Supporting Information

Asymmetric synthesis of the fully functionalized six-membered A-ring of siphonol A

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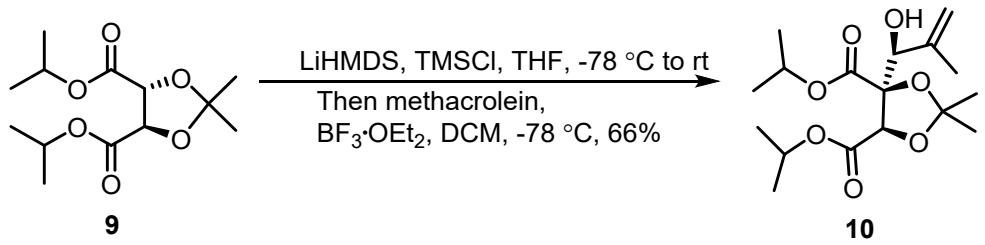
1. General Information

All reactions were performed under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. DCM，DIPA，DIPEA，Et_3N and PhMe were purified by distillation with calcium hydride under an argon atmosphere. THF was distilled firstly from sodium and then from $LiAlH_4$ under an argon atmosphere. All the other chemicals were purchased commercially and used without further purification, unless otherwise stated. Reactions performed at an ambient temperature of 20 - 25 °C are referred to as room temperature. Oil baths were employed as a heat source for reactions requiring elevated temperatures, while cryogenic reactors (ethanol baths) were utilized for reactions requiring cooling. Flash chromatography was performed using silica gel (200 - 300 mesh). Reactions were monitored by thin-layer chromatography (TLC), and visualization was achieved under a UV lamp (254 nm and 365 nm) and by developing the plates with *p*-anisaldehyde, ceric ammonium molybdate (CAM) or phosphomolybdic acid. ^1H and ^{13}C NMR were recorded on a Bruker DRX-400 MHz NMR spectrometer with TMS as an internal standard. Residual undeuterated solvent in the sample served as an internal reference for calibration ($CDCl_3$: ^1H NMR = 7.26 ppm，^{13}C NMR = 77.16 ppm; CD_2Cl_2: ^1H NMR = 5.32 ppm，^{13}C NMR = 53.87 ppm; CD_3OD: ^1H NMR = 3.31, 4.87 ppm，^{13}C NMR = 49.00 ppm;). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) were reported in Hertz (Hz). Optical rotations were measured at the sodium D line using a 100 mm path length cell and reported as $[\alpha]_D^T$ (*c*g/100 mL, in solvent). High resolution mass spectra (HRMS) were recorded on a LCMS-IT-TOF spectrometer, and samples were dissolved in dichloromethane. Infrared (IR) spectra were obtained using a Bruker TENSOR II IR spectrophotometer and reported in wave numbers (cm^{-1}). The melting point was obtained using the Hanon Instrument (MP 450 melting point meter).

2. Experimental Procedures

2.1. Procedure for preparation of compound 10



To a stirred solution of compound **9** (11.6 g, 42.3 mmol, 1.0 eq.) in dry THF (150 mL) at room temperature under an argon atmosphere was added TMSCl (7.0 mL, 55.0 mmol, 1.3 eq.). The temperature was cooled to -78 °C, then LiHMDS (116 mL, 59.2 mmol, 1.4 eq.) was added to the reaction mixture. The reaction was maintained at -78 °C for 1 h, after that the reaction was raised to room temperature and stirred for another 1.5 h. The resulting solution was concentrated under reduced pressure. The crude product was dried under vacuum for 1 h and then dissolved in dry DCM (150 mL) at room temperature under an argon atmosphere. This mixture was added methacrolein (4.6 mL, 55.0 mmol, 1.3 eq.) and cooled to -78 °C. $BF_3.OEt_2$ (6.9 mL, 55.0 mmol, 1.3 eq.) in dry DCM (20 mL) was added dropwise to above reaction mixture. The reaction was maintained at -78 °C for 2.5 h. Then the reaction was quenched slowly by adding saturated $NaHCO_3$ (40 mL). The resulting mixture was extracted with DCM (50 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 16:1) to obtain **10**[1] (9.6 g, 66%) as a yellow oily liquid.

Compound 10:

TLC: R_f = 0.5 (PE : EtOAc = 3:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 – 5.05 (m, 4H), 4.65 (s, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 2.80 (d, *J* = 8.3 Hz, 1H), 1.89 (s, 3H), 1.64 (s, 3H), 1.39 (s, 3H), 1.34 – 1.26 (m,

12H).

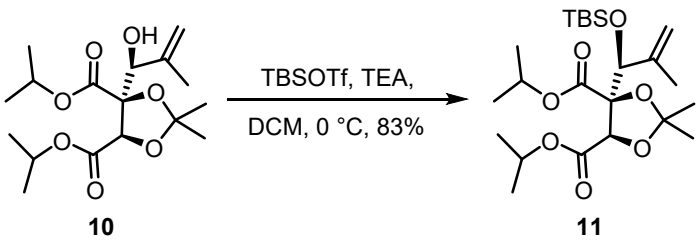
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 166.9, 143.3, 115.9, 112.3, 88.4, 79.6, 70.2, 69.6, 26.6, 26.6, 21.9, 21.7, 21.7, 21.6, 19.5.

HRMS (ESI-TOF) m/z Calculated for $C_{17}H_{29}O_7$ $[M + H]^+$: 345.1908, found 345.1908.

IR (thin film): 3517, 2978, 2933, 1754, 1372, 1200, 1100, 891 cm^{-1}.

$[\alpha]_D^{25}$ = + 51.6 (*c* 0.44 g/100 mL, DCM)

2.2. Procedure for preparation of compound 11



10 **11**

To a stirred solution of compound **10** (9.0 g, 26.1 mmol, 1.0 eq.) in dry DCM (200 mL) at 0 °C under an argon atmosphere was added Et_3N (4.4 mL, 31.3 mmol, 1.2 eq.) and TBSOTf (7.2 mL, 31.3 mmol, 1.2 eq.). The reaction was gradually increased to room temperature, and stirred for an additional 2.5 h. Then the reaction mixture was cooled to 0 °C, and quenched was quenched by slowly adding saturated $NaHCO_3$ (50 mL). The resulting mixture was extracted with EtOAc (50 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 40:1) to obtain **11** (9.9 g，83%) as a pale yellow oily liquid.

Compound 11:

TLC: R_f = 0.5 (PE : EtOAc = 10:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 – 5.10 (m, 2H), 5.08 (dd, *J* = 1.9, 1.0 Hz, 1H),

5.04 – 4.98 (m, 1H), 4.79 (s, 1H), 4.53 (s, 1H), 1.90 (s, 3H), 1.65 (s, 3H), 1.38 – 1.34 (m, 6H), 1.32 – 1.28 (m, 9H), 0.86 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H).

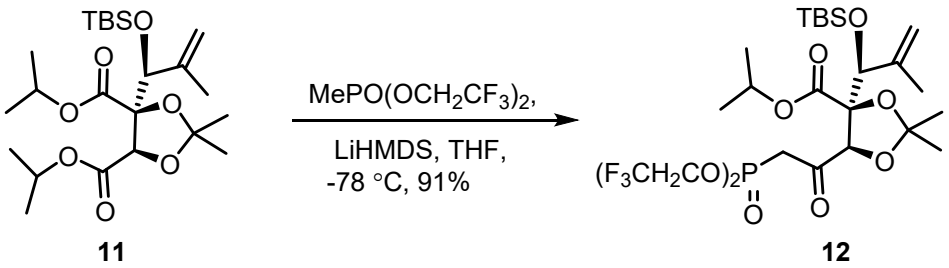
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 166.6, 145.0, 116.6, 111.6, 90.2, 78.8, 77.9, 77.3, 77.0, 76.7, 69.8, 69.2, 26.6, 26.3, 25.8, 22.0, 22.0, 21.8, 18.9, 18.2, -4.9, -5.4.

HRMS (ESI-TOF) m/z Calculated for $C_{23}H_{43}O_7Si$ $[M + H]^+$: 459.2773, found 459.2776.

IR (thin film): 2932, 1756, 1723, 1372, 1248, 1206, 1076, 840, 773 cm^{-1}.

$[\alpha]_D^{25}$ = + 34.2 (*c* 1.06 g/100 mL, DCM)

2.3. Procedure for preparation of compound 12



To a stirred solution of compound **11** (3.7 g, 8.1 mmol, 1.0 eq.) and bis(2,2,2-trifluoroethyl) methylphosphonate (6.3 g, 24.3 mmol, 3.0 eq.) in dry THF (50 mL) at -78 °C under an argon atmosphere. Then LiHMDS (90 mL, 32.4 mmol, 4.0 eq.) was cooled at -78 °C and added to the above solution. The reaction was maintained at -78 °C for 3.5 h. Then the reaction was quenched by slowly adding saturated NH_4Cl (20 mL). The resulting mixture was extracted with EtOAc (20 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 10:1 to 6:1) to obtain **12** (4.8 g, 91%) as a pale yellow oily liquid.

Compound 12:

TLC: R_f = 0.5 (PE : EtOAc = 3:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (dd, *J* = 5.6, 1.2 Hz, 2H), 5.03 – 4.95 (m, 1H), 4.64 (s, 1H), 4.56 – 4.39 (m, 5H), 3.62 (dd, A of AB, *J* = 19.5, 16.5 Hz, 1H), 3.23 (dd, B of AB, *J* = 21.0, 16.5 Hz, 1H), 1.85 (s, 3H), 1.59 (s, 3H), 1.35 – 1.28 (m, 9H), 0.86 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4 (d, $J_{P,C}$ = 7.1 Hz), 170.8, 144.2, 117.2, 111.8, 91.3, 82.9, 82.9, 77.6, 70.4, 62.6 (qd, $J_{F,C}$ = 37.4 Hz, $J_{P,C}$ = 5.1 Hz), 38.8, 37.3, 26.7, 26.2, 25.8, 21.9, 21.7, 18.9, 18.2, -5.0, -5.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.3, -75.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 23.8

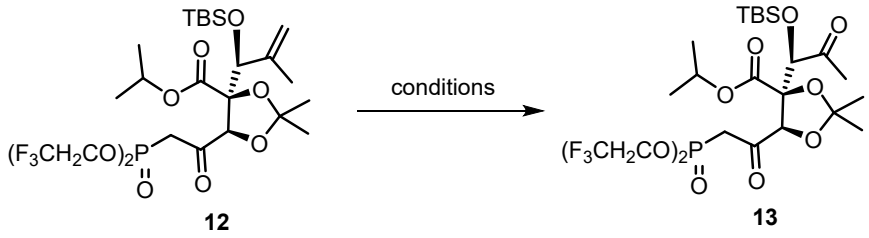
HRMS (ESI-TOF) m/z Calculated for $C_{25}H_{42}F_6O_9PSi$ $[M + H]^+$: 659.2234, found 659.2236.

IR (thin film): 2937, 2353, 1717, 1288, 1248, 1168, 1068, 836 cm^{-1}.

$[\alpha]_D^{25}$ = + 80.9 (*c* 0.23 g/100 mL, DCM)

2.4. Procedure for preparation of compound 13

2.4.1 Table S1 the ozonation of 12



12 **13**

entry	conditions	results[a]
1	O_3, MeOH, - 20 ℃, 25 min, then Me_2S	trace
2	O_3, MeOH, - 40 ℃, 25 min, then Me_2S	minor
3	O_3, MeOH/DCM, - 40 ℃, 25 min, then Me_2S	minor
4	O_3, MeOH, - 78 ℃, 1.5 h, then Me_2S	38%[b, c]

5	O_3, MeOH/DCM, -78 ℃, 1.5 h, then Me_2S	34%[b, c]
6	O_3, DCM, - 78 ℃, 1.5 h, then Me_2S	trace
7	O_3, *i*PrOH, - 78 ℃, 1.5 h then Me_2S	18%[b, c]
8	O_3, EtOH, - 78 ℃, 40 min then Me_2S,	94%[b]
9	O_3, MeOH, Py, - 78 ℃, 1.5 h then Me_2S	NP
10	O_3, MeOH/DCM, Py, - 78 ℃, 1.5 h then Me_2S	NP
11	O_3, EtOH, Py, - 78 ℃, 1.5 h then Me_2S	NP
12	O_3, DCM, Py, - 78 ℃ 1.5 h then Me_2S	NP

[a] The results were determined via TLC; [b] Isolated yield; [c] Compound **12** remained; [d] Py: Pyridine; NP: No desired product.

Procedure for entries 1-3:

To a stirred solution of compound **12** (0.02 M) in EtOH at - 20 ℃ or - 40 ℃ was imported O_3/O_2 gas for 25 min. The reaction was quenched by adding Me_2S and slowly warmed up to room temperature within 10 h. The compound **12** in entries 1-3 were fully consumed while a small amount of products were generated.

Procedure for entries 4-7:

To a stirred solution of compound **12** (0.02 M) in EtOH at -78 ℃ was imported O_3/O_2 gas for 1.5 h. The reaction was quenched by adding Me_2S and then slowly warmed up to room temperature within 10 h. In entry 4, the yield was 38%; in entry 5, the yield was 34%; in entry 6, only trace amounts of the product was produced; in entry 7, the yield was 18%.

Procedure for entries 9-12:

To a stirred solution of compound **12** (0.02 M) in EtOH at -78 ℃ was added pyridine (2.0 eq.). Then the reaction mixture was imported O_3/O_2 gas for 1.5 h. The reaction was quenched by adding Me_2S and then slowly warmed up to room temperature within 10 h. In entries 9-12, no product was identified.

Procedure for entry 8:

To a stirred solution of compound **12** (1.7 g, 2.6 mmol, 1.0 eq.) in EtOH (60 mL) at -78 ℃ was imported O_3/O_2 gas for 40 min. The reaction was then quenched by adding Me_2S and slowly warmed up to room temperature for 10 h. Then the reaction mixture was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 4:1) to obtain **13** (1.6 g，94%) as a colorless oily liquid.

Compound 13:

TLC: R_f = 0.5 (PE : EtOAc = 2.5:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 – 5.02 (m, 1H), 4.63 (s, 1H), 4.52 – 4.38 (m, 5H), 3.71 (dd, *J* = 19.5, A of AB, 16.5 Hz, 1H), 3.48 (dd, B of AB, *J* = 20.7, 16.5 Hz, 1H), 2.32 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.33 (d, *J* = 6.4 Hz, 3H), 1.29 (d, *J* = 6.3 Hz, 3H), 0.95 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 198.0 (d, $J_{P,C}$ = 6.1 Hz), 168.8, 111.6, 90.1, 80.3, 80.3, 77.6, 70.7, 62.3 (qd, $J_{F,C}$ = 37.4 Hz, $J_{P,C}$ = 5.1 Hz), 39.2, 37.8, 28.3, 27.0, 26.4, 25.8, 21.6, 21.5, 18.0, -4.7, -5.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.2, -75.4.

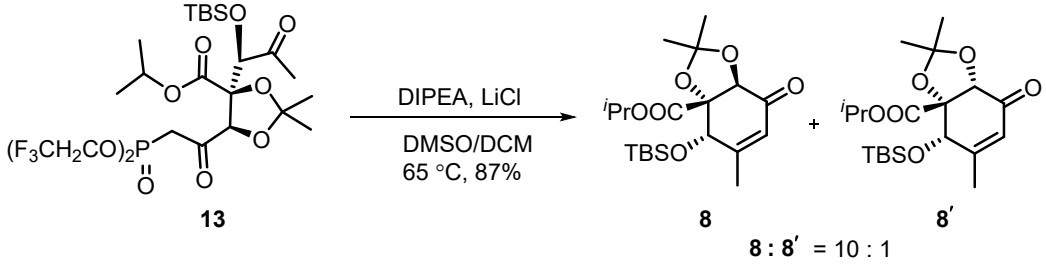
^{31}P NMR (162 MHz, $CDCl_3$) δ 24.1

HRMS (ESI-TOF) m/z Calculated for $C_{24}H_{40}F_6O_{10}PSi$ $[M + H]^+$: 661.2027, found 661.2027.

IR (thin film): 2936, 1719, 1374, 1296,1252, 1173, 1069, 838, 783 cm^{-1}.

$[\alpha]_D^{25}$ = + 58.0 (*c* 0.51 g/100 mL, DCM)

2.5. Procedure for preparation of compound 8



13 **8** **8′**

8 : 8′ = 10 : 1

To a stirred solution of compound **13** (610.0 mg, 0.9 mmol, 1.0 eq.) in DMSO (25 mL)/DCM (25 mL) at room temperature were added LiCl (381.5 mg, 9.0 mmol, 10.0 eq.) and DIPEA (0.6 mL, 3.6 mmol, 4.0 eq.). The reaction was heated to 65 ℃, and stirred for 24 h. Then the reaction solution was cooled to room temperature. DCM was evaporated under reduced pressure. The residue was added EtOAc (30 mL) and washed with H_2O (15 mL × 2). The combined aqueous phases were extracted with EtOAc (30 mL × 3), and then the organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 16:1) to obtain **8** (311.0 mg, 87%, **8** : **8′**= 10:1) as a yellow oily liquid.

Compound 8:

TLC: R_f = 0.5 (PE : EtOAc = 6:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (d, *J* = 1.2 Hz, 1H), 5.01 – 4.94 (m, 1H), 4.91 (s, 1H), 4.65 (s, 1H), 2.00 (d, *J* = 1.1 Hz, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.92 (s, 9H), 0.21 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 169.4, 156.0, 127.3, 113.5, 84.7, 76.4, 71.3, 69.8, 27.0, 26.4, 25.8, 22.4, 21.4, 21.1, 18.1, -3.6, -4.9.

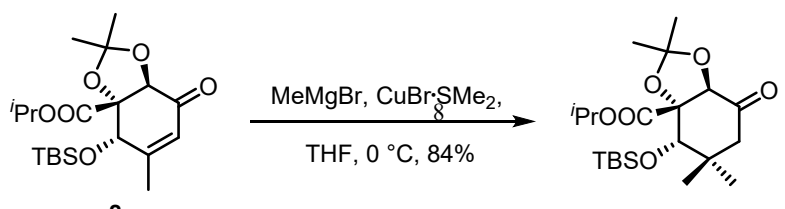
HRMS (ESI-TOF) m/z Calculated for $C_{20}H_{35}O_6Si$ $[M + H]^+$: 399.2197, found 399.2197.

IR (thin film): 2939, 1719, 1469, 1375, 1243, 1178, 1108, 1078, 1041, 858, 781 cm^{-1}.

Compound 8′:

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (d, *J* = 1.6 Hz, 1H), 5.11 – 5.04 (m, 1H), 4.74 (s, 1H), 4.63 (s, 1H), 2.08 (s, 3H), 1.52 (s, 3H), 1.43 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 0.88 (s, 9H), 0.13 (s, 3H), 0.08 (s, 3H).

2.6. Procedure for preparation of compound 14



8 **14**

To a stirred solution of $CuBr \cdot SMe_2$ (1.5 g, 7.2 mmol, 6.0 eq.) in dry THF (55 mL) at 0 °C under an argon atmosphere was slowly added MeMgBr (6.0 mL, 18.0 mmol, 15.0 eq.). After stirring at 0 °C for 1 h, compound **8** (478.0 mg, 1.2 mmol, 1.0 eq.) was dissolved in dry THF (15 mL) and added dropwise to the reaction mixture. The reaction was maintained at 0 °C for 9 h. Then the mixture was quenched by slowly adding saturated NH_4Cl (20 mL). After that the reaction was raised to room temperature and stirred for another 20 min. The reaction mixture was diluted by adding H_2O (10 mL), and the resulting mixture was extracted with EtOAc (30 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 10:1) to obtain **14** (417.5 mg，84%) as a white solid.

Compound 14:

TLC: R_f = 0.5 (PE : EtOAc = 6:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 – 4.93 (m, 1H), 4.87 (d, *J* = 1.6 Hz, 1H), 4.10 (s, 1H), 2.43 (dd, A of AB, *J* = 16.0, 1.5 Hz, 1H), 2.14 (d, B of AB, *J* = 16.0 Hz, 1H), 1.43 (s, 6H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.12 (s, 3H), 0.97 (s, 3H), 0.96 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 170.2, 112.5, 86.5, 78.3, 75.6, 69.8, 50.4, 40.2, 29.8, 28.5, 27.1, 26.6, 26.3, 21.5, 21.1, 18.3, -3.1, -4.38.

