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1,1-Dioxothiomorpholines with Asymmetric Environments: Protecting Group Directed Diastereoselectivity of Glyco Divinyl Sulfone Cyclization

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Experimental Section

General methods: Carbohydrates and other fine chemicals were obtained from commercial suppliers and used without purification. Solvents were dried and distilled following the standard procedures. TLC was carried out on precoated plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light or by charring the plates dipped in 5% H_2SO_4-MeOH solution. Column chromatography was performed on silica gel (230-400 mesh). ^1H and ^{13}C NMR for compounds were recorded at 400 MHz instrument and 100 MHz instrument respectively using $CDCl_3$ as the solvent. DEPT experiments were carried out to identify the methylene carbons. High resolution mass spectra were recorded using QTOF mass analyzer. Optical rotations were recorded at 589 nm.

Compound 9α: A mixture of mercaptoethanol (7.9 mL, 113.6 mmol) and TMG (10.5 mL, 90.9 mmol) in DMF (30 mL) was heated at 60 ^oC for 30 min. Compound **6α** (3 g, 11.36 mmol) was added to this mixture and the mixture was heated at 90-120 ^oC for 4-5 h with stirring under N_2. After completion (tlc), the reaction mixture was poured into satd. solution of $NaHCO_3$ (60 mL) and the product was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhyd. Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get a gummy residue. The residue was purified over silica gel column [Eluent: EtOAc : pet ether (1 : 1)] to get the sulfide **7α**. To a well-stirred solution of **7α** in dry MeOH (40 mL) was added MMPP (16.8 g, 34.08 mmol) and the mixture was stirred for 6 h under N_2. After completion of reaction (tlc), MeOH was evaporated to dryness under reduced pressure and the residue thus obtained was dissolved in satd. $NaHCO_3$ solution (30 mL). The solution was washed 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 column [Eluent: EtOAc : pet ether (3 : 2)] to obtain sulfone **8α**. To a well-stirred solution of **8α** in pyridine (35 mL) was added a solution of MsCl (3.9 mL, 34.08 mmol) in pyridine (10 mL) drop wise at 0 ^oC

under N_2. After completion of the addition, the reaction mixture was kept at +4 ^oC. After 24 h (tlc), the reaction mixture was poured into ice-cold water and the product 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 crude material was stirred at room temperature with Et_3N (2 mL) in DCM (10 mL). After 2h (tlc), the reaction mixture was concentrated under reduced pressure to get a residue. The residue was purified over silica gel column to get compound **9α** (2.11 g, 55% in three steps from **6α**). Eluent: EtOAc : pet ether (1 : 3); white solid; mp: 110 ^oC (from EtOH); $[\alpha]^{24.6}_D$ +85.6 (*c* 0.12 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.51 (s, 3H), 3.86-3.97 (m, 2H), 4.35-4.38 (m, 1H), 4.58-4.60 (m, 1H), 5.09 (d, *J* = 1.6 Hz, 1H), 5.67 (s, 1H), 5.98 (d, *J* = 9.6 Hz, 1H), 6.36 (d, *J* = 16.4 Hz, 1H), 6.65-6.72 (m, 1H), 6.81 (m, 1H), 7.37-7.39 (m, 3H), 7.45-7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 56.7, 64.0, 68.8 (CH_2), 73.9, 95.5, 102.1, 126.0, 128.3, 129.2, 129.7 (CH_2), 135.5, 136.7, 137.9, 141.4; Anal. Calcd for $C_{16}H_{18}O_6S$: C 56.79, H 5.36 Found: C 56.80, H 5.20.

Compound 9β: Compound **6β** (1 g, 3.78 mmol) was converted to **9β** (0.67 g, 53% in three steps) following the procedure described for the synthesis of compound **9α**. Eluent: EtOAc : pet ether (1 : 3); colorless gum; $[\alpha]^{25.5}_D$ +27.0 (*c* 0.36 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.50 (s, 3H), 3.76-3.82 (m, 1H), 3.95 (t, *J* = 10.4 Hz, 1H), 4.34-4.38 (m, 1H), 4.70-4.73 (m, 1H), 5.40-5.41 (m, 1H), 5.69 (s, 1H), 5.99 (d, *J* = 9.6 Hz, 1H), 6.37 (d, *J* = 16.4 Hz, 1H), 6.65-6.72 (m, 1H), 6.77 (d, *J* = 1.2 Hz, 1H), 7.37-7.39 (m, 3H), 7.44-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 55.7, 68.5 (CH_2), 69.9, 73.5, 98.6, 102.0, 125.9, 128.3, 129.2, 129.6 (CH_2), 136.6, 137.5, 138.1, 141.9; Anal. Calcd for $C_{16}H_{18}O_6S$: C 56.79, H 5.36 Found: C 56.83, H 4.96.

Compound 10: Benzylamine (0.043 mL, 0.41 mmol) was added to a solution of **9α** (0.14 g, 0.41 mmol) in MeOH (15 mL) and the mixture was stirred at room temperature for 3 h. Volatile matters were removed under reduced pressure. The product was purified over silica gel to afford **10** (0.146 g, 79%). Eluent: EtOAc : pet ether (1 : 4); white solid; mp: 124 ^{o}C (from EtOH); $[\alpha]^{25.2}_{D}$ +32.6 (*c* 1.46 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.00-3.05 (m, 2H), 3.35-3.39 (2H), 3.51 (s, 3H), 3.65-3.67 (m, 2H), 3.88 (t, *J* = 10.0 Hz, 1H), 3.96-4.00 (m, 1H), 4.36 (dd, *J* = 4.4, 10.4 Hz, 1H), 4.60 (d, *J* = 8.8 Hz, 1H), 5.08 (s, 1H), 5.67 (s, 1H), 6.78-6.80 (m, 1H), 7.21-52 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 42.1 (CH_2), 53.0 (CH_2), 55.5 (CH_2), 56.7, 63.9, 68.9 (CH_2), 74.1, 95.6, 102.2, 126.1, 127.1, 128.1, 128.4, 129.4, 136.7, 139.6, 140.5; HRMS [ES^+, $(M + H)^+$] for $C_{23}H_{28}NO_6S$ found 446.1631, calcd 446.1637.

Compound 11: DBU (0.13 mL, 0.887 mmol) was added to a solution of **9α** (0.1 g, 0.296 mmol) in THF-H_2O (5 mL) and the solution was stirred at room temperature for 7 h. Volatile matters were removed under reduced pressure. The product was purified over silica gel column to afford compound **11** (0.085 g, 81%). Eluent: EtOAc : pet ether (2 : 3); colorless gum; $[\alpha]^{25.5}_{D}$ -53.9 (*c* 0.58 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.95 (dd, *J* = 2.4, 14.4 Hz, 1H), 3.39 (s, 3H), 3.49-3.57 (m, 2H), 3.89 (d, *J* = 4.4 Hz, 2H), 4.03-4.34 (m, 5H), 4.73 (s, 1H), 5.64 (s, 1H), 7.32-7.38 (m, 3H), 7.51-7.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 49.2 (CH_2), 55.2, 61.2, 64.3, 65.9 (CH_2), 69.0 (CH_2), 74.1, 99.1, 101.6, 126.1, 128.4, 129.1, 137.0; HRMS [ES^+, $(M + H)^+$] for $C_{16}H_{21}O_7S$ found 357.1033, calcd 357.1008.

Compound 12: Aq. acetic acid (50%, 6 mL) was added to compound **11** (0.05 g, 0.14 mmol) and the mixture was stirred at 80 ^{o}C for 4 h. Volatile matters were evaporated and co-evaporated by addition of toluene under reduced pressure. The product was purified over

silica gel column to afford compound **12** (0.021 g, 66%). Eluent: EtOAc : pet ether (4 : 1); white solid; mp: 136 ^{o}C (from EtOH); $[\alpha]^{25.5}_{D}$ -37.0 (*c* 0.43 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.68-1.77 (m, 8H), 2.49 (bs, 4H), 2.69 (bs, 4H), 2.94 (bs, 2H), 3.16 (m, 1H), 3.24 (m, 1H), 3.32-3.36 (m, 1H), 3.39 (s, 3H), 3.59 (d, *J* = 10.8 Hz, 1H), 3.81-3.83 (m, 2H), 4.51 (bs, 1H), 5.09 (s, 1H), 7.21-7.32 (m, 9H), 7.46-7.48 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 49.4 (CH_2), 55.2, 62.1 (CH_2), 62.8, 63.2, 65.5 (CH_2), 71.3, 98.4; HRMS [ES^+, $(M + Na)^+$] for $C_9H_{16}O_7NaS$ found 291.0527, calcd 291.0514.

Compound 14a: Benzylamine (0.038 mL, 0.35 mmol) was added to a solution of **9β** (0.12 g, 0.35 mmol) in MeOH (10 mL) and the mixture was stirred at room temperature for 24 h. Volatile matters were removed under reduced pressure. The product was purified over silica gel to afford compound **14a** (0.098g, 62%). Eluent: EtOAc : pet ether (1 : 4); white solid; mp: 146 ^{o}C (from EtOH); $[\alpha]^{25.2}_{D}$ -50.8 (*c* 1.14 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.94-3.00 (m, 2H), 3.20-3.26 (m, 1H), 3.44-3.45 (m, 2H), 3.55 (s, 3H), 3.63-3.69 (m, 1H), 3.72 (d, *J* = 4.8 Hz, 1H), 3.85-3.92 (m, 2H), 4.22 (d, *J* = 13.2 Hz, 1H), 4.42 (dd, *J* = 4.6, 10.6 Hz, 1H), 4.69-4.75 (m, 2H), 5.72 (s, 1H), 7.28-7.40 (m, 8H), 7.55-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 46.7 (CH_2), 47.9 (CH_2), 56.5 (CH_2), 56.9, 61.0, 62.3, 69.6(CH_2), 74.1, 77.3, 101.5, 103.3, 126.1, 126.8, 127.8, 128.4, 128.7, 128.8, 129.1, 137.0, 138.8; HRMS [ES^+, $(M + H)^+$] for $C_{23}H_{28}NO_6S$ found 446.1638, calcd 446.1637.

Compound 14b: Butylamine (0.029 mL, 0.29 mmol) was added to a solution of **9β** (0.1g, 0.29mmol) in MeOH (10 mL) and the mixture was stirred at room temperature for 2 h. The mixture was then heated under reflux for 24 h. It was cooled and volatile matters were removed under reduced pressure. The product was purified over silica gel to afford compound **14b** (0.079 g, 65%). Eluent: EtOAc : pet ether (1 : 4); white solid; mp: 140 ^{o}C

(from EtOH); $[\alpha]^{25.2}_{D}$ -64.2 (*c* 1.12 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.84-0.94 (m, 3H), 1.28-1.51 (m, 4H), 2.72-2.79 (m, 1H), 2.91 (bs, 1H), 3.04-3.22 (m, 3H), 3.37 (bs, 1H), 3.48 (s, 4H), 3.62-3.68 (m, 2H), 3.82 (t, *J* = 10.2 Hz ,1H), 4.38 (dd, *J* = 4.8, 10.4 Hz, 1H), 4.60-4.66 (m, 2H), 5.66 (s, 1H), 7.32-7.38 (m, 3H), 7.51-7.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 20.3 (CH_2), 29.8 (CH_2), 47.1, 48.0 (CH_2), 52.8 (CH_2), 56.5, 60.5, 61.5, 69.6 (CH_2), 73.7, 101.3, 103.0, 126.1, 128.3, 129.0, 137.1; HRMS [ES^+, $(M + H)^+$] for $C_{20}H_{30}NO_6S$ found 412.1814, calcd 412.1794.

Compound 14c: Isobutylamine (0.024 mL, 0.25 mmol) was added to a solution of **9β** (0.084g, 0.25mmol) in MeOH (10 mL) and the mixture was stirred at room temperature for 2 h. The mixture was then heated under reflux for 36 h. It was cooled and volatile matters were removed under reduced pressure. The product was purified over silica gel to afford compound **14c** (0.081 g, 78%). Eluent: EtOAc : pet ether (1 : 3); white solid; mp: 192 ^oC (from EtOH); $[\alpha]^{25.2}_{D}$ -72.4 (*c* 1.2 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.86-0.91 (m, 6H), 1.68-1.74 (m, 1H), 2.37-2.42 (m, 1H), 2.64-2.68 (m, 1H), 2.93-2.99 (m, 1H), 3.11 (bs, 2H), 3.45 (s, 4H), 3.55-3.56 (m, 1H), 3.66-3.79 (m, 3H), 4.34-4.38 (m, 1H), 4.64 (s, 1H), 5.51 (t, *J* = 9.0 Hz, 1H), 5.65 (s, 1H), 7.31-7.37 (m, 3H), 7.50-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 20.5, 20.6, 27.2, 46.5 (CH_2), 48.6 (CH_2), 56.0, 60.8, 61.3 (CH_2), 67.2, 70.0 (CH_2), 73.4, 101.3, 102.2, 126.2, 128.3, 129.0, 137.1; HRMS [ES^+, $(M + H)^+$] for $C_{20}H_{30}NO_6S$ found 412.1811, calcd 412.1794.

Compound **15β:** Methyl β-D-glucopyranoside (5 g, 25.77 mmol) was converted to **15β** (2.1 g, 31%) following the procedure described for the synthesis of compound **15α** as mentioned in reference 18. Eluent: EtOAc : pet ether (1 : 10); glassy liquid; $[\alpha]^{25.5}_{D}$ +35.5 (*c* 0.9 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.21 (d, *J* = 3.8 Hz, 1H), 3.36 (d, *J* = 3.8 Hz, 1H), 3.50-3.67 (m, 7H), 4.47-4.56 (m, 3H),

4.70 (d, J = 11.3 Hz, 1H), 4.84 (s, 3H), 7.25-7.39 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 51.8, 56.7, 56.9, 69.0 (CH_2), 69.4, 71.7 (CH_2), 71.8, 73.2 (CH_2), 98.0, 127.5, 127.7, 127.8, 127.9, 128.3, 128.4, 137.7, 138.2; HRMS [ES^+, $(M + H)^+$] for $C_{21}H_{25}O_5$ found 357.1684, calcd 357.1702.

Compound 18α: Compound **15α** (2 g, 7.87 mmol) was converted to **18α** (1.48 g, 58%) following the procedure described for the synthesis of compound **9α**. Eluent: EtOAc : pet ether (1 : 4); glassy liquid; $[\alpha]^{25.2}_D$ +148.4 (*c* 0.17 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.47 (s, 3H), 3.73-3.83 (m, 2H), 3.95-3.99 (m, 1H), 4.44 (d, J = 10.8 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.69-4.73 (m, 2H), 4.87 (d, J = 10.8 Hz, 1H), 5.12 (d, J = 2.8 Hz, 1H), 5.82 (d, J = 10.0 Hz, 1H), 6.29 (d, J = 16.4 Hz, 1H), 6.61 (dd, J = 10.0, 16.8 Hz, 1H), 6.77-6.78 (m, 1H), 7.19-7.37 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 56.4, 68.0 (CH_2), 70.4 (2 x C), 73.6 (CH_2), 74.9 (CH_2), 94.9, 127.9, 127.9 (CH_2), 128.4, 128.4, 136.1, 137.2, 137.4, 138.7, 144.3; HRMS [ES^+, $(M + Na)^+$] for $C_{23}H_{26}O_6SNa$ found 453.1349, calcd 453.1348.

Compound 18β: Compound **15β** (1 g, 3.93 mmol) was converted to **18β** (0.65 g, 51%) following the procedure described for the synthesis of compound **9α**. Eluent: EtOAc : pet ether (1 : 4); glassy liquid; $[\alpha]^{25.5}_D$ +63.1 (*c* 0.84 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.47 (s, 3H), 3.52-3.57 (m, 1H), 3.61-3.69 (m, 1H), 4.27-4.35 (m, 1H), 4.48-4.53 (m, 3H), 4.62 (bs, 2H), 5.13 (d, J = 2.2 Hz, 1H), 5.91 (d, J = 9.4 Hz, 1H), 6.32 (d, J = 16.6 Hz, 1H), 6.54 (dd, J = 9.4, 16.6 Hz, 1H), 6.90 (d, J = 2.3 Hz, 1H), 7.26-7.40 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 56.0, 68.3, 69.3 (CH_2), 72.7 (CH_2), 73.4 (CH_2), 74.3, 94.7, 127.7, 127.8, 128.0, 128.4, 128.5, 128.5 (CH_2), 136.9, 137.4, 137.7, 137.9, 140.1; HRMS [ES^+, $(M + Na)^+$] for $C_{23}H_{26}O_6SNa$ found 453.1346, calcd 453.1348.

Compound 19a: Following the procedure described for **10**, in 48 h **18α** (0.05 g, 0.15 mmol) was converted to **19a** (0.06 g, 90%). Eluent: EtOAc : pet ether (1 : 4); white solid; mp: 142 ^{o}C (from EtOH); $[\alpha]^{25.2}_{D}$ +100.8 (*c* 1.30 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.95 (t, *J* = 15.2 Hz, 2H), 3.23-3.32 (m, 2H), 3.45 (s, 3H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.76-3.82 (m, 2H), 3.88 (d, *J* = 9.6 Hz, 1H), 3.96-4.00 (m, 1H), 4.04-4.07 (m, 1H), 4.20 (t, *J* = 13.2 Hz, 1H), 4.43-4.52 (m, 3H), 4.64 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 5.01 (d, *J* = 10.8 Hz, 1H), 7.26-7.36 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 44.9 (CH_2), 52.3 (CH_2), 54.8, 57.4, 58.4 (CH_2), 58.8, 65.8, 68.4 (CH_2), 72.2 (CH_2), 72.9, 73.5 (CH_2), 98.8, 127.5, 127.7, 128.2, 128.3, 128.6, 128.7, 137.4, 137.5, 137.9; HRMS [ES^+, $(M + H)^+$] for $C_{30}H_{36}NO_6S$ found 538.2276, calcd 538.2263.

