Electronic Supplementary Information

Divergent Total Synthesis of the Revised Structures of Marine Anti-Cancer Meroterpenoids (+)-Dysiherbols A–E

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I. General Methods

Dry solvents benzene, dichloromethane (CH_2Cl_2), 1,2-dichloroethane (DCE), dimethylformamide (DMF), dioxane, ethanol (EtOH), ethyl acetate (EtOAc), methanol (MeOH), and tetrahydrofuran (THF) were purchased from commercial suppliers and stored under argon. **Reagents** were purchased at the highest commercial quality and used without further purification, unless otherwise noted.

All reactions were carried out under an argon atmosphere with dry solvent under anhydrous conditions, unless otherwise noted. **Reactions** were monitored by thin layer chromatography (TLC) carried out on 0.25 mm Huanghai silica gel plates (HSGF254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid (PMA), an aqueous solution of cerium sulfate ($Ce(SO_4)_2$) or a basic aqueous solution of potassium permanganate ($KMnO_4$) as developing agents. Huanghai silica gel (200–300 mesh) was used for flash column chromatography (FCC). **Yields** refer to chromatographically and spectroscopically (^{1}H NMR) homogenous material, unless otherwise stated.

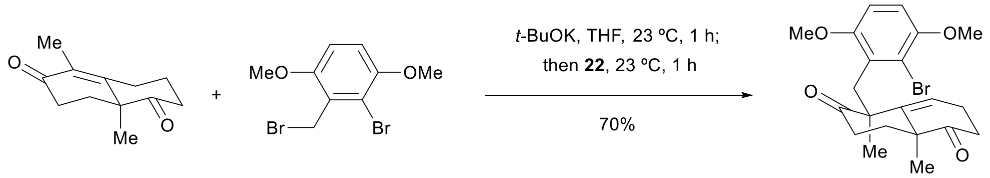
Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 or Bruker AV 500 instrument and calibrated using residual undeuterated solvent ($CDCl_3$, $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; C_6D_6, $\delta_H = 7.16$ ppm, $\delta_C = 128.06$ ppm; CD_3OD, $\delta_H = 3.31$ ppm, $\delta_C = 49.00$ ppm; pyridine-d_5, $\delta_H = 8.74$ ppm, $\delta_C = 150.35$ ppm) as an internal reference, unless otherwise noted. The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. **Melting points (M.P.)** were recorded on a Shanghai YiCe WRX-4 melting-point apparatus with microscope. **Infrared (IR)** spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. **High resolution mass spectrometry (HRMS)** spectra were recorded on Varian 7.0 T FTMS mass spectrometer using ESI (electrospray ionization). **Optical rotations** were recorded on an InsMark IP120 polarimeter. **X-ray diffractions** were recorded on a Rigaku XtalAB PRO MM007 DW apparatus. **Chiral high performance liquid chromatography (HPLC)** analyses were recorded on a Shimadzu LC 20A apparatus. **Experimental ECD** spectra were recorded on a BioLogic MOS-450 apparatus.

ECD Calculations: Systematic conformational searches of each compound were applied using MOE software, and the appropriate conformation was subjected to geometry optimizations and re-optimizations, which were performed at the B3LYP/6-31+G(d, p) level using Gaussian 09. TDDFT calculations for the optimized conformers were conducted at the CAM-B3LYP/SVP level with a

CPCM solvent model in MeOH. The extract of the calculated ECD curves was finished by SpecDis 1.62 software, and a half-bandwidth of ~0.4 eV was used to simulate the calculated ECD spectra of different conformers. Boltzmann distribution was used to weigh the ECD curves of each compound after UV correction.

II. Experimental Procedures and Physical Data of Compounds

Preparation of diketone 17:



21 22 17

To a stirred solution of Wieland–Miescher ketone derivative (+)-**21** (1.49 g, 7.74 mmol, 1.2 equiv.) in THF (10 mL) was added *t*-BuOK (7.10 mL, 7.10 mmol, 1.0 M in THF, 1.1 equiv.) at 0 °C. The resulting mixture was warmed to 23 °C and allowed to stir at this temperature for 1 h. A solution of benzyl bromide **22** (2.00 g, 6.45 mmol, 1.0 equiv.) in THF (2 mL) was added to the above solution at 23 °C. Then the resulting solution was allowed to stir at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 10:1→8:1) to give diketone **17** (1.90 g, 4.52 mmol, 70%).

Characterization of diketone 17:

Physical state: white solid;

M.P.: 151–153 °C;

TLC: $R_f = 0.39$ (silica gel, petroleum ether:EtOAc = 2:1);

Optical rotation: $[\alpha]_D^{23} = +88.4$ ($c = 1.0$, $CHCl_3$);

FT-IR (KBr): ν_{max} = 2996, 2884, 2833, 1867, 1721, 1476, 1435, 1261, 1110, 1062, 1030, 820 cm^{-1};

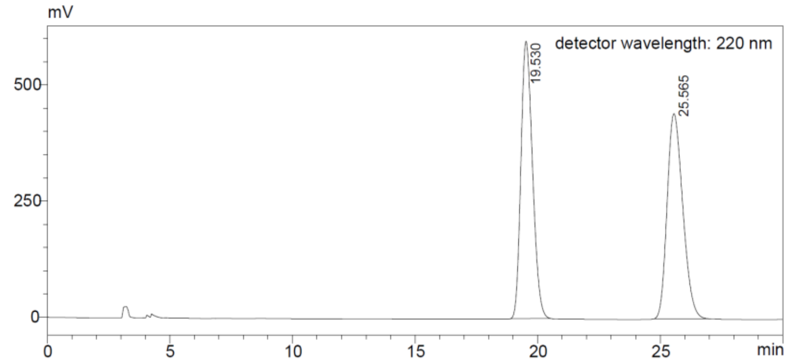
^{1}H NMR (400 MHz, C_6D_6): δ = 6.32 (d, *J* = 9.0 Hz, 1H), 6.27 (d, *J* = 9.0 Hz, 1H), 5.60 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.31 (s, 3H), 3.26 (d, *J* = 13.5 Hz, 1H), 3.18 (s, 3H), 2.74 (ddd, *J* = 17.8, 8.0, 1.8 Hz, 1H), 2.48–2.23 (m, 3H), 2.18–2.04 (m, 2H), 2.06–1.84 (m, 2H), 1.45 (s, 3H), 0.89 (s, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 211.8, 210.6, 152.9, 150.9, 148.6, 128.2, 122.2, 118.4, 110.6, 109.4, 56.2, 54.9, 53.8, 47.1, 40.9, 34.4, 33.8, 27.5, 24.3, 23.6, 23.2 ppm;

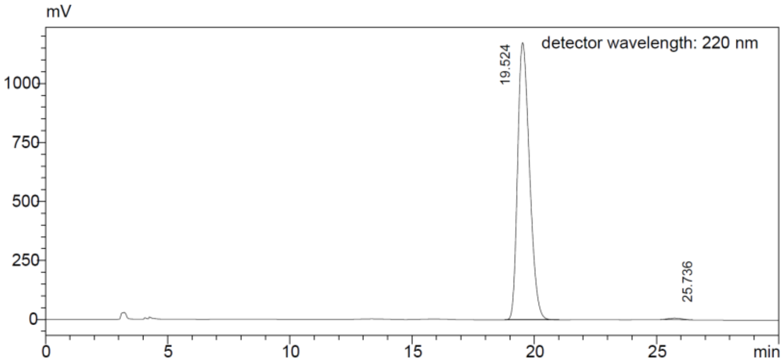
HRMS (ESI-TOF): calcd for $C_{21}H_{26}BrO_4^+$ $[M+H]^+$ 421.1009, found 421.1008.

Chiral HPLC traces:

Racemate



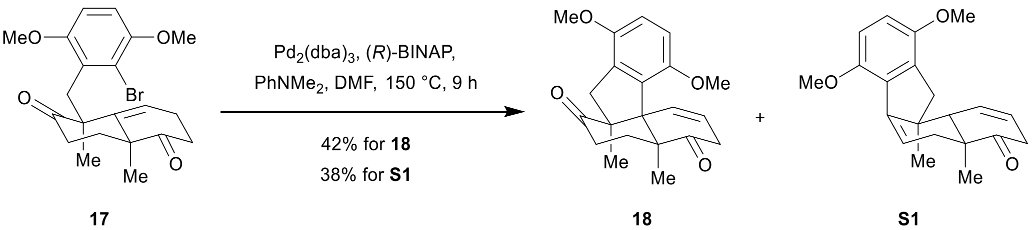
Sample of ketone **17**



Sample	Peak area (t = 19.3 min)	Peak area (t = 25.8 min)	ee[a]
Racemate	50.0%	50.0%	0%
Sample of ketone **17**	99.4%	0.6%	98.8%

[a] The ee values were determined by Chiral HPLC (column: CHIRALCEL® OZH0CE-PF10, φ0.46 cm × 25.0 cm × 5 μm), *n*-hexane:*i*-PrOH = 90:10, temperature: 35 °C, flow rate: 1 mL/min, detector wavelength: 220 nm).

Preparation of tetracyclic diketone 18 and tetracyclic diene S1[1]:



To a stirred solution of diketone **17** (50.3 mg, 119 μmol, 1.0 equiv.), $Pd_2(dba)_3$ (54.5 mg, 59.5 μmol, 0.5 equiv.), and (*R*)-BINAP (74.1 mg, 119 μmol, 1.0 equiv.) in DMF (5 mL) was added $PhNMe_2$ (2.5 mL) at 23 °C. The resulting mixture was heated to 150 °C and stirred at this temperature for 9 h. The reaction mixture was diluted with 3 M HCl (50 mL) and then extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 30:1→5:1) to give tetracyclic diketone **18** (17.1 mg, 50.1 μmol, 42%) and tetracyclic diene **S1** (14.7 mg, 45.4 μmol, 38%).

Characterization of tetracyclic diketone 18:

Physical state: white solid;

M.P.: 193–195 °C;

TLC: R_f = 0.46 (silica gel, petroleum ether:EtOAc = 2:1);

Optical rotation: $[\alpha]_D^{23}$ = +350 (c = 1.0, $CHCl_3$);

FT-IR (KBr): ν_{max} = 3032, 2962, 2935, 2833, 1692, 1496, 1452, 1263, 1144, 1097, 1066, 984, 954, 798, 720, 691 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.31 (d, J = 8.7 Hz, 1H), 6.25 (d, J = 8.7 Hz, 1H), 5.40 (dt, J = 10.3, 2.1 Hz, 1H), 5.32 (dt, J = 10.3, 3.3 Hz, 1H), 3.39 (d, J = 17.3 Hz, 1H), 3.31 (s, 3H), 3.23 (s, 3H), 2.88–2.78 (m, 1H), 2.82–2.77 (m, 1H), 2.71 (dt, J = 22.3, 2.7 Hz, 1H), 2.24 (ddd, J = 15.7, 9.6, 4.3 Hz, 1H), 2.10–1.87 (m, 3H), 1.43 (s, 3H), 0.96 (s, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 215.1, 206.3, 150.2, 150.2, 135.3, 130.5, 127.3, 122.4, 109.9, 109.7, 61.7, 58.8, 55.1, 53.4, 49.0, 43.1, 37.3, 34.6, 26.5, 22.1, 21.4 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{25}O_4^+$ $[M+H]^+$ 341.1747, found 341.1743.

Characterization of tetracyclic diene S1:

Physical state: colorless oil;

TLC: R_f = 0.41 (silica gel, petroleum ether:EtOAc = 5:1);

Optical rotation: $[\alpha]_D^{23}$ = +112 (c = 1.0, $CHCl_3$);

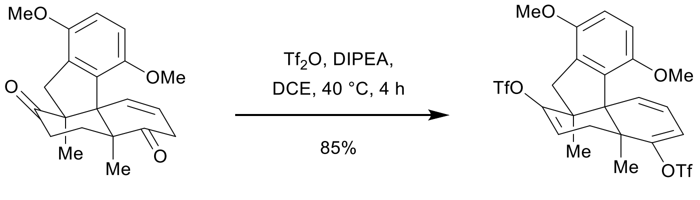
FT-IR (KBr): ν_{max} = 3040, 2945, 2902, 2833, 1707, 1497, 1459, 1258, 1099, 1078, 1001, 828, 792, 717 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.83 (dd, J = 6.5, 3.1 Hz, 1H), 6.45 (d, J = 8.8 Hz, 1H), 6.42 (d, J = 8.8 Hz, 1H), 5.49 (dd, J = 6.8, 2.9 Hz, 1H), 3.58 (dd, J = 17.5, 6.5 Hz, 1H), 3.47 (s, 3H), 3.37 (s, 3H), 3.25 (d, J = 15.8 Hz, 1H), 3.03 (d, J = 15.7 Hz, 1H), 2.28 (ddd, J = 17.0, 6.9, 3.2 Hz, 1H), 2.17 (dd, J = 17.5, 3.1 Hz, 1H), 2.14–2.03 (m, 1H), 1.97 (dt, J = 16.9, 7.6 Hz, 1H), 1.86–1.73 (m, 1H), 1.26 (s, 3H), 1.17 (s, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 210.9, 151.7, 151.1, 148.8, 146.5, 132.9, 129.0, 120.4, 120.4, 109.5, 109.3, 55.2, 55.0, 49.4, 49.3, 42.7, 34.2, 32.4, 27.4, 25.7, 22.8 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{25}O_4^+$ $[M+H]^+$ 325.1798, found 325.1795.

Preparation of bistriflate 23:



18 **23**

To a stirred solution of diketone **18** (322 mg, 0.947 mmol, 1.0 equiv.) in DCE (10 mL) were added DIPEA (1.61 mL, 9.47 mmol, 10.0 equiv.) and Tf_2O (1.60 mL, 9.47 mmol, 10.0 equiv.) at 0 °C. Then the reaction mixture was heated to 40 °C and allowed to stir at this temperature for 4 h. The reaction mixture was diluted with saturated aqueous citric acid (100 mL). After extraction with CH_2Cl_2 (3 × 10 mL), the combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed in vacuo and the residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 80:1→40:1) to give bistriflate **23** (486 mg, 0.805 mmol, 85%).

Characterization of triflate 23:

Physical state: yellow oil;

TLC: $R_f = 0.48$ (silica gel, petroleum ether:EtOAc = 5:1);

Optical rotation: $[\alpha]_D^{23} = +366.9$ ($c = 1.0$, $CHCl_3$);

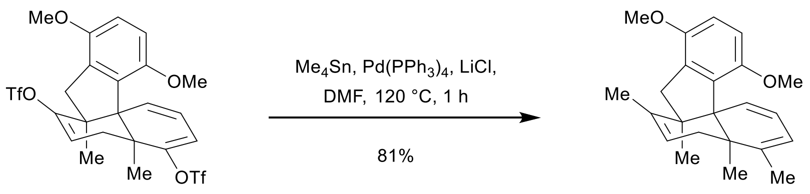
FT-IR (KBr): ν_{max} = 3434, 2943, 2841, 1589, 1494, 1465, 1413, 1253, 1213, 1141, 1078, 989, 868, 605 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.34 (d, J = 8.8 Hz, 1H), 6.26 (d, J = 8.8 Hz, 1H), 5.71 (d, J = 6.3 Hz, 1H), 5.34–5.25 (m, 2H), 5.12 (d, J = 9.6 Hz, 1H), 3.42 (d, J = 16.8 Hz, 1H), 3.35 (s, 3H), 3.27 (s, 3H), 2.59 (d, J = 16.8 Hz, 1H), 2.34–2.25 (m, 1H), 1.79 (dd, J = 17.6, 6.4 Hz, 1H), 1.36 (s, 3H), 1.30 (s, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 156.2, 152.0, 150.8, 150.7, 134.9, 129.6, 124.6, 120.6, 119.1 (q, J = 319.9 Hz), 119.0 (q, J = 319.6 Hz), 118.4, 111.6, 109.7, 106.2, 63.9, 55.1, 54.9, 52.7, 39.3, 38.6, 29.6, 20.2, 18.4 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{22}F_6O_8S_2Na^+$ $[M+Na]^+$ 627.0552, found 627.0558.

Preparation of triene 24:



23 **24**

To a stirred solution of bistriflate **23** (365 mg, 0.604 mmol, 1.0 equiv.) and LiCl (126 mg, 3.02 mmol, 5.0 equiv.) in DMF (10 mL) were added Pd(PPh$_3$)$_4$ (140 mg, 121 μmol, 0.2 equiv.) and Me$_4$Sn (215 mg, 166 μL, 1.21 mmol, 2.0 equiv.) at 23 °C. The resulting mixture was heated to 120 °C and stirred at this temperature for 1 h. The reaction mixture was diluted with saturated aqueous NH$_4$Cl (20 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 500:1→200:1) to give triene **24** (164 mg, 0.489 mmol, 81%).

Characterization of triene 24:

Physical state: white powder;

TLC: R_f = 0.44 (silica gel, petroleum ether:EtOAc = 20:1);

Optical rotation: $[\alpha]_{D}^{23}$ = +709.6 (c = 1.0, CHCl$_3$);

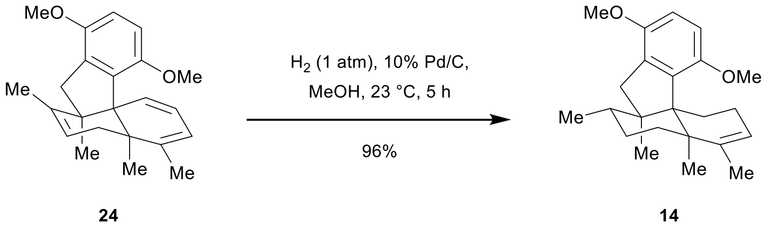
FT-IR (KBr): ν_{max} = 3427, 3004, 2961, 2927, 1586, 1491, 1444, 1370, 1260, 1093, 1060, 1026, 800, 701 cm^{-1};

^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 6.49 (d, J = 8.7 Hz, 1H), 6.32 (d, J = 8.7 Hz, 1H), 5.81 (dd, J = 9.6, 5.4 Hz, 1H), 5.63–5.56 (m, 1H), 5.53 (dq, J = 5.4, 1.4 Hz, 1H), 5.28 (dt, J = 6.2, 1.6 Hz, 1H), 3.37 (s, 3H), 3.34 (d, J = 16.1 Hz, 1H), 3.32 (s, 3H), 2.81 (dd, J = 16.2, 1.1 Hz, 1H), 2.49 (dt, J = 16.8, 2.5 Hz, 1H), 1.90–1.82 (m, 1H), 1.81 (s, 3H), 1.66 (dt, J = 2.6, 1.3 Hz, 3H), 1.47 (s, 3H), 1.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, C$_6$D$_6$): δ = 151.6, 150.9, 145.8, 139.5, 137.3, 131.2, 124.8, 124.3, 123.5, 115.0, 112.3, 108.4, 60.8, 55.4, 55.1, 52.8, 39.3, 38.9, 33.3, 21.1, 20.9, 18.8, 17.9 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{29}O_2^+$ [M+H]$^+$ 337.2162, found 337.2157.

Preparation of dimethyl predysiherbol 14 from triene 24:



To a stirred solution of olefin **24** (161 mg, 479 μmol, 1.0 equiv.) in MeOH (10 mL) was added 10% Pd/C (1.13 g, 479 μmol, wetted with *ca.* 55% water, 1.0 equiv.) at 23 °C. The resulting mixture was stirred at this temperature for 5 h under H_2. The reaction mixture was filtered through Celite® and the residue was washed with EtOAc (3 × 20 mL). Then the combined filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 500:1→300:1) to give dimethyl predysiherbol **14** (157 mg, 460 μmol, 96%).

Characterization of dimethyl predysiherbol 14:

Physical state: white solid;

M.P.: 112–114 °C;

TLC: $R_f = 0.49$ (silica gel, petroleum ether:EtOAc = 20:1);

Optical rotation: $[\alpha]_D^{23} = +22.0$ ($c = 1.0$, $CHCl_3$);

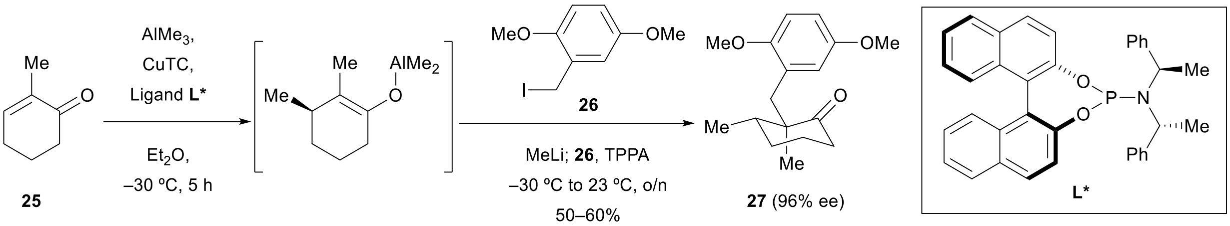
FT-IR (KBr): ν_{max} = 2946, 2907, 2830, 1489, 1462, 1380, 1253, 1177, 1070, 1041, 790, 719 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.58 (d, J = 8.8 Hz, 1H), 6.49 (d, J = 8.8 Hz, 1H), 5.18–5.12 (m, 1H), 3.43 (s, 3H), 3.38 (s, 3H), 2.93 (d, J = 16.2 Hz, 1H), 2.76 (d, J = 16.2 Hz, 1H), 2.08 (td, J = 12.0, 6.1 Hz, 1H), 1.99–1.87 (m, 2H), 1.83–1.68 (m, 1H),1.76 (s, 3H), 1.63–1.50 (m, 2H), 1.50–1.40 (m, 1H), 1.44–1.35 (m, 1H), 1.33–1.17 (m, 1H), 1.28 (s, 3H), 1.04 (s, 3H), 0.75 (d, J = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 152.8, 151.8, 144.7, 140.3, 132.2, 116.7, 111.7, 109.1, 60.3, 55.2, 55.1, 49.7, 40.6, 39.5, 35.0, 31.2, 28.3, 26.4, 24.3, 24.2, 19.5, 17.6, 17.2 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{33}O_2^+$ $[M+H]^+$ 341.2475, found 341.2476.

Preparation of ketone 27:



In a flame-dried *Schlenk* flask, a solution of (10 mg, 0.052 mmol, 0.12 equiv.) of copper(I) thiophene-

2-carboxylate (CuTC) and (10 mg, 0.019 mmol, 0.043 equiv.) of the phosphoramidite ligand **L*** in 1.2 mL of dry Et_2O was stirred at 23 °C for 30 min. The salmon-colored solution was cooled to −30 °C and (49 mg, 0.44 mmol, 1.0 equiv.) of enone **25** was added. Then, (0.27 mL, 0.54 mmol, 1.2 equiv., 2.0 M in hexanes) of $AlMe_3$ were added via syringe over a period of 10 min. The reaction mixture was stirred at −30 °C for 5 h, until TLC indicated full conversion of the starting material. The solvents were removed in vacuo at −30 °C (using Schlenk line) until a small volume remained, which was dissolved in 0.45 mL of tripyrrolidinophosphoric acid triamide (TPPA) before (0.39 mL, 0.55 mmol, 1.3 equiv., 1.4 M in Et_2O) of methyllithium were added (still at −30 °C). Finally, (0.21 g, 0.76 mmol, 1.7 equiv.) of iodide **26** was added and the stirred suspension was allowed to slowly warm up to 23 °C overnight. At this point, GC-MS analysis indicated full conversion of the 1,4-addition intermediate and a diastereoselectivity of 6:1 dr. The reaction mixture was carefully quenched by addition of 2 mL of sat. aqueous NH_4Cl at 0 °C before 20 mL of H_2O and 10 mL of sat. aqueous Na K tartrate solution were added (to facilitate phase separation). The aqueous phase was extracted with 3 × 20 mL of c-Hex, 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 33:1) to give (38 mg, 0.14 mmol, 32%) of the pure *trans*-product **27**. This product showed an enantiomeric excess of 96% ee as determined by chiral HPLC using a racemic standard (see below). In addition, (7 mg, 0.025 mmol, 6%) *cis*–byproduct *epi*-**27** was obtained.

Note: When the reaction was performed on a 5 g scale, the pure ketone **27** was obtained in 50–60% yield after chromatography.

Characterization of ketone 27:

Physical state: pale yellow oil;

TLC: $R_f = 0.28$ (silica gel, *c*-Hex:EtOAc = 9:1);

Optical rotation: $[\alpha]_D^{20} = -22$ ($c = 0.6$, $CHCl_3$);

FT-IR (ATR): ν_{max} = 2988, 2936, 2874, 2833, 1700, 1609, 1589, 1498, 1462, 1426, 1382, 1351, 1313, 1222, 1179, 1159, 1122, 1091, 1048, 1027, 946, 918, 874, 801, 716, 624, 590, 558, 533 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.74–6.71 (m, 1H), 6.71–6.67 (m, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 3.17 (d, *J* = 13.6 Hz, 1H), 2.90 (d, *J* = 13.6 Hz, 1H), 2.73 (ddd, *J* = 14.5, 9.8, 6.5 Hz, 1H), 2.33 (dt, *J* = 14.5, 5.8 Hz, 1H), 2.09 (ddt, *J* = 13.7, 9.0, 4.4 Hz, 1H), 1.98 (td, *J* = 6.8, 4.1 Hz, 1H), 1.88 (dtt, *J* =

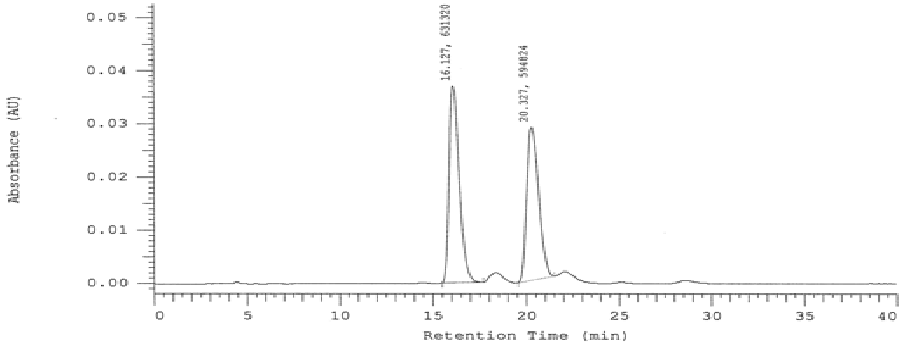
14.5, 9.4, 4.1 Hz, 1H), 1.82–1.75 (m, 1H), 1.49 (ddd, *J* = 13.3, 11.1, 6.5 Hz, 1H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 3H) ppm;

^{13}C NMR (126 MHz, CDCl$_3$): δ = 216.2, 153.1, 152.3, 128.2, 118.5, 111.8, 111.2, 55.7, 55.5, 53.6, 40.2, 38.4, 37.2, 28.7, 23.0, 18.9, 16.4 ppm;

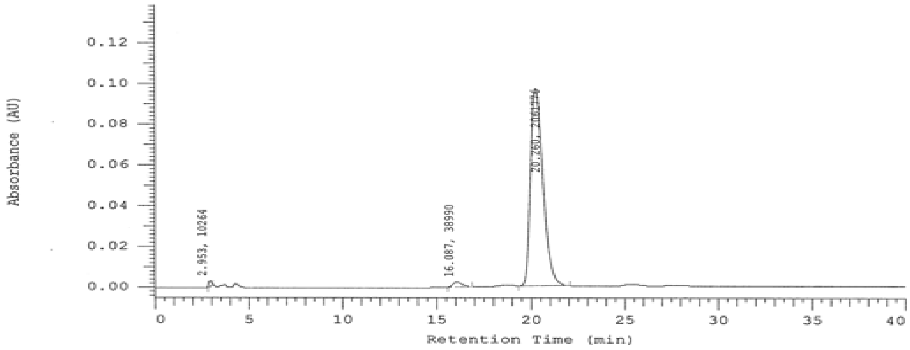
HRMS (ESI): calcd for $C_{17}H_{24}O_3^+$ [M+H]$^+$ 277.17982, found 277.18007.

Chiral HPLC traces:

Racemate



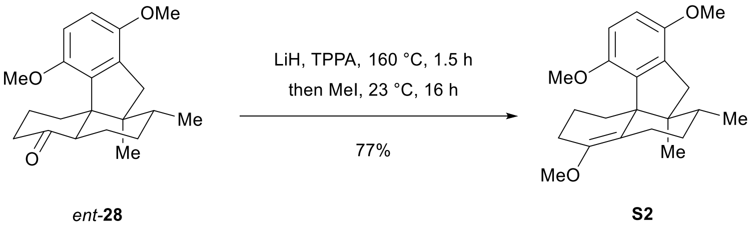
Sample of ketone **27**



Sample	Peak area (*t* = 16.1 min)	Peak area (*t* = 20.3 min)	ee[a]
Racemate	51.5%	48.5%	3.0%
Sample of ketone **27**	1.9%	98.1%	96.2%

[a]The ee values were determined by Chiral HPLC (column: CHIRALPAK AD-H), *n*-hexane:*i*-PrOH = 99:1, temperature: 18 °C, flow rate: 1 mL/min, detector wavelength: 250 nm).

Preparation of enol ether S2[2]:



In a flame-dried *Schlenk* flask, ketone *ent*-**28** (194 mg, 0.590 mmol, 1.00 equiv.) was dissolved in TPPA (2.8 mL). LiH (107 mg, 13.5 mmol, 23.1 equiv.) was added and the stirred suspension was heated to 160 °C for 1.5 h. Then the mixture was cooled to 0 °C and MeI (1.73 g, 760 µL, 12.2 mmol, 20.9 equiv.) was added. The mixture was allowed to reach 23 °C and stirred for 16 h, before excess LiH was carefully quenched by addition of 25% aqueous NH_4OH (5 mL). After addition of H_2O (60 mL) and extraction with MTBE (3 × 40 mL) 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 enol ether **S2** (155 mg, 0.453 mmol, 77%).

Characterization of enol ether S2:

Physical state: colorless, crystalline solid;

M.P.: 78–80 °C;

TLC: R_f = 0.64 (silica gel, *c*-Hex:EtOAc = 9:1);

Optical rotation: $[\alpha]_D^{20}$ = +152 (*c* = 0.5, $CHCl_3$);

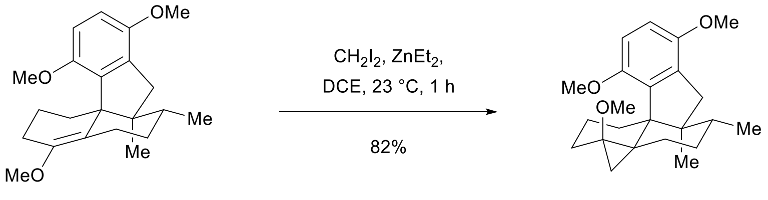
FT-IR (ATR): ν_{max} = 2930, 2909, 2874, 2850, 2830, 1708, 1673, 1595, 1491, 1462, 1437, 1380, 1360, 1326, 1305, 1282, 1253, 1208, 1170, 1149, 1125, 1111, 1093, 1070, 1056, 1022, 971, 945, 936, 907, 871, 854, 789, 737, 715, 666, 646, 518 cm^{-1};

^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.62 (s, 2H), 3.77 (s, 3H), 3.66 (s, 3H), 3.53 (s, 3H), 2.89 (dt, *J* = 13.6, 3.2 Hz, 1H), 2.83 (d, *J* = 15.8 Hz, 1H), 2.51 (d, *J* = 15.8 Hz, 1H), 2.20–2.10 (m, 2H), 1.84 (ddd, *J* = 13.2, 10.0, 3.6 Hz, 1H), 1.70–1.59 (m, 2H), 1.49 (tq, *J* = 13.6, 2.9 Hz, 1H), 1.41–1.37 (m, 2H), 1.33 (dt, *J* = 12.8, 3.5 Hz, 1H), 1.11 (qd, *J* = 12.7, 3.6 Hz, 1H), 0.97 (s, 3H), 0.82 (d, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (126 MHz, CDCl$_3$): δ = 151.7, 150.8, 149.0, 140.7, 131.7, 120.3, 109.9, 108.8, 56.8, 55.8, 55.7, 55.6, 51.7, 38.5, 36.0, 32.2, 31.0, 25.7, 24.1, 20.1, 18.2, 14.1 ppm;

HRMS (ESI): calcd for $C_{22}H_{31}O_3^+$ $[M+H]^+$ 343.22677, found 343.22754.

Preparation of cyclopropane *ent*-29[2]:



S2 *ent*-**29**

In an argon-flushed flask, enol ether **S2** (155 mg, 0.453 mmol, 1.00 equiv.) was dissolved in DCE (9.8 mL). The solution was cooled to 0 °C and $ZnEt_2$ (1.80 mL, 1.62 mmol, 3.58 equiv., 0.9 M in hexane) was added slowly. Then CH_2I_2 (1.0 g, 0.30 mL, 3.7 mmol, 8.2 equiv.) was added and the arising milk-like suspension was allowed to reach 23 °C and stirred for 1 h. Excess reagent was quenched with sat. aqueous $NaHCO_3$ (3 mL). After addition of H_2O (35 mL) and extraction with MTBE (3 × 25 mL) 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 50:1) to provide cyclopropane *ent*-**29** (132 mg, 0.370 mmol, 82%) as a colorless sticky oil, crystallizing upon repetitive dissolving in CH_2Cl_2 and solvent removal *in vacuo*.

Characterization of cyclopropane *ent*-29:

Physical state: colorless, crystalline solid;

M.P.: 87–90 °C;

TLC: $R_f = 0.37$ (silica gel, *c*-Hex:EtOAc = 19:1);

Optical rotation: $[\alpha]_D^{20} = +30$ ($c = 1.0$, $CHCl_3$);

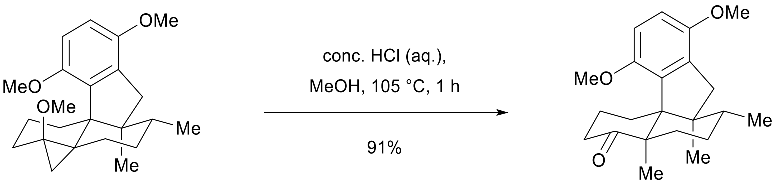
FT-IR (ATR): ν_{max} = 3061, 2991, 2931, 2902, 2874, 2847, 2829, 1595, 1492, 1459, 1437, 1379, 1353, 1324, 1300, 1282, 1255, 1214, 1201, 1174, 1160, 1135, 1097, 1081, 1049, 1016, 998, 985, 970, 951, 915, 886, 838, 822, 789, 759, 738, 716, 649, 635, 510 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.65 (s, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.32 (s, 3H), 2.72 (d, *J* = 15.7 Hz, 1H), 2.44 (d, *J* = 15.7 Hz, 1H), 2.08–2.01 (m, 2H), 1.56–1.50 (m, 1H), 1.39–1.33 (m, 6H), 1.27–1.25 (m, 1H), 1.12 (dd, *J* = 9.4, 3.2 Hz, 1H), 1.00 (s, 3H), 0.82 (d, *J* = 6.0 Hz, 3H), 0.65 (dd, *J* = 5.1, 1.7 Hz, 1H), 0.41 (d, *J* = 4.3 Hz, 1H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4, 151.1, 139.0, 132.1, 109.0, 108.9, 65.1, 55.8, 55.5, 54.7, 53.8, 50.9, 38.5, 36.1, 32.3, 30.4, 29.0, 27.9, 27.5, 21.3, 18.2, 17.1, 14.0 ppm;

HRMS (ESI): calcd for $C_{23}H_{32}O_3Na^+$ $[M+Na]^+$ 379.22437, found 379.22467.

Preparation of ketone *ent*-30[2]:



ent-**29** *ent*-**30**

In an argon-flushed flask, cyclopropane *ent*-**29** (132 mg, 0.370 mmol, 1.00 equiv.) was dissolved in MeOH (4.5 mL) under gentle warming, HCl (conc., aq., 4.0 mL) was added and the mixture was refluxed for 1 h. The solution was allowed to cool to 23 °C before it was neutralized with sat. aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with MTBE (3 × 40 mL), the combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure to provide ketone *ent*-**30** (115 mg, 0.336 mmol, 91%).

Characterization of ketone *ent*-30

Physical state: colorless, crystalline solid;

M.P.: 125–128 °C;

TLC: $R_f = 0.24$ (silica gel, *c*-Hex:EtOAc = 9:1);

Optical rotation: $[\alpha]_D^{20} = +0$ ($c = 0.5$, $CHCl_3$);

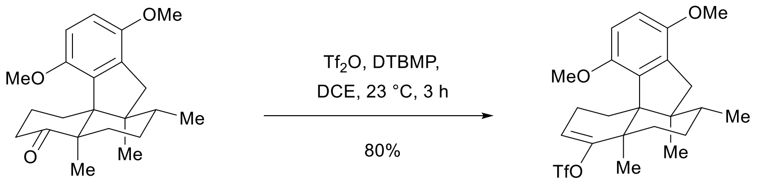
FT-IR (ATR): ν_{max} = 3028, 2935, 2881, 2833, 1701, 1595, 1493, 1460, 1415, 1386, 1347, 1321, 1277, 1256, 1194, 1172, 1151, 1128, 1115, 1091, 1065, 1056, 1045, 1023, 1005, 974, 957, 927, 853, 827, 798, 720, 676, 648, 578, 560, 523 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.64 (d, J = 8.7 Hz, 1H), 6.59 (d, J = 8.7 Hz, 1H), 3.76 (s, 3H), 3.55 (s, 3H), 2.72 (d, J = 15.9 Hz, 1H), 2.55–2.47 (m, 1H), 2.51 (d, J = 15.9 Hz, 1H), 2.27 (dd, J = 17.1, 6.0 Hz, 1H), 2.17 (td, J = 13.4, 4.2 Hz, 1H), 1.97–1.91 (m, 1H), 1.75–1.69 (m, 1H), 1.56–1.48 (m, 1H), 1.45–1.37 (m, 4H), 1.37–1.33 (m, 1H), 1.31 (s, 3H), 1.15 (s, 3H), 0.84 (d, J = 6.5 Hz, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$): δ = 212.2, 151.4, 151.1, 138.3, 131.7, 109.20, 109.18, 59.7, 55.7, 53.2, 50.7, 50.3, 40.1, 36.4, 35.1, 28.8, 27.3, 27.2, 22.8, 20.7, 17.7, 17.4 ppm;

HRMS (ESI): calcd for $C_{22}H_{31}O_3^+$ $[M+H]^+$ 343.22677, found 343.22720.

Preparation of enol triflate S3[2]:



ent-**30** **S3**

In a flame-dried *Schlenk* flask, ketone *ent*-**30** (115 mg, 0.336 mmol, 1.00 equiv.) was dissolved in DCE (1.6 mL). After the addition of DTBMP (196 mg, 0.955 mmol, 2.84 equiv.), the solution was cooled to 0 °C and Tf_2O (202 mg, 120 µL, 0.717 mmol, 2.13 equiv.) was added. The arising suspension was allowed to reach 23 °C and stirred for 3 h. After quenching with sat. aqueous $NaHCO_3$ (2 mL) and addition of H_2O (25 mL), the aqueous phase was extracted with MTBE (3 × 25 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (*c*-Hex/EtOAc 50:1) afforded enol triflate **S3** (127 mg, 0.268 mmol, 80%).

Characterization of enol triflate S3:

Physical state: colorless, viscous oil;

TLC: $R_f = 0.80$ (silica gel, *c*-Hex:EtOAc = 9:1);

Optical rotation: $[\alpha]_D^{20} = +0.5$ ($c = 0.5$, $CHCl_3$);

FT-IR (ATR): ν_{max} = 3025, 2956, 2913, 2836, 1683, 1586, 1491, 1463, 1439, 1407, 1345, 1313, 1256, 1208, 1177, 1144, 1079, 1063, 1041, 1023, 1000, 981, 944, 910, 885, 792, 740, 720, 687, 652, 616, 600, 516 cm^{-1};

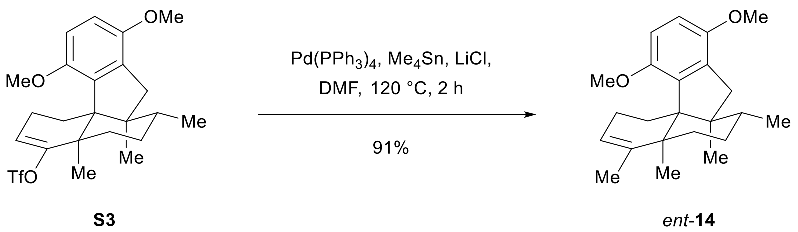
^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.66 (s, 2H), 5.38 (t, J = 3.9 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 2.67 (d, J = 16.2 Hz, 1H), 2.57 (d, J = 16.2 Hz, 1H), 2.13–2.02 (m, 2H), 1.81–1.74 (m, 1H), 1.74–1.67 (m, 1H), 1.60–1.55 (m, 1H), 1.50–1.44 (m, 1H), 1.42–1.34 (m, 3H), 1.40 (s, 3H), 1.10 (s, 3H), 0.81 (d, J = 6.0 Hz, 3H) ppm;

^{13}C NMR (126 MHz, CDCl$_3$): δ = 157.3, 151.8, 151.1, 137.7, 131.6, 118.6 (q, J = 319.2 Hz), 110.5, 110.0, 109.5, 61.4, 55.7, 55.1, 49.5, 40.2, 40.1, 34.5, 28.9, 27.3, 25.2, 23.6, 22.1, 17.4, 17.0 ppm;

^{19}F NMR (471 MHz, CDCl$_3$): δ = –75.1 ppm;

HRMS (ESI): calcd for $C_{23}H_{29}F_3O_5Na^+$ $[M+Na]^+$ 497.15800, found 497.15874.

Preparation of dimethyl predysiherbol *ent*-14 from enol triflate S3^2:



In a flame-dried *Schlenk* flask, enol triflate **S3** (123 mg, 0.259 mmol, 1.00 equiv.) was dissolved in DMF (2 mL). LiCl (57 mg, 1.3 mmol, 5.0 equiv.), $Pd(PPh_3)_4$ (62 mg, 0.054 mmol, 0.21 equiv.) and $SnMe_4$ (95 mg, 74 µL, 0.53 mmol, 2.0 equiv.) were added and the reaction mixture was heated to 120 °C for 2 h. After cooling to 23 °C, the excess reagent was quenched with sat. aqueous NH_4Cl (10 mL) and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (*c*-Hex/toluene 5:1) afforded dimethyl predysiherbol *ent*-**14** (80.0 mg, 0.235 mmol, 91%).

Characterization of dimethyl predysiherbol *ent*-14:

Physical state: colorless, viscous oil;

TLC: $R_f = 0.41$ (silica gel, *c*-Hex:EtOAc = 4:1);

Optical rotation: $[\alpha]_D^{20} = -24$ ($c = 0.4$, $CHCl_3$);

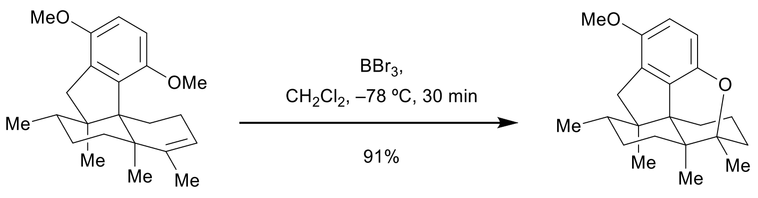
FT-IR (ATR): ν_{max} = 3014, 2940, 2909, 2831, 1585, 1489, 1463, 1450, 1437, 1385, 1377, 1314, 1254, 1176, 1162, 1149, 1123, 1090, 1074, 1045, 1035, 1017, 997, 988, 969, 904, 878, 790, 742, 720, 663, 651, 515 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.66 (d, *J* = 8.8 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 5.04 (s, 1H), 3.76 (s, 3H), 3.62 (s, 3H), 2.62 (d, *J* = 16.1 Hz, 1H), 2.57 (d, *J* = 16.1 Hz, 1H), 2.10 (td, *J* = 12.5, 6.1 Hz, 1H), 1.93–1.85 (m, 1H), 1.72–1.66 (m, 1H), 1.69–1.67 (m, 3H), 1.60–1.54 (m, 1H), 1.54–1.49 (m, 1H), 1.49–1.43 (m, 1H), 1.42–1.37 (m, 2H), 1.35–1.29 (m, 1H), 1.24 (s, 3H), 1.10 (s, 3H), 0.79 (d, *J* = 6.4 Hz, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4, 151.0, 144.9, 140.3, 131.9, 116.2, 111.4, 108.9, 60.1, 55.6, 55.6, 49.4, 40.0, 39.2, 34.7, 30.8, 27.9, 26.1, 24.0, 23.9, 19.2, 17.5, 17.0 ppm;

HRMS (ESI): calcd for $C_{23}H_{33}O_2^+$ $[M+H]^+$ 341.24751, found 341.24774.

Preparation of dysiherbol A methyl ether 31 from dimethyl predysiherbol 14 with BBr_3[3]:



14 **31**

To a stirred solution of dimethyl predysiherbol **14** (25.6 mg, 75.2 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added BBr_3 (150 μL, 150 μmol, 1.0 M in CH_2Cl_2, 2.0 equiv.) at –78 °C. The resulting mixture was stirred at this temperature for 30 min before it was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give dysiherbol A methyl ether **31** (22.3 mg, 68.4 μmol, 91%).

Characterization of dysiherbol A methyl ether 31:

Physical state: colorless oil;

TLC: $R_f = 0.38$ (silica gel, petroleum ether:EtOAc = 50:1);

Optical rotation: $[\alpha]_D^{23} = +22.4$ ($c = 1.0$, $CHCl_3$);

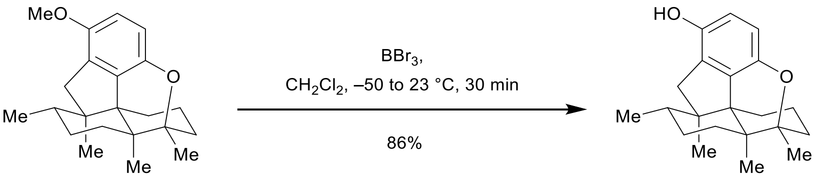
FT-IR (KBr): ν_{max} = 3431, 2934, 2360, 2338, 1734, 1716, 1635, 1540, 1457, 1383, 1183, 1106, 1031 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.78 (d, J = 8.6 Hz, 1H), 6.44 (d, J = 8.6 Hz, 1H), 3.43 (s, 3H), 2.85 (d, J = 15.4 Hz, 1H), 2.66 (d, J = 15.4 Hz, 1H), 1.78–1.67 (m, 2H), 1.64–1.54 (m, 1H), 1.54–1.41 (m, 2H), 1.36–1.27 (m, 2H), 1.27–1.22 (m, 2H), 1.21 (s, 3H), 1.19–1.10 (m, 1H), 1.04 (dq, J = 13.6, 3.5 Hz, 1H), 0.93 (s, 3H), 0.91 (s, 3H), 0.71 (d, J = 6.8 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 150.9, 149.2, 133.6, 128.3, 111.1, 110.6, 82.2, 55.4, 51.7, 49.4, 40.6, 37.5, 36.1, 35.8, 30.3, 26.8, 26.7, 22.3, 20.2, 18.5, 17.9, 15.0 ppm;

HRMS (ESI-TOF): calcd for $C_{22}H_{31}O_2^+$ $[M+H]^+$ 327.2319, found 327.2319.

Preparation of dysiherbol A (6) from dysiherbol A methyl ether 31:



31

6: (+)-dysiherbol A
(revised structure)

To a stirred solution of dysiherbol A methyl ether **31** (10.2 mg, 31.2 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added BBr_3 (156 μL, 156 μmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −50 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 25:1) to give dysiherbol A (**6**) (8.4 mg, 26.9 μmol, 86%).

Characterization of dysiherbol A (6):

Physical state: pale yellow oil;

TLC: $R_f = 0.49$ (silica gel, petroleum ether:EtOAc = 5:1);

Optical rotation: $[\alpha]_D^{23} = +22.9$ ($c = 1.0$, MeOH);

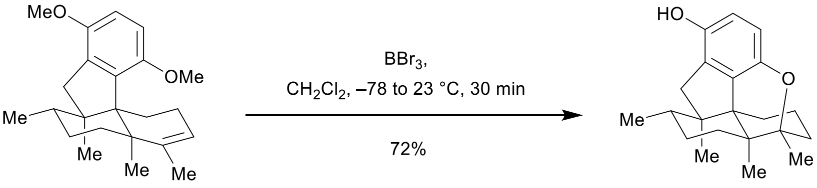
FT-IR (KBr): ν_{max} = 3307, 2949, 2870, 1491, 1462, 1380, 1263, 1184, 1105, 959, 938, 868, 800 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.49 (d, J = 8.5 Hz, 1H), 6.42 (d, J = 8.5 Hz, 1H), 4.24 (s, 1H), 2.57 (d, J = 15.4 Hz, 1H), 2.53 (d, J = 15.4 Hz, 1H), 1.96 (td, J = 13.9, 6.5 Hz, 1H), 1.84 (td, J = 12.8, 4.6 Hz, 1H), 1.68 (dd, J = 15.0, 5.8 Hz, 1H), 1.54–1.46 (m, 1H), 1.42–1.37 (m, 1H), 1.37–1.33 (m, 1H), 1.34–1.32 (m, 1H), 1.32–1.30 (m, 1H), 1.30–1.27 (m, 1H), 1.26–1.23 (m, 1H), 1.23–1.22 (m, 1H), 1.22 (s, 3H), 1.21 (s, 3H) 1.08 (s, 3H), 0.83 (d, J = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.5, 145.7, 133.2, 126.0, 114.4, 111.2, 82.5, 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 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{29}O_2^+$ $[M+H]^+$ 313.2162, found 313.2162.

Preparation of dysiherbol A (6) directly from dimethyl predysiherbol 14:



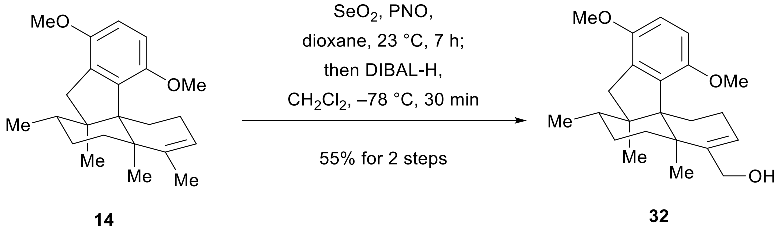
14

6: (+)-dysiherbol A
(revised structure)

To a stirred solution of dimethyl predysiherbol **14** (15.6 mg, 45.8 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added BBr_3 (229 μL, 229 μmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −78 °C. The resulting mixture was allowed to warm to 23 °C gradually and stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 25:1) to give dysiherbol A (**6**) (10.3 mg, 33.0 μmol, 72%).

The analytical data of dysiherbol A (**6**) was described above.

Preparation of allylic alcohol 32 from dimethyl predysiherbol 14:



To a stirred solution of dimethyl predysiherbol **14** (4.6 mg, 13.5 μmol, 1.0 equiv.) in dioxane (1 mL) was added PNO (5.1 mg, 54.0 μmol, 4.0 equiv.) and SeO_2 (1.5 mg, 13.5 μmol, 1.0 equiv.) at 23 °C. The resulting mixture was stirred at this temperature for 7 h. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was used to the next step without further purification.

To a stirred solution of the resulting crude product in CH_2Cl_2 (1 mL) was added DIBAL-H (27.0 μL, 27.0 μmol, 1.0 M in toluene, 2.0 equiv.) at −78 °C. The resulting mixture was stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) and saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 15:1→10:1) to give allylic alcohol **32** (2.6 mg, 7.43 μmol, 55%).

Characterization of allylic alcohol 32:

Physical state: white foam;

TLC: R_f = 0.48 (silica gel, petroleum ether:EtOAc = 3:1);

Optical rotation: $[\alpha]_D^{23}$ = +17.1 (c = 1.0, $CHCl_3$);

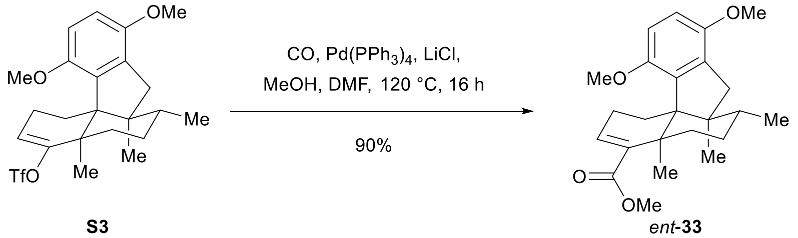
FT-IR (KBr): ν_{max} = 3854, 3820, 3748, 3673, 3566, 2940, 1747, 1716, 1700, 1650, 1541, 1490, 1457, 1421, 1385, 1254 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.54 (d, J = 8.8 Hz, 1H), 6.46 (d, J = 8.8 Hz, 1H), 5.42 (t, J = 3.4 Hz, 1H), 4.24 (d, J = 12.8 Hz, 1H), 4.17 (d, J = 12.8 Hz, 1H), 3.41 (s, 3H), 3.37 (s, 3H), 2.93 (d, J = 16.2 Hz, 1H), 2.72 (d, J = 16.2 Hz, 1H), 1.96 (m, 3H), 1.75 (ddt, J = 15.0, 6.0, 2.6 Hz, 1H), 1.67 (dt, J = 12.9, 3.5 Hz, 1H), 1.53 (ddd, J = 12.0, 6.7, 4.9 Hz, 1H), 1.40 (tdd, J = 13.3, 10.9, 3.3 Hz, 2H), 1.28 (s, 3H), 1.23 (dq, J = 12.0, 3.9 Hz, 1H), 1.02 (s, 3H), 0.73 (d, J = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 152.6, 151.9, 147.5, 140.0, 132.1, 117.6, 112.2, 109.2, 64.4, 60.7, 55.6, 55.0, 49.6, 40.7, 39.0, 34.9, 30.8, 28.0, 26.2, 25.5, 24.0, 17.5, 17.4 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{32}O_3Na^+$ $[M+Na]^+$ 379.2244, found 379.2241.

Preparation of methyl ester *ent*-33[2]:



To a solution of triflate **S3** (10 mg, 0.021 mmol, 1.0 equiv.) in DMF (0.28 mL) were added $Pd(PPh_3)_4$ (11 mg, 9.5 µmol, 0.45 equiv.), LiCl (10 mg, 0.24 mmol, 11 equiv.) and MeOH (0.28 mL). The resulting suspension was degassed in 3 freeze-pump-thaw cycles and stirred under a CO atmosphere at 120 °C for 16 h. The mixture was then allowed to reach room temp. before H_2O (0.5 mL) and EtOAc (1 mL) were added. The aqueous layer was extracted with EtOAc (3 × 1 mL) and the combined organic phases were dried over $MgSO_4$ before the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether:EtOAc = 100:1→50:1) to provide *ent*-**33** (7.3 mg, 0.019 mmol, 90%).

Characterization of methyl ester *ent*-33:

Physical state: pale yellow, viscous oil;

TLC: R_f = 0.20 (silica gel, *c*-Hex:EtOAc = 20:1);

Optical rotation: $[\alpha]_D^{20}$ = −14 (c = 0.48, $CHCl_3$);

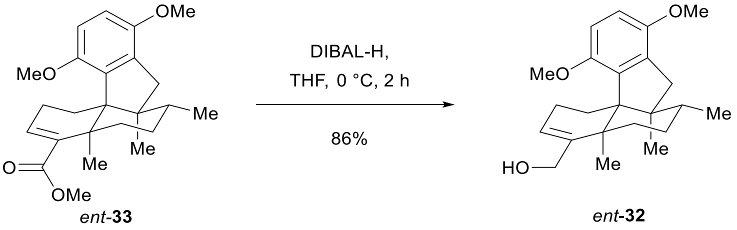
FT-IR (ATR): ν_{max} = 3019, 2947, 2858, 2831, 1709, 1638, 1586, 1488, 1461, 1436, 1385, 1377, 1355, 1315, 1291, 1253, 1224, 1174, 1158, 1126, 1081, 1061, 1036, 1015, 999, 989, 972, 958, 948, 934, 912, 885, 866, 852, 823, 790, 772, 761,739, 720, 711, 652, 599, 530, 453 cm^{-1};

^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.64 (d, *J* = 8.8 Hz, 1H), 6.61 (d, *J* = 8.9 Hz, 1H), 6.53 (dd, *J* = 4.4, 2.6 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.60 (s, 3H), 2.65 (d, *J* = 16.1 Hz, 1H), 2.58 (d, *J* = 16.2 Hz, 1H), 2.29 (dt, *J* = 12.6, 3.2 Hz, 1H), 2.14–2.03 (m, 2H), 1.75–1.65 (m, 1H), 1.58 (qd, *J* = 13.2, 3.4 Hz, 1H), 1.52–1.47 (m, 2H), 1.45 (s, 3H), 1.42–1.36 (m, 1H), 1.36–1.34 (m, 1H), 1.11 (s, 3H), 0.80 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (126 MHz, CDCl$_3$): δ = 168.1, 152.4, 150.9, 141.9, 139.1, 134.0, 131.9, 110.3, 109.1, 60.6, 55.7, 55.5, 51.1, 49.8, 40.3, 38.7, 34.6, 29.7, 28.0, 25.2, 24.9, 24.5, 17.5, 17.3 ppm;

HRMS (ESI-TOF): calcd for $C_{24}H_{32}O_4Na^+$ $[M+Na]^+$ 407.2193, found 407.2195.

Synthesis of alcohol *ent*-32[2]:



To a solution of ester *ent*-**33** (5.3 mg, 0.014 mmol, 1.0 equiv.) in THF (0.16 mL) was added DIBAL-H (85 µL, 0.085 mmol, 6.2 equiv., 1.0 M in hexanes) at 0 °C. The resulting mixture was stirred at this temperature for 2 h. The reaction mixture was quenched with MeOH (0.3 mL). aqueous Rochelle's salt solution (0.3 mL) and extracted with EtOAc (3 × 1 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was used to the next step without further purification. The crude product was purified by silica gel column chromatography (petroleum ether:EtOAc = 20:1→9:1) to provide *ent*-**32** (4.1 mg, 0.012 mmol, 86%).

