Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

A Stereocontrolled Synthesis of the C9-C19 Subunit of (+)-Peloruside A

Sadagopan Raghavan,* V. Vinoth Kumar

Division of Natural Product Chemistry, Indian Institute of Chemical Technology, Hyderabad 500007, India

Table of Contents

General Information

All materials were used as received from a commercial supplier without further purification. All anhydrous reactions were performed using oven-dried or flame dried glassware, which was then cooled under nitrogen gas. Tetrahydrofuran (THF), toluene was distilled over Na/Ph_2CO under nitrogen atmosphere. Dichloromethane (CH_2Cl_2), hexane, acetonitrile, dimethylsulfoxide, dimethylformamide, triethylamine (TEA), 2,6-lutidine and diethyl ether (Et_2O) were dried over CaH_2 and distilled prior to use. 4 Å Molecular sieves were flame dried and then cooled under high vacuum prior to use. All reactions were monitored by E. Merck analytical thin layer chromatography (TLC) plates and analyzed with 254 nm UV light and/or anisaldehyde–sulfuric acid or potassium permanganate or PMA treatment. Silica gel for column chromatography was purchased from Acme (Silica Gel 60-120, 100-200 mesh). All ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Gemini 200, Avance 300, Inova 400, Inova 500 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual $CHCl_3$ as an internal reference (^{1}H: δ 7.26 ppm, ^{13}C: δ 77.00 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Enantiomeric excess were recorded using Waters HPLC instrument. For the preparation of dienol silyl ketene acetal an inert atmosphere filtration setup was employed. Sealed tube was purchased from Aldrich Company. Mass spectra were recorded using Waters Mass spectrometer. HPLC spectra were recorded

using Waters 2998 spectrometer. High resolution mass (HRMS) were recorded using Applied Bio-Sciences HRMS spectrometer and Thermo LTQ-Orbitrap mass spectrometer. All IR-spectra were recorded using Nexus 870-FT-IR Thermo Nicolet spectrometer.

Experimental section

Compound 11. To a suspension of NaH (4 g, 60% in Nujol, 100 mmol) in anhydrous THF (300 mL) cooled at 0 ^{o}C was added a solution of neopentyl glycol **10** (10.4 g, 100 mmol) in anhydrous THF (100 mL) dropwise over 30 minutes. The mixture was stirred for 16 h at rt during which a white color thick mono anion was formed. TBDPS-Cl (27.3 mL, 105 mmol) was added slowly at 0 ^{o}C over 20 minutes, the mixture stirred for an additional 3 h and quenched with aq NH_4Cl solution at 0 ^{o}C. The layers were separated and the aqueous layer extracted with ethyl acetate (3×200 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using hexanes/EtOAc (9:1, v/v) to afford pure mono protected alcohol **11** (29 g, 85 mmol) in 85% yield as a viscous oil. TLC R_f = 0.25 (15% EtOAc/Hexanes). IR (KBr): 3446, 3070, 2957, 2860, 1469, 1108, 821, 703, 506 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69-7.40 (m, 4H), 7.46-7.38 (m, 6H), 3.51 (s, 2H), 3.47 (s, 2H), 1.06 (s, 9H), 0.89 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6, 133.1, 129.7, 127.7, 71.9, 71.0, 37.0, 26.8, 21.4, 19.2. MS (ESI) 365 $[M+Na]^+$. HRMS (ESI) *m/z* calcd for $C_{21}H_{30}O_2NaSi$ 365.1912; found 365.1921.

Compound 9. The mixture of mono protected alcohol **11** (6.8 g, 20 mmol) and IBX (6.2 g, 24 mmol) in ethyl acetate (60 mL) was heated at reflux for 6 h. The solid material was

filtered and washed with ethyl acetate (2×30 mL). The combined filtrates were concentrated and the residue purified by flash column chromatography using hexanes/EtOAc (9:1, v/v) to afford pure aldehyde **9** (6.5 g, 19 mmol) in 95% yield as a viscous oil. TLC R_f = 0.35 (15% EtOAc/Hexanes). IR (KBr): 2959, 2932, 2859, 1706, 1471, 1427, 1110, 822, 704, 505 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.62-7.58 (m, 4H), 7.42-7.34 (m, 6H), 3.60 (s, 2H), 1.06 (s, 6H), 1.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6, 135.6, 133.0, 129.7, 127.7, 68.8, 48.3, 26.7, 19.2, 18.5. MS (ESI) 379 $[K]^+$.

Compound 8. To a solution of *i*Pr_2NH (5.6 mL, 40.0 mmol) in anhydrous THF (40 mL) cooled at 0 °C was added *n*-BuLi (15.4 mL, 40.0 mmol, 2.6 M in hexane) over 5 minutes. The clear, colorless solution was stirred at 0 °C for 20 minutes and then cooled to -78 °C. Freshly distilled 2,2,6-trimethyl-[1,3]dioxine-4-one (4.7 mL, 36.0 mmol) was added neat over 10 minutes and the resulting yellowish solution was stirred at -78 °C for 60 minutes. Freshly distilled TMS-Cl (5.3 mL, 42 mmol) was added slowly over 10 min and the reaction mixture was stirred for an additional 30 minutes at -78 °C. The thick, orange suspension was allowed to warm to rt over 90 minutes and was then filtered over anhydrous Na_2SO_4 under nitrogen atmosphere. The filter cake was rinsed twice with anhydrous hexane (2×15 mL) and the clear, orange filtrate was concentrated under reduced pressure at low temperature (30-35 ^oC). The remaining red oil was distilled under reduced pressure (0.4 mm/Hg, 60 °C) to yield **8** (29.3 g, 78% yield) as a colorless liquid. The silyl ether **8** was stored at 0 ^oC and used within a week. ^1H NMR (300 MHz, $CDCl_3$): δ 4.55 (s, 1H), 4.00 (s, 1H), 3.80 (s, 1H), 1.53 (s, 6H), 0.26 (s, 9H).

***Anti–1,3-acetonide of 15*.** To a solution of diol **15** (45 mg, 0.1 mmol) in anhydrous dichloromethane (2 mL) was added 2,2-dimethoxypropane (0.1 mL) and catalytic amounts of CSA. The mixture was stirred at rt for 1 h. Few drops of Et_3N, enough to neutralize CSA, were added and the volatiles removed under reduced pressure. The residue was purified by column chromatography using 10% hexanes/EtOAc (v/v) as the eluent to afford the corresponding acetonide (45 mg, 0.095 mmol) in 95% yield. TLC R_f = 0.4 (20% EtOAc/Hexanes). IR (KBr): 2960, 2860, 1735, 1469, 1428, 1369, 1257, 1169, 1107, 822, 703, 505 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73-7.64 (m, 4H), 7.48-7.37 (m, 6H), 4.21-4.15 (m, 1H), 3.87 (dd, *J* = 9.9, 5.9 Hz, 1H), 3.69 (s, 3H), 3.52 (d, *J* = 8.9 Hz, 1H), 3.33 (d, *J* = 8.9 Hz, 1H), 2.54 (dd, *J* = 15.9, 7.9 Hz, 1H), 2.43 (dd, *J* = 15.9, 4.9 Hz, 1H), 1.92-1.86 (m, 1H), 1.47-1.40 (m, 1H), 1.37 (s, 3H), 1.30 (s, 3H), 1.07 (s, 9H), 0.87 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 135.7, 133.7, 129.5, 127.5, 100.5, 69.3, 69.0, 63.9, 51.6, 40.6, 38.7, 32.6, 26.9, 24.6, 24.1, 20.2, 19.4, 19.1. MS (ESI) 521 $[M+Na]^+$. HRMS (ESI) *m/z* calcd for $C_{29}H_{42}O_5NaSi$ 521.26937; found 521.26853.

***Compound 23*.** To a stirred suspension of $LiAlH_4$ (7.4 g, 200 mmol) in anhydrous THF (300 mL) cooled at -10 ^oC was added a solution of diethyl ethyl malonate **22** (18.8 g, 100 mmol) in THF (300 mL) dropwise over 30 minutes. The reaction mixture was stirred at rt for 16 h. The reaction mixture was cooled to -10 °C and an additional 200 mL of THF was added. The reaction was quenched with aq 20% NaOH solution followed by H_2O. This mixture was further diluted with THF (300 mL), filtered through a pad of Celite and the precipitated aluminum salts were washed with THF repeatedly until all the diol was removed from the aluminum salt (It required 6 to 8 times of washing). The combined

filtrates were concentrated under reduced pressure to give an yellow oil which was distilled under reduced pressure at 110 °C, to provide diol **23** as a colorless liquid (6.8 g, 65 mmol) in 65% yield.^{1}H NMR (500 MHz, $CDCl_3$): δ 3.82-3.69 (m, 2H), 3.62-3.58 (m, 2H), 1.64-1.56 (m, 1H), 1.32-1.24 (m, 2H), 0.92 (t, *J* = 7.9 Hz, 3H).

***Compound 24*.** To a suspension of NaH (2 g, 60% in Nujol, 50 mmol) in anhydrous THF (100 mL) cooled at 0 ^{o}C was added a solution of diol **23** (5.2 g, 50 mmol) in anhydrous THF (100 mL) dropwise over 30 minutes. Stirring was continued for 16 h at rt. TBS-Cl (9 g, 60 mmol) in anhydrous THF (30 mL) was added at 0 ^{o}C slowly. After 3 h of stirring at rt, the reaction was quenched with aq NH_4Cl at 0 ^{o}C. The layers were separated and the aqueous layer was extracted with ethyl acetate (3×60 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated and the residue purified by column chromatography using hexanes/EtOAc (9:1, v/v) to afford alcohol **24** (7.7 g, 35 mmol) in 70% yield as a colorless oil. TLC R_f = 0.15 (20% EtOAc/Heaxanes). IR (KBr): 3421, 3210, 2894, 1983, 1739, 1643, 1526, 1120, 709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (dd, *J* = 9.8, 3.9 Hz, 1H), 3.69 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.64-3.54 (m, 2H), 1.66-1.56 (m, 1H), 1.36-1.22 (m, 2H), 0.98-0.90 (m, 12H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 67.0, 66.2, 43.5, 25.7, 20.5, 18.1, 11.6, -3.7, -5.7. MS (ESI) 241 $[M+Na]^+$. HRMS (ESI) *m/z* calcd for $C_{11}H_{26}O_2NaSi$, 241.1599; found 241.1608.

***Compounds 25 and 26*.** To a solution of racemic alcohol **24** (6.6 g, 30 mmol) and Amano lipase (0.50 g) in diisopropyl ether (90 mL) was added freshly distilled vinyl acetate (4 mL, 75 mmol). The heterogeneous mixture was stirred at rt for 12 h before being filtered through Celite to remove the enzyme. The filter cake was washed with Et_2O (2×40 mL) and the combined filtrates were concentrated under reduced pressure. Purification of the

residue by column chromatography using hexanes/EtOAc (95:5, v/v) afforded initially (*R*)-acetate **26** (3.4 g, 13 mmol) in 43% yield as an oil and later (*S*)-alcohol **25** (2.7 gm, 12.3 mmol) in 41% yield as an oil. ***Compound 26.*** TLC R_f = 0.15 (20% EtOAc/Heaxnes). $[\alpha]_D^{35}$ = +6.2 (*c* 1, $CHCl_3$). IR (KBr): 2890, 2856, 1798, 1734, 1640, 1529, 1109, 708 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.06 (d, *J* = 5.6 Hz, 2H), 3.60-3.54 (m, 2H), 2.04 (s, 3H), 1.78-1.64 (m, 1H), 1.42-1.24 (m, 2H), 0.98-0.88 (m, 12H), 0.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 64.5, 62.3, 41.8, 25.8, 20.9, 20.7, 18.3, 11.4, -5.5. MS (ESI) 283 $[M+Na]^+$. HRMS (ESI) *m/z* calcd for $C_{13}H_{28}O_3NaSi$ 283.1705; found 283.1712. ***Compound 25.*** $[\alpha]_D^{35}$ = -3.9 (*c* 1, $CHCl_3$), all other physical characteristics were identical to compound **24**.

Compound epi-25. To a solution of acetate **26** (3.1 g, 12 mmol) in MeOH (24 mL) was added K_2CO_3 (163 mg, 1.2 mmol). The reaction mixture was stirred for 2 h at rt. The mixture was filtered through a pad of Celite and the filtrate concentrated in *vacuo*. The product was purified by column chromatography using hexanes/EtOAc (95:5, v/v) as the eluent to afford alcohol *epi*-**25** (2.4 g, 11 mmol) in 92% yield. $[\alpha]_D^{35}$ = +4.4 (*c* 1, $CHCl_3$), all other physical characteristics were identical to compound **25**.

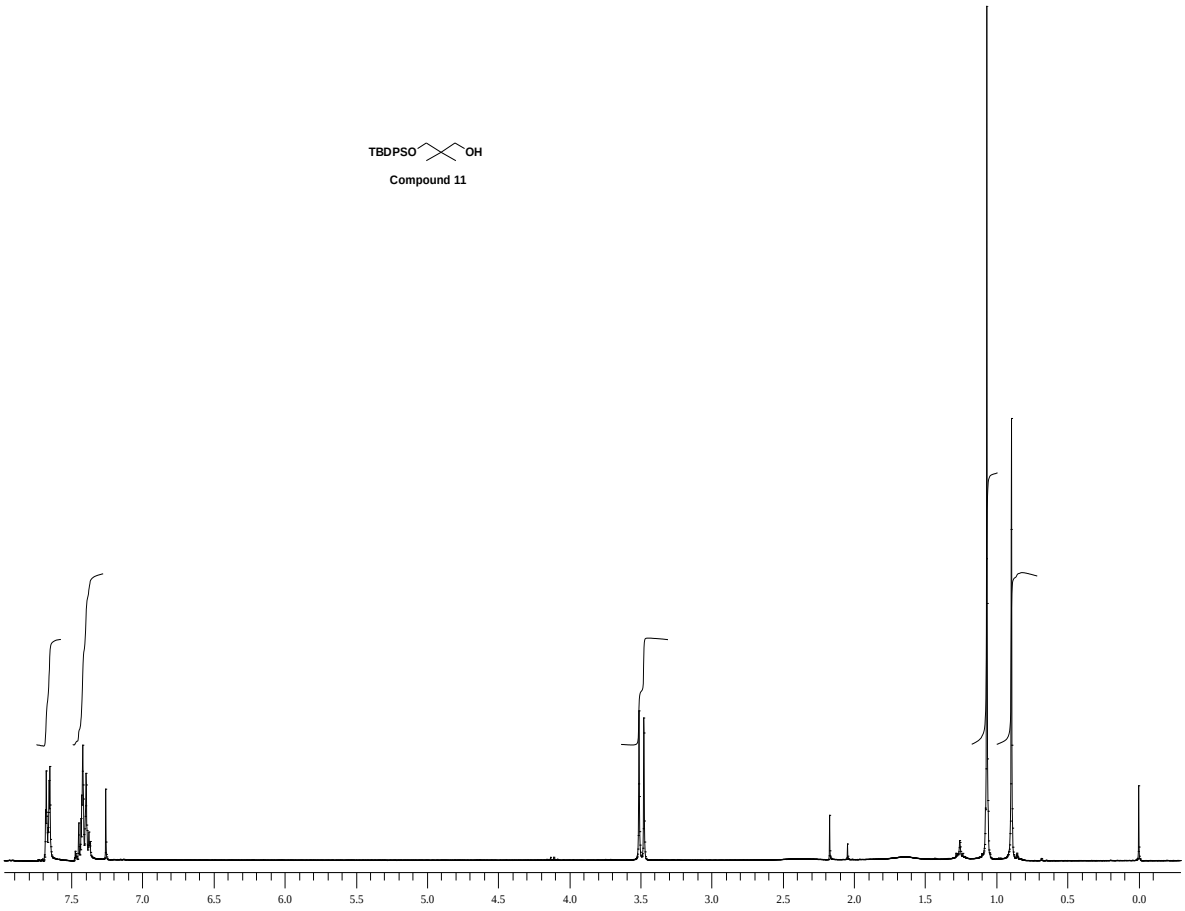
Alcohol epi 33 by resolution. Obtained by an identical route as detailed for racemic alcohol **24**. Yield 41%. TLC R_f = 0.24 (20% EtOAc/Hexanes). $[\alpha]_D^{37}$ = -5.3 (*c* 1.5, $CHCl_3$). IR (KBr): 3420, 2959, 2931, 2858, 1467, 1109, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.80-7.64 (m, 4H), 7.44-7.32 (m, 6H), 3.76 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.35 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.67-3.61 (m, 2H), 1.68-1.62 (m, 1H), 1.38-1.24 (m, 2H), 1.08 (s, 9H), 0.75 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.5, 134.8, 129.8,

127.7, 67.2, 65.9, 43.8, 26.8, 20.5, 19.1, 11.7. MS (ESI) 365 $[M+Na]^+$. HRMS (ESI) *m/z* calcd for $C_{21}H_{30}O_2NaSi$ 365.19073; found 365.19115.

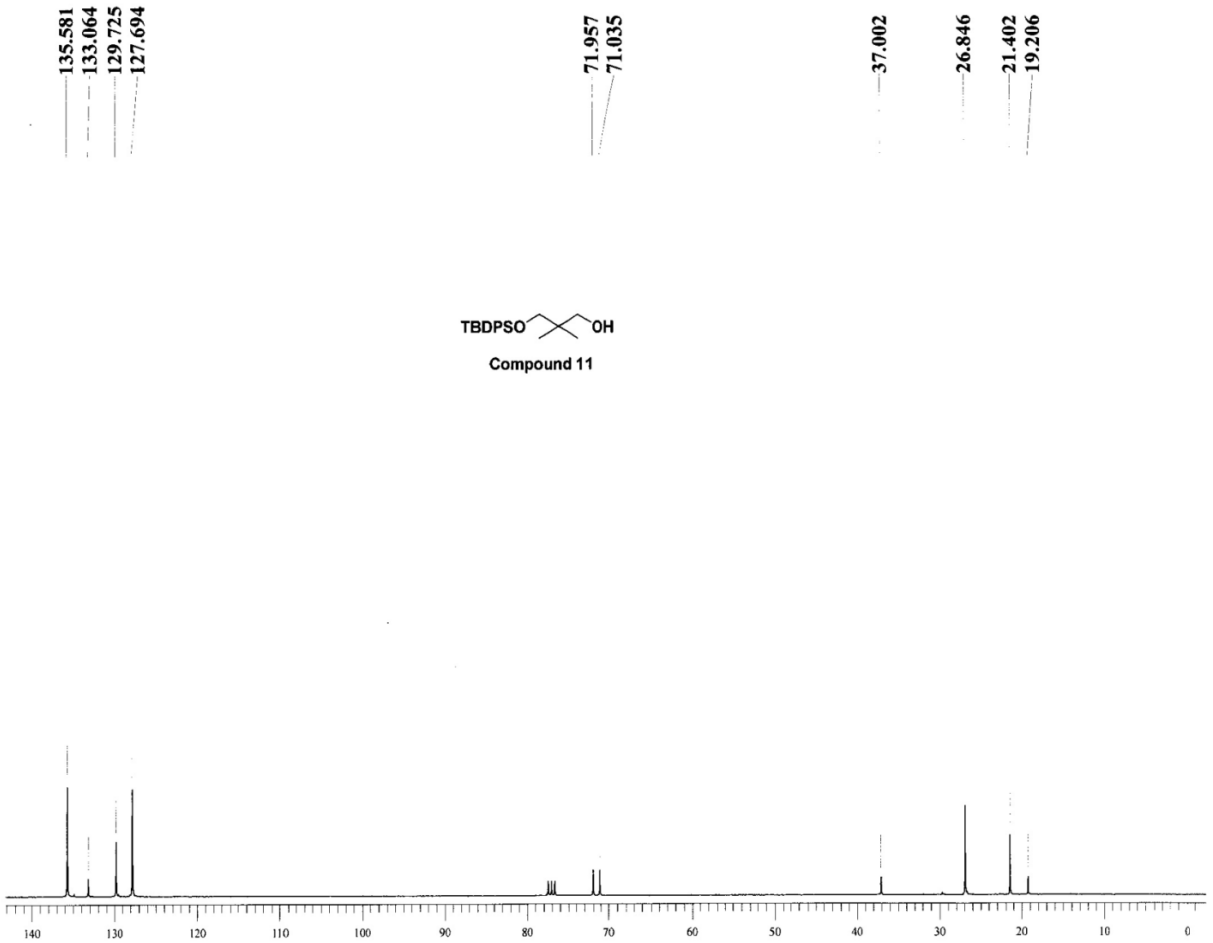
***Acetate via resolution*.** Yield 43%. TLC R_f = 0.32 (20% EtOAc/Hexanes). $[\alpha]_D^{37}$ = +2.9 (*c* 1.3, $CHCl_3$). IR (KBr): 2959, 2932, 1741, 1240, 1110, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74-7.62 (m, 4H), 7.48-7.32 (m, 6H), 4.18-4.09 (m, 2H), 3.72-3.58 (m, 2H), 1.98 (s, 3H), 1.80-1.68 (m, 1H), 1.48-1.30 (m, 2H), 1.03 (s, 9H), 0.87 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 135.5, 133.5, 129.5, 127.5, 64.3, 62.8, 41.8, 26.7, 26.5, 20.7, 19.2, 11.3. MS (ESI) 407 $[M+Na]^+$. HRMS (ESI) *m/z* calcd for $C_{23}H_{33}O_3Si$ 385.21935; found 385.21866.

***Compound 33*.** Prepared by K_2CO_3 catalyzed hydrolysis as described for compound **26**. Yield 90%. $[\alpha]_D^{37}$ = +5.1 (*c* 1.2, $CHCl_3$). The IR, NMR data were identical to that of *epi*-**33.**

