Supporting Information

Asymmetric Total Synthesis of (+)-Attenol B

Jingyun Ren, Jian Wang and Rongbiao Tong*

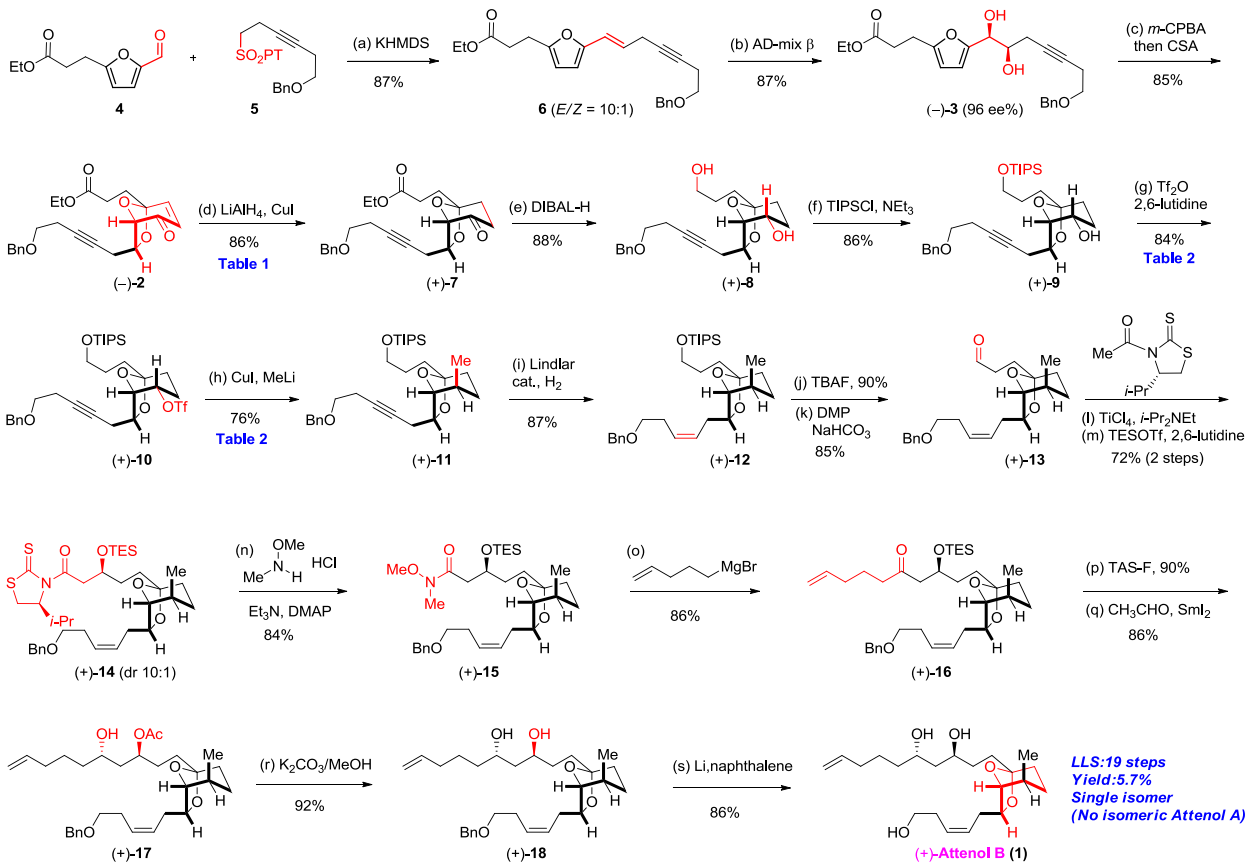
Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

rtong@ust.hk

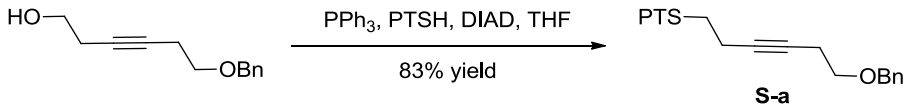
Table of Contents

General Information: Reactions were carried out in oven or flame-dried glassware under a nitrogen atmosphere, unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Dichloromethane (CH_2Cl_2) was freshly distilled before use from calcium hydride (CaH_2). All other anhydrous solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Grace. Infrared spectra were collected on a Bruker model TENSOR27 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) and benzene (7.16 ppm for ^{1}H and 128.06 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Optical rotations were measured on a JASCO Perkin-Elmer model P-2000 polarimeter. High resolution mass spectra were measured at the Hong Kong University of Science and Technology Mass Spectrometry Service Center on either an Agilent GC/MS 5975C System or an API QSTAR XL System. HPLC (Agilent technologies, 1260 Infinity) was used to determine enantiomeric excess of chiral compounds with eluents of hexane/*i*-PrOH.

Asymmetric Total Synthesis of (+)-Attenol B



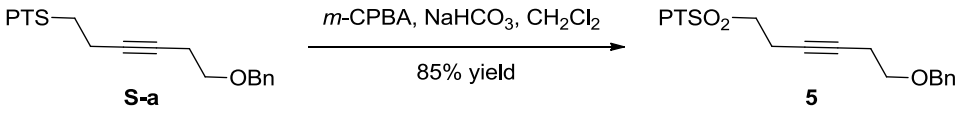
Preparation of Phenyltetrazole Sulfide S-a



To a solution of 6-(benzyloxy)hex-3-yn-1-ol (8.19 g, 40.0 mmol) in THF (400 mL) at 0 °C were added PPh_3 (15.8 g, 60.0 mmol), 1-phenyl-1H-tetrazole-5-thiol (PTSH, 10.7 g, 60.0 mmol) and diisopropyl azodicarboxylate (DIAD, 12.1 g, 60.0 mmol). The reaction mixture was stirred at room temperature for 6 h and then the solvent was evaporated directly in vacuo. The residue was dissolved in saturated aqueous NH_4Cl (100 mL) and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the desired sulfide product **S-a** (12.1 g, 33.2 mmol, 83% yield) as colorless oil.

IR (neat, cm^{-1}): 3063, 3031, 2934, 1728, 1499, 1238, 1077, 762, 696. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.57 – 7.54 (m, 5H), 7.40 – 7.24 (m, 5H), 4.53 (s, 2H), 3.52 (dt, *J* = 11.8, 6.9 Hz, 4H), 2.76 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 154.1, 138.2, 133.7, 130.3 (2 × C), 129.9 (2 × C), 128.5 (2 × C), 127.8 (2 × C), 123.9 (2 × C), 79.6, 78.2, 73.0, 68.6, 32.7, 20.3, 19.8. **HRMS** (TOF, Cl^+) m/z calculated for $C_{20}H_{21}N_4OS$, $[M+H]^+$ 365.1431, found 365.1418.

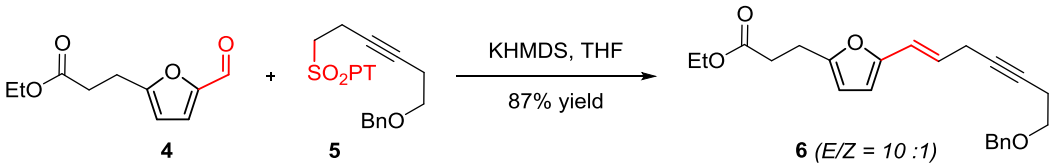
Preparation of Phenyltetrazole Sulfone 5



To a solution of **S-a** (12.1 g, 33.2 mmol) in CH_2Cl_2 (500 mL) were added $NaHCO_3$ (13.9 g, 166 mmol) and 3-chloroperbenzoic acid (*m*-CPBA, 13.5 g, 66.4 mmol, ca. 85 wt%) at 0 °C. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by addition of saturated aqueous Na_2SO_3 solution (100 mL). The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford the desired sulfone product **5** (11.2 g, 28.2 mmol, 85% yield) as colorless oil.

IR (neat, cm^{-1}): 3034, 3031, 2932, 1725, 1407, 1354, 1232, 1108, 739, 694. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.72 – 7.54 (m, 5H), 7.40 – 7.27 (m, 5H), 4.54 (s, 2H), 3.84 (t, *J* = 7.4 Hz, 2H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 6.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 153.3, 138.1, 133.0, 131.6 (2 × C), 129.8 (2 × C), 128.5 (2 × C), 127.8 (2 × C), 125.3 (2 × C), 80.7, 75.0, 73.0, 68.2, 54.9, 20.1, 13.7. **HRMS** (TOF, Cl^+) m/z calculated for $C_{20}H_{21}N_4O_3S$, $[M+H]^+$ 397.1329, found 397.1322.

Preparation of Alkene 6 via Julia-Kocienski Olefination

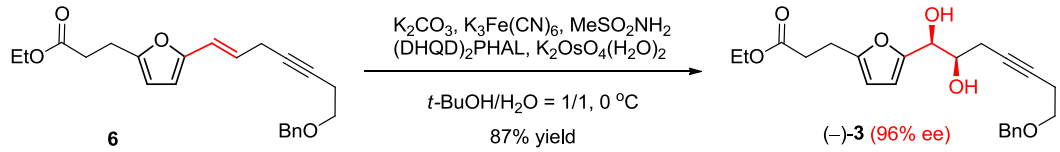


To a solution of sulfone **5** (11.2 g, 28.2 mmol) in dried THF (300 mL) at –78 °C, was added potassium bis(trimethylsilyl)amide (KHMDS, 0.5 M in toluene, 67.6 mL, 33.8 mmol) slowly. The

reaction mixture was stirred at −78 °C for 30 min and the aldehyde **4**[1] (8.67 g, 45.0 mmol) was added very slowly. After the completion of addition, the reaction mixture was stirred at −78 °C for additional 2 h. Then, the reaction was quenched by addition of saturated aqueous NH_4Cl (50 mL). The organic phase was collected and the aqueous phase was extracted with Et_2O (3 x 100 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the desired alkene product **6** (9.00 g, 24.5 mmol, 87% yield, ratio of *E/Z* isomers 10/1) as a pale yellow oil.

IR (neat, cm^{-1}): 3030, 2981, 2866, 1733, 1678, 1299, 1187, 795, 739. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.09 – 6.01 (m, 2H), 5.98 (d, *J* = 2.7 Hz, 1H), 4.57 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.07 (d, *J* = 3.0 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.6, 153.6, 151.6, 138.3, 128.5 (2 × C), 127.8, 127.7 (2 × C), 122.6, 119.7, 108.0, 107.1, 79.6, 77.8, 73.0, 68.8, 60.6, 32.8, 23.7, 22.1, 20.3, 14.3. **HRMS** (TOF, Cl^+) m/z calculated for $C_{23}H_{27}O_4$, $[M+H]^+$ 367.1904, found 367.1907.

Preparation of Diol (-)-3 via Sharpless Asymmetric Dihydroxylation of Alkene 6

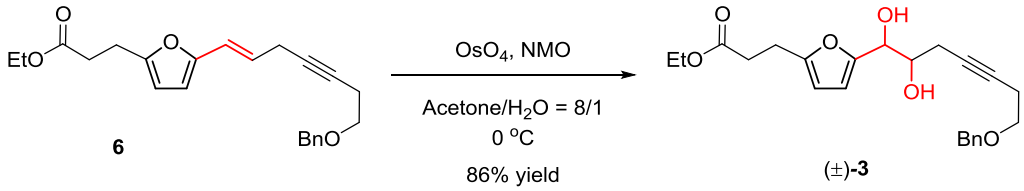


To a solution of alkene **6** (9.00 g, 24.5 mmol) in *t*-BuOH/H_2O (1/1, 100mL/100mL) solution at 0 °C were added sequentially K_2CO_3 (10.1 g, 73.5 mmol), $K_3Fe(CN)_6$(24.2 g, 73.5 mmol), $(DHQD)_2PHAL$(190 mg, 0.245 mmol) and $K_2OsO_4{\cdot}(H_2O)_2$ (92.0 mg, 0.245 mmol) and $MeSO_2NH_2$(2.33 g, 24.5 mmol). The reaction mixture was stirred at 0 °C for 4 days. The reaction was quenched by addition of saturated aqueous Na_2SO_3 (50 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the desired diol (–)-**3** (8.52 g, 21.3 mmol, 87% yield, 96 ee%) as a yellow oil.

[1] (a) Zhu, L.; Song, L.; Tong, R. *Org. Lett.* **2012**, *14*, 5892-5898. (b) Ren, J.; Tong, R. *J. Org. Chem.* **2014**, *79*, 6987-6995.

$[\alpha]_D^{20}$ = –13.4 (*c* 1.00, $CHCl_3$). **IR** (neat, cm^{-1}): 3421, 3034, 2914, 2868, 1731, 1156, 1018, 790, 743, 699. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 5.97 (d, *J* = 3.1 Hz, 1H), 4.61 (d, *J* = 5.9 Hz, 1H), 4.55 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.99 (dd, *J* = 11.5, 6.1 Hz, 1H), 3.57 (t, *J* = 6.8 Hz, 2H), 2.93 (d, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.51 – 2.46 (m, 2H), 2.45 – 2.40 (m, 1H), 2.35 – 2.27 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.6, 154.2, 152.1, 138.0, 128.5 (3 × C), 127.8 (2 × C), 108.7, 106.2, 80.0, 77.4, 73.0, 71.7, 69.9, 68.6, 60.7, 32.7, 23.8, 23.6, 20.3, 14.3. **HRMS** (TOF, Cl^+) m/z calculated for $C_{23}H_{32}NO_6$, $[M+NH_4]^+$ 418.2224, found 418.2235.

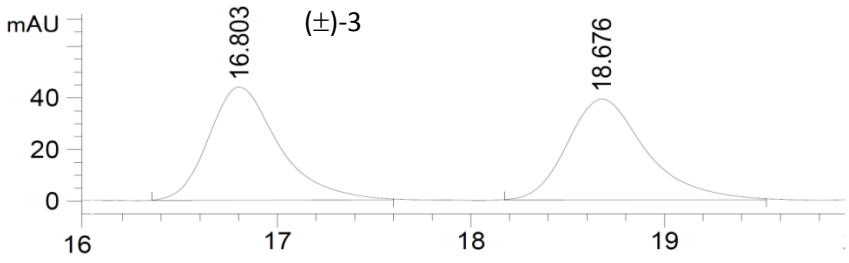
Preparation of Racemic Diol (±)-3 via Upjohn Oxidation of Alkene 6



Following the procedure described in the literature[2], to a solution of alkene **6** (37 mg, 0.10 mmol) in acetone/H_2O (0.8 mL/0.1mL) solution at 0 °C were added OsO_4 solution (17 mg, 0.0013 mmol, ca. 2.0 wt% in water) and 4-methylmorpholine N-oxide (NMO, 18 mg, 0.15 mmol). After 2 h, the reaction was quenched by addition of saturated aqueous Na_2SO_3 (2 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic fractions were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the desired diol-product (±)-**3** (34 mg, 0.086 mmol, 86% yield) as a yellow oil.

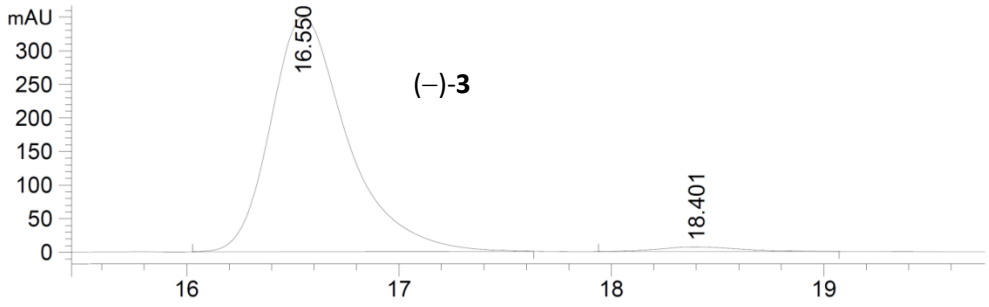
HPLC Data of Diol 3

HPLC conditions: Daicel CHIRALPAK AD-H column; 10% *i*-PrOH in hexanes; 1.0 mL/min



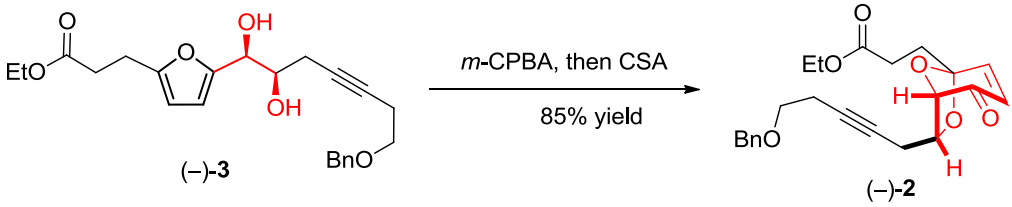
[2] For a review in dihydroxylation, see: Schröder, M. *Chem. Rev.* **1980**, *80*, 187-213. For a representative example, see: Molander, G. A.; Figueroa, R. *Org. Lett.* **2006**, *8*, 75-78.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.803	BB	0.3801	1106.65308	43.90429	49.8486
2	18.676	BB	0.4270	1113.37585	39.24723	50.1514
Totals :				2220.02893	83.15152	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.550	BB	0.3786	8772.62598	349.76163	98.0480
2	18.401	BB	0.3963	174.64885	6.78407	1.9520
Totals :				8947.27483	356.54570	

Preparation of 6,8-Dioxabicyclo[3.2.1]octane (–)-2 via Sequential Achmatowicz Rearrangement/Bicycloketalization of (–)-3



To a solution of diol (–)-**3** (8.52 g, 21.3 mmol) in CH_2Cl_2 (50 mL) was added 3-chloroperbenzoic acid (*m*-CPBA, 5.40 g, 27.0 mmol, ca. 85.0 wt%) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, and then CSA (5.10 g, 22.0 mmol) was added. The reaction mixture was stirred at 0 °C for additional 20 min. Then the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (30 mL) and $NaHCO_3$ solution (30 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure.

The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford the desired product (–)-**2** (7.20 g, 18.1 mmol, 85% yield) as a yellow oil.

$[\alpha]_D^{20}$ = –15.2 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 3031, 2933, 1732, 1703, 1314, 1181, 1096, 1012, 897, 699, 680. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 6.97 (d, *J* = 9.8 Hz, 1H), 6.04 (dd, *J* = 9.8, 1.3 Hz, 1H), 4.55 (s, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.99 – 3.89 (m, 1H), 3.57 (t, *J* = 6.9 Hz, 2H), 2.63 – 2.38 (m, 6H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.27 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 194.3, 172.9, 150.2, 138.2, 128.5 (2 × C), 127.8 (2 × C), 127.8, 126.6, 105.1, 83.9, 80.1, 75.7, 74.6, 73.1, 68.6, 60.8, 29.5, 27.3, 24.2, 20.2, 14.3. **HRMS** (TOF, Cl^+) m/z calculated for $C_{23}H_{27}O_6$, $[M+H]^+$ 399.1802, found 399.1795.

Preparation of Bicyclic Ketone (+)-7 via Chemoselctive Reduction of Enone (-)-2

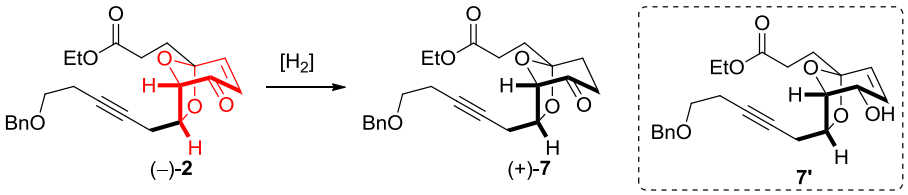


Table S1

Entry	*[H_2]*	*Temp (^{o}C)*	*Time*	*Yield (**7**,%)*
1	$TiCl_4$/Hantzsch ester	–78 → 60	8 h	<5
2	TFA/Hantzsch ester	–78 → 60	8 h	<5
3	L-selectride	–78	2 h	<20[b]
4[a]	MeLi/CuI, DIBAL-H	–78	10 min	0[b]
5[a]	CuI/DIBAL-H	–78 → rt	4 h	0
6[a]	CuI/$LiAlH_4$	–78	10 min	86

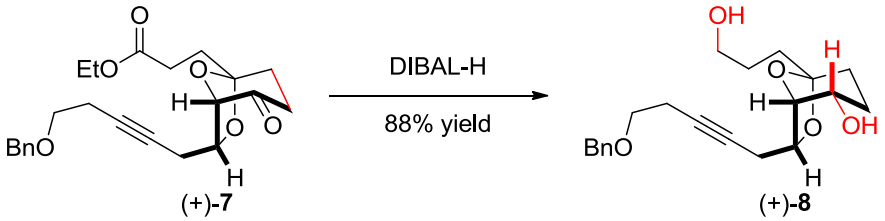
Note: [a] THF/HMPA = 4/1 as the solvent. [b] Compound **7'** was isolated as a major or only product. TFA: trifluoroacetic acid; DIBAL-H: diisobutylaluminum hydride.

Based on the results in Table **S1**, we performed the conjugate reduction on a gram scale under the condition of the entry 6 to achieve the desired product (+)-**7**. Flame-dried CuI was dissolved in HMPA at 50 °C, and the solution was cooled to room temperature. To a vigorously stirred suspension of $LiAlH_4$ (1.21 g, 32.0 mmol) in anhydrous THF (200 mL) was added dropwise the solution of CuI (6.08 g, 32.0 mmol) in HMPA (30 mL) at –78 °C. The generated orange suspension gradually turned to brown. The stirring continued for additional 1 h, and then enone (–)-**2** (6.36 g, 16.0 mmol) in anhydrous THF (20 mL) was added dropwise at the same

temperature. Within 10 min, the enone was completely consumed. The reaction mixture was quenched with an aqueous saturated solution of NH_4Cl (5 mL) at –78 °C, and the resulting mixture was warmed to room temperature. The reaction mixture was filtered through a pad of silica gel, which was washed with EtOAc (200 mL). The combined filtrates were washed with water (200 mL) and brine (20 mL), dried with anhydrous Na_2SO_4, and filtered. The solvents were evaporated under reduced pressure to give the crude product, which was purified by column chromatography (hexane/EtOAc, 9:1) to give bicyclic ketone (+)-**7** (5.50 g, 13.7 mmol, 86%) as a colorless oil.

$[\alpha]_D^{20}$ = +10.2 (*c* 0.75, $CHCl_3$). **IR** (neat, cm^{-1}): 2979, 2935, 2863, 1732, 1221, 1112, 1076, 743, 699. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 4.0 Hz, 4H), 7.32 – 7.26 (m, 1H), 4.55 (s, 2H), 4.32 (s, 1H), 4.19 – 4.13 (m, 3H), 3.56 (t, *J* = 6.8 Hz, 2H), 2.60 – 2.33 (m, 8H), 2.23 – 2.19 (m, 2H), 2.15 – 2.04 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 204.9, 173.1, 138.2, 128.4 (2 × C), 127.8 (2 × C), 127.7, 109.3, 83.3, 79.9, 77.6, 75.8, 73.0, 68.6, 60.6, 34.5, 32.5, 31.4, 28.2, 24.6, 20.2, 14.3. **HRMS** (TOF, Cl^+) m/z calculated for $C_{23}H_{32}NO_6$, $[M+NH_4]^+$ 418.2224, found 418.2221.

Preparation of Diol (+)-8 by DIBAL-H Reduction of Bicyclic Ketone (+)-7



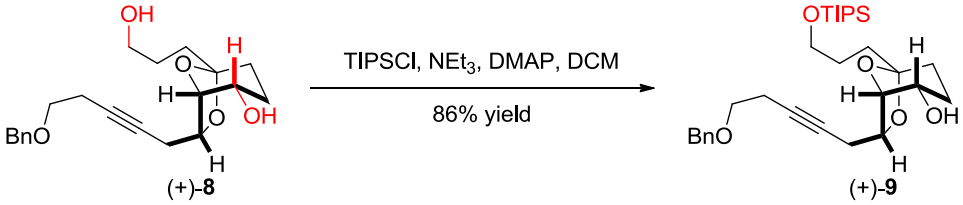
(+)-**7** (+)-**8**

To a solution of bicyclic ketone (+)-**7** (5.00 g, 12.5 mmol) in CH_2Cl_2 (100 mL) at –78 °C was added diisobutylaluminum hydride solution (DIBAL-H, 1.0 M, 62.5 mL, 62.5 mmol) dropwise. After stirring at –78 °C for 2 h, the reaction was quenched by addition of saturated aqueous Rochelle salt (sodium potassium tartrate) solution (50 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford desired diol (+)-**8** (3.96 g, 11.0 mmol, 88% yield) as a yellow oil.

$[\alpha]_D^{20}$ = +9.80 (*c* 0.72, $CHCl_3$). **IR** (neat, cm^{-1}): 3476, 3031, 2873, 1642, 1435, 1076, 1059, 1027, 799, 738. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.25 (t, *J* = 8.2 Hz, 2H), 7.20 (t, *J* = 8.2 Hz, 2H), 7.10 (t, *J* = 7.1 Hz, 1H), 4.53 (dd, *J* = 8.3, 5.7 Hz, 1H), 4.27 (s, 2H), 4.20 (d, *J* = 3.1 Hz, 1H), 3.70 (s, 1H),

3.47 (d, *J* = 6.1 Hz, 2H), 3.41 – 3.35 (m, 2H), 2.53 – 2.34 (m, 4H), 2.08 (br s, 1H), 1.80 – 1.60 (m, 6H), 1.55 – 1.38 (m, 2H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 138.7, 128.6, 128.3, 128.1, 128.0, 127.8, 109.4, 81.0, 79.5, 78.0, 74.9, 72.8, 69.0, 66.1, 62.7, 34.0, 33.6, 26.8, 26.6, 25.7, 20.4. **HRMS** (TOF, Cl^+) m/z calculated for $C_{21}H_{29}O_5$, $[M+H]^+$ 361.2010, found 361.2002.

