Supporting information for:

# A Diastereoselective Formal Synthesis of Berkelic Acid

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**I. General Techniques** – In reactions, where water was *not* present as solvent, reagent, or by-product, vessels were flame-dried under a slow nitrogen flow. A slight positive pressure of dry nitrogen was maintained via rubber septum seal during the course of the reaction. The nitrogen stream originated from a regulated high pressure 55 L $N_2$ *(l)* tank and was further dried by passage through a Drierite® tube. Reagents were purified according to the procedures described in *Purification of Laboratory Chemicals* (W.L. F. Armarego and C. L. L. Chai).

Reactions were monitored by analytical thin-layer chromatography on EM-Science hard layer silica gel-60$^{F-250}$ plates cut into 1x2.5cm pieces. Visualization was effected by ultraviolet light (254 nm), followed by staining [Seebach or permanganate] the plate, followed by drying on a *Fisher*® micro-hot plate. The Seebach stain was made with 25 g of phosphomolybdic acid, 10 g of cerium sulfate, 60 mL $H_2SO_4$, and 940 mL of $H_2O$. The potassium permanganate stain was made with 200 mL $H_2O$, 1.33 g $KMnO_4$, 13.33 g of $K_2CO_3$, and 4 mL of 5% NaOH.

All reactions were stirred with Teflon®-coated magnetic stir bars and *Thomas*® Magna-Matic magnetic stirrers. Removal of solvents was typically accomplished using a *Buchi*® rotary evaporator (model #R-114) connected to a Fisher KNF®-vacuum pump (model #UN820-3). The condenser was cooled to 0 °C by a Fisher® chiller circulator bath (model #1013S). If the product was non-volatile, trace solvents were removed using a *Labconco*® freeze dryer system at a pressure of approximately 0.01 mmHg.

For distillation, a specific low pressure (760 – 1 mm Hg) was obtained and monitored with a *Buchi*®-vacuum controller (model #B-721) in combination with a *Welch*® direct drive pump (model #8915A). Lower pressures were achieved using a vacuum manifold connected to an oil-diffusion pump and backed by a *Welch*® direct drive vacuum pump, (model #8910A). Bulb-to-bulb distillation was performed using a Buchi Glass Oven (model #B-580). Chromatography was performed following the method prescribed by W. C. Still (*J. Org. Chem.* **1977**, *42*, 1258-1259).

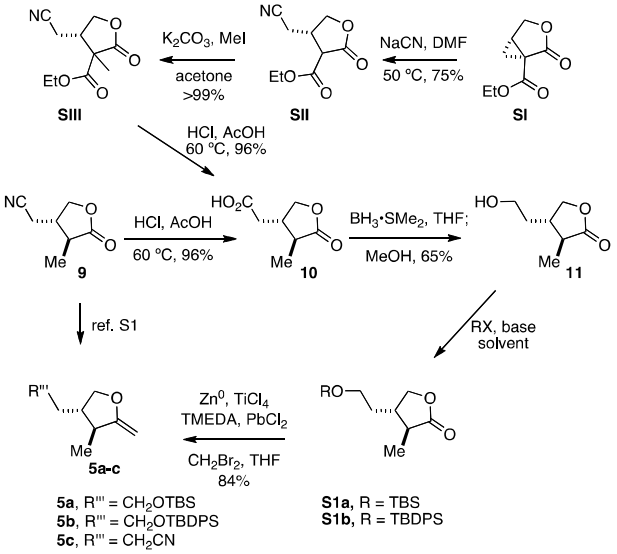
Deuterated chloroform was filtered through basic alumina prior to use. Solvents were distilled before use, under a slight positive pressure of nitrogen. Diethyl ether, tetrahydrofuran, benzene, and toluene were

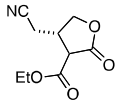
distilled from sodium and benzophenone. Dichloromethane was distilled from $CaH_2$. Atmosphere (1 atm) hydrogenations were carried out using a balloon.

$^1$H-NMR spectra were recorded at 400 MHz or 500 MHz on a *Varian*® Unity Inova spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance of $CDCl_3$ (7.27 ppm). $^{13}$C NMR spectra were recorded at (100 MHz or 125 MHz) with a solvent resonance of $CDCl_3$ (77.23 ppm). Infrared spectra were recorded on a *Shimadzu*® FTIR-8300 Fourier transform infrared spectrometer with 2 cm resolution in a solution cell ($CH_2Cl_2$). Infrared frequencies are reported in reciprocal centimeters ($cm^{-1}$). Silica columns for HPLC, supplied by *Jones Chromatography,*® were 25 cm long in length and contained 5 µm spherisorb. In some instances, flash chromatography was performed using a Jones Flashmaster Solo model 605. Mass spectra were recorded on a VG-7035 mass spectrometer at an ionizing voltage of either 70 or 20 eV.

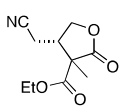
## II. Experimental Procedures

### A. Synthesis of Enol Ethers 5a-c:





SII

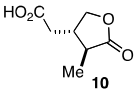
**Lactone SII:** To a solution of cyclopropyl lactone **SI**[1] (8 g, 46.88 mmol) in DMF (78 mL) was added NaCN (2.76 g, 56.25 mmol) in one portion. The resulting solution was warmed to 50 ºC and stirred overnight. After completion as judged by TLC (iodine stain), the solution was cooled to room temperature and quenched with 1 M $NH_4Cl$ (20 mL). The mixture was extracted with EtOAc (3 x 50 mL), and the combined extracts were washed with $H_2O$ (2x), brine (2x), dried ($Na_2SO_4$), filtered, and concentrated *in* vacuo to afford 6.92 g of crude cyano lactone **SII** that was taken on without further purification. Isolated yield: 75%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 4.60 (dd, *J* = 9.3, 7.6 Hz, 1H), 4.33-4.28 (m, 2H), 4.12-4.08 (m, 1H), 3.44 (d, *J* = 9.1 Hz, 1H), 3.39-3.31 (m, 1H), 2.67 (d, *J* = 6.3 Hz, 1H), 1.35 (t, *J* = 7.2 Hz, 2H) ppm; $^{13}$C NMR [$CDCl_3$, 100 MHz] δ 169.9, 166.2, 116.2, 69.8, 63.1, 50.7, 36.2, 19.5, 14.2 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ $cm^{-1}$] 2985, 2249, 1782, 1732, 1153, 1153, 1026; HRMS (ESI+/TOF) *m/z* calculated for $C_9H_{11}NO_4$ $(M)^+$ 197.0688, found 220.0580 $(M+Na)^+$.


SIII

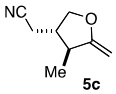
**Lactone SIII:** To a solution of cyano lactone **SII** (2 g, 10.17 mmol) in acetone (34 mL) was added $K_2CO_3$ (2.8 g, 20.23 mmol) and MeI (0.95 mL, 15.18 mmol). The resulting solution was warmed to reflux and stirred overnight. After completion as judged by TLC (iodide stain), the solution was cooled to room temperature and filtered through Celite®. The clear solution was concentrated *in* vacuo to afford 2.2 g of crude lactone **SIII** as a single diastereomer that was taken on without further purification. Isolated yield: >99%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 4.55 (dd, *J* = 8.9, 7.9 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.16-4.12 (m, 1H), 2.80-2.73 (m, 1H), 2.64 (dd, *J* = 17.1, 8.3 Hz, 1H), 2.45 (dd, *J* = 17.1, 8.3 Hz,

[1] Pirrung, M. C.; Dunlap, S. E.; Trinks, U. P. *Helv. Chim. Acta* **1989**, *72*, 1301.

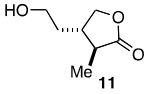
1H), 1.57 (s, 3H), 1.32 (t, $J$ = 7.2 Hz, 3H) ppm; $^{13}$C NMR [$CDCl_3$, 100 MHz] δ 174.3, 167.9, 116.2, 69.1, 63.1, 53.1, 43.4, 39.9, 19.5, 16.2, 14.2 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm$^{-1}$] 2985, 2939, 2253, 1782, 1736, 1230, 1103, 1022, 737; HRMS (ESI+/TOF) *m/z* calculated for $C_{10}H_{13}NO_4$ $(M)^+$ 211.2145, found 234.0740 $(M+Na)^+$.



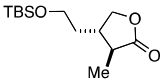

**Lactone 10**: To a solution of lactone **9**[2] or lactone SIII (326.1 mg, 2.34 mmol) in AcOH (0.13 mL) was added conc. HCl (1 mL), and the resulting solution was heated to 60 ºC and stirred overnight. After completion as judged by TLC (iodine stain), the solution was cooled to room temperature and diluted with $H_2O$ (5 mL). The solution was extracted with EtOAc (3 x 10mL), and the combined extracts were washed with $H_2O$ (2x), brine (2x), dried ($Na_2SO_4$), filtered, and concentrated *in* vacuo. The crude mixture was azeotroped with toluene to remove residual AcOH and concentrated to afford 339 mg of crude acid **10** that was taken on without further purification. Isolated yield: 96%. $^1$H NMR [$CDCl_3$, 500 MHz] δ 4.59 (dd, $J_1$ = 9.1 Hz, $J_2$ = 7.5 Hz, 1H), 3.97 (t, $J$ = 9.2 Hz, 1H), 2.74 (dd, $J_1$ = 16.2 Hz, $J_2$ = 4.2 Hz, 1H), 2.61-2.53 (m, 1H), 2.51 (dd, $J_1$ = 16.2 Hz, $J_2$ = 4.2 Hz, 1H), 2.32-2.27 (m, 1H), 1.30 (d, $J$ = 7.2 Hz, 3 H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 178.9, 176.6, 71.0, 40.0, 39.8, 36.1, 13.9 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm$^{-1}$] 3500, 2977, 2918, 1766, 1735, 1188, 1010; HRMS (EI) *m/z* calculated for $C_7H_{10}O_4$ (M+) = 158.0579, found 158.0581.




**Enol Ether 5c** was constructed by literature precedent.[1]

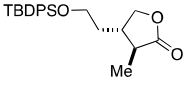



**Alcohol 11**: To a solution of acid **10** (1.25 g, 7.89 mmol) in THF (78 mL) at 0 ºC was added $BH_3$•$SMe_2$ (8.7 mL, 2 M in THF), and the resulting solution was stirred overnight. After completion as judged by TLC (iodine stain), the solution was cooled to 0 ºC and quenched with MeOH (10 mL). The mixture was concentrated *in* vacuo, and the crude mixture was purified by chromatography on silica gel (60% EtOAc/Hexanes) to afford 742.6 mg of alcohol **11**. Isolated yield: 65%. $^1$H NMR [$CDCl_3$, 500 MHz] δ 4.50 (dd, $J_1$ = 9.5 Hz, $J_2$ = 7.3 Hz, 1H), 3.97 (t, $J$ = 9.2 Hz, 1H), 3.80-3.70 (m, 2H), 2.30-2.23 (m, 2H), 1.94-1.90 (m, 1H), 1.69-1.62 (m, 1H), 1.48 (br s, 1H), 1.28 (d, $J$ = 6.0 Hz, 3 H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 176.8, 72.1, 61.1, 41.9, 40.6, 34.7, 14.1 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm$^{-1}$] 3423, 2970, 2933, 2881, 1770, 1388, 1176, 1101, 1047, 1006, 711, 582; HRMS (ESI+/TOF) *m/z* calculated for $C_7H_2O_3Na$ $(M+Na)^+$ = 167.0678, found 167.0685.




**S1a**, R = TBS

**Lactone S1a:** To a solution of alcohol **11** (1.33 g, 9.246 mmol) in DMF (23 mL) was added TBSCl (1.46 g, 9.71 mmol) and imidazole (660 mg, 9.71 mmol), and the resulting solution was stirred at room temperature overnight. After completion as judged by TLC (iodine stain), the reaction was diluted with $H_2O$ (20 mL) and extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with $H_2O$ (2x), brine (2x), dried ($Na_2SO_4$), filtered, and concentrated. The crude oil was purified by chromatography on silica gel (7% EtOAc/Hexanes) to afford 1.62 g of silyloxy lactone **130**. Isolated yield: 68%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 4.45 (td, $J$ = 7.2, 2.0 Hz, 1H), 3.86 (td, $J$ = 8.1, 3.3 Hz, 1H), 3.73-3.67 (m, 1H), 3.67-3.60 (m, 1H), 2.25-2.18 (m, 2H), 1.86-1.81 (m, 1H), 1.63-1.55 (m, 1H), 1.27-1.21 (m, 3H), 0.88 (s, 9H), 0.04 (s, 6H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 179.8, 72.4, 61.5, 42.5, 40.5, 35.1, 26.1, 18.3, 13.9, -5.3 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm$^{-1}$] 2955, 2931, 2858, 1778, 1254, 1103, 1011, 837, 779; HRMS (ESI+/TOF) *m/z* calculated for $C_{13}H_{26}O_3Si$ $(M)^+$ = 258.1651, found 281.1548 $(M+Na)^+$.




**S1b**, R = TBDPS

**Lactone S1b:** Prepared in the same way as Lactone **S1a**. All data matched those reported in the literature.[3]

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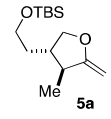
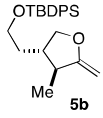
[2] Marsini, M. A.; Huang, Y.; Lindsey, C. C.; Wu, K. L.; Pettus, T. R. R. *Org. Lett.* **2008**, *10*, 1477.

[3] (a) Wu, X.; Zhou, J.; Snider, B. B. *Angew. Chem. Int. Ed.* **2009**, *48*, 1283. (b) Wu, X.; Zhou, J.; Snider, B. B. *J. Org. Chem.* **2009**, *74*, 6245.



5a

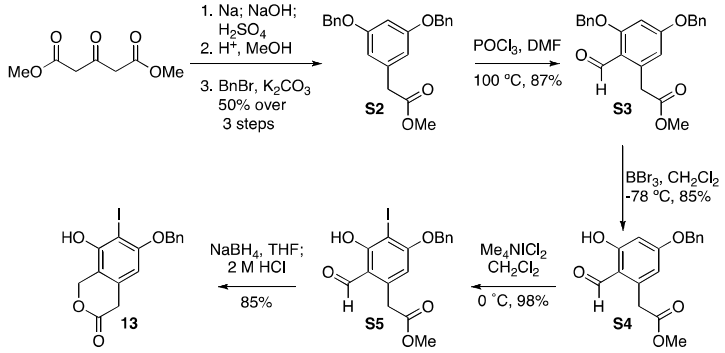
**Enol Ether 5a:** To a flame dried flask with a stirbar under $N_2$ was added THF (46 mL) that was cooled to 0 ºC. $TiCl_4$ (9.2 mL, 1 M in $CH_2Cl_2$) was added, resulting in a yellow precipitate. This mixture was warmed pulled from the ice bath, and TMEDA (2.7 mL, 17.83 mmol) was added to afford a clear, brown solution that was stirred for 20 minutes. Activated Zn metal (1.3 g, 19.99 mmol) and $PbCl_2$ (30 mg, 0.11 mmol) was added, resulting in a blue-green solution that was stirred for 30 minutes. Lactone **S1a** (280 mg, 1.08 mmol) and $CH_2Br_2$ (0.36 mL, 5.08 mmol) in THF (2.2 mL) was added via canula, and the resulting solution was stirred at room temperature overnight. After completion as judged by TLC, the reaction was cooled to 0 ºC and quenched with sat. aq. $K_2CO_3$ (1.3 mL) and $Et_2O$ (10 mL). After stirring for 20 minutes, the black heterogeneous mixture was filtered through a thin pad alumina, which was further eluted with $Et_2O/Et_3N$ (200:1). The filtrate was concentrated *in vacuo* at room temperature. The resulting oil, which contained a white precipitate, was dissolved in hexanes/$Et_3N$ (200:1) and the heterogeneous mixture was filtered through a second, thin pad of alumina. The resulting solution was concentrated *in vacuo* at room temperature to afford 234 mg of pure enol ether **5a**. Isolated yield: 84%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 4.61 (t, *J* = 1.7 Hz, 1H), 4.19 (dd, *J* = 8.4, 7.4 Hz, 1H), 3.92 (t, *J* = 1.5 Hz, 1H), 3.50 (t, *J* = 9.0 Hz, 1H), 3.35-3.23 (m, 2H), 2.06 (ddt, *J* = 7.8, 4.5, 2.1 Hz, 1H), 1.69 (ddd, *J* = 9.7, 7.1, 4.0 Hz, 1H), 1.51-1.44 (m, 1H), 1.16-1.07 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.92 (s, 9H), -0.03 (s, 6H).

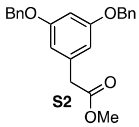


5b

**Enol Ether 5b:** To the lactone **S1b** (0.3761 g, 0.983 mmol) was added $Cp_2TiMe_2$ (1.01 M in toluene, 2.42 mL) and toluene (5.0 mL). The flask was covered with aluminum foil and the solution was heated at 65 ˚C for 24 h. The toluene was removed under reduced pressure, and to the residue was added hexanes (ca 15 mL). Celite was added and the mixture was stirred until the gummy residue dissipated, leaving a yellow precipitate (10 min). The solution was filtered through a pad of celite and washed with hexanes (ca 5 mL). $NaHCO_3$ (0.142 g, 1.69 mmol), $H_2O$ (0.070 mL, 3.9 mmol), and MeOH (ca 0.8 mL) was added and the mixture was stirred at 40 ˚C for 32 h. The mixture was filtered through celite, concentrated, redissolved in hexanes, and filtered through a short pad of grade III alumina, washing with $Et_3N$:$Et_2O$ (1:200). The filtrate was concentrated and the residue was purified by flash chromatography ($Et_3N$ doped $SiO_2$) using 1% EtOAc/hexanes as the eluent to afford **5b** (0.3218 g, 86%) as a light yellow oil. $^1$H NMR [$C_6D_6$, 500 MHz] δ 7.74 (m, 4H), 4.59 (s, 1H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.90 (s, 1H), 3.48–3.40 (m, 3H), 2.03 (m, 1H), 1.68 (m, 1H), 1.53 (m, 1H), 1.19–1.12 (m, 10H), 0.95 (d, *J* = 6.7 Hz, 3H) ppm; $^{13}$C NMR [$C_6D_6$, 125 MHz] δ 168.6, 136.3, 130.4, 128.9, 128.7, 78.8, 74.4, 63.3, 44.1, 42.2, 34.9, 27.4, 19.7, 16.7 ppm; IR [thin film, $\nu_{max}$ cm$^{-1}$] 3048, 2932, 2863, 1666, 1466, 1427, 1111, 1034, 702; HRMS (FI) *m/z* calculated for $C_{24}H_{32}O_2Si$ = 380.2172, found 380.2177.

**B: Synthesis of Isochromanone 13:**



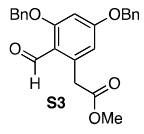




**Methyl Ester S2:** To a flame dried flask with a stirbar under $N_2$ was added dimethylacetone dicarboxylate (20 mL, 140 mmol). Sodium (250 mg, 10.89 mmol) is added in incremental portions, and the resulting mixture is allowed to stir at room temperature for 20 hours. The mixture is then

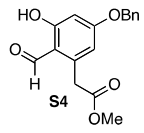
heated for 2 hours to an internal temperature of 140 ºC, whereby the volatile components are distilled off. After distillation ceases, 12% aq. NaOH (128 mL) is cautiously added, and again volatile components (MeOH) are removed by distillation over 2 hours. The solution is then cooled to 80 ºC and is slowly treated with conc. $H_2SO_4$ (11.2 mL) (Caution: gas evolution and temperature increase!). After complete addition, the resulting mixture was refluxed for 3 hours, cooled, and, after saturation with NaCl, extracted with EtOAc (4 x 100 mL). The combined organic extracts were washed with $H_2O$, brine (4x), dried ($Na_2SO_4$), filtered, and concentrated. The crude acid (10.94 g, 48% yield) was taken directly on to the next step.

To a solution of crude acid (6.92 g, 41.17 mmol) in MeOH (137 mL) was added $H_2SO_4$ (10 drops), and the resulting mixture was heated to reflux for 4 hours, after which it was stirred overnight at room temperature. The mixture was then concentrated *in vacuo*, redissolved in EtOAc (150 mL), and washed with 1 M $NaHCO_3$ (150 mL). The aqueous layer was extracted with EtOAc (3 x 50 mL), and the combined organic extracts were washed with $H_2O$ until the aqueous layer was clear, followed by brine. The organic extracts were dried ($Na_2SO_4$), filtered, and concentrated to afford 5.31 g of the crude methyl ester, which was taken directly on to the next step.

To a solution of the above ester (6 g, 32.93 mmol) in acetone (118 mL) was added $K_2CO_3$ (9.56 g, 69.16 mmol) and BnBr (8.37 mL, 69.96 mmol). The resulting solution was heated to reflux overnight. After completion by TLC, the reaction mixture was cooled to room temperature, filtered through Celite®, and concentrated *in vacuo*. Purification by chromatography on silica gel (7% EtOAc/Hexanes) affords 11.32 g of pure methyl ester **S2** as a white solid. All spectral data matched those reported in the literature.[4] Isolated yield: 95%.



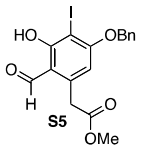

**Aldehyde S3:** To a solution of ester **S2** (15.02 g, 41.62 mmol) in DMF (20 mL) at 50 ºC was added $POCl_3$ (5.84 mL, 62.42 mmol). The resulting mixture is then warmed to 100 ºC and stirred at this temperature for 10 minutes, after which it was allowed to warm to room temperature and stirred overnight (~16 hours). The resulting viscous mixture was cooled to 0 ºC with vigorous stirring and quenched slowly with 10% aq. NaOAc (100 mL). After stirring for ~3 hours, the completely heterogeneous mixture is filtered and washed thoroughly with $H_2O$. The resulting tan solid is recrystallized from 95% EtOH to afford 14.12 g of pure aldehyde **S3** as a white solid. Isolated yield: 87%. $^1$H NMR [$CDCl_3$, 500 MHz] δ 10.53 (s, 1H), 7.42-7.36 (m, 10H), 6.60 (d, *J* = 2.0 Hz, 1H), 6.46 (d, *J* = 2.0 Hz, 1H), 5.12 (s, 2H), 5.10 (s, 2H), 3.97 (s, 2H), 3.73 (s, 3H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 190.3, 171.8, 164.6, 164.1, 139.4, 136.0, 135.9, 129.0, 128.9, 128.6, 128.5, 127.8, 127.6, 117.6, 111.3, 99.3, 70.9, 70.5, 52.2, 40.8 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm$^{-1}$] 2951, 2881, 2789, 1732, 1674, 1597, 1578, 1319, 1153; HRMS (ESI+/TOF) *m/z* calculated for $C_{22}H_{22}O_5$ $(M+Na)^+$ = 390.1467, found 413,1365 $(M+Na)^+$.



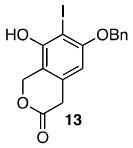

**Aldehyde S4:** To a solution of aldehyde **S3** (5 g, 12.87 mmol) in dry $CH_2Cl_2$ (86 mL) at -78 ºC was added $BBr_3$ (12.9 mL, 1.1 M in $CH_2Cl_2$). The mixture was allowed to slowly warm to room temperature and stirred overnight. The resulting solution was then cooled to 0 ºC and quenched dropwise with 2 M aq. HCl (30 mL). After stirring for 3 hours, the solution is extracted with $CH_2Cl_2$ (3 x 70 mL). The combined organic extracts were dried ($MgSO_4$), and the mixture was filtered through a wide plug of sand, silica gel, and sand that was washed copiously with $CH_2Cl_2$. The clear solution was concentrated *in vacuo* and azeotroped with toluene to provide 3.26 g of pure phenol **S4** as an off-white solid. Isolated yield: 85%. $^1$H NMR [$CDCl_3$, 500 MHz] δ 12.52 (s, 1H), 10.06 (s, 1H), 7.42-7.37 (m, 5H), 6.45 (s, 2H), 5.09 (s, 3H), 3.85 (s, 2H), 3.72 (s, 3H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 192.9, 170.8, 166.8, 165.7, 139.4, 135.6, 128.9, 128.6, 127.8, 113.2, 112.2, 101.1, 70.5, 52.8, 37.7 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm$^{-1}$]

[4] (a) Theilacker W.; Schmid, W. *Annalen* **1950**, *570*, 15. (b) Ichinose, K.; Ebizuka, Y.; Sankawa, U. *Chem. Pharm. Bull.* **2001**, *49*, 192.

3421, 3032, 2951, 1736, 1628, 1292, 1165; HRMS (ESI+/TOF) *m/z* calculated for $C_{17}H_{16}O_5$ ($M^+$) = 300.0998, found 323.0893 $(M+Na)^+$.



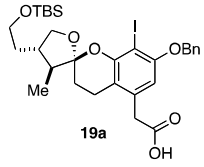

**Iodide S5:** To a solution of phenol **S4** (500 mg, 1.68 mmol) in $CH_2Cl_2$ (11.2 mL) was added $NaHCO_3$ (283 mg, 3.36 mmol), and the resulting mixture was cooled 0 ºC. $Me_4NICl_2$ (548 mg, 1.85 mmol) was added in one portion, and the resulting solution was allowed to stir for 16 hours. The solution was quenched with 1 M aq. HCl and stirred for 15 minutes, after which it was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic extracts were washed with 1 M aq. $Na_2S_2O_3$, dried ($Na_2SO_4$), filtered, and concentrated. The crude residue was purified by chromatography on silica gel (20% EtOAc/Hexanes) to afford 630 mg of iodophenol **S5**. Isolated yield: 98%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 13.21 (s, 1H), 10.00 (s, 1H), 6.43 (s, 1H), 5.28 (s, 2H), 3.88 (s, 2H), 3.71 (s, 3H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 192.7, 170.3, 164.6, 164.1, 140.3, 135.4, 128.9, 128.7, 128.4, 127.1, 113.8, 107.8, 71.3, 52.9, 37.9 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ $cm^{-1}$] 3445, 3040, 2970, 1732, 1636, 1393, 1296, 1192, 783; HRMS (ESI+/TOF) *m/z* calculated for $C_{17}H_{15}O_5I$ $(M)^+$ = 425.9964, found 448.9861 $(M+Na)^+$.



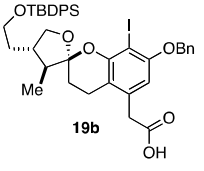

**Isochromanone 13:** To a solution of phenol **S5** (585.3 mg, 1.527 mmol) in THF (7.6 mL) at 0 ºC was added $NaBH_4$ (86.7 mg, 2.291 mmol), and the solution was allowed to stir for 30 minutes. After completion as judged by TLC, the solution was quenched at 0 ºC with 2 M aq. HCl (2 mL) and stirred overnight. The resulting mixture was extracted with EtOAc (3 x 10 mL), and the combined organic extracts were washed with $H_2O$ and brine, dried ($Na_2SO_4$), filtered, dried, and concentrated. The crude residue was recrystallized from 1:1 $Et_2O$/pentane to afford 460.2 mg of pure iodolactone **13**. Isolated yield: 85%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 7.49-7.35 (m, 5H), 6.34 (s, 1H), 5.74 (s, 1H), 5.41 (s, 2H), 5.16 (s, 2H), 3.64 (s, 2H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 170.4, 162.7, 157.9, 151.8, 136.1, 133.9, 128.9, 128.3, 127.1, 111.1, 103.6, 71.3, 65.9, 36.2 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm-1] 3446, 3063, 3032, 1736, 1601, 1346, 1157, 1030, 737; HRMS (ESI+/TOF) *m/z* calculated for $C_{16}H_{13}IO_4$ $(M)^+$ = 395.9859, found 418.9764 $(M+Na)^+$.

### C. Diastereoselective Formal Synthesis of Berkelic Acid

**General Procedure for *o*-QM cycloaddition:** The enol ether (2.0 equiv.) was dissolved in dry solvent ($Et_2O$ or toluene, 0.1 M) and added to a stirring solution of the benzyl alcohol (1.0 equiv.) in dry $Et_2O$ or toluene (0.1 M) at -78 °C. Next, *t*-butylmagnesium chloride (1.1 equiv, 1 M in THF) was added slowly, and the reaction was allowed to warm up to room temperature over 3 hours. Upon completion by TLC, the reaction was then quenched by 0.1 M HCl and extracted with EtOAc (3X). The combined organic extracts were washed with $H_2O$, brine, dried ($Mg_2SO_4$), and concentrated. Purification by flash chromatography afforded the products.

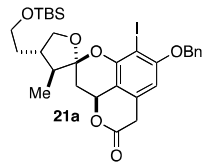



**Spiroketal 19a:** Following the general procedure for cycloaddition using enol ether **5a**, spiroketal **19a** was obtained in 60% yield after equilibration with TFA. $^1$H NMR [$CDCl_3$, 400 MHz] δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.40-7.37 (m, 2H), 7.32-7.29 (m, 1H), 6.44 (s, 1H), 5.12 (s, 2H), 4.17 (t, *J* = 8.5 Hz, 1H), 3.73-3.54 (m, 6H), 2.91-2.84 (m, 1H), 2.75-2.71 (m, 1H), 2.54 (ddt, *J* = 11.2, 7.0, 3.5 Hz, 1H), 2.07-1.98 (m, 2H), 1.94-1.87 (m, 2H), 1.70 (dq, *J* = 10.8, 6.6 Hz, 1H), 1.51 (ddt, *J* = 13.4, 10.4, 6.7 Hz, 1H), 1.19 (d, *J* = 6.7 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 175.9, 156.9, 136.9, 132.9, 128.7, 127.9, 127.2, 115.4, 107.7, 107.1, 78.8, 73.2, 71.2, 62.5, 48.8, 42.2, 38.3, 36.3, 29.9, 27.9, 26.2, 19.8, 18.5, 12.5, 1.2 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm-1] 3429, 2955, 2928, 1709, 1593, 1404, 1254, 1165, 1095, 1072, 1007, 891, 837; HRMS (ESI+/TOF) *m/z* calculated for $C_{30}H_{41}O_6ISi$ $(M)^+$ = 652.1717, found 675.1582 $(M+Na)^+$.

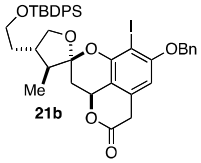



**Spiroketal 19b:** Following the general procedure for cycloaddition using enol ether **5b**, spiroketal **19b** was obtained in 58% yield after equilibration with TFA. $^1$H NMR [$CDCl_3$, 500 MHz] δ 7.69 (d, *J* = 7.4 Hz, 4H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.43–7.37 (m, 8H), 7.32 (m, 1H),

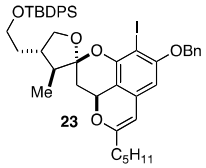
6.45 (s, 1H), 5.13 (s, 1H), 4.18 (t, *J* = 8.5 Hz, 1H), 3.71 (m, 2H), 3.64–3.54 (m, 3H), 2.88 (dt, *J* = 14.9, 6.5 Hz, 1H), 2.73 (dd, *J* = 15.7, 6.0 Hz, 1H), 2.64 (t, *J* = 8.3 Hz, 1H), 2.10–1.86 (m, 3H), 1.69 (m, 1H), 1.53 (m, 1H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.07 (s, 9H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ: 176.8, 156.9, 153.9, 136.9, 135.8, 133.8, 132.9, 129.8, 128.7, 127.9, 127.3, 115.4, 107.8, 107.2, 78.9, 73.2, 71.3, 68.0, 63.3, 48.8, 42.0, 38.4, 36.0, 27.9, 27.1, 19.8, 19.4, 12.4 ppm; IR [thin film, $\nu_{max}$ cm$^{-1}$] 2932, 2857, 1709, 1593, 1427, 1404, 1163, 1111, 889, 735, 702. HRMS (ESI+/TOF) *m/z* calculated for $C_{40}H_{45}IO_6SiNa$ = 799.1928, found 799.1921.




**Tetracycle 21a:** To a solution of iodo-acid **19a** (10 mg, .01532 mmol) in $CDCl_3$ (2 mL) was added DDQ (16 mg, .0705 mmol). The resulting blue-green mixture was then heated to 65 ºC for 24 hours. After completion, the mixture was cooled and poured into 1 M aq. $NaHCO_3$. The mixture was extracted with $CHCl_3$ (3 x 5 mL), and the organic extracts were washed with $H_2O$, dried ($MgSO_4$), filtered, and concentration. Purification by flash chromatography (15% EtOAc/hexanes) affords tetracycle **21a**. Isolated yield: 65%. $^1$H NMR [$CDCl_3$, 400 MHz] δ 7.50-7.32 (m, 5H), 6.36 (s, 1H), 5.67-5.62 (m, 1H), 5.17 (s, 2H), 4.19 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.74-3.62 (m, 5H), 2.54-2.49 (m, 1H), 2.43-2.39 (m, 1H), 2.26 (dd, *J* = 12.3, 11.5 Hz, 1H), 2.05-2.02 (m, 1H), 1.96-1.90 (m, 1H), 1.80-1.77 (m, 1H), 1.24-1.21 (m, 3H), 0.91 (s, 9H), 0.07 (s, 6H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 170.3, 159.4, 136.4, 132.4, 128.8, 128.2, 127.1, 110.9, 109.2, 103.9, 74.1, 71.3, 70.9, 62.4, 49.2, 41.8, 37.1, 35.9, 33.9, 29.9, 26.2, 18.5, 12.3, -5.1 ppm; IR [$CH_2Cl_2$ solution, $\nu_{max}$ cm-1] 2951, 2928, 2854, 1755, 1605, 1423, 1188, 1099, 833; HRMS (ESI+/TOF) *m/z* calculated for $C_{30}H_{39}O_6ISi$ $(M)^+$ = 650.1561, found 673.1441 $(M+Na)^+$.



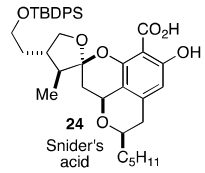

**Tetracycle 21b:** To a solution of **19b** (0.0766 g, 0.0986 mmol) in $CHCl_3$ (2 mL) was added DDQ (0.0246 g, 0.108 mmol). The resulting blue-green mixture was then heated to 60 ºC for 24 hours. Additional DDQ (0.0246 g, 0.108 mmol) was added and the reaction was heated for an additional 36 h. The mixture was filtered through a pad of celite and concentrated. The crude residue was purified by chromatography using 5% EtOAc/hexanes to 30% EtOAc/hexanes to afford tetracycle **21b** (0.0497 g, 65% yield) as a colorless oil. $^1$H NMR [$CDCl_3$, 500 MHz] δ 7.68 (d, *J* = 6.3 Hz, 4H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.41 (m, 8H), 7.34 (d, *J* = 7.3 Hz, 1H), 6.37 (s, 1H), 5.64 (dd, *J* = 11.1, 6.5 Hz, 1H), 5.17 (s, 2H), 4.17 (t, *J* = 8.5 Hz, 1H), 3.72 (m, 2H), 3.64 (m, 3H), 2.61 (m, 1H), 2.41 (dd, *J* = 12.5, 6.7, 1H), 2.26 (t, *J* = 11.9 Hz, 1H), 1.95 (m, 1H), 1.78 (m, 1H), 1.54 (m, 1H), 1.22 (d, *J* = 6.7 Hz, 3H), 1.07 (s, 9H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 170.2. 159.4, 151.6, 135.8, 135.7, 132.4, 129.9, 128.8, 128.2, 127.9, 127.1, 111.0, 109.3, 75.7, 74.0, 71.3, 70.9, 63.2, 49.2, 41.5, 37.0, 35.6, 33.9, 27.1, 27.0, 19.4, 12.3 ppm; IR [thin film, $\nu_{max}$ cm$^{-1}$] 2931, 1753, 1604, 1425, 1188, 1099, 735, 702; HRMS (ESI+/TOF) *m/z* calculated for $C_{40}H_{43}IO_6SiNa$ = 797.1771, found 797.1755.




**Isobenzopyran 23:** $CeCl_3$ • 2LiCl (0.52 M in THF, 0.572 mL, 0.286 mmol) was further diluted in THF (1.5 mL) and cooled to 0 ˚C. $C_5H_{11}MgBr$ (1.25 M in $Et_2O$, 0.218 mL, 0.273 mmol) was added and the resulting off-white and slightly opaque solution was stirred at 0 ˚C for 45 min. In a separate flask, the lactone **21b** (0.0384 g, 0.0496 mmol) was dissolved in THF (1 mL). $CeCl_3$ • 2LiCl solution (0.52 M in THF, 0.114 mL, 0.0572 mmol) was added lactone and the solution was cooled to –78 ˚C. The organocerium solution was added to the lactone/$CeCl_3$ solution via cannula over several minutes. The reaction mixture was stirred for 45 min. at –78 ˚C, quenched with satd aq $NH_4Cl$ and diluted with EtOAc. The flask was removed from the cold bath and celite was added to the mixture and allowed to stir for 15 min while warming to rt. The mixture was filtered and the aqueous layer was extracted with EtOAc four times. The combined organics layers were washed with brine, dried with $Na_2SO_4$ and concentrated. The crude residue was sufficiently pure for the subsequent reaction.

