Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Total synthesis of conosilane A via site-selective C-H functionalization strategy

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Contents:

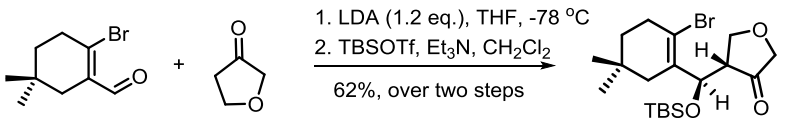
1. General Information……S2
2. Experimental Procedures……S3-10
3. NMR Spectra of New Compounds……S11-70
4. X-ray data of (±)-1……S71

1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction.

Melting points were determined with a digital Koffer apparatus and were uncorrected. NMR spectra were recorded on (^{1}H at 300MHz and 400 MHz, ^{13}C at 75 MHz and 100 MHz, HMBC at 400 MHz and NOE study at 600 MHz) Bruker spectrometers. Chemical shifts (δ) are given in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.0)] and coupling constants (J) in Hz. IR spectra were recorded on a Nicolet FT-170SX spectrometer. High-resolution mass spectra (HRMS) were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer. The X-ray single-crystal determination was performed on an Agilent SuperNova Eos diffractometer.

Experimental Procedures



5 **6** **8** (*anti: syn* = 2.8:1)

To a stirred solution of diisopropylamine (1.25 eq., 8.8 mL) in anhydrous THF (200 mL) at -78 ℃ under an argon atmosphere was added *n*-BuLi (1.2 eq., 24.0 mL, 2.5 M in hexanes) and the solution was stirred at 0 ℃ for 30 min. Then the freshly prepared LDA was cooled to -78 ℃ and a solution of **6**[1] (1.2 eq., 5.16 g) in anhydrous THF (50 mL) was added and then stirred for 1 h, after which **5**[2] (1.0 eq., 10.85 g, 50 mmol) in THF (50 mL) solution was added dropwise to the reaction mixture, and the resulting solution was stirred at the same temperature for 24 hours, when TLC analysis of the crude mixture showed full conversion. The reaction was quenched with saturated aqueous NH_4Cl and extracted with 300 mL ethyl ether. The combined organic phase was dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was chromatographed on silica-gel column quickly with petroleum/EtOAc (5:1) to give the product as pale-green oil (9.89 g, 65% yield).

To a stirred solution of hydroxyl ketone (1.0eq., 9.89 g, 32.62 mmol) in CH_2Cl_2 (150 mL) were added triethylamine (1.5 eq., 6.8 mL), and tert-butyldimethylsilyl trifluoromethanesulfonate (1.1 eq., 8.2 mL) at 0 ℃, and the mixture was stirred for 30 min at the same temperature. The reaction was quenched with sat.$NaHCO_3$ aqueous solution, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography petroleum/ether (50:1) to afford separated *anti*-**8** (9.534g, 70% yield), *syn*-**8** (3.405 g, 25% yield) as colorless oil.

Data for *anti*-**8:**

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.25 (d, *J* = 4.0 Hz, 1H), 4.29 (d, *J* = 8.3 Hz, 2H), 3.95 (dd, *J* = 16.8, 0.9 Hz, 1H), 3.71 (d, *J* = 16.8 Hz, 1H), 2.66-2.52 (m, 1H), 2.48 (t, *J* = 5.8 Hz, 2H), 2.00 (d, *J* = 16.9 Hz, 1H), 1.67 (d, *J* = 17.0 Hz, 1H), 1.42 (dt, *J* = 6.0, 3.7 Hz, 2H), 0.93 (s, 3H), 0.91 (s, 3H), 0.84 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 213.30, 134.62, 118.61, 71.90, 70.93, 67.83, 52.32, 39.81, 37.05, 34.51, 28.94, 27.81, 27.76, 25.70, 17.93, -4.63, -5.48.

HRMS (ESI): calcd for $C_{19}H_{33}BrO_3Si$ ($[M + Na]^+$) 439.1275, found 439.1280.

IR: 2953.8, 2928.5, 2857.9, 1763.5, 1652.7, 1471.9, 1254.1, 1216.0, 1147.6.

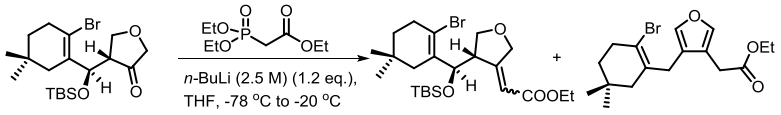
Data for *syn*-**8:**

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.96 (d, *J* = 7.8 Hz, 1H), 4.13 (dd, *J* = 9.7, 7.5 Hz, 1H), 4.00-3.95 (m, 1H), 3.92 (dd, *J* = 6.2, 4.2 Hz, 2H), 2.61 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.56-2.47 (m, 2H), 2.09 (d, *J* = 17.1 Hz, 1H), 1.87 (d, *J* = 17.1 Hz, 1H), 1.44-1.37 (m, 2H), 0.93 (s, 3H), 0.88 (s, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.02 (s, 3H).

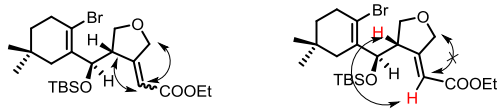
^{13}C NMR (75 MHz, $CDCl_3$): δ 213.52, 134.78, 119.75, 72.87, 71.42, 69.49, 51.38, 39.00, 37.16, 34.67, 28.88, 27.85, 27.72, 25.69, 17.96, -4.76, -5.08.

HRMS (ESI): calcd for $C_{19}H_{33}BrO_3Si$ ($[M + Na]^+$) 439.1275, found 439.1283.

IR: 2953.0, 2928.1, 2857.0, 1762.0, 1650.7, 1471.4, 1252.5, 1077.7, 777.4.



anti-**8** | **4** (**Z**:***E*** = 2.9:1) 82% yield from *anti*-**8** | **9** 5%



H-H COSY | NOE of the major isomer (*Z*-isomer)

To a stirred solution of triethyl phosphonoacetate (1.2 eq., 5.2 mL) in 120 mL THF was added *n*-BuLi (1.2 eq., 2.5 M in hexane, 10.5 mL) dropwise at -78 °C over a period of 10 min and stirred at the same temperature for 30 min. The solution of *anti*-**8** (1.0 eq., 9.20 g, 22.04 mmol) in 60 mL THF was added over a period of 30 min at the same temperature and then warmed to -20 °C over a period of 1 h. After which time TLC analysis showed full conversion, the reaction was quenched with 20 mL saturated aqueous NH_4Cl and the water phase was extracted with 150 mL ethyl ether. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica-gel column with petroleum/EtOAc (50:1 to 30:1) to give product **4** (8.81 g, 82% yield, *Z*/*E* = 2.9/1) as colorless oil combined with the aromatized by-product **9** (392 mg, 5% yield) as yellow-wish oil.

Data for **4** (*Z*/*E* = 2.9/1, mixture):

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.98 (d, *J* = 1.3 Hz, 1H), 5.78-5.69 (m, 3H), 4.82 (d, *J* = 7.4 Hz, 3H), 4.73 (s, 5H), 4.59 (d, *J* = 8.6 Hz, 1H), 4.28 (d, *J* = 8.5 Hz, 1H), 4.23-4.09 (m, 7H), 4.05 (dd, *J* = 8.7, 4.4 Hz, 3H), 3.98 (d, *J* = 5.6 Hz, 1H), 3.81 (dd, *J* = 8.7, 6.2 Hz, 3H), 3.26-3.10 (m, 1H), 3.10-2.94 (m, 1H), 2.94-2.82 (m, 3H), 2.51 (t, *J* = 6.2 Hz, 8H), 2.16 (s, 2H), 2.09 (d, *J* = 12.4 Hz, 3H), 1.91 (d, *J* = 16.7 Hz, 1H), 1.78 (d, *J* = 17.1 Hz, 3H), 1.55-1.36 (m, 8H), 1.26 (t, *J* = 7.1 Hz, 10H), 0.98 (s, 7H), 0.96 (s, 4H), 0.93 (s, 7H), 0.92 (s, 4H), 0.89 (s, 9H), 0.87 (s, 23H), 0.07 (s, 7H), 0.01 (s, 9H), -0.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.25, 165.95, 161.75, 160.98, 133.97, 133.80, 121.01, 120.45, 113.64, 112.92, 81.77, 74.64, 74.27, 72.07, 68.85, 68.18, 60.03, 59.76, 50.23, 39.39, 38.80, 37.20, 34.87, 34.55, 31.59, 28.96, 28.80, 27.19, 26.98, 25.87, 25.73, 17.96, 14.32, -4.51, -4.57, -4.96, -5.20.

HRMS (ESI): calcd for $C_{23}H_{39}BrO_4Si$ ($[M + Na]^+$) 509.1693, found 509.1690.

IR: 2953.6, 2928.7, 1716.7, 1666.2, 1471.9, 1462.0, 1256.8, 1206.8, 1079.3, 835.6

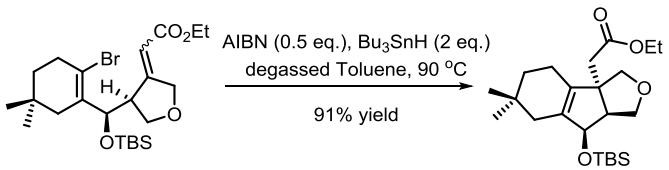
Data for **9**:

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (s, 1H), 6.17 (t, *J* = 2.4 Hz, 1H), 4.89 (d, *J* = 2.6 Hz, 2H), 4.62 (s, 2H), 4.18 (dt, *J* = 14.3, 5.5 Hz, 3H), 2.66 (s, 2H), 2.04 (s, 2H), 1.47 (t, *J* = 6.5 Hz, 2H), 1.34-1.24 (m, 4H), 0.95 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.55, 157.30, 136.42, 130.68, 128.21, 125.27, 106.76, 72.08, 70.28, 60.25, 43.19, 36.46, 35.44, 29.35, 27.70, 14.29.

HRMS (ESI): calcd for $C_{17}H_{23}BrO_3$ ($[M + Na]^+$) 377.0723, found 377.0723.

IR: 2955.7, 2928.1, 1737.1, 1707.8, 1591.3, 1465.0, 1370.1, 1156.0.



4 (**Z**:***E*** = 2.9:1) | **10**

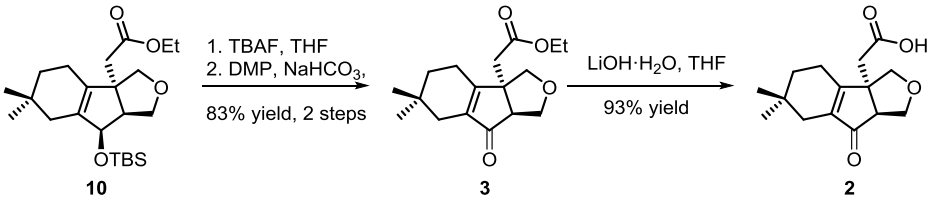
To a flame-dried two-necked round-bottom flask equipped with a stir bar and a condenser was added **4** (1.0 eq., 1.421 g, 2.915 mmol) and anhydrous degassed toluene (60 mL). The resulting solution was heated to 90 °C before Bu_3SnH (2.0 eq., 1.6 mL) and AIBN (0.5 eq., 239 mg) was added as a solution in degassed toluene (20 mL) to the reaction mixture dropwise over a period of 3.5 h using a syringe pump. The resulting solution was allowed to stir for 6 hour at this temperature, after which time TLC analysis showed full conversion, the reaction mixture was concentrated, and the crude residue was purified by silica gel chromatography using petroleum/EtOAc (50:1 to 20:1) to give **10** (1.084 g, 91% yield) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67 (d, *J* = 7.5 Hz, 1H), 4.31-4.20 (m, 1H), 4.14-3.99 (m, 2H), 3.91 -3.81 (m, 1H), 3.64 (dd, *J* = 16.7, 8.0 Hz, 1H), 3.38 (t, *J* = 7.7 Hz, 1H), 2.90 (td, *J* = 7.9, 4.3 Hz, 1H), 2.52 (dt, *J* = 18.2, 9.8 Hz, 2H), 1.90 (dd, *J* = 16.8, 10.1 Hz, 3H), 1.59-1.49 (m, 1H), 1.48-1.38 (m, 1H), 1.38-1.30 (m, 2H), 1.27-1.19 (m, 3H), 0.93 (s, 3H), 0.90 (s, 9H), 0.84 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.53, 139.02, 135.18, 77.98, 75.93, 68.87, 60.38, 60.27, 51.34, 39.51, 37.33, 35.59, 29.39, 29.18, 27.24, 25.90, 19.75, 18.31, 14.21, -4.66, -4.84.

HRMS (ESI): calcd for $C_{23}H_{40}O_4Si$ ($[M + Na]^+$) 431.2588, found 431.2594.

IR: 2954.1, 2929.3, 2857.3, 1736.0, 1471.9, 1364.3, 1255.1, 836.7.



10 **3** **2**

To a stirred solution of **10** (1.0 eq., 765 mg, 1.872 mmol) in THF (20 mL) was added dropwise tetra-*n*-butylammonium fluoride (1.2 eq.,1.0 M in THF, 2.2 mL) at 0 ℃, and the mixture was stirred at 0 ℃, after which time TLC analysis showed full conversion, the reaction was quenched with sat.NH_4Cl aqueous solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was used in the next step without further purification.

To the crude product in CH_2Cl_2 (30 mL) was added $NaHCO_3$ (3.0 eq., 466 mg), Dess–Martin periodinane (1.1 eq., 873 mg) at 0 ℃, and the mixture was stirred for 45 min at the same temperature. The reaction was then quenched with sat.$Na_2S_2O_3$ and sat.$NaHCO_3$ aqueous solution, then stirred for 30min, and extracted with with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane/AcOEt = 5:1) to afford **3** (454 mg, 83%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13-3.99 (m, 3H), 3.89 (d, *J* = 9.3 Hz, 1H), 3.73 (dd, *J* = 9.1, 7.5 Hz, 1H), 3.38 (d, *J* = 9.3 Hz, 1H), 2.94-2.88 (m, 1H), 2.66 (d, *J* = 1.3 Hz, 2H), 2.42-2.30 (m, 1H), 2.23 (dt, *J* = 19.4, 5.6 Hz, 1H), 1.91 (s, 2H), 1.48 (dd, *J* = 9.4, 4.3 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.49, 171.76, 170.21, 140.11, 73.43, 70.51, 60.81, 55.90, 54.83, 37.73, 35.13, 33.69, 28.87, 28.56, 26.89, 22.00, 14.11.

HRMS (ESI): calcd for $C_{17}H_{24}O_4$ ($[M + Na]^+$) 315.1567, found 315.1562.

IR: 2954.0, 2925.6, 1732.8, 1700.9, 1647.4, 1368.0, 1253.1, 1086.3.

To a stirred solution of **3** (1.0 eq., 216 mg, 0.739 mmol) in THF/H_2O (V/V, 8mL/2mL) was added the LiOH·H_2O (5.0 eq., 155 mg) at 0 ℃, and the reaction was stirred at the same temperature, after which time TLC analysis showed full conversion, the reaction was quenched with 1 N HCl (2 mL) and the water phase

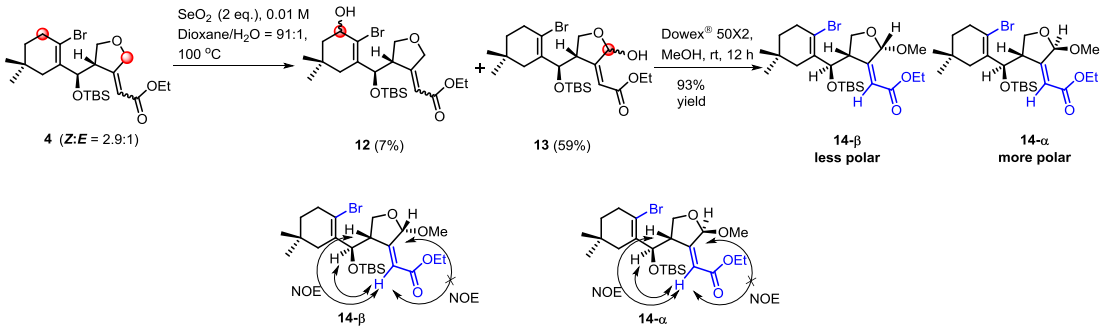
was extracted with 50 mL CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica-gel column chromatography with petroleum /EtOAc (3:1 to 2:1) to give compound 2 (182 mg, 93% yield) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 1H), 4.07 (d, *J* = 8.9 Hz, 1H), 3.92 (d, *J* = 9.3 Hz, 1H), 3.81 -3.67 (m, 1H), 3.40 (d, *J* = 9.3 Hz, 1H), 2.92 (d, *J* = 7.1 Hz, 1H), 2.71 (s, 1H), 2.44-2.19 (m, 2H), 1.92 (s, 1H), 1.49 (t, *J* = 6.6 Hz, 2H), 0.94 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.09, 175.43, 172.37, 140.24, 73.32, 70.48, 55.73, 54.53, 37.18, 34.99, 33.58, 28.88, 28.82, 26.56, 22.11.

HRMS (ESI): calcd for $C_{15}H_{20}O_4$ ([M + H]$^+$) 265.1434, found 265.1441.

IR: 3057.6, 2955.1, 2926.2, 2868.5, 1731.6, 1699.8, 1637.6, 1394.4.



NOTE: the stereochemistry of C12 could be confirmed that we could get compound **15-α** and **15-β** when **14-β** and **14-α** was subjected to the radical cyclization reaction, respectively. Also the C12 isomers of **15-α** and **15-β** was confirmed by the NOE study and HMBC of **14-β**, **14-α**, **15-α** and **15-β**.

To a stirred solution of **4** (1.0 eq., 2 g, 4.102 mmol) in dioxane (405 mL) and H_2O (4.5 mL) was added SeO_2 (2.0 eq., 902 mg) portionwise. The resulting solution was stirred in a preheated oil bath at 100 °C. After 24 hours, the reaction was cooled to room temperature and quenched by the sequential addition of brine and EtOAc. The organic and aqueous layers were separated and the aqueous layer was extracted with EtOAc. The combined organic phase was dried with Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on silica-gel column with petroleum/EtOAc (50:1 to 10:1 to 5:1) to give product **13** (1.25 g, 59% yield) as colorless oil and combined with **12** (148 mg, 7% yield) as a white solid (Mp=88-89 ℃).

Dowex®50WX2 (CAS: 12612-37-2) (0.25 g/1 mmol, 605 mg) was added to a suspension of **13** (1.25 g, 2.42 mmol) in Methanol (10 mL) at room temperature. The suspension was then stirred at room temperature, after which time TLC analysis showed full conversion. The mixture was filtered through a pad of celite and the filtrate was concentrated under reduced pressure. The residue was purified through flash chromatography with petroleum/EtOAc (50:1) to yield **14** (1.16 g, 93% yield) as colorless oil.

Data for **12**:

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.14 (t, *J* = 1.7 Hz, 1H), 5.17-5.07 (m, 1H), 4.75-4.68 (m, 1H), 4.60 (d, *J* = 8.7 Hz, 1H), 4.42 (d, *J* = 8.7 Hz, 1H), 4.32-4.10 (m, 3H), 3.89 (dd, *J* = 10.0, 3.6 Hz, 1H), 2.51 (s, 2H), 2.06 (d, *J* = 16.7 Hz, 1H), 1.89 (d, *J* = 16.7 Hz, 1H), 1.49 (dd, *J* = 13.4, 6.6 Hz, 1H), 1.39 (dd, *J* = 11.9, 6.3 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 3H), 0.91 (s, 3H), 0.89 (s, 9H), 0.01 (s, 3H), -0.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.49, 164.75, 133.57, 121.38, 116.10, 81.47, 74.62, 73.98, 71.25, 60.92, 38.76, 37.13, 34.87, 28.91, 28.66, 27.11, 25.85, 17.92, 14.10, -4.45, -4.95.

HRMS (ESI): calcd for $C_{23}H_{39}BrO_5Si$ ([M + Na]$^+$) 525.1642, found 525.1639.

IR: 3427.9, 2953.4, 2928.9, 1720.9, 1369.2, 1253.7, 1217.5, 1095.8, 1051.8.

Data for **13**:

HRMS (ESI): calcd for $C_{23}H_{39}BrO_5Si$ ([M + Na]$^+$) 525.1642, found 525.1646.

Data for **14**:

Less polar 14-β:

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.80 (s, 1H), 4.94 (d, *J* = 5.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 8.4 Hz, 2H), 3.43 (s, 3H), 2.98 (d, *J* = 7.8 Hz, 1H), 2.53 (s, 2H), 2.12 (d, *J* = 17.0 Hz, 1H), 1.78 (d, *J* = 16.9 Hz, 1H), 1.64 (s, 1H), 1.45 (d, *J* = 3.0 Hz, 3H), 1.28 (dd, *J* = 9.0, 5.2 Hz, 4H), 0.96 (s, 3H), 0.92 (s, 3H), 0.86 (s, 9H), 0.05 (s, 3H), -0.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$):δ 165.13, 157.28, 134.88, 119.86, 116.03, 102.05, 75.46, 66.66, 60.23, 55.09, 47.09, 39.58, 37.20, 34.67, 29.00, 28.68, 27.16, 25.74, 17.94, 14.28, -4.49, -5.03.

HRMS (ESI): calcd for $C_{24}H_{41}BrO_5Si$ ([M + Na]$^+$) 539.1799, found 539.1805.

IR: 2953.7, 2928.7, 2857.3, 2369.7, 1723.8, 1375.3, 1214.3, 1132.4.

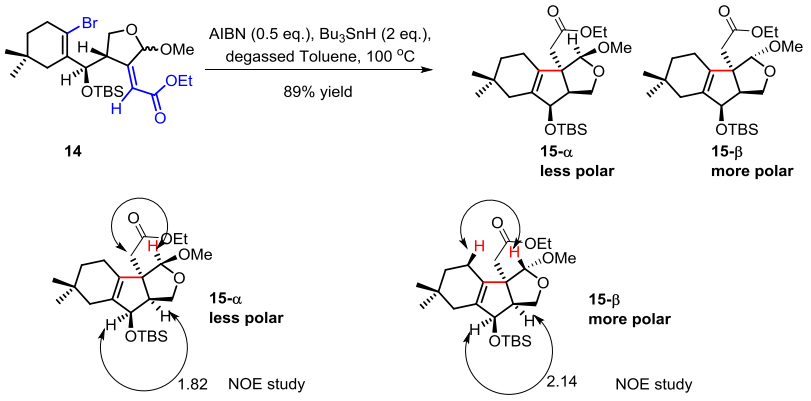
More polar 14-α:

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (d, *J* = 1.2 Hz, 1H), 5.79 (t, *J* = 1.6 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 1H), 4.24-4.14 (m, 2H), 4.12 (dd, *J* = 9.0, 1.6 Hz, 1H), 3.99 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.46 (s, 3H), 2.92-2.80 (m, 1H), 2.51 (s, 2H), 2.17 (d, *J* = 15.7 Hz, 1H), 1.77 (d, *J* = 17.3 Hz, 1H), 1.56- 1.36 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.98 (s, 3H), 0.92 (s, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.79, 156.78, 133.57, 121.15, 117.51, 102.81, 75.06, 66.67, 60.24, 55.65, 47.69, 39.26, 37.19, 34.61, 29.33, 28.97, 26.77, 25.73, 17.95, 14.28, -4.48, -5.13.

HRMS (ESI): calcd for $C_{24}H_{41}BrO_5Si$ ([M + Na]$^+$) 539.1799, found 539.1808.

IR: 2953.6, 2929.3, 2857.7, 1724.8, 1677.4, 1371.8, 1253.4, 1211.0.



To a flame-dried two-necked round-bottom flask equipped with a stir bar and a condenser was added **14** (1.0 eq., 655 mg, 1.266 mmol) and anhydrous toluene (25 mL). The resulting solution was heated to 100 °C before Bu_3SnH (2.0 eq., 0.7 mL) and AIBN (0.5 eq., 105 mg) was added as a solution in degassed toluene (20 mL) to the reaction mixture drop-wise over a period of 3.5 h using a syringe pump. The resulting solution was allowed to stir for 12-18 hours at this temperature, after which time TLC analysis showed full conversion. The reaction mixture was concentrated, and the crude residue was purified by silica gel chromatography using petroleum /EtOAc (50:1) to give **15** (495 mg, 89% yield) as colorless oil.

Data for **15**:

Less polar 15-α:

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.67 (s, 1H), 4.27 (s, 1H), 4.21-4.03 (m, 3H), 3.73-3.61 (m, 1H), 3.27 (s, 3H), 2.73 (ddd, *J* = 9.3, 6.9, 2.7 Hz, 1H), 2.62-2.47 (m, 2H), 2.08-1.89 (m, 2H), 1.84 (d, *J* = 18.2 Hz, 1H), 1.58 (d, *J* = 17.1 Hz, 2H), 1.34 (t, *J* = 6.2 Hz, 3H), 1.23 (dd, *J* = 12.5, 5.4 Hz, 3H), 0.91 (s, 3H), 0.89 (s, 3H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.25, 138.25, 134.65, 107.65, 83.99, 70.18, 64.97, 60.40, 57.17, 55.11, 41.17, 37.33, 35.63, 29.42, 28.61, 27.71, 25.79, 21.22, 18.07, 14.23, -4.48, -4.71.

