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Supporting Information

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Enantioselective Total Synthesis of the Reported Structures of (−)-9-*epi*-Presilphiperfolan-1-ol and (−)-Presilphiperfolan-1-ol: Structural Confirmation and Reassignment and Biosynthetic Insights**

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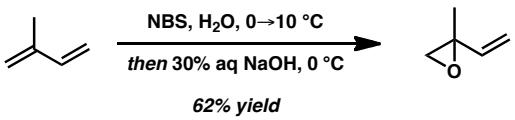
Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC). THF, Et_2O, CH_2Cl_2, toluene, benzene, CH_3CN, $CyCH_3$, and dioxane were dried by passage through an activated alumina column under argon. Triethylamine was distilled over CaH_2 prior to use. Purified water was obtained using a Barnstead NANOpure Infinity UV/UF system. Brine solutions are saturated aqueous solutions of sodium chloride. $Zn(CH_3)_2$ (1.0 M in heptanes) and TBAF (1.0 M in THF) were purchased from Sigma-Aldrich. CDI was purchased from Sigma-Aldrich or Combi-blocks, Inc. Adam's catalyst (PtO_2-hydrate) was purchased from Strem. Anhydrous lithium hydroxide and $P(NMe_2)_3$ were purchased from Acros Organics. LiHMDS, CH_3Ph_3PBr, pinacolborane, $Pd(P\textit{t}\text{-}Bu_3)_2$, and Crabtree's catalyst ($[Ir(cod)(PCy_3)(py)]PF_6$) were purchased from Sigma-Aldrich and stored in a N_2-filled glove box. $Ni(cod)_2$, CuCN, PCy_3, $P\textit{t}\text{-}Bu_3$, and Cy-Johnphos (CAS# [247940-06-3]) were purchased from Strem and stored in a N_2-filled glove box. NBS from Sigma-Aldrich was ground into a fine white powder with a mortar and pestle before use. NaH (60% wt. dispersion in mineral oil) from Sigma-Aldrich was purified by trituration with hexanes under a N_2 atmosphere and removal of residual solvent under vacuum. Isobutoxy-2-cyclohepten-1-one (#T271322) is commercially available from Sigma-Aldrich, but was prepared by a modified procedure[1] of Ragan.[2] 2-Methyl-2-vinyloxirane was purchased from Sigma-Aldrich or prepared by a modification of the procedure of Isobe.[3] 2-methylene-3-buten-1-ol (isoprenol) was prepared by the procedure of Isobe.[3] Phosphinooxazoline (PHOX) ligands were prepared by methods described in our previous work.[4] Tris(4,4'-methoxydibenzylideneacetone)dipalladium(0) ($Pd_2(pmdba)_3$) was prepared according to the method of Ibers[5] or Fairlamb.[6] $Pd(PPh_3)_4$ was prepared according to the procedure of Coulson.[7] TBSOTf was prepared according to the procedure of Corey and stored under a N_2 or Ar atmosphere in a –25 °C freezer.[8] $FeCl_2$(py-imine) complex **SI-4** and [2-(N,N-dimethylaminomethyl)phenyl]lithium (**SI-5**) were prepared according the method of Ritter and stored in a N_2-filled glove box.[9a] DMDO was prepared according to the procedure of Singh.[10] All other reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag temperature modulator unless otherwise indicated. Microwave-assisted reactions were performed in a Biotage Initiator 2.5 microwave reactor. Glove box manipulations were performed under a N_2 atmospere. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash column chromatography. Silica gel was deactivated by prestirring with 1% Et_3N in hexanes for 30 min to 1 h before use for flash column chromatography. Solutions of potentially volatile reaction products were concentrated under reduced pressure (25 mm Hg) in a 0 °C ice/water bath using a rotary evaporator. ^1H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm), C_6H_6 (δ 7.16 ppm), or CH_2Cl_2 (δ 5.32 ppm). ^{13}C NMR spectra are recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm) or C_6H_6 (δ 128.06 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained using a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm) using a 100 mm path-

length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent, ee). Melting points were measured using a Büchi B-545 capillary melting point apparatus and the reported values are uncorrected. Preparatory HPLC was performed with an Agilent 1100 Series HPLC utilizing an Agilent ZORBAX RX-SIL 5μm column (9.4 x 250 mm), part number 880975-201. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralcel AD column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries Ltd. with visualization at 254 nm. Analytical UHPLC-LCMS was performed with an Agilent 1290 Infinity Series UHPLC/Agilent 6140 Quadrupole LCMS utilizing an Agilent Eclipse Plus C18 RRHD 1.8 μm column (2.1 x 50 mm), part number 959757-902. High-resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility (EI+ or FAB+) or on an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed (MM: ESI-APCI+) ionization mode.

List of Abbreviations. The following abbreviations are used in experimental procedures:

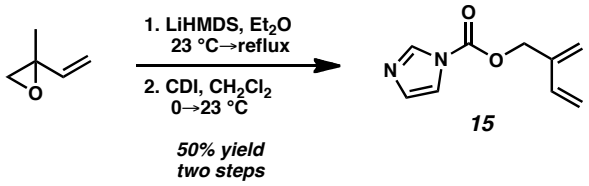
CDI = 1,1'-carbonyldiimidazole
cod = 1,5-cyclooctadiene
Cy-Johnphos = (2-biphenyl)dicyclohexylphosphine
$CyCH_3$ = methylcyclohexane
DMAP = 4-(dimethylamino)pyridine
EtOAc = ethyl acetate
i-Bu = isobutyl
IPA = isopropanol, 2-propanol
$[Ir(cod)(PCy_3)(py)]PF_6$ = (1,5-cyclooctadiene)(pyridine)(tricyclohexylphosphine)-iridium(I) hexafluorophosphate, Crabtree's catalyst
HBPin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane)
HMDS = hexamethyldisilazane
LiHMDS = lithium bis(trimethylsilyl)amide
$Ni(cod)_2$ = bis(1,5-cyclooctadiene)nickel(0)
PCy_3 = tricyclohexylphosphine
P*t*-Bu_3 = tri-*tert*-butylphosphine
$Pd_2(pmdba)_3$ = tris(4,4'-methoxydibenzylideneacetone)dipalladium(0)
PHOX = phosphinooxazoline ligand
PPTS = pyridinium *p*-toluenesulfonate
t-Bu = *tert*-butyl
TBAF = tetrabutylammonium fluoride
TBS = *tert*-butyldimethylsilyl
TBSOTf = *tert*-butyldimethylsilyl trifluoromethanesulfonate
TFE = 2,2,2-trifluoroethanol
THF = tetrahydrofuran
TMS = trimethylsilyl
TMSCl = chlorotrimethylsilane
μwaves = microwave irradiation

Procedures for the Synthesis of the Reported Structures of Presilphiperfolan-1-ol (1) and 9-*epi*-Presilphiperfolan-1-ol (2)



2-Methyl-2-vinyloxirane.[3] To a 3-neck 1 L round-bottom flask with mechanical stirrer was added H_2O (300 mL). The flask was cooled to 0 °C using an ice/water bath and stirred for 10 min. Isoprene (81 mL, 0.81 mol, 1.00 equiv) was added and glass stoppers were attached to the side necks. The biphasic mixture was stirred vigorously for 5 min at 0 °C. Finely powdered NBS (140.52 g, 0.790 mol, 0.975 equiv) was added portionwise through a side neck over 35 min to give a pale tan suspension. The glass stopper was reattached to the side neck and the reaction was stirred at 0 °C for 2.5 h. Subsequent warming of the reaction to 10 °C led to clarification of the reaction mixture. If stirring was halted, a clear, colorless upper aqueous phase and a clear, pale yellow lower organic phase could be observed. The reaction was cooled to 0 °C and stirred for 9 h. Chilled, ice-cold 10 M aqueous NaOH (160 mL) was added to the reaction over 15 min through an addition funnel to give a turbid white biphasic mixture. Internal temperature was maintained below 5 °C during addition. The reaction was stirred at 0 °C for 15 min. If stirring was halted, a clear, colorless organic upper phase could be observed. The phases were separated and the organic phase was washed with H_2O (2 x 15 mL) and brine (2 x 15 mL). The organic phase was transferred to a 100 mL round-bottom flask and the crude product was distilled (80 °C, 760 mmHg) to yield the first portion of 2-methyl-2-vinyloxirane (34.66 g).

A second portion of product was isolated by extraction of the aqueous phase with Et_2O (3 x 40 mL). The combined organic phases were washed with H_2O (2 x 15 mL) and brine (2 x 15 mL), dried over $MgSO_4$, filtered into a 200 mL pear-shaped flask. The flask was fitted with a short-path distillation head and immersed in a 45 °C oil bath to remove Et_2O by distillation. Once Et_2O was removed, the crude product was distilled (80 °C, 760 mmHg) to yield the second portion of 2-methyl-2-vinyloxirane (7.24 g). The portions of 2-methyl-2-vinyloxirane (41.90 g, 0.498 mol, 62% yield) were combined to give a clear, colorless liquid. The spectral data match data for commercially available material.

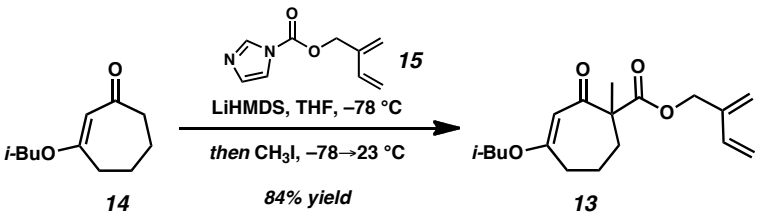


Carbamate 15. Isoprenol was prepared according to the method of Isobe[3a] and converted to carbamate **15** using the general procedure of Sarpong.[11]

To a 500 mL 3-neck round-bottom flask equipped with a magnetic stir bar, rubber septum, and two glass stoppers was added LiHMDS (24.09 g, 143.97 mmol, 1.20 equiv) in a N_2-filled glove box. The flask was sealed with a rubber septum and removed from the glove box. One of the glass stoppers was replaced with a reflux condenser connected to a N_2 inlet. The flask was cooled to –78 °C using an acetone/CO_2(s) bath. Et_2O (160 mL) was added and the suspension was stirred vigorously for 5 min. The cooling bath was removed and the flask was allowed to warm to 23 °C, giving a white suspension. A solution of 2-methyl-2-vinyloxirane

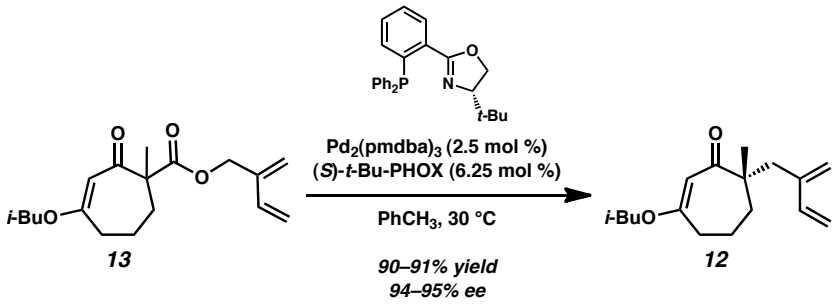
(10.0 g, 119.97 mmol, 1.00 equiv) in Et_2O (50 mL) in a 100 mL conical flask was added to the reaction by positive pressure cannulation, leading to the formation of a turbid pale yellow solution. The reaction was heated to reflux in a 45 °C oil bath. After 22 h of stirring, the reaction was cooled to 0 °C and stirred for 10 min. Chilled, ice-cold 2 M aqueous HCl (80 mL) was added and the reaction was stirred vigorously for 1 h. The phases were separated and the aqueous phase was extracted with Et_2O (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure (150 mmHg) in a 0 °C ice/water bath to a volume of ca. 50 mL. The solution of volatile isoprenol was used directly in the next step.

To a 1 L round-bottom flask with a magnetic stir bar were added CDI (29.7 g, 179.96 mmol, 1.50 equiv) and CH_2Cl_2 (400 mL). An addition funnel was attached and the apparatus was connected to a N_2 inlet. The flask was cooled to 0 °C and stirred for 10 min. The solution of crude isoprenol in Et_2O (50 mL) was transferred to the addition funnel and added dropwise with vigorous stirring at 0 °C. The cooling bath was removed and the flask was allowed to warm to 23 °C. After 1 h of stirring, the reaction was quickly washed with H_2O (2 x 100 mL) and brine (2 x 100 mL). The aqueous phases were extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, 8 x 15 cm, 20%→30%→50% EtOAc in hexanes) to afford carbamate **15** (10.74 g, 60.26 mmol, 50% yield over two steps) as a pale yellow oil which solidifies upon storage in a –25 °C freezer. (Note: The reagent is moisture sensitive. Storage under N_2 in a sealed container in a –25 °C freezer is recommended for maintaining reagent quality, but the reagent is typically used shortly after generation.); $R_f = 0.15$ (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.45–7.37 (m, 1H), 7.09–7.02 (m, 1H), 6.40 (dd, *J* = 17.8, 11.1 Hz, 1H), 5.38–5.34 (m, 1H), 5.34–5.31 (m, 1H), 5.30 (d, *J* = 17.9 Hz, 1H), 5.20 (d, *J* = 11.2 Hz, 1H), 5.06 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 139.2, 137.1, 135.6, 130.8, 119.9, 117.1, 115.4, 67.2; IR (Neat Film NaCl) 3132, 3091, 3010, 2952, 2929, 2855, 1763, 1599, 1526, 1472, 1403, 1390, 1318, 1290, 1281, 1240, 1172, 1095, 1058, 1007, 916, 897, 835, 768, 746 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_9H_{11}N_2O_2$ $[M+H]^+$: 178.0815; found 178.0818.



***β*-Ketoester 13.** To a 1 L round-bottom flask with a magnetic stir bar was added LiHMDS (25.83 g, 154.40 mmol, 3.00 equiv) in a N_2-filled glove box. The flask was sealed with a rubber septum and removed from the glove box, connected to a N_2 inlet, and cooled to –78 °C using an acetone/CO_2(s) bath. THF (360 mL) was added and the suspension was stirred vigorously for 5 min. The cooling bath was removed and the flask was allowed to warm until the solids completely dissolved. The pale tan solution was cooled to –78 °C. A solution of vinylogous ester **14**[1] (9.38 g, 51.47 mmol, 1.00 equiv) in THF (80 mL) in a 100 mL conical flask was added to the reaction dropwise over 1 h using positive pressure cannulation. The orange solution was stirred at –78 °C for 30 min. A solution of carbamate **15** (11.46 g, 64.33 mmol, 1.25 equiv) in THF (25 mL) in a 50 mL conical flask was added to the reaction dropwise over 15 min using positive pressure cannulation. The orange solution was stirred at –78 °C for 2.5 h. CH_3I (38.4

mL, 617.58 mmol, 12.00 equiv) was added dropwise. The cooling bath was allowed to expire and the reaction warmed to 23 °C over 7 h. After 13 h of stirring, the reaction was quenched with 50% sat. aqueous NH_4Cl (190 mL) and Et_3N (7.5 mL). The biphasic mixture was stirred vigorously for 12 h. The phases were separated and the organic phase was washed with brine (2 x 200 mL). The combined aqueous phases were washed with EtOAc (3 x 150 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The oil was taken up in Et_2O, leading to the precipitation of solids. The suspension was filtered through a silica gel plug (3 x 5 cm), eluting with Et_2O and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (SiO_2, 8 x 32 cm, 3%→10%→20%→40% EtOAc in hexanes) to afford *β*-ketoester **13** (13.22 g, 43.15 mmol, 84% yield) as a pale yellow oil; R_f = 0.54 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.29 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.37–5.31 (m, 1H), 5.22–5.18 (m, 1H), 5.16 (d, *J* = 18.2 Hz, 1H), 5.16–5.12 (m, 1H), 5.06 (d, *J* = 11.1 Hz, 1H), 4.77 (d, *J* = 13.3 Hz, 1H), 4.69 (d, *J* = 13.3 Hz, 1H), 3.44 (dd, *J* = 9.3, 6.6 Hz, 1H), 3.42 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.53 (ddd, *J* = 17.8, 9.9, 3.8 Hz, 1H), 2.43–2.28 (m, 2H), 2.00–1.87 (m, 2H), 1.81–1.68 (m, 1H), 1.65 (ddd, *J* = 14.4, 7.3, 4.3 Hz, 1H), 1.39 (s, 3H), 0.90 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 173.9, 173.5, 140.4, 136.1, 118.4, 114.8, 105.1, 74.8, 64.3, 59.1, 34.4, 33.9, 27.9, 24.2, 21.3, 19.3; IR (Neat Film NaCl) 3090, 2859, 2935, 2874, 1735, 1653, 1649, 1613, 1471, 1456, 1424, 1401, 1384, 1309, 1275, 1233, 1197, 1169, 1114, 1084, 1032, 994, 969, 910, 869, 768 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{27}O_2$ $[M+H]^+$: 307.1904; found 307.1899.

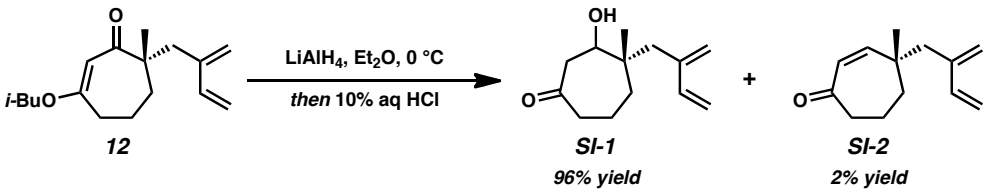


Vinylogous ester 12 (*2 mmol scale*). A 20 mL scintillation vial was loaded with *β*-ketoester **13** (527 mg, 1.72 mmol, 1.00 equiv). A separate 20 mL scintillation vial was loaded with a magnetic stir bar, $Pd_2(pmdba)_3$[5,6] (47.2 mg, 0.043 mmol, 2.5 mol %), and (*S*)-*t*-Bu-PHOX[4] (41.7 mg, 0.108 mmol, 6.25 mol %). The two vials and a teflon-lined hard cap were placed in a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the items were transferred into the glove box. Toluene (10 mL) was added to the vial containing $Pd_2(pmdba)_3$ and (*S*)-*t*-Bu-PHOX. The vial was capped and the reaction was stirred for 30 min in a 30 °C heating block. During this time, the reaction changed from a deep purple-black suspension to a deep red-orange color. *β*-Ketoester **13** was dissolved in toluene (7 mL) and added to the catalyst solution dropwise, causing the solution to turn olive green. The reaction was sealed with a teflon-lined hard cap and stirred at 30 °C. After 16.5 h of stirring, the reaction became a deep red-orange color. The capped vial was removed from the glove box and the reaction was concentrated under reduced pressure. The crude oil was purified by flash column chromatography (SiO_2, 3 x 25 cm, 40:1→20:1→15:1 hexanes:EtOAc) to afford vinylogous ester **12** (143.9 mg, 1.57 mmol, 91% yield, 94.7% ee) as a pale yellow oil.

Vinylogous ester 12 (*40 mmol scale*). To a 1 L round-bottom flask with a magnetic stir bar were added $Pd_2(pmdba)_3$[5,6] (1.18 g, 1.08 mmol, 2.5 mol %), (*S*)-*t*-Bu-PHOX[4] (1.04 g, 2.70 mmol, 6.25 mol %), and toluene (430 mL) in a N_2-filled glove box. The flask was sealed with a rubber septum, removed from the glove box, connected to a N_2 inlet, and immersed in a 30 °C oil bath. The deep purple-black suspension gradually became became a deep red-orange solution after 50 min of stirring. *β*-Ketoester **13** (13.22 g, 43.14 mmol, 1.00 equiv) in a 100 mL conical flask was freeze-pump-thawed using an acetone/CO_2(s) bath (3 cycles, 5 min evacuation per cycle), dissolved in toluene (30 mL), and added to the reaction dropwise using positive pressure cannulation. The solution became a deep olive-green solution. After 33 h of stirring, the reaction was a deep red-orange solution. The reaction was concentrated under reduced pressure and the crude oil was purified by flash column chromatography (SiO_2, 8 x 32 cm, 3%→5%→10% EtOAc in hexanes) to afford vinylogous ester **12** (10.20 g, 38.87 mmol, 90% yield, 95.3% ee) as a pale tan oil.

R_f = 0.35 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.32 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.29 (s, 1H), 5.25 (d, *J* = 17.5 Hz, 1H), 5.17–5.11 (m, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.93–4.87 (m, 1H), 3.48 (dd, *J* = 9.3, 6.6 Hz, 1H), 3.44 (dd, *J* = 9.3, 6.4 Hz, 1H), 2.56 (d, *J* = 13.7 Hz, 1H), 2.50–2.35 (m, 2H), 2.42 (d, *J* = 13.8 Hz, 1H), 1.96 (app. sept, *J* = 6.7 Hz, 1H), 1.88–1.74 (m, 2H), 1.74–1.61 (m, 1H), 1.54 (ddd, *J* = 14.5, 8.9, 1.3 Hz, 1H), 1.13 (s, 3H), 0.93 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.0, 171.0, 143.1, 140.3, 119.2, 113.9, 105.4, 74.4, 52.2, 41.1, 36.2, 35.1, 28.0, 26.3, 19.7, 19.3, 19.3; IR (Neat Film NaCl) 3085, 2959, 2934, 2873, 1811, 1722, 1699, 1614, 1470, 1464, 1455, 1423, 1402, 1387, 1373, 1317, 1260, 1212, 1187, 1174, 1110, 1083, 1019, 992, 969, 951, 898, 887, 851, 822 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{27}O_2$ $[M+H]^+$: 263.2006; found 263.2006; $[\alpha]_D^{26.0}$ –73.44 (*c* 0.92, $CHCl_3$, 94.7% ee); HPLC conditions: 2.0% IPA in hexanes, 1.0 mL/min, OD-H column, t_R (min): major = 6.41, minor = 7.53.

(Note: $Pd_2(pmdba)_3$ is preferable to $Pd_2(dba)_3$ in this reaction for ease of separation of pmdba from the reaction products during purification. The racemic reaction was carried out with $Pd(PPh_3)_4$[7] (5 mol %) in toluene (0.1 M) at 30 °C or with $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol %) and dppe (6.25 mol %) in toluene (0.1 M) at 30 °C.)

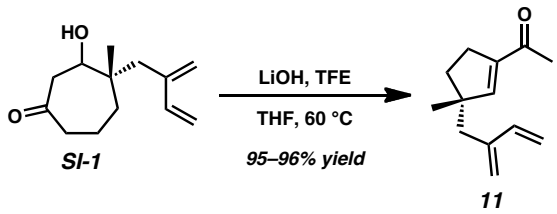


***β*-Hydroxyketone SI-1** and **Cycloheptenone SI-2.** A 1 L round-bottom flask with a magnetic stir bar was charged with $LiAlH_4$ (862.6 mg, 22.97 mmol, 0.60 equiv) and evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle). Et_2O (600 mL) was added and the gray suspension was cooled to 0 °C using an ice/water bath. A solution of vinylogous ester **12** (10.05 g, 38.28 mmol, 1.00 equiv) in Et_2O (80 mL) in a conical 100 mL flask was added to the reaction dropwise over 20 min using positive pressure cannulation. The flask was washed with THF (2 x 10 mL) and washes were added to the reaction. The gray suspension was stirred at 0 °C. After 15 min of stirring, the reaction was quenched by slow dropwise addition of 10% aqueous HCl (59.4 mL). Gas evolution was observed. The reaction was stirred at 0 °C for 5 min and the phases were

separated. The aqueous phase was extracted with Et_2O (3 x 30 mL). Combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (SiO_2, 3 x 25 cm, 10:1→3:1→2:1 hexanes:EtOAc) to afford cycloheptenone **SI-2** (174.9 mg, 0.919 mmol, 2% yield) as a pale yellow oil and *β*-hydroxyketone **SI-1** (7.65 g, 36.73 mmol, 96% yield, 1.26:1 d.r.) as a pale tan oil. (Note: Storage in a sealed container in a –25 °C freezer is recommended, but the compound is typically used shortly after generation.)

***β*-Hydroxyketone SI-1:** R_f = 0.15 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) mixture of two overlapping diastereomers, see Figure SI-4A; ^{13}C NMR (125 MHz, $CDCl_3$) mixture of two diastereomers: δ 214.0, 213.0, 143.4, 143.1, 140.7, 140.6, 119.5, 119.3, 113.9, 113.9, 73.5, 72.1, 47.7, 46.8, 44.1, 43.9, 41.5, 41.4, 40.7, 38.8, 36.4, 36.0, 22.1, 21.9, 19.2, 18.4; IR (Neat Film NaCl) 3447, 3084, 2966, 2933, 2873, 1810, 1696, 1628, 1590, 1465, 1457, 1400, 1351, 1321, 1252, 1166, 1113, 1064, 993, 899, 853, 802, 759, 729 cm^{-1}; HRMS (APCI+) *m/z* calc'd for $C_{13}H_{18}O$ [M–OH]$^+$: 191.1430; found 191.1426; $[\alpha]_D^{26.0}$ –30.27 (*c* 1.66, $CHCl_3$, 94.7% ee).

Cycloheptenone SI-2: R_f = 0.60 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (ddd, *J* = 17.6, 10.9, 0.8 Hz, 1H), 6.05 (dd, *J* = 13.0, 1.0 Hz, 1H), 5.77 (d, *J* = 13.0 Hz, 1H), 5.23–5.20 (m, 1H), 5.20 (d, *J* = 17.5 Hz, 1H), 5.05 (dm, *J* = 10.9 Hz, 1H), 4.99–4.94 (m, 1H), 2.66–2.49 (m, 2H), 2.38 (d, *J* = 13.6 Hz, 1H), 2.27 (dd, *J* = 13.6, 0.9 Hz, 1H), 1.90–1.75 (m, 3H), 1.73–1.60 (m, 1H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 152.8, 142.3, 140.1, 128.0, 120.0, 114.3, 45.1, 43.3, 43.2, 39.0, 27.9, 18.4; IR (Neat Film NaCl) 3087, 3008, 2962, 2930, 2869, 1811, 1707, 1658, 1591, 1457, 1400, 1373, 1346, 1336, 1261, 1208, 1146, 1092, 1020, 900, 876, 801 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{13}H_{18}O$ [M+H]$^+$: 191.1430; found 191.1428; $[\alpha]_D^{25.0}$ –5.31 (*c* 1.20, $CHCl_3$, 94.7% ee).

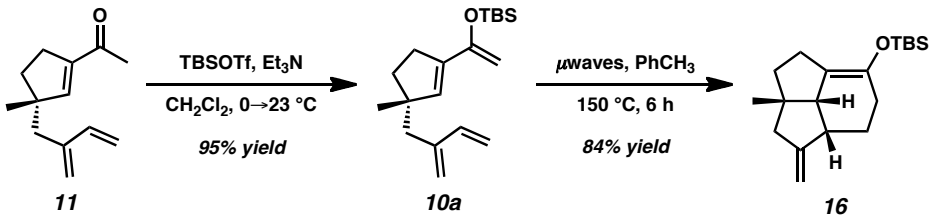


Acylcyclopentene 11 (*0.4 mmol scale*). *β*-Hydroxyketone **SI-1** (89.3 mg, 0.428 mmol, 1.00 equiv) was dissolved in THF (4.3 mL) in a 20 mL scintillation vial with a magnetic stir bar. The solution was treated with 2,2,2-trifluoroethanol (46.9 μL, 0.643 mmol, 1.50 equiv) and anhydrous LiOH (15.4 mg, 0.643 mmol, 1.50 equiv). The headspace of the vial was purged with Ar. The vial was sealed with a teflon-lined hard cap and inserted into a 60 °C heating block. After 14 h of stirring, the fine suspension was allowed to cool to ambient temperature, diluted with Et_2O (4 mL), dried over Na_2SO_4 with stirring for 30 min, filtered, and carefully concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The crude product was purified using flash column chromatography (SiO_2, 2 x 25 cm, 15:1 hexanes:Et_2O) to afford acylcyclopentene **11** (77.1 mg, 0.405 mmol, 95% yield) as a fragrant pale tan oil.

Acylcyclopentene 11 (*30 mmol scale*). *β*-Hydroxyketone **SI-1** (6.46 g, 31.0 mmol, 1.00 equiv) was dissolved in THF (310 mL) in a 1 L round-bottom flask with a magnetic stir bar. The solution was treated with 2,2,2-trifluoroethanol (3.39 mL, 46.5 mmol, 1.50 equiv) and anhydrous

LiOH (1.116 g, 46.53 mmol, 1.50 equiv). The flask was fitted with a reflux condenser, purged with N_2, and immersed in a 60 °C oil bath. After 34 h of stirring, the fine suspension was allowed to cool to ambient temperature, diluted with Et_2O (300 mL), dried over Na_2SO_4 with stirring for 30 min, filtered, and carefully concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The crude product was purified using flash column chromatography (SiO_2, 5 x 25 cm, 15:1 hexanes:Et_2O) to afford acylcyclopentene **11** (5.703 g, 29.97 mmol, 96% yield) as a fragrant pale tan oil.

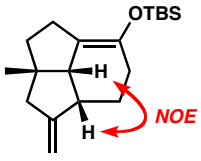
R_f = 0.61 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.45 (app. t, *J* = 1.8 Hz, 1H), 6.35 (ddm, *J* = 17.6, 10.8 Hz, 1H), 5.16–5.12 (m, 1H), 5.16 (d, *J* = 17.8 Hz, 1H), 5.04 (dm, *J* = 10.9 Hz, 1H), 4.97–4.91 (m, 1H), 2.55–2.43 (m, 2H), 2.38 (d, *J* = 13.5 Hz, 1H), 2.32 (dd, *J* = 13.6, 0.9 Hz, 1H), 2.23 (s, 3H), 1.91 (ddd, *J* = 12.9, 7.6, 6.8 Hz, 1H), 1.65 (ddd, *J* = 12.9, 7.8, 6.8 Hz, 1H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 152.7, 143.4, 142.9, 140.1, 119.3, 114.0, 50.3, 41.5, 37.0, 29.4, 26.7, 26.2; ^{1}H NMR (500 MHz, C_6D_6) δ 6.25 (ddd, *J* = 17.6, 10.8, 0.8 Hz, 1H), 6.07 (app. t, *J* = 1.8 Hz, 1H), 5.03 (d, *J* = 17.3 Hz, 1H), 5.03–4.99 (m, 1H), 4.90 (dm, *J* = 10.9 Hz, 1H), 4.79–4.75 (m, 1H), 2.65–2.52 (m, 2H), 2.17 (d, *J* = 13.5 Hz, 1H), 2.07 (dd, *J* = 13.5, 0.8 Hz, 1H), 1.98 (s, 3H), 1.69 (ddd, *J* = 12.8, 7.9, 6.8 Hz, 1H), 1.41 (ddd, *J* = 12.9, 7.9, 6.6 Hz, 1H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 195.3, 150.9, 143.8, 143.4, 140.4, 119.3, 114.0, 50.2, 41.6, 37.2, 30.0, 26.4, 26.1; IR (Neat Film NaCl) 3084, 2954, 2927, 2864, 1807, 1669, 1617, 1591, 1457, 1437, 1424, 1377, 1366, 1307, 1267, 1227, 1200, 1160, 1092, 1043, 1019, 992, 934, 898, 867, 806 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{13}H_{19}O$ $[M+H]^+$: 191.1430; found 191.1427; $[\alpha]_D^{26.0}$ –63.18 (*c* 1.02, $CHCl_3$, 94.7% ee).



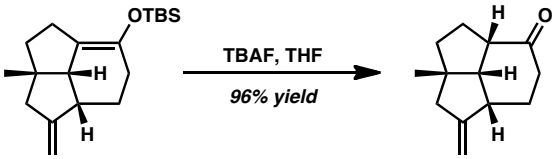
Silyl Dienol Ether 10a. A 20 mL scintillation vial with a magnetic stir bar was charged with acylcyclopentene **11** (41.7 mg, 0.219 mmol, 1.00 equiv), sealed with a septum-fitted screw cap, and connected to a N_2 inlet. The headspace of the vial was gently purged with N_2 through a venting needle for 1 min. CH_2Cl_2 (2.2 mL) was added and the reaction was cooled to 0 °C using an ice/water bath. After 5 min of stirring, Et_3N (122 μL, 0.877 mmol, 4.00 equiv) was added dropwise. After 2 min of stirring, TBSOTf[18] (101 μL, 0.438 mmol, 2.00 equiv) was added dropwise. The formation of vapor was observed. The clear, colorless solution was stirred at 0 °C for 20 min. The reaction was diluted with CH_2Cl_2 (2.2 mL) and quenched by addition of ice-cold sat. aqueous $NaHCO_3$ (1.5 mL) and stirred for 5 min at 0 °C. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography with deactivated silica gel (SiO_2, 3 x 12 cm, deactivated with 1% Et_3N in hexanes, 1% Et_3N in hexanes→20% Et_2O in hexanes eluent) to afford silyl dienol ether **10a** (63.1 mg, 0.207 mmol, 95% yield) as a colorless oil. (Note: Silyl dienol ether **10a** appears to be sensitive to moisture. The compound was stored as a solidified benzene solution under N_2 in a –25 °C freezer.); R_f = 0.73 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 6.35 (ddd, *J* = 17.5, 10.8, 0.8 Hz, 1H), 6.06 (app. t, *J* = 1.8 Hz, 1H), 5.20 (dm, *J* = 17.5 Hz, 1H), 5.11–5.08 (m,

1H), 4.98 (dm, *J* = 10.9 Hz, 1H), 4.94–4.91 (m, 1H), 4.37–4.35 (m, 1H), 4.36–4.34 (m, 1H), 2.49–2.36 (m, 2H), 2.31 (d, *J* = 13.4 Hz, 1H), 2.24 (dd, *J* = 13.4, 0.9 Hz, 1H), 1.87 (ddd, *J* = 12.6, 8.2, 6.9 Hz, 1H), 1.59 (ddd, *J* = 12.6, 8.0, 5.9 Hz, 1H), 1.05 (s, 3H), 1.02 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.7, 144.5, 140.6, 139.1, 138.0, 118.8, 114.0, 92.8, 49.3, 42.4, 38.2, 31.4, 26.9, 26.1, 18.5, –4.4, –4.5; IR (Neat Film NaCl) 3119, 3084, 2956, 2928, 2857, 1802, 1631, 1589, 1472, 1462, 1389, 1373, 1361, 1315, 1284, 1256, 1225, 1210, 1164, 11121, 1092, 1063, 1016, 1005, 991, 939, 895, 865, 838, 830, 812, 779 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{33}OSi$ $[M+H]^+$: 305.2301; found 305.2287; $[\alpha]_D^{25.0}$ –32.17 (*c* 1.02, CH_2Cl_2, 94.9% ee).

Silyl Enol Ether 16. To a 5 mL microwave vial with magnetic stir bar under N_2 were added silyl dienol ether **10a** (88.3 mg, 0.290 mmol, 1.00 equiv) and toluene (4 mL). The reaction was sealed with a microwave crimp cap and subjected to microwave irradiation in a Biotage Initiator microwave reactor (temperature: 150 °C, sensitivity: low) with a gradual temperature increase over 10 min (10 °C increments). After 6 h of stirring, the vial was cooled to ambient temperature and uncapped. The reaction was concentrated under reduced pressure. The residue was purified by flash column chromatography with deactivated silica gel (SiO_2, 3 x 12 cm, deactivated with 1% Et_3N in hexanes, 1% Et_3N in hexanes→20% Et_2O in hexanes eluent) to afford silyl enol ether **16** (74.6 mg, 0.245 mmol, 84% yield) as a colorless oil; R_f = 0.60 (1% Et_2O in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 4.99–4.95 (m, 1H), 4.91–4.86 (m, 1H), 2.75–2.70 (m, 1H), 2.70–2.62 (m, 1H), 2.32–2.09 (m, 4H), 2.01 (dm, *J* = 16.8 Hz, 1H), 1.97–1.83 (m, 2H), 1.83–1.71 (m, 1H), 1.61 (ddd, *J* = 13.1, 9.2, 3.9 Hz, 1H), 1.48 (ddd, *J* = 12.9, 11.3, 6.7 Hz, 1H), 1.02 (s, 3H), 1.01 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.4, 143.0, 120.7, 106.1, 55.3, 47.2, 45.4, 40.3, 36.9, 26.1, 25.9, 25.9, 25.8, 24.1, 18.4, –3.5, –3.8; IR (Neat Film NaCl) 2928, 2859, 1696, 1653, 1472, 1461, 1378, 1356, 1285, 1257, 1215, 1171, 1108, 1090, 1070, 1029, 1006, 978, 990, 959, 933, 890, 874, 834, 813, 777 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{19}H_{32}O_{Si}$ $[M]^{+\bullet}$: 304.2223; found 304.2209; $[\alpha]_D^{26.0}$ +114.41 (*c* 1.06, CH_2Cl_2, 94.7% ee). ^{1}H-NOESY-2D (500 MHz, C_6D_6) spectra were obtained for **16** and selected NOE interactions are shown below:



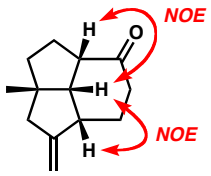
16



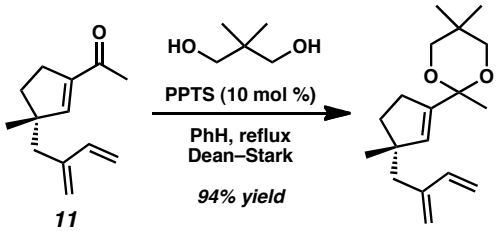
16 *SI-3*

Ketone SI-3. To a 20 mL scintillation vial with magnetic stir bar and silyl enol ether **16** (55.4 mg, 0.182 mmol, 1.00 equiv) was added THF (10 mL) to give a clear, colorless solution. TBAF (1.0 M in THF, 364 μL, 0.364 mmol, 2.00 equiv) was added dropwise, leading to a pale tan solution. After 20 min of stirring, the reaction was concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The pale yellow residue was purified by flash column chromatography (SiO_2, 3 x 12 cm, 2%→5%→10%→20% Et_2O in hexanes) to afford ketone **SI-3**

(36.2 mg, 0.176 mmol, 96% yield) as a colorless oil; R_f = 0.30 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.93–4.89 (m, 1H), 4.80–4.76 (m, 1H), 2.89–2.79 (m, 1H), 2.70 (ddd, *J* = 9.8, 9.8, 8.7 Hz, 1H), 2.51 (ddd, *J* = 16.6, 7.8, 7.8 Hz, 1H), 2.43 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.29 (ddd, *J* = 16.2, 2.9, 1.9 Hz, 1H), 2.24 (ddd, *J* = 16.1, 1.7, 1.7 Hz, 1H), 2.14 (ddd, *J* = 16.8, 5.8, 5.8 Hz, 1H), 2.06 (dd, *J* = 5.6, 5.6 Hz, 1H), 2.04 (dd, *J* = 5.6, 5.6 Hz, 1H), 1.87 (dd, *J* = 8.5, 8.5 Hz, 1H), 1.86 (dd, *J* = 8.5, 8.5 Hz, 1H), 1.63 (ddd, *J* = 12.6, 5.4, 5.4 Hz, 1H), 1.48 (ddd, *J* = 12.7, 8.5, 8.5 Hz, 1H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.3, 154.7, 105.2, 55.6, 52.1, 50.0, 47.8, 40.8, 40.8, 35.4, 30.5, 28.3, 24.9; IR (Neat Film NaCl) 3071, 2925, 2861, 1708, 1660, 1456, 1436, 1408, 1375, 1341, 1319, 1293, 1260, 1245, 1201, 1189, 1146, 1096, 1074, 1042, 968, 882, 802 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{13}H_{19}O$ [M+H]$^+$: 191.1430; found 191.1429; $[\alpha]_D^{25.0}$ +79.03 (*c* 1.01, $CHCl_3$, 94.9% ee). ^{1}H-NOESY-2D (500 MHz, $CDCl_3$) spectra were obtained for **SI-3** and selected NOE interactions are shown below:



SI-3

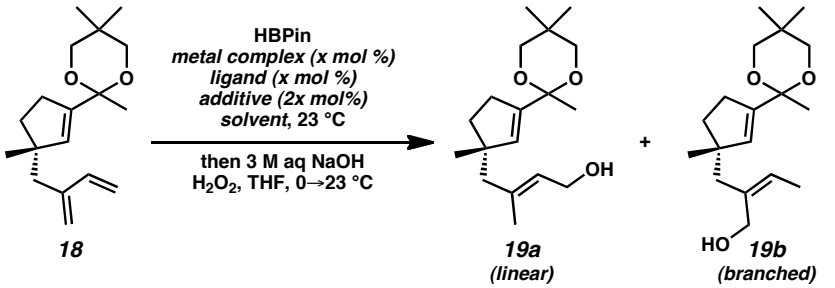


11 ***18***

Ketal 18. To a 250 mL round-bottom flask with a magnetic stir bar were added acylcyclopentene **11** (2.08 g, 11.0 mmol, 1.00 equiv), benzene (110 mL), neopentyl glycol (6.85 g, 65.74 mmol, 6.00 equiv), and PPTS (137.7 mg, 0.548 mmol, 0.05 equiv). A Dean–Stark trap and reflux condenser connected to a N_2 inlet was attached and the flask was immersed in a 100 °C oil bath. The suspension gradually became a clear, colorless solution. After 4.5 h of stirring, the reaction was cooled to 0 °C using an ice/water bath and poured into 50% sat. aqueous $NaHCO_3$ (25 mL) and stirred for 5 min. The phases were separated and the organic phase was washed with brine (3 x 40 mL). The combined aqueous phases were extracted with EtOAc (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a white semisolid. The crude product was purified using flash column chromatography (SiO_2, 8 x 20 cm, 1%→2%→5% EtOAc in hexanes) to afford ketal **18** (2.84 g, 10.3 mmol, 94% yield) as a pale tan oil; R_f = 0.65 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.38 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.54 (app. t, *J* = 1.9 Hz, 1H), 5.24 (d, *J* = 17.5 Hz, 1H), 5.16–5.13 (m, 1H), 5.05 (d, *J* = 10.7 Hz, 1H), 5.00–4.93 (m, 1H), 3.58 (d, *J* = 10.9 Hz, 1H), 3.50 (d, *J* = 11.0 Hz, 1H), 3.35–3.26 (m, 2H), 2.35 (d, *J* = 13.5 Hz, 1H), 2.33 (d, *J* = 13.5 Hz, 1H), 2.31–2.19 (m, 2H), 1.95 (ddd, *J* = 12.7, 8.4, 6.6 Hz, 1H), 1.65 (ddd, *J* = 12.7, 8.2, 5.6 Hz, 1H), 1.39 (s, 3H), 1.16 (s, 3H), 1.08 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 140.6, 140.4, 138.7, 118.7, 113.9, 98.8, 71.8, 71.8, 49.5, 41.9, 37.2, 31.1, 29.8, 27.6, 27.6, 22.9, 22.2; IR (Neat Film NaCl) 3084, 2951, 2865, 1631, 1591, 1472, 1458, 1395, 1369, 1352, 1319, 1298, 1257, 1240, 1180, 1117, 1083, 1040, 1014, 991, 949, 895, 862, 806, 793 cm^{-1}; HRMS

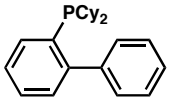
(MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{29}O_2$ $[M+H]^+$: 277.2162; found 277.2169; $[\alpha]_D^{25.0}$ –6.24 (*c* 0.950, $CHCl_3$, 94.9% ee).

Table SI-1. Metal-Catalyzed 1,4-Hydroboration/Oxidation Screen

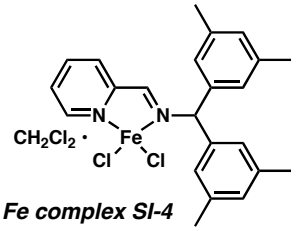


entry	metal complex (mol %)	ligand or additive (mol %)	solvent	time (h)	yield (%)[c]	*l* : *b*[d]
1[a]	$Ni(cod)_2$ (5%)	PCy_3 (5%)	$PhCH_3$	52	89	3.0 : 1
2[a]	$Ni(cod)_2$ (10%)	PCy_3 (10%)	$PhCH_3$	9.5	89	3.2 : 1
3[a]	$Ni(cod)_2$ (5%)	P*t*-Bu_3 (5%)	$PhCH_3$	6.5	57	8.3 : 1
4[a]	$Ni(cod)_2$ (10%)	P*t*-Bu_3 (10%)	$PhCH_3$	9.5	60	9.0 : 1
5[a]	$Ni(cod)_2$ (5%)	Cy-Johnphos (5%)	$PhCH_3$	6.5	50	3.1 : 1
6[a]	$Ni(cod)_2$ (5%)	$P(NMe_2)_3$ (5%)	$PhCH_3$	6.5	14	2.8 : 1
7[a]	$Pd(PPh_3)_4$ (5%)	—	PhH	41	0	n.d.
8[a]	$Pd(Pt\text{-}Bu_3)_2$ (5%)	—	PhH	41	< 5	n.d.
9[b]	Fe complex *SI-4* (8%)	Mg powder (16%)	Et_2O	42	0	n.d.
10[b]	Fe complex *SI-4* (4%)	aryllithium *SI-5* (8%)	Et_2O	10	62	1.1 : 1

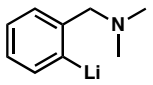
[a] *Conditions*: 1,3-Diene (1.0 equiv), pinacolborane (1.05 equiv), metal complex (x mol %), ligand (x mol %) in solvent (0.1 M) at 23 °C in a N_2-filled glove box. [b] *Conditions*: 1,3-Diene (1.0 equiv), pinacolborane (1.50 equiv), metal complex (x mol %), additive (2x mol %) in solvent (0.15 M) at indicated 23 °C in a N_2-filled glove box. [c] Combined isolated yield of ***19a*** and ***19b***. [d] Ratio of linear : branched allylic alcohols ***19a*** and ***19b***, determined by relative integration by ^1H NMR.



Cy-Johnphos



Fe complex SI-4



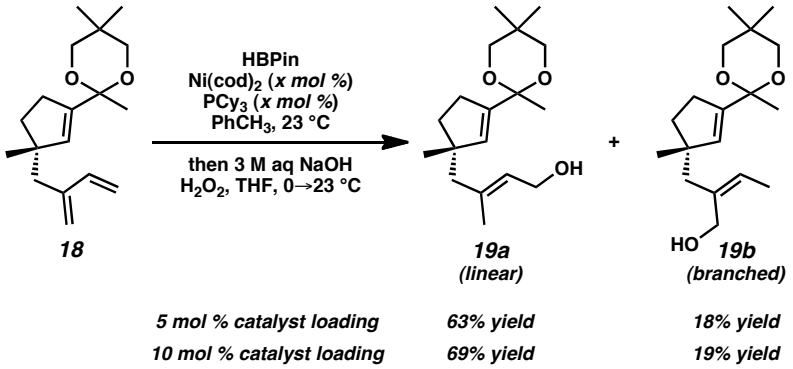
SI-5

Ni- and Pd-catalyzed 1,4-Hydroboration Screening Procedure ***(0.1 mmol scale, Table SI-1, entries 1–8).*** To a 2 dram vial with magnetic stir bar were added metal source (20–100 mM solution of Ni[13] or Pd[12] source in solvent, x mol %) and ligand (20–100 mM solution of ligand in solvent, x mol %) in a N_2-filled glove box. Additional solvent was added to bring the reaction concentration to 0.10 M relative to substrate. The reaction was stirred for 5 min at 23 °C. Pinacolborane (13.8 μL, 0.0950 mmol, 1.05 equiv) was added and the reaction was stirred for an additional 5 min. Diene substrate **18** (25.0 mg, 0.0904 mmol, 1.00 equiv) was added and the reaction was capped with a teflon-lined hard cap. Reaction progress was monitored by TLC. Once the reaction was complete, the reaction was diluted with an equal volume of THF relative to reaction solvent. The vial was capped, removed from the glove box, and cooled to 0 °C using an ice/water bath. The reaction was quenched by dropwise addition of 3 M aqueous NaOH (0.54 mL) and 30% wt. aqueous H_2O_2 (0.43 mL), stirred at 0 °C for 5 min, and then warmed to 23 °C. Once the oxidation was complete, the reaction was cooled to 0 °C, treated with sat. aqueous

$Na_2S_2O_3$ (0.54 mL), stirred for 5 min at 0 °C, and then warmed to 23 °C. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 2 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 2 x 25 cm, 6:1→4:1→2:1 hexanes:EtOAc) to afford branched allylic alcohol **19b** and linear allylic alcohol **19a**. The ratio of products was analyzed by ^{1}H NMR (300 or 500 MHz, C_6D_6) by comparing the relative integrations of the peaks corresponding to linear isomer **19a** (δ 5.39 (t, *J* = 6.6 Hz, 1H)) and branched isomer **19b** (δ 5.29 (q, *J* = 6.9 Hz, 1H)). Alternatively, the ratio of *allylborane intermediates* can be analyzed by ^{1}H NMR (300 or 500 MHz, C_6D_6) by comparing the relative integrations of the peaks corresponding to the linear allylborane isomer (δ 5.53 (br t, *J* = 7.4 Hz, 1H)) and the branched allylborane isomer (δ 5.32 (br q, *J* = 6.4 Hz, 1H)).

