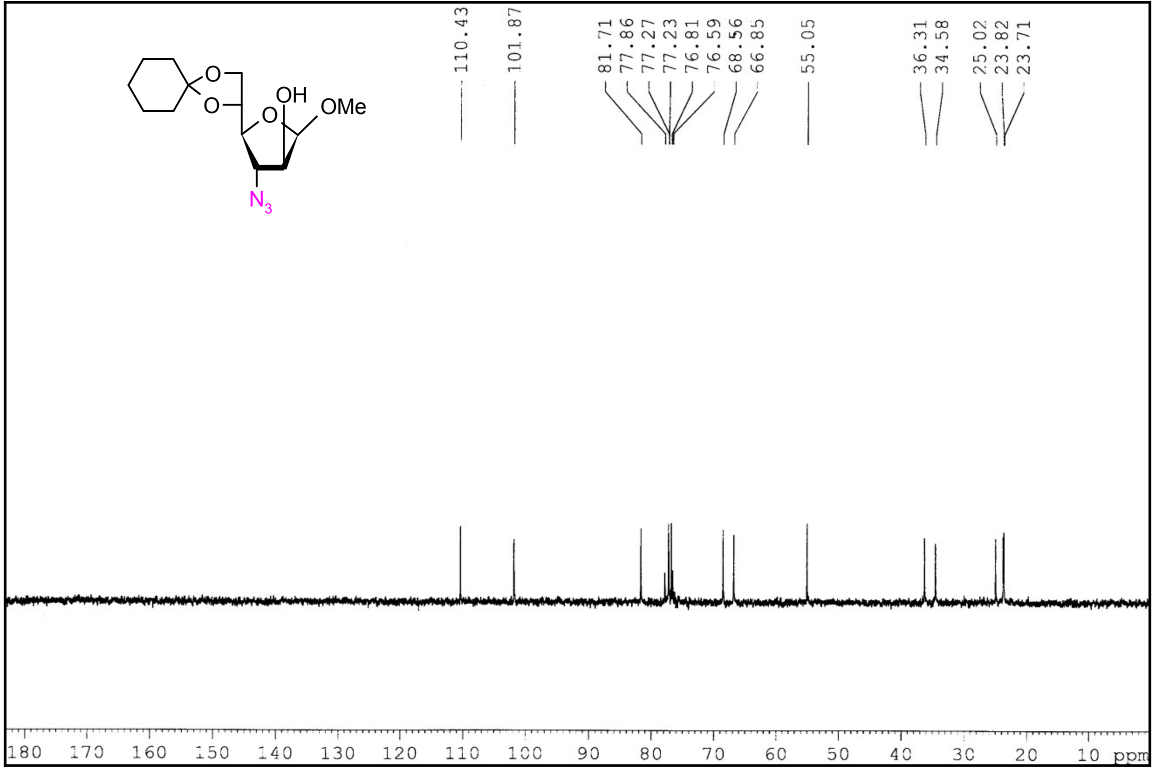
DEPT spectrum of 20a



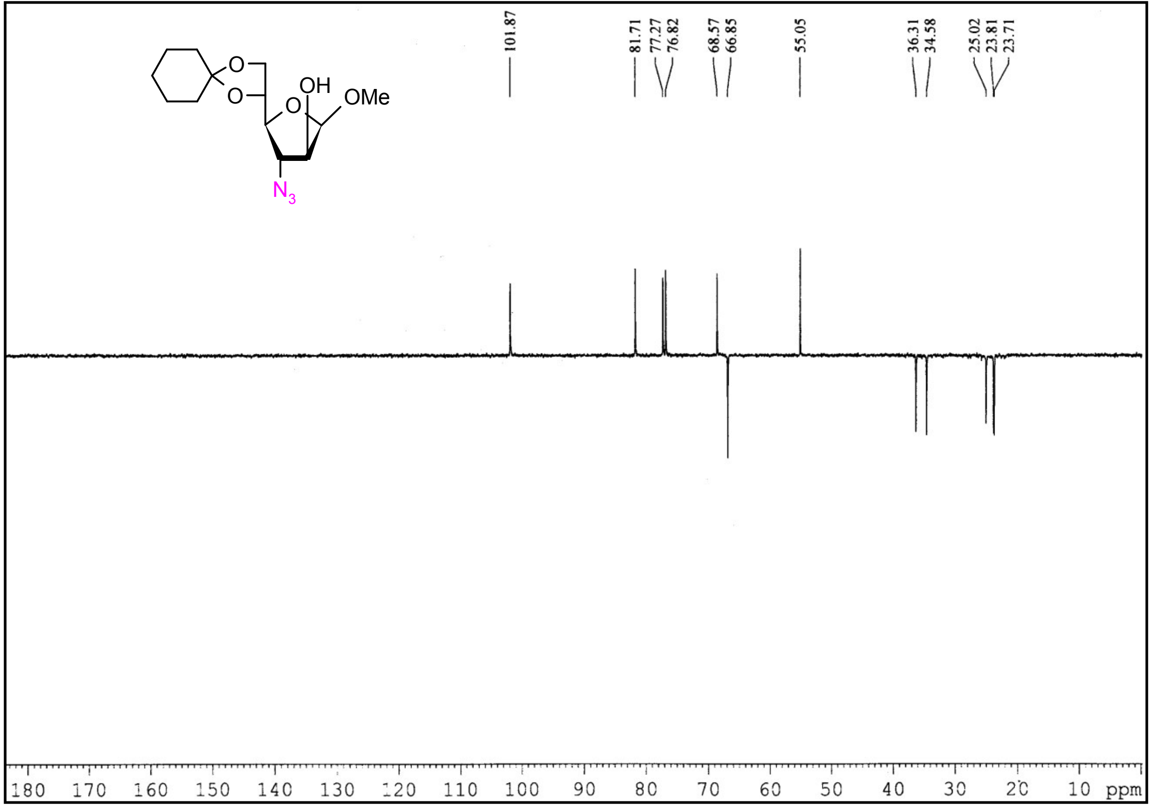
^{1}H NMR spectrum of 20b



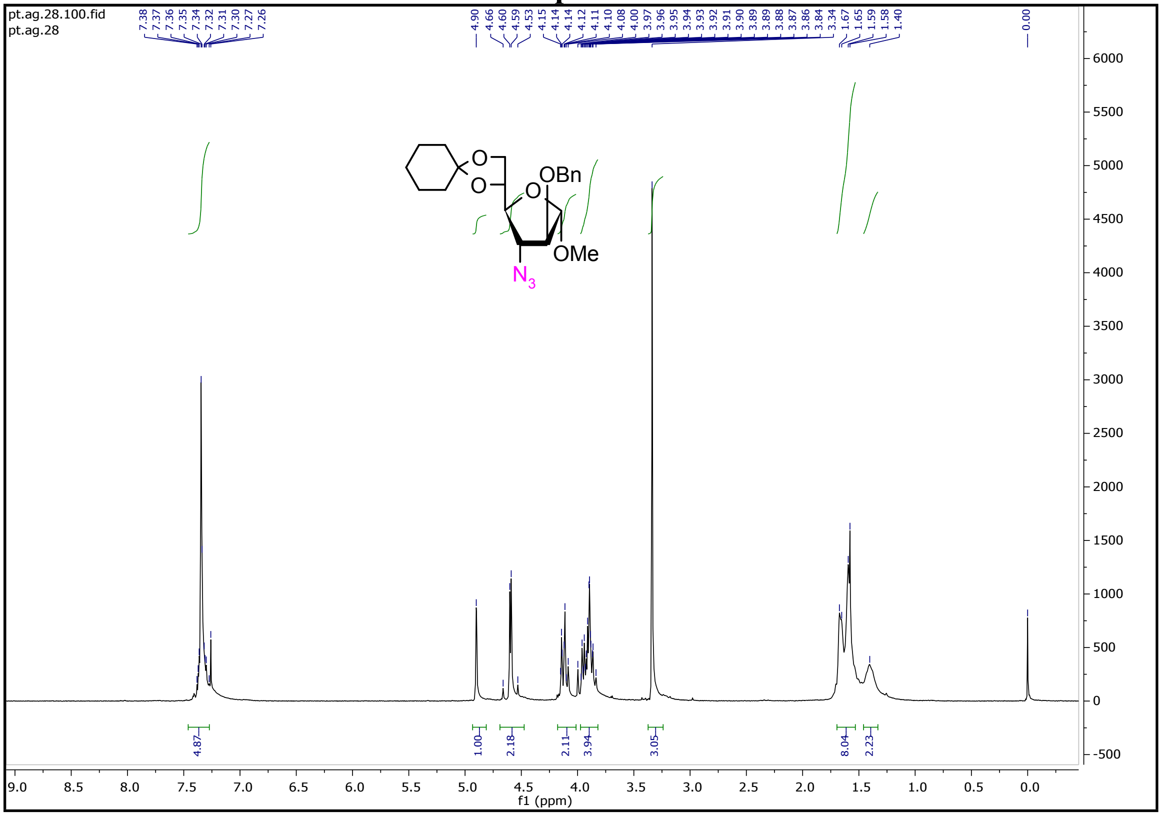
^{13}C NMR spectrum of 20b



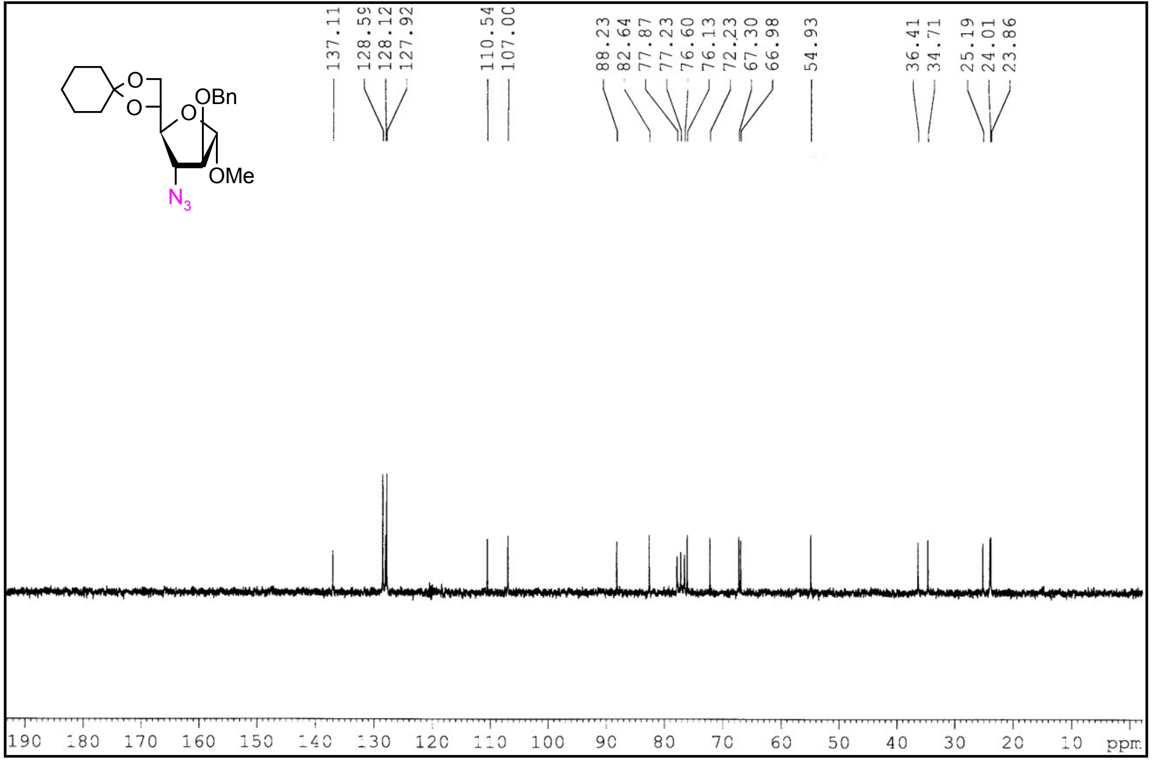
DEPT spectrum of 20b



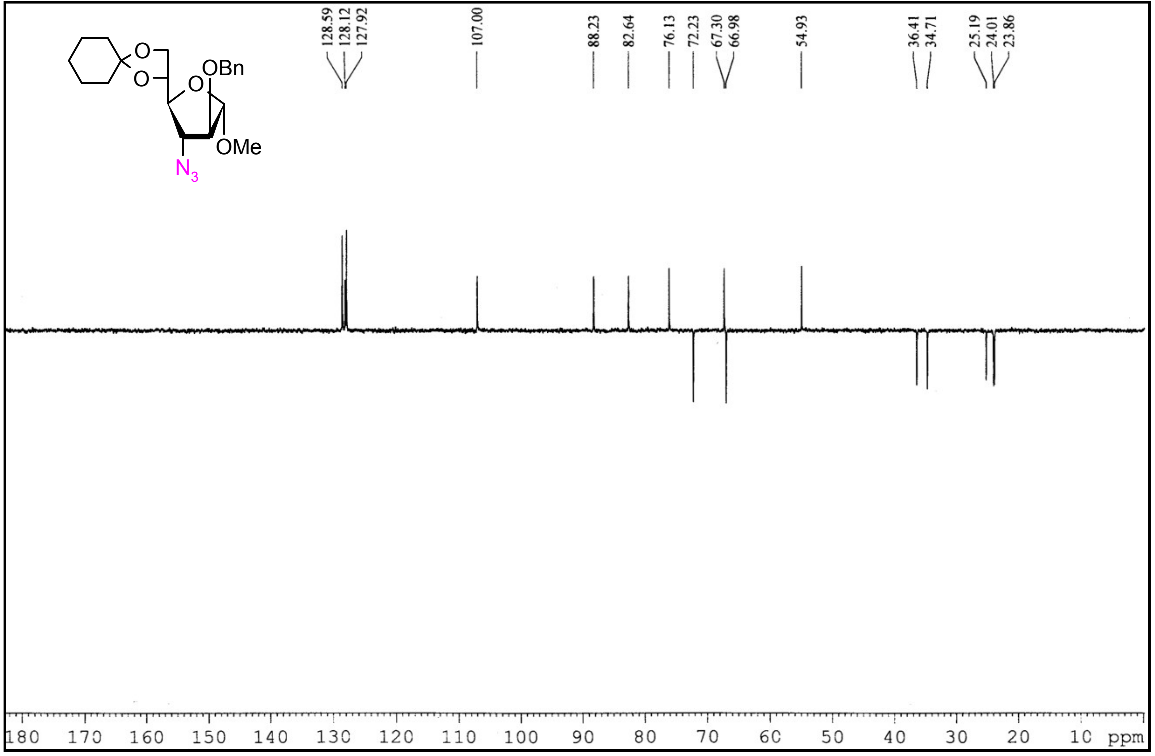
^{1}H NMR spectrum of 14



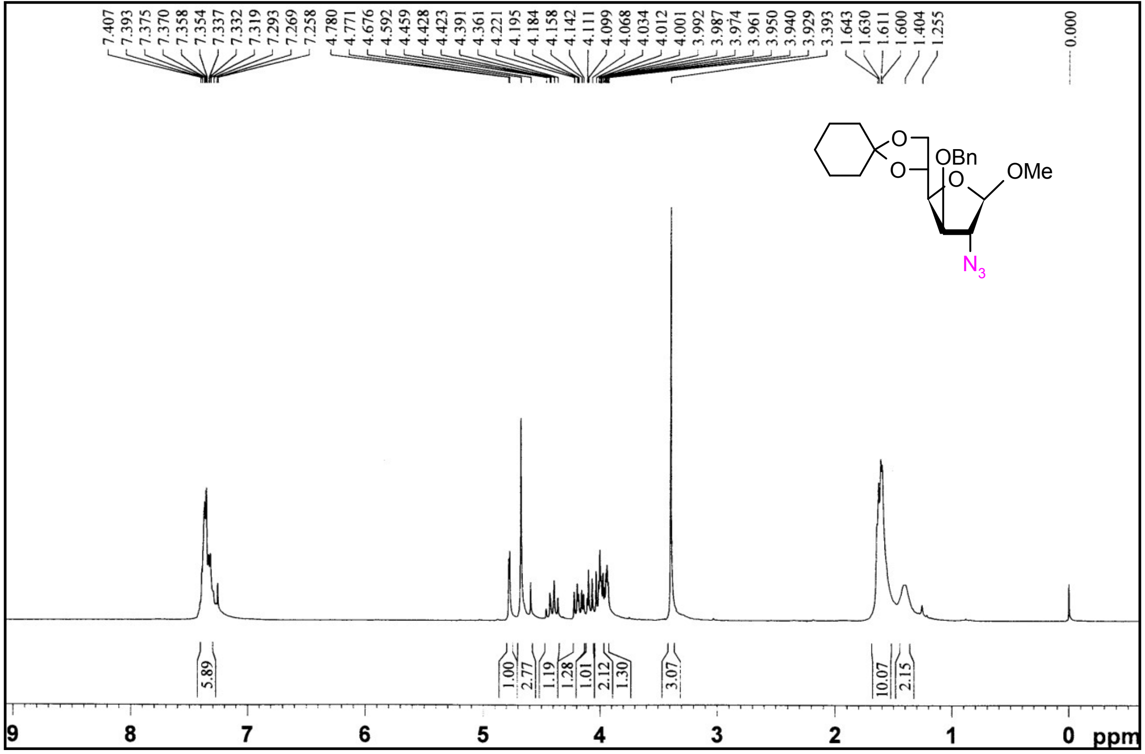
^{13}C NMR spectrum of 14



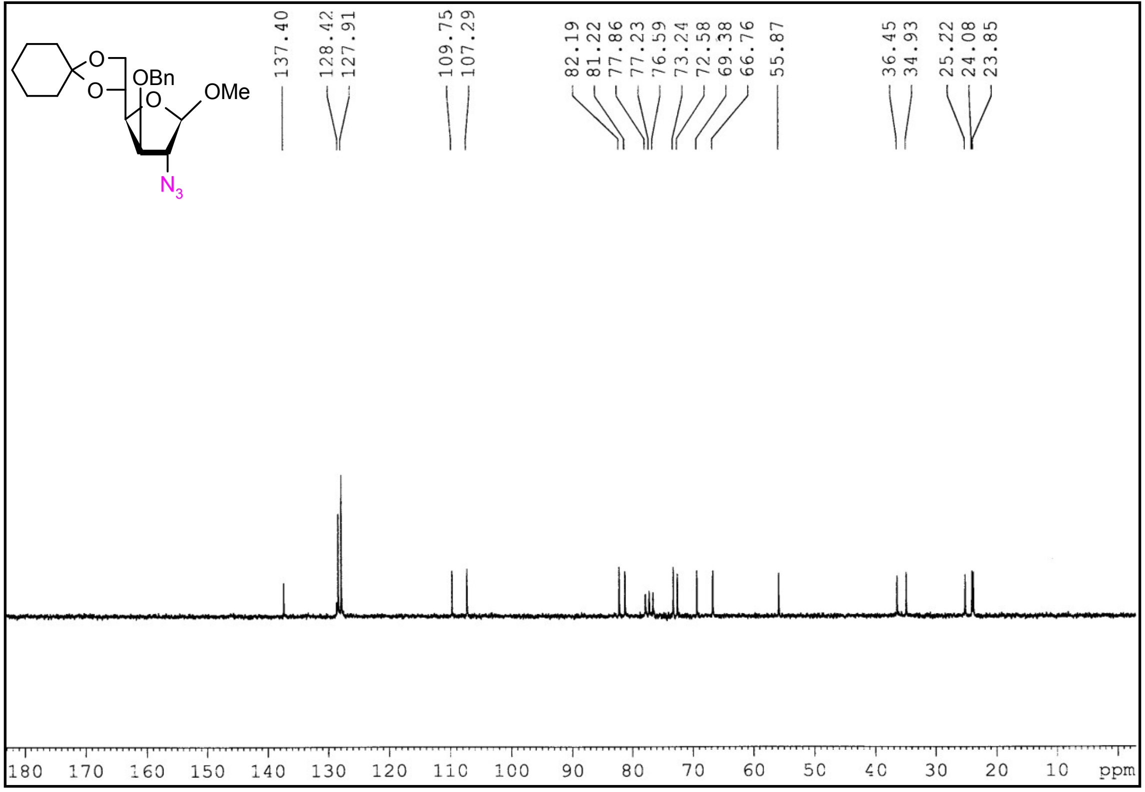
DEPT spectrum of 14



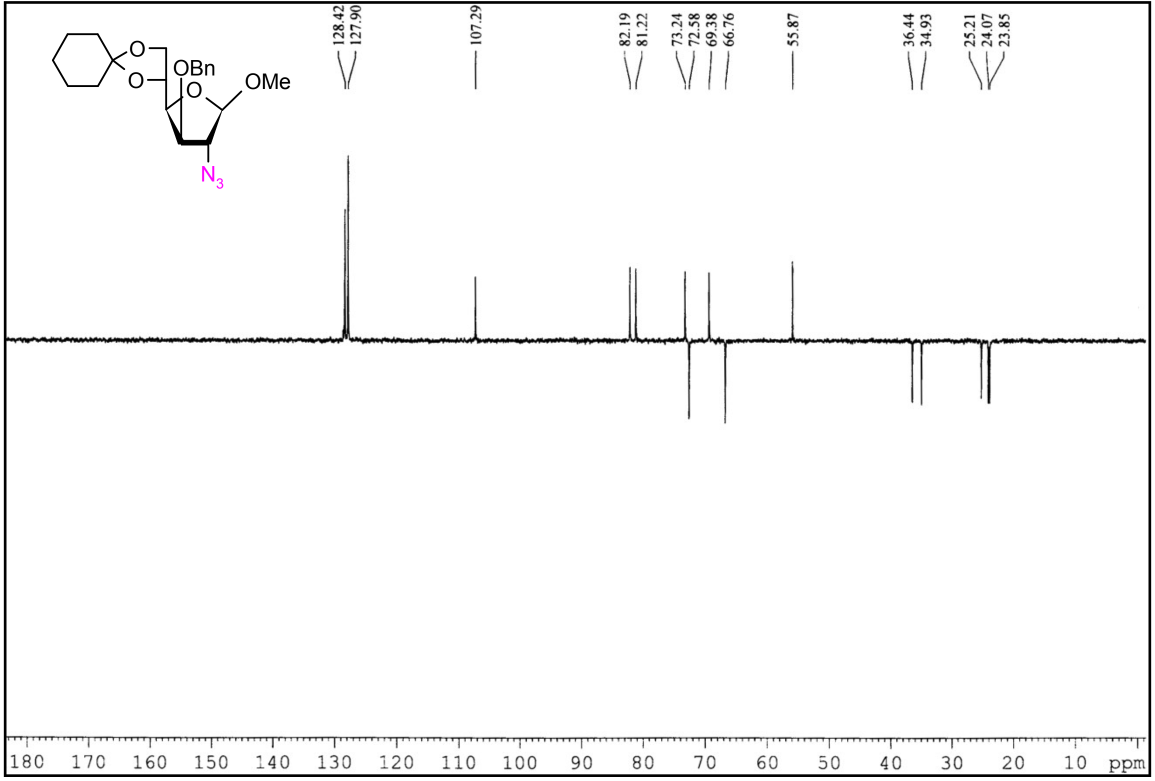
^{1}H NMR spectrum of 21a



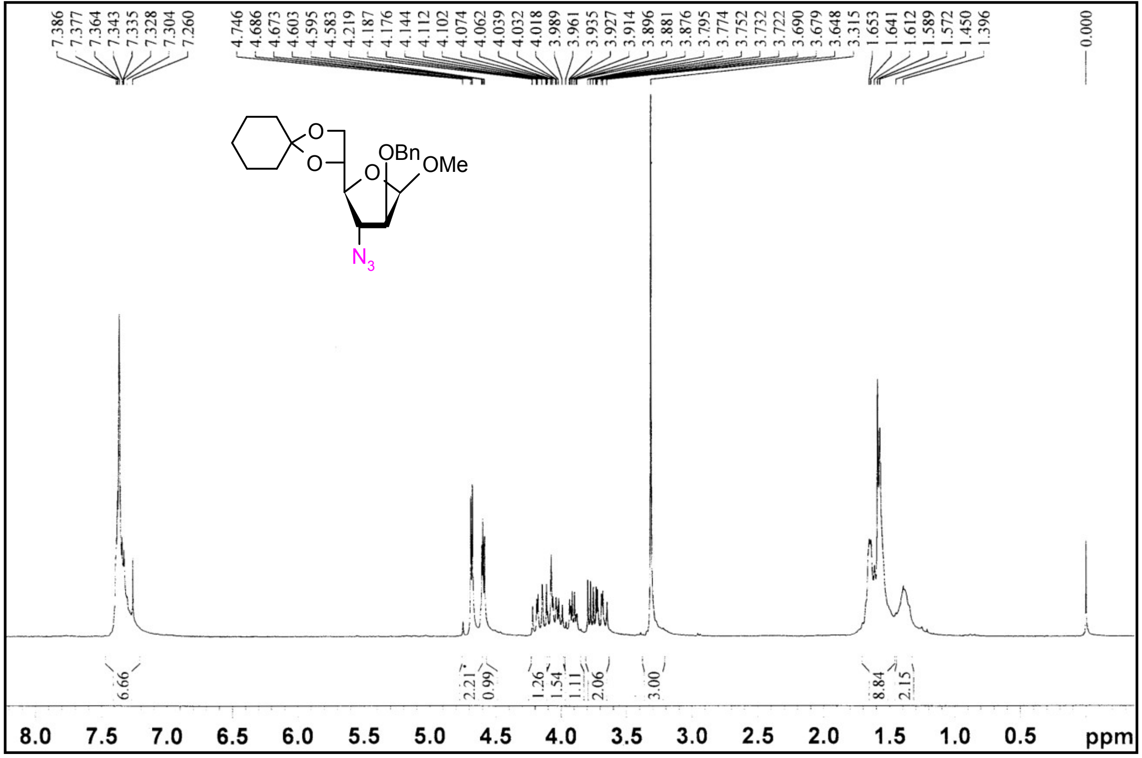
^{13}C NMR spectrum of 21a



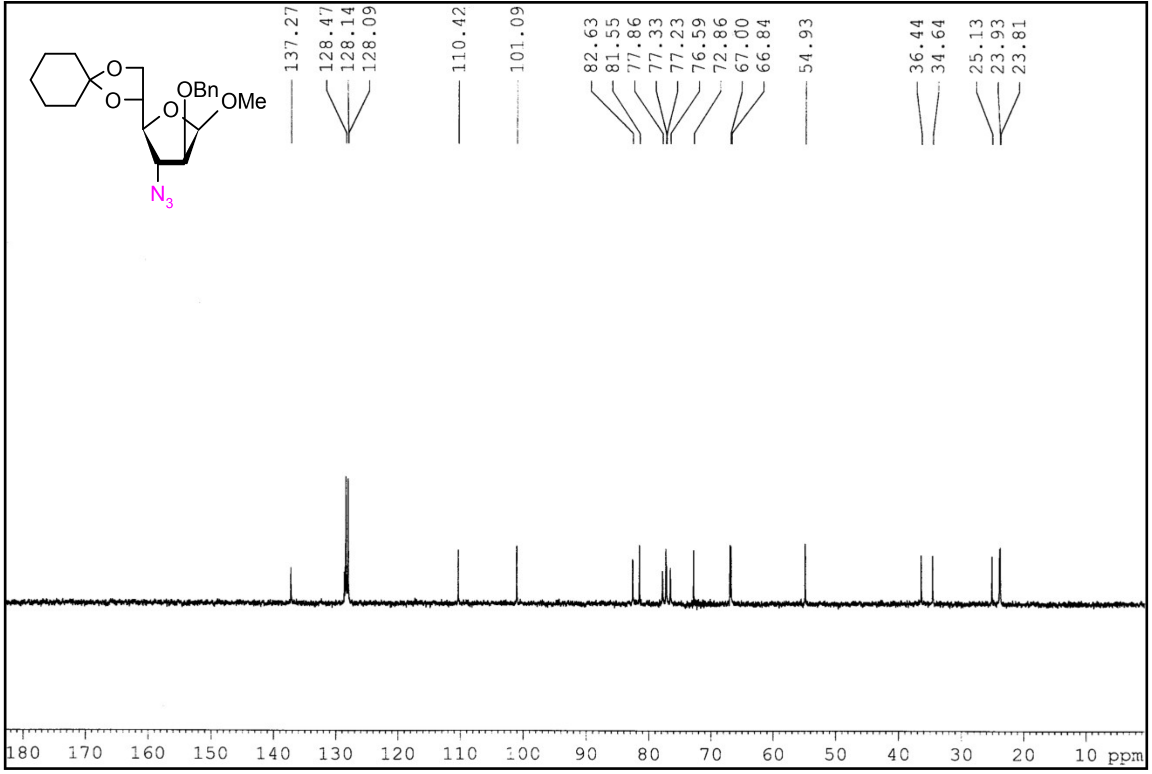
DEPT spectrum of 21a



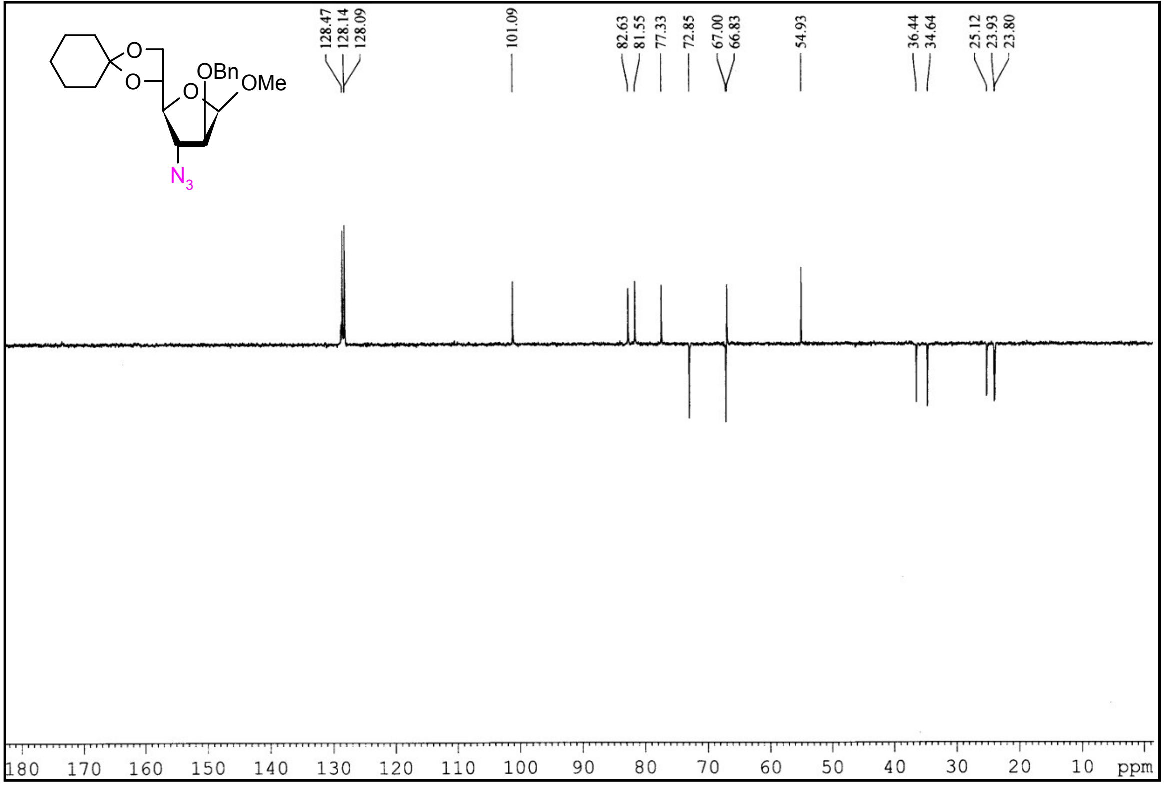