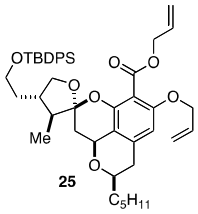
To a solution of the hemiketal in $CH_2Cl_2$ at –78 ˚C was added TFA (0.0005 mL, 0.0075 mmol). The solution was stirred for 15 min then quenched with satd aq $NaHCO_3$ and diluted with $CH_2Cl_2$. The aqueous layer was extracted with $CH_2Cl_2$ and the combined organic layers were dried with $Na_2SO_4$ and concentrated. The crude material was purified by flash chromatography on silica doped with $Et_3N$ using 5% EtOAc/hexanes

as the eluent to afford **23** (0.0329 g, 80% yield from **21b**) as a colorless oil. $^1$H NMR [$C_6D_6$, 500 MHz] δ 7.78 (d, *J* = 6.2 Hz, 4H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.27–7.17 (m, 8H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.01 (s, 1H), 5.62 (dd, *J* = 11.1, 6.1 Hz, 1H), 5.55 (s, 1H), 4.77 (s, 12H), 4.18 (t, *J* = 8.4 Hz, 1H), 3.55 (m, 2H), 3.47 (m, 2H), 2.67 (m, 1H), 2.32 (t, *J* = 12.1 Hz, 1H), 2.23 (dd, *J* = 12.3, 6.3 Hz, 1H), 2.16 (m, 2H), 1.70 (m, 1H), 1.58 (m, 2H), 1.34–1.19 (m, 6H), 1.17 (s, 9H), 1.08 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm; $^{13}$C NMR [$C_6D_6$, 125 MHz] δ 160.4, 159.4, 151.6, 137.9, 136.4, 136.3, 134.3, 133.5, 130.2, 129.1, 128.5, 127.5, 109.9, 106.9, 102.3, 100.9, 73.7, 71.3, 70.0, 63.6, 49.9, 41.8, 36.4, 34.8, 34.6, 32.1, 27.5, 27.4, 23.2, 19.8, 14.6, 12.6 ppm; IR [thin film, $\nu_{max}$ cm$^{-1}$] 2930, 2857, 1633, 1568, 1470, 1414, 1188, 1103, 997, 880, 735, 702; HRMS (ESI+/TOF) calculated for *m/z* $C_{45}H_{53}IO_5SiNa$ = 851.2605, found 851.2598.

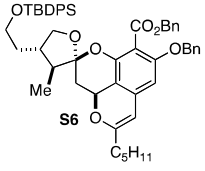



**Snider's acid 24:** Iodide **23** (0.00494 g, 0.00596 mmol) was dissolved in THF (1.0 mL) and cooled to –110 ˚C. *t*-BuLi (0.0077 mL, 0.0131 mmol, 1.7 M in pentane) was added, forming a light yellow solution, which was allowed to stir for 5 min at –110 ˚C. Then $CO_2$ was bubbled through the solution for 1 h, allowing the temperature to slowly increase to 0 ˚C. It was quenched with satd aq $NH_4Cl$ and diluted with EtOAc. The aqueous layer was extracted six times with EtOAc. The combined organic extracts were washed with brine, dried with $Na_2SO_4$, and concentrated. The crude residue was used for the subsequent hydrogenation reaction.

The crude product from above was dissolved in EtOAc (1 mL). Pd/C (cat.) was added and the reaction was stirred under a $H_2$ filled balloon for 4 hours. The reaction mixture was filtered through celite and concentrated. The crude residue was purified by chromatography using 20% EtOAc/hexanes + 1% HOAc to 40% EtOAc/hexanes + 1% HOAc to afford **24** (0.00243 g, 62% yield from **23**) as a colorless oil. $^1$H NMR [$CDCl_3$, 500 MHz] δ 11.88 (s, 1H), 7.66 (d, *J* = 5.4 Hz, 4H), 7.42 (m, 6H), 6.45 (s, 1H), 4.80 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.29 (t, *J* = 8.3 Hz, 1H), 3.84 (m, 1H), 3.76 (t, *J* = 8.8 Hz, 1H), 3.71 (m, 2H), 2.82 (d, *J* = 17.5 Hz, 1H), 2.63 (dd, *J* = 11.7, 18.6 Hz, 1H), 2.36 (t, 7.3 Hz, 1H), 2.22 (m, 2H), 1.87 (m, 2H), 1.73–1.19 (m, 6H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.06 (s, 9H), 0.97 (t, *J* = 6.4 Hz, 3H) ppm; $^{13}$C NMR [$CDCl_3$, 200 MHz] δ 171.0, 162.9, 152.2, 142.6, 135.9, 133.7, 130.1, 128.1, 112.8, 112.5, 110.7, 98.9, 75.6, 74.5, 67.7, 63.1, 49.1, 42.2, 35.6, 33.5, 32.2, 32.0, 30.0, 27.1, 25.3, 23.0, 19.3, 14.4, 12.3 ppm; IR [thin film, $\nu_{max}$ cm$^{-1}$] 3233, 2924, 2853, 1699, 1456, 1246, 1111, 702; HRMS (ESI+/TOF) calculated for *m/z* $C_{39}H_{50}O_7SiNa$ = 681.3224, found 681.3193.

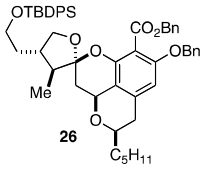



**Allyl ester 25:** The compound was prepared from **24** by the method reported in the literature.[2] $^1$H NMR [$CDCl_3$, 400 MHz] δ 7.66 (d, *J* = 6.7 Hz, 4H), 7.48–7.34 (m, 6H), 6.23 (s, 1H), 6.03–5.89 (m, 2H), 5.35 (m, 2H), 5.22 (d, *J* = 10.4 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.84–4.65 (m, 2H), 4.51 (d, *J* = 4.9 Hz, 2H), 4.21 (t, *J* = 8.5 Hz, 1H), 3.80 (m, 1H), 3.72–3.60 (m, 2H), 2.75 (dd, *J* = 17.1, 3.7 Hz, 1H), 2.60 (dd, *J* = 17.1, 10.7 Hz, 1H), 2.30–2.18 (m, 1H), 2.15 (dd, *J* = 12.1, 4.9 Hz, 1H), 1.98 (m, 1H), 1.89–1.79 (m, 1H), 1.72 (m, 2H), 1.55 (m, 3H), 1.43 (m, 5H), 1.05 (s, 9H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.90 (m, 3H).




**Benzyl ester S6:** Iodide **23** (0.0324 g, 0.0391 mmol) was dissolved in THF (3.0 mL) and cooled to –110 ˚C. *t*-BuLi (0.0506 mL, 0.0860 mmol, 1.7 M in pentane) was added dropwise, forming a light yellow solution which was allowed to stir for 5 min at –110 ˚C. $CO_2$ was bubbled through the solution for 1 h, allowing the temperature to slowly increase to 0 ˚C. The source of $CO_2$ was removed, and the solvent was evaporated at rt with the aid of gentle flowing $N_2$. The residue was taken up in $CH_3CN$ (3.0 mL) and benzyl bromide (0.0232 mL, 0.196 mmol) was added. The solution was stirred at 80 ˚C for 12 h. The solution was concentrated and the residue was purified by flash chromatography (5% EtOAc/Hexanes) to afford **S6** (0.0275 g, 84% yield) as a colorless oil. $^1$H NMR [$CDCl_3$, 400 MHz] δ 7.68 (d, *J* = 6.3 Hz, 4H), 7.43–7.39 (m, 7H), 7.37–7.29 (m, 6H), 7.19 (m, 3H), 6.15 (s, 1H), 5.57 (s, 1H), 5.28 (s, 2H), 5.22 (dd, *J* = 10.9, 6.6 Hz, 1H), 5.08 (s, 2H), 4.08 (t, *J* = 8.4 Hz, 1H), 3.66–3.54 (m, 3H), 2.36–2.27 (m, 2H), 2.16 (m, 3H), 2.03 (m, 1H), 1.80 (m, 1H), 1.65 (m, 1H), 1.55–1.48 (m, 2H), 1.27 (m, 2H), 1.06 (s, 9H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.90 (m, 5H) ppm; $^{13}$C NMR [$CDCl_3$, 125 MHz] δ 165.7, 160.8,

157.3, 148.7, 137.1, 136.3, 135.7, 133.8, 129.9, 128.6, 128.5, 128.2, 128.1, 127.9, 127.8, 127.1, 109.9, 108.9, 105.3, 101.6, 99.6, 73.4, 70.8, 68.7, 66.8, 63.3, 49.4, 41.4, 36.2, 34.1, 34.0, 31.6, 27.1, 27.0, 22.7, 19.4, 14.3, 12.1 ppm (1 carbon unresolved); IR [thin film, $\nu_{max}$ $cm^{-1}$] 2932, 2863, 1728, 1613, 1435, 1265, 1180, 1103, 741, 702; HRMS (ESI+/TOF) calculated for *m/z* $C_{53}H_{60}O_7SiNa$ = 859.4006, found 859.3983.

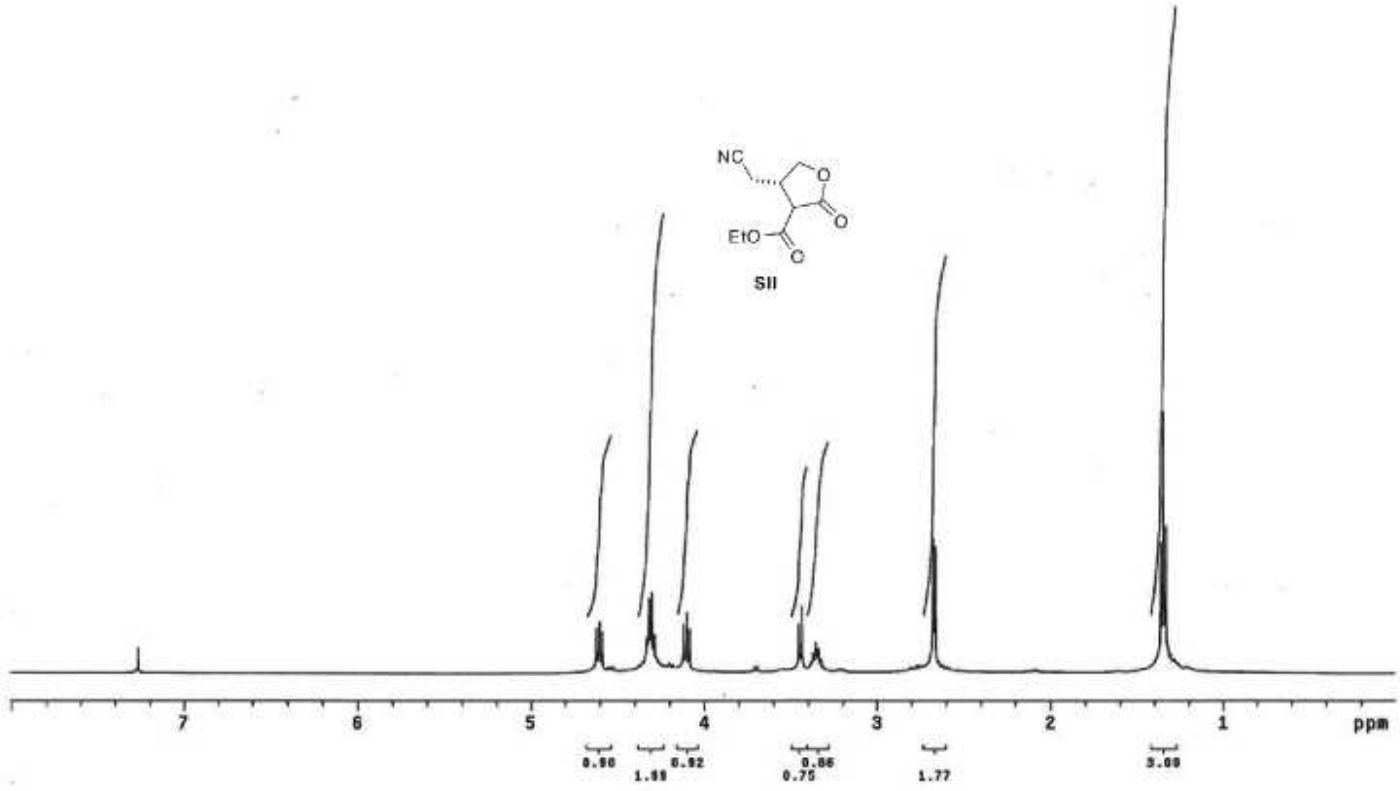



**Benzyl ester 26:** To a solution of compound **S6** (0.0203 g, 0.0242 mmol) in toluene (1.0 mL) was added Rh/C (0.0020 g, 5%). The system was pressurized to 60 psi of $H_2$ and the solution was shaken for 10 h. The solution was filtered through celite and concentrated. The crude residue was purified by column chromatography using 5% EtOAc/Hexanes as the mobile phase to afford **26** (0.0173 g, 85% yield) as a colorless oil. $^1$H NMR [$CDCl_3$, 400 MHz] δ 7.68 (d, *J* = 6.9 Hz, 4H), 7.44–7.39 (m, 8H), 7.34 (m, 7H), 7.19 (m, 2H), 6.28 (s, 1H), 5.28 (q, *J* = 12.1 Hz, 2H), 5.05 (s, 2H), 4.79 (dd, *J* = 12.7, 5.9 Hz, 1H), 4.13 (t, *J* = 8.5 Hz, 1H), 3.8 (m, 1H), 3.68–3.55 (m, 3H), 2.73 (dd, *J* = 16.6, 4.0 Hz, 1H), 2.58 (dd, *J* = 16.9, 10.8 Hz, 1H), 2.13 (dd, *J* = 12.0, 5.2 Hz, 1H) 2.04 (m, 2H), 1.95 (t, *J* = 12.3 Hz, 1H), 1.80 (m, 2H), 1.64 (m, 2H), 1.51–1.43 (m, 4H), 0.98 (m, 3H), 0.90 (m, 5H) ppm; $^{13}$C NMR [$CDCl_3$, 200 MHz] δ 166.0, 156.0, 149.3, 137.1, 136.4, 136.3, 128.6, 128.5, 128.2, 127.9, 127.2, 115.1, 109.9, 109.1, 75.6, 73.1, 70.7, 69.3, 66.9, 62.1, 49.2, 40.9, 36.6, 36.0, 34.7, 32.0, 25.4, 22.8, 21.7, 14.3, 11.8 ppm (some aromatic carbons unresolved); IR [thin film, $\nu_{max}$ $cm^{-1}$] 2924, 2855, 1728, 1597, 1435, 1273, 1103, 702; HRMS (ESI+/TOF) calculated for *m/z* $C_{53}H_{62}O_7SiNa$ = 861.4163, found 861.4133.

**III. Spectroscopic Data:**

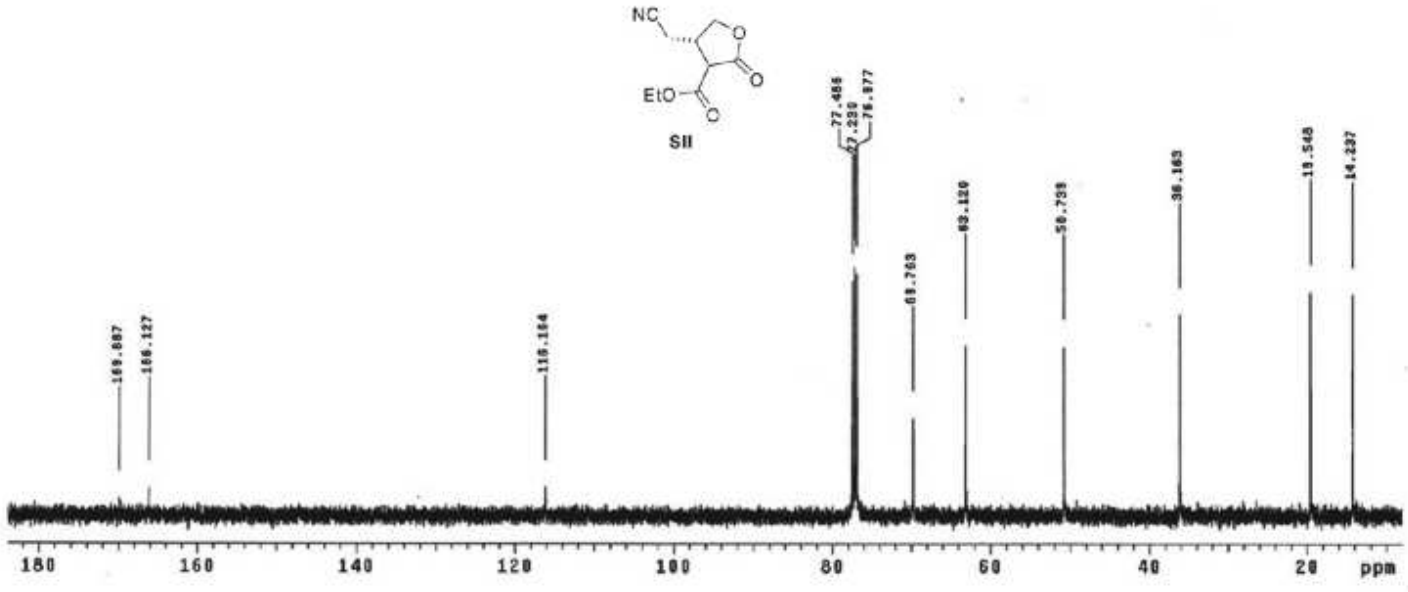
**Lactone SII:**

$^{1}$H NMR:



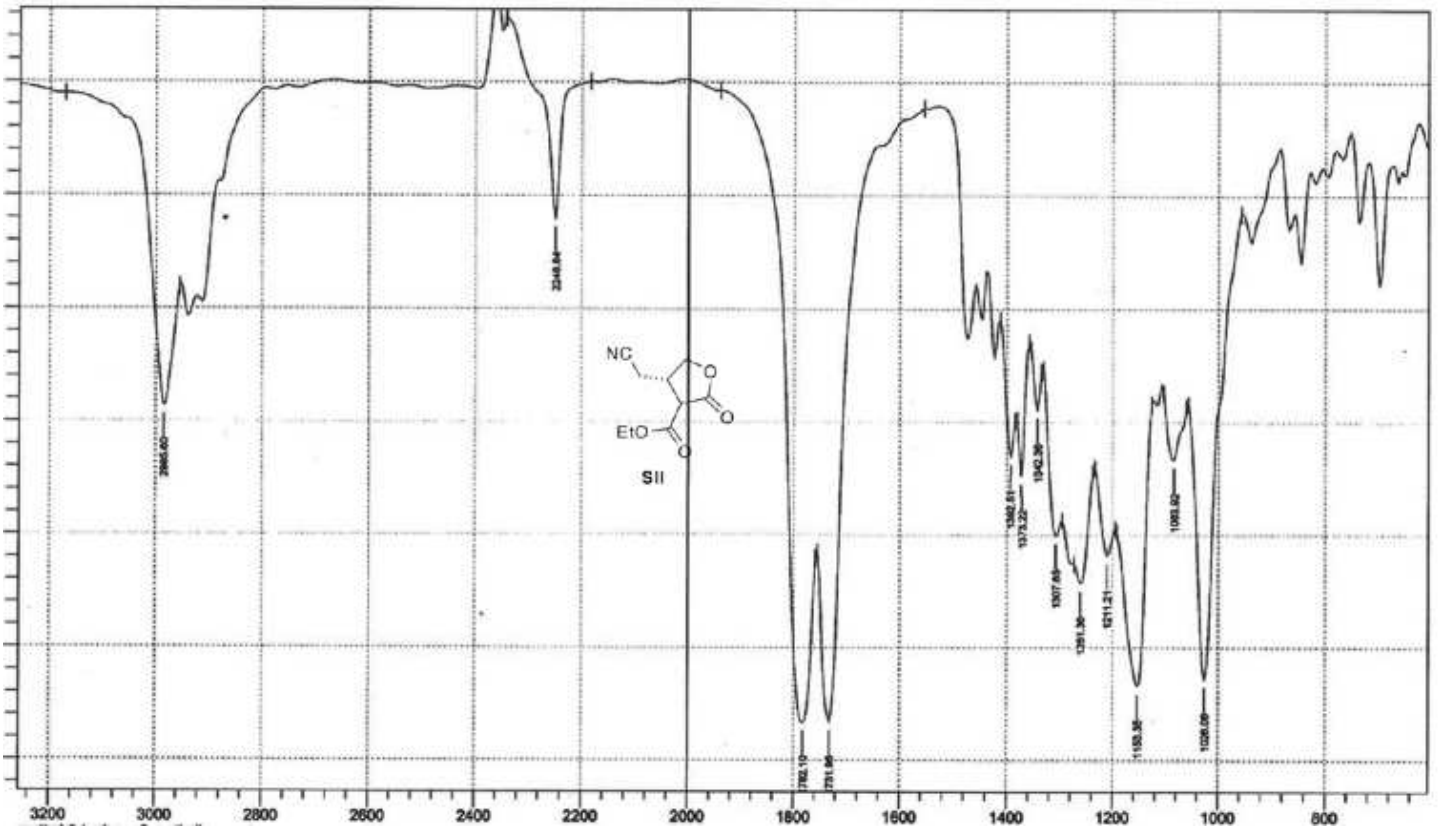
**Lactone SII:**

$^{13}$C NMR:



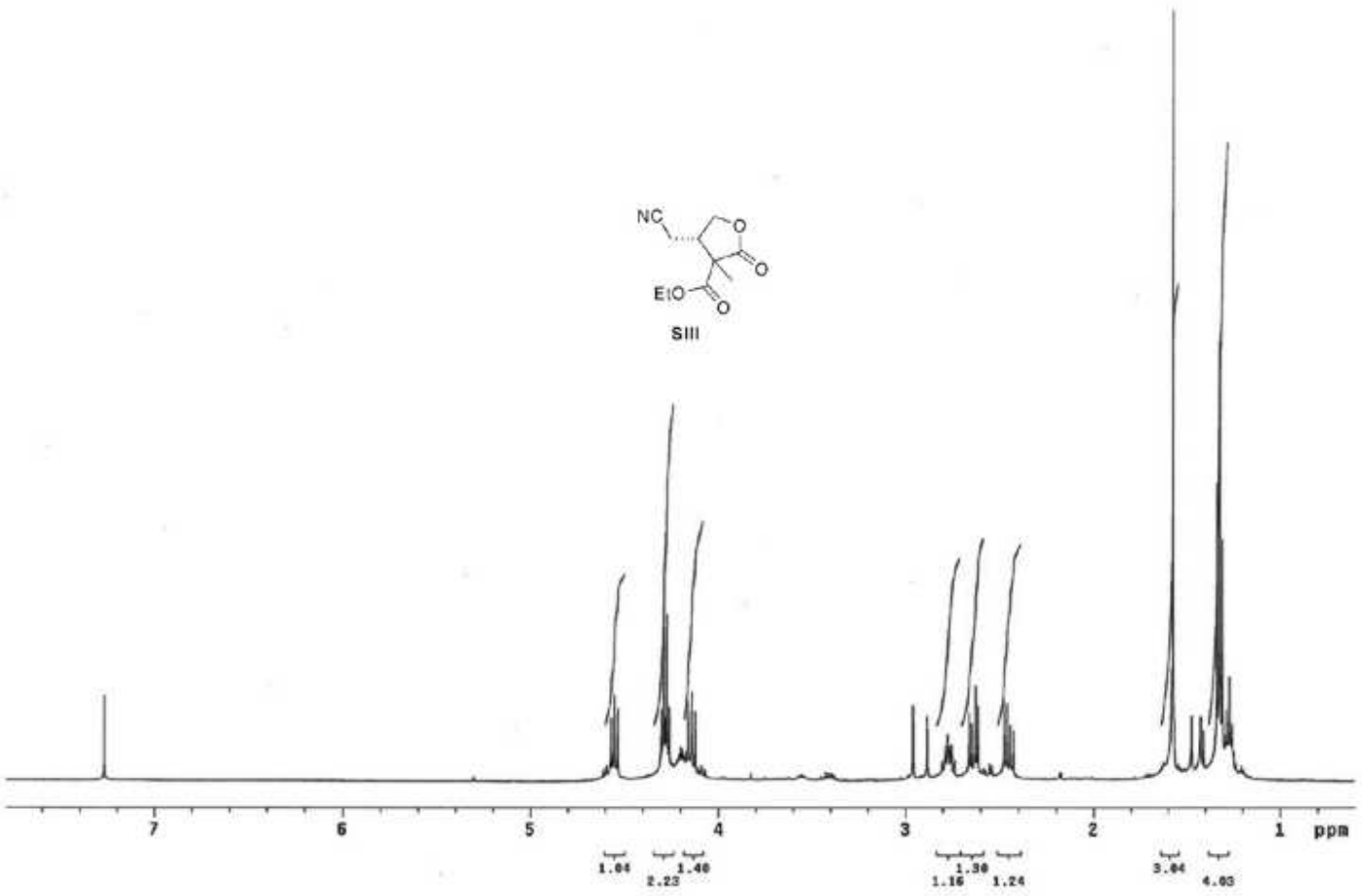
**Lactone SII:**

FTIR:



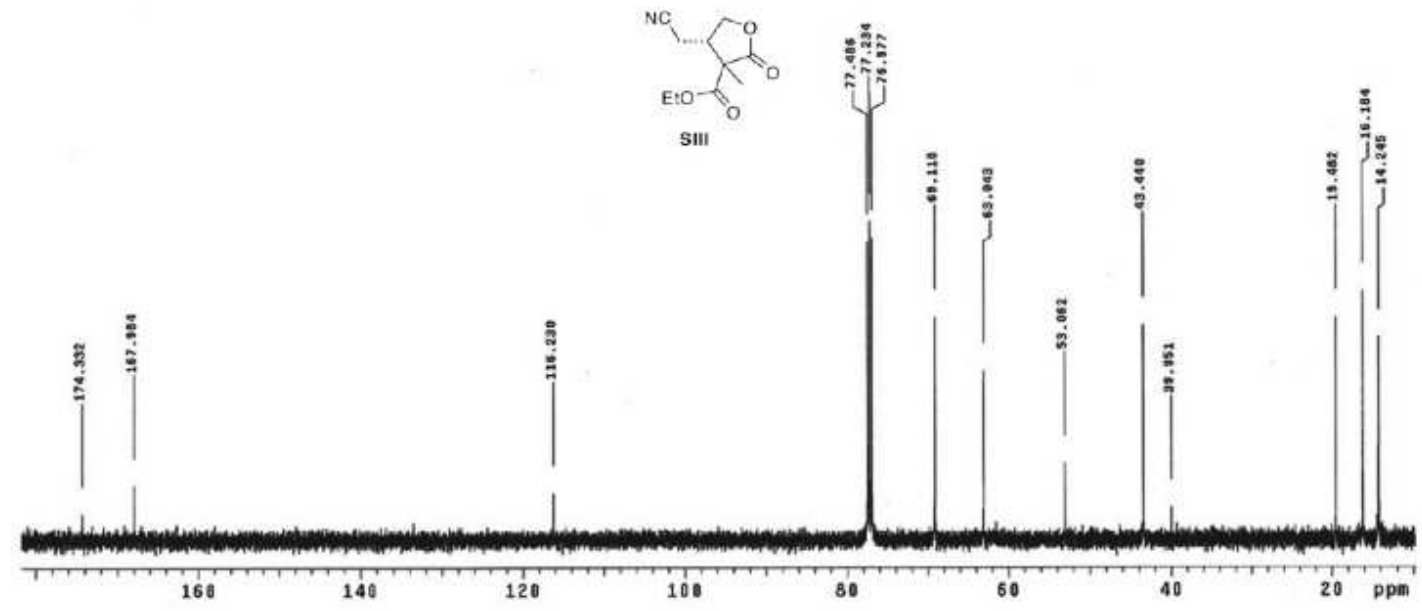
**Lactone SIII:**

$^{1}$H NMR:



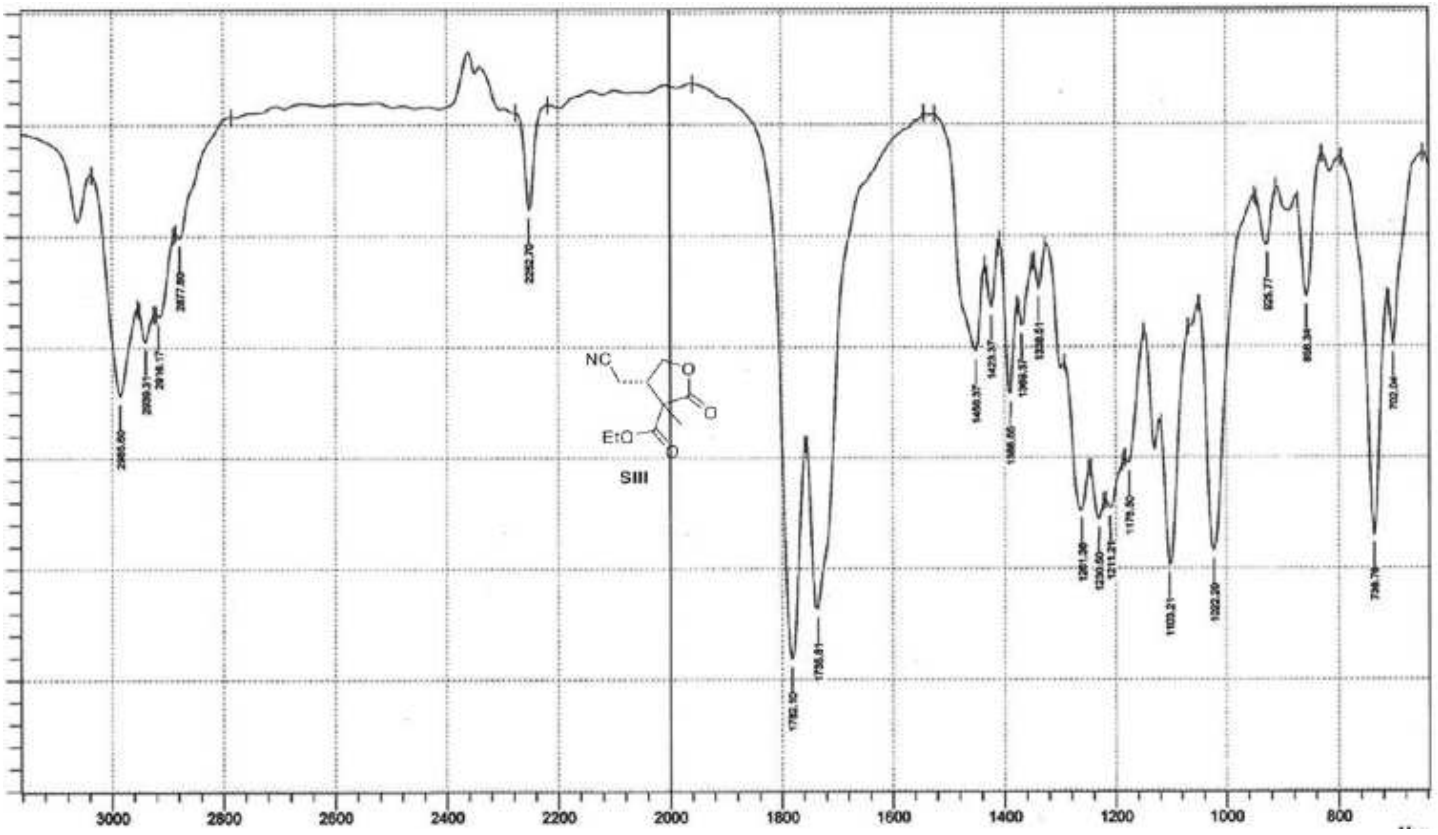
**Lactone SIII:**

$^{13}$C NMR:



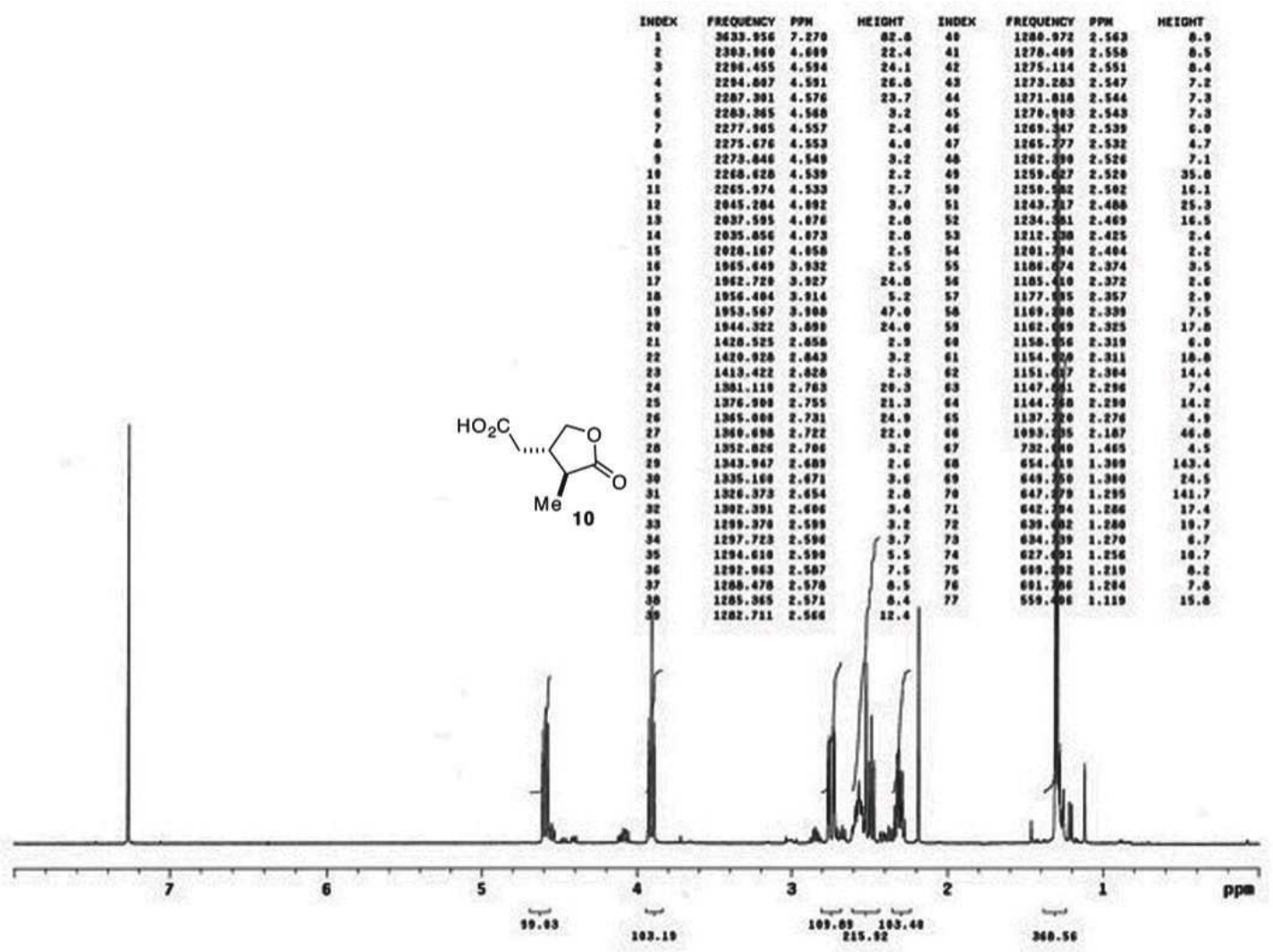
**Lactone SIII:**

FTIR:



