Electronic Supplementary Information

Total Syntheses of (±)-Musellarins A-C

Zhilong Li, Tsz-Fai Leung, and Rongbiao Tong*

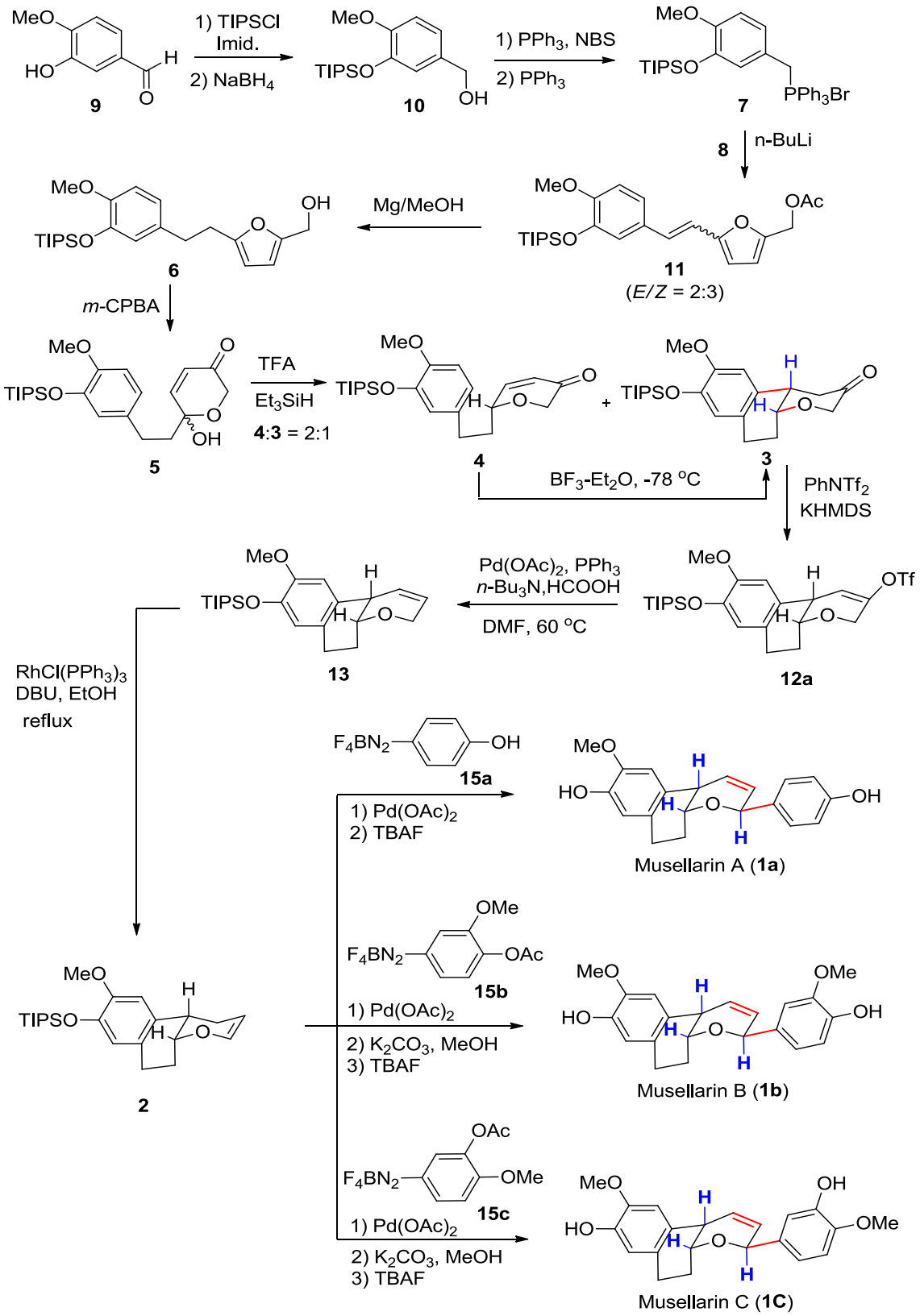
Department of Chemistry, The Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong, China

rtong@ust.hk

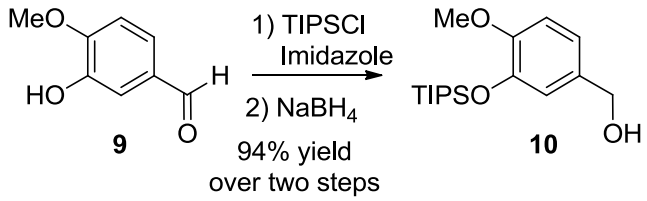
Table of Contents

General Information: Reactions were carried out in oven or flame-dried glassware under a nitrogen atmosphere, unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Dichloromethane (DCM) was freshly distilled before use from calcium hydride (CaH_2). All other anhydrous solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040–0.062 mm) supplied by Grace. Infrared spectra were collected on a Bruker model TENSOR27 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C), benzene (7.16 ppm for ^{1}H and 128.06 ppm for ^{13}C), methanol (3.31 ppm for ^{1}H and 49.00 ppm for ^{13}C), DMSO (2.54 ppm for ^{1}H and 40.45 ppm for ^{13}C) or acetone (2.09 ppm for ^{1}H and 30.60 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Optical rotations were measured on a JASCO Perkin-Elmer model P-2000 polarimeter. High resolution mass spectra were measured at the Hong Kong University of Science and Technology Mass Spectrometry Service Center on either an Agilent GC/MS 5975C System or an API QSTAR XL System.

Total Syntheses of Musellarin A-C



Preparation of Compound 10

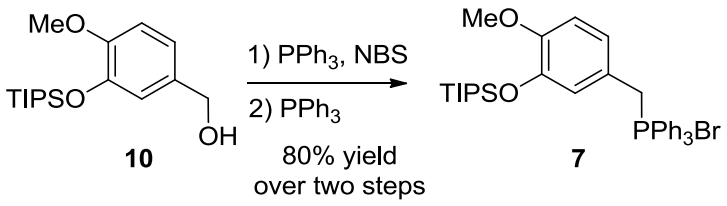


To a stirred solution of isovanillin **9** (15.2 g, 100 mmol) in anhydrous DCM (150 mL) were added imidazole (17.0 g, 250 mmol) and triisopropoylsilyl chloride(TIPSCl, 25.6 mml, 120 mmol) at 0 °C. After completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of water (60 mL). The organic fractions were collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions were washed with saturated aqueous NH_4Cl solution and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude protection product was used for next step without further purification.

To a stirred solution of the crude product obtained above in anhydrous MeOH (100 mL) was added $NaBH_4$ (4.54 g, 120 mmol) portionwise at 0 °C. After completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for additional 2 hr. The solvent (methanol) was removed under reduced pressure and the residue was dissolved in water (50 mL). Then, the aqueous phase was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic fractions were washed with 1 M HCl solution and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford the desired product **10** (29.0 g, 94.0 mmol, 94% yield over two steps) as a colorless oil. The analytical data were identical to those reported in the literature.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.88 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.56 (s, 2H), 3.80 (s, 3H), 1.27–1.22 (m, 3H), 1.10–1.00 (m, 18H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 145.7, 133.7, 120.3, 119.8, 112.1, 65.3, 55.7, 18.1 (6 x C), 13.1 (3 x C).

[1] N. Blank, B. F. Straub and T. Opatz, *Eur. J. Org. Chem.* **2011**, 7355.

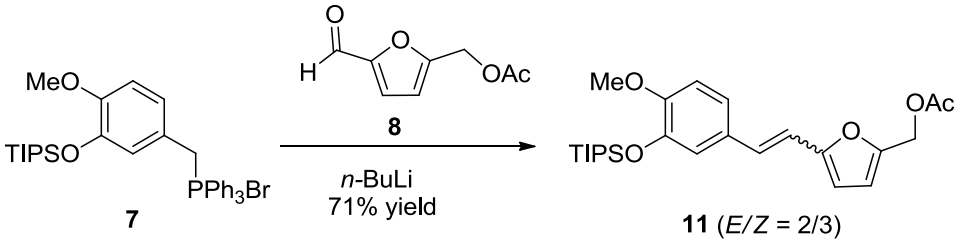
Preparation of Phosphonium Salt 7



To a stirred solution of **10** (8.45 g, 27.3 mmol) in anhydrous DCM (100 mL) were added PPh_3 (10.7 g, 40.9 mmol) and *N*-bromosuccinimide (NBS, 7.28 g, 40.9 mmol) portionwise at 0 °C. After completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for additional 2 hr. The reaction was quenched by addition of water (60 mL). The organic fractions were collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL). The combined organic fractions was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was dissolved in hexane/EtOAc (20:1) solution and the precipitate was removed by filtration through a pad of Celite. The filtrate was concentrated under reduced pressure and the crude product was used for next step without further purification.

To a stirred solution of the crude product obtained above in toluene (100 mL) was added PPh_3 (20.1 g, 76.7 mmol) at room temperature. After completion of the addition, the reaction mixture was heated to reflux for 2 days. The white precipitate was collected from filtration and dried under reduced pressure to afford the desired phosphonium salt **7** (13.8 g, 21.7 mmol, 80% yield over two steps), which was used for next step without further purification.

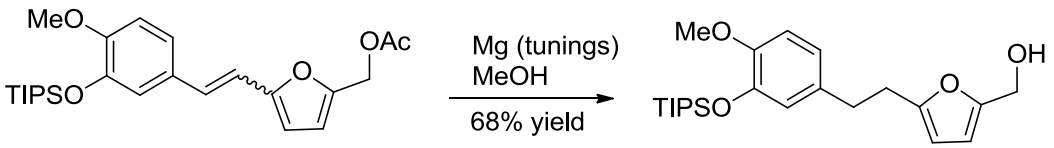
Preparation of Compound 11



To a stirred solution of phosphonium salt **7** (12.8 g, 20.2 mmol) in anhydrous THF (120 mL) was added *n*-BuLi (2.4 M in hexane, 8.40 mL, 20.2 mmol) slowly at −78 °C. The reaction mixture was stirred for 30 min at −78 °C and the aldehyde **8** (2.82 g, 16.8 mmol) dissolved in anhydrous THF (30 mL) was added very slowly. After completion of the addition, the reaction

mixture was stirred for additional 2 hr. The reaction was quenched by addition of saturated aqueous NH_4Cl (100 mL). The organic phase was collected and the aqueous phase was extracted with ethyl acetate (3 x 40 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the desired alkene products *cis*-**11** and *trans*-**11** (5.31 g, 12.0 mmol, 71% yield, ratio of *E/Z* isomers = 2:3) as a colorless oil. A small amount of pure *cis*-**11** could be obtained by careful and repeated preparative TLC. **IR** (neat, cm^{-1}): 2945, 2867, 1744, 1510, 1278, 1233, 996. Data for *cis*-**11**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.01 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.96 (d, *J* = 1.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 12.8 Hz, 1H), 6.30 (d, *J* = 3.2 Hz, 1H), 6.26 (d, *J* = 12.4 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 5.00 (s, 2H), 3.82 (s, 3H), 2.07 (s, 3H), 1.28–1.18 (m, 3H), 1.11–1.04 (m, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.7, 153.0, 150.6, 148.1, 145.2, 129.9, 129.4, 122.2, 120.7, 117.0, 112.3, 111.7, 110.0, 58.3, 55.5, 21.0, 18.0 (6 x C), 12.9 (3 x C). Data for *trans*-**11**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.02–7.00 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 6.30–6.21 (m, 2H), 5.07 (s, 2H), 3.82 (s, 3H), 2.10 (s, 3H), 1.28–1.18 (m, 3H), 1.11–1.04 (m, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.3, 154.5, 151.1, 150.7, 148.6, 145.8, 128.1, 120.8, 118.2, 114.3, 112.9, 112.1, 108.5, 58.4, 55.6, 21.1, 18.1 (6 x C), 13.1 (3 x C). **HRMS** (TOF, CI^+) m/z calcd for $C_{25}H_{36}O_5Si$ $[M]^+$ 444.2332, found 444.2321.

Preparation of Furfuryl Alcohol 6

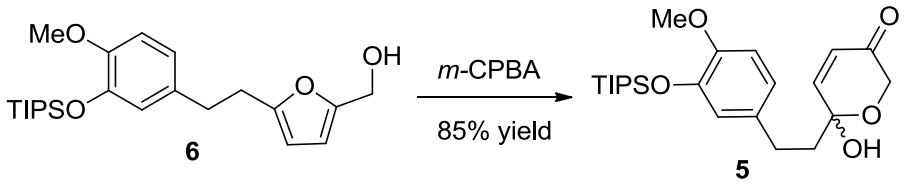


11 (*E/Z* = 2:3) **6**

To a stirred solution of **11** (3.35 g, 7.55 mmol) in anhydrous MeOH (40 mL) was added Mg (turning, 1.36 g, 56.6 mmol) slowly at room temperature. The reaction mixture was stirred overnight. Then, the reaction was quenched by addition of saturated aqueous NH_4Cl (50 mL). The organic phase was collected and the aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to afford the desired furfuryl alcohol **6** (2.18

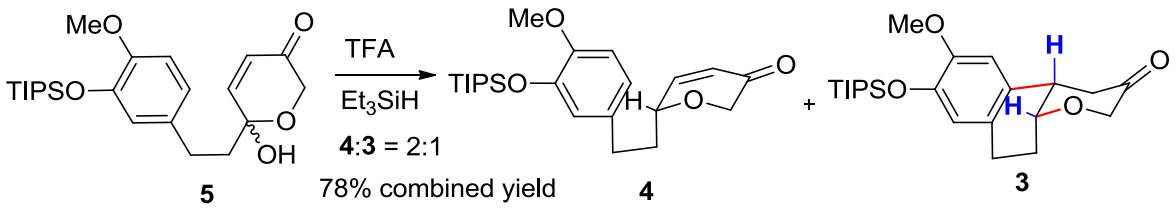
g, 5.16 mmol, 68% yield) as a yellow oil. **IR** (neat, cm^{-1}): 3346, 2943, 2866, 1513, 1465, 1347, 1136, 1009. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.87 (d, *J* = 2.4 Hz, 1H), 6.62 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 5.94 (d, *J* = 3.2 Hz, 1H), 5.75 (d, *J* = 2.8 Hz, 1H), 4.28 (s, 2H), 3.34 (s, 3H), 2.81 (s, 4H), 1.33–1.25 (m, 3H), 1.22 (d, *J* = 6.8 Hz, 18H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 155.5, 153.5, 149.7, 145.9, 134.1, 121.4, 121.1, 112.5, 108.3, 106.4, 57.6, 55.1, 34.0, 30.7, 18.3 (6 x C), 13.4 (3 x C). **HRMS** (TOF, CI^+) m/z calcd for $C_{23}H_{36}O_4Si$ $[M]^+$ 404.2383, found 404.2374.

Preparation of Dihydropyranone Acetal 5



To a stirred solution of **6** (2.18 g, 5.16 mmol) in CH_2Cl_2 (30 mL) was added 3-chloroperbenzoic acid (*m*-CPBA, 0.98 g, 5.68 mmol, ca. 85 wt%) at 0 °C. The reaction mixture was stirred at 0 °C for 2 hr. Then the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (30 mL) and $NaHCO_3$ solution (30 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford the desired dihydropyranone acetal **5** (1.84 g, 4.38 mmol, 85% yield) as a yellow oil. **IR** (neat, cm^{-1}): 3628, 2944, 2893, 2866, 1685, 1512, 1289, 1016. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.95 (s, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.18 (d, *J* = 10.0 Hz, 1H), 5.77 (d, *J* = 10.0 Hz, 1H), 4.40 (d, *J* = 17.2 Hz, 1H), 4.01 (d, *J* = 16.8 Hz, 1H), 3.36 (s, 3H), 2.75–2.67 (m, 1H), 2.61–2.51 (m, 1H), 2.00–1.86 (m, 2H), 1.34–1.25 (m, 3H), 1.15 (d, *J* = 7.4 Hz, 18H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 194.8, 150.1, 148.8, 146.4, 134.5, 127.2, 121.7, 121.45, 112.9, 94.3, 67.0, 55.5, 43.1, 29.7, 18.6 (6 x C), 13.8 (3 x C). **HRMS** (TOF, CI^+) m/z calcd for $C_{23}H_{37}O_5Si$ $[M+H]^+$ 421.2405, found 421.2397.

Preparation of Bicyclic Pyranone 4 and Tricyclic Pyranone 3

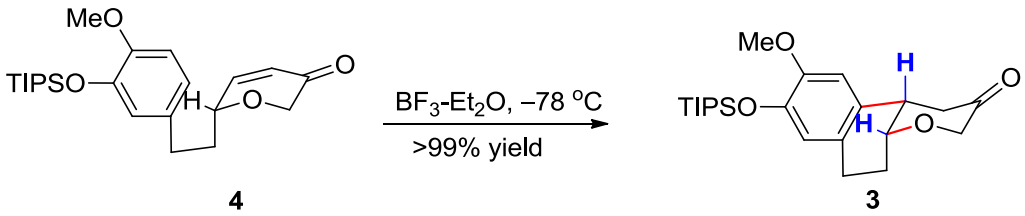


To a stirred solution of **5** (80.0 mg, 0.19 mmol) in CH_2Cl_2 (2 mL) were added Et_3SiH (0.24 g, 2.02 mmol) and trifluoroacetic acid (TFA, 0.23 g, 2.02 mmol) at –40 °C. The reaction mixture was stirred at –40 °C for 1 hr. Then the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (5 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified carefully by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford the bicyclic pyranone **4** (40 mg, 52% yield) as a colorless oil and the tricyclic pyranone **3** (20 mg, 26% yield) as a white solid.

Data for **4**: **IR** (neat, cm^{-1}): 3156, 2944, 2865, 1698, 1583, 1423, 1228, 1033. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.93 (d, *J* = 2.0 Hz, 1H), 6.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.04 (dd, *J* = 10.4, 1.6 Hz, 1H), 5.85 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.15 (d, *J* = 16.4 Hz, 1H), 3.74–3.65 (m, 2H), 3.37 (s, 3H), 2.61–2.53 (m, 2H), 1.75–1.65 (m, 1H), 1.59–1.48 (m, 1H), 1.37–1.25 (m, 3H), 1.22–1.15 (m, 18H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 193.7, 151.0, 149.8, 146.1, 134.1, 126.8, 121.5, 121.3, 112.5, 72.4, 71.4, 55.2, 36.2, 30.8, 18.3 (6 x C), 13.5 (3 x C). **HRMS** (TOF, CI^+) m/z calcd. for $C_{23}H_{37}O_4Si$ $[M+H]^+$ 405.2456, found 405.2473.

Data for **3**: Mp = 72 °C. **IR** (neat, cm^{-1}): 2941, 2892, 2865, 1727, 1631, 1512, 1333, 1108. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.77 (s, 1H), 6.31 (s, 1H), 3.87 (d, *J* = 16.8 Hz, 1H), 3.65 (d, *J* = 16.8 Hz, 1H), 3.61 (dt, *J* = 6.4, 4.0 Hz, 1H), 3.34 (s, 3H), 2.81 (dt, *J* = 9.6, 6.4 Hz, 1H), 2.70 (ddd, *J* = 15.7, 8.3, 4.7 Hz, 1H), 2.54–2.41 (m, 2H), 2.34 (ddd, *J* = 16.0, 7.6, 5.2 Hz, 1H), 1.89–1.79 (m, 1H), 1.58 (ddd, *J* = 12.4, 8.4, 4.4 Hz, 1H), 1.34–1.24 (m, 3H), 1.18 (d, *J* = 6.8 Hz, 18H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 208.7, 150.0, 144.5, 129.7, 129.2, 120.5, 111.9, 72.9, 72.3, 55.3, 43.6, 37.2, 27.9, 25.8, 18.3 (6 x C), 13.4 (3 x C). **HRMS** (TOF, CI^-) m/z calcd. for $C_{23}H_{35}O_4Si$ $[M-H]^-$ 403.2310, found 403.2232. X-ray data for **3** was provided in page S-20.

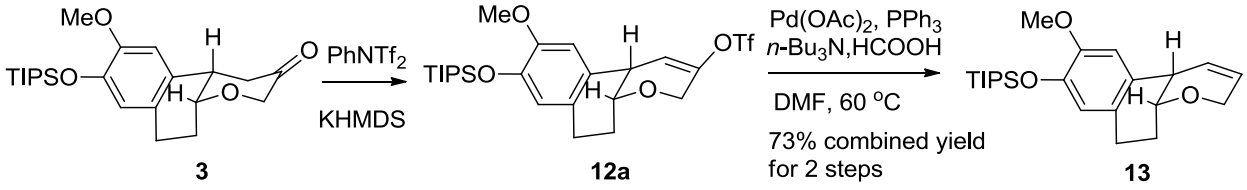
Preparation of Tricyclic Pyranone 3 from Bicyclic Pyranone 4



4 **3**

To a stirred solution of the bicyclic pyranone **4** (48.0 mg, 0.12 mmol) in CH_2Cl_2 (2 mL) was added BF_3-OEt_2 (0.05 mL, 0.36 mmol ca. 48 wt%) at −78 °C. The reaction mixture was stirred at −78 °C for 3 hr. Then the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (5 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford the desired tricyclic pyranone **3** (47.0 mg, 0.12 mmol, 100% yield) as a white solid.

Preparation of Tricyclic Dihydropyran 13



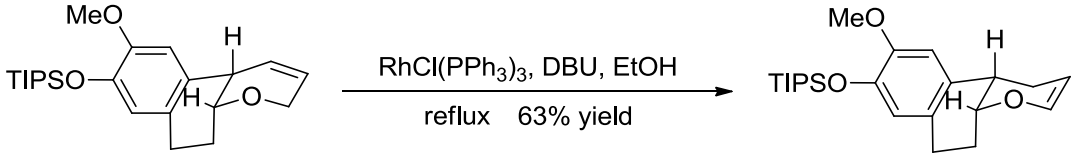
3 **12a** **13**

To a stirred solution of potassium bis(trimethylsilyl) amide (KHMDS, 0.5 M in toluene, 2.0 mL, 0.99 mmol) in anhydrous THF (3 mL) was slowly added **3** (0.20 g, 0.49 mmol) dissolved in anhydrous THF (4 mL) at −78 °C. The reaction mixture was stirred for 30 min at −78 °C and then a solution of $PhNTf_2$ (0.44 g, 1.24 mmol) in anhydrous THF (1.5 mL) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU, 1.5 mL) was added. After completion of the addition, the reaction mixture was stirred for additional 2 hr. Then, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (5 mL). The organic phase was collected and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product (**12a**) was used directly for next step without further purification.

To a stirred solution of crude product (**12a**) above in anhydrous DMF (10 mL) were added $Pd(OAc)_2$ (22.2 mg, 0.10 mmol), PPh_3 (51.8 mg, 0.20 mmol), *n*-Bu_3N (0.28 g, 1.48 mmol) and

formic acid (45.7 mg, 0.99 mmol) at room temperature. After completion of the addition, the reaction mixture was heated to 60 °C and stirred overnight. Then, the reaction was quenched by addition of water (5 mL). The reaction mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the desired tricyclic dihydropyran **13** (0.14 g, 0.36 mmol, 73% yield over two steps) as a colorless oil. **IR** (neat, cm^{-1}): 2930, 2866, 1731, 1512, 1410, 1220, 1124. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.80 (s, 1H), 6.64 (s, 1H), 6.10–5.99 (m, 1H), 5.49 (ddd, *J* = 10.0, 4.4, 2.0 Hz, 1H), 4.02–3.92 (m, 2H), 3.90–3.82 (m, 1H), 3.42 (s, 3H), 3.12–2.99 (m, 2H), 2.43 (dt, *J* = 15.6, 5.2 Hz, 1H), 2.06 (dq, *J* = 13.2, 5.2 Hz, 1H), 1.64 (dddd, *J* = 13.2, 10.4, 5.2, 2.8 Hz, 1H), 1.33–1.24 (m, 3H), 1.18 (dd, *J* = 7.2, 1.6 Hz, 18H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 150.2, 144.4, 131.0, 129.2, 128.5, 126.8, 121.0, 112.7, 71.3, 64.6, 55.8, 37.6, 28.1, 25.6, 18.6 (6 x C), 13.8 (3 x C). **HRMS** (TOF, CI^+) m/z calcd for $C_{23}H_{36}O_3Si$ $[M]^+$ 388.2434, found 388.2432.

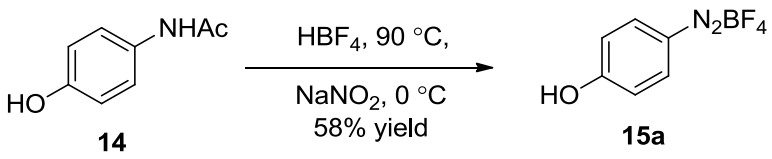
Preparation of Tricyclic Enol Ether 2



13 **2**

To a stirred solution of **13** (96.0 mg, 0.25 mmol) in anhydrous ethanol (3 mL) were added $RhCl(PPh_3)_3$ (11.4 mg, 12.0 *μ*mol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.11 g, 0.74 mmol) at room temperature. The reaction mixture was heated to reflux for 6 hr. The solvent (ethanol) was removed under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to afford the desired tricyclic enol ether **2** (60.0 mg, 63% yield) as a colorless oil. **IR** (neat, cm^{-1}): 2926, 2866, 1736, 1611, 1515, 1262, 1081. **^{1}H NMR** (400 MHz, C_6D_6) δ: 6.74 (s, 1H), 6.46 (dt, *J* = 6.4, 1.6 Hz, 1H), 6.37 (s, 1H), 4.54 (ddd, *J* = 6.4, 4.8, 2.8 Hz, 1H), 4.27 (dt, *J* = 11.2, 4.0 Hz, 1H), 3.37 (s, 3H), 2.92–2.85 (m, 1H), 2.69–2.48 (m, 2H), 2.11 (dt, *J* = 17.2, 5.6 Hz, 1H), 2.06–1.92 (m, 2H), 1.73 (dtd, *J* = 10.0, 6.8, 3.2 Hz, 1H), 1.36–1.25 (m, 3H), 1.19 (d, *J* = 6.8 Hz, 18H). **^{13}C NMR** (100 MHz, C_6D_6) δ: 149.6, 144.5, 142.8, 132.6, 127.0, 120.7, 112.1, 97.4, 73.1, 55.2, 35.6, 27.4, 26.8, 25.1, 18.3 (6 x C), 13.4 (3 x C). **HRMS** (TOF, CI^-) m/z calcd for $C_{23}H_{35}O_3Si$ $[M-H]^-$ 387.2361, found 387.2362.

