Supporting Information

Synthetic Strategies Toward the Decalin Motif of Maklamicin and Related Spirotetronates

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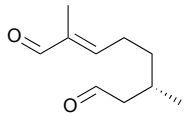
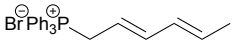
General Procedures

Unless indicated, all commercially available reagents and anhydrous solvents were purchased at the highest commercial quality and were used as received without further purification. All non-aqueous reactions were carried out under argon atmosphere using dry glassware that had been flame-dried under a stream of argon unless otherwise noted. Anhydrous tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and dimethylformamide (DMF) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Flash column chromatography was performed on silica gel (Merck Kieselgel 60, 230-400 mesh) using Hexanes-EtOAc or CH_2Cl_2-MeOH mixtures of increasing polarity. The progress of all the reactions were monitored by thin-layer chromatography (TLC) using glass plates precoated with silica gel-60 F_{254} to a thickness of 0.5 mm (Merck), and compounds were visualized by irradiation with UV light and/or by treatment with a solution of $KMnO_4$ stain or Seebach's stain followed by heating. ^{13}C NMR and ^{1}H NMR spectra were recorded on either 500 MHz Varian instrument or 500 MHz JEOL instrument. $CDCl_3$ was treated with flame dried K_2CO_3, chemical shifts (δ) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak reference ($CDCl_3$), with the abbreviations s, br s, d, t, q, m, td, dt and qd denoting singlet, broad singlet, doublet, triplet, quartet, multiplet, quartet of doublets, triplet of doublets, doublet of triplets and quartet of doublets respectively. *J* = coupling constants given in Hertz (Hz). IR spectras were collected on a Jasco 4100 FTIR. High resolution Mass spectra (HRMS) were recorded on a trisector WG AutoSpecQ spectrometer. Optical rotation data were collected on a Jasco P-1010 polarimeter using HPLC grade anhydrous $CHCl_3$.



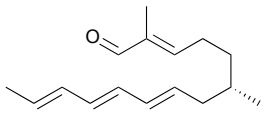
Dialdehyde (11) (Method 1): To a solution of (*S*)-(–)-citronellal (1.45 mL, 1.23 g, 8.0 mmol, purchased from TCI America, > 96.0%, $[\alpha]_D^{20} = -15.5$, neat) in CH_2Cl_2 (150 mL) was added methacrolein (1.32 mL, 16.0 mmol) and Grubbs catalyst (2nd generation, 340 mg, 0.4 mmol). The reaction mixture was refluxed for 24 hours under argon atmosphere. The reaction was allowed to cool to room temperature and concentrated. The residue was purified via silica column chromatography (hexanes: EtOAc, 100:1 to 10:1) to recover the (*S*)-(–)-citronellal (205 mg, 17%) and yield the di-aldehyde **11** (1.01 g, 75%, 90% brsm) as a pale yellow oil.

Dialdehyde (11) (Method 2): To a solution of SeO_2 (416 mg, 3.7 mmol) and salicylic acid (1.99 g, 12.4 mmol) in CH_2Cl_2 (40 mL) was added *t*-butyl hydrogen peroxide slowly (70% in H_2O, 71.0 mL, 496 mmol). The mixture was stirred for 15 min then (*S*)-(–)-citronellal (18.8 g, 122 mmol) was added. The reaction was stirred at room temperature for 36 hours. The reaction was diluted with benzene (100 mL) and concentrated. The residue was diluted with ether (400 mL) and washed with 10% NaOH (2 x 130 mL) and brine (120 mL). The organic layer was dried over $MgSO_4$ filtered, concentrated and purified through silica column chromatography (hexanes:EtOAc, 200:1 to 5:1) to recover the (*S*)-(–)-citronellal (3.23 g, 17%) and yield the di-aldehyde **11** (2.80 g, 14%) and corresponding allylic alcohol (9.10 g, 44%) as a clear oil. To a solution of this allylic alcohol (1.60 g, 9.4 mmol) in DMSO (35 mL) was added IBX (3.76 g, 13.4 mmol) in one portion. The reaction was stirred for 1.5 hours, then was diluted with water (180 mL) and filtered through Celite® to remove the precipitate. The filtrate was extracted with diethyl ether (5 x 100 mL). The combined organic layers were washed with brine (100 mL) and 10% NaOH (2 x 100 mL), dried over $MgSO_4$, filtered and concentrated to yield **11** (1.35 g, 87 %) as a pale yellow oil. The analytical data were identical with the compound obtained from method 1. Characterization of this compound matched the literature data.[1]



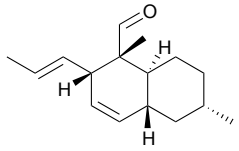
(2*E*,4*E*)-Hexa-2,4-dien-1-yltriphenylphosphonium bromide (**17**): To a stirred solution of (2*E*,4*E*)-hexadien-l-o1 (9.80 g, 100 mmol) in CH_2Cl_2 (20 mL) at –10 ºC was slowly

added a solution of phosphorus tribromide (9.20 g, 34.0 mmol) in CH_2Cl_2 (20 mL) dropwise via an addition funnel. After all the phosphorous tribromide was added, the reaction mixture was stirred for 3 hours before it was diluted with ether (150 mL) and quenched with a saturated $NaHCO_3$ (100 mL) solution. The mixture was separated with diethyl ether with the aid of brine. The aqueous phase was extracted with ether (2 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford crude (2*E*,4*E*)- hexadienylbromide (10.4 g, 65%) as a brown oil. The crude (2*E*,4*E*)- hexadienylbromide was then dissolved in anhydrous toluene (90 mL), followed by the addition of triphenyl phosphine (18.9 g, 72.0 mmol). This reaction was then stirred for 72 hours at room temperature, and the resulting crystalline product was collected by suction filtration, rinsing the solids with a small amount of toluene. After pumping under high vacuum at room temperature for 12 hours, the phosphonium salt **17** were obtained (27.2 g, 99%, 64% from (2*E*,4*E*)-hexadien-l-ol). mp: 159–160 °C. Characterization of this compound matched the literature data.[1]

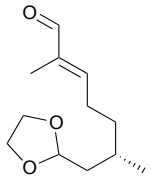


Triene (3): To a suspension of (2*E*,4*E*)-hexa-2,4-dien-1-yltriphenylphosphonium bromide **17** (20.6 g, 48.7 mmol) in THF (240 mL) was added dropwise *n*-BuLi (30.4 mL, 48.7 mmol, 1.6 M in hexane) via addition funnel at –78 ºC. The mixture was stirred for 1 hour at –60 ºC then re-cooled to –78 ºC and transferred via cannula, slowly dropwise to a solution of aldehyde **11** (8.2 g, 48.7 mmol) in THF (240 mL) at –78 ºC over 2 hours. After completion of addition, the reaction mixture was stirred at this temperature for 10 min, quenched with saturated NH_4Cl solution (250 mL), diluted with ethyl ether (350 mL) and allowed to reach room temperature. The layers were separated and the aqueous layer was extracted with ether (2 x 200 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated and purified through neutralized (Et_3N, 5%) silica column chromatography (pure hexanes, then hexanes:EtOAc, 500:1 to 50:1) to yield polyene **3** (6.8 g, 61%) as a pale yellow oil as an inseparable *E/Z* isomeric mixture (*E:Z* = ca. 3:2). To a solution of the (*E/Z*) **3** (113 mg, 0.28 mmol) in CH_2Cl_2 (5.6 mL) at RT was added iodine (3.5 mg, 14 μmol) in CH_2Cl_2 (0.2 mL). The reaction mixture was

irradiated with visible light (sunlamp, visible light) for 10 minutes. (caution: keep the flask a few feet from the light source to avoid the heating-induced IMDA reaction). Then the reaction was quenched with saturated sodium thiosulfate (11 mL). The mixture was extracted with CH_2Cl_2 (3 x 15 mL). All organic layers were washed with brine (15 mL), dried over Na_2SO_4 and concentrated to yield polyene **3** (112 mg, 99%) as a clear oil and inseparable *E/Z* isomeric mixture (*E:Z* = ca. 95:1). Characterization of this compound matched the literature data.[1]

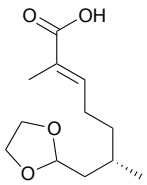


Decalin aldehyde (4): To a mixture of MacMillan's catalyst (20 mol%) (listed in Scheme 1) in MeCN or ethanol (0.86 mL) was added triene (**3**) (10 mg, 43 μmol) in ethanol (0.1 mL) followed by perchloric acid (0.52 μl, 8.61μmol, 0.2 eq, 70% in water) at –20°C. This reaction continued to stir at this temperature for 3 days and then was concentrated and purified via preparative thin layer chromatography (hexanes:EtOAc, 9:1) to yield decalin aldehyde **4** (6.0 mg, 60%) as a clear oil. Characterization of this compound matched the literature data.[1]

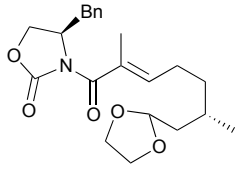


Acetal aldehyde (11_1): To a solution of the dialdehyde **11** (14 g, 83 mmol) in ethylene glycol (93 mL, 20 eq.) was added *p*-toluenesulfonic acid, *p*-TsOH (1.583 g, 8.32 mmol, 0.1 eq.) and stirred for 5 minutes. Then reaction was diluted with water (500 mL) and extracted with CH_2Cl_2 (3 x 500 mL). All organic layers were washed with water (2 x 750 mL), dried over Na_2SO_4 and concentrated to yield **11_1** (17.67 g, 100%). This compound was used directly to the next step without further purification. R_f = 0.65 (silica gel, hexanes:EtOAc, 3:1); $[\alpha]_D^{23}$ = –5.5 (*c* = 0.34, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 6.47 (t, *J* = 7.5 Hz, 1H), 4.88 (t, *J* = 5.2 Hz, 1H), 3.95 (m, 2H), 3.83 (m, 2H), 2.35 (m, 2H), 1.72 (s, 3H), 1.66-1.37 (m, 5H), 0.98 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 195.4, 154.8, 139.3, 103.6, 64.8, 64.8, 40.6, 35.7, 29.1, 26.6, 19.8, 8.9; HRMS (ESI) m/e 235.1301 [M+Na^+] calcd for $C_{12}H_{20}O_3Na^+$: 235.1305.

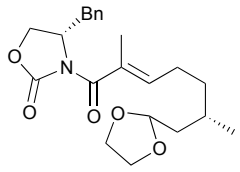


Carboxylic acid (12): To aldehyde **11_1** (17.67 g, 83 mmol) in THF (357 mL) was added at 0°C sulfamic acid (11.31 g, 117 mmol) dissolved in water (170 mL) followed by sodium chlorite (10.54 g, 117 mmol) dissolved in water (170 mL) and stirred for 30 minutes at room temperature. The reaction was acidified to pH 2 with 2N HCl (50 mL) and extracted with ethyl acetate (3 x 500 mL). All organic layers were washed with brine (500 mL), dried over Na_2SO_4 and concentrated. The resultant product was then purified through silica column chromatography (hexanes:EtOAc, 100:1 to 1:1) to yield carboxylic acid **12** (15.20 g, 80%) as a clear oil. R_f = 0.22 (silica gel, hexanes:EtOAc, 3:1); $[\alpha]_D^{23}$ = –28.5 (*c* = 0.32, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (t, *J* = 7.5 Hz, 1H), 4.88 (t, *J* = 4.9 Hz, 1H), 3.95 (m, 2H), 3.82 (m, 2H), 2.19 (m, 2H), 1.81 (s, 3H), 1.66 (m, 2H), 1.50 (m, 2H), 1.32 (m, 1H), 0.95 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 145.3, 127.0, 103.6, 64.8, 64.7, 40.7, 35.8, 29.2, 26.4, 19.8, 12.0; HRMS (ESI) m/e 251.1256 [M+Na^+] calcd for $C_{12}H_{20}O_4Na^+$: 251.1254.

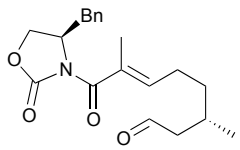


Acetal (12_1): To a suspension of (*R*)-4-benzyl-2-oxazolidinone (12.98 g, 73.2 mmol), 4-dimethylaminopyridine, DMAP (1.057 g, 8.66 mmol), and carboxylic acid **12** (15.20 g, 66.6 mmol) in CH_2Cl_2 (89 mL) at 0°C was added *N,N'*-dicyclohexylcarbodiimide, DCC (17.86 g, 87 mmol). The reaction stirred at this temp for 10 min and then rt overnight. The reaction was filtered through a fritted funnel to remove the urea byproduct and rinsed with 500 mL CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ (500 mL), dried over Na_2SO_4, and concentrated. The crude compound was purified by silica chromatography (hexane:EtOAc, 100:1 to 1:1) to yield **12_1** (19.35 g, 75%) as a clear oil. R_f = 0.42 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{23}$ = –40.5 (*c* = 0.27, $CHCl_3$); ^{1}H NMR

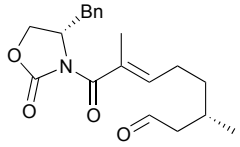
(500 MHz, $CDCl_3$) δ 7.33-7.18 (m, 5H), 6.07 (t, *J* = 7.5 Hz, 1H), 4.90 (t, *J* = 5.2 Hz, 1H), 4.71 (m, 1H) 4.22 (t, *J* = 8.6 Hz, 1H), 4.14 (dd, *J* = 5.2, 8.6 Hz, 1H), 3.96 (m, 2H), 3.84 (m, 2H), 3.33 (dd, *J* = 3.5, 13.8 Hz, 1H), 2.82 (dd, *J* = 9.2, 13.8 Hz, 1H), 2.20 (m, 2H), 1.90 (s, 3H), 1.71-1.17 (m, 5H), 0.98 (d, *J* =6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 153.3, 140.2, 135.3, 130.5, 129.6, 129.0, 127.4, 103.7, 66.4, 64.8, 64.7, 55.6, 40.8, 37.6, 35.8, 29.2, 26.0, 19.8, 13.6; HRMS (ESI) m/e 388.2119 [M+H^+] calcd for $C_{22}H_{30}O_5N^+$: 388.2118.



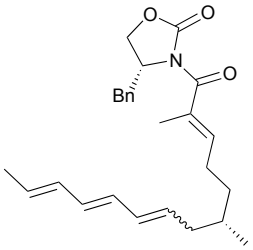
Acetal (12_2): To a suspension of (*S*)-4-benzyl-2-oxazolidinone (0.77 g, 4.3 mmol), 4-dimethylaminopyridine, DMAP (0.06 g, 0.5 mmol), and carboxylic acid **12** (0.9 g, 3.9 mmol) in CH_2Cl_2 (5.3 mL) at 0°C was added *N,N'*-dicyclohexylcarbodiimide, DCC (1.06 g, 5.1 mmol). The reaction stirred at this temp for 10 min and then rt overnight. The reaction was filtered through a fritted funnel to remove the urea byproduct and rinsed with CH_2Cl_2 (20 mL). The organic layer was washed with saturated $NaHCO_3$ (15 mL), dried over Na_2SO_4, and concentrated. The crude compound was purified by silica chromatography (hexane:EtOAc, 100:1 to 1:1) to yield **12_2** (1.15 g, 75%) as a clear oil. R_f = 0.5 (silica gel, hexanes:EtOAc, 3:2); $[\alpha]_D^{22}$ = +6.9 (*c* = 0.32, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.20 (m, 5H), 6.10 (t, *J* = 7.3 Hz, 1H), 4.92 (t, *J* = 5.1 Hz, 1H), 4.72 (m, 1H), 4.26 (t, *J* = 8.5 Hz, 1H), 4.16 (dd, *J* = 5.6, 9.0 Hz, 1H), 3.99 (m, 2H), 3.86 (m, 2H), 3.36 (dd, *J* = 3.4, 13.5 Hz, 1H), 2.83 (dd, *J* = 9.3, 13.5 Hz, 1H), 2.24 (m, 2H), 1.92 (s, 3H), 1.71-1.30 (m, 5H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 153.2, 140.1, 135.2, 130.4, 129.5, 128.9, 127.3, 103.6, 66.4, 64.8, 64.7, 55.5, 40.7, 37.5, 35.7, 29.2, 25.9, 19.8, 13.5; HRMS (ESI) m/e 410.1940 [M+Na^+] calcd for $C_{22}H_{30}NO_5Na^+$: 410.1938.



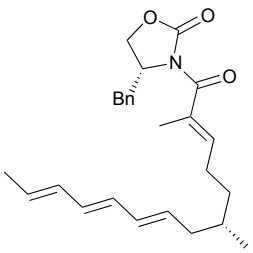
Aldehyde 15: To a solution of the acetal **12_1** (19.35 g, 49.9 mmol) in THF (333 mL) was added 18% aqueous HCl solution (333 mL). After 2 hrs the reaction was carefully quenched with saturated $NaHCO_3$ solution (1 L) and extracted with EtOAc (3 x 800 mL). All organic layers were washed with brine (700 mL), dried over Na_2SO_4 and concentrated to yield aldehyde **15** (17.15 g, 100%) as a clear oil. R_f = 0.42 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{23}$ = –48.0 (*c* = 2.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.30-7.16 (m, 5H), 6.00 (t, *J* = 7.5 Hz, 1H), 4.68 (m, 1H), 4.22 (t, *J* = 8.6 Hz, 1H), 4.12 (dd, *J* = 5.8, 9.2 Hz, 1H), 3.30 (d, *J* = 13.2 Hz, 1H), 2.80 (dd, *J* = 9.2, 13.2 Hz, 1H), 2.38 (dd, *J* = 5.8, 16.1 Hz, 1H), 2.23 (m, 2H), 2.10 (m, 1H), 1.88 (s, 3H), 1.71-1.30 (m, 3H), 0.96 (d, *J* =6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 171.8, 153.2, 138.8, 135.2, 131.1, 129.5, 129.0, 127.4, 66.5, 55.5, 50.9, 37.6, 35.3, 27.7, 25.9, 19.8, 13.6; HRMS (ESI) m/e 344.1859 [M+H$^+$] calcd for $C_{20}H_{26}O_4N^+$: 344.1856.



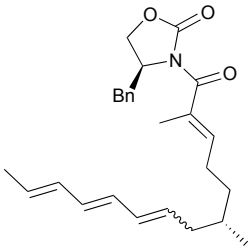
Aldehyde 16: To a solution of the acetal **12_2** (1.15 g, 2.97 mmol) in THF (20 mL) was added 18% aqueous HCl solution (20 mL). After 2 hrs the reaction was carefully quenched with saturated $NaHCO_3$ solution (100 mL) and extracted with EtOAc (3 x 20 mL). All organic layers were washed with brine (70 mL), dried over Na_2SO_4 and concentrated to yield aldehyde **16** (1.02 g, 100%) as a clear oil. R_f = 0.5 (silica gel, hexanes: EtOAc, 3:2); $[\alpha]_D^{24}$ = +2.1 (*c* = 0.37, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 2.2 Hz, 1H), 7.37-7.20 (m, 5H), 6.05 (t, *J* = 7.3 Hz, 1H), 4.72 (m, 1H), 4.26 (t, *J* = 8.5 Hz, 1H), 4.17 (dd, *J* = 5.4, 9.0 Hz, 1H), 3.36 (dd, *J* = 3.4, 13.5 Hz, 1H), 2.84 (dd, *J* = 9.3, 13.5 Hz, 1H), 2.43 (dd, *J* = 5.7, 16.3 Hz, 1H), 2.25 (m, 2H), 2.14 (m, 1H), 1.93 (s, 3H), 1.65-1.37 (m, 3H), 1.01 (d, *J* =6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 171.8, 153.2, 138.9, 135.1, 131.0, 129.5, 128.9, 127.4, 66.4, 55.5, 50.9, 37.5, 35.3, 27.7, 25.8, 19.8, 13.6; HRMS (ESI) m/e 366.1677 [M+Na$^+$] calcd for $C_{20}H_{25}NO_4Na^+$: 366.1676.



Polyene (18): To a stirred solution of phosphonate **17** (0.77 g, 1.8 mmol) in THF (9.7 mL) at -78°C was added *n*-butyl lithium (*n*-BuLi) (1.15 mL, 1.8 mmol, 1.6M) dropwise and this solution turned deep red in color and continued to stir for 1 hr at this temperature. Then aldehyde **15** (0.63 g, 1.8 mmol) in THF (9.6 mL) was added to this solution dropwise. After stirring at -78°C for 5 minutes the reaction was quenched with sat. NH_4Cl solution (10 mL) and warmed to RT. The reaction was extracted with ether (3 x 30 mL). All organic layers were washed with brine (30 mL), dried over Na_2SO_4, and concentrated. The resulting product was purified through neutralized (Et_3N, 5%) silica column chromatography (pure hexanes, then hexanes:EtOAc, 500:1 to 3:1) to yield polyene **18** (0.47 g, 63%) as a clear oil and inseparable *E/Z* isomeric mixture (*E:Z* = ca. 3:2). R_f = 0.63 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{23}$ = –18.2 (*c* = 0.52, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 7.37- 7.20 (m, 5H), 6.51-6.04 (m, 5H), 5.75-5.41 (m, 2H), 4.72 (m, 1H), 4.26 (t, *J* = 8.5 Hz, 1H), 4.16 (dd, *J* = 5.6, 8.9 Hz, 1H), 3.35 (dd, *J* = 3.5, 13.5 Hz, 1H), 2.84 (dd, *J* = 9.3, 13.5 Hz, 1H), 2.27-2.10 (m, 4H), 1.92 (s, 3H), 1.78 (m, 3H), 1.60-1.41 (m, 3H), 0.92 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 171.9, 153.2, 152.1, 140.4, 140.4, 140.4, 140.3, 135.2, 133.2, 132.9, 132.5, 131.9, 131.7, 130.9, 130.5, 130.4, 130.4, 130.1, 129.7, 129.7, 129.5, 129.0, 128.9, 127.3, 125.9, 125.8, 105.0, 66.4, 55.5, 40.2, 40.2, 37.5, 35.1, 35.0, 34.9, 33.2, 33.0, 26.2, 26.1, 19.4, 19.4, 18.4, 18.4, 13.5, 13.5; HRMS (ESI) m/e 408.2536 [M+H$^+$] calcd for $C_{26}H_{34}O_3N^+$: 408.2533.

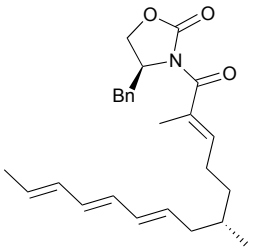


Polyene (18) isomerized: To a solution of the (*E/Z*) **18** (113 mg, 0.28 mmol) in CH_2Cl_2 (5.6 mL) at RT was added iodine (3.5 mg, 14 μmol) in CH_2Cl_2 (0.2 mL). The reaction mixture was irradiated with visible light (sunlamp, visible light) for 10 minutes. (caution: keep the flask a few feet from the light source to avoid the heating-induced IMDA reaction). Then the reaction was quenched with saturated sodium thiosulfate (11 mL). The mixture was extracted with CH_2Cl_2 (3 x 15 mL). All organic layers were washed with brine (15 mL), dried over Na_2SO_4 and concentrated to yield polyene **18** (112 mg, 99%) as a clear oil and inseparable *E/Z* isomeric mixture (*E:Z* = ca. 95:1). R_f = 0.63 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{24}$ = -21.4 (*c* = 3.04, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37- 7.20 (m, 5H), 6.51-6.04 (m, 5H), 5.75-5.41 (m, 2H), 4.72 (m, 1H), 4.26 (t, *J* = 8.5 Hz, 1H), 4.16 (dd, *J* = 5.6, 8.9 Hz, 1H), 3.35 (dd, *J* = 3.5, 13.5 Hz, 1H), 2.84 (dd, *J* = 9.3, 13.5 Hz, 1H), 2.27-2.10 (m, 4H), 1.92 (s, 3H), 1.78 (d, *J* = 5.9, 3H), 1.60-1.41 (m, 3H), 0.92 (d, *J* =6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 153.2, 152.1, 140.4, 135.3, 132.5, 132.0, 131.9, 131.0, 130.6, 130.5, 129.6, 129.0, 127.4, 66.4, 55.6, 40.3, 37.6, 35.1, 33.1, 26.2, 19.5, 18.4, 13.6; HRMS (ESI) m/e 344.1859 [M+H$^+$] calcd for $C_{26}H_{33}O_3N^+$: 344.1856.

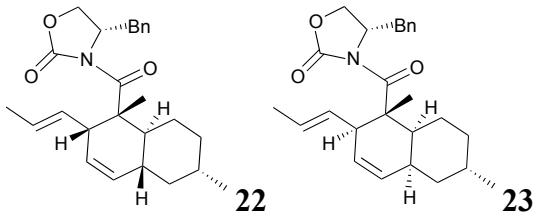


Polyene (19): To a stirred solution of phosphonate **17** (1.00 g, 2.36 mmol) in THF (12.4 mL) at –78°C was added *n*-butyl lithium (*n*-BuLi) (1.47 mL, 2.36 mmol, 1.6M in hexanes) dropwise and this solution turned deep red in color and continued to stir for 1 hr at this temperature. Then aldehyde **16** (0.81 g, 2.36 mmol) in THF (12.4 mL) was added to this solution dropwise. After stirring at -78°C for 5 minutes the reaction was quenched with saturated NH_4Cl solution (40 mL) and warmed to RT. The reaction was extracted with ether (3 x 40 mL). All organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated. The resulting product was purified through neutralized (Et_3N, 5%) silica column chromatography (pure hexanes, then hexanes:EtOAc, 500:1 to 3:1) to yield polyene **19** (0.61 g, 63%) as a clear oil and inseparable *E/Z* isomeric mixture (*E:Z* = ca.

3:2). R_f = 0.65 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{23}$ = +38.1 (*c* = 2.13, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 7.31- 7.18 (m, 5H), 6.51-5.19 (m, 7H), 4.69 (m, 1H), 4.23 (t, *J* = 8.3 Hz, 1H), 4.14 (m, 1H), 3.33 (d, *J* = 13.7 Hz, 1H), 2.82 (dd, *J* = 9.2, 13.2 Hz, 1H), 2.25-1.94 (m, 4H), 1.90 (s, 3H), 1.75 (m, 3H), 1.60-1.45 (m, 3H), 0.89 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 171.9, 153.2, 152.1, 140.4, 140.4, 140.4, 140.3, 135.2, 133.2, 132.9, 132.5, 131.9, 131.7, 130.9, 130.5, 130.4, 130.4, 130.1, 129.7, 129.7, 129.5, 129.0, 128.9, 127.3, 125.9, 125.8, 105.0, 66.4, 55.5, 40.2, 40.2, 37.5, 35.1, 35.0, 34.9, 33.2, 33.0, 26.2, 26.1, 19.4, 19.4, 18.4, 18.4, 13.5, 13.5; HRMS (ESI) m/e 408.2535 [M+H^+] calcd for $C_{26}H_{34}O_3N^+$: 408.2533.



Polyene (19) isomerized: To a solution of the (*E/Z*) **19** (68 mg, 0.17 mmol) in CH_2Cl_2 (3.3 mL) at RT was added iodine (2.1 mg, 8.3 μmol) in CH_2Cl_2 (0.1 mL). The reaction mixture was irradiated with visible light (sunlamp, visible light) for 10 minutes. (caution: keep the flask a few feet from the light source to avoid the heating-induced IMDA reaction). Then the reaction was quenched with saturated sodium thiosulfate (7 mL). The mixture was extracted with CH_2Cl_2 (3 x 7 mL). All organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated to yield polyene **19** (67 mg, 99%) as a clear oil and inseparable *E/Z* isomeric mixture (*E:Z* = ca. 95:1). R_f = 0.63 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{25}$ = +44.9 (*c* = 2.49, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31- 7.18 (m, 5H), 6.51-5.19 (m, 7H), 4.69 (m, 1H), 4.23 (t, *J* = 8.3 Hz, 1H), 4.14 (m, 1H), 3.33 (d, *J* = 13.7 Hz, 1H), 2.82 (dd, *J* = 9.2, 13.2 Hz, 1H), 2.25-1.94 (m, 4H), 1.90 (s, 3H), 1.75 (d, *J* = 6.9, 3H), 1.60-1.45 (m, 3H), 0.89 (d, *J* =6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 153.2, 140.3, 135.2, 132.5, 131.9, 131.7, 130.9, 130.5, 130.4, 129.5, 129.0, 128.9, 127.3, 66.4, 55.5, 40.2, 37.5, 35.0, 33.0, 26.1, 19.4, 18.4, 13.5; HRMS (ESI) m/e 408.2535 [M+H^+] calcd for $C_{26}H_{34}O_3N^+$: 408.2533.

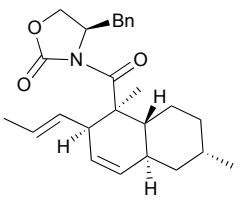


22 **23**

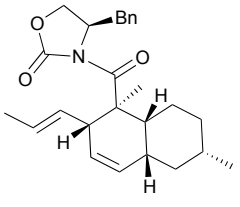
Decalin (22/23): Then to a stirred solution of polyene **19** (0.18 g, 0.44 mmol) in CH_2Cl_2 (6.3 mL) was added iodine (5.6 mg, 22 μmol, 0.05 eq.). The reaction mixture was irradiated with visible light (sunlamp, visible light) for 10 minutes. (caution: keep the flask a few feet from the light source to avoid the heating-induced IMDA reaction). The mixture was cooled to -78°C at which time Me_2AlCl (0.49 mL, 0.49 mmol, 1M in hexanes) was added dropwise. The reaction mixture was then warmed to -20°C and continued to stir at this temperature for 2 days. The reaction mixture was quenched with a 1:1 sat. $NaHCO_3$/sodium thiosulfate solution (20 mL) and the mixture was ran through a Celite® plug followed by rinse with CH_2Cl_2 (50 mL). The reaction was extracted with CH_2Cl_2 (3 x 20 mL). All organic layers were dried over Na_2SO_4 and concentrated. The crude compound was purified by silica column chromatography (hexanes:EtOAc, 200:1 to 5:1) to yield decalin **23** (74 mg, 41%) and decalin **22** (74 mg, 41%) as a white foam. Characterization of decalin **22:** R_f = 0.47 (silica gel, hexanes: EtOAc, 9:1); $[\alpha]_D^{24}$ = +168.1 (*c* = 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 5.51 (m, 1H), 5.40 (m, 2H), 5.26 (m, 1H), 4.47 (m, 1H), 4.08 (m, 2H), 3.86 (dd, *J* = 3.4, 9.7 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.46 (t, *J* = 12.3 Hz, 1H), 1.91- 0.99 (m, 9H), 1.58 (d, *J* = 6.3 Hz, 3H), 1.36 (s, 3H), 0.93 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 152.3, 136.5, 132.2, 129.9, 129.6, 129.0, 127.2, 127.0, 126.7, 65.9, 59.2, 50.6, 44.5, 42.5, 42.4, 38.0, 37.2, 35.8, 33.5, 28.1, 22.6, 17.9, 14.0; HRMS (ESI) m/e 408.2536 [M+H$^+$] calcd for $C_{26}H_{34}NO_3^+$: 408.2533.

Characterization of decalin **23:** R_f = 0.29 (silica gel, hexanes: EtOAc, 9:1); $[\alpha]_D^{24}$ = –26.8 (*c* = 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 5.66 (m, 1H), 5.50 (m, 2H), 5.42 (d, *J* = 10.3 Hz, 1H), 4.75 (m, 1H), 4.15 (t, *J* = 8.6 Hz, 1H), 4.10 (dd, *J* = 3.5, 9.2 Hz, 1H), 3.50 (br s, 1H), 3.20 (dd, *J* = 3.5, 13.2 Hz, 1H), 2.68 (dd, *J* = 9.8, 13.2 Hz, 1H), 2.59 (m, 1H), 2.24 (br s, 1H), 1.69 (d, *J* = 5.2 Hz, 3H), 1.67-0.86 (m, 7H), 1.42 (s, 3H), 0.82 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 152.7, 135.6, 131.3, 130.6, 129.5, 129.5, 129.0, 128.1, 127.3, 66.2, 58.0, 51.4, 44.9, 40.6, 38.2, 37.9,

35.5, 34.9, 28.4, 22.8, 22.6, 18.3, 18.2; HRMS (ESI) m/e 408.2535 [M+H$^+$] calcd for $C_{26}H_{34}NO_3^+$: 408.2533.



20

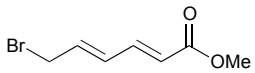


21

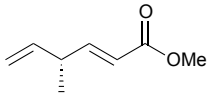
Decalin (20/21): Then to a stirred solution of **18** (0.37 g, 0.91 mmol) in CH_2Cl_2 (13 mL) was added iodine (12.0 mg, 45 μmol, 0.05 eq.). The reaction mixture was irradiated with visible light (sunlamp, visible light) for 10 minutes. (caution: keep the flask a few feet from the light source to avoid the heating-induced IMDA reaction). The mixture was cooled to -78°C at which time Me_2AlCl (1.00 mL, 1.0 mmol, 1M in hexanes) was added dropwise. The reaction mixture was then warmed to -20°C and continued to stir at this temperature for 2 days. The reaction mixture was quenched with a 1:1 sat. $NaHCO_3$/sodium thiosulfate solution (40 mL) and the mixture was ran through a Celite® plug followed by a rinse with CH_2Cl_2 (80 mL). The reaction was extracted with CH_2Cl_2 (3 x 30 mL). All organic layers were dried over Na_2SO_4 and concentrated. The crude compound was purified by silica column chromatography (hexanes:EtOAc, 200:1 to 5:1) to yield decalin **20** (0.15 g, 41%) and decalin **21** (0.15 g, 41%) as a white foam. Characterization for **20:** R_f = 0.47 (silica gel, hexanes:EtOAc, 9:1); $[\alpha]_D^{25}$ = –19.2 (*c* = 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35- 7.24 (m, 5H), 5.51 (m, 1H), 5.40 (m, 2H), 5.25 (m 1H), 4.47 (m, 1H), 4.08 (m, 2H), 3.86 (m, 1H), 3.37 (d, *J* = 12.6 Hz, 1H), 2.44 (t, *J* = 12.0 Hz, 1H), 2.08 (m, 2H), 1.80-1.19 (m, 7H), 1.58 (d, *J* = 6.3 Hz, 3H), 1.39 (s, 3H), 1.03 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 152.3, 136.5, 132.2, 130.2, 129.6, 129.0, 127.3, 127.2, 126.7, 65.8, 59.2, 50.6, 44.4, 43.4, 39.7, 37.2, 32.7, 31.9, 27.9, 22.7, 18.8, 17.9, 14.1; HRMS (ESI) m/e 408.2534 [M+H$^+$] calcd for $C_{26}H_{34}NO_3^+$: 408.2533.

Characterization for **21:** R_f = 0.10 (silica gel, hexanes:EtOAc, 9:1); $[\alpha]_D^{24}$ = +10.5 (*c* = 3.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31- 7.12 (m, 5H), 6.10 (m, 2H), 5.75 (m, 1H), 5.42 (dd, *J* = 8.0, 14.3 Hz, 1H), 4.45 (m, 1H), 4.32 (t, *J* = 8.3 Hz, 1H), 4.01 (t, *J* = 8.3 Hz, 1H), 3.51 (br s, 1H), 2.98 (dd, *J* = 6.3, 13.8 Hz, 1H), 2.73 (dd, *J* = 7.5, 13.8 Hz,

1H), 1.95-0.40 (m, 9H), 1.77 (d, J = 6.9 Hz, 3H), 1.58 (s, 3H), 0.88 (d, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 155.2, 136.2, 134.3, 130.9, 130.8, 129.1, 128.7, 128.0, 127.0, 106.9, 81.4, 67.8, 55.7, 43.6, 42.6, 40.0, 36.7, 35.2, 32.6, 29.5, 22.6, 18.2, 14.1; HRMS (ESI) m/e 408.2535 [M+H$^+$] calcd for $C_{26}H_{34}NO_3^+$: 408.2533.

