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Supporting Information

Enantioselective Total Synthesis and Structural Revision of Dysiherbol A

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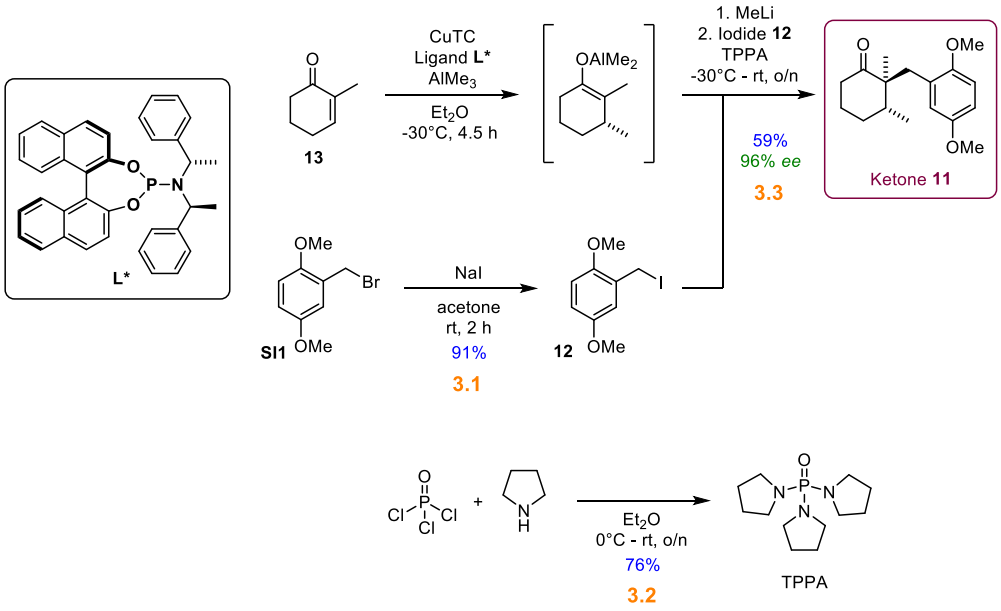

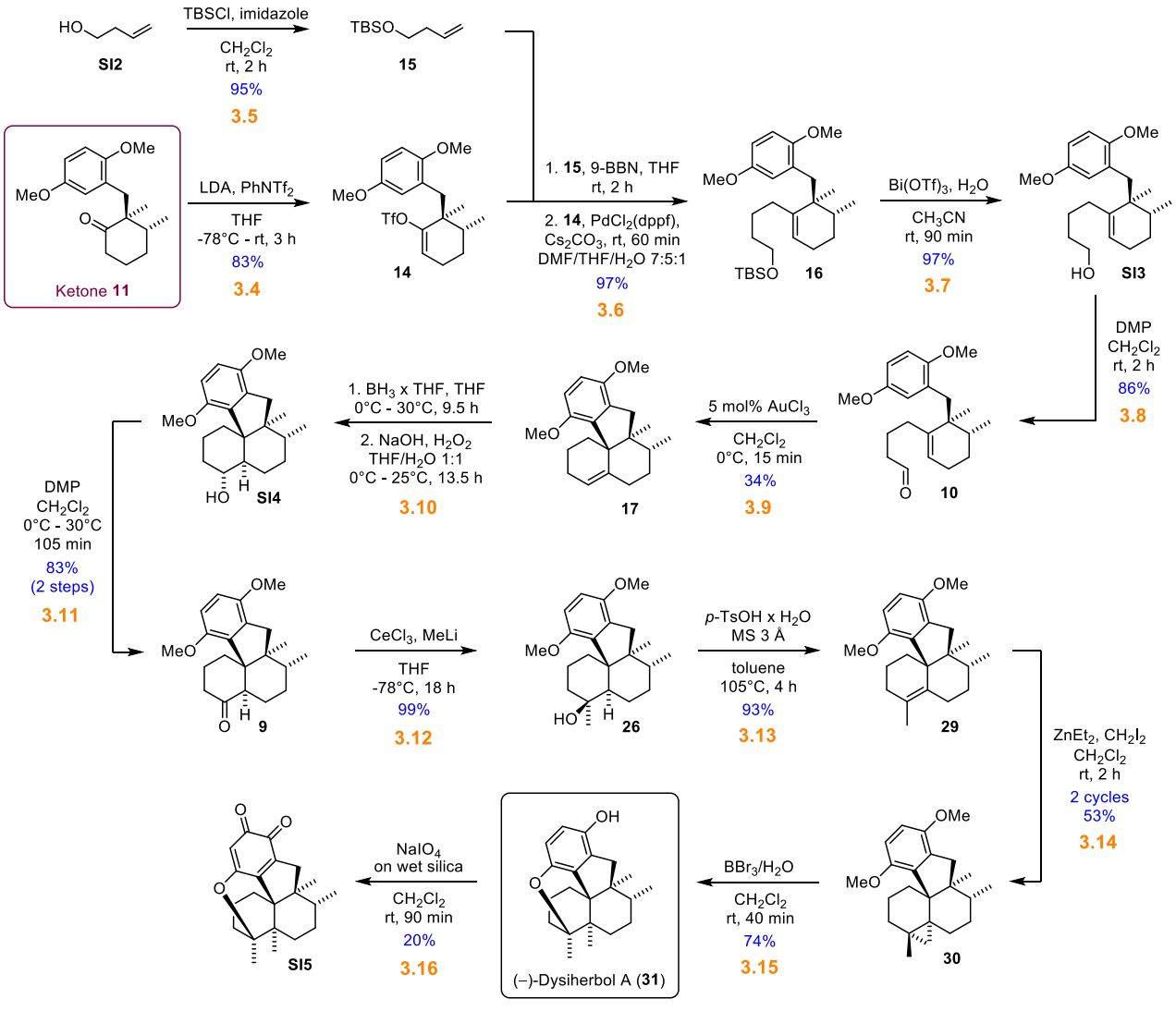

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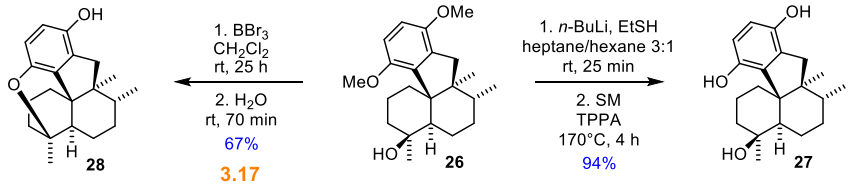

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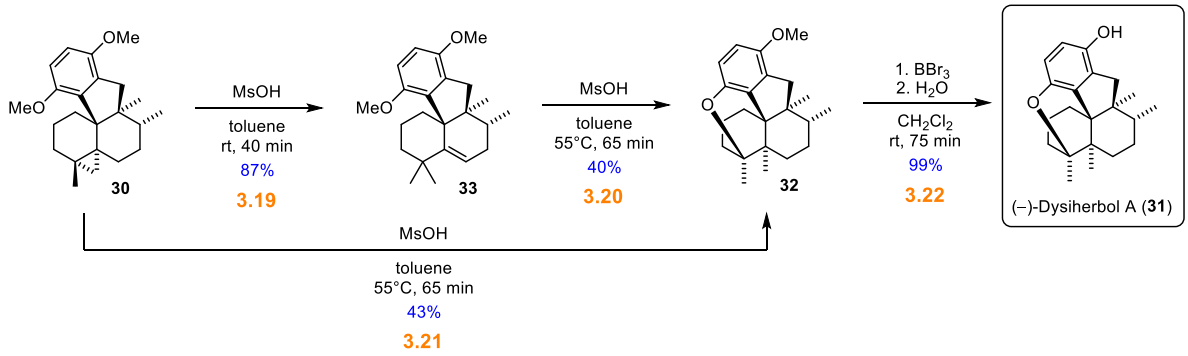

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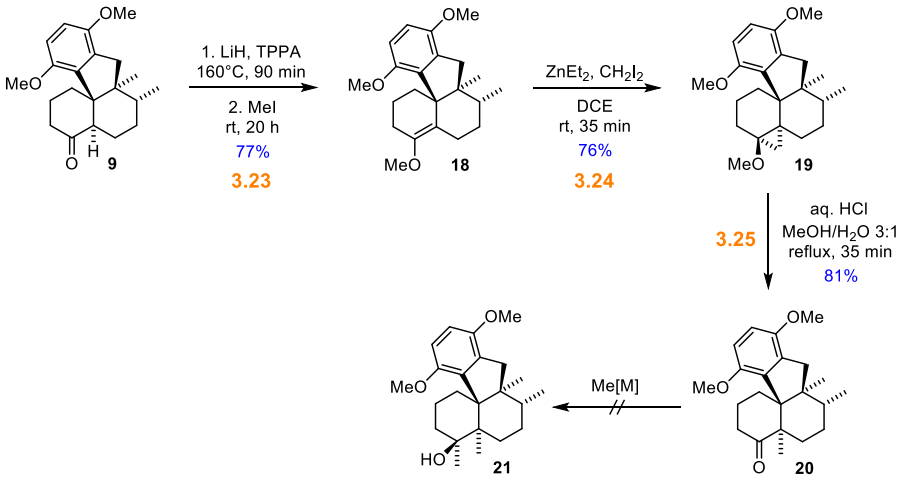

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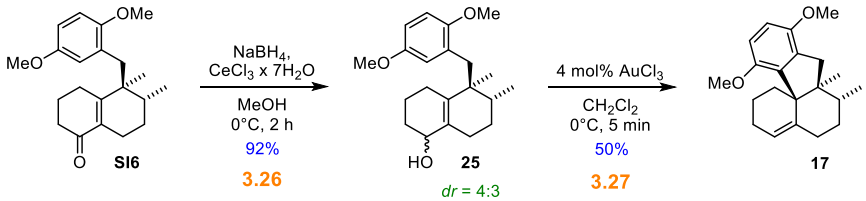


2. General Experimental Information

2.1. Reagents and Solvents

All reagents and reactants were purchased from *Acros Organics, Sigma-Aldrich, Merck, Alfa Aesar, Carbolution, ABCR, TCI Chemicals* or *Fluka* with a purity of ≥ 95% and used without further purification unless otherwise noted. The solvents were distilled before use. Dry THF, Et_2O and toluene were obtained by distillation from sodium/benzophenone, dry CH_2Cl_2 by distillation from CaH_2 under argon atmosphere. 2-Methylcyclohex-2-enone,[1] 2-bromomethyl-2,5-dimethoxybenzene[2] and the phosphoramidite ligand **L***[3] were synthesized on multi gram scale based on literature known procedures.

2.2. Working Techniques

Air sensitive reactions were performed in flame-dried glassware under argon using a *Schlenk* line. Substances were added through argon-flushed syringes via septa or by addition under an argon stream. Solvent evaporation was conducted using a *Büchi* Rotavapor RE 114 rotary evaporator at 40°C water bath temperature unless otherwise noted. Room temperature (r.t.) corresponds to 24±3 °C.

2.3. Chromatography

Reactions were monitored by thin layer chromatography (TLC) on plates from *Merck* (silica gel 60 F_{254} on aluminum foil, layer thickness 0.25 mm). Compounds were visualized under UV light (λ = 254 nm), with $KMnO_4$ or with ceric ammonium molybdate as staining agent. Flash column chromatography was carried out with silica gel (particle size: 35 – 70 µm, pore size: 60 Å) or ultrapure silica gel (particle size: 40 – 60 µm, pore size: 60 Å) purchased from *Acros Organics*.

2.4. Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H, ^{13}C (standard or DEPTQ), ^{31}P and ^{19}F NMR spectra were measured in $CDCl_3$ at r.t. on a *Bruker* Avance 300 (300 MHz), *Bruker* Avance II 300 (300 MHz), *Bruker* Avance II 500 (500 MHz), *Bruker* Avance III 500 (500 MHz) or *Bruker* Avance II+ 600 (600 MHz) spectrometer. Chemical shifts δ are given in parts per million (ppm) relative to tetramethylsilane (TMS; ^1H and ^{13}C), 85% phosphoric acid (^{31}P) or $CFCl_3$ (^{19}F) using the residual solvent (^1H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm) or TMS (0.00 ppm) as a reference. The information in parentheses report fine structures (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), scalar coupling constants (J, given in Hz), relative integration of signals and the signal assignment. The non-trivial assignments were determined with the help of 2D NMR experiments: ^1H,^1H-COSY, ^1H,^1H-NOESY, ^1H,^{13}C-HSQCed and ^1H,^{13}C-HMBC. Assignments of NMR signals refer to the given numbering und do not necessarily correspond to IUPAC nomenclature.

2.5. Fourier-Transform Infrared (FT-IR) Spectroscopy

IR spectra were obtained using a *PerkinElmer* Spectrum Two FT-IR instrument in the ATR mode at room temperature. Absorption bands are given in cm^{-1} (abbreviations: s = strong, m = medium, w = weak, br = broad).

2.6. Gas-Chromatography – Mass Spectroscopy (GC-MS)

GC-MS analysis was performed on a gas chromatograph *Agilent* HP6890 coupled with a mass detector (MSD) 5937 N. Capillary column: Optima-1-MS (*Macherey-Nagel*), 30 m x 0.25 mm Ø. Carrier gas: H_2, 30 mL/min, 1.2 bar. Temperature program: 50°C (2 min), 50°C – 300°C (10 min), 300°C (5 min).

2.7. High Resolution Electrospray Ionization – Mass Spectroscopy (HRMS)

High resolution mass spectra were recorded on a *Thermo Scientific* LTQ Orbitrap XL instrument. ESI conditions were set as 3.4 kV (spray voltage), 3.0 V (capillary voltage), 3.0 V (tube lens voltage) and 275°C (capillary temperature). For a stable electrospray, sheath gas and sweep gas were used (Nitrogen 5.0, ≥ 99.999%, *Linde*).

2.8. Specific Optical Rotation ($[\alpha]_\lambda^T$)

Optical rotation values were determined using an *Anton Paar* MCP 200 polarimeter with a cell length of 10 cm. All compounds were measured in $CHCl_3$ or MeOH with given concentrations at room temperature.

2.9. Melting Point (M.p.)

Melting points were determined on a *Büchi* B-545 instrument in open capillary tubes.

2.10. X-Ray Crystallography

X-ray data were obtained using a *Bruker* D8 VENTURE (Kappa geometry, microfocus source (Cu anode), λ = 1.54178 Å) apparatus with a PHOTON III M14 or PHOTON 100 detector. Structure solution and refinement were performed using SHELXT[4] software.

2.11. Chiral High Performance Liquid Chromatography (Chiral HPLC)

The enantiomeric excess (*ee*) was determined on a *VWR Hitachi* Chromaster HPLC system with a CHIRALPAK AD-H column (column temperature: 18°C, detection at 250 nm) using a racemic standard.

2.12. UV Spectroscopy

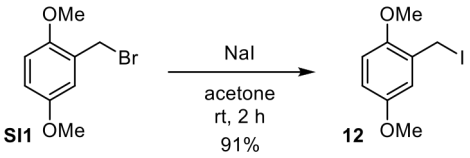
The UV spectrum of (–)-dysiherbol A was measured on a *PerkinElmer* Lambda 35 UV/VIS spectrometer in methanol (10^{-5} M solution).

2.13. ECD Spectroscopy

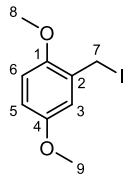
The ECD spectrum of (–)-dysiherbol A was measured on a *Jasco* j-715 CD spectropolarimeter in methanol (10^{-3} M solution).

3. Synthetic Procedures and Compound Data

3.1. 2-(Iodomethyl)-1,4-dimethoxybenzene (12)[5]



Note: Due to the light sensitivity of the product, all operations were performed under exclusion of sunlight in flasks wrapped with aluminum foil. To a solution of 45.8 g (198 mmol, 1.00 eq.) of 2-(bromomethyl)-1,4-dimethoxybenzene (**SI1**) in 280 mL of acetone were added 59.3 g (396 mmol, 2.00 eq.) of NaI and the suspension was stirred for 2 h at rt. Then, the precipitate was removed by filtration and the solution was concentrated under reduced pressure. The resulting pale yellow solid was immediately partitioned between 200 mL of sat. aqueous $Na_2S_2O_3$ and 400 mL of CH_2Cl_2 and the phases were separated. The organic layer was concentrated under reduced pressure to give 50.3 g (180 mmol, 91%) of **12** as a pale yellow solid. Alternative workup: Occasionally, the product crystallized during the first solvent removal. In this case, the flask was removed from the rotation evaporator and the crystallization process allowed to finished, before the crystals were washed with sat. aqueous $Na_2S_2O_3$, water and MeOH. The obtained colorless needles were finally dried *in vacuo*.



$C_9H_{11}IO_2$ (**M** = 278.09 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.53

M.p.: 59.5°C – 60.5°C

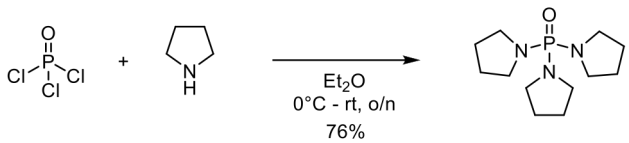
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.87 (d, *J* = 2.9 Hz, 1H, 3-H), 6.80 (dd, *J* = 8.9, 2.9 Hz, 1H, 5-H), 6.76 (d, *J* = 8.9 Hz, 1H, 6-H), 4.46 (s, 2H, 7-H), 3.87 (s, 3H, 8-H), 3.76 (s, 3H, 9-H).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 153.5 (C-4), 151.5 (C-1), 128.5 (C-2), 115.8 (C-3), 114.6 (C-5), 112.3 (C-6), 56.1 (C-8), 55.9 (C-9), 1.3 (C-7).

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3003 (w), 2988 (w), 2959 (w), 2934 (w), 2902 (w), 2832 (w), 1824 (w), 1605 (w), 1586 (w), 1491 (s), 1467 (m), 1439 (w), 1414 (m), 1318 (w), 1278 (m), 1263 (w), 1225 (s), 1185 (m), 1180 (m), 1148 (m), 1134 (m), 1084 (m), 1043 (s), 1019 (s), 927 (w), 875 (m), 825 (w), 801 (s), 757 (w), 730 (w), 714 (m), 576 (w), 550 (w).

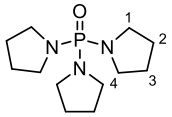
GC-MS (70 eV): *m/z* (%) = 278 (4, $[M]^+$), 151 (100), 137 (99), 121 (38), 91 (18), 77 (22), 66 (16), 39 (9).

3.2. Tris-(pyrrolidinyl)-phosphoramide (TPPA)[6]



A 1000 mL three-necked round flask equipped with a 300 mL dropping funnel and a reflux condenser connected to a bubble counter (containing 1 M aqueous NaOH), was charged with 48.0 mL (79.0 g, 515 mmol, 1.00 eq.) of $POCl_3$ dissolved in 250 mL of dry Et_2O. The magnetically stirred solution was cooled in an ice bath while 250 mL (213 g, 2.99 mol, 5.81 eq.) of pyrrolidine were added slowly over a period of 2 h through the dropping funnel. ((Note: Upon addition a white precipitate (pyrrolidine hydrochloride) forms immediately. As the reaction is exothermic, the dropping speed has to be controled carefully). After complete addition, the stirred suspension was allowed to warm up to rt overnight. The white precipitate was separated off by filtration, washed with dry Et_2O and the combined organic solutions were concentrated under reduced pressure. To the resulting yellow oil were added several grams of

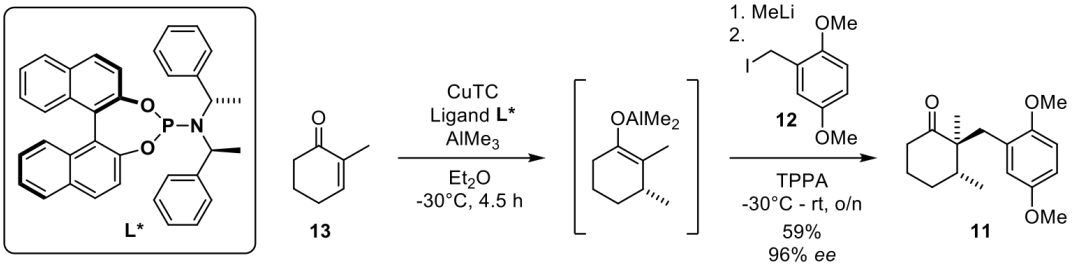
CaH_2 and the product was purified by fractional vacuum distillation (0.018 mbar, head temperature: 140°C) to provide 101 g (392 mmol, 76%) of TPPA as a colorless, viscous oil.



$C_{12}H_{24}N_3OP$ (**M** = 257.32 g/mol)

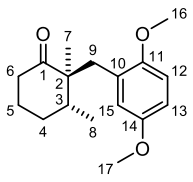
^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ [ppm] = 3.21 (td, J = 6.6, 4.2 Hz, 12H, 1-H, 4-H), 1.68 – 1.54 (m, 12H, 2-H, 3-H).
^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 46.3 (d, $J_{C,P}$ = 4.4 Hz, C-1, C-4), 26.5 (d, $J_{C,P}$ = 8.0 Hz, C-2, C-3).
^{31}P NMR (121 MHz, $CDCl_3$, 298 K): δ [ppm] = 14.2
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960 (m), 2864 (m), 1490 (w), 1449 (w), 1345 (w), 1292 (w), 1222 (s), 1202 (s), 1126 (m), 1076 (s), 1008 (s), 956 (w), 912 (m), 873 (w), 765 (m), 573 (s), 512 (w).
GC-MS (70 eV): *m/z* (%) = 257 (25, $[M]^+$), 187 (54), 145 (8), 118 (9), 89 (7), 70 (100), 41 (11).

3.3. (2*S*,3*R*)-2-(2,5-Dimethoxybenzyl)-2,3-dimethylcyclohexanone (11)



The reaction was performed in analogy to a literature procedure.[7] In a *Schlenk* flask a solution of 173 mg (0.908 mmol, 0.024 eq.) of CuTC and 980 mg (1.82 mmol, 0.047 eq.) of the phosphoramidite ligand **L*** in 100 mL of dry Et_2O was stirred at rt for 20 min. The salmon-colored solution was cooled to -30°C and 4.24 g (38.5 mmol, 1.00 eq.) of enone **13** were added. Then, 27.2 mL (54.5 mmol, 1.42 eq.) of $AlMe_3$ (2.0 M in heptane) were added via syringe over a period of 10 min. The reaction mixture was stirred at -30°C for 4.5 h, until TLC indicated full conversion of the starting material. The solvents were removed *in vacuo* at -30°C (using the *Schlenk* line) until a small volume remained, which was dissolved in 40 mL of TPPA before 34.1 mL (54.5 mmol, 1.42 eq.) of methyllithium (1.6 M in Et_2O) were added over 5 min (still at -30 °C). Finally, 20.2 g (72.6 mmol, 1.89 eq.) of iodide **12** were added and the stirred suspension was allowed to slowly warm up to rt overnight. At this point, GC-MS analysis indicated full conversion of the 1,4-addition intermediate and a diastereoselectivity of *dr* = 5:1. The reaction mixture was carefully quenched by addition of 20 mL of sat. aqueous NH_4Cl at 0°C before 200 mL of H_2O and 100 mL of sat. aqueous Na K tartrate solution were added (to facilitate phase separation). The aqueous phase was extracted with 4 x 200 mL of *c*-Hex, the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 33:1) to give 6.34 g (22.9 mmol, 59%) of the pure *trans*-product **11** as a pale yellow solid. This product showed an enantiomeric excess of 96% *ee* as determined by chiral HPLC using a racemic standard (for details see section 8). In addition, a sample of the separated *cis*-byproduct *epi*-**11** was obtained and used for analytical characterization (see below).

<u>*Data of the trans*-product **11:**</u>



$C_{17}H_{24}O_3$ (**M** = 276.38 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.32
m.p.: 50.4°C – 53.5°C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.72 (d, J = 8.9 Hz, 1H, 12-H), 6.70 – 6.66 (m, 2H, 13-H, 15-H), 3.72 (s, 3H, 17-H), 3.68 (s, 3H, 16-H), 3.17 (d, J = 13.6 Hz, 1H, 9-H_a), 2.90 (d, J = 13.6 Hz, 1H, 9-H_b), 2.72 (ddd, J = 14.5, 9.9, 6.6 Hz, 1H, 6-H_a), 2.32 (dt, J = 14.5, 5.8 Hz, 1H, 6-H_b), 2.08 (ddt, J = 13.7, 9.1, 4.4 Hz, 1H, 4-H_a), 2.01 – 1.93 (m, 1H, 3-H), 1.88 (dtt, J = 14.6, 9.8, 5.0 Hz, 1H, 5-H_a), 1.82 – 1.74 (m, 1H, 5-H_b), 1.49 (dtd, J = 13.4, 6.5, 4.5 Hz, 1H, 4-H_b), 0.91 (d, J = 7.0 Hz, 3H, 8-H), 0.89 (s, 3H, 7-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 216.2 (C-1), 153.1 (C-14), 152.3 (C-11), 128.2 (C-10), 118.5 (C-15), 111.8 (C-13), 111.2 (C-12), 55.7 (C-17), 55.5 (C-16), 53.6 (C-2), 40.2 (C-3), 38.4 (C-6), 37.2 (C-9), 28.7 (C-4), 23.0 (C-5), 18.9 (C-7), 16.4 (C-8).

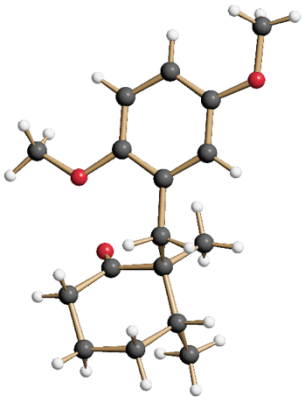
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2988 (w), 2935 (m), 2871 (w), 2833 (w), 1700 (s), 1610 (w), 1589 (w), 1498 (s), 1462 (m), 1426 (w), 1382 (w), 1351 (w), 1313 (w), 1222 (s), 1179 (w), 1158 (w), 1122 (w), 1107 (w), 1091 (w), 1048 (s), 1027 (w), 946 (w), 918 (w), 874 (w), 800 (m), 716 (m), 623 (w), 588 (w), 557 (w), 532 (w).

GC-MS (70 eV): *m/z* (%) = 276 (29, $[M]^+$), 151 (100), 121 (22), 91 (12), 77 (9), 65 (6), 55 (9).

HRMS (ESI):	Calc. [amu]	Found [amu]
	277.17982 $[M+H]^+$	277.18007 $[M+H]^+$
	299.16177 $[M+Na]^+$	299.16179 $[M+Na]^+$

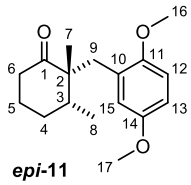
$[\alpha]^{20}_{\lambda}$ (c = 0.65 g/100 mL, $CHCl_3$): + 76° (436 nm), + 35° (546 nm), + 29° (579 nm), + 27° (589 nm).

X-ray crystal structure (CCDC 2077905)**:**



Data of the cis-product *epi*-**11:**

$C_{17}H_{24}O_3$ (**M** = 276.38 g/mol)



***epi*-11**

R_f (c-Hex/EtOAc 9:1) = 0.25

m.p.: 61 °C – 63 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.70 – 6.64 (m, 2H, 12-H, 13-H), 6.57 (d, J = 2.6 Hz, 1H, 15-H), 3.71 (s, 3H, 17-H), 3.63 (s, 3H, 16-H), 3.22 (d, J = 13.5 Hz, 1H, 9-H_a), 3.06 (td, J = 13.4, 6.4 Hz, 1H, 6-H_a), 2.60 (d, J = 13.5 Hz, 1H, 9-H_b), 2.36 – 2.30 (m, 1H, 6-H_b), 2.02 (ddq, J = 9.3, 6.1, 3.1 Hz, 1H, 5-H_a), 1.84 – 1.75 (m, 1H, 4-H_a), 1.75 – 1.68 (m, 1H, 3-H), 1.68 – 1.60 (m, 2H, 4-H_b, 5-H_b), 1.10 (d, J = 6.4 Hz, 3H, 8-H), 0.88 (s, 3H, 7-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 214.9 (C-1), 153.0 (C-14), 152.1 (C-11), 127.5 (C-10), 118.5 (C-15), 111.6 (C-13), 110.9 (C-12), 55.7 (C-17), 55.2 (C-16), 53.1 (C-2), 44.7 (C-3), 38.5 (C-6), 31.8 (C-9), 29.8 (C-4), 26.4 (C-5), 19.9 (C-7), 16.1 (C-8).

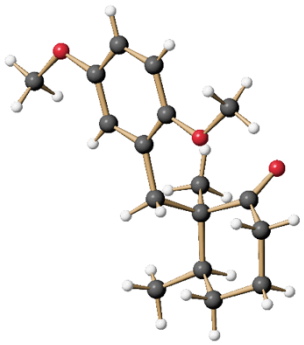
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2964 (m), 2919 (m), 2859 (w), 2834 (w), 1696 (s), 1607 (w), 1501 (s), 1465 (m), 1450 (m), 1417 (w), 1382 (w), 1371 (w), 1356 (w), 1339 (w), 1323 (w), 1313 (w), 1297 (w), 1267 (w), 1222 (s), 1194 (w), 1179 (m), 1159 (w), 1125 (w), 1099 (w), 1089 (w), 1068 (w), 1037 (s), 1017 (m), 947 (w), 915 (w), 874 (m), 855 (w), 832 (w), 803 (m), 742 (w), 708 (m), 629 (w), 595 (w), 573 (w), 538 (w).

GC-MS (70 eV): *m/z* (%) = 276 (27, $[M]^+$), 151 (100), 121 (24), 91 (14), 77 (11), 65 (8), 55 (12).

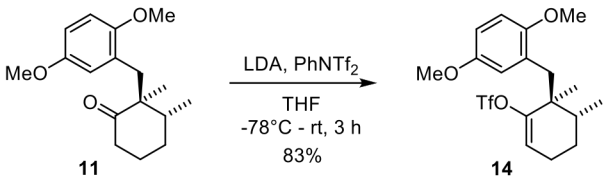
HRMS (ESI):	Calc. [amu]	Found [amu]
	277.17982 $[M+H]^+$	277.17961 $[M+H]^+$
	299.16177 $[M+Na]^+$	299.16133 $[M+Na]^+$

[α]$^{20}_{\lambda}$ (*c* = 0.53 g/100 mL, $CHCl_3$): – 111° (436 nm), – 62° (546 nm), – 54° (579 nm), – 53° (589 nm).

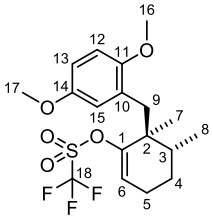
X-ray crystal structure (CCDC 2077912)**:**



3.4. Synthesis of enol triflate 14



In a *Schlenk* flask a solution of 5.78 g (54.0 mmol, 1.70 eq.) of LDA in 250 mL of dry THF was cooled to -78°C before 8.77 g (31.7 mmol, 1.00 eq.) of ketone **11** in 100 mL of dry THF were added. After stirring the mixture for 10 min at -78°C, 19.3 g (54.0 mmol, 1.70 eq.) of $PhNTf_2$ were added portionwise at that temperature. Stirred was continued at 0°C for 50 min and at rt for 2 h before excess reagents were quenched by addition of sat. aqueous NH_4Cl. After extracting with 3 x 200 mL of EtOAc the combined organic phases were washed with H_2O, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (*c*-Hex/EtOAc 30:1 → 20:1) afforded 10.7 g (26.2 mmol, 83%) of enol triflate **14** as a yellow, viscous oil.



$C_{18}H_{23}F_3O_5S$ (**M** = 408.43 g/mol)

R_f (*c*-Hex/EtOAc 20:1) = 0.29

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): *δ* [ppm] = 6.78 – 6.75 (m, 1H, 12-H), 6.75 – 6.71 (m, 2H, 13-H, 15-H), 5.77 (dd, *J* = 5.3, 3.0 Hz, 1H, 6-H), 3.74 (s, 3H, 16-H), 3.73 (s, 3H, 17-H), 3.00 (d, *J* = 13.9 Hz, 1H, 9-H_a), 2.70 (d, *J* = 13.8 Hz, 1H, 9-H_b), 2.08 (dtd, *J* = 17.8, 5.4, 4.3 Hz, 1H, 5-H_a), 1.94 (dddd, *J* = 17.8, 8.8, 5.6, 3.0 Hz, 1H, 5-H_b), 1.64 (dqd, *J* = 9.8, 6.8, 3.0 Hz, 1H, 3-H), 1.60 – 1.53 (m, 1H, 4-H_a), 1.42 – 1.33 (m, 1H, 4-H_b), 1.11 (s, 3H, 7-H), 0.97 (d, *J* = 6.8 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): *δ* [ppm] = 154.5 (C-1), 153.3 (C-14), 152.7 (C-11), 127.2 (C-10), 118.6 (q, $J_{C,F}$ = 319.3 Hz, C-18), 118.0 (C-6), 117.1 (C-15), 112.7 (C-13), 111.3 (C-12), 55.7*4* (C-16), 55.6*5* (C-17), 43.9 (C-2), 35.2 (C-9), 34.6 (C-3), 26.2 (C-4), 23.3 (C-5), 20.1 (C-7), 16.2 (C-8).

^{19}F NMR (282 MHz, $CDCl_3$, 298 K): *δ* [ppm] = –75.0

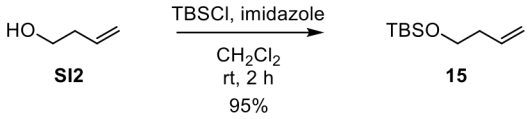
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2935 (br), 2835 (w), 1674 (w), 1609 (w), 1589 (w), 1501 (m), 1465 (m), 1408 (m), 1386 (m), 1347 (w), 1314 (w), 1301 (w), 1284 (w), 1270 (w), 1245 (m), 1208 (s), 1189 (m), 1141 (m), 1103 (w), 1081 (w), 1049 (m), 1029 (m), 1012 (m), 983 (s), 959 (w), 918 (m), 904 (m), 869 (s), 855 (s), 802 (m), 773 (w), 756 (m), 737 (w), 716 (m), 709 (m), 689 (m), 689 (w), 648 (w), 605 (s).

GC-MS (70 eV): *m/z* (%) = 408 (20, $[M]^+$), 151 (100), 121 (19), 91 (9), 69 (9), 55 (5).

HRMS (ESI):	Calc. [amu]	Found [amu]
	431.11105 $[M+Na]^+$	431.11125 $[M+Na]^+$

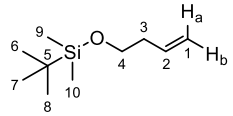
[α]$^{20}_{\lambda}$ (*c* = 0.59 g/100 mL, $CHCl_3$): + 44° (436 nm), + 26° (546 nm), + 23° (579 nm), + 23° (589 nm).

3.5. But-3-en-1-yloxy(*tert*-butyl)dimethylsilane (15)[8]



To a solution of 5.89 mL (4.94 g, 69.3 mmol, 1.00 eq.) of homoallylic alcohol (**SI2**) in 150 mL of dry CH_2Cl_2 were added 9.44 g (139 mmol, 2.00 eq.) of imidazole and the resulting suspension was stirred under argon until a clear solution was obtained. Then, 11.5 g (76.3 mmol, 1.10 eq.) of TBSCl were added and stirring was continued for 2 h at rt before 200 mL of H_2O were added. The aqueous phase was extracted with 2 x 100 mL of CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Filtration through a short plug of silica gel (*c*-Hex/EtOAc 5:1) afforded 12.3 g (66.0 mmol, 95%) of **15** as a volatile, colorless liquid.

$C_{10}H_{22}OSi$ (**M** = 186.37 g/mol)



R_f (*c*-Hex/EtOAc 3:1) = 0.90

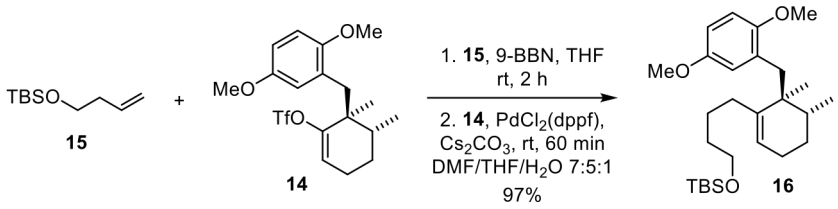
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 5.81 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H, 2-H), 5.07 (dq, J = 17.2, 1.5 Hz, 1H, 1-H_a), 5.03 – 5.00 (m, 1H, 1-H_b), 3.66 (t, J = 6.8 Hz, 2H, 4-H), 2.28 (qt, J = 6.8, 1.2 Hz, 2H, 3-H), 0.90 (s, 9H, 6-H, 7-H, 8-H), 0.05 (s, 6H, 9-H, 10-H).

^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ [ppm] = 135.5 (C-2), 116.4 (C-1), 62.9 (C-4), 37.6 (C-3), 26.1 (C-6, C-7, C-8), –5.1 (C-9, C-10).

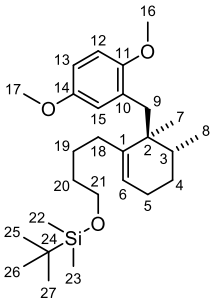
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3080 (w), 2955 (w), 2929 (m), 2897 (w), 2858 (m), 1642 (w), 1472 (w), 1463 (w), 1432 (w), 1408 (w), 1384 (w), 1361 (w), 1254 (m), 1228 (w), 1096 (s), 1005 (w), 986 (m), 938 (w), 909 (m), 833 (s), 810 (m), 733 (w), 678 (w), 664 (w), 626 (w).

GC-MS (70 eV): *m/z* (%) = 129 (66), 101 (100), 89 (18), 73 (30), 59 (16), 41 (18).

3.6. Synthesis of silyl ether 16 through Suzuki cross coupling



The reaction was performed in analogy to a literature protocol.[9] In a *Schlenk* flask, a solution of 7.14 g (38.3 mmol, 1.50 eq.) of olefin **15** in 55 mL of dry THF was cooled to 0°C. Then, 92.0 mL (46.0 mmol, 1.80 eq.) of 9-BBN (0.5 M in THF) were added and the mixture was stirred at rt for 2 h. The solution was then cooled to 0 °C before 27.5 mL of H_2O were added and stirring was continued for 60 min at 0 °C. This borane solution was then transferred via needle to a second *Schlenk* flask charged with a solution of 625 mg (0.765 mmol, 0.030 eq.) of $PdCl_2$(dppf) x CH_2Cl_2, 20.8 g (63.8 mmol, 2.50 eq.) of Cs_2CO_3 and 10.4 g (25.5 mmol, 1.00 eq.) of the enol triflate **14** in 190 mL of dry DMF at rt. The black reaction mixture was stirred at rt for 60 min before 0.40 g of QuadraSil AP® were added as a metal scavenger and the suspension was stirred for further 30 min. Then the solids were separated by decantation and H_2O and brine were added to the product solution. After extraction with with EtOAc (4x) the combined organic layers were washed with H_2O, dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (*c*-Hex/EtOAc 20:1) to yield 11.1 g (24.8 mmol, 97%) of silyl ether **16** as a yellow, viscous oil.



$C_{27}H_{46}O_3Si$ (**M** = 446.75 g/mol)

R_f (*c*-Hex/EtOAc 15:1) = 0.42

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.78 (d, *J* = 3.1 Hz, 1H, 15-H), 6.75 (d, *J* = 8.8 Hz, 1H, 12-H), 6.68 (dd, *J* = 8.8, 3.1 Hz, 1H, 13-H), 5.46 (t, *J* = 3.8 Hz, 1H, 6-H), 3.75 (s, 3H, 16-H), 3.72 (s, 3H, 17-H), 3.62 (t, *J* = 6.3 Hz, 2H, 21-H), 2.93 (d, *J* = 14.6 Hz, 1H, 9-H_a), 2.66 (d, *J* = 14.6 Hz, 1H, 9-H_b), 2.04 (t, *J* = 7.1 Hz, 2H, 18-H), 2.02 – 1.91 (m, 2H, 5-H), 1.78 (dtd, *J* = 12.9, 6.5, 3.2 Hz, 1H, 4-H_a), 1.70 (quint of d, *J* = 7.0, 3.1 Hz, 1H, 3-H), 1.59 – 1.53 (m, 2H, 20-H), 1.53 – 1.42 (m, 2H, 19-H), 1.40 – 1.32 (m, 1H, 4-H_b), 0.93 (s, 3H, 7-H), 0.90 (s, 9H, 25-H, 26-H, 27-H), 0.80 (d, *J* = 6.8 Hz, 3H, 8-H), 0.05 (s, 6H, 22-H, 23-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 153.1 (C-14), 152.6 (C-11), 143.3 (C-1), 129.6 (C-10), 121.4 (C-6), 117.3 (C-15), 111.2*4* (C-12), 111.1*9* (C-13), 63.5 (C-21), 56.0 (C-16), 55.7 (C-17), 42.0 (C-2), 36.3 (C-9), 33.8 (C-3), 33.3 (C-20), 31.3 (C-18), 26.5 (C-4), 26.1 (C-25, C-26, C-27), 25.5 (C-19), 23.9 (C-5), 21.8 (C-7), 18.5 (C-24), 16.1 (C-8), –5.1 (C-22, C-23).

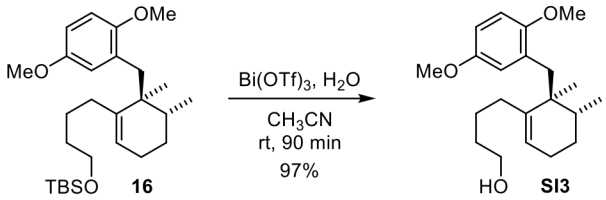
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2951 (br), 2929 (m), 2906 (w), 2857 (w), 2833 (w), 1609 (w), 1588 (w), 1498 (m), 1463 (m), 1426 (w), 1380 (w), 1360 (w), 1298 (w), 1282 (w), 1254 (m), 1219 (s), 1179 (w), 1158 (w), 1099 (m), 1051 (m), 1030 (m), 1005 (w), 964 (w), 939 (w), 901 (w), 834 (s), 804 (m), 795 (m), 773 (s), 732 (w), 714 (m), 686 (w), 661 (w), 606 (w).

GC-MS (70 eV): *m/z* (%) = 446 (17, $[M]^+$), 389 (17), 295 (8), 237 (7), 163 (100), 152 (48), 147 (10), 121 (22), 107 (16), 91 (15), 75 (14).

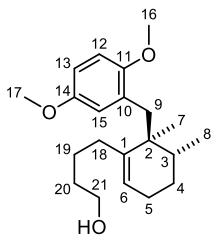
HRMS (ESI):	Calc. [amu]	Found [amu]
	447.32889 $[M+H]^+$	447.32930 $[M+H]^+$
	469.31084 $[M+Na]^+$	469.31088 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.51 g/100 mL, $CHCl_3$): – 51° (436 nm), – 27° (546 nm), – 24° (579 nm), – 21° (589 nm).

3.7. Synthesis of alcohol SI3



In an argon-flushed flask 11.1 g (24.8 mmol, 1.00 eq.) of silyl ether **16** were dissolved in 400 mL of CH_3CN and 4.5 mL (4.5 g, 250 mmol, 10 eq.) of H_2O. Then, 650 mg (0.99 mmol, 0.04 eq.) of $Bi(OTf)_3$ were added and the reaction mixture was stirred at rt for 90 min. 200 mL of H_2O were added and the aqueous phase was extracted with 3 x 200 mL of CH_2Cl_2. The combined organic phases were washed with H_2O, dried over $MgSO_4$ and the solvent was removed under reduced pressure. 7.98 g (24.0 mmol, 97%) of alcohol **SI3**, together with 1.48 g of TBSOH/TBSOTBS were obtained as a pale yellow, viscous oil. The crude alcohol **SI3** was used for the following reaction without further purification. For analytical characterization, a sample of was purified by silica gel column chromatography (*c*-Hex/MTBE 2:1).



$C_{21}H_{32}O_3$ (**M** = 332.48 g/mol)

R_f (*c*-Hex/EtOAc 4:1) = 0.22

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.77 (d, J = 3.5 Hz, 1H, 15-H), 6.76 (d, J = 9.1 Hz, 1H, 12-H), 6.68 (dd, J = 8.8, 3.1 Hz, 1H, 13-H), 5.47 (t, J = 3.6 Hz, 1H, 6-H), 3.75 (s, 3H, 16-H), 3.73 (s, 3H, 17-H), 3.65 (t, J = 6.4 Hz, 2H, 21-H), 2.92 (d, J = 14.6 Hz, 1H, 9-H_a), 2.66 (d, J = 14.5 Hz, 1H, 9-H_b), 2.07 – 2.02 (m, 2H, 18-H), 2.02 – 1.92 (m, 2H, 5-H), 1.79 (dtd, J = 13.0, 6.6, 3.2 Hz, 1H, 4-H_a), 1.71 (quint of d, J = 7.0, 3.2 Hz, 1H, 3-H), 1.65 – 1.57 (m, 2H, 20-H), 1.57 – 1.44 (m, 2H, 19-H), 1.36 (td, J = 13.5, 6.3 Hz, 1H, 4-H_b), 0.93 (s, 3H, 7-H), 0.81 (d, J = 6.9 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 153.1 (C-14), 152.6 (C-11), 143.0 (C-1), 129.6 (C-10), 121.5 (C-6), 117.5 (C-15), 111.2 (C-12), 111.1 (C-13), 63.2 (C-21), 56.0 (C-16), 55.7 (C-17), 42.0 (C-2), 36.4 (C-9), 33.8 (C-3), 33.2 (C-20), 31.2 (C-18), 26.4 (C-4), 25.4 (C-19), 23.8 (C-5), 21.8 (C-7), 16.0 (C-8).