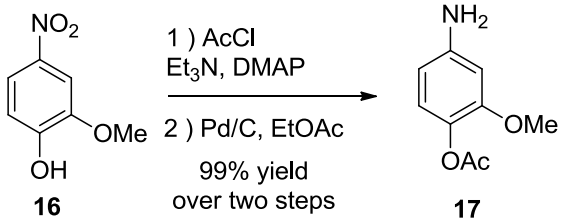
Preparation of Diazonium Salt 15a



14 **15a**

Following the procedure reported in the literature,[2] to a stirred solution of 4-acetoamidophenol **14** (2.50 g, 16.5 mmol) in 2-propanol (2.5 mL) was added HBF_4 (3.50 mL, 27.1 mmol, ca 50 wt%) at room temperature. The reaction mixture was heated to 90 °C and stirred for 3 hr. The reaction mixture was cooled down to 0 °C and then $NaNO_2$ (1.52 g, 22.0 mmol) was added portionwise to the mixture. After completion of the addition, the reaction was allowed to stir at 0 °C for 30 min. The yellow precipitates were filtered and dried under reduced pressure to afford the yellow diazonium salt **15a** (2.01 g, 9.67 mmol, 58% yield). The analytical data were identical to those reported in the literature.[2] **^{1}H NMR** (400 MHz, DMSO) δ: 8.20–8.07 (m, 2H), 6.75–6.63 (m, 2H), 5.93–5.45 (m, 1H). **^{13}C NMR** (100 MHz, DMSO) δ: 175.0, 134.4 (2 x C), 121.8 (2 x C), 87.9.

Preparation of Aniline 17



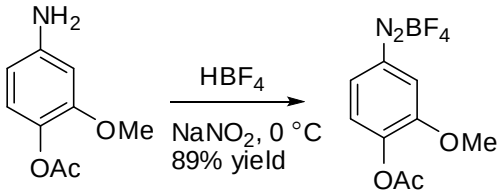
16 **17**

To a stirred solution of **16** (3.00 g, 17.7 mmol) in anhydrous CH_2Cl_2 (60 mL) were added triethyl amine (4.71 g, 44.3 mmol), 4-dimethylaminopyridine (DMAP, 0.22 g, 1.77 mmol) and acetyl chloride (1.67 g, 21.3 mmol) at 0 °C. After completion of the addition, the reaction mixture was allowed to warm up to room temperature and stirred for 4 hr. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (50 mL). The organic fractions were collected and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was used for next step without further purification.

[2] B. Schmidt, F. Hölter, R. Berger and S. Jessel, *Adv. Synth. Catal.,* 2010, **352**, 2463.

To a stirred solution of the crude product obtained above in ethyl acetate (50 mL) was added Pd/C (1.89 g, 0.89 mmol, 5.0 wt% Pd on activated carbon) under N_2 atmosphere at room temperature. The reaction mixture was bubbled by H_2 (g) for 10 min, and then the gas outlet was closed and the reaction mixture was stirred at room temperature overnight under H_2 atmosphere (balloon) before filtration through celite. The solvent (EtOAc) was removed under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the aniline **17** (3.18 g, 17.6 mmol, 99% yield over two steps) as a white powder. The analytical data were identical to those reported in the literature.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.79 (d, *J* = 8.4 Hz, 1H), 6.29 (d, *J* = 2.8 Hz, 1H), 6.21 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.76 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 169.9, 151.6, 145.6, 132.0, 123.2, 106.7, 100.1, 55.8, 20.8.

Preparation of Diazonium Salt 15b

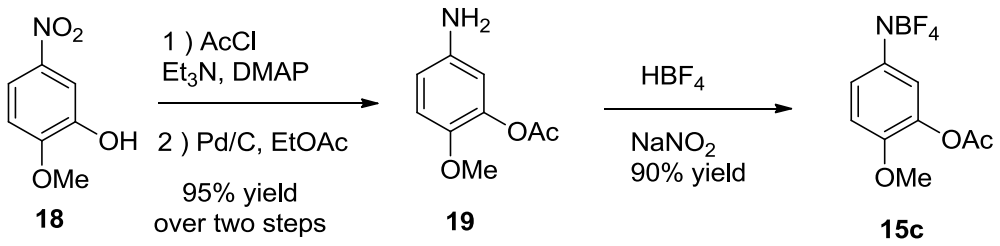


17 **15b**

To a stirred solution of **17** (0.44 g, 2.42 mmol) in 2-propanol (0.8 mL) was added HBF_4 (3.6 M solution in water, 1.01 mL, 3.63 mmol) under N_2 atmosphere at 0 °C. After completion of the addition, the reaction mixture was allowed to stir at 0 °C for 30 min and then $NaNO_2$ (1.52 g, 22.0 mmol) was added portionwise to the mixture. After completion of the addition, the reaction mixture was allowed to stir at 0 °C for 30 min. The precipitates were collected by filtration and the resulting solid was washed with MeOH twice and dried under reduced pressure to afford the white diazonium salt **15b** (0.60 g, 2.14 mmol, 89% yield). It was noted that **15b** was unstable and consequently spectra of IR and HRMS could not be obtained. **^{1}H NMR** (400 MHz, DMSO) δ: 8.52 (d, *J* = 2.4 Hz, 1H), 8.43 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 3.92 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ: 167.5, 152.0, 149.1, 127.7, 125.9, 115.8, 113.1, 57.4, 20.4.

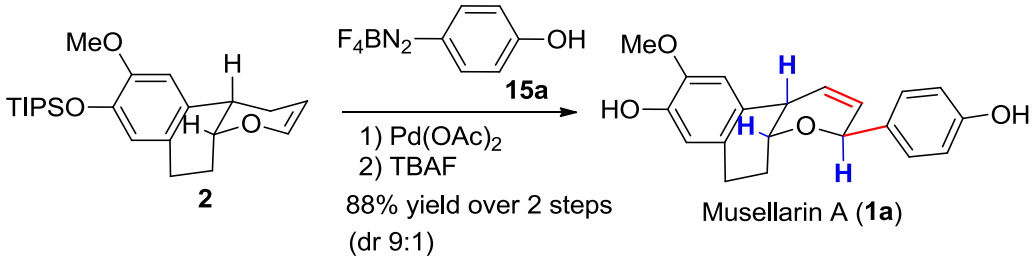
[3] C. S. J. Walpole, R. Wrigglesworth, S. Bevan, E. A. Campbell, A. Dray, I. F. James, K. J. Masdin, M. N. Perkins and J. Winter, *J. Med. Chem.,* 2010, **352**, 2463.

Preparation of Diazonium Salt 15c



Following the similar procedure for synthesis of **15b**, diazonium salt **15c** (0.25 g, 0.89 mmol) was prepared from **18** (0.18 g, 1.03 mmol) in 86% over yield as a brown solid. It was also noted that **15c** was unstable and consequently spectra of IR and HRMS could not be obtained. **^{1}H NMR** (400 MHz, DMSO) δ: 8.68 (dd, *J* = 9.2, 2.4 Hz, 1H), 8.51 (d, *J* = 2.4 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 4.08 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, DMSO) δ: 168.0, 161.7, 139.3, 135.1, 127.0, 115.4, 103.8, 58.2, 20.2.

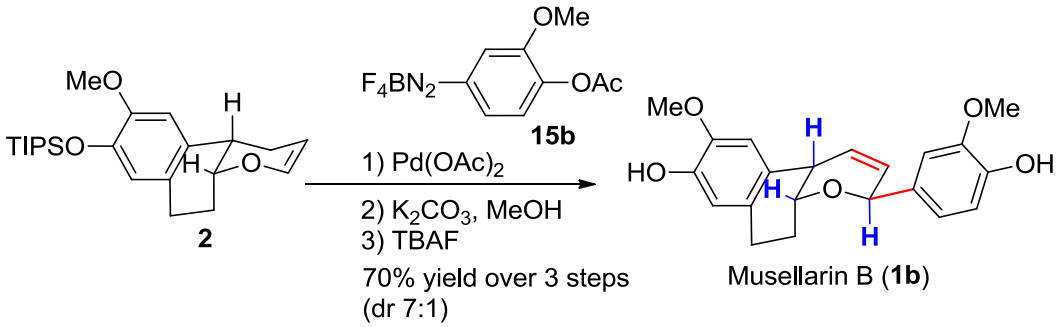
Synthesis of Musellarin A (1a)



To a stirred solution of tricyclic enol ether **2** (12.0 mg, 30.9 *μ*mol) in anhydrous acetonitrile (2 mL) were added $Pd(OAc)_2$ (1.73 mg, 7.71 *μ*mol), NaOAc (7.6 mg, 0.09 mmol) and aryl diazonium salt **15a** (7.7 mg, 0.04 mmol) at room temperature. The reaction mixture was stirred for 3 hr. Then, the reaction was quenched by addition of saturated aqueous NH_4Cl (5 mL). The organic phase was collected and the aqueous phase was extracted with ethyl acetate (3 x 2 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The ^{1}H NMR of the crude products indicated the ratio of the diastereomeric mixture was 9:1, favoring the desired *trans* diastereomer. To a stirred solution of the crude products obtained above in THF (1 mL) at 0 °C was added tetrabutylammonium fluoride hydrate solution (TBAF, 1.0 M in THF, 0.04 mmol). The reaction mixture was allowed to warm up to room temperature and stirred for additional 1 hr. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (2 mL). The organic

phase was collected and the aqueous phase was extracted with ethyl acetate (3 x 3 mL). The combined organic fractions were washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford **Musellarin A** (**1a**) (8.8 mg, 27.1 μmol, 88% yield over two steps) as a yellow oil. After careful preparative TLC, the minor diastereomer could be removed and the analytically pure musellarin A was obtained. Spectroscopic data comparison with those reported for the natural musellarin A was provided in Table S1 in page S-17. **IR** (neat, cm^{-1}): 3406, 2929, 1728, 1658, 1512, 1369, 1170, 952. ^1H NMR (400 MHz, CD_3OD) δ: 7.24 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.52 (s, 1H), 6.26 (ddd, *J* = 10.4, 4.0, 2.0 Hz, 1H), 5.86 (dt, *J* = 10.4, 2.4 Hz, 1H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.21–4.14 (m, 1H), 3.84 (s, 3H), 3.42 (brs, 1H), 2.89–2.78 (m, 1H), 2.62–2.53 (m, 1H), 2.08–2.01 (m, 1H), 1.89–1.83 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ: 158.4, 147.8, 145.7, 133.0, 130.5 (2 x C), 130.3, 129.9, 129.7, 128.5, 116.0 (2 x C), 115.9, 112.7, 73.7, 69.7, 56.6, 38.2, 27.2, 26.9. **HRMS** (TOF, Cl^-) m/z calcd for $C_{20}H_{19}O_4$ $[M-H]^-$ 323.1289, found 323.1278.

Synthesis of Musellarin B (1b)



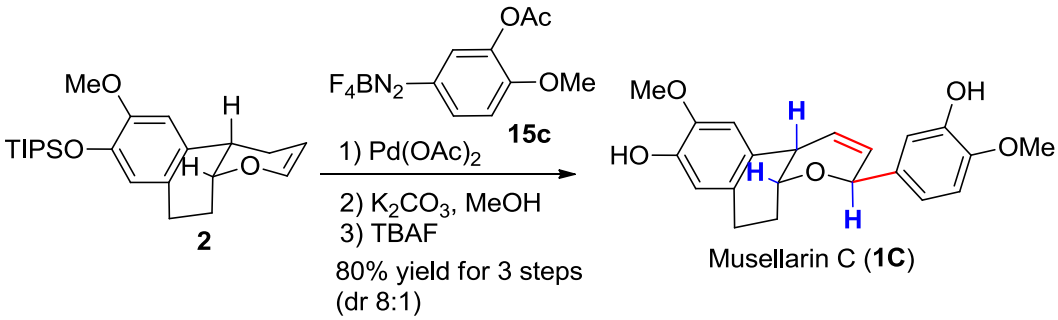
Following the similar procedure for the synthesis of musellarin A (**1a**) via Heck coupling, **Musellarin B** (**1b**) was prepared in 70% yield (4.1 mg, 11.6 μmol) from tricyclic enol ether **2** (6.4 mg, 16.5 μmol) and aryl diazonium salt **15b** (7.1 mg, 0.03 mmol) via Heck coupling, deacetylation by K_2CO_3 in methanol, and desilylation by TBAF.

Deacetylation: to a stirred solution of the crude products obtained by Heck coupling in methanol (2 mL) was added K_2CO_3 (4.2 mg, 0.03 mmol) at room temperature. The reaction mixture was stirred for 3 hr. Then, the reaction was quenched by addition of 1 M aqueous HCl (5 mL). The aqueous reaction mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic fractions were washed with brine, dried over Na_2SO_4, filtered and

concentrated under reduced pressure. The crude product was used directly for desilylation with TBAF without further purification.

The ^{1}H NMR of the crude products of Heck coupling indicated the ratio of the diastereomeric mixture was 7:1, favoring the desired *trans* diastereomer. After careful preparative TLC, the minor diastereomer could be removed and the analytically pure musellarin B was obtained as a yellow oil. Spectroscopic data comparison with those reported for the natural musellarin B was provided in Table S2 in page S-18. **IR** (neat, cm^{-1}): 3423, 2927, 2852, 1731, 1604, 1512, 1463, 1272, 1115, 1033, 734. ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.02 (d, *J* = 2.0 Hz, 1H), 6.90 (s, 1H), 6.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.55 (s, 1H), 6.30 (ddd, *J* = 10.0, 4.0, 2.0 Hz, 1H), 5.91 (dt, *J* = 10.0, 2.4 Hz, 1H), 5.06 (d, *J* = 2.4 Hz, 1H), 4.15 (ddd, *J* = 7.6, 4.8, 2.8 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.37 (brs, 1H), 2.90–2.83 (m, 1H) (overlapped with the signals of water in acetone-d_6), 2.61–2.50 (m, 1H), 2.08–1.96 (m, 1H) (overlapped with the signals of acetone-d_6), 1.84–1.76 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6) δ: 148.2, 147.1, 146.9, 145.5, 133.9, 129.9, 129.5, 129.4, 128.6, 121.4, 115.5, 115.4, 112.5, 112.3, 73.1, 68.2, 56.4, 56.3, 37.6, 27.3, 26.3. **HRMS** (TOF, CI^{+}) m/z calcd for $C_{21}H_{22}O_5$ $[M]^{+}$ 354.1467, found 354.1474.

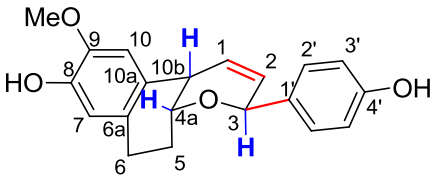
Synthesis of Musellarin C (1c)



Following the similar procedure for the synthesis of musellarin B (**1b**) via Heck coupling, **Musellarin C** (**1c**) was prepared in 80% yield (11 mg, 31.0 *μ*mol) from tricyclic enol ether **2** (15 mg, 38.6 *μ*mol) and aryl diazonium salt **15b** (13 mg, 0.05 mmol) via Heck coupling, deacetylation by K_2CO_3 in methanol, and desilylation by TBAF. The ^{1}H NMR of the crude products of Heck coupling indicated the ratio of the diastereomeric mixture was 8:1, favoring the desired *trans* diastereomer. After careful preparative TLC, the minor diastereomer could be removed and the analytically pure musellarin C was obtained as a yellow oil. Spectroscopic data comparison with those reported for the natural musellarin C was provided in Table S3 in page

S-19. **IR** (neat, cm^{-1}): 3415, 2918, 2850, 1636, 1510, 1441, 1275, 1128, 1025. ^{1}H NMR (400 MHz, CD_3OD) δ: 6.91–6.89 (m, 2H), 6.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.83 (s, 1H), 6.52 (s, 1H), 6.26 (ddd, *J* = 10.4, 4.0, 2.0 Hz, 1H), 5.87 (dt, *J* = 10.4, 2.4 Hz, 1H), 5.05 (d, *J* = 2.0 Hz, 1H), 4.18 (ddd, *J* = 7.8, 4.8, 3.2 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.40 (brs, 1H), 2.84 (ddd, *J* = 16.0, 7.8, 5.2 Hz, 1H), 2.63–2.51 (m, 1H), 2.10–2.02 (m, 1H), 1.84 (tdd, *J* = 8.0, 5.6, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ: 148.8, 147.8, 147.5, 145.7, 135.1, 130.2, 129.8, 129.7, 128.4, 120.5, 116.1, 115.9, 112.7, 112.4, 73.7, 69.7, 56.6, 56.4, 38.2, 27.3, 26.8. **HRMS** (TOF, CI^{+}) m/z calcd for $C_{21}H_{22}O_5$ $[M]^{+}$ 354.1467, found 354.1480.

Spectroscopic Data Comparison of Our Synthetic Musellarin A with Those Reported for Natural Musellarin A



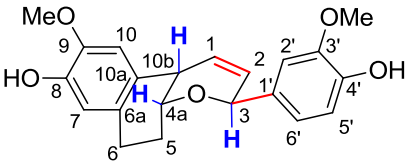
Musellarin A (**1a**)

Table S1. NMR Comparison

NO.	^{13}C NMR (CD_3OD)		^{1}H NMR (CD_3OD)	
	Natural Musellarin A[4] ^{13}C NMR (75 MHz)	Synthetic Musellarin A (Our Sample) ^{13}C NMR (100 MHz)	Natural Musellarin A[5] ^{1}H NMR (300 MHz)	Synthetic Musellarin A (Our Sample) ^{1}H NMR (400 MHz)
1	130.4	130.3	6.21, ddd (10.3, 3.8, 2.1)	6.26, ddd (10.4, 4.0, 2.0)
2	128.6	128.5	5.82, dt (10.3, 2.1)	5.86, dt (10.4, 2.4)
3	73.7	73.7	5.07, d (2.1)	5.09, d (2.4)
4a	69.8	69.7	4.14, m	4.14, m
5	27.3	27.2	1.80, m; 1.99, m	1.83, m; 2.01, m
6	27.0	26.9	2.52, m; 2.79, m	2.53, m; 2.78, m
6a	130.0	129.9		
7	116.0	115.9	6.53, s	6.52, s
8	145.8	145.7		
9	147.9	147.8		
10	112.9	112.7	6.82, s	6.83, s
10a	129.9	129.7		
10b	38.3	38.2	3.40, brs	3.42, brs
1’	133.2	133.0		
2’/6’	130.6	130.5	7.23, d (8.5)	7.24 d (8.8)
3’/5’	116.2	116.0	6.78, d (8.5)	6.78 d (8.4)
4’	158.4	158.4		
OMe-9	56.7	56.6	3.83, s	3.84, s

[4] D. S. Jang, E. J. Park, M. E. Hawthorne, J. S. Vigo, J. G. Graham, F. Cabieses, B. D. Santarsiero, A. D. Mesecar, H. H. S. Fong, R. G. Mehta, J. M. Pezzuto and A. D. Kinghorn, *J. Agric. Food Chem.,* 2002, **50**, 6330.

Spectroscopic Data Comparison of Our Synthetic Musellarin B with Those Reported for Natural Musellarin B



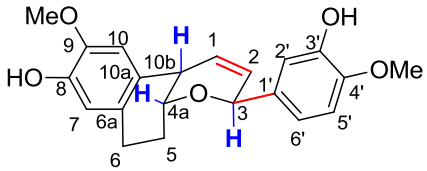
Musellarin B (**1b**)

Table S2. NMR Comparison

NO.	^{13}C NMR (acetone-d_6)		^{1}H NMR (acetone-d_6)	
	Natural Musellarin B[5] ^{13}C NMR (100 MHz)	Synthetic Musellarin B (Our Sample) ^{13}C NMR (100 MHz)	Natural Musellarin B[6] ^{1}H NMR (400 MHz)	Synthetic Musellarin B (Our Sample) ^{1}H NMR (400 MHz)
1	129.8, CH	129.8, CH	6.28, ddd (10.2, 4.0, 2.0)	6.30, ddd (10.0, 4.0, 2.0)
2	128.5, CH	128.6, CH	5.90, dt (10.2, 2.0)	5.90, dt (10.0, 2.4)
3	73.0, CH	73.1, CH	5.05, br s	5.06, d (2.4)
4a	68.1, CH	68.2, CH	4.14, m	4.15, ddd (7.6, 4.8, 2.8)
5	27.2, CH2	27.3, CH2	1.79, m (α); 2.03, m (β)	1.80, m (α); 2.03, m (β)
6	26.2, CH2	26.3, CH2	2.55, m (α); 2.85, m (β)	2.56, m (α); 2.85, m (β)
6a	129.4, C	129.5, C		
7	115.4, CH	115.5, CH	6.54, s	6.55, s
8	145.5, C	145.5, C		
9	147.0, C	146.9, C		
10	112.4, CH	112.5, CH	6.89, s	6.90, s
10a	129.4, C	129.4, C		
10b	37.5, CH	37.6, CH	3.36, br s	3.37, br s
1’	133.8, C	133.9, C		
2’	112.1, CH	112.3, CH	7.01, br s	7.01, d (2.0)
3’	148.1, C	148.2, C		
4’	147.0, C	147.1, C		
5’	115.3, CH	115.4, CH	6.80, d (8.0)	6.81, d (8.4)
6’	121.3, CH	121.4, CH	6.86, br d (8.0)	6.87, dd (8.0, 1.6)
9-OCH_3	56.3, CH3	56.4, CH3	3.82, s	3.83, s
3’-OCH_3	56.2, CH3	56.3, CH3	3.84, s	3.85, s

[5] L.-B. Dong, J. He, X.-Y. Li, X.-D. Wu, X. Deng, G. Xu, L.-Y. Peng, Y. Zhao, Y. Li, X. Gong and Q.-S. Zhao, *Nat. Prod. Bioprospect.,* 2011, **1**, 41.

Spectroscopic Data Comparison of Our Synthetic Musellarin C with Those Reported for Natural Musellarin C



Musellarin C (**1C**)

Table S3. NMR Comparison

NO.	^{13}C NMR (CD_3OD)		^{1}H NMR (CD_3OD)	
	Natural Musellarin C[6] ^{13}C NMR (125 MHz)	Synthetic Musellarin C (Our Sample) ^{13}C NMR (100 MHz)	Natural Musellarin C[6] ^{1}H NMR (500 MHz)	Synthetic Musellarin C (Our Sample) ^{1}H NMR (400 MHz)
1	130.2, CH	130.2, CH	6.26, ddd (10.2, 4.0, 2.0)	6.26, ddd (10.4, 4.0, 2.0)
2	128.4, CH	128.4, CH	5.87, dt (10.2, 2.0)	5.87, dt (10.4, 2.4)
3	73.7, CH	73.7, CH	5.05, d (1.5)	5.05, d (2.0)
4a	69.6, CH	69.7, CH	4.18, m	4.18, ddd (7.8, 4.8, 3.2)
5	27.3, CH2	27.3, CH2	1.84, m (*α*); 2.05, m (*β*)	1.84. tdd (8.0, 5.6, 3.2) (*α*); 2.06, m (*β*)
6	26.8, CH2	26.8, CH2	2.58, m (*α*); 2.84, m (*β*)	2.57, m (*α*); 2.84, ddd (16.0, 7.8, 5.2) (*β*)
6a	129.8, C	129.8, C		
7	115.9, CH	115.9, CH	6.52, s	6.52, s
8	145.6, C	145.7, C		
9	147.8, C	147.8, C		
10	112.7, CH	112.7, CH	6.83, s	6.83, s
10a	129.7, C	129.7, C		
10b	38.1, CH	38.2, CH	3.41, br s	3.40, br s
1’	135.1, C	135.1, C		
2’	116.1, CH	116.1, CH	6.89, overlap	6.89, overlap
3’	147.5, C	147.5, C		
4’	148.8, C	148.8, C		
5’	112.4, CH	112.4, CH	6.90, overlap	6.90, overlap
6’	120.5, CH	120.5, CH	6.85, dd (8.0, 1.5)	6.85, dd (8.4, 2.0)
9-OCH_3	56.5, CH3	56.6, CH3	3.84, s	3.84, s
4’-OCH_3	56.4, CH3	56.4, CH3	3.85, s	3.85, s

X-Ray Structure and Data for Compound 3

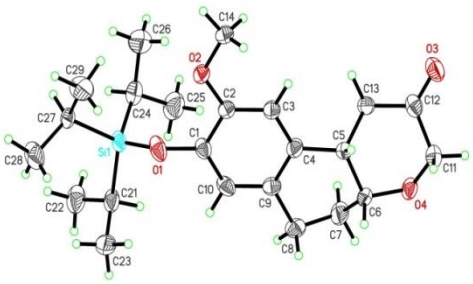


Table 1. Crystal data and structure refinement for Compound **3**.