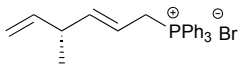


6-bromo methyl sorbate (25): A mixture of methyl sorbate (20.2 g, 160 mmol) and *N*-bromosuccinimide (29.6 g, 167 mmol) in dry chlorobenzene (136 mL) was heated to 100 °C over 1 hour. Benzoylperoxide (1.75 g, 7.21 mmol) was then cautiously added portionwise. After the addition was complete, the reaction mixture was heated under reflux for 3 hr. The reaction was cooled and the chlorobenzene was concentrated. The residual paste was dissolved with Et_2O (300 mL) and was washed with sodium hydroxide (75 mL of a 5% aqueous solution) until the washings were colorless. The organic layer was then dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by silica column chromatography (0 to 10% ethyl acetate in hexane) to afford bromide **25** (29.5 g 90 %) as light yellow oil. This material matched what was previously reported in the literature.[2]



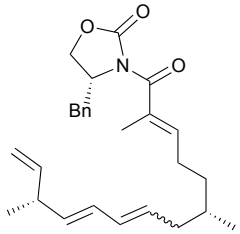
Skipped Diene (27): Optimization of literature protocol: Copper (I) bromide dimethylsulfide complex (25 mg, 0.12 mmol, 2.5 mol%) and *S,S*-TANIAPHOS (100 mg, 0.15 mmol, 3 mol%, purchased from Strem Chemicals Inc.) were dissolved in CH_2Cl_2 (49 mL) at room temperature and stirred for 15 minutes. Then the reaction was cooled to -78°C and methyl magnesium bromide, MeMgBr (2 mL, 5.85 mmol, 3M in diethyl ether) was added dropwise. Then the bromo methyl sorbate (**25**) (1 g, 4.88 mmol) was dissolved in CH_2Cl_2 (20 mL) and was added to reaction dropwise at a rate of 1mL/hr. The reaction was stirred at –60 °C for additional 48 hours and then was quenched with saturated NH_4Cl solution (100 mL). This mixture was then warmed up to room temperature, extracted with CH_2Cl_2 (100 mL x 2), dried over $MgSO_4$ and carefully concentrated at reduced pressure (150 torr). The residue was purified via silica column (pentane:ether, 100:1 to 20:1) to afford the skipped diene **27** as colorless oil (0.615 g, 91%, ee > 97%).

The skipped diene ester matched characterization data provided in the literature with our optimized preparation.[3]

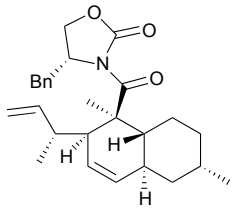


Skipped Diene Wittig Salt (28): The skipped diene ester **27** (0.615 g, 4.39 mmol) was dissolved in CH_2Cl_2 (25 mL) and cooled to 0 °C. A solution of DIBAL-H (17.6 mL, 17.6 mmol, 1M in hexanes) was added in dropwise. After 5 min the reaction was diluted with ether (50 mL), and sequentially added water (0.8 mL), aqueous 15% NaOH solution (0.8 mL), and water (0.5 mL). The reaction was warmed to RT and stirred at this temperature for 30 minutes. Some $MgSO_4$ was added and continued to stir for another 15 min. The reaction was filtered and carefully concentrated at reduced pressure (150 torr). The afforded allylic alcohol was essentially pure to be used directly in next step. The allylic alcohol (0.492 g, 4.39 mmol) was dissolved in CH_2Cl_2 (25 mL) and cooled to 0°C. PPh_3 (1.265 g, 4.82 mmol, 1.1 eq.) and CBr_4 (1.60 g, 4.82 mmol, 1.1 eq.) were added subsequently. After stirring for 5 min the reaction was diluted with pentane (100 mL) and filtered through a short Celite® pad, which was washed with pentane (200 mL). The filtrate was carefully concentrated at reduced pressure (350 torr). The resultant residue was dissolved in pentane (150 mL) and the mixture was sonicated for 2 min, which was filtered through a short Celite® pad and washed with pentane (200 mL). The filtrate was carefully concentrated at reduced pressure (350 torr). The resultant allylic bromide was essentially pure and was dissolved in acetonitrile (30 mL) and triphenylphosphine (1.5 g, 5.70 mmol, 1.3 eq.) was added. The clear mixture stirred for 16 hours at RT. The reaction was extracted with hexanes (6 x 50 mL) to remove excess PPh_3 and the acetonitrile layer was dried over $MgSO_4$ and concentrated. The compound was dissolved in benzene (15 mL) and concentrated to yield Wittig salt **28** (1.40 g, 73% over 3 steps) as a white foam. Note: Precursor compounds were carried through with residual solvent to avoid removing compound during concentration and yields are based on total isolated yield of Wittig salt **28** at the end. $[\alpha]_D^{23}$ = +4.7 (*c* = 0.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.59 (m, 15H), 5.79 (m, 1H), 5.54 (m, 1H), 5.27 (m, 1H), 4.86-4.55 (m, 4H), 2.77 (m, 1H), 0.92 (d, *J* = 8.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8 (d, *J* = 13.1 Hz), 141.0 (d, *J* = 3.3 Hz), 134.9 (d, *J* = 5.5 Hz), 134.1, 134.0, 132.9 (d, *J* = 2.7 Hz), 132.5, 132.4, 130.3,

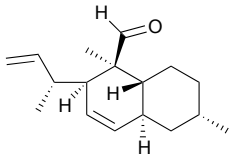
130.2, 129.1, 128.9, 128.8, 118.6, 117.9, 113.7, 113.1 (d, J = 9.8 Hz), 40.7 (d, J = 2.4 Hz), 28.0 (d, J= 48.2 Hz), 19.2; HRMS (ESI) m/e 357.1769 [M–Br^+] calcd for $C_{25}H_{26}P^+$: 357.1767.



Polyene (29): To a stirred solution of phosphonate **28** (1.40 g, 2.72 mmol) in THF (13.6 mL) at -78°C was added *n*-butyl lithium (*n*-BuLi) (1.8 mL, 2.72 mmol, 1.6M in hexanes) dropwise and this solution turned deep red in color and continued to stir for 1 hr at this temperature. Then aldehyde **15** (0.93 g, 2.72 mmol) in THF (13.6 mL) was added to this solution dropwise. After stirring at -78°C for 5 minutes the reaction was quenched with sat. NH_4Cl solution (40 mL) and warmed to RT. The reaction was extracted with ether (3 x 100 mL). All organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated. The resulting product was purified through neutralized (Et_3N, 5%) silica column chromatography (pure hexanes, then hexanes:EtOAc, 500:1 to 3:1) to yield polyene **29** (0.68 g, 59%) as a clear oil and inseparable *E/Z* isomeric mixture (*E:Z* = ca. 3:2). R_f = 0.50 (silica gel, hexanes:EtOAc, 5:1); $[\alpha]_D^{23}$ = –19.5, (c = 2.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 7.35-7.25 (m, 5H), 7.18 (d, J = 6.9 Hz, 2H), 6.10-5.97 (m, 2H), 5.77 (m, 1H), 5.56 (m, 1H), 5.38-4.92 (m, 2H), 4.70 (m, 1H), 4.23 (t, J = 8.6 Hz, 1H), 4.14 (dd, J = 5.8, 9.2 Hz, 1H), 3.33 (dd, J = 3.5, 13.8 Hz, 1H), 2.88 (m, 1H), 2.81 (dd, J = 9.7, 13.8 Hz, 1H), 2.23-1.90 (m, 4H), 1.90 (s, 3H), 1.55-1.24 (m, 3H), 1.10 (d, J =6.9 Hz, 3H), 0.90 (d, J =6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E:Z* = ca. 3:2). δ 171.9, 153.1, 152.1, 142.6, 142.5, 140.3, 140.2, 138.0, 135.7, 135.2, 131.7, 131.2, 130.4, 129.5, 129.4, 129.1, 128.9, 128.9, 127.3, 124.4, 113.1, 112.9, 105.9, 66.3, 55.5, 40.5, 40.3, 40.0, 37.6, 35.0, 35.0, 34.7, 33.2, 33.0, 26.1, 26.1, 19.8, 19.7, 19.4, 19.4, 13.5, 13.5; HRMS (ESI) m/e 444.2510 [M+Na^+] calcd for $C_{27}H_{35}NO_3Na^+$: 444.2509.

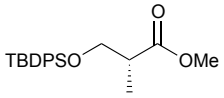


Decalin (30): To a stirred solution of **29** (0.68 g, 1.61 mmol) in CH_2Cl_2 (161 mL) at -78°C was added Me_2AlCl (8.1 mL, 8.06 mmol, 1M in hexanes, 5 eq.) dropwise. The reaction mixture was then warmed to 0°C and continued to stir at this temperature for 3 hrs. The reaction was quenched with saturated $NaHCO_3$ solution (100 mL) and the mixture was ran through a Celite® plug followed by a rinse with CH_2Cl_2 (100 mL). The reaction was extracted with CH_2Cl_2 (3 x 50 mL). All organic layers were dried over Na_2SO_4 and concentrated. The crude residue was purified by silica column chromatography (hexanes: EtOAc, 200:1 to 3:1) to yield decalin **30** (171 mg, 42% from the *E* isomer) as a white foam. R_f = 0.50 (silica gel, hexanes:EtOAc, 4:1); $[\alpha]_D^{23}$ = –75.5, (c = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 5H), 5.92 (m, 1H), 5.44 (m, 2H) 4.97 (m, 2H), 4.48 (m, 1H), 4.14 (m, 2H), 3.57 (d, *J* = 13.2 Hz, 1H), 3.28 (br s, 1H), 2.71 (dd, *J* = 10.9, 13.2 Hz, 1H), 2.22 (s, 1H), 2.08-1.90 (m, 3H), 1.82-1.31 (m, 6H), 1.34 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 152.6, 144.1, 136.1, 132.0, 129.6, 129.0, 127.3, 123.6, 113.3, 66.3, 59.5, 52.0, 45.8, 44.9, 39.9, 39.3, 37.2, 32.9, 31.8, 27.8, 23.4, 18.8, 16.4, 13.8; HRMS (ESI) m/e 444.2510 [M+Na^+] calcd for $C_{27}H_{35}NO_3Na^+$: 444.2509.

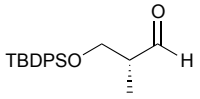


Decalin aldehyde (31): To a stirred solution of **30** (170 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) at 0°C was added diisobutylaluminum hydride (DIBAL-H) (2.02 mL, 2.02 mmol, 1M in hexanes) dropwise. This solution stirred at room temperature for 3 hours before being cooled down to 0°C. The reaction was diluted with ether (15 mL) and then water (0.1 mL), aqueous 15% NaOH (0.1 mL), and water (0.2 mL) were added subsequently dropwise. The solution was warmed to room temperature and stirred for 30 minutes. Then magnesium sulfate was added and stirred for an additional 15 minutes. The solution was filtered, concentrated and ran through a short silica plug (hexanes:EtOAc, 4:1) to

yield the crude alcohol. The resultant crude alcohol was dissolved in CH_2Cl_2 (5 mL) and sodium bicarbonate (203 mg, 2.42 mmol) and Dess-Martin periodinane (341 mg, 0.81 mmol) were subsequently added at room temperature. After stirring for 30 minutes the reaction was diluted with a 1:1 mixture of water and saturated sodium thiosulfate solution (10 mL) and stirred at rt for 30 minutes. Then the solution was extracted with CH_2Cl_2 (3 x 20 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by silica column chromatography (pure hexanes, then hexanes:EtOAc, 100:1 to 5:1) to yield aldehyde **31** (77 mg, 78% over 2 steps) as a clear oil. R_f = 0.55 (silica gel, hexanes:EtOAc, 4:1); $[\alpha]_D^{24}$ = –46.6 (*c* = 0.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 5.79 (m, 1H), 5.50 (m, 2H) 4.97 (m, 2H), 2.43 (m, 1H), 2.07 (m, 2H), 1.70-1.16 (m, 8H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.03 (s, 3H), 0.99 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 143.9, 133.0, 124.5, 114.0, 50.8, 50.2, 41.3, 38.9, 38.5, 32.2, 31.0, 27.7, 21.9, 18.3, 17.2, 15.8; HRMS (ESI) m/e 247.2054 [M+H$^+$] calcd for $C_{17}H_{27}O^+$: 247.2056.

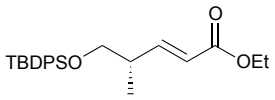


TBDPS Roche ester (32_1): To methyl (*R*)-(−)-3-hydroxy-2-methylpropionate (10.00 g, 85 mmol) in DMF (106 mL) at 0°C was added imidazole (11.53 g, 169 mmol) followed *tert*-butyldiphenylchlorosilane (23.1 mL, 89 mmol) dropwise. After stirring at RT for 2 hrs the reaction was diluted water (75 mL) and hexanes (200 mL). The aqueous layer was extracted with hexanes (3 × 75 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. The crude compound was purified by silica column chromatography (hexanes:Et_2O, 200:1 to 5:1) to yield **32_1** (30.2 g, 100%) as a clear oil. R_f = 0.50 (silica gel, hexanes:EtOAc, 9:1); $[\alpha]_D^{23}$ = –9.8 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.37 (m, 10H), 3.83 (dd, *J* = 7.0, 9.8 Hz, 1H), 3.73 (dd, *J* = 5.8, 9.8 Hz, 1H), 3.70 (s, 3H), 2.73 (m, 1H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 135.6, 133.4, 129.7, 127.7, 65.9, 51.6, 42.4, 26.7, 19.2, 13.5; HRMS (ESI) m/e 379.1705 [M$^+$Na$^+$] calcd for $C_{21}H_{28}O_3SiNa^+$: 379.1700.[4]

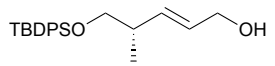


Aldehyde (33): To methyl ester **32_1** (30.2 g, 85 mmol) dissolved in hexanes (607 mL) at -78°C was added DIBAL-H (93 mL, 93 mmol, 1M in hexanes) via a syringe pump

over 3 hours. This reaction continued to stir at -78°C for 2 hrs until the reaction was diluted with ether (300 mL) and water (3.7 mL), aqueous 15% NaOH (3.7 mL), and water (4.8 mL) were added slowly. The mixture warmed to rt for 30 minutes and then $MgSO_4$ was added and stirred for an additional 15 minutes. The solution was filtered and concentrated to yield aldehyde **33** (24.89 g, 90%). This compound was used as is to the next step. R_f = 0.50 (silica gel, hexanes:EtOAc, 9:1); $[\alpha]_D^{23}$ = –11.1 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (d, *J* = 1.8 Hz, 1H), 7.64-7.36 (m, 10H), 3.90 (dd, *J* = 4.0, 9.8 Hz, 1H), 3.84 (dd, *J* = 6.9, 10.3 Hz, 1H), 2.56 (m, 1H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.6, 135.7, 133.2, 129.9, 127.9, 64.2, 48.9, 26.8, 19.3, 10.4; HRMS (ESI) m/e 349.1602 [M+Na^+] calcd for $C_{20}H_{26}O_2SiNa^+$: 349.1600.[4]

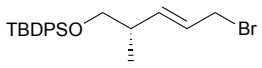


Ethyl ester (33_1): To a solution of aldehyde **33** (24.89 g, 76 mmol) in CH_2Cl_2 (305 mL) was added (carbethoxymethylene)triphenylphosphorane (27.9 g, 80 mmol) portionwise at RT. The reaction stirred overnight and upon completion the reaction was concentrated and then taken up in hexanes (500 mL) and sonicated for 2 minutes before filtering the solution through a Celite® plug. The Celite® plug was rinsed with hexanes (200 mL) and concentrated. This procedure was repeated 1-2 more times until the triphenylphosphine oxide was removed to yield ethyl ester **33_1** (26.9 g, 89%) as a clear oil. R_f = 0.50 (silica gel, hexanes:EtOAc, 9:1); $[\alpha]_D^{23}$ = –10.1 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.36 (m, 10H), 6.97 (dd, *J* = 7.2, 15.8 Hz, 1H), 5.84 (dd, *J* = 1.2, 15.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.58 (m, 2H), 2.56, (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$); δ 166.7, 151.4, 135.6, 133.5, 129.7, 127.7, 121.0, 67.5, 60.2, 39.1, 26.8, 19.3, 15.6, 14.3; HRMS (ESI) m/e 419.2010 [M+Na^+] calcd for $C_{24}H_{32}O_3SiNa^+$: 419.2013.[4]

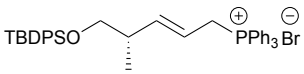


Allylic alcohol (34): To a solution of ethyl ester **33_1** (26.9 g, 67.8 mmol) in CH_2Cl_2 (136 mL) at 0°C was added DIBAL-H (203 mL, 203 mmol, 1M in hexanes) dropwise via an addition funnel. About 5 minutes later the reaction was diluted with ether (400 mL)

and water (8.1 mL), aqueous 15% NaOH (8.1 mL), and water (10 mL) were added slowly. The mixture warmed to rt for 30 minutes and then $MgSO_4$ was added and stirred for an additional 15 minutes. The solution was filtered and concentrated to yield alcohol **34** (21.88 g, 91%). This compound was used as is to the next step. R_f = 0.39 (silica gel, hexanes:EtOAc, 4:1); $[\alpha]_D^{23}$ = –9.2 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.34 (m, 10H), 5.62 (m, 2H), 4.06 (t, *J* = 5.2 Hz, 2H), 3.55 (dd, *J* = 6.3, 10.3 Hz, 1H), 3.50 (dd, *J* = 6.3, 9.7 Hz, 1H), 2.40, (m, 1H), 1.05 (s, 9H), 1.03 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7, 133.9, 132.3, 129.5, 128.7, 127.6, 68.5, 63.9, 39.0 26.7, 19.3, 16.4; HRMS (ESI) m/e 377.1899 [M+Na^+] calcd for $C_{22}H_{30}O_2SiNa^+$: 377.1907.[4]

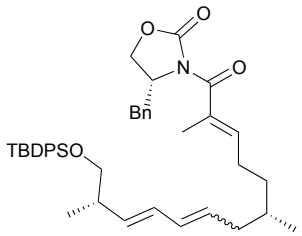


Bromide (34_1): To a solution of alcohol **34** (21.88 g, 61.7 mmol) in CH_2Cl_2 (617 mL) at 0°C was added PPh_3 (17.80 g, 67.9 mmol) and CBr_4 (22.51 g, 67.9 mmol) portionwise. After 10 minutes the reaction was diluted with hexanes (500 mL) and filtered through a Celite® plug, which was rinsed with additional hexanes (200 mL) and concentrated. The crude extract dissolved in hexanes (400 mL) and sonicated for 2 minutes before being filtered through a Celite® plug which was rinsed with additional hexanes (100 mL) and concentrated. This procedure was repeated 1-2 more times until the triphenylphosphine oxide was removed to yield bromide **34_1** (22.67 g, 88%) as a light yellow oil. R_f = 0.62 (silica gel, hexanes: EtOAc, 9:1); $[\alpha]_D^{23}$ = –8.7 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.36 (m, 10H), 5.72 (m, 2H), 3.95 (dd, *J* = 1.6, 3.7 Hz, 2H), 3.53 (dd, *J* = 1.2, 6.5 Hz, 2H), 2.43 (m, 1H), 1.06 (s, 9H), 1.03 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 135.6, 133.7, 129.6, 127.6, 126.1 68.2, 38.9, 33.6, 26.9, 19.3, 16.1; HRMS (ESI) m/e 439.1070 [M+Na^+] calcd for $C_{22}H_{29}OSiBrNa^+$: 439.1069.

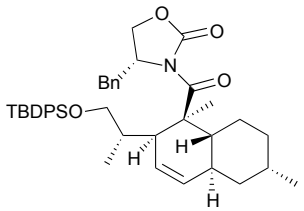


Wittig salt (35): To a solution of bromide **34_1** (22.67 g, 54.3 mmol) in MeCN (272 mL) was added PPh_3 (15.67 g, 59.7 mmol) and stirred for 18 hours at rt. Then the reaction was extracted with hexanes (6 x 300 mL) and the MeCN layer was dried over Na_2SO_4 and concentrated. The compound was dissolved in benzene (50 mL) and concentrated to yield Wittig salt **35** (35.1 g, 95%) as a white foam. $[\alpha]_D^{23}$ = –4.3 (*c* = 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.60 (m, 25H), 5.71 (m, 1H), 5.34 (m, 1H), 4.74 (m, 2H), 3.36

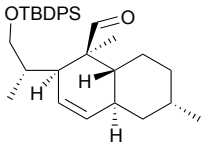
(dd, J = 5.8, 9.9 Hz, 1H), 3.26 (dd, J = 7.2, 10.0 Hz, 1H), 2.29 (m, 1H), 0.98 (s, 9H), 0.89 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.5, 135.5, 134.9, 134.9, 134.0, 134.0, 130.3, 130.2, 129.7, 128.3, 127.7, 127.7, 118.6, 117.9, 67.8 (d, J = 4.4 Hz), 39.8 (d, J = 2.5 Hz), 28.1 (d, J = 48.2 Hz), 26.8, 19.2, 16.4; HRMS (ESI) m/e 599.2896 [M–Br$^+$] calcd for $C_{40}H_{44}O_PSi^+$: 599.2899.



Polyene 36: To a stirred solution of phosphonate **35** (11.6 g, 17.1 mmol) in THF (90 mL) at -78°C was added *n*-butyl lithium (*n*-BuLi) (6.83 mL, 17.1 mmol, 2.5M in hexanes) dropwise and this solution turned deep red in color and continued to stir for 1 hr at this temperature. Then aldehyde **15** (5.86 g, 17.1 mmol) in THF (90 mL) was added to this solution dropwise. After stirring at -78°C for 5 minutes the reaction was quenched with sat. NH_4Cl solution (160 mL) and warmed to rt. The reaction was extracted with ether (3 x 300 mL). All organic layers were washed with brine (200 mL), dried over Na_2SO_4, and concentrated. The resulting product was purified through neutralized (Et_3N, 5%) silica column chromatography (pure hexanes, then hexanes:EtOAc, 500:1 to 5:1) to yield polyene **36** (6.91 g, 61%) as a clear oil and inseparable isomeric mixture (*E:Z* = ca. 3:2). R_f = 0.63 (silica gel, hexanes:EtOAc, 7:3); $[\alpha]_D^{23}$ = -10.0, (c = 0.75, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 7.65-7.18 (m, 15H), 6.30-5.97 (m, 3H), 5.62-5.46 (m, 2H), 4.70 (m, 1H), 4.22 (m, 1H), 4.13 (m, 1H), 3.56-3.44 (m, 2H), 3.33 (m, 1H), 2.80 (m, 1H), 2.53 (br s, 1H), 2.44-2.00 (m, 5H), 1.90 (s, 3H), 1.72-1.30 (m, 2H), 1.05 (d, J =7.5 Hz, 3H), 1.04 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) (*E:Z* = ca. 3:2) δ 171.9, 153.2, 140.4, 135.6, 135.2, 134.8, 134.6, 134.0, 133.9, 131.9, 131.0, 130.4, 130.0, 129.7, 129.5, 129.5, 128.9, 127.7, 127.6, 127.3, 68.6, 66.3, 55.5, 40.0, 39.3, 37.5, 35.0, 33.0, 26.9, 26.6, 26.1, 19.3, 16.6, 13.5; HRMS (ESI) m/e 686.3637 [M+Na$^+$] calcd for $C_{42}H_{53}O_4SiNa^+$: 686.3636.



Decalin (37): To a stirred solution of **36** (6.91 g, 10.41 mmol) in CH_2Cl_2 (210 mL) was added iodine (132 mg, 0.52 mmol). The reaction mixture was irradiated with visible light (sunlamp, visible light) for 10 minutes. (caution: keep the flask a few feet from the light source to avoid the heating-induced IMDA reaction). The mixture was further diluted with CH_2Cl_2 (830 mL) and cooled to -78°C at which time Me_2AlCl (52 mL, 52.0 mmol, 1M in hexanes) was added dropwise. The reaction mixture was then warmed to 0°C and continued to stir at this temperature for 2 hrs. The reaction mixture was quenched with sat. $NaHCO_3$ solution (300 mL) and the mixture was ran through a Celite® plug followed by a rinse with CH_2Cl_2 (300 mL). The reaction was extracted with CH_2Cl_2 (2 x 100 mL). All organic layers were dried over Na_2SO_4 and concentrated. The crude extract was purified by silica column chromatography (hexanes:EtOAc, 200:1 to 2:1) to yield decalin **37** (3.67 g, 52%) as a white foam. R_f = 0.66 (silica gel, hexanes:EtOAc, 4:1); $[\alpha]_D^{24}$ = -70.5 (*c* = 0.63, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72- 7.31 (m, 15H), 5.44 (d, *J* = 9.7 Hz, 1H), 5.32 (m, 1H), 4.51 (m, 1H), 4.11 (m, 2H), 3.64 (dd, *J* = 5.2, 9.7 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.46 (t, *J* = 9.2 Hz, 1H), 3.38 (s, 1H), 2.59 (t, *J* = 12.6 Hz, 1H), 2.19 (s, 1H), 2.07-1.43 (m, 9H), 1.36 (s, 3H), 1.07 (s, 9H), 1.02 (d, *J* = 7.5 Hz, 3H), 0.92 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 152.1, 136.1, 135.6, 134.8, 134.1, 133.9, 131.9, 129.5, 128.9, 127.1, 123.8, 68.7, 66.0, 59.1, 51.7, 44.8, 42.6, 39.7, 39.0, 36.9, 32.9, 31.9, 27.8, 26.8, 23.4, 19.3, 18.8, 15.9, 13.1; HRMS (ESI) m/e 686.3637 [M+Na^+] calcd for $C_{42}H_{53}O_4SiNa^+$: 686.3636.



Decalin (38): To a solution of **37** (600 mg, 0.9 mmol) in CH_2Cl_2 (18.1 mL) at -78°C was added DIBAL-H (4.52 mL, 4.52 mmol, 1M in hexanes) dropwise. This solution continued to stir at this temperature for 1 hr and then at 0°C for 1 hr before being diluted with ether (20 mL) and then water (0.18 mL) was added dropwise and then warmed to

RT for 30 minutes. Then some $MgSO_4$ was added and stirred for an additional 15 minutes before being filtered and ran through a silica plug (hexanes, then hexanes:EtOAc 9:1) to isolate the crude alcohol (244 mg). Then the alcohol was dissolved in DMSO (2.2 mL) and cooled to 0°C and IBX (209 mg, 0.75 mmol) was added in one portion. The reaction continued to stir at RT for 1 hrs before being diluted with water (5 mL). Then the solution was filtered through a Celite® plug which was rinsed with ether (10 mL). The filtrate was extracted with ether (5 x 5 mL) and all organic layers were washed with brine (10 mL) and 10% NaOH solution (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to yield decalin aldehyde **38** (216 mg, 49% over two steps) as a clear oil. R_f = 0.57 (silica gel, hexanes:EtOAc, 9:1); $[\alpha]_D^{23}$ = -54.4 (*c* = 1.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.69-7.38 (m, 10H), 5.52 (d, *J* = 10.3 Hz, 1H), 5.36 (m, 1H), 3.43 (m, 2H), 2.50 (m, 1H), 2.19 (s, 1H), 2.07 (m, 1H), 2.01-1.22 (m, 9H), 1.08 (s, 3H), 1.06 (s, 9H), 1.02 (d, *J* = 7.3 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 135.6, 133.6, 133.2, 129.7, 127.7, 123.2, 67.3, 50.6, 44.6, 41.6, 38.9, 36.7, 32.3, 31.1, 27.7, 26.9, 22.0, 19.3, 18.4, 16.1, 14.2; HRMS (ESI) m/e 511.3009 [M+Na^+] calcd for $C_{32}H_{44}O_2SiNa^+$: 511.3008.

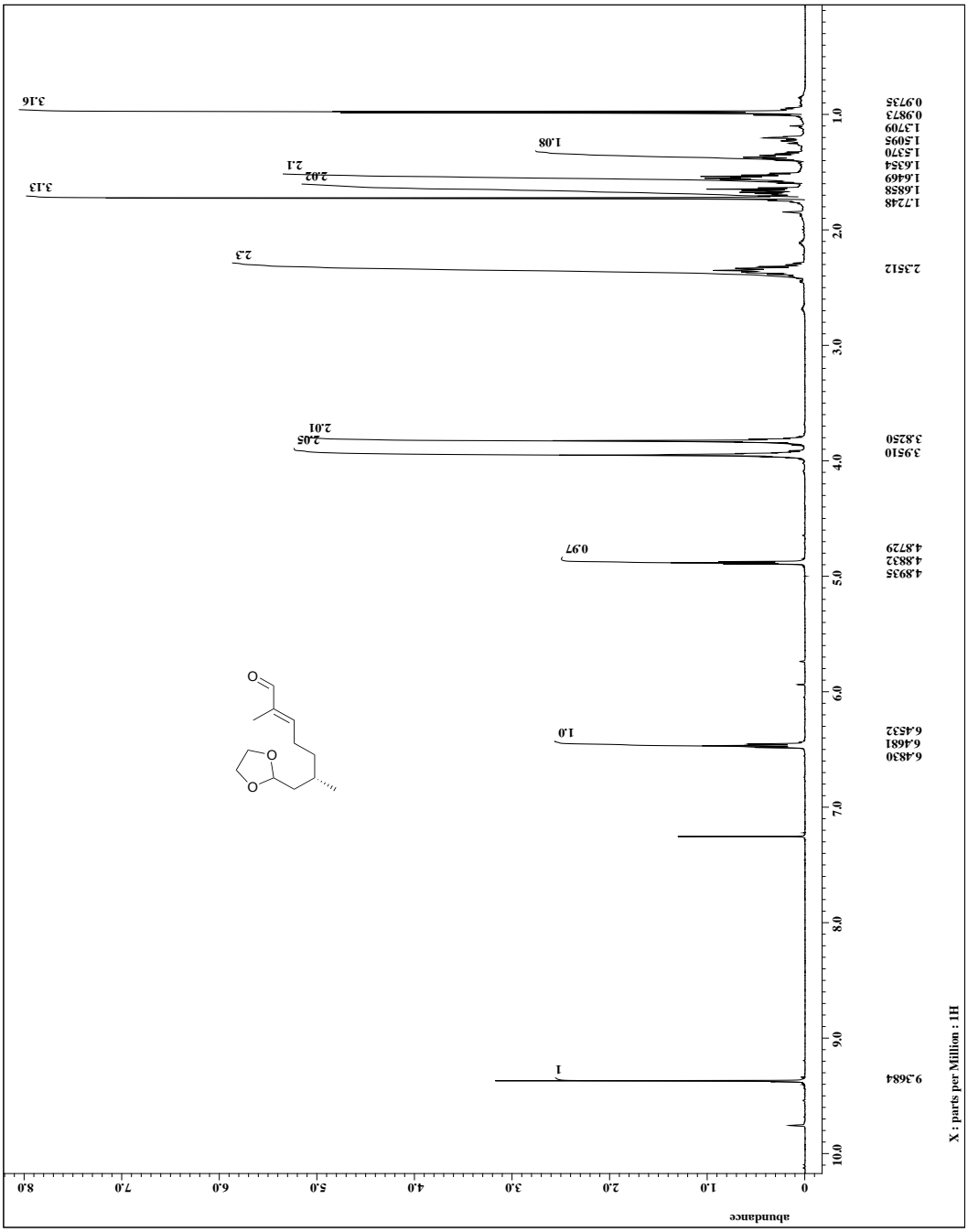
Reference:

(1) (a) Xu, J.; Caro-Diaz, E. J. E.; Lacoske, M. H.; Hung, C. I.; Jamora, C.; Theodorakis, E. A. *Chem. Sci.* **2012**, *3*, 3378-3386. (b) Xu, J.; Caro-Diaz, E. J. E.; Trzoss, L.; Theodorakis, E. A. *J. Am. Chem. Soc.* **2012**, *134*, 5072-5075.

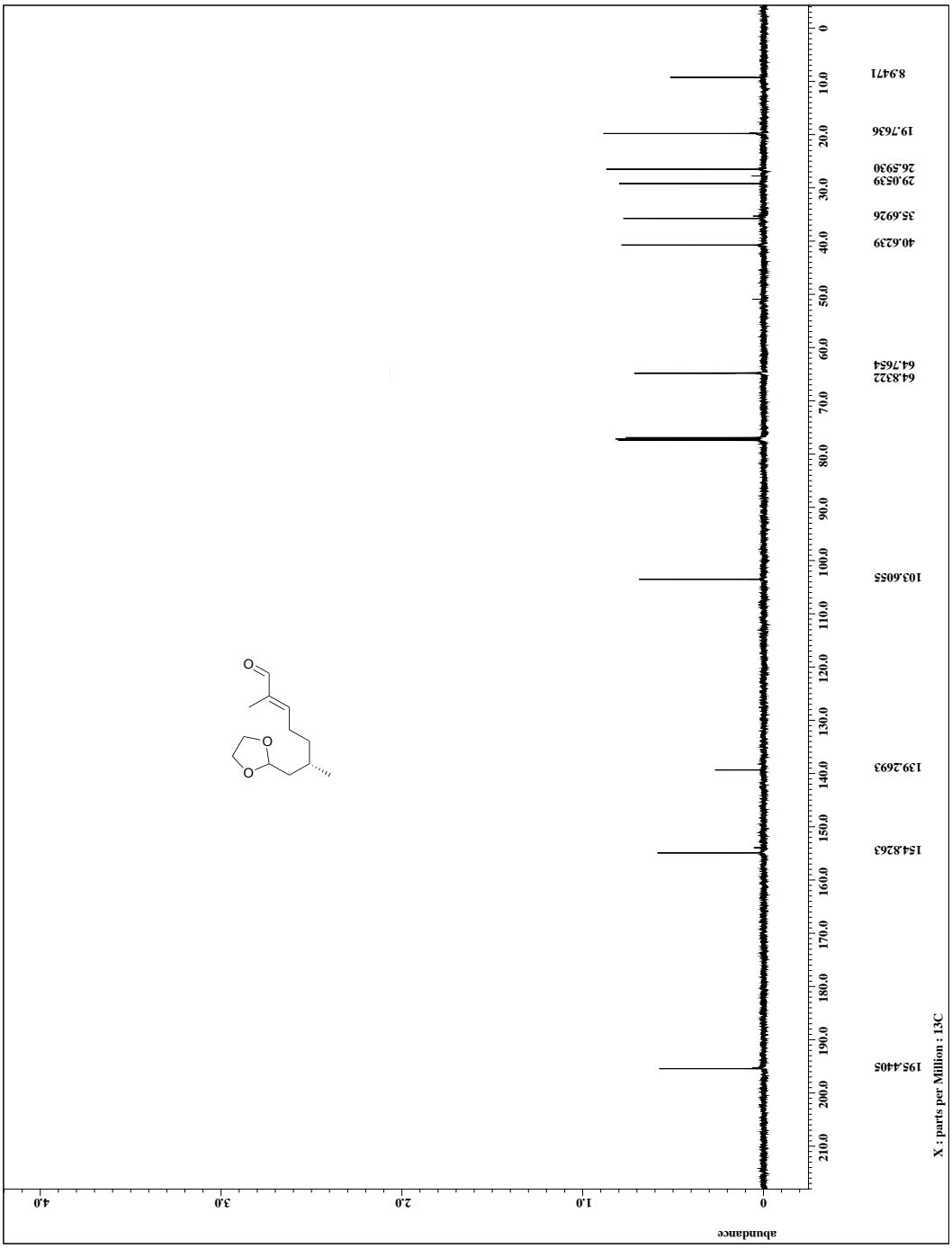
(2) Caravano, A.; Field, R. A.; Percy, J. M.; Rinaudo, G.; Roig, R.; Singh, K. *Org. Biomol. Chem.* **2009**, *7*, 996-1008.

(3) Huang, Y. G.; Fananas-Mastral, M.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun.* **2013**, *49*, 3309-3311.

