Supporting Information

Forging the tricyclic core framework of euphordraculoate B via a Barbier-type allyl addition

Lingduan Meng, Jingjing Liu, Zeying Sun, Yangdong Hou*, Qingyun Huang*, Pingping Tang*

State Key Laboratory and Institute of Elemento-Organic Chemistry

College of Chemistry, Nankai University, Tianjin 300071, China

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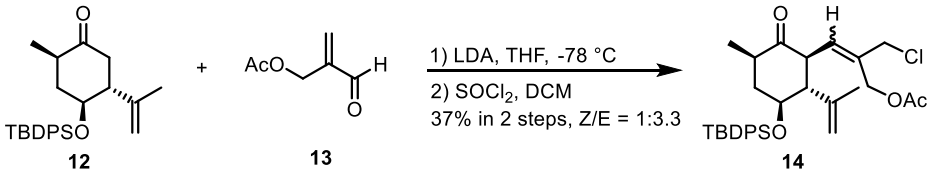
1. General method

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) and toluene were distilled immediately before use from sodium-benzophenone ketyl. Methylene chloride (CH_2Cl_2) and triethylamine (Et_3N) were distilled from calcium hydride and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Tianjin Reagents Chemical. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel Huanghai HSGF254 plates using UV light as visualizing agent and aqueous phosphomolybdic acid or basic aqueous potassium permanganate as developing agent. 200–300 mesh silica gel purchased from Qingdao Haiyang Chemical Co., China was used for flash column chromatography. NMR spectra were recorded on Bruker AVANCE AV 400, 600, 800 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{1}H: 800 MHz, ^{13}C: 201 MHz) instrument and calibrated by using residual undeuterated chloroform (δH = 7.26 ppm) and $CDCl_3$ (δC = 77.16 ppm) as internal references. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quint = quintet. High–resolution mass spectra (HRMS) were obtained on Varian 7.0T FTMS. X–ray diffraction was realized on a Rigaku 007 Saturn 70 instrument.

2. Experimental Procedures

Compound **10**, **11** and **12** were synthesized based on a literature procedure [1][2].

Synthesis of 14



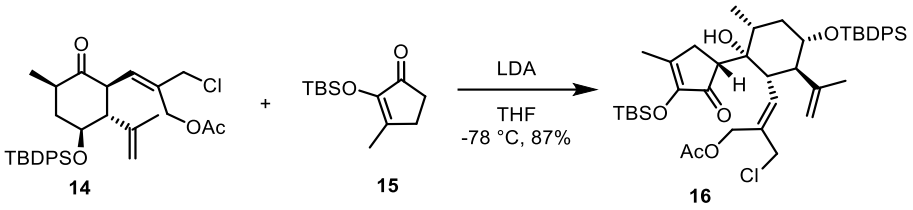
To a solution of ketone **12** (6.27 g, 15.4 mmol, 1.0 equiv) in THF (250 mL), LDA (2.0 M THF solution, 9.3 mL, 18.5 mmol, 1.2 equiv) was added at -78 °C. After stirring at -78 °C for 15 minutes, a solution of **13** (4 g, 30.8 mmol, 2.0 equiv) in 50 mL THF was slowly added to the mixture under nitrogen. The reaction mixture was stirred at -78 °C for 2 hours, and then saturated ammonium chloride solution was added to the mixture. The resultant mixture was raised to room temperature and stirred for additional 30 minutes. The reaction mixture was extracted with EA for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was used in the next reaction without further purification.

2, 6-Lutidine (16.1 mL, 138.6 mmol, 9.0 equiv) was added to the solution of crude product in DCM (300 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 5 minutes, $SOCl_2$ (10 mL, 138.6 mmol, 9.0 equiv) was slowly added to the mixture. The resultant mixture was raised to room temperature and stirred for 30 minutes, and then the mixture was cooled to 0 °C again. Saturated $NaHCO_3$ solution was added dropwise until foaming stopped, extracted with DCM for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to obtain the product **14** 3.1 g in 37% yield over 2 steps, colorless oil, Z:E = 1:3.3.

$[\alpha]_D^{20}$ = +10.1 (*c* = 2.5, CH_2Cl_2).

(*E*)-**14**: R_f = 0.51 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (800 MHz, Chloroform-*d*) δ 7.72 – 7.69 (m, 2H), 7.66 – 7.63 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.37 (m, 4H), 5.58 (d, *J* = 9.4 Hz, 1H), 4.88 (s, 1H), 4.82 (s, 1H), 4.55 (d, *J* = 12.5 Hz, 1H), 4.41 (d, *J* = 12.5 Hz, 1H), 4.16 (d, *J* = 11.3 Hz, 1H), 4.10 (d, *J* = 11.3 Hz, 1H), 4.05 – 4.01 (m, 1H), 3.23 (dd, *J* = 12.4, 9.4 Hz, 1H), 2.47 (dd, *J* = 12.4, 9.8 Hz, 1H), 2.28 – 2.22 (m, 1H), 1.97 (s, 4H), 1.49 (s, 3H), 1.32 – 1.28 (m, 1H), 1.00 (s, 9H), 0.84 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (201 MHz, $CDCl_3$) δ 209.1, 170.7, 142.3, 136.0, 135.9, 134.5, 133.4, 133.1, 131.8, 129.9, 129.6, 127.6, 127.4, 115.4, 71.2, 60.0, 59.3, 49.6, 47.3, 43.9, 41.9, 26.8, 20.8, 19.2, 14.1.

Synthesis of 16

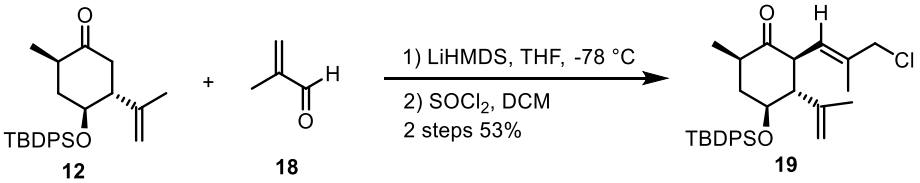


LDA (2.0 M THF solution, 2.5 mL, 5.04 mmol, 3.2 equiv) was added to a solution of ketone **15** (1.06 g, 4.72 mmol, 3.0 equiv) in THF (25 mL) at -78 °C. After the reaction mixture was stirred at -78 °C for 15 minutes, a solution of **14** (870 mg, 1.57 mmol, 1.0 equiv) in 10 mL THF was slowly added to the mixture under nitrogen. The reaction mixture was stirred at -78 °C for 2 hours, and then saturated ammonium chloride solution was added to the mixture. The resultant mixture was raised to room temperature and stirred for additional 30 minutes. The reaction mixture was extracted with EA for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to obtain the product **16** 1.0 g in 87% yield, colorless oil, d.r. = 9:1.

$[\alpha]_D^{20}$ = +124.2 (*c* = 0.3, CH_2Cl_2).

R_f = 0.73 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (m, 4H), 7.45 – 7.32 (m, 6H), 5.96 (s, 1H), 5.28 (s, 1H), 4.78 (s, 1H), 4.60 – 4.52 (m, 2H), 4.10 (s, 2H), 3.49 (m, 1H), 2.50 (s, 1H), 2.21 – 2.17 (m, 1H), 2.08 (m, 1H), 2.04 (s, 3H), 1.99 (t, *J* = 11.4 Hz, 1H), 1.89 (s, 3H), 1.80 (q, *J* = 11.9 Hz, 1H), 1.37 – 1.21 (m, 3H), 1.25 (s, 3H), 0.97 (s, 9H), 0.92 (s, 9H), 0.48 (d, *J* = 6.7 Hz, 3H), 0.15 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.9, 170.7, 150.9, 148.2, 136.0, 135.1, 129.5, 129.3, 127.4, 127.2, 77.2, 59.6, 47.8, 47.4, 39.2, 36.1, 29.7, 29.6, 29.4, 26.8, 25.6, 20.8, 19.3, 18.2, 17.6, 14.7. HRMS-ESI (m/z): Calcd. for $C_{44}H_{63}ClNaO_6Si_2$ $[M + Na]^+$: 801.3749. Found, 801.3751.

Synthesis of 19



LiHMDS (1.0 M THF solution, 16.0 mL, 16.01 mmol, 1.3 equiv) was added to a solution of ketone **12** (5 g, 12.3 mmol, 1.0 equiv) in THF (100 mL) at -78 °C. After the reaction mixture was stirred at -78 °C for 15 minutes, a solution of **18** (5.0 mL, 61.5 mmol, 5.0 equiv) in 20 mL THF

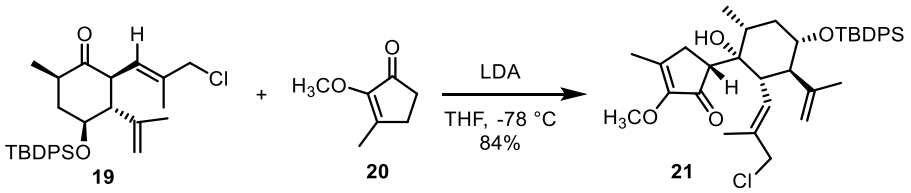
solution was slowly added to the mixture under nitrogen. The reaction mixture was stirred at -78 °C for 2 hours, and then saturated ammonium chloride solution was added to the mixture. The resultant mixture was raised to room temperature and stirred for additional 30 minutes. The reaction mixture was extracted with EA for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was used in the next reaction without further purification.

2, 6-Lutidine (12.8 mL, 110.9 mmol, 9.0 equiv) was added to a solution of aldol crude product in DCM (250 mL) at 0 °C. After the reaction mixture was stirred at 0 °C for 5 minutes, $SOCl_2$ (8.0 mL, 110.9 mmol, 9.0 equiv) was slowly added to the mixture. The resultant mixture was raised to room temperature and stirred for 30 minutes, and then the mixture was cooled to 0 °C again. Saturated $NaHCO_3$ solution was added dropwise until foaming stopped, extracted with DCM for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to obtain the product **19** 3.1 g in 53% yield over 2 steps, colorless oil, only E.

$[\alpha]_D^{20}$ = +110.5 (*c* = 0.2, CH_2Cl_2).

R_f = 0.55 (petroleum ether/ethyl acetate = 3/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.56 (m, 4H), 7.35 (m, 6H), 5.25 (d, *J* = 9.3 Hz, 1H), 4.80 (s, 1H), 4.74 (s, 1H), 3.99 – 3.91 (m, 3H), 2.97 (dd, *J* = 12.4, 9.3 Hz, 1H), 2.39 (dd, *J* = 12.3, 9.9 Hz, 1H), 2.15 (dt, *J* = 13.1, 6.1 Hz, 1H), 1.90 (dt, *J* = 12.8, 4.8 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 0.93 (s, 9H), 0.77 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 142.4, 136.0, 135.9, 134.6, 134.2, 133.2, 129.8, 129.6, 127.6, 127.4, 126.4, 115.2, 71.3, 60.1, 51.8, 49.8, 43.4, 42.0, 26.8, 19.3, 19.1, 14.6, 14.2. HRMS-ESI (m/z): Calcd. for $C_{30}H_{39}ClNaO_2Si$ $[M + Na]^+$: 517.2306. Found, 517.2305.