Identification code	Compound **3**	
Empirical formula	C23 H36 O4 Si	
Formula weight	404.61	
Temperature	99.98(10) K	
Wavelength	1.5418 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4432(3) Å	α= 82.362(2) °.
	b = 10.8187(3) Å	β= 86.419(2) °.
	c = 12.5225(3) Å	γ = 85.558(2) °.
Volume	1128.73(5) $Å^3$	
Z	2	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	1.112 mm^{-1}	
F(000)	440	
Crystal size	0.20 x 0.20 x 0.18 mm^3	
Theta range for data collection	5.10 to 67.50 °.	
Index ranges	-10<=h<=10, -12<=k<=12, -14<=l<=14	
Reflections collected	16557	
Independent reflections	3970 [R(int) = 0.0214]	
Completeness to theta = 66.50 °	99.95 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.86420	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3970 / 1 / 326	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1224	
R indices (all data)	R1 = 0.0557, wR2 = 0.1262	
Largest diff. peak and hole	0.378 and -0.580 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Compound **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	8441(1)	2132(1)	1386(1)	47(1)
O(1)	7770(2)	2511(1)	2577(1)	51(1)
O(2)	5073(2)	1752(1)	3534(1)	41(1)
O(3)	-958(2)	6525(2)	4601(2)	56(1)
O(3A)	-182(6)	6880(5)	5594(5)	59(1)
O(4)	2330(3)	8329(2)	3898(2)	41(1)
O(4A)	3285(7)	8071(5)	4210(4)	39(1)
C(1)	6629(2)	3412(2)	2847(2)	38(1)
C(2)	5206(2)	3020(2)	3367(1)	35(1)
C(3)	4088(2)	3900(2)	3695(2)	41(1)
C(4)	4330(2)	5181(2)	3500(2)	40(1)
C(5)	3190(4)	6078(2)	4041(2)	30(1)
C(5A)	2699(9)	6118(6)	3593(7)	35(2)
C(6)	3694(3)	7425(3)	3886(2)	33(1)
C(6A)	2968(8)	7532(6)	3285(6)	44(1)
C(7)	4536(3)	7760(2)	2733(2)	58(1)
C(8)	6044(2)	6945(2)	2775(2)	43(1)
C(9)	5728(2)	5575(2)	2978(1)	36(1)
C(10)	6870(2)	4671(2)	2670(2)	41(1)
C(11)	1083(4)	7932(3)	4646(2)	42(1)
C(11A)	1884(9)	8180(6)	4891(6)	40(2)
C(12)	379(3)	6809(2)	4311(2)	40(1)
C(12A)	1119(7)	6957(6)	5137(5)	41(1)
C(13)	1507(3)	6075(2)	3618(2)	35(1)
C(13A)	2132(8)	5863(6)	4773(5)	42(1)
C(14)	3661(2)	1324(2)	4094(2)	46(1)
C(21)	9909(3)	3284(2)	788(2)	53(1)
C(22)	10647(3)	3031(2)	-315(2)	67(1)
C(23)	11191(3)	3464(2)	1553(2)	65(1)
C(24)	6778(3)	2197(2)	436(2)	64(1)
C(25)	5994(3)	3504(2)	140(2)	72(1)

C(26)	5491(3)	1284(3)	782(3)	77(1)
C(27)	9263(3)	457(2)	1560(3)	39(1)
C(27A)	9492(9)	559(7)	2178(7)	51(2)
C(28)	11008(3)	240(3)	1682(3)	67(1)
C(28A)	10210(20)	-158(15)	1316(12)	67(4)
C(29)	8377(3)	-279(2)	2597(3)	79(1)

Table 3. Bond lengths [Å] and angles [º] for Compound **3**.

Si(1)-O(1)	1.6536(17)
Si(1)-C(21)	1.878(2)
Si(1)-C(24)	1.887(3)
Si(1)-C(27)	1.879(2)
Si(1)-C(27A)	2.024(8)
O(1)-C(1)	1.376(2)
O(2)-C(2)	1.371(2)
O(2)-C(14)	1.422(2)
O(3)-C(12)	1.214(3)
O(3A)-C(12A)	1.210(8)
O(4)-C(6)	1.453(3)
O(4)-C(11)	1.418(4)
O(4A)-C(6A)	1.413(8)
O(4A)-C(11A)	1.421(9)
C(1)-C(2)	1.398(2)
C(1)-C(10)	1.379(3)
C(2)-C(3)	1.372(3)
C(3)-C(4)	1.404(2)
C(4)-C(5)	1.508(3)
C(4)-C(5A)	1.653(7)
C(4)-C(9)	1.383(3)
C(5)-C(6)	1.533(4)
C(5)-C(13)	1.548(4)
C(5A)-C(6A)	1.558(9)

C(5A)-C(13A)	1.520(10)
C(6)-C(7)	1.579(4)
C(6A)-C(7)	1.477(7)
C(7)-C(8)	1.492(3)
C(8)-C(9)	1.511(2)
C(9)-C(10)	1.394(3)
C(11)-C(12)	1.511(5)
C(11A)-C(12A)	1.504(9)
C(12)-C(13)	1.502(4)
C(12A)-C(13A)	1.510(9)
C(21)-C(22)	1.528(3)
C(21)-C(23)	1.529(4)
C(24)-C(25)	1.523(3)
C(24)-C(26)	1.529(4)
C(27)-C(28)	1.488(4)
C(27)-C(29)	1.606(4)
C(27A)-C(28A)	1.485(17)
C(27A)-C(29)	1.389(8)

O(1)-Si(1)-C(21)	108.28(9)
O(1)-Si(1)-C(24)	111.34(10)
O(1)-Si(1)-C(27)	108.80(11)
O(1)-Si(1)-C(27A)	87.5(3)
C(21)-Si(1)-C(24)	108.44(11)
C(21)-Si(1)-C(27)	114.58(10)
C(21)-Si(1)-C(27A)	112.8(2)
C(24)-Si(1)-C(27A)	125.8(3)
C(27)-Si(1)-C(24)	105.43(12)
C(27)-Si(1)-C(27A)	24.3(2)
C(1)-O(1)-Si(1)	130.84(12)
C(2)-O(2)-C(14)	117.00(14)
C(11)-O(4)-C(6)	113.4(2)
C(6A)-O(4A)-C(11A)	110.5(6)
O(1)-C(1)-C(2)	118.07(16)
O(1)-C(1)-C(10)	122.52(16)
C(10)-C(1)-C(2)	119.34(17)

O(2)-C(2)-C(1)	115.78(15)
O(2)-C(2)-C(3)	125.20(16)
C(3)-C(2)-C(1)	118.99(16)
C(2)-C(3)-C(4)	121.45(17)
C(3)-C(4)-C(5)	118.57(18)
C(3)-C(4)-C(5A)	114.8(3)
C(5)-C(4)-C(5A)	25.5(2)
C(9)-C(4)-C(3)	119.80(17)
C(9)-C(4)-C(5)	120.72(18)
C(9)-C(4)-C(5A)	122.8(3)
C(4)-C(5)-C(6)	113.8(2)
C(4)-C(5)-C(13)	110.1(2)
C(6)-C(5)-C(13)	108.8(2)
C(6A)-C(5A)-C(4)	114.2(5)
C(13A)-C(5A)-C(4)	104.0(6)
C(13A)-C(5A)-C(6A)	110.2(5)
O(4)-C(6)-C(5)	111.8(2)
O(4)-C(6)-C(7)	103.79(19)
C(5)-C(6)-C(7)	111.0(2)
O(4A)-C(6A)-C(5A)	110.3(6)
O(4A)-C(6A)-C(7)	94.7(5)
C(7)-C(6A)-C(5A)	113.3(5)
C(6A)-C(7)-C(6)	37.6(3)
C(6A)-C(7)-C(8)	129.4(3)
C(8)-C(7)-C(6)	103.64(19)
C(7)-C(8)-C(9)	111.66(16)
C(4)-C(9)-C(8)	121.25(17)
C(4)-C(9)-C(10)	118.18(16)
C(10)-C(9)-C(8)	120.53(16)
C(1)-C(10)-C(9)	122.21(17)
O(4)-C(11)-C(12)	110.1(2)
O(4A)-C(11A)-C(12A)	111.5(5)
O(3)-C(12)-C(11)	122.5(3)
O(3)-C(12)-C(13)	124.0(3)
C(13)-C(12)-C(11)	113.4(2)
O(3A)-C(12A)-C(11A)	122.0(6)

O(3A)-C(12A)-C(13A)	124.3(6)
C(11A)-C(12A)-C(13A)	113.7(5)
C(12)-C(13)-C(5)	107.6(2)
C(12A)-C(13A)-C(5A)	111.8(5)
C(22)-C(21)-Si(1)	113.85(16)
C(22)-C(21)-C(23)	111.11(19)
C(23)-C(21)-Si(1)	113.66(16)
C(25)-C(24)-Si(1)	113.96(17)
C(25)-C(24)-C(26)	109.3(2)
C(26)-C(24)-Si(1)	115.6(2)
C(28)-C(27)-Si(1)	116.5(2)
C(28)-C(27)-C(29)	108.0(2)
C(29)-C(27)-Si(1)	108.94(17)
C(28A)-C(27A)-Si(1)	104.9(8)
C(29)-C(27A)-Si(1)	111.3(5)
C(29)-C(27A)-C(28A)	97.3(8)
C(27A)-C(29)-C(27)	31.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Compound **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	34(1)	21(1)	82(1)	0(1)	12(1)	5(1)
O(1)	38(1)	39(1)	68(1)	15(1)	13(1)	10(1)
O(2)	40(1)	26(1)	55(1)	-6(1)	7(1)	-4(1)
O(3)	37(1)	47(1)	77(2)	6(1)	6(1)	5(1)
O(3A)	41(3)	58(3)	81(4)	-23(3)	19(3)	-8(2)
O(4)	46(1)	25(1)	50(1)	-3(1)	2(1)	5(1)
O(4A)	45(3)	31(3)	38(2)	-2(2)	9(2)	-5(2)
C(1)	33(1)	34(1)	43(1)	3(1)	2(1)	3(1)
C(2)	35(1)	29(1)	39(1)	-3(1)	0(1)	-4(1)
C(3)	38(1)	31(1)	53(1)	-7(1)	11(1)	-8(1)
C(4)	42(1)	30(1)	46(1)	-6(1)	9(1)	-5(1)
C(5)	31(2)	28(1)	30(2)	0(1)	-6(1)	-2(1)
C(5A)	30(5)	35(3)	41(4)	-11(3)	-4(3)	-5(3)
C(6)	36(1)	25(1)	39(1)	-7(1)	-2(1)	0(1)
C(7)	58(1)	27(1)	85(2)	-3(1)	22(1)	-6(1)
C(8)	50(1)	35(1)	44(1)	2(1)	2(1)	-12(1)
C(9)	39(1)	32(1)	36(1)	0(1)	-2(1)	-7(1)
C(10)	30(1)	40(1)	50(1)	8(1)	3(1)	-3(1)
C(11)	41(2)	38(2)	43(2)	-3(1)	4(1)	7(1)
C(11A)	33(4)	28(3)	54(4)	-6(3)	9(3)	8(3)
C(12)	37(1)	35(1)	44(1)	9(1)	-3(1)	8(1)
C(12A)	30(3)	44(4)	50(4)	-13(3)	6(3)	-5(3)
C(13)	33(2)	30(1)	42(1)	-2(1)	-7(1)	-1(1)
C(13A)	42(3)	36(3)	47(3)	-11(3)	7(3)	-9(3)
C(14)	43(1)	29(1)	67(1)	-9(1)	8(1)	-10(1)
C(21)	50(1)	26(1)	78(2)	-4(1)	22(1)	1(1)
C(22)	75(2)	39(1)	81(2)	0(1)	30(1)	1(1)
C(23)	52(1)	51(1)	96(2)	-22(1)	23(1)	-20(1)
C(24)	55(1)	44(1)	95(2)	-24(1)	5(1)	7(1)
C(25)	73(2)	55(1)	87(2)	-14(1)	-19(1)	15(1)
C(26)	61(2)	69(2)	106(2)	-24(2)	-13(2)	-6(1)

C(27)	37(1)	22(1)	56(2)	-3(1)	-2(1)	8(1)
C(28)	47(2)	45(2)	100(2)	15(2)	-5(2)	17(1)
C(29)	57(1)	27(1)	143(3)	23(1)	-6(2)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Compound **3**.

	x	y	z	U(eq)
H(3)	3128	3636	4061	49
H(5)	3128	5780	4832	36
H(5A)	1883	5874	3130	41
H(6)	4423	7540	4458	40
H(6A)	2072	7998	2883	53
H(7AA)	3872	7571	2159	70
H(7AB)	4755	8655	2602	70
H(7BC)	4817	8560	2948	70
H(7BD)	4324	7939	1957	70
H(8A)	6680	7150	3358	52
H(8B)	6673	7112	2084	52
H(10)	7846	4930	2328	50
H(11A)	246	8621	4679	50
H(11B)	1499	7713	5374	50
H(11C)	1119	8821	4535	47
H(11D)	2155	8460	5575	47
H(13A)	1495	6462	2856	42
H(13B)	1191	5207	3660	42
H(13C)	1509	5114	4879	50
H(13D)	3067	5684	5223	50
H(14A)	2735	1693	3701	69
H(14B)	3586	1574	4821	69
H(14C)	3690	411	4146	69
H(21)	9285	4110	660	63
H(22A)	11213	2201	-248	101
H(22B)	11396	3665	-578	101
H(22C)	9806	3065	-825	101
H(23A)	10692	3580	2264	98
H(23B)	11760	4202	1264	98
H(23C)	11943	2724	1621	98
H(24)	7288	1946	-252	77

H(25A)	5518	3821	794	108
H(25B)	5165	3471	-367	108
H(25C)	6796	4062	-197	108
H(26A)	5981	428	884	115
H(26B)	4716	1357	222	115
H(26C)	4951	1481	1461	115
H(27)	9003	76	912	46
H(27A)	10263	718	2711	61
H(28A)	11576	684	1057	100
H(28B)	11313	-658	1726	100
H(28C)	11286	549	2342	100
H(28D)	9371	-532	986	100
H(28E)	10968	-821	1627	100
H(28F)	10767	404	764	100
H(29A)	8558	108	3239	118
H(29B)	7233	-241	2492	118
H(29C)	8799	-1154	2694	118
H(29D)	7630	112	3105	118
H(29E)	7794	-510	2009	118
H(29F)	8919	-1030	2974	118

Table 6. Torsion angles [º] for Compound **3**.

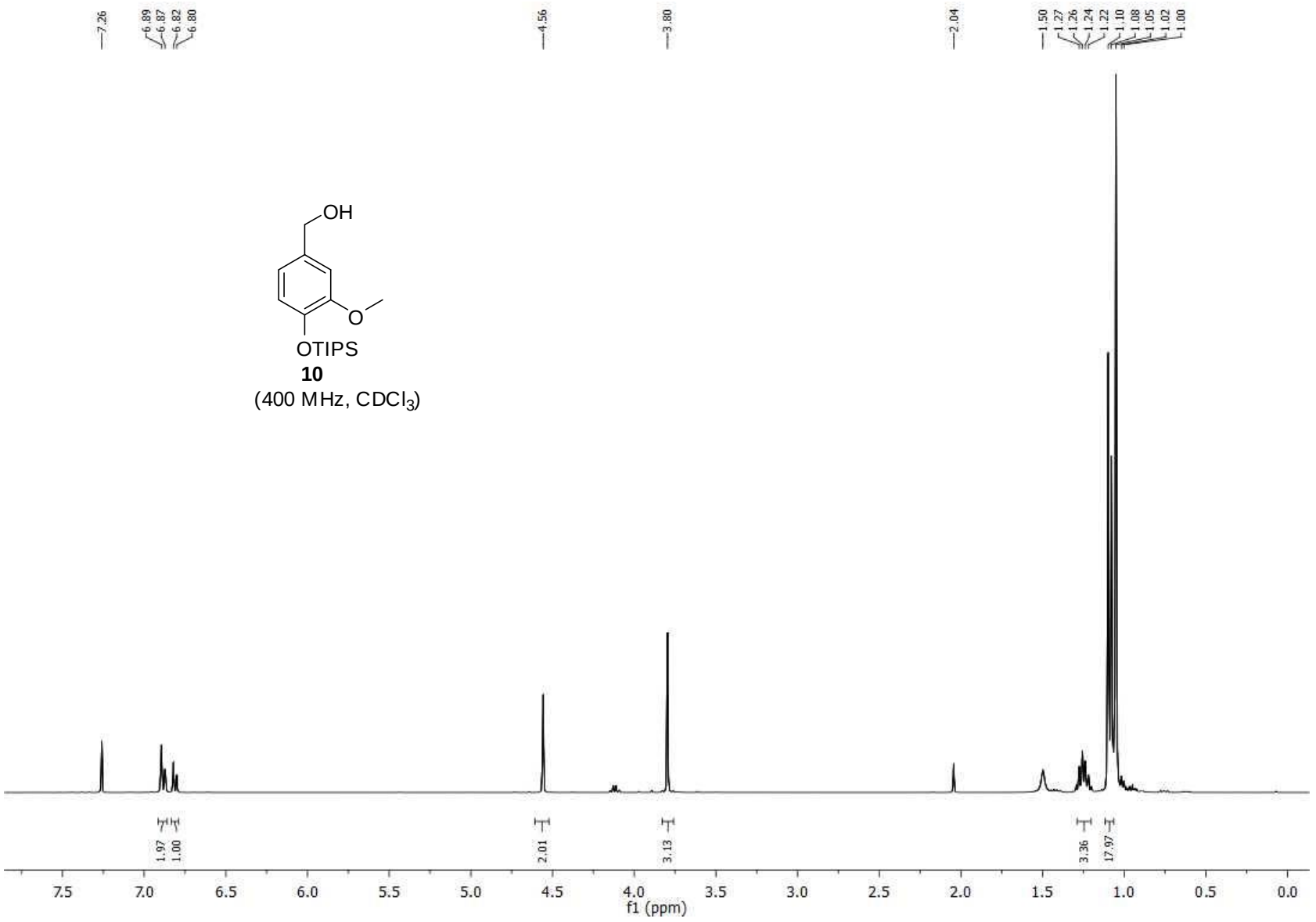
Si(1)-O(1)-C(1)-C(2)	111.39(18)
Si(1)-O(1)-C(1)-C(10)	-71.7(3)
Si(1)-C(27)-C(29)-C(27A)	-75.5(7)
Si(1)-C(27A)-C(29)-C(27)	65.9(6)
O(1)-Si(1)-C(21)-C(22)	179.15(16)
O(1)-Si(1)-C(21)-C(23)	50.58(16)
O(1)-Si(1)-C(24)-C(25)	65.1(2)
O(1)-Si(1)-C(24)-C(26)	-62.77(19)

O(1)-Si(1)-C(27)-C(28)	-95.5(3)
O(1)-Si(1)-C(27)-C(29)	26.9(2)
O(1)-Si(1)-C(27A)-C(28A)	176.2(8)
O(1)-Si(1)-C(27A)-C(29)	72.0(5)
O(1)-C(1)-C(2)-O(2)	-1.6(2)
O(1)-C(1)-C(2)-C(3)	176.64(17)
O(1)-C(1)-C(10)-C(9)	-177.94(17)
O(2)-C(2)-C(3)-C(4)	179.24(17)
O(3)-C(12)-C(13)-C(5)	-141.1(3)
O(3A)-C(12A)-C(13A)-C(5A)	128.6(7)
O(4)-C(6)-C(7)-C(6A)	-48.1(4)
O(4)-C(6)-C(7)-C(8)	172.82(19)
O(4)-C(11)-C(12)-O(3)	-157.2(3)
O(4)-C(11)-C(12)-C(13)	24.4(3)
O(4A)-C(6A)-C(7)-C(6)	34.6(3)
O(4A)-C(6A)-C(7)-C(8)	90.1(5)
O(4A)-C(11A)-C(12A)-O(3A)	-171.0(7)
O(4A)-C(11A)-C(12A)-C(13A)	9.7(9)
C(1)-C(2)-C(3)-C(4)	1.2(3)
C(2)-C(1)-C(10)-C(9)	-1.1(3)
C(2)-C(3)-C(4)-C(5)	-169.8(2)
C(2)-C(3)-C(4)-C(5A)	161.8(4)
C(2)-C(3)-C(4)-C(9)	-0.6(3)
C(3)-C(4)-C(5)-C(6)	172.6(2)
C(3)-C(4)-C(5)-C(13)	-65.0(3)
C(3)-C(4)-C(5A)-C(6A)	-175.3(5)
C(3)-C(4)-C(5A)-C(13A)	64.6(5)
C(3)-C(4)-C(9)-C(8)	-178.72(17)
C(3)-C(4)-C(9)-C(10)	-0.8(3)
C(4)-C(5)-C(6)-O(4)	150.5(2)
C(4)-C(5)-C(6)-C(7)	35.1(3)
C(4)-C(5)-C(13)-C(12)	170.63(19)
C(4)-C(5A)-C(6A)-O(4A)	-91.5(7)
C(4)-C(5A)-C(6A)-C(7)	13.2(8)
C(4)-C(5A)-C(13A)-C(12A)	155.7(5)
C(4)-C(9)-C(10)-C(1)	1.6(3)

C(5)-C(4)-C(5A)-C(6A)	80.0(7)
C(5)-C(4)-C(5A)-C(13A)	-40.0(6)
C(5)-C(4)-C(9)-C(8)	-9.8(3)
C(5)-C(4)-C(9)-C(10)	168.2(2)
C(5)-C(6)-C(7)-C(6A)	72.1(5)
C(5)-C(6)-C(7)-C(8)	-66.9(3)
C(5A)-C(4)-C(5)-C(6)	-99.1(7)
C(5A)-C(4)-C(5)-C(13)	23.3(6)
C(5A)-C(4)-C(9)-C(8)	20.3(4)
C(5A)-C(4)-C(9)-C(10)	-161.8(4)
C(5A)-C(6A)-C(7)-C(6)	-79.8(7)
C(5A)-C(6A)-C(7)-C(8)	-24.3(8)
C(6)-O(4)-C(11)-C(12)	-65.8(3)
C(6)-C(5)-C(13)-C(12)	-64.1(3)
C(6)-C(7)-C(8)-C(9)	60.6(2)
C(6A)-O(4A)-C(11A)-C(12A)	52.1(8)
C(6A)-C(5A)-C(13A)-C(12A)	32.9(8)
C(6A)-C(7)-C(8)-C(9)	29.5(5)
C(7)-C(8)-C(9)-C(4)	-25.4(3)
C(7)-C(8)-C(9)-C(10)	156.75(19)
C(8)-C(9)-C(10)-C(1)	179.58(17)
C(9)-C(4)-C(5)-C(6)	3.5(3)
C(9)-C(4)-C(5)-C(13)	126.0(2)
C(9)-C(4)-C(5A)-C(6A)	-13.4(8)
C(9)-C(4)-C(5A)-C(13A)	-133.5(4)
C(10)-C(1)-C(2)-O(2)	-178.60(16)
C(10)-C(1)-C(2)-C(3)	-0.4(3)
C(11)-O(4)-C(6)-C(5)	37.0(3)
C(11)-O(4)-C(6)-C(7)	156.8(2)
C(11)-C(12)-C(13)-C(5)	37.3(3)
C(11A)-O(4A)-C(6A)-C(5A)	-71.5(7)
C(11A)-O(4A)-C(6A)-C(7)	171.5(4)
C(11A)-C(12A)-C(13A)-C(5A)	-52.1(8)
C(13)-C(5)-C(6)-O(4)	27.4(3)
C(13)-C(5)-C(6)-C(7)	-88.0(3)
C(13A)-C(5A)-C(6A)-O(4A)	25.0(8)

