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Supporting Information

A Unified Approach to the Daucane and Sphenolobane Bicyclo[5.3.0]decane Core: Enantioselective Total Syntheses of Daucene, Daucenal, Epoxydaucenal B, and 14-*para*-Anisoyloxydauc-4,8-diene

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Materials and Methods

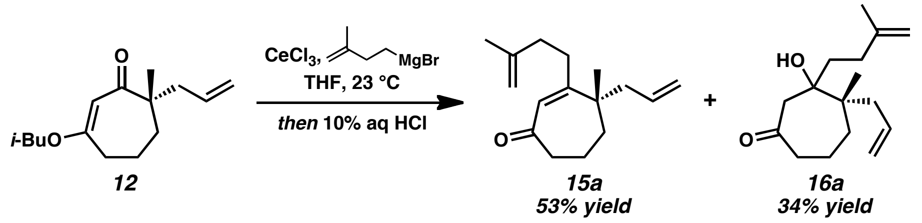
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Methanol (MeOH) was distilled over Mg and I_2 according to the procedure of Lund and Bjerrum.[2] Brine solutions are saturated aqueous solutions of sodium chloride. Vinylogous ester **12** was prepared following the method found in our previous report.[3] Triisopropylsilyl triflate was distilled immediately before use. Oxotrischlorobis(tetrahydrofuran)molybdenum(V) was prepared according to the procedure of McUliffe.[4] All other reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, Alfa Aesar, or TCI America and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag temperature modulator. Microwave-assisted reactions were performed in a Biotage Initiator 2.5 microwave reactor. Glove box manipulations were performed under a N_2 atmosphere. Reaction progress was monitored by thin-layer chromatography (TLC). TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde staining, and/or $KMnO_4$ staining. ICN silica gel (particle size 0.032-0.0653 mm) or Silicycle Silia*Flash* P60 Academic silica gel (particle size 0.040-0.063 mm) was used for flash column chromatography. ^1H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm) or benzene-d_6 (C_6D_6, δ 7.16 ppm). ^{13}C NMR spectra are recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and are reported relative to $CDCl_3$ (δ 77.16 ppm) or benzene-d_6 (C_6D_6, δ 128.06 ppm). 2D NMR experiments were performed on a Varian Inova 400 MHz or Varian Inova 500 MHz spectrometer and are reported relative to residual solvent. Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration, assignment (if applicable)). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, dm = doublet of multiplets, br = broad (e.g. br s = broad singlet), app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility (EI+, GC-EI+, 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 ionization mode (MM: ESI-APCI+). 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*).

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

Ar = argon
i-Bu = isobutyl
n-Bu = *n*-butyl
t-Bu = *tert*-butyl
DMAP = 4-dimethylaminopyridine
Me = methyl
µwaves = microwave irradiation
SiO_2 = silica gel
TBAF = tetrabutylammonium fluoride
TBME = *tert*-butyl methyl ether
TFE = 2,2,2-trifluoroethanol
THF = tetrahydrofuran
Tf = triflate
TIPS = triisopropylsilyl

Preparative Procedures

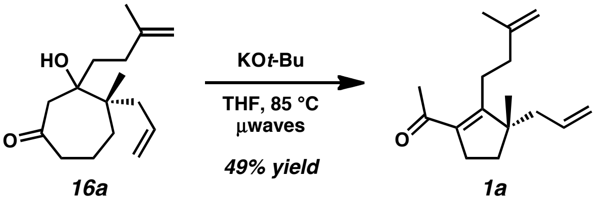
Procedures Associated with Initial Approach



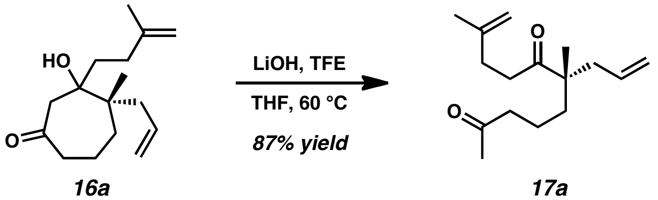
Cycloheptenone 15a and β-Hydroxyketone 16a. A flame-dried 250 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with anhydrous cerium chloride (2.66 g, 10.79 mmol, 2.54 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, and charged with THF (50 mL). After 24 h of stirring, (3-methylbut-3-en-1-yl)magnesium bromide[5] (0.24 M in THF, 52.85 mL, 12.69 mmol, 2.99 equiv) was added to the flask, causing the slurry to initially turn yellow and orange over time. After 3 h, the flask was charged with additional THF (20 mL), and vinylogous ester **12** (1.00 g, 4.25 mmol, 1.00 equiv) was transferred from a conical flask to the round-bottom flask using several THF rinses (3 x 10 mL, total added = 106 mL, 0.04 M). TLC analysis indicated no starting material remained after 5 min. After 40 min, the reaction was quenched with HCl (10% w/w aq, 50 mL) and transferred to a separatory funnel where the aqueous layer was extracted five times with EtOAc. The combined organics were rinsed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 3 cm, 100% hexanes→5%→10%→20% EtOAc in hexanes) to afford cycloheptenone **15a** (473.0 mg, 2.04 mmol, 53% yield) as a pale yellow oil and β-hydroxyketone **16a** (325.3 mg, 1.30 mmol, 34% yield) as a pale yellow oil.

Cycloheptenone 15a. Characterization data matches that previously reported.

β-hydroxyketone 16a. R_f = 0.55 (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) mixture of two diastereomers, see Figure SI-1.1; IR (Neat Film NaCl) 3464, 3072, 2965, 2936, 2866, 1694, 1647, 1638, 1452, 1375, 1342, 1299, 1229, 1186, 1110, 1073, 1029, 997, 967, 917, 884, 793 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{27}O_2$ $[M+H]^+$: 251.2006, found 251.2007.



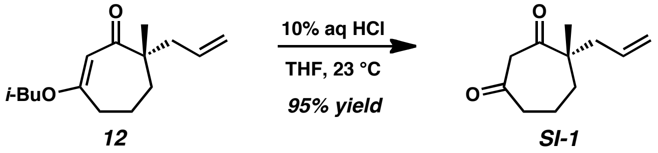
Acylcyclopentene 1a. KO*t*-Bu (269.4 mg, 2.40 mmol, 1.65 equiv) and THF (10 mL, 0.10 M), were added to a flame-dried 20 mL microwave vial with a stir bar. β-hydroxyketone **16a** (364.9 mg, 1.46 mmol, 1.00 equiv) was transferred to the vial using benzene (200 μL) and THF (2 x 1 mL). Another portion of THF (3 mL, total added = 15 mL, 0.10 M) was added to the vial. The pale yellow solution was subjected to microwave irradiation in a Biotage Initiator microwave reactor (temperature: 85 °C, sensitivity: normal). After 5 min of irradiation, the crimp cap was removed and Na_2SO_4 was added to the vial. The reaction contents were transferred to a separatory funnel, quenched with HCl (10% w/w aq, 10 mL), and extracted four times with Et_2O. The combined organics (300 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 28.5 x 3 cm, 100% pentane→5%→10%→15%→20% Et_2O in pentane) to afford acylcyclopentene **1a** (164.3 mg, 0.71 mmol, 49% yield) as a yellow oil; R_f = 0.75 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (dddd, J = 16.8, 10.3, 7.6, 7.0 Hz, 1H), 5.08–5.01 (m, 2H), 4.74 (dq, J = 2.2, 1.1 Hz, 1H), 4.73 (td, J = 1.4, 0.7 Hz, 1H), 2.61–2.52 (m, 3H), 2.33 (tdt, J = 12.2, 5.0, 1.1 Hz, 1H), 2.21 (s, 3H), 2.20–2.04 (m, 4H), 1.88 (ddd, J = 12.9, 7.5, 6.3 Hz, 1H), 1.80 (dd, J = 1.4, 1.0 Hz, 3H), 1.61–1.53 (m, 1H), 1.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.7, 163.5, 146.3, 135.0, 134.9, 117.7, 109.9, 52.6, 43.7, 37.5, 35.0, 31.6, 30.4, 26.6, 24.7, 22.5; IR (Neat Film NaCl) 3074, 2957, 2929, 2864, 1676, 1648, 1602, 1453, 1373, 1355, 1313, 1273, 1252, 1208, 1113, 995, 960, 913, 885 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{25}O$ $[M+H]^+$: 233.1900, found 233.1903; $[\alpha]_D^{25.0}$ –7.12 (c 1.53, $CHCl_3$, 88% ee).



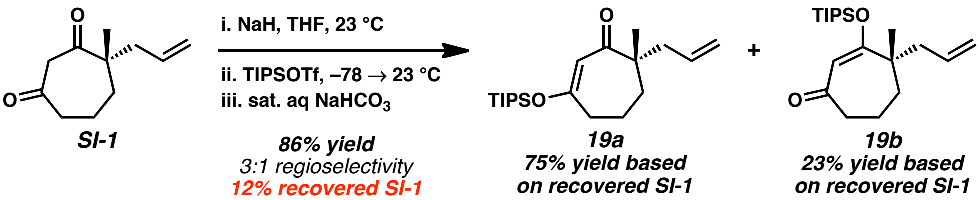
16a **17a**

Dione 17a. β-Hydroxyketone **16a** (50.6 mg, 0.20 mmol, 1.00 equiv) was transferred to a flame-dried 15 mL round-bottom flask equipped with a stir bar and water condenser using several THF rinses (4 x 1 mL, total = 4 mL, 0.05 M). TFE (58 μL, 0.81 mmol, 4.00 equiv) and LiOH (14.2 mg, 0.59 mmol, 2.93 equiv) were added, generating a pale yellow solution. The flask was lowered into a preheated oil bath (60 °C) and heated for 2 h. After cooling to room temperature, the reaction was filtered through a short silica gel plug (2 x 10 cm) rinsing with Et_2O. The combined organics were concentrated under reduced pressure at 0 °C (ice/water) and purified by flash column chromatography (SiO_2, 25 x 2 cm, 100% pentane→2%→5%→10%→15% Et_2O in pentane) to afford dione **17a** (44.1 mg, 0.81 mmol, 87% yield) as a yellow oil; R_f = 0.56 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68–5.59 (m, 1H), 5.06–5.01 (m, 2H), 4.72 (dqt, J = 2.2, 1.5, 0.8 Hz, 1H), 4.67 (qq, J = 1.3, 0.8 Hz, 1H), 2.61–2.57 (m, 2H), 2.40 (dd, J = 7.3, 6.0 Hz, 2H), 2.33 (ddt, J = 14.0, 7.2, 1.2 Hz, 1H), 2.24 (t, J = 7.9 Hz, 2H), 2.21 (ddt, J = 14.0, 7.5, 1.2 Hz, 1H), 2.12 (s, 3H), 1.74 (dd, J = 1.4, 0.8 Hz, 3H), 1.63–1.54 (m, 1H), 1.52–1.33 (m, 3H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.2, 208.6, 145.2, 133.9, 118.3, 110.2, 51.1, 44.0, 42.6, 37.4, 36.1, 31.5, 30.1, 22.9, 21.1, 18.7; IR (Neat Film NaCl) 3076, 2968, 2935, 1717, 1703, 1648, 1640, 1458, 1437, 1410, 1358, 1271, 1229, 1174, 1076, 996, 917, 889, 725 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{27}O_2$ $[M+H]^+$: 251.2006, found 251.2006; $[\alpha]_D^{25.0}$ 6.64 (c 0.96, $CHCl_3$, 88% ee).

Siloxyenone Efforts Toward Acyclic Dione 17a



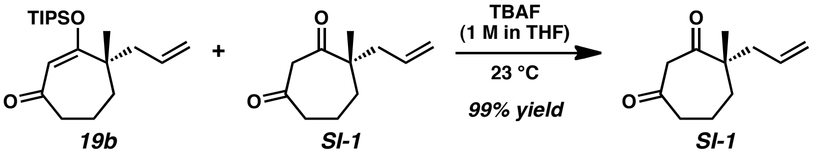
Dione SI-1. The following procedure affords a higher yield than our previous report.[6] A flame-dried 50 mL round-bottom flask equipped with a stir bar was charged with vinylogous ester **12** (1.83 g, 7.73 mmol, 1.00 equiv), THF (12.5 mL, 0.6 M), and hydrochloric acid (10% w/w aq = 2.87 M, 12.5 mL, 35.9 mmol, 4.64 equiv). The reaction mixture was initially a cloudy suspension that became a colorless solution over time. TLC analysis indicated no starting material remained after 4.5 h. Consequently, the reaction was transferred to a separatory funnel, diluted with water, and extracted six times with CH$_2$Cl$_2$. The combined organics (150 mL) were dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO$_2$, 27 x 3 cm, 100% hexanes→15% EtOAc in hexanes) to afford dione **SI-1** (1.33 g, 7.37 mmol, 95% yield) as a yellow oil. Characterization data matches that previously reported.[6]



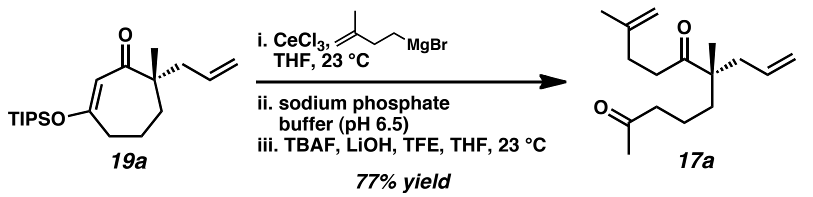
Siloxyenones 19a and b. A flame-dried 50 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with NaH (80.9 mg, 3.20 mmol, 1.05 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, and charged with THF (9 mL). Dione **SI-1** (547.3 mg, 3.04 mmol, 1.00 equiv) was transferred via cannula from a scintillation vial to the round-bottom flask using several THF rinses (1 x 5 mL + 5 x 1 mL, total added = 19 mL, 0.16 M). The reaction was stirred at room temperature for 30 min before the flask was lowered into a –78 °C bath (dry ice/acetone) and TIPSOTf (850 μL, 3.16 mmol, 1.04 equiv) was added dropwise over 20 min. After the addition was complete, the bath was removed and the reaction was allowed to warm to room temperature. After 13 h of stirring, the reaction was poured into a separatory funnel containing Et$_2$O (20 mL), sat. aq NaHCO$_3$ (20 mL), and water (10 mL). The aqueous layer was extracted once with Et$_2$O and four times with CH$_2$Cl$_2$. The combined organics were dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO$_2$, 26 x 3 cm, 100% hexanes→2%→15% EtOAc in hexanes) to afford siloxyenone **19a** (669.9 mg, 1.99 mmol, 66% yield, 75% yield based on recovered dione **SI-1**) as a yellow oil, a mixed fraction of siloxyenone **19b** with dione **SI-1** (206.5 mg total, 50:1 = **19b**:**SI-1**, siloxyenone **19b**: 204.3 mg, 0.6069 mmol, 20% yield, 23% yield based on recovered dione **SI-1**) as a yellow oil, and recovered dione **SI-1** (66.0 mg, 0.366 mmol, 12% recovered) as a yellow oil.

Siloxyenone 19a. R$_f$ = 0.76 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 5.87–5.74 (m, 1H), 5.78 (s, 1H), 5.06–5.00 (m, 2H), 2.51 (ddt, J = 13.5, 7.1, 1.3 Hz, 1H), 2.25 (ddt, J = 13.5, 7.7, 1.1 Hz, 1H), 2.21–2.16 (m, 2H), 1.67–1.59 (m, 1H), 1.44–1.37 (m, 2H), 1.34–1.28 (m, 1H), 1.20 (s, 3H), 1.13–1.00 (m, 21H); ^{13}C NMR (125 MHz, C_6D_6) δ 204.3, 167.5, 135.1, 117.8, 113.9, 51.8, 46.0, 38.2, 35.1, 25.4, 19.98, 18.1, 18.1, 12.9; IR (Neat Film NaCl) 3075, 2944, 2893, 2867, 1700, 1613, 1464, 1419, 1385, 1301, 1249, 1204, 1137, 1109, 1070, 1016, 996, 917, 883, 823, 782, 741 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{20}H_{37}O_2Si$ $[M+H]^+$: 337.2557, found 337.2566; $[\alpha]_D^{25.0}$ –60.52 (c 1.01, $CHCl_3$, 88% ee).

Siloxyenone 19b. R_f = 0.64 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 5.72 (s, 1H), 5.78–5.65 (m, 1H), 5.06–4.98 (m, 2H), 2.54 (ddt, J = 13.6, 6.5, 1.5 Hz, 1H), 2.49 (dm, J = 18.0 Hz, 1H), 2.42 (ddd, J = 17.9, 9.4, 5.1 Hz, 1H), 2.05 (ddt, J = 13.6, 8.1, 1.1 Hz, 1H), 1.62 (ddd, J = 14.4, 9.9, 1.4 Hz, 1H), 1.44 (dtdd, J = 14.6, 9.8, 4.7, 1.4 Hz, 1H), 1.41–1.30 (m, 1H), 1.26 (ddt, J = 14.4, 9.0, 1.2 Hz, 1H), 1.19–1.06 (m, 3H), 1.11 (s, 3H), 1.04 (d, J = 3.1 Hz, 9H), 1.02 (d, J = 3.0 Hz, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 199.3, 172.1, 134.6, 118.1, 113.9, 46.3, 45.3, 44.5, 37.0, 25.9, 18.3, 18.3, 17.9, 13.1; IR (Neat Film NaCl) 2944, 2892, 2867, 1636, 1592, 1464, 1378, 1351, 1283, 1249, 1207, 1170, 1071, 1016, 996, 917, 883, 855, 782 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{20}H_{37}O_2Si$ $[M+H]^+$: 337.2557, found 337.2559; $[\alpha]_D^{25.0}$ –46.35 (c 1.35, $CHCl_3$, 88% ee).

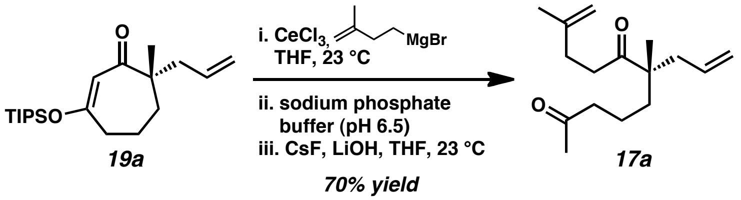


Dione SI-1. To a scintillation vial containing a mixed fraction of siloxyenone **19b** (262.6 mg, 0.780 mmol, 1.00 equiv) and dione **SI-1** (12.0 mg, 0.0666 mmol) was added a stir bar and TBAF (1.0 M in THF, 2 mL, 2.00 mmol, 2.56 equiv). After 4 h, no siloxyenone **19b** was observed by TLC. Consequently, the reaction was quenched with water (10 mL) and transferred to a separatory funnel where the aqueous layer was extracted six times with CH_2Cl_2. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 27.5 x 5 cm, 100% hexanes→5%→15% EtOAc in hexanes) to afford dione **SI-1** (151.7 mg, 0.842 mmol, 99% yield) as a yellow oil. Characterization data matches that previously reported.[6]



Dione 17a. A flame-dried 50 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with anhydrous cerium chloride (589.5 mg, 2.39 mmol, 2.50 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, placed under full vacuum, and lowered into an oil bath set to 140 °C. After 12.5 h, the flask was removed from the bath, allowed to cool to room temperature, and charged with THF (12 mL). After 3 h of stirring, (3-methylbut-3-en-1-yl)magnesium bromide^5 (0.59 M in THF, 4.86 mL, 2.87 mmol, 3.00 equiv) was added and the slurry initially turned yellow and then orange over time. After 40 min, siloxyenone **19a** (321.8 mg, 0.956 mmol, 1.00 equiv) was transferred from a

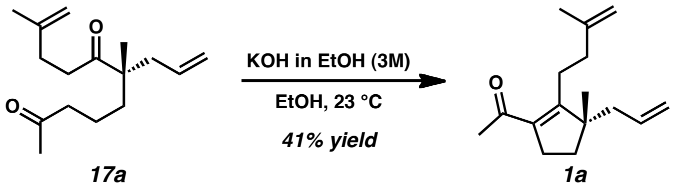
scintillation vial to the round-bottom flask using several THF rinses (1 x 6 mL + 3 x 2 mL, total added = 24 mL, 0.04 M). TLC analysis indicated no starting material remained after 10 min. Consequently, the reaction was quenched with sodium phosphate buffer (20 mM, pH 6.5, 20 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics (150 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was transferred to a scintillation vial equipped with a stir bar and backfilled with Ar. The vial was charged with TBAF (1.0 M in THF, 1.43 mL, 1.43 mmol, 1.50 equiv), TFE (210 μL, 2.88 mmol, 3.01 equiv), and LiOH (34.4 mg, 1.44 mmol, 1.50 equiv). After 4 h, the reaction was quenched with water (10 mL) and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified twice by flash column chromatography (SiO_2, 27.5 x 2 cm, 100% hexanes→5%→10% TBME in hexanes ***then*** SiO_2, 28 x 2 cm, 100% hexanes→2%→5%→20% TBME in hexanes) to afford dione **17a** (185.0 mg, 0.739 mmol, 77% yield) as a pale yellow oil. (For characterization data, see p. SI 4).