Synthesis of 21



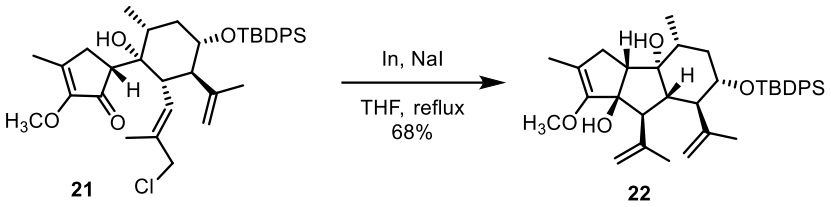
LDA (2.0 M THF solution, 3.2 mL, 6.47 mmol, 3.2 equiv) was added to a solution of enone **20** (760 mg, 6.07 mmol, 3.0 equiv) in THF (30 mL) at -78 °C. After the reaction mixture was stirred at -78 °C for 15 minutes, a solution of **19** (1 g, 2.02 mmol, 1.0 equiv) in 10 mL THF was slowly added to the mixture under nitrogen. The reaction mixture was stirred at -78 °C for 2 hours, and then saturated ammonium chloride solution was added to the mixture. The resultant mixture was raised to room temperature and stirred for additional 30 minutes. The reaction mixture was extracted with EA for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to obtain the product **21** 1.05 g in 84% yield, colorless oil, d.r. = 8:1.

$[\alpha]_D^{20}$ = +173.0 (*c* = 0.2, CH_2Cl_2).

R_f = 0.35 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 4H), 7.45 – 7.31 (m, 6H), 5.64 (d, *J* = 10.6 Hz, 1H), 5.22 (s, 1H), 4.76 (s, 1H), 4.68 (s, 1H), 4.01 (s, 2H), 3.81 (s, 3H), 3.51 (td, *J* = 10.7, 10.2, 3.9 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.54 (s, 1H), 2.30 – 2.06 (m, 2H), 1.95 (s, 3H), 1.81 (d, *J* = 11.8 Hz, 1H), 1.64 (s, 3H), 1.49 (m, 2H), 1.45 – 1.32 (m, 1H), 0.97 (s, 9H), 0.52 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.9, 153.9,

151.5, 136.1, 136.0, 135.2, 133.9, 129.4, 129.2, 127.3, 127.2, 77.7, 58.3, 52.5, 48.5, 39.5, 36.2, 30.4, 26.8, 19.3, 17.6, 15.2, 14.8. HRMS-ESI (m/z): Calcd. for $C_{37}H_{49}ClNaO_4Si$ $[M + Na]^+$: 643.2986. Found, 643.2985.

Synthesis of 22



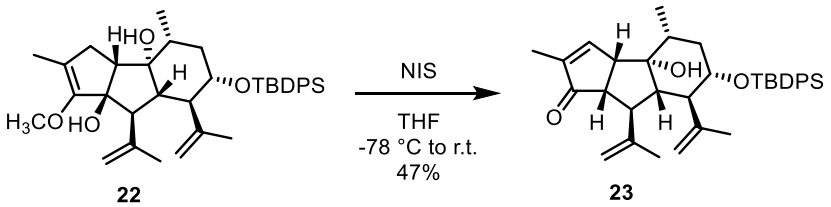
In powder (376 mg, 3.22 mmol, 20.0 equiv) and NaI (120 mg, 0.81 mmol, 5.0 equiv) were added to a solution of **21** (100 mg, 0.16 mmol, 1.0 equiv) in THF (3.2 mL) under nitrogen. The reaction mixture was stirred at 90 °C for 30 minutes, and then cooled to room temperature. 10 mL Et_2O was added into the mixture, and filtered through a pad of Celite with Et_2O washing (5 mL*3). The filtrate was washed by saturated $Na_2S_2O_3$ solution, and dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to obtain the product **22** 63mg in 68% yield, white solid, d.r.>20:1.

Note: The product **22** is sensitive to acid. During the column chromatography process, the silica gel should be alkalized with petroleum ether containing 1% Et_3N.

$[\alpha]_D^{20}$ = +87.9 (*c* = 0.5, CH_2Cl_2).

R_f = 0.35 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.30 (m, 6H), 5.11 (s, 1H), 4.87 (s, 1H), 4.66 (s, 1H), 4.63 (s, 1H), 3.74 (s, 3H), 3.57 (td, *J* = 10.9, 10.4, 4.7 Hz, 1H), 2.87 (s, 1H), 2.63 (t, *J* = 10.5 Hz, 1H), 2.45 (m, 2H), 2.10 (d, *J* = 16.2 Hz, 1H), 2.02 (d, *J* = 8.2 Hz, 1H), 1.83 (s, 3H), 1.73 (s, 3H), 1.68 (t, *J* = 12.2 Hz, 1H), 1.57 (m, 2H), 1.45 – 1.38 (m, 1H), 1.26 (s, 3H), 0.98 (s, 9H), 0.75 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.1, 144.7, 136.0, 135.9, 135.3, 134.2, 129.4, 129.2, 127.3, 127.1, 115.5, 114.9, 113.6, 88.3, 78.9, 72.9, 60.1, 54.9, 53.5, 39.3, 39.0, 32.0, 26.9, 19.3, 15.6, 13.1. HRMS-ESI (m/z): Calcd. for $C_{37}H_{50}NaO_4Si$ $[M + Na]^+$: 609.3376. Found, 609.3375. Mp: 104-106℃.

Synthesis of 23



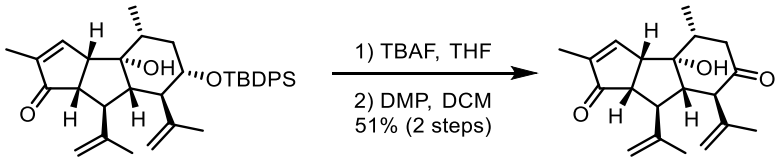
NIS (6.9 mg, 0.03 mmol, 1.0 equiv) was added to a solution of **22** (18 mg, 0.03 mmol, 1.0 equiv) in THF (1.5 mL) at -78 °C under nitrogen. After the reaction mixture was stirred at -78 °C for 1 hour, the resultant mixture was slowly raised to room temperature and stirred for 30 minutes. Saturated $Na_2S_2O_3$ solution was added to the mixture to quench the reaction. The reaction mixture was extracted with EA for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to obtain the product **23** 7.8 mg in 47% yield, white solid.

Note: The product **23** is sensitive to acid. During the column chromatography process, the silica gel should be alkalized with petroleum ether containing 1% Et_3N.

$[\alpha]_D^{20}$ = +102.2 (*c* = 0.15, CH_2Cl_2).

R_f = 0.45 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.38 (m, 6H), 6.97 (s, 1H),4.82 (s, 1H), 4.75 (s, 1H), 4.73 (s, 1H), 4.72 (s, 1H), 3.55 (td, *J* = 10.5, 4.5 Hz, 1H), 2.93 (s, 1H), 2.56 (m, 2H), 2.44 (t, *J* = 10.7 Hz, 1H), 1.78 (s, 3H), 1.71 (s, 3H), 1.67 (t, *J* = 11.4 Hz, 1H), 1.55 (m, 5H), 1.40 (m, 2H), 0.97 (s, 9H), 0.80 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.8, 151.5, 144.7, 136.0, 136.0, 135.3, 133.8, 129.5, 129.2, 127.3, 127.2, 78.9, 53.1, 39.4, 38.1, 26.8, 19.4, 15.8, 10.6.

Synthesis of 24



23 **24**

TBAF (1.0 M THF, 0.1 mL, 0.1 mmol, 5.0 equiv) was added to a solution of **23** (12 mg, 0.02 mmol, 1.0 equiv) in THF (0.4 mL) at room temperature. After the reaction mixture was stirred for 4 hours, water (3 mL) was added. The reaction mixture was extracted with EA for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product, which was used in the next reaction without further purification.

DMP (42.4 mg, 0.1 mmol, 5.0 equiv) was added to a solution of the crude product in DCM (1 mL) at room temperature. The mixture was stirred for 4 hours. Then the mixture was filtered through a pad of Celite with DCM washing (5 mL*3). The filtrate was washed with saturated $NaHCO_3$ solution. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 3/1) to obtain the product **24** 3.2 mg in 51% yield over 2 steps, white solid.

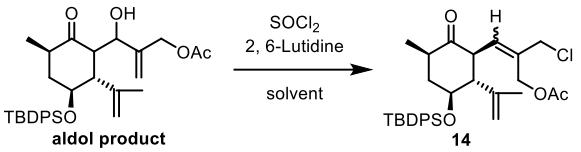
Note: The product **24** is sensitive to acid. During the column chromatography process, the silica gel should be alkalized with petroleum ether containing 1% Et_3N.

$[\alpha]_D^{20}$ = +115.6 (*c* = 0.15, CH_2Cl_2).

R_f = 0.65 (petroleum ether/ethyl acetate = 1/1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.09 (s, 1H), 4.87 (s, 2H), 4.84 (s, 1H), 4.74 (s, 1H), 3.31 (d, *J* = 12.2 Hz, 1H), 3.25 (d, *J* = 7.4 Hz, 1H), 2.78 (t, *J* = 7.2 Hz, 1H), 2.66 (dd, *J* = 11.1, 7.3 Hz, 1H), 2.41 (m, 1H), 2.33 (m, 2H), 2.14 (dt, *J* = 12.6, 6.3 Hz, 1H), 1.85 (s, 3H), 1.78 (s, 3H), 1.63 (s, 3H), 1.07 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.4, 208.0, 149.2, 145.0, 143.9, 139.5, 115.3, 112.5, 77.8, 58.1, 56.3, 54.9, 51.6, 48.8, 43.8, 37.8, 28.6, 19.6, 19.4, 15.0, 9.7. HRMS-ESI (m/z): Calcd. for $C_{20}H_{26}NaO_3$ $[M + Na]^+$: 337.1780. Found, 337.1788.

3. Reaction Exploration and Optimization

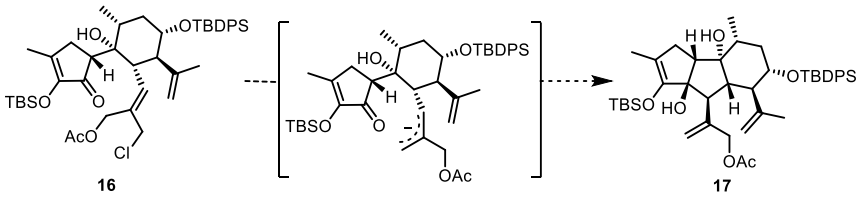
3.1 Optimization of **14**



Entry	Solvent	Result
1	Et_2O/*n*-Hexane = 3:2	61%, Z/E = 1:2.8
2	Et_2O	65%, Z/E = 1:3.3
3	DCM	72%, Z/E = 1:3.3
4	Toluene	56%, Z/E = 1:2.6
5	THF	33%, Z/E = 1:3.1
6	Acetone	8%, Z/E = 1:4.0
7	CH_3CN	6%, Z/E = 1:5.1

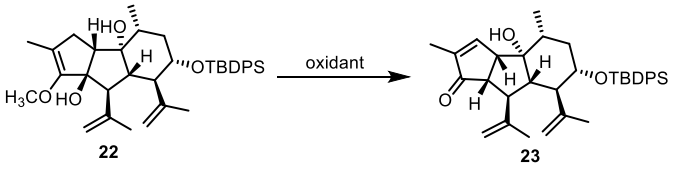
conditions: **aldol product** (1 equiv), $SOCl_2$ (9 equiv), 2, 6-Lutidine (9 equiv), solvents, c = 0.05 mol/L, 0 °C to r.t.