**Lactone 10:**

$^1$H NMR

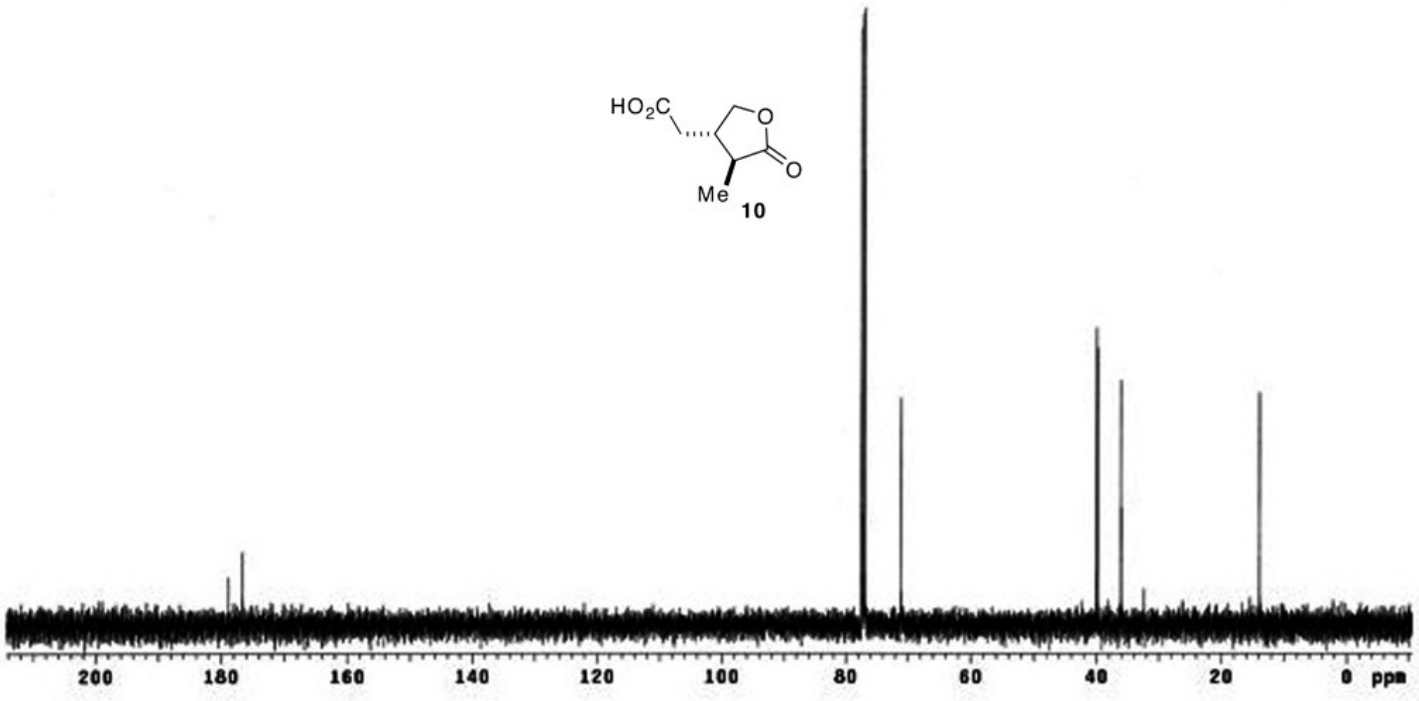



| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3633.956 | 7.270 | 82.8 | 40 | 1280.972 | 2.563 | 8.9 |
| 2 | 2303.960 | 4.609 | 22.4 | 41 | 1278.489 | 2.558 | 8.5 |
| 3 | 2298.455 | 4.594 | 24.1 | 42 | 1275.114 | 2.551 | 8.4 |
| 4 | 2294.807 | 4.591 | 26.8 | 43 | 1273.283 | 2.547 | 7.2 |
| 5 | 2287.301 | 4.576 | 23.7 | 44 | 1271.818 | 2.544 | 7.3 |
| 6 | 2283.365 | 4.568 | 3.2 | 45 | 1270.983 | 2.543 | 7.3 |
| 7 | 2277.965 | 4.557 | 2.4 | 46 | 1269.347 | 2.539 | 6.0 |
| 8 | 2275.676 | 4.553 | 4.8 | 47 | 1265.777 | 2.532 | 4.7 |
| 9 | 2273.846 | 4.549 | 3.2 | 48 | 1262.390 | 2.526 | 7.1 |
| 10 | 2268.628 | 4.539 | 2.2 | 49 | 1259.627 | 2.520 | 35.8 |
| 11 | 2265.974 | 4.533 | 2.7 | 50 | 1250.582 | 2.502 | 16.1 |
| 12 | 2045.284 | 4.092 | 3.0 | 51 | 1243.217 | 2.488 | 25.3 |
| 13 | 2037.595 | 4.076 | 2.8 | 52 | 1234.581 | 2.469 | 16.5 |
| 14 | 2035.856 | 4.073 | 2.8 | 53 | 1212.298 | 2.425 | 2.4 |
| 15 | 2028.167 | 4.058 | 2.5 | 54 | 1201.794 | 2.404 | 2.2 |
| 16 | 1965.649 | 3.932 | 2.5 | 55 | 1186.674 | 2.374 | 3.5 |
| 17 | 1962.729 | 3.927 | 24.8 | 56 | 1185.410 | 2.372 | 2.6 |
| 18 | 1956.404 | 3.914 | 5.2 | 57 | 1177.695 | 2.357 | 2.9 |
| 19 | 1953.567 | 3.908 | 47.0 | 58 | 1169.298 | 2.339 | 7.5 |
| 20 | 1944.322 | 3.889 | 24.0 | 59 | 1162.669 | 2.325 | 17.8 |
| 21 | 1428.525 | 2.858 | 2.9 | 60 | 1158.656 | 2.319 | 6.0 |
| 22 | 1420.928 | 2.843 | 3.2 | 61 | 1154.920 | 2.311 | 18.8 |
| 23 | 1413.422 | 2.828 | 2.3 | 62 | 1151.637 | 2.304 | 14.4 |
| 24 | 1381.119 | 2.763 | 20.3 | 63 | 1147.681 | 2.296 | 7.4 |
| 25 | 1376.900 | 2.755 | 21.3 | 64 | 1144.288 | 2.290 | 14.2 |
| 26 | 1365.088 | 2.731 | 24.9 | 65 | 1137.720 | 2.276 | 4.9 |
| 27 | 1360.698 | 2.722 | 22.0 | 66 | 1093.295 | 2.187 | 46.8 |
| 28 | 1352.826 | 2.706 | 3.2 | 67 | 732.640 | 1.465 | 4.5 |
| 29 | 1343.947 | 2.689 | 2.6 | 68 | 654.419 | 1.309 | 143.4 |
| 30 | 1335.168 | 2.671 | 3.6 | 69 | 649.750 | 1.300 | 24.5 |
| 31 | 1326.373 | 2.654 | 2.8 | 70 | 647.279 | 1.295 | 141.7 |
| 32 | 1302.391 | 2.606 | 3.4 | 71 | 642.794 | 1.286 | 17.4 |
| 33 | 1299.376 | 2.599 | 3.2 | 72 | 639.602 | 1.280 | 19.7 |
| 34 | 1297.723 | 2.596 | 3.7 | 73 | 634.739 | 1.270 | 6.7 |
| 35 | 1294.618 | 2.590 | 5.5 | 74 | 627.691 | 1.256 | 18.7 |
| 36 | 1292.963 | 2.587 | 7.5 | 75 | 609.292 | 1.219 | 8.2 |
| 37 | 1288.478 | 2.578 | 8.5 | 76 | 601.706 | 1.204 | 7.8 |
| 38 | 1285.365 | 2.571 | 8.4 | 77 | 559.496 | 1.119 | 15.8 |
| 39 | 1282.711 | 2.566 | 12.4 | | | | |

**Lactone 10:**

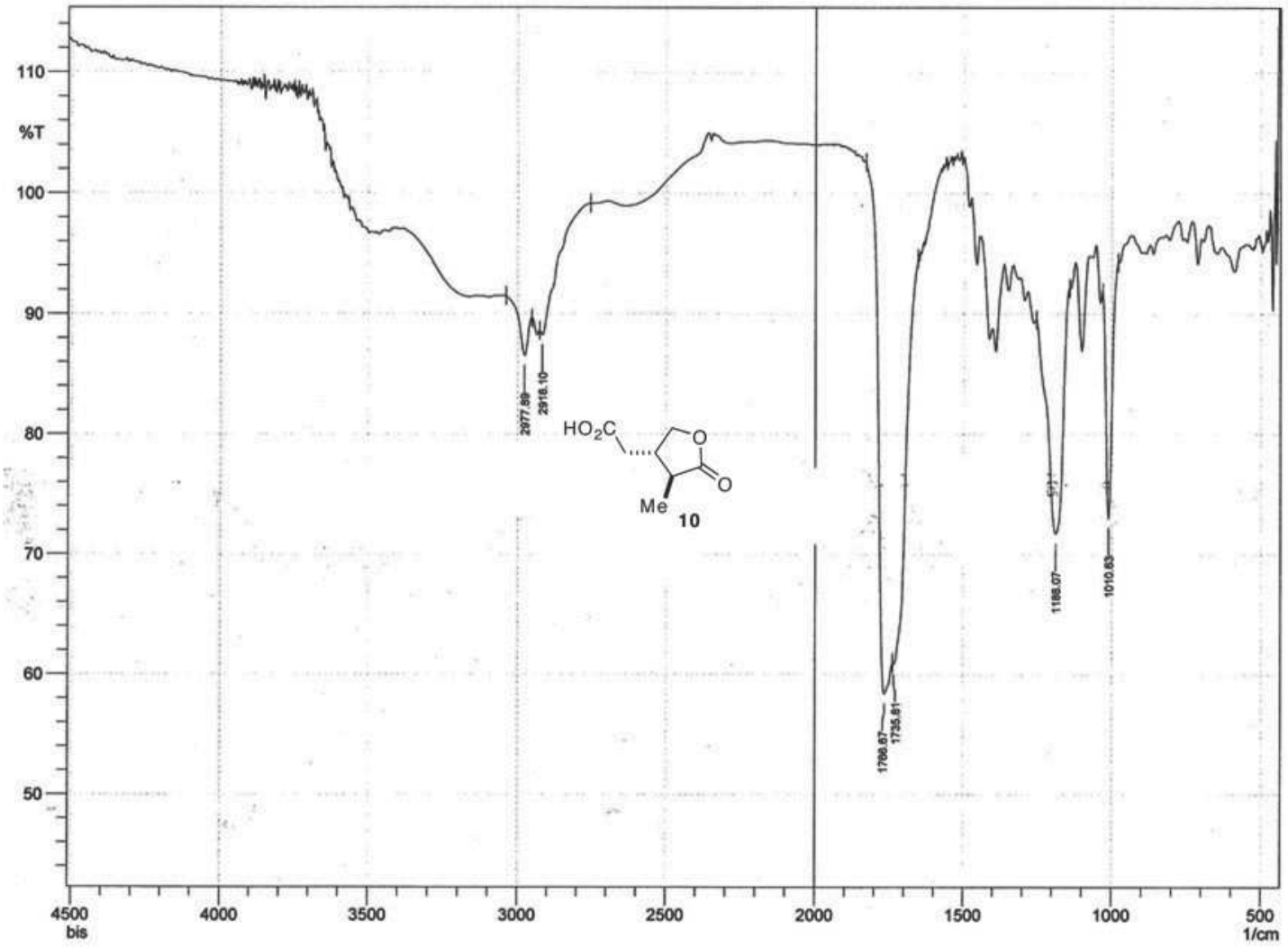
$^{13}$C NMR

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 22481.437 | 178.866 | 8.5 |
| 2 | 22201.594 | 176.639 | 12.9 |
| 3 | 9738.866 | 77.484 | 105.0 |
| 4 | 9706.958 | 77.230 | 107.5 |
| 5 | 9674.619 | 76.973 | 108.5 |
| 6 | 8929.520 | 71.045 | 40.0 |
| 7 | 5025.512 | 39.984 | 52.4 |
| 8 | 5000.503 | 39.785 | 48.8 |
| 9 | 4533.891 | 36.066 | 43.1 |
| 10 | 1747.594 | 13.904 | 41.0 |



**Lactone 10:**

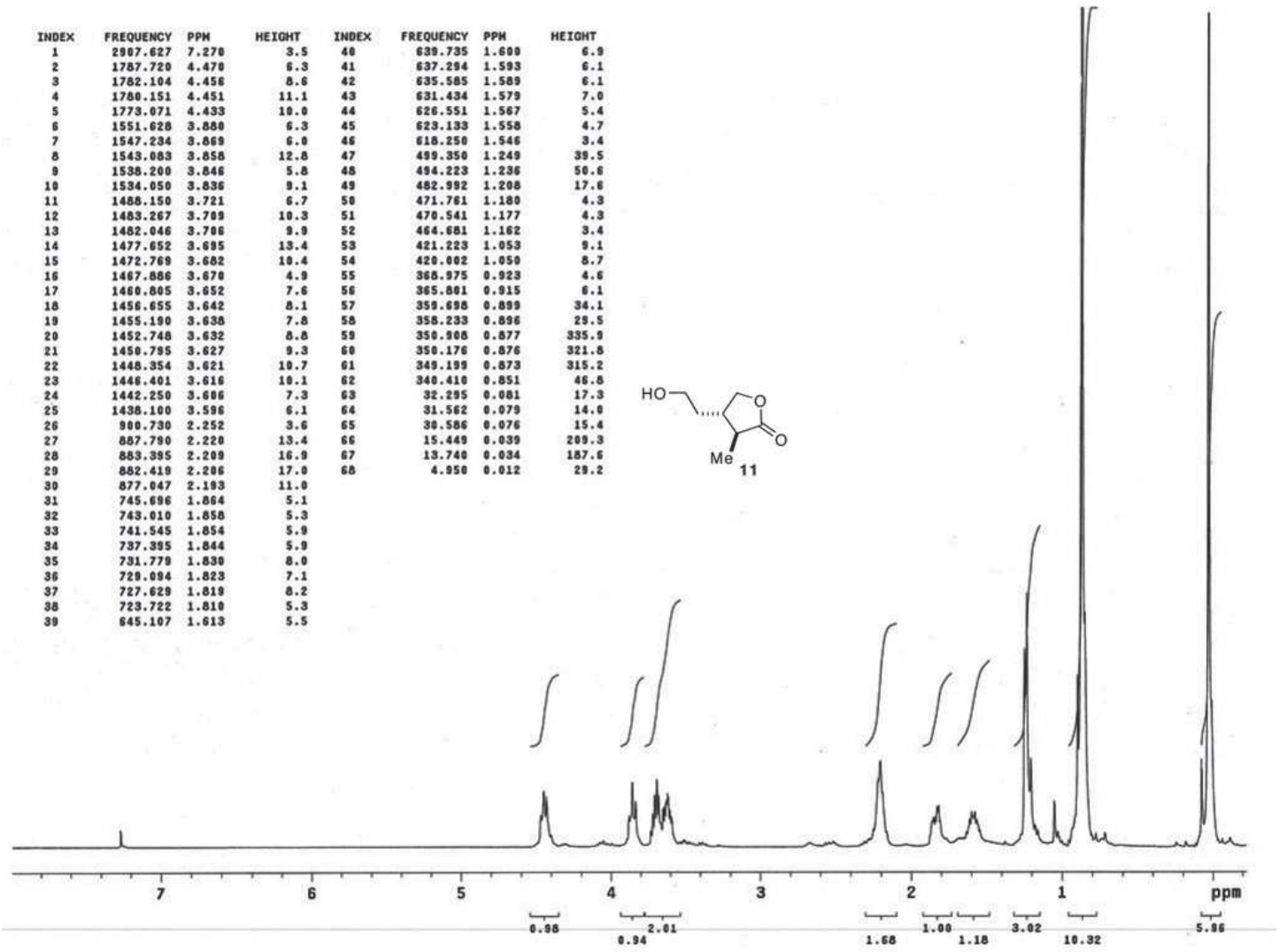
FTIR



**Alcohol 11:**

$^{1}$H NMR

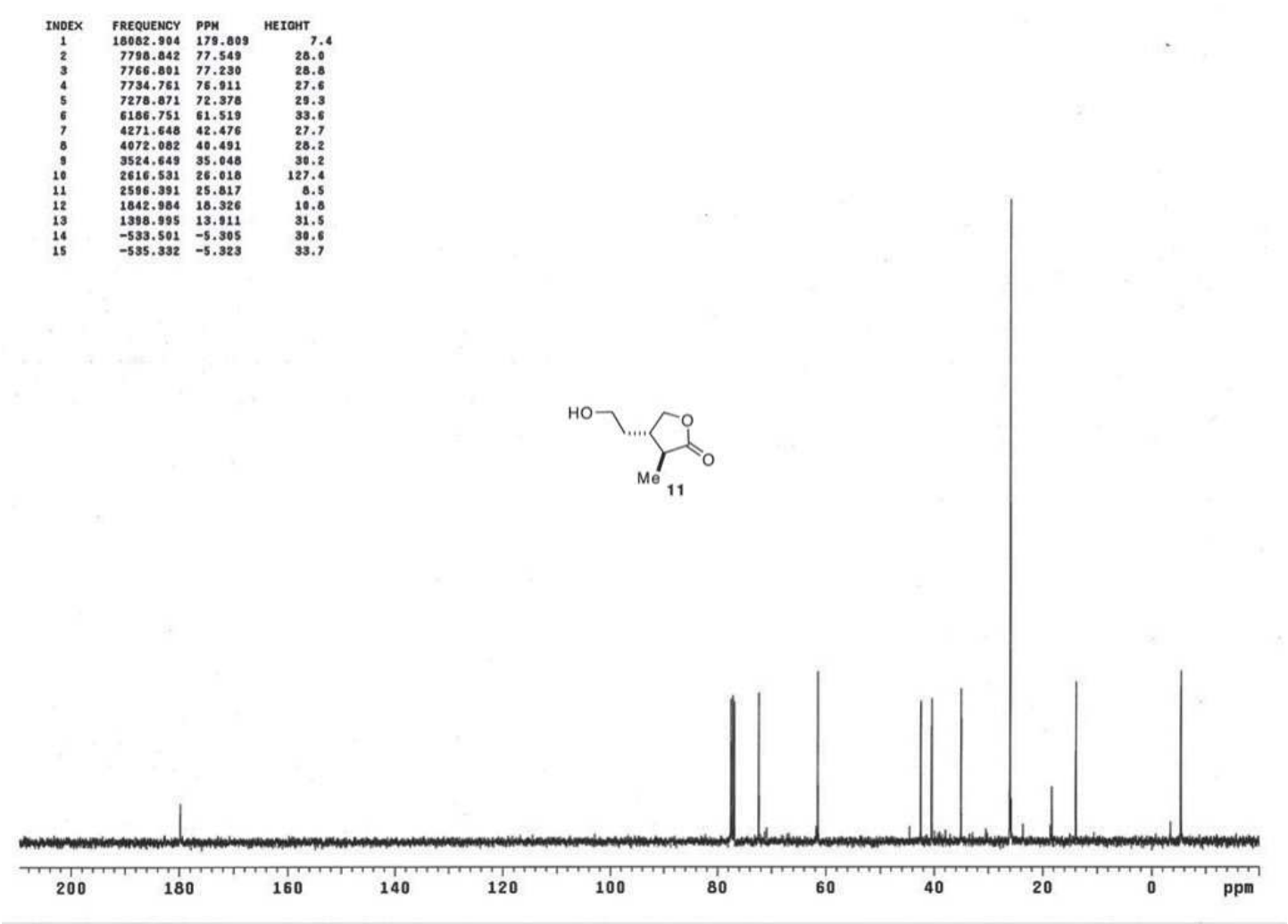
| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 2907.627 | 7.270 | 3.5 | 40 | 639.735 | 1.600 | 6.9 |
| 2 | 1787.720 | 4.470 | 6.3 | 41 | 637.294 | 1.593 | 6.1 |
| 3 | 1782.104 | 4.456 | 8.6 | 42 | 635.585 | 1.589 | 6.1 |
| 4 | 1780.151 | 4.451 | 11.1 | 43 | 631.434 | 1.579 | 7.0 |
| 5 | 1773.071 | 4.433 | 10.0 | 44 | 626.551 | 1.567 | 5.4 |
| 6 | 1551.628 | 3.880 | 6.3 | 45 | 623.133 | 1.558 | 4.7 |
| 7 | 1547.234 | 3.869 | 6.0 | 46 | 618.250 | 1.546 | 3.4 |
| 8 | 1543.083 | 3.858 | 12.8 | 47 | 499.350 | 1.249 | 39.5 |
| 9 | 1538.200 | 3.846 | 5.8 | 48 | 494.223 | 1.236 | 50.6 |
| 10 | 1534.050 | 3.836 | 9.1 | 49 | 482.992 | 1.208 | 17.6 |
| 11 | 1488.150 | 3.721 | 6.7 | 50 | 471.761 | 1.180 | 4.3 |
| 12 | 1483.267 | 3.709 | 10.3 | 51 | 470.541 | 1.177 | 4.3 |
| 13 | 1482.046 | 3.706 | 9.9 | 52 | 464.681 | 1.162 | 3.4 |
| 14 | 1477.652 | 3.695 | 13.4 | 53 | 421.223 | 1.053 | 9.1 |
| 15 | 1472.769 | 3.682 | 10.4 | 54 | 420.002 | 1.050 | 8.7 |
| 16 | 1467.886 | 3.670 | 4.9 | 55 | 368.975 | 0.923 | 4.6 |
| 17 | 1460.805 | 3.652 | 7.6 | 56 | 365.801 | 0.915 | 6.1 |
| 18 | 1456.655 | 3.642 | 8.1 | 57 | 359.698 | 0.899 | 34.1 |
| 19 | 1455.190 | 3.638 | 7.8 | 58 | 358.233 | 0.896 | 29.5 |
| 20 | 1452.748 | 3.632 | 8.8 | 59 | 350.906 | 0.877 | 335.9 |
| 21 | 1450.795 | 3.627 | 9.3 | 60 | 350.176 | 0.876 | 321.8 |
| 22 | 1448.354 | 3.621 | 10.7 | 61 | 349.199 | 0.873 | 315.2 |
| 23 | 1446.401 | 3.616 | 10.1 | 62 | 340.410 | 0.851 | 46.8 |
| 24 | 1442.250 | 3.606 | 7.3 | 63 | 32.295 | 0.081 | 17.3 |
| 25 | 1438.100 | 3.596 | 6.1 | 64 | 31.562 | 0.079 | 14.0 |
| 26 | 900.730 | 2.252 | 3.6 | 65 | 30.586 | 0.076 | 15.4 |
| 27 | 887.790 | 2.220 | 13.4 | 66 | 15.449 | 0.039 | 209.3 |
| 28 | 883.395 | 2.209 | 16.9 | 67 | 13.740 | 0.034 | 187.6 |
| 29 | 882.419 | 2.206 | 17.0 | 68 | 4.950 | 0.012 | 29.2 |
| 30 | 877.047 | 2.193 | 11.0 | | | | |
| 31 | 745.696 | 1.864 | 5.1 | | | | |
| 32 | 743.010 | 1.858 | 5.3 | | | | |
| 33 | 741.545 | 1.854 | 5.9 | | | | |
| 34 | 737.395 | 1.844 | 5.9 | | | | |
| 35 | 731.779 | 1.830 | 8.0 | | | | |
| 36 | 729.094 | 1.823 | 7.1 | | | | |
| 37 | 727.629 | 1.819 | 8.2 | | | | |
| 38 | 723.722 | 1.810 | 5.3 | | | | |
| 39 | 645.107 | 1.613 | 5.5 | | | | |



**Alcohol 11:**

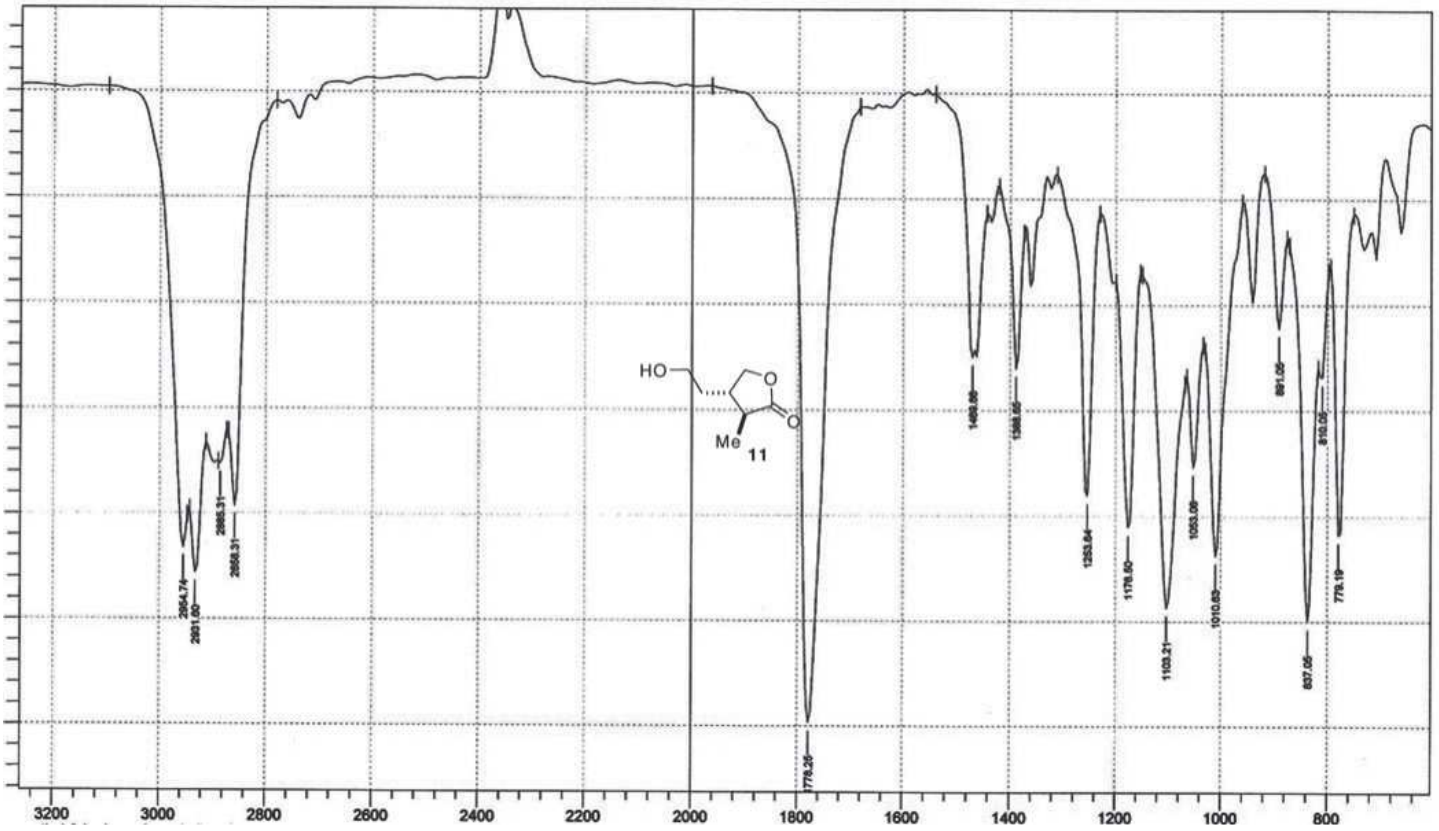
$^{13}$C NMR

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 18082.904 | 179.809 | 7.4 |
| 2 | 7798.842 | 77.549 | 28.0 |
| 3 | 7766.801 | 77.230 | 28.8 |
| 4 | 7734.761 | 76.911 | 27.6 |
| 5 | 7278.871 | 72.378 | 29.3 |
| 6 | 6186.751 | 61.519 | 33.6 |
| 7 | 4271.648 | 42.476 | 27.7 |
| 8 | 4072.082 | 40.491 | 28.2 |
| 9 | 3524.649 | 35.048 | 30.2 |
| 10 | 2616.531 | 26.018 | 127.4 |
| 11 | 2596.391 | 25.817 | 8.5 |
| 12 | 1842.984 | 18.326 | 10.8 |
| 13 | 1398.995 | 13.911 | 31.5 |
| 14 | -533.501 | -5.305 | 30.6 |
| 15 | -535.332 | -5.323 | 33.7 |



**Alcohol 11:**

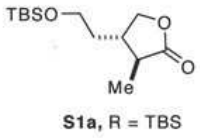
FTIR



**Lactone S1a:**

$^{1}$H NMR

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 2907.627 | 7.270 | 3.5 | 40 | 639.735 | 1.600 | 6.9 |
| 2 | 1787.720 | 4.470 | 6.3 | 41 | 637.294 | 1.593 | 6.1 |
| 3 | 1782.104 | 4.456 | 8.6 | 42 | 635.585 | 1.589 | 6.1 |
| 4 | 1780.151 | 4.451 | 11.1 | 43 | 631.434 | 1.579 | 7.0 |
| 5 | 1773.071 | 4.433 | 10.0 | 44 | 626.551 | 1.567 | 5.4 |
| 6 | 1551.628 | 3.880 | 6.3 | 45 | 623.133 | 1.558 | 4.7 |
| 7 | 1547.234 | 3.869 | 6.0 | 46 | 618.250 | 1.546 | 3.4 |
| 8 | 1543.083 | 3.858 | 12.8 | 47 | 499.350 | 1.249 | 39.5 |
| 9 | 1538.200 | 3.846 | 5.8 | 48 | 494.223 | 1.236 | 50.6 |
| 10 | 1534.050 | 3.836 | 9.1 | 49 | 482.992 | 1.208 | 17.6 |
| 11 | 1488.150 | 3.721 | 6.7 | 50 | 471.761 | 1.180 | 4.3 |
| 12 | 1483.267 | 3.709 | 10.3 | 51 | 470.541 | 1.177 | 4.3 |
| 13 | 1482.046 | 3.706 | 9.9 | 52 | 464.681 | 1.162 | 3.4 |
| 14 | 1477.652 | 3.695 | 13.4 | 53 | 421.223 | 1.053 | 9.1 |
| 15 | 1472.769 | 3.682 | 10.4 | 54 | 420.002 | 1.050 | 8.7 |
| 16 | 1467.886 | 3.670 | 4.9 | 55 | 368.975 | 0.923 | 4.6 |
| 17 | 1460.805 | 3.652 | 7.6 | 56 | 365.801 | 0.915 | 6.1 |
| 18 | 1456.655 | 3.642 | 8.1 | 57 | 359.698 | 0.899 | 34.1 |
| 19 | 1455.190 | 3.638 | 7.8 | 58 | 358.233 | 0.896 | 29.5 |
| 20 | 1452.748 | 3.632 | 8.8 | 59 | 356.908 | 0.877 | 335.9 |
| 21 | 1450.795 | 3.627 | 9.3 | 60 | 350.176 | 0.876 | 321.8 |
| 22 | 1448.354 | 3.621 | 10.7 | 61 | 349.199 | 0.873 | 315.2 |
| 23 | 1446.401 | 3.616 | 10.1 | 62 | 340.416 | 0.851 | 46.6 |
| 24 | 1442.250 | 3.606 | 7.3 | 63 | 32.295 | 0.081 | 17.3 |
| 25 | 1438.100 | 3.596 | 6.1 | 64 | 31.562 | 0.079 | 14.0 |
| 26 | 900.730 | 2.252 | 3.6 | 65 | 30.586 | 0.076 | 15.4 |
| 27 | 887.790 | 2.220 | 13.4 | 66 | 15.449 | 0.039 | 289.3 |
| 28 | 883.395 | 2.209 | 16.9 | 67 | 13.740 | 0.034 | 187.6 |
| 29 | 882.419 | 2.206 | 17.0 | 68 | 4.950 | 0.012 | 29.2 |
| 30 | 877.047 | 2.193 | 11.0 | | | | |
| 31 | 745.696 | 1.864 | 5.1 | | | | |
| 32 | 743.010 | 1.858 | 5.3 | | | | |
| 33 | 741.545 | 1.854 | 5.9 | | | | |
| 34 | 737.395 | 1.844 | 5.9 | | | | |
| 35 | 731.779 | 1.830 | 8.0 | | | | |
| 36 | 729.094 | 1.823 | 7.1 | | | | |
| 37 | 727.629 | 1.819 | 8.2 | | | | |
| 38 | 723.722 | 1.810 | 5.3 | | | | |
| 39 | 645.107 | 1.613 | 5.5 | | | | |

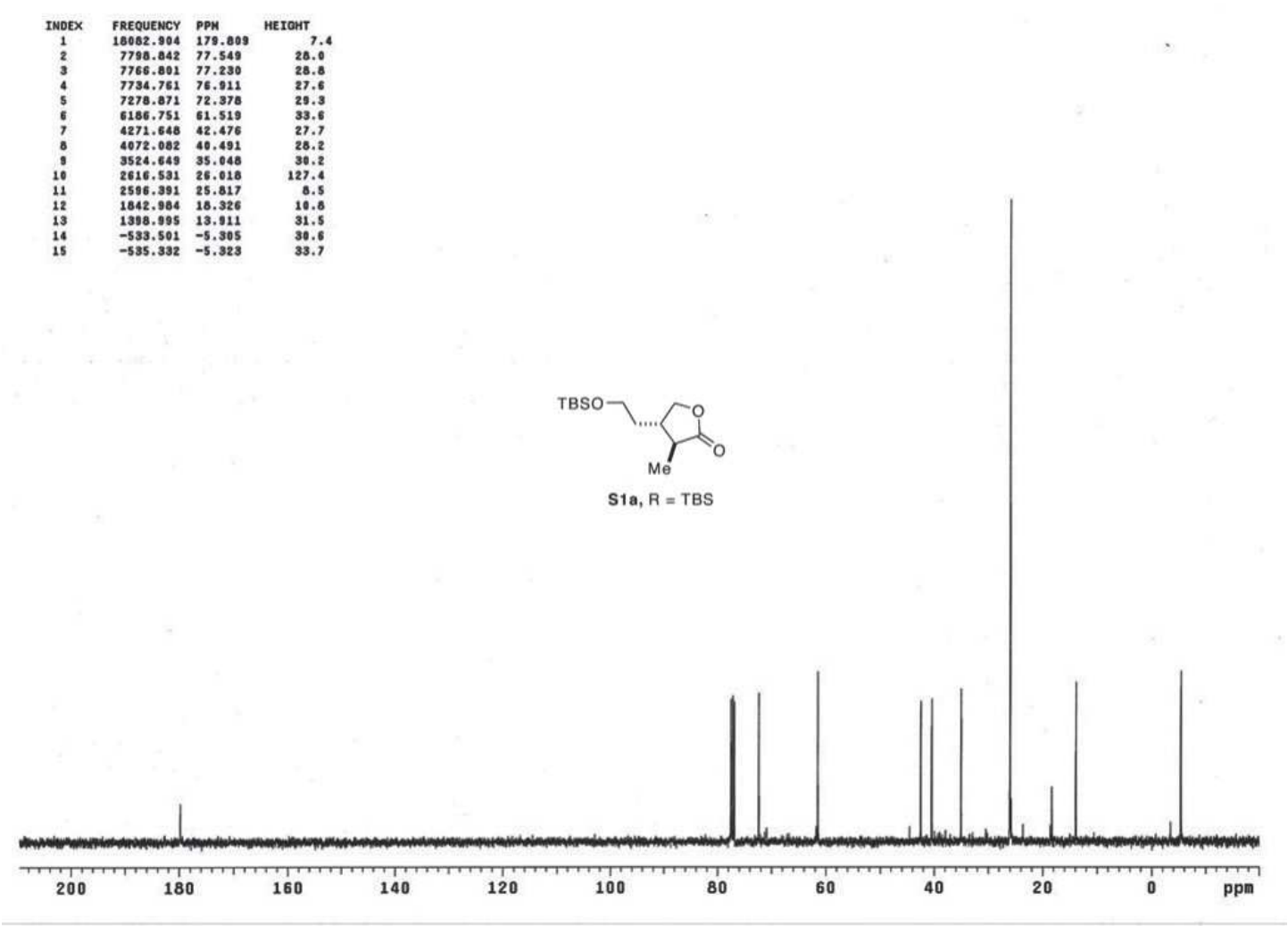



**S1a**, R = TBS

**Lactone S1a:**

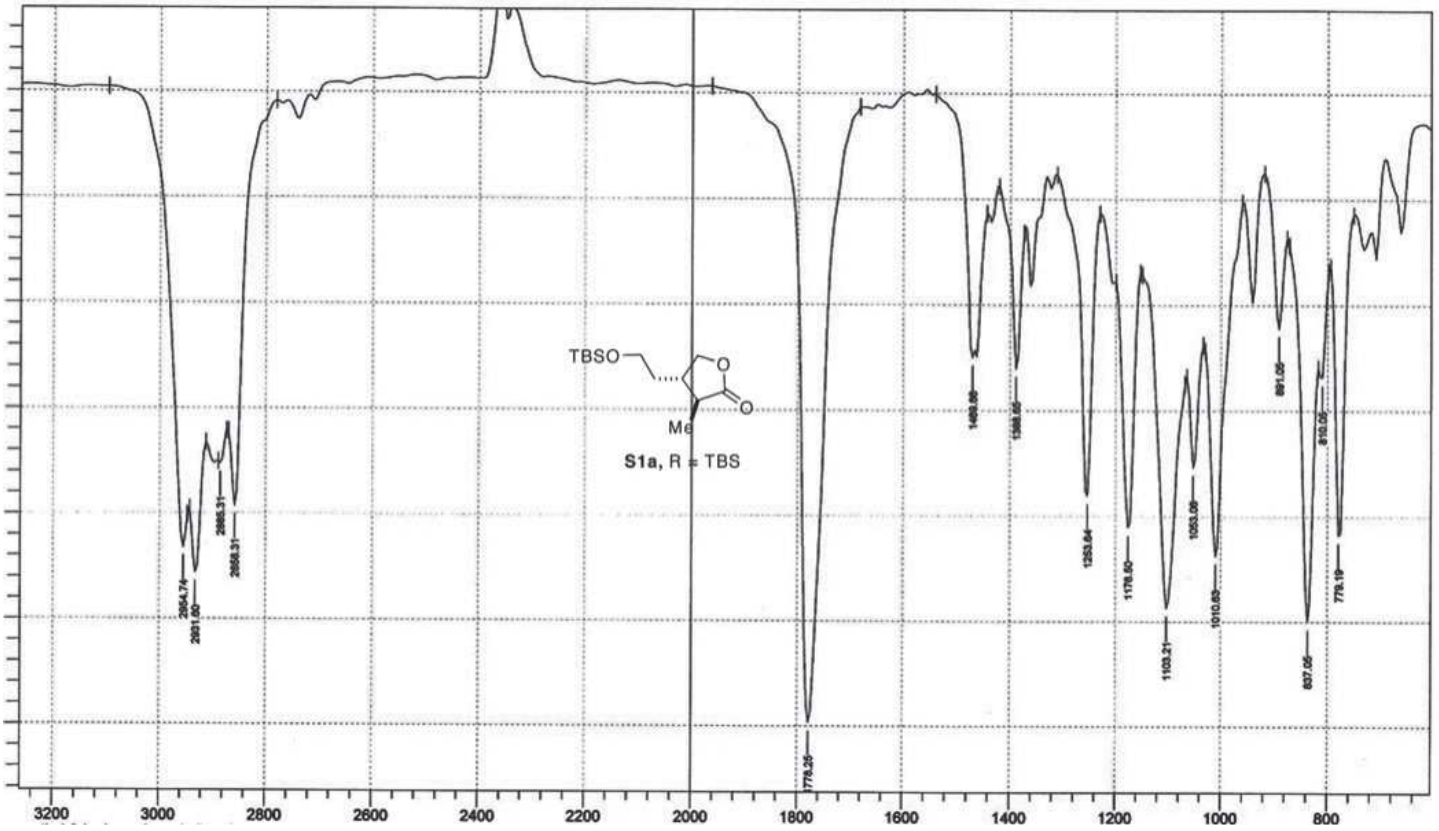
$^{13}$C NMR

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 18082.904 | 179.809 | 7.4 |
| 2 | 7798.842 | 77.549 | 28.0 |
| 3 | 7766.801 | 77.230 | 28.8 |
| 4 | 7734.761 | 76.911 | 27.6 |
| 5 | 7278.871 | 72.378 | 29.3 |
| 6 | 6186.751 | 61.519 | 33.6 |
| 7 | 4271.648 | 42.476 | 27.7 |
| 8 | 4072.082 | 40.491 | 28.2 |
| 9 | 3524.649 | 35.048 | 30.2 |
| 10 | 2616.531 | 26.018 | 127.4 |
| 11 | 2596.391 | 25.817 | 8.5 |
| 12 | 1842.984 | 18.326 | 10.8 |
| 13 | 1398.995 | 13.911 | 31.5 |
| 14 | -533.501 | -5.305 | 30.6 |
| 15 | -535.332 | -5.323 | 33.7 |