^{1}H NMR spectrum of 21b



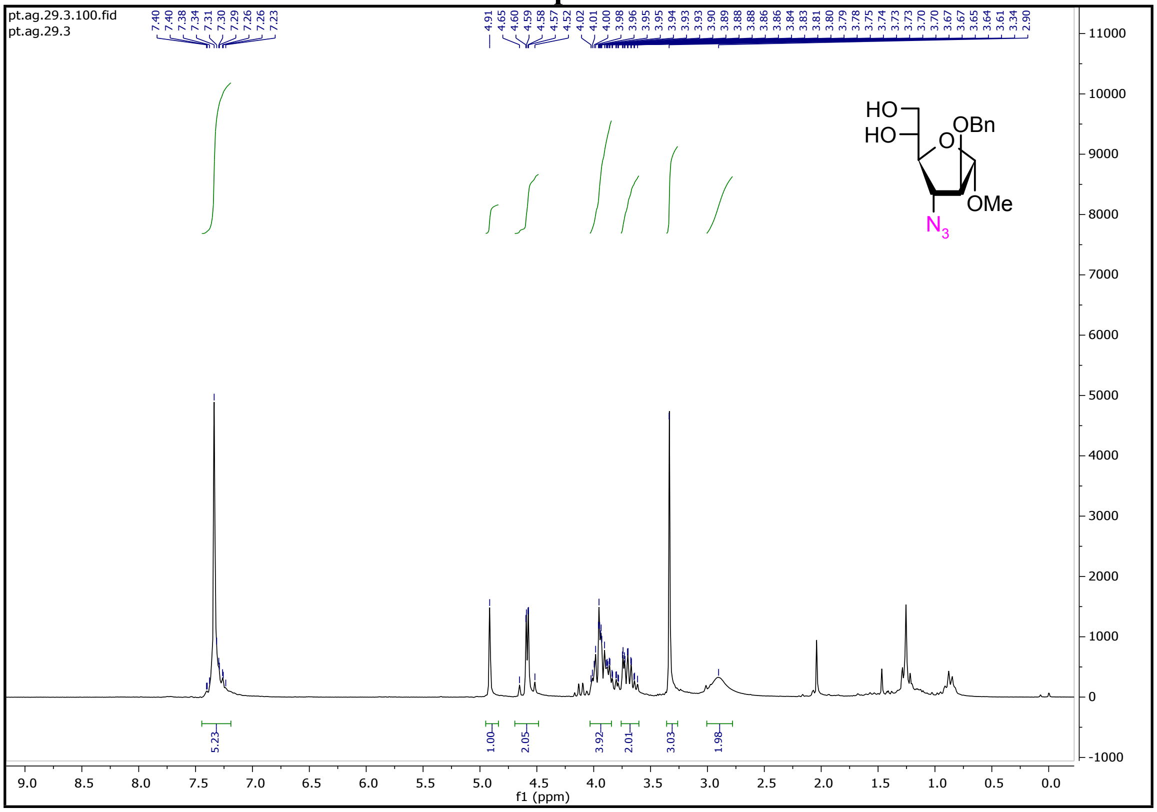
^{13}C NMR spectrum of 21b



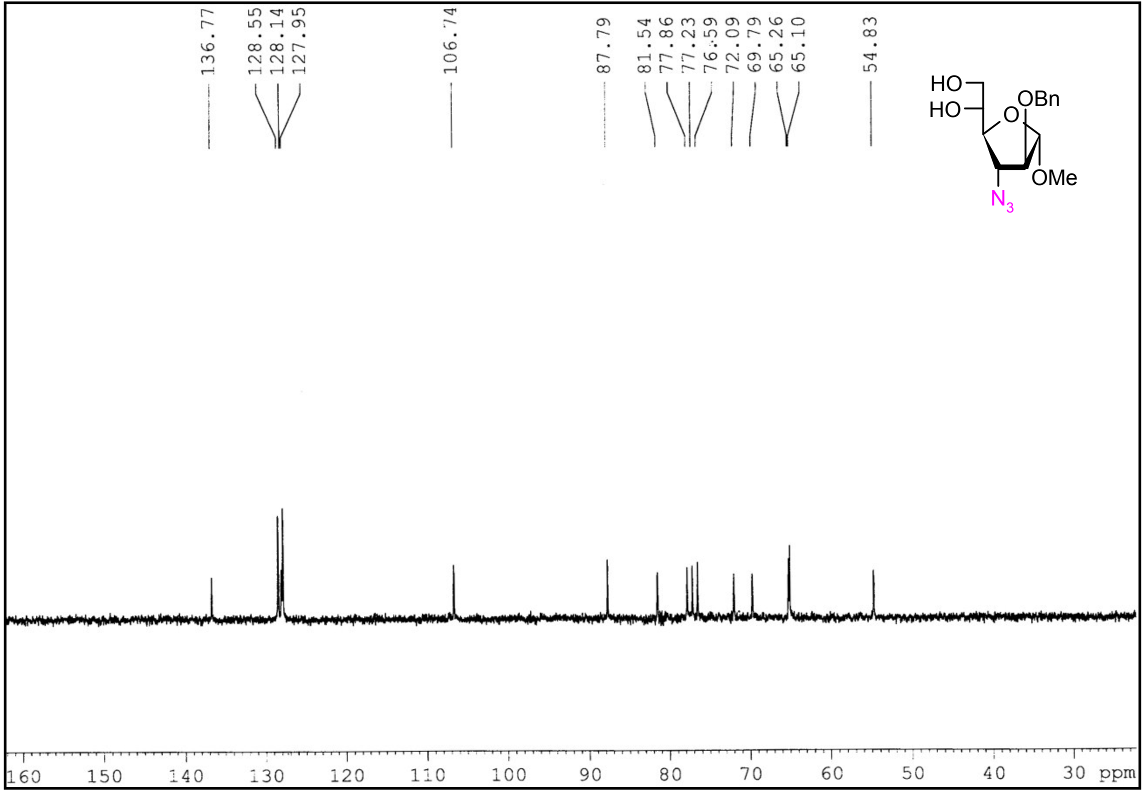
DEPT spectrum of 21b



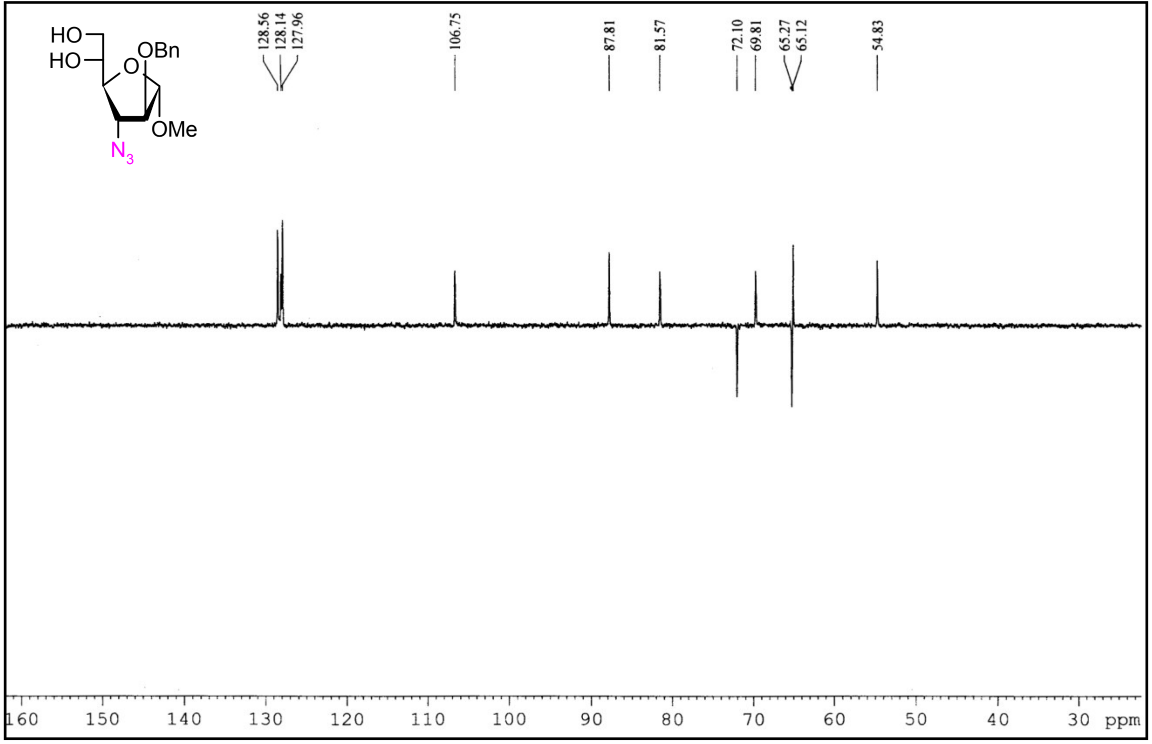
^{1}H NMR spectrum of 15



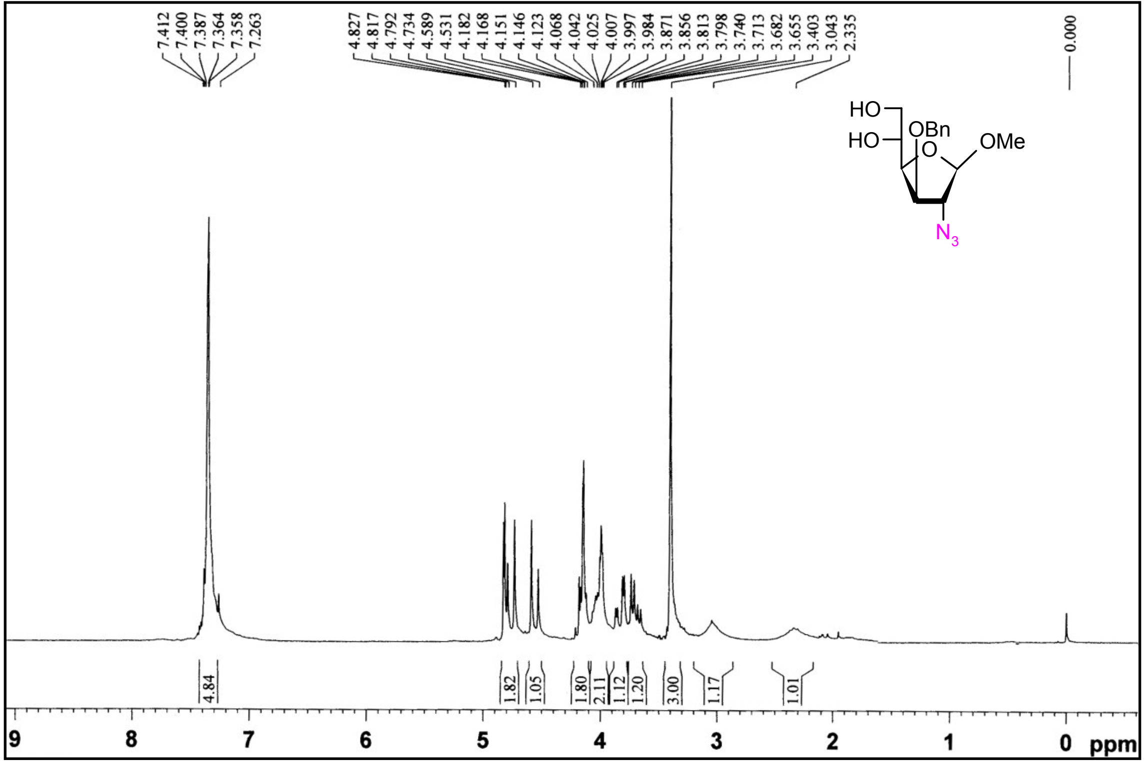
^{13}C NMR spectrum of 15



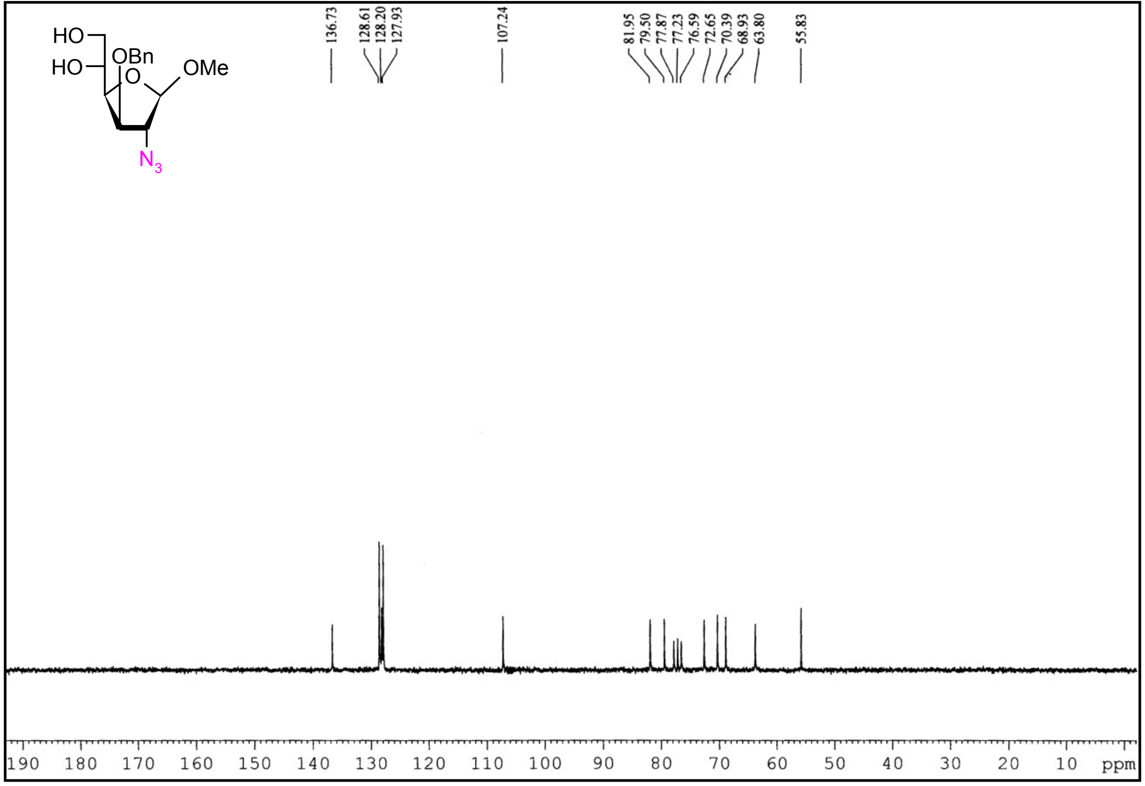
DEPT spectrum of 15



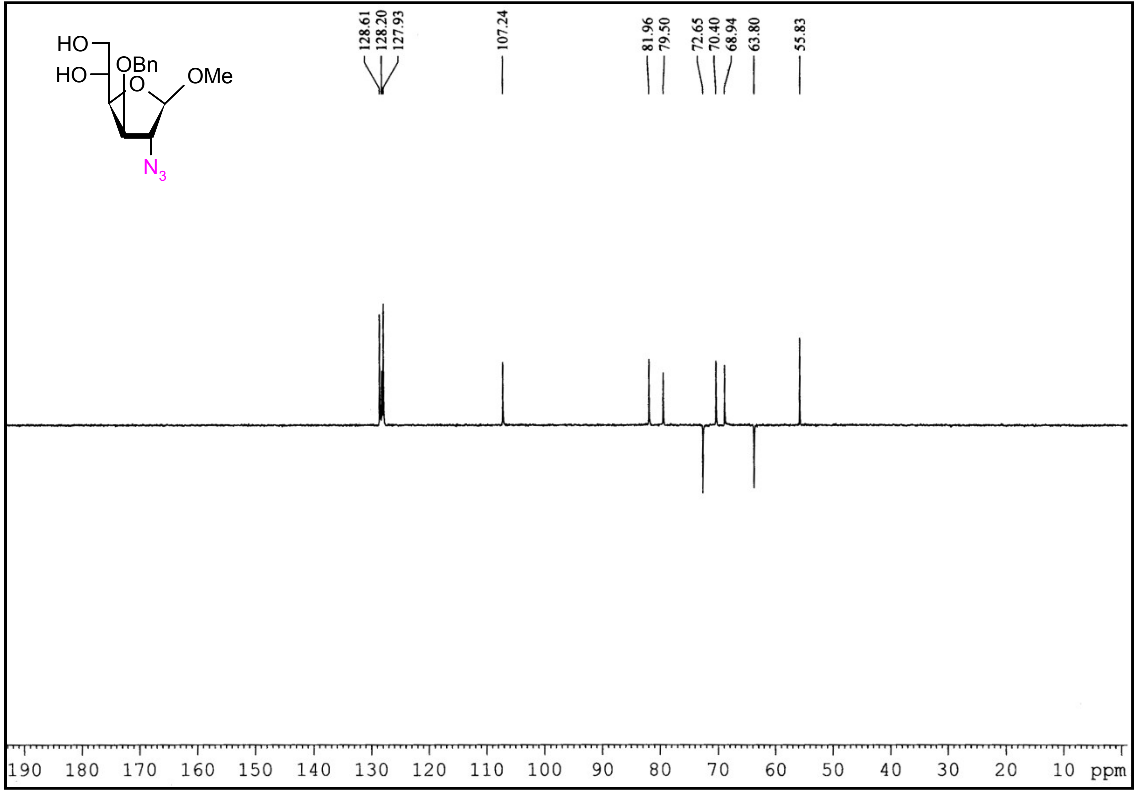
^{1}H NMR spectrum of 22a



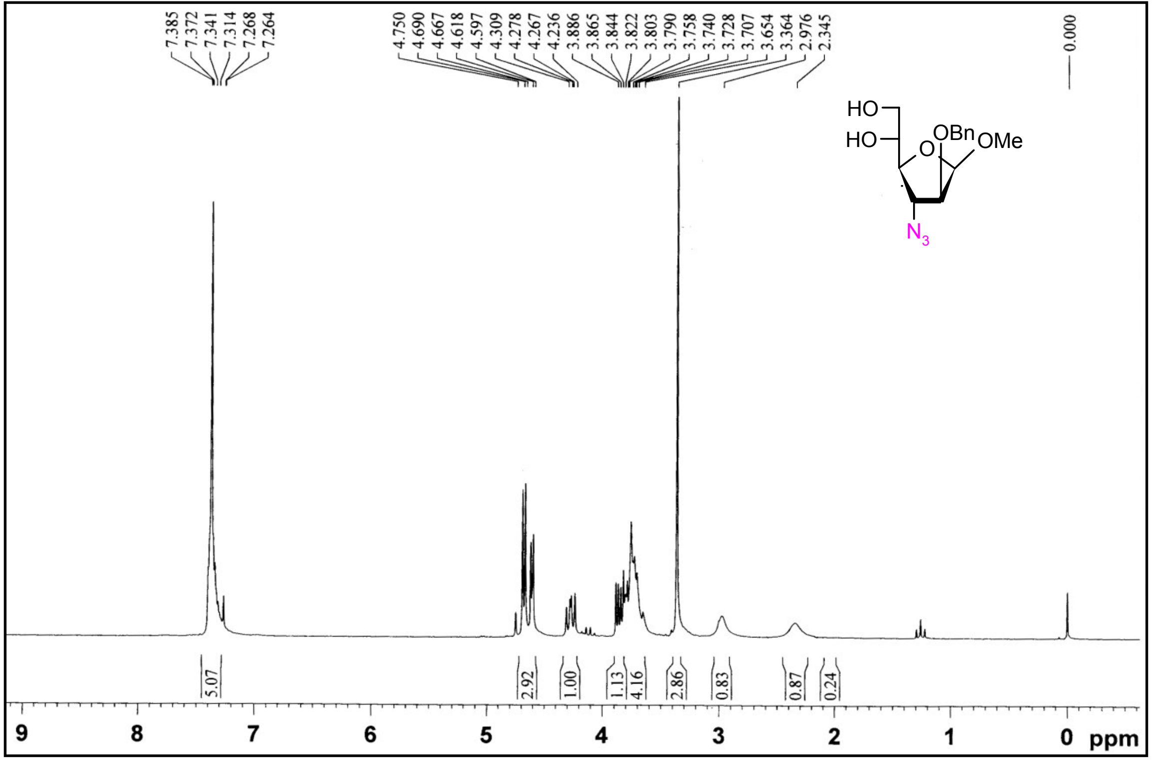
^{13}C NMR spectrum of 22a



DEPT spectrum of 22a



^{1}H NMR spectrum of 22b



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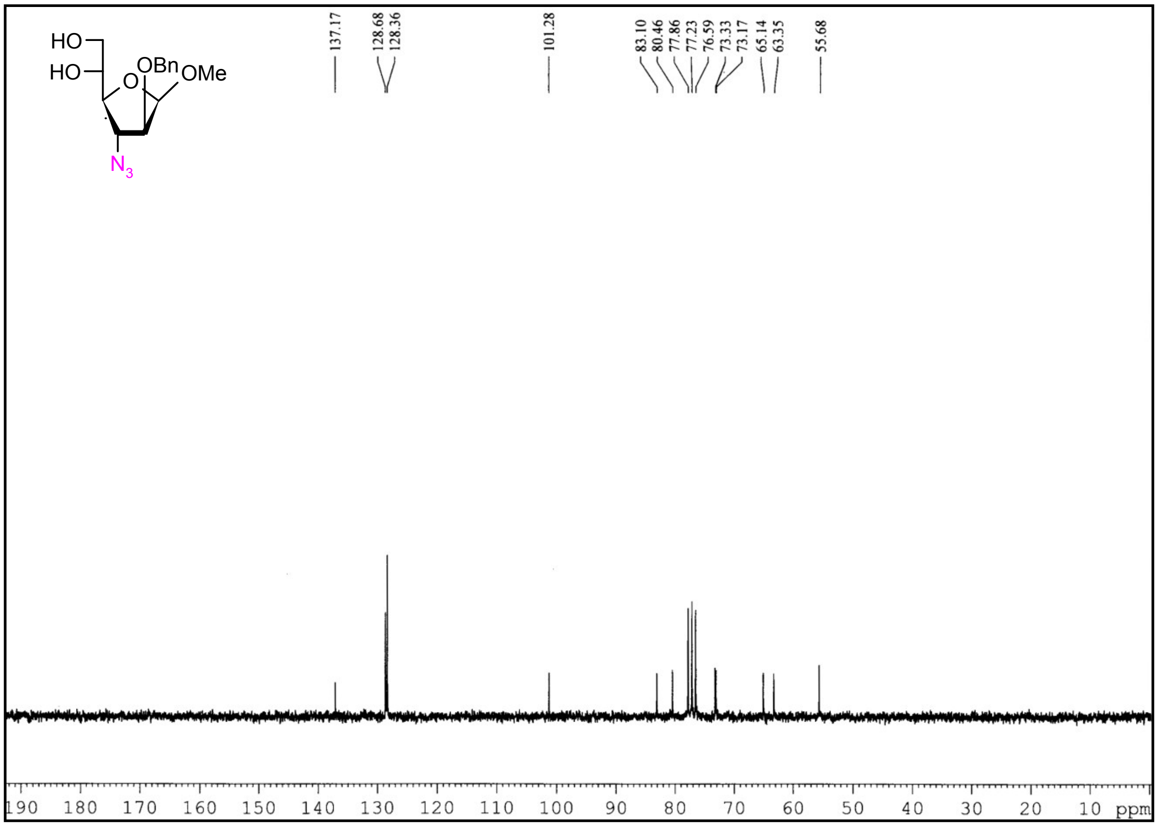
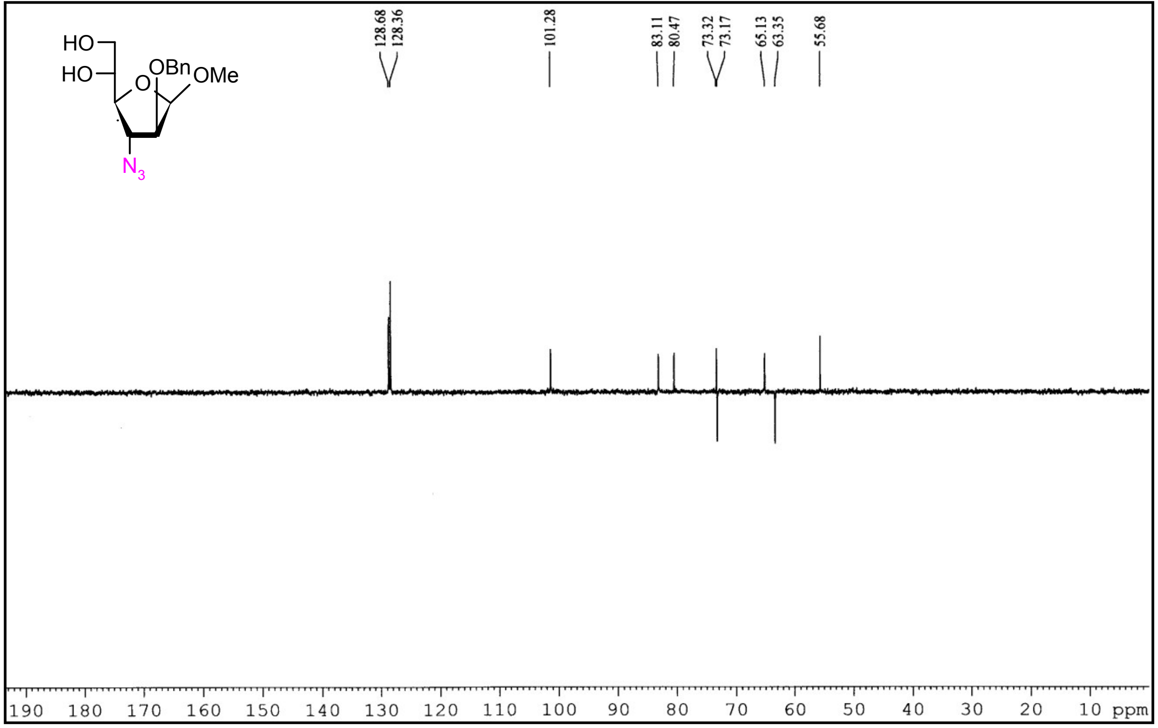
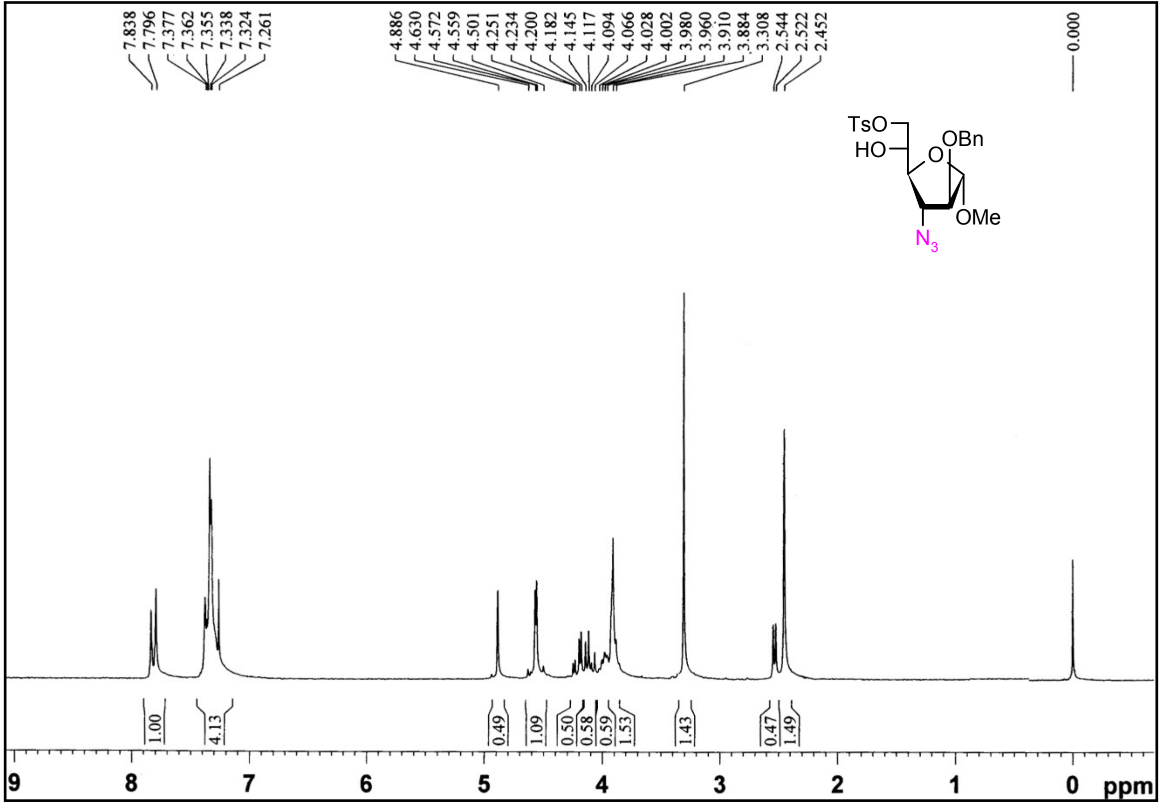