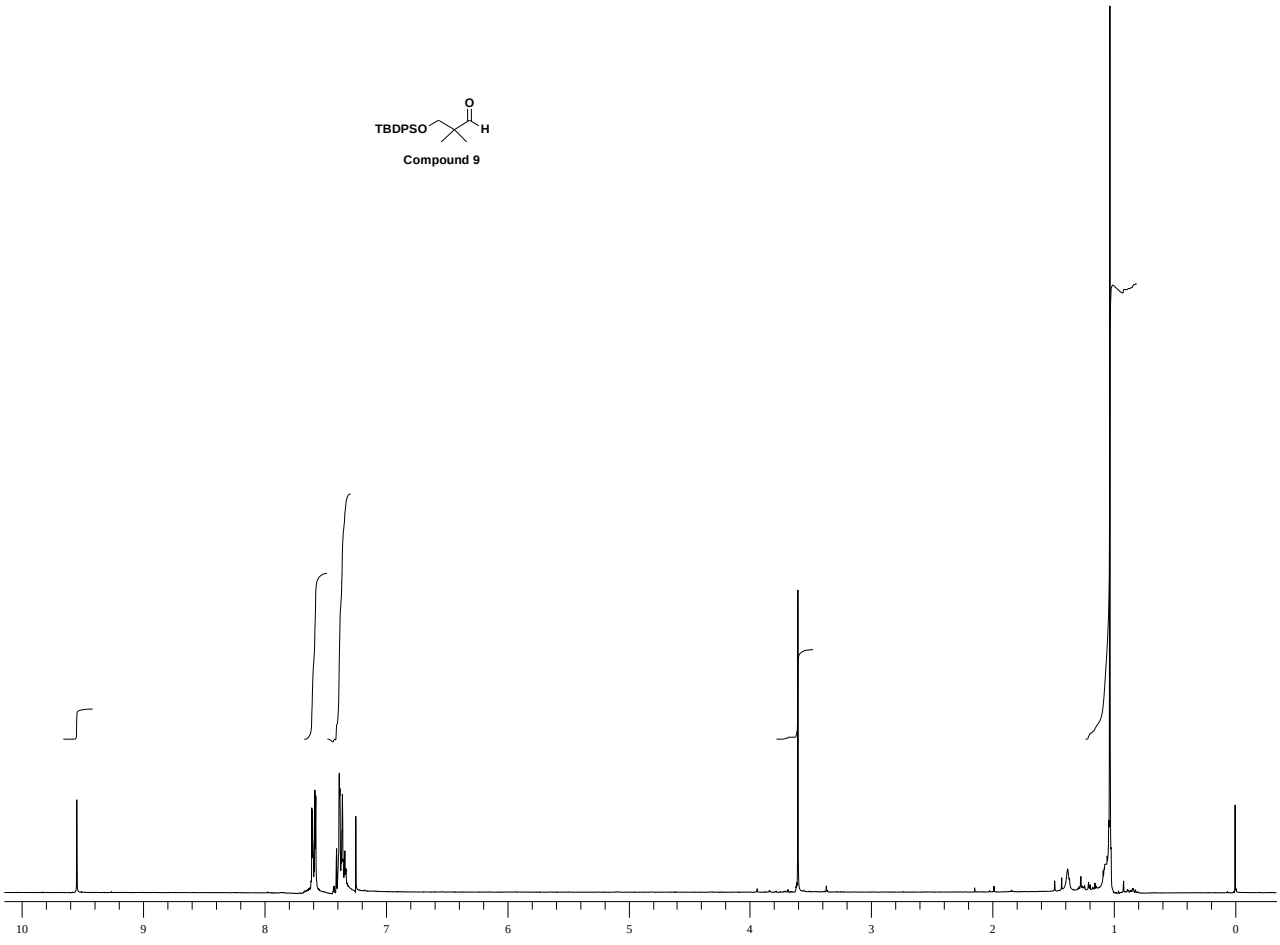
^{1}H NMR spectrum of Compound 11



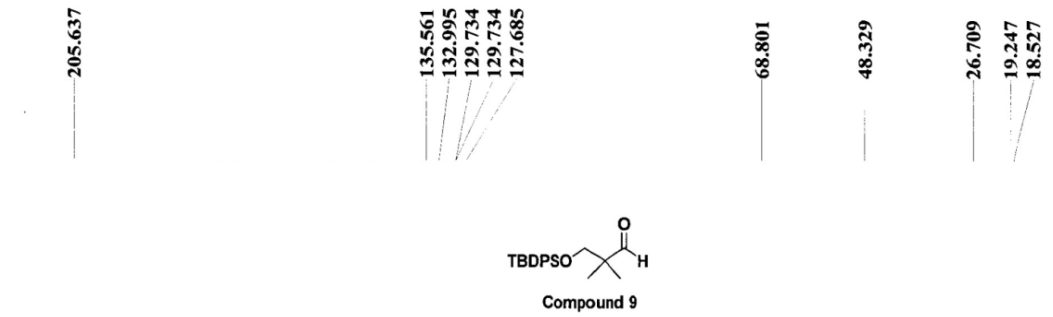
^{13}C NMR spectrum of Compound 11

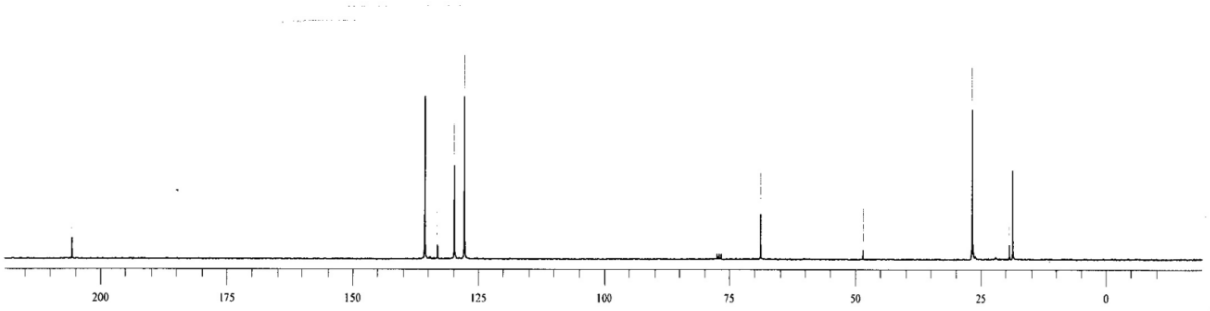


^{1}H NMR spectrum of Compound 9

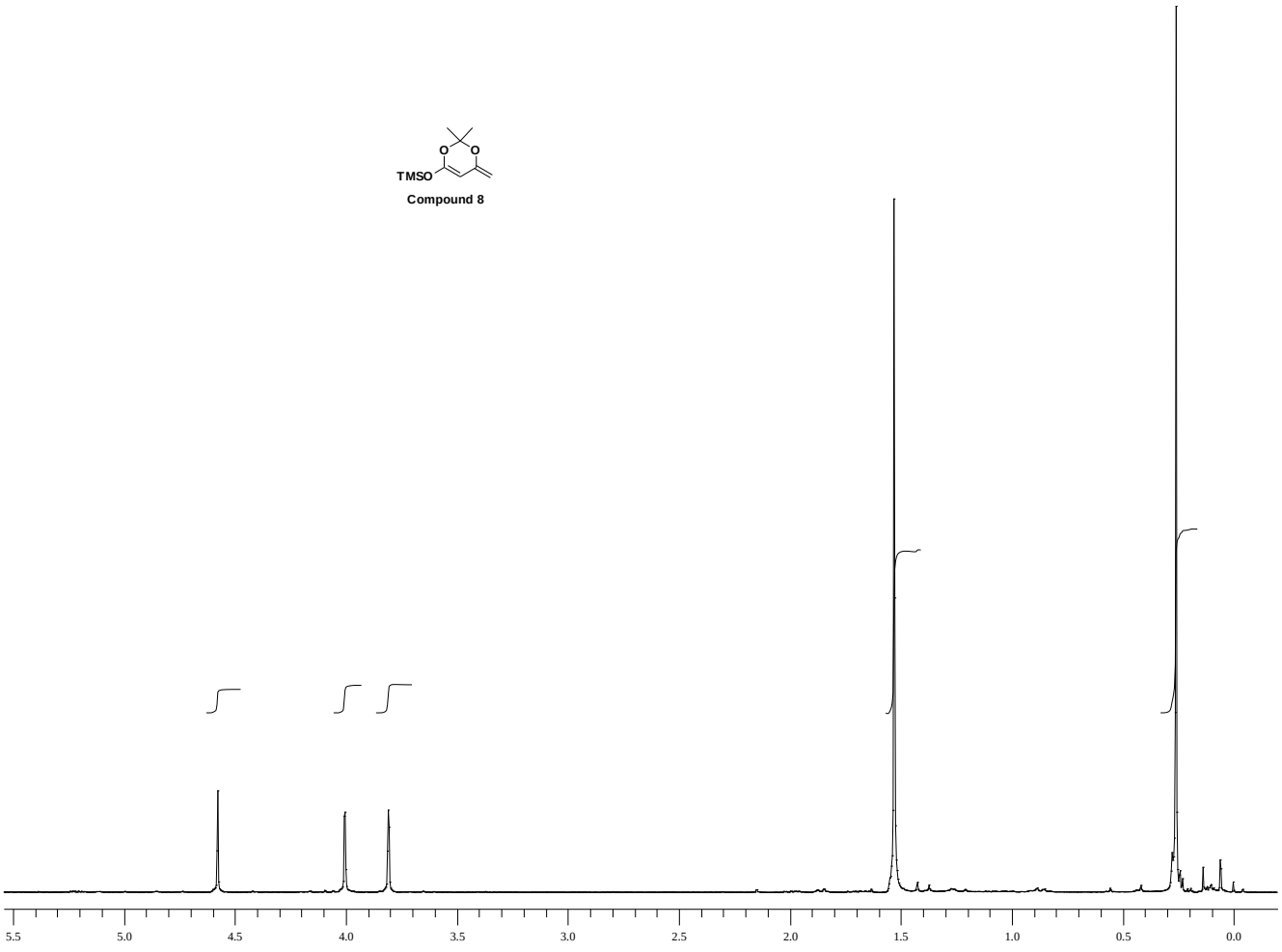


^{13}C NMR spectrum of Compound 9

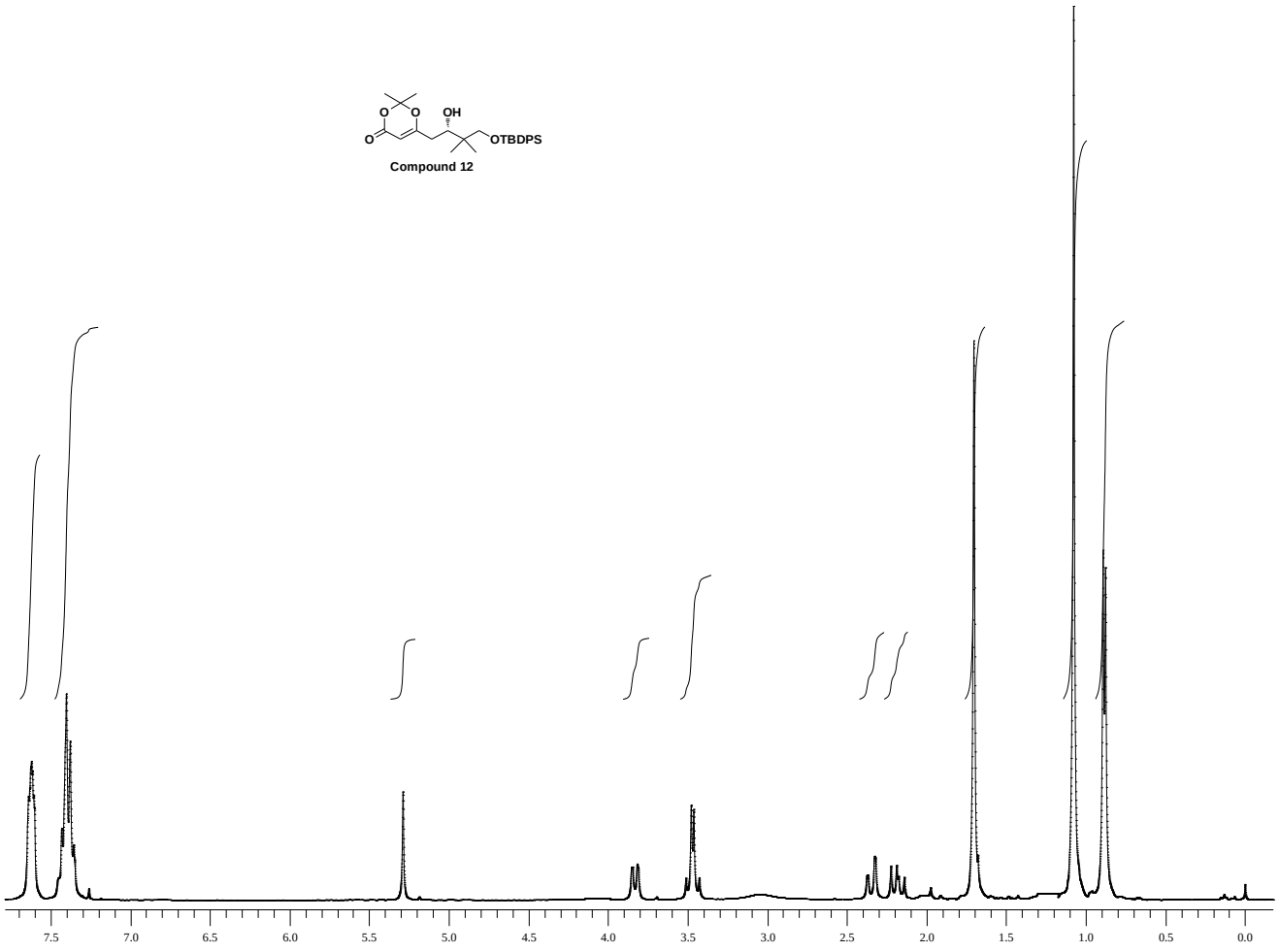




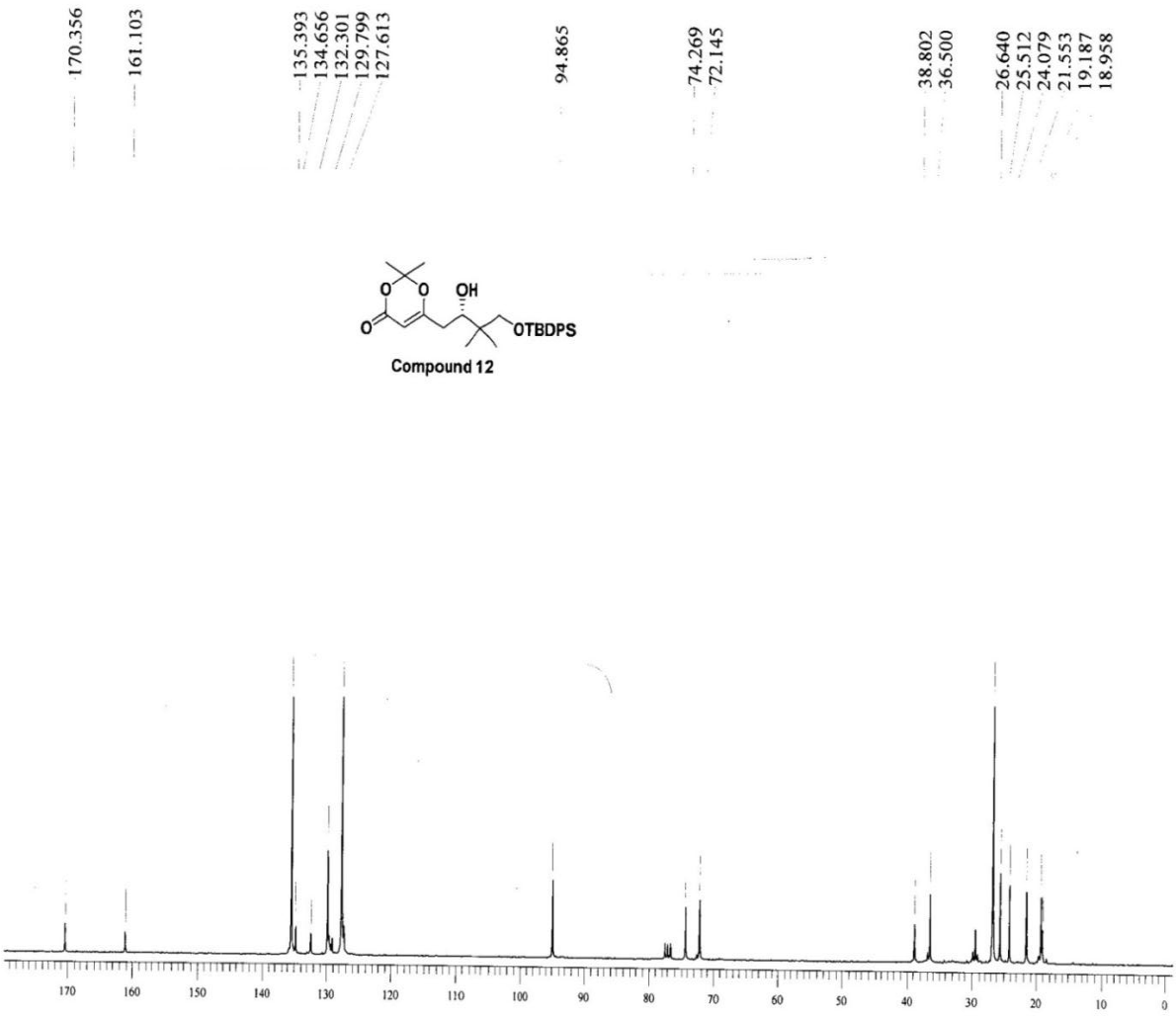
^{1}H NMR spectrum of Compound 8



^{1}H NMR spectrum of Compound 12



^{13}C NMR spectrum of Compound 12



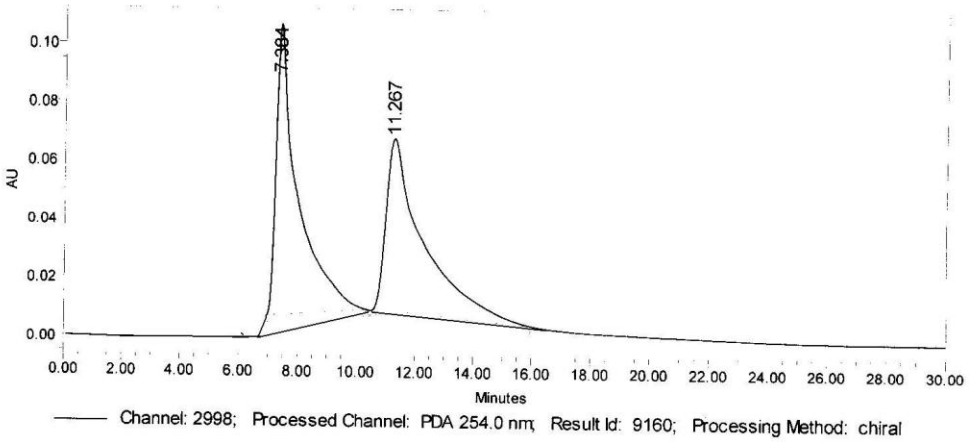
HPLC of Racemic compound 12

Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	VV MA RAC	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	
Vial:	1	Acq. Method Set:	VV 15% IPA
Injection #:	3	Processing Method:	chiral
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	6/24/2009 3:29:25 PM IST		
Date Processed:	6/24/2009 4:53:15 PM IST		



Channel: 2998; Processed Channel: PDA 254.0 nm; Result Id: 9160; Processing Method: chiral

Processed Channel Descr.: PDA 254.0 nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	PDA 254.0 nm	7.384	5030790	49.33	98878
2	PDA 254.0 nm	11.267	5167702	50.67	59006

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1005
Page: 1 of 1

Project Name: APRIL 2009
Date Printed: 9/5/2009
10:03:13 AM Asia/Calcutta

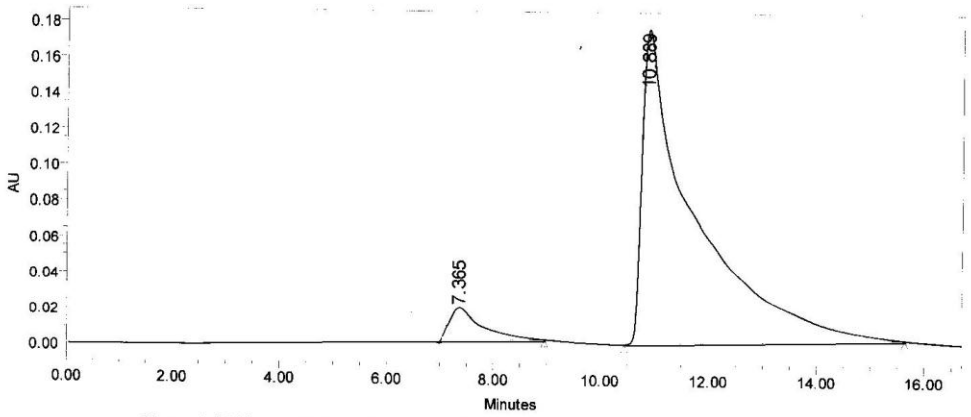
HPLC of compound 12

Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	VV MA CHIRAI Tol Binap	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	
Vial:	1	Acq. Method Set:	VV 15% IPA
Injection #:	5	Processing Method:	jk
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	6/24/2009 4:26:30 PM IST		
Date Processed:	6/26/2009 8:33:23 PM IST		



Channel: 2998; Processed Channel: PDA 254.0 nm; Result Id: 9212; Processing Method: jk

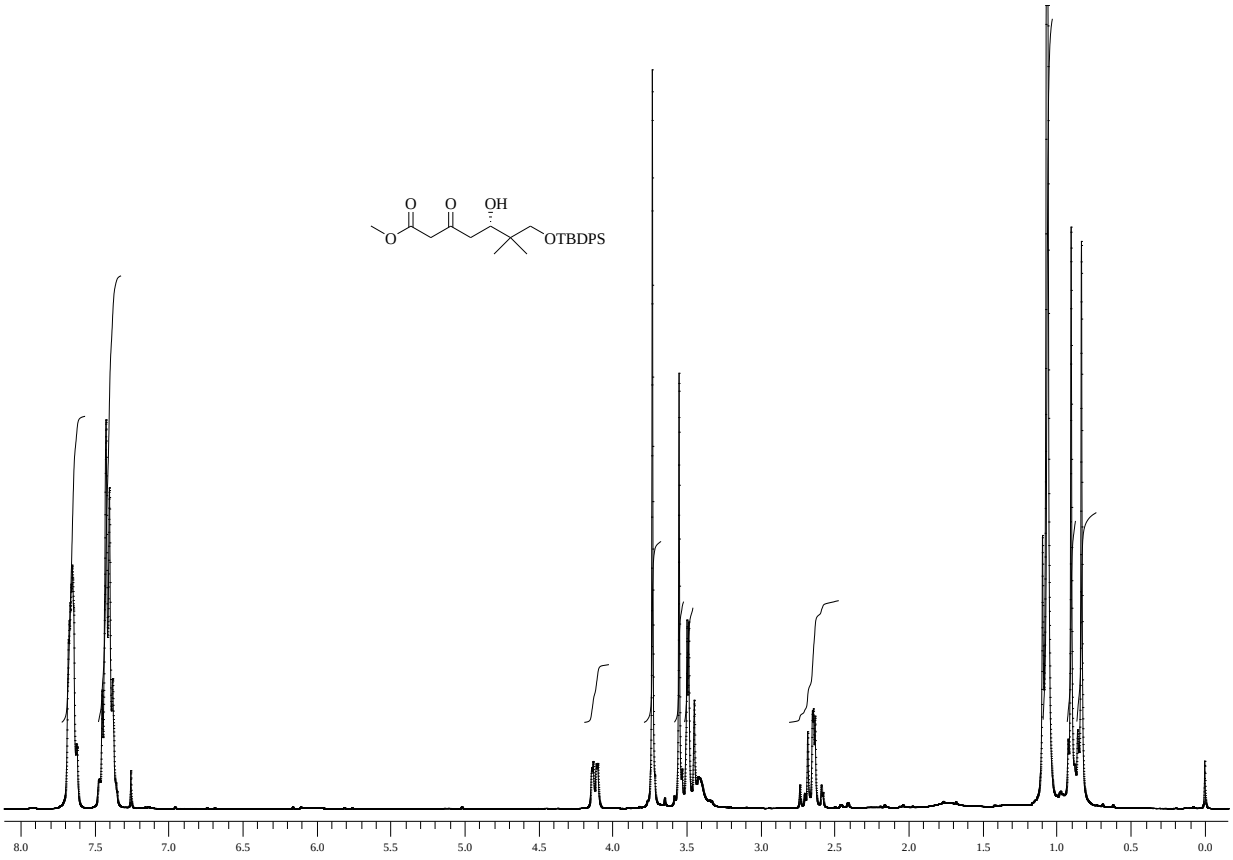
Processed Channel Descr.: PDA 254.0 nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	PDA 254.0 nm	7.365	831551	6.49	18744
2	PDA 254.0 nm	10.889	11989563	93.51	175782

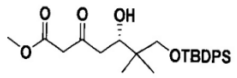
Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1005
Page: 1 of 1

Project Name: APRIL 2009
Date Printed:
9/5/2009
9:53:34 AM Asia/Calcutta

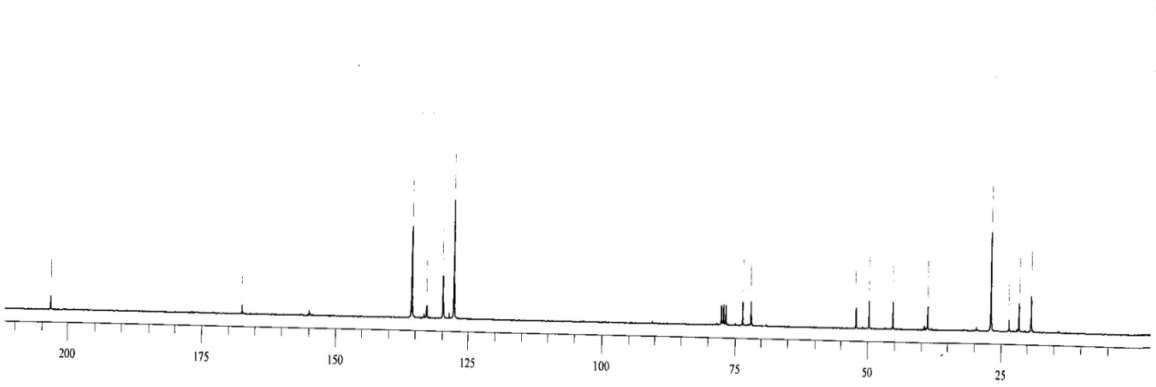
^{1}H NMR spectrum of Compound 13



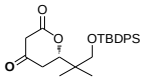
^{13}C NMR spectrum of Compound 13



Compound 13

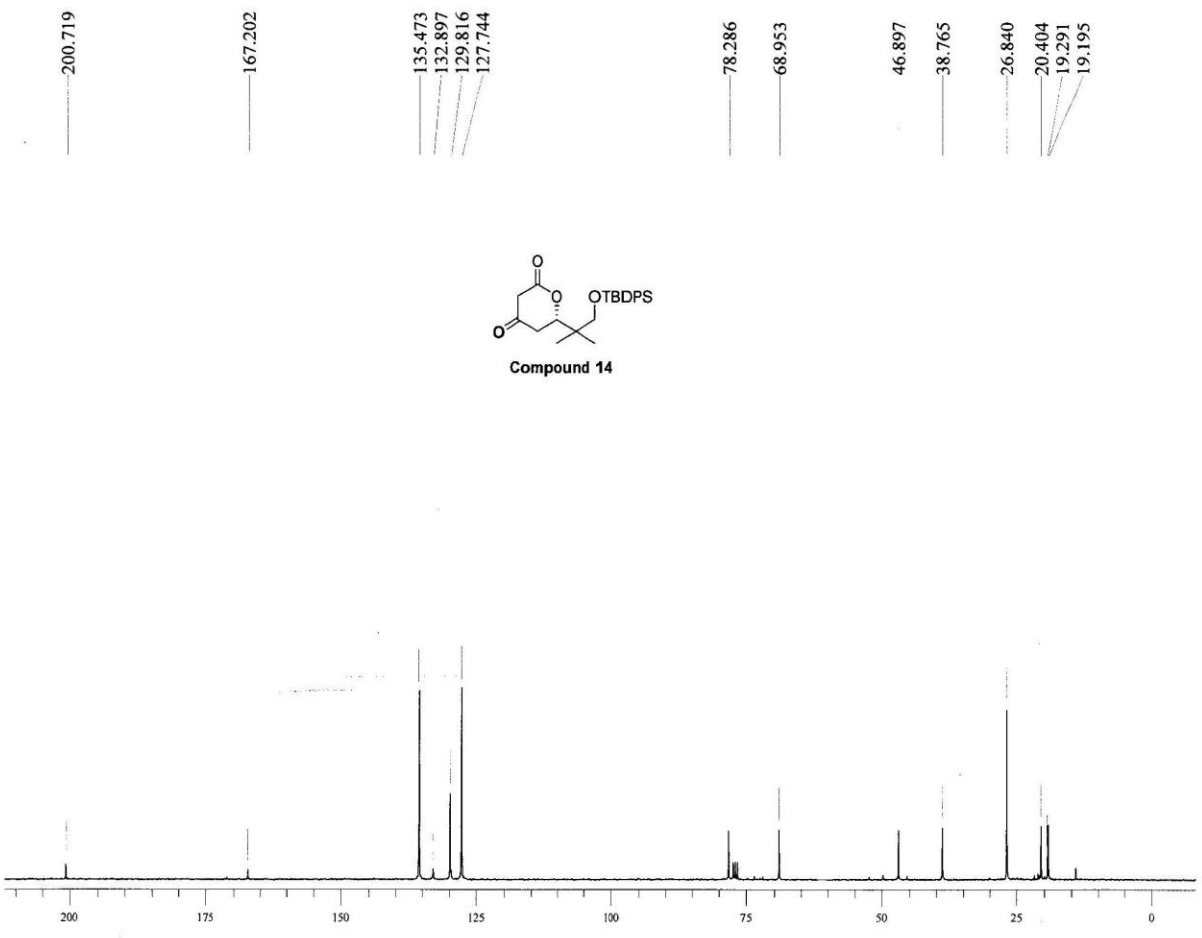


^{1}H NMR spectrum of Compound 14

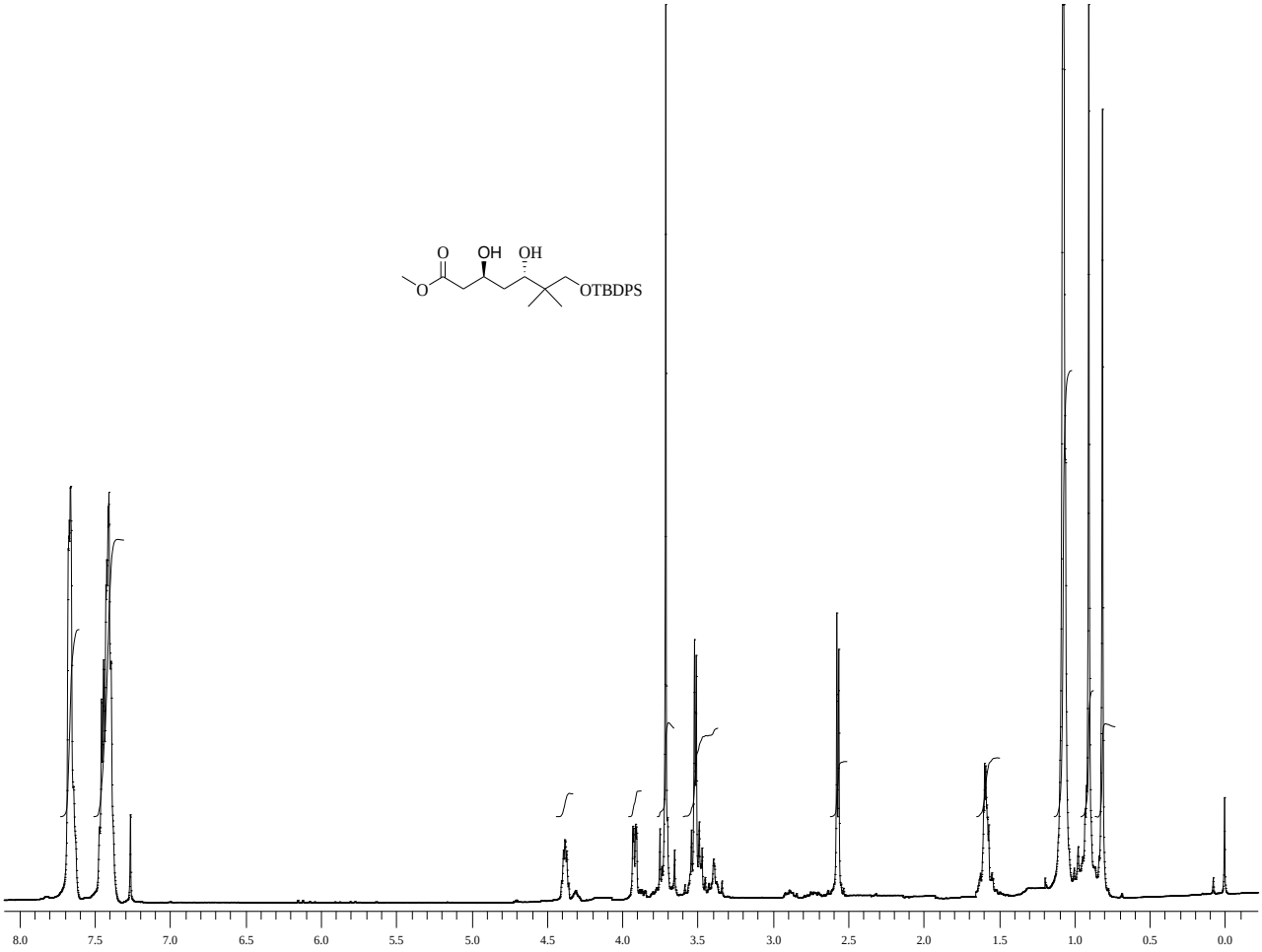


Compound 14

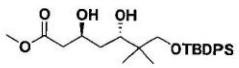
^{13}C NMR spectrum of Compound 14



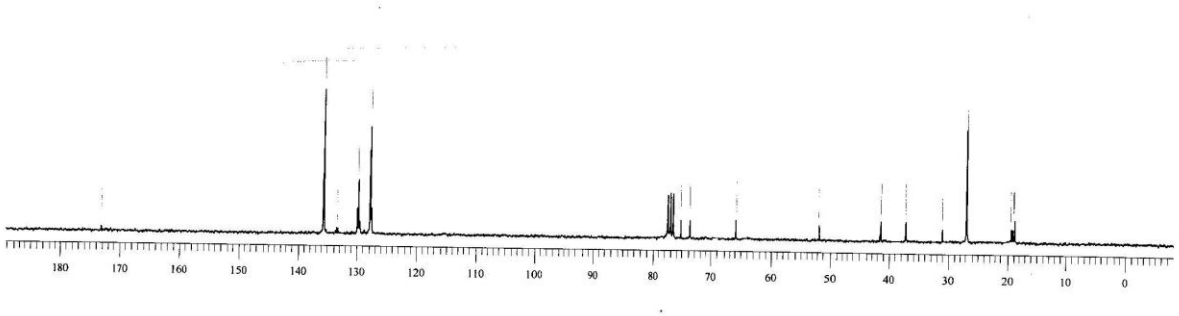
^{1}H NMR spectrum of Compound 15



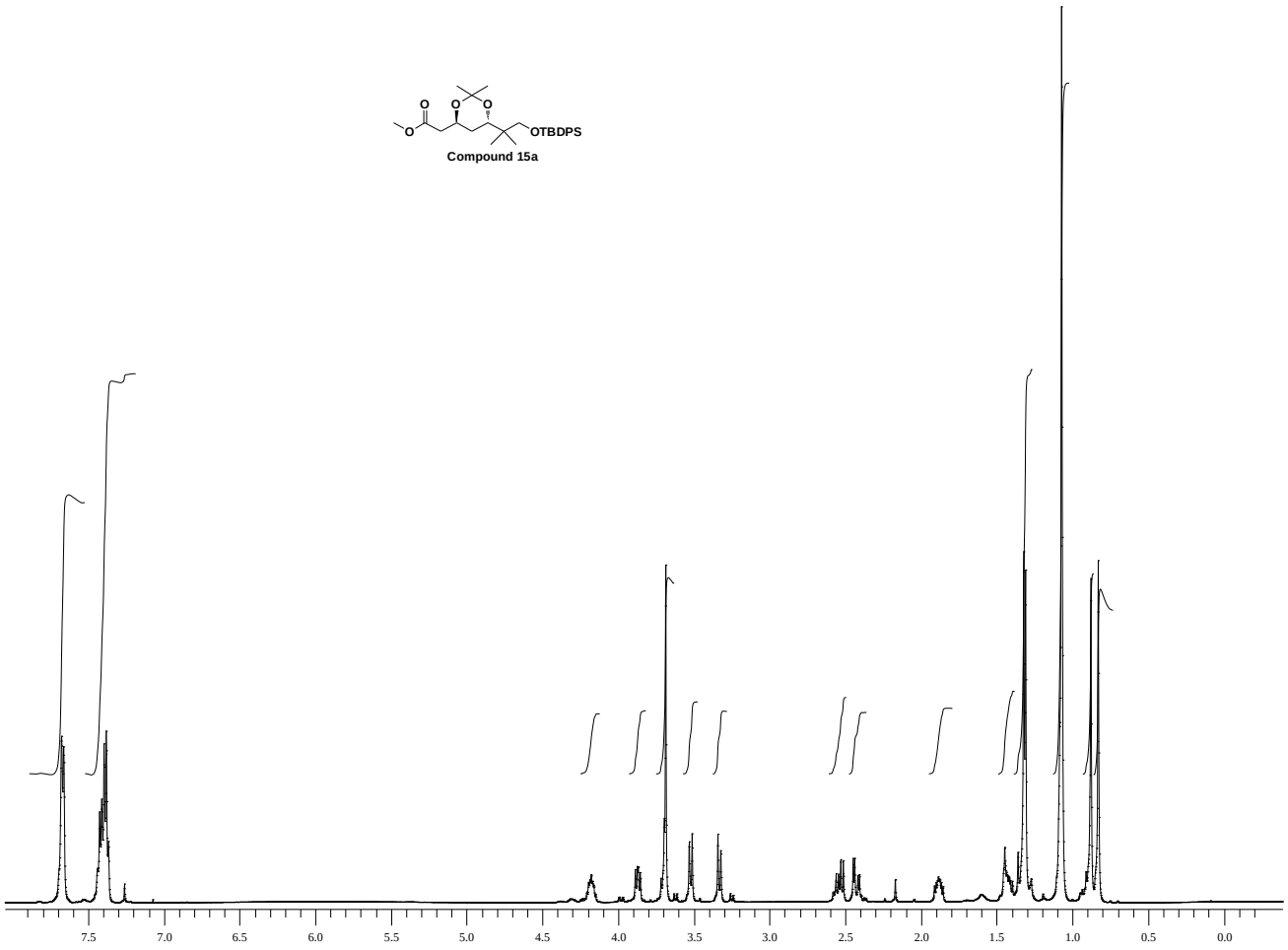
^{13}C NMR spectrum of Compound 15



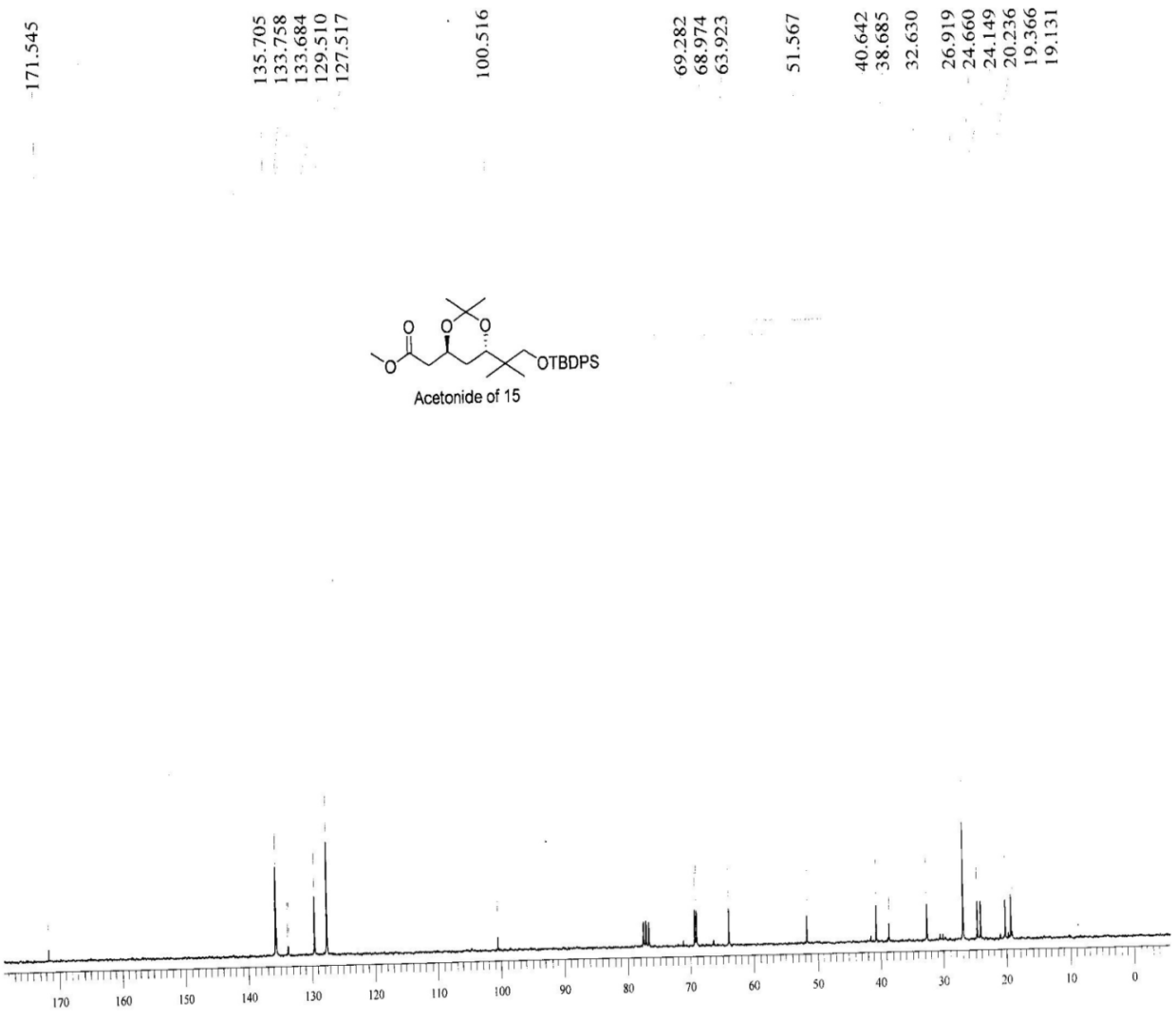
Compound 15



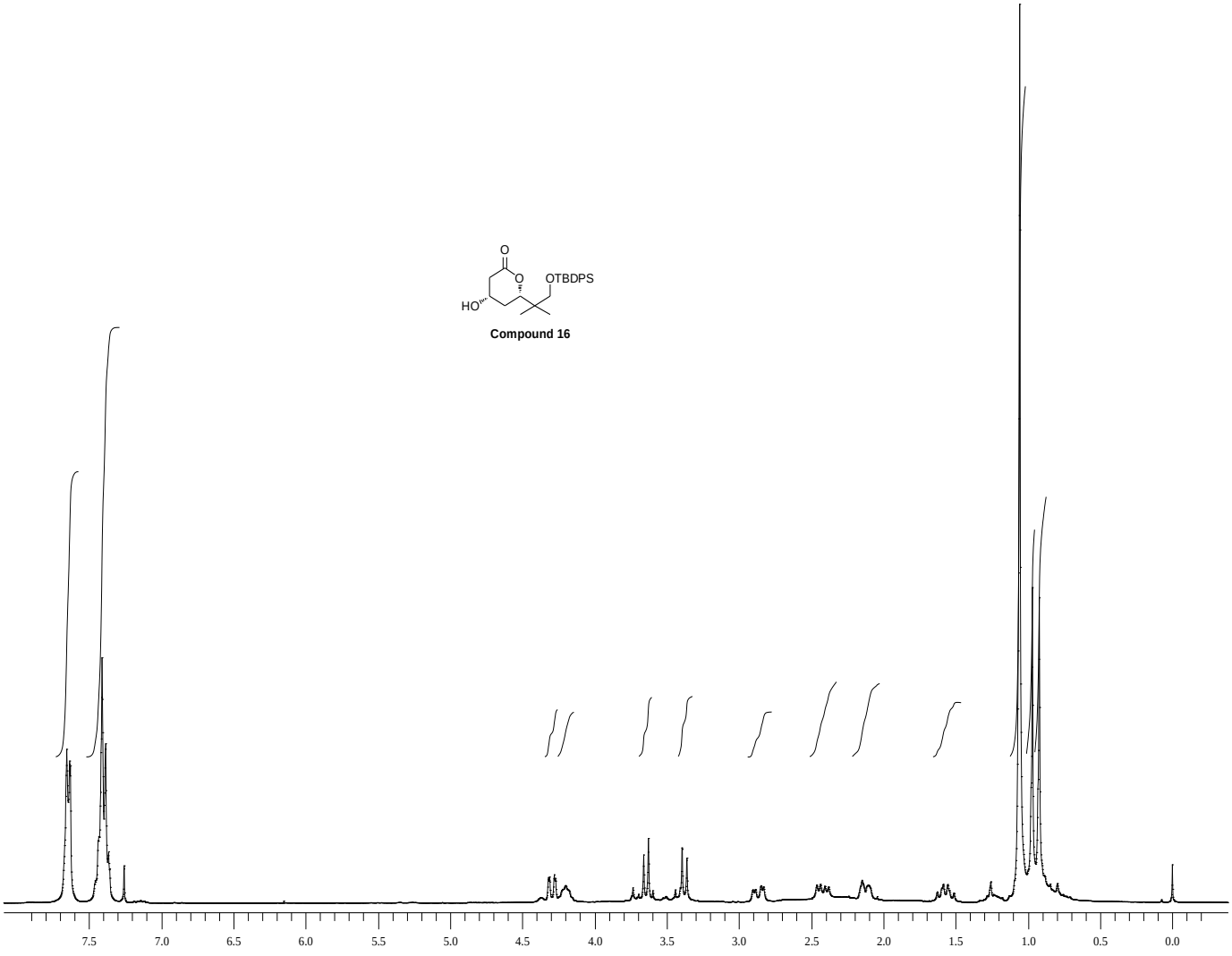
^{1}H NMR spectrum of Acetonide of Compound 15