HRMS (ESI): calcd for $C_{24}H_{42}O_5Si$ ([M + Na]$^+$) 461.2694, found 461.2692.

IR: 2952.1, 2929.3, 1735.4, 1471.8, 1363.7, 1255.4, 1089.7, 774.0.

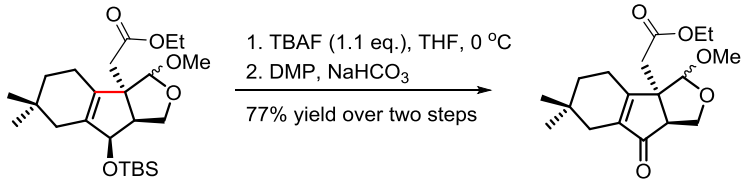
More polar 15-β:

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.19 (s, 1H), 4.13-4.01 (m, 3H), 3.61 (dd, *J* = 8.9, 2.3 Hz, 1H), 3.29 (s, 3H), 2.63 (d, *J* = 4.8 Hz, 2H), 2.60-2.49 (m, 1H), 2.12 (d, *J* = 18.4 Hz, 1H), 1.89 (d, *J* = 21.2 Hz, 2H), 1.79 (s, 1H), 1.63 (d, *J* = 17.0 Hz, 2H), 1.46-1.28 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.96 -0.82 (m, 15H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.19, 138.75, 137.72, 105.97, 85.22, 70.37, 63.49, 60.02, 55.25, 54.79, 37.94, 37.32, 35.65, 29.35, 28.94, 27.22, 25.79, 21.23, 18.09, 14.28, -4.43, -4.71.

HRMS (ESI): calcd for $C_{24}H_{42}O_5Si$ ([M + Na]$^+$) 461.2694, found 461.2697.

IR: 2952.7, 2929.1, 2857.8, 1736.7, 1471.8, 1364.5, 1251.3, 1187.1.



15 **16**

To a stirred solution of **15** (1.0 eq., 471 mg, 1.074 mmol) in THF (10 mL) was added dropwise tetra-*n*-butylammonium fluoride (1.2 eq., 1.0 M in THF, 1.3 mL) at 0 ℃, and the mixture was stirred at 0 ℃, after which time TLC analysis showed full conversion, the reaction was quenched with sat.NH_4Cl aqueous solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was used in the next step without further purification.

To the residues in CH_2Cl_2 (15 mL) was added $NaHCO_3$ (3 eq., 272 mg), Dess–Martin periodinane (1.5 eq., 684 mg) at 0 °C, and the mixture was stirred for 45 min at the same temperature. The reaction was then quenched with sat.$Na_2S_2O_3$ and sat.$NaHCO_3$ aqueous solution, stirred for 30min, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography hexane/EtOAc (5:1 to 3:1) to afford **16** (267 mg, 77%) as colorless oil.

Data for **16**:

Less polar:

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.68 (s, 1H), 4.07 (dt, *J* = 9.4, 6.1 Hz, 3H), 3.88 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.30 (s, 3H), 3.16 (dd, *J* = 9.3, 5.9 Hz, 1H), 2.73 (d, *J* = 1.7 Hz, 2H), 2.73 (d, *J* = 1.7 Hz, 2H), 2.33 (s, 2H), 1.90 (q, *J* = 17.1 Hz, 2H), 1.45 (dd, *J* = 15.2, 6.5 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 206.83, 170.18, 169.43, 139.13, 106.93, 65.36, 60.88, 59.50, 55.62, 55.18, 38.53, 35.23, 33.76, 28.97, 28.14, 27.46, 23.42, 14.17.

HRMS (ESI): calcd for $C_{18}H_{26}O_5$ ([M + Na]$^+$) 345.1672, found 345.1671.

IR: 2921.9, 2366.4, 1733.7, 1701.1, 1646.6, 1210.8, 1107.2, 1032.7.

More polar:

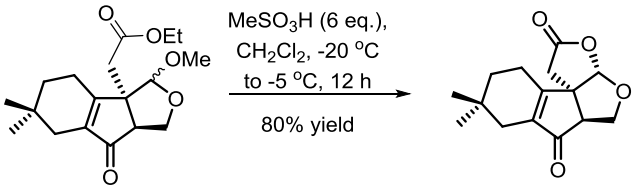
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.76 (d, *J* = 3.0 Hz, 1H), 4.01 (m, *J* = 8.8, 7.2, 3.1 Hz, 3H), 3.93-3.87 (m, 1H), 3.31 (s, 3H), 3.04 (dd, *J* = 7.8, 1.5 Hz, 1H), 2.93-2.80 (m, 1H), 2.64 (t, *J* = 9.0 Hz, 1H), 2.45 (dt, *J* = 19.3, 6.8 Hz, 1H), 2.24 (d, *J* = 19.5 Hz, 1H), 1.90 (s, 2H), 1.48 (t, *J* = 6.1 Hz, 2H), 1.15 (td,

J = 7.1, 3.3 Hz, 3H), 0.91 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 207.98, 171.05, 170.89, 140.65, 104.38, 67.30, 60.58, 59.13, 54.74, 54.38, 35.21, 35.13, 33.73, 28.85, 28.51, 26.98, 22.80, 14.12.

HRMS (ESI): calcd for $C_{18}H_{26}O_5$ ($[M + Na]^+$) 345.1672, found 345.1668.

IR: 2926.1, 2368.7, 1734.2, 1704.0, 1212.3, 1112.5, 1057.9.



16 **11**

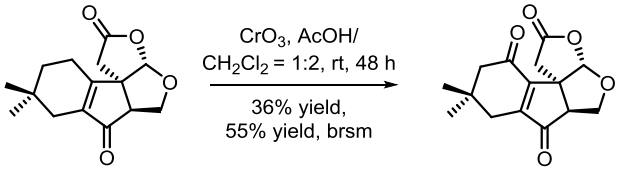
A solution of **16** (1.0 eq., 220 mg, 0.682 mmol) in CH_2Cl_2 (5 mL) was cooled to -20 °C. $MeSO_3H$ (6.0 eq., 0.27 mL) was added dropwise and the solution was left to stir at -20 °C for 30 min. The solution was then allowed to warm to -5 °C over a period of 1 hour and kept at this temperature for 12 h. The reaction mixture was then quenched with tri-ethylamine and sat.$NaHCO_3$ aqueous solution at -5 °C. The solution was diluted with EtOAc and washed with water. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by column chromatography petroleum /EtOAc (5:1 to 3:1) to afford **11** (144 mg, 80%) as a white solid (Mp = 170-172 ℃).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (d, *J* = 2.8 Hz, 1H), 4.30 (dd, *J* = 9.6, 1.5 Hz, 1H), 4.17 (dd, *J* = 9.6, 7.4 Hz, 1H), 3.15-3.02 (m, 1H), 2.83 (s, 1H), 2.80-2.70 (m, 2H), 2.46 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.26 (d, *J* = 19.5 Hz, 1H), 1.98 (d, *J* = 2.1 Hz, 2H), 1.58 (t, *J* = 6.0 Hz, 2H), 0.95 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 204.69, 172.43, 166.18, 141.88, 107.41, 68.45, 60.84, 56.80, 35.76, 34.89, 33.82, 28.85, 28.02, 27.38, 22.37.

HRMS (ESI): calcd for $C_{15}H_{18}O_4$ ($[M + Na]^+$) 285.1097, found 285.1090.

IR: 2955.4, 2922.6, 1791.9, 1706.4, 1647.8, 1174.4, 964.4.



11 **Conosilane A (1)**

To a solution of **11** (1.0 eq., 26mg, 0.1 mmol) in AcOH/CH_2Cl_2 (V/V = 1:2, 3mL) was added dry CrO_3 (5.0 eq., 50 mg) portion-wise at room temperature. After addition, the suspension was stirred at the same temperature. After being stirred for 2 days, the solution was diluted with ethyl ether, quenched with Sat.$Na_2S_2O_3$, and extracted with ethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by column chromatography petroleum/EtOAc (5:1 to 3:1) to afford conosilane A (**1**) (10 mg, 36%, 55 % brsm) as a white solid (Mp = 159-160 ℃) and recoved the starting material **11** (9 mg, 34%) as a white solid.

Data for conosilane A (**1**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (s, 1H), 4.30 (dd, *J* = 9.8, 1.6 Hz, 1H), 4.21 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.60 (d, *J* = 17.9 Hz, 1H), 2.85 (dd, *J* = 7.6, 1.5 Hz, 1H), 2.75 (d, *J* = 17.9 Hz, 1H), 2.49 (q, *J* = 16.3 Hz, 2H), 2.38 (d, *J* = 1.6 Hz, 2H), 1.14 (s, 3H), 1.04 (s, 3H).

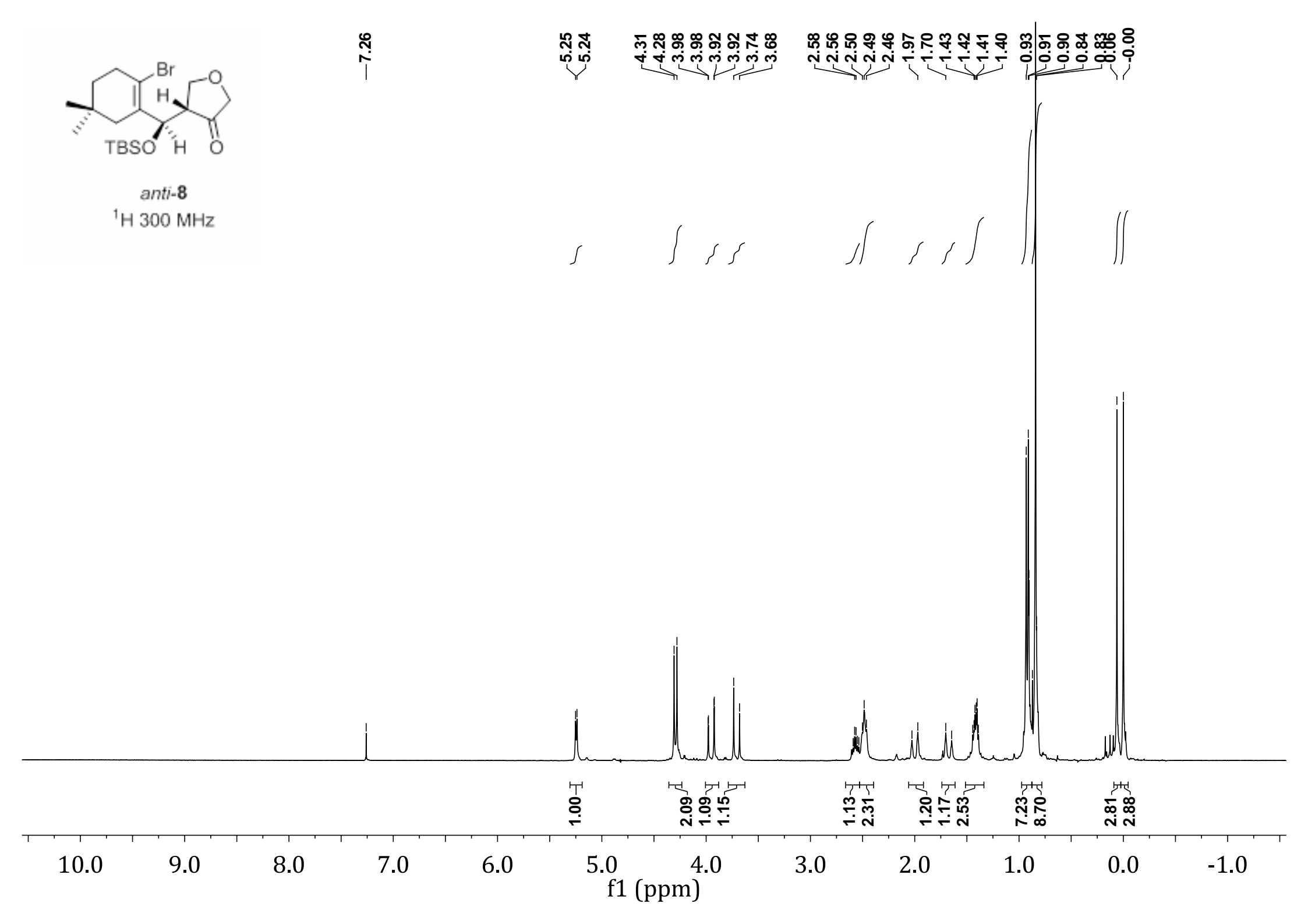
^{13}C NMR (100 MHz, $CDCl_3$): δ 206.56, 198.80, 172.21, 155.11, 153.16, 107.44, 68.38, 57.86, 57.82, 53.09, 36.54, 35.19, 34.38, 28.75, 27.47.

HRMS (ESIMS): calcd for $C_{15}H_{16}O_5$ ($[M+H]^+$) 277.1071, found 277.1069;
IR: 2958.8, 1790.1, 1719.7, 1678.1, 1305.2, 1212.5, 1114.2, 965.4.

References:

(1) Kraus, G. A.; Chen, L. *J. Am. Chem. Soc.* 1990, **112**, 3464.

(2) Park, C.-M.; Bruncko, M.; Adickes, J.; Bauch, J.; Ding, H.; Kunzer, A.; Marsh, K. C.; Nimmer, P.; Shoemaker, A. R.; Song, X.; Tahir, S. K.; Tse, C.; Wang, X.; Wendt, M. D.; Yang, X.; Zhang, H.; Fesik, S. W.; Rosenberg, S. H.; Elmore, S. W. *J. Med. Chem.* 2008, **51**, 6902.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O
H
TBSO
H
O
anti-8
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5.25
5.24
4.31
4.28
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3.98
3.92
3.92
3.74
3.68
2.58
2.56
2.50
2.49
2.46
1.97
1.70
1.43
1.42
1.41
1.40
0.93
0.91
0.90
0.84
0.83
0.06
-0.00
1.00
2.09
1.09
1.15
1.13
2.31
1.20
1.17
2.53
7.23
8.70
2.81
2.88
10.0
9.0
8.0
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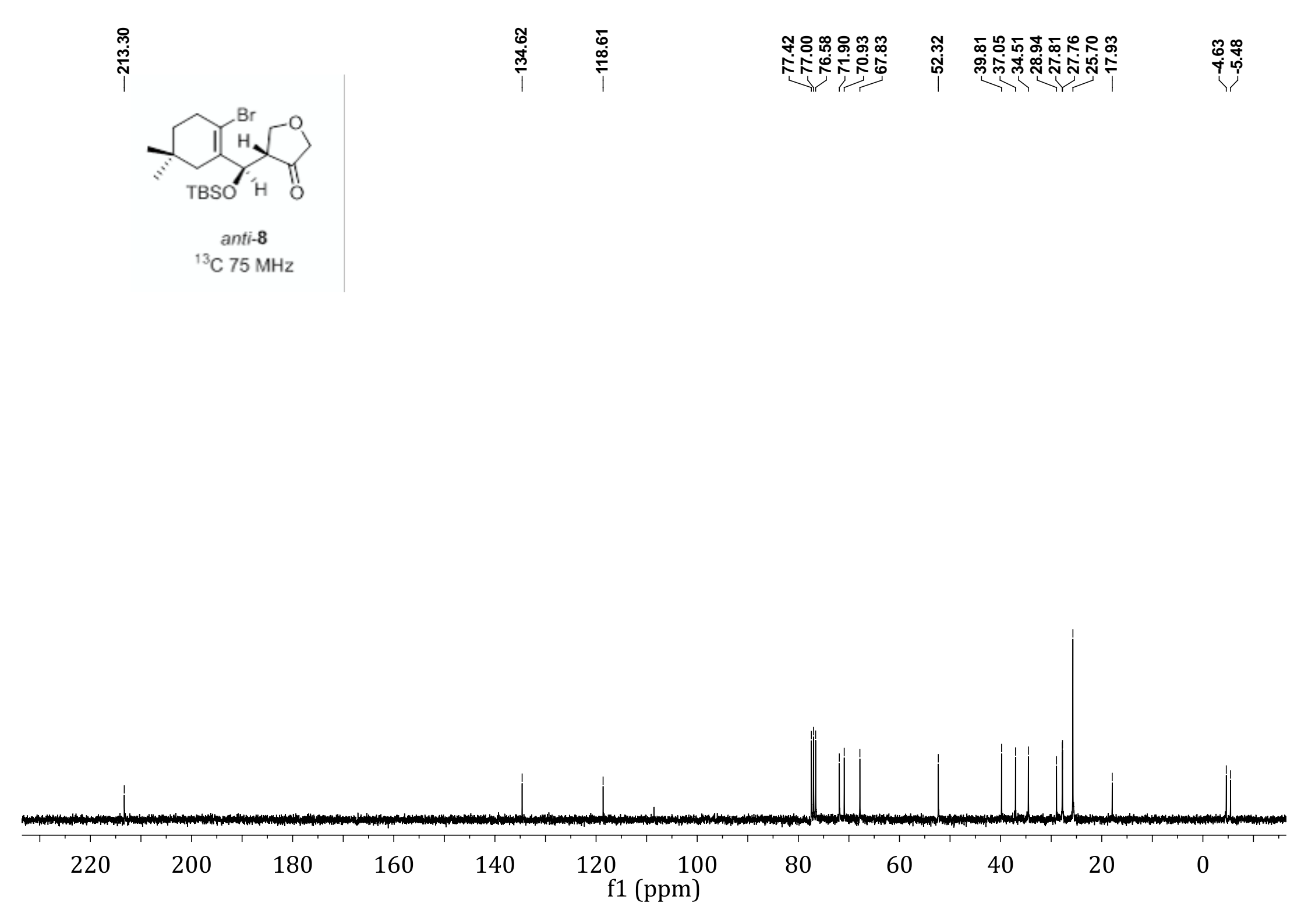
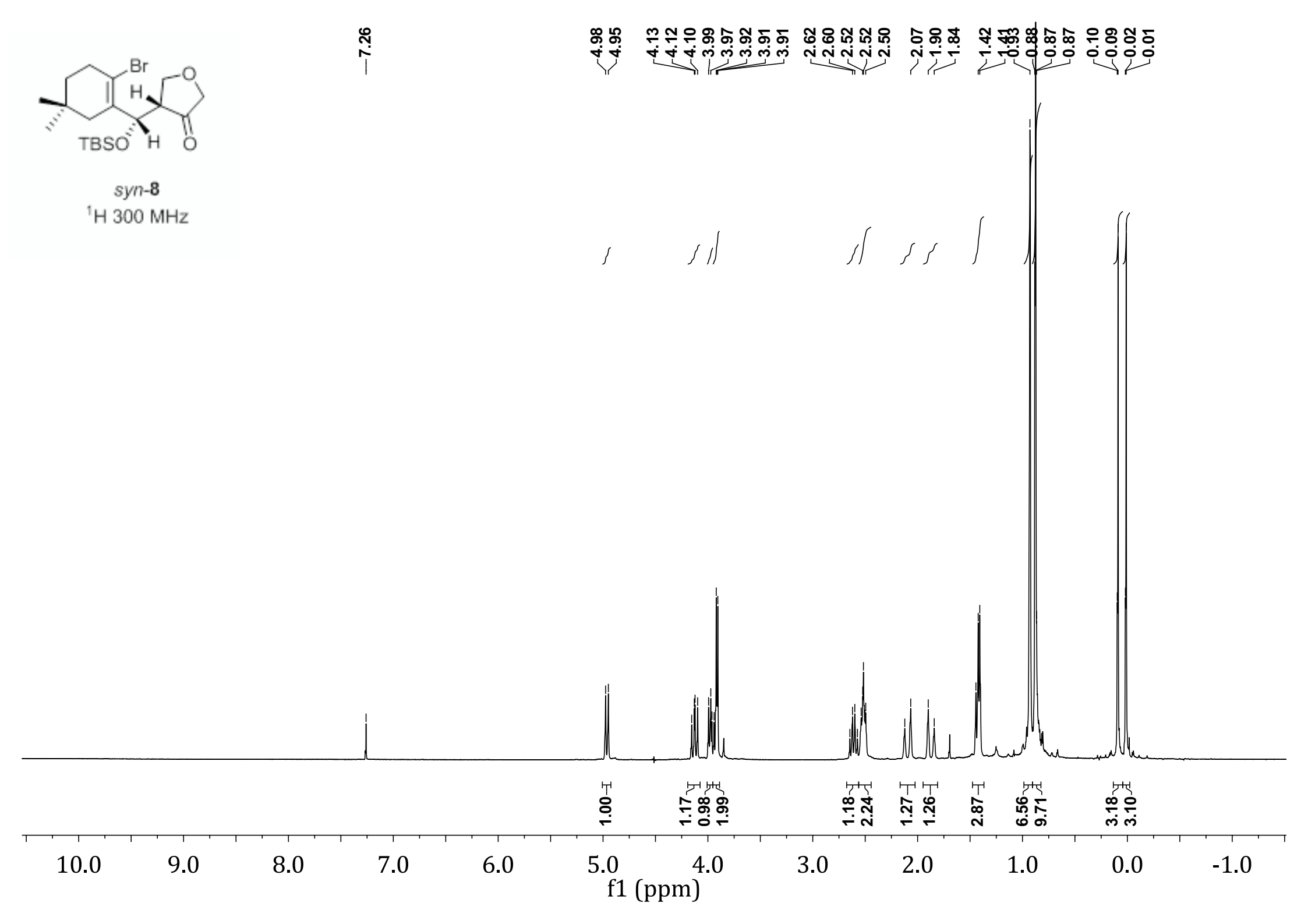
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


213.30
134.62
118.61
77.42
77.00
76.58
71.90
70.93
67.83
52.32
39.81
37.05
34.51
28.94
27.81
27.76
25.70
17.93
-4.63
-5.48
Br
O
H
TBSO
H
O
anti-8
13C 75 MHz
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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O
H
TBSO
H
O
syn-8
1H 300 MHz
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4.98
4.95
4.13
4.12
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3.97
3.92
3.91
3.91
2.62
2.60
2.52
2.52
2.50
2.07
1.90
1.84
1.42
1.41
0.93
0.88
0.87
0.87
0.10
0.09
0.02
0.01
1.00
1.17
0.98
1.99
1.18
2.24
1.27
1.26
2.87
6.56
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3.18
3.10
10.0
9.0
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6.0
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4.0
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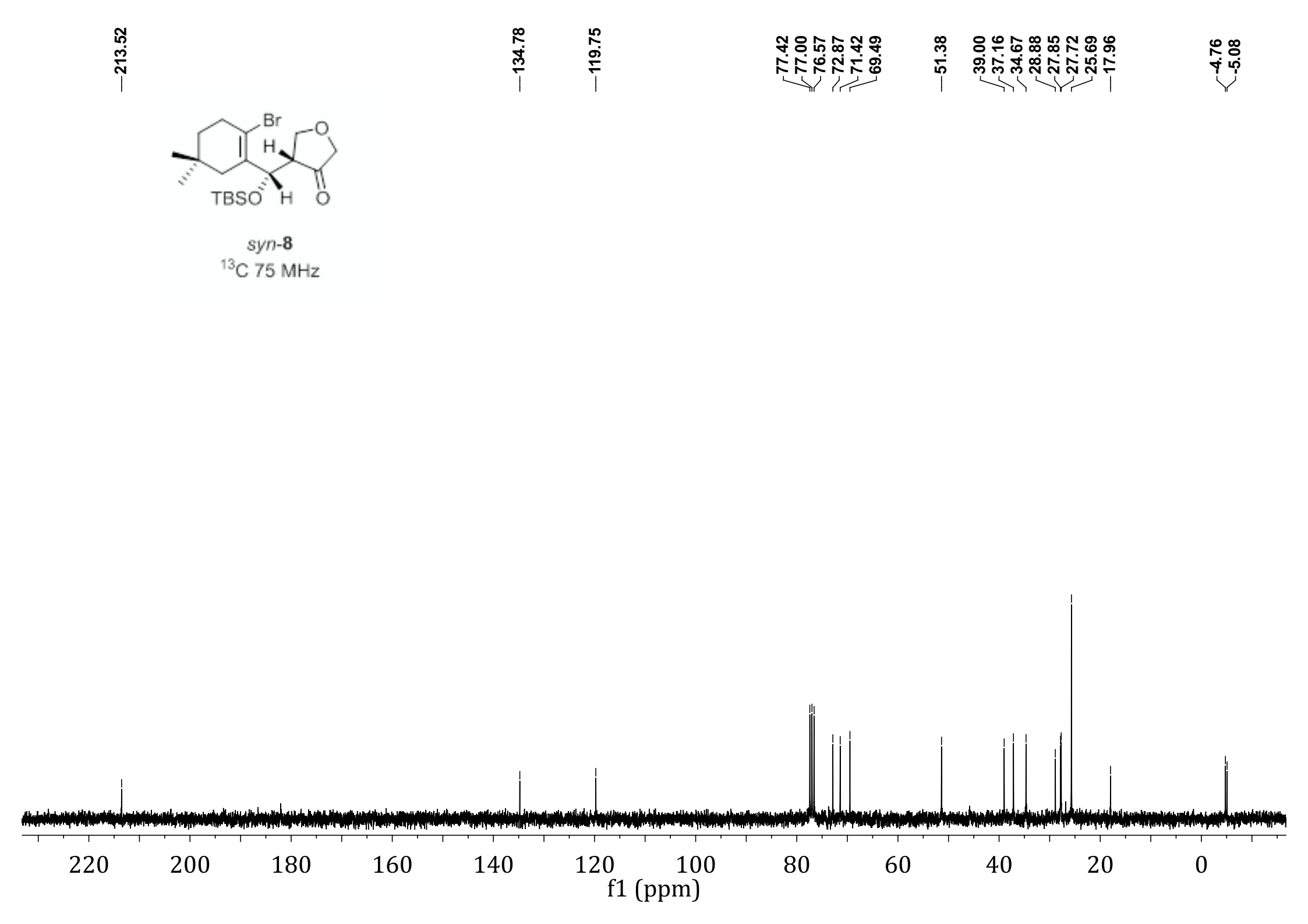
2.0
1.0
0.0
-1.0
f1 (ppm)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39.00
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34.67
28.88
27.85
27.72
25.69
17.96
-4.76
-5.08
Br
H
O
TBSO
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O
syn-8
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220
200
180
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140
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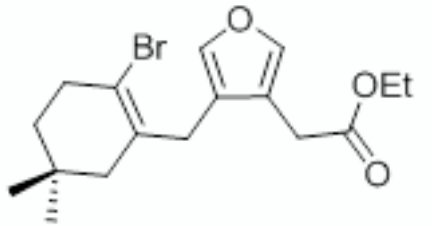
100
80
60
40
20
0
f1 (ppm)