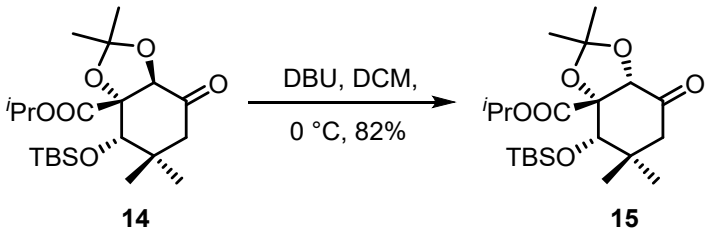
HRMS (ESI-TOF) m/z Calculated for $C_{21}H_{39}O_6Si$ $[M + H]^+$: 415.2510, found 415.2510.

IR (thin film): 2940, 2853, 1755, 1476, 1368, 1253, 1107, 1067, 860, 838, 782 cm^{-1}.

$[\alpha]_D^{25}$ = + 196.4 (*c* 0.22 g/100 mL, DCM)

Melting point range: 99.1 – 99.8 °C

2.7. Procedure for preparation of compound 15



To a stirred solution of compound **14** (414.0 mg, 1.0 mmol, 1.0 eq.) in DCM (50 mL) at 0 °C was slowly added DBU (2.2 mL, 15.0 mmol, 15.0 eq.). The reaction was maintained at 0 °C for 36 h. Then the reaction was quenched by slowly adding saturated NH_4Cl (20 mL) and H_2O (10 mL). The resulting mixture was extracted with EtOAc (30 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 10:1) to obtain **15** (339.5 mg，82%) as a white solid.

Compound 15:

TLC: R_f = 0.5 (PE : EtOAc = 7:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 – 5.06 (m, 1H), 5.03 (s, 1H), 4.15 (s, 1H), 2.40 (d, A of AB, *J* = 17.0 Hz, 1H), 2.17 (d, B of AB, *J* = 17.0 Hz, 1H), 1.44 (s, 3H), 1.40 (s, 3H), 1.32 (t, 6H), 1.08 (s, 3H), 1.06 (s, 3H), 0.89 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 171.7, 113.4, 87.6, 80.0, 75.7, 70.0, 47.4, 37.7, 28.2, 27.7, 27.5, 27.4, 26.3, 21.6, 21.4, 18.4, -3.0, -4.4.

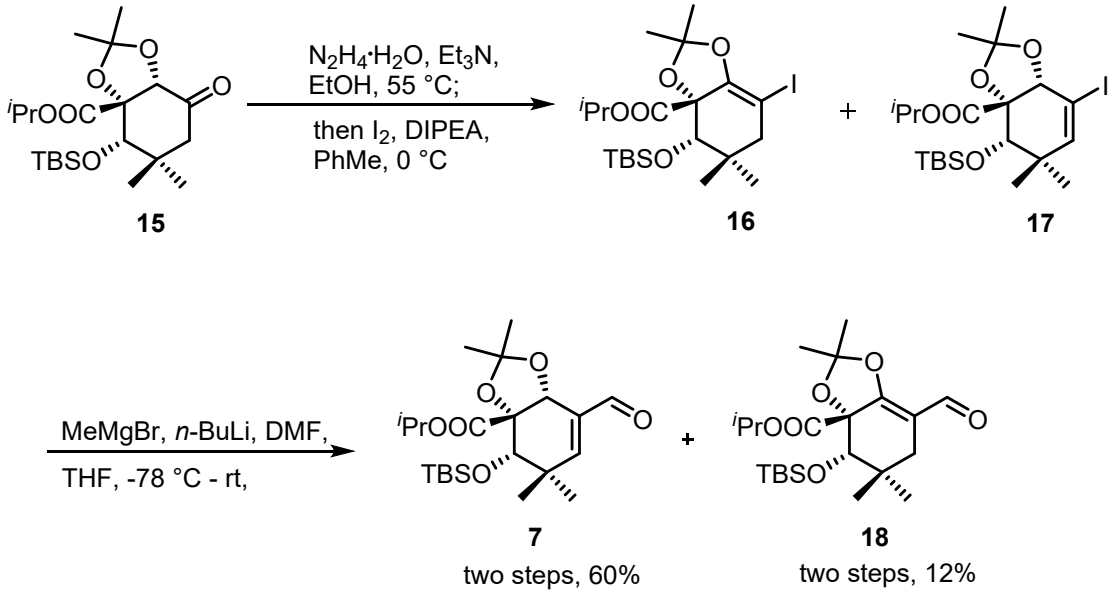
HRMS (ESI-TOF) m/z Calculated for $C_{21}H_{39}O_6Si$ $[M + H]^+$: 415.2510, found 415.2510.

IR (thin film): 2925, 2851, 1728, 1461, 1368, 1234, 1107, 857, 835, 775 cm^{-1}.

$[\alpha]_D^{25}$ = + 124.3 (*c* 0.21 g/100 mL, DCM)

Melting point range: 86.7 – 87.8 °C

2.8. Procedure for preparation of compound 7

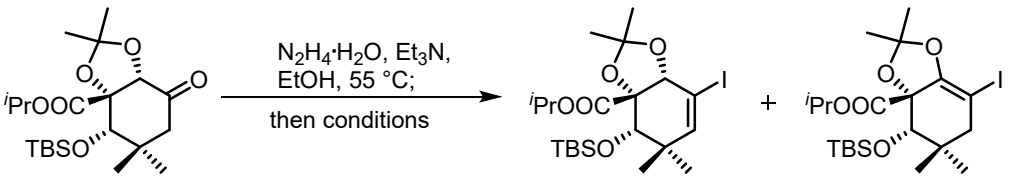


15 **16** **17**

7 two steps, 60%

18 two steps, 12%

2.8.1 Table S2 the iodination of 15



15 **17** **16**

entry	conditions	results (**17**:**16**) [a]
1	I_2, Et_3N, THF, 0 °C	1.7:1
2	I_2, Et_3N, THF, -30 °C	trace [b]
3	I_2, Et_3N, THF, - 78 °C	trace [b]
4	I_2, DBU, THF, 0 °C	1:1
5	I_2, DMAP, THF, 0 °C	1:1
6	I_2, TMEDA, THF, 0 °C	2.5:1
7	I_2, DIPEA, THF, 0 °C	2:1
8	I_2, 2,6-(tBu)$_2$Py, THF, 0 °C	NP [b]
9	I_2, 2,6-(tBu)$_2$,4-Me-Py, THF, 0 °C	NP [b]

10	I_2, TMEDA, THF, -78 °C	trace [b]
11	I_2, DIPEA, THF, -78 °C	trace [b]
12	I_2, TMEDA, PhMe, 0 °C	2.9:1
13	I_2, DIPEA, PhMe, 0 °C	5:1

[a] The results were confirmed by NMR; [b] The results were determined via TLC; [c] Et_3N: Triethylamine; DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene; DMAP: 4-Dimethylaminopyridine; TMEDA: N,N,N',N'-Tetramethylethylenediamine; DIPEA: N,N-Diisopropylethylamine; 2,6-(*t*Bu)$_2$Py: 2,6-Di-tert-butylpyridine; 2,6-(*t*Bu)$_2$-4-Me-Py: 2,6-Di-tert-butyl-4-methylpyridine; NP: No desired product.

Procedure for entries 1-13:

To a stirred solution of compound **15** (0.01 M) in EtOH at room temperature was added $N_2H_4 \cdot H_2O$ (4.0 eq.) and Et_3N (1.2 eq.). The solution was heated to 55 °C and stirred for 13 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was diluted with EtOH. The resulting solution was concentrated under reduced pressure and this process was repeated for three times. Finally, the crude product was dried under vacuum for 30 min and redissolved in dry PhMe or THF and cooled to 0 °C (entry 2 in -30 °C; entries 3, 10 and 11 in -78 °C) under argon atmosphere. Different bases (10.0 eq.) were added, followed by addition of a solution of I_2 (2.0 eq.) in dry PhMe or THF. The reaction mixture was maintained at 0 °C (entry 2 in -30 °C; entries 3, 10 and 11 in -78 °C) for 15 min, and then quenched by slowly pouring into a solution of $Na_2S_2O_3$ at 0 °C (entry 2 in -30 °C; entries 3, 10 and 11 in -78 °C). The mixture was extracted with EtOAc. The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel. The results showed that: entries 1, 4-7, 12-13 detected the formation of product where entry 13 was the optimized ratio (**17**:**16** = 5:1); entries 2-3, 10-11 led to trace amounts of product; entries 8-9 have no desired product.

Procedure for 18, 7

To a stirred solution of compound **15** (248.0 mg, 0.6 mmol, 1.0 eq.) in EtOH (23 mL) at room temperature was added $N_2H_4 \cdot H_2O$ (0.1 ml, 2.4 mmol, 4.0 eq.) and Et_3N (0.1 ml, 0.7 mmol, 1.2 eq.). The solution was heated to 55 °C and stirred for 13 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was diluted with EtOH (15 mL). The resulting solution was concentrated under reduced pressure and this process was repeated for three times. Finally, the product was dried under vacuum for 30 min. The crude product was dissolved in dry PhMe (20 mL) and cooled to 0 °C under argon atmosphere. DIPEA (1.0 ml, 6.0 mol, 10.0 eq.) was added, followed by addition of a solution of I_2 (304.6 mg, 1.2 mmol, 2.0 eq.) in dry PhMe (10 mL). The reaction mixture was maintained at 0 °C for 15 min, and then quenched by slowly pouring into a solution of $Na_2S_2O_3$ (15 mL) at 0 °C. The mixture was extracted with EtOAc (20 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 60:1) to obtain **17**[2] as mixture with regioisomer **16**. The crude product was directly used for the next step without further purification.

To a stirred solution of **17** as mixture with regioisomer **16** in dry THF (25 mL) at 0 °C under argon atmosphere was slowly added MeMgBr (1.0 mL, 3.0 mmol, 5.0 eq.). The reaction was maintained at 0 °C for 15 min. Then the reaction mixture was cooled at -78 °C and maintained at -78 °C for 10 min. The *n*BuLi (1.7 mL, 4.2 mmol, 7.0 eq.) was added dropwise to the reaction mixture and maintained at -78 °C for 25 min. Then the DMF (0.7 mL, 9.0 mmol, 15.0 eq.) was added dropwise to the reaction mixture and raised to room temperature for another 30 min. Then the reaction was quenched by slowly adding saturated NH_4Cl (20 mL). The resulting mixture was extracted with EtOAc (20 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 15:1) to obtain **18** (30.1 mg, 12% yield in two steps) as a colorless oily liquid and **7**[3] (153.4 mg, 60% yield in two steps) as a colorless oily liquid.

Compound 18:

TLC: R_f = 0.5 (PE : EtOAc = 10:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 5.10 – 5.00 (m, 1H), 4.13 (s, 1H), 2.26 (d, A of AB, *J* = 16.3 Hz, 1H), 1.96 (d, B of AB, *J* = 16.3 Hz, 1H), 1.59 (s, 3H), 1.52 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 0.98 (s, 3H), 0.94 (s, 3H), 0.87 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7, 169.4, 161.9, 116.9, 111.2, 85.3, 75.9, 70.3, 35.7, 31.8, 28.3, 27.4, 26.9, 26.2, 21.4, 21.3, 18.3, -3.1, -4.6.

HRMS (ESI-TOF) m/z Calculated for $C_{22}H_{39}O_6Si$ $[M + H]^+$: 427.2510, found 427.2510.

IR (thin film): 2932, 2862, 1732, 1660, 1474, 1389, 1231, 1100, 1038, 860, 832, 775 cm^{-1}.

$[\alpha]_D^{25}$ = + 76.0 (*c* 0.40 g/100 mL, DCM)

Compound 7:

TLC: R_f = 0.5 (PE : EtOAc = 8:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 6.56 (s, 1H), 5.17 (s, 1H), 5.12 – 5.01 (m, 1H), 4.12 (s, 1H), 1.53 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.22 (s, 3H), 0.93 (s, 9H), 0.10 (s, 3H), 0.01 (s, 3H).

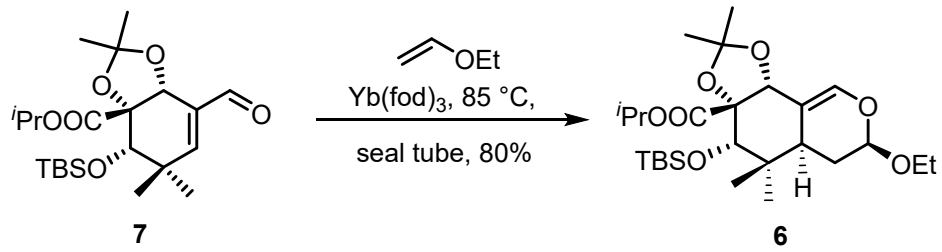
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 172.7, 158.8, 135.7, 113.5, 87.1, 76.5, 75.8, 69.8, 38.9, 29.6, 28.3, 27.8, 26.4, 21.6, 21.6, 20.2, 18.9, -3.9, -4.6.

HRMS (ESI-TOF) m/z Calculated for $C_{22}H_{39}O_6Si$ $[M + H]^+$: 427.2510, found 427.2510.

IR (thin film): 2939, 2855, 1751, 1690, 1475, 1368, 1240, 1104, 1049, 839, 783 cm^{-1}.

$[\alpha]_D^{25}$ = + 94.8 (*c* 0.23 g/100 mL, DCM)

2.9. Procedure for preparation of compound 6



7 6

To a stirred solution of compound **7** (127.8 mg, 0.3 mmol, 1.0 eq.) in ethyl vinyl ether (15 mL) at room temperature was added $Yb(fod)_3$ (63.5 mg, 0.06 mmol, 0.2 eq.). The solution was heated at 85 °C in the seal tube for 80 h. Then the resulting mixture was cooled to room temperature. The reaction mixture was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 40:1 to 20:1) to obtain **6** (119.4 mg, 80%) as a colorless oily liquid.

Compound 6:

TLC: R_f = 0.5 (PE : EtOAc = 10:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.13 (s, 1H), 5.08 – 5.02 (m, 1H), 4.99 (d, *J* = 8.5 Hz, 1H), 4.07 (s, 1H), 4.00 – 3.93 (m, 1H), 3.63 – 3.56 (m, 1H), 2.91 (dd, A of AB, *J* = 11.1, 7.2 Hz, 1H), 1.92 (dd, B of AB, *J* = 11.8, 7.2 Hz, 1H), 1.56 – 1.50 (m, 4H), 1.37 (s, 3H), 1.30 – 1.25 (m, 9H), 0.97 (s, 3H), 0.95 (s, 9H), 0.54 (s, 3H), 0.15 (s, 3H), 0.09 (s, 3H).

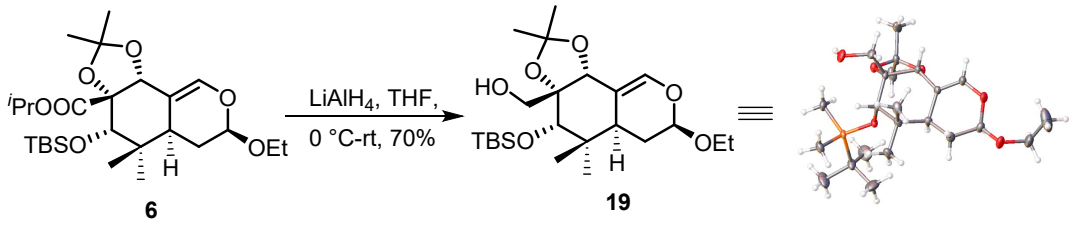
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 146.8, 111.4, 110.4, 102.8, 82.8, 78.1, 76.3, 71.3, 40.8, 32.8, 31.7, 31.1, 28.9, 28.7, 28.2, 27.8, 27.3, 23.5, 23.4, 20.7, 20.4, 17.2, 2.0, -2.0.

HRMS (ESI-TOF) m/z Calculated for $C_{26}H_{47}O_7Si$ $[M + H]^+$: 499.3086, found 499.3086.

IR (thin film): 2931, 2848, 1729, 1664, 1459, 1373, 1243, 1126, 1091, 1062, 1038, 867, 832, 773 cm^{-1}.

$[\alpha]_D^{25}$ = + 34.2 (*c* 0.26 g/100 mL, DCM)

2.10. Procedure for preparation of compound 19



To a stirred solution of compound **6** (100.0 mg, 0.2 mmol, 1.0 eq.) in dry THF (18 mL) at 0 °C under argon atmosphere was slowly added $LiAlH_4$ (1.6 mL, 1.6 mmol, 8.0 eq.). The reaction was maintained at 0 °C for 1 h. Then the reaction was gradually raised to room temperature and stirred for 10 h. The reaction was quenched by slowly adding 1.6 mL THF/H_2O (7:1) mixed solution. After filtration via silica gel, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 10:1) to obtain **19** (61.7 mg, 70%) as a white solid.

Compound 19:

TLC: R_f = 0.5 (PE : EtOAc = 6:1; CAM).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (d, *J* = 1.7 Hz, 1H), 4.95 (dd, *J* = 9.8, 1.9 Hz, 1H), 4.26 (s, 1H), 3.99 – 3.91 (m, 1H), 3.63 – 3.50 (m, 3H), 3.44 (s, 1H), 2.90 (ddd, A of AB, *J* = 11.7, 7.6, 1.9 Hz, 1H), 1.95 (ddd, B of AB, *J* = 13.0, 7.5, 1.9 Hz, 1H), 1.59 (d, *J* = 1.5 Hz, 1H), 1.52 (s, 3H), 1.41 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.00 (s, 3H), 0.94 (s, 9H), 0.71 (s, 3H), 0.10 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 112.7, 109.6, 102.6, 84.0, 77.3, 70.3, 66.6, 40.5, 33.3, 31.4, 31.1, 28.9, 28.8, 28.6, 27.9, 27.9, 22.7, 20.5, 16.9, 1.7, -2.3.

HRMS (ESI-TOF) m/z Calculated for $C_{23}H_{43}O_6Si$ $[M + H]^+$: 443.2823, found 443.2820.

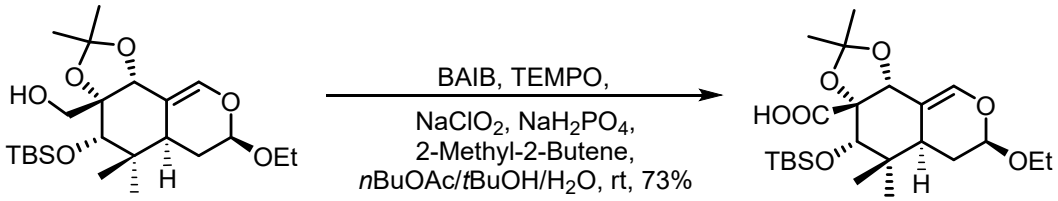
IR (thin film): 2922, 2848, 1653, 1456, 1359, 1251, 1141, 1082, 1054, 870, 830, 774

cm^{-1}.

$[\alpha]_D^{25}$ = + 125.0 (*c* 0.04 g/100 mL, DCM)

Melting point range: 133.7 – 134.6 °C

2.11. Procedure for preparation of compound 20



19 **20**

To a stirred solution of compound **19** (62.0 mg, 0.14 mmol, 1.0 eq.) in *n*BuOAc (17 mL), *t*BuOH (1 mL) and H_2O (1 mL) at room temperature were added TEMPO (32.8 mg, 0.21 mmol, 1.5 eq.) and $PhI(OAc)_2$ (135.3 mg, 0.42 mmol, 3.0 eq.). The reaction was maintained at room temperature for 24 h. Then the reaction solution at room temperature were added H_2O (1 mL), NaH_2PO_4 (119.2 mg, 0.84 mmol, 6.0 eq.), 2-Methyl-2-butene (0.6 mL, 5.60 mmol, 40.0 eq.) and $NaClO_2$ (76.0 mg, 0.84 mmol, 6.0 eq.) in sequence. The reaction was maintained at room temperature for 10 h. The reaction was quenched by slowly adding saturated $Na_2S_2O_3$ (10 mL). The resulting mixture was extracted with EtOAc (10 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 1:1) to obtain **20**[4] (46.7 mg, 73%) as a colorless oily liquid.