3.2 Exploration of cyclization reactions



Entry	Conditions	Result
1	Zn, NaI, reflux	n.d.
2	$SnCl_2$, NaI, DMF, 60 °C	n.r.
3	$CrCl_2$, Mn, 60 °C	n.r.
4	SmI_2, r.t.	retro-aldol
5	SmI_2, 50 °C	retro-aldol
6	SmI_2, HMPA, r.t.	retro-aldol

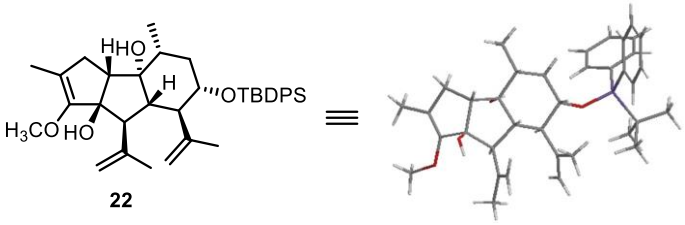
3.3 Optimization of **23**



Entry	Conditions	Result
1	Br_2, DCM, -30 °C	trace
2	Br_2, DCM, -78 °C	5%
3	NBS, THF, -78 °C	trace
4	$PyHBr_3$, DCM, -78 °C	n.d.
5	NIS, THF, -78 °C to r.t.	47%
6	NIS, DCM, -78 °C to r.t.	7%
7	NIS, THF, -30 °C to r.t.	trace
8	NIS, THF, 0 °C to r.t.	trace

conditions: **22** (1 equiv), oxidant (1.2 equiv), solvents, c = 0.02 mol/L

4. X-Ray data



22

Table 1 Crystal data and structure refinement for 22 (CCDC 2354348).

Identification code	22
Empirical formula	$C_{37}H_{50}O_4Si$
Formula weight	586.86
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.62167(13)
b/Å	10.50225(11)
c/Å	15.14865(15)
α/°	90
β/°	93.6459(10)
γ/°	90
Volume/Å^3	1686.43(3)
Z	2
ρ_{calc}g/cm^3	1.156
μ/mm^{-1}	0.106
F(000)	636.0

Crystal size/mm^3	0.28 × 0.26 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.842 to 59.15
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -21 ≤ l ≤ 20
Reflections collected	38186
Independent reflections	9443 [R_{int} = 0.0623, R_{sigma} = 0.0438]
Data/restraints/parameters	9443/3/395
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1083
Final R indexes [all data]	R_1 = 0.0464, wR_2 = 0.1097
Largest diff. peak/hole / e Å^{-3}	0.41/-0.25
Flack parameter	0.06(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 22. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Si1	-7538.3(5)	-4477.2(5)	-1508.8(3)	16.07(12)
O1	-6514.1(13)	-4501.7(15)	-2272.3(9)	20.2(3)
O2	-5729.2(14)	-4290.3(13)	-5096.6(9)	18.0(3)
O3	-2947.5(15)	-7225.5(14)	-5545.6(10)	20.7(3)
O4	-2146.6(16)	-4691.9(16)	-6115.3(10)	28.1(3)

C1	-6891.9(18)	-6111.1(19)	-4528.7(13)	18.0(4)
C2	-7249.8(18)	-5373(2)	-3703.4(13)	17.8(4)
C3	-6219.6(18)	-5378.7(19)	-2950.4(12)	16.0(3)
C4	-4916.0(17)	-4983.1(18)	-3248.3(12)	14.7(3)
C5	-4609.6(17)	-5768.5(18)	-4065.2(12)	14.3(3)
C6	-3386.2(18)	-5434.8(19)	-4506.9(12)	16.3(3)
C7	-3622(2)	-6043.8(18)	-5450.5(12)	17.2(4)
C8	-5049.7(19)	-6300.2(18)	-5593.1(12)	17.7(4)
C9	-5637.0(18)	-5596.2(17)	-4826.6(12)	14.8(3)
C10	-5418(2)	-5821(2)	-6535.0(13)	24.1(4)
C11	-4297(2)	-5079(2)	-6816.6(14)	24.9(4)
C12	-3345(2)	-5175.0(19)	-6203.6(13)	21.5(4)
C13	-7972(2)	-6070(2)	-5248.7(15)	27.9(5)
C14	-3911.2(19)	-5070(2)	-2491.4(13)	19.3(4)
C15	-3184(2)	-4075(2)	-2271.7(17)	32.0(5)
C16	-3763(2)	-6304(2)	-2000.3(14)	27.4(5)
C17	-2140(2)	-5809(2)	-4030.2(14)	24.9(4)
C18	-1914(3)	-6971(3)	-3716.2(16)	34.4(5)
C19	-1142(2)	-4779(3)	-3967.1(19)	39.6(6)
C20	-4433(3)	-4441(3)	-7706.0(15)	39.3(6)
C21	-1728(3)	-3887(3)	-6793.2(19)	38.6(6)
C22	-6663(2)	-3769(2)	-492.8(13)	21.7(4)

C23	-6403(4)	-2370(3)	-688(2)	51.1(9)
C24	-7447(3)	-3865(3)	315.6(16)	41.7(7)
C25	-5389(2)	-4413(3)	-276.0(16)	38.8(6)
C26	-8857.8(19)	-3358.7(19)	-1853.1(13)	19.5(4)
C27	-8810(2)	-2616(2)	-2617.3(14)	23.2(4)
C28	-9733(2)	-1711(2)	-2838.3(17)	29.3(5)
C29	-10701(2)	-1497(2)	-2285.0(18)	31.5(5)
C30	-10760(2)	-2199(2)	-1517.9(17)	29.4(5)
C31	-9860(2)	-3137(2)	-1314.7(15)	25.1(4)
C32	-8195(2)	-6110(2)	-1311.3(13)	19.9(4)
C33	-9433(2)	-6425(2)	-1614.9(14)	24.3(4)
C34	-9931(2)	-7630(2)	-1479.7(15)	28.8(5)
C35	-9209(2)	-8551(2)	-1034.7(15)	29.0(5)
C36	-7986(2)	-8272(2)	-730.3(16)	29.2(5)
C37	-7484(2)	-7072(2)	-870.8(15)	26.0(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 22. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	16.0(2)	20.5(3)	11.9(2)	-1.66(19)	2.54(16)	-1.6(2)
O1	20.6(6)	24.9(7)	15.8(6)	-4.2(6)	7.1(5)	-3.1(6)
O2	24.4(7)	13.0(6)	16.8(6)	1.0(5)	3.4(5)	2.4(5)

O3	25.6(8)	14.7(6)	22.6(7)	-1.2(5)	8.1(6)	3.5(6)
O4	34.0(8)	27.5(8)	24.0(7)	5.0(6)	11.8(6)	-7.5(7)
C1	17.2(9)	19.4(9)	17.3(8)	-2.8(7)	0.3(7)	-3.1(7)
C2	16.0(8)	20.8(9)	17.0(8)	-1.0(7)	2.6(7)	-1.8(7)
C3	16.8(8)	17.7(8)	13.6(8)	-0.3(7)	3.2(6)	-1.5(7)
C4	15.5(8)	15.7(8)	13.2(8)	-0.6(6)	3.0(6)	-0.9(7)
C5	15.0(8)	13.9(8)	14.1(8)	0.4(6)	2.7(6)	-0.3(6)
C6	17.1(8)	17.0(8)	15.1(8)	-2.0(7)	4.5(6)	0.3(7)
C7	23.3(9)	14.2(8)	14.9(8)	-0.9(6)	6.5(7)	1.3(7)
C8	23.6(9)	14.2(8)	15.5(8)	-2.2(7)	3.5(7)	-0.7(7)
C9	19.1(8)	12.1(8)	13.3(8)	-0.6(6)	1.5(6)	-0.6(7)
C10	32.5(11)	25.1(10)	14.5(8)	-3.1(7)	-0.1(8)	0.3(9)
C11	40.0(12)	18.2(10)	17.4(9)	0.4(7)	7.5(8)	3.9(9)
C12	32.9(11)	15.2(9)	17.5(9)	-0.7(7)	10.5(8)	-0.5(8)
C13	22.0(10)	38.6(13)	22.6(10)	-7.0(9)	-3.3(8)	-6.4(9)
C14	17.5(9)	26.0(10)	14.6(8)	-0.1(7)	2.2(7)	2.4(8)
C15	27.6(11)	32.9(12)	34.1(12)	-2.3(10)	-10.1(9)	-3.0(9)
C16	28.0(11)	33.3(12)	20.6(10)	8.7(9)	-1.4(8)	1.3(9)
C17	19.0(9)	36.2(11)	19.9(9)	-5.2(8)	3.7(7)	3.4(8)
C18	32.5(12)	43.1(14)	27.1(11)	-1.3(10)	-0.8(9)	16.8(11)
C19	21.0(10)	59.2(18)	38.5(13)	-3.6(12)	1.6(9)	-6.8(11)
C20	62.4(17)	34.1(12)	21.7(10)	9.1(10)	3.7(10)	3.7(13)

C21	45.8(15)	30.8(13)	41.6(14)	13.9(11)	21.4(12)	-3.3(11)
C22	22.1(10)	25.7(10)	17.2(9)	-4.8(7)	-0.2(7)	-3.2(8)
C23	69(2)	32.5(14)	48.0(16)	-1.0(12)	-23.6(15)	-19.8(14)
C24	35.3(13)	71(2)	19.8(10)	-17.2(12)	6.1(9)	-7.4(13)
C25	27.7(11)	58.5(17)	28.6(11)	-15.7(13)	-9.3(9)	7.3(13)
C26	18.6(9)	21.3(10)	18.5(9)	-2.1(7)	1.2(7)	-2.4(7)
C27	23.6(10)	24.3(10)	21.6(10)	-1.4(8)	1.7(8)	-3.8(8)
C28	31.6(12)	24.1(10)	31.5(11)	4.9(9)	-2.9(9)	-0.5(9)
C29	24.6(11)	23.8(11)	45.5(14)	-1.3(10)	-3.8(10)	3.5(9)
C30	21.0(10)	31.1(11)	36.7(12)	-6.9(10)	5.9(9)	-0.9(9)
C31	23.4(10)	28.0(11)	24.4(10)	-1.2(8)	5.6(8)	-1.2(9)
C32	22.4(9)	23.7(9)	14.0(8)	-2.6(7)	5.7(7)	-2.0(8)
C33	23.0(10)	30.4(11)	19.5(9)	2.1(8)	2.4(8)	-3.7(9)
C34	27.2(11)	36.1(12)	23.3(10)	-2.1(9)	4.1(9)	-11.2(10)
C35	38.3(13)	26.1(10)	23.9(10)	-2.7(9)	12.8(9)	-9.2(9)
C36	33.0(12)	24.6(11)	30.8(11)	2.4(9)	8.2(9)	2.6(9)
C37	22.1(10)	27.6(10)	28.5(11)	0.4(9)	3.4(8)	-1.3(9)

Table 4 Bond Lengths for 22.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	O1	1.6376(14)	C8	C10	1.540(3)
Si1	C22	1.898(2)	C10	C11	1.508(3)

Si1	C26	1.877(2)	C11	C12	1.333(3)
Si1	C32	1.883(2)	C11	C20	1.503(3)
O1	C3	1.429(2)	C14	C15	1.330(3)
O2	C9	1.433(2)	C14	C16	1.498(3)
O3	C7	1.445(2)	C17	C18	1.325(4)
O4	C12	1.369(3)	C17	C19	1.514(4)
O4	C21	1.423(3)	C22	C23	1.527(4)
C1	C2	1.539(3)	C22	C24	1.527(3)
C1	C9	1.533(3)	C22	C25	1.530(3)
C1	C13	1.532(3)	C26	C27	1.399(3)
C2	C3	1.530(3)	C26	C31	1.401(3)
C3	C4	1.540(3)	C27	C28	1.391(3)
C4	C5	1.539(3)	C28	C29	1.386(4)
C4	C14	1.519(3)	C29	C30	1.381(4)
C5	C6	1.539(3)	C30	C31	1.394(3)
C5	C9	1.547(3)	C32	C33	1.405(3)
C6	C7	1.571(3)	C32	C37	1.404(3)
C6	C17	1.519(3)	C33	C34	1.392(3)
C7	C8	1.541(3)	C34	C35	1.383(4)
C7	C12	1.505(3)	C35	C36	1.381(4)
C8	C9	1.541(3)	C36	C37	1.390(3)