Characterization of allylic alcohol *ent*-32:

Physical state: colorless, viscous oil;

TLC: R_f = 0.081 (silica gel, *c*-Hex:EtOAc = 9:1);

Optical rotation: $[\alpha]_D^{20}$ = −5 (*c* = 0.37 , $CHCl_3$);

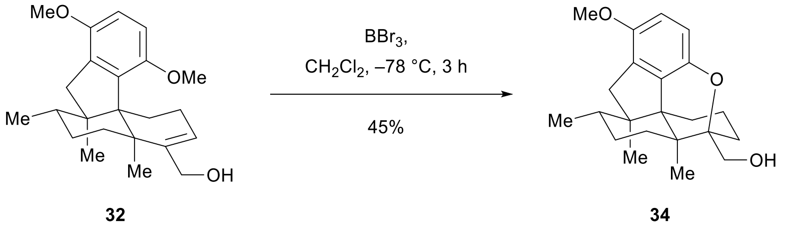
FT-IR (ATR): ν_{max} = 3674, 3444, 2988, 2954, 2927, 2870, 2832, 2215, 2028, 1987, 1734, 1674, 1489, 1463, 1438, 1383, 1253, 1175, 1149, 1131, 1073, 1065, 1040, 1002, 967, 879, 794, 743, 721, 653, 582, 551, 516 cm^{-1};

^{1}H NMR (600 MHz, CDCl$_3$): δ = 6.72 (d, J = 8.8 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 5.46 (dt, J = 3.4, 2.1 Hz, 1H), 4.28–4.25 (m, 1H), 4.18–4.14 (m, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 2.68 (d, J = 16.2 Hz, 1H), 2.59 (d, J = 16.2 Hz, 1H), 2.14 (td, J = 12.6, 6.2 Hz, 1H), 2.06–2.01 (m, 1H), 1.76 (td, J = 13.1, 3.7 Hz, 1H), 1.68–1.65 (m, 2H), 1.52–1.49 (m, 1H), 1.47–1.44 (m, 1H), 1.43–1.40 (m, 1H), 1.38–1.35 (m, 1H), 1.33 (s, 3H), 1.13 (s, 3H), 0.83 (d, J = 6.5 Hz, 3H) ppm;

^{13}C NMR (151 MHz, CDCl$_3$): δ = 152.3, 151.4, 146.9, 139.8, 132.0, 119.2, 112.2, 109.2, 64.9, 60.6, 56.2, 55.7, 49.5, 40.2, 38.9, 34.7, 30.9, 27.8, 25.9, 25.5, 23.8, 17.5, 17.4 ppm;

GC-MS (70 eV): m/z = 356 [M]$^+$, 338, 323, 297, 269, 255, 241, 217, 204, 187, 165, 151, 128, 115, 91, 69, 55.

Preparation of dysiherbol E methyl ether 34:



To a stirred solution of allylic alcohol **32** (5.5 mg, 15.4 µmol, 1.0 equiv.) in CH$_2$Cl$_2$ (1 mL) was added BBr$_3$ (18.5 µL, 18.5 µmol, 1.0 M in CH$_2$Cl$_2$, 1.2 equiv.) at −78 °C. The resulting mixture was stirred at this temperature for 3 h. The reaction mixture was quenched with saturated aqueous NaHCO$_3$ (10 mL) and extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 6:1→3:1) to give dysiherbol E methyl ether **34** (2.4 mg, 6.93 µmol, 45%).

Characterization of dysiherbol E methyl ether 34

Physical state: white foam;

TLC: R_f = 0.37 (silica gel, petroleum ether:EtOAc = 4:1);

Optical rotation: $[\alpha]_D^{23}$ = +26.7 (c = 0.5, CHCl$_3$);

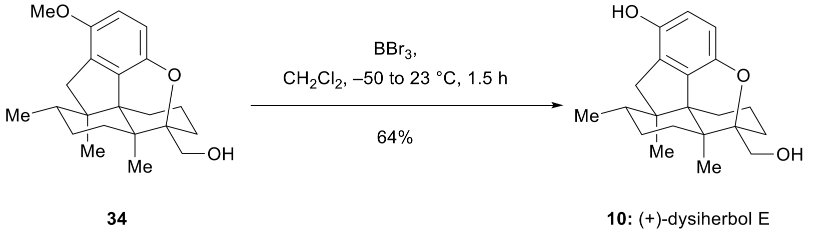
FT-IR (KBr): ν_{max} = 3221, 2999, 2939, 2877, 1494, 1452, 1259, 1158, 1107, 1050, 960, 921, 875, 801 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.71 (dd, *J* = 8.6, 1.0 Hz, 1H), 6.46 (d, *J* = 8.6 Hz, 1H), 3.79 (d, *J* = 11.3 Hz, 1H), 3.48–3.40 (m, 1H), 3.44 (s, 3H), 2.82 (d, *J* = 15.4 Hz, 1H), 2.62 (dd, *J* = 15.5, 1.0 Hz, 1H), 2.15–1.99 (m, 1H), 1.82 (s, 1H), 1.70–1.58 (m, 1H), 1.53 (ddd, *J* = 12.4, 10.7, 7.2 Hz, 1H), 1.37 (m, 3H), 1.29–1.13 (m, 3H), 1.12–1.06 (m, 1H), 0.97 (m, 3.7 Hz, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.68 (d, *J* = 6.8 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 151.2, 148.3, 133.6, 128.6, 111.1, 110.5, 83.9, 65.8, 55.4, 51.8, 49.5, 40.6, 37.1, 35.6, 30.7, 30.2, 26.8, 26.6, 19.6, 18.4, 17.8, 15.0 ppm;

HRMS (ESI-TOF): calcd for $C_{22}H_{30}O_3Na^+$ $[M+Na]^+$ 365.2087, found 365.2084.

Preparation of dysiherbol E (10) from dysiherbol E methyl ether 34:



34

10: (+)-dysiherbol E
(revised structure)

To a stirred solution of dysiherbol B methyl ether **34** (4.6 mg, 13.4 µmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (67.0 µL, 67.0 µmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −50 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 6:1→3:1) to give dysiherbol E (**10**) (2.8 mg, 8.52 µmol, 64%).

Characterization of dysiherbol E (10):

Physical state: white foam;

TLC: $R_f = 0.41$ (silica gel, CH_2Cl_2:MeOH = 40:1);

Optical rotation: $[\alpha]_D^{23} = +34.5$ (*c* = 0.5, MeOH);

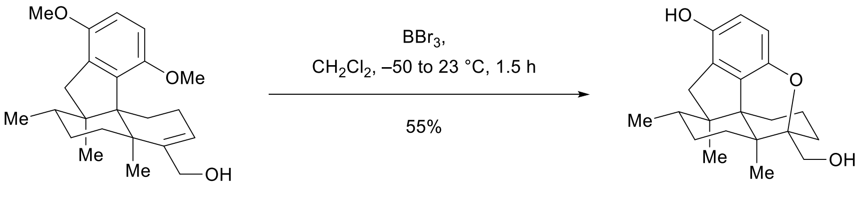
FT-IR (KBr): ν_{max} = 3901, 3854, 3820, 3801, 3711, 3615, 3276, 2871, 1772, 1716, 1622, 1492, 1317, 1185, 956, 802 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (d, *J* = 8.5 Hz, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 4.37 (s, 1H), 3.90 (d, J = 11.3 Hz, 1H), 3.51 (d, J = 11.3 Hz, 1H), 2.56 (s, 2H), 2.06 (s, 1H), 2.00 (dd, J = 14.8, 6.1 Hz, 1H), 1.85 (tdd, J = 14.8, 9.5, 5.7 Hz, 2H), 1.59 (dt, J = 12.1, 5.4 Hz, 2H), 1.44–1.29 (m, 5H), 1.24 (s, 3H), 1.21 (d, J = 8.2 Hz, 2H), 1.08 (s, 3H), 0.82 (d, J = 6.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$): δ = 147.7, 146.1, 133.1, 126.2, 114.5, 111.4, 83.6, 65.8, 52.2, 49.4, 39.5, 37.0, 35.4, 30.6, 30.0, 26.6, 26.4, 19.3, 18.6, 17.9, 15.1 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{28}O_3Na^+$ $[M+Na]^+$ 351.1931, found 351.1928.

Preparation of dysiherbol E (10) from allylic alcohol 32:



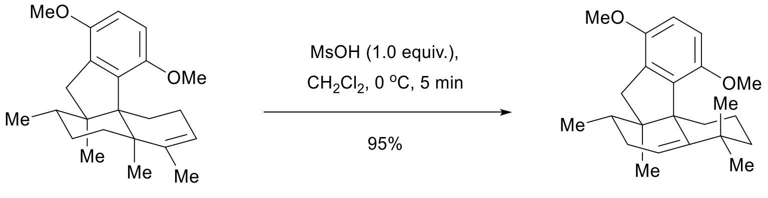
32

10: (+)-dysiherbol E
(revised structure)

To a stirred solution of allylic alcohol **32** (5.1 mg, 14.3 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (71.5 μL, 71.5 μmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −50 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 6:1→3:1) to give dysiherbol E (**10**) (2.6 mg, 7.86 μmol, 55%).

The analytical data of dysiherbol E (**10**) were described above.

Preparation of olefin 35[4]:



14

35

To a stirred solution of dimethyl predysiherbol **14** (15.2 mg, 44.6 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added MsOH (4.3 mg, 2.9 μL, 44.6 μmol, 1.0 equiv.) at 0 °C. The resulting mixture was allowed to stir at this temperature for 5 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give olefin **35** (14.4 mg, 42.4 μmol, 95%).

Characterization of olefin 35:

Physical state: white foam;

TLC: $R_f = 0.41$ (silica gel, petroleum ether:EtOAc = 50:1);

Optical rotation: $[\alpha]_D^{23} = +26.1$ ($c = 1.0$, $CHCl_3$);

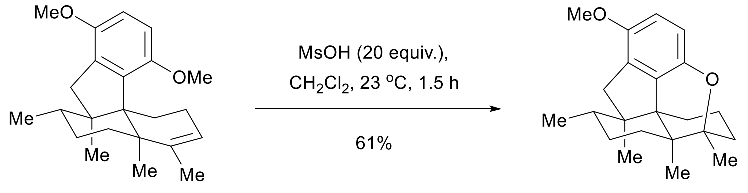
FT-IR (KBr): ν_{max} = 3801, 3689, 3628, 2953, 2861, 2360, 1651, 1540, 1437, 1397, 1376, 1253, 1112, 830 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.47 (d, J = 8.8 Hz, 1H), 6.45 (d, J = 8.8 Hz, 1H), 5.74 (t, J = 3.7 Hz, 1H), 3.44 (s, 3H), 3.32 (s, 3H), 3.16 (d, J = 16.1 Hz, 1H), 2.78 (d, J = 16.1 Hz, 1H), 2.52–2.39 (m, 1H), 1.98–1.89 (m, 1H), 1.88–1.79 (m, 2H), 1.73–1.60 (m, 2H), 1.59–1.50 (m, 2H), 1.43 (s, 3H), 1.37 (dt, J = 14.5, 3.0 Hz, 1H), 1.31 (s, 3H), 0.86 (s, 3H), 0.74 (d, J = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 152.1, 151.8, 145.6, 142.6, 131.5, 121.1, 109.7, 108.9, 56.0, 55.2, 54.9, 50.3, 38.3, 37.1, 35.0, 33.1, 32.9, 32.2, 30.7, 27.5, 17.1, 17.0, 12.4 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{33}O_2^+$ $[M+H]^+$ 341.2475, found 341.2477.

Preparation of dysiherbol A methyl ether 31 from dimethyl predysiherbol 14 with MsOH:

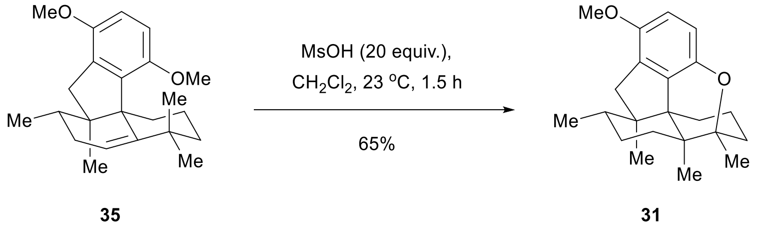


14 **31**

To a stirred solution of dimethyl predysiherbol **14** (10.7 mg, 31.4 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added MsOH (60.4 mg, 40.8 μL, 628 μmol, 20 equiv.) at 0 °C. The resulting mixture was warmed to 23 °C and allowed to stir at this temperature for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give dysiherbol A methyl ether **31** (6.3 mg, 19.2 μmol, 61%).

The analytical data of pentacyclic ether **31** was described above.

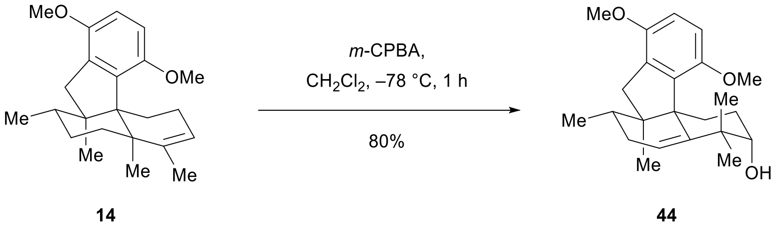
Preparation of dysiherbol A methyl ether 31 from olefin 35 with MsOH:



To a stirred solution of olefin **35** (10.2 mg, 30.0 µmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added MsOH (57.6 mg, 38.9 µL, 600 µmol, 20 equiv.) at 0 °C. The resulting mixture was warmed to 23 °C and allowed to stir at this temperature for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give dysiherbol A methyl ether **31** (6.4 mg, 19.5 µmol, 65%).

The analytical data of dysiherbol A methyl ether **31** was described above.

Preparation of homoallylic alcohol 44 from dimethyl predysiherbol 14 with *m*-CPBA:



To a stirred solution of dimethyl predysiherbol **14** (32.3 mg, 94.9 µmol, 1.0 equiv.) in CH_2Cl_2 (3 mL) was added *m*-CPBA (23.1 mg, 114 µmol, *ca.* 85%, 1.2 equiv.) at −78 °C. The resulting mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) saturated and aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 10:1→8:1) to give homoallylic alcohol **44** (27.1 mg, 75.9 µmol, 80%).

Characterization of homoallylic alcohol 44:

Physical state: white foam;

TLC: $R_f = 0.46$ (silica gel, petroleum ether:EtOAc = 2:1);

Optical rotation: $[\alpha]_D^{23} = -420$ (c = 1.0, $CHCl_3$);

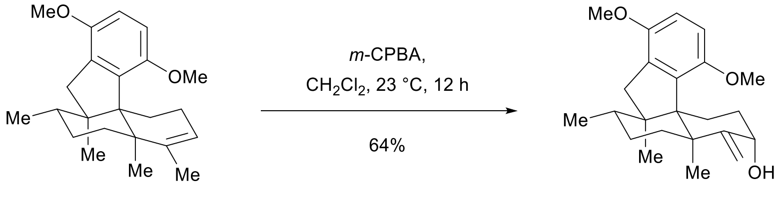
FT-IR (KBr): ν_{max} = 2962, 2930, 2826, 1494, 1462, 1436, 1379, 1255, 1090, 1062, 1024, 995, 965, 789 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.46 (d, J = 8.9 Hz, 1H), 6.43 (d, J = 8.9 Hz, 1H), 5.77 (t, J = 3.7 Hz, 1H), 4.61 (t, J = 7.4 Hz, 1H), 3.43 (s, 3H), 3.28 (s, 3H), 3.10 (d, J = 16.1 Hz, 1H), 2.73 (d, J = 16.1 Hz, 1H), 2.06–1.83 (m, 3H), 1.74 (dt, J = 11.2, 6.3 Hz, 1H), 1.64–1.45 (m, 2H), 1.51 (s, 3H), 1.45–1.33 (m, 1H), 1.24 (s, 3H), 0.95–0.89 (m, 1H), 0.80 (s, 3H), 0.70 (d, J = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 152.0, 151.6, 145.5, 142.7, 131.4, 121.6, 110.6, 109.3, 70.3, 55.4, 55.2, 50.7, 41.1, 37.1, 33.1, 30.4, 28.7, 27.8, 27.7, 27.6, 16.8, 12.4 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{33}O_3^+$ $[M+H]^+$ 357.2424, found 357.2423.

Preparation of allylic alcohol 45 from dimethyl predysiherbol 14 with *m*-CPBA:



14 **45**

To a stirred solution of dimethyl predysiherbol **14** (32.3 mg, 94.9 μmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added *m*-CPBA (23.1 mg, 114 μmol, *ca.* 85%, 1.2 equiv.) at −78 °C. The resulting mixture was allowed to warm to 23 °C gradually and stirred at this temperature for 12 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (10 mL) saturated and aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 15:1→10:1) to give allylic alcohol **45** (21.6 mg, 60.7 μmol, 64%).

Characterization of allylic alcohol 45:

Physical state: white solid;

M.P.: 131–133 °C;

TLC: R_f = 0.42 (silica gel, petroleum ether:EtOAc = 3:1);

Optical rotation: $[\alpha]_D^{23}$ = +54.5 (c = 1.0, $CHCl_3$);

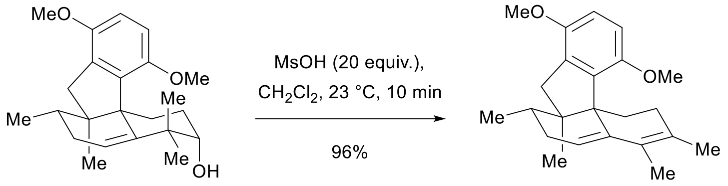
FT-IR (KBr): ν_{max} = 3649, 3523, 3078, 3026, 2932, 2875, 1491, 1455, 1254, 1093, 999, 882, 780, 717 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.47 (d, J = 8.8 Hz, 1H), 6.44 (d, J = 8.8 Hz, 1H), 4.72 (d, J = 1.3 Hz, 1H), 4.67 (d, J = 1.3 Hz, 1H), 4.33 (dd, J = 4.2, 1.8 Hz, 1H), 3.42 (s, 3H), 3.17 (s, 3H), 2.94 (d, J = 16.0 Hz, 1H), 2.62 (d, J = 16.0 Hz, 1H), 2.41 (td, J = 13.4, 3.9 Hz, 1H), 1.85–1.56 (m, 4H), 1.55 (s, 3H), 1.55–1.40 (m, 2H), 1.37–1.24 (m, 1H), 1.19 (dt, J = 13.0, 3.6 Hz, 1H), 1.06 (s, 3H), 1.04 (s, 1H), 0.76 (d, J = 6.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 163.7, 152.0, 151.5, 140.0, 132.5, 110.0, 109.1, 104.8, 73.3, 61.6, 55.1, 52.3, 50.3, 41.8, 40.9, 35.1, 32.4, 29.6, 28.4, 28.2, 24.5, 18.0, 17.7 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{33}O_3^+$ $[M+H]^+$ 357.2424, found 357.2424.

Preparation of tetracyclic diene 46 from homoallylic alcohol 44:



44 **46**

To a stirred solution of homoallylic alcohol **44** (8.4 mg, 23.6 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added MsOH (45.3 mg, 30.6 μL, 471 μmol, 20 equiv.) at 23 °C. The resulting mixture was allowed to stir at this temperature for 10 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give tetracyclic diene **46** (7.7 mg, 22.6 μmol, 96%).

Characterization of tetracyclic diene 46:

Physical state: white foam;

M.P.: 123–125 °C;

TLC: R_f = 0.55 (silica gel, petroleum ether:EtOAc = 10:1);

Optical rotation: $[\alpha]_D^{23}$ = −7.9 (c = 1.0, $CHCl_3$);

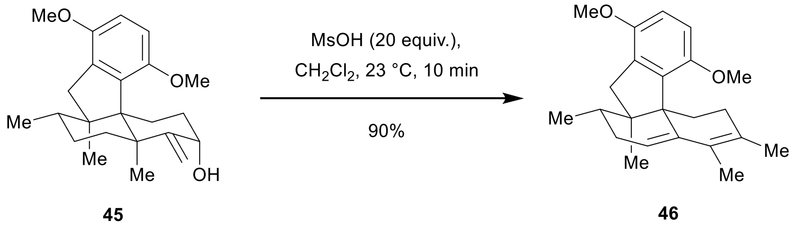
FT-IR (KBr): ν_{max} = 2964, 2934, 2904, 2883, 2826, 1489, 1463, 1431, 1256, 1090, 1049, 796 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.50 (d, *J* = 8.8 Hz, 1H), 6.46 (d, *J* = 8.8 Hz, 1H), 5.83–5.77 (m, 1H), 3.44 (s, 3H), 3.26 (s, 3H), 3.24 (d, *J* = 17.2 Hz, 1H), 2.75 (d, *J* = 16.1 Hz, 1H), 2.08 (t, *J* = 15.3 Hz, 1H), 2.02–1.92 (m, 1H), 1.97 (s, 3H), 1.90–1.83 (m, 1H), 1.85–1.80 (m, 2H), 1.82 (s, 3H), 1.75 (td, *J* = 12.2, 4.5 Hz, 1H), 1.63 (ddd, *J* = 12.0, 4.5, 2.4 Hz, 1H), 0.90 (s, 3H), 0.79 (d, *J* = 6.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 153.2, 151.7, 141.4, 137.4, 131.2, 129.5, 127.4, 120.0, 110.9, 109.0, 56.2, 55.4, 55.2, 49.3, 37.0, 32.9, 31.4, 31.1, 30.7, 21.0, 16.6, 15.1, 12.9 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{31}O_2^+$ [M+H]$^+$ 339.2319, found 339.2320.

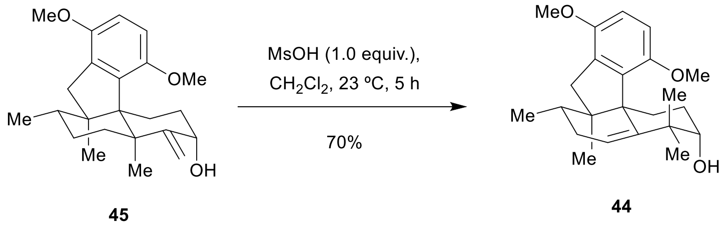
Preparation of tetracyclic diene 46 from allylic alcohol 45:



To a stirred solution of homoallylic alcohol **45** (7.8 mg, 21.9 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added MsOH (42.0 mg, 28.4 μL, 438 μmol, 20 equiv.) at 23 °C. The resulting mixture was allowed to stir at this temperature for 10 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give tetracyclic diene **46** (6.7 mg, 19.7 μmol, 90%).

The analytical data of tetracyclic diene **46** was described above.

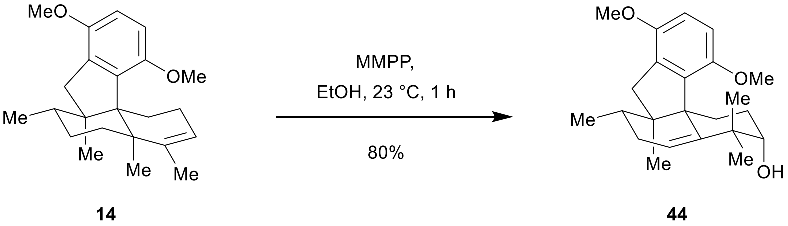
Preparation of homoallylic alcohol 44 from allylic alcohol 45 with MsOH:



To a stirred solution of allylic alcohol **45** (6.2 mg, 17.4 μmol, 1.0 equiv.) in CH_2Cl_2 (0.5 mL) was added MsOH (1.7 mg, 1.0 µL, 17.4 µmol, 1.0 equiv.) at 0 °C. The resulting mixture was warmed to 23 °C and allowed to stir at this temperature for 5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give homoallylic alcohol **44** (4.3 mg, 12.2 µmol, 70%).

The analytical data of homoallylic alcohol **44** was described above.

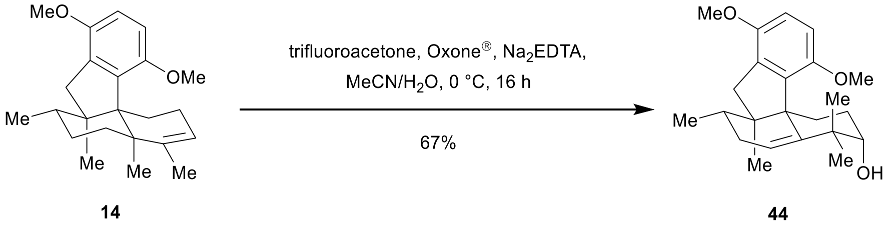
Preparation of homoallylic alcohol 44 from dimethyl predysiherbol 14 with MMPP:



To a stirred solution of dimethyl predysiherbol **14** (34.7 mg, 102 µmol, 1.0 equiv.) in EtOH (3 mL) was added MMPP (47.8 mg, 122 µmol, *ca.* 80%, 1.2 equiv.) at 0 °C. The resulting mixture was warmed to 23 °C and allowed to stir at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) saturated and aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 10:1→8:1) to give homoallylic alcohol **44** (29.1 mg, 81.6 µmol, 80%).

The analytical data of homoallylic alcohol **44** was described above.

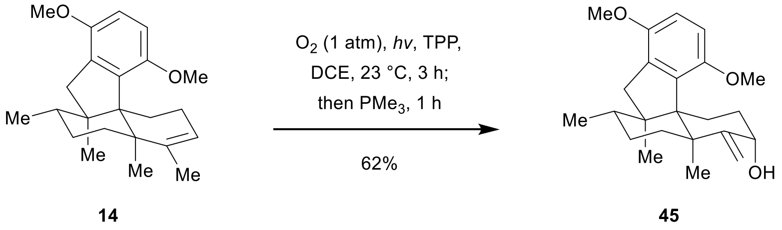
Preparation of homoallylic alcohol 44 from dimethyl predysiherbol 14 with trifluoroacetone-Oxone®-Na2EDTA:



To a stirred solution of dimethyl predysiherbol **14** (10.0 mg, 29.4 µmol, 1.0 equiv.) in MeCN (0.3 mL) was added a mixture of Na_2EDTA (0.22 mg, 0.59 µmol, 0.02 equiv.) in H_2O (6.0 µL) and 1,1,1-trifluoroacetone (33.9 mg, 26.9 µL, 0.294 mmol, 10 equiv.) at 0 °C. Then, a solid mixture of Oxone® (41.0 mg, 0.13 mmol, 4.5 equiv.) and $NaHCO_3$ (17.0 mg, 0.20 mmol, 6.9 equiv.) was added at 0 °C over a period of 20 min. The reaction mixture was stirred for 16 h at 0 °C, before the solid was filtered off and the filtrate was diluted with H_2O (2 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 3 mL). 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 = 9:1) to provide homoallylic alcohol **44** (7.0 mg, 19.7 µmol, 67%).

The analytical data of homoallylic alcohol **44** was described above.

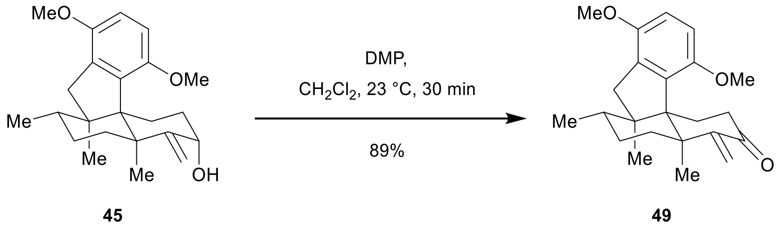
Preparation of allylic alcohol 45 from dimethyl predysiherbol 14 through O_2 ene reaction:



To a stirred solution of dimethyl predysiherbol **14** (49.6 mg, 146 µmol, 1.0 equiv.) in DCE (3 mL) was added TPP (9.0 mg, 14.6 µmol, 0.1 equiv.) at 23 °C under O_2. The resulting mixture was stirred at this temperature for 3 h, using a fluorescent lamp (Essential 23 W, PHILIPS®, distance ~5 cm) as the light. PMe_3 (291 µL, 291 µmol, 1.0 M in THF, 2.0 equiv.) was added to quench the reaction and stirred for 1 h. The solvent was removed in vacuo and the crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 15:1→10:1) to give allylic alcohol **45** (32.1 mg, 90.5 µmol, 62%).

The analytical data of allylic alcohol **45** was described above.

Preparation of ketone 49:



To a stirred solution of allylic alcohol **45** (22.1 mg, 62.0 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added Dess–Martin periodinane (52.6 mg, 124 μmol, 2.0 equiv.) at 0 °C. The resulting mixture was warmed to 23 °C and allowed to stir at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) and $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 15:1→10:1) to give ketone **49** (19.6 mg, 55.2 μmol, 89%).

Characterization of ketone 49:

Physical state: colorless oil;

TLC: $R_f = 0.47$ (silica gel, petroleum ether:EtOAc = 3:1);

Optical rotation: $[\alpha]_D^{23} = +68.9$ ($c = 1.0$, $CHCl_3$);

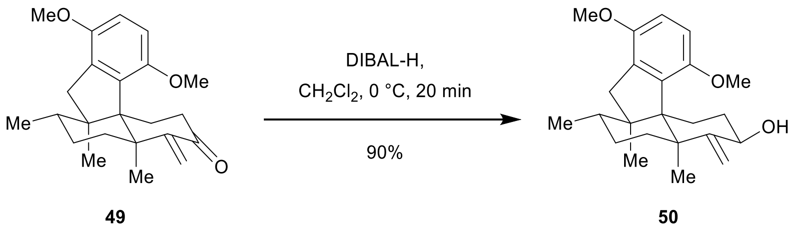
FT-IR (KBr): ν_{max} = 2947, 2906, 2832, 1688, 1603, 1492, 1460, 1385, 1260, 1092, 1066, 1029, 983, 919, 802, 721 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.43 (d, J = 8.8 Hz, 1H), 6.38 (d, J = 8.8 Hz, 1H), 6.26 (d, J = 1.6 Hz, 1H), 4.89 (d, J = 1.6 Hz, 1H), 3.41 (s, 3H), 3.11 (s, 3H), 2.96 (d, J = 16.1 Hz, 1H), 2.54 (d, J = 16.1 Hz, 1H), 2.38 (ddd, J = 18.2, 5.4, 1.8 Hz, 1H), 2.21 (ddd, J = 18.1, 13.7, 6.8 Hz, 1H), 1.92 (td, J = 13.5, 5.4 Hz, 1H), 1.63 (dd, J = 7.8, 3.2 Hz, 2H), 1.56–1.42 (m, 1H), 1.41–1.17 (m, 3H), 1.09 (s, 3H), 0.89 (s, 3H), 0.72 (d, J = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 197.7, 158.2, 151.5, 151.5, 138.2, 132.3, 110.0, 109.7, 109.4, 59.2, 55.1, 52.3, 50.4, 42.2, 40.5, 36.7, 35.0, 33.1, 28.5, 28.4, 27.3, 17.9, 17.5 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{31}O_3^+$ $[M+H]^+$ 355.2268, found 355.2263.

Preparation of allylic alcohol 50:



49 **50**

To a stirred solution of ketone **49** (10.3 mg, 29.1 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added DIBAL-H (58.1 μL, 58.1 μmol, 1.0 M in toluene, 2.0 equiv.) at −20 °C. The resulting mixture was allowed to warm to 0 °C and stirred at this temperature for 20 min. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 12:1) to give allylic alcohol **50** (9.0 mg, 25.3 μmol, 90%).

Characterization of allylic alcohol 50:

Physical state: white foam;

TLC: $R_f = 0.39$ (silica gel, petroleum ether:EtOAc = 3:1);

Optical rotation: $[\alpha]_D^{23} = +18.8$ ($c = 1.0$, $CHCl_3$);

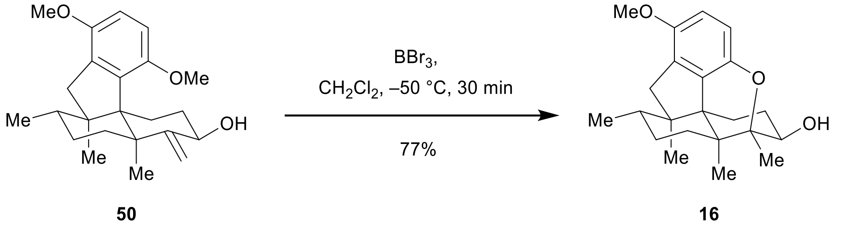
FT-IR (KBr): ν_{max} = 3475, 3027, 2934, 2867, 2831, 1738, 1492, 1458, 1384, 1255, 1148, 1049, 878, 791, 720 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.47 (d, J = 8.9 Hz, 1H), 6.45 (d, J = 8.9 Hz, 1H), 5.31 (t, J = 1.7 Hz, 1H), 4.82–4.77 (m, 1H), 4.47 (s, 1H), 3.41 (s, 3H), 3.18 (s, 3H), 2.95 (d, J = 16.0 Hz, 1H), 2.55 (d, J = 16.0 Hz, 1H), 1.83 (ddd, J = 10.0, 5.3, 2.7 Hz, 1H), 1.76 (ddd, J = 12.7, 5.7, 3.2 Hz, 2H), 1.61 (td, J = 12.8, 4.2 Hz, 1H), 1.56–1.33 (m, 3H), 1.32–1.27 (m, 1H), 1.27–1.24 (m, 2H), 1.18 (s, 3H), 0.94 (s, 3H), 0.74 (d, J = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 163.0, 151.9, 151.6, 140.0, 132.3, 111.2, 109.2, 97.7, 69.5, 61.7, 55.1, 53.0, 50.3, 42.7, 40.6, 34.9, 33.3, 32.8, 28.6, 28.3, 27.0, 18.0, 17.6 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{33}O_3^+$ $[M+H]^+$ 357.2424, found 357.2421.

Preparation of dysiherbol B methyl ether 16 from allylic alcohol 50:



To a stirred solution of allylic alcohol **50** (11.3 mg, 31.7 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (38.0 μL, 38.0 μmol, 1.0 M in CH_2Cl_2, 1.2 equiv.) at −50 °C. The resulting mixture was stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 15:1→10:1) to give dysiherbol B methyl ether **16** (8.4 mg, 24.4 μmol, 77%).

Characterization of dysiherbol B methyl ether 16:

Physical state: pale yellow oil;

TLC: $R_f = 0.41$ (silica gel, petroleum ether:EtOAc = 3:1);

Optical rotation: $[\alpha]_D^{23} = +13.5$ ($c = 1.0$, $CHCl_3$);

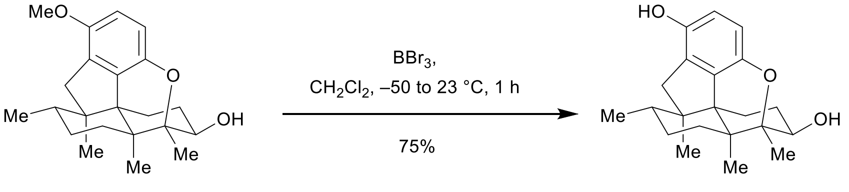
FT-IR (KBr): ν_{max} = 3432, 2961, 2926, 2855, 1492, 1457, 1401, 1381, 1261, 1102, 1074, 1028, 799 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.69 (d, J = 8.6 Hz, 1H), 6.41 (d, J = 8.6 Hz, 1H), 3.73 (td, J = 11.2, 6.7 Hz, 1H), 3.42 (s, 3H), 2.80 (d, J = 15.4 Hz, 1H), 2.57 (dd, J = 15.4, 1.0 Hz, 1H), 1.91 (d, J = 11.3 Hz, 1H), 1.82 (dtd, J = 10.5, 6.1, 1.5 Hz, 1H), 1.55–1.42 (m, 1H), 1.39 (s, 3H), 1.33 (dt, J = 12.9, 3.6 Hz, 1H), 1.27–1.11 (m, 4H), 1.14–1.02 (m, 1H), 0.97 (dq, J = 13.5, 3.6 Hz, 1H), 0.81 (s, 3H), 0.79–0.77 (s, 3H), 0.67 (d, J = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 151.3, 148.1, 133.7, 128.5, 111.3, 110.6, 84.6, 72.1, 55.4, 51.6, 48.6, 40.5, 37.6, 35.7, 30.7, 30.7, 27.1, 26.5, 17.8, 17.4, 15.0 ppm;

HRMS (ESI-TOF): calcd for $C_{22}H_{31}O_3^+$ $[M+H]^+$ 343.2268, found 343.2269.

Preparation of dysiherbol B (7) from dysiherbol B methyl ether 16:



16

7: (+)-dysiherbol B
(revised structure)

To a stirred solution of dysiherbol B methyl ether **16** (9.3 mg, 27.2 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (136 μL, 136 μmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −50 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 6:1→3:1) to give dysiherbol B (**7**) (6.7 mg, 20.4 μmol, 75%).

Characterization of dysiherbol B (7):

Physical state: white solid;

M.P.: 235–237 °C;

TLC: $R_f = 0.49$ (silica gel, petroleum ether:EtOAc = 1:1);

Optical rotation: $[\alpha]_D^{23} = +20.0$ ($c = 1.0$, MeOH);

FT-IR (KBr): ν_{max} = 3565, 3422, 2926, 2855, 1715, 1700, 1650, 1490, 1339, 1258, 1105, 1061, 1033 cm^{-1};

^{1}H NMR (400 MHz, pyridine-*d*$_5$): δ = 10.61 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.17 (dd, *J* = 11.8, 6.3 Hz, 1H), 2.96 (d, *J* = 15.2 Hz, 1H), 2.76 (d, *J* = 15.2 Hz, 1H), 2.12–2.04 (m, 1H), 1.86 (td, *J* = 13.1, 4.3 Hz, 1H), 1.68 (td, *J* = 12.7, 5.2 Hz, 1H), 1.61 (s, 3H), 1.54–1.46 (m, 1H), 1.45–1.40 (m, 1H), 1.40–1.35 (m, 1H), 1.35–1.32 (m, 1H), 1.31–1.23 (m, 1H), 1.13 (s, 3H), 1.12–1.07 (m, 1H), 0.99 (s, 3H), 0.73 (d, *J* = 6.2 Hz, 3H) ppm;

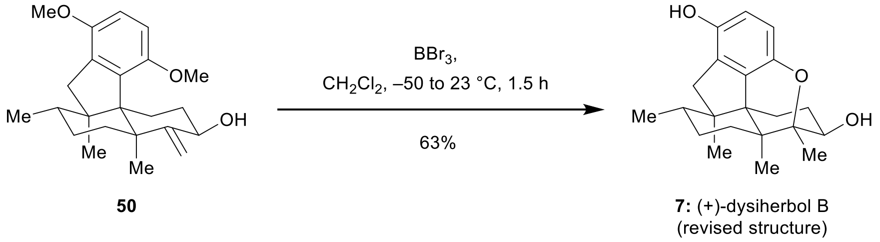
^{1}H NMR (400 MHz, CD$_3$OD): δ = 6.45 (d, *J* = 8.6 Hz, 1H), 6.41 (d, *J* = 8.6 Hz, 1H), 3.90 (dd, *J* = 12.0, 6.4 Hz, 1H), 2.62 (d, *J* = 15.3 Hz, 1H), 2.53 (d, *J* = 15.3 Hz, 1H), 1.96 (td, *J* = 13.3, 4.5 Hz, 1H), 1.86–1.77 (m, 1H), 1.49–1.38 (m, 3H), 1.38–1.31 (m, 1H), 1.29 (s, 3H), 1.26–1.22 (m, 1H), 1.21 (s, 3H), 1.20–1.12 (m, 2H), 1.09 (s, 3H), 0.86 (d, *J* = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, pyridine-*d*$_5$): δ = 149.4, 148.0, 133.9, 127.4, 115.6, 112.2, 85.1, 72.6, 52.1, 49.4, 41.2, 38.3, 36.2, 31.1, 31.0, 27.8, 27.1, 18.4, 18.3, 18.2, 15.5 ppm;

^{13}C NMR (101 MHz, CD$_3$OD): δ = 148.3, 148.2, 133.8, 127.2, 115.7, 112.4, 84.8, 73.1, 52.6, 49.7, 40.7, 38.7, 36.7, 31.5, 30.3, 27.9, 27.4, 18.3, 18.0, 17.5, 15.3 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{29}O_3^+$ [M+H]$^+$ 329.2111, found 329.2112.

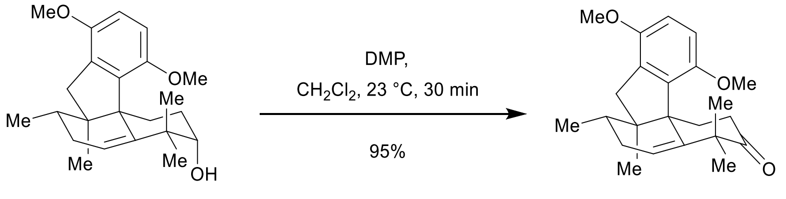
Preparation of dysiherbol B (7) from allylic alcohol 50:



To a stirred solution of allylic alcohol **50** (5.3 mg, 14.9 μmol, 1.0 equiv.) in CH$_2$Cl$_2$ (1 mL) was added BBr$_3$ (74.3 μL, 74.3 μmol, 1.0 M in CH$_2$Cl$_2$, 5.0 equiv.) at −50 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 1.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 6:1→3:1) to give dysiherbol B (**7**) (3.1 mg, 9.4 μmol, 63%).

The analytical data of dysiherbol B (**7**) was described above.

Preparation of ketone 51:



44 **51**

To a stirred solution of homoallylic alcohol **44** (30.1 mg, 84.4 μmol, 1.0 equiv.) in CH_2Cl_2 (3 mL) was added Dess–Martin periodinane (71.6 mg, 169 μmol, 2.0 equiv.) at 0 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) and $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 12:1→8:1) to give ketone **51** (28.4 mg, 80.2 μmol, 95%).

Characterization of ketone 51:

Physical state: colorless oil;

TLC: $R_f = 0.52$ (silica gel, petroleum ether:EtOAc = 2:1);

Optical rotation: $[\alpha]_D^{23} = -9.6$ (c = 1.0, $CHCl_3$);

FT-IR (KBr): ν_{max} = 2957, 2924, 2853, 1706, 1491, 1459, 1374, 1252, 1087, 1056, 1025, 787, 714 cm^{-1};

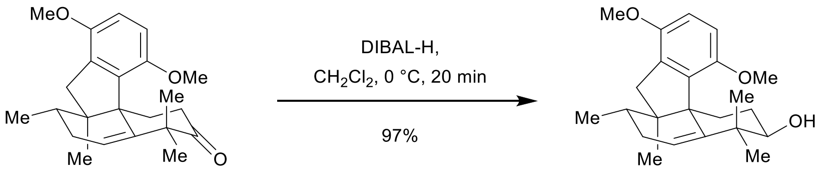
^{1}H NMR (400 MHz, C_6D_6): δ = 6.41 (d, J = 8.7 Hz, 1H), 6.32 (d, J = 8.7 Hz, 1H), 5.63 (t, J = 3.5 Hz, 1H), 3.43 (s, 3H), 3.26 (s, 3H), 3.21 (d, J = 16.1 Hz, 1H), 2.62 (d, J = 16.1 Hz, 1H), 2.27 (ddd, J = 19.3, 6.0, 1.8 Hz, 1H), 2.14 (ddd, J = 19.5, 13.7, 6.1 Hz, 1H), 1.77 (tt, J = 15.1, 5.9 Hz, 3H), 1.71 (s, 3H), 1.62–1.49 (m, 1H), 1.43 (ddd, J = 13.3, 6.1, 1.8 Hz, 1H), 1.23 (s, 3H), 0.78 (s, 3H), 0.73 (d,

J = 6.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 210.4, 151.5, 151.0, 144.3, 140.0, 130.8, 122.8, 109.1, 108.7, 55.3, 55.2, 53.3, 49.9, 49.4, 36.7, 34.3, 33.6, 32.5, 30.5, 27.9, 25.1, 16.6, 12.4 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{30}O_3Na^+$ $[M+Na]^+$ 377.2087, found 377.2084.

Preparation of homoallylic alcohol 52:



51

52

To a stirred solution of ketone **51** (19.8 mg, 55.9 μmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added DIBAL-H (112 μL, 112 μmol, 1.0 M in toluene, 2.0 equiv.) at −20 °C. The resulting mixture was allowed to warm to 0 °C and stirred at this temperature for 20 min. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 10:1) to give homoallylic alcohol **52** (19.3 mg, 54.2 μmol, 97%).

Characterization of homoallylic alcohol 52:

Physical state: white foam;

TLC: R_f = 0.42 (silica gel, petroleum ether:EtOAc = 2:1);

Optical rotation: $[\alpha]_D^{23}$ = −417 (c = 1.0, $CHCl_3$);

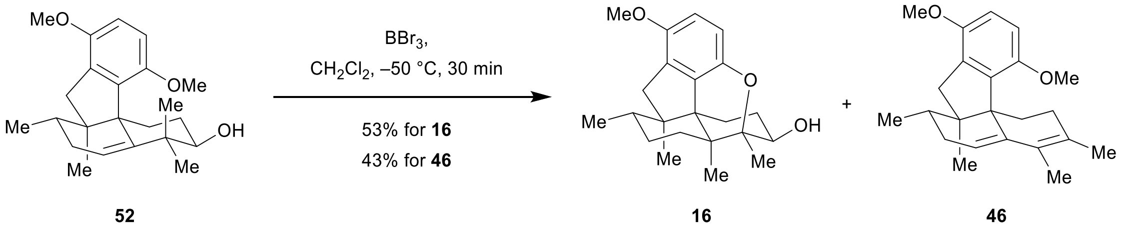
FT-IR (KBr): ν_{max} = 3522, 2959, 2935, 2866, 2842, 1494, 1458, 1378, 1254, 1082, 1058, 971, 790, 716 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.44 (d, J = 8.8 Hz, 1H), 6.38 (d, J = 8.8 Hz, 1H), 5.73 (t, J = 4.0 Hz, 1H), 3.85 (d, J = 11.5 Hz, 1H), 3.67 (ddd, J = 11.5, 8.5, 5.8 Hz, 1H), 3.40 (s, 3H), 3.28 (s, 3H), 3.05 (d, J = 15.9 Hz, 1H), 2.71 (d, J = 15.9 Hz, 1H), 2.20 (ddt, J = 13.5, 8.8, 4.4 Hz, 1H), 1.91 (ddd, J = 18.2, 6.6, 3.9 Hz, 1H), 1.83–1.66 (m, 2H), 1.65–1.48 (m, 2H)1.59 (s, 3H), 1.45 (dt, J = 13.2, 4.5 Hz, 1H), 1.19 (s, 3H), 0.81 (s, 3H), 0.70 (d, J = 6.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 152.8, 150.2, 145.1, 144.6, 131.4, 123.3, 113.8, 109.3, 74.3, 57.9, 55.8, 55.2, 50.7, 40.9, 38.3, 37.9, 33.4, 31.8, 30.9, 27.3, 27.3, 17.5, 12.8 ppm;

HRMS (ESI-TOF): calcd for $C_{23}H_{33}O_3^+$ $[M+H]^+$ 357.2424, found 357.2421.

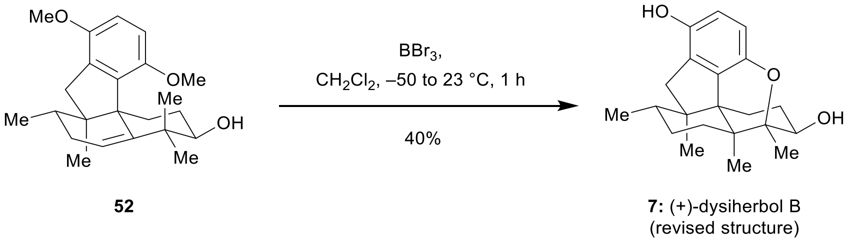
Preparation of dysiherbol B methyl ether 16 from homoallylic alcohol 52:



To a stirred solution of homoallylic alcohol **52** (10.9 mg, 30.6 µmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (36.7 µL, 36.7 µmol, 1.0 M in CH_2Cl_2, 1.2 equiv.) at −50 °C. The resulting mixture was stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 50:1→10:1) to give dysiherbol B methyl ether **16** (5.5 mg, 16.2 µmol, 53%) and tetracyclic diene **46** (4.5 mg, 13.2 µmol, 43%).

The analytical data of dysiherbol B methyl ether **16** and tetracyclic diene **46** were described above.

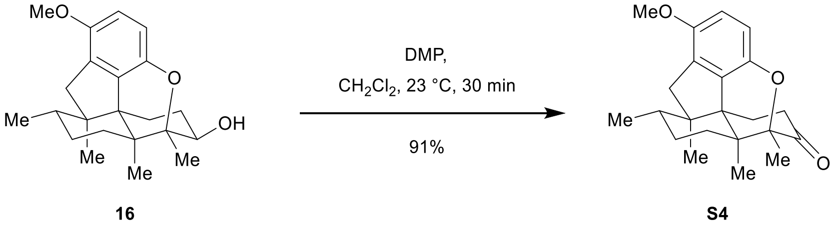
Preparation of dysiherbol B (7) from homoallylic alcohol 52:



To a stirred solution of homoallylic alcohol **52** (5.8 mg, 16.3 µmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (81.3 µL, 81.3 µmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −50 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 6:1→3:1) to give dysiherbol B (**7**) (2.1 mg, 6.5 µmol, 40%).

The analytical data of dysiherbol B (**7**) was described above.

Preparation of dysiherbol C methyl ether S4:



To a stirred solution of dysiherbol B methyl ether **16** (12.5 mg, 36.5 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added Dess–Martin periodinane (31.0 mg, 73.0 µmol, 2.0 equiv.) at 0 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 30 min. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL) and $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 25:1→15:1) to give dysiherbol C methyl ether **S4** (11.3 mg, 33.2 µmol, 91%).

Characterization of dysiherbol C methyl ether S4:

Physical state: colorless oil;

TLC: R_f = 0.48 (silica gel, petroleum ether:EtOAc = 5:1);

Optical rotation: $[\alpha]_D^{23}$ = +260 (*c* = 1.0, $CHCl_3$);

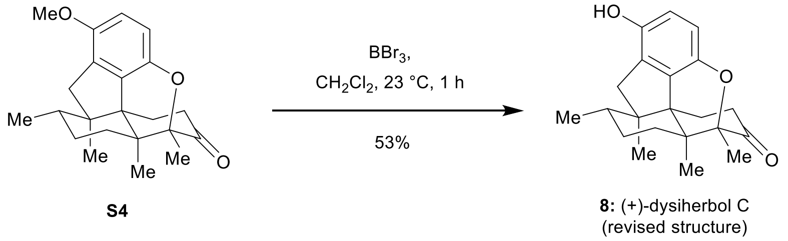
FT-IR (KBr): ν_{max} = 3418, 2953, 1716, 1492, 1456, 1383, 1341, 1312, 1254, 1186, 1106, 1072, 1038, 836, 798 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.73 (d, *J* = 8.7, 1H), 6.41 (d, *J* = 8.7 Hz, 1H), 3.41 (s, 3H), 2.83 (d, *J* = 15.6 Hz, 1H), 2.54 (dd, *J* = 15.6, 1.1 Hz, 1H), 2.22 (ddd, *J* = 15.6, 5.3, 1.7 Hz, 1H), 2.09 (ddd, *J* = 15.6, 12.8, 7.6 Hz, 1H), 1.59 (td, *J* = 12.9, 5.3 Hz, 1H), 1.49 (s, 3H), 1.38–1.10 (m, 3H), 1.10–0.87 (m, 3H), 0.74 (s, 3H), 0.68 (d, *J* = 0.8 Hz, 3H), 0.64 (d, *J* = 6.8 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 204.9, 151.4, 146.4, 132.5, 128.4 112.4, 111.2, 86.6, 55.3, 52.1, 48.3, 40.5, 38.1, 36.8, 35.8, 30.5, 29.2, 26.6, 18.3, 17.6, 15.2, 15.1 ppm;

HRMS (ESI-TOF): calcd for $C_{22}H_{29}O_3^+$ $[M+H]^+$ 341.2111, found 341.2113.

Preparation of dysiherbol C (8) from dysiherbol C methyl ether S4:



To a stirred solution of dysiherbol C methyl ether **S4** (10.3 mg, 30.3 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added BBr_3 (151 μL, 151 μmol, 1.0 M in CH_2Cl_2, 5.0 equiv.) at −20 °C. The resulting mixture was allowed to warm to 23 °C and stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 25:1→15:1) to give dysiherbol C (**8**) (5.2 mg, 16.0 μmol, 53%).

Characterization of dysiherbol C (8):

Physical state: white solid;

M.P.: 241–243 °C;

TLC: $R_f = 0.53$ (silica gel, petroleum ether:EtOAc = 5:1);

Optical rotation: $[\alpha]_D^{23} = +206$ ($c = 1.0$, MeOH);

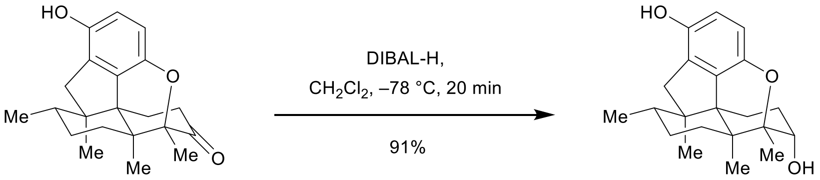
FT-IR (KBr): ν_{max} = 3384, 2957, 2938, 2857, 1705, 1494, 1460, 1385, 1324, 1280, 1251, 1177, 1100, 1021, 952, 907, 806 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$, 7.26): δ = 6.58 (d, J = 8.5 Hz, 1H), 6.53 (d, J = 8.5 Hz, 1H), 4.24 (s, 1H), 2.69 (d, J = 15.3 Hz, 1H), 2.64 (d, J = 15.4 Hz, 1H), 2.38 (dd, 12.0, 4.8 Hz, 1H), 2.20–2.12 (m, 1H), 2.12–2.04 (m, 1H), 1.80–1.69 (m, 1H), 1.40–1.37 (m, 1H), 1.37–1.34 (m, 1H), 1.33 (s, 3H), 1.33–1.31 (m, 1H), 1.31–1.27 (m, 1H), 1.27–1.23 (m, 1H), 1.12 (s, 3H), 1.02 (s, 3H), 0.87 (d, J = 6.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$, 77.16): δ = 206.6, 146.6, 145.7, 132.0, 126.1, 115.6, 112.8, 86.3, 52.6, 48.2, 39.6, 38.1, 36.8, 35.7, 30.5, 29.4, 26.5, 18.6, 17.7, 15.5, 14.7 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{27}O_2^+$ $[M+H]^+$ 327.1955, found 327.1956.

Preparation of *epi*-dysiherbol B S5:



8: (+)-dysiherbol C
(revised structure)

S5

To a stirred solution of dysiherbol C (**8**) (23.8 mg, 72.9 µmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added DIBAL-H (94.8 µL, 94.8 µmol, 1.0 M in toluene, 1.3 equiv.) at −78 °C. The resulting mixture was allowed to stir at this temperature for 20 min. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (3 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 10:1) to give *epi*-dysiherbol B **S5** (21.8 mg, 66.3 µmol, 91%).

Characterization of *epi*-dysiherbol B S5:

Physical state: white foam;

TLC: R_f = 0.49 (silica gel, petroleum ether:EtOAc = 2:1);

Optical rotation: $[\alpha]_D^{23}$ = +39.3 (*c* = 1.0, $CHCl_3$);

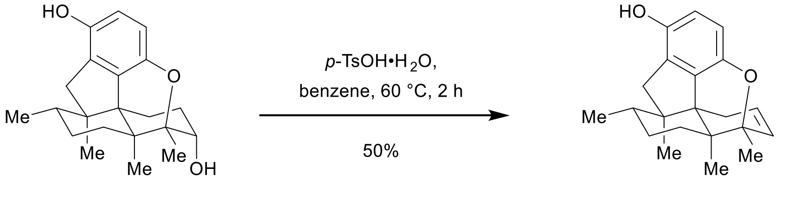
FT-IR (KBr): ν_{max} = 3210, 2981, 2958, 2929, 2860, 1488, 1452, 1382, 1262, 1208, 1103, 1057, 1031, 956, 927, 811 cm^{-1};

^{1}H NMR (400 MHz, C_6D_6): δ = 6.65 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 1H), 3.53 (s, 1H), 2.50 (d, *J* = 15.1 Hz, 1H), 2.43 (d, *J* = 15.1 Hz, 1H), 1.86 (td, *J* = 13.2, 4.5 Hz, 1H), 1.54 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.31–1.26 (m, 1H), 1.26–1.15 (m, 3H), 1.12–0.95 (m, 3H), 0.90 (s, 3H), 0.67 (d, *J* = 5.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, C_6D_6): δ = 147.7, 146.9, 133.4, 126.3, 114.9, 111.8, 83.3, 75.7, 51.8, 49.4, 39.9, 37.0, 35.8, 30.8, 29.6, 26.1, 23.1, 19.1, 17.9, 17.6, 15.0 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{29}O_3^+$ $[M+H]^+$ 329.2111, found 329.2107.

Preparation of dysiherbol D (9) from *epi*-dysiherbol B S5:



S5

9: (+)-dysiherbol D
(revised structure)

To a stirred solution of *epi*-dysiherbol B **S5** (7.7 mg, 23.4 µmol, 1.0 equiv.) in benzene (2 mL) was added *p*-TsOH•H_2O (13.5 mg, 70.2 µmol, 3.0 equiv.) at 23 °C. The resulting mixture was allowed to warm to 60 °C and stirred at this temperature for 2 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (3 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether:EtOAc = 100:1) to give dysiherbol D (**9**) (3.6 mg, 11.7 µmol, 50%).