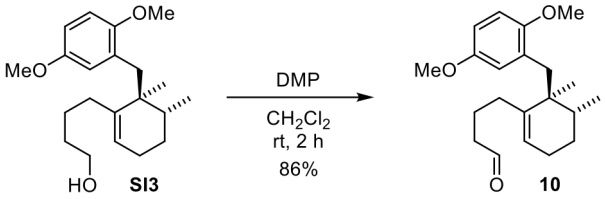
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3354 (br), 2933 (br), 2834 (w), 1611 (w), 1592 (w), 1499 (s), 1463 (m), 1379 (w), 1282 (w), 1271 (w), 1221 (s), 1179 (w), 1159 (w), 1126 (w), 1051 (m), 1045 (m), 1029 (m), 878 (w), 800 (w), 717 (w).

GC-MS (70 eV): *m/z* (%) = 332 (40, $[M]^+$), 181 (43), 152 (79), 151 (65), 137 (29), 121 (100), 107 (56), 91 (73), 79 (47), 71 (29), 55 (40).

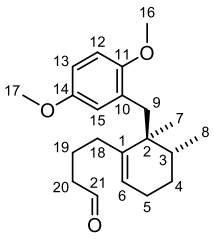
HRMS (ESI):	Calc. [amu]	Found [amu]
	355.22437 $[M+Na]^+$	355.22478 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (c = 0.67 g/100 mL, $CHCl_3$): – 59° (436 nm), – 30° (546 nm), – 26° (579 nm), – 25° (589 nm).

3.8. Synthesis of aldehyde 10



A solution of 7.98 g (24.0 mmol, 1.00 eq.) of alcohol **SI3** (in a mixture with 1.48 g of TBSOH/TBSOTBS) were dissolved in 630 mL of dry CH_2Cl_2. The solution was cooled to 0°C and 21.0 g (49.6 mmol, 2.00 eq.) of Dess Martin's reagent were added over 5 min and stirring was continued for 15 min at 0°C and 2 h at rt. Then, the mixture was cooled to 0°C before 200 mL of H_2O were added. The phases were separated and the aqueous phase was extracted with 3 x 200 mL of CH_2Cl_2. The combined organic phases were washed with H_2O, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (ultrapure SiO_2, *c*-Hex/EtOAc 9:1) to provide 6.83 g (20.7 mmol, 86%) of aldehyde **10** as a yellowish viscous oil.



$C_{21}H_{30}O_3$ (**M** = 330.47 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.27

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 9.77 (t, J = 1.8 Hz, 1H, 21-H), 6.75*4* (d, J = 8.6 Hz, 1H, 12-H), 6.74*9* (d, J = 3.6 Hz, 1H, 15-H), 6.68 (dd, J = 8.9, 3.0 Hz, 1H, 13-H), 5.48 (t, J = 3.7 Hz, 1H, 6-H), 3.75 (s, 3H, 16-H), 3.73 (s, 3H, 17-H), 2.90 (d, J = 14.5 Hz, 1H, 9-H_a), 2.64 (d, J = 14.4 Hz, 1H, 9-H_b), 2.46 (td, J = 7.2, 1.6 Hz, 2H, 20-H), 2.09 – 2.02 (m, 2H, 18-H), 2.02 – 1.92 (m, 2H, 5-H), 1.90 – 1.77 (m, 3H, 4-H_a, 19-H), 1.73 (qq, J = 7.0, 3.2 Hz, 1H, 3-H), 1.37 (ddt, J = 13.4, 7.5, 6.1 Hz, 1H, 4-H_b), 0.92 (s, 3H, 7-H), 0.81 (d, J = 6.9 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 203.0 (C-21), 153.1 (C-11), 152.6 (C-14), 142.3 (C-1), 129.4 (C-10), 122.1 (C-6), 117.6 (C-15), 111.2 (C-12/13), 111.1 (C-12/13), 56.0 (C-16), 55.7 (C-17), 44.1 (C-20), 42.0 (C-2), 36.6 (C-9), 33.8 (C-3), 30.9 (C-18), 26.3 (C-4), 23.7 (C-5), 21.8 (C-19), 21.7 (C-7), 16.0 (C-8).

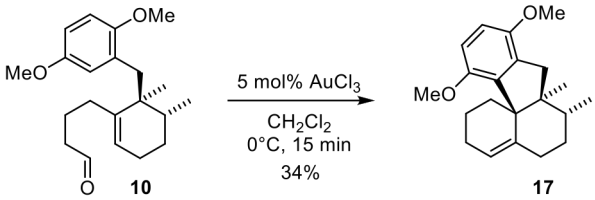
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2932 (br), 2833 (w), 2718 (w), 1723 (m), 1608 (w), 1588 (w), 1497 (s), 1463 (m), 1425 (w), 1379 (w), 1283 (w), 1268 (w), 1218 (s), 1179 (m), 1158 (w), 1127 (w), 1074 (w), 1048 (s), 1028 (m), 952 (w), 940 (w), 909 (w), 873 (w), 849 (w), 799 (m), 757 (w), 732 (w), 714 (m), 687 (w), 637 (w).

GC-MS (70 eV): *m/z* (%) = 330 (30, [M]$^+$), 207 (8), 179 (13), 161 (83), 151 (85), 135 (36), 121 (100), 105 (56), 91 (96), 77 (60), 55 (37).

HRMS (ESI):	Calc. [amu]	Found [amu]
	353.20871 [M+Na]$^+$	353.20897 [M+Na]$^+$

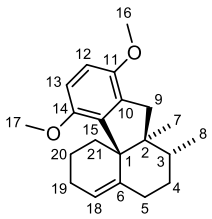
[α]$^{20}_{\lambda}$ (*c* = 0.57 g/100 mL, $CHCl_3$): – 80° (436 nm), – 41° (546 nm), – 34° (579 nm), – 32° (589 nm).

3.9. Synthesis of olefin 17



A solution of 2.00 g (6.05 mmol, 1.00 eq.) of aldehyde **10** in 600 mL of CH_2Cl_2 (HPLC grade) was cooled to 0°C and 94 mg (0.31 mmol, 0.051 eq.) of $AuCl_3$ were added. The dark green mixture was stirred for 15 min at 0 °C before 620 mg of QuadraSil TA® (0.5 mmol/g) were added and the suspension was stirred for further 30 min at 0 °C (discoloration). The solids were separated by filtration and the solvent was removed under reduced pressure. The resulting pale brown, viscous oil was purified by silica gel column chromatography (*c*-Hex/EtOAc 30:1) to give 825 mg of a colorless sticky oil, containing approximately 644 mg (2.06 mmol, 34%) of olefin **17** along with inseparable (at this stage) side products, as determined by integration of suitable ^{1}H NMR signals. On a 100 mg scale a yield of 38% of **17** was obtained (37% for a 300 mg scale). The oil crystallizes very slowly at rt. A sample of the ketone side product **SI8** (single diastereomer) was also obtained and characterized (see below).

Data of **17:**



$C_{21}H_{28}O_2$ (**M** = 312.45 g/mol)

R_f (*c*-Hex/EtOAc 20:1) = 0.27

m.p.: 86°C – 88°C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.63 (s, 2H, 12-H, 13-H), 5.61 (td, *J* = 3.9, 1.7 Hz, 1H, 18-H), 3.78 (s, 3H, 16-H), 3.68 (s, 3H, 17-H), 2.83 (d, *J* = 15.8 Hz, 1H, 9-H$_a$), 2.54 (d, *J* = 15.8 Hz, 1H, 9-H$_b$), 2.09 (dt, *J* = 13.1, 3.3 Hz, 1H, 5-H$_a$), 2.05 – 2.01 (m, 2H, 19-H), 2.01 – 1.95 (m, 1H, 5-H$_b$), 1.92 (ddd, *J* = 12.8, 9.5, 2.9 Hz, 1H, 21-H$_a$), 1.64 (ddtd, *J* = 12.6, 9.4, 6.4, 2.9 Hz, 1H, 20-H$_a$), 1.57 – 1.49 (m, 1H, 20-H$_b$), 1.49 – 1.42 (m, 2H, 3-H, 21-H$_b$), 1.36 (dq, *J* = 12.7, 3.5 Hz, 1H, 4-H$_a$), 1.18 (qd, *J* = 12.9, 3.9 Hz, 1H, 4-H$_b$), 1.00 (s, 3H, 7-H), 0.83 (d, *J* = 6.7 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 151.6 (C-14), 150.9 (C-11), 141.2 (C-15), 138.3 (C-6), 131.8 (C-10), 122.5 (C-18), 110.3 (C-13), 108.8 (C-12), 56.0 (C-17), 55.8 (C-16), 55.4 (C-1), 52.2 (C-2), 38.4 (C-9), 36.3 (C-3), 35.0 (C-5), 32.5 (C-21), 32.3 (C-4), 25.9 (C-19), 20.3 (C-20), 18.2 (C-8), 14.2 (C-7).

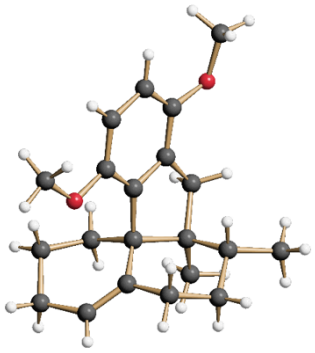
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924 (br), 2851 (m), 2830 (m), 1596 (w), 1491 (s), 1462 (m), 1437 (m), 1379 (w), 1323 (w), 1278 (w), 1254 (s), 1189 (w), 1157 (w), 1141 (w), 1110 (w), 1095 (m), 1070 (m), 1055 (m), 1012 (w), 972 (w), 914 (w), 883 (w), 865 (w), 788 (m), 715 (w), 669 (w), 638 (w).

GC-MS (70 eV): *m/z* (%) = 312 (100, [M]$^+$), 297 (38), 255 (16), 241 (15), 227 (16), 165 (17), 115 (16), 55 (15).

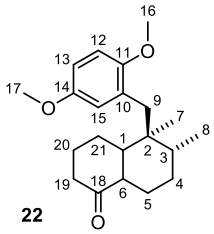
HRMS (ESI):	Calc. [amu]	Found [amu]
	313.21620 $[M+H]^+$	313.21688 $[M+H]^+$

$[\alpha]^{20}_{\lambda}$ (c = 0.45 g/100 mL, $CHCl_3$): + 249° (436 nm), + 131° (546 nm), + 113° (579 nm), + 107° (589 nm).

X-ray crystal structure (CCDC 2077903)**:**



Data of the ketone side product **SI8:**



22

$C_{21}H_{30}O_3$ (**M** = 330.47 g/mol)

R_f (c-Hex/EtOAc 5:1) = 0.36

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.74 (d, J = 8.8 Hz, 1H, 12-H), 6.71 (dd, J = 8.8, 2.9 Hz, 1H, 13-H), 6.68 (d, J = 2.8 Hz, 1H, 15-H), 3.74 (s, 3H, 17-H), 3.71 (s, 3H, 16-H), 2.82 (d, J = 14.0 Hz, 1H, 9-H_a), 2.62 (d, J = 14.0 Hz, 1H, 9-H_b), 2.46 – 2.41 (m, 1H, 21-H_a), 2.35 (ddt, J = 13.6, 4.2, 2.1 Hz, 1H, 19-H_a), 2.30 – 2.22 (m, 1H, 19-H_b), 2.15 – 2.07 (m, 2H, 6-H, 20-H_a), 1.73 (dq, J = 13.5, 3.1 Hz, 1H, 5-H_a), 1.53 – 1.49 (m, 1H, 20-H_b), 1.49 – 1.43 (m, 2H, 4-H_a, 21-H_b), 1.38 – 1.30 (m, 1H, 3-H), 1.23 – 1.18 (m, 1H, 1-H), 1.18 – 1.10 (m, 1H, 4-H_b), 1.10 – 1.04 (m, 1H, 5-H_b), 1.02 (d, J = 6.5 Hz, 3H, 8-H), 0.89 (s, 3H, 7-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 214.2 (C-18), 152.9 (C-14), 152.8 (C-11), 127.9 (C-10), 119.0 (C-15), 111.3 (C-13), 110.9 (C-12), 55.7 (C-17), 55.5 (C-16), 51.3 (C-6), 47.7 (C-1), 42.1 (C-19), 41.8 (C-2), 35.6 (C-9), 35.3 (C-3), 29.9 (C-4), 27.6 (C-21), 26.1 (C-20), 25.2 (C-5), 17.6 (C-8), 14.9 (C-7).

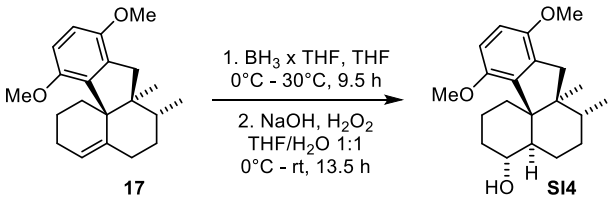
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2927 (s), 2855 (m), 2837 (w), 1734 (w), 1709 (m), 1590 (w), 1498 (s), 1464 (s), 1400 (w), 1379 (w), 1260 (s), 1221 (s), 1179 (w), 1159 (w), 1090 (m), 1049 (s), 1028 (m), 870 (w), 799 (s), 715 (w).

GC-MS (70 eV): m/z (%) = 330 (72, $[M]^+$), 161 (15), 151 (100), 121 (24), 105 (13), 91 (27), 77 (17).

HRMS (ESI):	Calc. [amu]	Found [amu]
	353.20872 $[M+Na]^+$	353.20896 $[M+Na]^+$

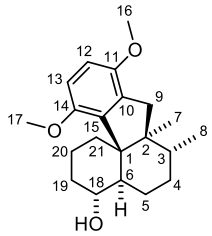
$[\alpha]^{20}_{\lambda}$ (c = 0.25 g/100 mL, $CHCl_3$): – 2.7° (436 nm), + 4.7° (546 nm), + 2.7° (579 nm), – 2.7° (589 nm).

3.10. Synthesis of alcohol SI4



17 **SI4**

A solution of 644 mg (2.06 mmol, 1.00 eq.) of olefin **17** in 60 mL of dry THF was cooled to 0°C and 13.5 mL (13.5 mmol, 6.55 eq.) of BH_3 x THF (1.0 M in THF) were added. The mixture was stirred at 0°C for 2 h and at 30°C for 7.5 h. Then, the solution was cooled to 0 °C before 20 mL of 10% (w/w) aqueous NaOH and 40 mL of aqueous 30% (w/V) H_2O_2 were slowly added successively (CAUTION: The reaction with NaOH is exothermic!). The stirred mixture was left in the cooling bath overnight to slowly reach 25°C (14 h). After re-cooling to 0 °C and careful addition of sat. aqueous $Na_2S_2O_3$ the mixture was allowed to reach rt before the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a colorless, viscous oil. The crude alcohol **SI4** was used for the following reaction without further purification. For analytical characterization, a sample of the crude product was purified by silica gel column chromatography (CH_2Cl_2/*c*-Hex 4:1). The configuration of the two newly formed stereocenters was verified by ^{1}H,^{1}H-NOESY NMR analysis.



$C_{21}H_{30}O_3$ (**M** = 330.47 g/mol)

R_f (*c*-Hex/EtOAc 4:1) = 0.41

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.67 (s, 2H, 12-H, 13-H), 4.50 (td, *J* = 10.0, 5.9 Hz, 1H, 18-H), 3.77 (s, 3H, 16-H), 3.75 (s, 3H, 17-H), 2.77 (d, *J* = 15.9 Hz, 1H, 9-H_a), 2.43 (d, *J* = 15.9 Hz, 1H, 9-H_b), 2.17 – 2.10 (m, 1H, 19-H_a), 1.97 – 1.92 (m, 1H, 5-H_a), 1.53 – 1.46 (m, 1H, 21-H_a), 1.46 – 1.39 (m, 3H, 4-H_a, 20-H_a, 21-H_b), 1.35 – 1.28 (m, 3H, 3-H, 6-H, 20-H_b), 1.22 – 1.10 (m, 3H, 4-H_b, 5-H_b, 19-H_b), 1.02 (s, 3H, 7-H), 0.77 (d, *J* = 6.7 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 151.3 (C-11), 150.8 (C-14), 138.8 (C-15), 132.9 (C-10), 109.7 (C-12), 109.2 (C-13), 71.1 (C-18), 59.4 (C-1), 55.8 (C-16), 55.1 (C-17), 50.9 (C-2), 47.4 (C-6), 37.7 (C-9), 36.5 (C-19), 35.2 (C-3), 35.1 (C-21), 32.0 (C-4), 25.6 (C-5), 20.9 (C-20), 18.1 (C-8), 13.3 (C-7).

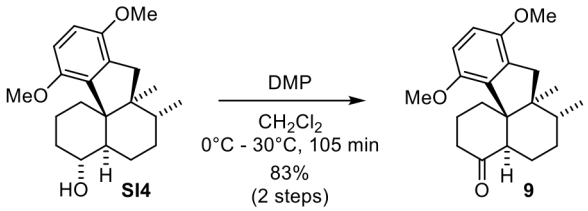
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3363 (br), 2931 (s), 2854 (m), 2043 (w), 1971 (w), 1735 (br), 1594 (w), 1492 (s), 1462 (m), 1380 (w), 1324 (w), 1281 (w), 1255 (s), 1171 (w), 1148 (w), 1071 (m), 1047 (w), 1034 (w), 1004 (w), 968 (w), 941 (w), 873 (w), 848 (w), 790 (w), 719 (w).

GC-MS (70 eV): *m/z* (%) = 330 (52, $[M]^+$), 312 (100), 297 (34), 258 (18), 255 (22), 243 (25), 227 (18), 203 (23), 189 (21).

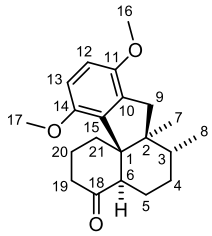
HRMS (ESI):	Calc. [amu]	Found [amu]
	353.20872 $[M+Na]^+$	353.20865 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.76 g/100 mL, $CHCl_3$): – 75° (436 nm), – 44° (546 nm), – 39° (579 nm), – 37° (589 nm).

3.11. Synthesis of ketone 9



A solution of the crude alcohol **SI4** of the previous reaction (≤2.06 mmol) in 72 mL of CH_2Cl_2 (HPLC grade) was cooled to 0°C before 2.46 g (5.80 mmol, 2.82 eq.) of DMP were added over 5 min. The mixture was stirred at 0°C for 30 min and at 30°C for 75 min. After addition of H_2O, the phases were separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic layers were washed with sat. aqueous $NaHCO_3$ and H_2O, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (*c*-Hex/EtOAc 9:1) to provide 559 mg (1.70 mmol, 83% over 2 steps) of ketone **9** as a yellow sticky oil, which crystallized very slowly at rt.



$C_{21}H_{28}O_3$ (**M** = 328.45 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.24

m.p.: 127 °C – 128 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.65 (d, *J* = 8.7 Hz, 1H, 12-H), 6.61 (d, *J* = 8.8 Hz, 1H, 13-H), 3.77 (s, 3H, 16/17-H), 3.56 (s, 3H, 16/17-H), 2.82 (d, *J* = 15.8 Hz, 1H, 9-H_a), 2.53 (d, *J* = 15.8 Hz, 1H, 9-H_b), 2.47 (ddt, *J* = 16.6, 5.0, 1.7 Hz, 1H, 19-H_a), 2.24 – 2.19 (m, 1H, 5-H_a), 2.19 – 2.13 (m, 1H, 19-H_b), 2.09 – 2.05 (m, 1H, 6-H), 1.81 – 1.74 (m, 1H, 21-H_a), 1.74 – 1.65 (m, 2H, 20-H_a, 21-H_b), 1.63 – 1.53 (m, 1H, 20-H_b), 1.47 – 1.41 (m, 1H, 4-H_a), 1.28 – 1.20 (m, 1H, 3-H), 1.13 – 1.06 (m, 1H, 4-H_b), 1.05 (s, 3H, 7-H), 1.04 – 0.98 (m, 1H, 5-H_b), 0.81 (d, *J* = 6.7 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 209.6 (C-18), 151.3 (C-11/14), 151.2 (C-11/14), 136.7 (C-15), 131.8 (C-10), 109.4 (C-12), 109.2 (C-13), 58.4 (C-1), 55.8 (C-16/17), 53.8 (C-16/17), 51.9 (C-6), 50.9 (C-2), 40.4 (C-19), 38.0 (C-9), 35.2 (C-3), 33.4 (C-21), 30.9 (C-4), 22.6 (C-5), 21.1 (C-20), 18.1 (C-8), 12.7 (C-7).

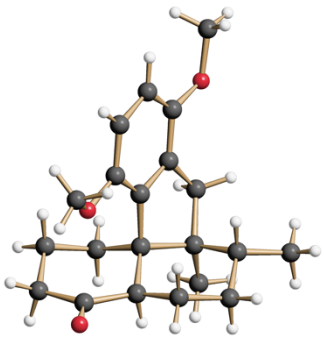
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2924 (br), 2851 (m), 1706 (s), 1597 (w), 1493 (s), 1460 (m), 1381 (w), 1354 (w), 1320 (w), 1293 (w), 1279 (m), 1259 (s), 1251 (s), 1187 (w), 1171 (w), 1146 (w), 1129 (w), 1094 (m), 1083 (m), 1068 (m), 1051 (m), 1024 (w), 1007 (w), 967 (w), 954 (w), 898 (w), 879 (w), 842 (w), 792 (m), 738 (w), 716 (w), 678 (w), 648 (w).

GC-MS (70 eV): *m/z* (%) = 328 (100, $[M]^+$), 297 (97), 285 (100), 258 (31), 243 (49), 227 (18), 201 (22), 189 (20), 115 (21), 91 (12), 55 (16).

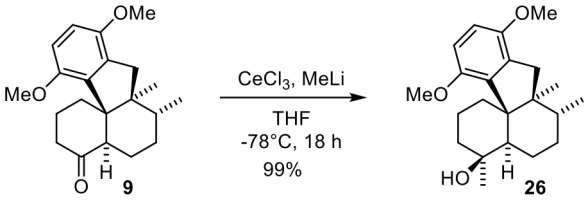
HRMS (ESI):	Calc. [amu]	Found [amu]
	329.21112 $[M+H]^+$	329.21094 $[M+H]^+$
	351.19307 $[M+Na]^+$	351.19257 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.55 g/100 mL, $CHCl_3$): – 39° (436 nm), – 20° (546 nm), – 17° (579 nm), – 17° (589 nm).

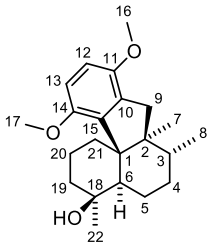
X-ray crystal structure (CCDC 2077914)**:**



3.12. Synthesis of alcohol 26



According to *Imamoto*,[10] a suspension of 311 mg (1.26 mmol, 2.30 eq.) of $CeCl_3$ in 7.2 mL of dry THF was stirred at rt for 2.5 h (activation). Then, the mixture was cooled to -78°C and 0.88 mL (1.1 mmol, 2.1 eq.) of MeLi (1.3 M in Et_2O) were added over 2 min. After stirring at -78°C for 35 min, 180 mg (0.548 mmol, 1.00 eq.) of ketone **9** in 1.8 mL of dry THF were added over 1 min. and the mixture was stirred for further 18 h at -78 °C the allowed to reach rt over 20 min. After additional 30 min excess reagent was quenched by addition of 20 mL of sat. aqueous NH_4Cl and 70 mL of H_2O. After extraction with 3 x 50 mL of MTBE the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to give 189 mg (0.548 mmol, 99%) of alcohol **26** as a colorless, crystalline solid.



$C_{22}H_{32}O$ (**M** = 344.50 g/mol)

R_f (*c*-Hex/EtOAc 3:1) = 0.35

m.p.: 149 °C – 151 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.74 (d, *J* = 8.9 Hz, 1H, 13-H), 6.70 (d, *J* = 8.8 Hz, 1H, 12-H), 6.33 (s, 1H, OH), 3.85 (s, 3H, 17-H), 3.78 (s, 3H, 16-H), 2.76 (d, *J* = 16.0 Hz, 1H, 9-H_a), 2.40 (d, *J* = 16.0 Hz, 1H, 9-H_b), 1.92 – 1.83 (m, 2H, 5-H_a, 19-H_a), 1.60 – 1.55 (m, 1H, 6-H), 1.54 – 1.49 (m, 1H, 4-H_a), 1.49 – 1.44 (m, 3H, 19-H_b, 21-H), 1.44 – 1.37 (m, 1H, 20-H_a), 1.37 – 1.28 (m, 2H, 3-H, 20-H_b), 1.25 (d, *J* = 1.1 Hz, 3H, 22-H), 1.24 – 1.16 (m, 2H, 4-H_b, 5-H_b), 0.99 (s, 3H, 7-H), 0.76 (d, *J* = 6.7 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 152.0 (C-11), 149.5 (C-14), 139.6 (C-15), 133.6 (C-10), 110.2 (C-13), 109.2 (C-12), 69.8 (C-18), 59.5 (C-1), 56.2 (C-17), 55.8 (C-16), 52.2 (C-2), 47.5 (C-6), 42.7 (C-19), 37.2 (C-9), 35.8 (C-21), 35.3 (C-3), 33.5 (C-4), 31.2 (C-22), 24.6 (C-5), 19.1 (C-20), 18.0 (C-8), 13.6 (C-7).

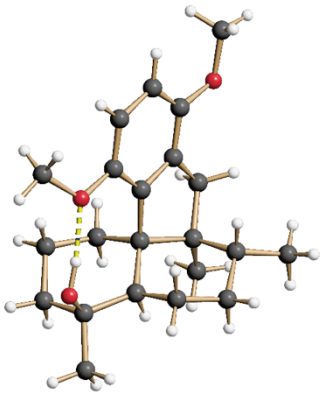
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3462 (br), 2930 (s), 2873 (w), 2848 (w), 1588 (w), 1490 (s), 1462 (m), 1385 (w), 1374 (w), 1359 (w), 1317 (w), 1298 (w), 1266 (w), 1253 (s), 1190 (w), 1171 (w), 1162 (w), 1149 (w), 1077 (m), 1047 (m), 997 (w), 962 (m), 923 (w), 898 (w), 863 (w), 789 (m), 726 (m), 665 (w), 647 (w), 580 (w), 537 (w).

GC-MS (70 eV): *m/z* (%) = 344 (21, $[M]^+$), 326 (11), 269 (19), 259 (100), 243 (8), 203 (22), 189 (16), 71 (9), 55 (13).

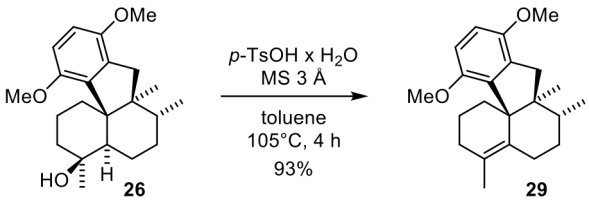
HRMS (ESI):	Calc. [amu]	Found [amu]
	367.22437 $[M+Na]^+$	367.22418 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.40 g/100 mL, $CHCl_3$): – 72° (436 nm), – 42° (546 nm), – 36° (579 nm), – 35° (589 nm).

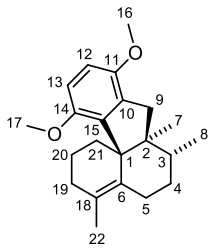
X-ray crystal structure (CCDC 2077910)**:**



3.13. Synthesis of olefin 29



A *Schlenk* flask was charged with 2.2 g of freshly activated MS 3 Å powder before a solution of 504 mg (1.46 mmol, 1.00 eq.) of alcohol **26** in 42 mL of toluene (HPLC grade) and 2.93 g (15.4 mmol, 10.5 eq.) of *p*-TsOH x H_2O were added. Then, the mixture was stirred at 105°C for 4 h. After cooling to rt and addition of sat. aqueous $NaHCO_3$ the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic phases were washed with H_2O, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 50:1) to afford 442 mg (1.35 mmol, 93%) of olefin **29** as a colorless, crystalline solid.



$C_{22}H_{30}O_2$ (**M** = 326.48 g/mol)

R_f (*c*-Hex/EtOAc 49:1) = 0.39

m.p.: 80 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.61 (s, 2H, 12-H, 13-H), 3.77 (s, 3H, 16-H), 3.64 (s, 3H, 17-H), 2.80 (d, *J* = 15.8 Hz, 1H, 9-H_a), 2.61 (dt, *J* = 13.8, 3.3 Hz, 1H, 5-H_a), 2.52 (d, *J* = 15.8 Hz, 1H, 9-H_b), 2.08 – 1.99 (m, 1H, 19-H_a), 1.99 – 1.92 (m, 1H, 19-H_b), 1.88 (ddd, *J* = 13.0, 10.1, 3.1 Hz, 1H, 21-H_a), 1.71 (s, 3H, 22-H), 1.65 – 1.59 (m, 1H, 5-H_b), 1.59 – 1.56 (m, 1H, 20-H_a), 1.55 – 1.47 (m, 1H, 20-H_b), 1.47 – 1.39 (m, 2H, 3-H, 21-H_b), 1.33 (dq, *J* = 12.8, 3.5 Hz, 1H, 4-H_a), 1.10 (dtd, *J* = 13.9, 12.6, 3.4 Hz, 1H, 4-H_b), 0.96 (s, 3H, 7-H), 0.82 (d, *J* = 6.8 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 151.7 (C-14), 150.9 (C-11), 142.0 (C-15), 131.7 (C-10), 130.0 (C-6), 126.8 (C-18), 110.4 (C-13), 108.7 (C-12), 56.3 (C-17), 56.1 (C-1), 55.8 (C-16), 52.1 (C-2), 38.5 (C-9), 36.4 (C-3), 33.1 (C-19), 32.9 (C-21), 31.5 (C-4), 27.9 (C-5), 20.3 (C-20), 20.2 (C-22), 18.2 (C-8), 14.3 (C-7).

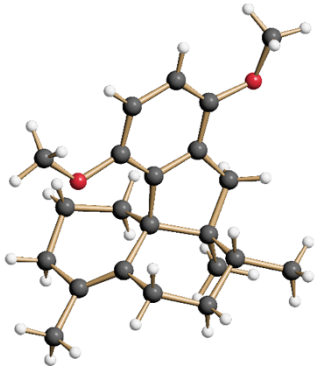
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2951 (w), 2931 (m), 2908 (m), 2871 (w), 2852 (m), 2829 (m), 2044 (w), 1973 (w), 1595 (w), 1492 (s), 1463 (m), 1437 (m), 1379 (w), 1325 (w), 1255 (s), 1194 (w), 1172 (w), 1157 (w), 1142 (w), 1125 (w), 1094 (m), 1074 (m), 1057 (m), 1011 (w), 971 (w), 945 (w), 897 (w), 866 (w), 789 (m), 715 (m), 665 (w).

GC-MS (70 eV): *m/z* (%) = 326 (100, $[M]^+$), 311 (69), 267 (19), 258 (24), 241 (27), 227 (11), 225 (11), 211 (13), 175 (15), 165 (11), 152 (10), 115 (11), 91 (11), 71 (13), 55 (15).

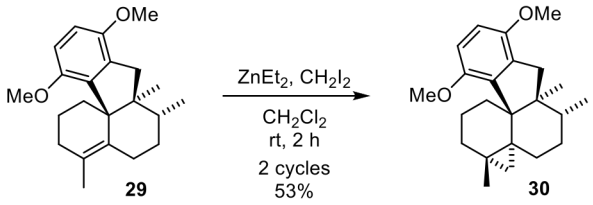
HRMS (ESI):	Calc. [amu]	Found [amu]
	327.23186 $[M+H]^+$	327.23177 $[M+H]^+$
	349.21380 $[M+Na]^+$	349.21378 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.49 g/100 mL, $CHCl_3$): + 338° (436 nm), + 180° (546 nm), + 156° (579 nm), + 149° (589 nm).

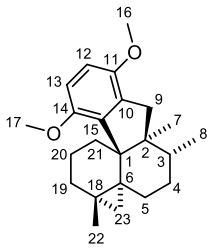
X-ray crystal structure (CCDC 2077904)**:**



3.14. Synthesis of cyclopropane 30



In a flame-dried *Schlenk* flask 105 mg (0.322 mmol, 1.00 eq.) of olefin **29** were dissolved in 750 µL of CH_2Cl_2 (HPLC grade). Then, 430 µL (0.387 mmol, 1.20 eq.) of $ZnEt_2$ (0.9 M in hexane) and 32.0 µL (106 mg, 0.396 mmol, 1.23 eq.) of CH_2I_2 were simultaneously added at rt and the addition procedure (same amounts) was repeated 3 more times with an interval of 20 minutes. The mixture was stirred for further 60 min at rt before excess reagent was quenched ba addition of H_2O and sat. aqueous $NaHCO_3$. After extraction with with EtOAc (2x) and CH_2Cl_2 the combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (*c*-Hex/toluene 8:1 → 4:1) to provide 48 mg (0.14 mmol, 44%) of cyclopropane **30** besides 40 mg (0.12 mmol, 38%) of reisolated olefin **29** which again subjected to the same cyclopropanation procedure. After the two cycles, 58 mg (0.17 mmol, 53%) of cyclopropane **30** were obtained as a colorless sticky oil, which solidified very slowly at rt.



$C_{23}H_{32}O_2$ (**M** = 340.51 g/mol)

R_f (*c*-Hex/toluene 1:1) = 0.62

m.p.: 76 °C – 80 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.66 (d, *J* = 8.9 Hz, 1H, 13-H), 6.64 (d, *J* = 8.8 Hz, 1H, 12-H), 3.78 (s, 3H, 17-H), 3.77 (s, 3H, 16-H), 2.70 (d, *J* = 15.7 Hz, 1H, 9-H_a), 2.46 (d, *J* = 15.7 Hz, 1H, 9-H_b), 1.73 (ddd, *J* = 13.9, 11.1, 8.6 Hz, 1H, 19-H_a), 1.62 (dd, *J* = 13.8, 8.7 Hz, 1H, 19-H_b), 1.58 – 1.47 (m, 2H, 5-H_a, 21-H_a), 1.41 – 1.23 (m, 4H, 3-H, 4-H_a, 5-H_b, 20-H_a), 1.20 (ddd, *J* = 9.8, 4.6, 3.5 Hz, 1H, 20-H_b), 1.14 (s, 3H, 22-H), 1.13 – 1.06 (m, 2H, 4-H_b, 21-H_b), 1.01 (s, 3H, 7-H), 0.81 (d, *J* = 6.2 Hz, 3H, 8-H), 0.72 (dd, *J* = 4.3, 1.7 Hz, 1H, 23-H_a), –0.01 (d, *J* = 4.4 Hz, 1H, 23-H_b).

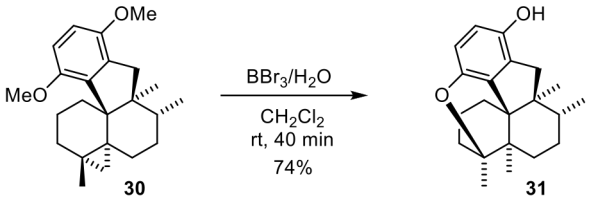
^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 152.4 (C-14), 151.1 (C-11), 139.7 (C-15), 132.3 (C-10), 108.8 (C-12), 108.7 (C-13), 55.7 (C-17), 55.6 (C-16), 55.0 (C-1), 51.0 (C-2), 38.5 (C-9), 36.1 (C-3), 31.4 (C-19), 30.5 (C-5), 30.3 (C-4), 28.5 (C-6), 28.1 (C-21), 23.6 (C-23), 23.4 (C-22), 20.7 (C-18), 18.6 (C-20), 18.2 (C-8), 14.0 (C-7).

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3676 (br), 3053 (w), 2946 (w), 2928 (s), 2904 (w), 2849 (w), 2830 (w), 1594 (w), 1492 (s), 1462 (m), 1438 (w), 1407 (w), 1395 (w), 1380 (w), 1322 (w), 1255 (s), 1175 (w), 1147 (w), 1085 (m), 1062 (m), 978 (w), 893 (br), 808 (w), 788 (w), 716 (w), 649 (w).

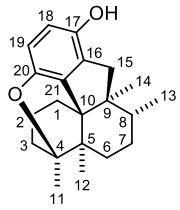
GC-MS (70 eV): *m/z* (%) = 340 (100, $[M]^+$), 272 (26), 258 (40), 257 (51), 255 (37), 243 (27), 215 (31), 201 (29), 189 (38), 55 (30).

$[\alpha]^{20}_{\lambda}$ (*c* = 1.00 g/100 mL, $CHCl_3$): + 132° (436 nm), + 73° (546 nm), + 63° (579 nm), + 60° (589 nm).

3.15. Synthesis of (–)-dysiherbol A (31)



To solution of 43 mg (0.13 mmol, 1.0 eq.) of cyclopropane **30** in 1.6 mL of CH_2Cl_2 were added 23 µL (23 mg, 1.3 mmol, 10 eq.) of H_2O and 1.6 mL (1.3 mmol, 10 eq.) of BBr_3 (0.78 M in heptane) and the mixture was stirred at rt for 40 min. After addition of H_2O the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 20:1) to provide 29 mg (0.092 mmol, 74%) of (–)-dysiherbol A (**31**) as a yellow, sticky oil. Slow evaporation of an Et_2O/MeOH solution of **31** at rt delivered crystalline (–)-dysiherbol A (as MeOH complex) as a yellowish, crystalline solid.



$C_{21}H_{28}O_2$ (**M** = 312.45 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.31

m.p.: 97 °C – 100 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.49 (d, *J* = 8.5 Hz, 1H, 18-H), 6.43 (d, *J* = 8.5 Hz, 1H, 19-H), 4.20 (br, 1H, OH), 2.57 (d, *J* = 15.2 Hz, 1H, 15-H_a), 2.54 (d, *J* = 15.0 Hz, 1H, 15-H_b), 1.96 (td, *J* = 14.1, 6.5 Hz, 1H, 3-H_a), 1.85 (td, *J* = 12.7, 4.4 Hz, 1H, 1-H_a), 1.68 (dd, *J* = 14.6, 5.8 Hz, 1H, 3-H_b), 1.54 – 1.47 (m, 1H, 2-H_a), 1.41 – 1.37 (m, 1H, 6-H_a), 1.37 – 1.27 (m, 4H, 1-H_b, 2-H_b, 6-H_b, 7-H_a), 1.25 – 1.17 (m, 2H, 7-H_b, 8-H), 1.22 (s, 3H, 11-H), 1.21 (s, 3H, 12-H), 1.08 (s, 3H, 14-H), 0.83 (d, *J* = 6.6 Hz, 3H, 13-H).

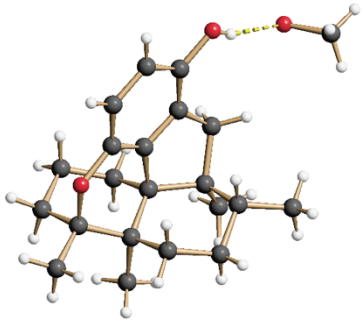
^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 148.5 (C-20), 145.7 (C-17), 133.2 (C-21), 126.0 (C-16), 114.4 (C-18), 111.2 (C-19), 82.6 (C-4), 52.0 (C-9), 49.3 (C-10), 39.5 (C-15), 37.4 (C-5), 35.8 (C-3), 35.6 (C-8), 30.1 (C-6), 26.6 (C-7), 26.5 (C-1), 22.1 (C-11), 19.9 (C-2), 18.6 (C-12), 17.9 (C-13), 15.0 (C-14).

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3389 (br), 2929 (s), 2870 (m), 2856 (m), 1710 (br), 1633 (w), 1489 (s), 1461 (s), 1382 (m), 1349 (w), 1324 (w), 1312 (w), 1263 (s), 1196 (m), 1183 (s), 1164 (m), 1131 (w), 1106 (s), 1087 (w), 1061 (w), 1045 (w), 1027 (w), 1010 (w), 988 (w), 959 (s), 937 (w), 911 (w), 887 (w), 869 (s), 800 (s), 763 (w), 738 (m), 704 (w), 594 (w).

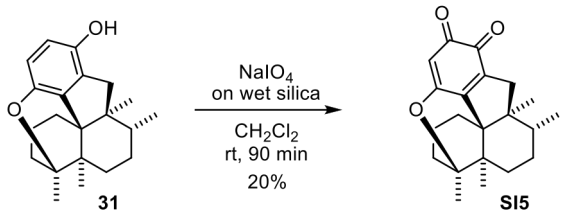
GC-MS (70 eV): *m/z* (%) = 312 (100, $[M]^+$), 243 (9), 225 (9), 213 (8), 199 (8), 187 (10), 173 (33), 161 (8), 119 (15), 115 (8), 55 (14).

$[\alpha]^{20}_{\lambda}$ (*c* = 0.50 g/100 mL, MeOH): – 27° (546 nm), – 24° (579 nm), – 23° (589 nm).

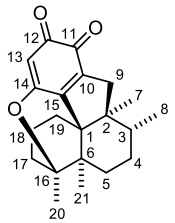
X-ray crystal structure (CCDC 2077913)**:**



3.16. Synthesis of quinone SI5



According to a procedure of *Baran*,[11] a solution of 10 mg (0.032 mmol, 1.0 eq.) of (–)-dysiherbol A (**31**) in 1.1 mL of dry CH_2Cl_2 was cooled to 0°C before 0.13 g (0.083 mmol, 2.6 eq.) of $NaIO_4$ on wet silica gel were added (preparation:[12] A solution of 2.59 g (12.1 mmol) of $NaIO_4$ in 6.0 mL of H_2O was heated to 70°C to give an almost clear solution. To the hot solution were added 10 g of silica gel and the mixture was shaken vigorously until a homogenous, free-flowing powder (0.65 mmol $NaIO_4$/g) was obtained). The stirred reaction mixture was allowed to warm to rt and stirred for 90 min. The red suspension was filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (*c*-Hex/EtOAc 5:1) to provide 2.1 mg (20%) of quinone **SI5** as a dark red, viscous oil.



$C_{21}H_{26}O_3$ (**M** = 326.44 g/mol)

R_f (*c*-Hex/EtOAc 4:1) = 0.23

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 5.61 (s, 1H, 13-H), 2.50 (d, J = 17.0 Hz, 1H, 9-H_a), 2.37 (d, J = 16.8 Hz, 1H, 9-H_b), 2.04 (ddd, J = 14.9, 13.2, 6.3 Hz, 1H, 17-H_a), 1.92 – 1.83 (m, 1H, 19-H_a), 1.79 – 1.70 (m, 2H, 17-H_b, 18-H_a), 1.64 – 1.50 (m, 3H, 5-H_a, 18-H_b, 19-H_b), 1.45 – 1.32 (m, 4H, 3-H, 4-H, 5-H_b), 1.30 (s, 3H, 20-H), 1.19 (s, 3H, 21-H), 1.05 (s, 3H, 7-H), 0.87 (d, J = 6.5 Hz, 3H, 8-H).

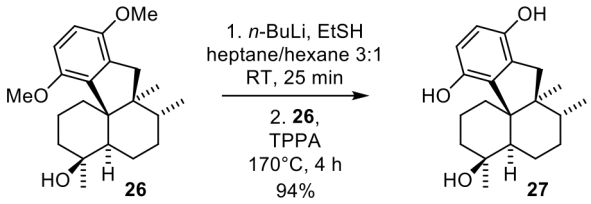
^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 181.3 (C-11), 178.7 (C-12), 166.1 (C-14), 156.3 (C-15), 138.2 (C-10), 102.8 (C-13), 88.0 (C-16), 52.2 (C-1), 50.8 (C-2), 39.6 (C-9), 39.5 (C-6), 36.3 (C-3), 33.9 (C-17), 30.5 (C-5), 27.1 (C-19), 25.8 (C-4), 21.7 (C-20), 19.5 (C-18), 18.8 (C-21), 17.7 (C-8), 15.0 (C-7).

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952 (w), 2926 (s), 2872 (m), 2856 (m), 1723 (w), 1677 (m), 1646 (s), 1578 (s), 1458 (m), 1395 (s), 1351 (w), 1293 (w), 1262 (w), 1235 (m), 1196 (w), 1178 (m), 1129 (w), 1102 (w), 1078 (w), 1041 (w), 1028 (w), 1015 (w), 965 (w), 920 (w), 912 (w), 856 (w), 836 (w), 798 (w), 777 (w), 731 (w), 680 (w).

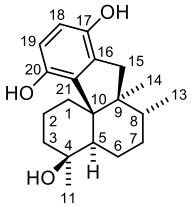
HRMS (ESI):	Calc. [amu]	Found [amu]
	327.19547 $[M+H]^+$	327.19532 $[M+H]^+$
	349.17742 $[M+Na]^+$	349.17730 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.02 g/100 mL, MeOH): + 125° (579 nm), + 107° (589 nm).

3.17. Synthesis of triol 27



In a *Schlenk* flask, 0.40 mL (0.88 mmol, 10 eq.) of *n*-BuLi (2.2 M in hexane) were diluted with 1.2 mL of heptane and the solution was cooled to 0 °C before 77 µL (65 mg, 1.0 mmol, 12 eq.) of EtSH were added. [13] The resulting suspension was stirred for 5 min at 0 °C and for 25 min at rt. Then, the solvents were removed *in vacuo* and the residual colorless solid was dried for 45 min before 0.45 mL of TPPA and 30 mg (0.087 mmol, 1.0 eq.) of alcohol **26** were added and the stirred mixture was heated to 170°C for 4 h under argon. After cooling to 25 °C, 3 mL of sat. aqueous NH_4Cl and 35 mL of H_2O were added and the aqueous phase was extracted with 3 x 25 mL of MTBE. The combined organic layers were washed with 80 mL of H_2O, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (*c*-Hex/EtOAc 4:1) afforded 26 mg (0.082 mmol, 94%) of triol **27** as a colorless solid. Slow evaporation of an Et_2O solution of **27** at rt delivered the triol (as Et_2O complex) as a colorless, crystalline solid.