Fe-catalyzed 1,4-Hydroboration Screening Procedure *(0.1 mmol scale, Table SI-1, entries 9–10).* To a 2 dram vial with magnetic stir bar were added diene substrate **18** (25.0 mg, 0.0904 mmol, 1.00 equiv) and $FeCl_2$(py-imine) complex **SI-4**[9] (x mol %). Et_2O (0.6 mL) was added, followed by additive (2x mol %) in a N_2-filled glove box. Finely divided Mg powder[9a] was added as a solid and aryllithium **SI-5**[9b] was added as a solution in THF (1.0 M). The reaction was stirred for 5 min at 23 °C. Pinacolborane (19.7 μL, 0.136 mmol, 1.50 equiv) was added and the reaction was capped with a teflon-lined hard cap. Reaction progress was monitored by TLC. Once the reaction was complete, the reaction was diluted with an equal volume of THF relative to reaction solvent. The vial was capped, removed from the glove box, and cooled to 0 °C using an ice/water bath. The reaction was quenched by dropwise addition of 3 M aqueous NaOH (0.54 mL) and 30% wt. aqueous H_2O_2 (0.43 mL), stirred at 0 °C for 5 min, and then warmed to 23 °C. Once the oxidation was complete, the reaction was cooled to 0 °C, treated with sat. aqueous $Na_2S_2O_3$ (0.54 mL), stirred for 5 min at 0 °C, and then warmed to 23 °C. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 2 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 2 x 25 cm, 6:1→4:1→2:1 hexanes:EtOAc) to afford branched allylic alcohol **19b** and linear allylic alcohol **19a**. The ratio of products was analyzed by ^{1}H NMR (300 or 500 MHz, C_6D_6) by comparing the relative integrations of the peaks corresponding to linear isomer **19a** (δ 5.39 (t, *J* = 6.6 Hz, 1H)) and branched isomer **19b** (δ 5.29 (q, *J* = 6.9 Hz, 1H)). Alternatively, the ratio of *allylborane intermediates* can be analyzed by ^{1}H NMR (300 or 500 MHz, C_6D_6) by comparing the relative integrations of the peaks corresponding to the linear allylborane isomer (δ 5.53 (br t, *J* = 7.4 Hz, 1H)) and the branched allylborane isomer (δ 5.32 (br q, *J* = 6.4 Hz, 1H)).

(Note: Control reactions were performed with isoprene as substrate. With a $Ni(cod)_2/PCy_3$ catalyst system, a 1.26:1 linear:branched ratio was observed. With a $FeCl_2$·**SI-4**·CH_2Cl_2 catalyst system, the reported 10:1 linear:branched ratio was observed. The C(4) quaternary stereocenter is likely responsible for the differences in regioselectivity in our case.)



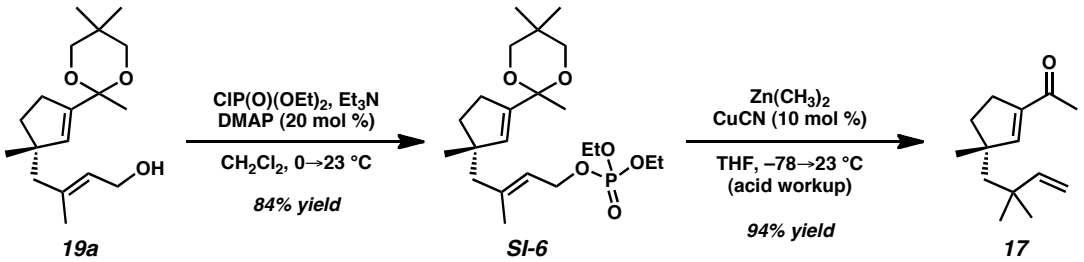
Linear Allylic Alcohol 19a and Branched Allylic Alcohol 19b *(5 mol % catalyst loading).*[13] To a 250 mL round-bottom flask with magnetic stir bar were added $Ni(cod)_2$ (113.9 mg, 0.414 mmol, 5 mol %), PCy_3 (116.1 mg, 0.414 mmol, 5 mol %), and toluene (25 mL) in a N_2-filled glove box. The pale orange solution was stirred for 5 min. Pinacolborane (1.26 mL, 8.69 mmol, 1.05 equiv) was added dropwise, causing the reaction to become a dark orange solution. Diene **18** (2.29 g, 8.28 mmol, 1.00 equiv) in toluene (8 mL) was added, causing further darkening of the reaction to a red-orange solution. The reaction was sealed with a rubber septum and stirred at 23 °C in the glove box. After 96 h of stirring, the reaction reverted to an orange color. The reaction was diluted with toluene (33 mL) and THF (33 mL), sealed with a rubber septum, removed from the glove box, and connected to a N_2 inlet. The reaction was cooled to 0 °C using an ice/water bath and 3 M aqueous NaOH (52.2 mL) was added dropwise over 5 min. Chilled, ice cold 30% wt. aqueous H_2O_2 (39.4 mL) was added dropwise over 20 min, giving a yellow biphasic mixture. The reaction was stirred at 0 °C until the oxidation was complete by TLC (5 min). At 0 °C, sat. aqueous $Na_2S_2O_3$ (52.2 mL) was added dropwise over 20 min, causing the biphasic mixture to become colorless. The reaction was stirred at 0 °C for 15 min, warmed to 23 °C, and stirred for 15 min. The phases were separated and the organic phase was washed with H_2O (2 x 20 mL) and brine (2 x 20 mL). The combined aqueous phases were extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 8 x 35 cm, 10:1→8:1→6:1→4:1→2:1 hexanes:EtOAc) to afford branched allylic alcohol **19b** (427.2 mg, 1.45 mmol, 18% yield) as a yellow oil and linear allylic alcohol **19a** (1.535 g, 5.212 mmol, 63% yield) as a yellow oil.

Linear Allylic Alcohol 19a and Branched Allylic Alcohol 19b *(10 mol % catalyst loading).*[13] To a 1 L round-bottom flask with magnetic stir bar were added $Ni(cod)_2$ (660 mg, 2.40 mmol, 10 mol %), PCy_3 (674 mg, 2.40 mmol, 10 mol %), and toluene (65 mL) in a N_2-filled glove box. The pale orange solution was stirred for 5 min. Pinacolborane (3.66 mL, 25.2 mmol, 1.05 equiv) was added dropwise, causing the reaction to become a dark orange solution. Diene **18** (6.64 g, 24.0 mmol, 1.00 equiv) in toluene (30 mL) was added, causing further darkening of the reaction to a red-orange solution. The reaction was sealed with a rubber septum and stirred at 23 °C in the glove box. After 48 h of stirring, the reaction reverted to an orange color. The reaction was diluted with toluene (95 mL) and THF (95 mL), sealed with a rubber septum, removed from the glove box, and connected to a N_2 inlet. The reaction was cooled to 0 °C using an ice/water bath and 3 M aqueous NaOH (153 mL) was added dropwise over 5 min. Chilled, ice cold 30% wt. aqueous H_2O_2 (114 mL) was added dropwise over 45 min, giving a yellow biphasic mixture. The reaction was stirred at 0 °C until the oxidation was complete by TLC (5 min). At 0 °C, sat. aqueous $Na_2S_2O_3$ (153 mL) was added dropwise over 1 h, causing the biphasic mixture to

become colorless. The reaction was stirred at 0 °C for 15 min, warmed to 23 °C, and stirred for 15 min. The phases were separated and the organic phase was washed with H_2O (2 x 50 mL) and brine (2 x 50 mL). The combined aqueous phases were extracted with EtOAc (3 x 60 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 8 x 35 cm, 10:1→8:1→6:1→4:1→2:1 hexanes:EtOAc) to afford branched allylic alcohol **19b** (1.358 g, 4.6133 mmol, 19% yield) as a yellow oil and linear allylic alcohol **19a** (4.876 g, 16.562 mmol, 69% yield) as a yellow oil.

Linear Allylic Alcohol 19a: R_f = 0.15 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.63 (app. t, *J* = 1.9 Hz, 1H), 5.39 (br t, *J* = 6.6 Hz, 1H), 4.00 (d, *J* = 6.6 Hz, 2H), 3.51 (d, *J* = 11.0 Hz, 1H), 3.49 (d, *J* = 11.0 Hz, 1H), 3.30 (dd, *J* = 6.9, 2.4 Hz, 1H), 3.28 (dd, *J* = 6.9, 2.4 Hz, 1H), 2.42–2.31 (m, 2H), 2.05 (s, 2H), 1.87 (ddd, *J* = 12.6, 8.1, 6.8 Hz, 1H), 1.63–1.51 (m, 1H), 1.59 (s, 3H), 1.55 (br s, 3H), 1.16 (s, 3H), 1.01 (s, 3H), 0.50 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.9, 138.7, 136.3, 128.7, 98.9, 71.7, 59.4, 51.2, 49.4, 37.4, 31.5, 29.7, 27.5, 22.9, 22.2, 18.6; IR (Neat Film NaCl) 3413, 3039, 2951, 2866, 2737, 2962, 1726, 1663, 1471, 1454, 1395, 1369, 1352, 1319, 1297, 1254, 1240, 1179, 1116, 1082, 1040, 1013, 950, 929, 911, 861, 808, 7793, 755 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{29}O_3$ $[M]^{+\bullet}$: 277.2162; found 277.2155; $[\alpha]_D^{25.0}$ –0.82 (*c* 0.84, $CHCl_3$, 94.9% ee).

Branched Allylic Alcohol 19b: R_f = 0.21 (4:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.71 (app. t, *J* = 1.9 Hz, 1H), 5.29 (br q, *J* = 6.9 Hz, 1H), 4.05 (s, 2H), 3.52 (d, *J* = 10.9 Hz, 1H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.35–3.25 (m, 2H), 2.44–2.33 (m, 2H), 2.29 (d, *J* = 13.4 Hz, 1H), 2.18 (d, *J* = 13.3 Hz, 1H), 1.95 (ddd, *J* = 12.6, 7.7, 7.7 Hz, 1H), 1.64–1.56 (m, 1H), 1.58 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H), 1.13 (s, 3H), 1.05 (s, 3H), 0.53 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.1, 138.6, 138.6, 125.7, 99.0, 71.7, 60.7, 49.6, 46.5, 37.0, 31.5, 29.8, 27.6, 27.2, 22.9, 22.2, 13.4; IR (Neat Film NaCl) 3435, 3036, 2950, 2866, 2739, 2693, 1877, 1723, 1649, 1471, 1455, 1395, 1369, 1353, 1297, 1282, 1255, 1240, 1178, 1139, 1116, 1082, 1039, 1013, 950, 929, 911, 860, 808, 793, 739 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{29}O_3$ $[M]^{+\bullet}$: 277.2162; found 277.2155; $[\alpha]_D^{25.0}$ –6.27 (*c* 1.08, $CHCl_3$, 94.9% ee).



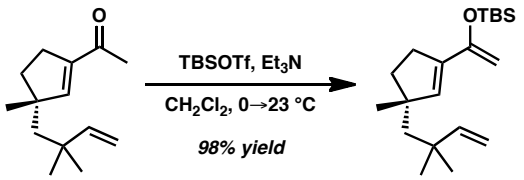
Allylic Phosphate SI-6.[14] To a 300 mL round-bottom flask with a magnetic stir bar containing linear allylic alcohol **19a** (1.522 g, 5.17 mmol, 1.00 equiv) in CH_2Cl_2 (103 mL) under N_2 at 0 °C (ice/water bath) were added Et_3N (1.08 mL, 7.76 mmol, 1.5 equiv) and DMAP (126.3 mg, 1.03 mmol, 0.2 equiv). The pale tan solution was stirred for 5 min. Diethylchlorophosphate (1.12 mL, 7.76 mmol, 1.50 equiv) was added dropwise and the reaction was stirred for 5 min. The cooling bath was removed and the reaction was allowed to warm to 23 °C. After 3 h of stirring, the reaction was quenched with sat. aqueous NH_4Cl (50 mL). The reaction was stirred for 5 min and the phases were separated. The organic phase was washed with brine (20 mL). The combined

aqueous phases were extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 5 x 25 cm, 30%→40%→50% EtOAc in hexanes) to afford allyl phosphate **SI-6** (1.86 g mg, 4.32 mmol, 84% yield) as a pale tan oil; R_f = 0.20 (2:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (app. t, *J* = 1.9 Hz, 1H), 5.40 (br t, *J* = 7.0 Hz, 1H), 4.56 (dd, *J* = 7.5, 7.5 Hz, 2H), 4.10 (dq, *J* = 7.9, 7.1 Hz, 4H), 3.52 (dd, *J* = 11.1, 3.5 Hz, 2H), 3.33 (ddd, *J* = 11.1, 3.9, 2.5 Hz, 2H), 2.38–2.21 (m, 2H), 2.17 (s, 2H), 1.90 (ddd, *J* = 12.7, 8.6, 6.5 Hz, 1H), 1.73 (br s, 3H), 1.64 (ddd, *J* = 12.6, 8.4, 5.4 Hz, 1H), 1.40 (s, 3H), 1.33 (td, *J* = 7.1, 1.0 Hz, 6H), 1.16 (s, 3H), 1.05 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 140.7, 138.7, 122.8 ($J_{C–P}$ = 5.7 Hz), 98.7, 71.8 ($J_{C–P}$ = 5.3 Hz), 64.1 ($J_{C–P}$ = 5.7 Hz), 63.7 ($J_{C–P}$ = 5.8 Hz), 51.0, 49.2, 37.2, 31.1, 29.8, 27.4, 27.2, 22.8, 22.3, 18.8, 16.3 ($J_{C–P}$ = 6.8 Hz); IR (Neat Film NaCl) 2980, 2951, 2867, 1660, 1473, 1457, 1395, 1369, 1277, 1262, 1180, 1116, 1100, 1082, 1035, 1000, 911, 862, 807, 746 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{39}O_6PNa$ $[M+Na]^+$: 453.2376; found 453.2385; $[\alpha]_D^{25.0}$ –3.77 (*c* 0.85, $CHCl_3$, 94.9% ee).

(Note: A small amount of ketal deprotection of the phosphorylated product may be observed during work-up. The resulting acylcyclopentene can also be converted to *gem*-dimethyl acylcyclopentene **17** smoothly and chemoselectively using the Cu-catalyzed allylic substitution reaction conditions below.)

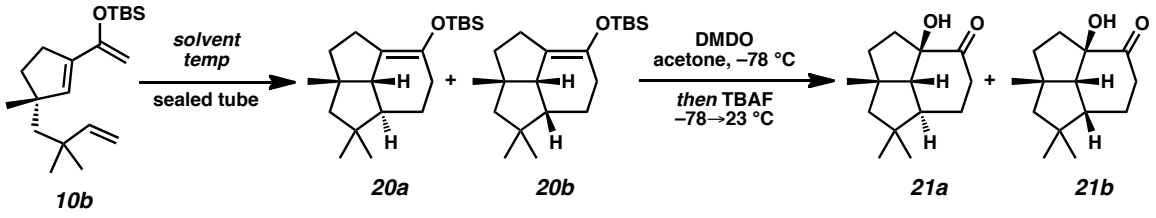
Acylcyclopentene 17.[15] To a 250 mL Schlenk flask with Kontes teflon valve and 14/20 joint with rubber septum were added a magnetic stir bar and CuCN (101 mg, 1.129 mmol, 10 mol %) in a N_2-filled glove box. The flask was sealed and removed from the glove box. A solution of allyl phosphate **SI-6** (4.86 g, 11.29 mmol, 1.00 equiv) in THF (120 mL) in a 100 mL conical flask was transferred to the Schlenk flask by positive pressure cannulation. Additional THF (30 mL) was added to the Schlenk flask. The reaction was a pale tan solution with insoluble pale green solids. The reaction was cooled to –78 °C using an acetone/CO_2(s) bath and stirred for 15 min. $Zn(CH_3)_2$ (1.0 M in heptanes, 33.9 mL, 33.9 mmol, 3.00 equiv) was added dropwise by syringe over 15 min. The reaction became a darker tan-grey solution with insoluble pale green solids. The flask was sealed and cooling bath was allowed to slowly expire and reach 23 °C over 16 h. After an additional 48 h of stirring, the reaction was a black suspension. The reaction was cooled to –78 °C and stirred for 10 min. The reaction was diluted with Et_2O (100 mL) and stirred for 15 min. The reaction was quenched by slow dropwise addition of 10% aqueous HCl (47 mL). The –78 °C acetone/CO_2(s) cooling bath was exchanged for a 0 °C ice/water bath and the reaction was stirred for 30 min. The ice/water cooling bath was removed and the reaction was allowed to warm to 23 °C. After 2 h of stirring, the majority of the metal salts were dissolved and TLC analysis indicated that the intermediate ketal had been converted to the corresponding acylcyclopentene. The phases were separated and the organic phase was washed with H_2O (30 mL) and sat. aqueous $NaHCO_3$ (30 mL). The combined aqueous phases were extracted with Et_2O (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The residue was purified by flash column chromatography (SiO_2, 5 x 25 cm, 15:1 hexanes:Et_2O) to afford acylcyclopentene **17** (2.218 g, 10.750 mmol, 95% yield) as a fragrant pale tan oil; R_f = 0.41 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (app. t, *J* = 1.8 Hz, 1H), 5.92–5.81 (m, 1H), 4.93–4.87 (m, 2H), 2.51 (dd, *J* = 7.1, 1.8 Hz, 1H), 2.49 (dd, *J* = 7.1, 1.8 Hz, 1H), 2.27 (s, 3H), 1.94 (ddd, *J* = 12.9, 7.8, 7.8 Hz, 1H), 1.67 (d, *J* = 14.4 Hz, 1H), 1.67–1.59 (m, 1H), 1.59 (d, *J* = 14.4 Hz, 1H), 1.11 (s, 3H), 1.07 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 154.1, 149.7,

142.2, 110.0, 53.5, 50.7, 38.8, 38.0, 29.7, 29.1, 28.7, 27.9, 26.8; ^{1}H NMR (500 MHz, C_6D_6) δ 6.16 (app. t, *J* = 1.8 Hz, 1H), 5.74–5.65 (m, 1H), 4.86–4.79 (m 2H), 2.61 (dd, *J* = 7.7, 1.8 Hz, 1H), 2.60 (dd, *J* = 7.7, 1.8 Hz, 1H), 2.02 (s, 3H), 1.72 (ddd, *J* = 12.9, 7.7, 7.7 Hz, 1H), 1.45–1.36 (m, 1H), 1.39 (d, *J* = 14.4 Hz, 1H), 1.29 (d, *J* = 14.4 Hz, 1H), 0.92 (s, 3H), 0.91 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 195.0, 151.7, 149.3, 142.2, 109.5, 53.0, 50.2, 38.4, 37.5, 29.3, 29.3, 28.1, 27.3, 26.1; IR (Neat Film NaCl) 3080, 2956, 2926, 2872, 1730, 1711, 1668, 1636, 1617, 1455, 1431, 1413, 1377, 1366, 1302, 1269, 1232, 1215, 1190, 1120, 1010, 971, 934, 908, 861, 803 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{23}O$ $[M]^{+\bullet}$: 207.1743; found 207.1753; $[\alpha]_D^{25.0}$ –10.580 (*c* 1.12, $CHCl_3$, 94.9% ee).



Silyl Dienol Ether 10b. A 100 mL pear-shaped flask with a magnetic stir bar under N_2 was charged with acylcyclopentene **17** (400 mg, 1.93 mmol, 1.00 equiv) and CH_2Cl_2 (40 mL). The colorless solution was cooled to 0 °C using an ice/water bath. After 5 min of stirring, Et_3N (1.08 mL, 7.75 mmol, 4.00 equiv) was added dropwise. After 2 min of stirring, TBSOTf[8] (891 μL, 3.88 mmol, 2.00 equiv) was added dropwise. The formation of vapor was observed. The clear, colorless solution was stirred at 0 °C for 15 min. The reaction was quenched by addition of ice-cold sat. aqueous $NaHCO_3$ (12 mL) and stirred for 5 min at 0 °C. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic phases washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography with deactivated silica gel (SiO_2, 3 x 25 cm, deactivated with 1% Et_3N in hexanes, 1% Et_3N in hexanes→20% Et_2O in hexanes eluent) to afford silyl dienol ether **10b** (607.2 mg, 1.894 mmol, 98% yield) as a colorless oil. (Note: Silyl dienol ether **10b** appears to be sensitive to moisture. The compound was stored as a solidified benzene solution under N_2 in a –25 °C freezer.); R_f = 0.78 (10:1 hexanes:EtOAc, 1% Et_3N in hexanes deactivated silica TLC plates); ^{1}H NMR (500 MHz, C_6D_6) δ 6.17 (app. t, *J* = 1.8 Hz, 1H), 5.89 (dd, *J* = 17.5, 10.7 Hz, 1H), 4.94 (dd, *J* = 17.5, 1.4 Hz, 1H), 4.92 (dd, *J* = 10.7, 1.4 Hz, 1H), 4.41–4.35 (m, 1H), 4.40–4.34 (m, 1H), 2.50–2.35 (m, 2H), 1.88 (ddd, *J* = 12.7, 8.7, 7.0 Hz, 1H), 1.60 (ddd, *J* = 12.7, 8.3, 5.2 Hz, 1H), 1.56 (d, *J* = 14.3 Hz, 1H), 1.47 (d, *J* = 14.3 Hz, 1H), 1.08 (s, 3H), 1.05–1.02 (m, 12H), 1.03 (s, 3H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.8, 150.0, 139.2, 138.3, 109.7, 92.7, 54.3, 49.8, 40.1, 38.0, 31.1, 29.9, 28.7, 28.3, 26.1, 18.5, -4.4, -4.4; IR (Neat Film NaCl) 3119, 3081, 2956, 2929, 2896, 2858, 1818, 1636, 1586, 1472, 1463, 1412, 1389, 1373, 1361, 1330, 1309, 1283, 1256, 1201, 1129, 1090, 1060, 1016, 1005, 939, 907, 838, 812, 779 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{37}OSi$ $[M+H]^+$: 321.2614; found 321.2607; $[\alpha]_D^{25.0}$ –7.57 (*c* 0.95, CH_2Cl_2, 94.9% ee).

Table SI-2. Intramolecular Diels–Alder/Rubottom Oxidation Screening



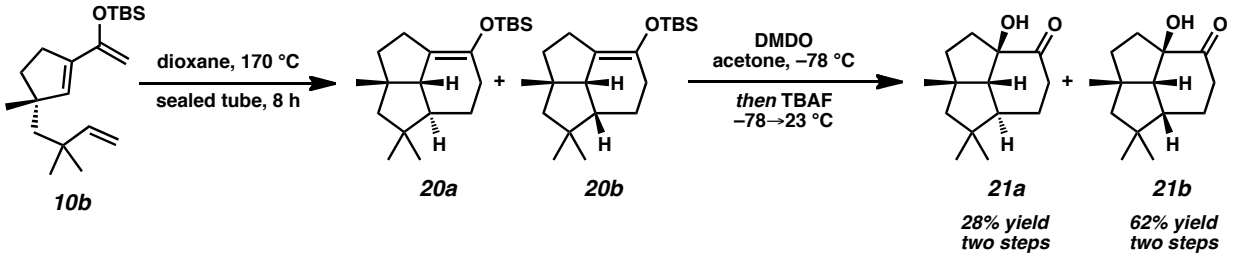
entry[a]	temp (°C)	heating mechanism	solvent	time (h)	overall yield (%)[b]	*21a* : *21b*[c]
1	110	oil bath	$PhCH_3$	96	78	1 : 8.25
2	130	oil bath	$PhCH_3$	24	83	1 : 3.58
3	150	oil bath	$PhCH_3$	6	79	1 : 3.26
4	160	oil bath	$PhCH_3$	2	58	1 : 2.68
5	170	sand bath	$PhCH_3$	3	92	1 : 2.55
6	190	metal block	$PhCH_3$	1	90	1 : 2.64
7	200	oil bath	dioxane	1	95	1 : 2.02
8	200	oil bath	$CyCH_3$	1	93	1 : 2.31
9	200	microwave irradiation	PhCl	1	95	1 : 3.26
10	170	metal block	dioxane	2	91	1 : 2.03
11	170	metal block	$CyCH_3$	2	93	1 : 2.07
12	170	metal block	PhCl	3	94	1 : 2.73
13	170	metal block	CH_3CN	2	91	1 : 2.27
14	170	metal block	DCE	2	83	0 : 1.00

[a] *Conditions*: silyl dienol ether ***10b*** (1.0 equiv), solvent (0.01 M) in a sealed tube at the indicated temperature for the indicated time. [b] Combined isolated yield over two steps for ***21a*** and ***21b***. [c] Ratio of *trans* : *cis* α-hydroxyketones ***21a*** and ***21b***, determined by relative integration by ^{1}H NMR.

Intramolecular Diels–Alder/Rubottom Oxidation Screening Procedure *(0.05 mmol scale, Table SI-2, entries 1–14).* To a 5 mL microwave vial was added a solution of silyl dienol ether **10b** in benzene (100 mg/mL, 20.0 mg, 0.0623 mmol, 1.00 equiv). The solvent was removed under reduced pressure. The vial, a magnetic stir bar, crimp cap, and crimper were placed in a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the items were transferred into the glove box. Solvent (6 mL) was added by syringe and the vial was sealed with a crimp cap. The vial was removed from the glove box and heated according to the indicated conditions for the indicated time interval. A blast shield was set up as a precaution. The vial was uncapped and the reaction was concentrated under reduced pressure. The crude reaction mixture was analyzed by ^{1}H NMR to confirm the complete consumption of starting material before use in the next step.

The crude mixture of silyl enol ethers **20a** and **20b** was dissolved in acetone (3 mL) in a 20 mL scintillation vial with magnetic stir bar and sealed with a screw cap. The vials were cooled to –78 °C and stirred for 5 min. A solution of DMDO in acetone[10] (0.103 M, 607 μL, 0.0624 mmol, 1.00 equiv) was added dropwise over 5 min. The reaction was stirred for 5 min, allowed to warm to 23 °C, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 3 x 12 cm, 10% EtOAc in hexanes) to afford mixture of α-hydroxyketones **21a** and **21b** as a pale yellow solid. The ratio of products was analyzed by ^{1}H NMR (300 or 500 MHz, C_6D_6) by comparing the relative integrations of the peaks corresponding to *trans* isomer **21a** (δ 0.64 (s, 3H)) and *cis* isomer **21b** δ 0.68 (s, 3H)).

(Note: Incomplete silyl transfer to the tertiary alcohol was observed during the Rubottom oxidation, so TBAF was added to simplify the reaction mixture. Attempts to reinstall the silyl group with α-hydroxyketone **21a** led to a mixture of bis-, mono-, and unsilylated products. Lower overall yields were observed with *m*-CPBA as the oxidant.)



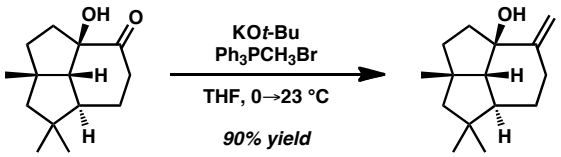
α-Hydroxyketones 21a and 21b. To a 20 mL microwave vial was added a solution of silyl dienol ether **10b** in benzene (100 mg/mL, 98.1 mg, 0.306 mmol, 1.00 equiv). The solvent was removed under reduced pressure. The vial, a magnetic stir bar, crimp cap, and crimper were placed in a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the items were transferred into the glove box. Dioxane (12.5 mL) was added by syringe and the vial was sealed with a crimp cap. The vial was removed from the glove box and immersed in a preheated 170 °C heating mantle-supported sand bath regulated by a J-KEM Scientific Model 210 Temperature Controller. A blast shield was set up as a precaution. The reaction was stirred for 8 h at 170 °C. The reaction was allowed to cool to 23 °C and the vial was uncapped. The reaction was diluted with hexanes (24 mL) and concentrated under reduced pressure to give a mixture of silyl enol ethers **20a** and **20b**.

To a 50 mL round-bottom flask with magnetic stir bar was added the mixture of silyl enol ethers **20a** and **20b.** The flask was evacuated and backfilled with N_2 (3 cycles, 5 min evacuation per cycle). Acetone (12.5 mL) was added and the reaction was cooled to –78 °C. After 15 min of stirring, a solution of DMDO in acetone[10] (0.0734 M, 5.0 mL, 0.367 mmol, 1.20 equiv) was added dropwise over 10 min. After an additional 5 min of stirring, TBAF (1.0 M in THF, 367 μL, 0.367 mmol, 1.20 equiv). The reaction was stirred at –78 °C for 5 min, the cooling bath was removed, and the reaction was allowed to warm to 23 °C. After 15 min of stirring at 23 °C, the reaction was concentrated under reduced pressure to give a pale orange residue, which was purified by flash column chromatography (SiO_2, 5 x 30 cm, 2.5%→5%→10% EtOAc in hexanes) to afford α-hydroxyketones **21a** (19.2 mg, 0.0864 mmol, 28% yield over two steps) and **21b** (42.3 mg, 0.190 mmol, 62% yield over two steps) as a faint yellow solids. X-ray quality crystals of alcohol **21b** (colorless to pale yellow) were grown by slow evaporation from benzene.

α-Hydroxyketone 21a (*trans*-isomer): R_f = 0.18 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (br s, 1H), 2.62 (ddd, *J* = 16.2, 4.4, 1.8 Hz, 1H), 2.47 (ddd, *J* = 16.2, 12.4, 6.8 Hz, 1H), 2.43–2.35 (m, 1H), 2.03–1.97 (m, 2H), 1.86 (dddd, *J* = 12.0, 6.9, 1.9, 1.9 Hz, 1H), 1.86–1.74 (m, 2H), 1.77 (d, *J* = 13.4 Hz, 1H), 1.66 (d, *J* = 13.4 Hz, 1H), 1.57 (ddd, *J* = 12.6, 12.6, 2.3 Hz, 1H), 1.48 (dddd, *J* = 12.3, 12.3, 12.3, 4.4 Hz, 1H), 1.28 (s, 3H), 1.05 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.2, 87.9, 67.6, 59.8, 54.2, 47.5, 42.0, 40.2, 39.1, 38.8, 31.0, 28.8, 24.0, 22.3; ^{1}H NMR (500 MHz, C_6D_6) δ 3.90 (br s, 1H), 2.33 (ddd, *J* = 15.9, 4.4, 1.8 Hz, 1H), 2.04–1.86 (m, 3H), 1.85 (br d, *J* = 11.6 Hz, 1H), 1.68–1.53 (m, 2H), 1.56 (d, *J* = 13.2 Hz, 1H), 1.50 (d, *J* = 13.2 Hz, 1H), 1.38 (s, 3H), 1.25 (dddd, *J* = 12.1, 6.7, 2.5, 1.8 Hz, 1H), 1.15 (ddd, *J* = 12.6, 12.6, 2.5 Hz, 1H), 0.92 (dddd, *J* = 12.5, 12.5, 12.5, 4.4 Hz, 1H), 0.84 (s, 3H), 0.64

(s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 213.8, 87.7, 67.7, 59.9, 53.9, 47.5, 42.2, 40.0, 39.1, 38.5, 31.1, 28.6, 23.8, 22.2; IR (Neat Film NaCl) 3496, 2947, 2930, 2866, 1701, 1457, 1420, 1371, 1364, 1349, 1319, 1303, 1267, 1243, 1221, 1211, 1196, 1179, 1148, 1114, 1074, 1056, 1040, 1012, 986, 974, 950, 932, 909, 878, 837, 816, 751 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{22}O_2$ $[M]^{+\bullet}$: 222.1620; found 222.1625; $[\alpha]_D^{25.0}$ +2.96 (*c* 0.67, $CHCl_3$, 94.9% ee).

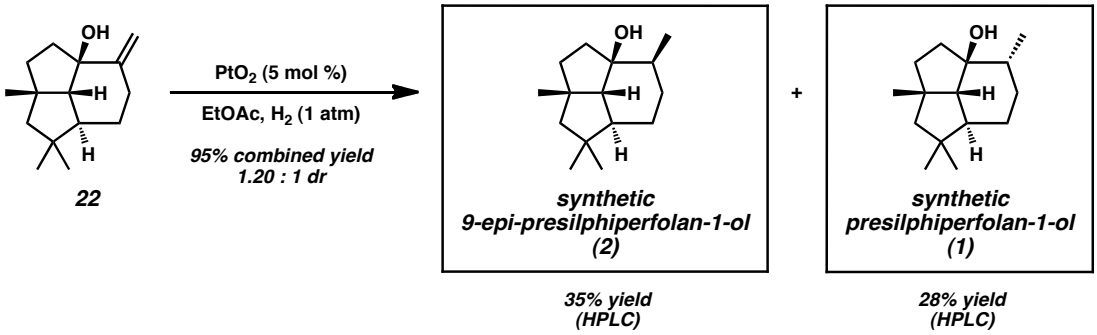
α-Hydroxyketone 21b (*cis*-isomer): R_f = 0.14 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (br s, 1H), 2.60 (ddd, *J* = 19.8, 5.0, 2.2 Hz, 1H), 2.45 (dd, *J* = 8.7, 2.0 Hz, 1H), 2.28 (ddd, *J* = 19.7, 11.6, 7.6 Hz, 1H), 2.05 (ddd, *J* = 13.3, 12.2, 8.5 Hz, 1H), 1.88 (ddd, *J* = 12.4, 12.4, 7.5 Hz, 1H), 1.86–1.71 (m, 4H), 1.69 (d, *J* = 13.1 Hz, 1H), 1.61 (dddd, *J* = 12.9, 7.1, 1.3, 1.3 Hz, 1H), 1.52 (d, *J* = 13.2 Hz, 1H), 1.39 (s, 3H), 1.10 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.2, 86.1, 63.9, 54.0, 52.4, 48.6, 43.9, 42.0, 40.3, 35.0, 32.1, 30.6, 25.3, 22.6; ^{1}H NMR (500 MHz, C_6D_6) δ 4.04 (br s, 1H), 2.34 (dd, *J* = 8.8, 1.4 Hz, 1H), 2.16–2.08 (m, 1H), 1.95 (ddd, *J* = 12.0, 12.0, 1.4 Hz, 1H), 1.95–1.82 (m, 1H), 1.68–1.58 (m, 1H), 1.55 (dd, *J* = 12.0, 8.3 Hz, 1H), 1.50–1.43 (m, 1H), 1.40 (s, 3H), 1.35 (d, *J* = 13.1 Hz, 1H), 1.33–1.22 (m, 1H), 1.26 (d, *J* = 13.1 Hz, 1H), 1.17–1.05 (m, 2H), 0.88 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 213.7, 85.8, 64.0, 53.9, 52.2, 48.3, 43.6, 42.1, 40.3, 34.8, 32.1, 30.5, 25.2, 22.6; IR (Neat Film NaCl) 3415, 2970, 2948, 2866, 2759, 2717, 2658, 1708, 1485, 1467, 1456, 1443, 1399, 1384, 1368, 1363, 1331,1304, 1254, 1242, 1223, 1211, 1180, 1167, 1153, 1137, 1114, 1071, 1054, 1017, 997, 985, 961, 949, 937, 920, 903, 874, 861, 841, 799, 788, 735 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{14}H_{23}O_2$ $[M+H]^+$: 224.1698; found 224.1693; $[\alpha]_D^{25.0}$ –53.99 (*c* 0.98, $CHCl_3$, 94.9% ee); mp = 51–52 °C (benzene).



21a ***22***

Allylic Alcohol 22.[16] To a 20 mL scintillation vial with magnetic stir bar was added Ph_3PCH_3Br (138.8 mg, 0.3885 mmol, 2.6 equiv) in a N_2-filled glove box. KO*t*-Bu (1.0 M in THF, 358.7 μL, 0.3587 mmol, 2.4 equiv) was added and the bright yellow suspension was diluted with THF (2 mL). The mixture was stirred for 30 min. α-Hydroxyketone **21a** (33.2 mg, 0.149 mmol, 1.00 equiv) was dissolved in THF (6 mL) and added to the reaction. The reaction was capped with a teflon-lined hard cap and stirred in the glove box. After 8.5 h, the reaction was removed from the glove box and quenched with sat. aqueous NH_4Cl (1 mL) and H_2O (1 mL). The phases were separated and the aqueous phase was extracted with Et_2O (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The residue was purified by flash column chromatography (SiO_2, 3 x 25 cm, 1%→3%→5% EtOAc in hexanes) to afford faintly fragrant allylic alcohol **22** (29.8 mg, 0.135 mmol, 90% yield) as a colorless crystalline solid; R_f = 0.34 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.29–5.25 (m, 1H), 4.93–4.90 (m, 1H), 2.42 (dddd, *J* = 14.5, 4.8, 3.0, 0.8 Hz, 1H), 2.11–1.97 (m, 3H), 1.83–1.75 (m, 1H), 1.65–1.57 (m, 1H), 1.53 (d, *J* = 13.2 Hz, 1H), 1.51 (d, *J* = 13.1 Hz, 1H), 1.41 (dddd, *J* = 11.3, 5.8, 2.7, 2.7 Hz, 1H), 1.34 (s, 3H), 1.31 (br d, *J* = 12.2 Hz, 1H), 1.04 (ddd, *J* = 12.2, 12.2, 2.5 Hz, 1H), 1.02–0.93 (m, 1H), 0.92 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.6, 109.7, 85.0, 67.6, 60.3, 55.5, 46.5, 42.8, 40.1, 38.1, 34.8, 32.3, 28.5, 25.2, 22.2; IR (Neat Film NaCl) 3351, 2950, 2944, 2923, 2856, 1816, 1730,

1636, 1457, 1452, 1377, 1370, 1363, 1344, 1316, 1303, 1276, 1248, 1222, 1196, 1183, 1151, 1137, 1127, 1114, 1077, 1044, 1007, 987, 979, 962, 942, 931, 908, 862, 836, 815, 756, 722 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{25}O$ $[M+H]^+$: 221.1905; found 221.1898; $[\alpha]_D^{25.0}$ +2.96 (*c* 0.67, $CHCl_3$, 94.9% ee).

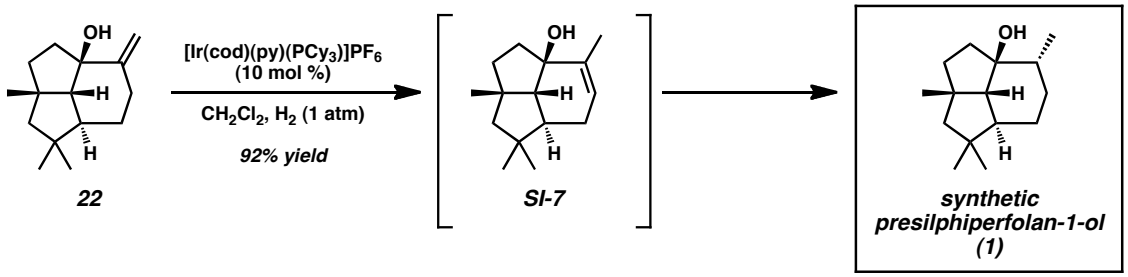


Synthetic (–)-9-*epi*-Presilphiperfolan-1-ol[17] **(2) and Synthetic (–)-Presilphiperfolan-1-ol**[18] **(1).** To a 20 mL scintillation vial with magnetic stir bar were added allylic alcohol **22** (6.8 mg, 0.031 mmol, 1.0 equiv), EtOAc (1.2 mL), and Adam's catalyst (PtO_2-hydrate, 0.35 mg, 0.0015 mmol, 5 mol %). A brown suspension was obtained. The reaction was capped with a septum-fitted screw cap and the solution was sparged with H_2 (1 atm, balloon) through a long metal needle until a fine black suspension was formed. After 45 min, the needle connected to the H_2 balloon was raised above the surface of the reaction and the venting needle was removed. After 1 h of stirring, the H_2 balloon was removed and Celite (5 mg) was added. The reaction was stirred briefly, filtered through a Celite pipet plug (0.5 x 1 cm), and eluted with EtOAc. The clear filtrate was concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The residue was purified by flash column chromatography (SiO_2, 3 x 12 cm, 15:1 hexanes:Et_2O) to afford a mixture of faintly fragrant alcohols **2** and **1** (6.5 mg, 0.029 mmol, 95% combined yield, 1.20:1 d.r. (**2**:**1**)) as a white amorphous solid. Alcohols **2** and **1** can be separated by normal phase preparatory HPLC (SiO_2, 10%→25% Et_2O in pentane, 5.0 mL/min, ZORBAX RX-SIL column, 5 μm, 9.4 x 250 mm, manual collection every 0.2 min). The purity of fractions was analyzed by UHPLC-MS (C18, 33.5–36.0% CH_3CN in H_2O, 1.2 mL/min, Agilent Eclipse Plus C18, 1.8 μm, 2.1 x 50 mm, t_R (min): **2** = 7.22 (*m/z* = 205.2), **1** = 7.78 (*m/z* = 205.2). X-ray quality crystals of alcohol **1** (colorless to pale yellow) were grown by slow evaporation from hexanes.

The NMR spectra (C_6D_6) for synthetic compound **2** match spectral data for reported natural **2**,[17] but the NMR spectra (C_6D_6) for synthetic compound **1** do not match spectral data for reported natural **1**.[18] The NMR spectra (CD_2Cl_2) for synthetic compound **1** match spectral data for reported synthetic **1**.[19]

Synthetic (–)-9-*epi*-Presilphiperfolan-1-ol (2): R_f = 0.32 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 1.89–1.78 (m, 2H), 1.73–1.64 (m, 1H), 1.63–1.55 (m, 2H), 1.55 (br d, *J* = 12.3 Hz, 1H), 1.50 (s, 2H), 1.48–1.38 (m, 1H), 1.36–1.25 (m, 2H), 1.33 (s, 3H), 1.19–1.05 (m, 2H), 0.94 (s, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.80 (s, 3H), 0.58 (br s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 84.5, 63.9, 59.4, 51.7, 46.2, 42.7, 40.5, 39.7, 36.9, 31.4, 29.9, 28.8, 22.3, 20.3, 15.8; IR (Neat Film NaCl) 3468, 2952, 2923, 2853, 1725, 1463, 1456, 1377, 1300, 1259, 1188, 1156, 1095, 1077, 104, 1008, 970, 945, 801, 720 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{26}O$ $[M]^{+\bullet}$: 222.1984; found 222.1978; $[\alpha]_D^{25.0}$ –47.245 (*c* 0.63, $CHCl_3$, 94.9% ee).

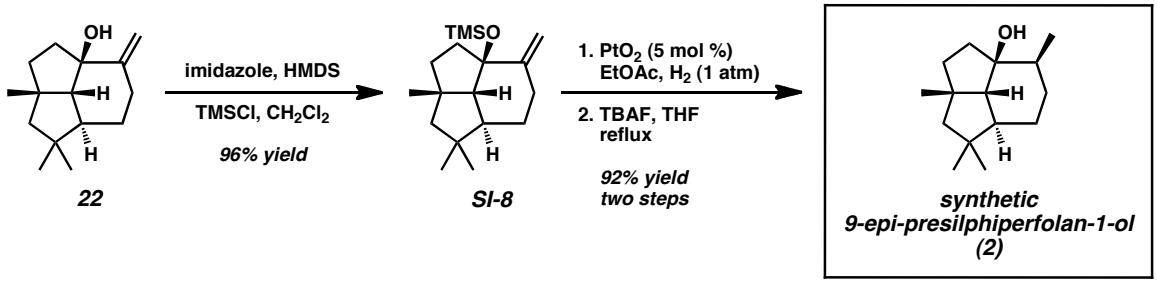
Synthetic (–)-Presilphiperfolan-1-ol (1): R_f = 0.32 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 1.96 (ddd, *J* = 13.3, 9.1, 9.1 Hz, 1H), 1.75 (ddd, *J* = 13.5, 10.1, 9.0 Hz, 1H), 1.70–1.61 (m, 1H), 1.59 (ddd, *J* = 13.4, 10.2, 1.9 Hz, 1H), 1.53 (s, 2H), 1.52–1.34 (m, 3H), 1.39 (s, 3H), 1.27 (br d, *J* = 11.9 Hz, 1H), 0.95 (s, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.91–0.82 (m, 3H), 0.81 (s, 3H), 0.52 (br s, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 85.7, 66.2, 60.6, 56.2, 46.1, 42.2, 41.6, 40.4, 35.1, 32.5, 32.1, 28.7, 24.7, 22.3, 15.9; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.96 (ddd, *J* = 13.6, 9.8, 9.8 Hz, 1H), 1.84 (ddd, *J* = 13.6, 9.1, 9.1 Hz, 1H), 1.82–1.76 (m, 1H), 1.65 (ddd, *J* = 13.5, 10.3, 1.9 Hz, 1H), 1.61–1.42 (m, 6H), 1.25 (s, 3H), 1.14–1.11 (br s, 1H), 1.08–0.96 (m, 3H), 0.95 (s, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.81 (s, 3H); IR (Neat Film NaCl) 3325, 2949, 2921, 2853, 1734, 1460, 138, 1335, 1304, 1283, 1276, 1258, 1250, 1218, 1189, 1181, 1145, 1126, 1069, 1053, 1030, 1002, 995, 974, 964, 947, 926, 907, 859, 843, 801, 778, 743 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{26}O$ $[M]^{+\bullet}$: 222.1984; found 222.1977; $[\alpha]_D^{25.0}$ –3.24 (*c* 0.19, $CHCl_3$, 94.9% ee); $[\alpha]_D^{22.0}$ –2.73 (*c* 0.68, $CHCl_3$, 94.9% ee); mp = 113–116 °C (hexanes).



Synthetic (–)-Presilphiperfolan-1-ol (1). To a 20 mL scintillation vial with magnetic stir bar were added allylic alcohol **22** (6.8 mg, 0.034 mmol, 1.0 equiv) and $[Ir(cod)(py)(PCy_3)]PF_6$ (2.9 mg, 0.0034 mmol, 10 mol %). A septum-fitted screw cap was attached and the vial was evacuated for 5 min and backfilled with an H_2 (1 atm, balloon). CH_2Cl_2 (8 mL) was added, giving a golden yellow-orange solution. The solution was freeze-pump-thawed using a $N_2(l)$ bath (3 cycles, 5 min evacuation per cycle), backfilling with H_2 (1 atm, balloon) for each cycle. The golden yellow-orange solution was stirred at 23 °C for 27 h. The reaction was filtered through a silica plug (0.5 x 2 cm), eluting with Et_2O. The filtrate was concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The residue was purified by flash column chromatography (SiO_2, 1.5 x 25 cm, 5%→10% EtOAc in hexanes) to afford faintly fragrant alcohol **1** (6.9 mg, 0.031 mmol, 92% combined yield) as a white amorphous solid.

The NMR spectra (C_6D_6) for synthetic compound **1** do not match spectral data for reported natural **1**.[18] The NMR spectra (CD_2Cl_2) for synthetic compound **1** match spectral data for reported synthetic **1**.[19]

(Note: Competitive olefin isomerization to a endocyclic trisubstituted alkene (**SI-7**) is observed if the reaction is stopped at incomplete conversion, but with sufficient time, only reduced product **1** is observed.)



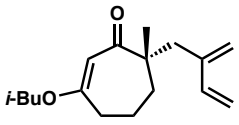
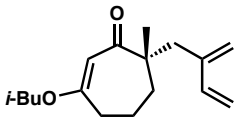
Trimethylsilyl Ether SI-8.[20] To a 20 mL scintillation vial with magnetic stir bar was added allylic alcohol **22** (10.8 mg, 0.049 mmol, 1.00 equiv). A septum-fitted screw cap was attached and the vial was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle). CH_2Cl_2 (4 mL) was added. HMDS (41.1 μL, 0.196 mmol, 4.00 equiv) and TMSCl (12 μL, 0.098 mmol, 2.0 equiv) were added dropwise, followed by imidazole (6.5 mg, 0.098 mmol, 2.0 equiv) in one portion. The clear, colorless solution turned into a turbid white solution several seconds after the addition of imidazole. After 24 h of stirring, the reaction was quenched by the addition of sat. aqueous $NaHCO_3$ (2 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, 1.5 x 25 cm, 0%→1%→2% EtOAc in hexanes) to afford trimethylsilyl ether **SI-8** (13.8 mg, 0.04717 mmol, 96% yield) as a nearly colorless pale yellow oil; R_f = 0.73 (10:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.14–5.12 (m, 1H), 4.93–4.91 (m, 1H), 2.55–2.42 (m, 1H), 2.12–2.01 (m, 3H), 1.98–1.83 (m, 2H), 1.66–1.55 (m, 1H), 1.53 (d, *J* = 13.0 Hz, 1H), 1.47 (br d, *J* = 13.0 Hz, 1H), 1.48–1.40 (m, 1H), 1.36 (s, 3H), 1.29–1.17 (m, 1H), 0.98 (ddd, *J* = 12.8, 12.8, 5.7 Hz, 1H), 0.88 (s, 3H), 0.81 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.3, 113.1, 87.9, 67.0, 59.6, 52.3, 45.8, 42.6, 40.1, 38.5, 32.0, 31.3, 28.4, 23.3, 22.2, 2.5; IR (Neat Film NaCl) 3073, 2950, 2929, 2865, 1813, 1730, 1648, 1458, 1440, 1412, 1384, 1368, 1335, 1300, 1248, 1202, 1186, 1142, 1115, 1071, 1062, 1034, 1012, 997, 976, 950, 935, 921, 906, 889, 876, 838, 812, 751 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{18}H_{32}OSi$ $[M]^{+\bullet}$: 292.2223; found 292.2211; $[\alpha]_D^{25.0}$ –94.32 (*c* 0.98, CH_2Cl_2, 94.9% ee).

Synthetic 9-*epi*-Presilphiperfolan-1-ol (2). To a 20 mL scintillation vial with magnetic stir bar containing trimethylsilyl ether **SI-8** (13.8 mg, 0.0472 mmol, 1.00 equiv) was added Adam's catalyst (PtO_2-hydrate, 0.54 mg, 0.0024 mmol, 5 mol %). The reaction was capped with a septum-fitted screw cap, evacuated for 5 min, and backfilled with an H_2 (1 atm, balloon). EtOAc (2.5 mL) was added and the reaction was stirred vigorously. After 10 min, the brown solids turned black. After 13.5 h of stirring, the H_2 balloon was removed. The reaction was filtered through a Celite pipet plug (0.5 x 1 cm) and eluted with EtOAc. The clear filtrate was concentrated under reduced pressure. The residue was taken up in THF (5 mL) and treated with TBAF (1.0 M in THF, 189 μL, 0.189 mmol, 4.00 equiv). The reaction was sealed with a teflon-lined hard cap and inserted into a 100 °C heating block. After 10.5 h of stirring, the reaction was a tan solution. The vial was cooled to 23 °C and an additional portion of TBAF (1.0 M in THF, 95 μL, 0.094 mmol, 2.0 equiv) was added. The vial was resealed and inserted into a 100 °C heating block. After an additional 16 h of stirring, the vial was cooled to 23 °C and concentrated under reduced pressure (25 mmHg) in a 0 °C ice/water bath. The residue was purified by flash column chromatography (SiO_2, 2 x 20 cm, 1%→3%→5% EtOAc in hexanes) to afford faintly fragrant alcohol **2** (9.6 mg, 0.043 mmol, 92% yield) as a clear, colorless, faintly fragrant oil which solidifies upon storage in a –25 °C freezer.