Characterization of dysiherbol D (9):

Physical state: white foam;

TLC: $R_f = 0.42$ (silica gel, petroleum ether:EtOAc = 10:1);

Optical rotation: $[\alpha]_D^{23} = +40.3$ ($c = 0.5$, MeOH);

FT-IR (KBr): ν_{max} = 3367, 3024, 2919, 2851, 1489, 1461, 1380, 1259, 1197, 1161, 1097, 1080, 962, 893, 801 cm^{-1};

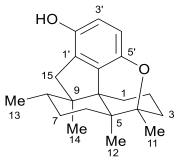
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (d, J = 8.5 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 5.82 (ddd, J = 9.7, 5.3, 2.1 Hz, 1H), 5.37 (ddd, J = 9.7, 2.8, 1.2 Hz, 1H), 4.20 (s, 1H), 2.64 (d, J = 15.2 Hz, 1H), 2.60 (d, J = 15.2 Hz, 1H), 2.46 (dt, J = 17.6, 2.5 Hz, 1H), 2.00 (dd, J = 17.6, 5.3 Hz, 1H), 1.44–1.37 (m, 1H), 1.37–1.26 (m, 3H), 1.35 (s, 4H), 1.13 (s, 3H), 1.11 (s, 3H), 1.11–1.06 (m, 1H), 0.82 (d, J = 6.8 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.2, 145.8, 135.7, 129.7, 129.7, 126.5, 115.0, 113.4, 80.0, 51.9, 49.1, 39.5, 36.3, 35.3, 32.1, 29.5, 26.4, 19.9, 18.2, 17.8, 15.8 ppm;

HRMS (ESI-TOF): calcd for $C_{21}H_{27}O_2^+$ $[M+H]^+$ 311.2006, found 311.2002.

III. Comparison of Spectroscopic Data of Natural and Synthetic (+)-Dysiherbols A–E.

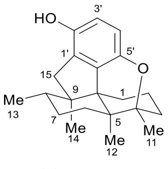
Table S1. Comparison of ^{1}H NMR spectroscopic data (CDCl$_3$) of natural and synthetic (+)-dysiherbol A (6).



6: (+)-dysiherbol A
(revised structure)

Position	**Natural**[5] δ ^{1}H [ppm; mult; *J* (Hz)] 600 MHz, CDCl$_3$, 7.26	**Synthetic** δ ^{1}H [ppm; mult; *J* (Hz)] 400 MHz, CDCl$_3$, 7.26	**Deviation** (synthetic−natural) Δδ (ppm)
1*α*	1.84; td; 12.6, 4.8	1.84; td; 12.8, 4.6	0
1*β*	1.22; m	1.23–1.22; m	-
2*α*	1.49; m	1.54–1.46; m	-
2*β*	1.30; m	1.32–1.30; m	-
3*α*	1.36; td; 13.2, 4.2	1.37–1.33; m	-
3*β*	1.28; m	1.30–1.27; m	-
6*α*	1.68; dd; 14.4, 6.0	1.68; dd; 15.0, 5.8	0
6*β*	1.95; td; 13.8, 6.6	1.96; td; 13.9, 6.5	0.01
7*α*	1.32; m	1.34–1.32; m	-
7*β*	1.37; m	1.42–1.37; m	-
8	1.24; m	1.26–1.23; m	-
11	1.22; s	1.22; s	0
12	1.21; s	1.21; s	0
13	0.83; d; 6.6	0.83; d; 6.5	0
14	1.07; s	1.08; s	0.01
15*α*	2.57; d; 14.4	2.57; d; 15.4	0
15*β*	2.54; d; 14.4	2.53; d; 15.4	−0.01
3'	6.49; d; 8.4	6.49; d; 8.5	0
4'	6.43; d; 8.4	6.42; d; 8.5	−0.01
2'-OH	4.23; br s	4.24; s	0.01

Table S2. Comparison of ^{13}C NMR spectroscopic data ($CDCl_3$) of natural and synthetic (+)-dysiherbol A (6).

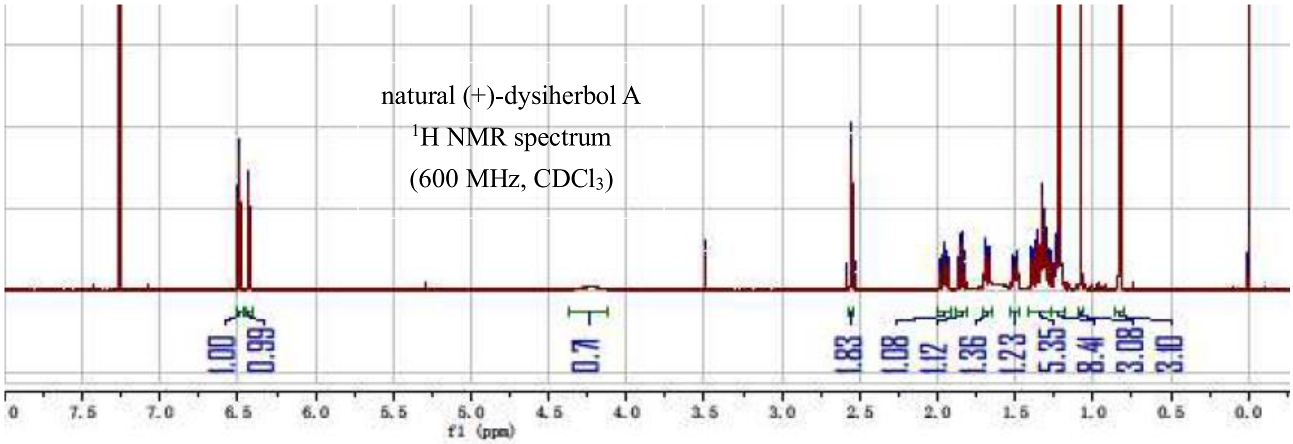


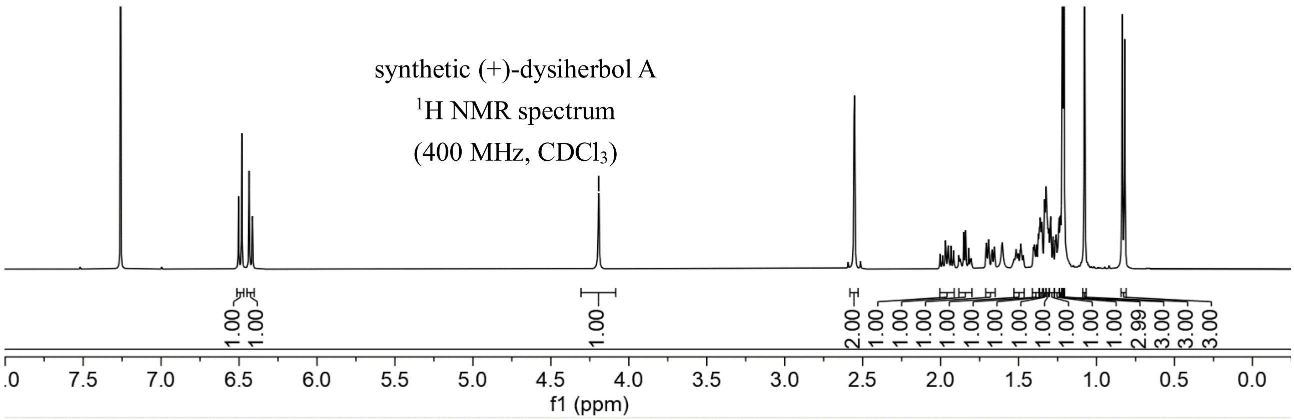
6: (+)-dysiherbol A
(revised structure)

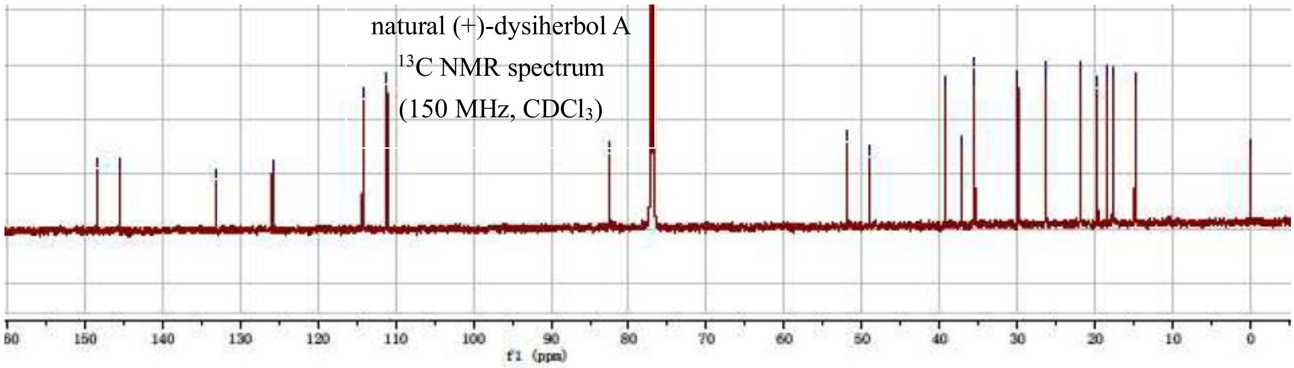
Position	Natural[5] δ ^{13}C [ppm] 150 MHz $CDCl_3$, 77.00	Synthetic δ ^{13}C [ppm] 101 MHz $CDCl_3$, 77.16	Deviation (synthetic−natural) Δδ (ppm)	Deviation (synthetic−natural) Δδ (ppm)[a]
1	26.41	26.58	0.17	0
2	19.7	19.9	0.2	0
3	29.9	30.1	0.2	0
4	82.4	82.5	0.2	0
5	37.2	37.4	0.2	0
6	35.7	35.8	0.2	0
7	26.36	26.52	0.16	0
8	35.5	35.6	0.1	0
9	51.9	52.0	0.1	−0.1
10	49.1	49.3	0.2	0
11	21.9	22.1	0.2	0
12	18.5	18.6	0.1	0
13	17.8	17.9	0.1	0
14	14.9	15.0	0.1	0
15	39.3	39.5	0.2	0
1'	125.8	126.0	0.2	0.1
2'	145.5	145.7	0.2	0.1
3'	114.2	114.4	0.2	0.1
4'	111.1	111.2	0.1	0
5'	148.3	148.5	0.2	0
6'	133.1	133.2	0.2	−0.1

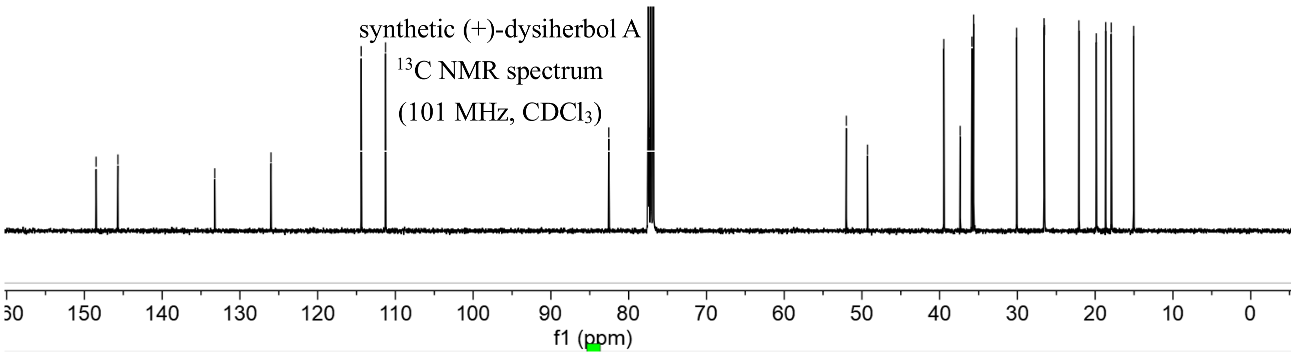
[a] To compare the ^{13}C NMR spectroscopic data of the synthetic (+)-dysiherbol A (**6**) with the natural one, the internal reference of $CDCl_3$ used in the synthetic sample was adjusted from 77.16 ppm to 77.00 ppm, which is consistent with that used in the natural sample.

Comparison of NMR spectra of natural and synthetic (+)-dysiherbol A (6).

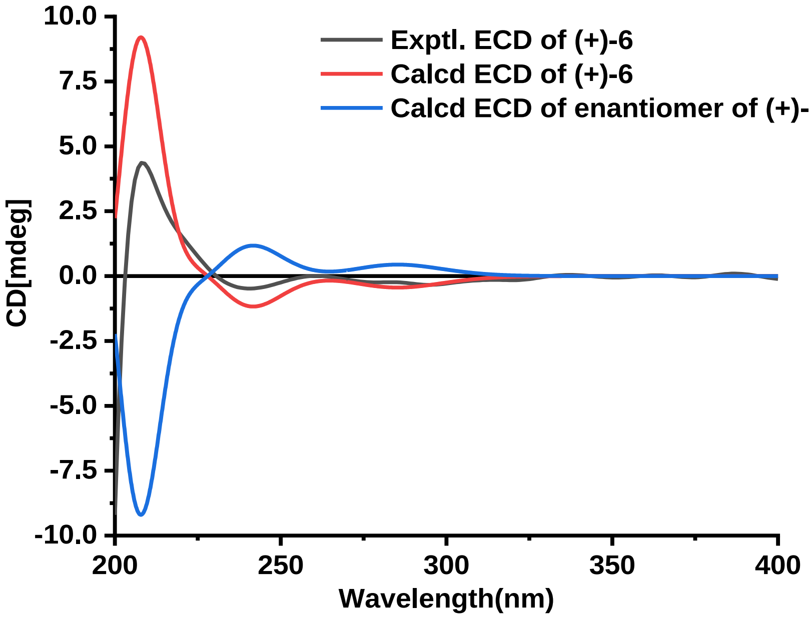


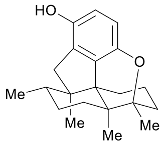






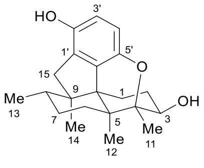
Experimental and calculated ECDs of the revised structure of (+)-dysiherbol A (6).





6: (+)-dysiherbol A
(revised structure)

Table S3. Comparison of ^{1}H NMR spectroscopic data (pyridine-d_5) of natural and synthetic (+)-dysiherbol B (7).

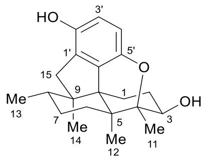


7: (+)-dysiherbol B
(revised structure)

Position	**Natural**[5] δ ^{1}H [ppm; mult; *J* (Hz)] 600 MHz, pyridine-d_5, 8.71	**Synthetic** δ ^{1}H [ppm; mult; *J* (Hz)] 400 MHz, pyridine-d_5, 8.74	**Deviation** (synthetic−natural) Δδ (ppm)	 Δδ (ppm)[a]
1*α*	1.85; td; 13.2, 4.4	1.86; td; 13.1, 4.3	0.01	−0.02
1*β*	1.39; m	1.45–1.40; m	-	-
2*α*	2.05; m	2.12–2.04; m	-	-
2*β*	1.64; td; 12.8, 5.6	1.68; td; 12.7, 5.2	0.04	0.01
3*α*	4.15; dd; 12.0, 6.4	4.17; dd; 11.8, 6.3	0.02	−0.01
6*α*	1.46; m	1.54–1.46; m	-	-
6*β*	1.39; m	1.40–1.35; m	-	-
7*α*	1.30; m	1.31–1.23; m	-	-
7*β*	1.09; m	1.12–1.07; m	-	-
8	1.31; m	1.35–1.32; m	-	-
11	1.58; s	1.61; s	0.03	0
12	1.12; s	1.13; s	0.01	−0.02
13	0.72; d; 6.0	0.73; d; 6.2	0.01	−0.02
14	0.97; s	0.99; s	0.02	−0.01
15*α*	2.93; d; 15.2	2.96; d; 15.2	0.03	0
15*β*	2.74; d; 15.2	2.76; d; 15.2	0.02	−0.01
3'	6.91; d; 8.4	6.92; d; 8.4	0.01	−0.02
4'	6.62; d; 8.4	6.64; d; 8.4	0.02	−0.01
-OH	-	10.61; s	-	-

[a] To compare the ^{1}H NMR spectroscopic data of the synthetic (+)-dysiherbol B (**7**) with the natural one, the internal reference of pyridine-d_5 used in the synthetic sample was adjusted from 8.74 ppm to 8.71 ppm, which is consistent with that used in the natural sample.

Table S4. Comparison of ^{13}C NMR spectroscopic data (pyridine-d_5) of natural and synthetic (+)-dysiherbol B (7).

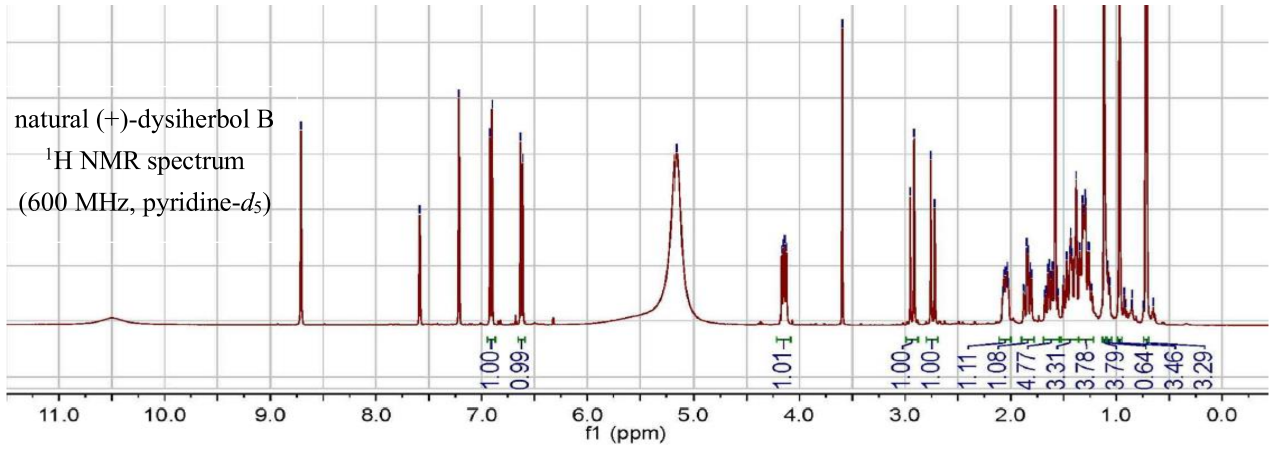


7: (+)-dysiherbol B
(revised structure)

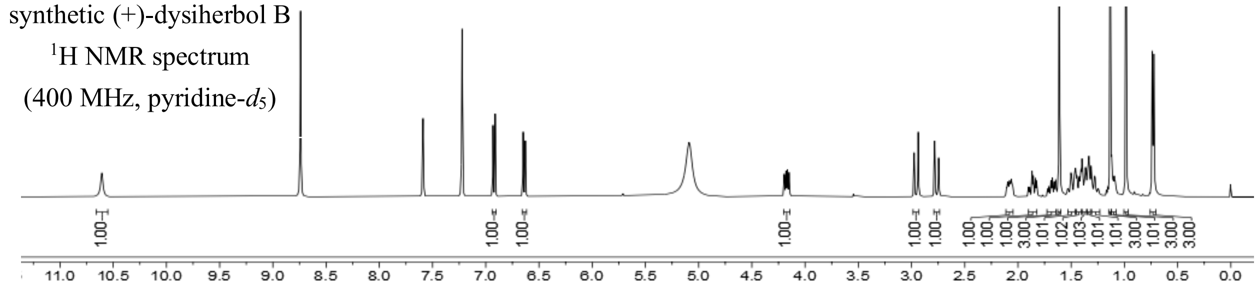
Position	**Natural**[5] δ ^{13}C [ppm] 150 MHz pyridine-d_5, 149.20	**Synthetic** δ ^{13}C [ppm] 101 MHz pyridine-d_5, 150.35	**Deviation** (synthetic−natural)	
			Δδ (ppm)	Δδ (ppm)[a]
1	26.7	27.8	1.1	0
2	29.8	31.0	1.2	0
3	71.5	72.6	1.1	−0.1
4	84.0	85.1	1.1	−0.1
5	37.2	38.3	1.1	−0.1
6	30.1	31.1	1.0	−0.1
7	26.0	27.1	1.1	−0.1
8	35.1	36.2	1.1	−0.1
9	51.0	52.1	1.1	−0.1
10	48.3	49.4	1.1	−0.1
11	17.1	18.2	1.1	−0.1
12	17.3	18.4	1.1	−0.1
13	17.2	18.3	1.1	−0.1
14	14.5	15.5	1.0	−0.1
15	40.1	41.2	1.1	−0.1
1'	126.3	127.4	1.1	−0.1
2'	148.2	149.4	1.2	0
3'	114.6	115.6	1.0	−0.1
4'	111.1	112.2	1.1	−0.1
5'	146.9	148.0	1.1	−0.1
6'	132.8	133.9	1.1	0

[a] To compare the ^{13}C NMR spectroscopic data of the synthetic (+)-dysiherbol B (**7**) with the natural one, the internal reference of pyridine-d_5 used in the synthetic sample was adjusted from 150.35 ppm to 149.20 ppm, which is consistent with that used in the natural sample.

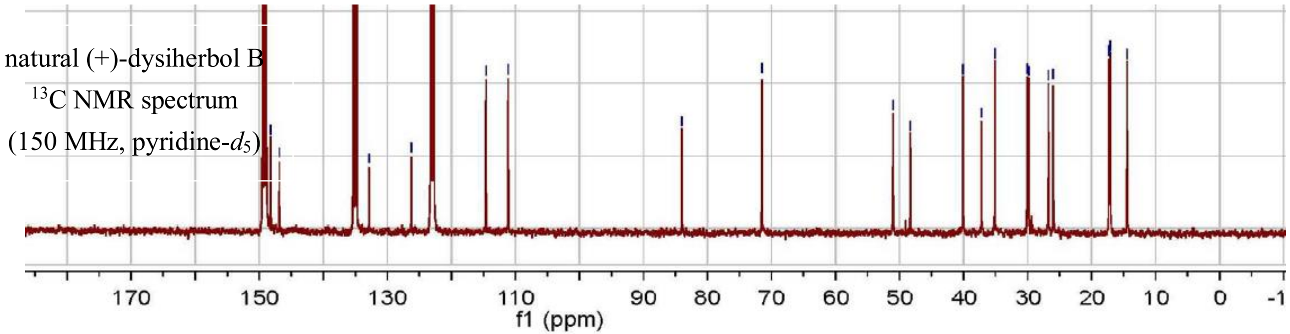
Comparison of NMR spectra of natural and synthetic (+)-dysiherbol B (7).



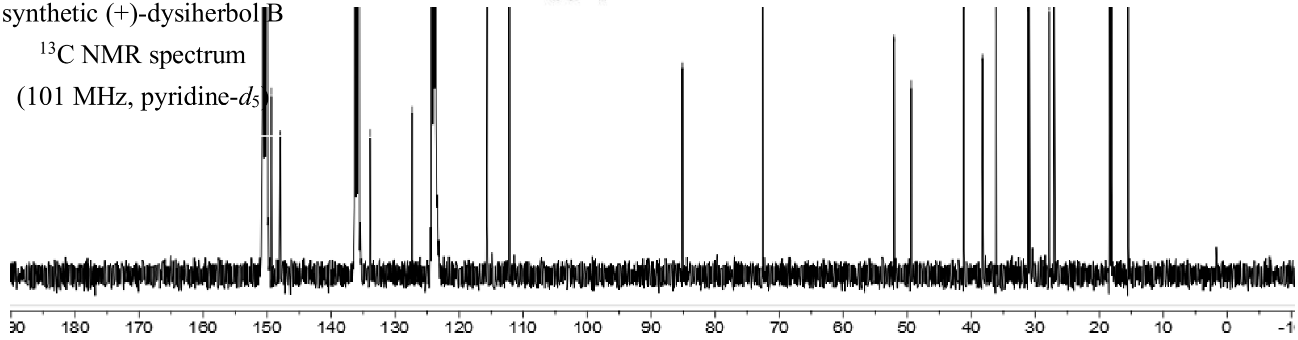
natural (+)-dysiherbol B
^{1}H NMR spectrum
(600 MHz, pyridine-d_5)



synthetic (+)-dysiherbol B
^{1}H NMR spectrum
(400 MHz, pyridine-d_5)

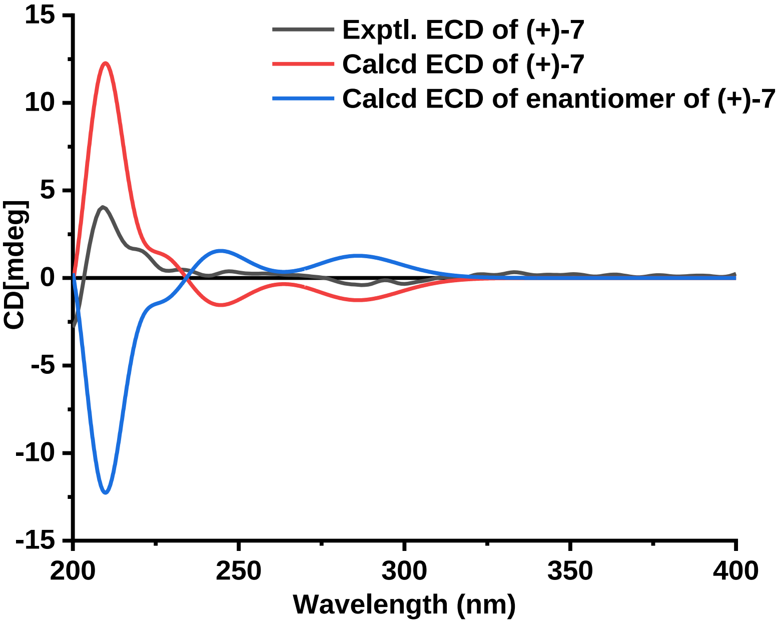


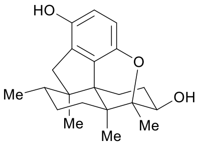
natural (+)-dysiherbol B
^{13}C NMR spectrum
(150 MHz, pyridine-d_5)



synthetic (+)-dysiherbol B
^{13}C NMR spectrum
(101 MHz, pyridine-d_5)

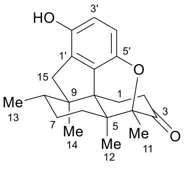
Experimental and calculated ECDs of the revised structure of (+)-dysiherbol B (7).





7: (+)-dysiherbol B
(revised structure)

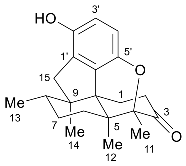
Table S5. Comparison of ^{1}H NMR spectroscopic data (CDCl$_3$) of natural and synthetic (+)-dysiherbol C (8).



8: (+)-dysiherbol C
(revised structure)

Position	**Natural**[5] δ ^{1}H [ppm; mult; *J* (Hz)] 600 MHz, CDCl$_3$, 7.26	**Synthetic** δ ^{1}H [ppm; mult; *J* (Hz)] 400 MHz, CDCl$_3$, 7.26	**Deviation** (synthetic−natural) Δδ (ppm)
1*α*	2.09; m	2.12–2.04; m	-
1*β*	1.74; m	1.80–1.69; m	-
2*α*	2.39; dd; 14.4, 4.8	2.38; dd; 12.0, 4.8	−0.01
2*β*	2.16; m	2.20–2.12; m	-
6*α*	1.37; m	1.40–1.37; m	-
6*β*	1.31; m	1.33–1.31; m	-
7*α*	1.28; m	1.31–1.27; m	-
7*β*	1.34; m	1.37–1.34; m	-
8	1.24; m	1.27–1.23; m	-
11	1.33; s	1.33; s	0
12	1.03; s	1.02; s	−0.01
13	0.87; d; 6.6	0.87; d; 6.4	0
14	1.12; s	1.12; s	0
15*α*	2.70; d; 12.6	2.69; d; 15.3	−0.01
15*β*	2.65; d; 12.6	2.64; d; 15.3	−0.01
3'	6.58; d; 8.4	6.58; d; 8.5	0
4'	6.53; d; 8.4	6.53; d; 8.5	0
2'-OH	4.38; br s	4.24; s	−0.14

Table S6. Comparison of ^{13}C NMR spectroscopic data (CDCl$_3$) of natural and synthetic (+)-dysiherbol C (8).

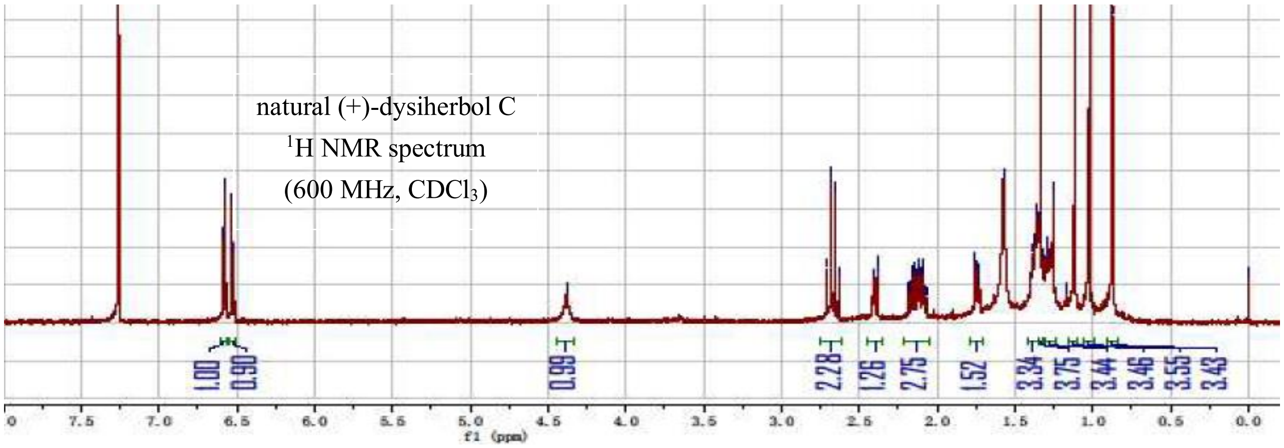


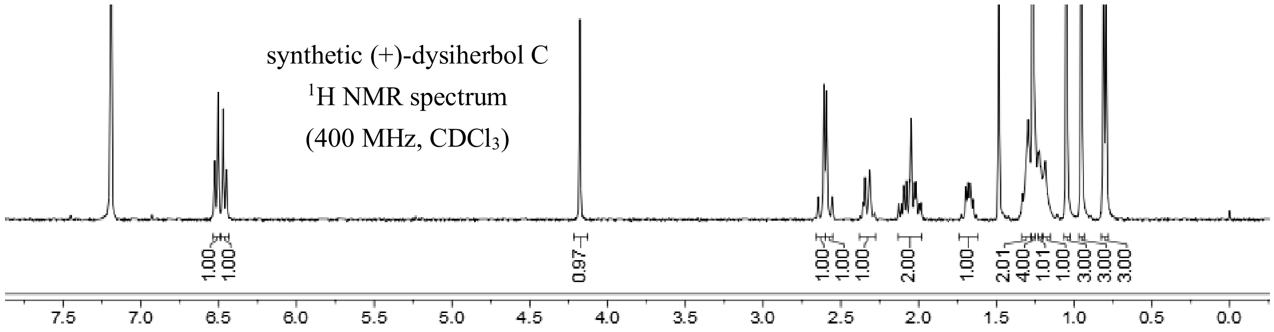
8: (+)-dysiherbol C
(revised structure)

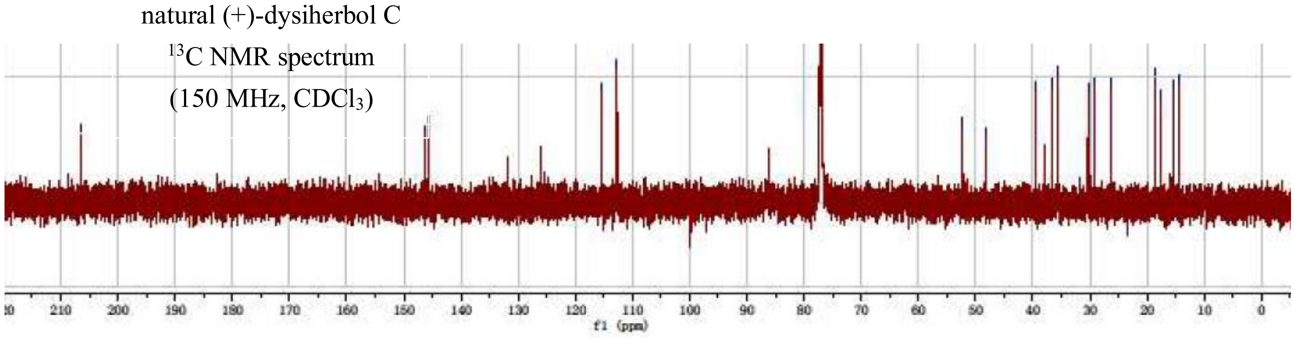
Position	Natural[5] δ ^{13}C [ppm] 150 MHz CDCl$_3$, 77.00	Synthetic δ ^{13}C [ppm] 101 MHz CDCl$_3$, 77.16	Deviation (synthetic−natural)	
			Δδ (ppm)	Δδ (ppm)[a]
1	29.2	29.4	0.2	0
2	36.6	36.8	0.2	0
3	206.2	206.6	0.4	0.2
4	86.2	86.3	0.1	−0.1
5	38.0	38.1	0.1	−0.1
6	30.3	30.5	0.2	0
7	26.3	26.5	0.2	0
8	35.6	35.7	0.1	0
9	52.5	52.6	0.1	−0.1
10	48.1	48.2	0.1	0
11	14.5	14.7	0.2	0
12	18.4	18.6	0.2	0
13	17.5	17.7	0.2	0
14	15.3	15.5	0.2	0
15	39.4	39.6	0.2	0
1'	125.9	126.1	0.2	0
2'	146.4	146.6	0.2	0
3'	115.5	115.6	0.2	0
4'	112.7	112.8	0.2	0
5'	145.6	145.7	0.2	−0.1
6'	131.8	132.0	0.2	0

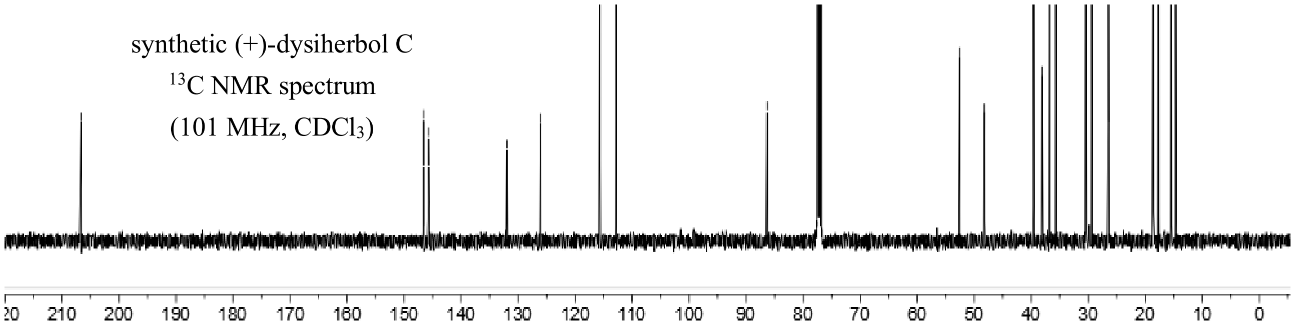
[a] To compare the ^{13}C NMR spectroscopic data of the synthetic (+)-dysiherbol C (**8**) with the natural one, the internal reference of CDCl$_3$ used in the synthetic sample was adjusted from 77.16 ppm to 77.00 ppm, which is consistent with that used in the natural sample.

Comparison of NMR spectra of natural and synthetic (+)-dysiherbol C (8).

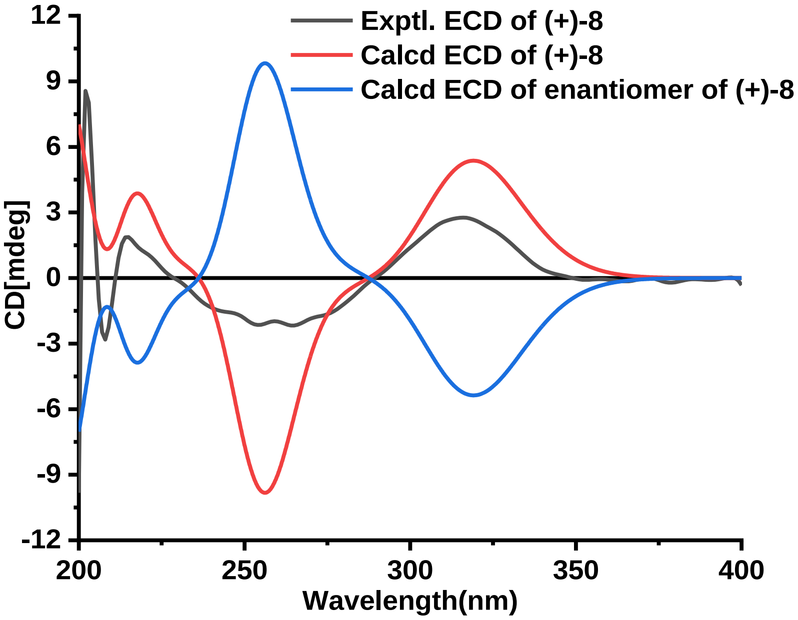

natural (+)-dysiherbol C
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)

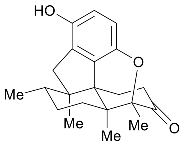

synthetic (+)-dysiherbol C
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)


natural (+)-dysiherbol C
^{13}C NMR spectrum
(150 MHz, $CDCl_3$)


synthetic (+)-dysiherbol C
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)

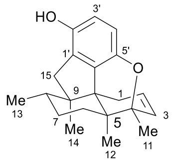
Experimental and calculated ECDs of the revised structure of (+)-dysiherbol C (8).





8: (+)-dysiherbol C
(revised structure)

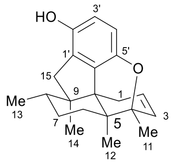
Table S7. Comparison of ^{1}H NMR spectroscopic data (CDCl$_3$) of natural and synthetic (+)-dysiherbol D (9).



9: (+)-dysiherbol D
(revised structure)

Position	Natural[6] δ ^{1}H [ppm; mult; *J* (Hz)] 600 MHz, CDCl$_3$, 7.26	Synthetic δ ^{1}H [ppm; mult; *J* (Hz)] 400 MHz, CDCl$_3$, 7.26	Deviation (synthetic−natural) Δδ (ppm)
1*α*	2.00; dd; 17.4, 4.8	2.00; dd; 17.6, 5.3	0
1*β*	2.45; d; 18.0	2.46; d; 17.6	0.01
2	5.82; ddd; 9.6, 5.4, 1.8	5.82; ddd; 9.7, 5.3, 2.0	0
3	5.37; dd; 9.6, 2.4	5.37; ddd; 9.7, 2.8, 1.2	0
6*α*	1.41; dd; 9.0, 3.6	1.44–1.37; m	-
6*β*	1.32; m	1.37–1.26; m	-
7*α*	1.32; m	1.37–1.26; m	-
7*β*	1.32; m	1.37–1.26; m	-
8	1.08; m	1.11–1.06; m	-
11	1.35; s	1.35; s	0
12	1.11; s	1.11; s	0
13	0.82; d; 6.8	0.82; d; 6.8	0
14	1.13; s	1.11; s	−0.02
15*α*	2.59; d; 15.2	2.60; d; 15.2	0.01
15*β*	2.63; d; 15.2	2.64; d; 15.2	0.01
3'	6.52; d; 9.0	6.52; d; 9.5	0
4'	6.45; d; 8.4	6.45; d; 8.5	0
2'-OH	-	4.20, s	-

Table S8. Comparison of ^{13}C NMR spectroscopic data ($CDCl_3$) of natural and synthetic (+)-dysiherbol D (9).

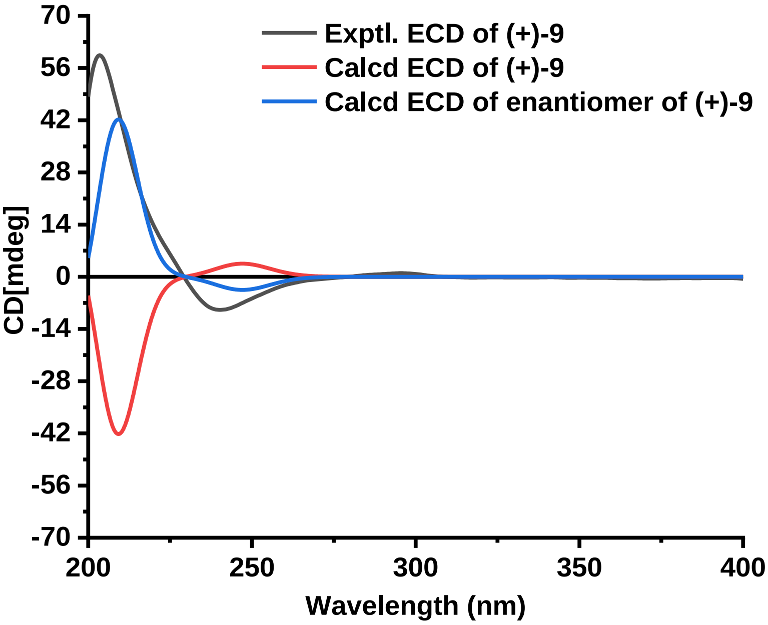


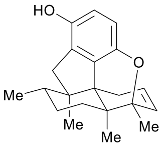
9: (+)-dysiherbol D
(revised structure)

Position	Natural[6] δ ^{13}C [ppm] 150 MHz $CDCl_3$, 77.00	Synthetic δ ^{13}C [ppm] 101 MHz $CDCl_3$, 77.16	Deviation (synthetic−natural)	
			Δδ (ppm)	Δδ (ppm)[a]
1	32.1	32.1	0	−0.2
2	129.7	129.7	0	−0.1
3	129.7	129.7	0	−0.1
4	80.0	80.0	0	−0.1
5	36.3	36.3	0	−0.1
6	29.5	29.5	0	−0.2
7	26.4	26.4	0	−0.1
8	35.3	35.3	0	−0.1
9	51.9	51.9	0	−0.2
10	49.1	49.1	0	−0.1
11	19.8	19.9	0.1	−0.1
12	18.2	18.2	0	−0.2
13	17.8	17.8	0	−0.1
14	15.9	15.8	−0.1	−0.3
15	39.5	39.5	0	−0.2
1'	126.5	126.5	0	−0.2
2'	146.2	146.2	0	−0.2
3'	115.0	115.0	0	−0.2
4'	113.3	113.4	0.1	−0.1
5'	145.7	145.7	0	−0.1
6'	135.7	135.7	0	−0.1

[a] To compare the ^{13}C NMR spectroscopic data of the synthetic (+)-dysiherbol D (**9**) with the natural one, the internal reference of $CDCl_3$ used in the synthetic sample was adjusted from 77.16 ppm to 77.00 ppm, which is consistent with that used in the natural sample.

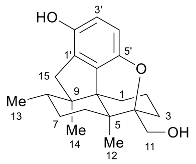
Experimental and calculated ECDs of the revised structure of (+)-dysiherbol D (9).





9: (+)-dysiherbol D
(revised structure)

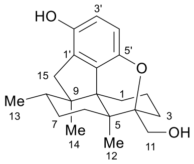
Table S9. Comparison of ^{1}H NMR spectroscopic data ($CDCl_3$) of natural and synthetic (+)-dysiherbol E (10).



10: (+)-dysiherbol E
(revised structure)

	Natural[6]	**Synthetic**	**Deviation**
Position	δ ^{1}H [ppm; mult; *J* (Hz)]	δ ^{1}H [ppm; mult; *J* (Hz)]	(synthetic−natural)
	600 MHz, $CDCl_3$, 7.26	400 MHz, $CDCl_3$, 7.26	Δδ (ppm)
1*α*	1.87; dd; 12.6, 4.2	1.87; m	0
1*β*	1.34; m;	1.36–1.32; m;	-
2	1.59; m	1.59; dt; 12.1, 5.4	0
3*α*	2.00; dd; 14.4, 5.4	2.00; dd; 14.8, 6.1	0
3*β*	1.83; dd; 14.4, 6.0	1.83; m	0
6	1.39; m	1.42–1.35; m	-
7	1.26; m	1.30–1.22; m	-
8	1.22; m	1.26–1.18; m	-
11*α*	3.90; d; 10.8	3.90; d; 11.3	0
11*β*	3.52; d; 10.8	3.51; d; 11.3	−0.01
12	1.24; s	1.24; s	0
13	0.82; d; 6.6	0.82; d; 6.4	0
14	1.08; s	1.08; s	0
15	2.56; s	2.56; s	0
3'	6.51, d, 8.4	6.51; d, 8.5	0
4'	6.46; d; 8.4	6.46; d; 8.5	0
-OH	-	4.37; s	-

Table S10. Comparison of ^{13}C NMR spectroscopic data ($CDCl_3$) of natural and synthetic (+)-dysiherbol E (10).

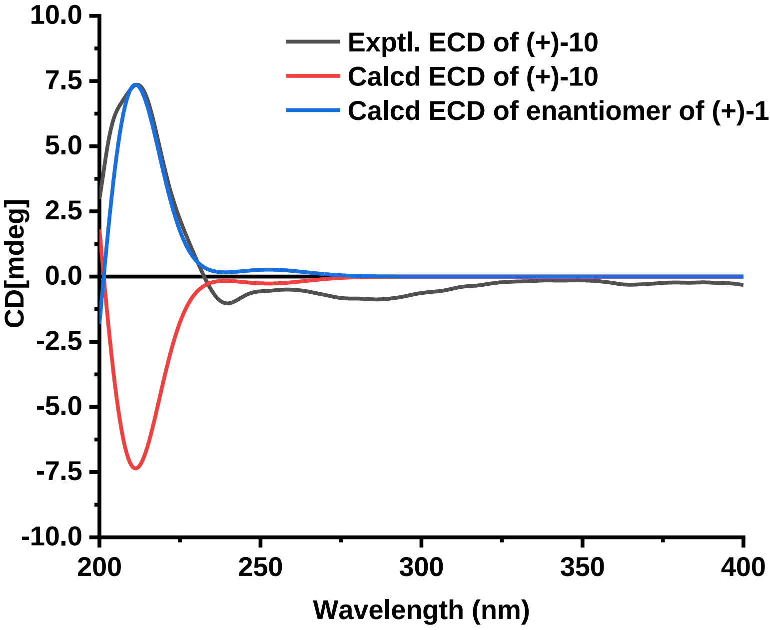


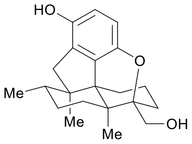
10: (+)-dysiherbol E
(revised structure)

Position	Natural[6] δ ^{13}C [ppm] 150 MHz $CDCl_3$ 77.00	Synthetic δ ^{13}C [ppm] 101 MHz $CDCl_3$ 77.16	Deviation (synthetic−natural)	
			Δδ (ppm)	Δδ (ppm)[a]
1	26.5	26.6	0.1	−0.1
2	19.2	19.3	0.1	0
3	29.9	30.0	0.1	0
4	83.5	83.6	0.1	−0.1
5	36.9	37.0	0.1	0
6	30.5	30.6	0.1	0
7	26.3	26.4	0.1	0
8	35.3	35.4	0.1	−0.1
9	52.1	52.2	0.1	−0.1
10	49.2	49.4	0.2	0
11	65.6	65.8	0.2	0
12	18.4	18.6	0.2	0
13	17.7	17.9	0.2	0
14	14.9	15.1	0.2	0
15	39.3	39.5	0.2	0
1'	126.0	126.2	0.2	0
2'	146.0	146.1	0.1	0
3'	114.4	114.5	0.1	0
4'	111.3	111.4	0.1	−0.1
5'	147.6	147.7	0.1	−0.1
6'	132.9	133.1	0.2	0

[a] To compare the ^{13}C NMR spectroscopic data of the synthetic (+)-dysiherbol E (**10**) with the natural one, the internal reference of $CDCl_3$ used in the synthetic sample was adjusted from 77.16 ppm to 77.00 ppm, which is consistent with that used in the natural sample.

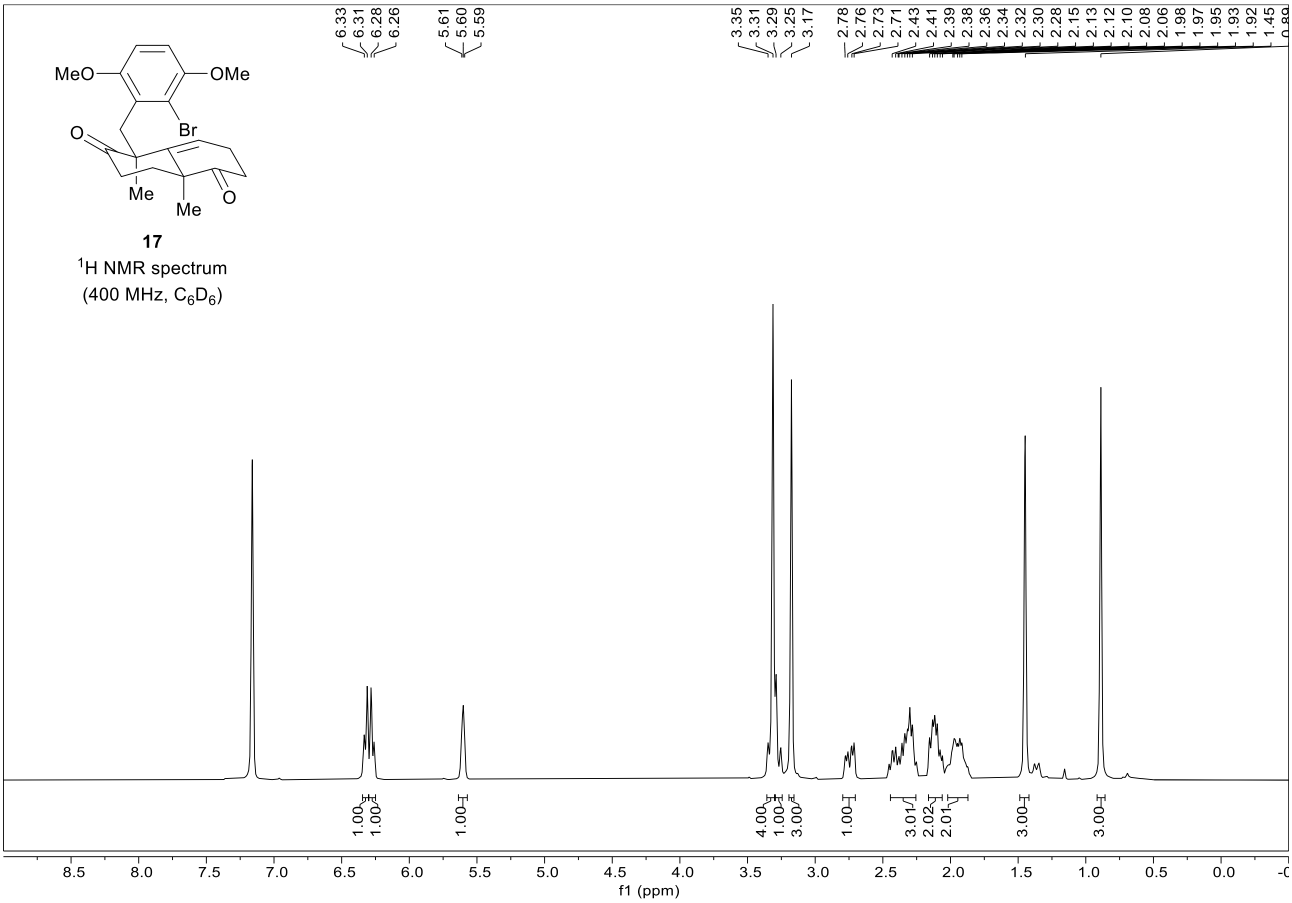
Experimental and calculated ECDs of the revised structure of (+)-dysiherbol E (10).