Compound 20:

TLC: R_f = 0.5 (PE : EtOAc = 1:1; CAM).

^{1}H NMR (400 MHz, CD_3OD) δ 6.63 (d, *J* = 1.8 Hz, 1H), 5.14 (s, 1H), 4.97 (dd, *J* = 9.7, 1.9 Hz, 1H), 4.14 (s, 1H), 3.98 – 3.90 (m, 1H), 3.68 – 3.61 (m, 1H), 2.88 (ddd, A of AB, *J* = 11.7, 7.0, 1.9 Hz, 1H), 1.91 (ddd, B of AB, *J* = 13.0, 7.0, 1.9 Hz, 1H), 1.55

– 1.48 (m, 4H), 1.39 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.05 (s, 3H), 0.98 (s, 9H), 0.66 (s, 3H), 0.18 (s, 3H), 0.13 (s, 3H).

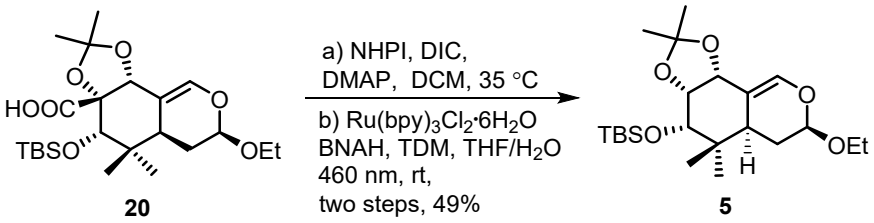
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 145.0, 109.5, 108.3, 100.8, 81.7, 76.1, 75.9, 64.8, 38.3, 32.5, 29.7, 26.7, 26.4, 25.8, 25.1, 20.6, 18.7, 15.2, -2.5, -3.9.

HRMS (ESI-TOF) m/z Calculated for $C_{23}H_{41}O_7Si$ $[M + H]^+$: 457.2616, found 457.2616.

IR (thin film): 2936, 2863, 2367, 1747, 1651, 1469, 1373, 1127, 1104, 1055, 1015, 863, 835, 776 cm^{-1}.

$[\alpha]_D^{25}$ = + 114.0 (*c* 0.05 g/100 mL, DCM)

2.12. Procedure for preparation of compound 5



To a stirred solution of compound **20** (20.0 mg, 0.04 mmol, 1.0 eq.) in dry DCM (2.5 mL) at room temperature under argon atmosphere were added DMAP (4.9 mg, 0.04 mmol, 1.0 eq.), NHPI (11.4 mg, 0.07 mmol, 1.8 eq.) and DIC (0.01 mL, 0.07 mmol, 1.8 eq.). The solution was heated at 35 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 6:1) to obtain the crude product. The crude product was directly used for the next step without further purification.

To a stirred solution of the crude product in THF (2.0 mL)/ H_2O (0.2 mL) at room temperature under an argon atmosphere were added 1-Benzyl-1,4-dihydronicotinamide (BNAH) (12.9 mg, 0.060 mmol, 1.5 eq.), $Ru(bpy)_3Cl_2.6H_2O$ (5.0 mg, 0.008 mmol, 0.2 eq.) and tert-dodecylthiol (TDM) (0.02 mL, 0.080 mmol, 2.0 eq.). After the reaction

was irradiated for 3 h at room temperature under a blue light lamp (λ = 460 nm). The resulting mixture was diluted with water (3 mL) and extracted with EtOAc (5 mL × 3). The organic phases were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (PE : EtOAc = 40:1 to 30:1) to obtain **5**[5] (8.1 mg, 49% yield in two steps) as a colorless oily liquid.

Compound 5:

TLC: R_f = 0.5 (PE : EtOAc = 10:1; CAM).

^{1}H NMR (400 MHz, CD_3OD/CD_2Cl_2) δ 6.59 (d, *J* = 1.9 Hz, 1H), 4.96 (dd, *J* = 9.7, 1.8 Hz, 1H), 4.60 (d, *J* = 7.2 Hz, 1H), 4.21 (dd, *J* = 7.2, 5.0 Hz, 1H), 3.97 – 3.89 (m, 1H), 3.66 – 3.58 (m, 1H), 3.55 (d, *J* = 4.9 Hz, 1H), 2.87 (ddd, A of AB, *J* = 11.8, 6.8, 1.1 Hz, 1H), 1.89 (ddd, B of AB, *J* = 12.9, 6.8, 1.8 Hz, 1H), 1.49 (s, 4H), 1.35 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.01 (s, 3H), 0.96 (s, 9H), 0.71 (s, 3H), 0.14 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD/CD_2Cl_2) δ 144.8, 109.6, 107.6, 100.9, 75.3, 73.5, 72.6, 64.4, 38.3, 31.9, 29.0, 25.9, 25.0, 23.8, 18.6, 18.1, 14.2, -3.2, -5.0.

HRMS (ESI-TOF) m/z Calculated for $C_{22}H_{41}O_5Si$ $[M + H]^+$: 413.2718, found 413.2718.

IR (thin film): 2934, 2914, 2365, 1455, 1374, 1116, 1056, 1015, 871, 832, 791 cm^{-1}.

$[\alpha]_D^{25}$ = + 145.0 (*c* 0.06 g/100 mL, DCM)

3. References

[1] J. Feng, T. Yu, Z. Zhang, J. Li, S. Fu, J. Chen and B. Liu, *Chem. Commun.,* 2018, **54**, 7665.

[2] Y. Sun, J. Feng, S. Qin, S. Fu and B. Liu, *Org. Lett.,* 2023, **25**, 8072.

[3] A. S. Burns and S. D. Rychnovsky, *J. Am. Chem. Soc.,* 2019, **141**, 13295.

[4] M. Shibuya, *Tetrahedron Lett.,* 2020, **61**, 151515.

[5] (a) K. Okada, K. Okamoto and M. Oda, *J. Am. Chem. Soc.,* 1988, **110**, 8736; (b) K.

Okada, K. Okubo, N. Morita and M. Oda, *Tetrahedron Lett.,* 1992, **33**, 7377.

4. X-ray Crystallographic Data for compound 19

The single crystal for compound **19** was obtained by slow vaporization of a mixture solvent of dichloromethane and petroleum ether (1:6). Displacement ellipsoids are drawn at the 30% probability level.

Experimental Single crystal of **19** was used as supplied. The colourless crystal in block-shape, with approximate dimensions of 0.150 × 0.177 × 0.797 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by

Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (Kα = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.

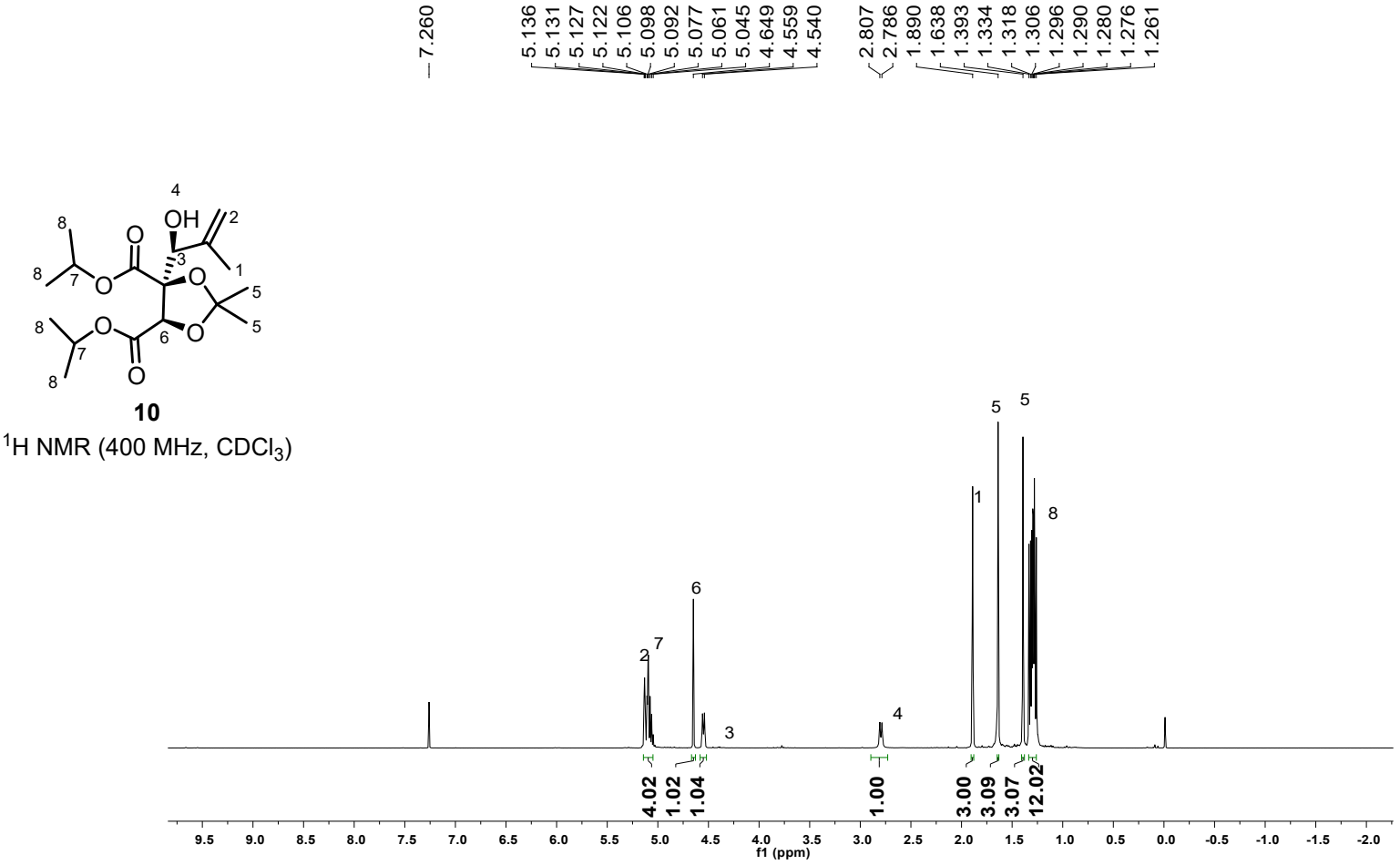
Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 2299440).

Crystal data and structure refinement for CCDC 2299440

Empirical formula	$C_{23}H_{42}O_6Si$
Formula weight	442.65
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.7582(2)
b/Å	12.2091(2)
c/Å	18.8089(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2470.51(8)
Z	4
ρ_{calc}g/cm^3	1.190
μ/mm^{-1}	1.115
F(000)	968.0
Crystal size/mm^3	0.797 × 0.177 × 0.150

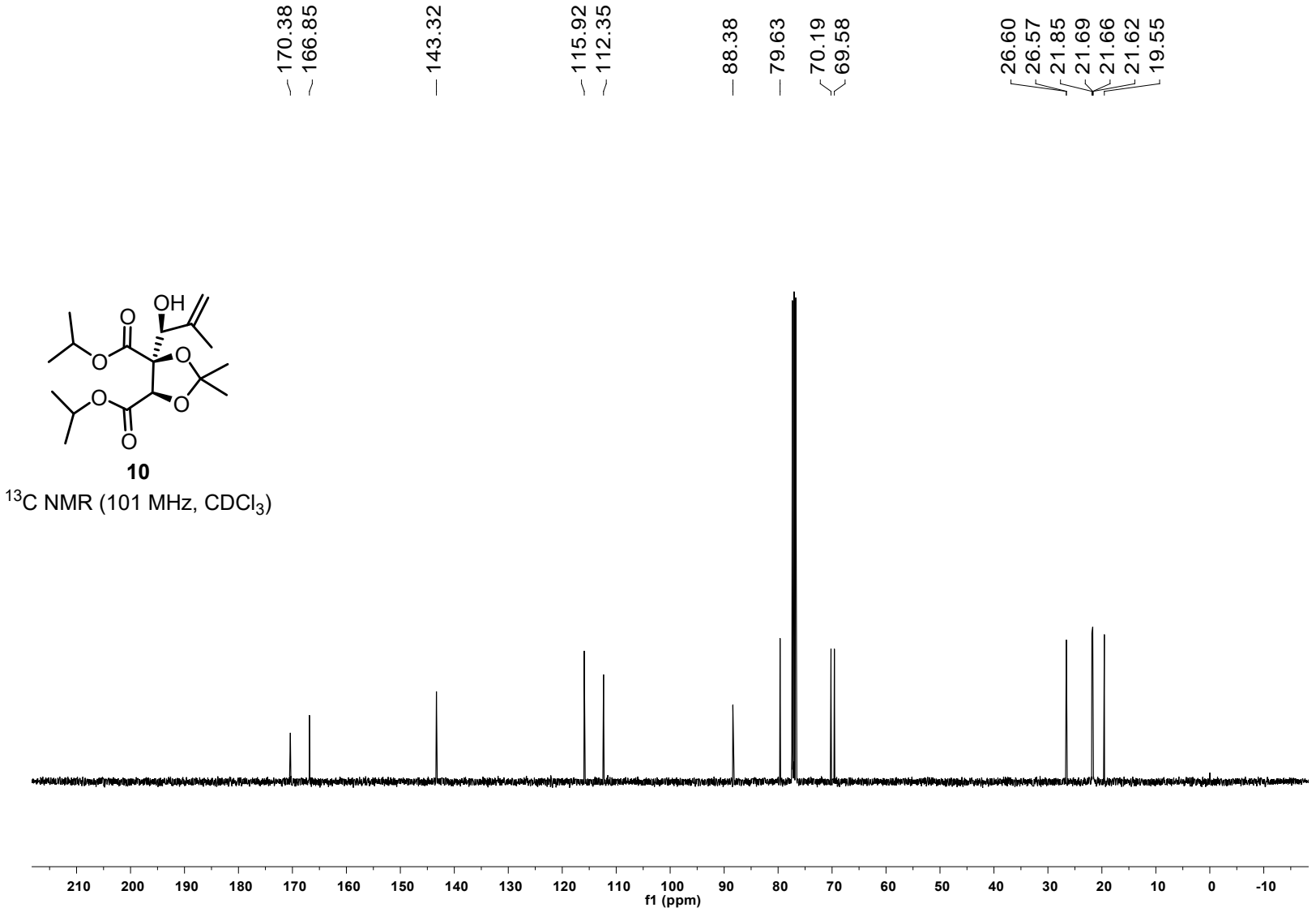
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.634 to 158.84
Index ranges	$-13 \leq h \leq 13$, $-15 \leq k \leq 12$, $-23 \leq l \leq 23$
Reflections collected	16699
Independent reflections	5182 [R_{int} = 0.0576, R_{sigma} = 0.0504]
Data/restraints/parameters	5182/1/285
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1046
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.1060
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.38
Flack parameter	0.058(12)

5. Spectra for Compounds



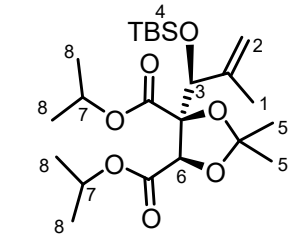
10

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



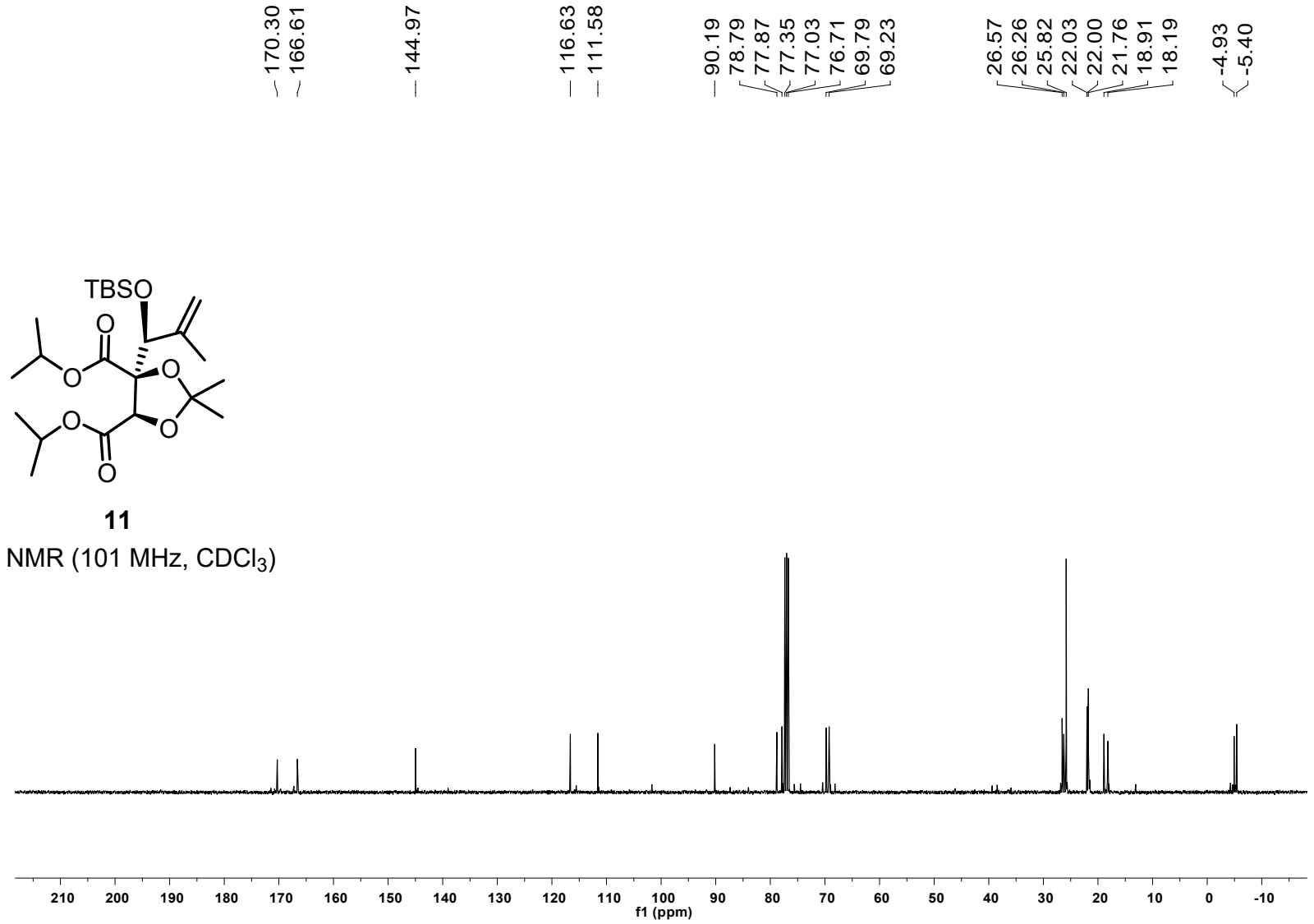
10

^{13}C NMR (101 MHz, $CDCl_3$)