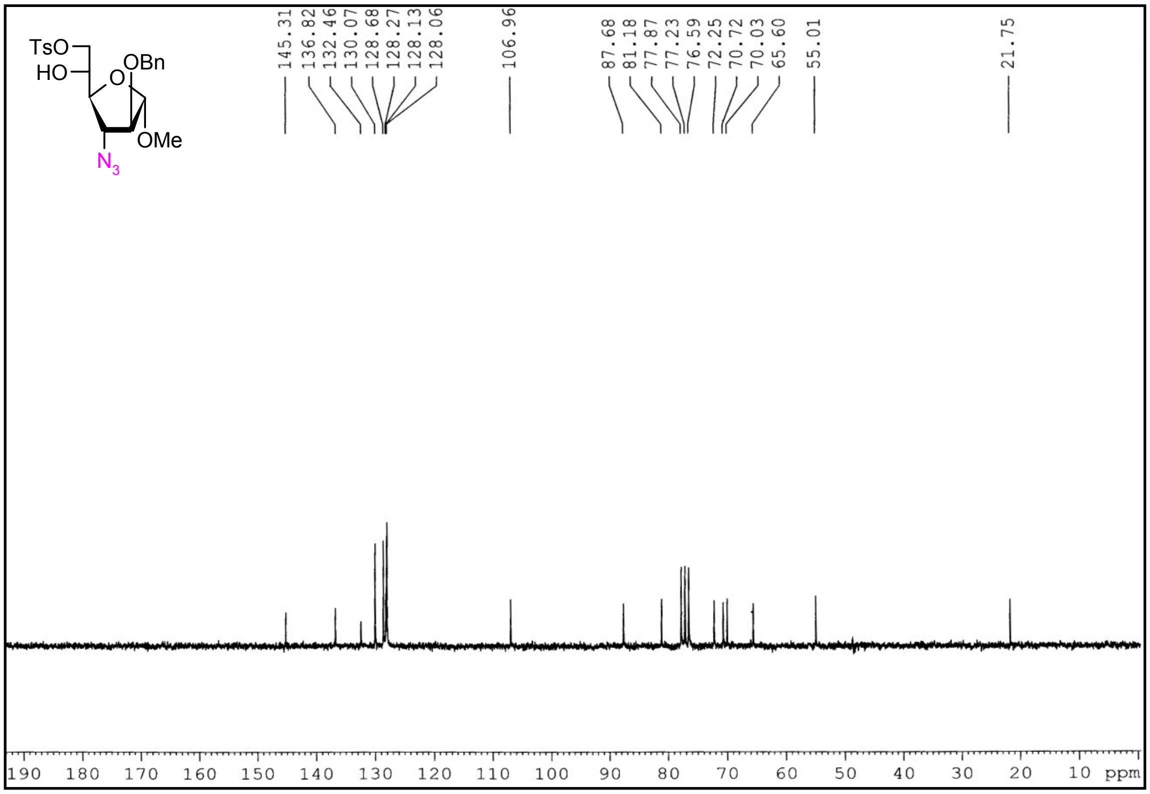
DEPT spectrum of 22b



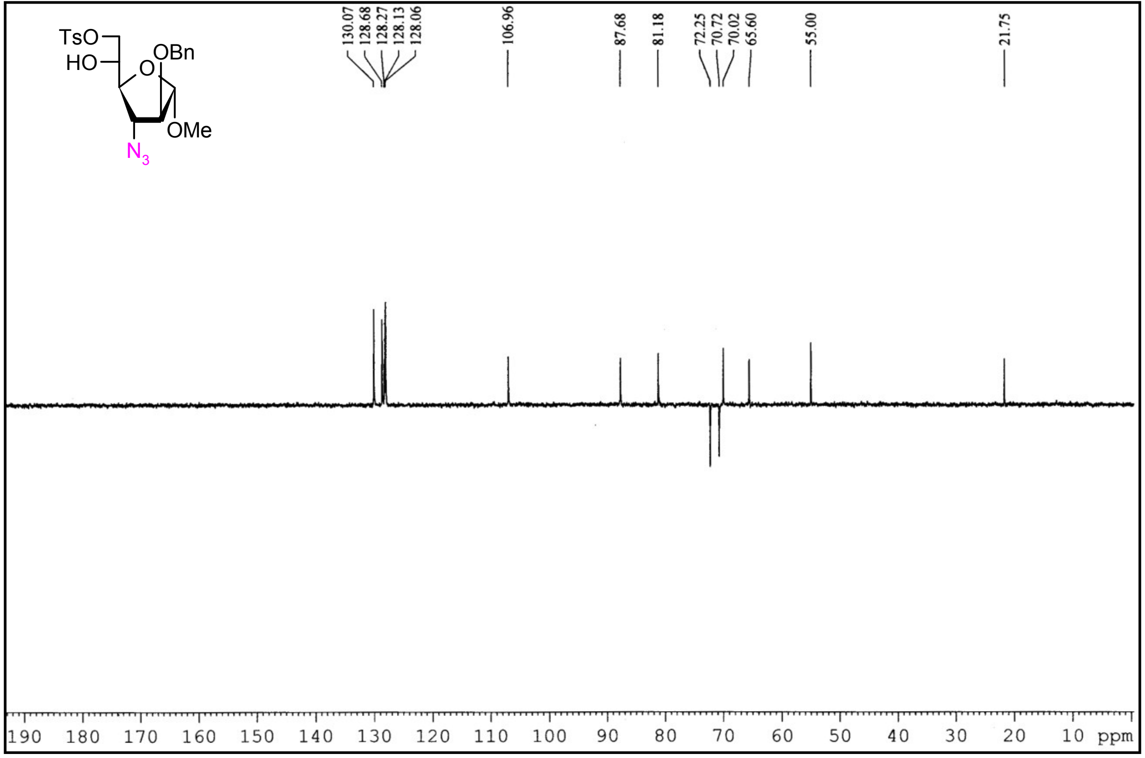
^{1}H NMR spectrum of 16



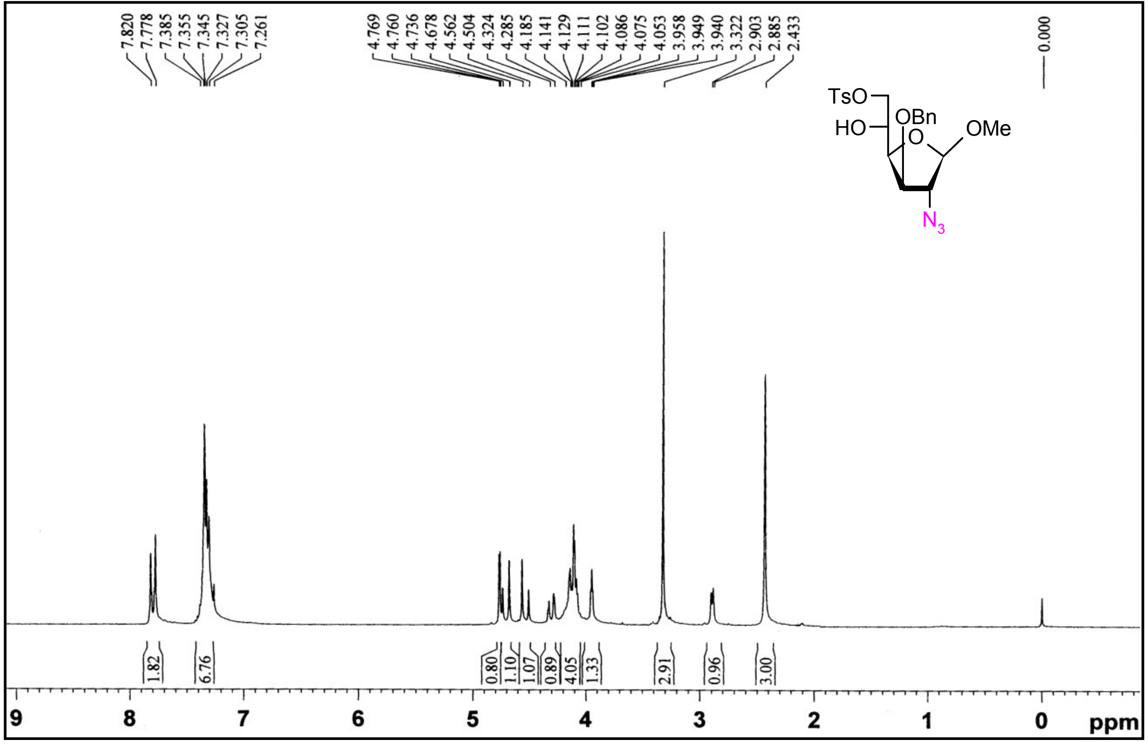
^{13}C NMR spectrum of 16



DEPT spectrum of 16



^{1}H NMR spectrum of 23a



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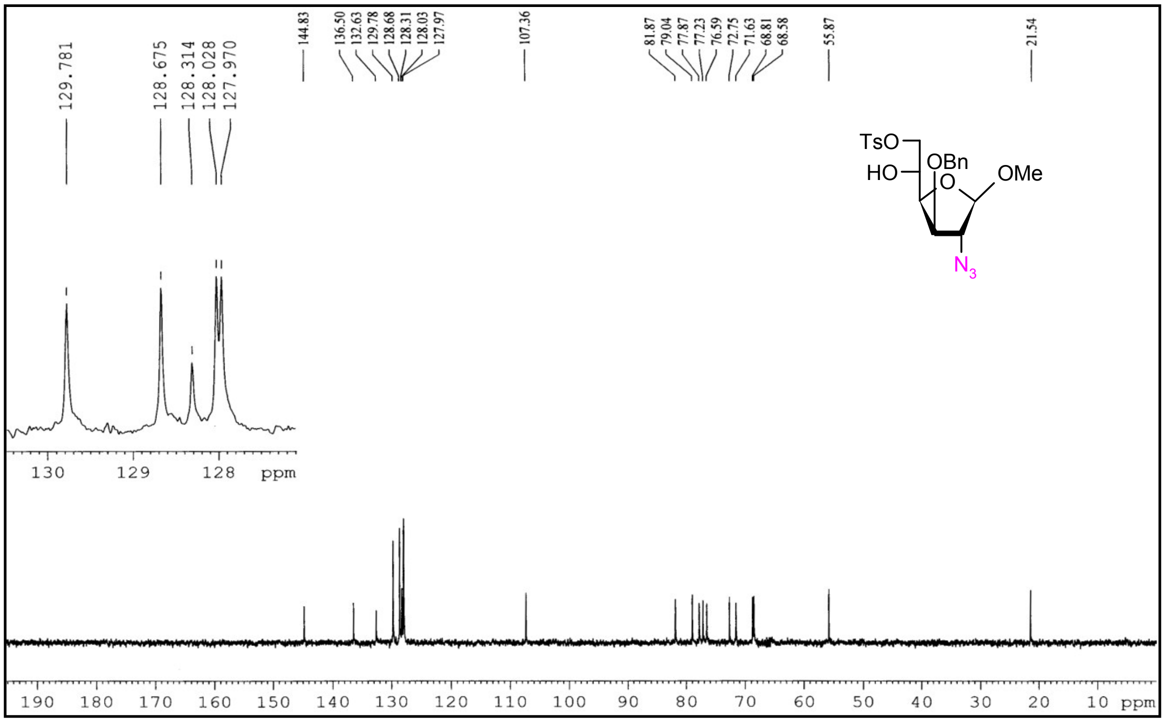
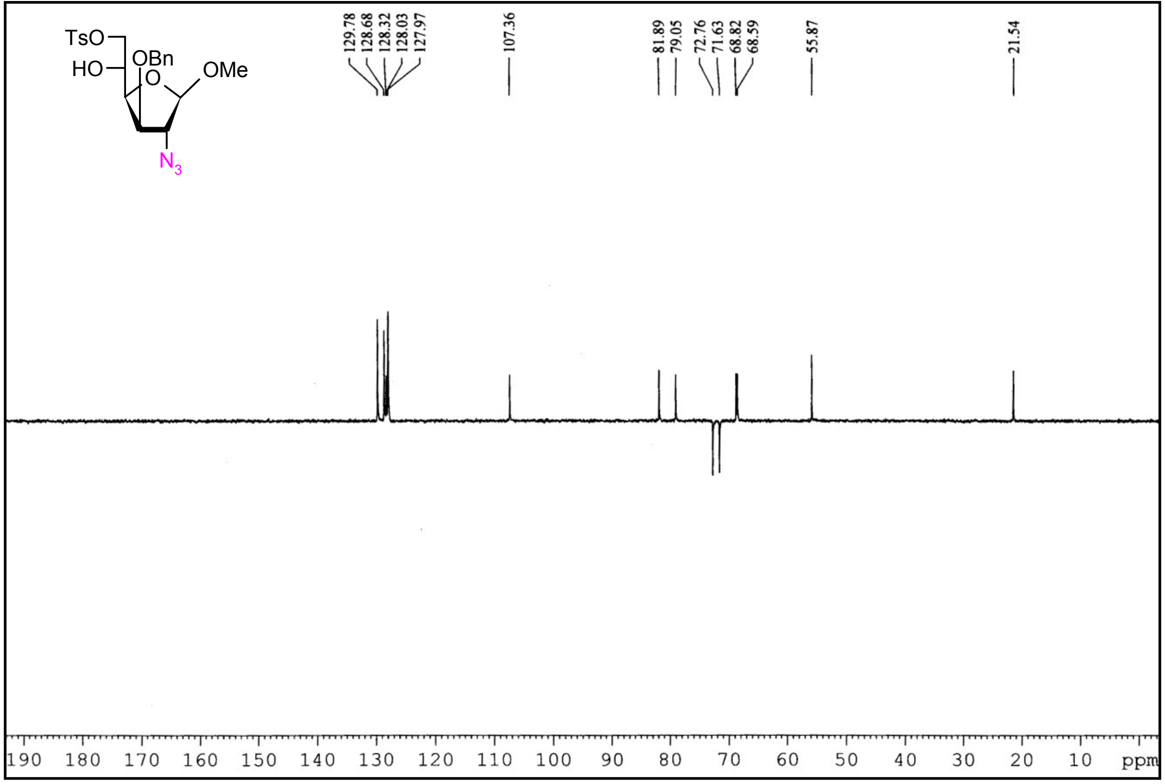


DEPT spectrum of 23a



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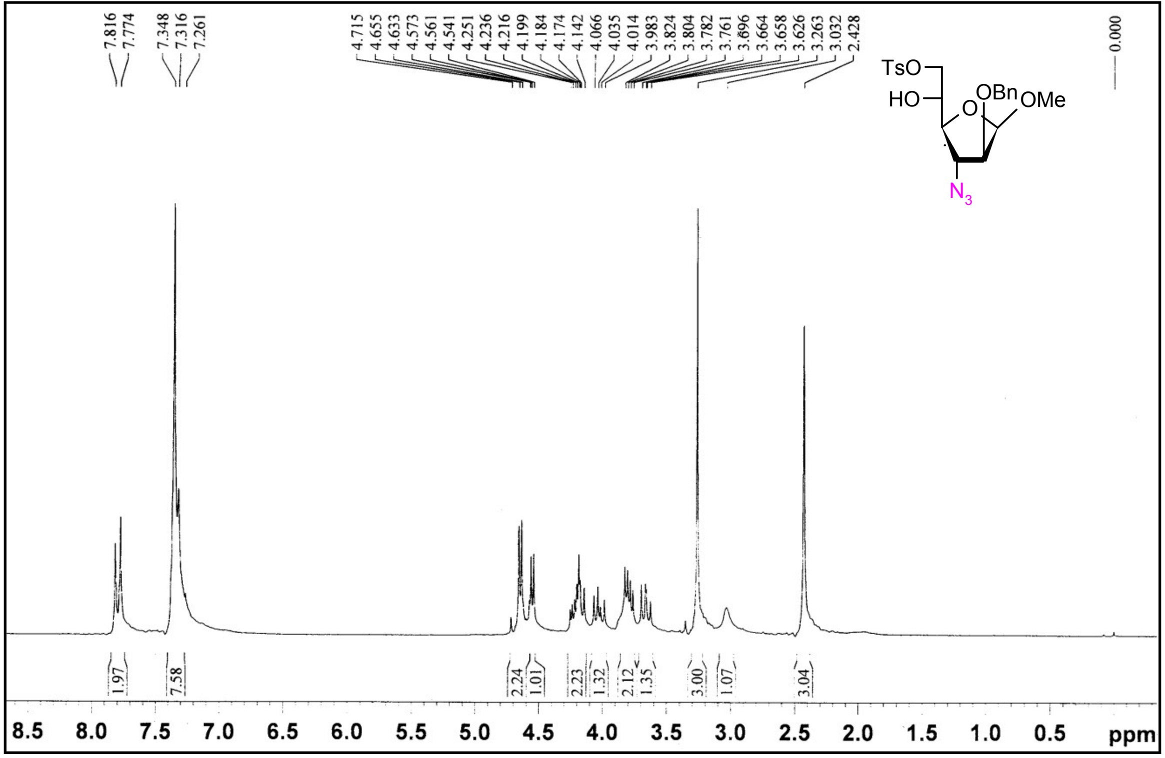

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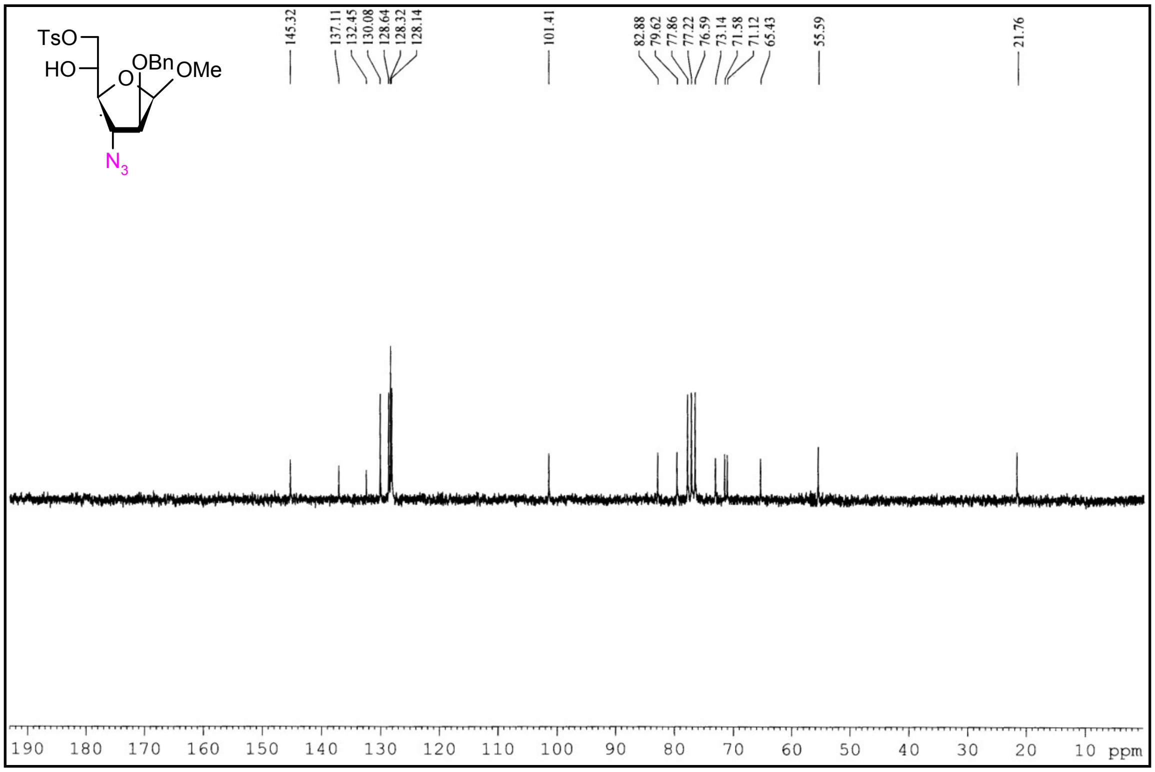
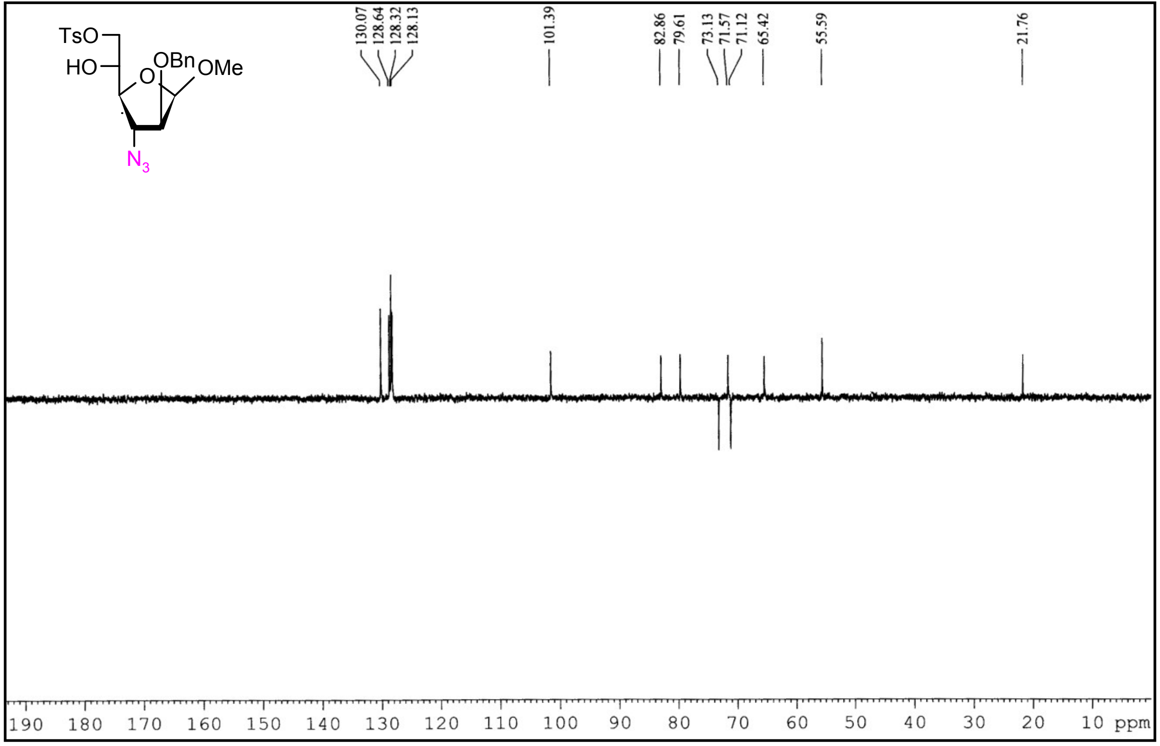


DEPT spectrum of 23b



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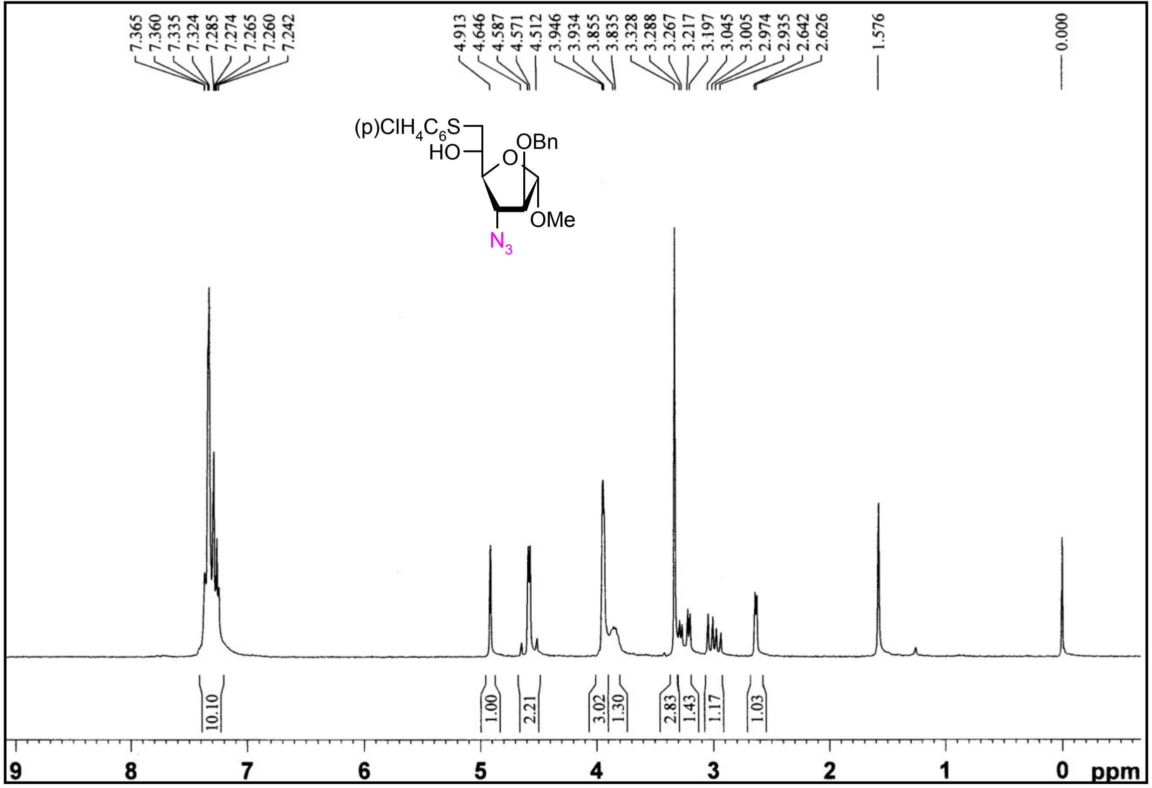

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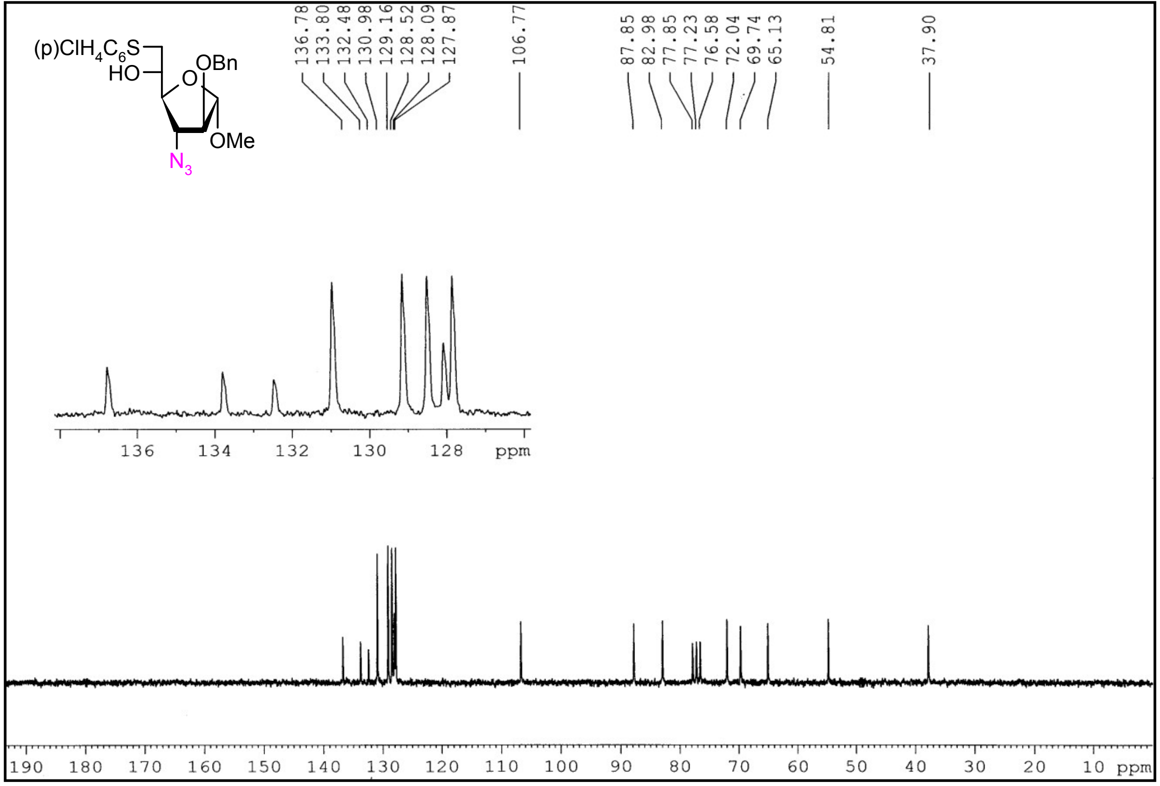
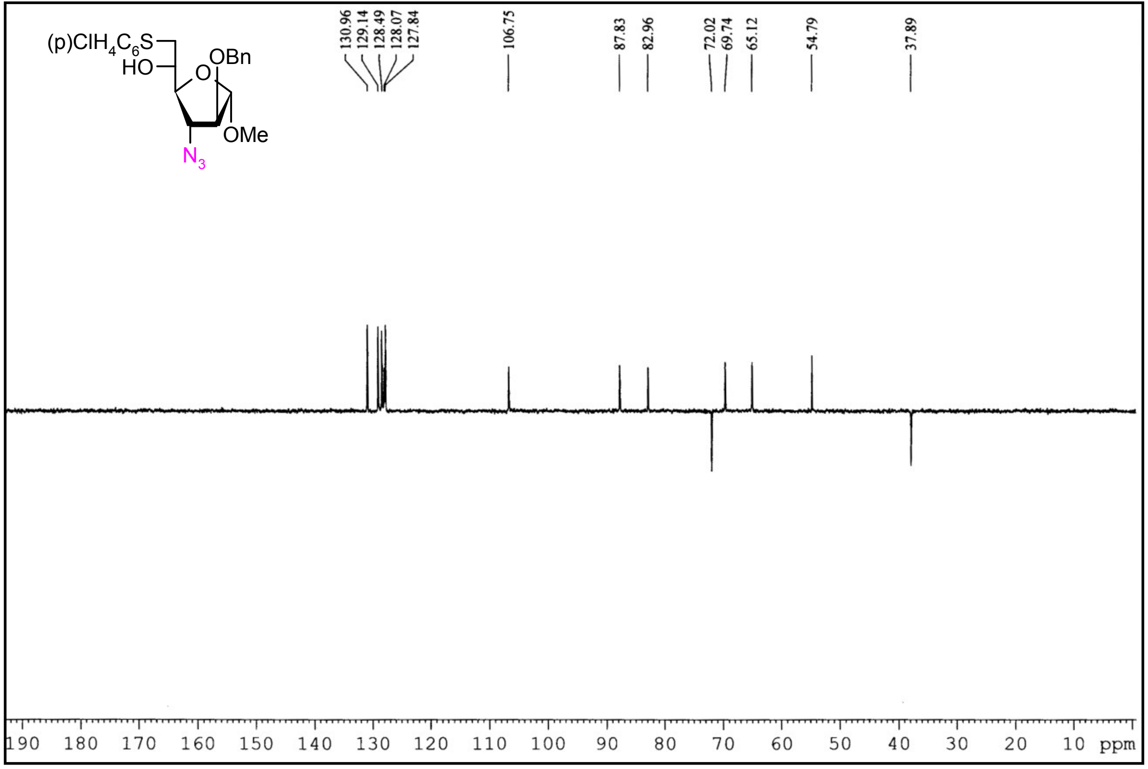
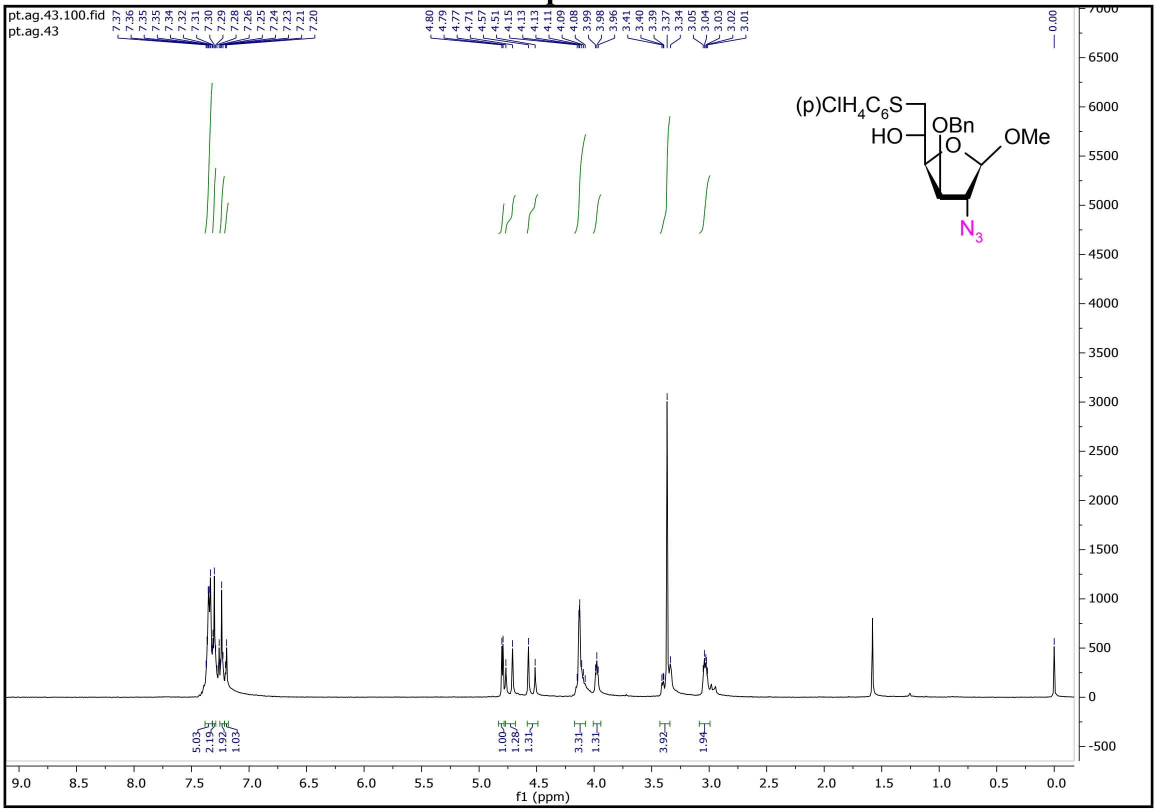


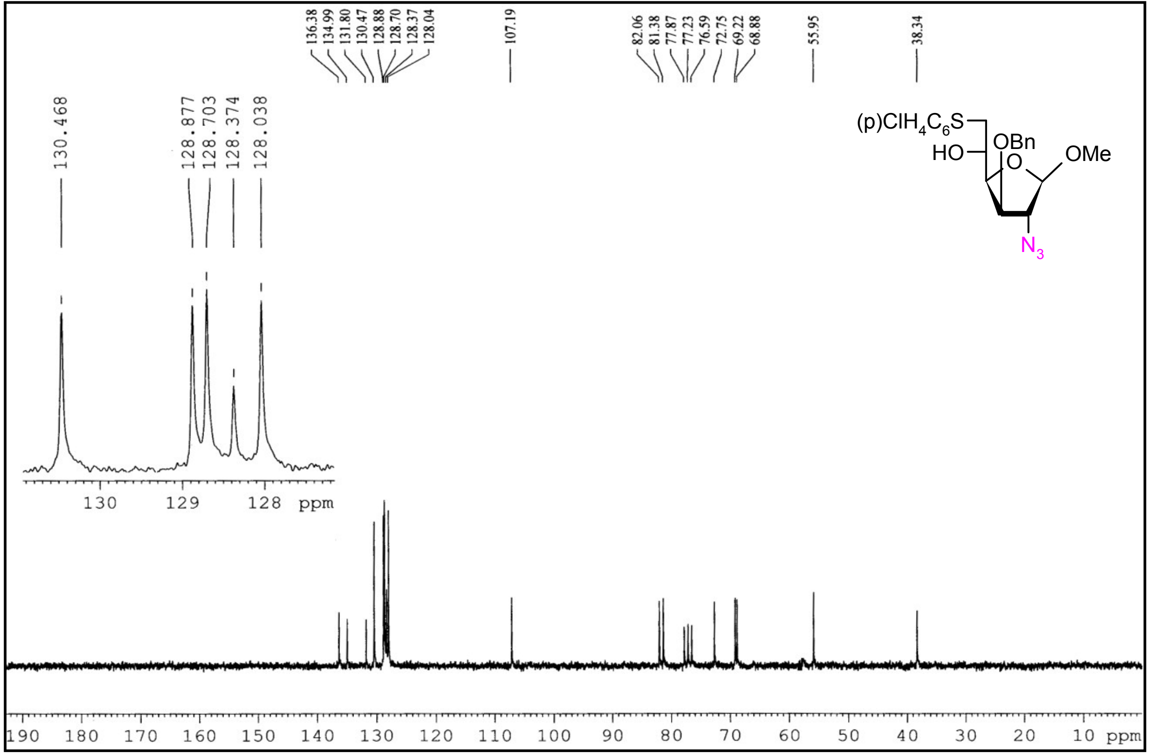
DEPT spectrum of 17



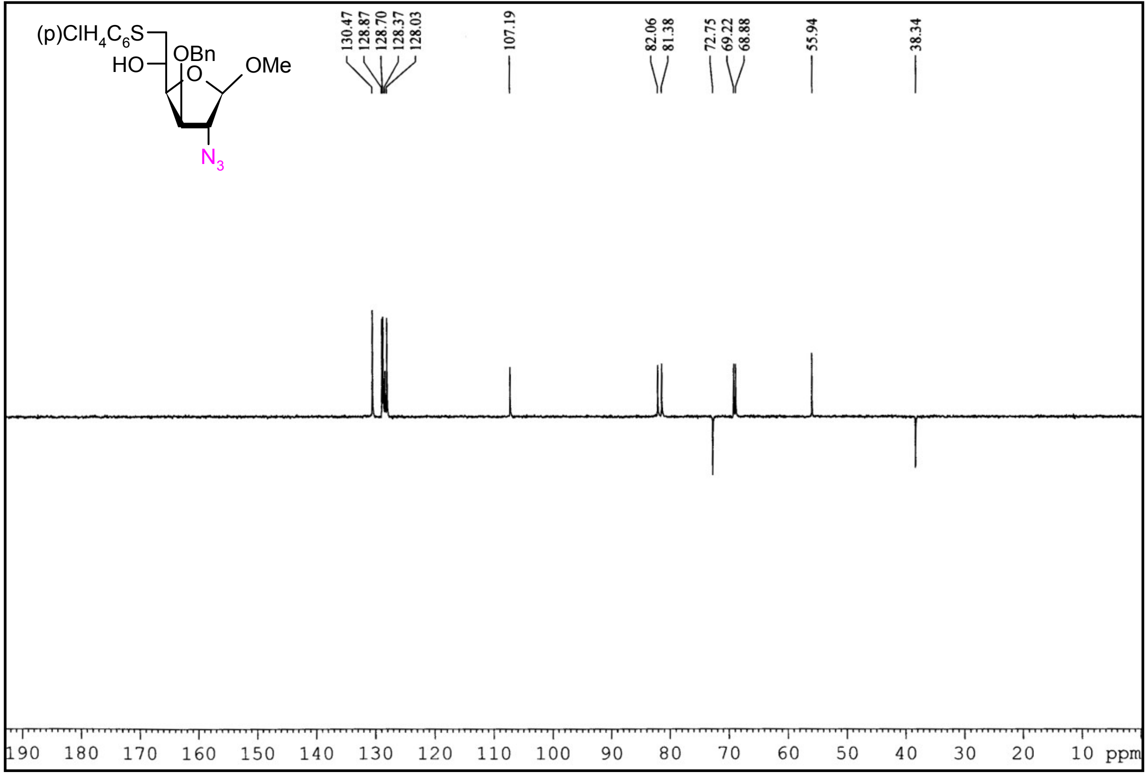
^{1}H NMR spectrum of 24a



^{13}C NMR spectrum of 24a



DEPT spectrum of 24a



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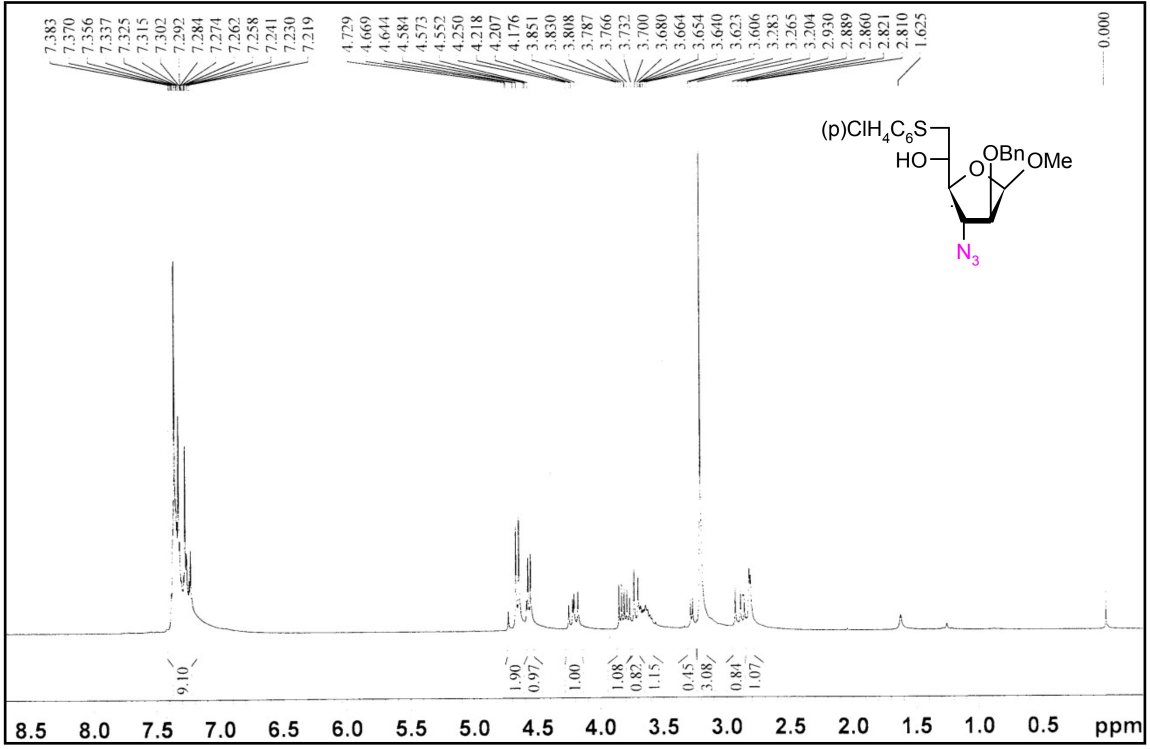