Table 5 Bond Angles for 22.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Si1	C22	105.42(8)	C1	C9	C8	116.99(15)
O1	Si1	C26	109.36(9)	C8	C9	C5	101.85(15)
O1	Si1	C32	111.57(9)	C11	C10	C8	105.79(18)
C26	Si1	C22	107.36(9)	C12	C11	C10	109.98(18)
C26	Si1	C32	109.66(9)	C12	C11	C20	133.2(2)
C32	Si1	C22	113.29(9)	C20	C11	C10	116.8(2)
C3	O1	Si1	134.70(13)	O4	C12	C7	112.11(18)
C12	O4	C21	118.7(2)	C11	C12	O4	134.40(19)
C9	C1	C2	109.02(15)	C11	C12	C7	113.45(19)
C13	C1	C2	110.59(17)	C15	C14	C4	120.73(19)
C13	C1	C9	113.95(17)	C15	C14	C16	121.0(2)
C3	C2	C1	113.70(16)	C16	C14	C4	118.27(18)
O1	C3	C2	110.77(16)	C18	C17	C6	122.8(2)
O1	C3	C4	106.19(15)	C18	C17	C19	121.7(2)
C2	C3	C4	113.22(15)	C19	C17	C6	115.5(2)
C5	C4	C3	109.33(15)	C23	C22	Si1	107.77(16)
C14	C4	C3	111.36(15)	C23	C22	C25	107.3(2)
C14	C4	C5	113.60(15)	C24	C22	Si1	111.14(15)
C4	C5	C6	117.06(15)	C24	C22	C23	109.5(2)
C4	C5	C9	111.19(15)	C24	C22	C25	108.6(2)

C6	C5	C9	102.95(14)	C25	C22	Si1	112.42(15)
C5	C6	C7	102.26(15)	C27	C26	Si1	120.86(16)
C17	C6	C5	117.95(17)	C27	C26	C31	117.2(2)
C17	C6	C7	114.27(16)	C31	C26	Si1	121.58(16)
O3	C7	C6	112.88(16)	C28	C27	C26	121.2(2)
O3	C7	C8	109.00(15)	C29	C28	C27	120.2(2)
O3	C7	C12	108.84(15)	C30	C29	C28	119.8(2)
C8	C7	C6	107.30(15)	C29	C30	C31	119.7(2)
C12	C7	C6	114.54(16)	C30	C31	C26	121.7(2)
C12	C7	C8	103.76(17)	C33	C32	Si1	120.74(17)
C9	C8	C7	104.60(15)	C37	C32	Si1	122.49(16)
C10	C8	C7	105.24(16)	C37	C32	C33	116.8(2)
C10	C8	C9	116.74(17)	C34	C33	C32	121.5(2)
O2	C9	C1	112.14(16)	C35	C34	C33	120.2(2)
O2	C9	C5	110.91(15)	C36	C35	C34	119.7(2)
O2	C9	C8	105.53(15)	C35	C36	C37	120.2(2)
C1	C9	C5	108.94(15)	C36	C37	C32	121.7(2)

Table 6 Torsion Angles for 22.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Si1	O1	C3	C2	72.6(2)	C8	C7	C12	C11	-10.8(2)
Si1	O1	C3	C4	-164.09(14)	C8	C10	C11	C12	5.3(2)

Si1	C26	C27	C28	-174.70(17)		C8	C10	C11	C20	-176.94(19)
Si1	C26	C31	C30	172.33(18)		C9	C1	C2	C3	-54.4(2)
Si1	C32	C33	C34	179.56(17)		C9	C5	C6	C7	-38.79(17)
Si1	C32	C37	C36	179.94(18)		C9	C5	C6	C17	-165.04(17)
O1	Si1	C22	C23	68.3(2)		C9	C8	C10	C11	104.0(2)
O1	Si1	C22	C24	-171.73(18)		C10	C8	C9	O2	-34.8(2)
O1	Si1	C22	C25	-49.8(2)		C10	C8	C9	C1	90.7(2)
O1	Si1	C26	C27	-5.56(19)		C10	C8	C9	C5	-150.72(17)
O1	Si1	C26	C31	-178.98(16)		C10	C11	C12	O4	-178.9(2)
O1	Si1	C32	C33	-106.52(17)		C10	C11	C12	C7	3.6(2)
O1	Si1	C32	C37	72.61(19)		C12	C7	C8	C9	-110.45(16)
O1	C3	C4	C5	-172.38(15)		C12	C7	C8	C10	13.11(19)
O1	C3	C4	C14	61.26(19)		C13	C1	C2	C3	179.61(17)
O3	C7	C8	C9	133.70(15)		C13	C1	C9	O2	60.4(2)
O3	C7	C8	C10	-102.74(17)		C13	C1	C9	C5	-176.41(17)
O3	C7	C12	O4	-72.9(2)		C13	C1	C9	C8	-61.7(2)
O3	C7	C12	C11	105.1(2)		C14	C4	C5	C6	-59.6(2)
C1	C2	C3	O1	169.79(16)		C14	C4	C5	C9	-177.55(15)
C1	C2	C3	C4	50.6(2)		C17	C6	C7	O3	25.6(2)
C2	C1	C9	O2	-63.63(19)		C17	C6	C7	C8	145.68(18)
C2	C1	C9	C5	59.53(19)		C17	C6	C7	C12	-99.7(2)
C2	C1	C9	C8	174.26(16)		C20	C11	C12	O4	3.8(4)

C2	C3	C4	C5	-50.6(2)	C20	C11	C12	C7	-173.7(2)
C2	C3	C4	C14	-176.98(16)	C21	O4	C12	C7	177.83(19)
C3	C4	C5	C6	175.29(16)	C21	O4	C12	C11	0.4(4)
C3	C4	C5	C9	57.38(19)	C22	Si1	O1	C3	140.68(18)
C3	C4	C14	C15	-126.1(2)	C22	Si1	C26	C27	108.33(18)
C3	C4	C14	C16	53.9(2)	C22	Si1	C26	C31	-65.08(19)
C4	C5	C6	C7	-161.07(15)	C22	Si1	C32	C33	134.70(17)
C4	C5	C6	C17	72.7(2)	C22	Si1	C32	C37	-46.2(2)
C4	C5	C9	O2	60.7(2)	C26	Si1	O1	C3	-104.18(18)
C4	C5	C9	C1	-63.22(19)	C26	Si1	C22	C23	-48.2(2)
C4	C5	C9	C8	172.57(15)	C26	Si1	C22	C24	71.8(2)
C5	C4	C14	C15	109.9(2)	C26	Si1	C22	C25	-166.32(18)
C5	C4	C14	C16	-70.1(2)	C26	Si1	C32	C33	14.79(19)
C5	C6	C7	O3	-103.03(17)	C26	Si1	C32	C37	-166.09(17)
C5	C6	C7	C8	17.07(19)	C26	C27	C28	C29	2.1(3)
C5	C6	C7	C12	131.66(18)	C27	C26	C31	C30	-1.3(3)
C5	C6	C17	C18	49.7(3)	C27	C28	C29	C30	-0.9(4)
C5	C6	C17	C19	-132.7(2)	C28	C29	C30	C31	-1.4(4)
C6	C5	C9	O2	-65.48(18)	C29	C30	C31	C26	2.5(4)
C6	C5	C9	C1	170.63(15)	C31	C26	C27	C28	-1.0(3)
C6	C5	C9	C8	46.42(17)	C32	Si1	O1	C3	17.3(2)
C6	C7	C8	C9	11.15(19)	C32	Si1	C22	C23	-169.5(2)

C6	C7	C8	C10	134.72(16)	C32	Si1	C22	C24	-49.5(2)
C6	C7	C12	O4	54.5(2)	C32	Si1	C22	C25	72.5(2)
C6	C7	C12	C11	-127.48(19)	C32	Si1	C26	C27	-128.19(17)
C7	C6	C17	C18	-70.5(3)	C32	Si1	C26	C31	58.39(19)
C7	C6	C17	C19	107.1(2)	C32	C33	C34	C35	0.3(3)
C7	C8	C9	O2	80.99(17)	C33	C32	C37	C36	-0.9(3)
C7	C8	C9	C1	-153.53(16)	C33	C34	C35	C36	-0.5(3)
C7	C8	C9	C5	-34.91(18)	C34	C35	C36	C37	0.0(4)
C7	C8	C10	C11	-11.5(2)	C35	C36	C37	C32	0.7(4)
C8	C7	C12	O4	171.12(16)	C37	C32	C33	C34	0.4(3)

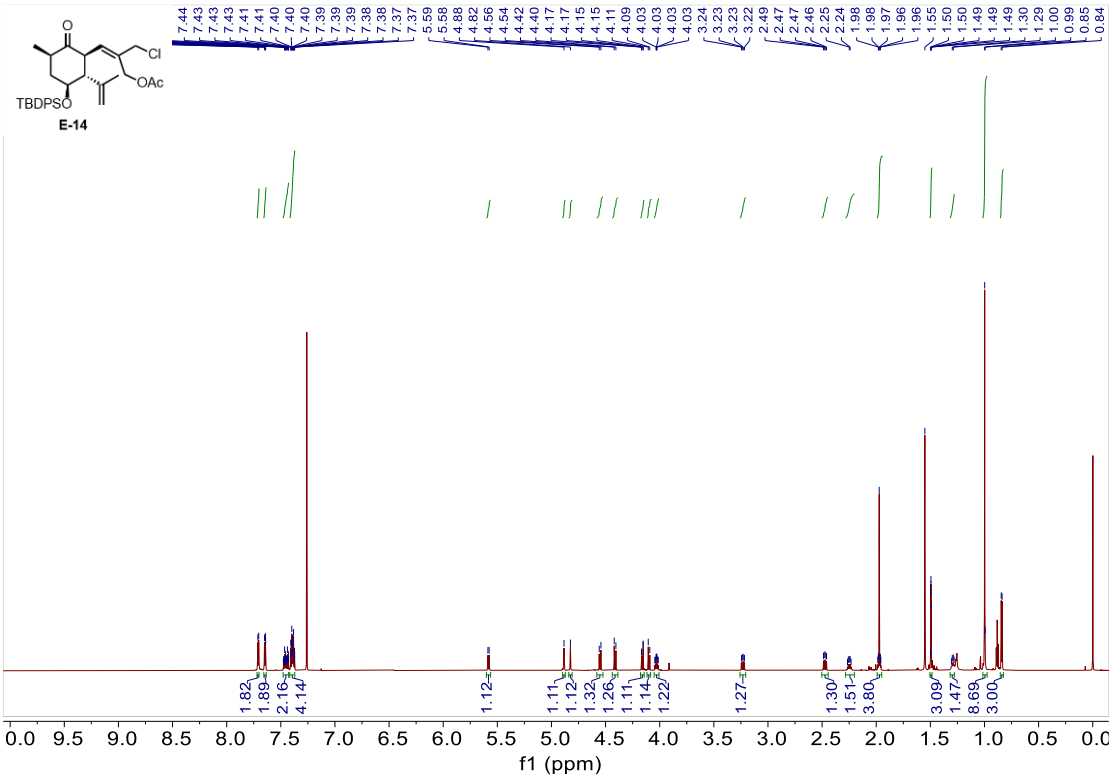
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 22.