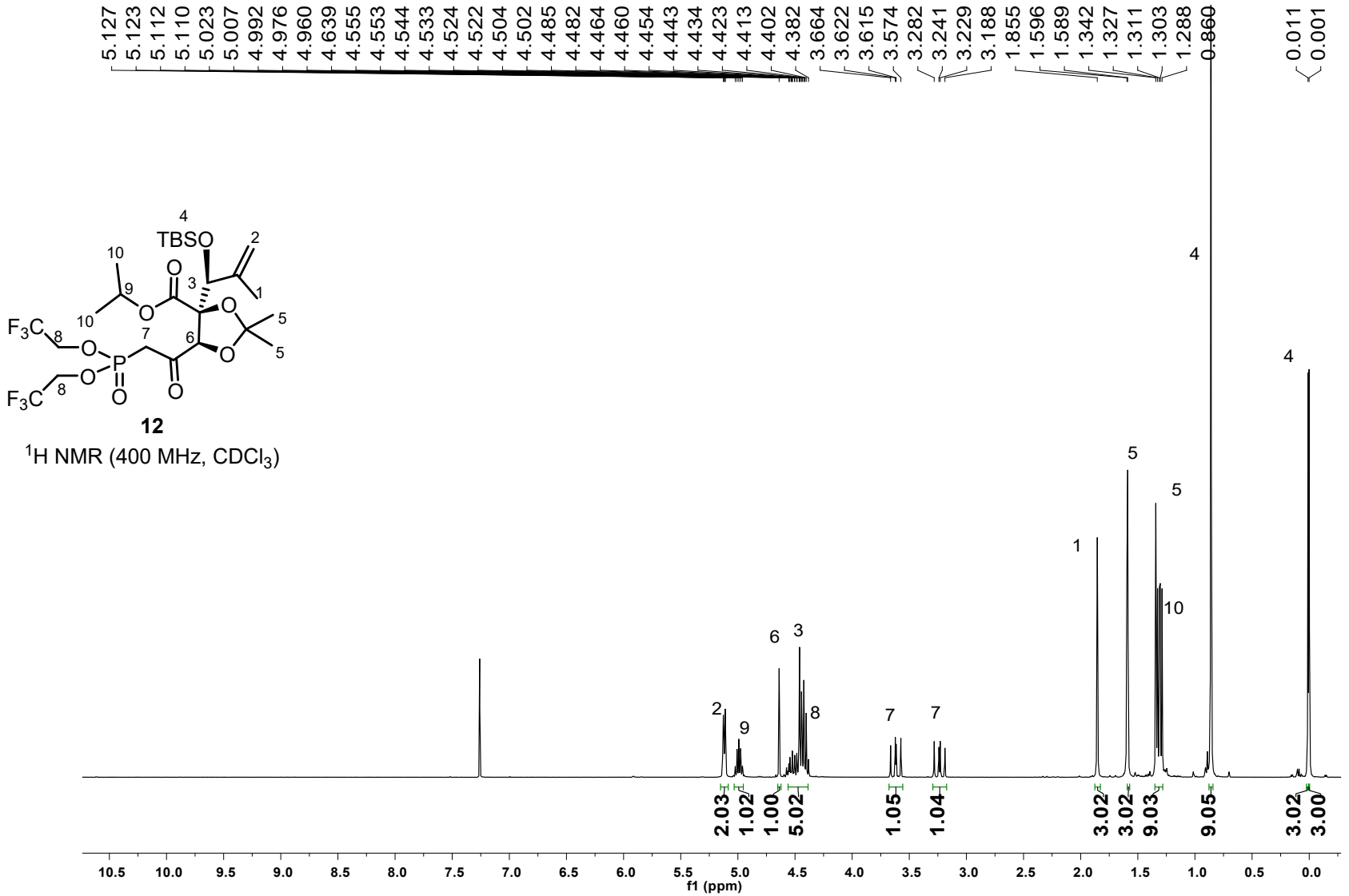
11

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



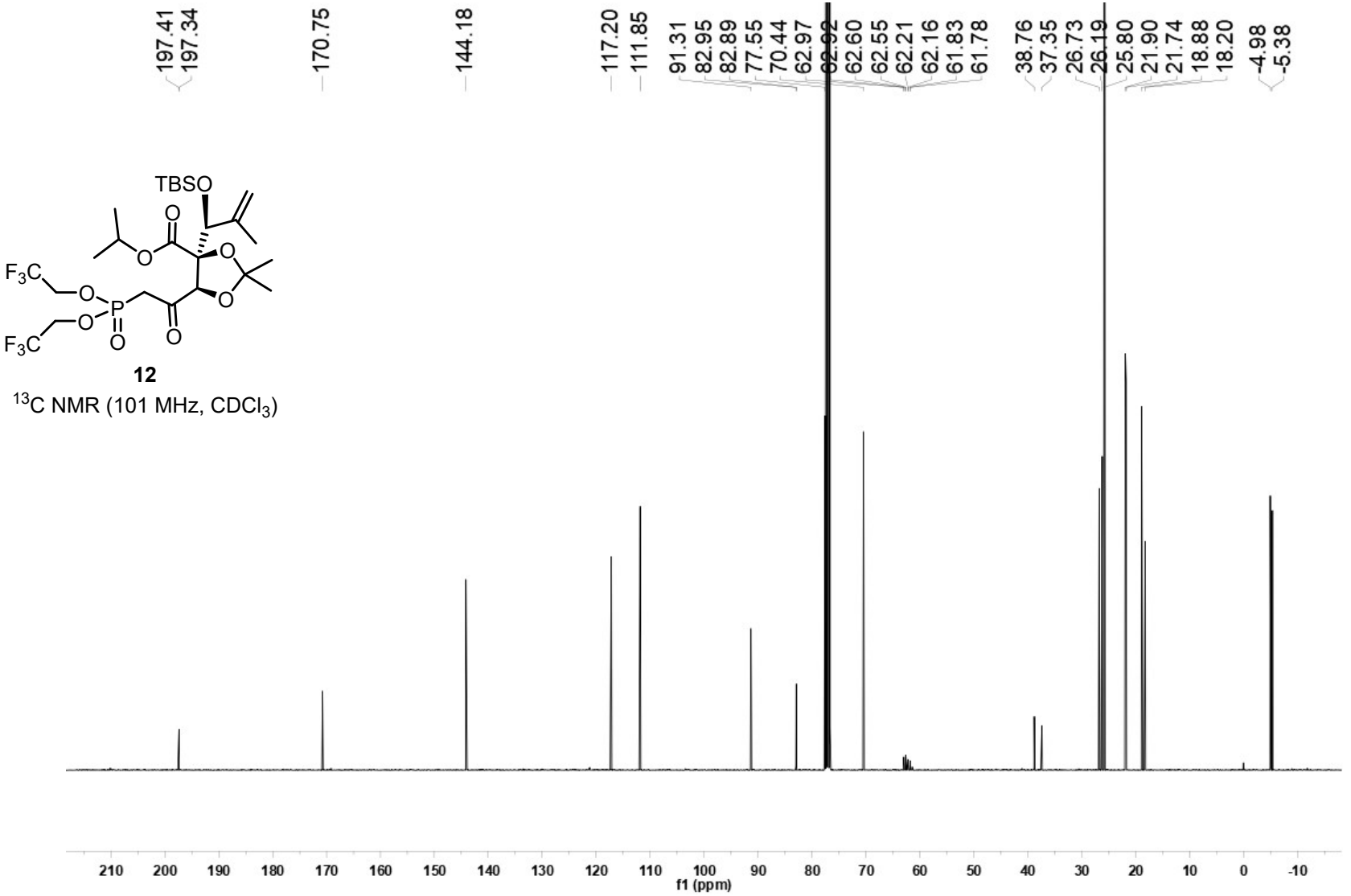
11

^{13}C NMR (101 MHz, $CDCl_3$)



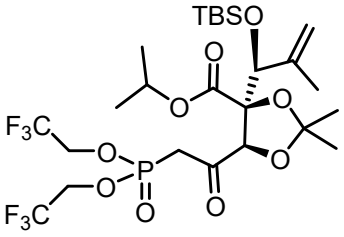
12

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



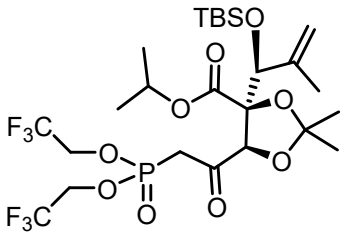
12

^{13}C NMR (101 MHz, $CDCl_3$)



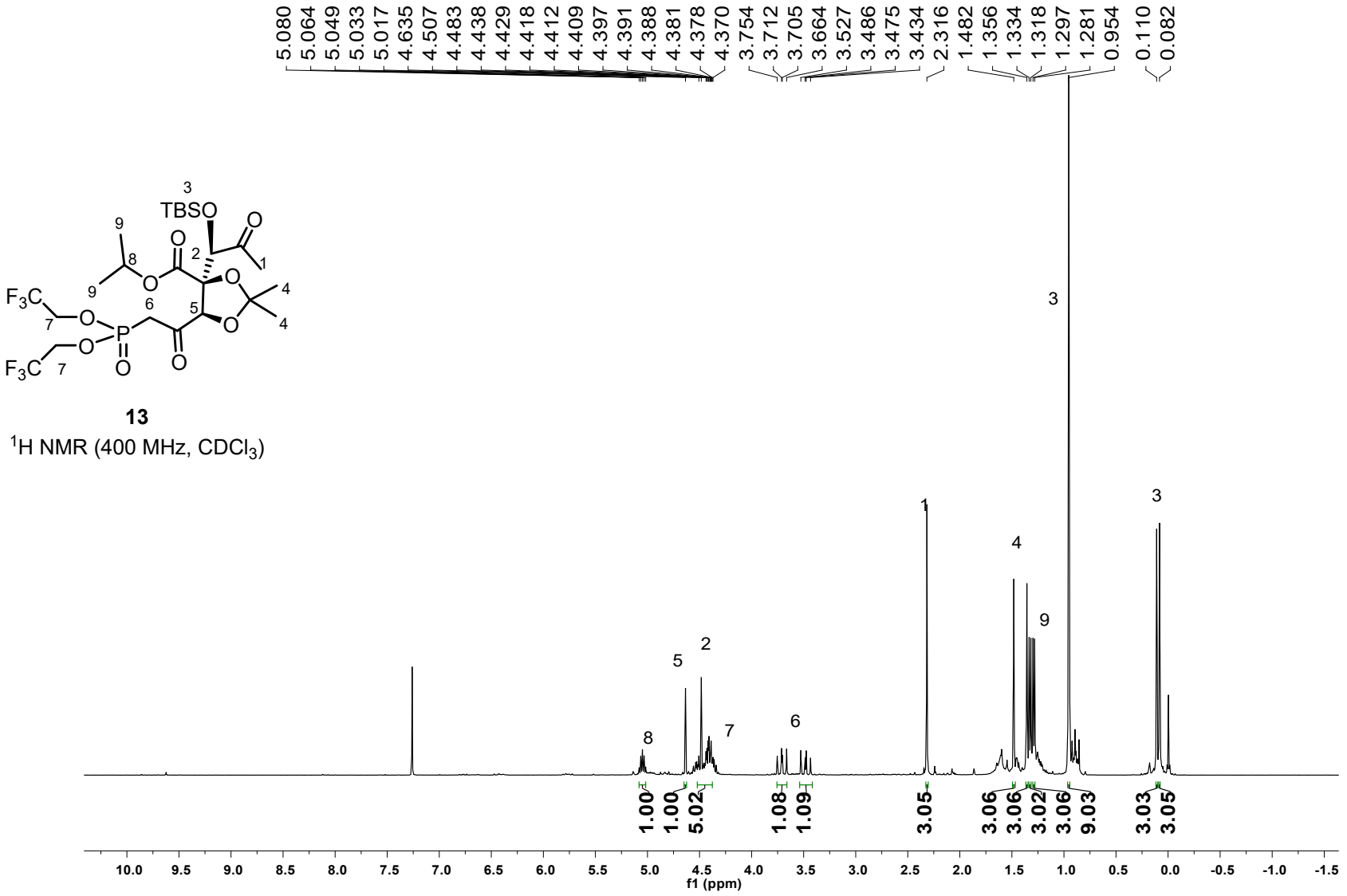
12

^{19}F NMR (376 MHz, $CDCl_3$)



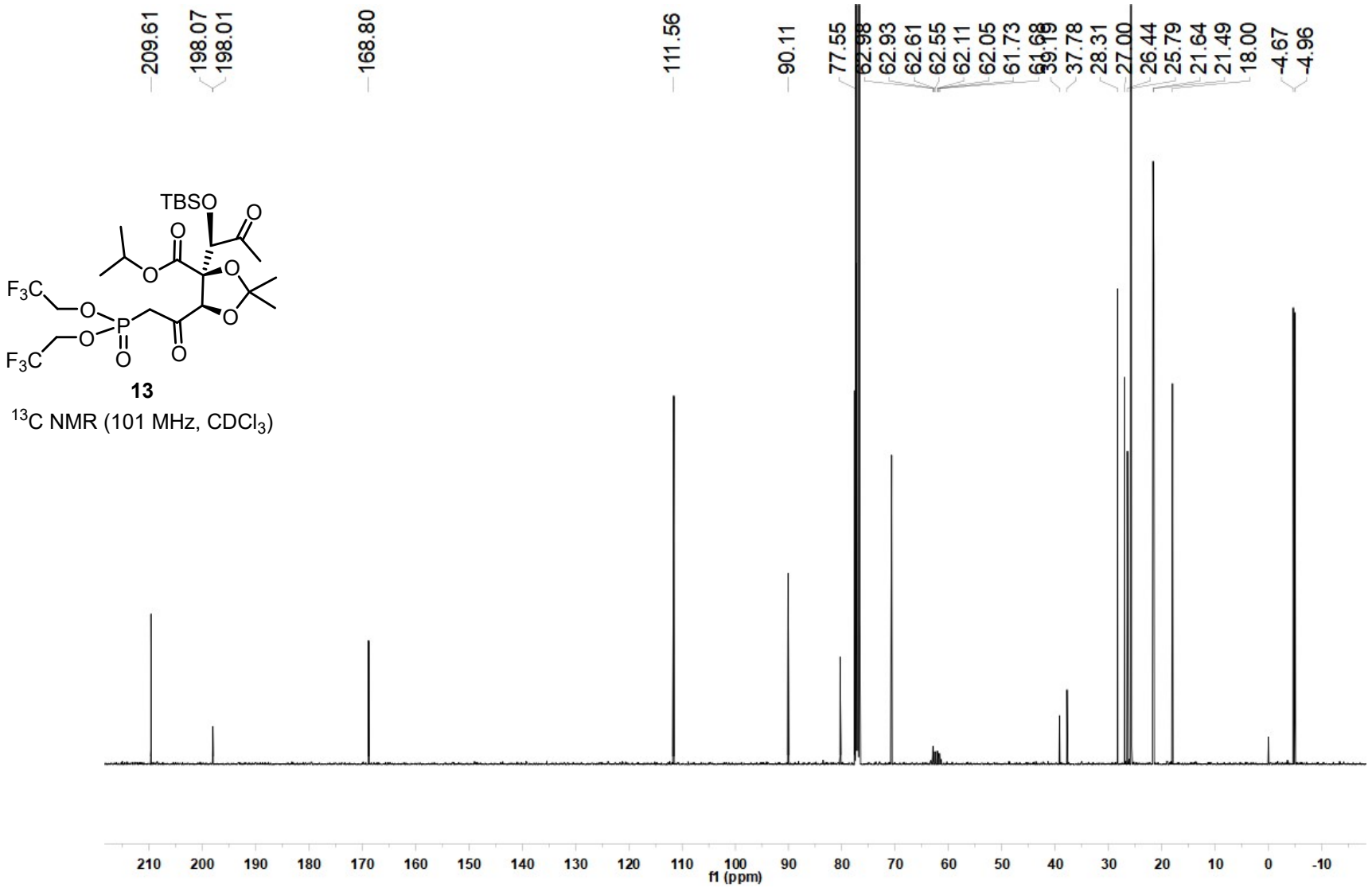
12

^{31}P NMR (162 MHz, $CDCl_3$)



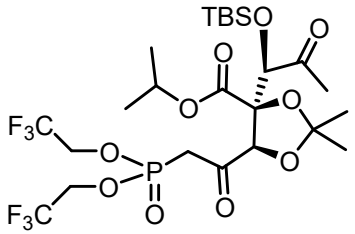
13

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



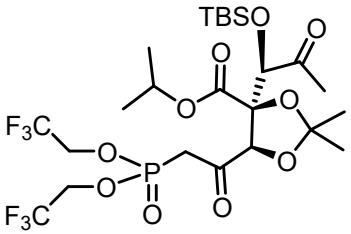
13

^{13}C NMR (101 MHz, $CDCl_3$)



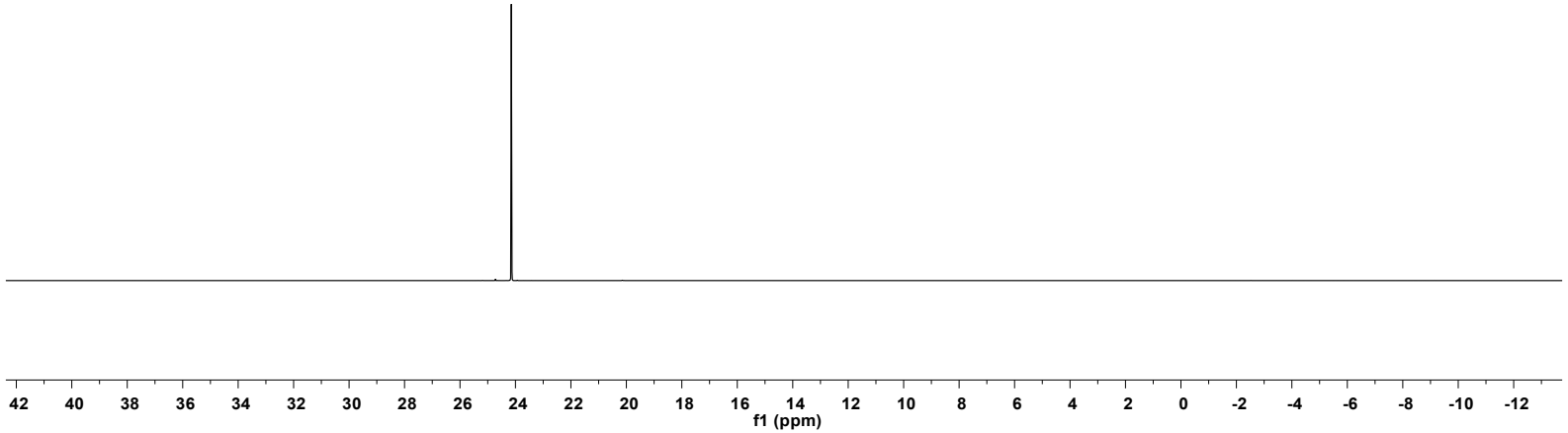
13

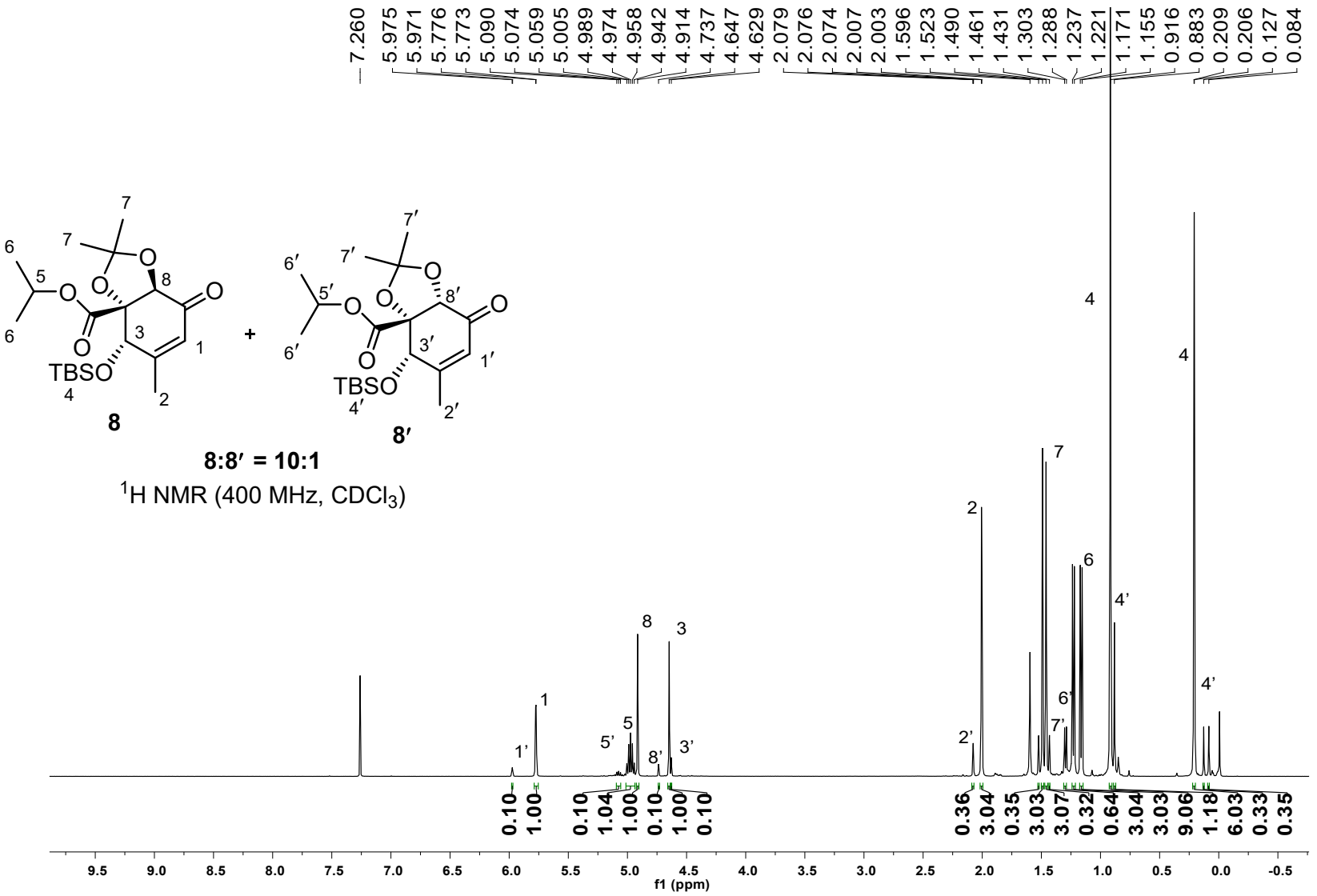
^{19}F NMR (376 MHz, $CDCl_3$)