Preparation of Compound (+)-9



To a solution of (+)-**8** (3.60 g, 10.0 mmol) in dry CH_2Cl_2 (200 mL) at 0 °C were added triethylamine (NEt_3, 1.51 g, 15.0 mmol), triisopropylsilyl chloride (TIPSCl, 2.09 g, 11.0 mmol) and 4-(dimethylamino)pyridine (DMAP, 122 mg, 1.00 mmol). After the completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of water (60 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford the desired product (+)-**9** (4.43 g, 8.60 mmol, 86% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +24.2 (*c* 1.00, $CHCl_3$). **IR** (neat, cm^{-1}): 3440, 2958, 2865, 1512, 1288, 1100, 1027, 800, 733. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38 – 7.28 (m, 5H), 4.53 (d, *J* = 3.5 Hz, 2H), 4.33 (dd, *J* = 9.1, 5.3 Hz, 1H), 4.14 (d, *J* = 3.1 Hz, 1H), 3.82 – 3.79 (m, 1H), 3.69 (t, *J* = 6.1 Hz, 2H), 3.61 – 3.52 (m, 2H), 2.49 – 2.36 (m, 3H), 2.28 (dd, *J* = 16.1, 9.2 Hz, 1H), 2.19 (br s, 1H), 1.90 (t, *J* = 6.0 Hz, 1H), 1.76 – 1.61 (m, 7H), 1.10 – 1.03 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.0, 128.6 (2 × C), 128.0, 127.9, 127.8, 109.4, 80.5, 79.1, 77.6, 74.6, 72.9, 68.8, 66.0, 63.4, 33.8, 33.1, 26.8, 26.1, 25.2, 20.1, 18.1 (6 × C), 12.1 (3 × C). **HRMS** (TOF, Cl^+) m/z calculated for $C_{30}H_{49}O_5Si$, $[M+H]^+$ 517.3344, found 517.3331.

Preparation of Compound (+)-11 via S_N2 Substitution of 9 with Methyl Nucleophile

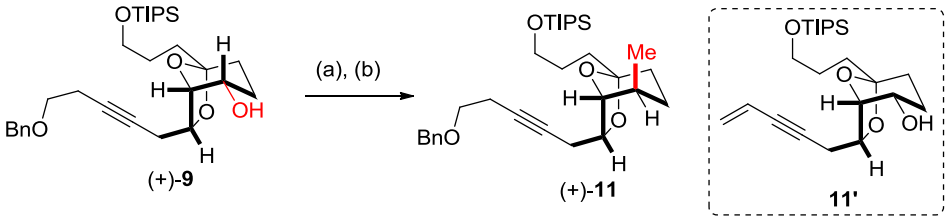


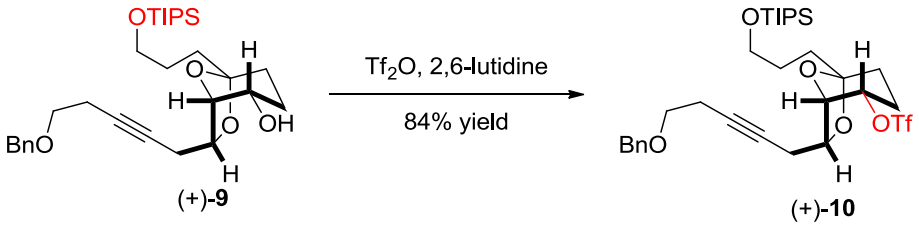
Table S2

Entry	*(a)*	*(b)*	*Temp (°C)*	*Time*	*Yield (**11**,%)*
1	Ms_2O	MeLi	−20 → 60	4 h	0[a]
2	Ms_2O	Me_2CuLi	−20 → rt	4 h	0[b]
3	Ms_2O	MeMgBr/CuBr-Me_2S	−20 → rt	4 h	0[b,c]
4	TsCl	MeLi	−20 → rt	4 h	0[c]
5	TsCl	Me_2CuLi	−20 → rt	4 h	0[c]
6	Picolinate	MeMgBr/$ZnCl_2$/CuBr-Me_2S	−20 → rt	2 h	0[a]
7	Tf_2O	MeLi/CuI	−10 → rt	4 h	64[d]

Note: [a] No S_N2 substitution reaction occurred at −20 °C to 0 °C, and decomposition was observed at reflux. [b] Starting material **9** was isolated probably due to desulfonation by methyl nucleophile. [c] **11'** was isolated as the major product. [d] Isolated yield for two steps

Based on the results in Table **S2**, we performed S_N2 substitution of **9** with methyl nucleophile on a gram scale under the conditions of the entry 7 to achieve the desired product (+)-**11**.

Preparation of Compound (+)-10

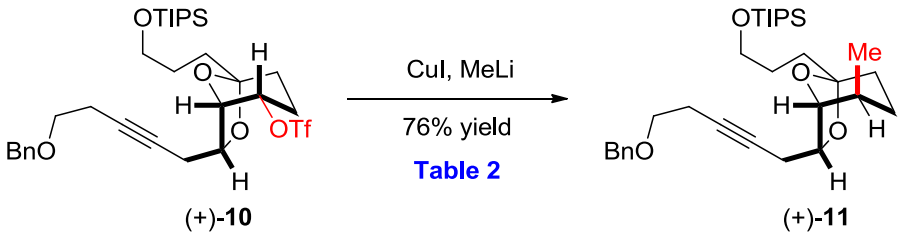


To a solution of (+)-**9** (4.12 g, 8.00 mmol) in dry CH_2Cl_2 (100 mL) at −78 °C were added 2,6-lutidine (1.03 g, 9.60 mmol) and trifluoromethanesulfonic anhydride (Tf_2O, 1.0 M in CH_2Cl_2, 9.60 mL, 9.60 mmol). After the completion of addition, the reaction mixture was stirred for 30 min at −78 °C. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (60 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL).

The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the desired product (+)-**10** (4.35 g, 6.72 mmol, 84% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +8.20 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 2942, 2892, 1416, 1210, 1146, 938, 883. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.27 (d, *J* = 7.5 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.09 (t, *J* = 7.1 Hz, 1H), 4.85 – 4.73 (m, 1H), 4.38 (d, *J* = 3.4 Hz, 1H), 4.33 (s, 2H), 4.17 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.59 (d, *J* = 5.8 Hz, 2H), 3.47 (t, *J* = 7.1 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.34 (d, *J* = 14.0 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.80 – 1.59 (m, 5H), 1.53 – 1.49 (m, 1H), 1.39 – 1.21 (m, 2H), 1.16 – 0.91 (m, 21H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 139.0, 128.5, 128.3, 128.1 (2 × C), 127.8, 127.7, 109.8, 82.6, 80.3, 77.6, 76.1, 75.3, 72.9, 68.9, 63.4, 34.2, 33.0, 27.1, 25.0, 23.9, 20.4, 18.3 (6 × C), 12.3 (3 × C). **HRMS** (TOF, Cl^+) m/z calculated for $C_{31}H_{47}F_3O_7SSi$, $[M]^+$ 648.2758, found 648.2771.

Preparation of Compound (+)-11 via S_N2 substitution of (+)-10



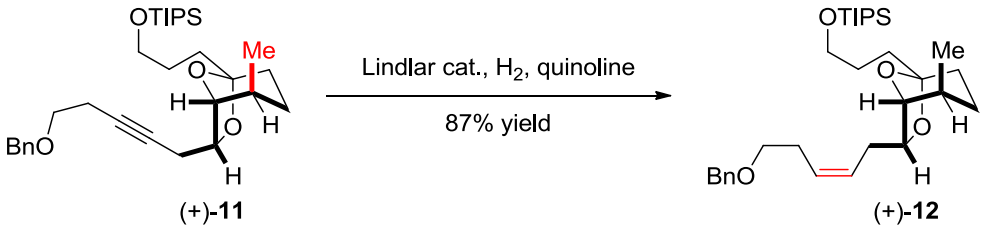
(+)-**10** (+)-**11**

To a stirred suspension of CuI (1.90 g, 10.0 mmol) in THF (20 mL) at 0 °C was added methyllithium (1.60 M, 12.5 mL, 20.0 mmol) dropwise. After 30 min a solution of (+)-**10** (4.35 g, 6.72 mmol) in THF (50 mL) was added dropwise. The resulting yellow suspension was stirred at 0 °C for 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (60 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the desired product (+)-**11** (2.62 g, 5.10 mmol, 76% yield) as a colorless oil.

(+)-**11:** $[\alpha]_D^{20}$ = +18.0 (*c* 1.00, $CHCl_3$). **IR** (neat, cm^{-1}): 3030, 2890, 1432, 1103, 1039, 969, 734. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 4.54 (s, 2H), 4.08 (dd, *J* = 8.8, 5.4 Hz, 1H), 4.02 (s, 1H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.55 (t, *J* = 7.0 Hz, 2H), 2.46 (t, *J* = 4.7 Hz, 2H), 2.38 (dd, *J* = 5.1, 2.4 Hz, 1H), 2.32 – 2.20 (m, 1H), 2.04 – 2.00 (m, 1H), 1.79 – 1.62 (m, 6H), 1.46 (dd, *J* = 13.4, 5.7 Hz, 1H), 1.38 – 1.25 (m, 1H), 1.12 (d, *J* = 7.1 Hz, 3H), 1.09 – 0.95

(m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.3, 128.5 (2 × C), 127.8 (3 × C), 110.3, 82.8, 78.9, 78.4, 77.7, 73.1, 68.9, 63.6, 34.1, 31.3, 30.4, 26.6, 25.6, 23.4, 20.3, 18.2 (6 × C), 17.2, 12.1 (3 × C). **HRMS** (TOF, Cl^+) m/z calculated for $C_{31}H_{51}O_4Si$, $[M+H]^+$ 515.3551, found 515.3541.

Preparation of *cis*-Alkene (+)-12 via Lindlar-Catalyzed Hydrogenation of (+)-11

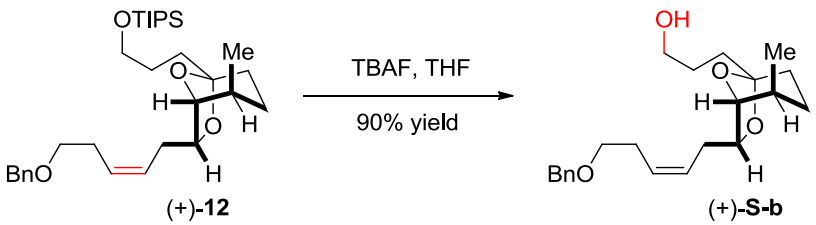


(+)-**11** (+)-**12**

To a solution of alkyne (+)-**11** (2.62 g, 5.10 mmol) in ethyl acetate was added Lindlar catalyst (540 mg, 0.255 mmol, 5.00 wt% Pd) and quinoline (1.97 g, 15.3 mmol) under N_2 (g) at room temperature. The reaction flask was flushed by H_2 (balloon) for 10 min, and then the gas outlet was closed and the reaction mixture was stirred under H_2 (balloon, 1 atm) atmosphere at room temperature for 2 h before filtration through celite. The solvent (EtOAc) was removed under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to afford (+)-**12** (2.29 g, 4.43 mmol, 87% yield) as a yellow oil.

$[\alpha]_D^{20}$ = +25.8 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 3034, 3027, 2891, 1585, 1173, 969, 733. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 5.59 – 5.45 (m, 2H), 4.51 (s, 2H), 3.99 (t, *J* = 6.8 Hz, 1H), 3.87 (s, 1H), 3.71 (t, *J* = 5.6 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 2.40 (q, *J* = 6.6 Hz, 2H), 2.26 (tq, *J* = 14.1, 7.1 Hz, 2H), 2.11 – 1.94 (m, 1H), 1.78 – 1.67 (m, 5H), 1.65 – 1.56 (m, 1H), 1.46 (dd, *J* = 13.3, 5.7 Hz, 1H), 1.30 (dd, *J* = 13.6, 4.9 Hz, 1H), 1.10 (d, *J* = 6.9 Hz, 3H), 1.08 – 0.96 (m, 21H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.6, 128.5 (2 × C), 127.7 (2 × C), 127.6 (2 × C), 127.0, 109.7, 82.9, 80.1, 73.0, 69.9, 63.7, 34.3, 33.8, 31.4, 30.4, 28.3, 26.8, 23.4, 18.2 (6 × C), 17.2, 12.1 (3 × C). **HRMS** (TOF, Cl^+) m/z calculated for $C_{31}H_{53}O_4Si$, $[M+H]^+$ 517.3708, found 517.3706.

Preparation of Compound (+)-S-b

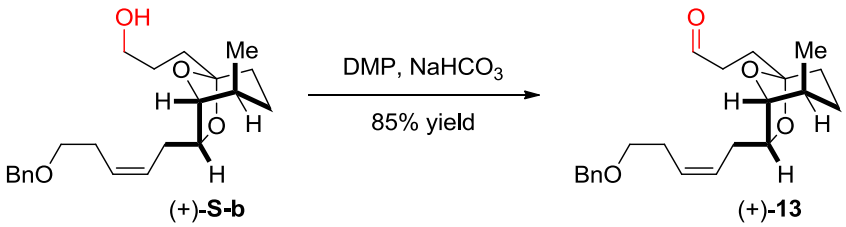


(+)-**12** (+)-**S-b**

To a solution of the (+)-**12** (2.29 g, 4.43 mmol) in THF (50 mL) at 0 °C was added tetrabutylammonium fluoride hydrate solution (TBAF, 1.0 M in THF, 6.65 mL 6.65 mmol). The reaction was allowed to warm to room temperature. After 1 h, the reaction was quenched by addition of a saturated aqueous NH_4Cl solution (20 mL). The organic phase was collected and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic fractions were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford (+)-**S-b** (1.43 g, 3.99 mmol, 90% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +10.6 (*c* 0.50, $CHCl_3$). **IR** (neat, cm^{-1}): 3432, 3063, 2870, 1495, 1453, 1250, 1107, 969, 734, 698. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.34 – 7.24 (m, 2H), 7.24 – 7.16 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 5.64 – 5.44 (m, 2H), 4.32 (s, 2H), 3.85 (t, *J* = 6.8 Hz, 1H), 3.74 (s, 1H), 3.55 (s, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.38 – 2.34 (m, 2H), 2.34 – 2.24 (m, 2H), 1.89 (dt, *J* = 19.1, 6.3 Hz, 1H), 1.81 – 1.74 (m, 4H), 1.59 (dt, *J* = 12.7, 6.4 Hz, 1H), 1.36 (dd, *J* = 13.2, 5.9 Hz, 1H), 1.27 – 1.19 (m, 1H), 1.07 (dd, *J* = 14.7, 6.5 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 139.3, 128.9, 128.6, 128.3, 128.1, 127.8, 127.6, 127.2, 109.7, 82.8, 80.3, 73.0, 70.0, 63.0, 34.9, 34.1, 31.5, 30.7, 28.7, 26.9, 23.7, 17.2. **HRMS** (TOF, Cl^+) m/z calculated for $C_{22}H_{33}O_4$, $[M+H]^+$ 361.2373, found 361.2375.

Preparation of Aldehyde (+)-13 via Dess-Martin Periodinane Oxidation of (+)-S-b

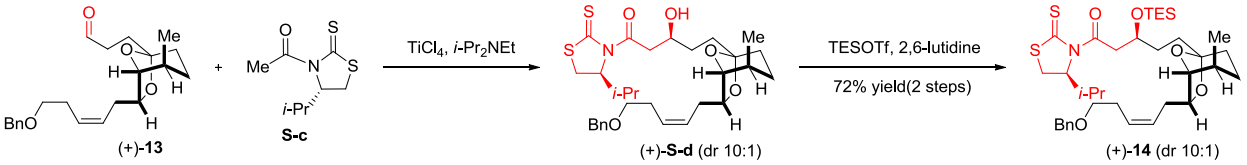


(+)-**S-b** (+)-**13**

To a solution of alcohol (+)-**S-b** (1.43 g, 3.99 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C were added $NaHCO_3$ (1.66 g, 20.0 mmol) and Dess-Martin periodinane (DMP, 3.38 g, 7.98 mmol). The reaction mixture was stirred at 0 °C for 2 h. Then, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ (50 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford the desired aldehyde (+)-**13** (1.21 g, 3.39 mmol, 85% yield) as a pale yellow oil.

$[\alpha]_D^{20}$ = +22.6 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 3028, 2935, 2870, 1723, 1453, 1172, 1102, 991, 735, 698. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.34 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 5.62 – 5.40 (m, 2H), 4.51 (s, 2H), 3.99 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 1H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.55 (d, *J* = 6.4 Hz, 2H), 2.39 (q, *J* = 6.9 Hz, 2H), 2.24 (t, *J* = 6.3 Hz, 2H), 2.07 – 1.98 (m, 3H), 1.71 (td, *J* = 12.9, 5.6 Hz, 1H), 1.61 (dd, *J* = 13.1, 6.4 Hz, 1H), 1.47 (dd, *J* = 13.3, 5.9 Hz, 1H), 1.35 – 1.26 (m, 1H), 1.08 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 202.6, 138.5, 128.8, 128.5 (2 × C), 127.7 (2 × C), 127.6, 126.6, 108.6, 82.8, 80.3, 73.0, 69.8, 37.6, 33.5, 31.3, 30.9, 29.6, 28.4, 23.2, 17.0. **HRMS** (TOF, Cl^+) m/z calculated for $C_{22}H_{31}O_4$, $[M+H]^+$ 359.2217, found 359.2229.

Preparation of Compound (+)-14 via Asymmetric Acetate Aldol Reaction

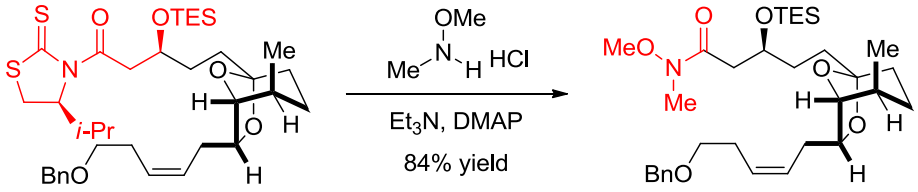


To a solution of (S)-1-(4-isopropyl-2-thioxothiazolidin-3-yl)ethanone **S-c** (1.37 g, 6.78 mmol) in CH_2Cl_2 (50 mL) at –40 °C was added $TiCl_4$ (1.0 M, 6.78 mL, 6.78 mmol) dropwise followed by N,N-diisopropylethylamine (*i*-Pr_2NEt, 787 mg, 6.10 mmol) dropwise. After stirring at –40 °C for 2h, the reaction mixture is cooled to –78 °C and aldehyde (+)-**13** (1.21 g, 3.39 mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 30 min. The reaction was quenched by addition of pH 7.0 phosphate buffer and warm to room temperature. The aqueous layer is extracted with CH_2Cl_2 and the combined organic extracts are dried over Na_2SO_4 and concentrated under reduced pressure to get the crude desired product (+)-**S-d**, which was used directly in next step without further purification.

To a solution of the crude (+)-**S-d** in dry CH_2Cl_2 (50 mL) at –78 °C were added 2,6-lutidine (543 mg, 5.08 mmol) and triethylsilyl trifluoromethanesulfonate (TESOTf, 1.0 M in CH_2Cl_2, 5.08 mL, 5.08 mmol). After the completion of addition, the reaction mixture was stirred for 30 min at –78 °C. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (60 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) with the minor isomer being removed to afford the desired product (+)-**14** (1.65 g, 2.44 mmol, 72% yield, 2 steps,) as a colorless oil.

$[\alpha]_D^{20}$ = +24.1 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 3027, 2954, 2874, 1697, 1495, 1455, 1312, 1281, 1168, 1041, 733, 699. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 – 7.30 (m, 4H), 7.28 – 7.26 (m, 1H), 5.51 (dt, *J* = 17.8, 8.5 Hz, 2H), 5.25 – 4.97 (m, 1H), 4.52 (s, 2H), 3.76 (t, *J* = 6.6 Hz, 1H), 3.61 (dd, *J* = 17.2, 5.9 Hz, 1H), 3.53 – 3.42 (m, 3H), 3.34 (t, *J* = 10.9 Hz, 1H), 3.00 (d, *J* = 11.4 Hz, 1H), 2.48 – 2.19 (m, 5H), 2.16 – 2.00 (m, 2H), 1.96 – 1.73 (m, 2H), 1.75 – 1.40 (m, 7H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.6 Hz, 12H), 0.86 (d, *J* = 6.2 Hz, 3H), 0.70 – 0.51 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 202.4, 172.0, 138.8, 129.1 (2 × C), 128.5 (2 × C), 127.8, 127.6, 127.0, 106.3, 76.6, 73.4, 73.0, 71.7, 70.2, 46.3, 38.8, 34.4, 31.6, 31.0, 30.9, 30.5, 30.2, 29.8, 29.7, 28.4, 19.2, 17.9, 17.8, 7.3 (2 × C), 7.2, 5.6 (2 × C), 5.5. **HRMS** (TOF, Cl^+) m/z calculated for $C_{36}H_{58}NO_5S_2Si$, $[M+H]^+$ 676.3520, found 676.3513.

Preparation of Weinreb Amide (+)-15



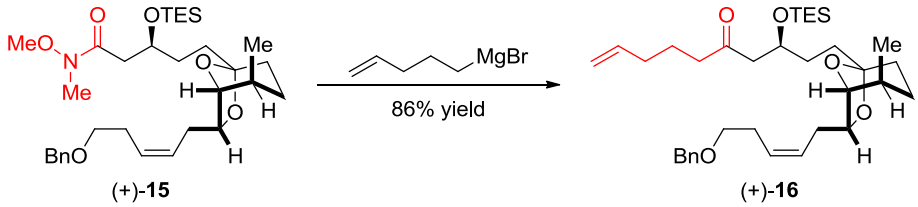
(+)-**14** (+)-**15**

To a solution of MeO(Me)NH·HCl (476 mg, 4.88 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C were added triethylamine (NEt_3, 591 mg, 5.86 mmol). The solution was stirred at 0 °C for 30 min. Then the compound (+)-**14** (1.65 g, 2.44 mmol) and DMAP (24.4 mg, 0.20 mmol) was added to the reaction mixture. After the completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of water (60 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the desired product (+)-**15** (1.18 g, 2.05 mmol, 84% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +16.0 (*c* 1.00, $CHCl_3$). **IR** (neat, cm^{-1}): 2951, 2874, 1823, 1663, 1458, 1364, 1098, 976, 731, 696. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 – 7.29 (m, 4H), 7.28 – 7.26 (m, 1H), 5.60 – 5.42 (m, 2H), 4.51 (s, 2H), 4.28 (s, 1H), 3.97 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 1H), 3.67 (s, 3H), 3.48 (t, *J* = 6.8 Hz, 2H), 3.16 (s, 3H), 2.74 (s, 1H), 2.48 – 2.33 (m, 3H), 2.24 (t, *J* = 6.7 Hz, 2H), 2.06 – 1.94 (m, 1H), 1.78 – 1.58 (m, 6H), 1.44 (dd, *J* = 13.3, 5.7 Hz, 1H), 1.35 – 1.30 (m, 1H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.59 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.6,

128.5 (3 × C), 127.7 (2 × C), 127.6 (2 × C), 127.0, 109.5, 82.8, 80.1, 73.0, 69.9, 69.2, 61.4, 33.7, 33.5, 33.1, 31.4, 31.3, 30.5, 29.5, 28.3, 23.4, 17.2, 7.0 (3 × C), 5.0 (3 × C). **HRMS** (TOF, Cl^+) m/z calculated for $C_{32}H_{54}NO_6Si$, $[M+H]^+$ 576.3715, found 576.3707.

Preparation of Ketone (+)-16 via Grignard Addition

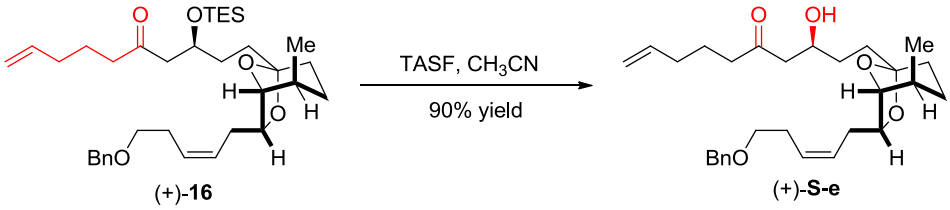


(+)-**15** (+)-**16**

To a suspension of magnesium turnings (240 mg, 10.0 mmol) in dry THF (10 mL) was added 5-bromo-1-pentene (1.49 g, 10.0 mmol) dropwise over a period time of 10 min at room temperature. After complete addition, the mixture was allowed to stir for another 2h. Then to a solution of Weinreb amid (+)-**15** (1.18 g, 2.05 mmol) in THF (50 mL) was added the Grignard reagent at −78 °C dropwise. After 5 min, the mixture was warmed to 0 °C and stirred for 1h. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl (60 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to afford the desired ketone (+)-**16** (1.03 g, 1.76 mmol, 86% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +21.0 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 2952, 2875, 1714, 1495, 1381, 1239, 1096, 1006, 910, 734, 697. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.34 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 5.81 – 5.69 (m, 1H), 5.59 – 5.41 (m, 2H), 4.98 (t, *J* = 15.0 Hz, 2H), 4.51 (s, 2H), 4.23 (s, 1H), 3.96 (t, *J* = 6.8 Hz, 1H), 3.84 (s, 1H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.60 (dd, *J* = 15.3, 7.4 Hz, 1H), 2.40 (dt, *J* = 14.9, 7.3 Hz, 4H), 2.23 (t, *J* = 6.7 Hz, 1H), 2.07 – 2.01 (m, 3H), 1.67 – 1.63 (m, 8H), 1.43 (dd, *J* = 12.8, 4.6 Hz, 2H), 1.34 – 1.24 (m, 2H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 209.7, 138.6, 138.2, 128.5 (2 × C), 128.4 (2 × C), 127.7, 127.6, 126.9, 115.3, 109.4, 82.8, 80.1, 73.0, 69.9, 68.8, 50.2, 43.8, 33.7, 33.2, 33.0, 31.4, 31.1, 30.5, 28.3, 23.4, 22.6, 17.2, 7.0 (3 × C), 5.1 (3 × C). **HRMS** (TOF, Cl^+) m/z calculated for $C_{35}H_{57}O_5Si$, $[M+H]^+$ 585.3970, found 585.3951.