The NMR spectra (C_6D_6) for synthetic compound **2** match spectral data for reported natural **2**.[17]

Methods for Determination of Enantiomeric Excess

Table SI-3. Methods for the Determination of Enantiomeric Excess (Chiral HPLC and SFC).

entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
1	 *12*	 *12*	HPLC Chiralcel OD-H 2.0% IPA in hexane isocratic, 1.0 mL/min	6.41	7.53	95

Comparison of Spectral Data for Synthetic and Reported 1 and 2

Spectral data for synthetic presilphiperfolan-1-ol (**1**) and 9-*epi*-presilphiperfolan-1-ol (**2**) (^{1}H NMR, ^{13}C NMR, $[\alpha]_D^T$) were compared with reported spectral data for the natural samples.[17,18] Tables comparing compound data are shown in Tables SI-4–SI-7. Superimposed NMR spectra are shown in Figures SI-22–SI-24. Additionally, we compared the spectra of our synthetic presilphiperfolan-1-ol (**1**) to a reported synthetic compound.[19] The results are shown in Tables SI-8–SI-9. ^{1}H and ^{13}C NMR spectra for naturally isolated 9-*epi*-presilphiperfolan-1-ol (**2**)[17] were generously provided by Prof. Suzana G. Leitao. A ^{1}H NMR spectrum of naturally isolated presilphiperfolan-1-ol (**1**) was published in a dissertation.[18b] Unfortunately, attempts to obtain samples or spectra of naturally isolated presilphiperfolan-1-ol (**1**) were unsuccessful.

The NMR spectra (C_6D_6) for synthetic compound **2** match spectral data for reported natural **2**,[17] but the NMR spectra (C_6D_6) for synthetic compound **1** do not match spectral data for reported natural **1**.[18] The NMR spectra (C_6D_6) of reported natural **1**[18] appear to match spectral data for reported natural **2**.[17] The NMR spectra (CD_2Cl_2) for synthetic compound **1** match spectral data for reported synthetic **1**.[19] Based on our analysis of spectral data, we believe that reported natural **1** is misassigned at C(9) and should have the same true structure as natural **2** with a 9β-methyl configuration.

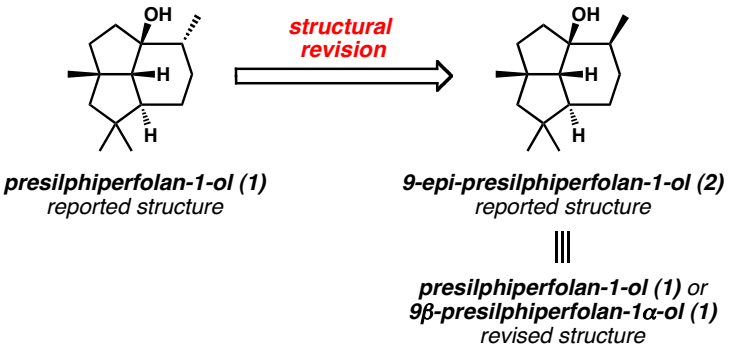
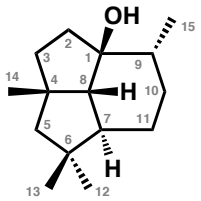


Table SI-4. Comparison of Optical Rotation Data for Synthetic and Reported Natural[18] Presilphiperfolan-1-ol (**1**) and Reported Natural[17] 9-*epi*-Presilphiperfolan-1-ol (**2**)

Compound	Reported Natural Sample	Synthetic Sample
Presilphiperfolan-1-ol (**1**)	$[\alpha]_D^{25} = -66.0$ (*c* 0.0015)	$[\alpha]_D^{25} = -47.25$ (*c* 0.63, $CHCl_3$, 94.9% ee)
9-*epi*-Presilphiperfolan-1-ol (**2**)	*(not reported)*	$[\alpha]_D^{25} = -2.73$ (*c* 0.68, $CHCl_3$, 94.9% ee)

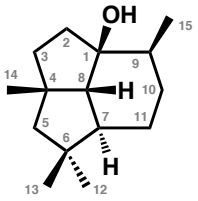


presilphiperfolan-1-ol (1)
reported structure

Table SI-5. Comparison of ^{1}H NMR Data for Synthetic and Reported Natural[18] Presilphiperfolan-1-ol (**1**)[a]

Assignment	Synthetic **1**[b] (ppm)	Multiplicity, *J* (Hz)	Natural **1**[c] (ppm)	Multiplicity, *J* (Hz)
C1	—	—	—	—
C2	1.75	ddd, 13.5, 10.1, 9.0	1.92–1.77	m
	1.52–1.34	m	1.72–1.62	m
C3	1.96	ddd, 13.3, 9.1, 9.1	1.92–1.77	m
	1.59	ddd, 13.4, 10.2, 1.9	1.62–1.53	m
C4	—	—	—	—
C5	1.53	s	1.50	s
C6	—	—	—	—
C7	0.91–0.82	m	1.17–1.08	m
C8	1.27	br d, 11.9	1.62–1.53	m
C9	1.52–1.34	m	1.62–1.53	m
C10	1.70–1.61	m	1.45–1.39	m
	0.91–0.82	m	1.33–1.20	m
C11	1.52–1.34	m	1.33–1.20	m
	0.91–0.82	m	1.17–1.08	m
C12	0.81	s	0.80	s
C13	0.95	s	0.94	s[d]
C14	1.39	s	1.32	s
C15	0.94	d, 7.0	0.89	d, 7

[a] For a comparison of ^{1}H NMR spectra of synthetic and natural samples, see Figure SI-22
[b] ^{1}H NMR spectra were obtained at 500 MHz in C_6D_6 and standardized relative to residual C_6D_6
[c] ^{1}H NMR spectra were obtained at 500 MHz in C_6D_6 and standardized relative to TMS
[d] Peak multiplicity was originally reported as d, *J* = 7 Hz in ref. 18a, but corrected in ref. 18b

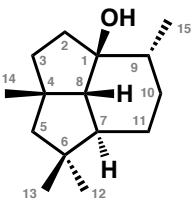


9-epi-presilphiperfolan-1-ol (2)
reported structure

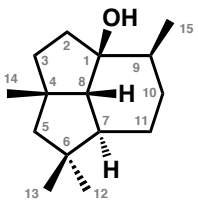
Table SI-6. Comparison of ^{1}H NMR Data for Synthetic and Reported Natural[17] 9-*epi*-Presilphiperfolan-1-ol (**2**) [a]

Assignment	**Synthetic 2** [b] (ppm)	**Multiplicity, *J*** (Hz)	**Natural 2** [c] (ppm)	**Multiplicity, *J*** (Hz)
C1	—	—	—	—
C2	1.87–1.78	m	1.87–1.79	m
	1.73–1.64	m	1.72–1.61	m
C3	1.89–1.81	m	1.87–1.79	m
	1.63–1.55	m	1.61–1.54	m
C4	—	—	—	—
C5	1.50	s	1.50	s
C6	—	—	—	—
C7	1.15–1.05	m	1.16–1.09	m
C8	1.55	br d, 12.3	1.61–1.54	m
C9	1.63–1.55	m	1.61–1.54	m
C10	1.48–1.38	m	1.45–1.39	m
	1.36–1.27	m	1.34–1.24	m
C11	1.33–1.25	m	1.34–1.24	m
	1.19–1.09	m	1.16–1.09	m
C12	0.80	s	0.80	s
C13	0.94	s	0.93	s
C14	1.33	s	1.32	s
C15	0.90	d, 7.0	0.89	d, 7

[a] For a comparison of ^{1}H NMR spectra of synthetic and natural samples, see Figure SI-24A
[b] ^{1}H NMR spectra were obtained at 500 MHz in C_6D_6 and standardized relative to residual C_6D_6
[c] ^{1}H NMR spectra were obtained at 400 MHz in C_6D_6 and standardized relative to TMS



presilphiperfolan-1-ol (1)
reported structure

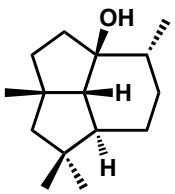


9-epi-presilphiperfolan-1-ol (2)
reported structure

Table SI-7. Comparison of ^{13}C NMR Data for Synthetic and Reported[18] Natural Presilphiperfolan-1-ol (**1**), Synthetic and Reported Natural 9-*epi*-Presilphiperfolan-1-ol[17] (**2**) [a]

Assignment	**Synthetic 1** [b] (ppm)	**Natural 1** [c] (ppm)	**Synthetic 2** [b] (ppm)	**Natural 2** [d] (ppm)
C1	85.7	89.0	84.5	84.3
C2	32.1	39.7	39.7	39.5
C3	42.2	42.6	42.7	42.4
C4	46.1	46.2	46.2	46.0
C5	60.6	59.4	59.4	59.2
C6	40.4	41.0	40.5	40.2
C7	56.2	51.7	51.7	51.5
C8	66.2	63.9	63.9	63.7
C9	41.6	36.9	36.9	36.7
C10	35.1	29.9	29.9	29.7
C11	24.7	20.3	20.3	20.1
C12	22.3	22.3	22.3	22.1
C13	28.7	28.7	28.8	28.5
C14	32.5	31.4	31.4	31.1
C15	15.9	15.7	15.8	15.5

[a] For a comparison of ^{13}C NMR spectra of synthetic and natural **2**, see Figure SI-24B
[b] ^{13}C NMR spectra were obtained at 125 MHz in C_6D_6 and standardized relative to residual C_6D_6
[c] ^{13}C NMR spectra were obtained at 125 MHz in C_6D_6 and standardized relative to TMS
[d] ^{13}C NMR spectra were obtained at 100 MHz in C_6D_6 and standardized relative to TMS



synthetic compound 1

Table SI-8. Comparison of ^{1}H NMR Data for Synthetic and Reported Synthetic[19] Presilphiperfolan-1-ol (**1**)

Synthetic 1 [a] (ppm)	**Multiplicity, *J*** (Hz)	**Reported 1** [b] (ppm)	**Multiplicity, *J*** (Hz)
1.25	s	1.26	s
0.95	s	0.95	s
0.93	d, 6.8	0.94	d, 7
0.81	s	0.82	s

[a] ^{1}H NMR spectra were obtained at 500 MHz in CD_2Cl_2 and standardized relative to residual CH_2Cl_2

[b] ^{1}H NMR spectra were obtained at 100 or 200 MHz in CD_2Cl_2

Table SI-9. Comparison of ^{13}C NMR Data for Synthetic and Reported Synthetic[19] Presilphiperfolan-1-ol (**1**)

Synthetic 1 [a] (ppm)	**Reported 1** [b] (ppm)
85.7	85.4
66.2	65.8
60.6	60.3
56.2	55.8
46.1	45.7
42.2	41.5
41.6	41.1
40.4	40.1
35.1	34.7
32.5	32.1
32.1	31.7
28.7	28.5
24.7	24.8
22.3	22.0
15.9	15.5

[a] ^{13}C NMR spectra were obtained at 125 MHz in C_6D_6 and standardized relative to residual C_6D_6

[b] ^{13}C NMR spectra were obtained at 23 or 50 MHz in C_6D_6/CCl_4 and standardized relative to CCl_4

References

[1] (a) Hong, A. Y.; Krout, M. R.; Jensen, T.; Bennett, N. B.; Harned, A. M.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 2756 – 2760.
(b) Hong, A. Y.; Bennett, N. B.; Krout, M. R.; Jensen, T.; Harned, A. M.; Stoltz, B. M. *Tetrahedron* **2011**, *67*, 10234 – 10248.
(c) Bennett, N. B.; Hong, A. Y.; Harned, A. M.; Stoltz, B. M. *Org. Biomol. Chem.* **2012**, *10,* 56 – 59.

[2] (a) Ragan, J. A.; Makowski, T. W.; am Ende, D. J.; Clifford, P. J.; Young, G. R.; Conrad, A. K.; Eisenbeis, S. A. *Org. Process Res. Dev.* **1998**, *2*, 379 – 381.
(b) Ragan, J. A.; Murry, J. A.; Castaldi, M. J.; Conrad, A. K.; Jones, B. P.; Li, B.; Makowski, T. W.; McDermott, R.; Sitter, B. J.; White, T. D.; Young, G. R. *Org. Process. Res. Dev.* **2001**, *5*, 498 – 507.
(c) Do, N.; McDermott, R. E.; Ragan, J. A. *Org. Synth.* **2008**, *85*, 138 – 146.

[3] Satake, Y.; Nishikawa, T.; Hiramatsu, T.; Araki, H.; Isobe. M. *Synthesis* **2010**, *12*, 1992 – 1998.

[4] (a) Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044 – 15045.
(b) Tani, K.; Behenna, D. C.; McFadden, R. M.; Stoltz, B. M. *Org. Lett.* **2007**, *9*, 2529 – 2531.
(c) Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth.* **2009**, *86*, 181 – 193.

[5] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organometallic Chem.* **1999**, *65*, 253 – 266.

[6] Fairlamb, I. J. S.; Kapdi, A. R.; Lee, A. F. *Org. Lett.* **2004**, *6*, 4435 – 4438.

[7] Coulson, D. R.; Satek, L. C.; Grim, S. O. *Inorg. Synth.* **1972**, *13*, 121 – 124.

[8] Corey, E. J.; Cho, H.; Rücker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455 – 3458.

[9] (a) Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915 – 12917.
(b) Wu, J. Y.; Stanzl, B. N.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 13214 – 13216.

[10] Murray, R. W.; Singh, M. *Org. Synth.* **1997**, *74*, 91 – 96.

[11] (a) Heller, S. T.; Sarpong, R. *Org. Lett.* **2010**, *12*, 4572 – 4575.
(b) Heller, S. T.; Sarpong, R. *Tetrahedron* **2011**, *67*, 8851 – 8859.
(c) Heller, S. T.; Fu, T.; Sarpong, R. *Org. Lett.* **2012**, *14*, 1970 – 1973.

[12] Satoh, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1989**, *30*, 3789 – 3792.

[13] (a) Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534 – 2535.
(b) Ely, R. J.; Morken, J. P. *Org. Synth.* **2011**, *88*, 342 – 352.

[14] Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 8656 – 8659.

[15] Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2001**, *40*, 1456 – 1460.

[16] Knapp, S.; Yu, Y. *Org Lett.* **2007**, *9*, 1359 – 1362.

[17] (a) Pinto, S. C.; Leitão, G. G.; Bizzo, H. R.; Martinez, N.; Dellacassa, E.; dos Santos Jr.; F. M.; Costa, F. L. P.; de Amorim, M. B.; Leitão, S. G. *Tetrahedron Lett.* **2009**, *50*, 4785 – 4787.
(b) Joseph-Nathan, P.; Leitão, S. G.; Pinto, S. C.; Leitão, G. G.; Bizzo, H. R.; Costa, F. L. P.; de Amorim, M. B.; Martinez, N.; Dellacassa, E.; Hernández-Barragán, A.; Pérez-Hernández, N. *Tetrahedron Lett.* **2010**, *51*, 1963 – 1965.

[18] (a) Melching, S.; König, W. A. *Phytochem*. **1999**, *51*, 517 – 523.
(b) Melching, S. Isolierung, Strukturaufklärung und stereochemische Untersuchungen neuer sesquiterpenoider Verbindungen aus vier Chemotypen des Lebermooses *Conocephalum conicum*. Ph.D. Thesis, Universität Hamburg, April 1999.

[19] (a) Khomenko, T. M.; Bagryanskaya, I. Y.; Gatilov, Y. V.; Korchagina, D. V.; Gatilova, V. P.; Dubovenko, Z. V.; Barkhash, V. A. *Zh. Org. Khim*. **1985**, *21*, 677 – 678. *Russ. J. Org. Chem*. (*Engl. Transl*.) **1985**, *21*, 614 – 615;
(b) Khomenko, T. M.; Korchagina, D. V.; Gatilov, Y. V.; Bagryanskaya, Y. I.; Tkachev, A. V.; Vyalkov, A. I.; Kun, O. B.; Salenko, V. L.; Dubovenko, Z. V.; Barkash, V. A. *Zh. Org. Khim*. **1990**, *26*, 2129 – 2145; *Russ. J. Org. Chem*. (*Engl. Transl*.) **1990**, *26*, 1839 – 1852.

[20] Kotoku, N.; Sumii, Y.; Kobayashi, M. *Org. Lett.* **2011**, *13*, 3514 – 3514.

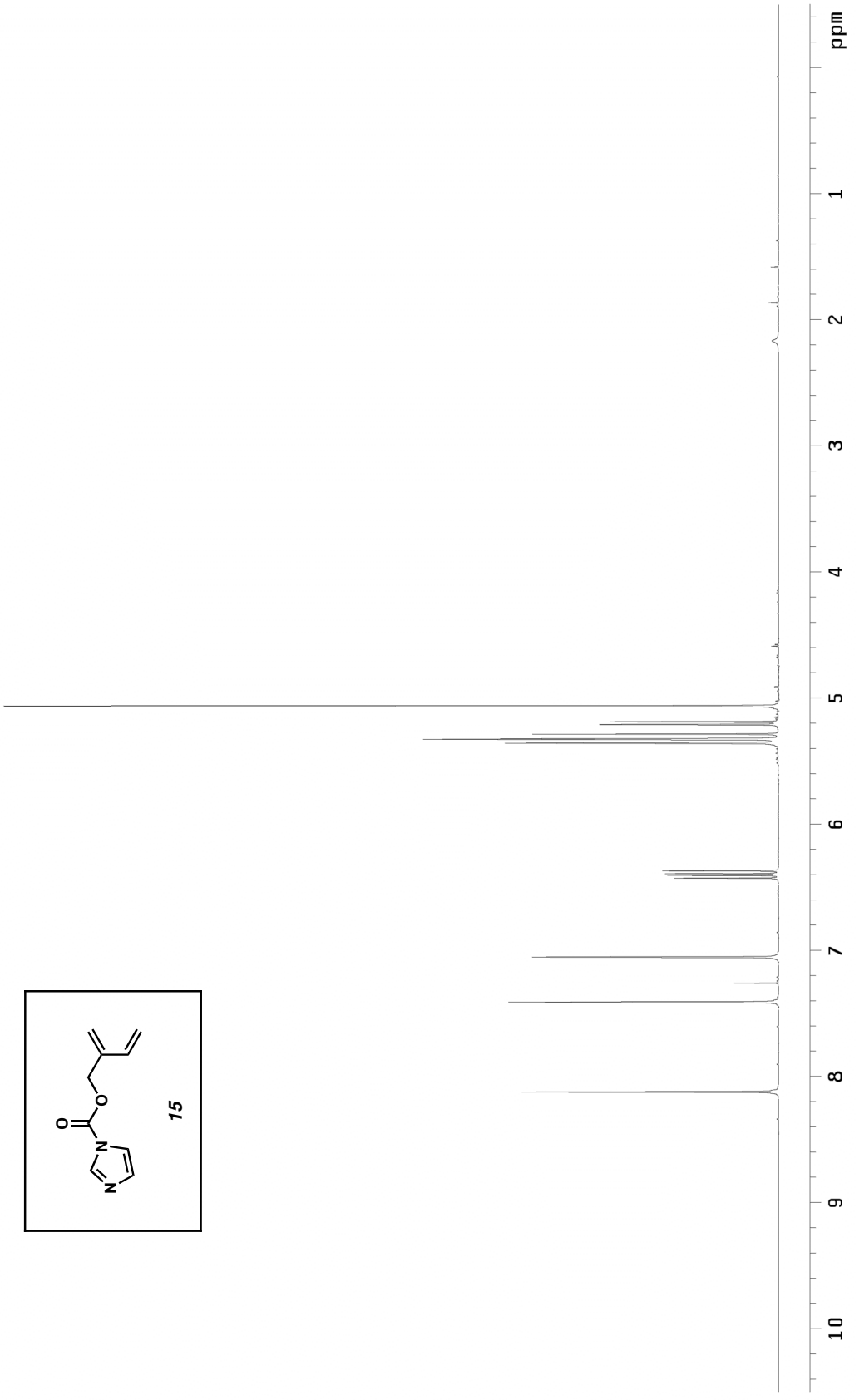


Figure SI-1A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **15**.

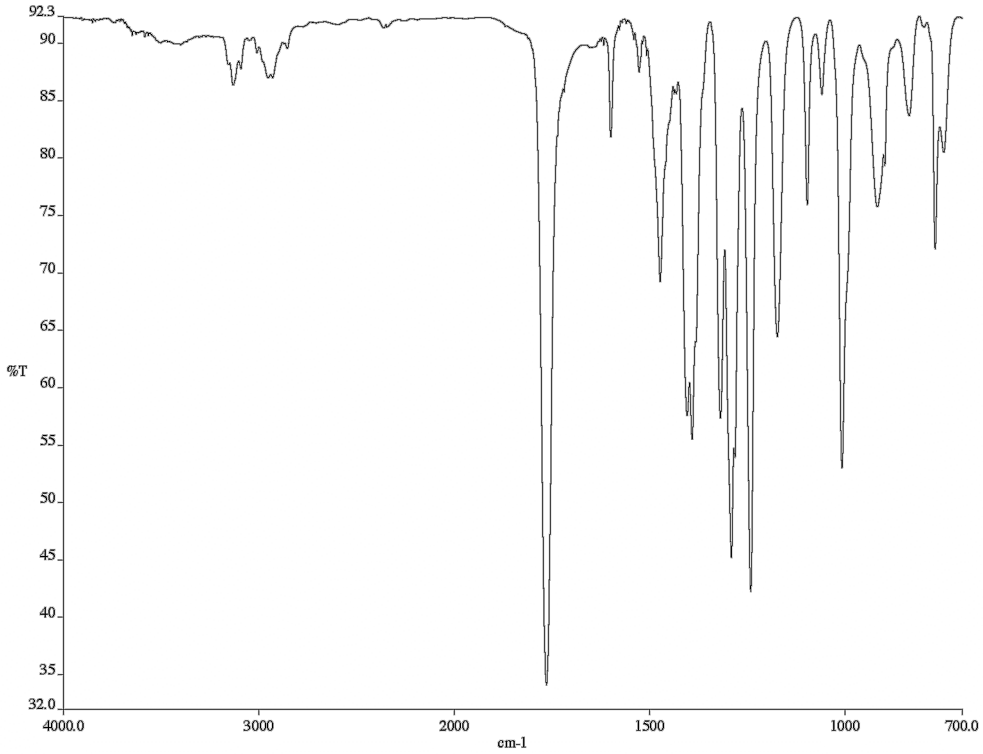


Figure SI-1B. Infrared spectrum (thin film/NaCl) of compound **15**.

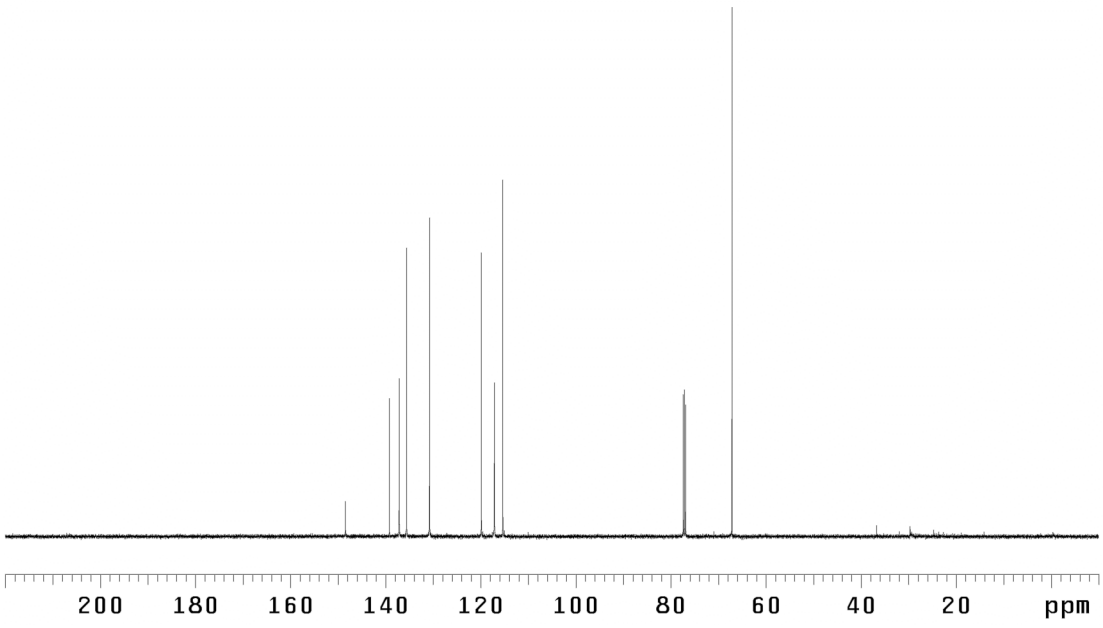


Figure SI-1C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **15**.

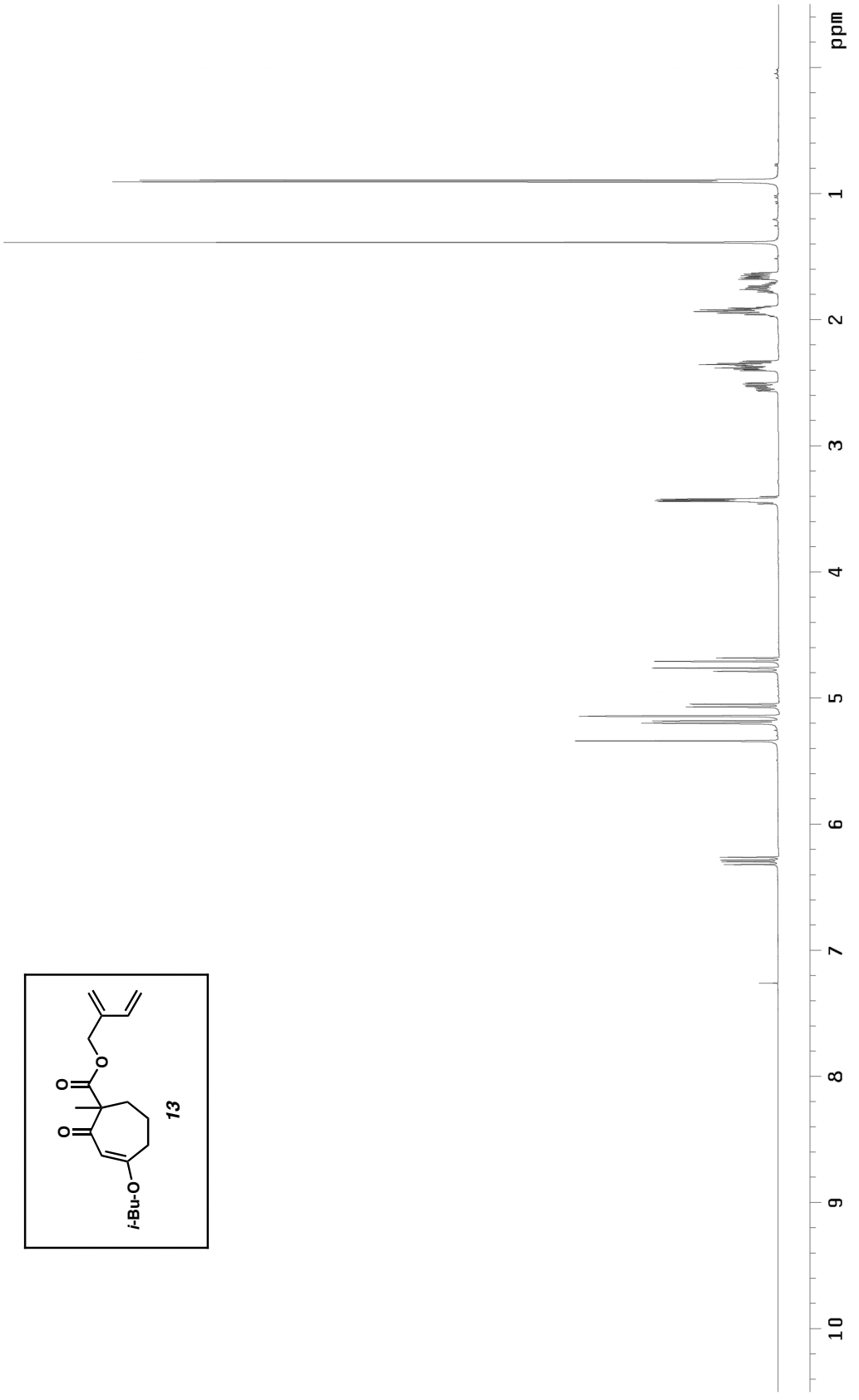


Figure SI-2A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **13**.

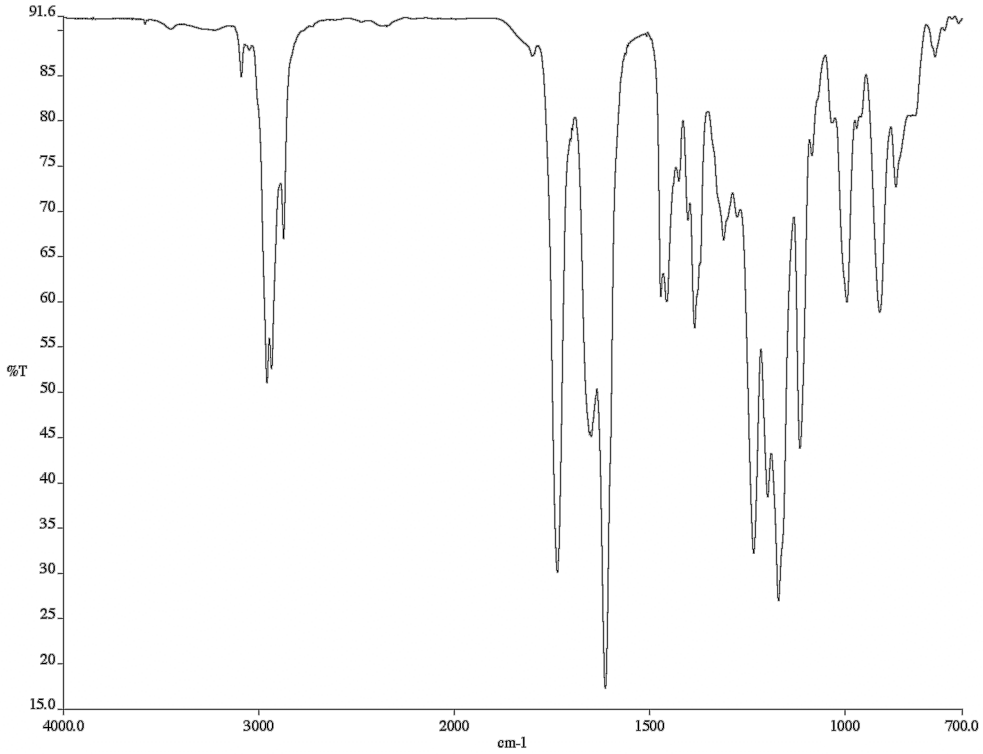


Figure SI-2B. Infrared spectrum (thin film/NaCl) of compound **13**.

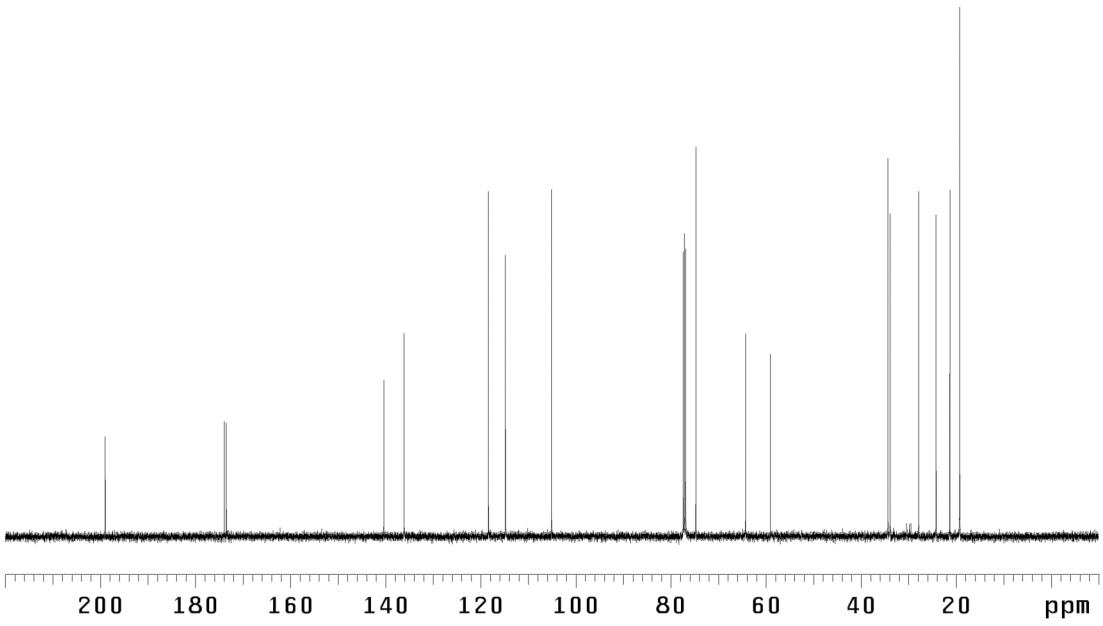


Figure SI-2C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **13**.

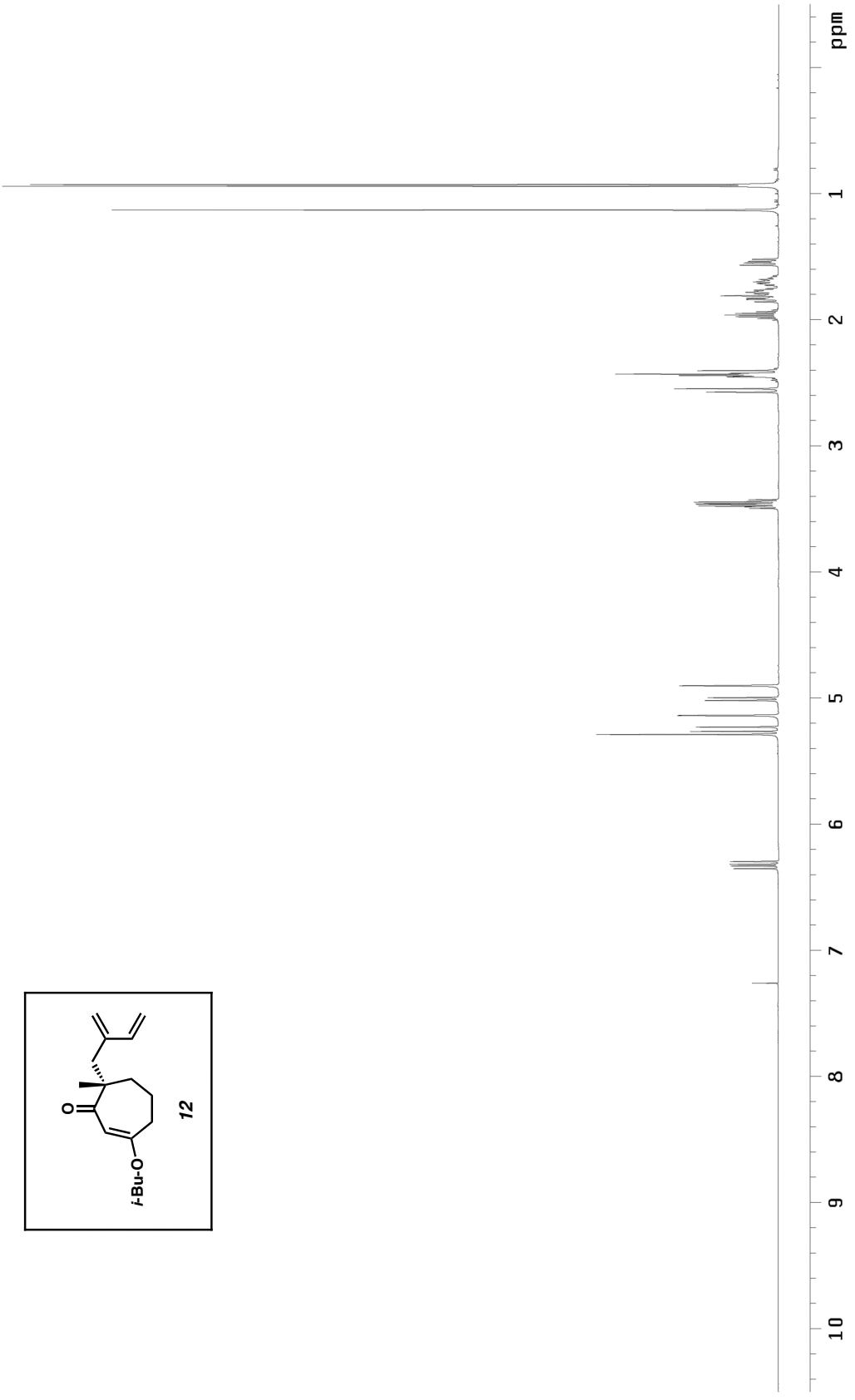


Figure SI-3A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **12**.

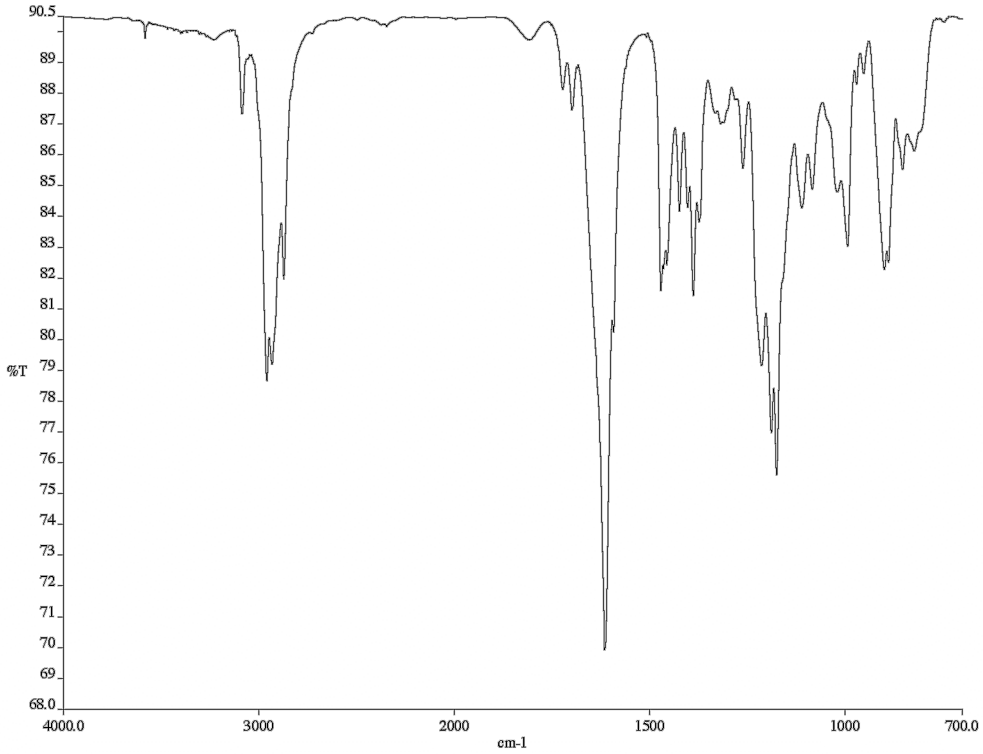


Figure SI-3B. Infrared spectrum (thin film/NaCl) of compound **12**.

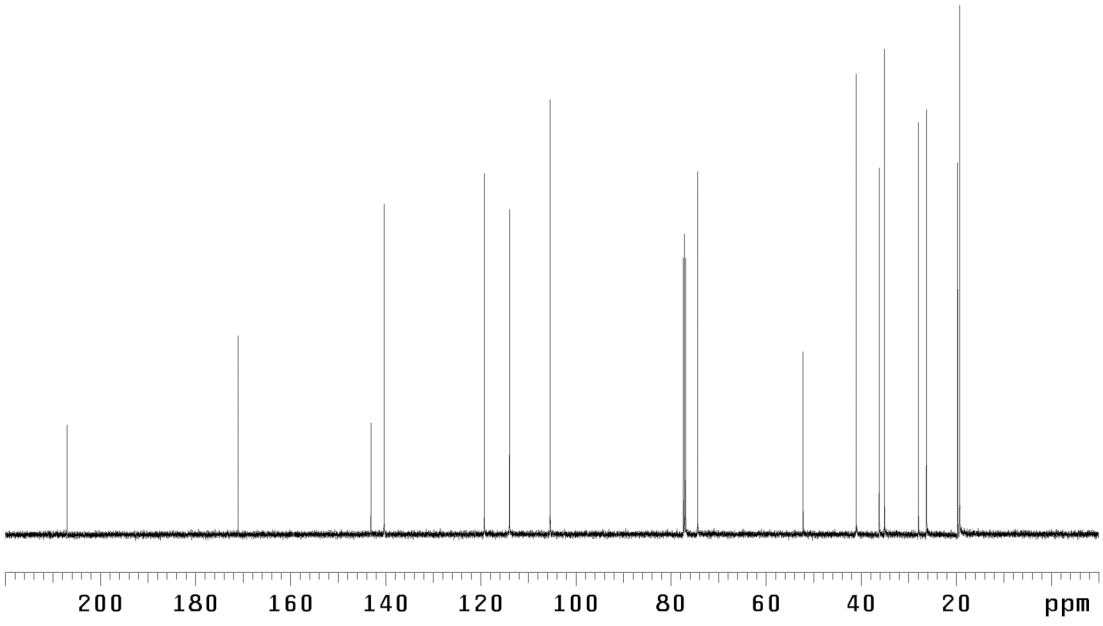


Figure SI-3C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **12**.

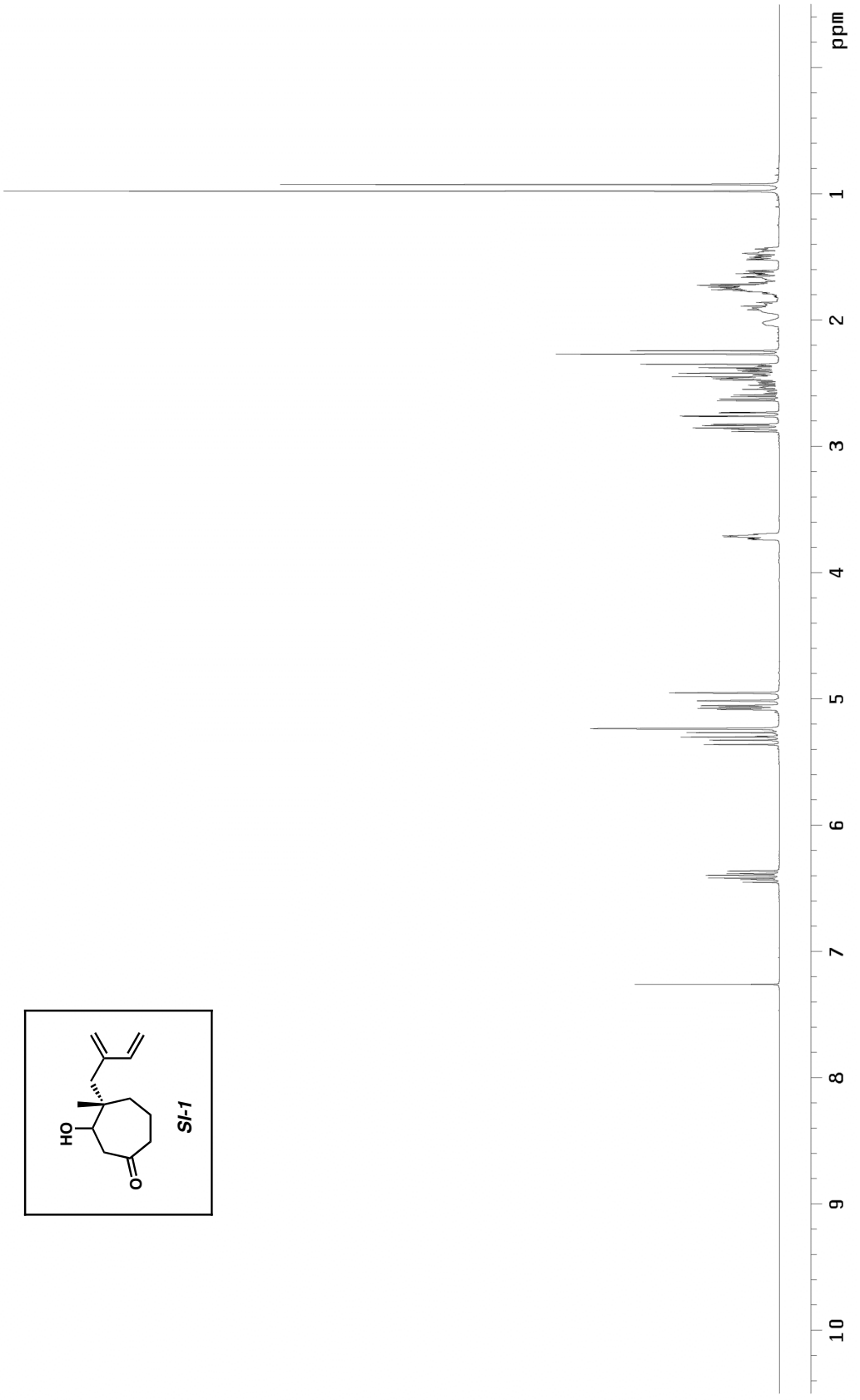


Figure SI-4A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-1**.

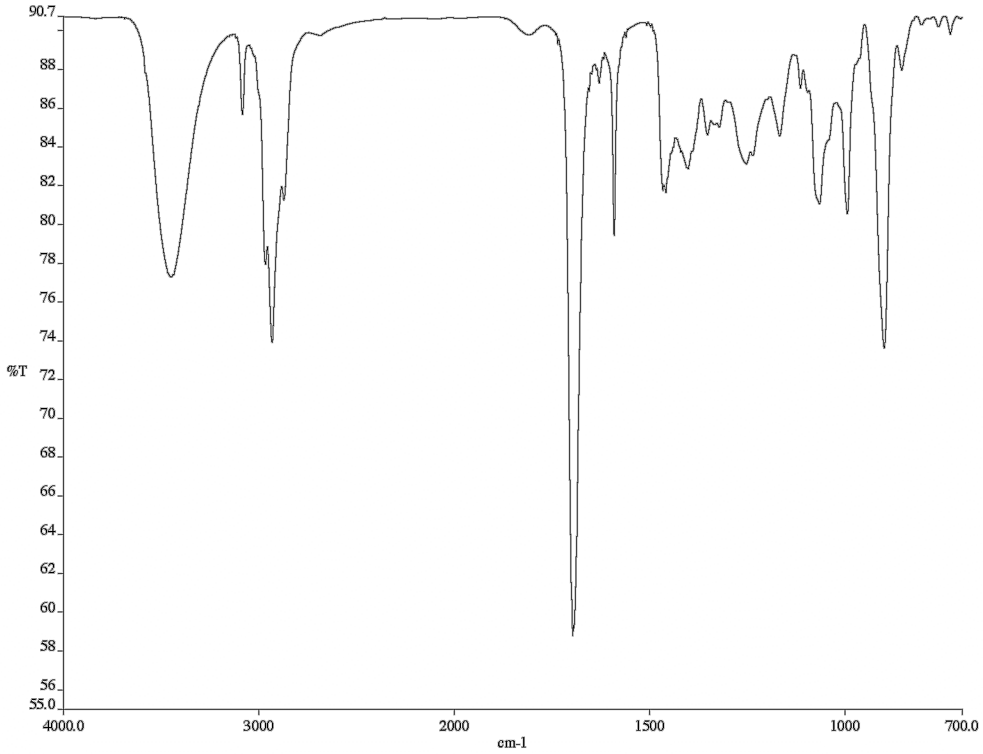


Figure SI-4B. Infrared spectrum (thin film/NaCl) of compound **SI-1**.

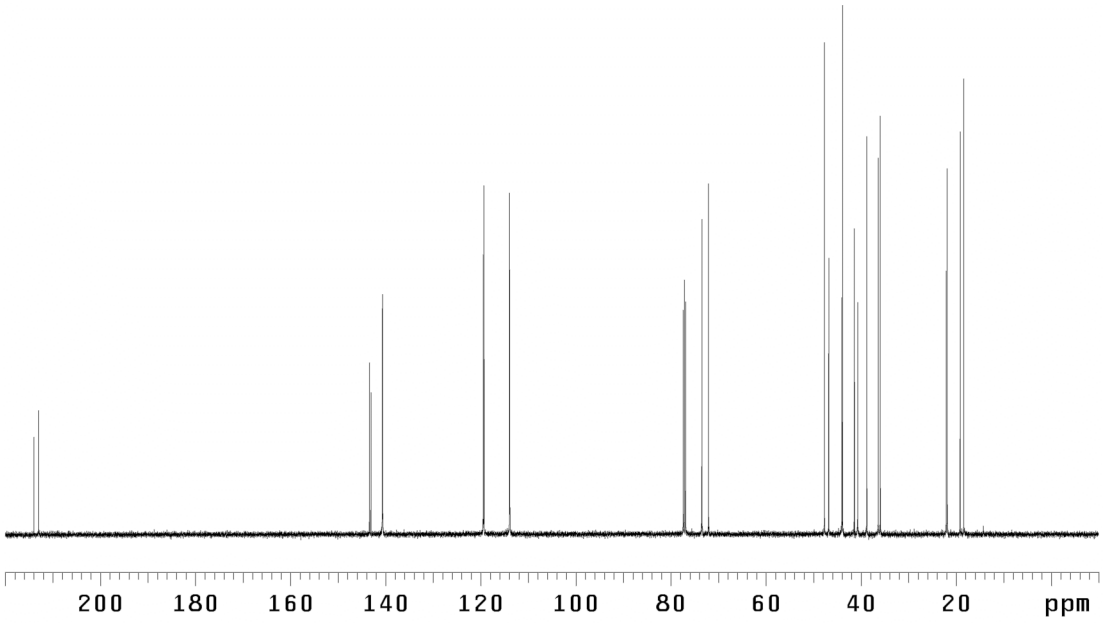


Figure SI-4C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-1**.