$C_{20}H_{28}O_3$ (**M** = 316.44 g/mol)

R_f (*c*-Hex/EtOAc 2:1) = 0.44

m.p.: 116 °C – 118 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.58 (d, *J* = 8.6 Hz, 1H, 18-H), 6.54 (d, *J* = 8.6 Hz, 1H, 19-H), 4.51 (br, 1H, OH), 2.66 (d, *J* = 15.3 Hz, 1H, 15-H_a), 2.42 (d, *J* = 15.3 Hz, 1H, 15-H_b), 1.92 – 1.87 (m, 1H, 3-H_a), 1.87 – 1.82 (m, 1H, 6-H_a), 1.64 – 1.50 (m, 5H, 1-H_a, 2-H_a, 3-H_b, 5-H, 7-H_a), 1.50 – 1.46 (m, 1H, 1-H_b), 1.46 – 1.40 (m, 2H, 2-H_b, 8-H), 1.39 (s, 3H, 11-H), 1.33 (td, *J* = 12.6, 3.3 Hz, 1H, 6-H_b), 1.19 (qd, *J* = 12.8, 3.9 Hz, 1H, 7-H_b), 0.99 (s, 3H, 14-H), 0.76 (d, *J* = 6.7 Hz, 3H, 13-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 148.2 (C-20), 145.6 (C-17), 134.9 (C-21), 129.4 (C-16), 116.5 (C-19), 115.0 (C-18), 72.7 (C-4), 58.1 (C-10), 52.0 (C-9), 46.9 (C-5), 41.6 (C-3), 36.8 (C-15), 35.6 (C-1), 34.9 (C-8), 33.1 (C-7), 31.5 (C-11), 24.2 (C-6), 19.0 (C-2), 17.9 (C-13), 13.5 (C-14).

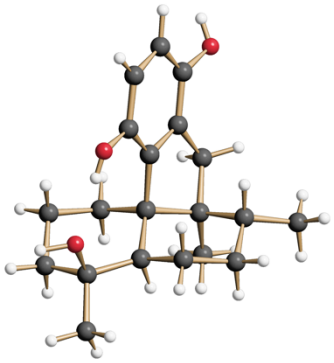
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3319 (br), 2930 (s), 2874 (m), 2853 (m), 2678 (br), 2248 (br), 1701 (br), 1648 (w), 1619 (w), 1592 (w), 1485 (w), 1461 (s), 1376 (m), 1329 (w), 1301 (w), 1262 (m), 1230 (s), 1185 (m), 1167 (m), 1125 (w), 1087 (w), 1053 (w), 1022 (m), 996 (w), 957 (w), 907 (s), 871 (m), 826 (w), 804 (m), 785 (w), 758 (w), 731 (s), 648 (w), 591 (w), 531 (w), 512 (w).

GC-MS (70 eV): *m/z* (%) = 316 (4, $[M]^+$), 298 (100), 283 (18), 255 (82), 239 (10), 213 (13), 173 (15), 161 (9), 115 (8), 55 (11).

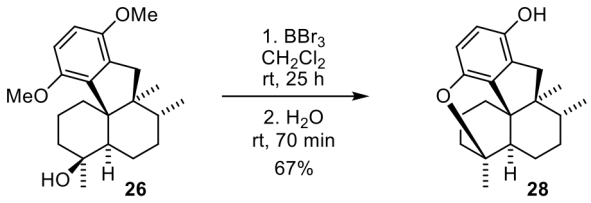
HRMS (ESI):	Calc. [amu]	Found [amu]
	339.19307 $[M+Na]^+$	339.19383 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 1.00 g/100 mL, MeOH): – 24° (546 nm), – 22° (579 nm), – 22° (589 nm).

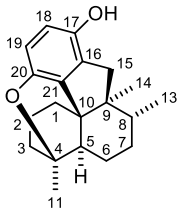
X-ray crystal structure (CCDC 2082956)**:**



3.18. Synthesis of nor-(–)-dysiherbol A (28)



A solution of 26 mg (0.075 mmol, 1.0 eq.) of alcohol **26** in 1.0 mL of dry CH_2Cl_2 was cooled to 0°C before 0.29 mL (0.29 mmol, 3.9 eq.) of BBr_3 (1.0 M in CH_2Cl_2) were added over 1 min. The solution was then stirred for 5 min at 0 °C and for 25 h at rt before, 3 drops of H_2O were added causing discoloration. The suspension was stirred for further 70 min at rt, before it was hydrolyzed by addition 3 mL of sat. aqueous $NaHCO_3$ and 15 mL of H_2O. The aqueous phase was extracted with 3 x 15 mL of MTBE, the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 10:1) to provide 15 mg (0.050 mmol, 67%) of **28** as a colorless solid.



$C_{20}H_{26}O_2$ (**M** = 298.43 g/mol)

R_f (*c*-Hex/EtOAc 3:1) = 0.66

m.p.: 67 °C – 69 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.50 (d, *J* = 8.5 Hz, 1H, 18-H), 6.45 (d, *J* = 8.5 Hz, 1H, 19-H), 4.24 (s, 1H, OH), 2.64 (d, *J* = 15.1 Hz, 1H, 15-H_a), 2.59 (d, *J* = 15.0 Hz, 1H, 15-H_b), 1.95 – 1.89 (m, 1H, 3-H_a), 1.69 – 1.62 (m, 2H, 6-H_a, 1-H_a), 1.59 (dd, *J* = 12.4, 5.1 Hz, 1H, 5-H), 1.56 – 1.46 (m, 2H, 3-H_b, 2-H_a), 1.43 (dd, *J* = 12.4, 3.6 Hz, 1H, 1-H_b), 1.39 – 1.33 (m, 1H, 2-H_b), 1.31 (s, 3H, 11-H), 1.30 – 1.28 (m, 1H, 7-H_a), 1.16 – 1.10 (m, 1H, 8-H), 1.08 (dd, *J* = 12.6, 2.7 Hz, 1H, 7-H_b), 1.03 (s, 3H, 14-H), 0.91 – 0.84 (m, 1H, 6-H_b), 0.82 (d, *J* = 6.5 Hz, 3H, 13-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 148.9 (C-20), 145.6 (C-17), 131.1 (C-21), 126.5 (C-16), 114.5 (C-18), 111.4 (C-19), 79.2 (C-4), 51.8 (C-9), 47.8 (C-10), 42.7 (C-5), 41.3 (C-3), 38.8 (C-15), 35.7 (C-8), 33.5 (C-1), 29.4 (C-7), 26.0 (C-11), 23.3 (C-6), 20.5 (C-2), 18.0 (C-13), 13.1 (C-14).

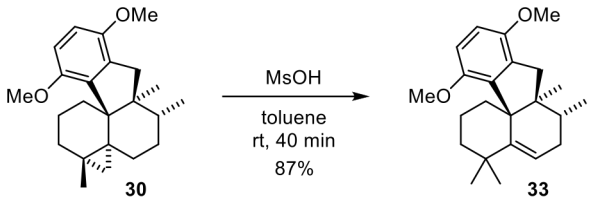
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3370 (br), 2928 (s), 2872 (w), 2849 (w), 2246 (w), 1630 (w), 1486 (s), 1462 (s), 1377 (m), 1351 (w), 1332 (w), 1308 (w), 1277 (m), 1263 (w), 1242 (s), 1213 (m), 1189 (s), 1175 (w), 1148 (w), 1137 (w), 1114 (m), 1074 (w), 1036 (w), 1023 (w), 1013 (w), 994 (w), 956 (m), 942 (m), 910 (m), 895 (w), 880 (w), 871 (m), 797 (s), 762 (w), 733 (s), 648 (w), 593 (w).

GC-MS (70 eV): *m/z* (%) = 298 (100, $[M]^+$), 283 (15), 255 (74), 239 (11), 213 (12), 173 (11), 161 (7), 115 (8), 91 (7), 55 (9).

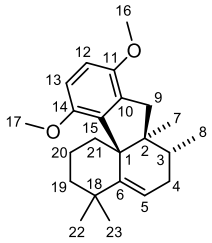
HRMS (ESI):	Calc. [amu]	Found [amu]
	299.20056 $[M+H]^+$	299.20111 $[M+H]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.68 g/100 mL, $CHCl_3$): – 66° (436 nm), – 40° (546 nm), – 35° (579 nm), – 33° (589 nm).

3.19. Synthesis of olefin 33



To a solution of 15 mg (0.044 mmol, 1.0 eq.) of cyclopropane **30** in 1.1 mL toluene were added 5.7 µL (8.5 mg, 0.088 mmol, 2.0 eq.) of MsOH and the mixture was stirred for 40 min at rt. After addition of 3 mL of sat. aqueous $NaHCO_3$ and 30 mL of H_2O the aqueous phase was extracted with 3 x 20 mL of MTBE. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/toluene 2:1) to give 13 mg (0.038 mmol, 87%) of olefin **33** as a colorless, crystalline solid.



$C_{23}H_{32}O_2$ (**M** = 340.51 g/mol)

R_f (toluene) = 0.63

m.p.: 166 °C – 168 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): *δ* [ppm] = 6.61 (s, 2H, 12-H, 13-H), 5.68 (t, *J* = 3.6 Hz, 1H, 5-H), 3.77 (s, 3H, 16-H), 3.68 (s, 3H, 17-H), 2.83 (d, *J* = 16.0 Hz, 1H, 9-H_a), 2.59 (d, *J* = 16.0 Hz, 1H, 9-H_b), 2.16 (ddd, *J* = 13.3, 12.0, 6.1 Hz, 1H, 19-H_a), 2.03 (dt, *J* = 17.7, 4.8 Hz, 1H, 4-H_a), 1.83 (td, *J* = 13.3, 6.7 Hz, 1H, 21-H_a), 1.70 – 1.56 (m, 3H, 3-H, 4-H_b, 20-H_a), 1.48 (ddd, *J* = 13.1, 6.4, 2.0 Hz, 1H, 21-H_b), 1.37 – 1.30 (m, 1H, 20-H_b), 1.30 – 1.24 (m, 1H, 19-H_b), 1.21 (s, 3H, 22-H), 1.18 (s, 3H, 23-H), 0.87 (s, 3H, 7-H), 0.79 (d, *J* = 6.5 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): *δ* [ppm] = 151.9 (C-14), 151.2 (C-11), 145.5 (C-6), 142.5 (C-15), 131.2 (C-10), 120.8 (C-5), 109.6 (C-13), 108.8 (C-12), 55.8 (C-16), 55.6*3* (C-1), 55.5*6* (C-17), 50.1 (C-2), 38.3 (C-23), 36.6 (C-9), 34.8 (C-18), 32.9 (C-4), 32.5 (C-19), 31.8 (C-22), 30.4 (C-3), 27.2 (C-21), 17.0 (C-8), 16.8 (C-20), 12.3 (C-7).

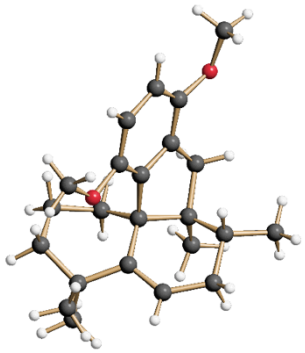
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3676 (br), 3001 (w), 2954 (s), 2913 (w), 2899 (w), 2864 (w), 2835 (w), 1606 (w), 1492 (s), 1461 (m), 1441 (w), 1380 (w), 1357 (w), 1321 (w), 1279 (w), 1254 (s), 1178 (w), 1148 (w), 1114 (w), 1090 (m), 1075 (w), 1058 (m), 1042 (w), 1030 (w), 985 (w), 967 (w), 952 (w), 832 (w), 789 (m), 718 (w), 680 (w), 630 (w), 517 (w).

GC-MS (70 eV): *m/z* (%) = 340 (41, $[M]^+$), 271 (100), 253 (18), 239 (32), 201 (97), 189 (24), 173 (15), 152 (67), 119 (66), 83 (16), 55 (20).

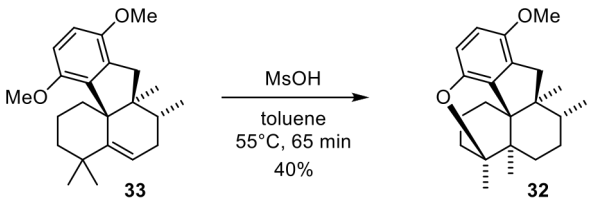
HRMS (ESI):	Calc. [amu]	Found [amu]
	341.24751 $[M+H]^+$	341.24765 $[M+H]^+$
	363.22945 $[M+Na]^+$	363.22941 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.50 g/100 mL, $CHCl_3$): + 106° (436 nm), + 57° (546 nm), + 49° (579 nm), + 47° (589 nm).

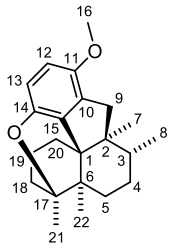
X-ray crystal structure (CCDC 2077909)**:**



3.20. Synthesis of (–)-dysiherbol A methyl ether (32) from olefin 33



To a solution of 12 mg (0.035 mmol, 1.0 eq.) of olefin **33** in 0.90 mL dry toluene was added 46 µL (68 mg, 0.70 mmol, 20 eq.) of MsOH and the mixture was stirred at 55 °C for 65 min under argon. After cooling to rt 3 mL of sat. aqueous $NaHCO_3$ and 35 mL of H_2O the aqueous phase was extracted with 3 x 25 mL of MTBE, the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/toluene 1:1) to provide 4.6 mg (0.014 mmol, 40%) of **32** as a colorless viscous oil, which crystallized upon slowly evaporation of a pentane solution at rt to form needles.



$C_{22}H_{30}O_2$ (**M** = 326.48 g/mol)

R_f (*c*-Hex/toluene 1:1) = 0.22

m.p.: 83 °C – 86 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.56 (d, *J* = 8.6 Hz, 1H, 12-H), 6.48 (d, *J* = 8.6 Hz, 1H, 13-H), 3.75 (s, 3H, 16-H), 2.62 (d, *J* = 15.4 Hz, 1H, 9-H_a), 2.57 (d, *J* = 15.4 Hz, 1H, 9-H_b), 1.96 (td, *J* = 14.0, 6.5 Hz, 1H, 18-H_a), 1.84 (td, *J* = 12.8, 4.6 Hz, 1H, 20-H_a), 1.68 (dd, *J* = 14.5, 5.8 Hz, 1H, 18-H_b), 1.53 – 1.46 (m, 1H, 19-H_a), 1.42 – 1.35 (m, 2H, 5-H_a, 20-H_b), 1.35 – 1.28 (m, 3H, 4-H_a, 5-H_b, 19-H_b), 1.24 – 1.17 (m, 2H, 3-H, 4-H_b), 1.22 (s, 3H, 21-H), 1.21 (s, 3H, 22-H), 1.07 (s, 3H, 7-H), 0.83 (d, *J* = 6.7 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 150.2 (C-11), 148.7 (C-14), 133.6 (C-15), 128.2 (C-10), 110.4 (C-13), 110.3 (C-12), 82.6 (C-17), 56.1 (C-16), 51.6 (C-2), 49.2 (C-1), 40.1 (C-9), 37.4 (C-6), 35.9 (C-18), 35.7 (C-3), 30.1 (C-5), 26.6*0* (C-4), 26.57 (C-20), 22.1 (C-21), 19.9 (C-19), 18.7 (C-22), 18.0 (C-8), 15.0 (C-7).

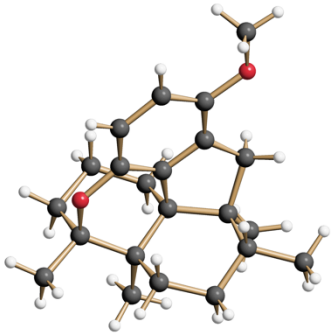
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2933 (s), 2871 (w), 2832 (w), 1725 (w), 1623 (w), 1492 (s), 1457 (m), 1382 (w), 1348 (w), 1340 (w), 1325 (w), 1313 (w), 1297 (w), 1261 (s), 1229 (w), 1185 (w), 1164 (w), 1140 (w), 1126 (w), 1106 (m), 1068 (m), 1031 (w), 1011 (w), 966 (w), 925 (w), 911 (w), 888 (w), 862 (w), 794 (m), 758 (w), 720 (w), 658 (w), 632 (w), 587 (w), 505 (w).

GC-MS (70 eV): *m/z* (%) = 326 (100, $[M]^+$), 257 (16), 201 (8), 187 (38), 175 (7), 119 (18), 115 (8), 91 (7), 83 (7), 69 (6), 55 (16).

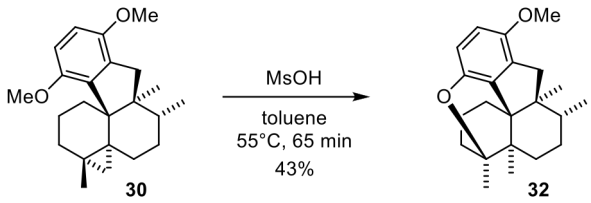
HRMS (ESI):	Calc. [amu]	Found [amu]
	349.21380 $[M+Na]^+$	349.21371 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.50 g/100 mL, $CHCl_3$): – 79° (436 nm), – 43° (546 nm), – 36° (579 nm), – 35° (589 nm).

X-ray crystal structure (CCDC 2077906)**:**



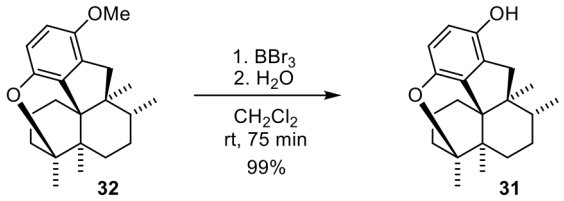
3.21. Synthesis of (–)-dysiherbol A methyl ether (32) from cyclopropane 30



To a solution of 16 mg (0.047 mmol, 1.0 eq.) of cyclopropane **30** in 1.2 mL of dry toluene were added 61 µL (90 mg, 0.94 mmol, 20 eq.) of MsOH and the mixture was stirred at 55 °C for 65 min. After cooling to rt, 3 mL of sat. aqueous $NaHCO_3$ and 25 mL of H_2O were added and the aqueous phase was extracted with 3 x 20 mL of MTBE. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/toluene 1:1) to provide 6.6 mg (0.020 mmol, 43%) of **32** as a pale yellow viscous oil, which crystallized upon slow evaporation of a pentane solution at rt to form needles.

The analytical data were identical to those given above (section **3.20**).

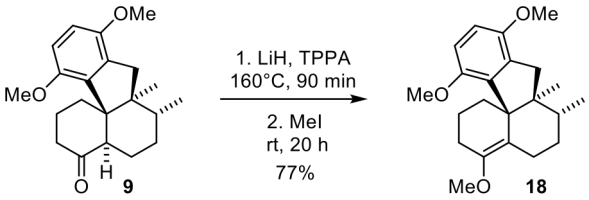
3.22. Synthesis of (–)-dysiherbol A (31) from its methyl ether 32



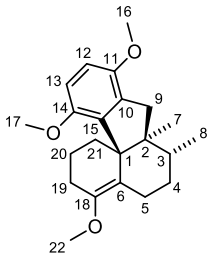
A solution of 15 mg (0.046 mmol, 1.0 eq.) of **32** in 0.6 mL of dry CH_2Cl_2 was cooled to 0°C before 0.13 mL (0.098 mmol, 2.1 eq.) of BBr_3 (0.78 M in heptane) were added via syringe over 20 s. After stirring the mixture for 75 min at rt, 0.10 mL of H_2O were added and stirred was continued for 10 min at rt before excess reagent was hydrolyzed by addition of 3 mL of sat. aqueous $NaHCO_3$ and 20 mL of H_2O. The aqueous phase was extracted with 3 x 20 mL of MTBE, the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 10:1) to provide 15 mg (0.046 mmol, 99%) of (–)-dysiherbol A (**31**) as a yellow, sticky oil.

The analytical data were identical to those given above (section **3.15**).

3.23. Synthesis of enol ether 18



To a solution of 80 mg (0.24 mmol, 1.0 eq.) of ketone **9** in 1.1 mL of TPPA were added 43 mg (5.4 mmol, 22 eq.) of LiH and the stirred suspension was heated to 160°C for 90 min. Then, the mixture was cooled to 0° C and 0.30 mL (0.69 g, 4.9 mmol, 20 eq.) of MeI were added. The mixture was allowed to reach rt and stirred for another 20 h, before excess LiH was carefully quenched with 5 mL of 25% aqueous NH_4OH. After addition of 45 mL of H_2O and extraction with 3 x 20 mL of MTBE the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 20:1) to provide 64 mg (0.19 mmol, 77%) of enol ether **18** as a colorless, crystalline solid.



$C_{22}H_{30}O_3$ (**M** = 342.48 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.64

m.p.: 78 °C – 80 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.62 (s, 2H, 12-H, 13-H), 3.77 (s, 3H, 16-H), 3.67 (s, 3H, 17-H), 3.54 (s, 3H, 22-H), 2.90 (dt, *J* = 13.6, 3.3 Hz, 1H, 5-H_a), 2.84 (d, *J* = 15.8 Hz, 1H, 9-H_a), 2.52 (d, *J* = 15.8 Hz, 1H, 9-H_b), 2.22 – 2.09 (m, 2H, 19-H), 1.84 (ddd, *J* = 13.2, 10.0, 3.6 Hz, 1H, 21-H_a), 1.72 – 1.58 (m, 2H, 20-H), 1.50 (tq, *J* = 13.7, 2.9 Hz, 1H, 5-H_b), 1.45 – 1.37 (m, 2H, 3-H, 21-H_b), 1.34 (dq, *J* = 13.2, 3.7 Hz, 1H, 4-H_a), 1.12 (qd, *J* = 12.7, 3.7 Hz, 1H, 4-H_b), 0.97 (s, 3H, 7-H), 0.82 (d, *J* = 6.7 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 151.7 (C-14), 150.8 (C-11), 149.0 (C-18), 140.7 (C-15), 131.7 (C-10), 120.3 (C-6), 109.9 (C-13), 108.8 (C-12), 56.8 (C-22), 55.8 (C-16), 55.7 (C-1), 55.6 (C-17), 51.7 (C-2), 38.5 (C-9), 36.0 (C-3), 32.2 (C-21), 31.0 (C-4), 25.7 (C-19), 24.1 (C-5), 20.1 (C-20), 18.2 (C-8), 14.1 (C-7).

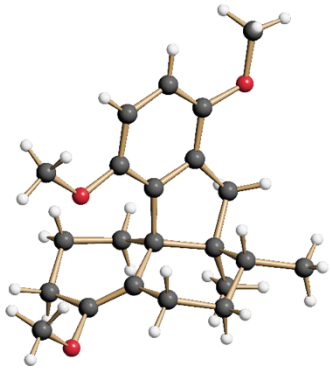
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2930 (m), 2909 (w), 2874 (w), 2850 (w), 2830 (m), 1708 (w), 1673 (m), 1595 (w), 1491 (s), 1462 (m), 1437 (m), 1380 (w), 1360 (w), 1326 (w), 1305 (w), 1282 (w), 1253 (s), 1208 (m), 1170 (m), 1149 (m), 1125 (m), 1111 (w), 1093 (m), 1070 (m), 1056 (m), 1022 (m), 971 (m), 945 (w), 936 (w), 907 (w), 871 (w), 854 (w), 789 (m), 737 (w), 715 (m), 666 (w), 646 (w), 518 (w).

GC-MS (70 eV): *m/z* (%) = 342 (30, $[M]^+$), 311 (100), 295 (22), 285 (9), 283 (9), 255 (4), 241 (9), 227 (4).

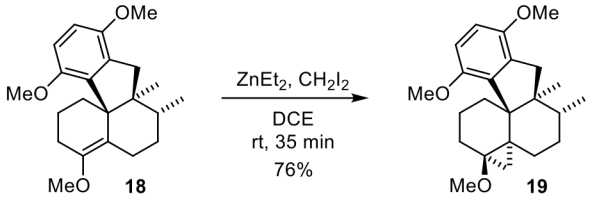
HRMS (ESI):	Calc. [amu]	Found [amu]
	343.22677 $[M+H]^+$	343.22754 $[M+H]^+$
	365.20872 $[M+Na]^+$	365.20848 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.50 g/100 mL, $CHCl_3$): + 346° (436 nm), + 185° (546 nm), + 159° (579 nm), + 152° (589 nm).

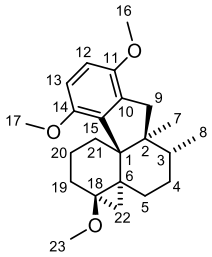
X-ray crystal structure (CCDC 2077907)**:**



3.24. Synthesis of cyclopropane 19



In an argon-flushed flask 61 mg (0.18 mmol, 1.0 eq.) of enol ether **18** were dissolved in 4.0 mL of dry DCE. The solution was cooled to 0°C and 0.71 mL (0.71 mmol, 4.0 eq.) of $ZnEt_2$ (1.0 M in hexanes) were added over 20 s. Then, 0.12 mL (0.38 g, 1.4 mmol, 8.0 eq.) of CH_2I_2 were added and the arising milk-like suspension was allowed to reach rt and stirred for 35 min. Excess reagent was quenched with 3 mL of sat. aqueous $NaHCO_3$. After addition of 55 mL of H_2O and extraction with 3 x 25 mL of MTBE the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 50:1) to provide 48 mg (0.14 mmol, 76%) of cyclopropane **19** as a colorless sticky oil, crystallizing upon repetitive dissolving in CH_2Cl_2 and solvent removal *in vacuo*.



$C_{23}H_{32}O_3$ (**M** = 356.51 g/mol)

R_f (*c*-Hex/EtOAc 19:1) = 0.37

m.p.: 87 °C – 90 °C

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.66 (d, *J* = 8.9 Hz, 1H, 13-H), 6.64 (d, *J* = 8.8 Hz, 1H, 12-H), 3.78 (s, 3H, 17-H), 3.77 (s, 3H, 16-H), 3.32 (s, 3H, 23-H), 2.72 (d, *J* = 15.6 Hz, 1H, 9-H_a), 2.44 (d, *J* = 15.7 Hz, 1H, 9-H_b), 2.10 – 2.00 (m, 2H, 19-H), 1.56 – 1.49 (m, 1H, 5-H_a), 1.44 – 1.31 (m, 6H, 3-H, 4-H, 5-H_b, 20-H_a, 21-H_a), 1.28 – 1.22 (m, 1H, 20-H_b), 1.12 (dd, *J* = 9.3, 3.6 Hz, 1H, 21-H_b), 1.00 (s, 3H, 7-H), 0.82 (d, *J* = 5.9 Hz, 3H, 8-H), 0.65 (dd, *J* = 5.2, 1.9 Hz, 1H, 22-H_a), 0.41 (dd, *J* = 5.1, 1.4 Hz, 1H, 22-H_b).

^{13}C NMR (151 MHz, $CDCl_3$, 298 K): δ [ppm] = 152.4 (C-14), 151.1 (C-11), 139.0 (C-15), 132.1 (C-10), 109.0 (C-13), 108.9 (C-12), 65.1 (C-18), 55.8 (C-17), 55.5 (C-16), 54.7 (C-1), 53.8 (C-23), 50.9 (C-2), 38.5 (C-9), 36.1 (C-3), 32.3 (C-6), 30.4 (C-4), 29.0 (C-5), 27.9 (C-19), 27.5 (C-21), 21.3 (C-22), 18.2 (C-8), 17.1 (C-20), 14.0 (C-7).

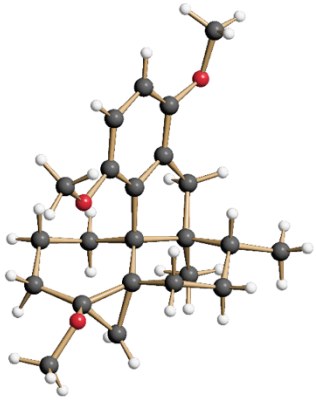
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3061 (w), 2991 (w), 2931 (m), 2902 (w), 2874 (w), 2847 (w), 2829 (w), 1595 (w), 1492 (s), 1459 (m), 1437 (w), 1379 (w), 1353 (w), 1324 (w), 1300 (w), 1282 (w), 1255 (s), 1214 (w), 1201 (w), 1174 (m), 1160 (w), 1135 (w), 1097 (m), 1081 (w), 1049 (m), 1016 (w), 998 (w), 985 (w), 970 (w), 951 (w), 915 (w), 886 (w), 838 (w), 822 (w), 789 (m), 759 (w), 738 (w), 716 (m), 649 (w), 635 (w), 510 (w).

GC-MS (70 eV): *m/z* (%) = 356 (100, $[M]^+$), 324 (28), 309 (26), 271 (51), 257 (25), 255 (26), 216 (29), 215 (42), 201 (26), 189 (26), 85 (18).

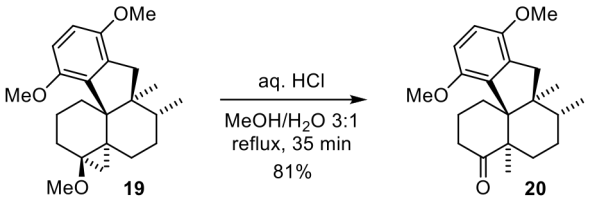
HRMS (ESI):	Calc. [amu]	Found [amu]
	379.22437 $[M+Na]^+$	379.22467 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 1.00 g/100 mL, $CHCl_3$): + 71° (436 nm), + 38° (546 nm), + 34° (579 nm), + 30° (589 nm).

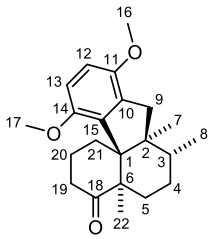
X-ray crystal structure (CCDC 2077911)**:**



3.25. Synthesis of ketone 20



In an argon-flushed flask 46 mg (0.13 mmol, 1.0 eq.) of cyclopropane **19** were dissolved in 4.5 mL of MeOH (under gentle warming), 1.5 mL of conc. $HCl_{(aq)}$ were added and the mixture was refluxed for 35 min. The solution was allowed to cool to rt, before it was neutralized with 20 mL of sat. aqueous $NaHCO_3$. The aqueous phase was extracted with 3 x 15 mL of MTBE, the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 10:1) to provide 36 mg (0.11 mmol, 81%) of ketone **20** as a colorless, crystalline solid.



$C_{22}H_{30}O_3$ (**M** = 342.48 g/mol)

R_f (*c*-Hex/EtOAc 9:1) = 0.24

m.p.: 125 °C – 128 °C

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ [ppm] = 6.64 (d, *J* = 8.7 Hz, 1H, 12-H), 6.59 (d, *J* = 8.7 Hz, 1H, 13-H), 3.76 (s, 3H, 16-H), 3.55 (s, 3H, 17-H), 2.72 (d, *J* = 15.9 Hz, 1H, 9-H_a), 2.56 – 2.46 (m, 1H, 19-H_a), 2.50 (d, *J* = 15.8 Hz, 1H, 9-H_b), 2.27 (dd, *J* = 17.2, 6.0 Hz, 1H, 19-H_b), 2.17 (td, *J* = 13.5, 4.2 Hz, 1H, 21-H_a), 1.99 – 1.90 (m, 1H, 5-H_a), 1.76 – 1.68 (m, 1H, 20-H_a), 1.57 – 1.46 (m, 1H, 20-H_b), 1.46 – 1.37 (m, 4H, 4-H, 5-H_b, 21-H_b), 1.37 – 1.32 (m, 1H, 3-H), 1.31 (s, 3H, 22-H), 1.15 (s, 3H, 7-H), 0.84 (d, *J* = 6.5 Hz, 3H, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ [ppm] = 212.2 (C-18), 151.4 (C-14), 151.1 (C-11), 138.3 (C-15), 131.7 (C-10), 109.2*0* (C-12), 109.1*8* (C-13), 59.7 (C-1), 55.7 (C-16), 53.2 (C-17), 50.7 (C-2), 50.3 (C-6), 40.1 (C-9), 36.4 (C-19), 35.1 (C-3), 28.8 (C-5), 27.3 (C-21), 27.2 (C-4), 22.8 (C-22), 20.7 (C-20), 17.7 (C-8), 17.4 (C-7).

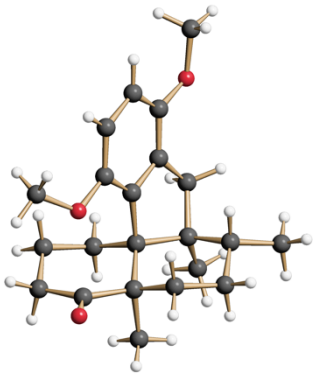
FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3028 (w), 2935 (m), 2881 (w), 2833 (w), 1701 (s), 1595 (w), 1493 (s), 1460 (m), 1415 (w), 1386 (w), 1347 (w), 1321 (w), 1277 (w), 1256 (s), 1194 (w), 1172 (w), 1151 (w), 1128 (w), 1115 (w), 1091 (m), 1065 (w), 1056 (w), 1045 (m), 1023 (w), 1005 (w), 974 (m), 957 (w), 927 (w), 853 (w), 827 (w), 798 (m), 720 (m), 676 (w), 648 (w), 578 (w), 560 (w), 523 (w).

GC-MS (70 eV): *m/z* (%) = 342 (100, $[M]^+$), 286 (12), 271 (8), 257 (11), 232 (10), 217 (9), 203 (8), 189 (8), 175 (7), 109 (7).

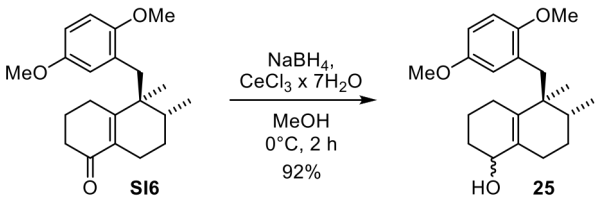
HRMS (ESI):	Calc. [amu]	Found [amu]
	343.22677 $[M+H]^+$	343.22720 $[M+H]^+$
	365.20872 $[M+Na]^+$	365.20884 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.50 g/100 mL, $CHCl_3$): + 8.6° (436 nm), + 0.9° (546 nm), + 0.4° (579 nm), + 0.0° (589 nm).

X-ray crystal structure (CCDC 2077908)**:**

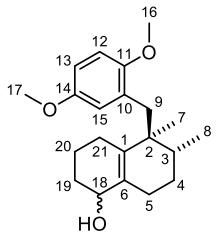


3.26. Synthesis of allylic alcohol 25



dr = 4:3

A solution of 27 mg (0.082 mmol, 1.0 eq.) of enone **SI6** in 0.80 mL of MeOH was cooled to 0°C before 37 mg (0.099 mmol, 1.2 eq.) of $CeCl_3$ x 7 H_2O and 8.0 mg (0.21 mmol, 2.6 eq.) of $NaBH_4$ were added and the mixture allowed to stirr for 2 h at 0°C. After addition of H_2O and extraction with 3x EtOAc the combined organic phases were washed with H_2O, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give 25 mg (0.076 mmol, 92%) of a diastereomeric mixture (*dr* = 4:3) of allylic alcohol **25** as a pale yellow oil.



$C_{21}H_{30}O_3$ (**M** = 330.47 g/mol)

R_f (*c*-Hex/EtOAc 1:1) = 0.61 (single spot for both diastereomers)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): Major diastereomer: δ [ppm] = 6.77 (d, *J* = 3.6 Hz, 1H, 15-H), 6.77 – 6.75 (m, 1H, 12-H), 6.70 – 6.66 (m, 1H, 13-H), 3.97 (t, *J* = 4.0 Hz, 1H, 18-H), 3.76 (s, 3H, 17-H), 3.69 (s, 3H, 16-H), 2.96 (d, *J* = 15.5 Hz, 1H, 9-H_a), 2.64 (d, *J* = 15.5 Hz, 1H, 9-H_b), 2.43 – 2.37 (m, 1H, 5-H_a), 2.17 – 2.14 (m, 1H, 4-H_a), 2.06 – 1.98 (m, 1H, 4-H_b)*, 1.91 – 1.85 (m, 1H, 21-H_a)*, 1.77 – 1.68 (m, 2H, 19-H), 1.74 – 1.70 (m, 2H, 3-H, 5-H_b), 1.67 – 1.54 (m, 2H, 20-H), 1.42 – 1.37 (m, 1H, 21-H_b)*, 0.96 (s, 3H, 7-H), 0.81 (d, *J* = 6.4 Hz, 3H, 8-H). Minor diastereomer: δ [ppm] = 6.77 – 6.75 (m, 0.8H, 12-H), 6.75 (d, *J* = 3.5 Hz, 0.8H, 15-H), 6.70 – 6.66 (m, 0.8H, 13-H), 3.90 (t, *J* = 4.0 Hz, 0.8H, 18-H), 3.75*3* (s, 2.3H, 17-H), 3.74*9* (s, 2.3H, 16-H), 2.95 (d, *J* = 14.3 Hz, 0.8H, 9-H_a), 2.61 (d, *J* = 14.3 Hz, 0.8H, 9-H_b), 2.06 – 1.98 (m, 0.8H, 4-H_a)*, 1.95 – 1.89 (m, 0.8H, 4-H_b)*, 1.91 – 1.85 (m, 0.8H, 21-H_a)*, 1.77 – 1.68 (m, 1.6H, 19-H), 1.71 – 1.66 (m, 0.8H, 5-H_a)*, 1.70 – 1.67 (m, 0.8H, 3-H), 1.67 – 1.54 (m, 1.6H, 20-H), 1.46 – 1.42 (m, 0.8H, 5-H_b)*, 1.42 – 1.37 (m, 0.8H, 21-H_b)*, 0.92 (s, 2.3H, 7-H), 0.80 (d, *J* = 6.5 Hz, 2.3H, 8-H). *Assignments possibly interconvertible.

^{13}C NMR (126 MHz, $CDCl_3$, 298 K): Major diastereomer: δ [ppm] = 153.2*1* (C-14), 152.5 (C-11), 138.9 (C-1), 131.1 (C-6), 129.5 (C-10), 116.1 (C-15), 111.3*3* (C-12), 111.3*1* (C-13), 69.3 (C-18), 56.1 (C-17), 55.7 (C-16), 41.4 (C-2), 34.4 (C-9), 33.6 (C-3), 32.3 (C-19), 26.7 (C-5), 26.6 (C-21), 25.6 (C-4), 22.2 (C-7), 19.1 (C-20), 16.2 (C-8). Minor diastereomer: δ [ppm] = 153.1*6* (C-14), 152.6 (C-11), 138.1 (C-1), 130.7 (C-6), 129.6 (C-10), 117.4 (C-15), 111.6 (C-12), 111.2 (C-13), 69.7 (C-18), 56.2 (C-17), 55.8 (C-16), 41.8 (C-2), 36.8 (C-9), 34.0 (C-3), 32.1 (C-19), 26.2 (C-5), 26.1 (C-21), 25.8 (C-4), 21.5 (C-7), 19.0 (C-20), 16.1 (C-8).

FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3407 (br), 2926 (s), 2856 (w), 2834 (w), 1730 (br), 1607 (w), 1589 (w), 1499 (s), 1464 (m), 1380 (m), 1346 (w), 1325 (w), 1274 (w), 1222 (s), 1179 (m), 1159 (w), 1123 (w), 1050 (m), 1030 (w), 996 (w), 926 (w), 880 (w), 868 (w), 803 (m), 715 (m).

GC-MS (70 eV): *m/z* (%) = 330 (1, $[M]^+$), 312 (15), 179 (45), 161 (100), 152 (62), 137 (61), 119 (38), 105 (38), 91 (52).

HRMS (ESI):	Calc. [amu]	Found [amu]
	353.20872 $[M+Na]^+$	353.20907 $[M+Na]^+$

$[\alpha]^{20}_{\lambda}$ (*c* = 0.50 g/100 mL, $CHCl_3$): + 0.3° (436 nm), + 0.7° (546 nm), + 0.4° (579 nm), + 0.1° (589 nm).

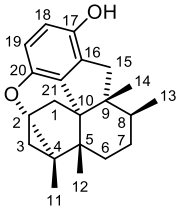
3.27. Synthesis of olefin 17 from allylic alcohol 25

In an argon-flushed flask 20 mg (0.061 mmol, 1.0 eq.) of a diastereomeric mixture (*dr* = 4:3) of allylic alcohol **25** were dissolved in 6.0 mL of CH_2Cl_2. The solution was cooled to 0°C, 0.73 mg (0.0024 mmol, 0.039 eq.) of $AuCl_3$ in 0.66 mL of CH_2Cl_2 were added and the green reaction mixture was stirred for 5 min at that temperature. 5 mg of QuadraSil TA® were added and the suspension was stirred for further 15 min at 0°C. The solids were separated by filtration and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (*c*-Hex/EtOAc 30:1) to give 11 mg as a colorless sticky oil, containing approximately 9.4 mg (0.030 mmol, 50%) of olefin **17** along with inseparable side products, which was determined by integration of suitable ^{1}H-NMR signals.

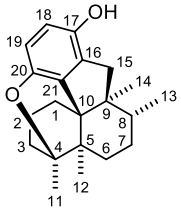
The analytical data of **17** were identical to those given above (section **3.9**).