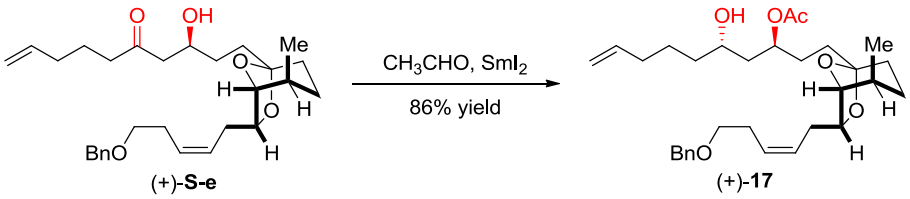
Preparation of Alcohol (+)-S-e via Desilylation of Ketone (+)-16



To a solution of ketone (+)-**16** (877 mg, 1.50 mmol) in wet CH_3CN (5 mL) was added a solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 825 mg, 3.00 mmol) in CH_3CN (4 mL) at room temperature. After stirring for 4 h, the mixture was filtered through a pad of silica gel which was carefully rinsed with EtOAc. The combined filtrates were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the desired alcohol (+)-**S-e** (636 mg, 1.35 mmol, 90% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +16.4 (*c* 0.90, $CHCl_3$). **IR** (neat, cm^{-1}): 3447, 2933, 2870, 1708, 1495, 1361, 1249, 1099, 1029, 992, 910, 735, 698. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.31 – 7.29 (m, 2H), 7.21 – 7.12 (m, 2H), 7.10 – 7.08 (m, 1H), 5.65 – 5.53 (m, 3H), 4.96 (dd, *J* = 13.1, 7.8 Hz, 2H), 4.33 (s, 2H), 4.07 (s, 1H), 3.88 (t, *J* = 6.7 Hz, 1H), 3.77 (s, 1H), 3.36 – 3.29 (m, 2H), 2.42 – 2.36 (m, 2H), 2.30 – 2.26 (m, 2H), 2.14 – 1.98 (m, 2H), 1.98 – 1.93 (m, 2H), 1.81 – 1.76 (m, 5H), 1.79 – 1.59 (m, 3H), 1.57 – 1.46 (m, 2H), 1.40 (dd, *J* = 13.1, 5.6 Hz, 2H), 1.30 – 1.16 (m, 1H), 1.09 (dd, *J* = 13.8, 5.1 Hz, 1H), 1.03 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 210.3, 139.3, 138.4, 128.9, 128.6, 128.3, 127.8, 127.7, 127.6, 127.3, 115.2, 109.6, 82.8, 80.3, 73.0, 70.0, 68.1, 49.7, 42.6, 34.3, 34.2, 33.4, 31.5, 30.9, 30.7, 28.8, 23.7, 22.8, 17.2. **HRMS** (TOF, Cl^+) m/z calculated for $C_{29}H_{43}O_5$, $[M+H]^+$ 471.3105, found 471.3133.

Preparation of 1,3-*anti*-Diol (+)-17 via Evans-Tishchenko Reaction

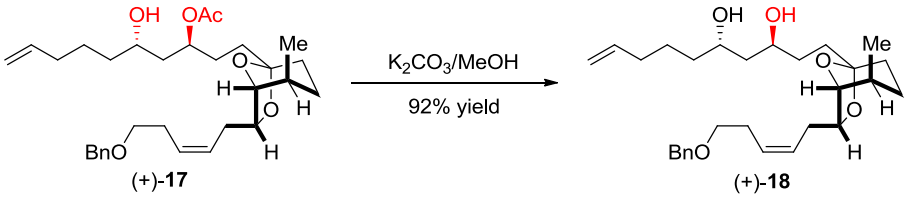


To a solution of acetaldehyde (440 mg, 10.0 mmol) in dry THF (10 mL) at 0 °C was added SmI_2 solution (0.1 M, 11.0 ml, 1.10 mmol) dropwise. The solution was stirred for 5 min before cooling to –20°C. A solution of compound (+)-**S-e** (471 mg, 1.00 mmol) in THF (10 mL) was added dropwise and the reaction was maintained at –20°C for 2h. The reaction was quenched

by addition of saturated aqueous $NaHCO_3$ (10 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford the 1,3-*anti*-diol (+)-**17** (442 mg, 0.860 mmol, 86% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +27.0 (*c* 1.00, $CHCl_3$). **IR** (neat, cm^{-1}): 3496, 2935, 2869, 1733, 1716, 1496, 1373, 1246, 1100, 1026, 993, 909, 736, 698. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.33 – 7.29 (m, 4H), 7.29 – 7.26 (m, 1H), 5.78 (dq, *J* = 10.1, 6.7 Hz, 1H), 5.59 – 5.40 (m, 2H), 5.07 (br s, 1H), 4.95 (dd, *J* = 22.7, 13.7 Hz, 2H), 4.50 (s, 2H), 3.97 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 1H), 3.50 – 3.44 (m, 4H), 2.40 – 2.36 (m, 2H), 2.26 – 2.20 (m, 2H), 2.07 (s, 3H), 2.05 – 1.95 (m, 3H), 1.75 – 1.68 (m, 3H), 1.62 – 1.57 (m, 3H), 1.41 (dd, *J* = 13.6, 5.6 Hz, 4H), 1.28 (dd, *J* = 17.6, 8.1 Hz, 3H), 1.17 (d, *J* = 4.5 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.5, 138.8, 138.5, 128.6 (2 × C), 128.4 (2 × C), 127.7, 127.6 (2 × C), 126.7, 114.6, 109.1, 82.9, 80.1, 72.9, 71.9, 69.8, 67.1, 43.1, 36.5, 33.8, 33.7, 33.4, 31.3, 30.6, 28.3, 25.2, 23.3, 21.2, 17.1. **HRMS** (TOF, Cl^+) m/z calculated for $C_{31}H_{47}O_6$, $[M+H]^+$ 515.3367, found 515.3376.

Preparation of 1,3-*anti*-Diol (+)-18

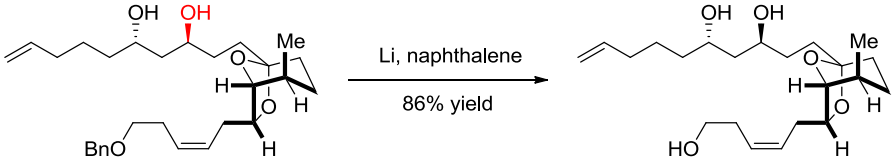


To a solution of (+)-**17** (103 mg, 0.200 mmol) in methanol (5 mL) at room temperature was added K_2CO_3 (276 mg, 2.00 mmol) dropwise. After stirring for 4h, the mixture was filtered through a pad of silica gel which was carefully rinsed with EtOAc. The combined filtrates were concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the desired 1,3-*anti*-diol (+)-**18** (86.8 mg, 0.184 mmol, 92% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +28.1 (*c* 0.80, $CHCl_3$). **IR** (neat, cm^{-1}): 3472, 3035, 2934, 2859, 1710, 1548, 1453, 1310, 1248, 1172, 1077, 992, 734, 614. **^{1}H NMR** (400 MHz, C_6D_6) δ: 7.30 (d, *J* = 7.7 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 5.83 – 5.76 (m, 1H), 5.66 – 5.47 (m, 2H), 5.02 (dd, *J* = 23.0, 13.6 Hz, 2H), 4.34 (s, 2H), 4.01 – 3.88 (m, 2H), 3.86 (t, *J* = 6.6 Hz, 1H), 3.76 (s, 1H), 3.45 (br s, 1H), 3.34 (t, *J* = 5.4 Hz, 2H), 2.91 (br s, 1H), 2.42 – 2.36 (m, 2H), 2.32 – 2.28 (m, 1H), 2.02 (d, *J* = 6.9 Hz, 2H), 1.88 – 1.72 (m, 4H), 1.59 – 1.48 (m, 6H), 1.46 – 1.31 (m, 4H), 1.25 –

1.18 (m, 1H), 1.06 (dd, *J* = 11.6, 6.4 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 139.3, 139.2, 129.1, 128.6, 128.3, 127.9, 127.8, 127.6, 127.1, 114.6, 109.7, 82.9, 80.4, 73.0, 70.0, 69.9, 69.1, 43.5, 37.5, 34.9, 34.3, 34.1, 31.5, 31.3, 30.8, 28.8, 25.6, 23.6, 17.2. **HRMS** (TOF, Cl^+) m/z calculated for $C_{29}H_{45}O_5$, $[M+H]^+$ 473.3262, found 473.3287.

Total Synthesis of (+)-Attenol B

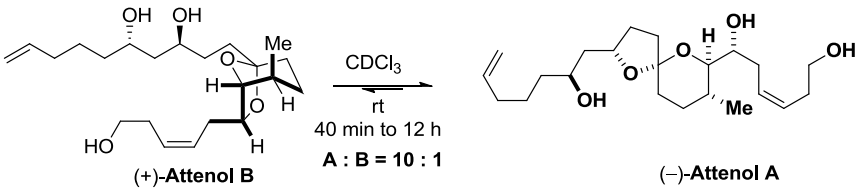


(+)-**18** (+)-**Attenol B (1)**

To a stirred solution of naphthalene (51 mg, 0.40 mmol) in THF (2 mL) was added lithium (2.1 mg, 0.30 mmol). The reaction mixture was stirred at room temperature until the lithium was completely dissolved. The resulting dark-green solution of lithium naphthalenide was cooled to −20 °C, and a solution of 1,3-*anti*-diol (+)-**18** (47 mg, 0.10 mmol) in THF (2 mL) was added dropwise. After stirring for 30 min, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl (10 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:3) to afford (+)-attenol B (33 mg, 0.086 mmol, 86% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +31.0 (*c* 0.10, $CHCl_3$). **IR** (neat, cm^{-1}): 3388, 3373, 2924, 2853, 1727, 1537, 1459, 1414, 1376, 1351, 1293, 1224, 1173, 1121, 1042, 993, 968, 908, 877, 858. **HRMS** (TOF, Cl^+) m/z calculated for $C_{22}H_{39}O_5$, $[M+H]^+$ 383.3792, found 383.2798. For other data: please see Table S3 and S4.

Equilibration of (-)-Attenol A and (+)-Attenol B in $CDCl_3$



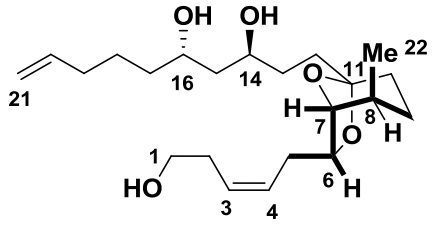
(+)-**Attenol B** (–)-**Attenol A**

The (+)-**attenol B** (5.0 mg, 0.013 mmol) in $CDCl_3$ (0.5 mL) was added into the NMR tube. The (–)-attenol A and (+)-attenol B equilibrated after 40 min with a constant A/B ratio of 10/1.

Separation of attenols A from B through column chromatography on silica gel (hexane/EtOAc = 1:3) to provide (–)-attenol A (4.5 mg, 0.012 mmol, 91% yield) as a colorless oil.

$[\alpha]_D^{20}$ = –10.2 (*c* 0.90, $CHCl_3$). **IR** (neat, cm^{-1}): 3367, 2927, 2859, 1639, 1488, 1457, 1375, 1249, 1087, 1043, 1012, 978. **HRMS** (TOF, Cl^+) m/z calculated for $C_{22}H_{38}O_5Na$, $[M+Na]^+$ 405.2611, found 405.2593. For other data: please see Table S5 and S6.

Spectroscopic Data Comparison of (+)-Attenol B



(+)-**Attenol B**

Table S3. ^{1}H NMR Comparison

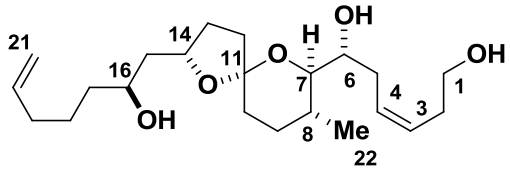
No.	Natural (+)-Attenol B (Reported by Daisuke Uemura[3]) ^{1}H NMR (600 MHz, $CDCl_3$)	Synthetic (+)-Attenol B (Reported Jhillu S. Yadav[4]) ^{1}H NMR (500 MHz, $CDCl_3$)	Synthetic (+)-Attenol B (Reported by Makoto Sasaki[5]) ^{1}H NMR (600 MHz, $CDCl_3$)	Synthetic (+)-Attenol B (Our Sample) ^{1}H NMR (400 MHz, $CDCl_3$)
1	3.63 (2H, m)	3.63 (2H, m)	3.61 (2H, m)	3.63 (2H, m)
2	2.31 (m), 2.39 (m)	2.29 (m), 2.39 (m)	2.29 (m), 2.38 (m)	2.29 (m), 2.40 (m)
3	5.53 (m)	5.53 (m)	5.52 (m)	5.54 (m)
4	5.54 (m)	5.53 (m)	5.52 (m)	5.54 (m)
5	2.31 (m), 2.39 (m)	2.29 (m), 2.39 (m)	2.29 (m), 2.38 (m)	2.29 (m), 2.40 (m)
6	4.09 (t, 6.7)	4.08 (t, 7.0)	4.07 (t, 6.5)	4.09 (t, 6.8)
7	3.92 (s)	3.93 (br s)	3.90 (s)	3.93 (s)
8	1.67 (m)	1.61 (m)	1.59 (m)	1.63 (m)
9	1.34 (dd, 15.2, 5.7), 2.02 (m)	1.34 (dd, 14.0, 5.4), 2.01 (m)	1.33 (dd, 15.2, 5.0), 2.00 (m)	1.34 (dd, 13.9, 5.0), 2.00 (m)
10	1.51 (m), 1.68 (m)	1.61 (m), 1.78 (m)	1.59 (2H, m)	1.53 (m), 1.63 (m)
12	1.85 (m), 1.90 (m)	1.87 (m), 2.01 (m)	1.85 (2H, m)	1.82 (2H, m)
13	1.61 (m), 1.81 (m)	1.61 (m), 1.87 (m)	1.59 (m), 1.85 (m)	1.63 (m), 1.84 (m)
14	3.95 (m)	3.95 (m)	3.94 (m)	3.96 (m)
15	1.58 (m), 1.65 (m)	1.61 (m), 1.78 (m)	1.59 (2H, m)	1.63 (2H, m)
16	3.93 (m)	3.95 (m)	3.94 (m)	3.96 (m)
17	1.43 (m), 1.54 (m)	1.43 (m), 1.61 (m)	1.42 (m), 1.59 (m)	1.45 (m), 1.63 (m)
18	1.40 (m), 1.53 (m)	1.43 (m), 1.61 (m)	1.42 (m), 1.59 (m)	1.45 (m), 1.63 (m)
19	2.08 (2H, m)	2.08 (2H, m)	2.06 (2H, m)	2.08 (2H, m)
20	5.81 (ddt, 17.2, 10.1, 6.8)	5.81 (ddt, 17.1, 10.1, 7.0)	5.79 (m)	5.81 (m)
21	4.95 (br d, 10.1), 5.01 (br d, 17.2)	4.95 (br d, 10.1), 5.01 (dd, 17.1, 1.6)	4.93 (d, 10.3), 4.98 (d, 17.0)	4.95 (d, 10.0), 5.01 (d, 17.3)
22	1.12 (3H, d, 7.0)	1.12 (3H, d, 7.0)	1.10 (3H, d, 7.0)	1.12 (3H, d, 7.1)

[3] Takada, N.; Suenaga, K.; Yamada, K.; Zheng, S.-Z.; Chen, H.-S.; Uemura, D. *Chem. Lett.* **1999**, 1025-1026.
[4] Yadav, J. S.; Narayana Reddy, P. A.; Jayasudhan Reddy, Y.; Meraj, S.; Prasad, A. R. *Eur. J. Org. Chem.* **2013**, 6317-6324.
[5] Fuwa, H.; Sasaki, M. *Org. Lett.* **2008**, *10*, 2549-2552.

Table S4. ^{13}C NMR Comparison

NO.	Natural (+)-Attenol B (Reported by Daisuke Uemura) ^{13}C NMR (150 MHz, $CDCl_3$)	Synthetic (+)-Attenol B (Reported by Jhillu S. Yadav) ^{13}C NMR (75 MHz, $CDCl_3$)	Synthetic (+)-Attenol B (Reported by Makoto Sasaki) ^{13}C NMR (150 MHz, $CDCl_3$)	Synthetic (+)-Attenol B (Our Sample) ^{13}C NMR (100 MHz, $CDCl_3$)
1	61.9	61.8	61.9	61.9
2	31.3	31.1	31.3	31.3
3	128.5	128.4	128.5	128.5
4	127.9	127.7	127.8	127.9
5	33.7	33.7	33.7	33.7
6	80.1	80.0	80.1	80.1
7	83.1	83.0	83.1	83.1
8	31.2	31.2	31.3	31.2
9	23.1	23.0	23.1	23.1
10	30.3	30.3	30.3	30.3
11	109.6	109.6	109.5	109.6
12	34.5	34.2	34.5	34.5
13	30.3	30.3	30.3	30.2
14	70.2	69.8	70.3	70.2
15	42.5	42.5	42.4	42.5
16	69.2	68.9	69.1	69.2
17	36.9	36.8	36.8	36.9
18	25.0	25.0	25.0	25.1
19	33.7	33.6	33.7	33.7
20	138.8	138.8	138.8	138.8
21	114.5	114.5	114.5	114.5
22	16.9	16.9	16.9	16.9

Spectroscopic Data Comparison of (–)-Attenol A



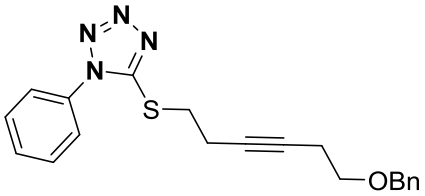
(–)-Attenol A

Table S5. ^{1}H NMR Comparison

No.	Natural (–)-Attenol A (Reported by Daisuke Uemura) ^{1}H NMR (400 MHz, $CDCl_3$)	Synthetic (–)-Attenol A (Reported by Jhillu S. Yadav) ^{1}H NMR (500 MHz, $CDCl_3$)	Synthetic (–)-Attenol A (Reported by Makoto Sasaki) ^{1}H NMR (600 MHz, $CDCl_3$)	Synthetic (–)-Attenol A (Our Sample) ^{1}H NMR (400 MHz, $CDCl_3$)
1	3.65 (2H, m)	3.66 (2H, m)	3.67 (2H, m)	3.68 (2H, m)
2	2.29 (m), 2.41 (m)	2.29 (m), 2.42 (m)	2.27 (m), 2.42 (m)	2.25 (m), 2.41 (m)
3	5.54 (m)	5.56 (m)	5.55 (m)	5.54 (m)
4	5.68 (m)	5.68 (m)	5.67 (m)	5.68 (m)
5	2.12 (m), 2.51 (br dt, 14.8, 8.8)	2.11 (m), 2.52 (m)	2.10 (m), 2.52 (m)	2.05 (m), 2.53 (m)
6	3.72 (m)	3.66 (m)	3.67 (m)	3.67 (m)
7	3.31 (dd, 10.4, 1.2)	3.32 (dd, 10.1, 1.4)	3.32 (d, 10.3)	3.31 (d, 10.1)
8	1.74 (m)	1.70 (m)	1.59 (m)	1.74 (m)
9	1.50 (m), 1.65 (m)	1.49 (m), 1.70 (m)	1.59 (2H, m)	1.51 (2H, m)
10	1.64 (m), 1.75 (m)	1.70 (2H, m)	1.59 (2H, m)	1.51 (2H, m)
12	1.70 (m), 2.02 (m)	1.70 (m), 2.01 (m)	1.59 (m), 2.10 (m)	1.51 (m), 2.05 (m)
13	1.84 (m), 2.02 (m)	1.84 (m), 2.01 (m)	1.83 (m), 2.10 (m)	1.74 (m), 2.05 (m)
14	4.31 (m)	4.32 (m)	4.31 (m)	4.32 (m)
15	1.72 (2H, m)	1.70 (2H, m)	1.59 (2H, m)	1.74 (2H, m)
16	3.83 (m)	3.83 (m)	3.82 (br s)	3.83 (m)
17	1.50 (2H, m)	1.49 (2H, m)	1.59 (2H, m)	1.51 (2H, m)
18	1.43 (m), 1.56 (m)	1.49 (2H, m)	1.59 (2H, m)	1.74 (2H, m)
19	2.09 (2H, m)	2.11 (2H, m)	2.10 (2H, m)	2.05 (2H, m)
20	5.81 (ddt, 17.2, 10.2, 6.8)	5.81 (ddt, 16.9, 10.2, 6.7)	5.81 (m)	5.81 (m)
21	4.95 (br d, 10.2), 5.01 (br d, 17.2)	4.95 (d, 10.1), 5.01 (dd, 17.2, 1.8)	4.96 (d, 10.0), 5.02 (d, 17.0)	4.96 (d, 10.2), 5.01 (d, 17.2)
22	0.87 (3H, d, 6.4)	0.88 (3H, d, 6.6)	0.88 (3H, d, 6.5)	0.88 (3H, d, 5.9)

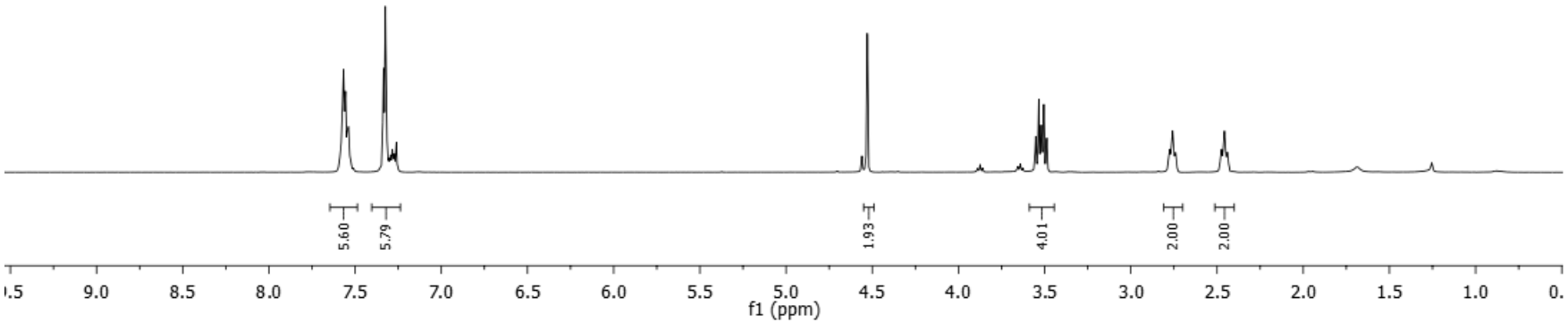
Table S6. ^{13}C NMR Comparison

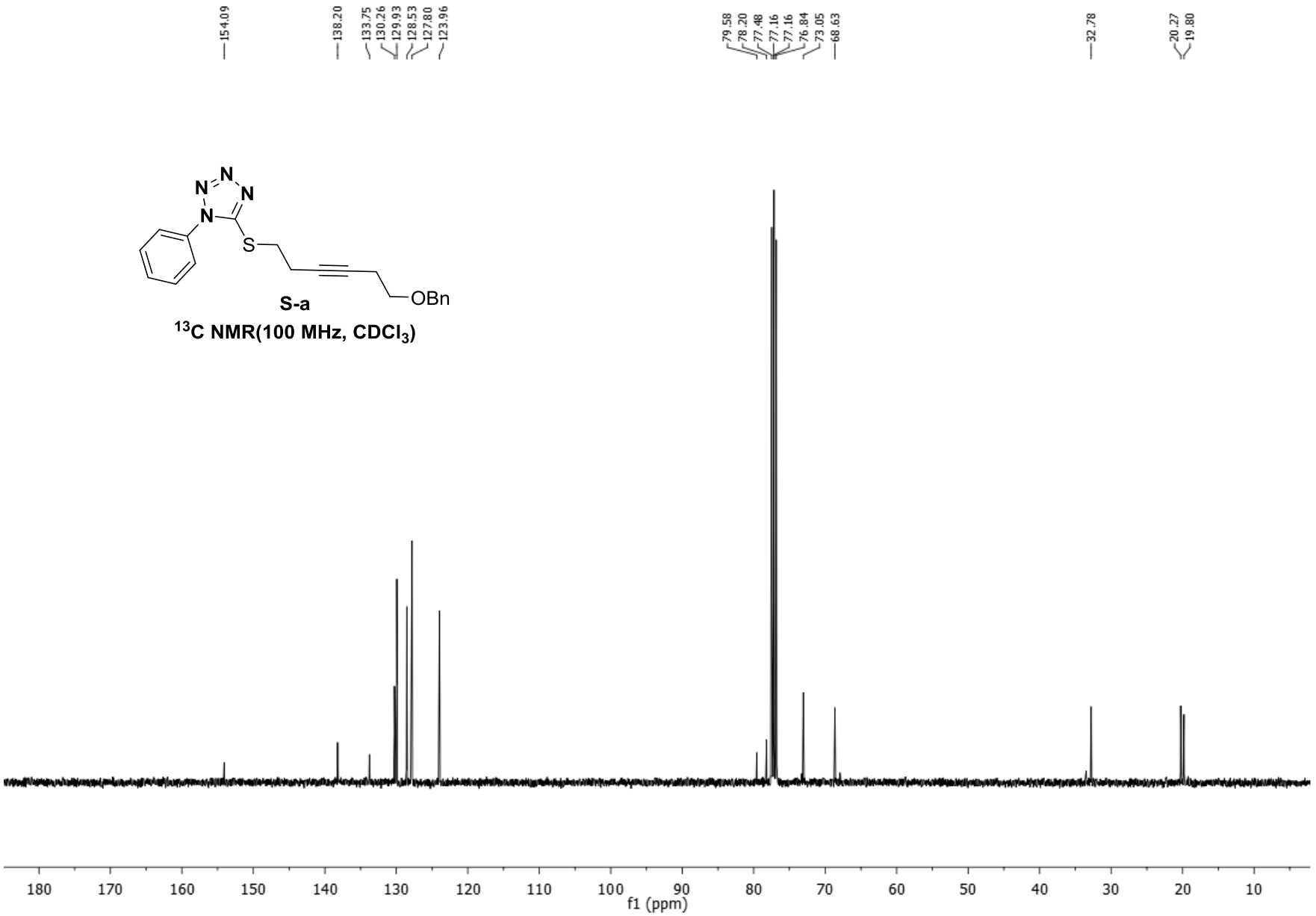
NO.	Natural (–)-Attenol A (Reported by Daisuke Uemura) ^{13}C NMR (100 MHz, $CDCl_3$)	Synthetic (–)-Attenol A (Reported by Jhillu S. Yadav) ^{13}C NMR (75 MHz, $CDCl_3$)	Synthetic (–)-Attenol A (Reported by Makoto Sasaki) ^{13}C NMR (150 MHz, $CDCl_3$)	Synthetic (–)-Attenol A (Our Sample) ^{13}C NMR (100 MHz, $CDCl_3$)
1	61.9	61.8	61.9	61.9
2	30.9	30.8	30.84	30.9
3	128.0	128.0	128.0	128.0
4	129.6	129.4	129.6	129.6
5	33.0	32.8	33.0	33.0
6	70.1	70.0	70.1	70.1
7	78.0	77.9	78.0	78.0
8	30.4	30.8	30.4	30.4
9	29.0	29.0	29.0	29.0
10	33.9	33.8	33.9	33.9
11	106.4	106.3	106.4	106.4
12	38.5	38.5	38.5	38.5
13	30.8	30.8	30.83	30.9
14	78.0	77.9	78.0	78.0
15	43.6	43.7	43.6	43.7
16	69.6	69.5	69.6	69.6
17	36.6	36.6	36.6	36.6
18	25.1	25.0	25.0	25.1
19	33.7	33.6	33.7	33.7
20	138.7	138.6	138.7	138.7
21	114.6	114.5	114.6	114.6
22	17.3	17.2	17.3	17.3