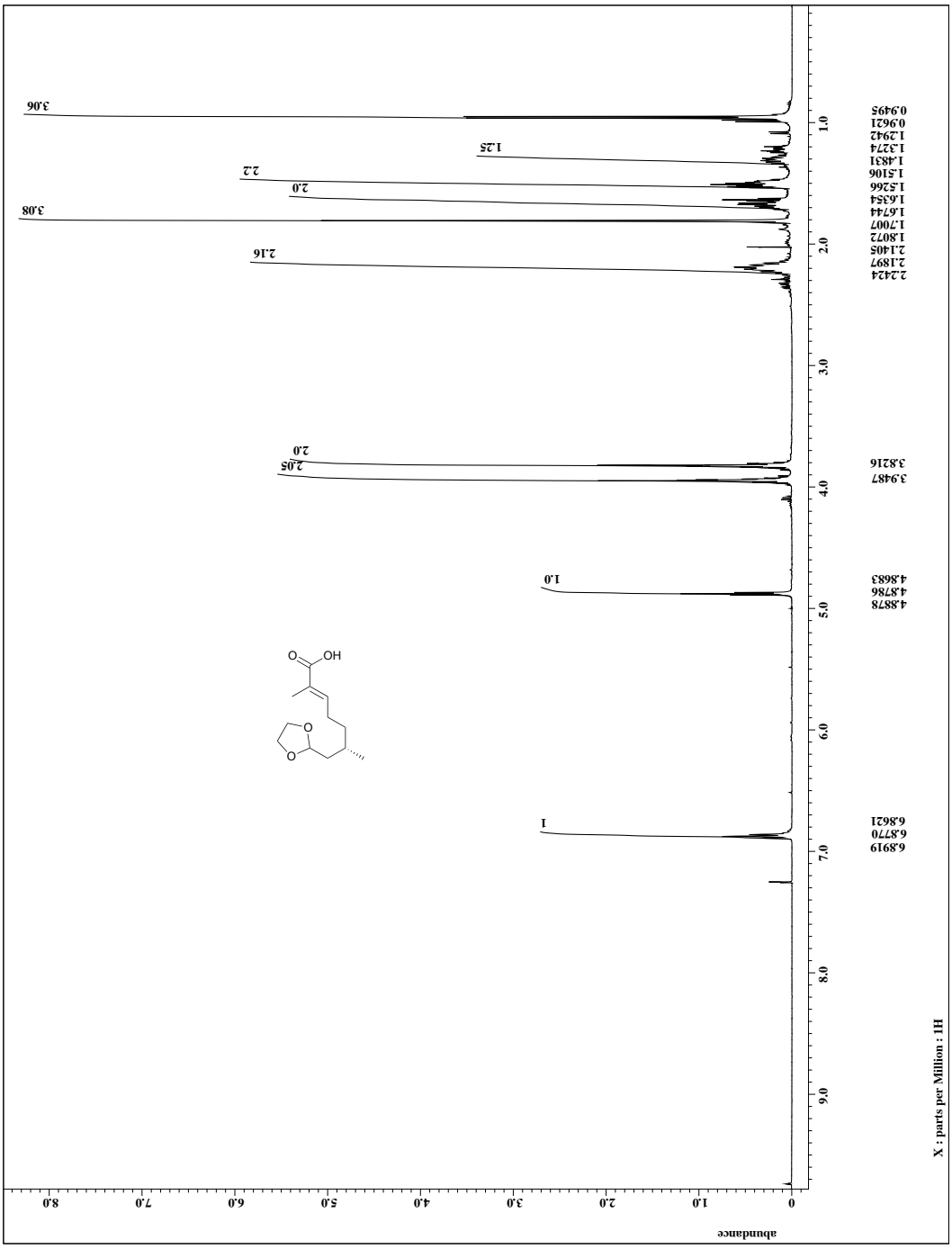
(4) (a) Yadav, J. S.; Venkatesh, M.; Thrimurtulu, N.; Prasad, A. R. *Synlett* **2010**, 1255-1259. (b) Chandrasekhar, S.; Yaragorla, S. R.; Sreelakshmi, L.; Reddy, C. R. *Tetrahedron* **2008**, *64*, 5174-5183. (c) Pasqua, A. E.; Ferrari, F. D.; Crawford, J. J.; Marquez, R. *Tetrahedron Lett.* **2012**, *53*, 2114-2116.



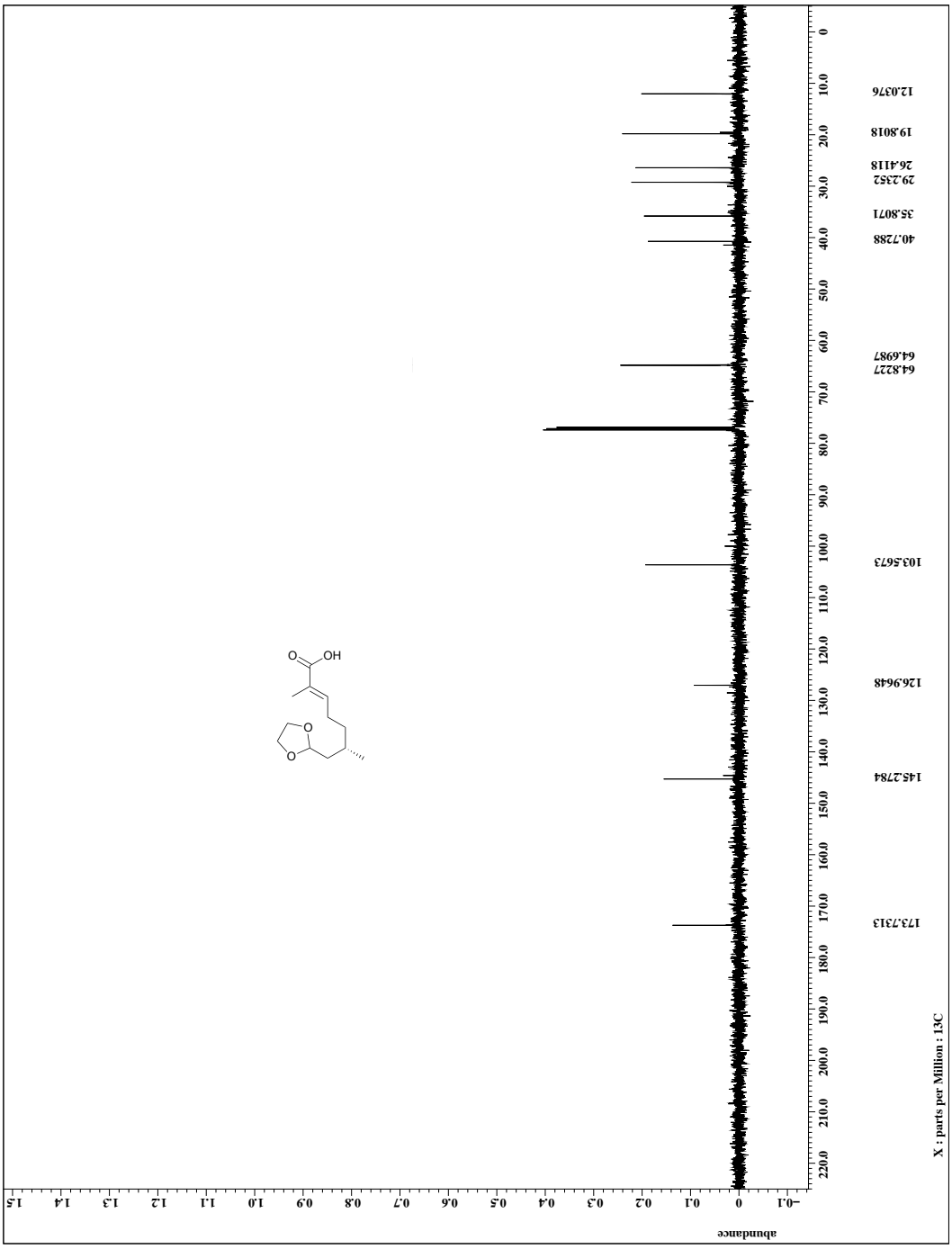
Spectrum 1 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **11_1**



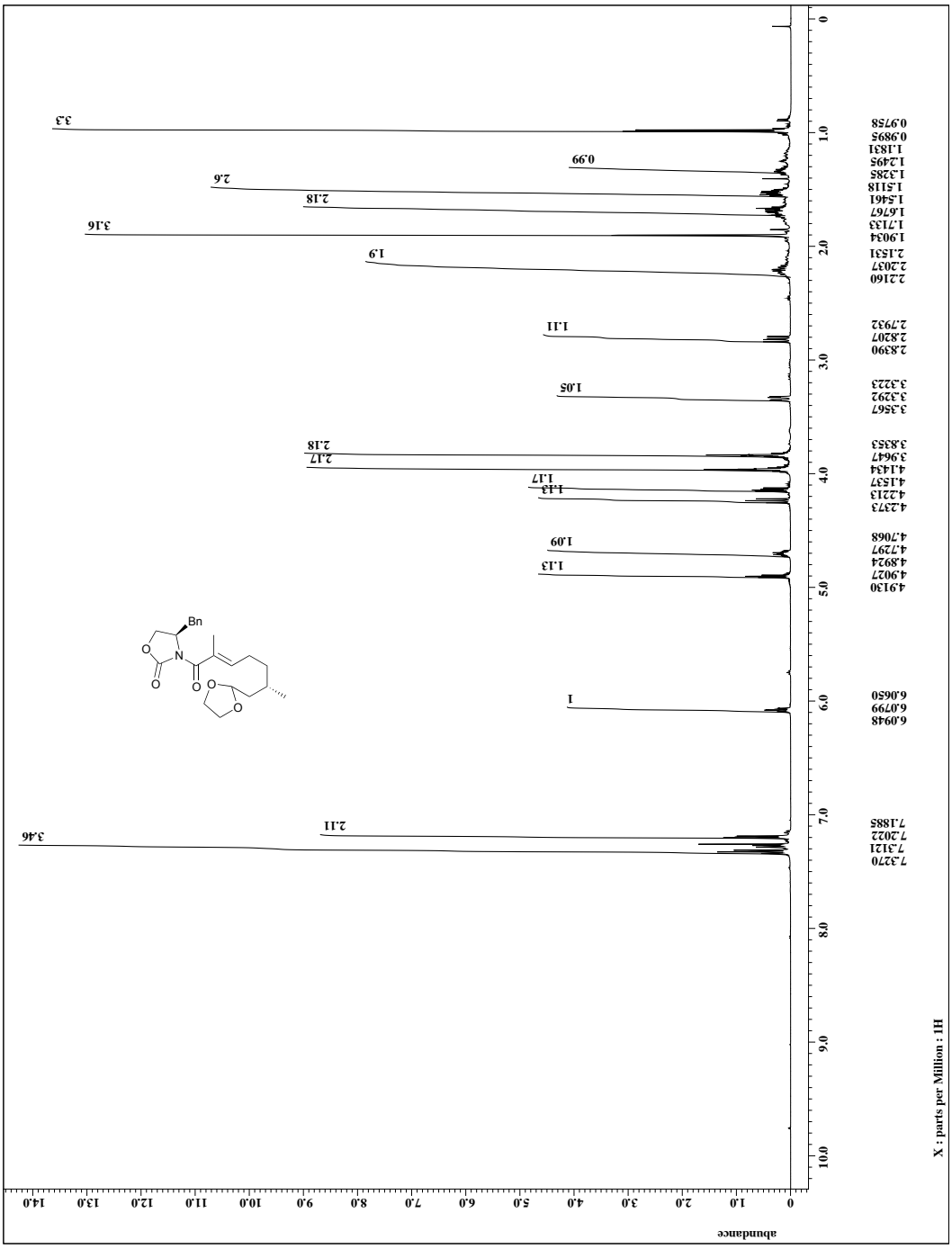
Spectrum 2 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **11_1**



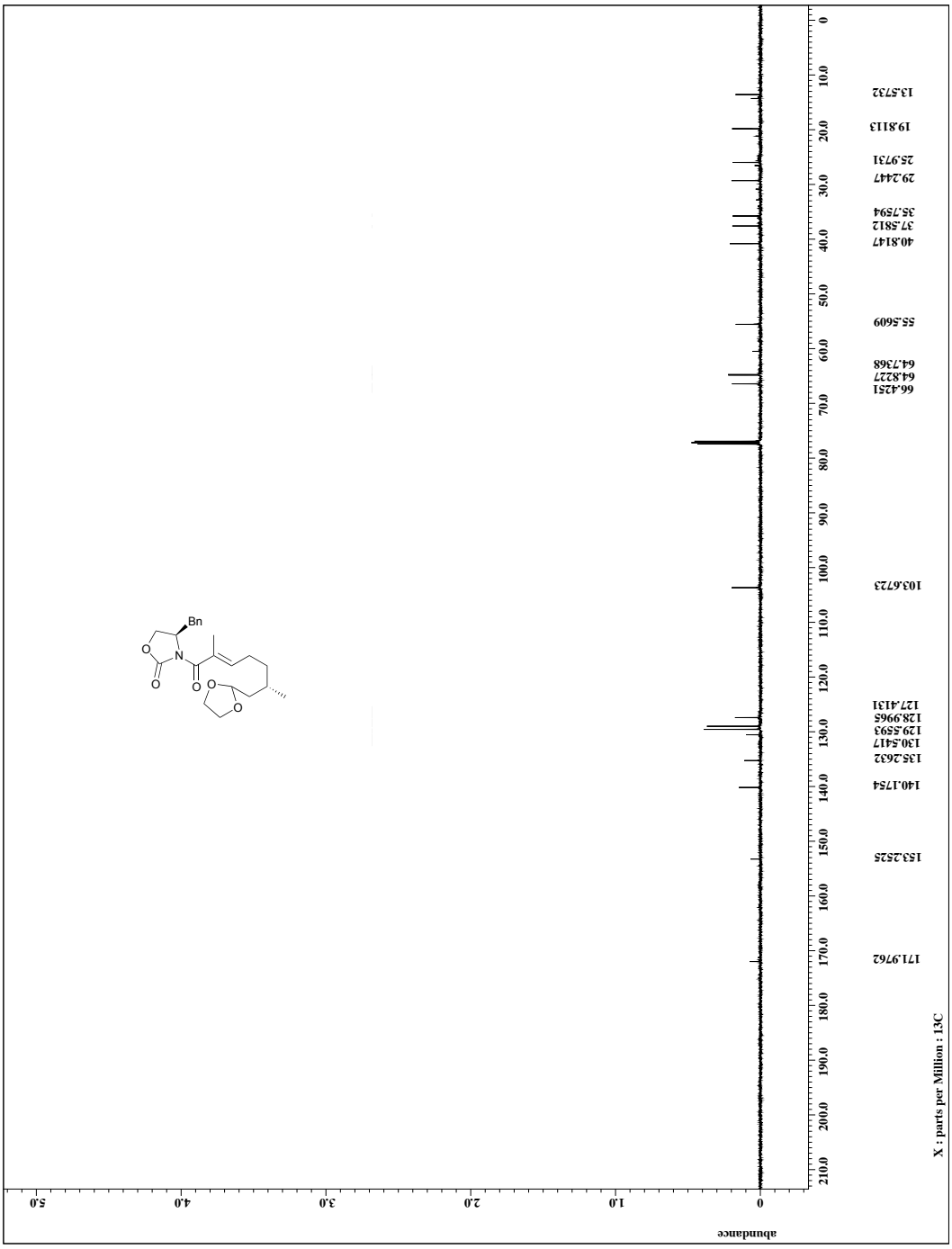
Spectrum 3 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **12**



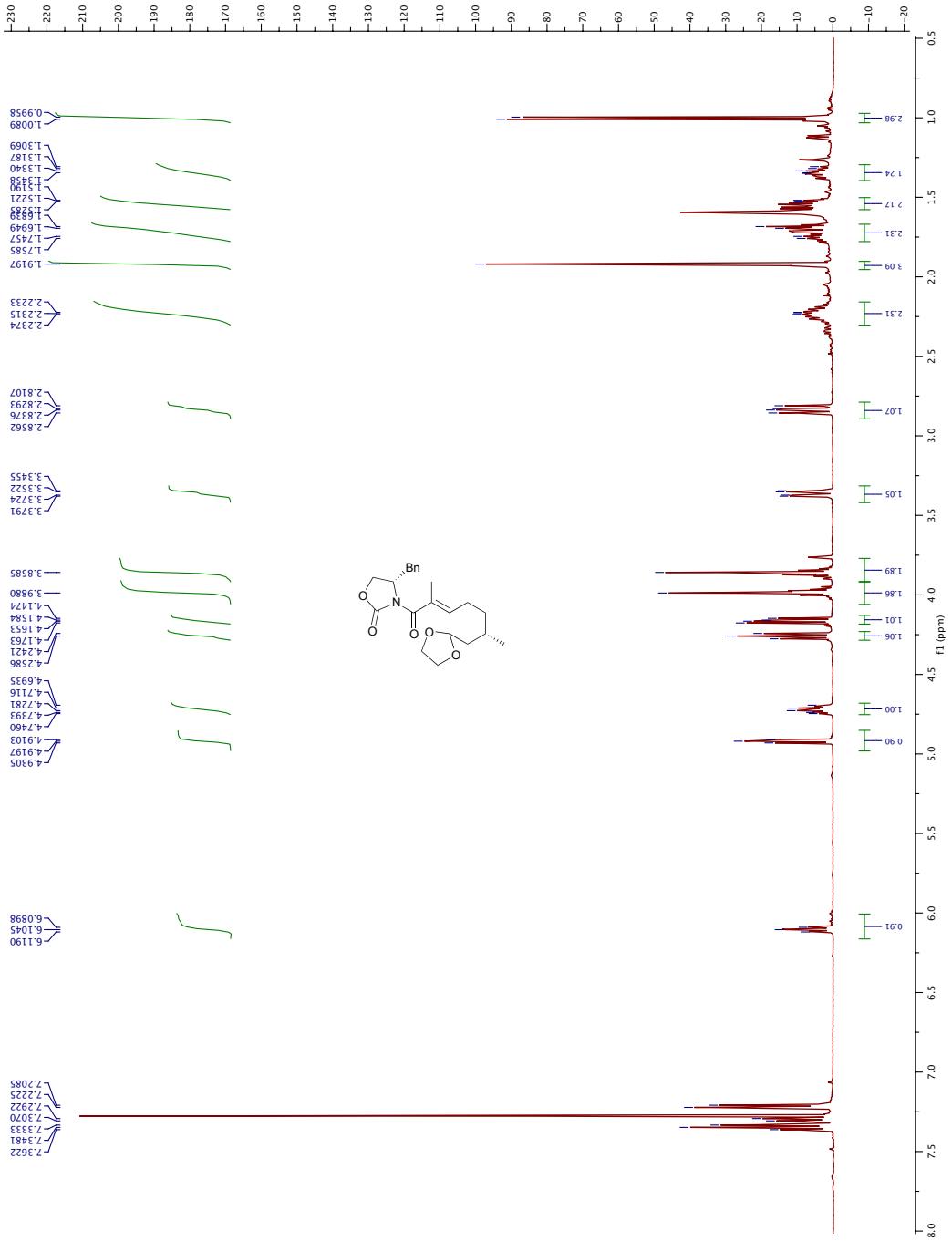
Spectrum 4 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **12**



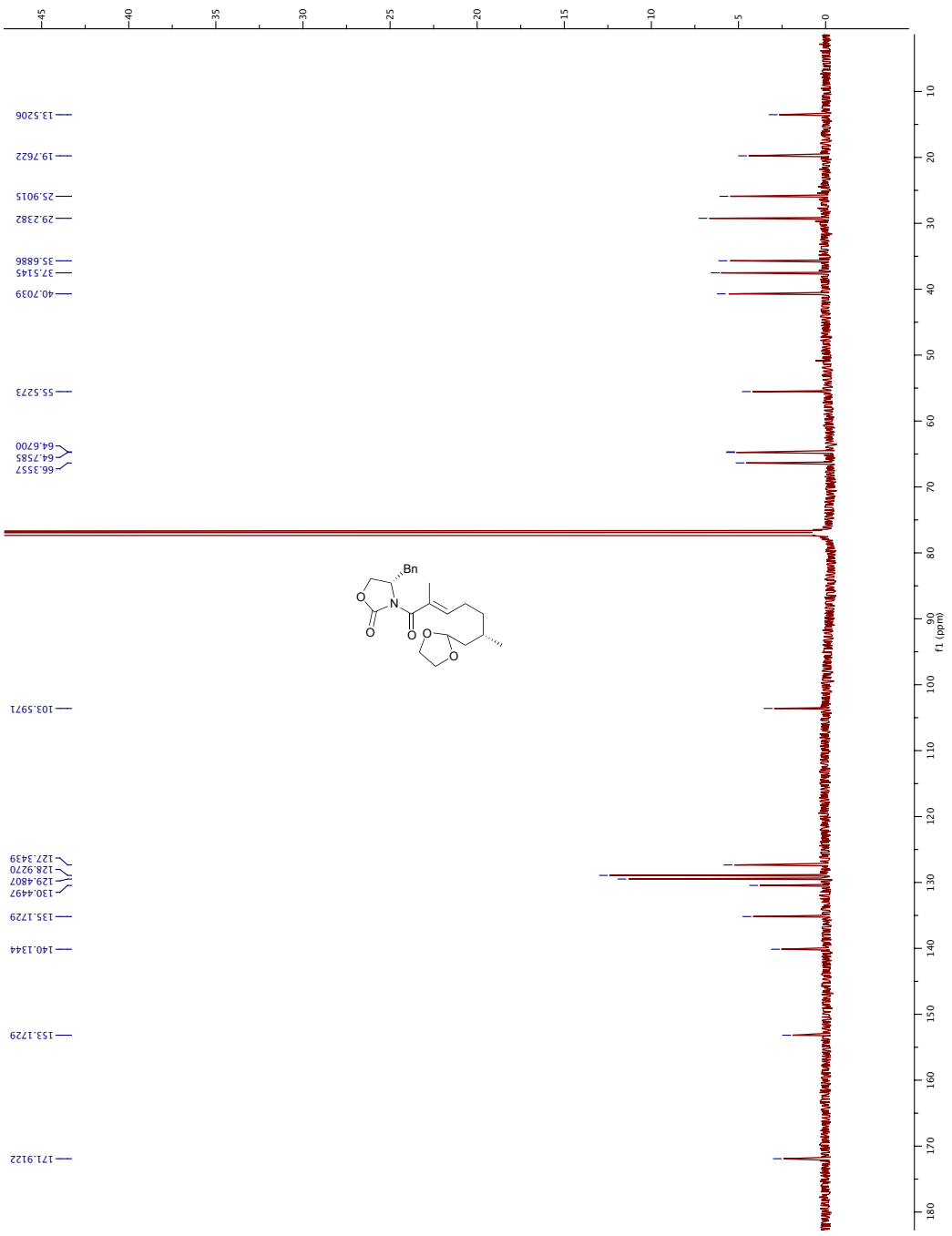
Spectrum 5 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **12_1**



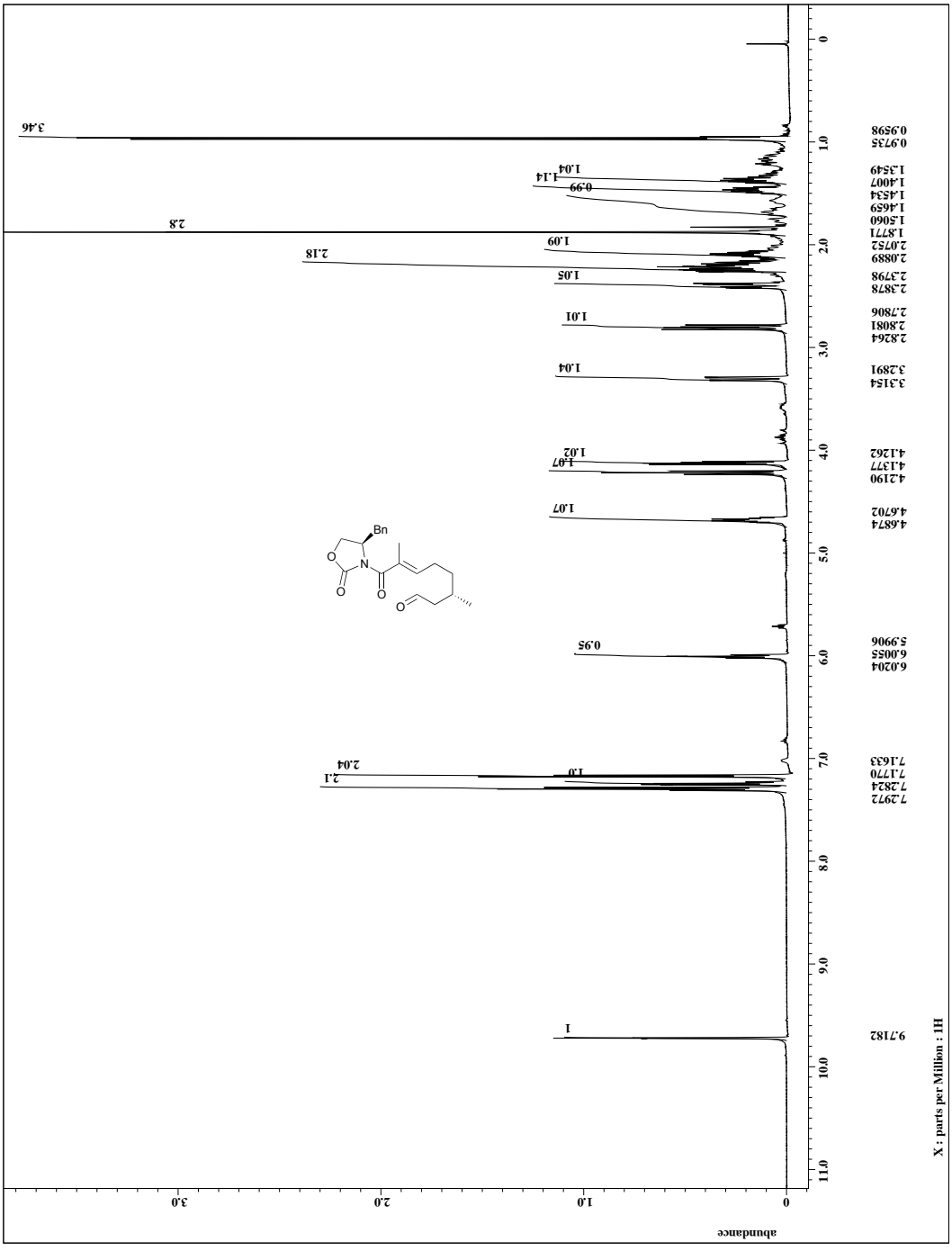
Spectrum 6 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **12_1**



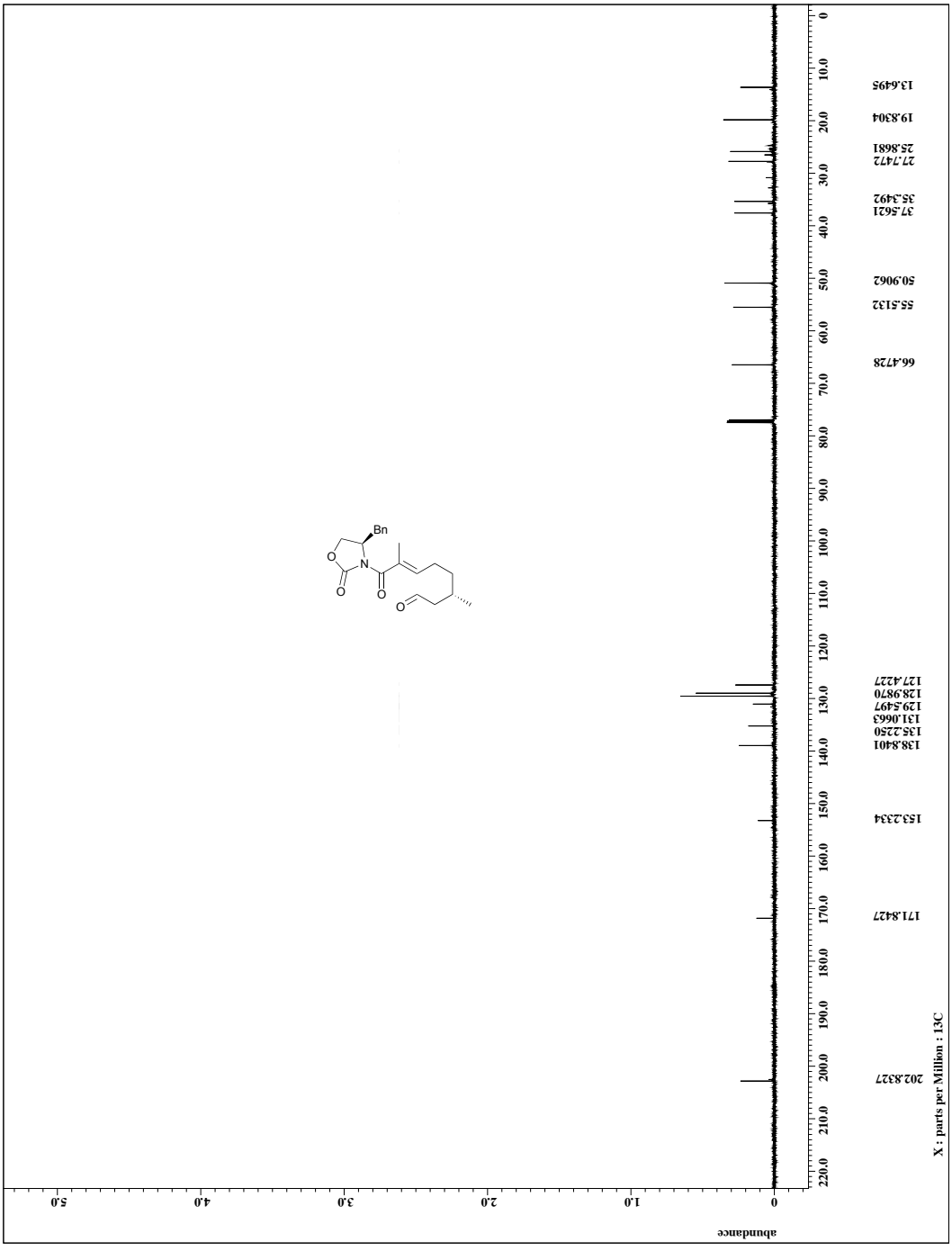
Spectrum 7 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **12_2**



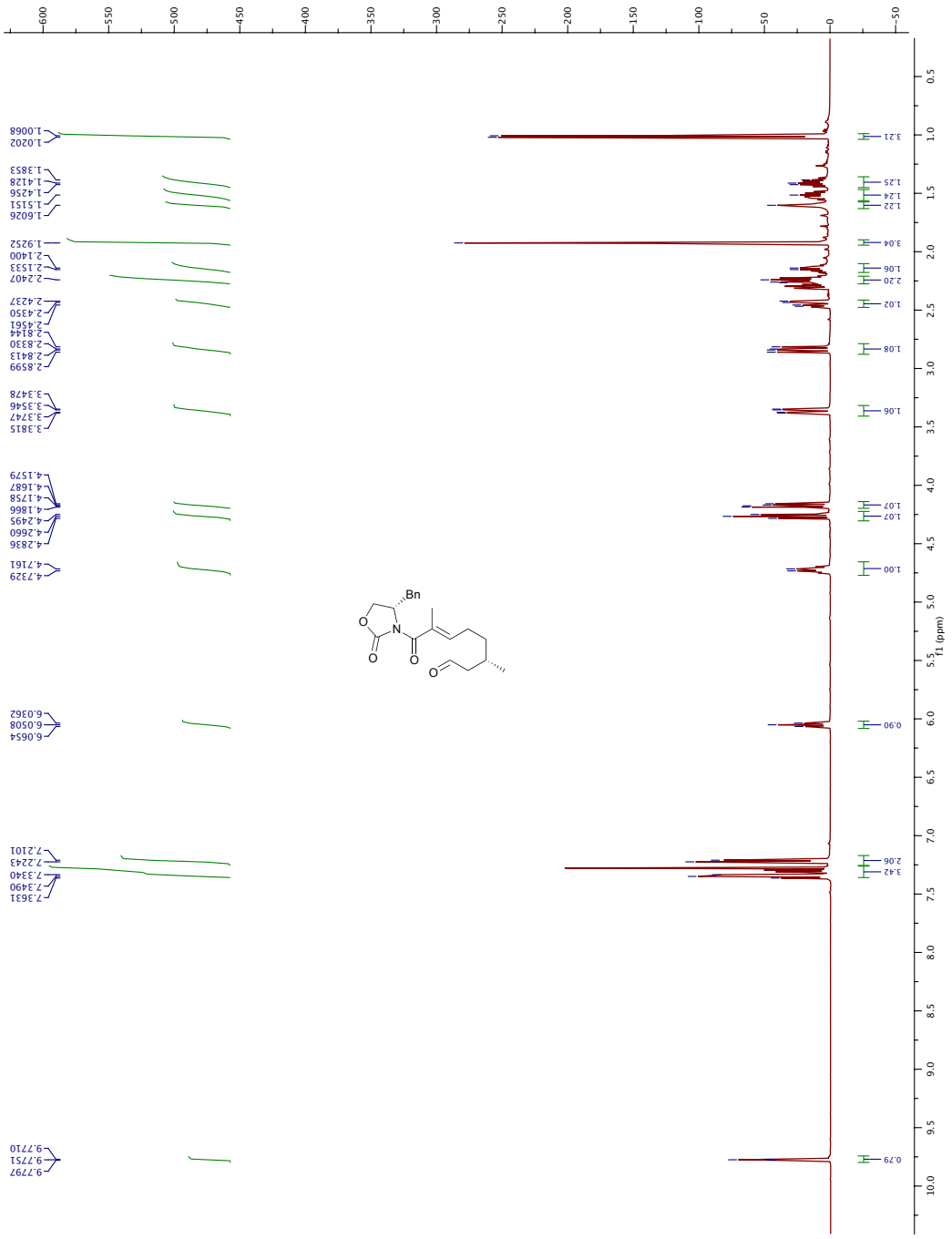
Spectrum 8 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **12_2**



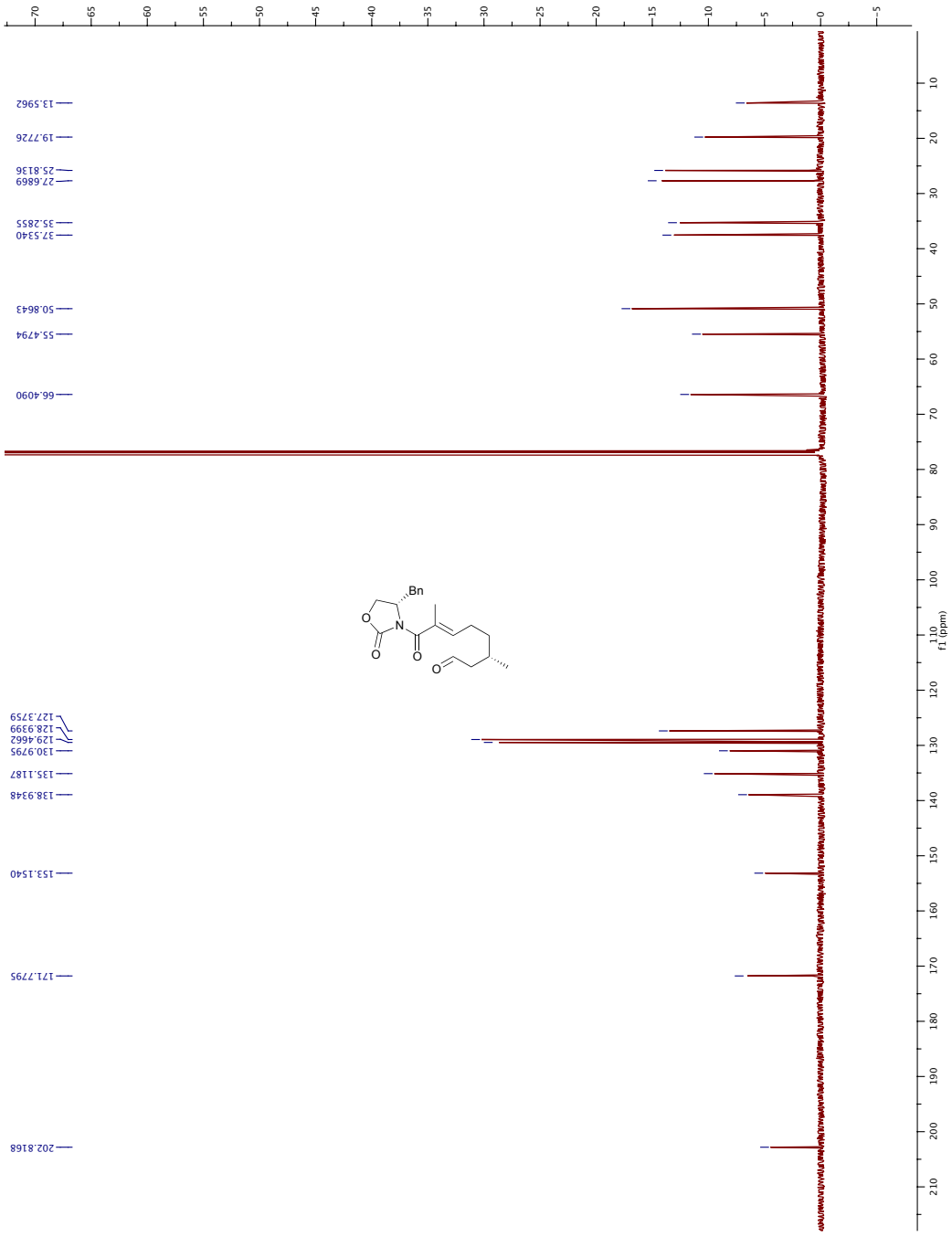
Spectrum 9 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **15**