4. Comparison of NMR Data of Natural (+)-dysiherbol A (*ent*-31) and Synthetic (–)-dysiherbol A (31)

4.1. Comparison of ^{1}H NMR spectroscopic data



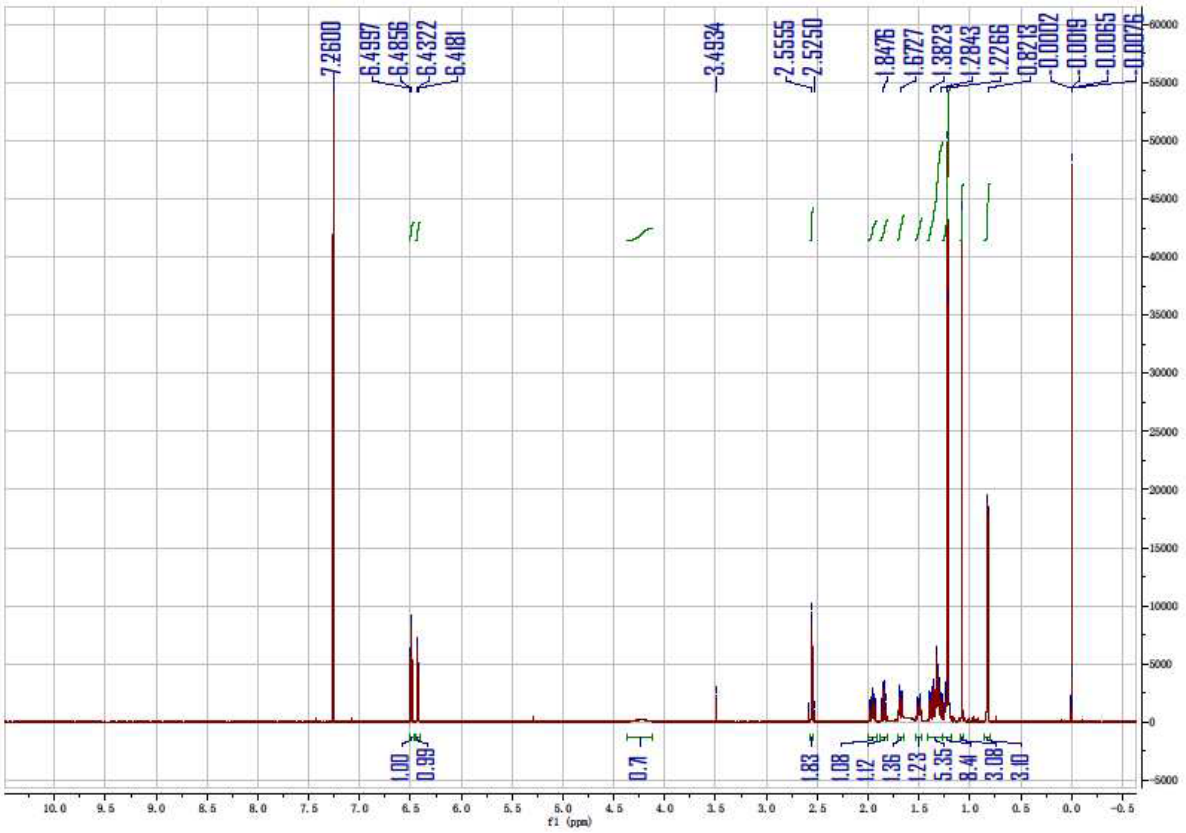
(+)-dysiherbol A (***ent*-31**)

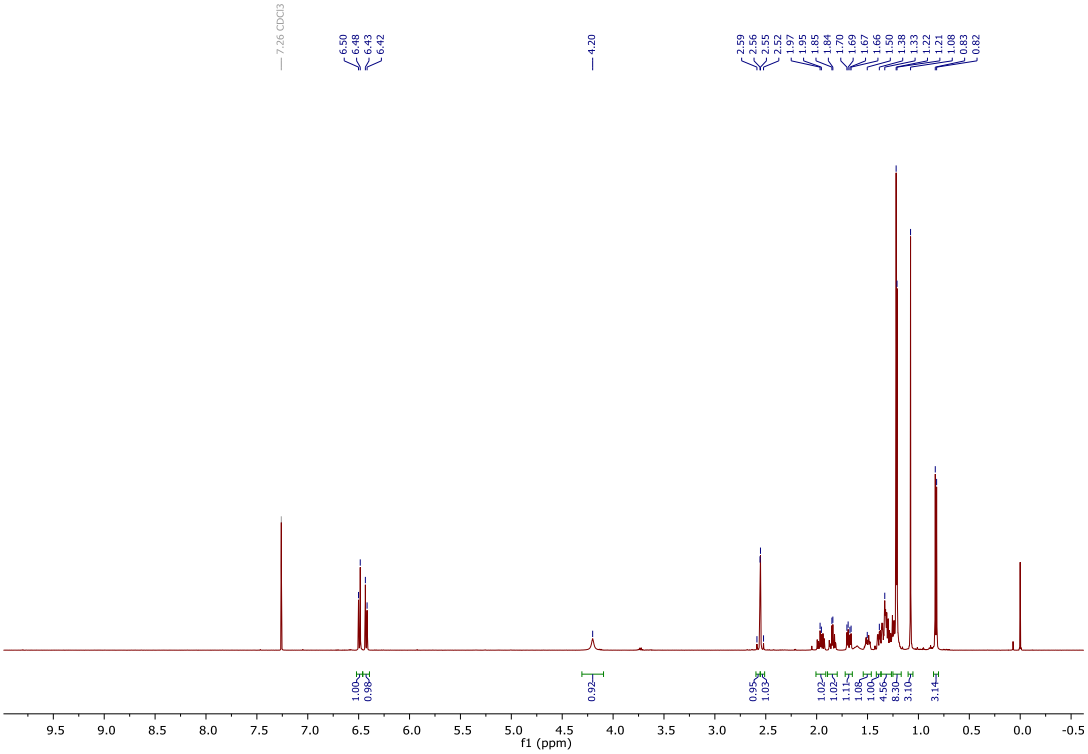


(–)-dysiherbol A (**31**)

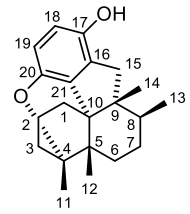
Position	Natural (+)-dysiherbol A (***ent*-31**)[14] δ_H ($CDCl_3$, 600 MHz)	Synthetic (–)-dysiherbol A (**31**) δ_H ($CDCl_3$, 500 MHz)	$\Delta\delta_H$
1*α*	1.84, td (12.6, 4.8 Hz)	1.85, td (12.7, 4.4 Hz)	+0.01
1*β*	1.37, m	1.35, m	–0.02
2	1.49, m	1.50, m	+0.01
	1.30, m	1.30, m	0.00
3*α*	1.95, td (13.8, 6.6 Hz)	1.96, td (14.1, 6.5 Hz)	+0.01
3*β*	1.68, dd (14.4, 6.0 Hz)	1.68, dd (14.6, 5.8 Hz)	0.00
4			
5			
6*α*	1.36, td (13.2, 4.2 Hz)	1.39, m	+0.03
6*β*	1.28, m	1.32, m	+0.04
7*α*	1.32, m	1.32, m	0.00
7*β*	1.22, m	1.23, m	+0.01
8	1.24, m	1.22, m	–0.02
9			
10			
11	1.22, s	1.22, s	0.00
12	1.21, s	1.21, s	0.00
13	0.83, d (6.6 Hz)	0.83, d (6.6 Hz)	0.00
14	1.07, s	1.08, s	+0.01
15	2.57, d (14.4 Hz)	2.57, d (15.2 Hz)	0.00
	2.54, d (14.4 Hz)	2.54, d (15.0 Hz)	0.00
16			
17			
17-OH	4.23, br	4.20, br	–0.03
18	6.49, d (8.4 Hz)	6.49, d (8.5 Hz)	0.00
19	6.43, d (8.4 Hz)	6.43, d (8.5 Hz)	0.00
20			
21			

4.2. Comparison of ^{1}H NMR Spectra (top: natural (+)-dysiherbol A (*ent*-31)[14], bottom: synthetic (–)-dysiherbol A (31))

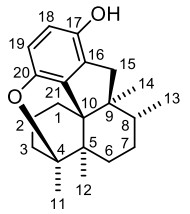




4.3. Comparison of ^{13}C NMR Spectroscopic Data



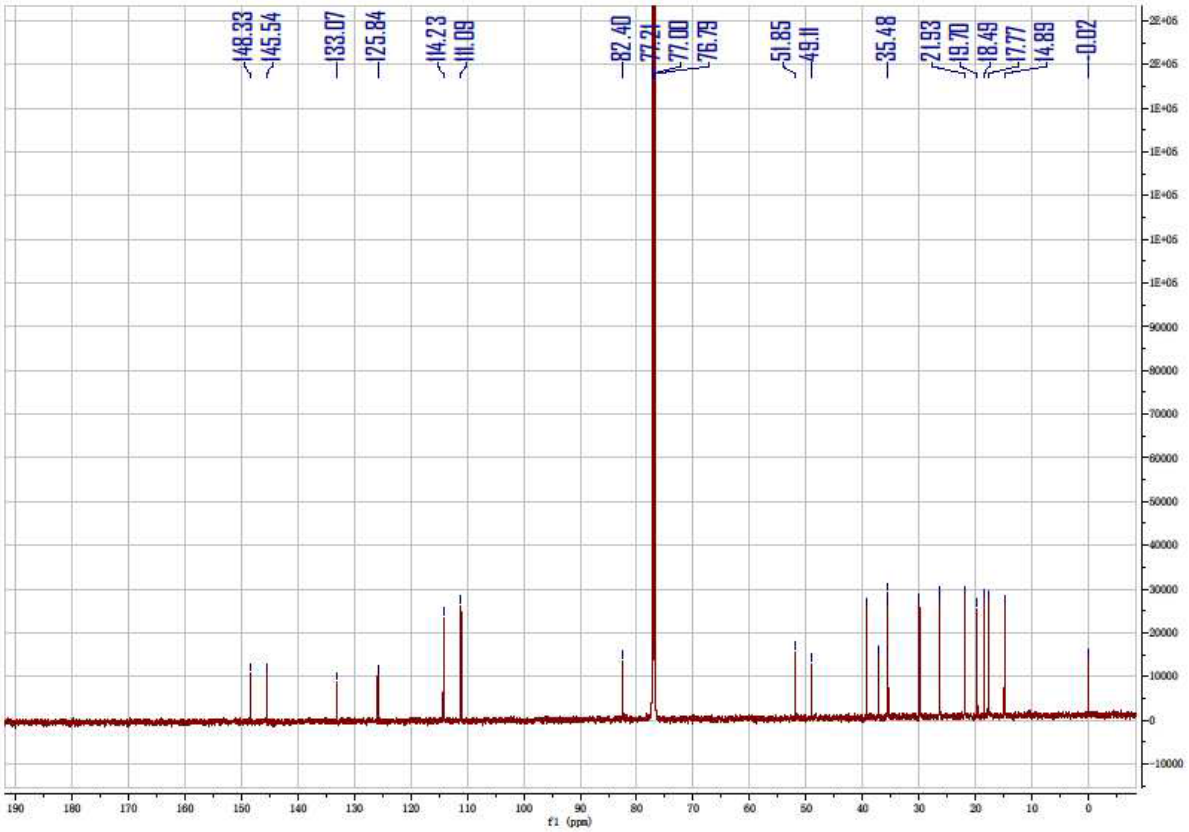
(+)-dysiherbol A (***ent*-31**)

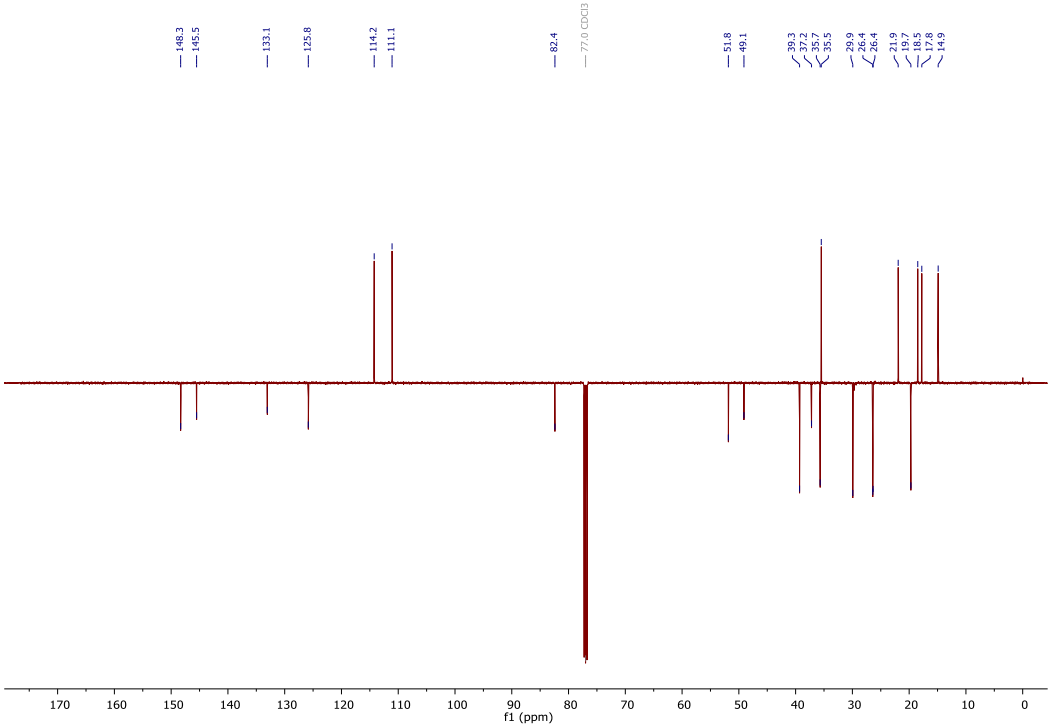


(–)-dysiherbol A (**31**)

	Natural (+)-dysiherbol A (***ent*-31**)[14] δ_C ($CDCl_3$, 150 MHz)	Synthetic (–)-dysiherbol A (**31**) δ_C ($CDCl_3$, 126 MHz)		$\Delta\delta_C$
Position	δ_{CDCl3} = 77.00	δ_{CDCl3} = 77.16	δ_{CDCl3} = 77.00	δ_{CDCl3} = 77.00
1	26.3*6*	26.5	26.3*6*	0.0
2	19.7	19.9	19.7	0.0
3	35.7	35.8	35.7	0.0
4	82.4	82.6	82.4	0.0
5	37.2	37.4	37.2	0.0
6	29.9	30.1	29.9	0.0
7	26.4*1*	26.6	26.4*1*	0.0
8	35.5	35.6	35.5	0.0
9	51.9	52.0	51.8	–0.1
10	49.1	49.3	49.1	0.0
11	21.9	22.1	21.9	0.0
12	18.5	18.6	18.5	0.0
13	17.8	17.9	17.8	0.0
14	14.9	15.0	14.9	0.0
15	39.3	39.5	39.3	0.0
16	125.8	126.0	125.8	0.0
17	145.5	145.7	145.5	0.0
18	114.2	114.4	114.2	0.0
19	111.1	111.2	111.1	0.0
20	148.3	148.5	148.3	0.0
21	133.1	133.2	133.1	0.0

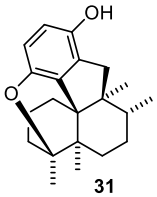
4.4. Comparison of ^{13}C NMR Spectra (top: natural (+)-dysiherbol A (*ent*-31)[14], bottom: synthetic (–)-dysiherbol A (31))



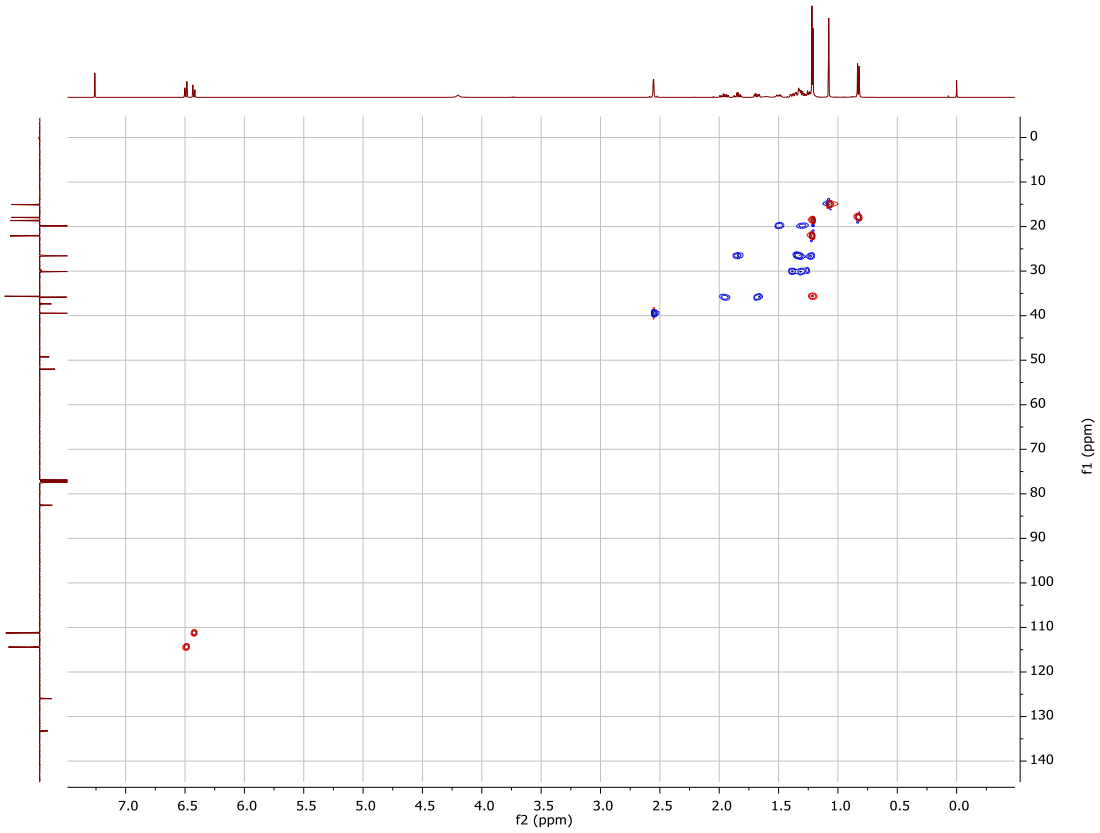


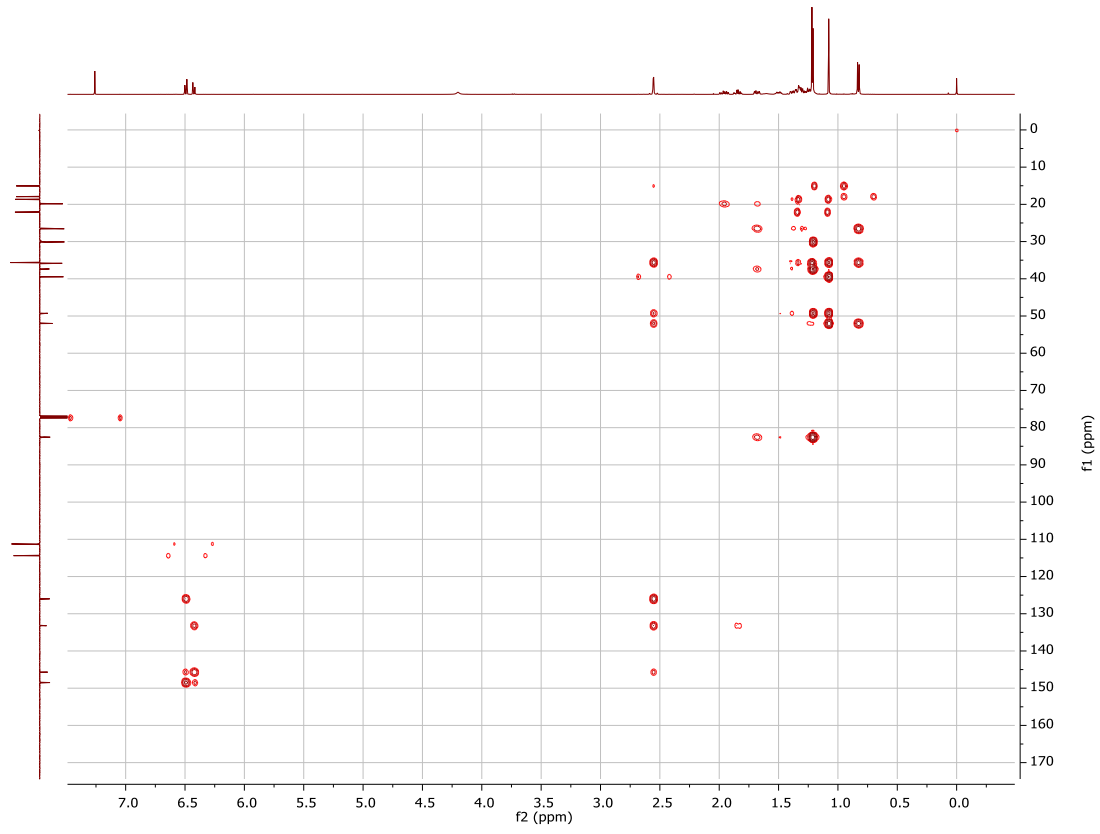
5. Further Analytical Spectra of (–)-dysiherbol A (31)

5.1. $^{1}H,^{13}C$-HSQCed and $^{1}H,^{13}C$-HMBC spectra of (–)-dysiherbol A (31)

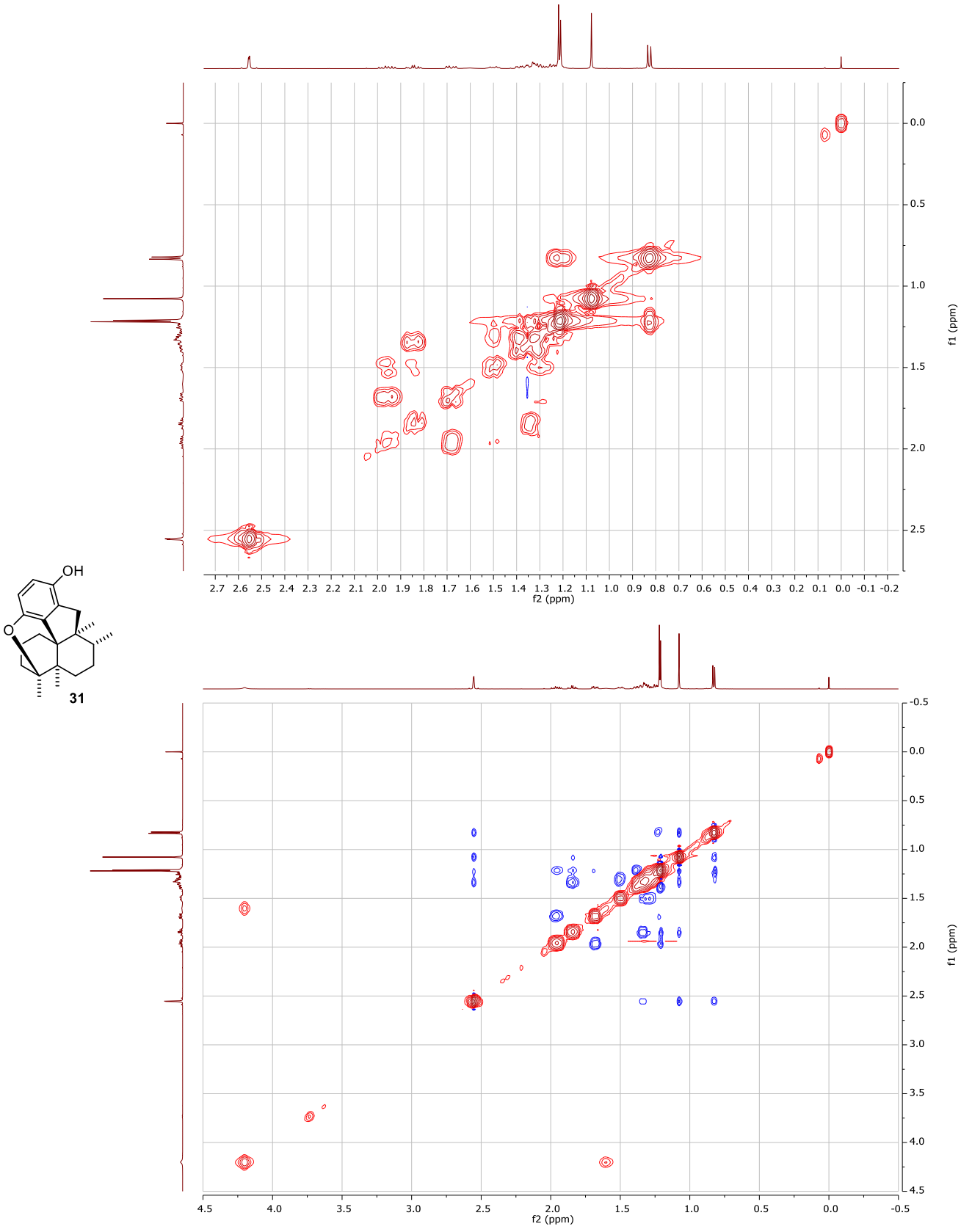


31

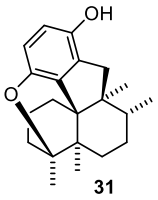


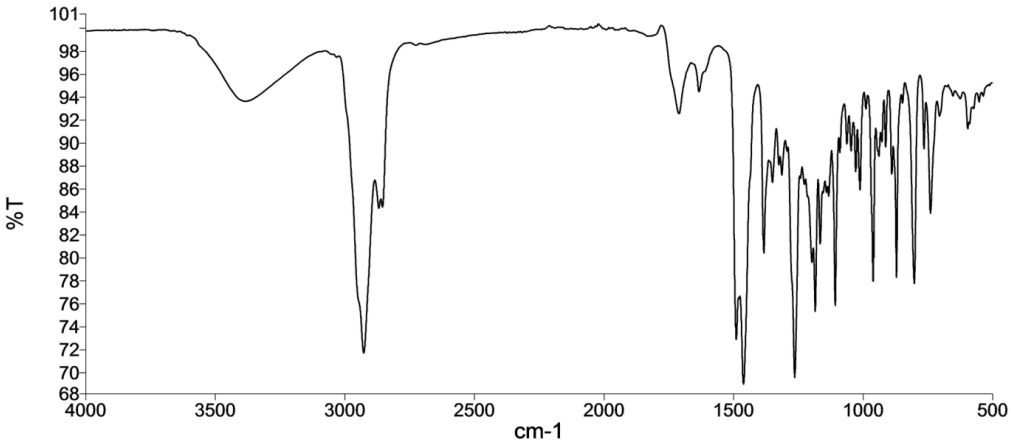


5.2. $^{1}H,^{1}H$-COSY and $^{1}H,^{1}H$-NOESY Spectrum of (–)-dysiherbol A (31)

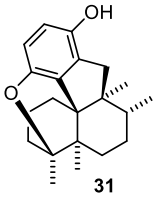


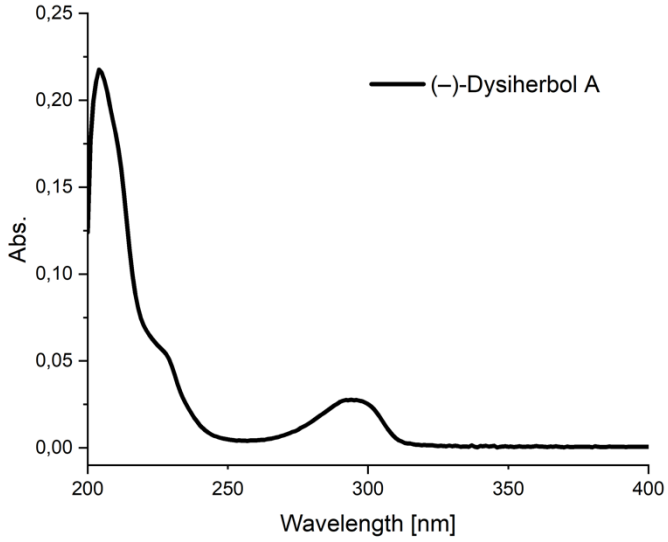
5.3. IR Spectrum of (–)-dysiherbol A (31)



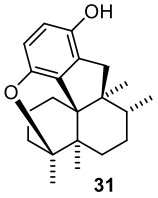


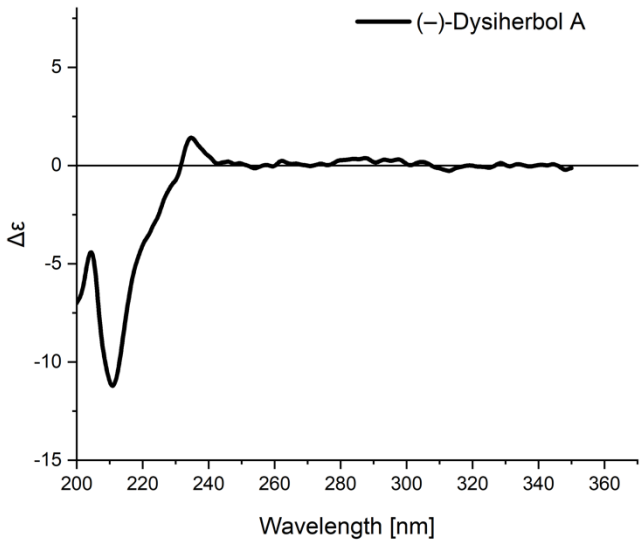
5.4. UV Spectrum of (–)-dysiherbol A (31)





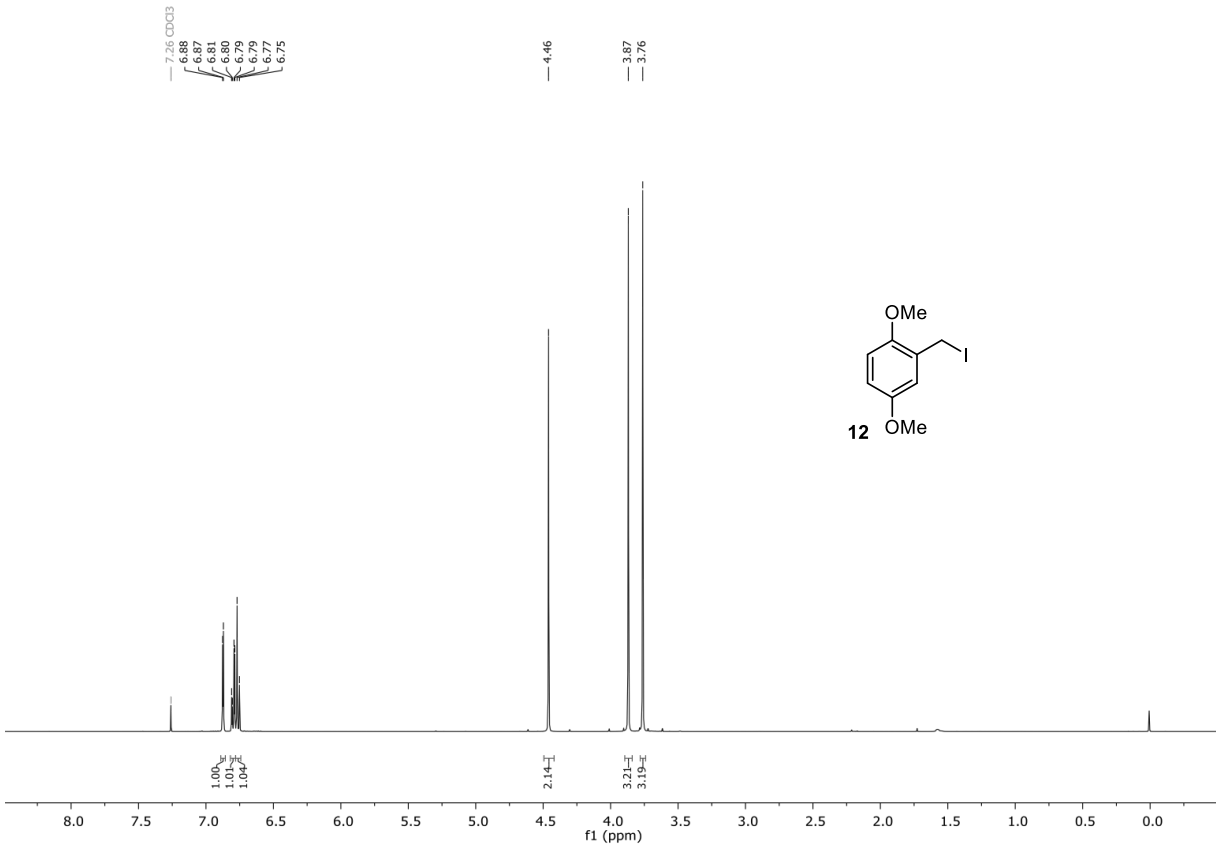
5.5. ECD Spectrum of (–)-dysiherbol A (31)

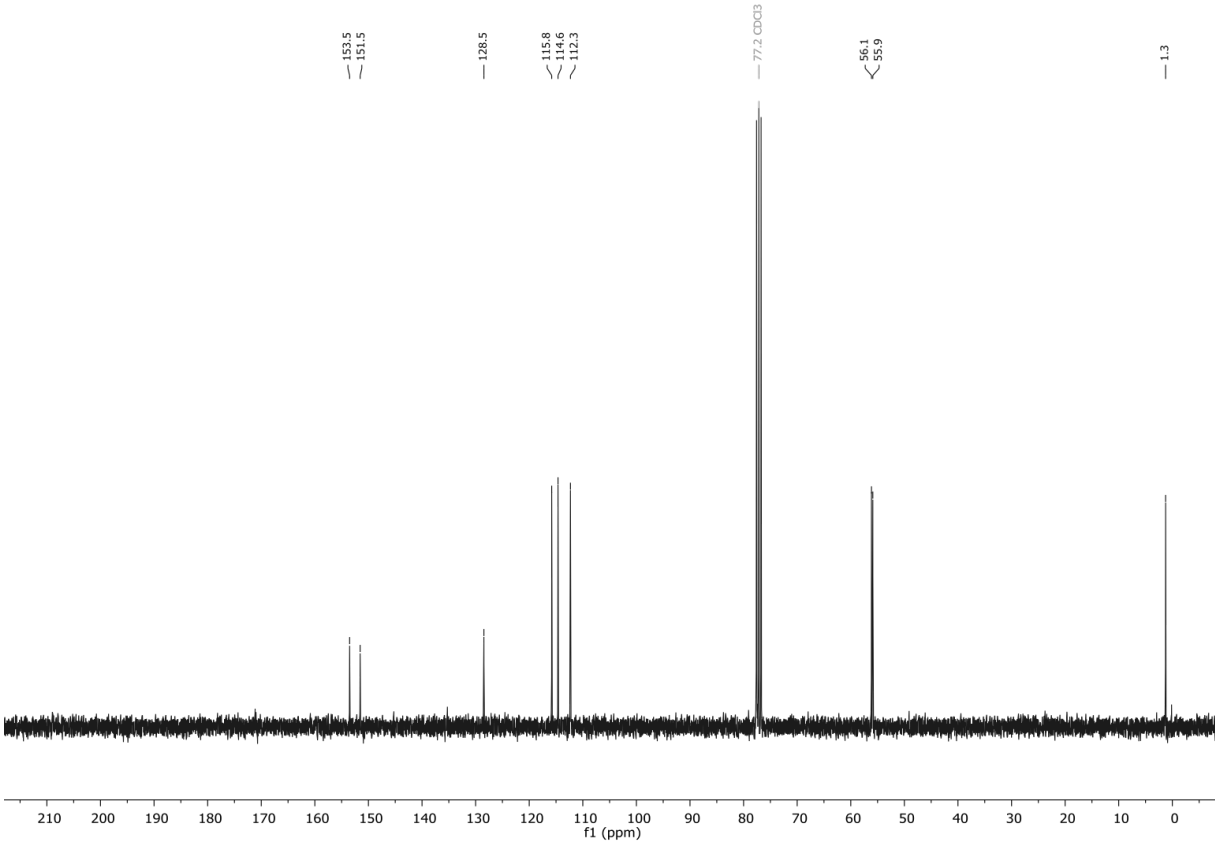




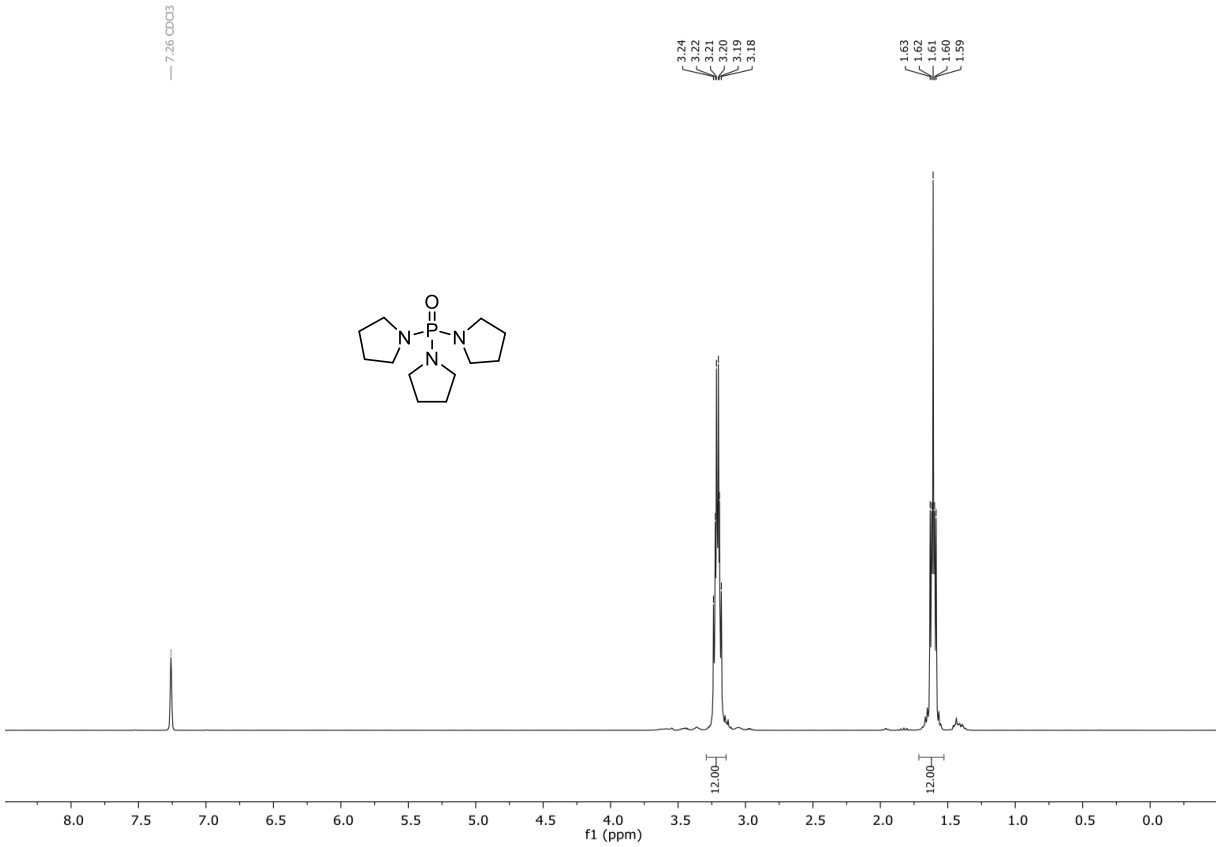
6. NMR Spectra

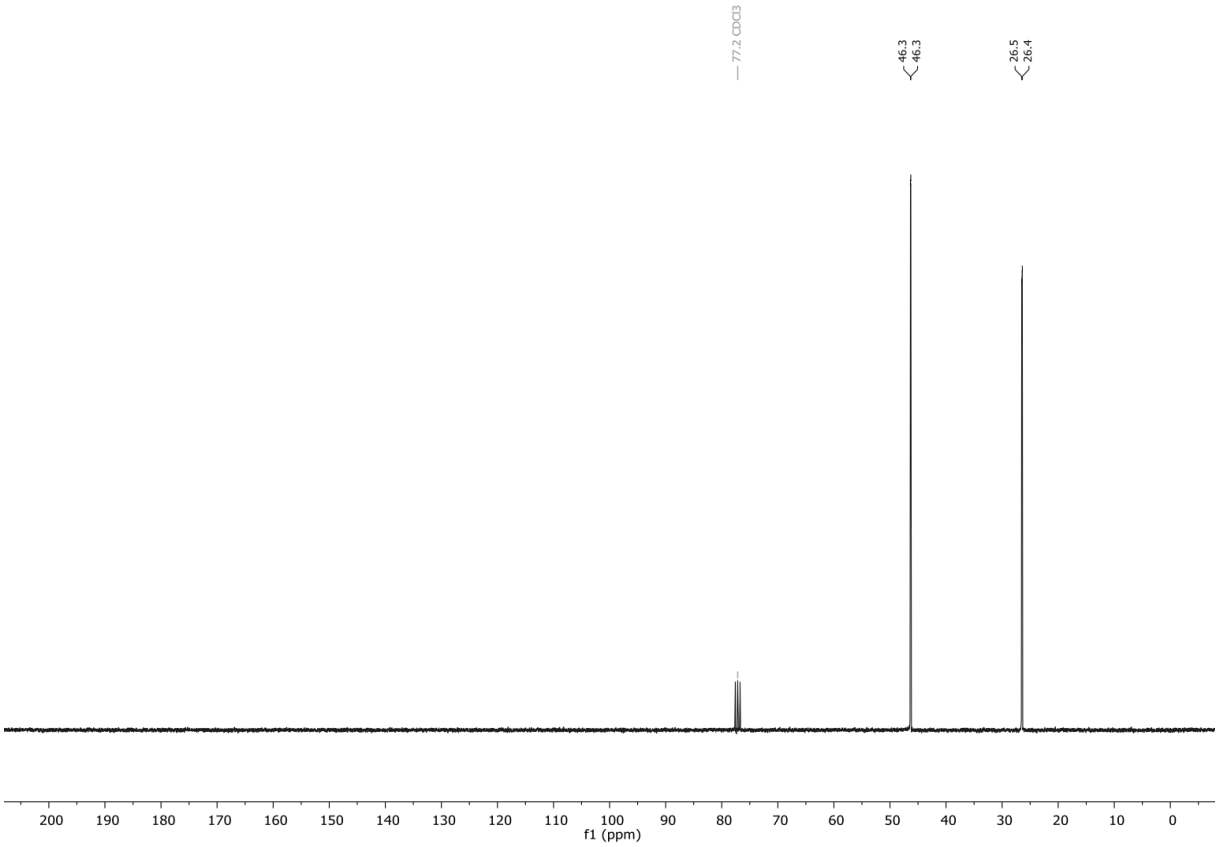
6.1. ^{1}H and ^{13}C NMR of 2-(Iodomethyl)-1,4-dimethoxybenzene (12)

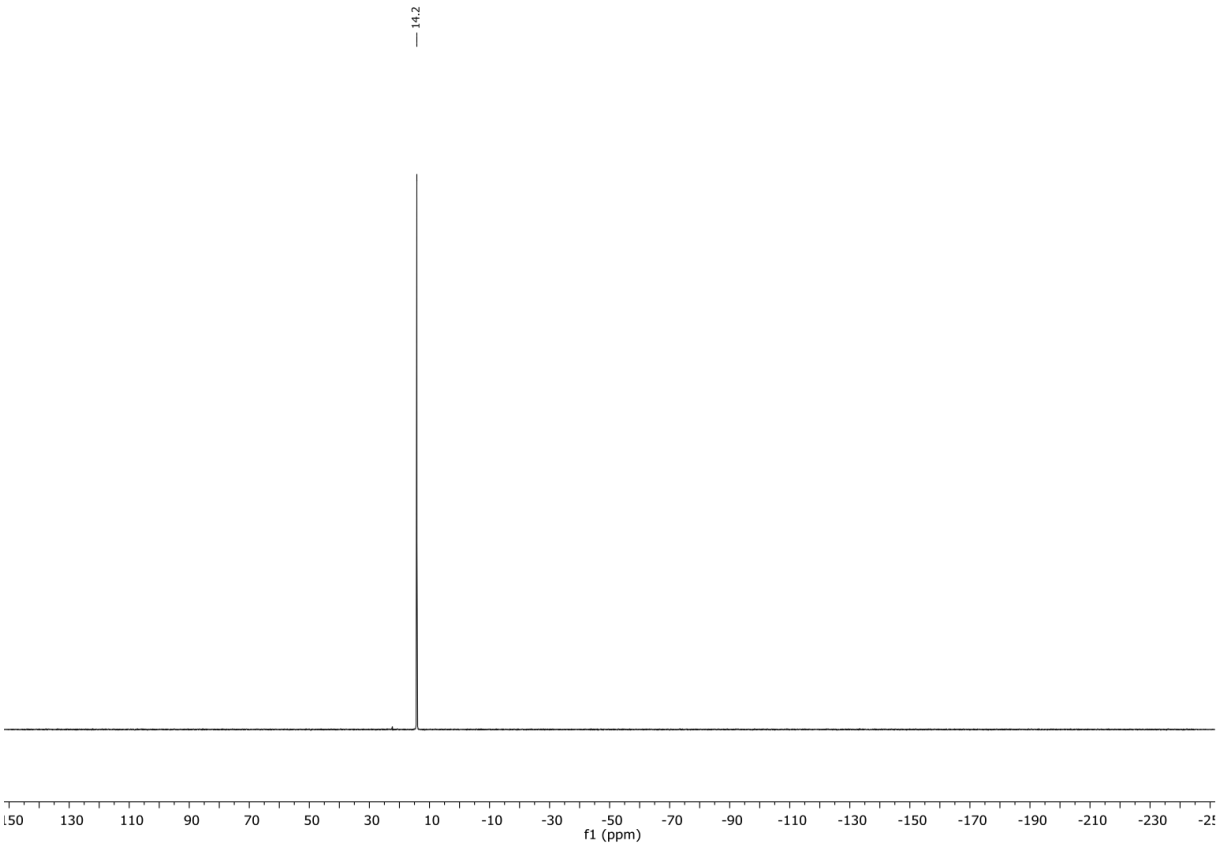




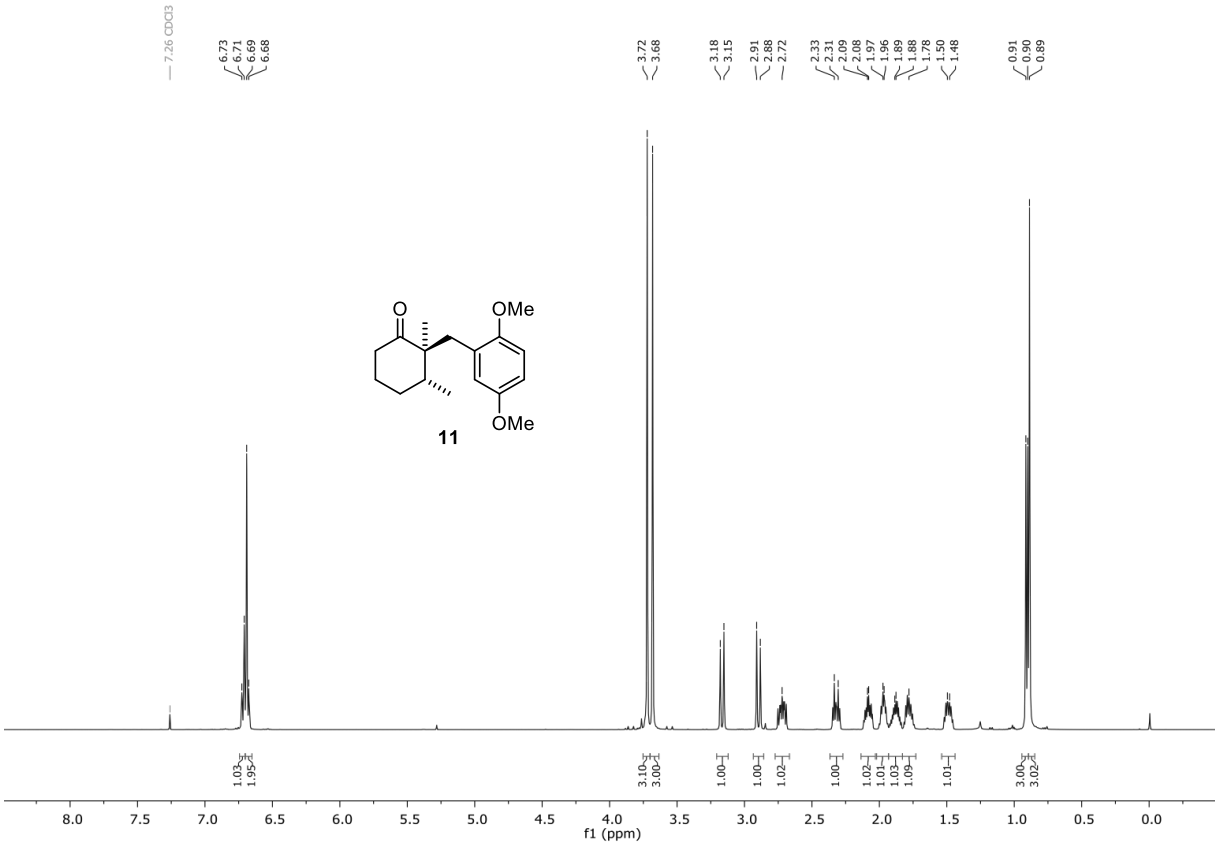
6.2. ^{1}H, ^{13}C and ^{31}P NMR of Tris-(pyrrolidinyl)-phosphoramide (TPPA)