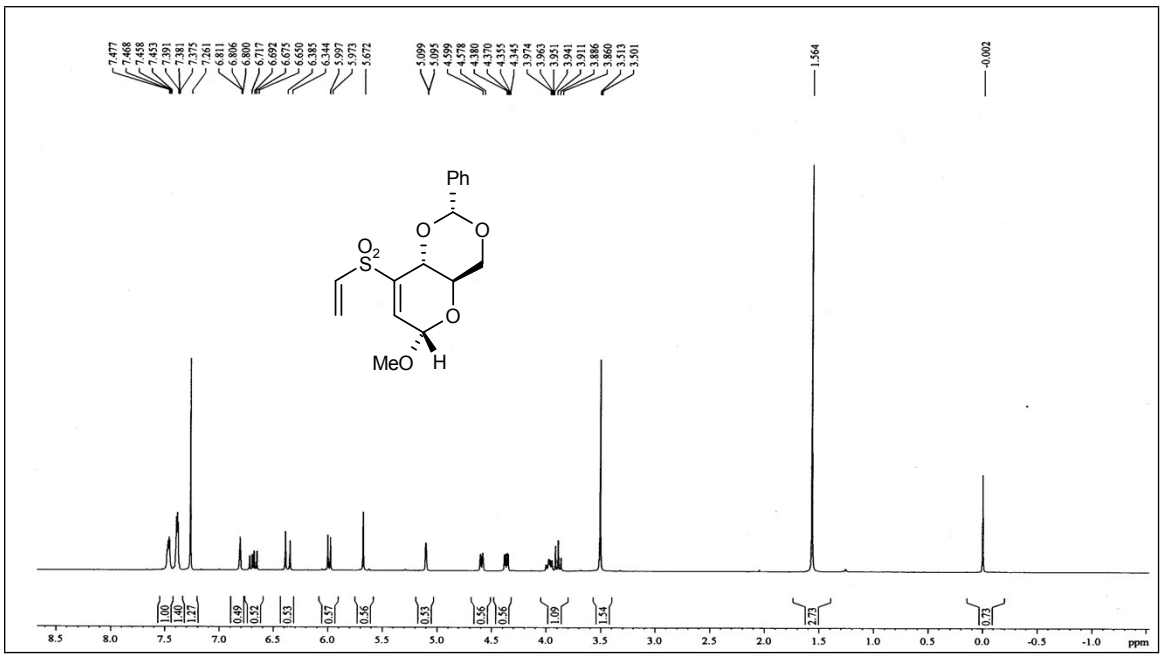
Compound 19b: Isopropylamine (0.013 mL, 0.15 mmol) was added to a solution of **18α** (0.05g, 0.15 mmol) in MeOH (15 mL) and the mixture was stirred at room temperature for 2 h. The mixture was then heated under reflux for 1 h. It was cooled and volatile matters were removed under reduced pressure. The product was purified over silica gel to afford compound **19b** (0.049 g, 83%). Eluent: EtOAc : pet ether (1 : 4); white solid; mp: 124 ^{o}C (from EtOH); $[\alpha]^{25.2}_{D}$ +108.1 (*c* 0.79 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.04-1.08 (m, 6H), 2.98-3.01 (m, 1H), 3.05-3.11 (m, 1H), 3.15-3.21 (m, 1H), 3.29-3.31 (m, 1H), 3.41 (s, 3H), 3.45-3.51 (m, 1H), 3.60-3.67 (m, 2H), 3.79-3.82 (m, 1H), 3.96-4.03 (m, 2H), 4.46-4.50 (m, 2H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.60 (bs, 1H), 4.62 (d, *J* = 3.6 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 7.26-7.37 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.7, 21.4, 41.4 (CH_2), 53.9, 54.6 (CH_2), 54.9, 57.2, 59.5, 65.4, 68.3 (CH_2), 72.1 (CH_2), 72.6, 73.6 (CH_2), 99.8, 127.6, 128.0, 128.2, 128.3, 128.4, 128.6, 137.3, 137.9; HRMS [ES^+, $(M + H)^+$] for $C_{26}H_{36}NO_6S$ found 490.2263, calcd 490.2263.

Compound 19c: Ethanolamine (0.018 mL, 0.31 mmol) was added to a suspension of **18α** (0.1 g, 0.31 mmol) in MeOH (15 mL) and the mixture was stirred at room temperature for 36 h. Volatile matters were removed under reduced pressure. It was dissolved in anhyd. pyridine (15 mL) and trityl chloride (0.17 g, 0.61 mmol) was added into it. The reaction mixture was stirred for 72 h at room temperature. The solution was then poured into satd. $NaHCO_3$ solution and the resulting solution was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhyd. Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure to get the crude product. Residual pyridine was co-evaporated with toluene. The product was purified over silica gel to afford **19c** (0.11 g, 53% in two steps). Eluent: EtOAc : pet ether (1 : 4); white solid; mp: 68 ^oC (from EtOH). $[\alpha]^{25.2}_D$ +56.6 (*c* 0.60 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.83-2.87 (m, 1H), 2.93-3.01 (m, 3H), 3.06-3.12 (m, 1H), 3.20 (bs, 2H), 3.39 (s, 3H), 3.49 (d, *J* = 4.0 Hz, 1H), 3.65 (d, *J* = 8.8 Hz, 1H), 3.78-3.80 (m, 1H), 3.95-4.06 (m, 3H), 4.32 (d, *J* = 10.8 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.58-4.61 (m, 1H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.91 (d, *J* =10.8 Hz, 1H), 7.21-7.44 (m, 25H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 45.4 (CH_2), 52.1 (CH_2), 54.8 (CH_2), 54.9, 57.2, 60.5, 62.7 (CH_2), 65.7, 68.6 (CH_2), 72.1 (CH_2), 72.9, 73.5 (CH_2), 86.9, 99.1, 127.1, 127.5, 127.7, 127.9, 128.2, 128.3, 128.5, 137.5, 138.0, 143.8; HRMS [ES^+, $(M + H)^+$] for $C_{44}H_{48}NO_7S$ found 734.3140, calcd 734.3152.

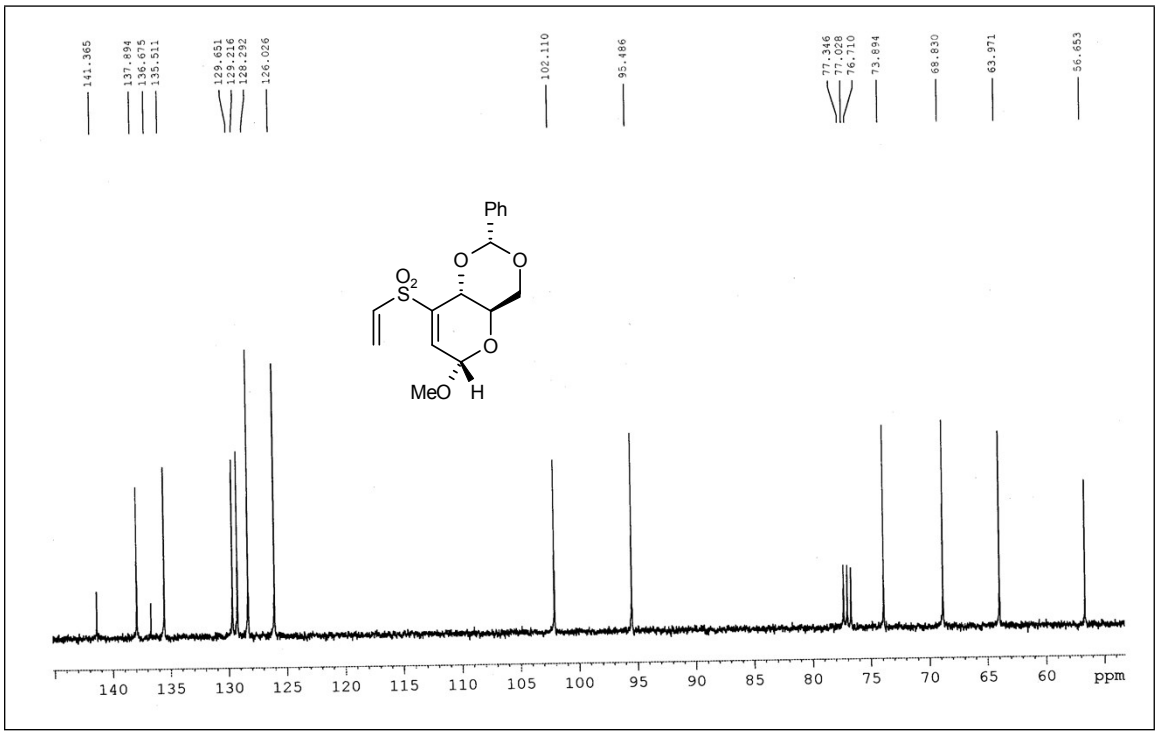
Compounds 20: Following the procedure described for **10**, in 6 h **18β** (0.03 g, 0.092mmol) was converted to a mixture of diastereomers **20** (0.025 g, 63%). Eluent: EtOAc : pet ether (1 : 4); white solid; ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.81-2.96 (m, 4H), 3.14-3.25 (m, 3H), 3.35-3.45 (m, 2H), 3.53-3.69 (m, 11H), 3.83 (d, *J* = 10.8 Hz, 1H), 3.91-4.08 (m, 6H), 4.39-4.64 (m, 8H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.94-4.99 (m, 2H), 5.52 (d, *J* = 7.2 Hz, 1H), 7.19-7.41 (m, 30H).

CCDC-935012 (for compound **12**), 1031469 (for compound **14b**) and 1031470 (for compound **19b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