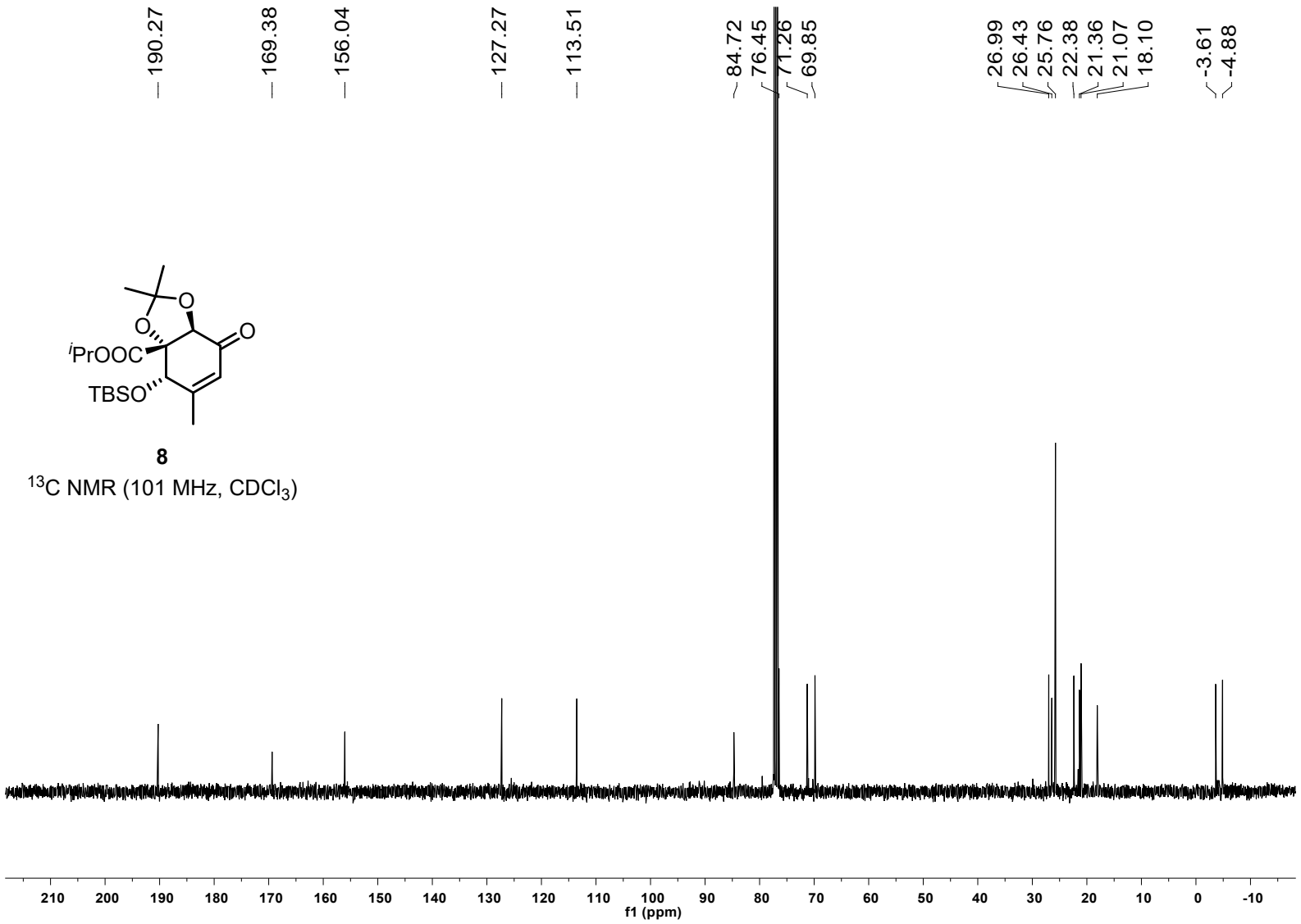


13

^{31}P NMR (162 MHz, $CDCl_3$)

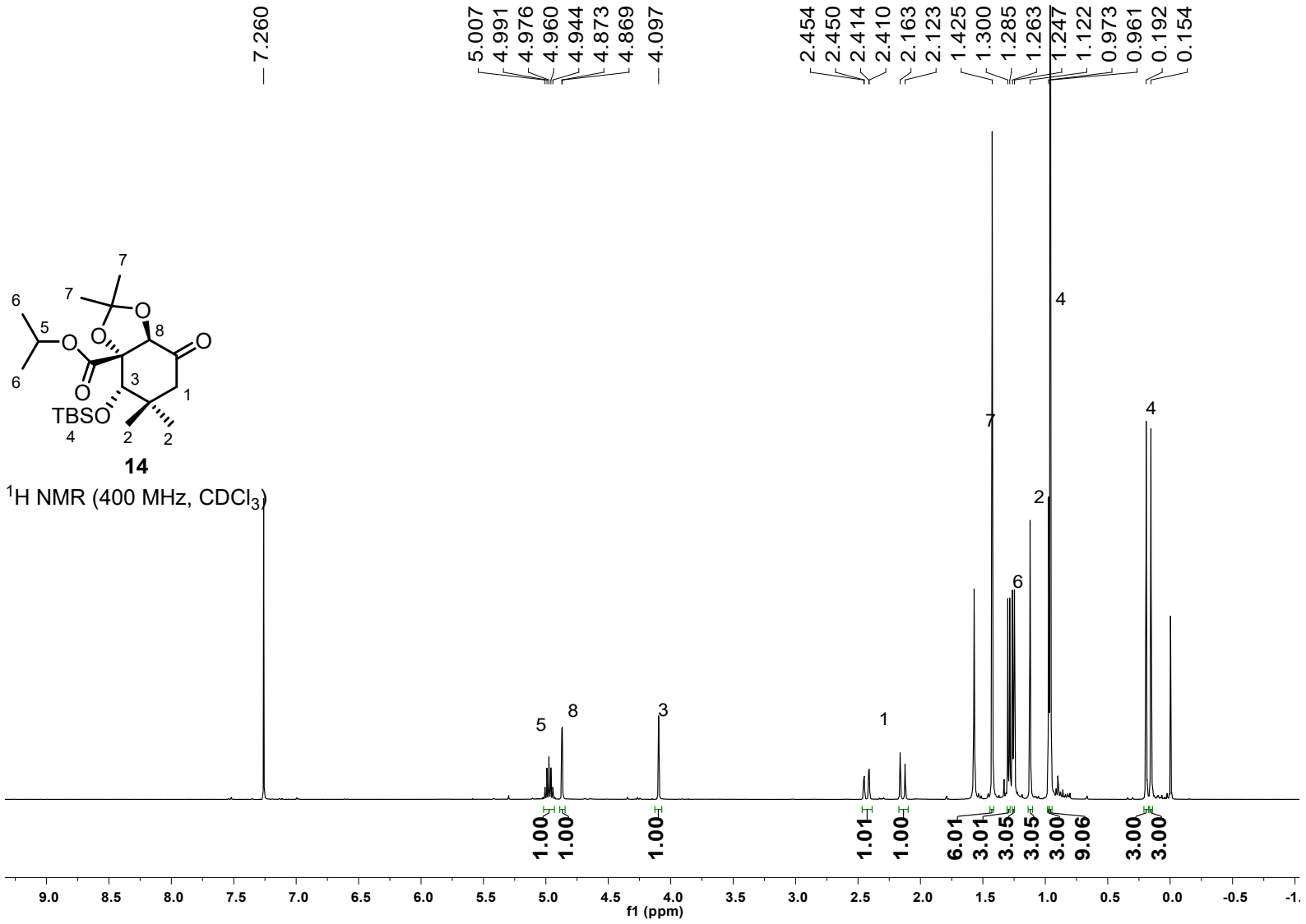


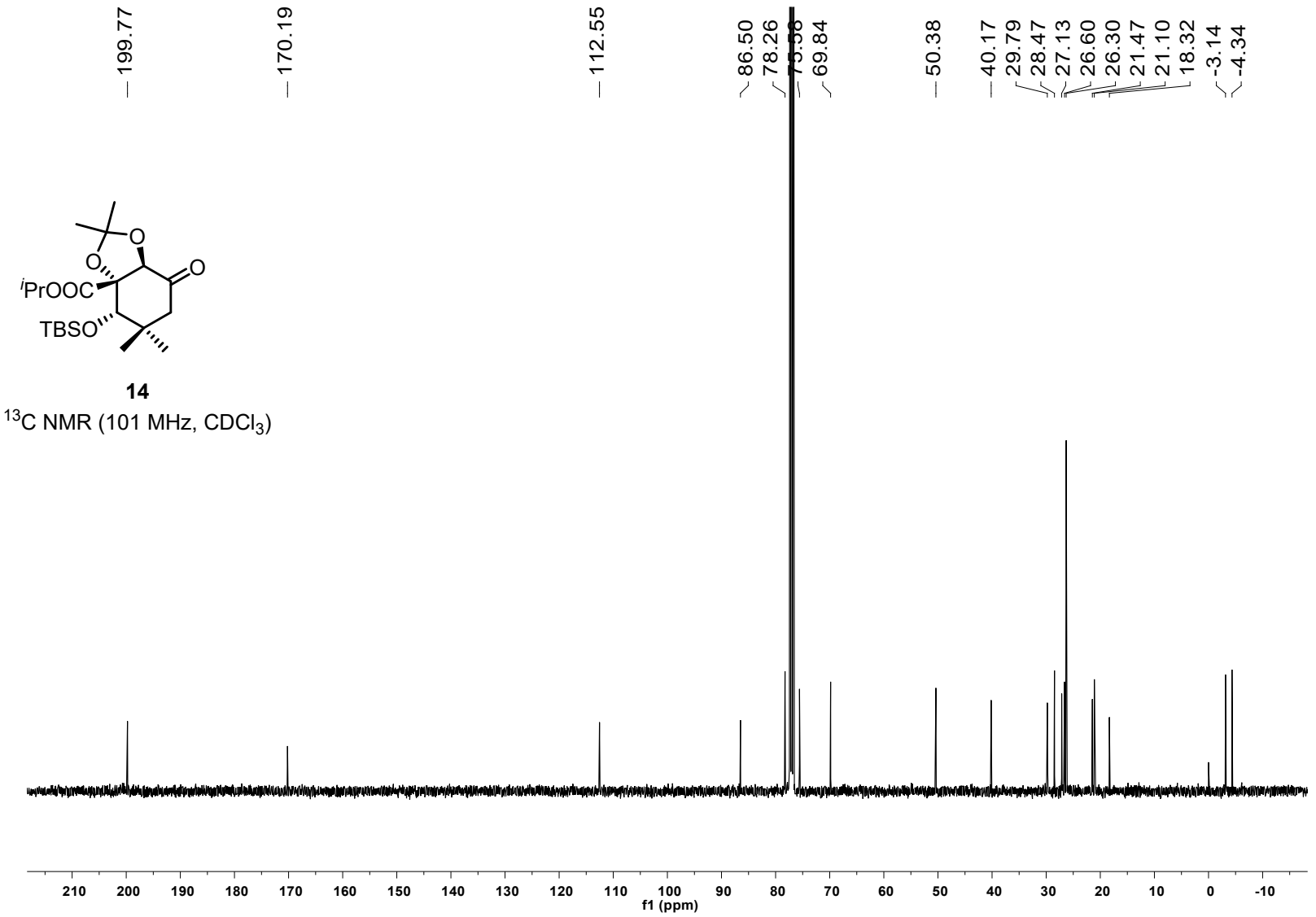

7.260
5.975
5.971
5.776
5.773
5.090
5.074
5.059
5.005
4.989
4.974
4.958
4.942
4.914
4.737
4.647
4.629
2.079
2.076
2.074
2.007
2.003
1.596
1.523
1.490
1.461
1.431
1.303
1.288
1.237
1.221
1.171
1.155
0.916
0.883
0.209
0.206
0.127
0.084
TBSO
8
TBSO
8′
8:8′ = 10:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)



8

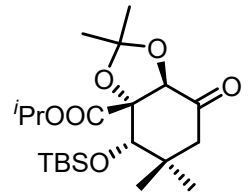
^{13}C NMR (101 MHz, $CDCl_3$)


7.260
5.007
4.991
4.976
4.960
4.944
4.873
4.869
4.097
2.454
2.450
2.414
2.410
2.163
2.123
1.425
1.300
1.285
1.263
1.247
1.122
0.973
0.961
0.192
0.154
TBSO
14
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.01
1.00
6.01
3.01
3.05
3.05
3.00
9.06
3.00
3.00
f1 (ppm)

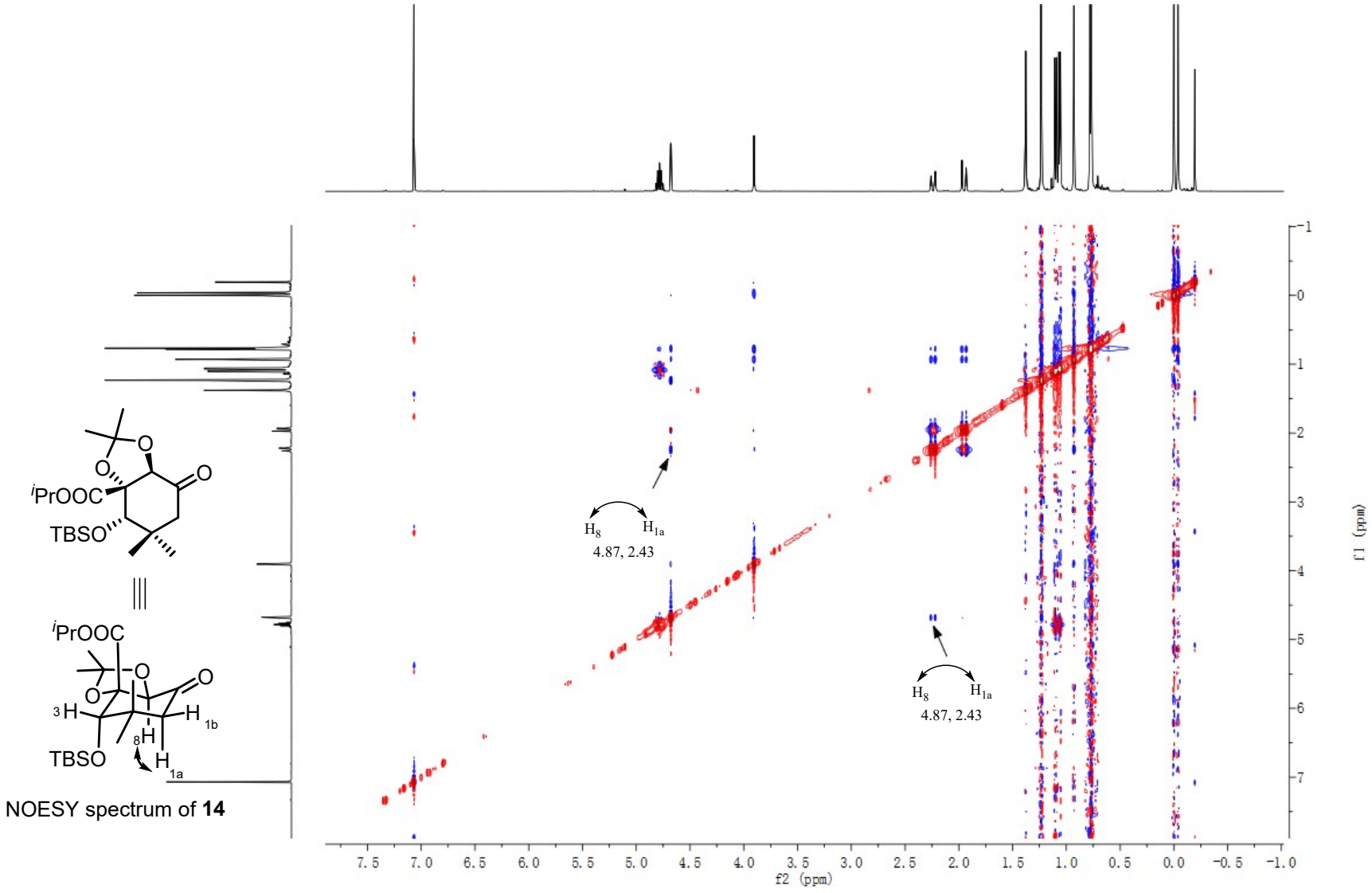


14

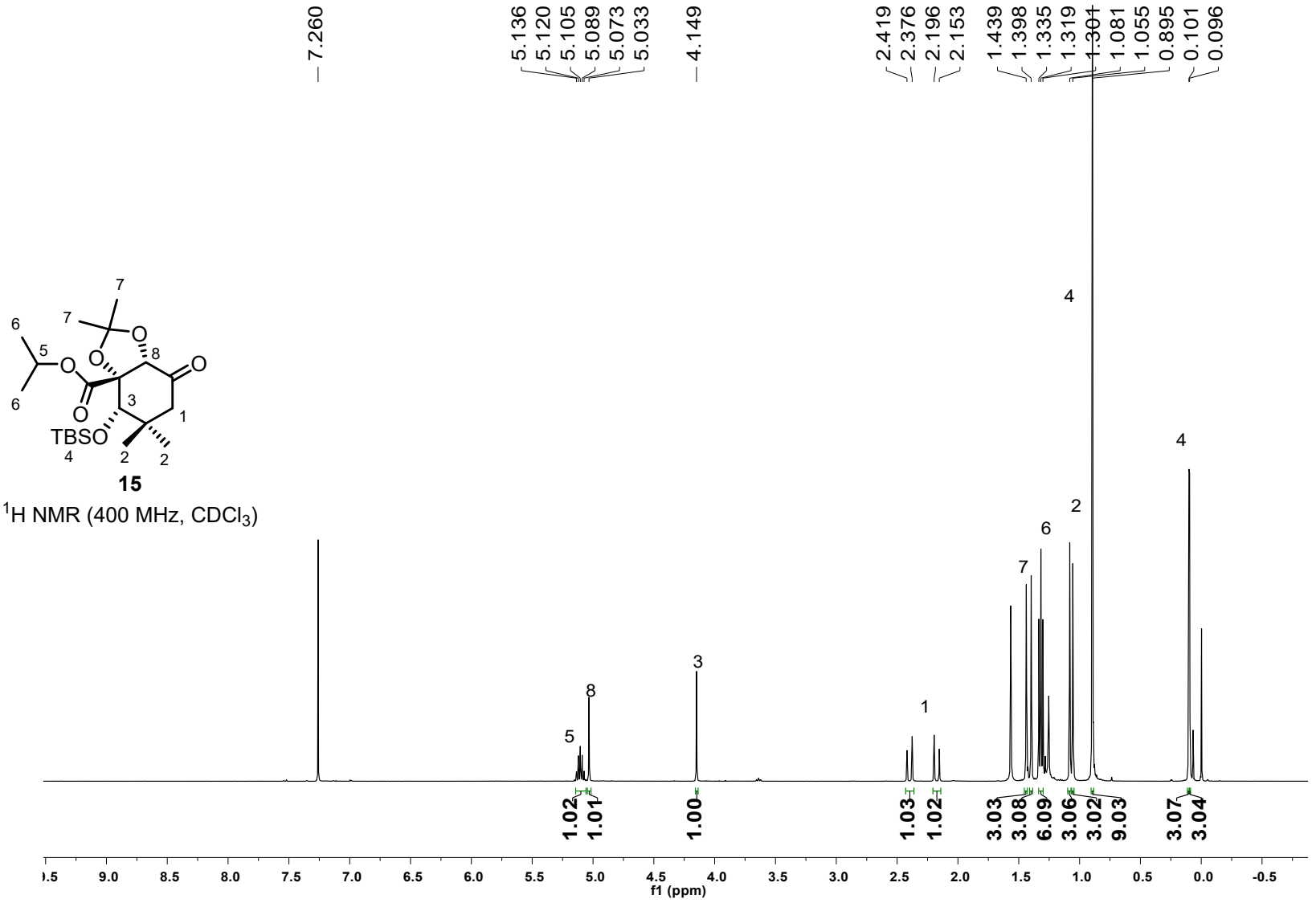
^{13}C NMR (101 MHz, $CDCl_3$)