9

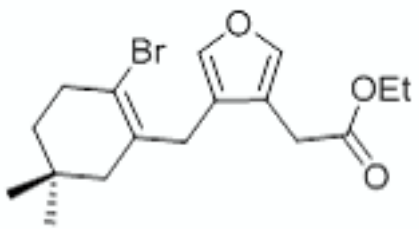
^{1}H 300 MHz

7.26 7.12 6.17 6.17 6.16 4.90 4.89 4.62 4.21 4.20 4.19 4.18 4.16 4.14 2.66 2.04 1.49 1.47 1.44 1.31 1.30 1.29 1.28 1.26 1.26 1.25 0.95 0.94

1.00 0.95 1.81 1.91 2.53 1.94 1.84 2.18 3.61 6.41

9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5

f1 (ppm)



9

^{13}C 75 MHz

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157.30
136.42
130.68
128.21
125.27
106.76
77.42
77.00
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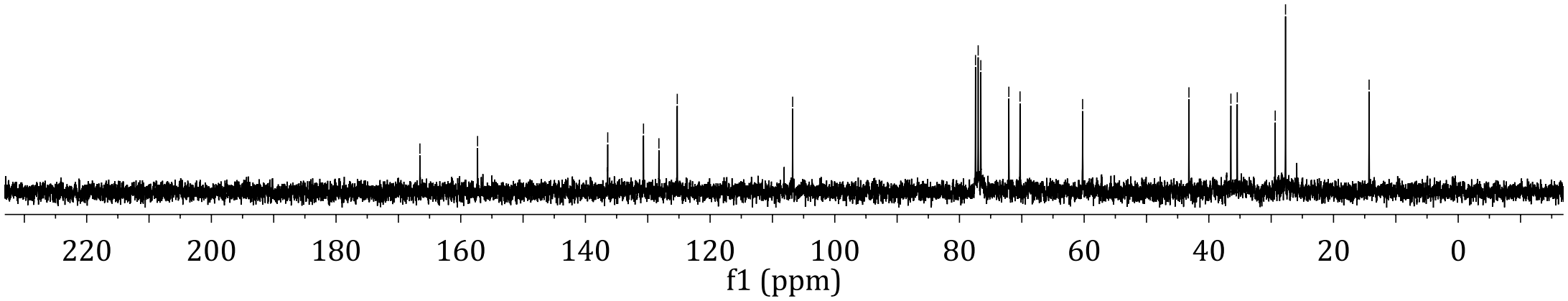
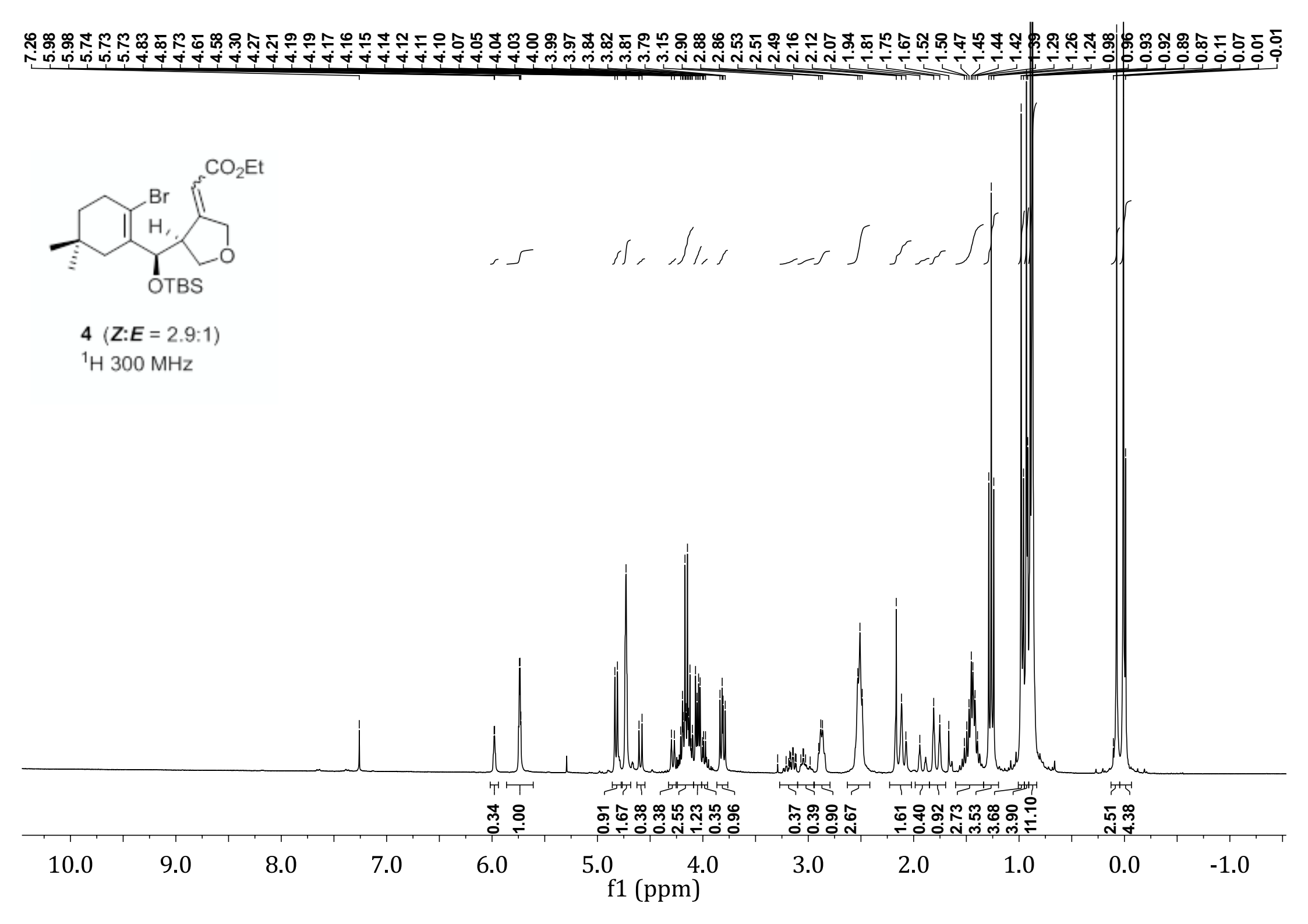
43.19
36.46
35.44
29.35
27.70
14.29

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CO2Et
Br
H
O
OTBS
4 (Z:E = 2.9:1)
1H 300 MHz
0.34 1.00 0.91 1.67 0.38 0.38 2.55 1.23 0.35 0.96 0.37 0.39 0.90 2.67 1.61 0.40 0.92 2.73 3.53 3.68 3.90 11.10 2.51 4.38
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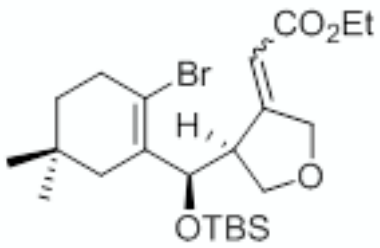
f1 (ppm)



4 (***Z*:*E*** = 2.9:1)
^{13}C 75 MHz

166.25
165.95
161.75
160.98
133.97
133.80
121.01
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113.64
112.92
81.77
77.43
77.00
76.58
74.64
74.27
72.07
68.85
68.18
60.03
59.76
50.23
37.20
34.55
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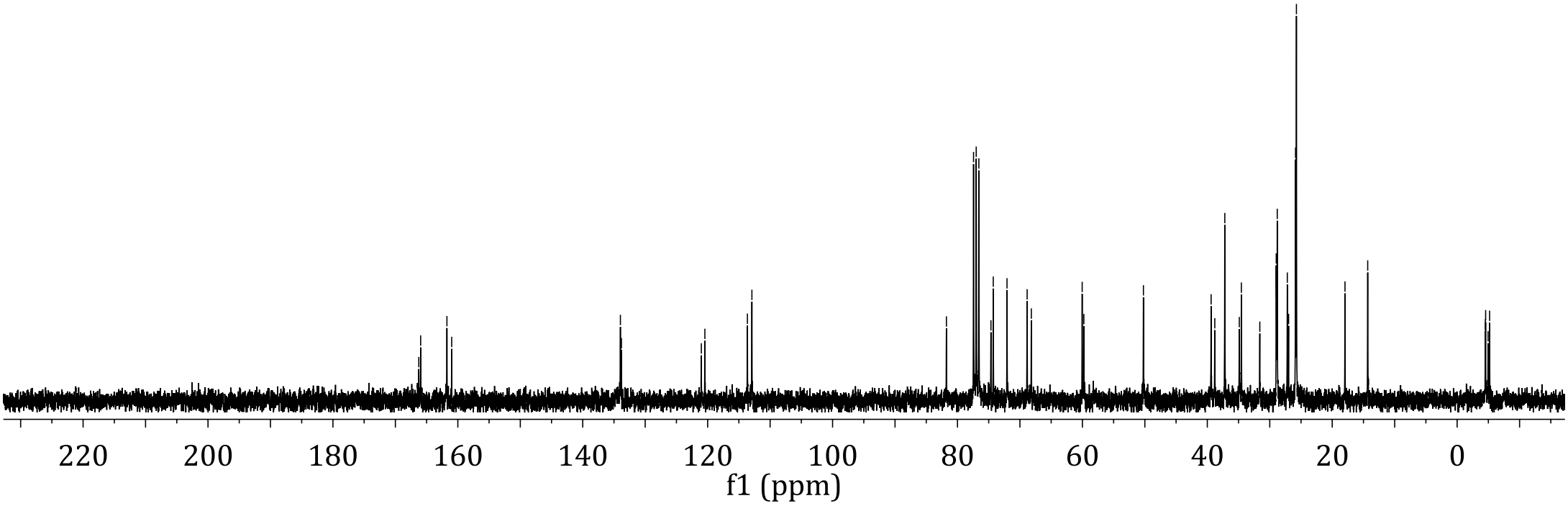

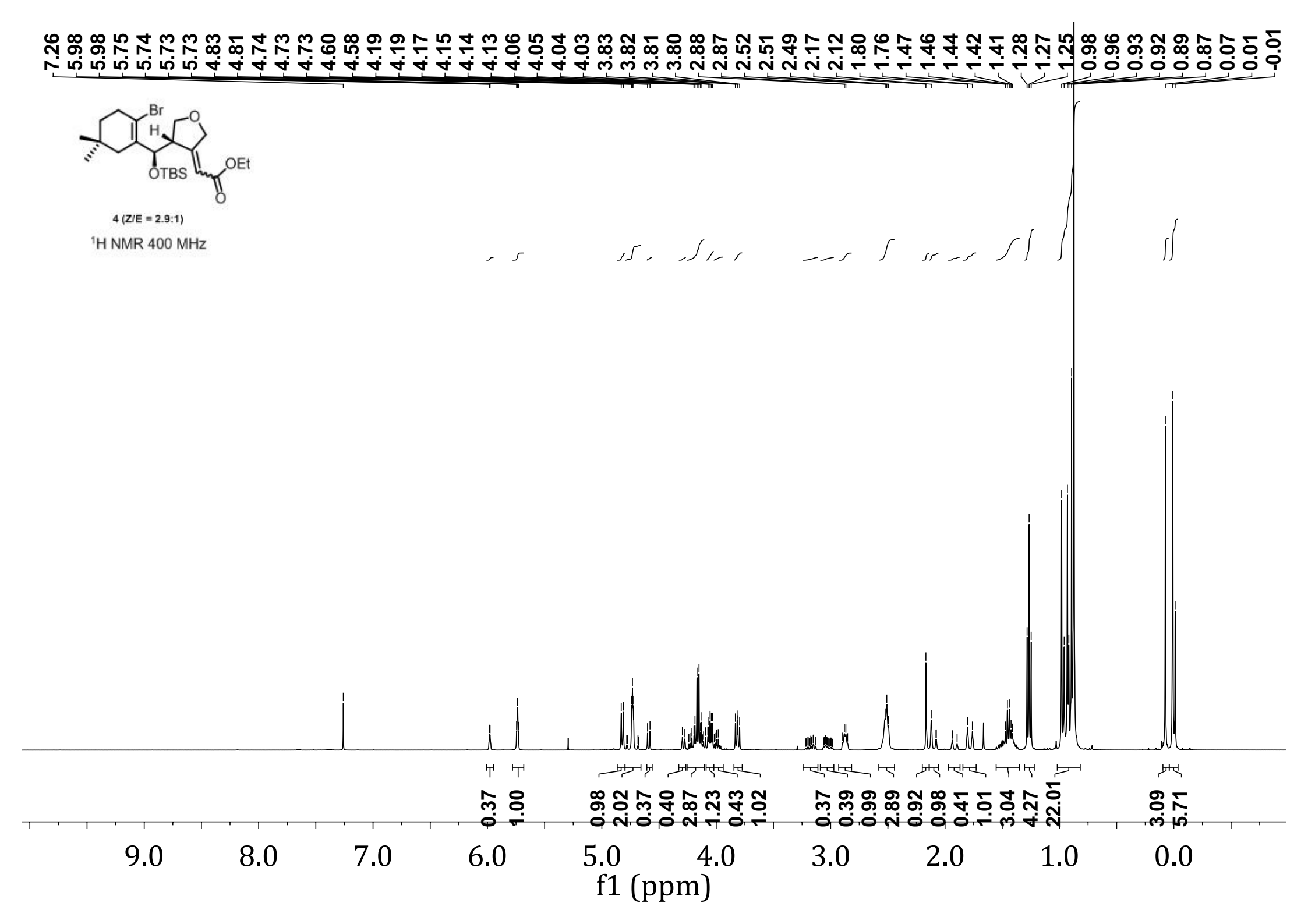
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Br
H
O
OTBS
OEt
O
4 (Z/E = 2.9:1)
1H NMR 400 MHz
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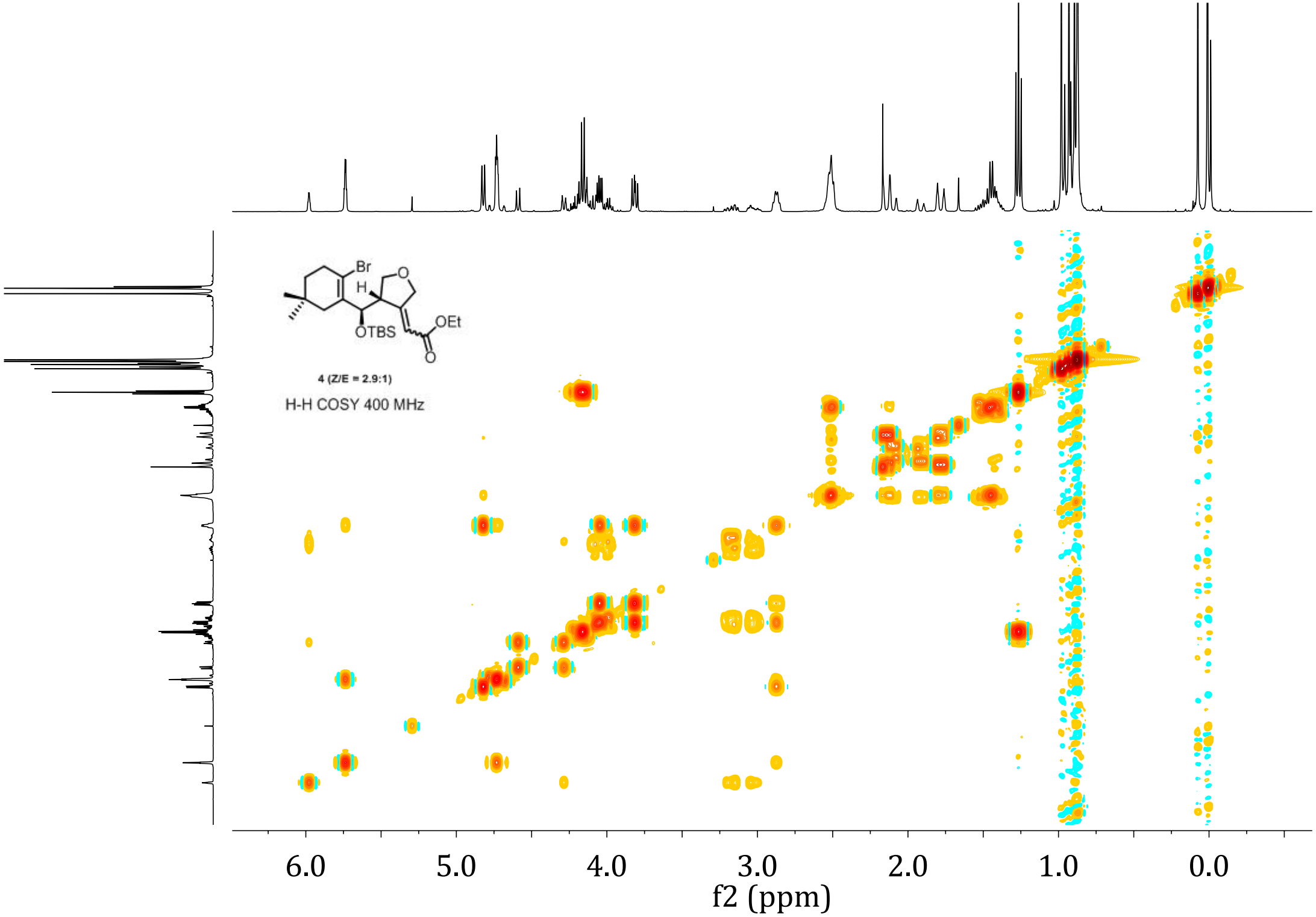
f1 (ppm)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O
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OEt
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H-H COSY 400 MHz
6.0
5.0
4.0
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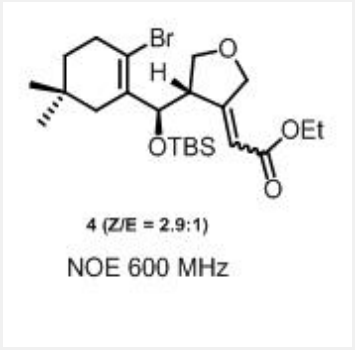
2.0
1.0
0.0
f2 (ppm)



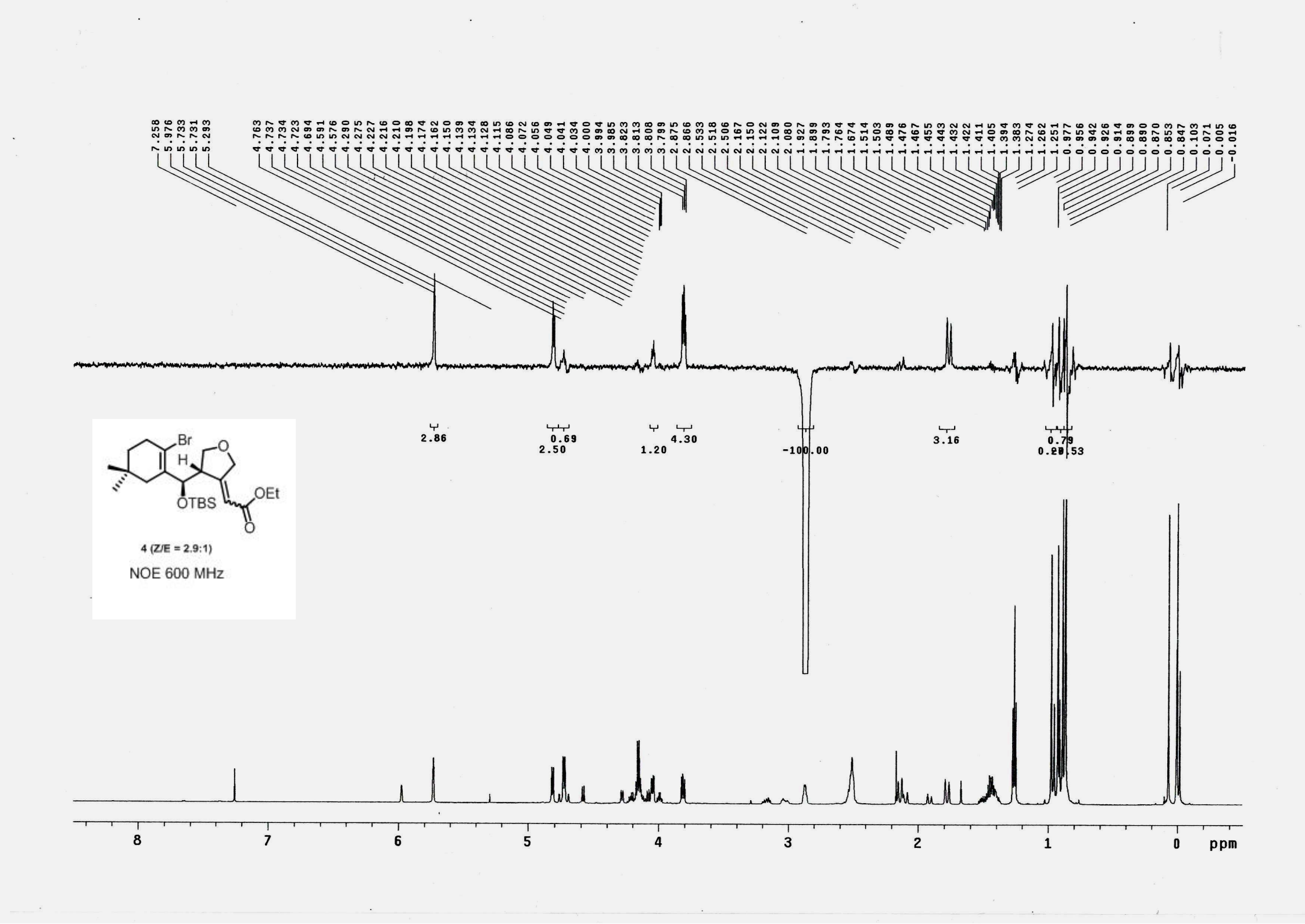
4 (Z/E = 2.9:1)