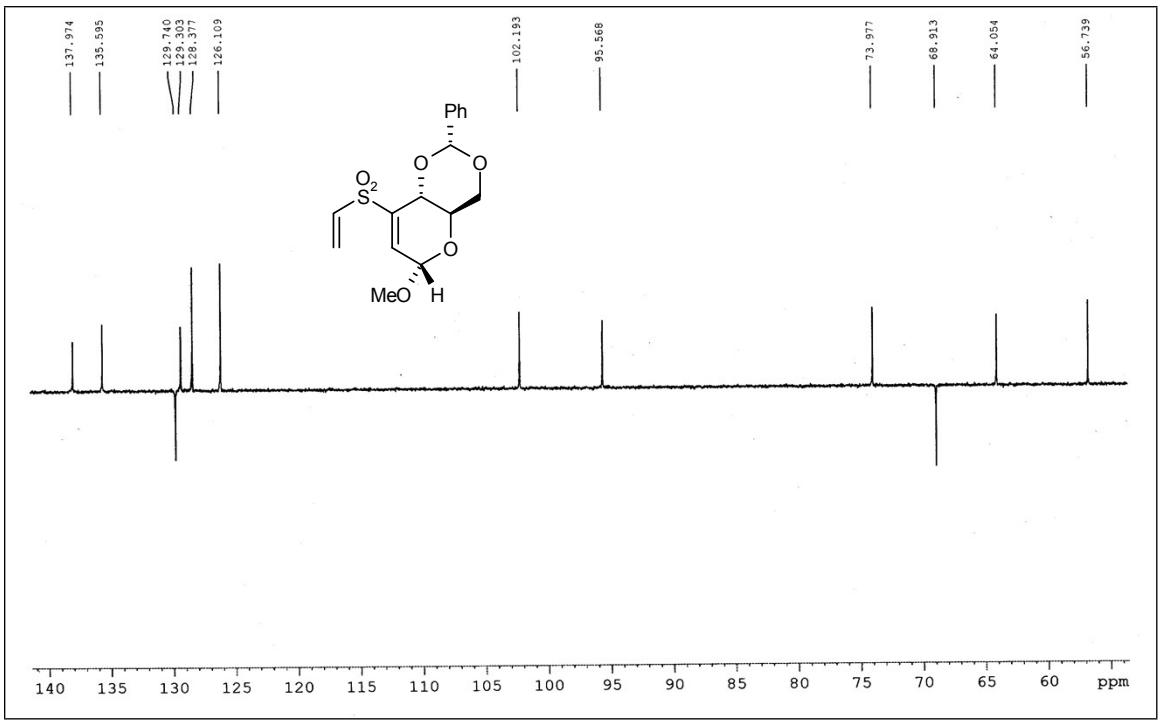
^{1}H NMR spectrum of compound **9α**



^{13}C NMR spectrum of compound **9α**

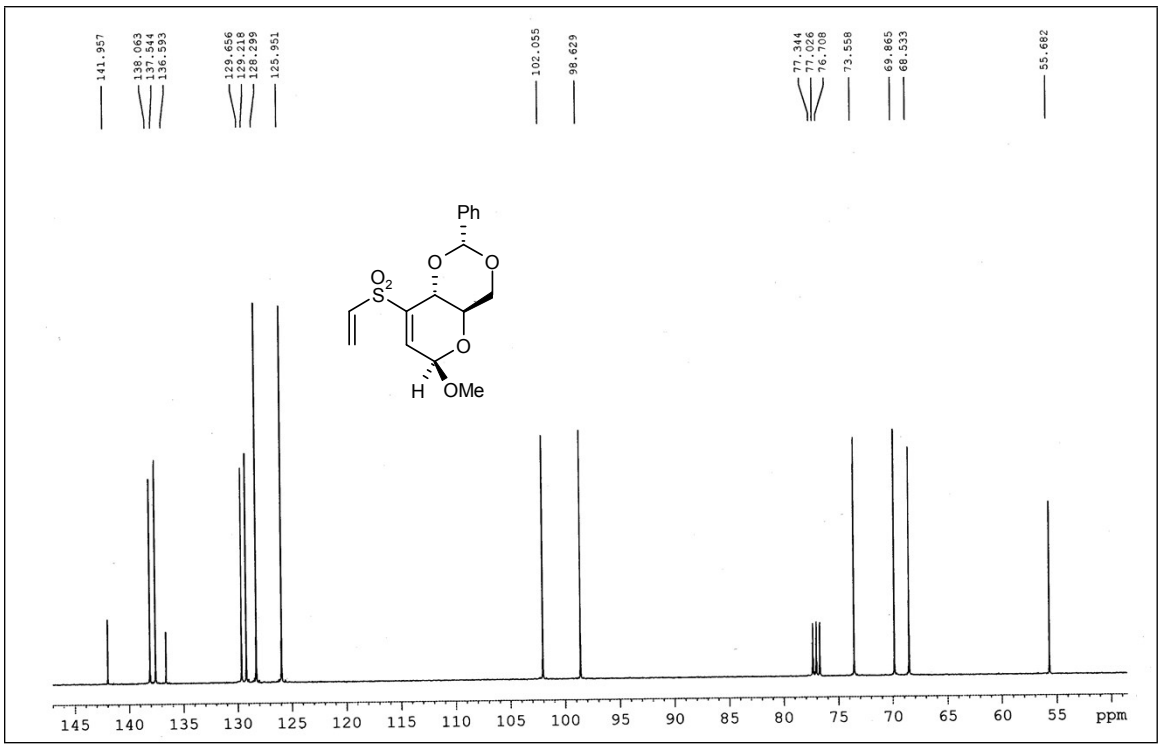


DEPT spectrum of compound **9α**

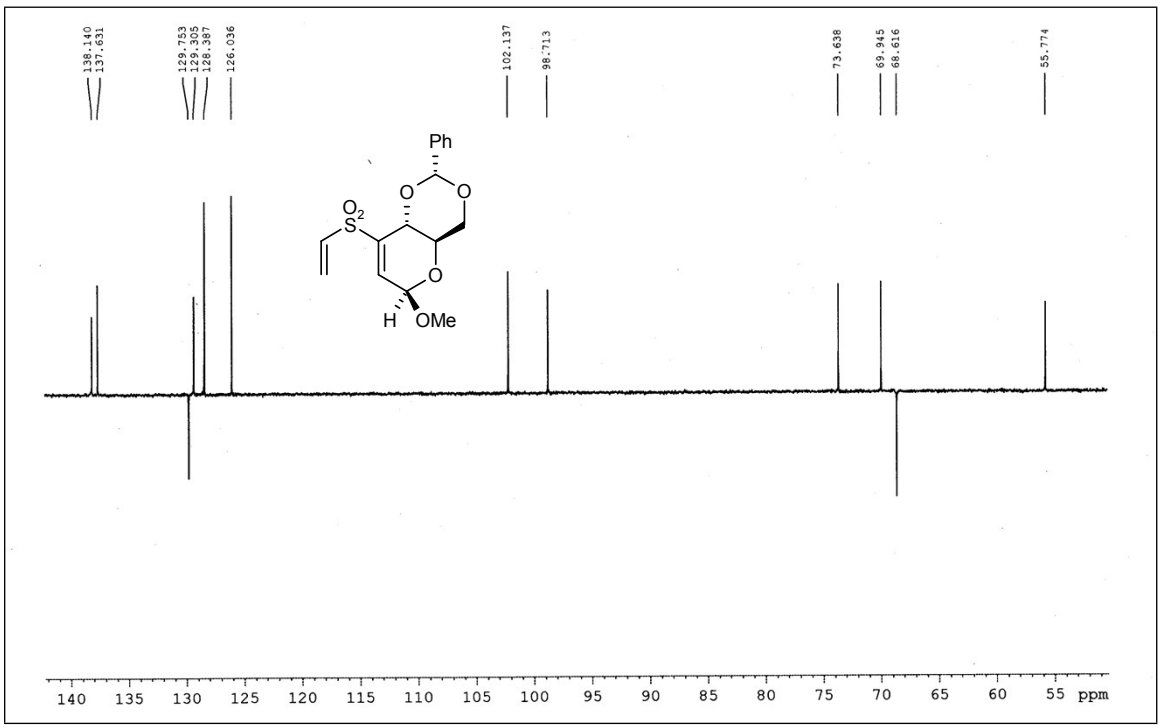


^{1}H NMR spectrum of compound **9β**

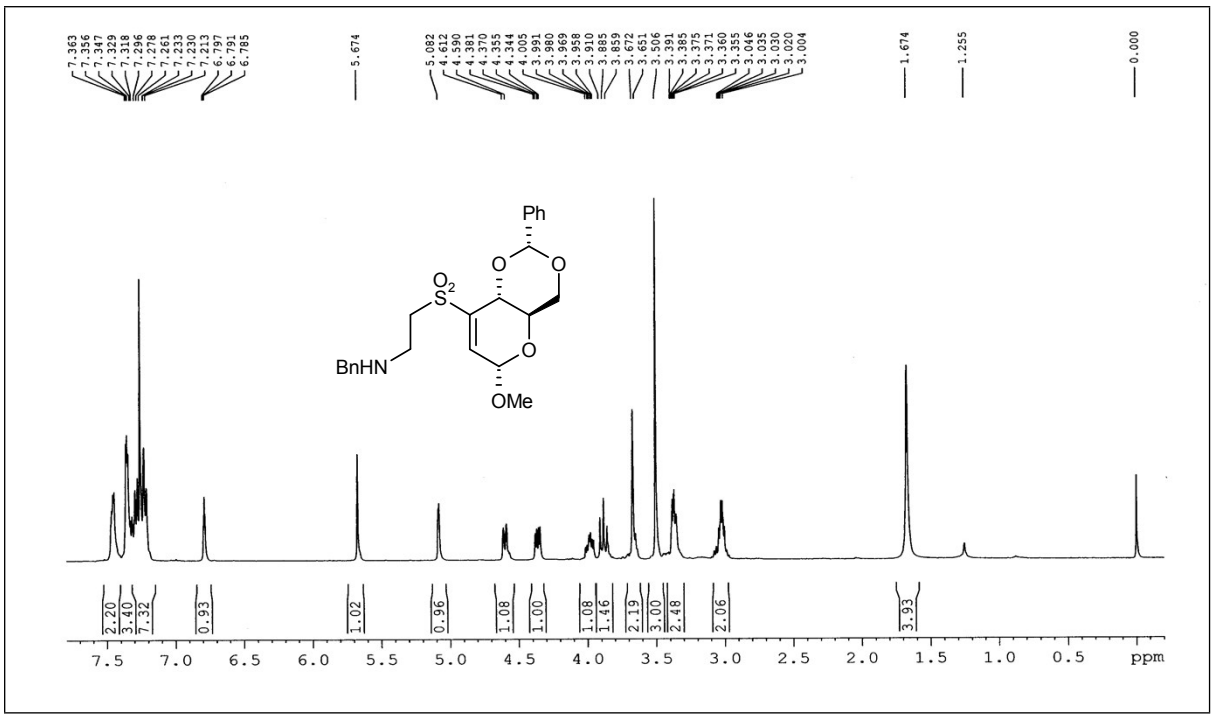
^{13}C NMR spectrum of compound **9β**



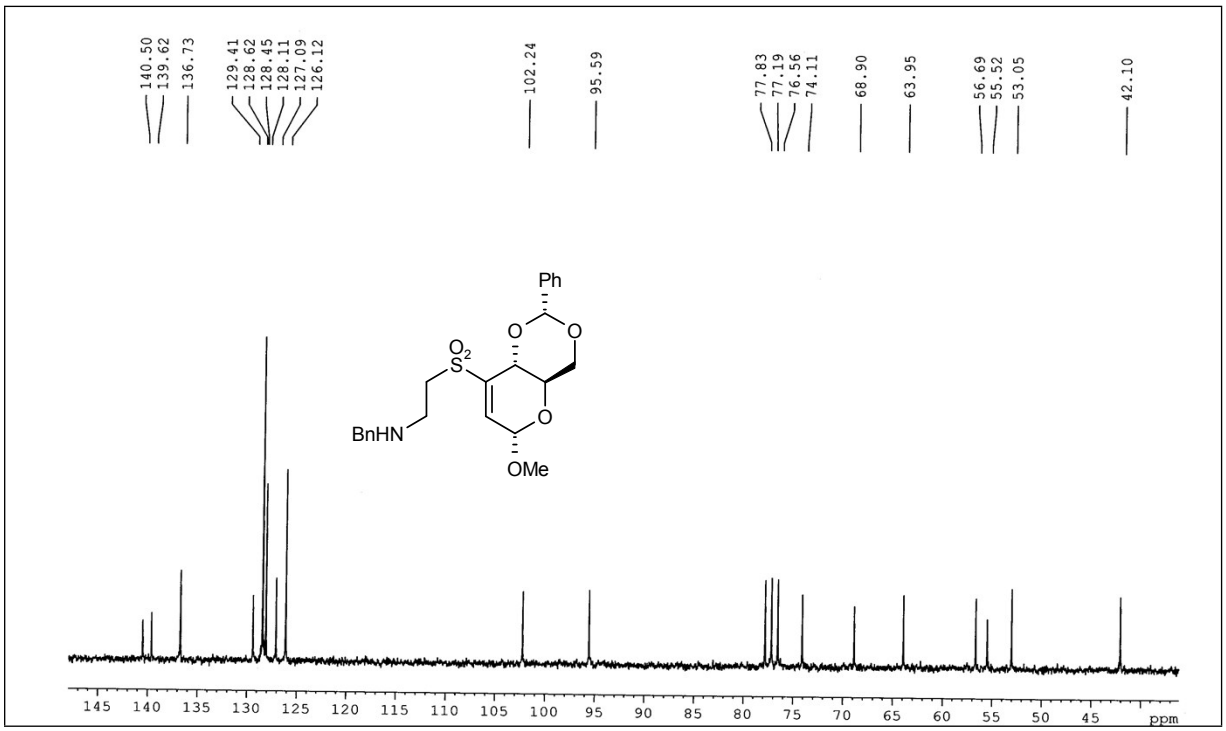
DEPT spectrum of compound **9β**



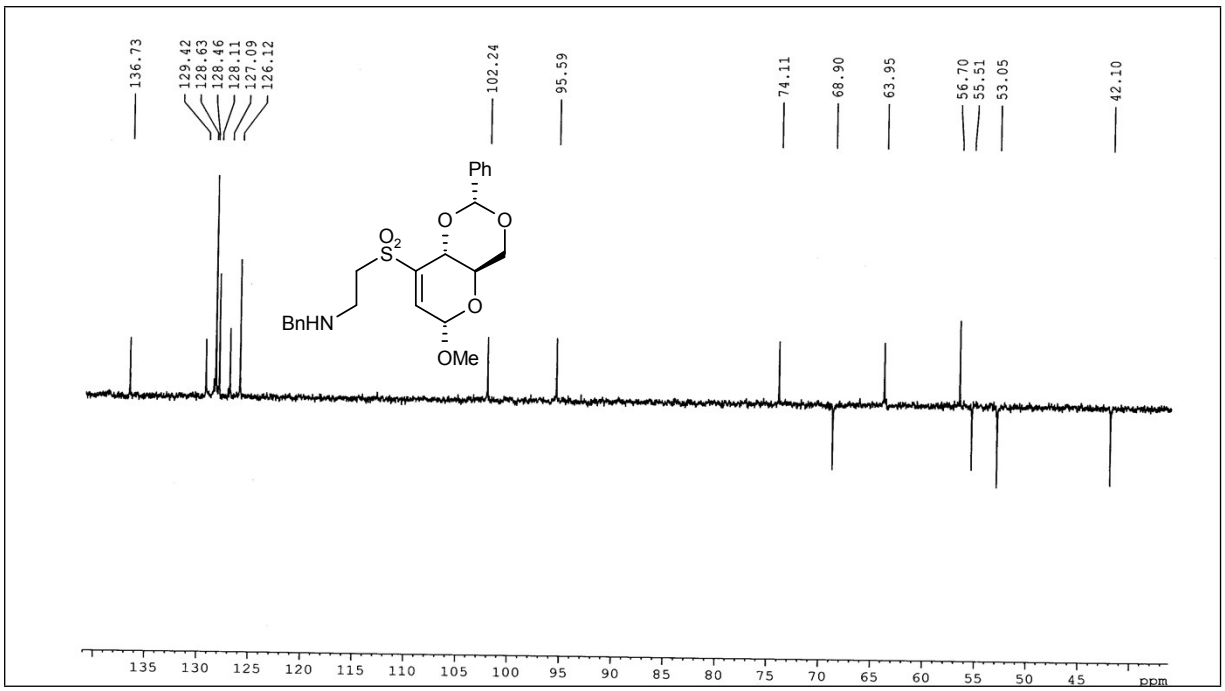
^{1}H NMR spectrum of compound **10**



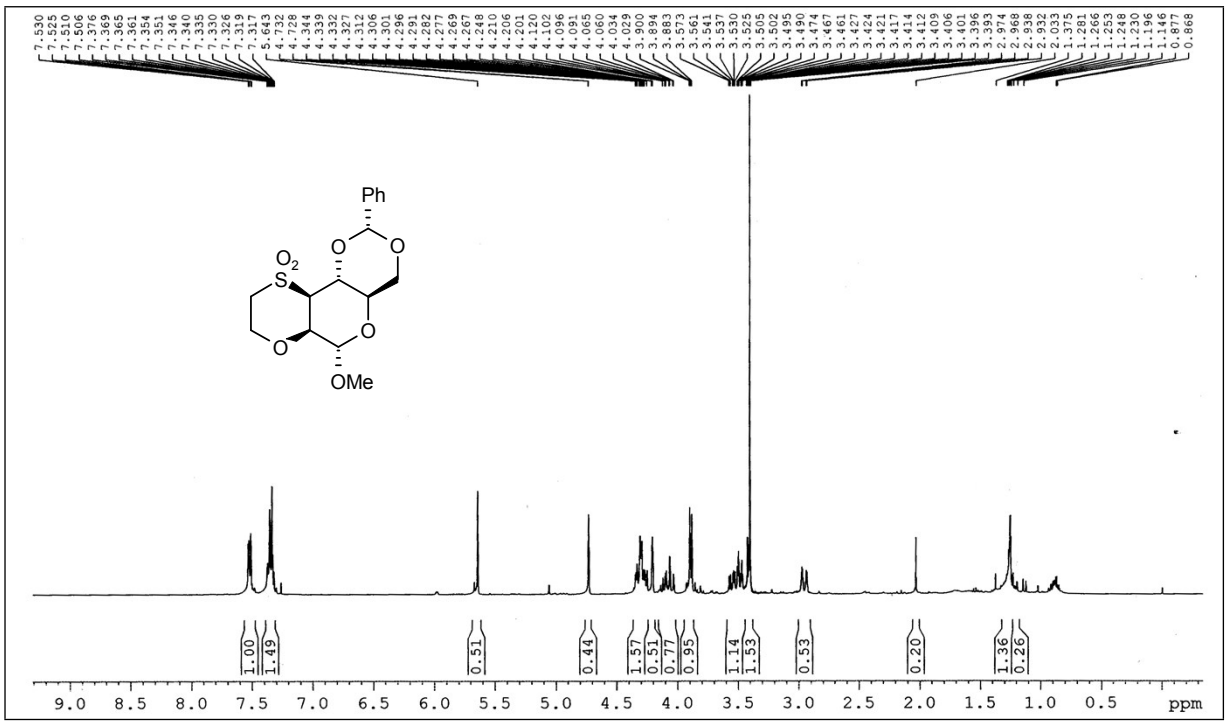
^{13}C NMR spectrum of compound **10**