**Lactone S1a:**

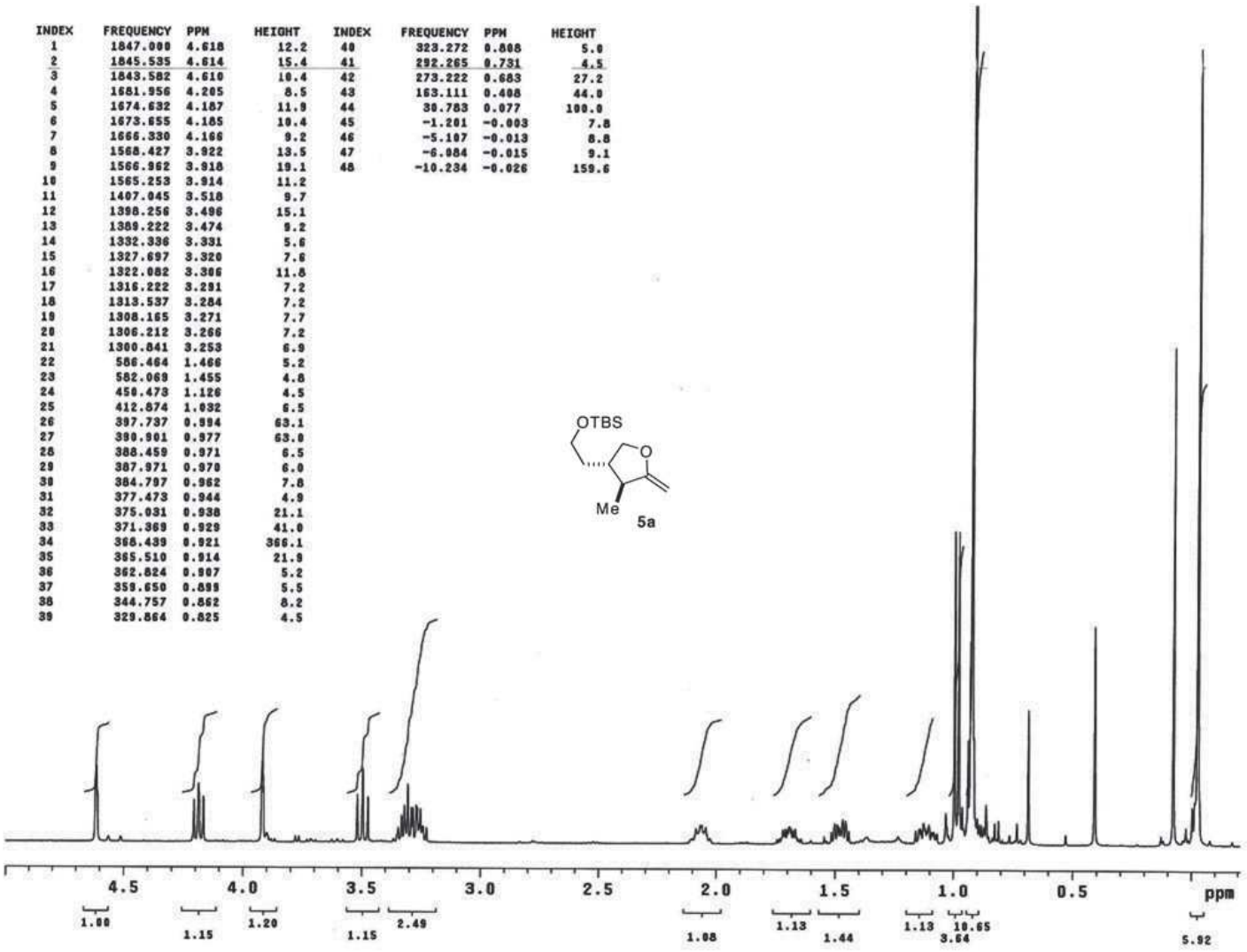
FTIR



**Enol ether 5a:**

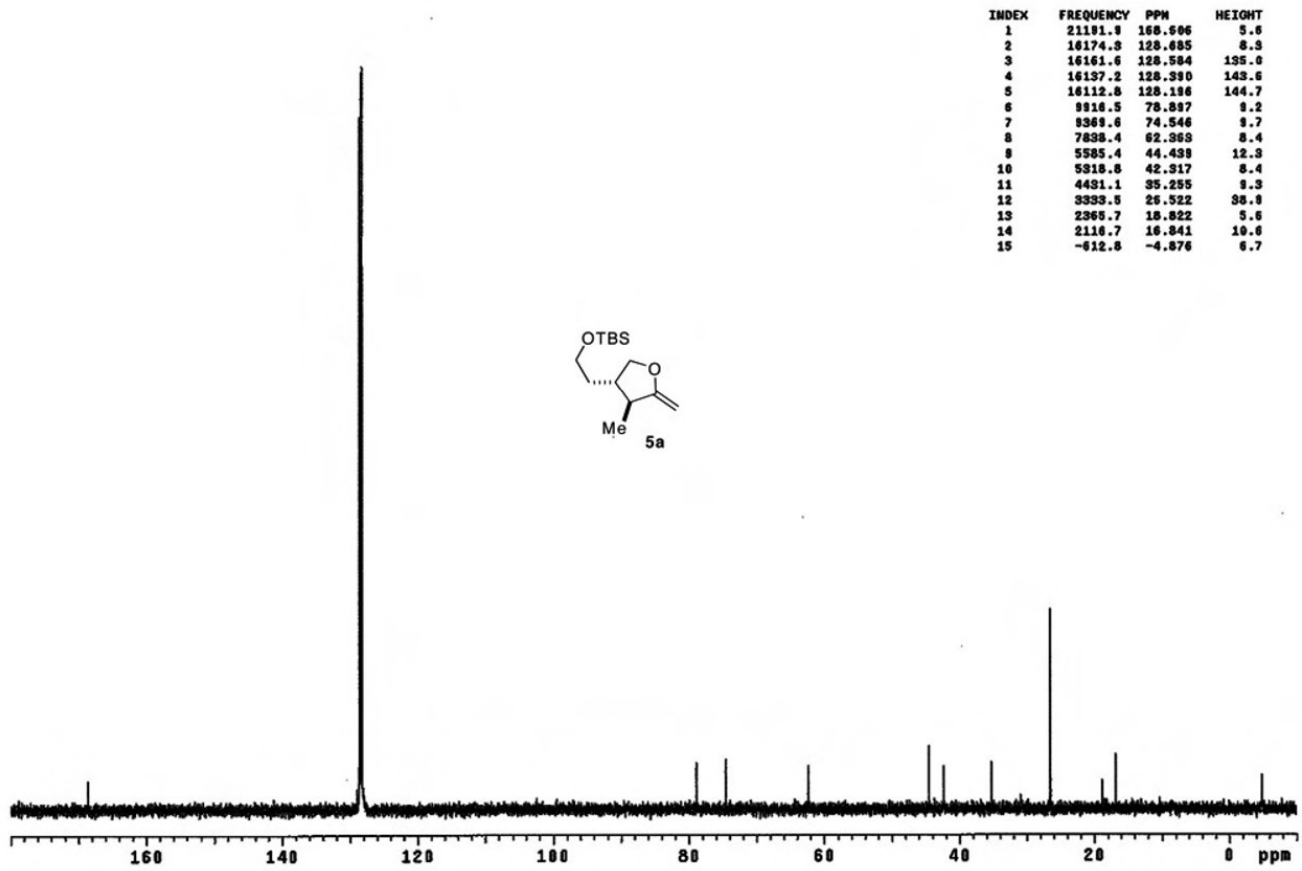
$^{1}$H NMR

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 1847.008 | 4.618 | 12.2 | 40 | 323.272 | 0.808 | 5.0 |
| 2 | 1845.535 | 4.614 | 15.4 | 41 | 292.265 | 0.731 | 4.5 |
| 3 | 1843.582 | 4.610 | 10.4 | 42 | 273.222 | 0.683 | 27.2 |
| 4 | 1681.956 | 4.205 | 8.5 | 43 | 163.111 | 0.408 | 44.0 |
| 5 | 1674.632 | 4.187 | 11.9 | 44 | 30.783 | 0.077 | 100.0 |
| 6 | 1673.655 | 4.185 | 10.4 | 45 | -1.201 | -0.003 | 7.8 |
| 7 | 1666.330 | 4.166 | 9.2 | 46 | -5.107 | -0.013 | 8.8 |
| 8 | 1568.427 | 3.922 | 13.5 | 47 | -6.084 | -0.015 | 9.1 |
| 9 | 1566.962 | 3.918 | 19.1 | 48 | -10.234 | -0.026 | 159.6 |
| 10 | 1565.253 | 3.914 | 11.2 | | | | |
| 11 | 1407.045 | 3.518 | 9.7 | | | | |
| 12 | 1398.256 | 3.496 | 15.1 | | | | |
| 13 | 1389.222 | 3.474 | 9.2 | | | | |
| 14 | 1332.336 | 3.331 | 5.6 | | | | |
| 15 | 1327.697 | 3.320 | 7.6 | | | | |
| 16 | 1322.082 | 3.306 | 11.8 | | | | |
| 17 | 1316.222 | 3.291 | 7.2 | | | | |
| 18 | 1313.537 | 3.284 | 7.2 | | | | |
| 19 | 1308.165 | 3.271 | 7.7 | | | | |
| 20 | 1306.212 | 3.266 | 7.2 | | | | |
| 21 | 1300.841 | 3.253 | 6.9 | | | | |
| 22 | 586.464 | 1.466 | 5.2 | | | | |
| 23 | 582.069 | 1.455 | 4.8 | | | | |
| 24 | 450.473 | 1.126 | 4.5 | | | | |
| 25 | 412.874 | 1.032 | 6.5 | | | | |
| 26 | 397.737 | 0.994 | 63.1 | | | | |
| 27 | 390.901 | 0.977 | 63.0 | | | | |
| 28 | 388.459 | 0.971 | 6.5 | | | | |
| 29 | 387.971 | 0.970 | 6.0 | | | | |
| 30 | 384.797 | 0.962 | 7.8 | | | | |
| 31 | 377.473 | 0.944 | 4.9 | | | | |
| 32 | 375.031 | 0.938 | 21.1 | | | | |
| 33 | 371.369 | 0.929 | 41.0 | | | | |
| 34 | 368.439 | 0.921 | 366.1 | | | | |
| 35 | 365.510 | 0.914 | 21.9 | | | | |
| 36 | 362.824 | 0.907 | 5.2 | | | | |
| 37 | 359.650 | 0.899 | 5.5 | | | | |
| 38 | 344.757 | 0.862 | 8.2 | | | | |
| 39 | 329.864 | 0.825 | 4.5 | | | | |



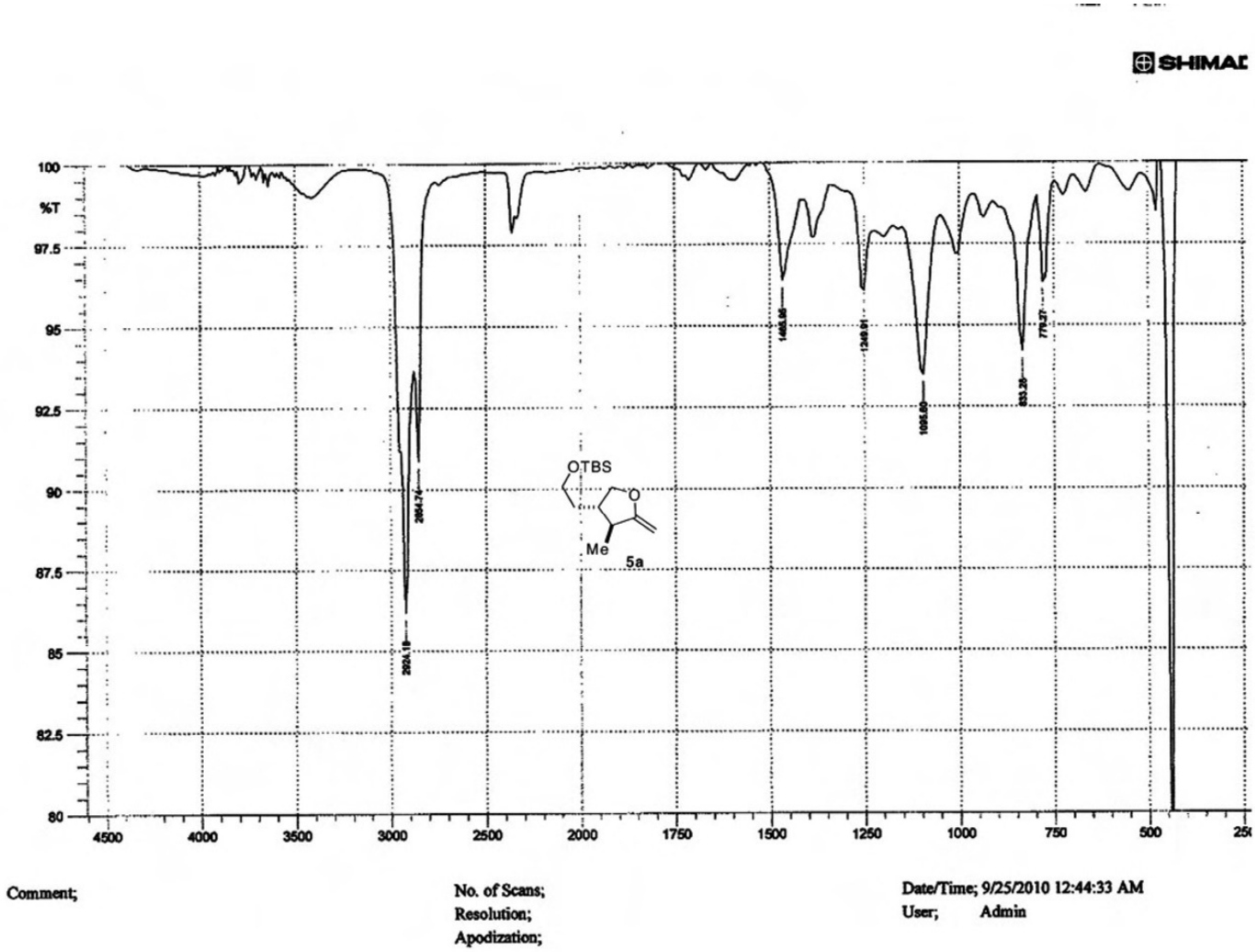
**Enol ether 5a:**

$^{13}$C NMR



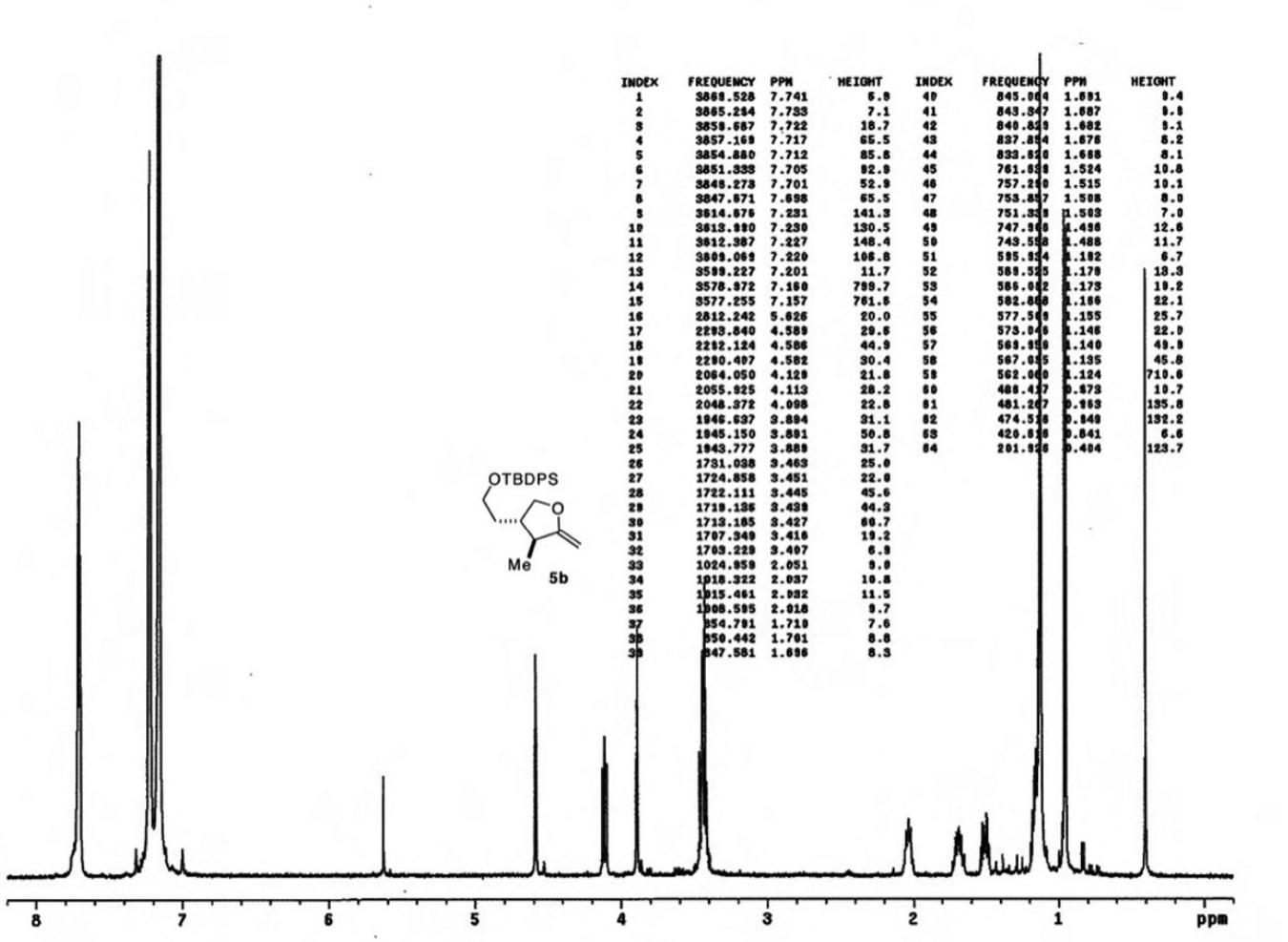
**Enol ether 5a:**

FTIR



**Enol ether 5b:**

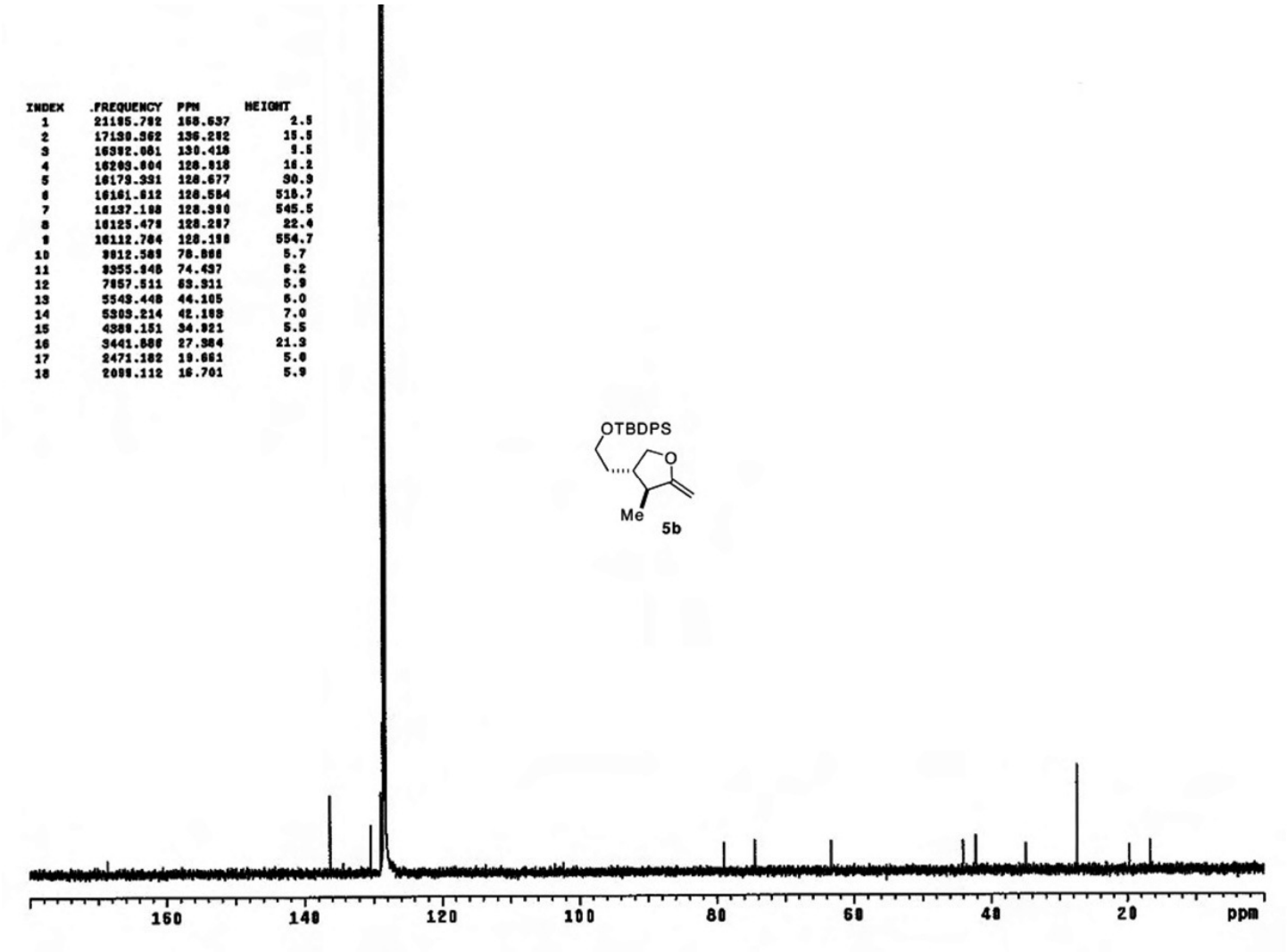
$^{1}$H NMR




| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 3868.528 | 7.741 | 6.8 | 40 | 845.064 | 1.691 | 9.4 |
| 2 | 3865.284 | 7.733 | 7.1 | 41 | 843.847 | 1.687 | 9.8 |
| 3 | 3858.687 | 7.722 | 18.7 | 42 | 840.829 | 1.682 | 9.1 |
| 4 | 3857.168 | 7.717 | 65.5 | 43 | 837.854 | 1.676 | 8.2 |
| 5 | 3854.880 | 7.712 | 85.8 | 44 | 833.820 | 1.668 | 8.1 |
| 6 | 3851.338 | 7.705 | 82.9 | 45 | 761.638 | 1.524 | 10.8 |
| 7 | 3848.278 | 7.701 | 52.9 | 46 | 757.290 | 1.515 | 10.1 |
| 8 | 3847.671 | 7.698 | 65.5 | 47 | 753.857 | 1.508 | 8.0 |
| 9 | 3814.876 | 7.231 | 141.3 | 48 | 751.338 | 1.503 | 7.0 |
| 10 | 3813.980 | 7.230 | 130.5 | 49 | 747.968 | 1.496 | 12.6 |
| 11 | 3812.387 | 7.227 | 148.4 | 50 | 743.558 | 1.488 | 11.7 |
| 12 | 3809.069 | 7.220 | 106.8 | 51 | 595.834 | 1.192 | 6.7 |
| 13 | 3589.227 | 7.201 | 11.7 | 52 | 588.525 | 1.178 | 18.3 |
| 14 | 3578.872 | 7.180 | 799.7 | 53 | 586.082 | 1.173 | 19.2 |
| 15 | 3577.255 | 7.157 | 761.8 | 54 | 582.868 | 1.166 | 22.1 |
| 16 | 2812.242 | 5.626 | 20.0 | 55 | 577.508 | 1.155 | 25.7 |
| 17 | 2293.840 | 4.589 | 29.8 | 56 | 573.048 | 1.146 | 22.9 |
| 18 | 2292.124 | 4.586 | 44.9 | 57 | 569.858 | 1.140 | 43.8 |
| 19 | 2290.407 | 4.582 | 30.4 | 58 | 567.055 | 1.135 | 45.8 |
| 20 | 2064.050 | 4.128 | 21.8 | 59 | 562.060 | 1.124 | 710.6 |
| 21 | 2055.925 | 4.113 | 28.2 | 60 | 488.427 | 0.978 | 10.7 |
| 22 | 2048.372 | 4.098 | 22.8 | 61 | 481.267 | 0.963 | 135.8 |
| 23 | 1946.637 | 3.894 | 31.1 | 62 | 474.538 | 0.949 | 132.2 |
| 24 | 1945.150 | 3.891 | 50.8 | 63 | 420.838 | 0.841 | 6.6 |
| 25 | 1943.777 | 3.888 | 31.7 | 64 | 201.928 | 0.404 | 123.7 |
| 26 | 1731.038 | 3.463 | 25.0 | | | | |
| 27 | 1724.858 | 3.451 | 22.8 | | | | |
| 28 | 1722.111 | 3.445 | 45.6 | | | | |
| 29 | 1719.136 | 3.439 | 44.3 | | | | |
| 30 | 1713.185 | 3.427 | 60.7 | | | | |
| 31 | 1707.349 | 3.416 | 19.2 | | | | |
| 32 | 1703.229 | 3.407 | 6.9 | | | | |
| 33 | 1024.959 | 2.051 | 9.9 | | | | |
| 34 | 1018.322 | 2.037 | 10.8 | | | | |
| 35 | 1015.461 | 2.032 | 11.5 | | | | |
| 36 | 1008.595 | 2.018 | 9.7 | | | | |
| 37 | 854.791 | 1.710 | 7.6 | | | | |
| 38 | 850.442 | 1.701 | 8.8 | | | | |
| 39 | 847.581 | 1.696 | 8.3 | | | | |

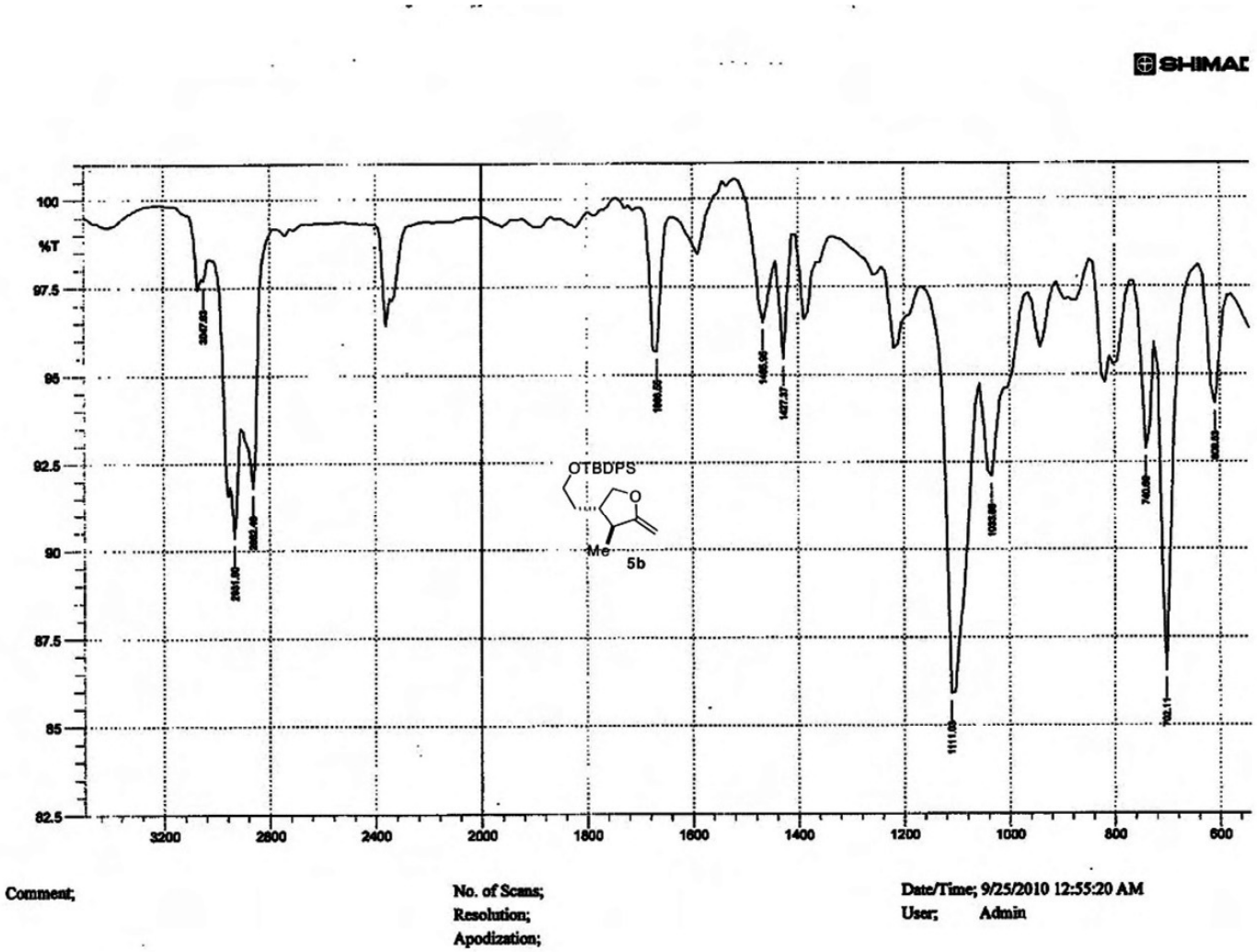
**Enol ether 5b:**

$^{13}$C NMR



**Enol ether 5b:**

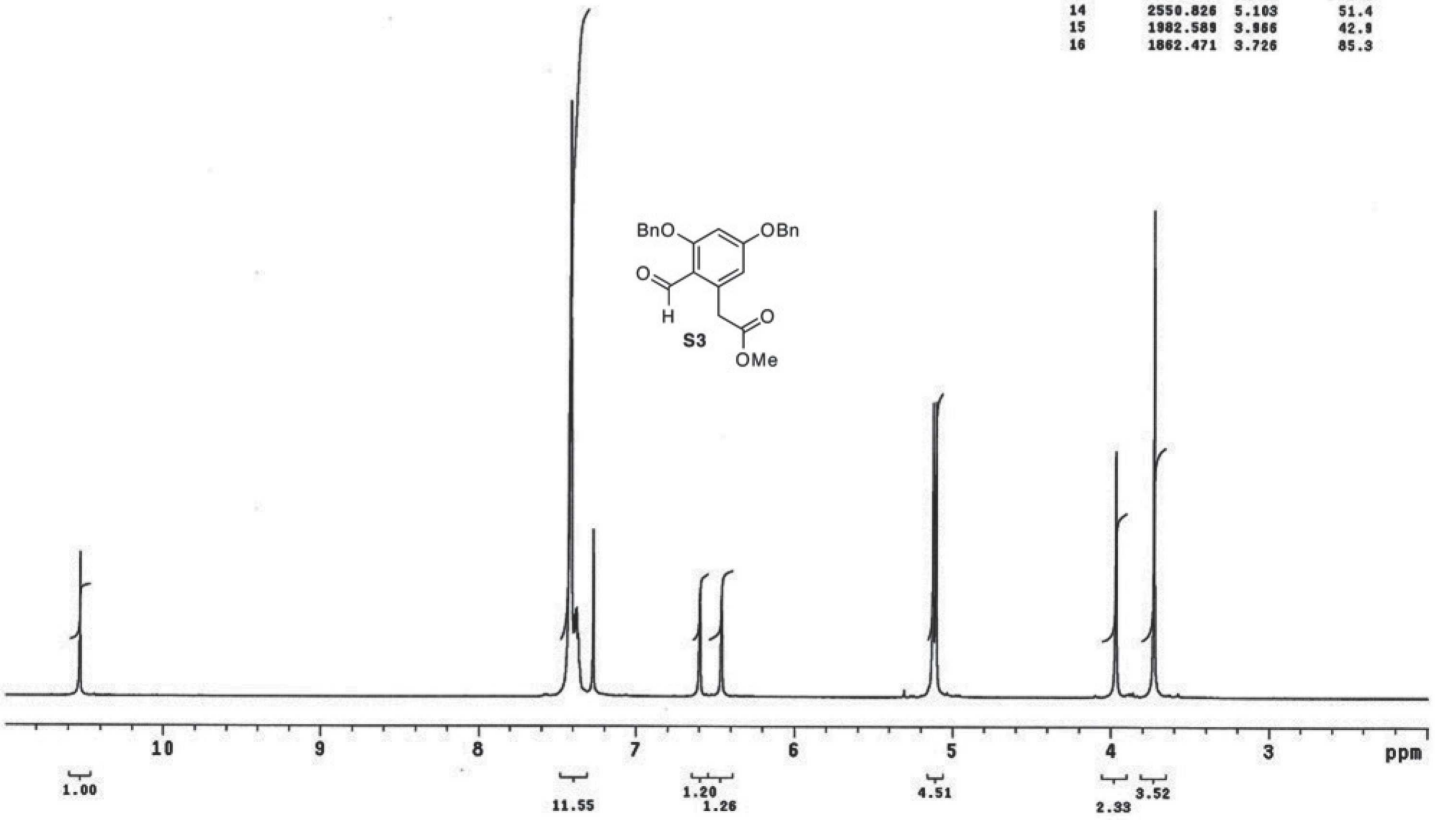
FTIR



**Aldehyde S3:**

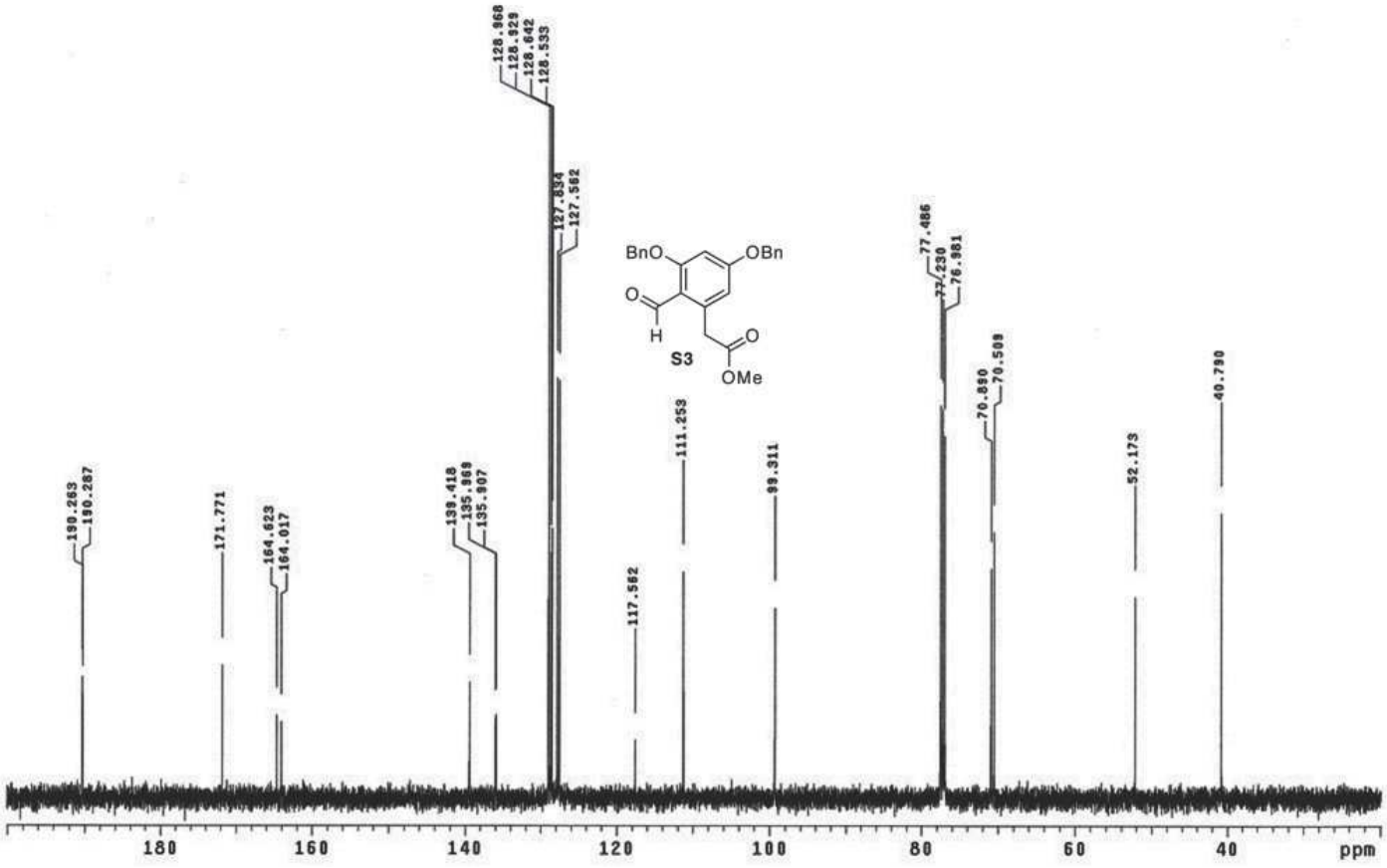
$^{1}$H NMR

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 5261.519 | 10.526 | 25.0 |
| 2 | 3710.616 | 7.423 | 58.6 |
| 3 | 3706.954 | 7.416 | 104.0 |
| 4 | 3703.780 | 7.410 | 62.3 |
| 5 | 3694.503 | 7.391 | 14.4 |
| 6 | 3690.108 | 7.382 | 15.3 |
| 7 | 3686.080 | 7.374 | 15.7 |
| 8 | 3681.441 | 7.365 | 11.1 |
| 9 | 3633.956 | 7.270 | 29.1 |
| 10 | 3297.652 | 6.597 | 18.1 |
| 11 | 3295.577 | 6.593 | 16.2 |
| 12 | 3229.171 | 6.460 | 17.3 |
| 13 | 2559.981 | 5.121 | 51.2 |
| 14 | 2550.826 | 5.103 | 51.4 |
| 15 | 1982.589 | 3.966 | 42.8 |
| 16 | 1862.471 | 3.726 | 85.3 |