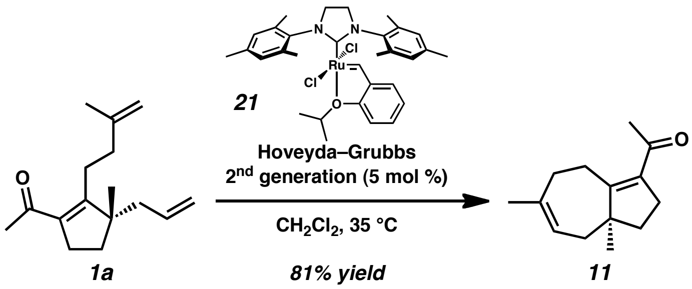
Dione 17a. A flame-dried 15 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with anhydrous cerium chloride (141.7 mg, 0.575 mmol, 2.50 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, placed under full vacuum, and lowered into an oil bath set to 140 °C. After 12 h, the flask was removed from the bath, allowed to cool to room temperature, and charged with THF (1.7 mL). After 2 h of stirring, (3-methylbut-3-en-1-yl)magnesium bromide[5] (0.59 M in THF, 1.17 mL, 0.690 mmol, 3.01 equiv) was added and the slurry initially tur ned yellow and then orange over time. After 30 min, siloxyenone **19a** (77.3 mg, 0.230 mmol, 1.00 equiv) was transferred from a scintillation vial to the round-bottom flask using several THF rinses (1 x 2 mL + 2 x 1 mL, total added = 5.7 mL, 0.04 M). TLC analysis indicated no starting material remained after 5 min. Consequently, the reaction was quenched with sodium phosphate buffer (20 mM, pH 6.5, 5 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

A separate flame-dried 10 mL round-bottom flask equipped with a stir bar was loaded with CsF (145.2 mg, 0.956 mmol, 4.16 equiv) and flame-dried again. Upon cooling, the crude oil from the previous step was transferred to the flask using several THF rinses (3 x 1 mL, total added = 3 mL, 0.08 M). As the reaction failed to progress by TLC analysis after 1 h, LiOH (18.5 mg, 0.772 mmol, 3.36 equiv) was added. TLC analysis indicated the desired product was mainly present after an additional 13 h. Consequently, the reaction was quenched with water (10 mL) and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 1.5 cm, 100% hexanes→2%→5%→10% TBME in hexanes) to afford dione **17a** (40.4 mg, 0.161 mmol, 70% yield) as a pale yellow oil. (For characterization data, see p. SI 4).

Routes to Key Intermediate Enone 11

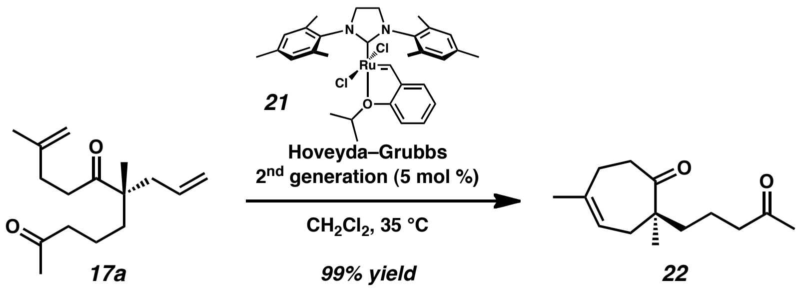


Enone 1a. A scintillation vial equipped with a stir bar and dione **17a** (40.4 mg, 0.161 mmol, 1.00 equiv) was charged with EtOH (950 μL, 0.17 M) and KOH solution (3 M in EtOH, 140 μL, 0.420 mmol, 2.60 equiv). The resulting yellow solution was stirred vigorously. Over the course of the reaction, an additional portion of the KOH solution (2 d = 140 μL, 3 d = 280 μL, 4 d = 1.4 mL, 5 d = 5.0 mL, total added = 7.66 mL, 23.0 mmol, 142 equiv) was added. After 6 days, the reaction was quenched with water (10 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 1.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford enone **1a** (15.3 mg, 0.0660 mmol, 41% yield) as a yellow oil. (For characterization data, see p. SI 4).

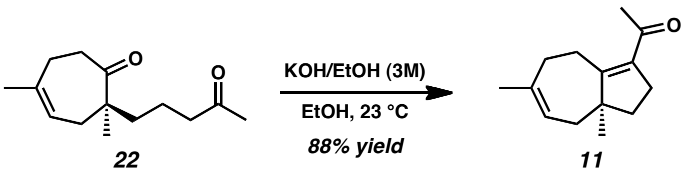


Enone 11. A flame-dried 25 mL round-bottom flask equipped with a stir bar and water condenser was charged with acylcyclopentene **1a** (1.0 M in benzene, 100 μL, 0.100 mmol, 1.00 equiv), CH_2Cl_2 (20 mL, 0.005 M, 30 min Ar sparge before use), and Grubbs–Hoveyda 2nd generation catalyst (**21**, 3.2 mg, 0.00511 mmol, 5 mol %), generating a pale green solution. The flask was lowered into a preheated oil bath (35 °C) and stirred for 5 h before the reaction was cooled to room temperature and quenched with ethyl vinyl ether. The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 21.5 x 1.3 cm, 100% hexanes→2% Et_2O in pentane) to afford enone **11** (16.5 mg, 0.081 mmol, 81% yield) as a yellow oil. Spectral data for enone **11** matches that previously reported by Urones[7]: $R_f = 0.73$ (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (ddt, J = 7.9, 6.7, 1.4 Hz, 1H), 3.21 (dt, J = 11.1, 5.9 Hz, 1H), 2.66–2.56 (m, 1H), 2.50 (ddd, J = 15.3, 8.7, 2.8 Hz, 1H), 2.29–2.16 (m, 1H), 2.21 (s, 3H), 2.17–2.11 (m, 3H), 2.02 (ddd, J = 14.4, 6.6, 1.2 Hz, 1H), 1.75–1.69 (m, 1H), 1.69 (d, J = 1.4 Hz, 3H), 1.64 (ddd, J = 12.3, 7.7, 2.8 Hz, 1H), 0.99 (s, 3H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 199.5, 165.0, 139.4, 133.4, 121.1, 52.7, 37.8, 37.3, 33.2, 30.8, 30.4, 26.1, 24.2, 23.7; IR (Neat Film NaCl) 2926, 2852, 1675, 1653, 1612, 1437, 1356, 1301, 1262, 1204, 945, 825 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{20}O$ $[M+•]^+$: 204.1514, found 204.1530; $[\alpha]_D^{25.0}$ –146.03 (c 0.98, $CHCl_3$, 88% ee).



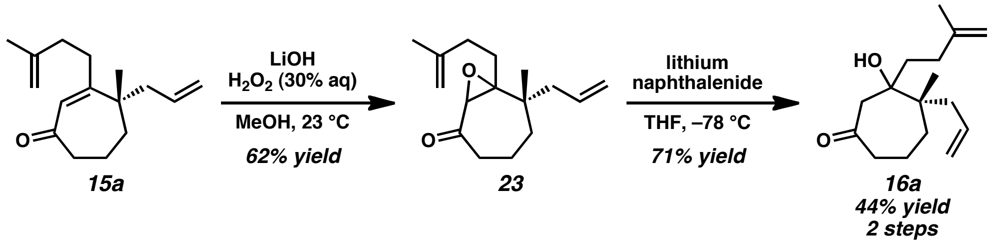
Dione 22. To a flame-dried 250 mL Schlenk flask equipped with a stir bar and water condenser was added dione **17a** (422.6 mg, 1.69 mmol, 1.00 equiv) via several CH_2Cl_2 rinses (5 x 6 mL, 30 min Ar sparge before use). The flask was charged with additional CH_2Cl_2 (130 mL) and Hoveyda–Grubbs 2nd generation catalyst (**21**, 53.0 mg, 0.0846 mmol, 5.0 mol %), generating a pale green solution. The flask was rinsed with CH_2Cl_2 (10 mL, total added = 170 mL, 0.01 M) and lowered into a preheated oil bath (35 °C). After 22 h, the reaction was quenched with ethyl vinyl ether (3 mL), removed from the oil bath, and allowed to cool to room temperature. The reaction contents were filtered through a short silica gel plug, rinsing with TBME, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 27.5 x 2 cm, 100% hexanes→5%→10%→15%→20%→30% TBME in hexanes) to afford dione **22** (370.5 mg, 1.67 mmol, 99% yield) as a yellow oil. Spectral data for dione **22** matches that previously reported by Urones[7a]: R_f = 0.39 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45 (dddd, J = 7.7, 6.2, 3.0, 1.5 Hz, 1H), 2.88 (ddd, J = 11.5, 9.5, 5.7 Hz, 1H), 2.59 (ddd, J = 11.5, 6.9, 5.4 Hz, 1H), 2.43 (dddd, J = 15.2, 6.1, 2.7, 1.3 Hz, 1H), 2.38 (t, J = 6.9 Hz, 2H), 2.34–2.20 (m, 2H), 2.11 (s, 3H), 2.08 (ddq, J = 15.4, 7.3, 1.0 Hz, 1H), 1.66 (q, J = 1.1 Hz, 3H), 1.56–1.38 (m, 4H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.0, 208.8, 137.0, 121.5, 53.8, 44.2, 38.0, 37.9, 34.7, 32.1, 30.1, 25.4, 22.4, 18.7; IR (Neat Film NaCl) 2963, 2931, 1714, 1705, 1436, 1360, 1314, 1215, 1173, 1123, 1071, 1011, 894, 826 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{23}O_2$ $[M+H]^+$: 223.1693, found 223.1696; $[\alpha]_D^{25.0}$ 52.49 (c 0.93, $CHCl_3$, 88% ee).



Enone 11. Procedure adapted from report by Urones.[7a] A flame-dried 25 mL round-bottom flask equipped with a stir bar was charged with dione **22** (255.6 mg, 1.15 mmol, 1.00 equiv), EtOH (6.74 mL, 0.17 M), and KOH solution (3 M in EtOH, 1.02 mL, 3.06 mmol, 2.66 equiv), generating a yellow solution that transitioned to orange over time. After 9 h, an additional portion of KOH (3 M in EtOH, 0.90 mL, total added = 1.92 mL, 5.76 mmol, 5.01 equiv) was added. After 22 h, no starting material remained by TLC. Consequently, the reaction was

diluted with water (15 mL) and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (100 mL) were rinsed with HCl (0.5 M, 15 mL) and water (15 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 26 x 2 cm, 100% hexanes→5% TBME in hexanes) to afford enone **11** (205.6 mg, 1.01 mmol, 88% yield) as a yellow oil. Spectral data for enone **11** matches that previously reported by Urones.[7a] (For characterization data, see p. SI 8).

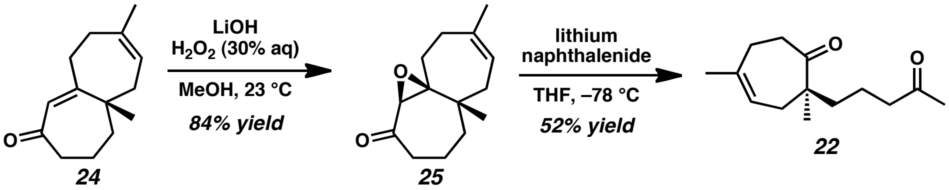
Routes to Reincorporate Cycloheptenone 15a into Synthetic Efforts



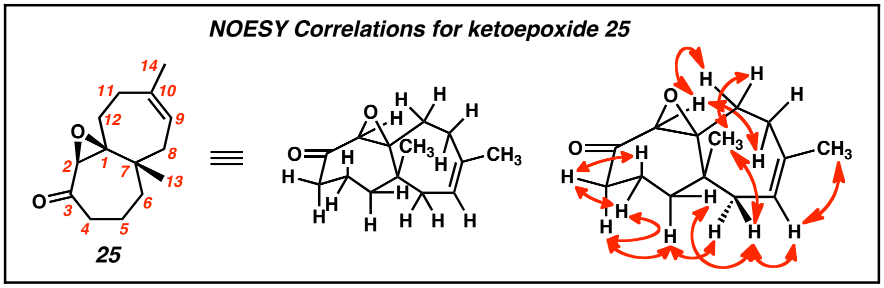
Epoxide 23. Procedure adapted from report by Stoltz.[3] To a scintillation vial containing a stir bar and cycloheptenone **15a** (216.6 mg, 0.932 mmol, 1.00 equiv) was added MeOH (3.6 mL), LiOH (56.1 mg, 2.34 mmol, 2.51 equiv), H_2O_2 (30% w/w aq, 950 µL, 9.30 mmol, 9.98 equiv), and additional MeOH (1.0 mL, total added = 4.6 mL, 0.2 M). During the course of the reaction, additional LiOH (7 h = 56.5 mg, 22 h = 55.8 mg, 31 h = 56.0 mg, 95.5 h = 55.9 mg, 142 h = 56.2 mg, total added = 336.5 mg, 14.0 mmol, 15.0 equiv) and H_2O_2 (950 µL more at 7 h, 22 h, 31 h, 71.5 h, 142 h, 151 h, total added = 7.6 mL, 74.4 mmol, 80 equiv) were added to the flask. The solvent level decreased over time and so more MeOH (47.5 h = 3 mL, 71.5 h = 2 mL, 77.5 h = 3 mL) was added when appropriate. After 10 days, TLC analysis indicated minor starting material remaining. Consequently, the reaction was diluted with CH_2Cl_2 (10 mL) and water (20 mL), quenched with sat. $NaHCO_3$ solution (10 mL), and transferred to a separatory funnel where the aqueous layer was extracted six times with CH_2Cl_2. The combined organics (125 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 2 cm, 100% hexanes→2%→5%→10%→20% EtOAc in hexanes) to afford recovered cycloheptenone **15a** (22.1 mg, 0.0951 mmol, 10% recovered) and epoxide **23** (142.8 mg, 0.575 mmol, 62% yield, 69% yield based on recovered cycloheptenone **15a**) as a cloudy yellow oil; R_f = 0.75 (30% EtOAc in hexanes); ^1H NMR (500 MHz, C_6D_6) mixture of two diastereomers, see Figure SI-8.1; IR (Neat Film NaCl) 3075, 2970, 2936, 1703, 1649, 1639, 1457, 1395, 1376, 1339, 1291, 1261, 1206, 1169, 1121, 996, 919, 890, 848 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{25}O_2$ $[M+H]^+$: 249.1855, found 249.1851.

β-Hydroxyketone 16a. Procedure adapted from report by Liu.[8] A flame-dried 25 mL round-bottom flask equipped with a stir bar was loaded with epoxide **23** (50.0 mg, 0.201 mmol, 1.00 equiv) and THF (5.8 mL, 0.10 M) and lowered into a –78 °C bath (dry ice/acetone). A lithium naphthalenide solution[9] (1.0 M in THF, 3.6 mL, 3.60 mmol, 6.26 equiv) was added dropwise to the flask, generating a dark green solution. During the course of the reaction, an additional portion of lithium naphthalenide (1.0 M in THF, 1 h = 1.0 mL, 5 h = 2.0 mL, 2.5 h = 0.58 mL, total added = 6.60 mL, 6.60 mmol, 11.5 equiv) was added. After 9 h, the reaction was quenched with water (10 mL), diluted with EtOAc, and stirred for 12 h. The reaction contents were transferred to a separatory funnel where the aqueous layer was extracted four times with CH_2Cl_2.

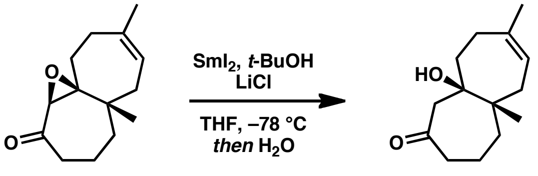
The combined organics (125 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified twice by flash column chromatography (SiO_2, 27.5 x 2 cm, 100% hexanes→5%→10%→20% EtOAc in hexanes ***then*** SiO_2, 27.5 x 2 cm, 100% hexanes→2%→5%→10%→15% EtOAc in hexanes) to afford β-hydroxyketone **16a** (102.6 mg, 0.410 mmol, 71% yield) as a yellow oil. (For characterization data, see p. SI 3).



Epoxide 25. A flame-dried 25 round-bottom flask equipped with a stir bar was charged with enone **24**[10] (110.3 mg, 0.540 mmol, 1.00 equiv), MeOH (4.8 mL, 0.11 M), LiOH (32.4 mg, 1.35 mmol, 2.50 equiv), and H_2O_2 (30% w/w aq, 550 μL, 5.38 mmol, 10.0 equiv). After 30.5 h, no starting material remained by TLC analysis. Consequently, the reaction was quenched with sat. aq $NaHCO_3$ (10 mL) and water (10 mL) and was transferred to a separatory funnel where the aqueous layer was extracted five times with CH_2Cl_2. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 1.5 cm, 100% hexanes→2%→5%→20% EtOAc in hexanes) to afford epoxide **25** (99.5 mg, 0.452 mmol, 84% yield) as a yellow oil that solidified upon freezing; $R_f = 0.68$ (30% EtOAc in hexanes); ^1H NMR (500 MHz, C_6D_6) δ 5.20 (ddt, J = 8.6, 5.1, 1.8 Hz, 1H, H-9), 3.18 (d, J = 1.3 Hz, 1H, H-2), 2.45 (td, J = 11.5, 5.3 Hz, 1H, H-4), 2.24–2.14 (m, 1H, H-4), 2.07 (ddd, J = 13.3, 12.4, 2.9 Hz, 1H, H-12), 2.00–1.89 (m, 1H, H-11), 1.82 (ddt, J = 14.9, 4.9, 1.8 Hz, 1H, H-8), 1.68 (ddd, J = 15.7, 5.6, 2.9 Hz, 1H, H-11), 1.67–1.58 (m, 1H, H-6), 1.56 (q, J = 1.4 Hz, 3H, H-14), 1.46 (dd, J = 14.8, 8.6 Hz, 1H, H-8), 1.29–1.20 (m, 1H, H-5), 1.13–1.04 (m, 2H, H-5 and H-6), 0.97 (s, 3H, H-13), 0.78 (ddd, J = 13.3, 5.5, 3.2 Hz, 1H, H-12); ^{13}C NMR (125 MHz, C_6D_6) δ 207.8, 138.0, 121.7, 72.0, 67.5, 40.6, 40.6, 40.1, 36.3, 33.8, 31.2, 26.1, 25.7, 18.1; IR (Neat Film NaCl) 2961, 2928, 2843, 1698, 1452, 1437, 1330, 1270, 841 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{20}O_2$ $[M+\bullet]^+$: 220.1463, found 220.1496; $[\alpha]_D^{25.0}$ –78.43 (c 1.06, $CHCl_3$, 88% ee).

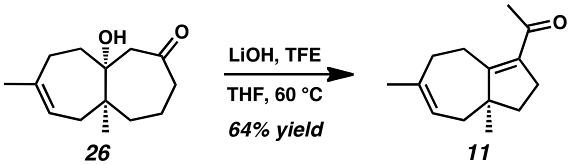

NOESY Correlations for ketoepoxide 25

Dione 22. To a 15 mL round-bottom flask equipped with a stir bar was loaded with epoxide **25** (35.6 mg, 0.162 mmol, 1.00 equiv) and THF (1.6 mL, 0.10 M) and lowered into a –78 °C bath (dry ice/acetone). A lithium naphthalenide solution[9] (1.0 M in THF, 680 μL, 0.680 mmol, 4.2 equiv) was added dropwise to the flask, generating a dark green solution. After 1.5 h, the reaction was quenched with water (5 mL), allowed to warm to room temperature, and transferred to a separatory funnel where the aqueous layer was extracted six times with CH_2Cl_2. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified twice by flash column chromatography (SiO_2, 29 x 1.5 cm, 100% hexanes→5%→10%→15%→20%→50% EtOAc in hexanes ***then*** SiO_2, 25.5 x 1.5 cm, 100% hexanes→10%→15% EtOAc in hexanes) to afford enone **22** (18.7 mg, 0.0842 mmol, 52% yield) as a yellow oil. (For characterization data, see p. SI 9).



25 *92% yield* **26**

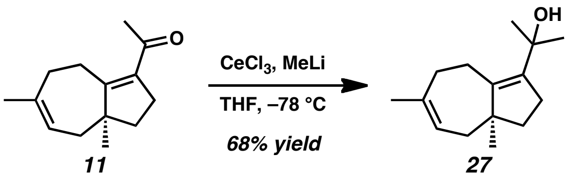
β-Hydroxyketone 26. A flame-dried 10 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with lithium chloride (52.6 mg, 1.24 mmol, 8.57 equiv). The flask was removed from the glove box and connected to an Ar-filled manifold. Epoxide **25** (31.9 mg, 0.145 mmol, 1.00 equiv) was transferred to the flask using several THF rinses (30 min Ar sparge before use, 3 x 0.5 mL, total added = 1.5 mL), *t*-BuOH (20 µL, 0.209 mmol, 1.44 equiv) was added, and the flask was lowered into a –78 °C bath (dry ice/acetone). A samarium diiodide solution[11] (0.1 M in THF, 3.04 mL, 0.304 mmol, 2.10 equiv) was added dropwise over 5 min down the side of the flask, generating a dark blue solution. TLC analysis indicated that no starting material remained after 5 min. After an additional 5 min, the reaction was quenched with water (2 mL), allowed to warm to room temperature, and transferred to a separatory funnel where the aqueous layer was extracted four times with EtOAc. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 25 x 1.5 cm, 100% hexanes→20% EtOAc in hexanes) to afford β-hydroxyketone **26** (29.7 mg, 0.133 mmol, 92% yield) as a yellow oil that solidified upon freezing; $R_f = 0.26$ (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.38 (tdd, J = 6.2, 2.6, 1.4 Hz, 1H), 3.10 (br s, 1H), 2.67 (br m, 1H), 2.43–2.32 (m, 2H), 2.20 (br m, 1H), 2.13 (br m, 1H), 2.04 (br m, 1H), 1.90 (dd, J = 15.4, 10.7 Hz, 1H), 1.84–1.76 (m, 2H), 1.73 (d, J = 1.3 Hz, 3H), 1.77–1.67 (m, 2H), 1.62 (br s, 1H), 1.57 (dd, J = 14.3, 10.5 Hz, 1H), 1.47 (ddd, J = 13.8, 8.9, 1.8 Hz, 1H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 140.0, 122.5, 77.3, 54.2, 43.1, 42.4, 40.1, 38.3, 36.4, 28.0, 25.4, 23.0, 18.2; IR (Neat Film NaCl) 3510, 2958, 2926, 2859, 1692, 1445, 1402, 1284, 1023, 903, 851, 828 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{22}O_2$ $[M+•]^+$: 222.1620, found 222.1629; $[\alpha]_D^{25.0}$ –39.67 (c 0.85, $CHCl_3$, 86% ee).