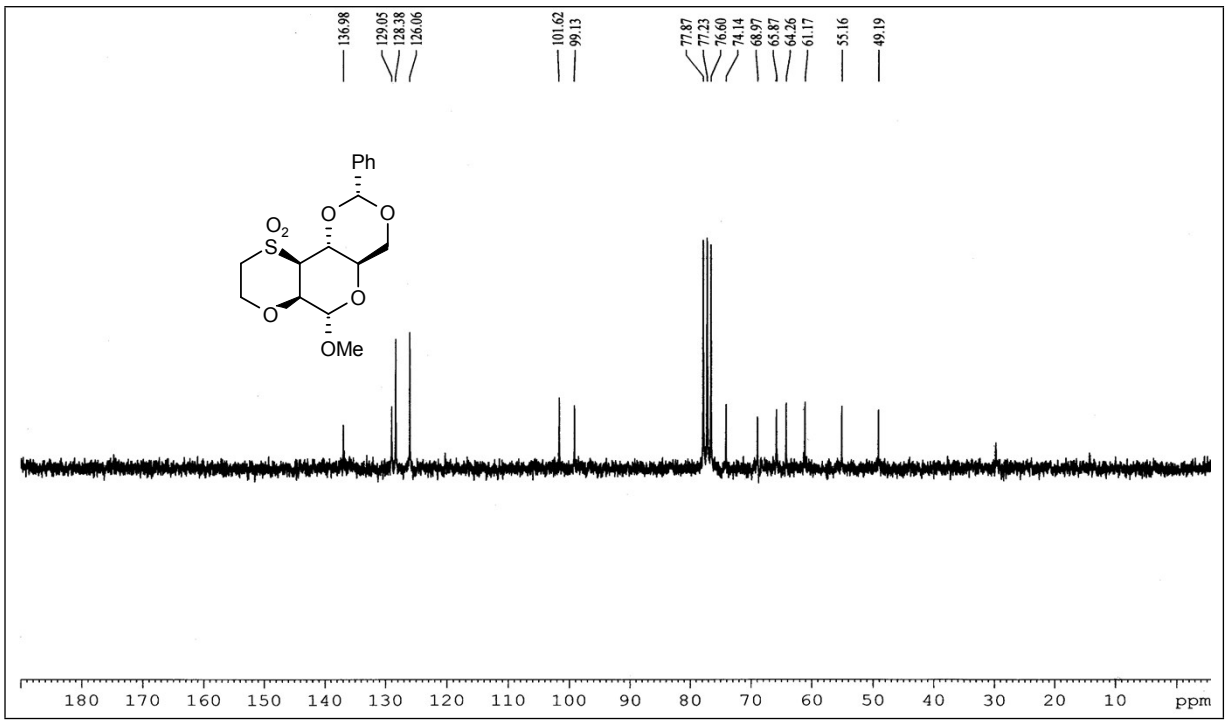
DEPT spectrum of compound **10**



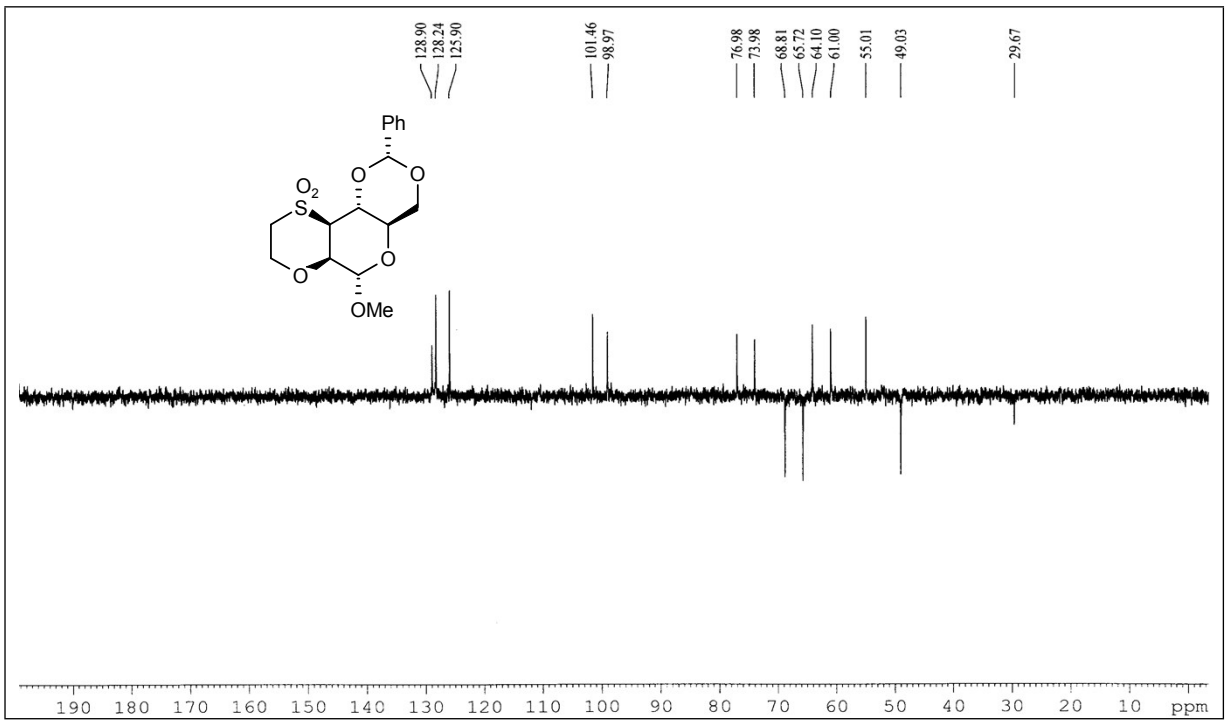
^{1}H NMR spectrum of compound **11**



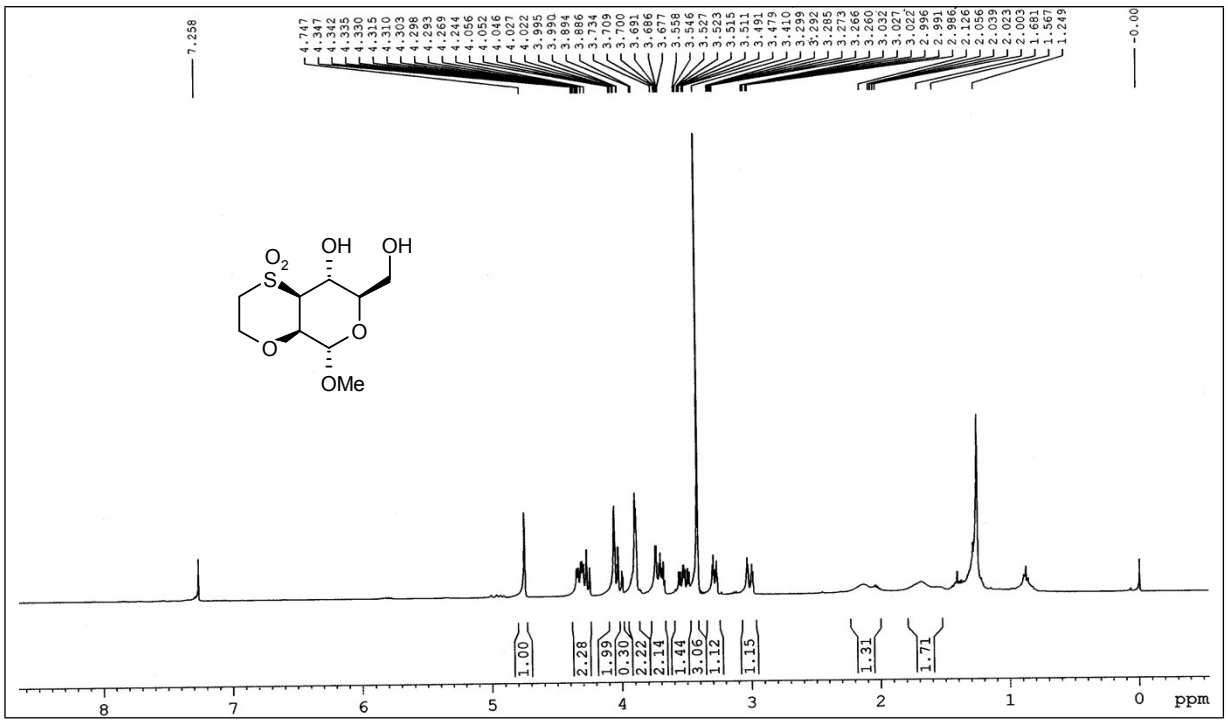
^{13}C NMR spectrum of compound **11**



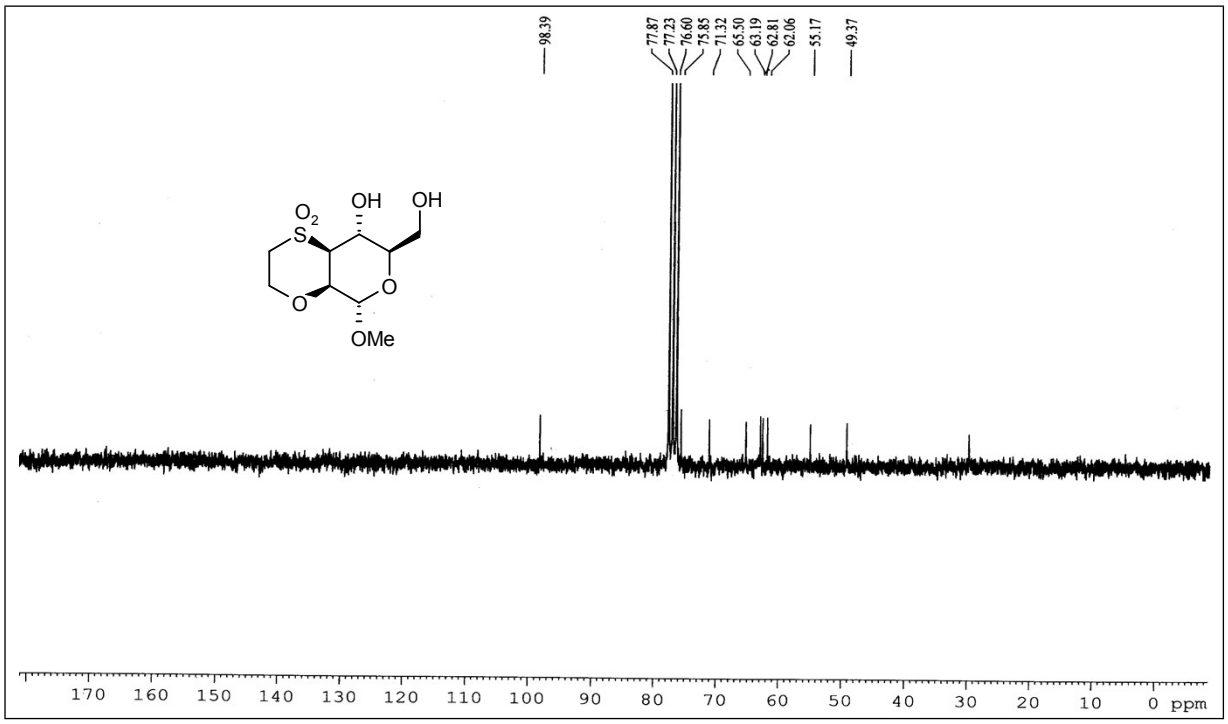
DEPT spectrum of compound **11**



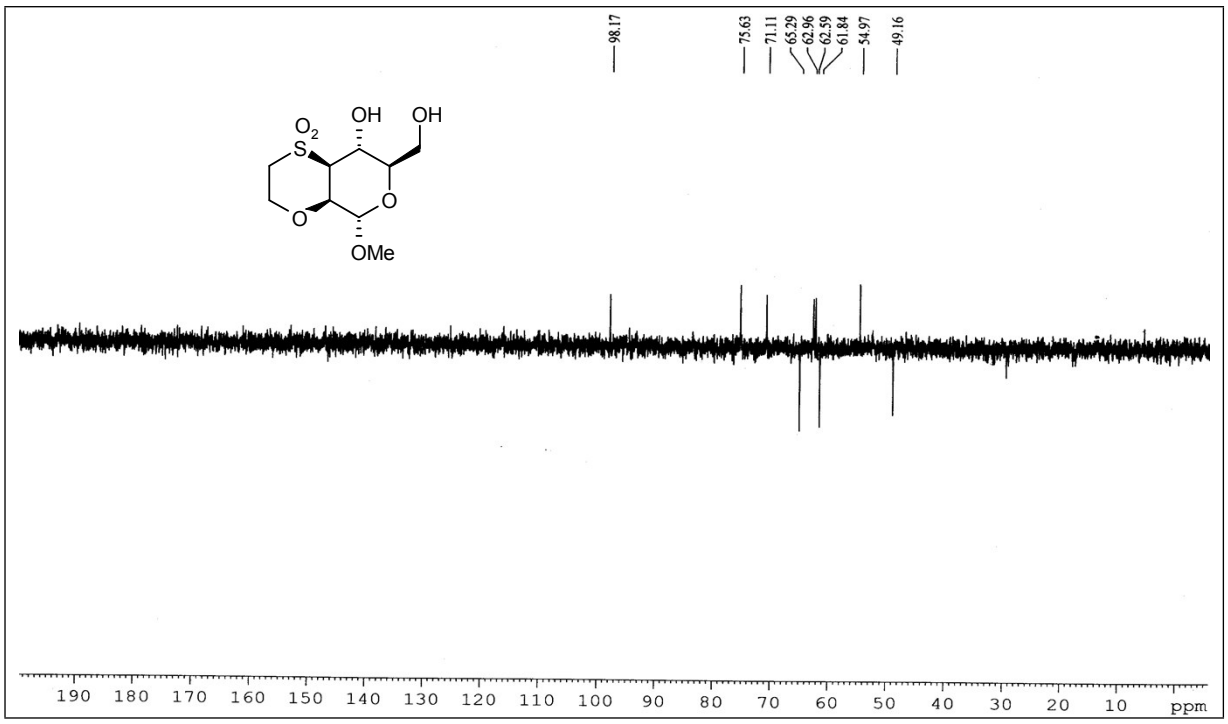
^{1}H NMR spectrum of compound **12**



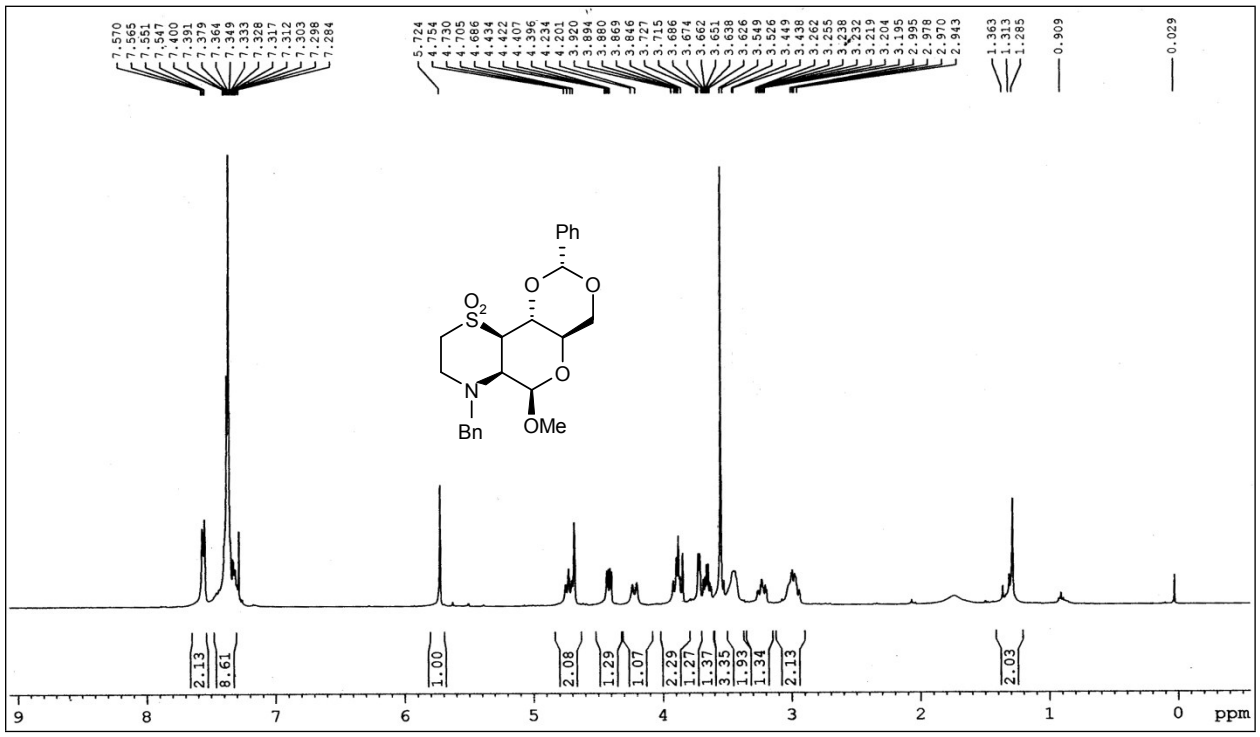
^{13}C NMR spectrum of compound **12**



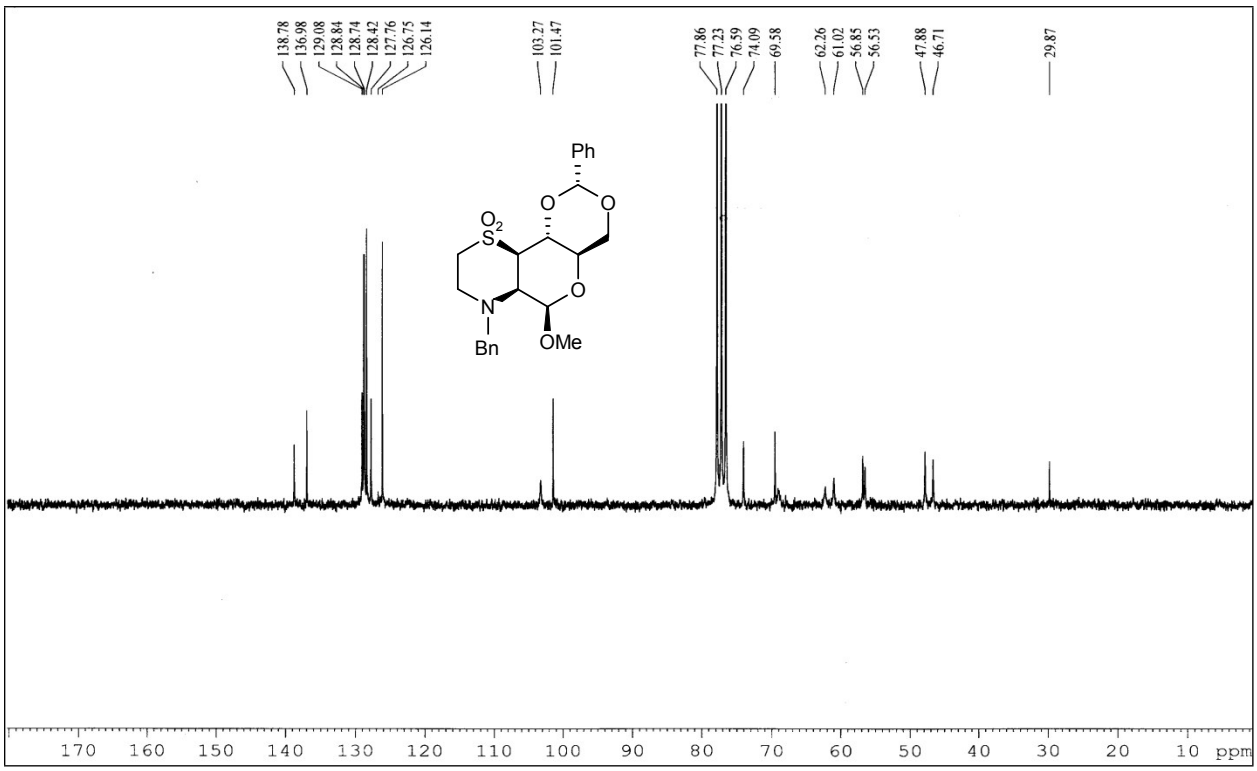
DEPT spectrum of compound **12**