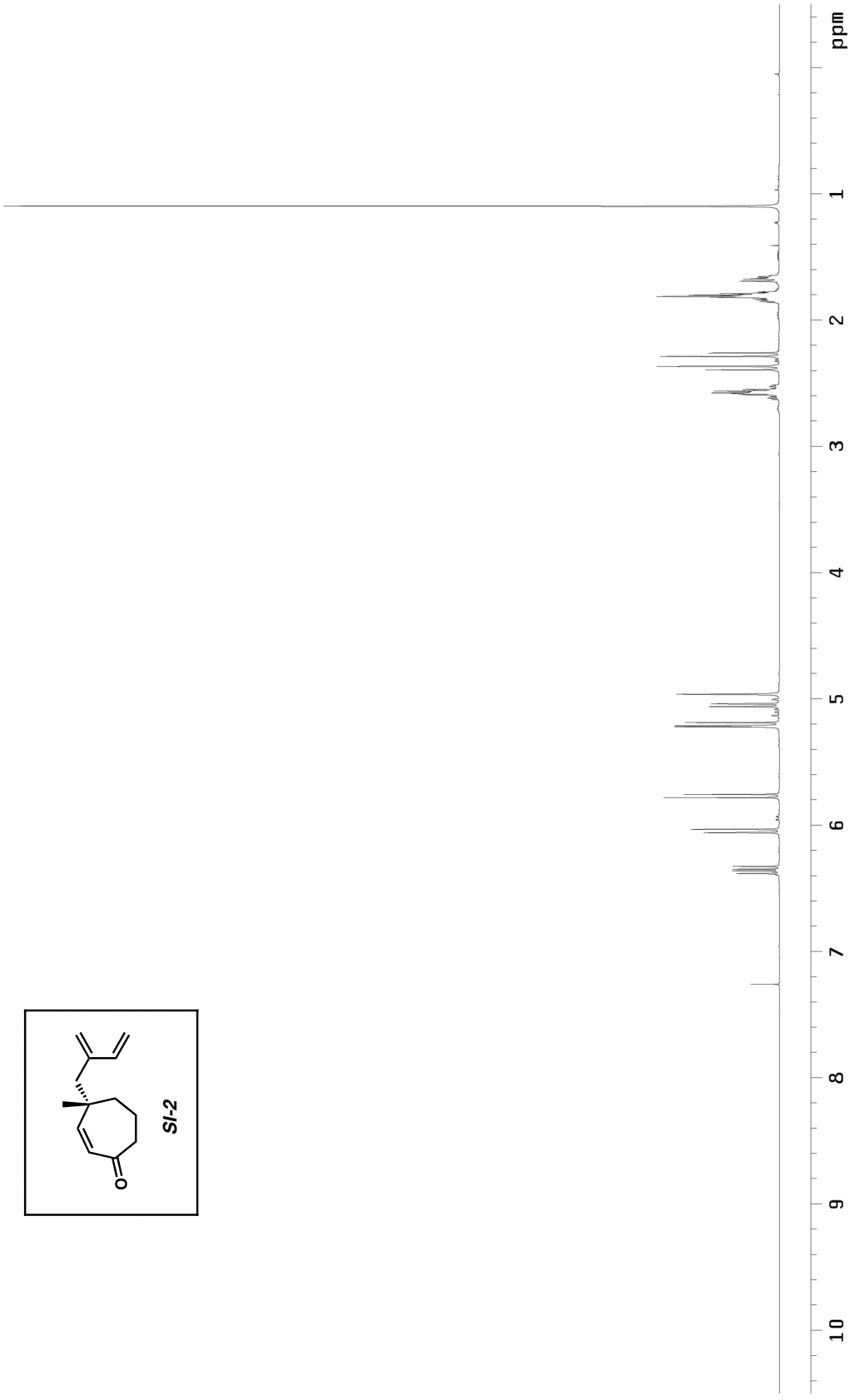


Figure SI-5A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-2**.

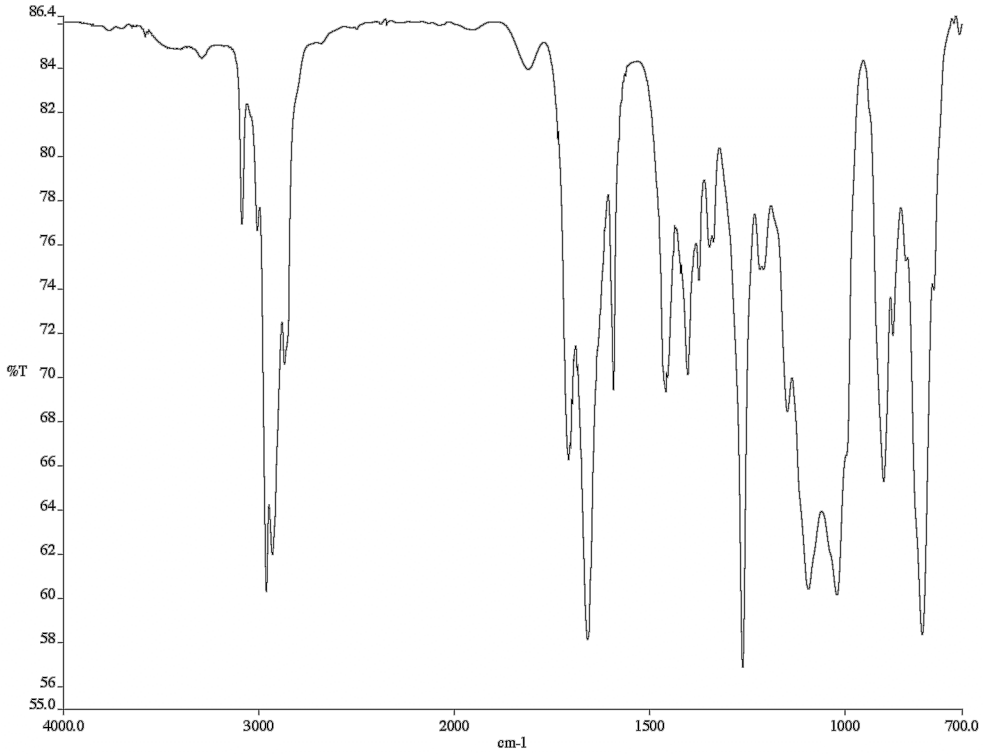


Figure SI-5B. Infrared spectrum (thin film/NaCl) of compound **SI-2**.

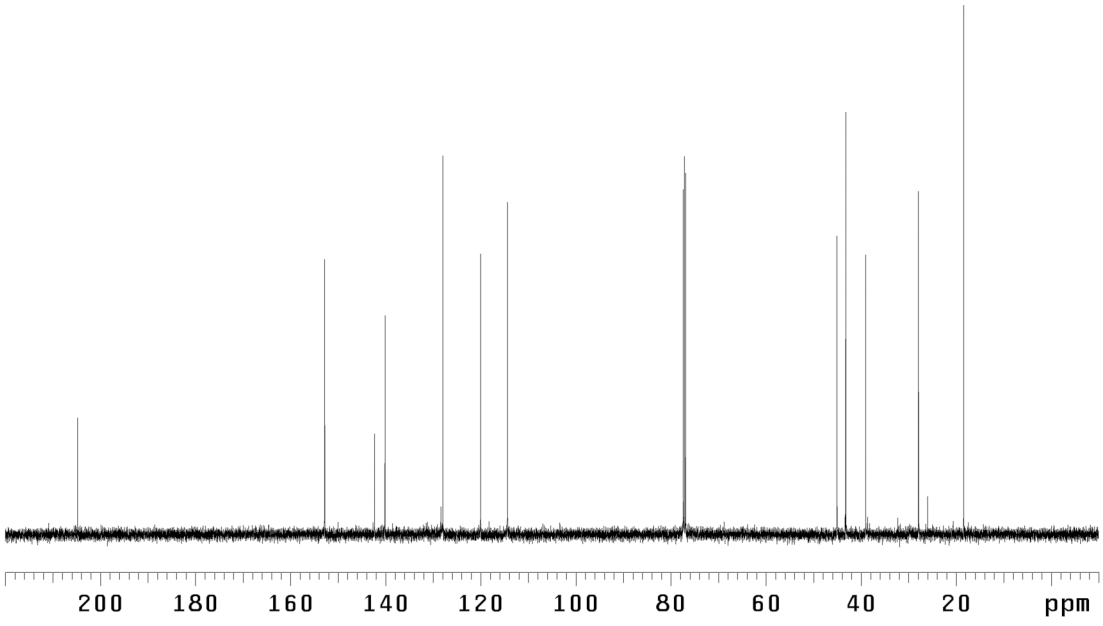


Figure SI-5C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-2**.

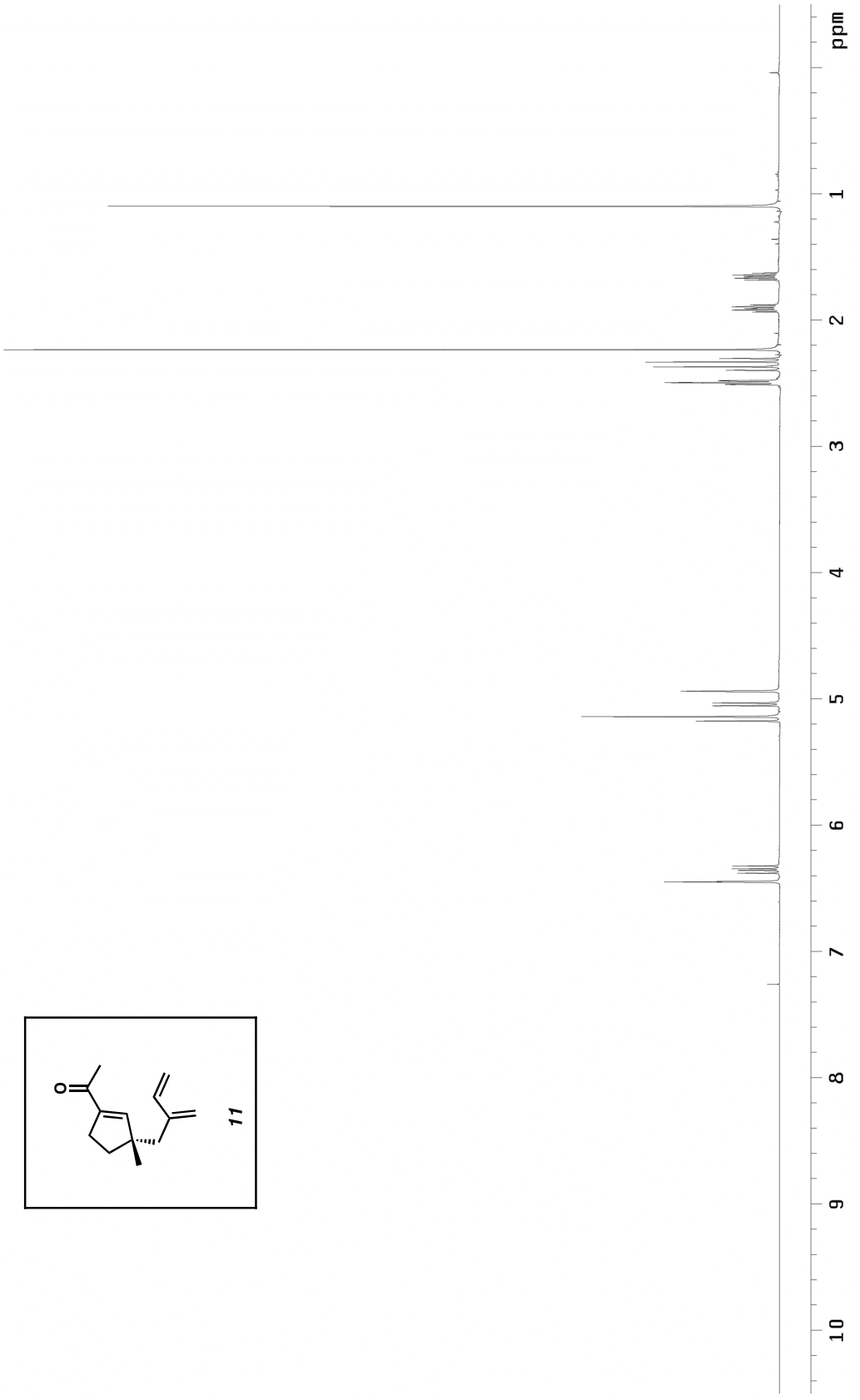


Figure SI-6A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.

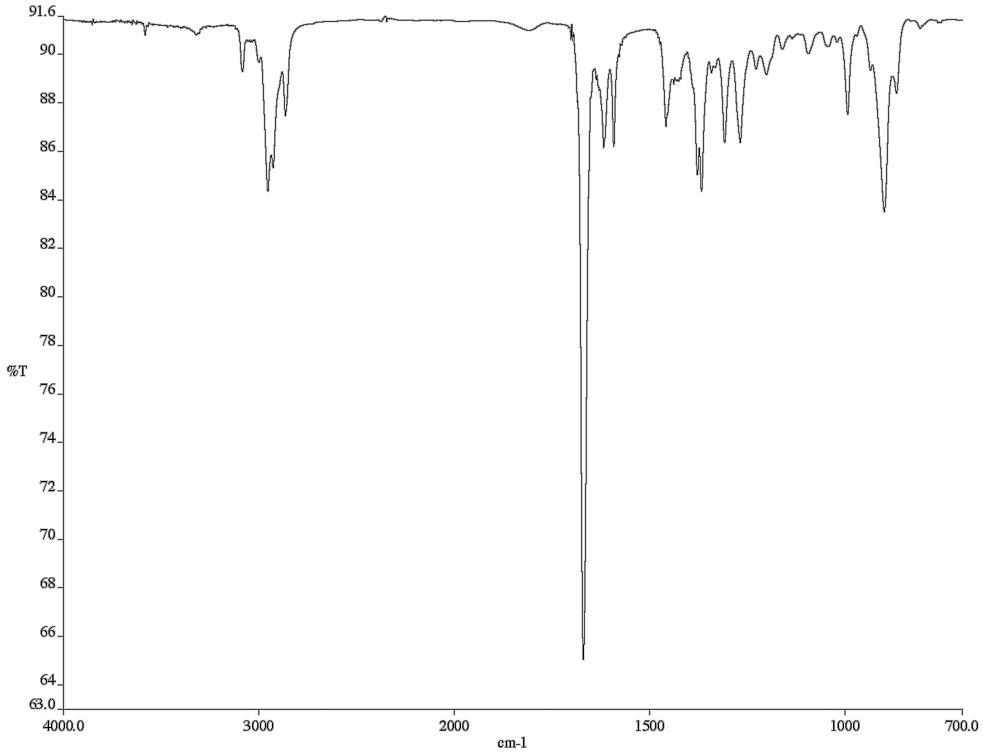


Figure SI-6B. Infrared spectrum (thin film/NaCl) of compound **11**.

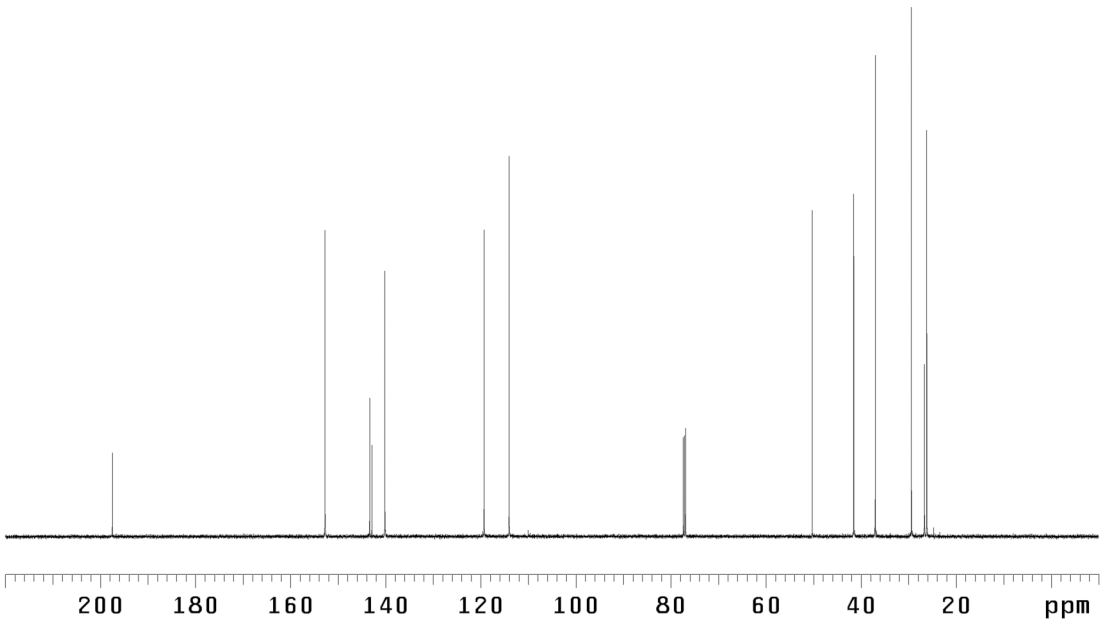


Figure SI-6C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **11**.

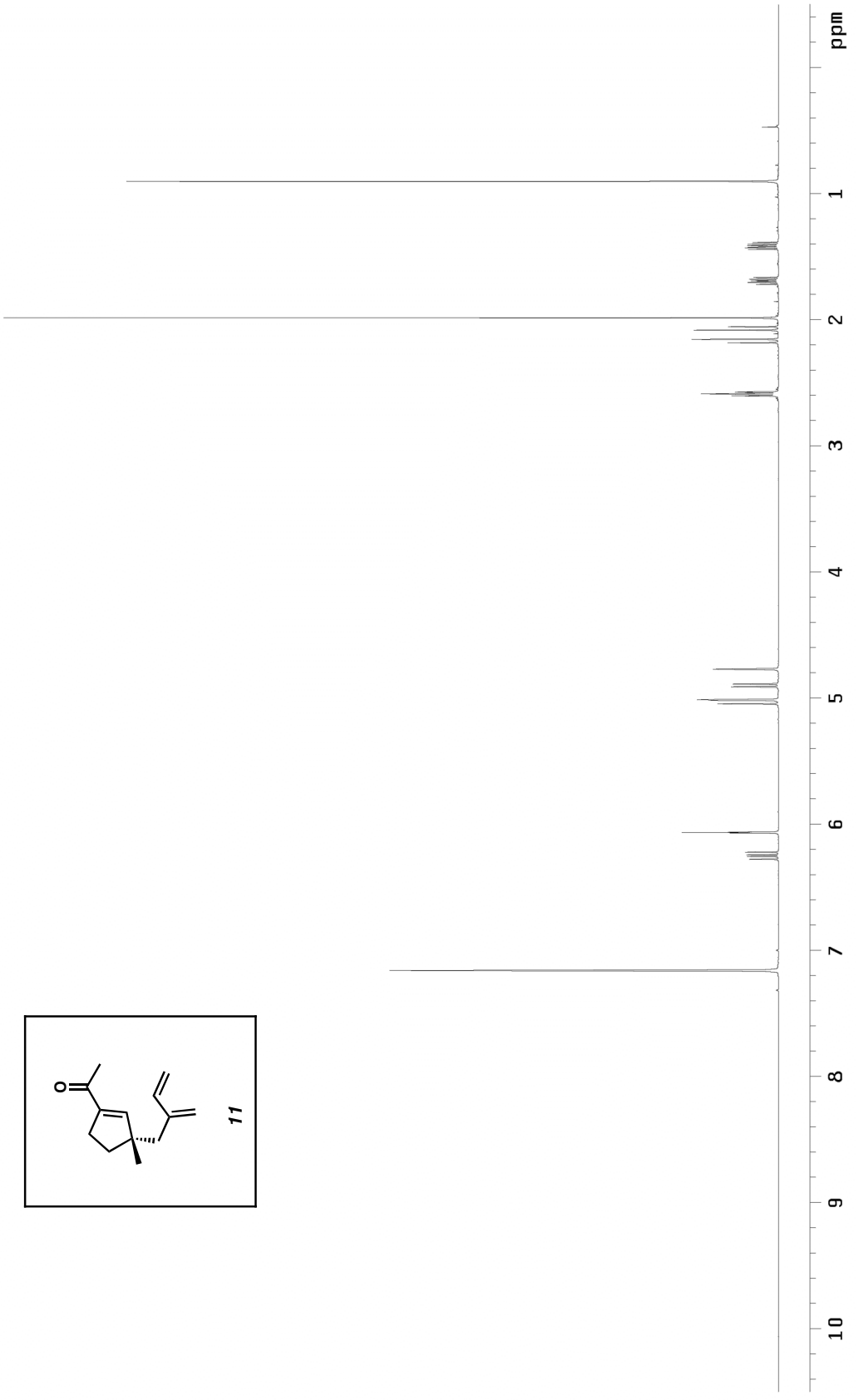


Figure SI-6D. ^{1}H NMR (500 MHz, C_6D_6) of compound **11**.

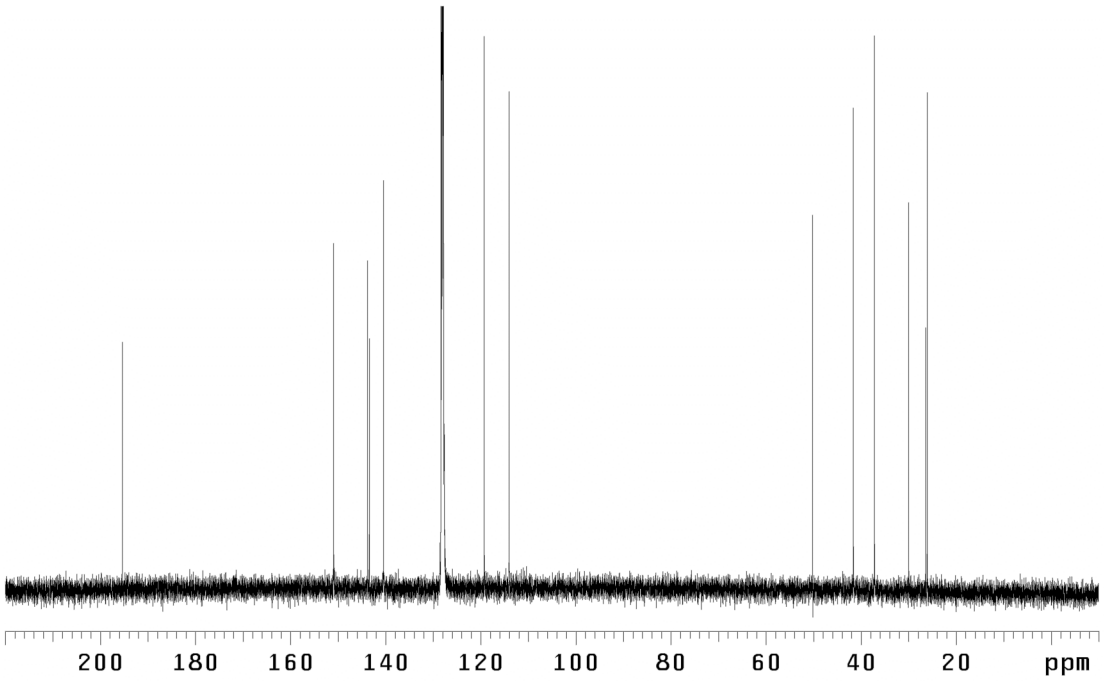


Figure SI-6E. ^{13}C NMR (125 MHz, C_6D_6) of compound **11**.

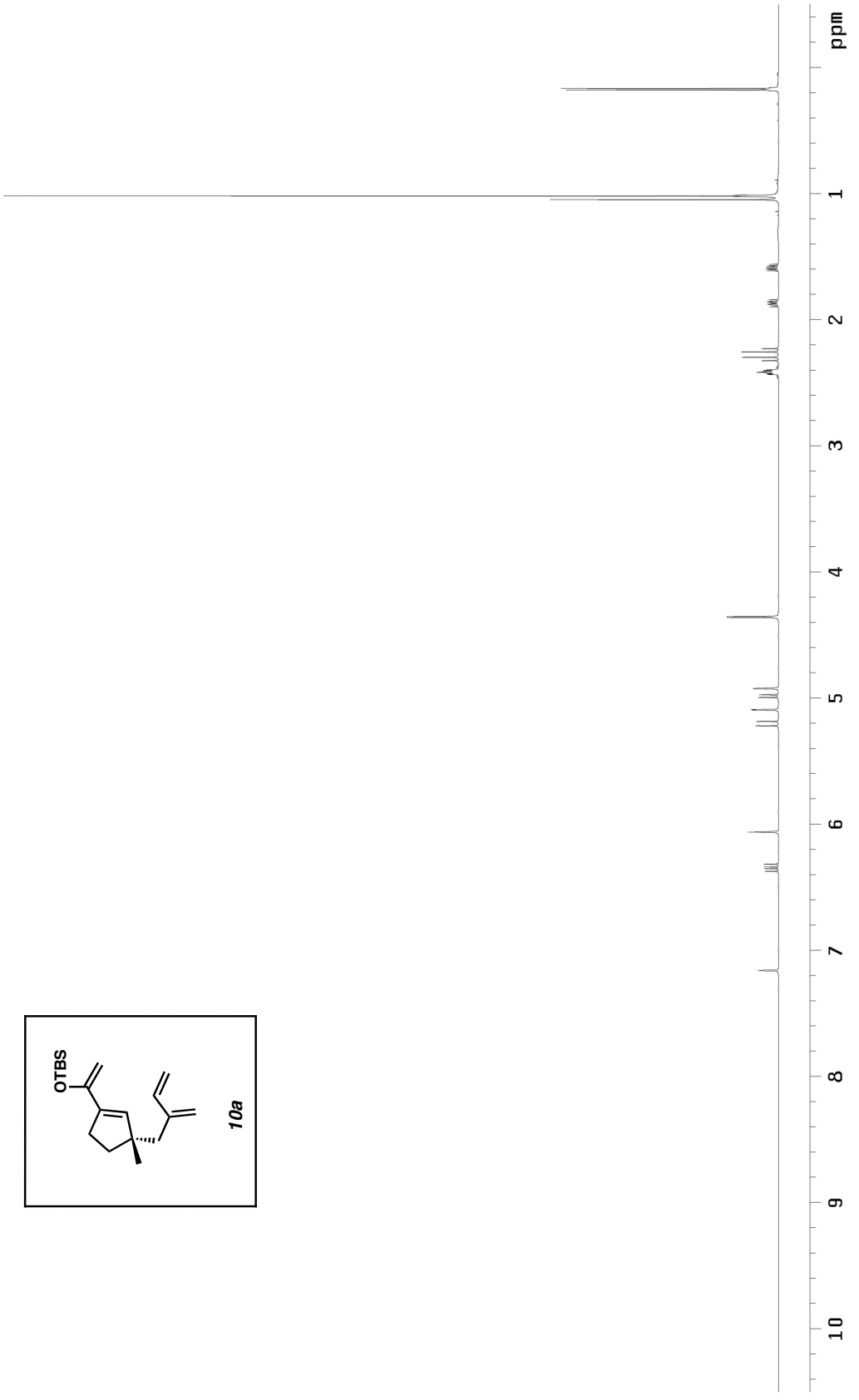


Figure SI-7A. ^{1}H NMR (500 MHz, C_6D_6) of compound **10a**.

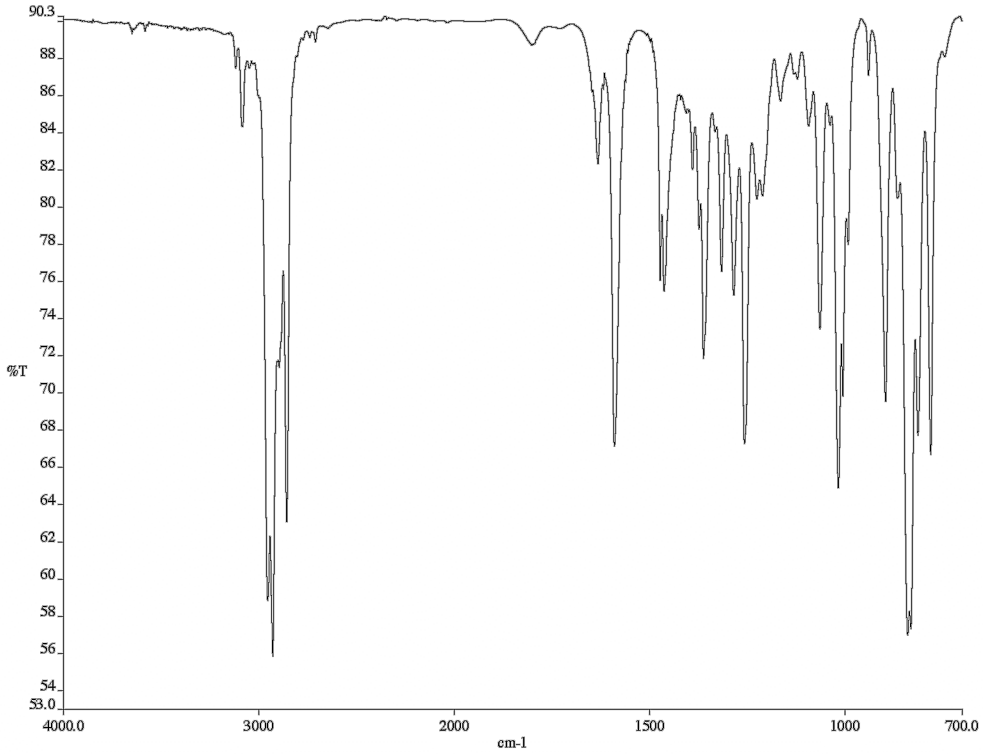


Figure SI-7B. Infrared spectrum (thin film/NaCl) of compound **10a.**

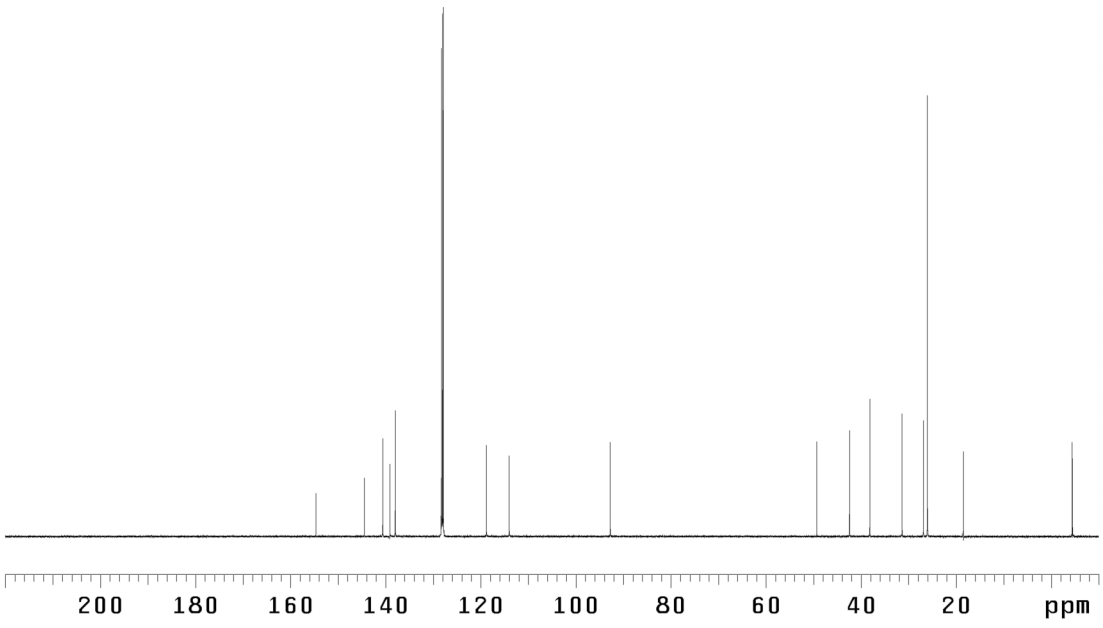


Figure SI-7C. ^{13}C NMR (125 MHz, C_6D_6) of compound **10a**.

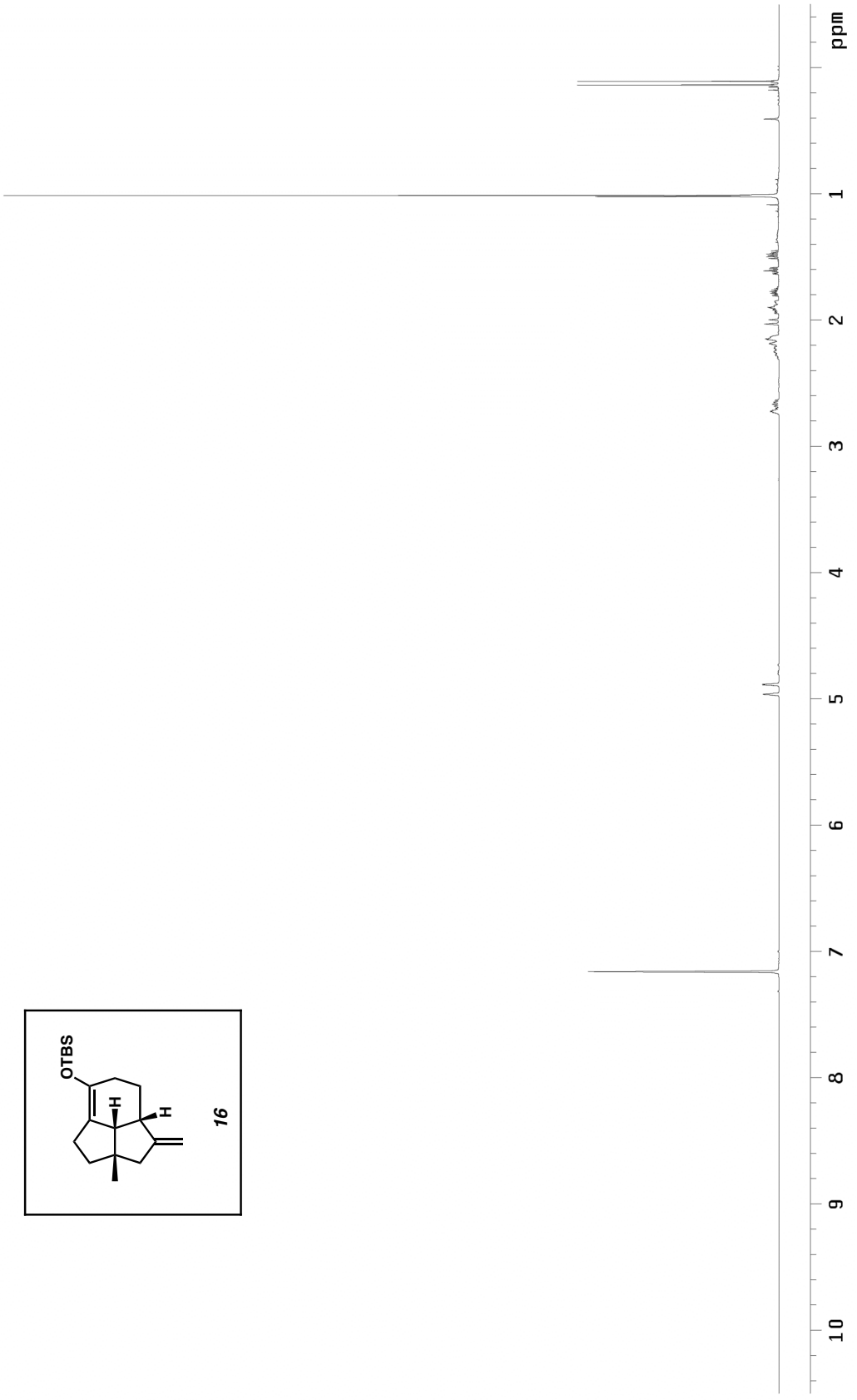


Figure SI-84. ^{1}H NMR (500 MHz, C_6D_6) of compound **16**.

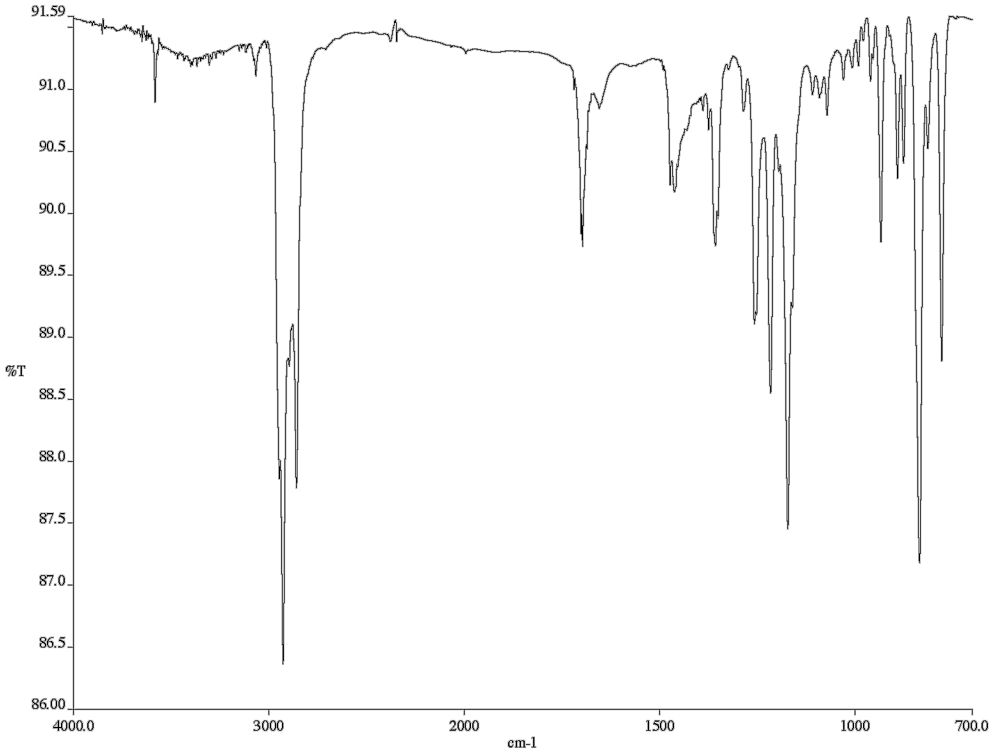


Figure SI-8B. Infrared spectrum (thin film/NaCl) of compound **16**.

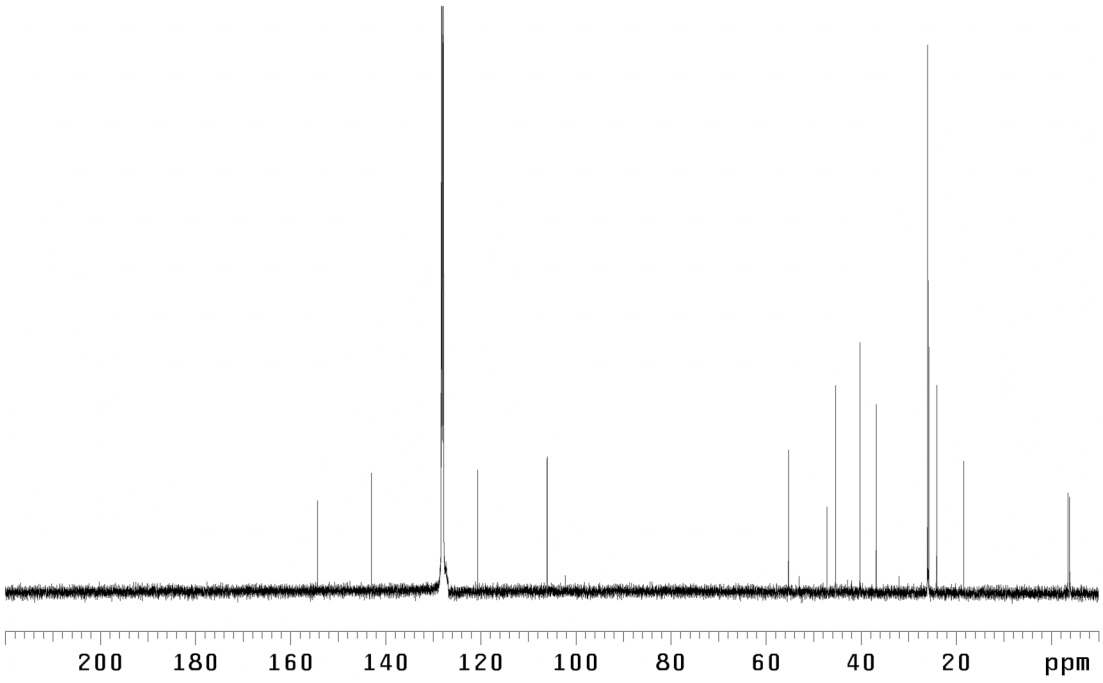


Figure SI-8C. ^{13}C NMR (125 MHz, C_6D_6) of compound **16**.

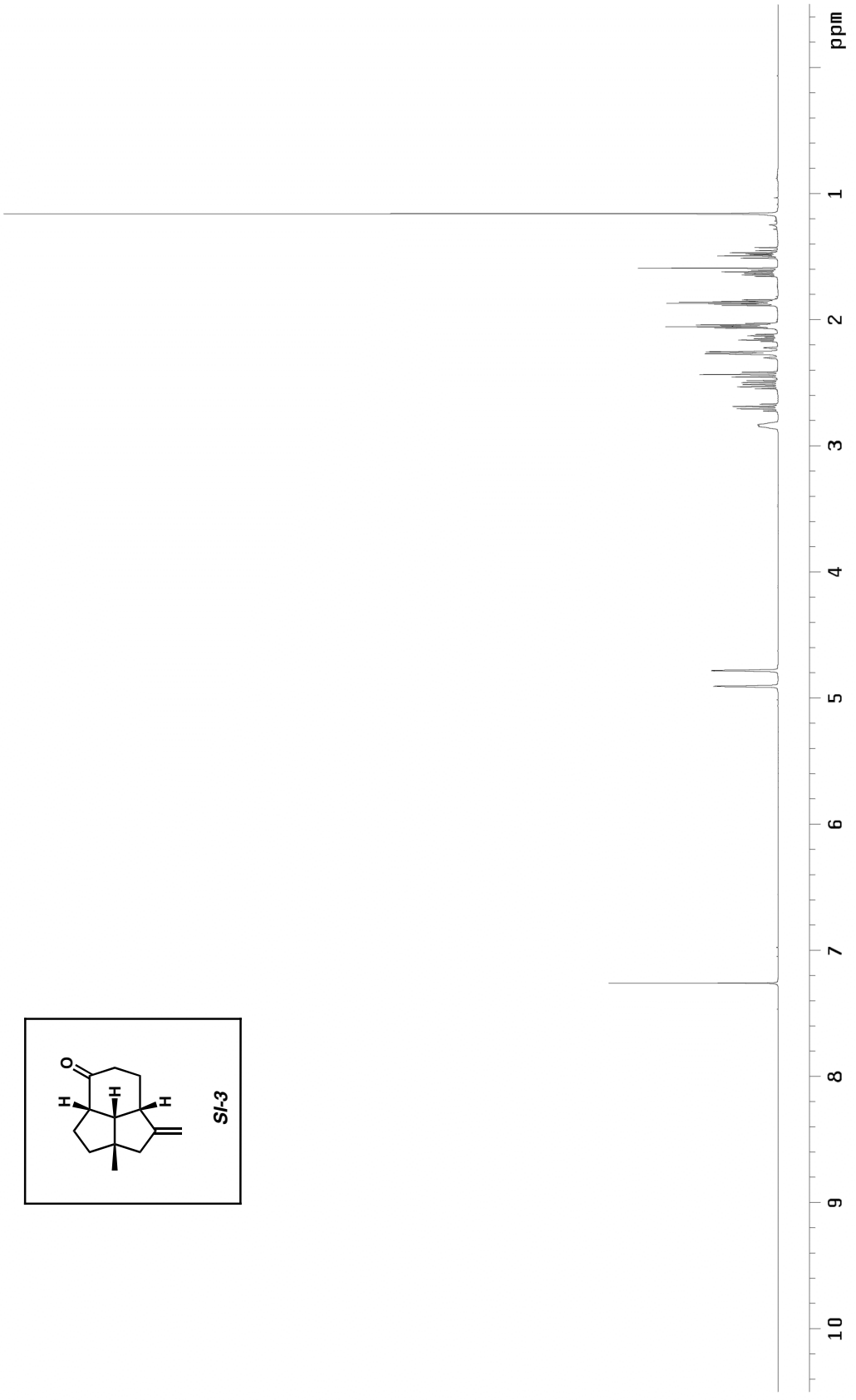


Figure SI-9A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-3**.

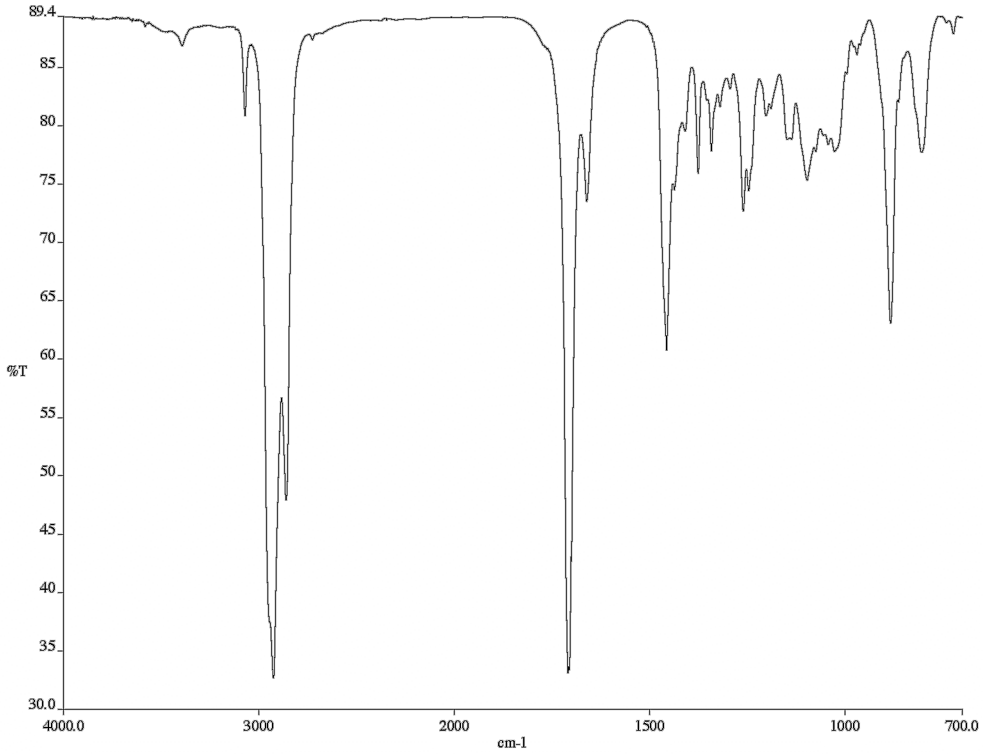


Figure SI-9B. Infrared spectrum (thin film/NaCl) of compound **SI-3**.

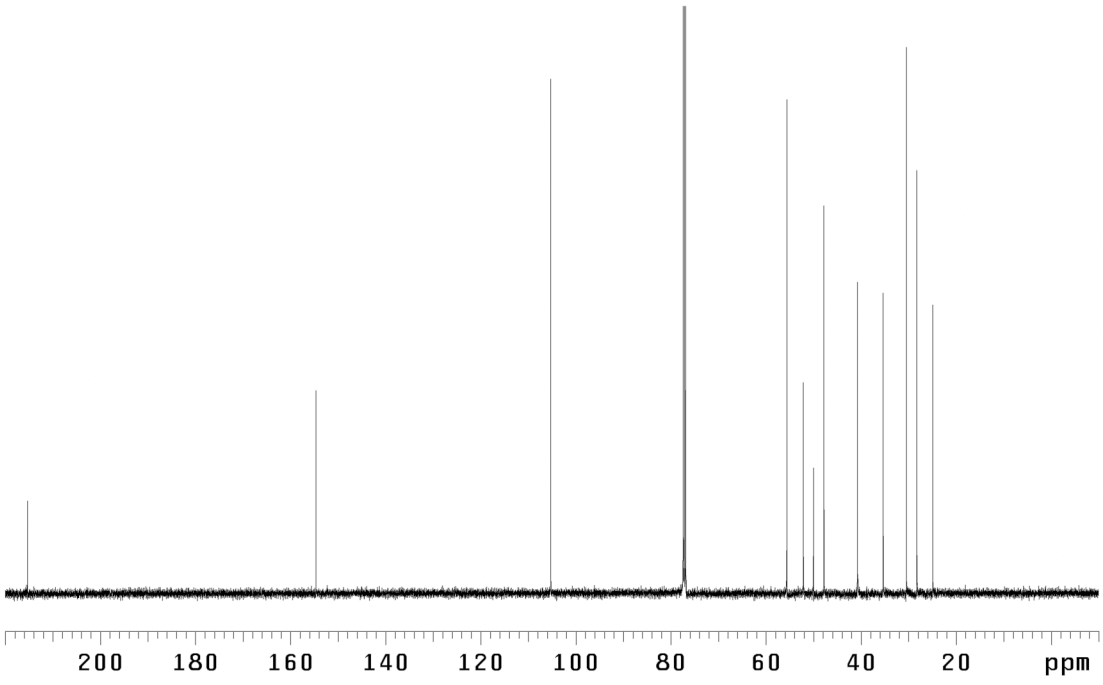


Figure SI-9C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-3**.