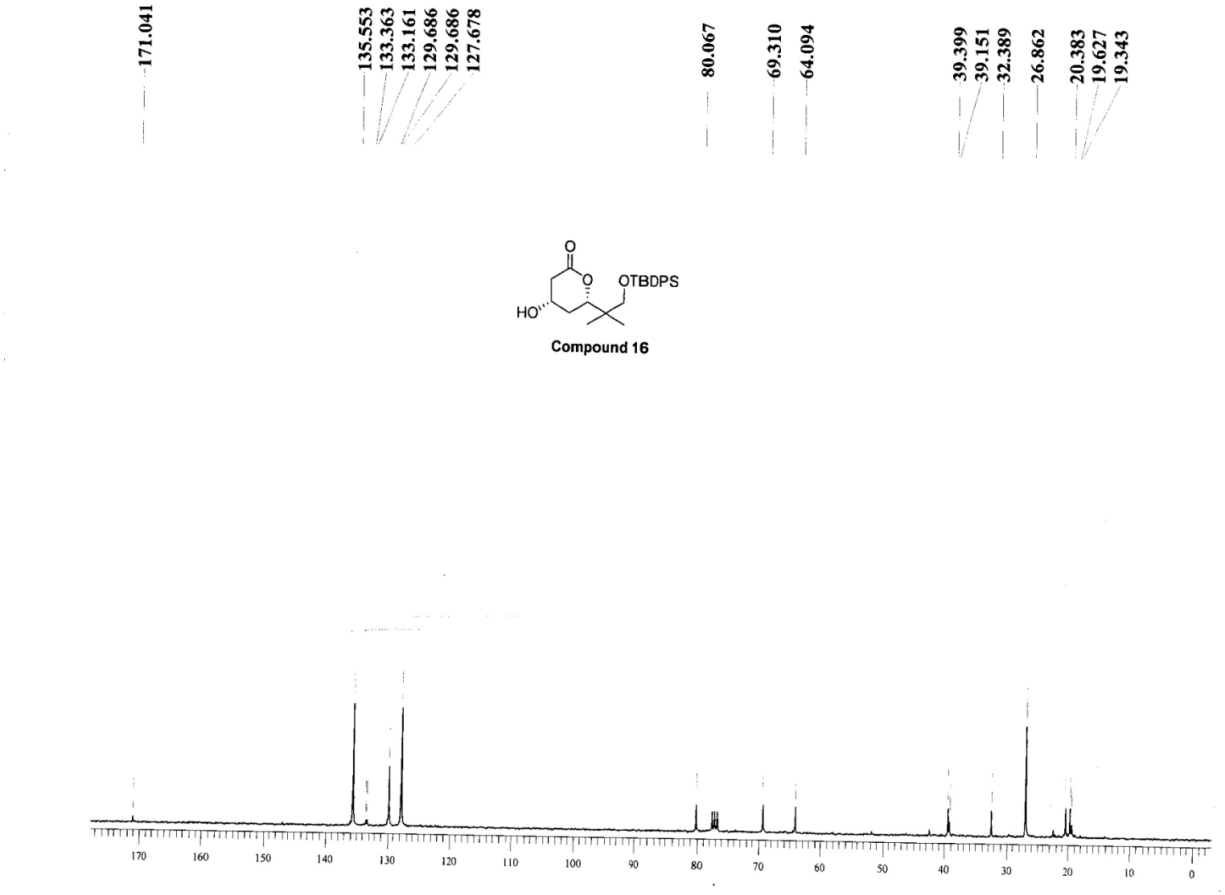
^{13}C NMR spectrum of Acetonide of Compound 15