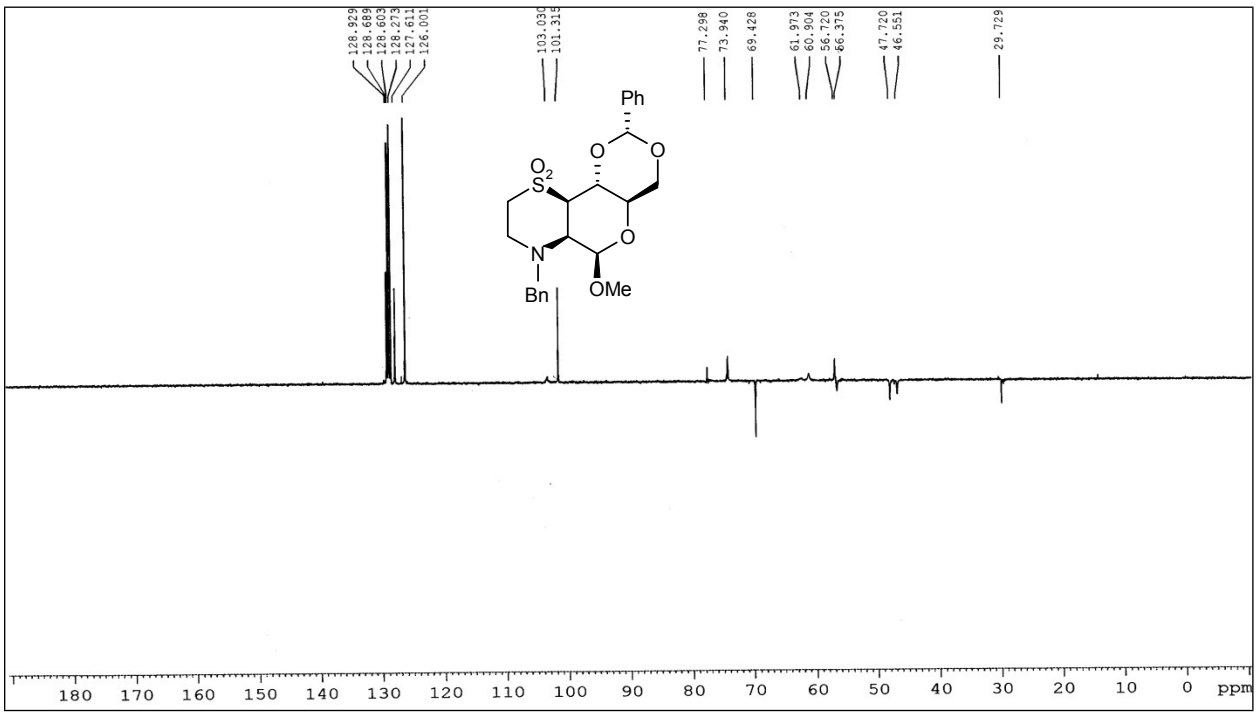
^{1}H NMR spectrum of compound **14a**



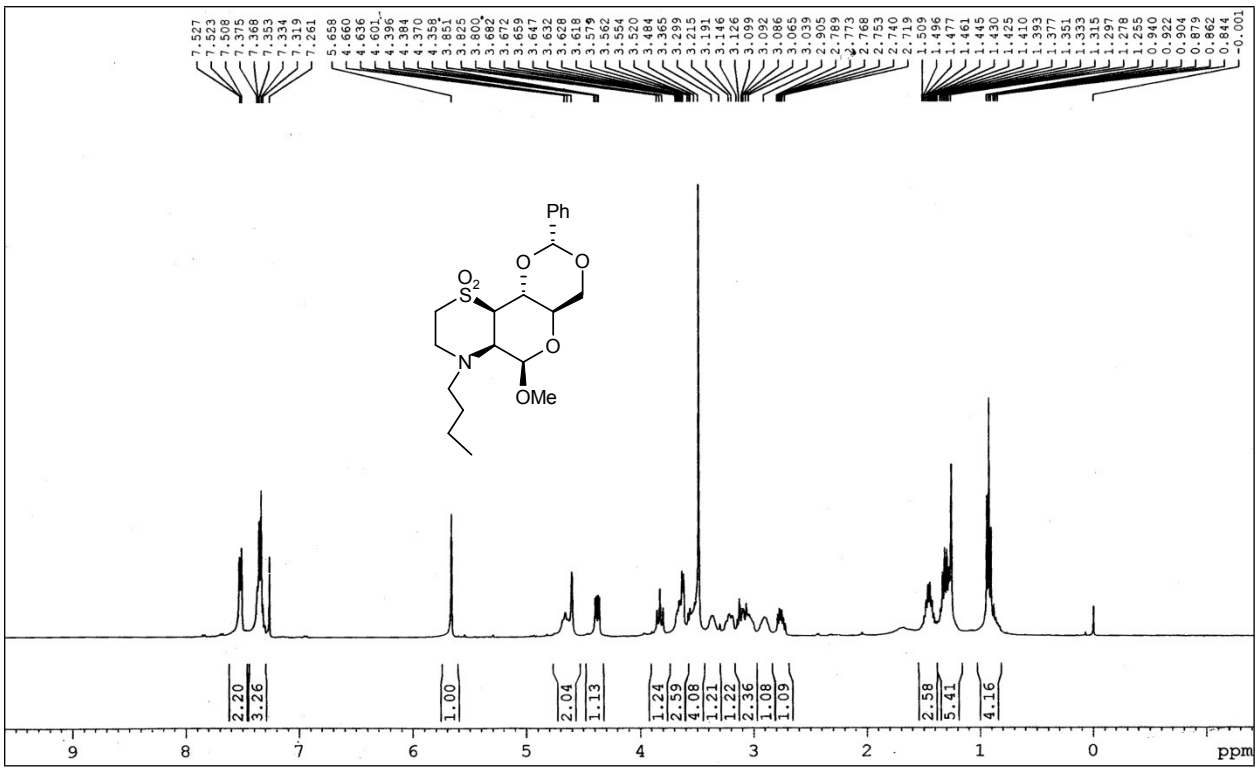
^{13}C NMR spectrum of compound **14a**



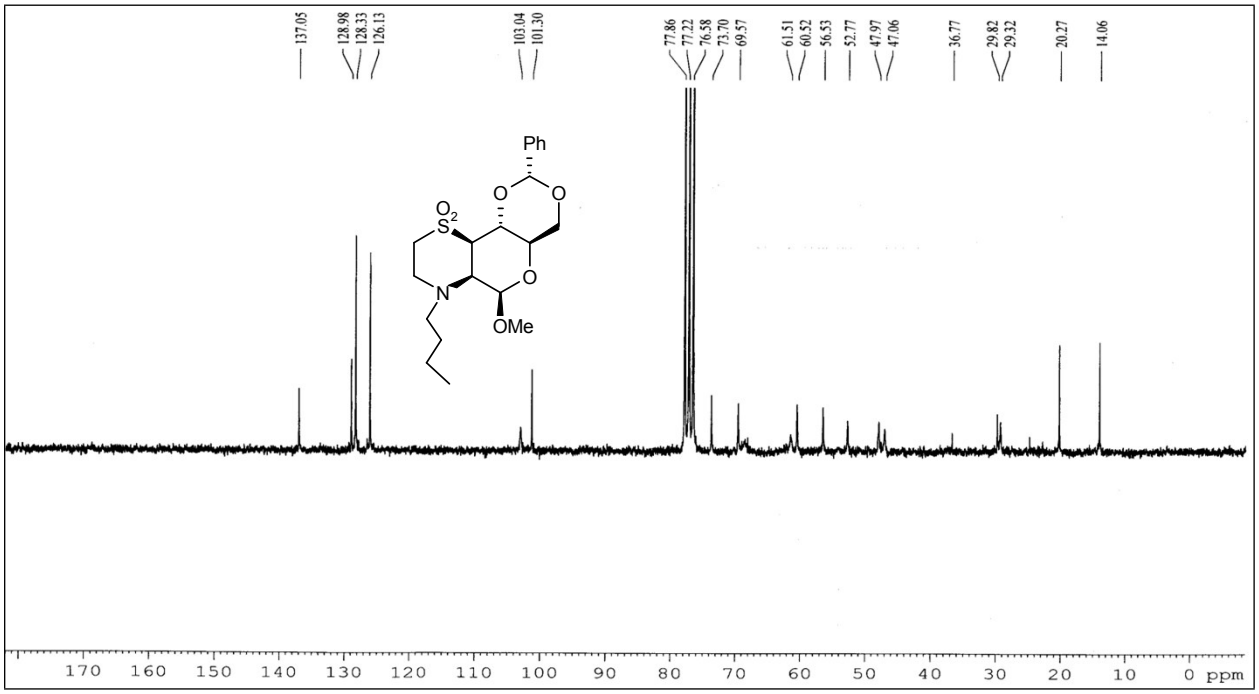
DEPT spectrum of compound **14a**



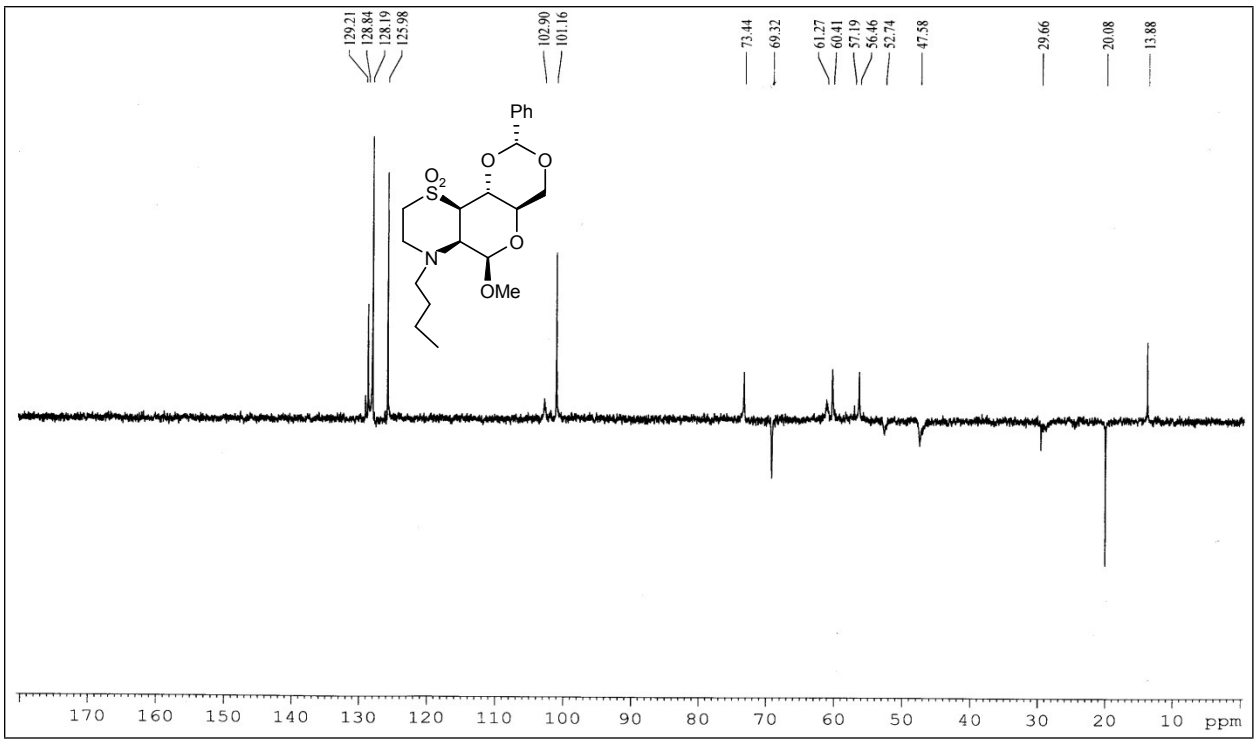
^{1}H NMR spectrum of compound **14b**



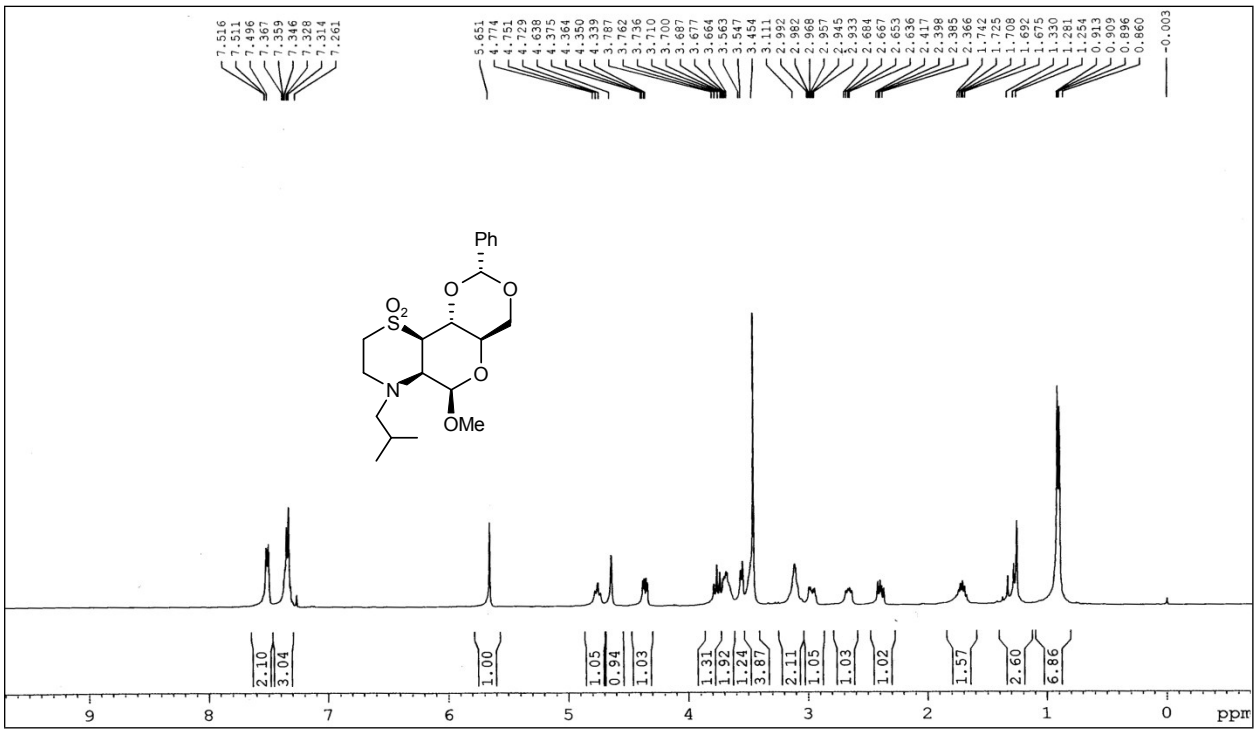
^{13}C NMR spectrum of compound **14b**



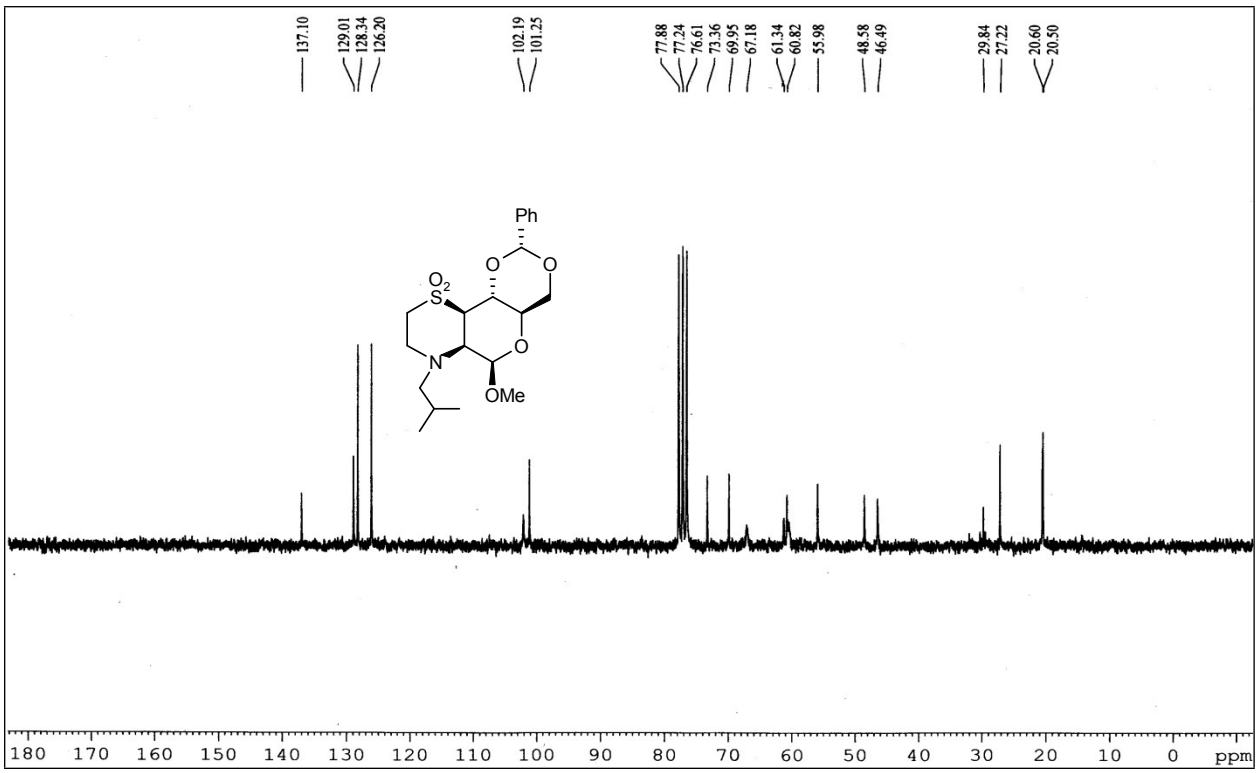
DEPT spectrum of compound **14b**



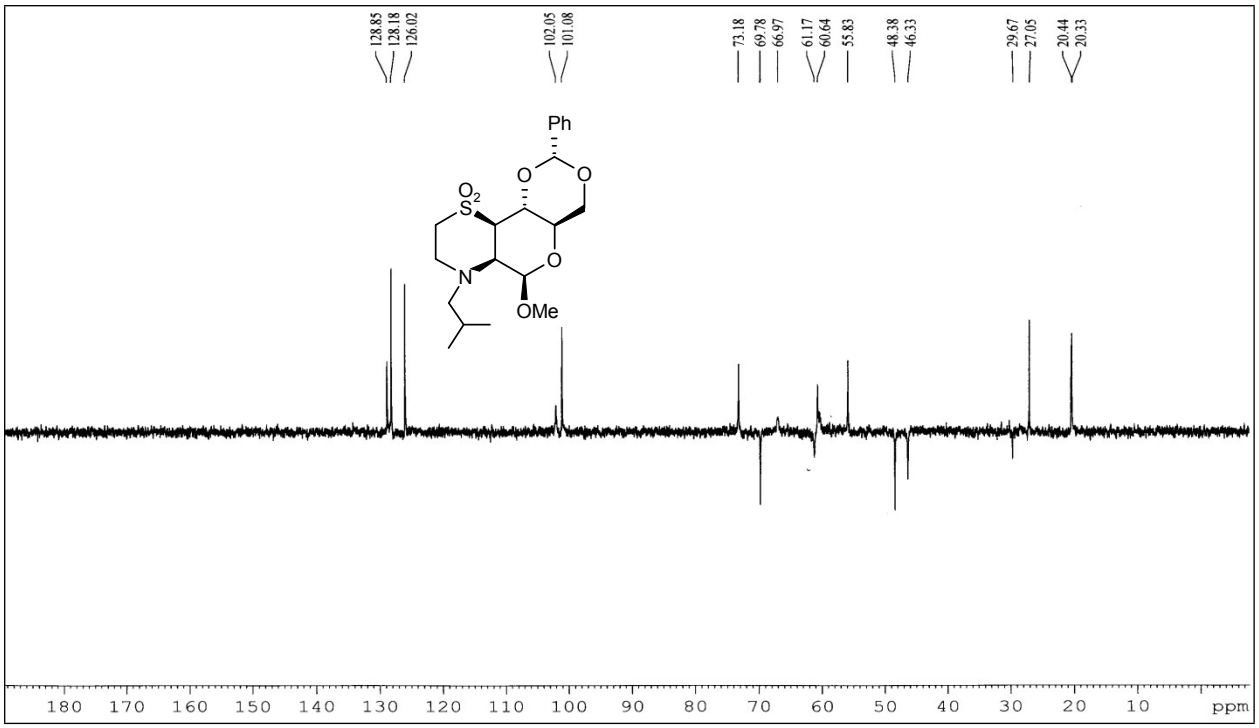
^{1}H NMR spectrum of compound **14c**



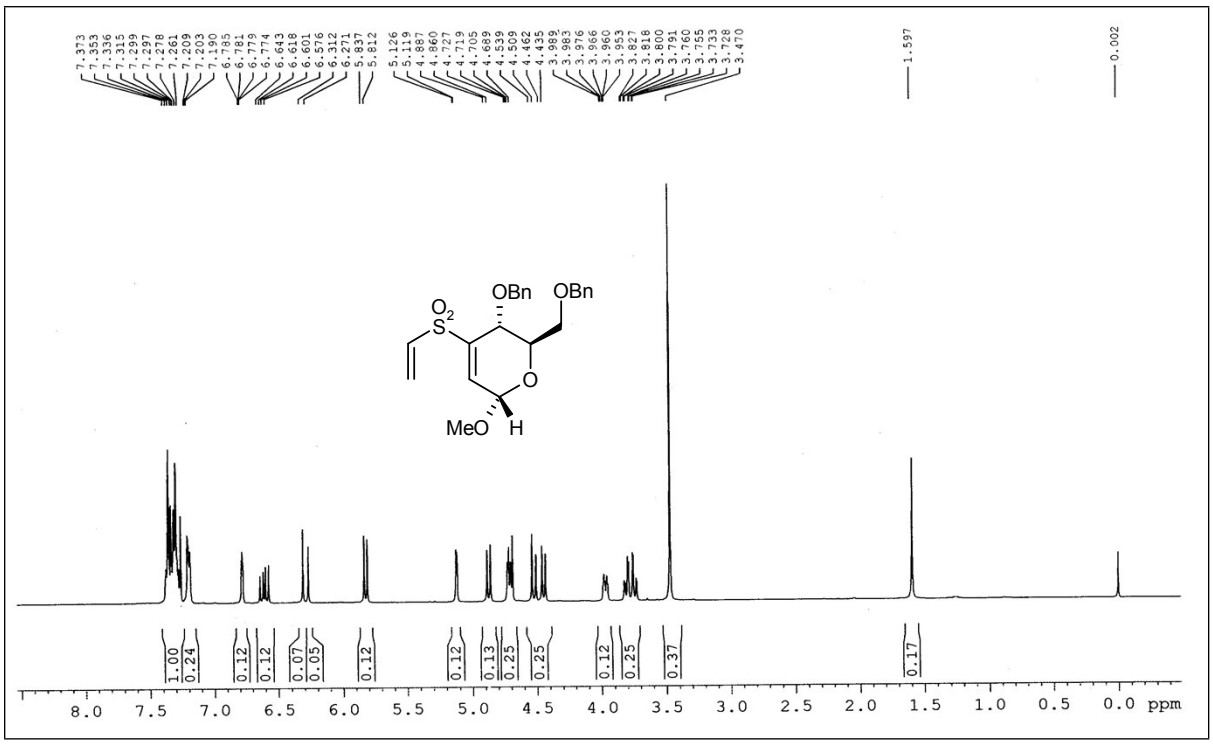