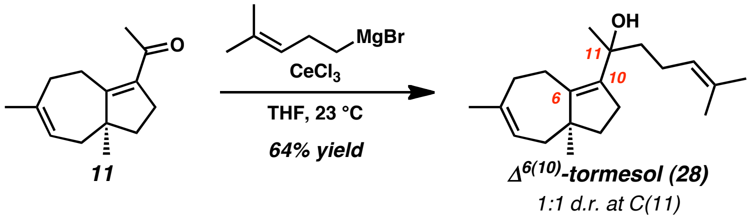
26 *64% yield* **11**

Enone 11. A 20 mL scintillation vial equipped with a stir bar and β-hydroxyketone **26** (13.6 mg, 0.0612 mmol, 1.00 equiv) was connected to an Ar-filled manifold and flushed with Ar. The vial was loaded with THF (1.5 mL, 0.04 M), TFE (10 µL, 0.137 mmol, 2.24 equiv), and LiOH (2.2 mg, 0.0919 mmol, 1.50 equiv) and lowered into a preheated oil bath (60 °C). After 72 h, the solvent had evaporated, and so the vial was charged with additional THF (1.5 mL). TLC analysis of the reaction after 75 h indicated no starting material or dione **22**. Consequently, the reaction was removed from the oil bath, allowed to cool to room temperature, filtered through a celite plug rinsing with Et_2O, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO2, 23 x 1.5 cm, 100% hexanes hexanes→5% TBME in hexanes) to afford enone **11** (8.0 mg, 0.0392 mmol, 64% yield) as a yellow oil. (For characterization data, see p. SI 8).

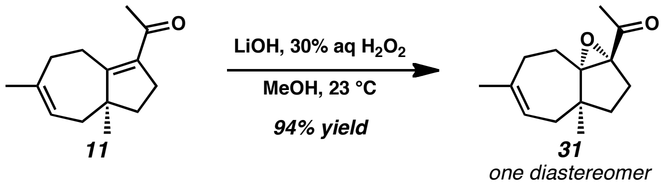
Derivatization of Enone 11 and Synthesis of (–)-Epoxydaucenal B (3b) and Δ^{11}-Carotol (34)



Alcohol 27. A flame-dried 15 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with anhydrous cerium chloride (76.4 mg, 0.310 mmol, 2.53 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, placed under full vacuum, and lowered into an oil bath set to 140 °C. After 13 h, the flask was removed from the bath, allowed to cool to room temperature, and charged with THF (3 mL). After 3 h of stirring, methyllithium (1.6 M in pentane, 310 µL, 0.496 mmol, 4.05 equiv) was added and the flask was lowered into a –78 °C bath (dry ice/acetone). The resulting slurry initially turned yellow and then orange over time. After 10 min, enone **11** (25.0 mg, 0.122 mmol, 1.00 equiv) was added neat. TLC analysis indicated no starting material remained after 5 min. Consequently, the reaction was quenched after 10 min with sat. aq NH_4Cl (20 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 27.5 x 2 cm, 100% hexanes→5% TBME in hexanes) to afford alcohol **27** (18.3 mg, 0.0829 mmol, 68% yield) as a pale yellow oil; R_f = 0.65 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (tp, J = 6.5, 1.5 Hz, 1H), 3.00 (ddd, J = 13.6, 4.9, 3.9 Hz, 1H), 2.37–2.26 (m, 1H), 2.21 (dddd, J = 15.6, 8.6, 3.4, 1.2 Hz, 1H), 2.14 (dt, J = 15.2, 4.6 Hz, 1H), 2.11–2.04 (m, 1H), 2.01 (dt, J = 7.0, 1.1 Hz, 2H), 1.99–1.94 (m, 1H), 1.71 (t, J = 1.3 Hz, 4H), 1.62–1.51 (m, 2H), 1.36 (s, 3H), 1.34 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 139.3, 139.0, 122.0, 72.5, 51.3, 39.3, 37.8, 34.1, 31.2, 30.7, 30.5, 26.1, 24.1, 23.3; IR (Neat Film NaCl) 3373, 2965, 2924, 2850, 1455, 1367, 1331, 1259, 1172, 1138, 1083, 1043, 1012, 984, 945, 887, 822 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{23}O$ $[(M+H)–H_2]^+$: 219.1749, found 219.1743; $[\alpha]_D^{25.0}$ –33.73 (c 1.83, $CHCl_3$, 88% ee).

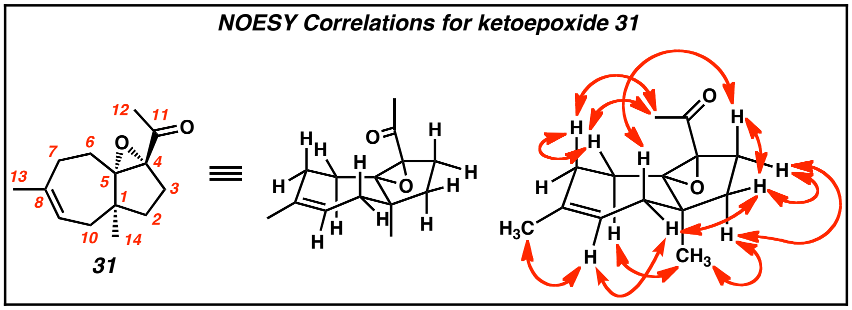


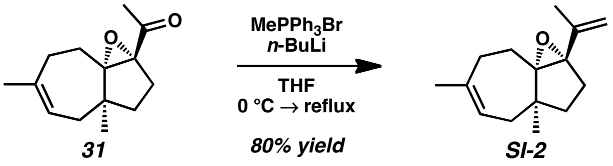
$\Delta^{6(10)}$-tormesol (28). A flame-dried 15 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with anhydrous cerium chloride (91.2 mg, 0.370 mmol, 2.52 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, placed under full vacuum, and lowered into an oil bath set to 140 °C. After 12 h, the flask was removed from the bath, allowed to cool to room temperature, and charged with THF (1.6 mL). After 3 h of stirring, (4-methylpent-3-en-1-yl)magnesium bromide (0.39 M in THF, 1.13 mL, 0.441 mmol, 3.00 equiv) was added and the slurry turned yellow. After 45 min, enone **11** (30.0 mg, 0.147 mmol, 1.00 equiv) was transferred from a scintillation vial to the round-bottom flask using several THF rinses (1 x 1.5 mL + 3 x 0.5 mL, total added = 4.6 mL, 0.03 M). TLC analysis indicated no starting material remained after 5 min. Consequently, the reaction was quenched with sat. NH_4Cl solution (3 mL) at –78 °C and allowed to warm to room temperature. The reaction contents were transferred to a separatory funnel where the aqueous layer was extracted four times with CH_2Cl_2 and three times with Et_2O. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 1.5 cm, 5% TBME in hexanes) to afford $\Delta^{6(10)}$-tormesol (**28**, 27.1 mg, 0.0941 mmol, 64% yield) as a yellow oil; R_f = 0.75 (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) mixture of two diastereomers, see Figure SI-12.1; IR (Neat Film NaCl) 3460, 2964, 2925, 2853, 1668, 1645, 1449, 1375, 1330, 1310, 1261, 1238, 1192, 1111, 1063, 1006, 983, 924, 825 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{20}H_{32}O$ $[M+\bullet]^+$: 288.2453, found 288.2451.



Ketoepoxide 31. Procedure adapted from report by Stoltz.[3] A flame-dried 25 mL round-bottom flask equipped with a stir bar and enone **11** (100.4 mg, 0.491 mmol, 1.00 equiv) was backfilled with Ar and charged with MeOH (3 mL), LiOH (29.5 mg, 1.23 mmol, 2.50 equiv), and H_2O_2 (30% w/w aq, 500 µL, 4.90 mmol, 10.0 equiv). Over the course of the reaction, additional LiOH (29.5 mg at 33 h, 46 h, 73 h and 29.6 mg at 80.5 h, total added = 147.6 mg, 6.15 mmol, 12.5 equiv) and H_2O_2 (500 µL at 33 h, 46 h, 73 h, 80.5 h, total added = 2.5 mL, 24.5 mmol, 50 equiv) were added. After 4 days, no starting material remained by TLC analysis. Consequently, CH_2Cl_2 (10 mL), water (10 mL), and sat. $NaHCO_3$ solution (10 mL) was added. The reaction contents were transferred to a separatory funnel where the aqueous layer was extracted four times with CH_2Cl_2. The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 28.5 x 1.5 cm, 100% hexanes→2%→5% TBME in hexanes) to afford ketoepoxide **31** (101.8 mg, 0.462 mmol, 94% yield) as a yellow oil; R_f = 0.70 (30% EtOAc in

hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 5.31 (ddq, J = 8.7, 5.2, 1.7 Hz, 1H, H-9), 2.22 (ddd, J = 13.8, 11.1, 8.2 Hz, 1H, H-3), 2.07 (dddd, J = 13.6, 3.8, 1.9, 1.0 Hz, 1H, H-10), 2.03–1.93 (m, 1H, H-7), 1.97 (s, 3H, H-12), 1.77 (tdd, J = 12.8, 2.0, 1.1 Hz, 1H, H-6), 1.73 (ddt, J = 13.8, 8.2, 0.9 Hz, 1H, H-3), 1.56 (td, J = 1.8, 0.7 Hz, 3H, H-13), 1.52 (dddd, J = 14.4, 6.6, 2.0, 1.2 Hz, 1H, H-7), 1.47 (dd, J = 14.4, 8.6 Hz, 1H, H-10), 1.41 (dddd, J = 12.4, 6.2, 5.5, 0.7 Hz, 1H, H-6), 1.37 (ddd, J = 12.4, 11.1, 8.2 Hz, 1H, H-2), 1.00 (ddt, J = 12.4, 8.2, 0.8 Hz, 1H, H-2), 0.96 (s, 3H, H-14); ^{13}C NMR (125 MHz, C_6D_6) δ 204.9, 139.9, 122.8, 78.3, 74.7, 44.5, 35.9, 35.8, 29.1, 27.9, 26.8, 26.1, 25.2, 19.4; IR (Neat Film NaCl) 2962, 2930, 2868, 1701, 1446, 1354, 1266, 1178, 1136, 1128, 1079, 1020, 994, 975, 954, 934, 882, 833 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{21}O_2$ $[M+H]^+$: 221.1536, found 221.1530; $[\alpha]_D^{25.0}$ –50.64 (c 1.24, $CHCl_3$, 88% ee).

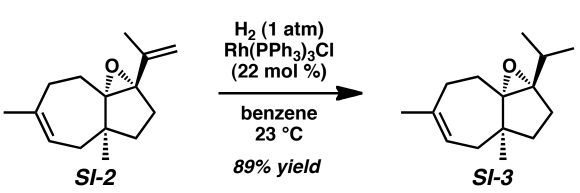

NOESY Correlations for ketoepoxide 31



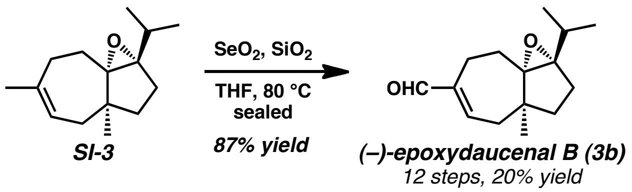
31 **SI-2**

Diene SI-2. A flame-dried 25 mL round-bottom flask equipped with a stir bar was cycled into a glove box and loaded with methyltriphenylphosphonium bromide (121.1 mg, 0.339 mmol, 1.54 equiv). The flask was removed from the glove box, connected to an Ar-filled manifold, charged with THF (1.4 mL), and lowered into a 0 °C bath (ice/water). *n*-BuLi (2.5 M in hexanes, 110 µL, 0.275 mmol, 1.25 equiv) was added dropwise to the flask, generating a bright yellow solution. After 15 min, ketoepoxide **31** (48.5 mg, 0.220 mmol, 1.00 equiv) was transferred via cannula to the flask using several THF rinses (3 x 1 mL, total added = 4.4 mL, 0.05 M) and the bath was allowed to warm to room temperature over time. After 1 h, significant starting material persisted by TLC analysis. Consequently, an additional solution (15 min prestir at 0 °C) of methyltriphenylphosphonium bromide (353.5 mg, 0.990 mmol, 4.50 equiv) and *n*-BuLi (2.5 M in hexanes, 330 µL, 0.275 mmol, 1.25 equiv) in THF (2 mL) was prepared and cannula transferred to the 25 mL flask. After 17 h, starting material was still present by TLC analysis, so a water condenser was attached to the flask and the reaction was heated to reflux. After 45 h, starting material was still observed by TLC analysis. Consequently, another solution (15 min prestir at 0 °C) of methyltriphenylphosphonium bromide (356.7 mg, 0.999 mmol, 4.53 equiv) and *n*-BuLi (2.5 M in hexanes, 330 µL, 0.275 mmol, 1.25 equiv) in THF (2 mL) was prepared and cannula transferred to the 25 mL flask. The solvent level decreased over time and more THF (2 mL at 47 h and 65 h) was added when appropriate. After 4 days, no starting material was observed by TLC analysis. Consequently, the reaction was quenched with H_2O (5 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 26.5

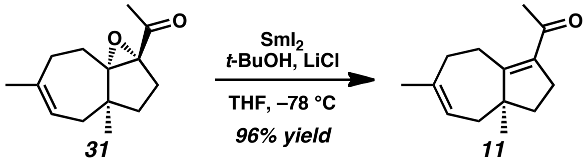
x 1.5 cm, 100% hexanes→2%→10% TBME in hexanes) to afford diene **SI-2** (38.5 mg, 0.176 mmol, 80% yield) as a yellow oil; R_f = 0.76 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (ddp, J = 8.6, 5.1, 1.6 Hz, 1H), 4.98 (q, J = 1.2 Hz, 2H), 2.14 (dddt, J = 14.2, 4.5, 1.8, 0.9 Hz, 1H), 2.06 (ddd, J = 13.7, 10.8, 8.3 Hz, 1H), 2.00 (br t, J = 13.8 Hz, 1H), 1.87 (t, J = 1.2 Hz, 3H), 1.87–1.83 (m, 1H), 1.82 (ddt, J = 13.8, 8.3, 1.0 Hz, 1H), 1.80–1.72 (m, 1H), 1.76 (td, J = 1.8, 0.6 Hz, 3H), 1.67 (dddd, J = 14.0, 13.0, 2.1, 1.1 Hz, 1H), 1.41 (ddd, J = 12.7, 10.8, 8.3 Hz, 1H), 1.39 (dddd, J = 13.7, 6.5, 1.9, 0.6 Hz, 1H), 1.23 (dd, J = 12.4, 8.2 Hz, 1H), 0.99 (d, J = 0.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 139.9, 123.0, 112.9, 78.6, 74.1, 43.9, 36.2, 36.1, 29.9, 28.4, 25.4, 24.6, 20.8, 19.7; IR (Neat Film NaCl) 2962, 2929, 2868, 2851, 1646, 1444, 1373, 960, 903, 831 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{22}O$ $[M+\bullet]^+$: 218.1671, found 218.1672; $[\alpha]_D^{25.0}$ –55.99 (c 1.11, $CHCl_3$, 88% ee).



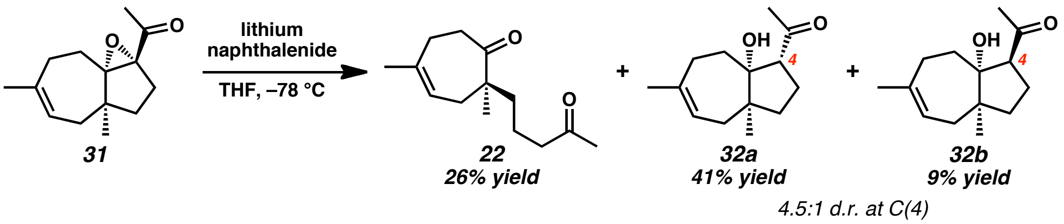
Epoxide SI-3. A flame-dried 10 mL round-bottom flask equipped with a stir bar was cycled into a glove box and loaded with Wilkinson's catalyst (13.1 mg, 0.0142 mmol, 15.0 mol %). The flask was removed from the glove box, connected to an Ar-filled manifold, and charged with benzene (30 min Ar sparge before use, 0.15 mL). Diene **SI-2** (20.6 mg, 0.0944 mmol, 1.00 equiv) was transferred to the flask via a cannula using several benzene rinses (3 x 1 mL, total added = 3.15 mL, 0.03 M). The reaction was disconnected from the manifold, connected to a hydrogen balloon, and flushed with hydrogen, generating an orange solution. After 4 h, no starting material was observed by TLC, so the stir bar was removed and rinsed with CH_2Cl_2, and the reaction was concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 24.5 x 1.5 cm, 100% hexanes→1% TBME in hexanes) to afford an oil that contained both epoxide **SI-3** and residual starting material (~10%). The reaction was set up again following the above procedure (Wilkinson's catalyst: 6.3 mg, 0.00681 mmol, 7 mol %; benzene: 3.15 mL, 0.03 M). After 3 h, a reaction aliquot was removed and ^{1}H NMR analysis revealed no starting material. Consequently, the stir bar was removed and rinsed with CH_2Cl_2, and the reaction was concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 27 x 1.5 cm, 100% hexanes→1% TBME in hexanes) to afford epoxide **SI-3** (18.4 mg, 0.0835 mmol, 89% yield) as a yellow oil; R_f = 0.69 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (ddq, J = 8.7, 5.3, 1.7 Hz, 1H), 2.17 (ttt, J = 13.3, 1.8, 0.8 Hz, 1H), 2.08 (dd, J = 14.7, 4.5 Hz, 1H), 1.94 (dddd, J = 14.4, 6.6, 1.9, 1.3 Hz, 1H), 1.82–1.74 (m, 1H), 1.77 (td, J = 1.8, 0.7 Hz, 3H), 1.76–1.66 (m, 4H), 1.43 (ddd, J = 14.1, 6.6, 1.9 Hz, 1H), 1.31 (ddd, J = 12.5, 10.5, 8.6 Hz, 1H), 1.15 (ddd, J = 12.3, 8.0, 1.0 Hz, 1H), 1.07 (d, J = 6.9 Hz, 6H), 0.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 123.2, 77.5, 76.3, 44.1, 36.2, 35.4, 30.1, 28.6, 25.5, 25.4, 22.9, 19.7, 19.5, 19.0; IR (Neat Film NaCl) 2961, 2930, 2869, 1709, 1454, 1368, 1022, 964, 828 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{24}O$ $[M+\bullet]^+$: 220.1827, found 220.1820; $[\alpha]_D^{25.0}$ –50.57 (c 1.25, $CHCl_3$, 88% ee).



(–)-Epoxydaucenal B (3b). Adapted from a procedure by Wood.[12] A 20 mL scintillation vial equipped with a stir bar and epoxide **SI-3** (10.8 mg, 0.0490 mmol, 1.00 equiv) was connected to an Ar-filled manifold and flushed with Ar. The vial was charged with THF (5.13 mL) and premixed selenium dioxide (10.9 mg, 0.0982 mmol, 2.00 equiv) and silica gel (117.8 mg, 1.96 mmol, 40.0 equiv). The vial was rinsed with THF (1 mL, total added = 6.13 mL, 0.008 M), sealed with a teflon cap, and lowered into a preheated sand bath (80 °C). After 30 min, starting material persisted by TLC analysis, so the vial was resealed and lowered back into the sand bath. After an additional 15 min, no starting material remained by TLC analysis. Consequently, the reaction was filtered through a short celite pad rinsing with Et_2O and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 26 x 1.5 cm, 100% hexanes→2%→5%→10% TBME in hexanes) to afford epoxydaucenal B[13] (**3b**, 10.0 mg, 0.0427 mmol, 87% yield) as a yellow oil; R_f = 0.58 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 9.22 (s, 1H), 6.03 (dddd, J = 8.7, 5.1, 2.2, 1.2 Hz, 1H), 3.11–3.03 (m, 1H), 1.85 (ddtd, J = 14.0, 5.1, 1.5, 0.8 Hz, 1H), 1.69–1.60 (m, 1H), 1.62–1.52 (m, 3H), 1.51 (sept, J = 7.0 Hz, 1H), 1.44–1.40 (m, 1H), 1.41–1.33 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 0.96–0.86 (m, 1H), 0.83 (s, 3H), 0.77 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 191.9, 152.5, 146.3, 75.7, 75.1, 44.3, 37.1, 35.7, 28.5, 25.4, 22.9, 20.1, 19.8, 19.6, 19.0; IR (Neat Film NaCl) 2961, 2931, 2869, 1687, 1683, 1644, 1455, 1444, 1378, 1229, 1149, 1023, 1003, 965, 876 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{22}O_2$ $[M+•]^+$: 234.1620, found 234.1630; $[\alpha]_D^{25.0}$ –20.52 (c 1.00, $CHCl_3$, 88% ee).