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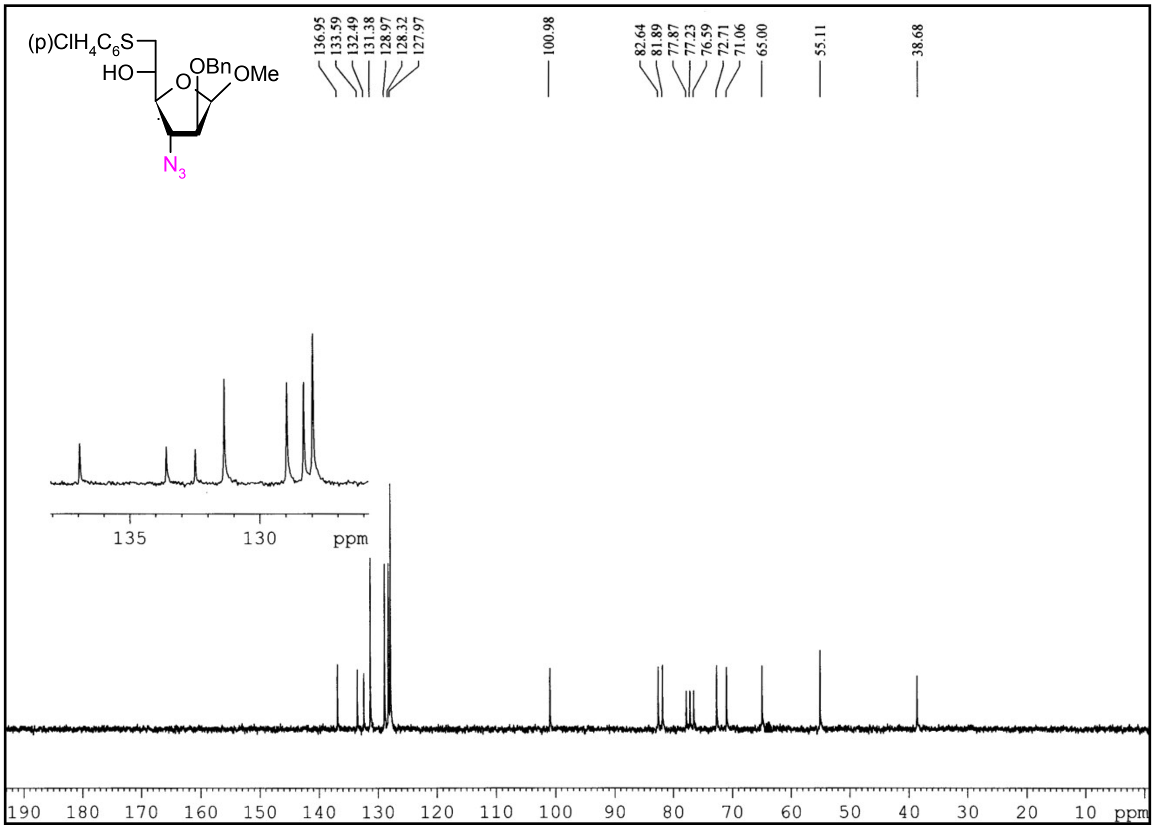
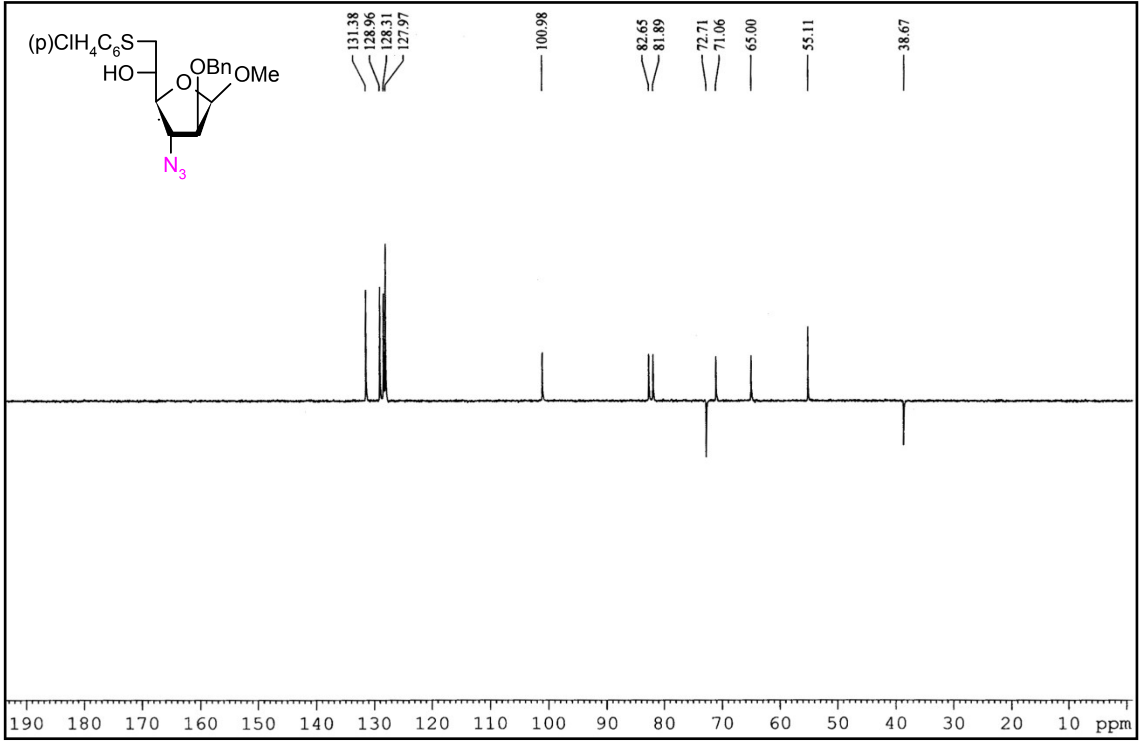
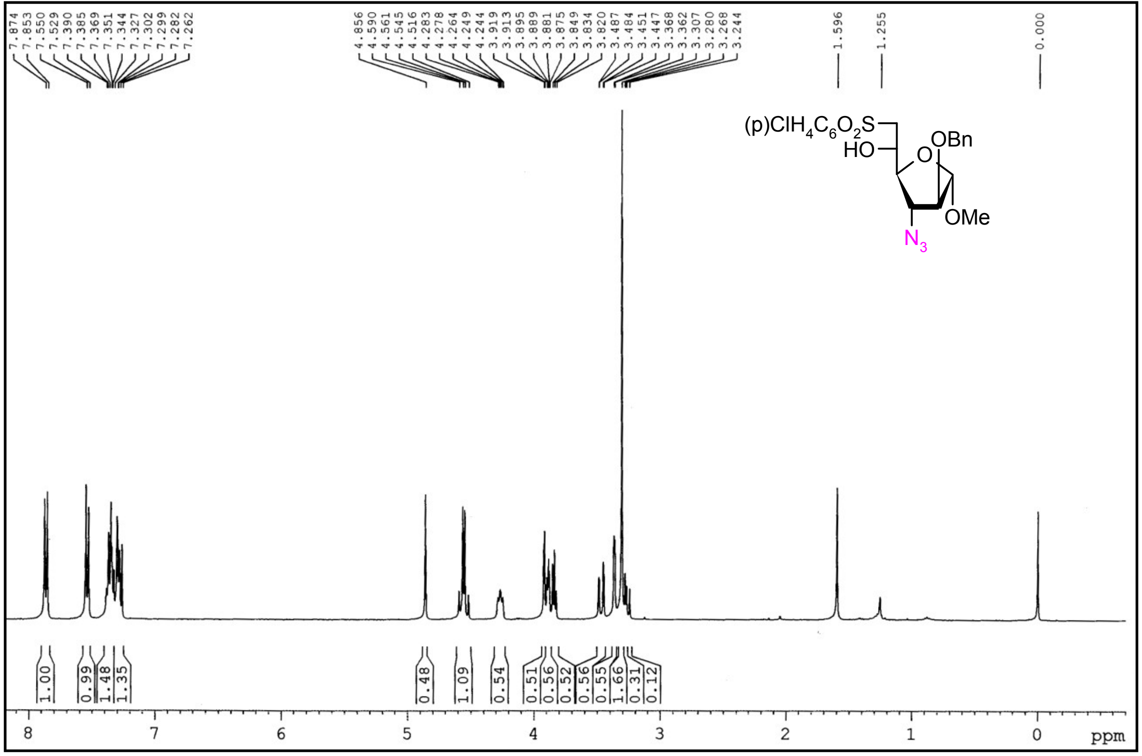