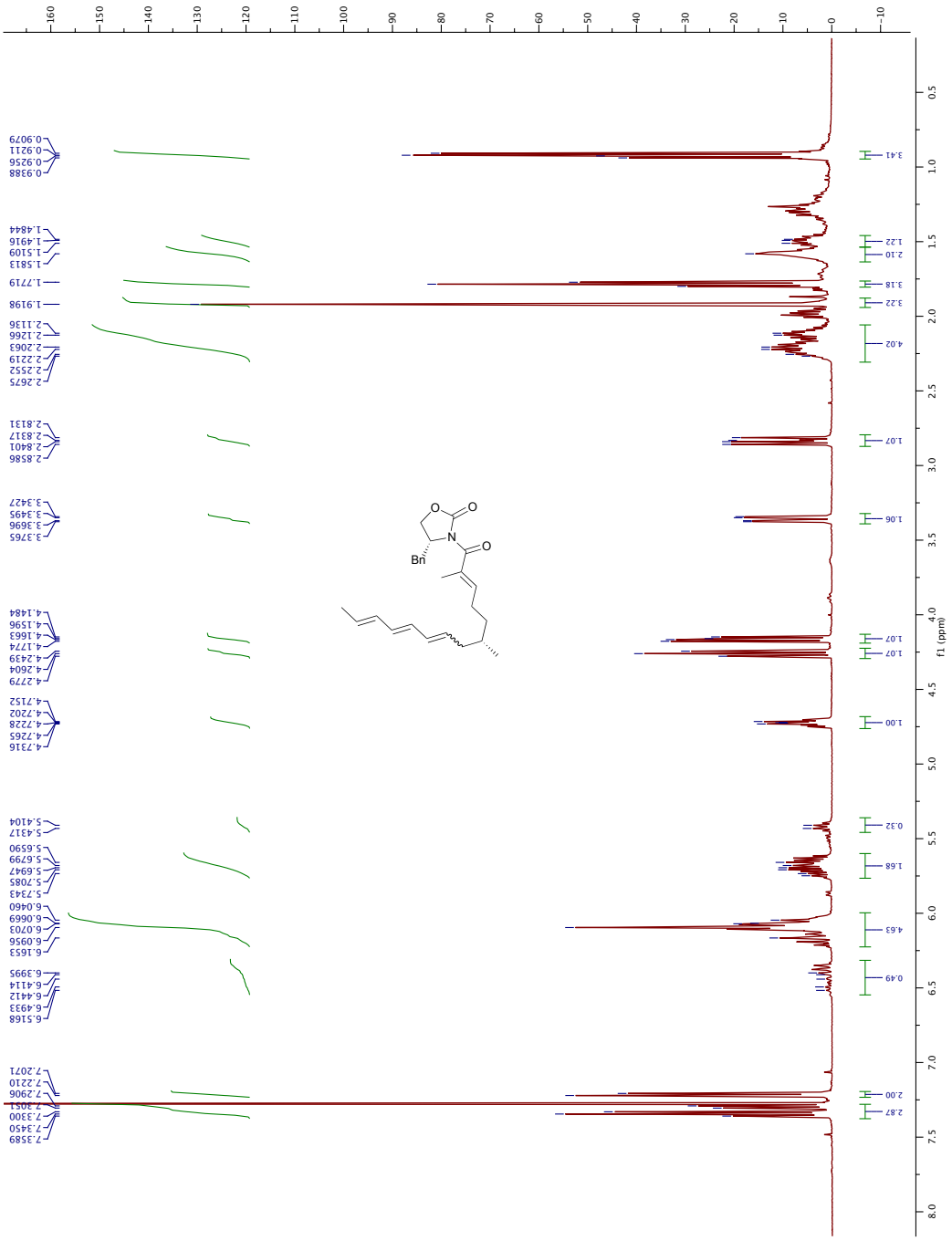
Spectrum 10 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **15**



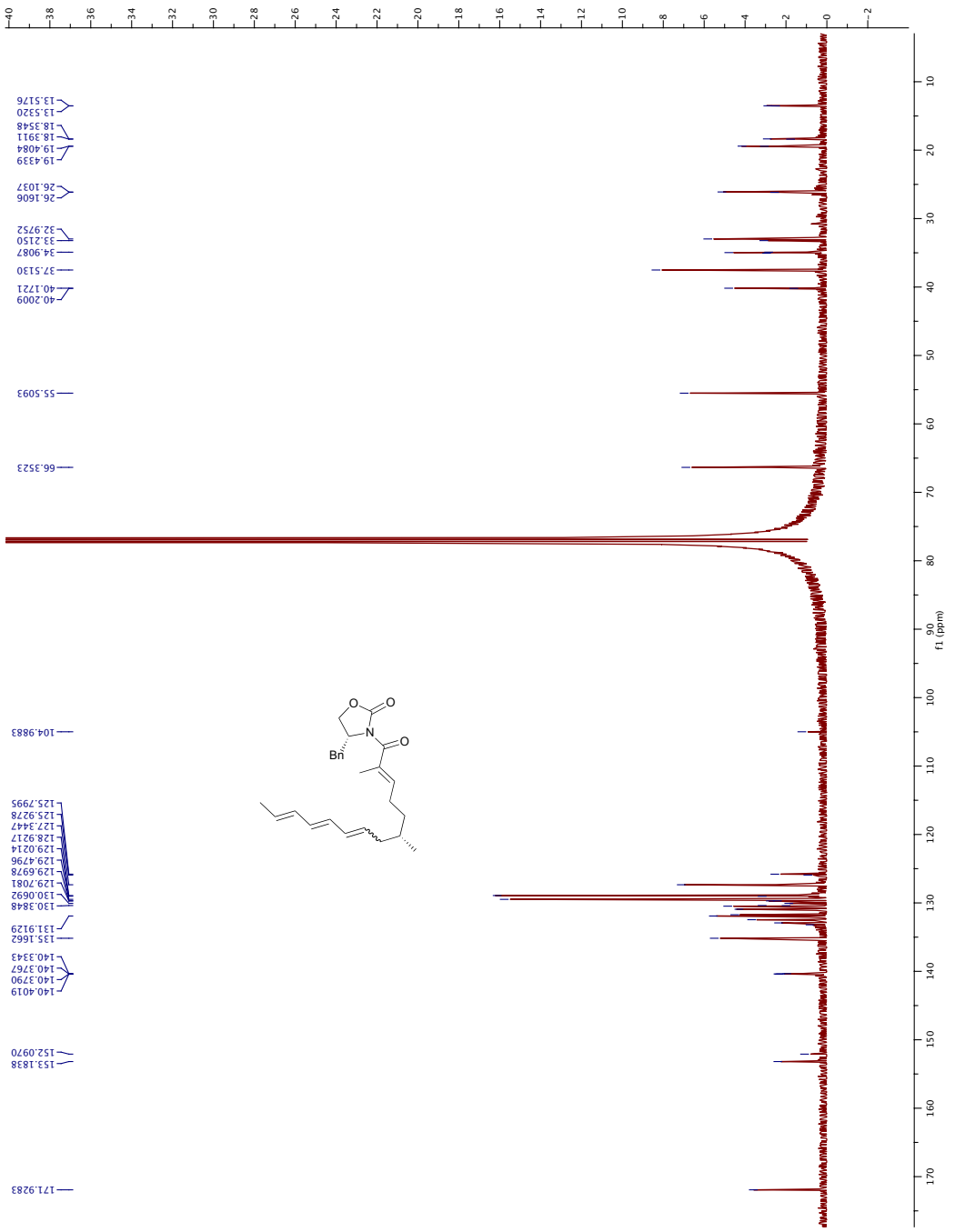
Spectrum 11 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **16**



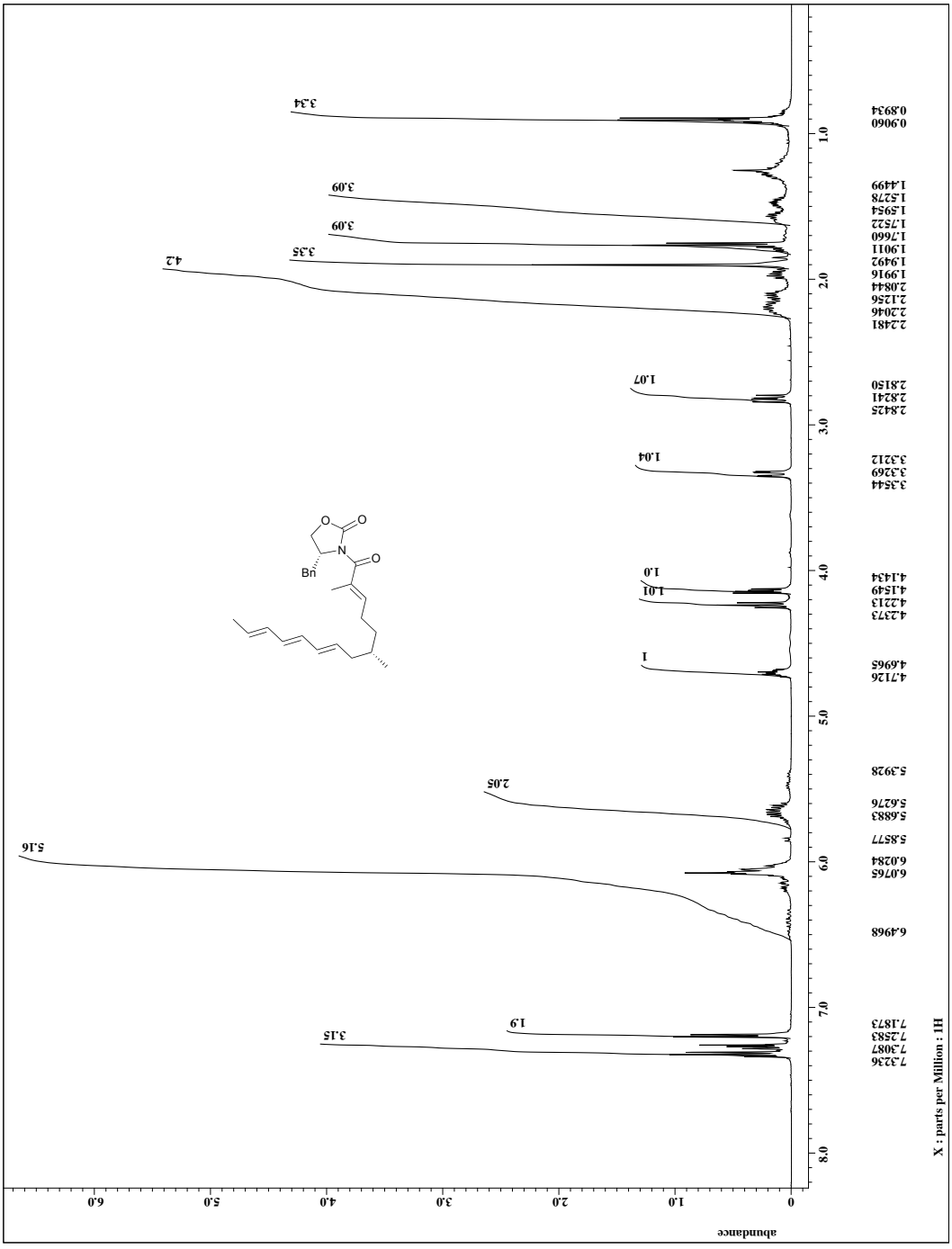
Spectrum 12 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **16**



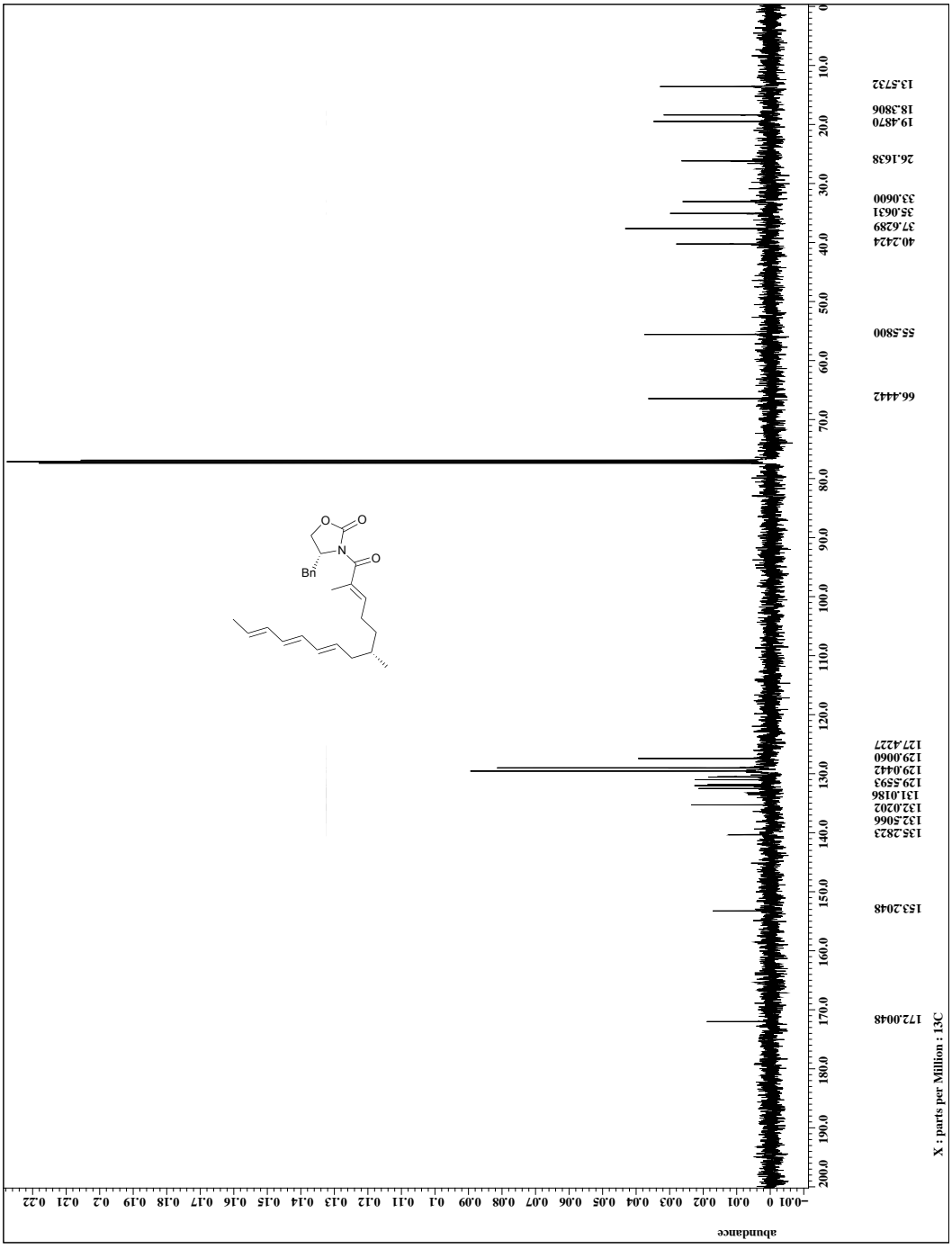
Spectrum 13 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **18**



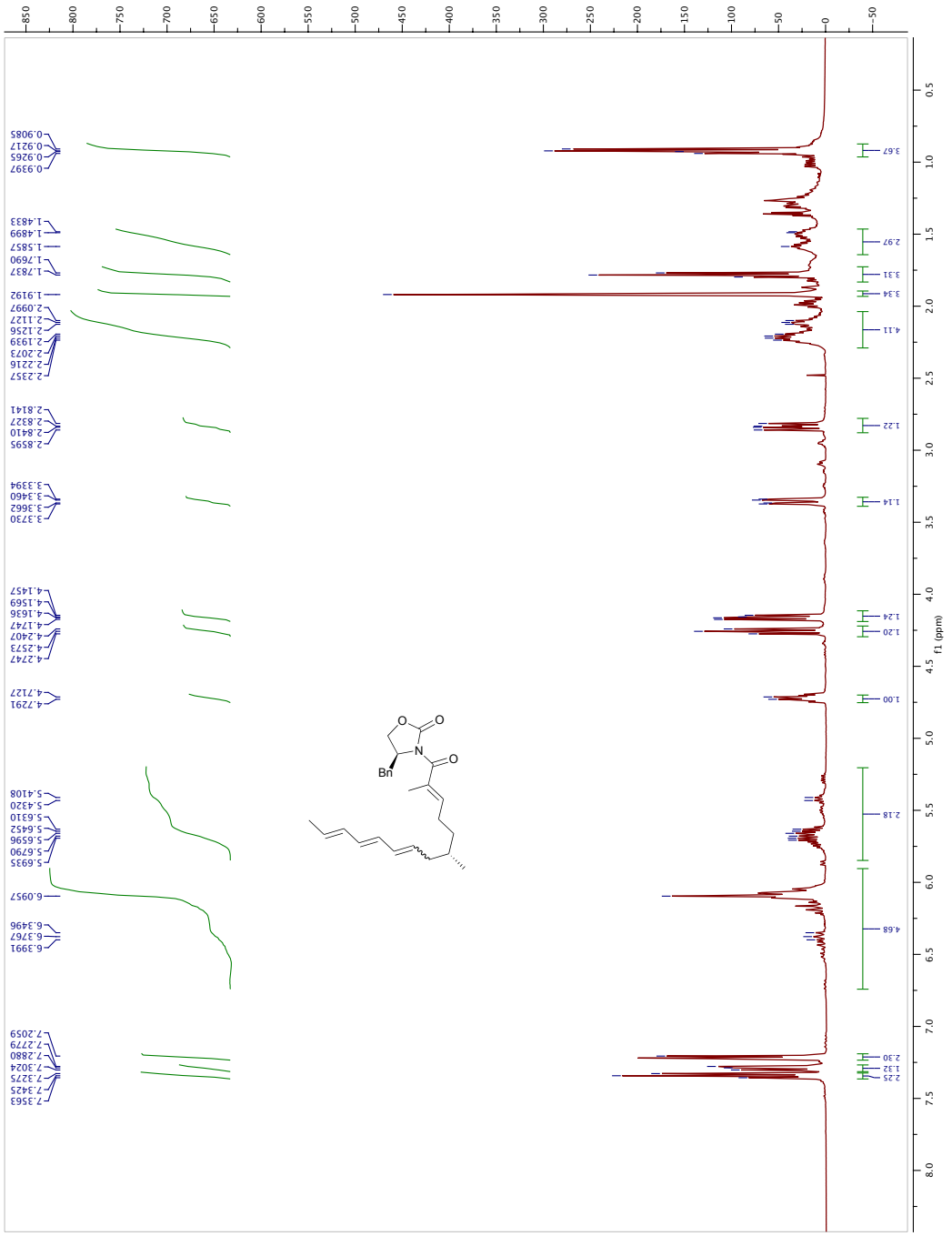
Spectrum 14 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **18**



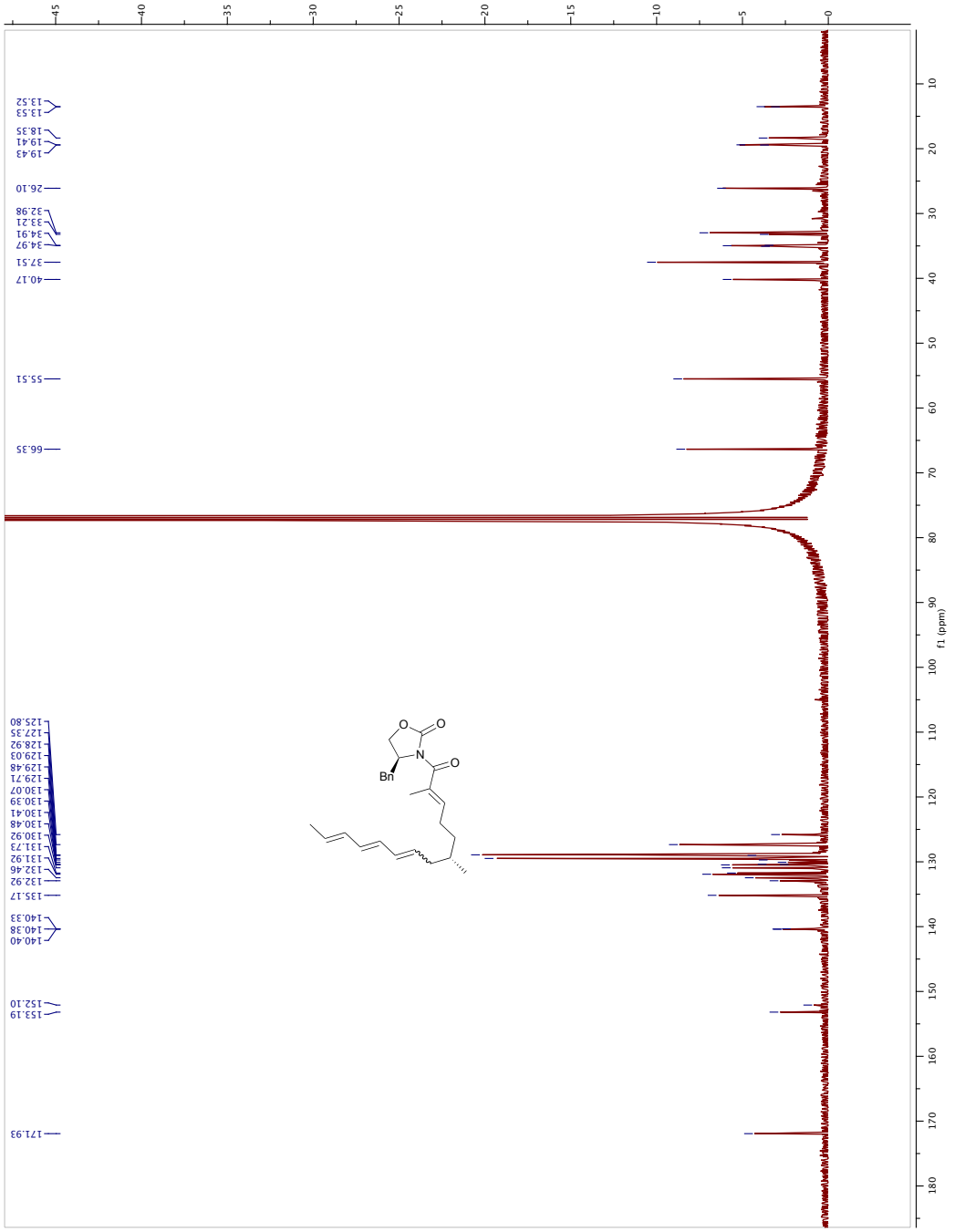
Spectrum 15 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **18 isomerized**



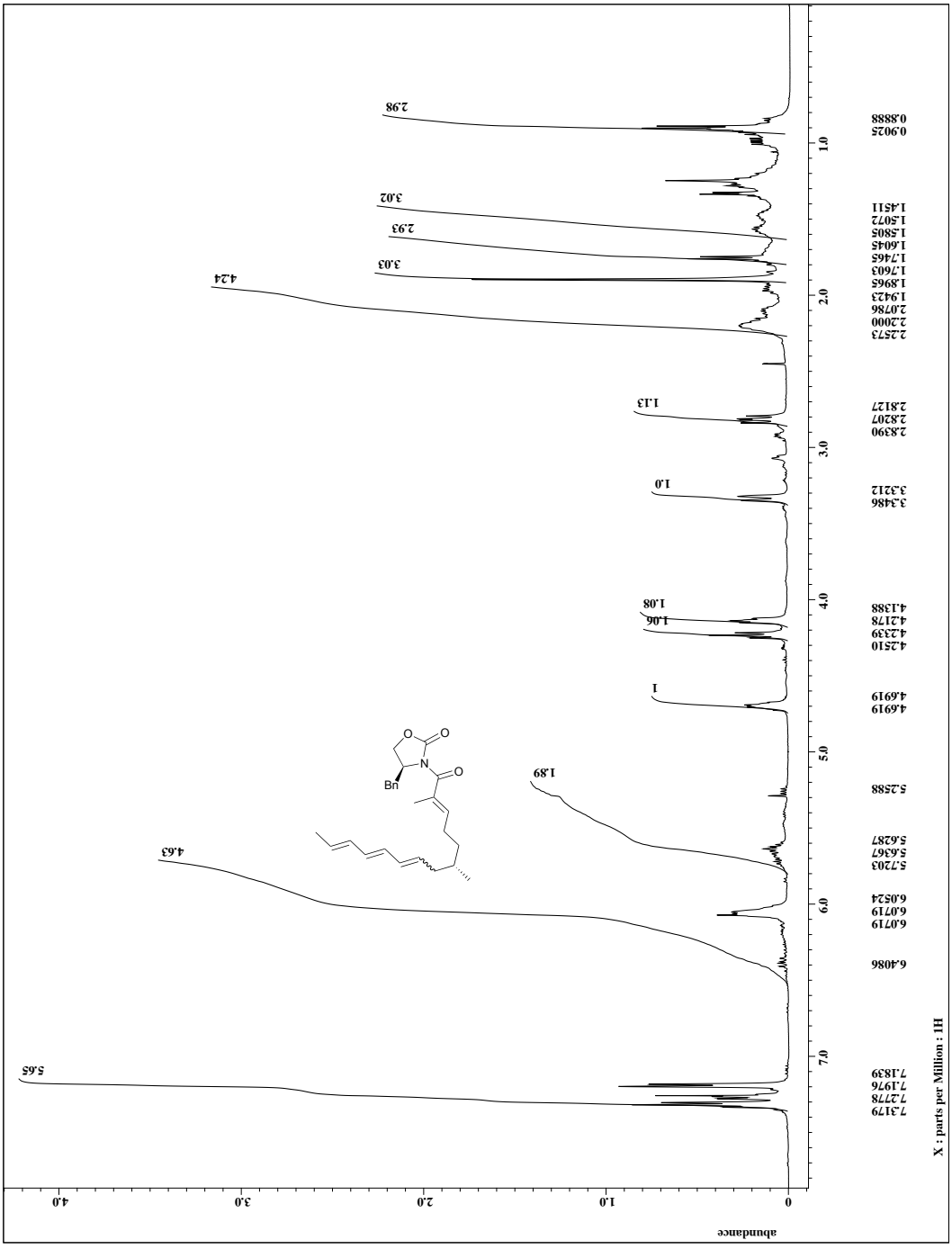
Spectrum 16 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **18 isomerized**



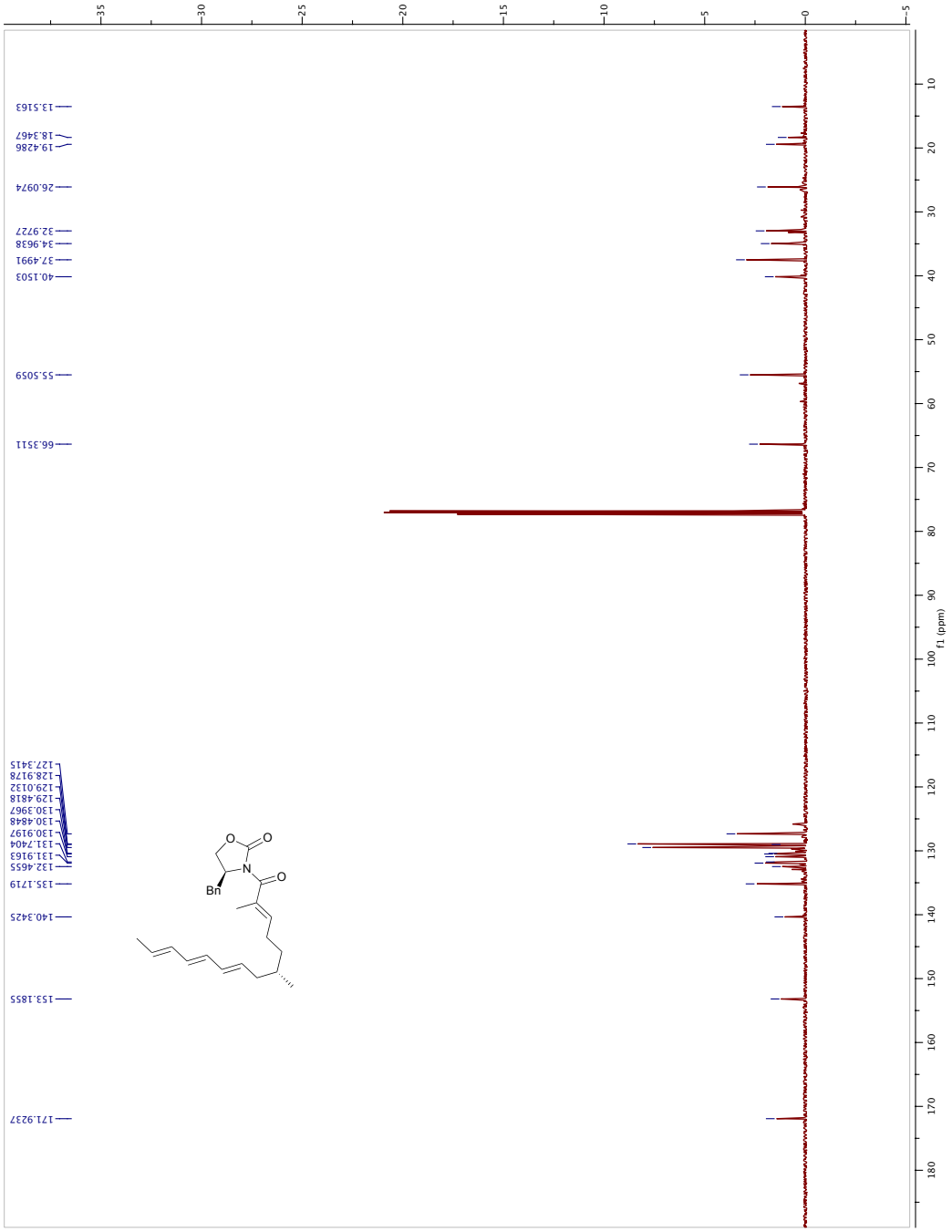
Spectrum 17 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **19**



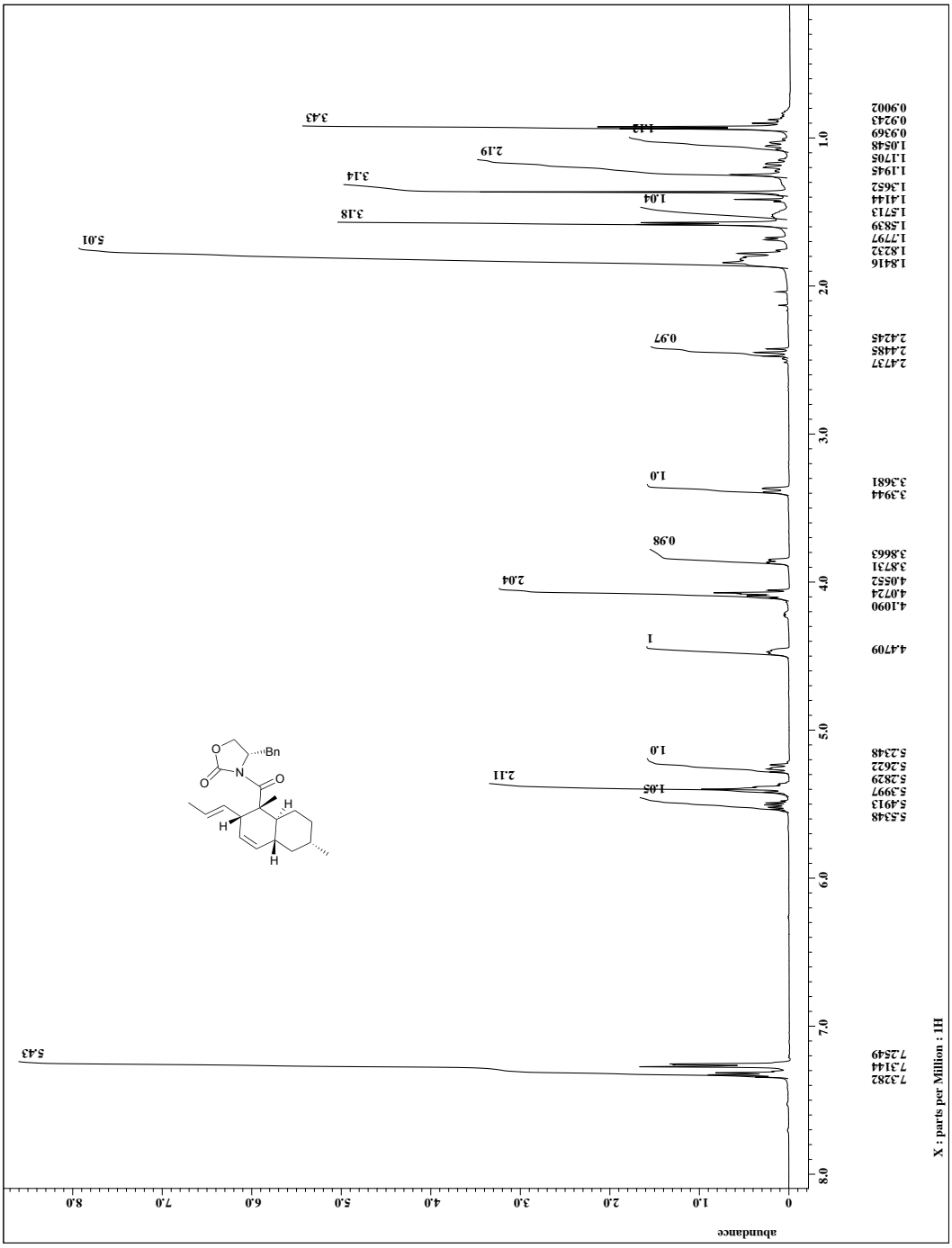
Spectrum 18 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **19**