COSY spectrum of **14**

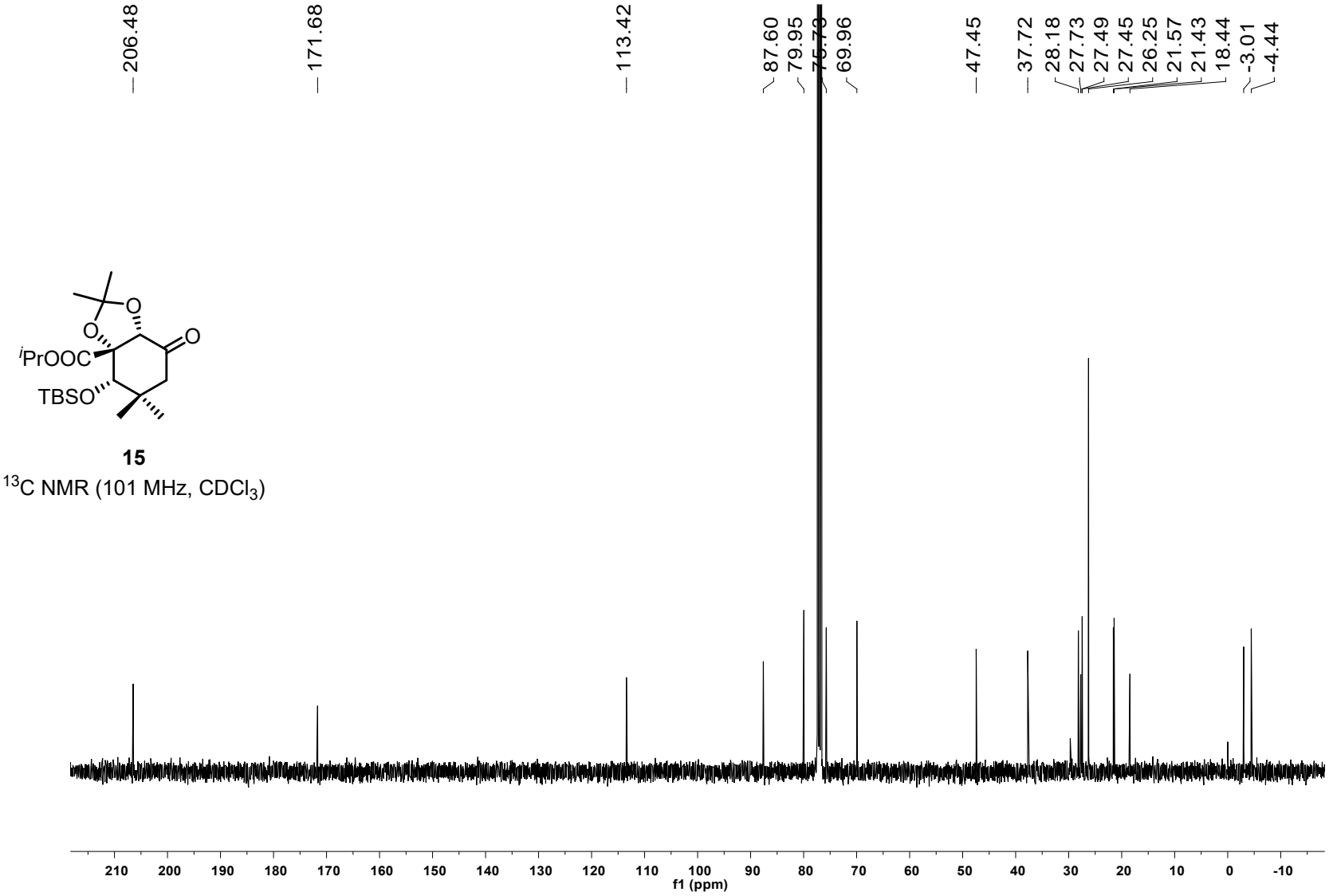


NOESY spectrum of **14**



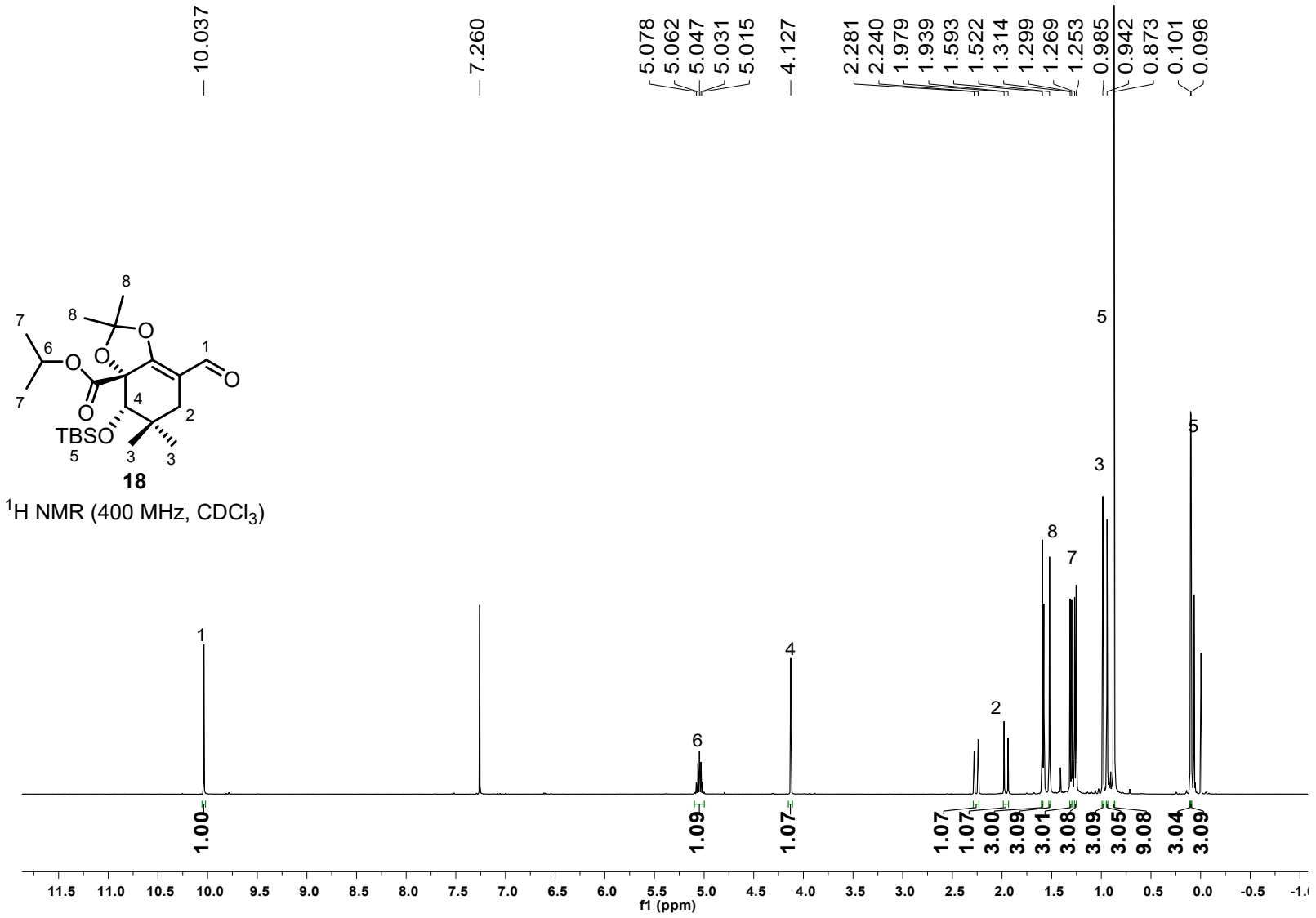
15

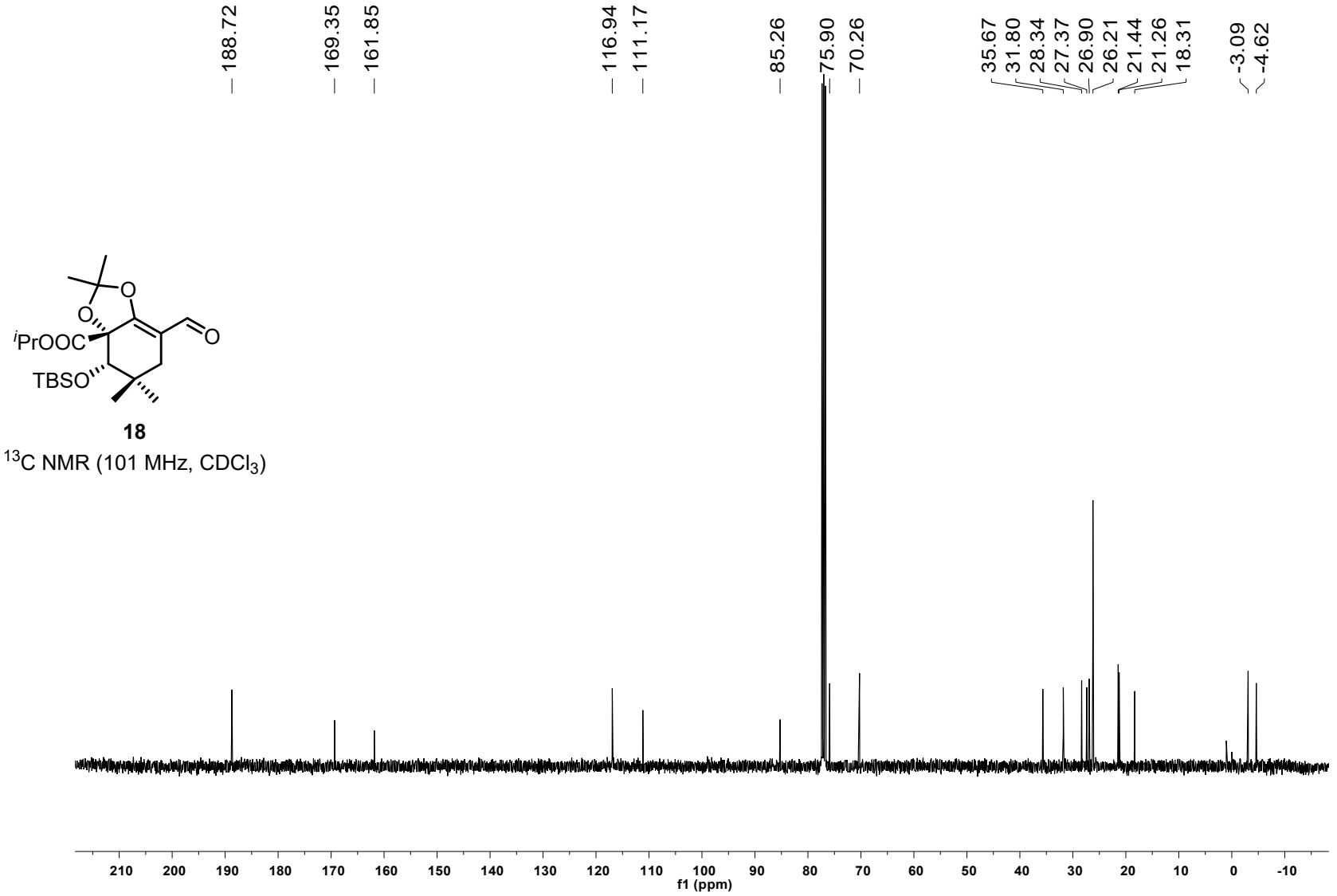
^{1}H NMR (400 MHz, $CDCl_3$)



15

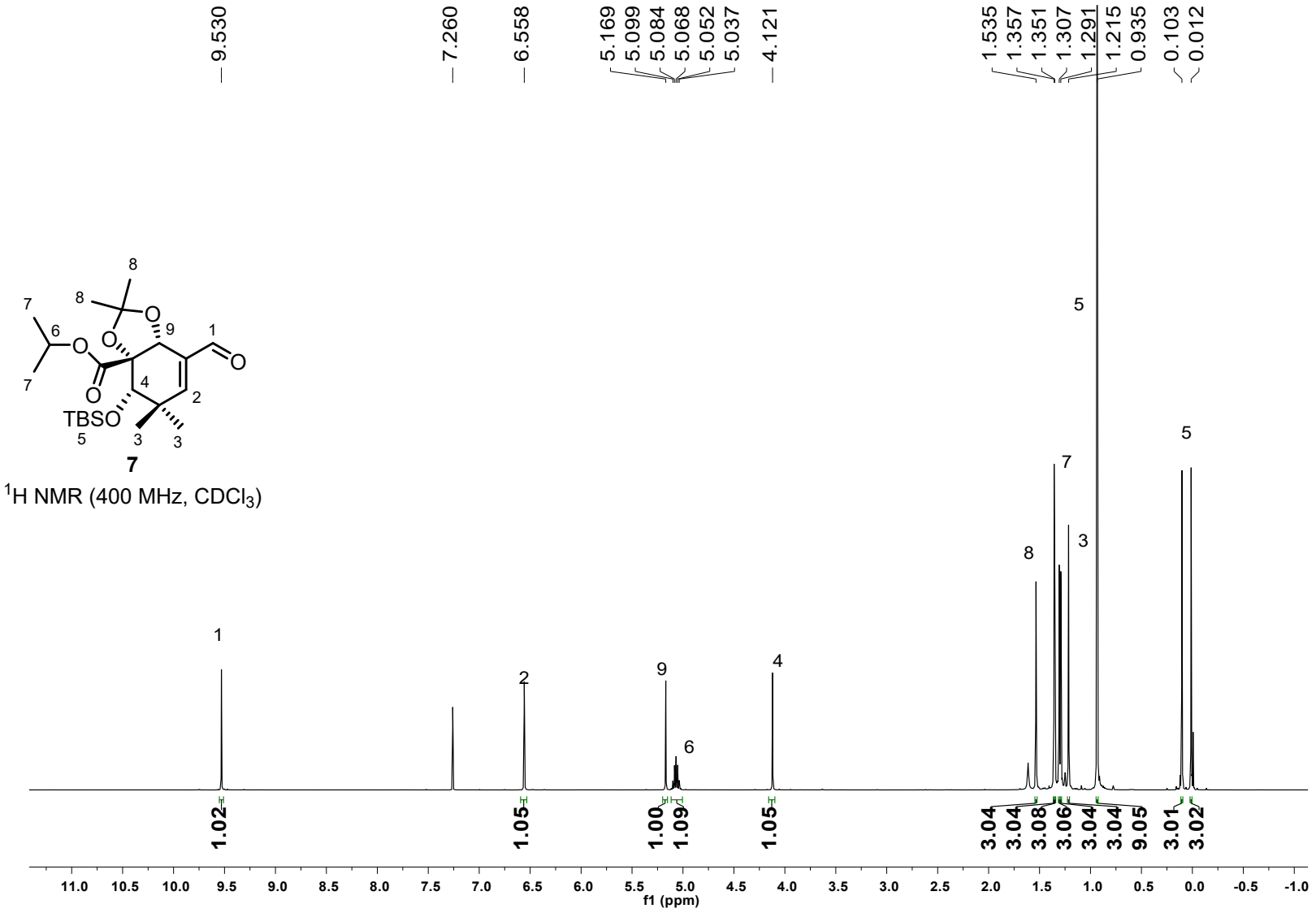
^{13}C NMR (101 MHz, $CDCl_3$)

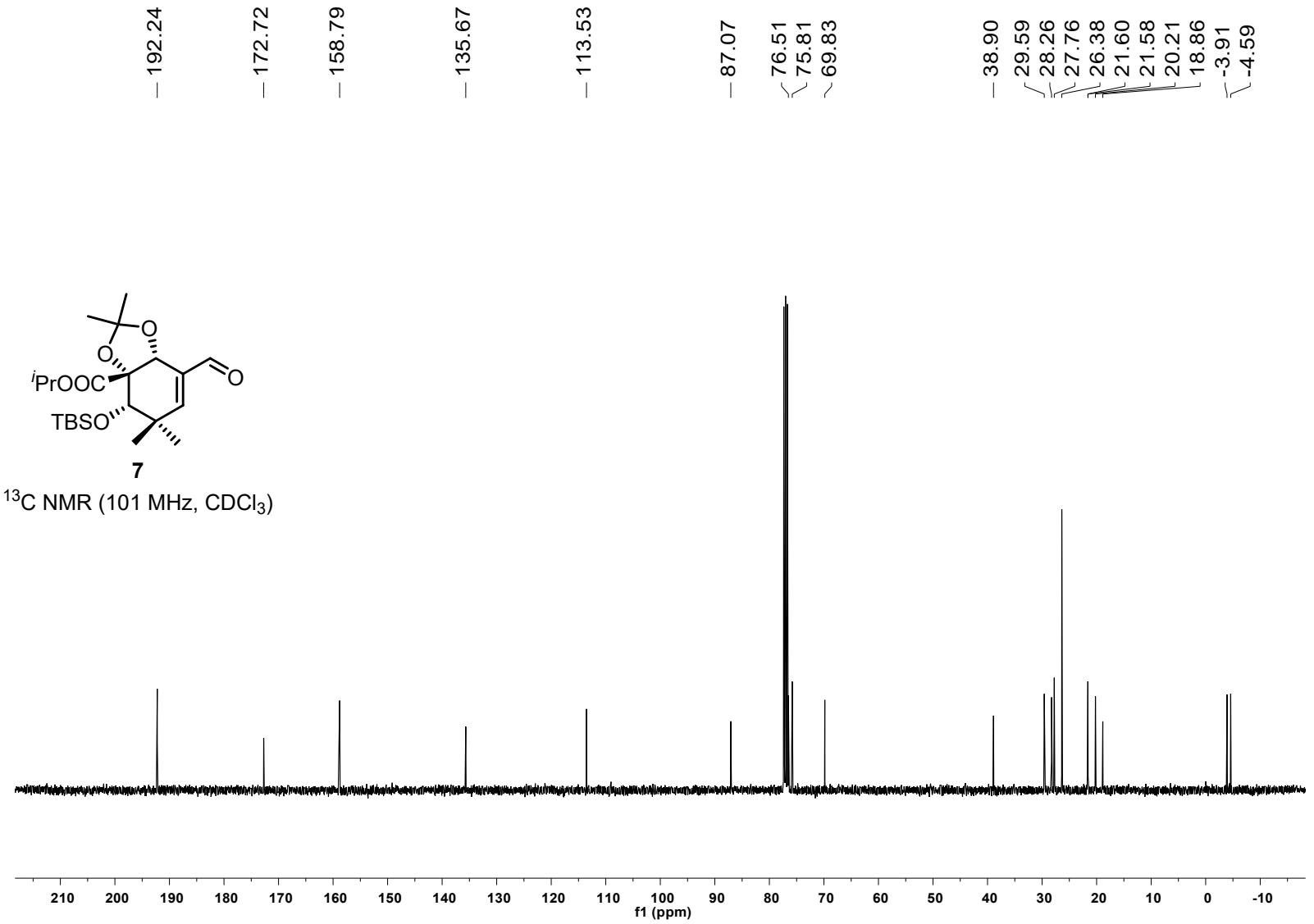

10.037
7.260
5.078
5.062
5.047
5.031
5.015
4.127
2.281
2.240
1.979
1.939
1.593
1.522
1.314
1.299
1.269
1.253
0.985
0.942
0.873
0.101
0.096
TBSO
18
1H NMR (400 MHz, CDCl3)
1.00
1.09
1.07
1.07
1.07
3.00
3.09
3.01
3.08
3.09
3.05
9.08
3.04
3.09
f1 (ppm)