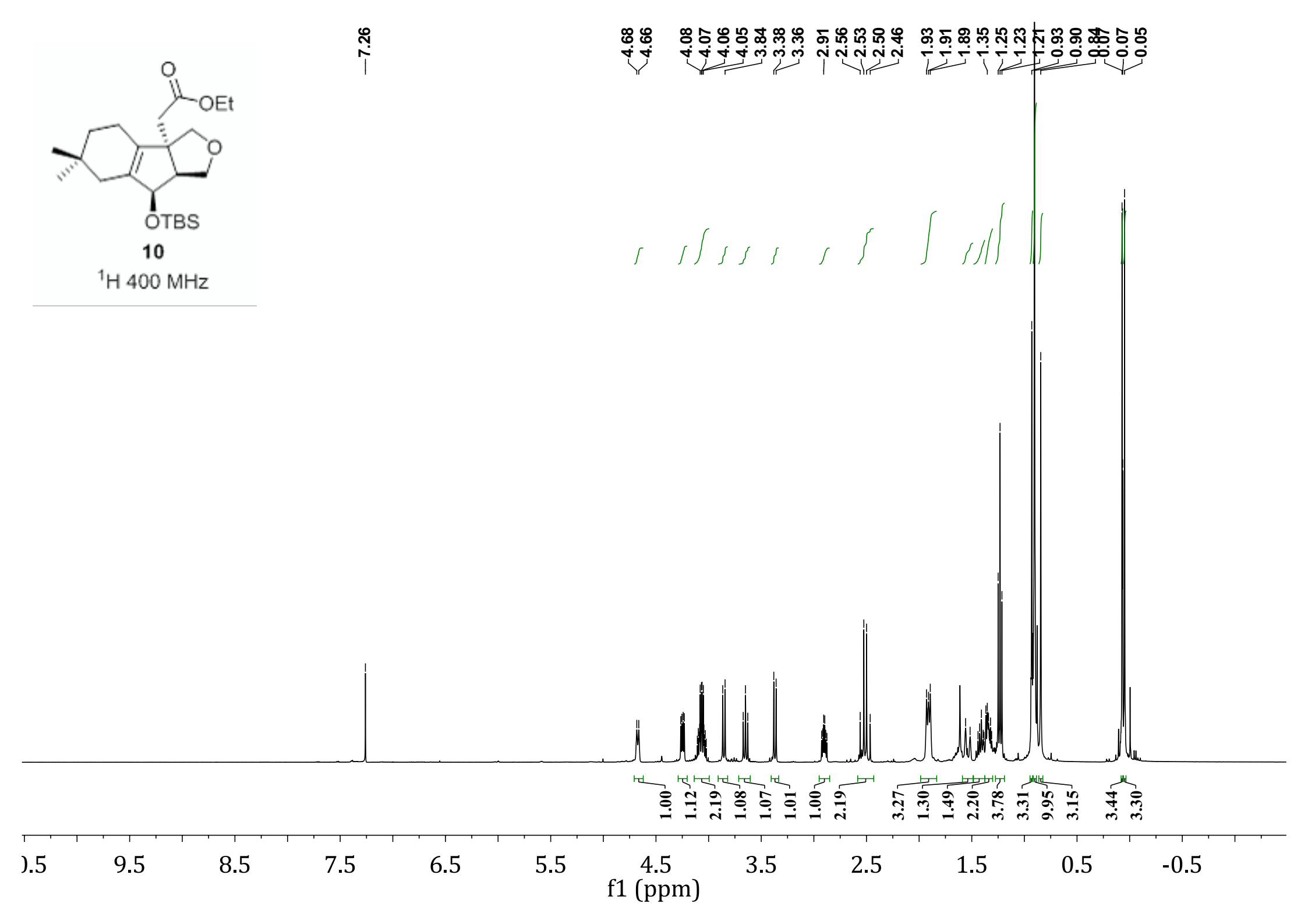
NOE 600 MHz

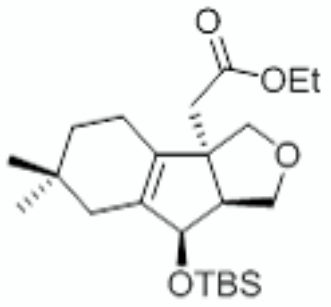
7.258 5.976 5.733 5.731 5.293 4.763 4.737 4.734 4.723 4.694 4.591 4.576 4.290 4.275 4.227 4.216 4.210 4.198 4.174 4.162 4.150 4.139 4.134 4.128 4.115 4.086 4.072 4.056 4.049 4.041 4.034 4.000 3.994 3.985 3.823 3.813 3.808 3.799 2.875 2.866 2.533 2.518 2.506 2.167 2.150 2.122 2.109 2.080 1.927 1.899 1.793 1.764 1.674 1.514 1.503 1.489 1.476 1.467 1.455 1.443 1.432 1.422 1.411 1.405 1.394 1.383 1.274 1.262 1.251 0.977 0.956 0.942 0.926 0.914 0.899 0.890 0.870 0.853 0.847 0.103 0.071 0.005 -0.016

-100.00 2.95 2.31 1.14 1.01 -0.17 0.46

8 7 6 5 4 3 2 1 0 ppm


7.258
5.976
5.733
5.731
5.293
4.763
4.737
4.734
4.723
4.694
4.591
4.576
4.290
4.275
4.227
4.216
4.210
4.198
4.174
4.162
4.150
4.139
4.134
4.128
4.115
4.086
4.072
4.056
4.049
4.041
4.034
4.000
3.994
3.985
3.823
3.813
3.808
3.799
2.875
2.866
2.533
2.518
2.506
2.167
2.150
2.122
2.109
2.080
1.927
1.899
1.793
1.764
1.674
1.514
1.503
1.489
1.476
1.467
1.455
1.443
1.432
1.422
1.411
1.405
1.394
1.383
1.274
1.262
1.251
0.977
0.956
0.942
0.926
0.914
0.899
0.890
0.870
0.853
0.847
0.103
0.071
0.005
-0.016
2.86
0.69
2.50
1.20
4.30
-100.00
3.16
0.79
0.28
0.53
Br
O
H
OEt
OTBS
O
4 (Z/E = 2.9:1)
NOE 600 MHz
8
7
6
5
4
3
2
1
0
ppm

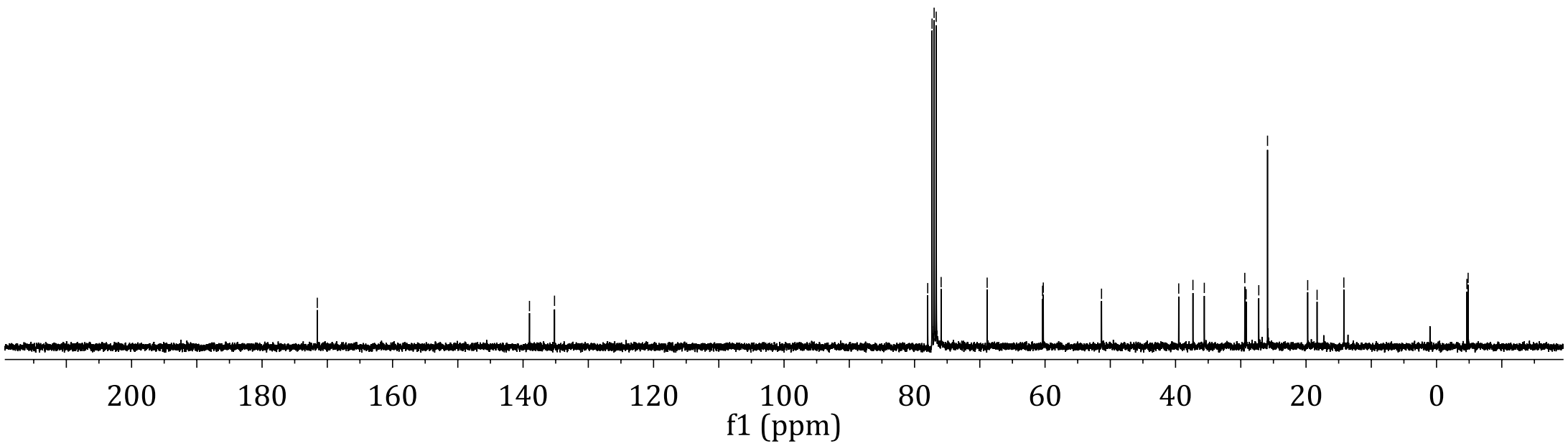

OEt
O
O
OTBS
10
1H 400 MHz
7.26
4.68
4.66
4.08
4.07
4.06
4.05
3.84
3.38
3.36
2.91
2.56
2.53
2.50
2.46
1.93
1.91
1.89
1.35
1.25
1.23
1.21
0.93
0.90
0.84
0.07
0.05
1.00
1.12
2.19
1.08
1.07
1.01
1.00
2.19
3.27
1.30
1.49
2.20
3.78
3.31
9.95
3.15
3.44
3.30
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

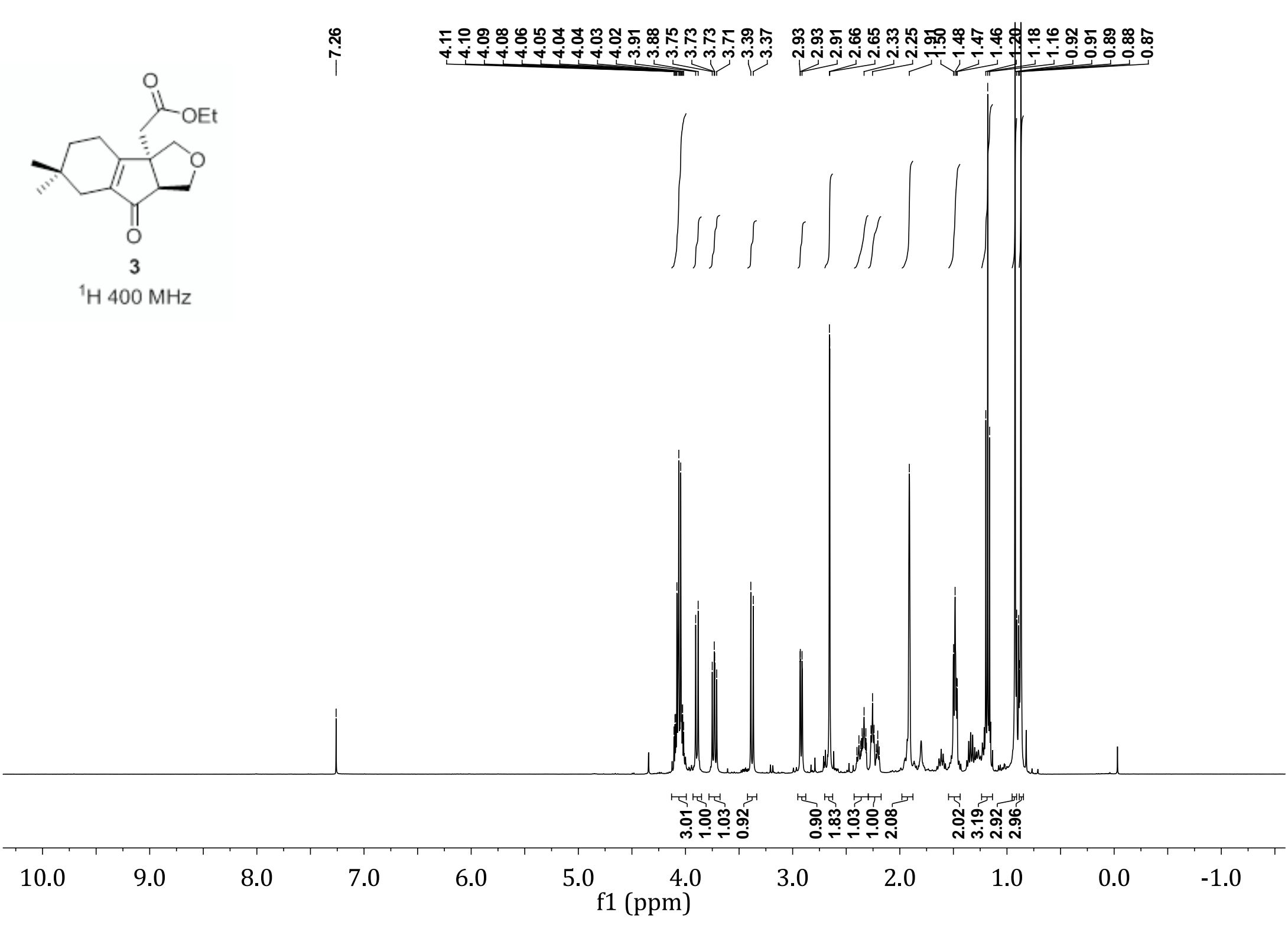


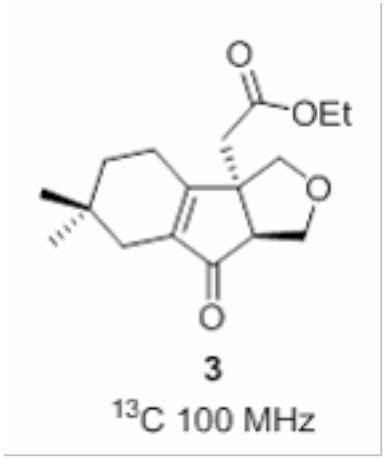
10

^{13}C 100 MHz

171.53
139.02
135.18
77.98
77.32
77.00
76.68
75.93
68.87
60.38
60.27
51.34
39.51
37.33
35.59
29.39
29.18
27.24
25.90
19.75
18.31
14.21
-4.66
-4.84



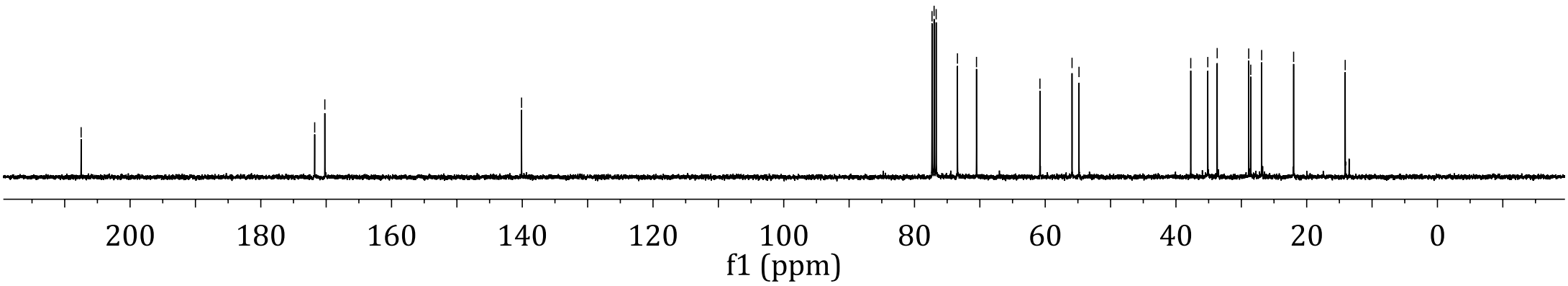

7.26
4.11
4.10
4.09
4.08
4.06
4.05
4.04
4.04
4.03
4.02
3.91
3.88
3.75
3.73
3.73
3.71
3.39
3.37
2.93
2.93
2.91
2.66
2.65
2.33
2.25
1.91
1.50
1.48
1.47
1.46
1.20
1.18
1.16
0.92
0.91
0.89
0.88
0.87
OEt
O
O
O
3
1H 400 MHz
3.01
1.00
1.03
0.92
0.90
1.83
1.03
1.00
2.08
2.02
3.19
2.92
2.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

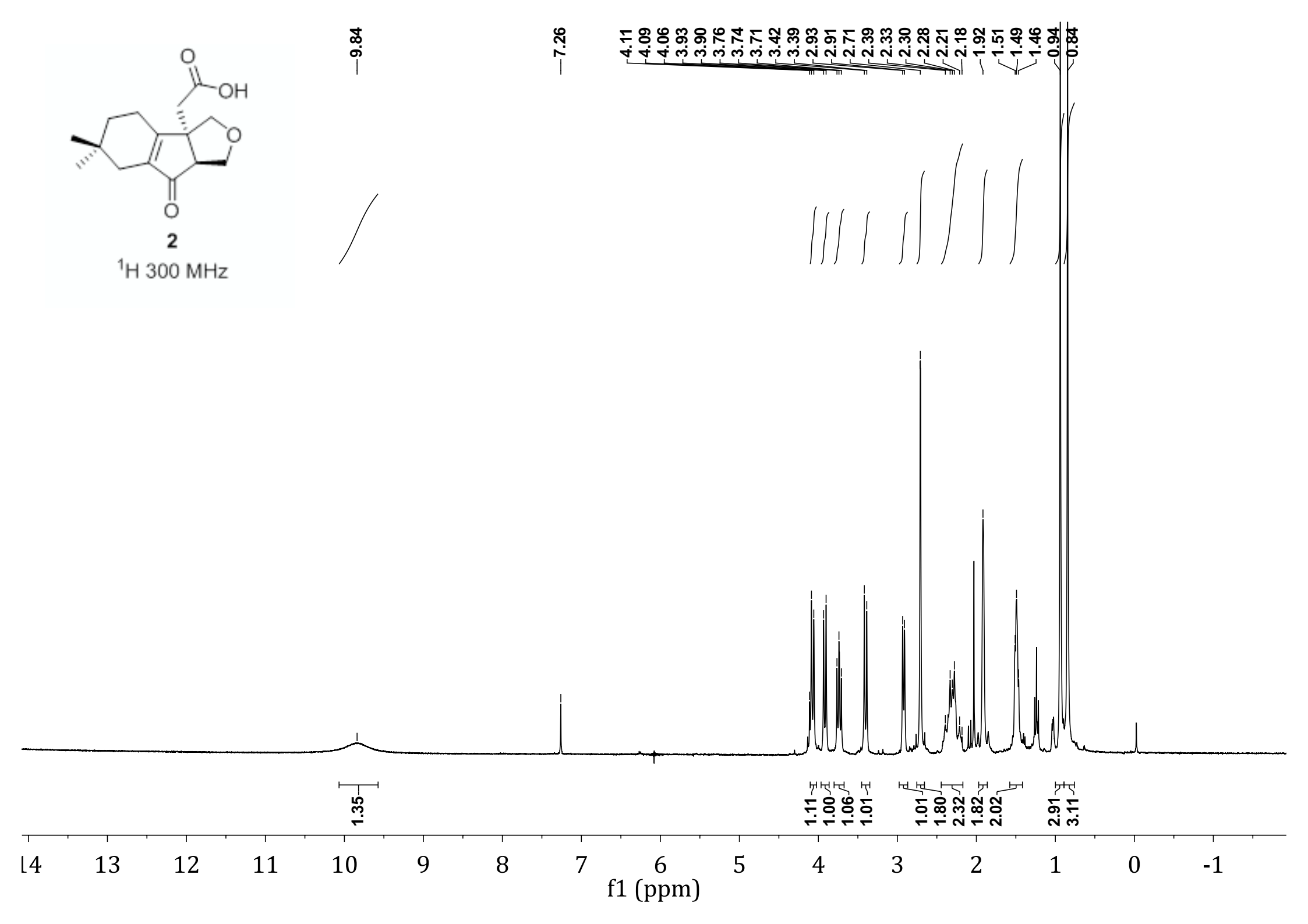


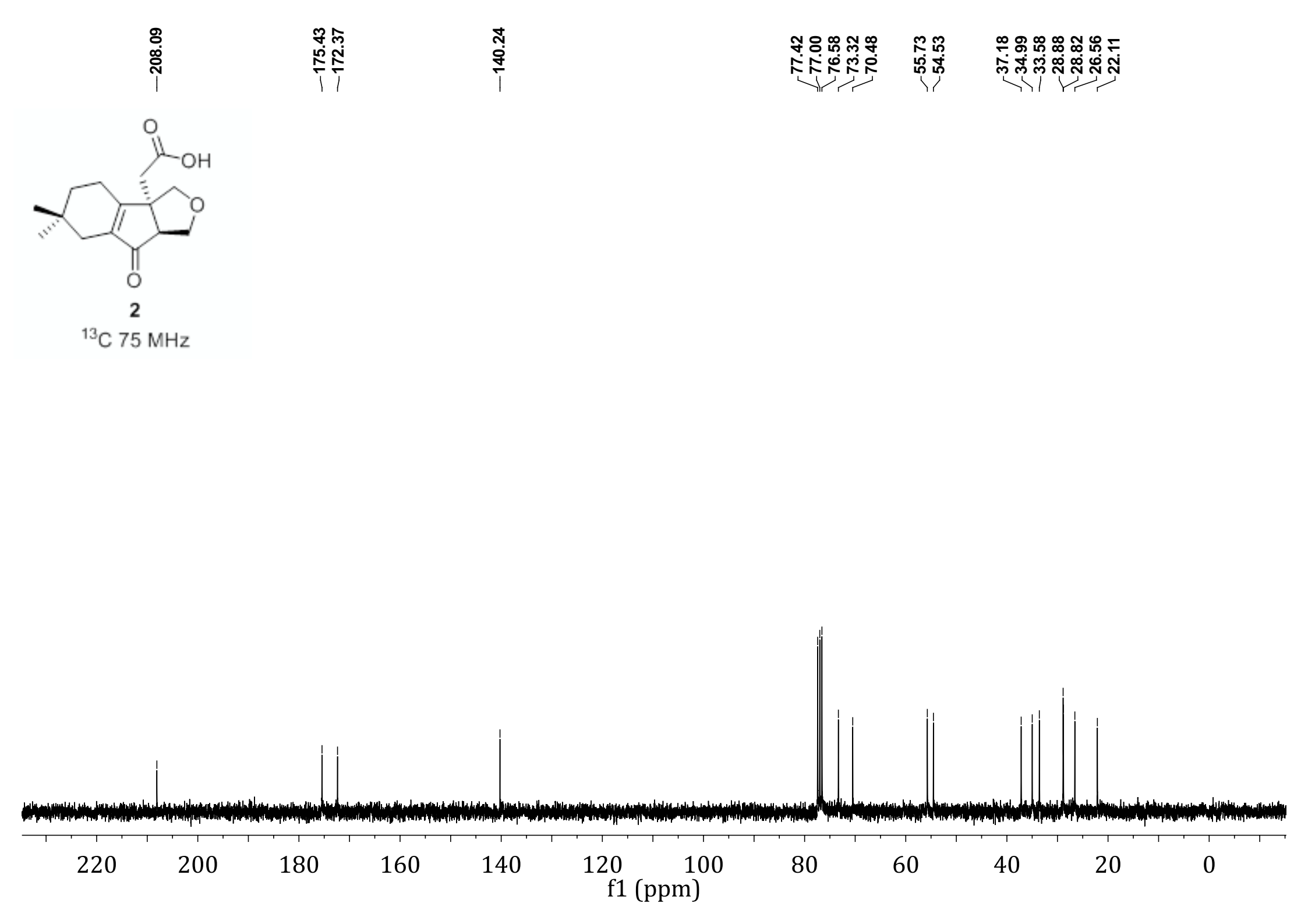
3

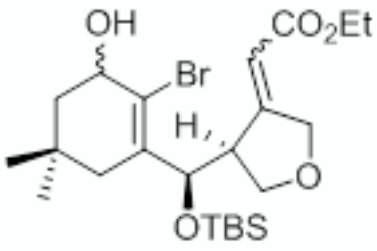
^{13}C 100 MHz

207.49
171.76
170.21
140.11
77.32
77.00
76.68
73.43
70.51
60.81
55.90
54.83
37.73
35.13
33.69
28.87
28.56
26.89
22.00
14.11




O
OH
O
O
2
1H 300 MHz
9.84
7.26
4.11
4.09
4.06
3.93
3.90
3.76
3.74
3.71
3.42
3.39
2.93
2.91
2.71
2.39
2.33
2.30
2.28
2.21
2.18
1.92
1.51
1.49
1.46
0.94
0.84
1.35
1.11
1.00
1.06
1.01
1.01
1.80
2.32
1.82
2.02
2.91
3.11
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

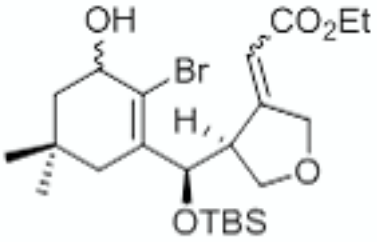

208.09
175.43
172.37
140.24
77.42
77.00
76.58
73.32
70.48
55.73
54.53
37.18
34.99
33.58
28.88
28.82
26.56
22.11
OH
O
O
O
2
13C 75 MHz
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