10: (+)-dysiherbol E
(revised structure)

IV. ^{1}H NMR and ^{13}C NMR Spectra of Compounds



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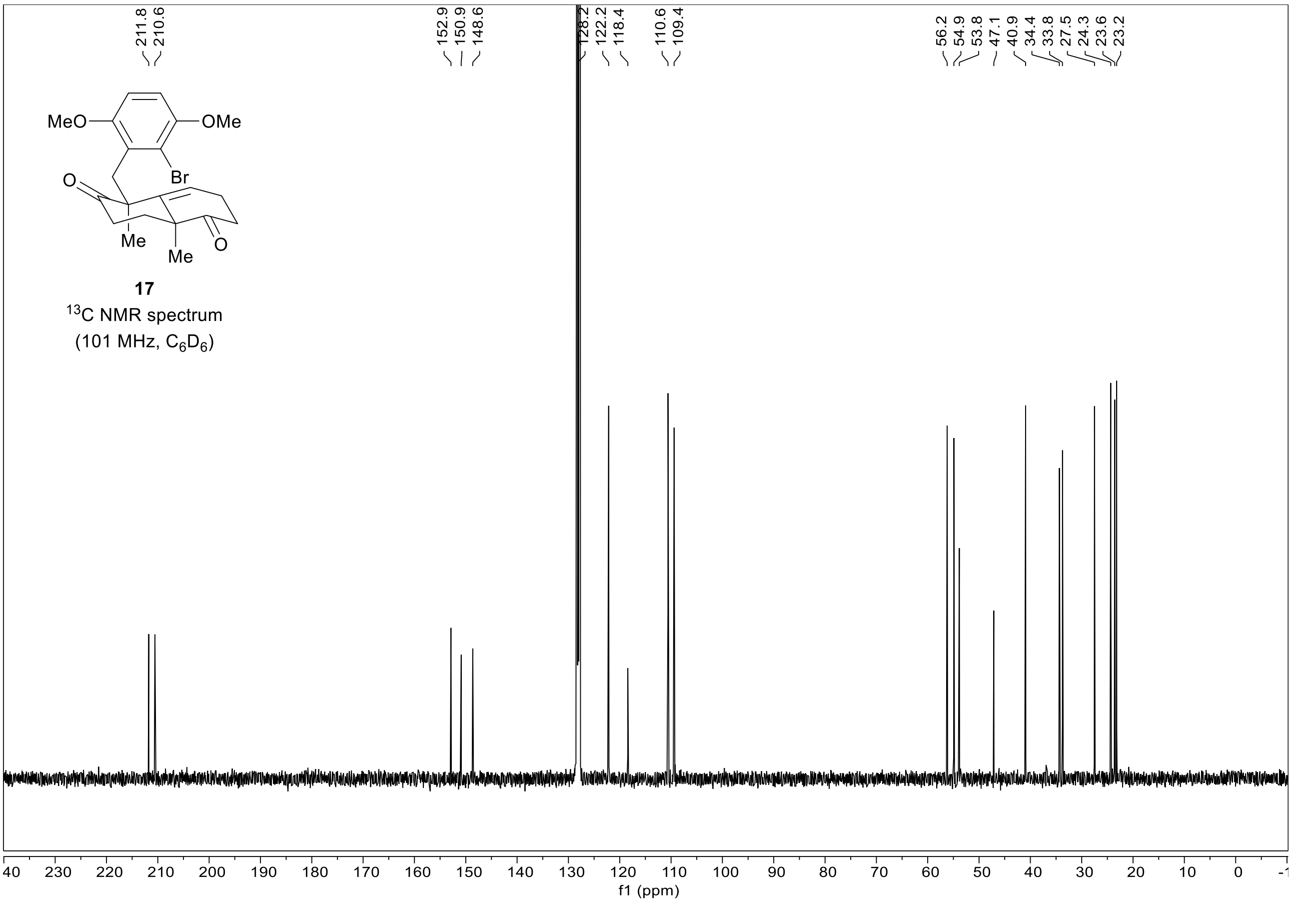
^{1}H NMR spectrum

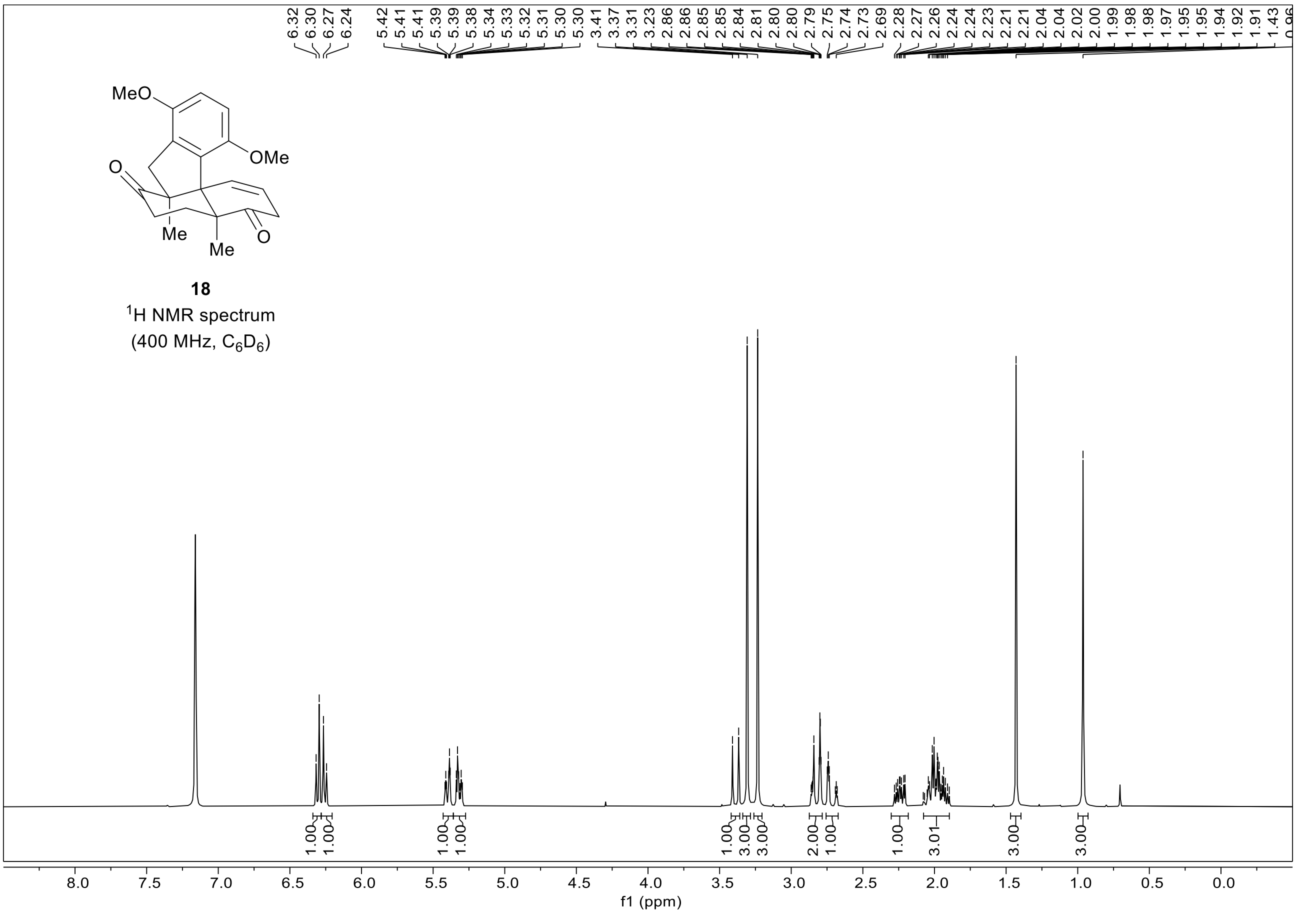
(400 MHz, C_6D_6)



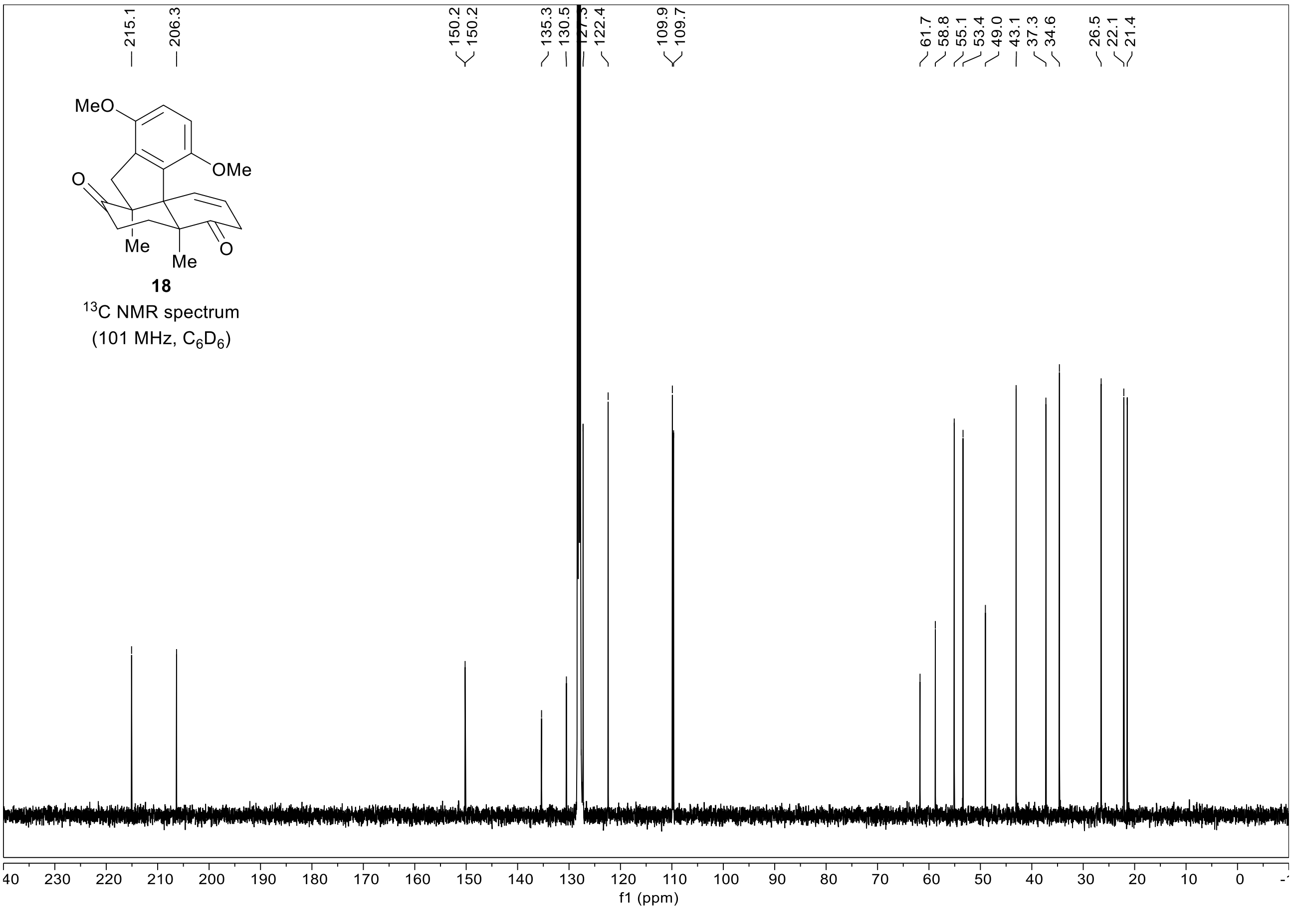
17

^{13}C NMR spectrum

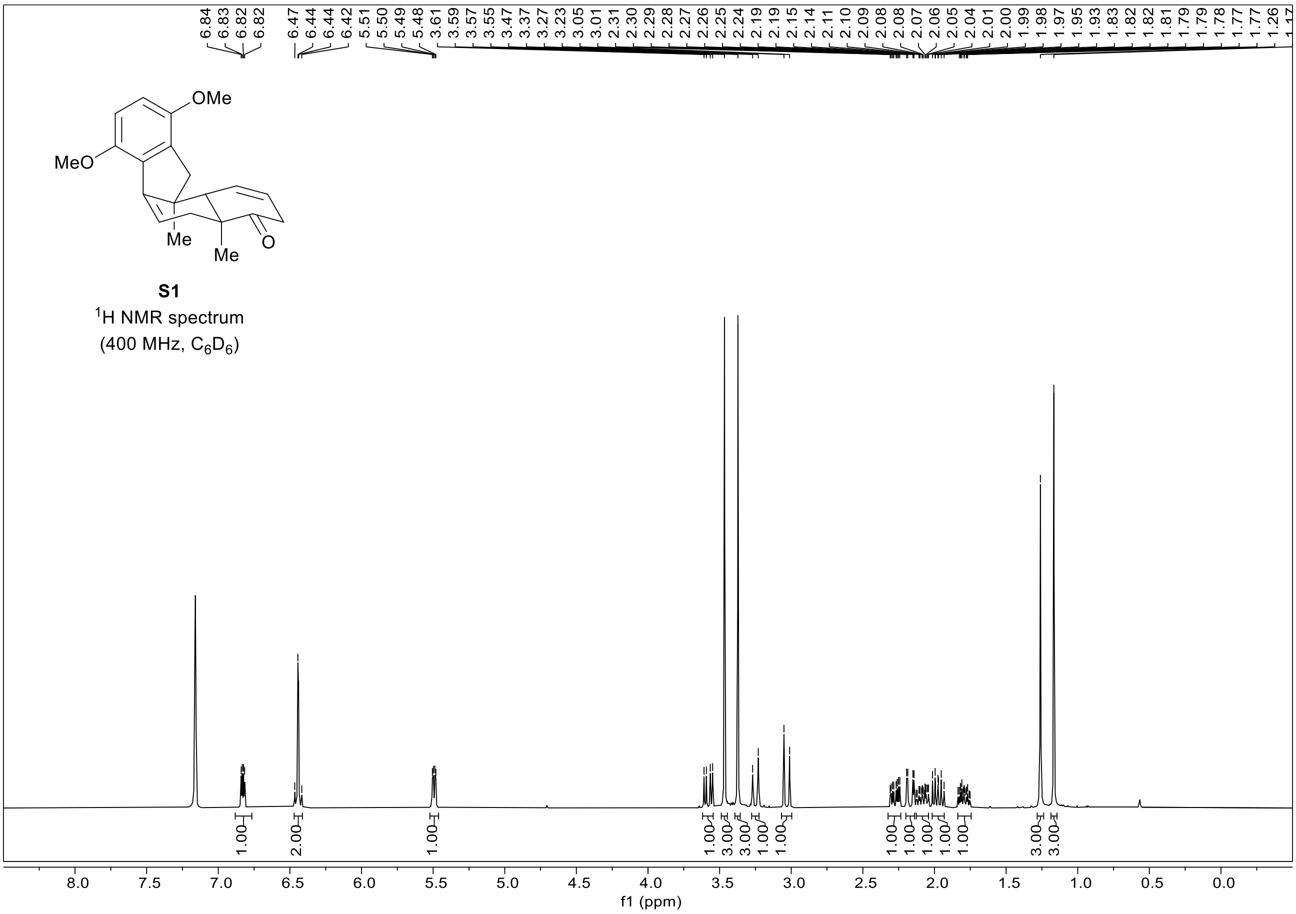
(101 MHz, C_6D_6)



18
^{1}H NMR spectrum
(400 MHz, C_6D_6)



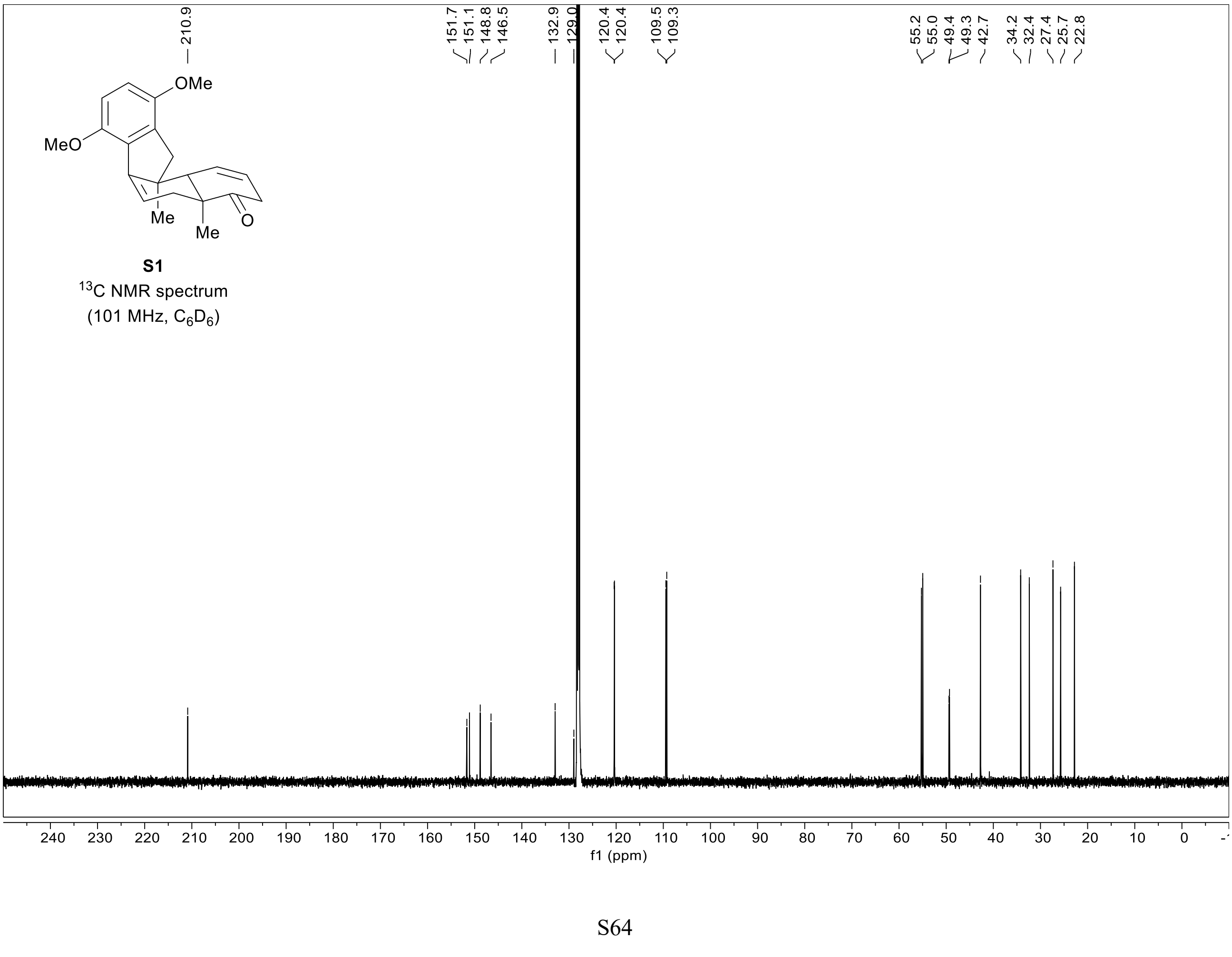
18
^{13}C NMR spectrum
(101 MHz, C_6D_6)



S1

^{1}H NMR spectrum

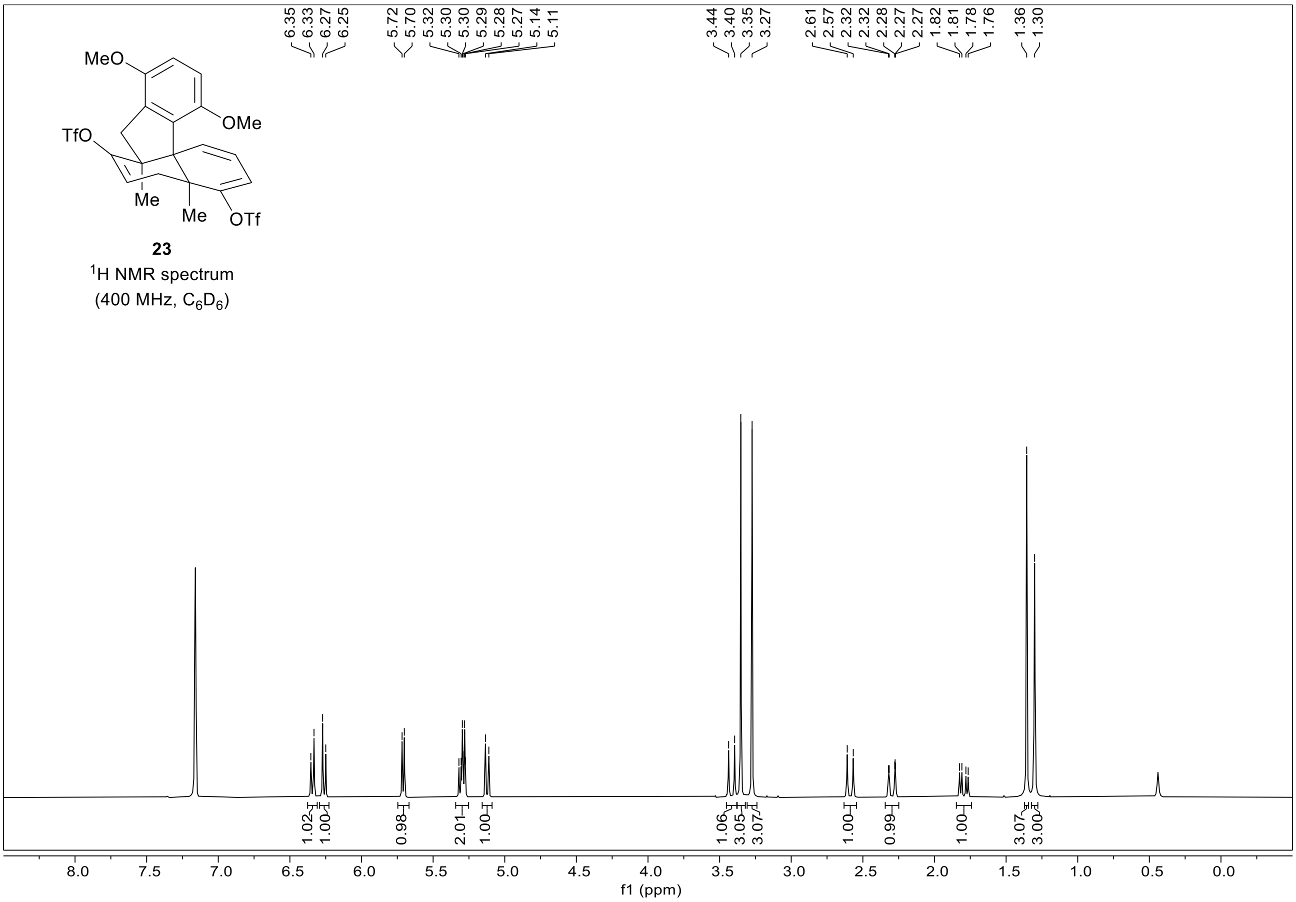
(400 MHz, C_6D_6)



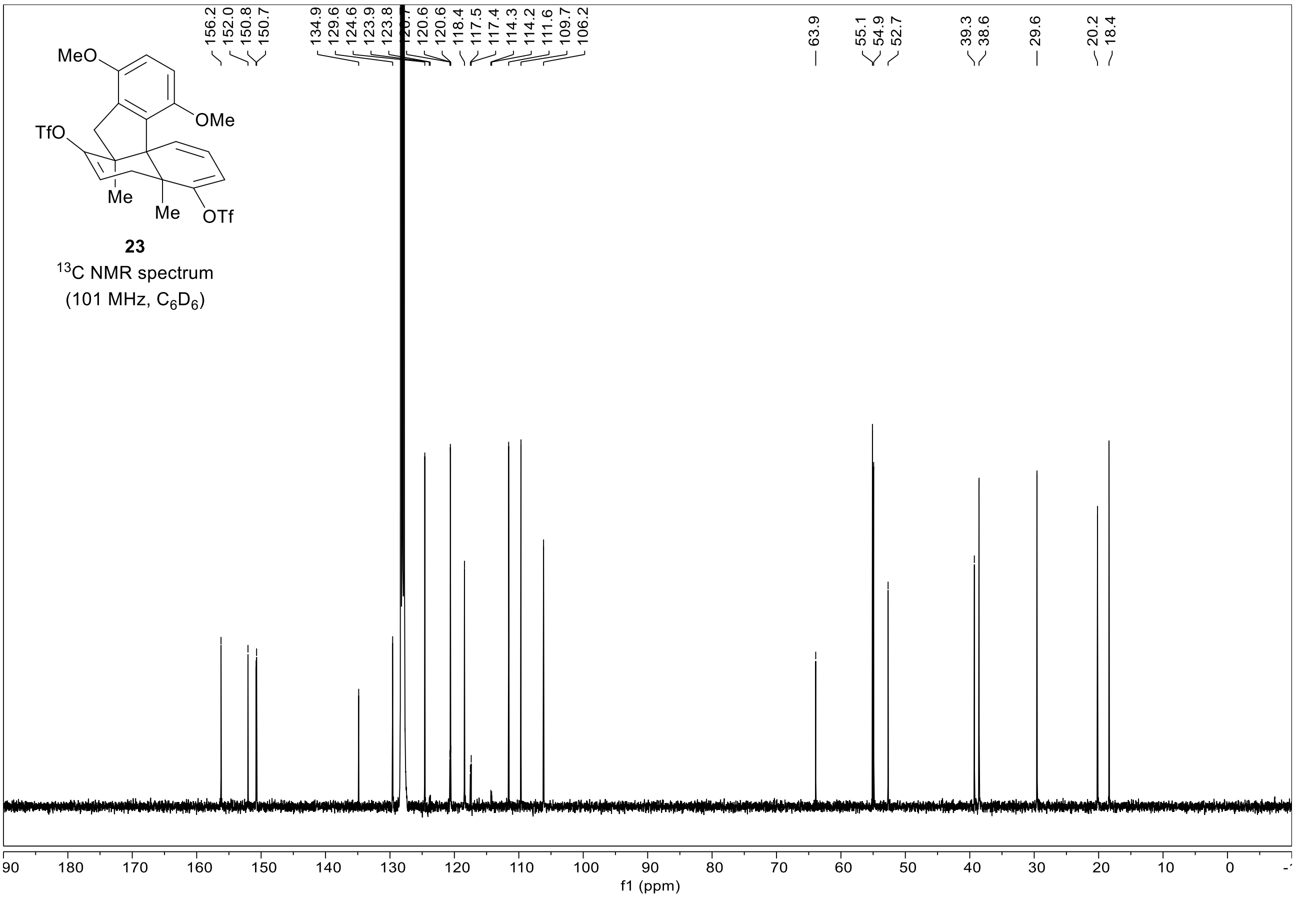
S1

^{13}C NMR spectrum

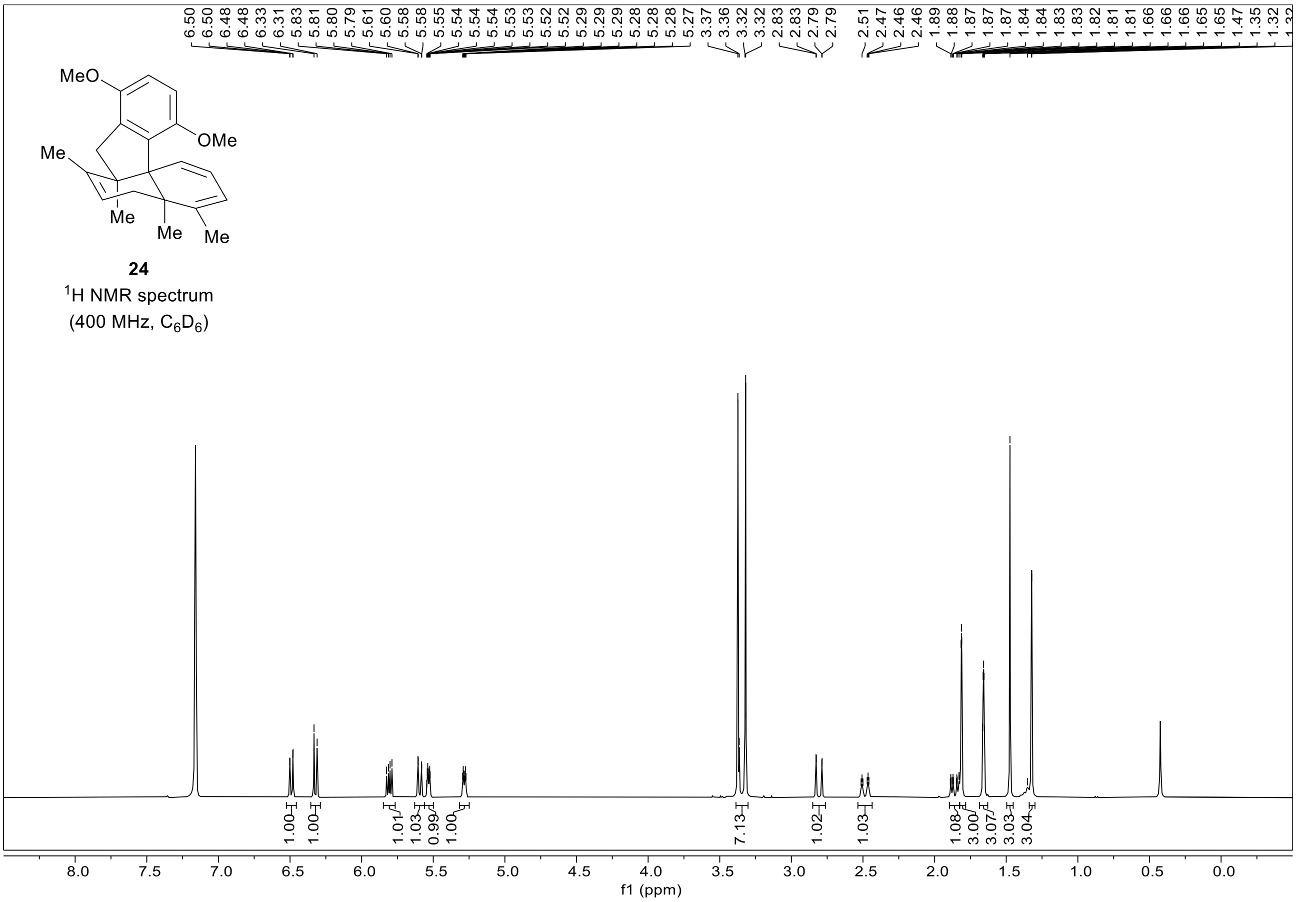
(101 MHz, C_6D_6)



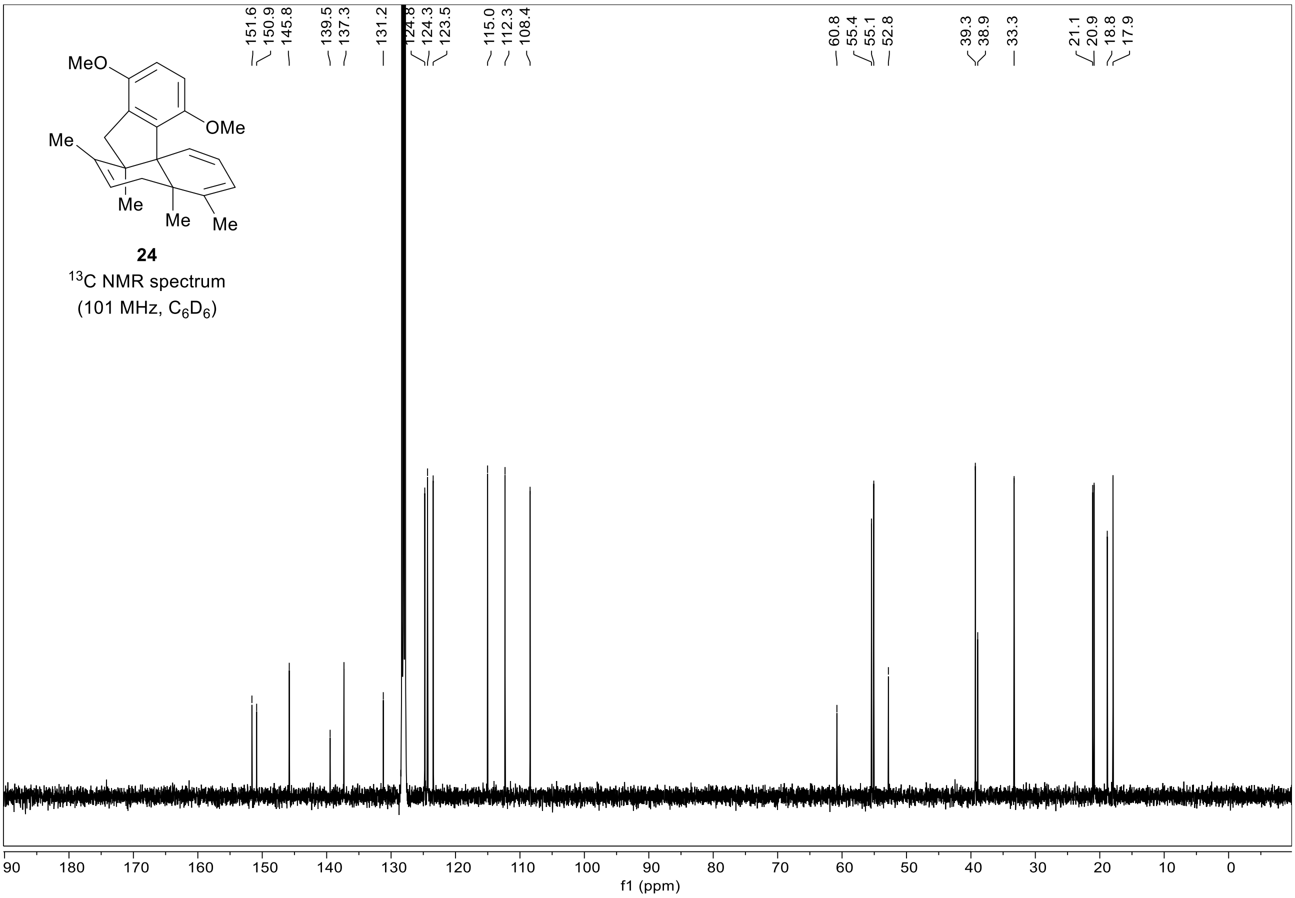
23
^{1}H NMR spectrum
(400 MHz, C_6D_6)



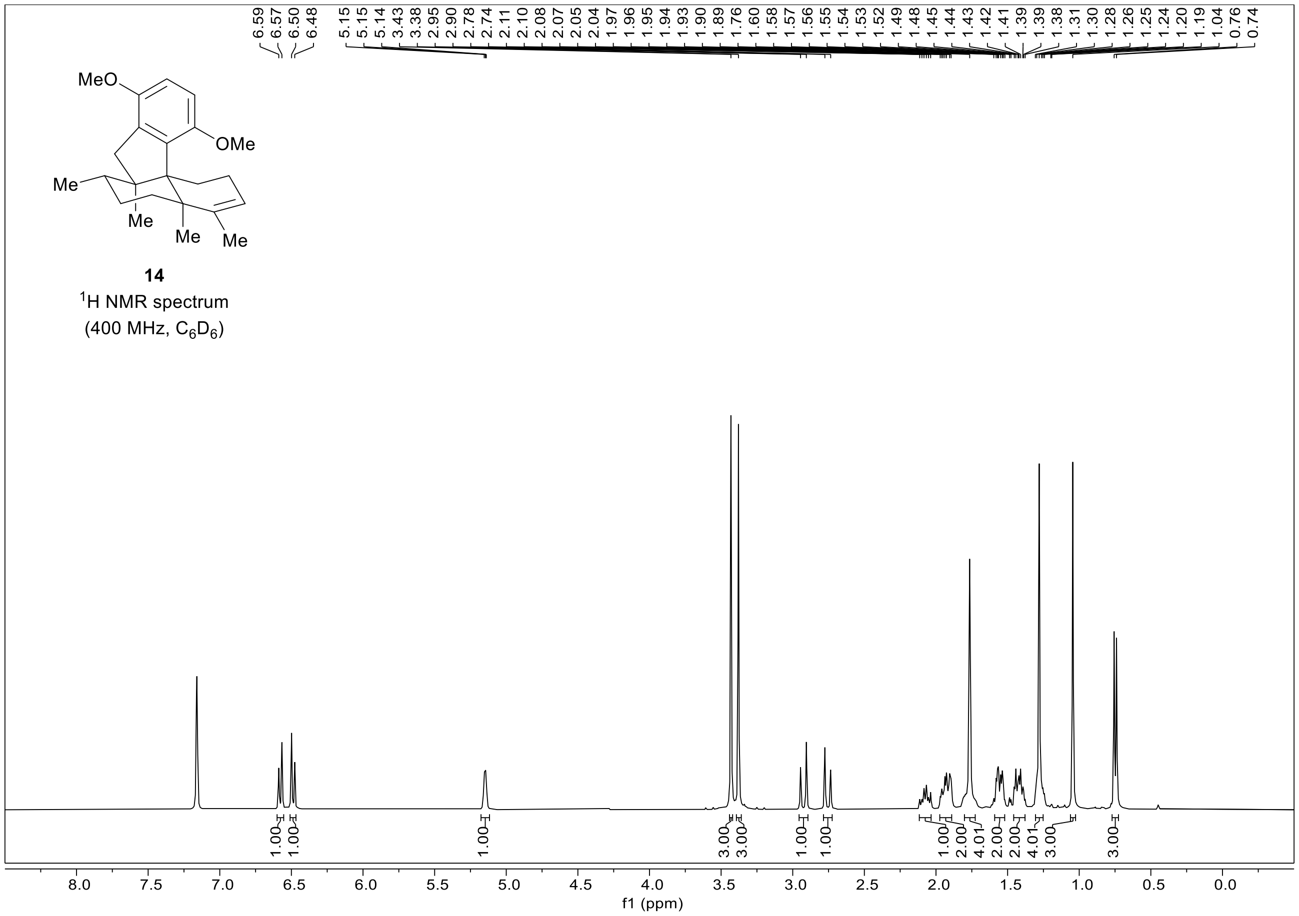
23
^{13}C NMR spectrum
(101 MHz, C_6D_6)



24
^{1}H NMR spectrum
(400 MHz, C_6D_6)



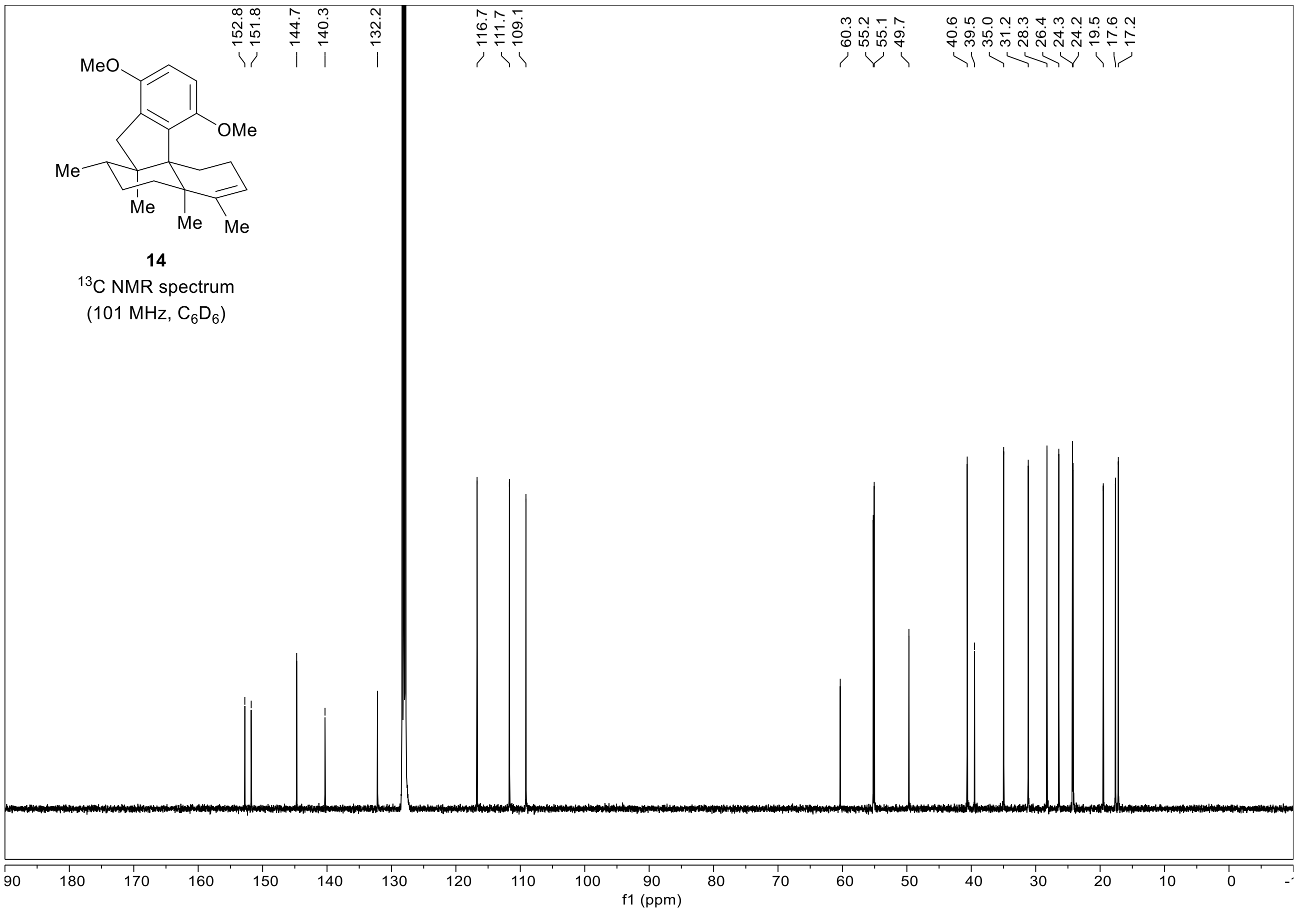
24
^{13}C NMR spectrum
(101 MHz, C_6D_6)



14

^{1}H NMR spectrum

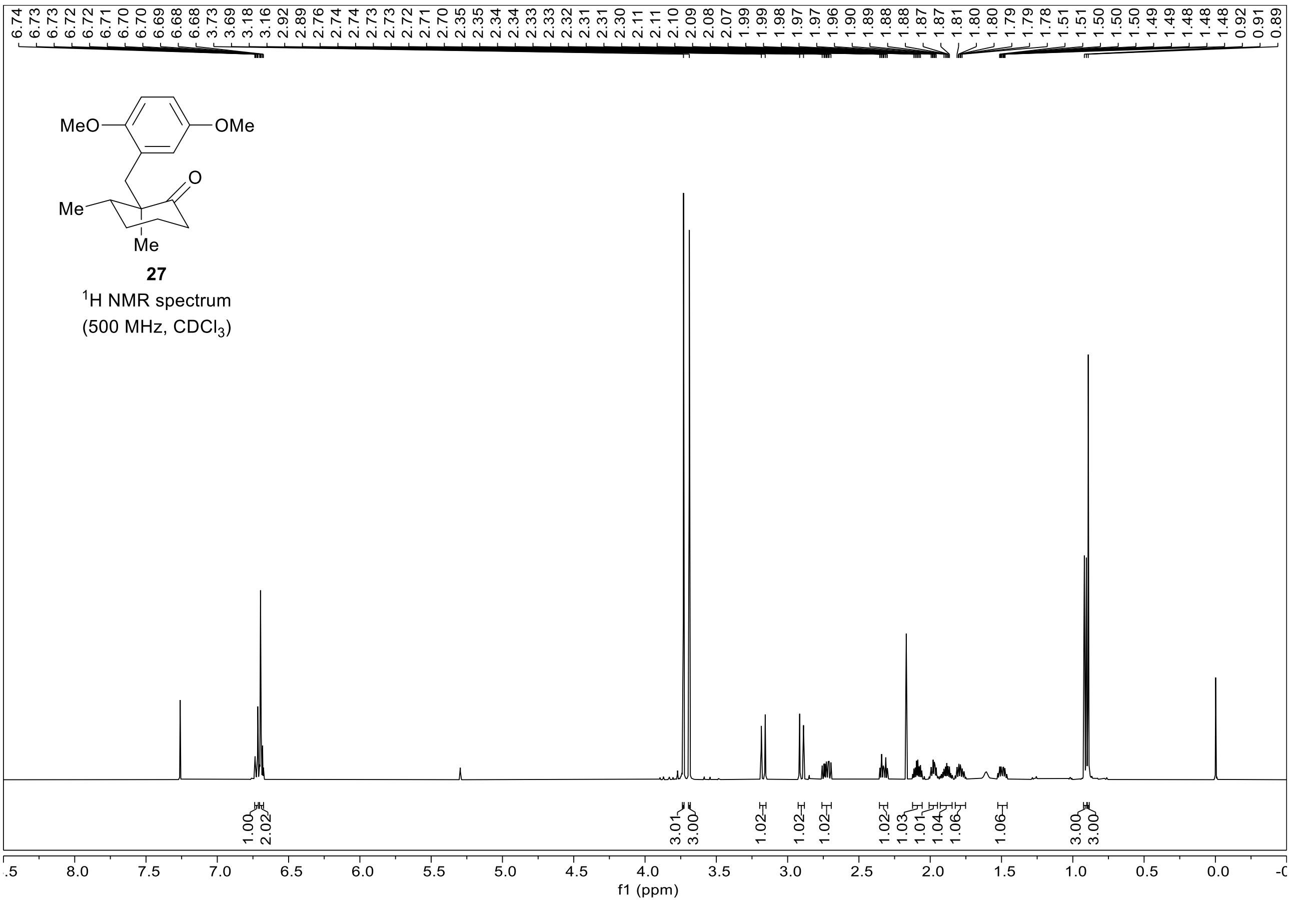
(400 MHz, C_6D_6)



14

^{13}C NMR spectrum

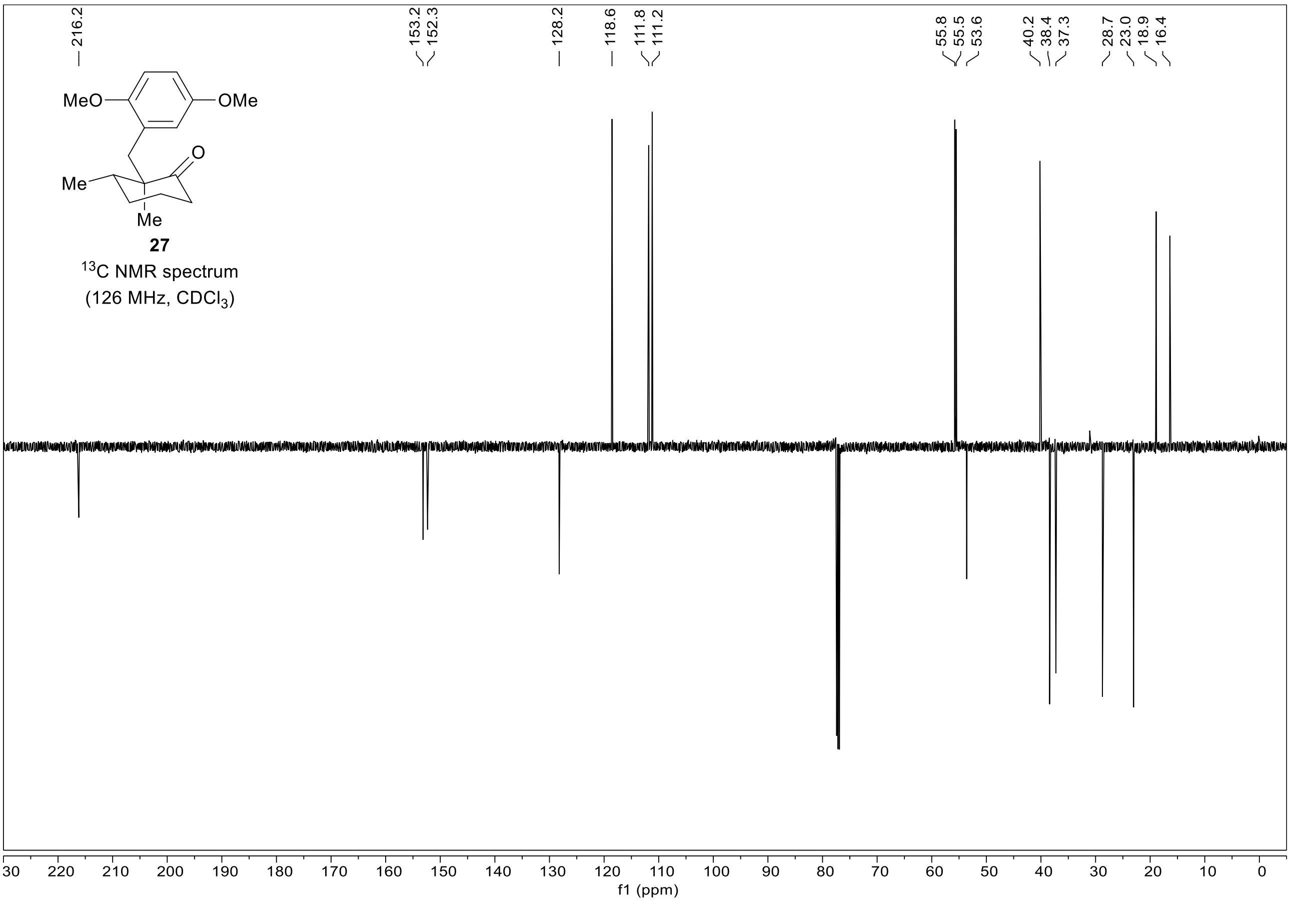
(101 MHz, C_6D_6)



27

^{1}H NMR spectrum

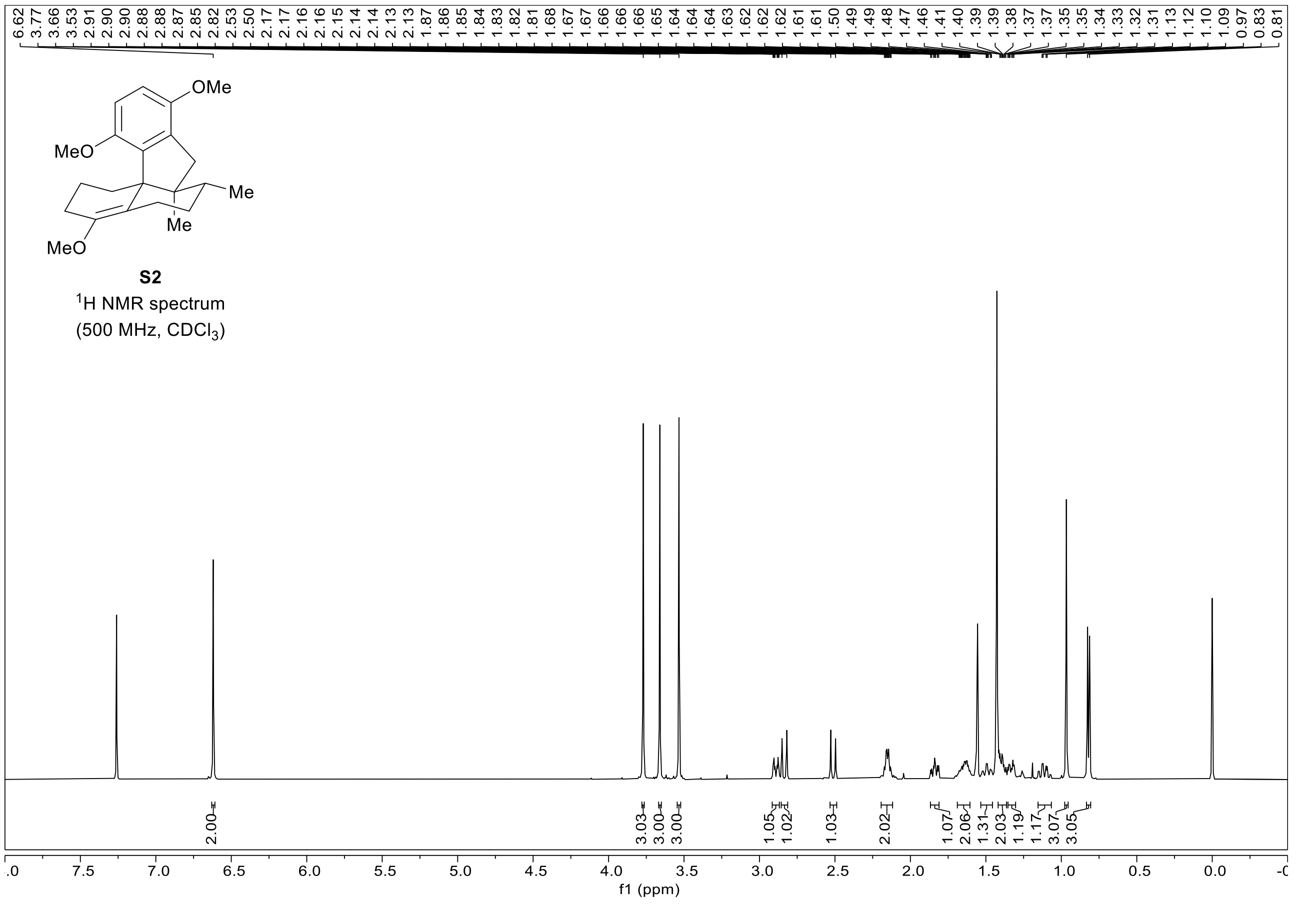
(500 MHz, $CDCl_3$)



27

^{13}C NMR spectrum

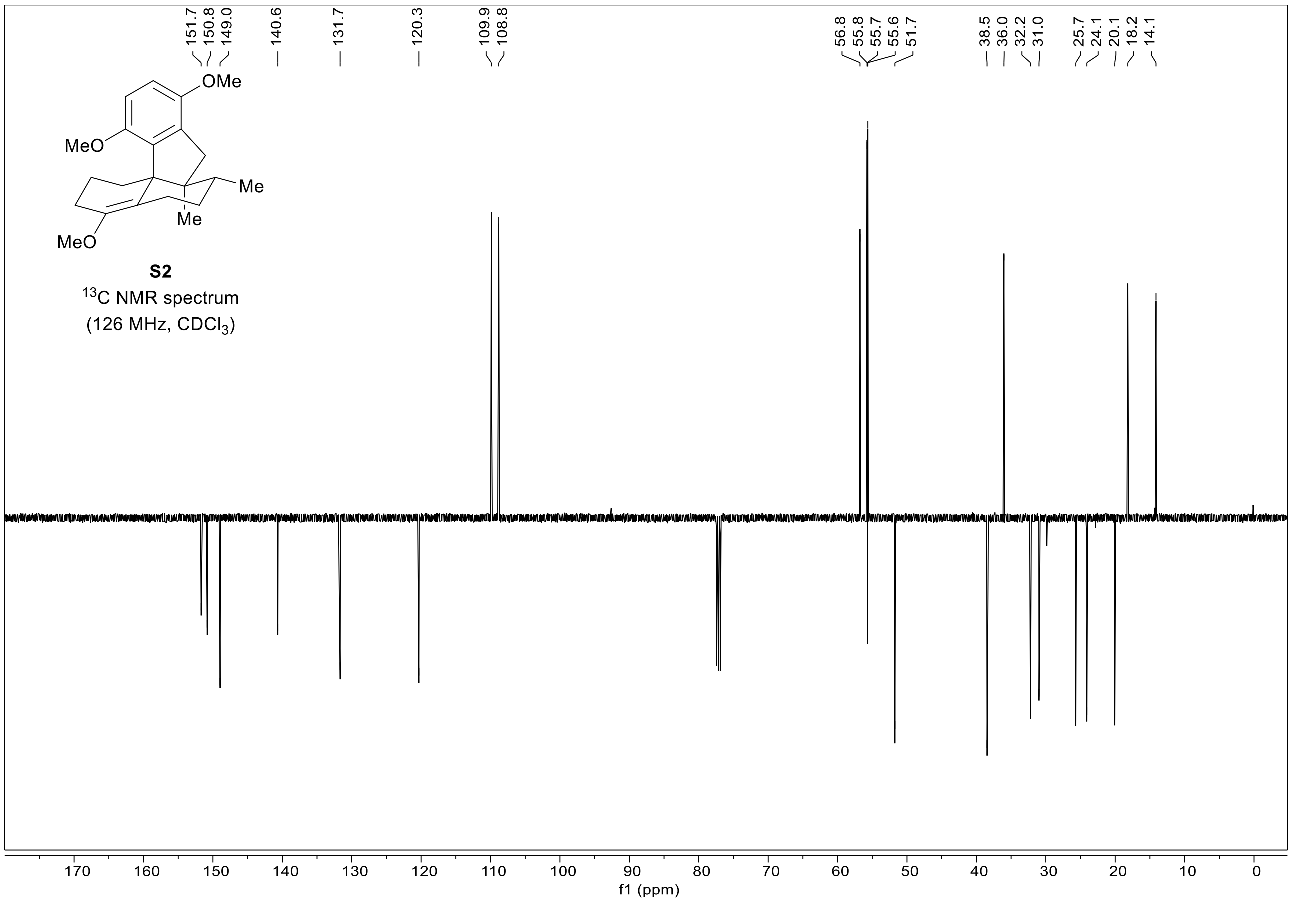
(126 MHz, $CDCl_3$)



S2

^{1}H NMR spectrum

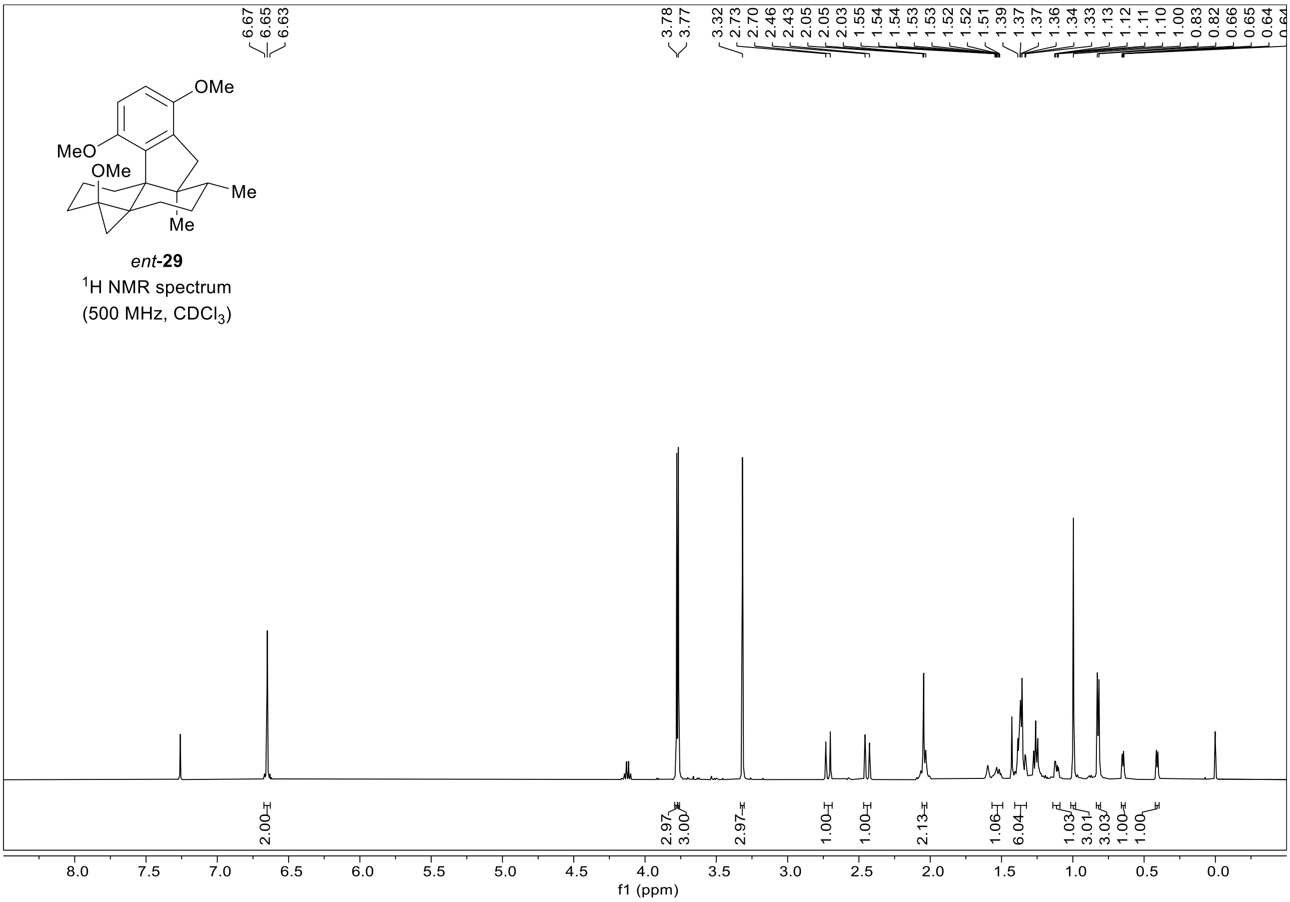
(500 MHz, $CDCl_3$)