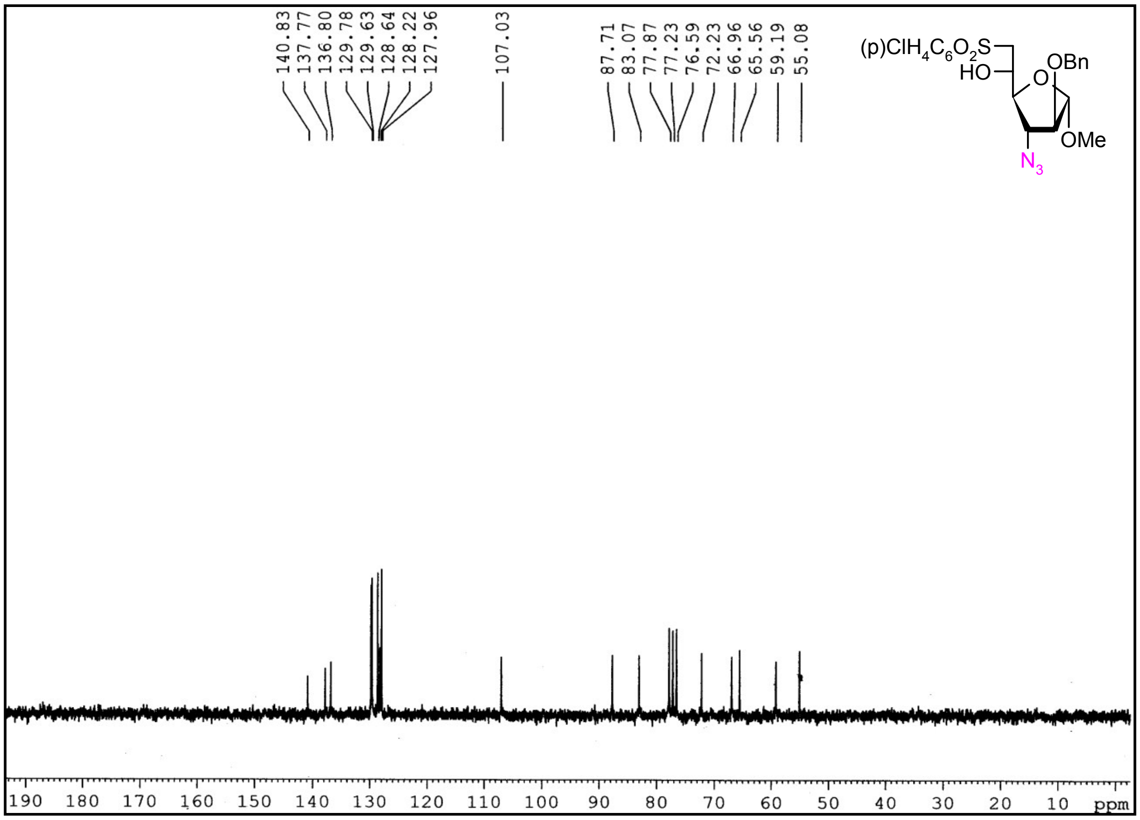
DEPT spectrum of 24b



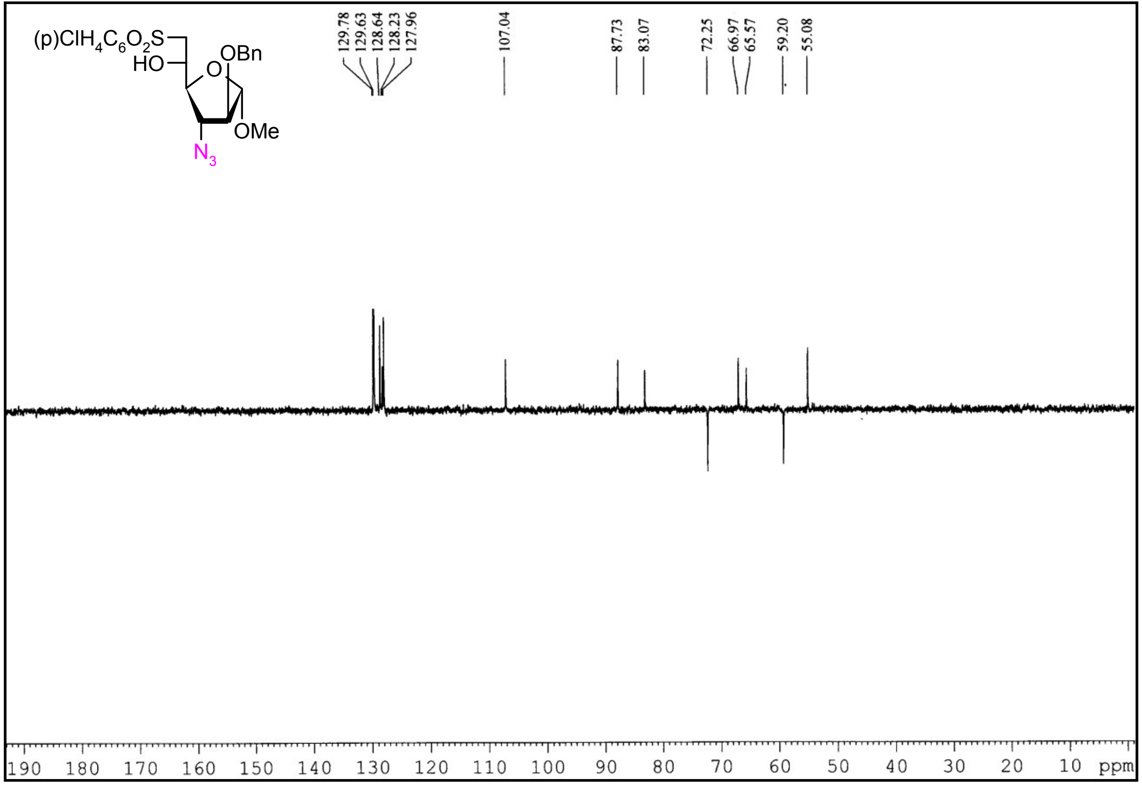
^{1}H NMR spectrum of 18



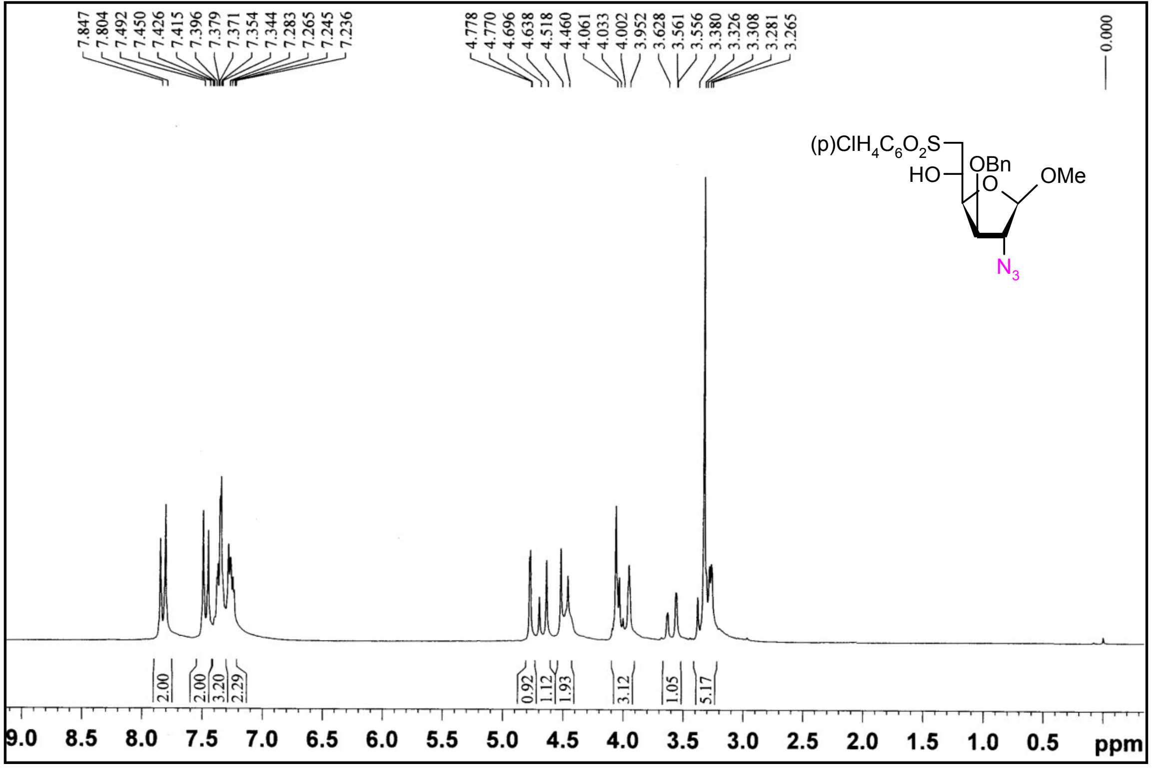
^{13}C NMR spectrum of 18



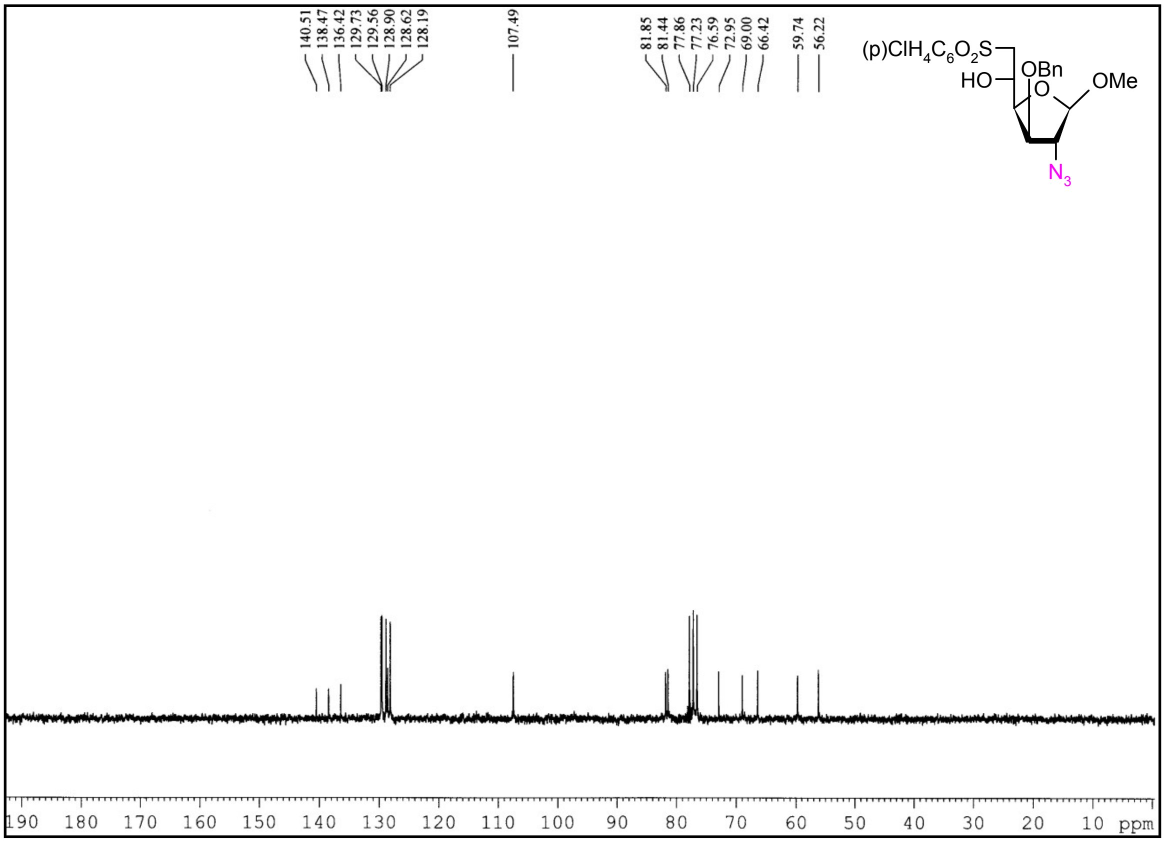
DEPT spectrum of 18



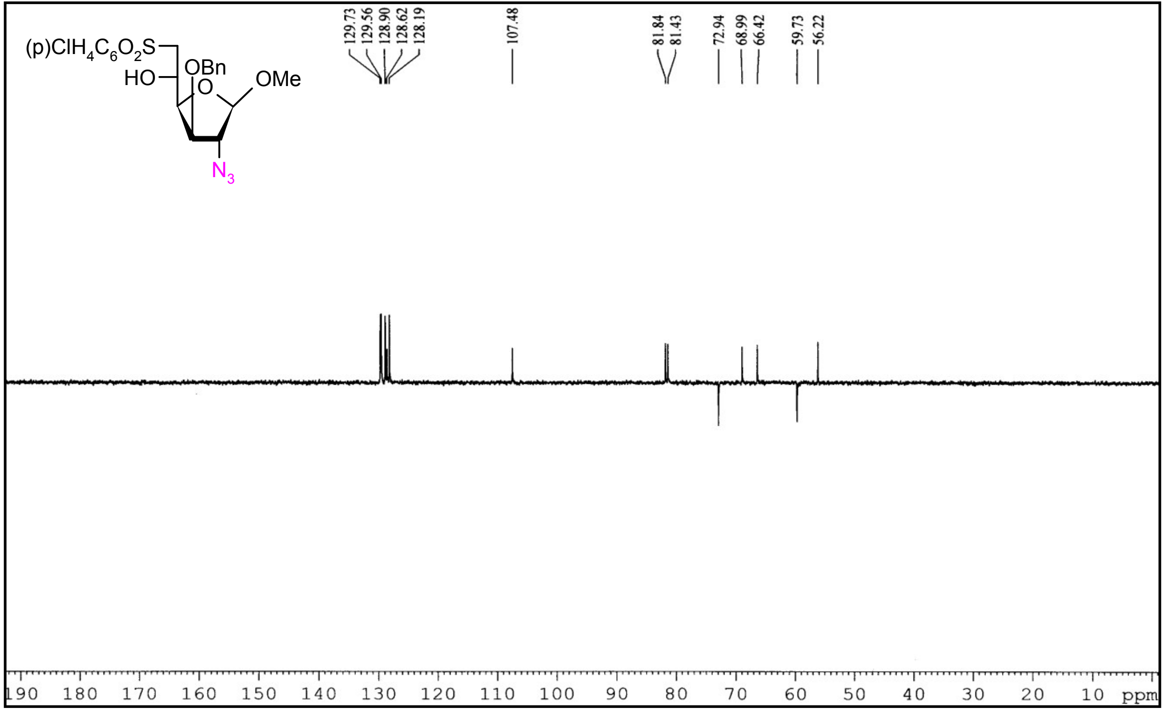
^{1}H NMR spectrum of 25a



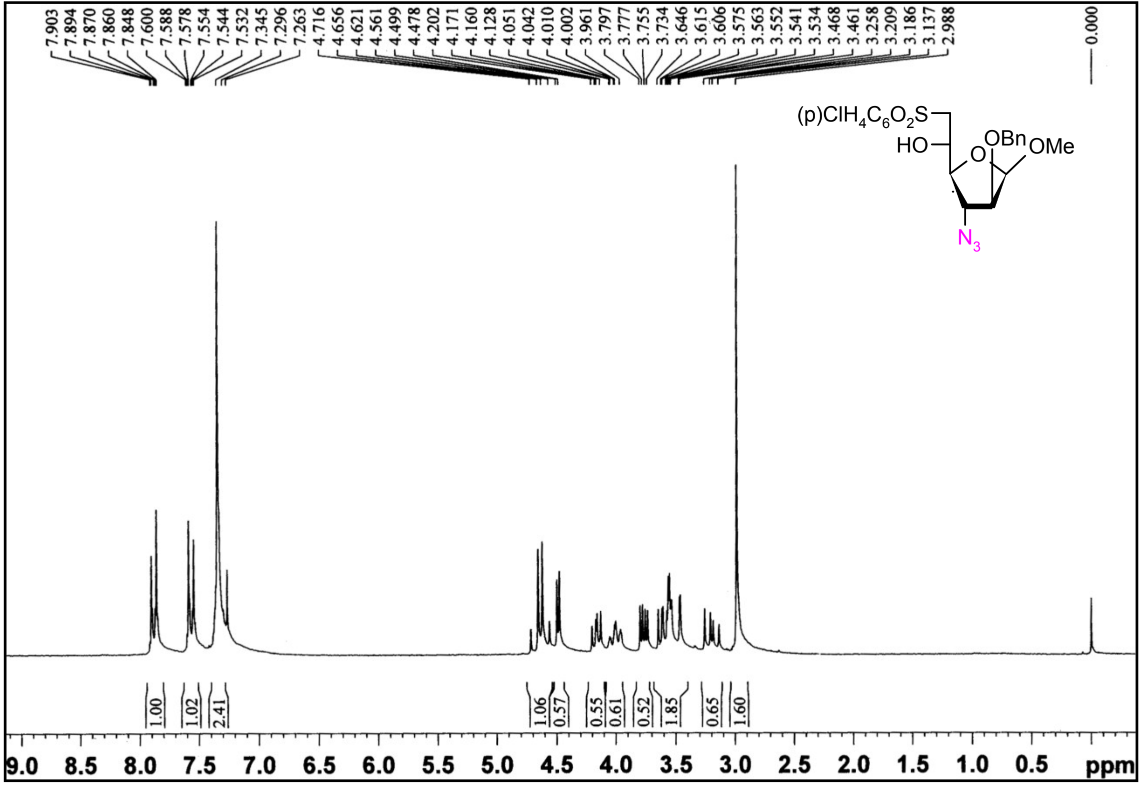
^{13}C NMR spectrum of 25a



DEPT spectrum of 25a



^{1}H NMR spectrum of 25b



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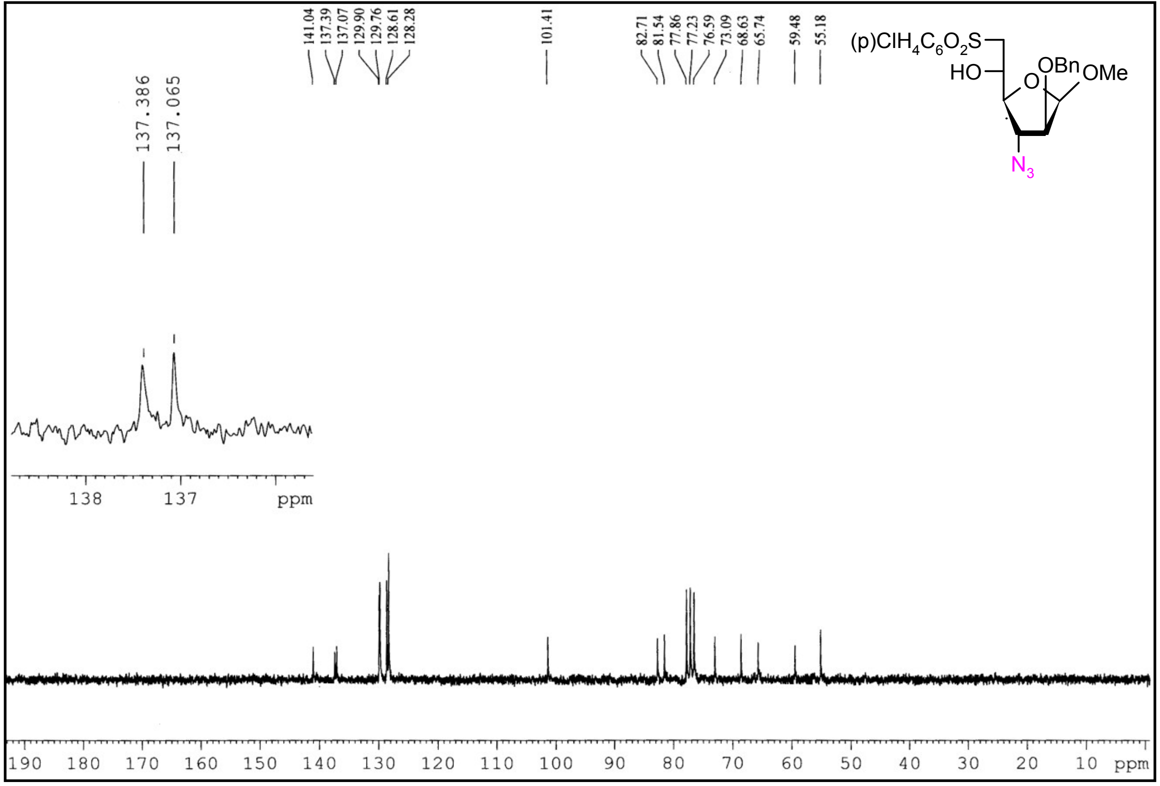
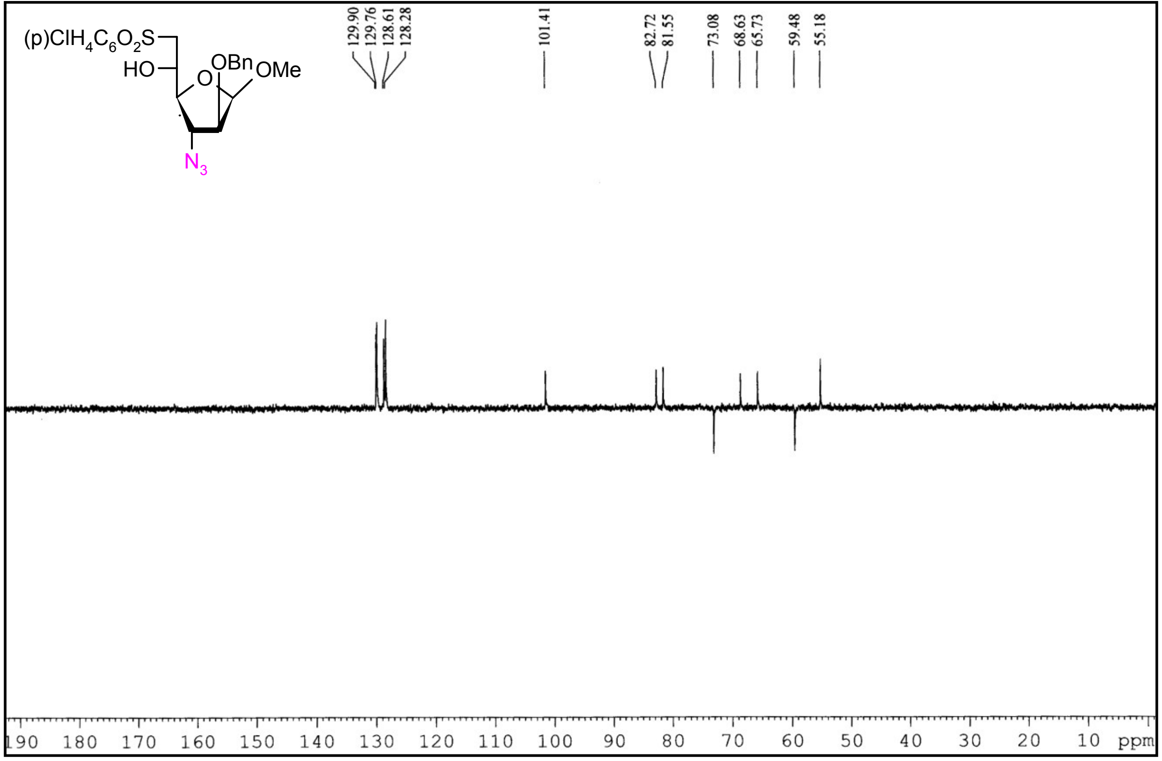
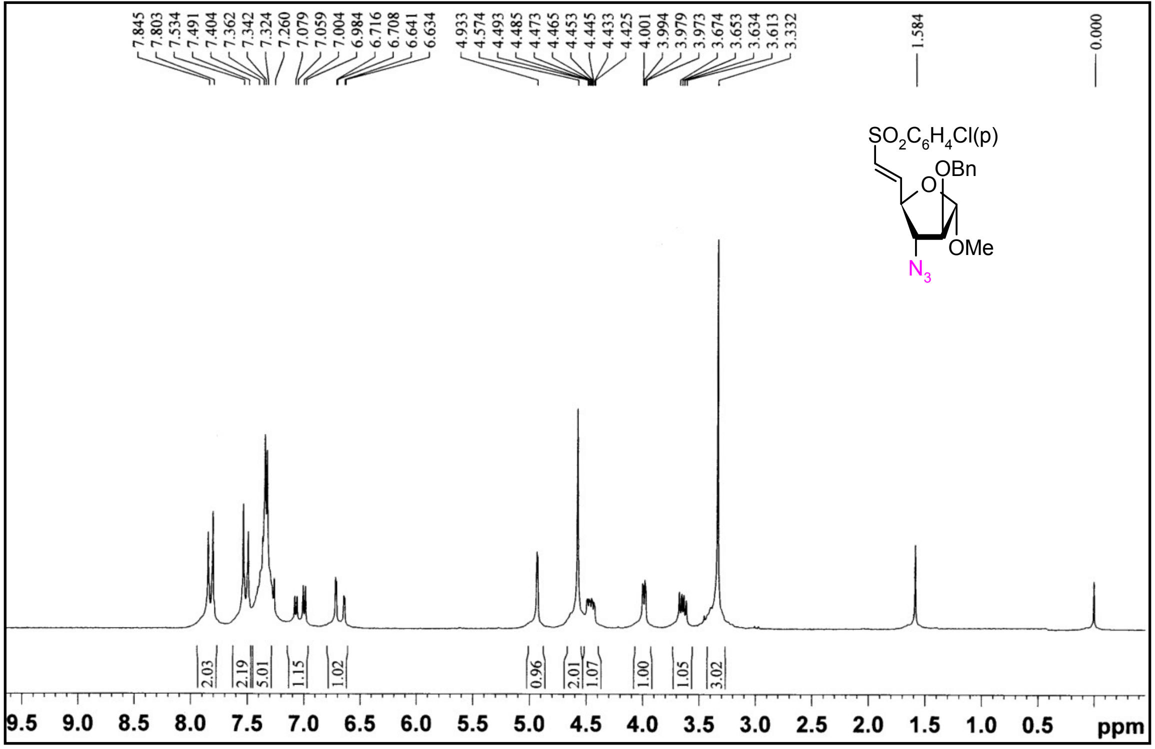


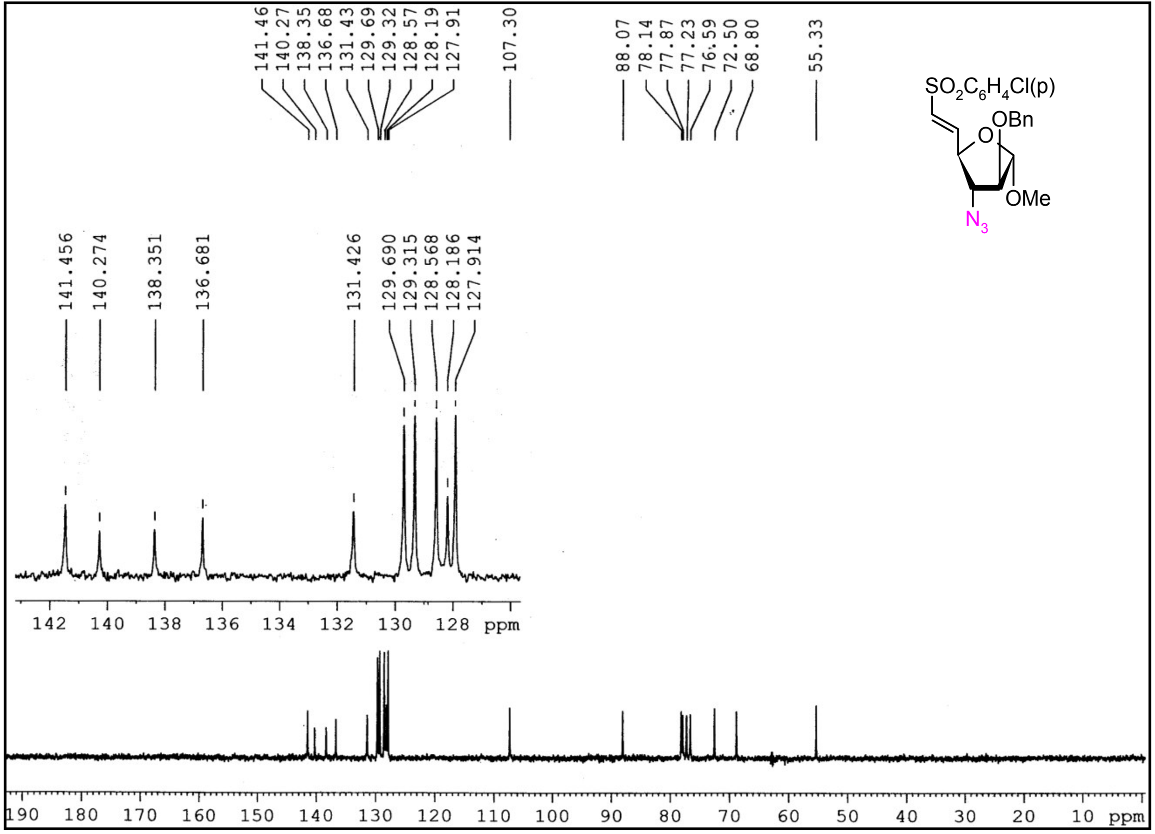
DEPT spectrum of 25b



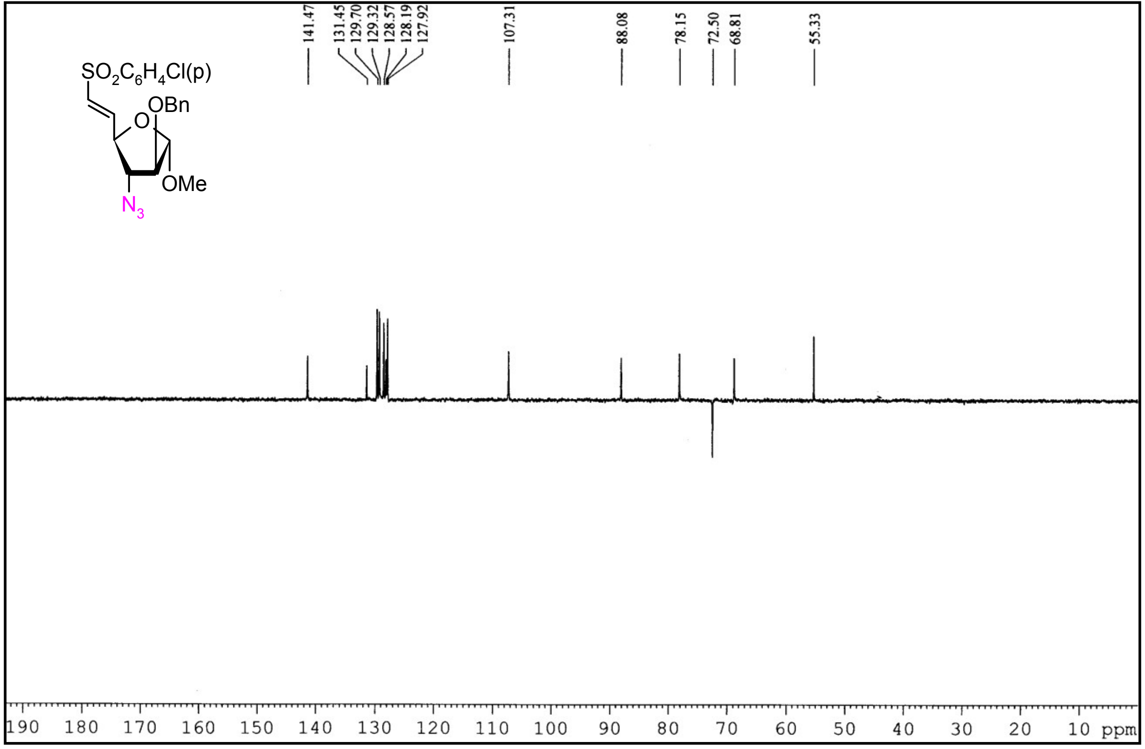
^{1}H NMR spectrum of 5



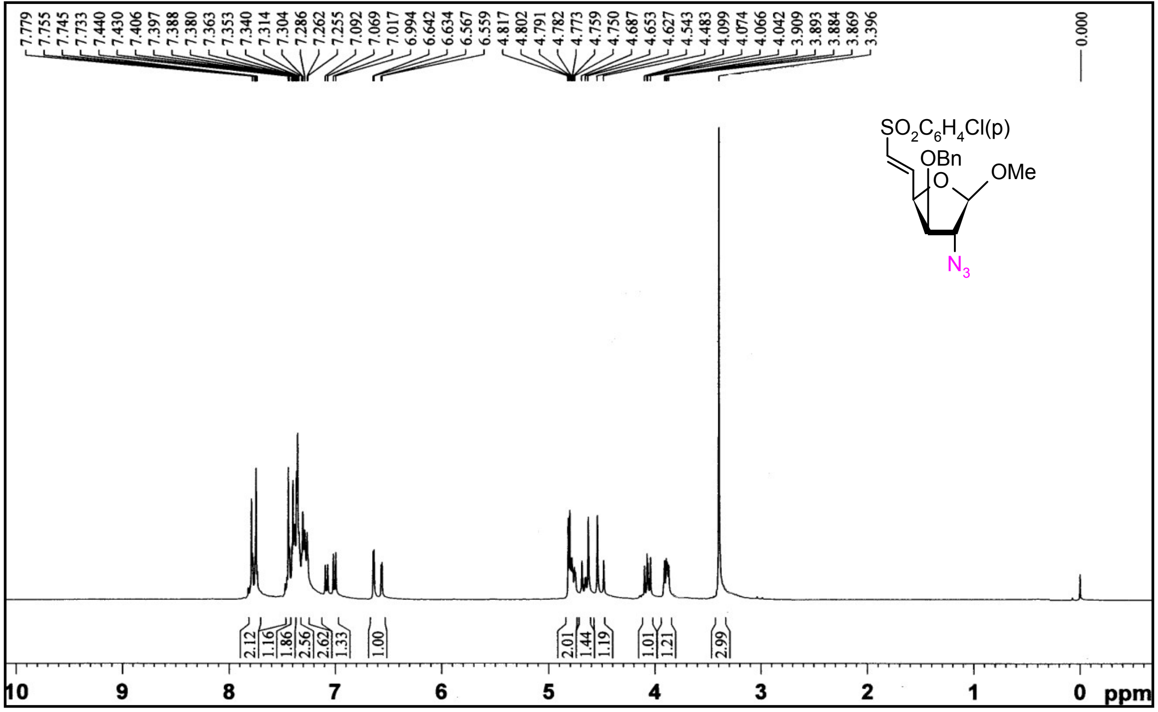
^{13}C NMR spectrum of 5



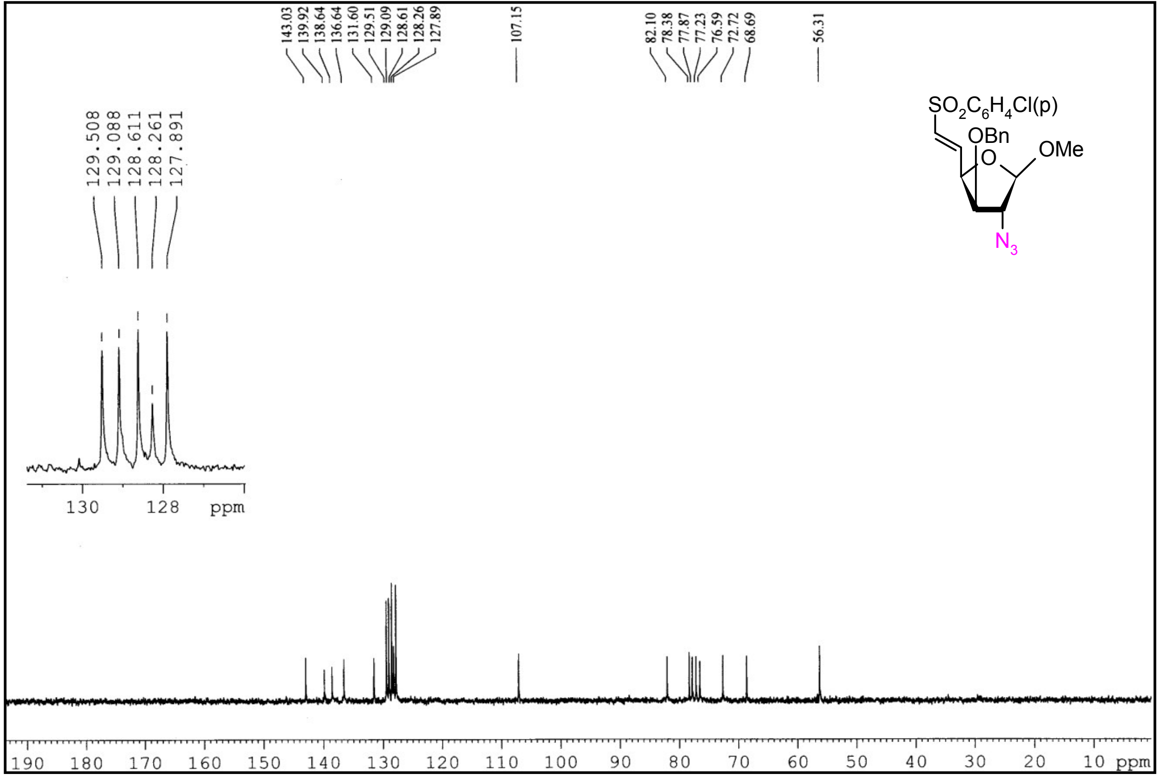
DEPT spectrum of 5



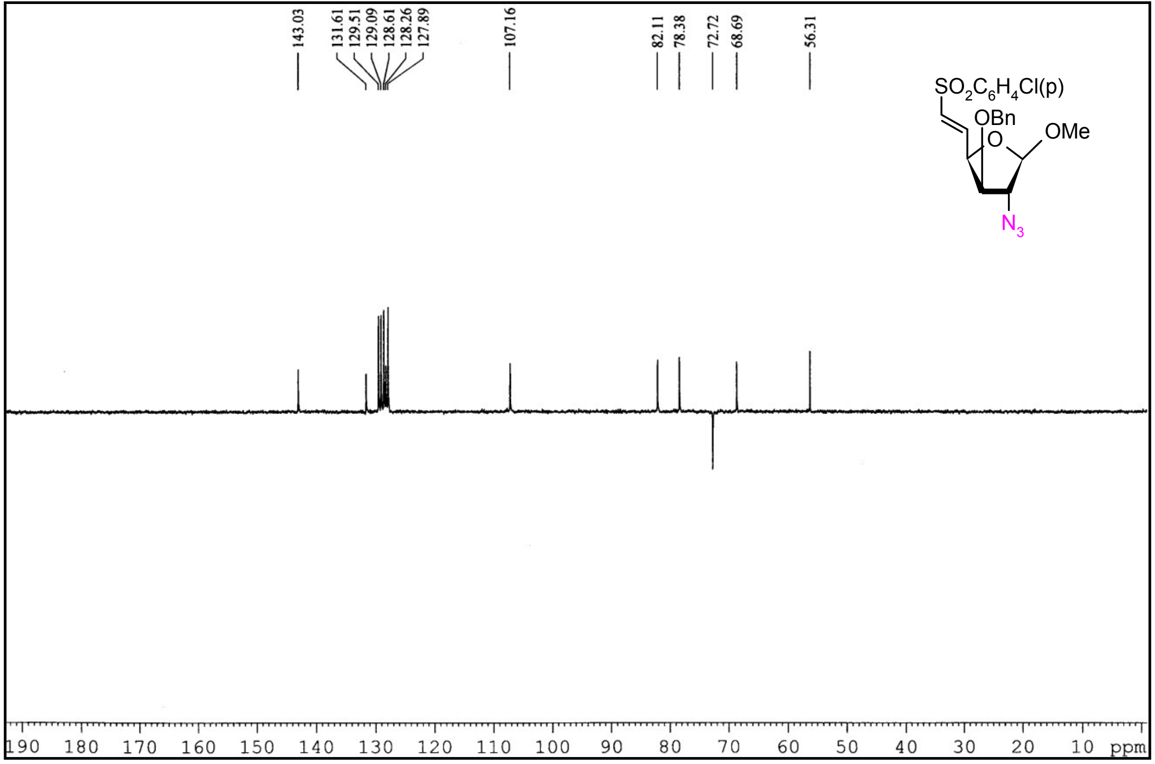
^{1}H NMR spectrum of 6



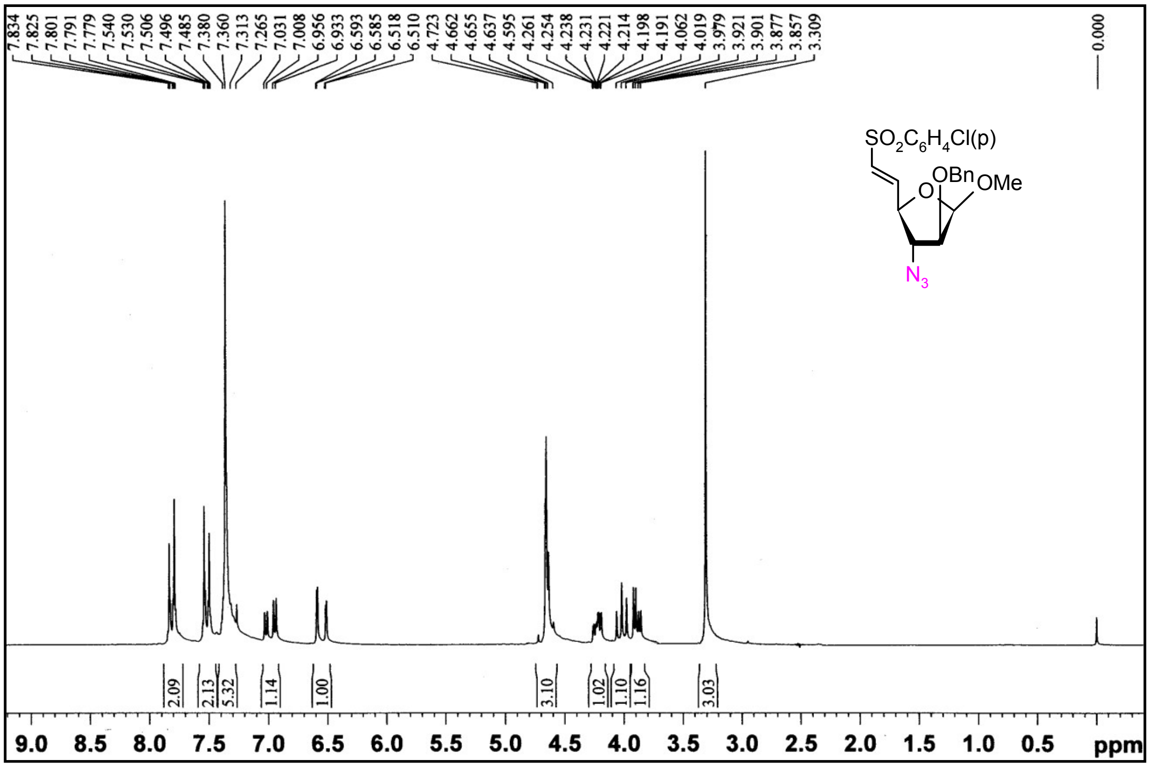
^{13}C NMR spectrum of 6



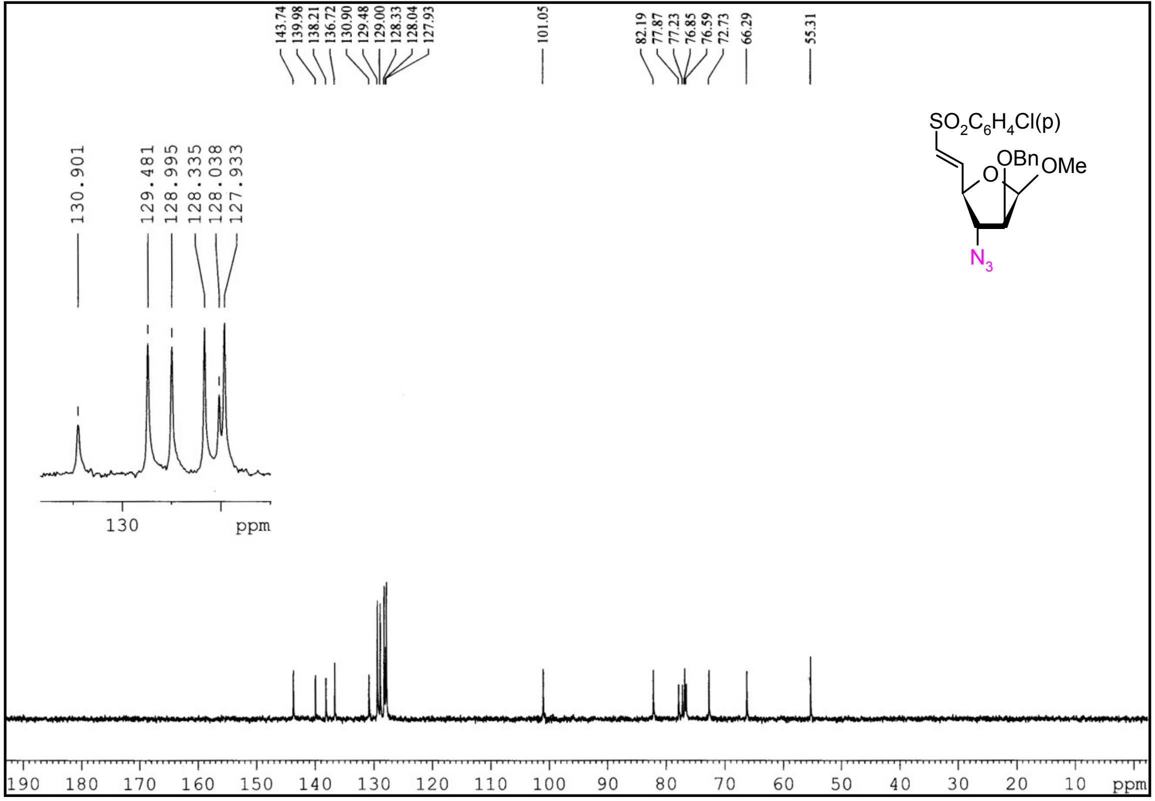
DEPT spectrum of 6



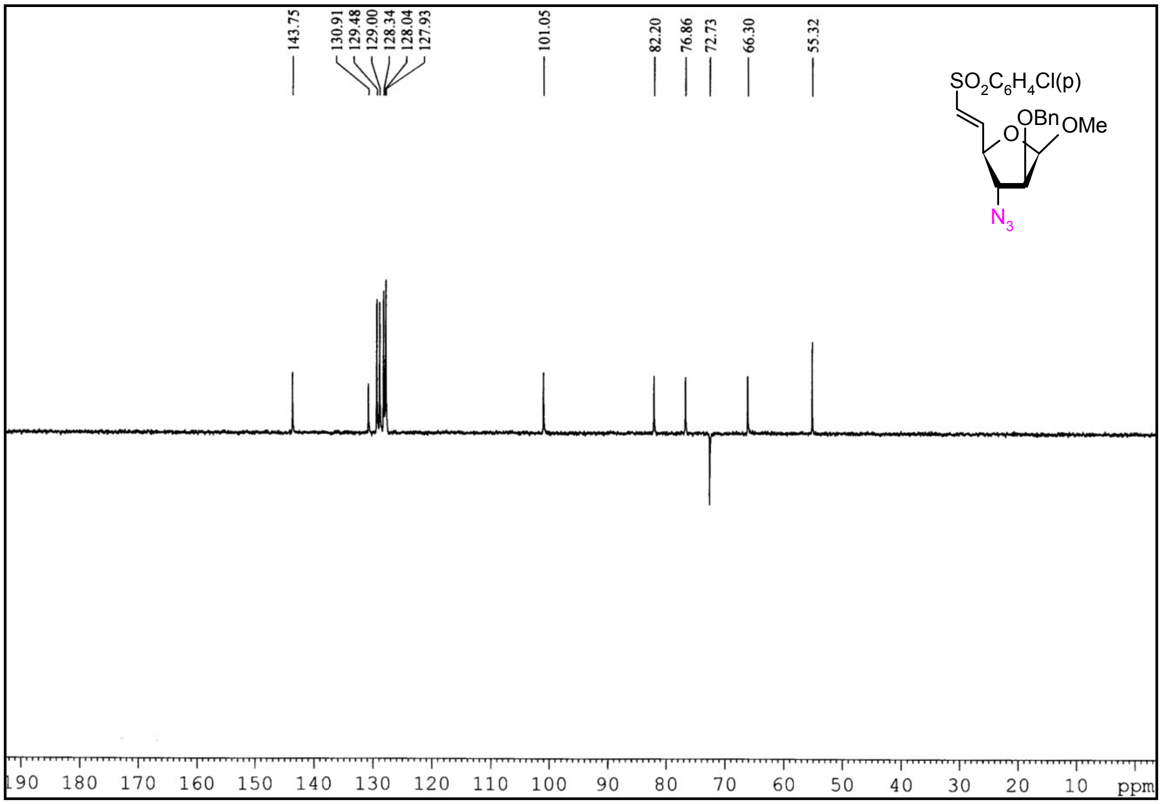
^{1}H NMR spectrum of 7



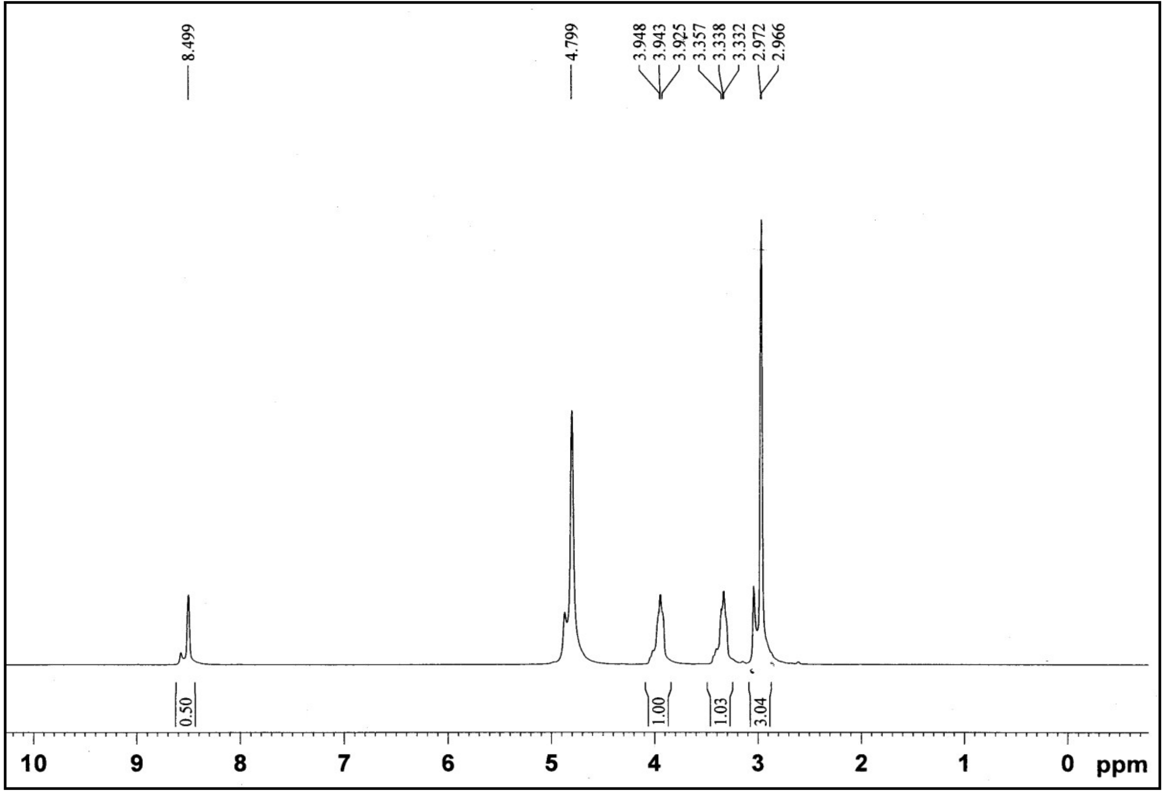
^{13}C NMR spectrum of 7



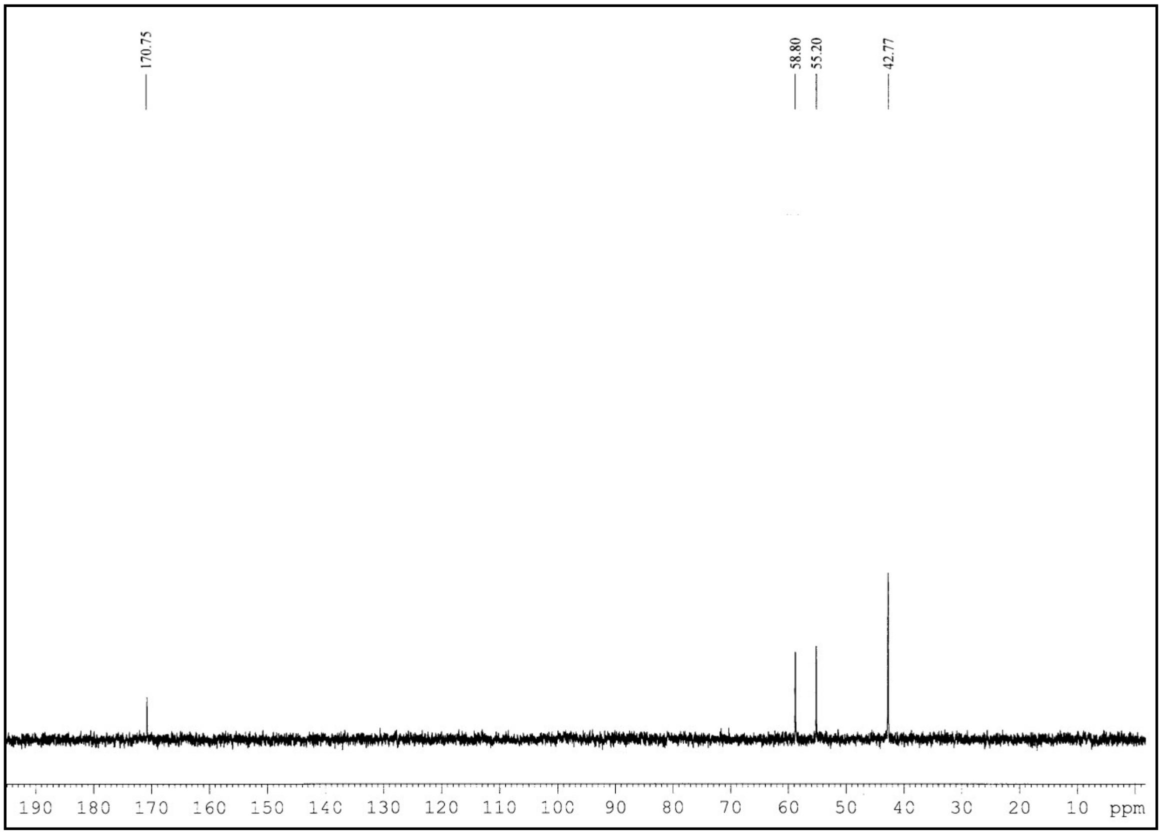
DEPT spectrum of 7


143.75
130.91
129.48
129.00
128.34
128.04
127.93
101.05
82.20
76.86
72.73
66.30
55.32
$SO_2C_6H_4Cl(p)$
OBn
OMe
O
N_3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