Atom	***x***	***y***	***z***	**U(eq)**
H2	-6220(30)	-3930(30)	-4770(20)	42(9)
H3	-2300(30)	-7190(40)	-5220(20)	50(10)
H1	-6757.87	-7021.33	-4353.17	22
H2A	-7440.72	-4480.27	-3873.44	21
H2B	-8026.67	-5749.93	-3486.31	21
H3A	-6155.95	-6254.02	-2691.62	19
H4	-4975.37	-4070.55	-3434.61	18
H5	-4577.39	-6688.52	-3895.07	17

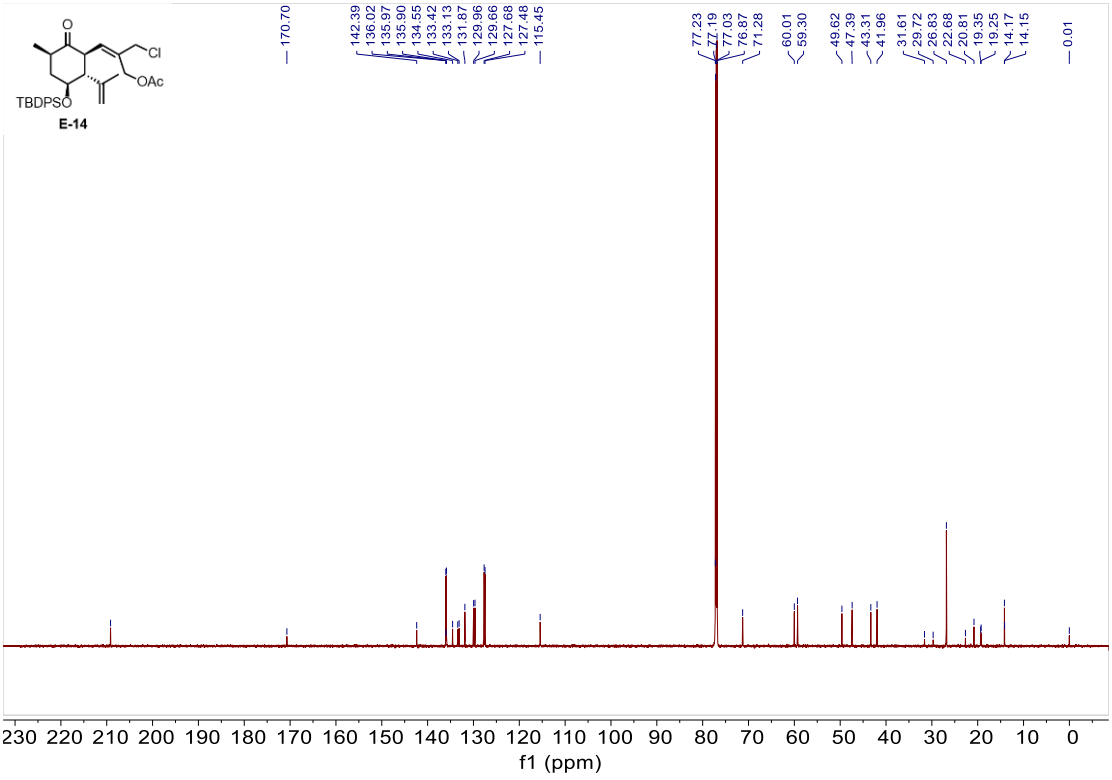
H6	-3373.67	-4489.77	-4586.74	20
H8	-5218.55	-7234.47	-5552.49	21
H10A	-5603.01	-6546.73	-6939.98	29
H10B	-6174.11	-5269.22	-6536.17	29
H13A	-8744.28	-6396.17	-5009.44	42
H13B	-7753.99	-6597.5	-5750.37	42
H13C	-8106.88	-5189.29	-5446.86	42
H15A	-2558.14	-4139.86	-1796.91	38
H15B	-3289.08	-3298.11	-2589.55	38
H16A	-4503.52	-6449.02	-1659.45	41
H16B	-3004.34	-6269.35	-1597.41	41
H16C	-3683.55	-7001.92	-2422.81	41
H18A	-1109.23	-7173.41	-3443.04	41
H18B	-2557.14	-7599.98	-3764.26	41
H19A	-1002.12	-4459	-4560.67	59
H19B	-352.62	-5131.34	-3699.72	59
H19C	-1424.24	-4079.3	-3599.96	59
H20A	-3661.56	-3966.41	-7807.45	59
H20B	-5151.53	-3854.08	-7722.41	59
H20C	-4575.83	-5087.8	-8168.1	59
H21A	-1749.2	-4358.04	-7352.49	58
H21B	-863.19	-3606.22	-6634.77	58

H21C	-2283.11	-3143.54	-6859.09	58
H23A	-5893.91	-2309.14	-1204.04	77
H23B	-5943.03	-1982.22	-174.99	77
H23C	-7203.63	-1921.34	-810.98	77
H24A	-8224.44	-3370.32	212.12	63
H24B	-6959.78	-3527.87	835.05	63
H24C	-7658.77	-4758.76	418.41	63
H25A	-5525.55	-5301.09	-108.2	58
H25B	-4938.55	-3964.46	215.65	58
H25C	-4887.49	-4385.77	-796.69	58
H27	-8135.57	-2732.76	-2992.05	28
H28	-9698.43	-1236.67	-3370.39	35
H29	-11323.34	-869.57	-2433.15	38
H30	-11412.08	-2043.71	-1130.31	35
H31	-9926.79	-3638.83	-798	30
H33	-9942.45	-5800.97	-1919.35	29
H34	-10769.61	-7820.77	-1693.9	35
H35	-9551.38	-9370.89	-938.78	35
H36	-7487.33	-8901.9	-424.08	35
H37	-6638.84	-6898.12	-663.54	31

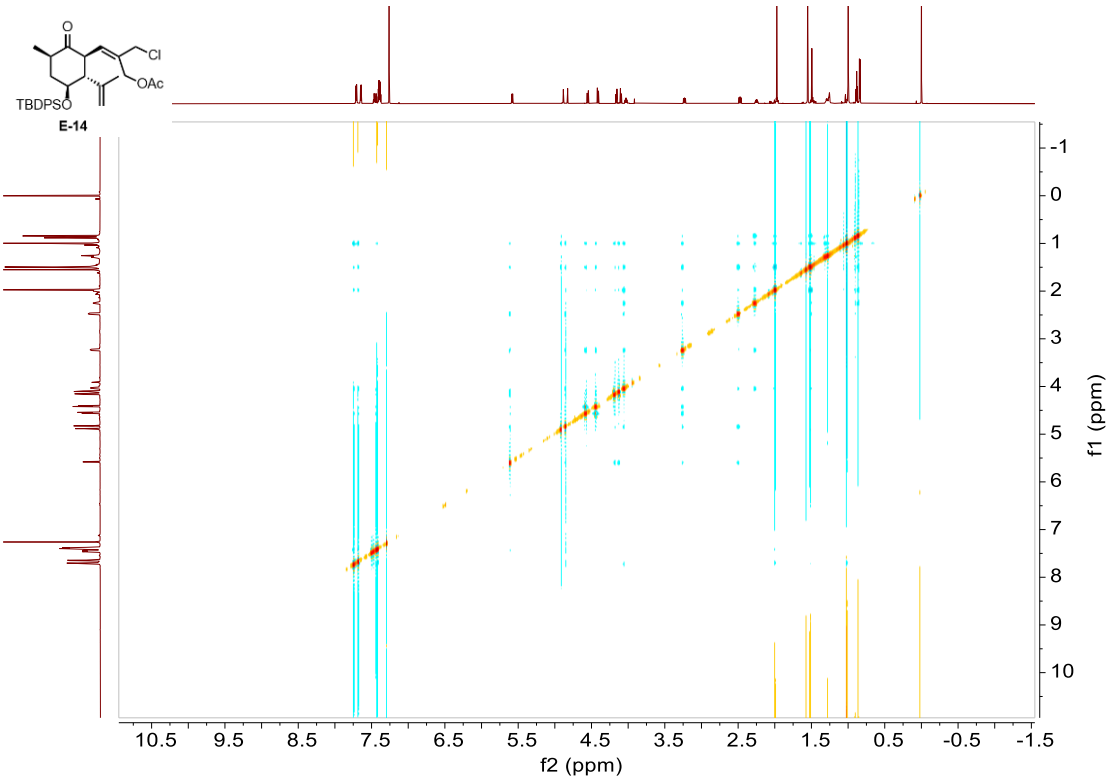
5. NMR Spectrum



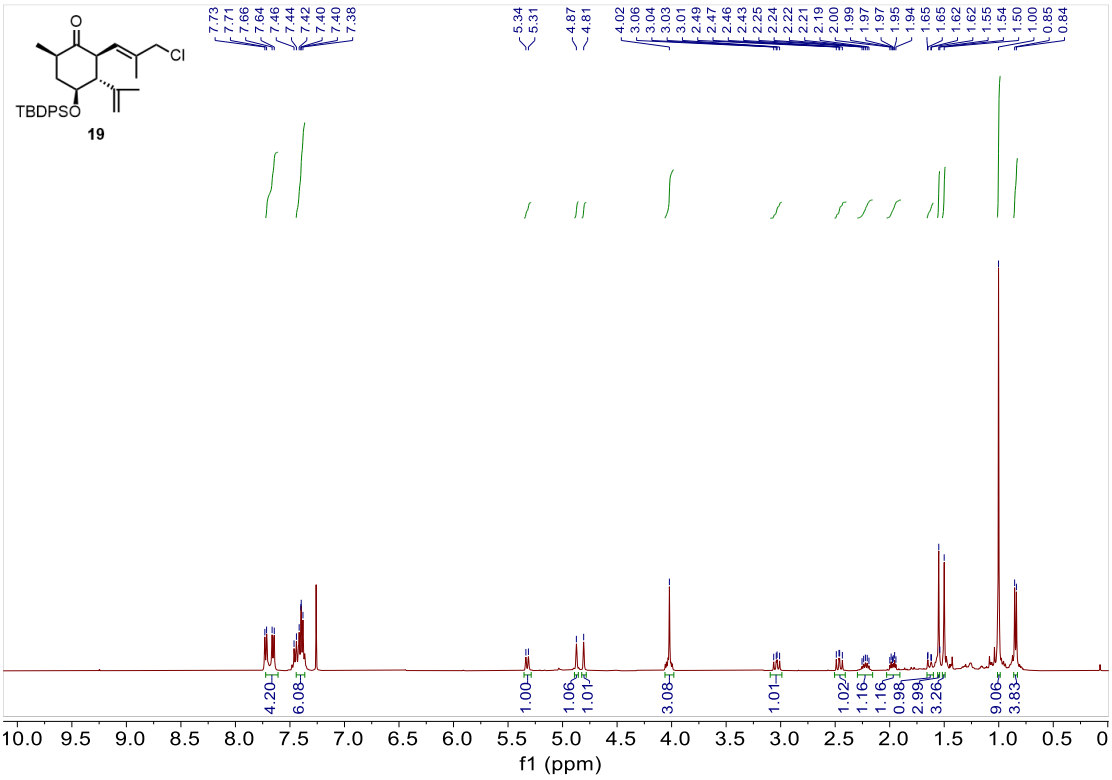
^{1}H NMR of compound (*E*)-**14** (800 MHz)