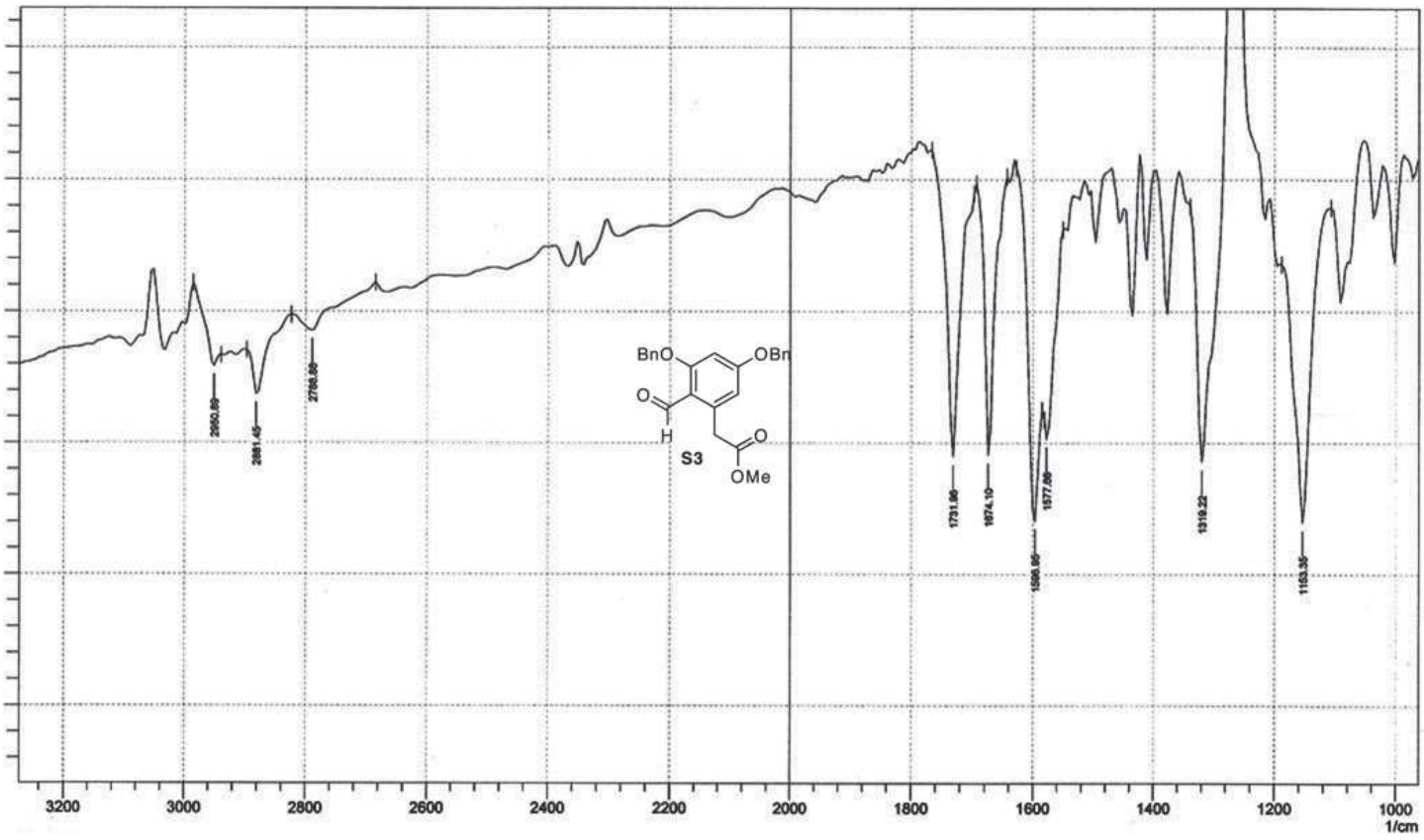
**Aldehyde S3:**

$^{13}$C NMR



**Aldehyde S3:**

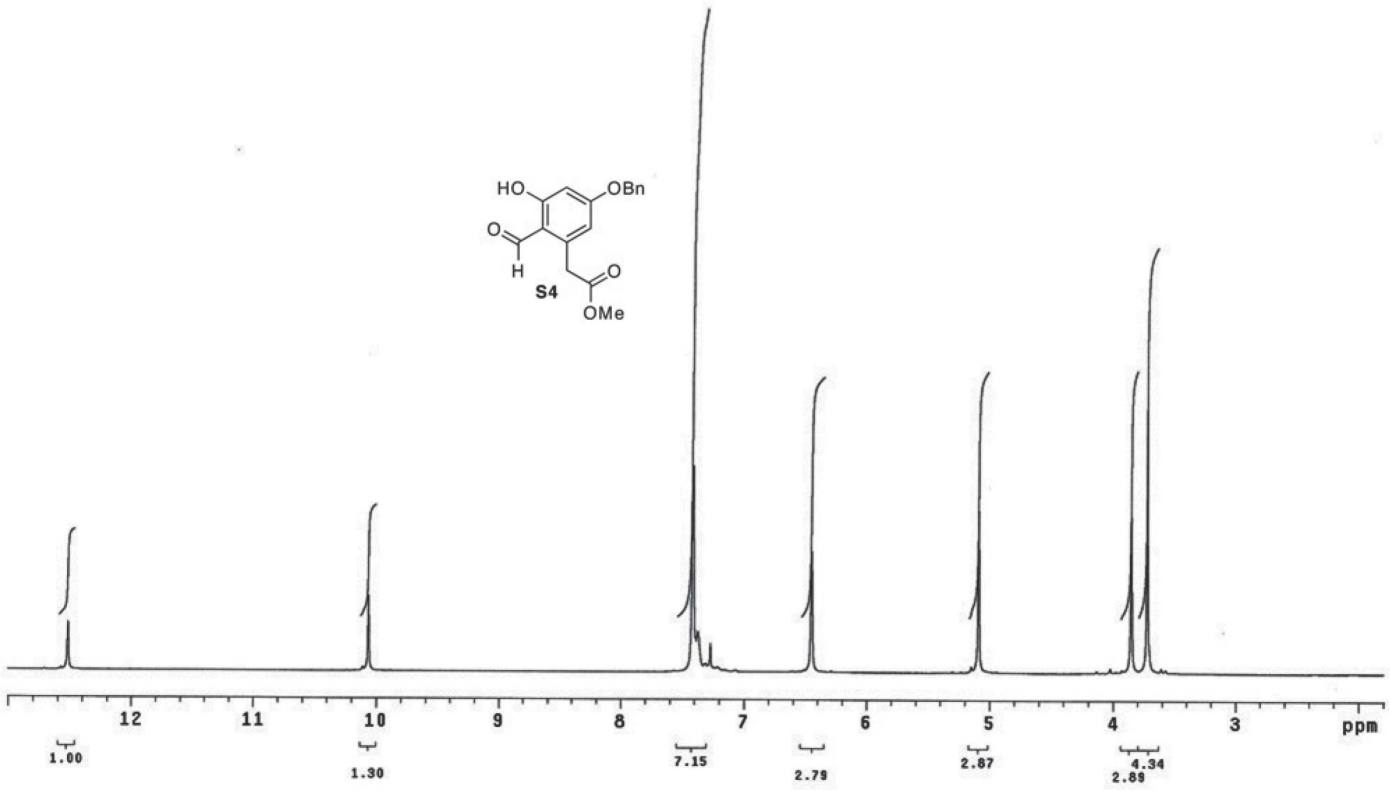
FTIR



**Aldehyde S4:**

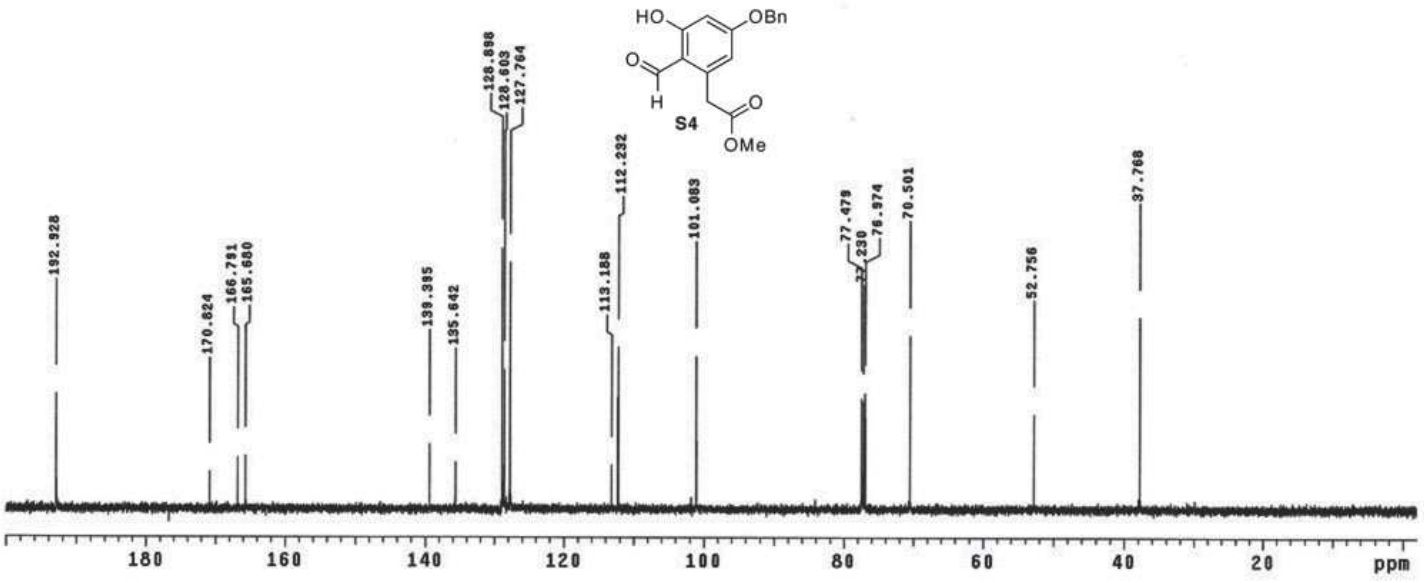
$^{1}$H NMR

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 6256.270 | 12.516 | 8.8 |
| 2 | 5029.586 | 10.062 | 13.7 |
| 3 | 3707.076 | 7.416 | 33.6 |
| 4 | 3703.414 | 7.409 | 37.1 |
| 5 | 3685.347 | 7.373 | 7.6 |
| 6 | 3224.410 | 6.451 | 21.9 |
| 7 | 2543.502 | 5.088 | 29.1 |
| 8 | 1924.849 | 3.851 | 29.2 |
| 9 | 1860.030 | 3.721 | 47.2 |



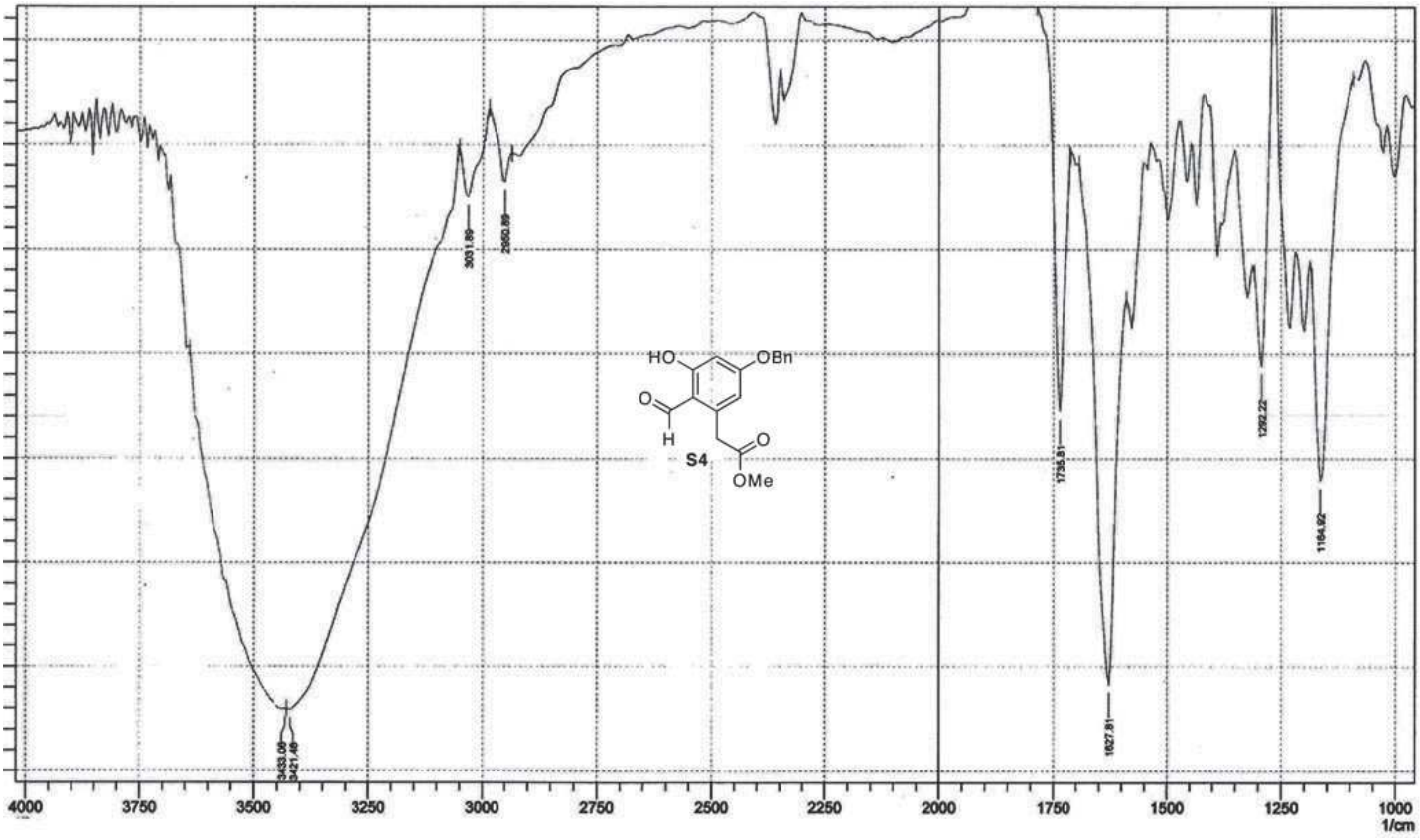
**Aldehyde S4:**

$^{13}$C NMR



**Aldehyde S4:**

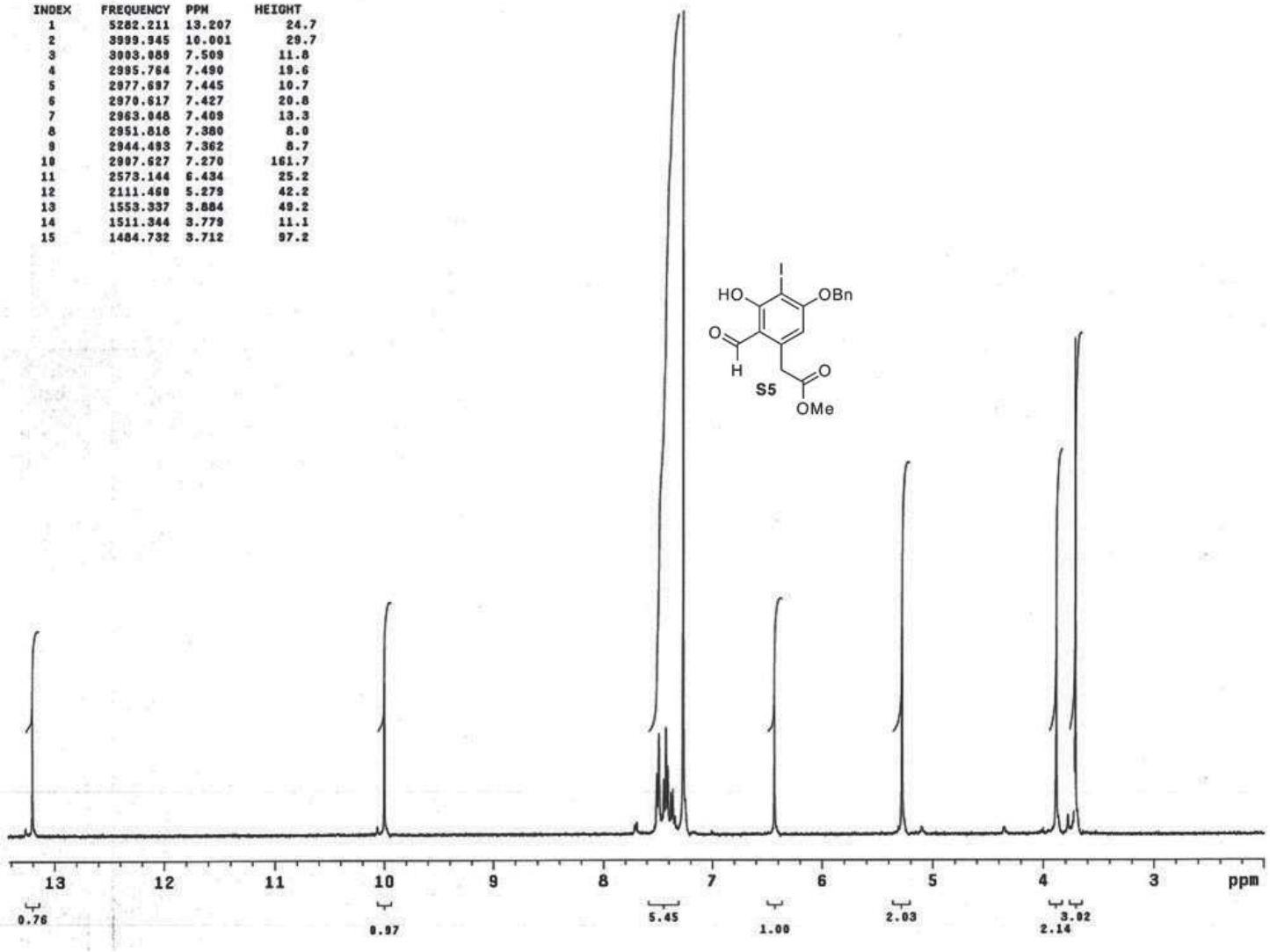
FTIR



**Iodide S5:**

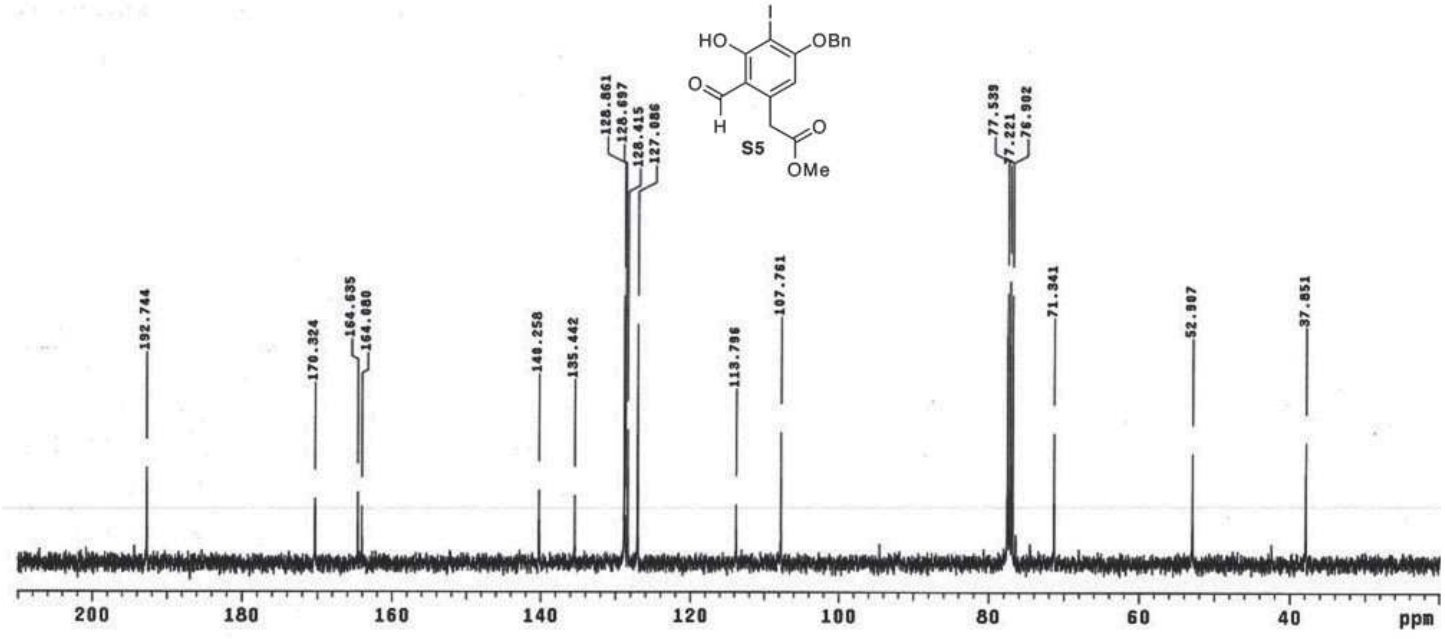
$^{1}$H NMR

| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 5282.211 | 13.207 | 24.7 |
| 2 | 3999.945 | 10.001 | 29.7 |
| 3 | 3003.989 | 7.509 | 11.8 |
| 4 | 2995.764 | 7.490 | 19.6 |
| 5 | 2977.697 | 7.445 | 10.7 |
| 6 | 2970.617 | 7.427 | 20.8 |
| 7 | 2963.948 | 7.409 | 13.3 |
| 8 | 2951.818 | 7.380 | 8.0 |
| 9 | 2944.493 | 7.362 | 8.7 |
| 10 | 2907.627 | 7.270 | 161.7 |
| 11 | 2573.144 | 6.434 | 25.2 |
| 12 | 2111.468 | 5.279 | 42.2 |
| 13 | 1553.337 | 3.884 | 49.2 |
| 14 | 1511.344 | 3.779 | 11.1 |
| 15 | 1484.732 | 3.712 | 97.2 |