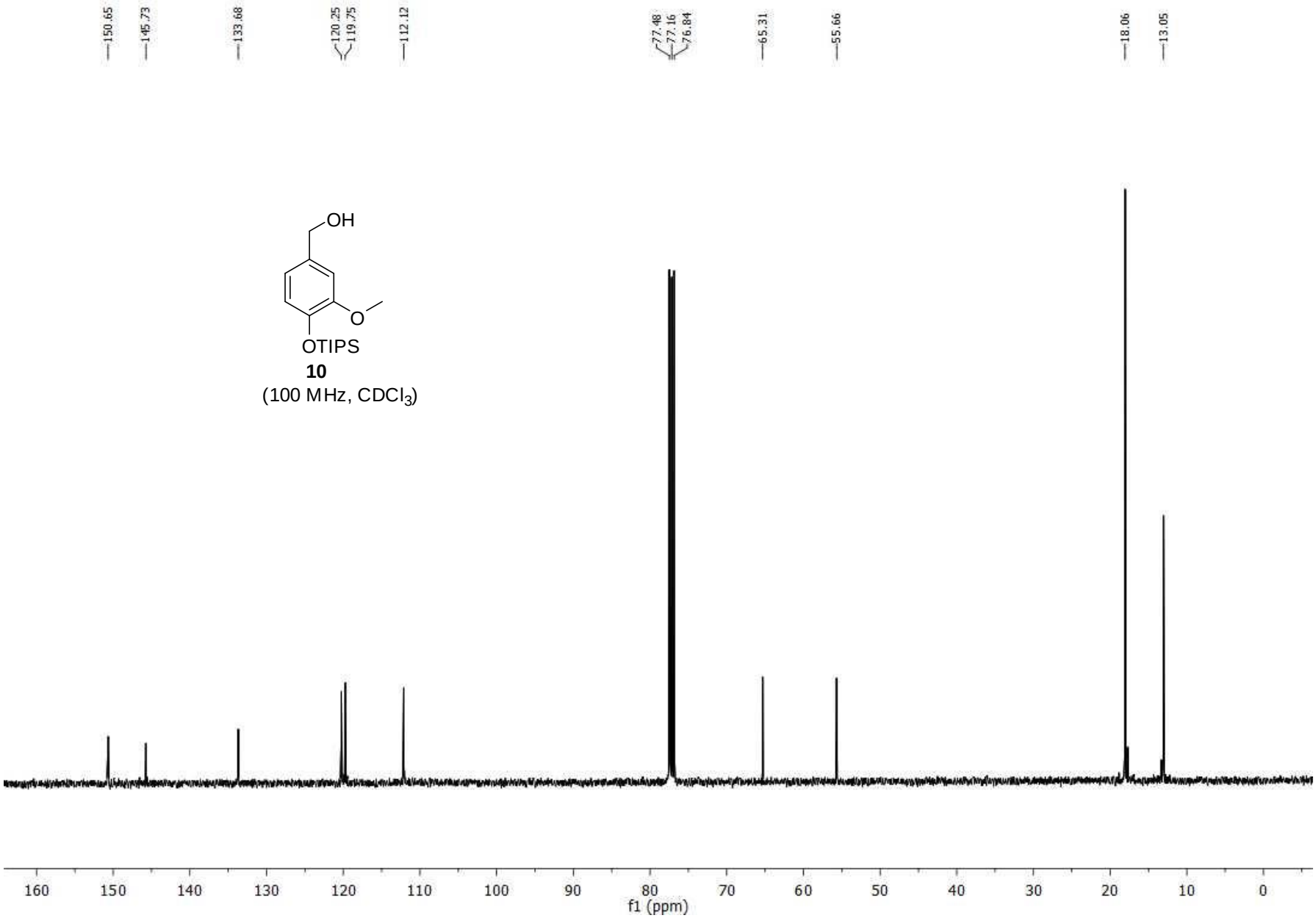
C(13A)-C(5A)-C(6A)-C(7)	129.7(6)
C(14)-O(2)-C(2)-C(1)	177.93(17)
C(14)-O(2)-C(2)-C(3)	-0.2(3)
C(21)-Si(1)-O(1)-C(1)	79.80(18)
C(21)-Si(1)-C(24)-C(25)	-54.0(2)
C(21)-Si(1)-C(24)-C(26)	178.20(17)
C(21)-Si(1)-C(27)-C(28)	25.8(3)
C(21)-Si(1)-C(27)-C(29)	148.22(19)
C(21)-Si(1)-C(27A)-C(28A)	-75.0(8)
C(21)-Si(1)-C(27A)-C(29)	-179.2(4)
C(24)-Si(1)-O(1)-C(1)	-39.32(19)
C(24)-Si(1)-C(21)-C(22)	-59.91(19)
C(24)-Si(1)-C(21)-C(23)	171.51(15)
C(24)-Si(1)-C(27)-C(28)	145.0(3)
C(24)-Si(1)-C(27)-C(29)	-92.6(2)
C(24)-Si(1)-C(27A)-C(28A)	61.5(8)
C(24)-Si(1)-C(27A)-C(29)	-42.7(7)
C(27)-Si(1)-O(1)-C(1)	-155.09(17)
C(27)-Si(1)-C(21)-C(22)	57.5(2)
C(27)-Si(1)-C(21)-C(23)	-71.0(2)
C(27)-Si(1)-C(24)-C(25)	-177.1(2)
C(27)-Si(1)-C(24)-C(26)	55.1(2)
C(27)-Si(1)-C(27A)-C(28A)	24.5(8)
C(27)-Si(1)-C(27A)-C(29)	-79.7(7)
C(27A)-Si(1)-O(1)-C(1)	-167.0(3)
C(27A)-Si(1)-C(21)-C(22)	84.0(3)
C(27A)-Si(1)-C(21)-C(23)	-44.6(3)
C(27A)-Si(1)-C(24)-C(25)	168.0(3)
C(27A)-Si(1)-C(24)-C(26)	40.2(4)
C(27A)-Si(1)-C(27)-C(28)	-65.5(6)
C(27A)-Si(1)-C(27)-C(29)	56.9(6)
C(28)-C(27)-C(29)-C(27A)	51.8(7)
C(28A)-C(27A)-C(29)-C(27)	-43.3(8)

Symmetry transformations used to generate equivalent atoms:



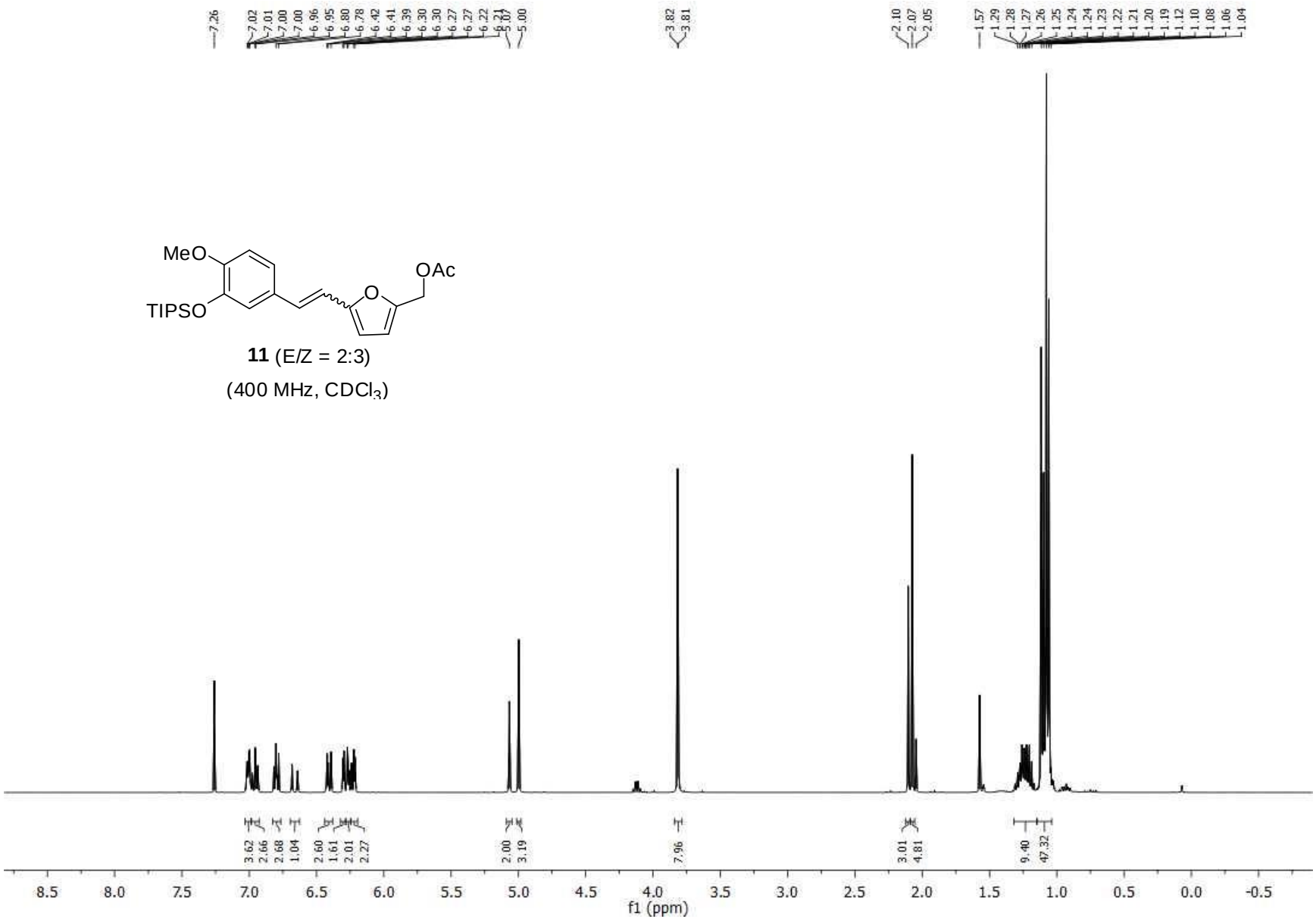
10

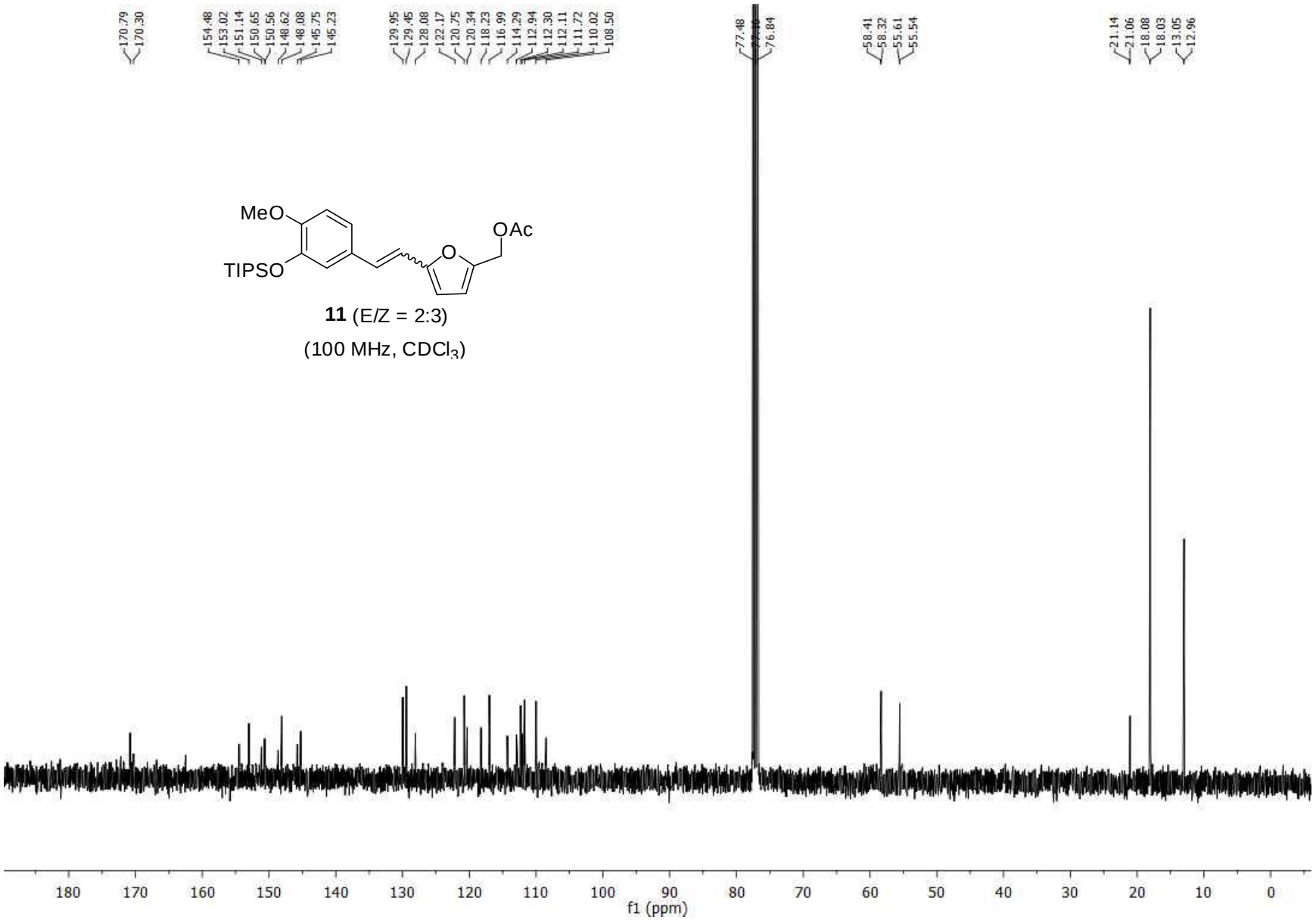
(400 MHz, $CDCl_3$)



10

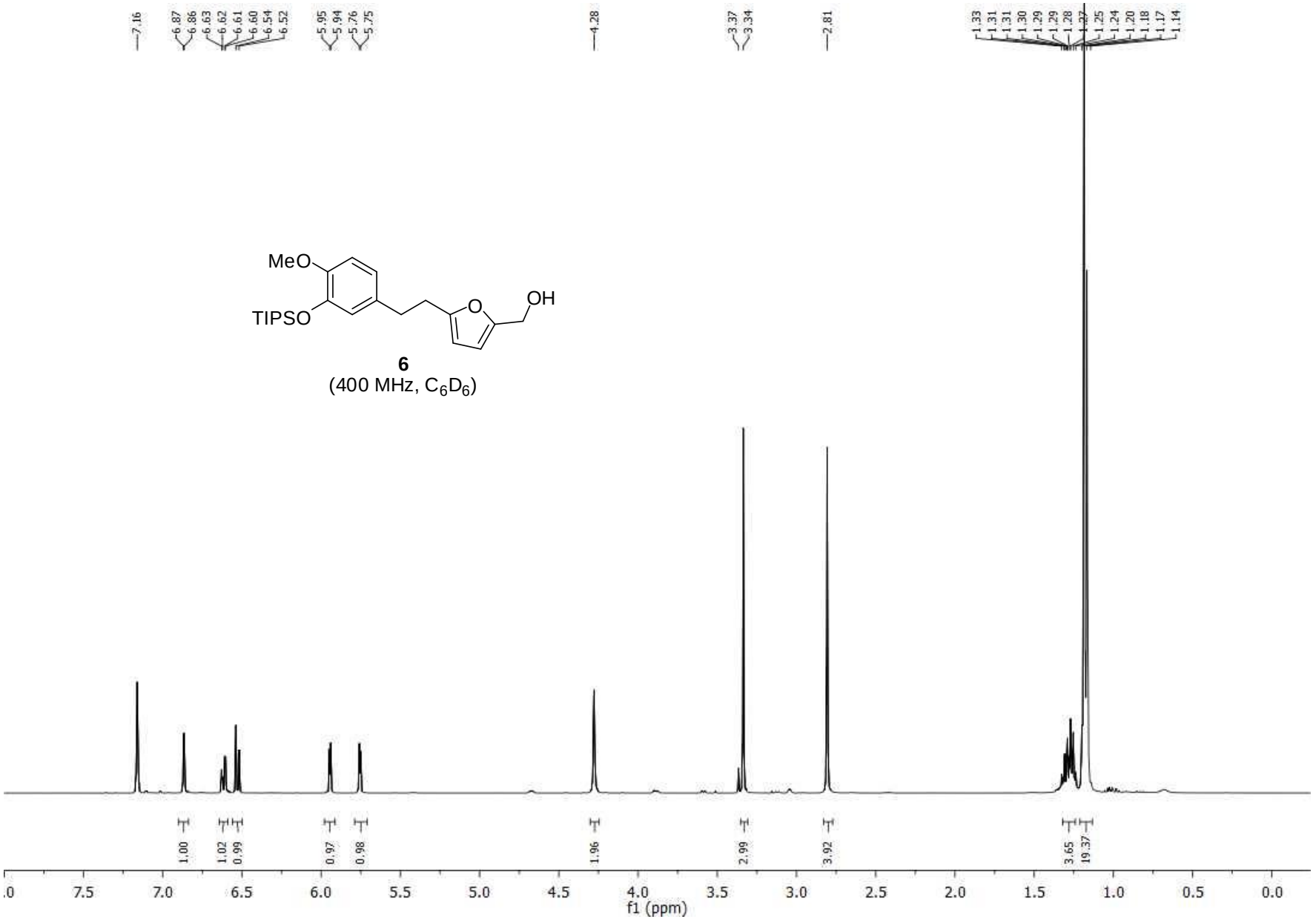
(100 MHz, $CDCl_3$)


MeO
TIPSO
OAc
O
11 (E/Z = 2:3)
(400 MHz, CDCl3)
f1 (ppm)

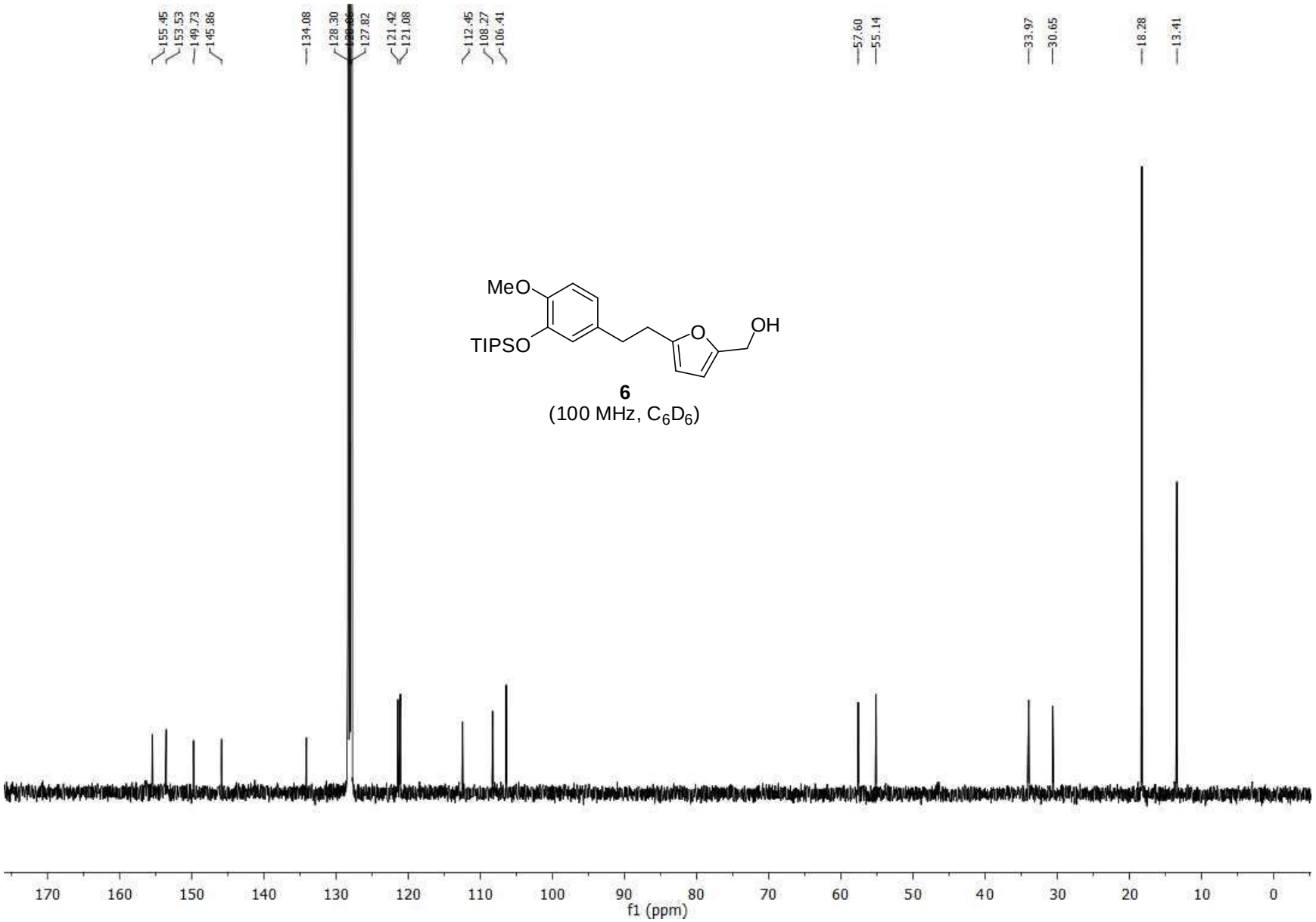


11 (E/Z = 2:3)

(100 MHz, $CDCl_3$)

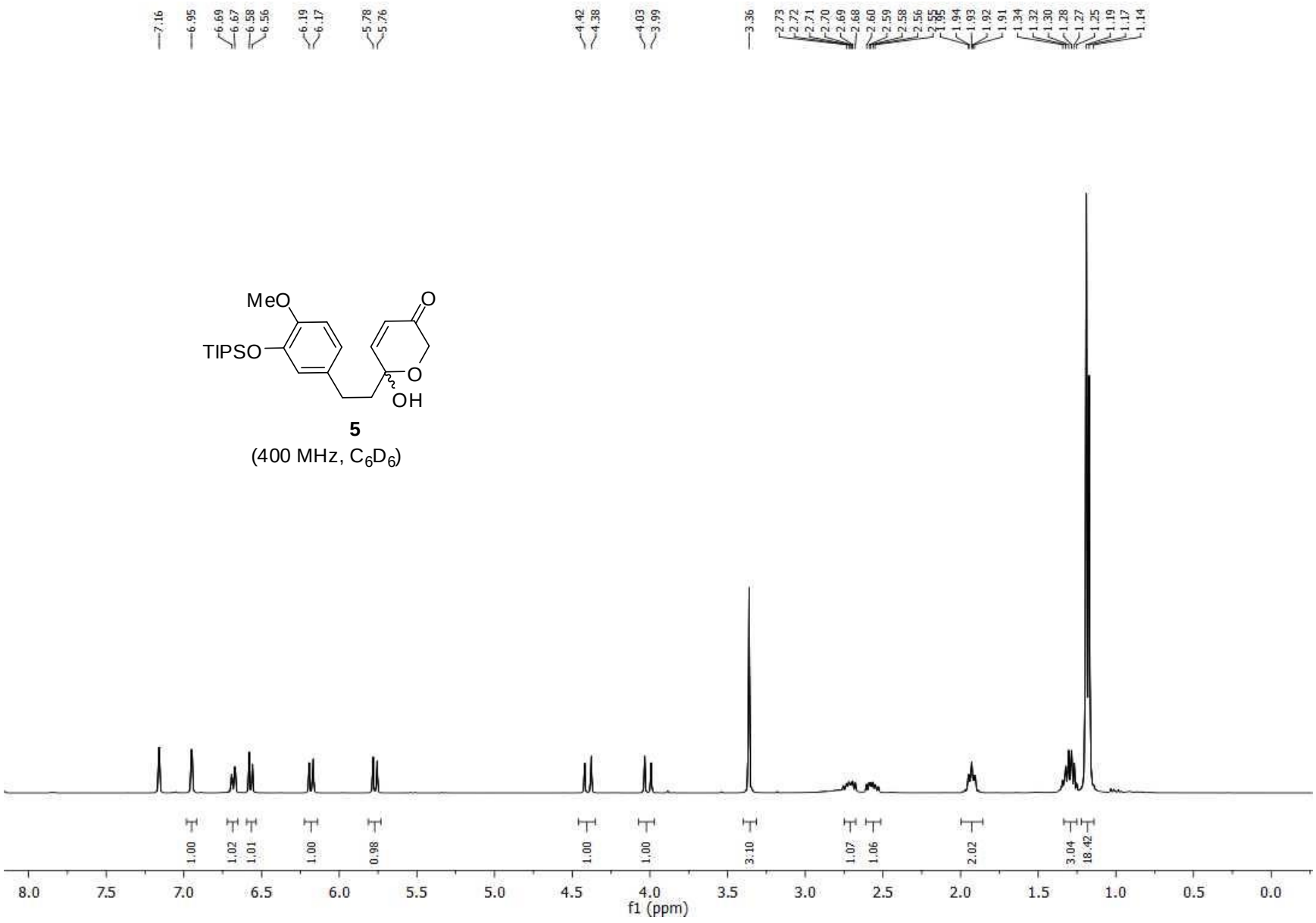


6
(400 MHz, C_6D_6)



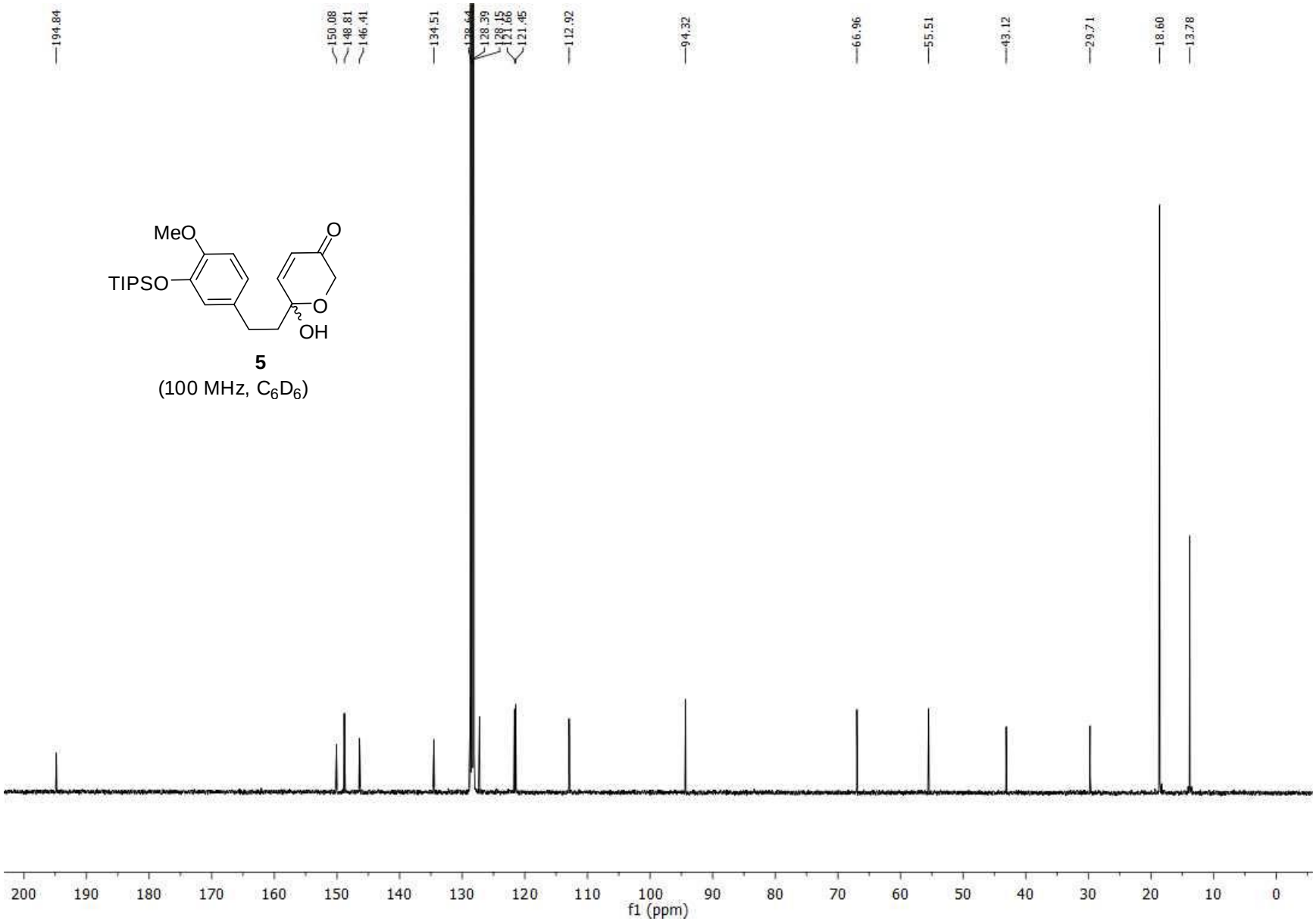
6

(100 MHz, C_6D_6)