Enone 11. A flame-dried 10 mL round-bottom flask equipped with a stir bar was cycled into a glove box where the flask was loaded with lithium chloride (77.0 mg, 1.82 mmol, 8.59 equiv). The flask was removed from the glove box and connected to an Ar-filled manifold. Epoxide **31** (46.6 mg, 0.212 mmol, 1.00 equiv) was transferred to the flask using several THF rinses (60 min Ar sparge before use, 1 x 0.6 mL + 3 x 0.5 mL, total added = 2.1 mL, 0.1 M), *t*-BuOH (20 µL, 0.209 mmol, 0.99 equiv) was added, and the flask was lowered into a –78 °C bath (dry ice/acetone). A samarium diiodide solution[11] (0.1 M in THF, 4.5 mL, 0.450 mmol, 2.13 equiv) was added dropwise over 5 min down the side of the flask, generating a dark blue solution. TLC analysis indicated that no starting material remained after 8 min. Consequently, the reaction was quenched with sat. aq NH_4Cl (2 mL), allowed to warm to room temperature, and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash column chromatography (SiO_2, 26 x 1.5 cm, 100% hexanes→5%→10%→15%→30%→50% TBME in hexanes) to afford enone **11** (41.5 mg, 0.203 mmol, 96% yield) as a yellow oil. (For characterization data, see p. SI 8).



31

22 *26% yield*

32a *41% yield*

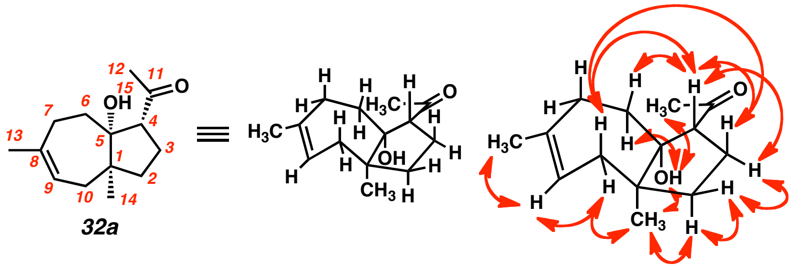
32b *9% yield*

4.5:1 d.r. at C(4)

β-hydroxyketone 32a and b. Procedure adapted from report by Liu.[8] A flame-dried 15 mL round-bottom flask equipped with a glass stir bar and ketoepoxide **31** (50.2 mg, 0.228 mmol, 1.00 equiv) was charged with THF (2.3 mL, 0.1 M) and lowered into a –78 °C bath (acetone/dry ice). A lithium naphthalenide solution[9] (1.0 M, 680 µL, 0.680 mmol, 2.98 equiv) was added dropwise and the reaction mixture turned dark green. Over the course of the reaction, an additional portion of lithium naphthalenide was added (680 µL at 1.5 h, 3 h, 4.5 h, total added = 2.72 mL, 2.72 mmol, 11.9 equiv). After 9 h, the reaction was quenched with H_2O and allowed to warm to room temperature. The reaction was transferred to a separatory funnel where the aqueous layer was extracted six times with CH_2Cl_2. The combined organics (50 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 1.5 cm, 100% hexanes→2%→5%→10%→20%→40% TBME in hexanes) to afford dione **22** (13.1 mg, 0.0588 mmol, 26% yield), β-hydroxyketone **32a** (20.7 mg, 0.0933 mmol, 41% yield) as a yellow oil, and β-hydroxyketone **32b** (4.6 mg, 0.0206 mmol, 9% yield) as a yellow oil. (For characterization data of dione **22**, see p. SI 9).

β-hydroxyketone 32a. R_f = 0.57 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 5.34 (ddt, J = 8.5, 4.5, 1.5 Hz, 1H, H-9), 3.95 (s, 1H, H-15), 2.77 (dd, J = 10.2, 9.1 Hz, 1H, H-4), 2.00 (dddd, J = 12.2, 3.4, 1.7, 0.9 Hz, 1H, H-10), 1.96 (dt, J = 8.6, 1.6 Hz, 1H, H-7), 1.90 (ddd, J = 12.3, 10.1, 5.1 Hz, 1H, H-2), 1.87–1.80 (m, 1H, H-6), 1.84–1.78 (m, 1H, H-7), 1.80–1.74 (m, 1H, H-3), 1.69 (ddd, J = 14.4, 10.7, 1.9 Hz, 1H, H-6), 1.68 (s, 3H, H-12), 1.63 (t, J = 1.7 Hz, 3H, H-13), 1.53 (ddd, J = 17.5, 12.4, 5.1 Hz, 1H, H-3), 1.57–1.47 (m, 1H, H-10), 1.24–1.15 (m, 1H, H-2), 1.19 (s, 3H, H-14); ^{13}C NMR (125 MHz, C_6D_6) δ 212.8, 139.5, 122.6, 84.1, 56.3, 48.7, 40.4, 38.3, 34.2, 31.0, 29.4, 25.4, 25.3, 20.5; IR (Neat Film NaCl) 3479, 2959, 2925, 2853, 1694, 1446, 1394, 1362, 1307, 1260, 1243, 1175, 1105, 1077, 1051, 1010, 832 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{23}O_2$ $[M+H]^+$: 223.1693, found 223.1692; $[\alpha]_D^{25.0}$ –193.24 (c 0.57, $CHCl_3$, 88% ee).

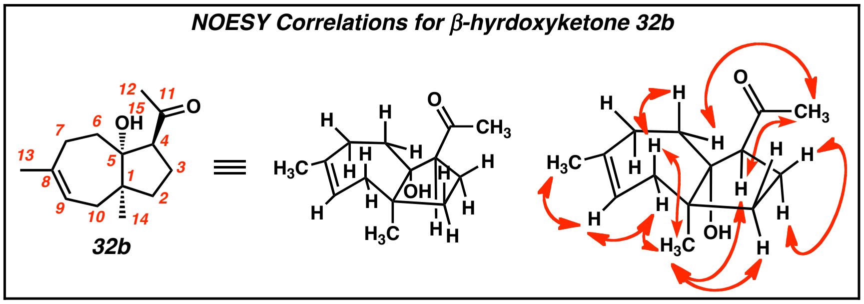
NOESY Correlations for β-hyrdoxyketone 32a



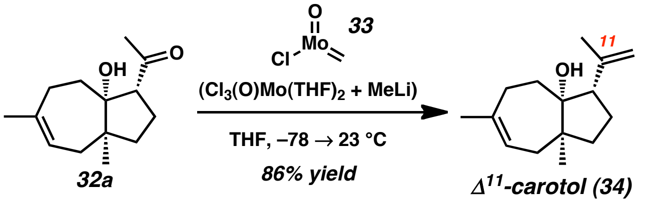
32a

β-hydroxyketone 32b. R_f = 0.36 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, C_6D_6) δ 5.21 (dddd, J = 8.6, 6.4, 3.2, 1.6 Hz, 1H, H-9), 2.83 (t, J = 9.6 Hz, 1H, H-4), 2.24 (br t, J = 14.2 Hz, 1H, H-7), 2.18 (dddd, J = 13.7, 10.5, 9.7, 5.4 Hz, 1H, H-3), 2.04 (dd, J = 15.1, 6.4 Hz, 1H, H-10), 1.98 (s, 3H, H-12), 1.85 (dd, J = 15.0, 7.4 Hz, 1H, H-10), 1.69–1.57 (m, 4H, H-2, H-6, H-7, and H-15), 1.53 (dt, J = 1.7, 0.8 Hz, 3H, H-13), 1.45 (dtd, J = 13.7, 9.4, 6.1 Hz, 1H, H-3), 1.26 (ddd, J = 14.9, 6.5, 2.6 Hz, 1H, H-6), 1.15 (ddd, J = 13.0, 9.3, 5.4 Hz, 1H, H-2), 0.87 (s, 3H, H-14); ^{13}C NMR (125 MHz, C_6D_6) δ 208.2, 140.4, 122.2, 84.2, 62.7, 47.5, 35.6, 34.2, 31.5, 31.1, 28.1, 25.2, 24.8, 20.6; IR (Neat Film NaCl) 3501, 2962, 2927, 2874, 1694, 1457, 1363, 1213, 1069, 1027, 833, 819 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{22}O_2$ $[M+\bullet]^+$: 222.1620, found 222.1623; $[\alpha]_D^{25.0}$ 67.43 (c 0.46, $CHCl_3$, 88% ee).

NOESY Correlations for β-hyrdoxyketone 32b



32b



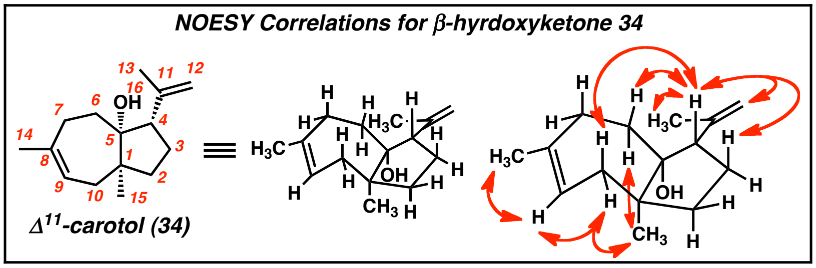
32a

Δ^{11}-carotol (34)

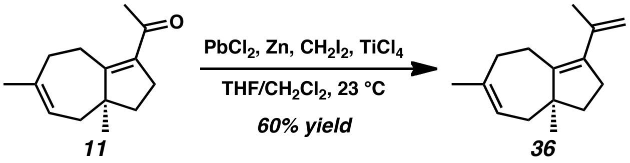
11 steps, 12% yield

Δ^{11}-carotol (34). A flame-dried 25 mL round-bottom flask equipped with a stir bar was cycled into a glove box, loaded with oxotrischlorobis(tetrahydrofuran)molybdenum(V)[14] (139.0 mg, 0.383 mmol, 4.11 equiv), removed from the glove box, and connected to an Ar-filled manifold. The flask was charged with THF (2 mL) and lowered into a –78 °C bath (dry ice/acetone). Methyllithium (1.58 M in Et_2O, 240 µL, 0.379 mmol, 4.06 equiv) was added dropwise to the flask causing the reaction mixture to transition from a bright green solution to a dark red/purple solution. After 1 h, β-hydroxyketone **32a** (20.7 mg, 0.0933 mmol, 1.00 equiv) was transferred to the flask via cannula using several THF rinses (2 x 1.5 mL + 1 mL, total added = 6 mL), and the bath was allowed to expire over time. After 29 h, starting material persisted by TLC analysis. Consequently, an additional solution (1 h prestir at –78 °C) of oxotrischlorobis(tetrahydrofuran)-molybdenum(V) (138.7 mg, 0.383 mmol, 4.10 equiv) and methyllithium (1.58 M in Et_2O, 240 µL, 0.275 mmol, 1.25 equiv) in THF (1 mL) was prepared and transferred via cannula to the 25 mL flask at –78 °C. The bath was once again allowed to expire over time. As starting material was still observed by TLC analysis after 40 h and 53 h, two additional solutions (*vide supra*) were prepared at –78 °C and transferred via cannula to the 25 mL flask at these times ($Cl_3(O)Mo(THF)_2$ total added = 556.1 mg, 1.52 mmol, 16.4 equiv; MeLi total added = 0.96 mL, 1.52 mmol, 16.3 equiv; THF total added = 9 mL). After 65 h, starting material was completely consumed by TLC analysis. The reaction was subsequently quenched with water (5 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics (50 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 25.5 x 1.5 cm, 100% hexanes→2% TBME in hexanes) to afford Δ^{11}-

carotol (**34**, 17.6 mg, 0.0799 mmol, 86% yield) as a yellow oil; R_f = 0.75 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (ddp, J = 8.8, 4.5, 1.5 Hz, 1H, H-9), 5.04 (p, J = 1.5 Hz, 1H, H-12), 4.86 (dq, J = 1.7, 0.9 Hz, 1H, H-12), 2.77 (dd, J = 11.0, 7.7 Hz, 1H, H-4), 2.32 (ddd, J = 15.7, 4.3, 2.1 Hz, 1H, H-10), 2.18–2.01 (m, 2H, H-7), 1.84 (dd, J = 1.5, 0.8 Hz, 3H, H-13), 1.87–1.75 (m, 2H, H-3 and H-6), 1.76–1.62 (m, 3H, H-2, H-3, and H-10), 1.69 (t, J = 1.7 Hz, 3H, 14), 1.51 (ddd, J = 14.2, 9.1, 2.5 Hz, 1H, 6), 1.47 (br s, 1H, 16), 1.35 (dd, J = 12.3, 8.0 Hz, 1H, H-2), 1.01 (d, J = 0.8 Hz, 3H, H-15); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 139.0, 122.2, 113.3, 83.2, 53.4, 48.3, 40.4, 39.3, 34.6, 29.5, 26.8, 25.4, 25.2, 21.9; IR (Neat Film NaCl) 3545, 3069, 2963, 2924, 2867, 1636, 1448, 1374, 1006, 898, 825 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{24}O$ $[M+\bullet]^+$: 220.1827, found 220.1834; $[\alpha]_D^{25.0}$ 17.49 (c 1.05, $CHCl_3$, 88% ee).

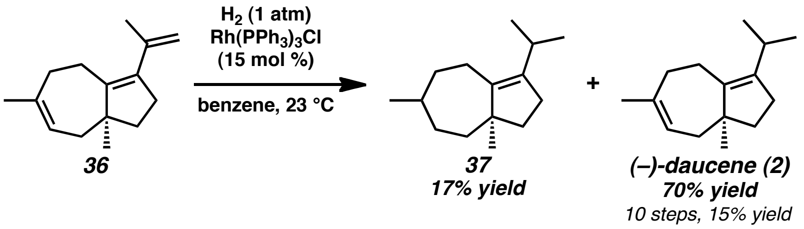

NOESY Correlations for β-hyrdoxyketone 34

Synthesis of (–)-Daucene (2), (+)-Daucenal (4), and (+)-14-*p*-Anisoyloxydauc-4,8-diene (5)



Triene 36. A flame-dried two-neck 25 mL round-bottom flask equipped with a stir bar and water condenser was loaded with lead(II) chloride (20.6 mg, 0.0740 mmol, 0.16 equiv) and zinc dust (437.5 mg, 6.69 mmol, 14.4 equiv) and backfilled with argon. The flask was charged with THF (6.5 mL) and diiodomethane (300 μL, 3.72 mmol, 8.02 equiv) and lowered into a preheated oil bath (70 °C). After 15 min, the bath was removed, the reaction was cooled to room temperature over 15 min and then lowered into a 0 °C bath (ice/water). Premixed titanium(IV) chloride (100 μL, 0.912 mmol, 1.96 equiv) and CH_2Cl_2 (830 μL) were added quickly, the bath was removed, and the reaction was allowed to warm to room temperature. After 1 h, enone **11** (94.9 mg, 0.464 mmol, 1.00 equiv) was transferred to the flask via cannula using several THF rinses (3 x 1 mL, total added = 9.5 mL, 0.05 M). No starting material remained after 1.5 h by TLC analysis, so the reaction was quenched with a sat. $NaHCO_3$ solution (10 mL) and filtered through a celite plug into a separatory funnel rinsing with Et_2O. The aqueous layer was extracted four times with Et_2O. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 28 x 1.5 cm, 100% hexanes) to afford triene **36** (56.5 mg, 0.279 mmol, 60% yield) as a pale yellow oil; R_f = 0.73 (0.3% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (ddp, J = 7.4, 5.9, 1.5 Hz, 1H), 4.90 (dq, J = 2.9, 1.5 Hz, 1H), 4.71 (dq, J = 2.5, 0.8 Hz, 1H), 2.65 (ddd, J = 13.8, 5.1, 3.6 Hz, 1H), 2.40 (dtd, J = 15.2, 8.3, 2.9 Hz, 1H), 2.29 (dddd, J = 15.4, 7.4, 4.7, 1.3 Hz, 1H), 2.11–2.04 (m, 3H), 2.01 (dd, J = 13.9, 7.6 Hz, 1H), 1.92 (ddddd, J = 16.7, 10.6, 4.7, 2.9, 1.4 Hz, 1H), 1.85 (dd, J = 1.5, 0.8 Hz, 3H), 1.74 (t, J = 1.5 Hz, 3H), 1.64–1.60 (m, 2H), 0.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 142.6, 139.9, 135.2, 122.4, 112.8, 50.5,

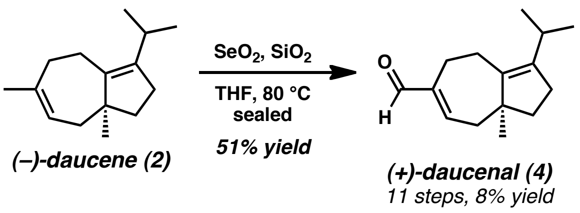
40.1, 38.4, 33.7, 32.6, 26.1, 23.7, 23.6, 22.8; IR (Neat Film NaCl) 3078, 2962, 2924, 2846, 1627, 1443, 1368, 891, 829 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{22}$ $[M+•]^+$: 202.1721, found 202.1703; $[\alpha]_D^{25.0}$ –76.62 (c 0.94, $CHCl_3$, 88% ee).



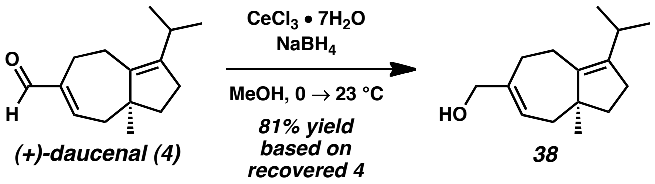
(–)-Daucene (2). A flame-dried 25 mL round-bottom flask equipped with a stir bar was cycled into a glove box and loaded with Wilkinson's catalyst (48.0 mg, 0.0519 mmol, 15.0 mol %). The flask was removed from the glove box, connected to an Ar-filled manifold, and charged with benzene (30 min Ar sparge before use, 3 mL). Triene **36** (70.0 mg, 0.346 mmol, 1.00 equiv) was transferred to the flask via cannula using several benzene rinses (1 x 2.5 mL + 3 x 2 mL, total added = 11.5 mL, 0.03 M). The flask was disconnected from the manifold, connected to a hydrogen balloon, and flushed with hydrogen, generating an orange solution. After 8 h, minimal starting material remained by TLC, so the stir bar was removed and rinsed with CH_2Cl_2 and the reaction was concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was loaded onto a silica gel column[15] using hexanes and minimal CH_2Cl_2 and purified by flash column chromatography (SiO_2, 27.5 x 2 cm, 100% hexanes) to afford alkene **37** (11.9 mg, 0.0576 mmol, 17% yield) as a clear colorless oil and daucene[13] (**2**, 49.5 mg, 0.242 mmol, 70% yield) as a clear colorless oil.

Alkene 37. R_f = 0.92 (0.3% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) mixture of two diastereomers, see Figure SI-22.1; IR (Neat Film NaCl) 2955, 2923, 2856, 1457, 1379, 1369, 1360 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{26}$ $[M+•]^+$: 206.2034, found 206.2040.

(–)-Daucene (2). R_f = 0.84 (0.3% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.42 (ddt, J = 9.2, 5.6, 1.5 Hz, 1H), 2.66 (sept, J = 6.8 Hz, 1H), 2.44–2.36 (m, 1H), 2.17 (ddt, J = 8.7, 6.7, 2.2 Hz, 2H), 2.08–2.03 (m, 1H), 2.05–1.99 (m, 2H), 1.94 (dd, J = 14.1, 7.8 Hz, 1H), 1.86–1.78 (m, 1H), 1.74 (t, J = 1.6 Hz, 3H), 1.62–1.48 (m, 2H), 0.98 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 139.9, 138.8, 122.8, 49.7, 40.5, 38.7, 33.7, 27.3, 26.6, 26.1, 23.7, 22.7, 22.0, 21.4; IR (Neat Film NaCl) 2959, 2932, 2845, 1444, 1366, 1330, 1303, 1202, 828 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{24}$ $[M+•]^+$: 204.1878, found 204.1878; $[\alpha]_D^{25.0}$ –24.95 (c 1.37, $CHCl_3$, 86% ee).