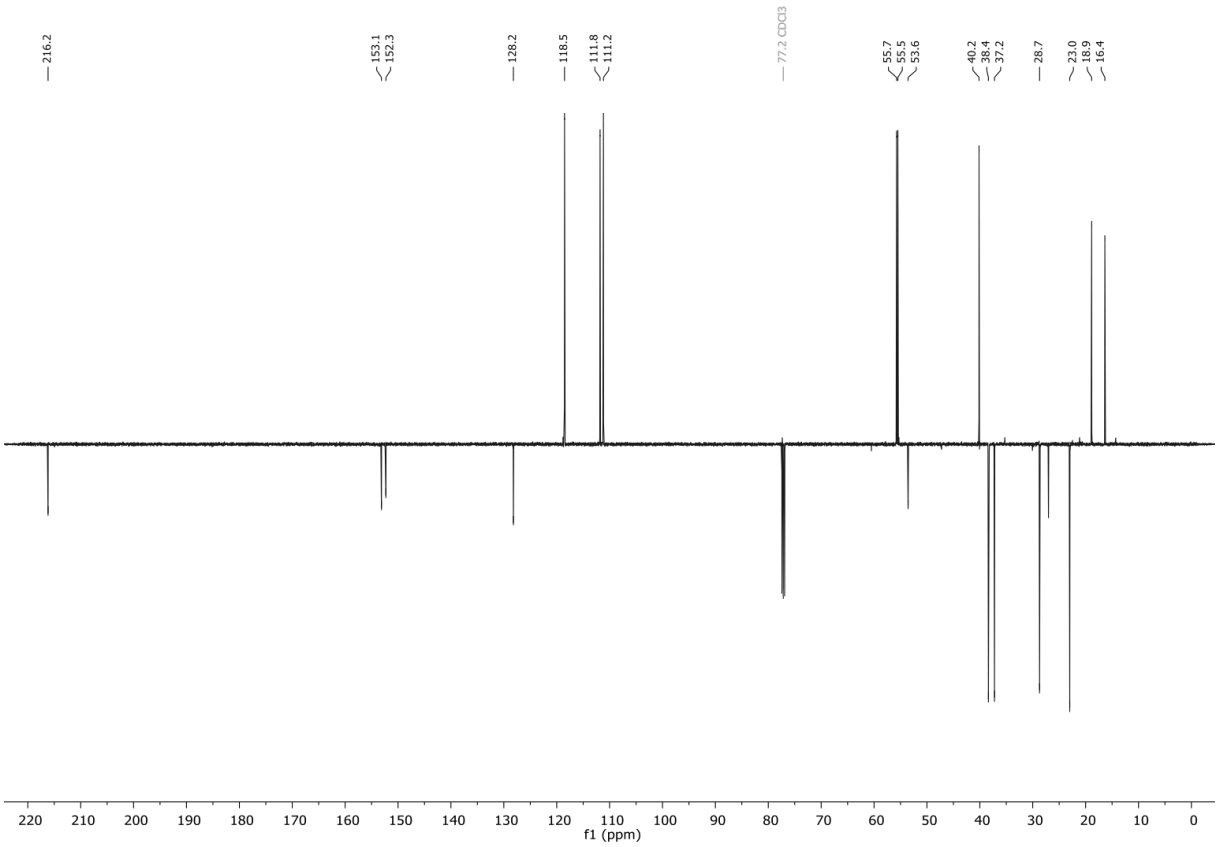




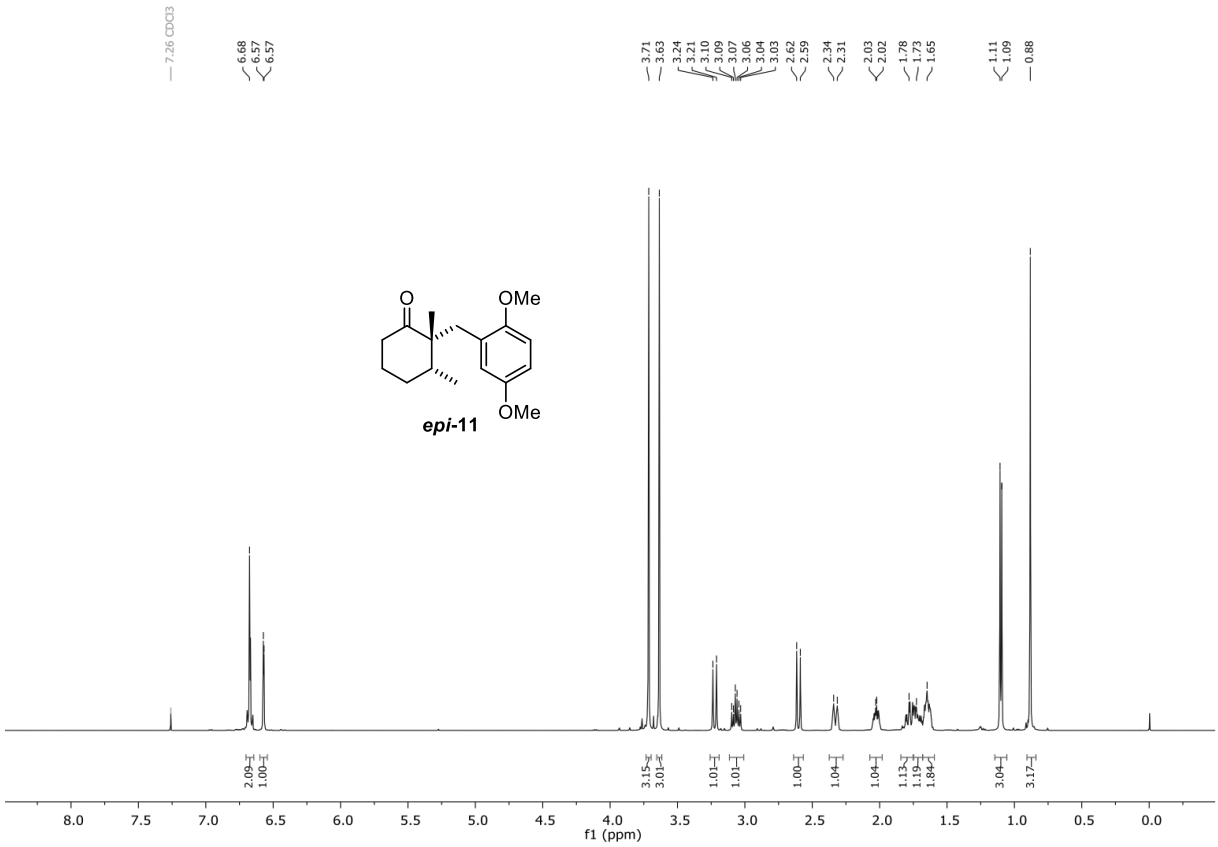

14.2
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

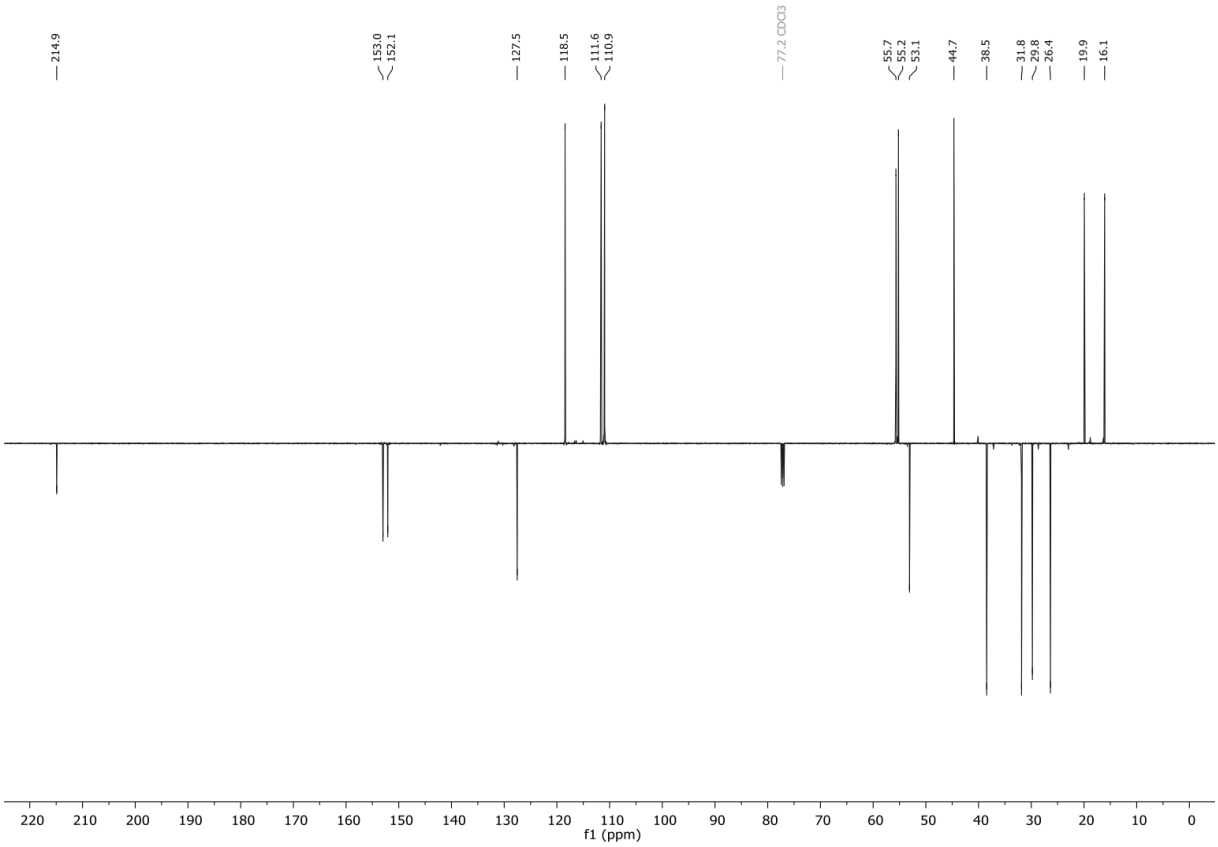
6.3. ^{1}H and ^{13}C NMR of (2*S*,3*R*)-2-(2,5-Dimethoxybenzyl)-2,3-dimethylcyclohexanone (11)



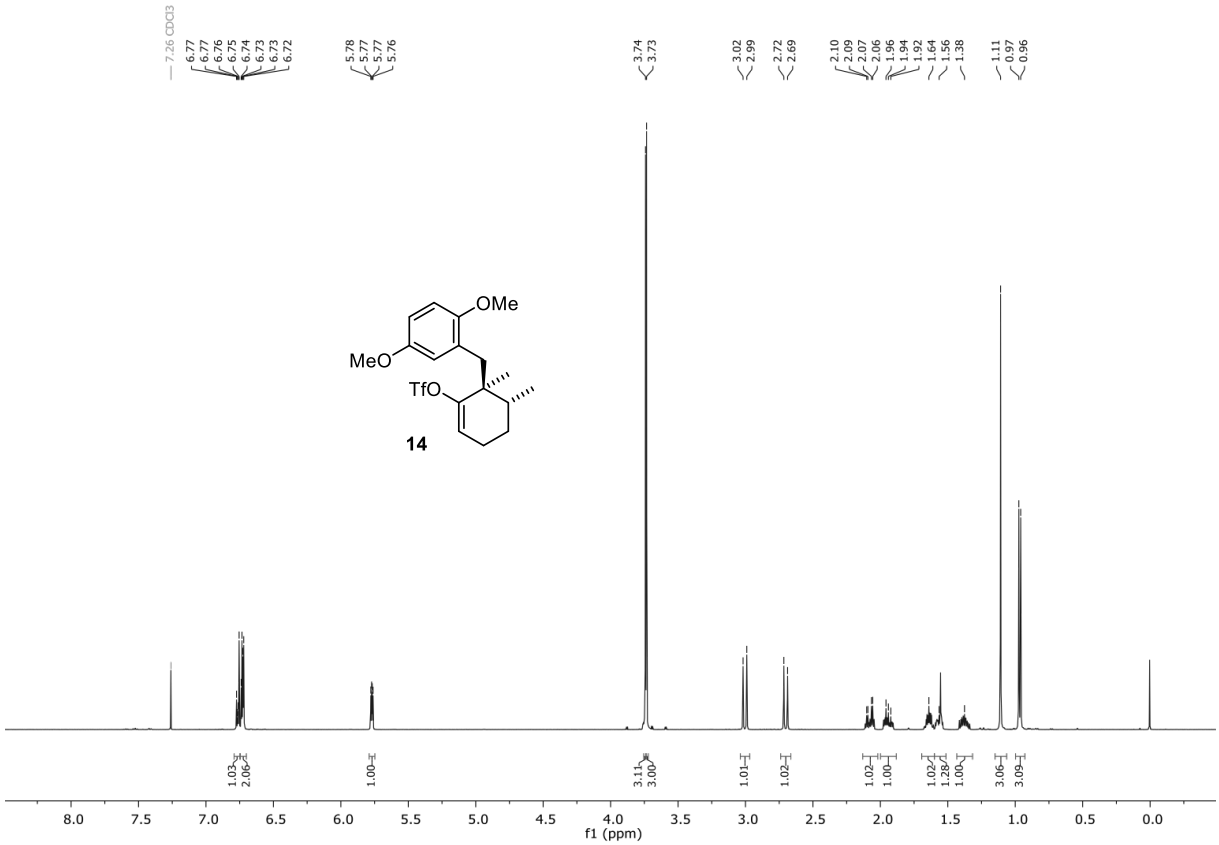


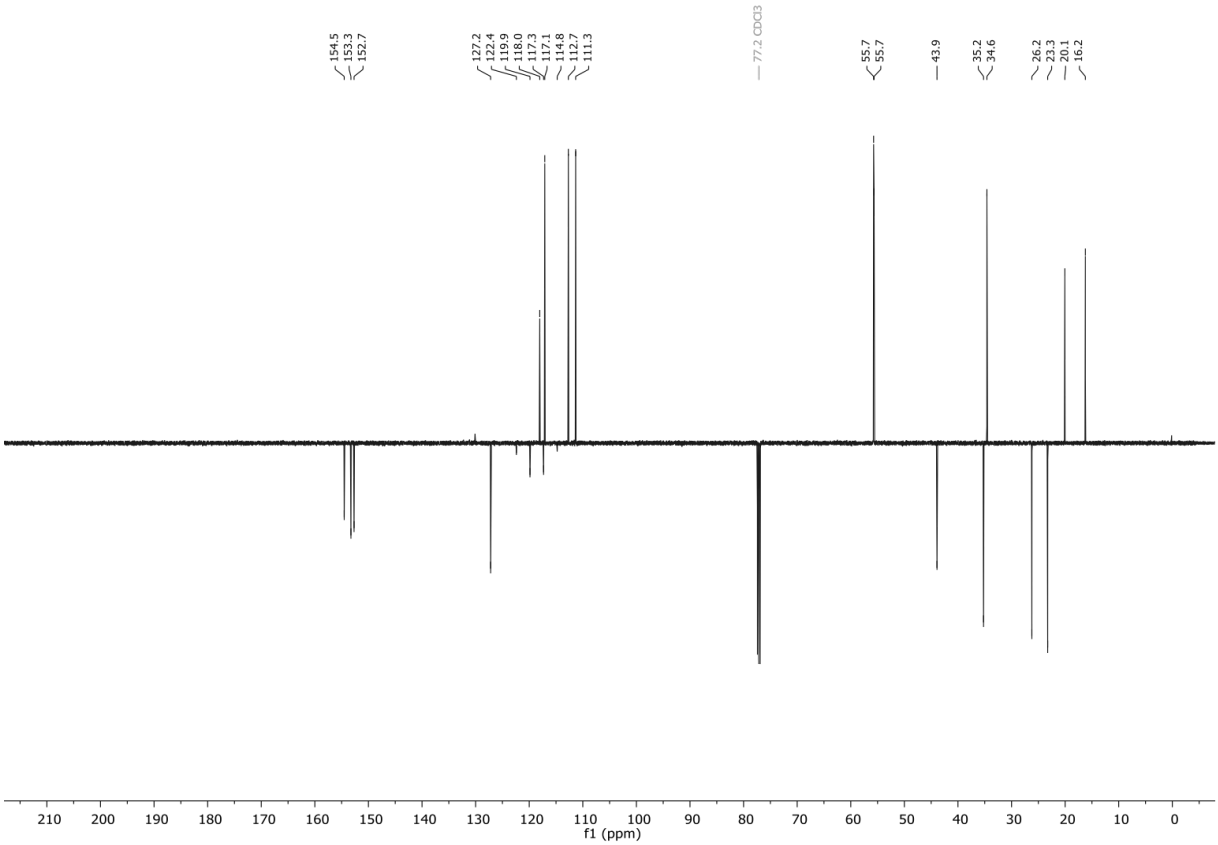
6.4. ^{1}H and ^{13}C NMR of (2*R*,3*R*)-2-(2,5-Dimethoxybenzyl)-2,3-dimethylcyclohexanone (*epi*-11)

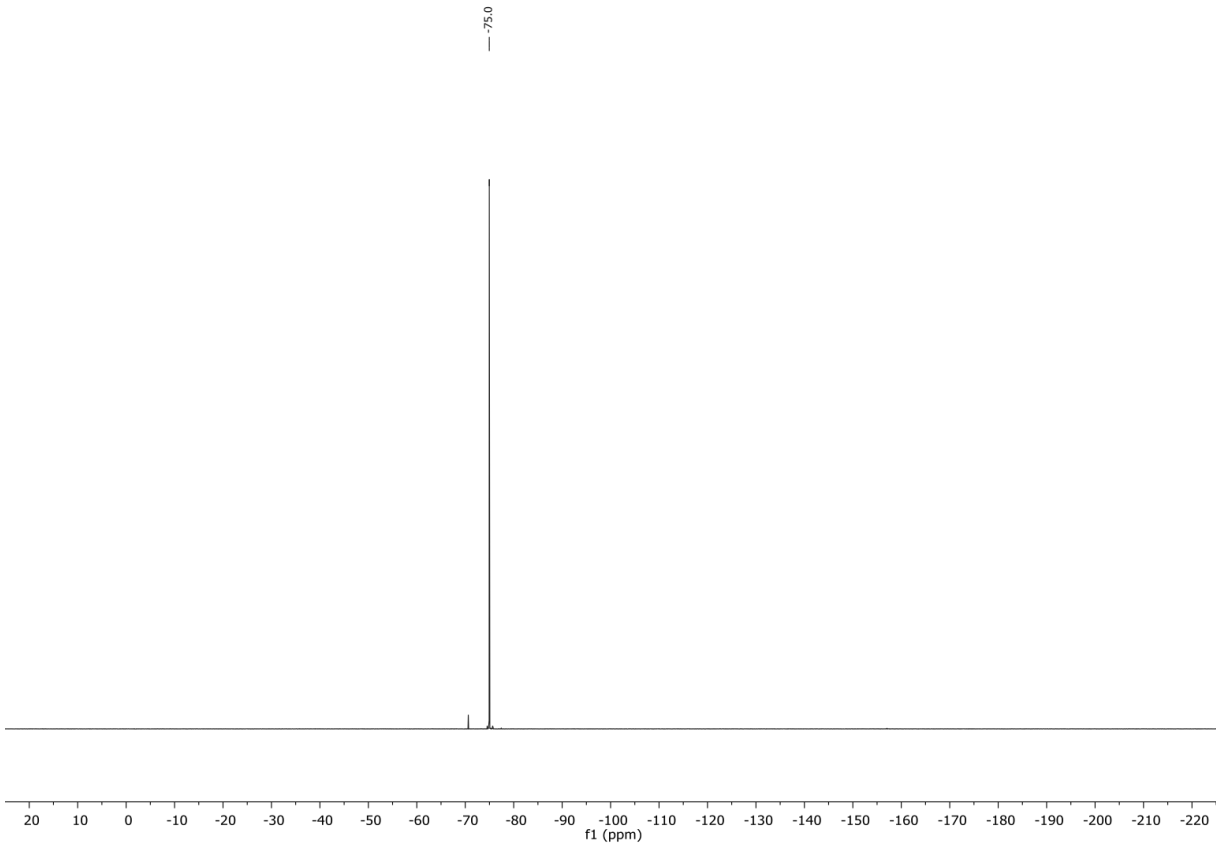




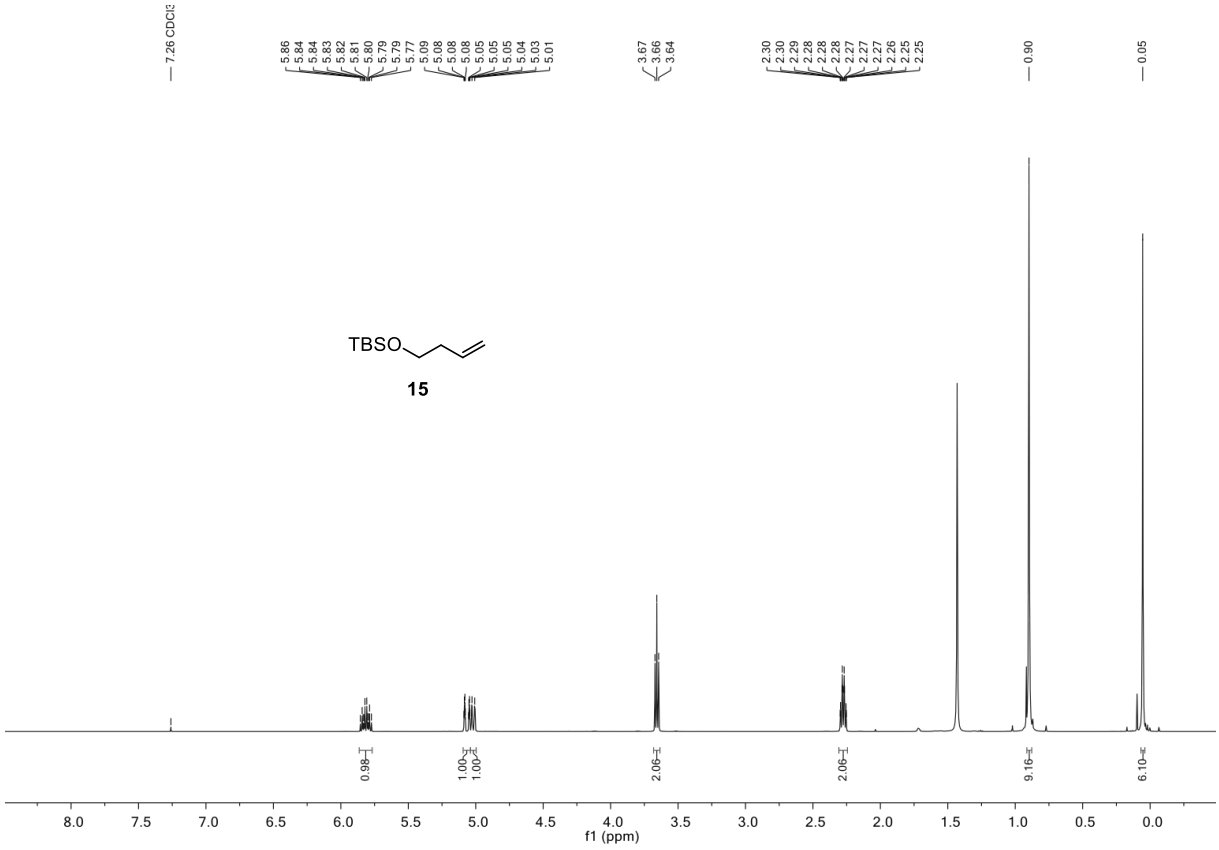
6.5. ^{1}H, ^{13}C and ^{19}F NMR of Enol Triflate 14

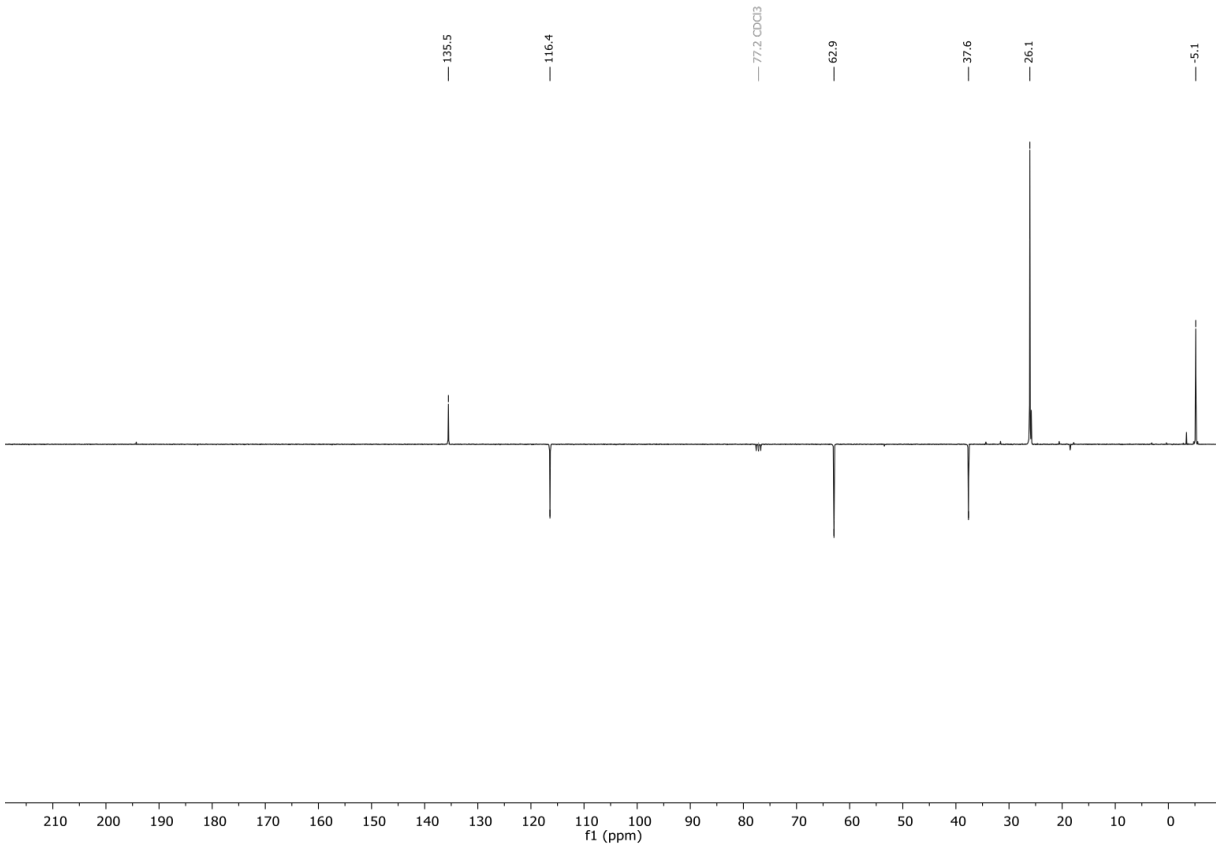




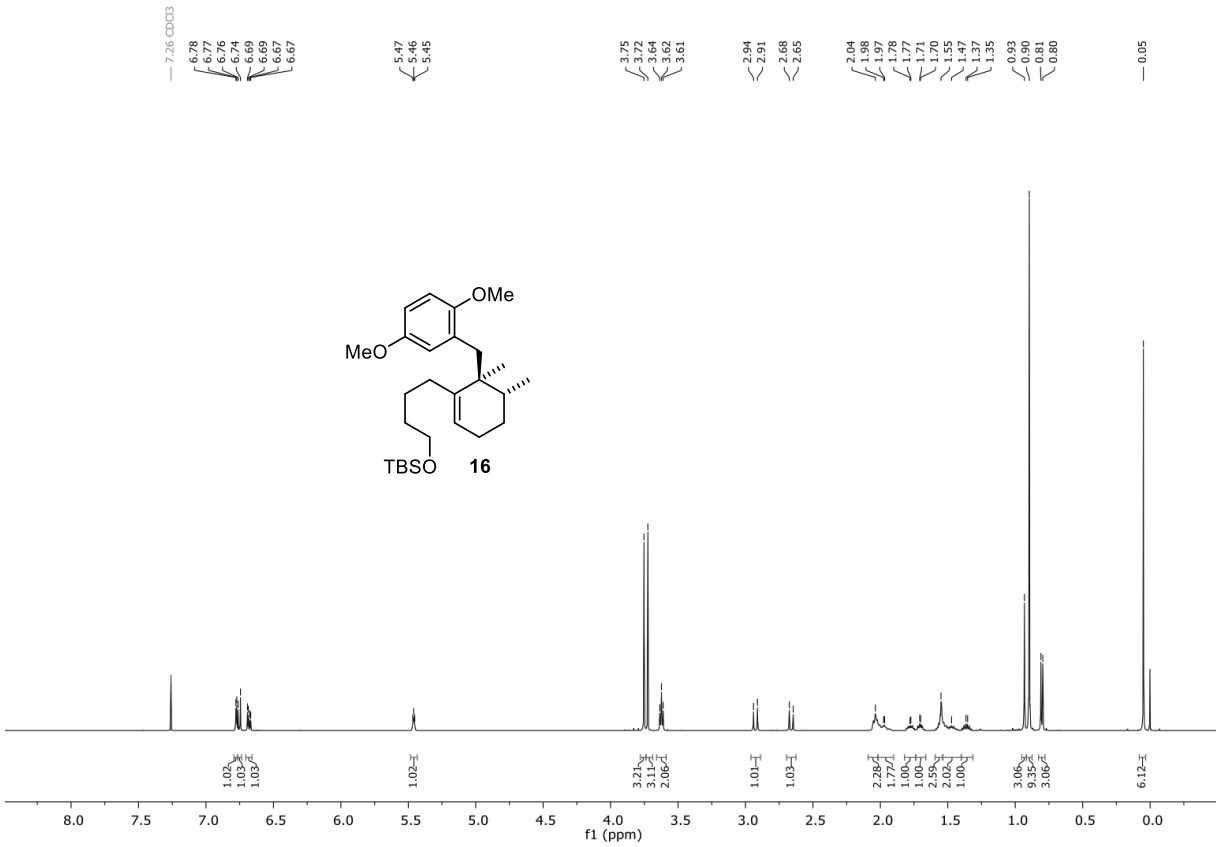

-75.0
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

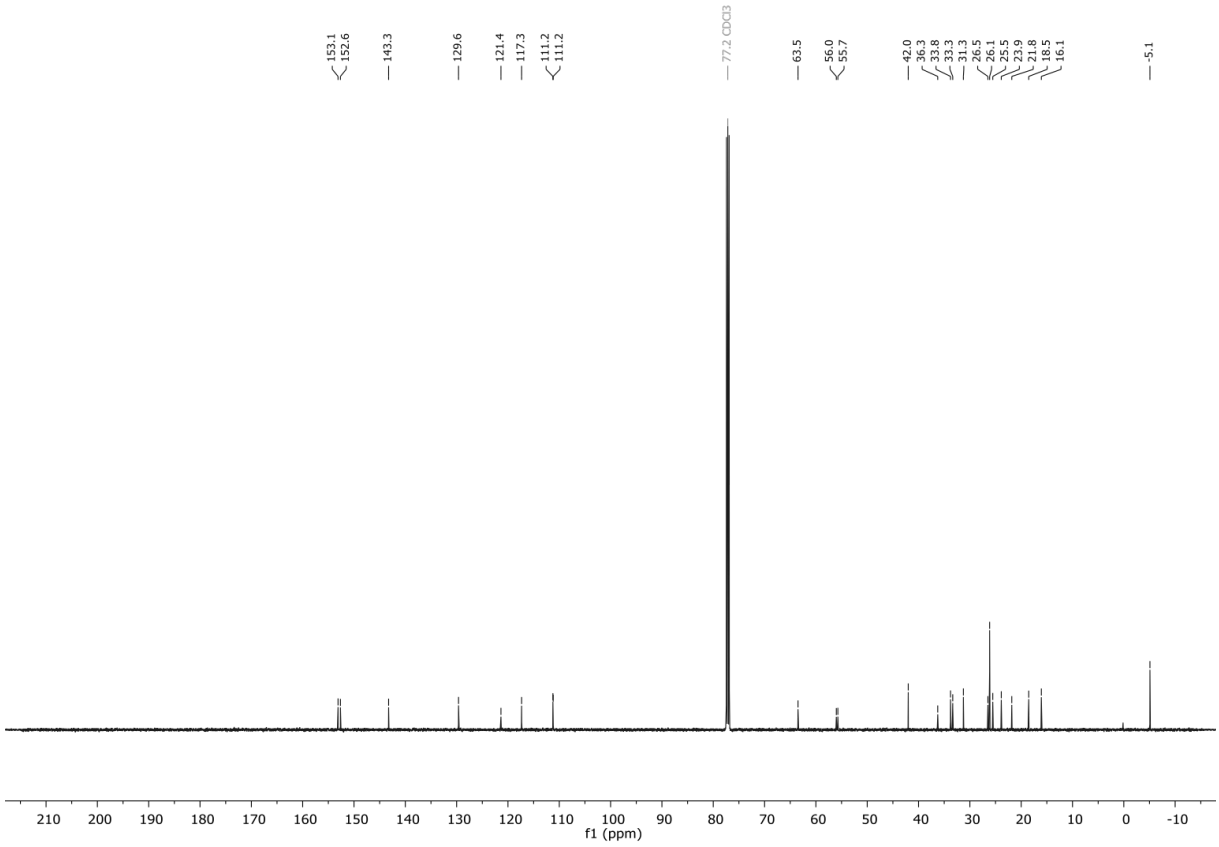
6.6. ^{1}H and ^{13}C NMR of But-3-en-1-yloxy(*tert*-butyl)dimethylsilane (15)



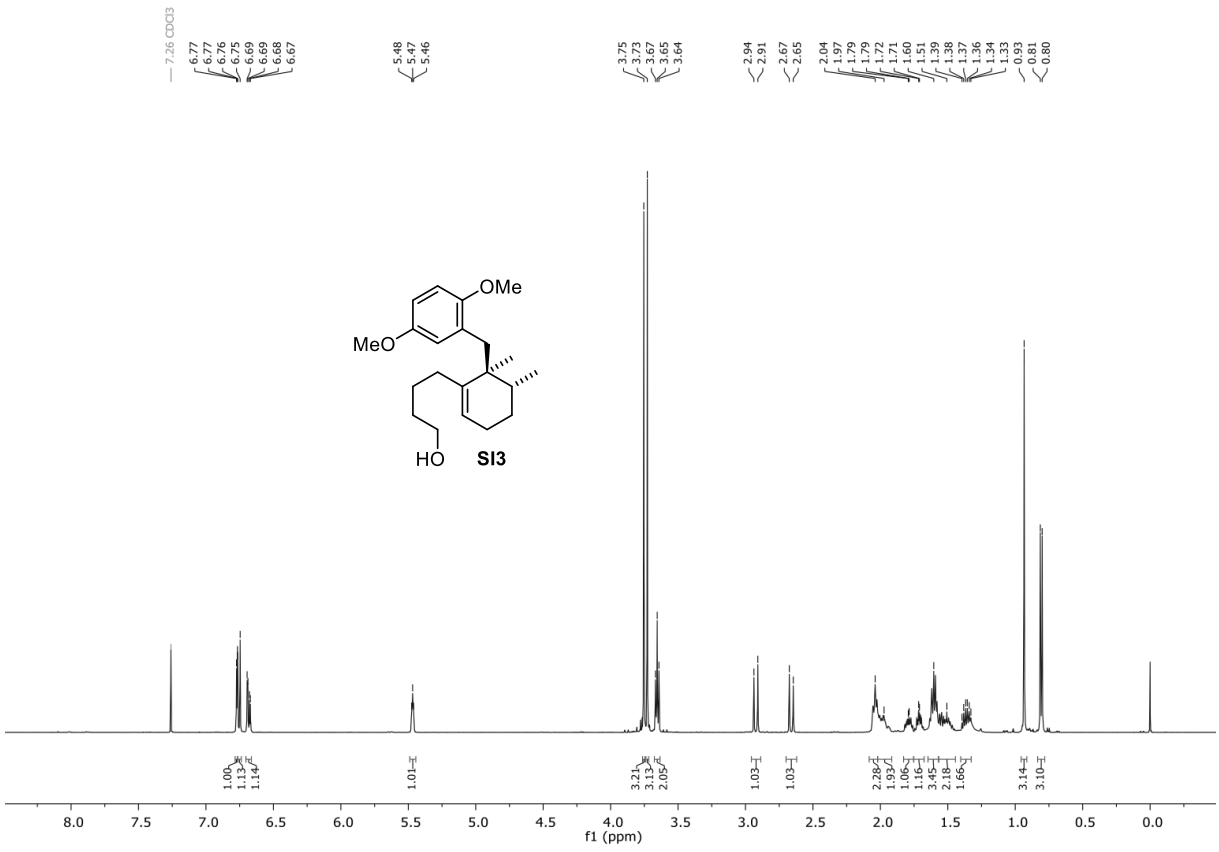


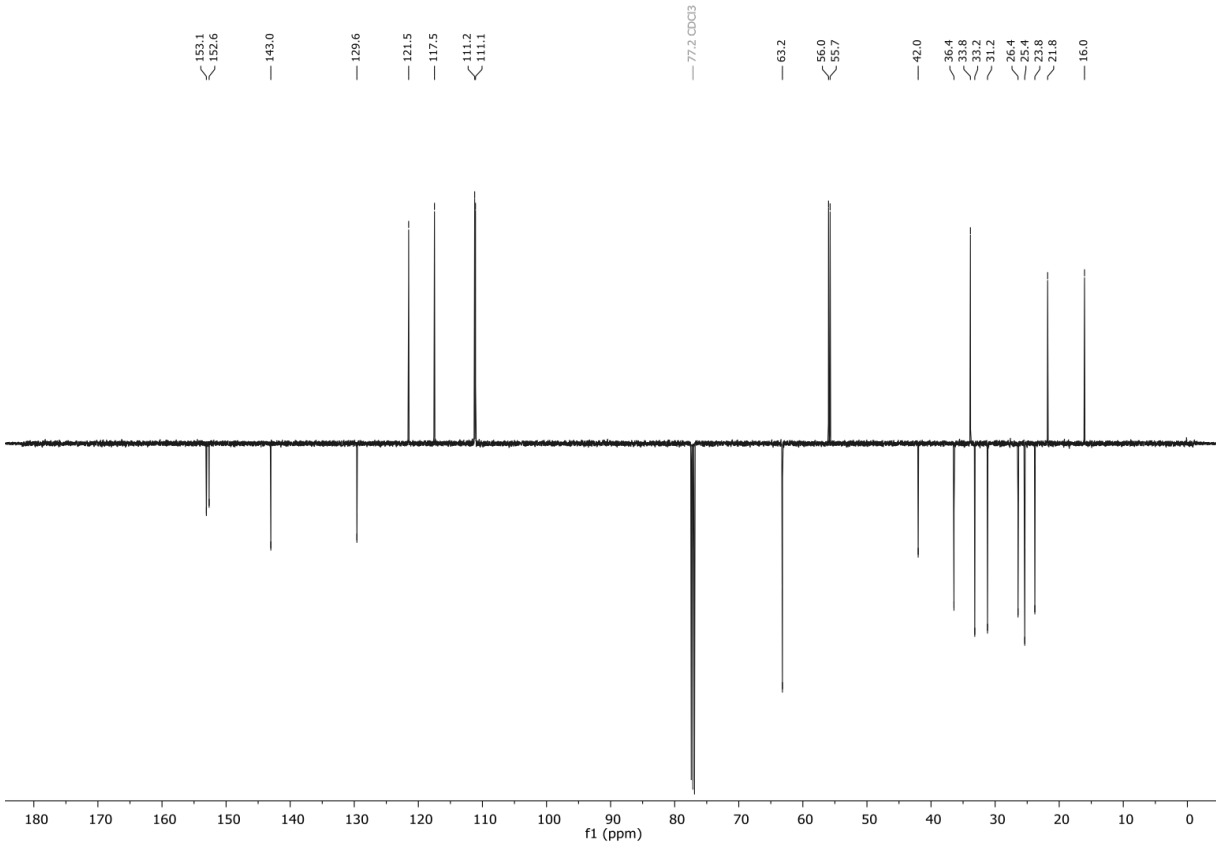
6.7. ^{1}H and ^{13}C NMR of Silyl Ether 16



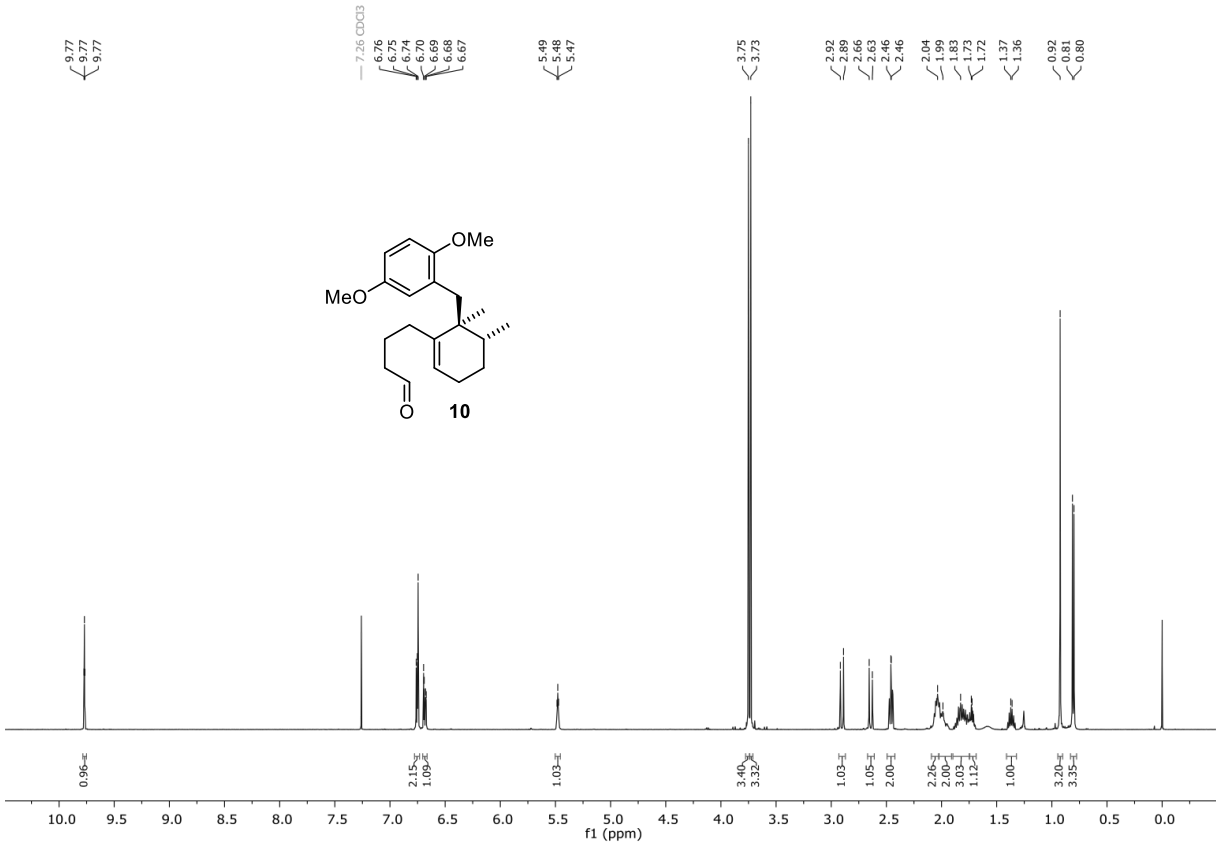


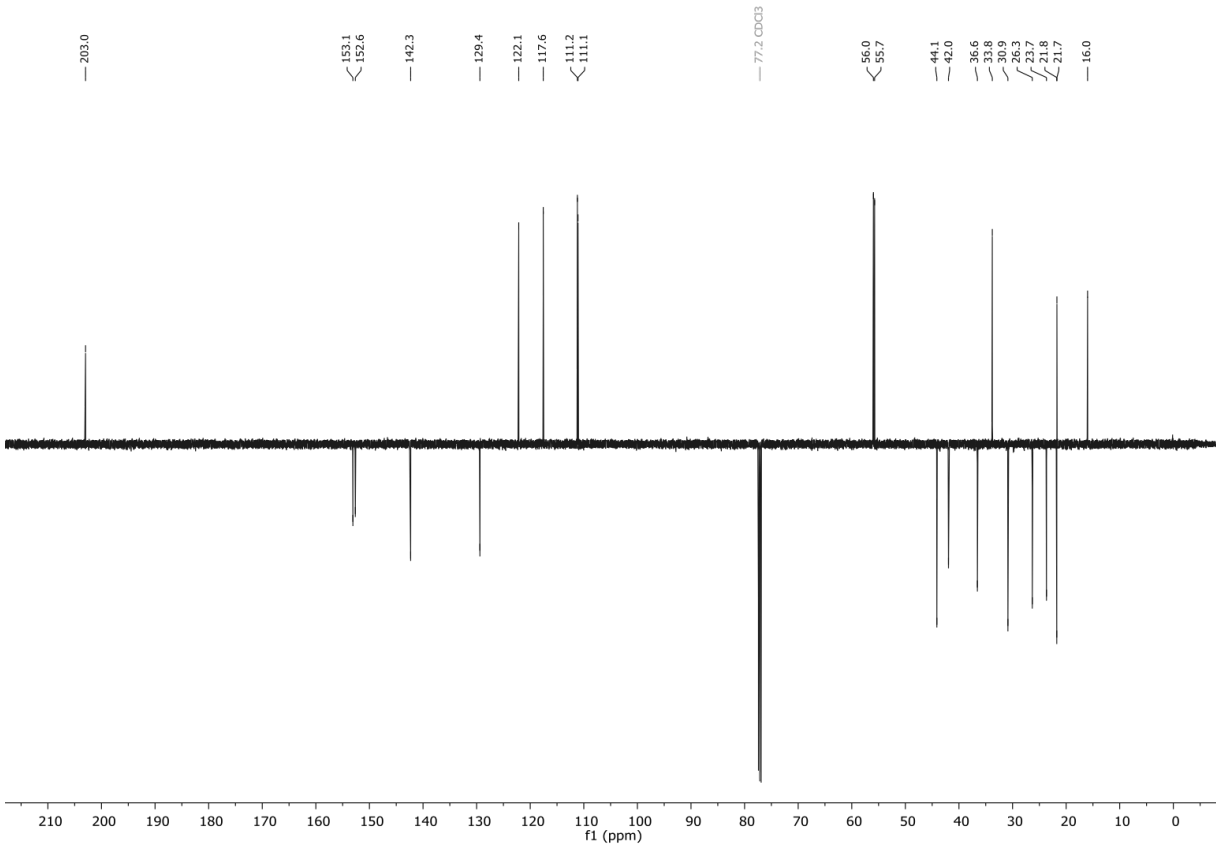
6.8. ^{1}H and ^{13}C NMR of Alcohol SI3