18

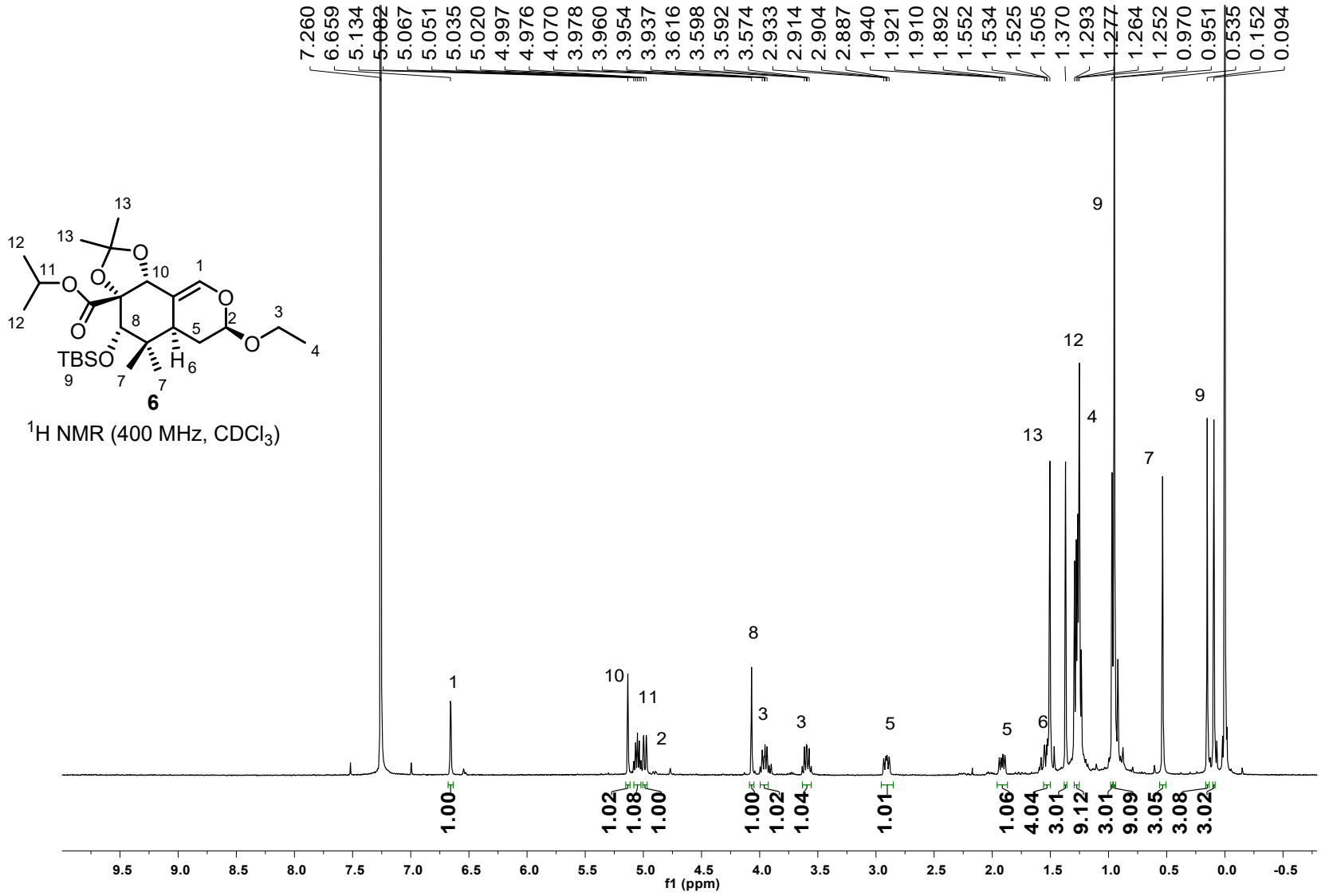
^{13}C NMR (101 MHz, $CDCl_3$)

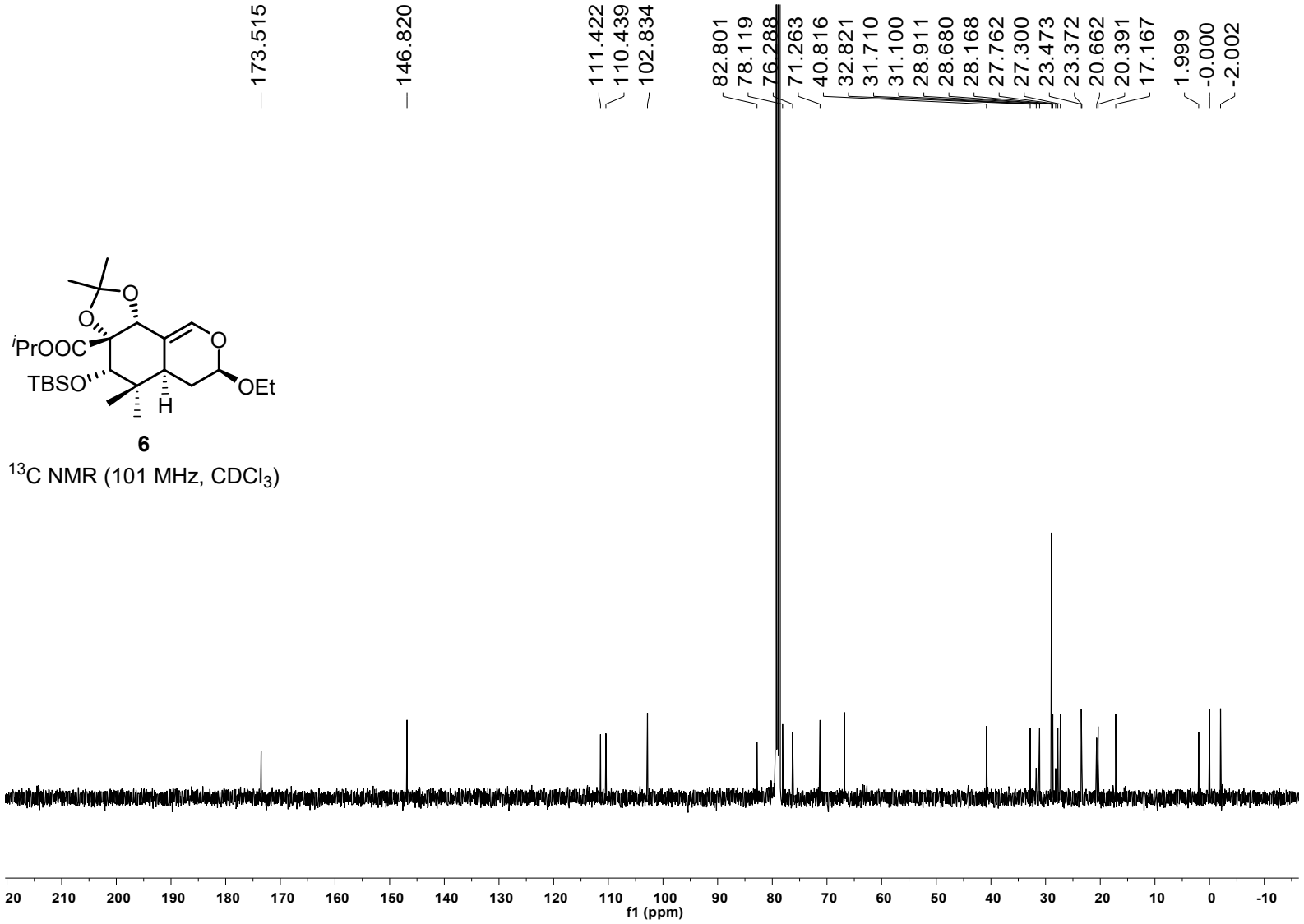

9.530
7.260
6.558
5.169
5.099
5.084
5.068
5.052
5.037
4.121
1.535
1.357
1.351
1.307
1.291
1.215
0.935
0.103
0.012
TBSO
7
1H NMR (400 MHz, CDCl3)
1.02
1.05
1.00
1.09
1.05
3.04
3.04
3.08
3.06
3.04
3.04
9.05
3.01
3.02
f1 (ppm)



7

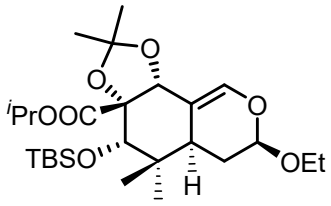
^{13}C NMR (101 MHz, $CDCl_3$)


7.260
6.659
5.134
5.082
5.067
5.051
5.035
5.020
4.997
4.976
4.070
3.978
3.960
3.954
3.937
3.616
3.598
3.592
3.574
2.933
2.914
2.904
2.887
1.940
1.921
1.910
1.892
1.552
1.534
1.525
1.505
1.370
1.293
1.277
1.264
1.252
0.970
0.951
0.535
0.152
0.094
TBSO
6
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.08
1.00
1.00
1.02
1.04
1.01
1.06
4.04
3.01
9.12
3.01
9.09
3.05
3.08
3.02
f1 (ppm)

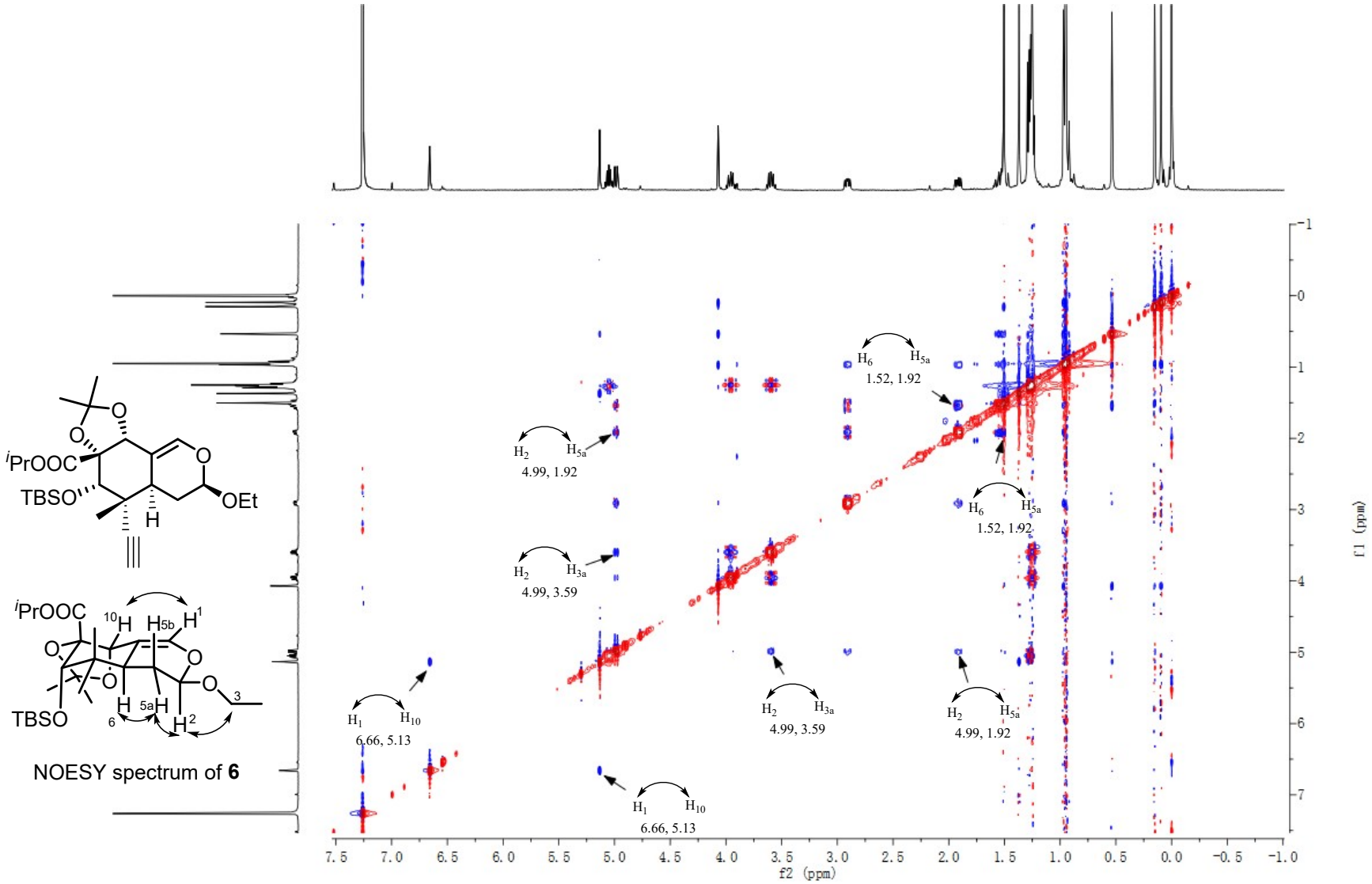


6

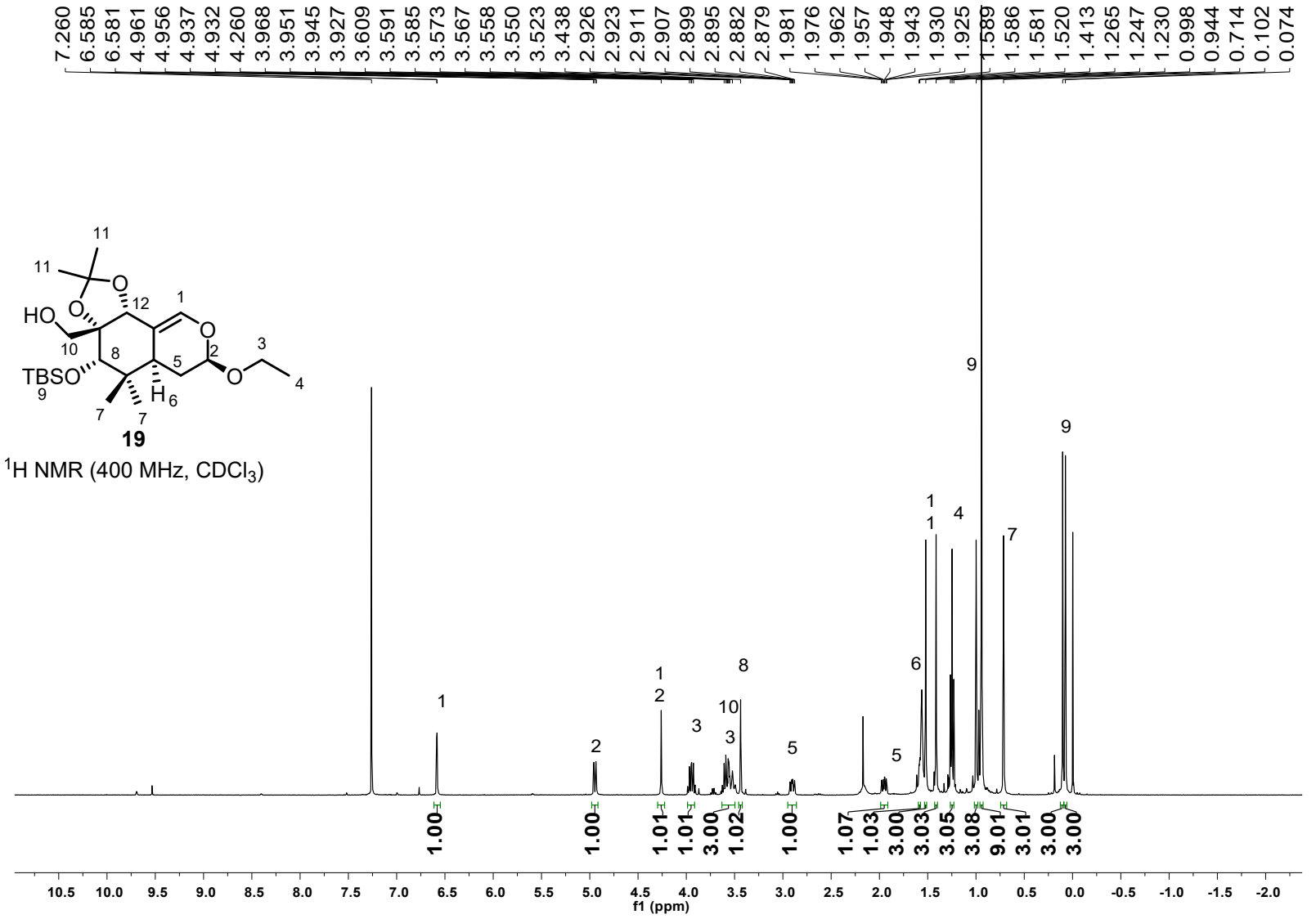
^{13}C NMR (101 MHz, $CDCl_3$)