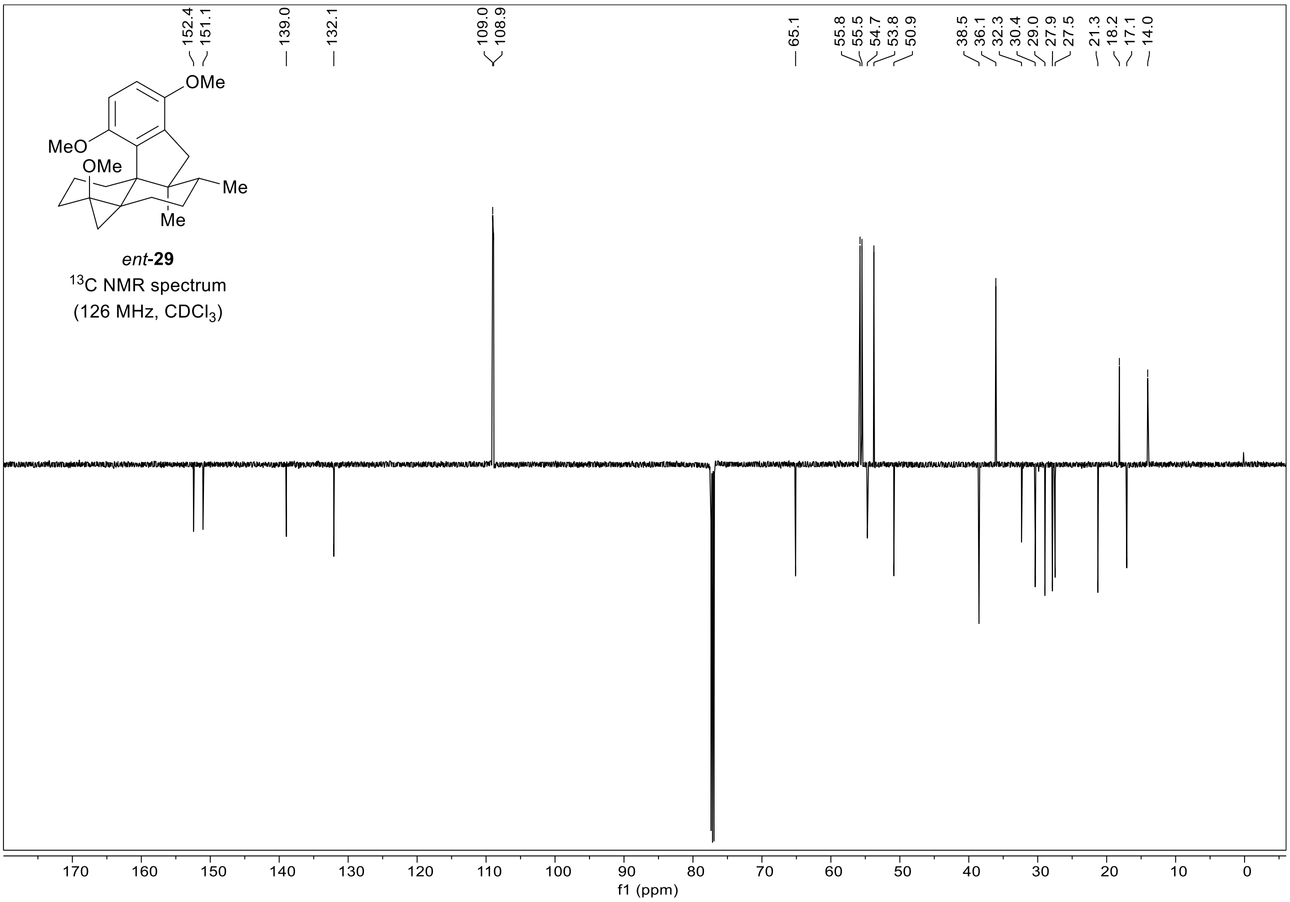


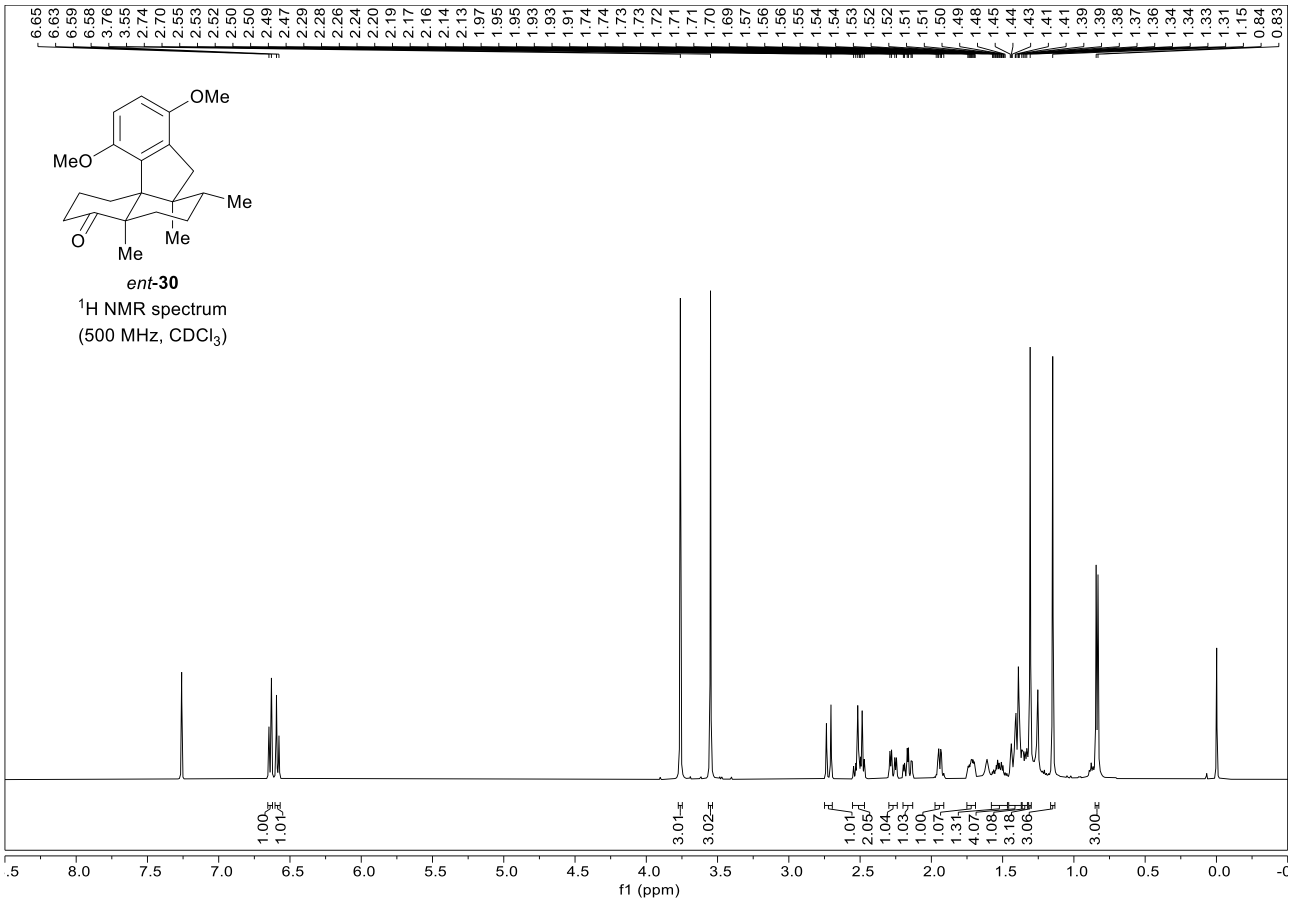
S2

^{13}C NMR spectrum

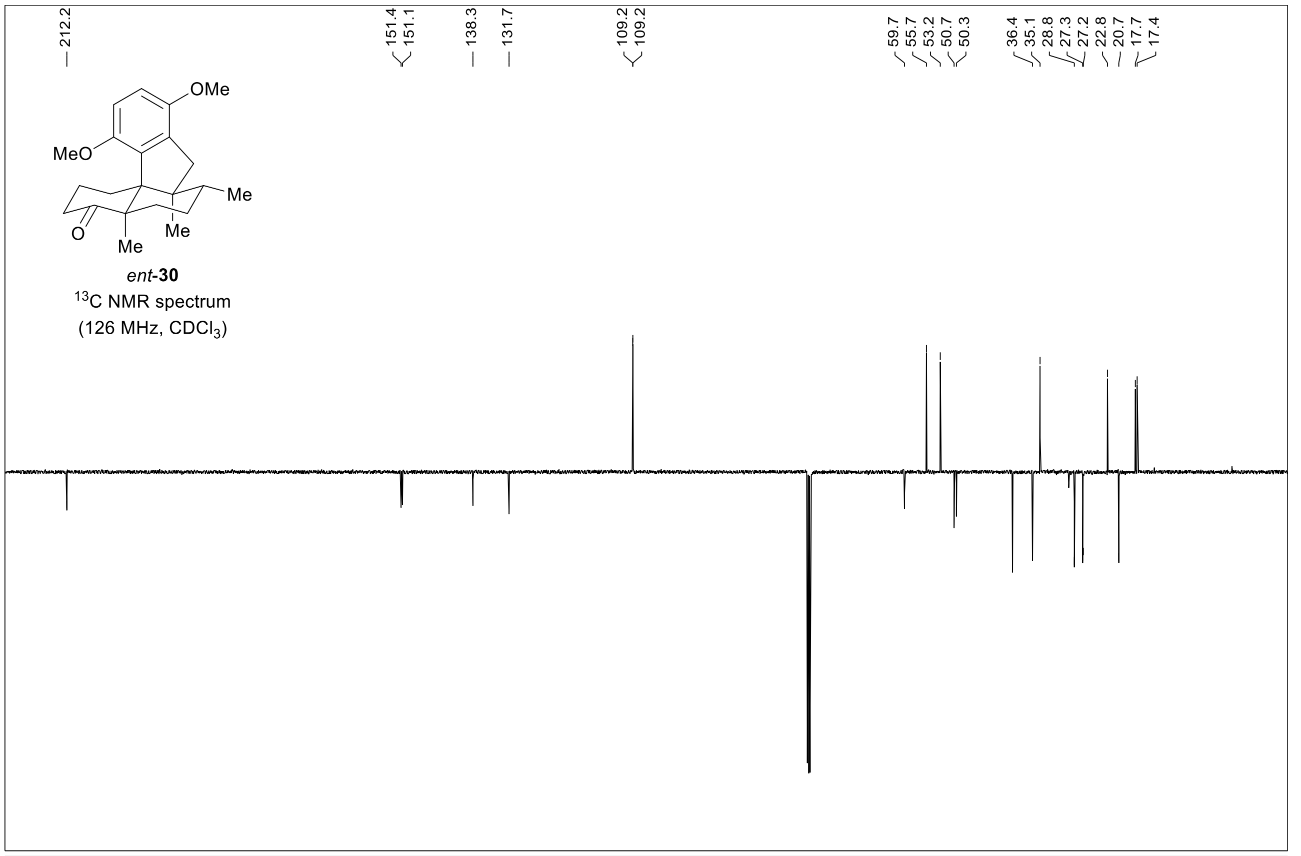
(126 MHz, $CDCl_3$)


6.67
6.65
6.63
3.78
3.77
3.32
2.73
2.70
2.46
2.43
2.05
2.03
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.39
1.37
1.37
1.36
1.34
1.33
1.13
1.12
1.11
1.10
1.00
0.83
0.82
0.66
0.65
0.64
OMe
MeO
OMe
Me
Me
ent-**29**
^{1}H NMR spectrum
(500 MHz, CDCl$_3$)
2.00
2.97
3.00
2.97
1.00
1.00
2.13
1.06
6.04
1.03
3.01
3.03
1.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

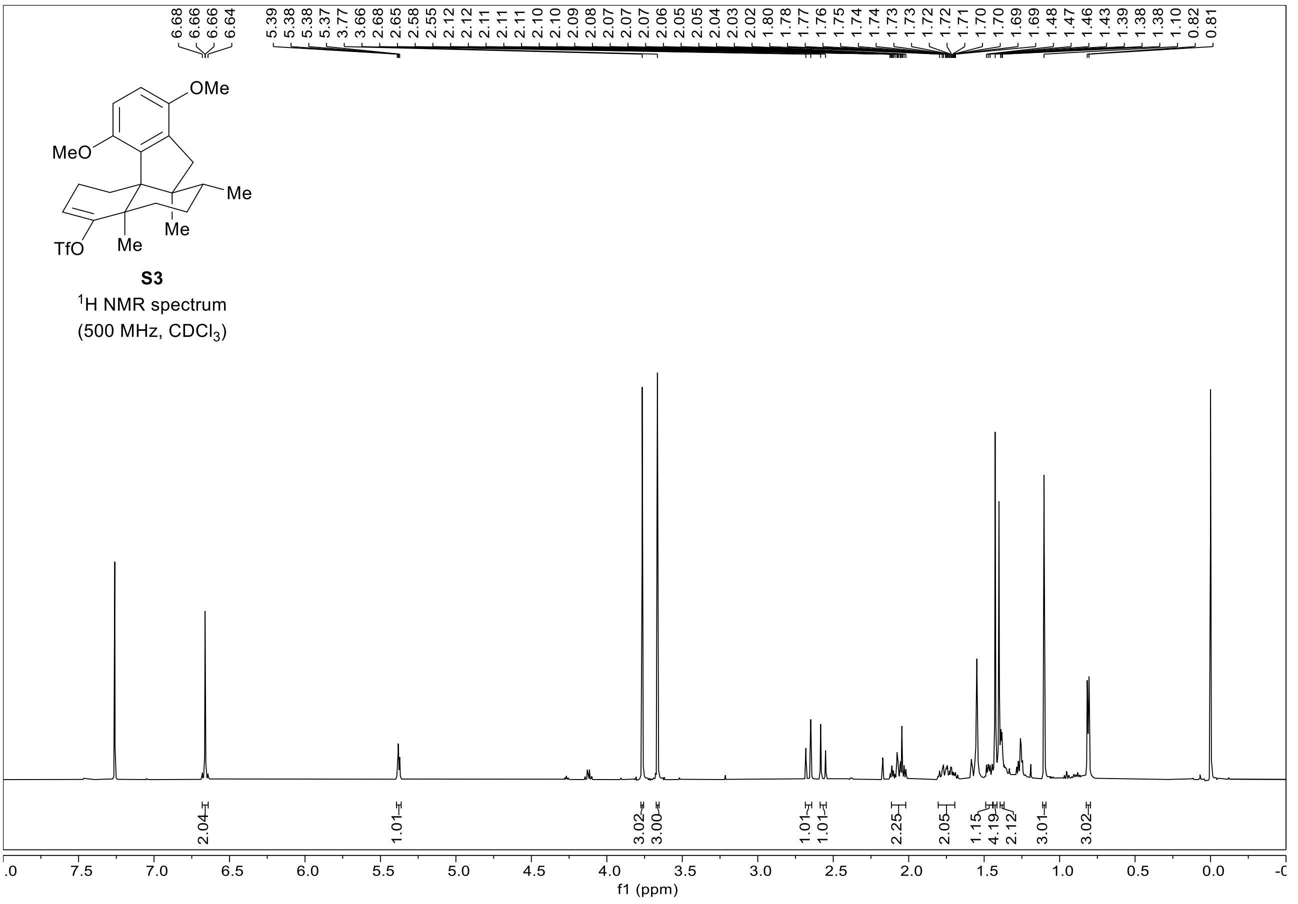

152.4
151.1
139.0
132.1
109.0
108.9
65.1
55.8
55.5
54.7
53.8
50.9
38.5
36.1
32.3
30.4
29.0
27.9
27.5
21.3
18.2
17.1
14.0
OMe
MeO
OMe
Me
Me
ent-**29**
^{13}C NMR spectrum
(126 MHz, CDCl$_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

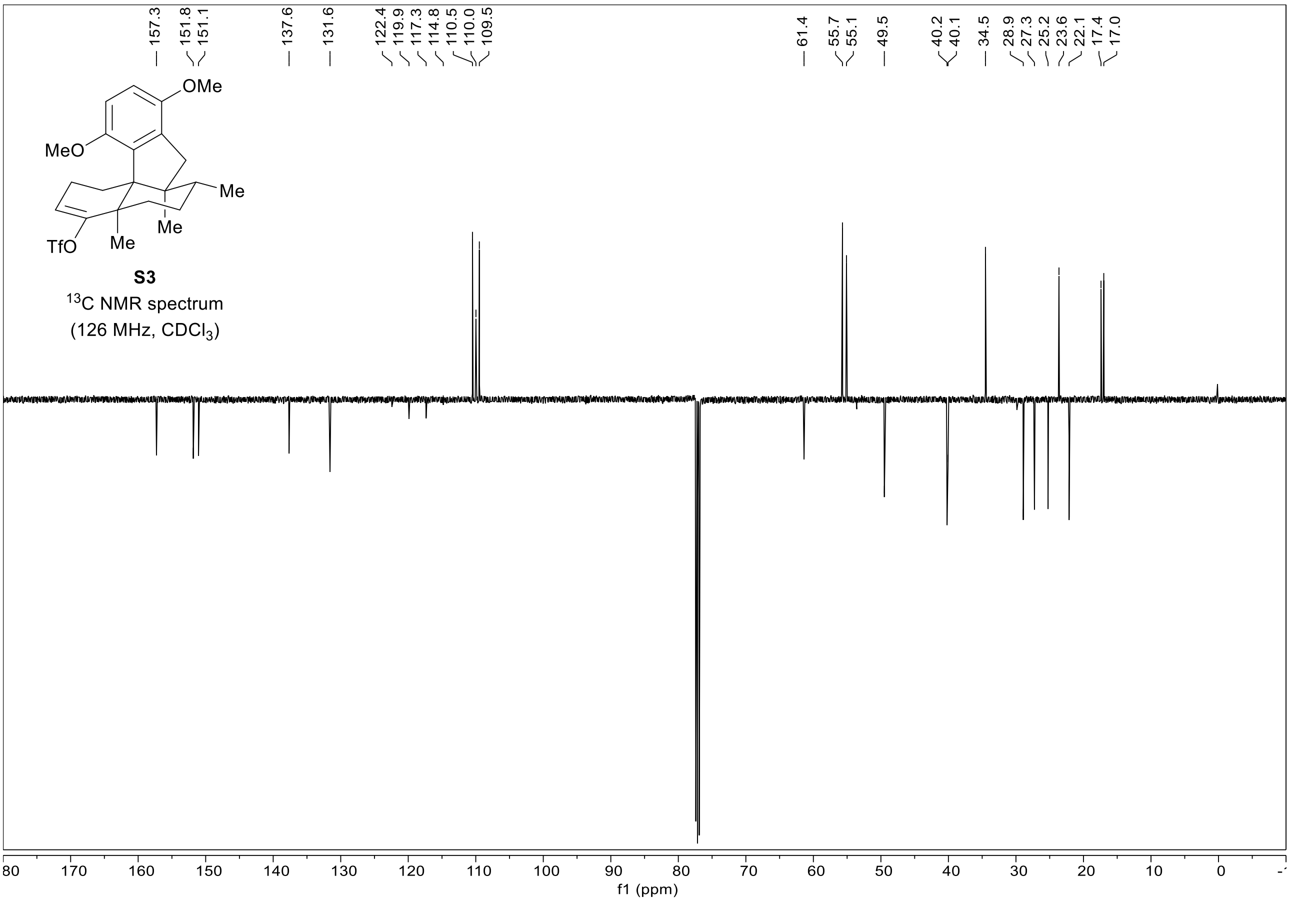


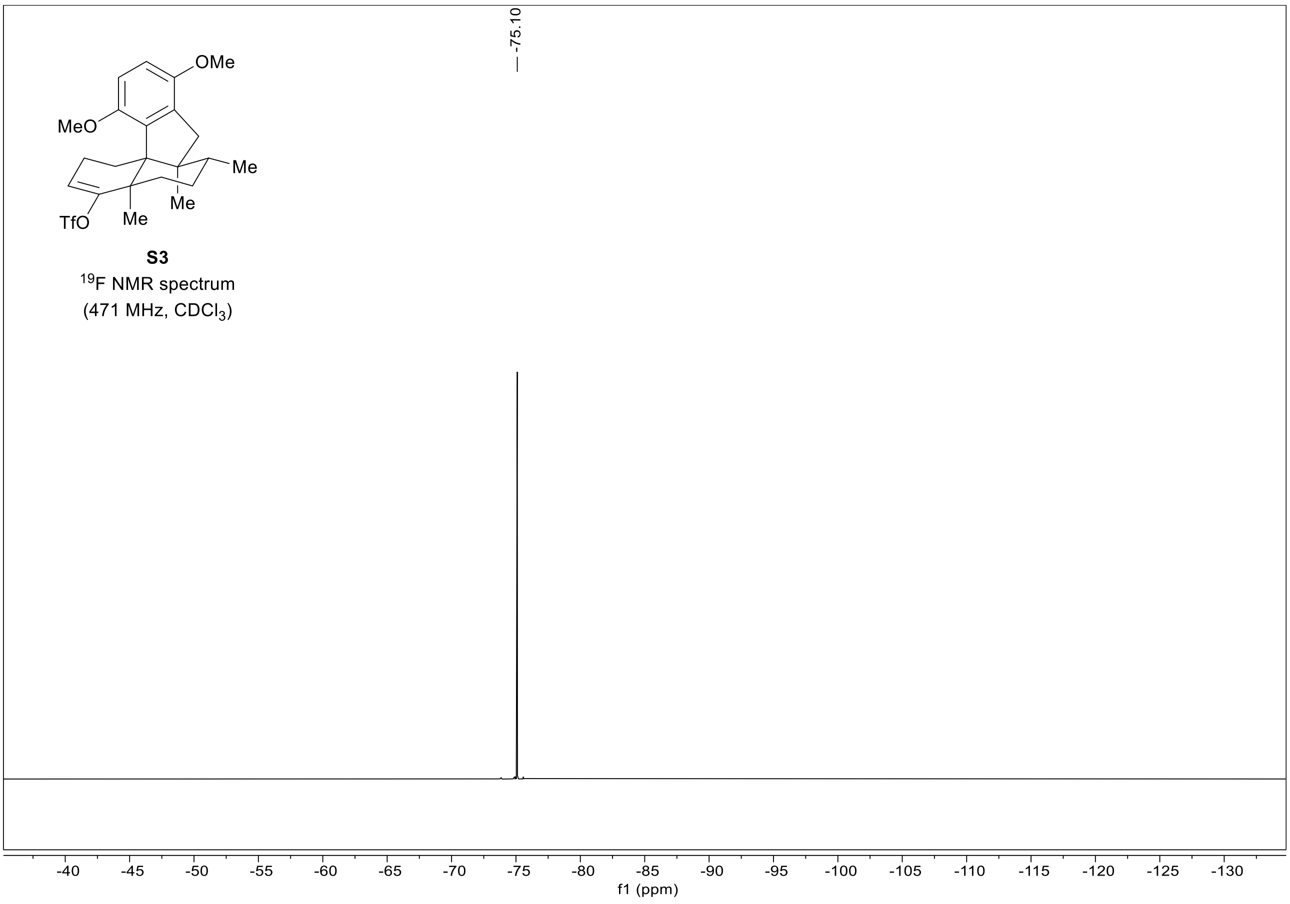
ent-**30**
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)



ent-**30**
^{13}C NMR spectrum
(126 MHz, $CDCl_3$)


6.68 6.66 6.66 6.64
5.39 5.38 5.38 5.37 3.77 3.66 2.68 2.65 2.58 2.55 2.12 2.12 2.11 2.11 2.11 2.10 2.09 2.08 2.07 2.07 2.06 2.05 2.05 2.04 2.03 2.02 1.80 1.78 1.77 1.76 1.75 1.74 1.73 1.73 1.72 1.72 1.71 1.70 1.70 1.69 1.69 1.48 1.47 1.46 1.43 1.39 1.38 1.38 1.10 0.82 0.81
OMe
MeO
Me
Me
TfO
Me
S3
^{1}H NMR spectrum
(500 MHz, CDCl$_3$)
2.04
1.01
3.02
3.00
1.01
1.01
2.25
2.05
1.15
4.19
2.12
3.01
3.02
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)

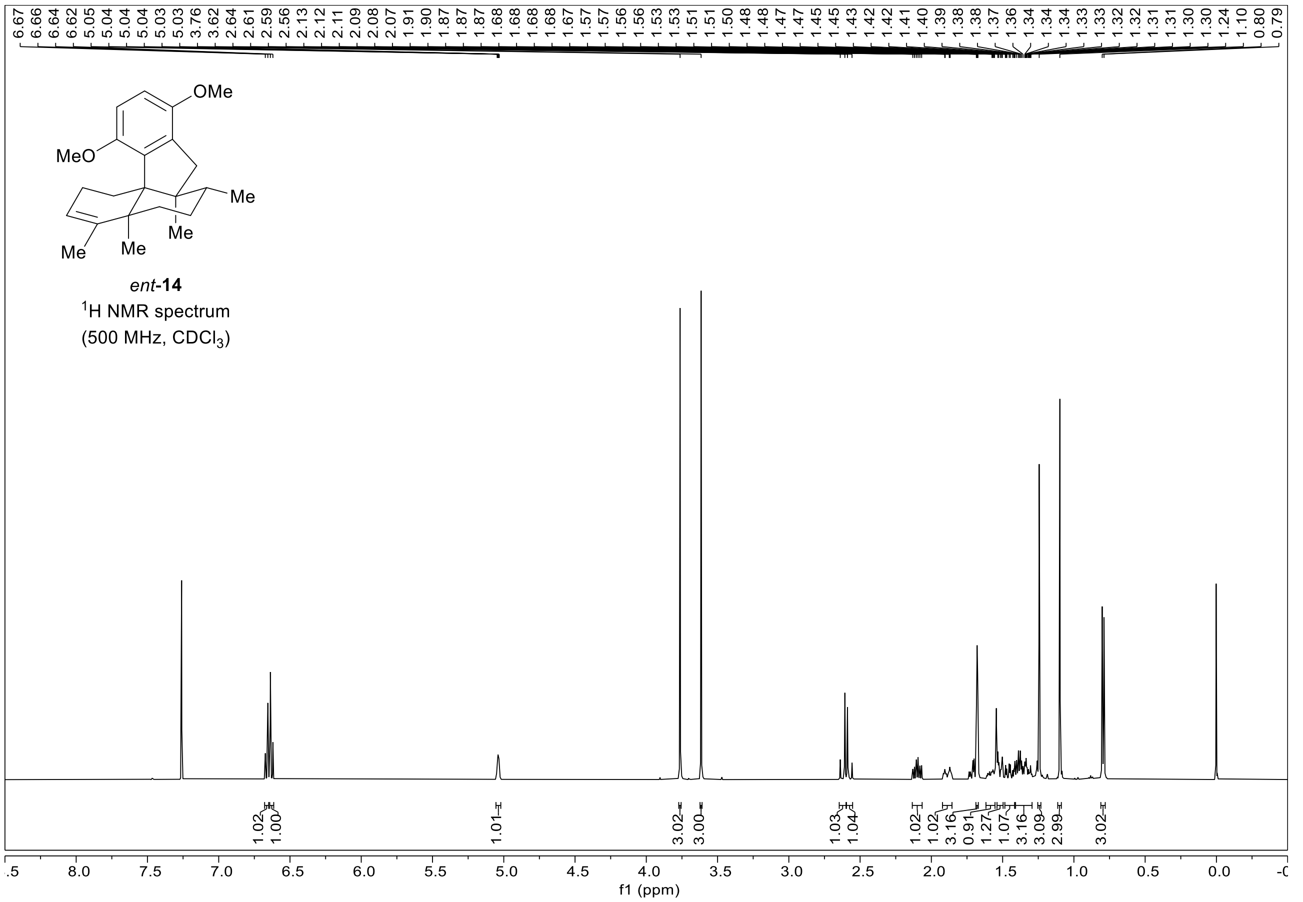

157.3 151.8 151.1 137.6 131.6 122.4 119.9 117.3 114.8 110.5 110.0 109.5
61.4 55.7 55.1 49.5 40.2 40.1 34.5 28.9 27.3 25.2 23.6 22.1 17.4 17.0
OMe
MeO
Me
Me
TfO
Me
S3
^{13}C NMR spectrum
(126 MHz, CDCl$_3$)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)



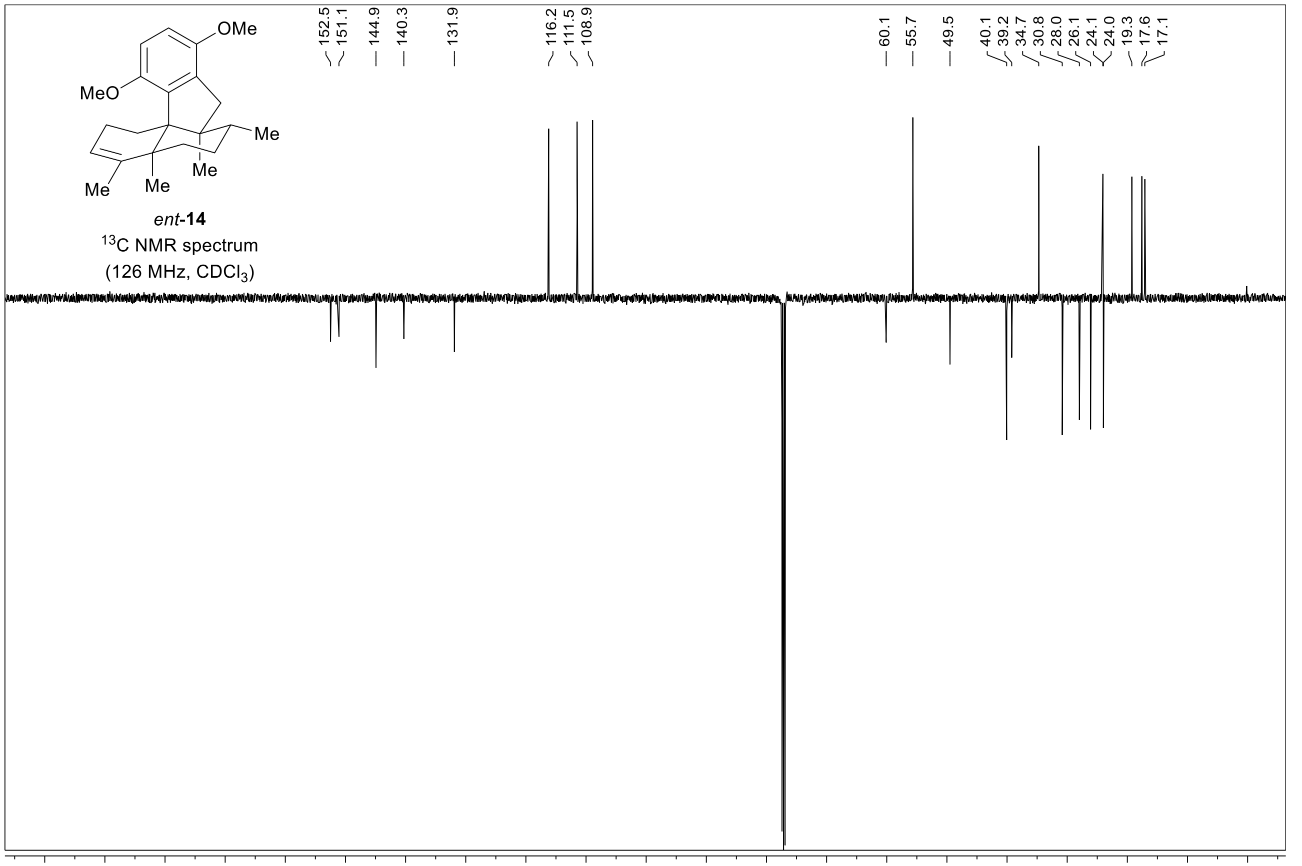
S3

^{19}F NMR spectrum

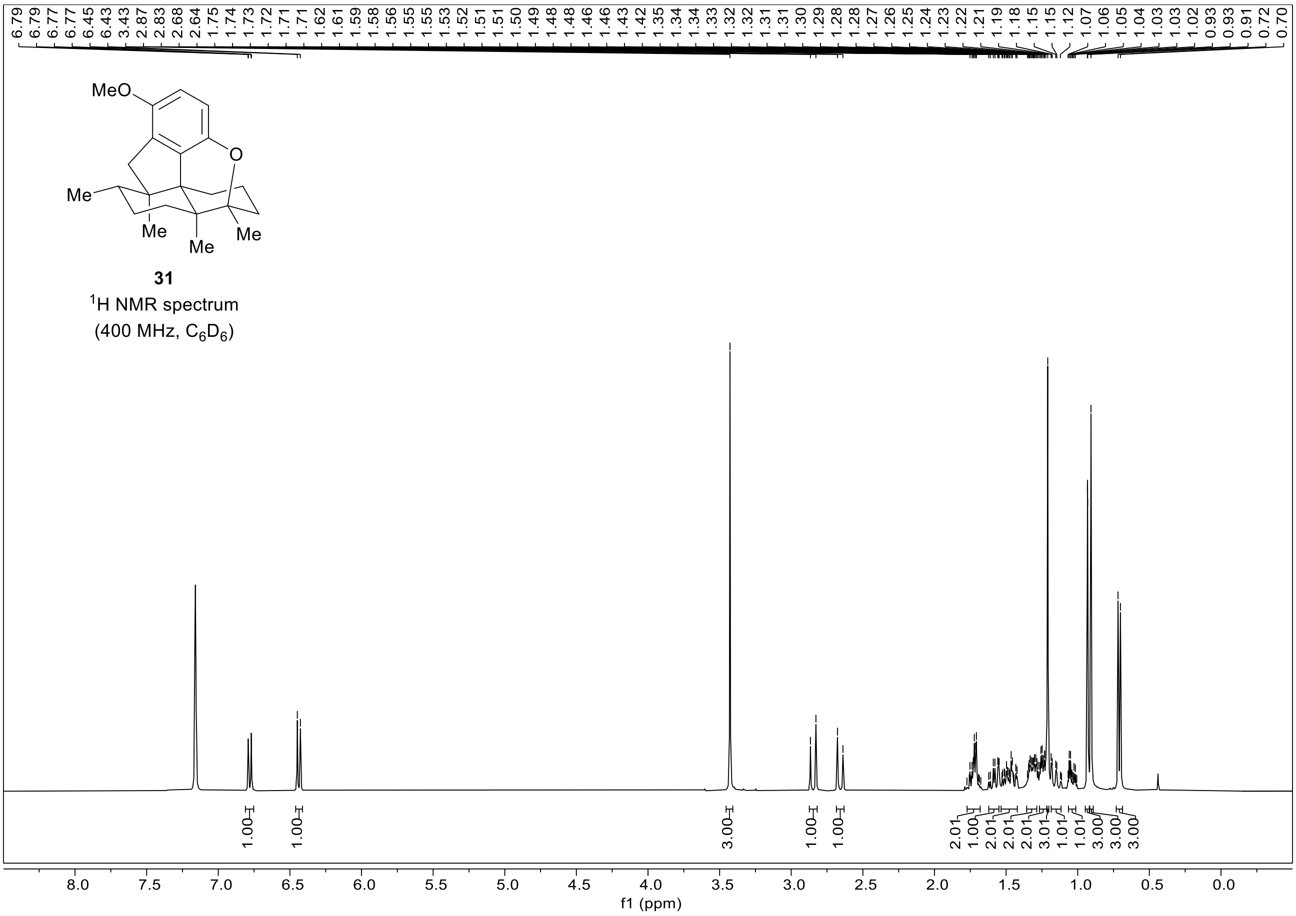
(471 MHz, $CDCl_3$)



ent-**14**
^{1}H NMR spectrum
(500 MHz, CDCl$_3$)



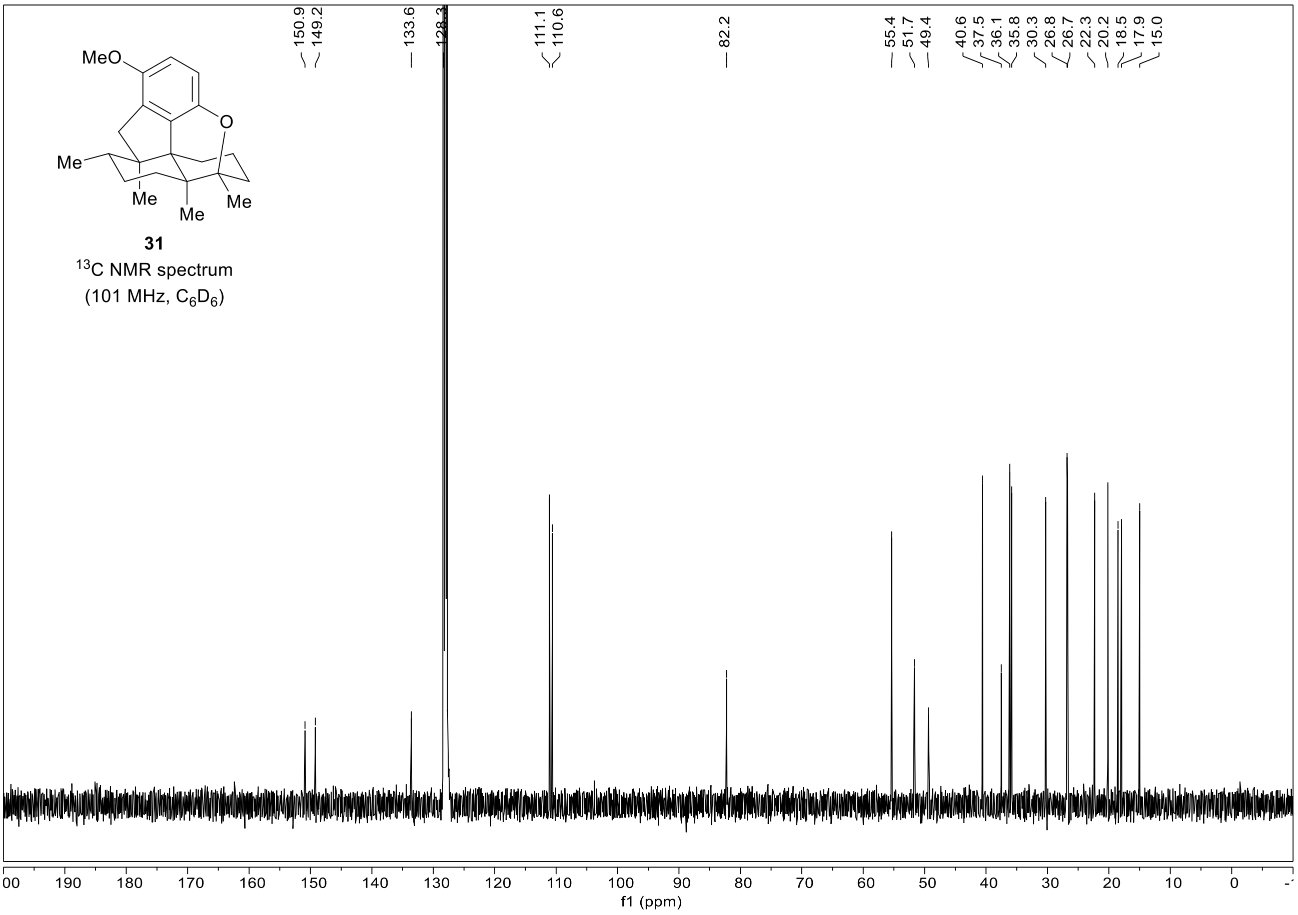
ent-**14**
^{13}C NMR spectrum
(126 MHz, CDCl$_3$)



31

^{1}H NMR spectrum

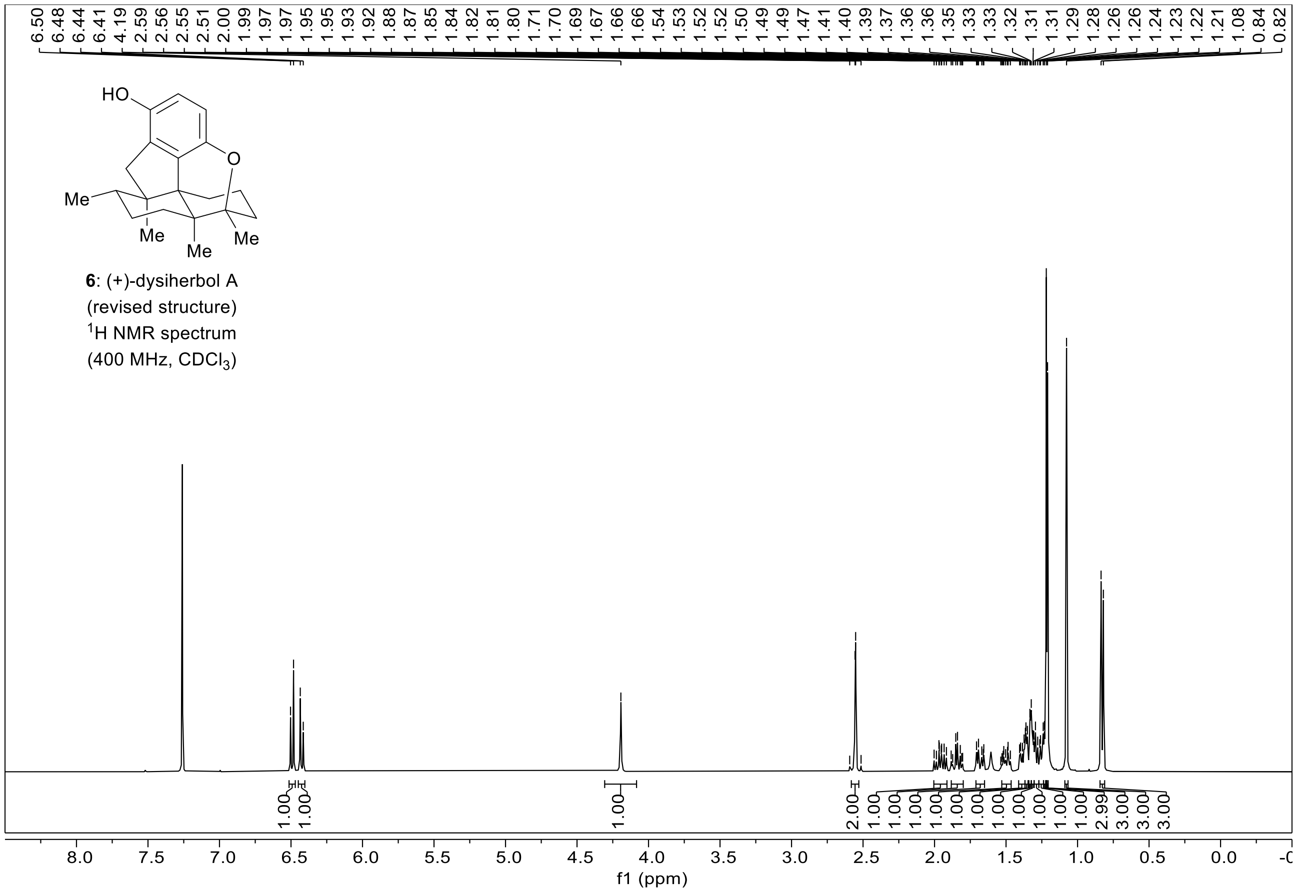
(400 MHz, C_6D_6)



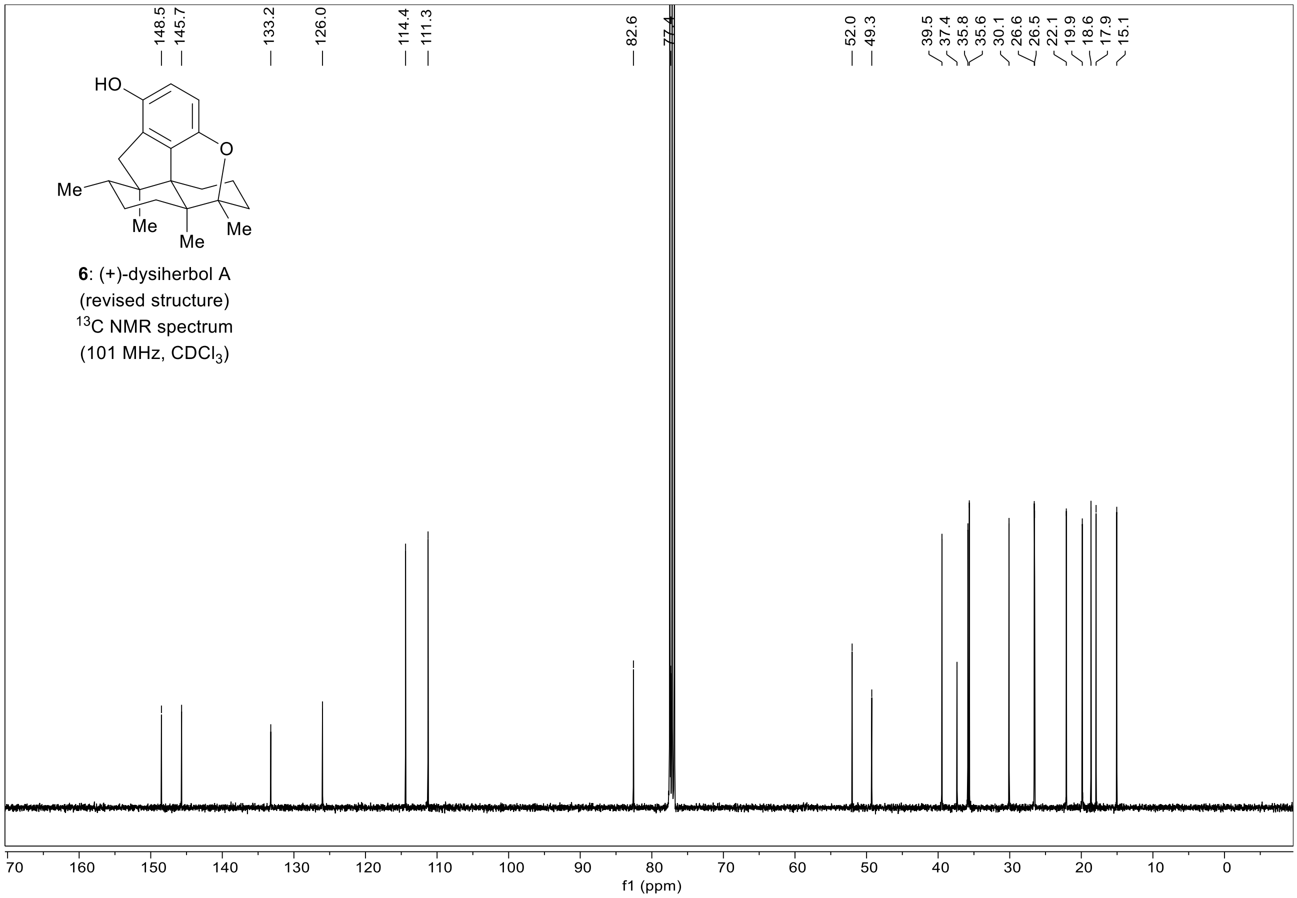
31

^{13}C NMR spectrum

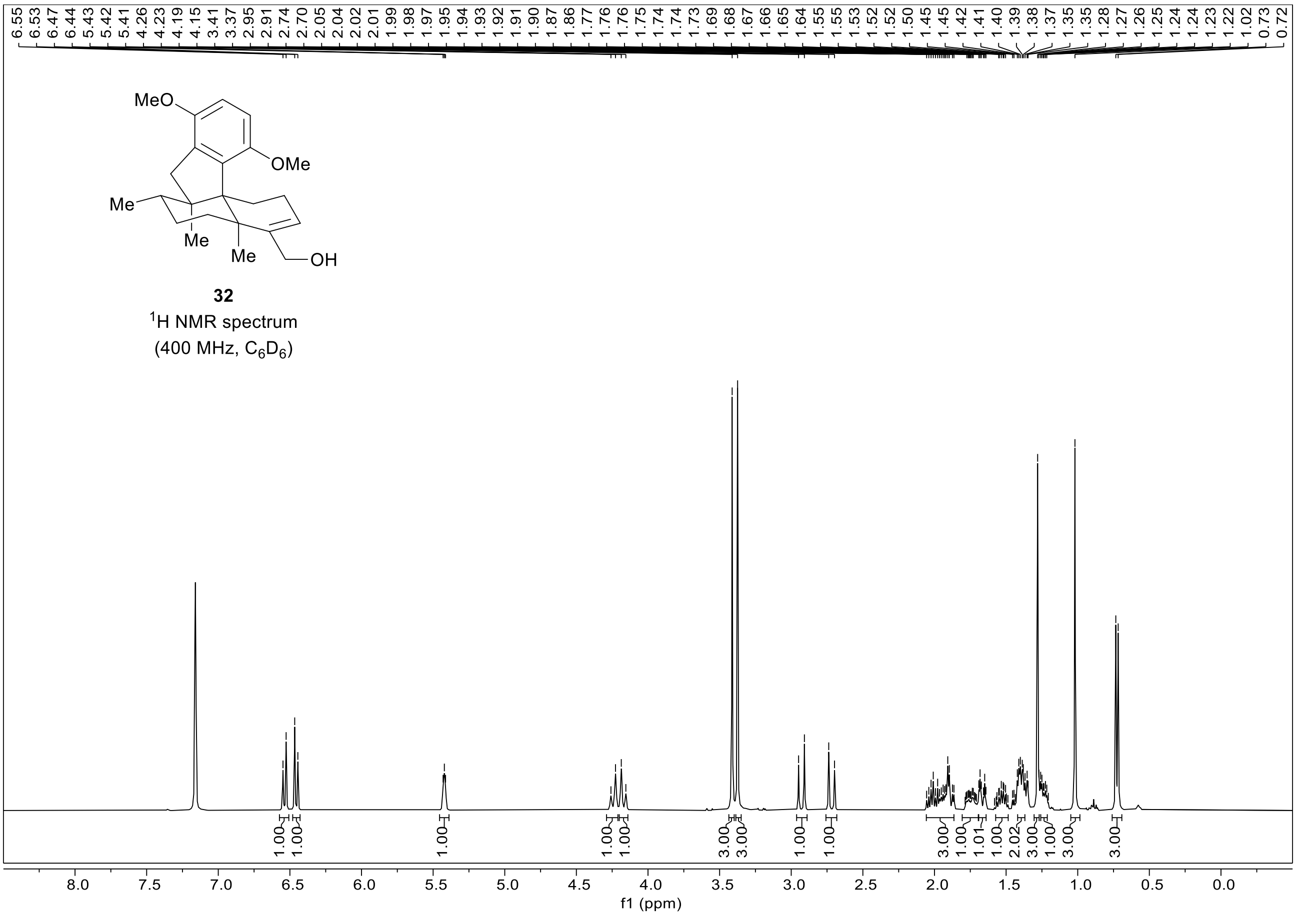
(101 MHz, C_6D_6)



6: (+)-dysiherbol A
(revised structure)
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



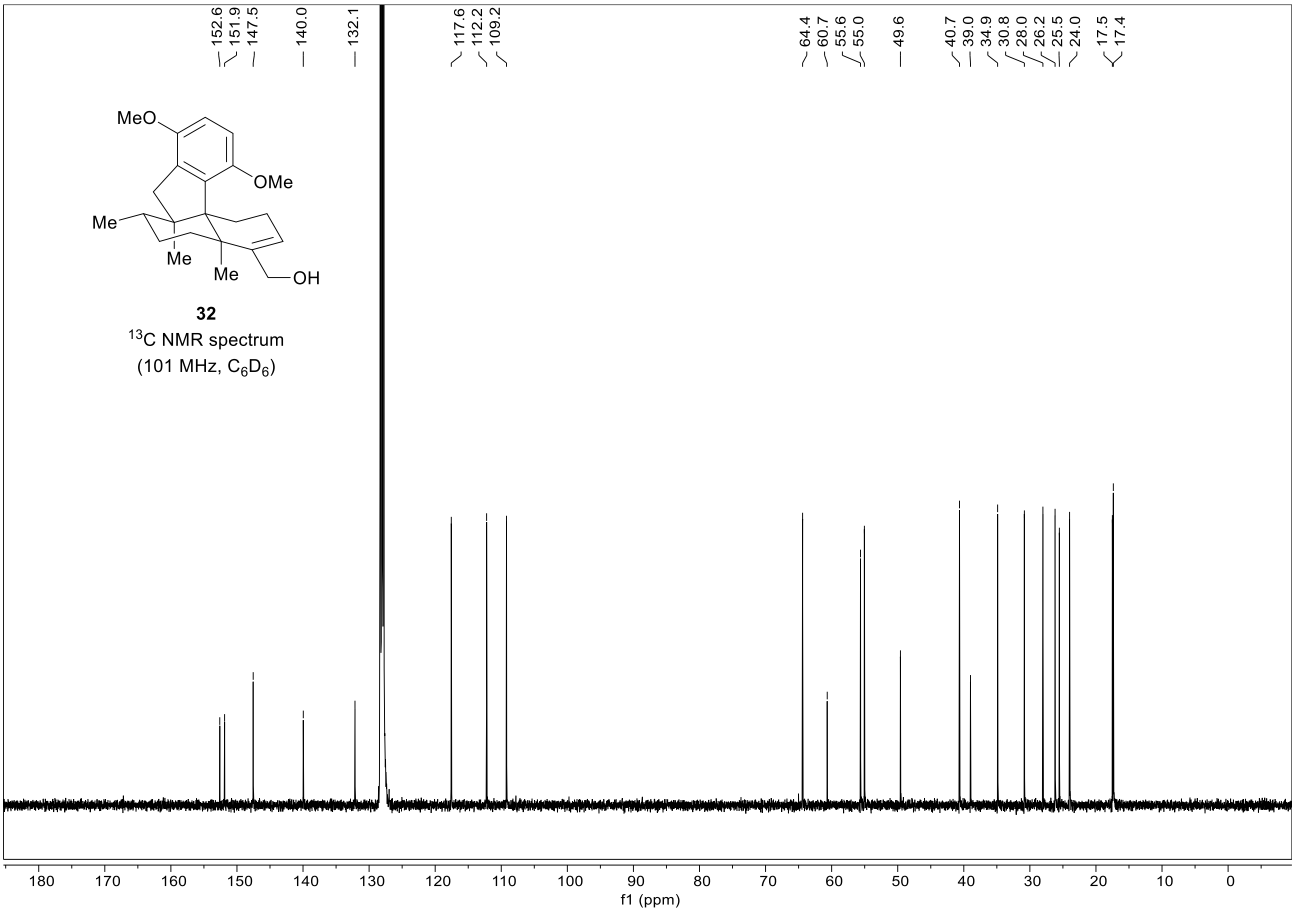
6: (+)-dysiherbol A
(revised structure)
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)



32

^{1}H NMR spectrum

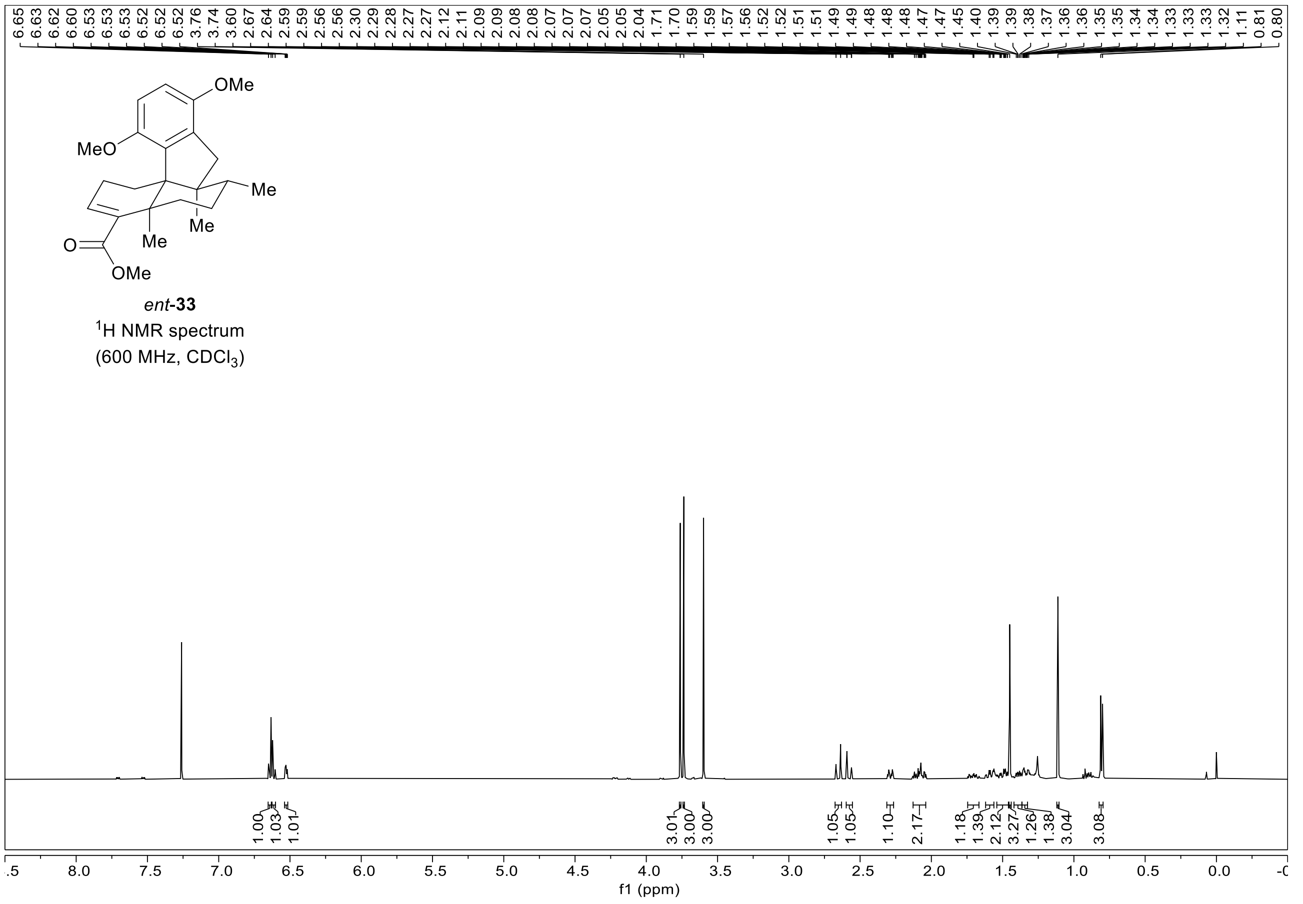
(400 MHz, C_6D_6)