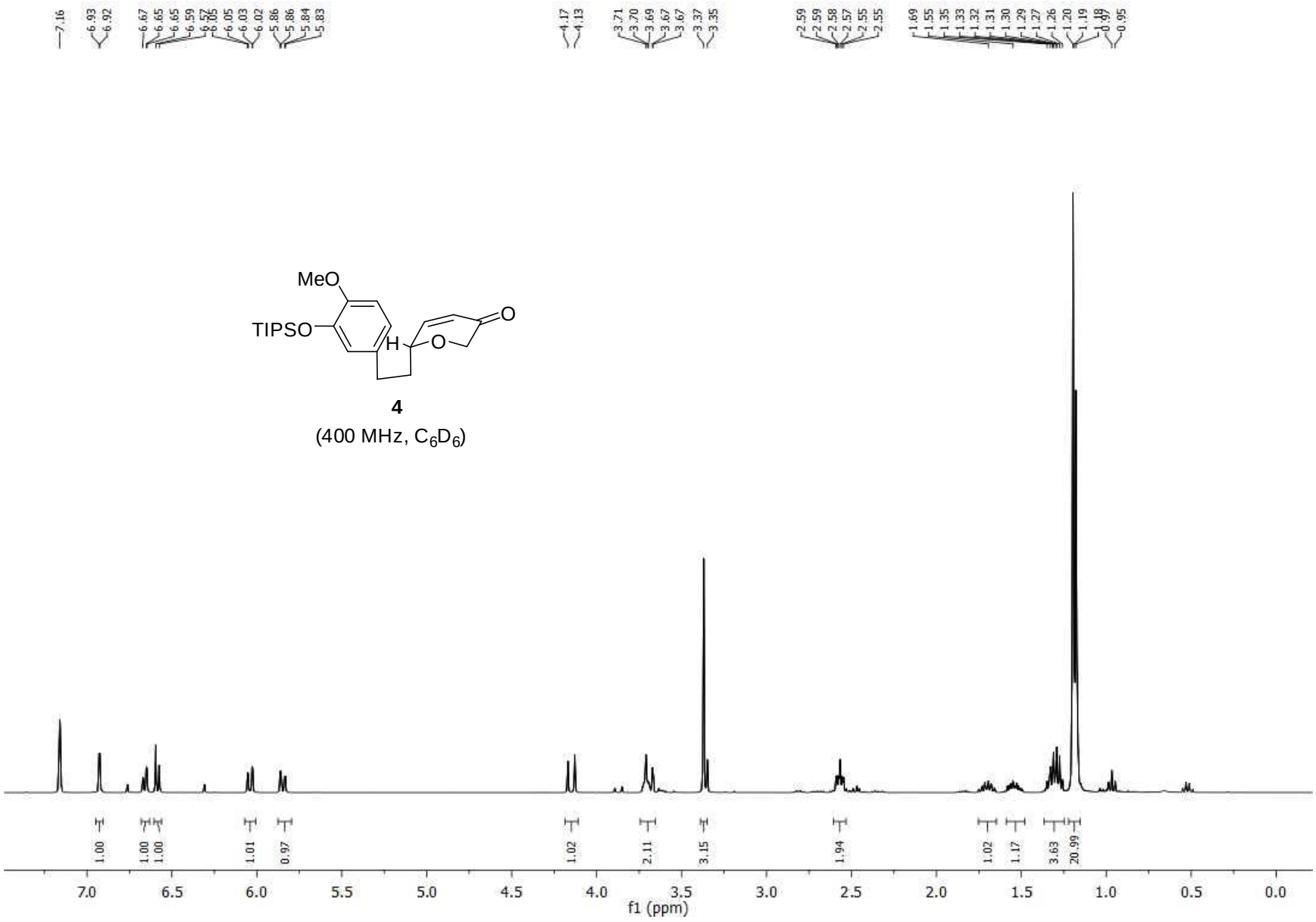
5

(400 MHz, C_6D_6)



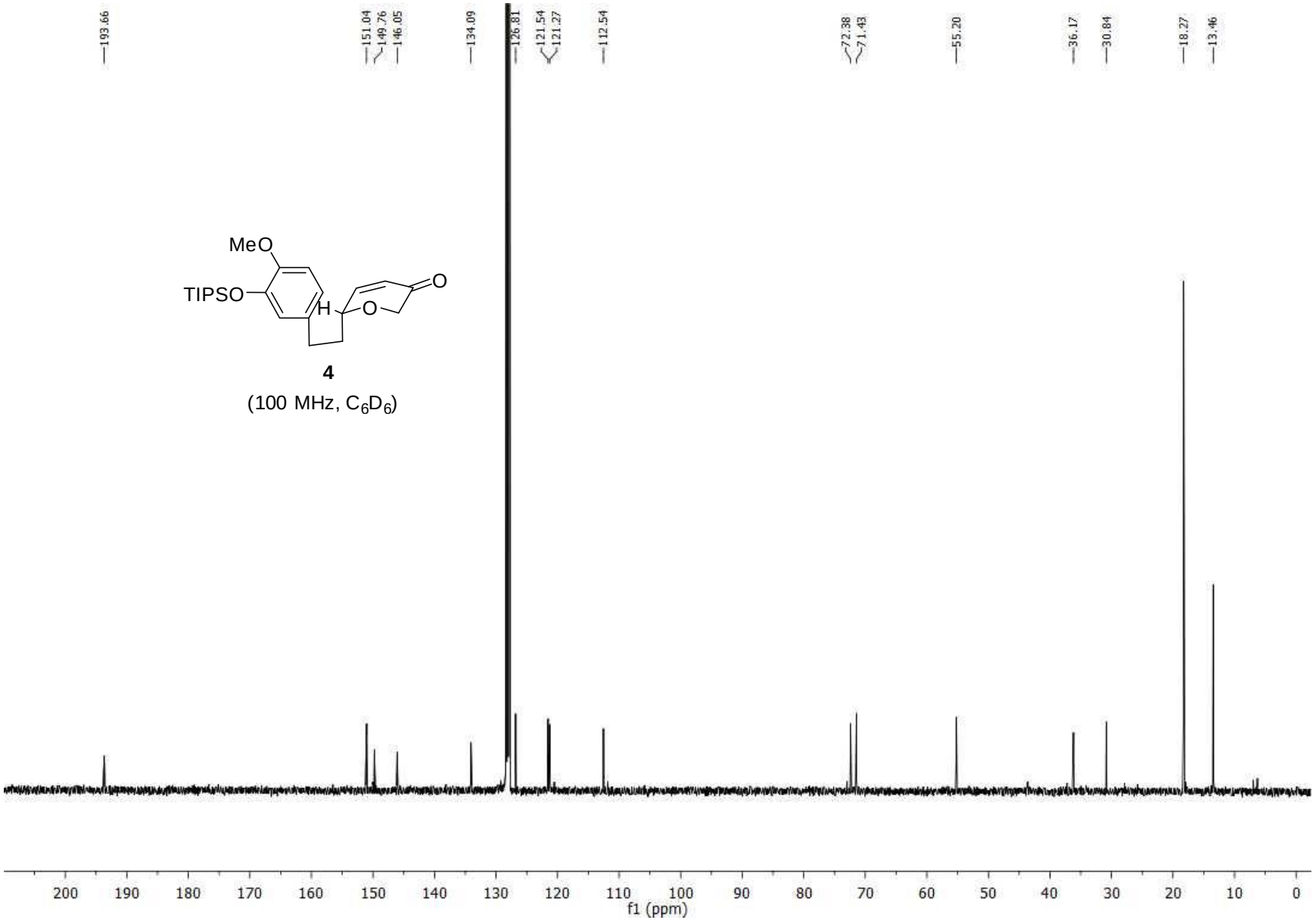
5

(100 MHz, C_6D_6)



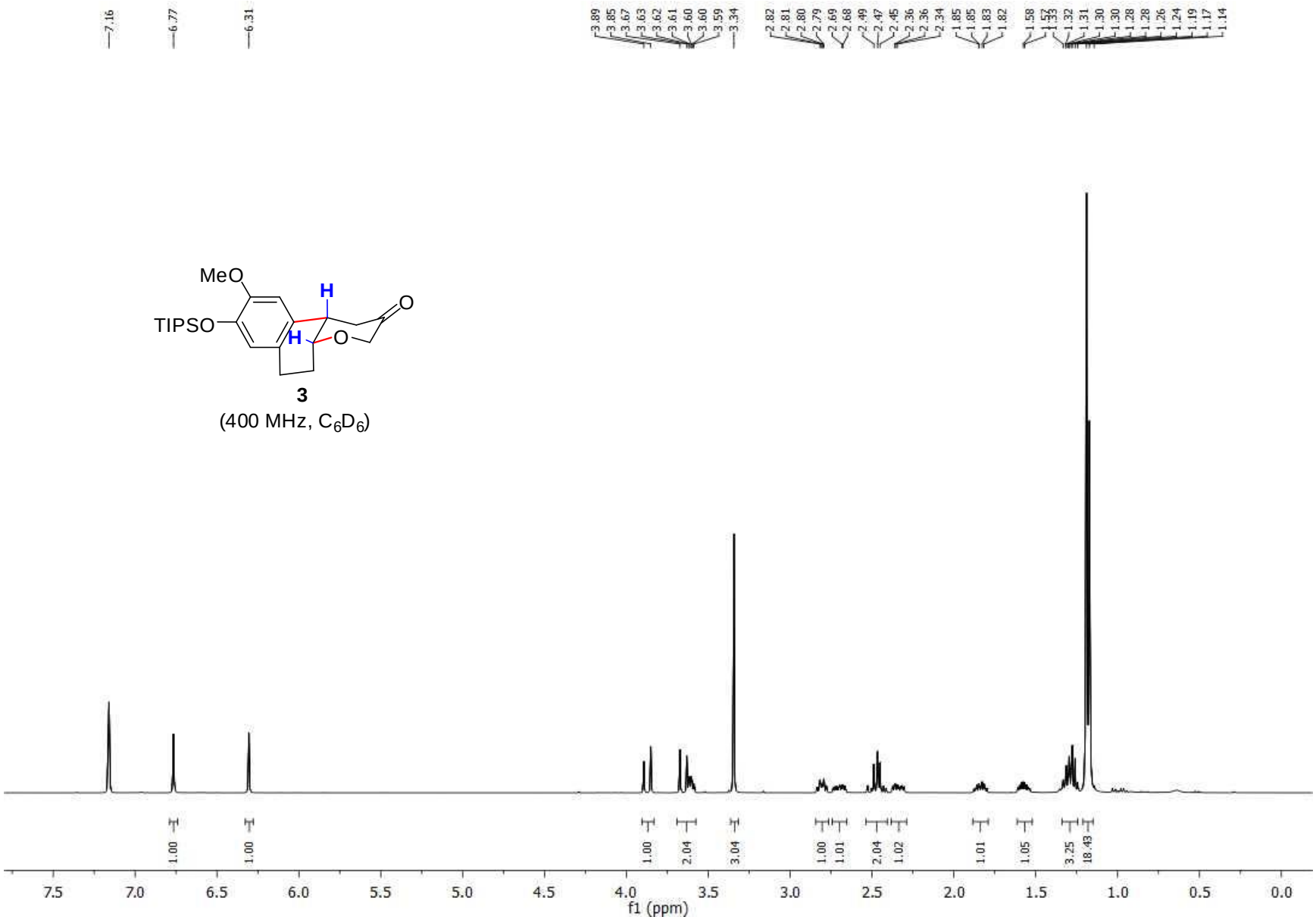
4

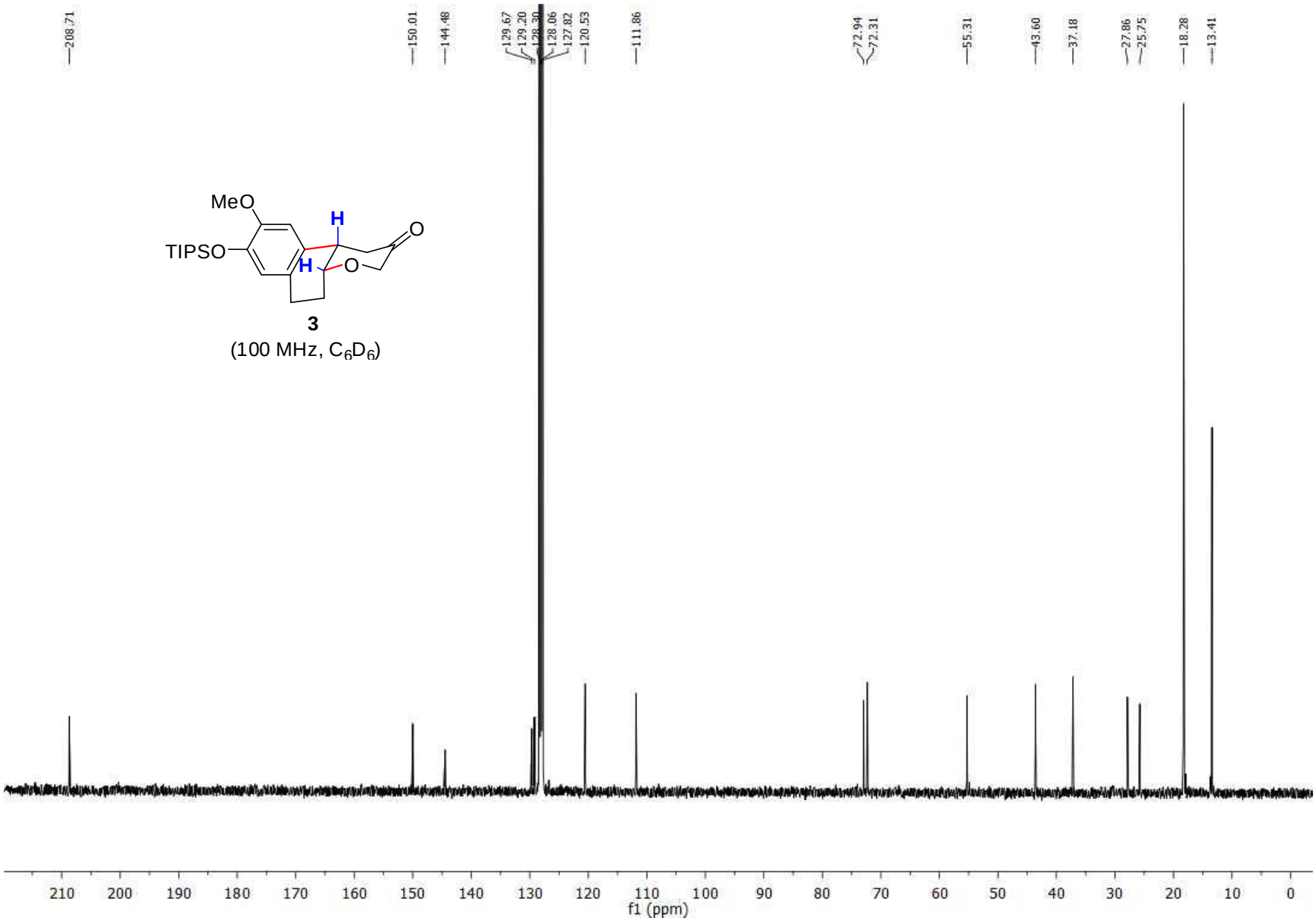
(400 MHz, C_6D_6)



4

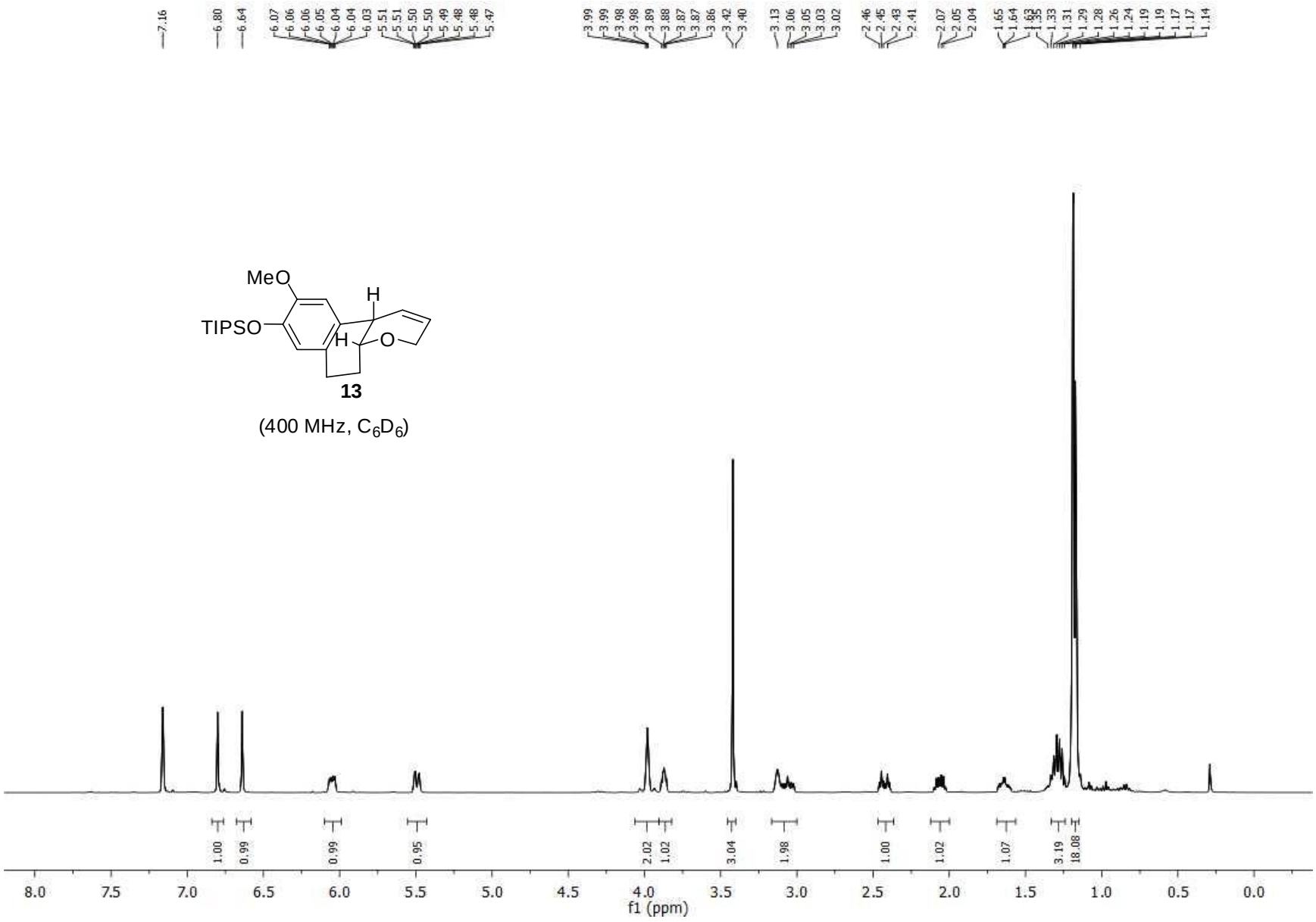
(100 MHz, C_6D_6)

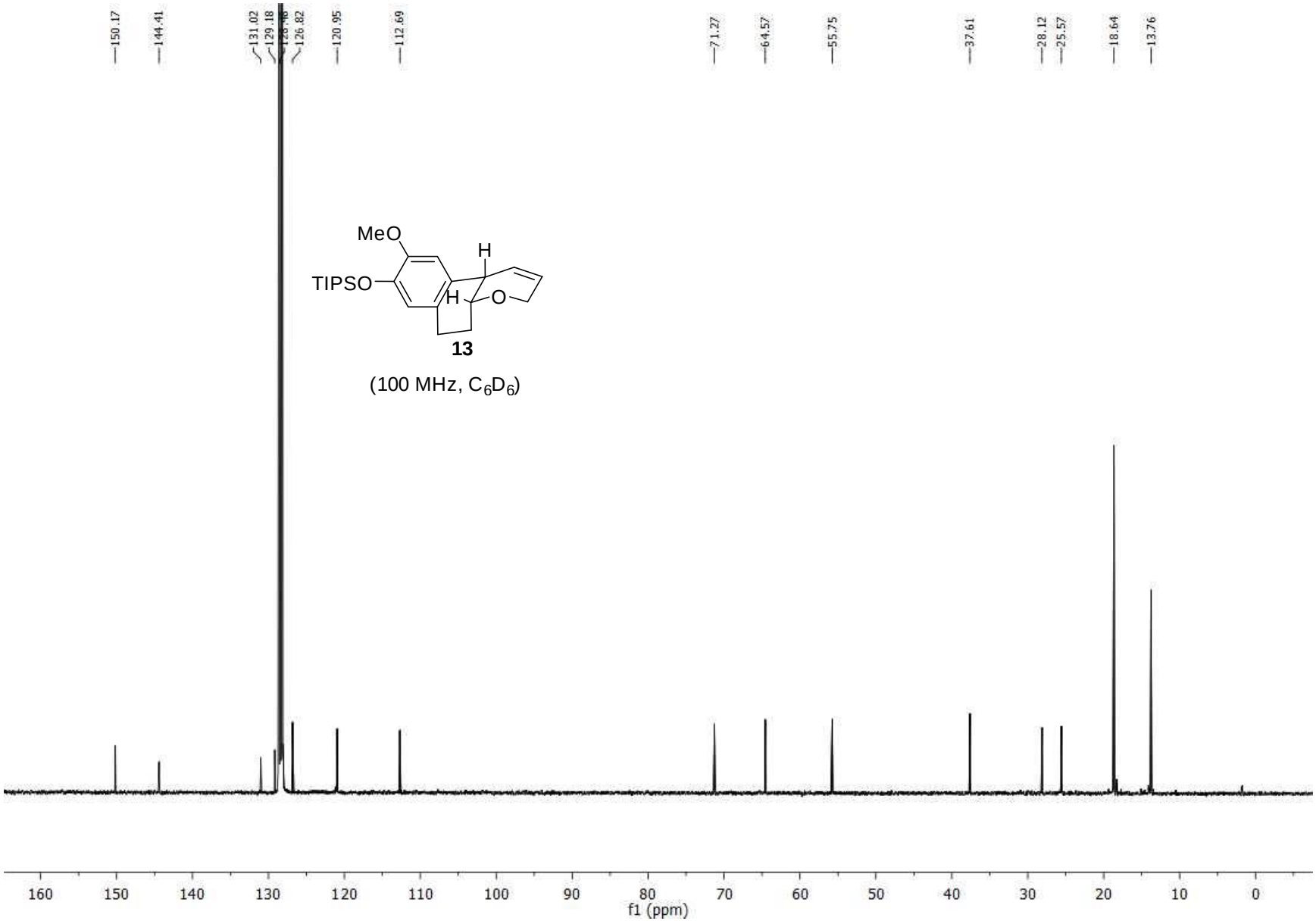

7.16
6.77
6.31
3.89
3.85
3.67
3.63
3.62
3.61
3.60
3.60
3.59
3.34
2.82
2.81
2.80
2.79
2.69
2.68
2.49
2.47
2.45
2.36
2.36
2.34
1.85
1.85
1.83
1.82
1.58
1.57
1.33
1.32
1.31
1.30
1.30
1.28
1.28
1.26
1.24
1.19
1.17
1.14
MeO
TIPSO
H
H
O
O
3
(400 MHz, C6D6)
1.00
1.00
1.00
2.04
3.04
1.00
1.01
2.04
1.02
1.01
1.05
3.25
18.43
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
f1 (ppm)