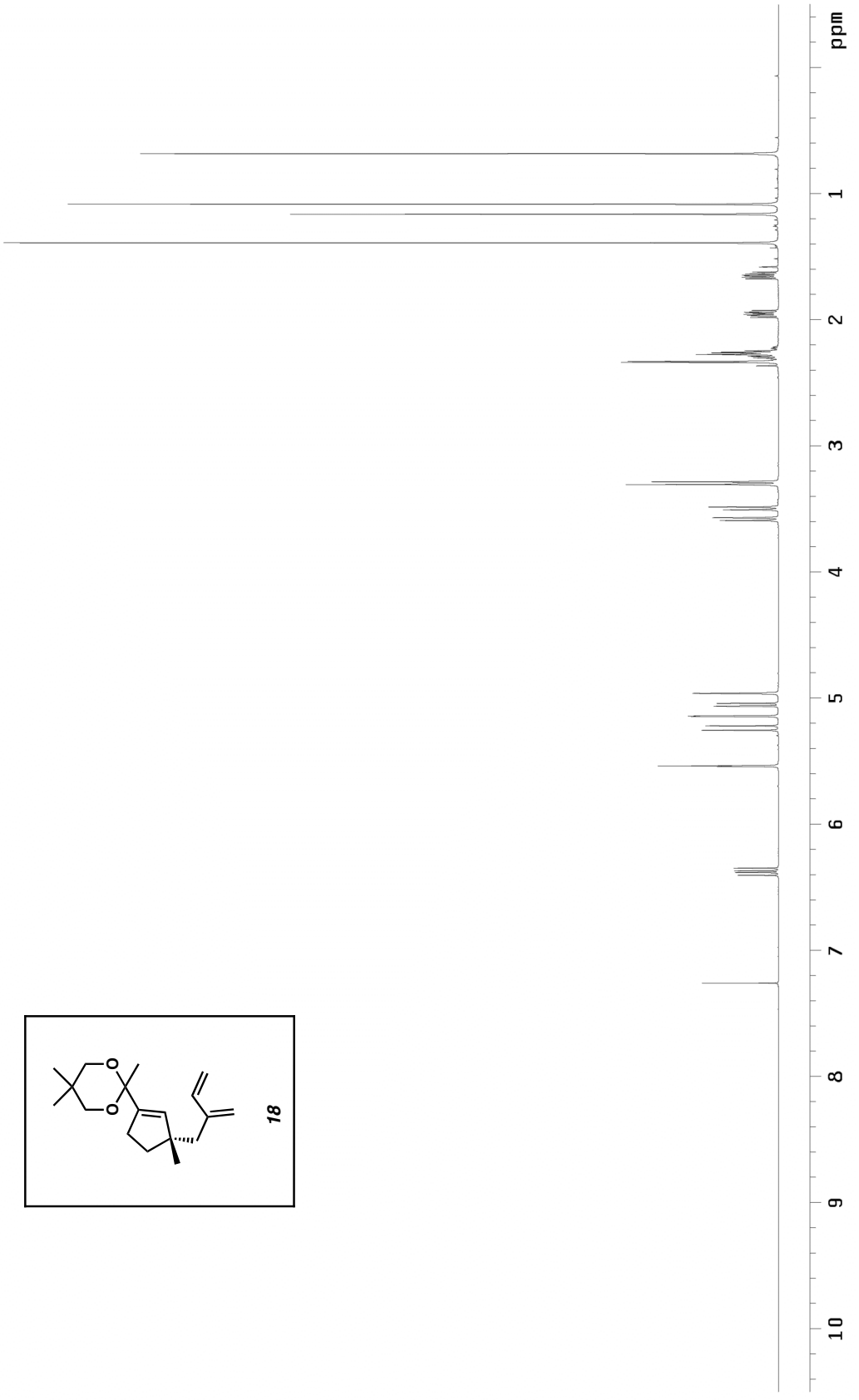


Figure SI-10A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **18**.

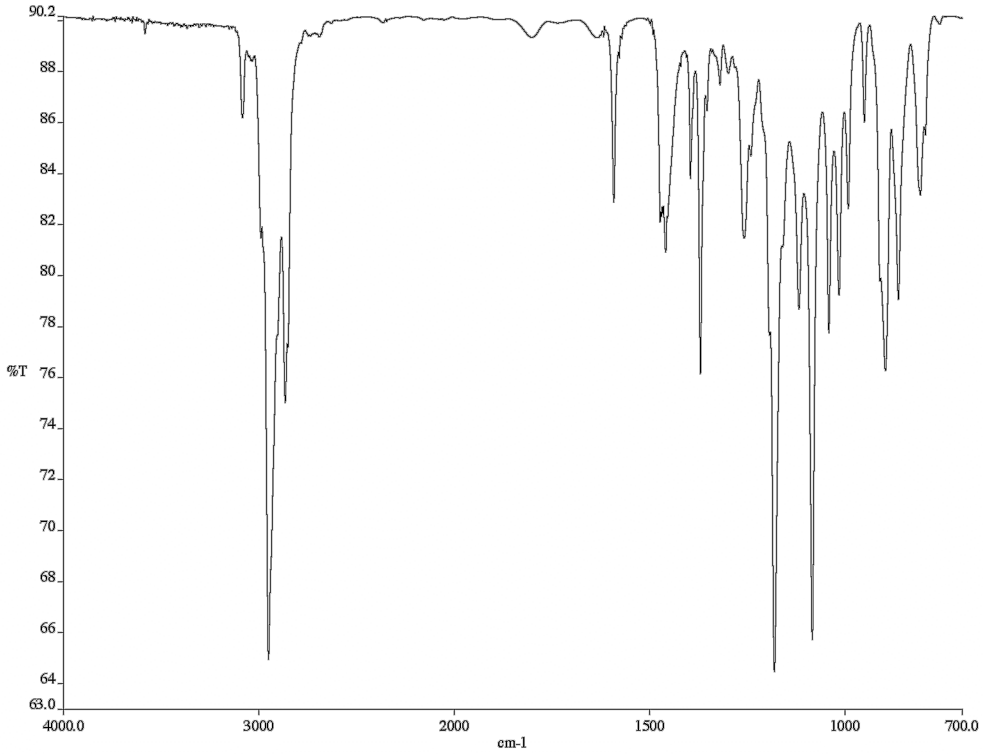


Figure SI-10B. Infrared spectrum (thin film/NaCl) of compound **18**.

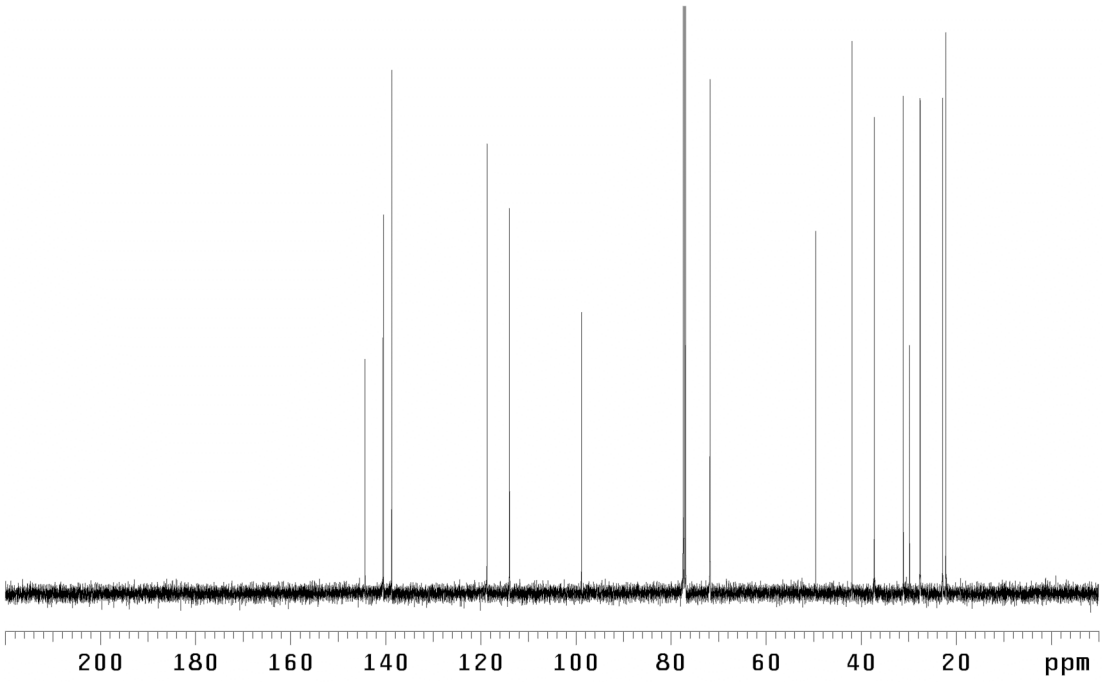


Figure SI-10C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **18**.

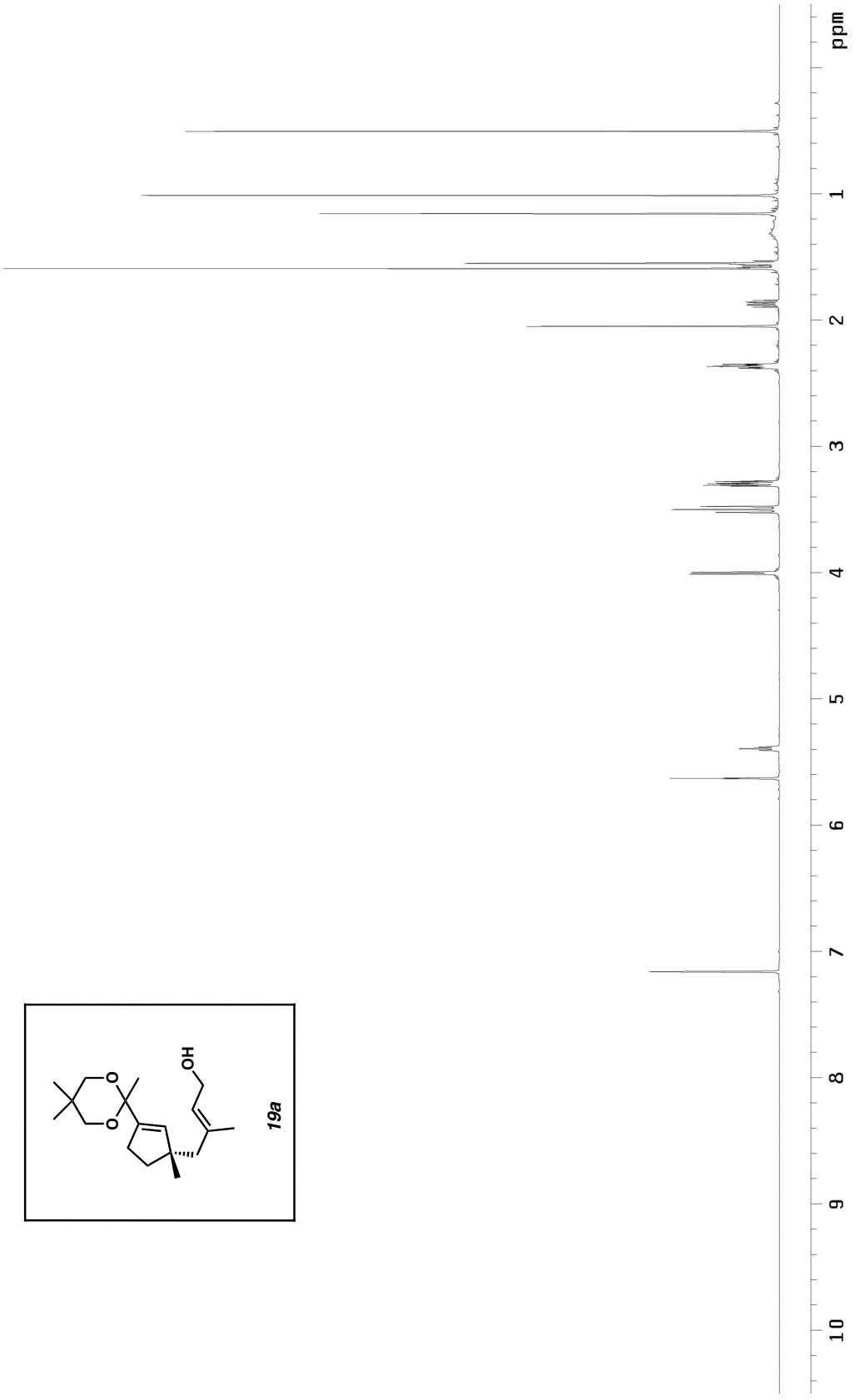


Figure SI-11A. ^{1}H NMR (500 MHz, C_6D_6) of compound **19a**.

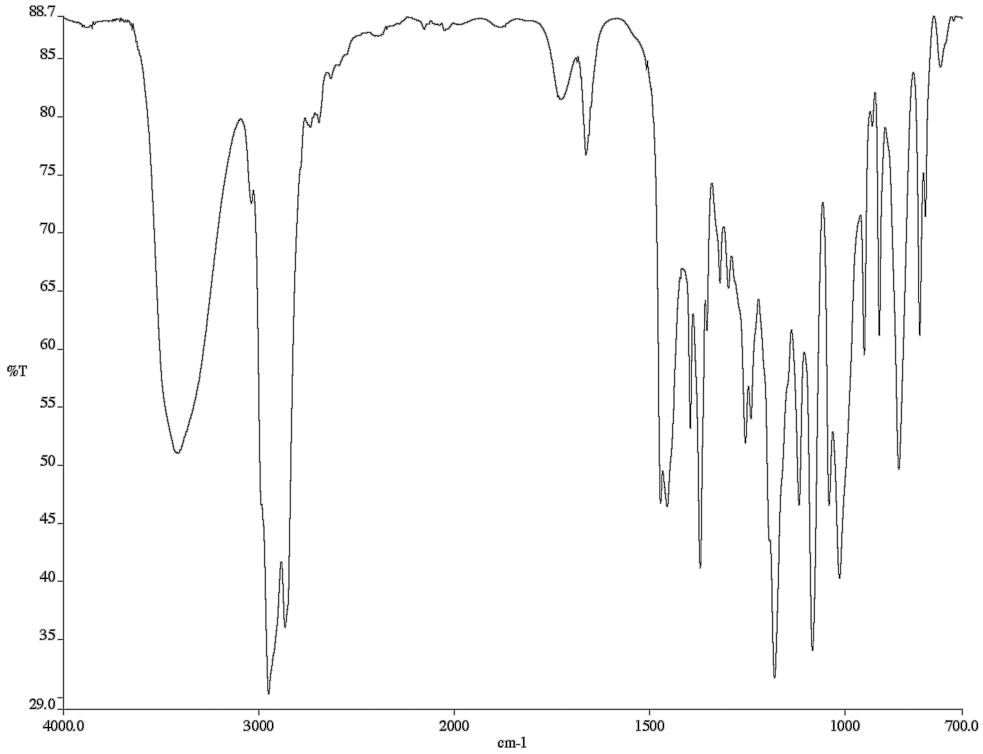


Figure SI-11B. Infrared spectrum (thin film/NaCl) of compound **19a**.

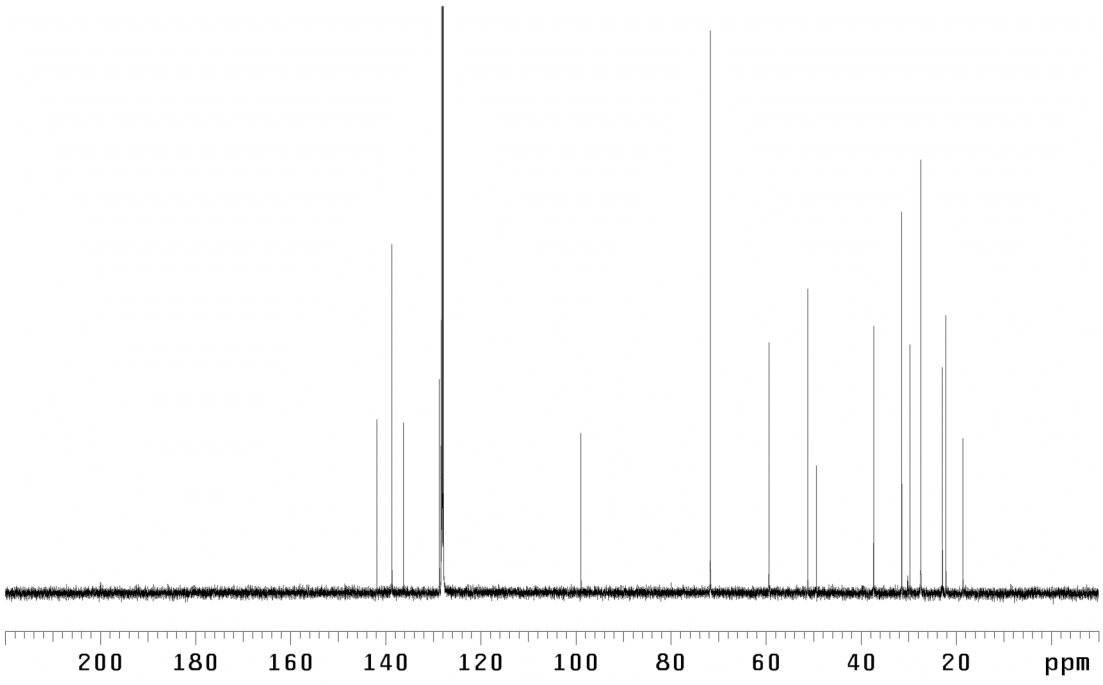


Figure SI-11C. ^{13}C NMR (125 MHz, C_6D_6) of compound **19a**.

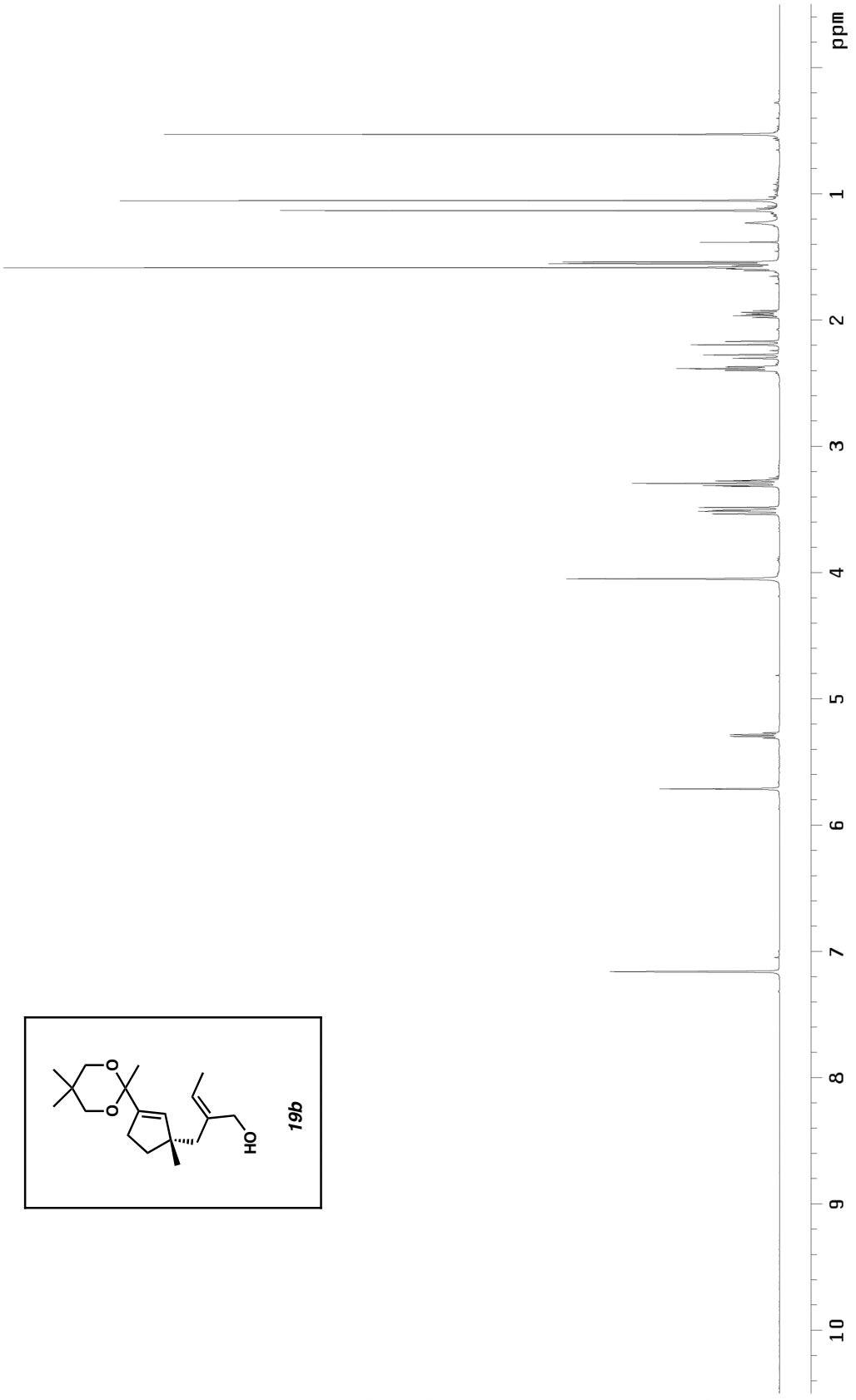


Figure SI-12A. ^{1}H NMR (500 MHz, C_6D_6) of compound **19b**.

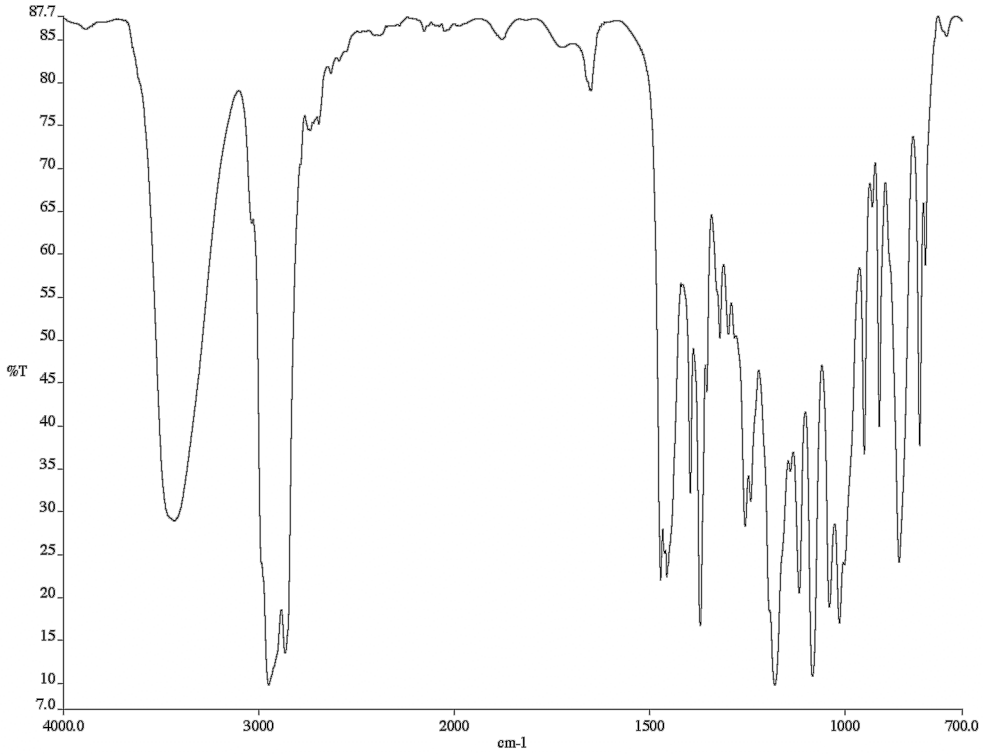


Figure SI-12B. Infrared spectrum (thin film/NaCl) of compound **19b**.

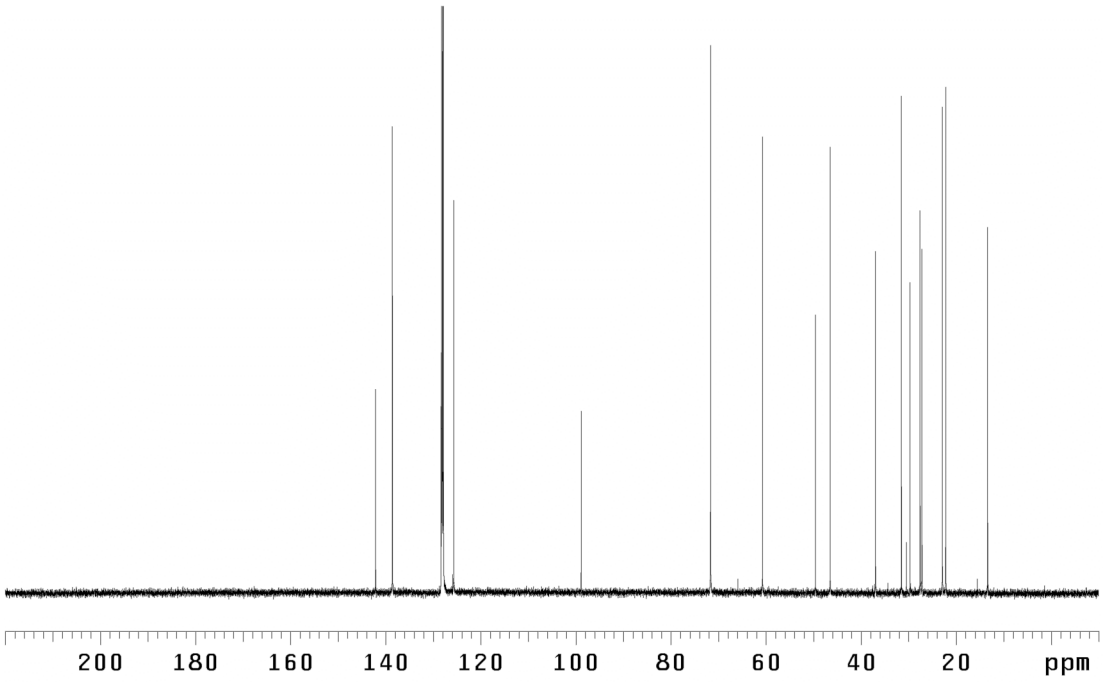


Figure SI-12C. ^{13}C NMR (125 MHz, C_6D_6) of compound **19b**.

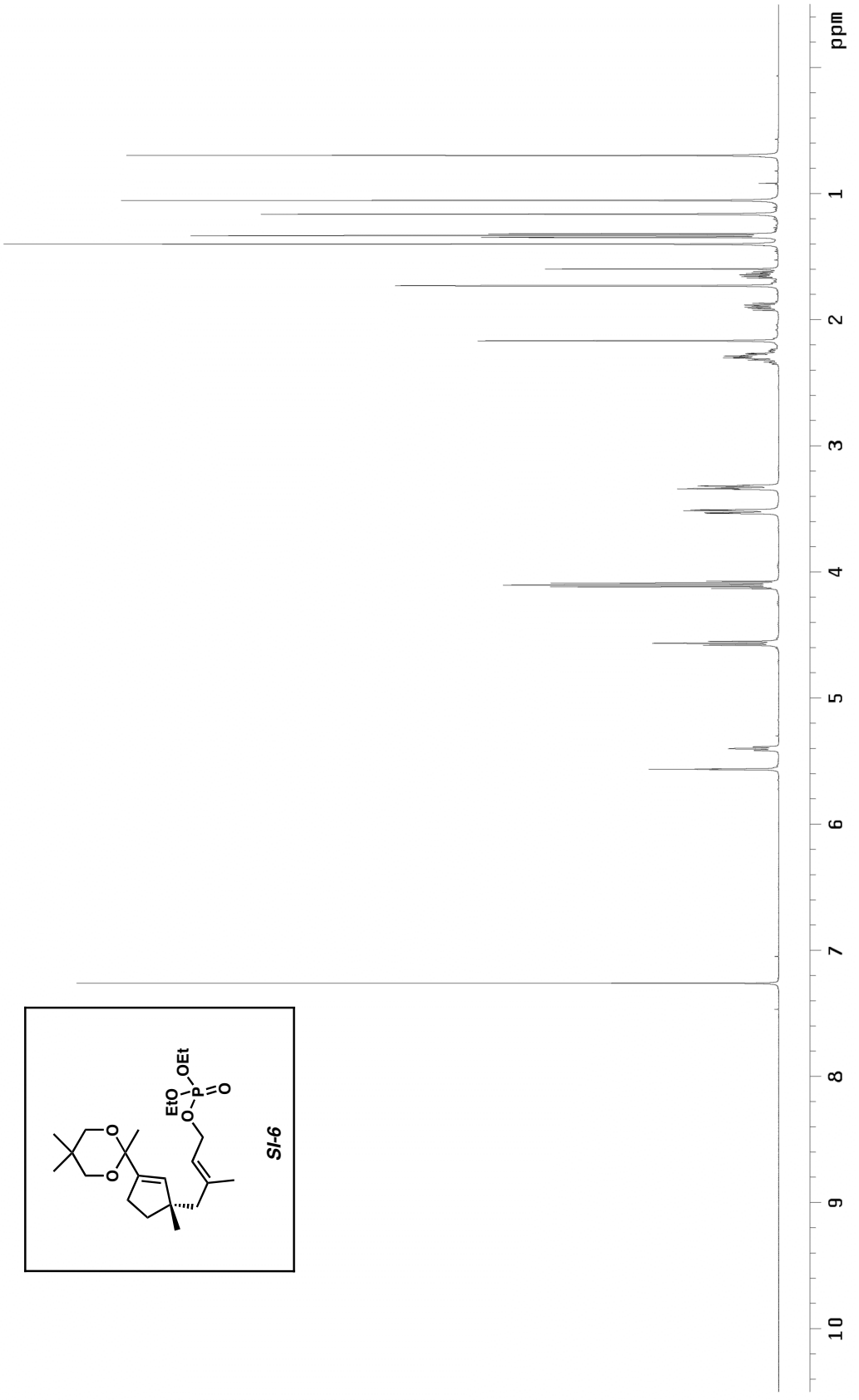


Figure SI-13A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-6**.

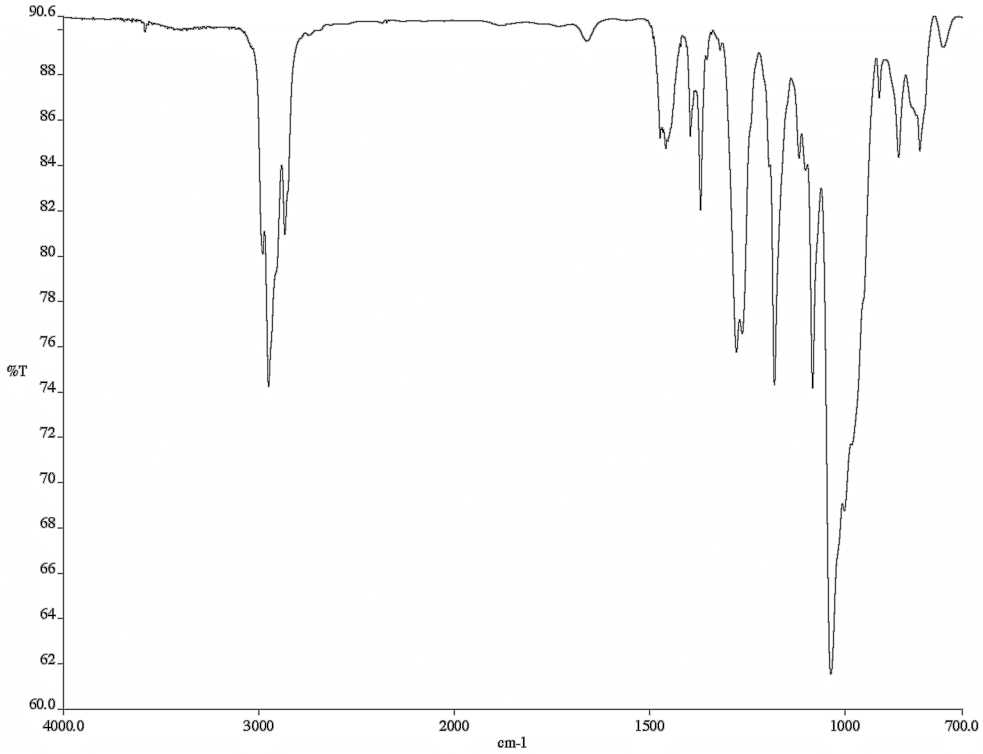


Figure SI-13B. Infrared spectrum (thin film/NaCl) of compound **SI-6**.

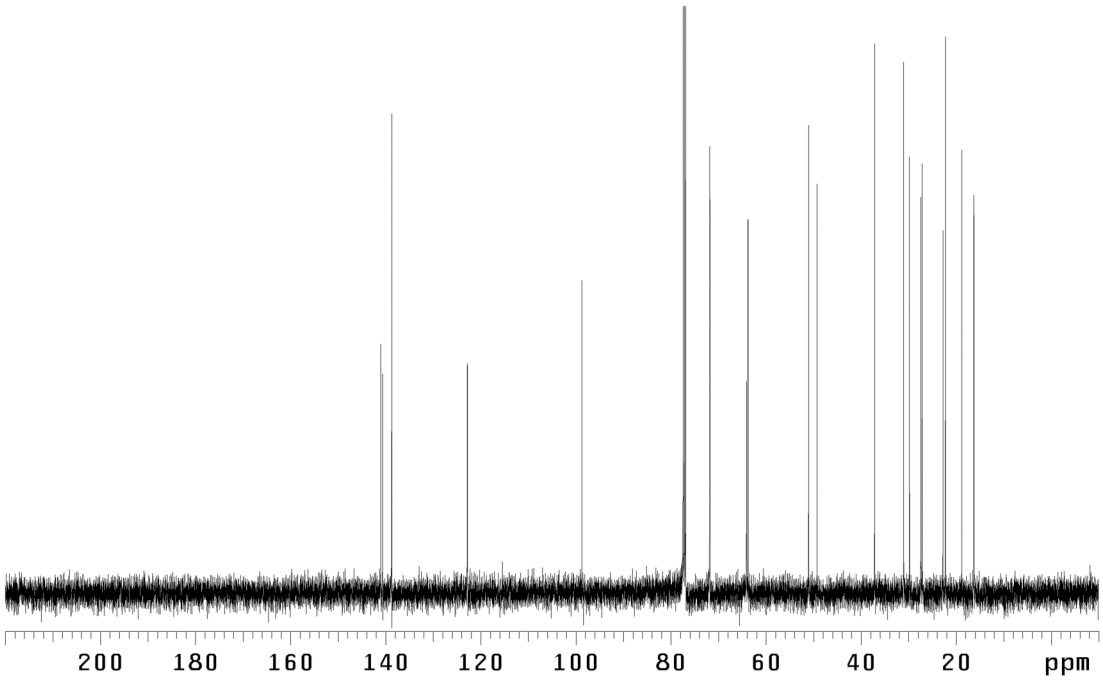


Figure SI-13C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **SI-6**.

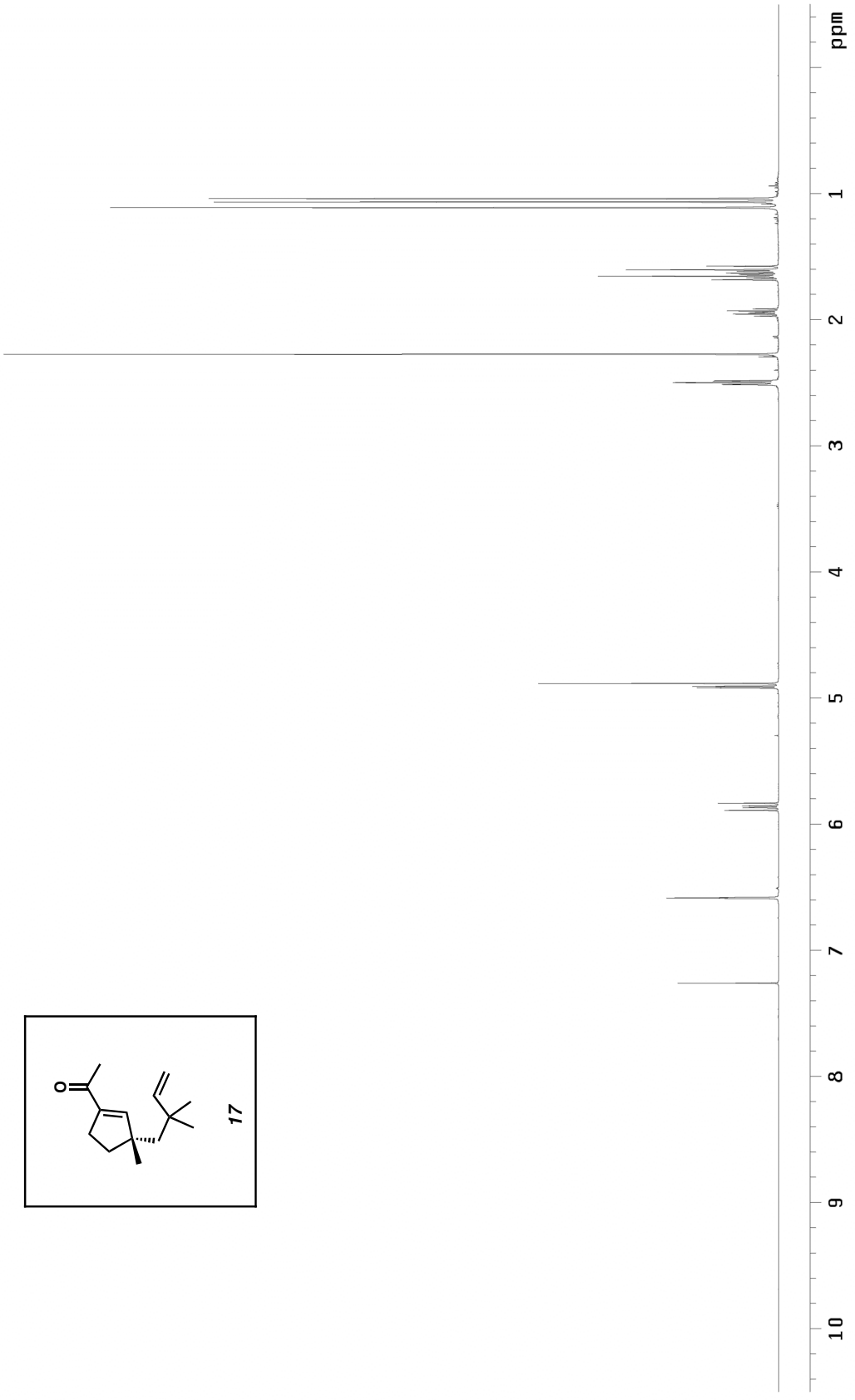


Figure SI-14A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17**.

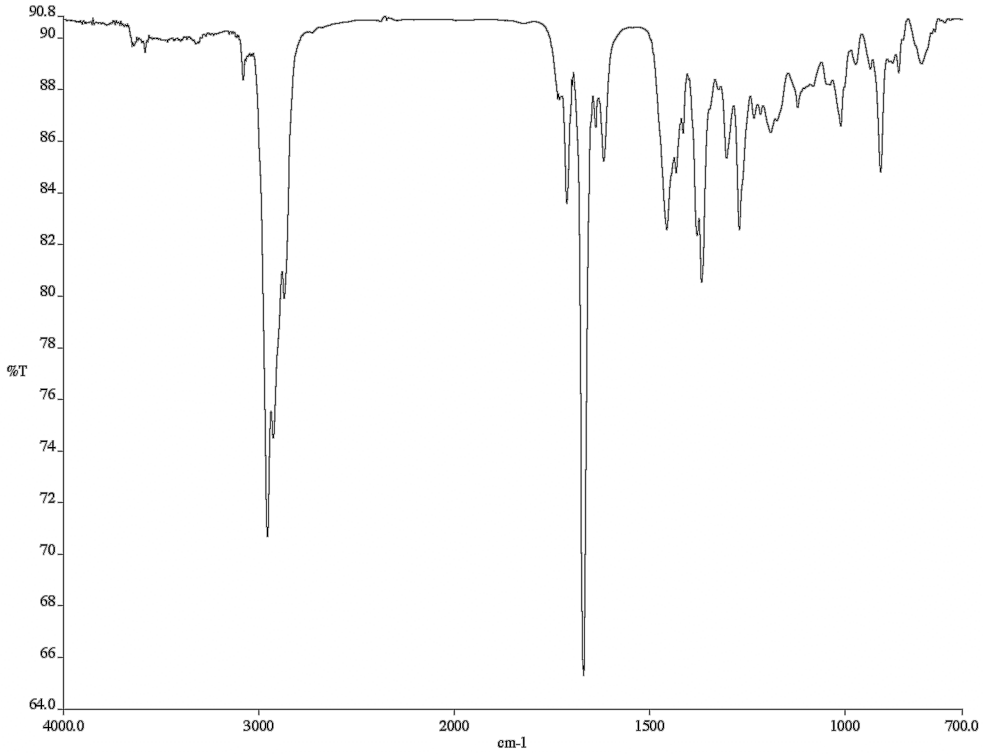


Figure SI-14B. Infrared spectrum (thin film/NaCl) of compound **17**.

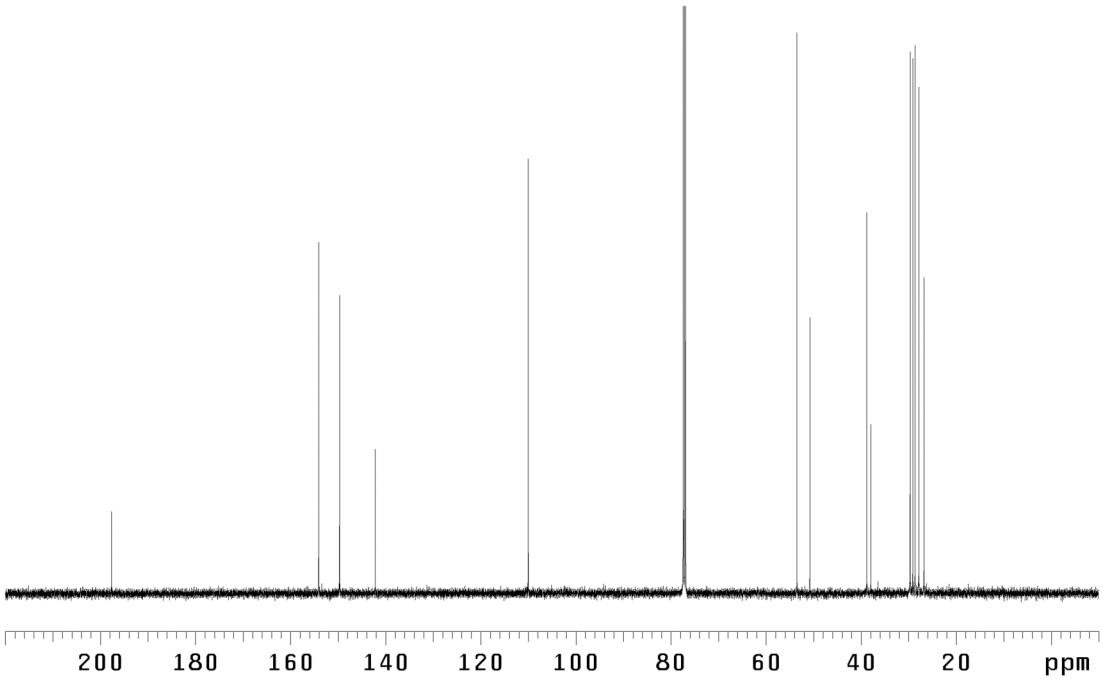


Figure SI-14C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **17**.

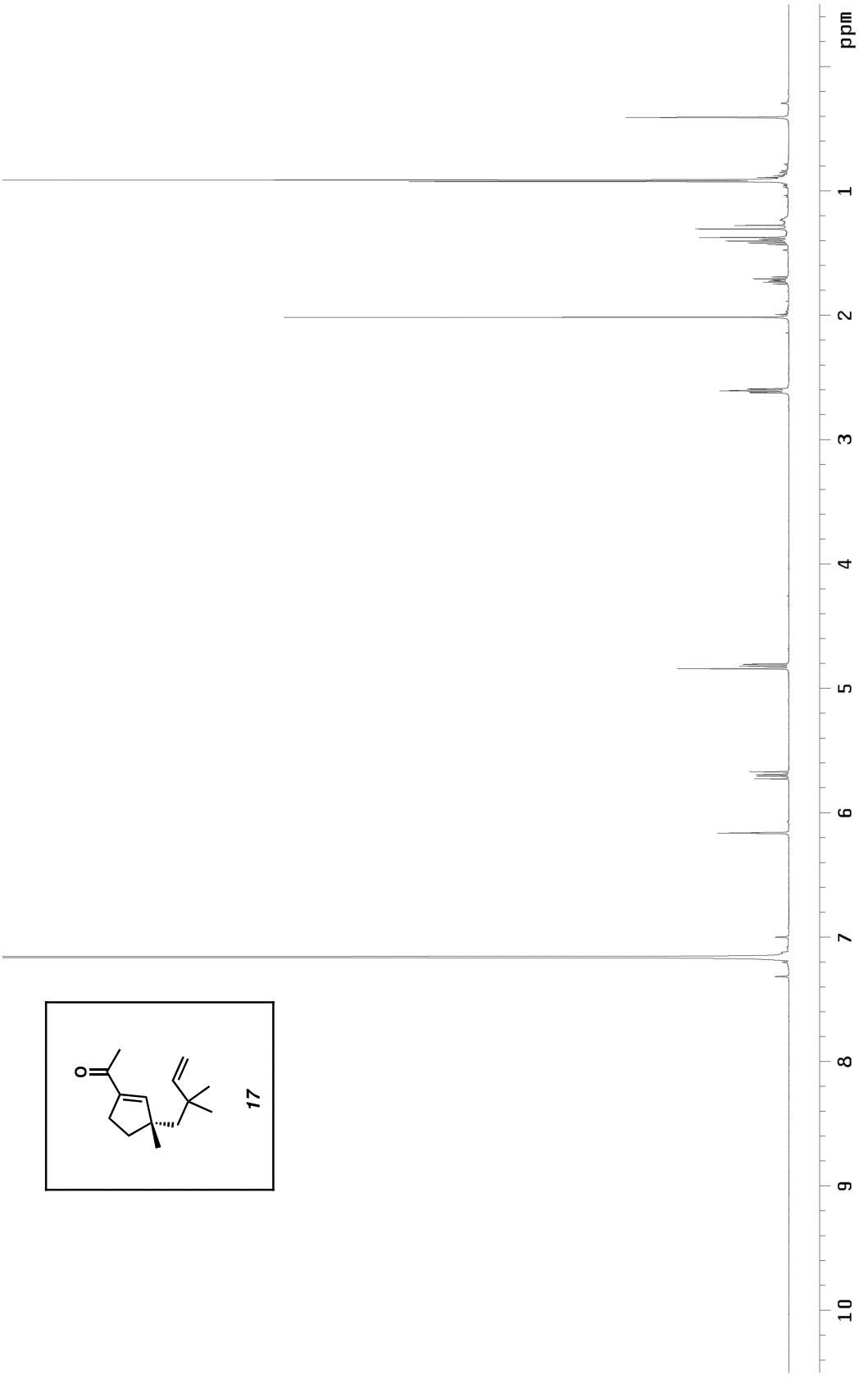


Figure SI-14D. ^{1}H NMR (500 MHz, C_6D_6) of compound **17**.

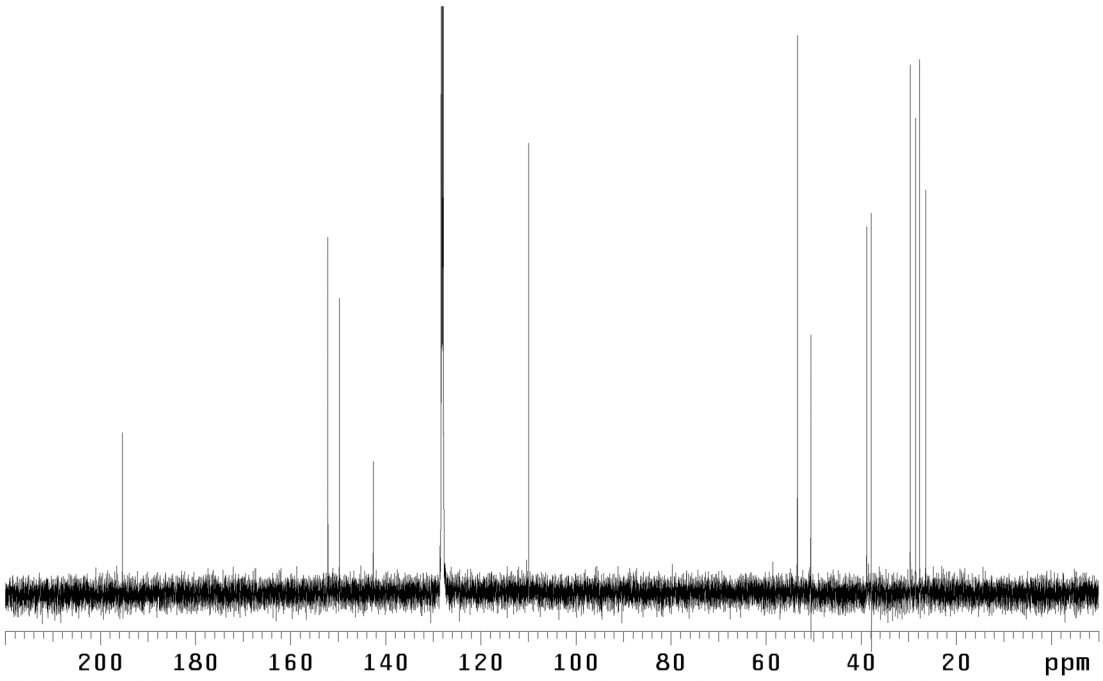


Figure SI-14E. ^{13}C NMR (125 MHz, C_6D_6) of compound **17**.