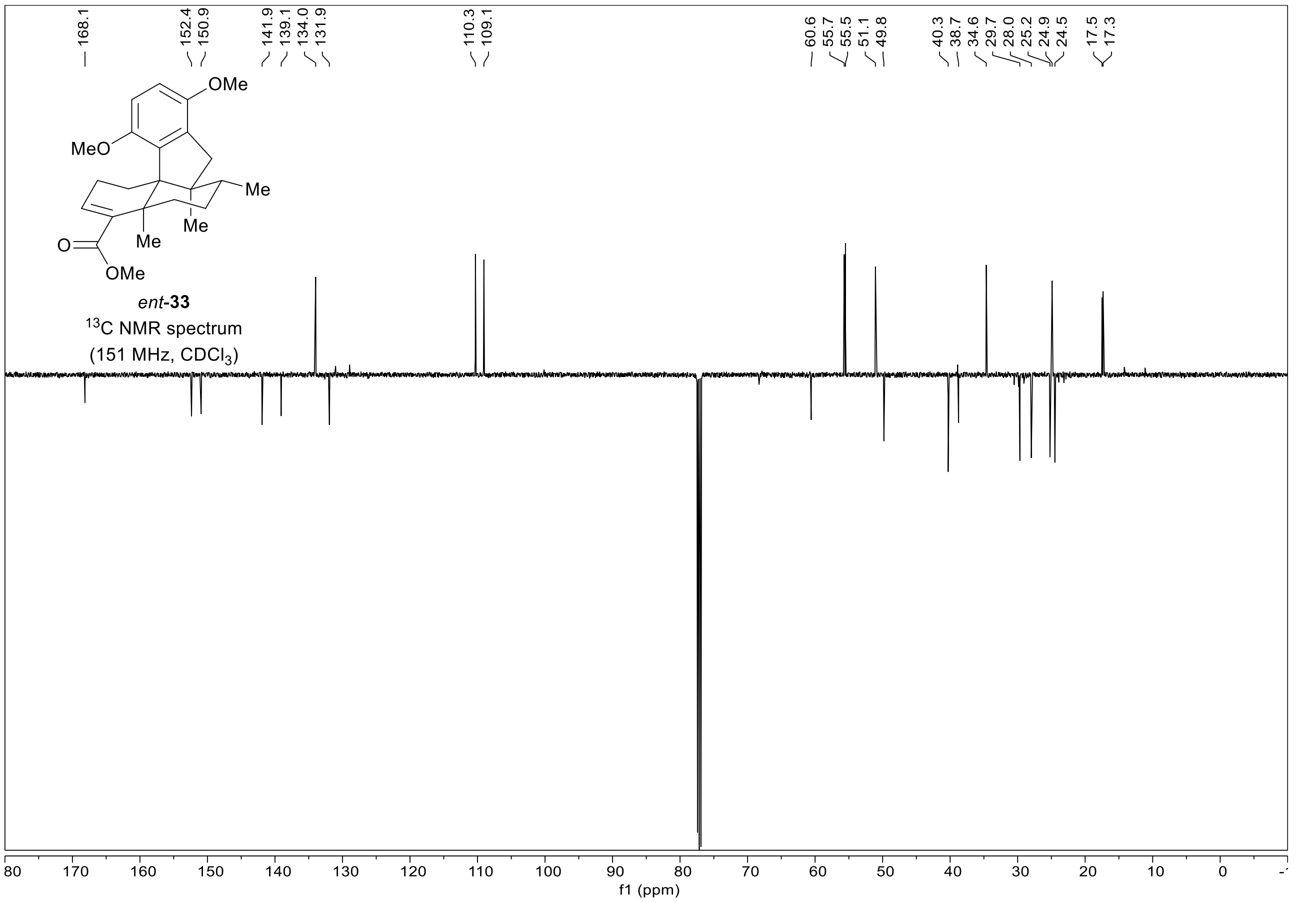
32

^{13}C NMR spectrum

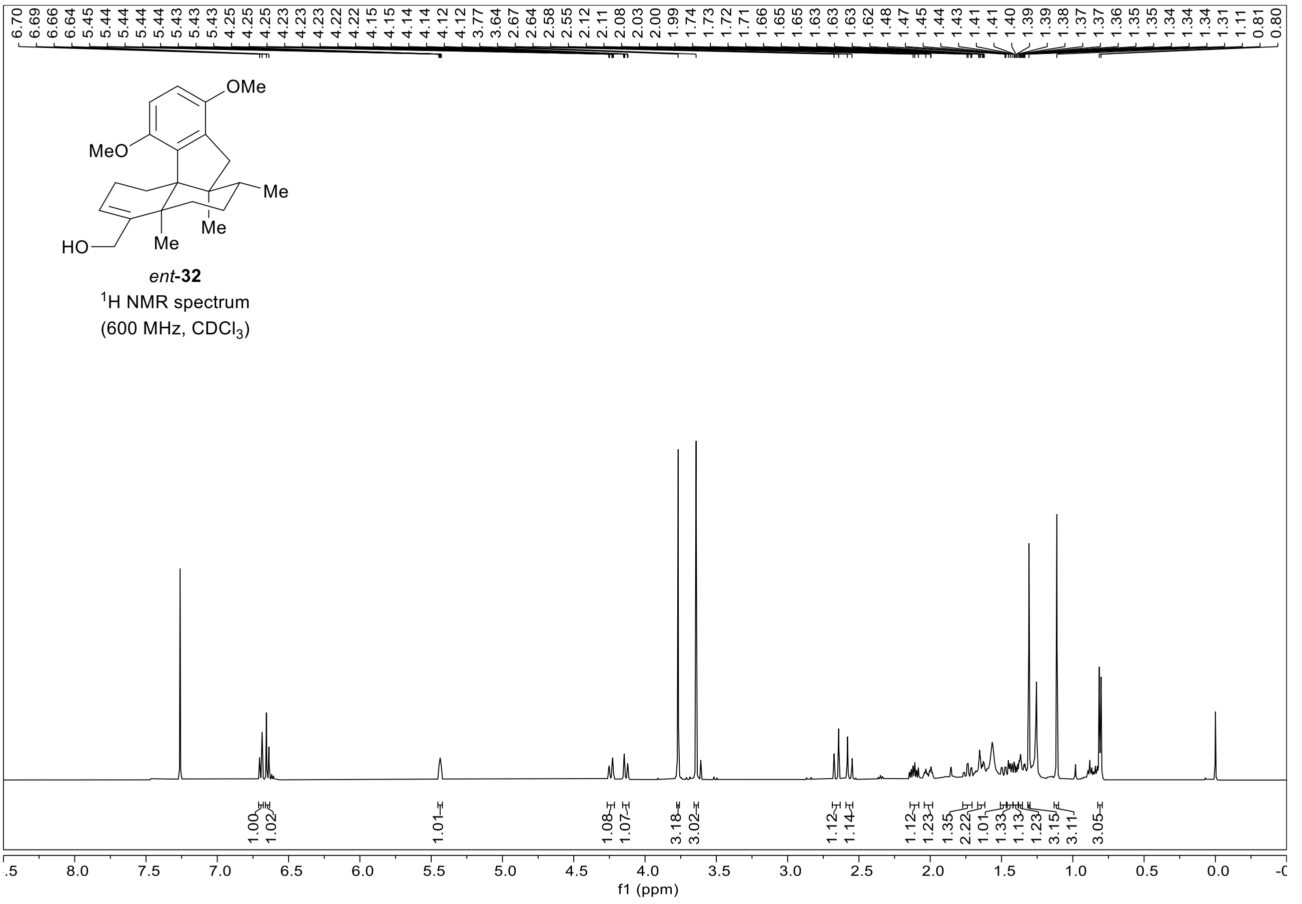
(101 MHz, C_6D_6)



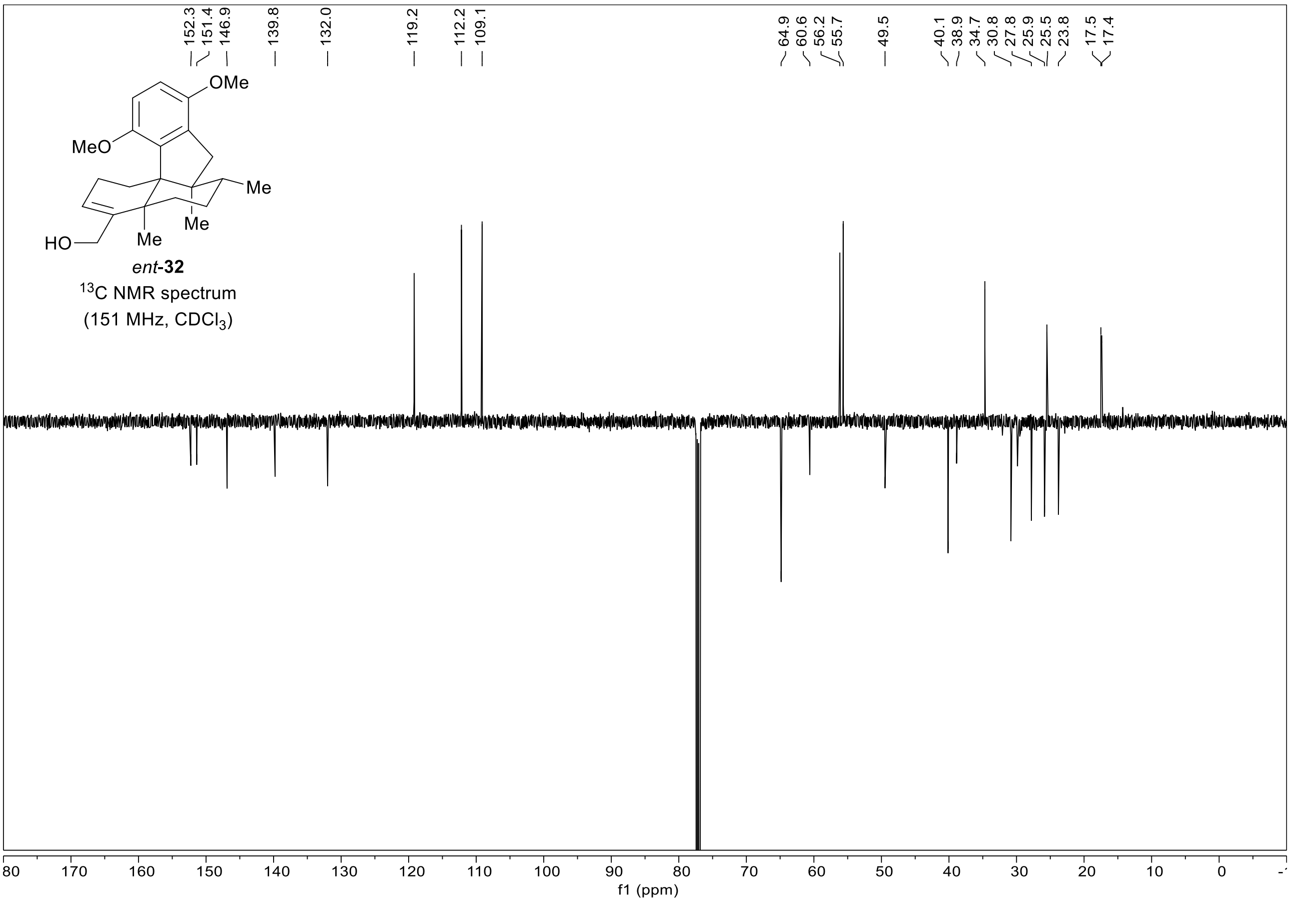
ent-**33**
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



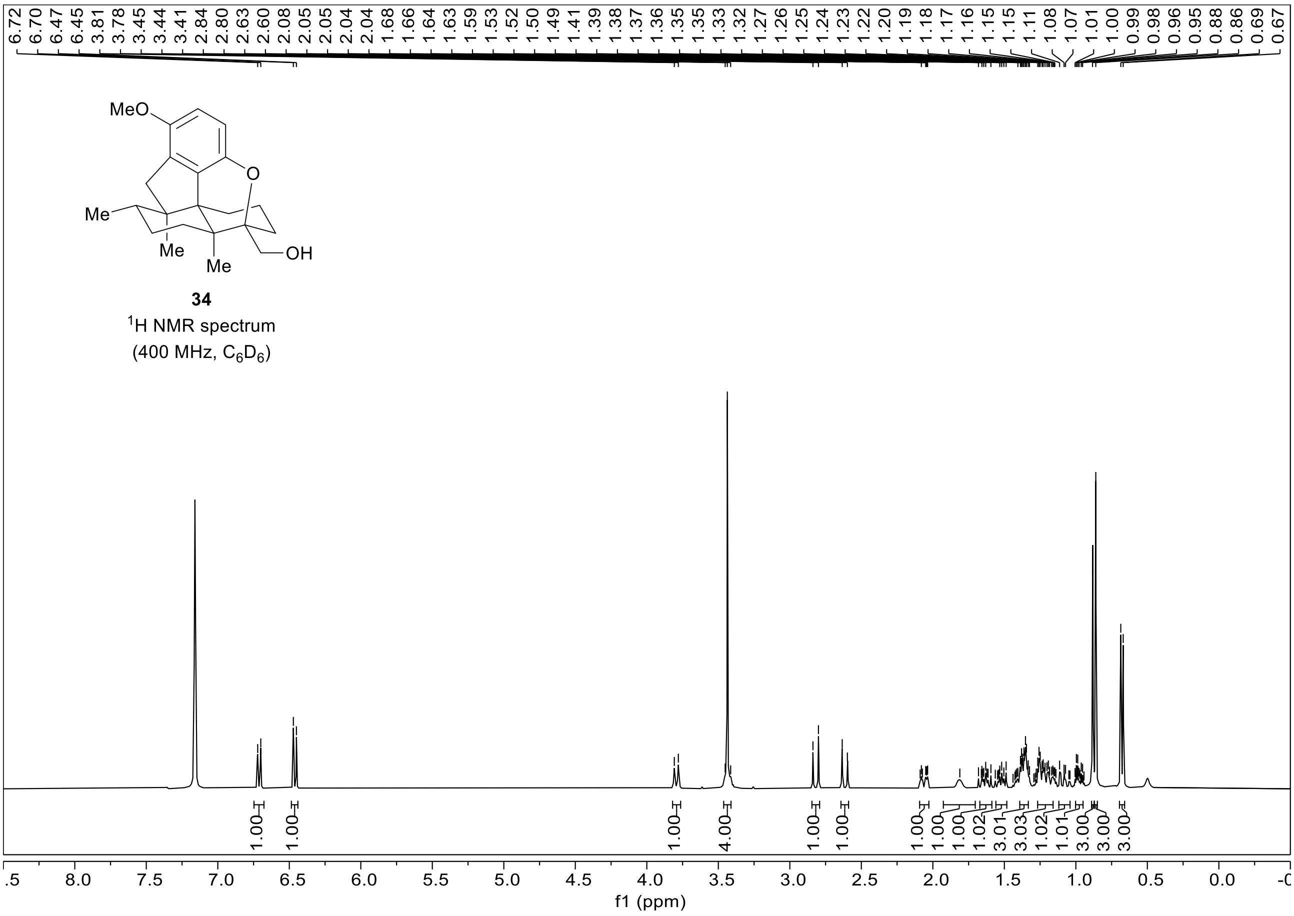
ent-**33**
^{13}C NMR spectrum
(151 MHz, $CDCl_3$)



ent-**32**
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



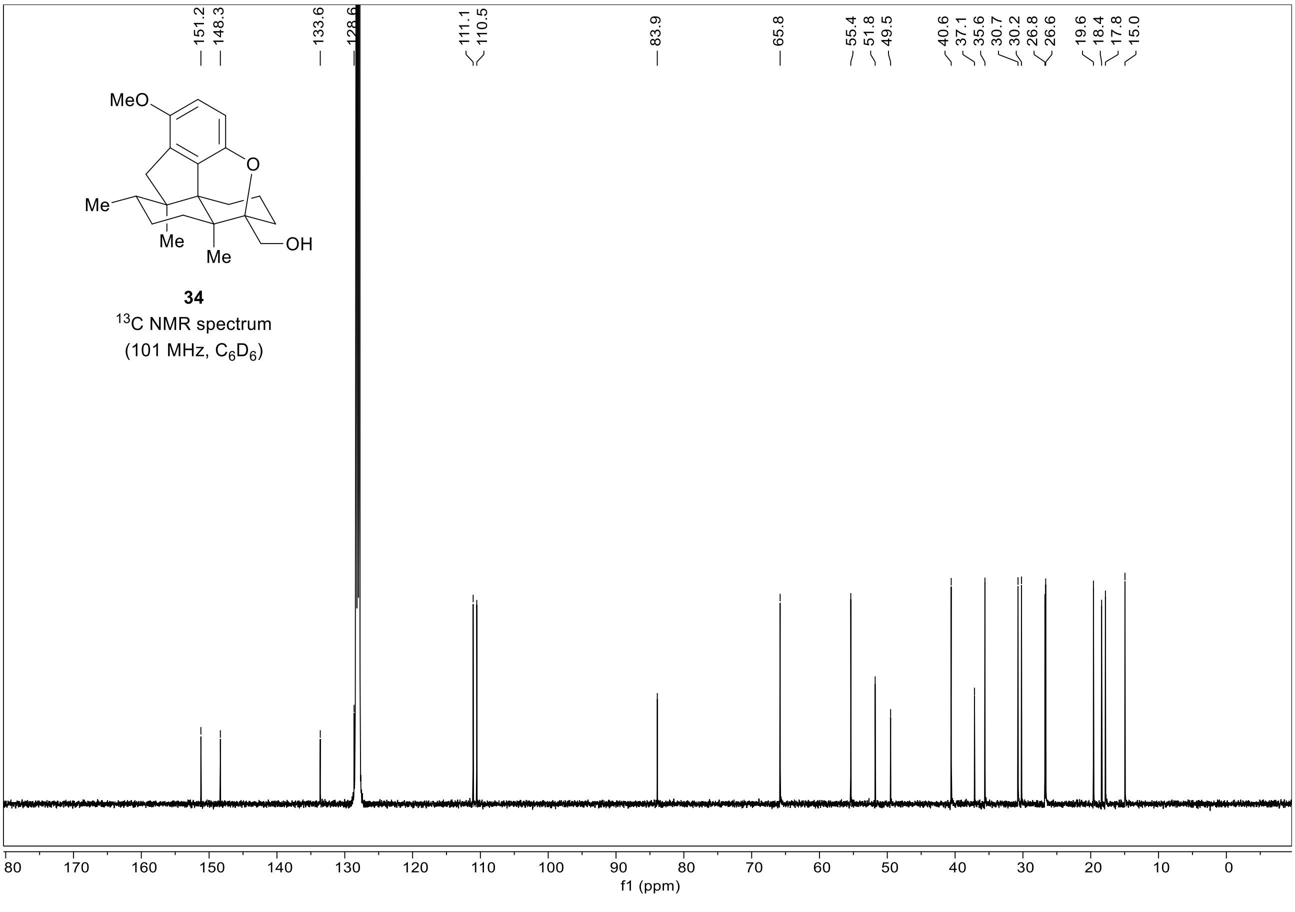
ent-**32**
^{13}C NMR spectrum
(151 MHz, $CDCl_3$)



34

^{1}H NMR spectrum

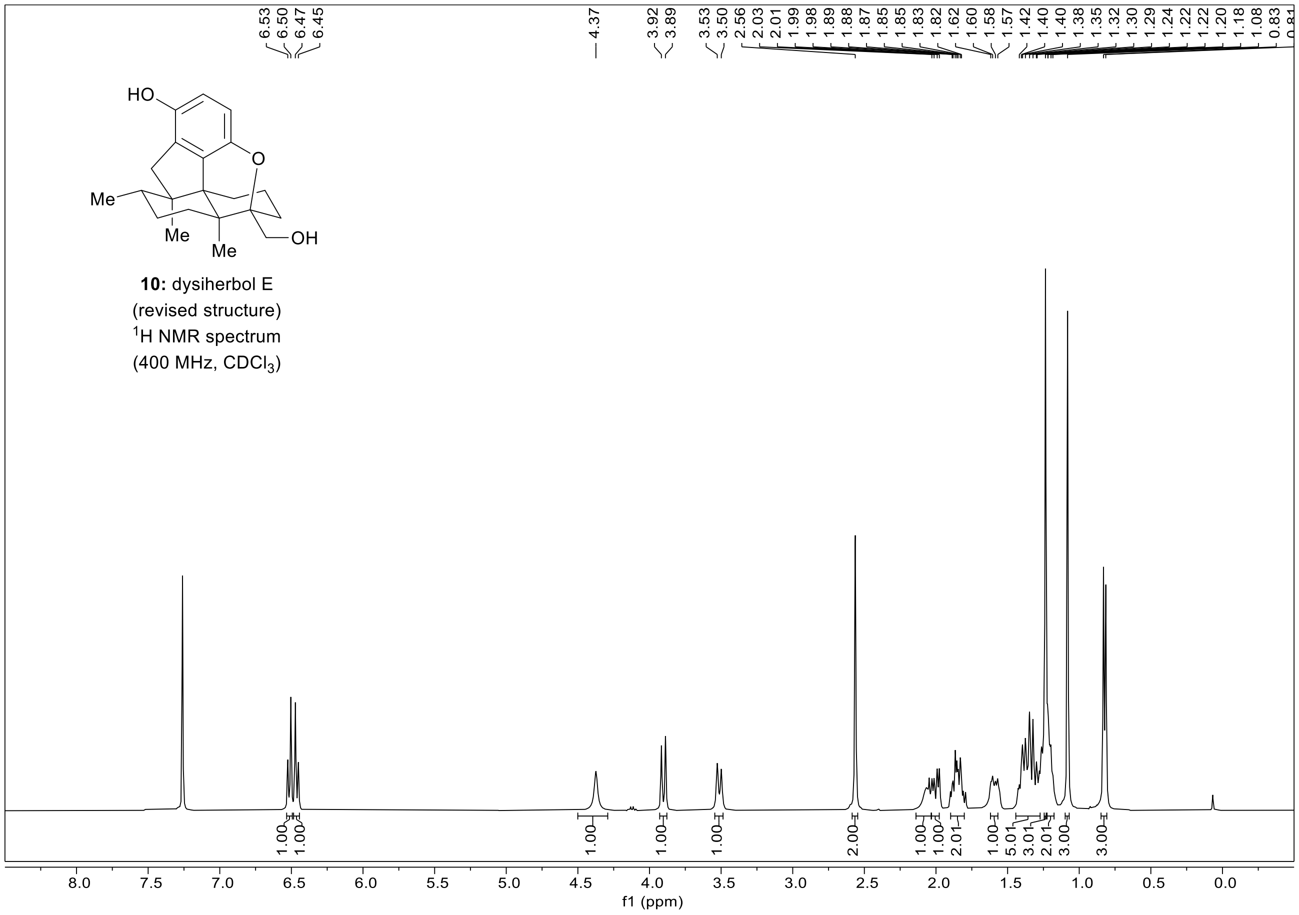
(400 MHz, C_6D_6)



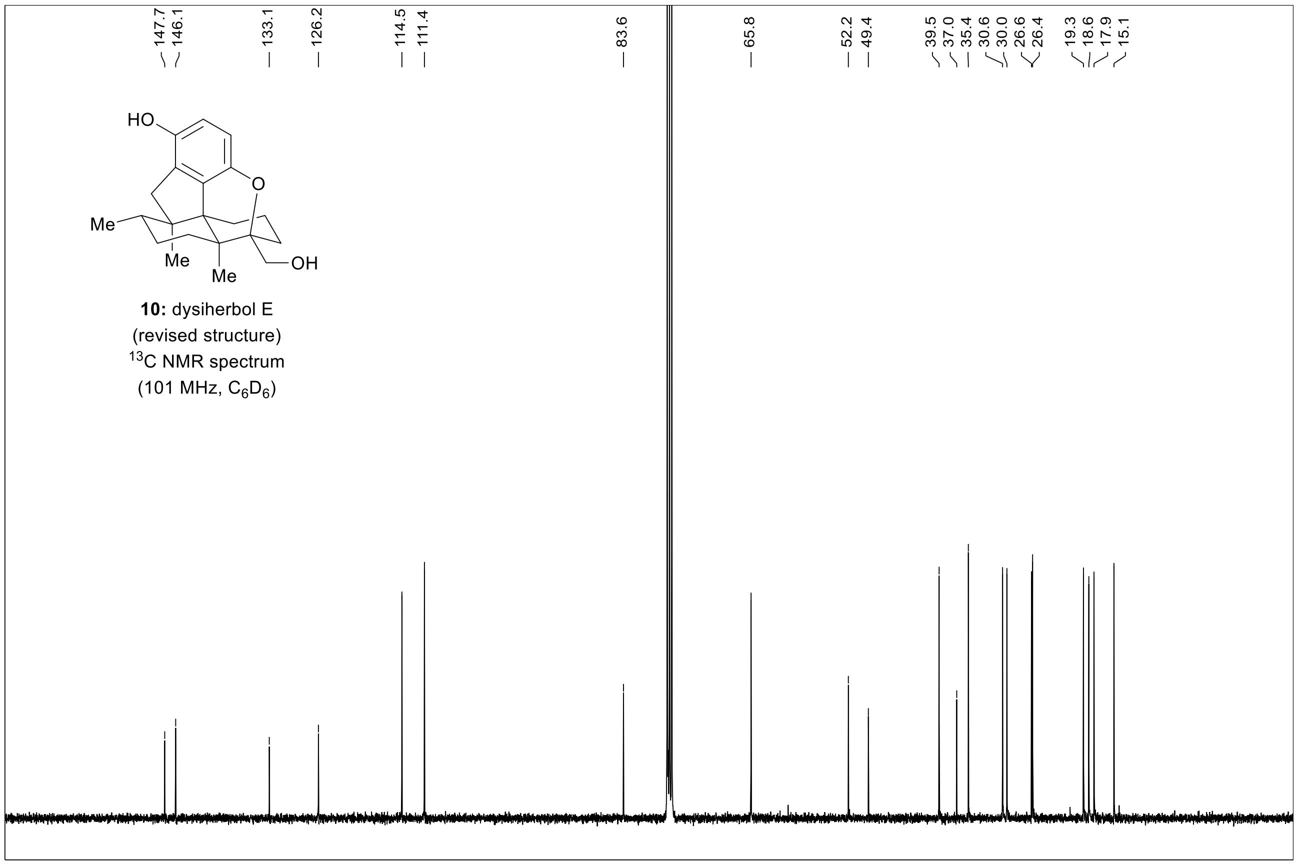
34

^{13}C NMR spectrum

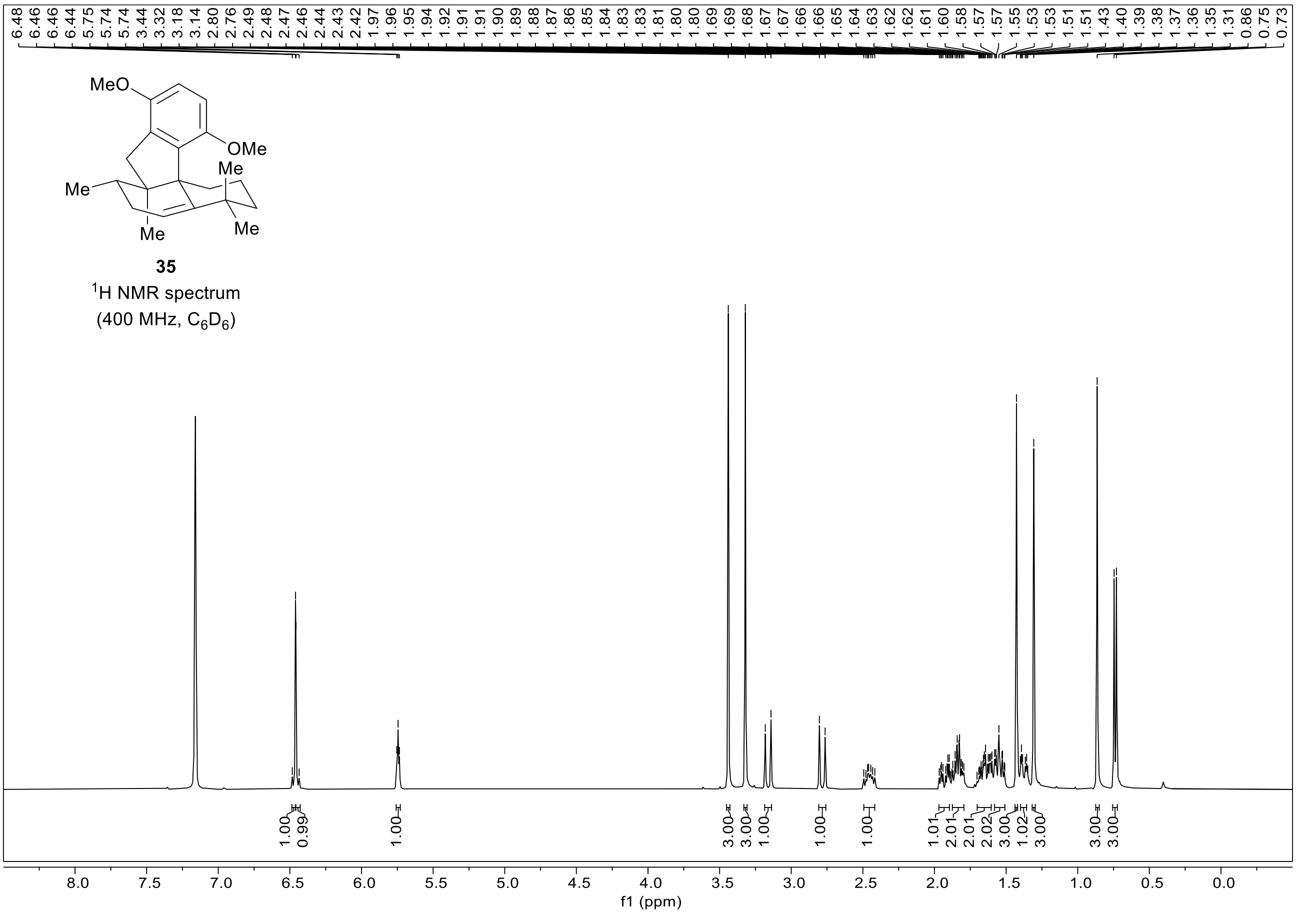
(101 MHz, C_6D_6)

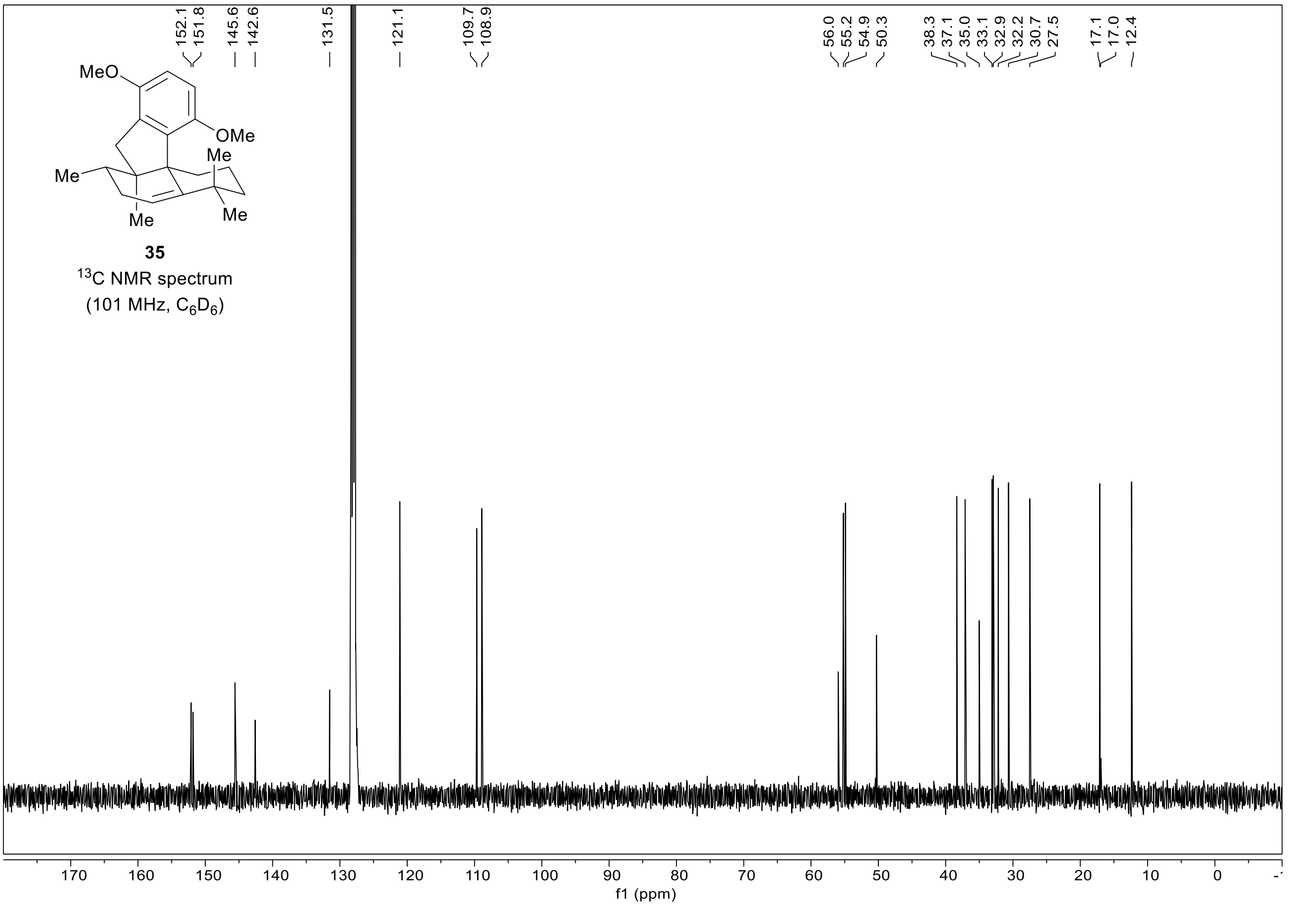


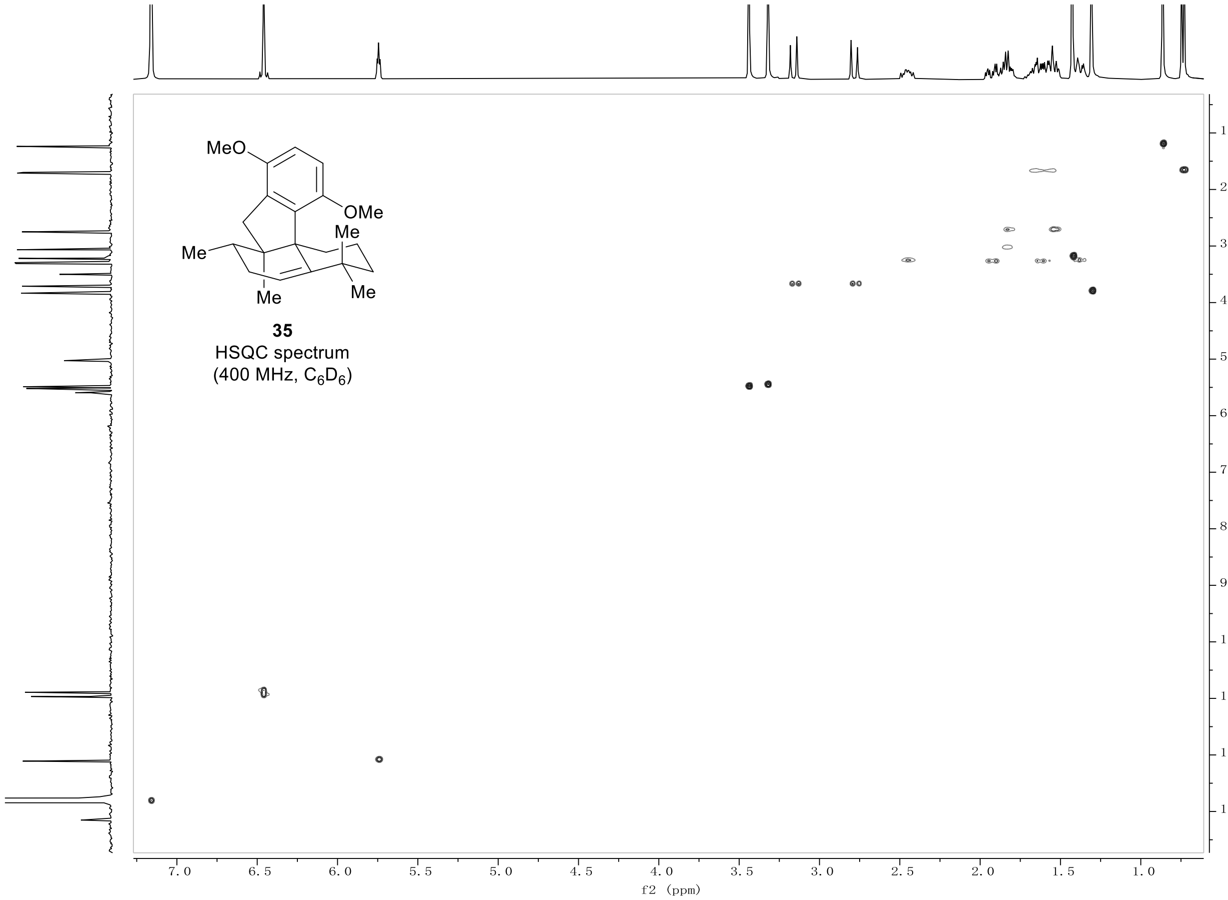
10: dysiherbol E
(revised structure)
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



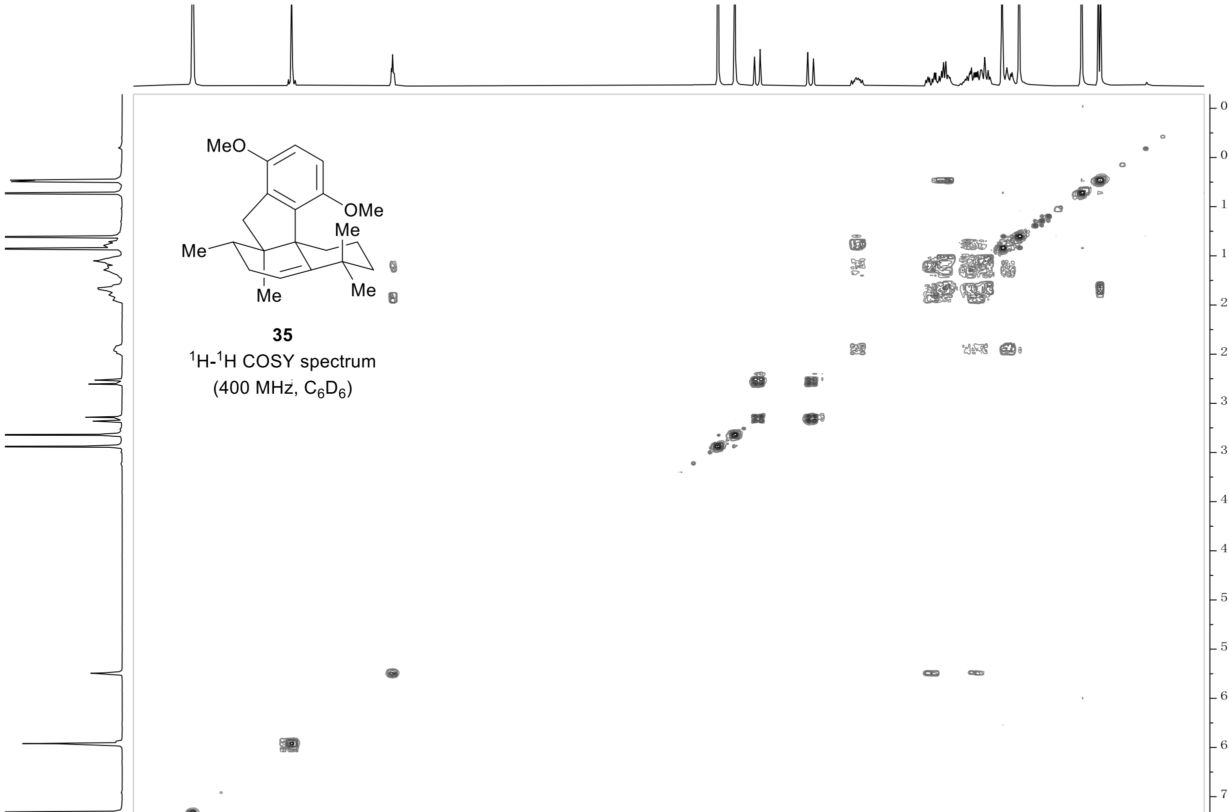
10: dysiherbol E
(revised structure)
^{13}C NMR spectrum
(101 MHz, C_6D_6)


6.48
6.46
6.46
6.44
5.75
5.74
3.44
3.32
3.18
3.14
2.80
2.76
2.49
2.48
2.47
2.46
2.44
2.43
2.42
1.97
1.96
1.95
1.94
1.92
1.91
1.91
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.83
1.81
1.80
1.80
1.69
1.69
1.68
1.67
1.67
1.66
1.66
1.65
1.64
1.63
1.62
1.62
1.61
1.60
1.58
1.57
1.57
1.55
1.53
1.53
1.51
1.51
1.43
1.40
1.39
1.38
1.37
1.36
1.35
1.31
0.86
0.75
0.73
MeO
OMe
Me
Me
Me
Me
35
^{1}H NMR spectrum
(400 MHz, C_6D_6)
1.00
0.99
1.00
3.00
3.00
1.00
1.00
1.00
1.01
2.01
2.01
2.02
3.00
1.02
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

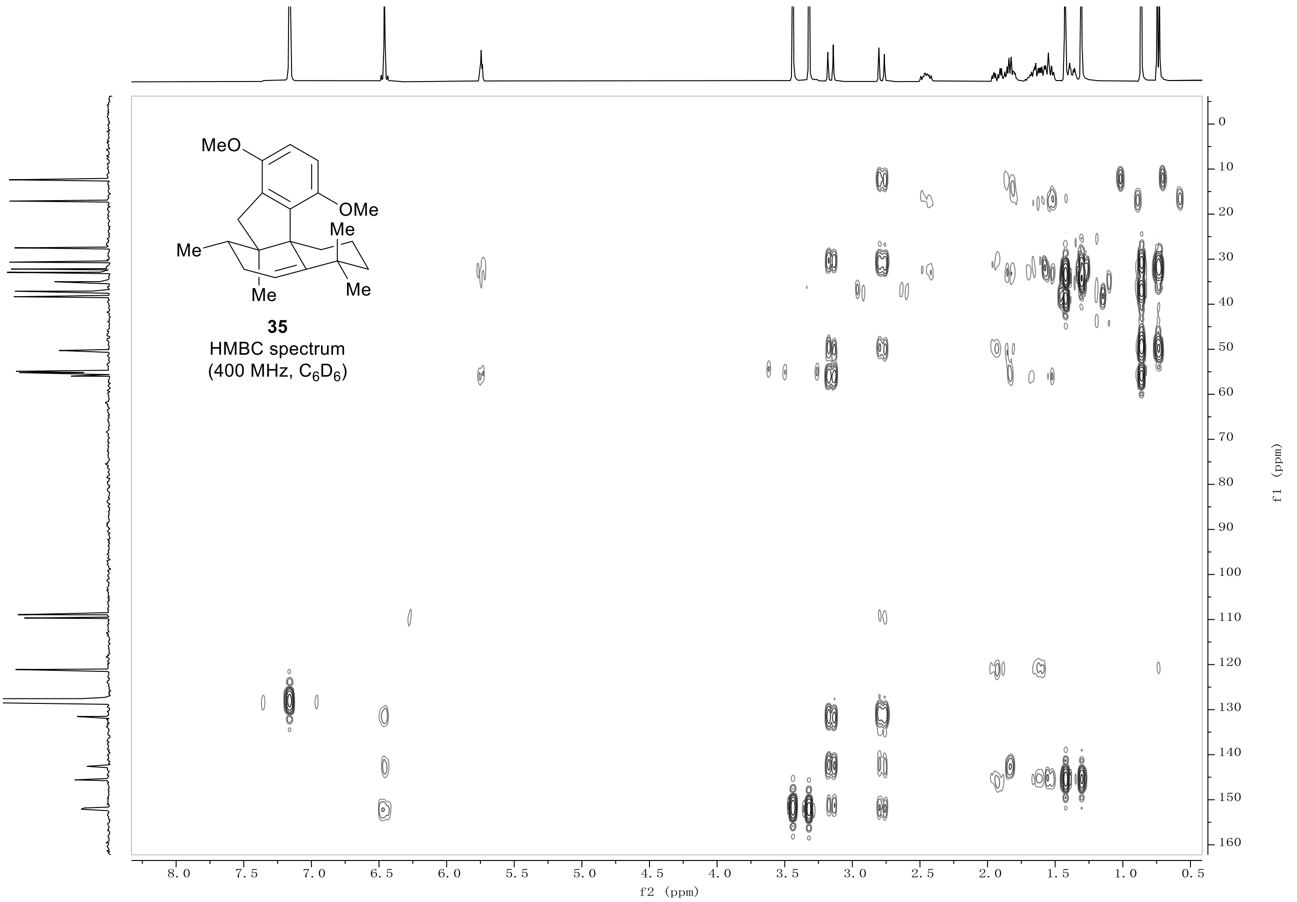

152.1
151.8
145.6
142.6
131.5
121.1
109.7
108.9
56.0
55.2
54.9
50.3
38.3
37.1
35.0
33.1
32.9
32.2
30.7
27.5
17.1
17.0
12.4
MeO
OMe
Me
Me
Me
Me
35
^{13}C NMR spectrum
(101 MHz, C_6D_6)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



35
HSQC spectrum
(400 MHz, C_6D_6)



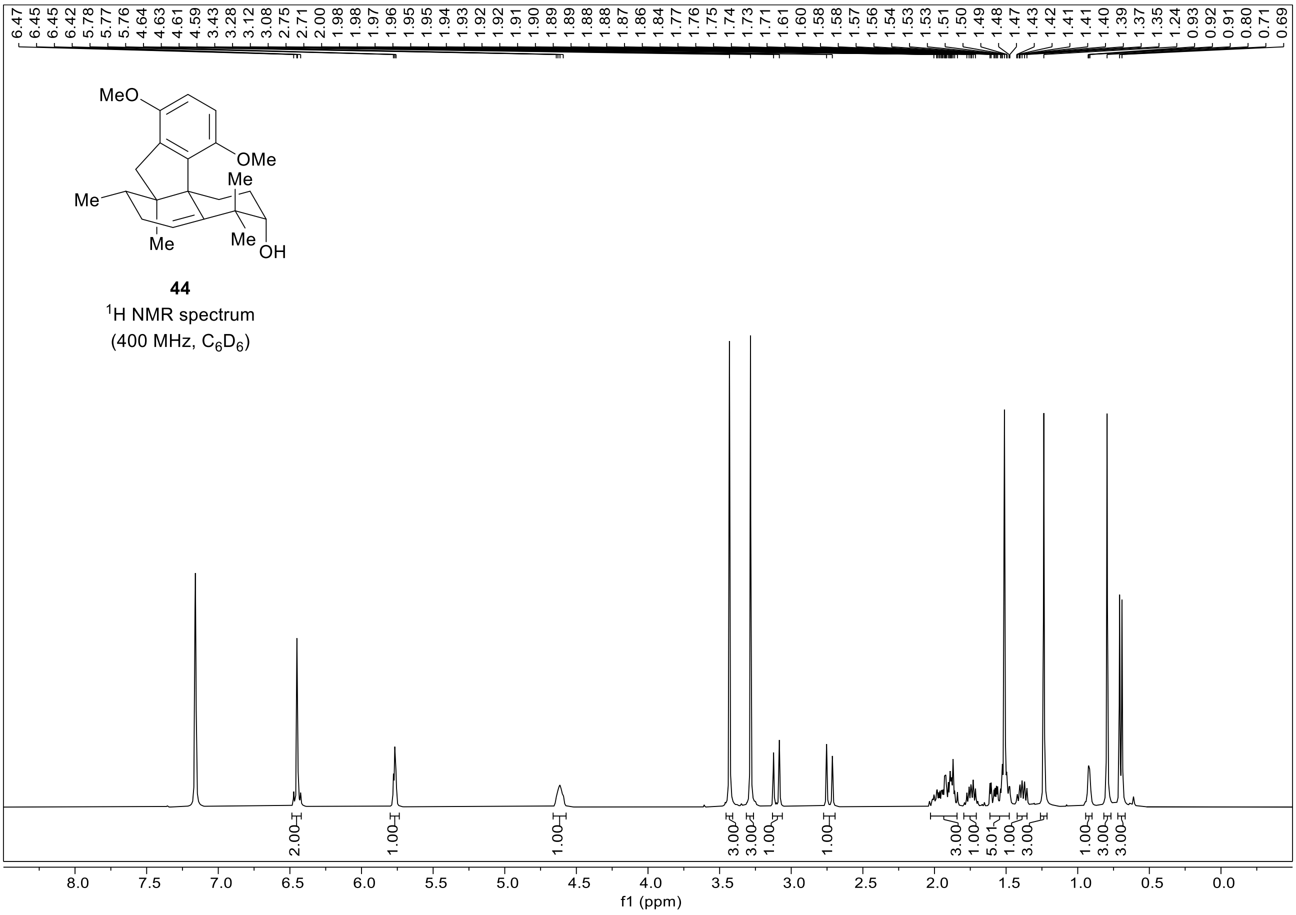
35
^{1}H-^{1}H COSY spectrum
(400 MHz, C_6D_6)



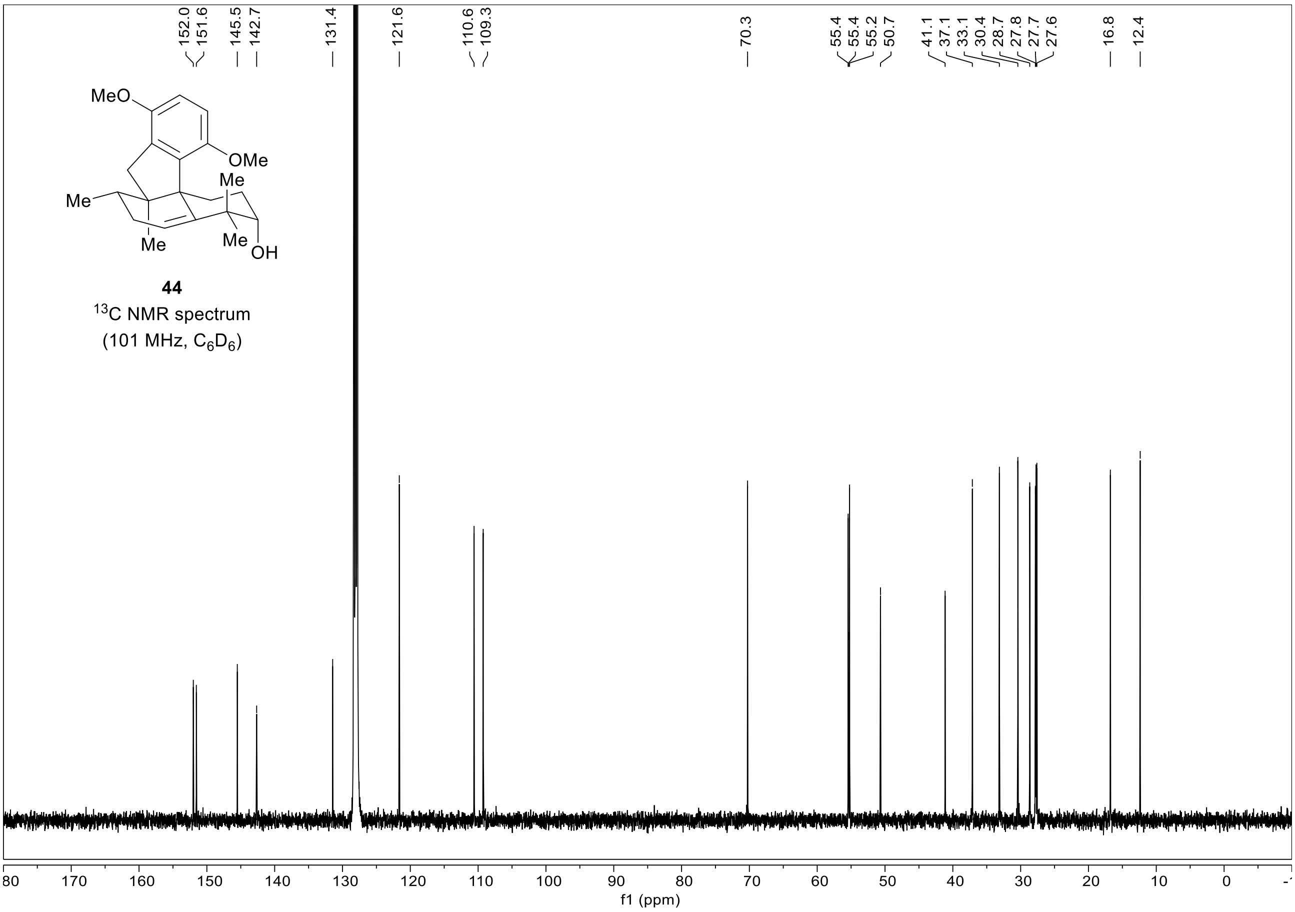
35

HMBC spectrum

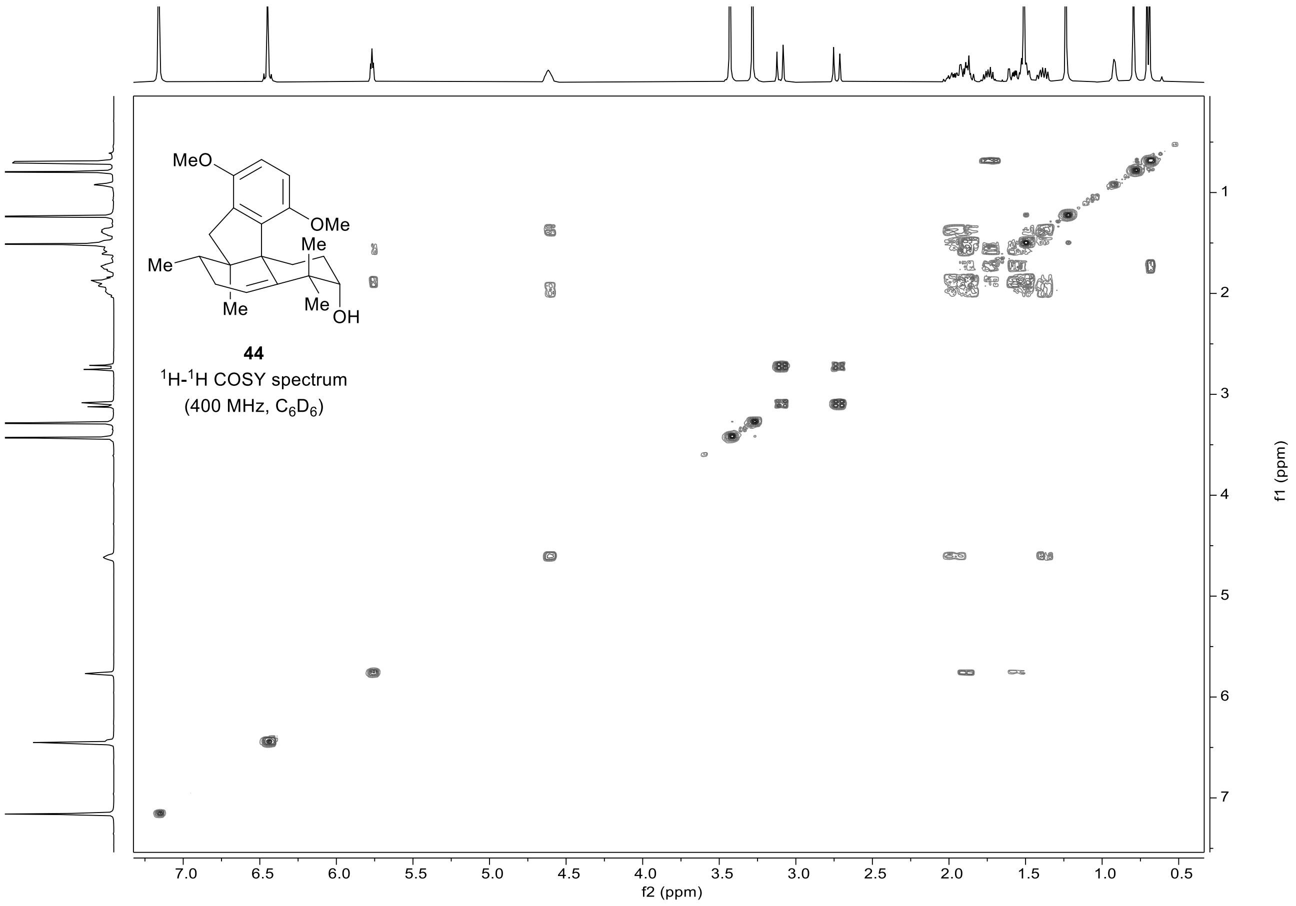
(400 MHz, C_6D_6)



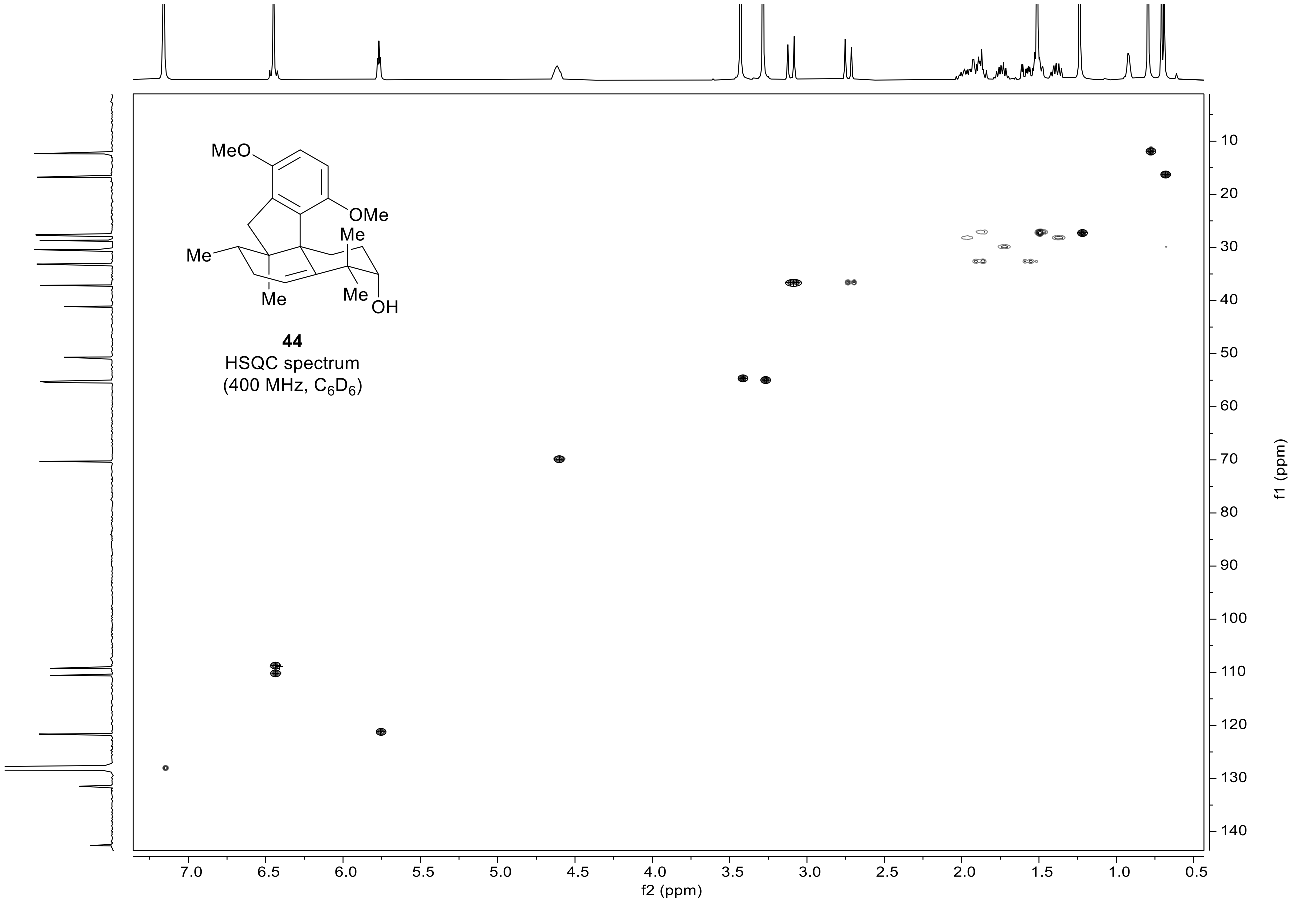
44
^{1}H NMR spectrum
(400 MHz, C_6D_6)