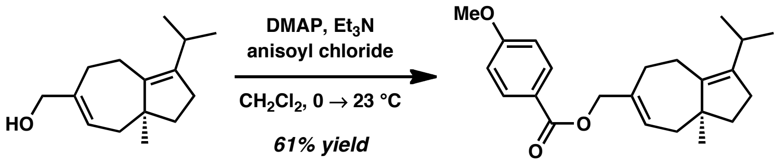
(+)-Daucenal (4). Adapted from a procedure by Wood.[12] A 20 mL scintillation vial equipped with a stir bar and daucene (**2**, 9.6 mg, 0.047 mmol, 1.00 equiv) was connected to an Ar-filled manifold and flushed with Ar. The vial was charged with THF (4.87 mL) and premixed selenium dioxide (10.4 mg, 0.0937 mmol, 2.00 equiv) and silica gel (113.9 mg, 1.896 mmol, 40.4 equiv). The vial was sealed with a teflon cap and lowered into a preheated sand bath (80 °C). After 20 min, starting material persisted by TLC analysis, so the vial was resealed and lowered back into the sand bath. After an additional 10 min, no starting material remained by TLC analysis. Consequently, the reaction was filtered through a short celite pad rinsing with Et_2O and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 27.5 x 1.5 cm, 100% hexanes→5%→10%→ 20% TBME in hexanes) to afford daucenal[13] (**4**, 5.2 mg, 0.0238 mmol, 51% yield) as a yellow oil; R_f = 0.77 (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 9.26 (d, J = 1.1 Hz, 1H), 6.10 (dddd, J = 8.4, 5.2, 2.0, 1.1 Hz, 1H), 3.05 (ddd, J = 15.2, 5.4, 2.7 Hz, 1H), 2.51 (sept, J = 6.7 Hz, 1H), 2.33 (ddd, J = 14.1, 5.5, 3.1 Hz, 1H), 2.13 (ddd, J = 8.5, 5.1, 1.9 Hz, 2H), 2.05 (dd, J = 14.3, 5.2 Hz, 1H), 1.94 (ddd, J = 14.3, 8.2, 1.1 Hz, 1H), 1.76 (br tdd, J = 14.2, 3.4, 1.6 Hz, 1H), 1.62 (br ddt, J = 14.5, 10.1, 2.4 Hz, 1H), 1.55 (dtd, J = 12.6, 6.8, 1.2 Hz, 1H), 1.47 (dtd, J = 12.4, 7.7, 1.1 Hz, 1H), 0.90 (dd, J = 6.9, 1.1 Hz, 3H), 0.88 (dd, J = 6.9, 1.1 Hz, 3H), 0.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 152.8, 146.8, 141.0, 140.3, 49.8, 41.7, 39.2, 27.4, 26.7, 24.2, 24.0, 22.4, 21.9, 21.3; IR (Neat Film NaCl) 2956, 2930, 2863, 1685, 1636, 1453, 1378, 1245, 1144, 929 cm^{-1}; HRMS (GC-EI+) *m/z* calc'd for $C_{15}H_{22}O$ $[M+\bullet]^+$: 218.1671, found 218.1680; $[\alpha]_D^{25.0}$ 33.65 (c 0.50, $CHCl_3$, 86% ee).



(+)-daucenal (4)

38

Allylic Alcohol 38. A 20 mL scintillation vial equipped with a stir bar and daucenal (**4**, 10.2 mg, 0.0467 mmol, 1.00 equiv) was connected to an Ar-filled manifold and flushed with Ar. The vial was charged with MeOH (930 µL) and cerium chloride heptahydrate (20.9 mg, 0.0561 mmol, 1.20 equiv). After 10 min of stirring, the cerium chloride heptahydrate had dissolved, generating a yellow solution. The vial was subsequently lowered into a 0 °C bath (ice/water) and sodium borohydride (4.1 mg, 0.108 mmol, 2.32 equiv) was added. The bath was allowed to expire over time. Additional sodium borohydride (35 min = 11.9 mg, 2 h 25 min = 12.3 mg, 6 h = 12.9 mg, 8 h = 50.2 mg; total added = 91.5 mg, 2.42 mmol, 51.8 equiv) and cerium chloride heptahydrate (8 h = 22.7 mg; total added = 43.6 mg, 0.117 mmol, 2.51 equiv) were added. After 20 h, the reaction was quenched with a sat. NH_4Cl solution (5 mL) and transferred to a separatory funnel where the aqueous layer was extracted four times with Et_2O. The combined organics were rinsed with 5% w/w HCl (10 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure at 0 °C (ice/water). The resulting crude oil was purified by flash column chromatography (SiO_2, 29 x 1.5 cm, 100% hexanes→5%→10%→20% TBME in hexanes) to afford recovered daucenal (**4**, 3.4 mg, 0.0156 mmol, 33% recovered) and alcohol **38** (5.6 mg, 0.0253 mmol, 54% yield, 81% yield based on recovered **4**) as a yellow oil; R_f = 0.42 (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.70 (ddtd, J = 8.0, 5.2, 2.0, 0.9 Hz, 1H), 4.03 (t, J = 1.5 Hz, 2H), 2.68 (sept, J = 6.8 Hz, 1H), 2.48 (ddd, J = 13.9, 5.7, 2.9 Hz, 1H), 2.22–2.16 (m, 4H), 2.14 (dd, J = 14.1, 5.3 Hz, 1H), 2.04 (dd, J = 14.1, 8.0 Hz, 1H), 2.05–1.95 (m, 1H), 1.86–1.77 (m, 1H), 1.62 (dt, J = 12.3, 6.2 Hz, 1H), 1.55 (dt, J = 12.3, 8.2 Hz, 1H), 0.98 (d, J = 6.9 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 141.6, 139.4, 124.7, 68.9, 49.4, 40.4, 38.8, 29.6, 27.3, 26.6, 23.8, 23.2, 22.0, 21.3; IR (Neat Film NaCl) 3325, 2957, 2930, 2859, 1710, 1455, 1380, 1367, 1360, 1261, 1055, 997, 841, 803 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{24}O$ [M+•]$^+$: 220.1827, found 220.1830; $[\alpha]_D^{25.0}$ –13.28 (c 0.56, $CHCl_3$, 86% ee).

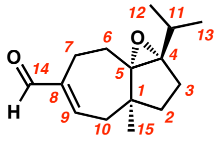


38 *(+)-14-p-anisoyloxydauc-4,8-diene (5)*
13 steps, 4% yield

14-*p*-Anisoyloxydauc-4,8-diene (5). A scintillation vial equipped with allylic alcohol **38** (5.6 mg, 0.0253 mmol, 1.00 equiv), a stir bar, and a Teflon cap was flushed with Ar and connected to an Ar-filled manifold. The vial was charged with CH_2Cl_2 (2 mL, 0.01 M) and lowered into a 0 °C bath (ice/water). DMAP (0.5 mg, 0.0041 mmol, 16 mol %), Et_3N (10 μL, 0.072 mmol, 2.8 equiv), and *p*-anisoyl chloride (10 μL, 0.074 mmol, 2.9 equiv) were added to the vial and the bath was allowed to expire over time. TLC analysis indicated starting material remained after 4 h, so additional Et_3N (10 μL, total added = 20 μL, 0.14 mmol, 5.7 equiv) and *p*-anisoyl chloride (10 μL, total added = 20 μL, 0.15 mmol, 5.8 equiv) were added. TLC analysis indicated no residual starting material after 18 h, so the reaction was loaded directly onto a column, and the crude material was purified by flash column chromatography (SiO_2, 28.5 x 2 cm, 100% hexanes→2% TBME in hexanes) to afford 14-p-anisoyloxydauc-4,8-diene[13] (**5**, 5.5 mg, 0.0155 mmol, 61% yield) as a yellow oil that solidified upon freezing; R_f = 0.70 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dm, J = 8.9 Hz, 2H), 6.92 (dm, J = 8.9 Hz, 2H), 5.85 (ddp, J = 7.3, 5.0, 1.1 Hz, 1H), 4.70 (d, J = 1.1 Hz, 2H), 3.86 (s, 3H), 2.67 (sept, J = 6.9 Hz, 1H), 2.49 (ddd, J = 13.9, 5.7, 2.8 Hz, 1H), 2.25 (ddd, J = 14.6, 5.8, 2.8 Hz, 1H), 2.19 (ddd, J = 8.2, 6.0, 2.2 Hz, 2H), 2.20–2.14 (m, 1H), 2.07 (dd, J = 14.1, 8.1 Hz, 1H), 2.07 (tm, J = 13.5 Hz, 1H), 1.88 (dddd, J = 14.6, 12.3, 5.0, 2.5 Hz, 1H), 1.64 (dt, J = 12.3, 6.1 Hz, 1H), 1.56 (dt, J = 12.4, 8.3 Hz, 1H), 0.98 (d, J = 6.9 Hz, 3H), 0.95 (s, 3H), 0.93 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 163.4, 141.5, 139.5, 138.6, 131.8, 128.4, 123.0, 113.7, 70.3, 55.6, 49.4, 40.5, 38.8, 29.9, 27.3, 26.6, 23.8, 23.0, 22.0, 21.3; IR (Neat Film NaCl) 2956, 2928, 2854, 1716, 1607, 1582, 1456, 1421, 1368, 1315, 1271, 1256, 1167, 1100, 1032, 846, 770 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{23}H_{30}O_3$ [M+•]$^+$: 354.2195, found 354.2193; $[\alpha]_D^{25.0}$ 2.27 (c 0.55, $CHCl_3$, 86% ee).

Comparison of Data for Synthetic and Reported Natural Products

Spectral data for synthetic (–)-epoxydaucenal B (**3b**), (–)-daucene (**2**), (+)-daucenal (**4**), and (+)-14-*p*-anisoyloxydauc-4,8-diene (**5**) (^{1}H NMR, ^{13}C NMR, $[\alpha]_D^T$) were compared with available reported spectral data for either natural or synthetic samples. Tables comparing compound data are shown in Tables SI-1–8.

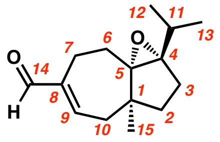


(–)-epoxydaucenal B (3b)

*Table SI-1. Comparison of ^{1}H NMR data for synthetic and natural epoxydaucenal B (**3b**).*[a–b]

Assignment	**Synthetic 3b** (ppm)[c]	**Multiplicity,** ***J*** (Hz)	**Natural**[16] **3b** (ppm)[d]	**Multiplicity,** ***J*** (Hz)
C1	—	—	—	—
C2	1.41–1.33	m		
	0.96–0.86	m		
C3	1.69–1.60	m		
	1.41–1.33	m		
C4	—	—	—	—
C5	—	—	—	—
C6	1.62–1.52	m		
	1.44–1.40	m		
C7	3.11–3.03	m	3.068	m
	1.62–1.52	m		
C8	—	—	—	—
C9	6.03	dddd, 8.7, 5.1, 2.2, 1.2	6.028	m
C10	1.85	ddtd, 14.0, 5.1, 1.5, 0.8	1.840	dd, 14.1, 5.0
	1.62–1.52	m		
C11	1.51	sept, 7.0	1.522	sept, 6.9
C12	1.03	d, 6.8	1.028	d, 6.9
C13	0.77	d, 7.0	0.763	d, 6.9
C14	9.22	s	9.211	s
C15	0.83	s	0.828	s

[a] See Figure SI-16.1 for ^{1}H NMR spectra. [b] Blank spaces in table represent neglected or unreported signals. [c] ^{1}H NMR spectra was obtained at 500 MHz in C_6D_6 and standardized to residual C_6H_6. [d] ^{1}H NMR spectra was obtained at 500 MHz in C_6D_6 and standardized to TMS.

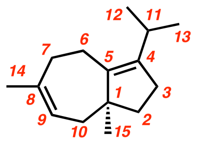


(–)-epoxydaucenal B (3b)

*Table SI-2. Comparison of ^{13}C NMR data for synthetic and natural epoxydaucenal B (**3b**).*[a]

Assignment	**Synthetic 3b** (ppm)[b]	**Natural[16] 3b** (ppm)[c]
C1	44.3	44.2
C2	35.7	35.7
C3	22.9	22.8[d]
C4	75.1	75.0
C5	75.7	75.7
C6	25.4	25.4[d]
C7	20.1	20.1
C8	146.3	146.3
C9	152.5	152.3
C10	37.1	37.1
C11	28.5	28.5
C12	19.0	18.9[e]
C13	19.6	19.5[e]
C14	191.9	191.8
C15	19.8	19.7

[a] See Figure SI-16.3 for ^{13}C NMR spectra. [b] ^{13}C NMR spectra was obtained at 125 MHz in C_6D_6 and standardized to residual C_6H_6. [c] ^{13}C NMR spectra was obtained at 125 MHz in C_6D_6 and standardized to TMS. [d] C(3) and C(6) were misassigned, see HSQC spectra, Figure SI-16.4. [e] C(12) and C(13) were misassigned, see HSQC spectra, Figure SI-16.4.

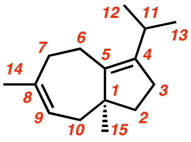


(–)-daucene (2)

*Table SI-3. Comparison of ^{1}H NMR data for synthetic and previously reported[17] daucene (**2**).*[a–b]

Assignment	**Synthetic 2** (ppm)[b]	**Multiplicity, *J*** (Hz)	**Little[18] 2** (ppm)[d]	**Multiplicity, *J*** (Hz)	**Seto[19] 2** (ppm)[e]	**Multiplicity, *J*** (Hz)	**Yamasaki[20] 2** (ppm)[e]	**Multiplicity, *J*** (Hz)	**Naegeli[21] 2** (ppm)[e]	**Multiplicity, *J*** (Hz)
C1	—	—	—	—	—	—	—	—	—	—
C2	1.59	ddd, 11.9, 6.7, 5.1	1.65–1.48[f]	m						
	1.52	dt, 12.2, 8.5								
C3	2.17	ddt, 8.7, 6.7, 2.2	2.21–2.12	m						
C4	—	—	—	—	—	—	—	—	—	—
C5	—	—	—	—	—	—	—	—	—	—
C6	2.44–2.36	m	2.39	m						
	1.86–1.78	m	1.81	m						
C7	2.05–1.99	m	2.05–1.90	m						
C8	—	—	—	—	—	—	—	—	—	—
C9	5.42	ddt, 9.2, 5.6, 1.5	5.42	m	5.43	br t, 6.6	5.37	t, 5	5.44	t, 6.5
C10	2.08–2.03	m	2.05–1.90	m						
	1.94	dd, 14.1, 7.8								
C11	2.66	sept, 6.8	2.66	sept, 6.75	2.67	sept, 6.8				
C12	0.98	d, 6.9	0.98	d, 6.75	0.98	d, 6.8	0.99	d, 5	1.00	d, 6.5
C13	0.92	d, 6.9	0.93	d, 6.75	0.92	d, 6.8	0.92	d, 5	0.92	d, 6.5
C14	1.74	t, 1.6	1.74	s	1.74	br s	1.73	s	1.75	br s
C15	0.91	s	0.91	s	0.91	s	0.94	s	0.91	s

[a] See Figure SI-21.1 for ^{1}H NMR spectra. [b] Blank spaces in table represent neglected or unreported signals. [c] ^{1}H NMR spectra was obtained at 500 MHz in $CDCl_3$ and standardized to residual $CHCl_3$. [d] ^{1}H NMR spectra was obtained at 400 MHz in $CDCl_3$ and standardized to residual $CHCl_3$. [e] ^{1}H NMR was obtained in $CDCl_3$ at unknown MHz. [f] Little reports this signal as 3H, however HSQC data indicates only 2H for this range (see Figure SI-21.4).

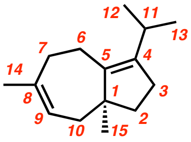


(–)-daucene (2)

*Table SI-4. Comparison of ^{13}C NMR data for synthetic and reported daucene (**2**).*[a]

Assignment	Synthetic 2 (ppm)[b]	Little[18] 2 (ppm)[c]	Seto[19] 2 (ppm)[d]
C1	49.7	49.7	49.7
C2	38.7	38.7	38.7
C3	27.3	27.3	27.3
C4	138.8	138.9	138.8
C5	142.0	142.1	142.0
C6	22.7	22.7	22.6
C7	33.7	33.7	33.6
C8	139.9	140.0	139.7
C9	122.8	122.9	122.8
C10	40.5	40.6	40.5
C11	26.6	26.6	26.5
C12	22.0	22.1	21.9
C13	21.4	21.4	21.2
C14	26.1	26.2	25.9
C15	23.7	23.7	23.6

[a] See Figure SI-21.3 for ^{13}C NMR spectra. [b] ^{13}C NMR spectra was obtained at 125 MHz in $CDCl_3$ and standardized to residual $CHCl_3$. [c] ^{13}C NMR spectra was obtained at 100 MHz in $CDCl_3$ and standardized to residual $CHCl_3$. [d] ^{13}C NMR was obtained in $CDCl_3$ at unknown MHz.

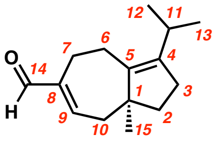


(–)-daucene (2)

*Table SI-5. Comparison of optical rotation data for synthetic and reported daucene (**2**).*[a]

Synthetic 2	(+)-Natural[22a] 2	Yamasaki [20] 2	Mehta[17] 2
$[\alpha]_D^{25} = –24.95$ (c 1.37, $CHCl_3$, 86% ee)	$[\alpha]_D^{25} = +23.32$ (c unspecified)	$[\alpha]_D^{25} = –21.5$ (c 0.8, EtOH)	$[\alpha]_D^{25} = –20$ (c 1.00)

[a] Daucene has been isolated from a number of sources.[22] Both (+)-[22a] and (–)-daucene[22b–c] have been isolated from nature, however the optical rotation has only been collected from natural (+)-daucene. Yamasaki and Mehta, though, have reported rotations for synthetic (–)-daucene.

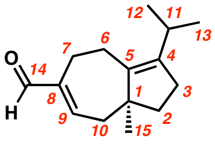


(+)-daucenal (4)

*Table SI-6. Comparison of ^{1}H NMR data for synthetic and natural daucenal (**4**).*[a]

Assignment	**Synthetic 4** (ppm)[b]	**Multiplicity, *J*** (Hz)	**Natural**[16] **4** (ppm)[c]	**Multiplicity, *J*** (Hz)
C1	—	—	—	—
C2	1.55	dtd, 12.6, 6.8, 1.2	1.550	dd, 12.4, 7.4
	1.47	dtd,12.4, 7.7, 1.1	1.471	dd, 12.4, 7.4
C3	2.13	ddd, 8.5, 5.1, 1.9	2.125	br ddd, 7.7, 7.4, 2.9
C4	—	—	—	—
C5	—	—	—	—
C6	2.33	ddd, 14.1, 5.5, 3.1	2.330	ddd, 14.0, 5.4, 3.0
	1.62	br ddt, 14.5, 10.1, 2.4	1.616	br ddd, 14.5, 14.0, 2.9
C7	3.06	ddd, 15.2, 5.4, 2.7	3.049	ddd, 14.9, 15.4, 2.9
	1.76	br tdd, 14.2, 3.4, 1.6	1.763	br dddd, 14.9, 14.5, 3.0, 2.0
C8	—	—	—	—
C9	6.10	dddd, 8.4, 5.2, 2.0, 1.1	6.101	ddd, 8.2, 5.2, 2.0
C10	2.05	dd, 14.3, 5.2	2.053	br dd, 14.3, 5.2
	1.94	ddd, 14.3, 8.2, 1.1	1.935	dd, 14.3, 8.2
C11	2.51	sept, 6.7	2.512	sept, 6.9
C12	0.90	dd, 6.9, 1.1	0.897	d, 6.9
C13	0.88	dd, 6.9, 1.1	0.869	d, 6.9
C14	9.26	d, 1.1	9.263	s
C15	0.81	s	0.811	s

[a] See Figure SI-23.1 for ^{1}H NMR spectra. [b] ^{1}H NMR spectra was obtained at 500 MHz in C_6D_6 and standardized to residual C_6H_6. [c] ^{1}H NMR spectra was obtained at 500 MHz in C_6D_6 and standardized to TMS.

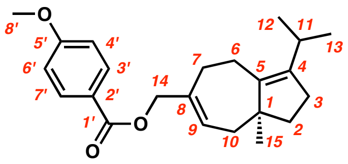


(+)-daucenal (4)

*Table SI-7. Comparison of ^{13}C NMR data for synthetic and natural daucenal (**4**).*[a]

Assignment	**Synthetic 4** (ppm)[b]	**Natural[16] 4** (ppm)[c]
C1	49.8	49.8
C2	39.2	41.7[d]
C3	27.4	27.4
C4	140.3	141.0
C5	141.0	146.7[e]
C6	22.4	24.0
C7	24.0	22.4
C8	146.8	140.2[e]
C9	152.8	152.8
C10	41.7	39.2[d]
C11	26.7	26.7
C12	21.9	21.7
C13	21.3	21.2
C14	193.0	193.0
C15	24.2	24.2

[a] See Figure SI-23.3 for ^{13}C NMR spectra. [b] ^{13}C NMR spectra was obtained at 125 MHz in C_6D_6 and standardized to residual C_6H_6. [c] ^{13}C NMR spectra was obtained at 125 MHz in C_6D_6 and standardized to TMS. [d] C2 and C10 were misassigned, see 2D NMR spectra, Figures SI-23.4–6. [e] C5 and C8 were misassigned, see 2D NMR spectra, Figures SI-23.4–6.



(+)-14-p-anisoyloxydauc-4,8-diene (5)

*Table SI-8. Comparison of ^{1}H NMR data for synthetic and natural[23] 14-p-anisoyloxydauc-4,8-diene (**5**).$^{a–b}$*

Assignment	**Synthetic 5** (ppm)^c	**Multiplicity, *J*** (Hz)	**Natural**[23a] **5** (ppm)^d	**Multiplicity, *J*** (Hz)
C1	—	—	—	—
C2	1.64	dt, 12.3, 6.1		
	1.56	dt, 12.4, 8.3		
C3	2.19	ddd, 8.2, 6.0, 2.2		
C4	—	—	—	—
C5	—	—	—	—
C6	2.49	ddd, 13.9, 5.7, 2.8		
	1.88	dddd, 14.6, 12.3, 5.0, 2.5		
C7	2.25	ddd, 14.6, 5.8, 2.8		
	2.07	tm, 13.5		
C8	—	—	—	—
C9	5.85	ddp, 7.3, 5.0, 1.1	5.86	br t, 6.5
C10	2.20–2.14	m		
	2.07	dd, 14.1, 8.1		
C11	2.67	sept, 6.9	2.69	sept
C12	0.98	d, 6.9	0.98	d, 7.2
C13	0.93	d, 6.8	0.93	d, 7.2
C14	4.70	d, 1.1	4.70	br s
C15	0.95	s	0.95	s
C1'	—	—	—	—
C2'	—	—	—	—
C3'/ C7'	6.92	dm, 8.9	6.93	d, 9.1
C4'/C6'	8.01	dm, 8.9	8.01	d, 9.1
C5'	—	—	—	—
C8'	3.86	s	3.86	s

[a] See Figure SI-25.1 for ^{1}H NMR spectra. [b] Blank spaces in table represent neglected or unreported signals. [c] ^{1}H NMR spectra was obtained at 500 MHz in CDCl$_3$ and standardized to residual CDCl$_3$. [d] ^{1}H NMR spectra was obtained at 200 MHz in CDCl$_3$ and standardized to TMS.