12

^{1}H 300 MHz

single diastereoisomer

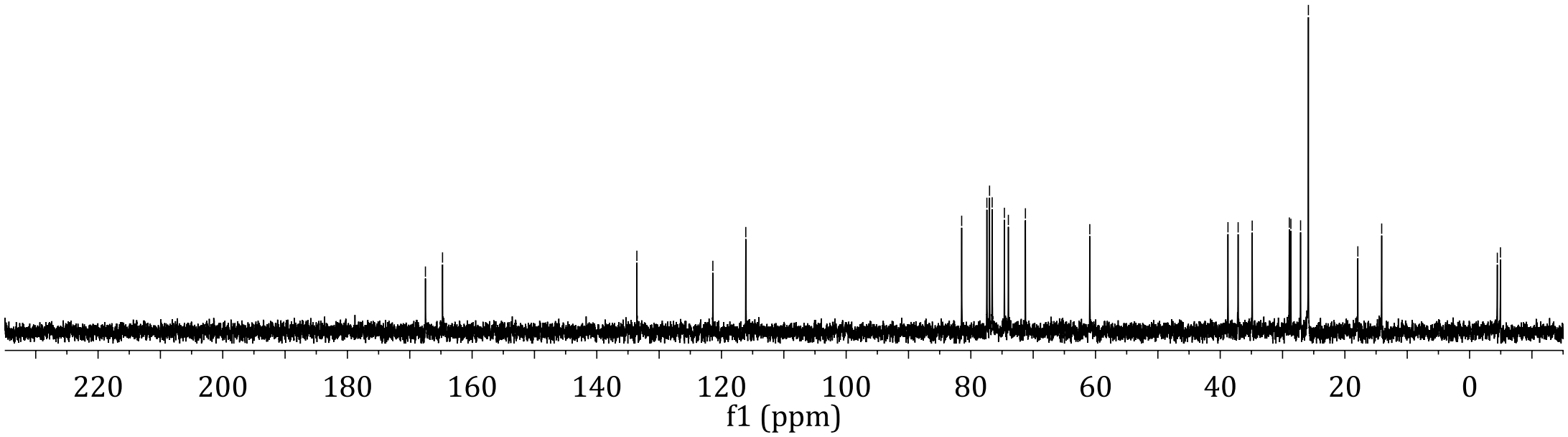


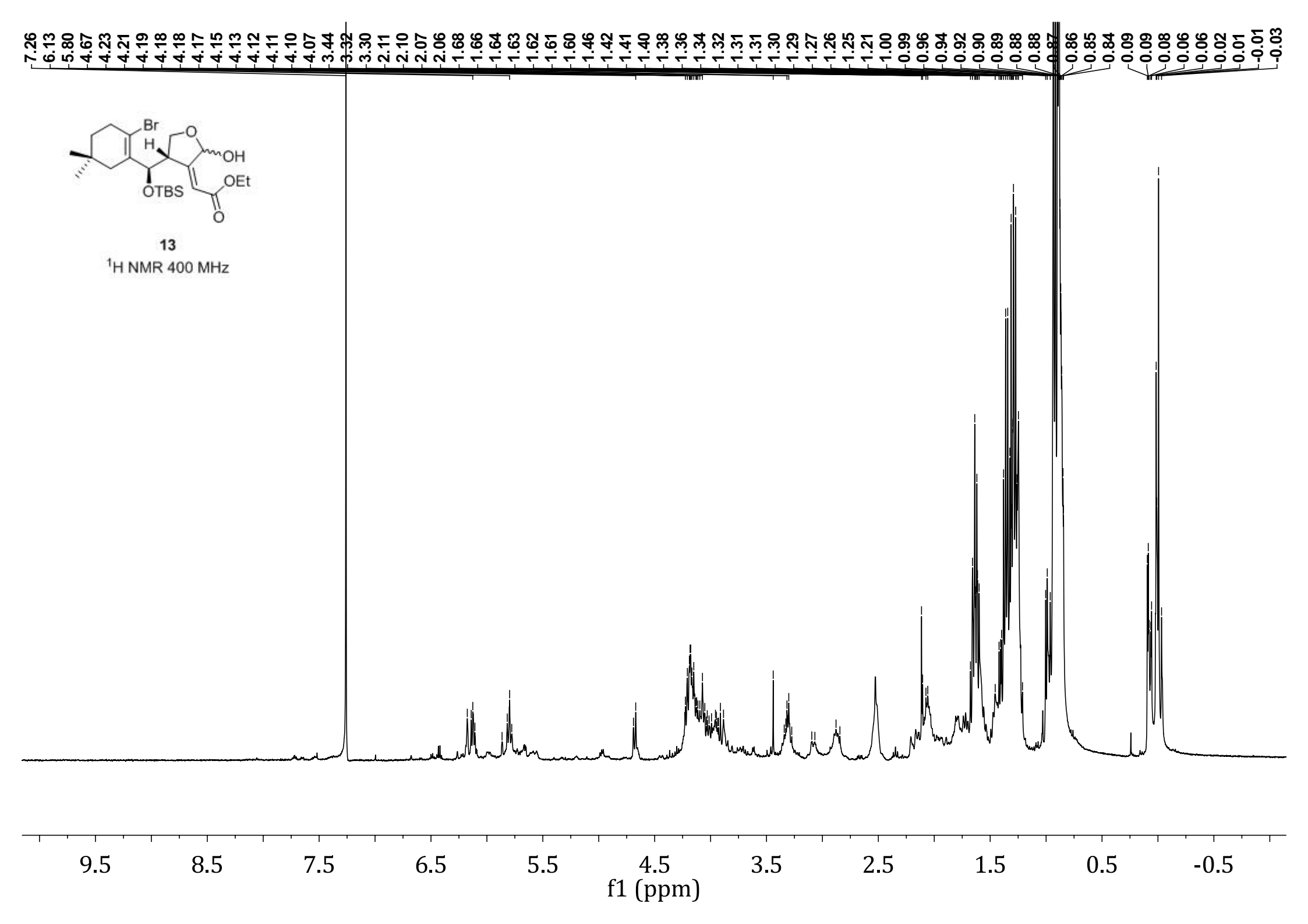
12

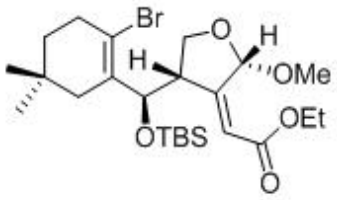
^{13}C 75 MHz

single diastereoisomer

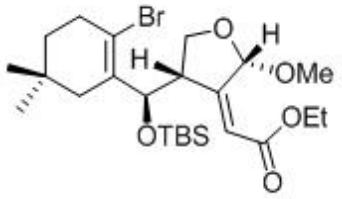
167.49
164.75
133.57
121.38
116.10
81.47
77.43
77.00
76.58
74.62
73.98
71.25
60.92
38.76
37.13
34.87
28.91
28.66
27.11
25.85
17.92
14.10
-4.45
-4.95



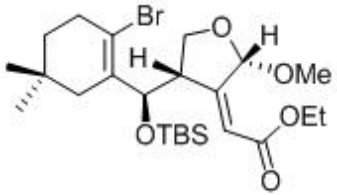

7.26 6.13 5.80 4.67 4.23 4.21 4.19 4.18 4.18 4.17 4.15 4.13 4.12 4.11 4.10 4.07 3.44 3.32 3.30 2.11 2.10 2.07 2.06 1.68 1.66 1.64 1.63 1.62 1.61 1.60 1.46 1.42 1.41 1.40 1.38 1.36 1.34 1.32 1.31 1.31 1.30 1.29 1.27 1.26 1.25 1.21 1.00 0.99 0.96 0.94 0.92 0.90 0.89 0.88 0.88 0.87 0.86 0.85 0.84 0.09 0.09 0.08 0.06 0.06 0.02 0.01 -0.01 -0.03
Br
H
O
OH
OEt
OTBS
O
13
1H NMR 400 MHz
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



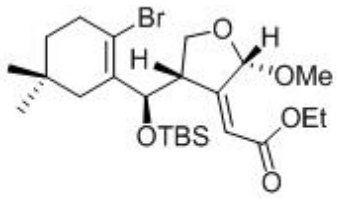
14-β less polar
^{1}H NMR 300 MHz



14-β less polar
^{13}C NMR 75 MHz

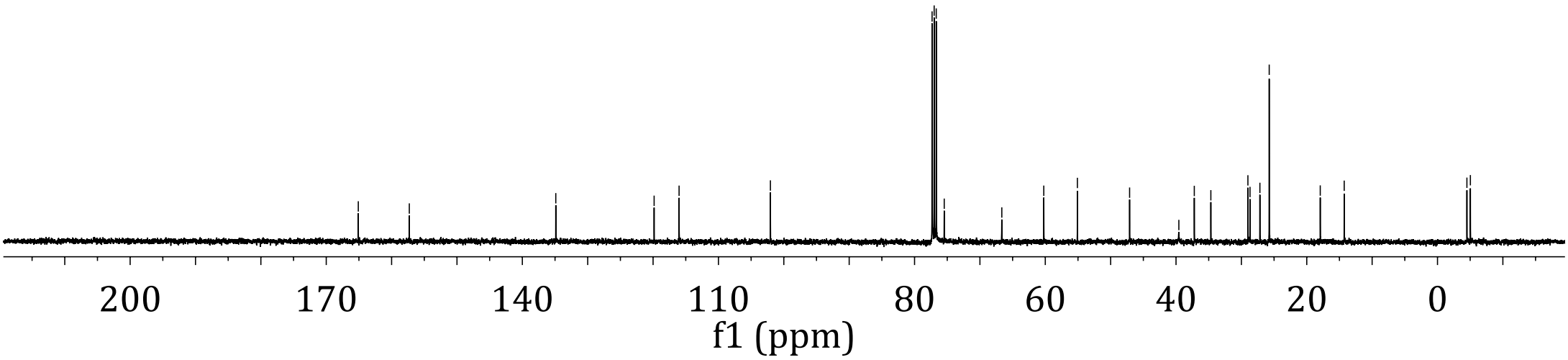


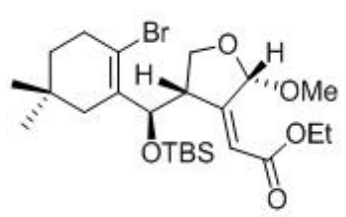
14-β less polar
^{1}H NMR 400 MHz



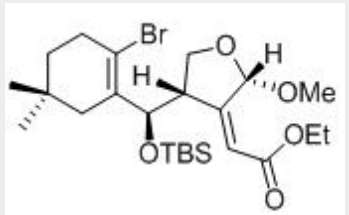
14-β less polar
^{13}C NMR 101 MHz

165.10
157.29
134.88
119.84
116.02
102.05
77.32
77.00
76.68
75.46
66.65
60.23
55.09
47.10
39.57
37.21
34.67
29.00
28.68
27.17
25.74
17.94
14.27
-4.50
-5.03





14-β less polar
HMBC 400 MHz

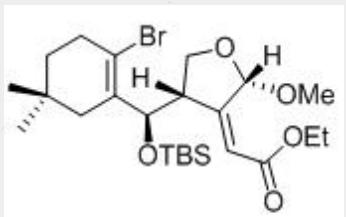


14-β less polar
NOE 600 MHz

7.257
5.876
5.797
4.938
4.930
4.196
4.184
4.173
4.160
4.005
3.990
3.422
2.975
2.965
2.528
2.517
2.125
2.095
1.789
1.761
1.464
1.452
1.440
1.435
1.425
1.288
1.276
1.264
0.959
0.920
0.856
0.832
0.048
-0.012

-100.00
4.26

8 7 6 5 4 3 2 1 0 ppm

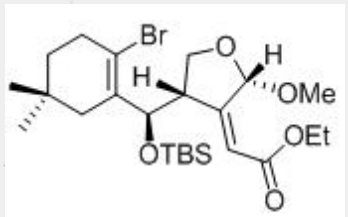


14-β less polar
NOE 600 MHz

7.257
5.876
5.797
4.938
4.930
4.196
4.184
4.173
4.160
4.005
3.990
3.422
2.975
2.965
2.528
2.517
2.125
2.095
1.789
1.761
1.464
1.452
1.440
1.435
1.425
1.288
1.276
1.264
0.959
0.920
0.856
0.832
0.048
-0.012

-100.00
3.61
1.83
1.02
0.16
0.66

8 7 6 5 4 3 2 1 0 ppm

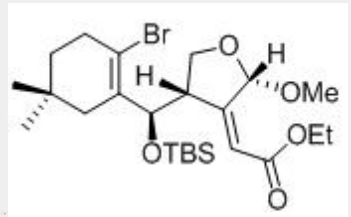


14-β less polar
NOE 600 MHz

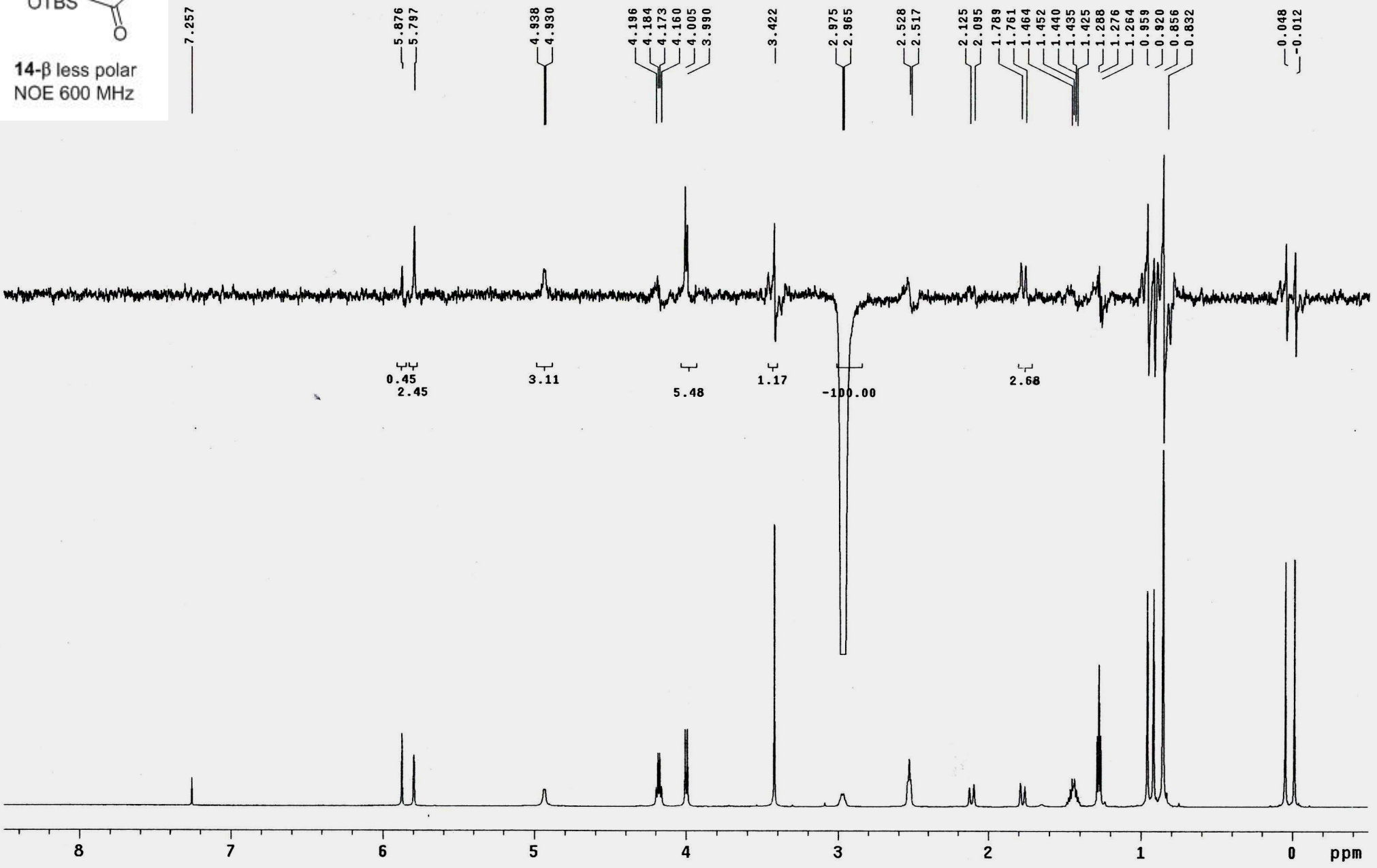
7.257
5.876
5.797
4.938
4.930
4.196
4.184
4.173
4.160
4.005
3.990
3.422
2.975
2.965
2.528
2.517
2.125
2.095
1.789
1.761
1.464
1.452
1.440
1.435
1.425
1.288
1.276
1.264
0.959
0.920
0.856
0.832
0.048
-0.012

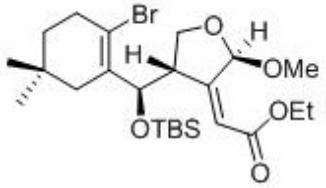
3.15
-100.00

8 7 6 5 4 3 2 1 0 ppm

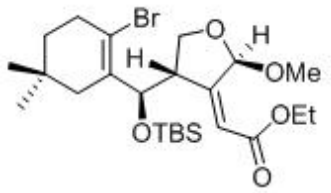


14-β less polar
NOE 600 MHz



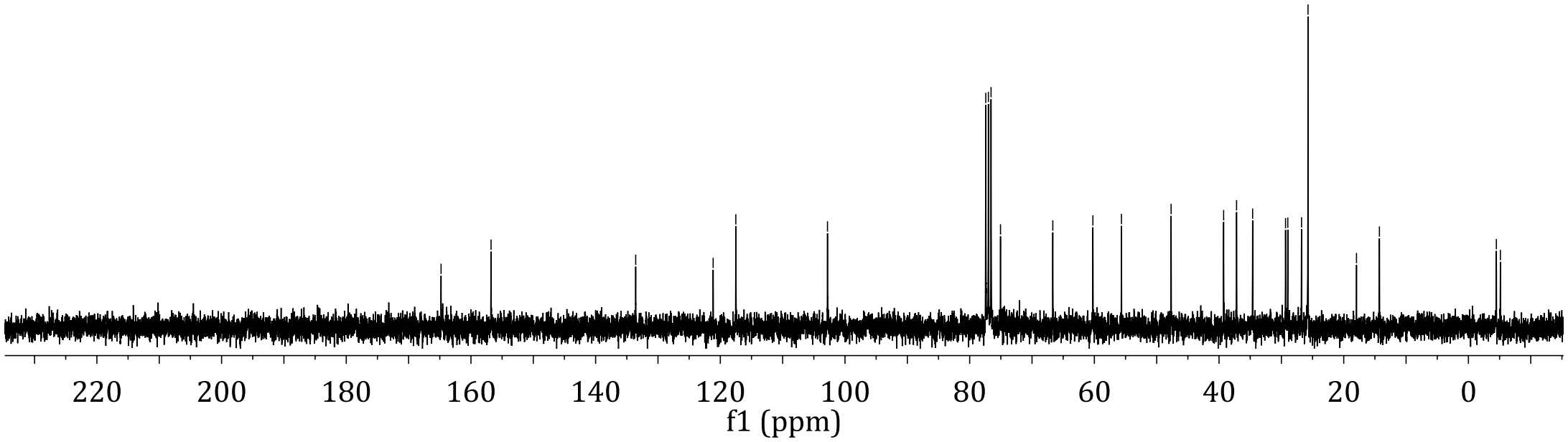


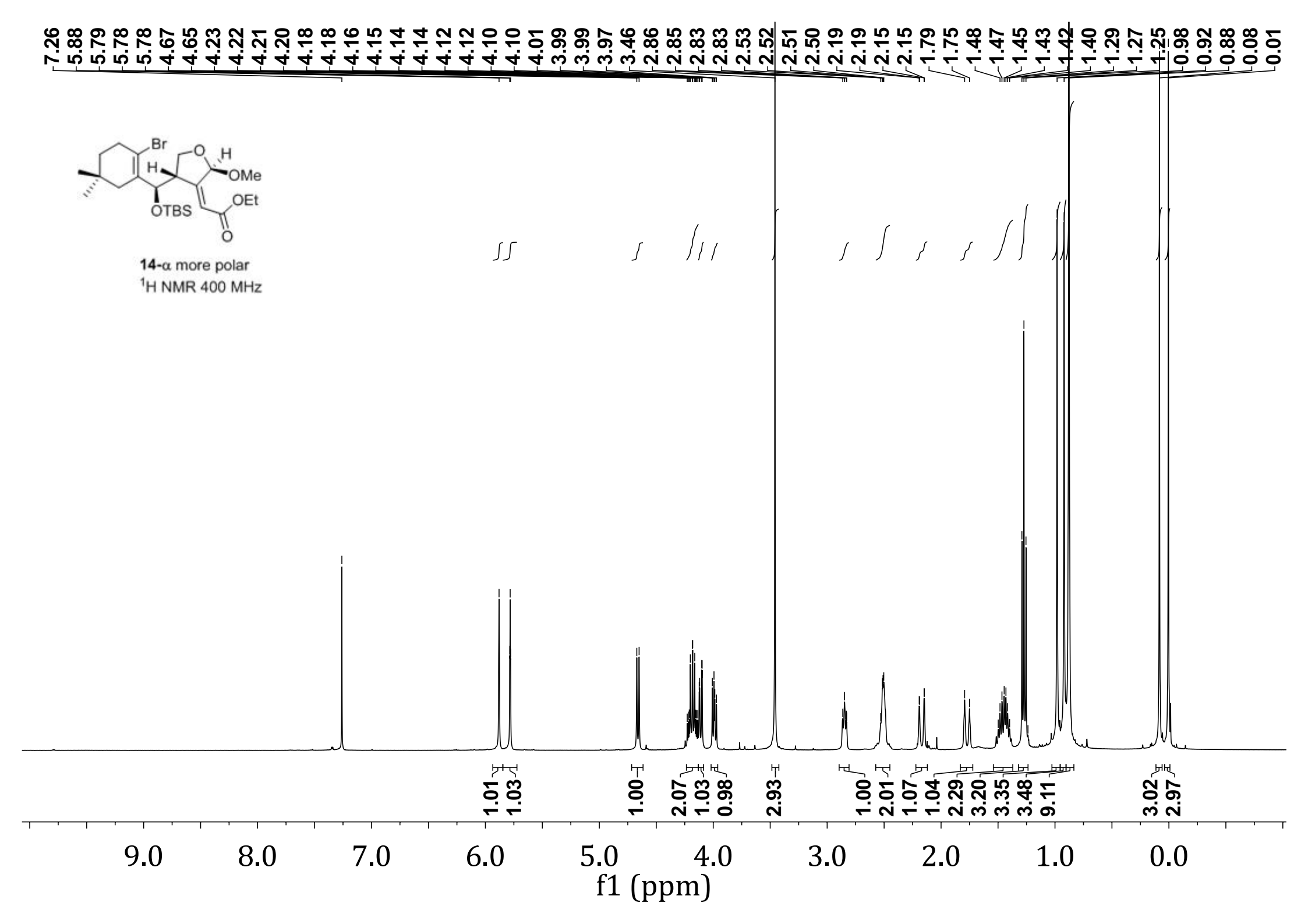
14-α more polar
^{1}H NMR 300 MHz

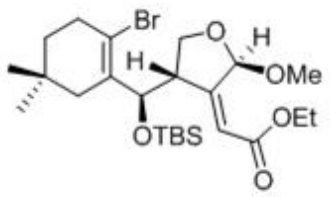


14-α more polar
^{13}C NMR 75 MHz

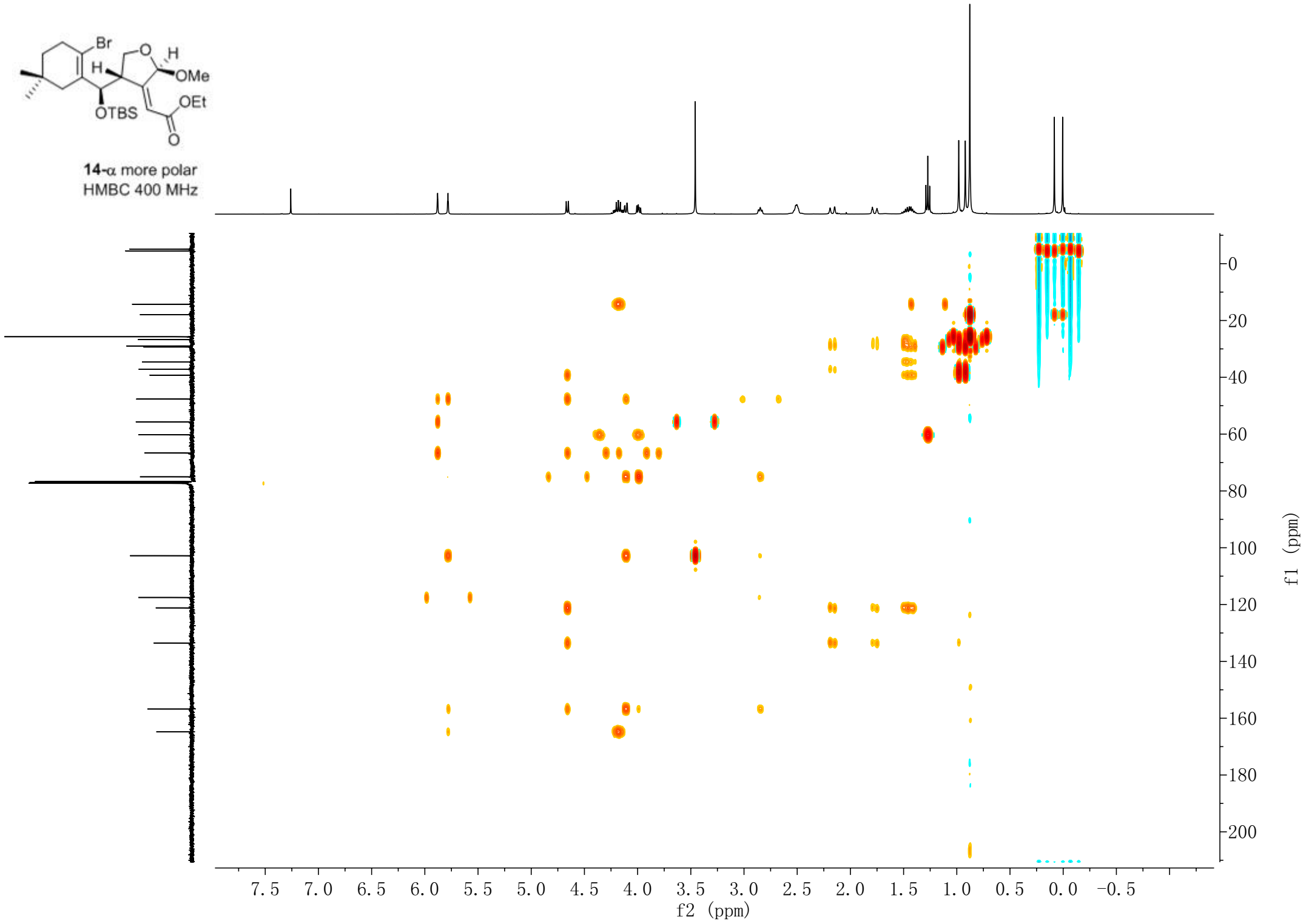
164.79
156.78
133.57
121.15
117.51
102.81
77.42
77.00
76.57
75.06
66.67
60.24
55.65
47.69
39.26
37.19
34.61
29.33
28.97
26.77
25.73
17.95
14.28
-4.48
-5.13