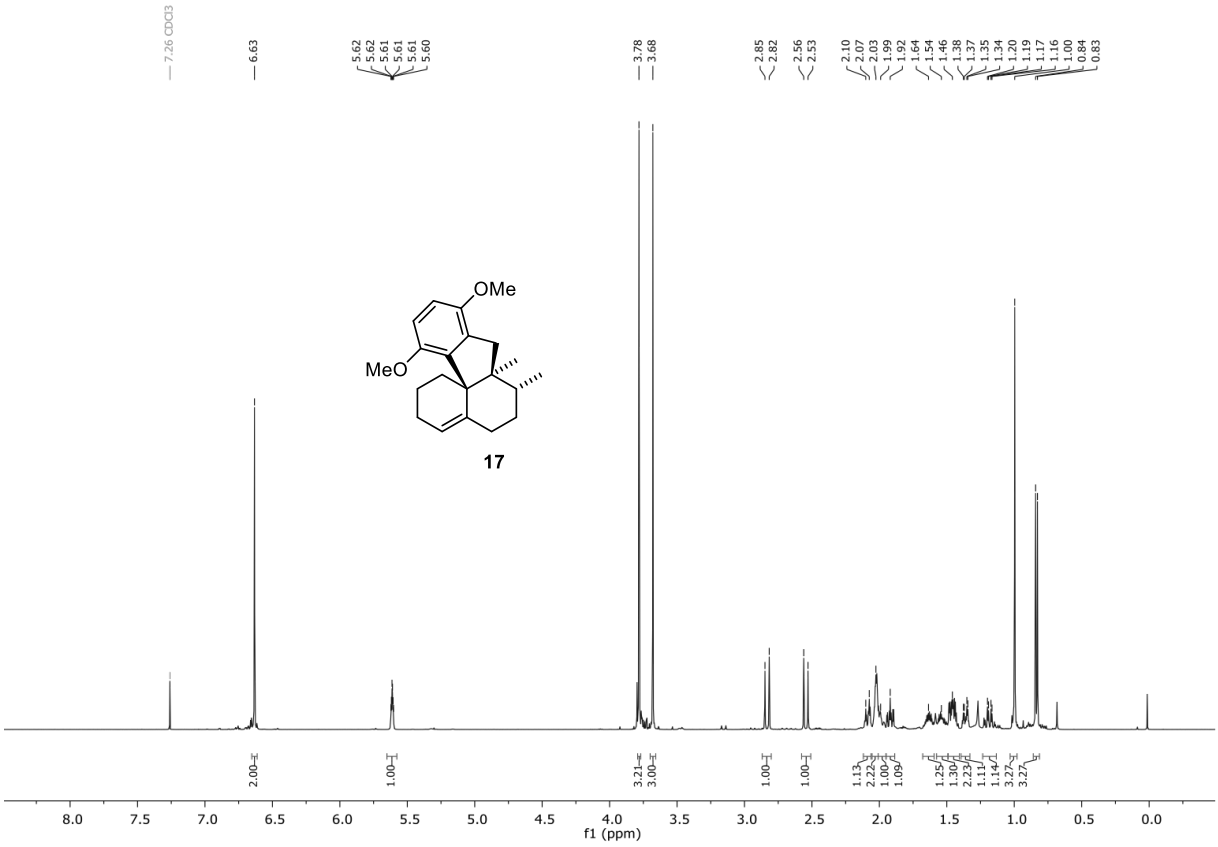


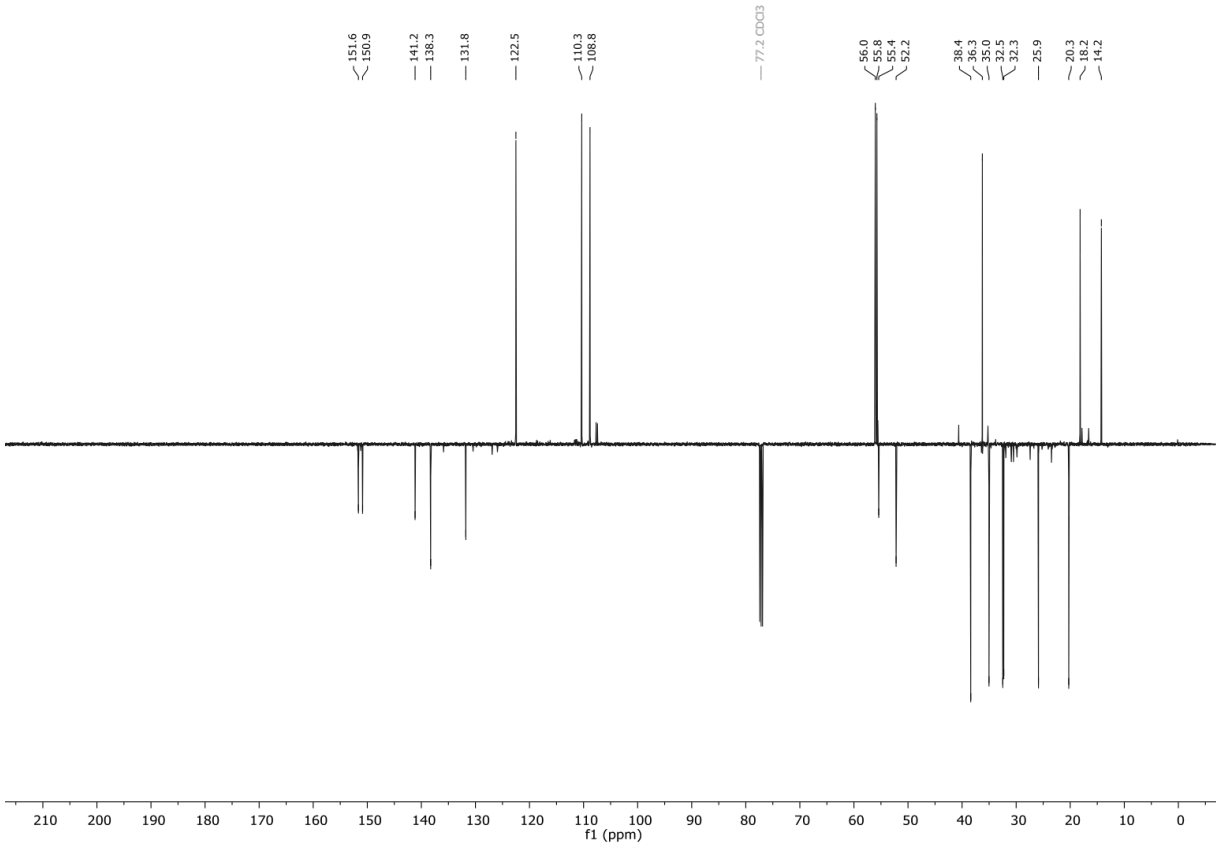
6.9. ^{1}H and ^{13}C NMR of Aldehyde 10



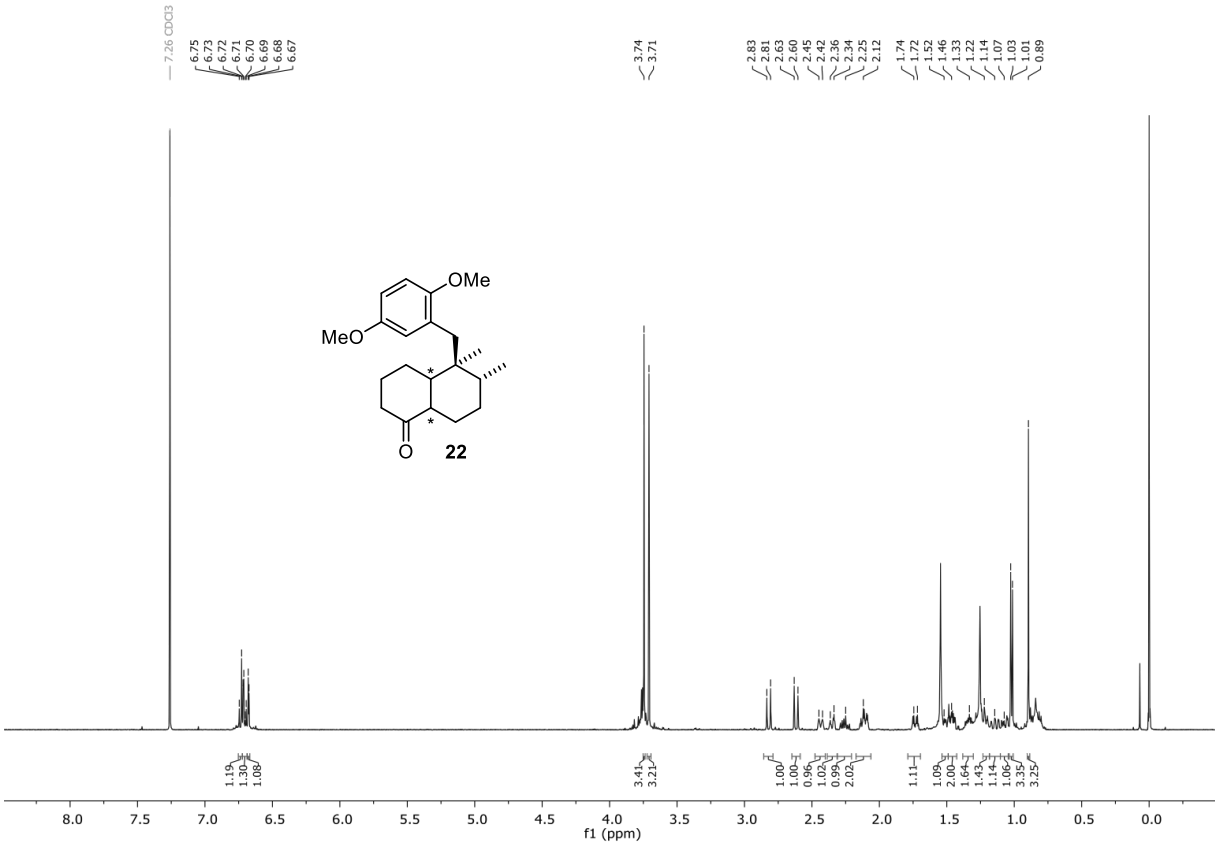


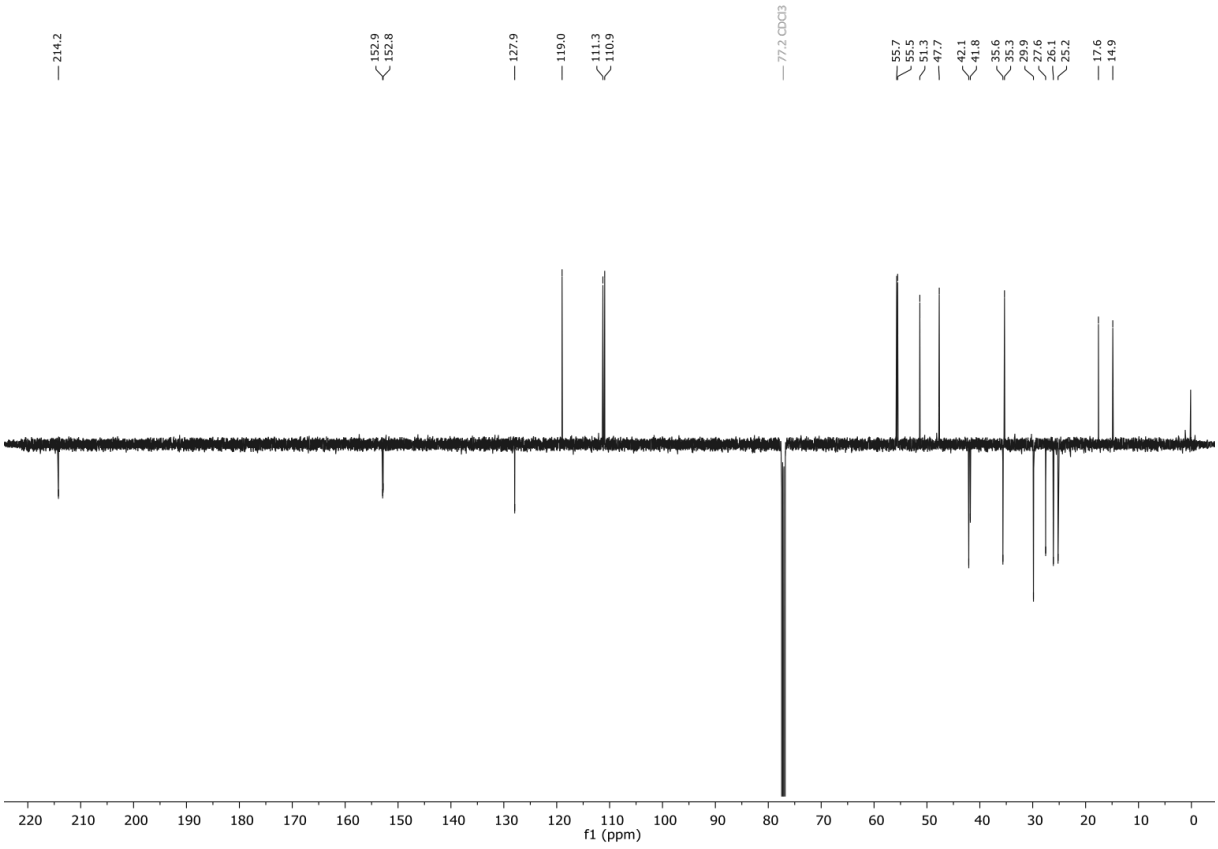
6.10. ^{1}H and ^{13}C NMR of Olefin 17



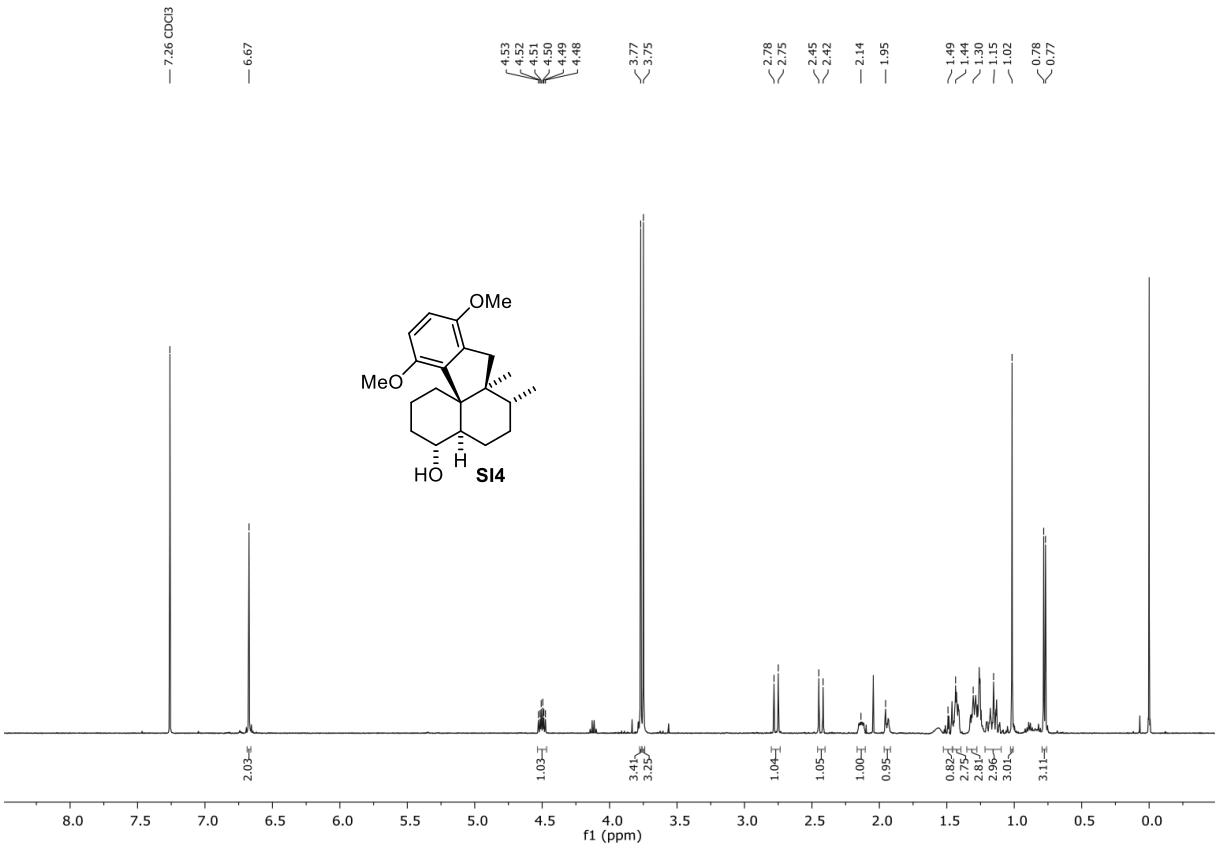


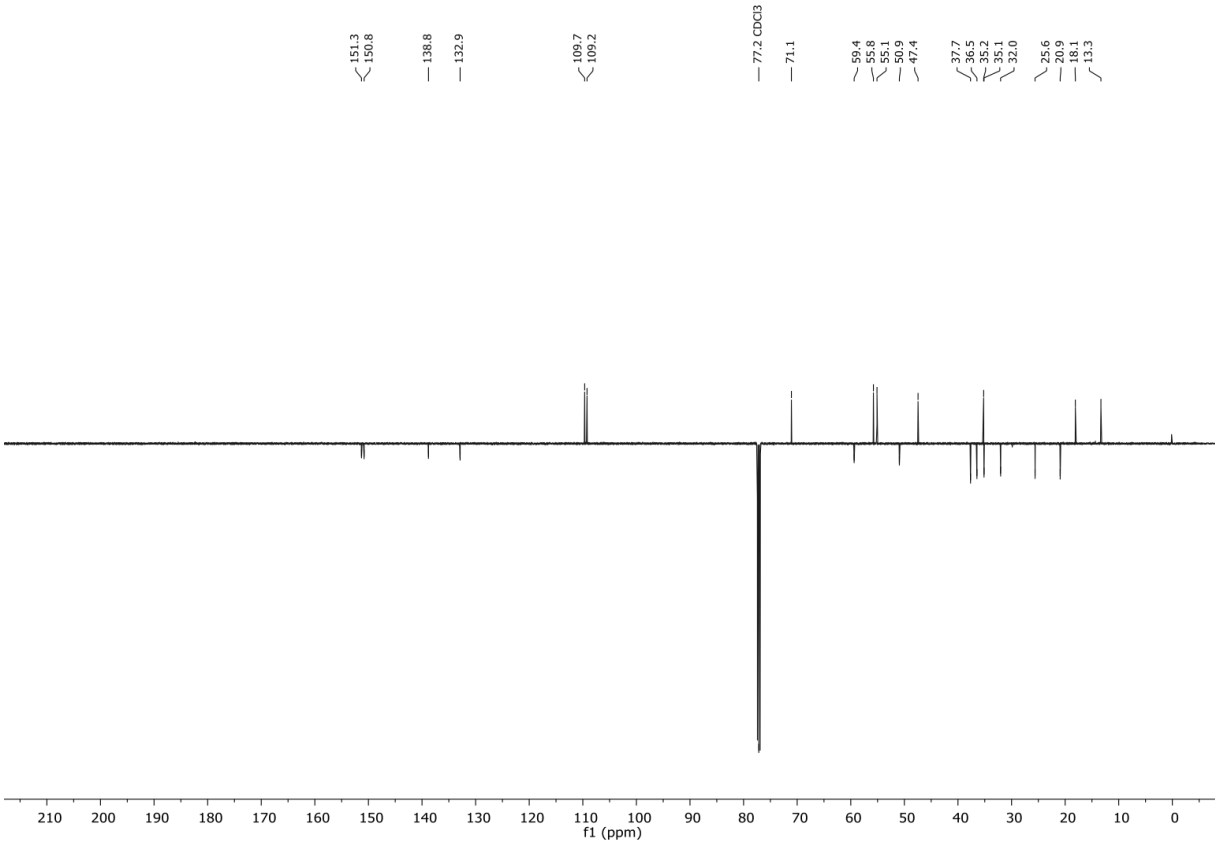
6.11. ^{1}H and ^{13}C NMR of Ketone 22



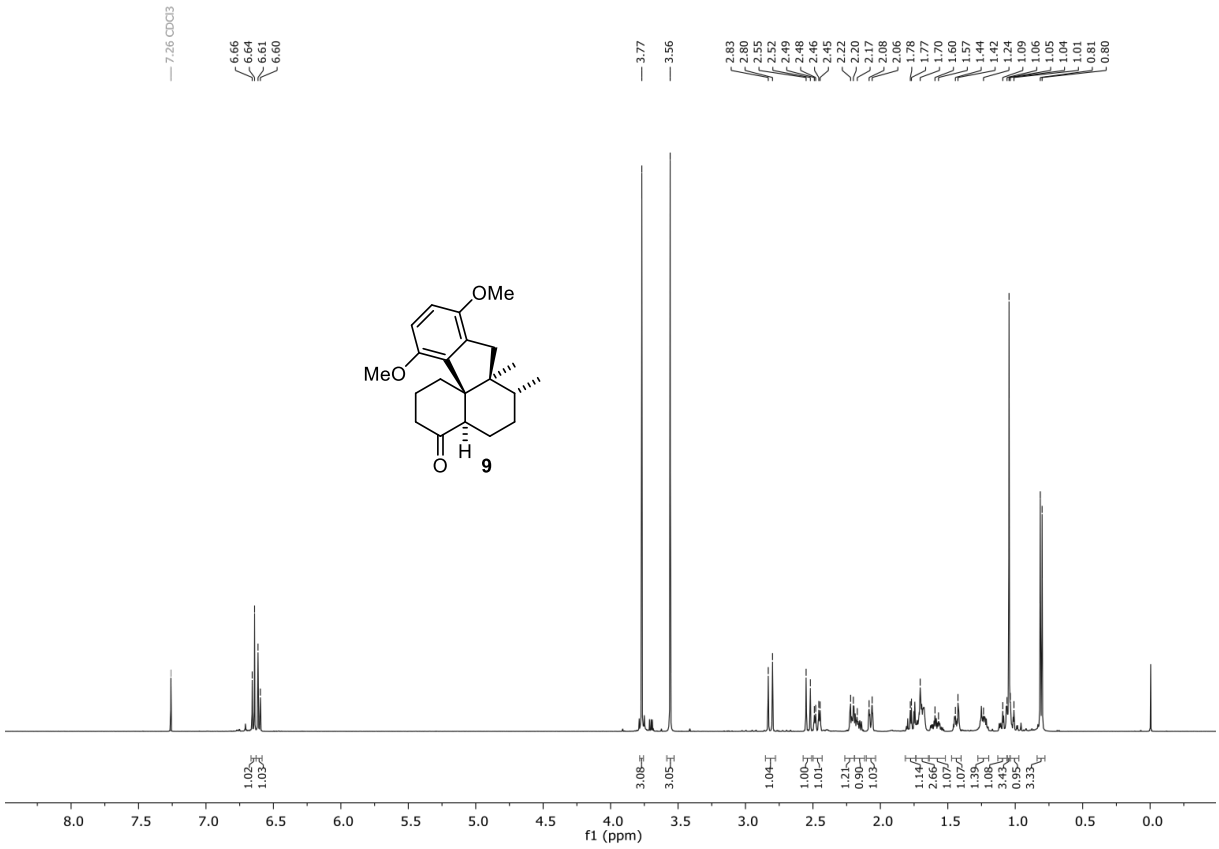


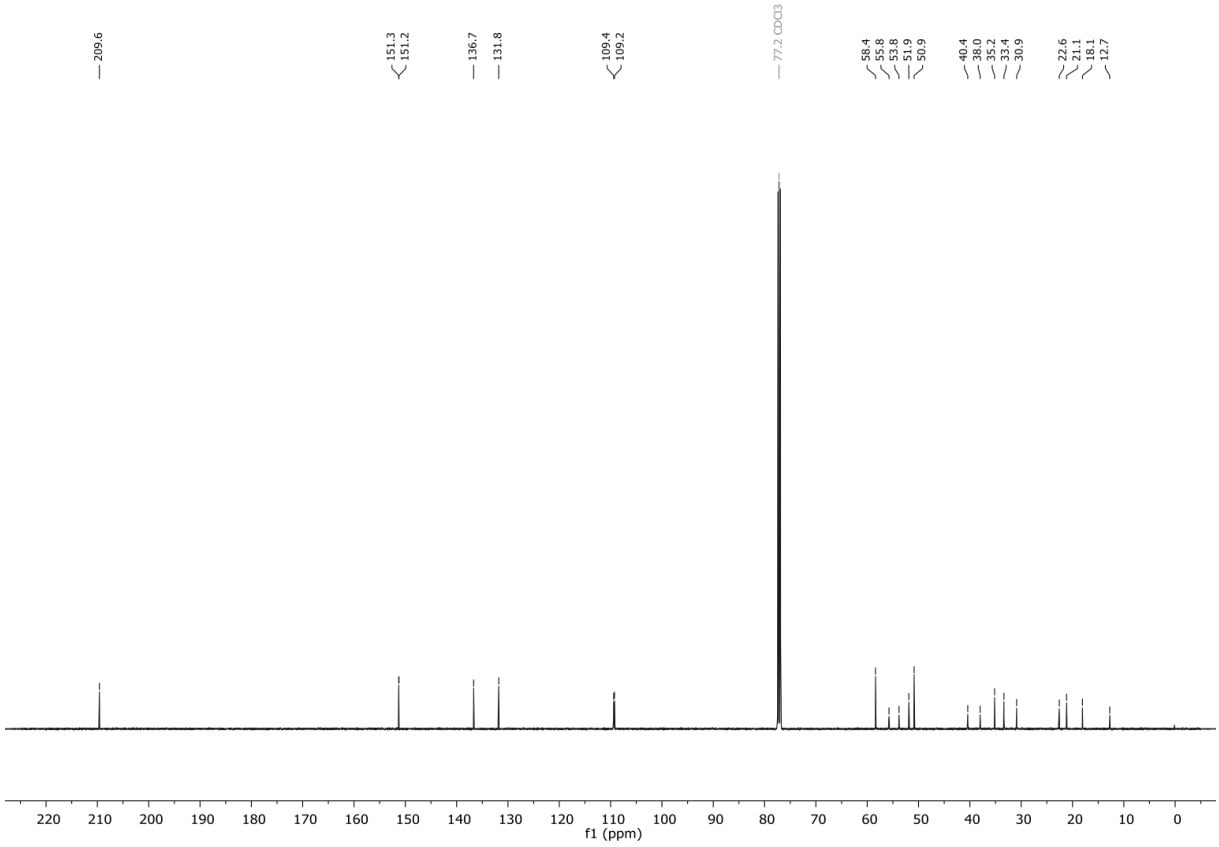
6.12. ^{1}H and ^{13}C NMR of Alcohol SI4



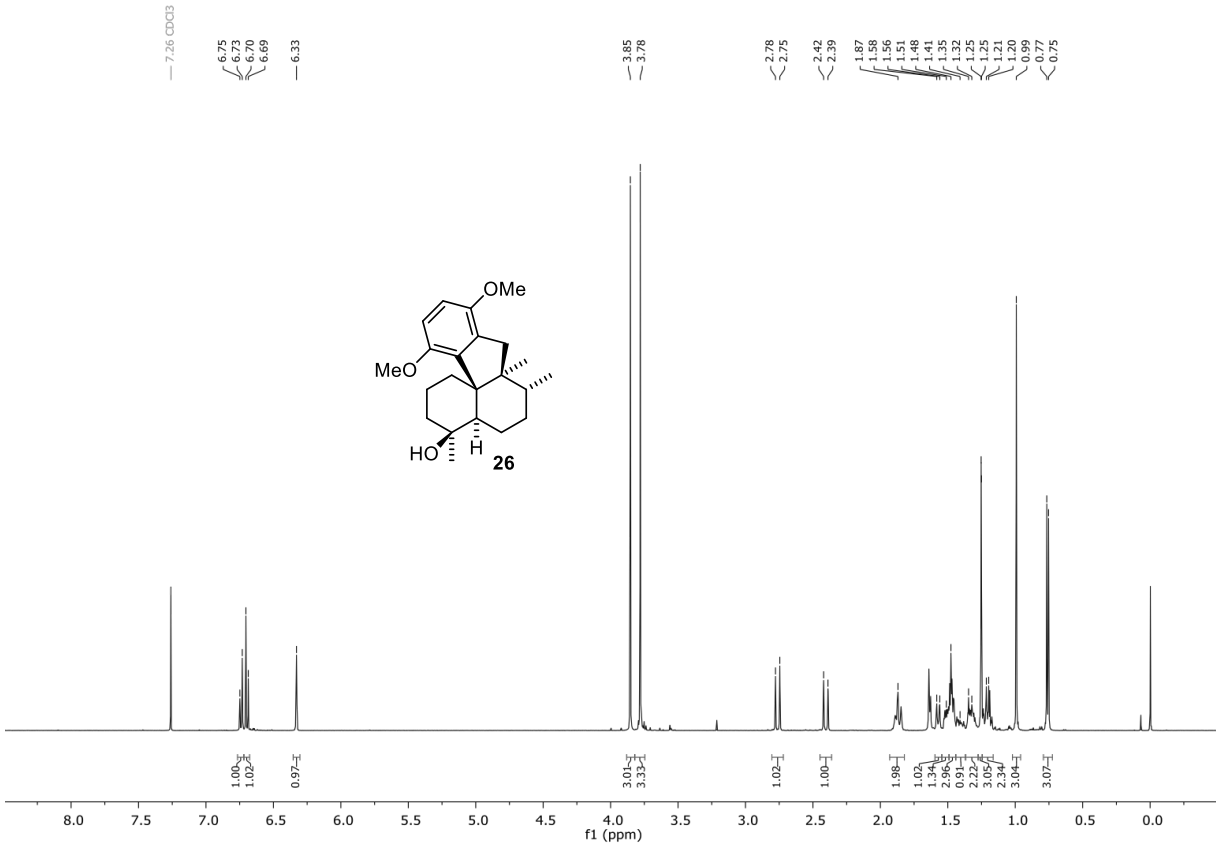


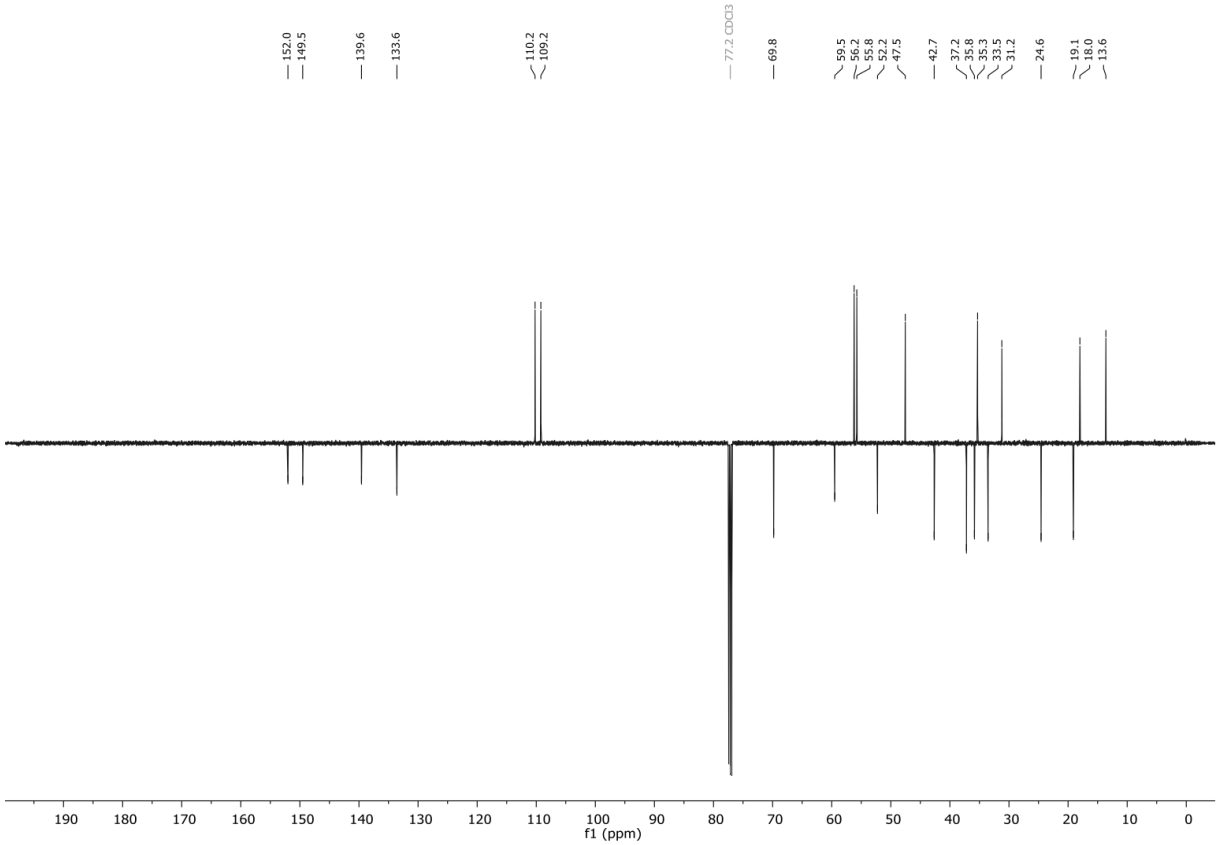
6.13. ^{1}H and ^{13}C NMR of Ketone 9



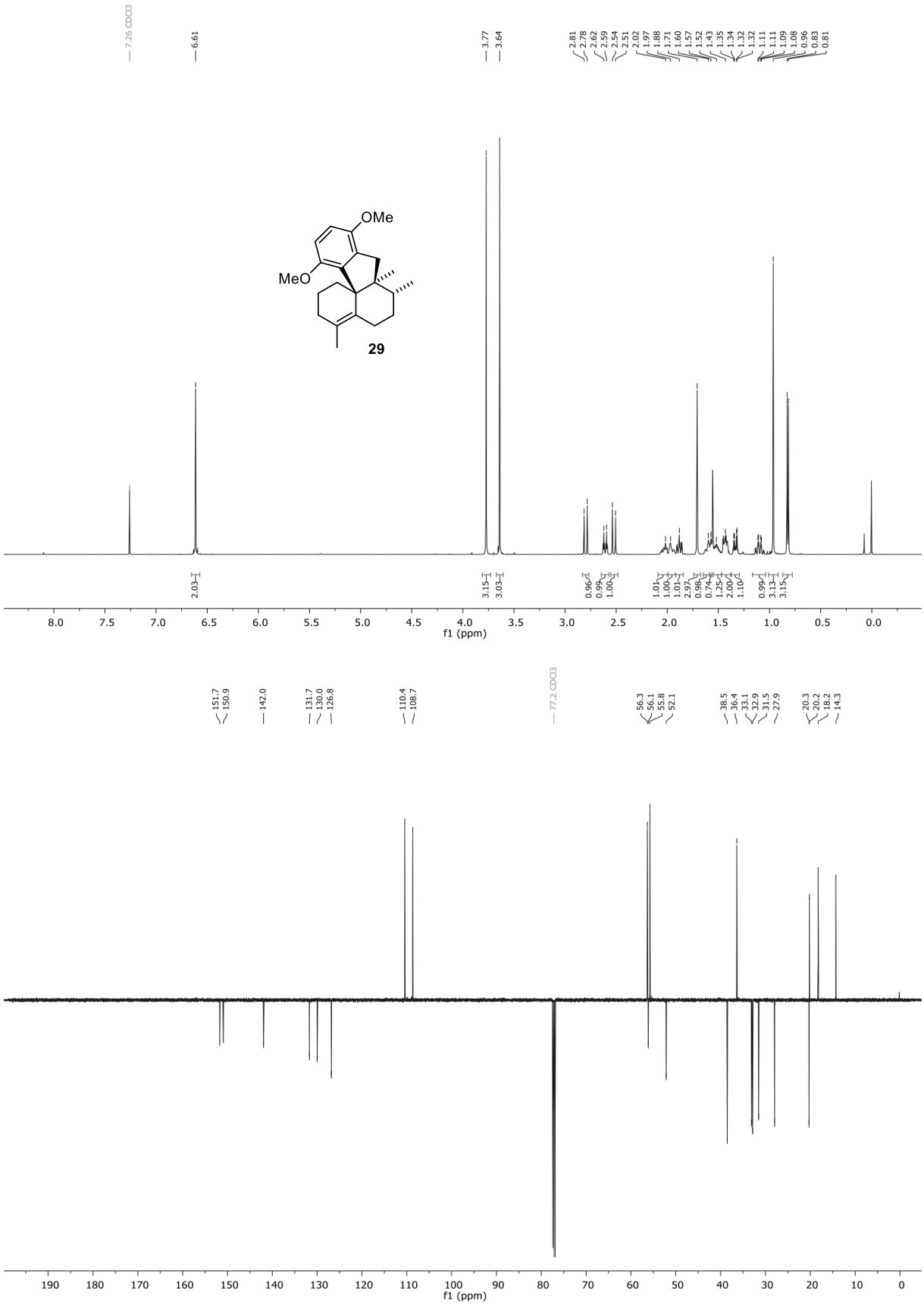


6.14. ^{1}H and ^{13}C NMR of Alcohol 26

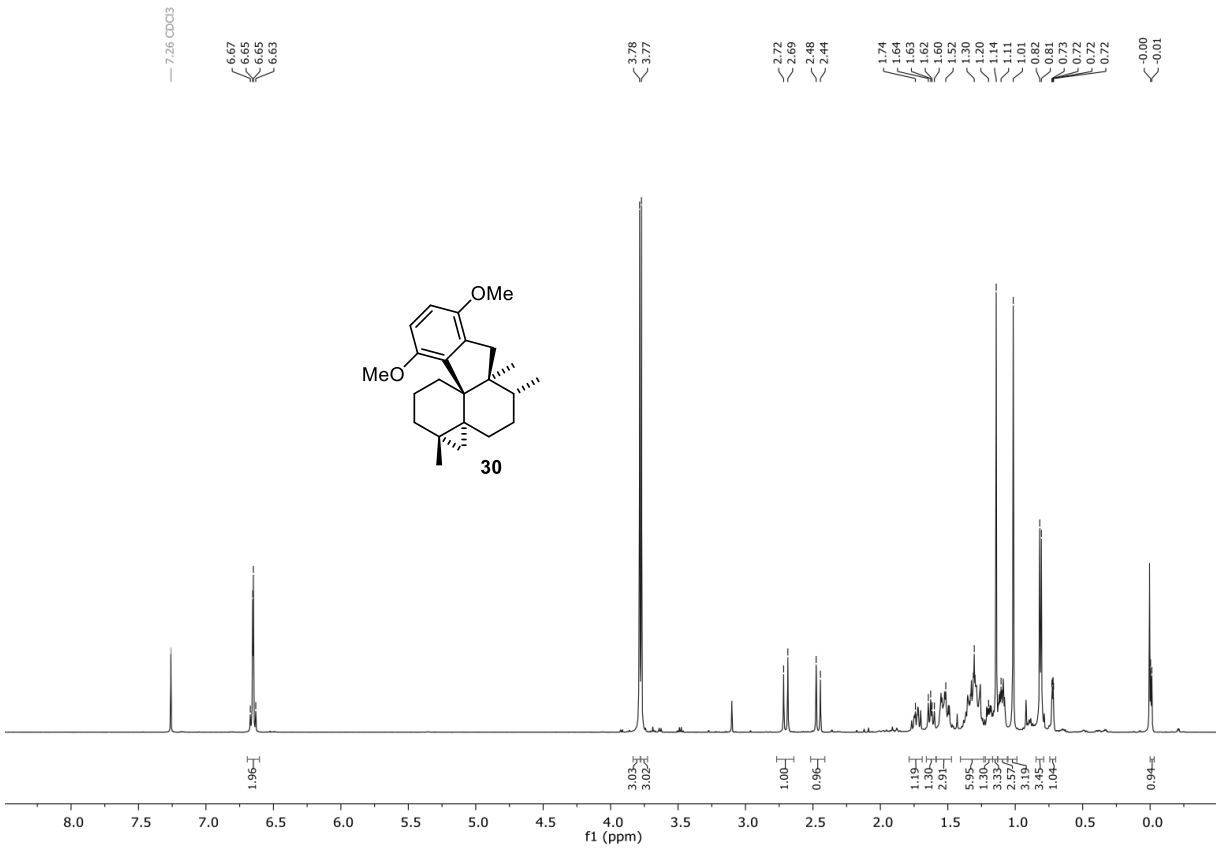


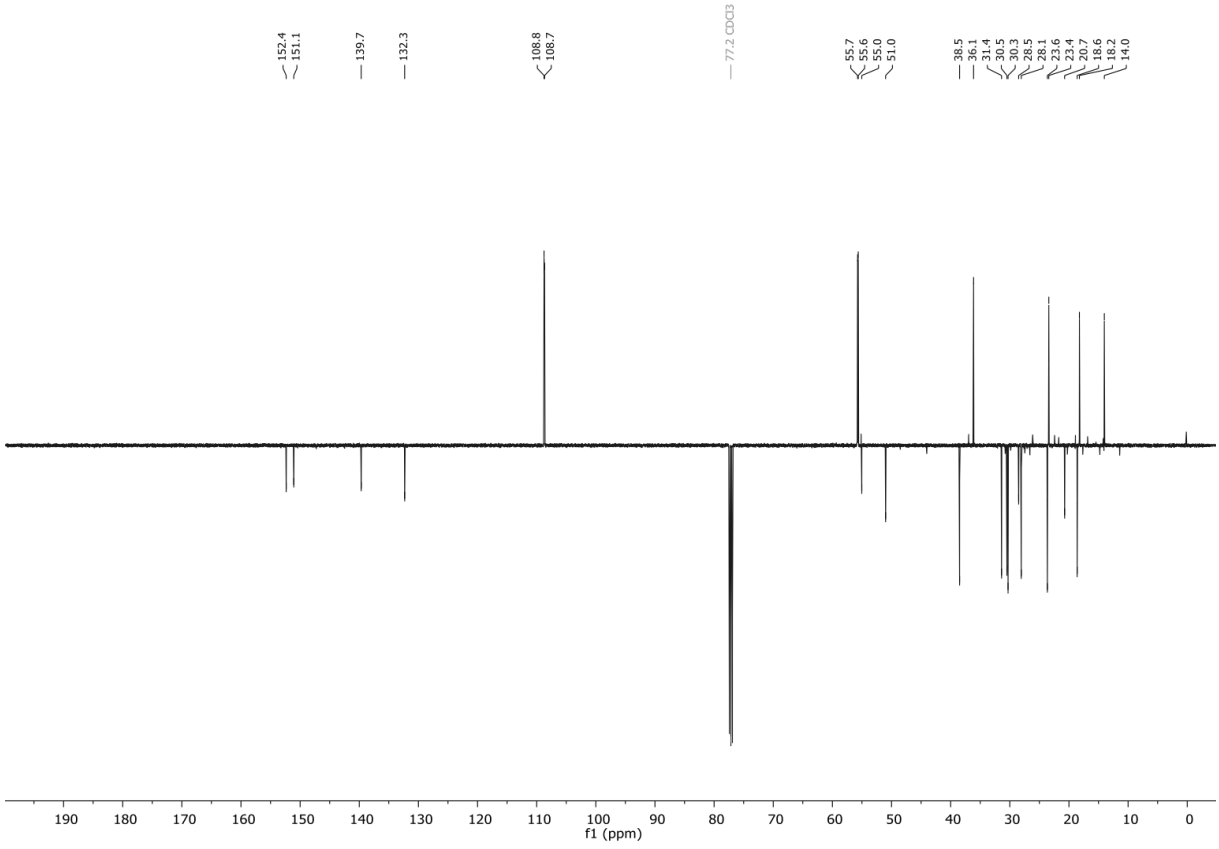


6.15. ^{1}H and ^{13}C NMR of Olefin 29

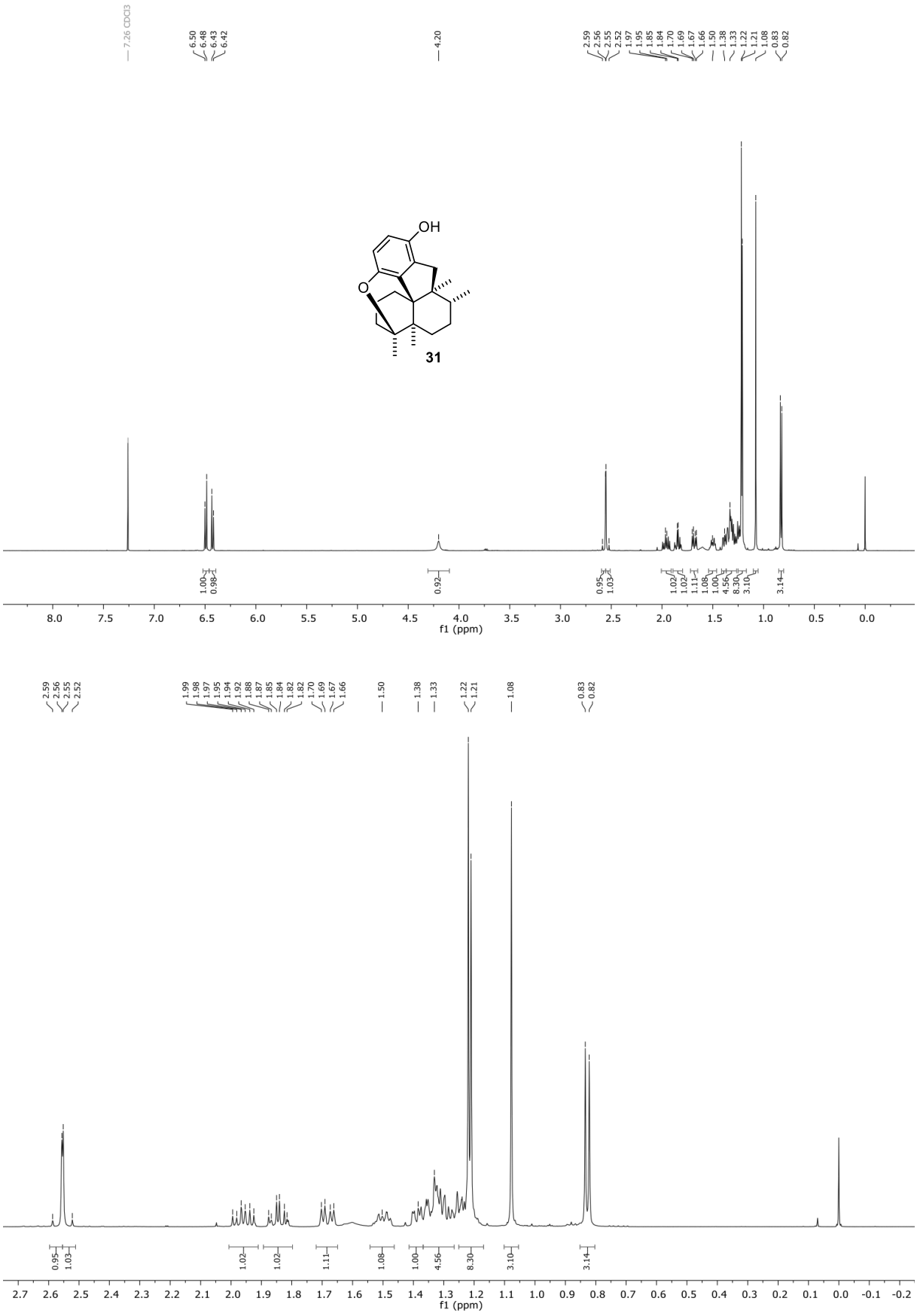


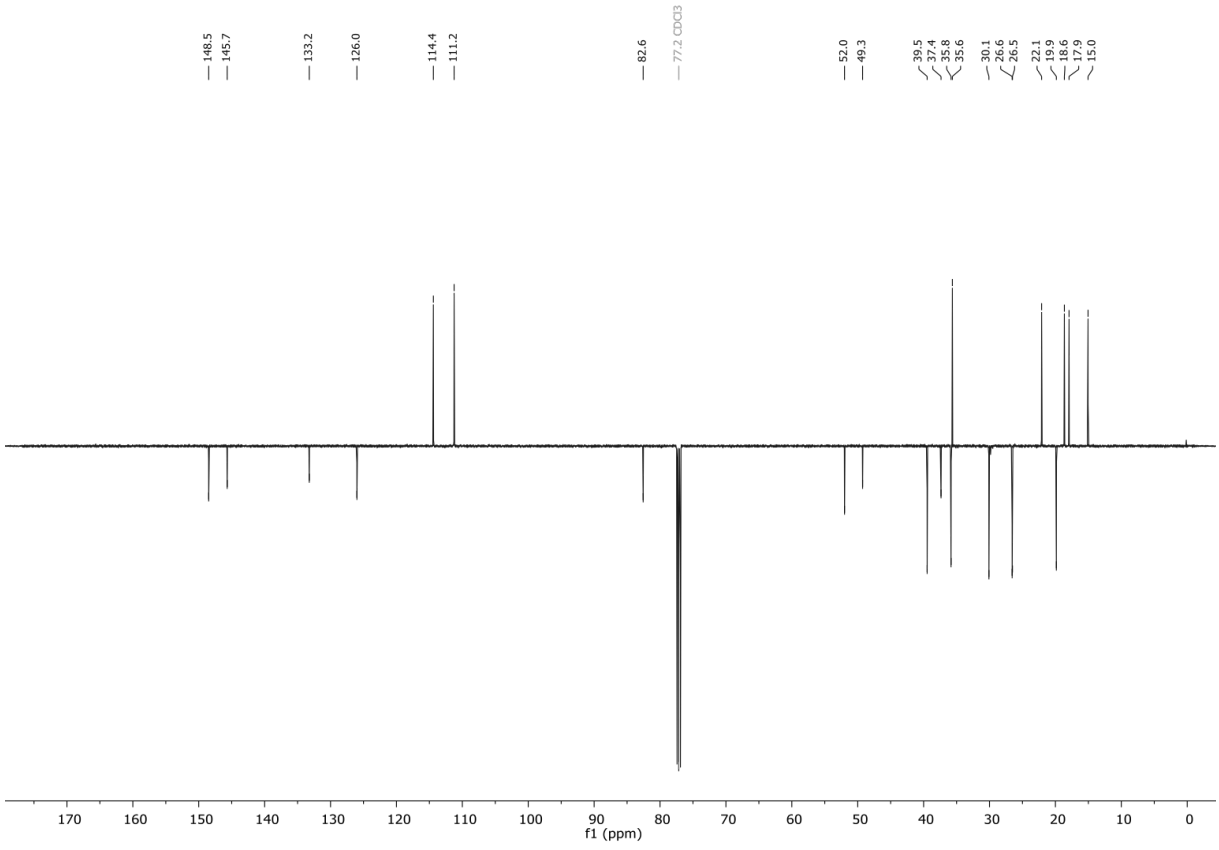
6.16. ^{1}H and ^{13}C NMR of Cyclopropane 30