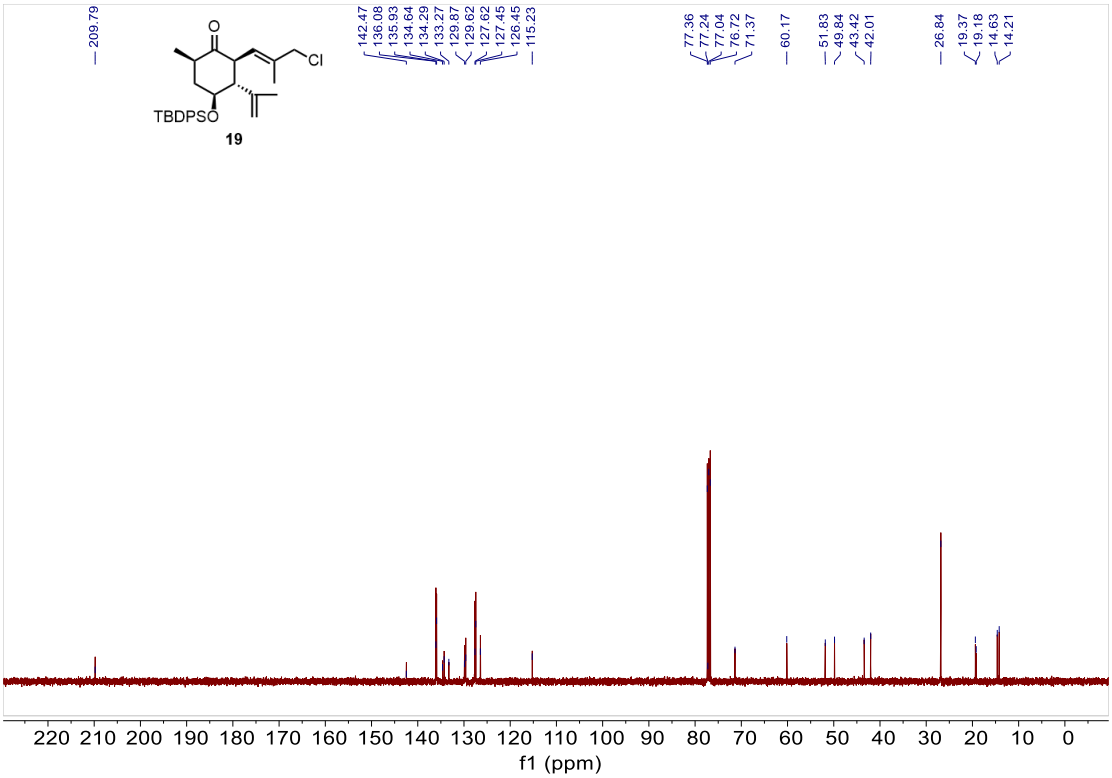
^{13}C NMR of compound (*E*)-**14** (201 MHz)



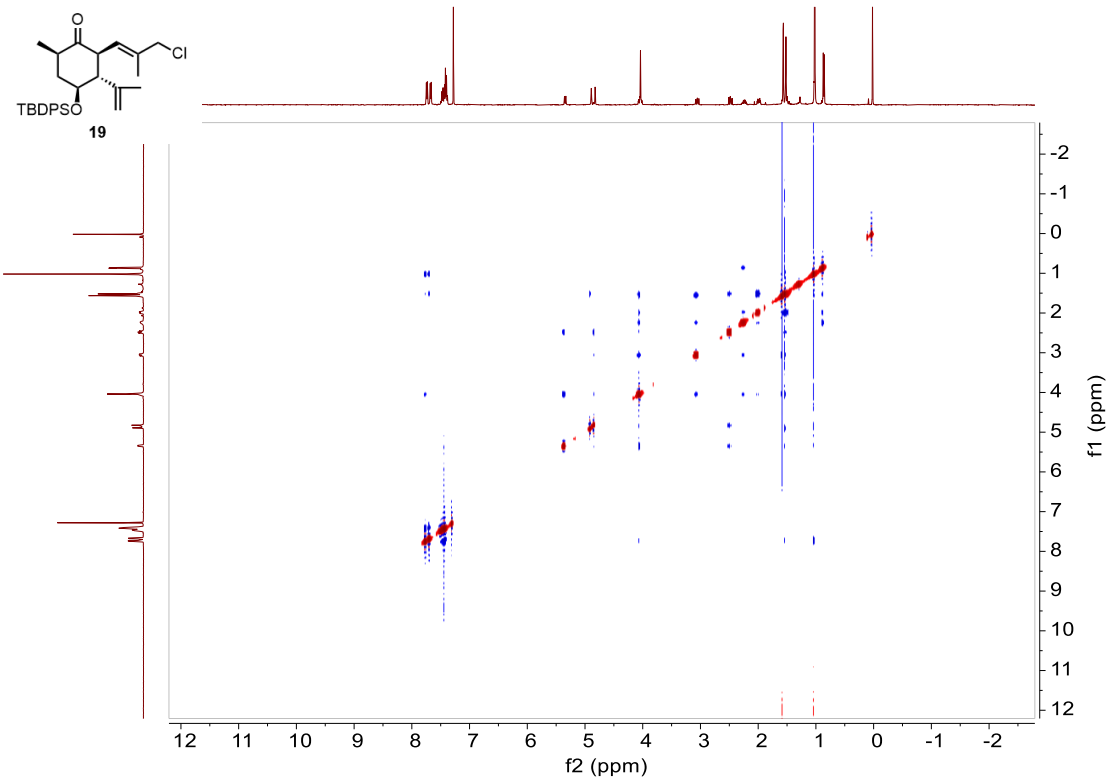
NOESY of compound (*E*)-**14**



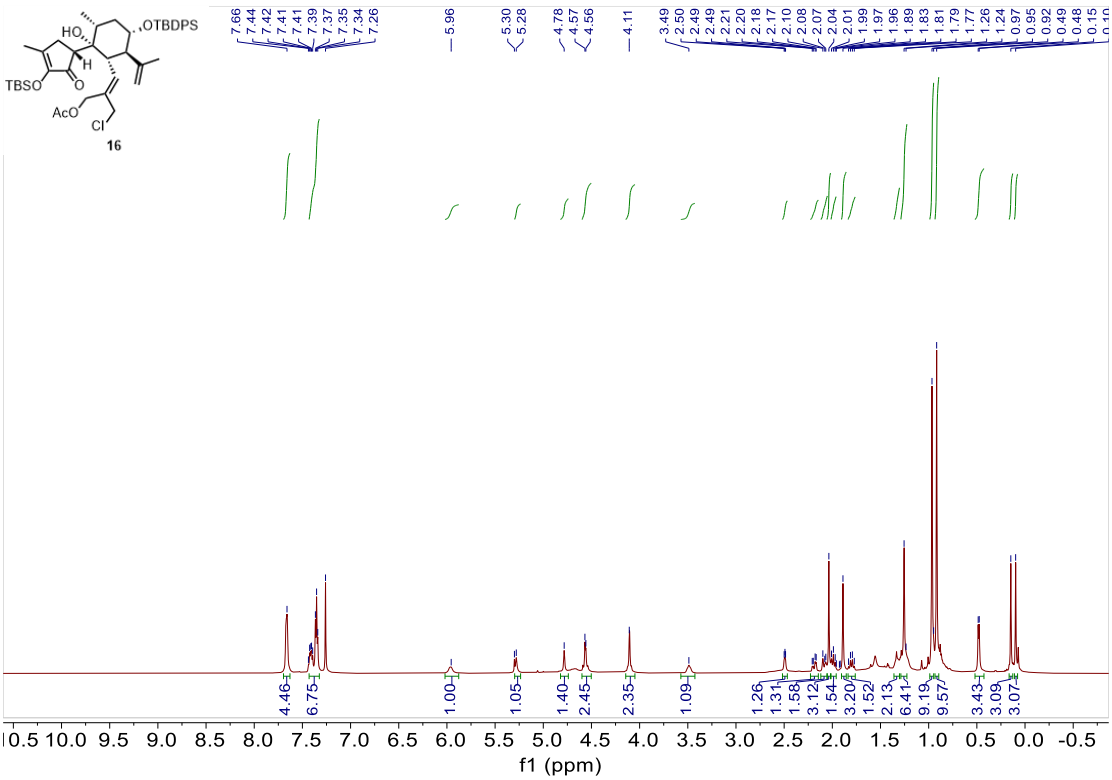
^{1}H NMR of compound **19** (400 MHz)



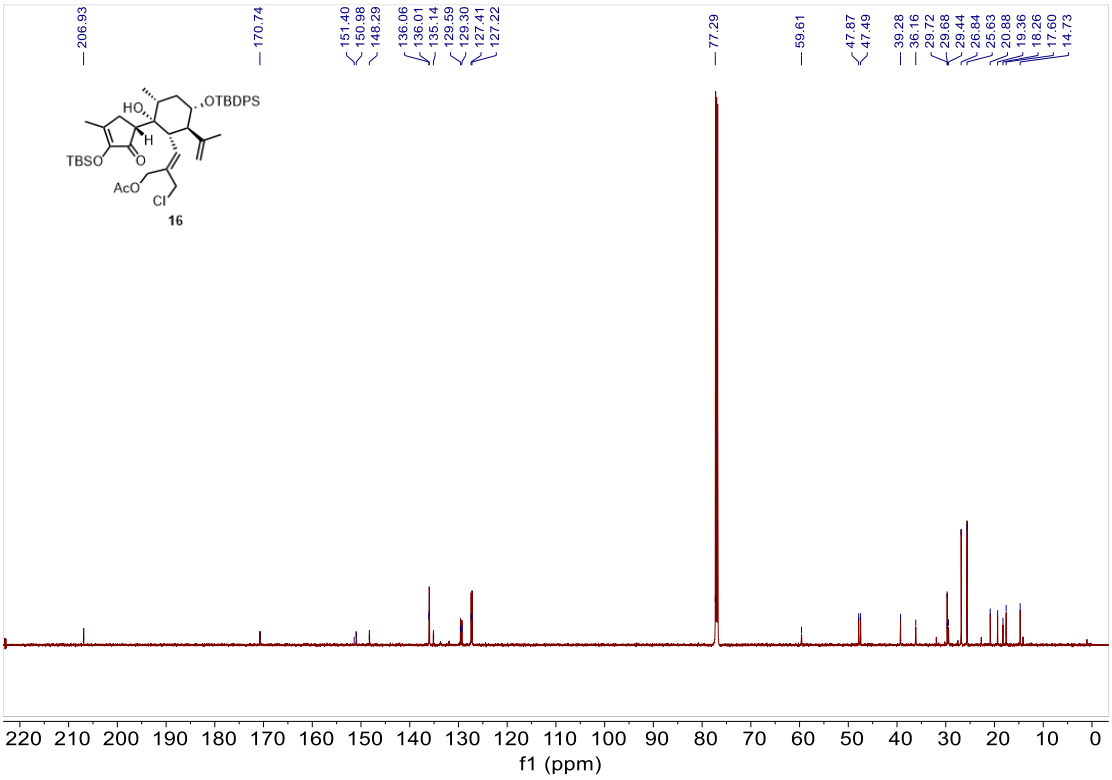
^{13}C NMR of compound **19** (101 MHz)