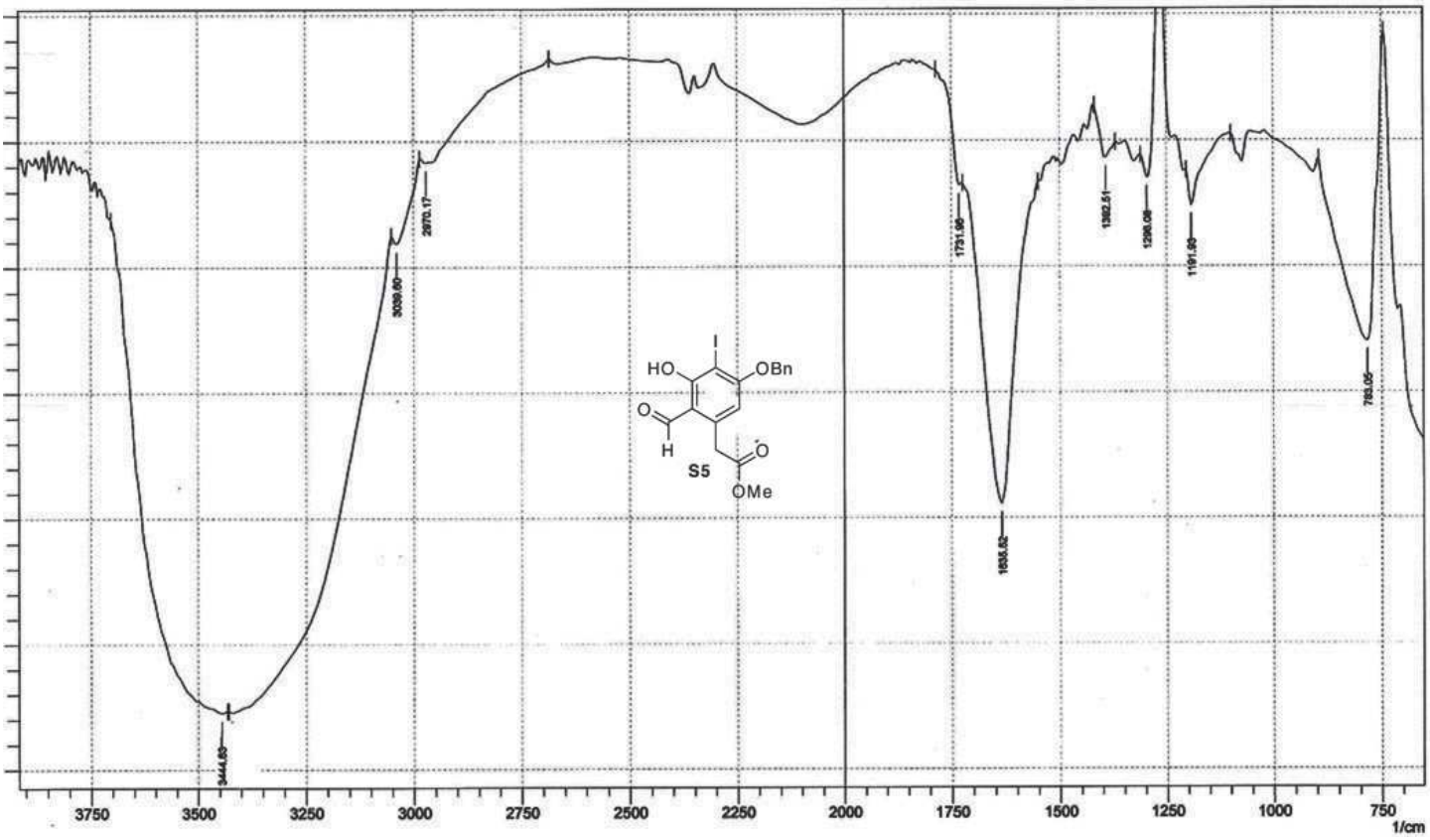
**Iodide S5:**

$^{13}$C NMR



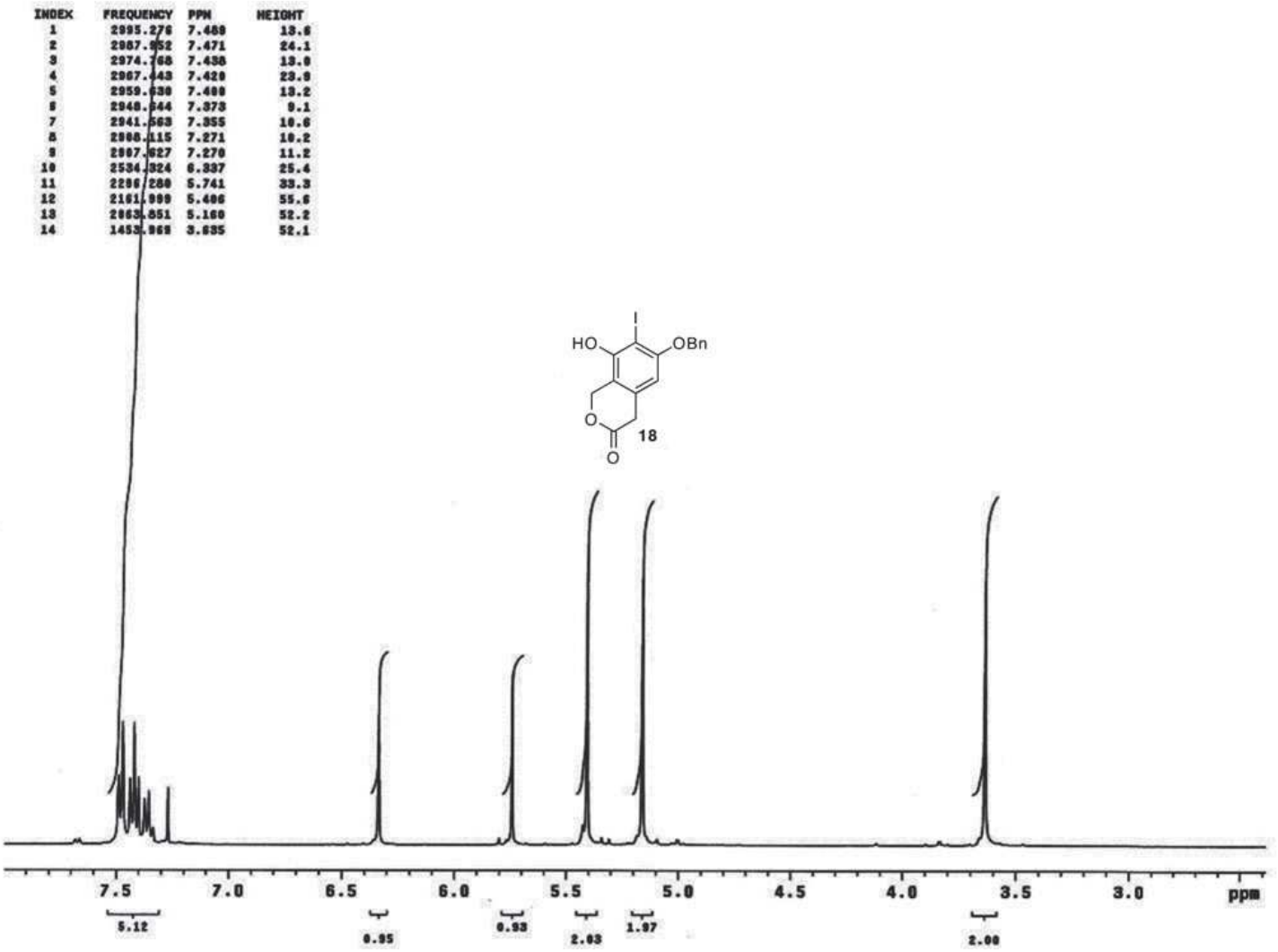
**Iodide S5:**

FTIR



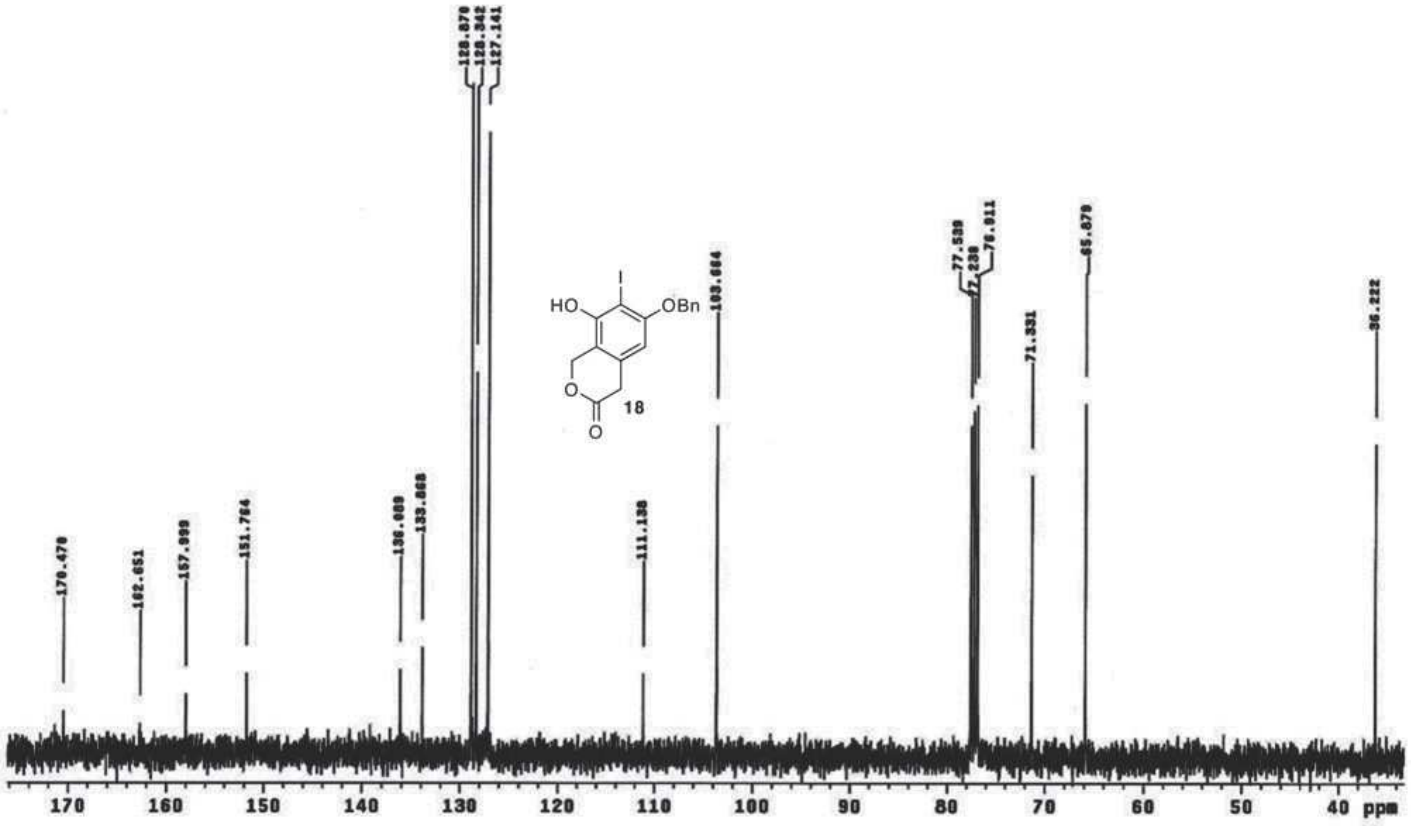
**Isochromanone 18:**

$^{1}$H NMR



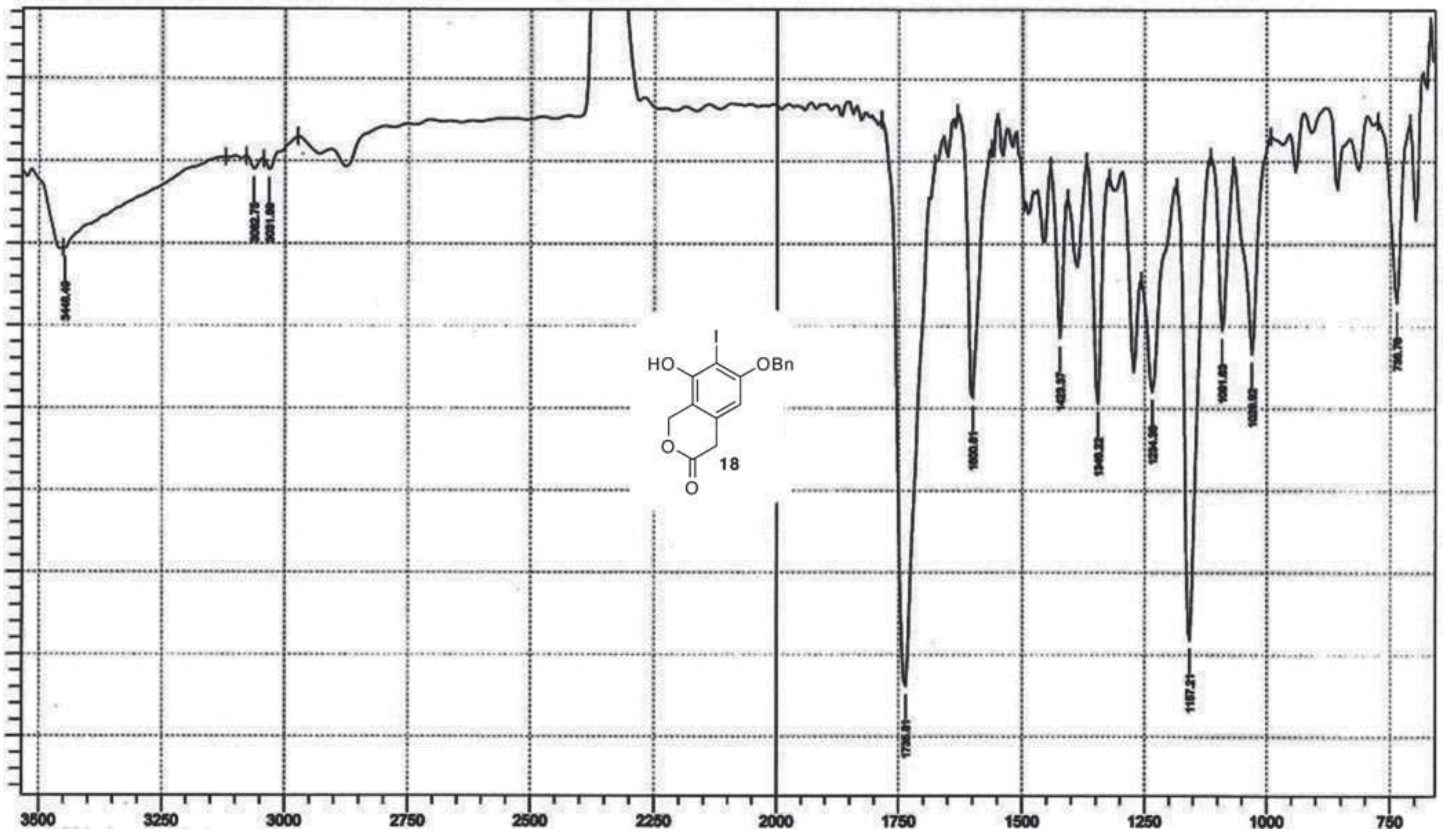
**Isochromanone 18:**

$^{13}$C NMR



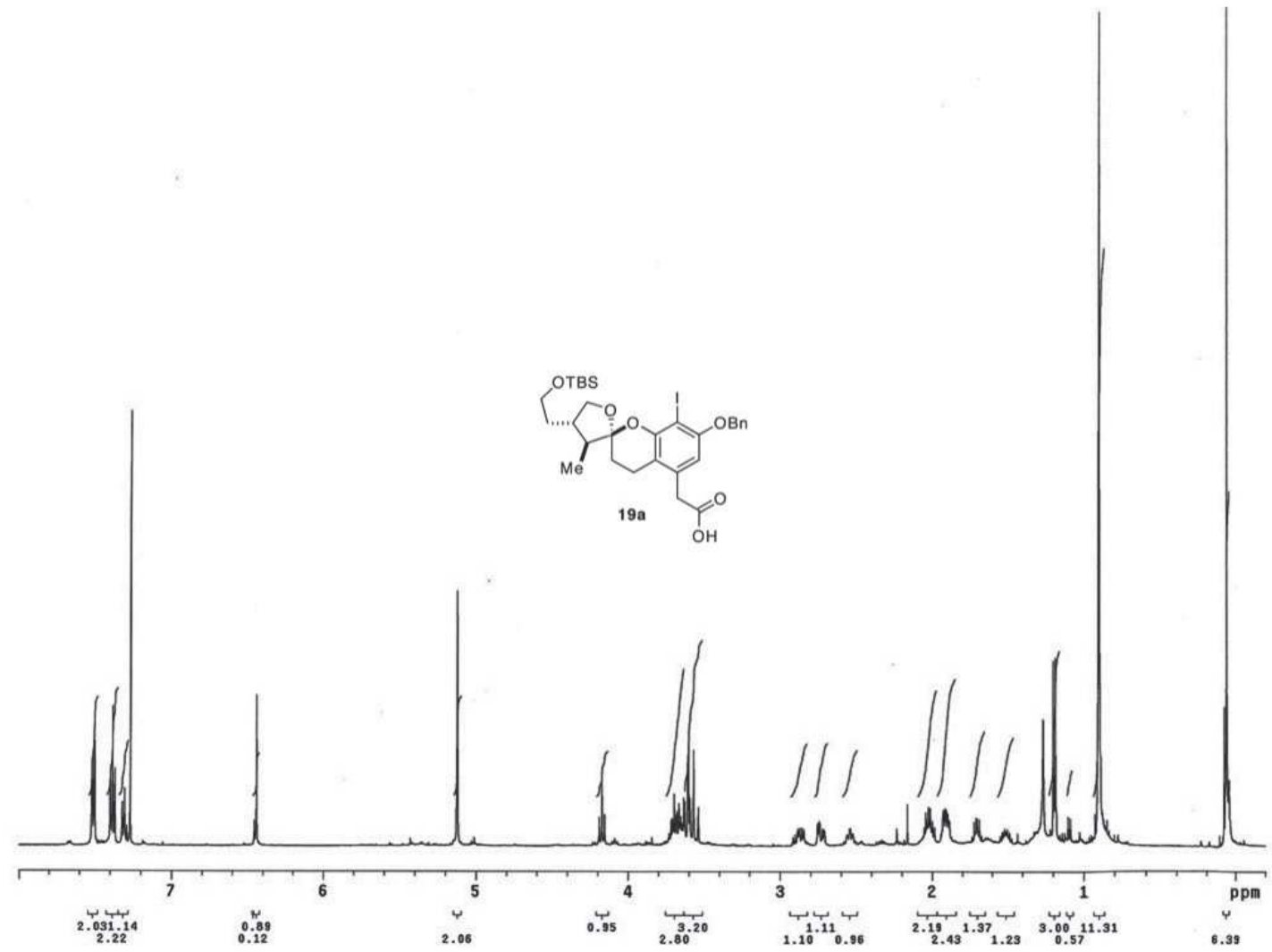
**Isochromanone 18:**

FTIR



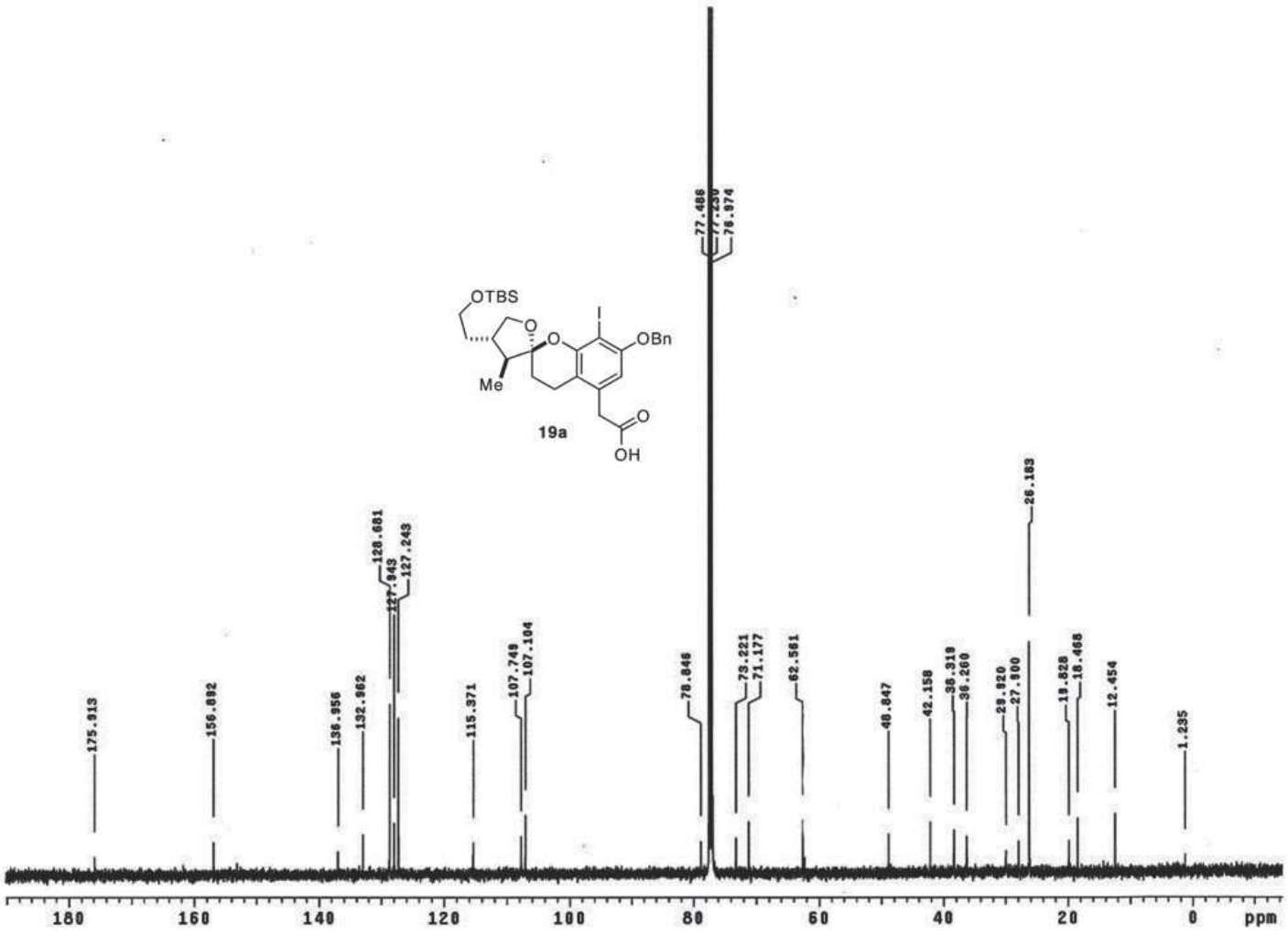
**Spiroketal 19a:**

$^{1}$H NMR



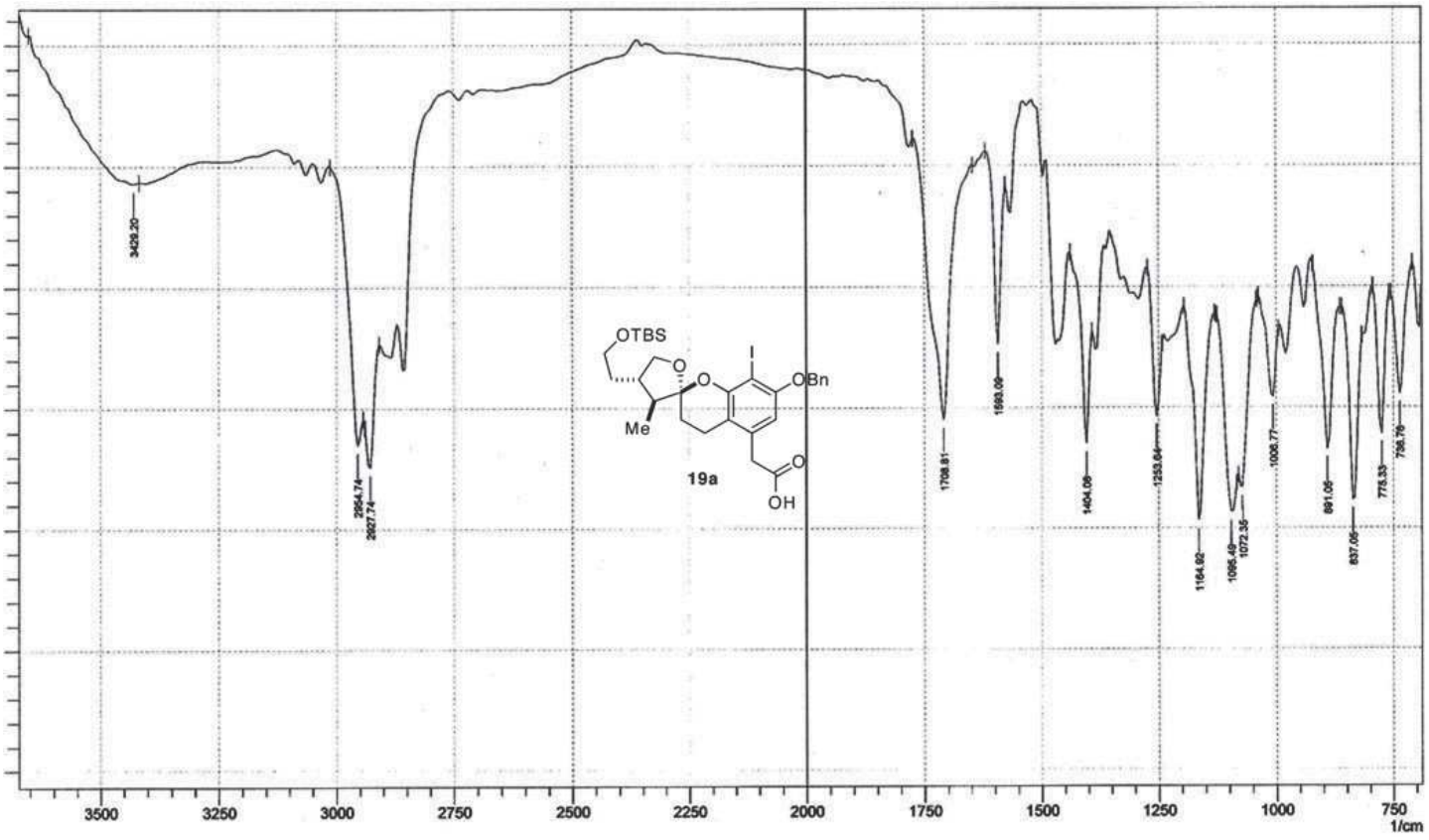
**Spiroketal 19a:**

$^{13}$C NMR



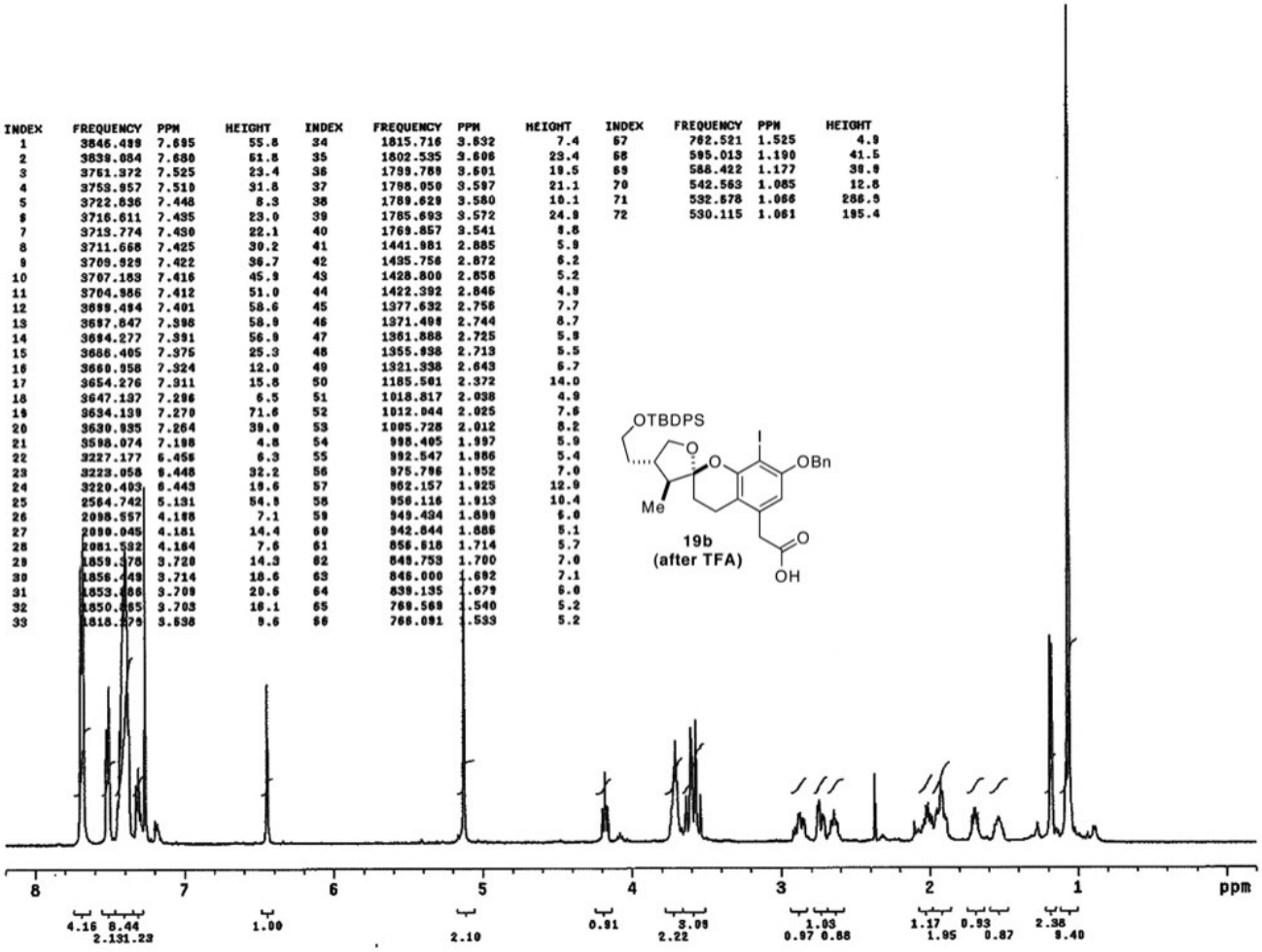
**Spiroketal 19a:**

FTIR



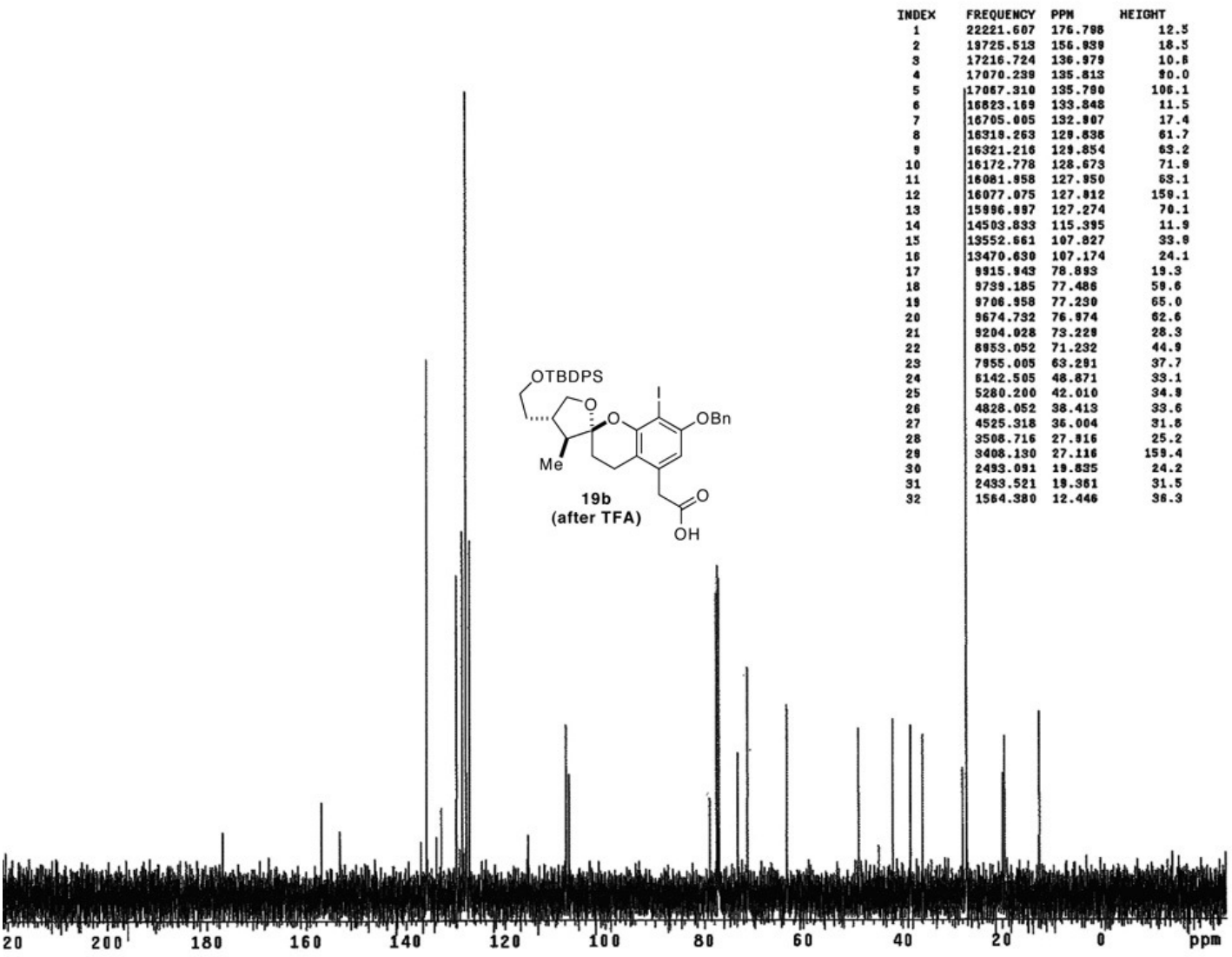
**Spiroketal 19b:**

$^{1}$H NMR



**Spiroketal 19b:**

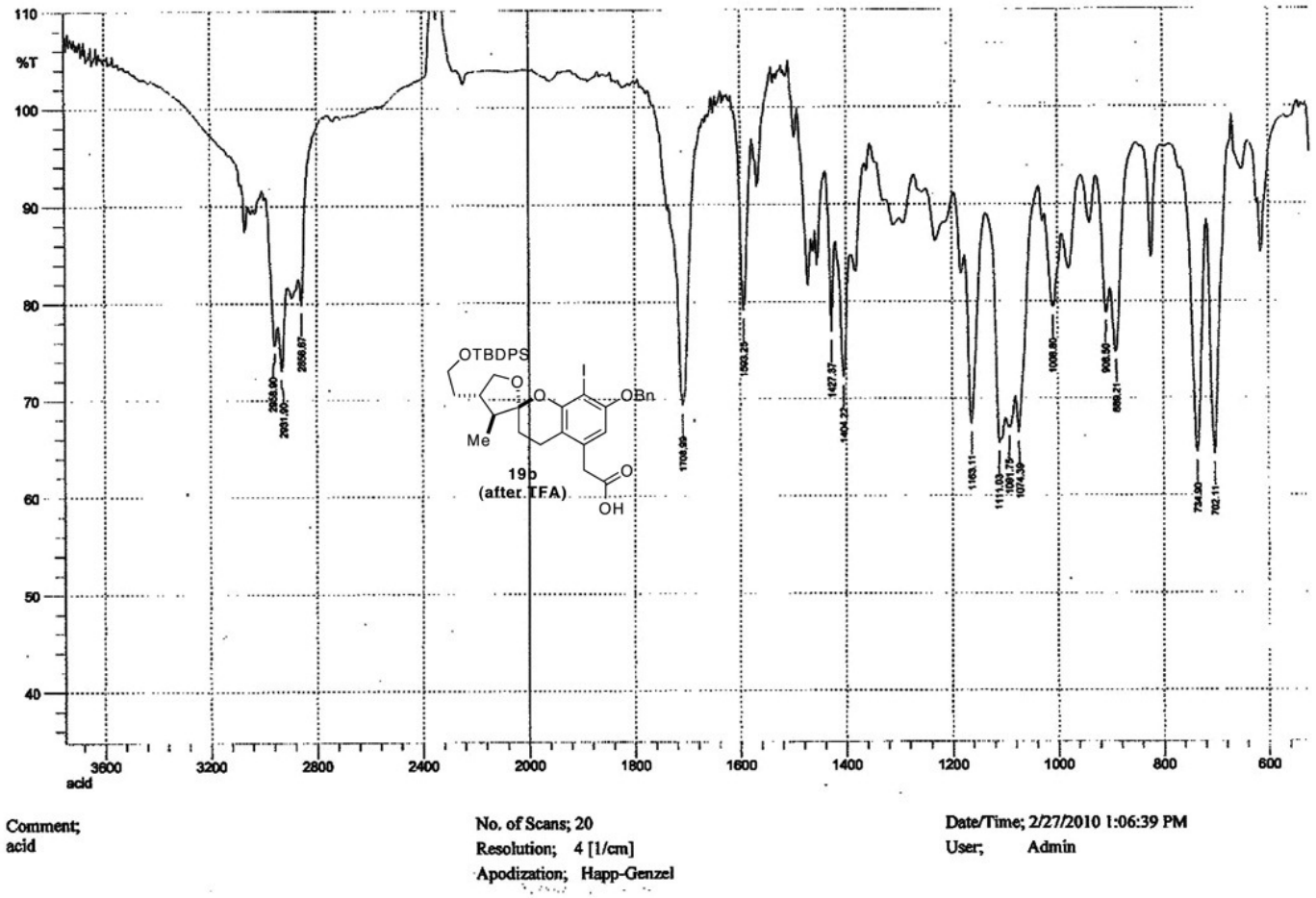
$^{13}$C NMR




| INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|
| 1 | 22221.607 | 176.798 | 12.5 |
| 2 | 19725.513 | 156.939 | 18.5 |
| 3 | 17216.724 | 136.979 | 10.8 |
| 4 | 17070.239 | 135.813 | 90.0 |
| 5 | 17067.310 | 135.790 | 106.1 |
| 6 | 16823.169 | 133.848 | 11.5 |
| 7 | 16705.005 | 132.907 | 17.4 |
| 8 | 16319.263 | 129.838 | 61.7 |
| 9 | 16321.216 | 129.854 | 63.2 |
| 10 | 16172.778 | 128.673 | 71.8 |
| 11 | 16081.958 | 127.950 | 63.1 |
| 12 | 16077.075 | 127.912 | 159.1 |
| 13 | 15996.997 | 127.274 | 70.1 |
| 14 | 14503.833 | 115.395 | 11.9 |
| 15 | 13552.661 | 107.827 | 33.9 |
| 16 | 13470.630 | 107.174 | 24.1 |
| 17 | 9915.943 | 78.893 | 19.3 |
| 18 | 9739.185 | 77.486 | 59.6 |
| 19 | 9706.958 | 77.230 | 65.0 |
| 20 | 9674.732 | 76.974 | 62.6 |
| 21 | 9204.028 | 73.228 | 28.3 |
| 22 | 8953.052 | 71.232 | 44.9 |
| 23 | 7955.005 | 63.291 | 37.7 |
| 24 | 6142.505 | 48.871 | 33.1 |
| 25 | 5280.200 | 42.010 | 34.8 |
| 26 | 4828.052 | 38.413 | 33.6 |
| 27 | 4525.318 | 36.004 | 31.8 |
| 28 | 3508.716 | 27.916 | 25.2 |
| 29 | 3408.130 | 27.116 | 159.4 |
| 30 | 2493.091 | 19.835 | 24.2 |
| 31 | 2433.521 | 19.361 | 31.5 |
| 32 | 1564.380 | 12.446 | 36.3 |