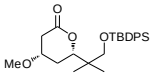
^{1}H NMR spectrum of Compound 16



^{13}C NMR spectrum of Compound 16

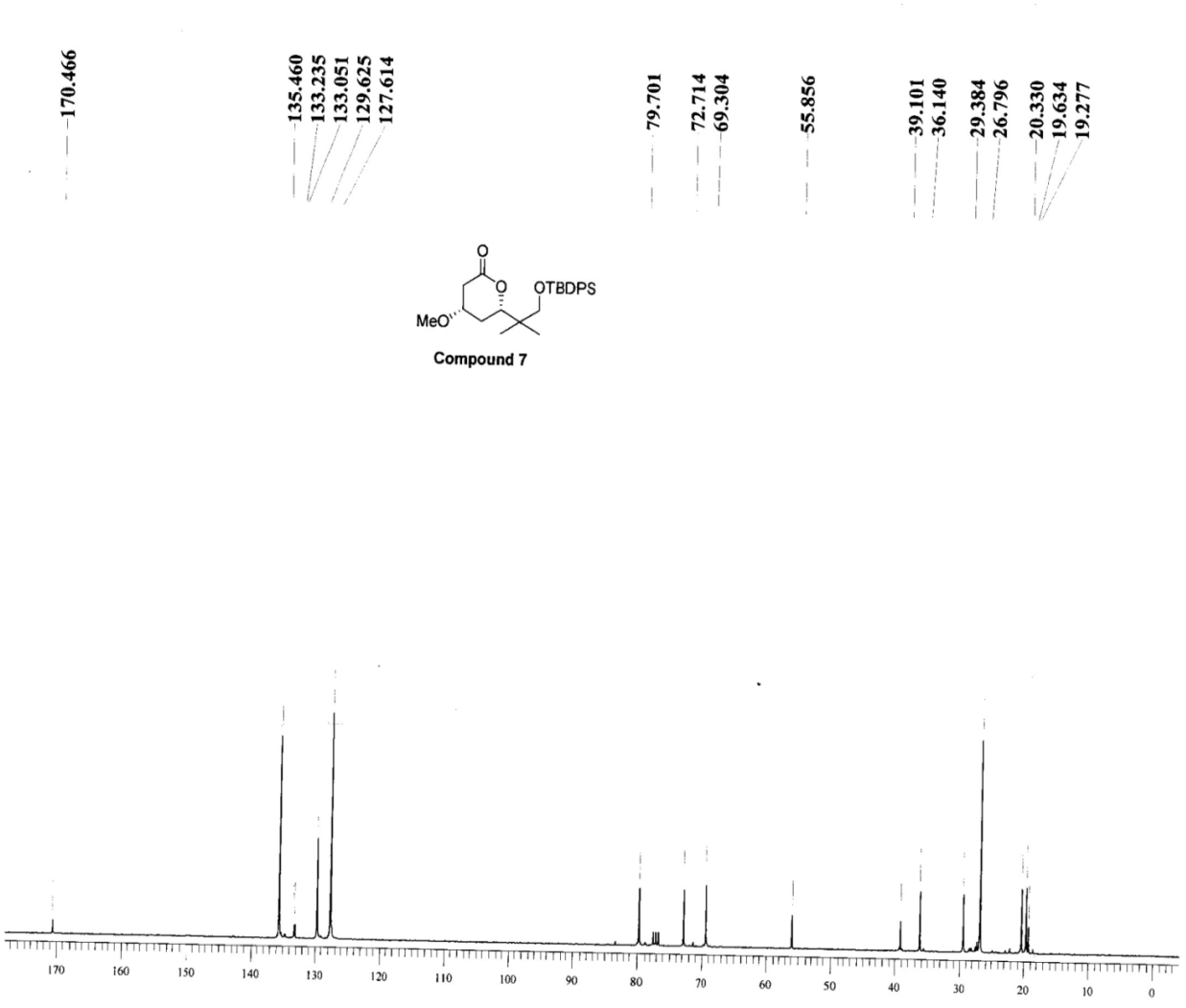


^{1}H NMR spectrum of Compound 7

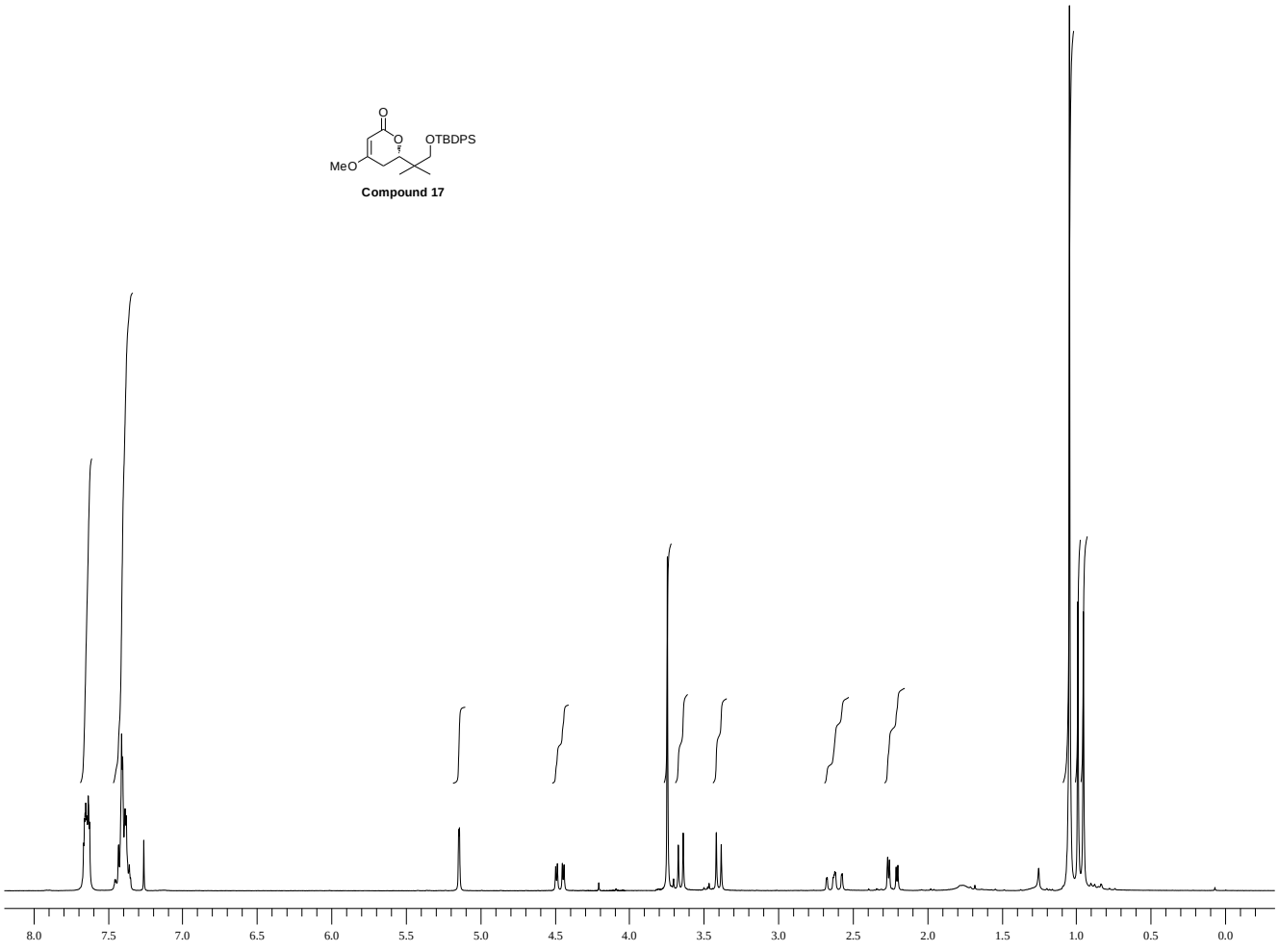


Compound 7

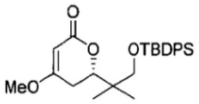
^{13}C NMR spectrum of Compound 7



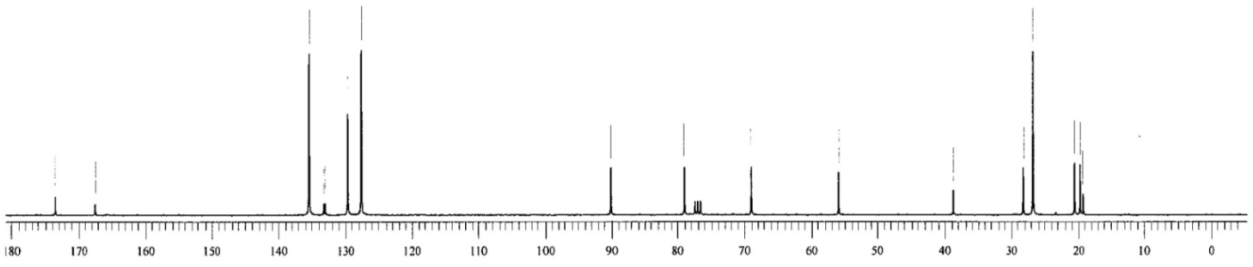
^{1}H NMR spectrum of Compound 17



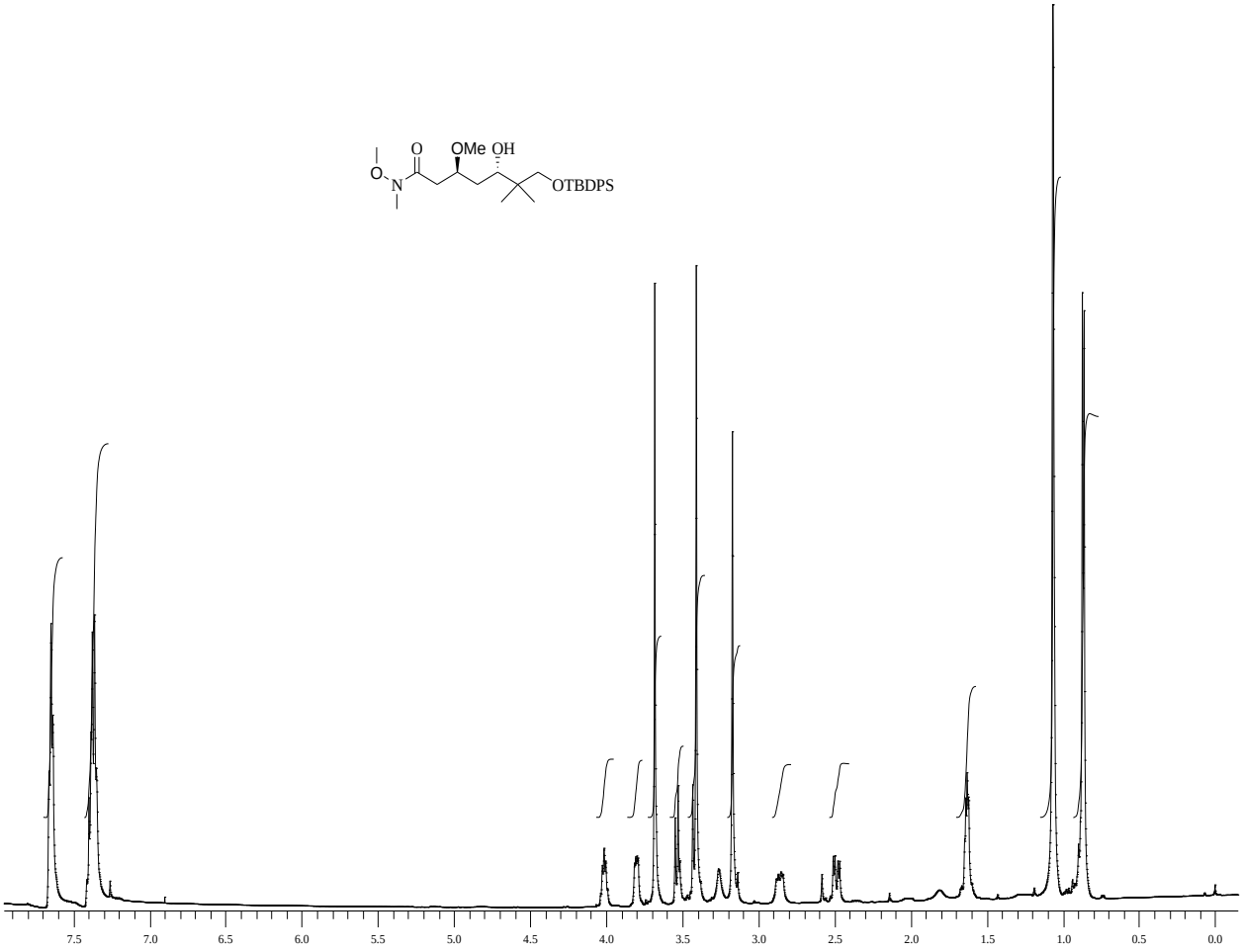
^{13}C NMR spectrum of Compound 17



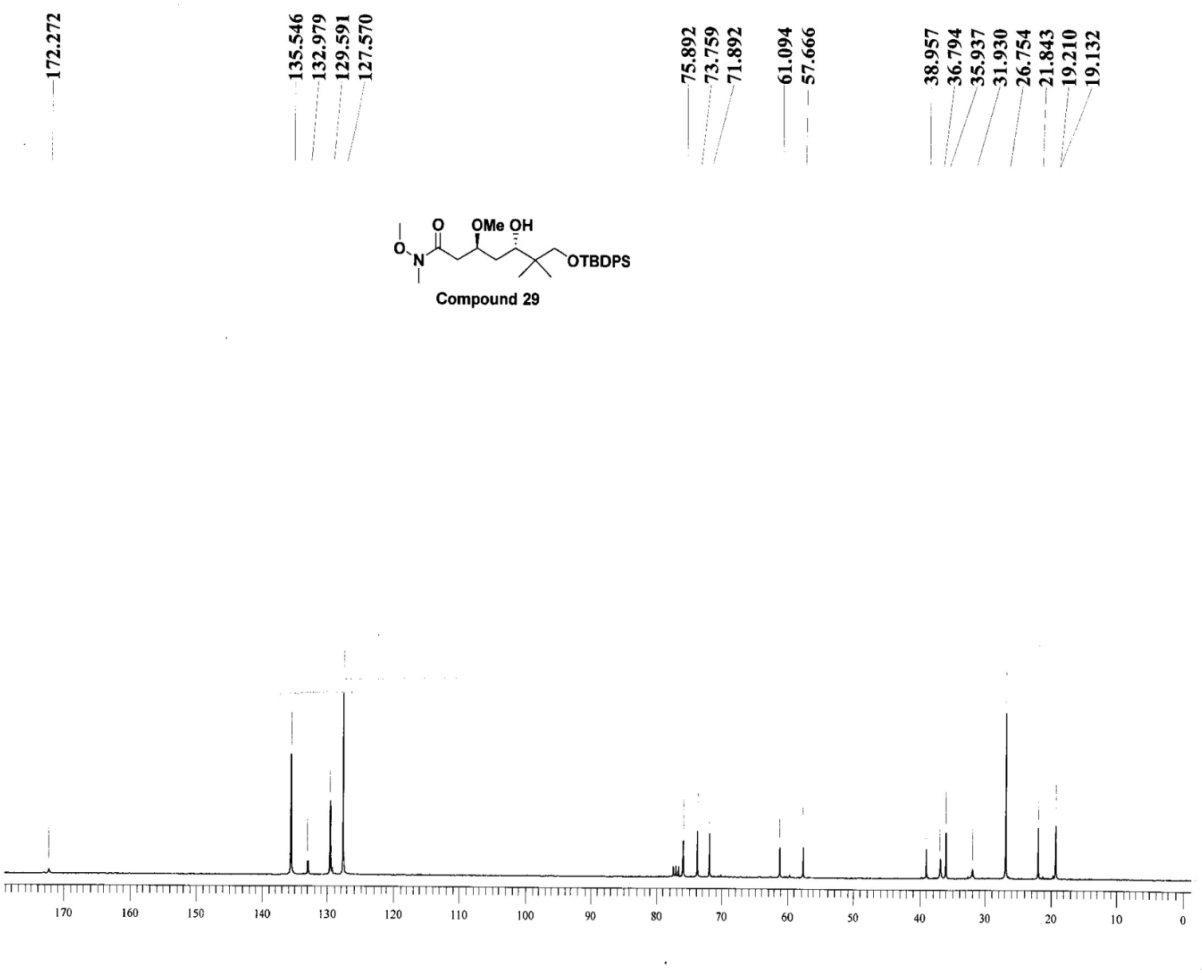
Compound 17



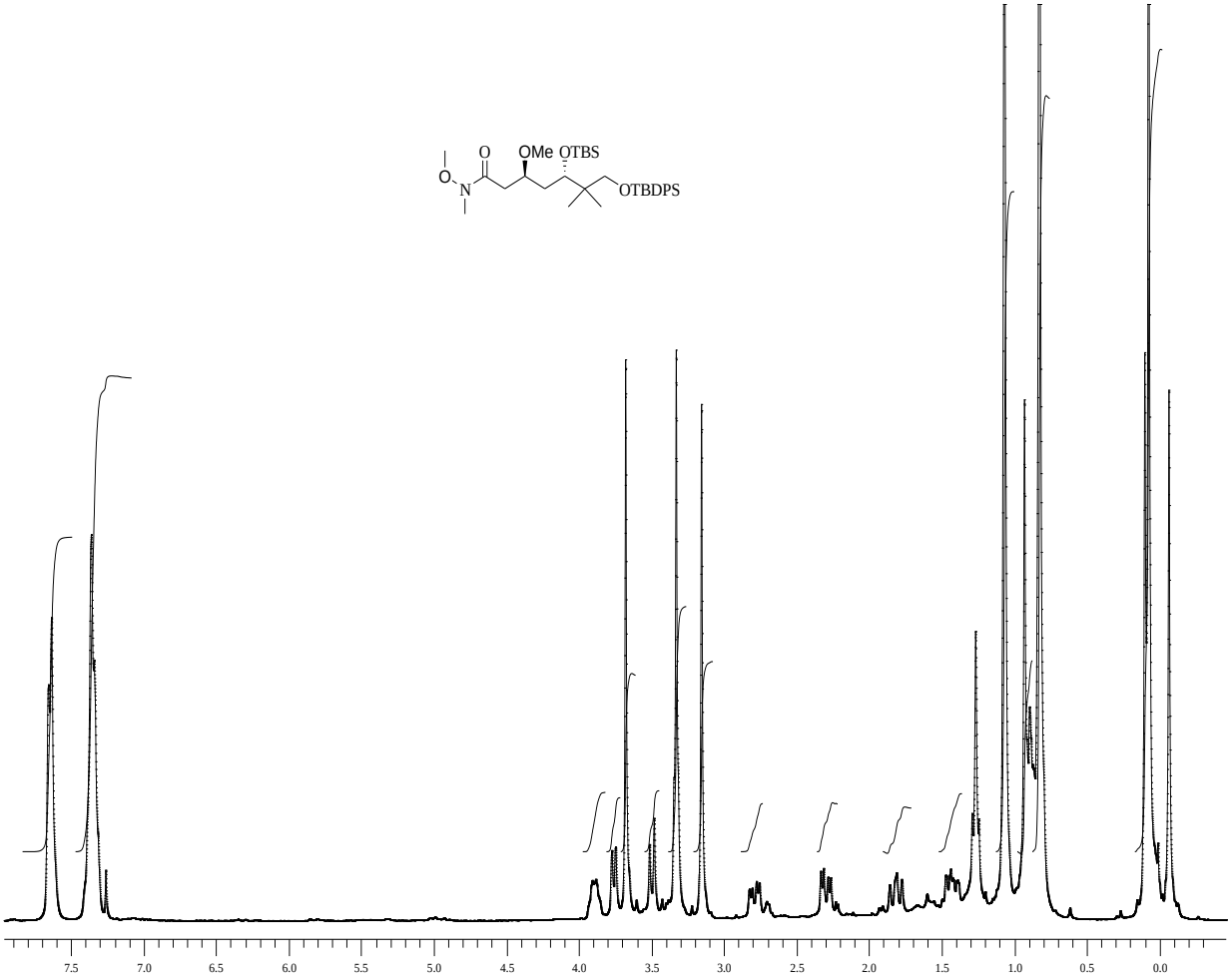
^{1}H NMR spectrum of Compound 29



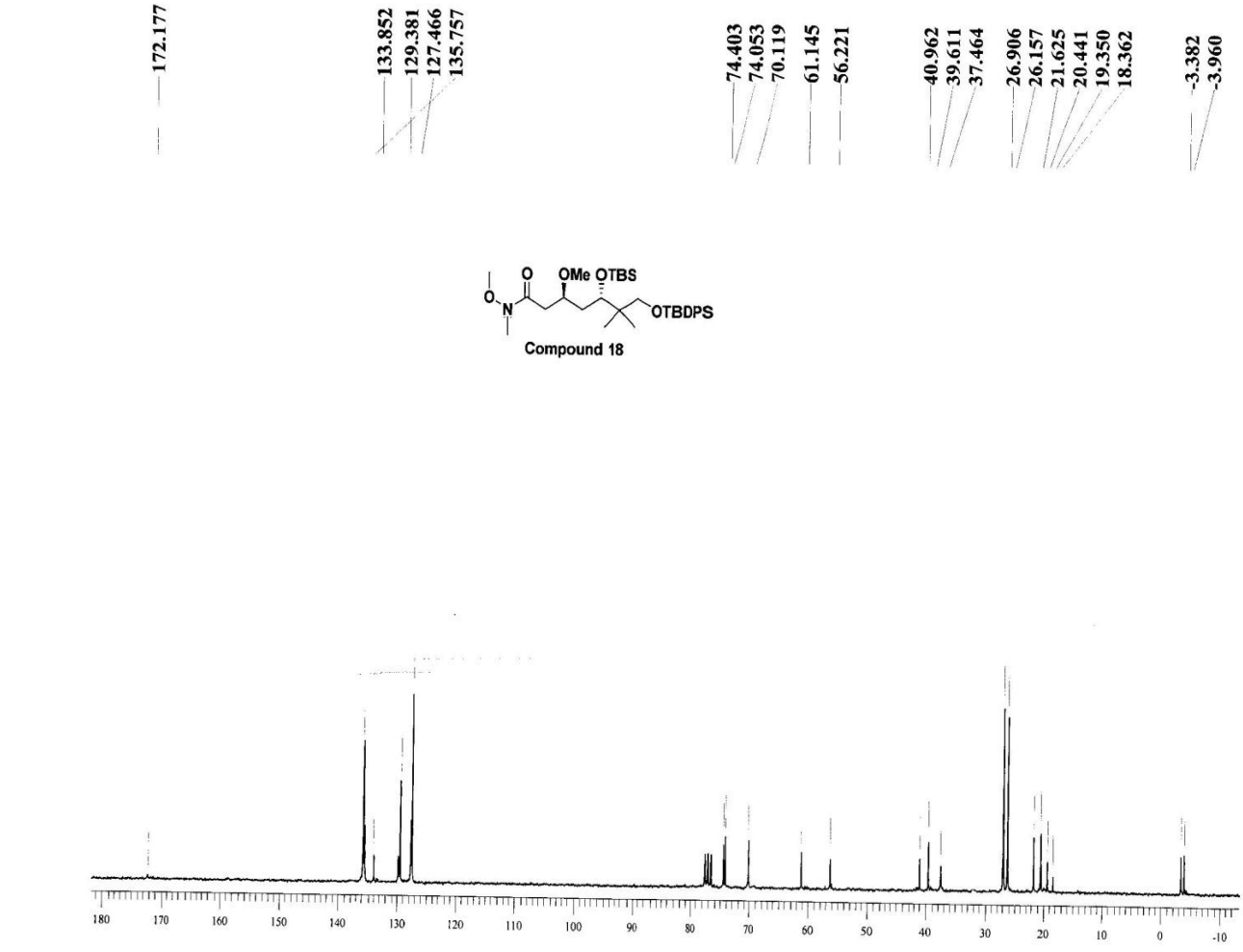
^{13}C NMR spectrum of Compound 29



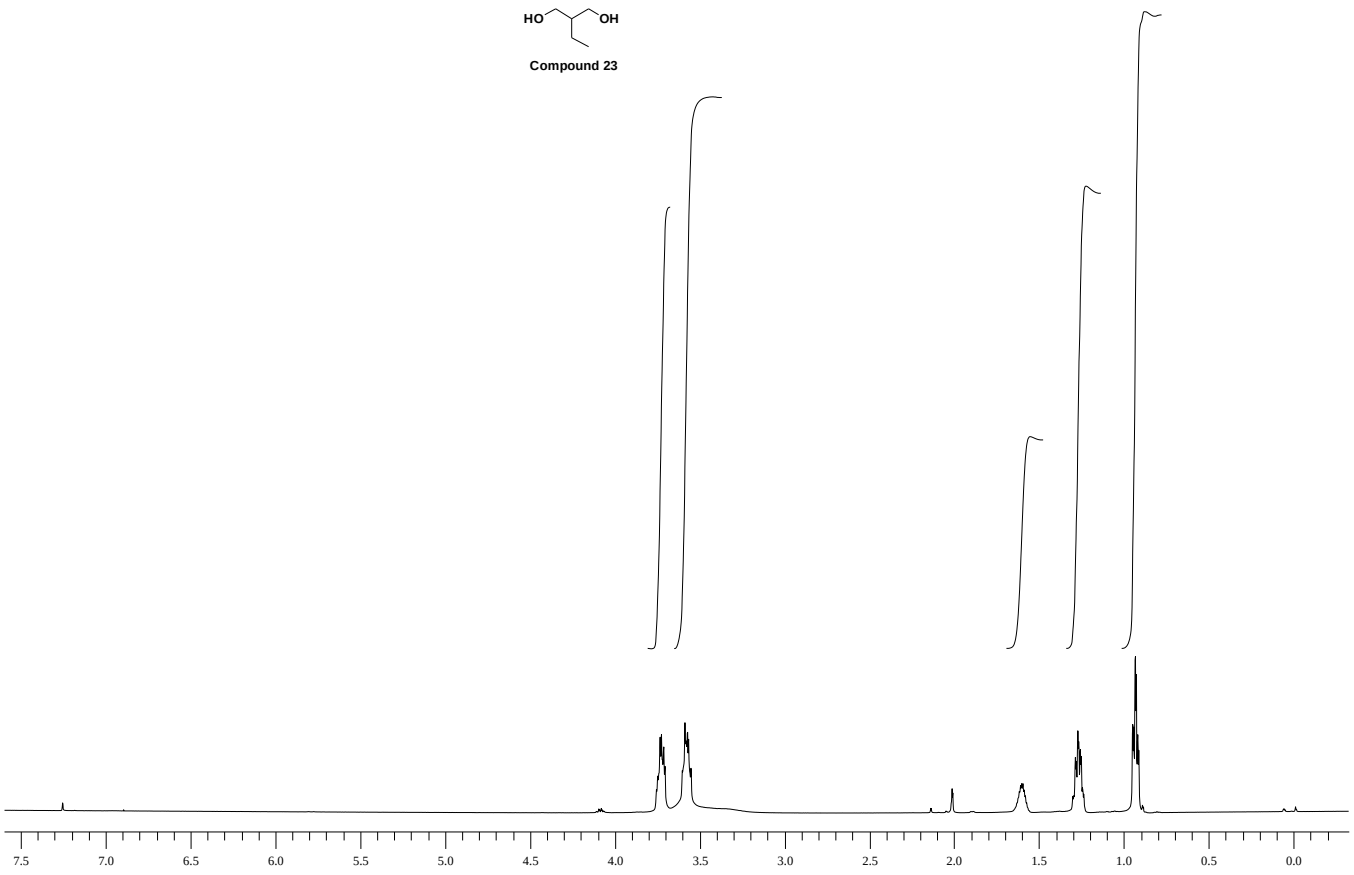
^{1}H NMR spectrum of Compound 18



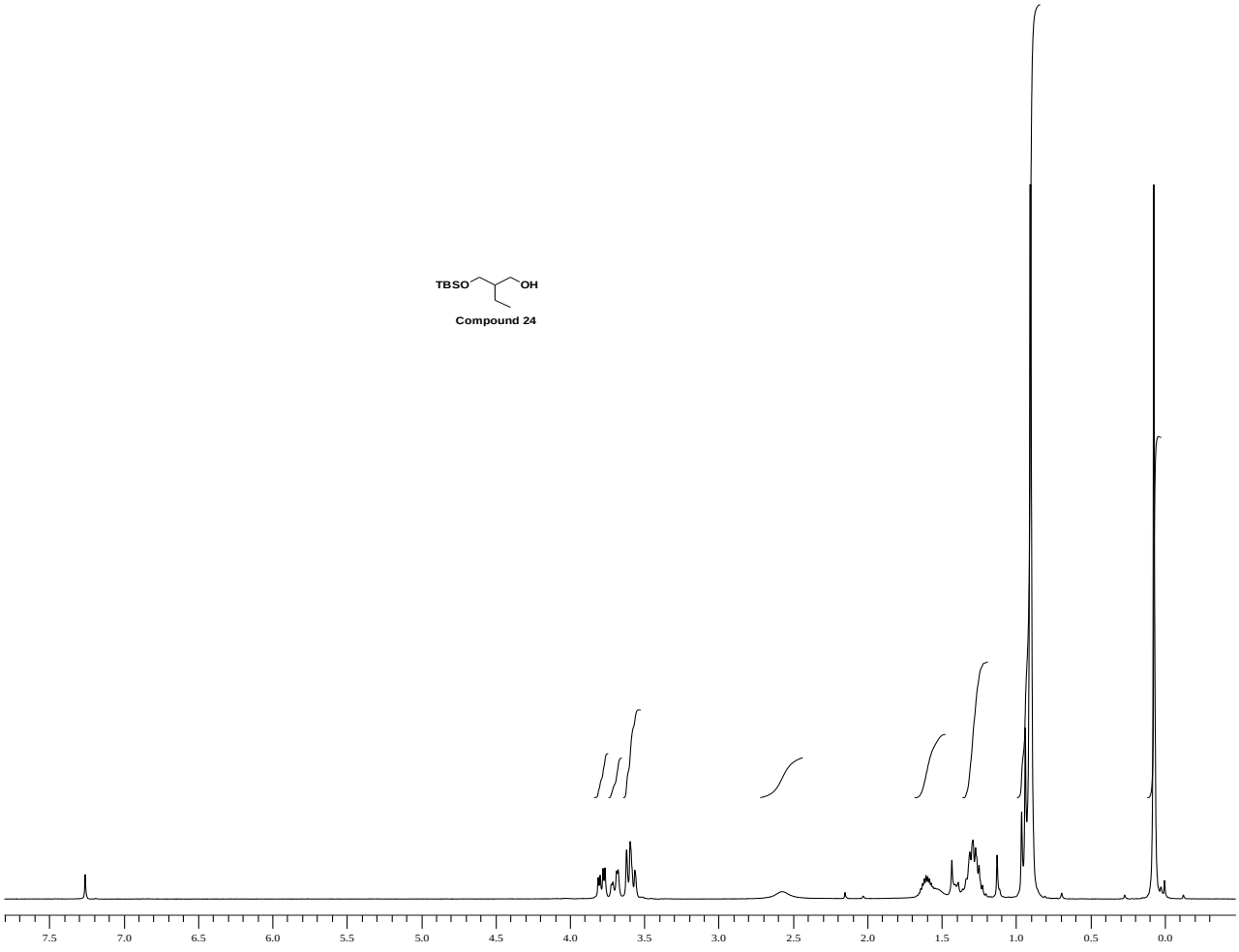
^{13}C NMR spectrum of Compound 18



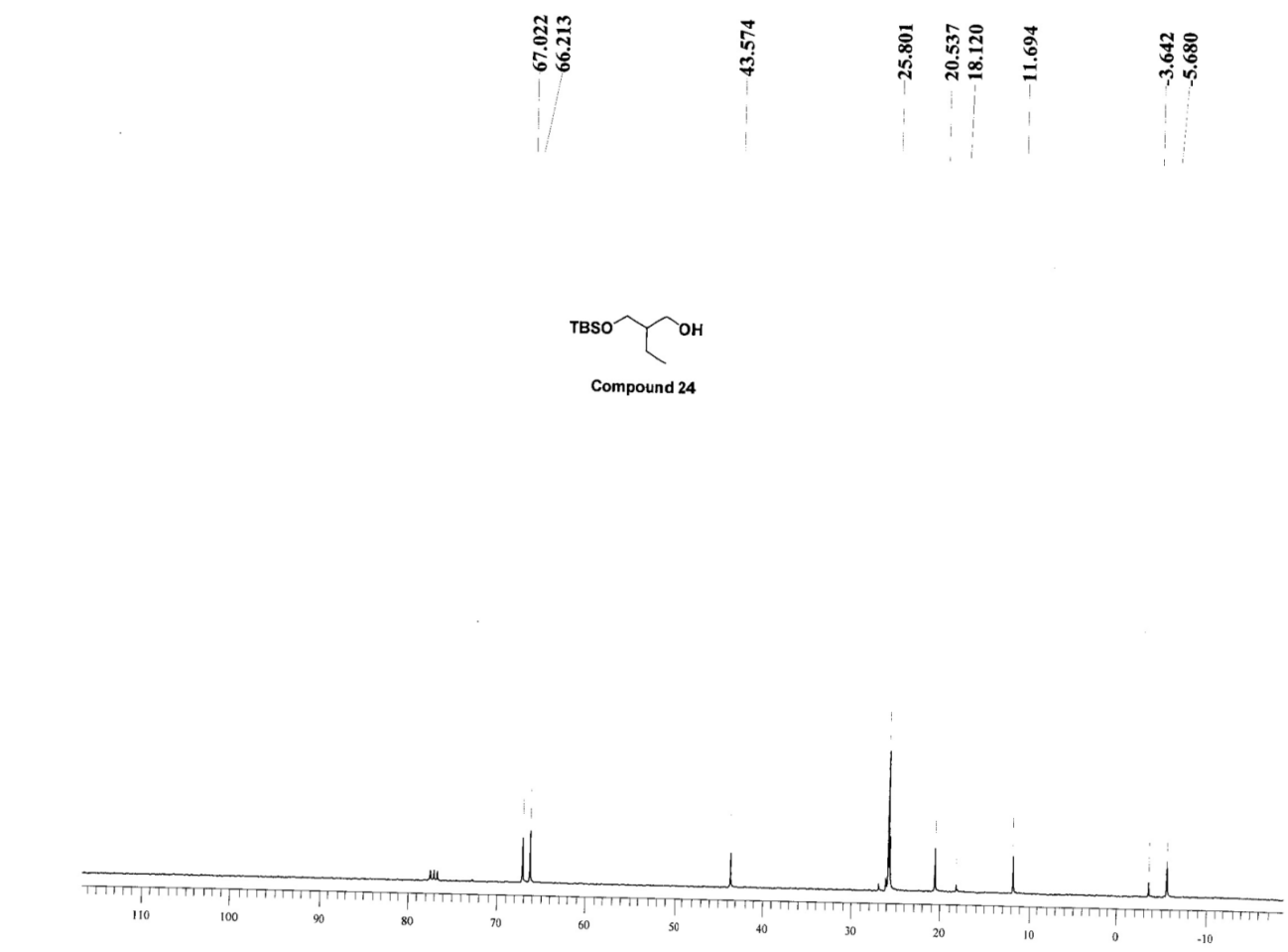
^{1}H NMR spectrum of Compound 23



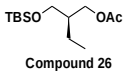
^{1}H NMR spectrum of Compound 24



^{13}C NMR spectrum of Compound 24

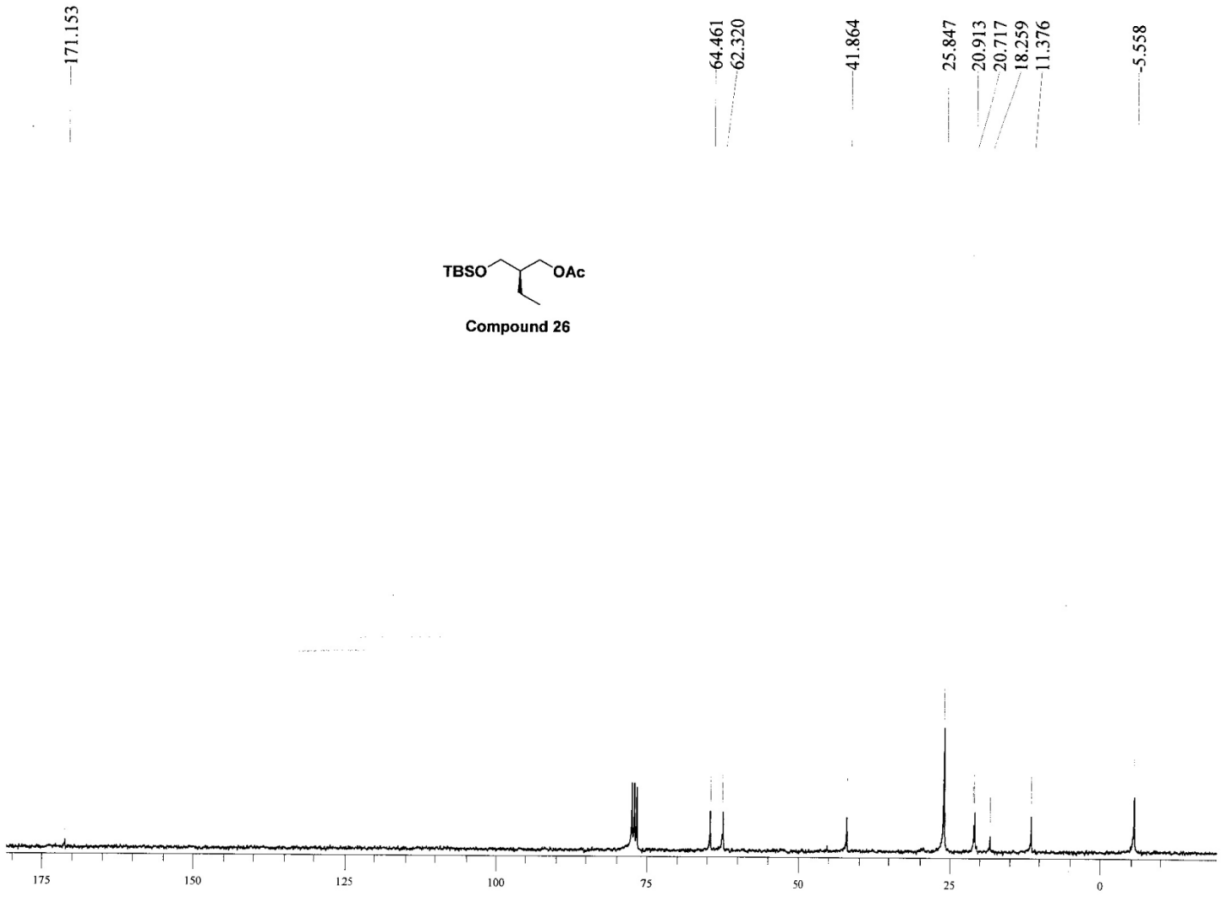


^{1}H NMR spectrum of Compound 26

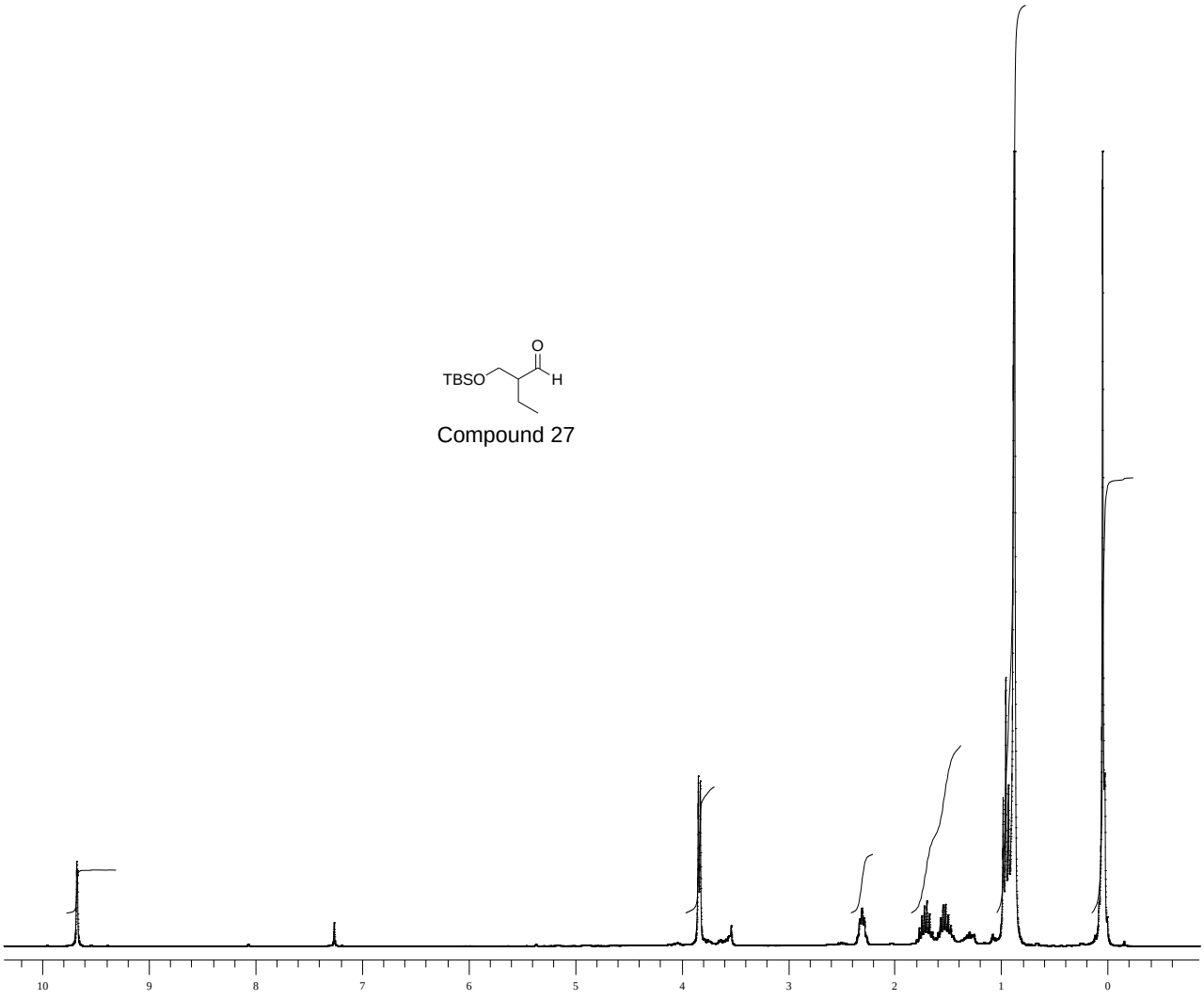


Compound 26

^{13}C NMR spectrum of Compound 26

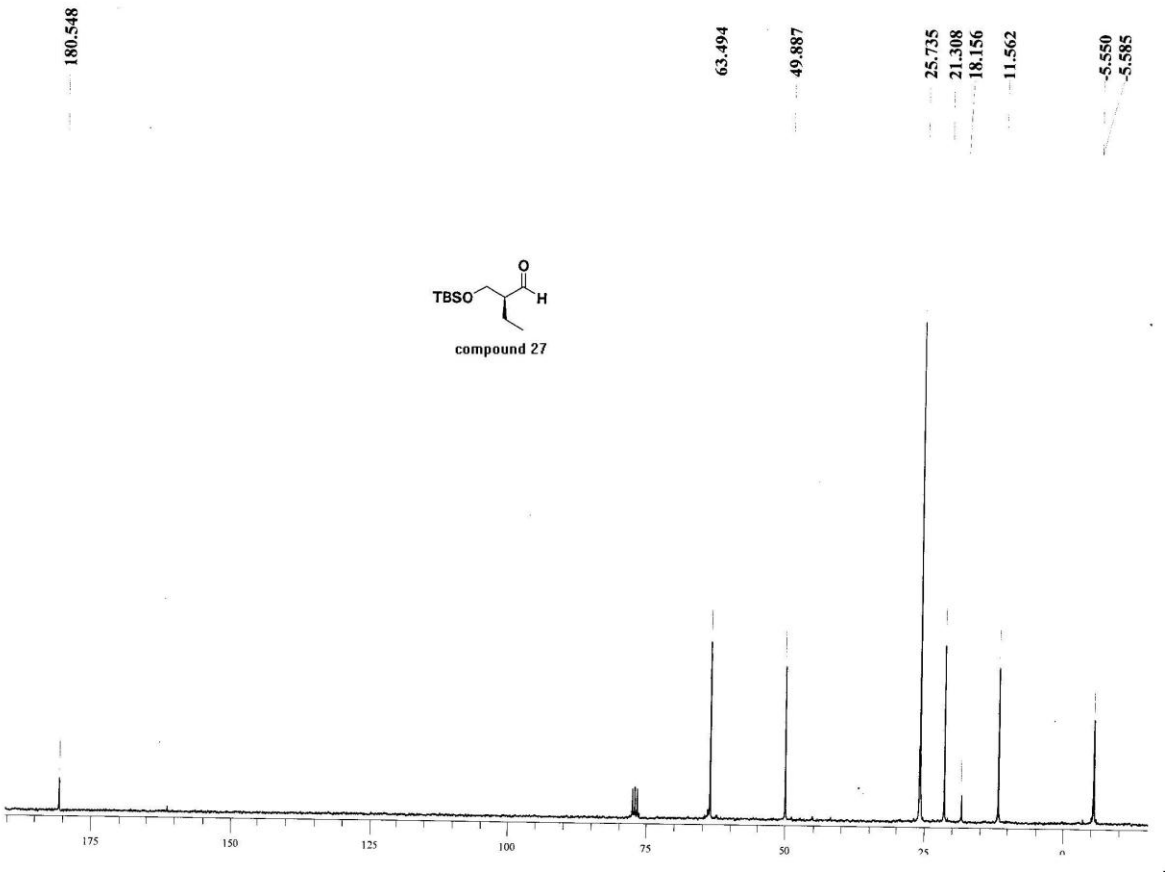


^{1}H NMR spectrum of Compound 27

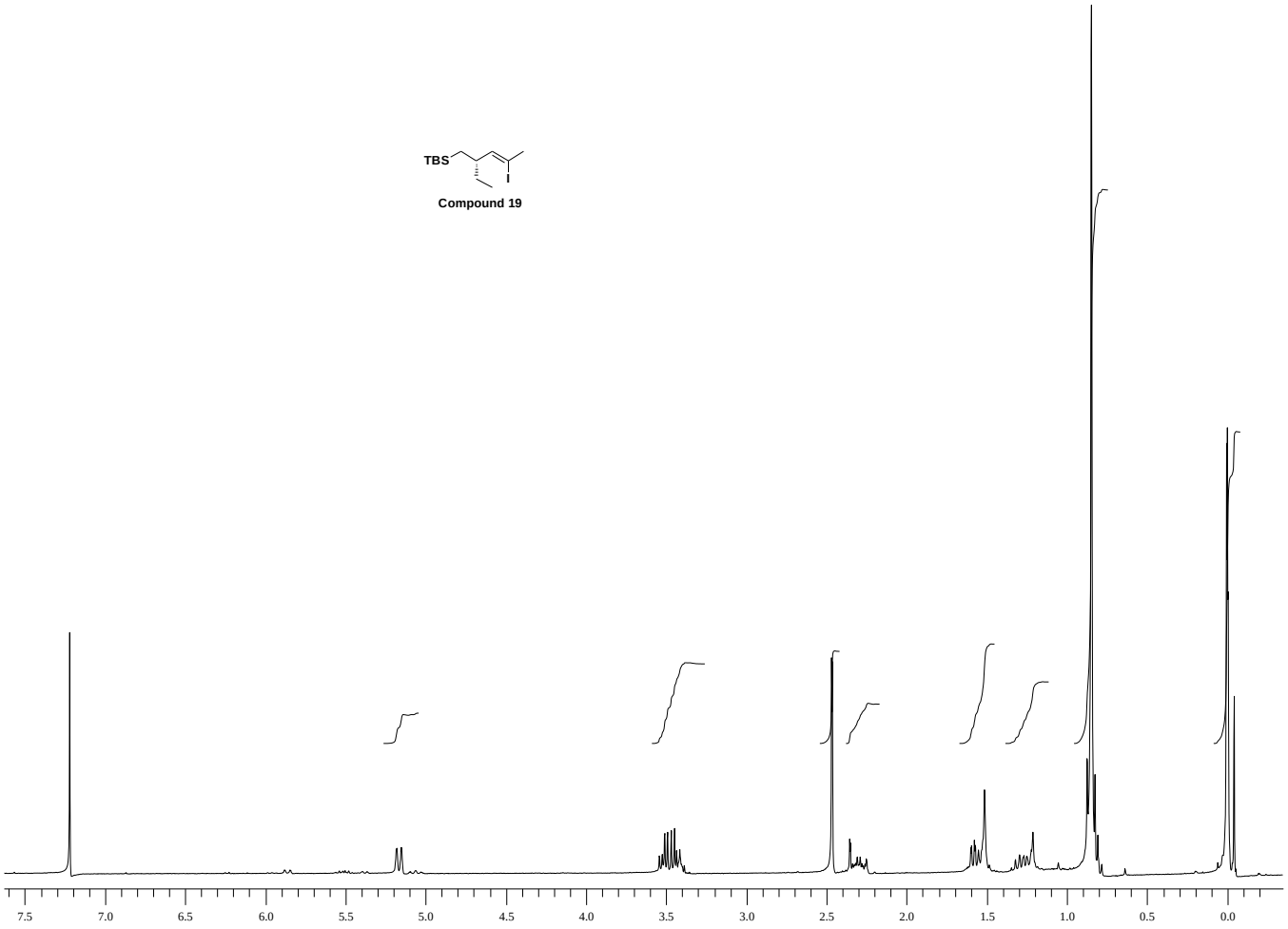


Compound 27

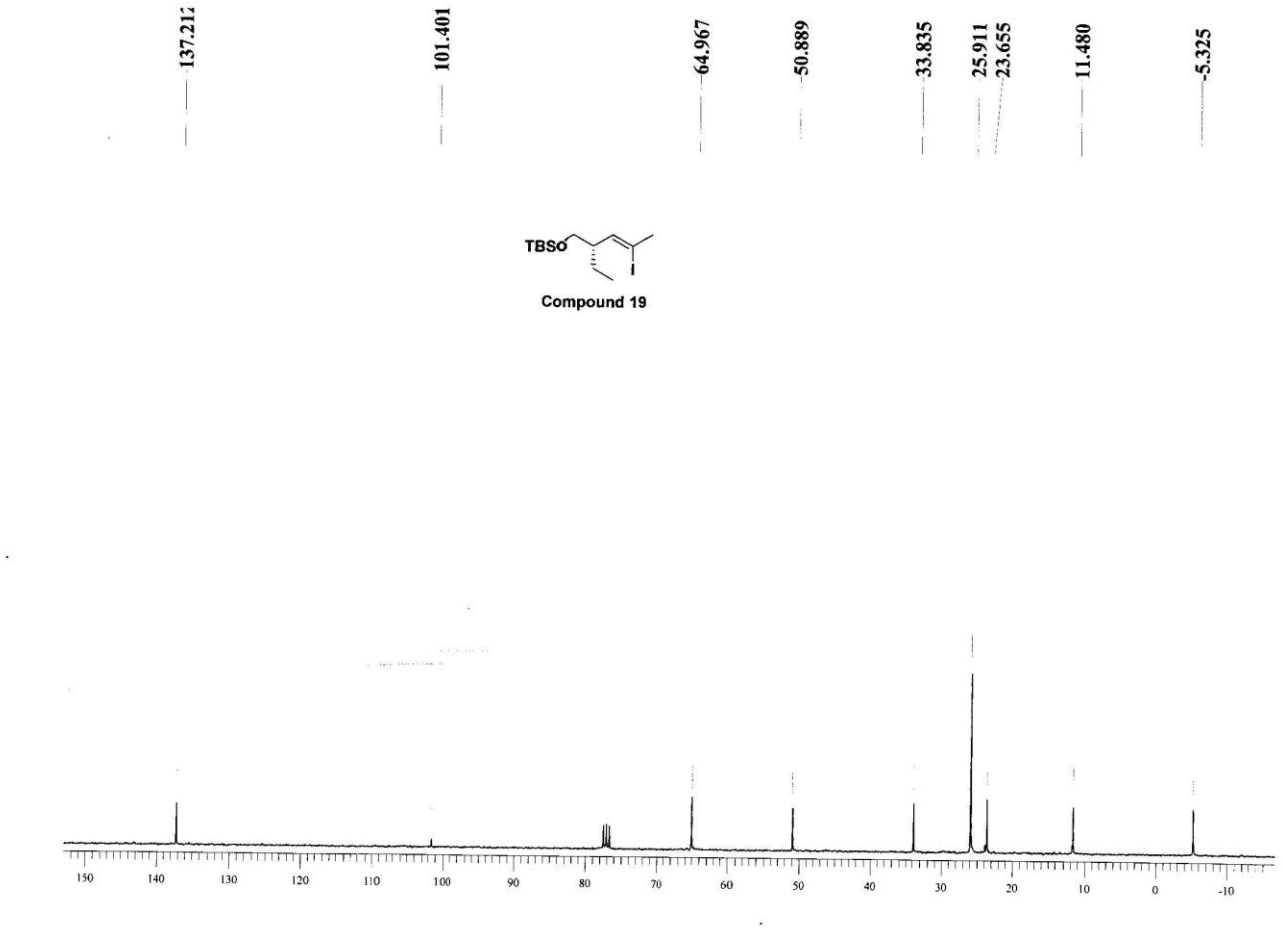
^{13}C NMR spectrum of Compound 27



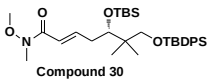
^{1}H NMR spectrum of Compound 19



^{13}C NMR spectrum of Compound 19

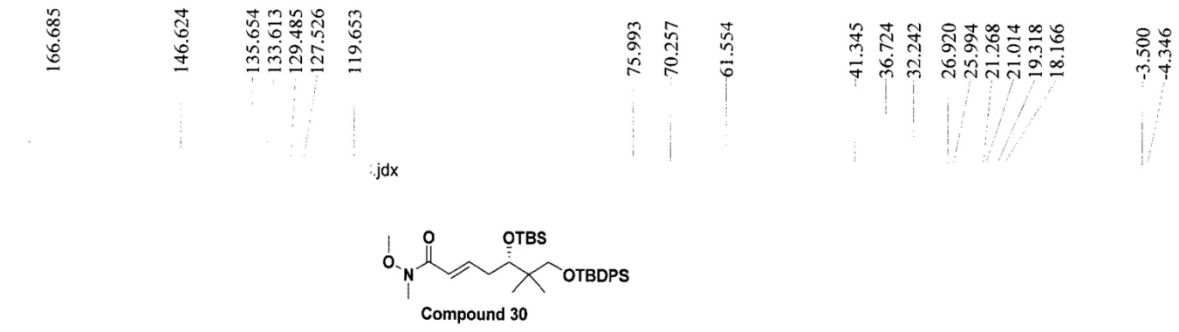


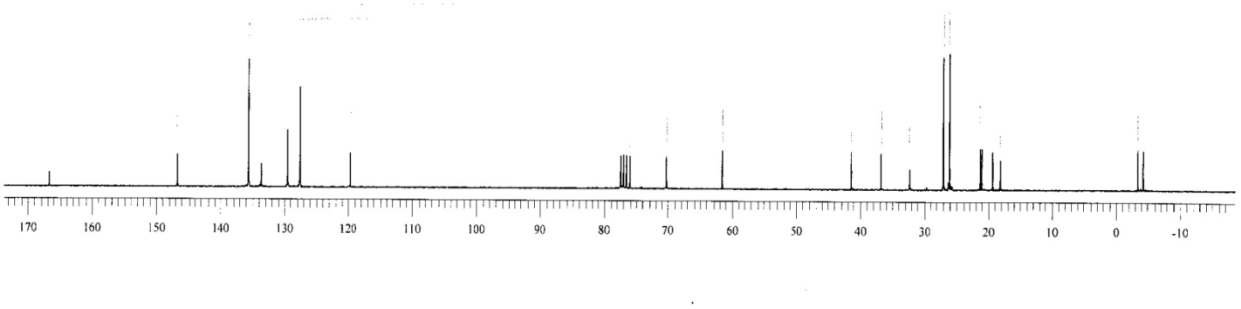
^{1}H NMR spectrum of Compound 30



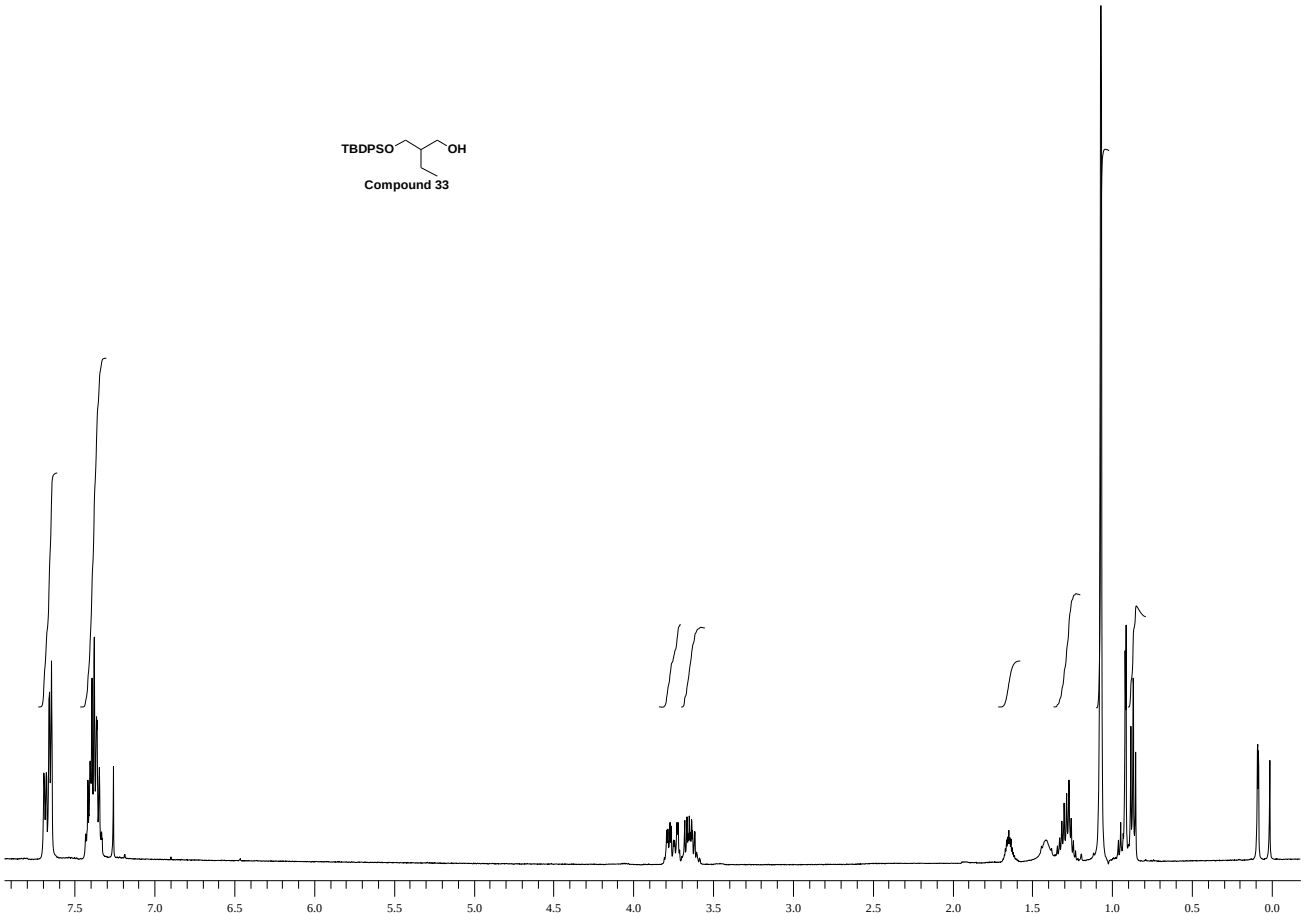
Compound 30

^{13}C NMR spectrum of Compound 30

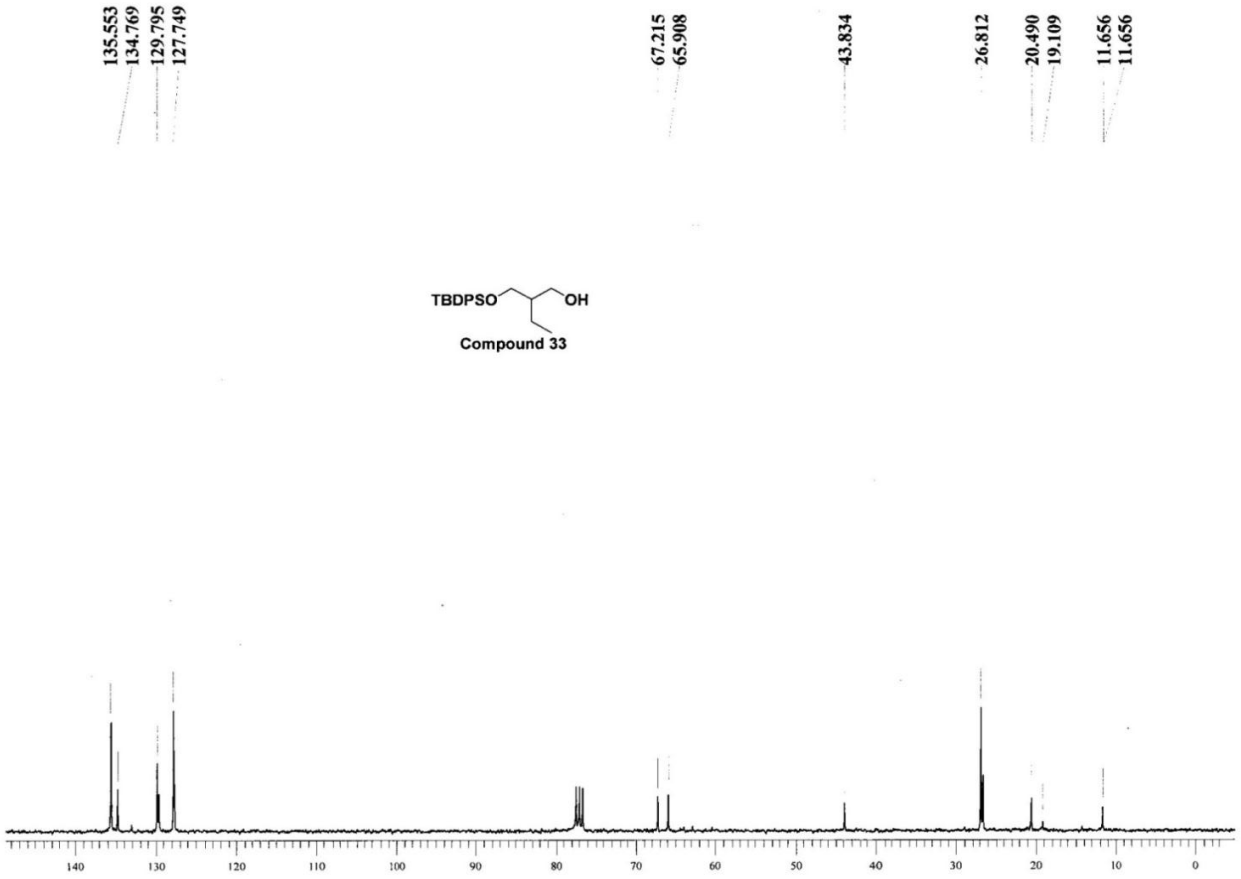




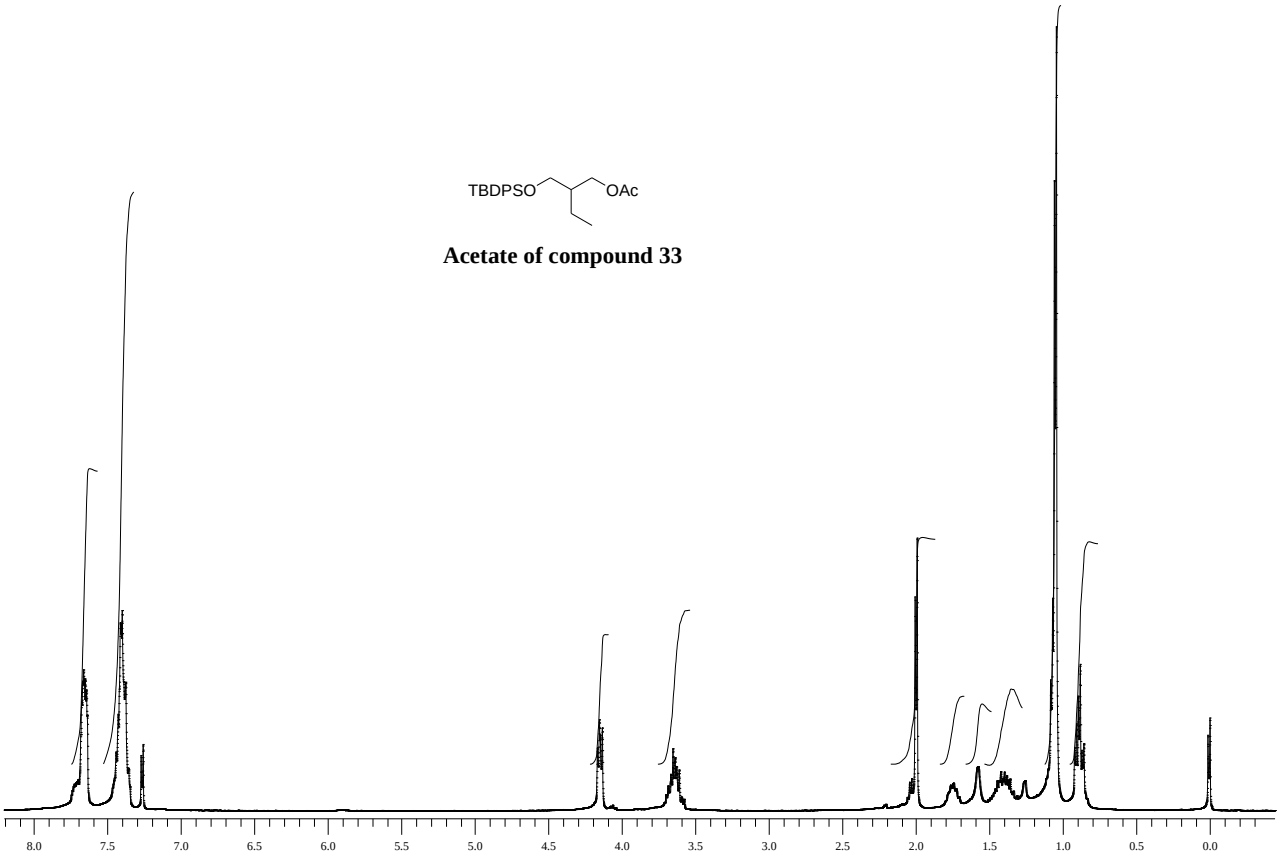
^{1}H NMR spectrum of Compound 33



^{13}C NMR spectrum of Compound 33



^{1}H NMR spectrum of Acetate of Compound 33



Acetate of compound 33

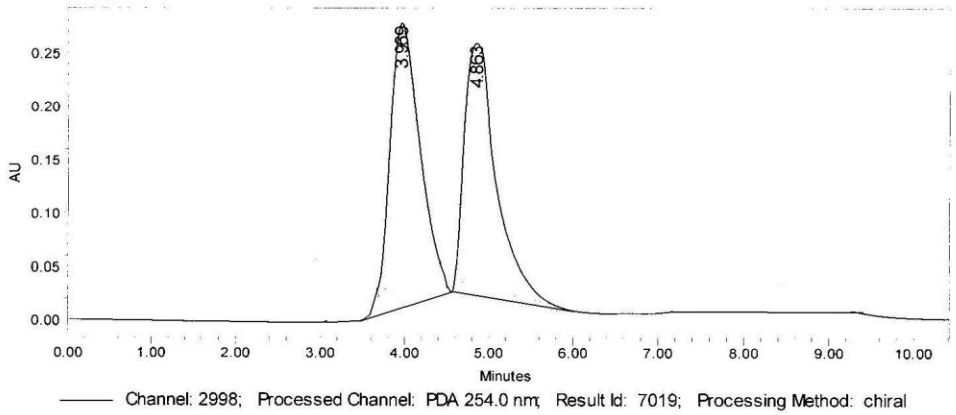
HPLC of Racemic compound of Acetate of 33

Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	Rac OAc 1% I etoh hep	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	
Vial:	1	Acq. Method Set:	VV 1% IPA
Injection #:	1	Processing Method:	chiral
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	29.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	8/31/2011 11:01:58 AM IST		