3

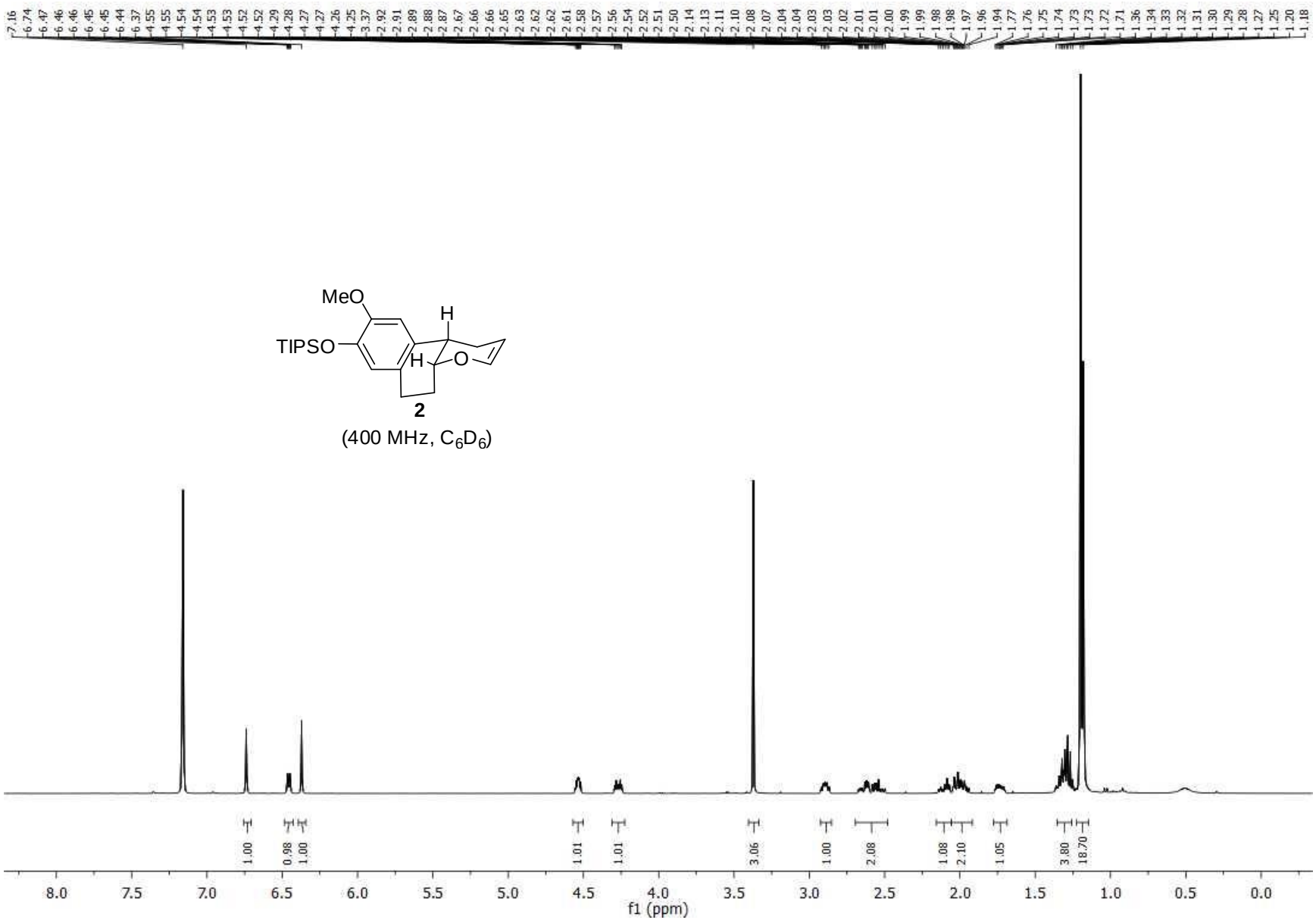
(100 MHz, C_6D_6)

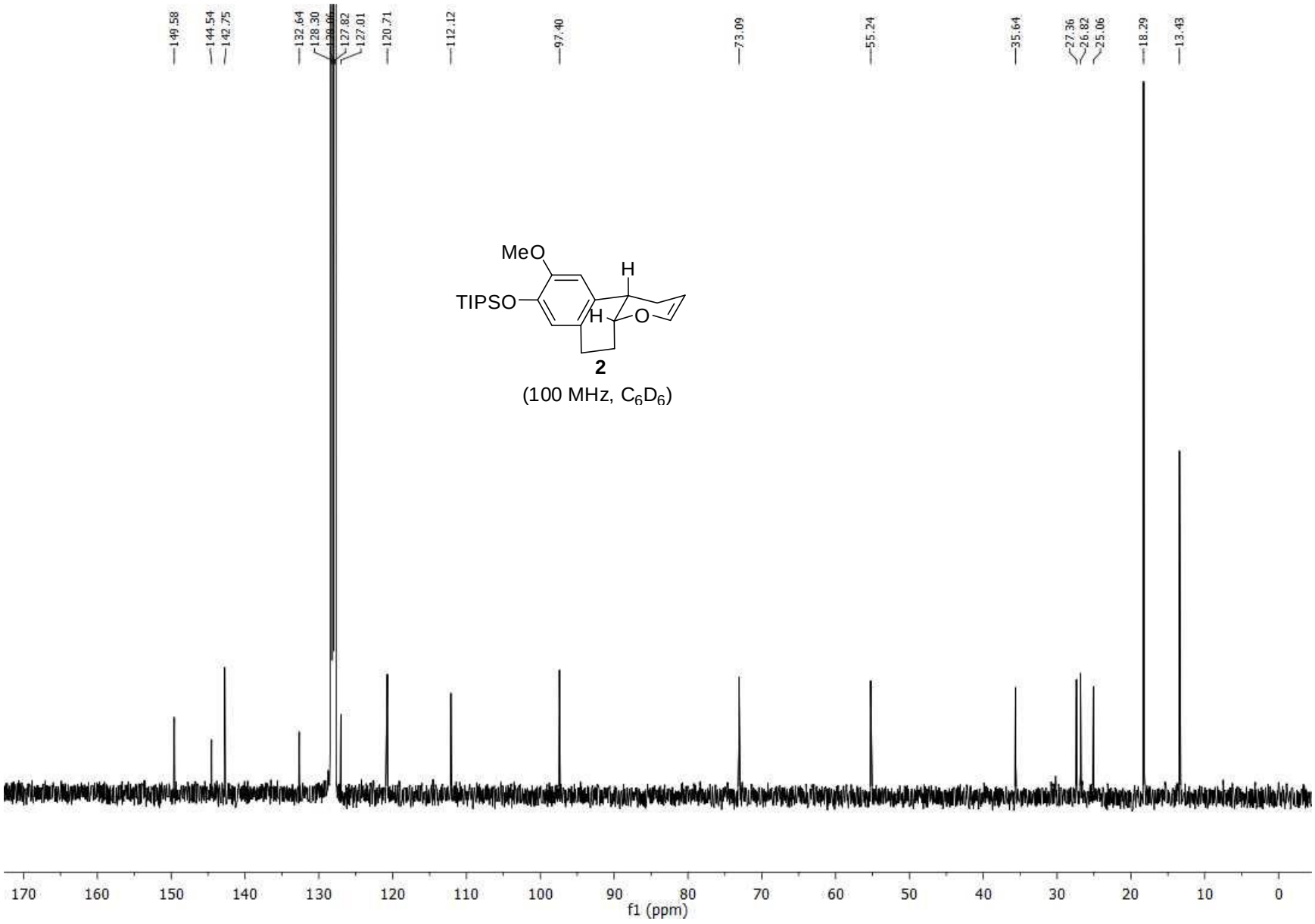

7.16
6.80
6.64
6.07
6.06
6.06
6.05
6.04
6.04
6.03
5.51
5.51
5.50
5.50
5.49
5.48
5.48
5.47
3.99
3.99
3.98
3.98
3.89
3.88
3.87
3.87
3.86
3.42
3.40
3.13
3.06
3.05
3.03
3.02
2.46
2.45
2.43
2.41
2.07
2.05
2.04
1.65
1.64
1.35
1.33
1.31
1.29
1.28
1.26
1.24
1.19
1.19
1.17
1.17
1.14
MeO
H
TIPSO
H
O
13
(400 MHz, C6D6)
1.00
0.99
0.99
0.95
2.02
1.02
3.04
1.98
1.00
1.02
1.07
3.19
18.08
8.0
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
f1 (ppm)

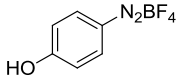


13

(100 MHz, C_6D_6)

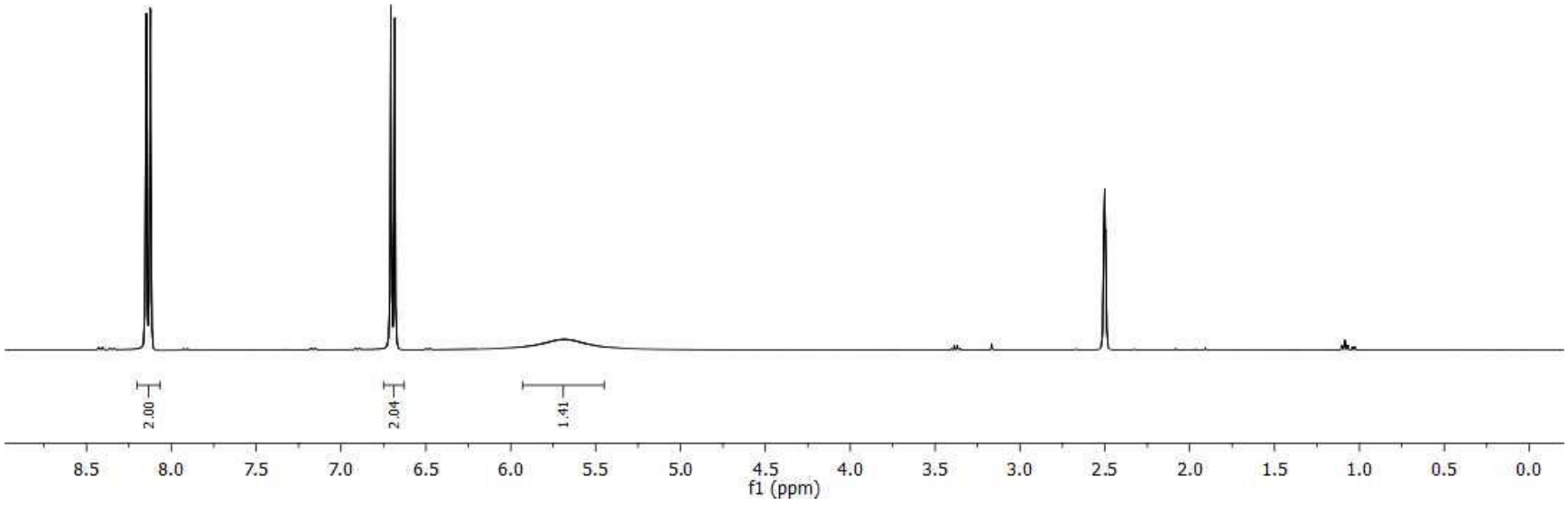

MeO
H
TIPSO
H
O
2
(400 MHz, C6D6)
1.00
0.98
1.00
1.01
1.01
3.06
1.00
2.08
1.08
2.10
1.05
3.80
18.70
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

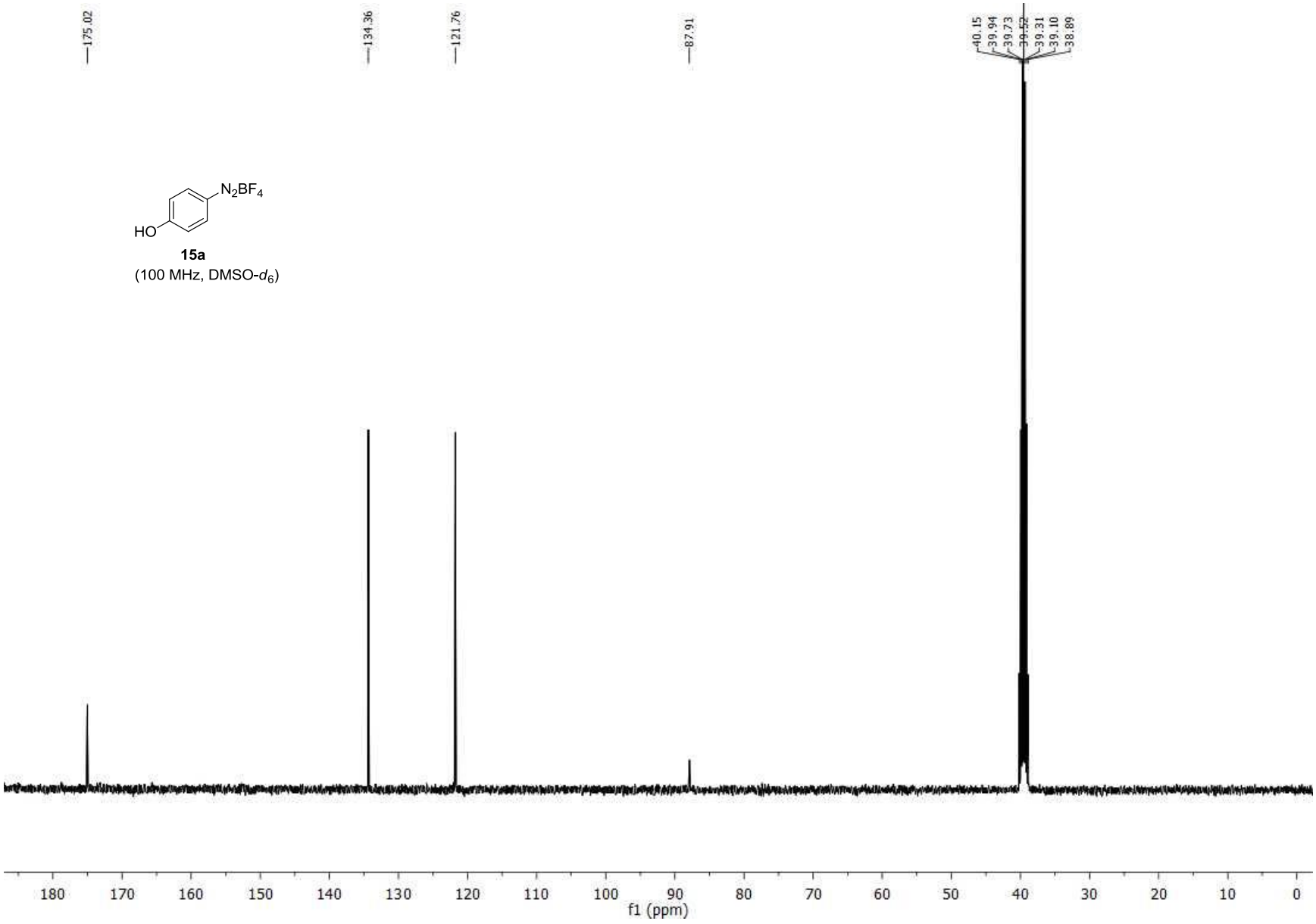

149.58
144.54
142.75
132.64
128.30
127.82
127.01
120.71
112.12
97.40
73.09
55.24
35.64
27.36
26.82
25.06
18.29
13.43
MeO
H
TIPSO
H
O
2
(100 MHz, C6D6)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

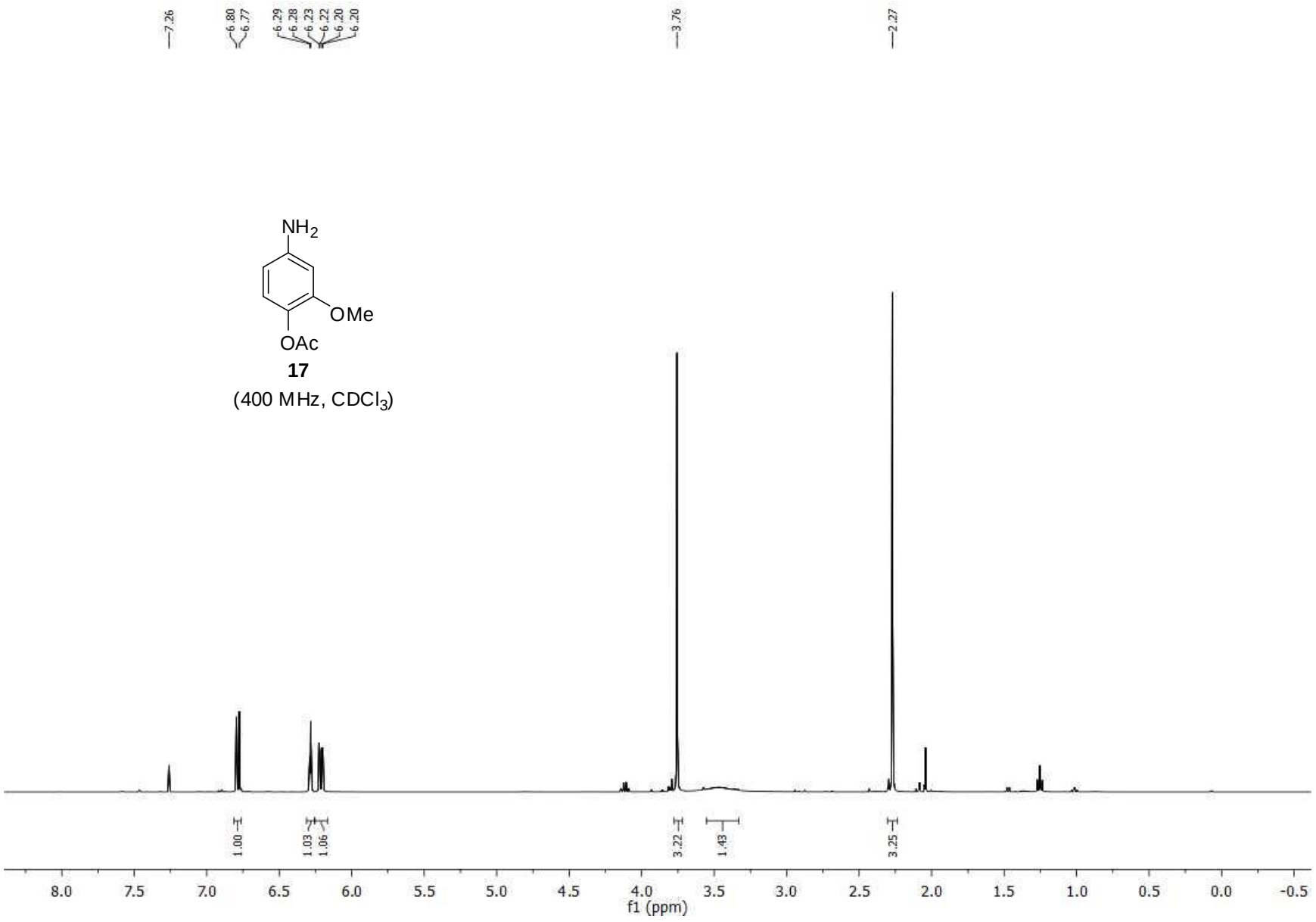


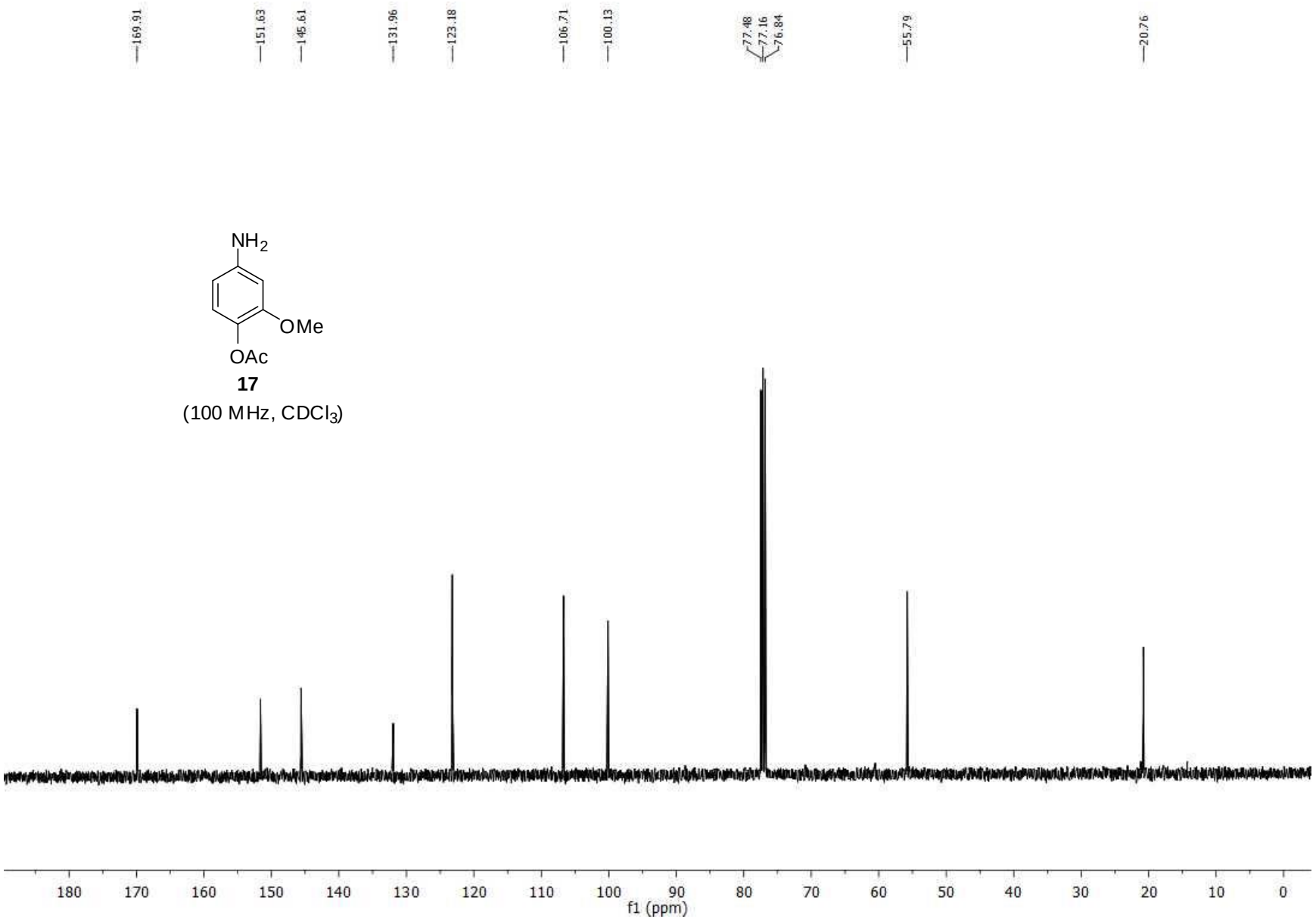
15a

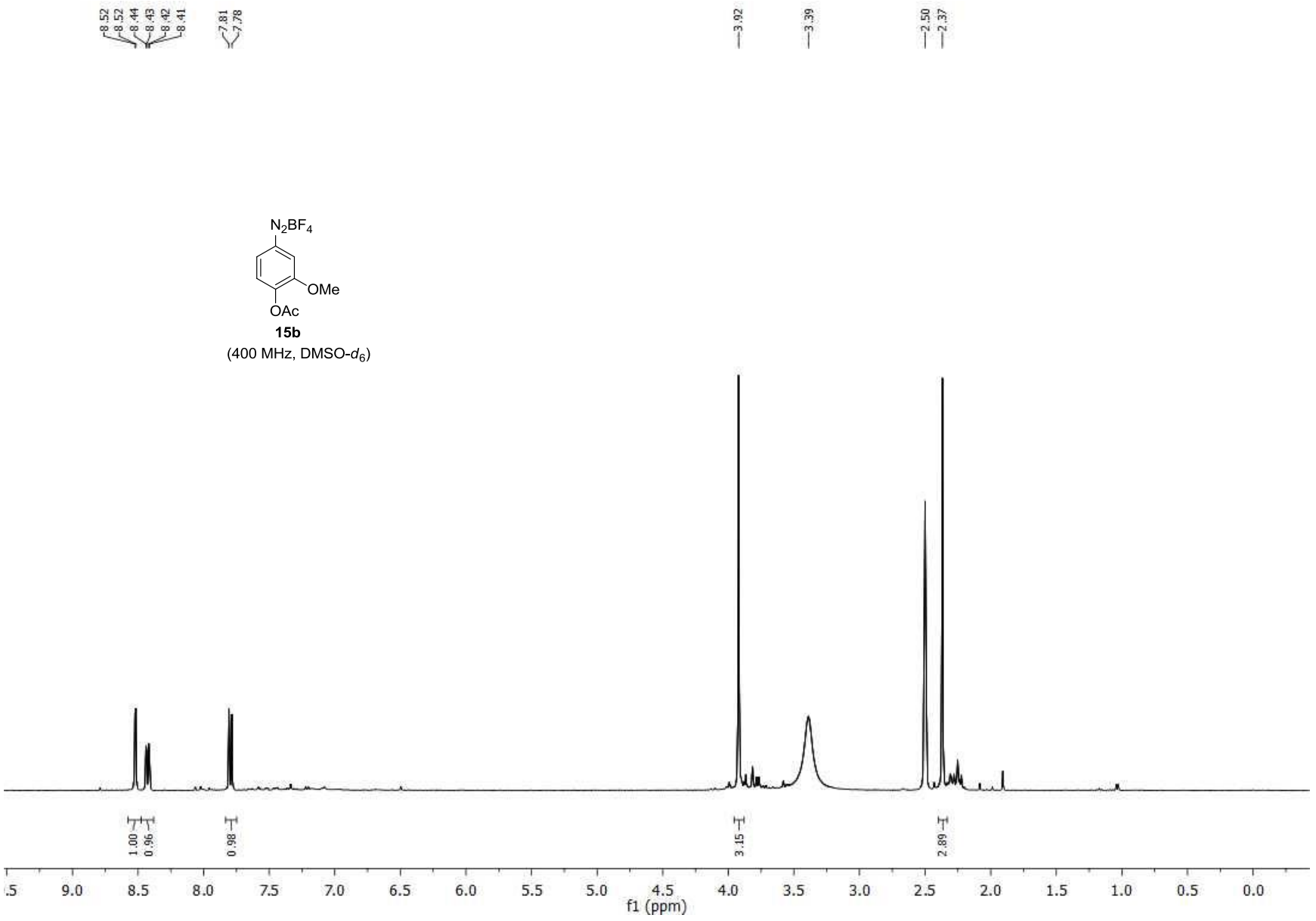
(400 MHz, DMSO-d_6)