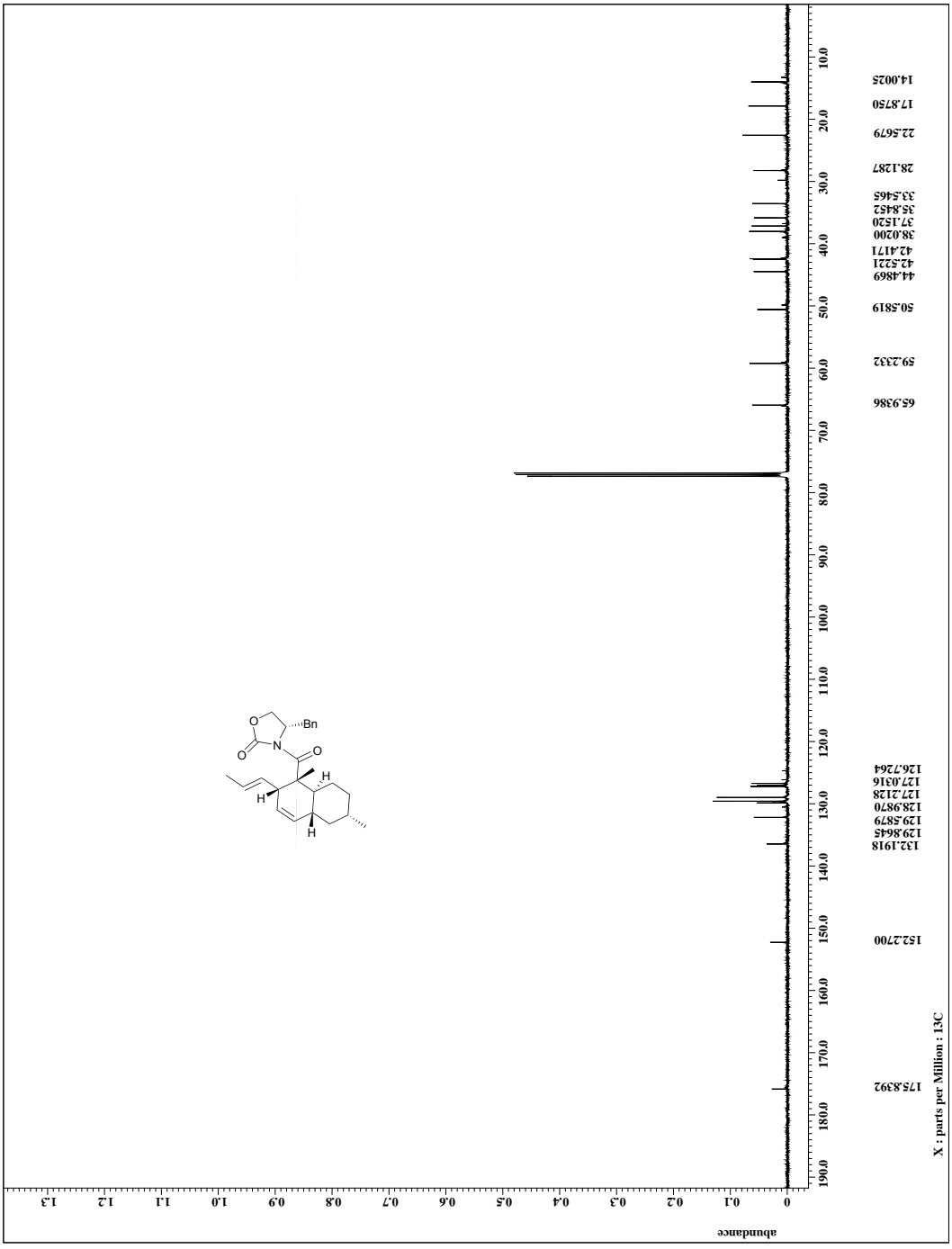
Spectrum 19 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **19 isomerized**



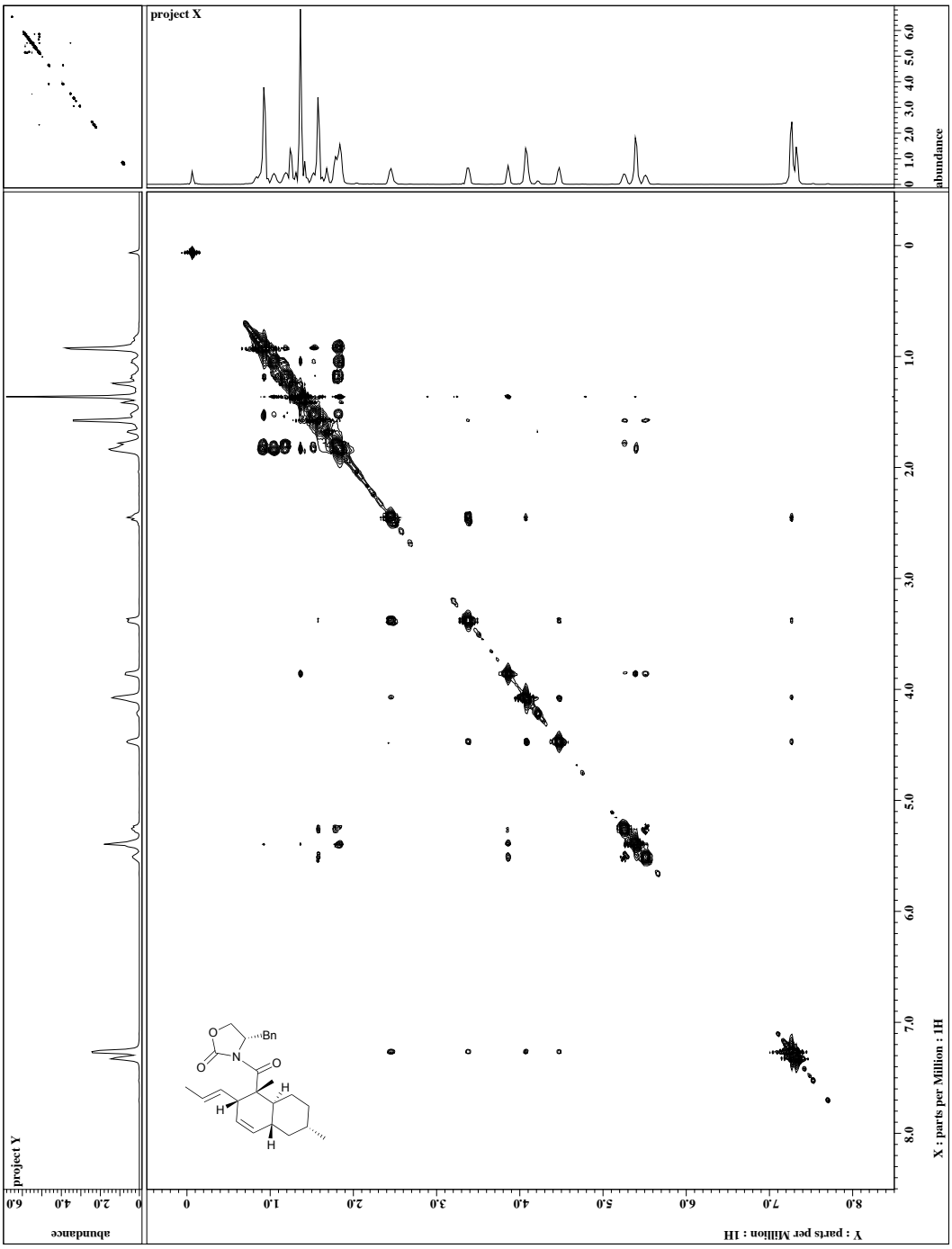
Spectrum 20 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **19 isomerized**



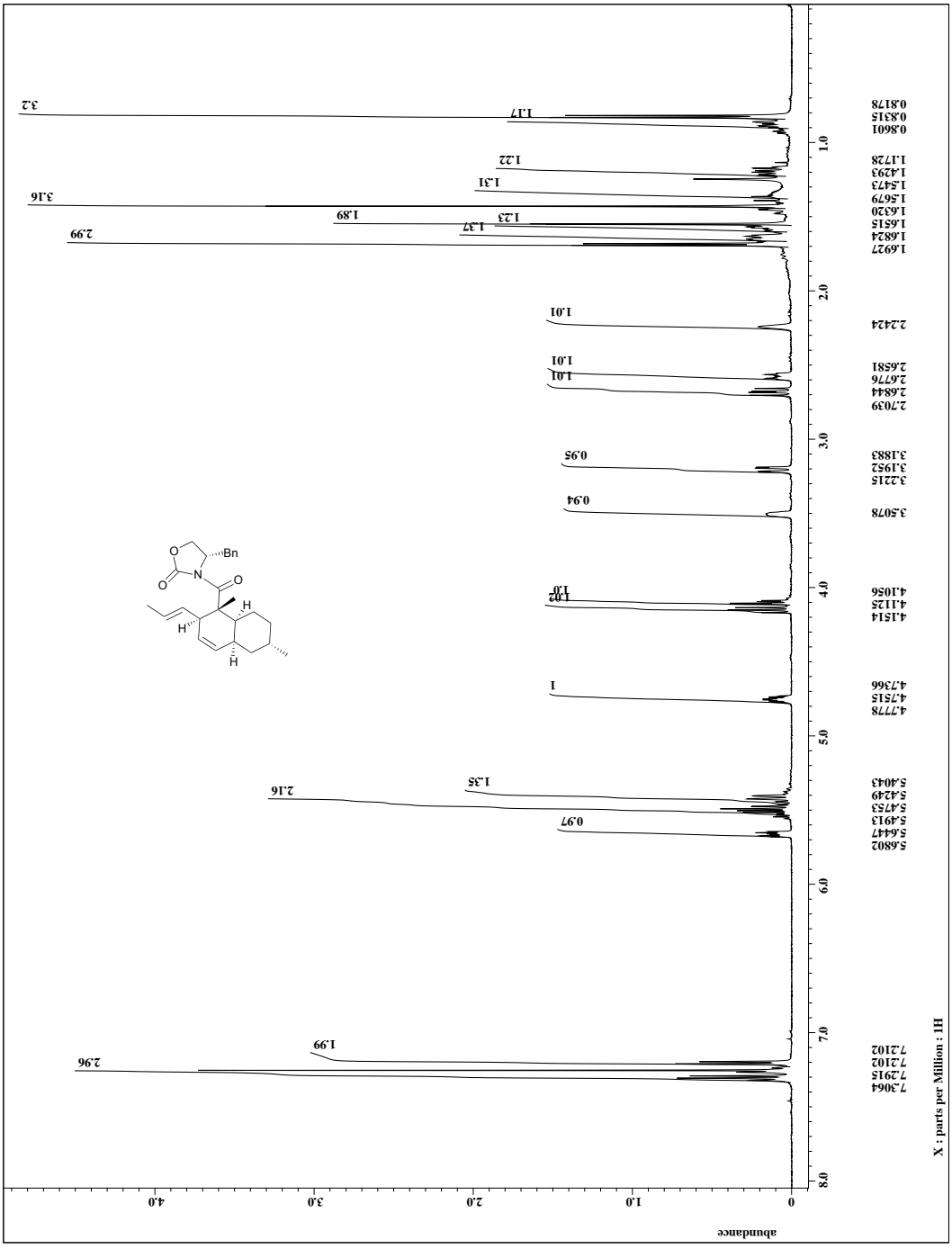
Spectrum 21 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **22**



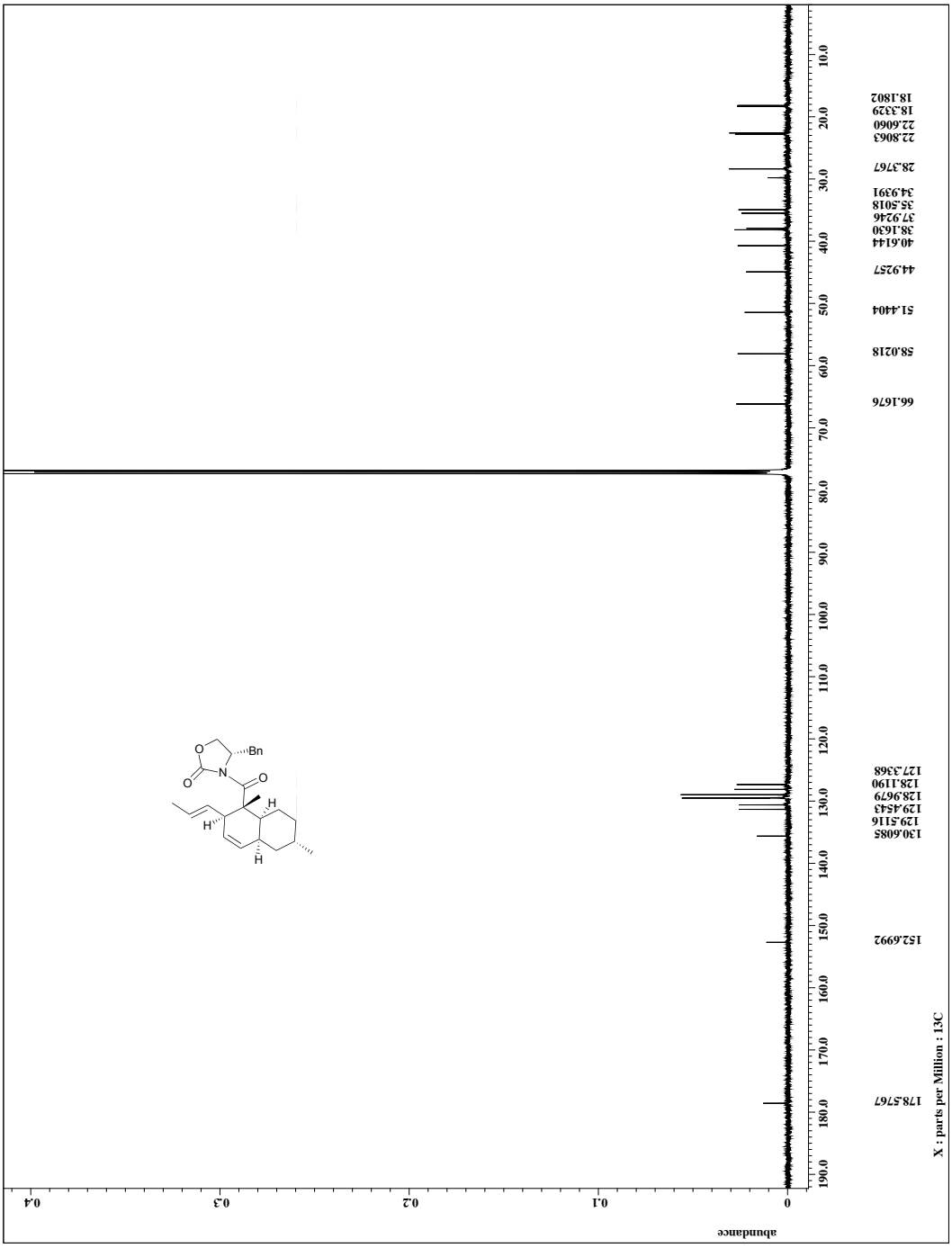
Spectrum 22 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **22**



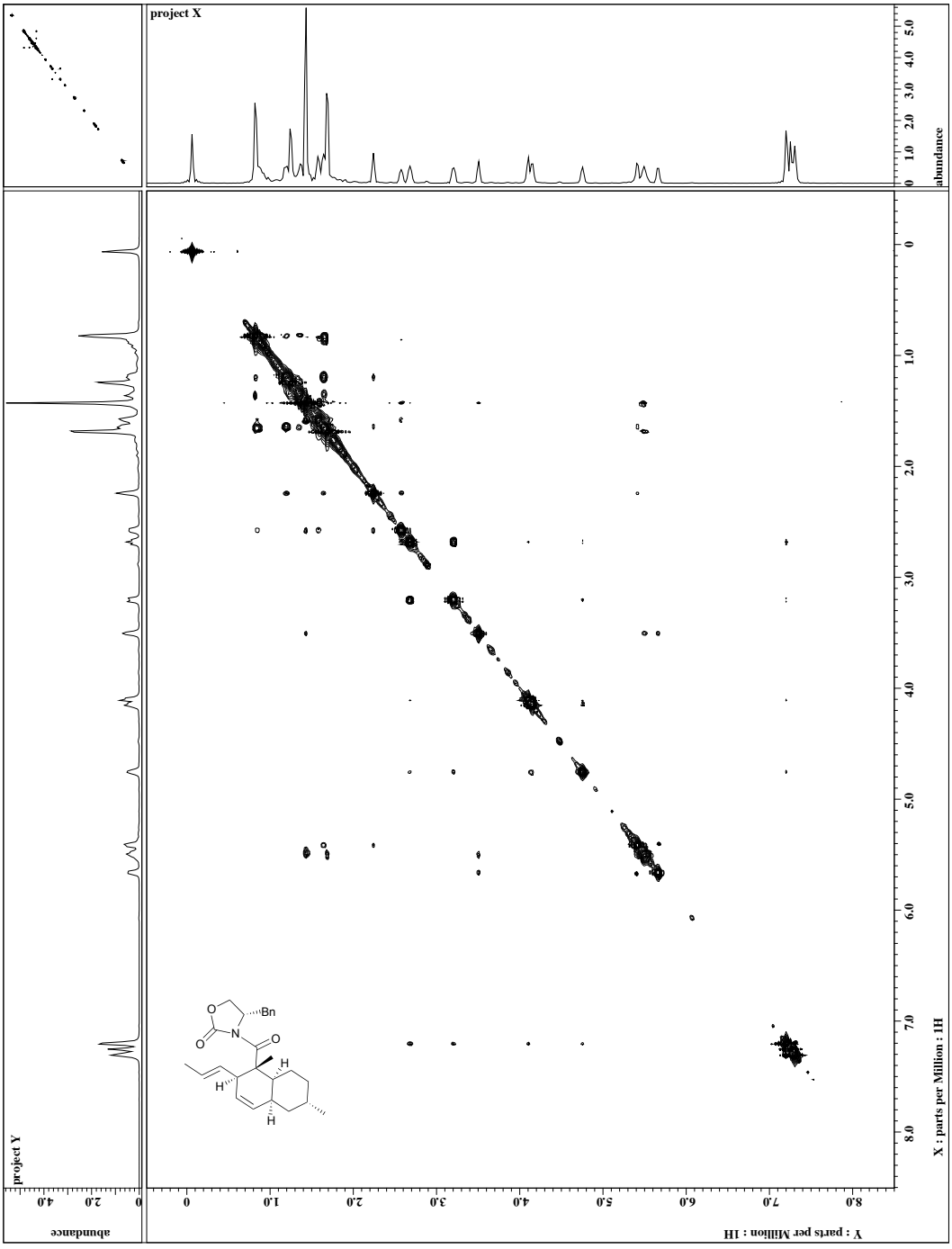
Spectrum 23 ^{1}H NOESY NMR ($CDCl_3$, 500 MHz) of compound **22**



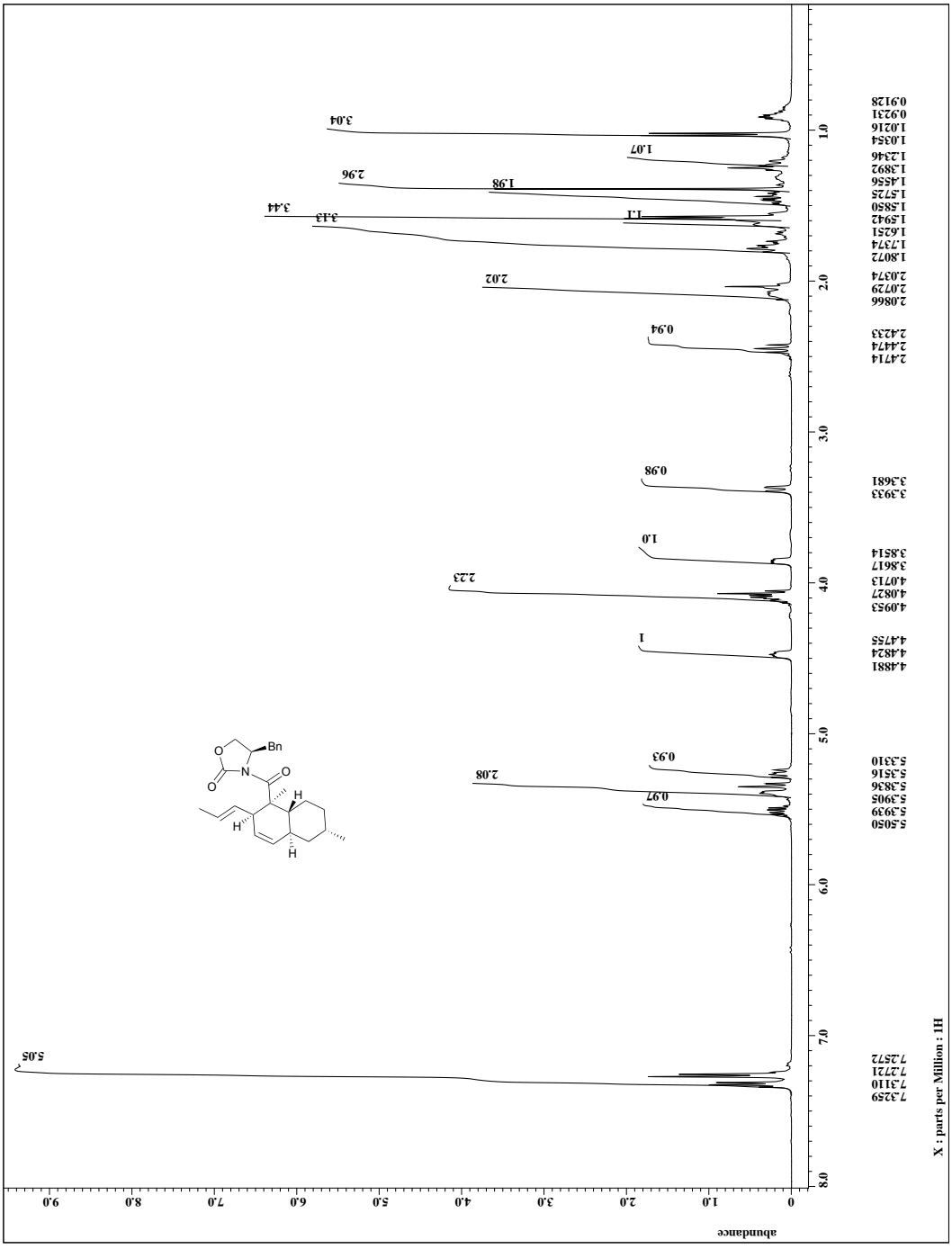
Spectrum 24 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **23**



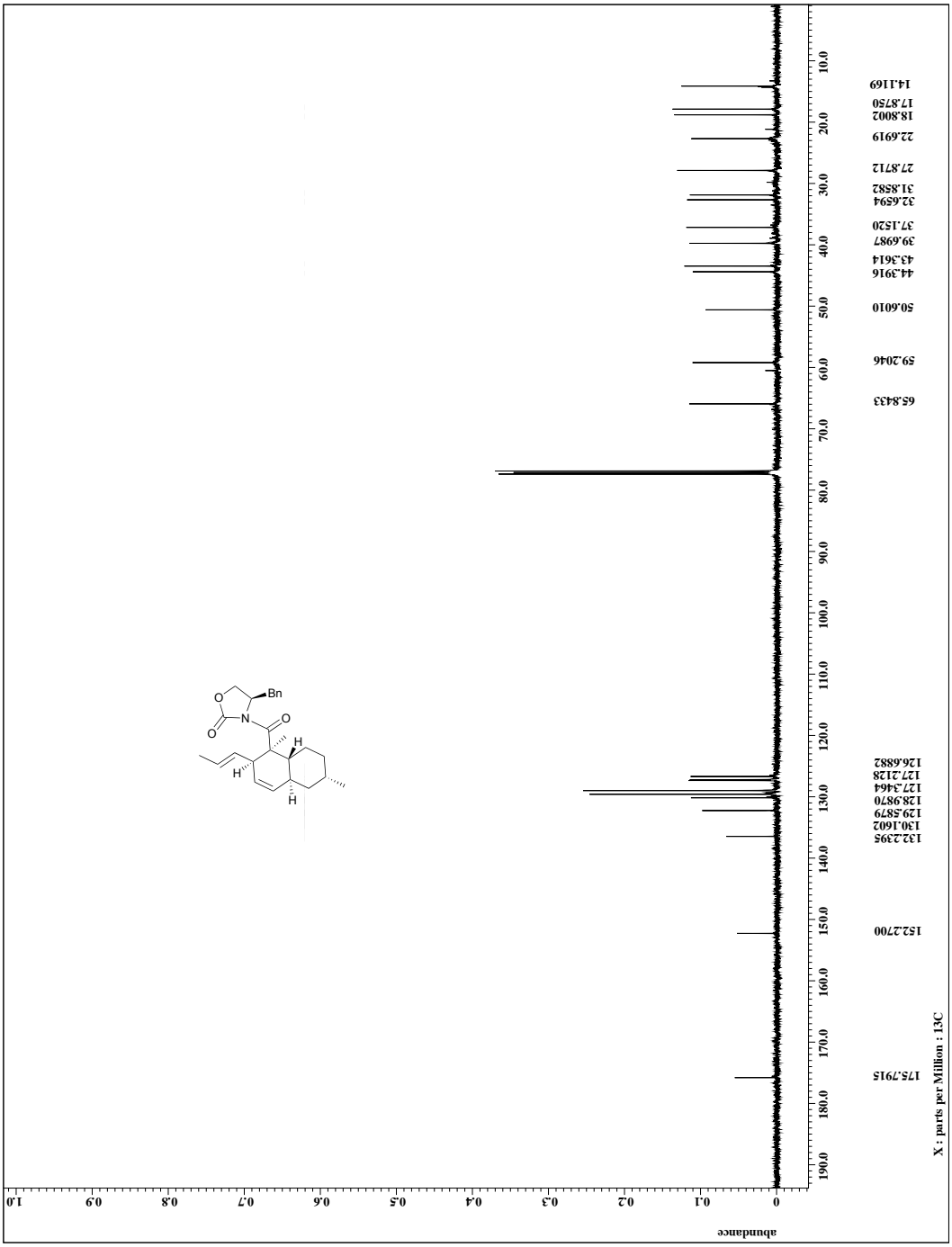
Spectrum 25 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **23**



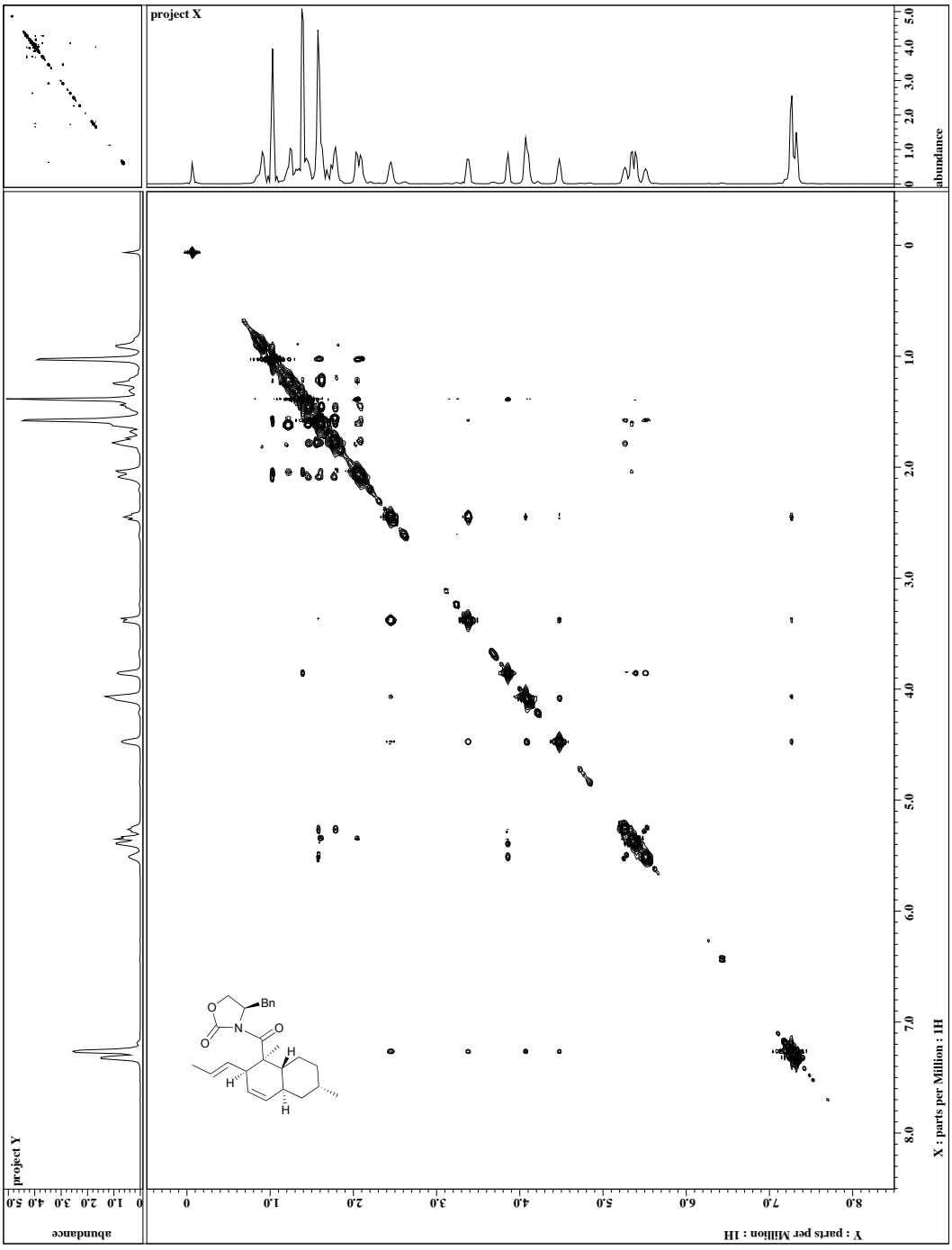
Spectrum 26 ^{1}H NOESY NMR ($CDCl_3$, 500 MHz) of compound **23**



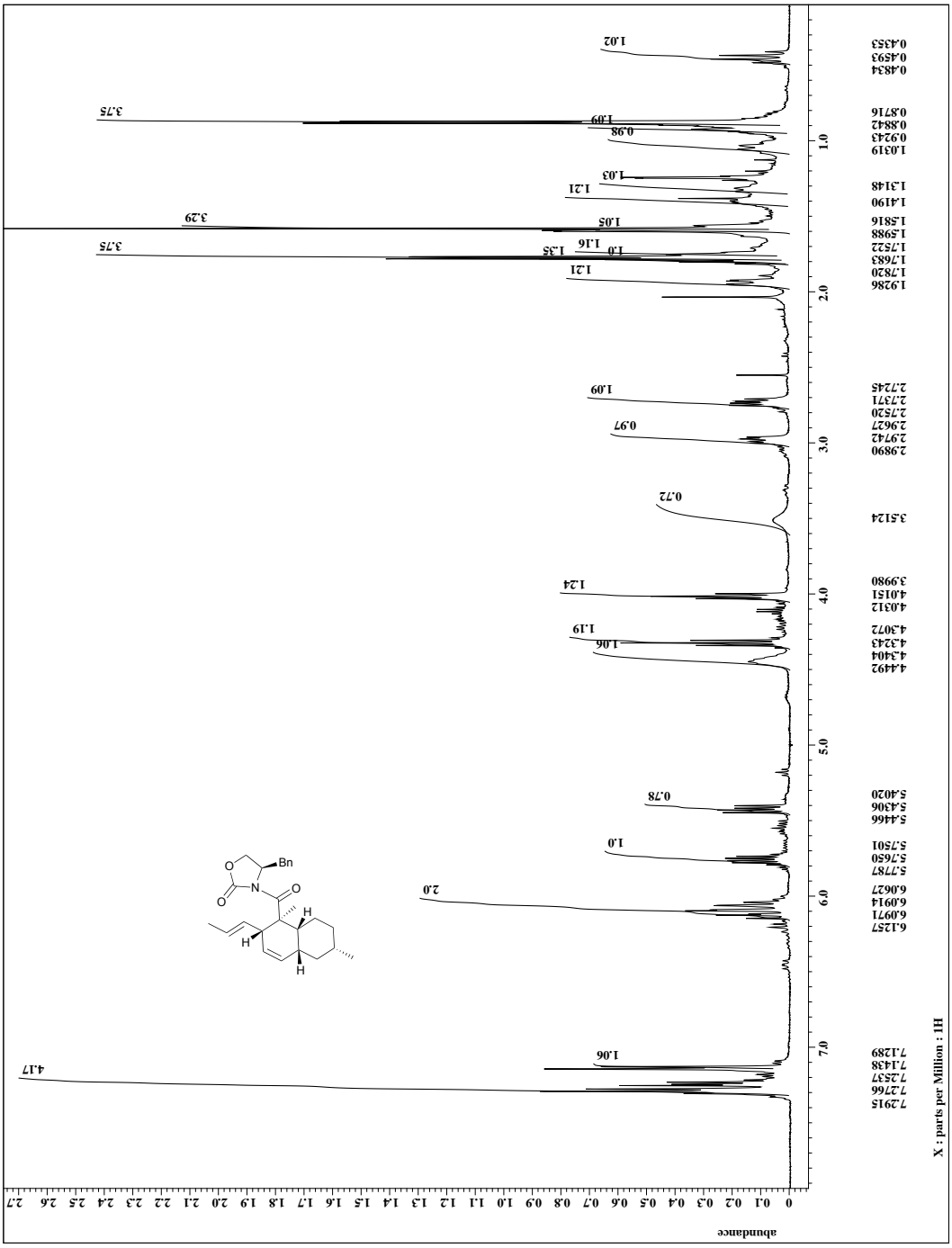
Spectrum 27 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **20**



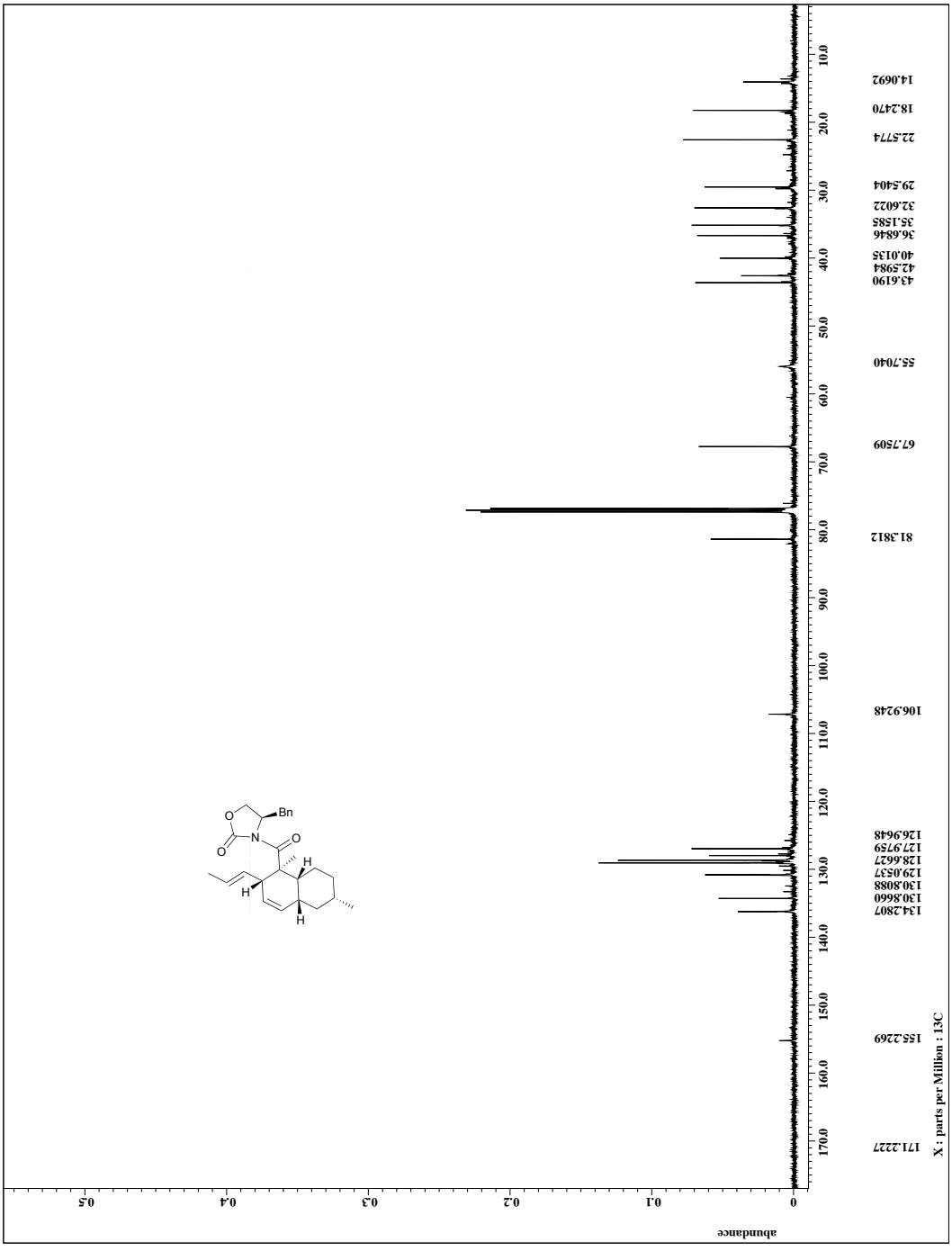
Spectrum 28 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **20**