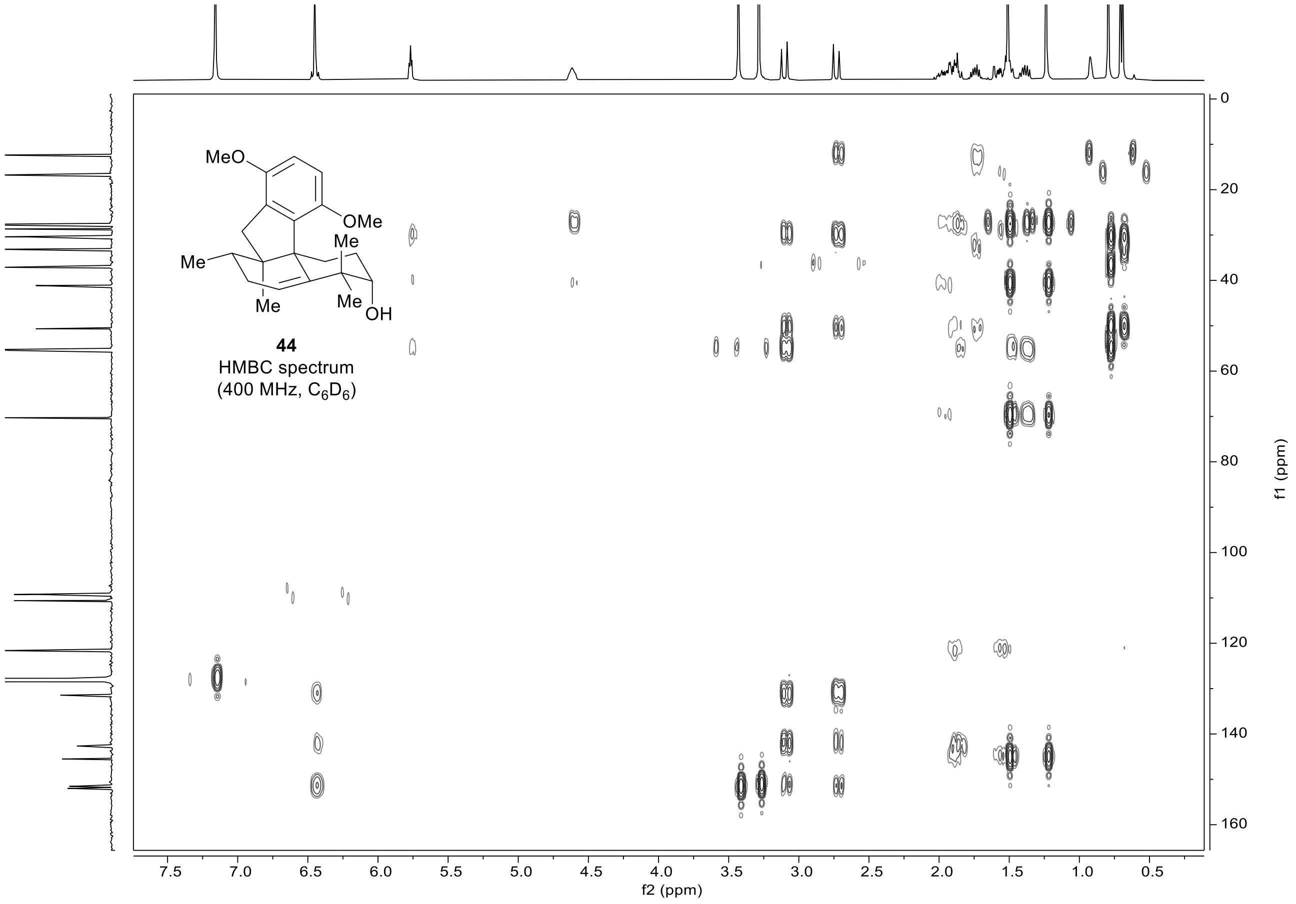
44
^{13}C NMR spectrum
(101 MHz, C_6D_6)

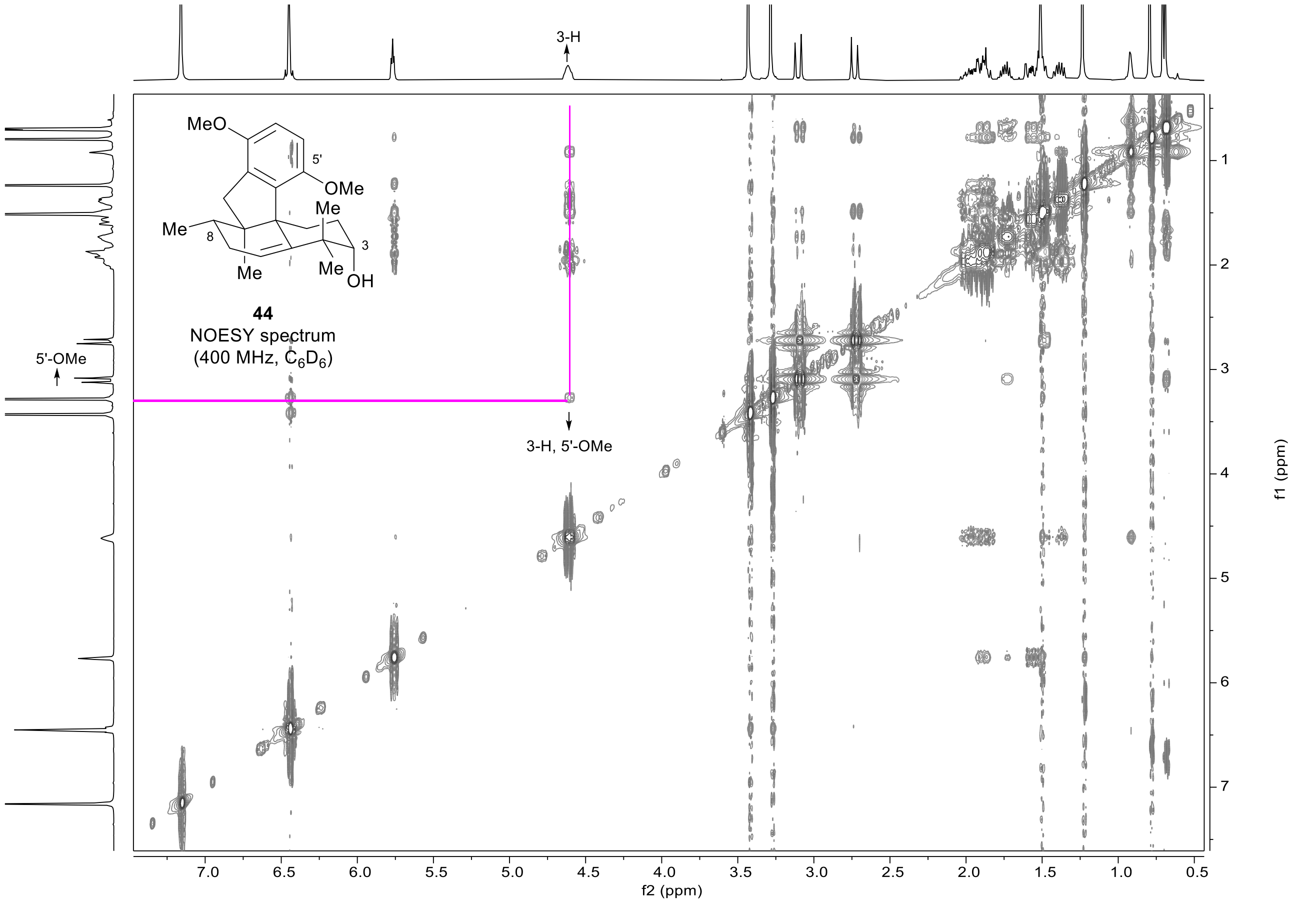


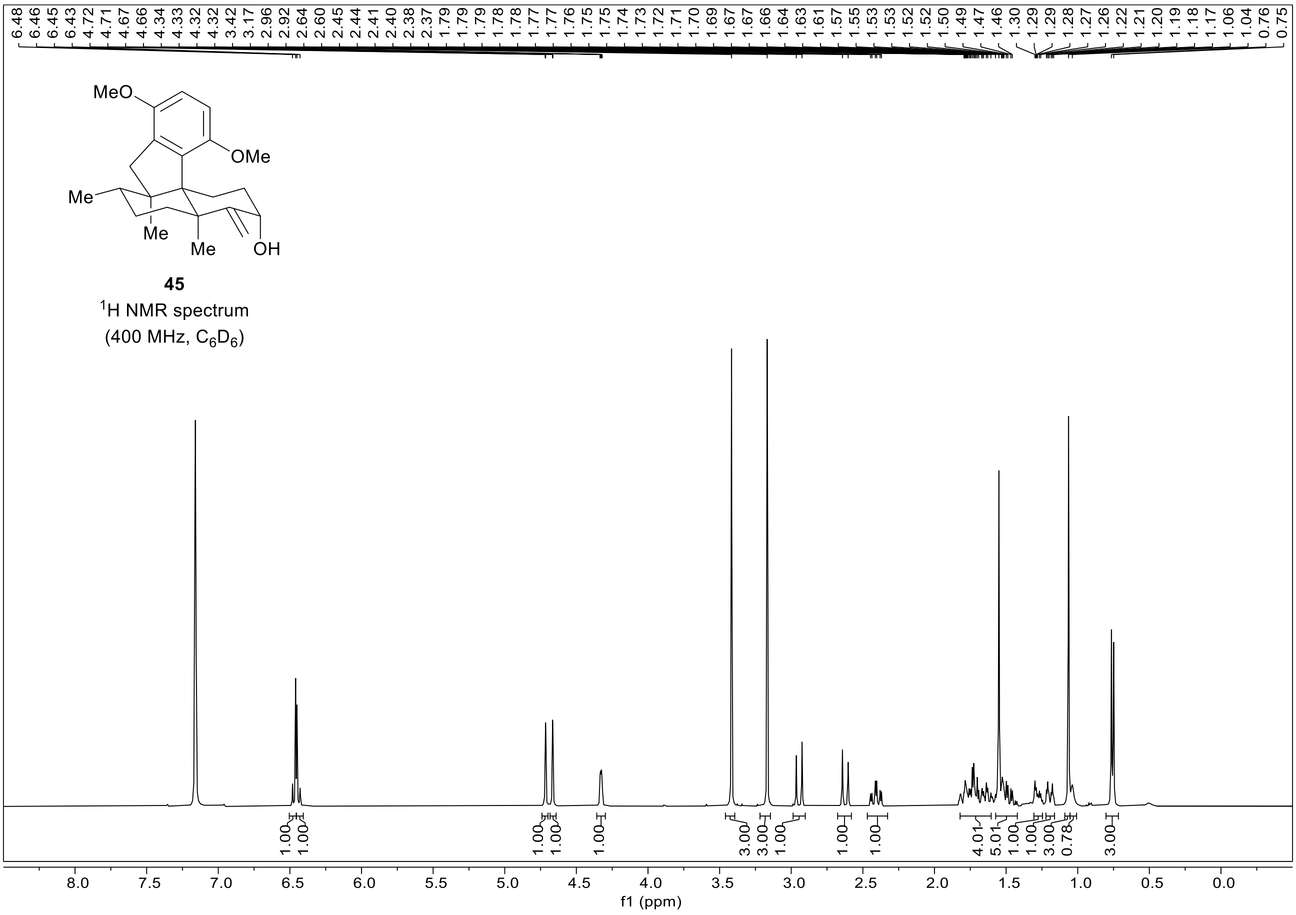
44
^{1}H-^{1}H COSY spectrum
(400 MHz, C_6D_6)



44
HSQC spectrum
(400 MHz, C_6D_6)


MeO
OMe
Me
Me
Me
Me
OH
44
HMBC spectrum
(400 MHz, C$_6$D$_6$)
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
20
40
60
80
100
120
140
160

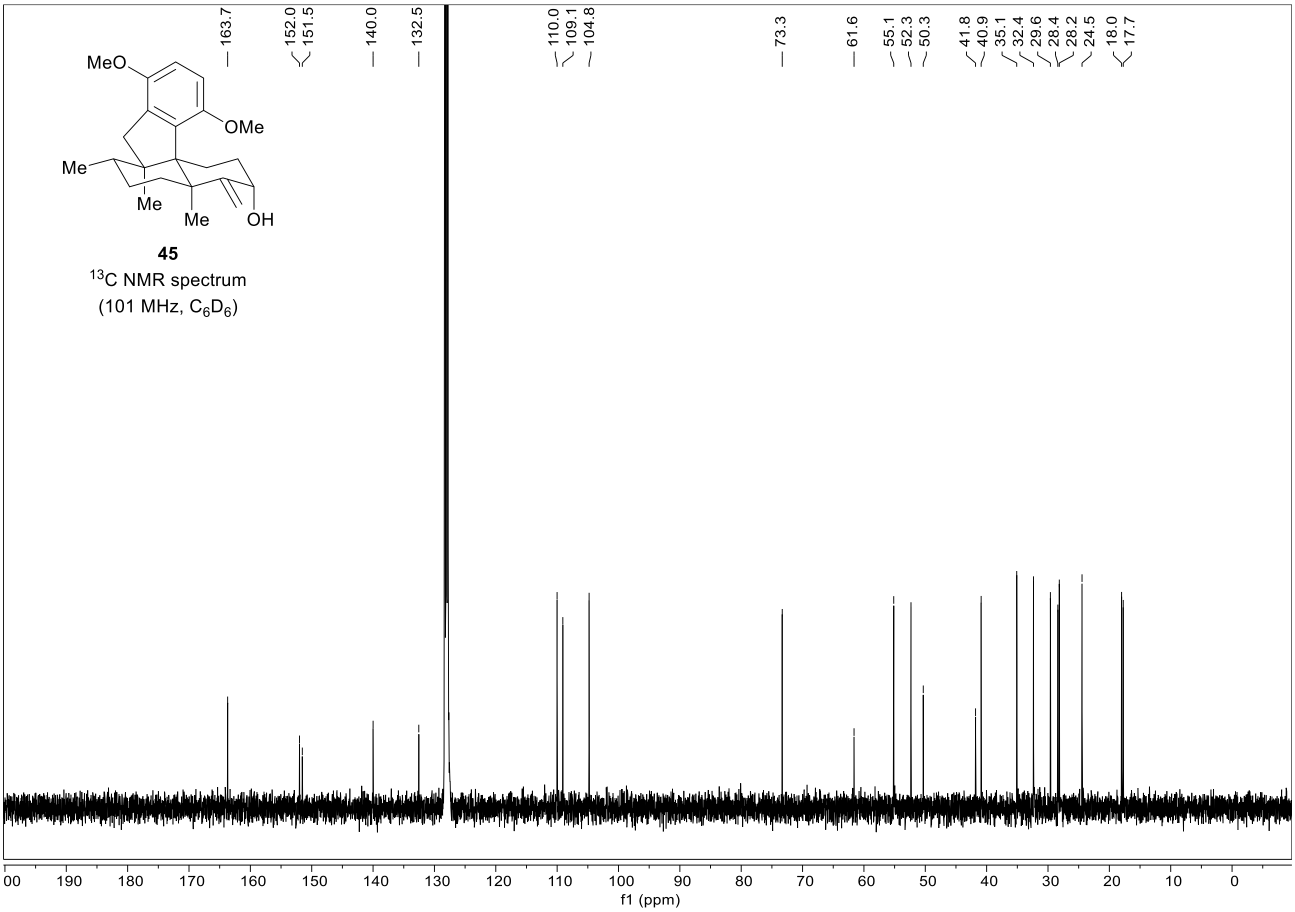

MeO
5'
OMe
Me
Me
8
3
Me
Me
OH
44
NOESY spectrum
(400 MHz, C$_6$D$_6$)
3-H
5'-OMe
3-H, 5'-OMe
f2 (ppm)
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1
2
3
4
5
6
7



45

^{1}H NMR spectrum

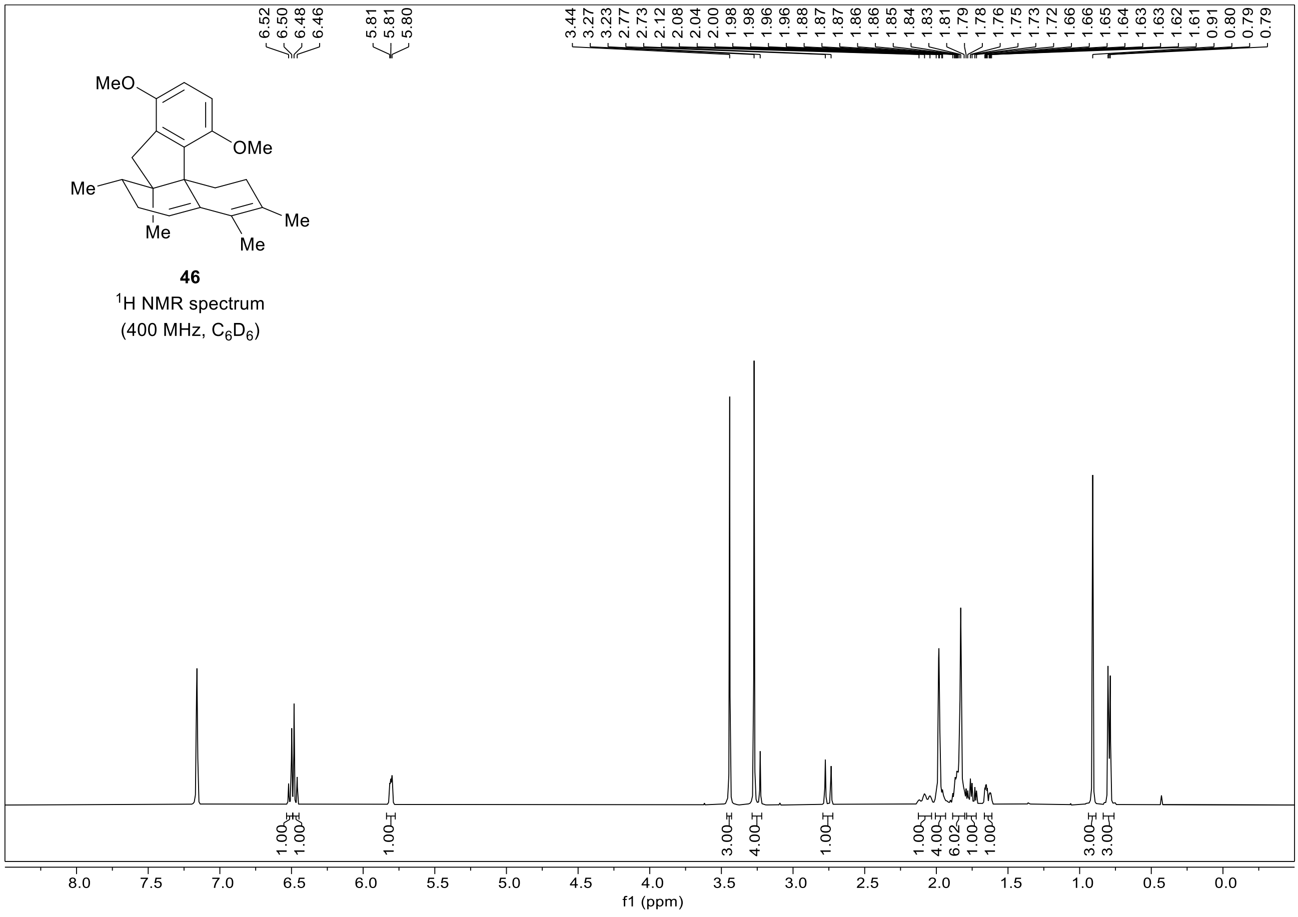
(400 MHz, C_6D_6)



45

^{13}C NMR spectrum

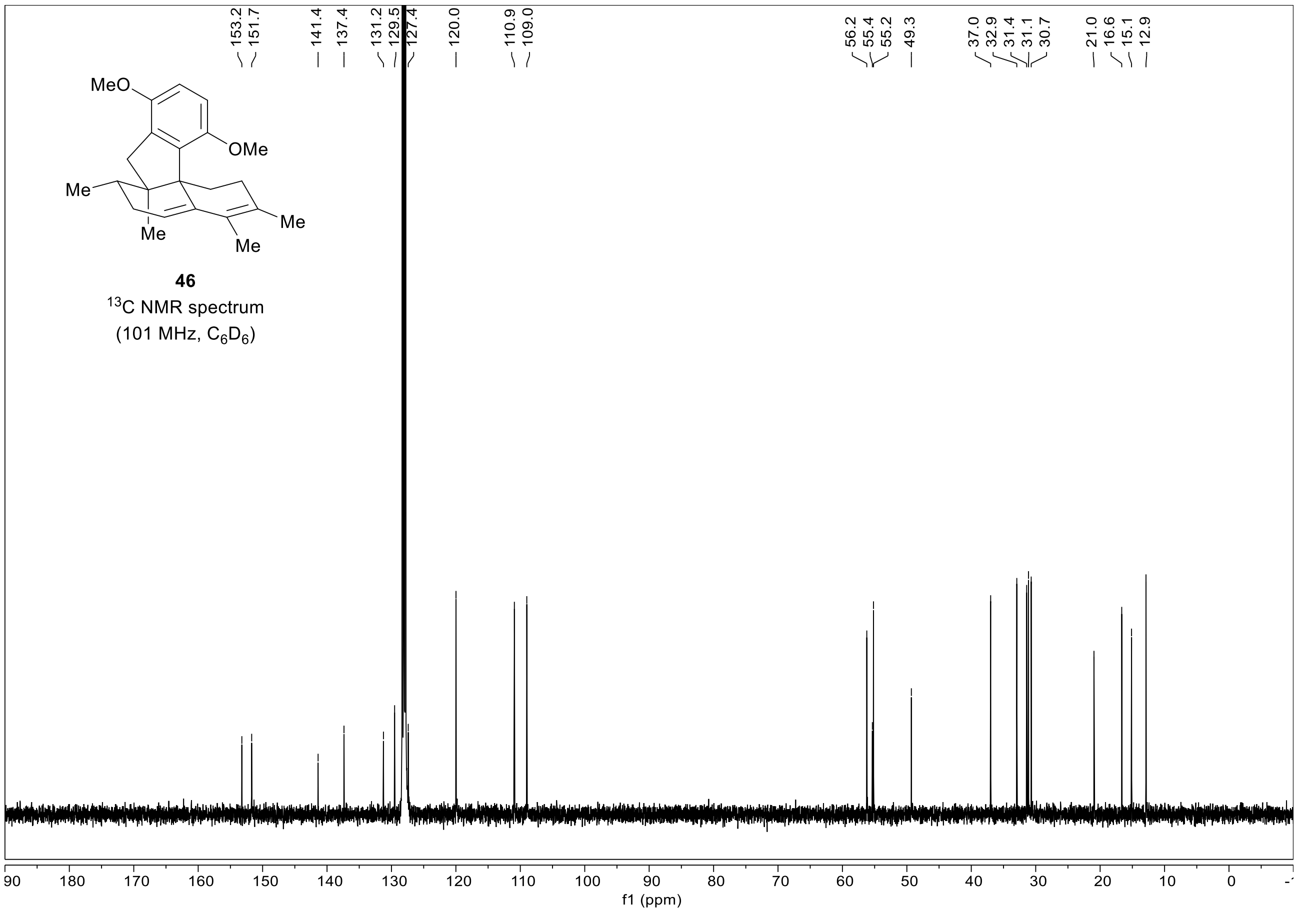
(101 MHz, C_6D_6)



46

^{1}H NMR spectrum

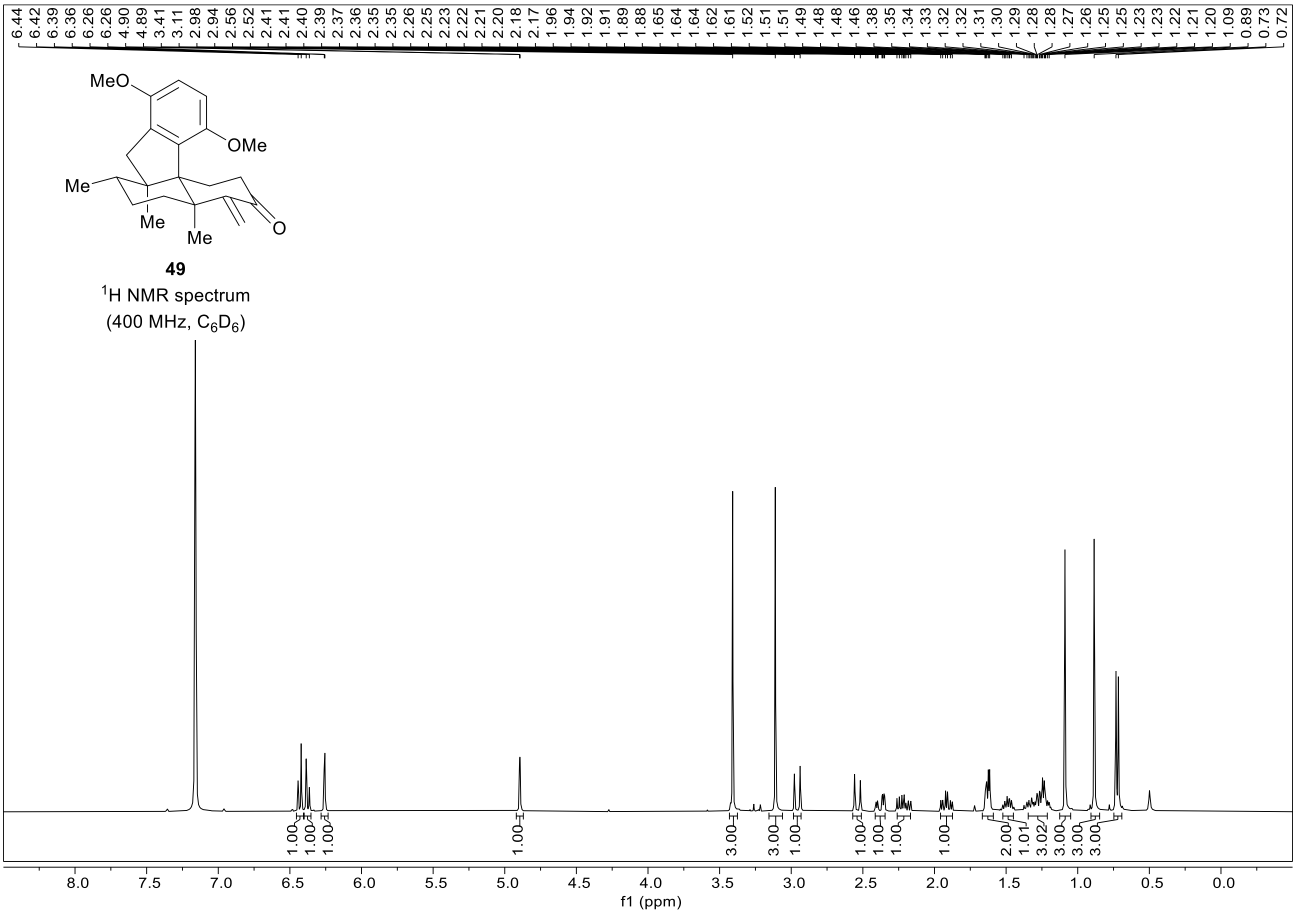
(400 MHz, C_6D_6)

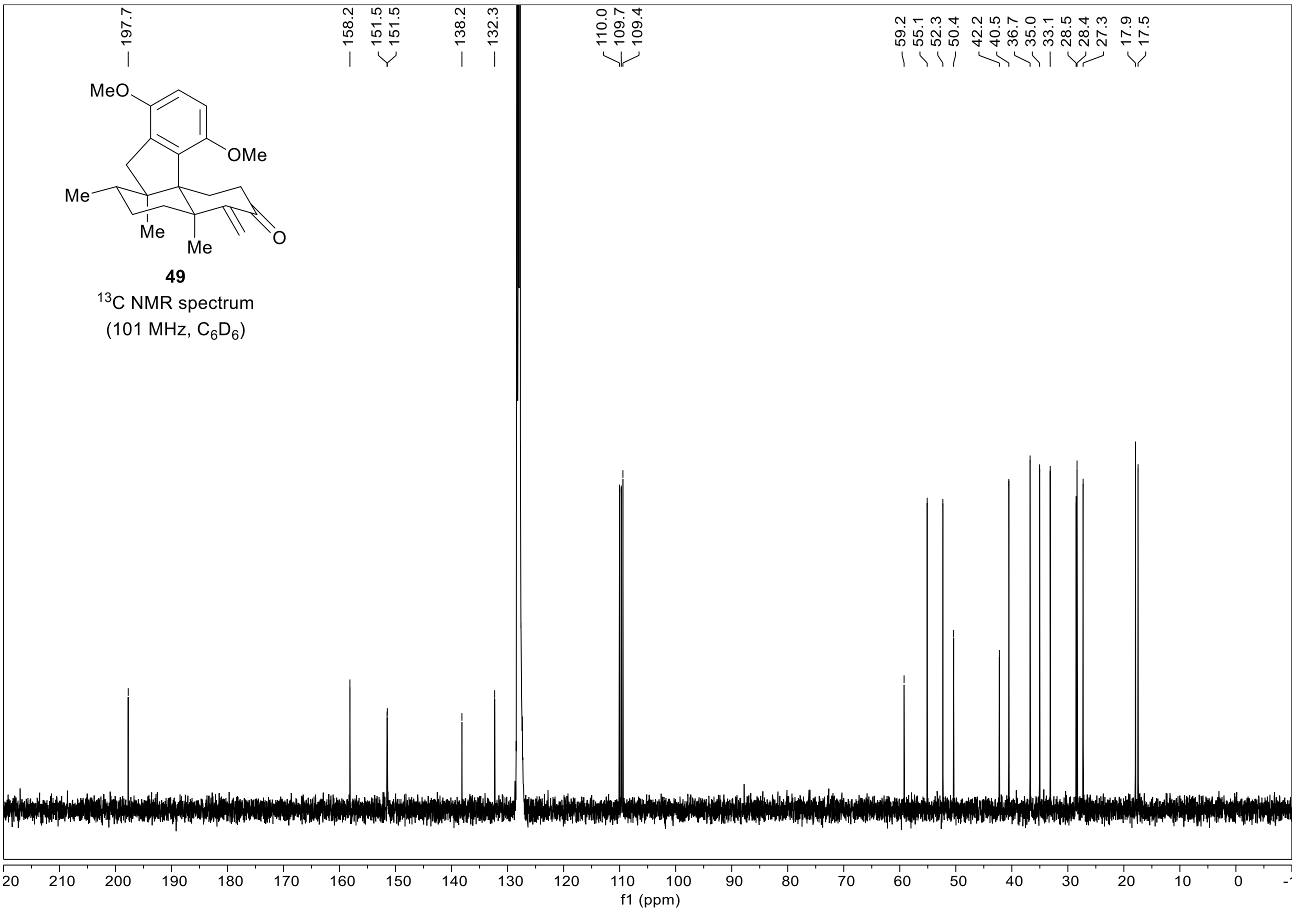


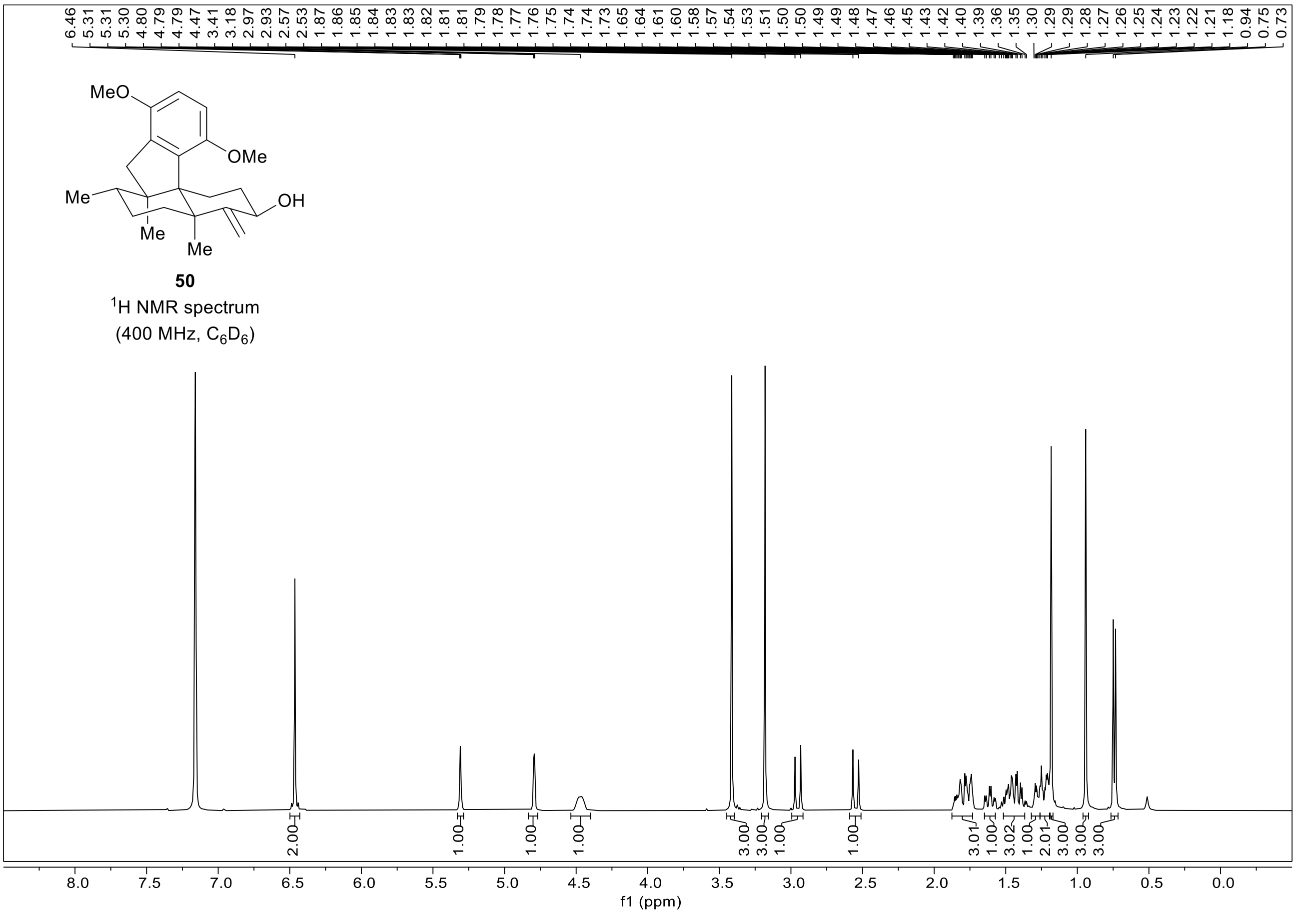
46

^{13}C NMR spectrum

(101 MHz, C_6D_6)


6.44 6.42 6.39 6.36 6.26 6.26 4.90 4.89 3.41 3.11 2.98 2.94 2.56 2.52 2.41 2.41 2.40 2.39 2.37 2.36 2.35 2.35 2.26 2.25 2.23 2.22 2.21 2.20 2.18 2.17 1.96 1.94 1.92 1.91 1.89 1.88 1.65 1.64 1.64 1.62 1.61 1.52 1.51 1.51 1.49 1.48 1.46 1.38 1.35 1.34 1.33 1.32 1.32 1.31 1.30 1.29 1.28 1.28 1.27 1.26 1.25 1.25 1.23 1.23 1.22 1.21 1.20 1.09 0.89 0.73 0.72
MeO
OMe
Me
Me
Me
O
49
^{1}H NMR spectrum
(400 MHz, C_6D_6)
1.00 1.00 1.00 1.00 3.00 3.00 1.00 1.00 1.00 1.00 1.00 2.00 1.01 3.02 3.00 3.00 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

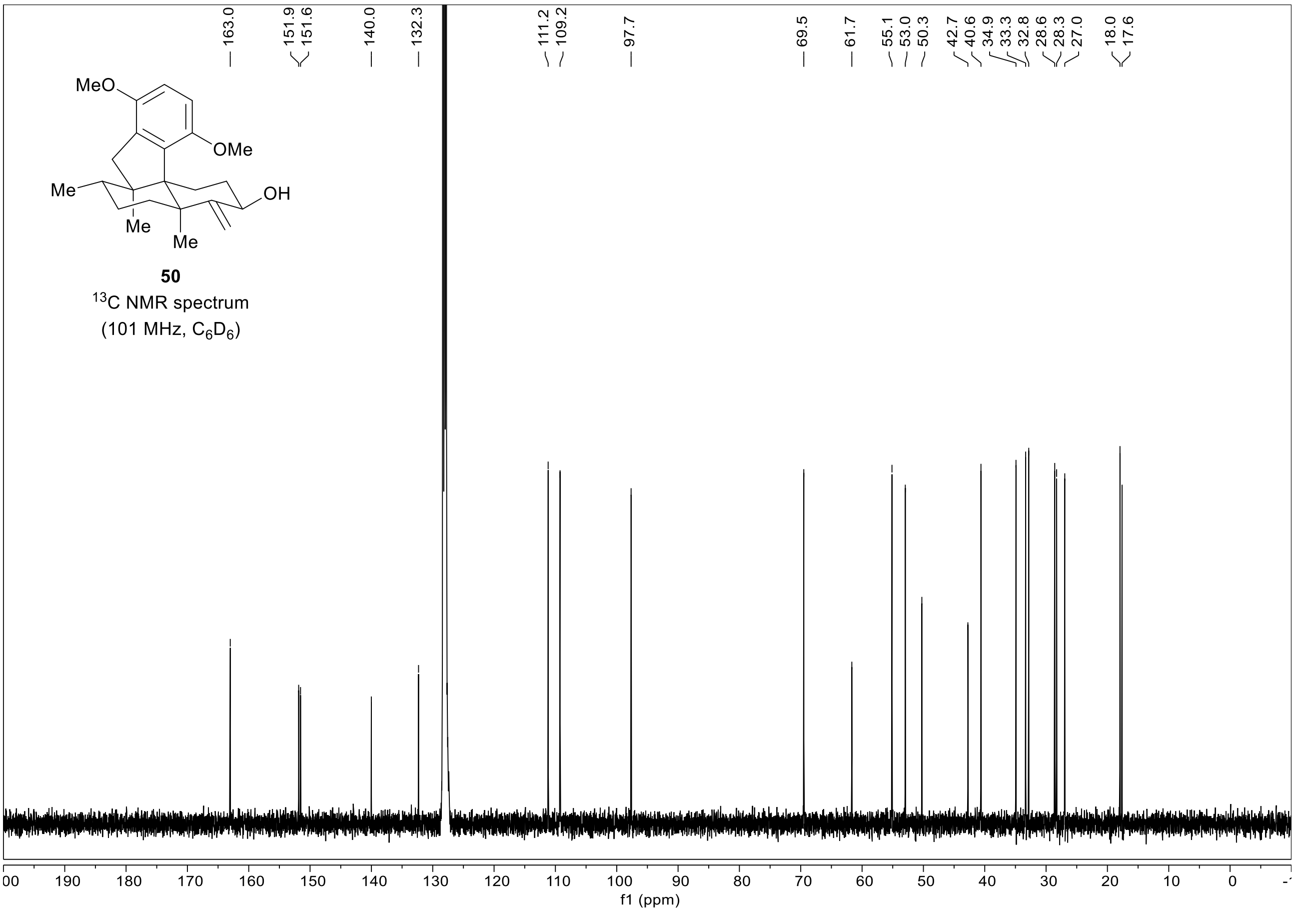

197.7
158.2 151.5 151.5
138.2 132.3
110.0 109.7 109.4
59.2 55.1 52.3 50.4 42.2 40.5 36.7 35.0 33.1 28.5 28.4 27.3 17.9 17.5
MeO
OMe
Me
Me
Me
O
49
^{13}C NMR spectrum
(101 MHz, C_6D_6)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



50

^{1}H NMR spectrum

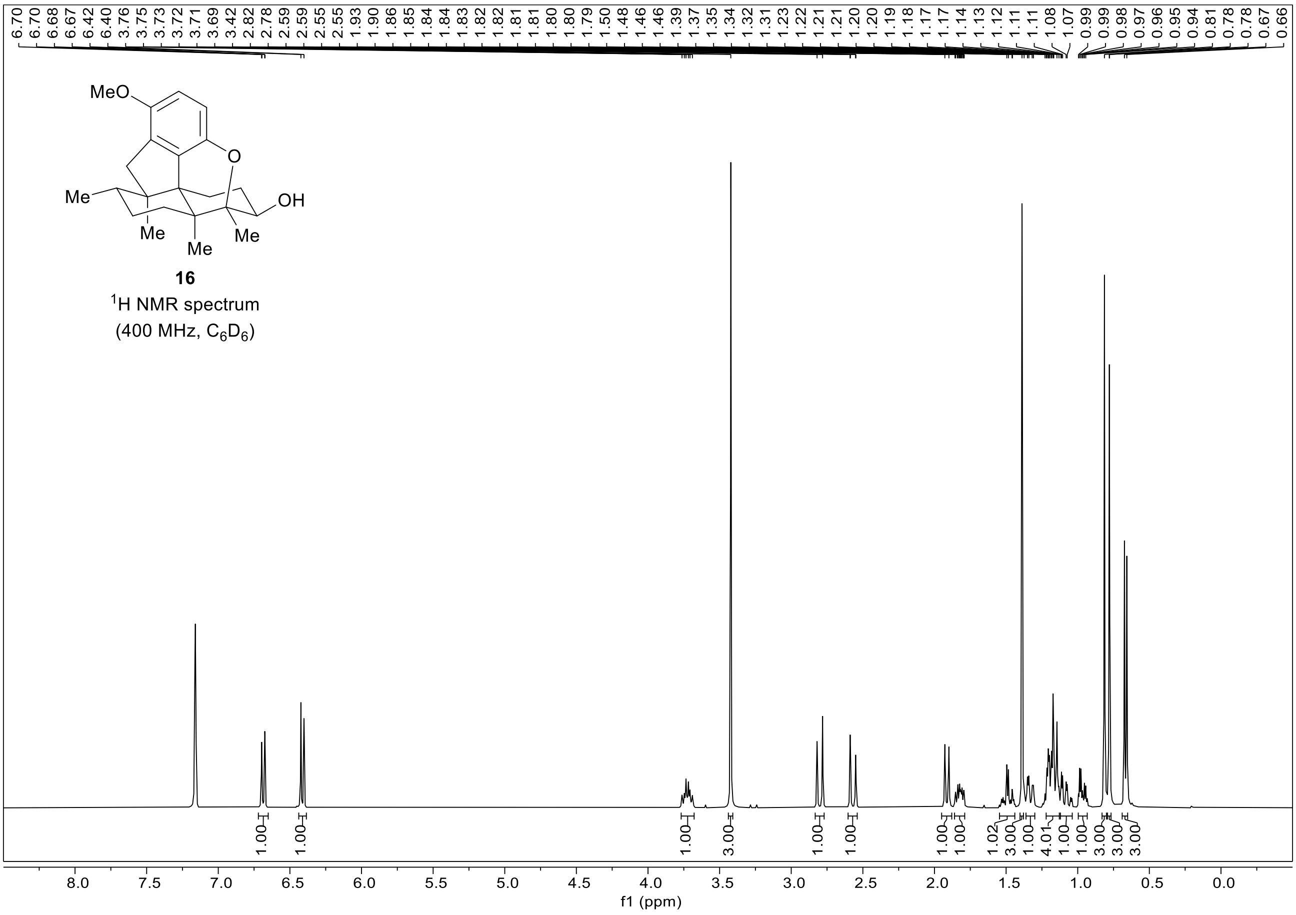
(400 MHz, C_6D_6)



50

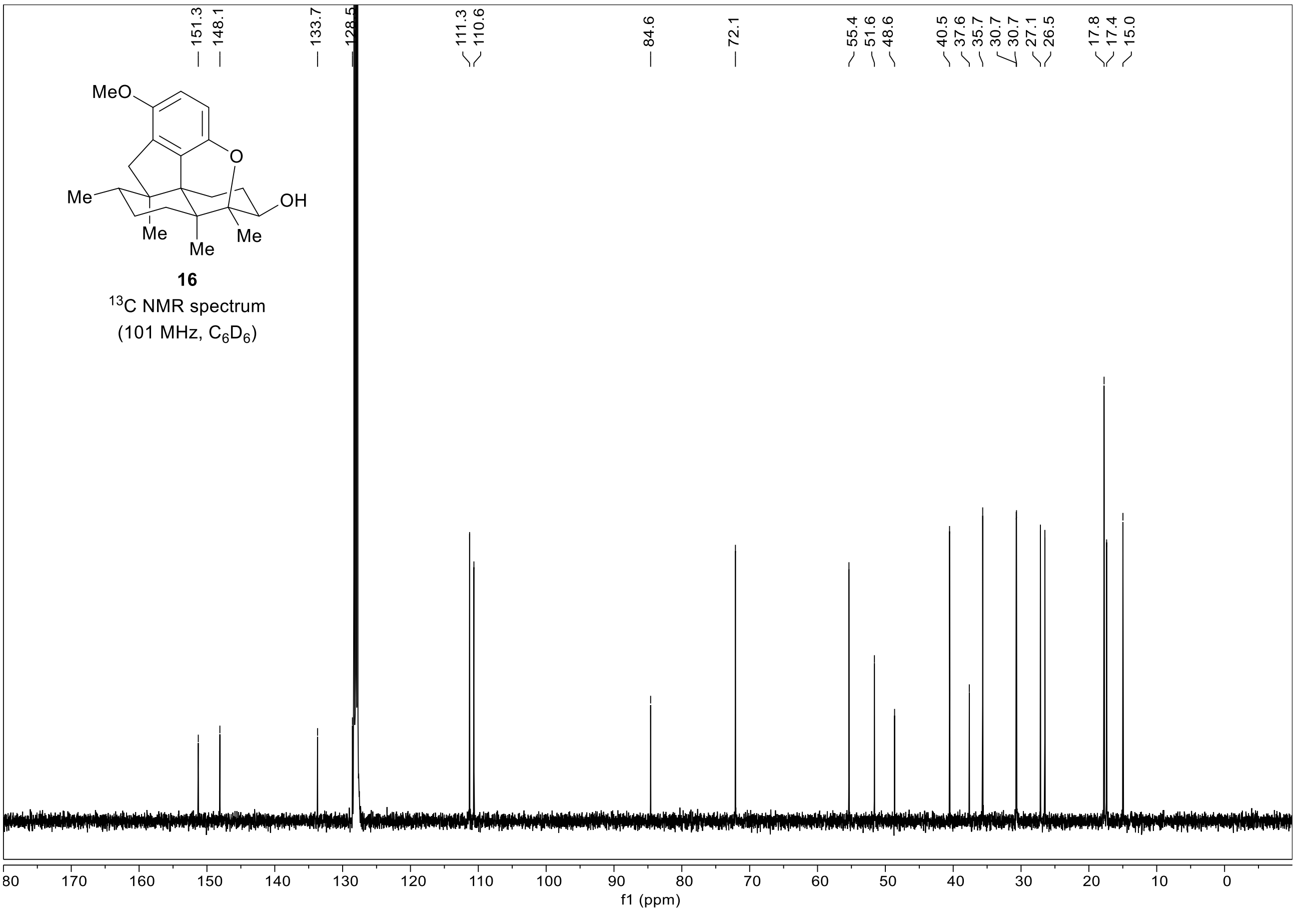
^{13}C NMR spectrum

(101 MHz, C_6D_6)



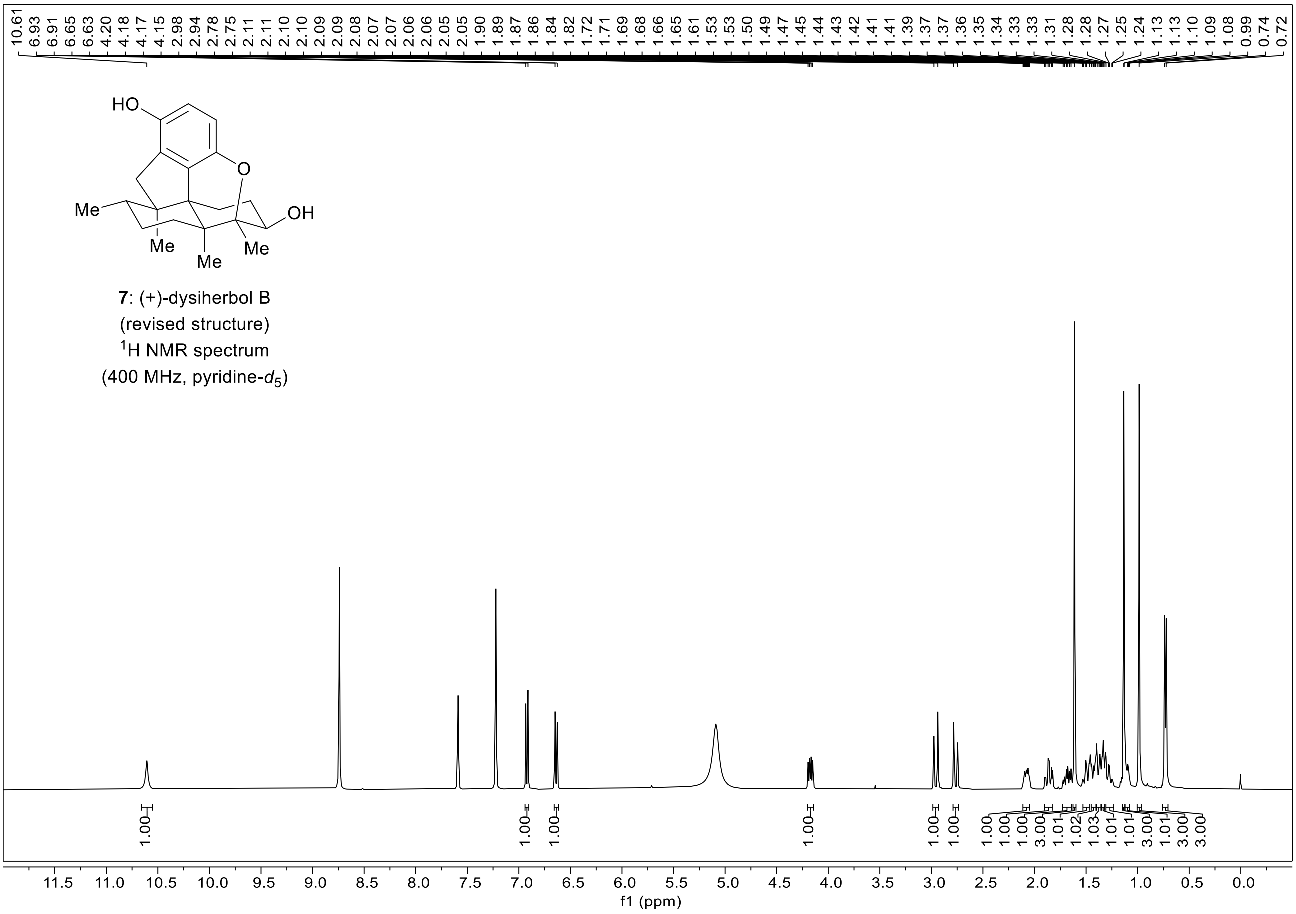
16

^{1}H NMR spectrum
(400 MHz, C_6D_6)

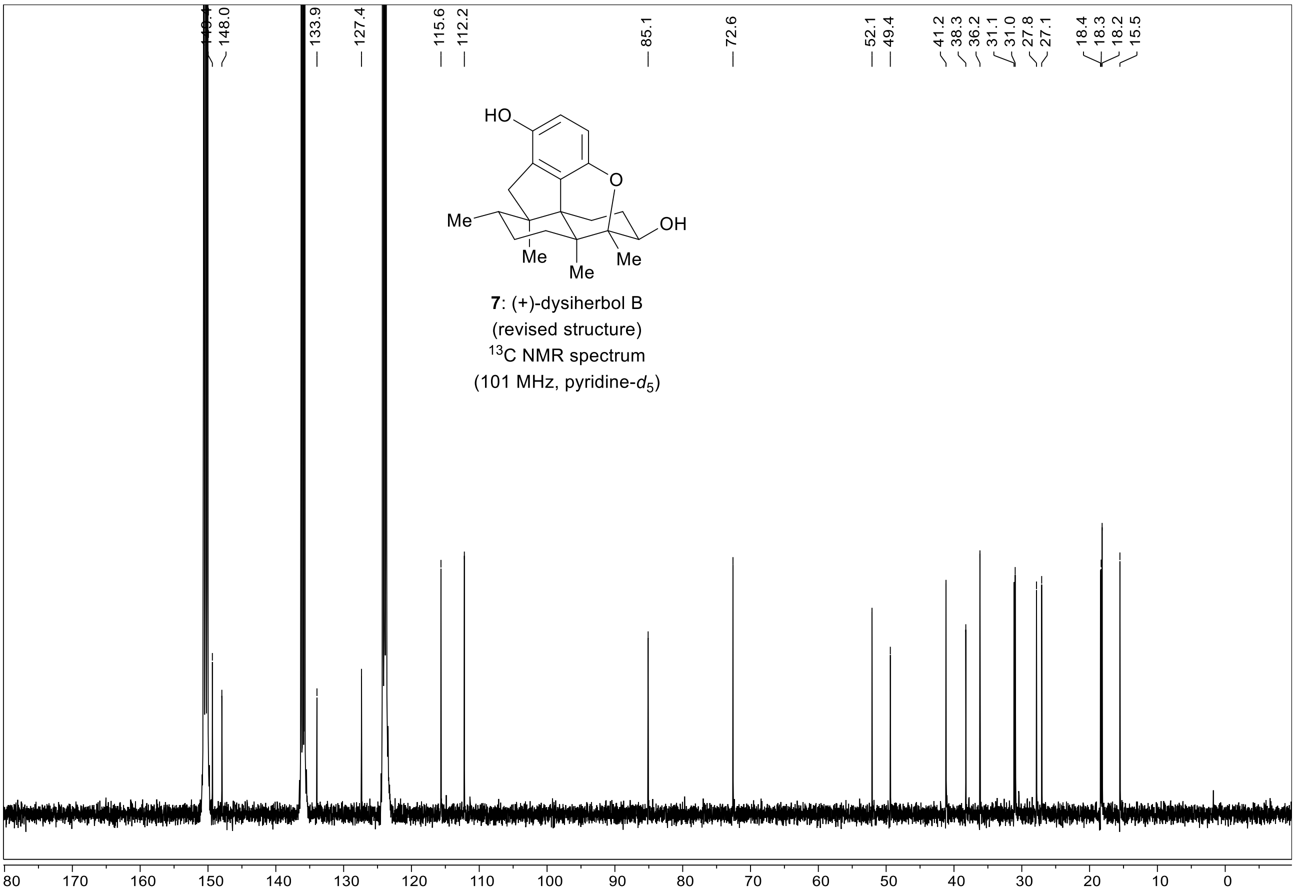


16

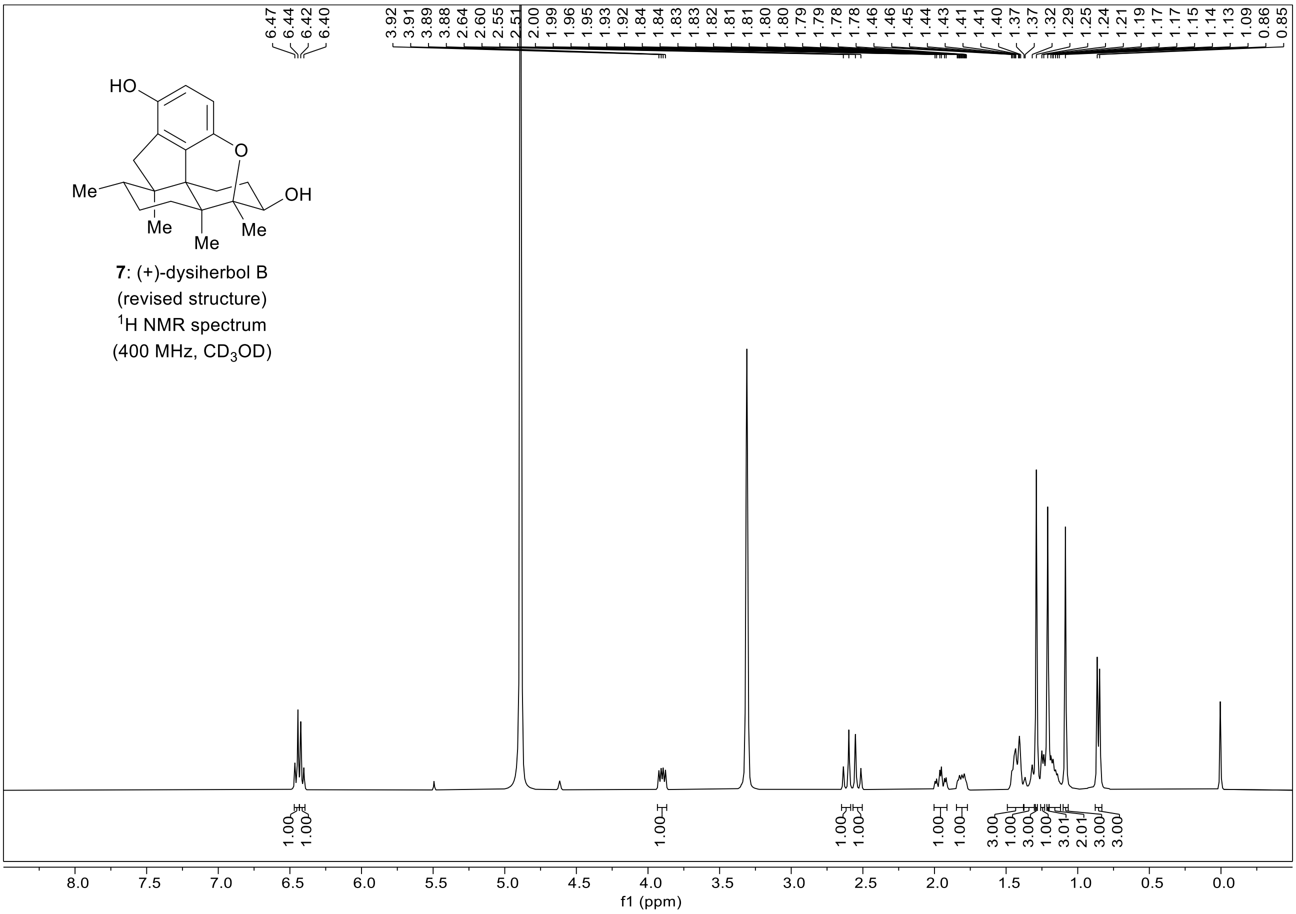
^{13}C NMR spectrum
(101 MHz, C_6D_6)