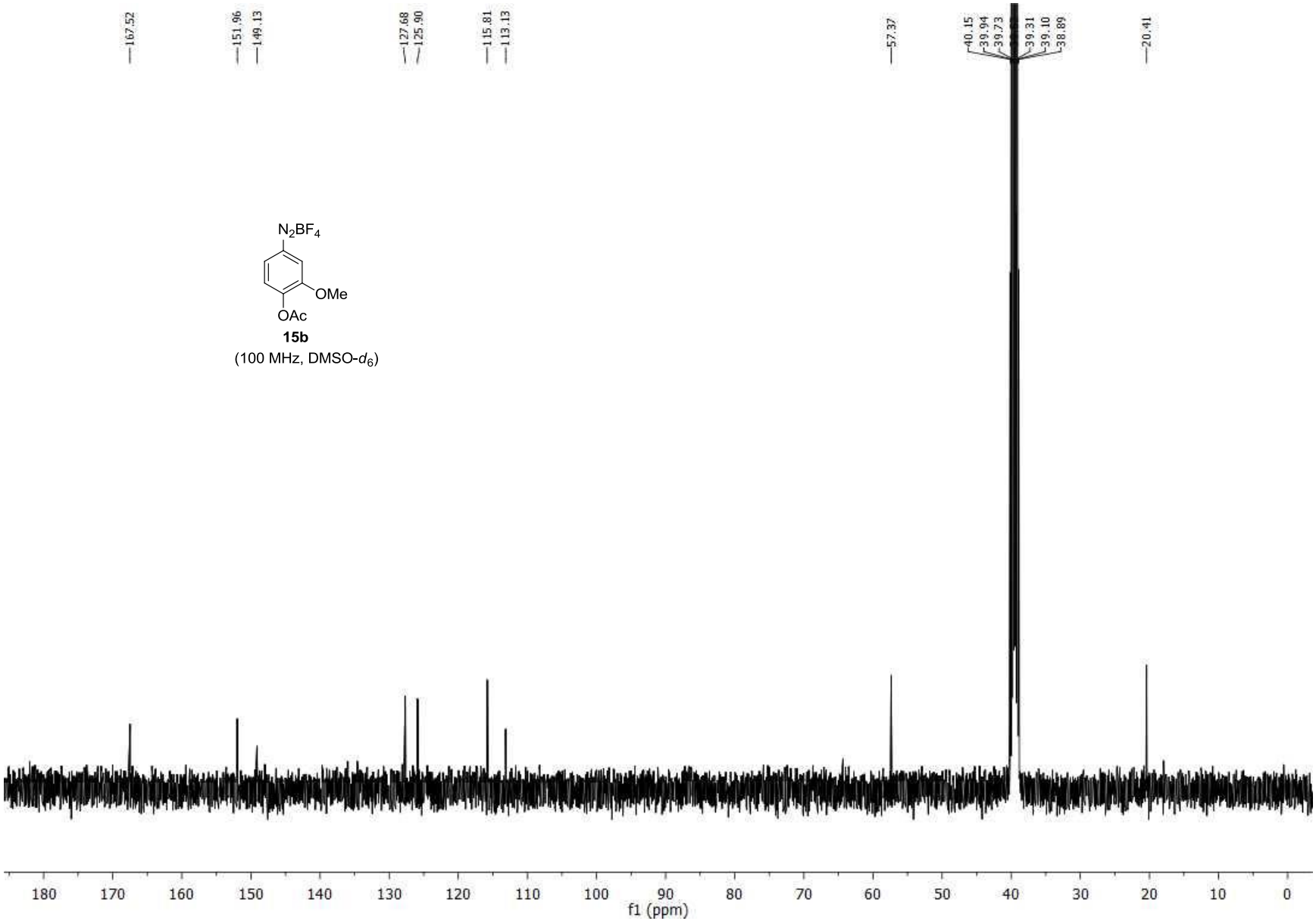


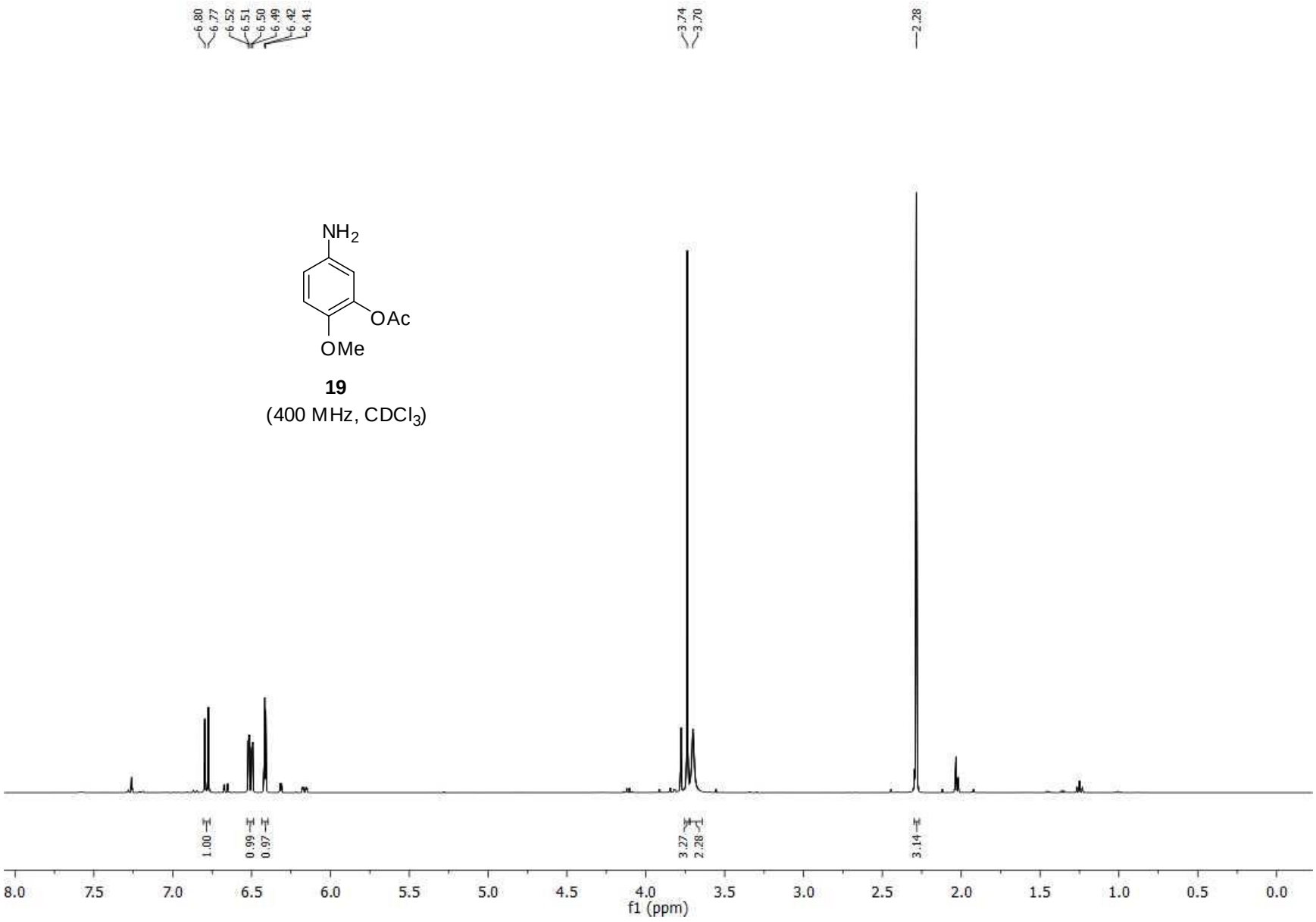

175.02
134.36
121.76
87.91
40.15
39.94
39.73
39.52
39.31
39.10
38.89
N2BF4
HO
15a
(100 MHz, DMSO-d6)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

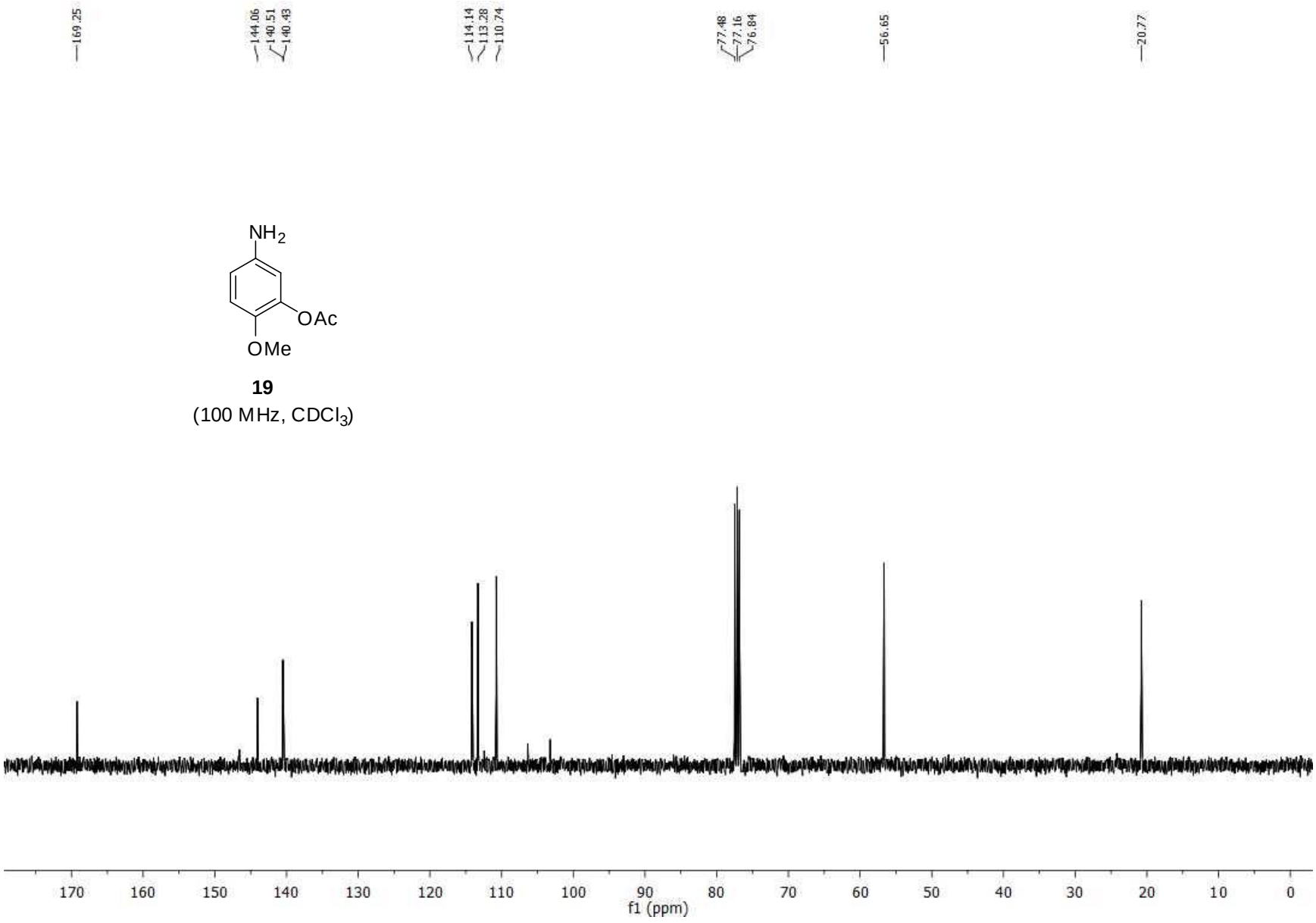

7.26
6.80
6.77
6.29
6.28
6.23
6.22
6.20
6.20
3.76
2.27
NH2
OMe
OAc
17
(400 MHz, CDCl3)
1.00
1.03
1.06
3.22
1.43
3.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


169.91
151.63
145.61
131.96
123.18
106.71
100.13
77.48
77.16
76.84
55.79
20.76
NH2
OMe
OAc
17
(100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.52
8.52
8.44
8.43
8.42
8.41
7.81
7.78
3.92
3.39
2.50
2.37
N2BF4
OMe
OAc
15b
(400 MHz, DMSO-d6)
1.00
0.96
0.98
3.15
2.89
f1 (ppm)

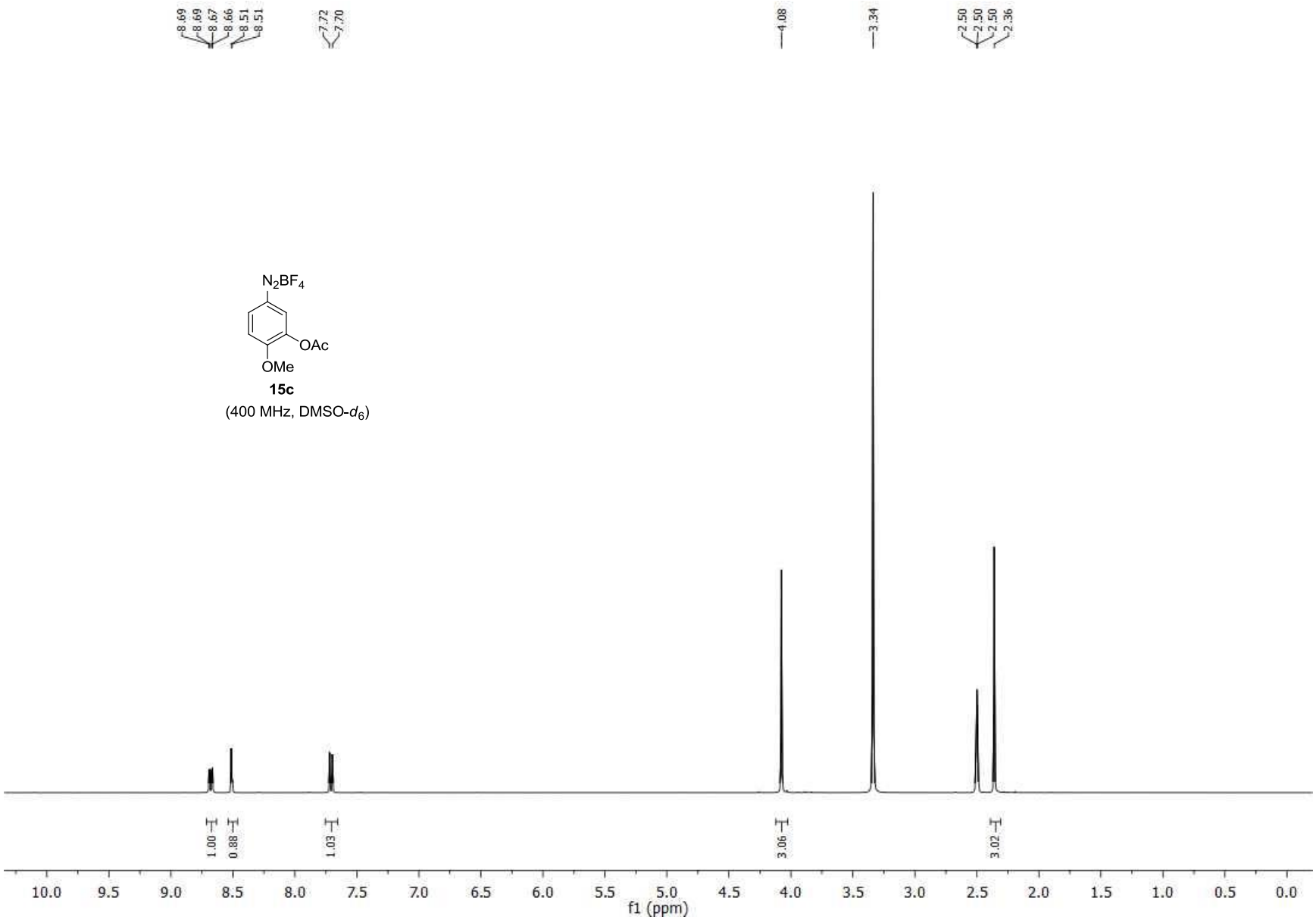

167.52
151.96
149.13
127.68
125.90
115.81
113.13
57.37
40.15
39.94
39.73
39.31
39.10
38.89
20.41
N2BF4
OMe
OAc
15b
(100 MHz, DMSO-d6)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

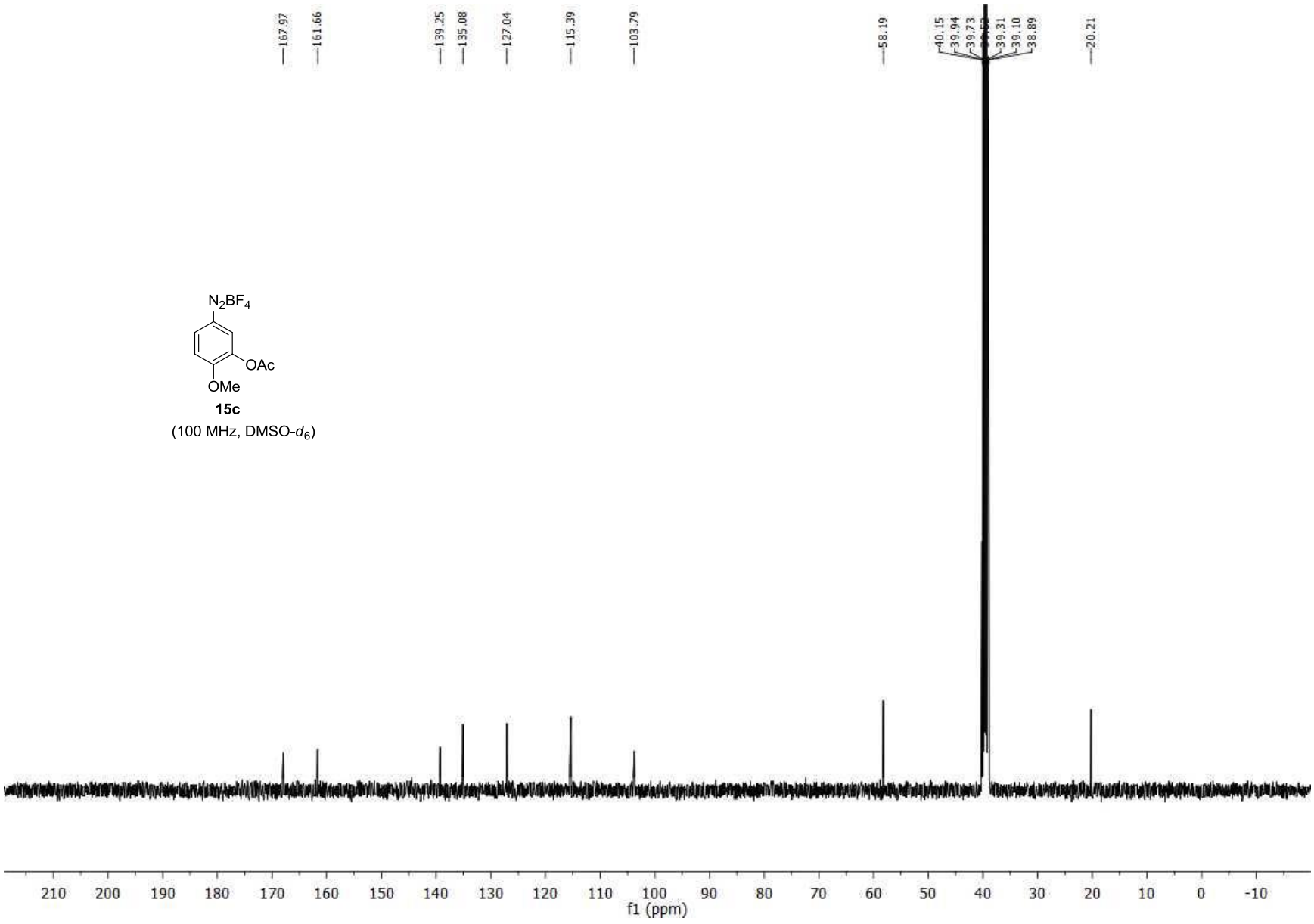

6.80
6.77
6.52
6.51
6.50
6.49
6.42
6.41
3.74
3.70
2.28
NH2
OAc
OMe
19
(400 MHz, CDCl3)
1.00
0.99
0.97
3.27
2.28
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

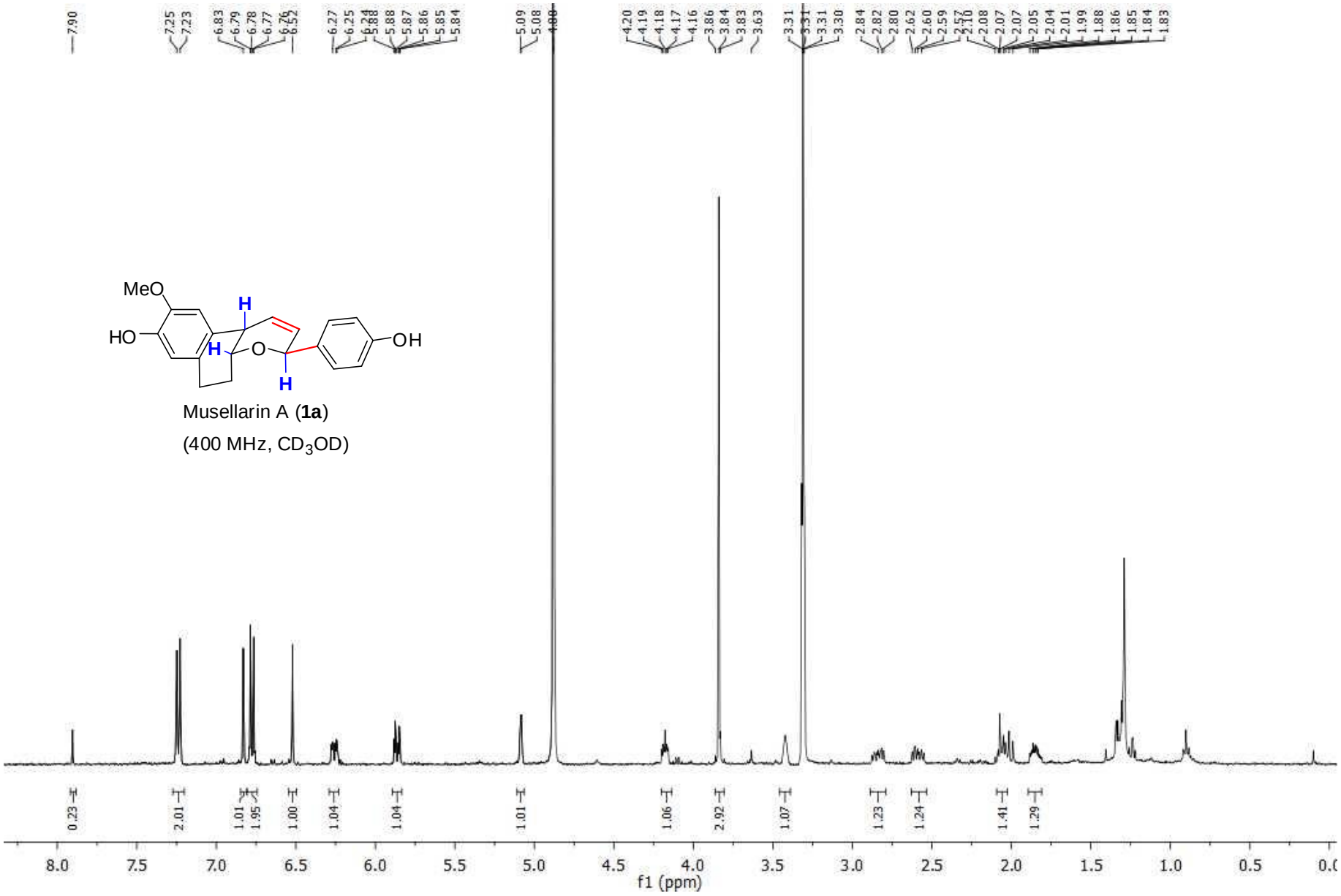


19

(100 MHz, $CDCl_3$)

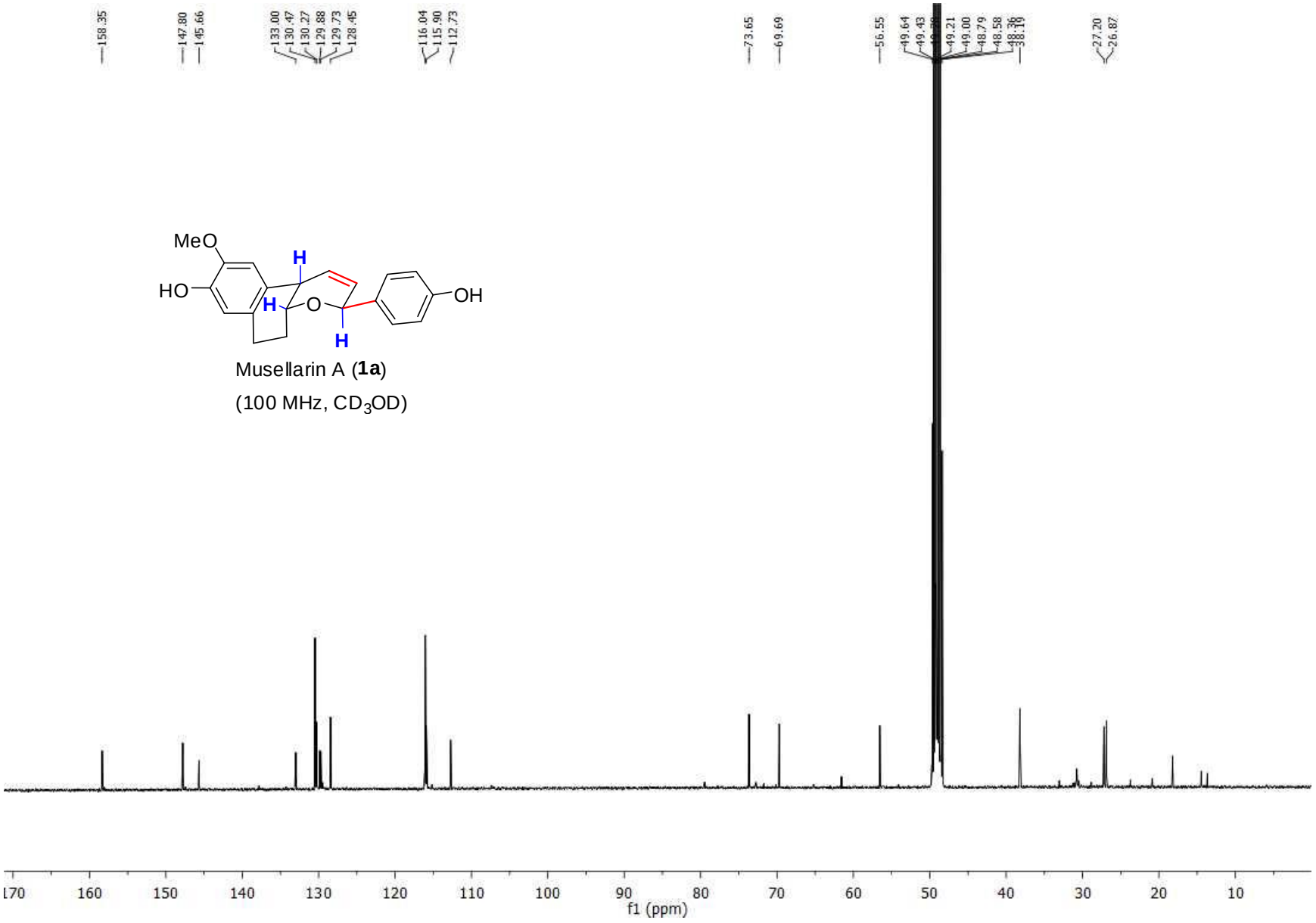

8.69
8.69
8.67
8.66
8.51
8.51
7.72
7.70
4.08
3.34
2.50
2.50
2.50
2.36
N2BF4
OAc
OMe
15c
(400 MHz, DMSO-d6)
1.00
0.88
1.03
3.06
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.97
161.66
139.25
135.08
127.04
115.39
103.79
58.19
40.15
39.94
39.73
39.31
39.10
38.89
20.21
N2BF4
OAc
OMe
15c
(100 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