Date Processed:	8/31/2011 11:14:09 AM IST		



Channel: 2998; Processed Channel: PDA 254.0 nm; Result Id: 7019; Processing Method: chiral

Processed Channel Descr.: PDA 254.0 nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	PDA 254.0 nm	3.969	5774325	49.79	247590
2	PDA 254.0 nm	4.863	5822600	50.21	227809

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1005
Page: 1 of 1

Project Name: APRIL 2009
Date Printed: 6/11/2012
8:32:13 PM Asia/Calcutta

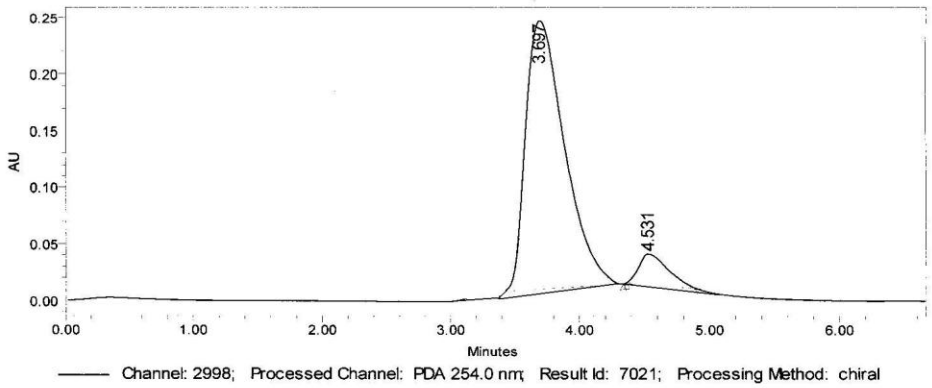
HPLC of Acetate of compound 33

Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	Chi OAc 1% Ietoh hep	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	
Vial:	1	Acq. Method Set:	VV 1% IPA
Injection #:	2	Processing Method:	chiral
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	29.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	8/31/2011 11:13:21 AM IST		
Date Processed:	8/31/2011 11:20:34 AM IST		



Channel: 2998; Processed Channel: PDA 254.0 nm; Result Id: 7021; Processing Method: chiral

Processed Channel Descr.: PDA 254.0 nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	PDA 254.0 nm	3.697	4943058	92.54	236227
2	PDA 254.0 nm	4.531	398419	7.46	26538

Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1005
Page: 1 of 1

Project Name: APRIL 2009
Date Printed: 6/11/2012
8:33:07 PM Asia/Calcutta

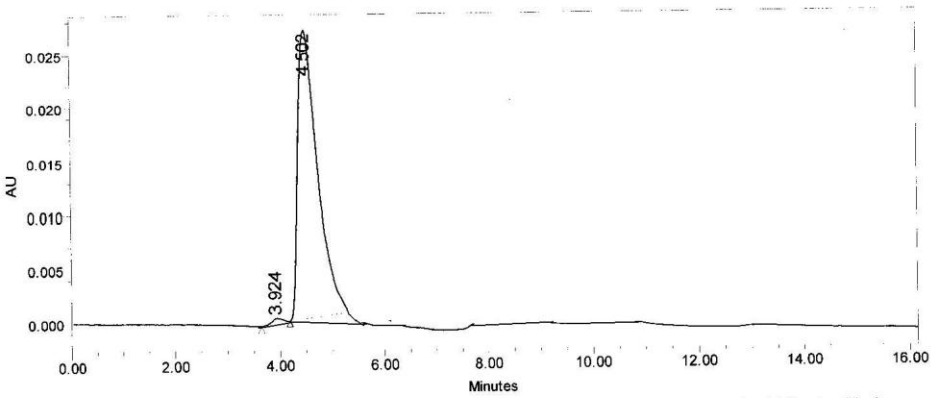
HPLC of Acetate of compound *epi*-33

Empower 2 software

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	VV-Ace-OH	Acquired By:	System
Sample Type:	Standard	Sample Set Name:	
Vial:	1	Acq. Method Set:	VV 1% IPA
Injection #:	5	Processing Method:	chiral
Injection Volume:	20.00 ul	Channel Name:	254.0nm
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	11/21/2012 7:47:57 PM IST		
Date Processed:	11/21/2012 8:15:08 PM IST		



Channel: 2998; Processed Channel: PDA 254.0 nm; Result Id: 9679; Processing Method: chiral

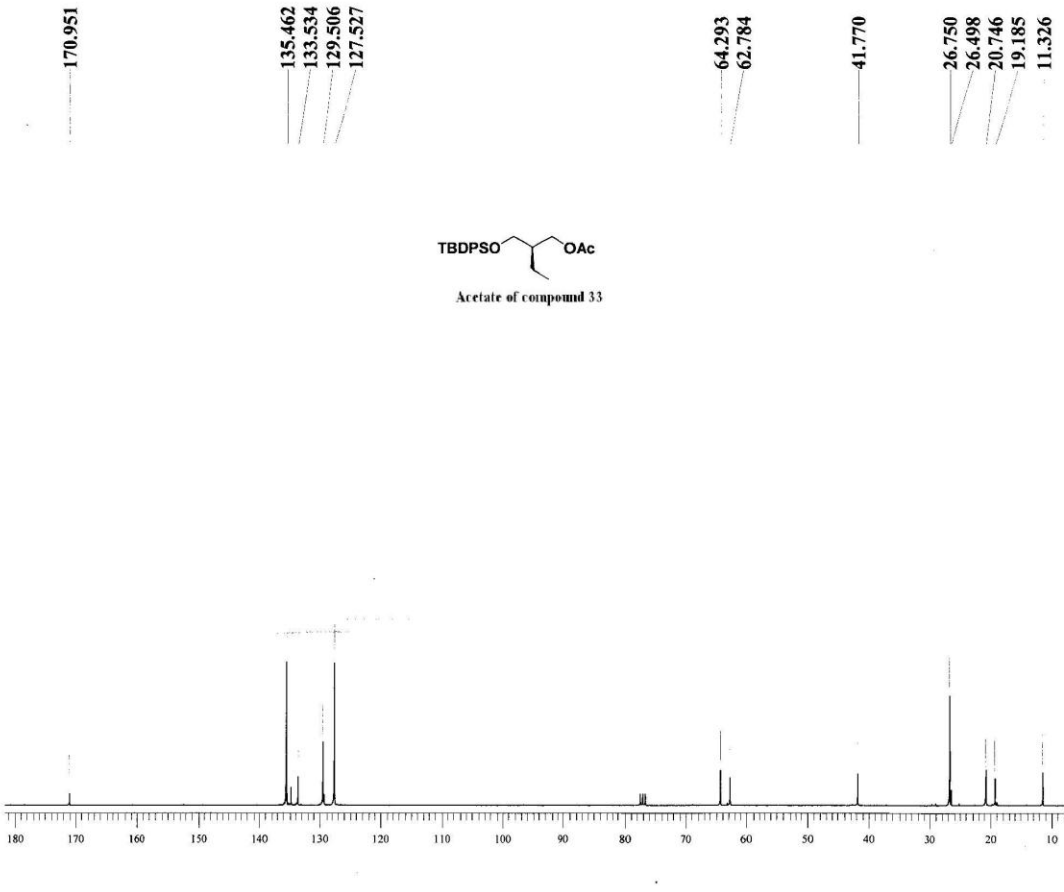
Processed Channel Descr.: PDA 254.0 nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	PDA 254.0 nm	3.924	7335	1.04	544
2	PDA 254.0 nm	4.502	696497	98.96	26872

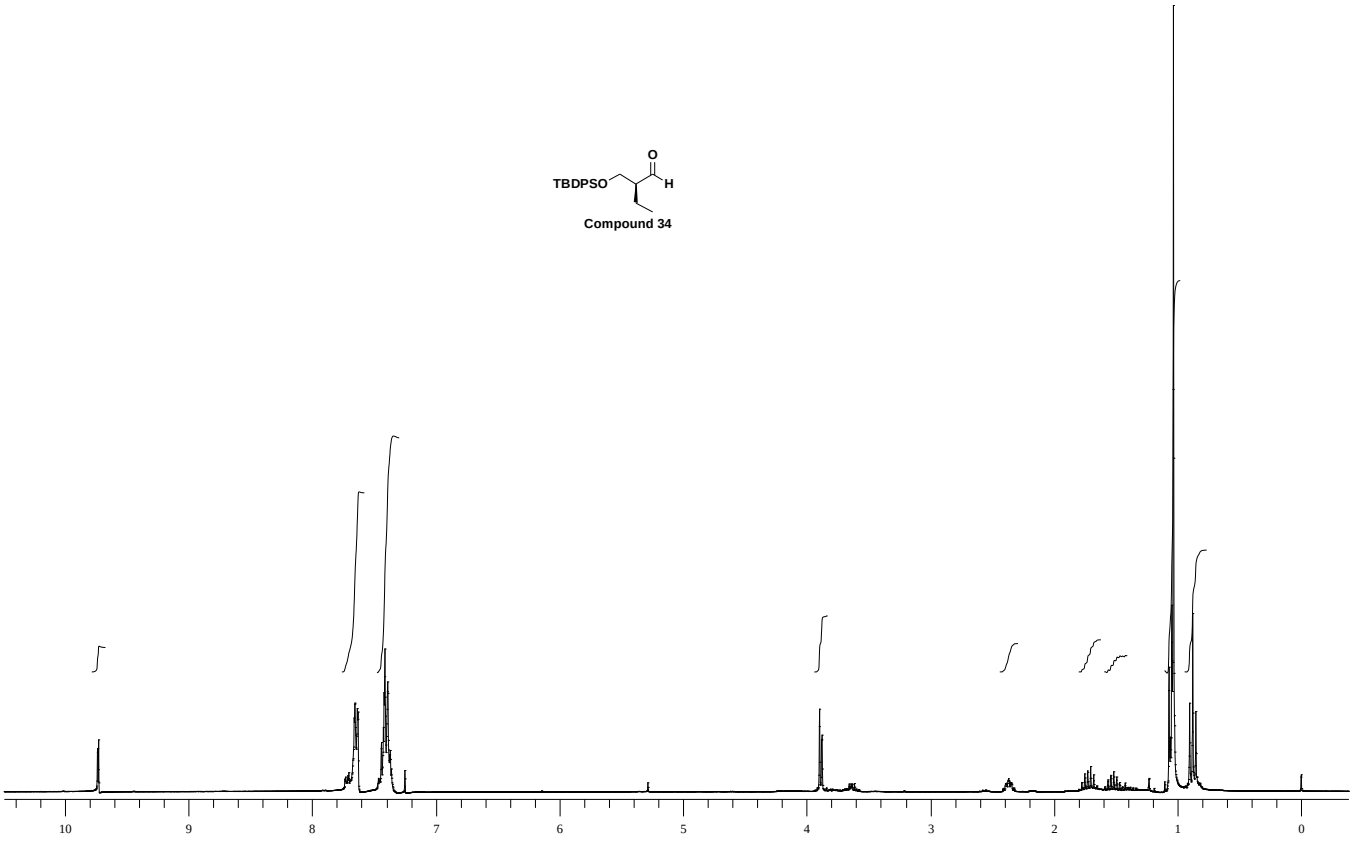
Reported by User: System
Report Method: Injection Summary Report
Report Method ID: 1005
Page: 1 of 1

Project Name: APRIL 2009
Date Printed:
11/21/2012
8:15:34 PM Asia/Calcutta

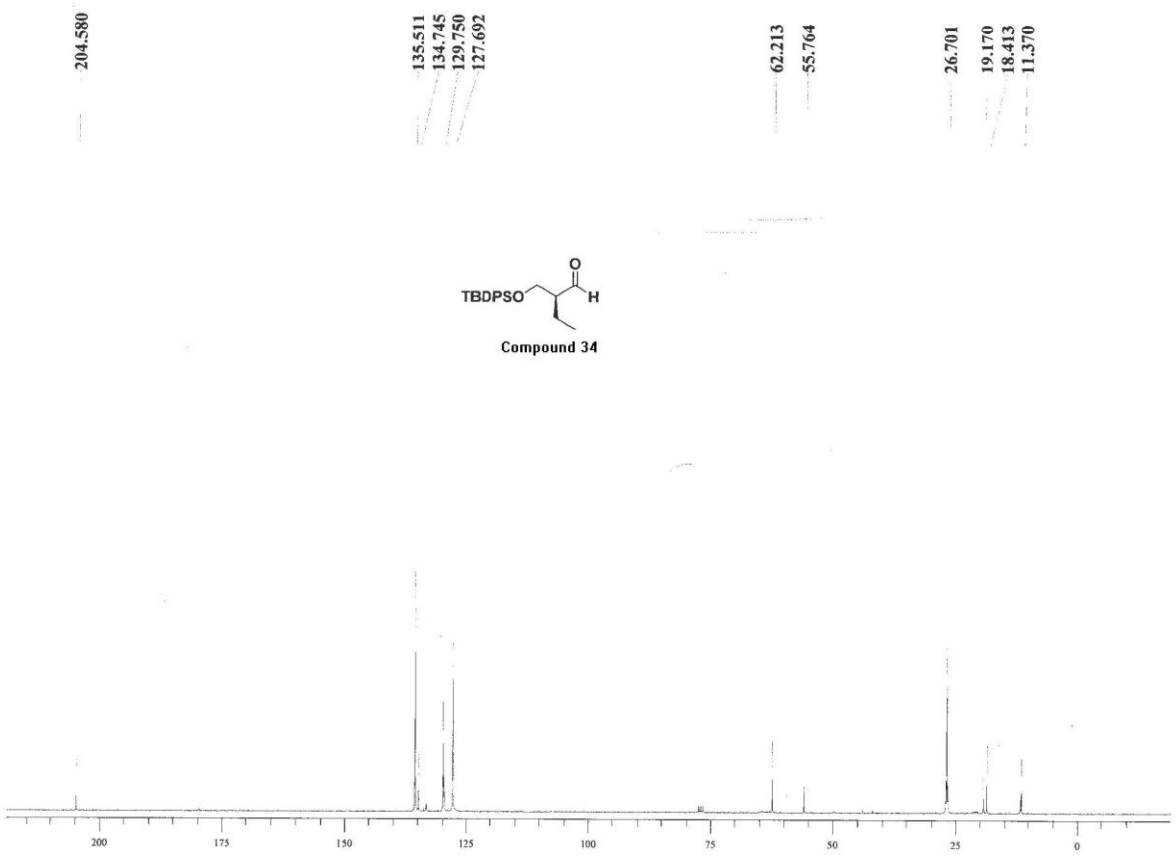
^{13}C NMR spectrum of Acetate of Compound 33