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[9] Example procedure for the preparation of a lithium naphthalenide solution: A flame-dried 50 mL round-bottom flask equipped with a stir bar was connected to an Ar-filled manifold and charged with naphthalene (1.84 g, 14.4 mmol, 1.11 equiv), lithium wire (90.2 mg, 13.0 mmol, 1.00 equiv), and THF (13 mL, 1.0 M). The reaction was sonicated for 0.5–1 h prior to use and administered as a 1.0 M solution.

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[11] Example procedure for the preparation of a samarium diiodide solution: A flame-dried 50 mL Schlenk tube equipped with a stir bar was connected to an Ar-filled manifold, loaded with samarium metal (311.3 mg, 2.07 mmol, 1.45 equiv), and backfilled with Ar three times. The flask was charged with THF (1 h Ar sparge before use, 14.3 mL, 0.1 M) and lowered into a 0 °C bath (ice/water). 1,2-Diiodoethane was added in two portions (203.0 mg and 30 min = 200.2 mg, total added = 403.2 mg, 1.43 mmol, 1.00 equiv), the ice bath was removed, and the reaction was allowed to warm to room temperature. After 1 h of vigorous stirring, the reaction had developed into a dark blue solution and was administered as a 0.1 M solution.

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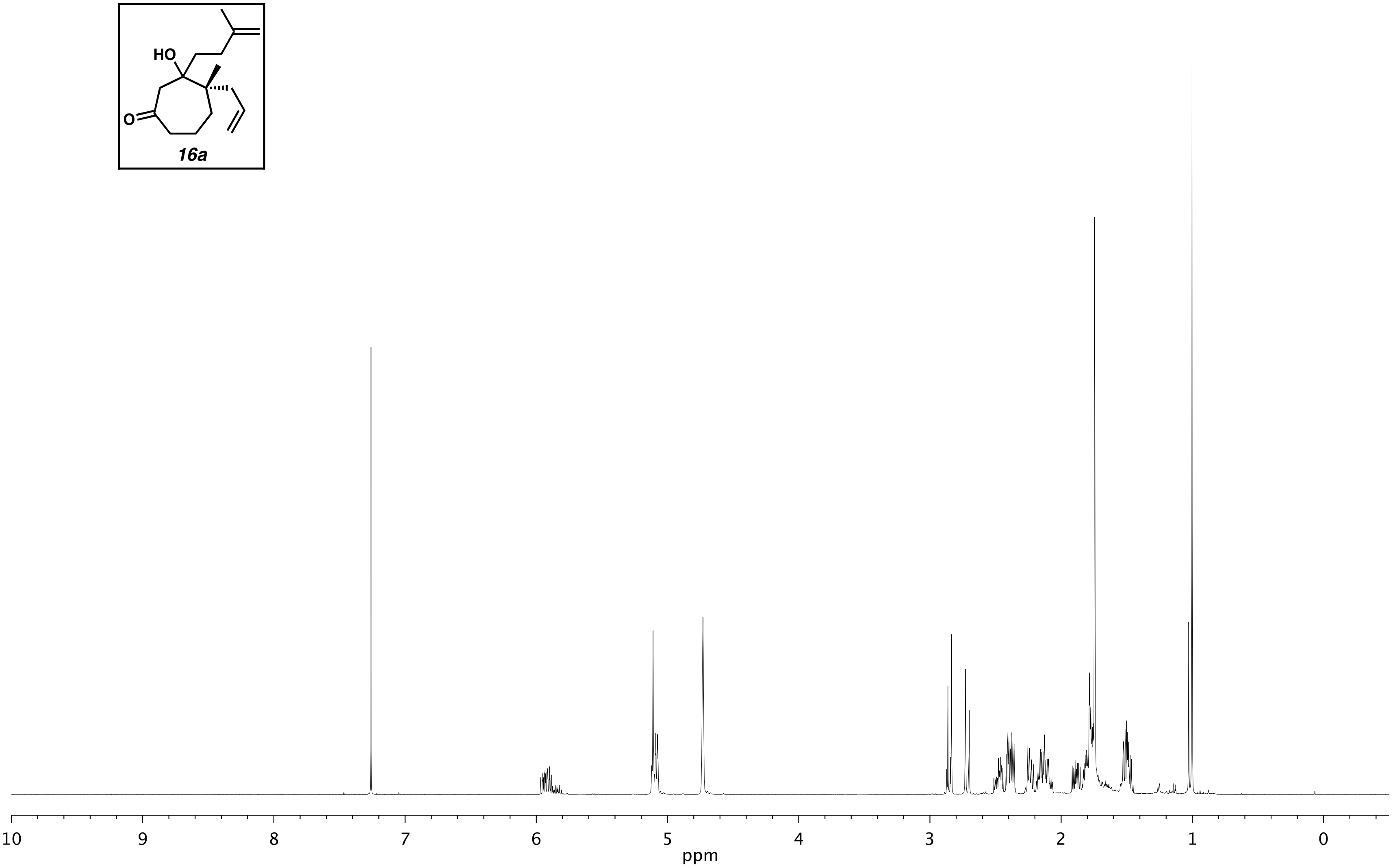


Figure SI-1.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **16a**.

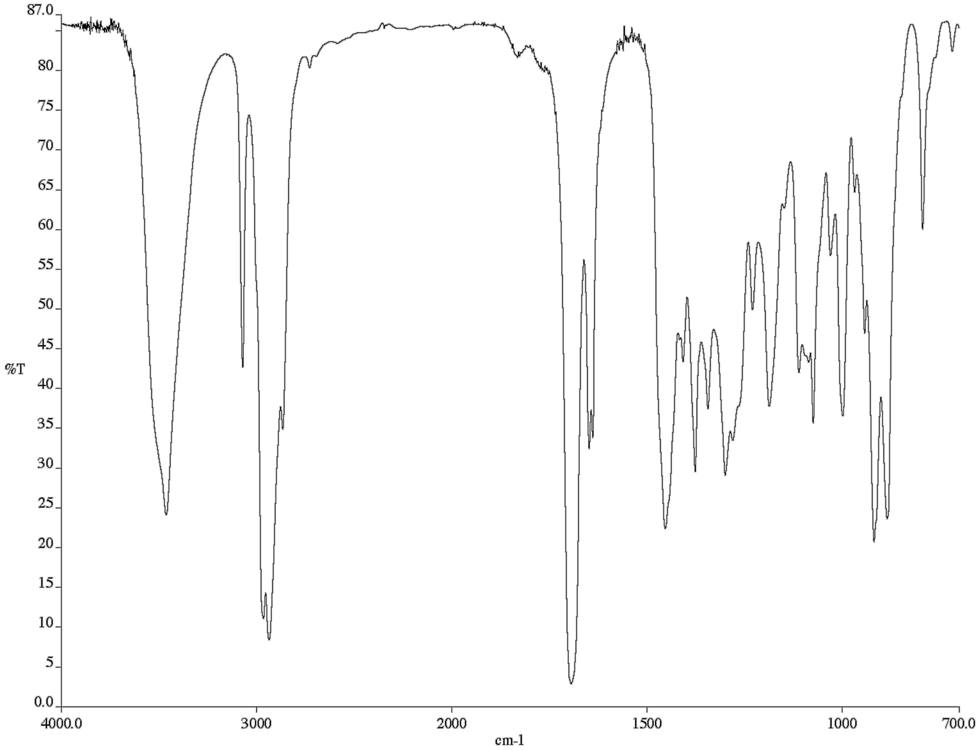


Figure SI-1.2. Infrared spectrum (thin film/NaCl) of compound **16a**.

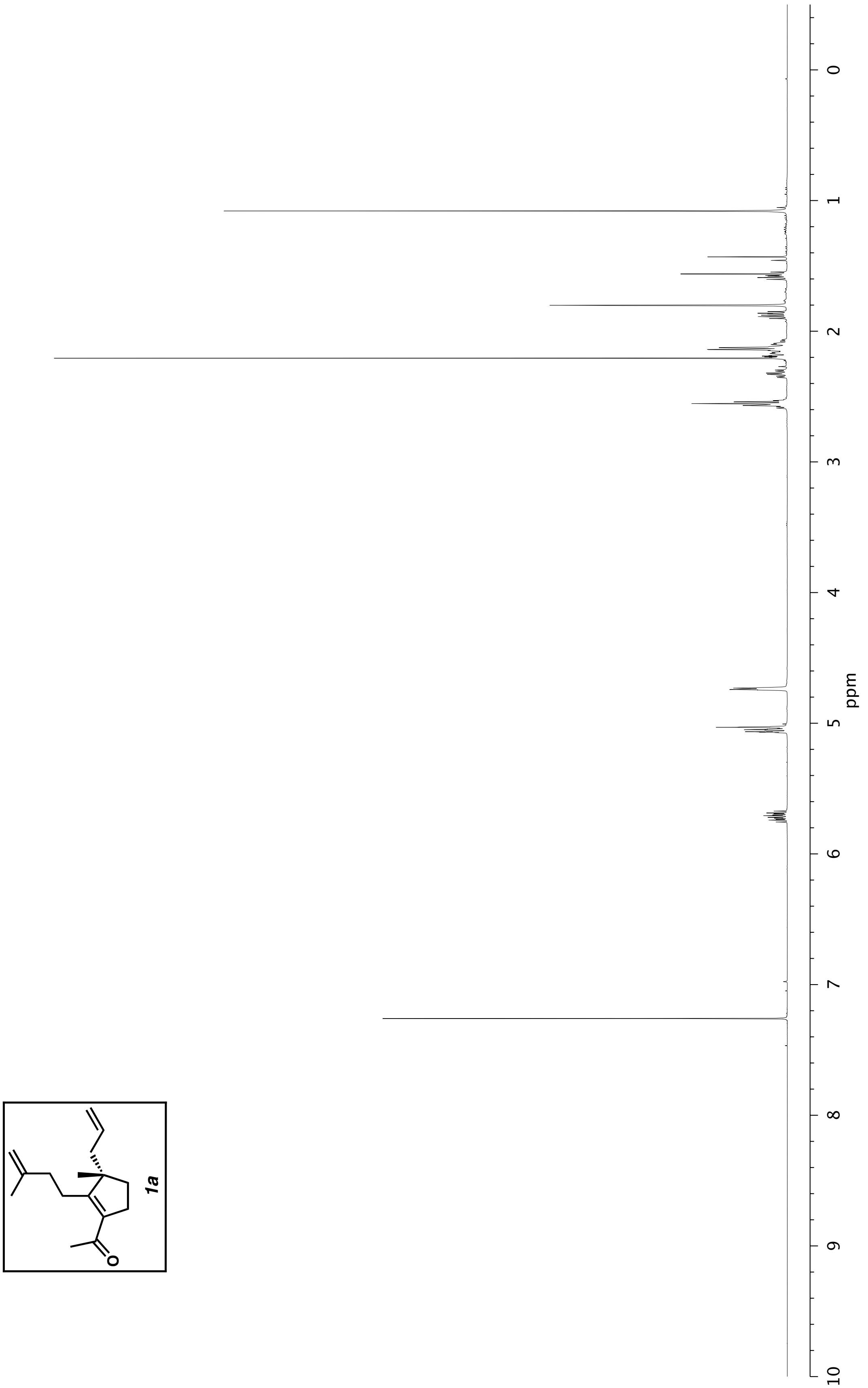


Figure SI-2.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1a**.

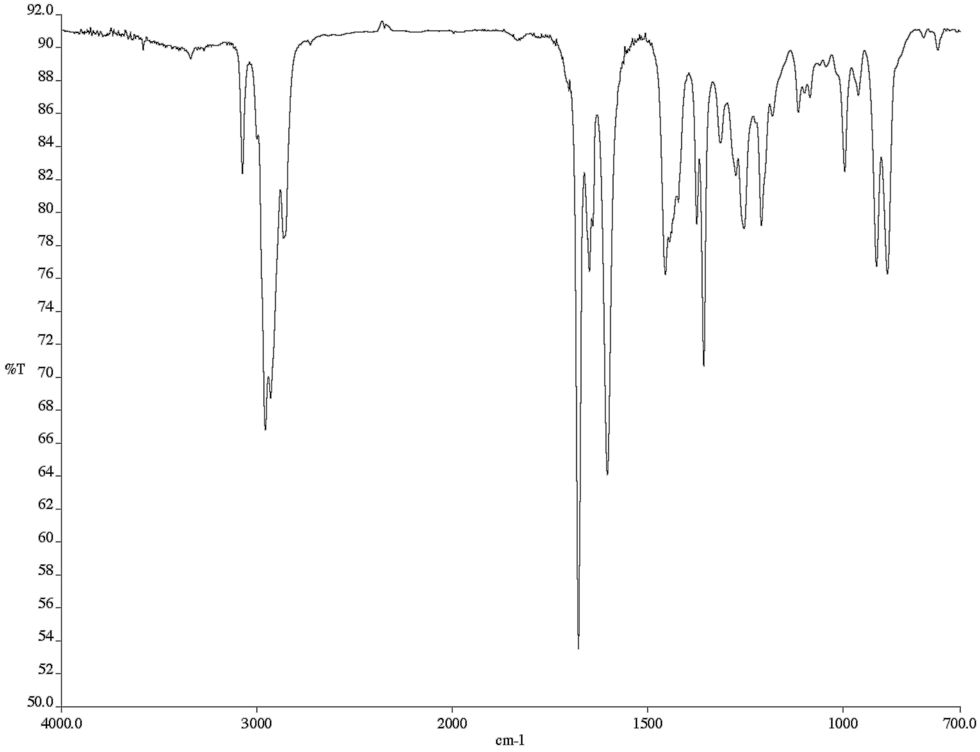


Figure SI-2.2. Infrared spectrum (thin film/NaCl) of compound **1a**.

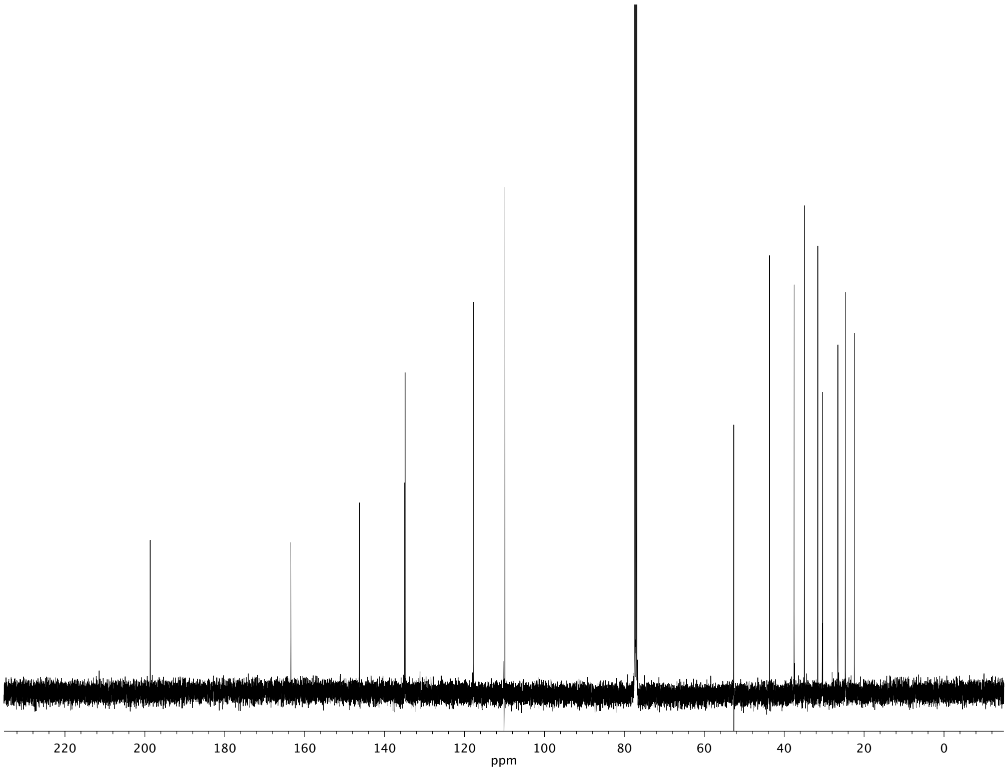


Figure SI-2.3. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **1a**.

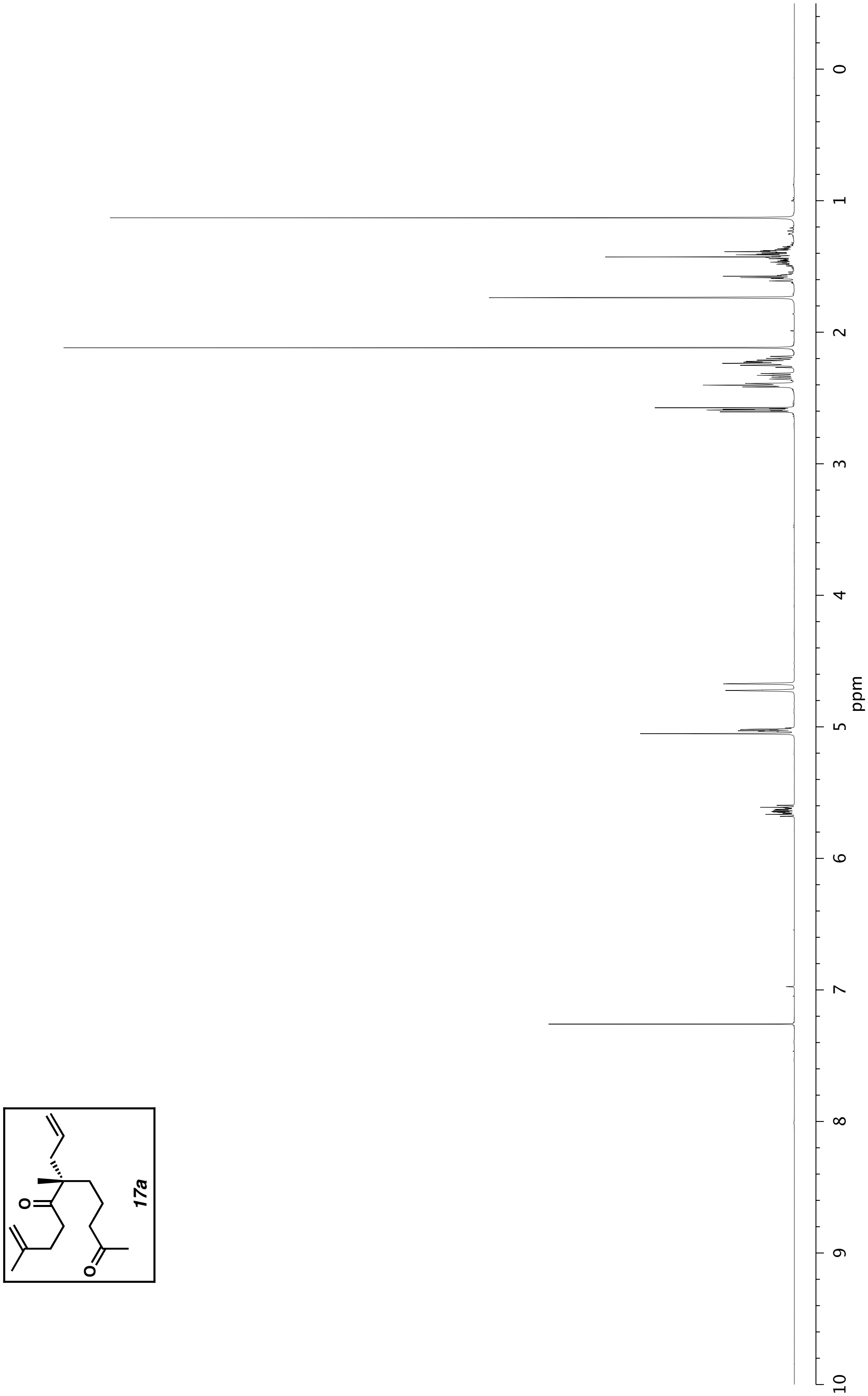


Figure SI-3.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17a**.