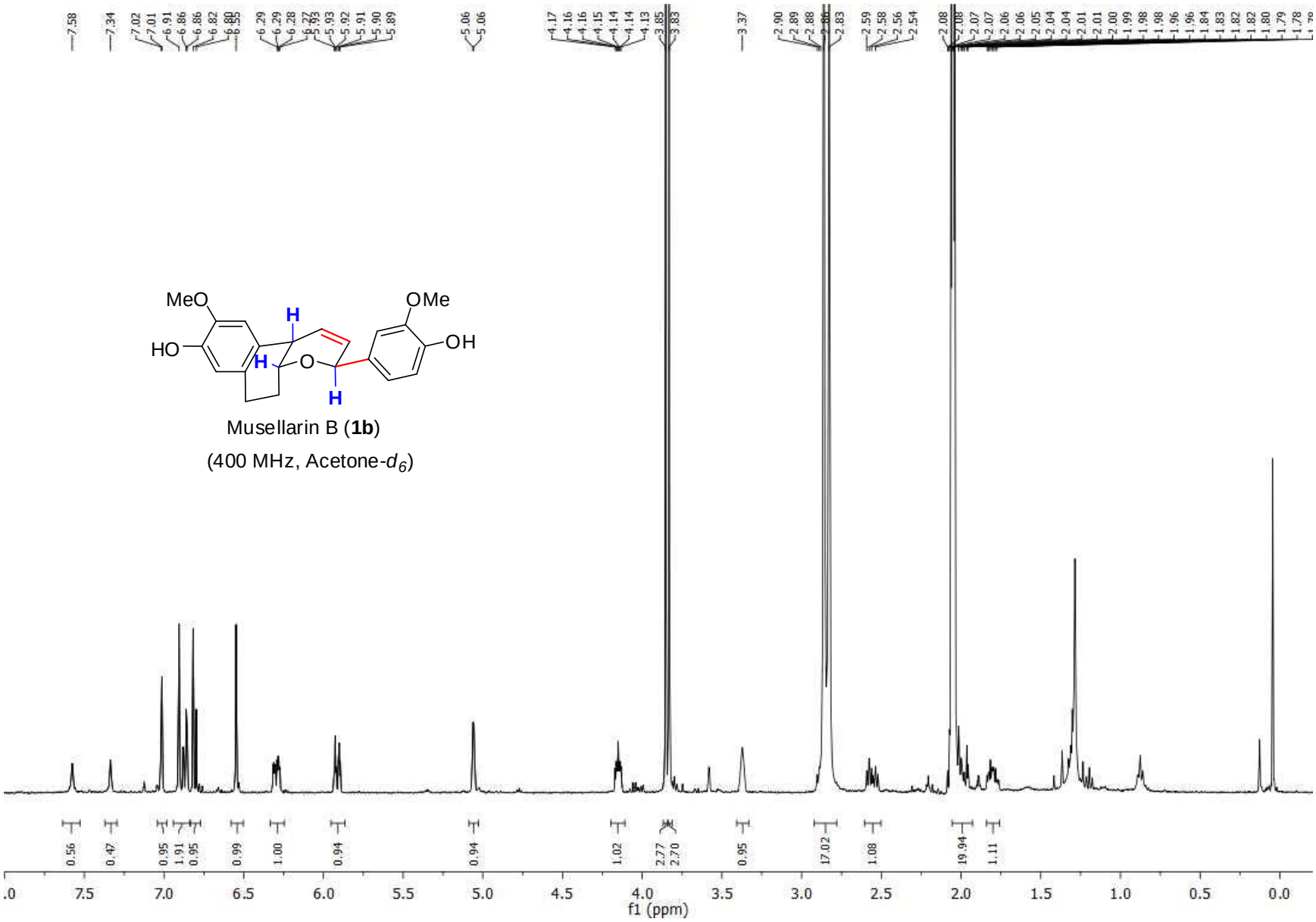
Musellarin A (**1a**)

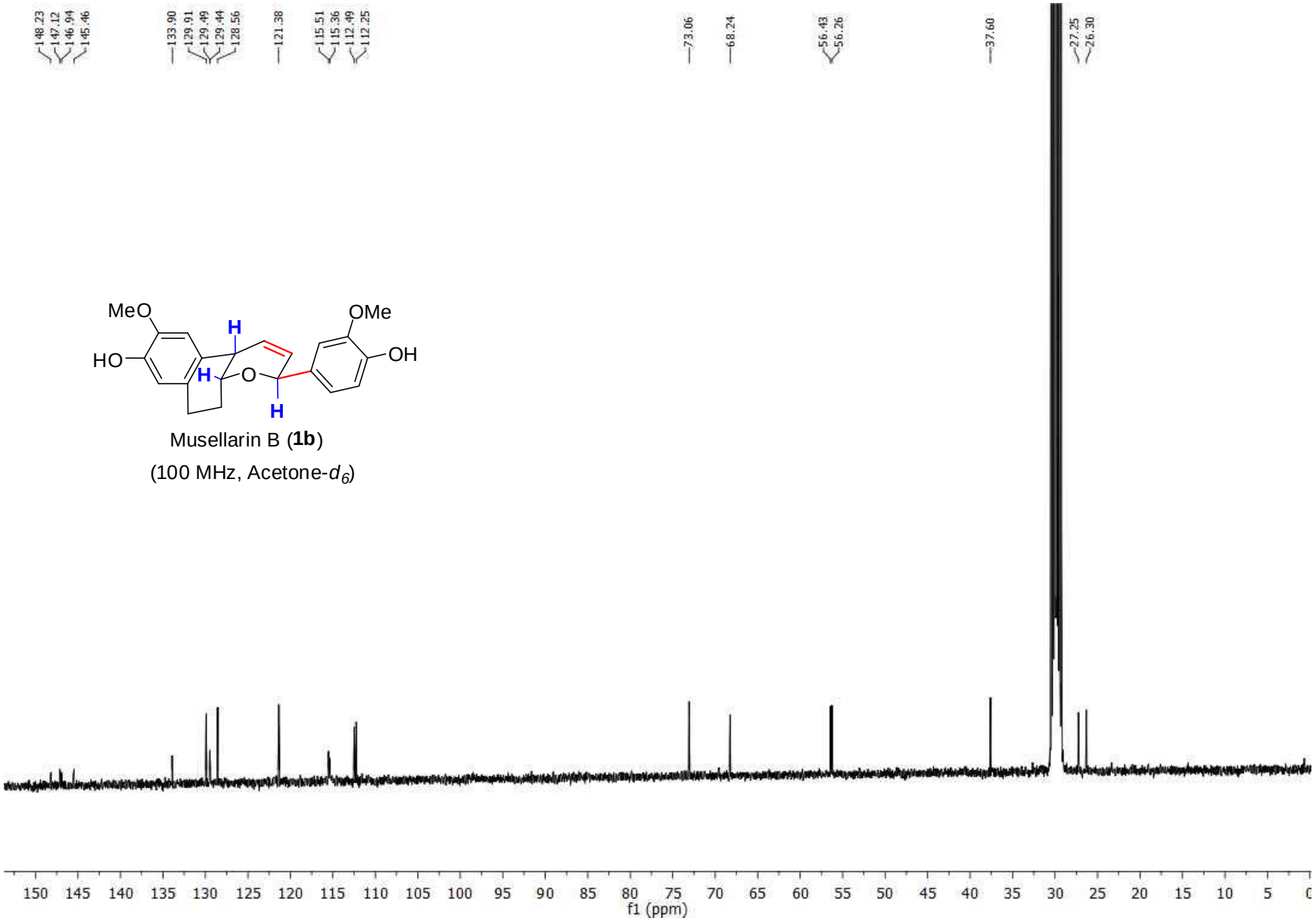
(400 MHz, CD_3OD)



Musellarin A (**1a**)

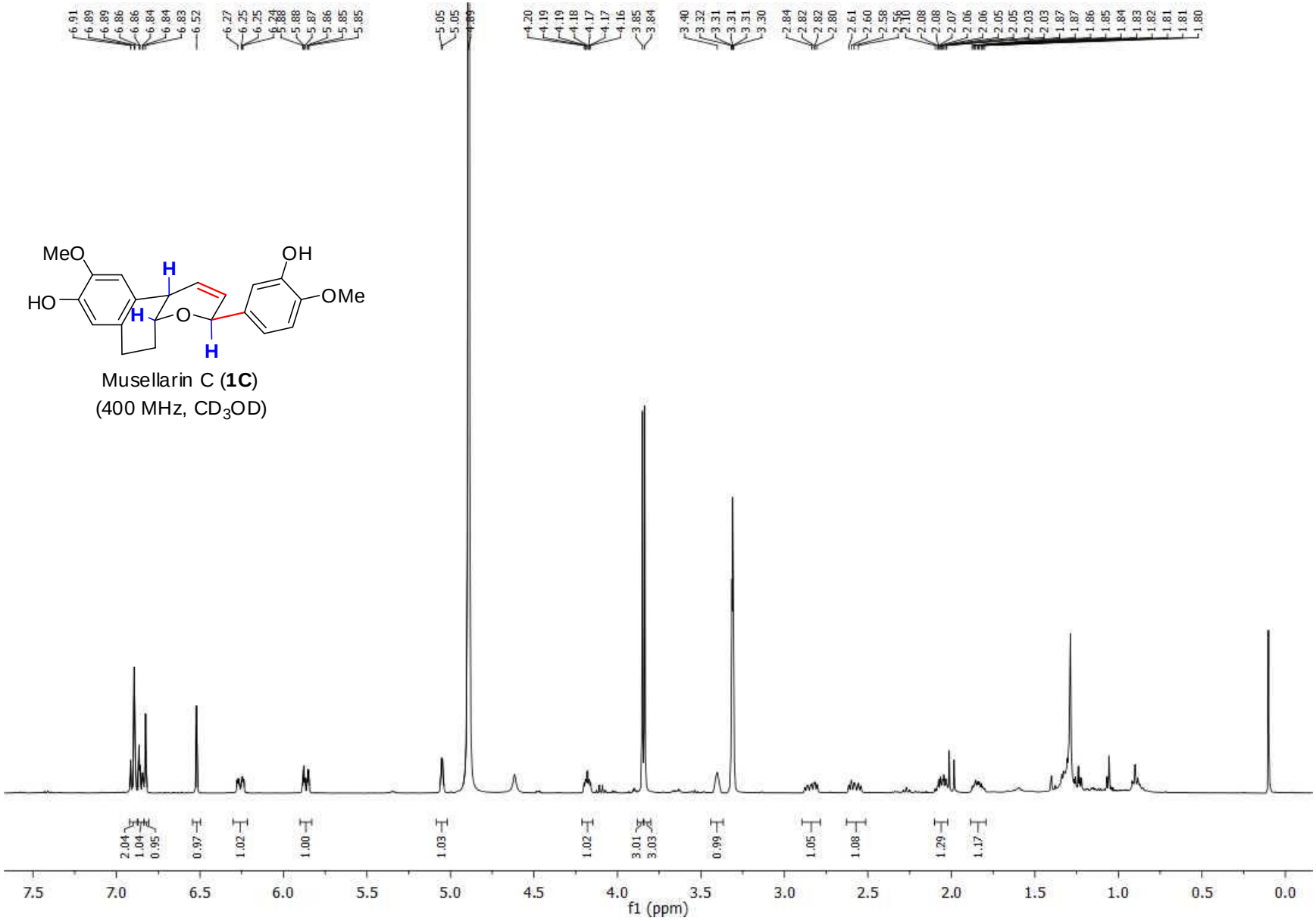
(100 MHz, CD_3OD)


MeO
HO
H
H
O
H
OMe
OH
Musellarin B (1b)
(400 MHz, Acetone-d6)
f1 (ppm)

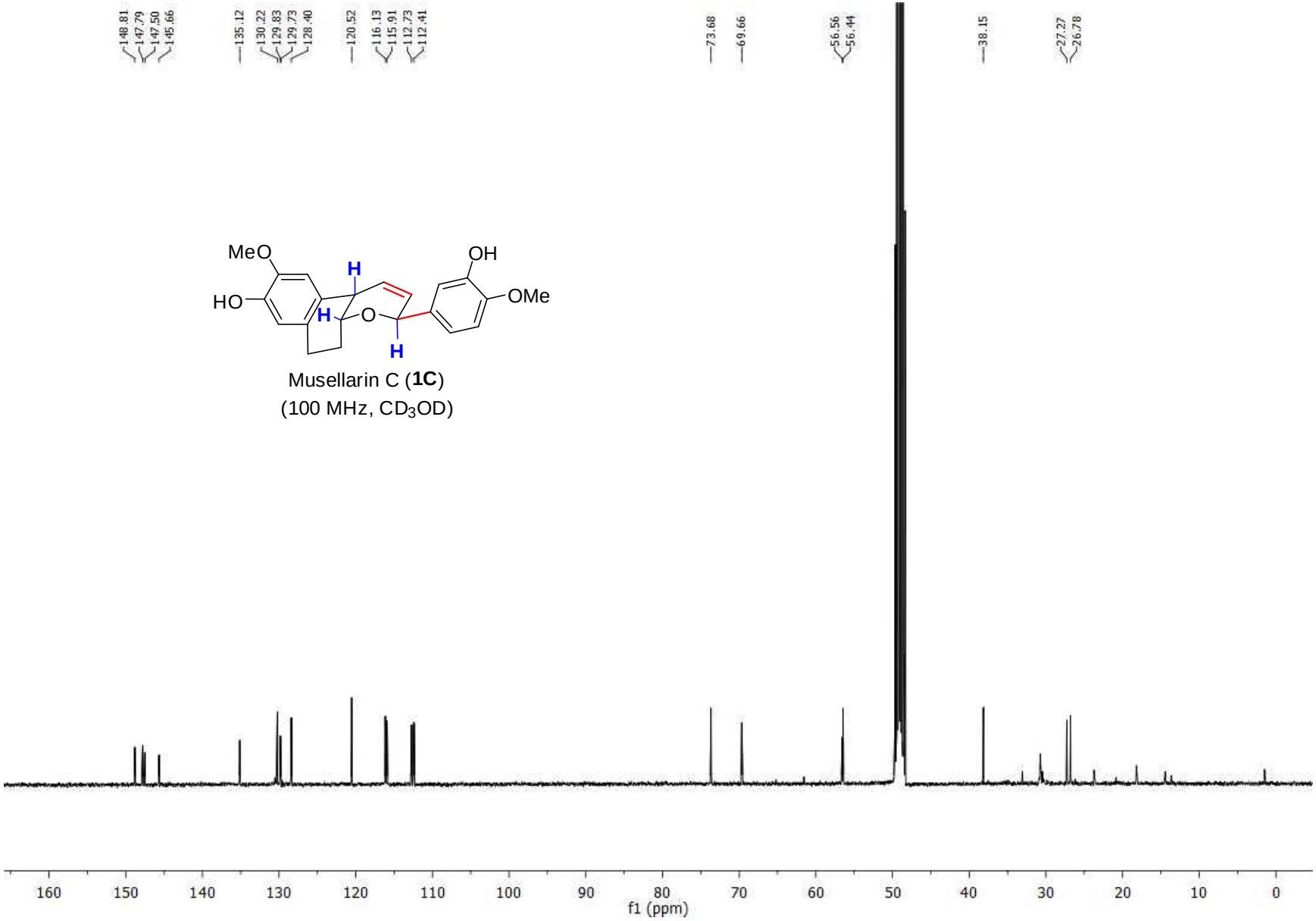


Musellarin B (**1b**)

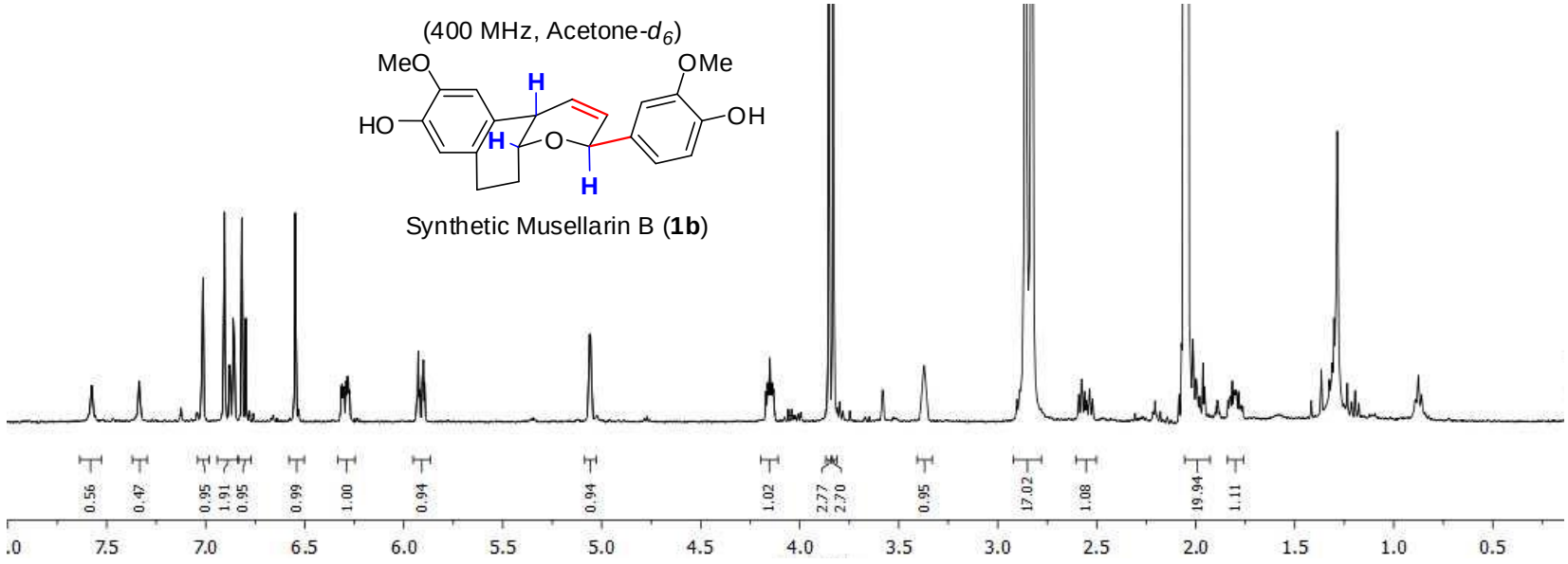
(100 MHz, Acetone-d_6)

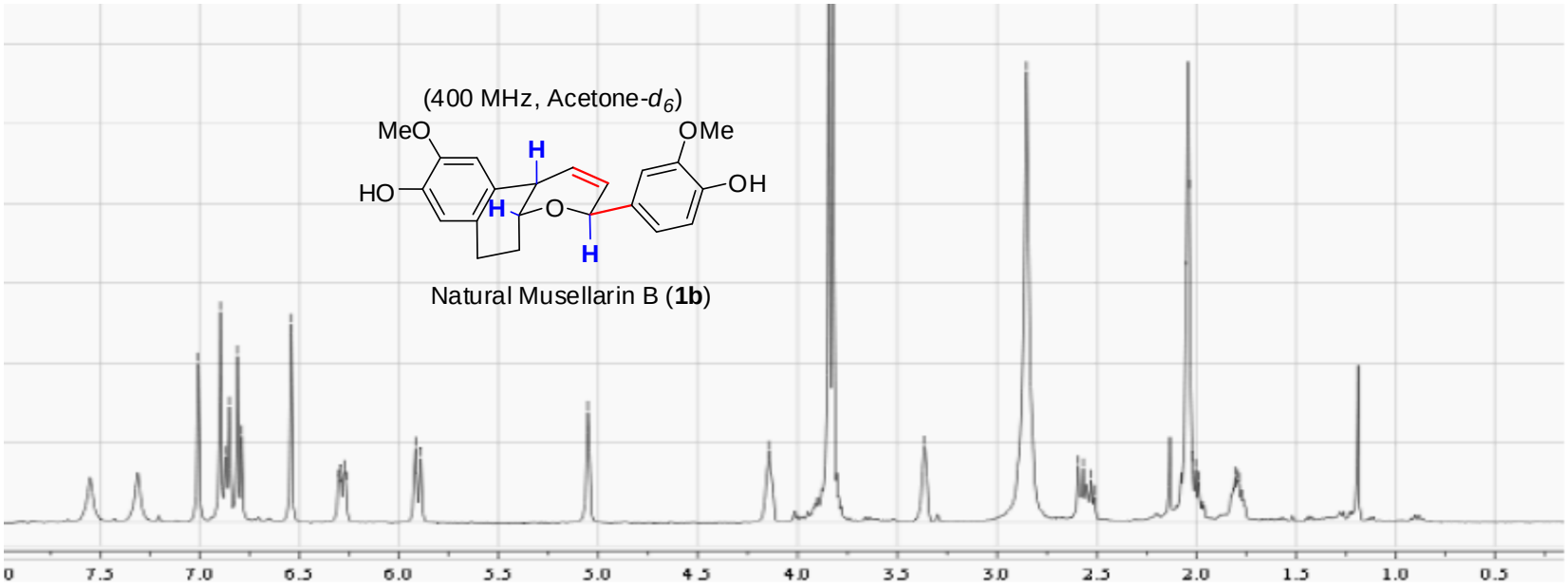


Musellarin C (**1C**)
(400 MHz, CD_3OD)

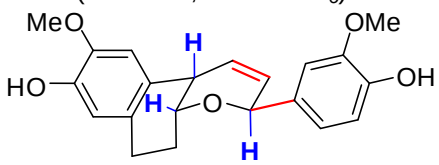


Musellarin C (**1C**)
(100 MHz, CD_3OD)


(400 MHz, Acetone-d_6)
MeO
OMe
HO
OH
H
H
O
H
Synthetic Musellarin B (**1b**)
0.56
0.47
0.95
1.91
0.95
0.99
1.00
0.94
0.94
1.02
2.77
2.70
0.95
17.02
1.08
19.94
1.11
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

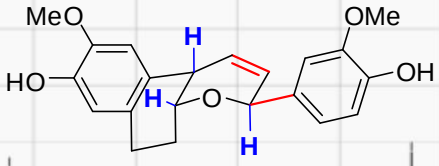

(400 MHz, Acetone-d_6)
MeO
OMe
HO
OH
H
H
O
H
Natural Musellarin B (**1b**)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

(100 MHz, Acetone-d_6)



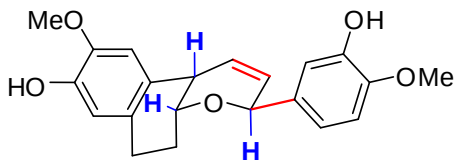
Synthetic Musellarin B (**1b**)

(100 MHz, Acetone-d_6)



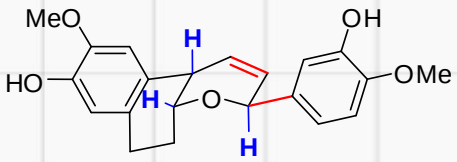
Natural Musellarin B (**1b**)

(400 MHz, CD_3OD)



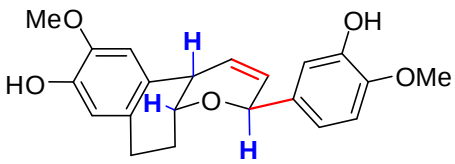
Synthetic Musellarin C (**1c**)

(500 MHz, CD_3OD)



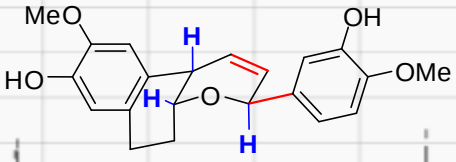
Natural Musellarin C (**1c**)

(100 MHz, CD_3OD)



Synthetic Musellarin C (**1c**)

(125 MHz, CD_3OD)



Natural Musellarin C (**1c**)