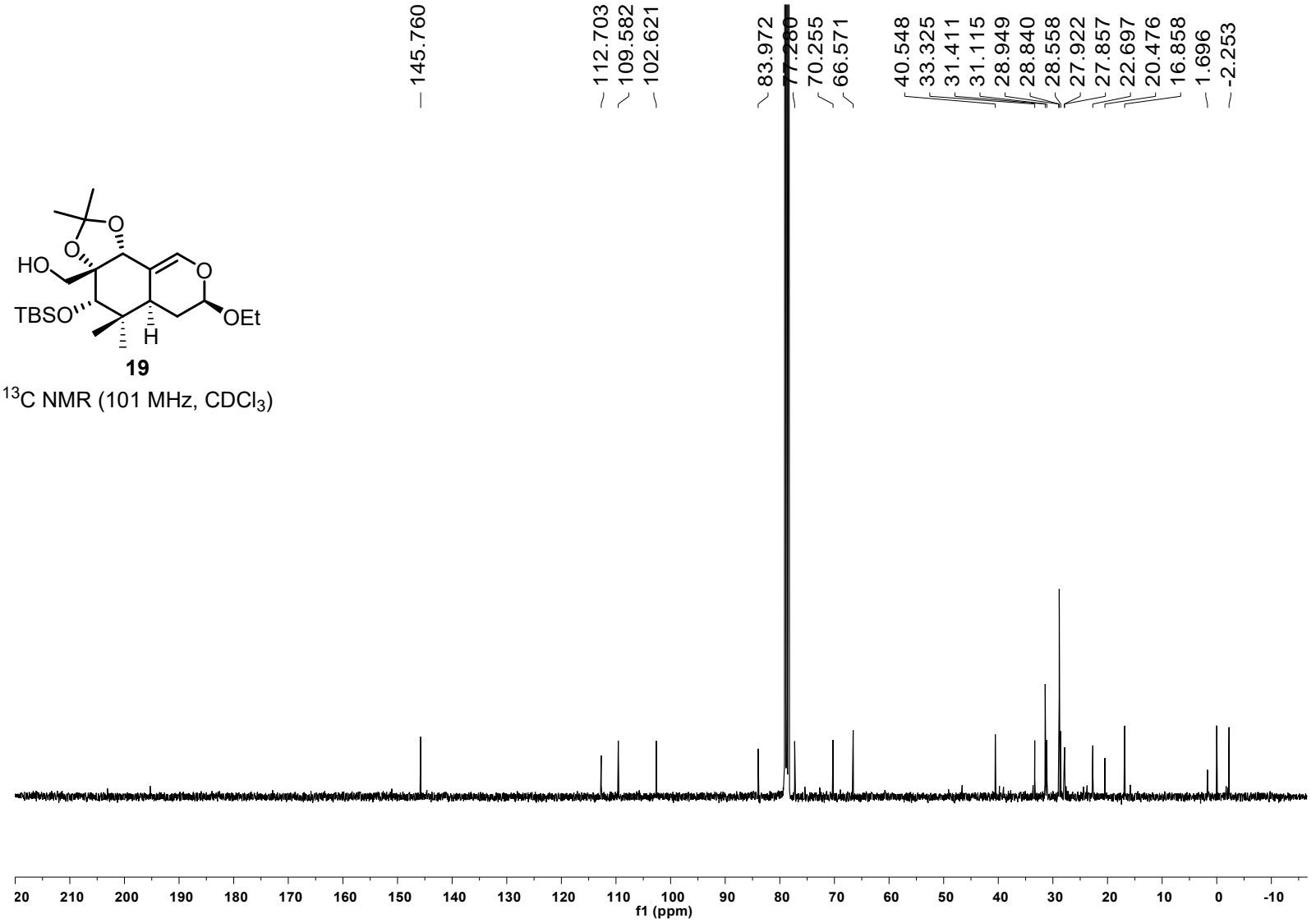


COSY spectrum of **6**



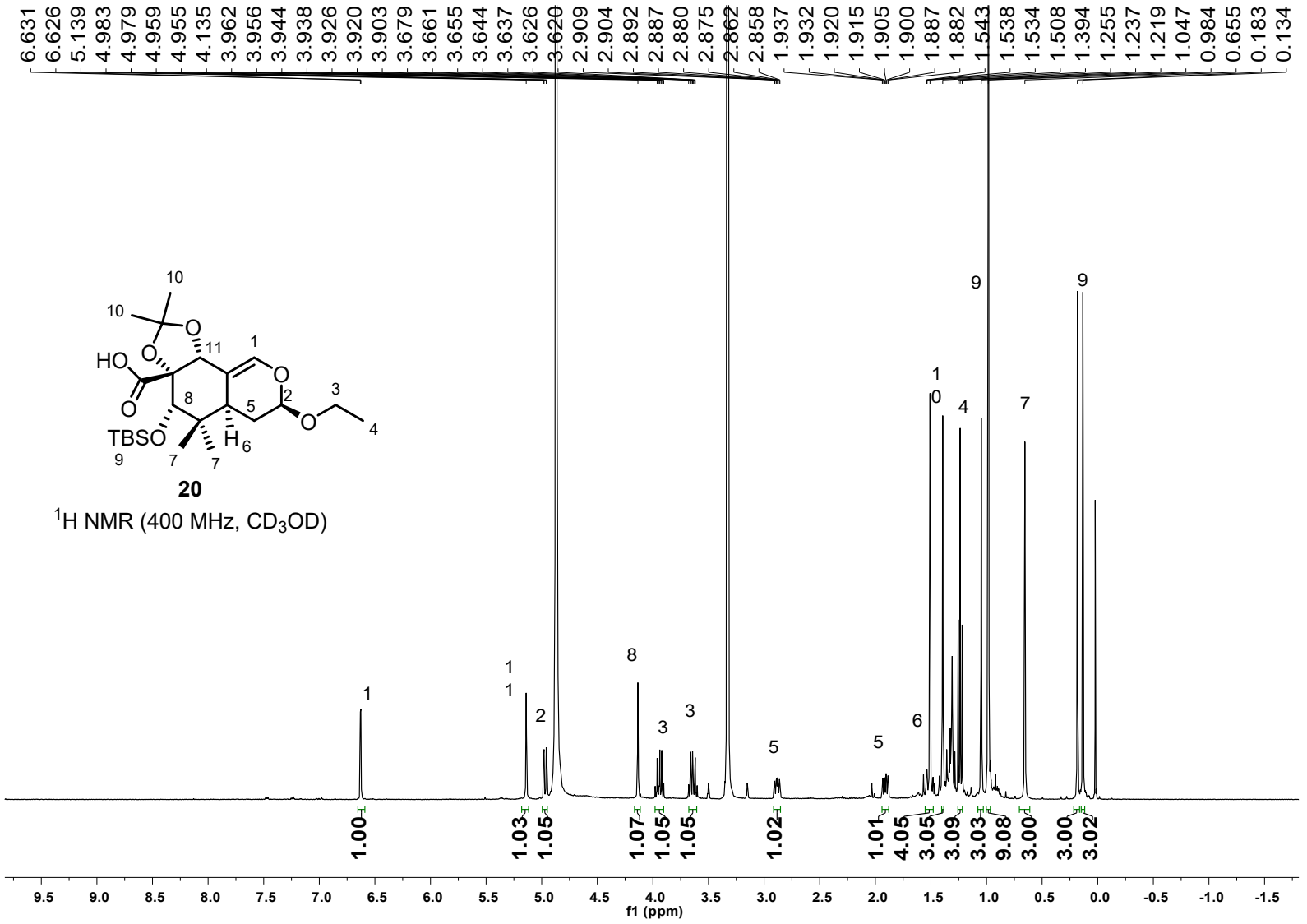
NOESY spectrum of **6**

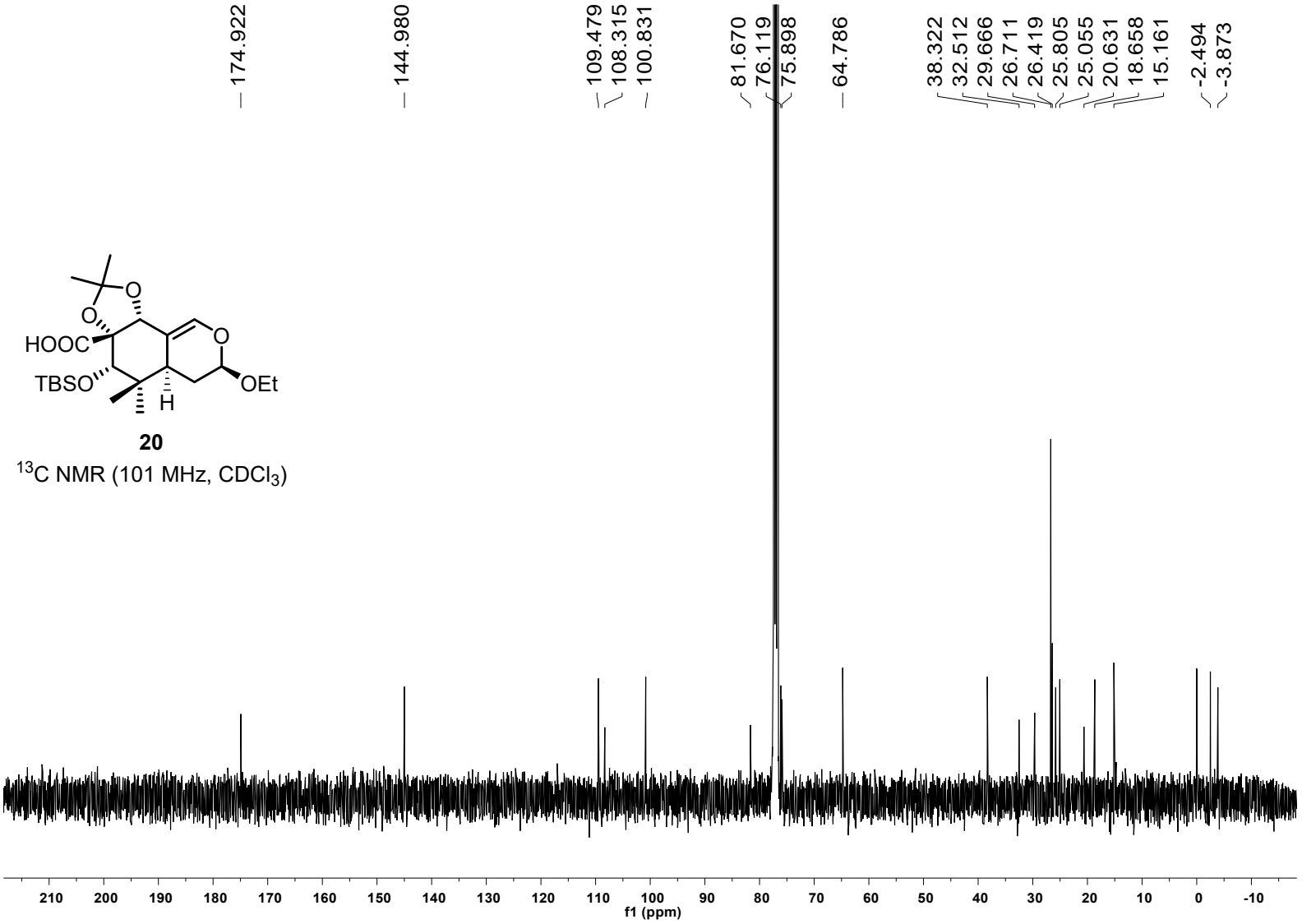

7.260
6.585
6.581
4.961
4.956
4.937
4.932
4.260
3.968
3.951
3.945
3.927
3.609
3.591
3.585
3.573
3.567
3.558
3.550
3.523
3.438
2.926
2.923
2.911
2.907
2.899
2.895
2.882
2.879
1.981
1.976
1.962
1.957
1.948
1.943
1.930
1.925
1.589
1.586
1.581
1.520
1.413
1.265
1.247
1.230
0.998
0.944
0.714
0.102
0.074
HO
TBSO
H6
19
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.01
1.01
3.00
1.02
1.00
1.07
1.03
3.00
3.03
3.05
3.08
9.01
3.01
3.00
3.00
f1 (ppm)



19

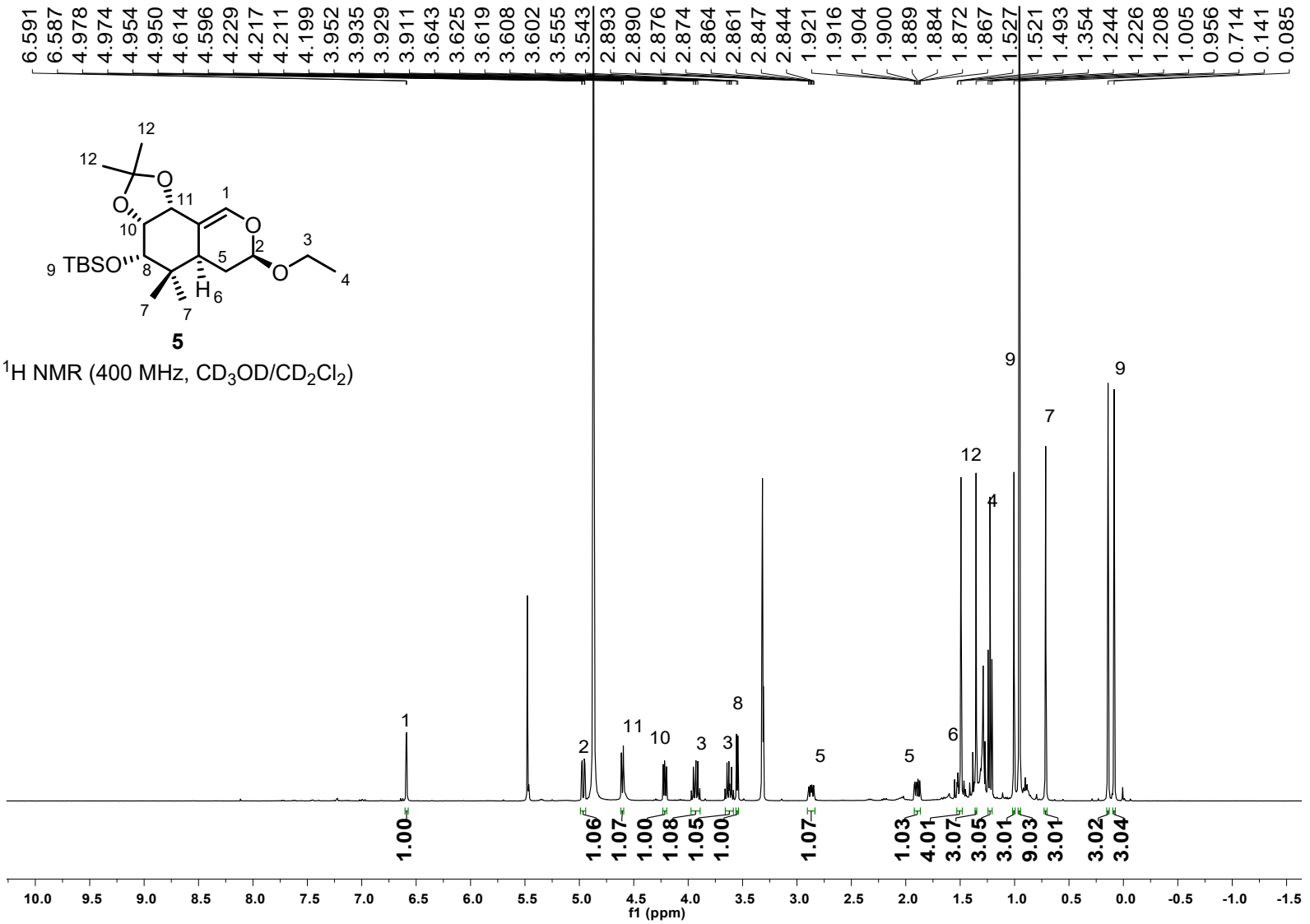
^{13}C NMR (101 MHz, $CDCl_3$)

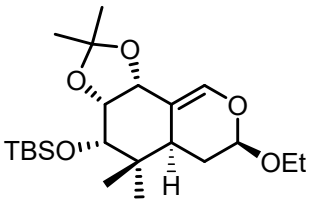

6.631
6.626
5.139
4.983
4.979
4.959
4.955
4.135
3.962
3.956
3.944
3.938
3.926
3.920
3.903
3.679
3.661
3.655
3.644
3.637
3.626
3.620
2.909
2.904
2.892
2.887
2.880
2.875
2.862
2.858
1.937
1.932
1.920
1.915
1.905
1.900
1.887
1.882
1.543
1.538
1.534
1.508
1.394
1.255
1.237
1.219
1.047
0.984
0.655
0.183
0.134
HO
TBSO
H6
20
1H NMR (400 MHz, CD3OD)
1.00
1.03
1.05
1.07
1.05
1.05
1.02
1.01
4.05
3.05
3.09
3.03
9.08
3.00
3.00
3.02
f1 (ppm)



20

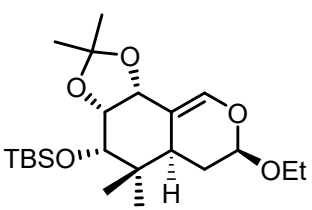
^{13}C NMR (101 MHz, $CDCl_3$)


6.591 6.587 4.978 4.974 4.954 4.950 4.614 4.596 4.229 4.217 4.211 4.199 3.952 3.935 3.929 3.911 3.643 3.625 3.619 3.608 3.602 3.555 3.543 2.893 2.890 2.876 2.874 2.864 2.861 2.847 2.844 1.921 1.916 1.904 1.900 1.889 1.884 1.872 1.867 1.527 1.521 1.493 1.354 1.244 1.226 1.208 1.005 0.956 0.714 0.141 0.085
9 TBSO
H6
5
1H NMR (400 MHz, CD3OD/CD2Cl2)
1.00 1.06 1.07 1.00 1.08 1.05 1.00 1.07 1.03 4.01 3.07 3.05 3.01 9.03 3.01 3.02 3.04
f1 (ppm)

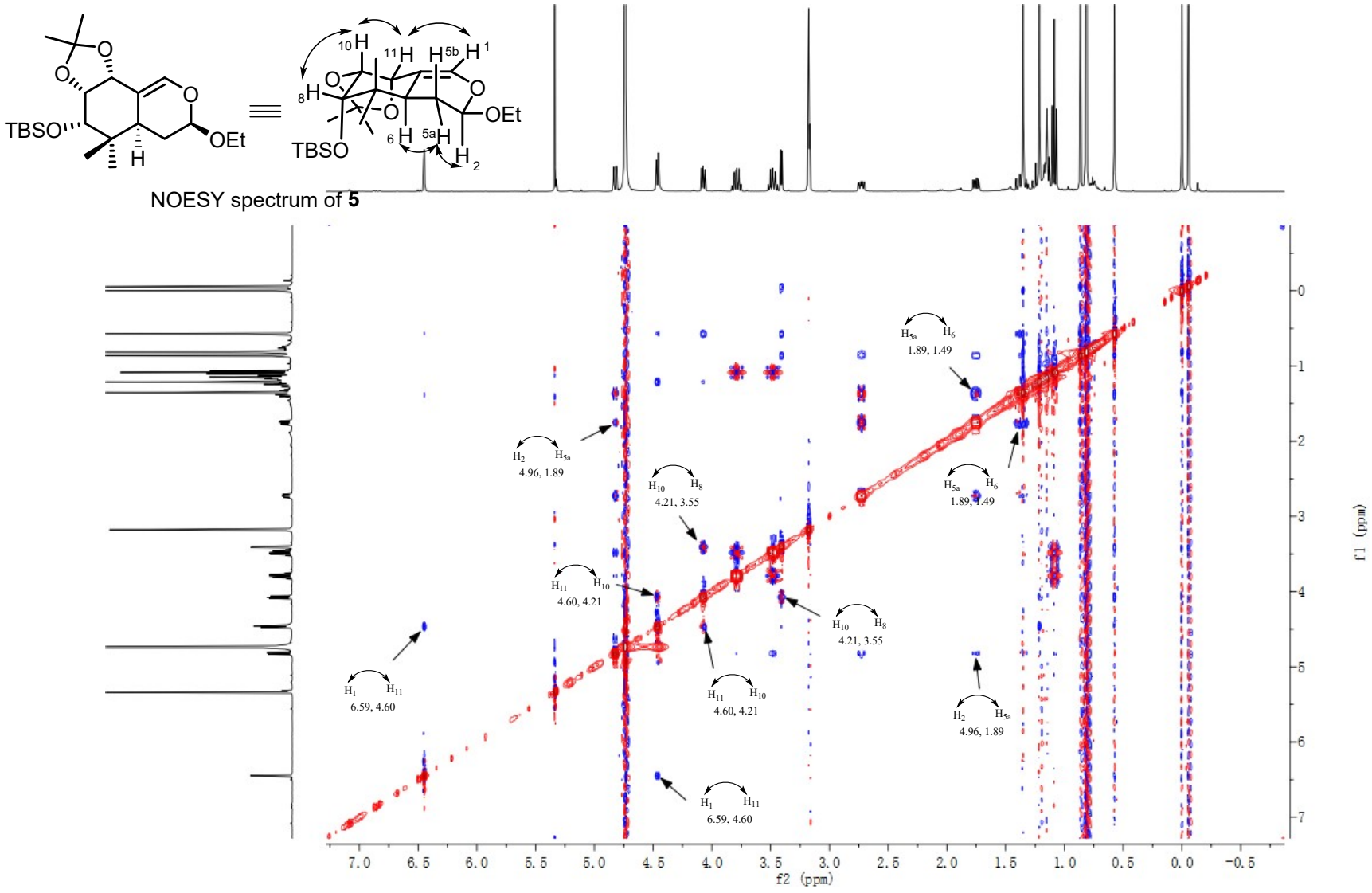


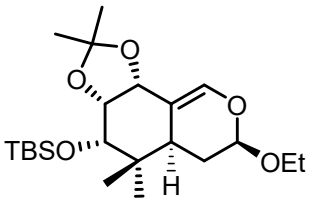
5

^{13}C NMR (101 MHz, CD_3OD/CD_2Cl_2)

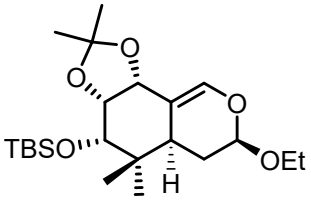


COSY spectrum of **5**


TBSO
OEt
H
TBSO
OEt
NOESY spectrum of 5
H2 H5a
4.96, 1.89
H10 H8
4.21, 3.55
H11 H10
4.60, 4.21
H1 H11
6.59, 4.60
H5a H6
1.89, 1.49
H10 H8
4.21, 3.55
H11 H10
4.60, 4.21
H5a H6
1.89, 1.49
H2 H5a
4.96, 1.89
H1 H11
6.59, 4.60
f2 (ppm)
f1 (ppm)



HMQC spectrum of **5**



HMBC spectrum of **5**