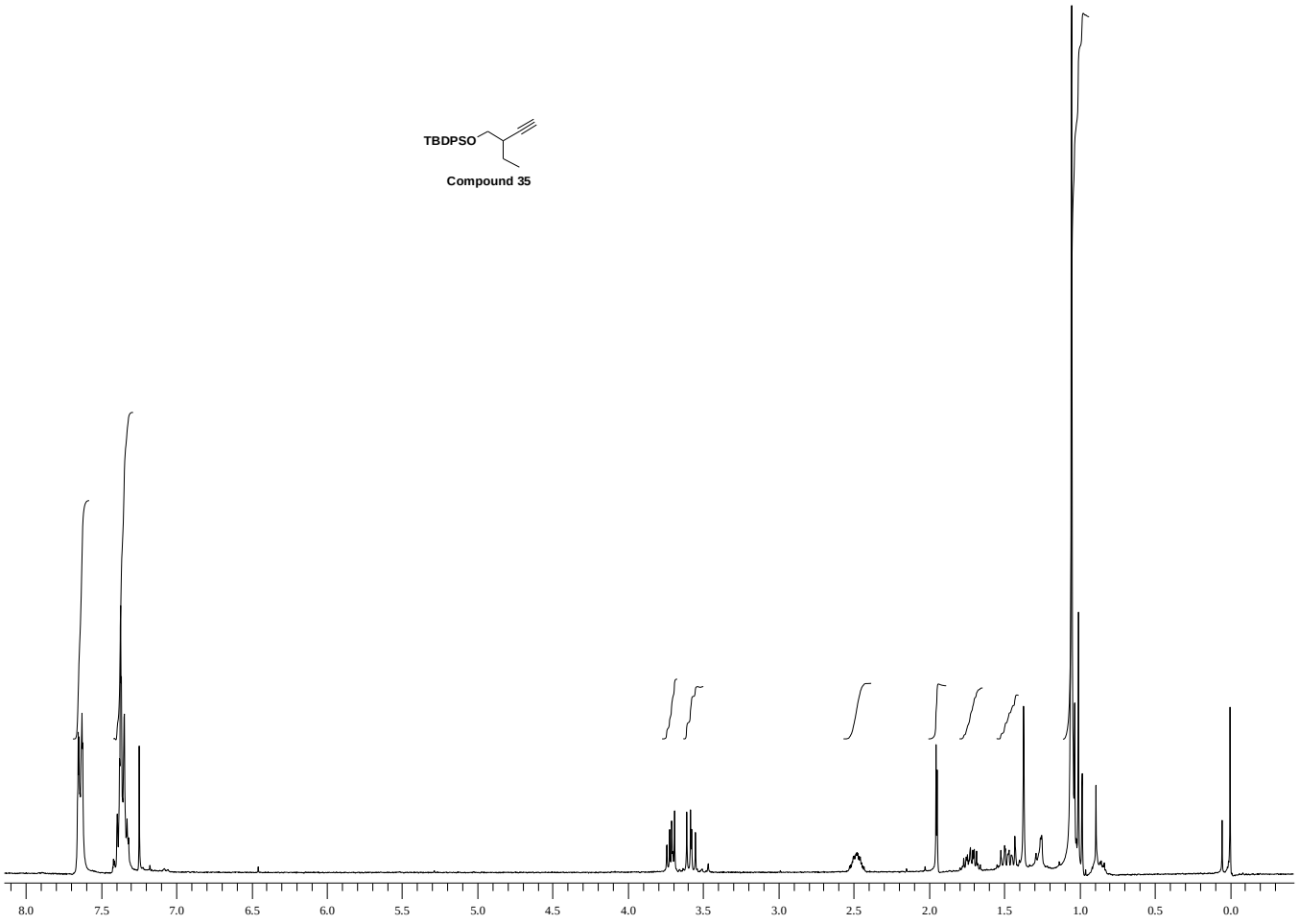
^{1}H NMR spectrum of Compound 34



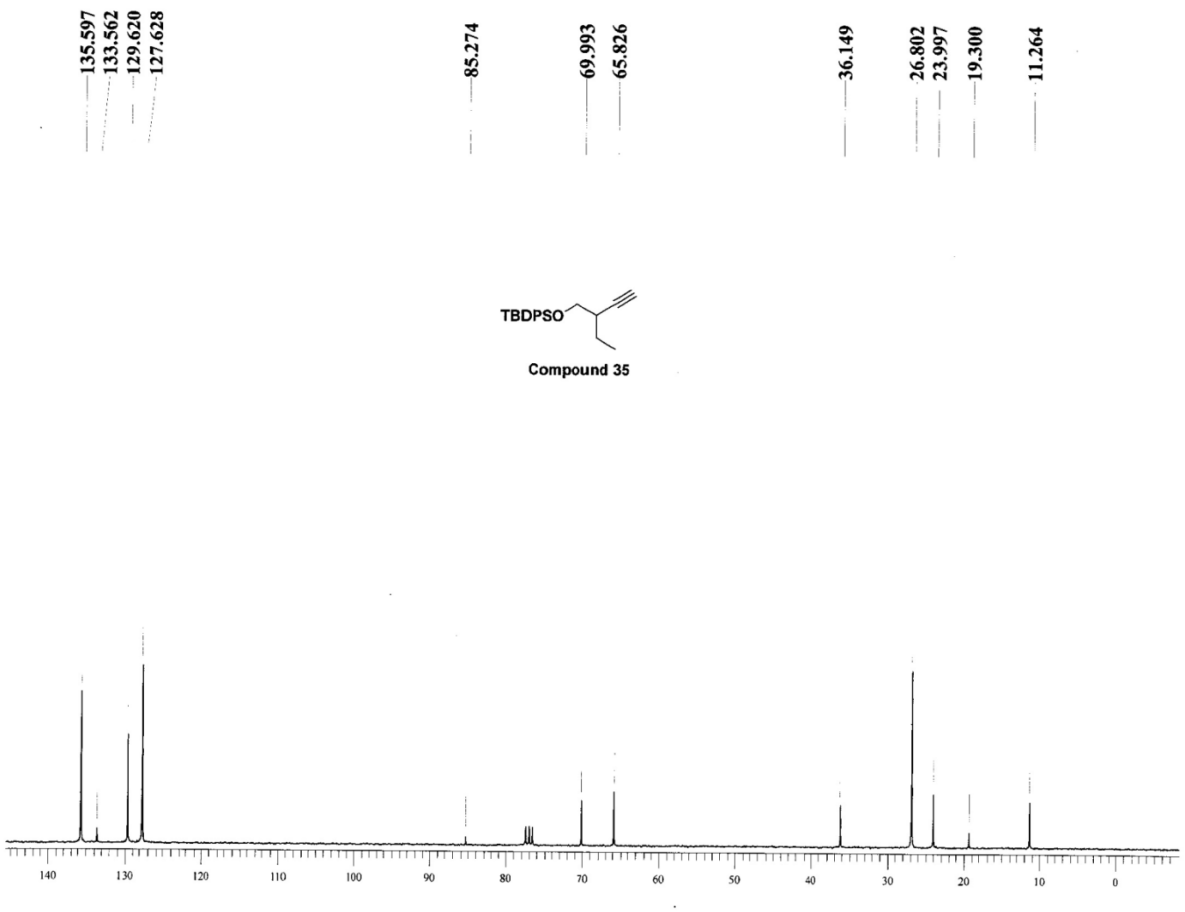
^{13}C NMR spectrum of Compound 34



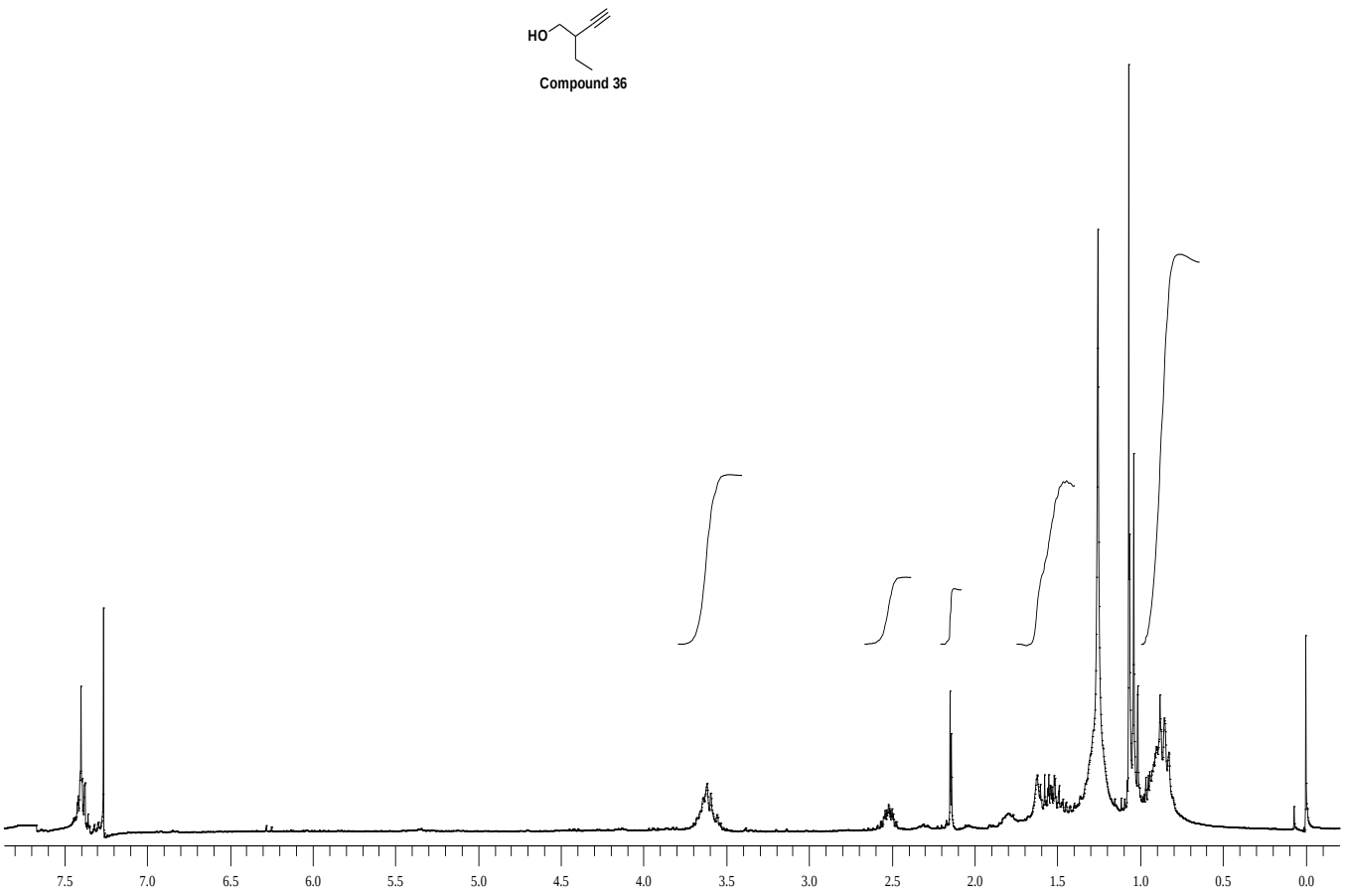
^{1}H NMR spectrum of Compound 35



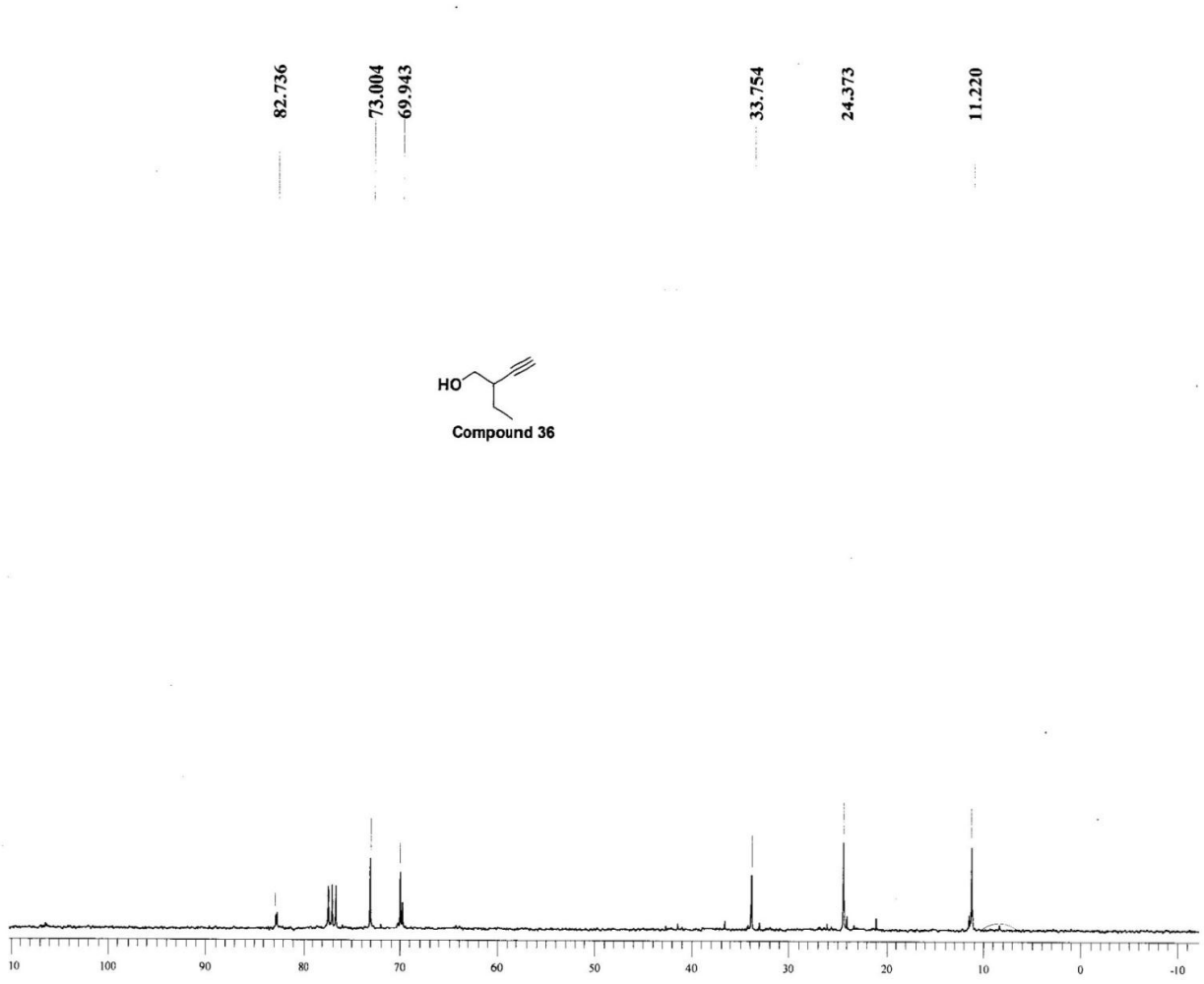
^{13}C NMR spectrum of Compound 35



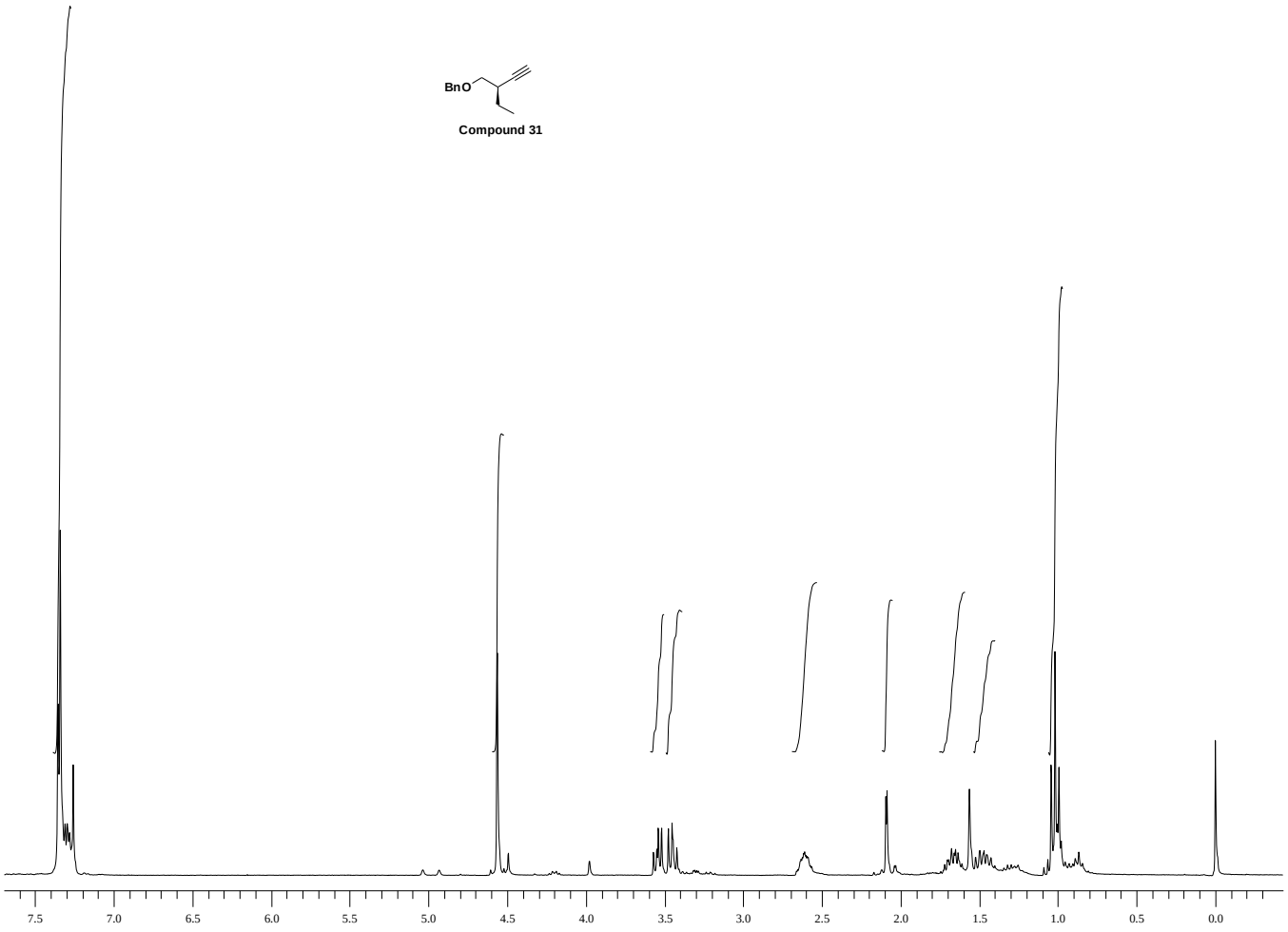
^{1}H NMR spectrum of Compound 36



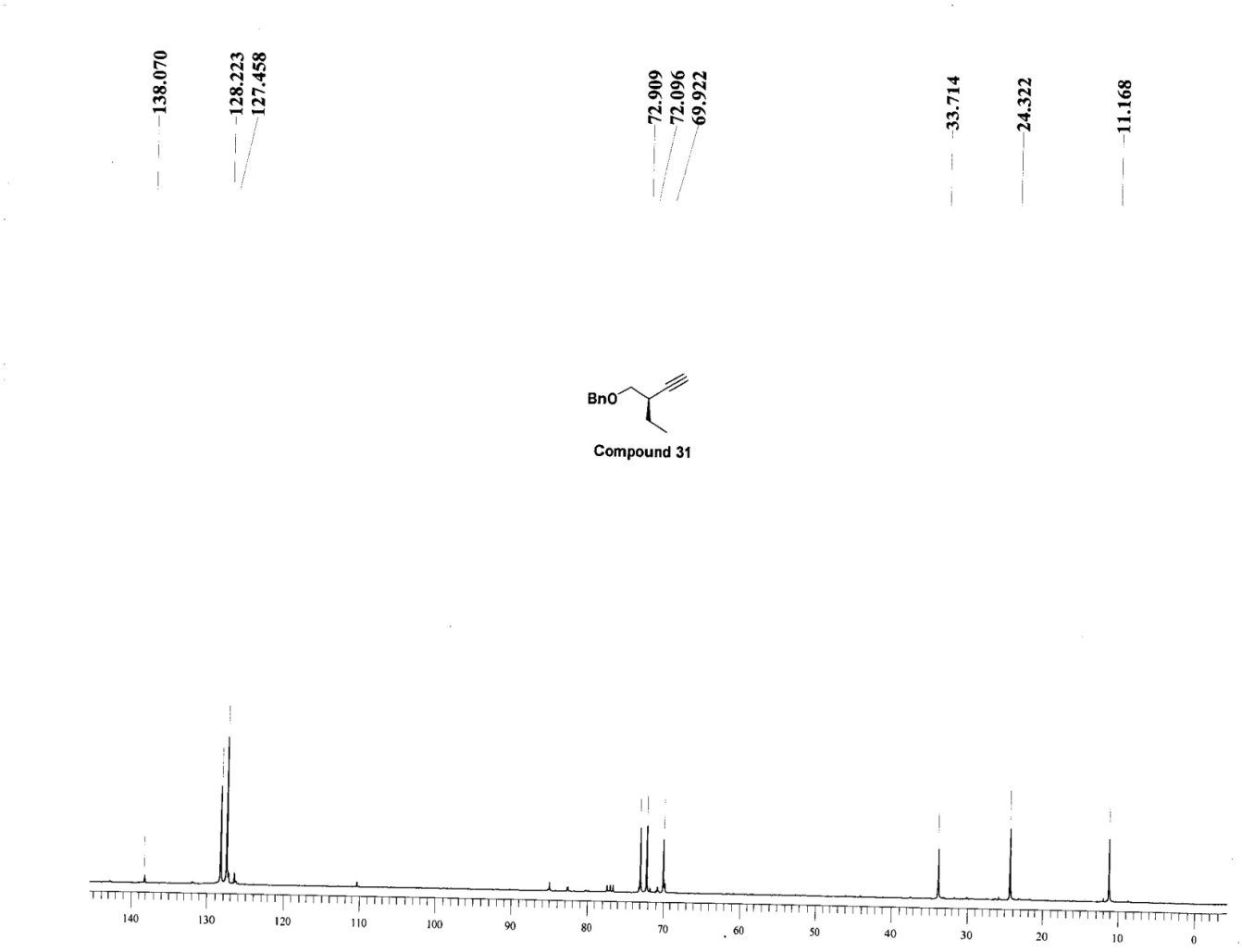
^{13}C NMR spectrum of Compound 36



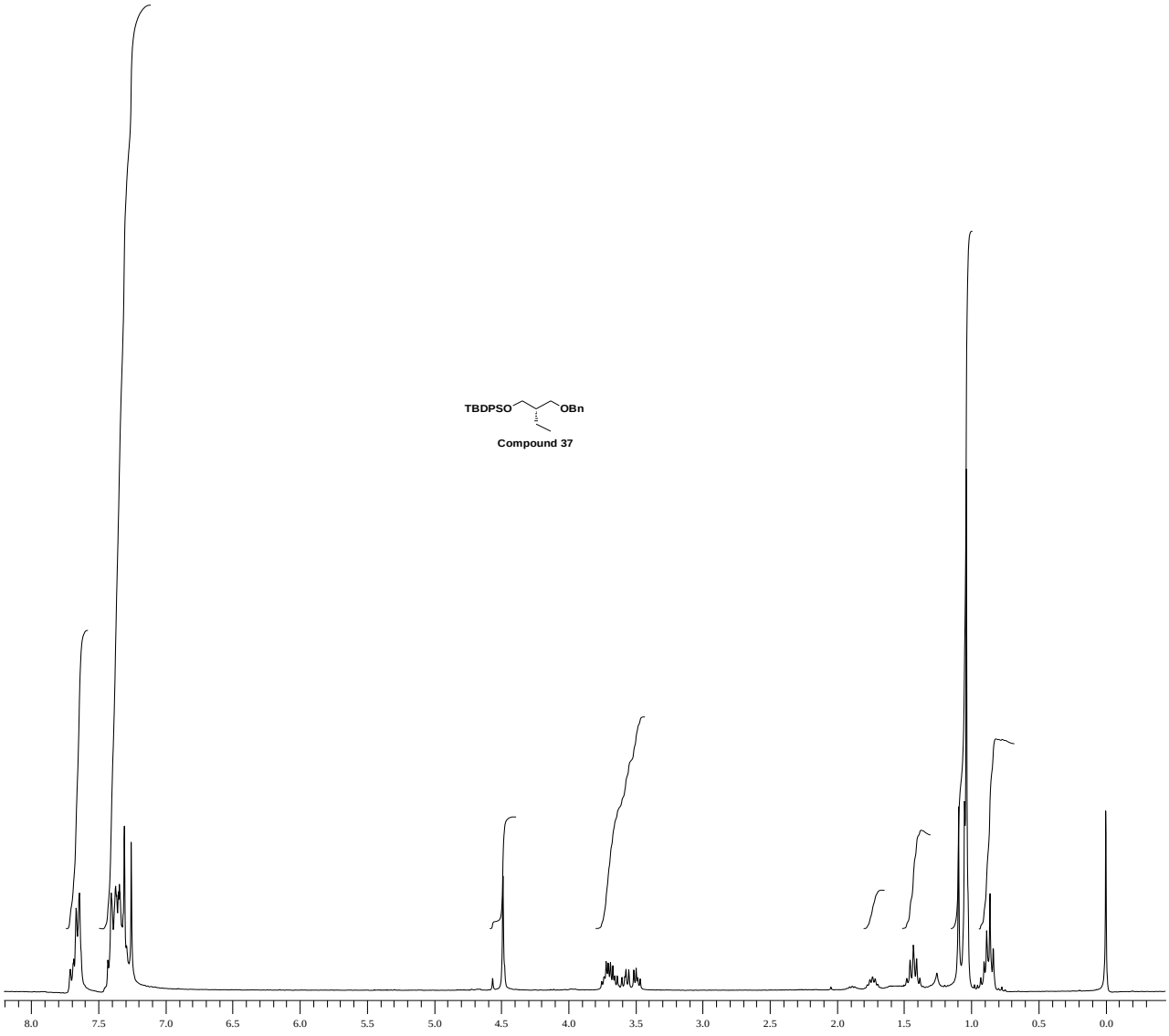
^{1}H NMR spectrum of Compound 31