S-a

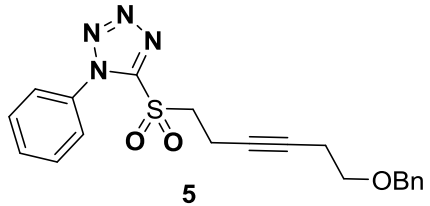
^{1}H NMR(400 MHz, $CDCl_3$)





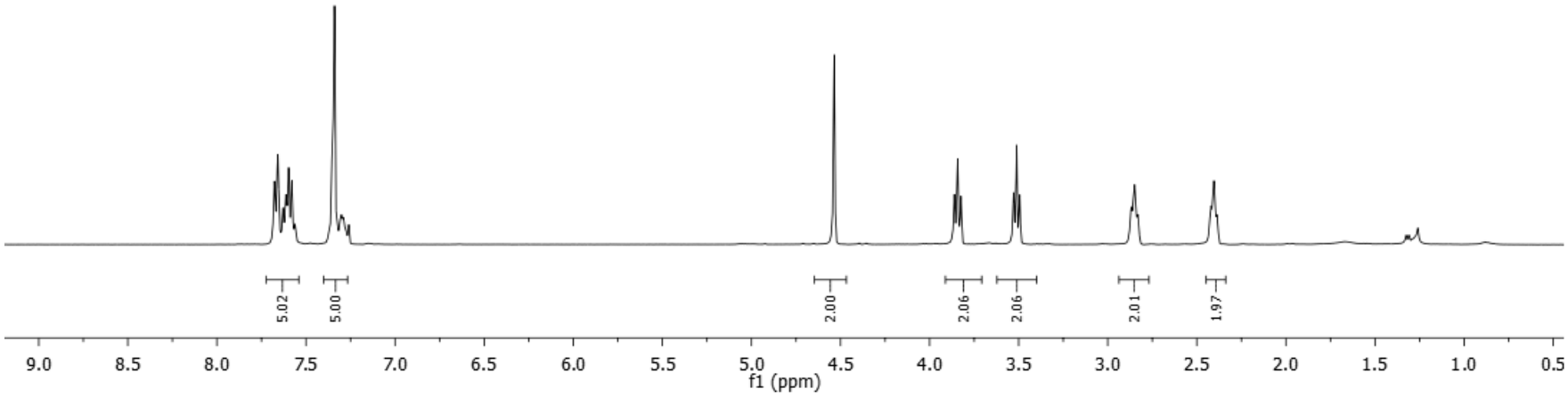
S-a

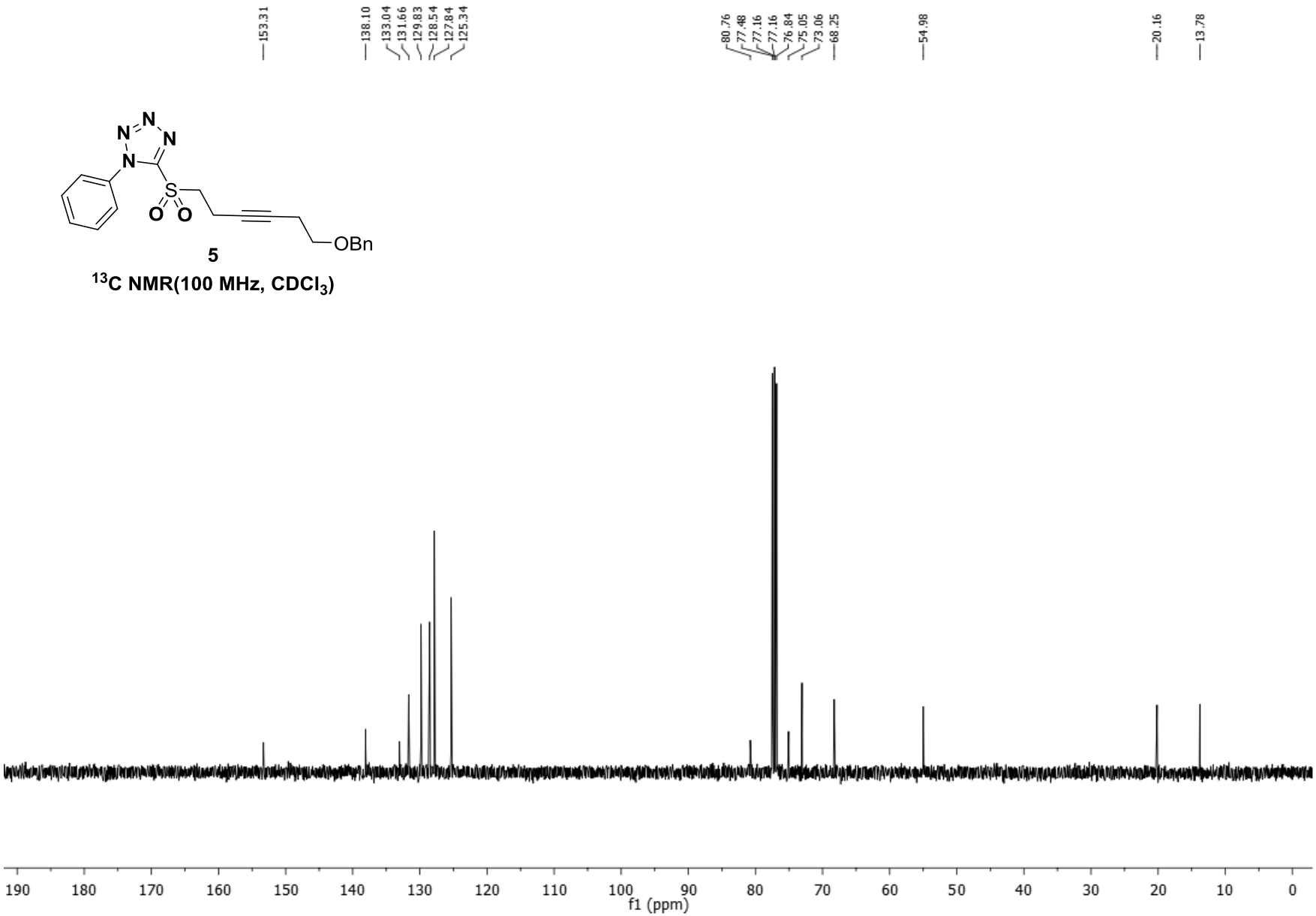
^{13}C NMR(100 MHz, $CDCl_3$)

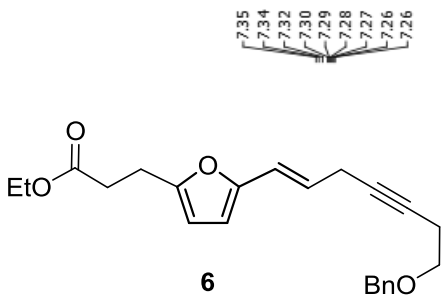


5

^{1}H NMR(400 MHz, $CDCl_3$)

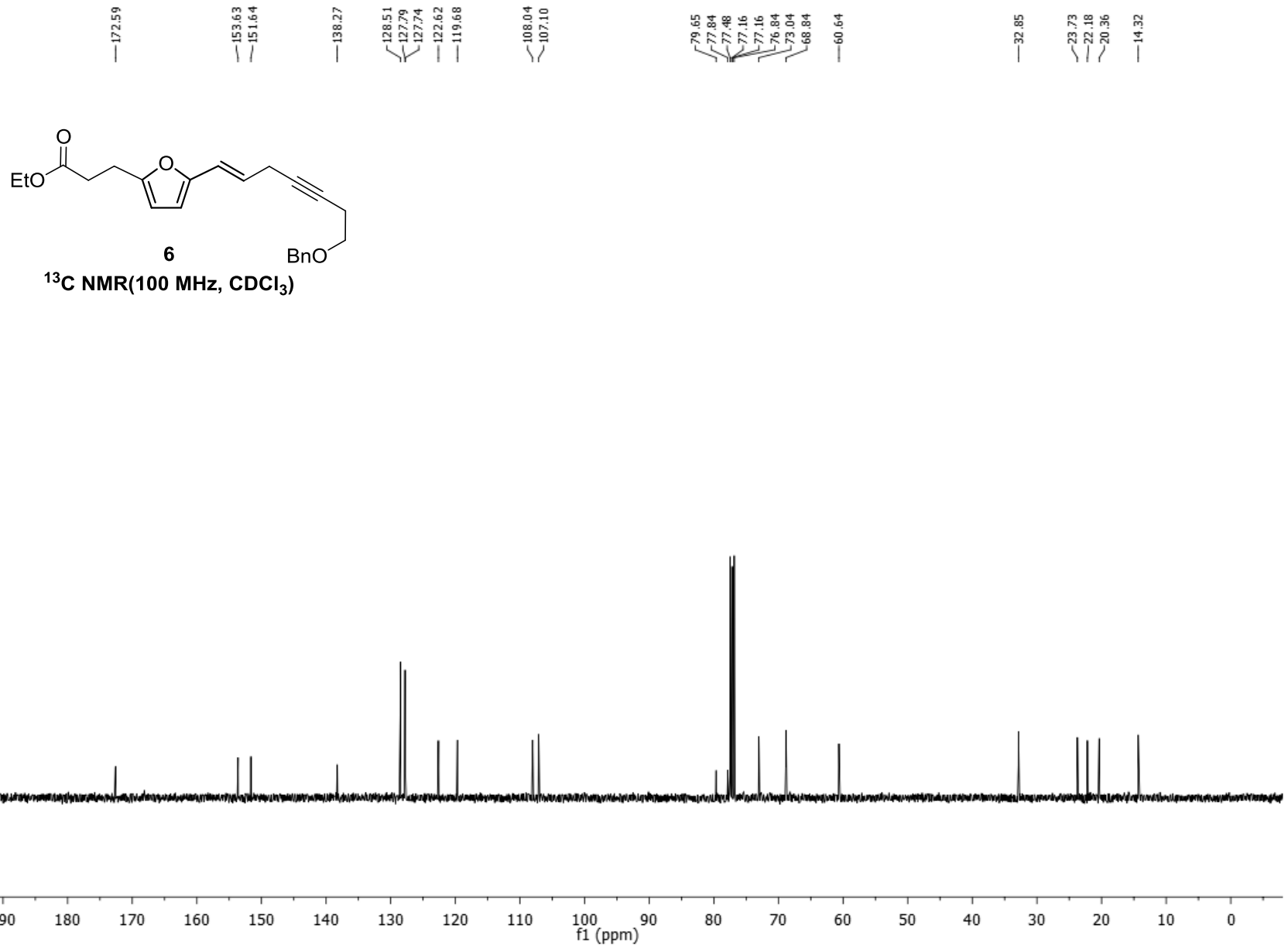



153.31
138.10
133.04
131.66
129.83
128.54
127.84
125.34
80.76
77.48
77.16
77.16
76.84
75.05
73.06
68.25
54.98
20.16
13.78
N
N
N
N
S
O
O
OBn
5
13C NMR(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



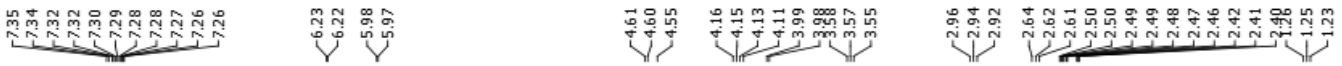
6

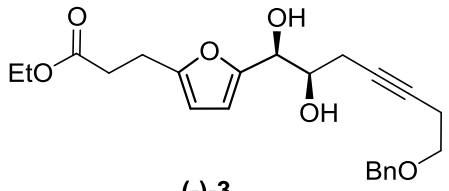
^{1}H NMR(400 MHz, $CDCl_3$)



6

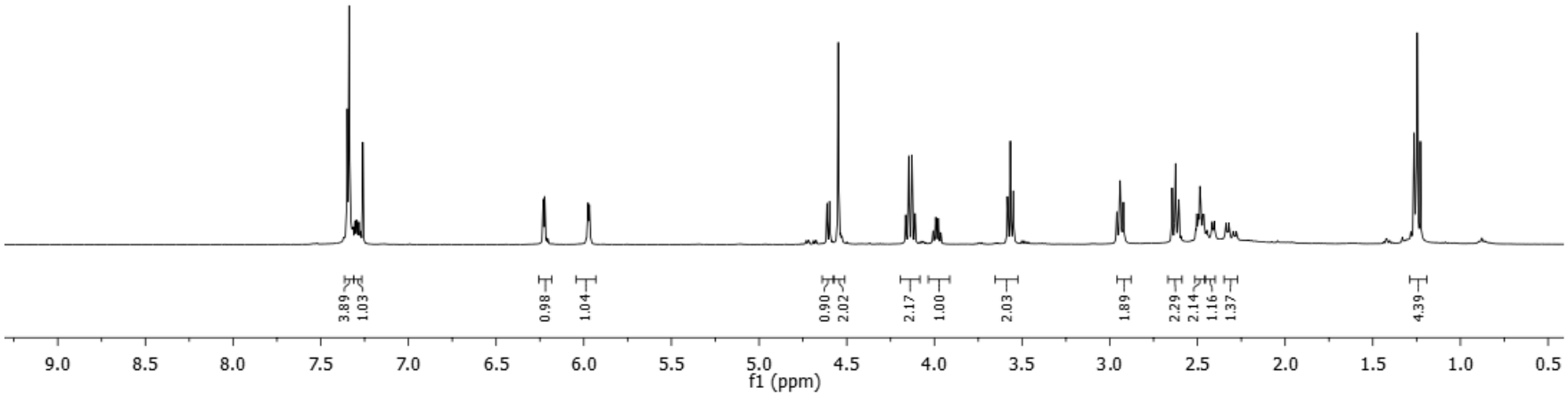
^{13}C NMR(100 MHz, $CDCl_3$)

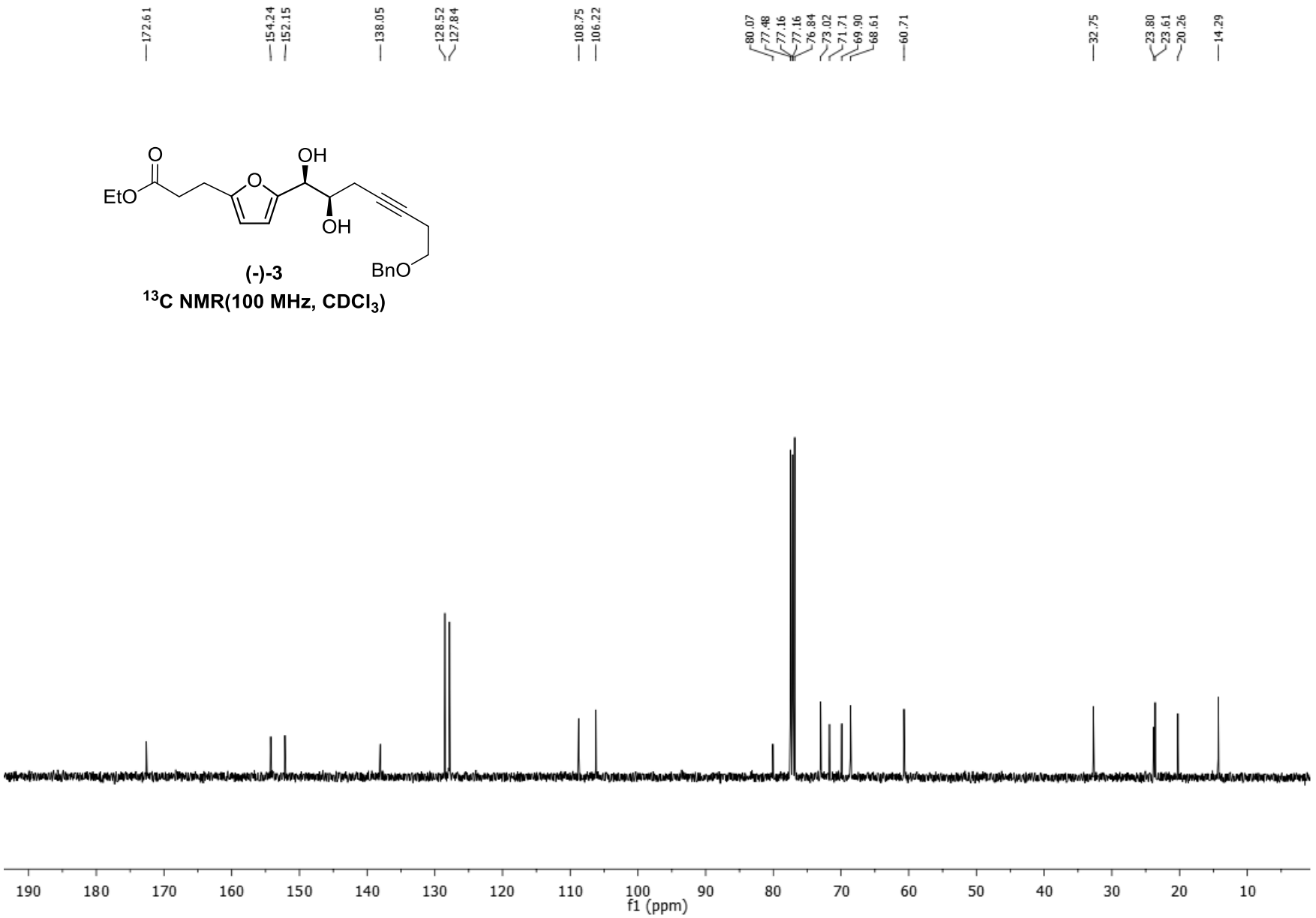




(-)-3

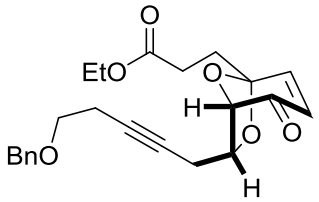
^{1}H NMR(400 MHz, $CDCl_3$)





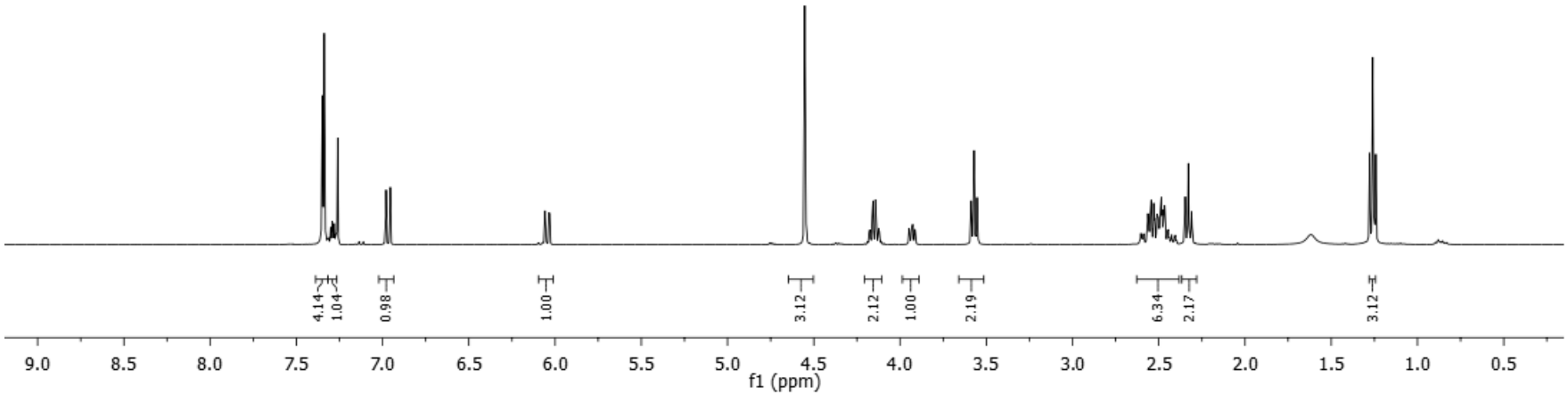
(-)-3

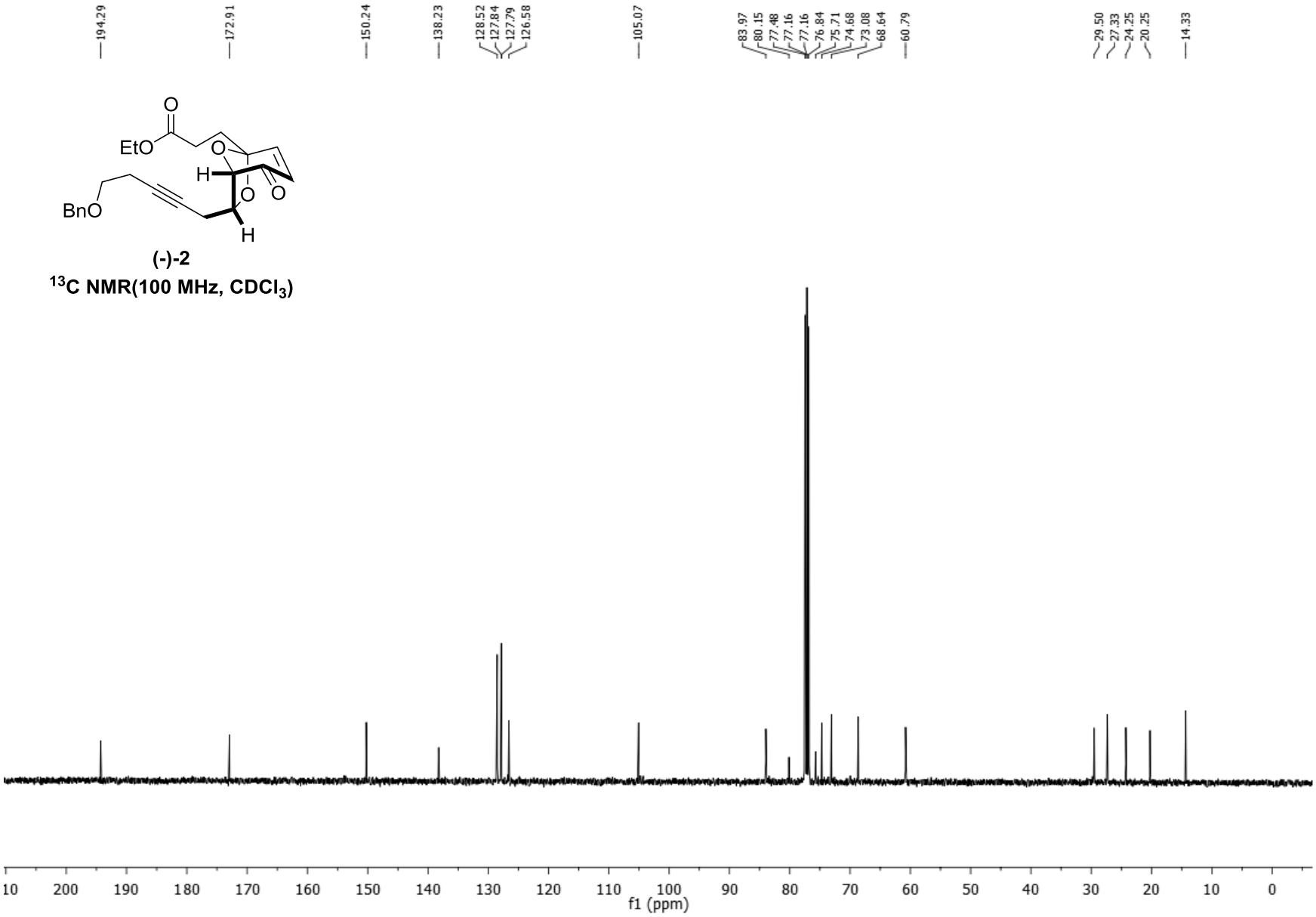
^{13}C NMR(100 MHz, $CDCl_3$)