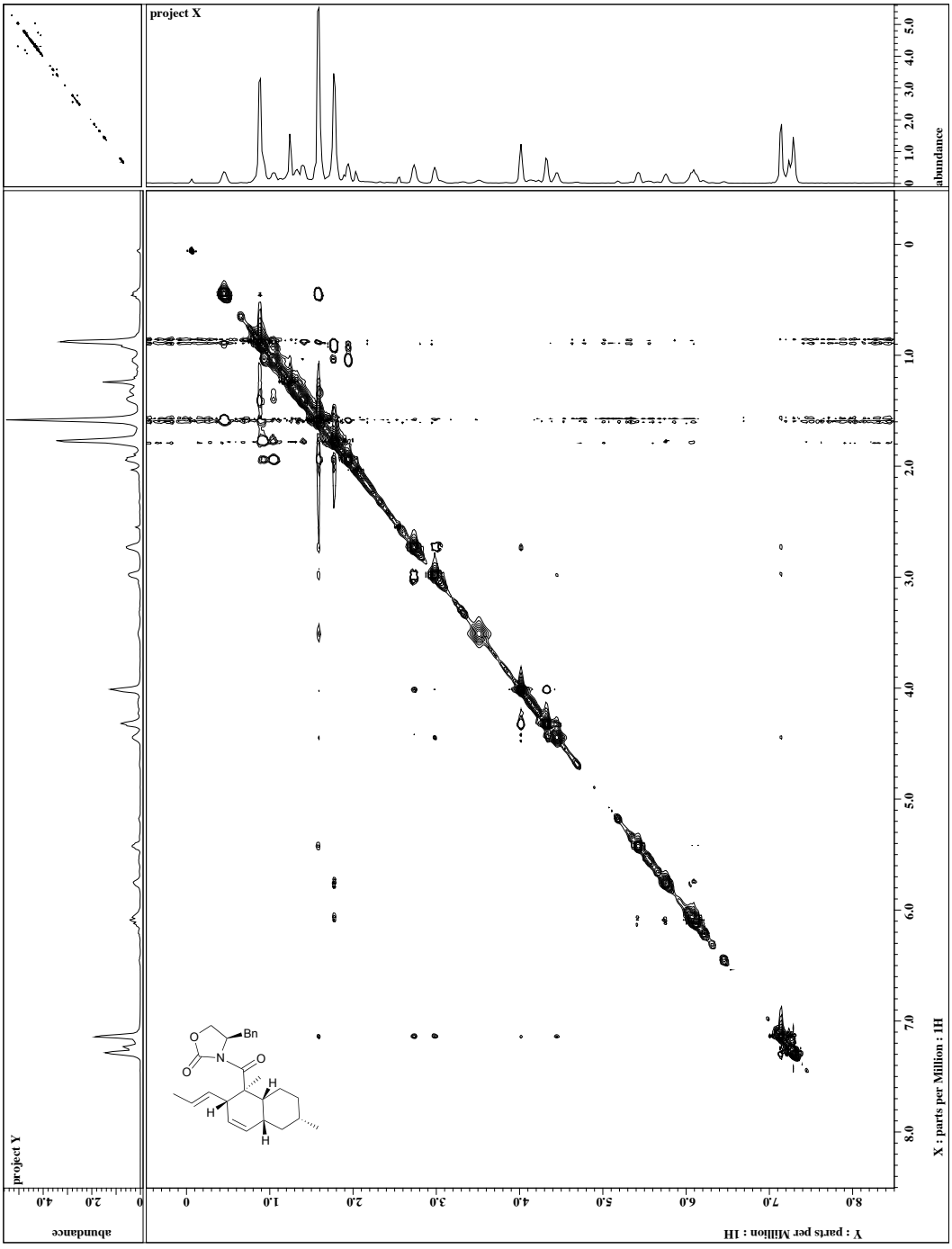
Spectrum 29 ^{1}H NOESY NMR ($CDCl_3$, 500 MHz) of compound **20**



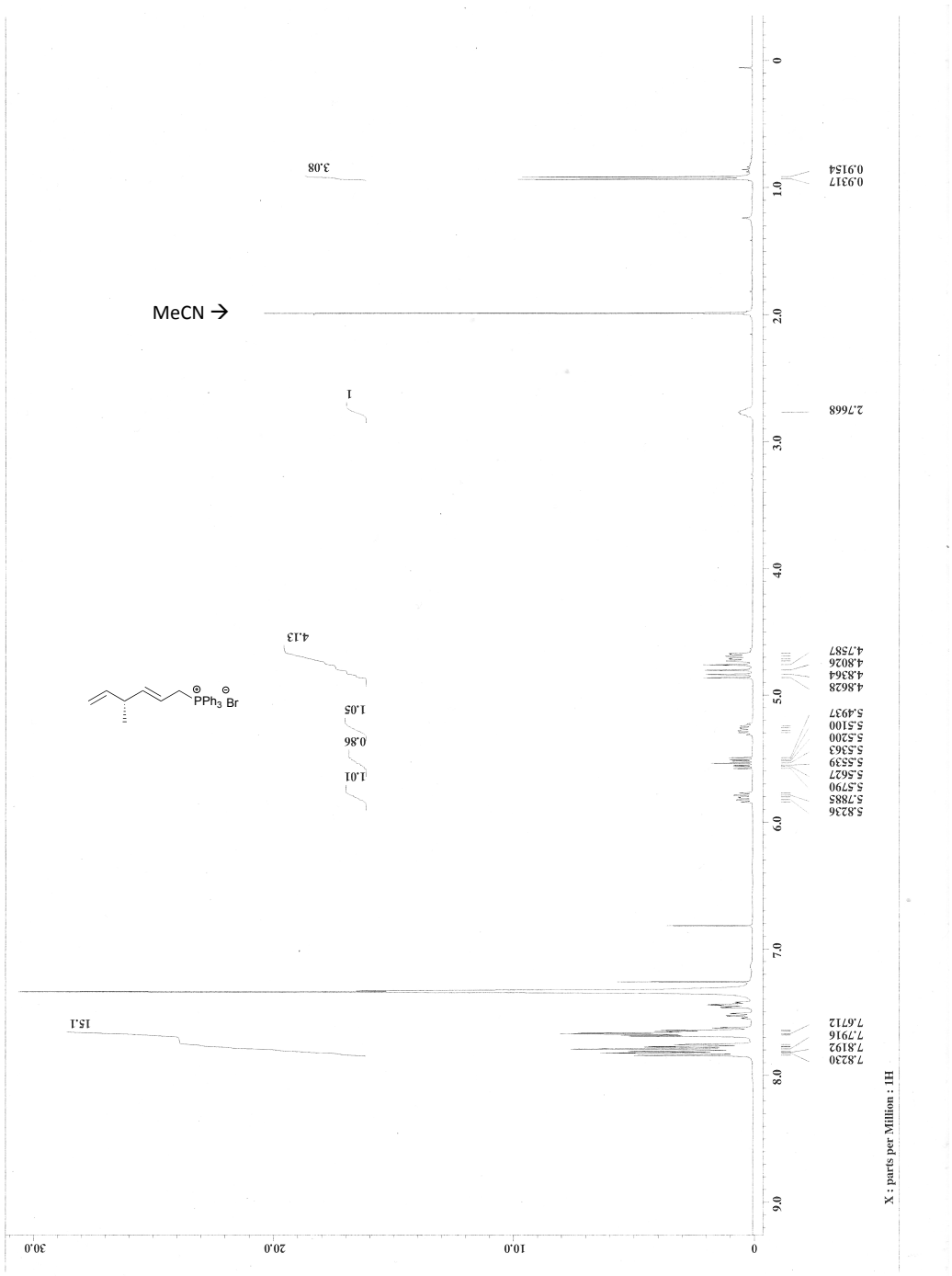
Spectrum 30 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **21**



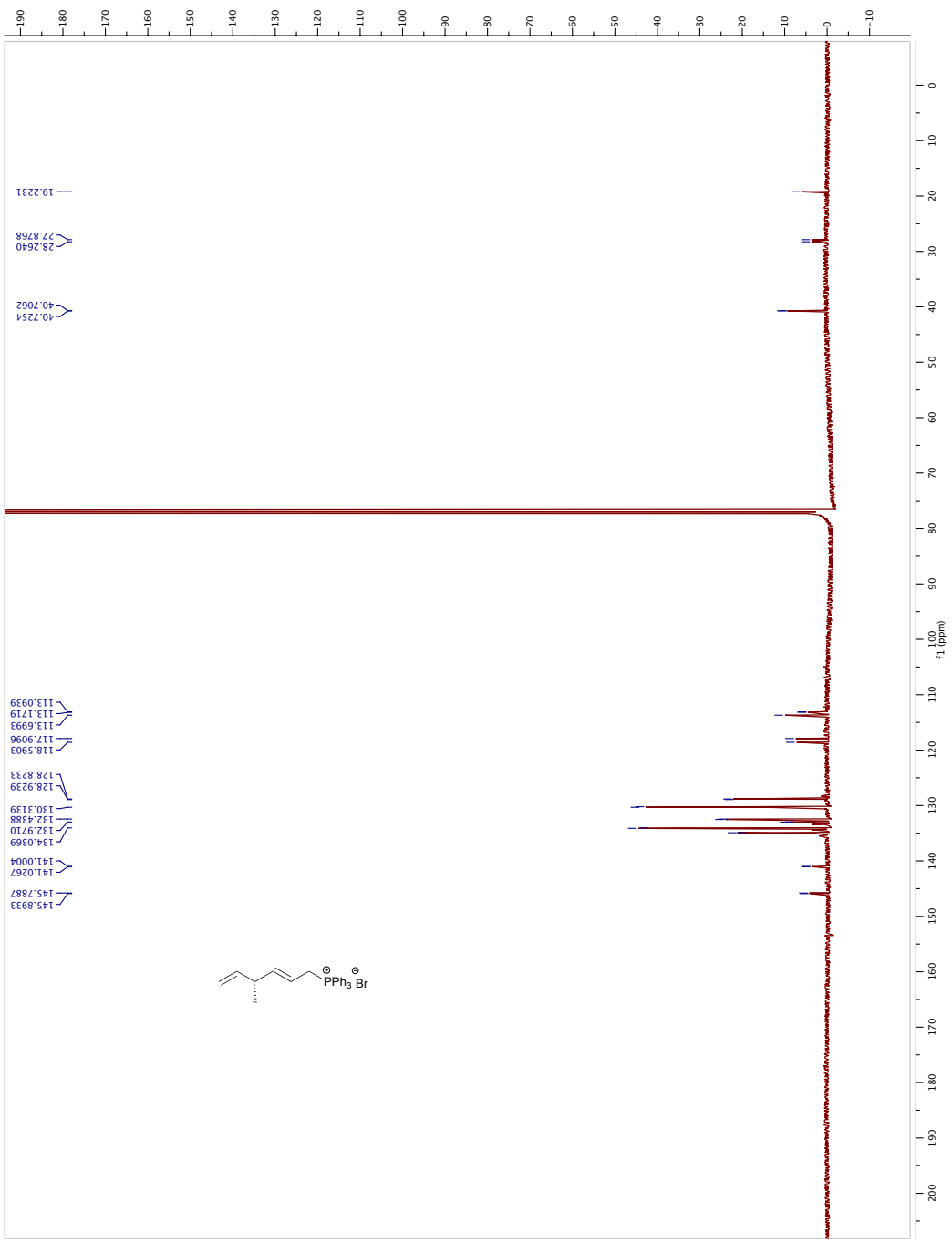
Spectrum 31 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **21**



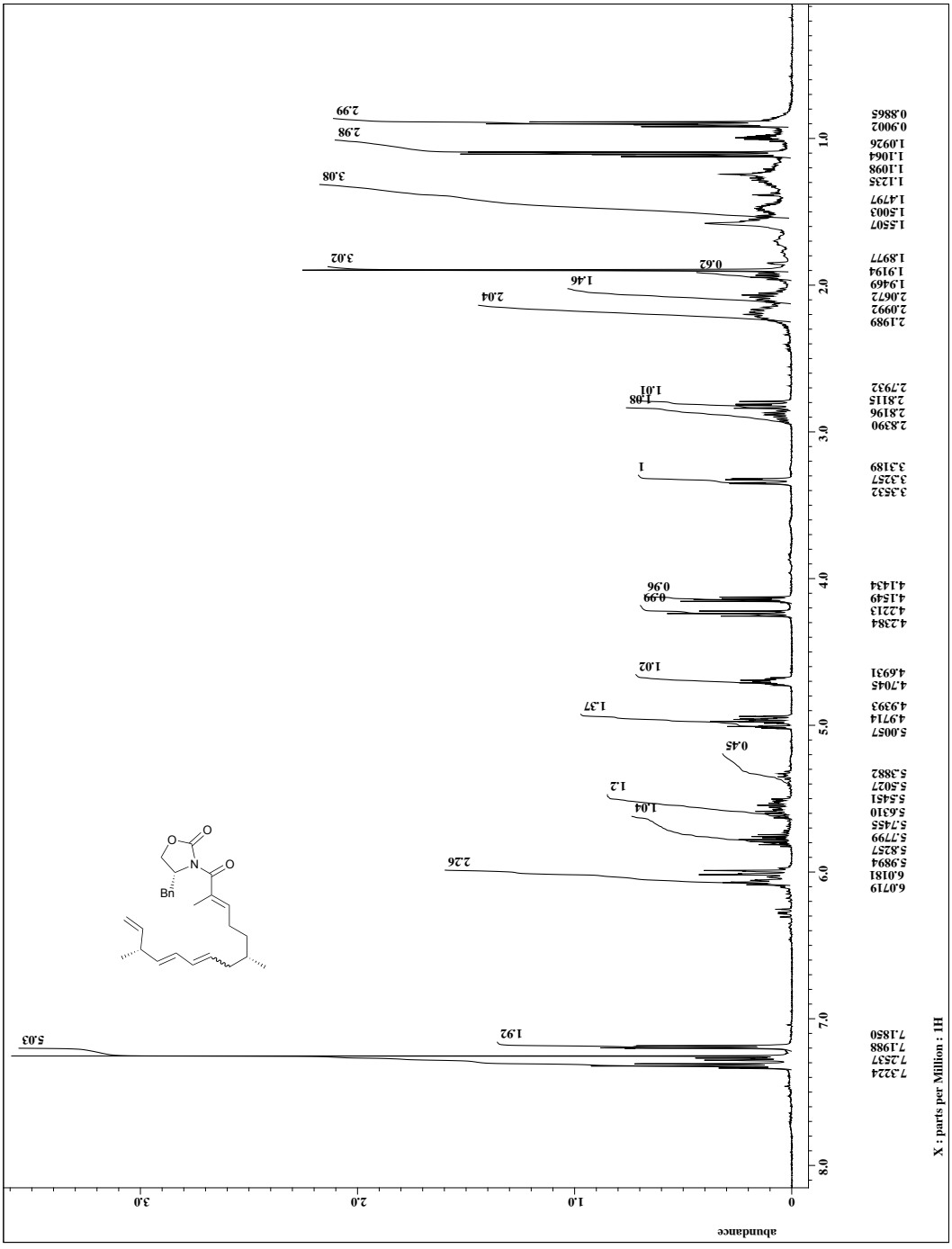
Spectrum 32 ^{1}H NOESY NMR ($CDCl_3$, 500 MHz) of compound **21**



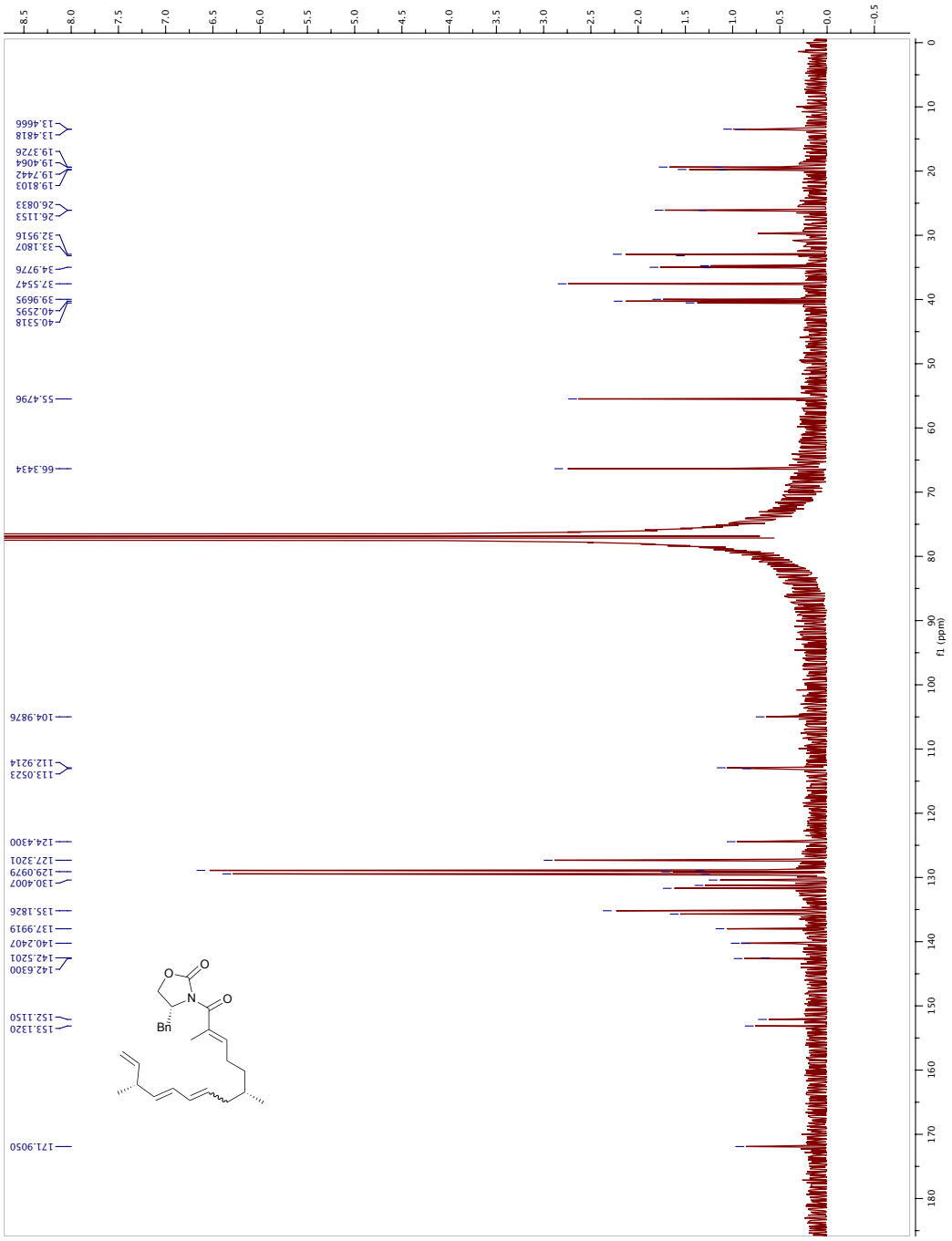
Spectrum 33 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **28**



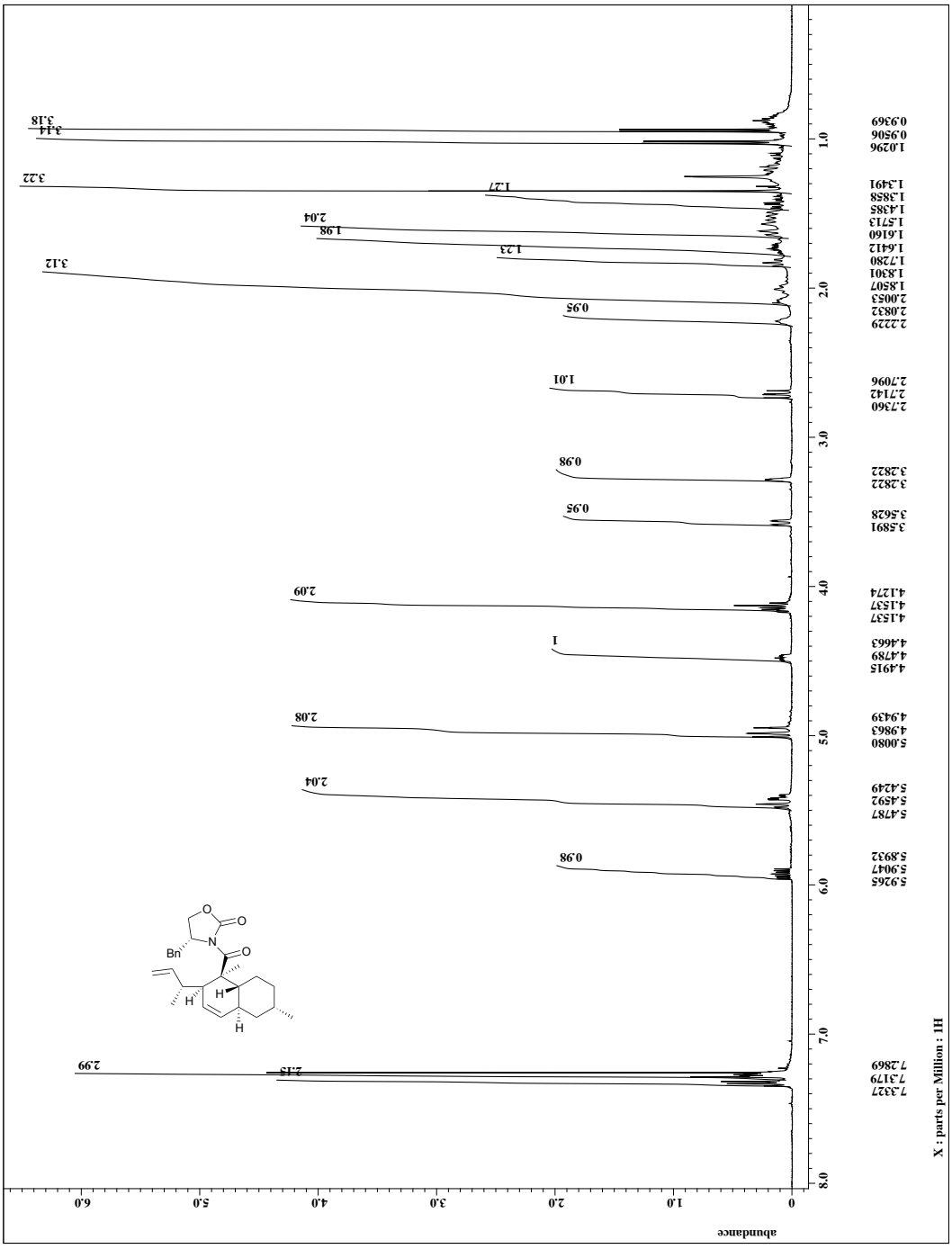
Spectrum 34 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **28**



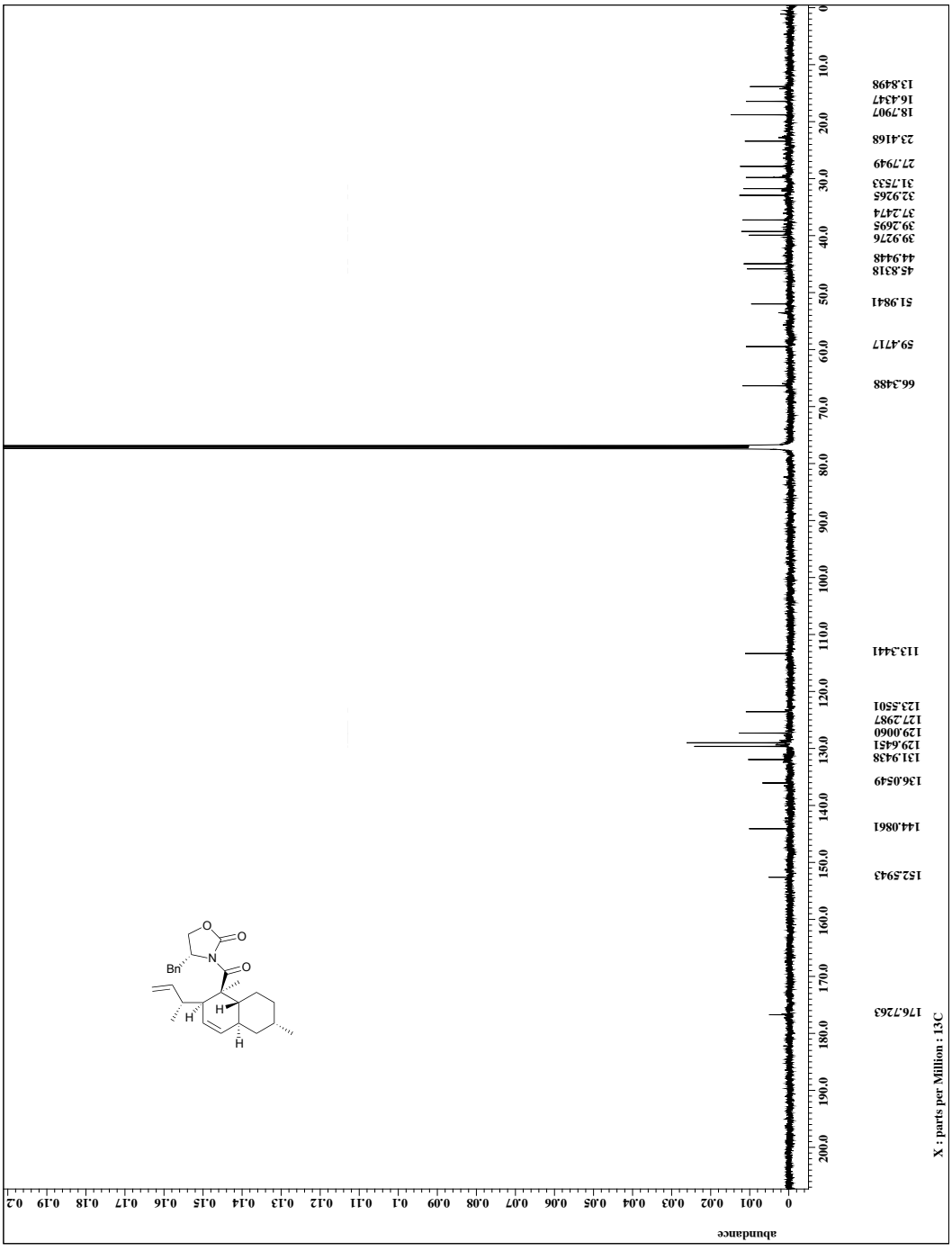
Spectrum 35 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **29**



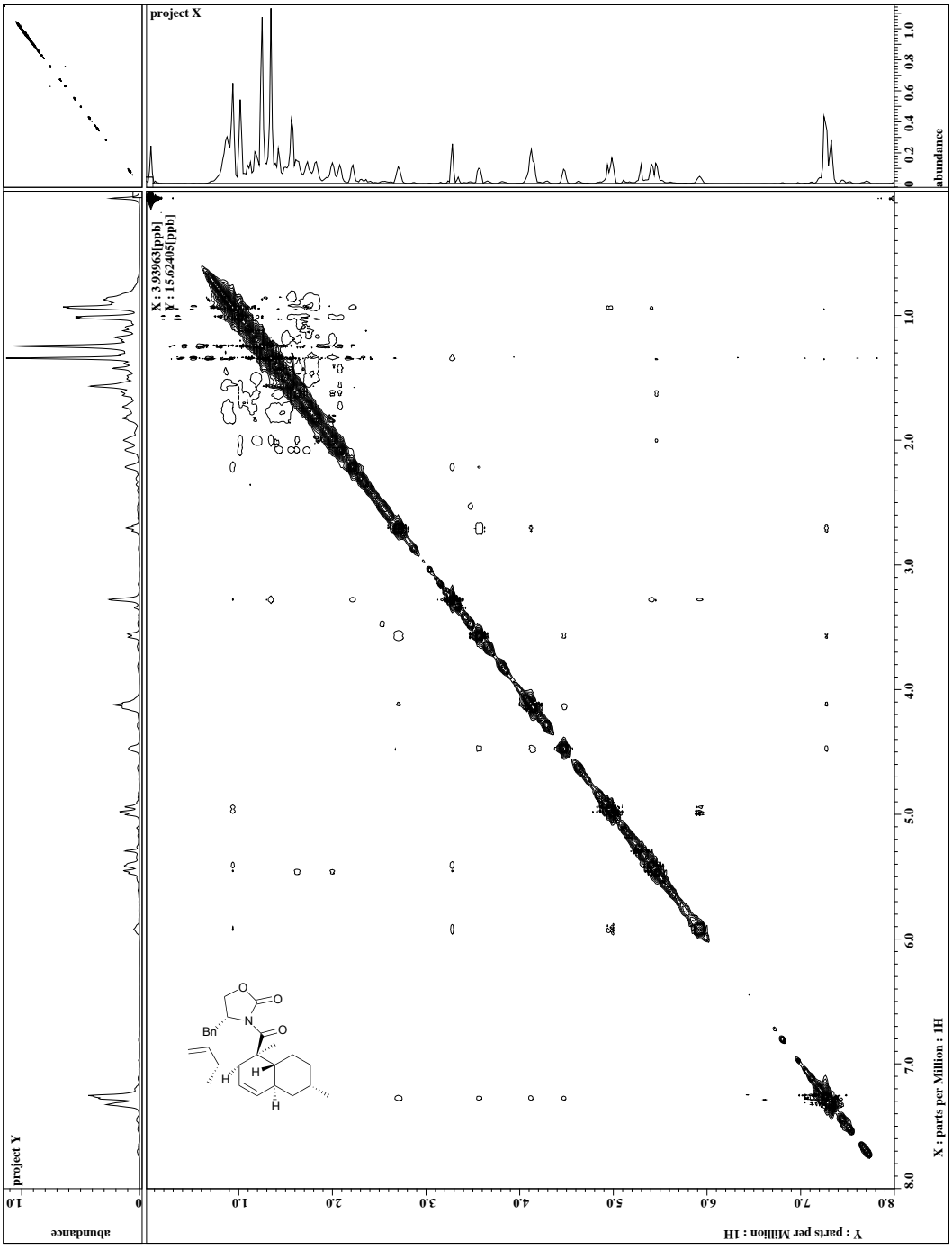
Spectrum 36 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **29**



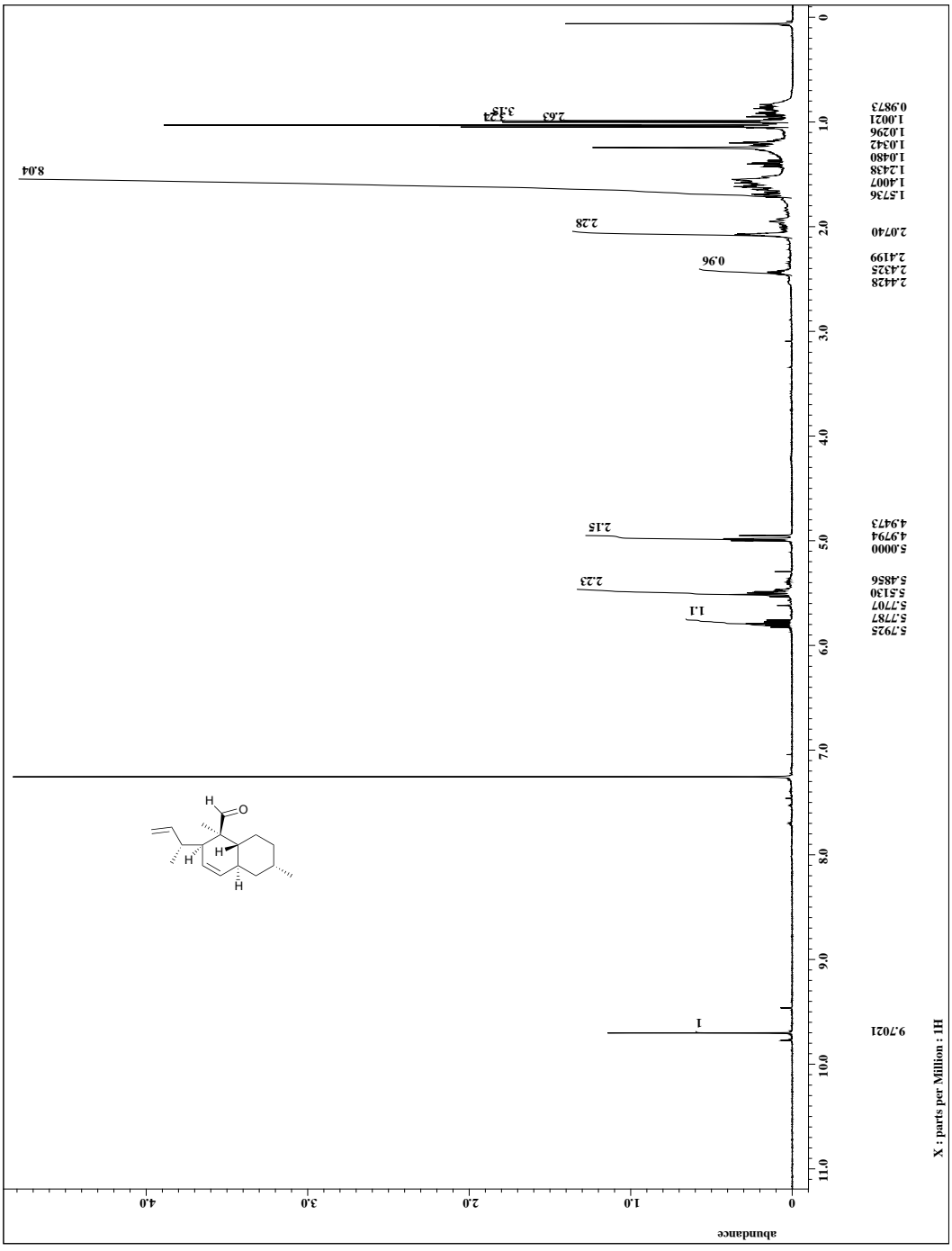
Spectrum 37 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **30**



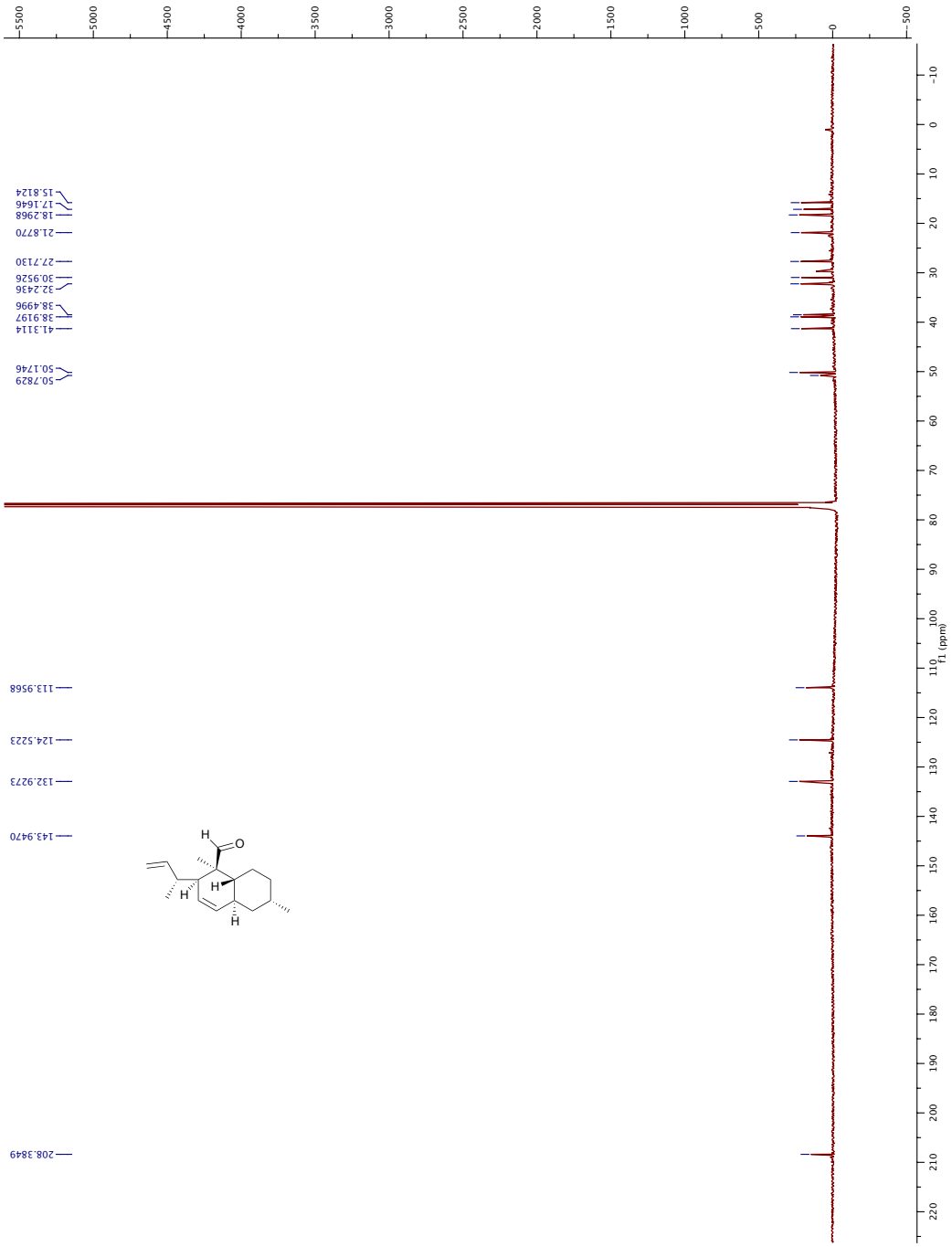
Spectrum 38 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **30**