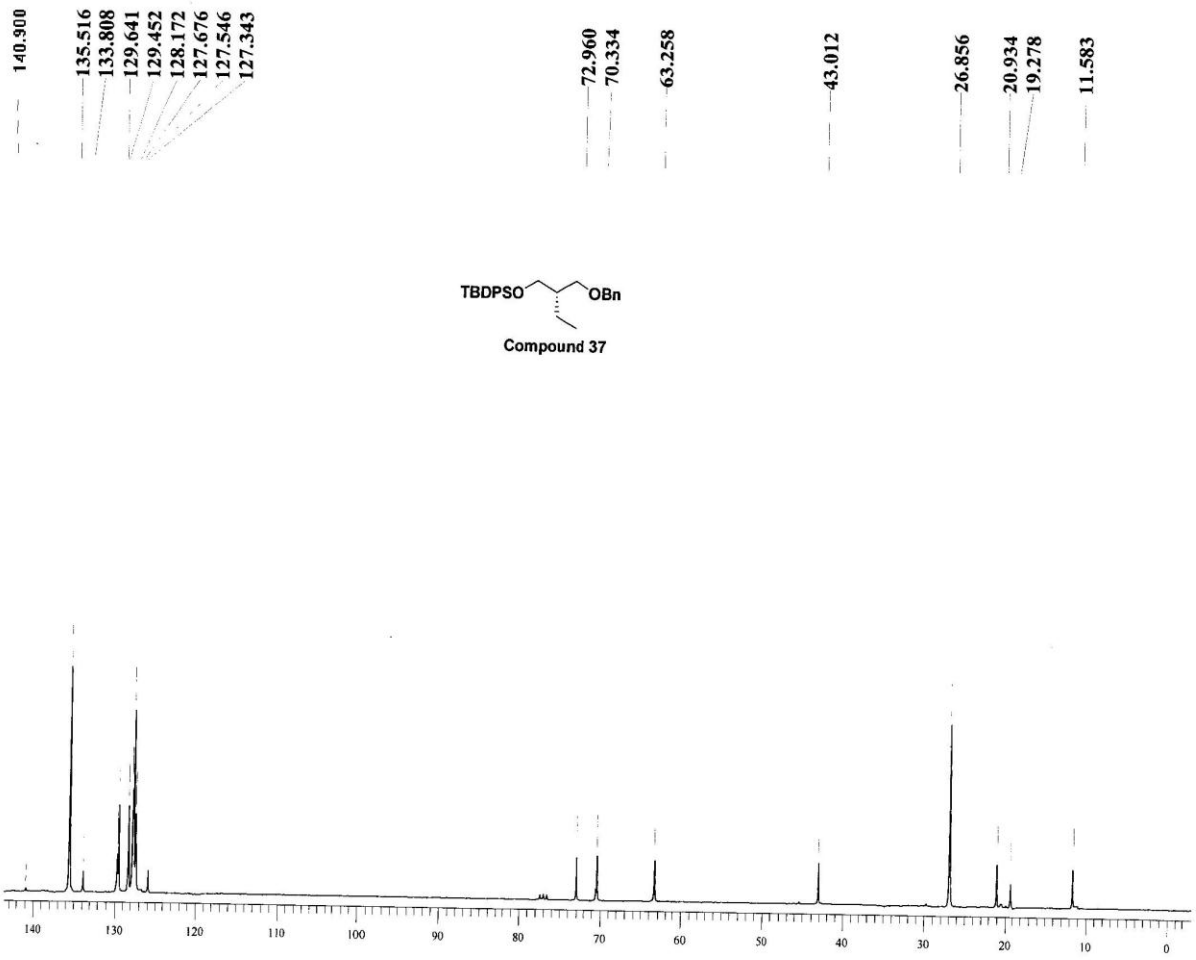
^{13}C NMR spectrum of Compound 31



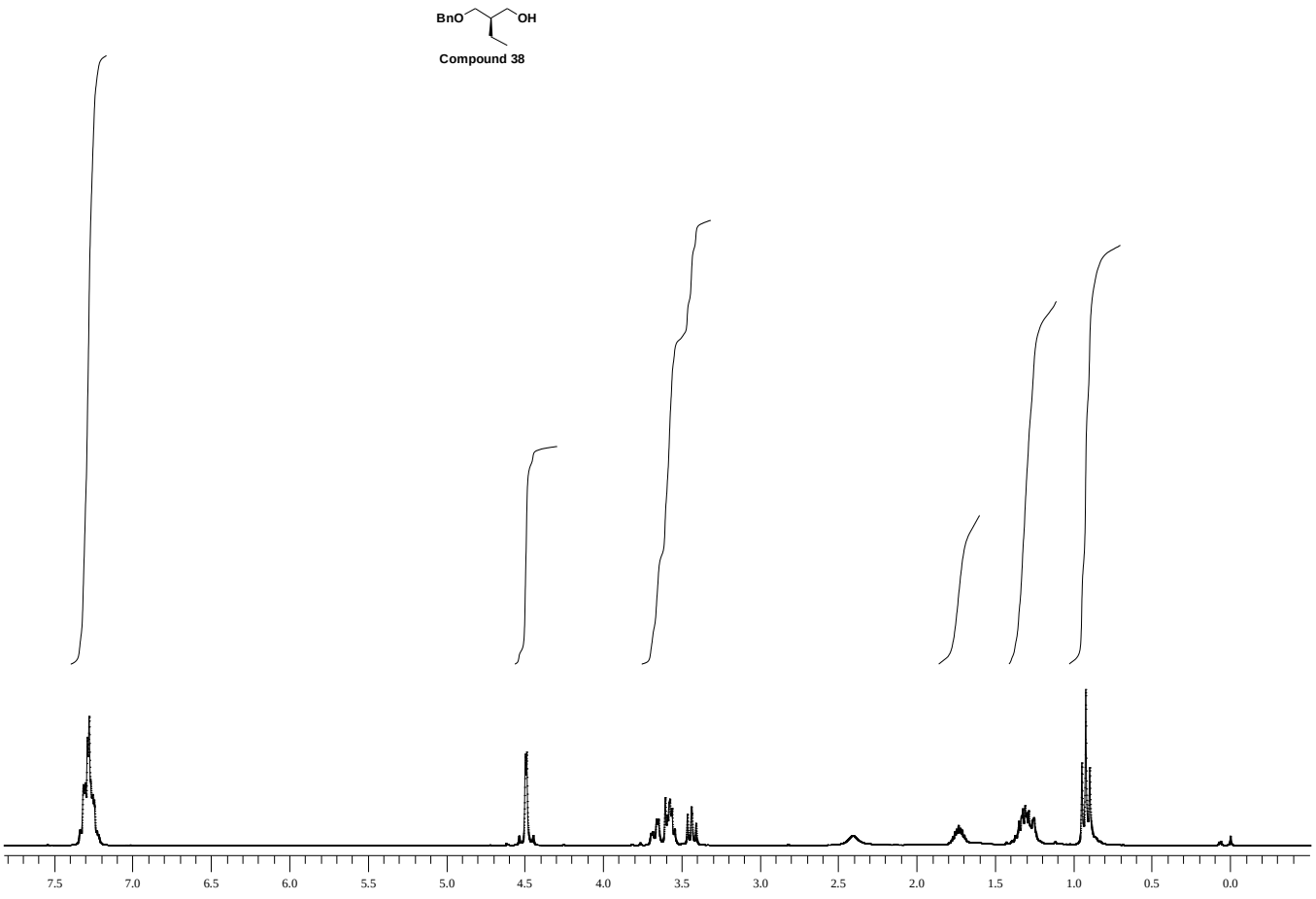
^{1}H NMR spectrum of Compound 37



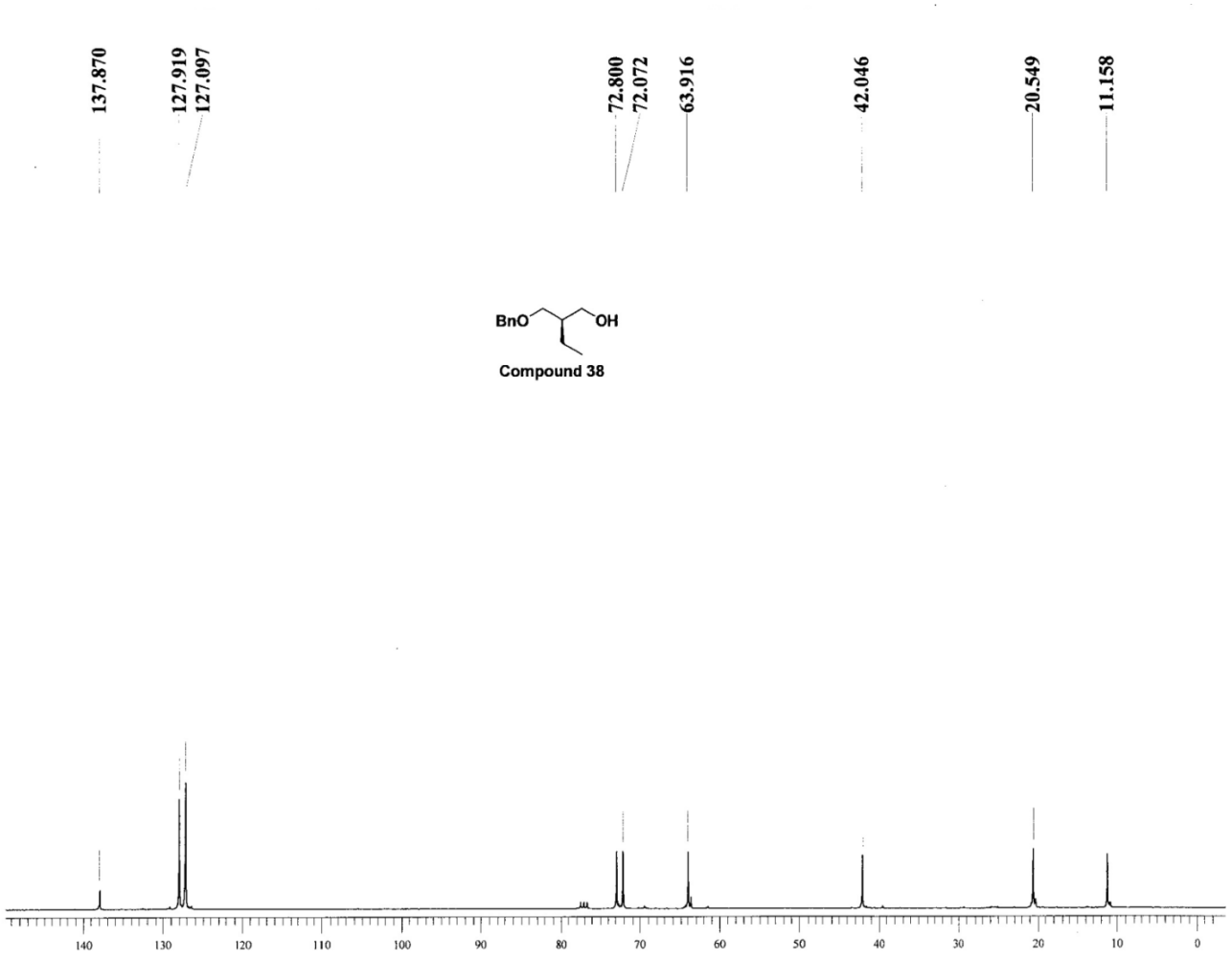
^{13}C NMR spectrum of Compound 37



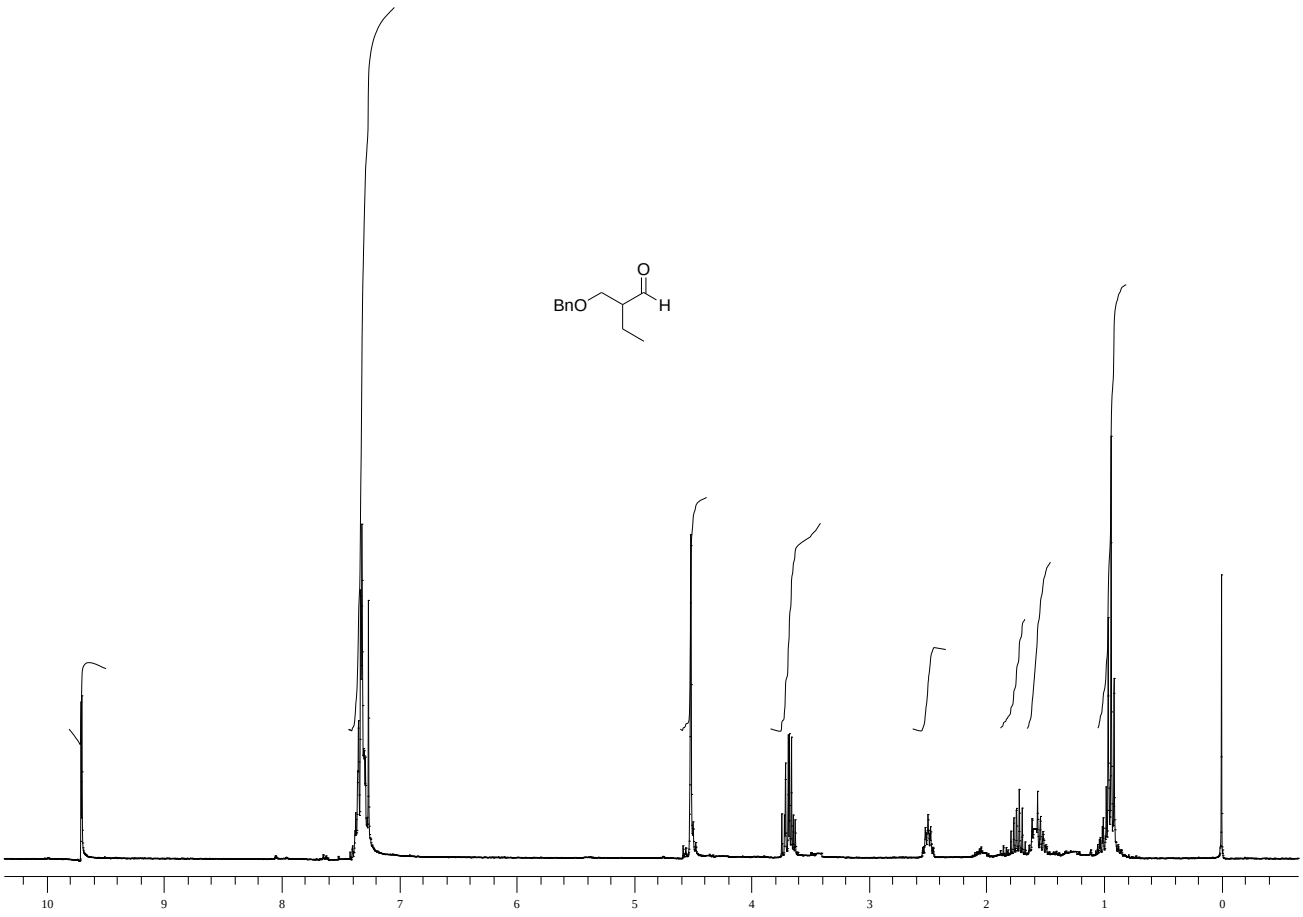
^{1}H NMR spectrum of Compound 38



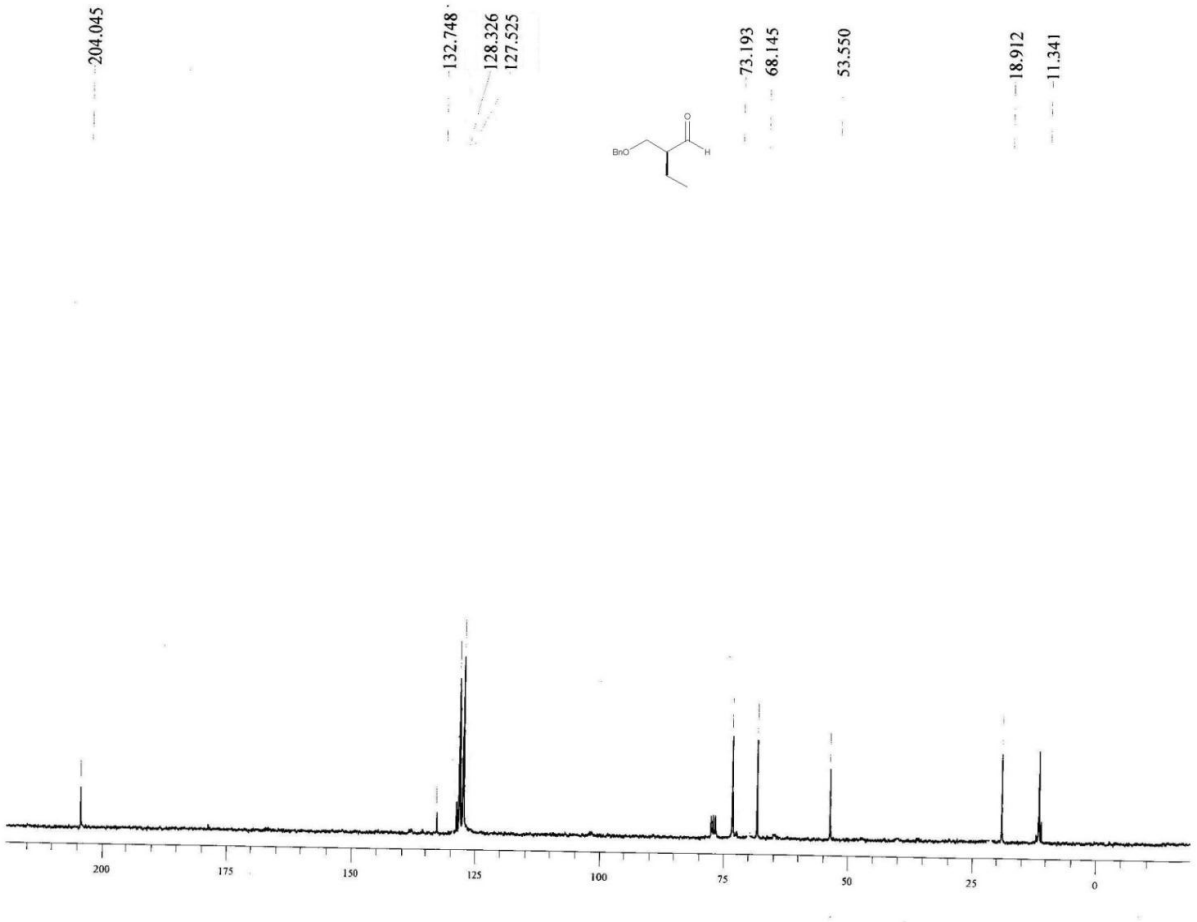
^{13}C NMR spectrum of Compound 38



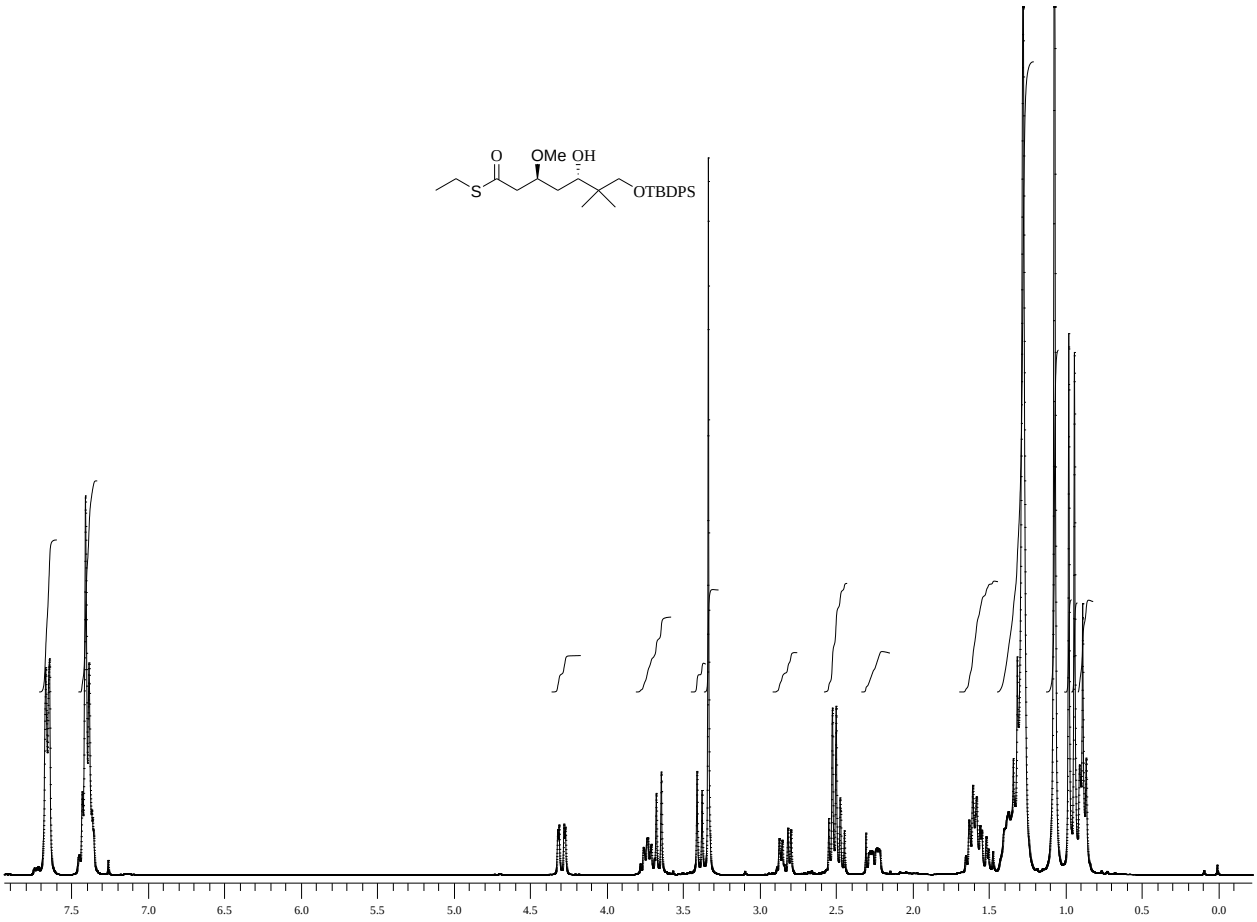
^{1}H NMR spectrum of aldehyde of Compound 38



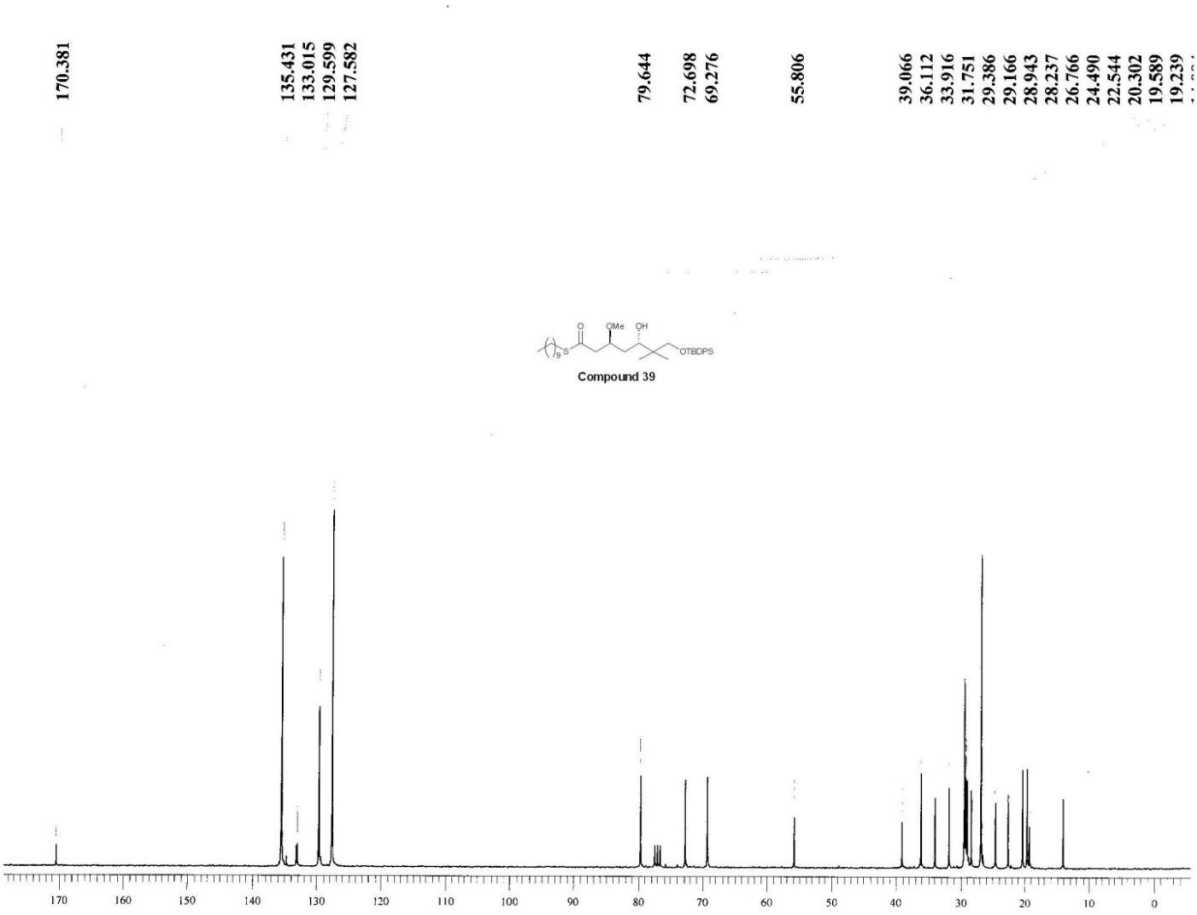
^{13}C NMR spectrum of aldehyde of Compound 38