(-)-2

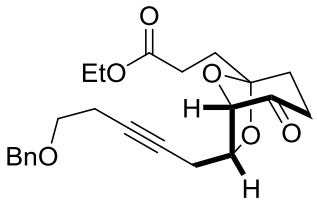
^{1}H NMR(400 MHz, $CDCl_3$)





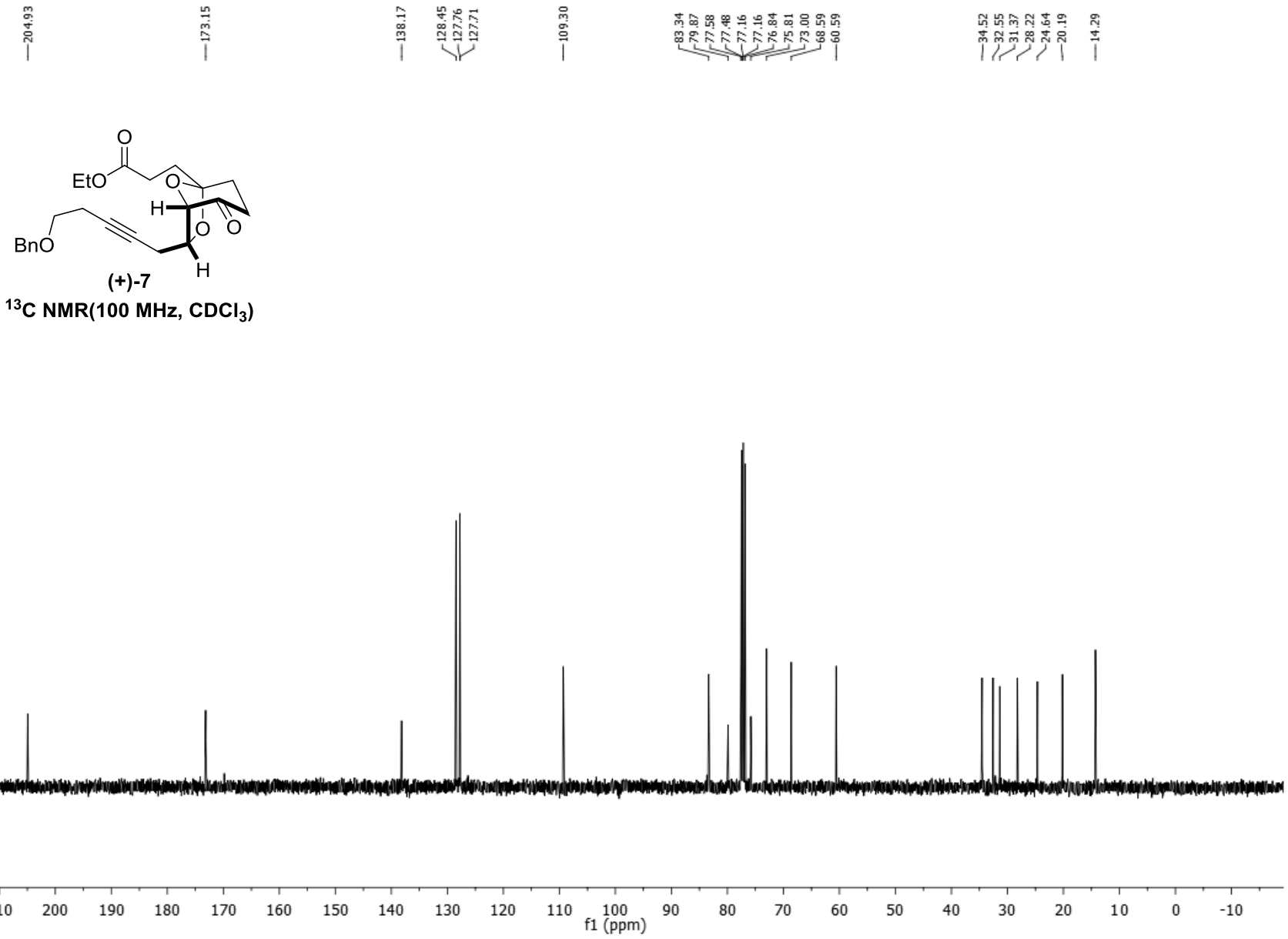
(-)-2

^{13}C NMR(100 MHz, $CDCl_3$)



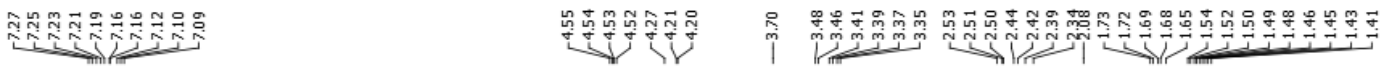
(+)-7

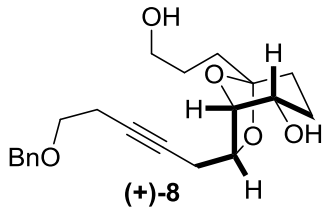
^{1}H NMR(400 MHz, $CDCl_3$)



(+)-7

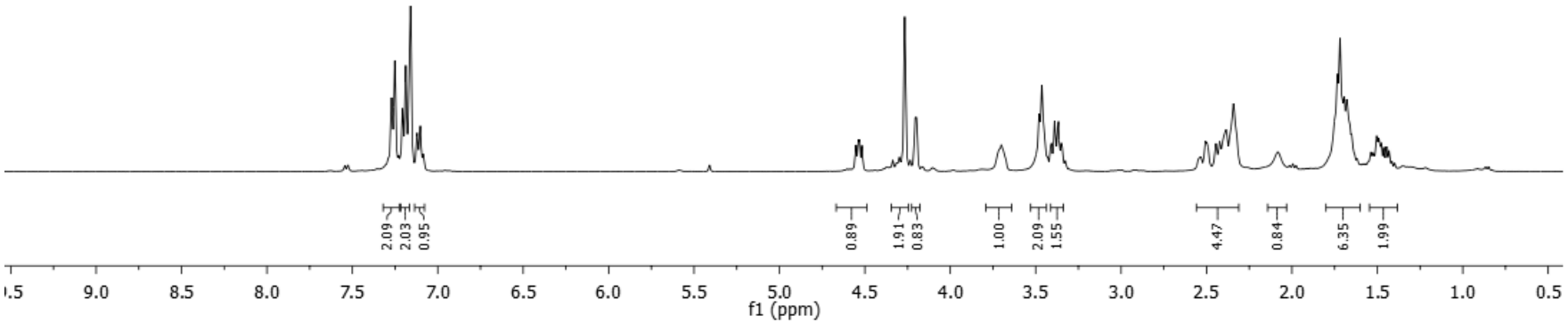
^{13}C NMR(100 MHz, $CDCl_3$)

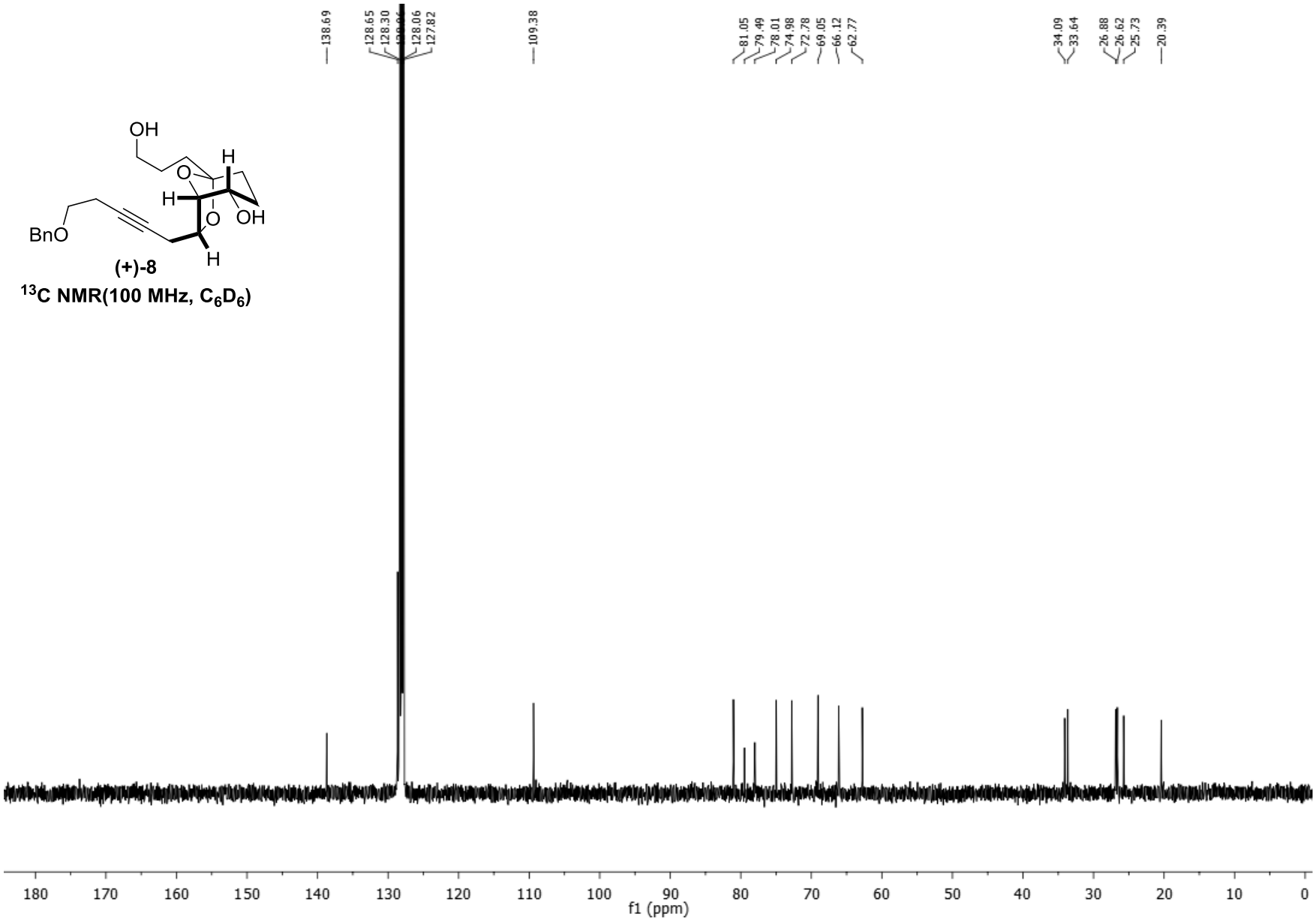




(+)-8

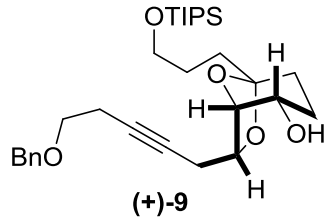
^{1}H NMR(400 MHz, C_6D_6)





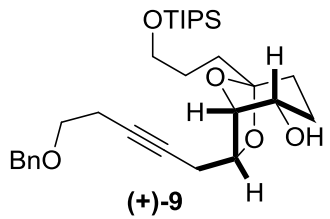
(+)-8

^{13}C NMR(100 MHz, C_6D_6)



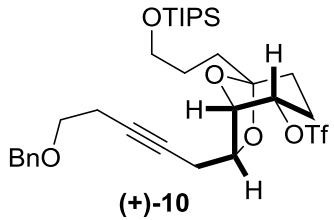
(+)-9

^{1}H NMR(400 MHz, $CDCl_3$)



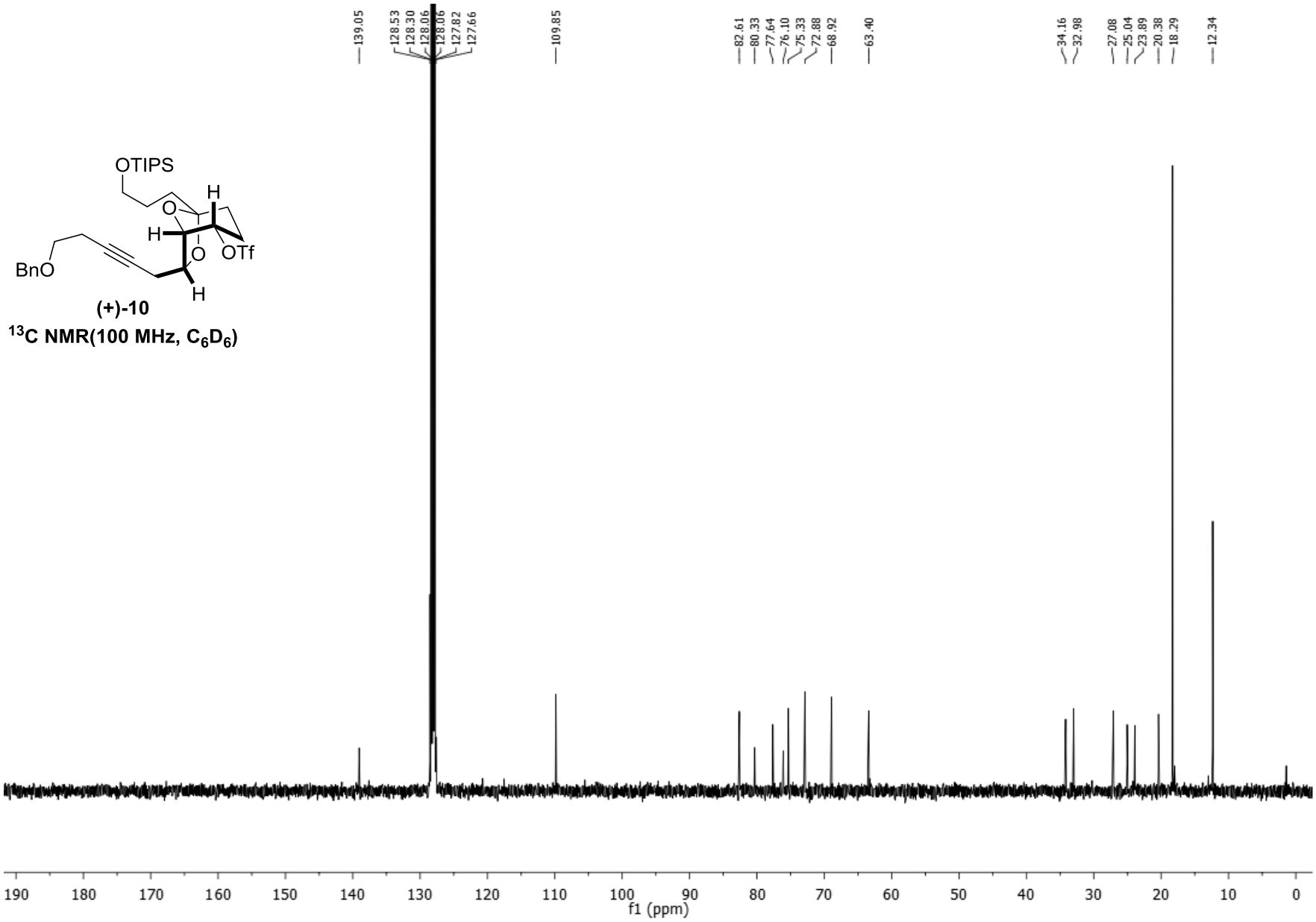
(+)-9

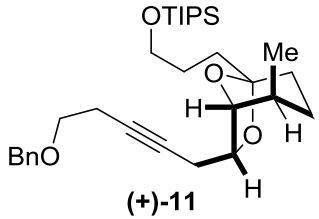
^{13}C NMR(100 MHz, $CDCl_3$)



(+)-10

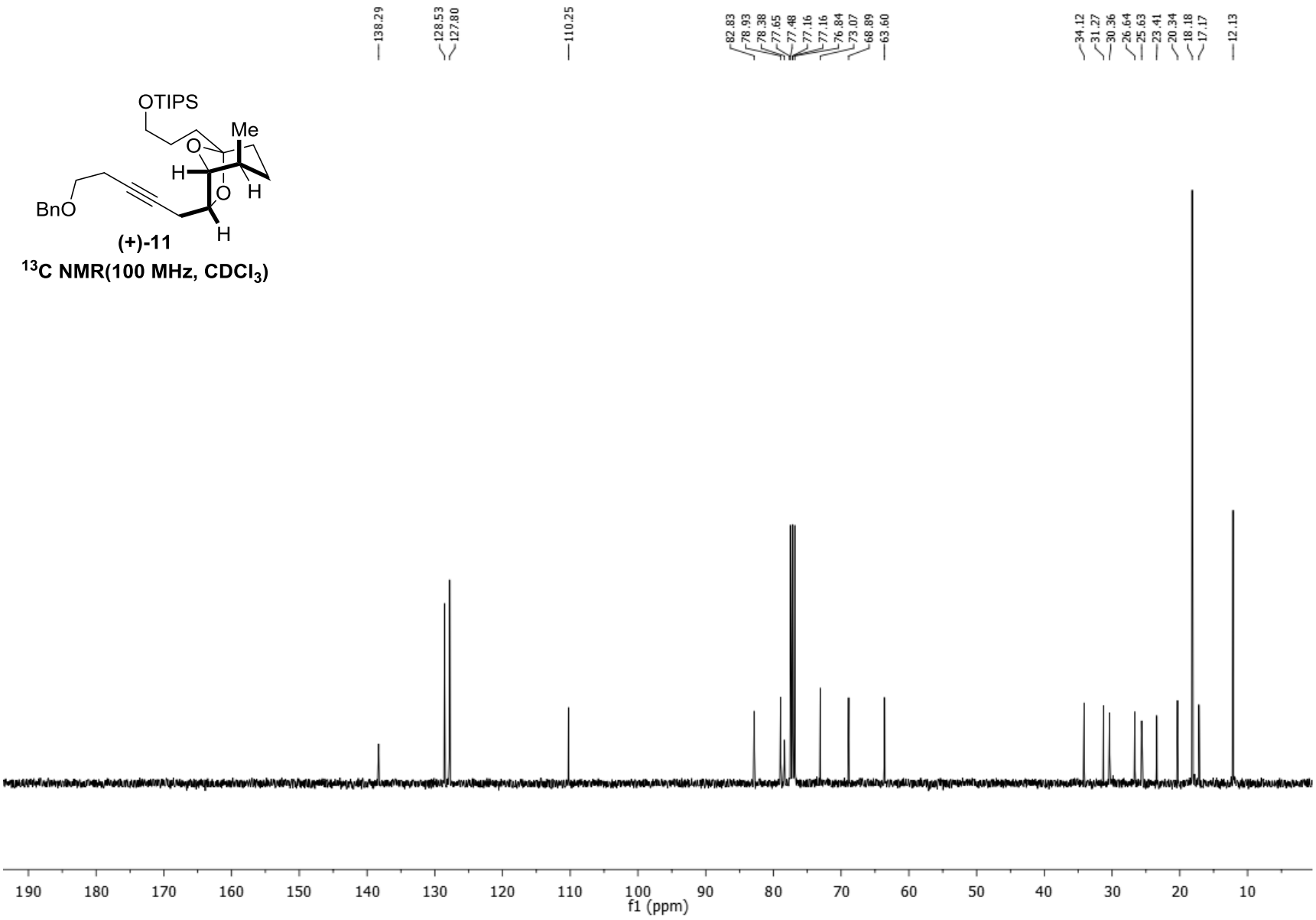
^{1}H NMR(400 MHz, C_6D_6)


OTIPS
H
O
H
O
OTf
BnO
H
(+)-10
^{13}C NMR(100 MHz, C_6D_6)
139.05
128.53
128.30
128.06
128.06
127.82
127.66
109.85
82.61
80.33
77.64
76.10
75.33
72.88
68.92
63.40
34.16
32.98
27.08
25.04
23.89
20.38
18.29
12.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



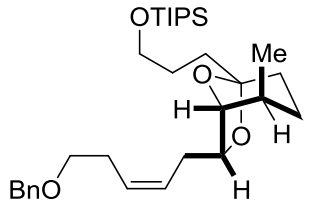
(+)-11

^{1}H NMR(400 MHz, $CDCl_3$)



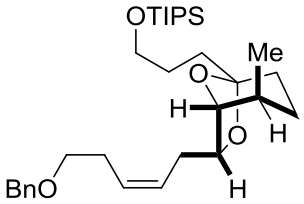
(+)-11

^{13}C NMR(100 MHz, $CDCl_3$)



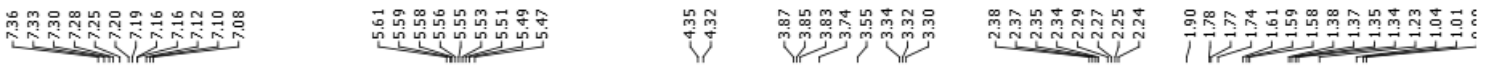
(+)-12

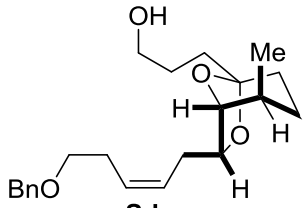
^{1}H NMR(400 MHz, $CDCl_3$)



(+)-12

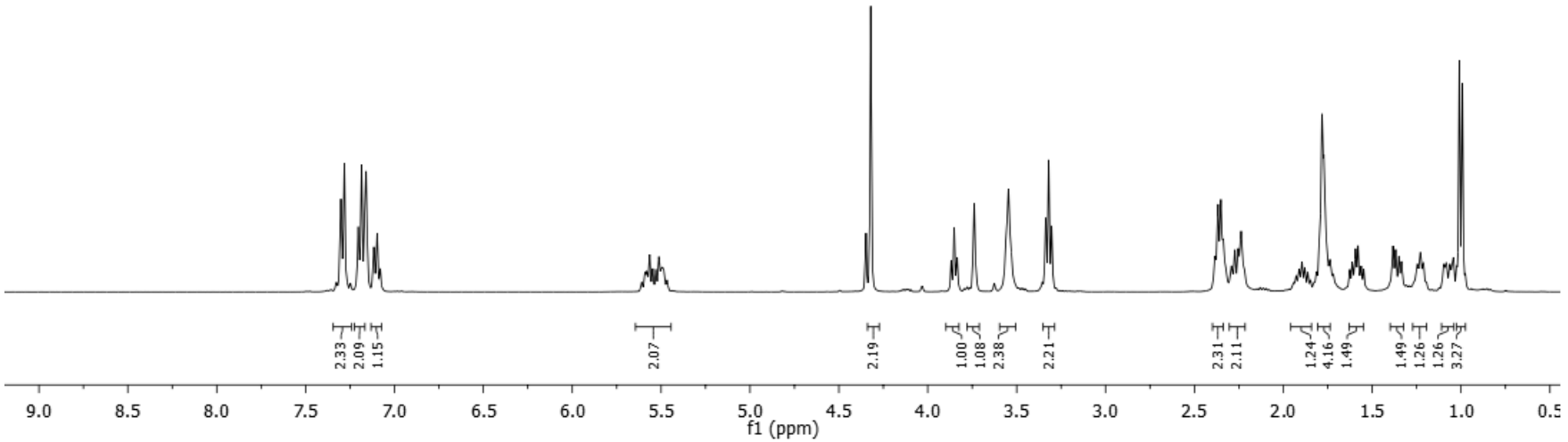
^{13}C NMR(100 MHz, $CDCl_3$)