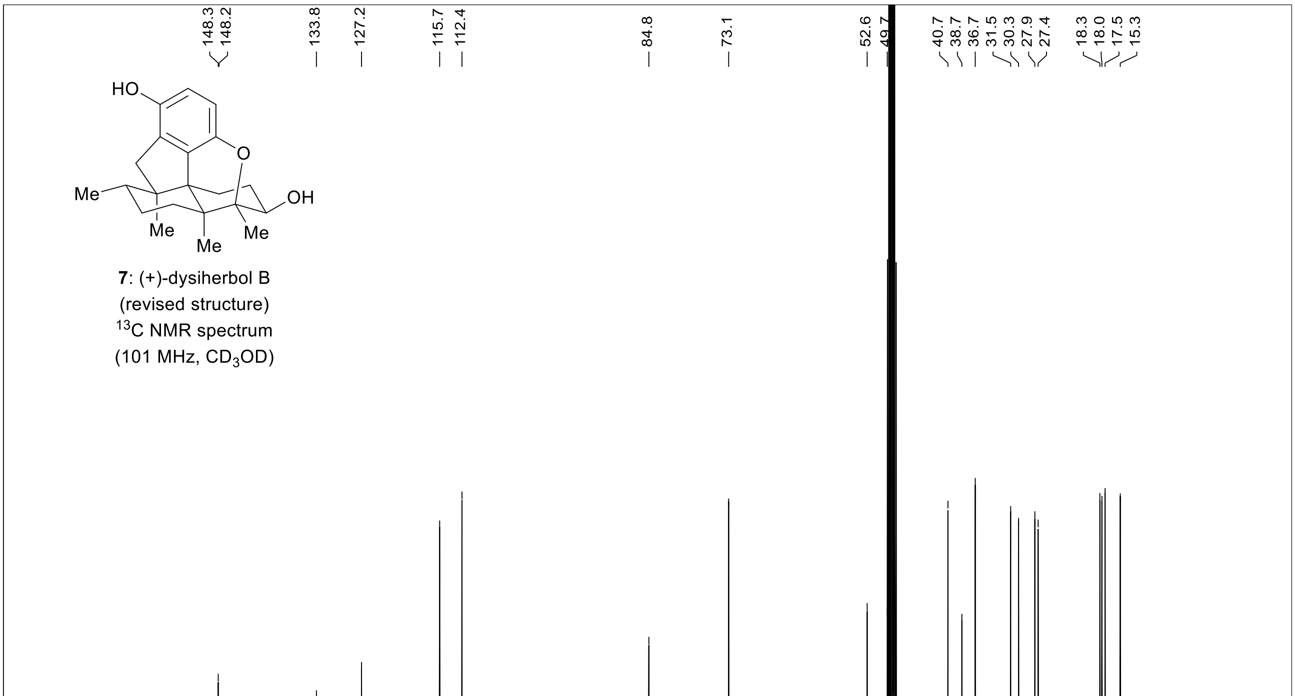
7: (+)-dysiherbol B
(revised structure)
^{1}H NMR spectrum
(400 MHz, pyridine-d_5)



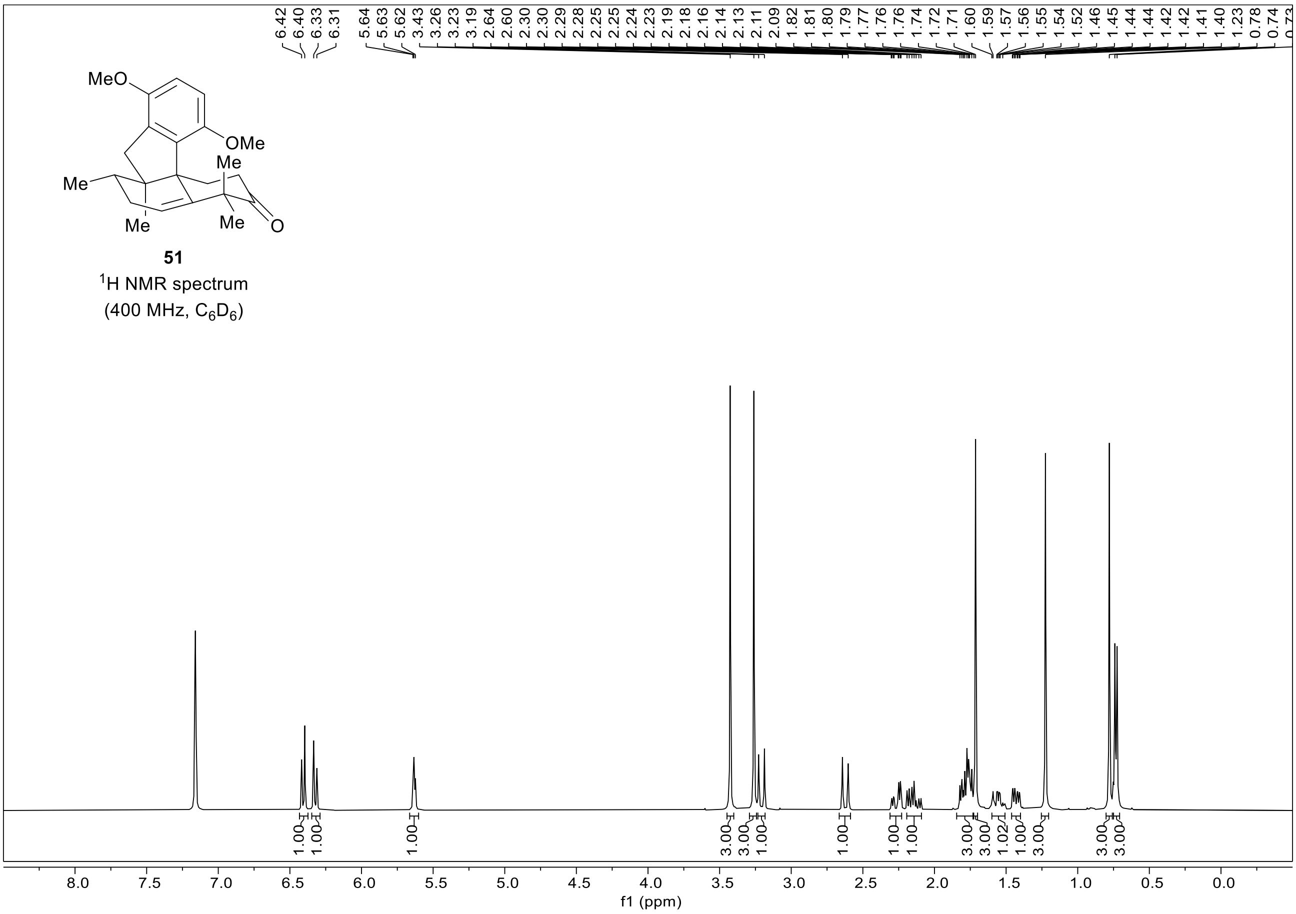
7: (+)-dysiherbol B
(revised structure)
^{13}C NMR spectrum
(101 MHz, pyridine-d_5)



7: (+)-dysiherbol B
(revised structure)
^{1}H NMR spectrum
(400 MHz, CD_3OD)



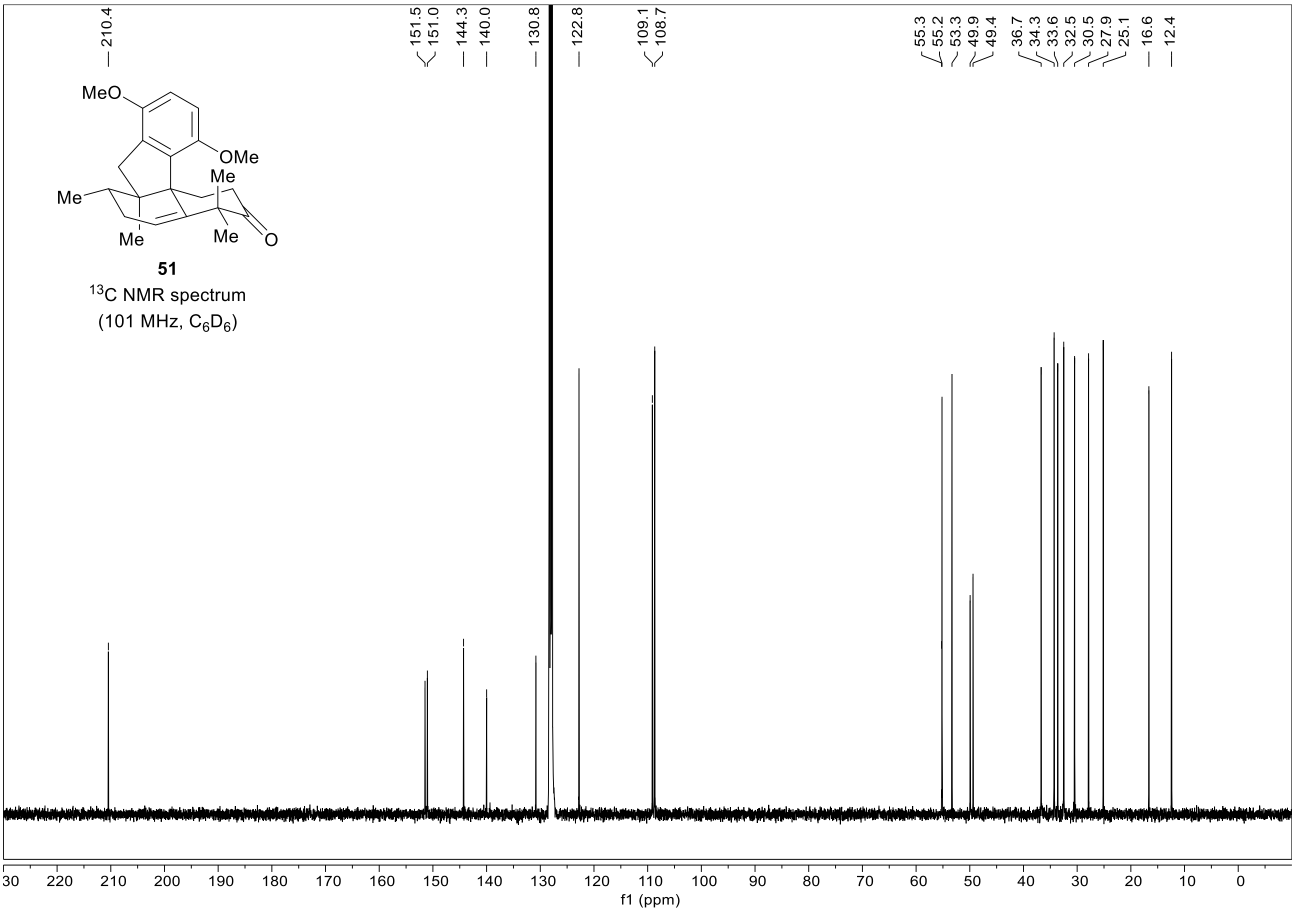
7: (+)-dysiherbol B
(revised structure)
^{13}C NMR spectrum
(101 MHz, CD_3OD)



51

^{1}H NMR spectrum

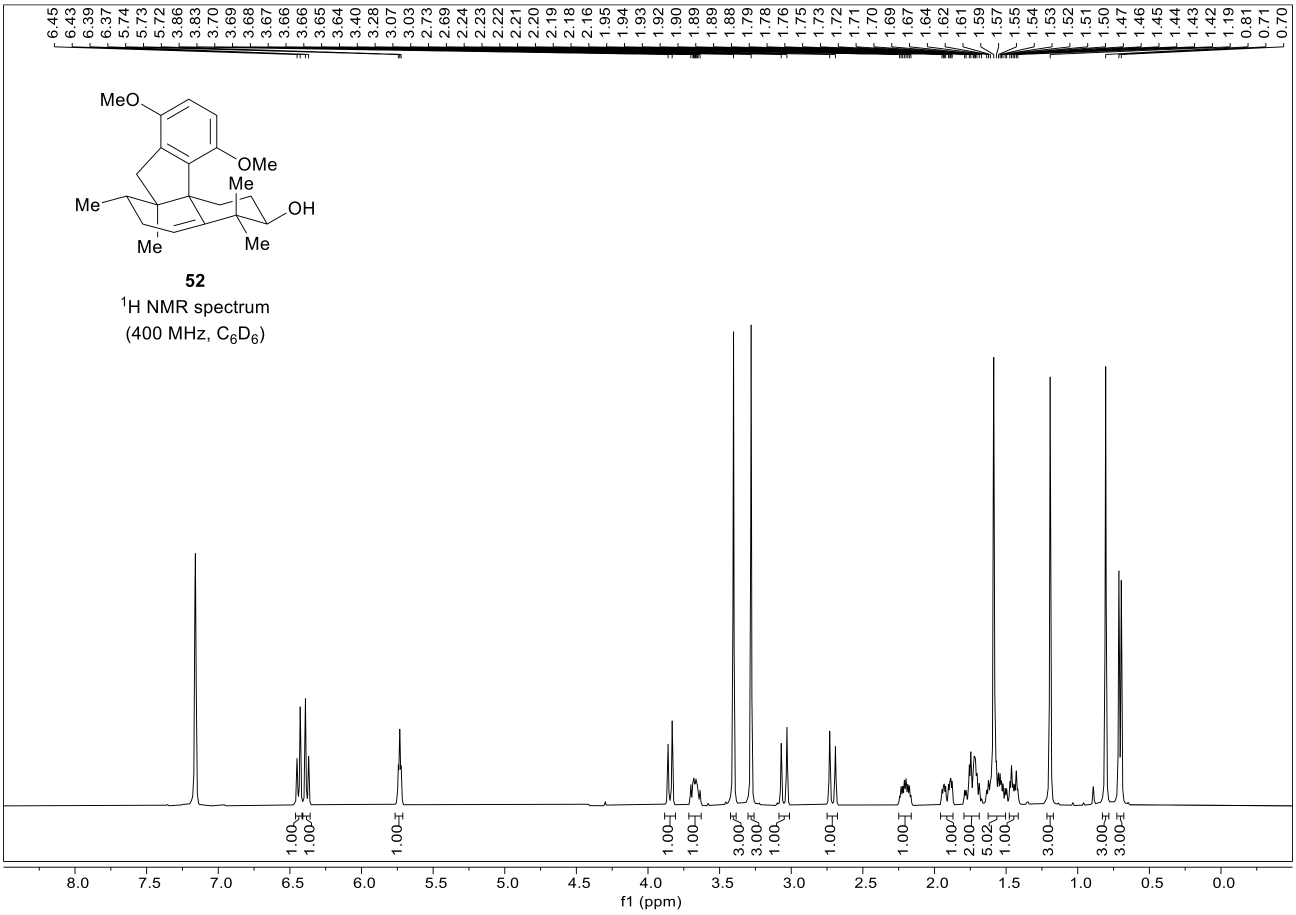
(400 MHz, C_6D_6)

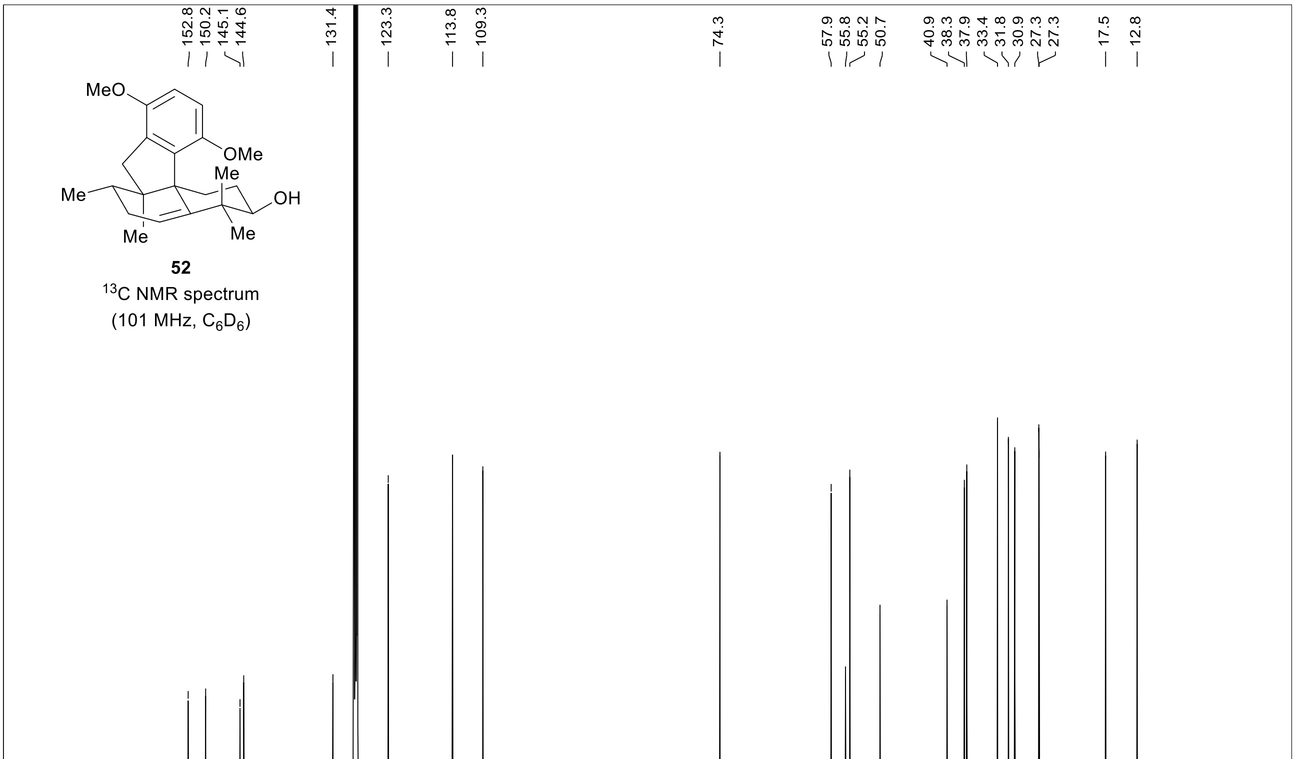


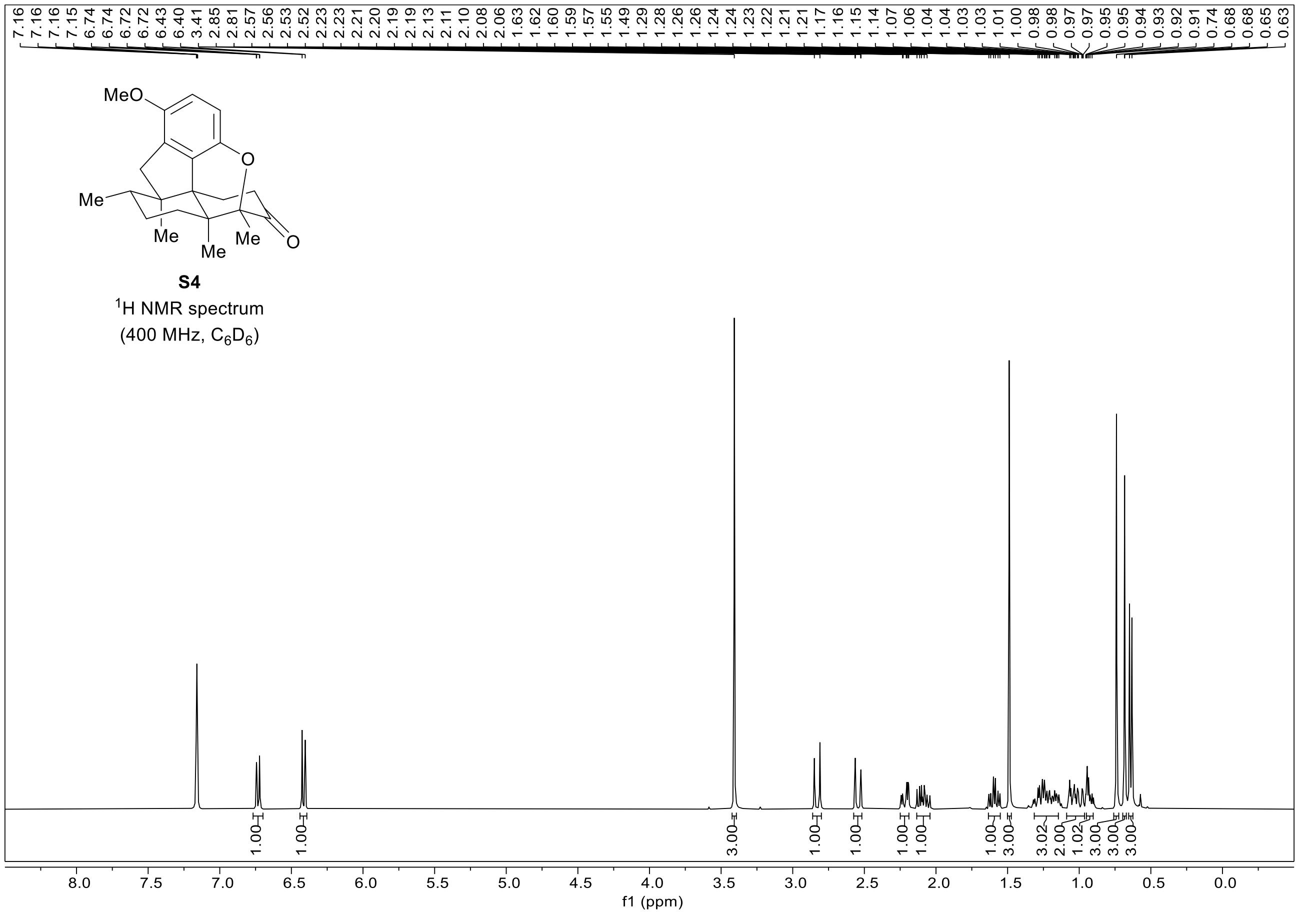
51

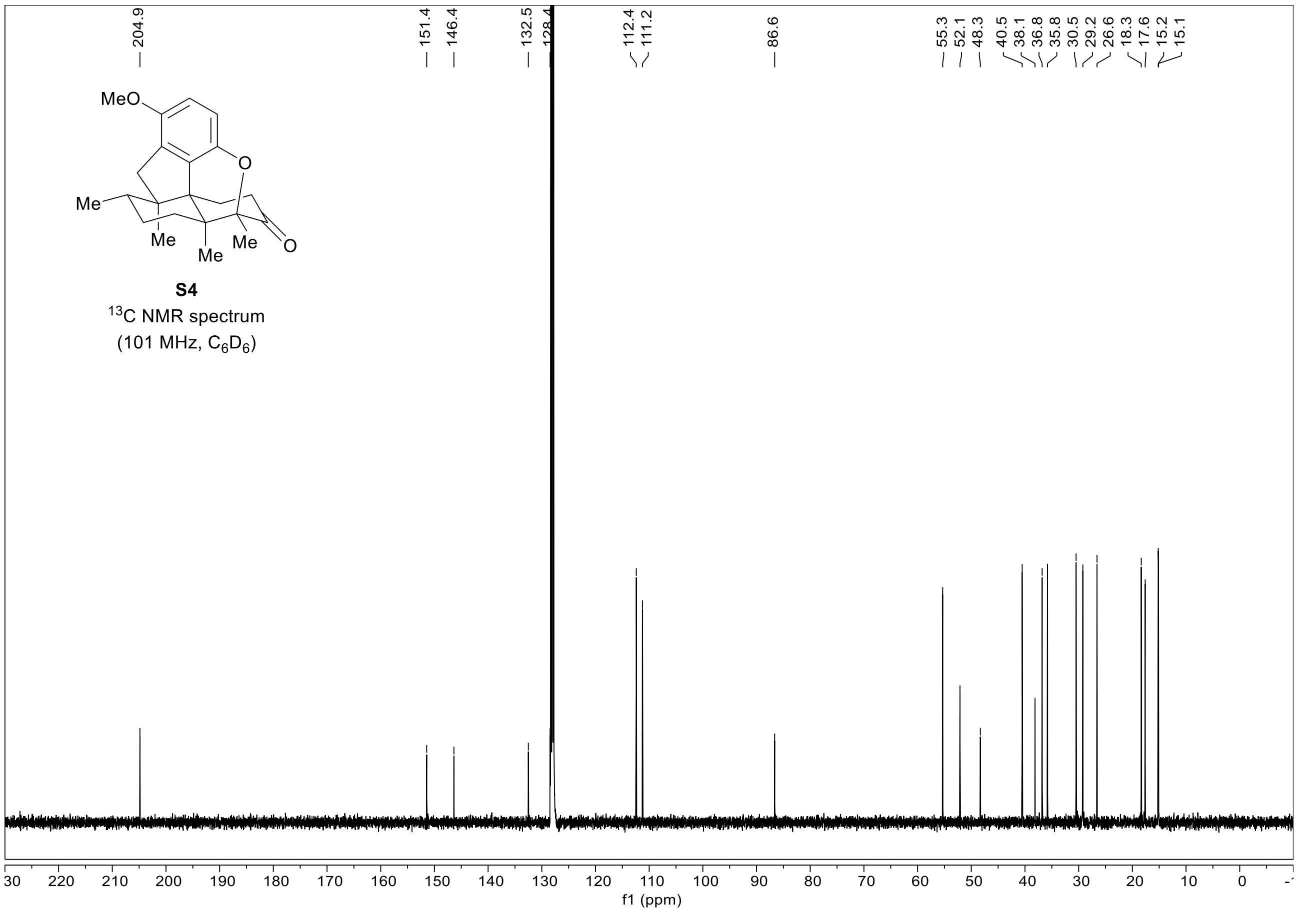
^{13}C NMR spectrum

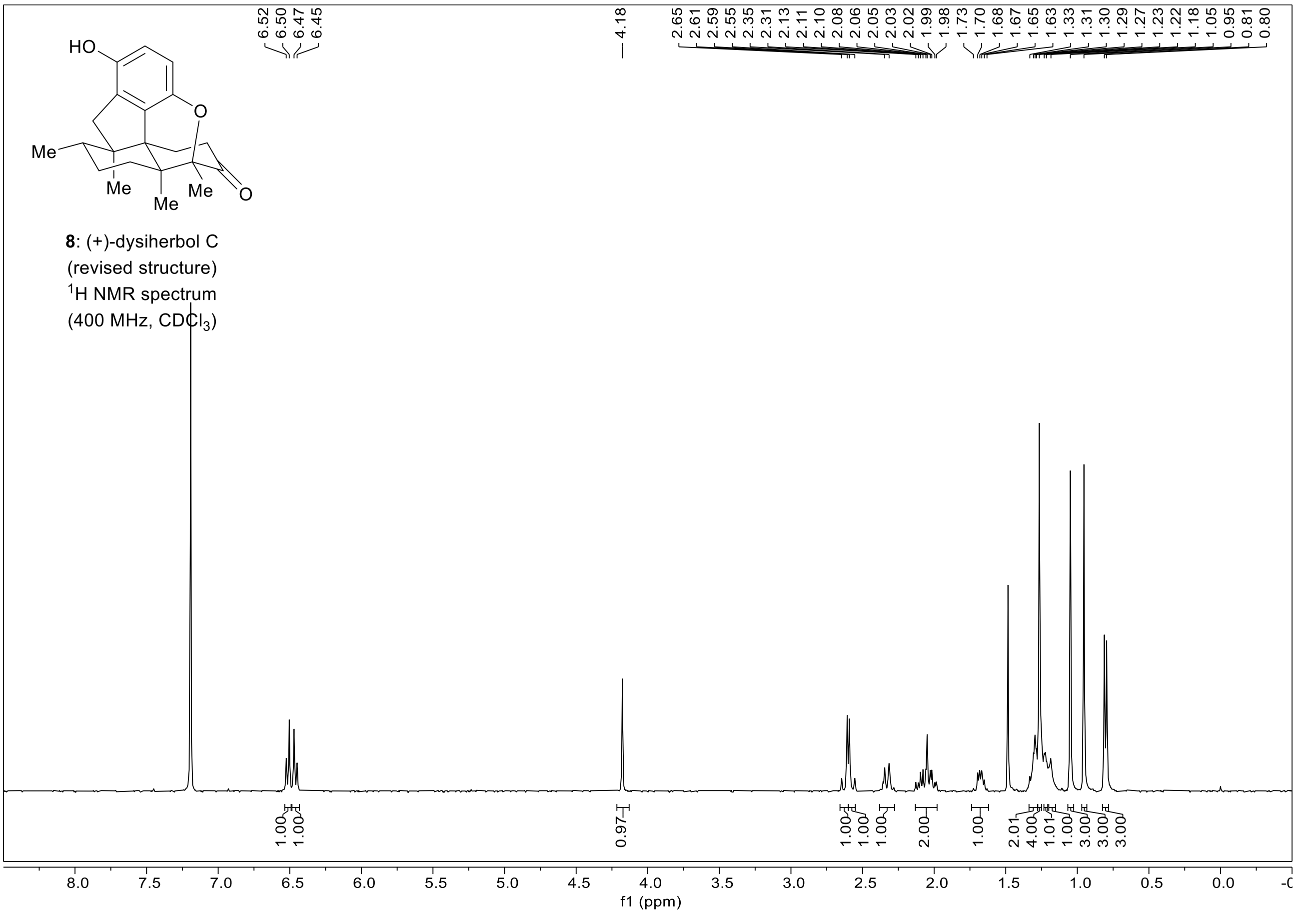
(101 MHz, C_6D_6)


6.45 6.43 6.39 6.37 5.74 5.73 5.72 3.86 3.83 3.70 3.69 3.68 3.67 3.66 3.66 3.65 3.64 3.40 3.28 3.07 3.03 2.73 2.69 2.24 2.23 2.22 2.21 2.20 2.19 2.18 2.16 1.95 1.94 1.93 1.92 1.90 1.89 1.89 1.88 1.79 1.78 1.76 1.75 1.73 1.72 1.71 1.70 1.69 1.67 1.64 1.62 1.61 1.59 1.57 1.55 1.54 1.53 1.52 1.51 1.50 1.47 1.46 1.45 1.44 1.43 1.42 1.19 0.81 0.71 0.70
MeO
OMe
Me
Me
OH
Me
Me
52
^{1}H NMR spectrum
(400 MHz, C_6D_6)
1.00 1.00 1.00 1.00 1.00 3.00 3.00 1.00 1.00 1.00 1.00 2.00 5.02 1.00 3.00 3.00 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

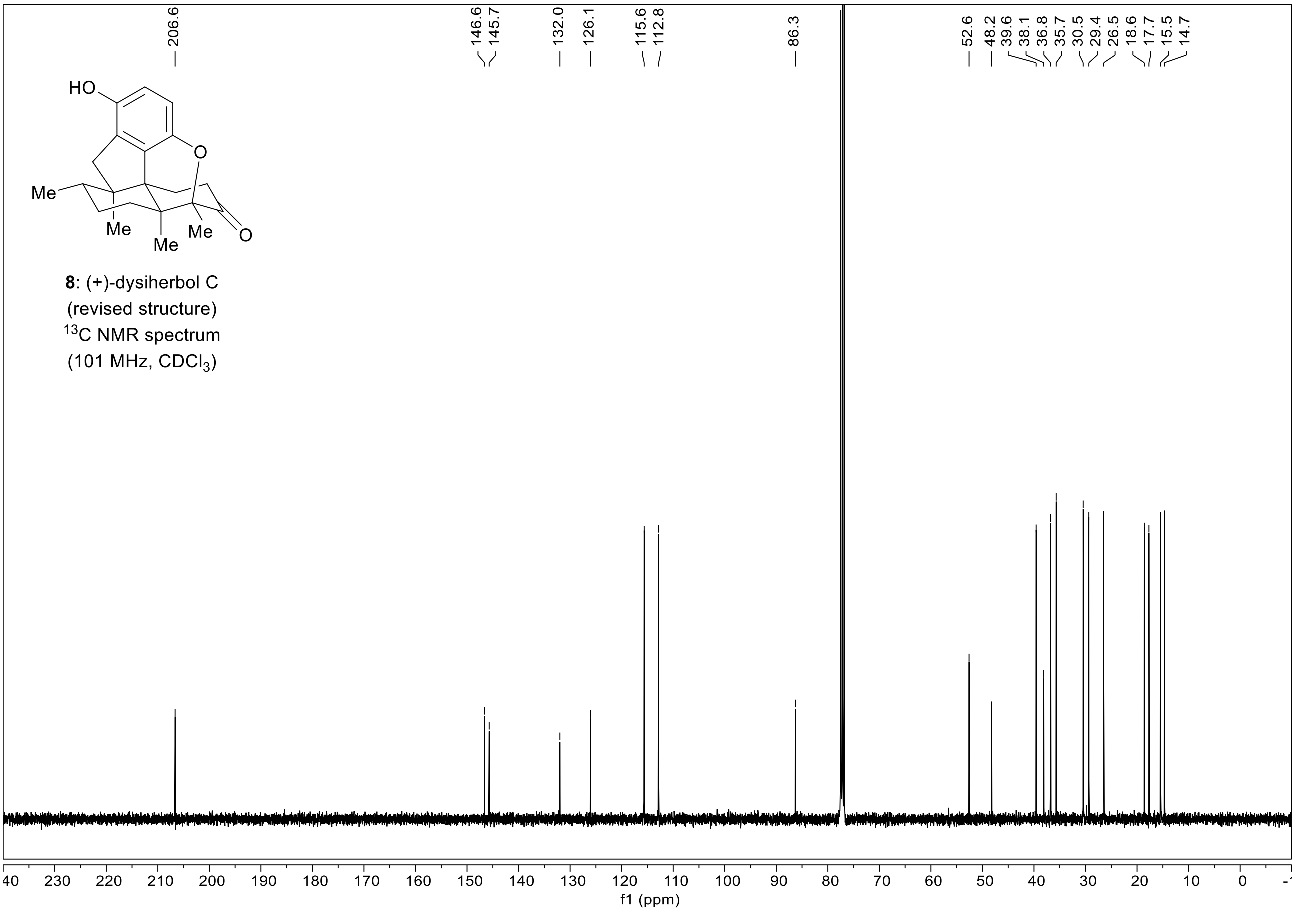

152.8 150.2 145.1 144.6 131.4 123.3 113.8 109.3 74.3 57.9 55.8 55.2 50.7 40.9 38.3 37.9 33.4 31.8 30.9 27.3 27.3 17.5 12.8
MeO
OMe
Me
Me
OH
Me
Me
52
^{13}C NMR spectrum
(101 MHz, C_6D_6)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.16
7.16
7.15
6.74
6.74
6.72
6.43
6.40
3.41
2.85
2.81
2.57
2.56
2.53
2.52
2.23
2.23
2.21
2.20
2.19
2.19
2.13
2.11
2.10
2.08
2.06
1.63
1.62
1.60
1.59
1.57
1.55
1.49
1.29
1.28
1.26
1.26
1.24
1.24
1.23
1.22
1.21
1.21
1.17
1.16
1.15
1.14
1.07
1.06
1.04
1.04
1.03
1.03
1.01
1.00
0.98
0.98
0.97
0.97
0.95
0.95
0.94
0.93
0.92
0.91
0.74
0.68
0.65
0.63
MeO
O
Me
Me
Me
Me
O
S4
¹H NMR spectrum
(400 MHz, C6D6)
1.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
3.00
3.02
2.00
1.02
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

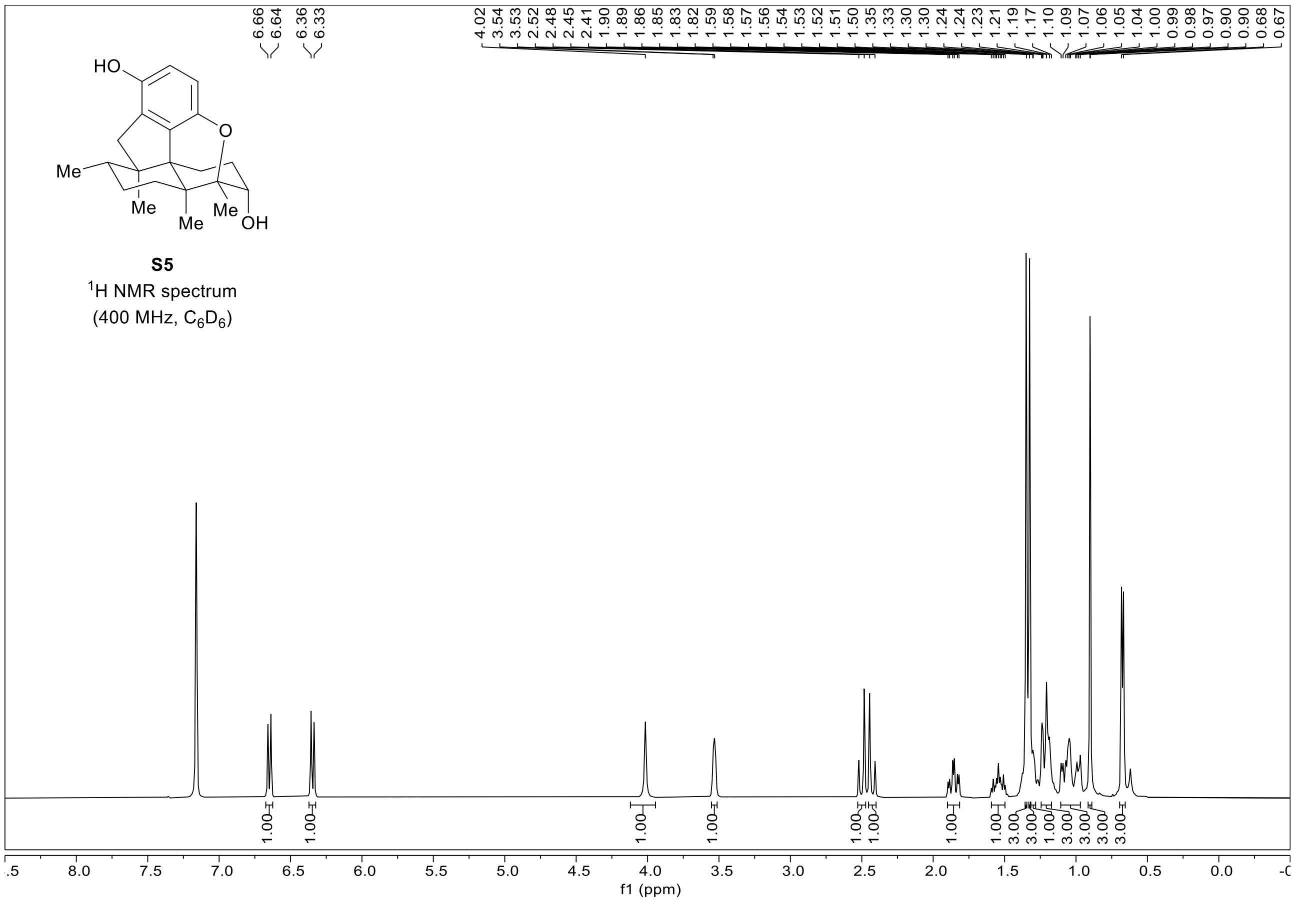

204.9
151.4
146.4
132.5
128.4
112.4
111.2
86.6
55.3
52.1
48.3
40.5
38.1
36.8
35.8
30.5
29.2
26.6
18.3
17.6
15.2
15.1
MeO
O
Me
Me
Me
Me
O
S4
¹³C NMR spectrum
(101 MHz, C6D6)
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)



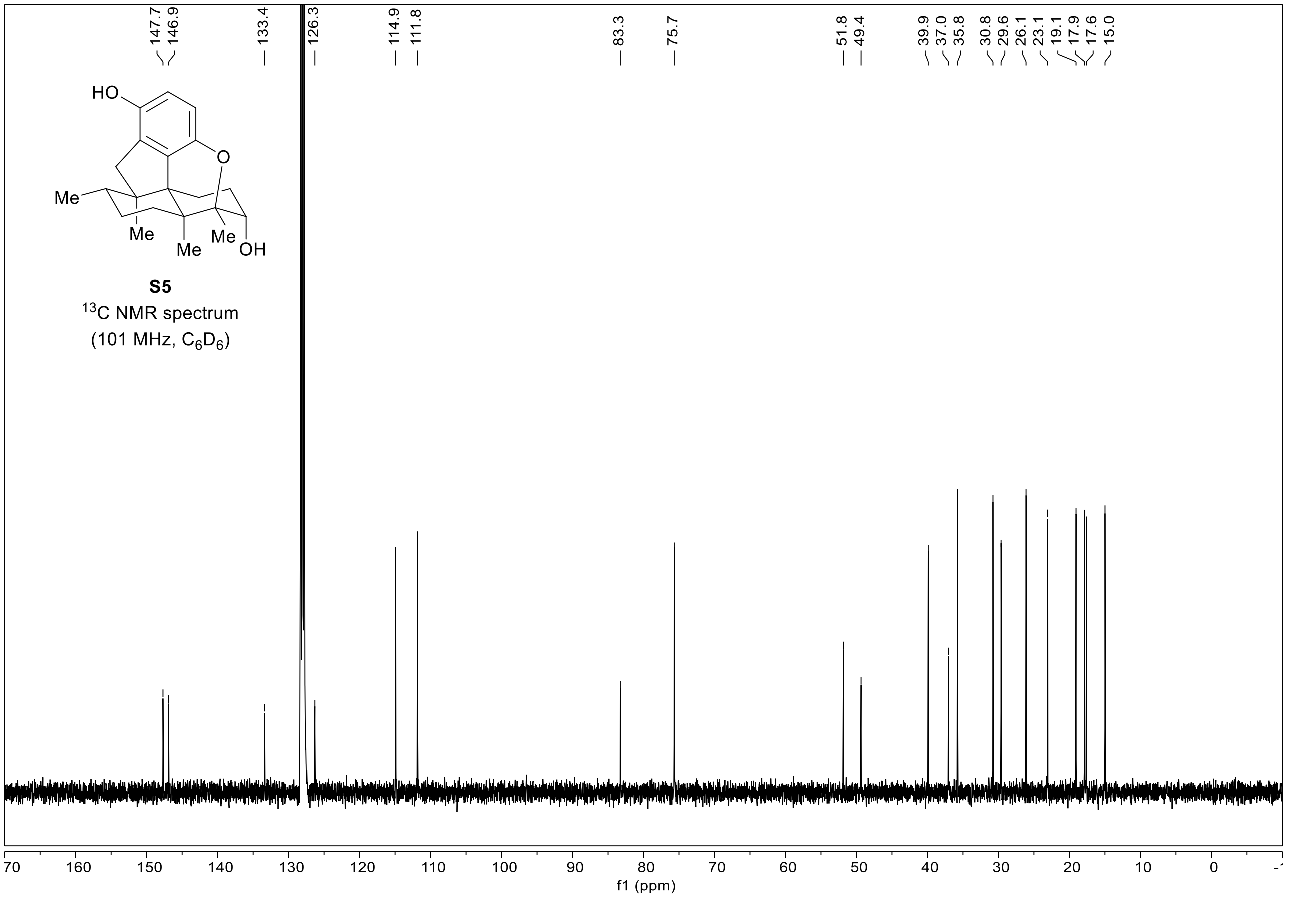
8: (+)-dysiherbol C
(revised structure)
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



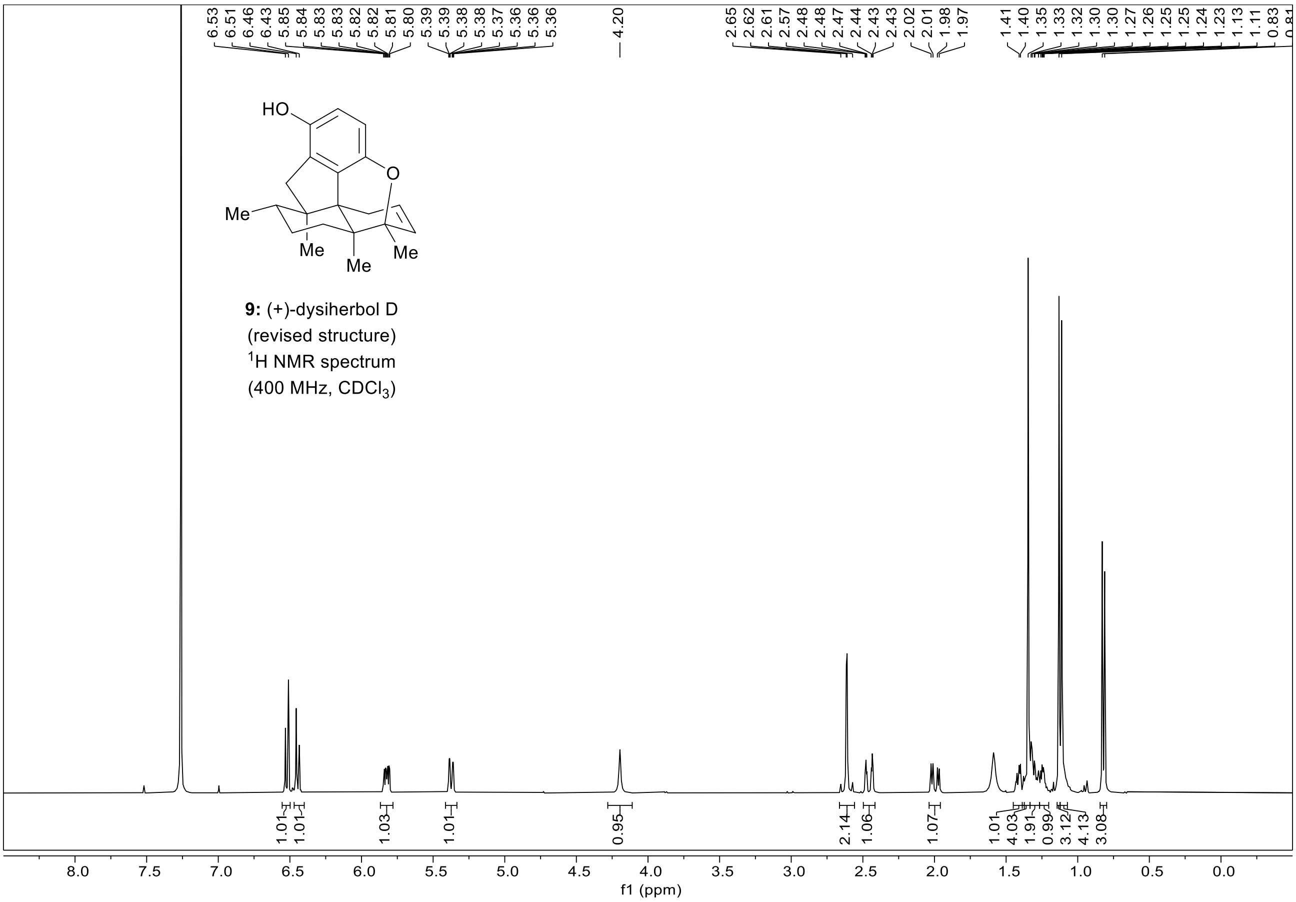
8: (+)-dysiherbol C
(revised structure)
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)



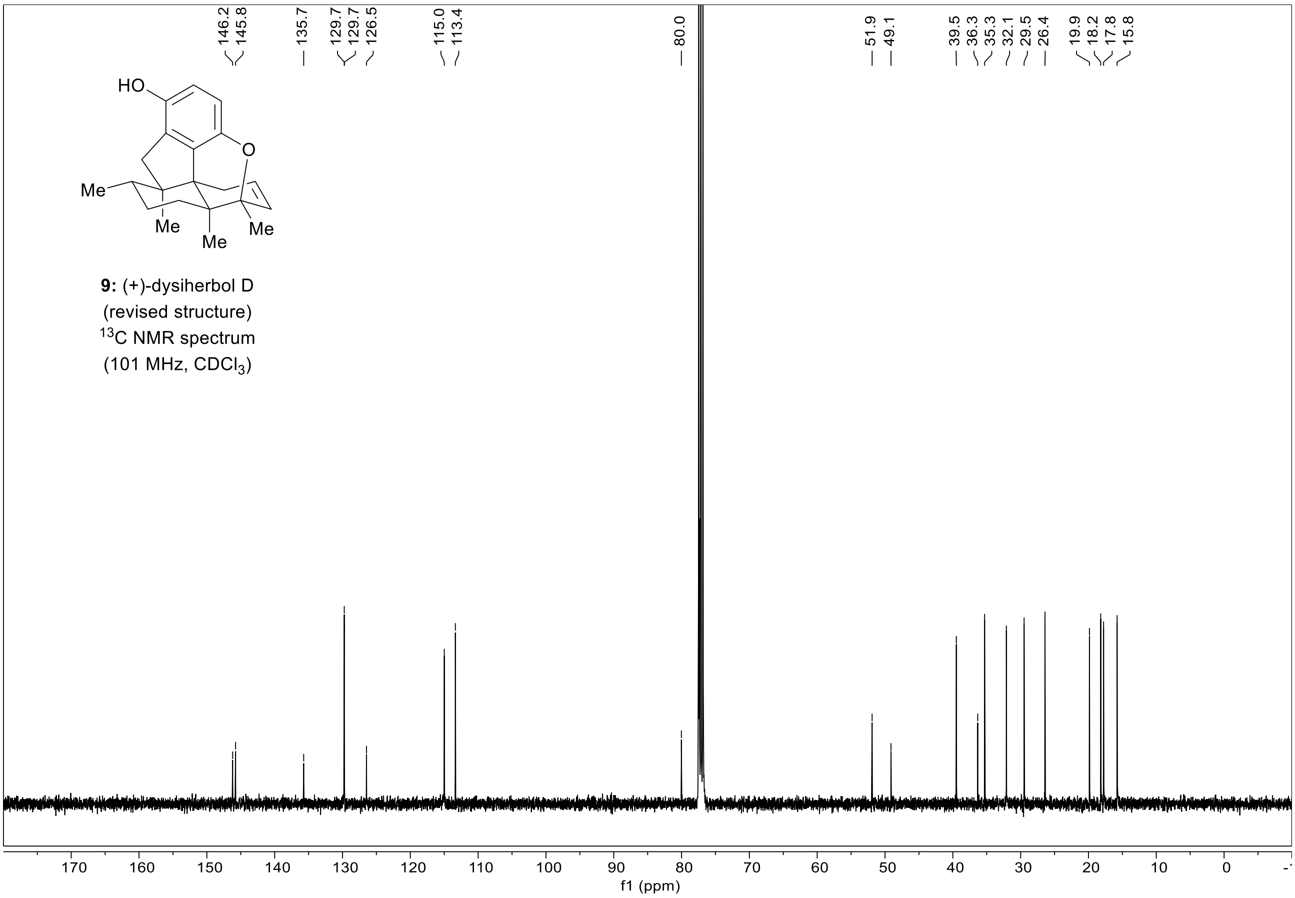
S5
^{1}H NMR spectrum
(400 MHz, C_6D_6)



S5
^{13}C NMR spectrum
(101 MHz, C_6D_6)



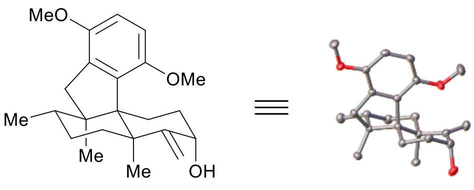
9: (+)-dysiherbol D
(revised structure)
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)



9: (+)-dysiherbol D
(revised structure)
^{13}C NMR spectrum
(101 MHz, $CDCl_3$)

V. X-Ray Crystallographic Data of Compounds

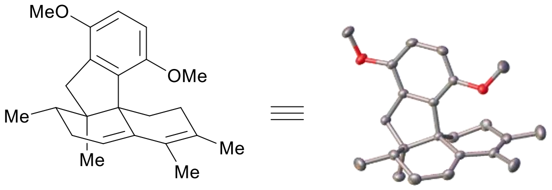
Table S11. Crystal data and structure refinement for allylic alcohol (±)-45.



(±)-**45**

Identification code	CCDC 2124205
Empirical formula	$C_{23}H_{32}O_3$
Formula weight	356.51
Temperature/K	100.00(10)
Crystal system	Orthorhombic
Space group	Pccn
a/Å	36.4809(3)
b/Å	14.42217(12)
c/Å	7.54283(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3968.54(6)
Z	8
$\rho_{calc.}$ g/cm^3	1.223
μ/mm^{-1}	0.636
F(000)	1592.0
Crystal size/mm^3	0.28 × 0.23 × 0.22
Radiation	CuKα (λ = 1.54184)
2^{Θ} range for data collection/°	13.202 to 151.754
Index ranges	$-42 \leq h \leq 45$, $-18 \leq k \leq 15$, $-8 \leq l \leq 5$
Reflections collected	18252
Independent reflections	4011 [R_{int} = 0.0223, R_{sigma} = 0.0184]
Data/restraints/parameters	4011/0/249
Goodness-of-fit on F^2	1.045
Final R indexes	R_1 = 0.0387, wR_2 = 0.1024
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.1041
Largest diff. peak/hole / e Å^{-3}	0.32/−0.32

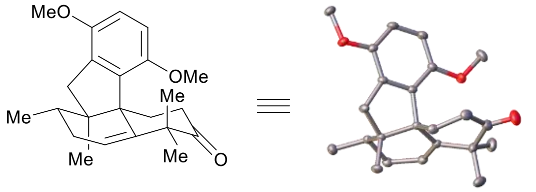
Table S12. Crystal data and structure refinement for diene (±)-(46).



(±)-**46**

Identification code	CCDC 2192301
Empirical formula	$C_{23}H_{30}O_2$
Formula weight	338.47
Temperature/K	113.15
Crystal system	monoclinic
Space group	Cc
a/Å	9.6931(4)
b/Å	25.8093(8)
c/Å	7.4931(3)
α/°	90
β/°	102.745(4)
γ/°	90
Volume/Å^3	1828.38(12)
Z	4
$\rho_{\mathrm{calc.}}$ g/cm^3	1.230
μ/mm^{-1}	0.076
F(000)	736.0
Crystal size/mm^3	0.25 × 0.2 × 0.16
Radiation	Mo Kα (λ = 0.71073)
2$^{\Theta}$ range for data collection/°	4.588 to 67.262
Index ranges	$-15 \leq h \leq 10$, $-39 \leq k \leq 39$, $-11 \leq l \leq 10$
Reflections collected	11231
Independent reflections	5088 [$R_{\mathrm{int}} = 0.0409$, $R_{\mathrm{sigma}} = 0.0531$]
Data/restraints/parameters	5088/2/233
Goodness-of-fit on F^2	1.031
Final R indexes	$R_1 = 0.0503$, $wR_2 = 0.1148$
Final R indexes [all data]	$R_1 = 0.0613$, $wR_2 = 0.1241$
Largest diff. peak/hole / e Å^{-3}	0.25/−0.20

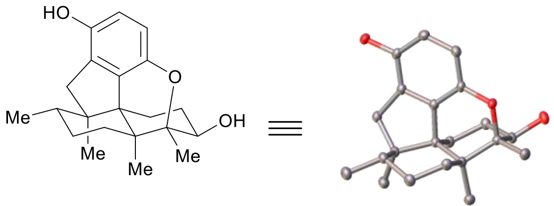
Table S13. Crystal data and structure refinement for ketone (±)-51.



(±)-**51**

Identification code	CCDC 2192302
Empirical formula	$C_{23}H_{30}O_3$
Formula weight	354.47
Temperature/K	113.15
Crystal system	orthorhombic
Space group	P212121
a/Å	9.4840(3)
b/Å	13.8807(3)
c/Å	14.0827(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1853.91(8)
Z	4
$\rho_{calc.}$ g/cm^3	1.270
μ/mm^{-1}	0.082
F(000)	768.0
Crystal size/mm^3	0.22 × 0.2 × 0.16
Radiation	Mo Kα (λ = 0.71073)
2$^\Theta$ range for data collection/°	4.12 to 65.634
Index ranges	$-14 \leq h \leq 14, -20 \leq k \leq 21, -21 \leq l \leq 20$
Reflections collected	23157
Independent reflections	6371 [R_{int} = 0.0330, R_{sigma} = 0.0296]
Data/restraints/parameters	6371/0/242
Goodness-of-fit on F^2	1.044
Final R indexes	R_1 = 0.0356, wR_2 = 0.0890
Final R indexes [all data]	R_1 = 0.0397, wR_2 = 0.0916
Largest diff. peak/hole / e Å^{-3}	0.27/−0.16

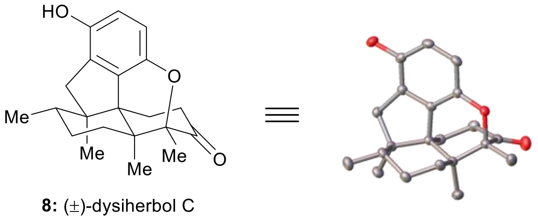
Table S14. Crystal data and structure refinement for (±)-dysiherbol B (7).



7: (±)-dysiherbol B
(revised structure)

Identification code	CCDC 2141304
Empirical formula	$C_{21}H_{28}O_3$
Formula weight	328.43
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_{1/C}$
a/Å	13.35230(10)
b/Å	7.54950(10)
c/Å	16.84080(10)
α/°	90
β/°	98.7890(10)
γ/°	90
Volume/Å^3	1677.69(3)
Z	4
$\rho_{calc.}$ g/cm^3	1.300
μ/mm^{-1}	0.672
F(000)	712.0
Crystal size/mm^3	0.22 × 0.21 × 0.08
Radiation	CuKα (λ = 1.54184)
2^{Θ} range for data collection/°	11.674 to 151.666
Index ranges	$-16 \le h \le 16$, $-9 \le k \le 9$, $-20 \le l \le 19$
Reflections collected	13374
Independent reflections	3407 [R_{int} = 0.0312, R_{sigma} = 0.0302]
Data/restraints/parameters	3407/0/223
Goodness-of-fit on F^2	1.083
Final R indexes	R_1 = 0.0404, wR_2 = 0.1079
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	0.25/−0.26

Table S15. Crystal data and structure refinement for (±)-dysiherbol C (8).



8: (±)-dysiherbol C
(revised structure)

Identification code	CCDC 2141326
Empirical formula	$C_{21}H_{26}O_3$
Formula weight	326.42
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.46953(17)
b/Å	17.2423(4)
c/Å	25.6766(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3306.93(13)
Z	8
$\rho_{calc.}$ g/cm^3	1.311
μ/mm^{-1}	0.681
F(000)	1408.0
Crystal size/mm^3	0.22 × 0.21 × 0.11
Radiation	CuKα (λ = 1.54184)
2^{Θ} range for data collection/°	13.37 to 133.996
Index ranges	$-8 \leq h \leq 8$, $-20 \leq k \leq 20$, $-25 \leq l \leq 30$
Reflections collected	9856
Independent reflections	2827 [R_{int} = 0.0423, R_{sigma} = 0.0401]
Data/restraints/parameters	2827/0/222
Goodness-of-fit on F^2	1.059
Final R indexes	R_1 = 0.0406, wR_2 = 0.1035
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1073
Largest diff. peak/hole / e Å^{-3}	0.18/−0.23

VI. References

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