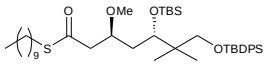
^{1}H NMR spectrum of Compound 39



^{13}C NMR spectrum of Compound 39

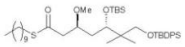


^{1}H NMR spectrum of Compound 40

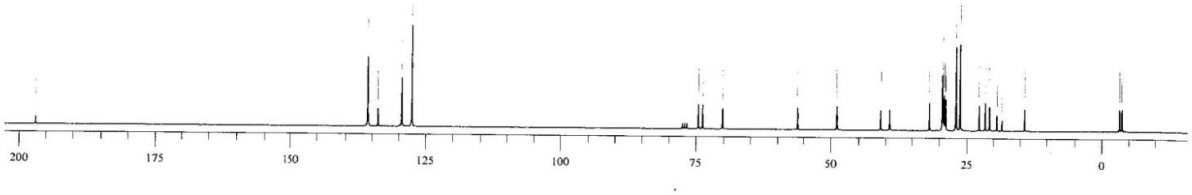


Compound 40

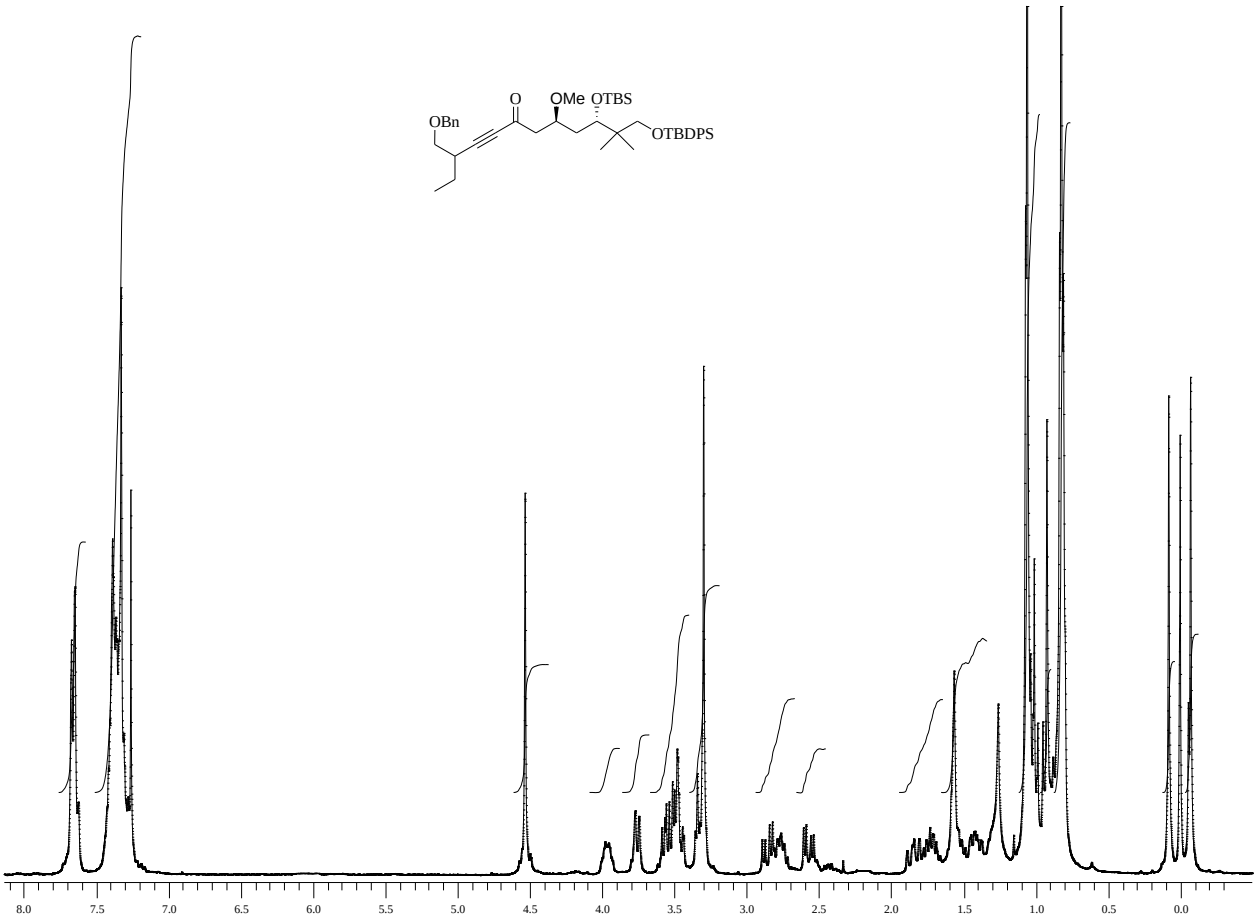
^{13}C NMR spectrum of Compound 40



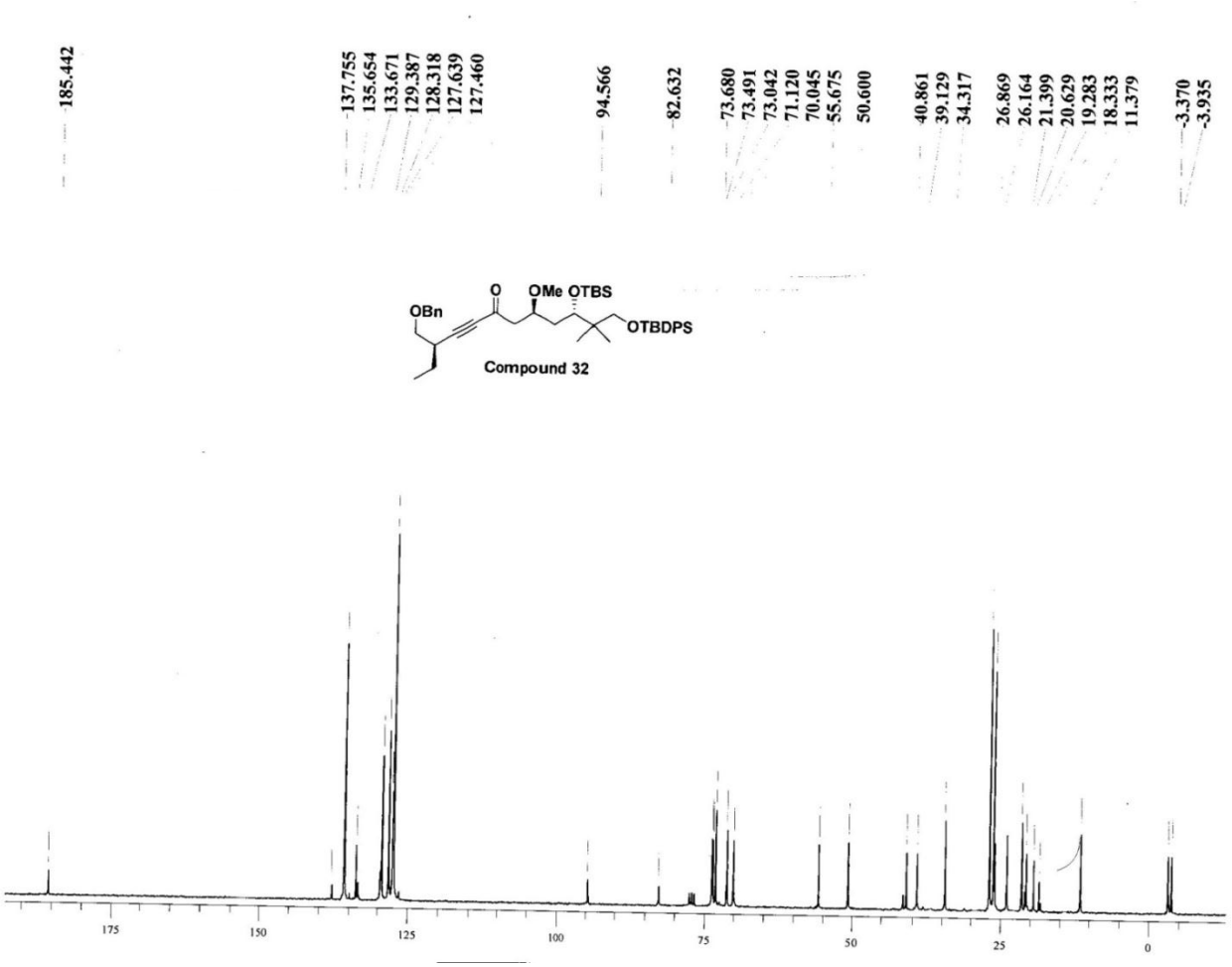
Compound 40



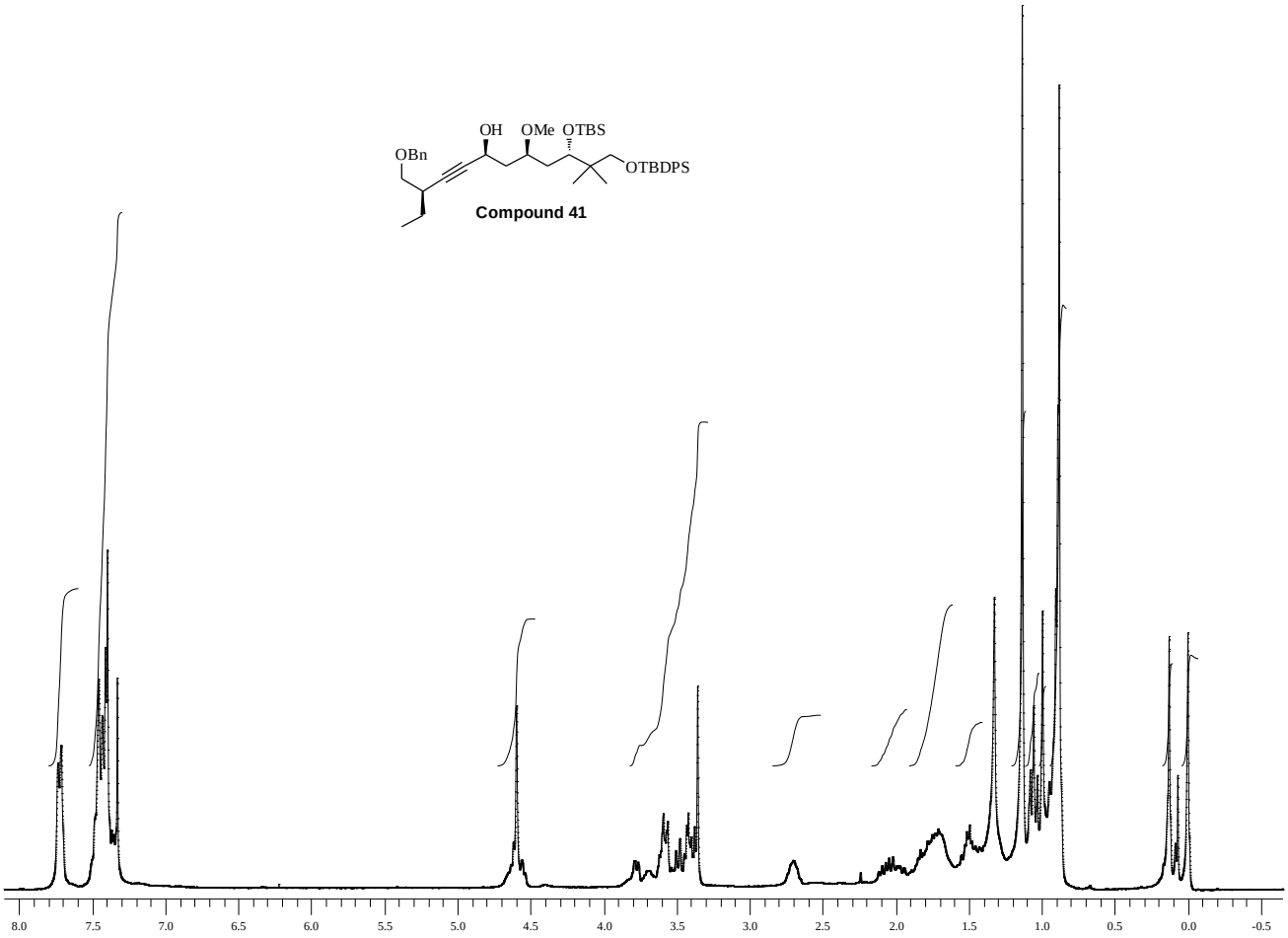
^{1}H NMR spectrum of Compound 32



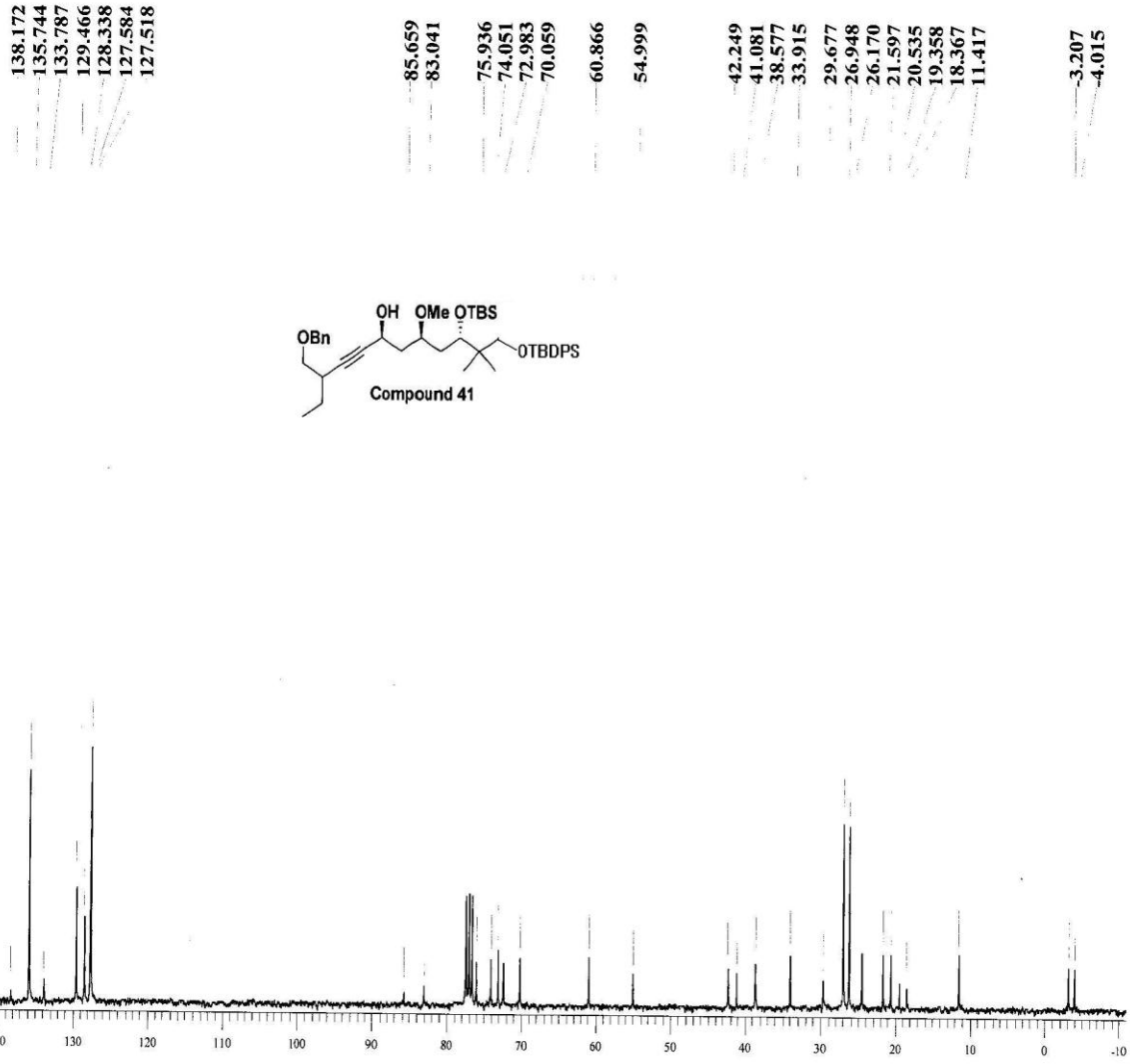
^{13}C NMR spectrum of Compound 32



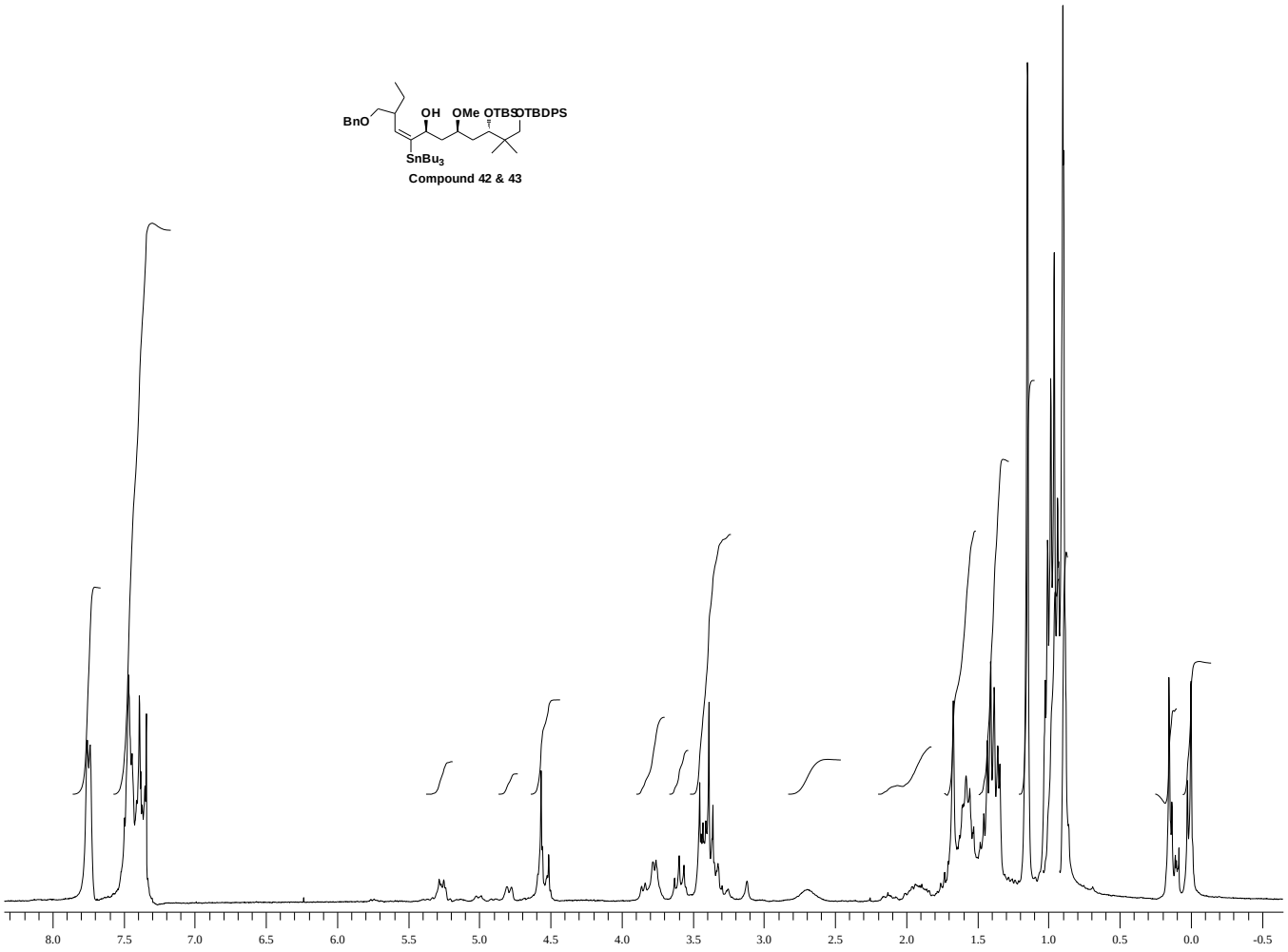
^{1}H NMR spectrum of Compound 41



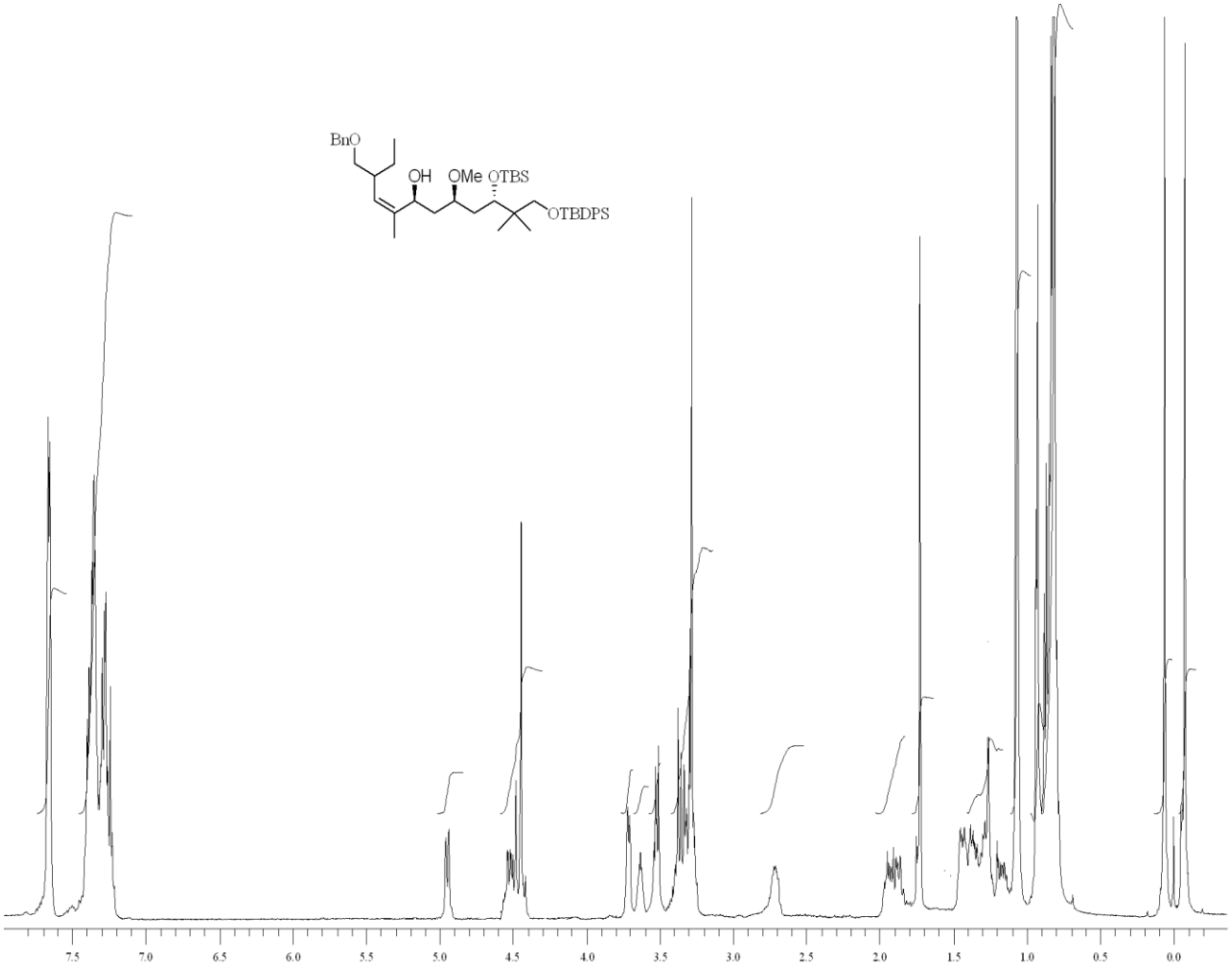
^{13}C NMR spectrum of Compound 41



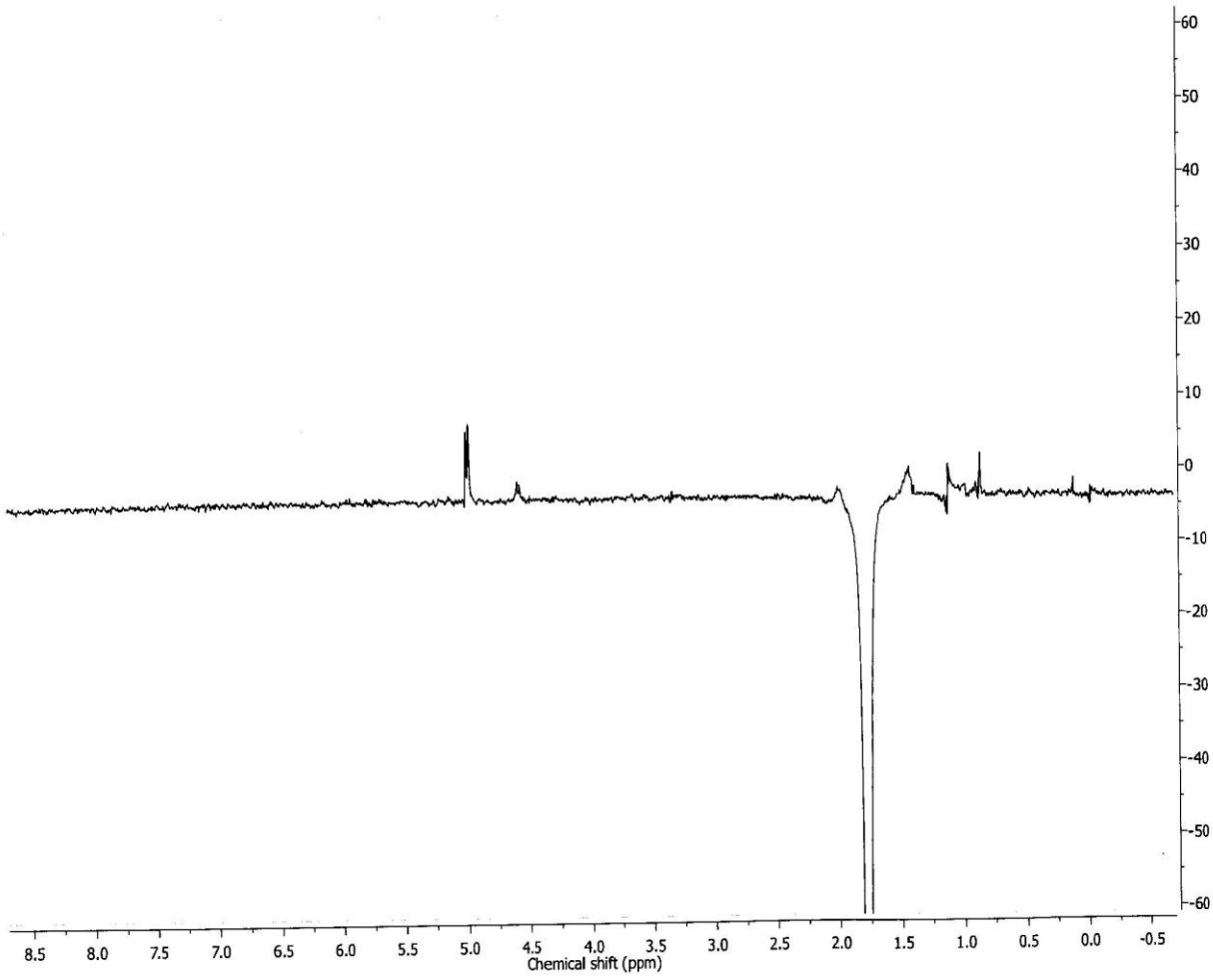
^{1}H NMR spectrum of mixture of Compound 42 and 43

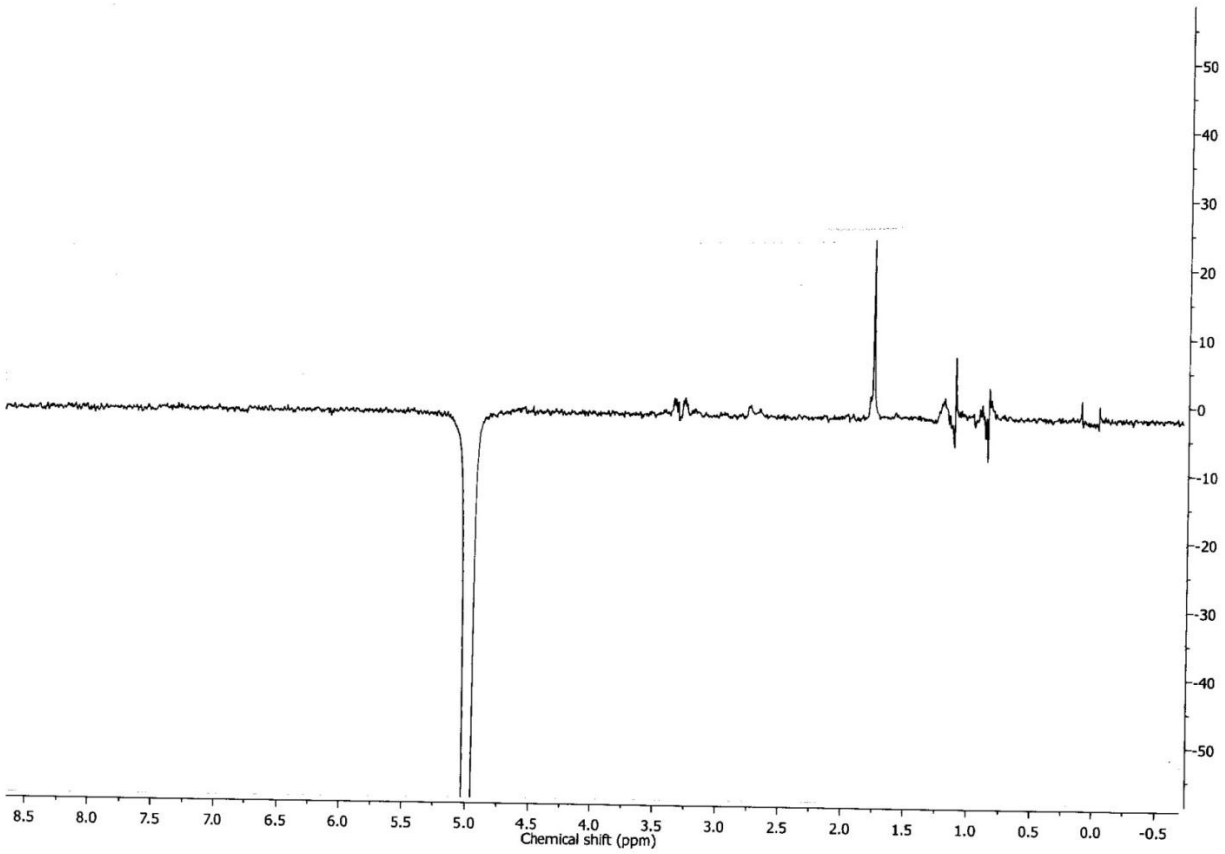


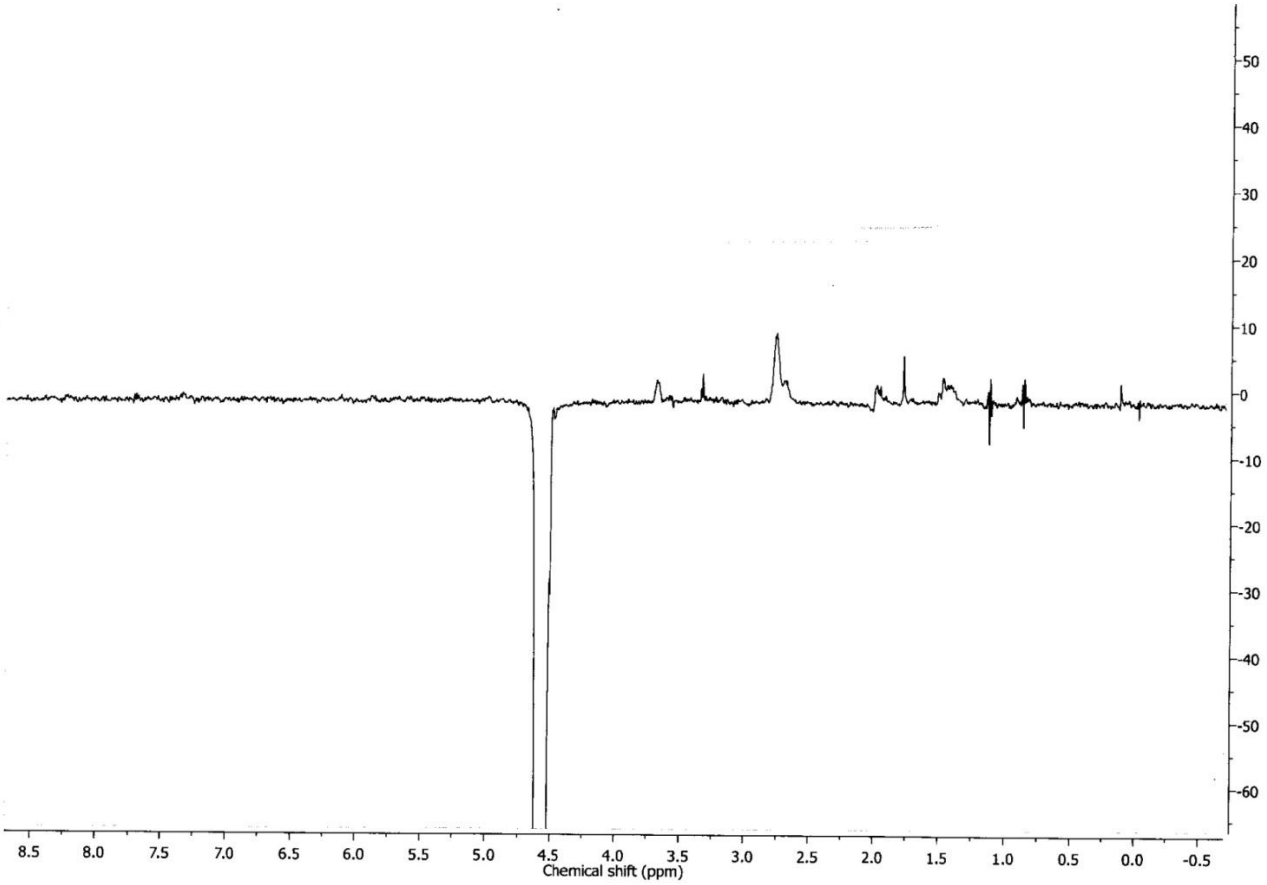
^{1}H NMR spectrum of Compound 44



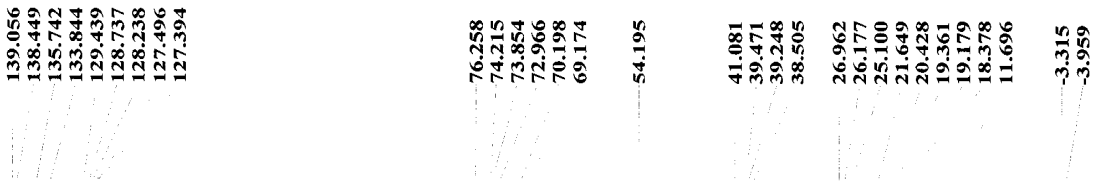
NOE for Compound 44

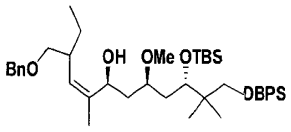




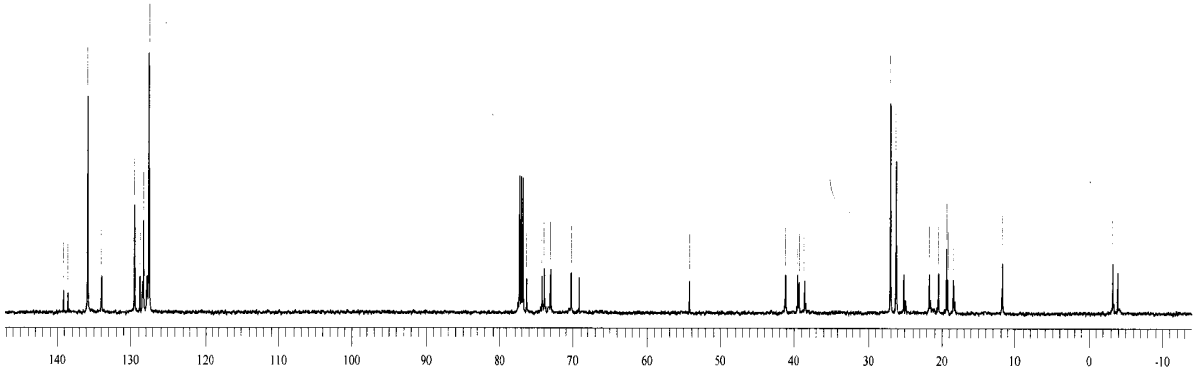


^{13}C NMR spectrum of Compound 44

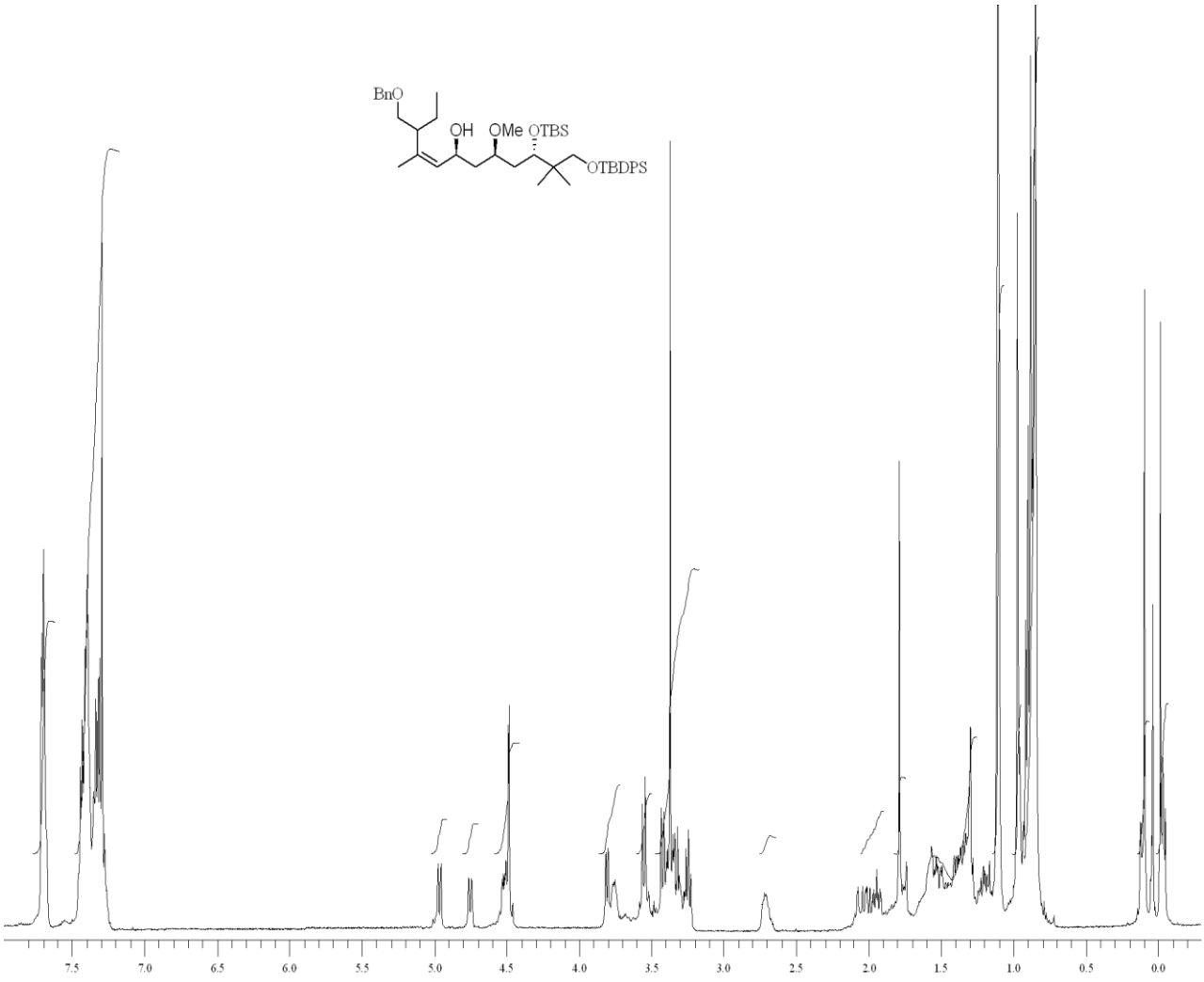




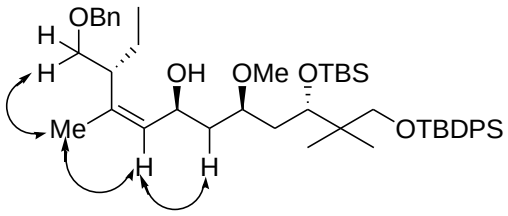
Compound 44



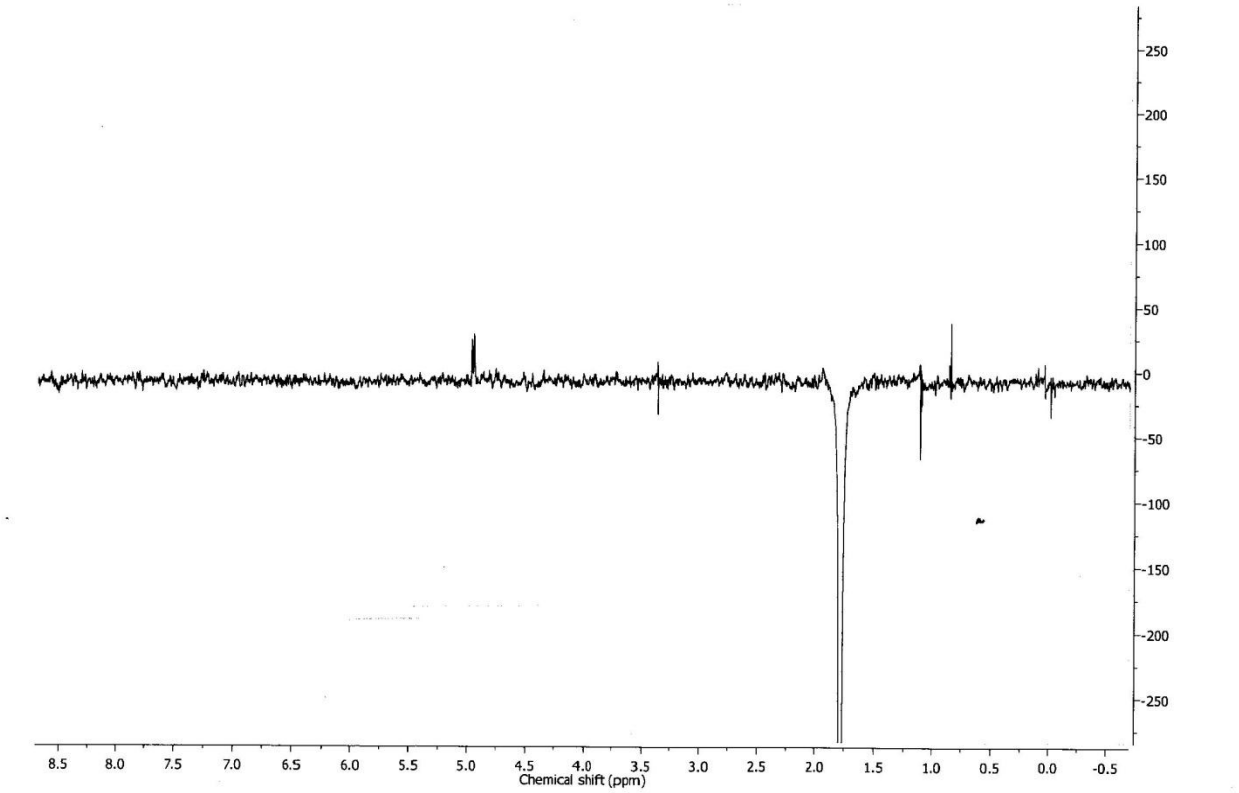
^{1}H NMR spectrum of Compound 45

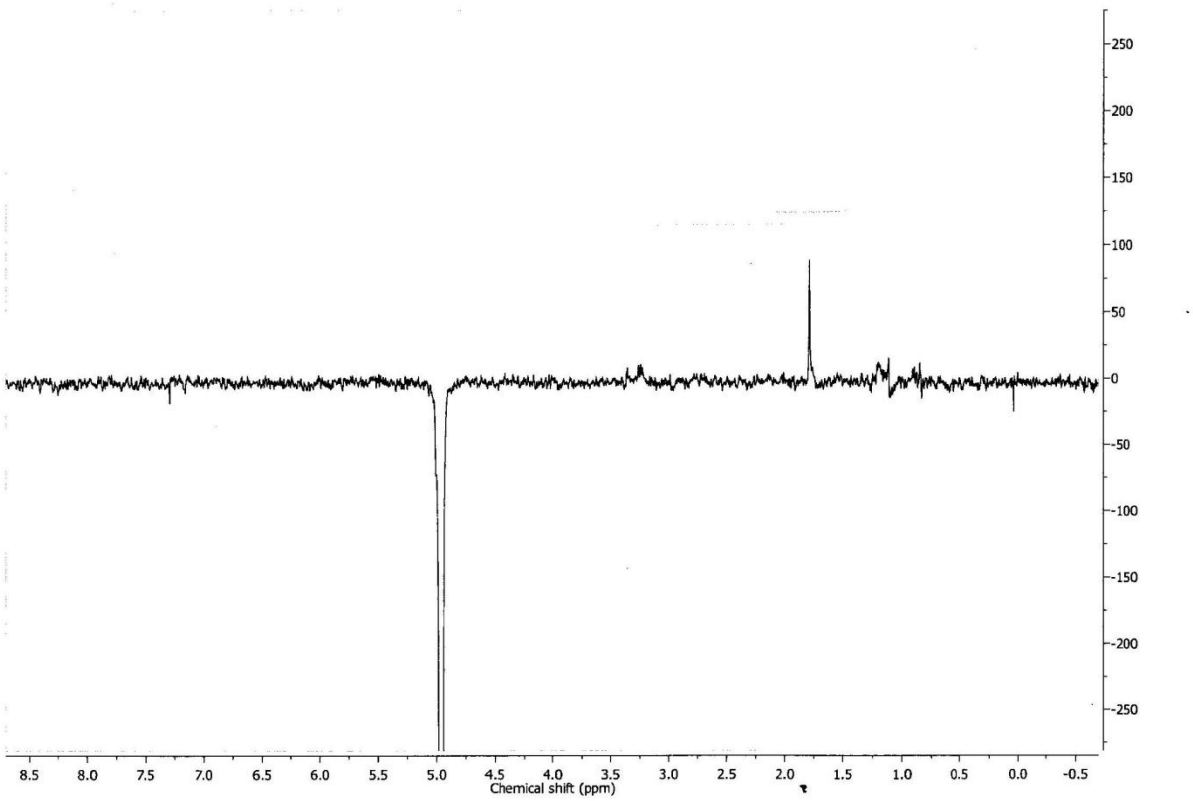


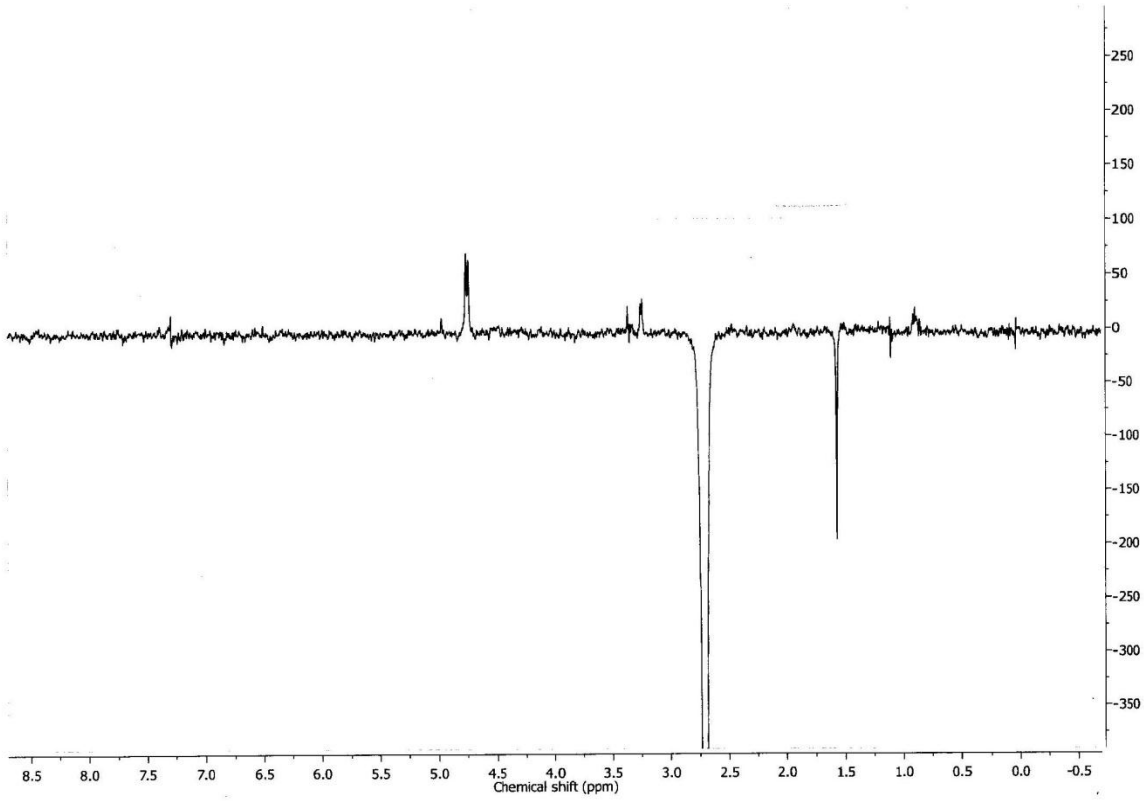
NOE for Compound 45



Compound **45**







^{13}C NMR spectrum of Compound 45