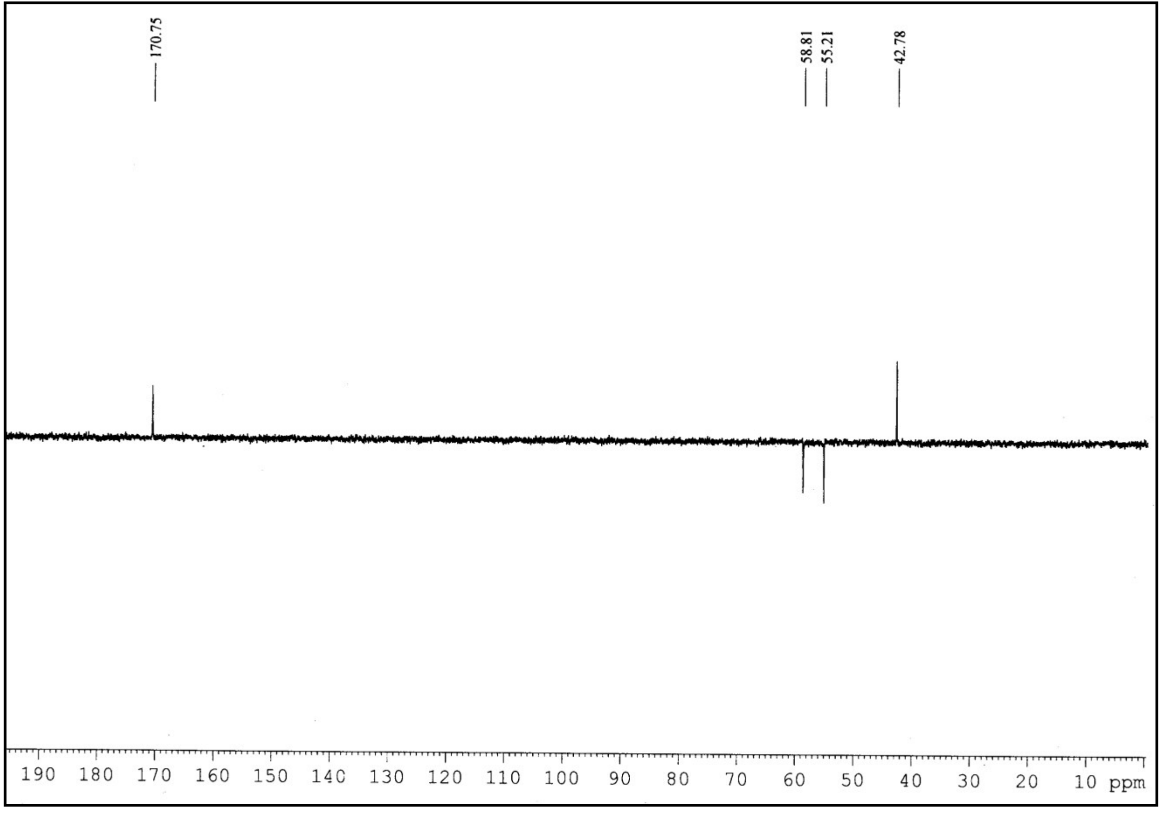
^{1}H NMR spectrum of DAF



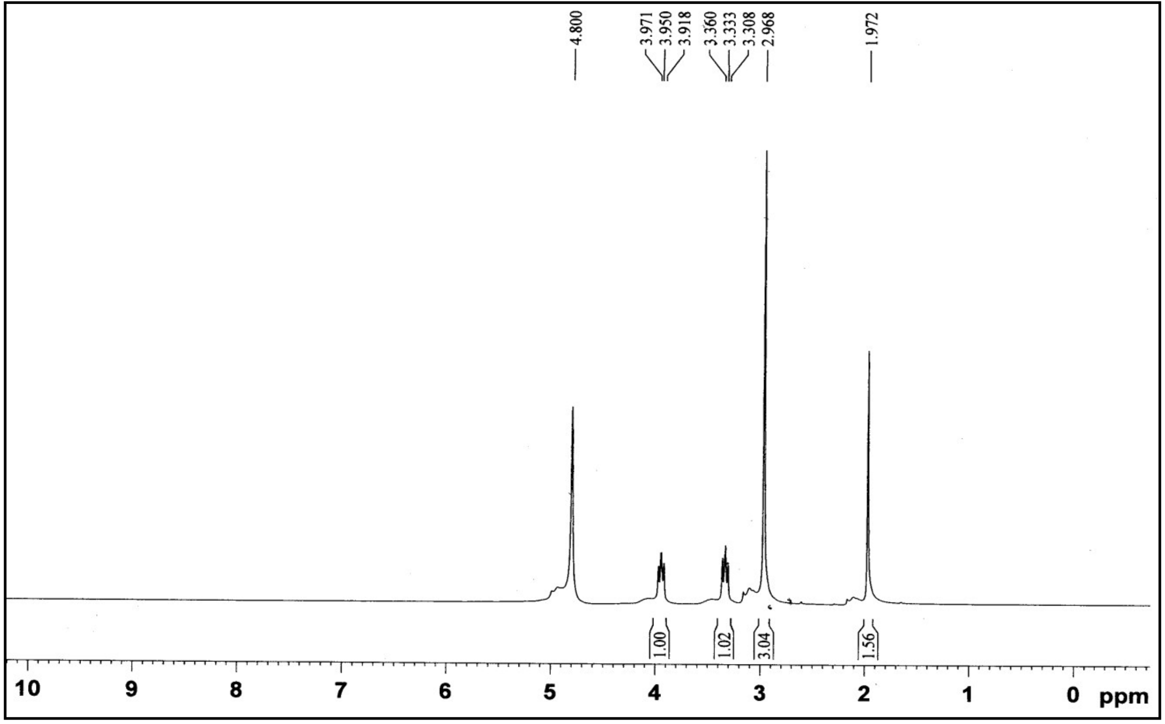
^{13}C NMR spectrum of DAF



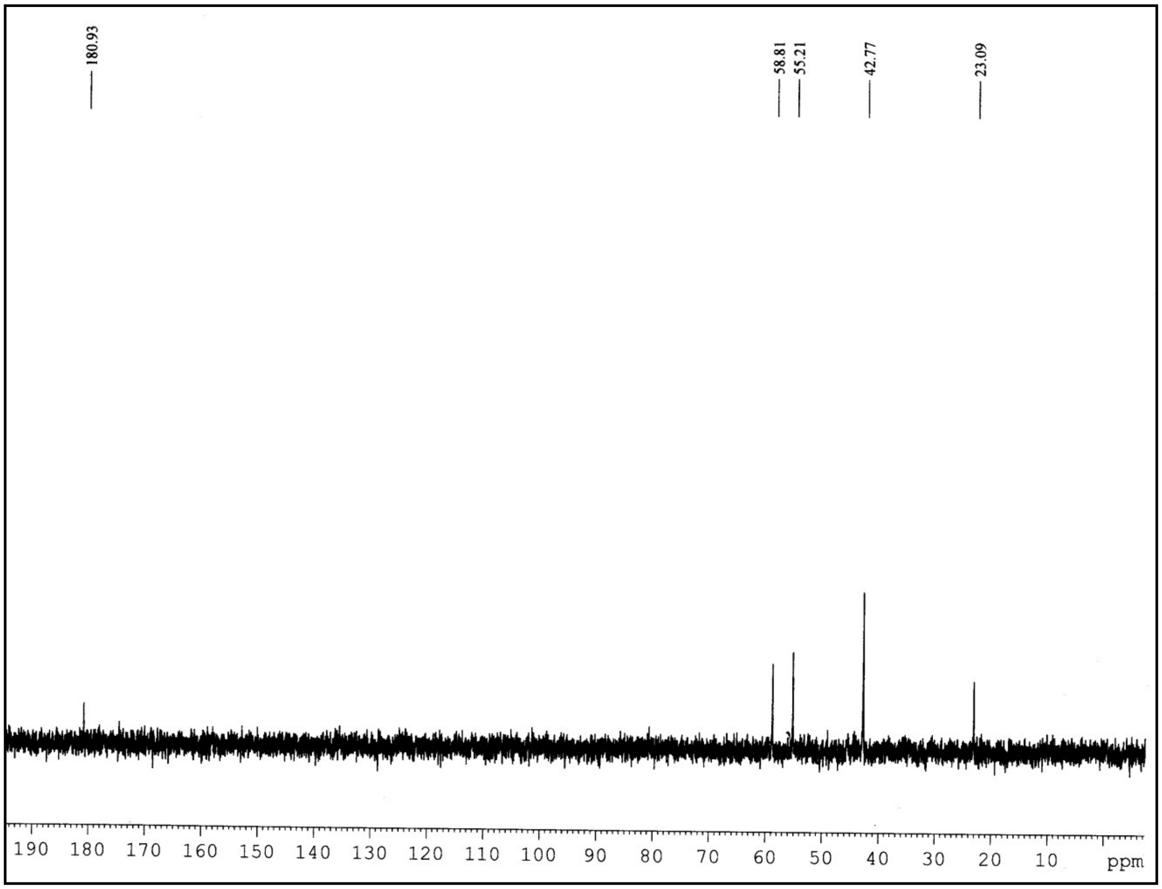
DEPT spectrum of DAF



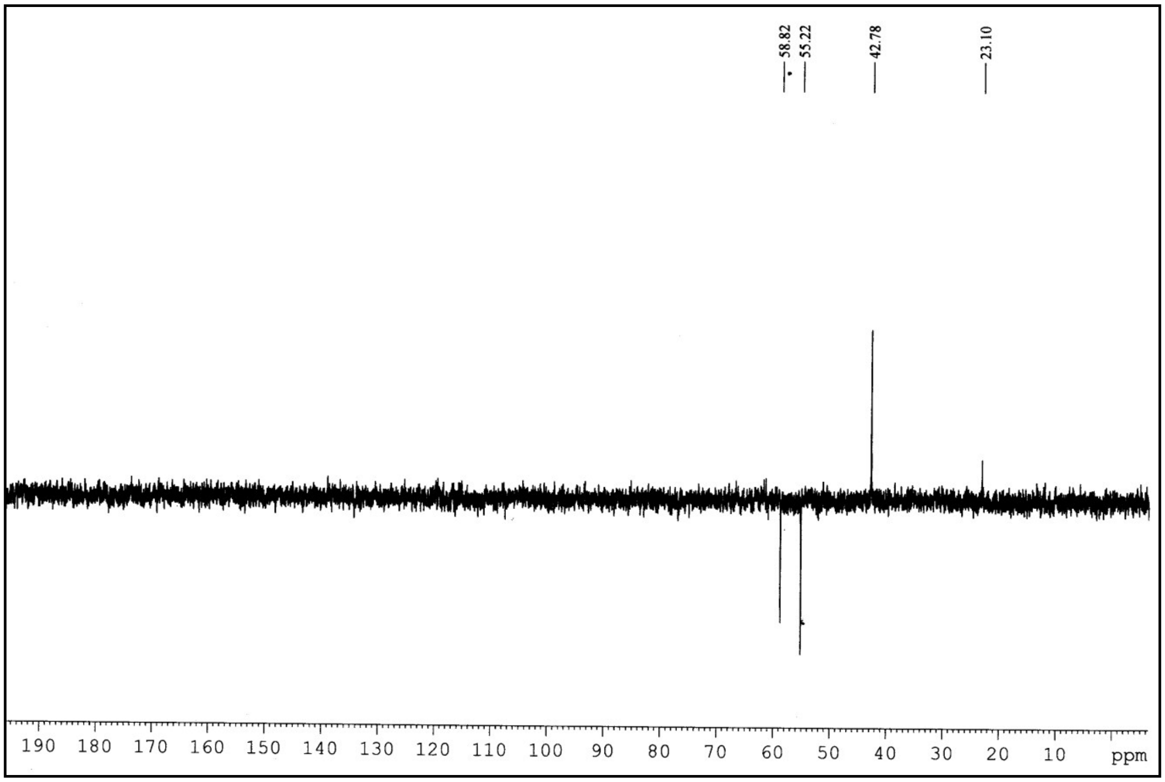
^{1}H NMR spectrum of DAA



^{13}C NMR spectrum of DAA

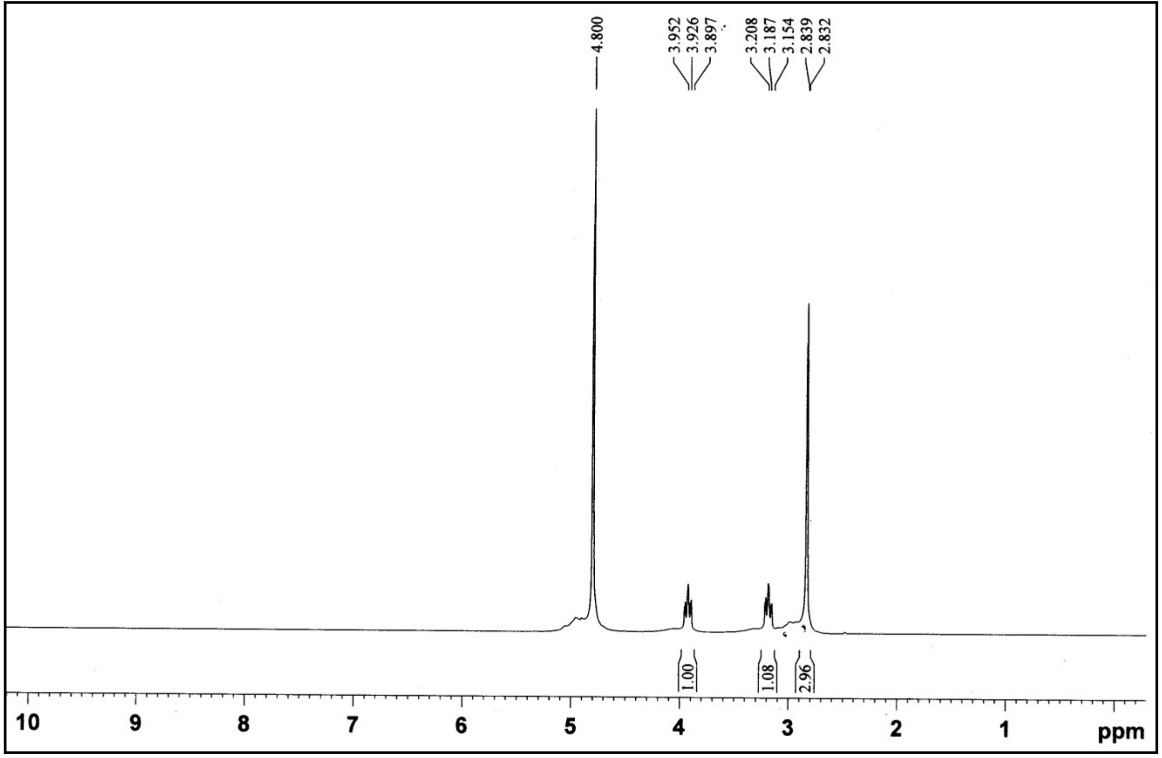


DEPT spectrum of DAA

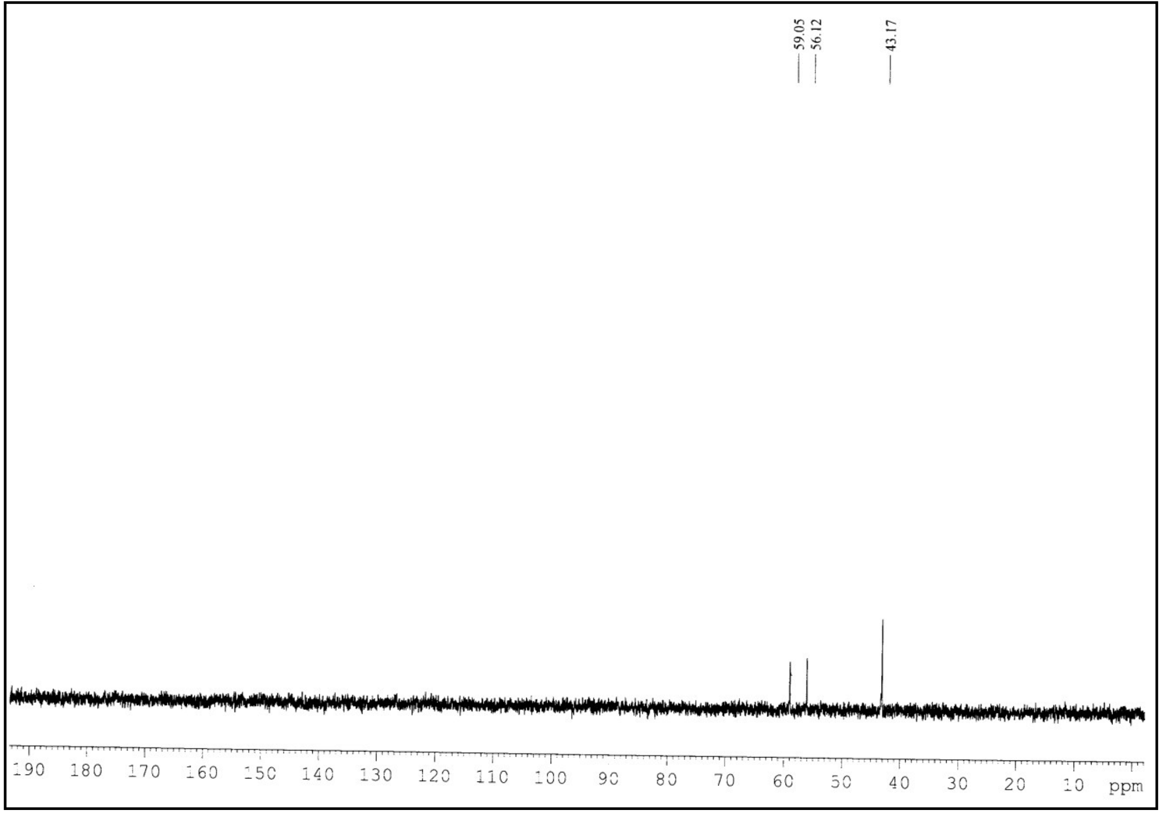


58.82
55.22
42.78
23.10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

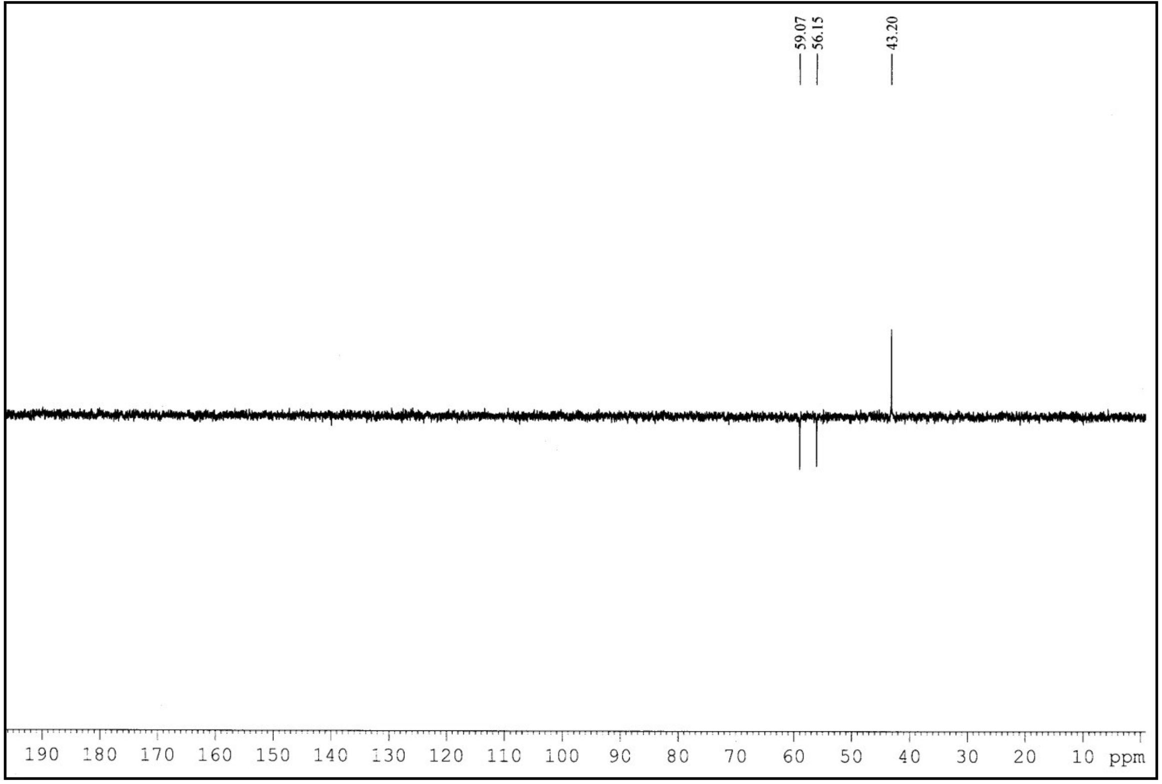
^{1}H NMR spectrum of DAC



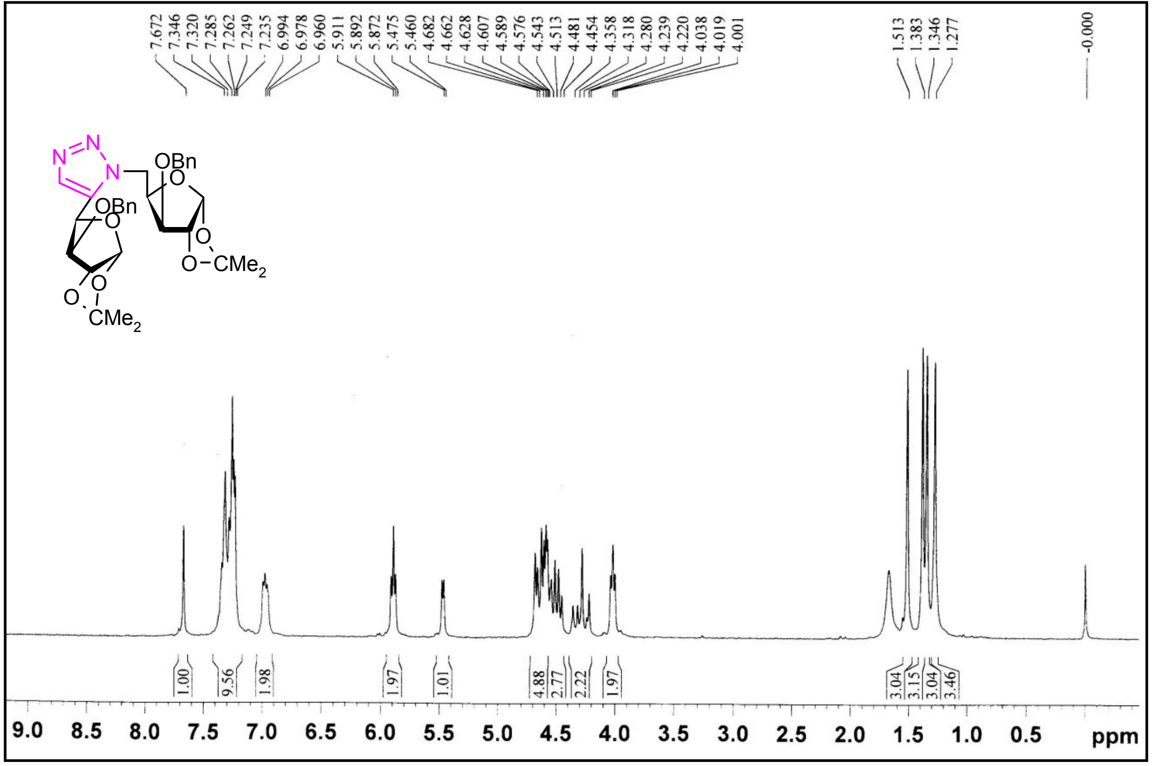
^{13}C NMR spectrum of DAC



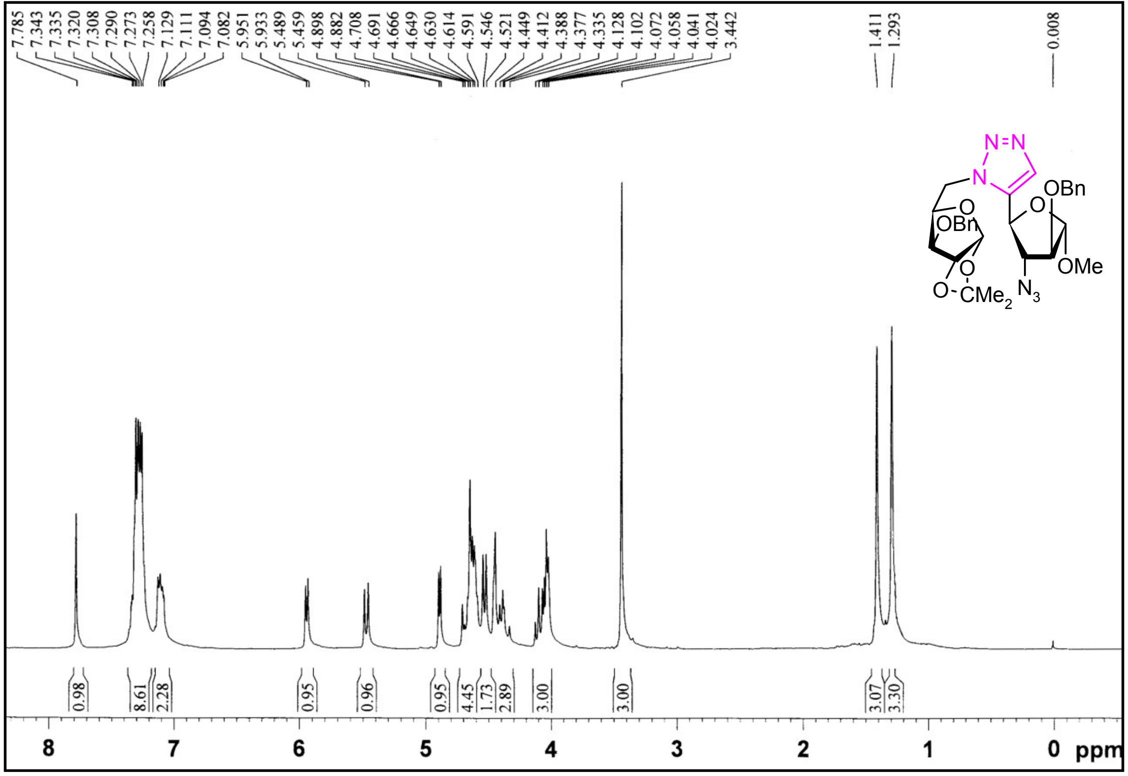
DEPT spectrum of DAC



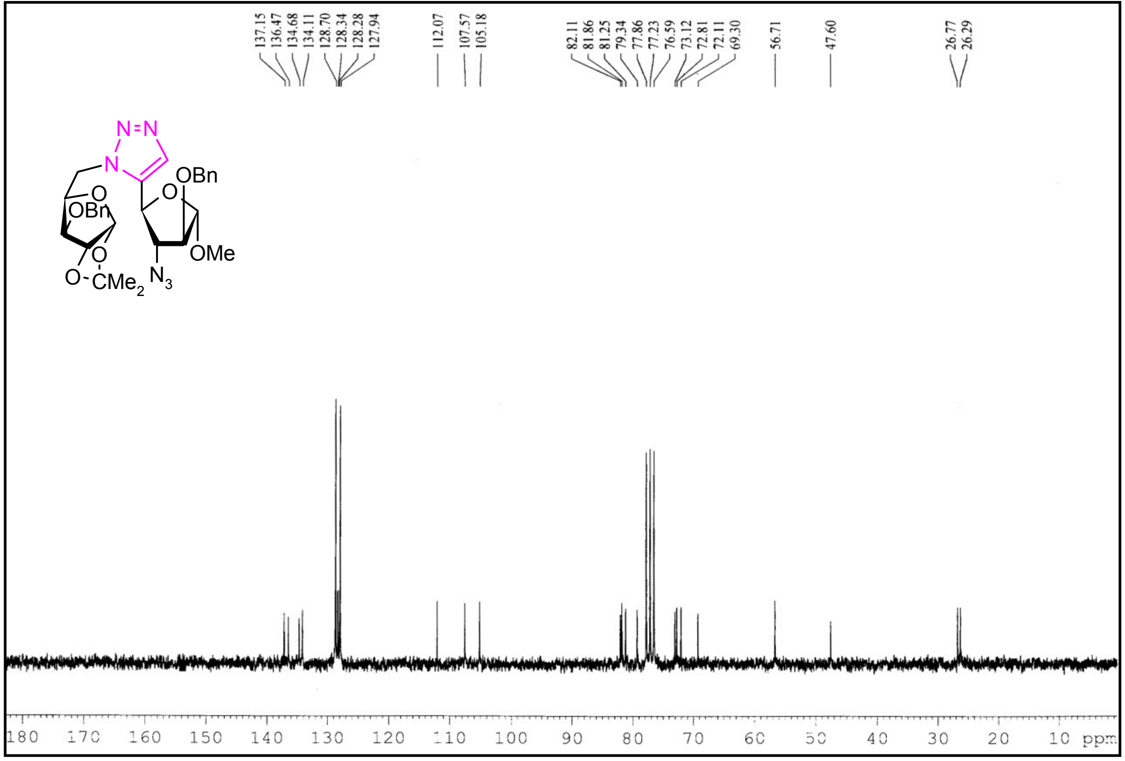
^{1}H NMR spectrum of 27



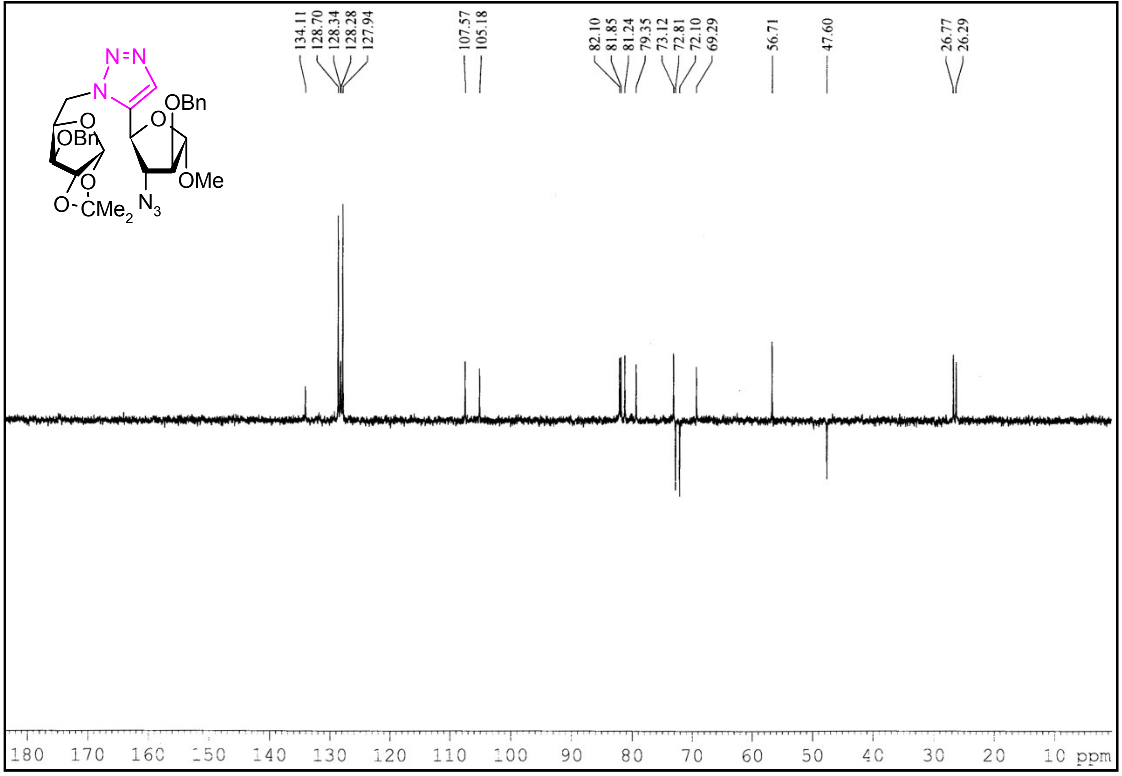
^{1}H NMR spectrum of 28