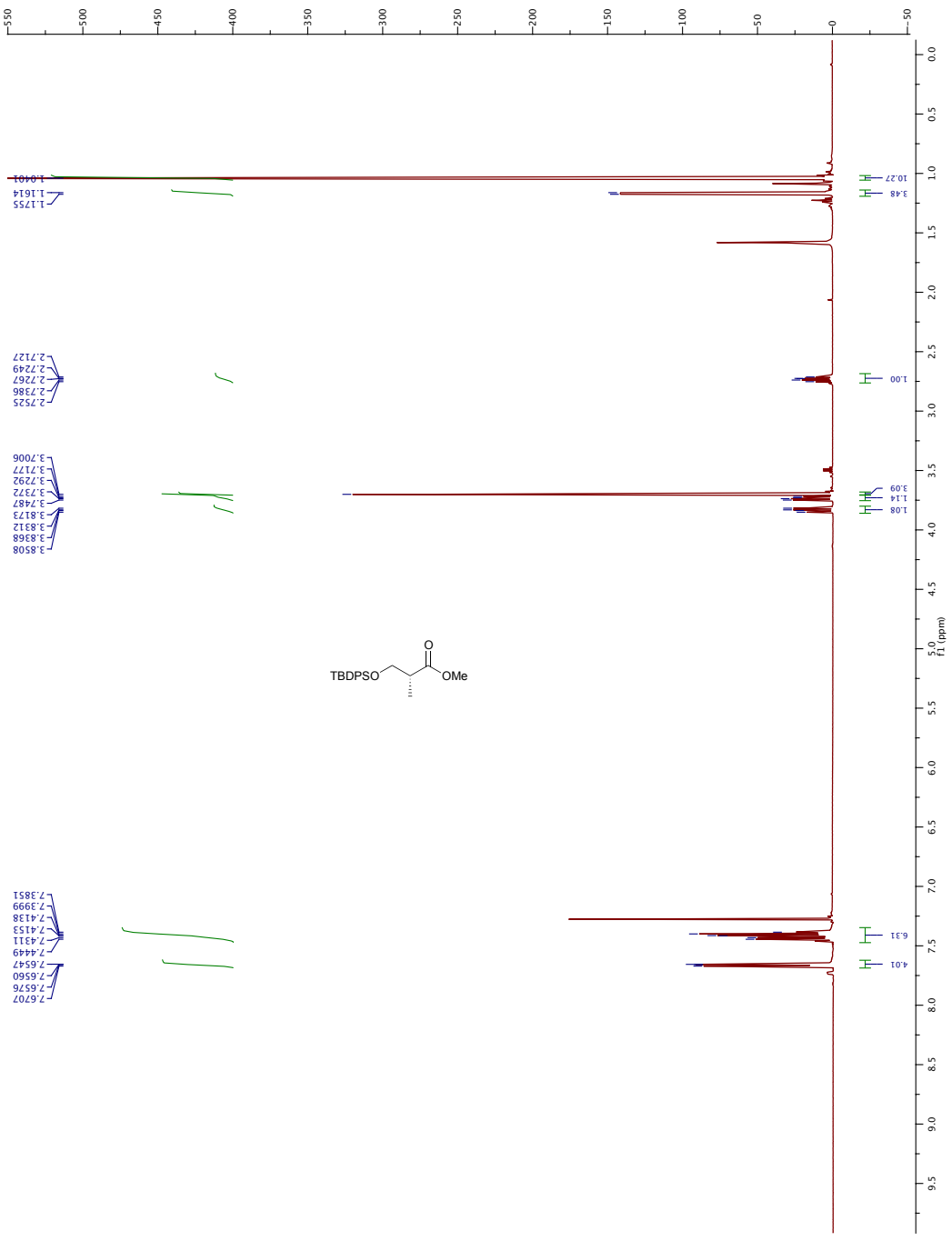
Spectrum 39 ^{1}H NOESY NMR ($CDCl_3$, 500 MHz) of compound **30**



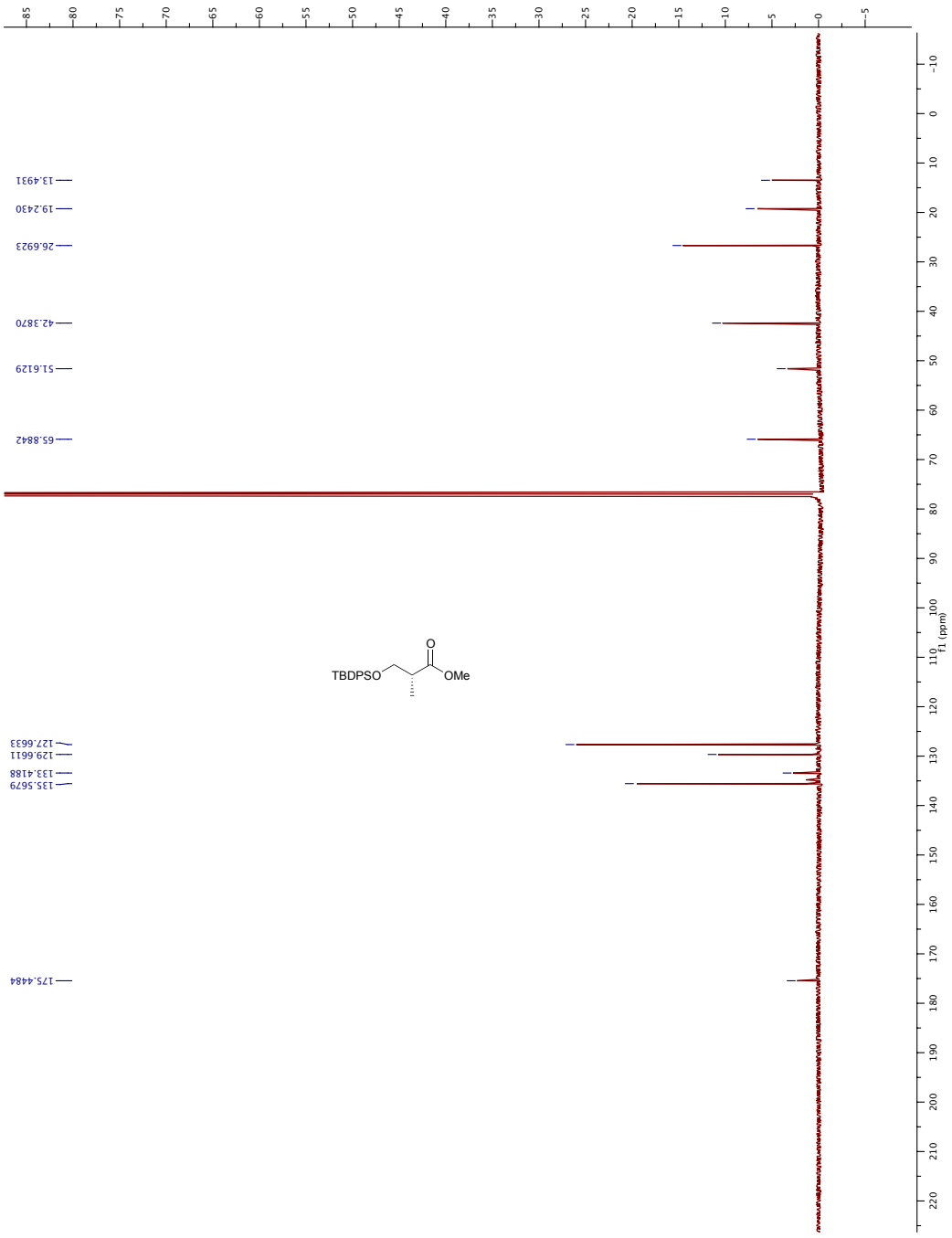
Spectrum 40 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **31**



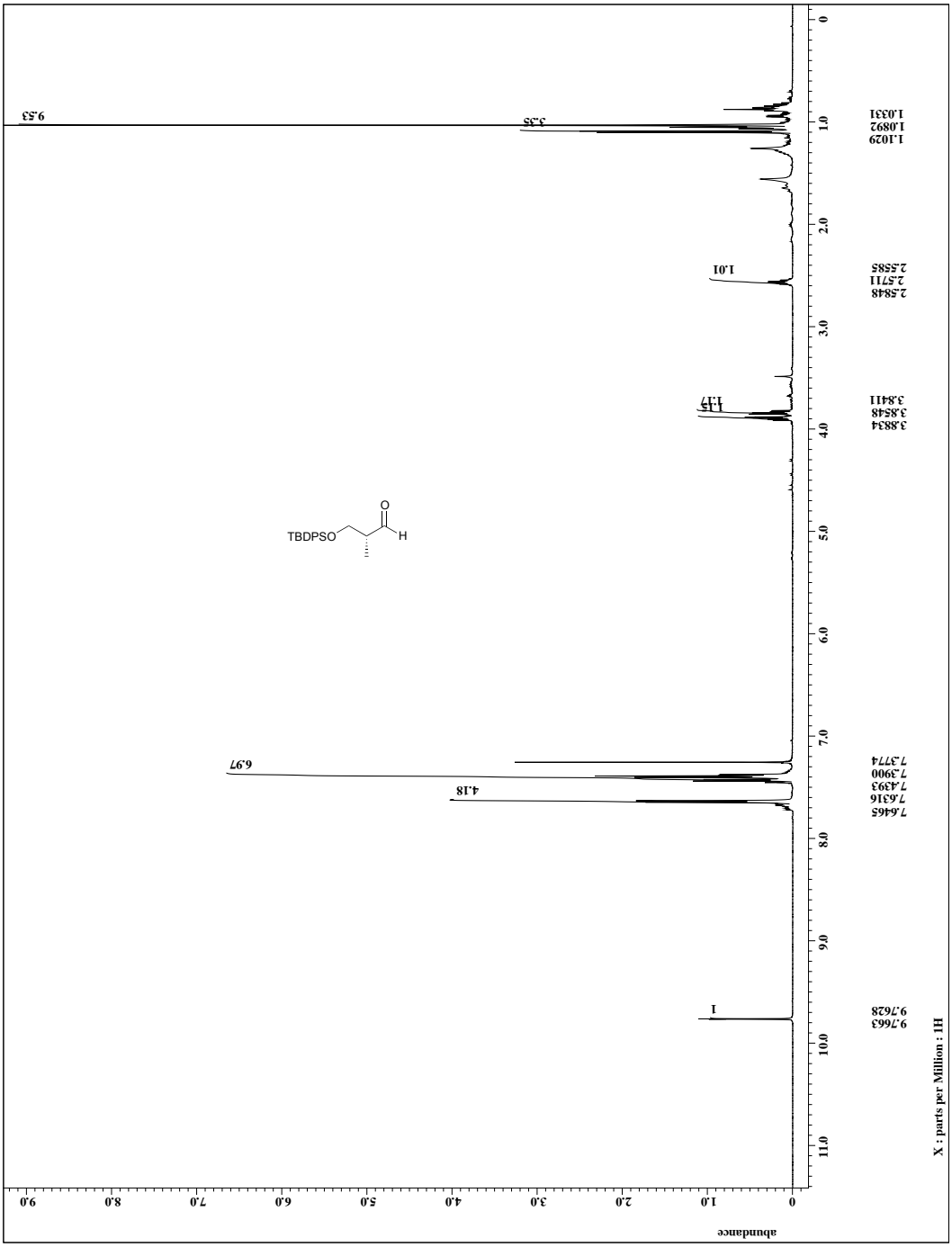
Spectrum 41 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **31**



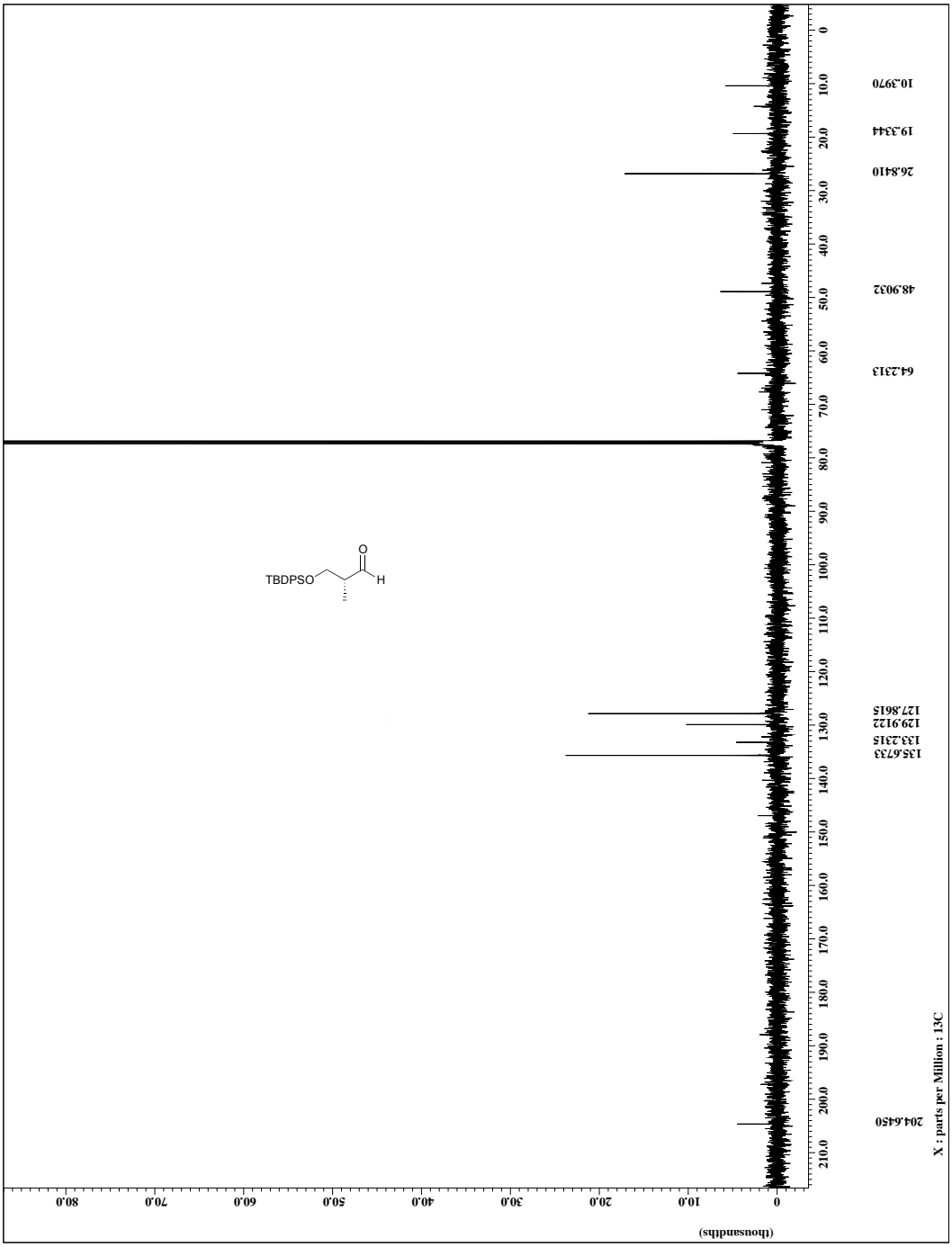
Spectrum 42 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **32_1**



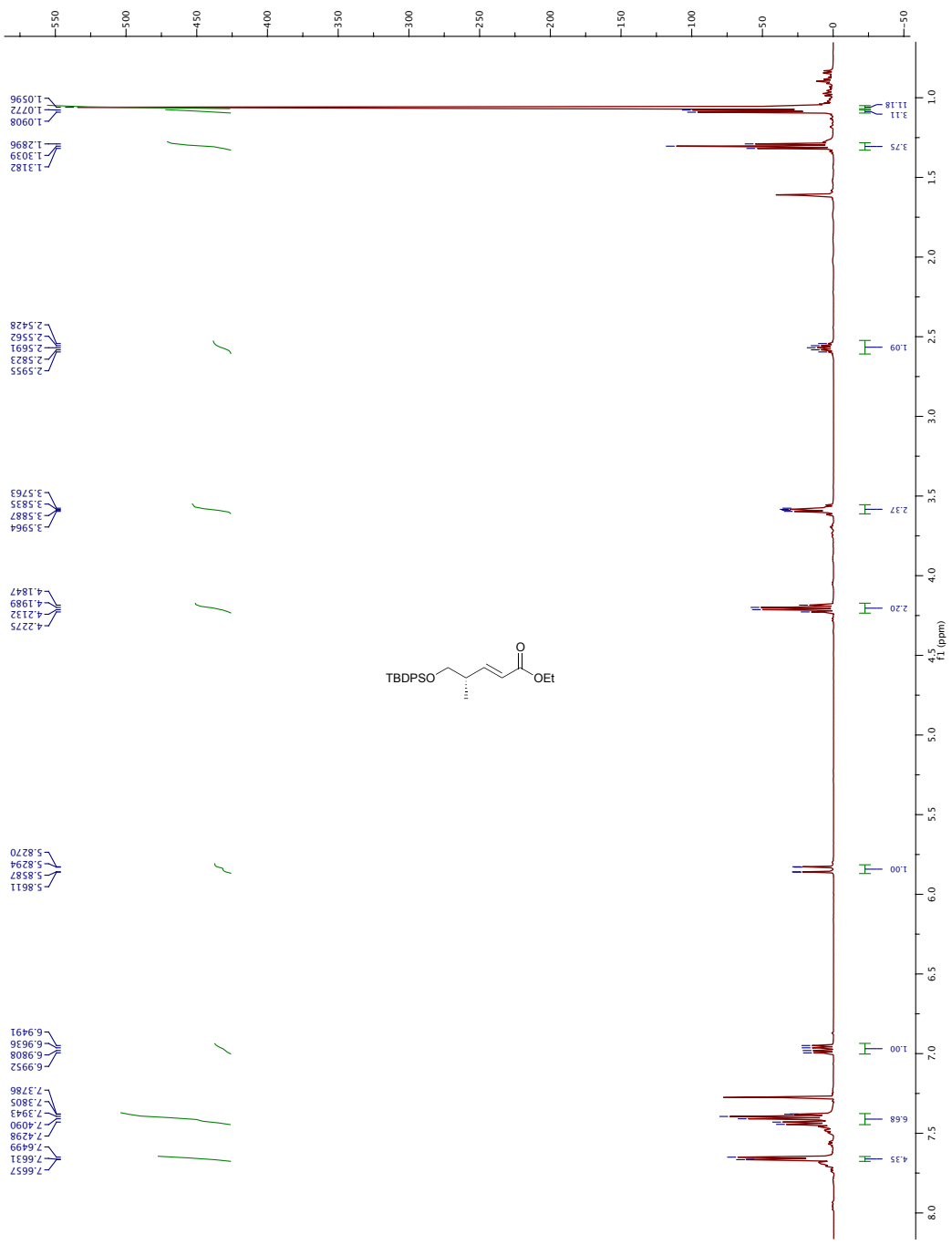
Spectrum 43 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **32_1**



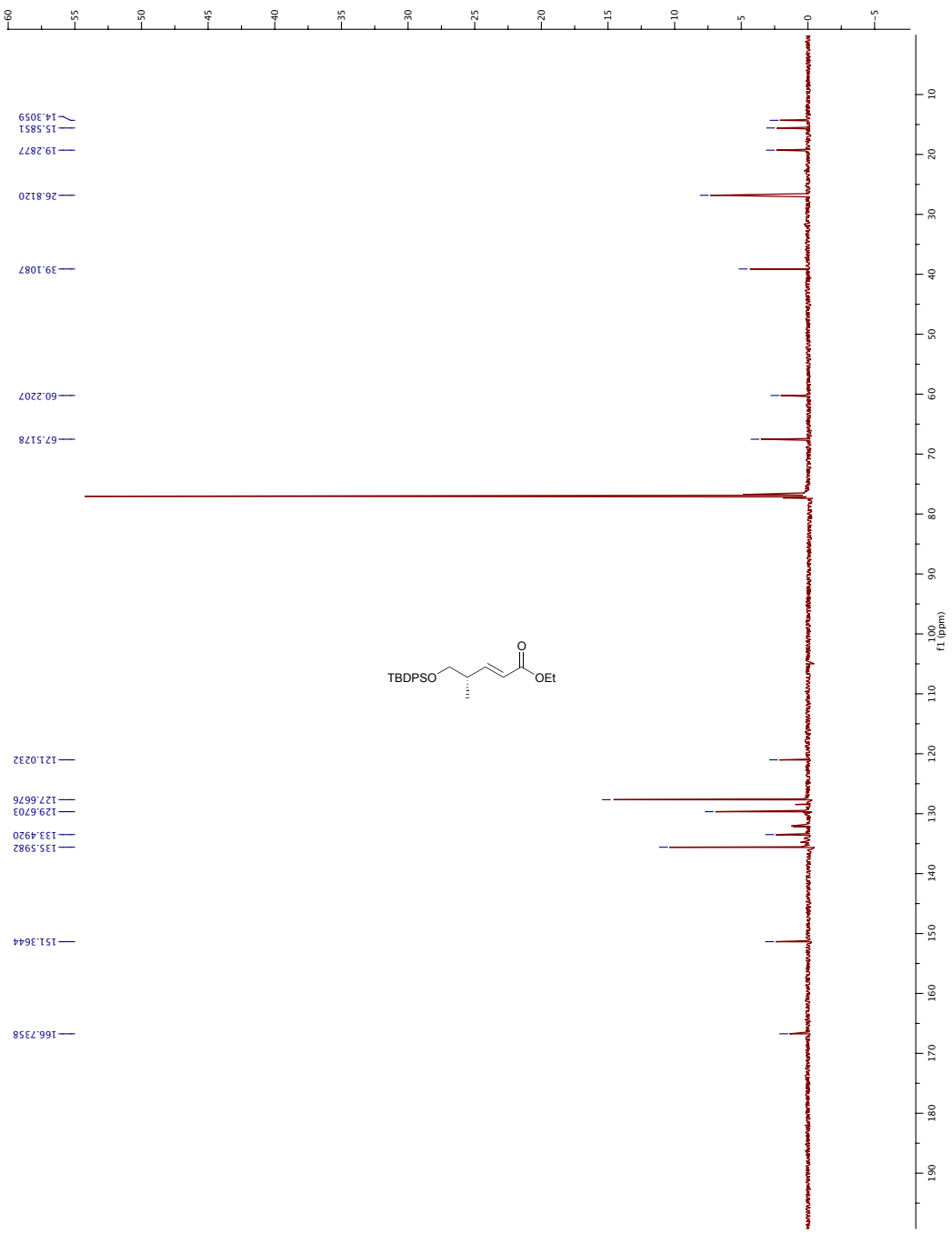
Spectrum 44 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **33**



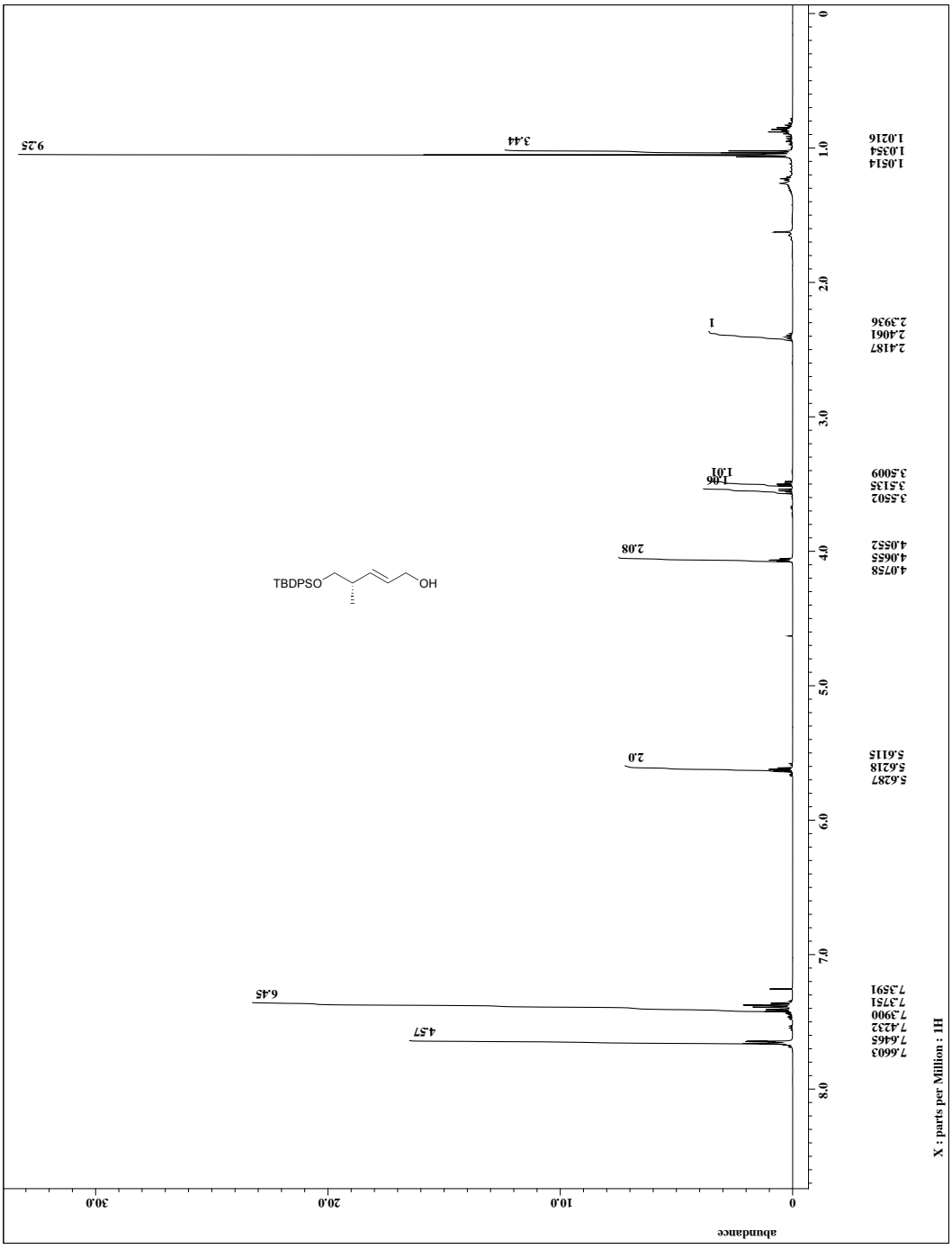
Spectrum 45 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **33**



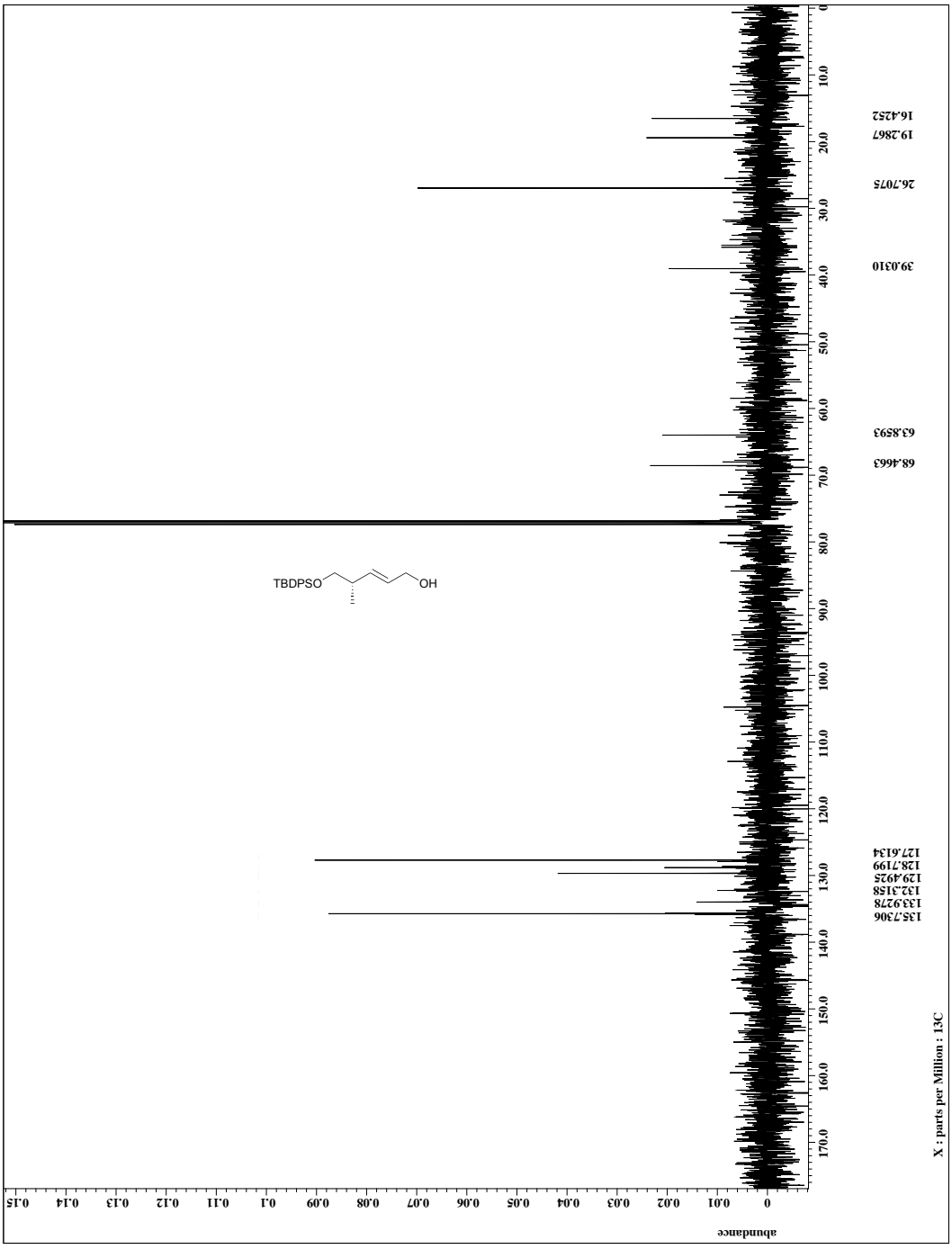
Spectrum 46 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **33_1**



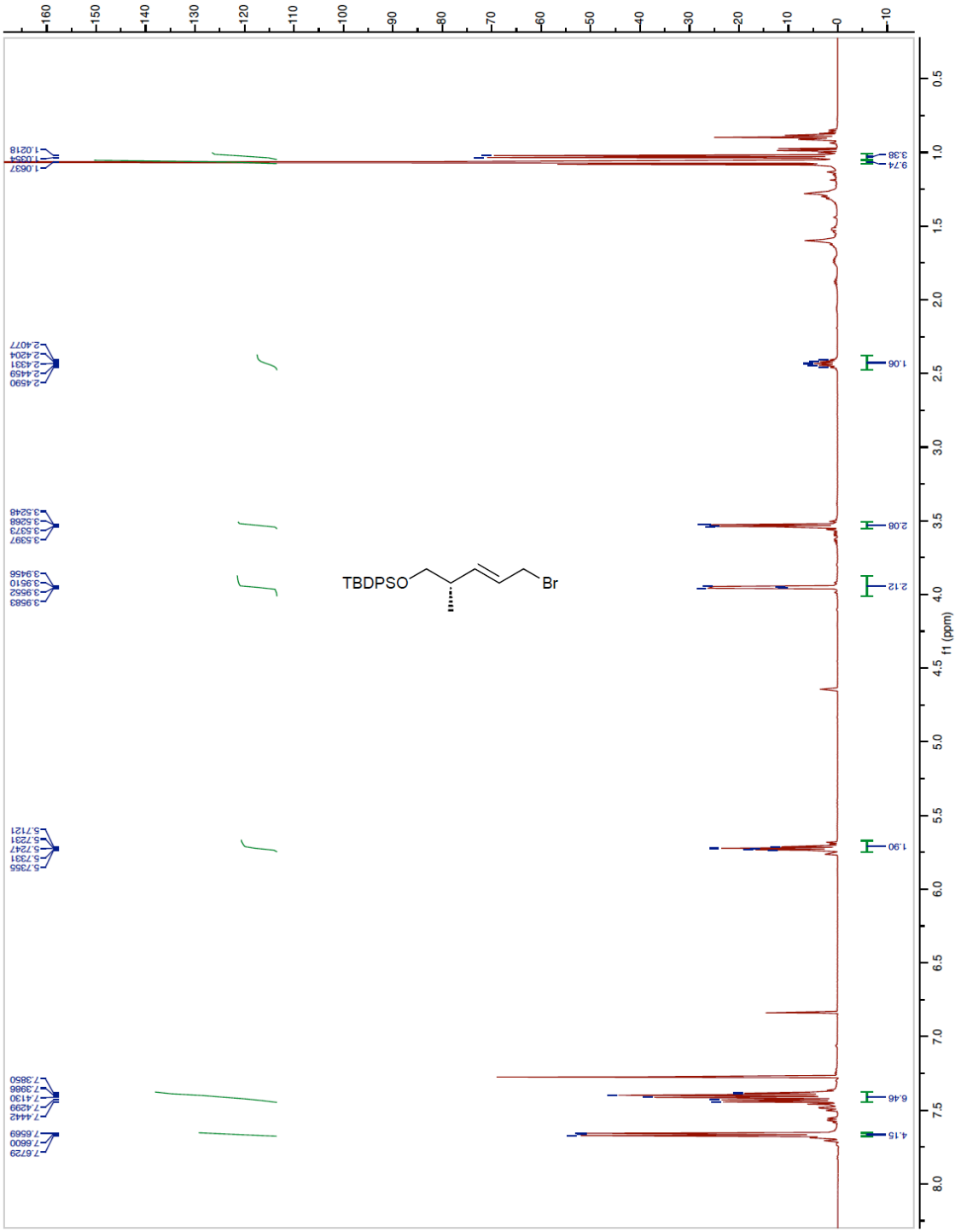
Spectrum 47 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **33_1**