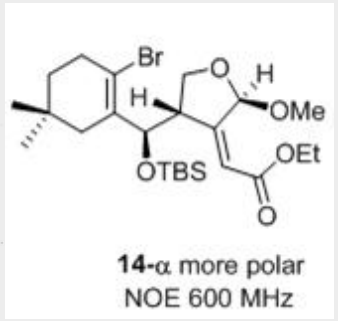



7.26 5.88 5.79 5.78 5.78 4.67 4.65 4.23 4.22 4.21 4.20 4.18 4.18 4.16 4.15 4.14 4.14 4.12 4.12 4.10 4.10 4.01 3.99 3.99 3.97 3.46 2.86 2.85 2.83 2.83 2.53 2.52 2.51 2.50 2.19 2.19 2.15 2.15 1.79 1.75 1.48 1.47 1.45 1.43 1.42 1.40 1.29 1.27 1.25 0.98 0.92 0.88 0.08 0.01
Br
O
H
H
OMe
OEt
OTBS
O
14-α more polar
1H NMR 400 MHz
1.01 1.03 1.00 2.07 1.03 0.98 2.93 1.00 2.01 1.07 1.04 2.29 3.20 3.35 3.48 9.11 3.02 2.97
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



14-α more polar
^{13}C NMR 101 MHz


Br
O
H
H
OMe
OEt
OTBS
O
14-α more polar
HMBC 400 MHz
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

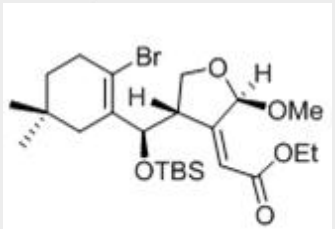


14-α more polar
NOE 600 MHz

7.257
5.877
5.777
4.662
4.648
4.196
4.184
4.171
4.159
4.152
4.112
4.099
3.999
3.989
3.984
3.974
3.455
2.853
2.843
2.832
2.508
2.497
2.179
2.151
1.783
1.754
1.476
1.465
1.425
1.414
1.281
1.268
1.257
0.978
0.916
0.874
0.080
0.001

-100.00
4.65

8 7 6 5 4 3 2 1 0 ppm



14-α more polar
NOE 600 MHz

7.257

5.877
5.777

4.662
4.648
4.196
4.184
4.171
4.159
4.152
4.112
4.099
3.999
3.989
3.984
3.974

3.455

2.853
2.843
2.832

2.508
2.497

2.179
2.151

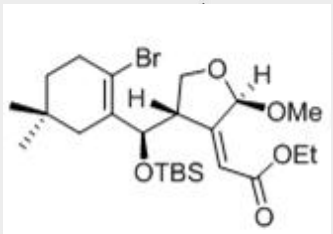
1.783
1.754
1.476
1.465
1.425
1.414
1.281
1.268
1.257

0.978
0.916
0.874

0.080
0.001

-100.00
2.45
2.46
1.90
1.12

8
7
6
5
4
3
2
1
0
ppm



14-α more polar
NOE 600 MHz

7.257

5.877
5.777

4.662
4.648
4.196
4.184
4.171
4.159
4.152
4.112
4.099
3.999
3.989
3.984
3.974

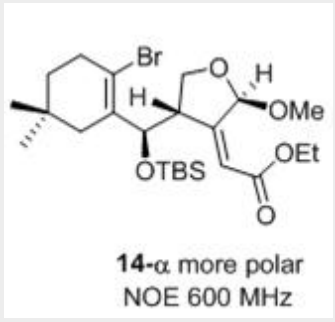
3.455

2.853
2.843
2.832
2.508
2.497
2.179
2.151
1.783
1.754
1.476
1.465
1.425
1.414
1.281
1.268
1.257
0.978
0.916
0.874

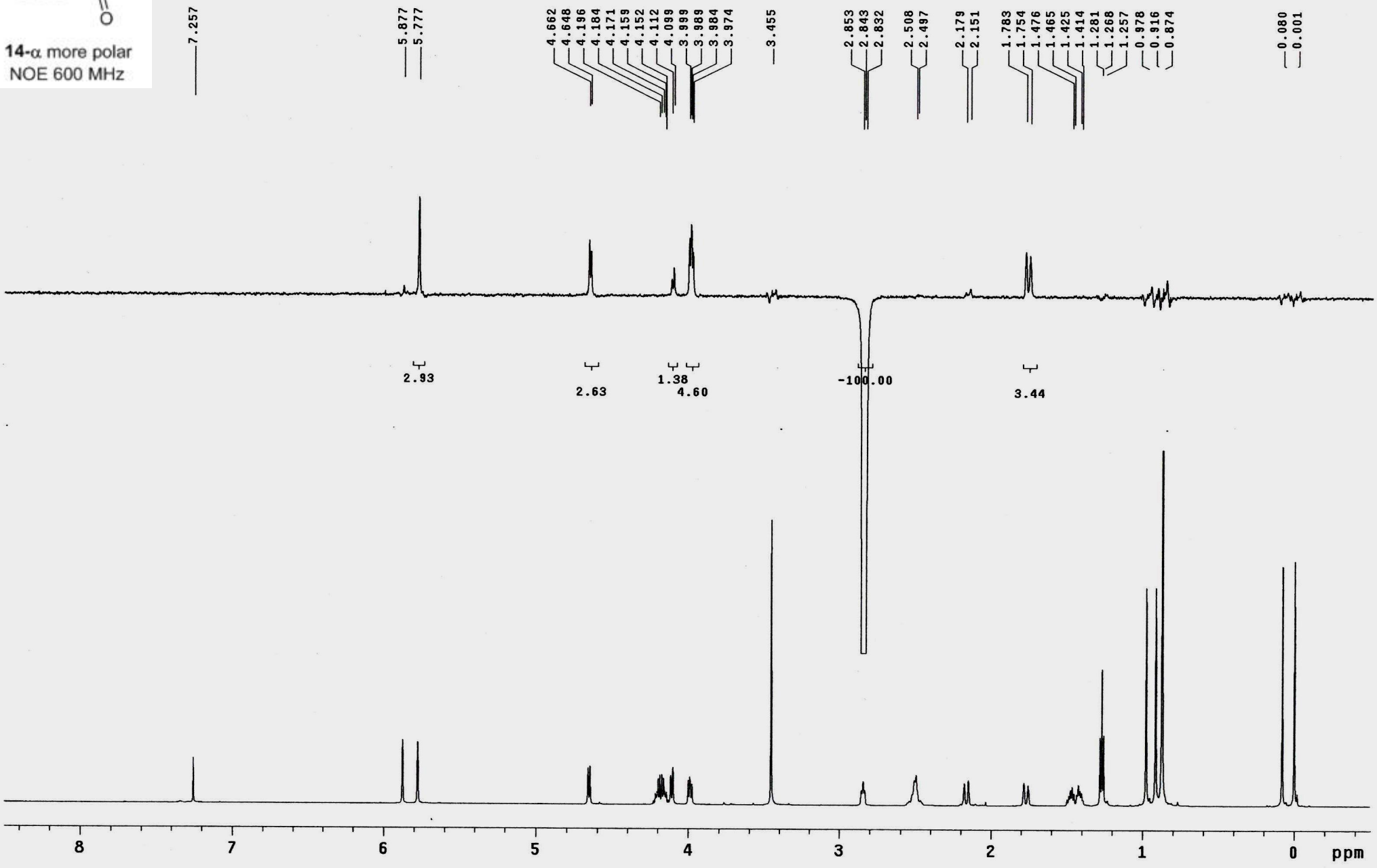
0.080
0.001

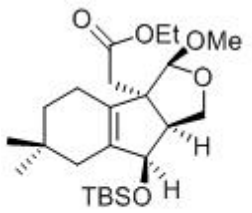
0.81
2.41
-100.00
1.74
2.12
0.64
1.96
1.20

8 7 6 5 4 3 2 1 0 ppm



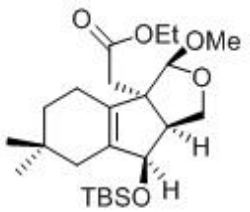
14-α more polar
NOE 600 MHz





15-α less polar

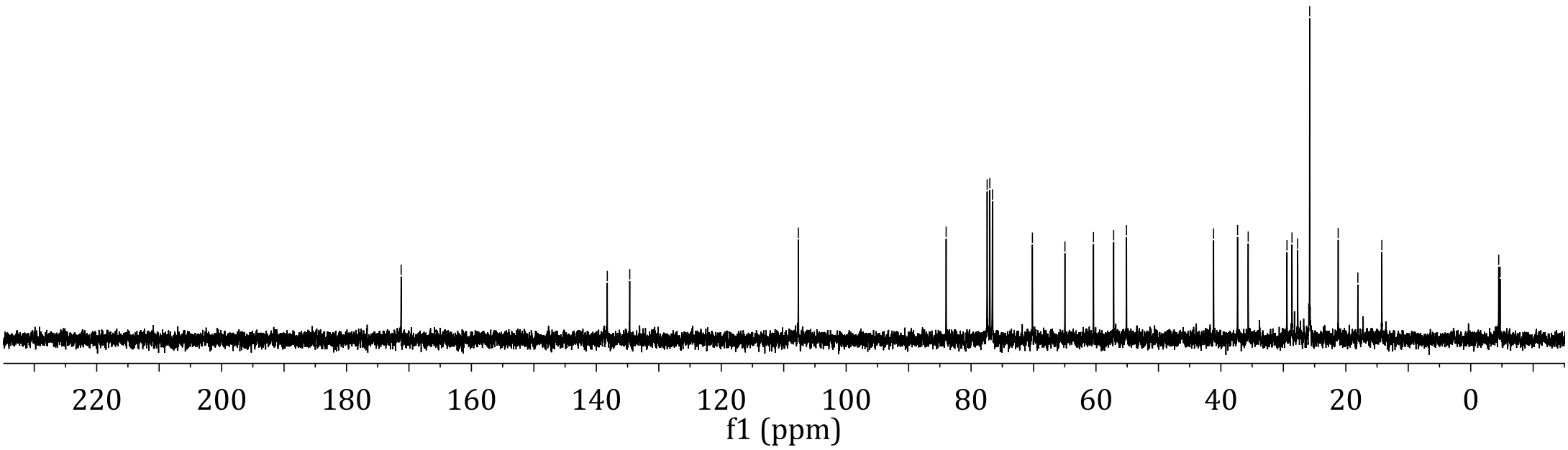
^{1}H NMR 300 MHz

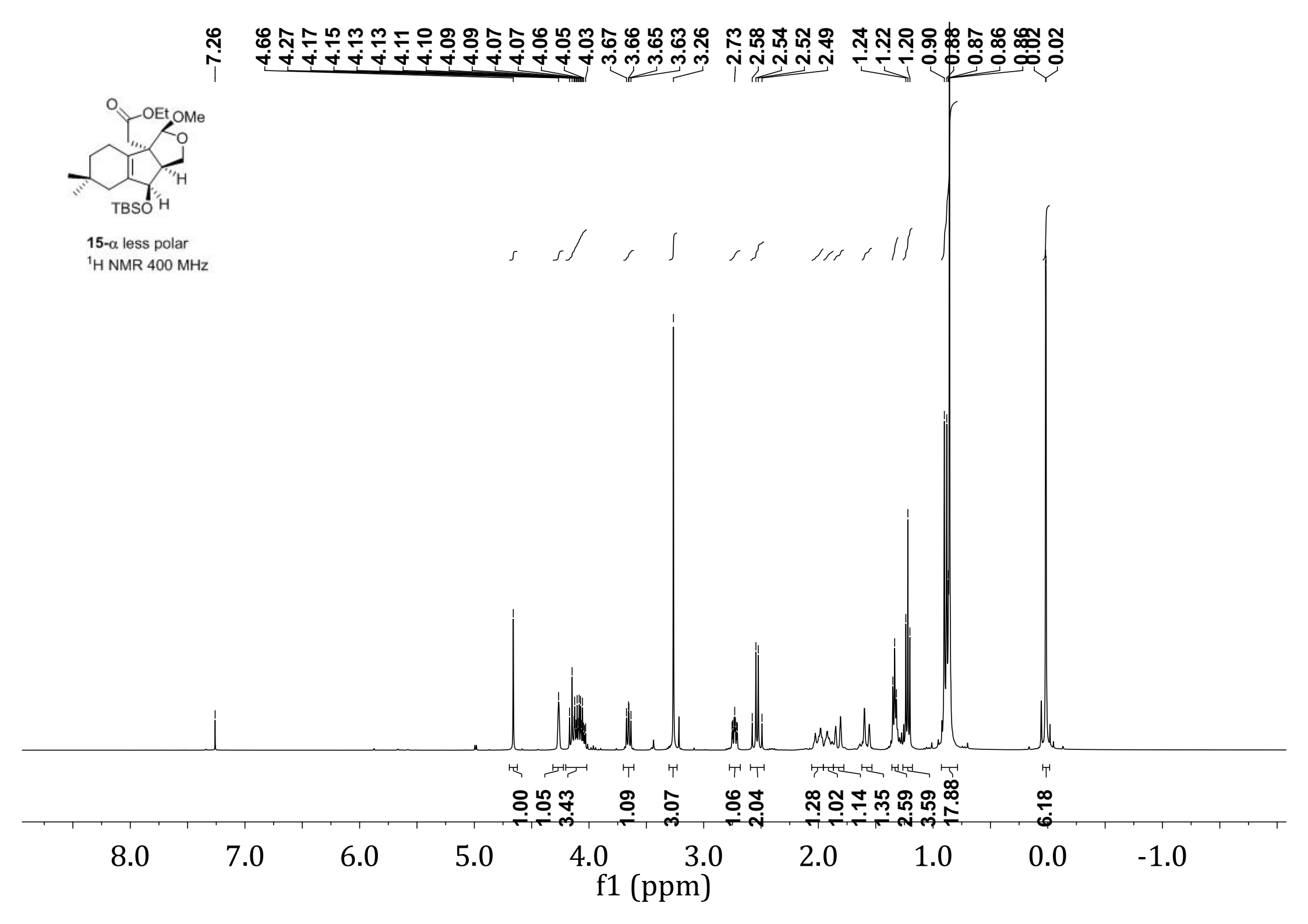


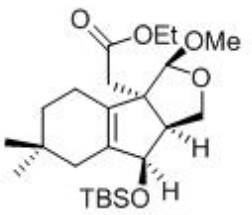
15-α less polar

^{13}C NMR 75 MHz

171.25
138.25
134.65
107.65
83.99
77.42
77.00
76.58
70.18
64.97
60.40
57.17
55.11
41.17
37.33
35.63
29.42
28.61
27.71
25.79
21.22
18.07
14.23
-4.48
-4.71

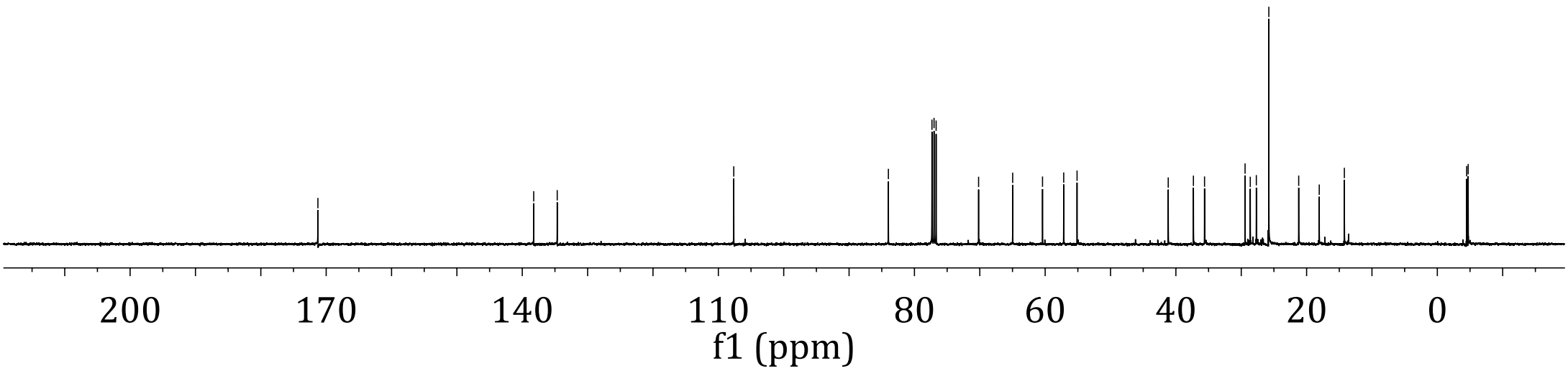


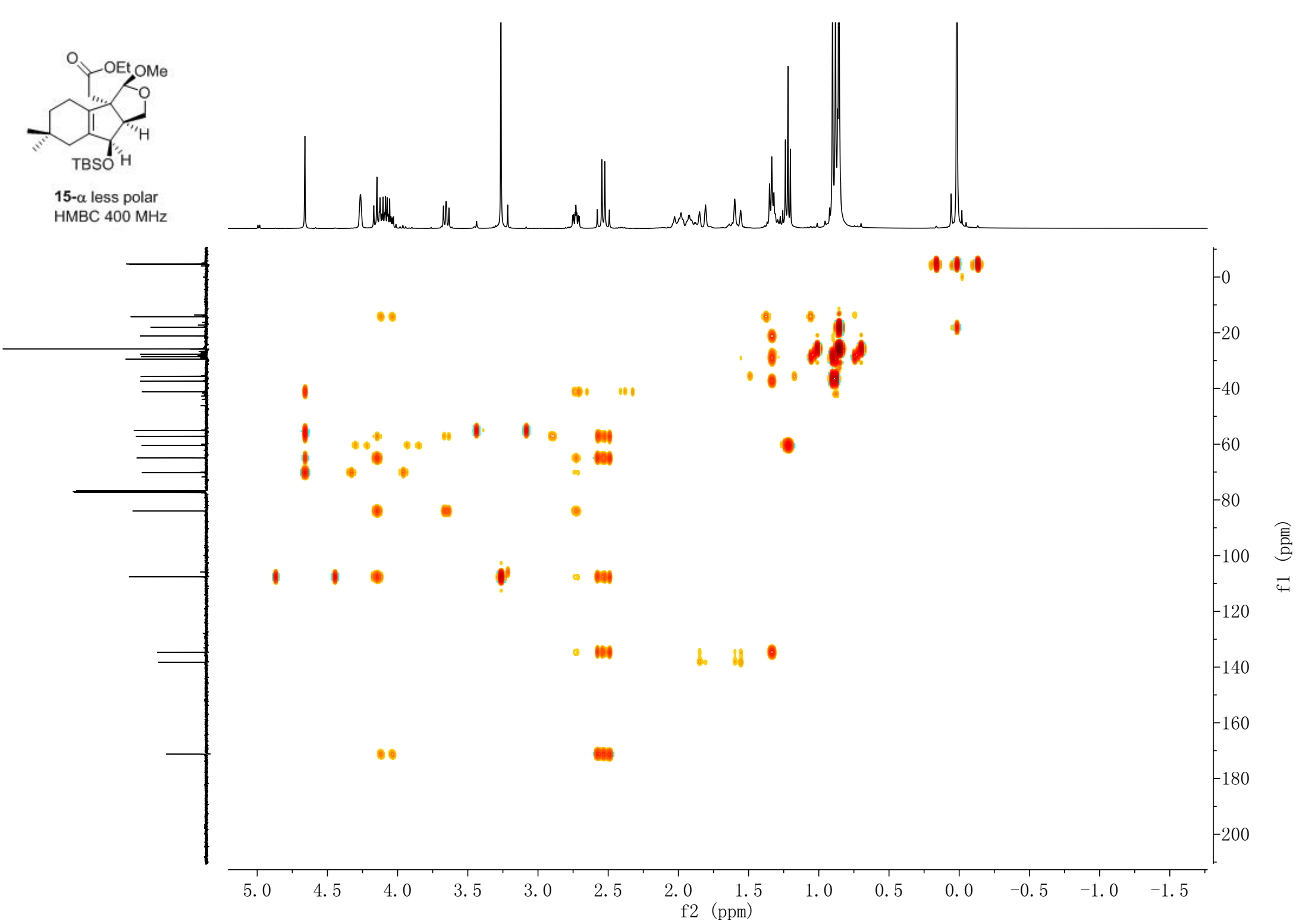

7.26
4.66
4.27
4.17
4.15
4.13
4.13
4.11
4.10
4.09
4.09
4.07
4.07
4.06
4.05
4.03
3.67
3.66
3.65
3.63
3.26
2.73
2.58
2.54
2.52
2.49
1.24
1.22
1.20
0.90
0.88
0.87
0.86
0.02
OEt
OMe
O
H
TBSO
H
15-α less polar
1H NMR 400 MHz
1.00
1.05
3.43
1.09
3.07
1.06
2.04
1.28
1.02
1.14
1.35
2.59
3.59
17.88
6.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