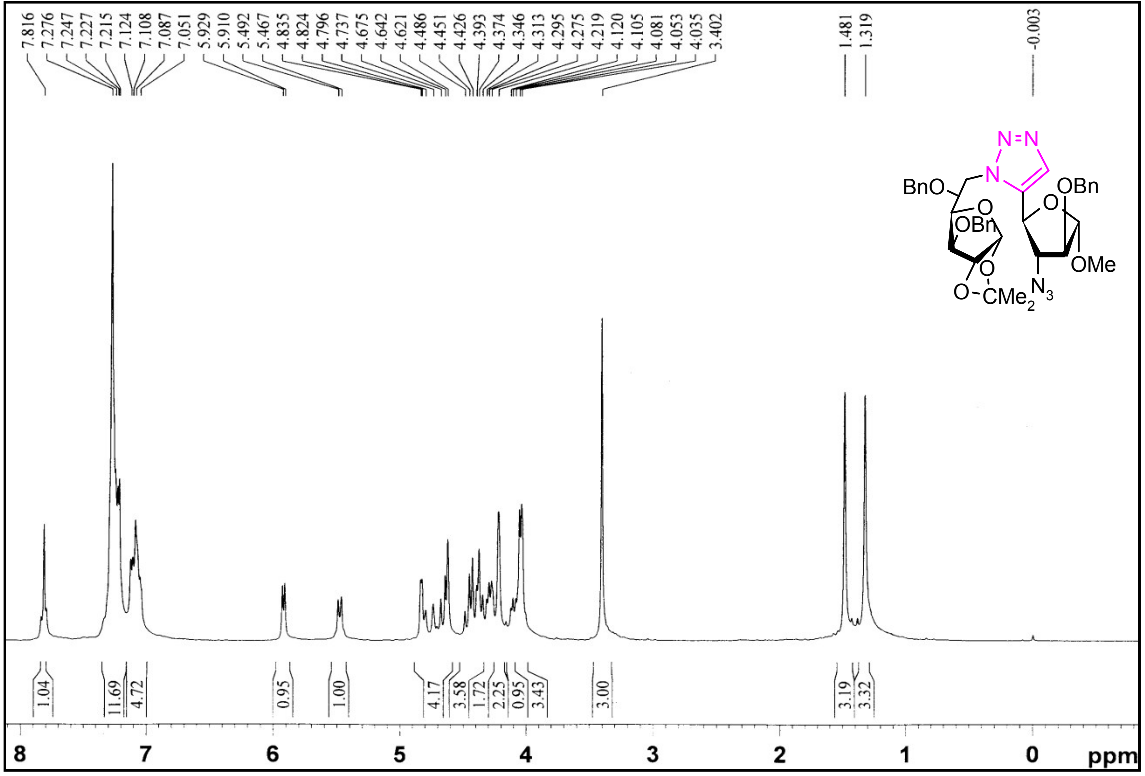
^{13}C NMR spectrum of 28



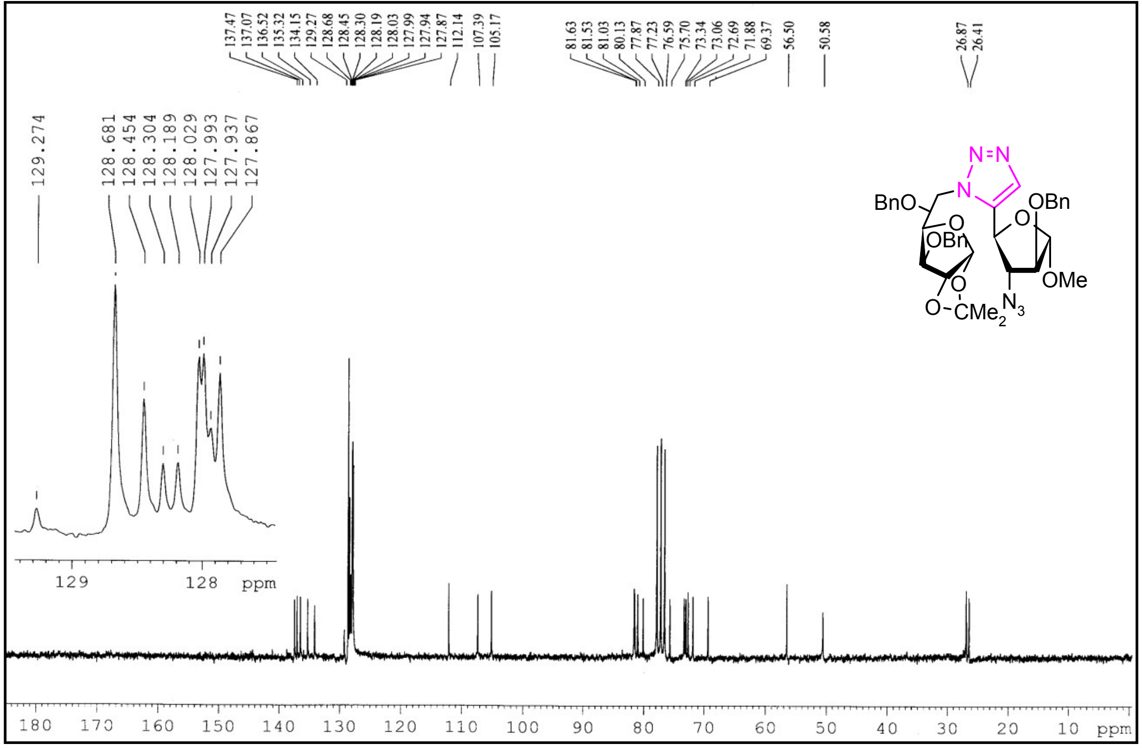
DEPT spectrum of 28



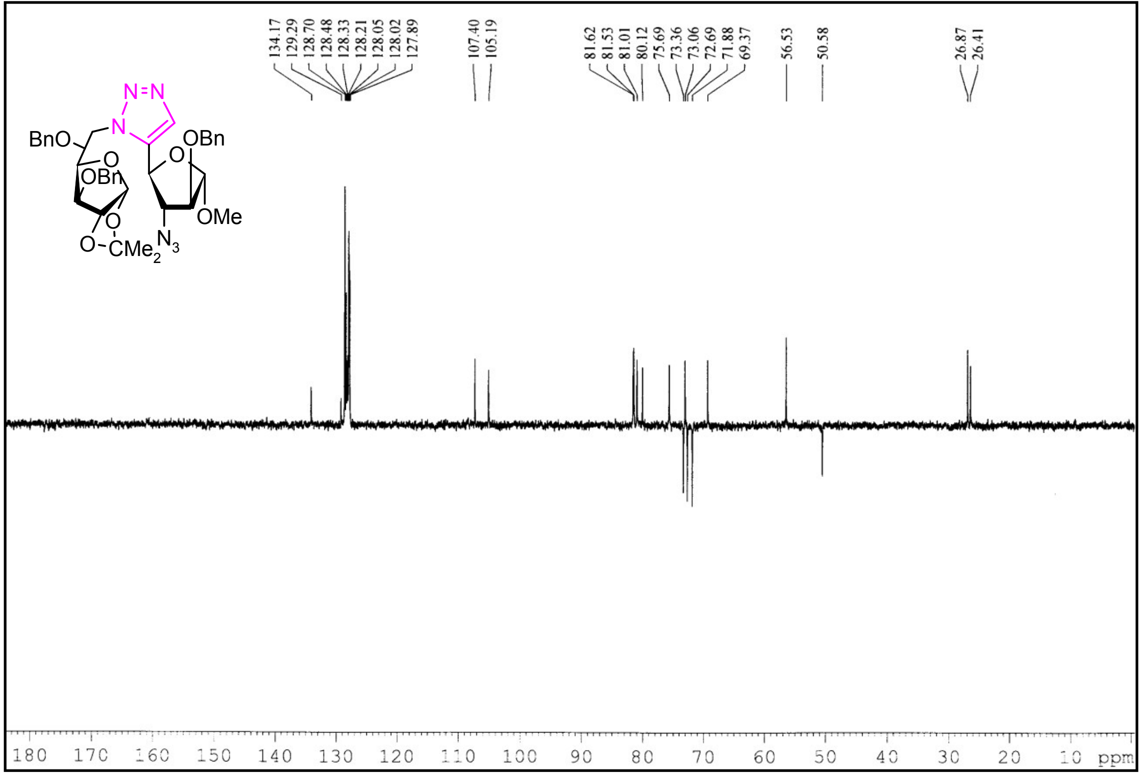
^{1}H NMR spectrum of 29



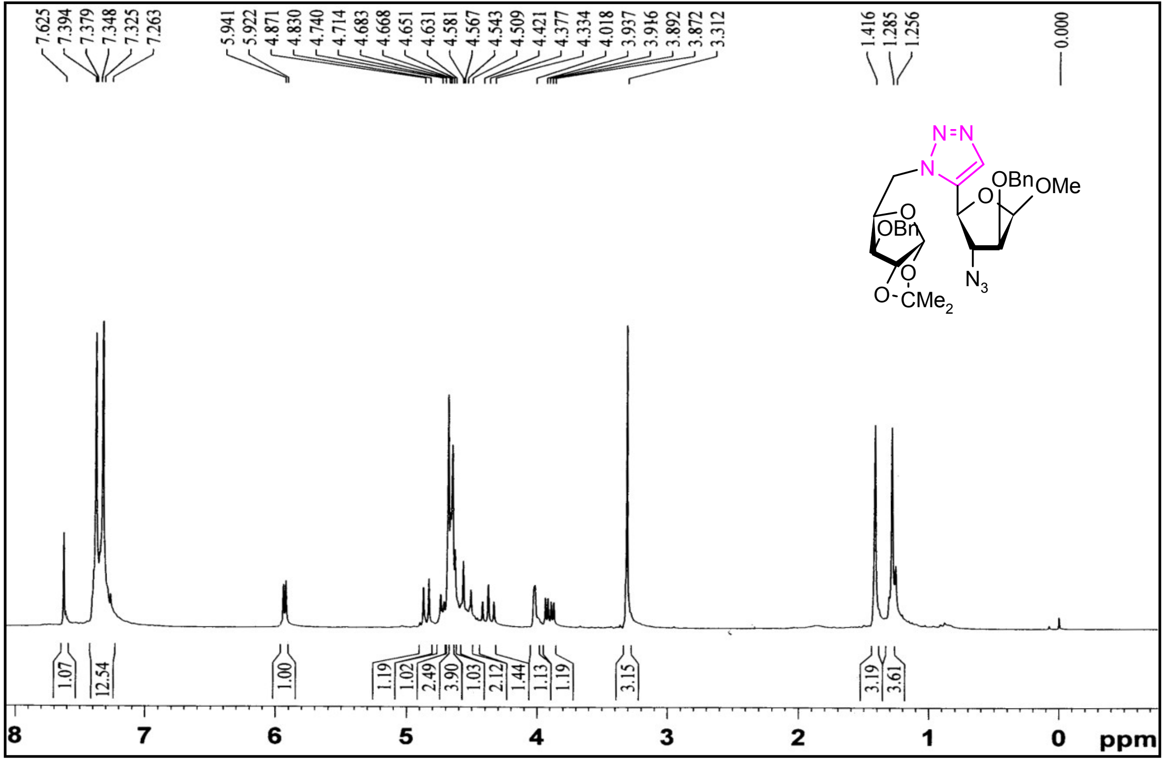
^{13}C NMR spectrum of 29



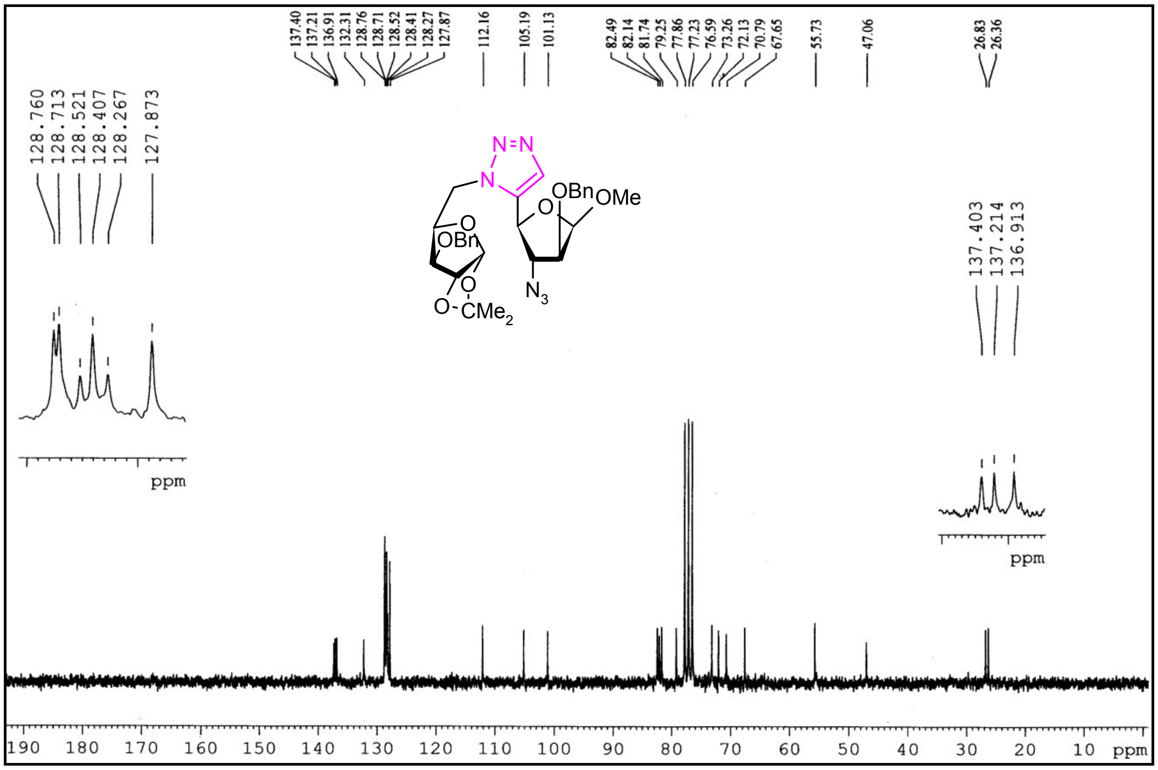
DEPT spectrum of 29



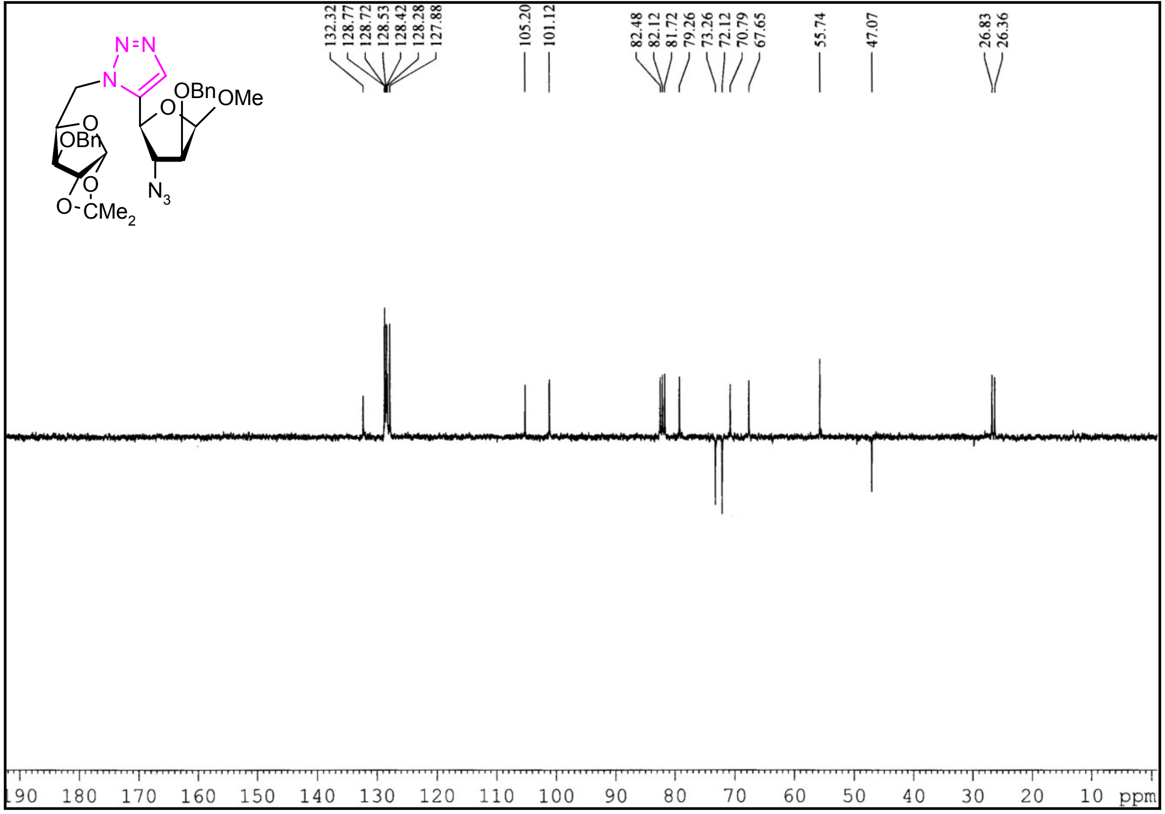
^{1}H NMR spectrum of 30



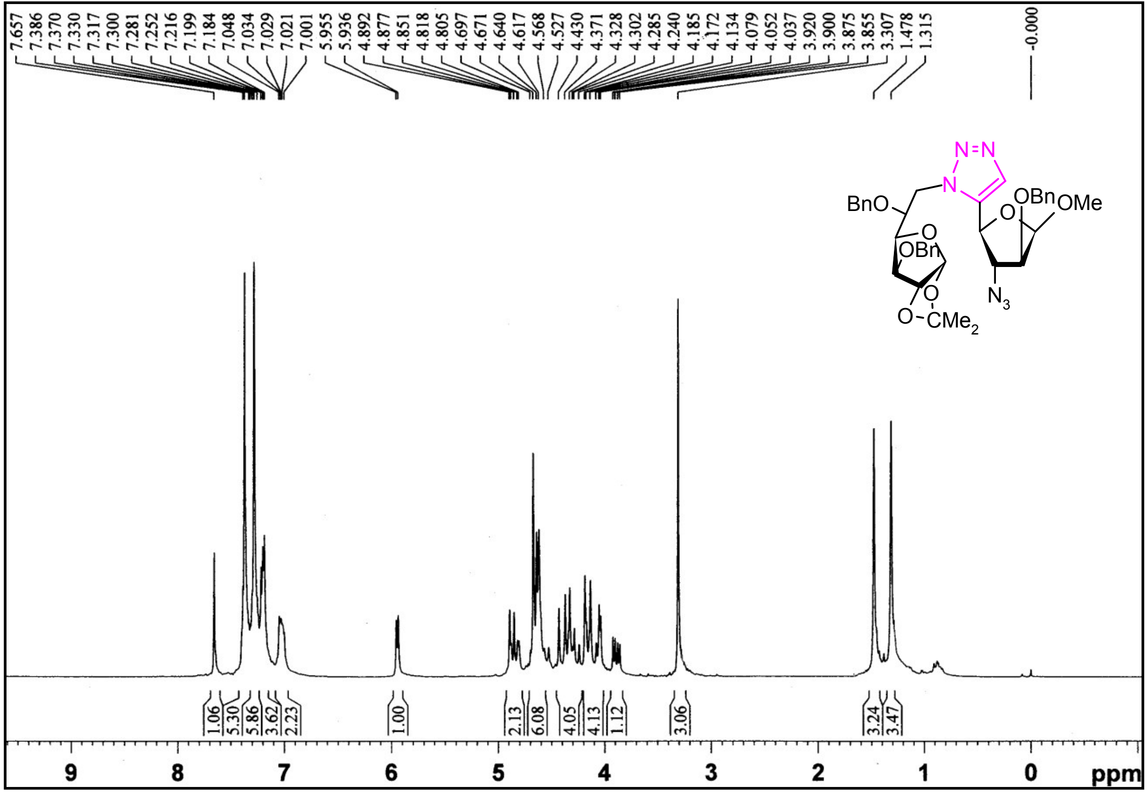
^{13}C NMR spectrum of 30



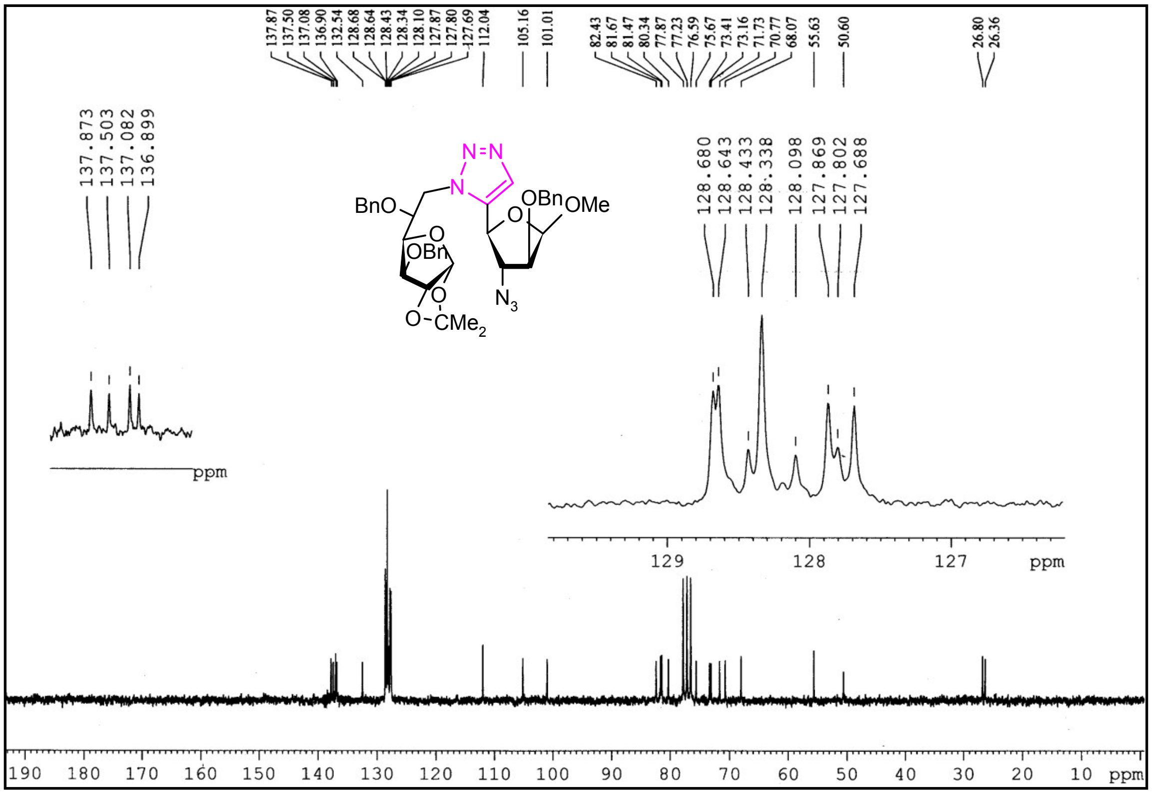
DEPT spectrum of 30



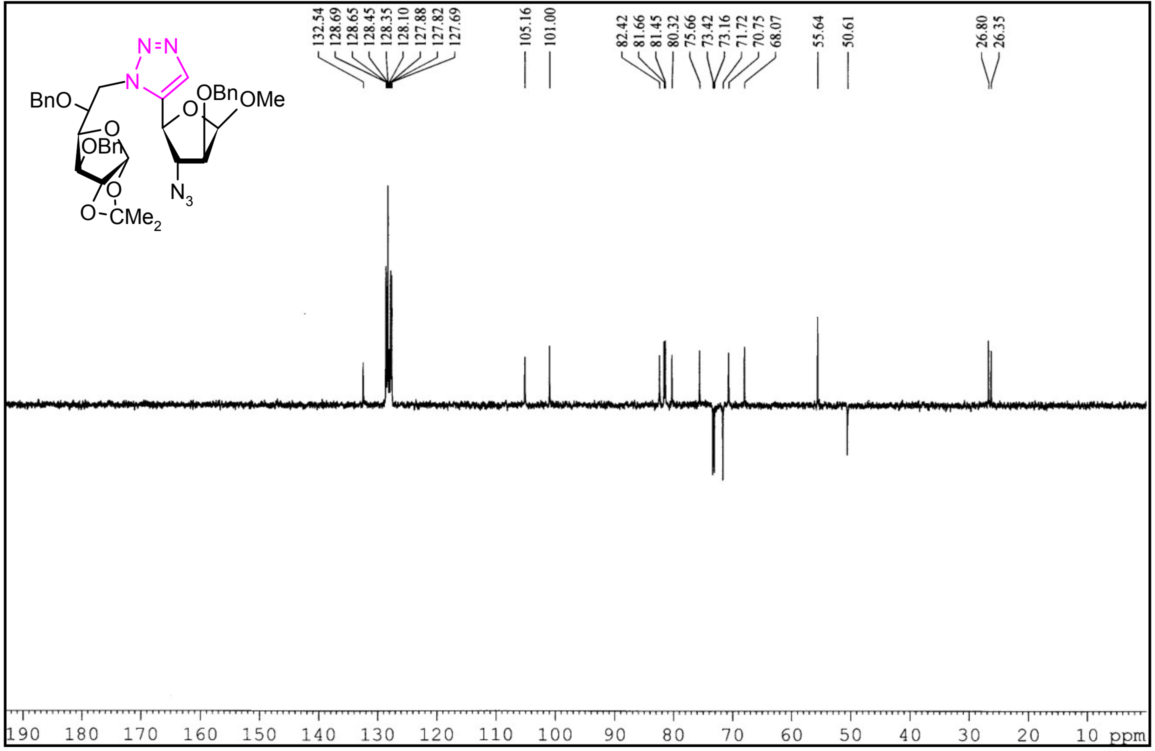
^{1}H NMR spectrum of 31



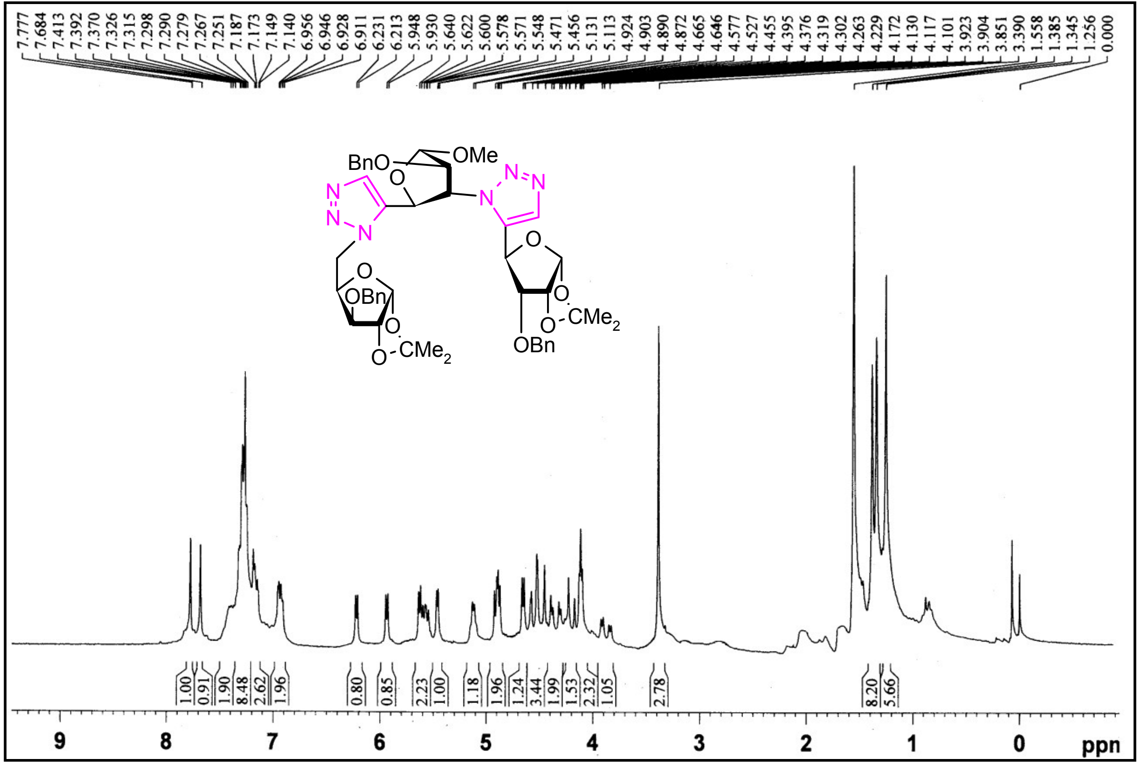
^{13}C NMR spectrum of 31



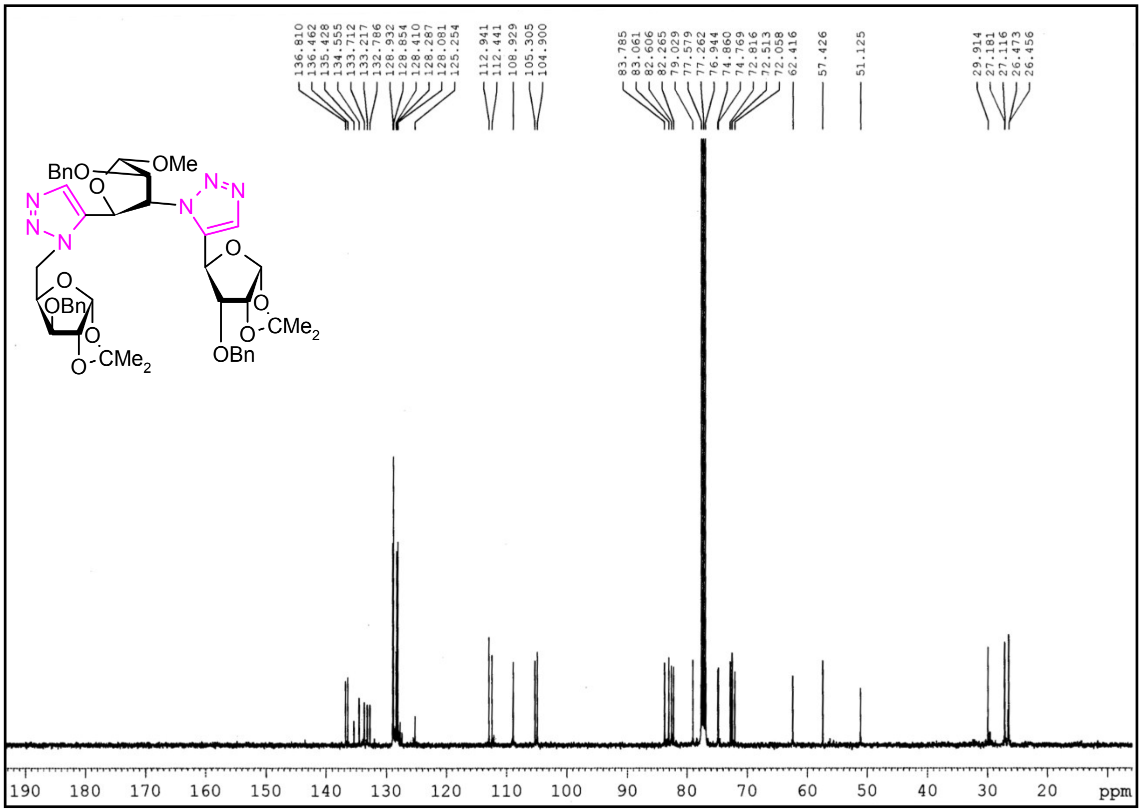
DEPT spectrum of 31



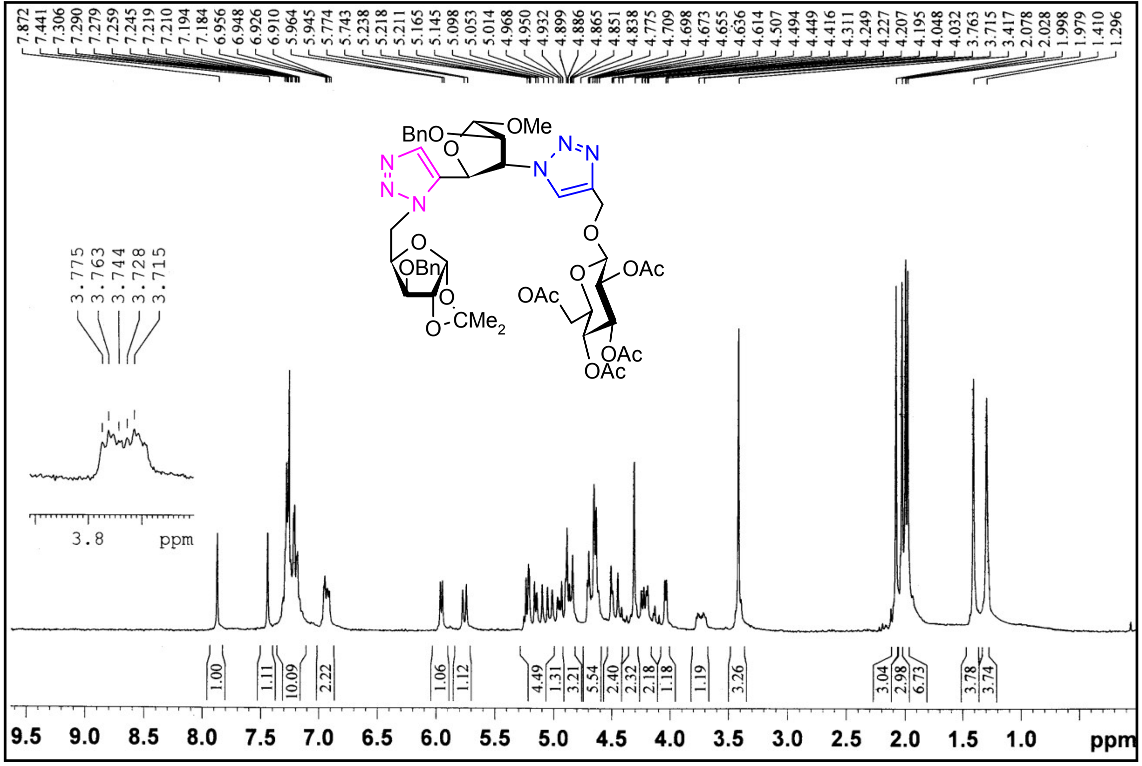
^{1}H NMR spectrum of 32