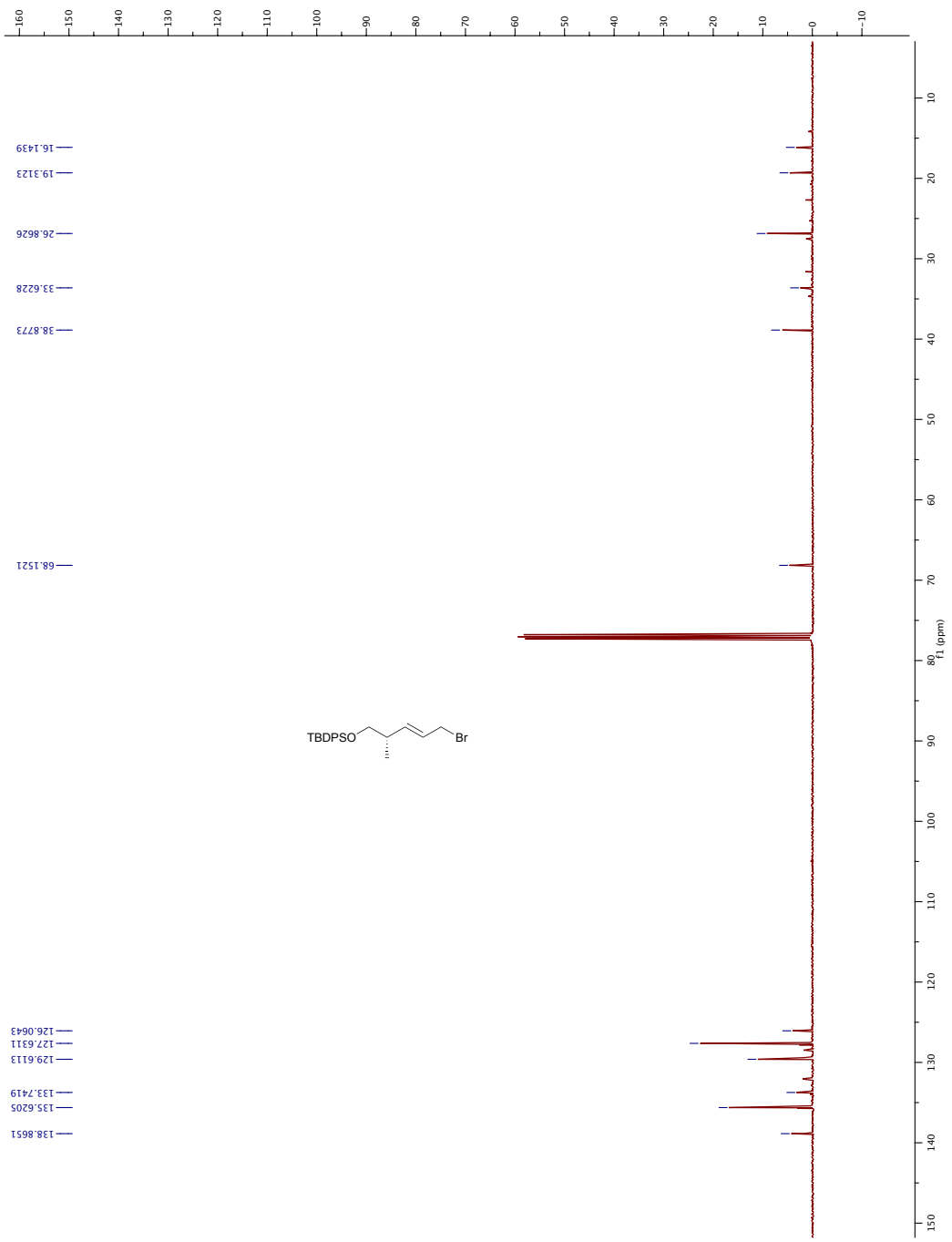
Spectrum 48 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **34**



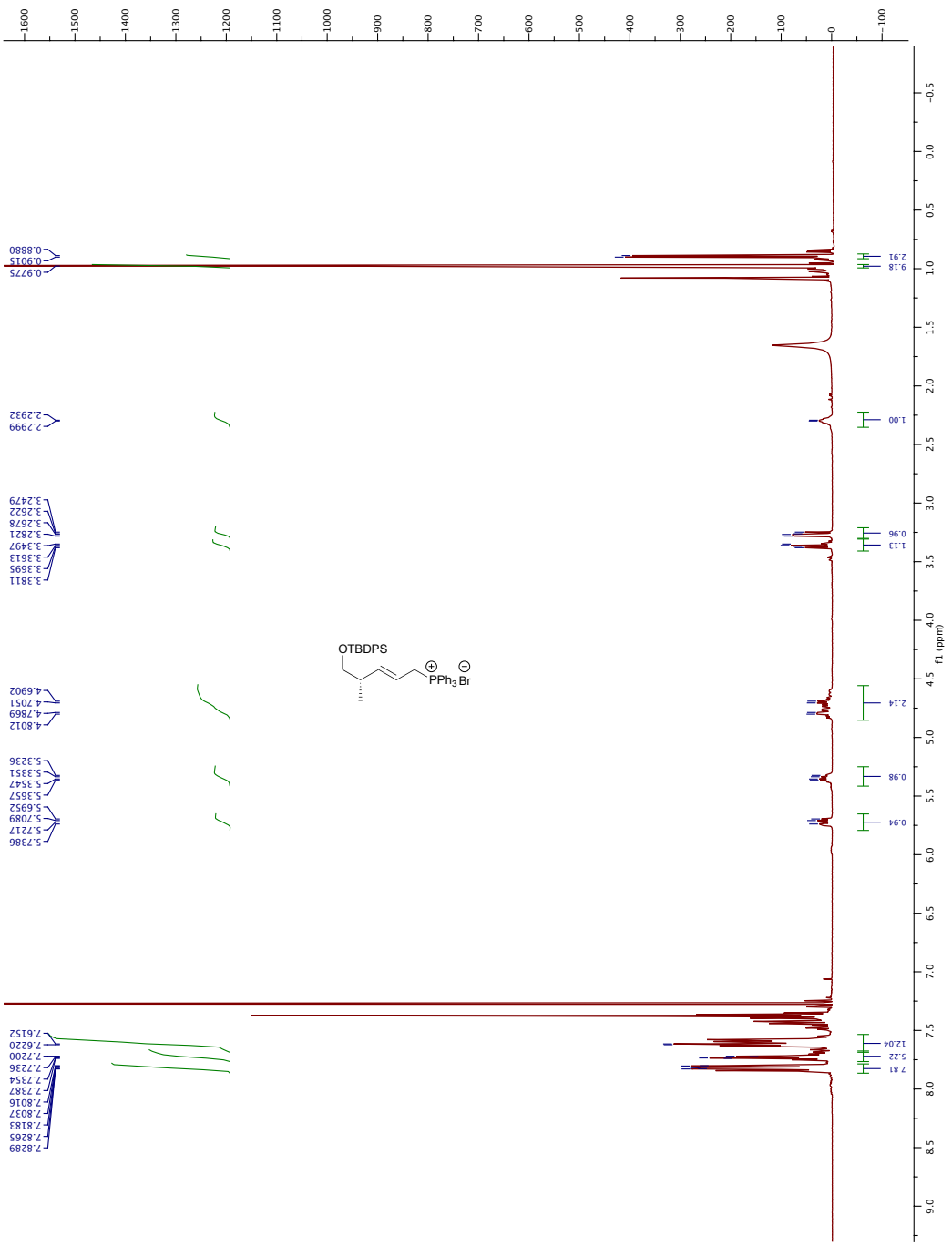
Spectrum 49 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **34**



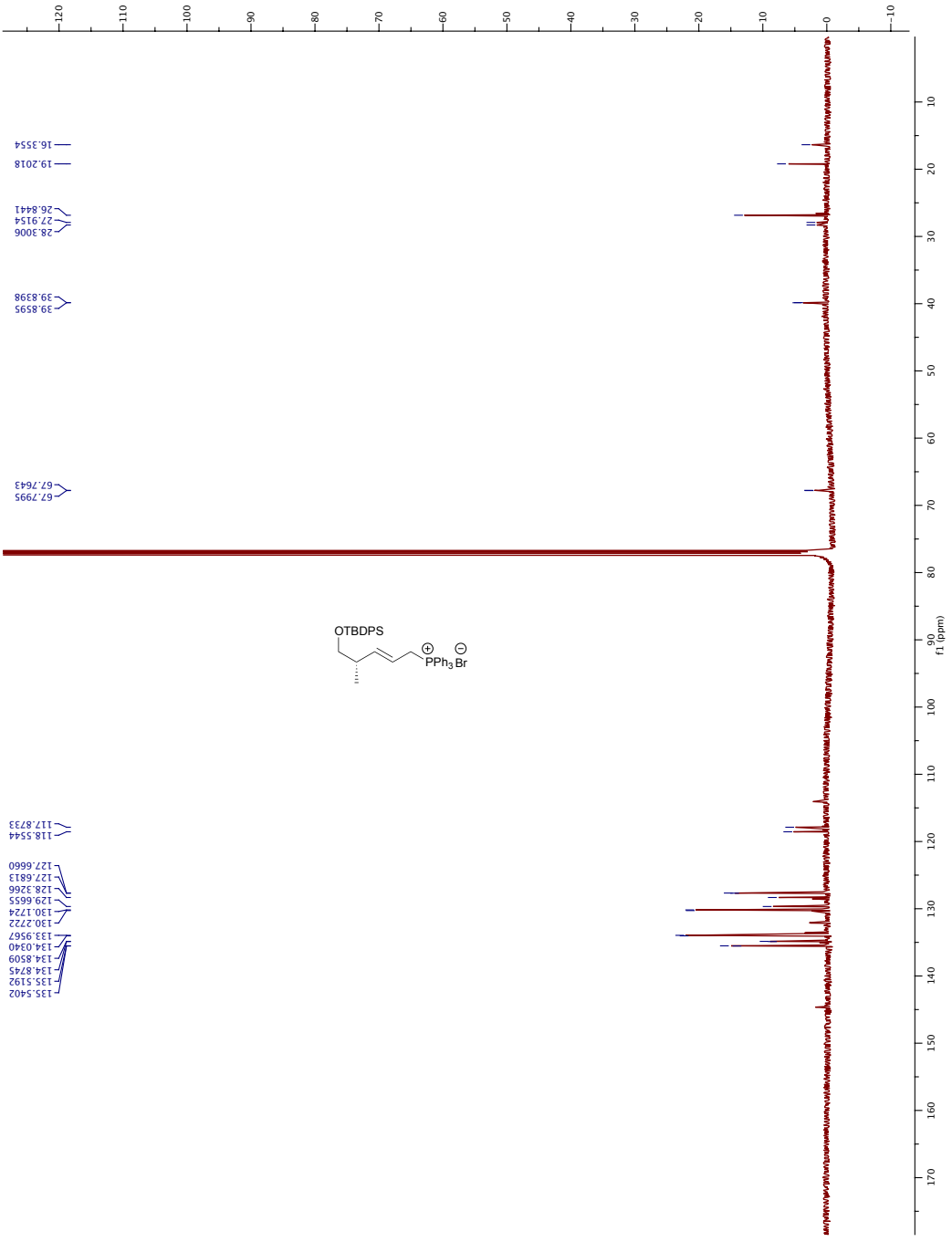
Spectrum 50 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **34_1**



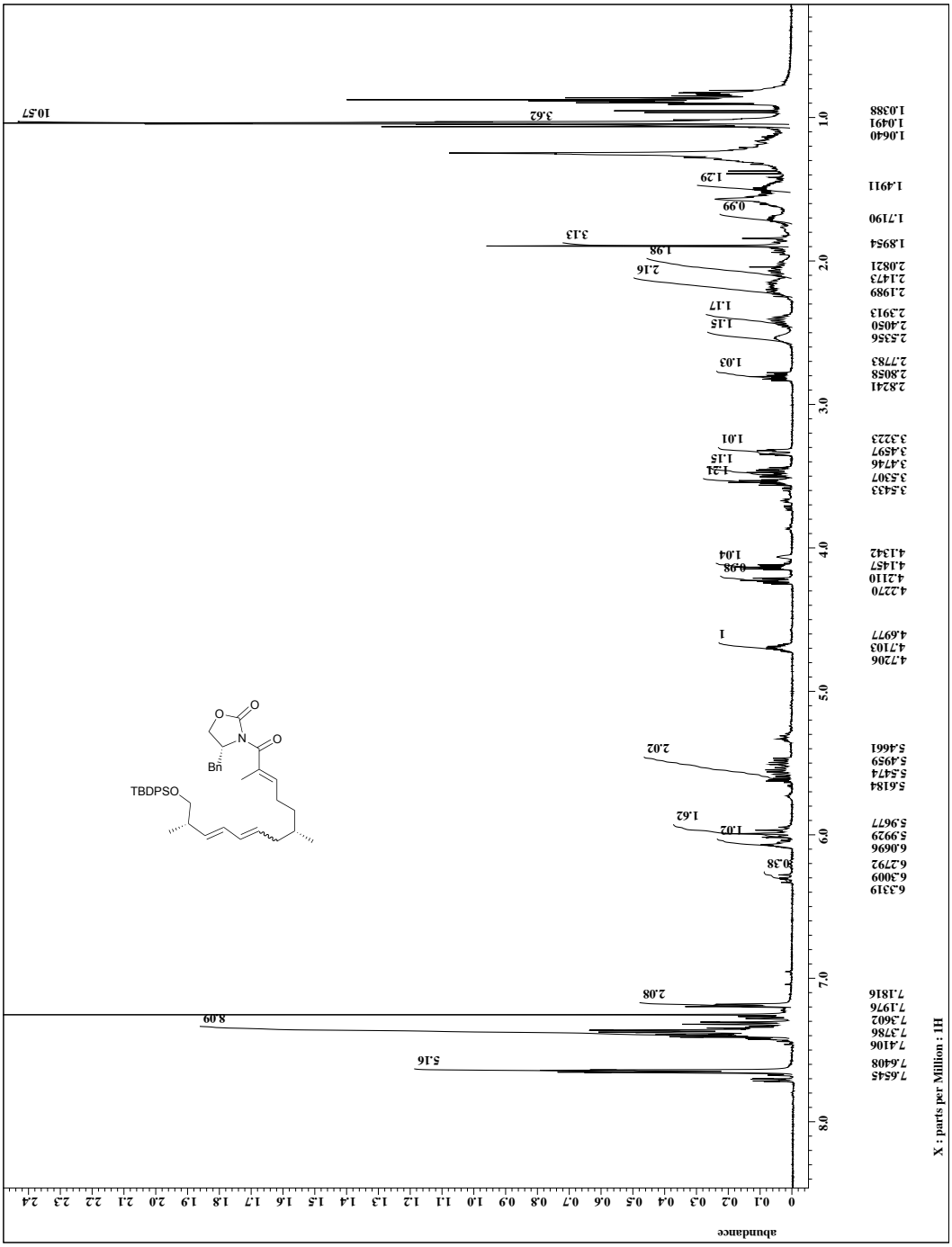
Spectrum 51 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **34_1**



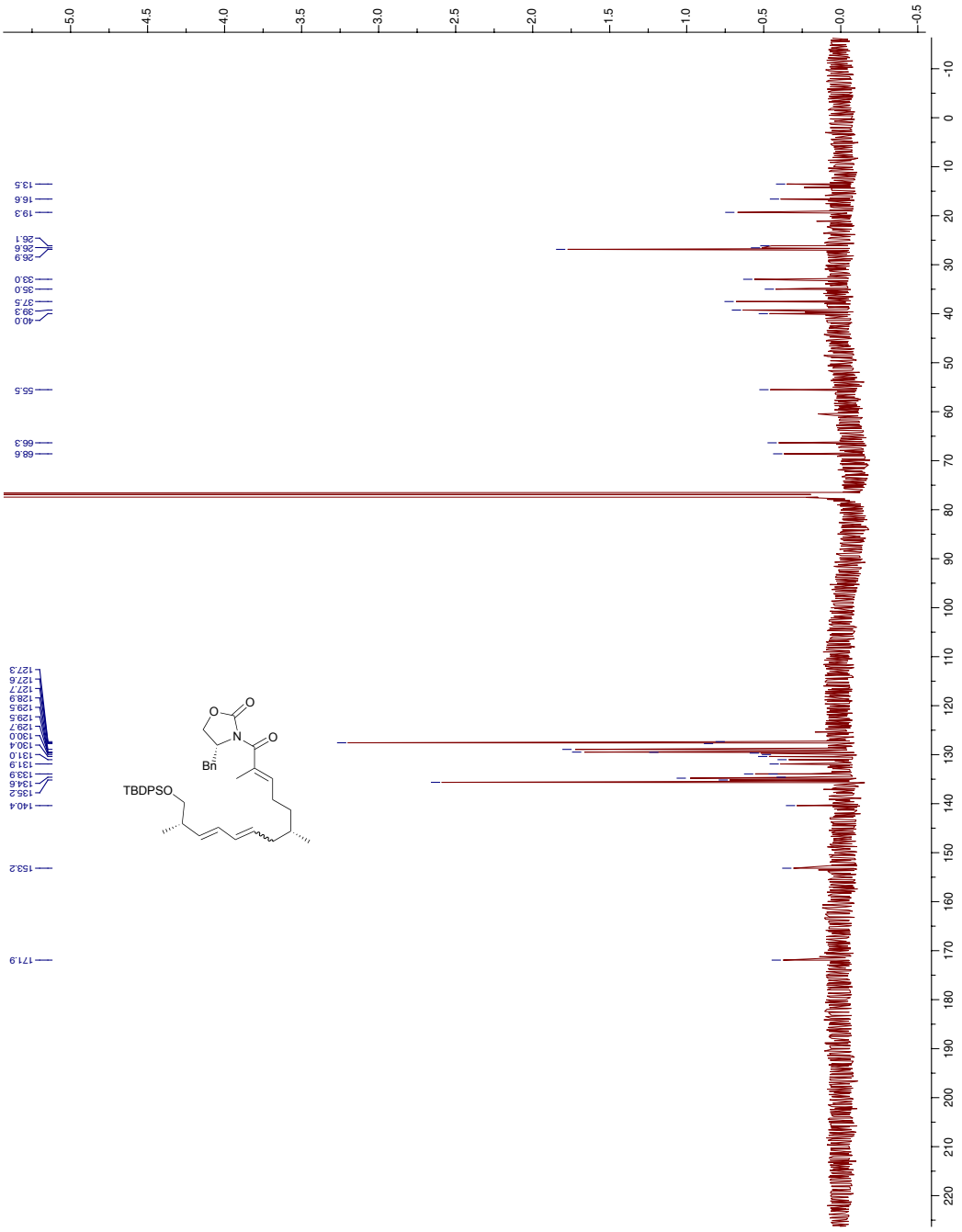
Spectrum 52 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **35**



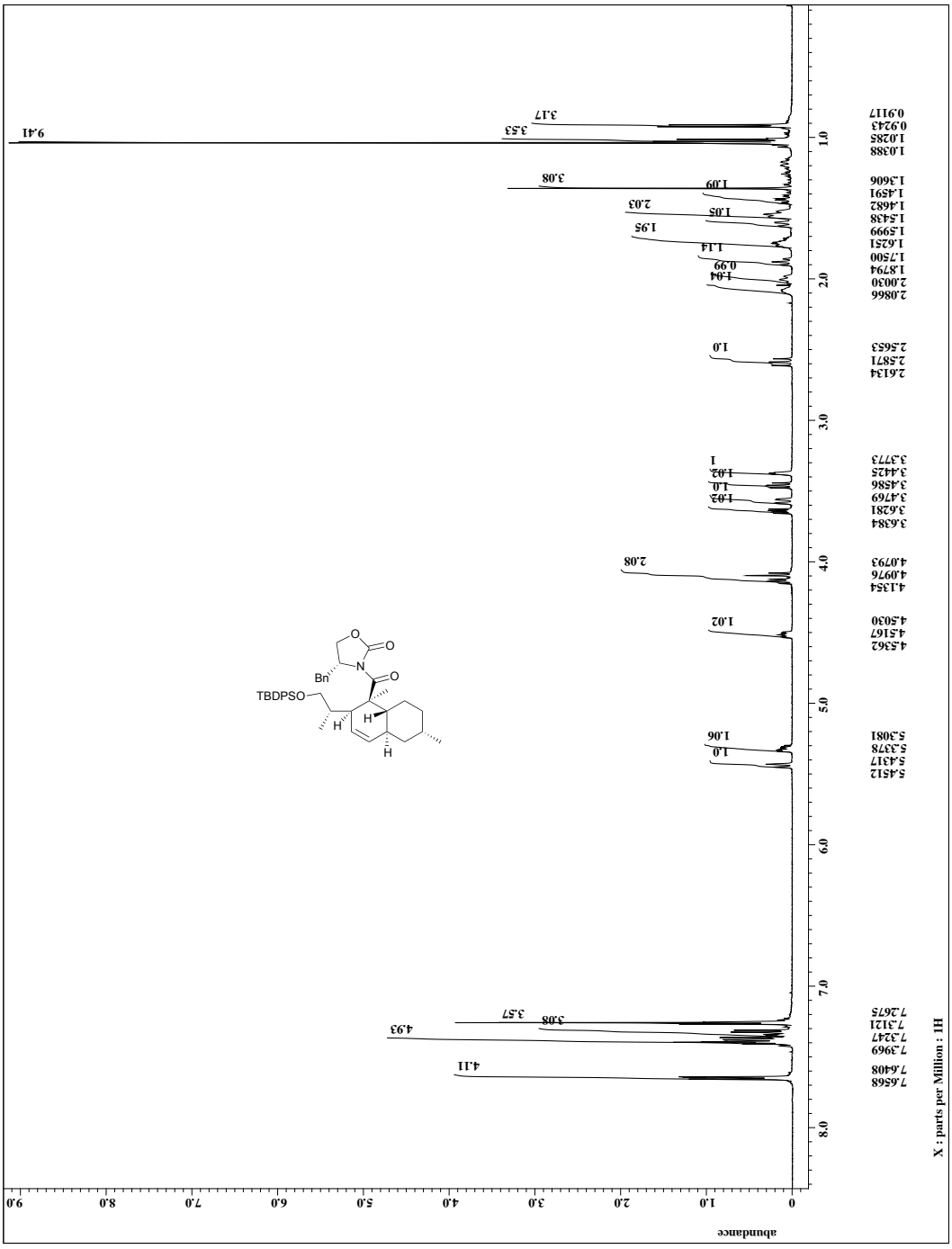
Spectrum 53 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **35**



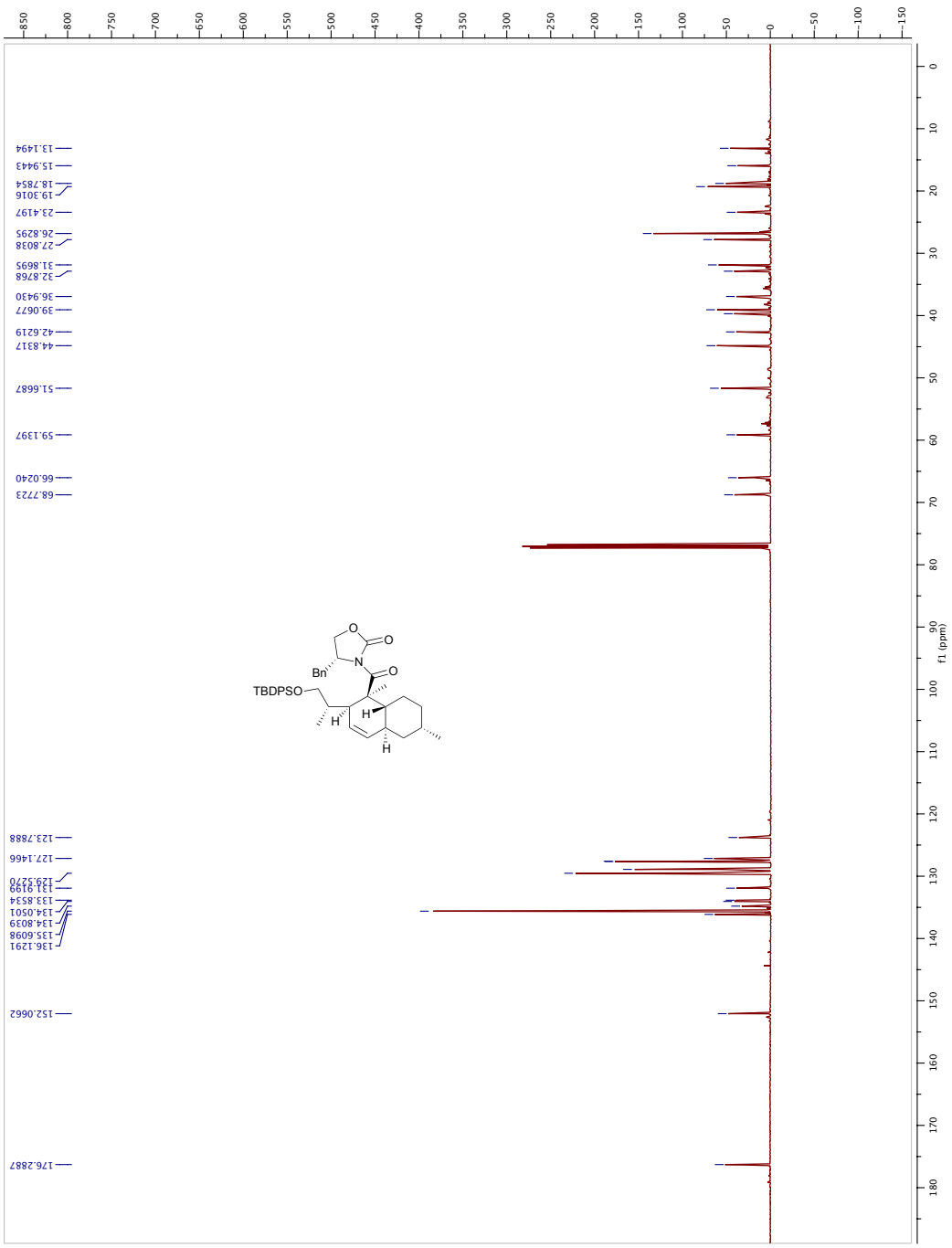
Spectrum 54 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **36**



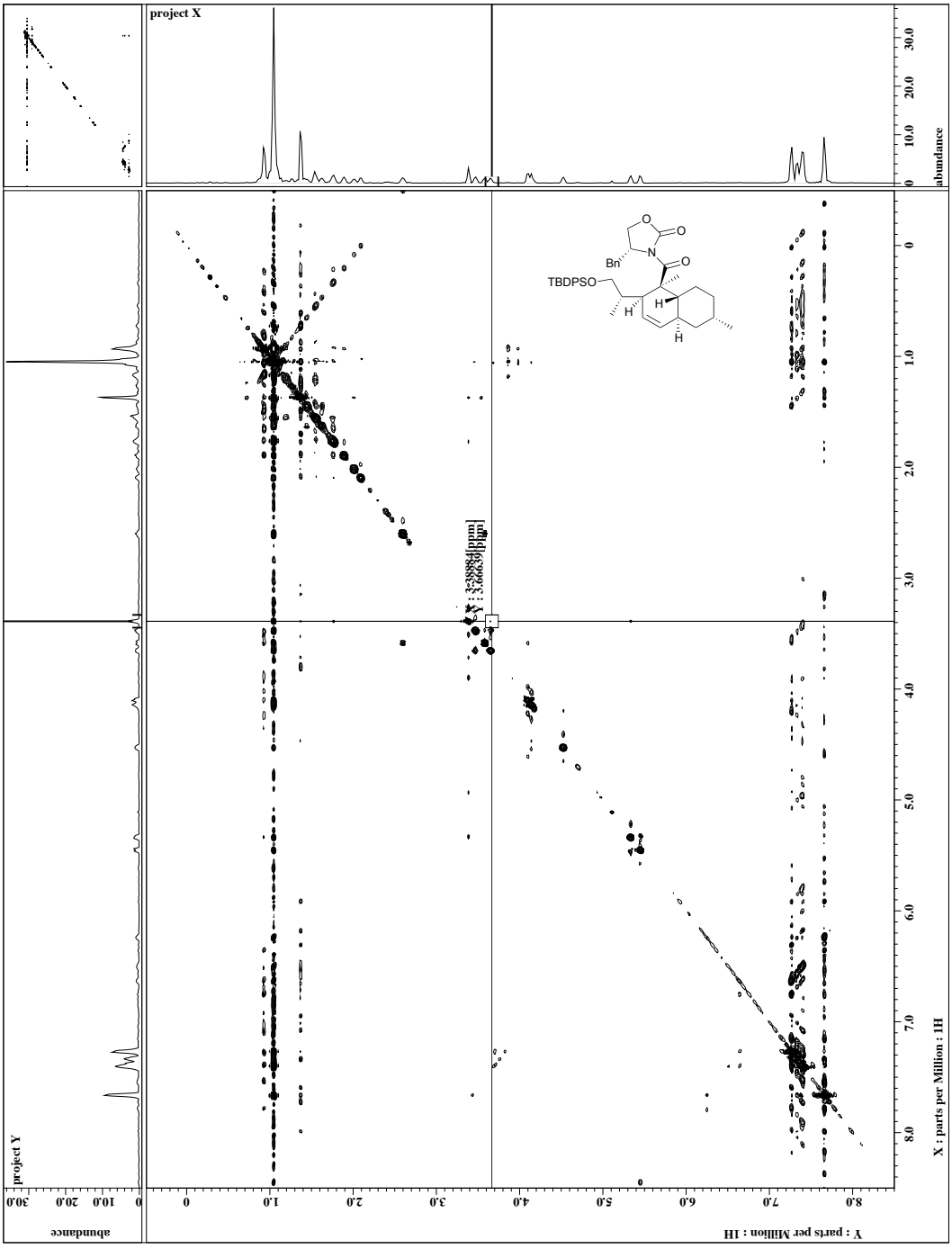
Spectrum 55 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **36**



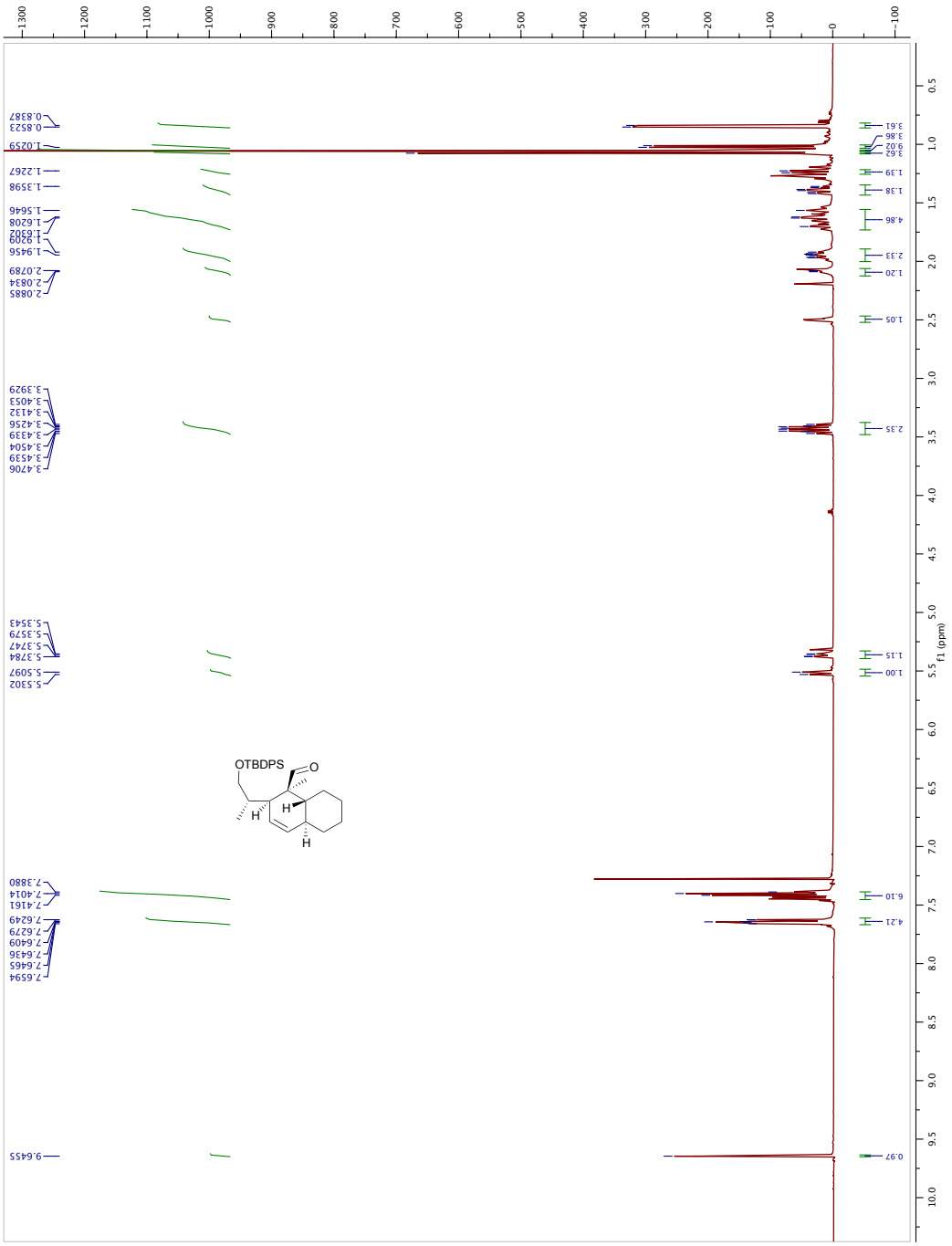
Spectrum 56 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **37**



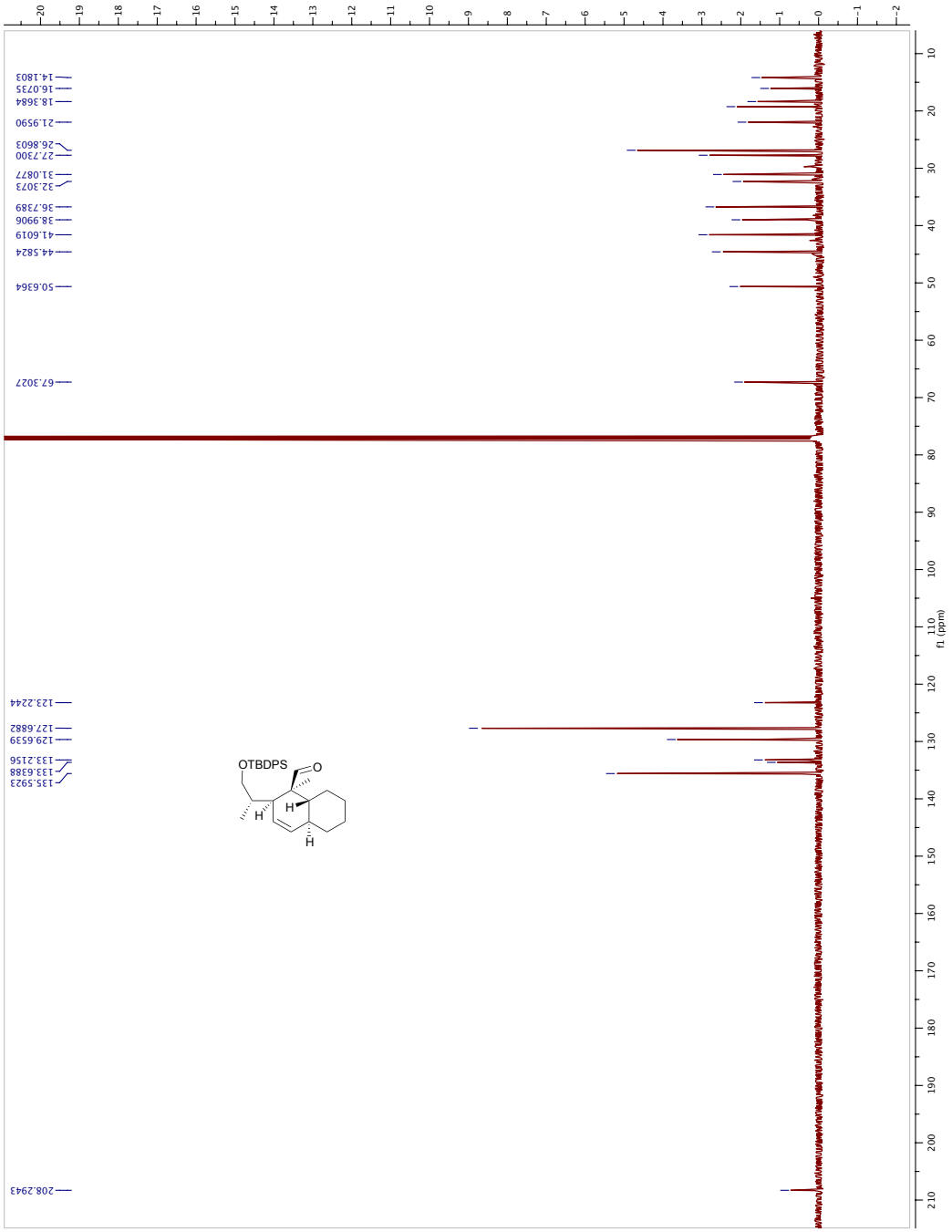
Spectrum 57 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **37**



Spectrum 58 ^{1}H NOESY NMR ($CDCl_3$, 500 MHz) of compound **37**



Spectrum 59 ^{1}H NMR ($CDCl_3$, 500 MHz) of compound **38**



Spectrum 60 ^{13}C NMR ($CDCl_3$, 125 MHz) of compound **38**