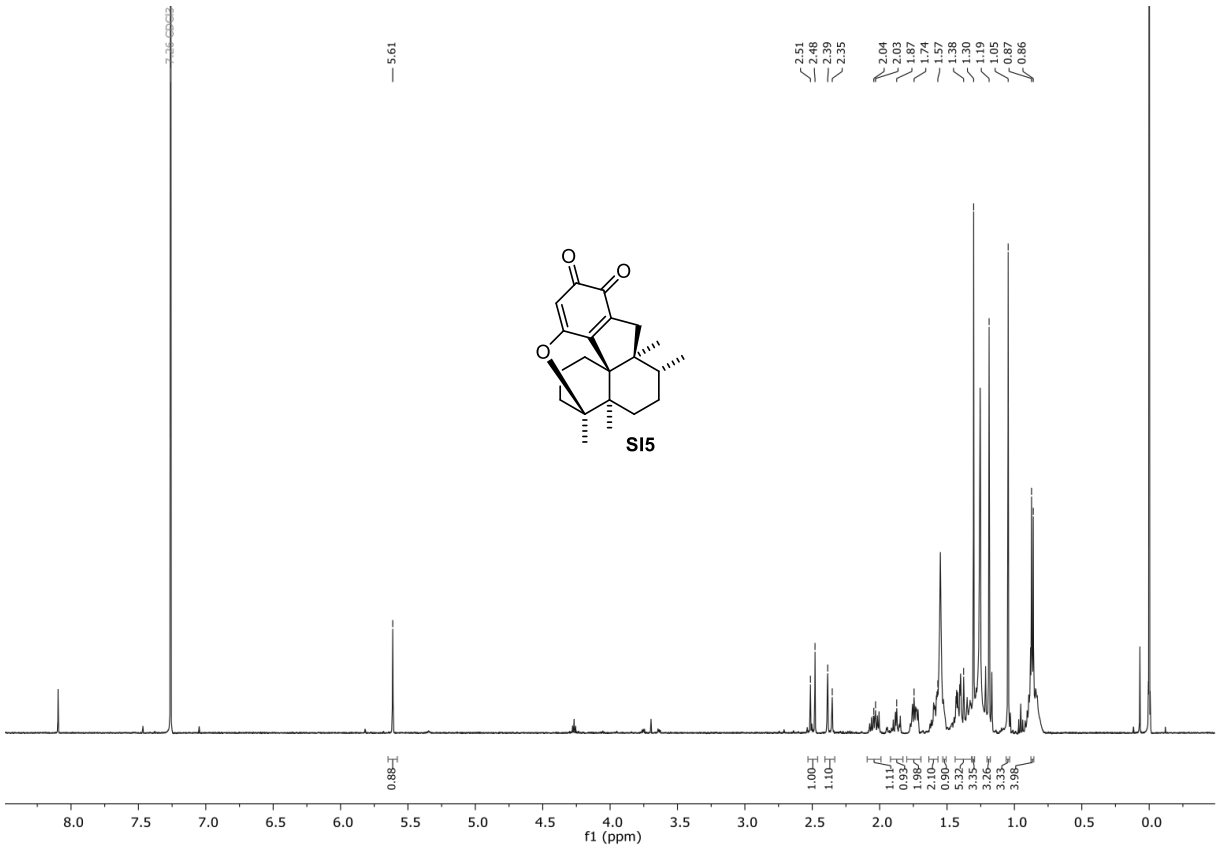


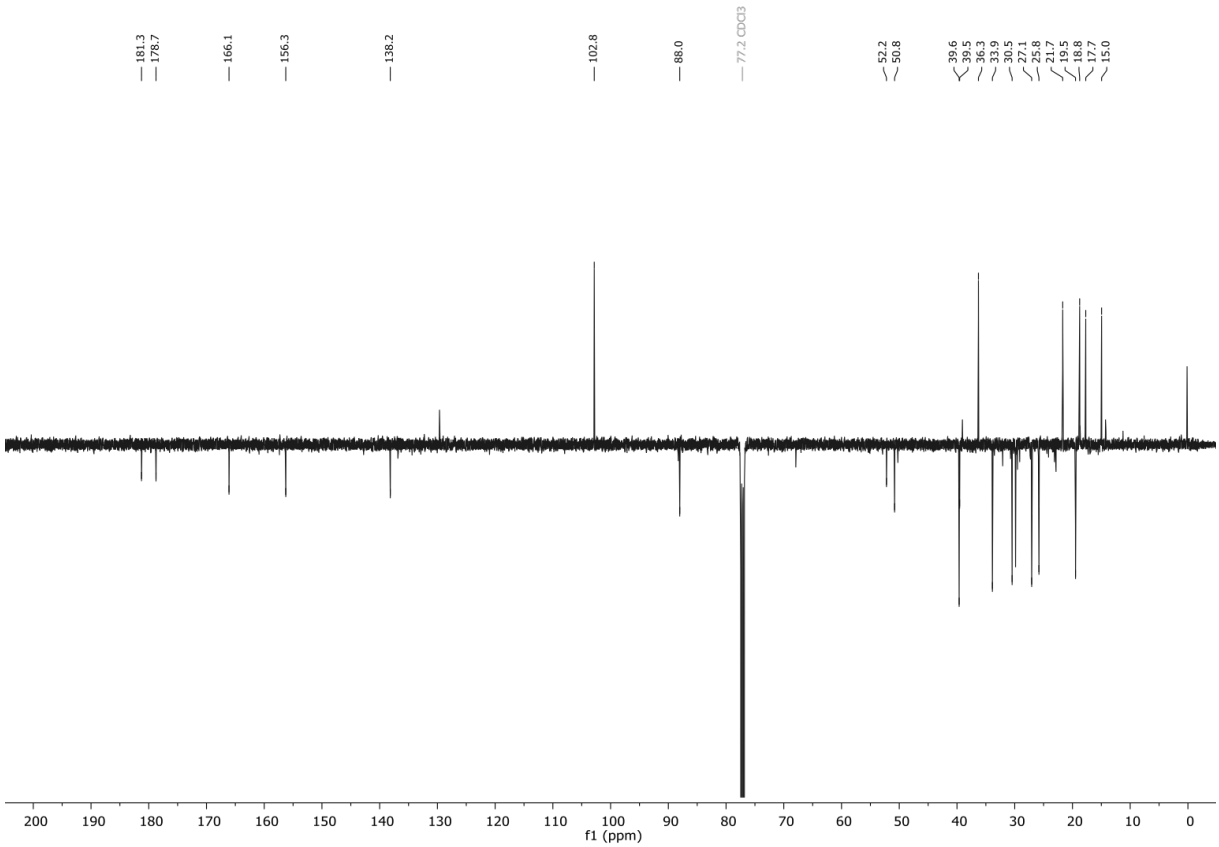
6.17. ^{1}H (full view and zoom in) and ^{13}C NMR of (–)-dysiherbol A (31)



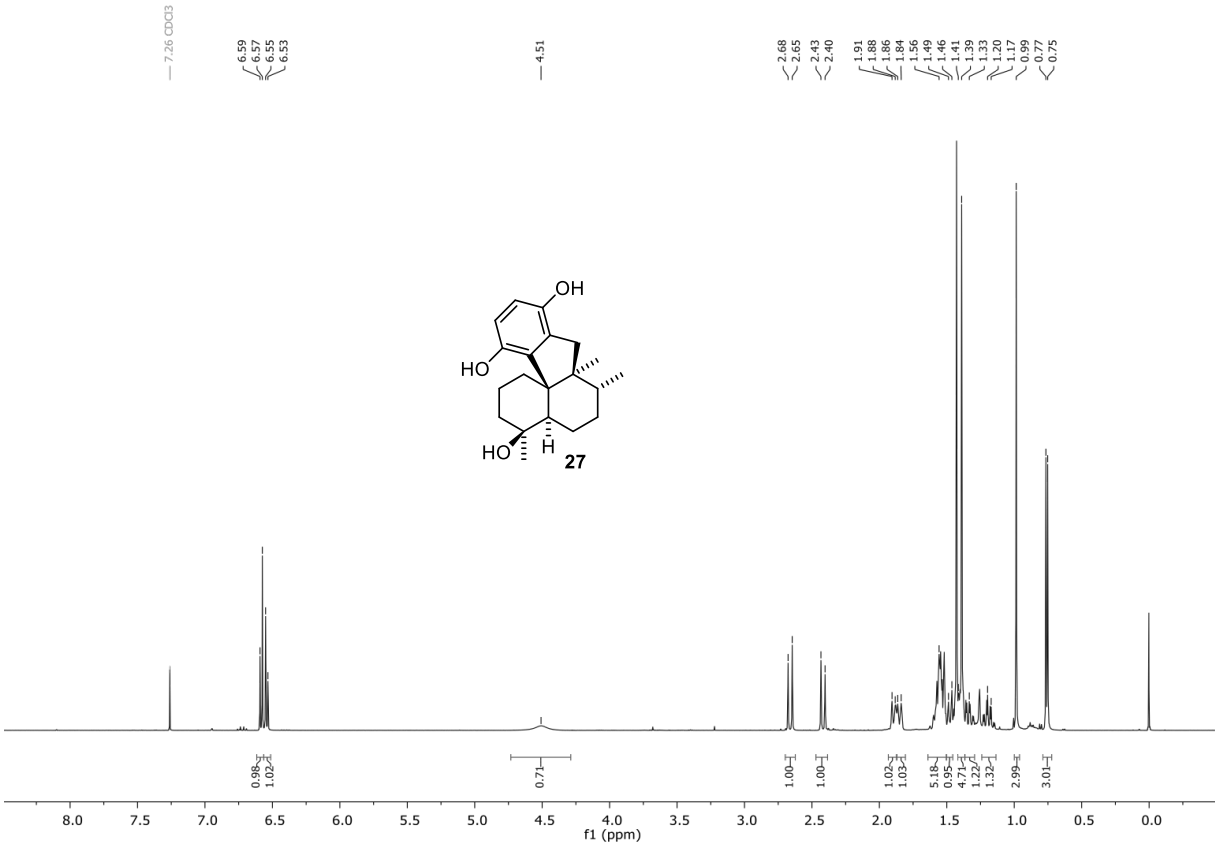

148.5
145.7
133.2
126.0
114.4
111.2
82.6
77.2 CDCl3
52.0
49.3
39.5
37.4
35.8
35.6
30.1
26.6
26.5
22.1
19.9
18.6
17.9
15.0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

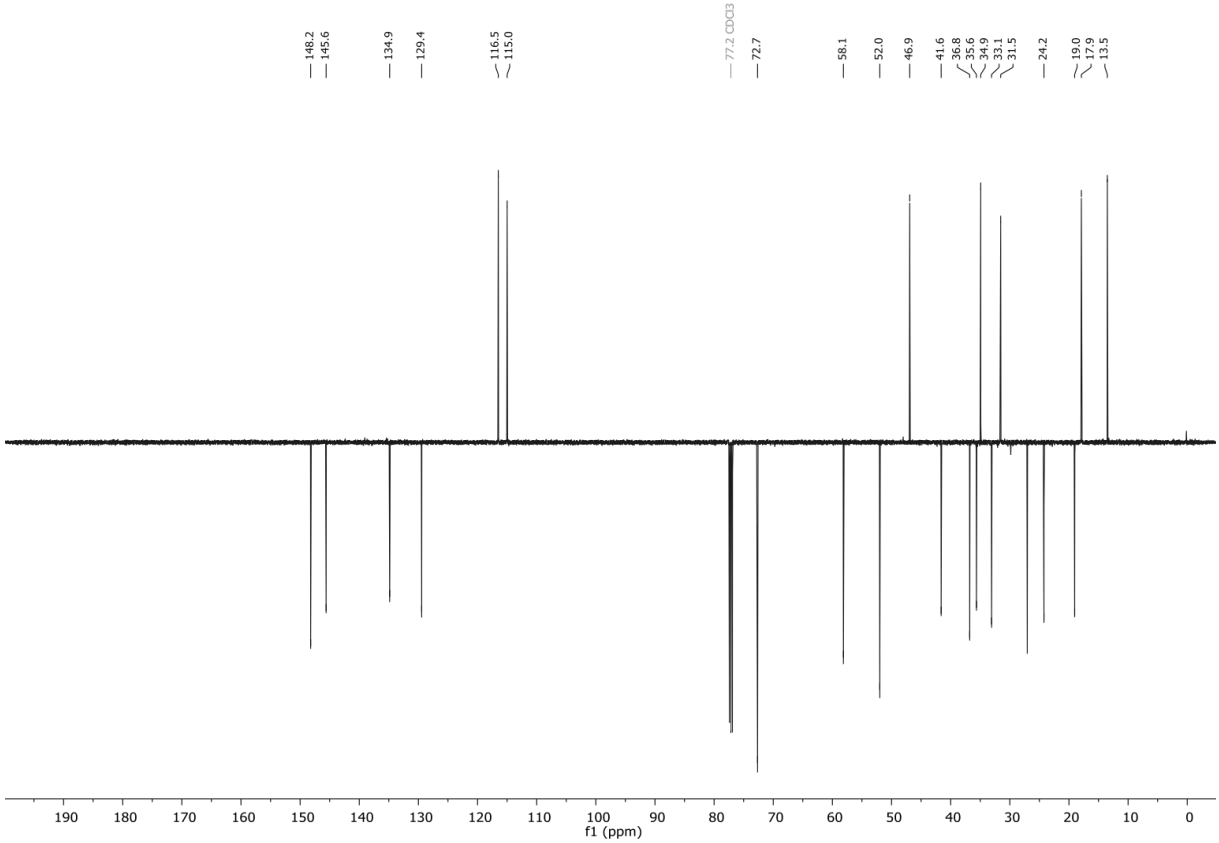
6.18. ^{1}H and ^{13}C NMR of Quinone SI5



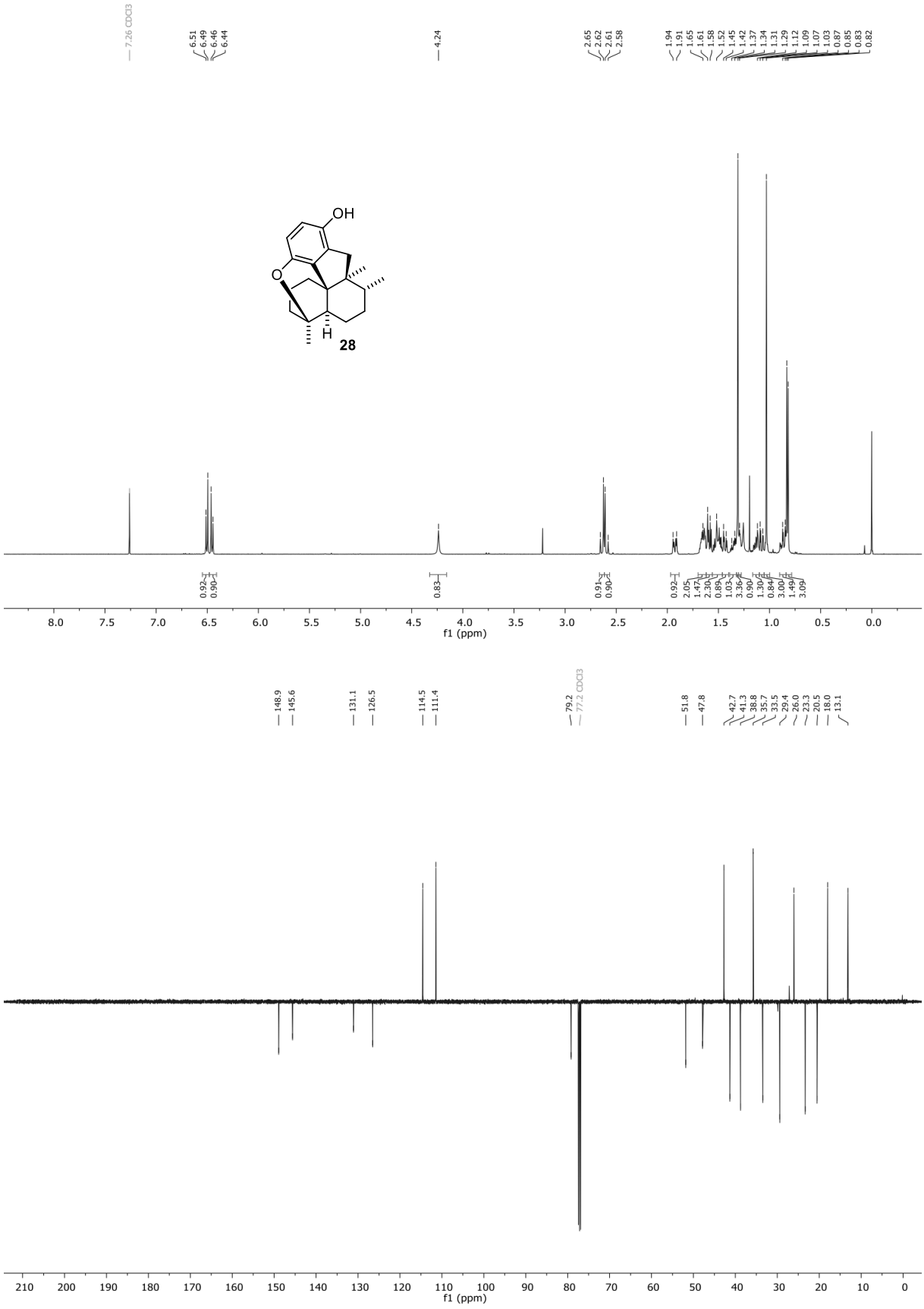


6.19. ^{1}H and ^{13}C NMR of Triol 27

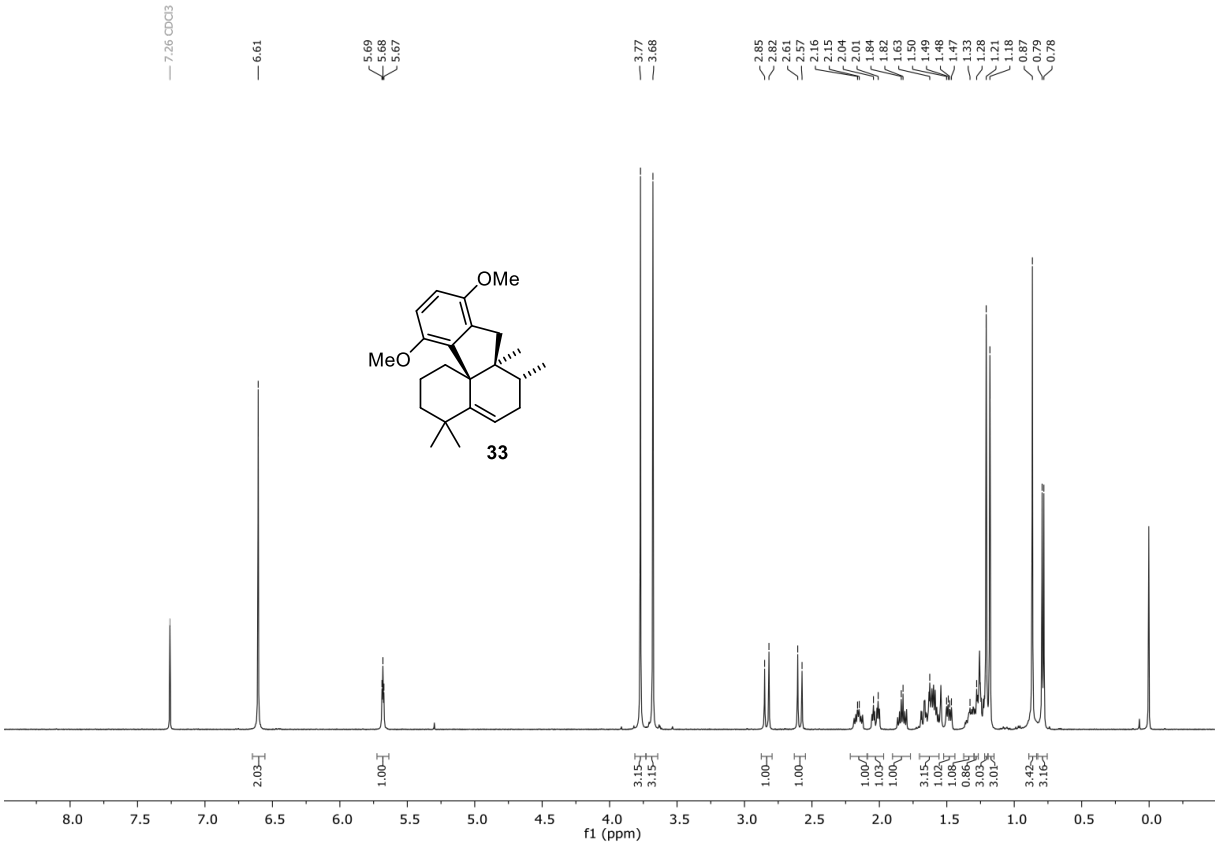


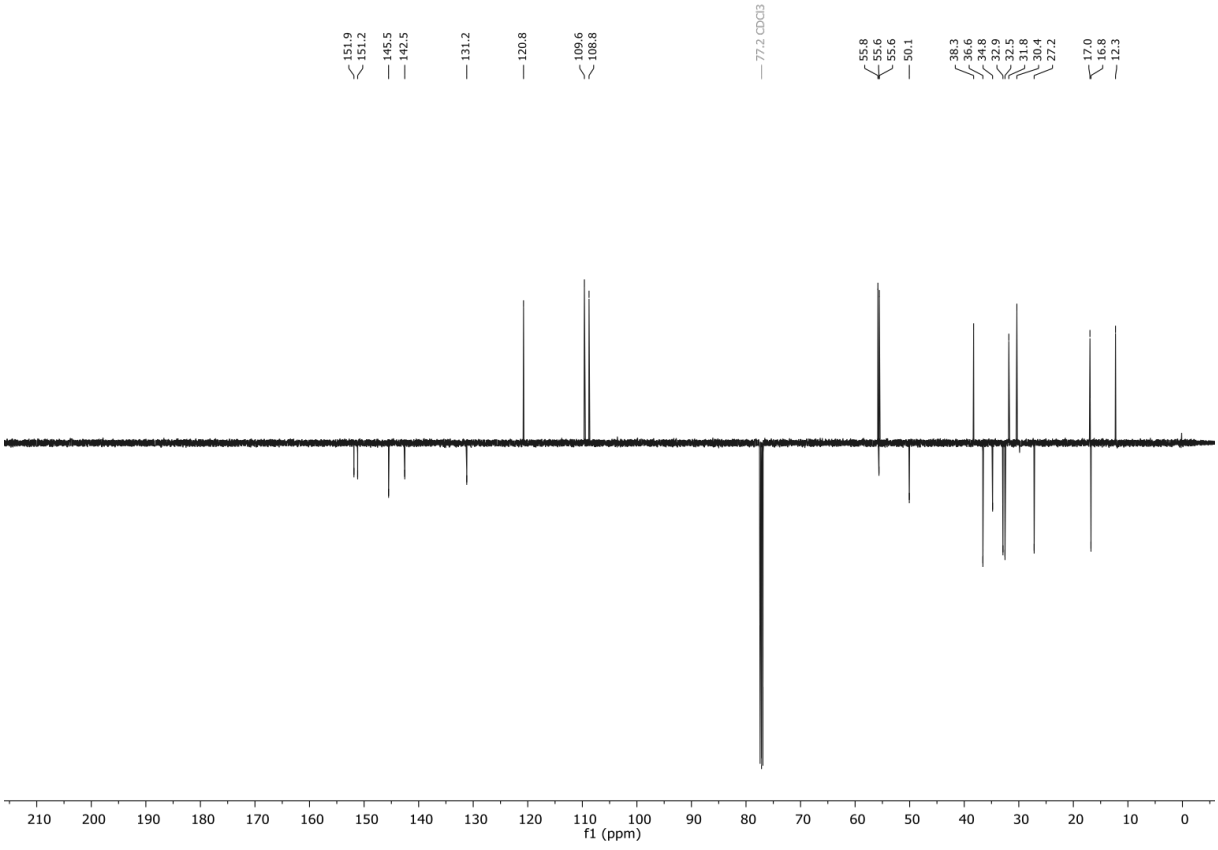


6.20. ^{1}H and ^{13}C NMR of nor-(–)-dysiherbol A 28

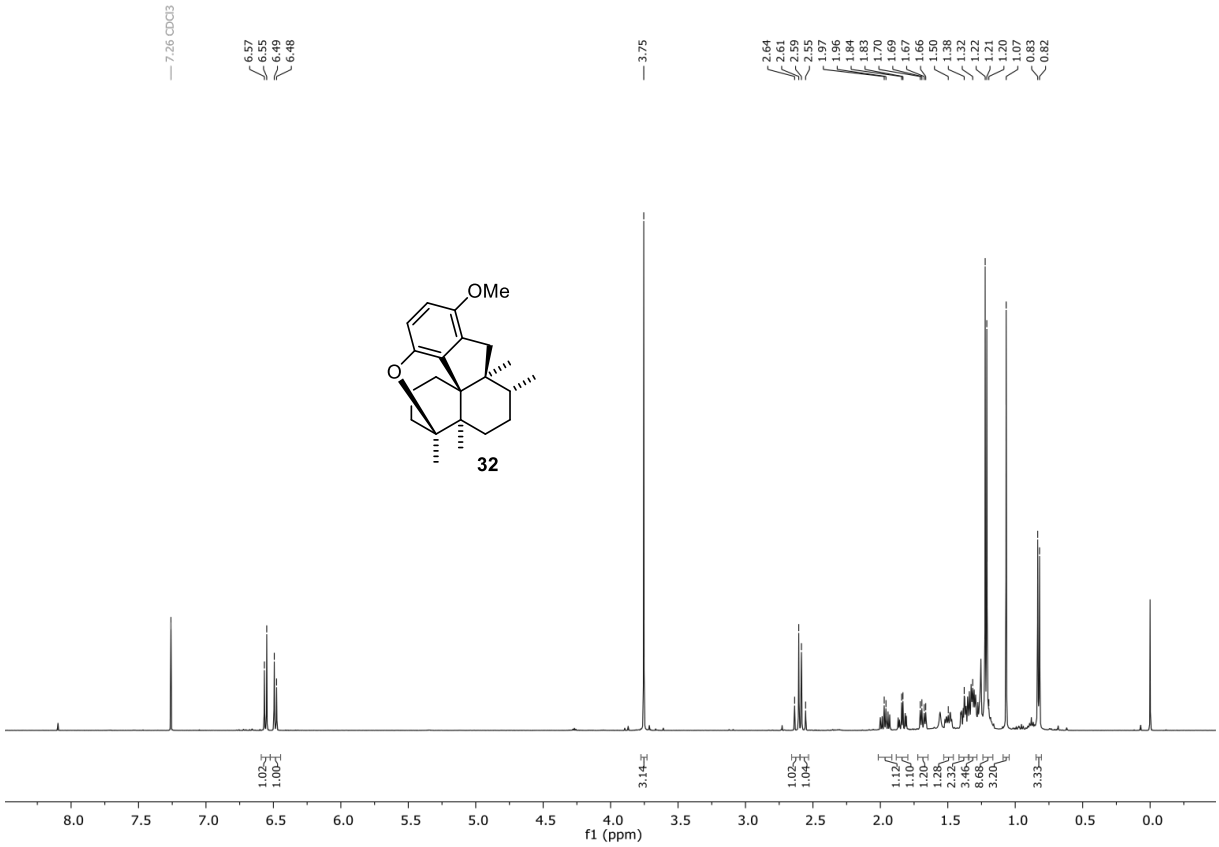


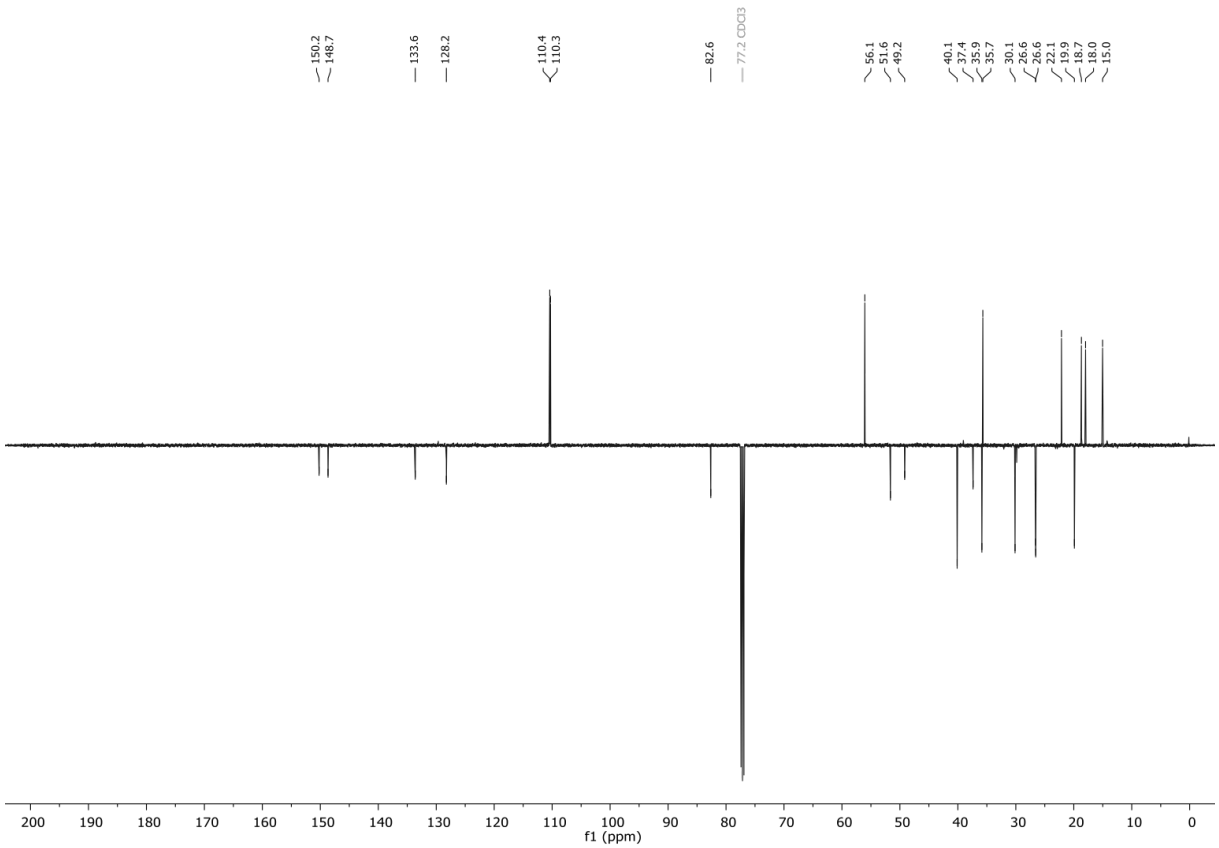
6.21. ^{1}H and ^{13}C NMR of Olefin 33



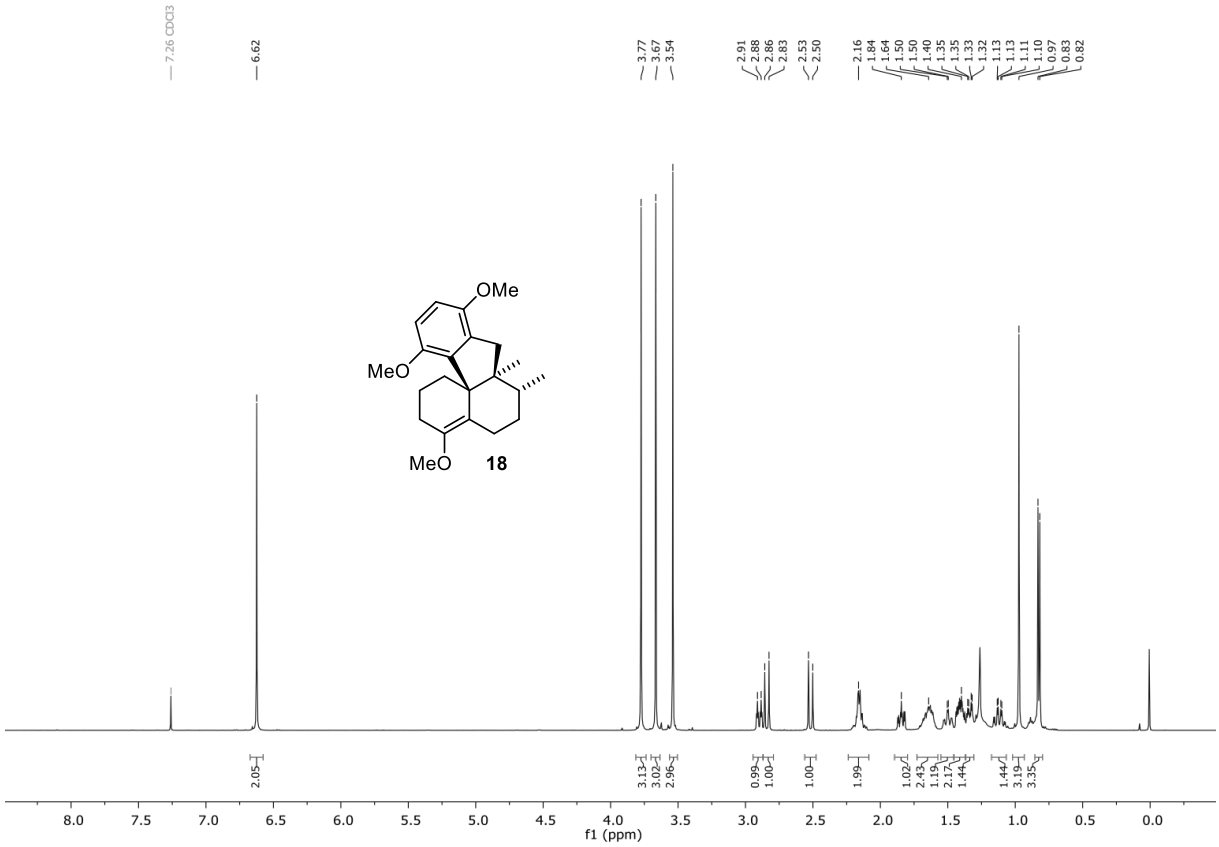


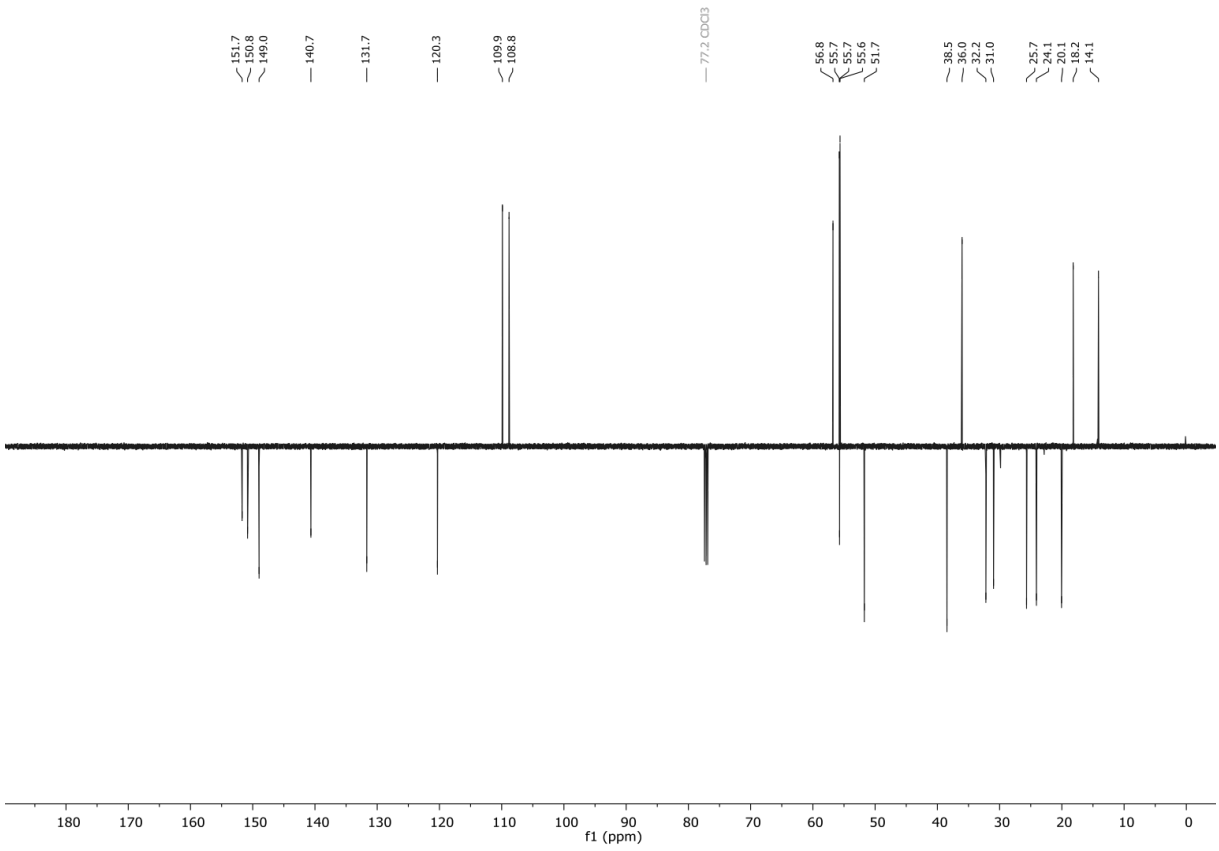
6.22. ^{1}H and ^{13}C NMR of (–)-dysiherbol A Methyl Ether (32)