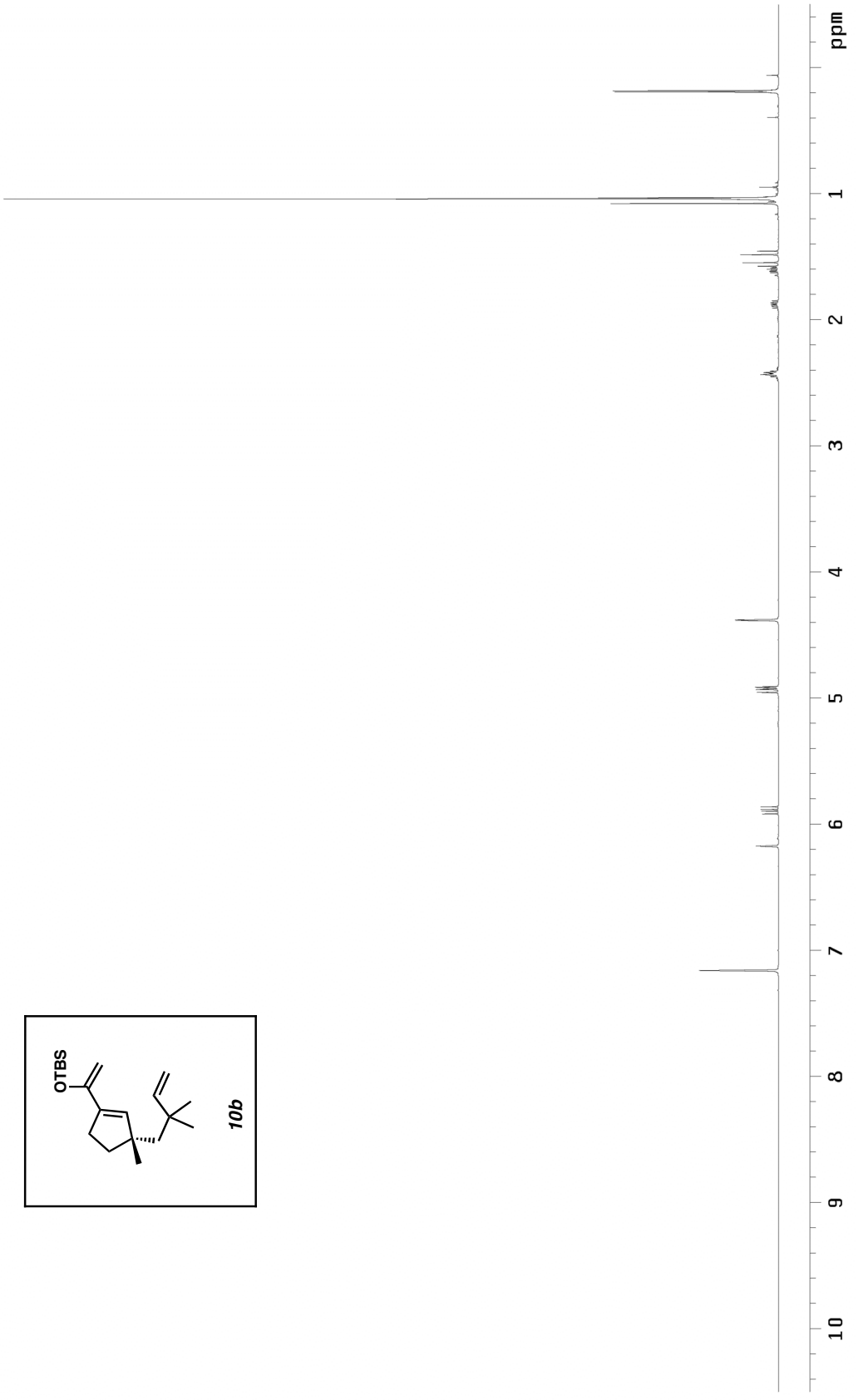


Figure SI-15A. ^{1}H NMR (500 MHz, C_6D_6) of compound **10b**.

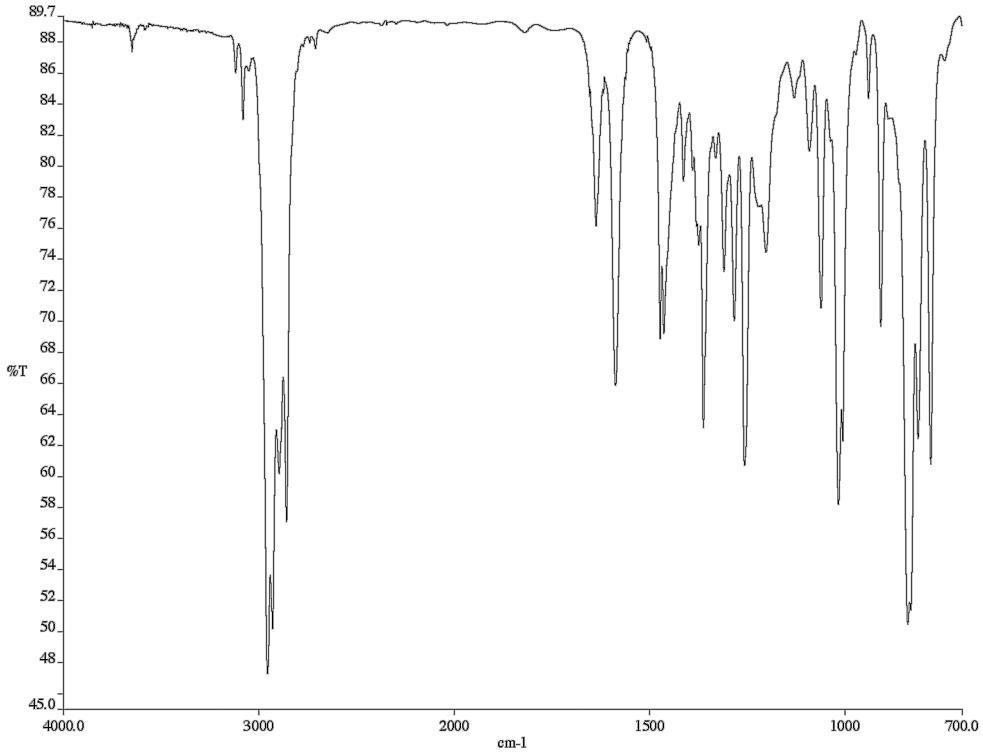


Figure SI-15B. Infrared spectrum (thin film/NaCl) of compound **10b**.

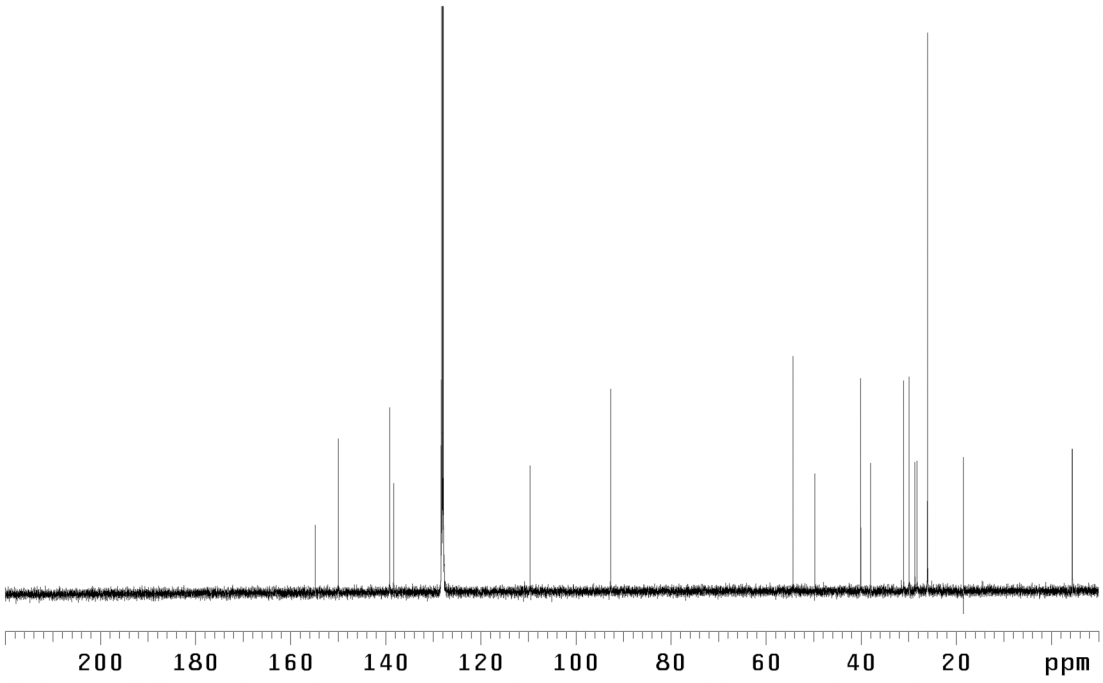


Figure SI-15C. ^{13}C NMR (125 MHz, C_6D_6) of compound **10b**.

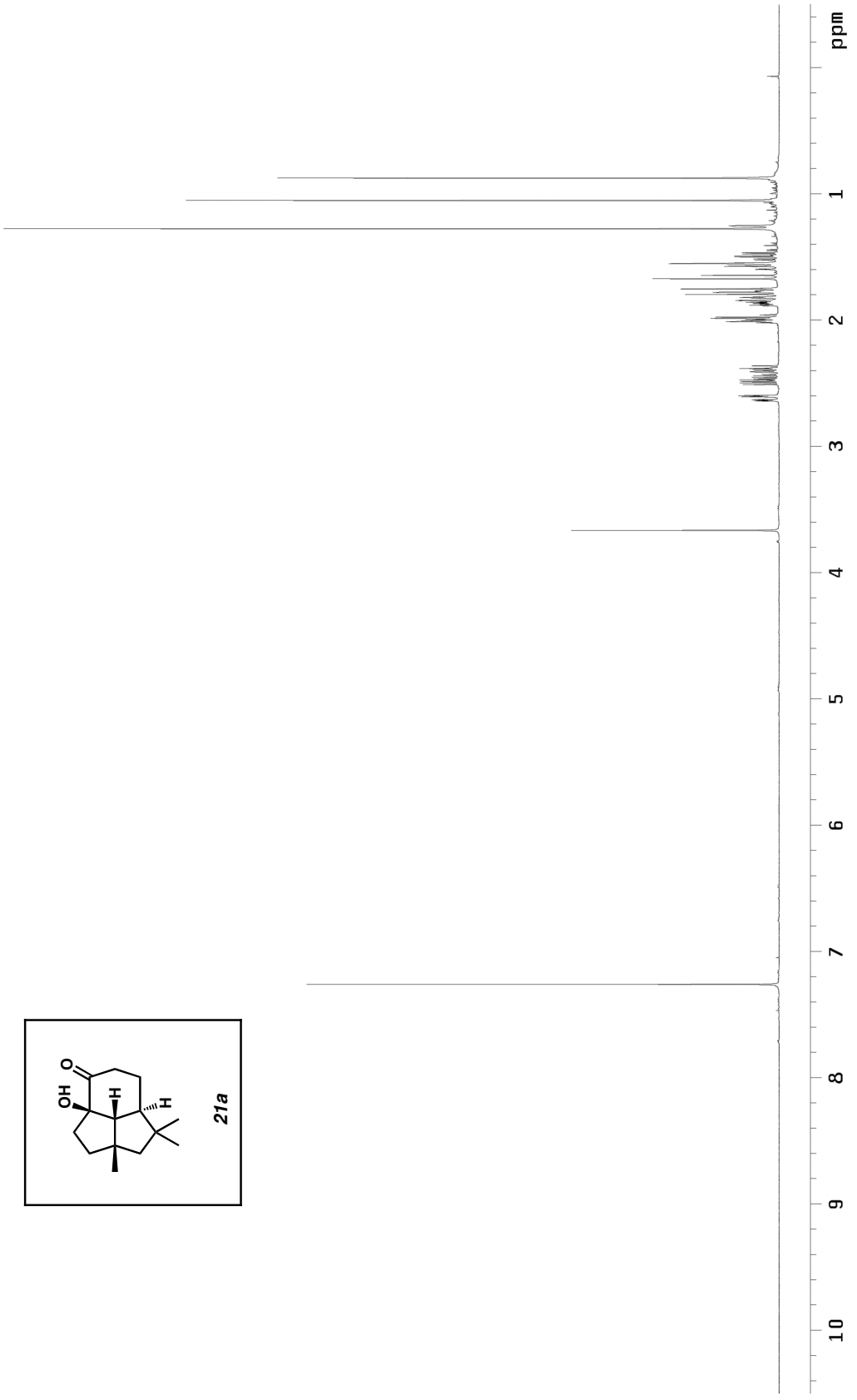


Figure SI-16A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **21a**.

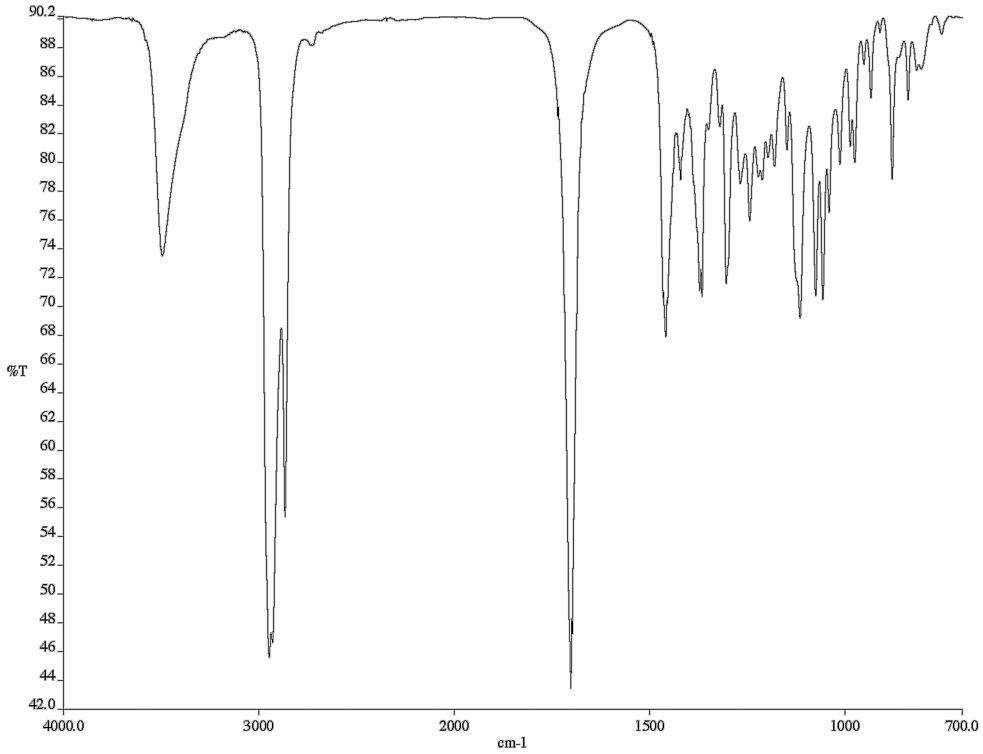


Figure SI-16B. Infrared spectrum (thin film/NaCl) of compound **21a**.

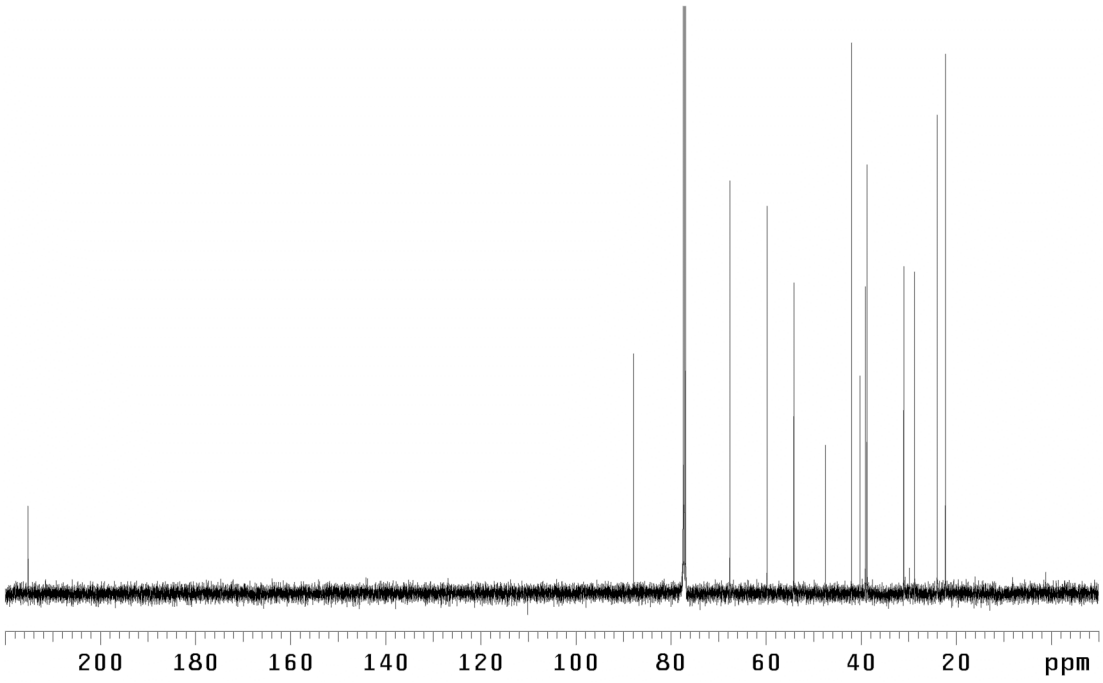


Figure SI-16C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **21a**.

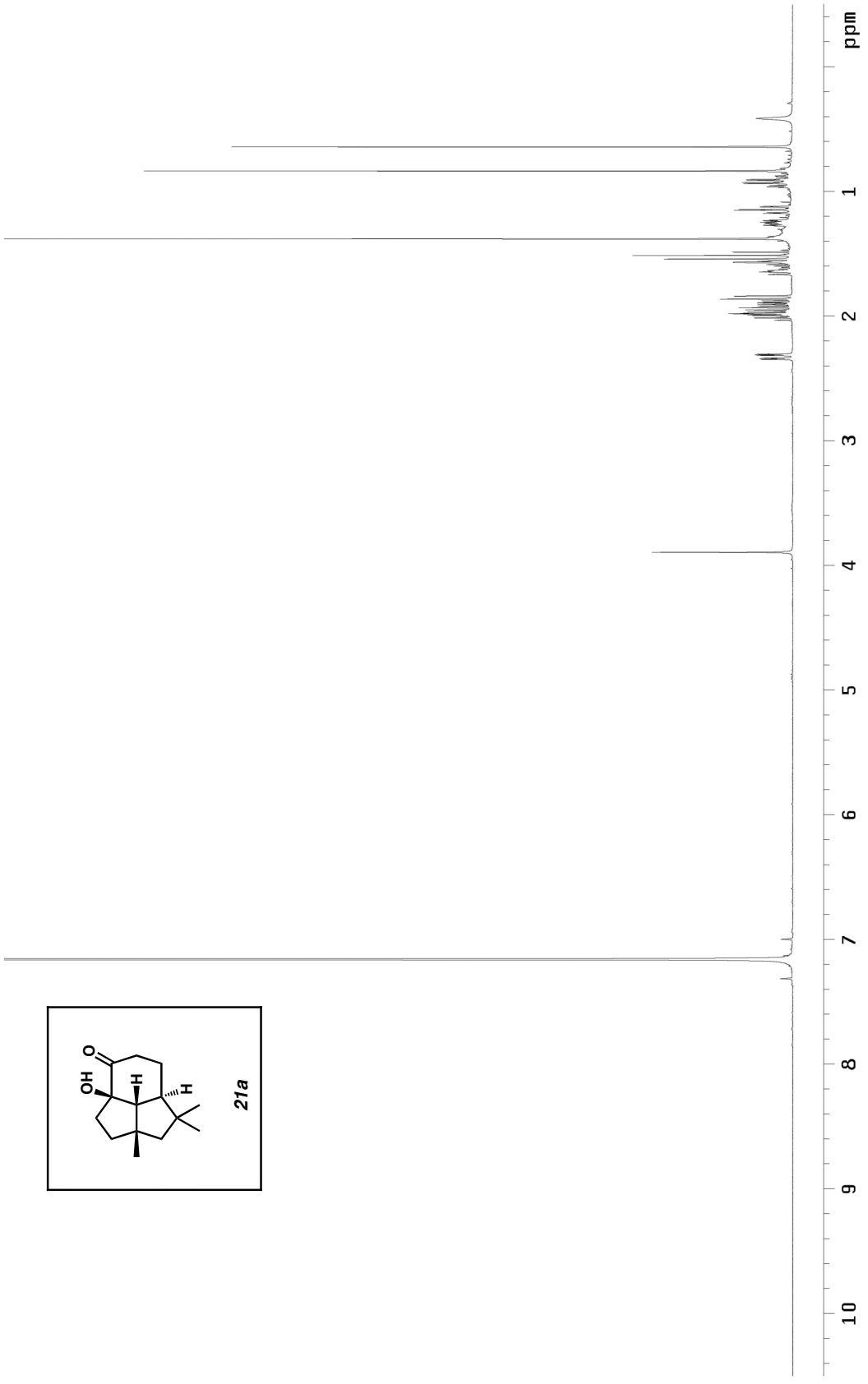


Figure SI-16D. ^{1}H NMR (500 MHz, C_6D_6) of compound **21a**.

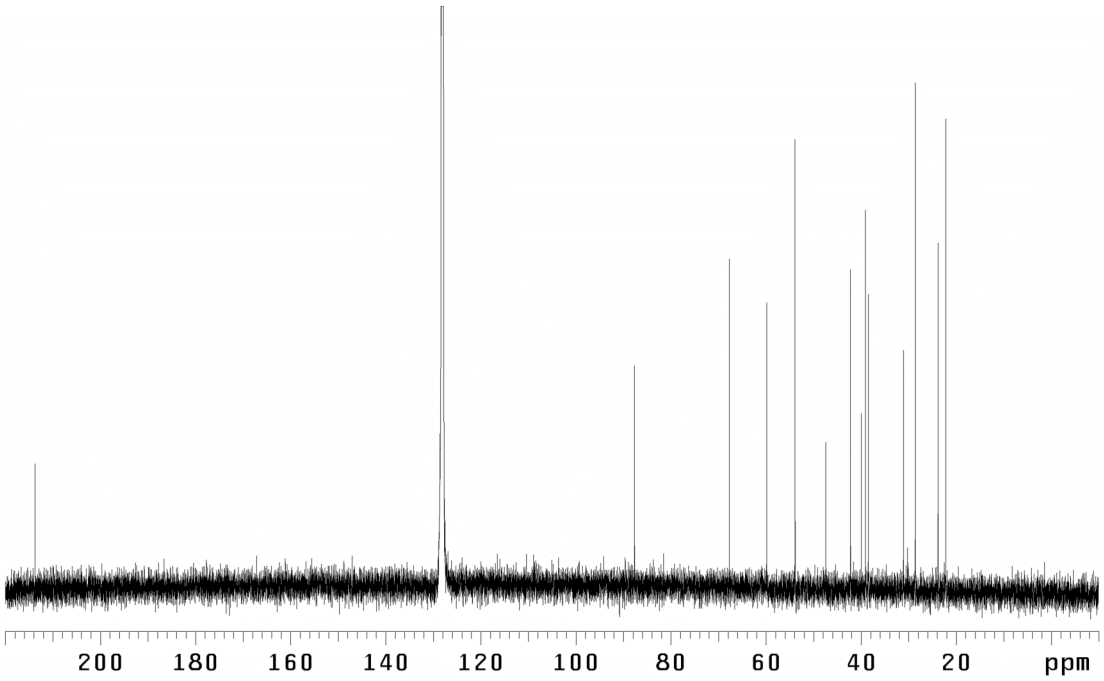


Figure SI-16E. ^{13}C NMR (125 MHz, C_6D_6) of compound **21a**.

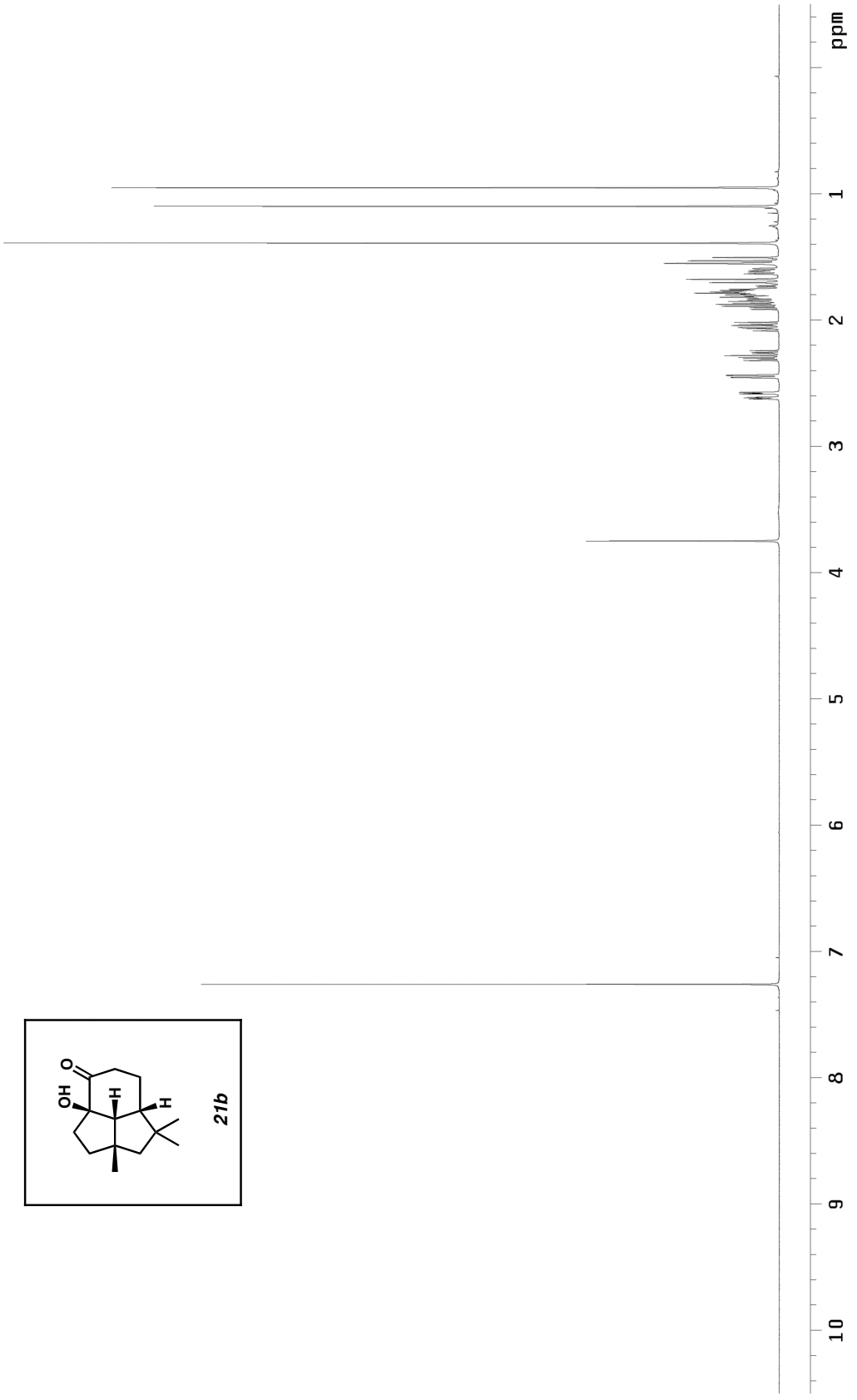


Figure SI-17A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **21b**.

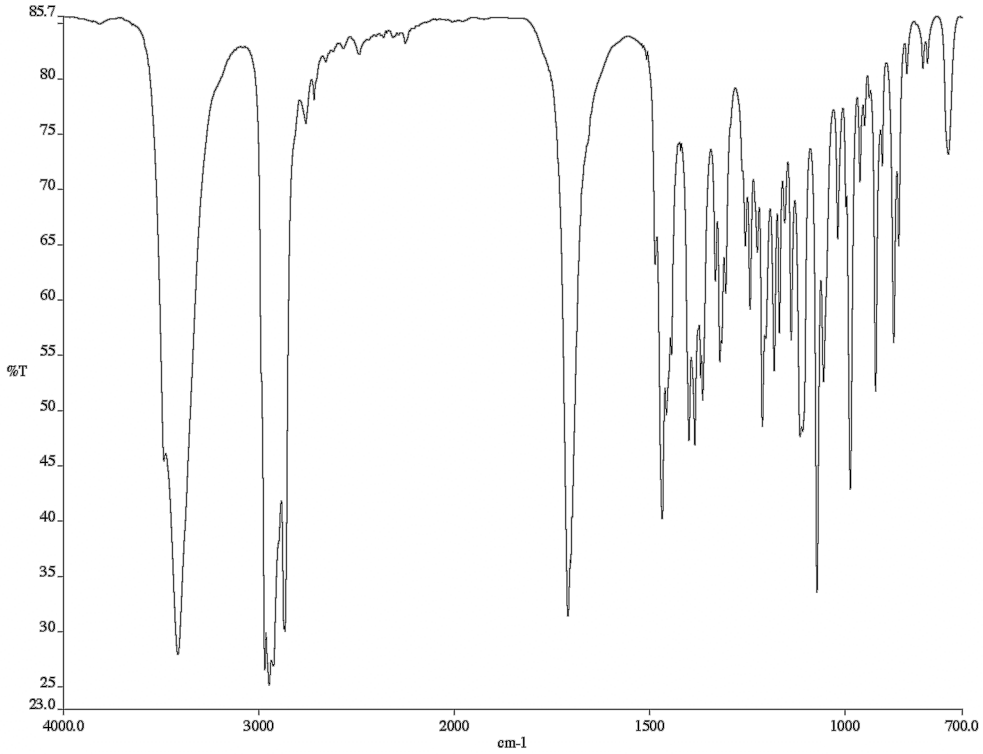


Figure SI-17B. Infrared spectrum (thin film/NaCl) of compound **21b**.

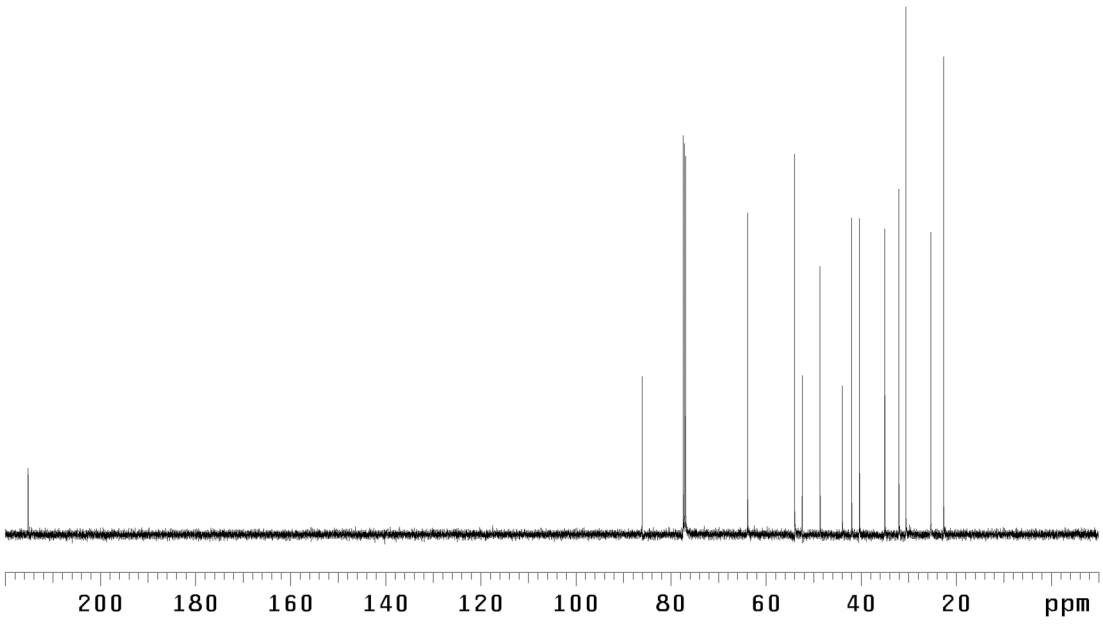


Figure SI-17C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **21b**.

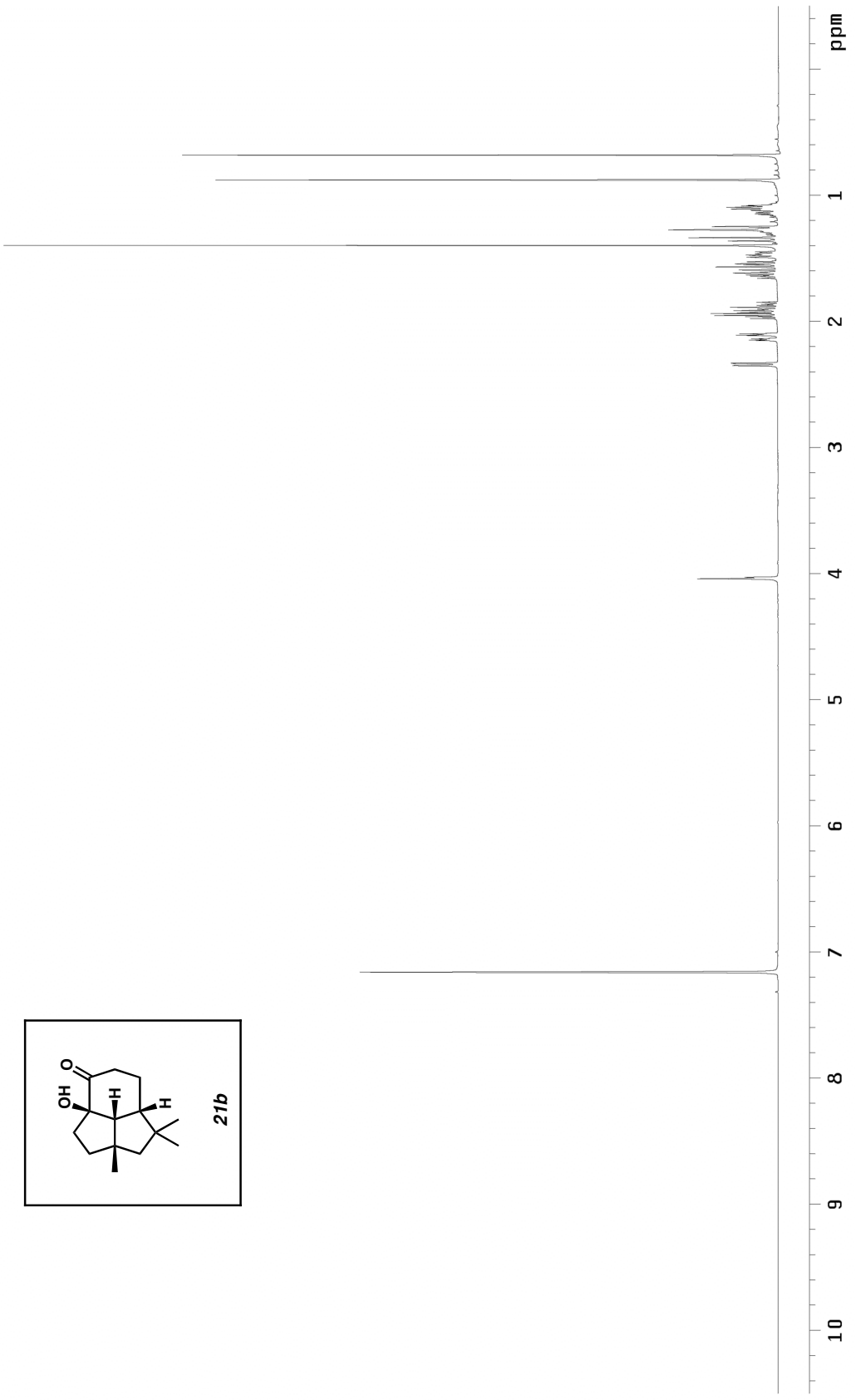


Figure SI-17D. ^{1}H NMR (500 MHz, C_6D_6) of compound **21b**.

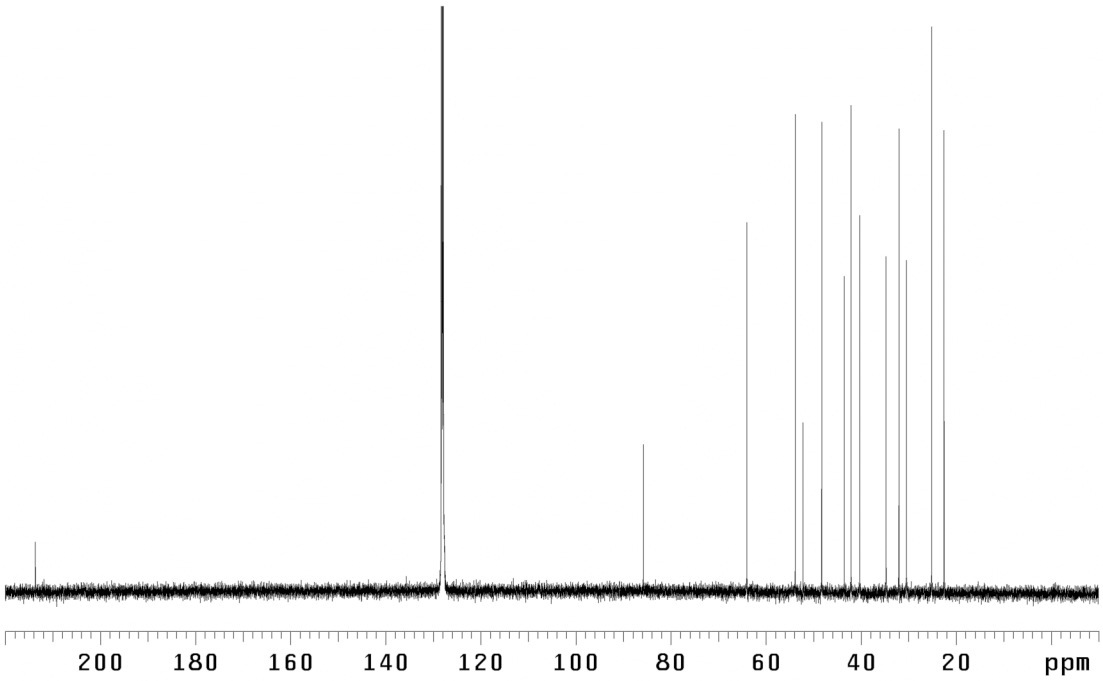


Figure SI-17E. ^{13}C NMR (125 MHz, C_6D_6) of compound **21b**.

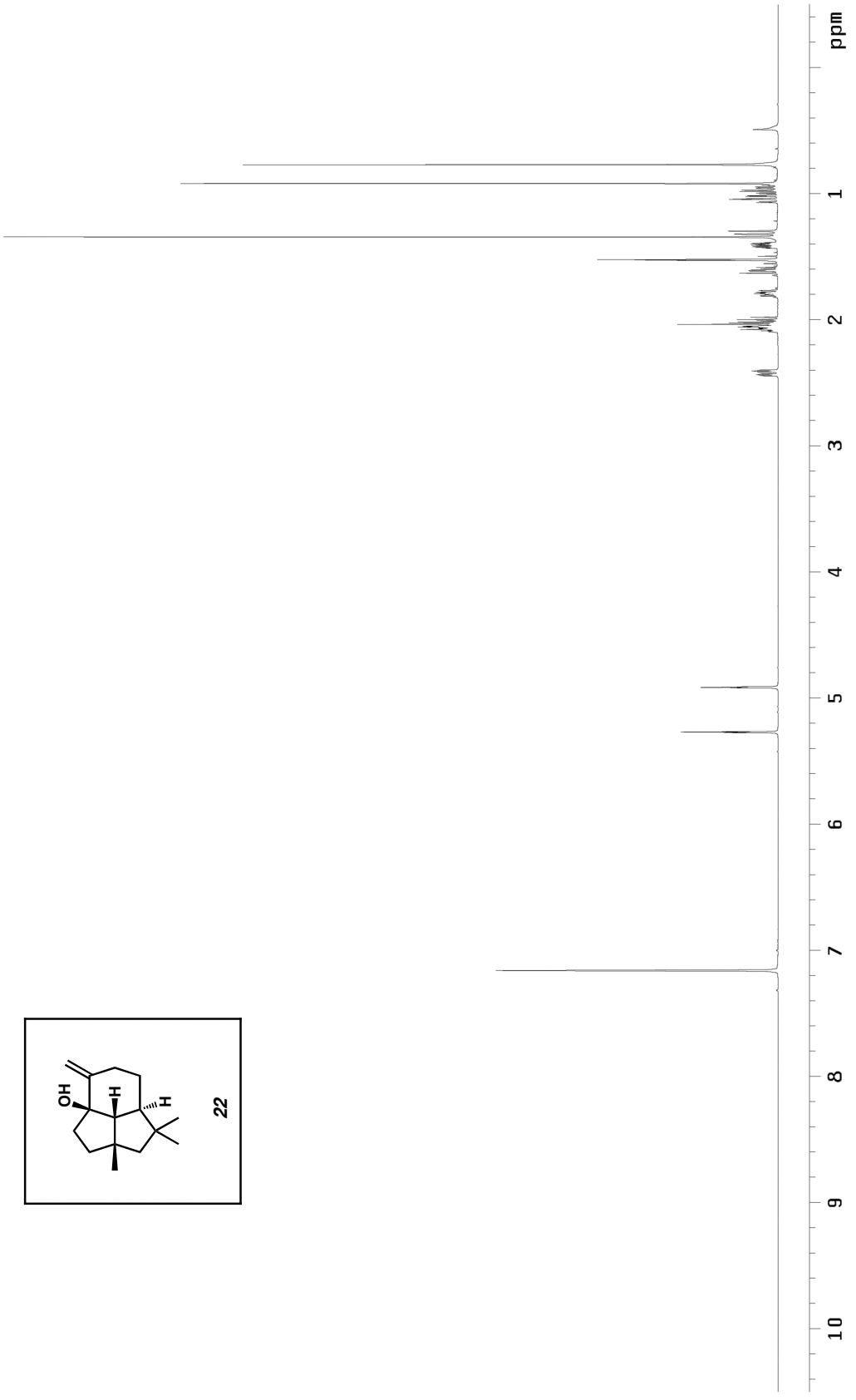


Figure SI-18A. ^{1}H NMR (500 MHz, C_6D_6) of compound **22**.

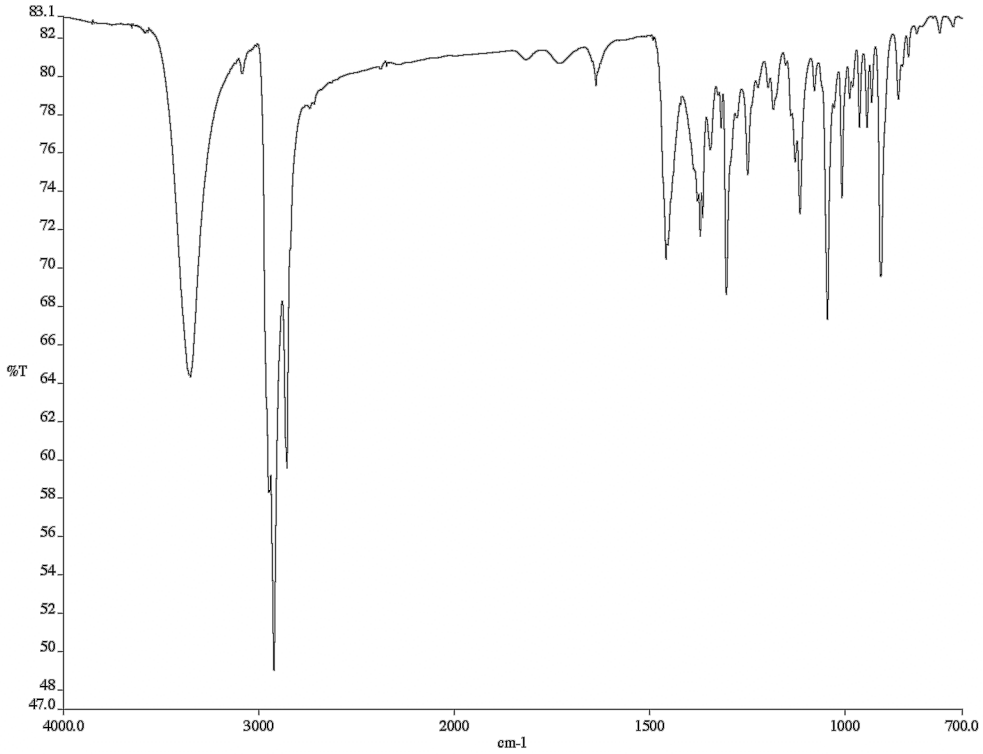


Figure SI-18B. Infrared spectrum (thin film/NaCl) of compound **22**.

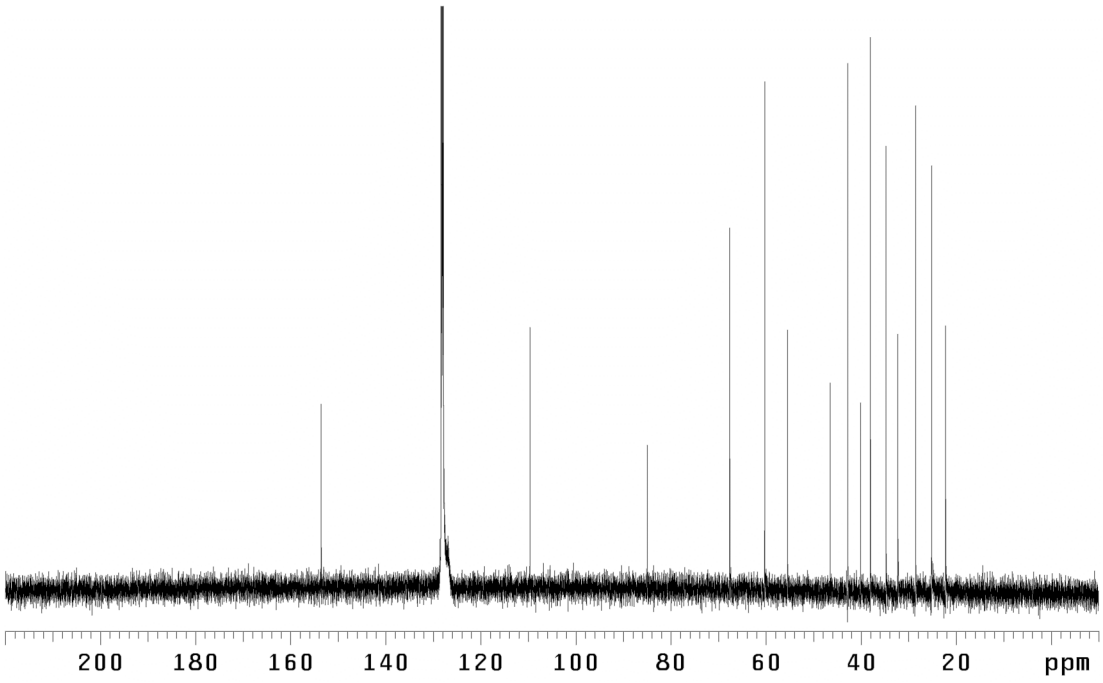


Figure SI-18C. ^{13}C NMR (125 MHz, C_6D_6) of compound **22**.

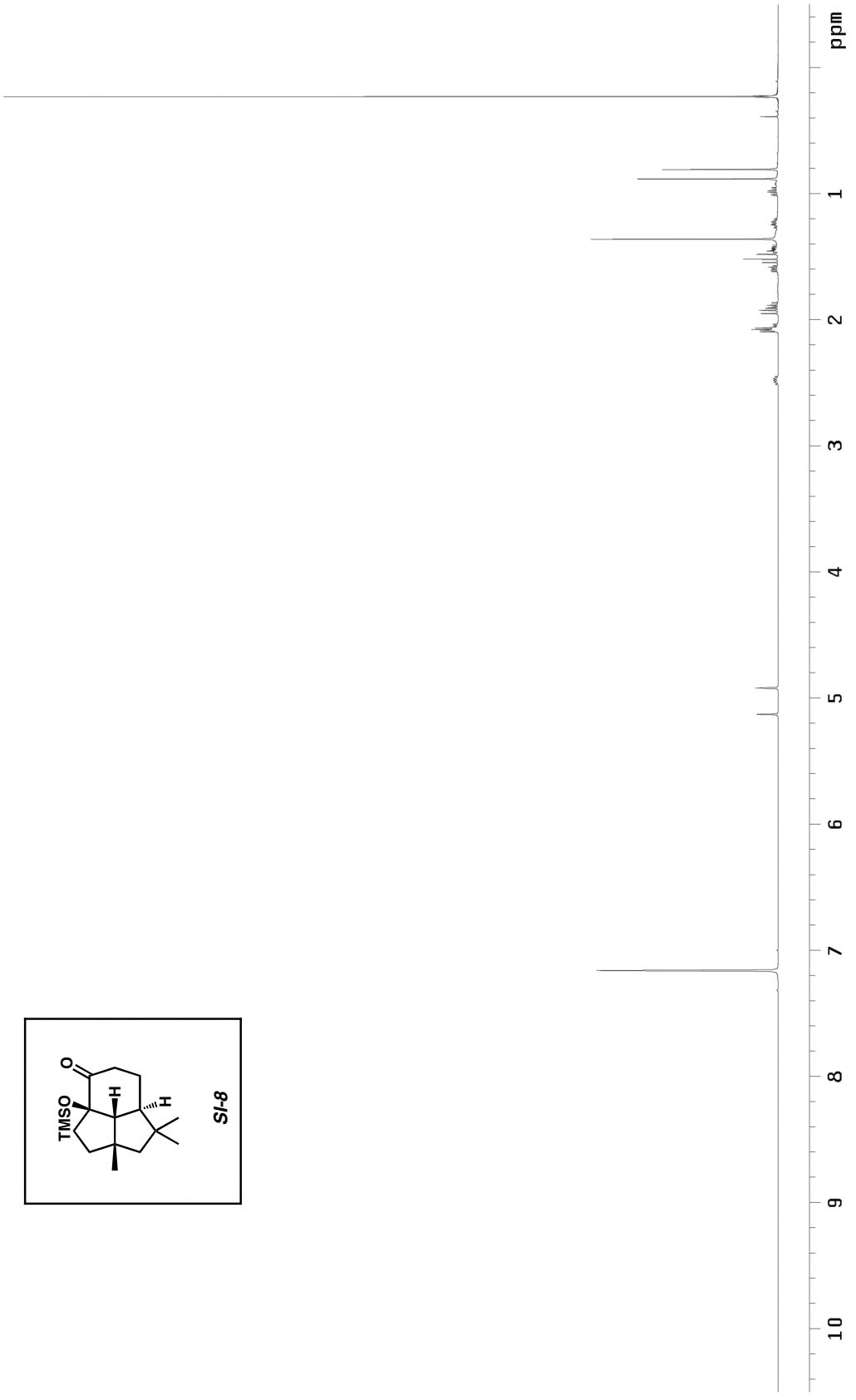


Figure SI-19A. ^{1}H NMR (500 MHz, C_6D_6) of compound **SI-8**.