^{13}C NMR spectrum of compound **14c**



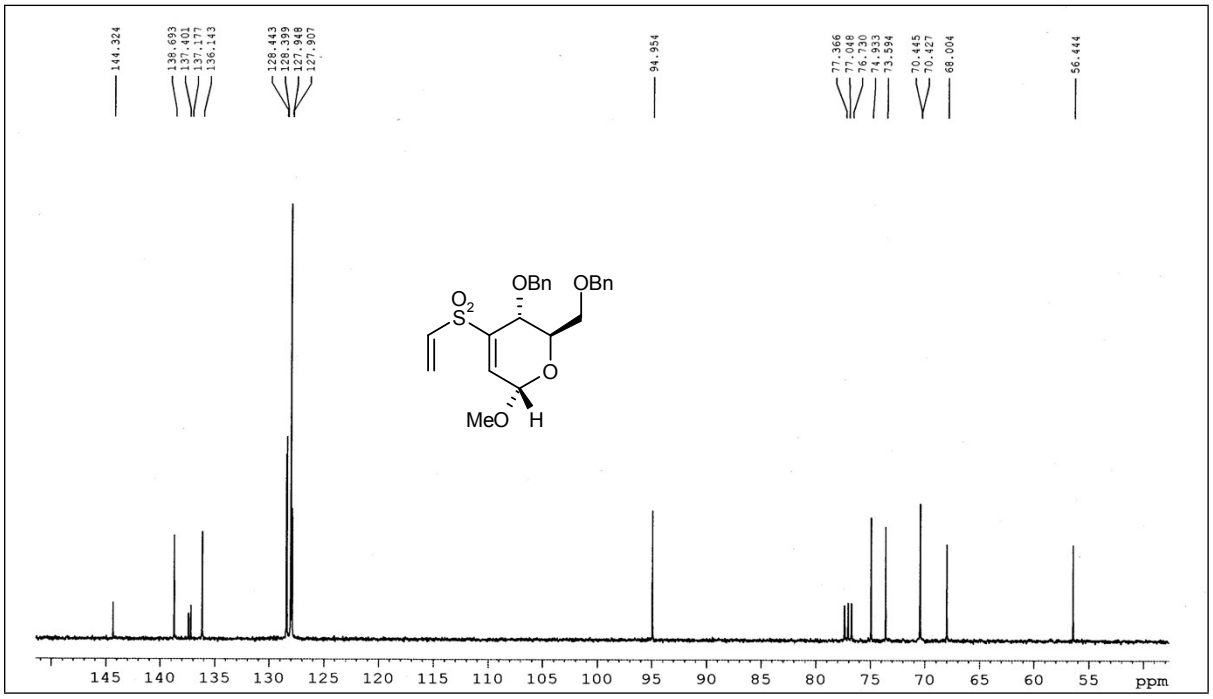
DEPT spectrum of compound **14c**



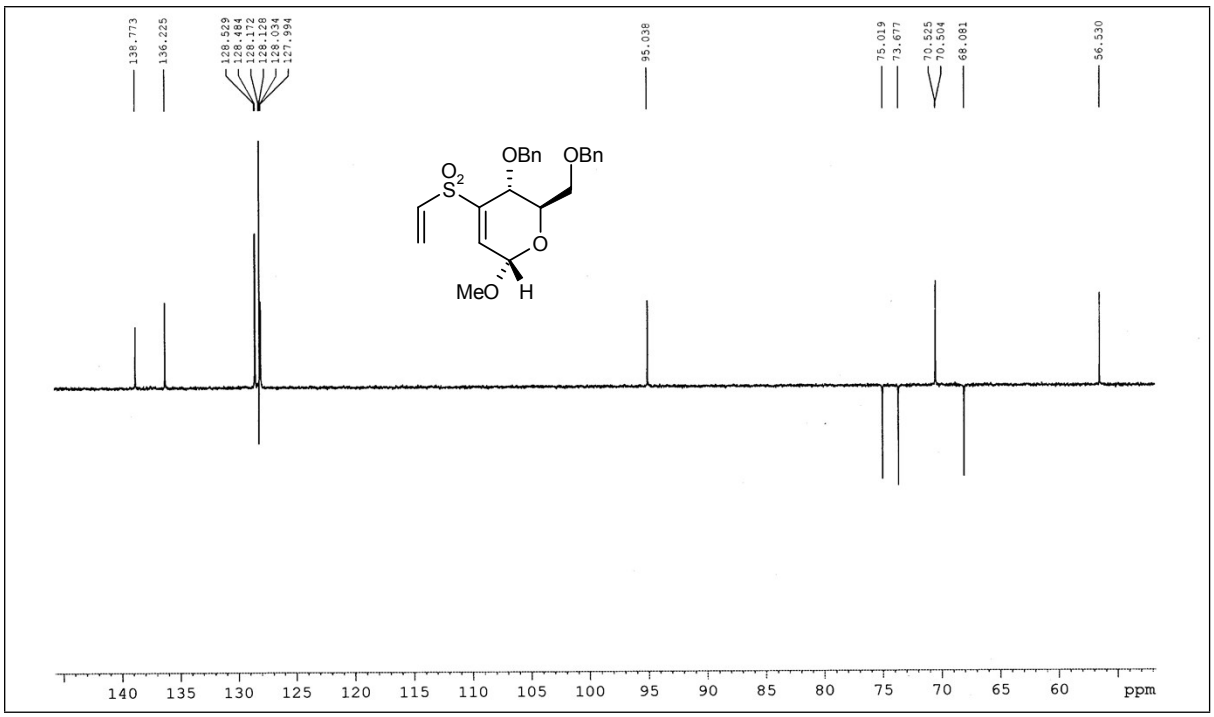
^{1}H NMR spectrum of compound **18α**



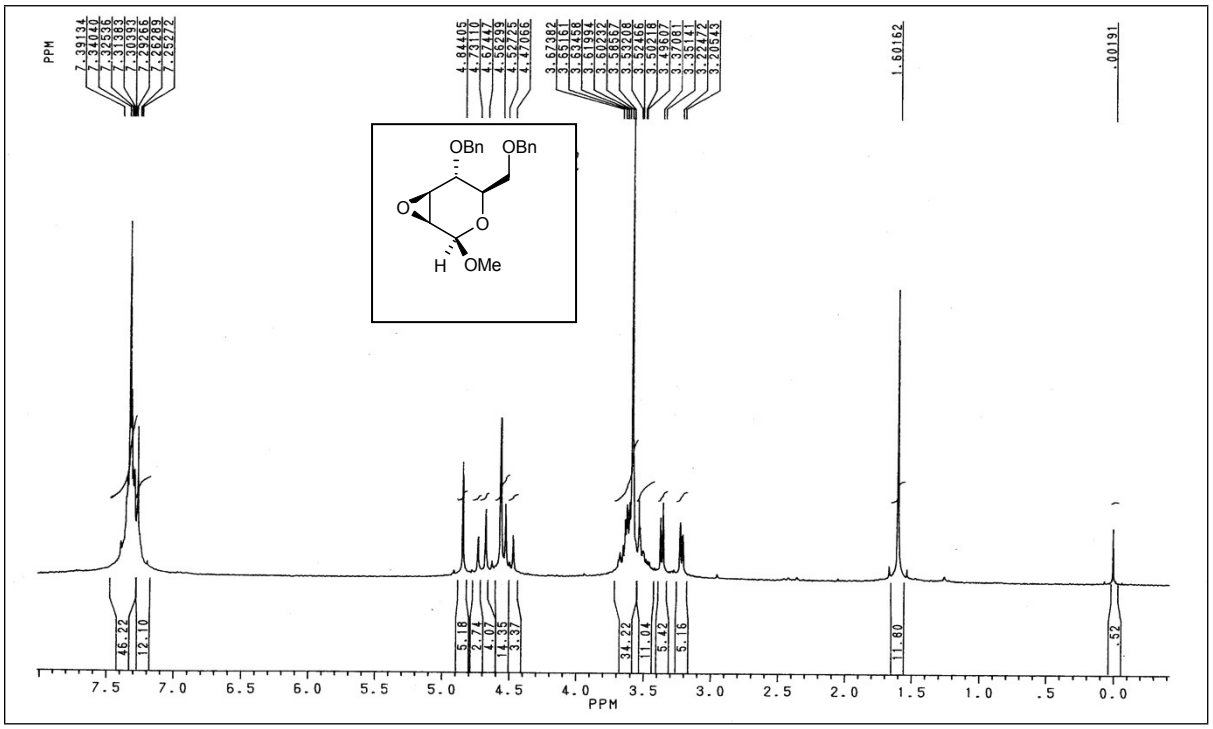
^{13}C NMR spectrum of compound **18α**



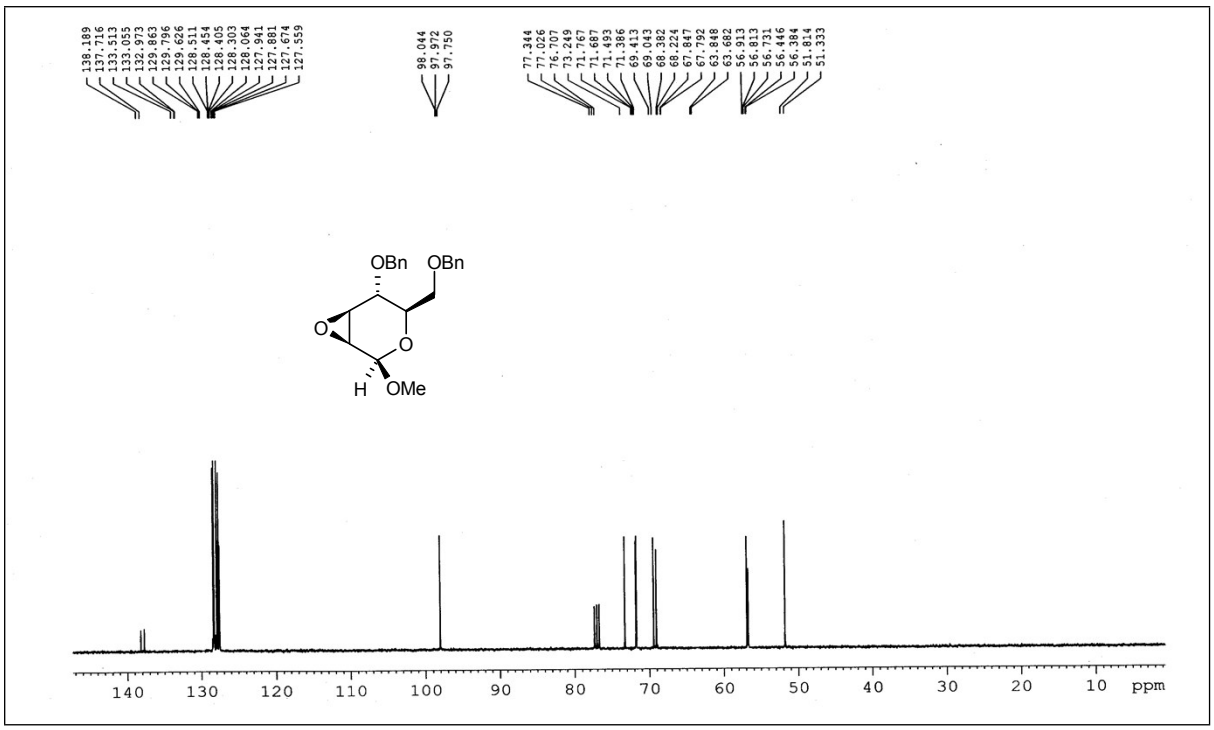
DEPT spectrum of compound **18α**



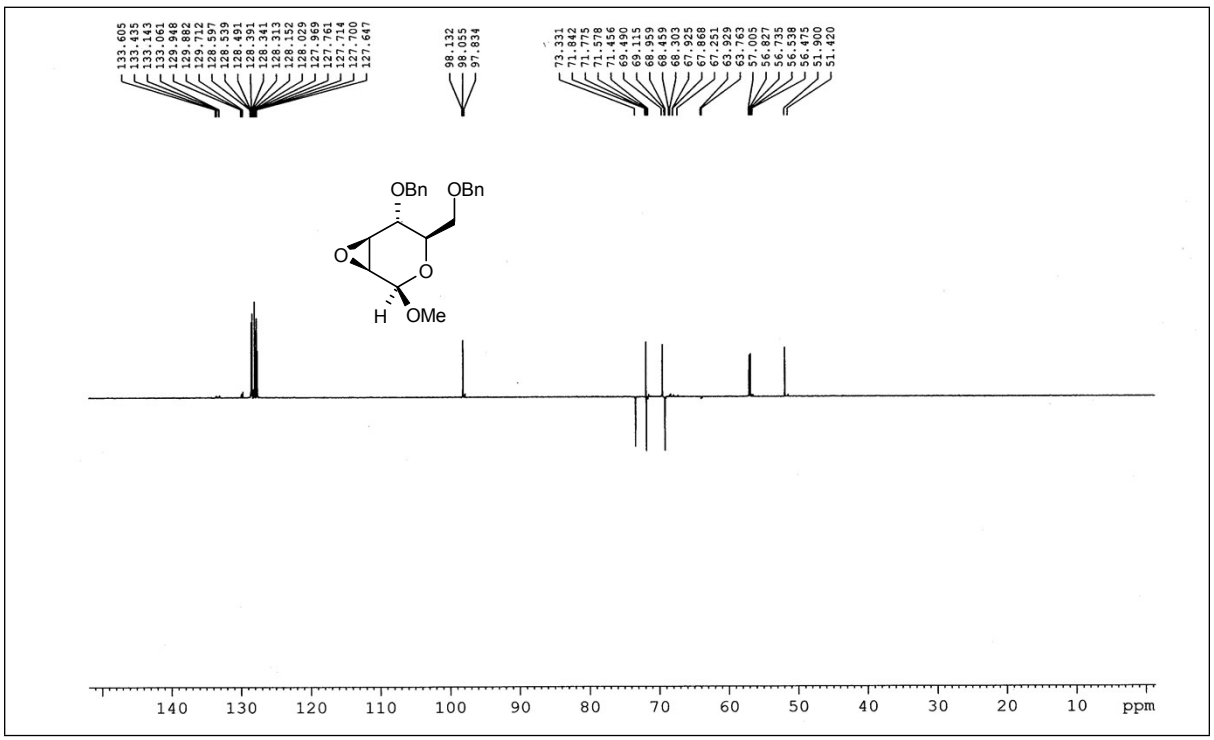
^{1}H NMR spectrum of compound **15β**



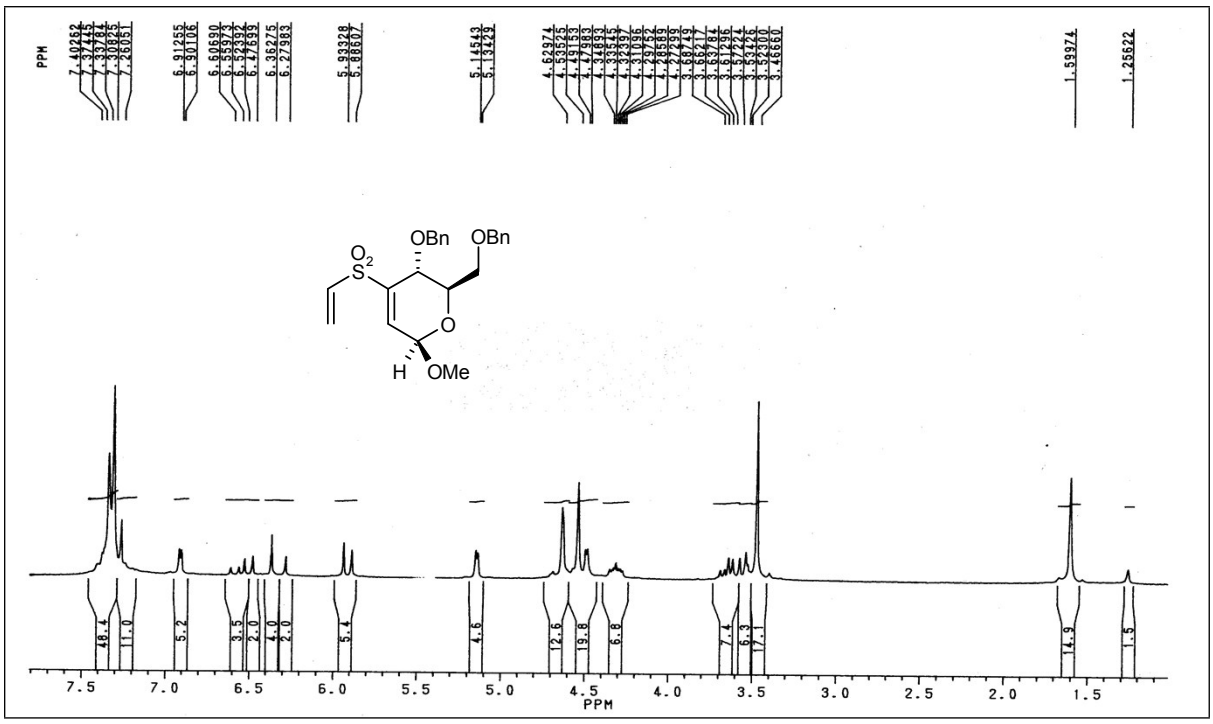
^{13}C NMR spectrum of compound **15β**



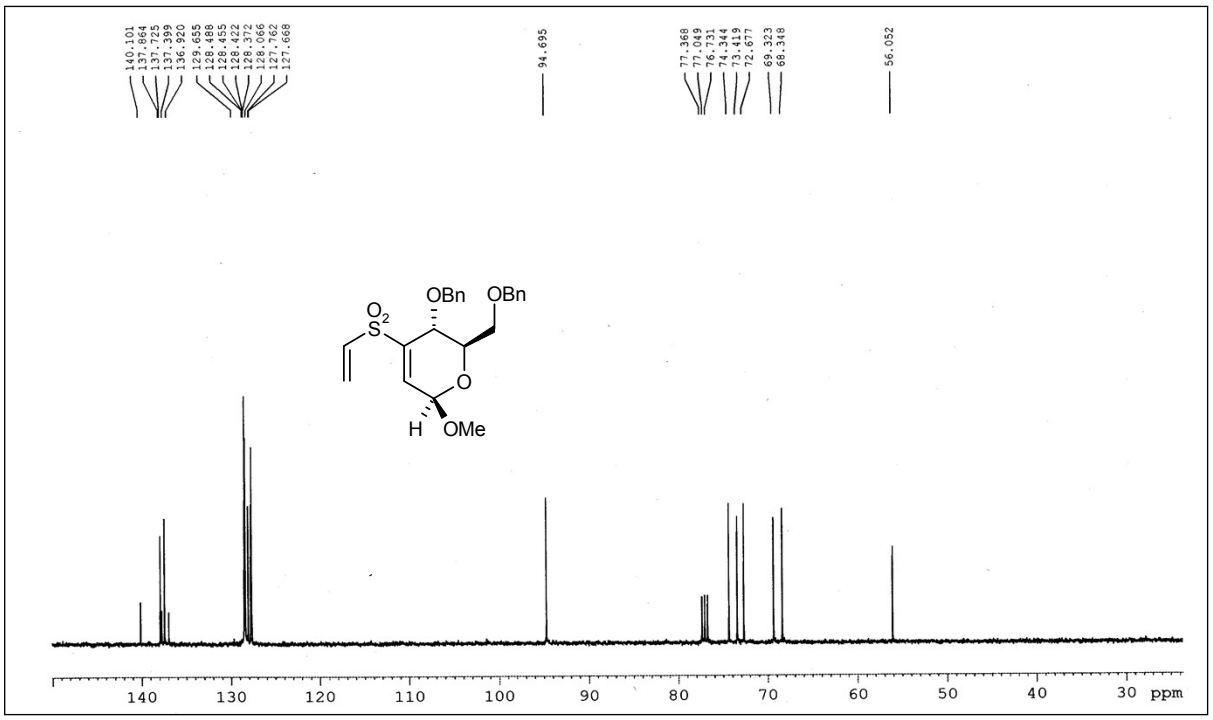