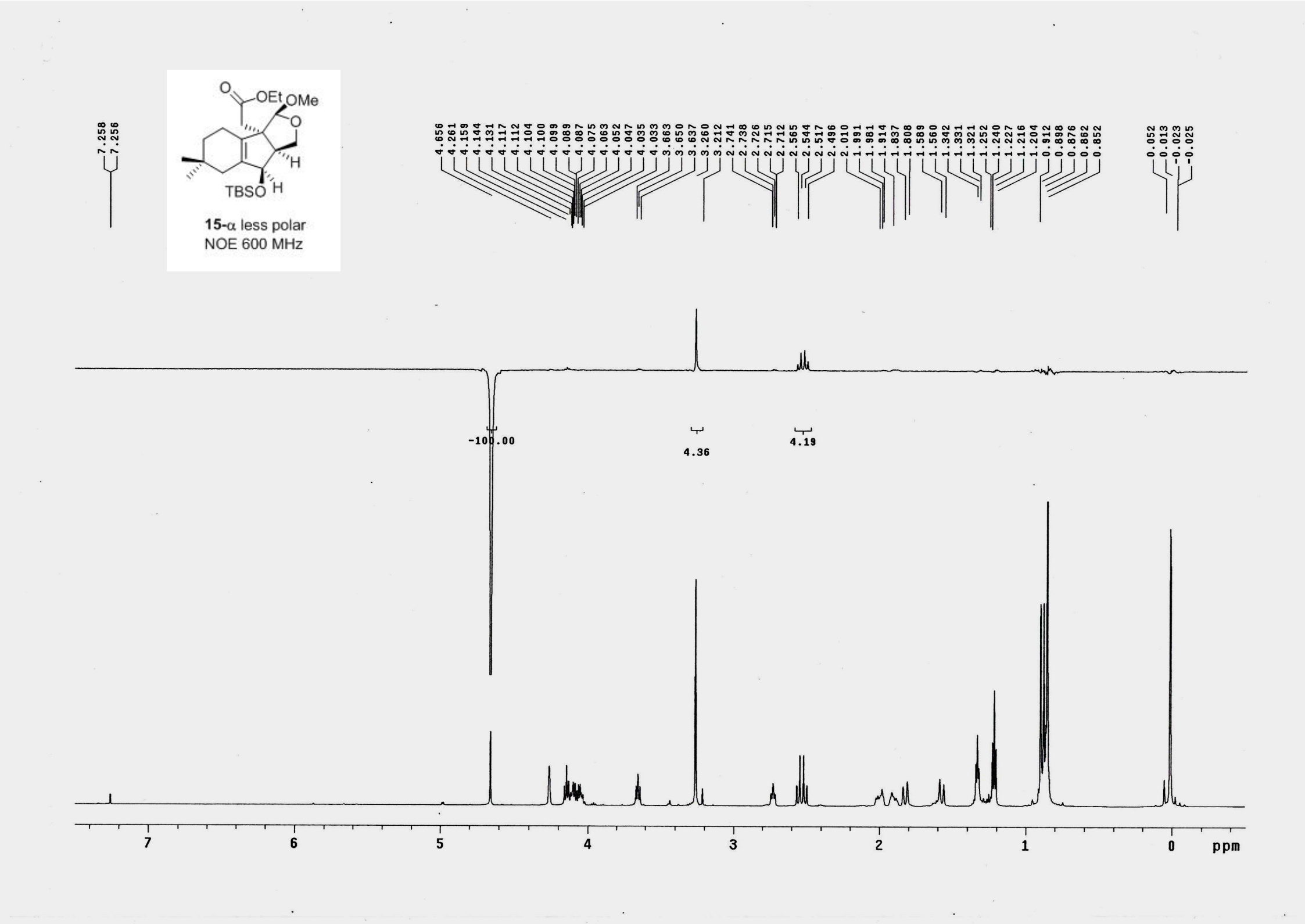


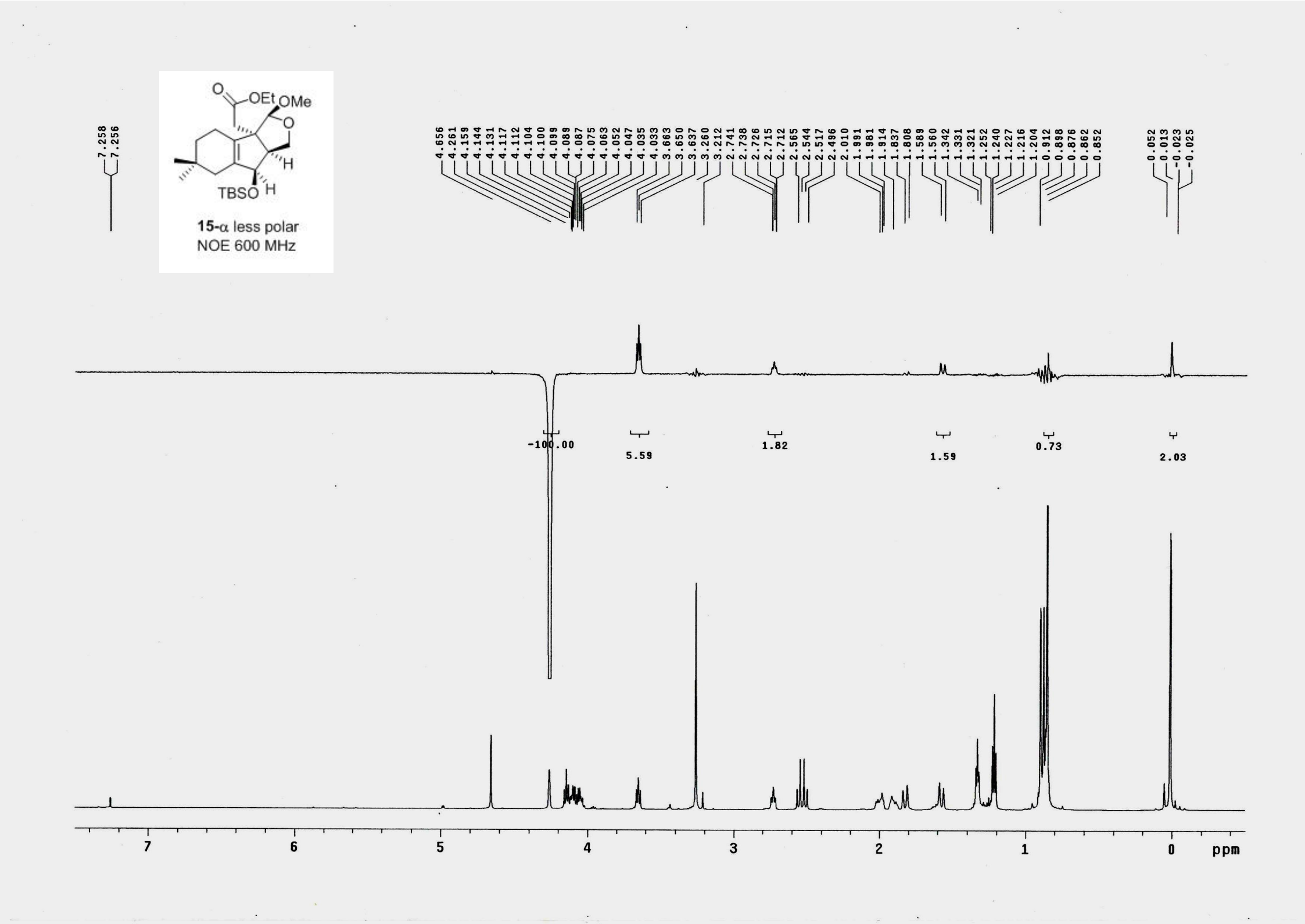
15-α less polar
^{13}C NMR 101 MHz

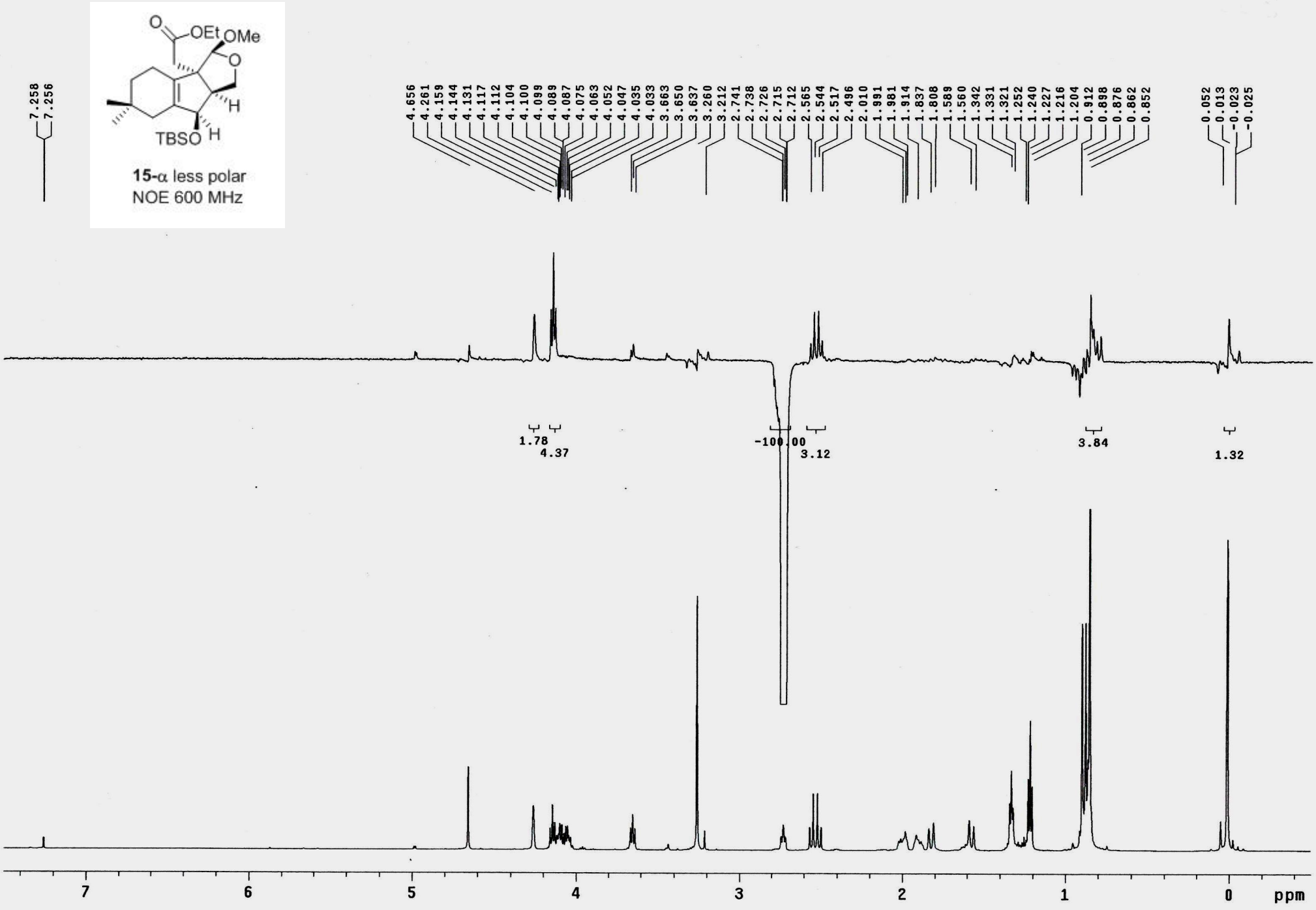
171.27
138.25
134.65
107.64
83.99
77.32
77.00
76.68
70.19
64.97
60.40
57.16
55.12
41.17
37.32
35.62
29.41
28.62
27.69
25.78
21.21
18.07
14.22
-4.49
-4.72

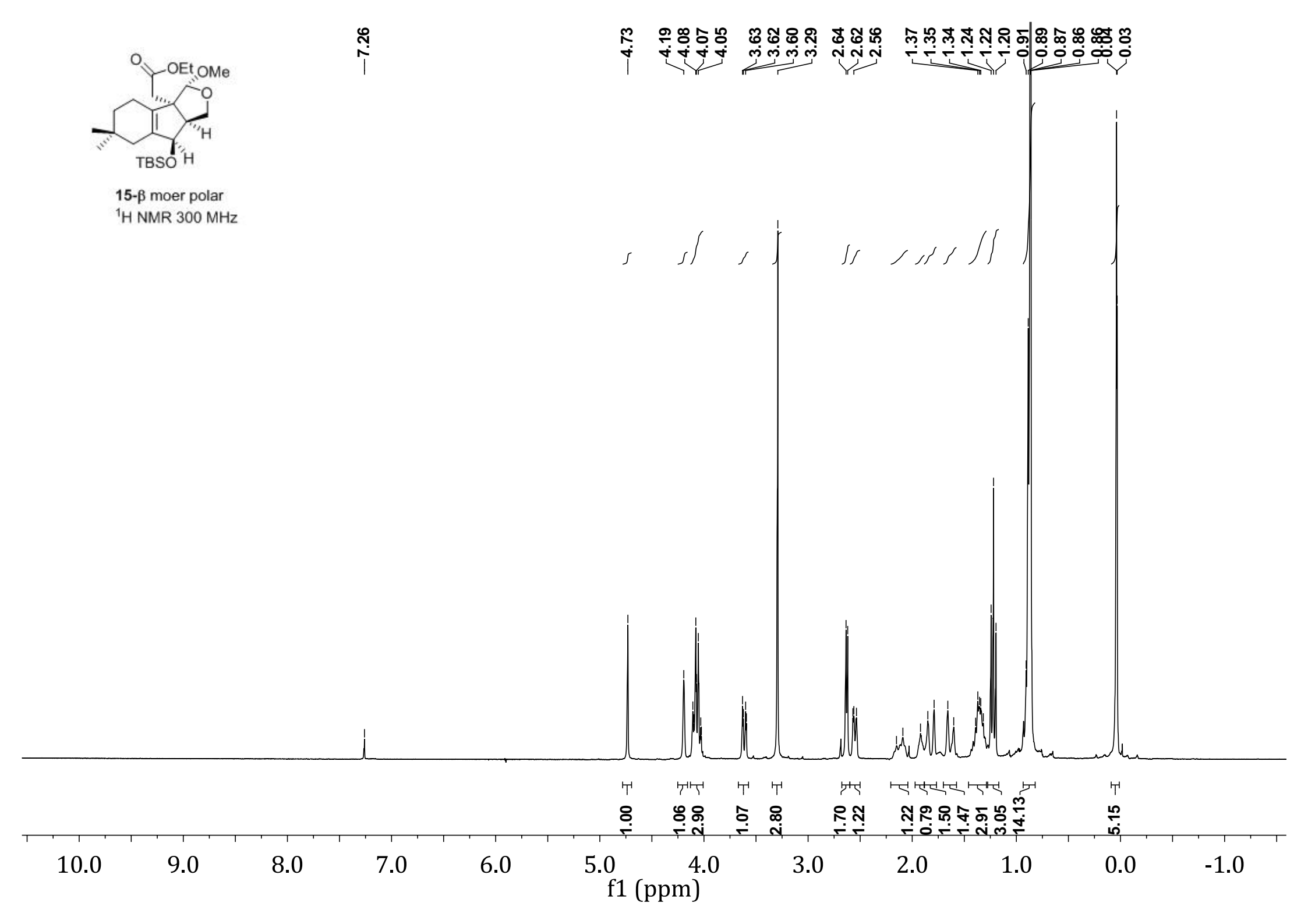


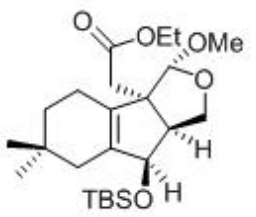

OEt
OMe
O
H
TBSO
H
15-α less polar
HMBC 400 MHz
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f2 (ppm)


OEt
OMe
O
H
TBSO
H
15-α less polar
NOE 600 MHz
7.258
7.256
4.656
4.261
4.159
4.144
4.131
4.117
4.112
4.104
4.100
4.099
4.089
4.087
4.075
4.063
4.052
4.047
4.035
4.033
3.663
3.650
3.637
3.260
3.212
2.741
2.738
2.726
2.715
2.712
2.565
2.544
2.517
2.496
2.010
1.991
1.981
1.914
1.837
1.808
1.589
1.560
1.342
1.331
1.321
1.252
1.240
1.227
1.216
1.204
0.912
0.898
0.876
0.862
0.852
0.052
0.013
-0.023
-0.025
-100.00
4.36
4.19
7
6
5
4
3
2
1
0
ppm


7.258
7.256
OEt
OMe
O
H
TBSO
H
15-α less polar
NOE 600 MHz
4.656
4.261
4.159
4.144
4.131
4.117
4.112
4.104
4.100
4.099
4.089
4.087
4.075
4.063
4.052
4.047
4.035
4.033
3.663
3.650
3.637
3.260
3.212
2.741
2.738
2.726
2.715
2.712
2.565
2.544
2.517
2.496
2.010
1.991
1.981
1.914
1.837
1.808
1.589
1.560
1.342
1.331
1.321
1.252
1.240
1.227
1.216
1.204
0.912
0.898
0.876
0.862
0.852
0.052
0.013
-0.023
-0.025
-100.00
5.59
1.82
1.59
0.73
2.03
7
6
5
4
3
2
1
0
ppm


OEt
OMe
O
H
TBSO
H
15-α less polar
NOE 600 MHz
7.258
7.256
4.656
4.261
4.159
4.144
4.131
4.117
4.112
4.104
4.100
4.099
4.089
4.087
4.075
4.063
4.052
4.047
4.035
4.033
3.663
3.650
3.637
3.260
3.212
2.741
2.738
2.726
2.715
2.712
2.565
2.544
2.517
2.496
2.010
1.991
1.981
1.914
1.837
1.808
1.589
1.560
1.342
1.331
1.321
1.252
1.240
1.227
1.216
1.204
0.912
0.898
0.876
0.862
0.852
0.052
0.013
-0.023
-0.025
1.78
4.37
-100.00
3.12
3.84
1.32
7
6
5
4
3
2
1
0
ppm

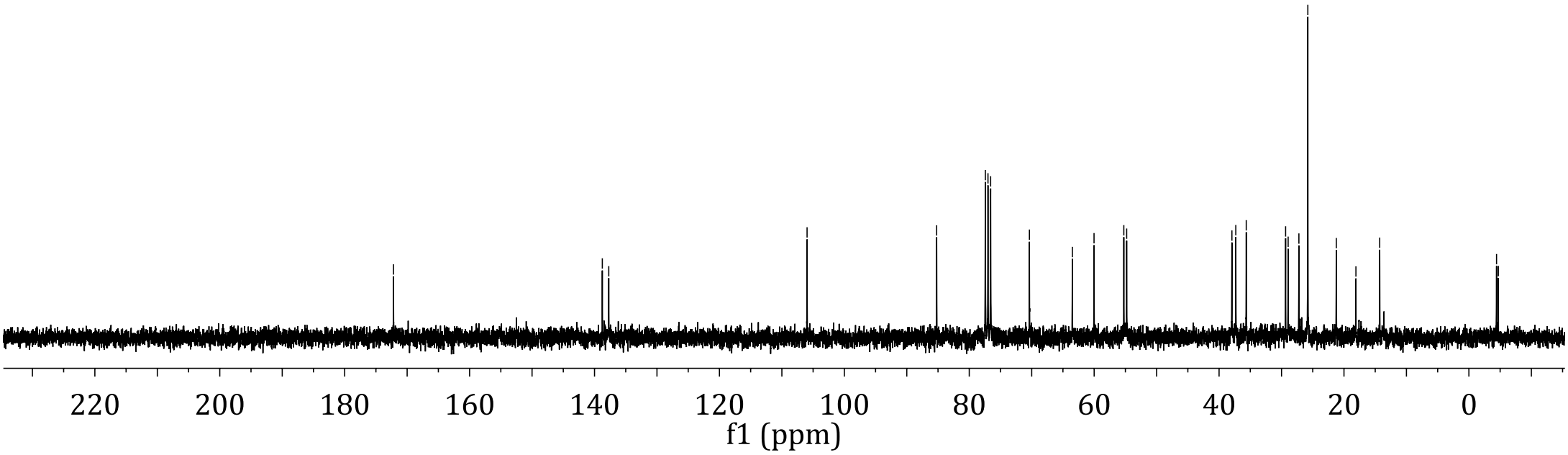

OEt
OMe
O
H
TBSO
H
15-β moer polar
1H NMR 300 MHz
7.26
4.73
4.19
4.08
4.07
4.05
3.63
3.62
3.60
3.29
2.64
2.62
2.56
1.37
1.35
1.34
1.24
1.22
1.20
0.91
0.89
0.87
0.86
0.04
0.03
1.00
1.06
2.90
1.07
2.80
1.70
1.22
1.22
0.79
1.50
1.47
2.91
3.05
14.13
5.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

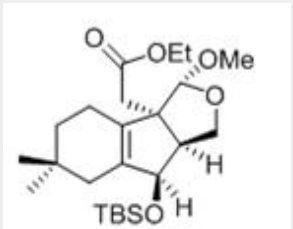


15-β moer polar

^{13}C NMR 75 MHz

172.19
138.75
137.72
105.97
85.22
77.42
77.00
76.58
70.37
63.49
60.02
55.25
54.79
37.94
37.32
35.65
29.35
28.94
27.22
25.79
21.23
18.09
14.28
-4.43
-4.71





15-β moer polar
NOE 600 MHz

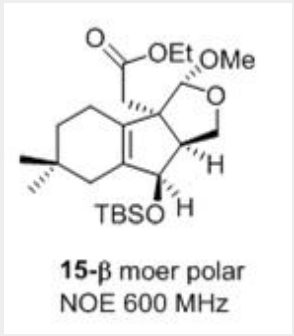
7.258
7.256

4.727

4.184
4.088
4.081
4.074
4.070
4.058
4.046
4.041
4.035
4.029
3.617
3.615
3.602
3.600
3.287
2.659
2.635
2.610
2.586
2.547
2.534
2.120
2.106
2.091
2.028
1.898
1.869
1.818
1.790
1.640
1.612
1.400
1.391
1.380
1.370
1.360
1.339
1.328
1.316
1.305
1.294
1.239
1.227
1.216
1.202
0.913
0.900
0.888
0.880
0.864
0.854
0.822
0.048
0.031
0.025
-0.023

-100.00
4.85
4.25

7
6
5
4
3
2
1
0
ppm



15-β moer polar
NOE 600 MHz

7.258
7.256

4.727

4.184
4.088
4.081
4.074
4.070
4.058
4.046
4.041
4.035
4.029
3.617
3.615
3.602
3.600
3.287
2.659
2.635
2.610
2.586
2.547
2.534
2.120
2.106
2.091
2.028
1.898
1.869
1.818
1.790
1.640
1.612
1.400
1.391
1.380
1.370
1.360
1.339
1.328
1.316
1.305
1.294
1.239
1.227
1.216
1.202
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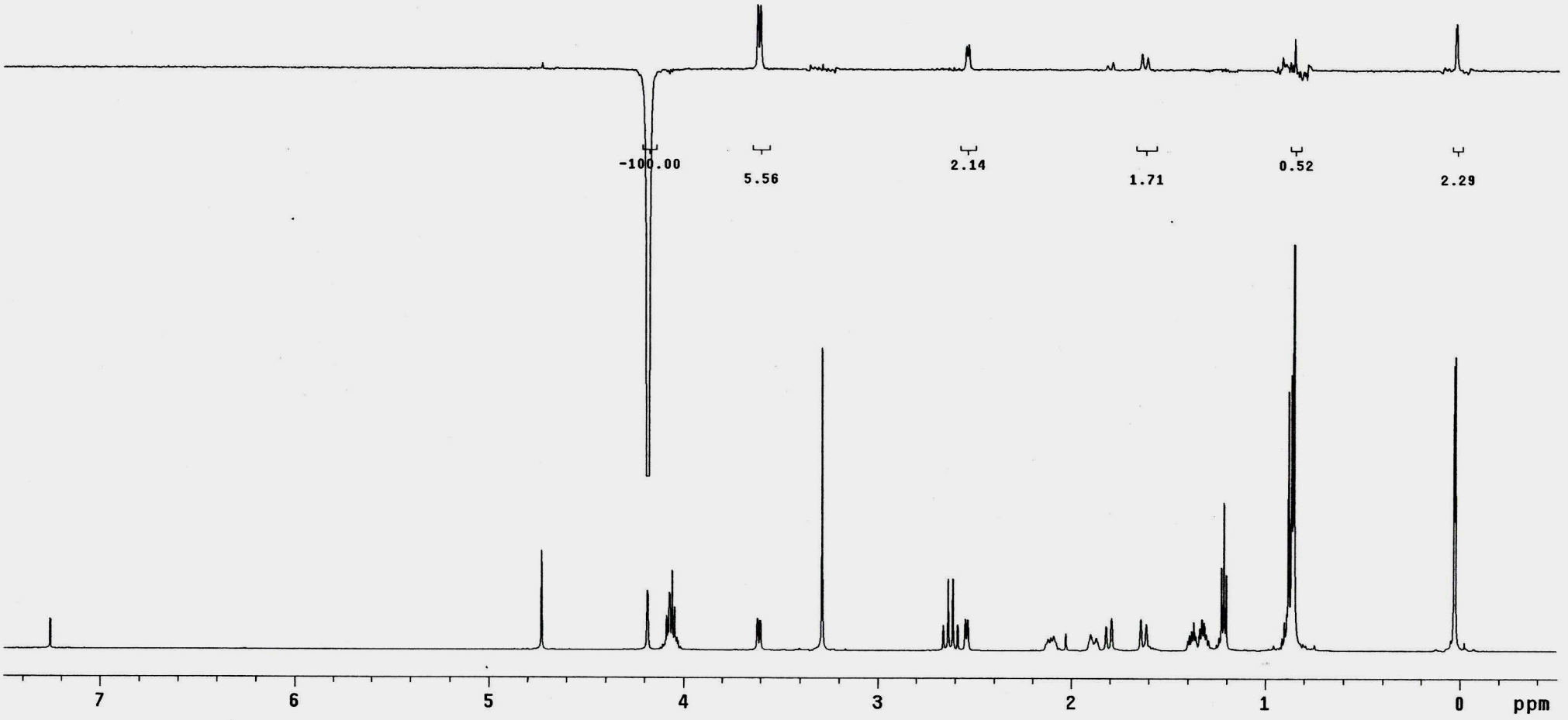
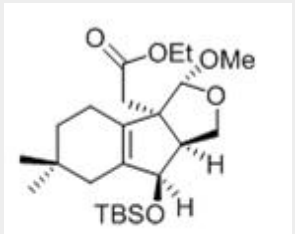
0.888
0.880
0.864
0.854
0.822
0.048
0.031
0.025
-0.023