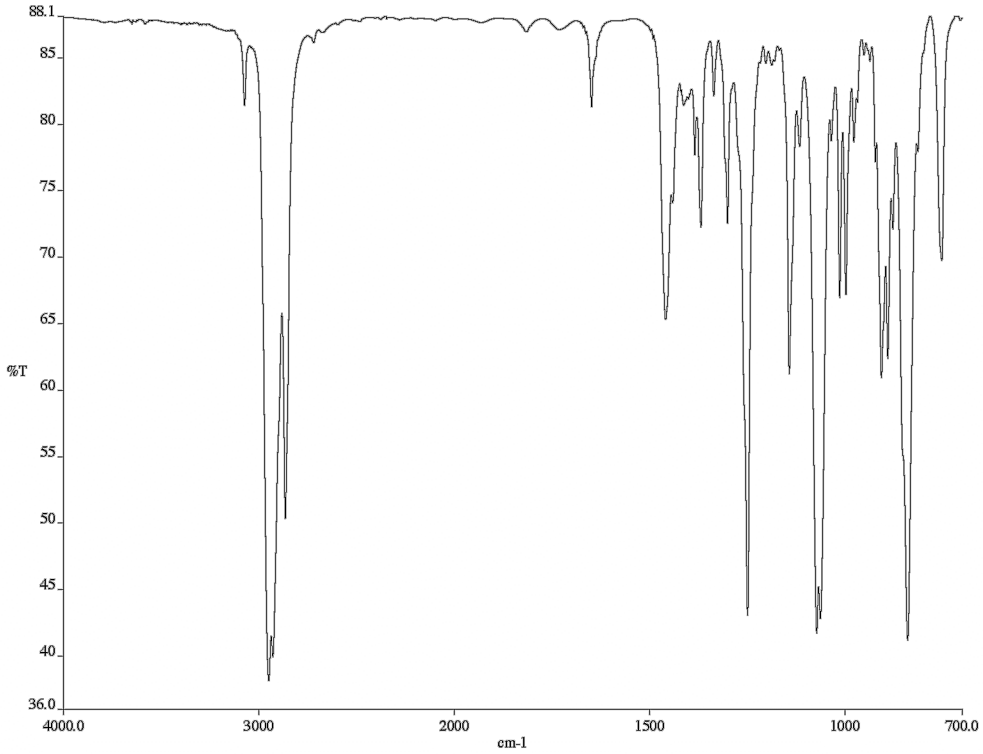


Figure SI-19B. Infrared spectrum (thin film/NaCl) of compound **SI-8**.

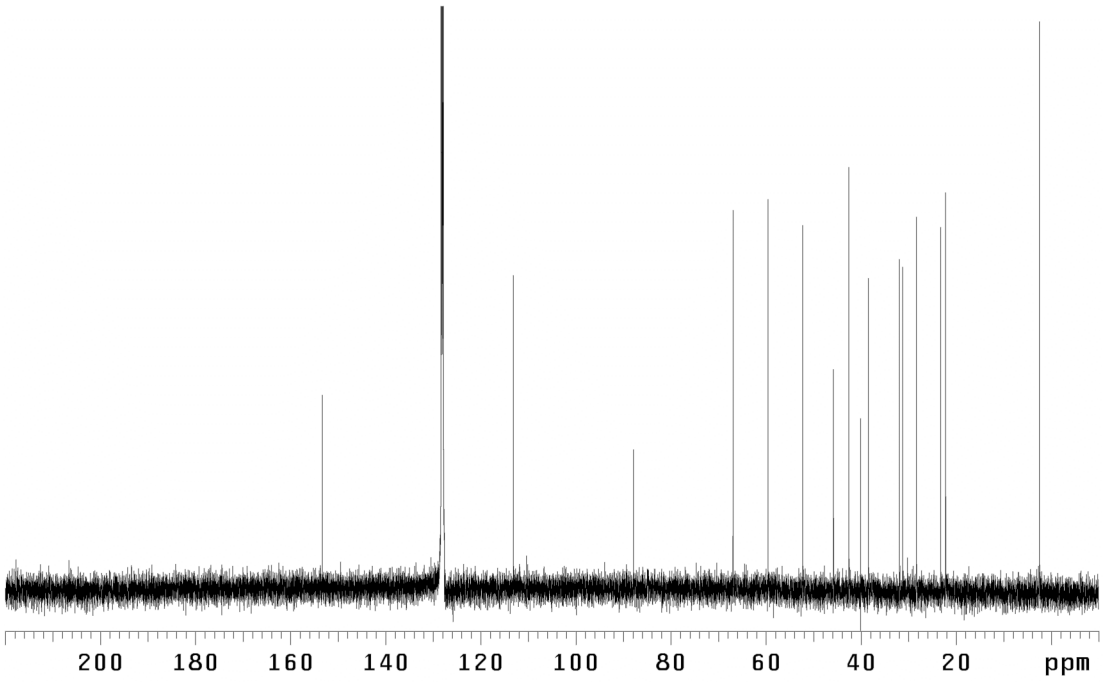


Figure SI-19C. ^{13}C NMR (125 MHz, C_6D_6) of compound **SI-8**.

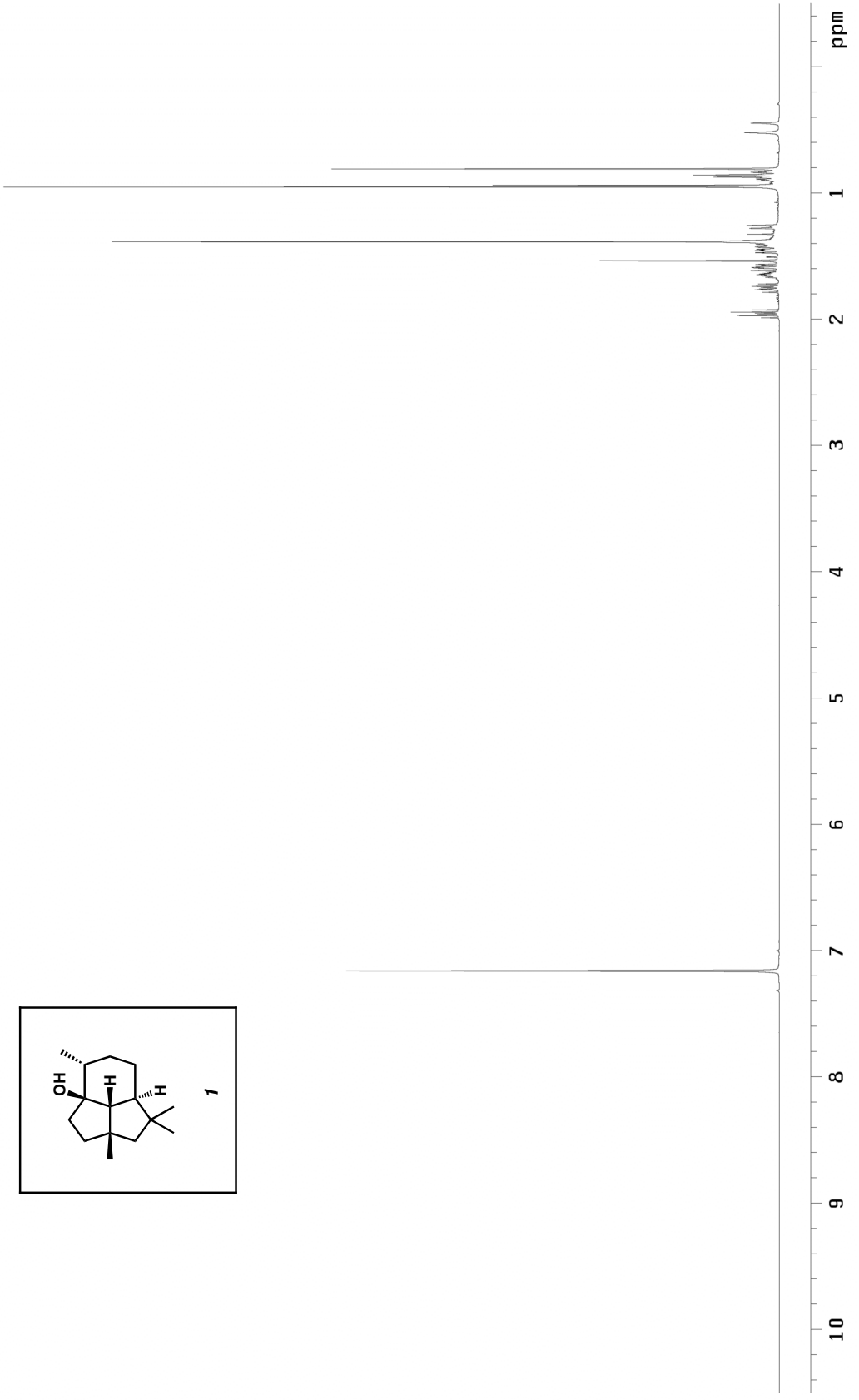


Figure SI-20A. ^{1}H NMR (500 MHz, C_6D_6) of compound **1**.

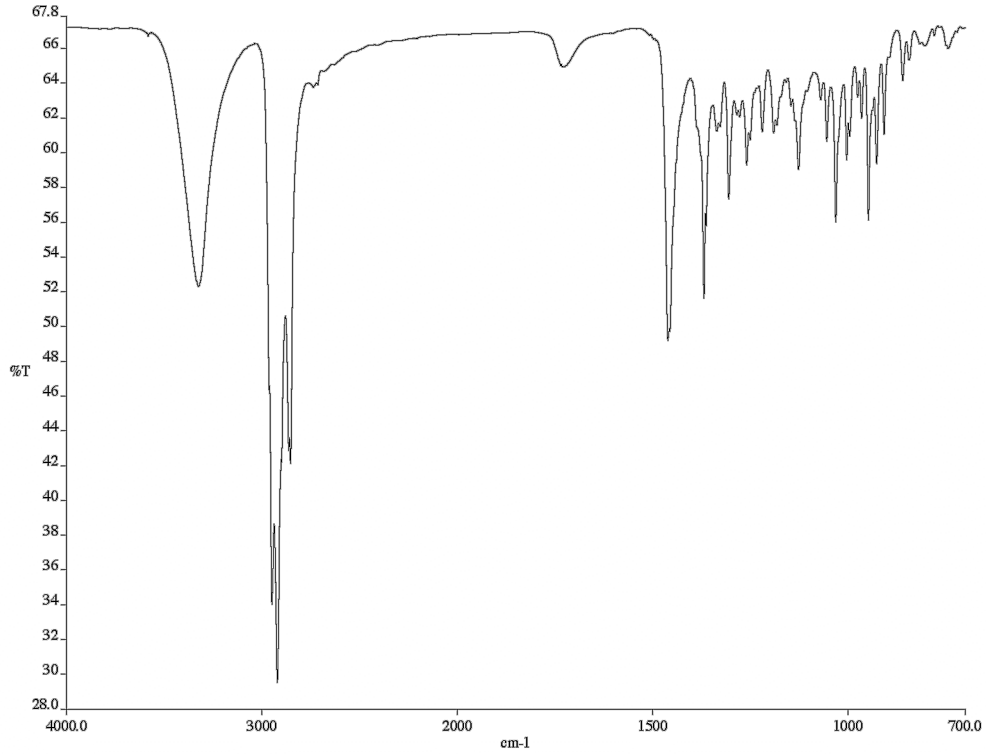


Figure SI-20B. Infrared spectrum (thin film/NaCl) of compound **1**.

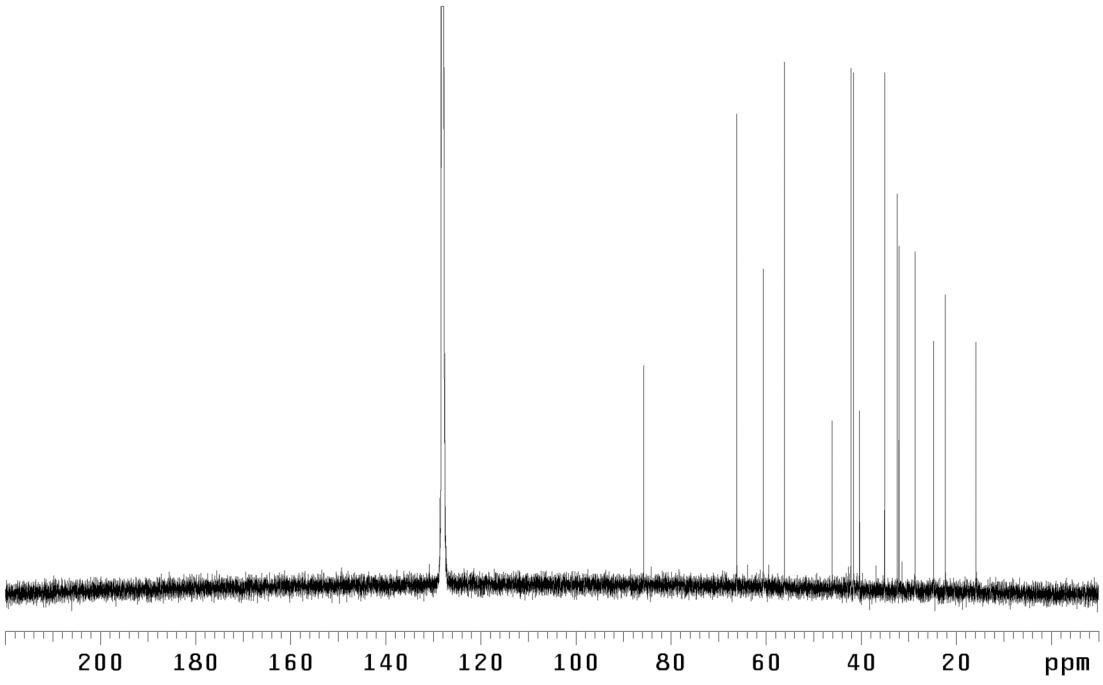


Figure SI-20C. ^{13}C NMR (125 MHz, C_6D_6) of compound **1**.

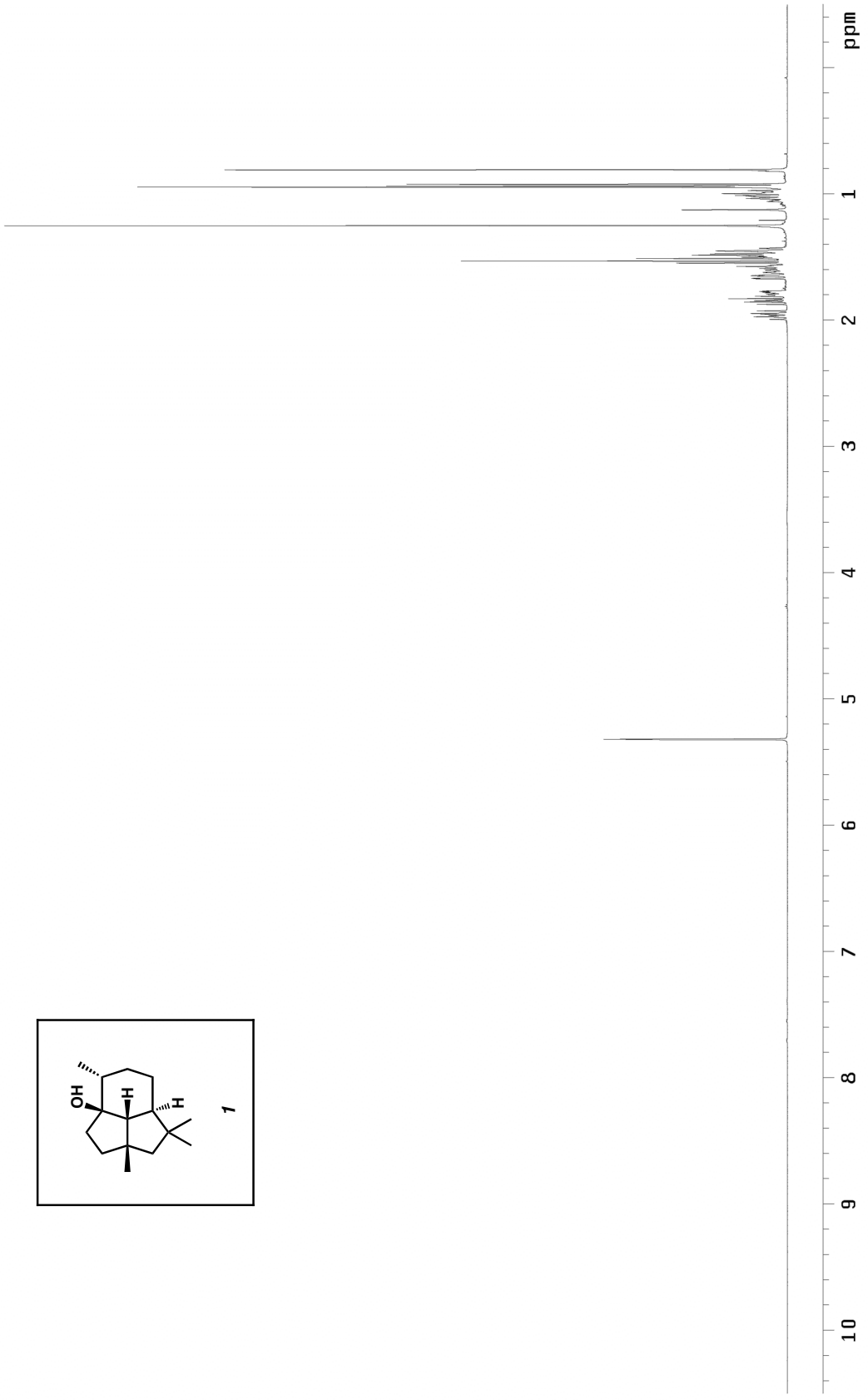


Figure SI-20D. ^{1}H NMR (500 MHz, CD_2Cl_2) of compound **1**.

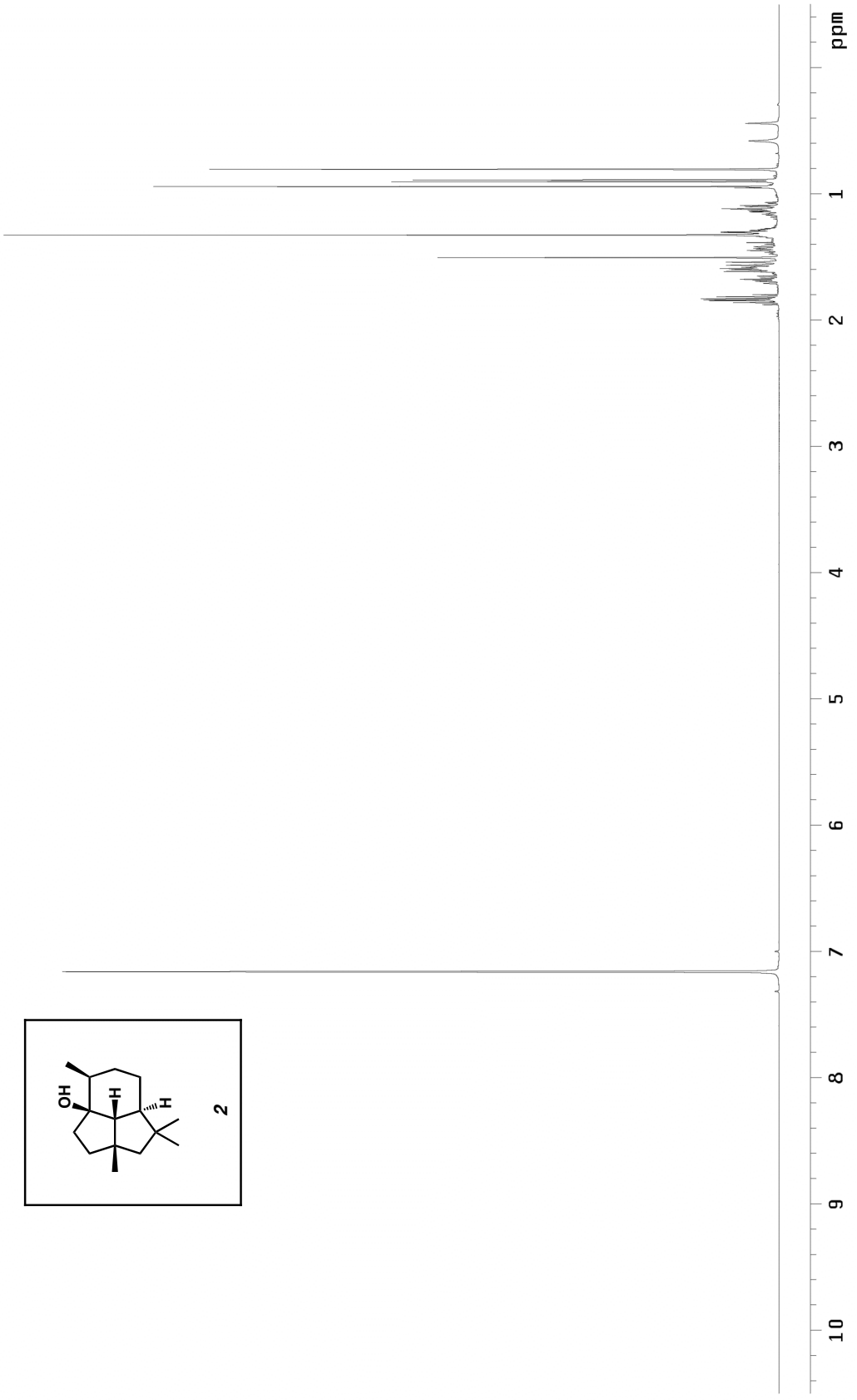


Figure SI-21A. ^{1}H NMR (500 MHz, C_6D_6) of compound **2**.

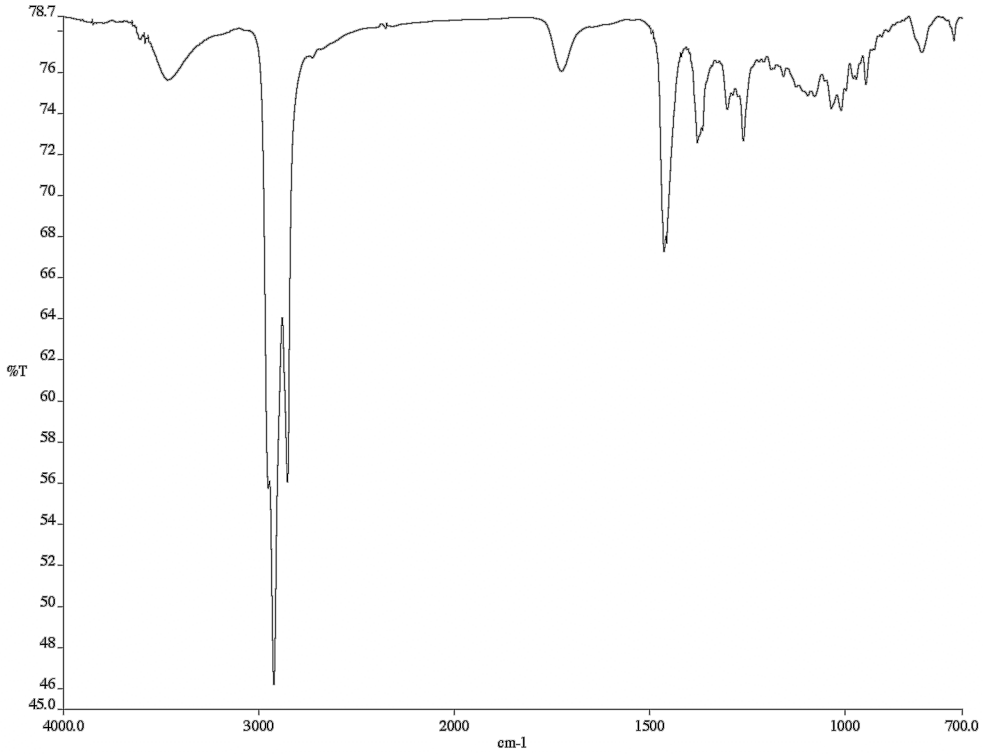


Figure SI-21B. Infrared spectrum (thin film/NaCl) of compound **2**.

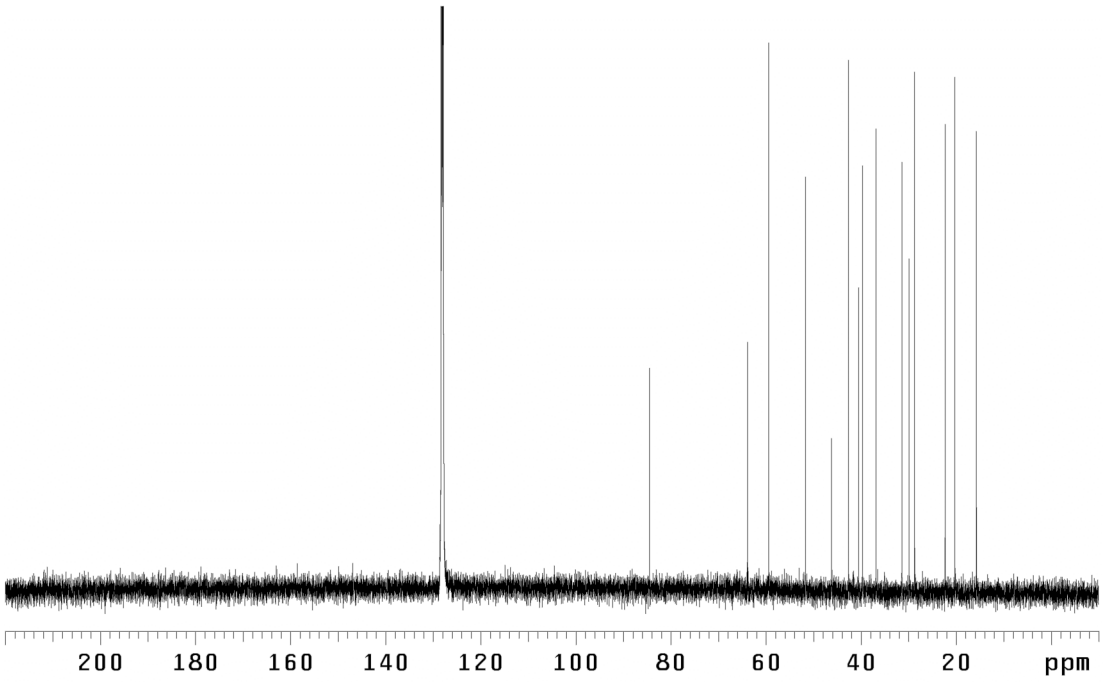


Figure SI-21C. ^{13}C NMR (125 MHz, C_6D_6) of compound **2**.

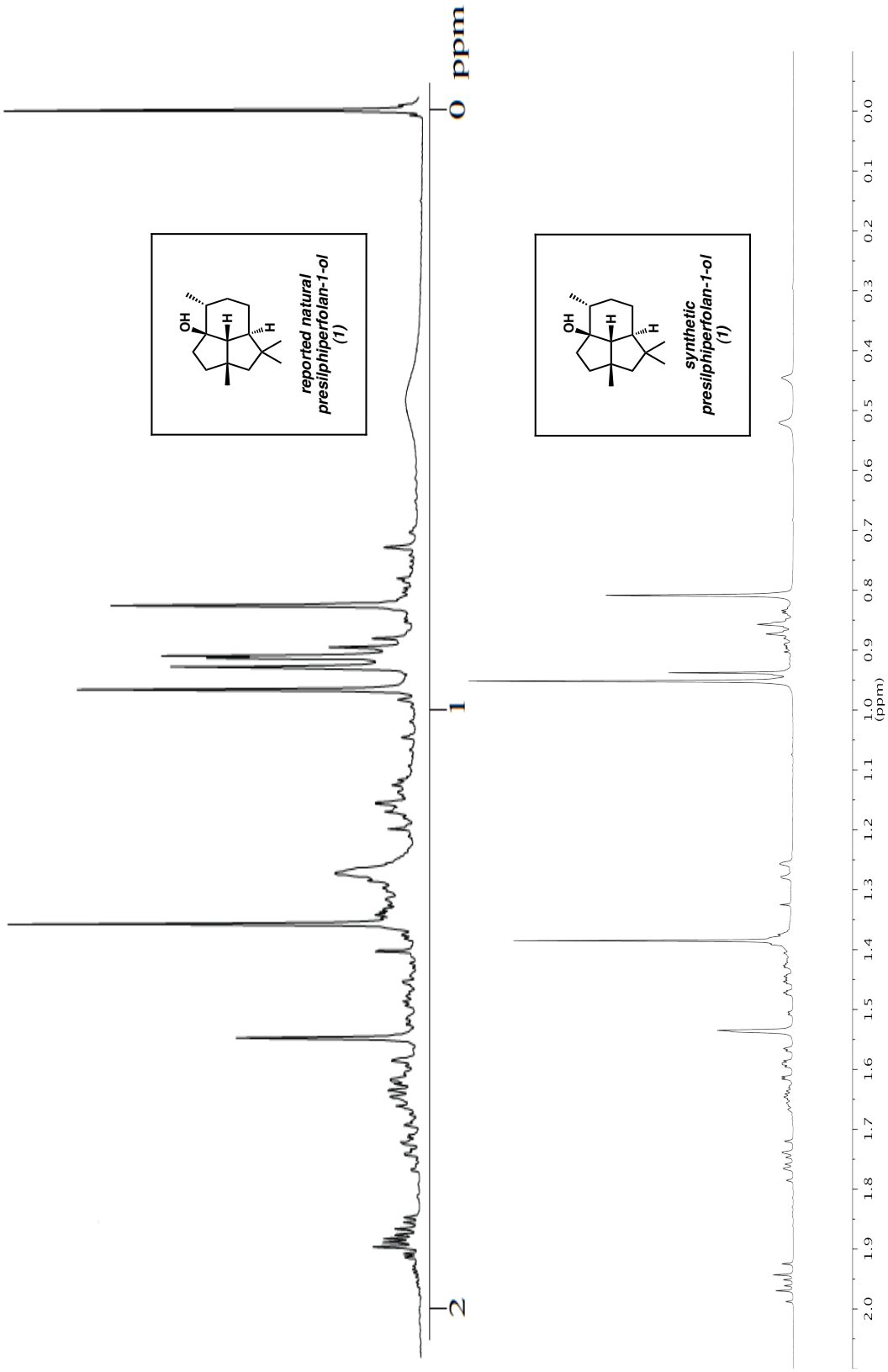


Figure SI-22. ^{1}H NMR comparison of reported natural compound **1** (500 MHz, C_6D_6) and synthetic compound **1** (500 MHz, C_6D_6).

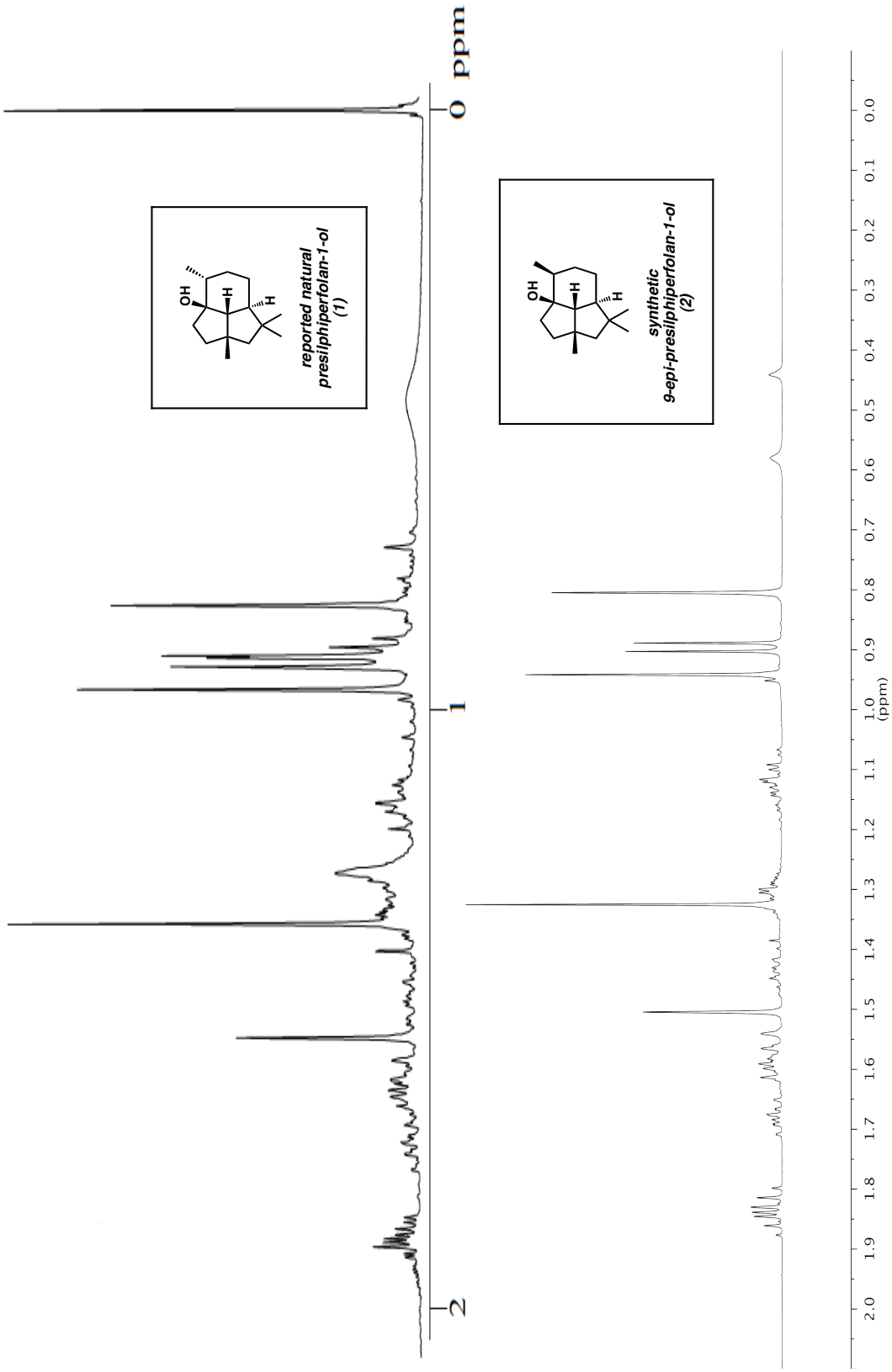


Figure SI-23. ^{1}H NMR comparison of reported natural compound **1** (500 MHz, C_6D_6) and synthetic compound **2** (500 MHz, C_6D_6).

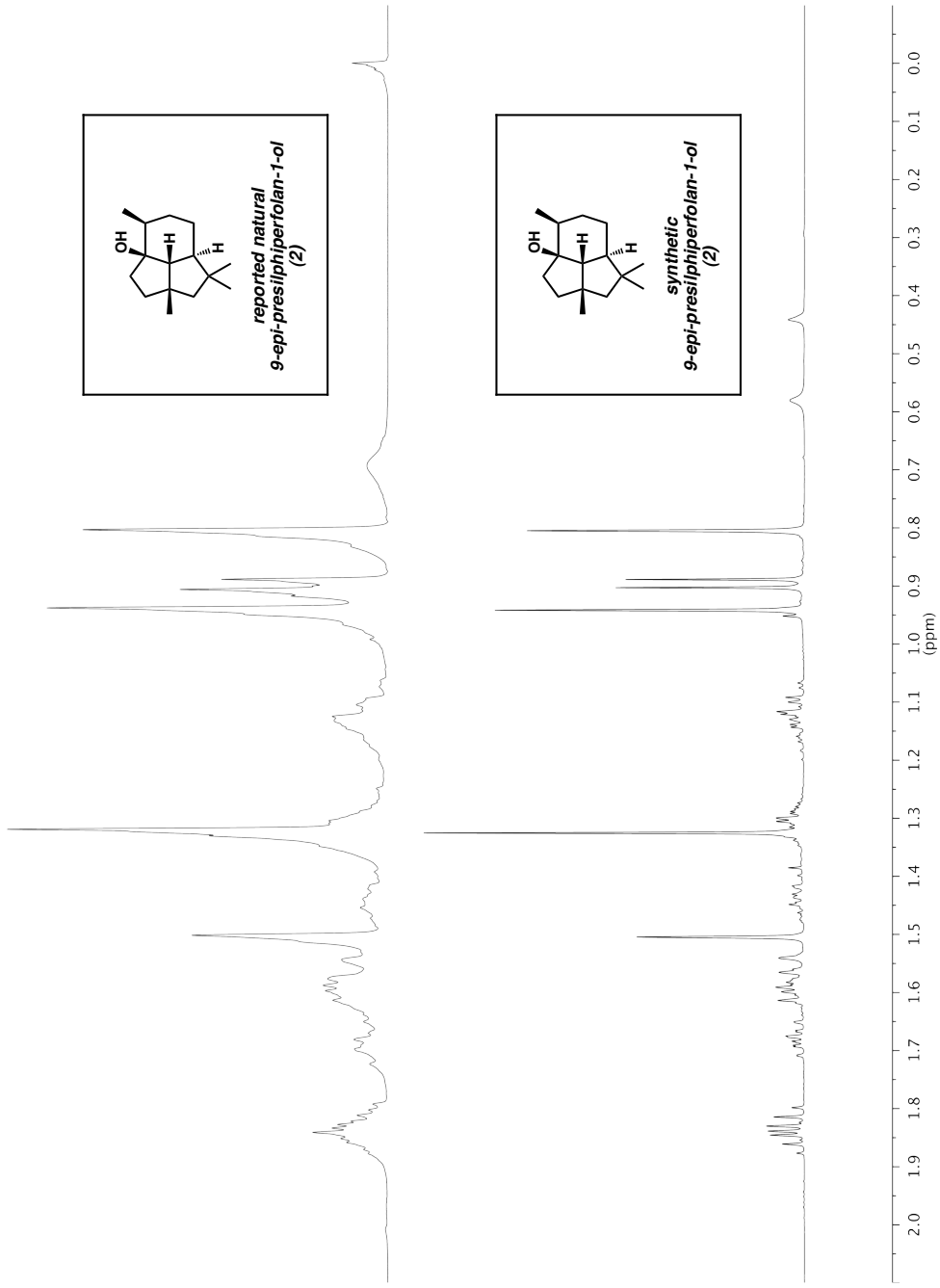


Figure SI-24A. ^{1}H NMR comparison of reported natural compound **2** (400 MHz, C_6D_6) and synthetic compound **2** (500 MHz, C_6D_6).