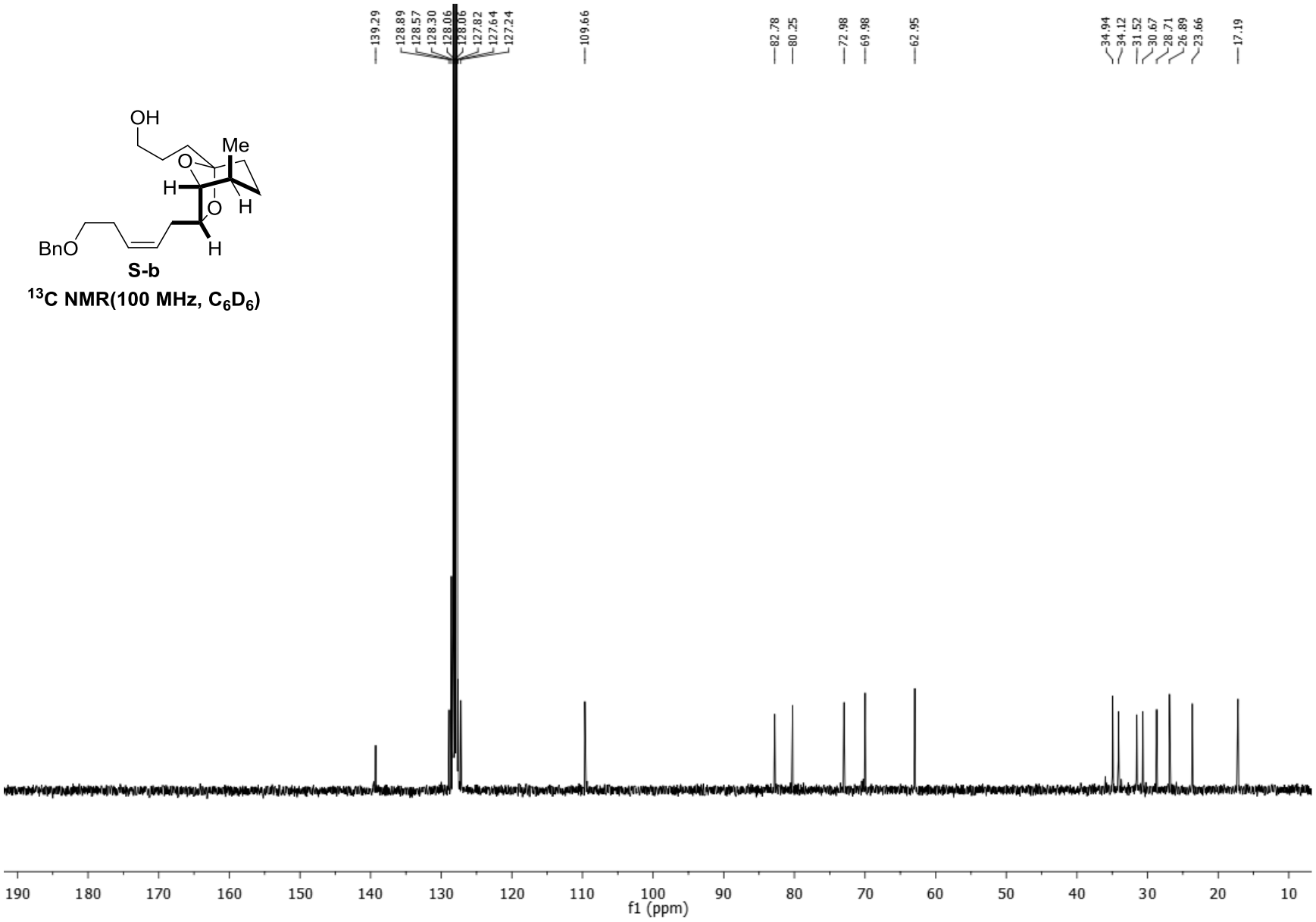




S-b

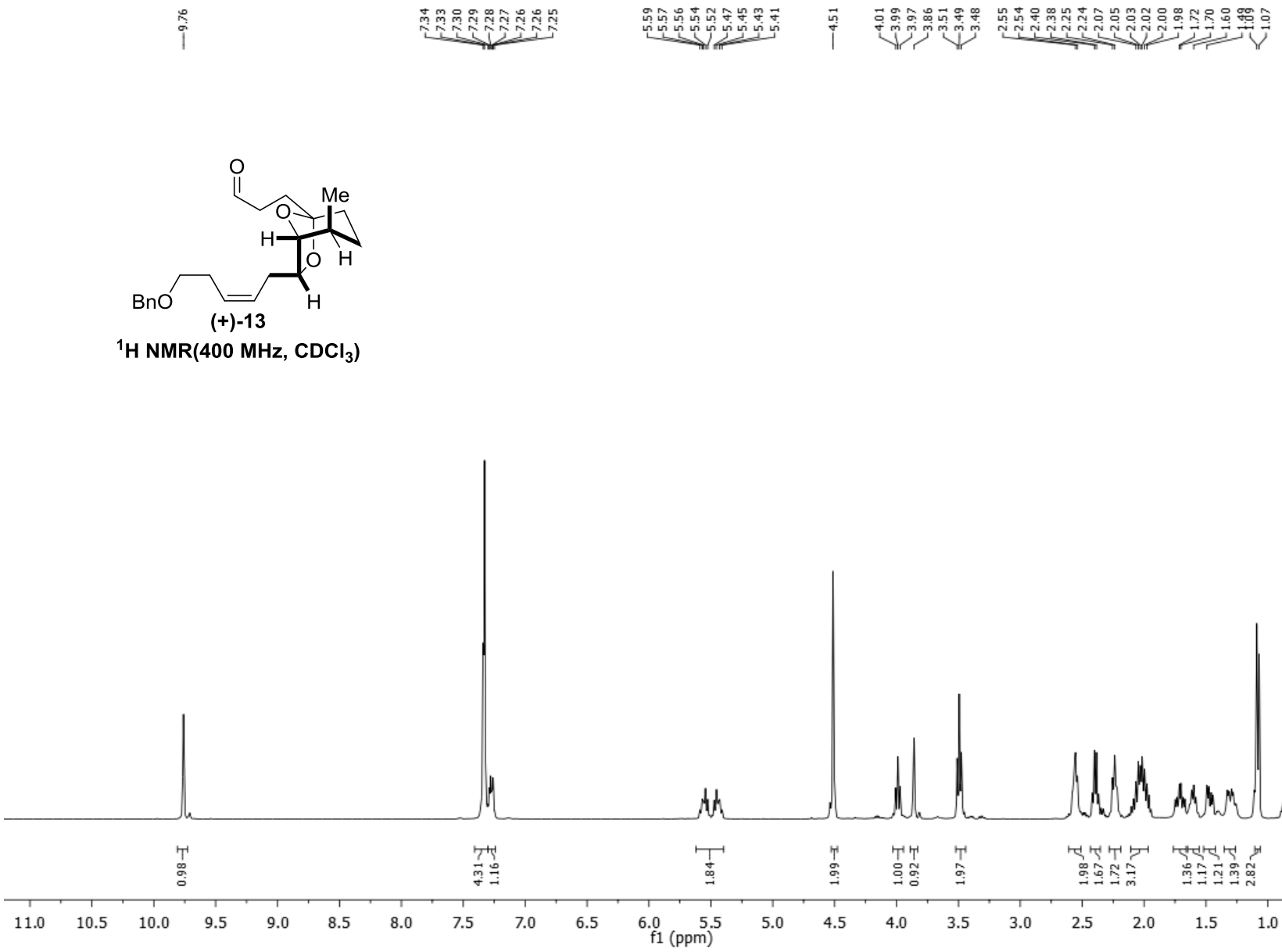
^{1}H NMR(400 MHz, C_6D_6)





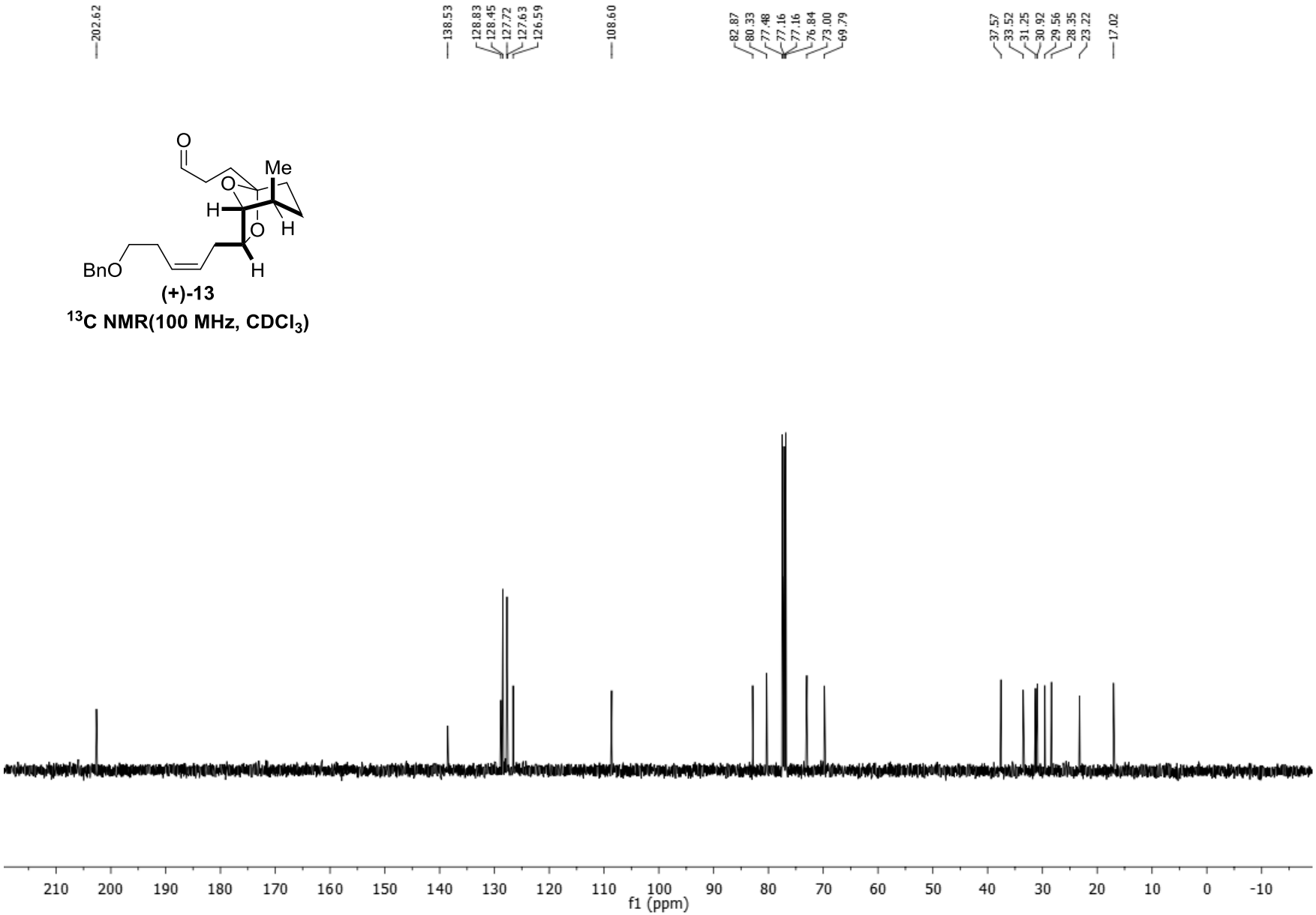
S-b

^{13}C NMR(100 MHz, C_6D_6)



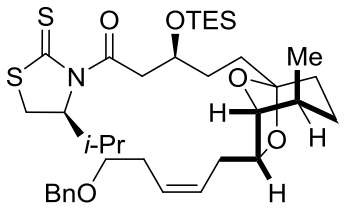
(+)-13

^{1}H NMR(400 MHz, $CDCl_3$)



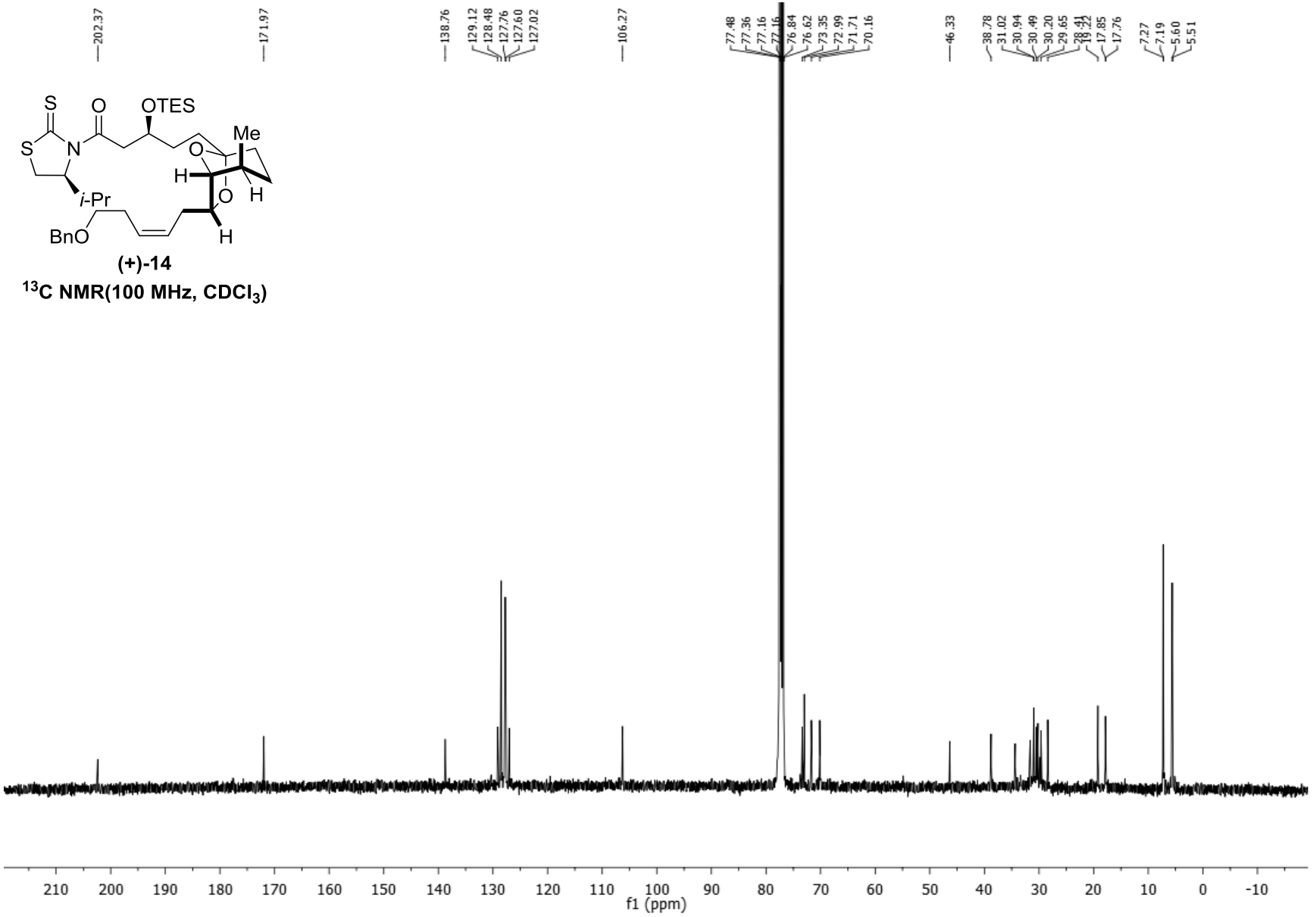
(+)-13

^{13}C NMR(100 MHz, $CDCl_3$)



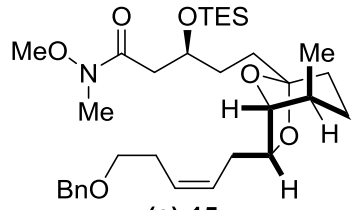
(+)-14

^{1}H NMR(400 MHz, $CDCl_3$)



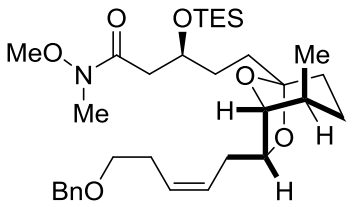
(+)-14

^{13}C NMR(100 MHz, $CDCl_3$)



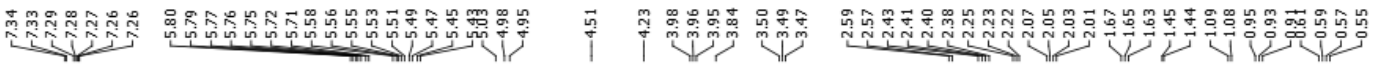
(+)-15

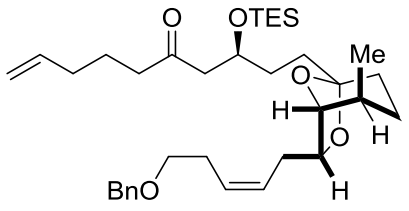
^{1}H NMR(400 MHz, $CDCl_3$)



(+)-15

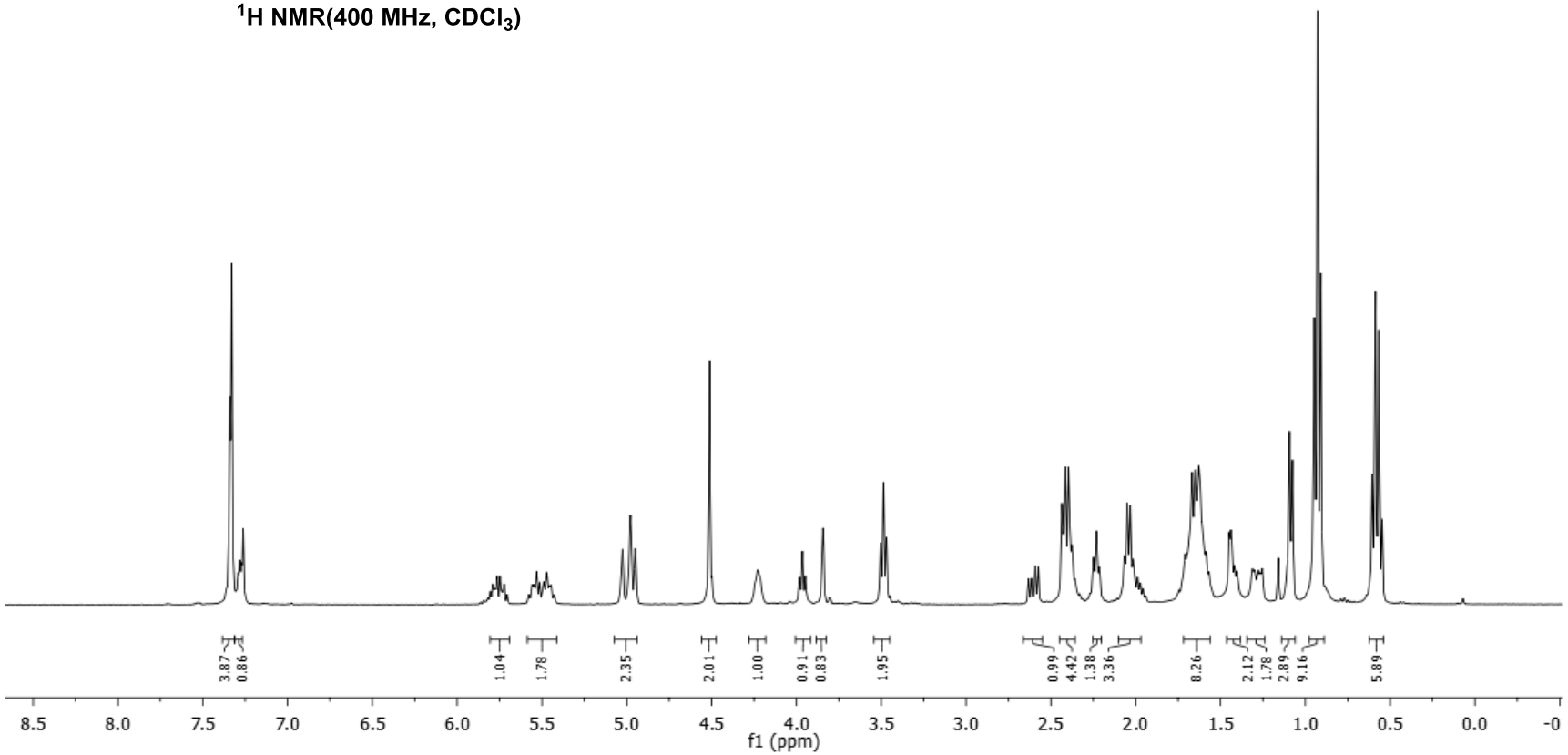
^{13}C NMR(100 MHz, $CDCl_3$)

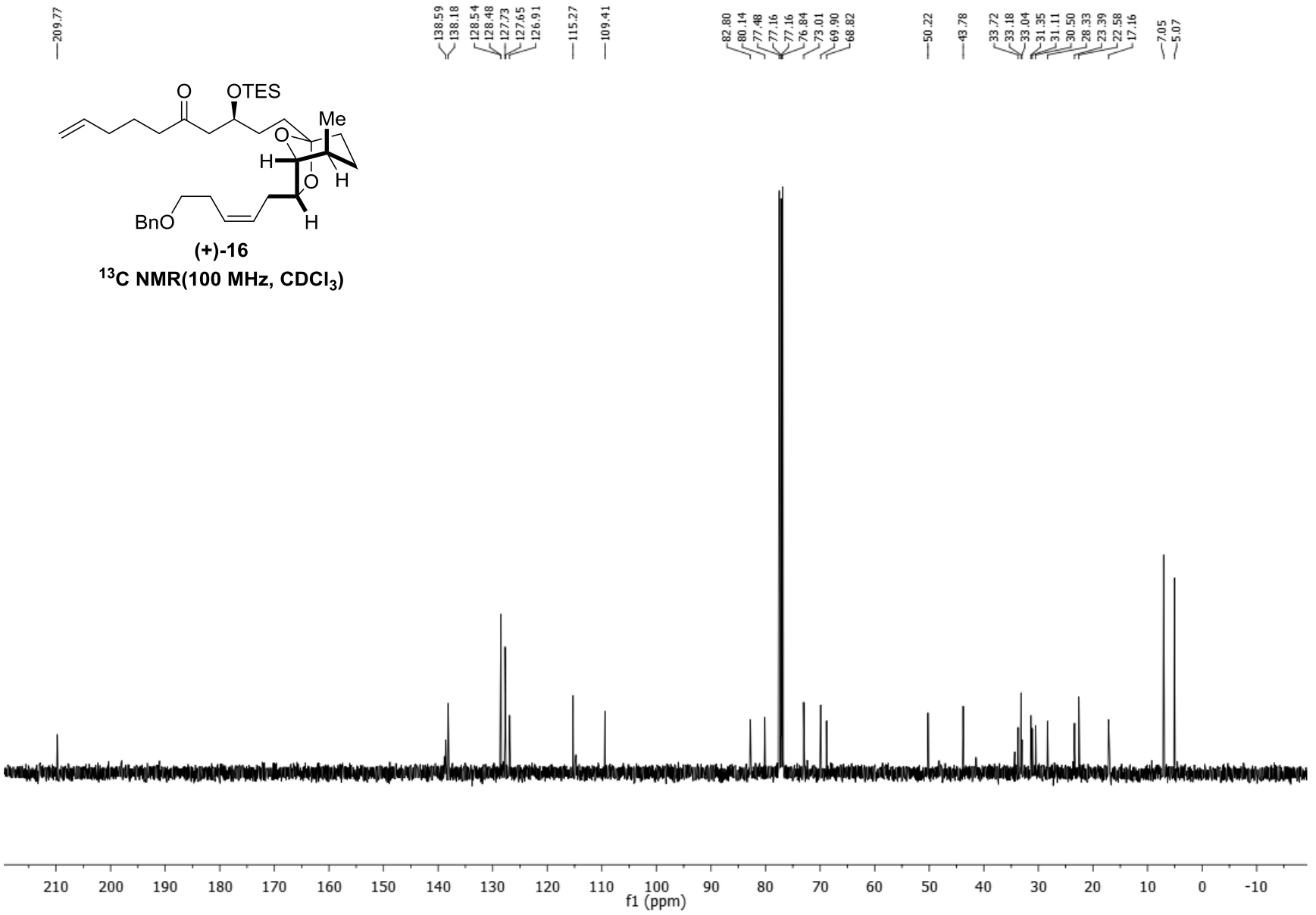




(+)-16

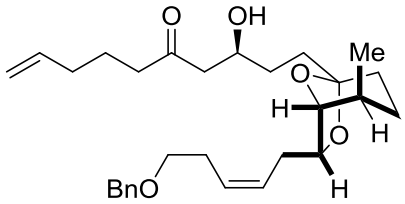
^{1}H NMR(400 MHz, $CDCl_3$)