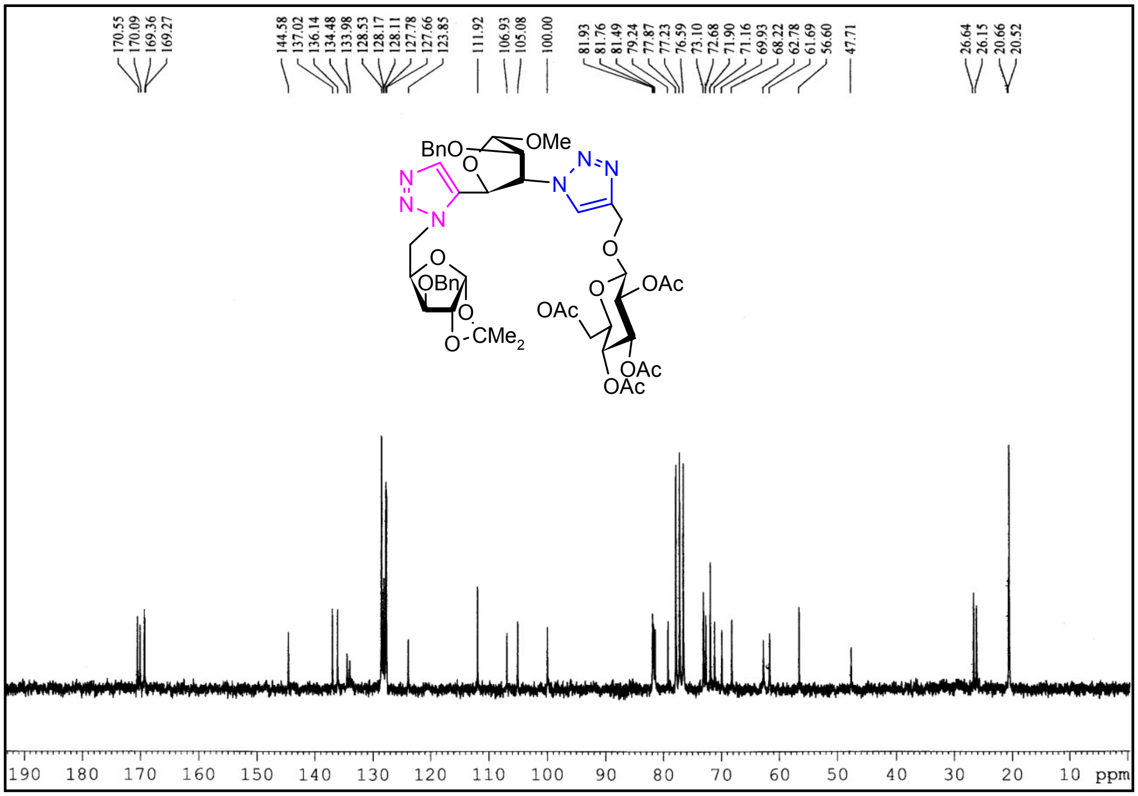
^{13}C NMR spectrum of 32



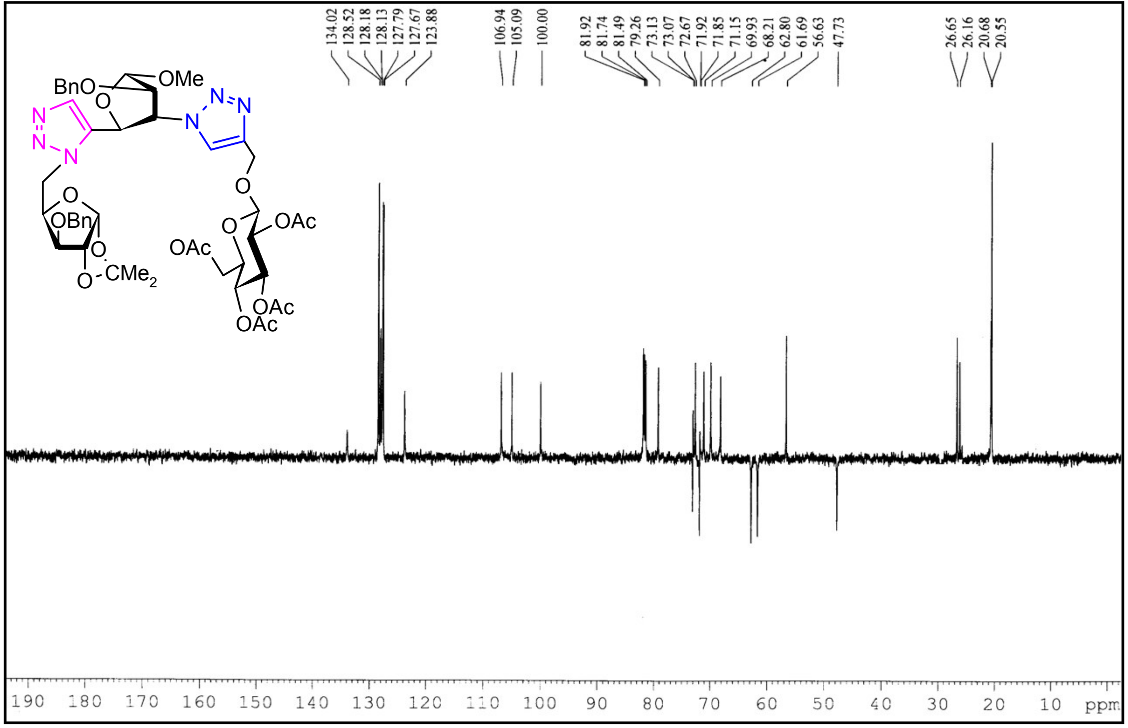
^{1}H NMR spectrum of 33



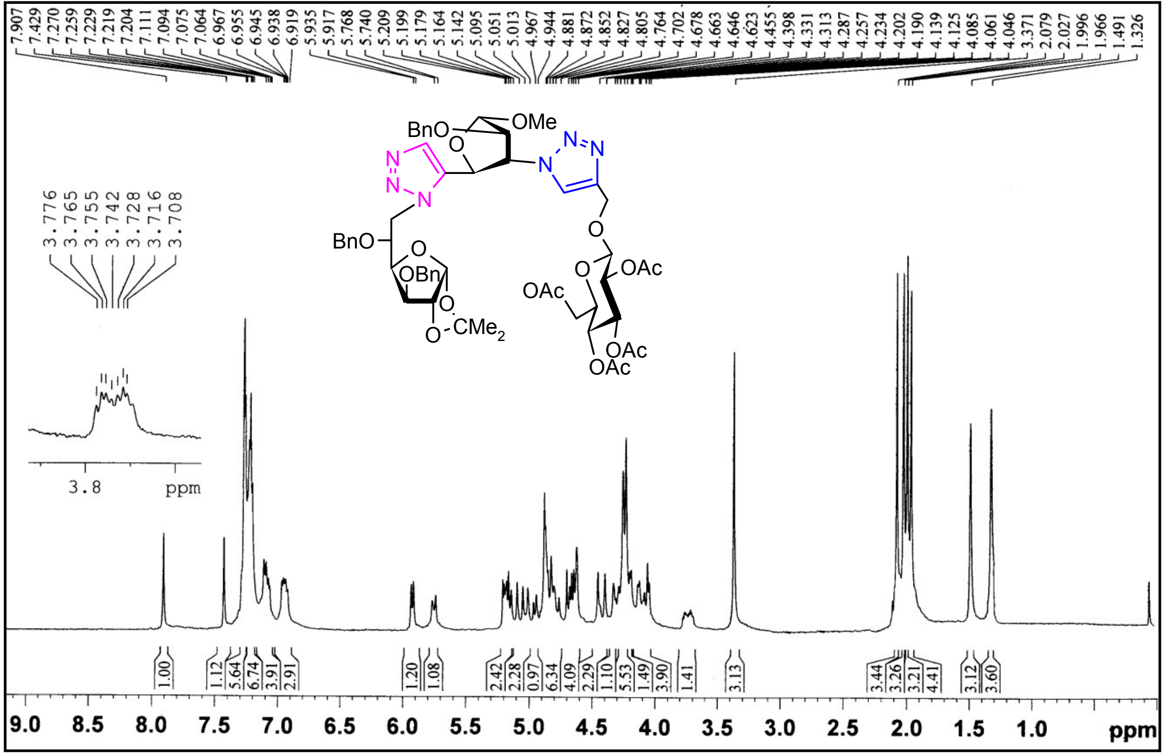
^{13}C NMR spectrum of 33



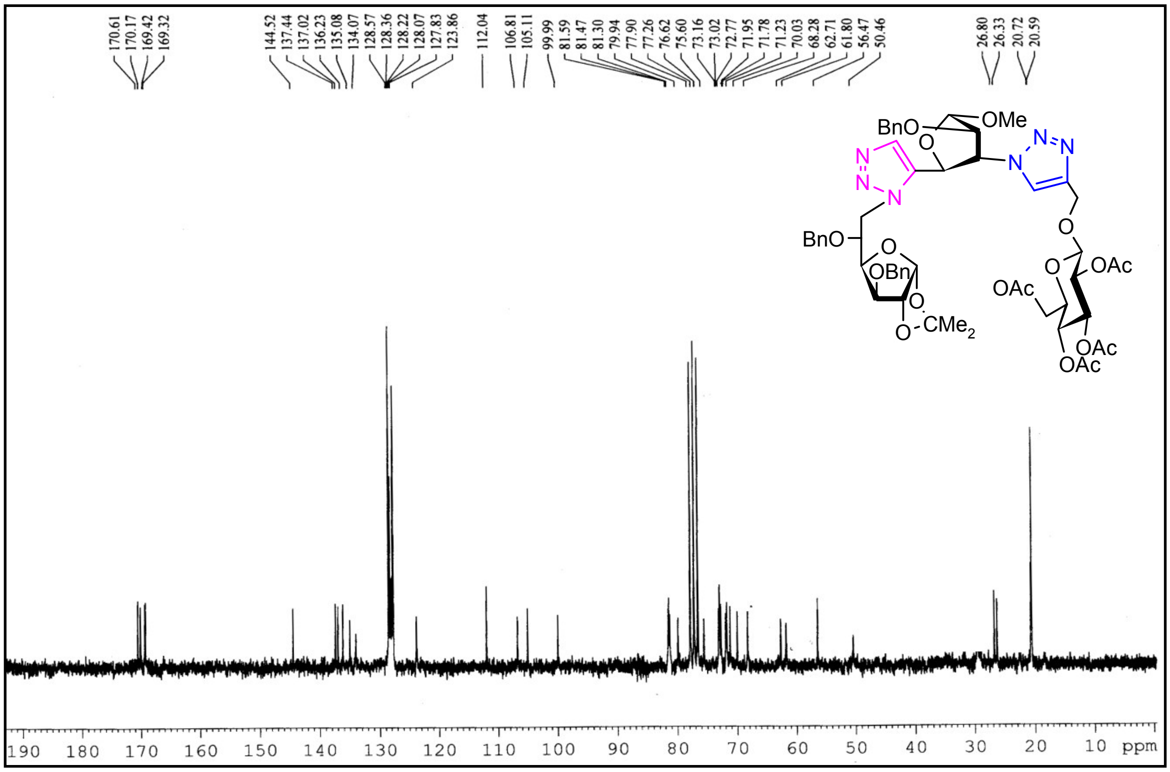
DEPT spectrum of 33



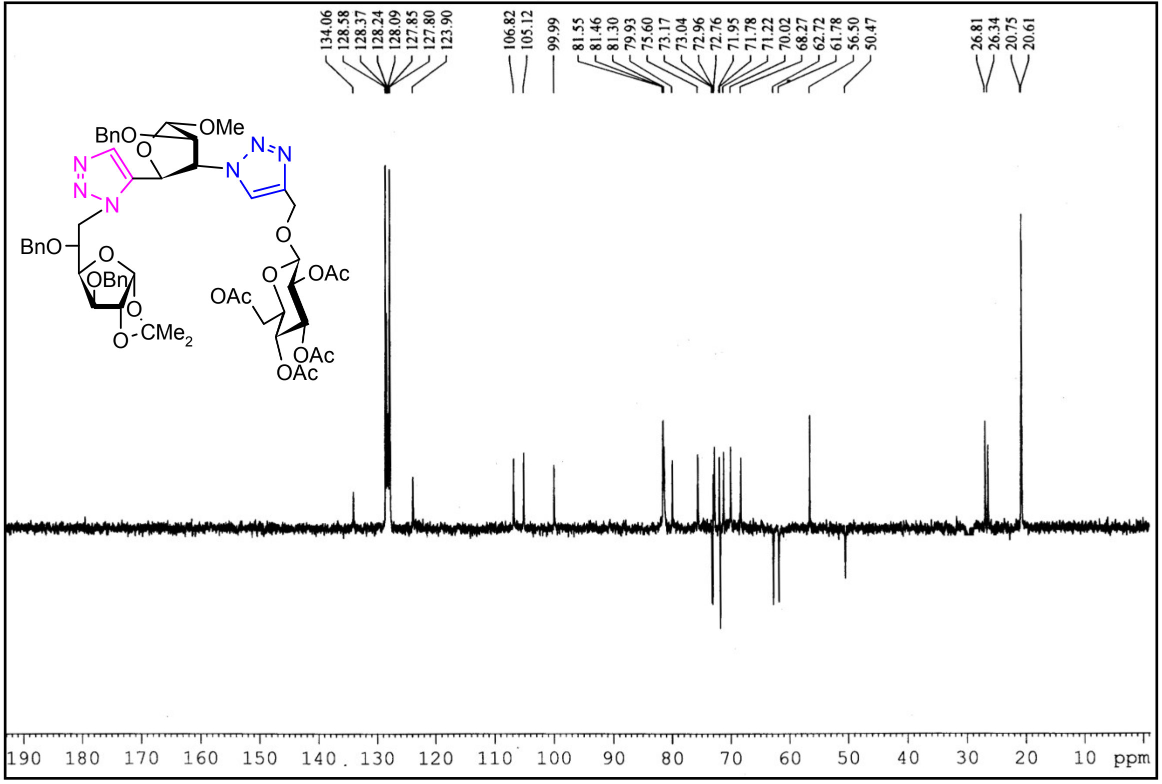
^{1}H NMR spectrum of 34



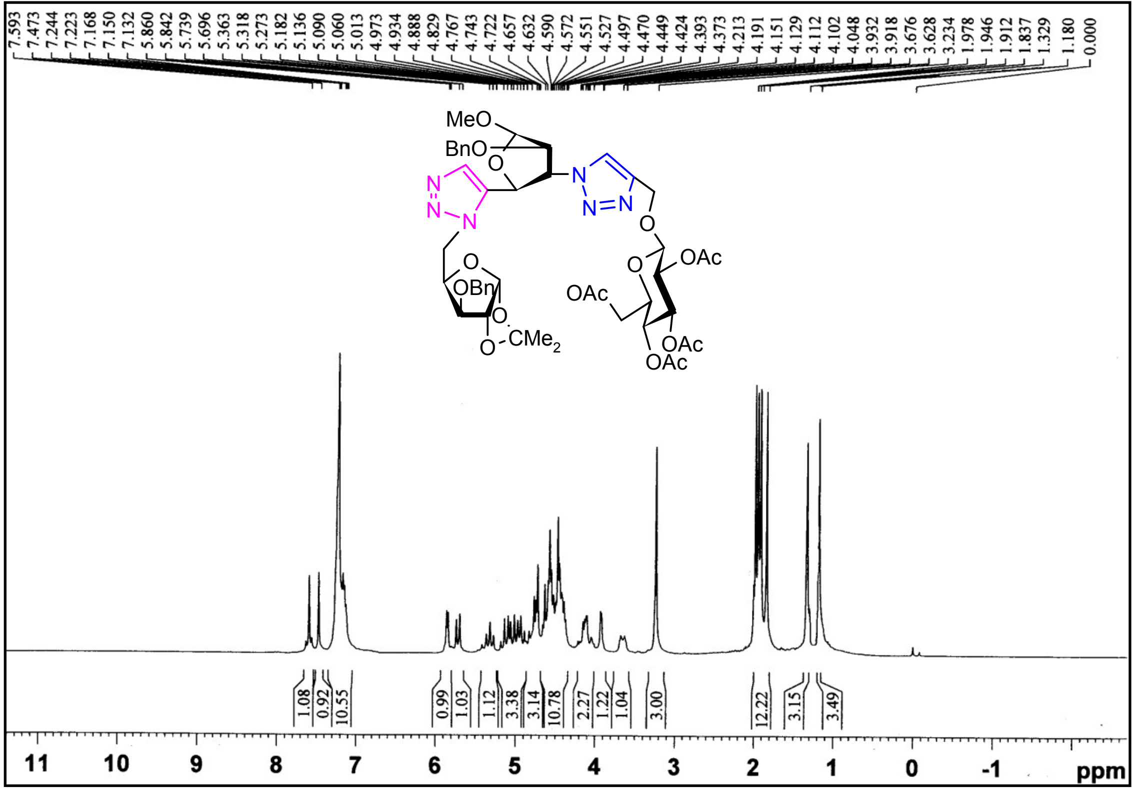
^{13}C NMR spectrum of 34



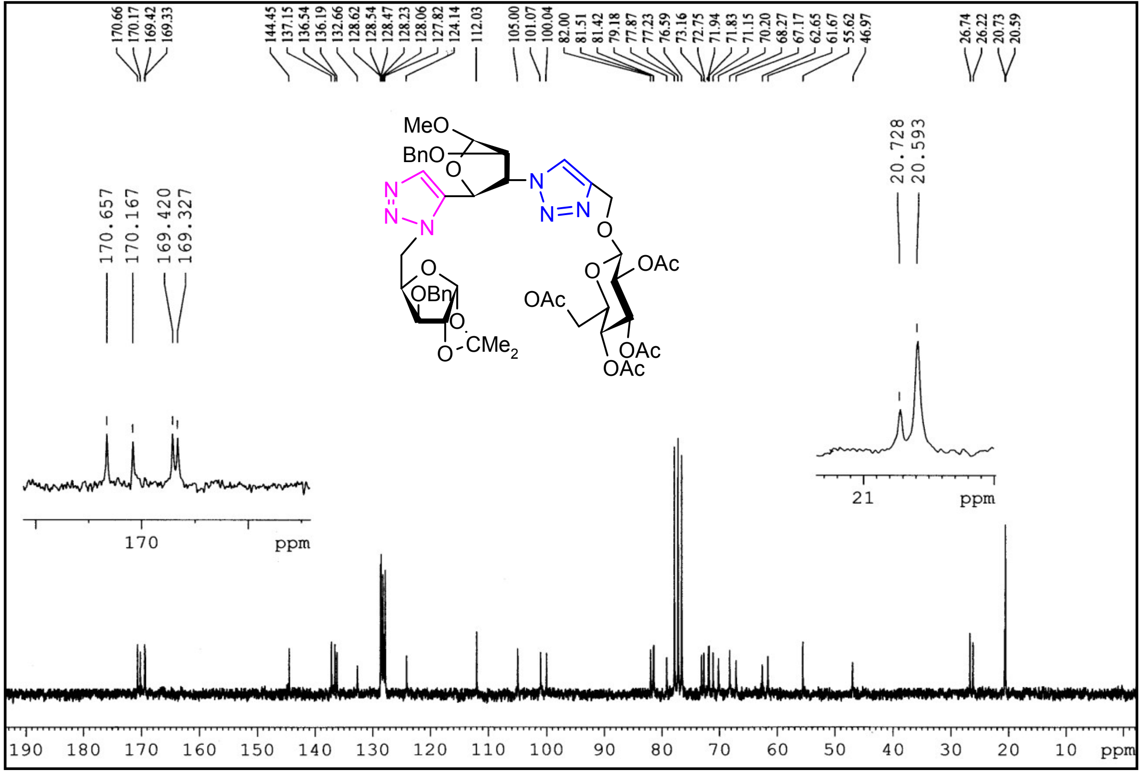
DEPT spectrum of 34



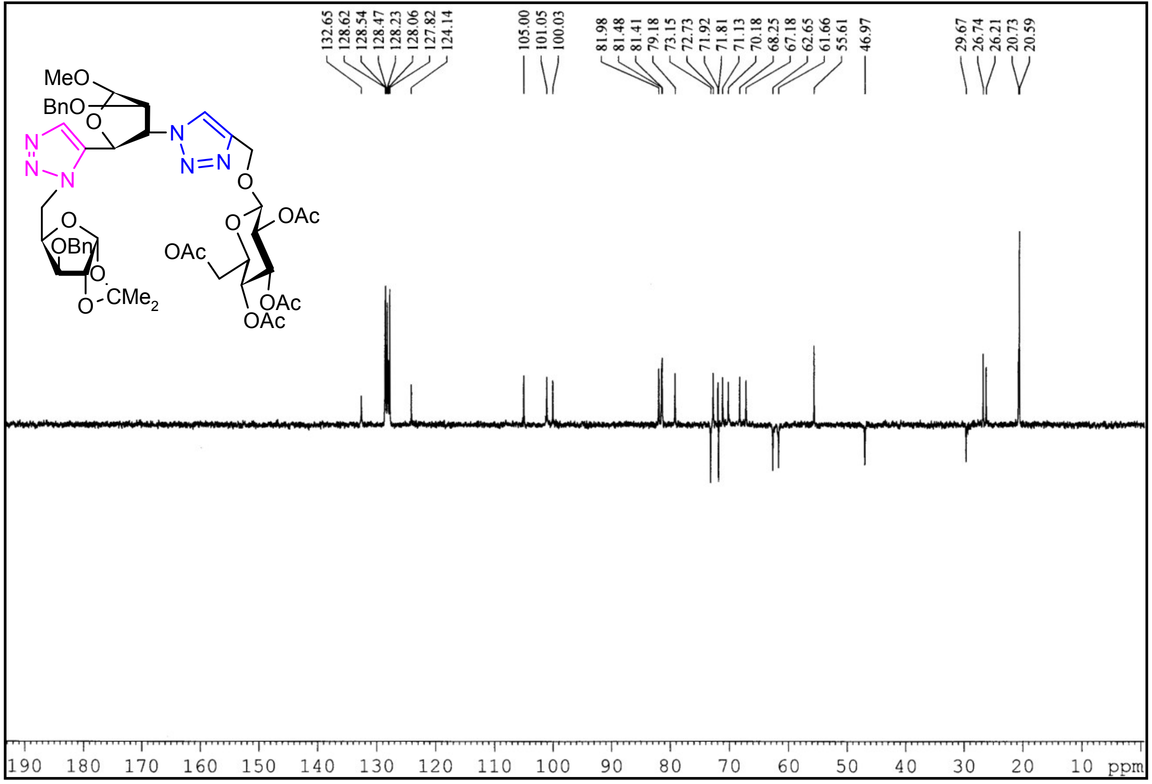
^{1}H NMR spectrum of 35



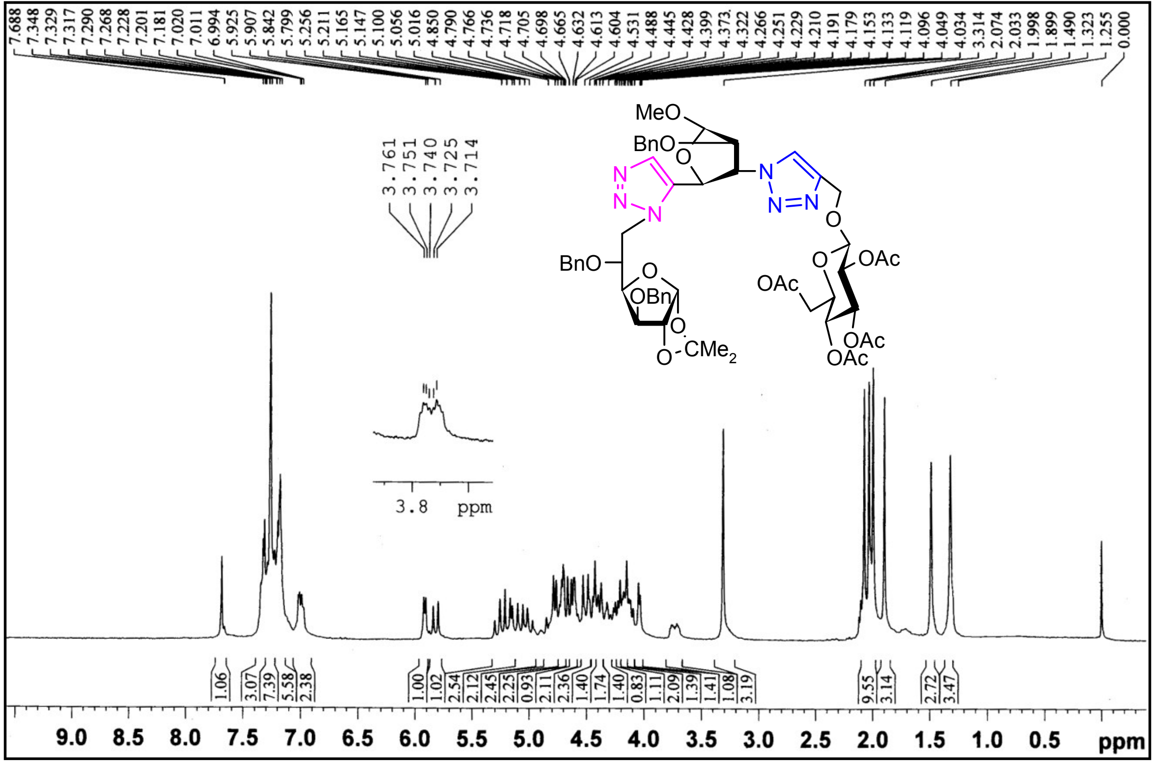
^{13}C NMR spectrum of 35



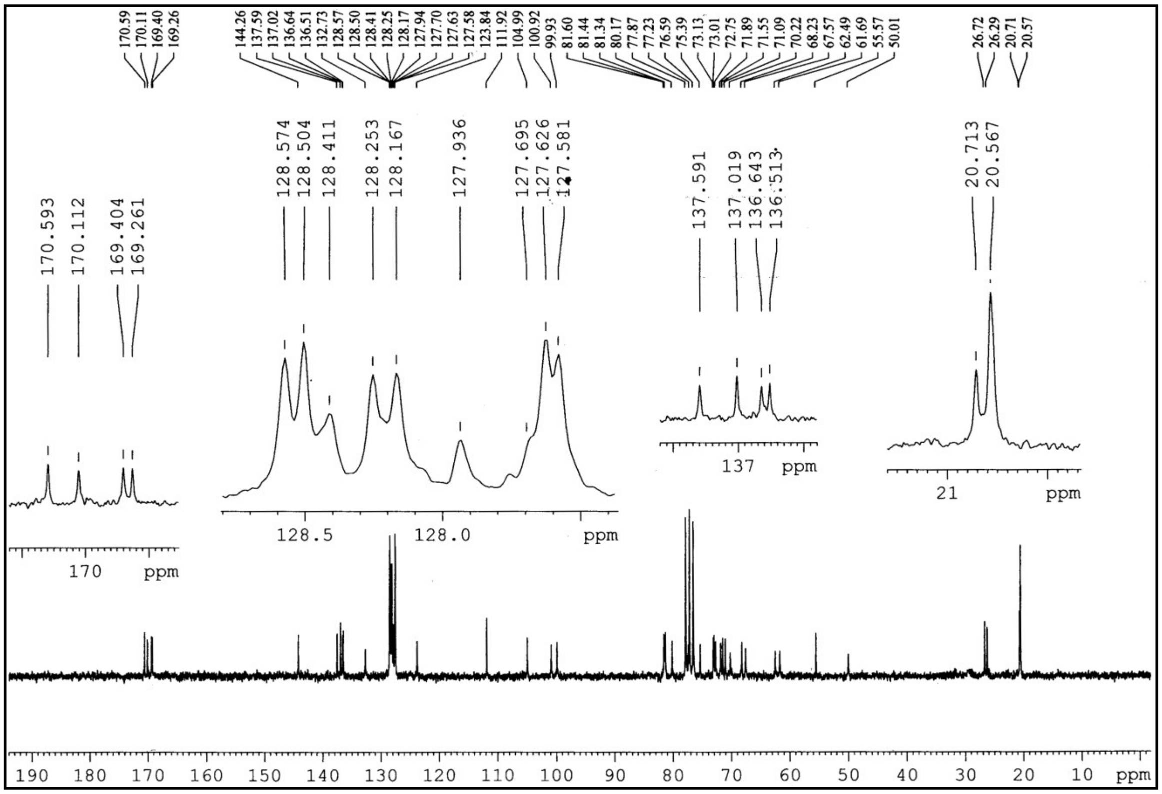
DEPT spectrum of 35



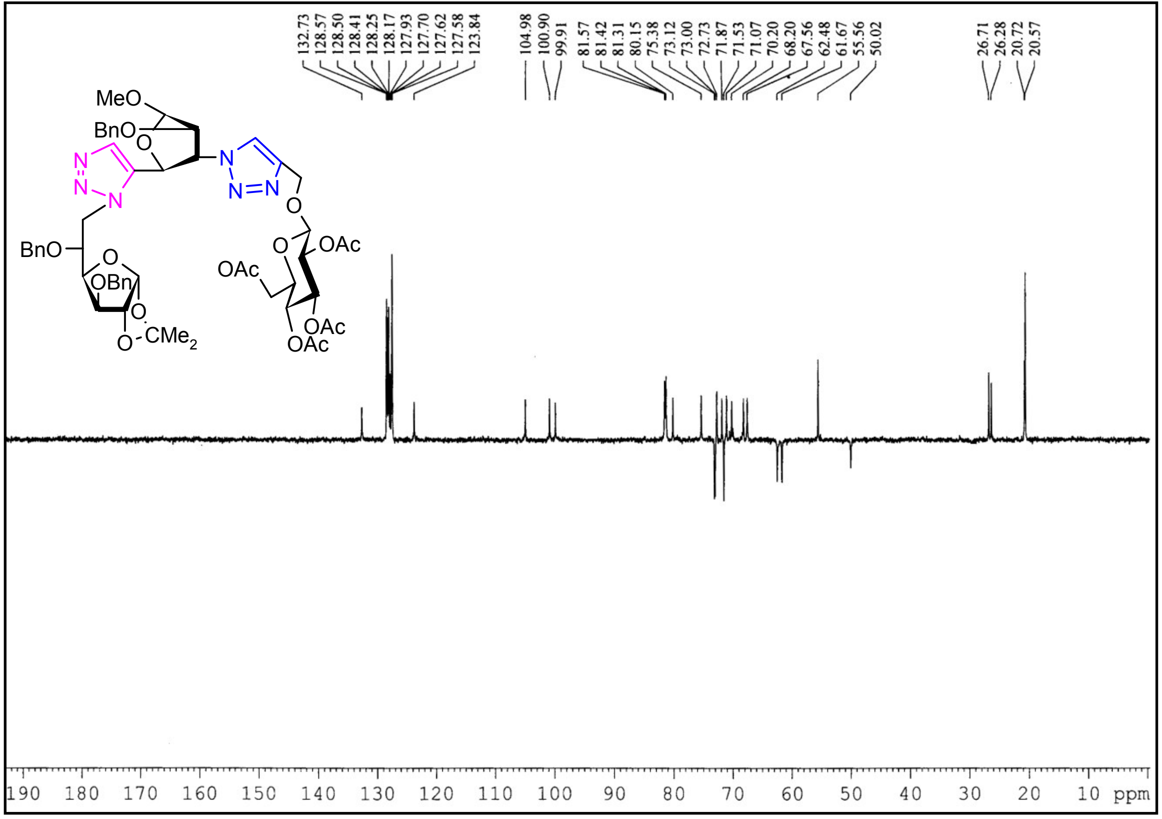
^{1}H NMR spectrum of 36



^{13}C NMR spectrum of 36



DEPT spectrum of 36



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