15-β moer polar
NOE 600 MHz

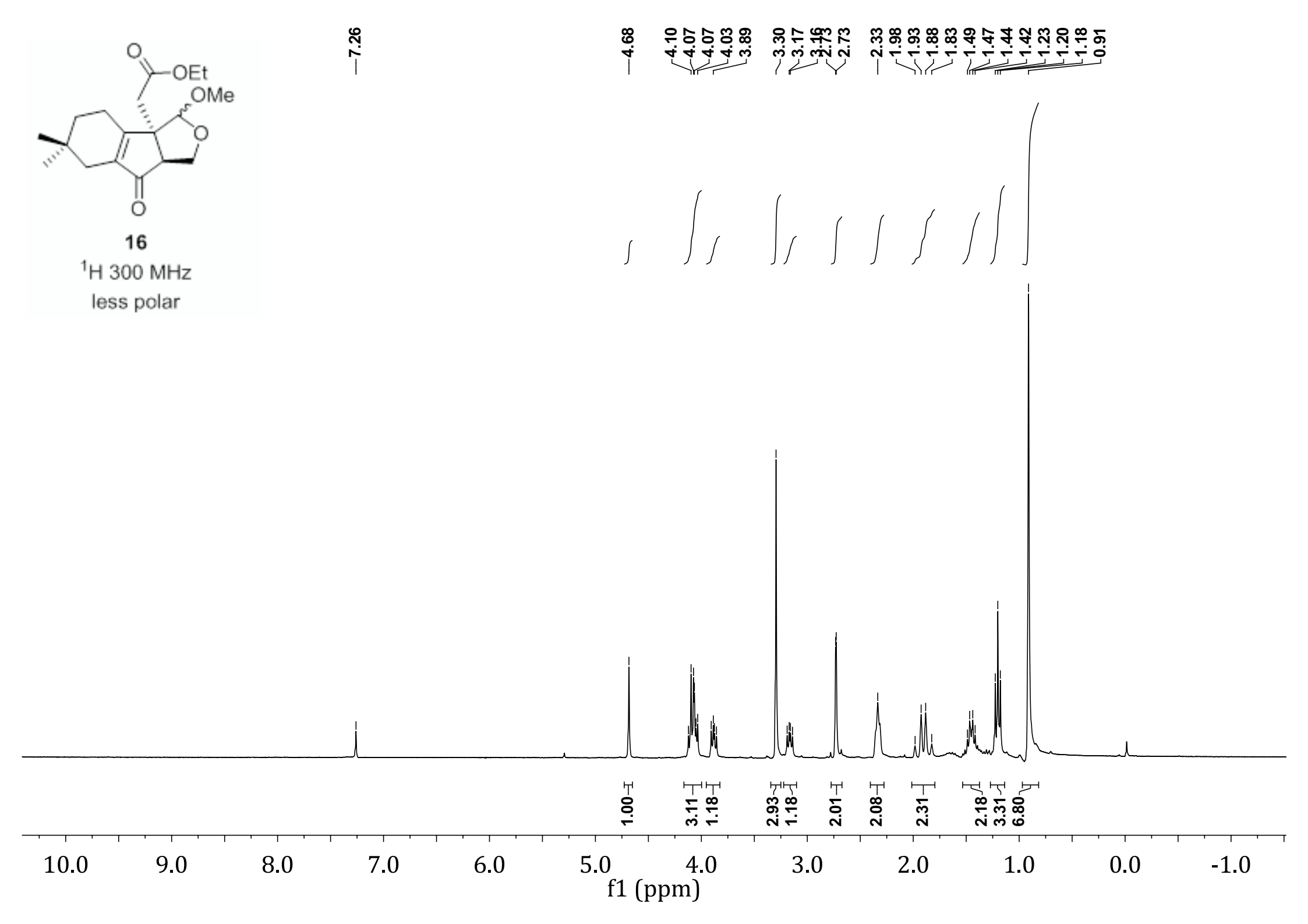
7.258
7.256

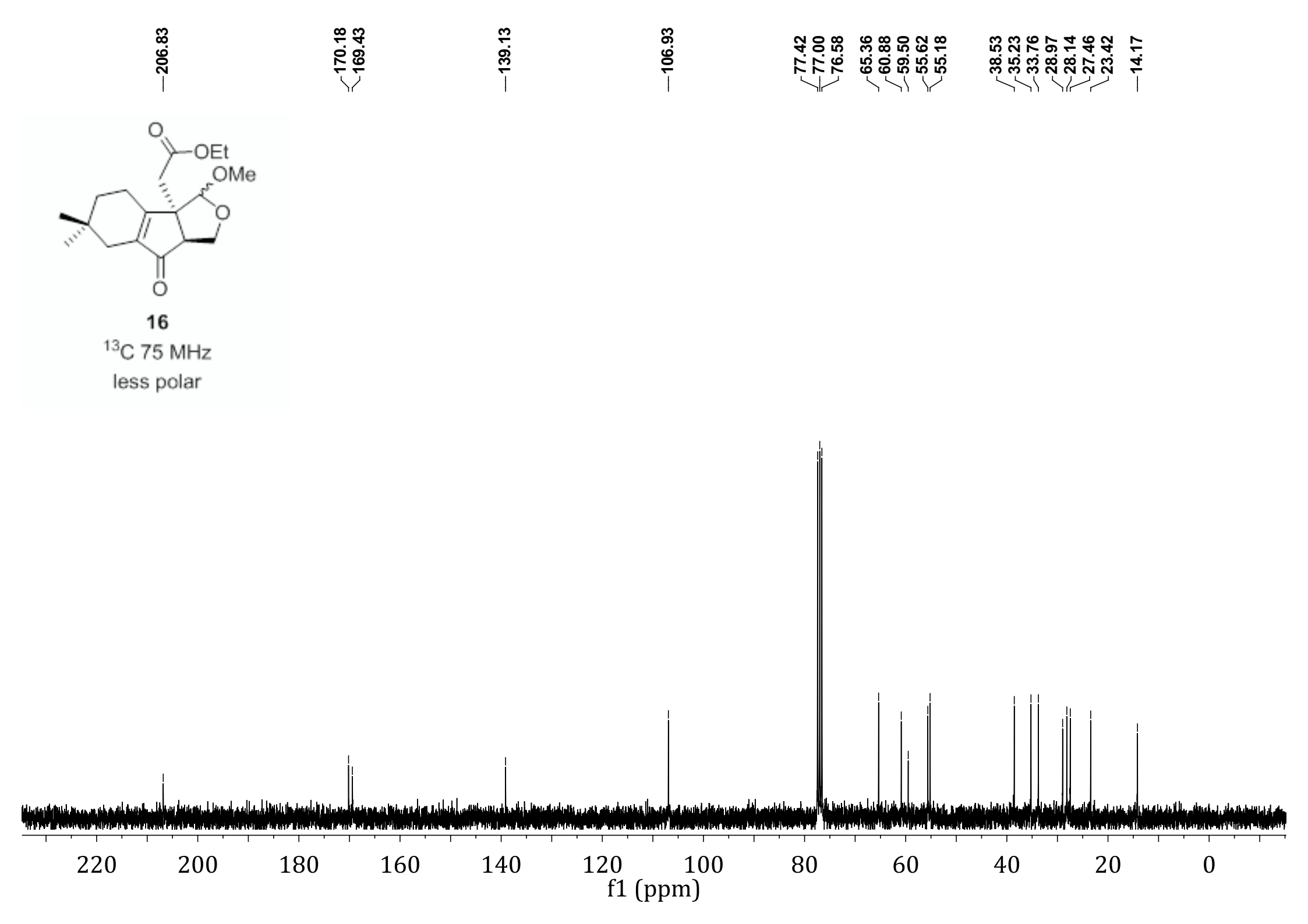
4.727

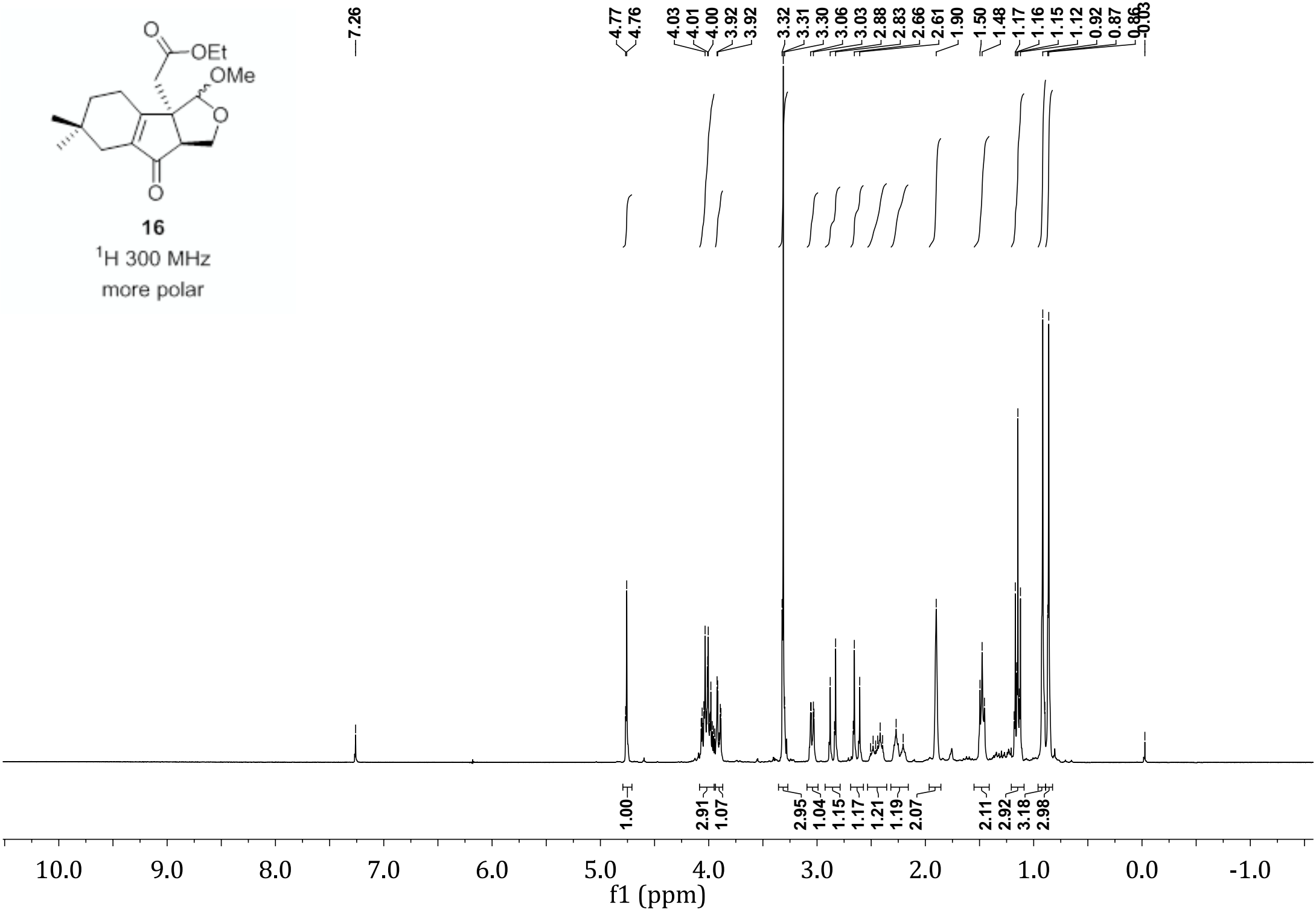
4.184
4.088
4.081
4.074
4.070
4.058
4.046
4.041
4.035
4.029
3.617
3.615
3.602
3.600
3.287
2.659
2.635
2.610
2.586
2.547
2.534
2.120
2.106
2.091
2.028
1.898
1.869
1.818
1.790
1.640
1.612
1.400
1.391
1.380
1.370
1.360
1.339
1.328
1.316
1.305
1.294
1.239
1.227
1.216
1.202
0.913
0.900
0.888
0.880
0.864
0.854
0.822
0.048
0.031
0.025
-0.023

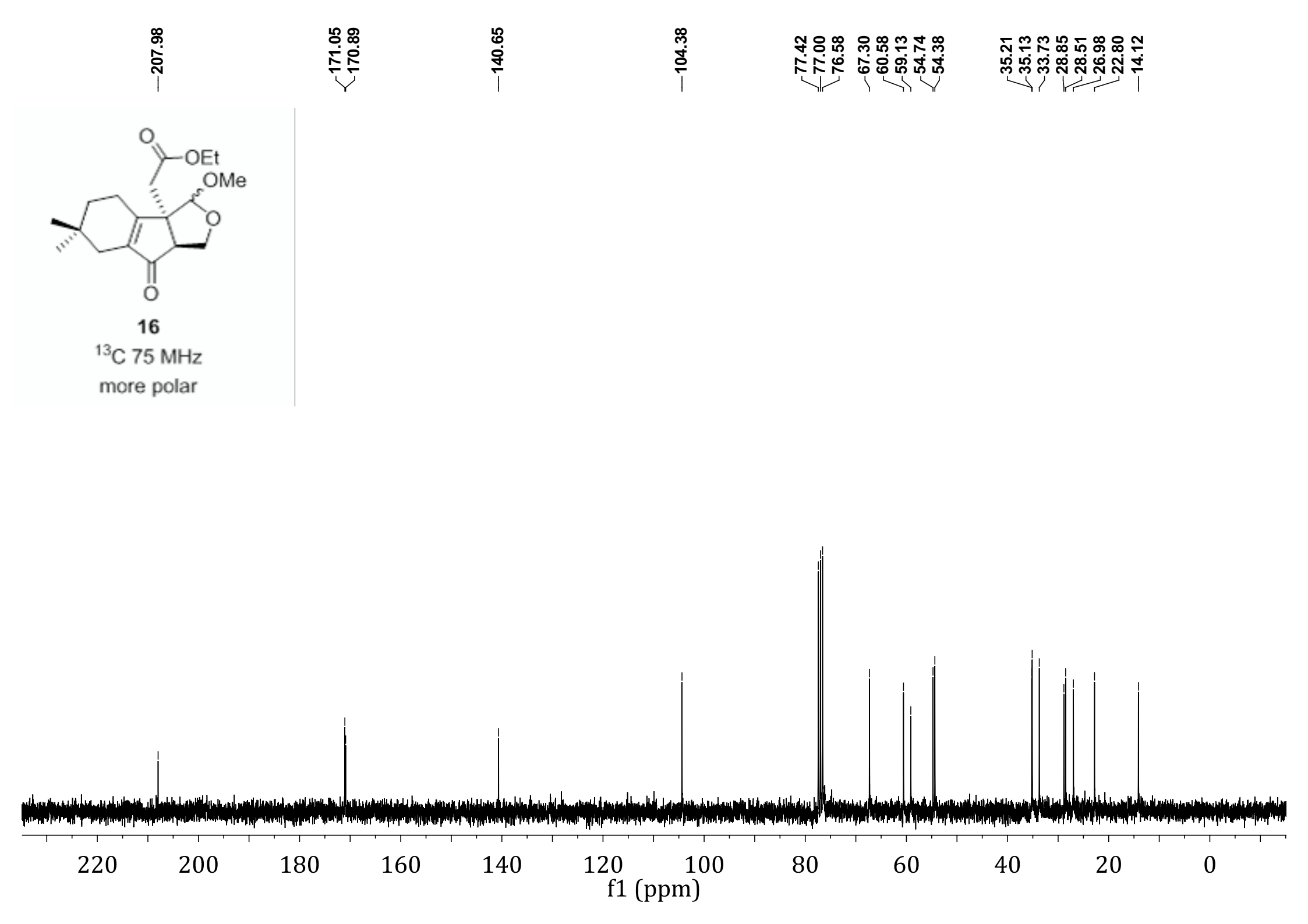
2.31
4.80
0.91
-100.00
1.09
0.45
1.23

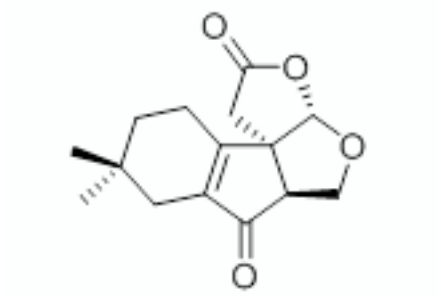
7
6
5
4
3
2
1
0
ppm


OEt
OMe
O
O
O
16
1H 300 MHz
less polar
7.26
4.68
4.10
4.07
4.07
4.03
3.89
3.30
3.17
3.16
2.73
2.73
2.33
1.98
1.93
1.88
1.83
1.49
1.47
1.44
1.42
1.23
1.20
1.18
0.91
1.00
3.11
1.18
2.93
1.18
2.01
2.08
2.31
2.18
3.31
6.80
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


206.83
170.18
169.43
139.13
106.93
77.42
77.00
76.58
65.36
60.88
59.50
55.62
55.18
38.53
35.23
33.76
28.97
28.14
27.46
23.42
14.17
OEt
OMe
O
O
O
16
13C 75 MHz
less polar
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


OEt
OMe
O
O
O
16
1H 300 MHz
more polar
7.26
4.77
4.76
4.03
4.01
4.00
3.92
3.92
3.32
3.31
3.30
3.06
3.03
2.88
2.83
2.66
2.61
1.90
1.50
1.48
1.17
1.16
1.15
1.12
0.92
0.87
0.86
0.03
1.00
2.91
1.07
2.95
1.04
1.15
1.17
1.21
1.19
2.07
2.11
2.92
3.18
2.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


207.98
171.05
170.89
140.65
104.38
77.42
77.00
76.58
67.30
60.58
59.13
54.74
54.38
35.21
35.13
33.73
28.85
28.51
26.98
22.80
14.12
OEt
OMe
O
O
O
16
13C 75 MHz
more polar
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



11

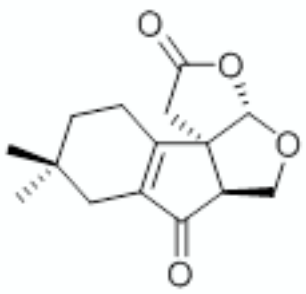
^{1}H 300 MHz

7.26 | 5.78 | 5.77 | 4.32 | 4.32 | 4.29 | 4.28 | 4.20 | 4.17 | 4.16 | 4.14 | 3.12 | 3.05 | 2.83 | 2.77 | 2.76 | 2.74 | 2.44 | 2.29 | 1.98 | 1.97 | 1.66 | 1.60 | 1.58 | 1.56 | 0.95 | 0.94 | -0.02

0.99 | 1.00 | 1.05 | 1.02 | 1.01 | 0.90 | 1.14 | 1.14 | 1.90 | 2.13 | 5.52

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

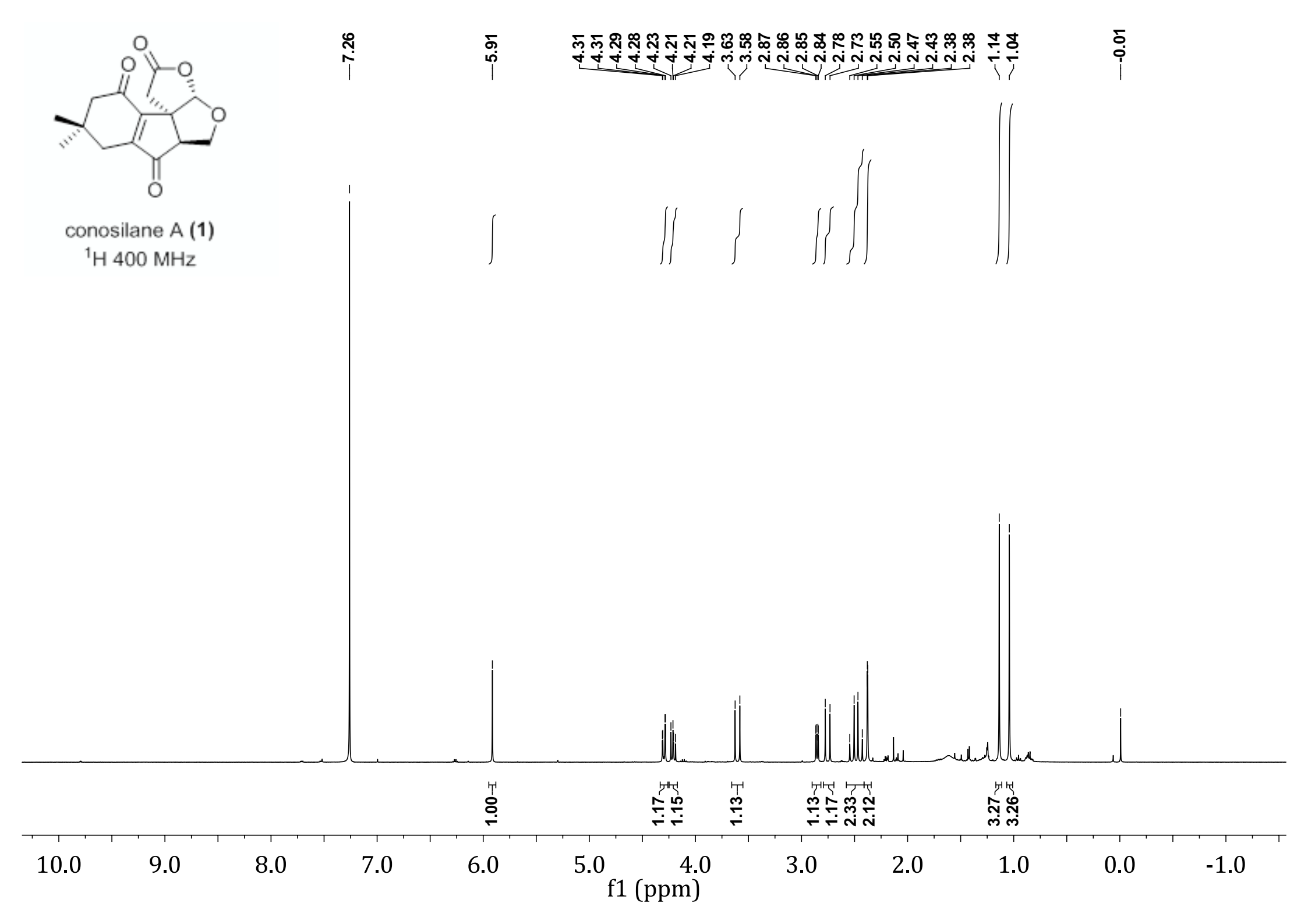
f1 (ppm)

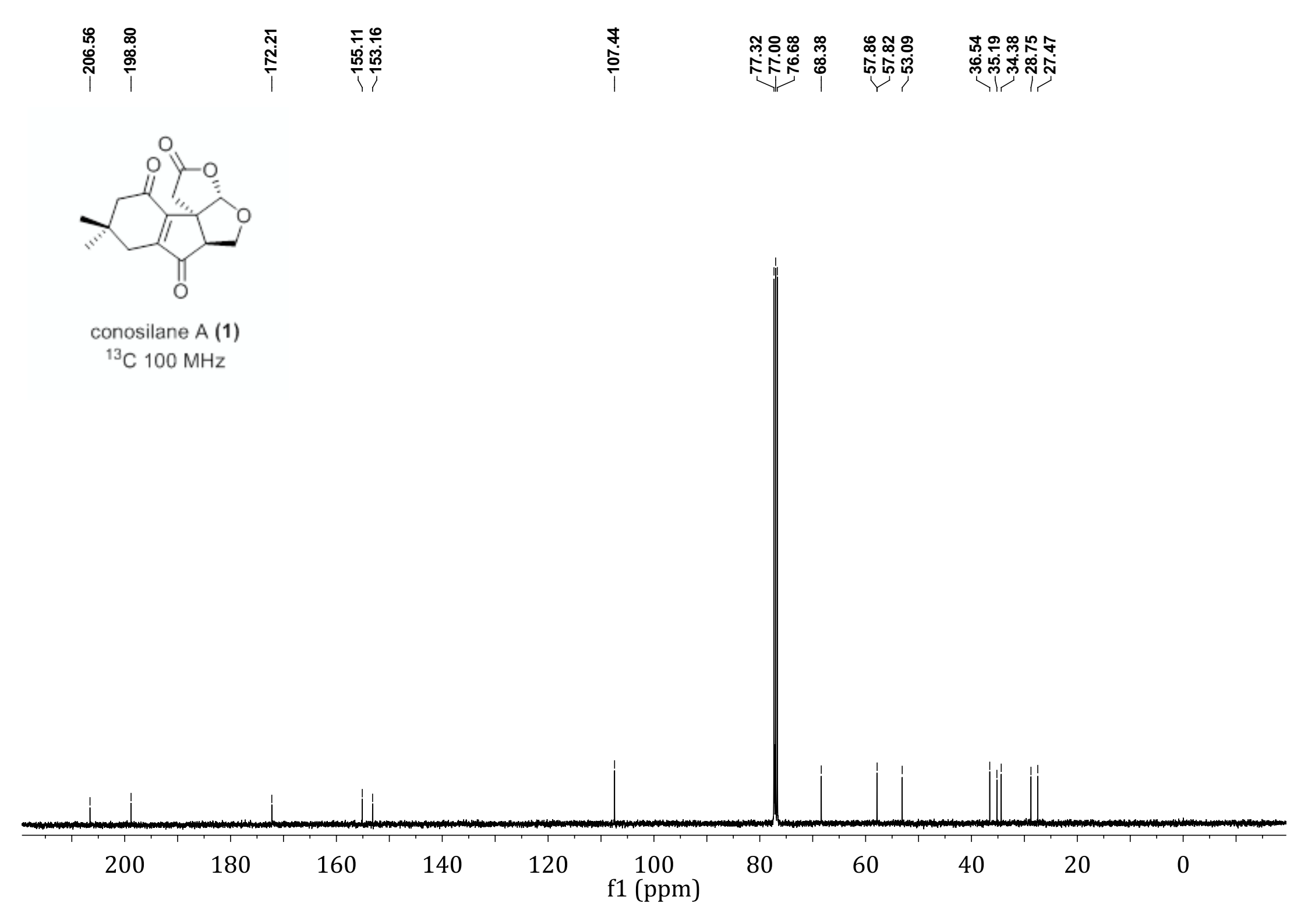


11

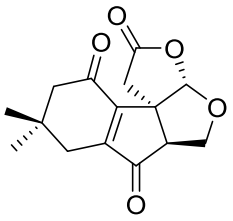
^{13}C 75 MHz

204.69
172.43
166.18
141.88
107.41
77.42
77.00
76.58
68.45
60.84
56.80
35.76
34.89
33.82
28.85
28.02
27.38
22.37
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

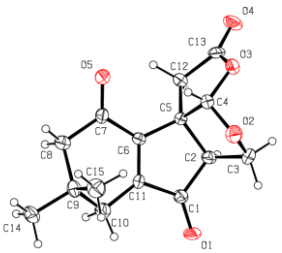

conosilane A (1)
1H 400 MHz
7.26
5.91
4.31
4.31
4.29
4.28
4.23
4.21
4.21
4.19
3.63
3.58
2.87
2.86
2.85
2.84
2.78
2.73
2.55
2.50
2.47
2.43
2.38
2.38
1.14
1.04
-0.01
1.00
1.17
1.15
1.13
1.13
1.17
2.33
2.12
3.27
3.26
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


206.56
198.80
172.21
155.11
153.16
107.44
77.32
77.00
76.68
68.38
57.86
57.82
53.09
36.54
35.19
34.38
28.75
27.47
O
O
O
O
O
conosilane A (1)
13C 100 MHz
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

X-ray data of conosilane A



conosilane A **(1)**



X-Ray of conosilane A
CCDC 1587221

Table 1 Crystal data and structure refinement for yuanzy_1113.

Identification code	yuanzy_1113
Empirical formula	$C_{15}H_{16}O_5$
Formula weight	276.28
Temperature/K	173.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.057(2)
b/Å	11.4810(18)
c/Å	12.6213(12)
α/°	87.520(11)
β/°	68.565(15)
γ/°	88.715(16)
Volume/Å^3	1355.3(4)
Z	4
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	0.102
F(000)	584.0
Crystal size/mm^3	0.23 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.714 to 52.042
Index ranges	-12 ≤ h ≤ 11, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	9272
Independent reflections	5320 [R_{int} = 0.1009, R_{sigma} = 0.2350]
Data/restraints/parameters	5320/0/365
Goodness-of-fit on F^2	0.979
Final R indexes [I>=2σ (I)]	R_1 = 0.0862, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.2400, wR_2 = 0.2114
Largest diff. peak/hole / e Å^{-3}	0.23/-0.32