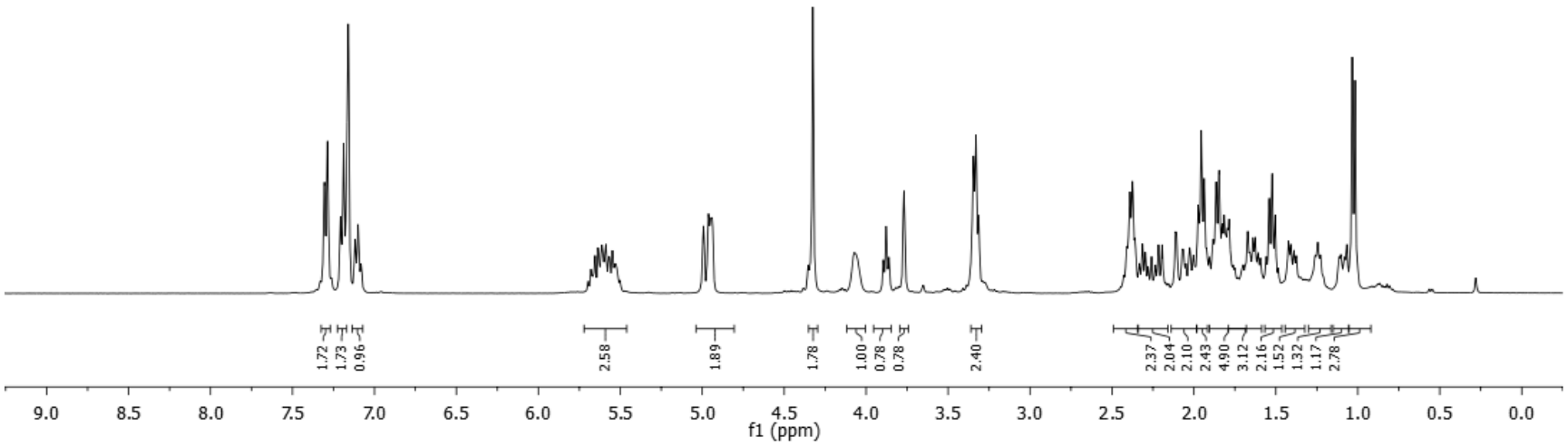
(+)-16

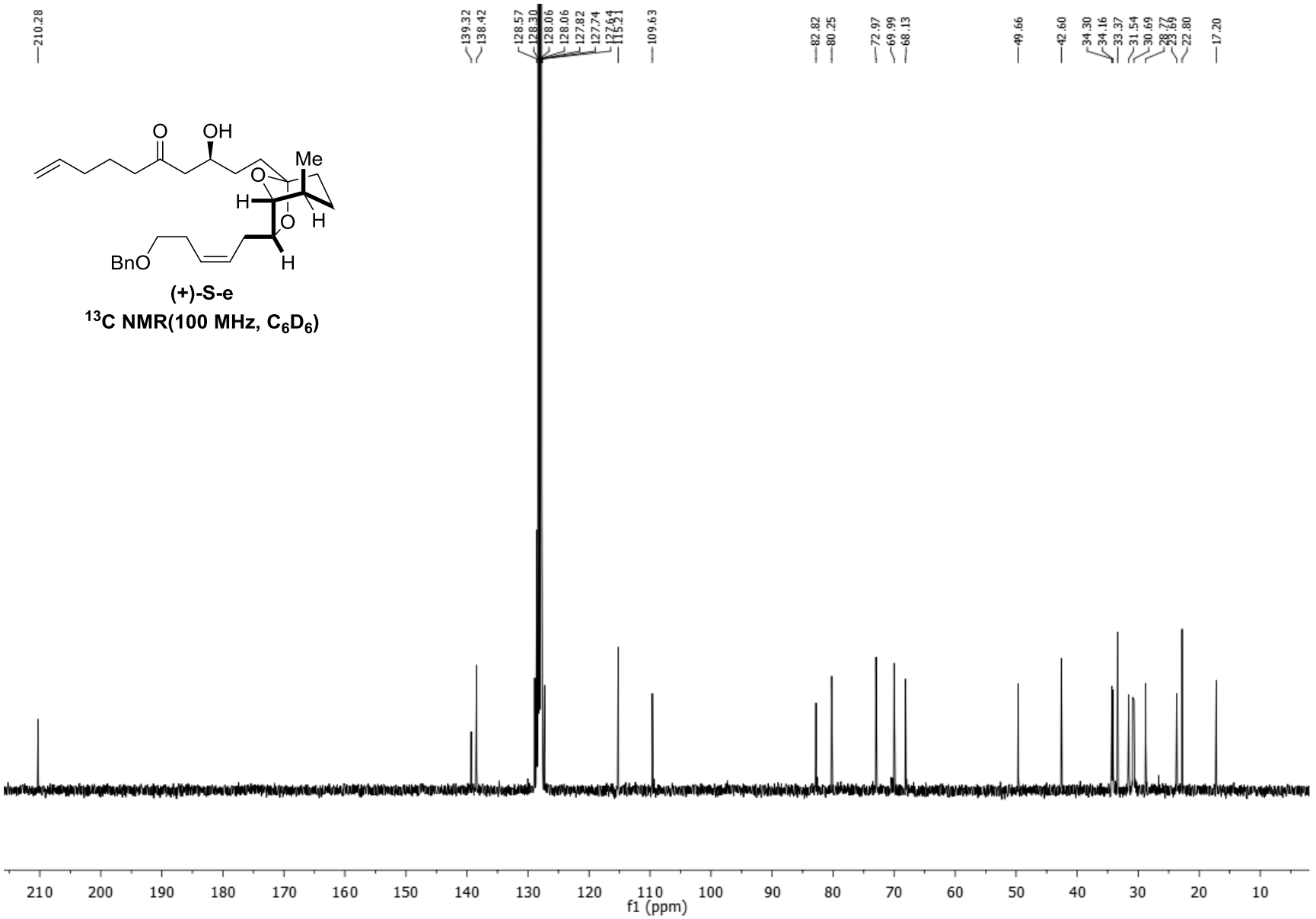
^{13}C NMR(100 MHz, $CDCl_3$)



(+)-S-e

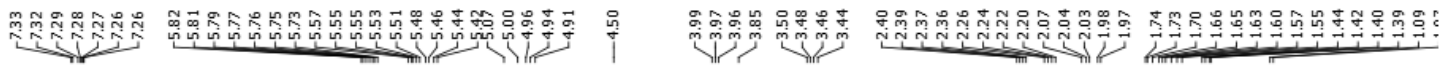
^{1}H NMR(400 MHz, C_6D_6)

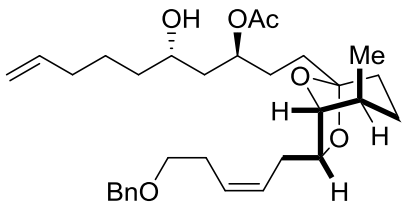




(+)-S-e

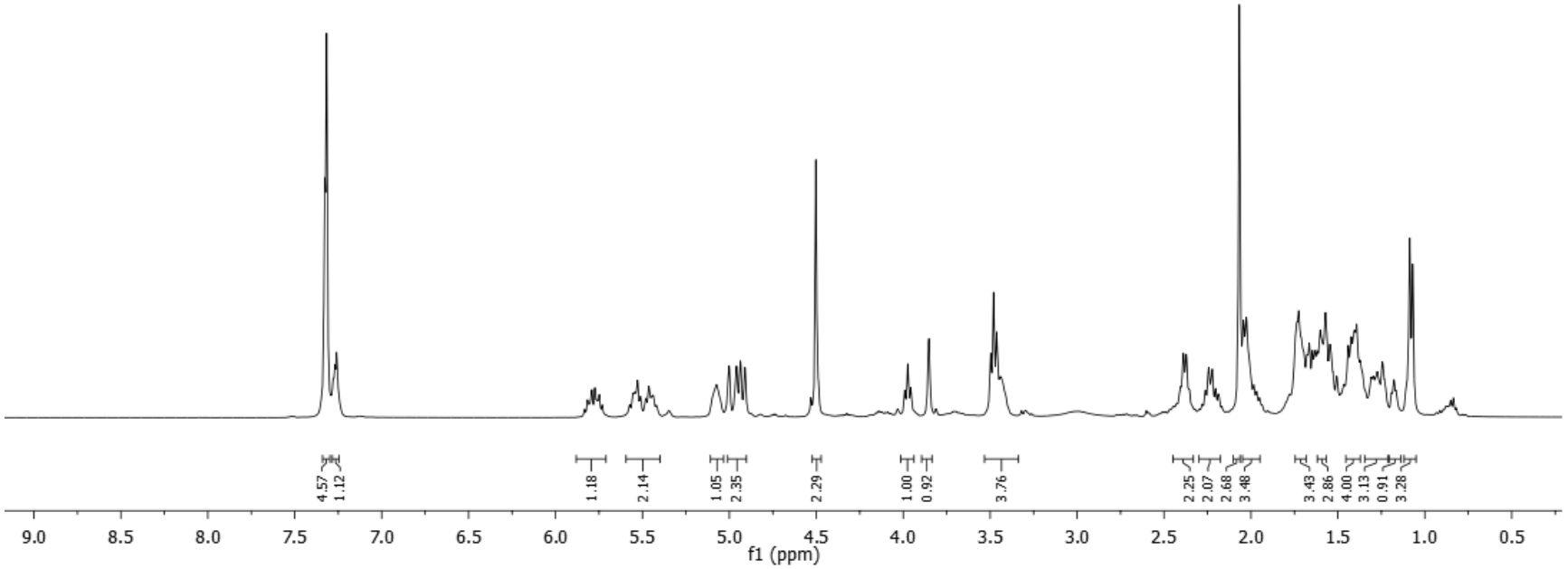
^{13}C NMR(100 MHz, C_6D_6)

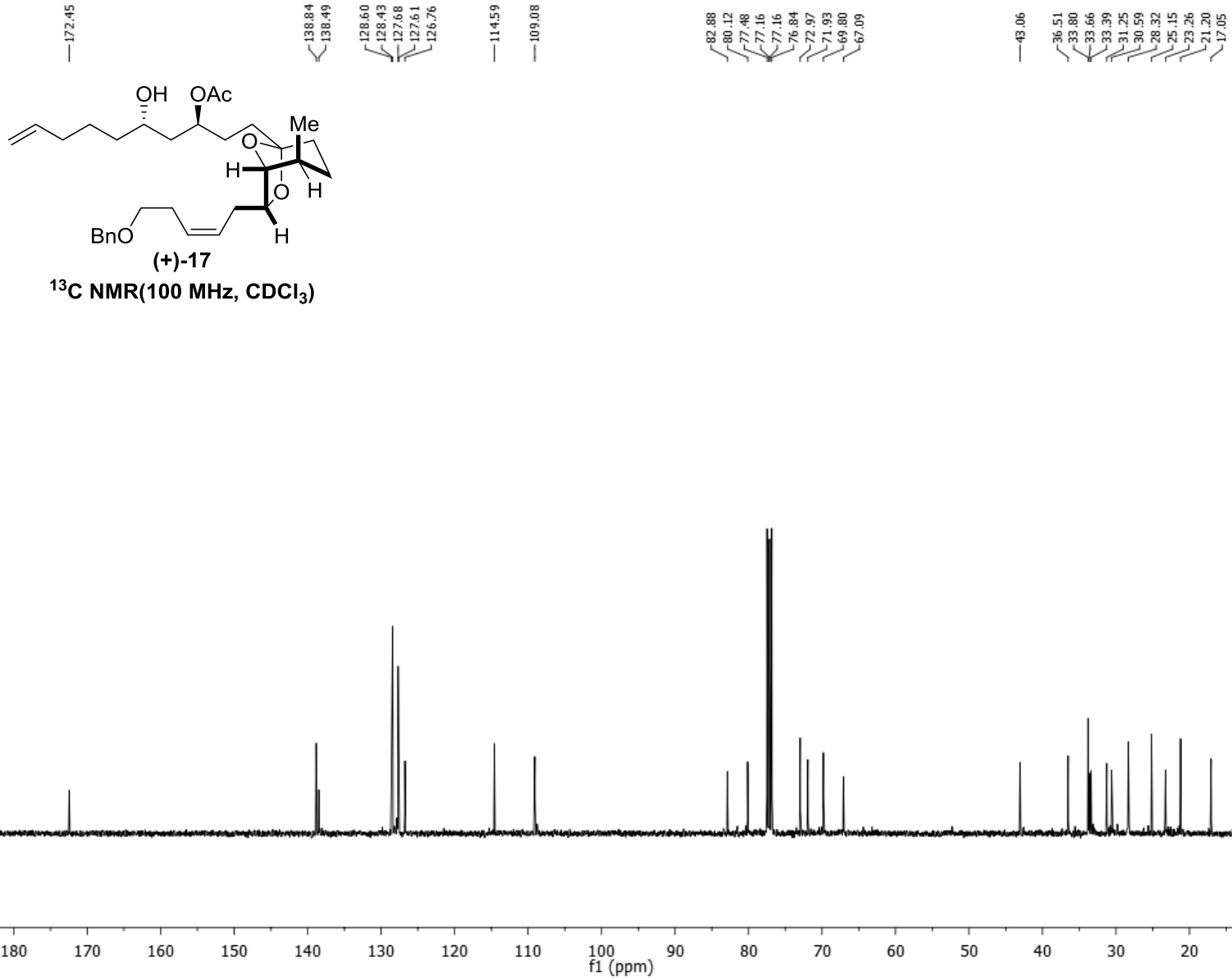




(+)-17

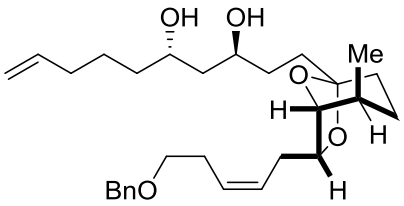
^{1}H NMR(400 MHz, $CDCl_3$)





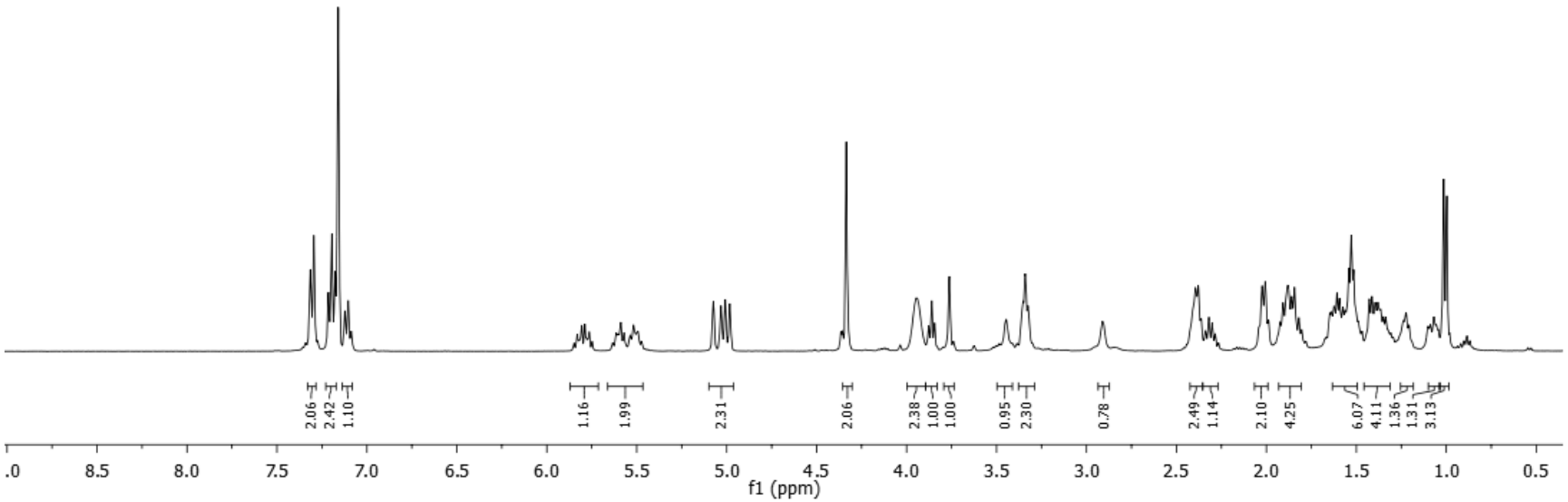
(+)-17

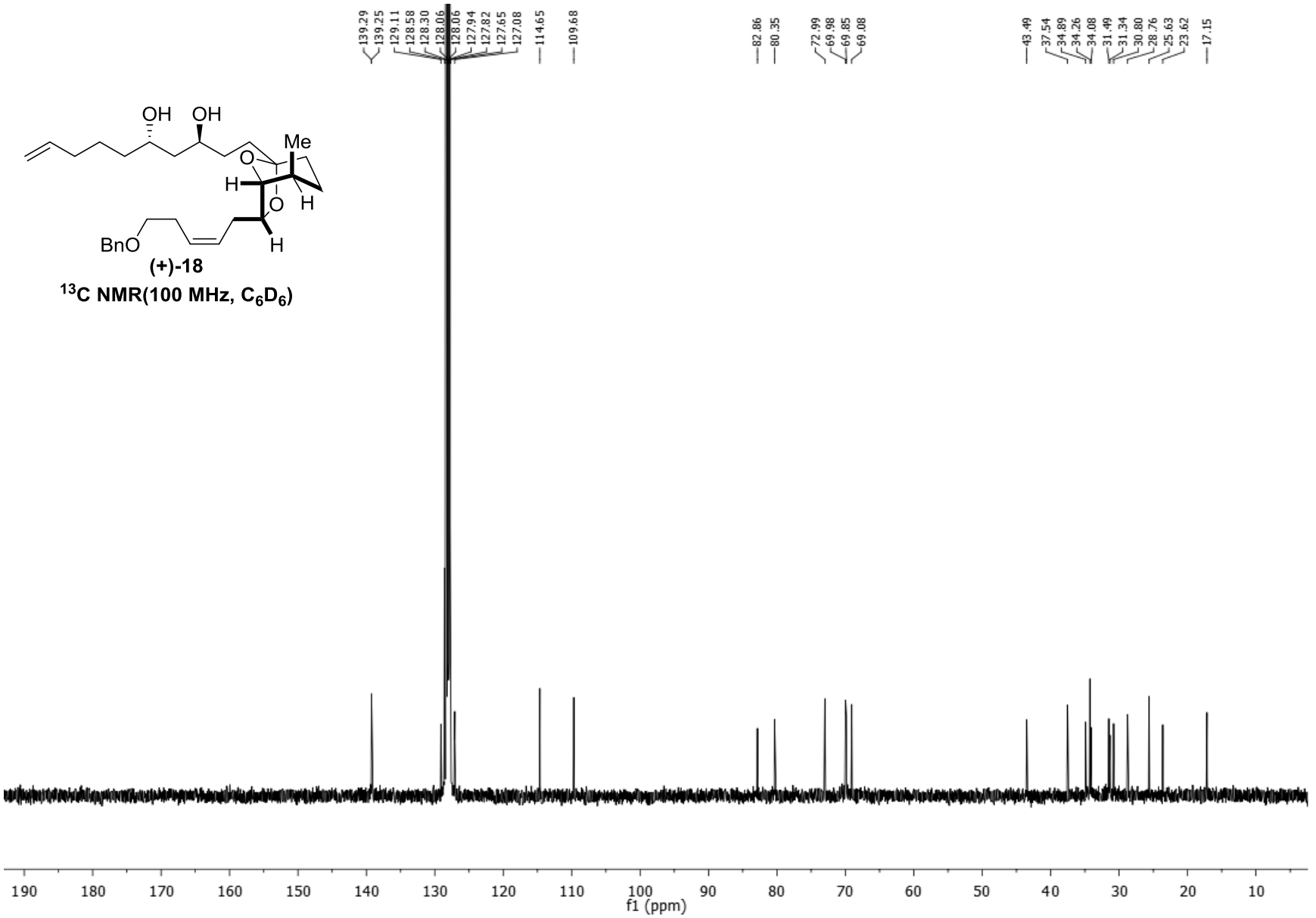
^{13}C NMR(100 MHz, $CDCl_3$)

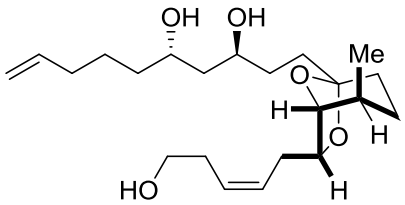


(+)-18

^{1}H NMR(400 MHz, C_6D_6)

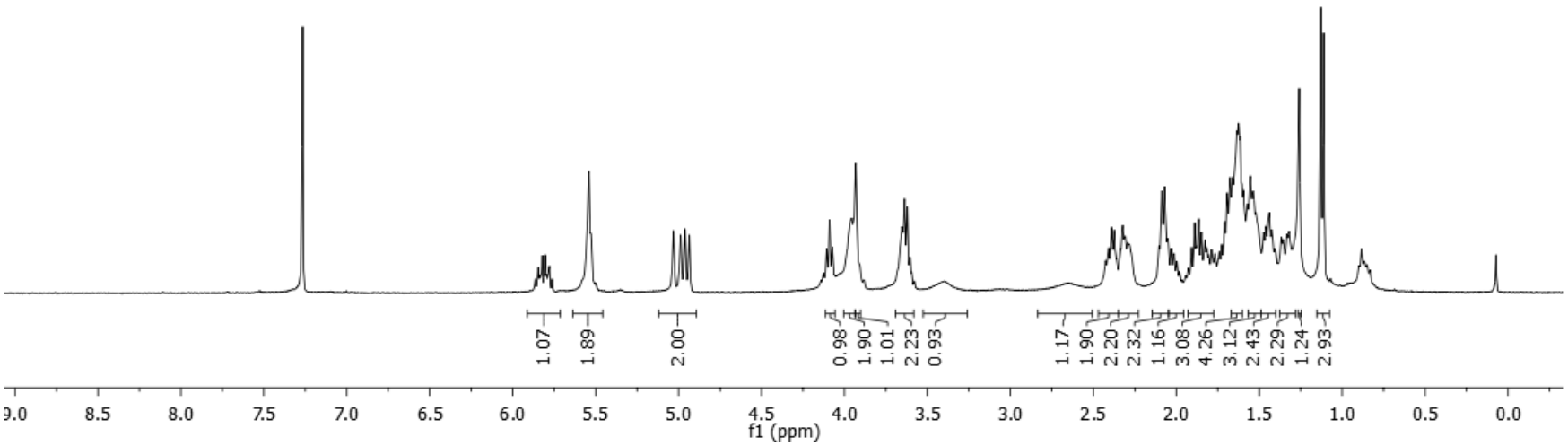


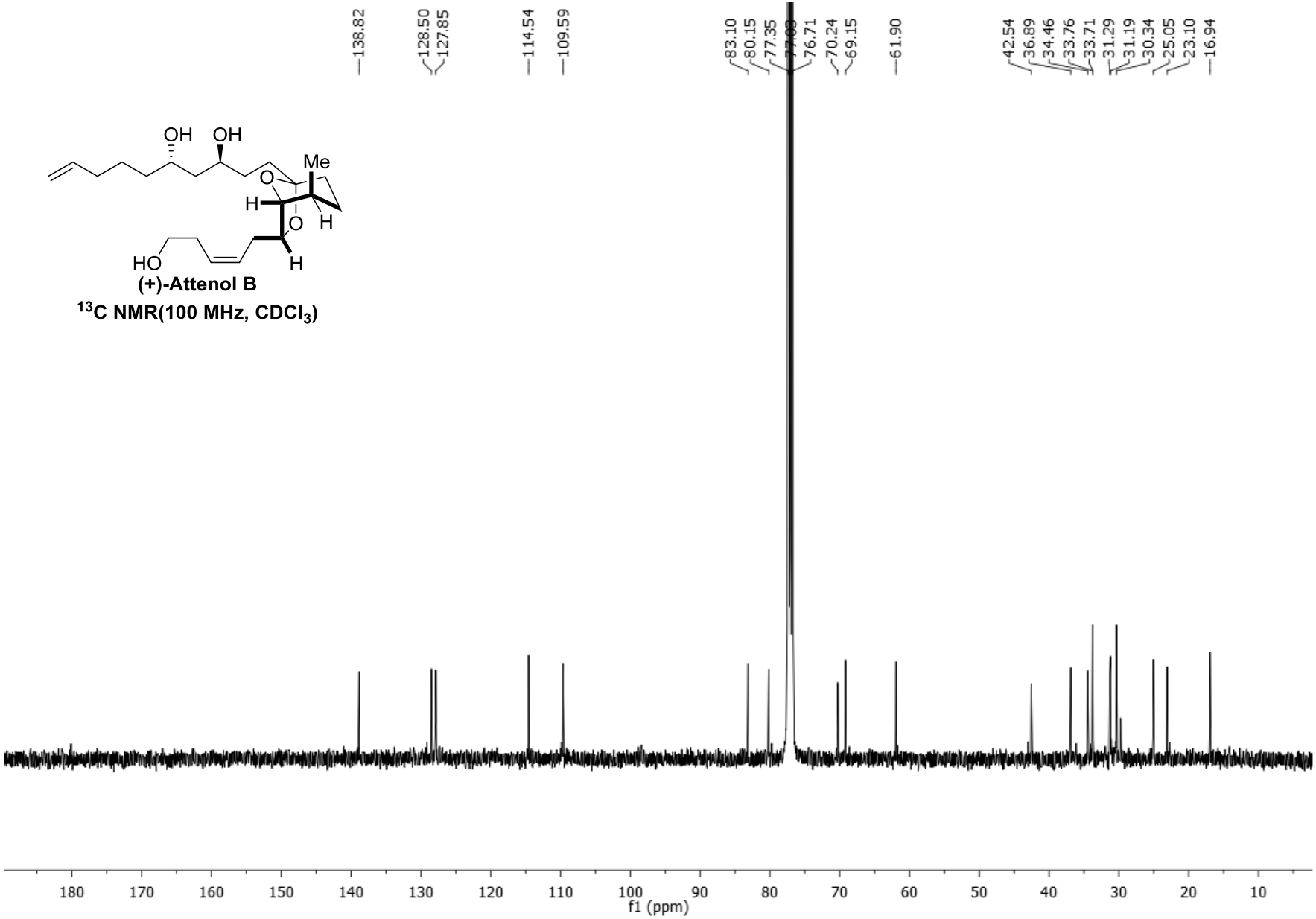

OH
OH
Me
O
H
O
H
BnO
H
(+)-18
^{13}C NMR(100 MHz, C_6D_6)
139.29
139.25
129.11
128.58
128.30
128.06
128.06
127.94
127.82
127.65
127.08
114.65
109.68
82.86
80.35
72.99
69.98
69.85
69.08
43.49
37.54
34.89
34.26
34.08
31.49
31.34
30.80
28.76
25.63
23.62
17.15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