DEPT spectrum of compound **15β**



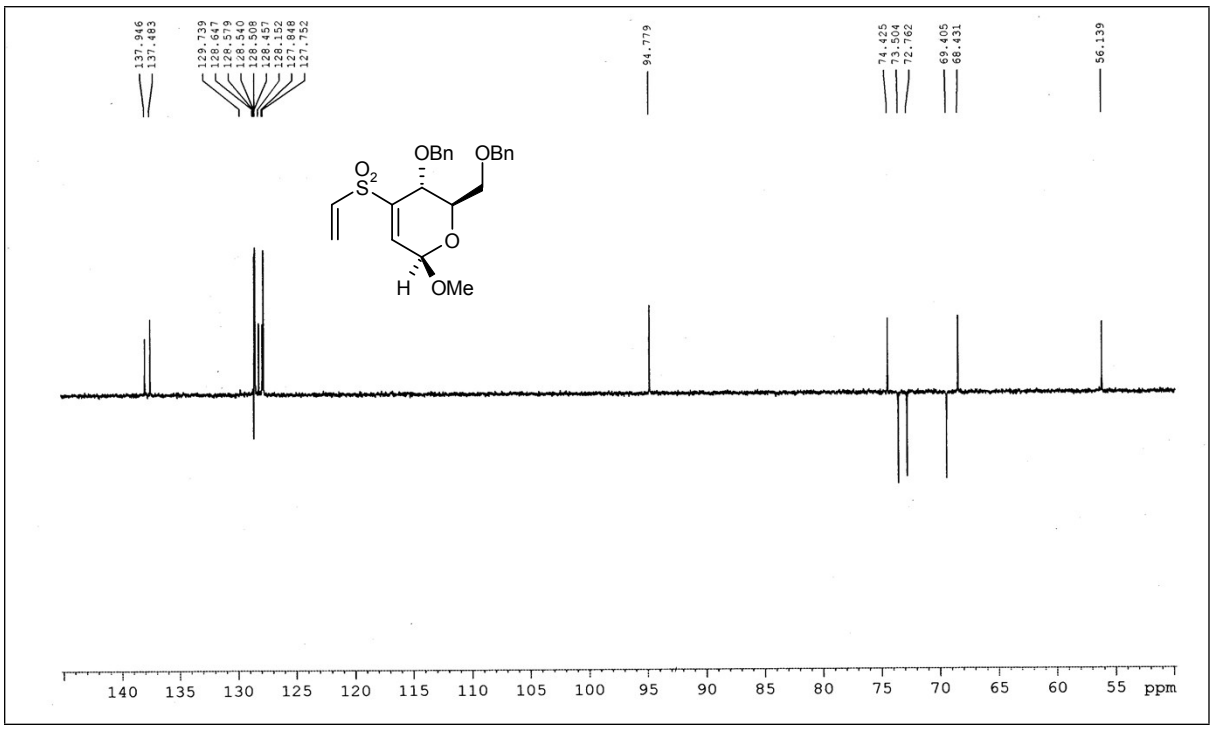
^{1}H NMR spectrum of compound **18β**



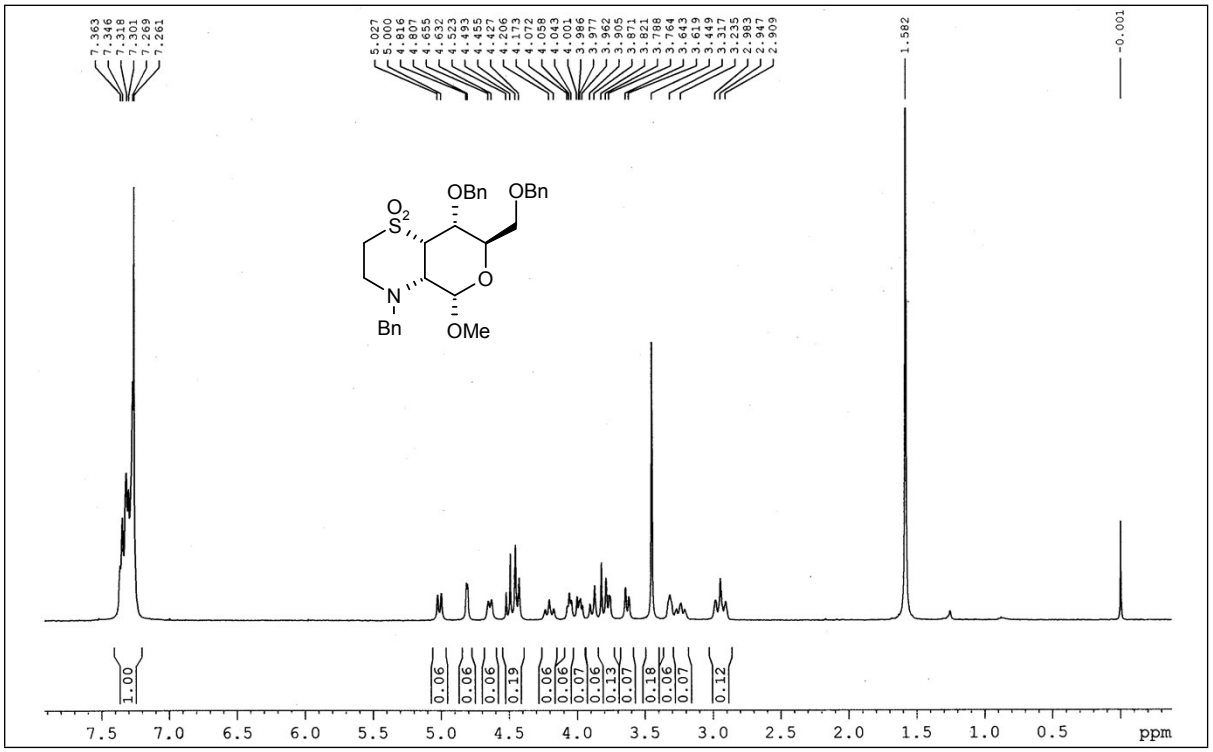
^{13}C NMR spectrum of compound **18β**



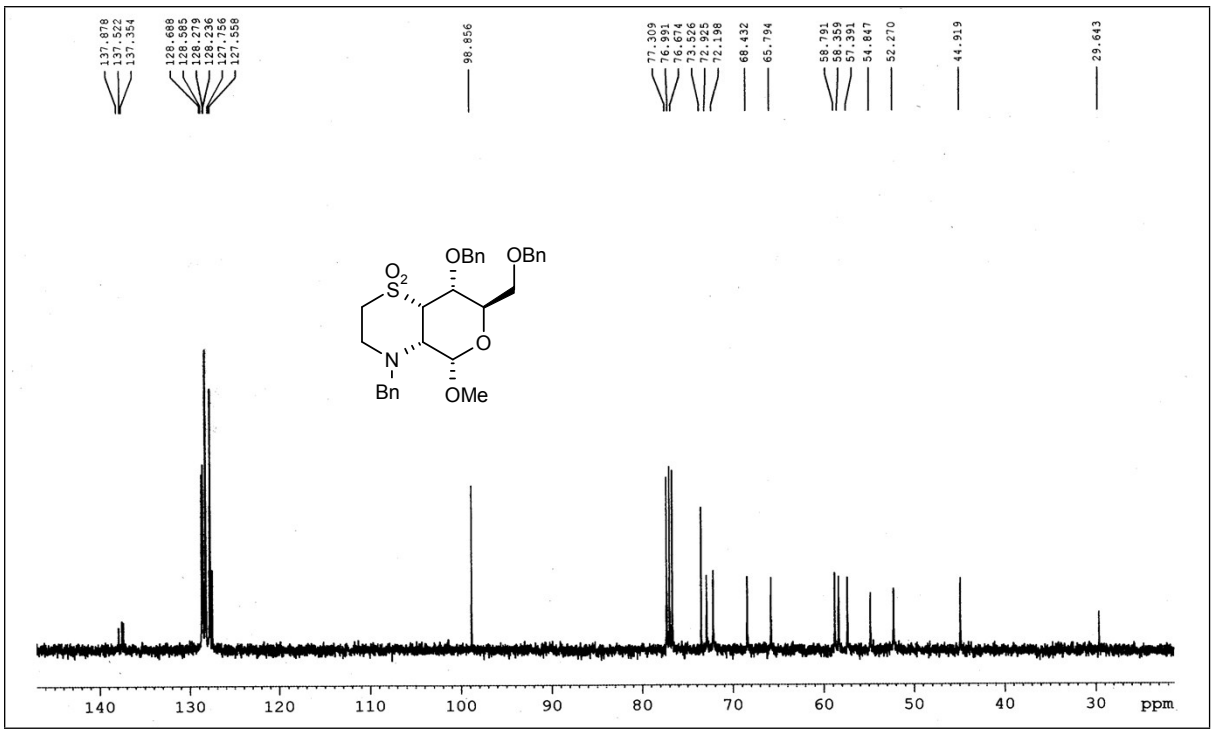
DEPT spectrum of compound **18β**



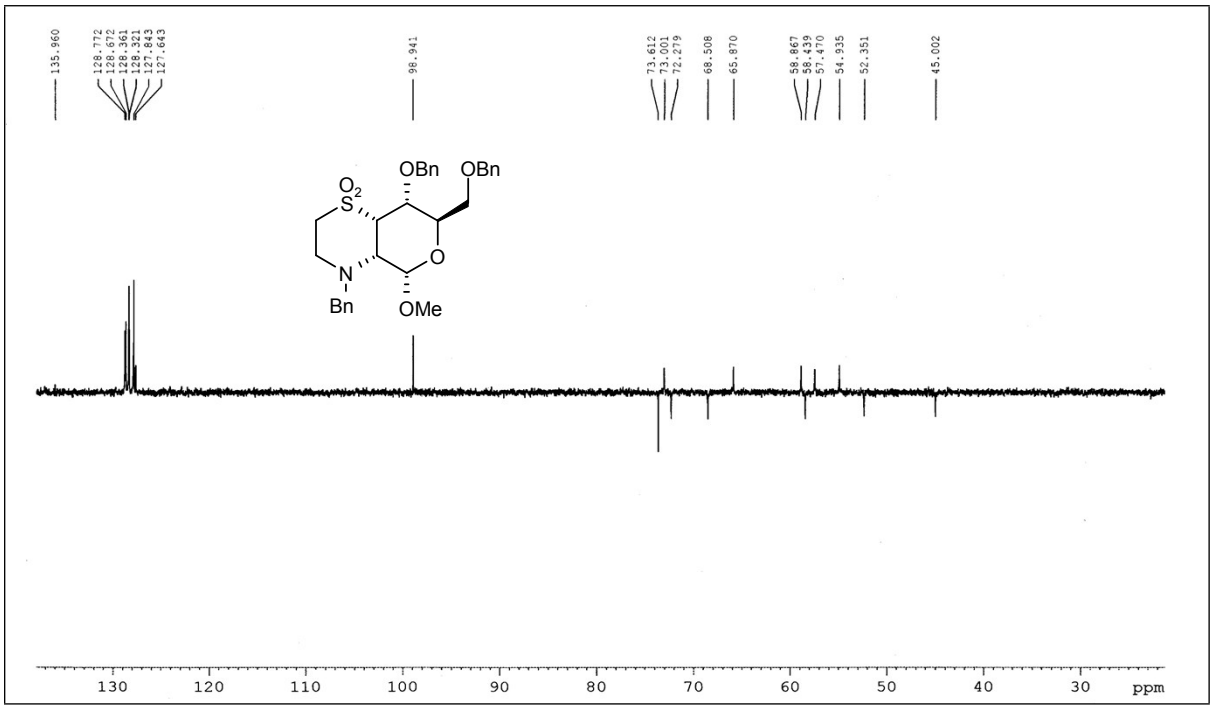
^{1}H NMR spectrum of compound **19a**



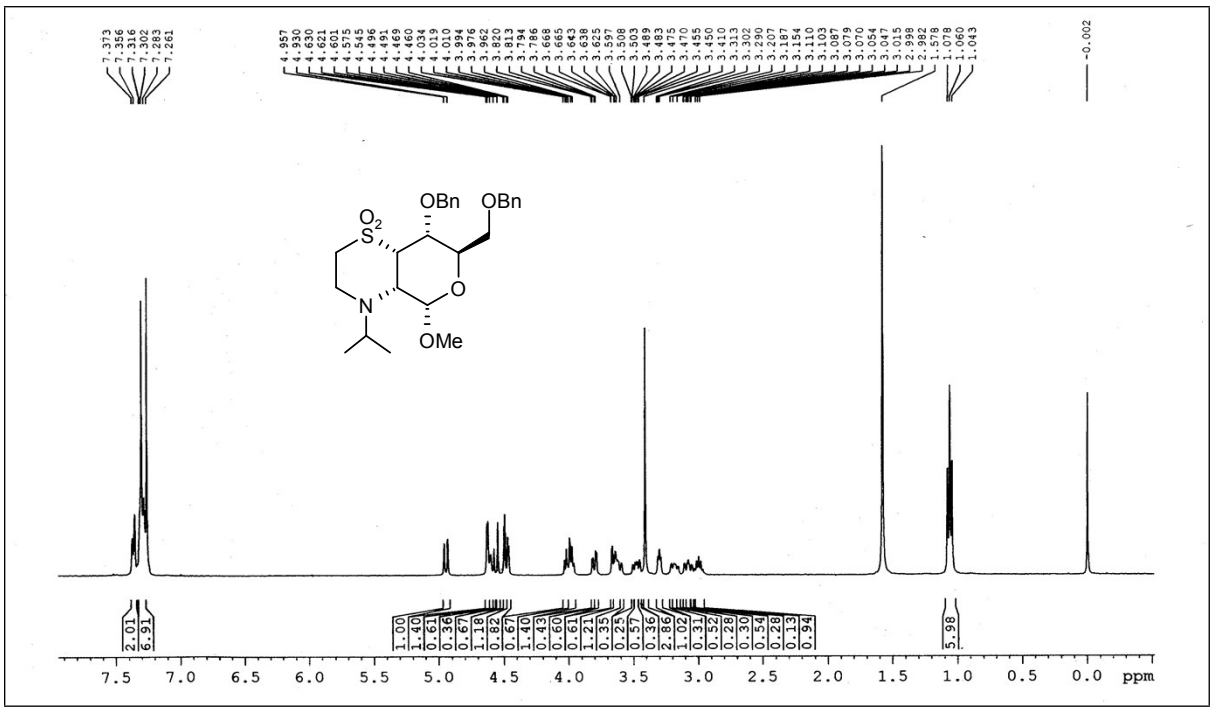
^{13}C NMR spectrum of compound **19a**



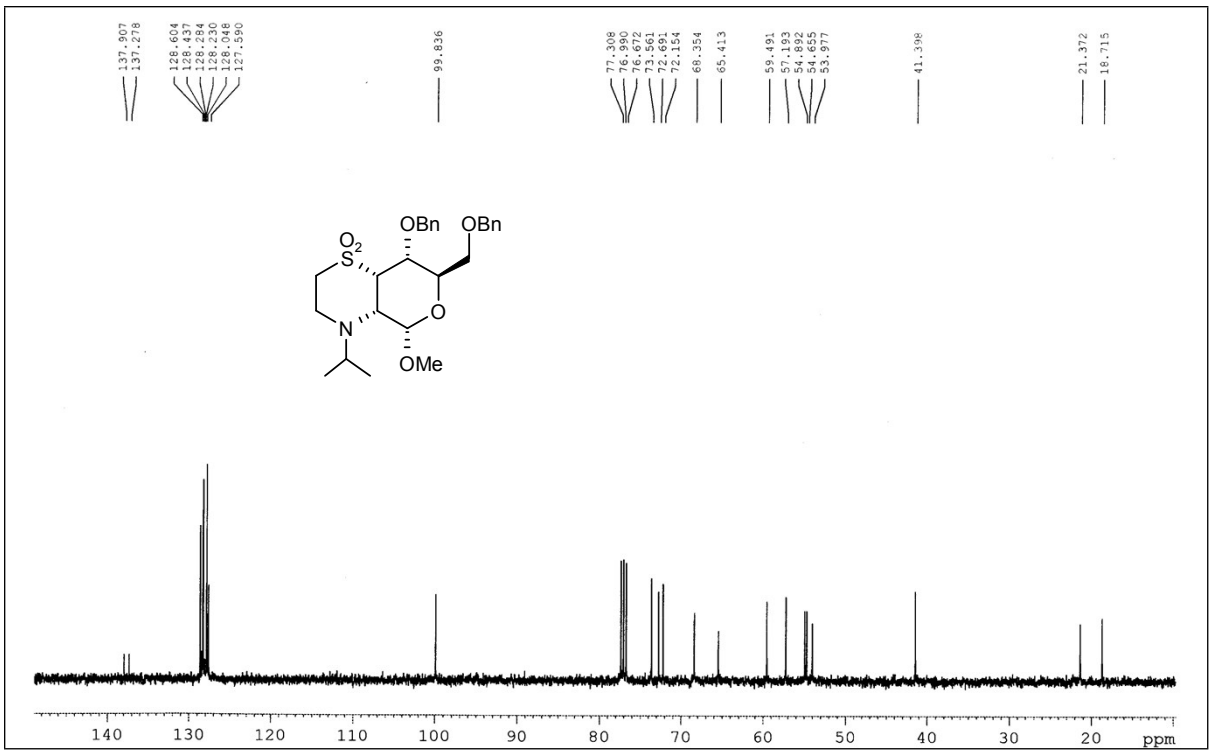
DEPT spectrum of compound **19a**



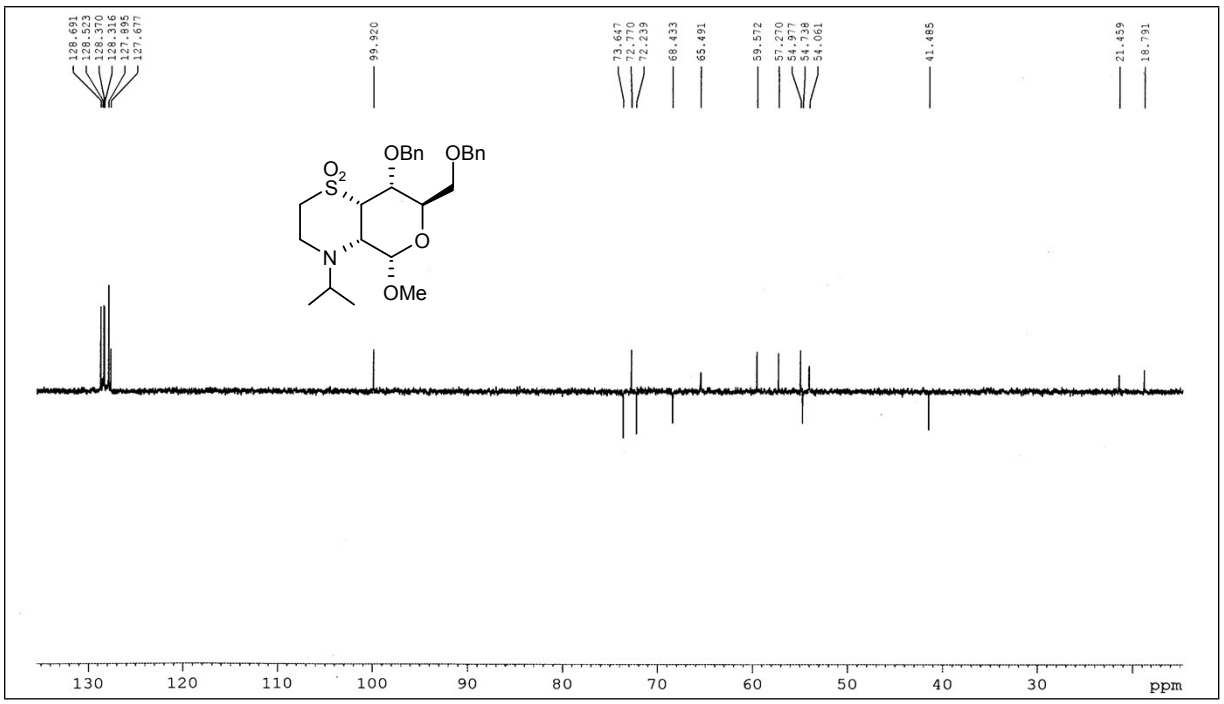
^{1}H NMR spectrum of compound **19b**