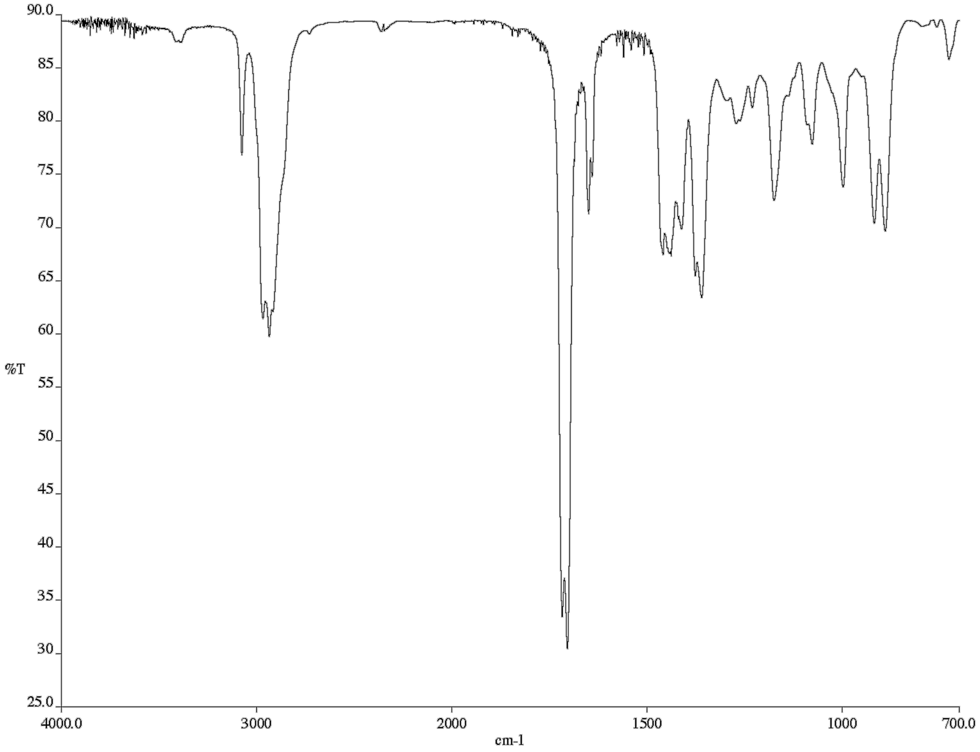


Figure SI-3.2. Infrared spectrum (thin film/NaCl) of compound **17a**.

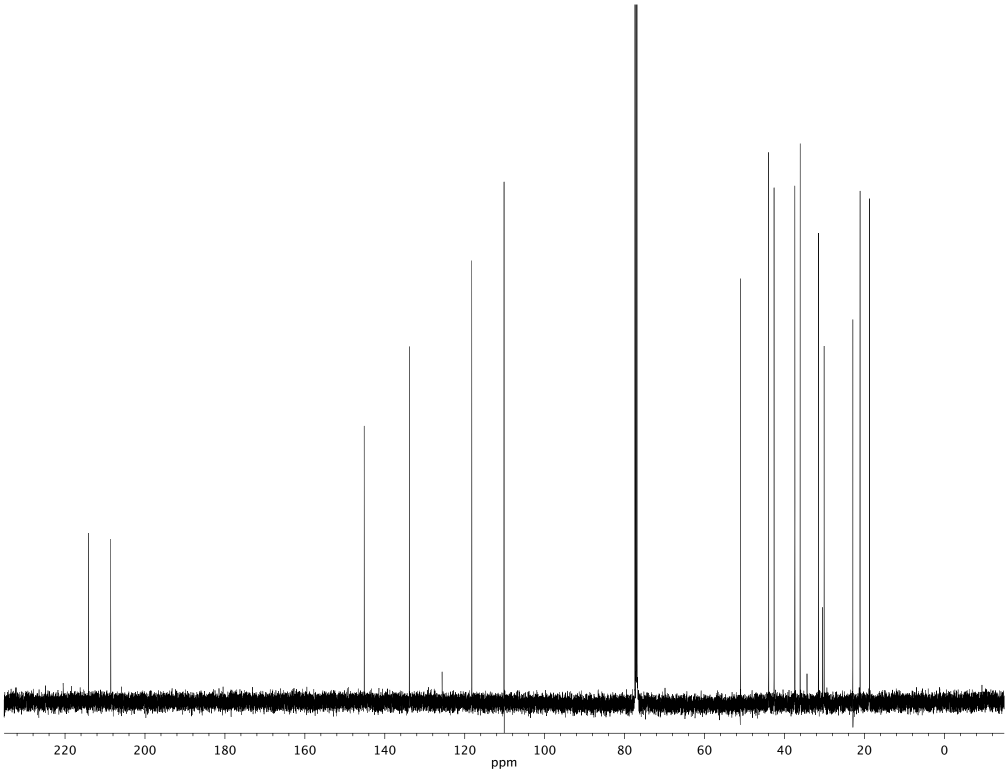


Figure SI-3.3. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **17a**.

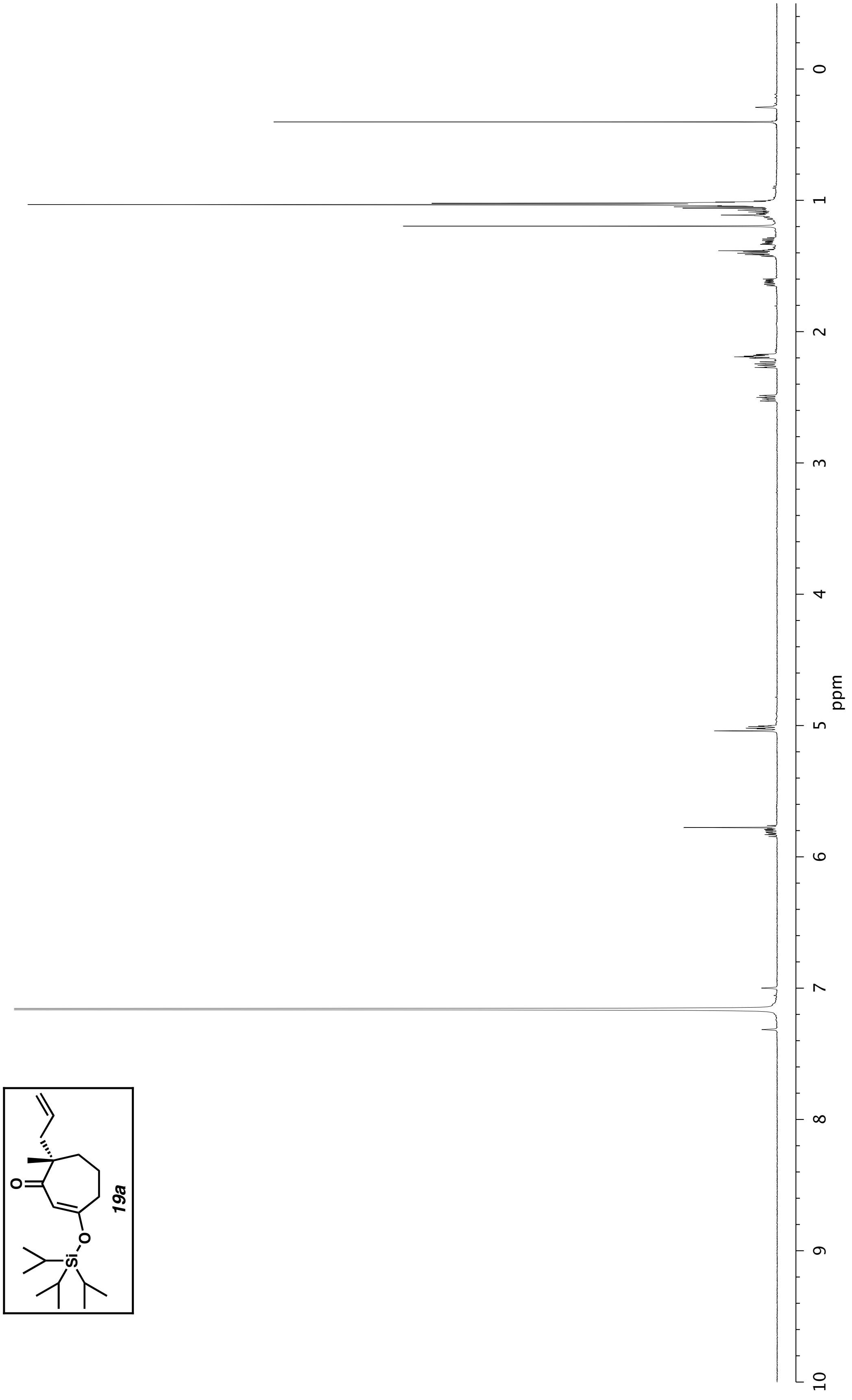


Figure SI-4.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **19a**.

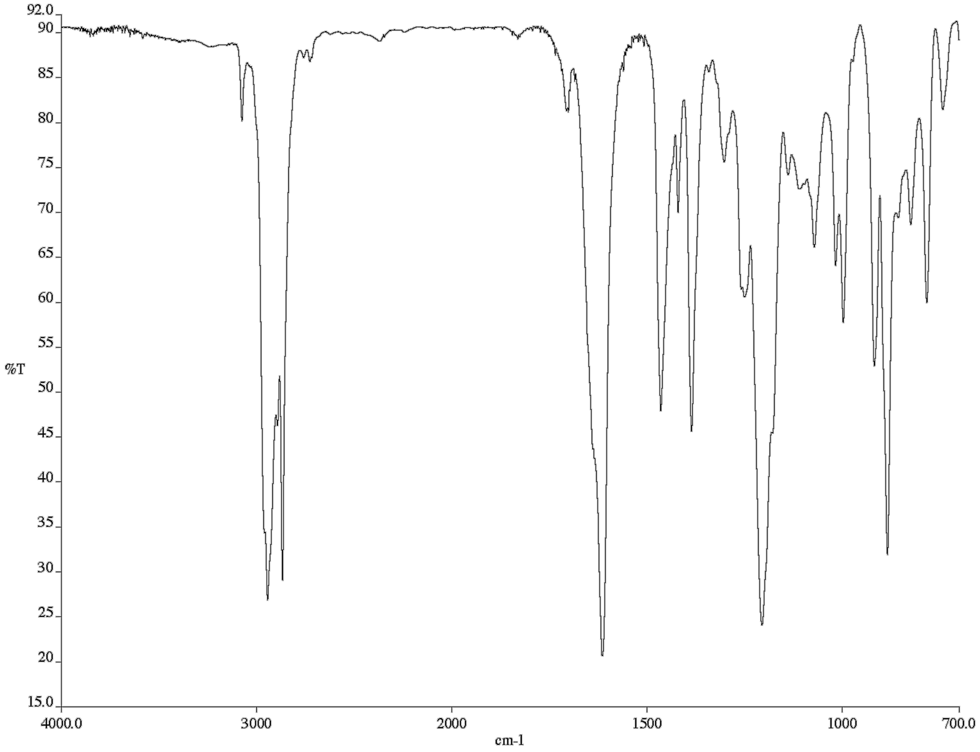


Figure SI-4.2. Infrared spectrum (thin film/NaCl) of compound **19a**.

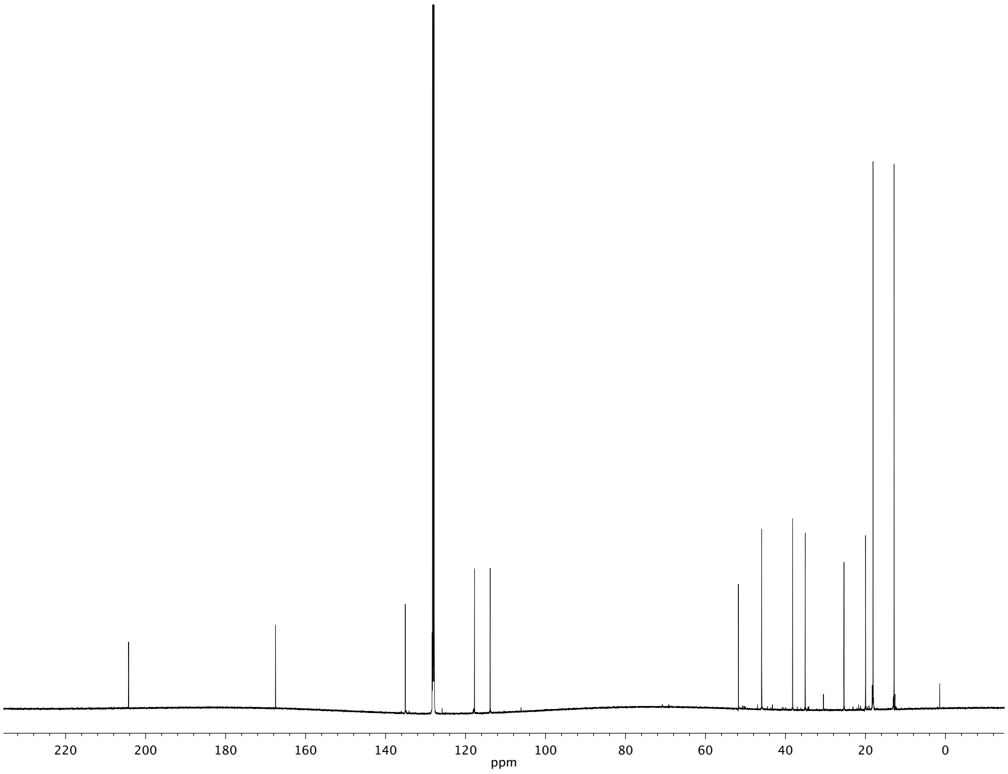


Figure SI-4.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **19a**.

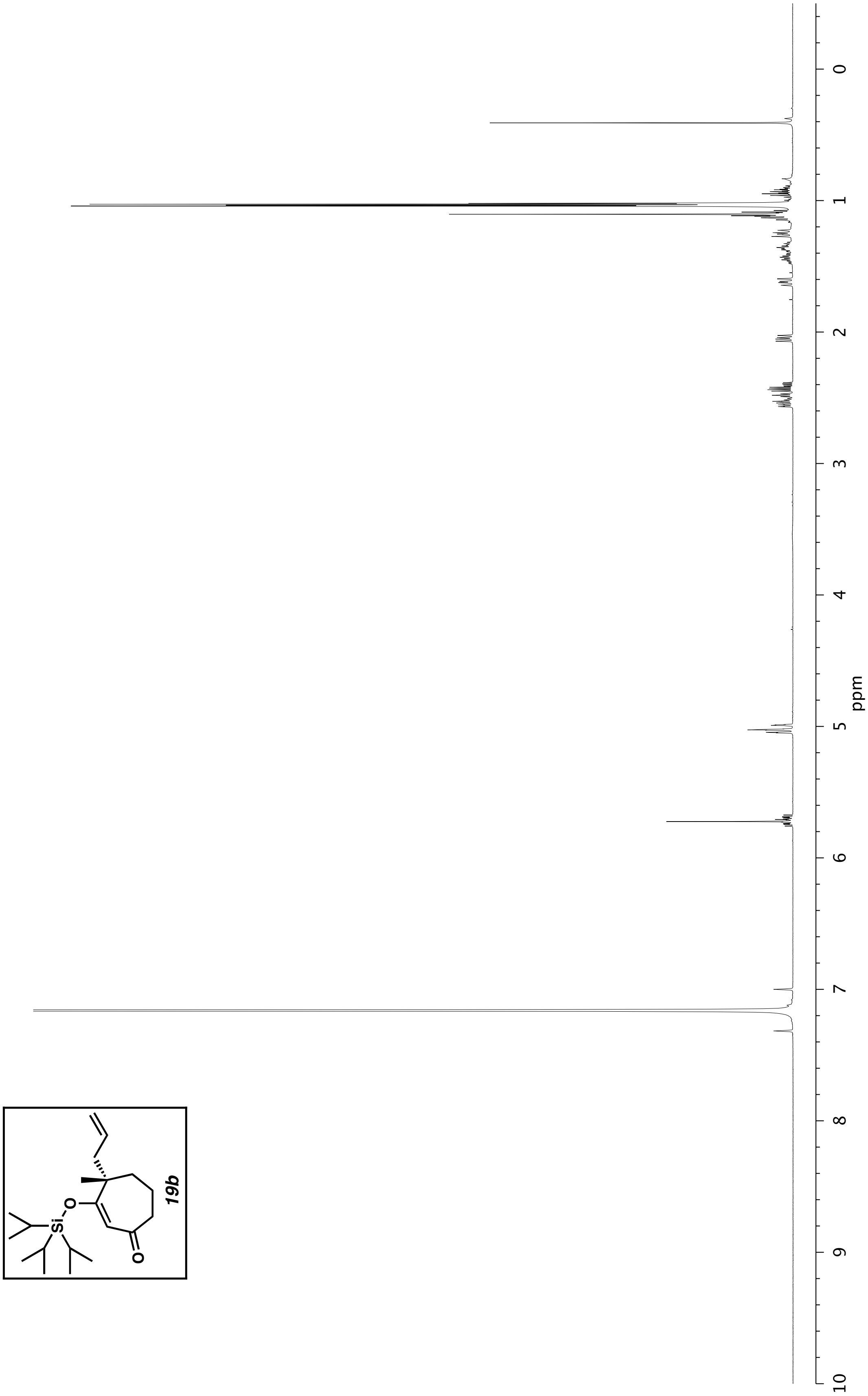


Figure SI-5.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **19b**.

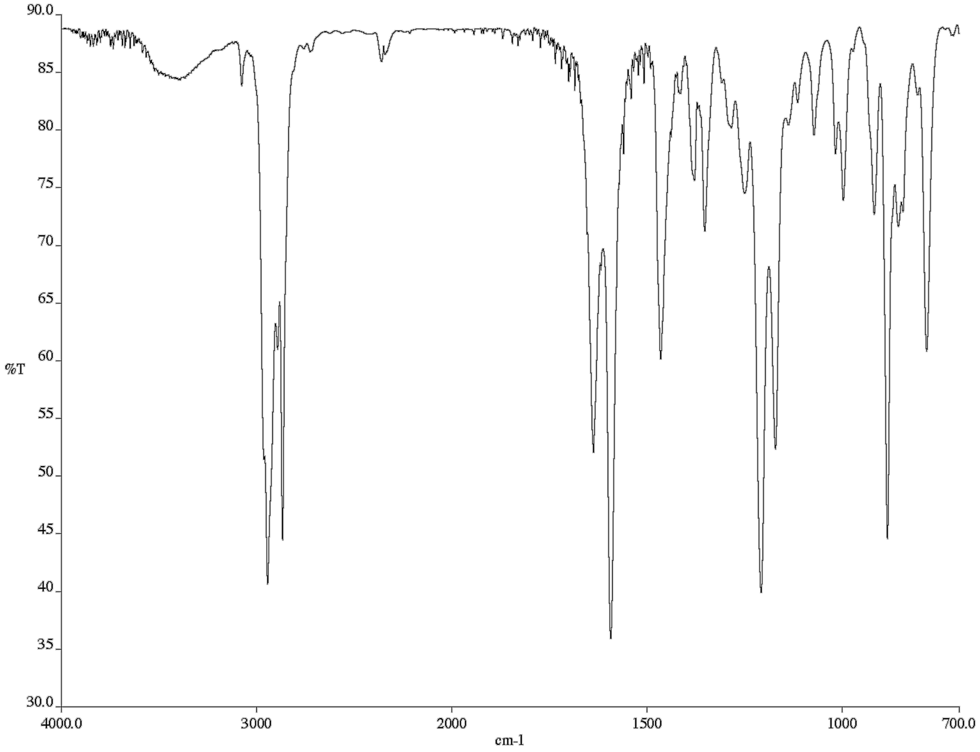


Figure SI-5.2. Infrared spectrum (thin film/NaCl) of compound **19b**.

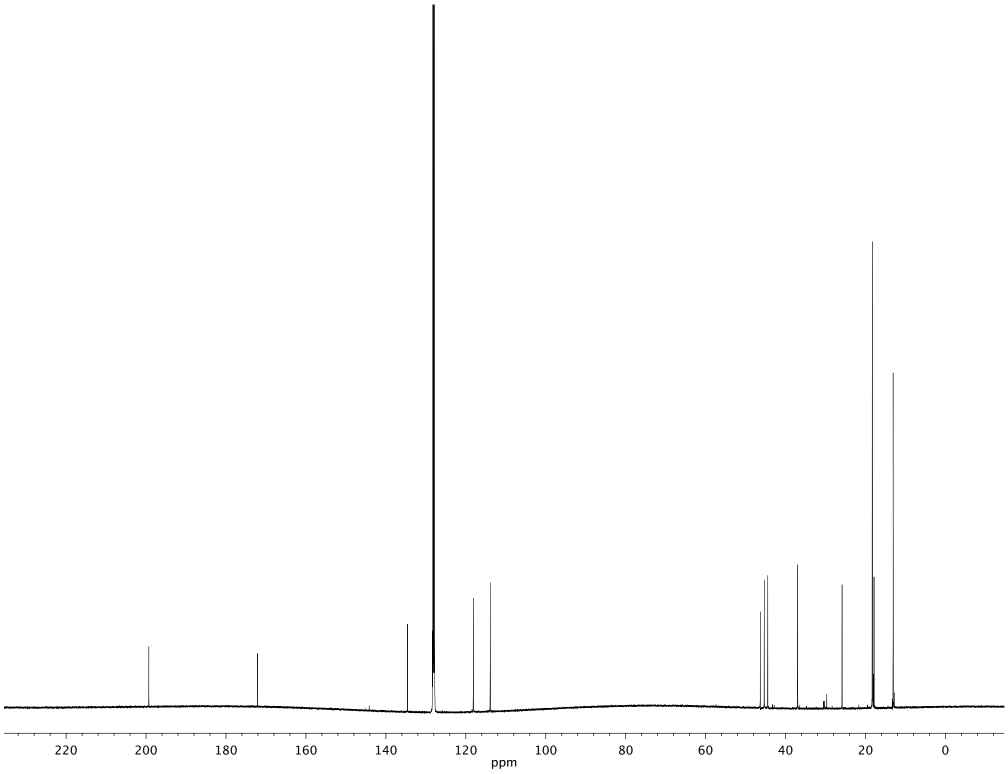


Figure SI-5.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **19b**.