(+)-Attenol B

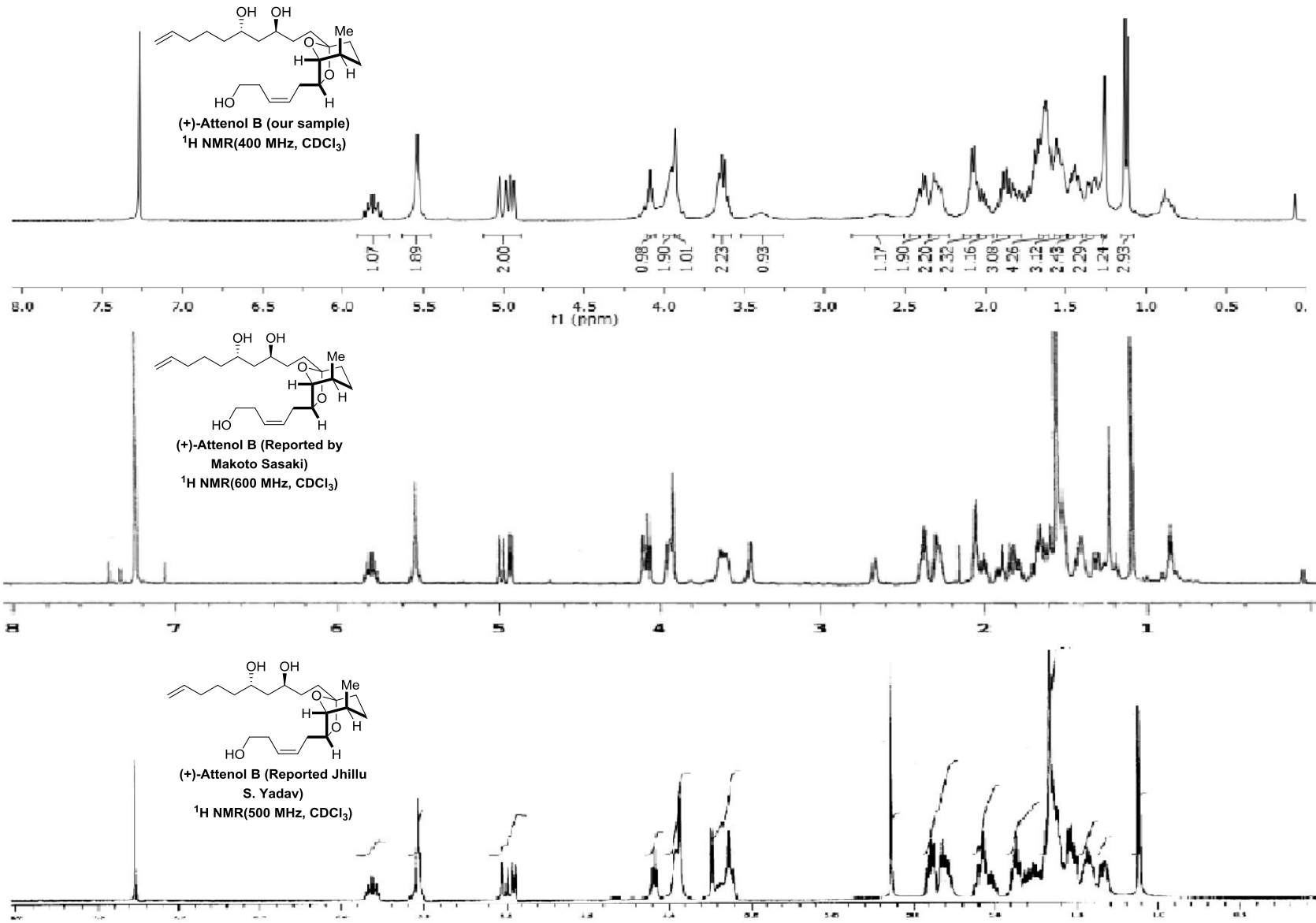
^{1}H NMR(400 MHz, $CDCl_3$)

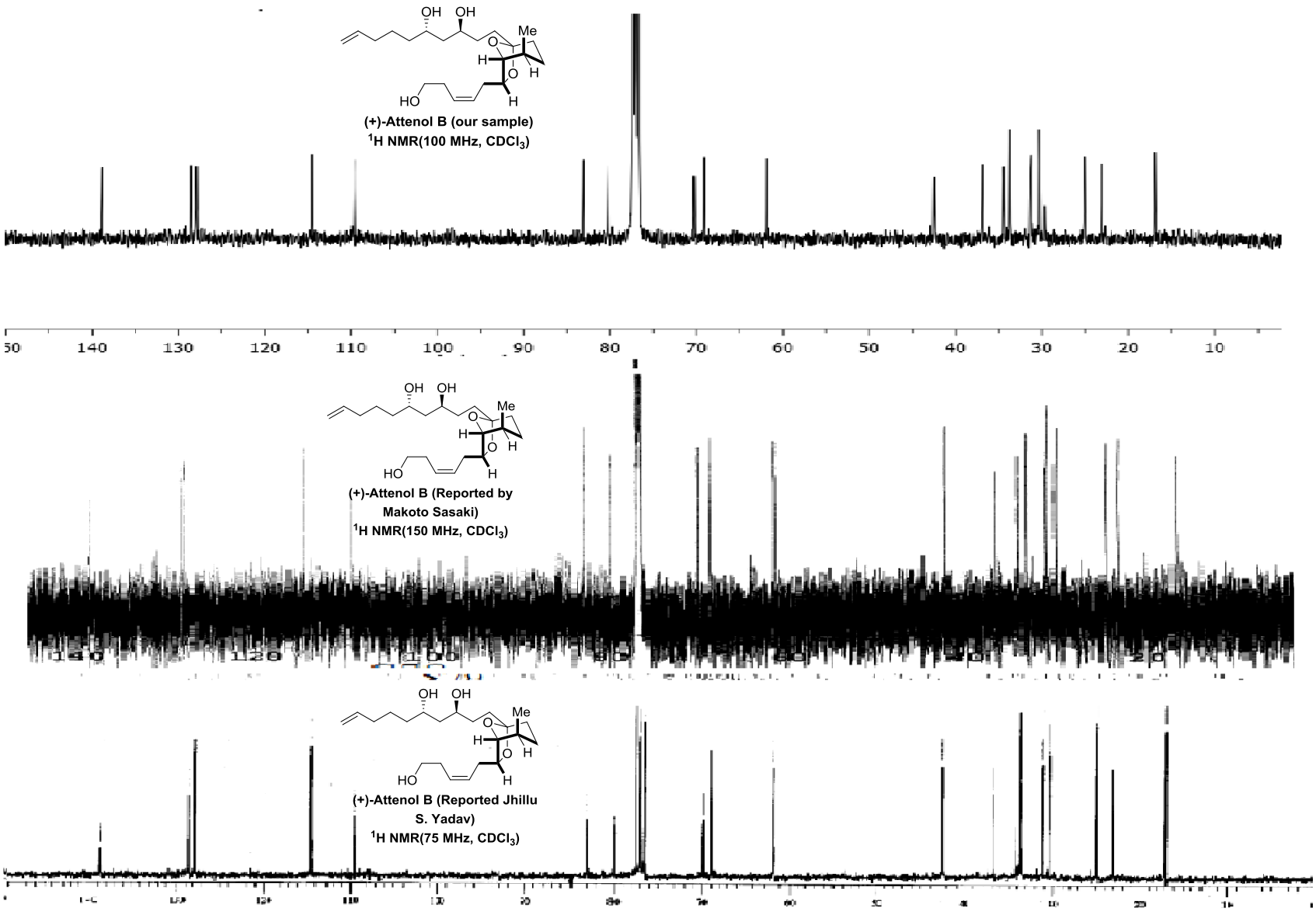


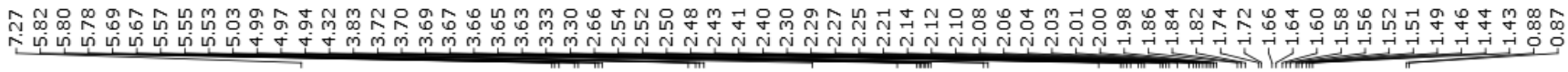


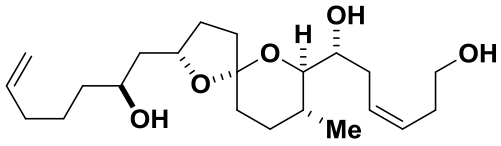
(+)-Attenol B

^{13}C NMR(100 MHz, $CDCl_3$)


(+)-Attenol B (our sample)
^{1}H NMR(400 MHz, CDCl$_3$)
f1 (ppm)
(+)-Attenol B (Reported by Makoto Sasaki)
^{1}H NMR(600 MHz, CDCl$_3$)
(+)-Attenol B (Reported Jhillu S. Yadav)
^{1}H NMR(500 MHz, CDCl$_3$)

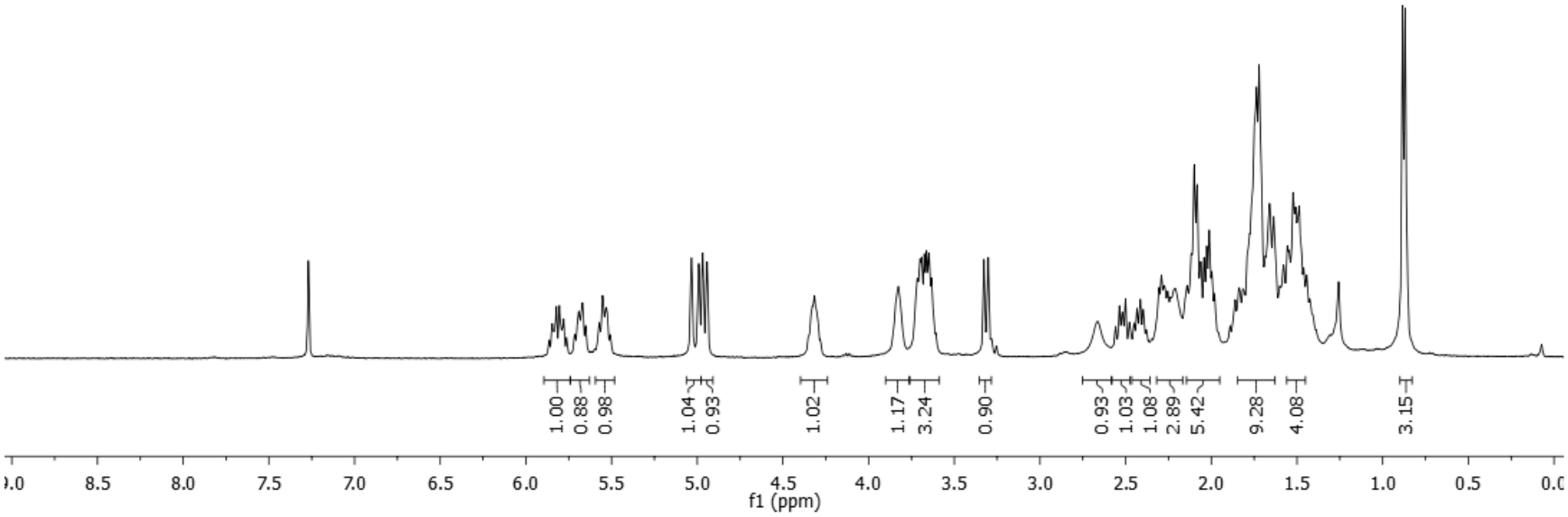

OH
OH
Me
O
H
O
H
HO
H
(+)-Attenol B (our sample)
1H NMR(100 MHz, CDCl3)
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(+)-Attenol B (Reported by
Makoto Sasaki)
1H NMR(150 MHz, CDCl3)
(+)-Attenol B (Reported Jhillu
S. Yadav)
1H NMR(75 MHz, CDCl3)

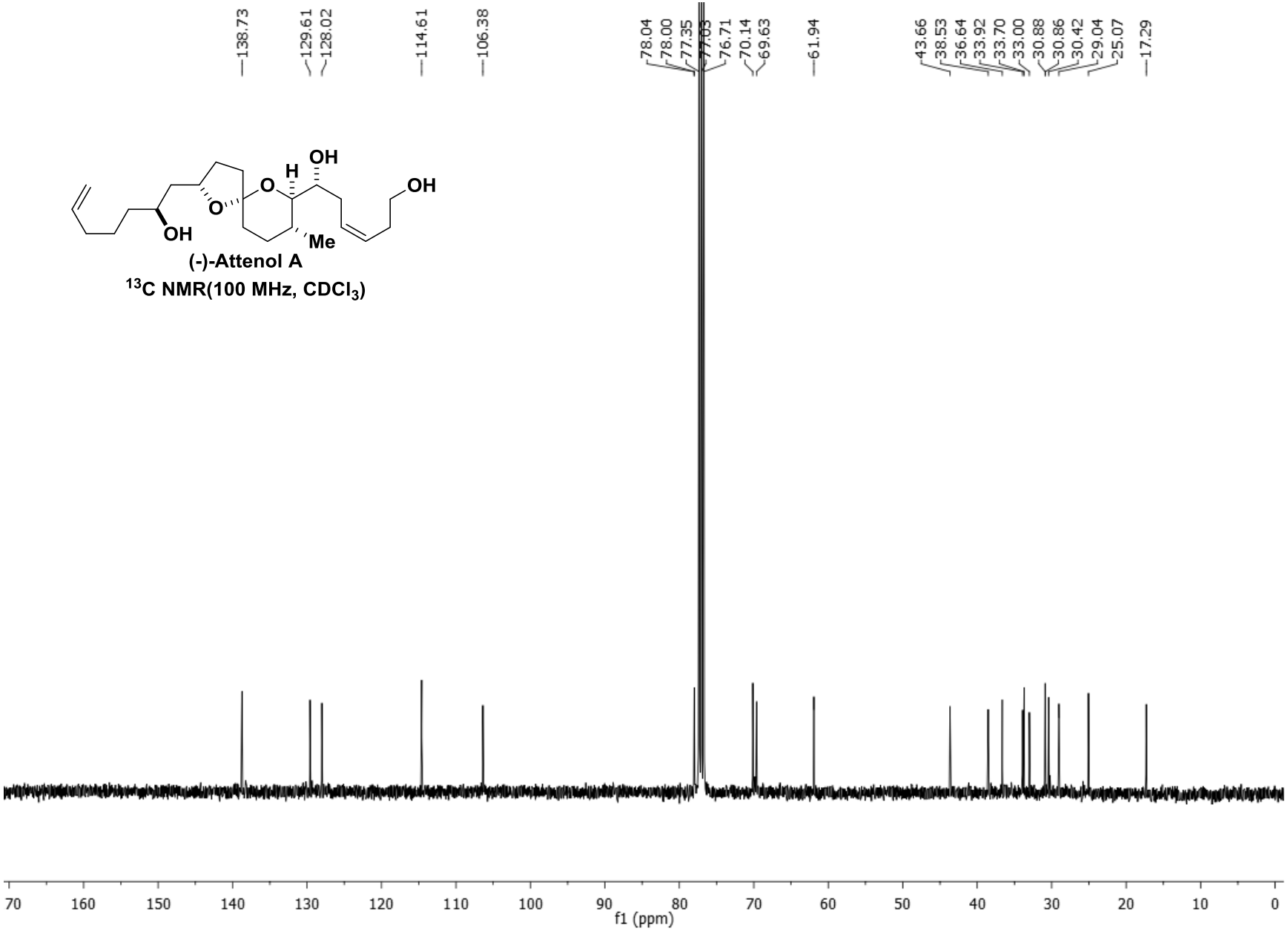


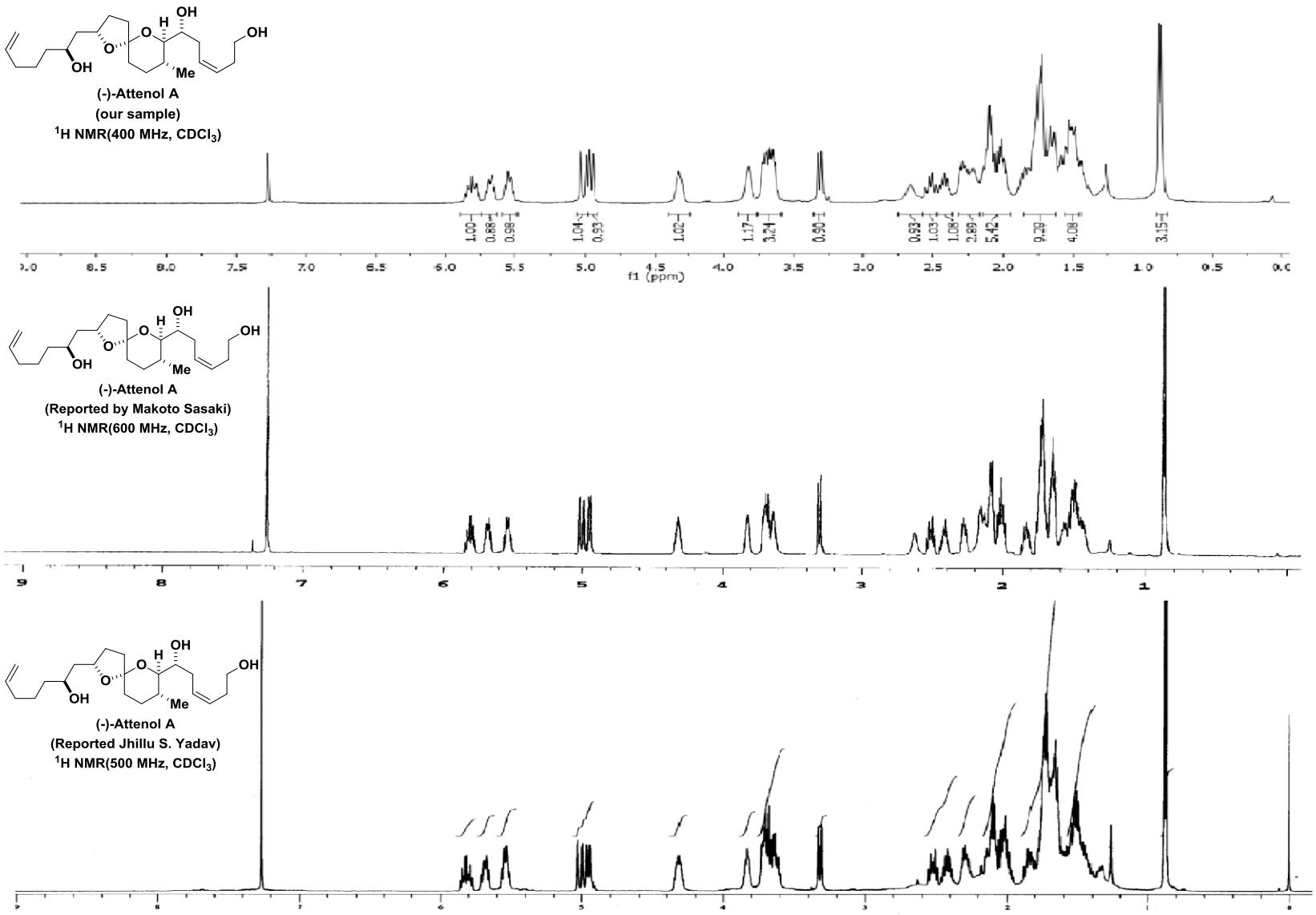


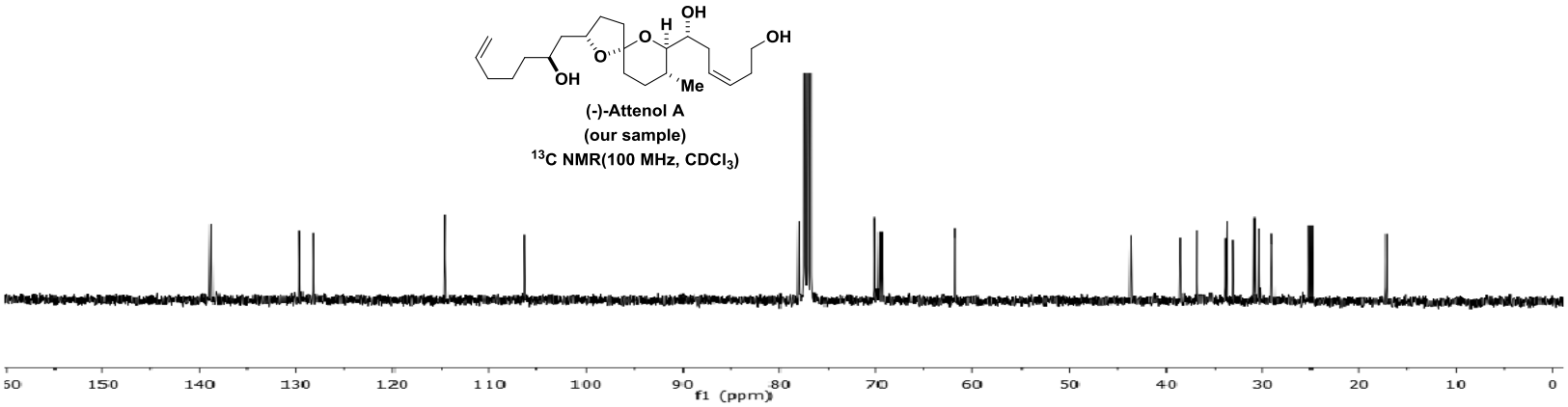
(-)-Attenol A

^{1}H NMR(400 MHz, $CDCl_3$)

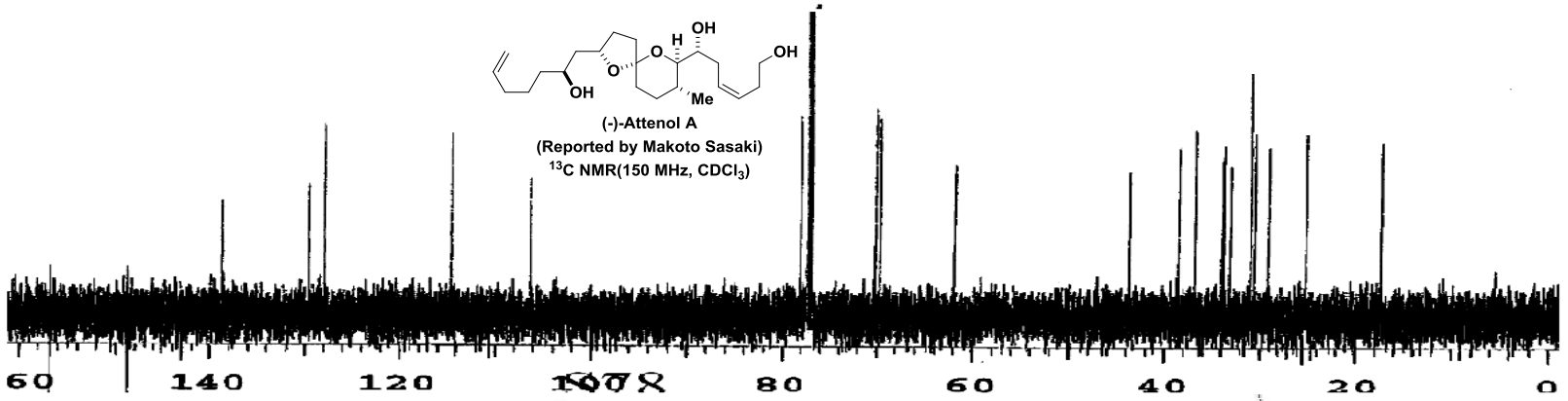



138.73
129.61
128.02
114.61
106.38
78.04
78.00
77.35
77.03
76.71
70.14
69.63
61.94
43.66
38.53
36.64
33.92
33.70
33.00
30.88
30.86
30.42
29.04
25.07
17.29
OH
H
O
OH
O
OH
Me
(-)-Attenol A
13C NMR(100 MHz, CDCl3)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

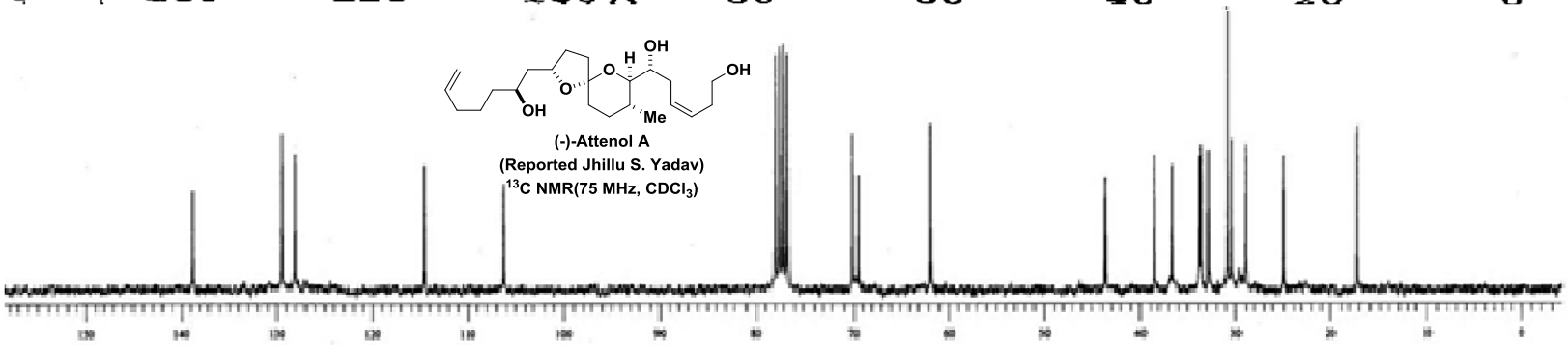

(-)-Attenol A
(our sample)
^{1}H NMR(400 MHz, CDCl$_3$)
f1 (ppm)
(-)-Attenol A
(Reported by Makoto Sasaki)
^{1}H NMR(600 MHz, CDCl$_3$)
(-)-Attenol A
(Reported Jhillu S. Yadav)
^{1}H NMR(500 MHz, CDCl$_3$)



(-)-Attenol A
(our sample)
^{13}C NMR(100 MHz, $CDCl_3$)



(-)-Attenol A
(Reported by Makoto Sasaki)
^{13}C NMR(150 MHz, $CDCl_3$)



(-)-Attenol A
(Reported Jhillu S. Yadav)
^{13}C NMR(75 MHz, $CDCl_3$)