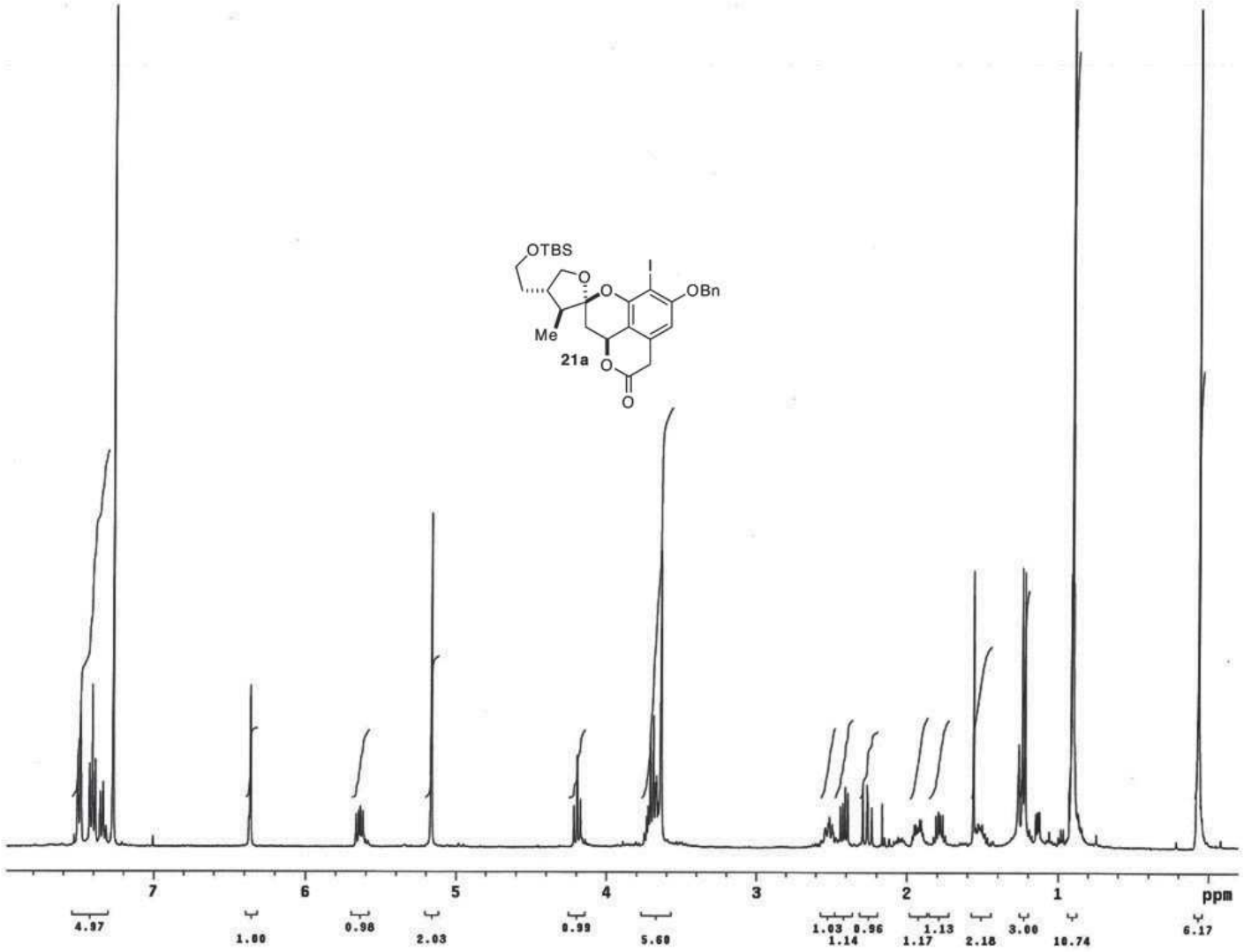
**Spiroketal 19b:**

FTIR



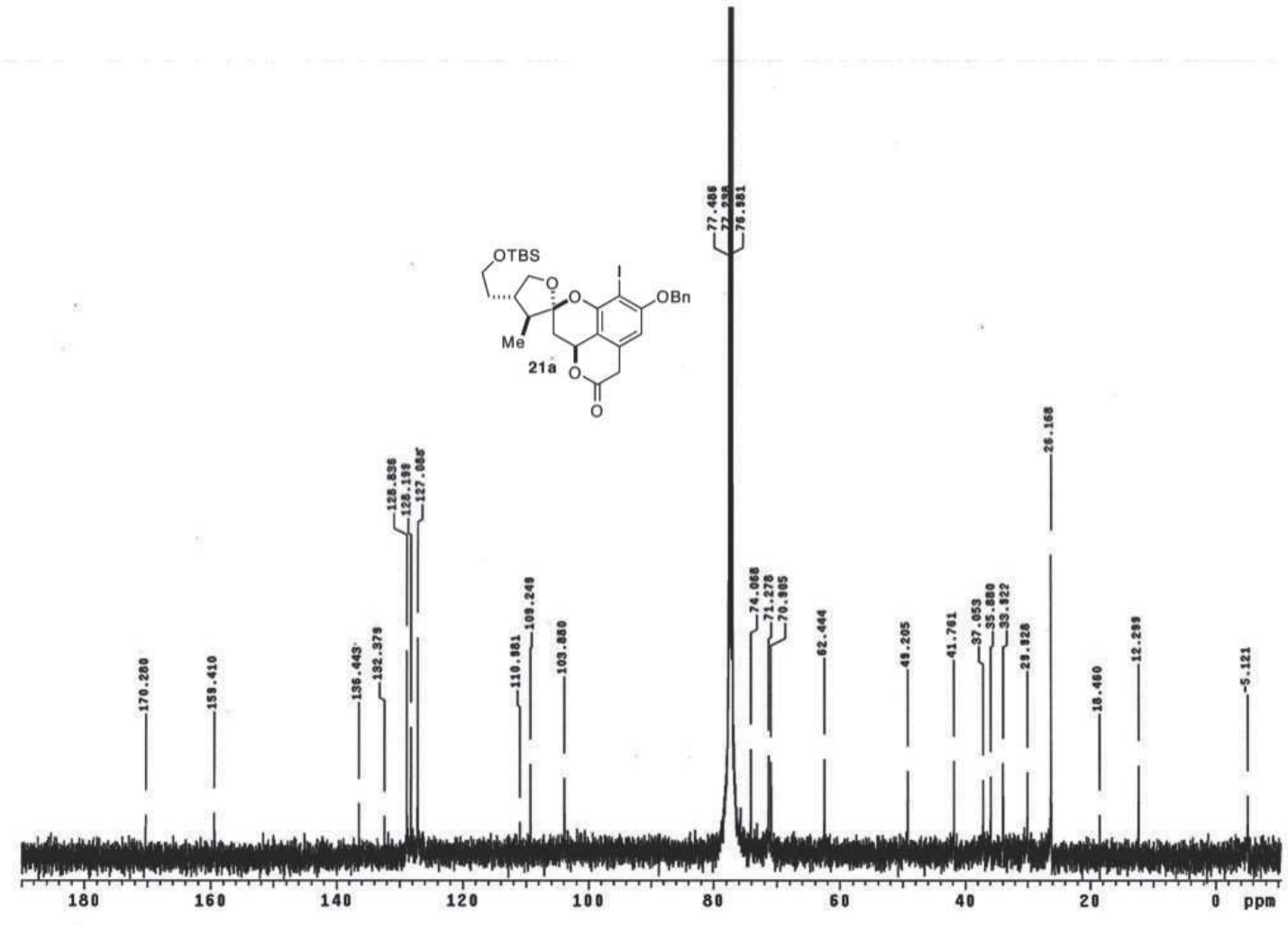
**Tetracycle 21a:**

$^{1}$H NMR



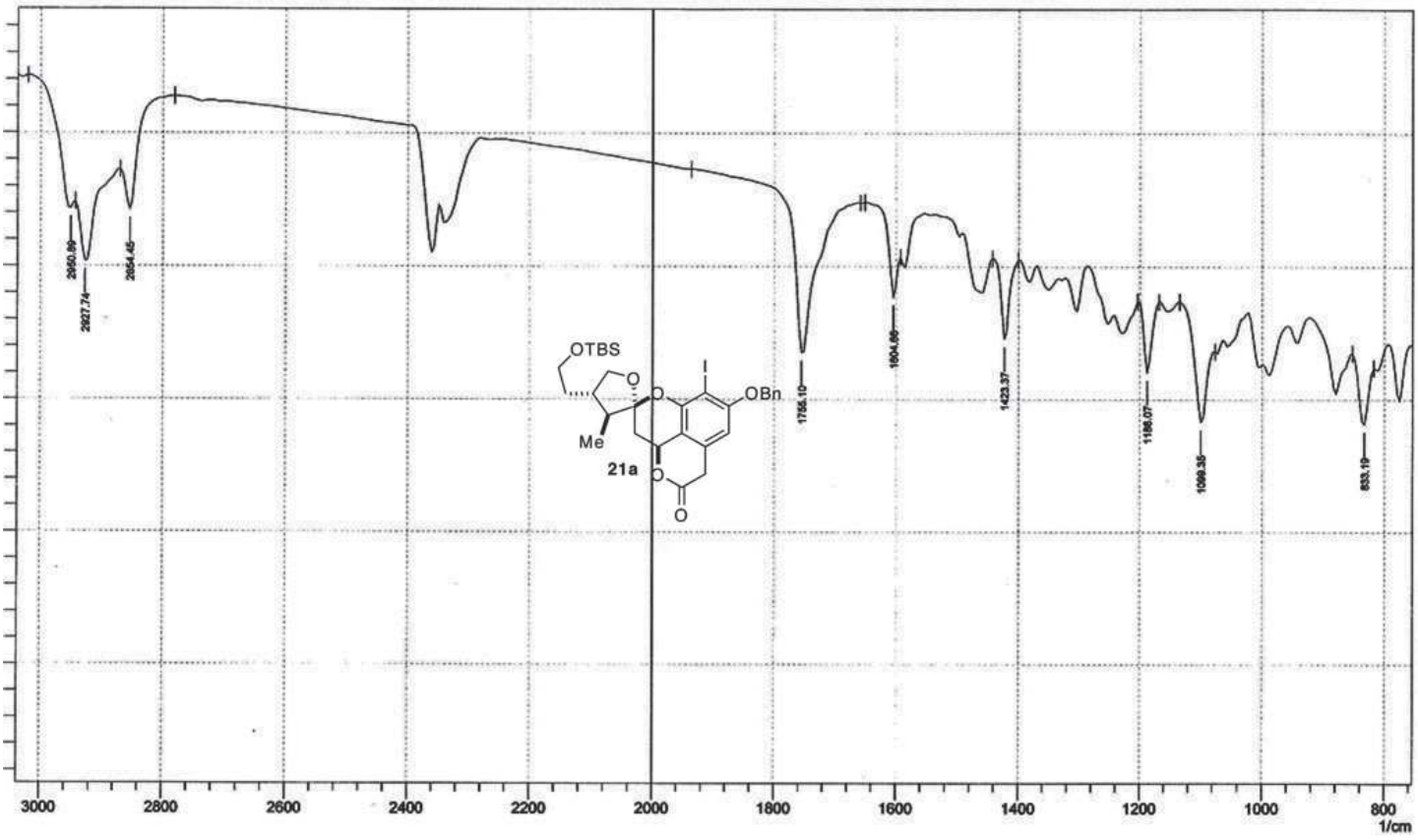
**Tetracycle 21a:**

$^{13}$C NMR



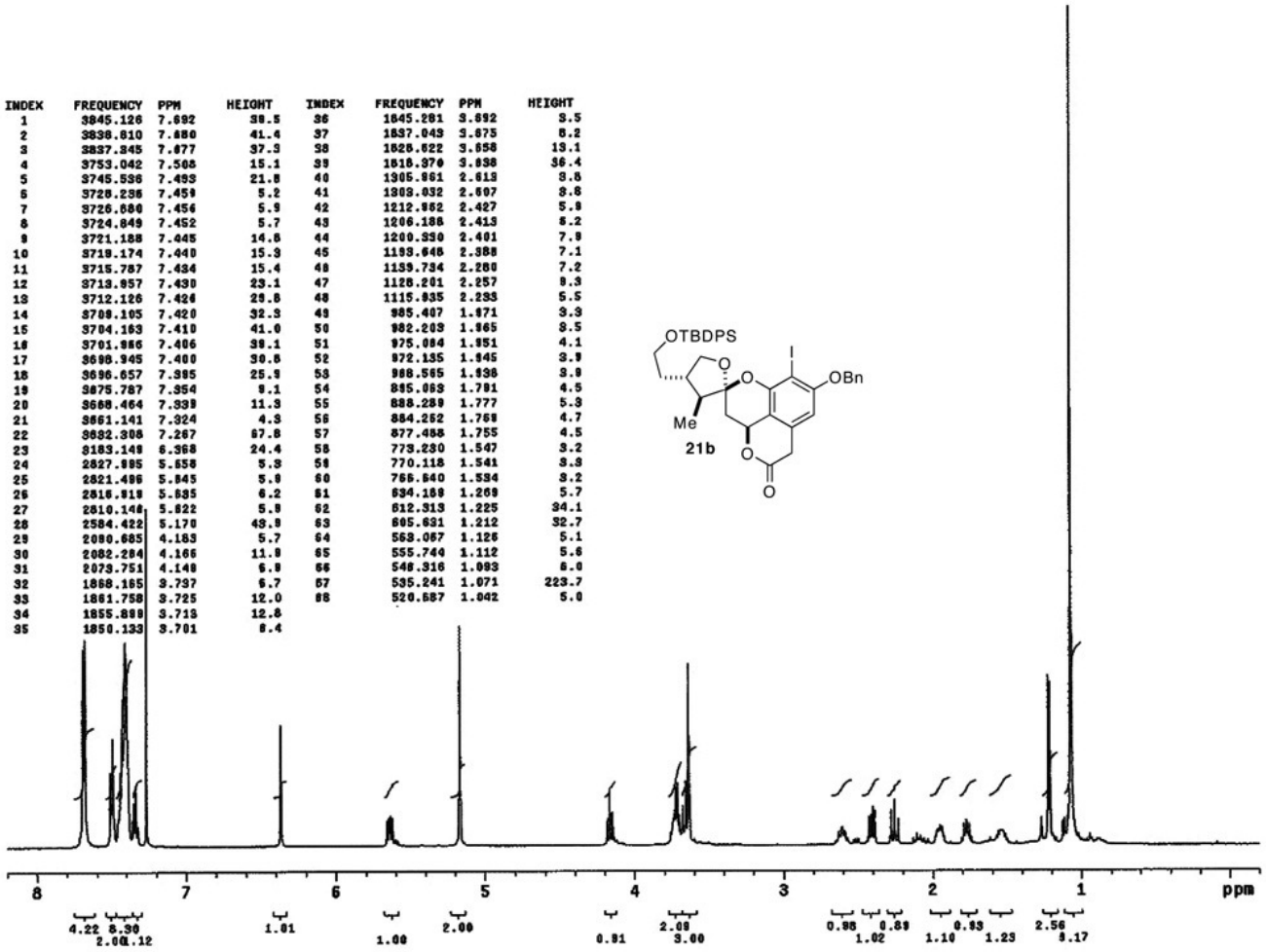
**Tetracycle 21a:**

FTIR



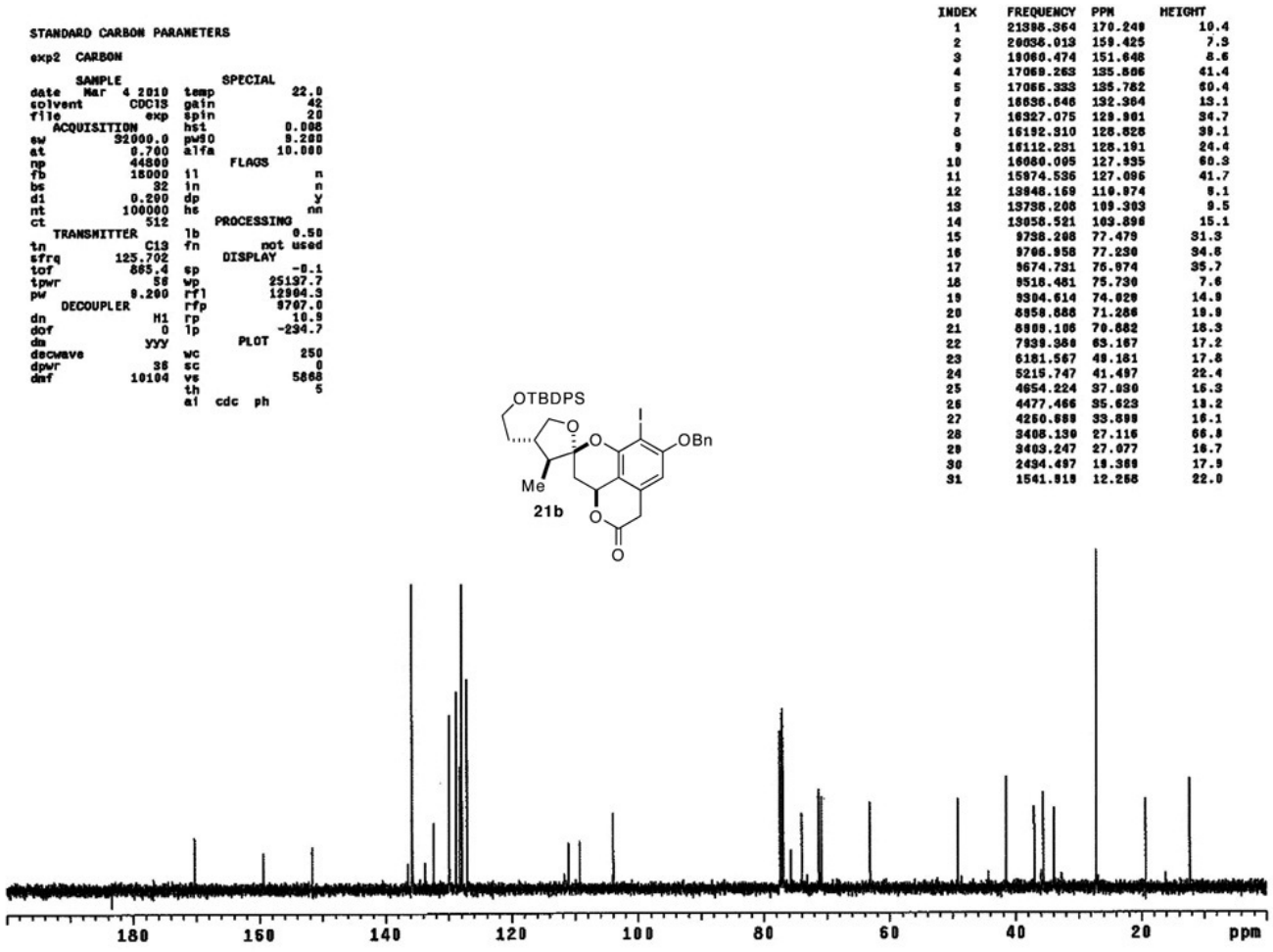
**Tetracycle 21b:**

$^{1}$H NMR



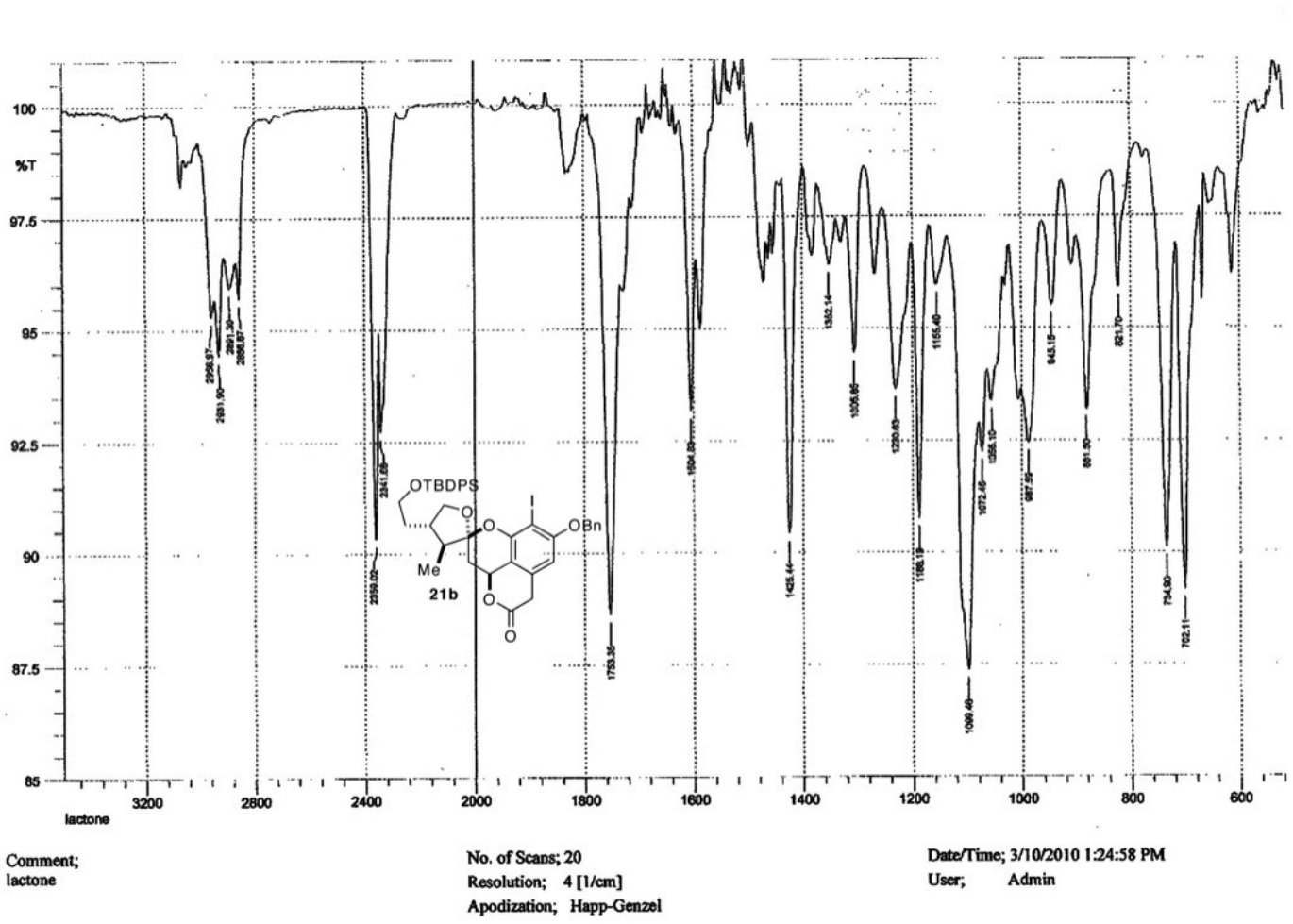
**Tetracycle 21b:**

$^{13}$C NMR



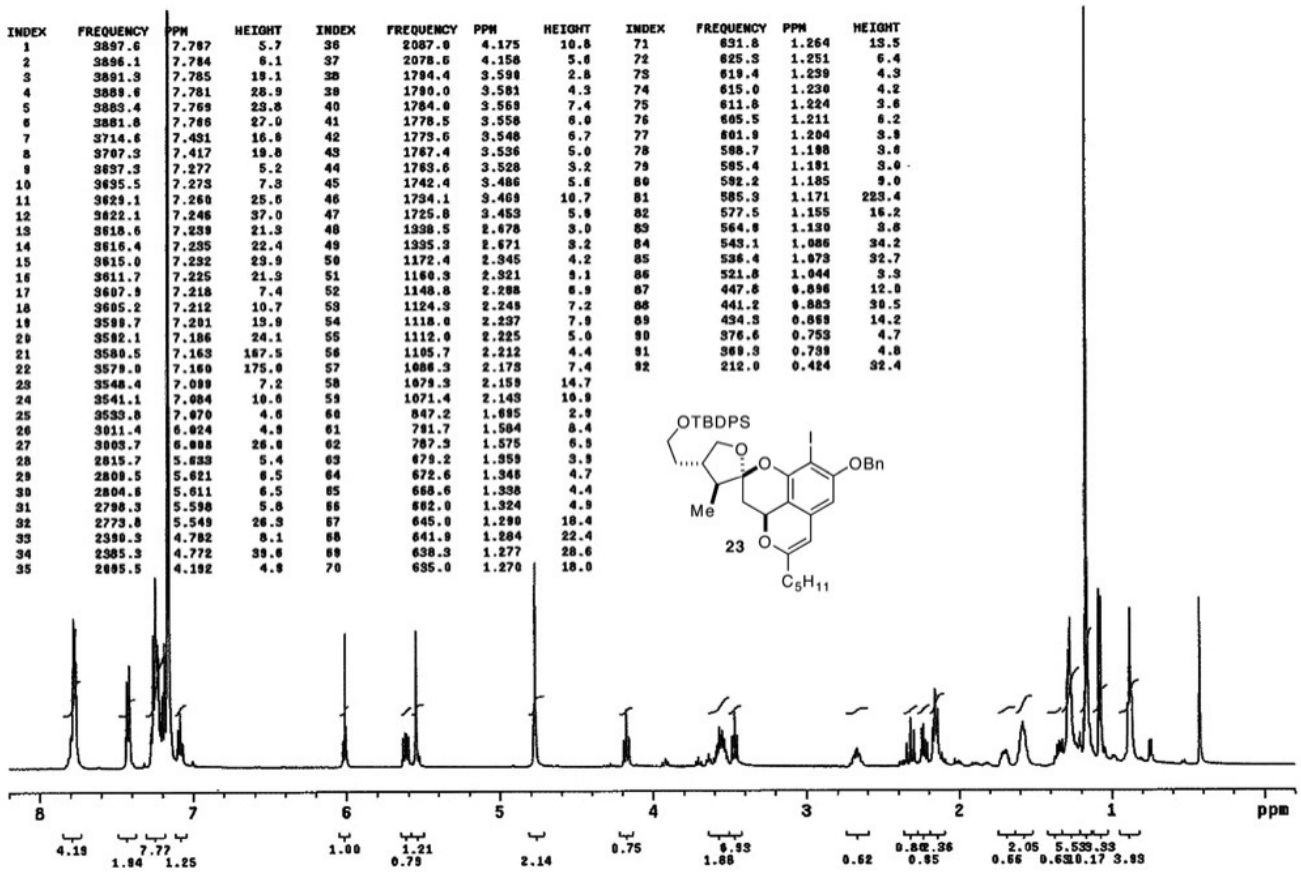
**Tetracycle 21b:**

FTIR



**Isobenzopyran 23:**

$^{1}$H NMR

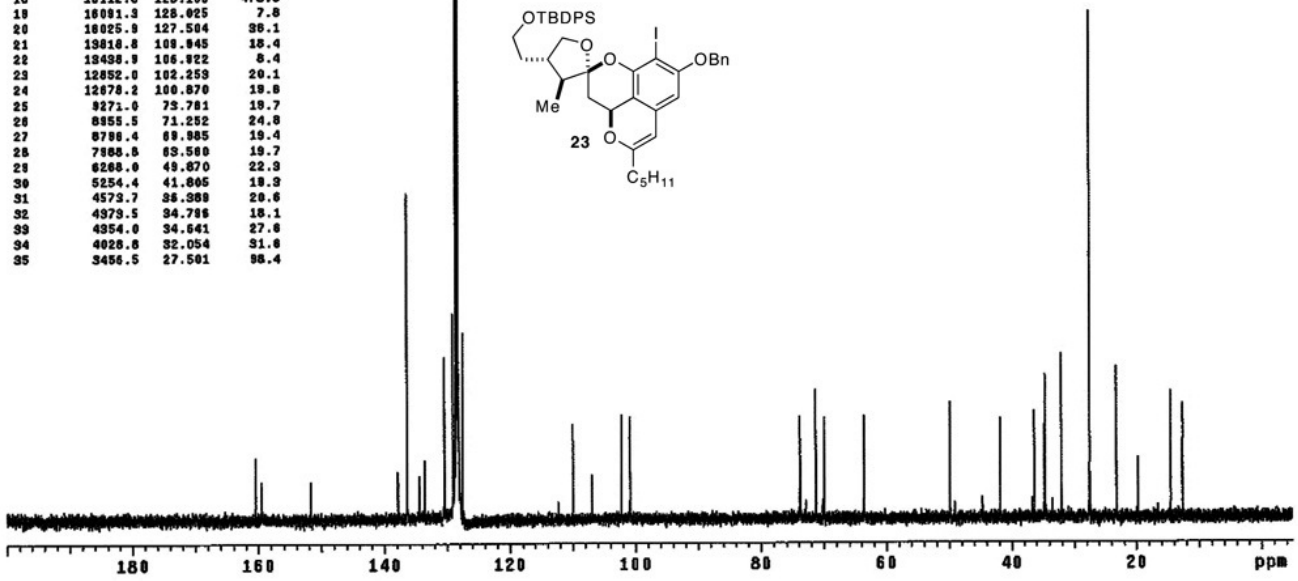


| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3897.6 | 7.787 | 5.7 | 36 | 2087.0 | 4.175 | 10.8 | 71 | 631.8 | 1.264 | 13.5 |
| 2 | 3896.1 | 7.784 | 6.1 | 37 | 2078.6 | 4.158 | 5.6 | 72 | 625.3 | 1.251 | 6.4 |
| 3 | 3891.3 | 7.785 | 18.1 | 38 | 1794.4 | 3.590 | 2.8 | 73 | 619.4 | 1.239 | 4.3 |
| 4 | 3889.6 | 7.781 | 28.9 | 39 | 1790.0 | 3.581 | 4.3 | 74 | 615.0 | 1.230 | 4.2 |
| 5 | 3883.4 | 7.769 | 23.8 | 40 | 1784.0 | 3.569 | 7.4 | 75 | 611.8 | 1.224 | 3.6 |
| 6 | 3881.8 | 7.766 | 27.0 | 41 | 1778.5 | 3.558 | 6.0 | 76 | 605.5 | 1.211 | 6.2 |
| 7 | 3714.6 | 7.431 | 16.6 | 42 | 1773.6 | 3.548 | 6.7 | 77 | 601.9 | 1.204 | 3.8 |
| 8 | 3707.3 | 7.417 | 19.8 | 43 | 1767.4 | 3.536 | 5.0 | 78 | 598.7 | 1.198 | 3.6 |
| 9 | 3697.3 | 7.277 | 5.2 | 44 | 1763.6 | 3.528 | 3.2 | 79 | 595.4 | 1.191 | 3.0 |
| 10 | 3695.5 | 7.273 | 7.3 | 45 | 1742.4 | 3.486 | 5.6 | 80 | 592.2 | 1.185 | 9.0 |
| 11 | 3629.1 | 7.260 | 25.6 | 46 | 1734.1 | 3.469 | 10.7 | 81 | 585.9 | 1.171 | 223.4 |
| 12 | 3622.1 | 7.246 | 37.0 | 47 | 1725.8 | 3.453 | 5.9 | 82 | 577.5 | 1.155 | 16.2 |
| 13 | 3618.6 | 7.239 | 21.3 | 48 | 1338.5 | 2.678 | 3.0 | 83 | 564.8 | 1.130 | 3.8 |
| 14 | 3616.4 | 7.235 | 22.4 | 49 | 1335.3 | 2.671 | 3.2 | 84 | 543.1 | 1.086 | 34.2 |
| 15 | 3615.0 | 7.232 | 23.9 | 50 | 1172.4 | 2.345 | 4.2 | 85 | 536.4 | 1.073 | 32.7 |
| 16 | 3611.7 | 7.225 | 21.3 | 51 | 1160.3 | 2.321 | 9.1 | 86 | 521.8 | 1.044 | 3.3 |
| 17 | 3607.9 | 7.218 | 7.4 | 52 | 1148.8 | 2.298 | 6.9 | 87 | 447.6 | 0.896 | 12.8 |
| 18 | 3605.2 | 7.212 | 10.7 | 53 | 1124.3 | 2.249 | 7.2 | 88 | 441.2 | 0.883 | 30.5 |
| 19 | 3598.7 | 7.201 | 15.9 | 54 | 1118.0 | 2.237 | 7.9 | 89 | 434.3 | 0.869 | 14.2 |
| 20 | 3592.1 | 7.186 | 24.1 | 55 | 1112.0 | 2.225 | 5.0 | 90 | 376.6 | 0.753 | 4.7 |
| 21 | 3580.5 | 7.163 | 167.5 | 56 | 1105.7 | 2.212 | 4.4 | 91 | 369.3 | 0.739 | 4.8 |
| 22 | 3579.0 | 7.160 | 175.0 | 57 | 1086.3 | 2.173 | 7.4 | 92 | 212.0 | 0.424 | 32.4 |
| 23 | 3548.4 | 7.099 | 7.2 | 58 | 1079.3 | 2.159 | 14.7 | | | | |
| 24 | 3541.1 | 7.084 | 10.6 | 59 | 1071.4 | 2.143 | 10.9 | | | | |
| 25 | 3533.8 | 7.070 | 4.6 | 60 | 847.2 | 1.695 | 2.9 | | | | |
| 26 | 3011.4 | 6.024 | 4.8 | 61 | 791.7 | 1.584 | 8.4 | | | | |
| 27 | 3003.7 | 6.008 | 26.6 | 62 | 787.3 | 1.575 | 6.5 | | | | |
| 28 | 2815.7 | 5.633 | 5.4 | 63 | 679.2 | 1.359 | 3.9 | | | | |
| 29 | 2809.5 | 5.621 | 6.5 | 64 | 672.6 | 1.346 | 4.7 | | | | |
| 30 | 2804.6 | 5.611 | 6.5 | 65 | 668.6 | 1.338 | 4.4 | | | | |
| 31 | 2798.3 | 5.598 | 5.8 | 66 | 662.0 | 1.324 | 4.9 | | | | |
| 32 | 2773.8 | 5.549 | 26.3 | 67 | 645.0 | 1.290 | 18.4 | | | | |
| 33 | 2390.3 | 4.782 | 8.1 | 68 | 641.9 | 1.284 | 22.4 | | | | |
| 34 | 2385.3 | 4.772 | 39.6 | 69 | 638.3 | 1.277 | 28.6 | | | | |
| 35 | 2895.5 | 4.192 | 4.8 | 70 | 695.0 | 1.270 | 18.0 | | | | |

**Isobenzopyran 23**:

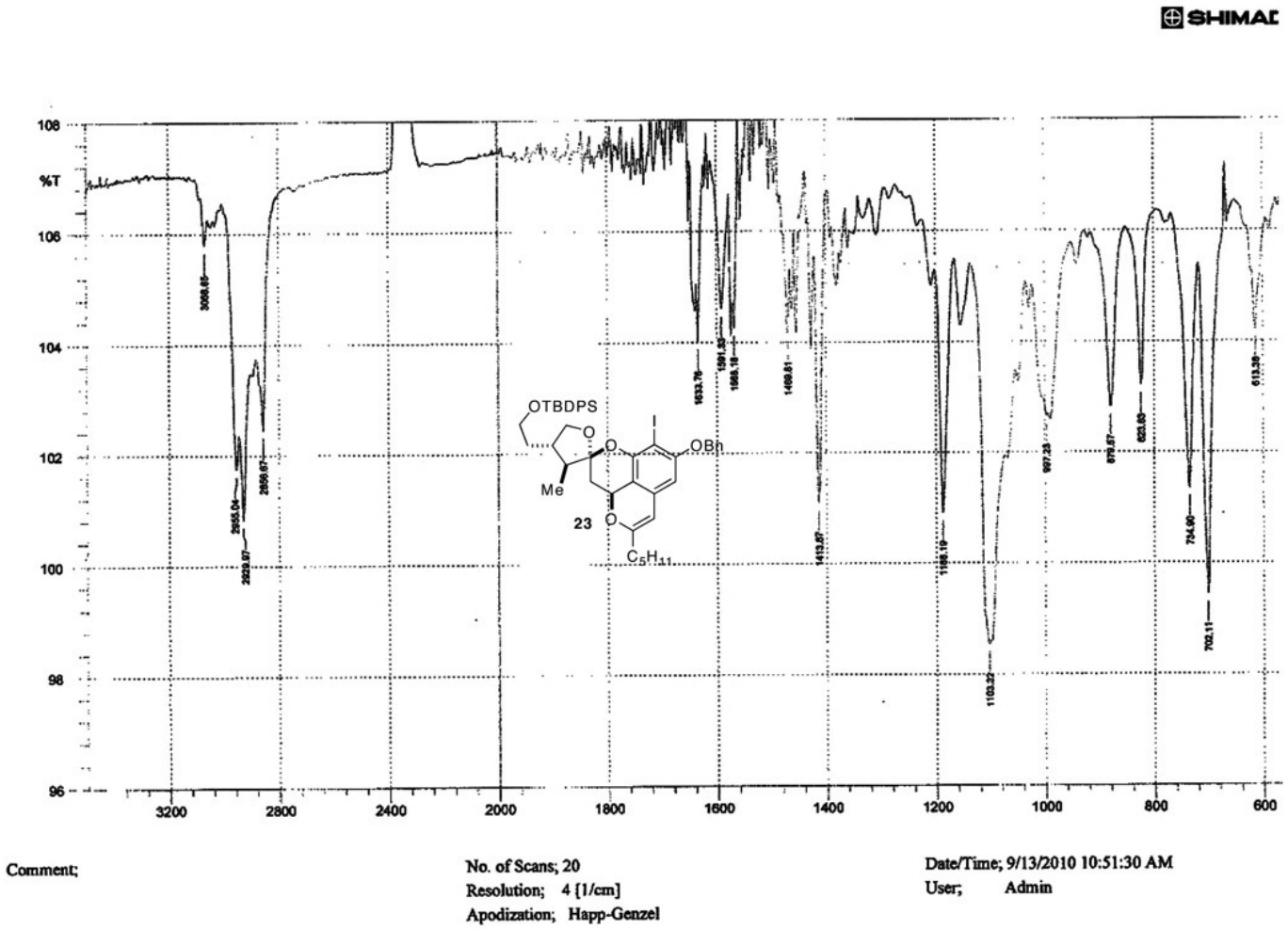
$^{13}$C NMR

| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 20183.6 | 160.424 | 11.7 | 36 | 3451.6 | 27.462 | 17.0 |
| 2 | 20045.4 | 159.484 | 7.0 | 37 | 2918.4 | 23.220 | 28.2 |
| 3 | 19058.1 | 151.614 | 7.1 | 38 | 2482.9 | 19.754 | 11.7 |
| 4 | 17328.8 | 137.853 | 8.1 | 39 | 1832.5 | 14.580 | 24.5 |
| 5 | 17143.0 | 136.383 | 62.2 | 40 | 1589.3 | 12.645 | 22.1 |
| 6 | 17141.1 | 136.377 | 69.2 | | | | |
| 7 | 16887.9 | 134.443 | 8.3 | | | | |
| 8 | 16785.6 | 133.549 | 11.3 | | | | |
| 9 | 16383.0 | 130.428 | 31.3 | | | | |
| 10 | 16381.1 | 130.410 | 29.7 | | | | |
| 11 | 16220.2 | 128.050 | 39.8 | | | | |
| 12 | 16203.6 | 128.818 | 14.6 | | | | |
| 13 | 16174.3 | 128.585 | 29.7 | | | | |
| 14 | 16161.6 | 128.584 | 417.2 | | | | |
| 15 | 16150.9 | 128.498 | 86.7 | | | | |
| 16 | 16137.2 | 128.390 | 455.0 | | | | |
| 17 | 16125.5 | 128.297 | 24.9 | | | | |
| 18 | 16112.8 | 128.198 | 473.8 | | | | |
| 19 | 16081.3 | 128.025 | 7.8 | | | | |
| 20 | 16025.9 | 127.584 | 36.1 | | | | |
| 21 | 13818.8 | 109.945 | 18.4 | | | | |
| 22 | 13438.9 | 106.922 | 8.4 | | | | |
| 23 | 12852.0 | 102.253 | 20.1 | | | | |
| 24 | 12678.2 | 100.870 | 19.8 | | | | |
| 25 | 9271.0 | 73.781 | 19.7 | | | | |
| 26 | 8955.5 | 71.252 | 24.8 | | | | |
| 27 | 8798.4 | 69.985 | 19.4 | | | | |
| 28 | 7868.8 | 63.580 | 19.7 | | | | |
| 29 | 6268.0 | 49.870 | 22.3 | | | | |
| 30 | 5254.4 | 41.805 | 19.3 | | | | |
| 31 | 4573.7 | 36.389 | 20.6 | | | | |
| 32 | 4373.5 | 34.796 | 18.1 | | | | |
| 33 | 4354.0 | 34.641 | 27.8 | | | | |
| 34 | 4026.8 | 32.054 | 31.6 | | | | |
| 35 | 3456.5 | 27.501 | 98.4 | | | | |