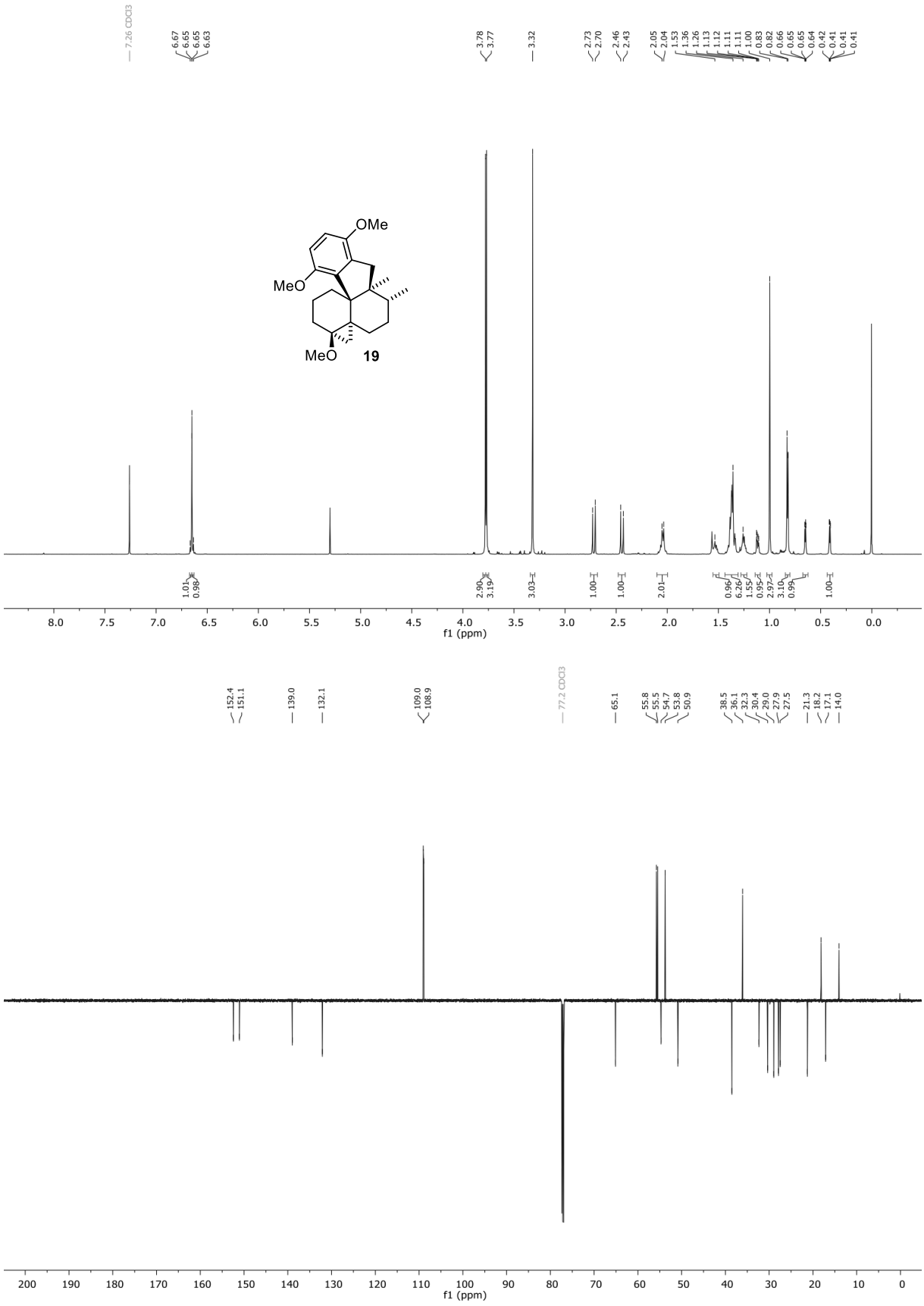


6.23. ^{1}H and ^{13}C NMR of Enol Ether 18

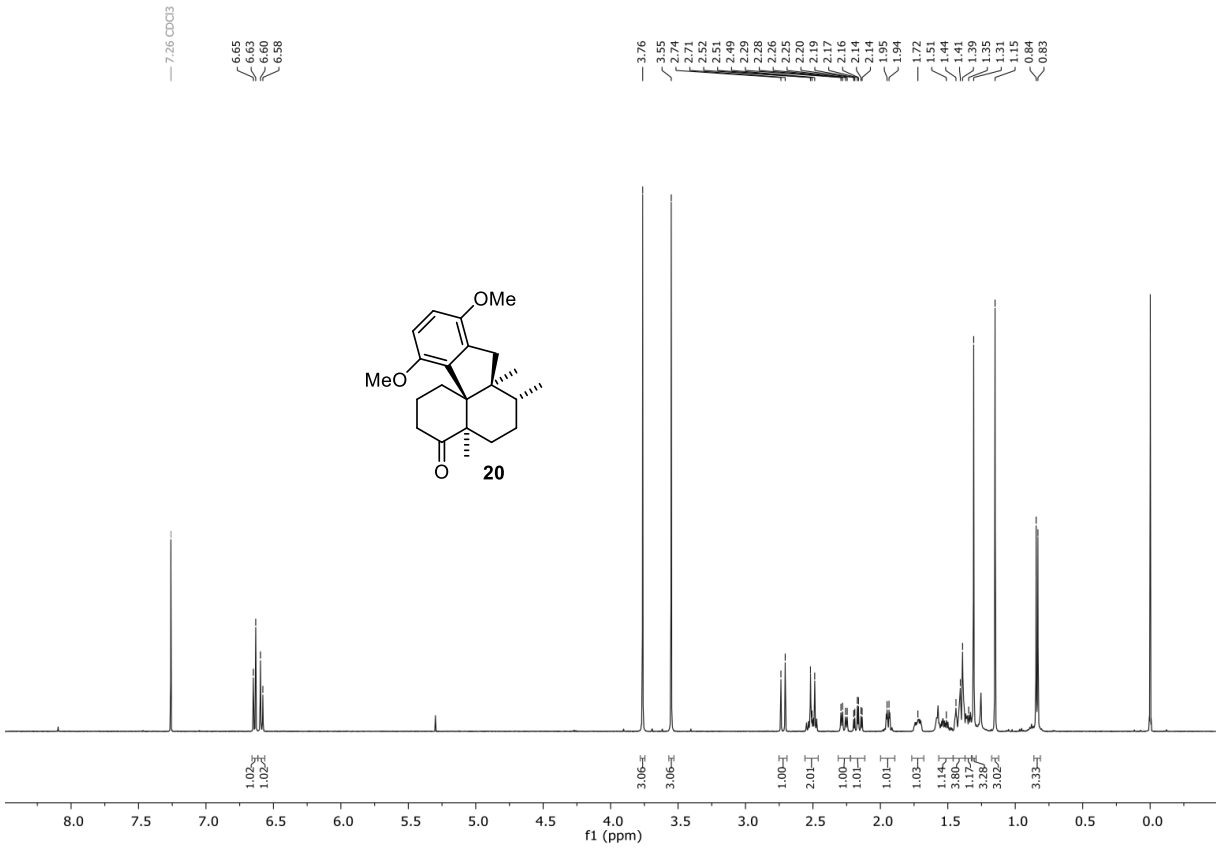


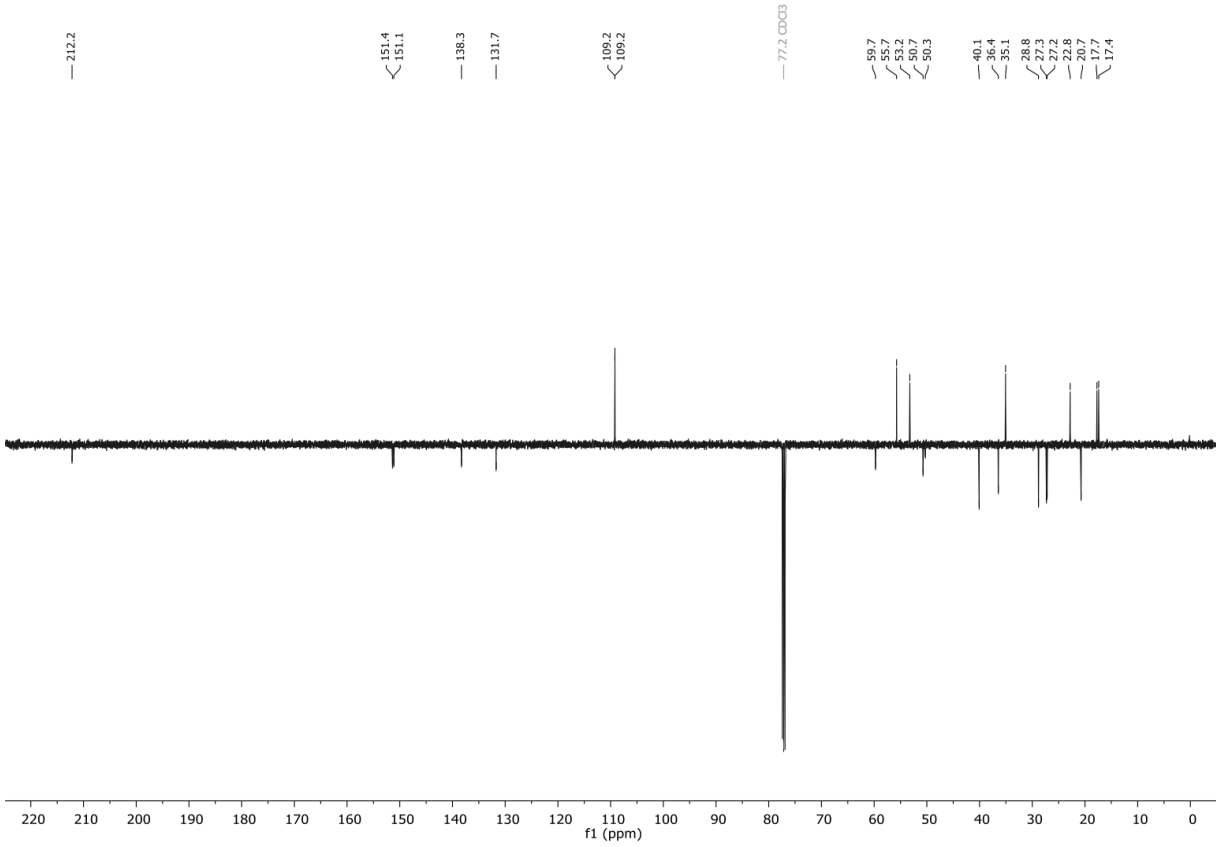


6.24. ^{1}H and ^{13}C NMR of Cyclopropane 19

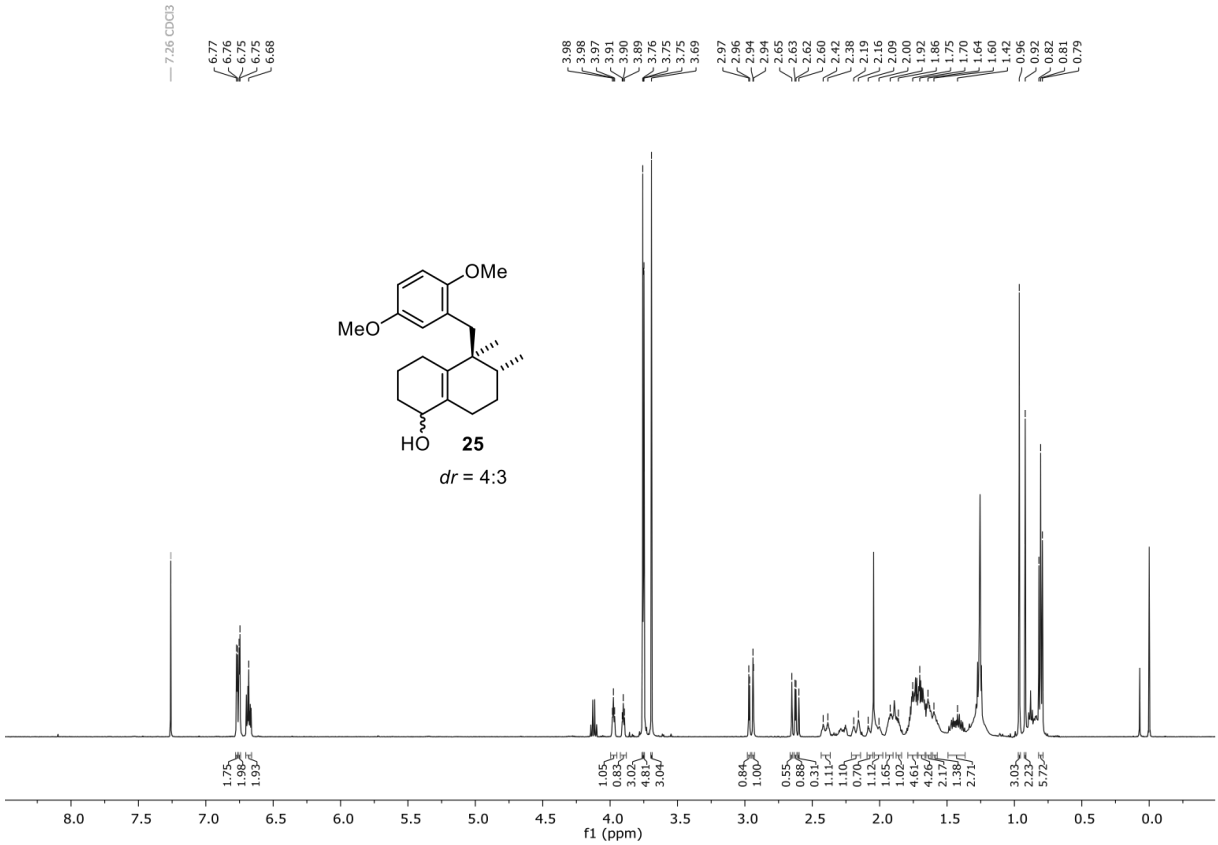


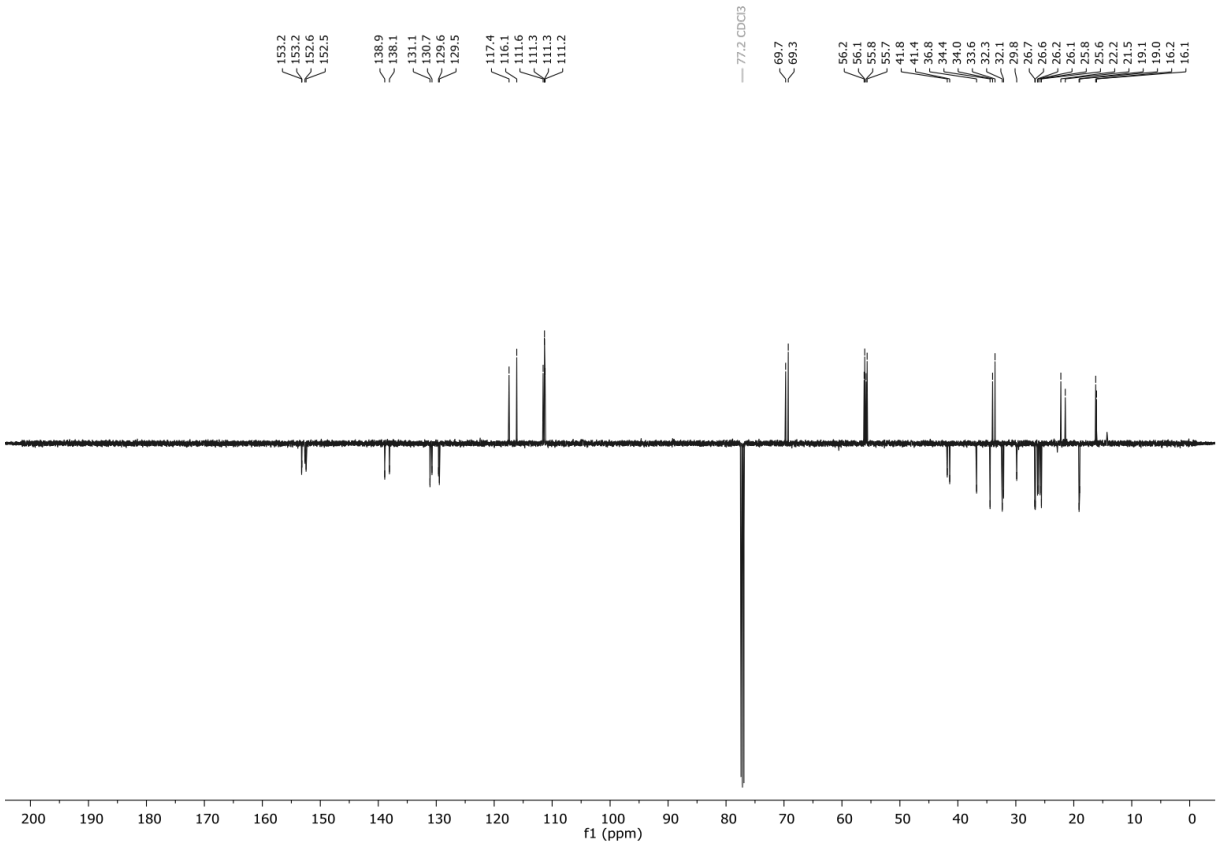
6.25. ^{1}H and ^{13}C NMR of Ketone 20





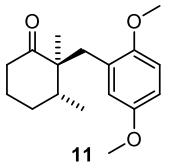
6.26. ^{1}H and ^{13}C NMR of Allylic Alcohol 25





7. X-ray Crystallographic Data

7.1. X-ray Crystallographic Data of (2*S*,3*R*)-2-(2,5-Dimethoxybenzyl)-2,3-dimethylcyclohexanone (11)



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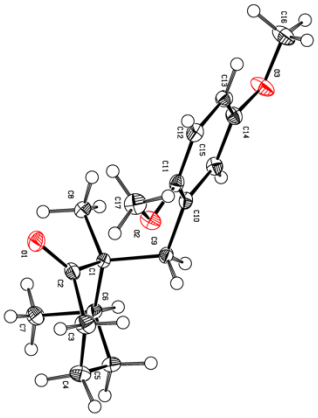
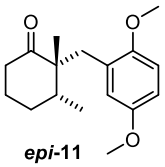


CCDC 2077905

Empirical formula	C17 H24 O3	
Formula weight	276.36	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.0055(3) Å	a= 90°.
	b = 12.6745(5) Å	b= 90°.
	c = 17.0091(6) Å	g = 90°.
Volume	1510.26(10) $Å^3$	
Z	4	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	0.650 mm^{-1}	
F(000)	600	
Crystal size	0.200 x 0.200 x 0.060 mm^3	
Theta range for data collection	4.350 to 72.086°.	
Index ranges	-8<=h<=8, -15<=k<=15, -20<=l<=20	
Reflections collected	45975	
Independent reflections	2980 [R(int) = 0.0348]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.6732	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2980 / 0 / 186	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0251, wR2 = 0.0667	
R indices (all data)	R1 = 0.0253, wR2 = 0.0668	
Absolute structure parameter	0.030(18)	
Extinction coefficient	0.0069(7)	
Largest diff. peak and hole	0.215 and -0.166 e.$Å^{-3}$	

7.2. X-ray Crystallographic Data of (2*R*,3*R*)-2-(2,5-Dimethoxybenzyl)-2,3-dimethylcyclohexanone (*epi*-11)



epi-11

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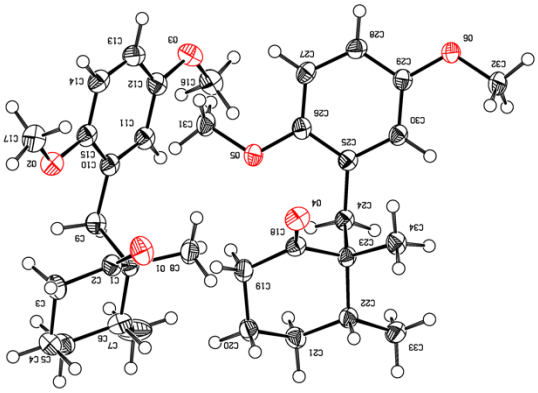
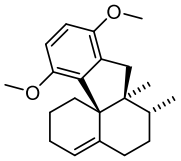


CCDC 2077912

Empirical formula	C17 H24 O3	
Formula weight	276.36	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.3458(9) Å	a= 103.635(5)°.
	b = 9.8517(11) Å	b= 91.317(5)°.
	c = 10.8463(12) Å	g = 90.511(5)°.
Volume	762.53(15) Å^3	
Z	2	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.644 mm^{-1}	
F(000)	300	
Crystal size	0.100 x 0.100 x 0.040 mm^3	
Theta range for data collection	4.195 to 72.398°.	
Index ranges	-9<=h<=9, -12<=k<=12, -13<=l<=13	
Reflections collected	23962	
Independent reflections	5683 [R(int) = 0.0763]	
Completeness to theta = 67.679°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5937	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5683 / 3 / 369	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1044	
R indices (all data)	R1 = 0.0409, wR2 = 0.1059	
Absolute structure parameter	0.11(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.197 and -0.242 e.Å^{-3}	

7.3. X-ray Crystallographic Data of Olefin 17



17

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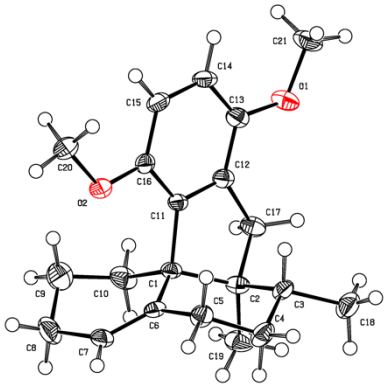
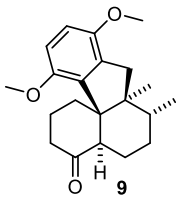


CCDC 2077903

Empirical formula	C21 H28 O2	
Formula weight	312.43	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_3$	
Unit cell dimensions	a = 13.3520(4) Å	a= 90°.
	b = 13.3520(4) Å	b= 90°.
	c = 17.1138(7) Å	g = 120°.
Volume	2642.22(19) $Å^3$	
Z	6	
Density (calculated)	1.178 Mg/m^3	
Absorption coefficient	0.571 mm^{-1}	
F(000)	1020	
Crystal size	0.200 x 0.100 x 0.070 mm^3	
Theta range for data collection	3.823 to 72.044°.	
Index ranges	-16<=h<=16, -16<=k<=16, -21<=l<=21	
Reflections collected	32133	
Independent reflections	3489 [R(int) = 0.0798]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5950	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3489 / 1 / 212	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1030	
R indices (all data)	R1 = 0.0490, wR2 = 0.1066	
Absolute structure parameter	0.17(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.487 and -0.212 $e.Å^{-3}$	

7.4. X-ray Crystallographic Data of Ketone 9



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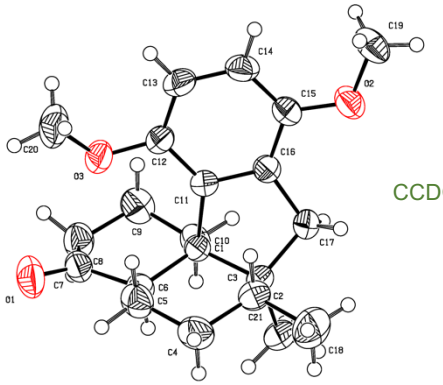
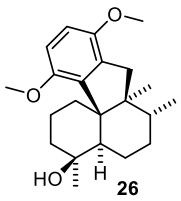


CCDC 2077914

Empirical formula	C21 H28 O3	
Formula weight	328.43	
Temperature	295(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.6575(2) Å	a= 90°.
	b = 11.2368(3) Å	b= 90°.
	c = 15.3203(4) Å	g = 90°.
Volume	1834.70(8) $Å^3$	
Z	4	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.614 mm^{-1}	
F(000)	712	
Crystal size	0.100 x 0.070 x 0.050 mm^3	
Theta range for data collection	4.881 to 72.208°.	
Index ranges	-13<=h<=11, -13<=k<=13, -18<=l<=18	
Reflections collected	40088	
Independent reflections	3616 [R(int) = 0.0534]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5789	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3616 / 0 / 221	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0886	
R indices (all data)	R1 = 0.0386, wR2 = 0.0980	
Absolute structure parameter	0.01(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.296 and -0.331 $e.Å^{-3}$	

7.5. X-ray Crystallographic Data of Alcohol 26



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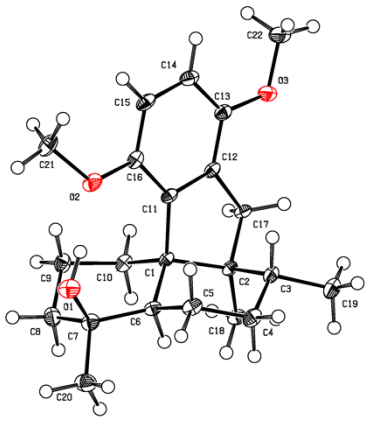
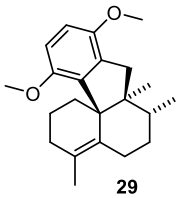


CCDC 2077910

Empirical formula	C22 H32 O3	
Formula weight	344.47	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.2318(4) Å	a= 90°.
	b = 7.4733(3) Å	b= 102.9009(13)°.
	c = 12.4504(4) Å	g = 90°.
Volume	927.99(6) $Å^3$	
Z	2	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	0.627 mm^{-1}	
F(000)	376	
Crystal size	0.200 x 0.200 x 0.100 mm^3	
Theta range for data collection	3.642 to 72.098°.	
Index ranges	-12<=h<=12, -8<=k<=9, -15<=l<=15	
Reflections collected	14198	
Independent reflections	3604 [R(int) = 0.0442]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.4307	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3604 / 1 / 239	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0832	
R indices (all data)	R1 = 0.0345, wR2 = 0.0846	
Absolute structure parameter	0.22(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.163 and -0.212 $e.Å^{-3}$	

7.6. X-ray Crystallographic Data of Olefin 29



29

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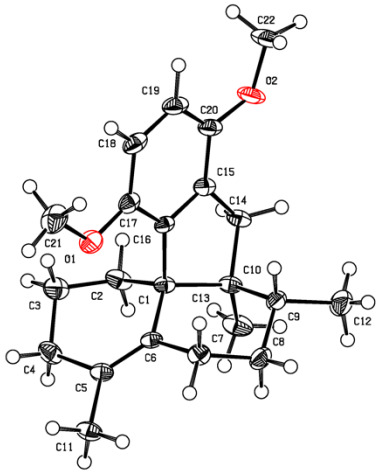
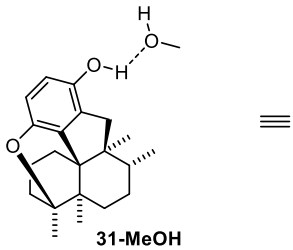
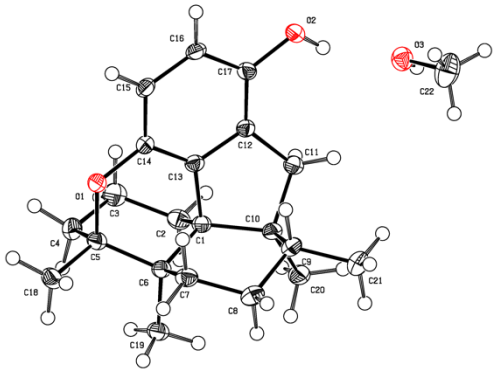


CCDC 2077904

Empirical formula	C22 H30 O2	
Formula weight	326.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_3$	
Unit cell dimensions	a = 13.5697(3) Å	a= 90°.
	b = 13.5697(3) Å	b= 90°.
	c = 17.4684(5) Å	g = 120°.
Volume	2785.63(15) $Å^3$	
Z	6	
Density (calculated)	1.168 Mg/m^3	
Absorption coefficient	0.561 mm^{-1}	
F(000)	1068	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	3.761 to 72.184°.	
Index ranges	-16<=h<=13, -16<=k<=16, -21<=l<=21	
Reflections collected	34153	
Independent reflections	3671 [R(int) = 0.0590]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5997	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3671 / 1 / 222	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0881	
R indices (all data)	R1 = 0.0394, wR2 = 0.0905	
Absolute structure parameter	0.12(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.205 and -0.181 $e.Å^{-3}$	

7.7. X-ray Crystallographic Data of (–)-dysiherbol A – MeOH complex (31-MeOH)

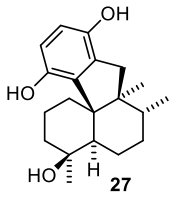




CCDC 2077913

Moiety formula	C21 H28 O2, C H4 O	
Formula weight	344.47	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.4931(5) Å	a= 90°.
	b = 12.8945(7) Å	b= 90°.
	c = 15.0694(9) Å	g = 90°.
Volume	1844.63(18) $Å^3$	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.631 mm^{-1}	
F(000)	752	
Crystal size	0.150 x 0.080 x 0.080 mm^3	
Theta range for data collection	4.513 to 72.088°.	
Index ranges	-11<=h<=11, -14<=k<=15, -18<=l<=18	
Reflections collected	108102	
Independent reflections	3629 [R(int) = 0.0575]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.6407	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3629 / 0 / 239	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0770	
R indices (all data)	R1 = 0.0289, wR2 = 0.0777	
Absolute structure parameter	0.04(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.235 and -0.128 $e.Å^{-3}$	

7.8. X-ray Crystallographic Data of Triol 27 (as a 4:3 complex with Et_2O)



27

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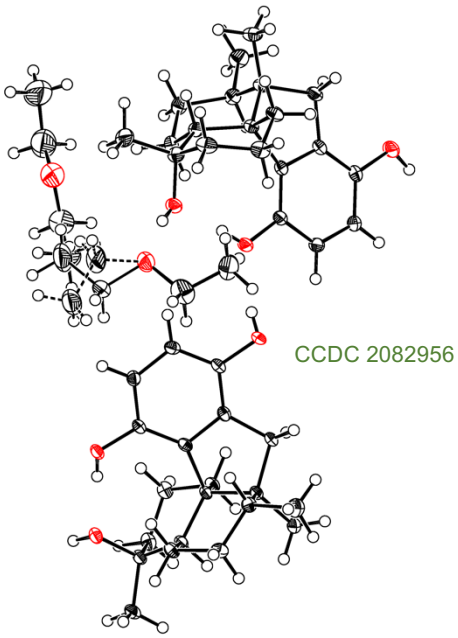
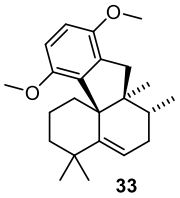


CCDC 2082956

Moiety formula	4(C20 H28 O3), 3(C4 H10 O)	
Formula weight	1488.05	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 34.7475(10) Å	a= 90°.
	b = 7.2447(2) Å	b= 125.6620(10)°.
	c = 20.4133(5) Å	g = 90°.
Volume	4175.1(2) $Å^3$	
Z	2	
Density (calculated)	1.184 Mg/m^3	
Absorption coefficient	0.619 mm^{-1}	
F(000)	1628	
Crystal size	0.150 x 0.150 x 0.020 mm^3	
Theta range for data collection	2.664 to 72.368°.	
Index ranges	-42<=h<=42, -8<=k<=8, -25<=l<=24	
Reflections collected	66221	
Independent reflections	8188 [R(int) = 0.0776]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5387	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8188 / 1 / 535	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1176	
R indices (all data)	R1 = 0.0468, wR2 = 0.1209	
Absolute structure parameter	-0.06(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.565 and -0.502 $e.Å^{-3}$	

7.9. X-ray Crystallographic Data of Olefin 33



33

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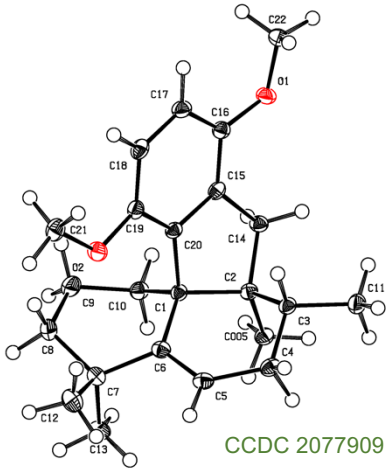
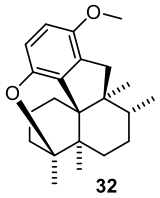


CCDC 2077909

Empirical formula	C23 H32 O2	
Formula weight	340.48	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.4580(2) Å	a= 90°.
	b = 13.6332(2) Å	b= 90°.
	c = 14.3762(2) Å	g = 90°.
Volume	1853.71(5) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.582 mm^{-1}	
F(000)	744	
Crystal size	0.300 x 0.080 x 0.080 mm^3	
Theta range for data collection	4.469 to 72.280°.	
Index ranges	-11<=h<=11, -16<=k<=16, -17<=l<=17	
Reflections collected	79725	
Independent reflections	3657 [R(int) = 0.0486]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.6367	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3657 / 0 / 232	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0677	
R indices (all data)	R1 = 0.0267, wR2 = 0.0681	
Absolute structure parameter	0.03(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.189 and -0.167 $e.Å^{-3}$	

7.10. X-ray Crystallographic Data of (–)-dysiherbol A Methyl Ether (32)



32

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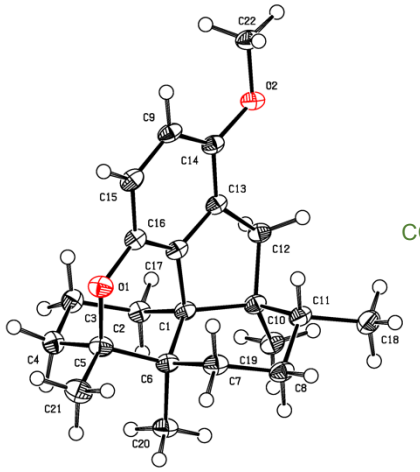
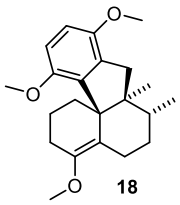


CCDC 2077906

Empirical formula	C22 H30 O2	
Formula weight	326.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.79900(10) Å	a= 90°.
	b = 15.8982(3) Å	b= 90°.
	c = 16.3340(3) Å	g = 90°.
Volume	1765.57(5) $Å^3$	
Z	4	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.590 mm^{-1}	
F(000)	712	
Crystal size	0.100 x 0.070 x 0.040 mm^3	
Theta range for data collection	3.880 to 72.071°.	
Index ranges	-8<=h<=8, -19<=k<=19, -20<=l<=20	
Reflections collected	75244	
Independent reflections	3480 [R(int) = 0.0654]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5811	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3480 / 0 / 222	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0273, wR2 = 0.0705	
R indices (all data)	R1 = 0.0280, wR2 = 0.0710	
Absolute structure parameter	0.10(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.160 and -0.140 $e.Å^{-3}$	

7.11. X-ray Crystallographic Data of Enol Ether 18



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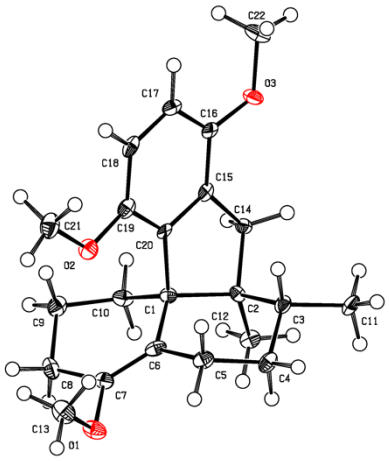
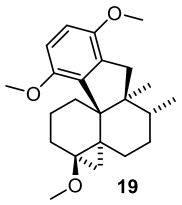


CCDC 2077907

Empirical formula	C22 H30 O3	
Formula weight	342.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.9440(3) Å	a= 90°.
	b = 11.1250(3) Å	b= 90°.
	c = 16.6670(5) Å	g = 90°.
Volume	1843.82(9) $Å^3$	
Z	4	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.631 mm^{-1}	
F(000)	744	
Crystal size	0.100 x 0.020 x 0.010 mm^3	
Theta range for data collection	4.779 to 72.276°.	
Index ranges	-12<=h<=12, -13<=k<=13, -20<=l<=20	
Reflections collected	31542	
Independent reflections	3629 [R(int) = 0.1326]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3629 / 0 / 231	
Goodness-of-fit on F^2	1.226	
Final R indices [I>2sigma(I)]	R1 = 0.0664, wR2 = 0.1171	
R indices (all data)	R1 = 0.0758, wR2 = 0.1202	
Absolute structure parameter	0.21(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.310 and -0.263 $e.Å^{-3}$	

7.12. X-ray Crystallographic Data of Cyclopropane 19



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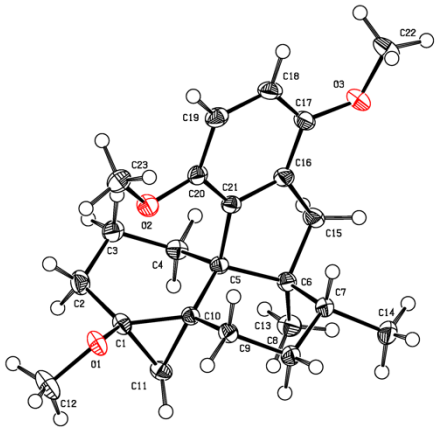
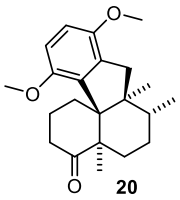


CCDC 2077911

Empirical formula	C23 H32 O3	
Formula weight	356.48	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.8315(3) Å	a= 90°.
	b = 7.4287(2) Å	b= 90.3890(10)°.
	c = 12.4592(4) Å	g = 90°.
Volume	1002.49(5) $Å^3$	
Z	2	
Density (calculated)	1.181 Mg/m^3	
Absorption coefficient	0.599 mm^{-1}	
F(000)	388	
Crystal size	0.150 x 0.080 x 0.040 mm^3	
Theta range for data collection	3.547 to 72.041°.	
Index ranges	-13<=h<=13, -9<=k<=9, -15<=l<=14	
Reflections collected	21086	
Independent reflections	3920 [R(int) = 0.0486]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5108	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3920 / 1 / 240	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0747	
R indices (all data)	R1 = 0.0304, wR2 = 0.0750	
Absolute structure parameter	0.09(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.162 and -0.143 $e.Å^{-3}$	

7.13. X-ray Crystallographic Data of Ketone 20



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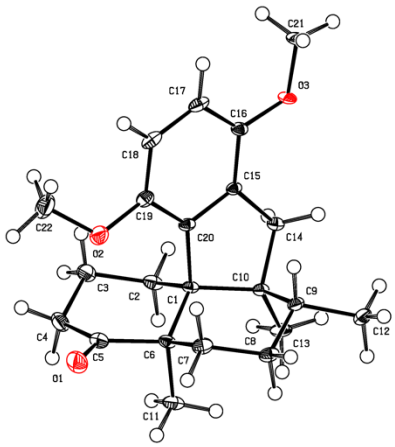
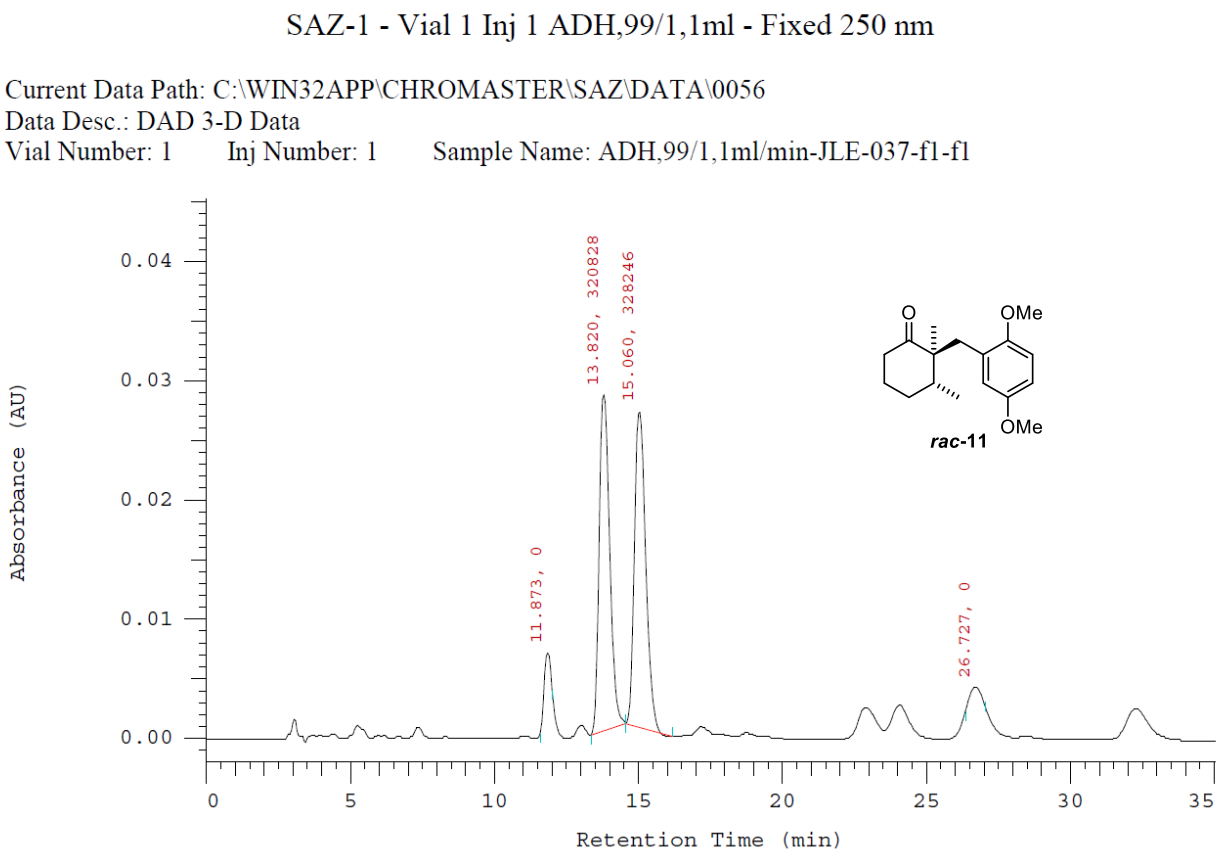


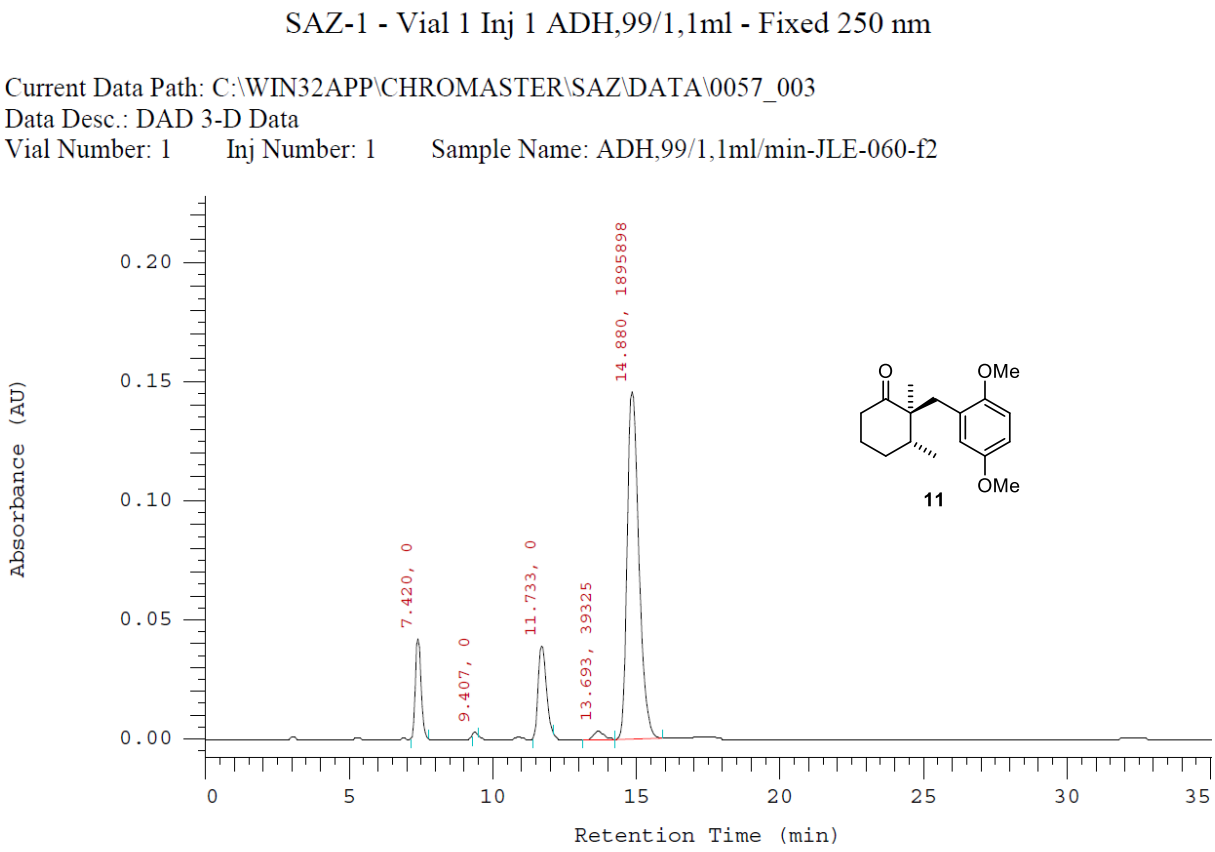
CCDC 2077908

Empirical formula	C22 H30 O3	
Formula weight	342.46	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.3013(4) Å	a= 90°.
	b = 12.7878(5) Å	b= 97.956(2)°.
	c = 15.5285(7) Å	g = 90°.
Volume	1829.23(13) $Å^3$	
Z	4	
Density (calculated)	1.244 Mg/m^3	
Absorption coefficient	0.636 mm^{-1}	
F(000)	744	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.873 to 72.359°.	
Index ranges	-10<=h<=11, -15<=k<=15, -18<=l<=19	
Reflections collected	21485	
Independent reflections	7042 [R(int) = 0.0482]	
Completeness to theta = 67.679°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5126	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7042 / 1 / 461	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0870	
R indices (all data)	R1 = 0.0383, wR2 = 0.0889	
Absolute structure parameter	0.05(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.180 and -0.257 $e.Å^{-3}$	

8. Chiral HPLC Analysis of (2*S*,3*R*)-2-(2,5-Dimethoxybenzyl)-2,3-dimethylcyclohexanone (11)



HPLC chromatogram of a racemic sample of ketone **11** on chiral stationary phase.
Column: CHIRALPAK AD-H
Column temperature: 18°C
Solvent: *n*-hexane/2-propanol 99:1
Flow: 1 mL/min
Detection: 250 nm



HPLC chromatogram of an enantioenriched sample of ketone **11** on chiral stationary phase.
Column: CHIRALPAK AD-H
Column temperature: 18°C
Solvent: *n*-hexane/2-propanol 99:1
Flow: 1 mL/min
Detection: 250 nm
Enantiomeric excess: 96%

9. References

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