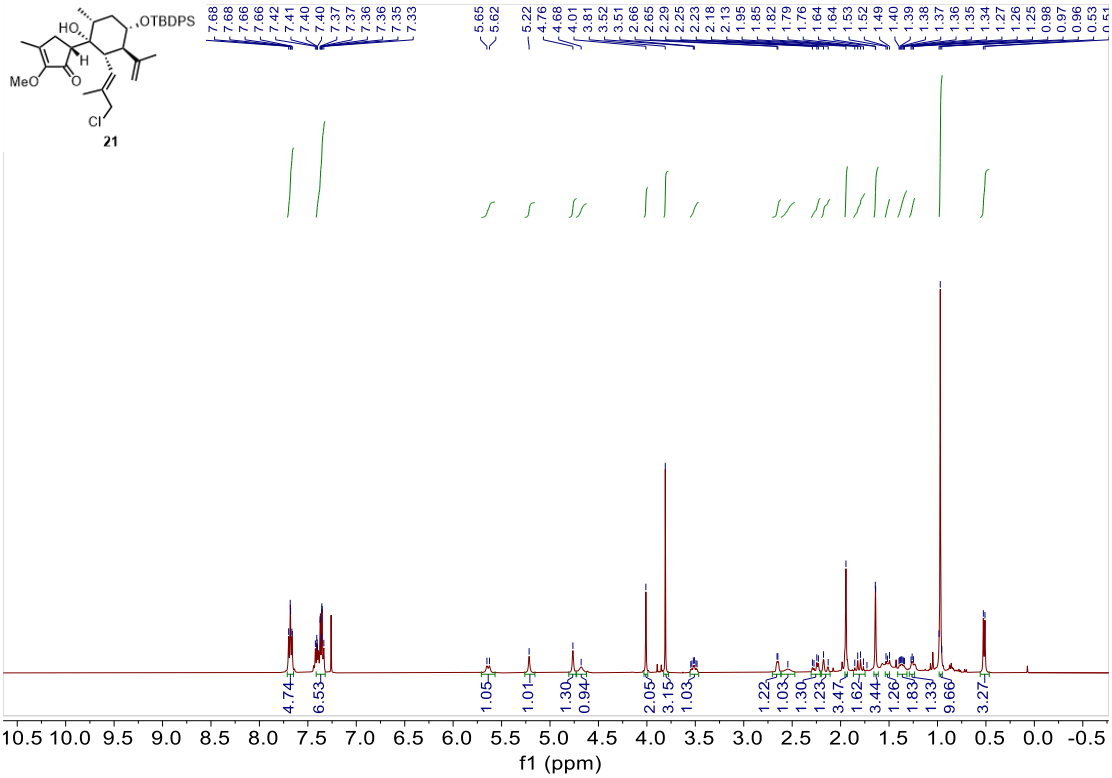
NOESY of compound **19**



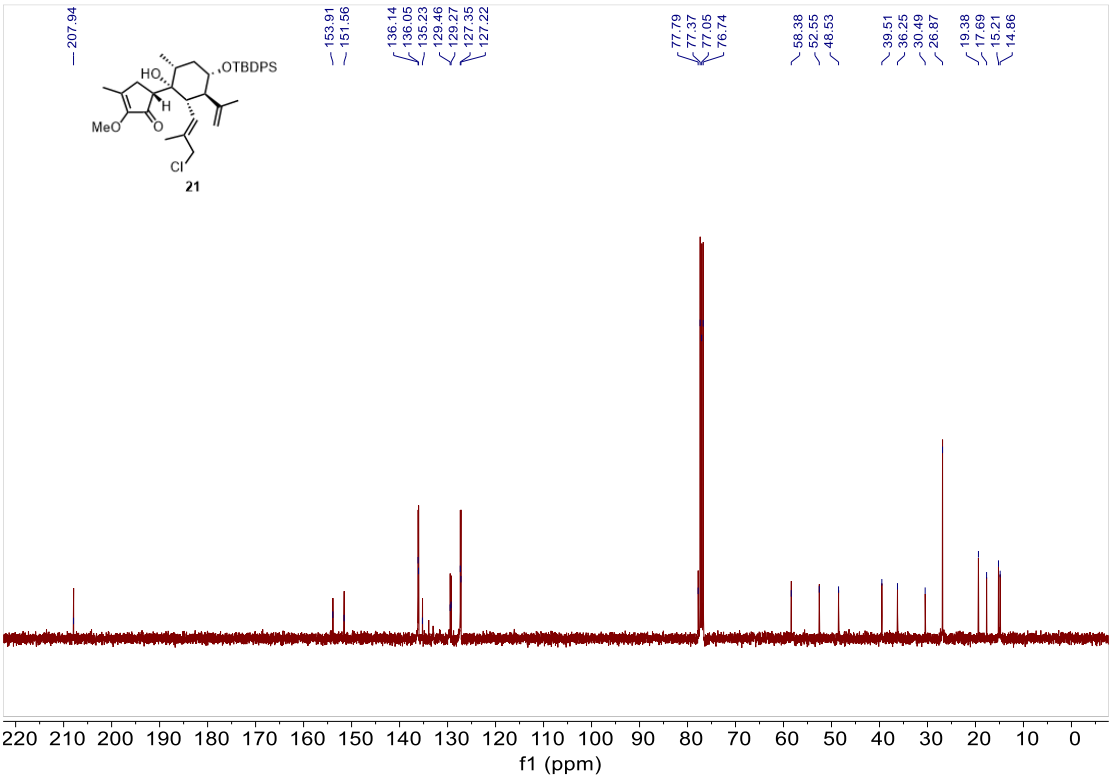
^{1}H NMR of compound **16** (600 MHz)



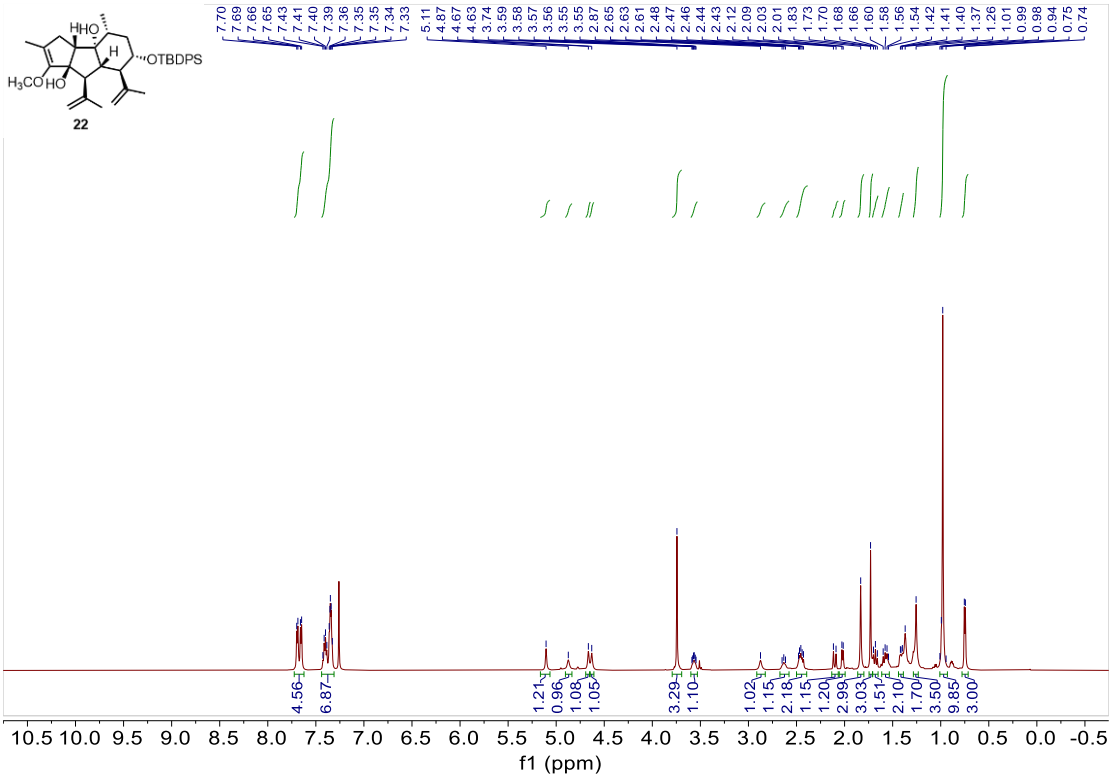
^{13}C NMR of compound **16** (151 MHz)



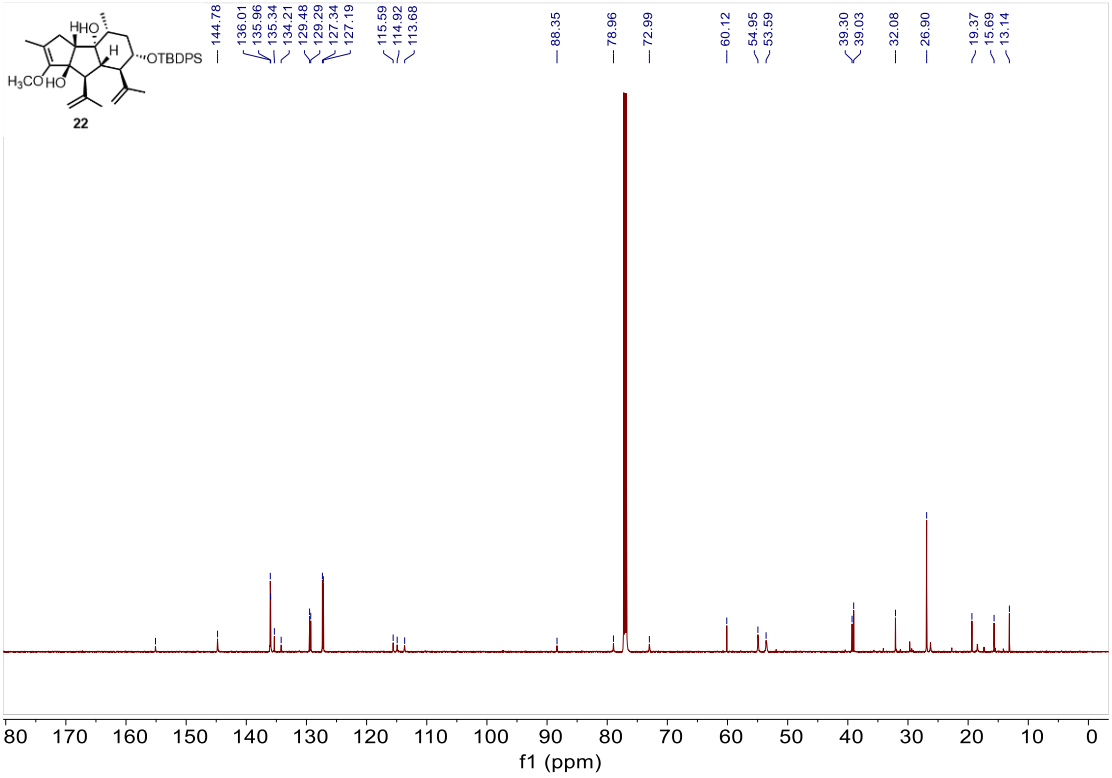
^{1}H NMR of compound **21** (400 MHz)



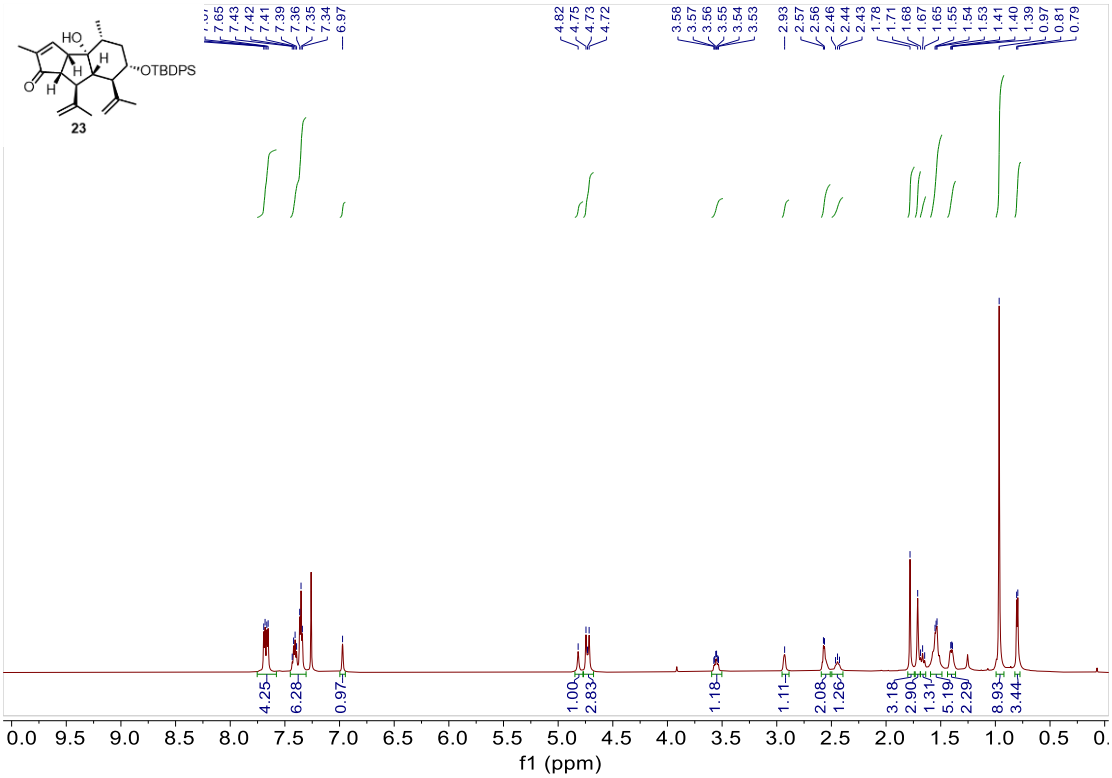
^{13}C NMR of compound **21** (101 MHz)