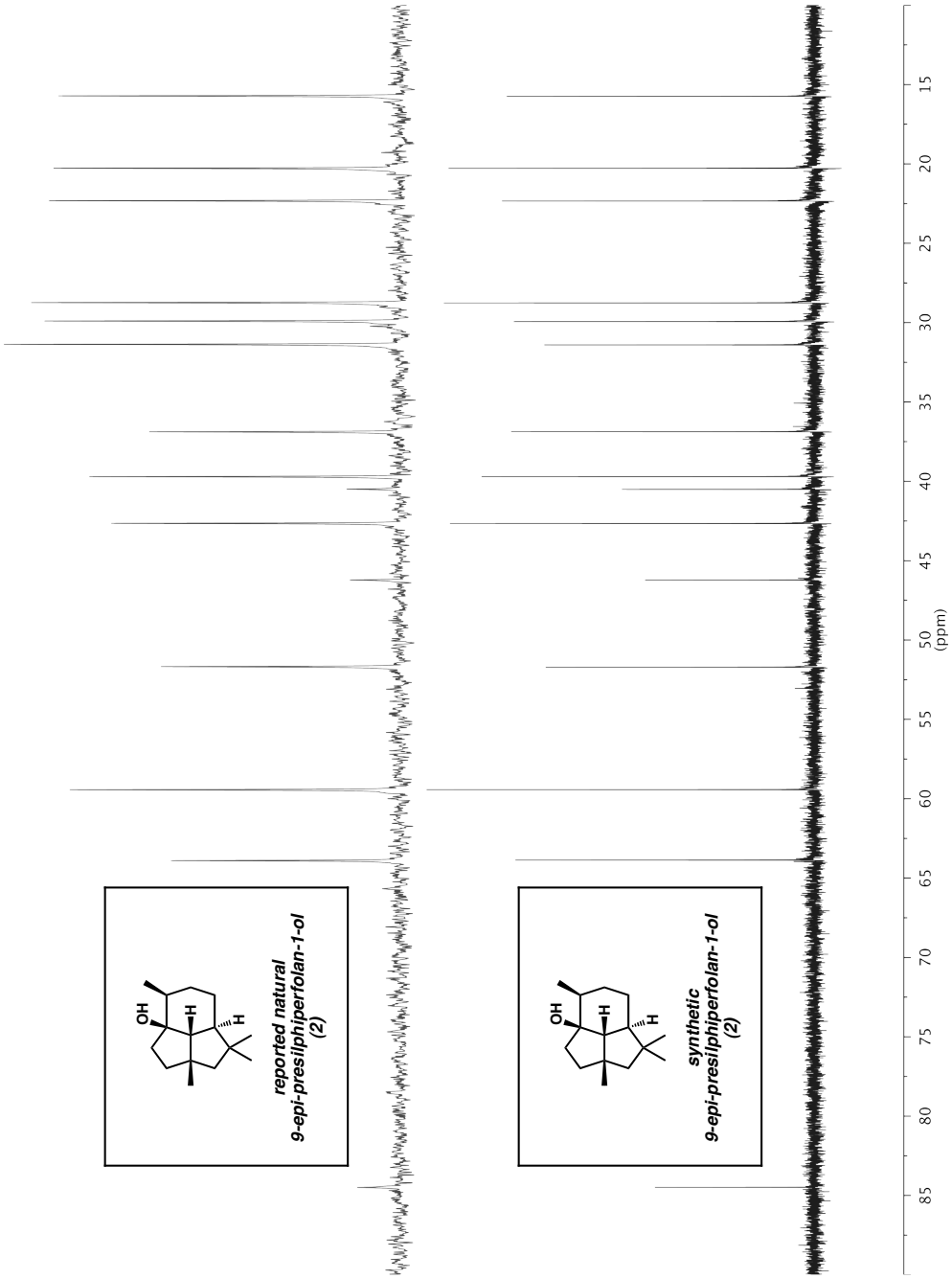


Figure SI-24B. ^{13}C NMR comparison of reported natural compound **2** (100 MHz, C_6D_6) and synthetic compound **2** (125 MHz, C_6D_6).

```
Data File C:\CHEM32\2\DATA\AYH10\AYHCOLUMNSCREEN 2011-08-09 16-00-41\AYH-X-277A-3-2.D
Sample Name: AYH-X-277A-3-2
    ======================================================================
    Acq. Operator   : AYH                              Seq. Line :  16
    Acq. Instrument : HPLC 2                          Location : Vial 71
    Injection Date  : 8/9/2011 6:51:13 PM                  Inj :   1
                                                     Inj Volume : 5.0 µl
    Acq. Method     : C:\CHEM32\2\DATA\AYH10\AYHCOLUMNSCREEN 2011-08-09 16-00-41\2IPA30_254.M
    Last changed    : 4/26/2010 8:32:06 PM
    Analysis Method : C:\CHEM32\2\METHODS\10IPA.M
    Last changed    : 5/11/2012 12:24:12 AM by AYH
                      (modified after loading)
    Method Info     : 10% IPA   10 min   Equil   1 mL/min

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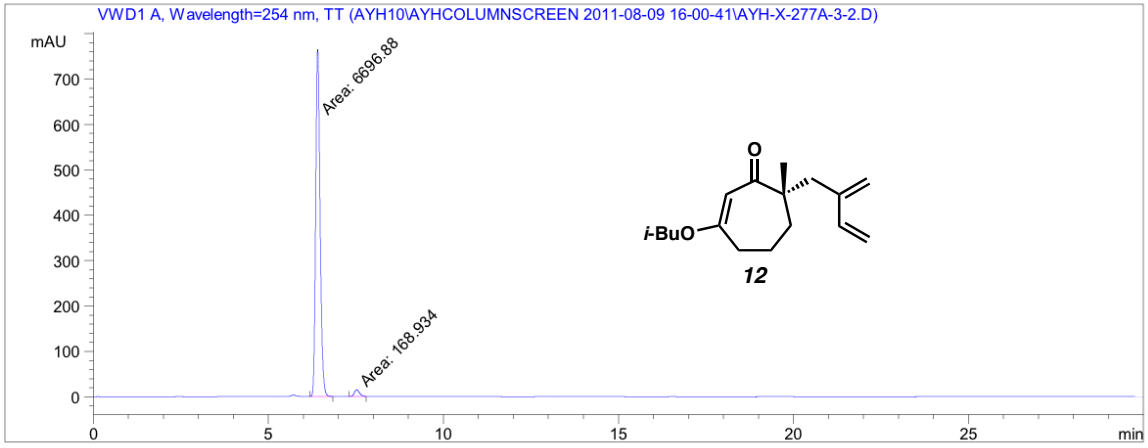


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    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm, TT

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s    [mAU   ]       %
    ----|-------|----|-------|----------|----------|--------|
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       2   7.525 MM    0.1817  168.93355   15.49775   2.4605

    Totals :                  6865.81685  780.91700


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    Acq. Instrument : HPLC 2                          Location : Vial 71
    Injection Date  : 8/8/2011 9:30:02 AM                  Inj :   1
                                                     Inj Volume : 5.0 µl
    Acq. Method     : C:\CHEM32\2\DATA\AYH10\AYHCOLUMNSCREEN 2011-08-08 01-43-08\2IPA30_254.M
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                      (modified after loading)
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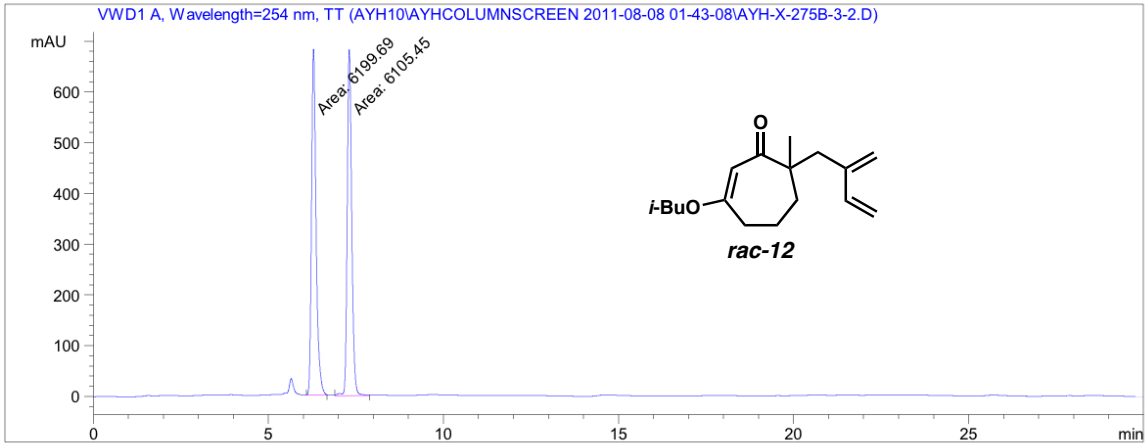


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                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm, TT

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s    [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   6.289 MF    0.1515 6199.69141  681.94836  50.3829
       2   7.312 MM    0.1491 6105.44824  682.45813  49.6171

    Totals :                  1.23051e4  1364.40649


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```

CALIFORNIA INSTITUTE OF TECHNOLOGY

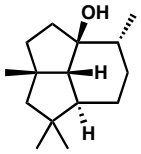
BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

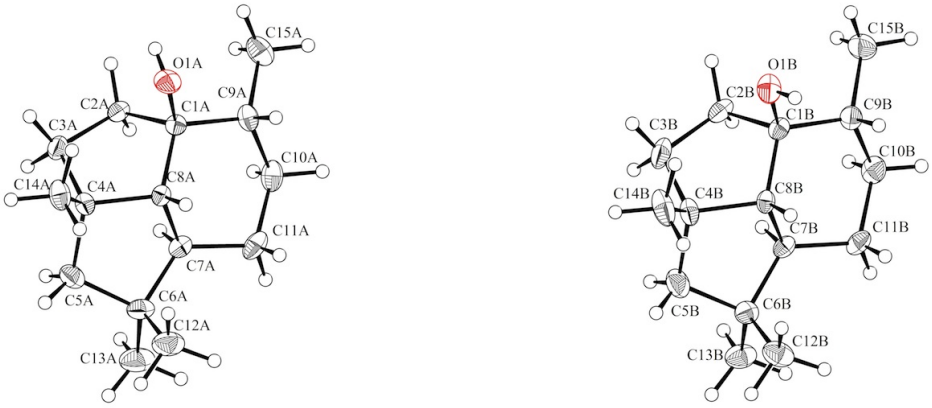
Crystal Structure Analysis of:

Compound **1**

(AYH01) (CCDC 889569)



Contents



AYH01

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC). The deposition number is 889569.

Table 1. Crystal Data and Structure Analysis Details for ayh01 (CCDC 889569).

Empirical formula	$C_{15}H_{26}O$
Formula weight	222.36
Crystallization solvent	hexanes, slow evaporation
Crystal shape	block
Crystal color	colourless
Crystal size	0.20 x 0.42 x 0.44 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data collection temperature	100 K	
Theta range for 9919 reflections used in lattice determination	2.35 to 33.56°	
Unit cell dimensions	a = 17.8200(13) Å b = 9.0182(4) Å c = 18.7656(9) Å	α= 90° β= 112.479(2)° γ = 90°
Volume	2786.6(3) $Å^3$	
Z	8	
Crystal system	Monoclinic	
Space group	I2 (# 5)	
Density (calculated)	1.060 g/cm^3	
F(000)	992	
Theta range for data collection	2.3 to 41.1°	
Completeness to theta = 25.00°	99.8%	
Index ranges	$-30 \le h \le 32$, $-16 \le k \le 16$, $-30 \le l \le 34$	
Data collection scan type	narrow omega and phi scans	
Reflections collected	66426	
Independent reflections	17149 [R_{int}= 0.0390]	
Reflections > 2σ(I)	11947	
Average σ(I)/(net I)	0.0568	
Absorption coefficient	0.06 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9874 and 0.9726	
Reflections monitored for decay	0	
Decay of standards	0%	

Table 1 (cont.)

Structure Solution and Refinement

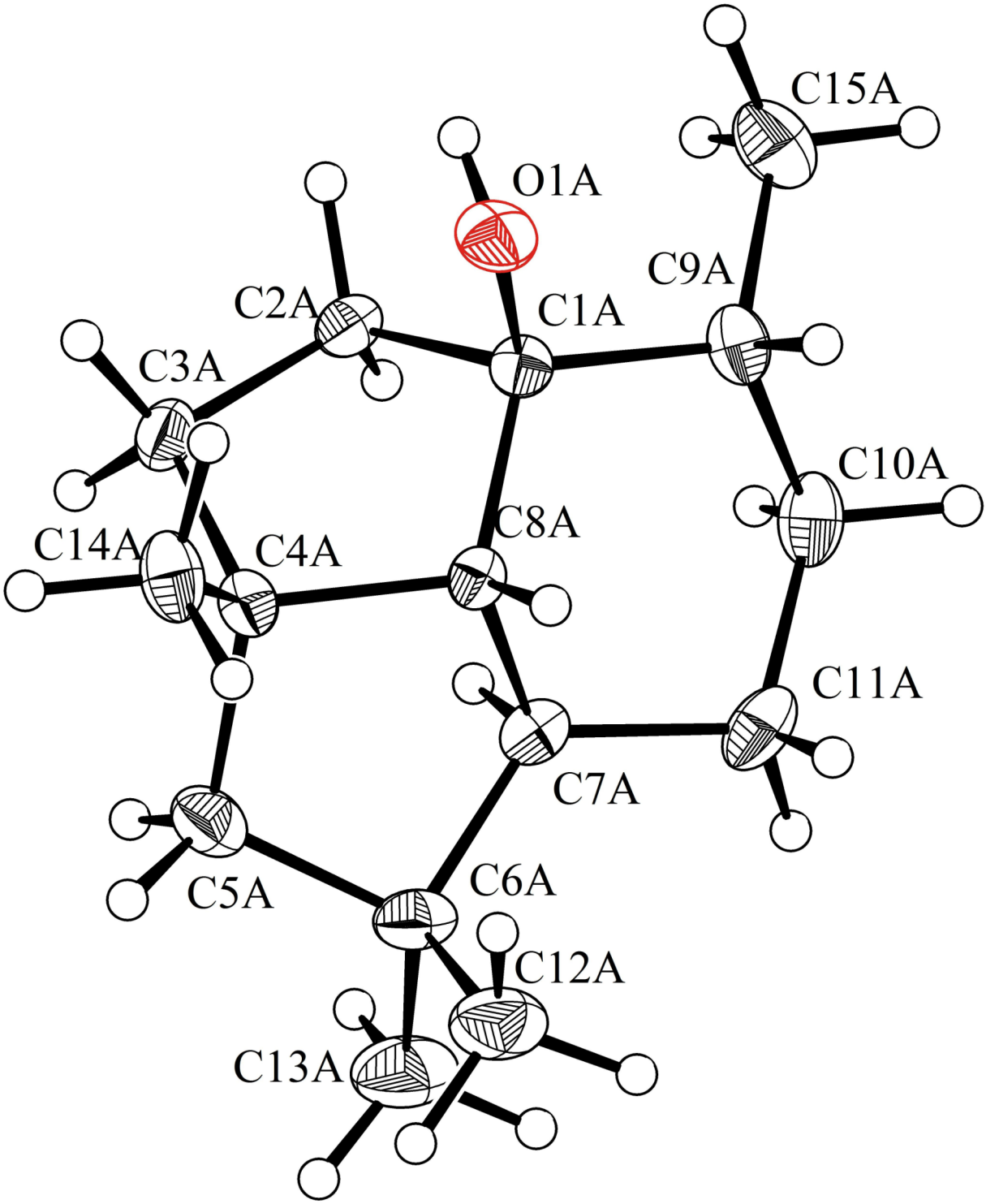
Primary solution method	direct
Secondary solution method	difmap
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17149 / 1 / 498
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	2.14
Final R indices [I>2σ(I), 11947 reflections]	R1 = 0.0566, wR2 = 0.0604
R indices (all data)	R1 = 0.0987, wR2 = 0.0618
Type of weighting scheme used	calc
Weighting scheme used	calc w=1/[^2^(Fo^2^)+(0.0000P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.4(5)
Extinction coefficient	0.00083(11)
Largest diff. peak and hole	0.62 and -0.30 e.$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.18C (Bruker-AXS, 2007)
Data collection	APEX2 2012.2-0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.18C (Bruker-AXS, 2007)
Structure solution	SHELXS-97 (Sheldrick, 1990)
Structure refinement	SHELXL-97 (Sheldrick, 1997)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

References

Special Refinement Details


C15A
O1A
C9A
C2A
C1A
C3A
C10A
C8A
C14A
C4A
C11A
C7A
C5A
C6A
C12A
C13A

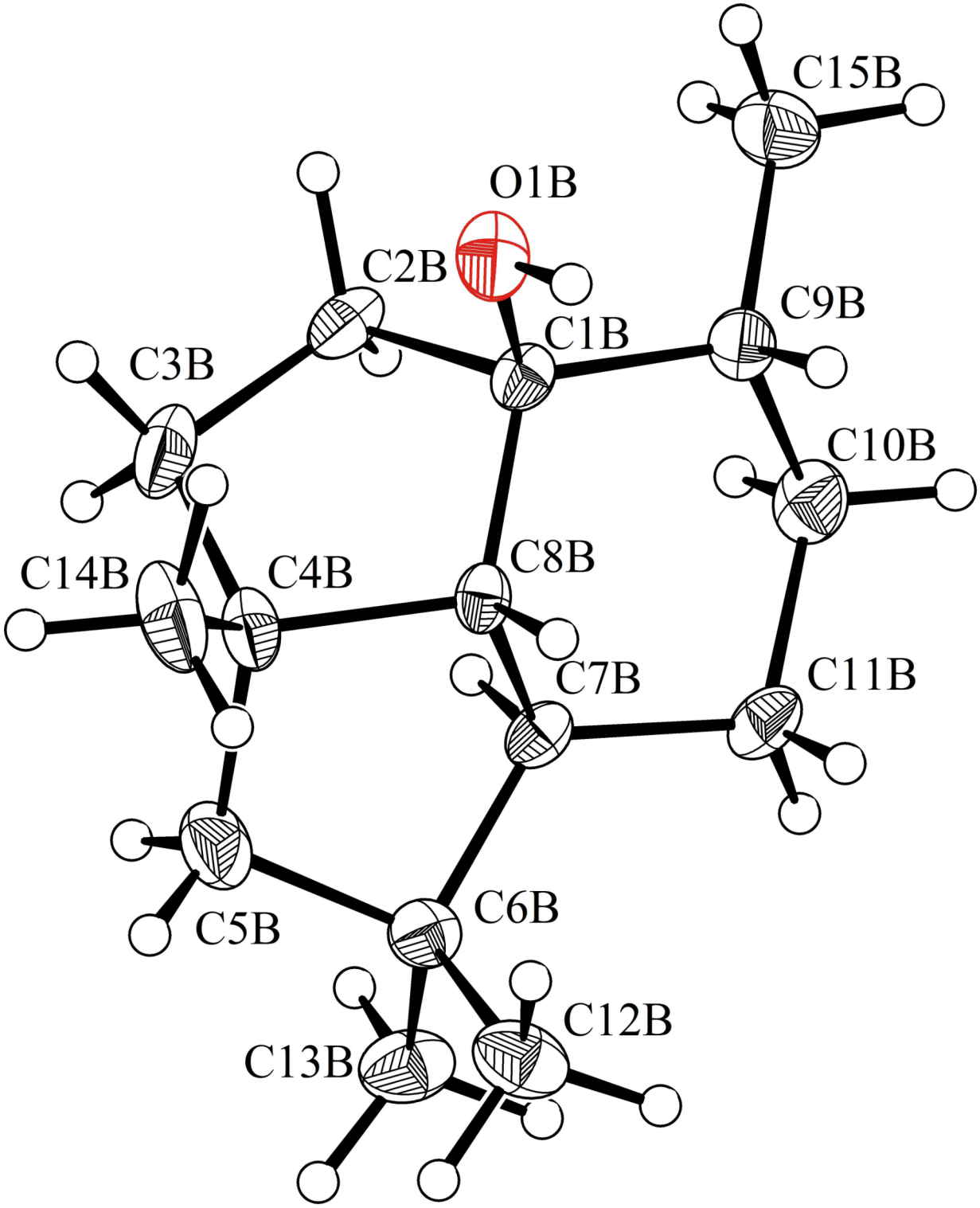

C15B
O1B
C2B
C9B
C1B
C3B
C10B
C14B
C4B
C8B
C7B
C11B
C5B
C6B
C12B
C13B

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ayh01 (CCDC 889569). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1A)	3956(1)	967(1)	101(1)	27(1)
C(1A)	3287(1)	100(1)	135(1)	17(1)
C(2A)	2590(1)	164(1)	-659(1)	20(1)
C(3A)	2207(1)	1716(1)	-689(1)	22(1)
C(4A)	2422(1)	2238(1)	158(1)	19(1)
C(5A)	1685(1)	2307(1)	413(1)	26(1)
C(6A)	1833(1)	1161(1)	1065(1)	25(1)
C(7A)	2330(1)	16(1)	827(1)	19(1)
C(8A)	2938(1)	944(1)	632(1)	16(1)
C(9A)	3615(1)	-1426(1)	480(1)	22(1)
C(10A)	3068(1)	-2264(1)	806(1)	27(1)
C(11A)	2742(1)	-1325(1)	1303(1)	28(1)
C(12A)	2309(1)	1842(1)	1857(1)	37(1)
C(13A)	1044(1)	514(1)	1063(1)	40(1)
C(14A)	2882(1)	3712(1)	315(1)	27(1)
C(15A)	3827(1)	-2400(1)	-80(1)	34(1)
O(1B)	5561(1)	934(1)	1119(1)	28(1)
C(1B)	5724(1)	1902(1)	1778(1)	18(1)
C(2B)	6641(1)	1788(1)	2244(1)	24(1)
C(3B)	6751(1)	344(1)	2714(1)	31(1)
C(4B)	5919(1)	-77(1)	2750(1)	23(1)
C(5B)	5896(1)	-2(1)	3573(1)	32(1)
C(6B)	5334(1)	1292(1)	3590(1)	22(1)
C(7B)	5432(1)	2293(1)	2970(1)	18(1)
C(8B)	5373(1)	1228(1)	2320(1)	17(1)
C(9B)	5359(1)	3445(1)	1494(1)	22(1)
C(10B)	5299(1)	4442(1)	2131(1)	28(1)
C(11B)	4935(1)	3678(1)	2654(1)	25(1)
C(12B)	4460(1)	773(1)	3385(1)	33(1)
C(13B)	5631(1)	2046(1)	4378(1)	32(1)
C(14B)	5634(1)	-1585(1)	2379(1)	36(1)
C(15B)	5790(1)	4240(1)	1045(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for ayh01 (CCDC 889569).

O(1A)-C(1A)	1.4471(9)
O(1A)-H(1A)	0.734(10)
C(1A)-C(8A)	1.5110(10)
C(1A)-C(2A)	1.5328(10)
C(1A)-C(9A)	1.5385(11)
C(2A)-C(3A)	1.5483(11)
C(2A)-H(2A)	0.968(8)
C(2A)-H(2B)	0.969(8)
C(3A)-C(4A)	1.5590(11)
C(3A)-H(3A)	0.999(8)
C(3A)-H(3B)	0.996(8)
C(4A)-C(14A)	1.5305(11)
C(4A)-C(8A)	1.5400(11)
C(4A)-C(5A)	1.5601(11)
C(5A)-C(6A)	1.5450(12)
C(5A)-H(5A)	1.001(8)
C(5A)-H(5B)	0.974(9)
C(6A)-C(13A)	1.5221(12)
C(6A)-C(12A)	1.5305(12)
C(6A)-C(7A)	1.5333(11)
C(7A)-C(11A)	1.5158(12)
C(7A)-C(8A)	1.5198(10)
C(7A)-H(7A)	0.998(7)
C(8A)-H(8A)	0.951(7)
C(9A)-C(15A)	1.5236(12)
C(9A)-C(10A)	1.5335(12)
C(9A)-H(9A)	0.977(8)
C(10A)-C(11A)	1.5288(13)
C(10A)-H(10A)	0.998(8)
C(10A)-H(10B)	1.018(9)
C(11A)-H(11A)	0.972(9)
C(11A)-H(11B)	0.999(9)
C(12A)-H(12A)	0.995(10)
C(12A)-H(12B)	0.992(9)
C(12A)-H(12C)	0.999(10)
C(13A)-H(13A)	0.977(11)
C(13A)-H(13B)	0.970(10)
C(13A)-H(13C)	0.942(11)
C(14A)-H(14A)	0.976(9)
C(14A)-H(14B)	0.983(9)
C(14A)-H(14C)	0.989(9)
C(15A)-H(15A)	0.979(10)
C(15A)-H(15B)	1.024(10)
C(15A)-H(15C)	0.987(10)
O(1B)-C(1B)	1.4494(10)
O(1B)-H(1B)	0.748(11)
C(1B)-C(8B)	1.5103(10)
C(1B)-C(2B)	1.5338(11)
C(1B)-C(9B)	1.5419(11)
C(2B)-C(3B)	1.5428(13)
C(2B)-H(2C)	0.977(8)
C(2B)-H(2D)	1.005(9)
C(3B)-C(4B)	1.5564(13)

C(3B)-H(3C)	0.977(10)
C(3B)-H(3D)	0.998(9)
C(4B)-C(14B)	1.5232(12)
C(4B)-C(8B)	1.5430(11)
C(4B)-C(5B)	1.5621(12)
C(5B)-C(6B)	1.5472(12)
C(5B)-H(5C)	0.959(10)
C(5B)-H(5D)	0.961(10)
C(6B)-C(13B)	1.5264(11)
C(6B)-C(12B)	1.5283(12)
C(6B)-C(7B)	1.5340(11)
C(7B)-C(11B)	1.5145(11)
C(7B)-C(8B)	1.5238(10)
C(7B)-H(7B)	0.984(7)
C(8B)-H(8B)	0.984(8)
C(9B)-C(15B)	1.5198(12)
C(9B)-C(10B)	1.5316(12)
C(9B)-H(9B)	0.967(7)
C(10B)-C(11B)	1.5329(12)
C(10B)-H(10C)	1.011(9)
C(10B)-H(10D)	0.966(10)
C(11B)-H(11C)	0.956(8)
C(11B)-H(11D)	0.967(8)
C(12B)-H(12D)	0.980(9)
C(12B)-H(12E)	0.968(9)
C(12B)-H(12F)	0.998(9)
C(13B)-H(13D)	0.994(10)
C(13B)-H(13E)	0.987(10)
C(13B)-H(13F)	0.976(9)
C(14B)-H(14D)	0.995(10)
C(14B)-H(14E)	0.964(10)
C(14B)-H(14F)	0.991(10)
C(15B)-H(15D)	1.014(11)
C(15B)-H(15E)	0.984(10)
C(15B)-H(15F)	0.962(10)

C(1A)-O(1A)-H(1A)	110.4(9)
O(1A)-C(1A)-C(8A)	107.21(6)
O(1A)-C(1A)-C(2A)	108.20(6)
C(8A)-C(1A)-C(2A)	102.06(6)
O(1A)-C(1A)-C(9A)	108.36(6)
C(8A)-C(1A)-C(9A)	111.76(6)
C(2A)-C(1A)-C(9A)	118.63(6)
C(1A)-C(2A)-C(3A)	104.58(6)
C(1A)-C(2A)-H(2A)	109.6(5)
C(3A)-C(2A)-H(2A)	111.5(5)
C(1A)-C(2A)-H(2B)	110.0(5)
C(3A)-C(2A)-H(2B)	111.5(5)
H(2A)-C(2A)-H(2B)	109.5(6)
C(2A)-C(3A)-C(4A)	107.62(6)
C(2A)-C(3A)-H(3A)	111.5(5)
C(4A)-C(3A)-H(3A)	111.5(4)
C(2A)-C(3A)-H(3B)	111.2(5)
C(4A)-C(3A)-H(3B)	109.2(5)
H(3A)-C(3A)-H(3B)	105.9(7)
C(14A)-C(4A)-C(8A)	112.91(6)

C(14A)-C(4A)-C(3A)	111.26(7)
C(8A)-C(4A)-C(3A)	102.70(6)
C(14A)-C(4A)-C(5A)	110.99(7)
C(8A)-C(4A)-C(5A)	103.88(6)
C(3A)-C(4A)-C(5A)	114.65(7)
C(6A)-C(5A)-C(4A)	107.85(6)
C(6A)-C(5A)-H(5A)	112.3(5)
C(4A)-C(5A)-H(5A)	111.2(5)
C(6A)-C(5A)-H(5B)	109.3(5)
C(4A)-C(5A)-H(5B)	110.6(5)
H(5A)-C(5A)-H(5B)	105.5(7)
C(13A)-C(6A)-C(12A)	108.90(8)
C(13A)-C(6A)-C(7A)	112.14(8)
C(12A)-C(6A)-C(7A)	112.71(7)
C(13A)-C(6A)-C(5A)	112.13(8)
C(12A)-C(6A)-C(5A)	111.38(8)
C(7A)-C(6A)-C(5A)	99.39(6)
C(11A)-C(7A)-C(8A)	110.62(7)
C(11A)-C(7A)-C(6A)	124.72(7)
C(8A)-C(7A)-C(6A)	104.02(6)
C(11A)-C(7A)-H(7A)	105.1(4)
C(8A)-C(7A)-H(7A)	105.6(4)
C(6A)-C(7A)-H(7A)	105.3(4)
C(1A)-C(8A)-C(7A)	111.77(6)
C(1A)-C(8A)-C(4A)	108.72(6)
C(7A)-C(8A)-C(4A)	103.50(6)
C(1A)-C(8A)-H(8A)	109.4(4)
C(7A)-C(8A)-H(8A)	108.5(4)
C(4A)-C(8A)-H(8A)	114.8(4)
C(15A)-C(9A)-C(10A)	110.76(7)
C(15A)-C(9A)-C(1A)	112.32(7)
C(10A)-C(9A)-C(1A)	114.30(7)
C(15A)-C(9A)-H(9A)	106.5(4)
C(10A)-C(9A)-H(9A)	107.2(4)
C(1A)-C(9A)-H(9A)	105.1(5)
C(11A)-C(10A)-C(9A)	114.74(7)
C(11A)-C(10A)-H(10A)	108.7(5)
C(9A)-C(10A)-H(10A)	110.0(5)
C(11A)-C(10A)-H(10B)	110.1(5)
C(9A)-C(10A)-H(10B)	108.3(5)
H(10A)-C(10A)-H(10B)	104.6(7)
C(7A)-C(11A)-C(10A)	107.07(7)
C(7A)-C(11A)-H(11A)	108.1(5)
C(10A)-C(11A)-H(11A)	110.8(5)
C(7A)-C(11A)-H(11B)	109.7(5)
C(10A)-C(11A)-H(11B)	111.6(5)
H(11A)-C(11A)-H(11B)	109.4(7)
C(6A)-C(12A)-H(12A)	109.7(6)
C(6A)-C(12A)-H(12B)	111.9(5)
H(12A)-C(12A)-H(12B)	108.4(8)
C(6A)-C(12A)-H(12C)	109.7(6)
H(12A)-C(12A)-H(12C)	106.1(7)
H(12B)-C(12A)-H(12C)	110.9(8)
C(6A)-C(13A)-H(13A)	111.6(6)
C(6A)-C(13A)-H(13B)	110.7(6)
H(13A)-C(13A)-H(13B)	107.8(8)

C(6A)-C(13A)-H(13C)	110.6(7)
H(13A)-C(13A)-H(13C)	107.4(8)
H(13B)-C(13A)-H(13C)	108.6(9)
C(4A)-C(14A)-H(14A)	109.6(5)
C(4A)-C(14A)-H(14B)	110.9(5)
H(14A)-C(14A)-H(14B)	108.3(7)
C(4A)-C(14A)-H(14C)	111.3(5)
H(14A)-C(14A)-H(14C)	108.5(7)
H(14B)-C(14A)-H(14C)	108.1(7)
C(9A)-C(15A)-H(15A)	109.1(5)
C(9A)-C(15A)-H(15B)	112.0(5)
H(15A)-C(15A)-H(15B)	108.4(8)
C(9A)-C(15A)-H(15C)	110.9(6)
H(15A)-C(15A)-H(15C)	110.3(8)
H(15B)-C(15A)-H(15C)	106.0(8)
C(1B)-O(1B)-H(1B)	109.6(8)
O(1B)-C(1B)-C(8B)	109.42(6)
O(1B)-C(1B)-C(2B)	105.54(6)
C(8B)-C(1B)-C(2B)	102.40(6)
O(1B)-C(1B)-C(9B)	109.12(6)
C(8B)-C(1B)-C(9B)	111.58(6)
C(2B)-C(1B)-C(9B)	118.31(7)
C(1B)-C(2B)-C(3B)	104.90(7)
C(1B)-C(2B)-H(2C)	110.2(5)
C(3B)-C(2B)-H(2C)	112.0(5)
C(1B)-C(2B)-H(2D)	109.8(5)
C(3B)-C(2B)-H(2D)	112.7(5)
H(2C)-C(2B)-H(2D)	107.3(7)
C(2B)-C(3B)-C(4B)	108.38(6)
C(2B)-C(3B)-H(3C)	111.3(5)
C(4B)-C(3B)-H(3C)	111.5(5)
C(2B)-C(3B)-H(3D)	108.0(5)
C(4B)-C(3B)-H(3D)	109.9(5)
H(3C)-C(3B)-H(3D)	107.7(7)
C(14B)-C(4B)-C(8B)	114.15(7)
C(14B)-C(4B)-C(3B)	110.72(8)
C(8B)-C(4B)-C(3B)	102.28(7)
C(14B)-C(4B)-C(5B)	111.10(8)
C(8B)-C(4B)-C(5B)	103.54(7)
C(3B)-C(4B)-C(5B)	114.67(7)
C(6B)-C(5B)-C(4B)	108.32(7)
C(6B)-C(5B)-H(5C)	110.3(6)
C(4B)-C(5B)-H(5C)	112.0(6)
C(6B)-C(5B)-H(5D)	107.5(6)
C(4B)-C(5B)-H(5D)	111.5(6)
H(5C)-C(5B)-H(5D)	107.2(8)
C(13B)-C(6B)-C(12B)	108.80(7)
C(13B)-C(6B)-C(7B)	112.00(7)
C(12B)-C(6B)-C(7B)	113.00(7)
C(13B)-C(6B)-C(5B)	111.61(7)
C(12B)-C(6B)-C(5B)	111.70(8)
C(7B)-C(6B)-C(5B)	99.55(6)
C(11B)-C(7B)-C(8B)	110.85(7)
C(11B)-C(7B)-C(6B)	124.21(7)
C(8B)-C(7B)-C(6B)	104.03(6)
C(11B)-C(7B)-H(7B)	105.4(4)

C(8B)-C(7B)-H(7B)	105.6(4)
C(6B)-C(7B)-H(7B)	105.3(4)
C(1B)-C(8B)-C(7B)	111.41(6)
C(1B)-C(8B)-C(4B)	108.52(6)
C(7B)-C(8B)-C(4B)	103.07(6)
C(1B)-C(8B)-H(8B)	110.3(4)
C(7B)-C(8B)-H(8B)	110.5(4)
C(4B)-C(8B)-H(8B)	112.9(4)
C(15B)-C(9B)-C(10B)	110.84(7)
C(15B)-C(9B)-C(1B)	112.46(7)
C(10B)-C(9B)-C(1B)	113.92(7)
C(15B)-C(9B)-H(9B)	109.4(4)
C(10B)-C(9B)-H(9B)	105.7(4)
C(1B)-C(9B)-H(9B)	104.0(4)
C(9B)-C(10B)-C(11B)	114.14(7)
C(9B)-C(10B)-H(10C)	108.9(5)
C(11B)-C(10B)-H(10C)	106.1(5)
C(9B)-C(10B)-H(10D)	110.2(5)
C(11B)-C(10B)-H(10D)	108.0(5)
H(10C)-C(10B)-H(10D)	109.3(7)
C(7B)-C(11B)-C(10B)	107.05(7)
C(7B)-C(11B)-H(11C)	110.3(5)
C(10B)-C(11B)-H(11C)	110.8(5)
C(7B)-C(11B)-H(11D)	111.4(5)
C(10B)-C(11B)-H(11D)	111.1(5)
H(11C)-C(11B)-H(11D)	106.2(6)
C(6B)-C(12B)-H(12D)	110.6(5)
C(6B)-C(12B)-H(12E)	111.3(5)
H(12D)-C(12B)-H(12E)	107.6(7)
C(6B)-C(12B)-H(12F)	111.6(5)
H(12D)-C(12B)-H(12F)	107.9(7)
H(12E)-C(12B)-H(12F)	107.7(8)
C(6B)-C(13B)-H(13D)	110.8(6)
C(6B)-C(13B)-H(13E)	111.4(5)
H(13D)-C(13B)-H(13E)	106.1(7)
C(6B)-C(13B)-H(13F)	109.9(5)
H(13D)-C(13B)-H(13F)	108.5(7)
H(13E)-C(13B)-H(13F)	110.2(8)
C(4B)-C(14B)-H(14D)	110.1(6)
C(4B)-C(14B)-H(14E)	108.0(5)
H(14D)-C(14B)-H(14E)	110.4(8)
C(4B)-C(14B)-H(14F)	111.5(6)
H(14D)-C(14B)-H(14F)	108.0(8)
H(14E)-C(14B)-H(14F)	108.9(8)
C(9B)-C(15B)-H(15D)	112.1(6)
C(9B)-C(15B)-H(15E)	112.4(6)
H(15D)-C(15B)-H(15E)	106.9(8)
C(9B)-C(15B)-H(15F)	111.9(5)
H(15D)-C(15B)-H(15F)	105.2(8)
H(15E)-C(15B)-H(15F)	107.9(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for ayh01 (CCDC 889569). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1A)	202(3)	283(3)	360(4)	20(3)	153(3)	-34(3)
C(1A)	139(3)	171(4)	191(3)	2(3)	62(3)	-36(3)
C(2A)	199(4)	235(4)	165(4)	12(3)	77(3)	-21(3)
C(3A)	218(4)	256(4)	177(4)	52(3)	56(3)	15(3)
C(4A)	163(3)	173(4)	208(4)	8(3)	55(3)	9(3)
C(5A)	192(4)	306(5)	278(5)	-26(4)	82(4)	40(4)
C(6A)	211(4)	343(5)	223(4)	-36(4)	115(3)	-30(4)
C(7A)	185(4)	224(4)	164(3)	-10(3)	58(3)	-53(3)
C(8A)	142(3)	168(4)	149(3)	2(3)	34(3)	-23(3)
C(9A)	190(4)	185(4)	248(4)	1(3)	34(3)	4(3)
C(10A)	286(5)	176(4)	292(5)	35(4)	40(4)	-28(4)
C(11A)	307(5)	284(5)	227(4)	71(4)	90(4)	-87(4)
C(12A)	356(5)	512(7)	248(5)	-87(5)	135(4)	16(5)
C(13A)	317(5)	561(7)	409(6)	-19(6)	231(5)	-58(5)
C(14A)	245(4)	167(4)	329(5)	26(4)	49(4)	1(3)
C(15A)	344(5)	260(5)	414(6)	-46(5)	137(5)	61(4)
O(1B)	319(4)	286(3)	183(3)	-61(3)	28(3)	61(3)
C(1B)	170(3)	198(4)	173(3)	-45(3)	54(3)	7(3)
C(2B)	166(4)	341(5)	223(4)	-81(4)	78(3)	20(3)
C(3B)	218(4)	365(5)	289(5)	-25(4)	35(4)	131(4)
C(4B)	268(4)	190(4)	170(4)	-6(3)	19(3)	64(3)
C(5B)	371(5)	351(5)	194(4)	42(4)	51(4)	98(5)
C(6B)	198(4)	276(4)	170(4)	-19(3)	49(3)	-12(3)
C(7B)	142(3)	206(4)	204(4)	-53(3)	64(3)	-15(3)
C(8B)	141(3)	165(4)	170(3)	-17(3)	21(3)	11(3)
C(9B)	194(4)	193(4)	254(4)	12(3)	81(3)	-12(3)
C(10B)	313(5)	171(4)	367(5)	-11(4)	151(4)	4(4)
C(11B)	256(4)	217(4)	316(5)	-56(4)	158(4)	29(3)
C(12B)	299(5)	406(6)	256(5)	24(5)	86(4)	-101(4)
C(13B)	270(5)	468(6)	212(4)	-72(4)	94(4)	-45(5)
C(14B)	500(6)	207(5)	255(5)	4(4)	1(4)	88(4)
C(15B)	330(5)	310(5)	345(6)	45(5)	160(4)	-32(4)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for ayh01 (CCDC 889569).

	x	y	z	U_{iso}
H(1A)	399(1)	87(1)	-27(1)	38(4)
H(2A)	220(1)	-62(1)	-70(1)	16(2)
H(2B)	280(1)	5(1)	-106(1)	19(2)
H(3A)	161(1)	170(1)	-98(1)	21(2)
H(3B)	243(1)	244(1)	-96(1)	21(2)
H(5A)	161(1)	333(1)	57(1)	21(2)
H(5B)	118(1)	206(1)	-2(1)	29(2)
H(7A)	195(1)	-40(1)	33(1)	14(2)
H(8A)	336(1)	123(1)	110(1)	9(2)
H(9A)	413(1)	-122(1)	91(1)	15(2)
H(10A)	260(1)	-271(1)	38(1)	22(2)
H(10B)	338(1)	-315(1)	112(1)	28(2)
H(11A)	234(1)	-187(1)	143(1)	31(2)
H(11B)	319(1)	-100(1)	179(1)	30(2)
H(12A)	196(1)	258(1)	198(1)	45(3)
H(12B)	281(1)	235(1)	187(1)	34(3)
H(12C)	244(1)	106(1)	226(1)	42(3)
H(13A)	114(1)	-24(1)	146(1)	52(3)
H(13B)	73(1)	6(1)	57(1)	45(3)
H(13C)	72(1)	126(1)	116(1)	51(3)
H(14A)	304(1)	398(1)	86(1)	29(2)
H(14B)	254(1)	451(1)	0(1)	32(2)
H(14C)	338(1)	364(1)	20(1)	29(2)
H(15A)	412(1)	-328(1)	19(1)	37(3)
H(15B)	418(1)	-186(1)	-31(1)	46(3)
H(15C)	333(1)	-270(1)	-52(1)	43(3)
H(1B)	511(1)	90(1)	89(1)	44(3)
H(2C)	683(1)	266(1)	258(1)	18(2)
H(2D)	694(1)	177(1)	188(1)	30(2)
H(3C)	717(1)	45(1)	323(1)	36(3)
H(3D)	693(1)	-45(1)	244(1)	35(3)
H(5C)	571(1)	-91(1)	371(1)	41(3)
H(5D)	642(1)	20(1)	396(1)	40(3)
H(7B)	600(1)	263(1)	319(1)	9(2)
H(8B)	480(1)	93(1)	203(1)	15(2)
H(9B)	480(1)	324(1)	116(1)	8(2)
H(10C)	586(1)	476(1)	248(1)	26(2)
H(10D)	497(1)	531(1)	191(1)	34(3)
H(11C)	495(1)	432(1)	307(1)	22(2)
H(11D)	437(1)	344(1)	237(1)	19(2)
H(12D)	443(1)	9(1)	378(1)	33(3)
H(12E)	426(1)	26(1)	289(1)	33(3)
H(12F)	409(1)	162(1)	335(1)	39(3)
H(13D)	527(1)	289(1)	438(1)	41(3)
H(13E)	618(1)	246(1)	451(1)	39(3)
H(13F)	563(1)	134(1)	477(1)	31(3)
H(14D)	509(1)	-182(1)	238(1)	47(3)
H(14E)	603(1)	-231(1)	267(1)	40(3)
H(14F)	559(1)	-160(1)	184(1)	43(3)

H(15D)	552(1)	521(1)	82(1)	57(3)
H(15E)	581(1)	364(1)	61(1)	44(3)
H(15F)	634(1)	450(1)	137(1)	40(3)

Table 6. Hydrogen bonds for ayh01 (CCDC 889569) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1A)-H(1A)...O(1B)#1	0.734(10)	2.033(10)	2.7380(9)	161.1(11)
O(1B)-H(1B)...O(1A)	0.748(11)	2.028(11)	2.7658(9)	168.8(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z

CALIFORNIA INSTITUTE OF TECHNOLOGY

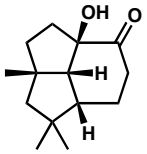
BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

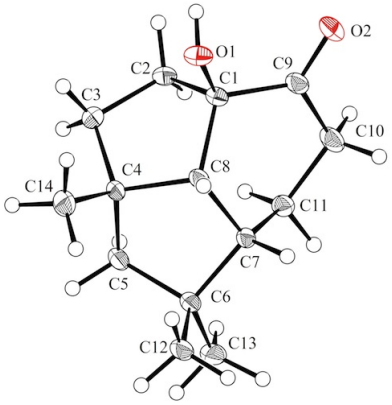
Crystal Structure Analysis of:

Compound **21b**

(AYH02) (CCDC 889570)



Contents



AYH02

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC). The deposition number is 889570.

Table 1. Crystal Data and Structure Analysis Details for ayh02 (CCDC 889570).

Empirical formula	$C_{14}H_{22}O_2$
Formula weight	222.32
Crystallization solvent	benzene, slow evaporation
Crystal shape	irregular
Crystal color	colourless
Crystal size	0.05 x 0.10 x 0.44 mm

Data Collection

Preliminary photograph(s)	rotation	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data collection temperature	100 K	
Theta range for 4413 reflections used in lattice determination	2.77 to 31.42°	
Unit cell dimensions	a = 5.8000(6) Å b = 7.3616(7) Å c = 29.454(3) Å	α= 90° β= 90° γ = 90°
Volume	1257.6(2) $Å^3$	
Z	4	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1) (# 19)	
Density (calculated)	1.174 g/cm^3	
F(000)	488	
Theta range for data collection	2.8 to 35.1°	
Completeness to theta = 25.00°	99.9%	
Index ranges	$-9 \le h \le 8$, $-11 \le k \le 7$, $-46 \le l \le 46$	
Data collection scan type	narrow omega and phi scans	
Reflections collected	19979	
Independent reflections	5133 [R_{int}= 0.0514]	
Reflections > 2σ(I)	4130	
Average σ(I)/(net I)	0.0579	
Absorption coefficient	0.08 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9962 and 0.9672	
Reflections monitored for decay	0	
Decay of standards	0%	

Table 1 (cont.)

Structure Solution and Refinement

Primary solution method	direct
Secondary solution method	difmap
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5133 / 0 / 233
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.56
Final R indices [I>2σ(I), 4130 reflections]	R1 = 0.0515, wR2 = 0.0685
R indices (all data)	R1 = 0.0713, wR2 = 0.0707
Type of weighting scheme used	calc
Weighting scheme used	calc w=1/[^2^(Fo^2^)+(0.0000P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	-0.4(8)
Largest diff. peak and hole	0.35 and -0.32 e.$Å^{-3}$

Programs Used

Cell refinement	SAINT V8.18C (Bruker-AXS, 2007)
Data collection	APEX2 2012.2-0 (Bruker-AXS, 2007)
Data reduction	SAINT V8.18C (Bruker-AXS, 2007)
Structure solution	SHELXS-97 (Sheldrick, 1990)
Structure refinement	SHELXL-97 (Sheldrick, 1997)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

References

Special Refinement Details

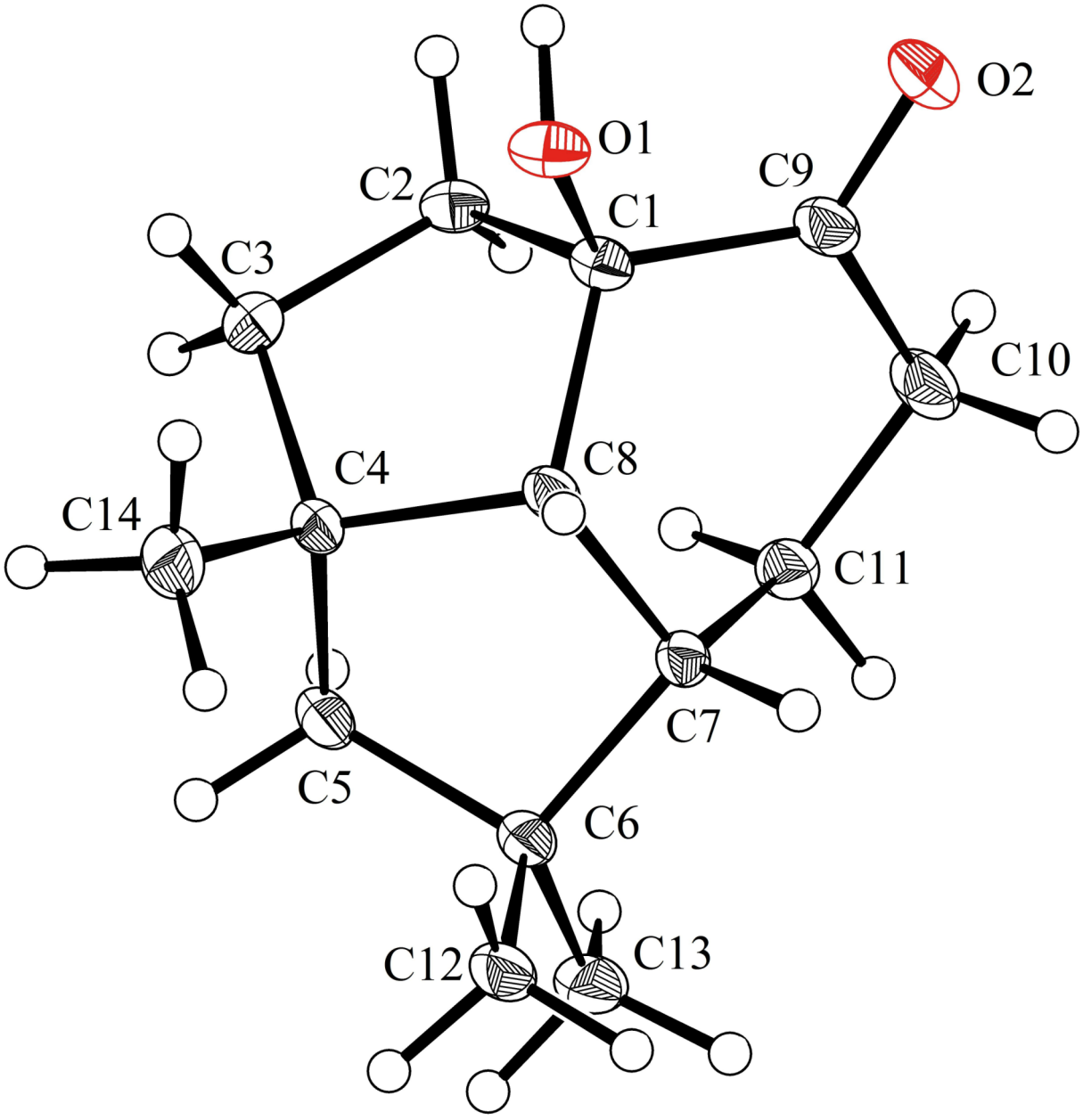

O1
O2
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ayh02 (CCDC 889570). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1)	3631(2)	7788(1)	1771(1)	15(1)
C(2)	1527(2)	6527(2)	1808(1)	16(1)
C(3)	1401(2)	5619(2)	1345(1)	18(1)
C(4)	2282(2)	7021(1)	996(1)	15(1)
C(5)	339(2)	8066(2)	754(1)	18(1)
C(6)	1024(2)	10078(1)	743(1)	16(1)
C(7)	2200(2)	10316(1)	1211(1)	14(1)
C(8)	3529(2)	8518(1)	1283(1)	14(1)
C(9)	3490(2)	9258(2)	2129(1)	18(1)
C(10)	1817(2)	10785(2)	2050(1)	23(1)
C(11)	531(2)	10713(2)	1601(1)	18(1)
C(12)	2788(2)	10465(2)	368(1)	21(1)
C(13)	-1040(2)	11316(2)	665(1)	23(1)
C(14)	3888(2)	6071(2)	660(1)	23(1)
O(1)	5704(1)	6782(1)	1805(1)	20(1)
O(2)	4656(2)	9193(1)	2472(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for ayh02 (CCDC 889570).

C(1)-O(1)	1.4155(13)
C(1)-C(9)	1.5143(15)
C(1)-C(8)	1.5351(14)
C(1)-C(2)	1.5375(15)
C(2)-C(3)	1.5225(15)
C(2)-H(2A)	0.961(11)
C(2)-H(2B)	0.993(11)
C(3)-C(4)	1.5429(16)
C(3)-H(3A)	0.958(12)
C(3)-H(3B)	1.000(11)
C(4)-C(14)	1.5291(15)
C(4)-C(5)	1.5406(15)
C(4)-C(8)	1.5654(15)
C(5)-C(6)	1.5334(15)
C(5)-H(5A)	0.980(12)
C(5)-H(5B)	1.000(12)
C(6)-C(13)	1.5227(16)
C(6)-C(12)	1.5328(16)
C(6)-C(7)	1.5483(14)
C(7)-C(11)	1.5301(15)
C(7)-C(8)	1.5462(15)
C(7)-H(7)	0.982(10)
C(8)-H(8)	0.956(10)
C(9)-O(2)	1.2164(13)
C(9)-C(10)	1.5036(16)
C(10)-C(11)	1.5186(16)
C(10)-H(10A)	1.000(13)
C(10)-H(10B)	0.965(13)
C(11)-H(11A)	0.997(11)
C(11)-H(11B)	0.997(11)
C(12)-H(12A)	0.968(12)
C(12)-H(12B)	1.033(13)
C(12)-H(12C)	0.981(12)
C(13)-H(13A)	1.007(12)
C(13)-H(13B)	1.020(13)
C(13)-H(13C)	0.961(13)
C(14)-H(14A)	0.980(12)
C(14)-H(14B)	1.001(12)
C(14)-H(14C)	0.977(13)
O(1)-H(1)	0.804(14)
O(1)-C(1)-C(9)	111.71(9)
O(1)-C(1)-C(8)	106.39(8)
C(9)-C(1)-C(8)	113.66(9)
O(1)-C(1)-C(2)	110.67(8)
C(9)-C(1)-C(2)	109.75(9)
C(8)-C(1)-C(2)	104.39(9)
C(3)-C(2)-C(1)	103.78(9)
C(3)-C(2)-H(2A)	112.8(6)
C(1)-C(2)-H(2A)	108.1(6)
C(3)-C(2)-H(2B)	110.7(6)
C(1)-C(2)-H(2B)	112.1(6)
H(2A)-C(2)-H(2B)	109.2(9)

C(2)-C(3)-C(4)	106.72(9)
C(2)-C(3)-H(3A)	113.5(7)
C(4)-C(3)-H(3A)	110.2(7)
C(2)-C(3)-H(3B)	108.2(6)
C(4)-C(3)-H(3B)	108.7(6)
H(3A)-C(3)-H(3B)	109.4(9)
C(14)-C(4)-C(5)	111.95(9)
C(14)-C(4)-C(3)	109.09(9)
C(5)-C(4)-C(3)	113.61(9)
C(14)-C(4)-C(8)	112.96(9)
C(5)-C(4)-C(8)	103.68(9)
C(3)-C(4)-C(8)	105.35(8)
C(6)-C(5)-C(4)	107.57(9)
C(6)-C(5)-H(5A)	114.9(7)
C(4)-C(5)-H(5A)	110.4(7)
C(6)-C(5)-H(5B)	109.9(7)
C(4)-C(5)-H(5B)	109.3(7)
H(5A)-C(5)-H(5B)	104.7(9)
C(13)-C(6)-C(12)	107.76(9)
C(13)-C(6)-C(5)	112.17(9)
C(12)-C(6)-C(5)	111.53(9)
C(13)-C(6)-C(7)	114.37(9)
C(12)-C(6)-C(7)	109.10(9)
C(5)-C(6)-C(7)	101.87(8)
C(11)-C(7)-C(8)	112.14(9)
C(11)-C(7)-C(6)	114.31(9)
C(8)-C(7)-C(6)	104.12(8)
C(11)-C(7)-H(7)	105.3(6)
C(8)-C(7)-H(7)	111.3(6)
C(6)-C(7)-H(7)	109.7(6)
C(1)-C(8)-C(7)	116.49(9)
C(1)-C(8)-C(4)	106.06(8)
C(7)-C(8)-C(4)	107.38(9)
C(1)-C(8)-H(8)	107.7(6)
C(7)-C(8)-H(8)	110.1(6)
C(4)-C(8)-H(8)	108.9(6)
O(2)-C(9)-C(10)	121.13(10)
O(2)-C(9)-C(1)	121.44(10)
C(10)-C(9)-C(1)	117.42(9)
C(9)-C(10)-C(11)	115.22(10)
C(9)-C(10)-H(10A)	106.4(7)
C(11)-C(10)-H(10A)	110.9(7)
C(9)-C(10)-H(10B)	108.4(8)
C(11)-C(10)-H(10B)	111.5(8)
H(10A)-C(10)-H(10B)	103.6(10)
C(10)-C(11)-C(7)	110.44(9)
C(10)-C(11)-H(11A)	109.4(6)
C(7)-C(11)-H(11A)	110.6(6)
C(10)-C(11)-H(11B)	111.1(6)
C(7)-C(11)-H(11B)	110.9(6)
H(11A)-C(11)-H(11B)	104.4(9)
C(6)-C(12)-H(12A)	112.4(7)
C(6)-C(12)-H(12B)	114.1(7)
H(12A)-C(12)-H(12B)	105.9(9)
C(6)-C(12)-H(12C)	110.5(7)
H(12A)-C(12)-H(12C)	108.0(10)

H(12B)-C(12)-H(12C)	105.5(10)
C(6)-C(13)-H(13A)	112.8(7)
C(6)-C(13)-H(13B)	113.7(7)
H(13A)-C(13)-H(13B)	107.3(10)
C(6)-C(13)-H(13C)	110.8(7)
H(13A)-C(13)-H(13C)	107.9(9)
H(13B)-C(13)-H(13C)	103.7(10)
C(4)-C(14)-H(14A)	109.7(7)
C(4)-C(14)-H(14B)	110.7(7)
H(14A)-C(14)-H(14B)	105.5(9)
C(4)-C(14)-H(14C)	113.0(7)
H(14A)-C(14)-H(14C)	109.2(10)
H(14B)-C(14)-H(14C)	108.4(10)
C(1)-O(1)-H(1)	110.1(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for ayh02 (CCDC 889570). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	143(5)	177(5)	124(5)	12(4)	-11(4)	17(5)
C(2)	186(5)	177(5)	132(5)	40(5)	16(5)	-4(5)
C(3)	231(6)	148(5)	171(6)	12(4)	-4(5)	-26(5)
C(4)	209(5)	144(5)	103(5)	-11(4)	0(4)	-24(5)
C(5)	225(6)	196(6)	124(5)	-16(5)	-29(5)	-36(5)
C(6)	188(6)	170(5)	131(5)	7(4)	-34(4)	-30(4)
C(7)	146(5)	138(5)	127(5)	0(4)	-11(4)	-28(4)
C(8)	156(5)	163(5)	99(5)	0(4)	13(4)	-19(5)
C(9)	219(5)	209(6)	112(5)	12(4)	15(4)	-39(5)
C(10)	296(7)	266(7)	128(6)	-55(5)	0(5)	73(6)
C(11)	204(5)	174(6)	148(5)	-3(5)	6(4)	27(5)
C(12)	296(6)	218(6)	121(6)	25(5)	-11(5)	-72(6)
C(13)	254(7)	228(6)	198(6)	43(5)	-84(5)	-21(5)
C(14)	313(7)	207(6)	170(6)	-39(5)	32(5)	0(6)
O(1)	186(4)	245(4)	176(4)	57(4)	-14(3)	43(4)
O(2)	389(5)	279(5)	174(4)	-32(4)	-114(4)	21(4)

Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for ayh02 (CCDC 889570).

	x	y	z	U_{iso}
H(2A)	181(2)	568(1)	205(1)	11(3)
H(2B)	8(2)	721(1)	187(1)	9(3)
H(3A)	-12(2)	522(2)	126(1)	17(3)
H(3B)	247(2)	456(2)	134(1)	13(3)
H(5A)	3(2)	753(2)	46(1)	24(3)
H(5B)	-113(2)	791(2)	93(1)	24(3)
H(7)	325(2)	1136(1)	120(1)	4(2)
H(8)	508(2)	864(1)	118(1)	7(3)
H(10A)	272(2)	1194(2)	208(1)	39(4)
H(10B)	77(2)	1084(2)	230(1)	40(4)
H(11A)	-28(2)	1189(2)	155(1)	15(3)
H(11B)	-73(2)	979(2)	161(1)	17(3)
H(12A)	223(2)	1013(2)	7(1)	30(4)
H(12B)	434(2)	979(2)	41(1)	27(3)
H(12C)	318(2)	1176(2)	36(1)	32(4)
H(13A)	-63(2)	1264(2)	69(1)	25(3)
H(13B)	-237(2)	1109(2)	88(1)	30(4)
H(13C)	-171(2)	1110(2)	37(1)	30(3)
H(14A)	307(2)	507(2)	51(1)	25(3)
H(14B)	522(2)	550(2)	82(1)	26(3)
H(14C)	450(2)	689(2)	43(1)	31(3)
H(1)	568(2)	615(2)	203(1)	37(4)

Table 6. Hydrogen bonds for ayh02 (CCDC 889570) [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O(1)-H(1)...O(2)#1	0.804(14)	2.071(15)	2.8653(12)	169.7(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1/2