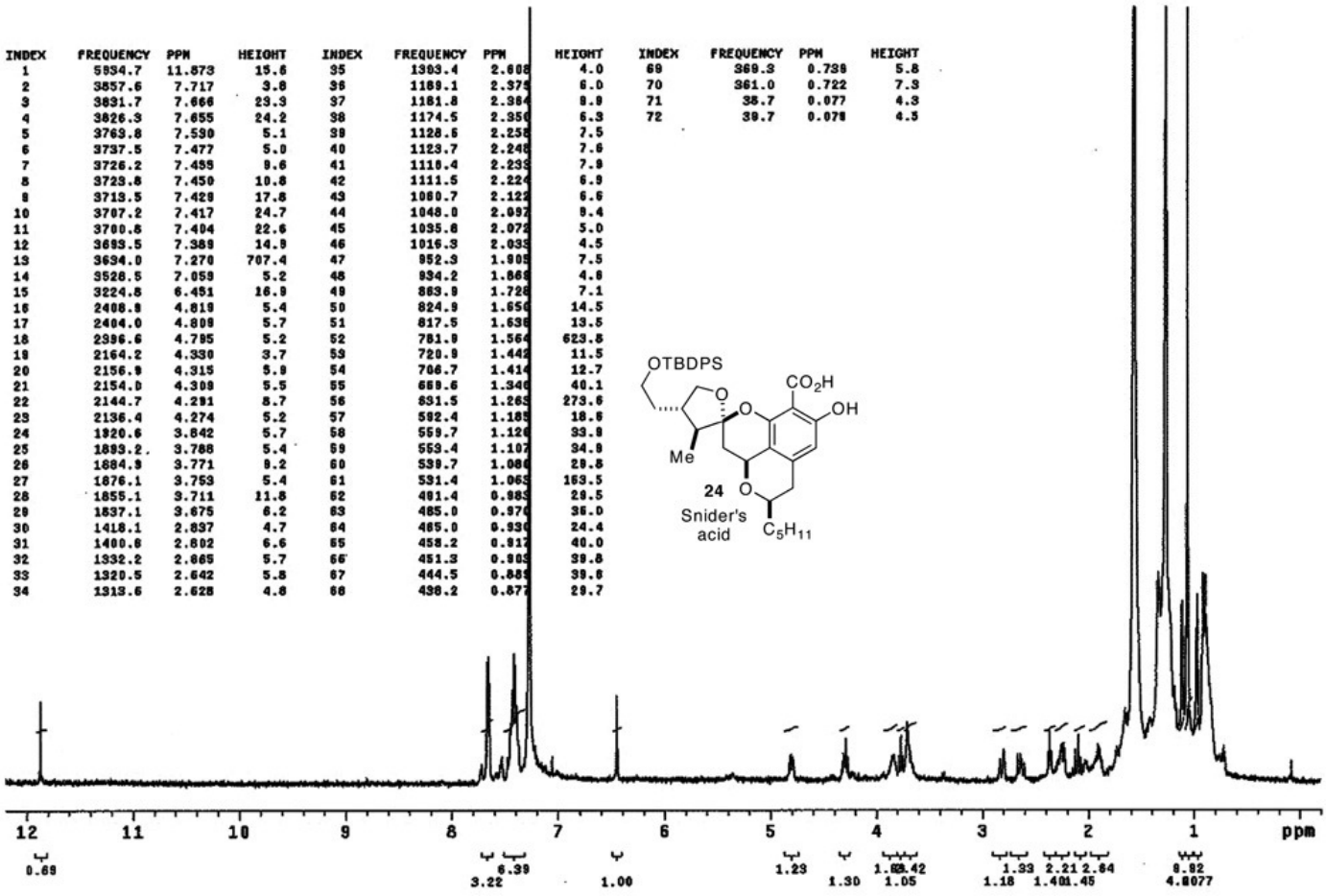
**Isobenzopyran 23:**

FTIR



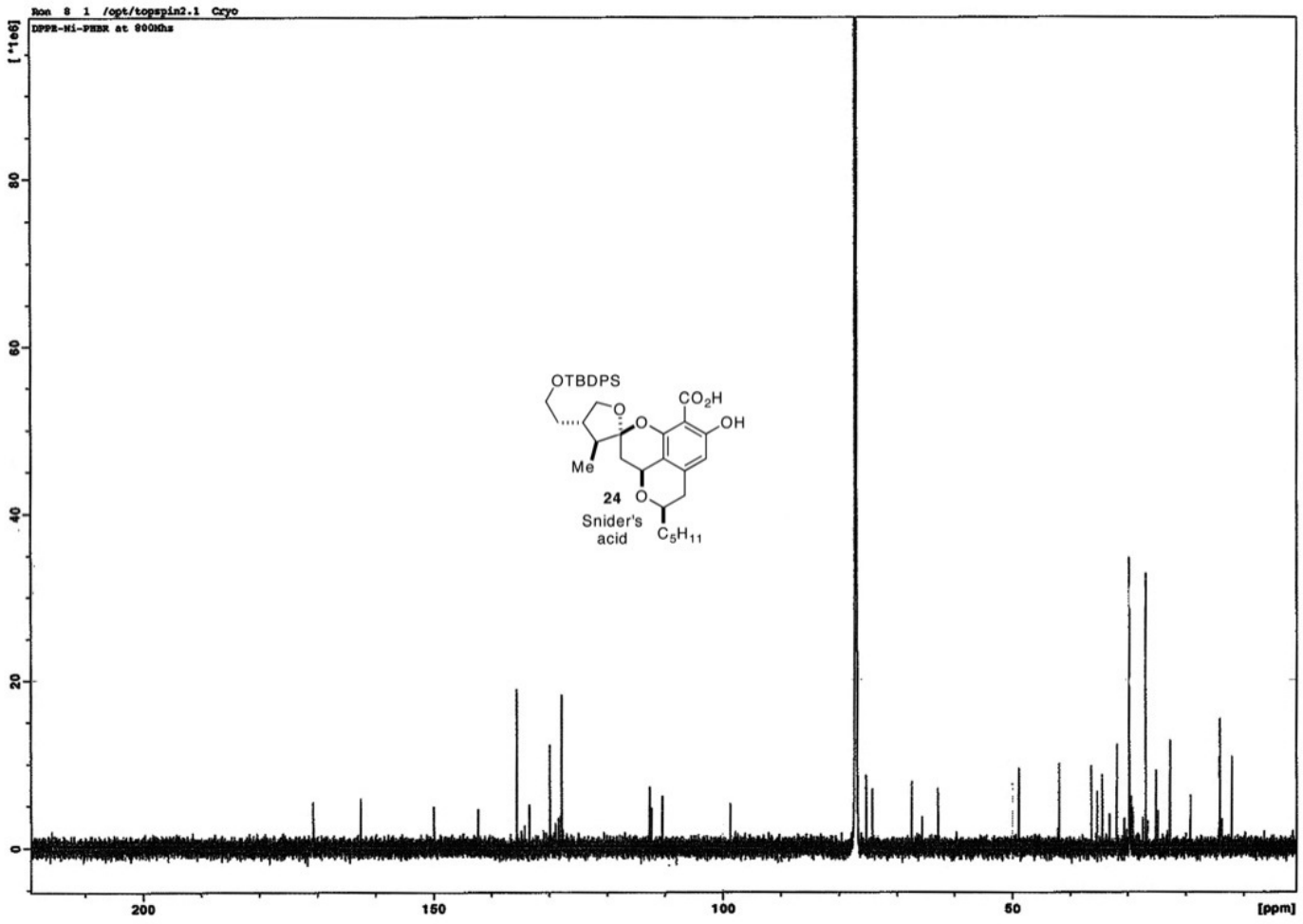
**Snider's Acid 24:**

$^{1}$H NMR



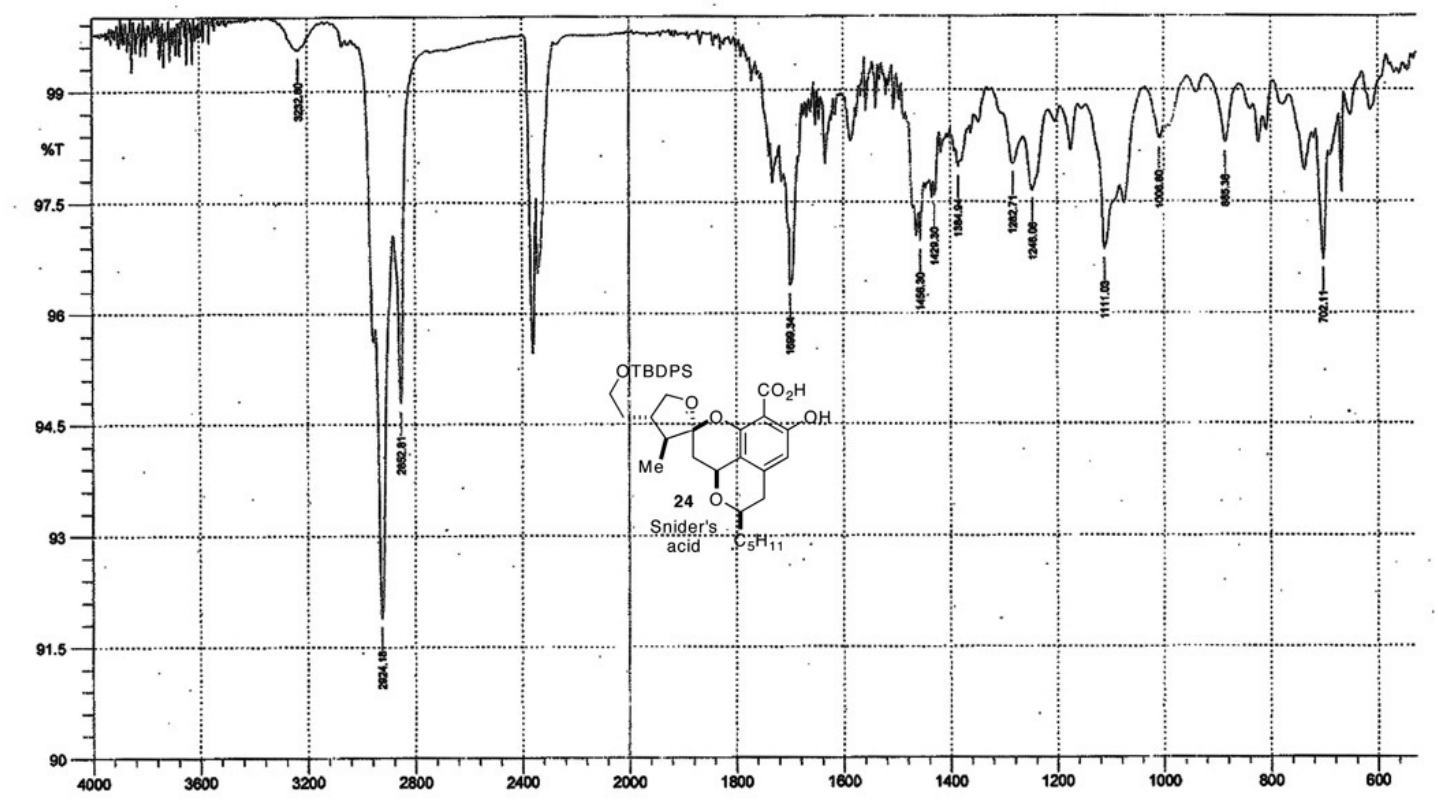
**Snider's Acid 24:**

$^{13}$C NMR



**Snider's Acid 24:**

FTIR



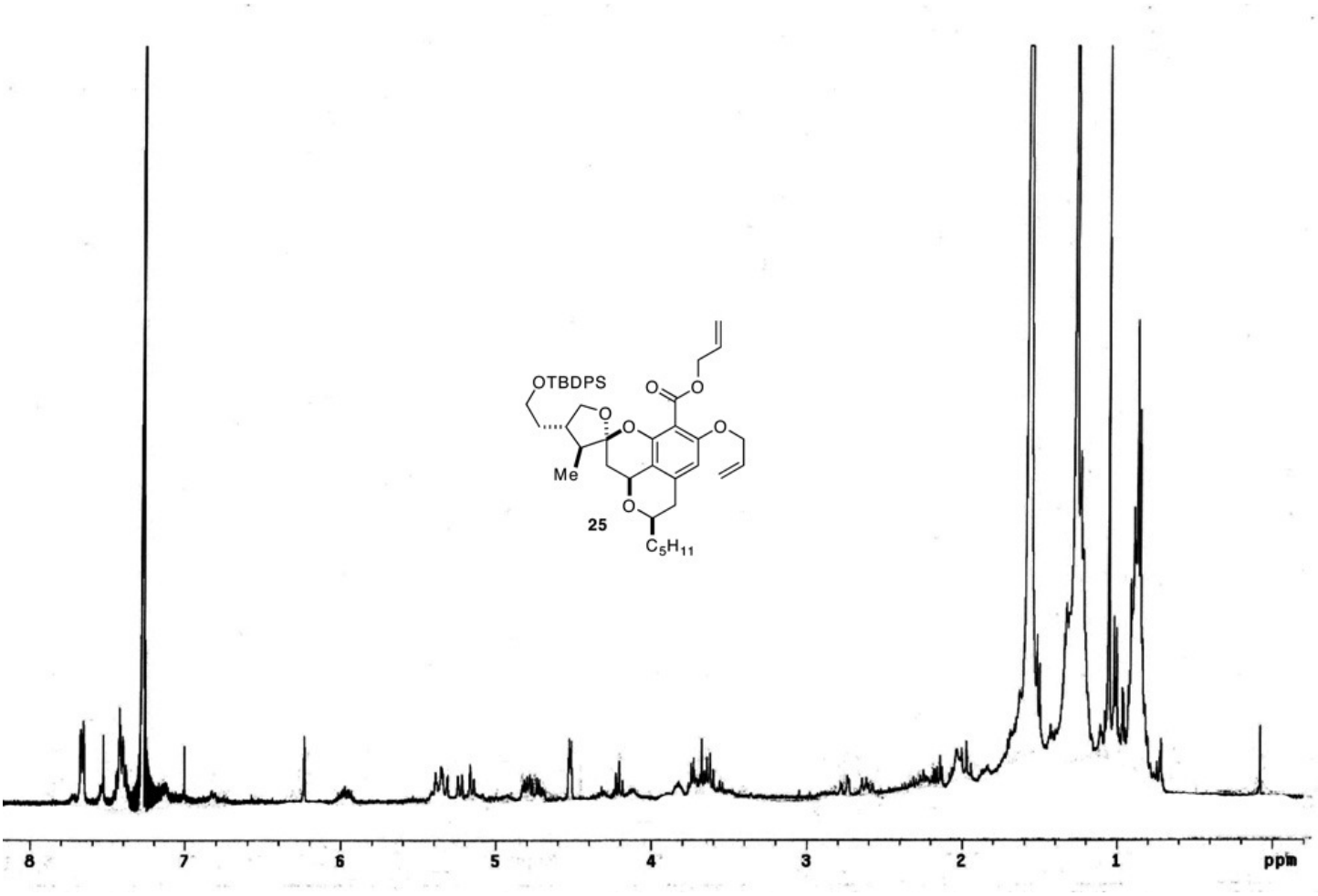

Comment;

No. of Scans;
Resolution;
Apodization;

Date/Time; 7/21/2010 11:09:12 AM
User; Admin

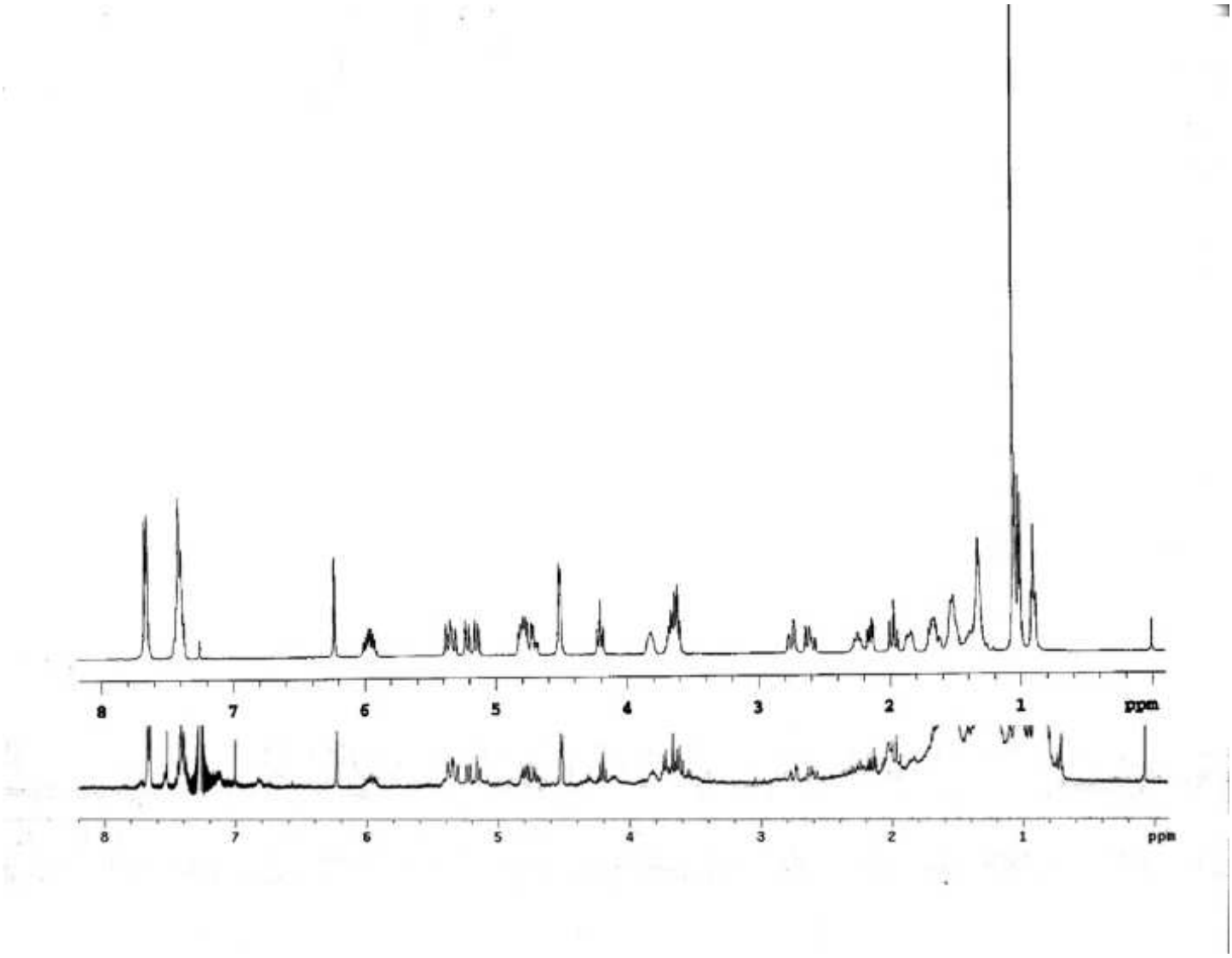
**Allyl ester 25:**

$^{1}$H NMR



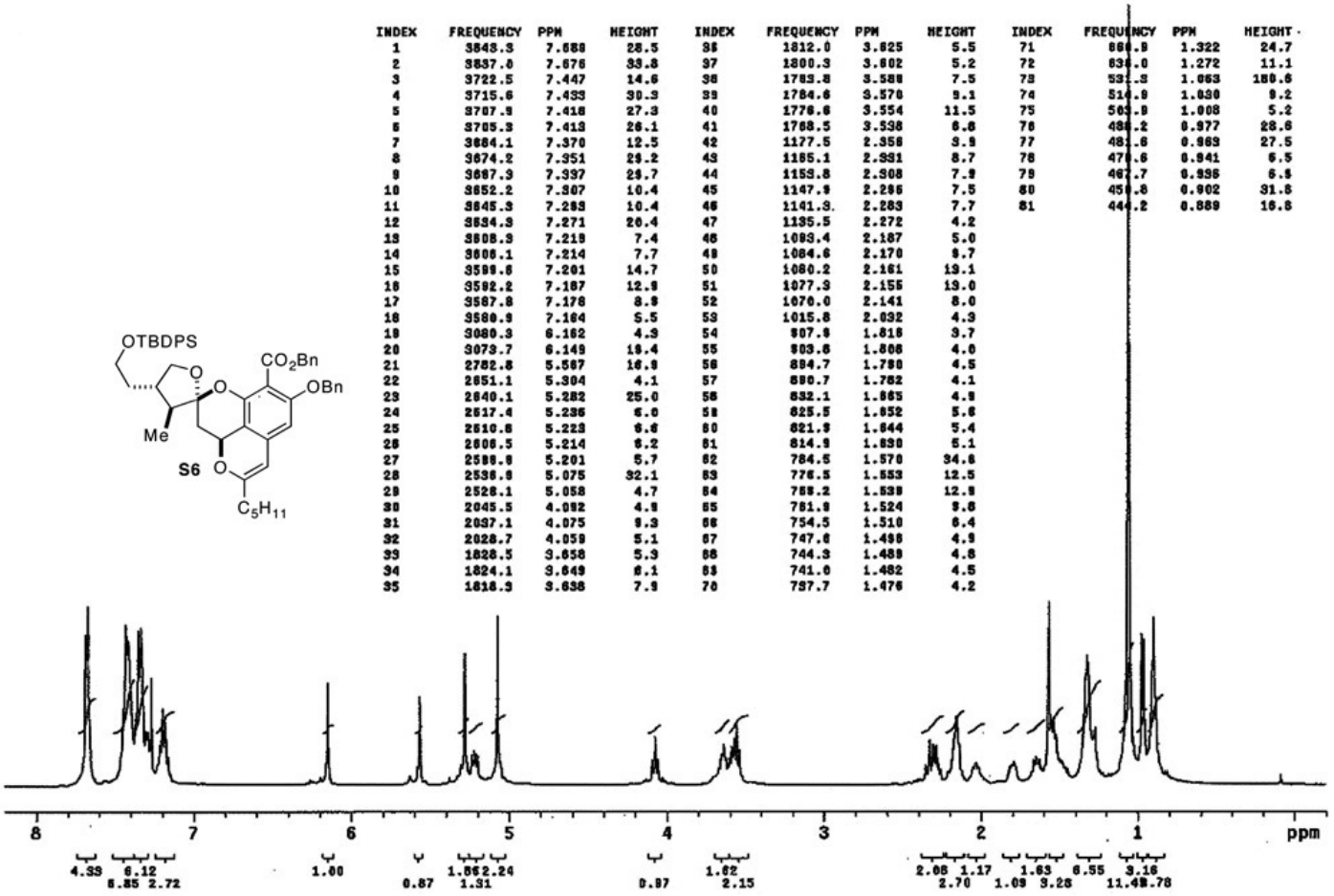
**Allyl ester 25:**

$^{1}$H NMR overlay with Snider's spectrum:
(Snider's is top, Pettus et al. is bottom)



**Benzyl Ester S6:**

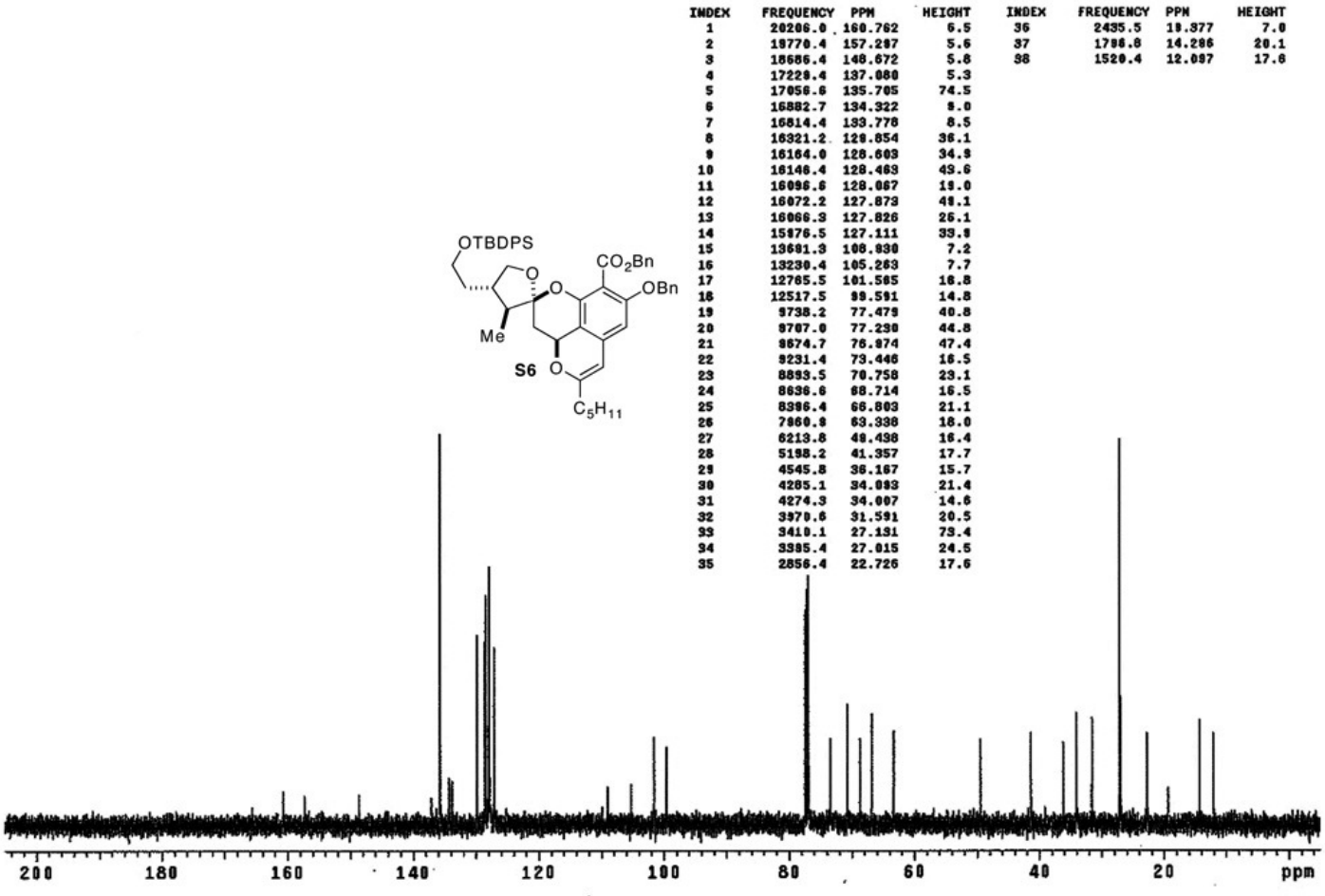
$^1$H NMR




| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3843.3 | 7.688 | 28.5 | 36 | 1812.0 | 3.625 | 5.5 | 71 | 660.9 | 1.322 | 24.7 |
| 2 | 3837.0 | 7.676 | 33.8 | 37 | 1800.3 | 3.602 | 5.2 | 72 | 636.0 | 1.272 | 11.1 |
| 3 | 3722.5 | 7.447 | 14.6 | 38 | 1783.8 | 3.568 | 7.5 | 73 | 531.8 | 1.063 | 186.6 |
| 4 | 3715.6 | 7.433 | 30.3 | 39 | 1784.6 | 3.570 | 9.1 | 74 | 514.9 | 1.030 | 9.2 |
| 5 | 3707.9 | 7.418 | 27.3 | 40 | 1776.6 | 3.554 | 11.5 | 75 | 503.9 | 1.008 | 5.2 |
| 6 | 3705.3 | 7.413 | 26.1 | 41 | 1768.5 | 3.538 | 6.6 | 76 | 488.2 | 0.977 | 28.6 |
| 7 | 3684.1 | 7.370 | 12.5 | 42 | 1177.5 | 2.356 | 3.9 | 77 | 481.6 | 0.963 | 27.5 |
| 8 | 3674.2 | 7.351 | 29.2 | 43 | 1165.1 | 2.331 | 8.7 | 78 | 470.6 | 0.941 | 6.5 |
| 9 | 3667.3 | 7.337 | 29.7 | 44 | 1153.8 | 2.308 | 7.9 | 79 | 467.7 | 0.935 | 6.5 |
| 10 | 3652.2 | 7.307 | 10.4 | 45 | 1147.9 | 2.296 | 7.5 | 80 | 450.8 | 0.902 | 31.6 |
| 11 | 3645.3 | 7.293 | 10.4 | 46 | 1141.3 | 2.283 | 7.7 | 81 | 444.2 | 0.889 | 16.6 |
| 12 | 3634.3 | 7.271 | 20.4 | 47 | 1135.5 | 2.272 | 4.2 | | | | |
| 13 | 3608.3 | 7.219 | 7.4 | 48 | 1093.4 | 2.187 | 5.0 | | | | |
| 14 | 3606.1 | 7.214 | 7.7 | 49 | 1084.6 | 2.170 | 8.7 | | | | |
| 15 | 3599.6 | 7.201 | 14.7 | 50 | 1080.2 | 2.161 | 19.1 | | | | |
| 16 | 3592.2 | 7.187 | 12.8 | 51 | 1077.3 | 2.155 | 19.0 | | | | |
| 17 | 3587.8 | 7.178 | 8.8 | 52 | 1070.0 | 2.141 | 8.0 | | | | |
| 18 | 3580.9 | 7.164 | 5.5 | 53 | 1015.8 | 2.032 | 4.3 | | | | |
| 19 | 3080.3 | 6.162 | 4.3 | 54 | 907.9 | 1.816 | 3.7 | | | | |
| 20 | 3073.7 | 6.149 | 18.4 | 55 | 903.6 | 1.808 | 4.0 | | | | |
| 21 | 2782.8 | 5.567 | 16.8 | 56 | 894.7 | 1.790 | 4.5 | | | | |
| 22 | 2651.1 | 5.304 | 4.1 | 57 | 890.7 | 1.782 | 4.1 | | | | |
| 23 | 2640.1 | 5.282 | 25.0 | 58 | 832.1 | 1.665 | 4.9 | | | | |
| 24 | 2617.4 | 5.236 | 6.6 | 59 | 825.5 | 1.652 | 5.6 | | | | |
| 25 | 2610.6 | 5.223 | 9.6 | 60 | 821.9 | 1.644 | 5.4 | | | | |
| 26 | 2606.5 | 5.214 | 9.2 | 61 | 814.9 | 1.630 | 5.1 | | | | |
| 27 | 2598.8 | 5.201 | 5.7 | 62 | 784.5 | 1.570 | 34.6 | | | | |
| 28 | 2536.9 | 5.075 | 32.1 | 63 | 776.5 | 1.553 | 12.5 | | | | |
| 29 | 2528.1 | 5.058 | 4.7 | 64 | 768.2 | 1.539 | 12.9 | | | | |
| 30 | 2045.5 | 4.092 | 4.9 | 65 | 761.9 | 1.524 | 9.6 | | | | |
| 31 | 2037.1 | 4.075 | 9.3 | 66 | 754.5 | 1.510 | 6.4 | | | | |
| 32 | 2028.7 | 4.059 | 5.1 | 67 | 747.6 | 1.496 | 4.9 | | | | |
| 33 | 1828.5 | 3.658 | 5.3 | 68 | 744.3 | 1.489 | 4.6 | | | | |
| 34 | 1824.1 | 3.649 | 8.1 | 69 | 741.0 | 1.482 | 4.5 | | | | |
| 35 | 1818.3 | 3.638 | 7.9 | 70 | 737.7 | 1.476 | 4.2 | | | | |

**Benzyl Ester S6:**

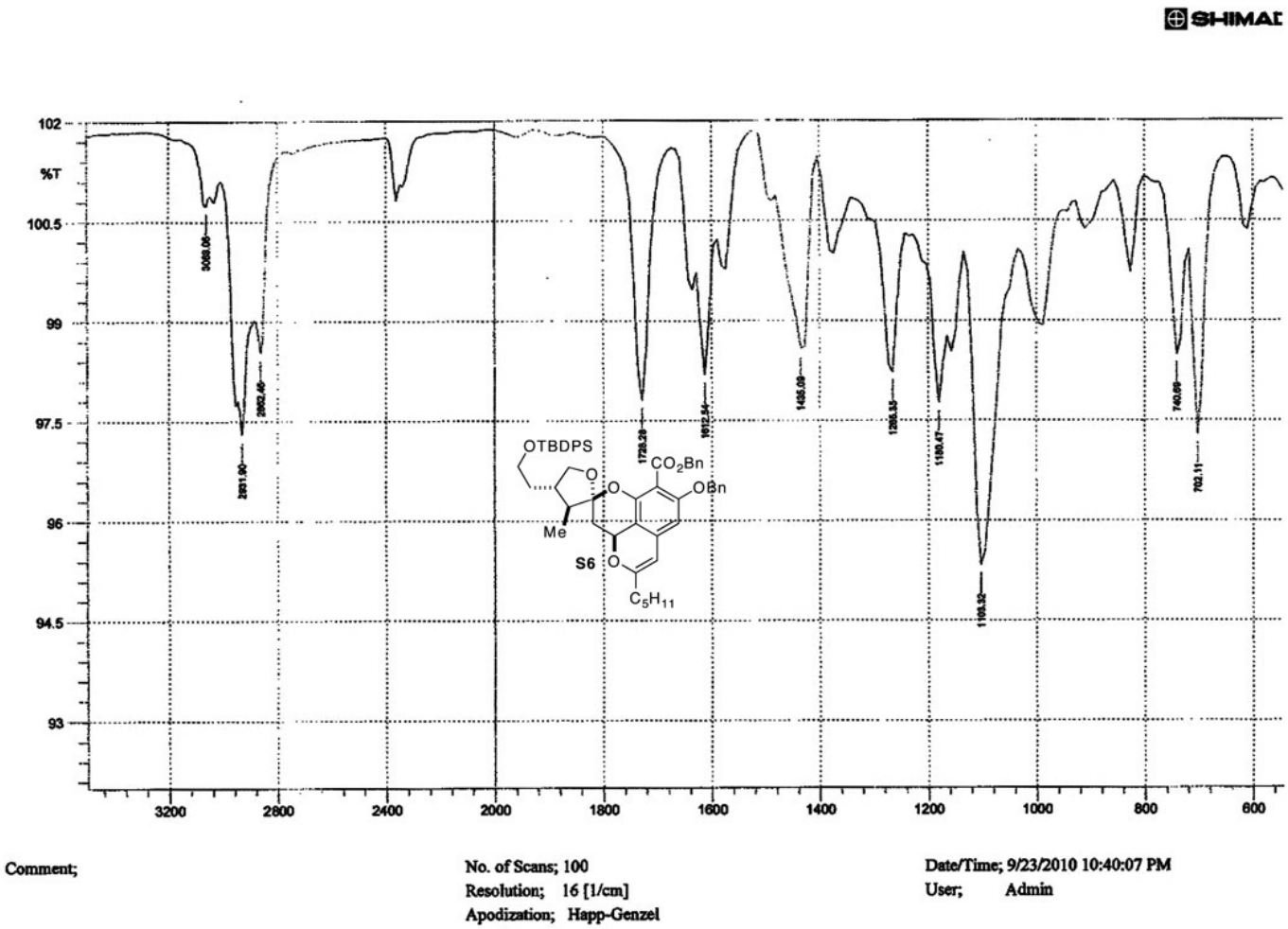
$^{13}$C NMR




| INDEX | FREQUENCY | PPM | HEIGHT | INDEX | FREQUENCY | PPM | HEIGHT |
|---|---|---|---|---|---|---|---|
| 1 | 20206.0 | 160.762 | 6.5 | 36 | 2435.5 | 19.377 | 7.0 |
| 2 | 19770.4 | 157.287 | 5.6 | 37 | 1786.8 | 14.286 | 20.1 |
| 3 | 18686.4 | 148.672 | 5.8 | 38 | 1520.4 | 12.097 | 17.6 |
| 4 | 17228.4 | 137.080 | 5.3 | | | | |
| 5 | 17058.6 | 135.705 | 74.5 | | | | |
| 6 | 16882.7 | 134.322 | 8.0 | | | | |
| 7 | 16814.4 | 133.778 | 8.5 | | | | |
| 8 | 16321.2 | 129.854 | 36.1 | | | | |
| 9 | 16164.0 | 128.603 | 34.8 | | | | |
| 10 | 16148.4 | 128.469 | 49.6 | | | | |
| 11 | 16096.6 | 128.057 | 19.0 | | | | |
| 12 | 16072.2 | 127.873 | 49.1 | | | | |
| 13 | 16066.3 | 127.826 | 25.1 | | | | |
| 14 | 15976.5 | 127.111 | 33.8 | | | | |
| 15 | 13691.3 | 108.930 | 7.2 | | | | |
| 16 | 13230.4 | 105.263 | 7.7 | | | | |
| 17 | 12765.5 | 101.565 | 16.8 | | | | |
| 18 | 12517.5 | 99.591 | 14.8 | | | | |
| 19 | 9738.2 | 77.479 | 40.8 | | | | |
| 20 | 9707.0 | 77.230 | 44.8 | | | | |
| 21 | 9674.7 | 76.974 | 47.4 | | | | |
| 22 | 9231.4 | 73.446 | 16.5 | | | | |
| 23 | 8893.5 | 70.758 | 23.1 | | | | |
| 24 | 8636.6 | 68.714 | 16.5 | | | | |
| 25 | 8396.4 | 66.803 | 21.1 | | | | |
| 26 | 7960.8 | 63.338 | 18.0 | | | | |
| 27 | 6213.8 | 49.438 | 16.4 | | | | |
| 28 | 5198.2 | 41.357 | 17.7 | | | | |
| 29 | 4545.8 | 36.167 | 15.7 | | | | |
| 30 | 4285.1 | 34.093 | 21.4 | | | | |
| 31 | 4274.3 | 34.007 | 14.6 | | | | |
| 32 | 3970.6 | 31.591 | 20.5 | | | | |
| 33 | 3410.1 | 27.131 | 73.4 | | | | |
| 34 | 3385.4 | 27.015 | 24.5 | | | | |
| 35 | 2856.4 | 22.726 | 17.6 | | | | |

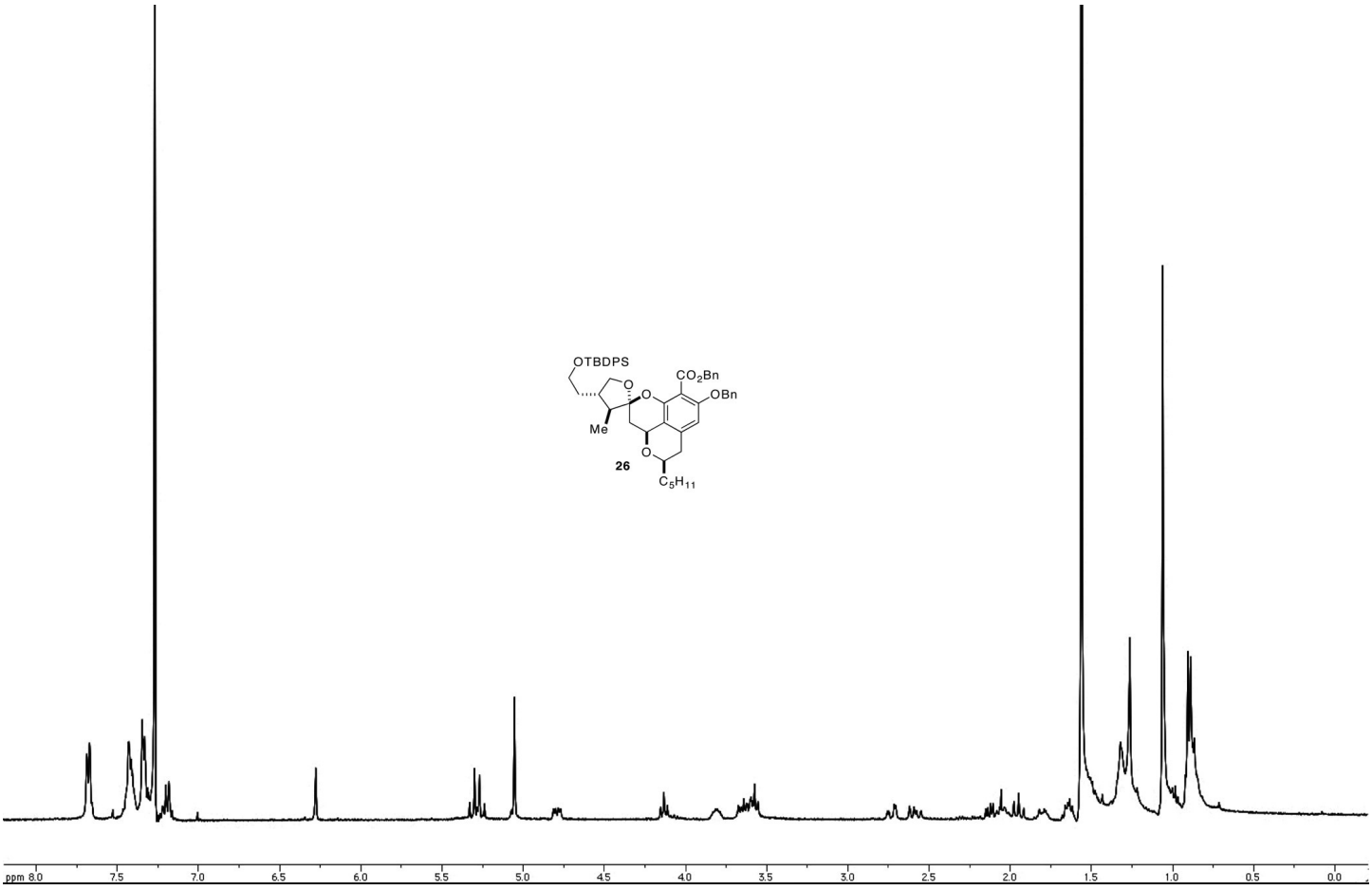
**Benzyl Ester S6:**

FTIR



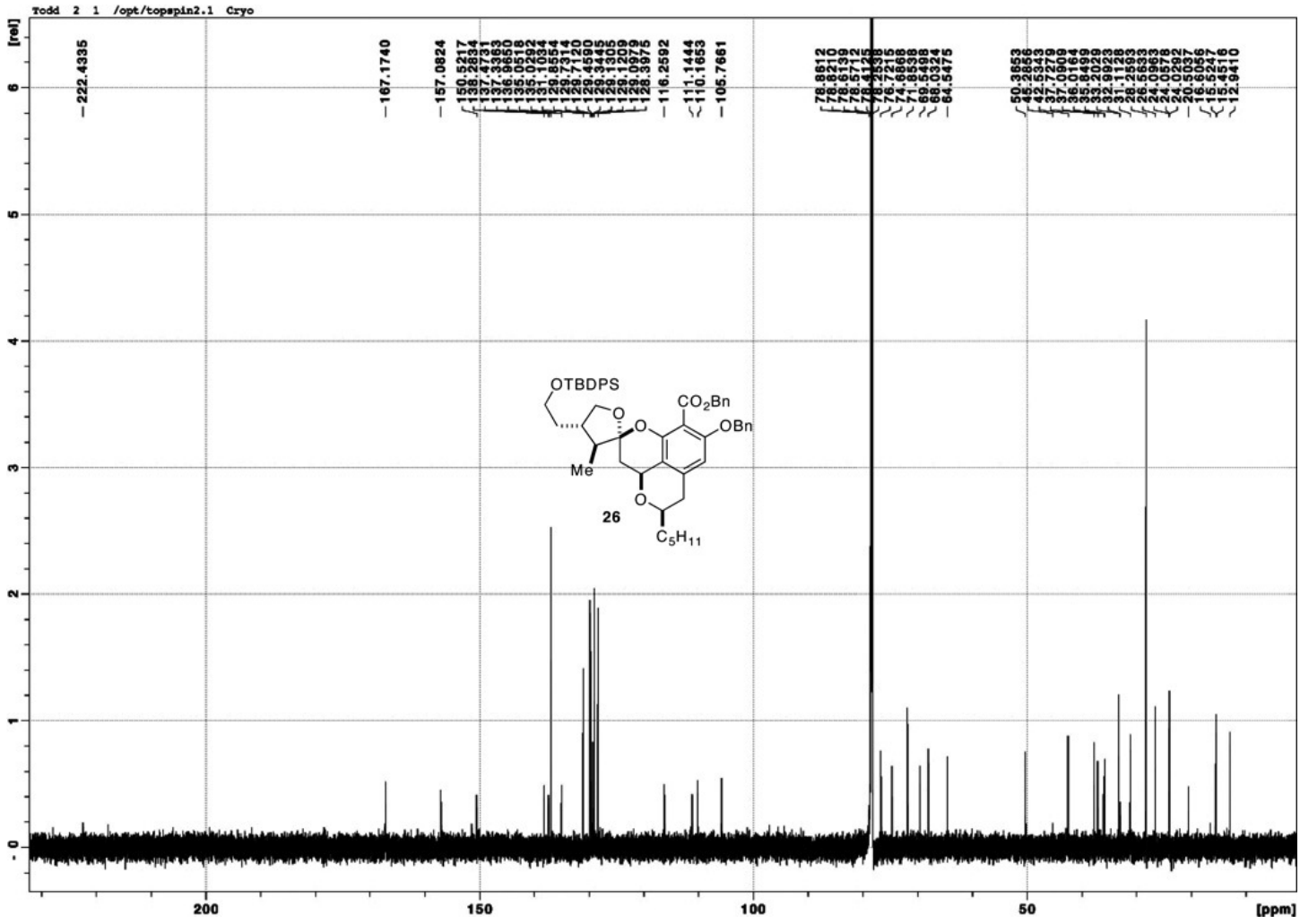
**Benzyl ester 26:**

$^{1}$H NMR



**Benzyl ester 26:**

$^{13}$C NMR



**Benzyl ester 26:**

FTIR