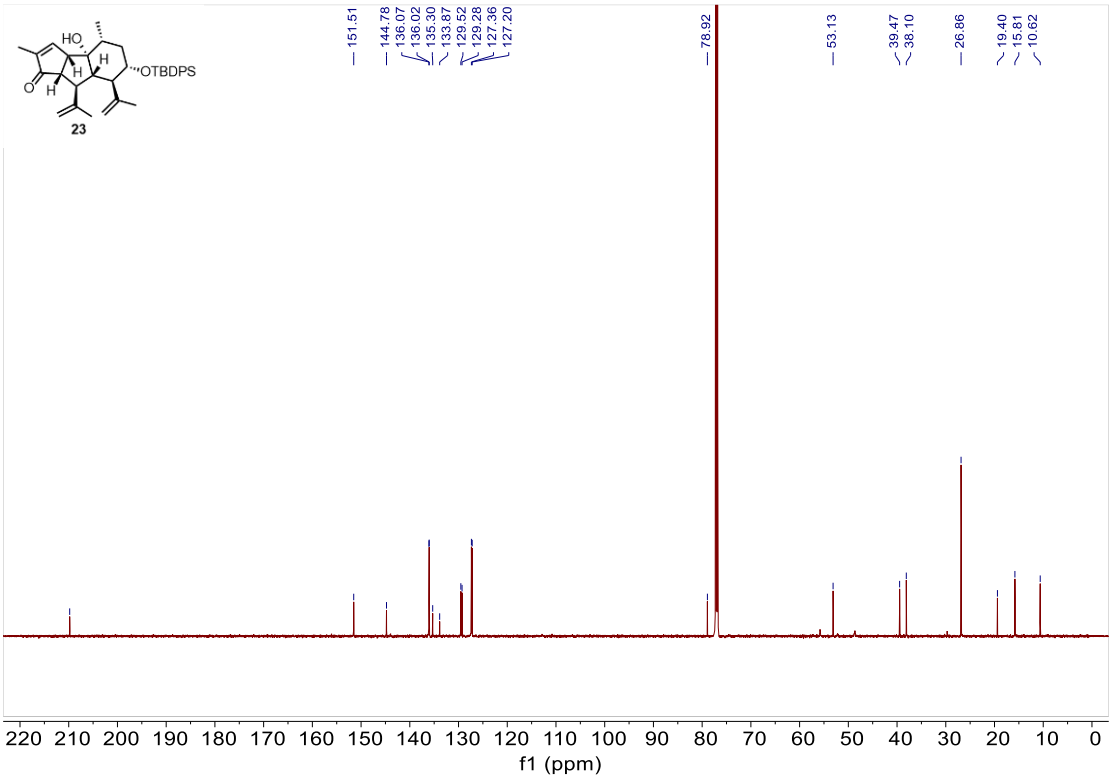
^{1}H NMR of compound **22** (600 MHz)



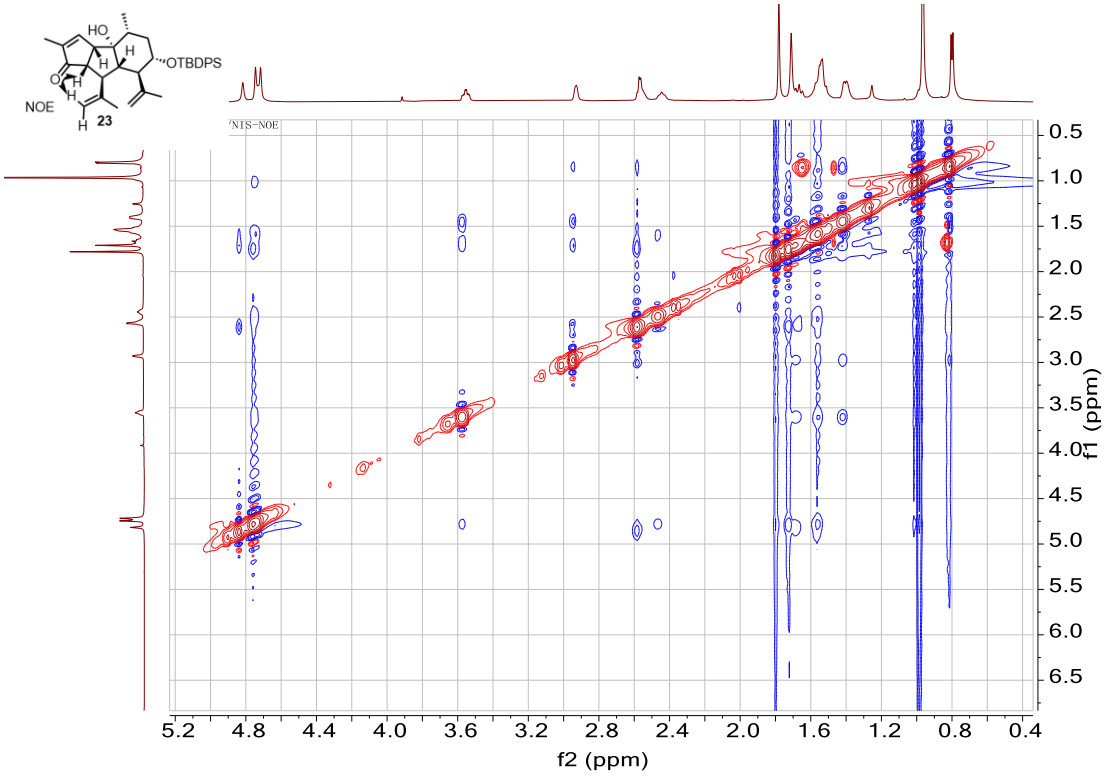
^{13}C NMR of compound **22** (151 MHz)



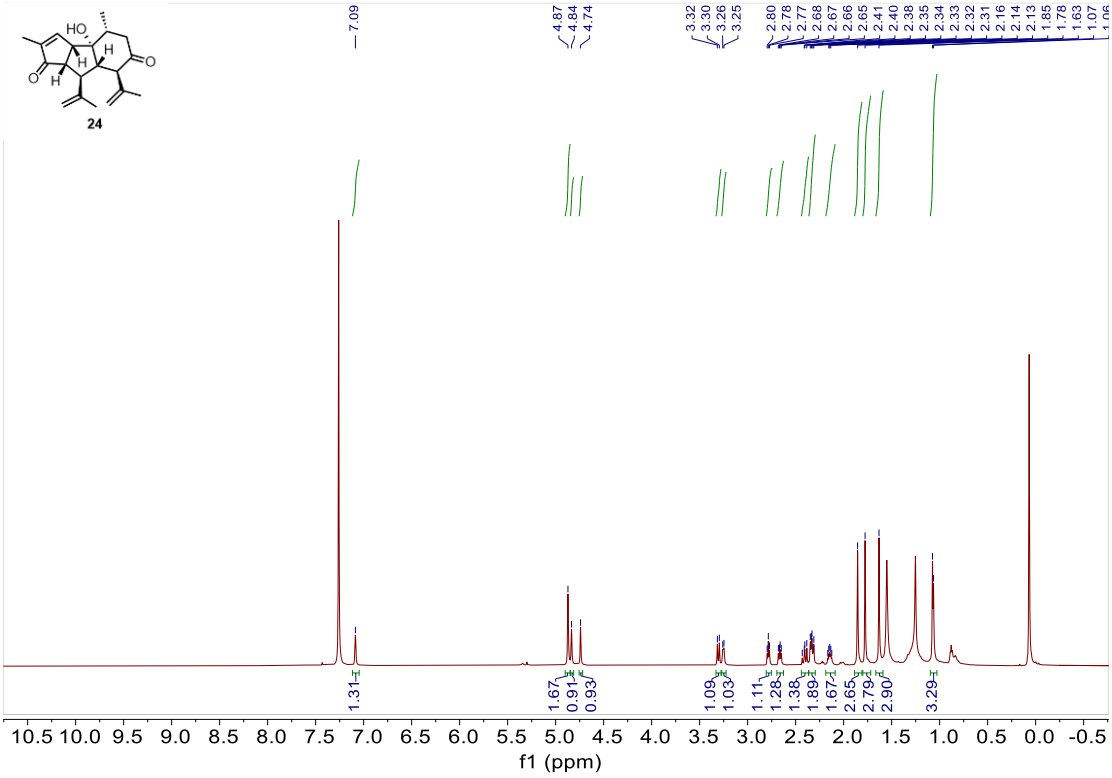
^{1}H NMR of compound **23** (600 MHz)



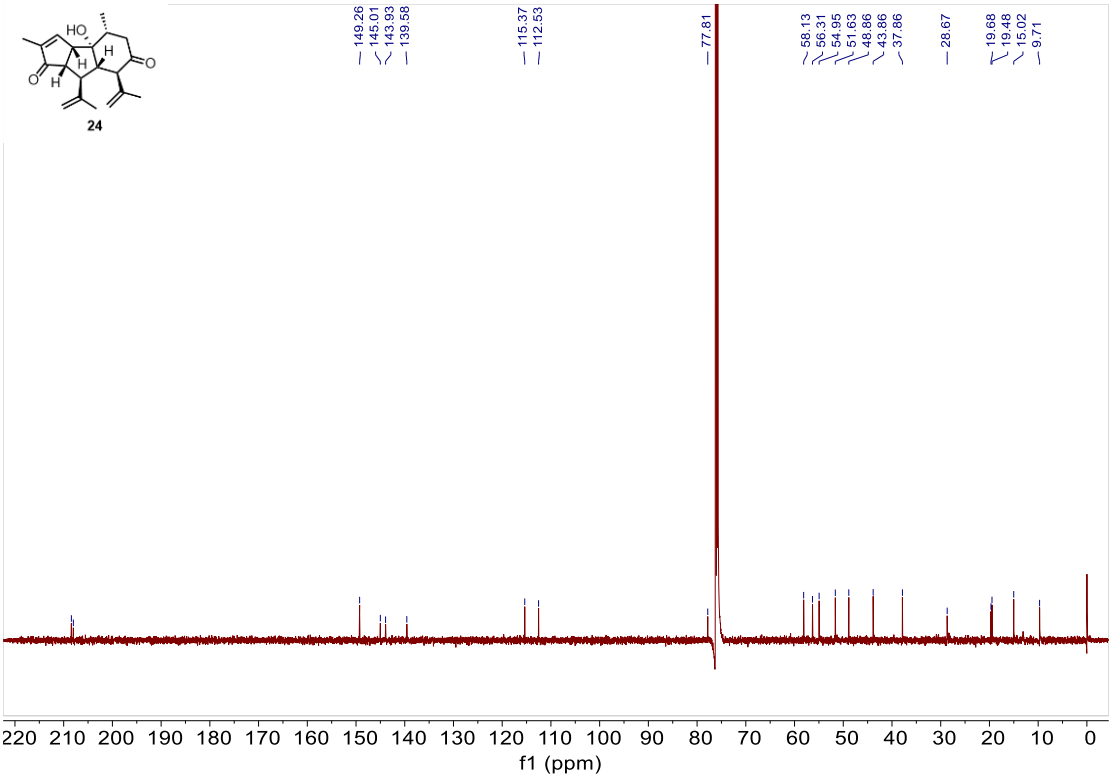
^{13}C NMR of compound **23** (151 MHz)



NOESY of compound **23**



^{1}H NMR of compound **24** (600 MHz)



^{13}C NMR of compound **24** (151 MHz)

6. Reference

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(2) T. Yu, Y. Sun, C. Tu, T. Chen, S. Fu, B. Liu, *Chem. Sci.*, 2020, **11**, 7177-7181.