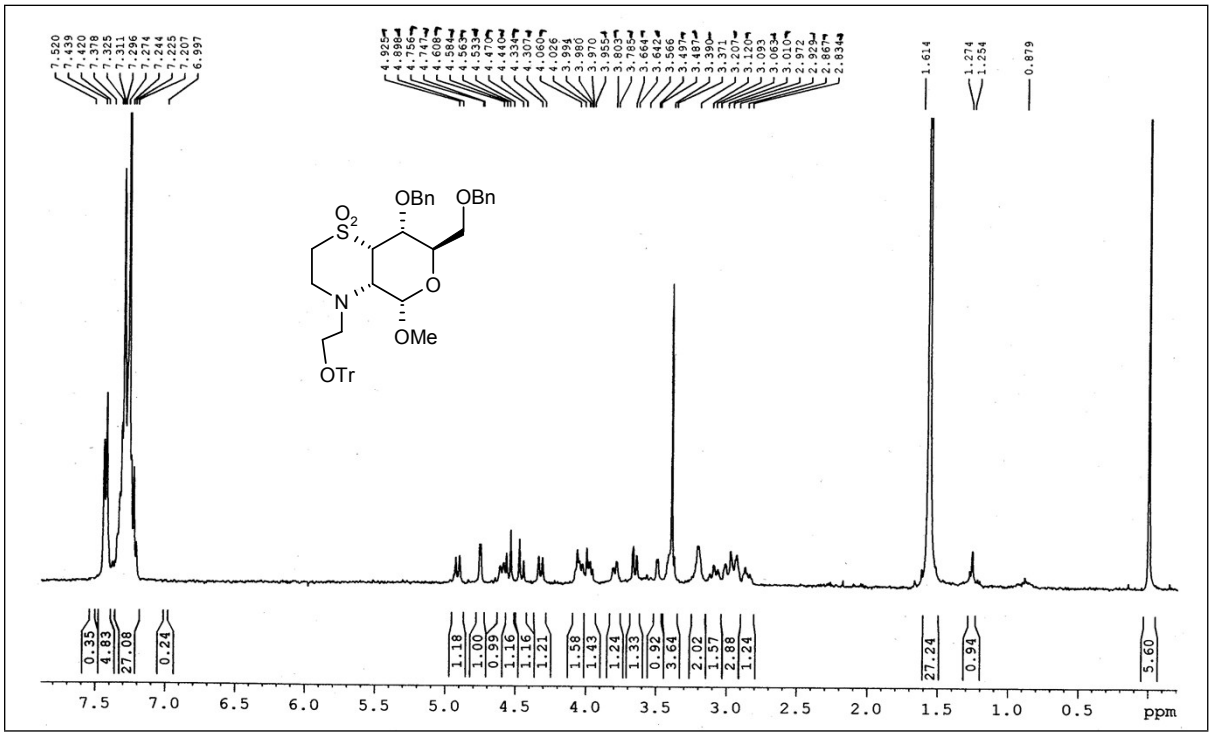
^{13}C NMR spectrum of compound **19b**



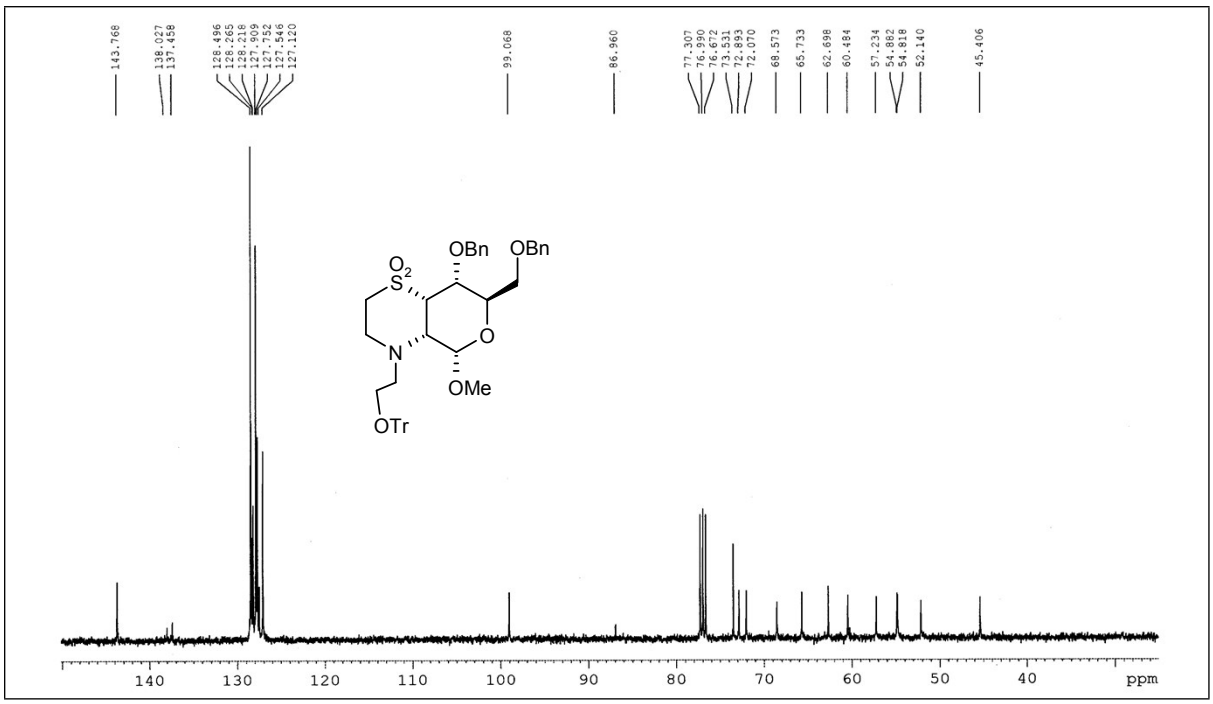
DEPT spectrum of compound **19b**



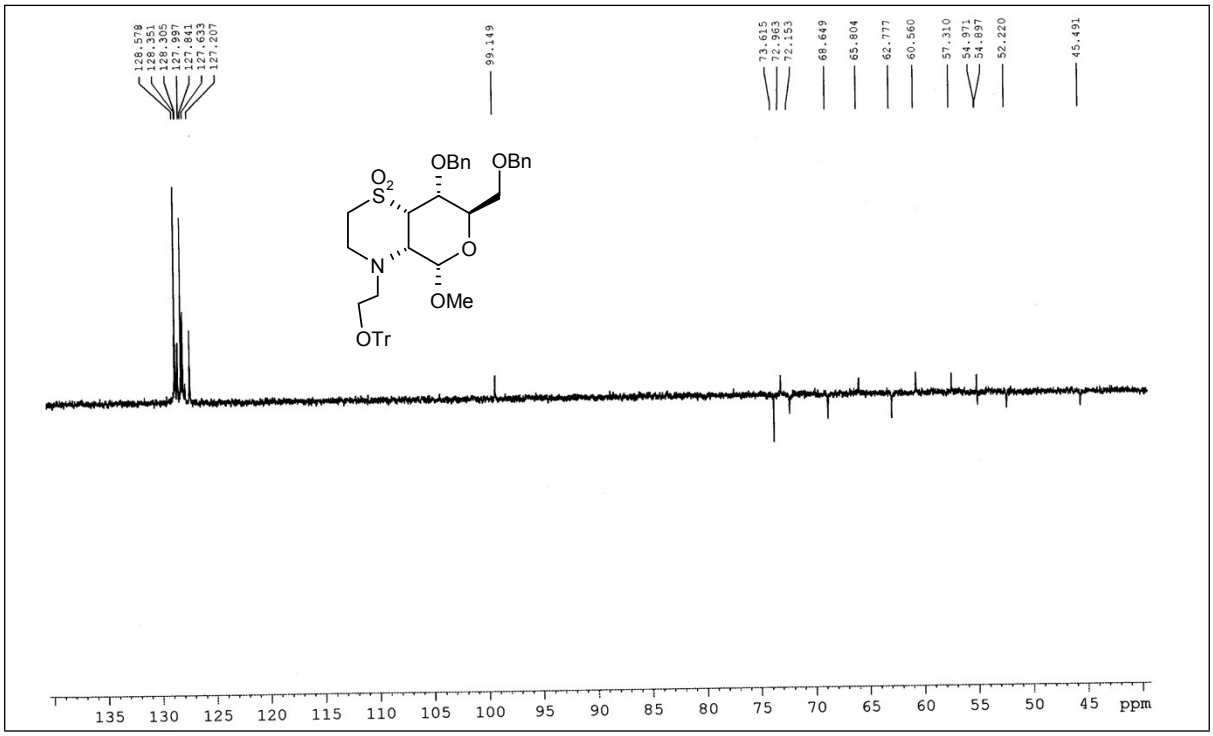
^{1}H NMR spectrum of compound **19c**



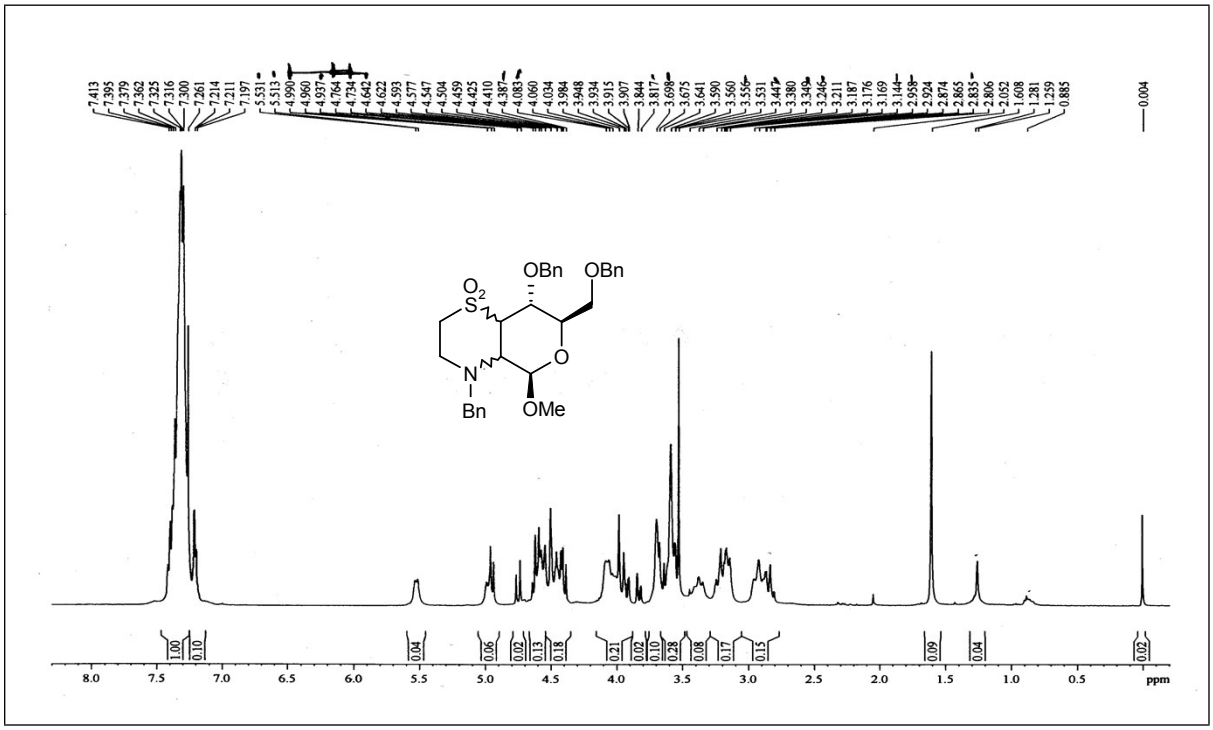
^{13}C NMR spectrum of compound **19c**



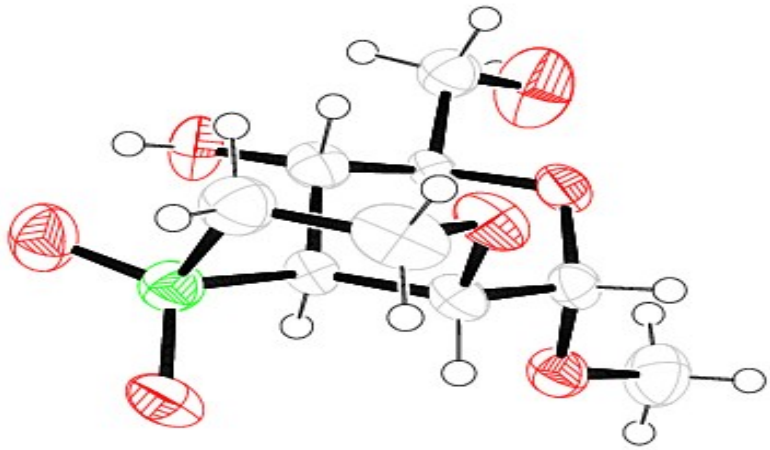
DEPT spectrum of compound **19c**



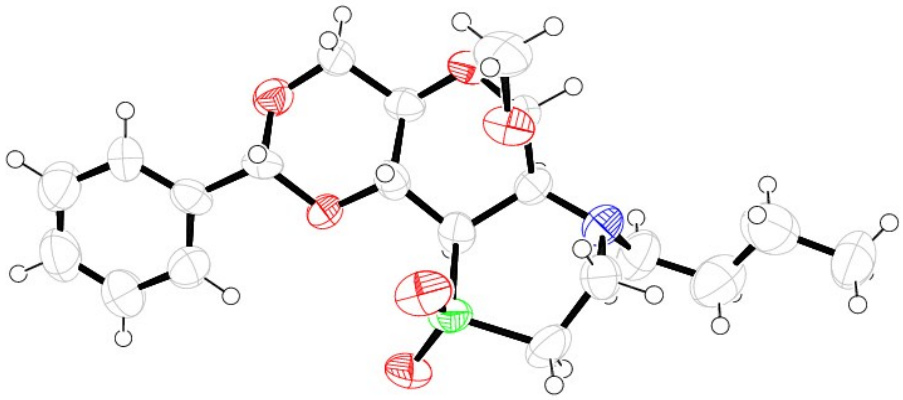
^{1}H NMR spectrum of compound **20**



ORTEP diagram of compound **12**



ORTEP diagram of compound **14b**



ORTEP diagram of compound **19b**