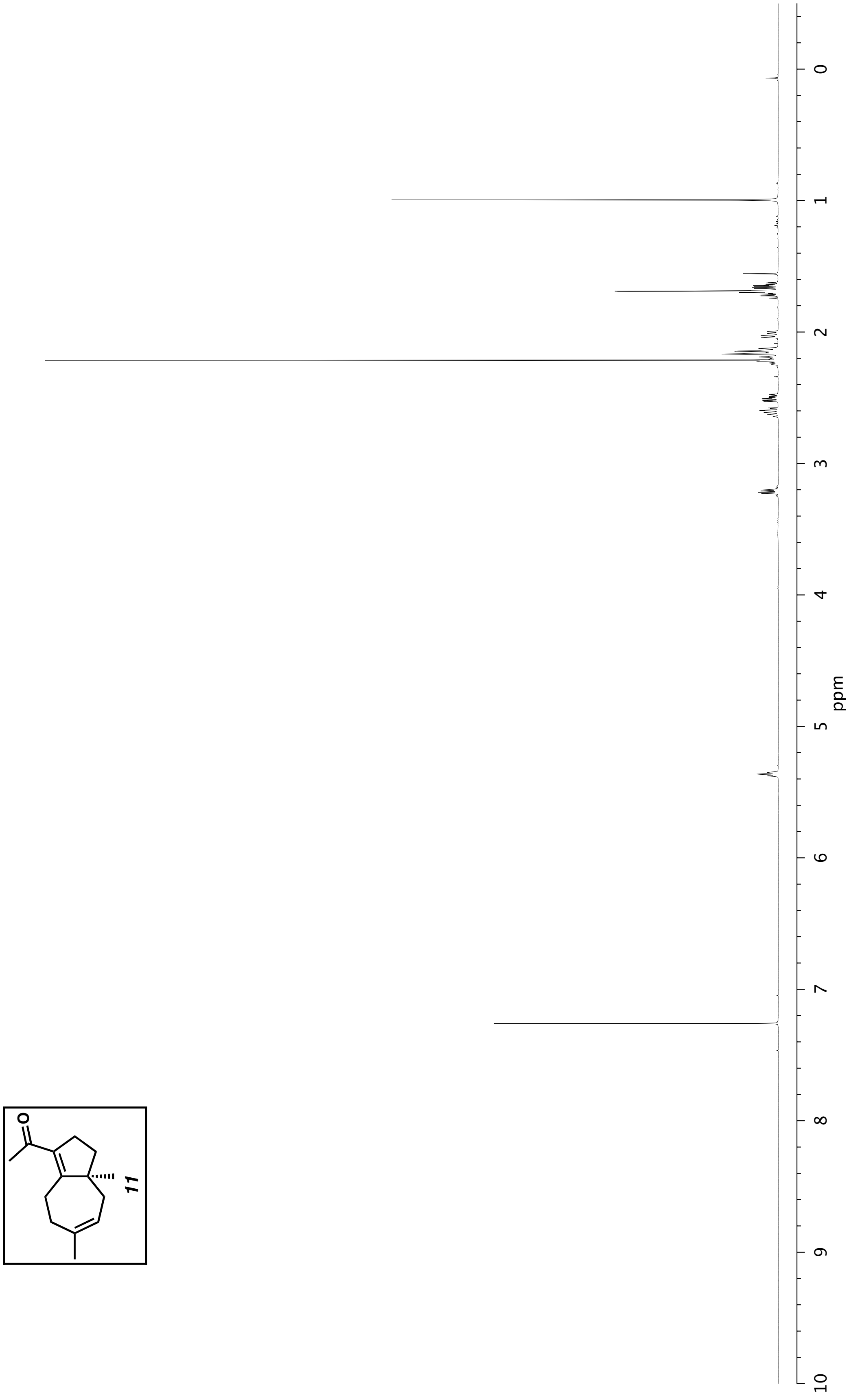


Figure SI-6.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.

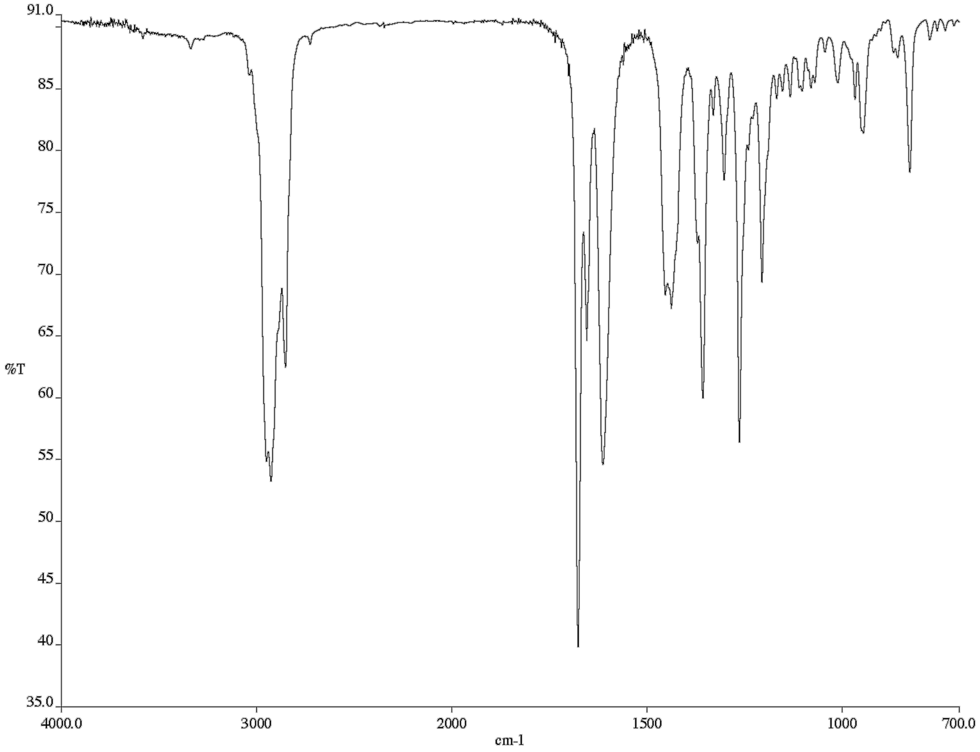


Figure SI-6.2. Infrared spectrum (thin film/NaCl) of compound **11**.

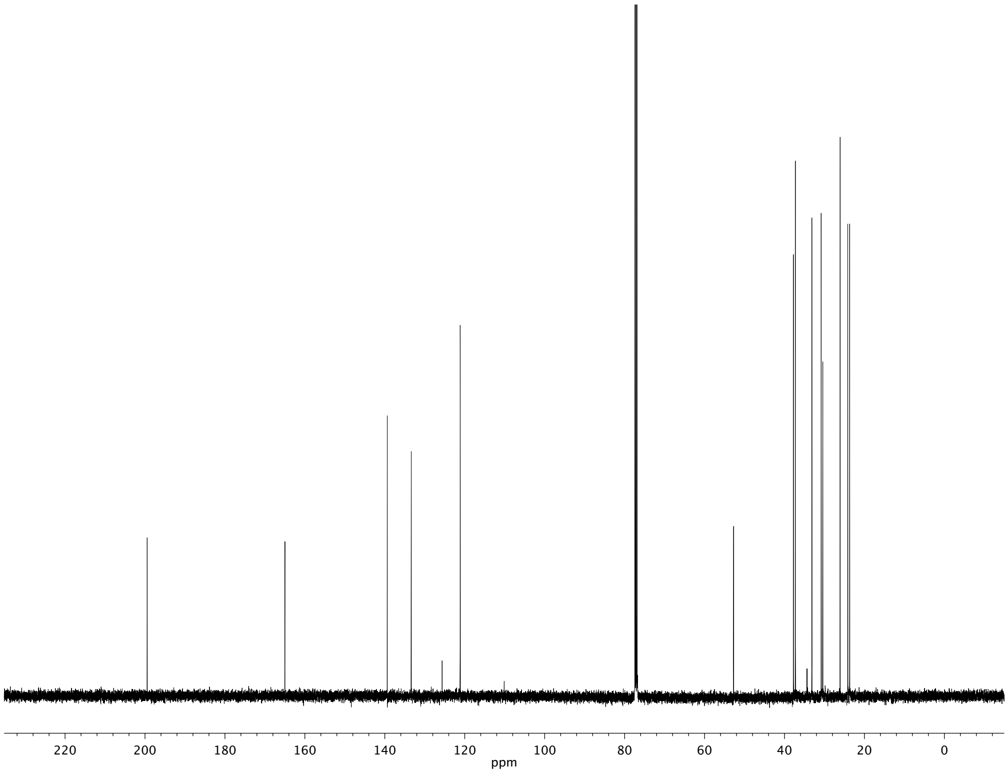


Figure SI-6.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **11**.

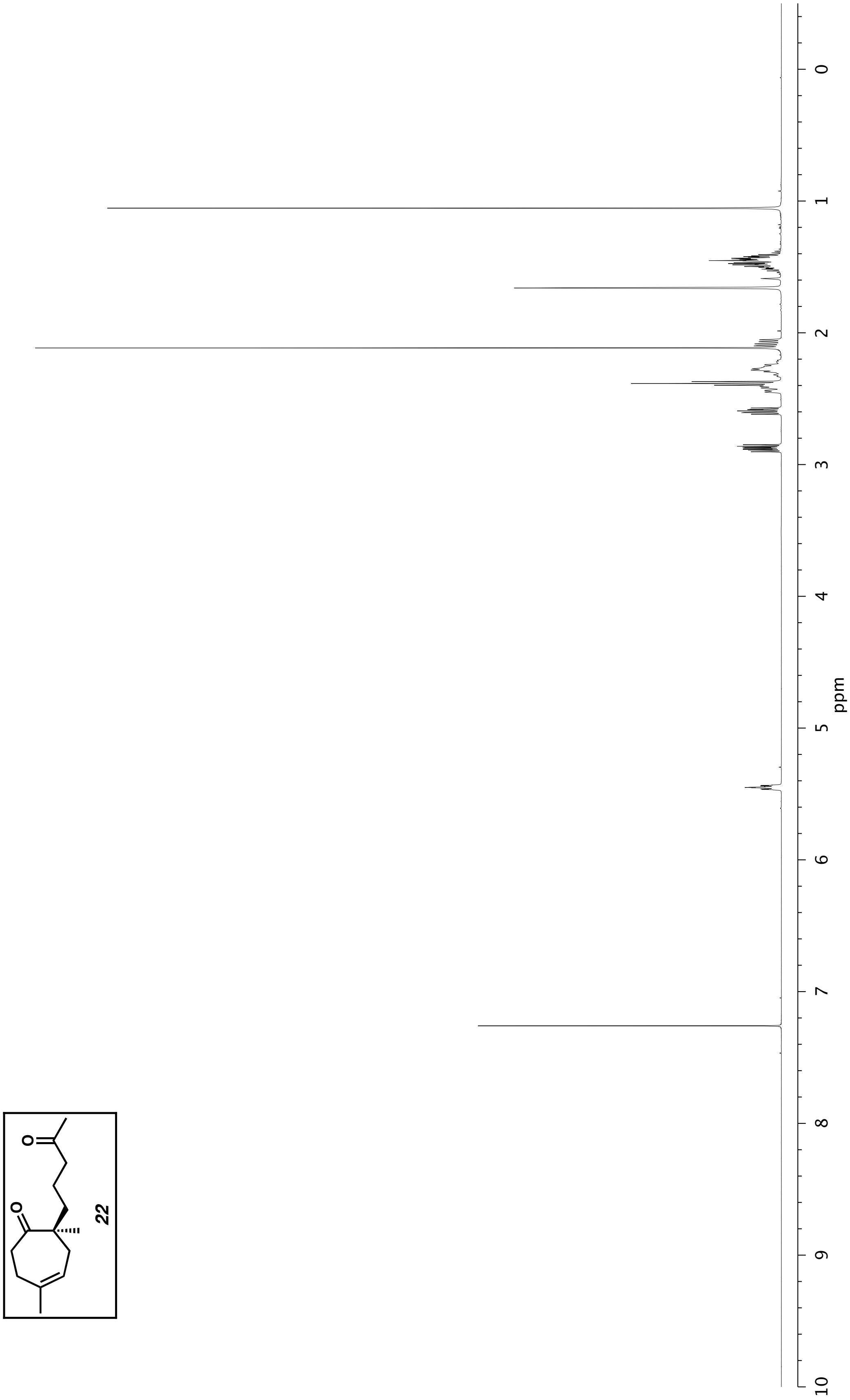


Figure SI-7.1. ^1H NMR (500 MHz, $CDCl_3$) of compound **22**.

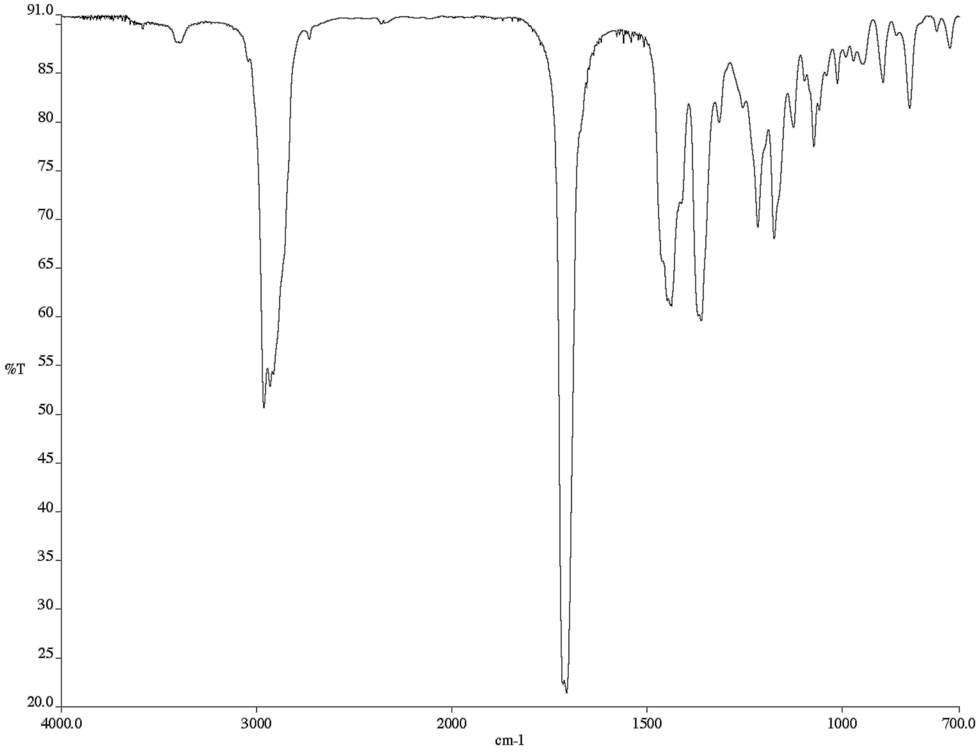


Figure SI-7.2. Infrared spectrum (thin film/NaCl) of compound **22**.

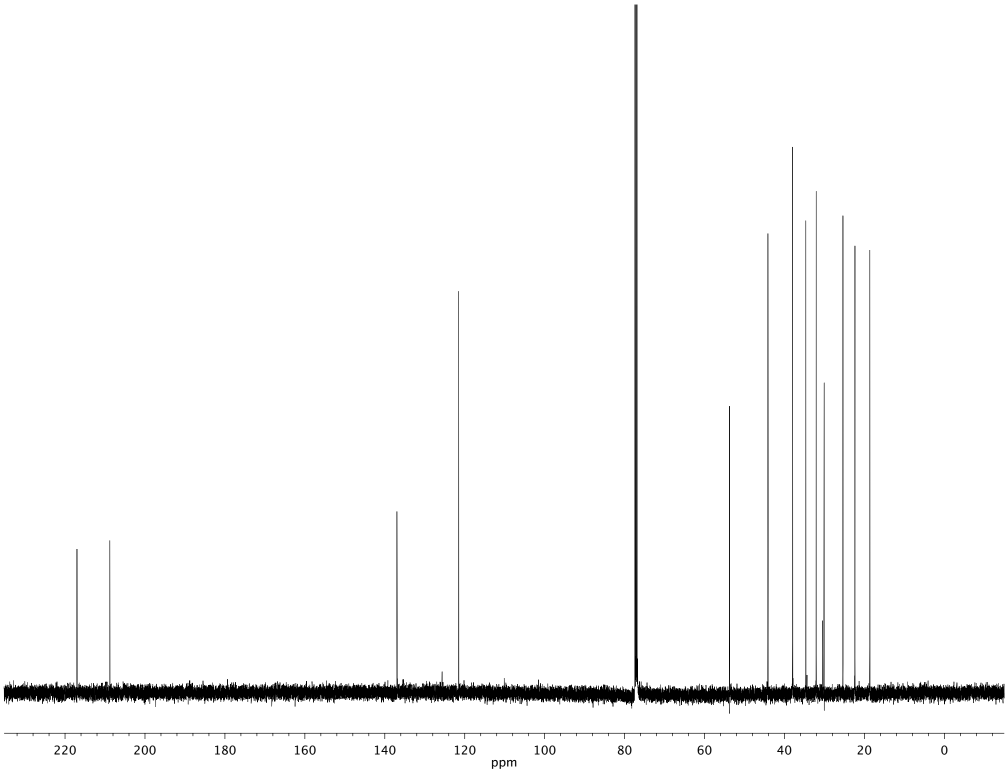


Figure SI-7.3. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **22**.

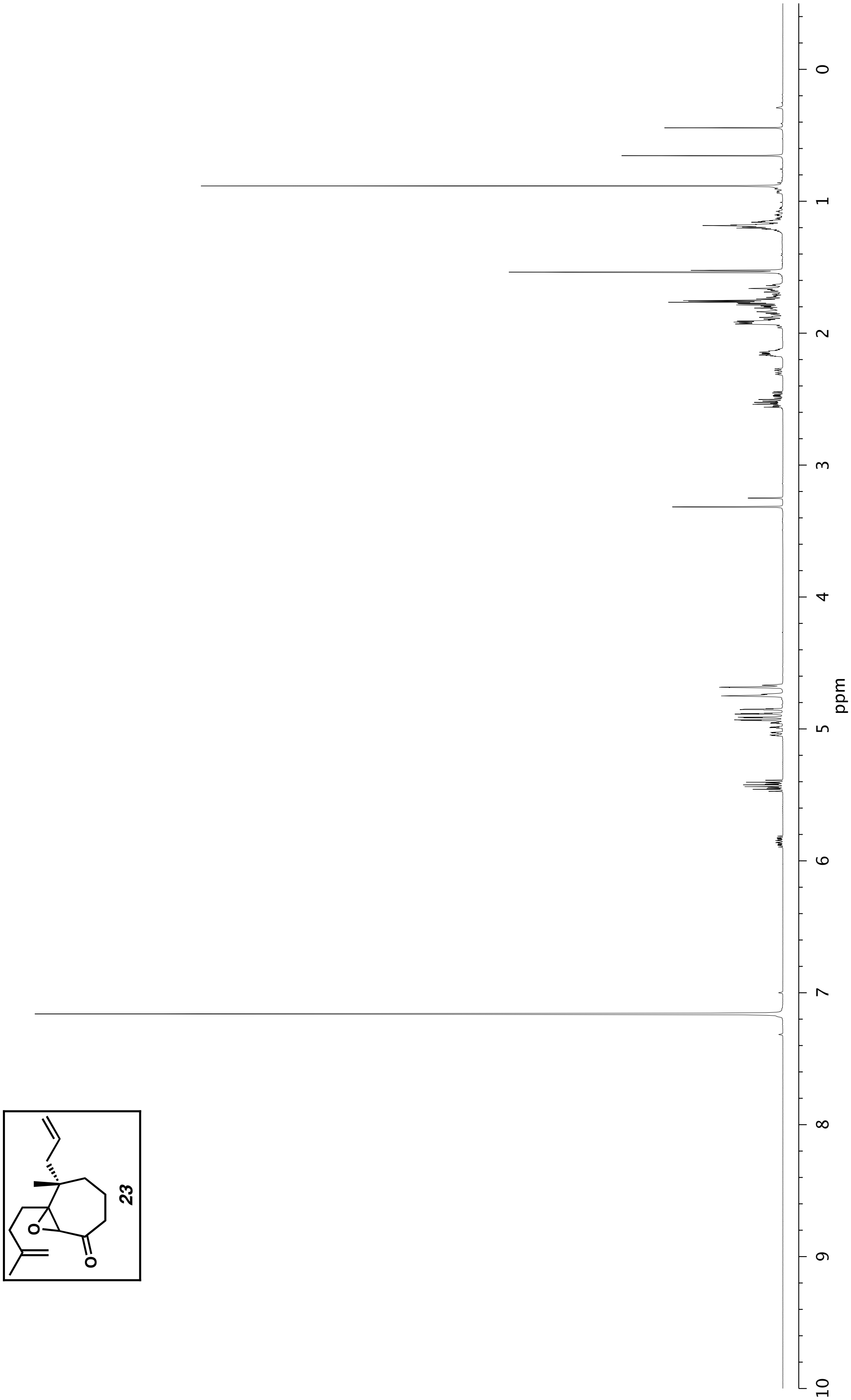


Figure SI-8.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **23**.

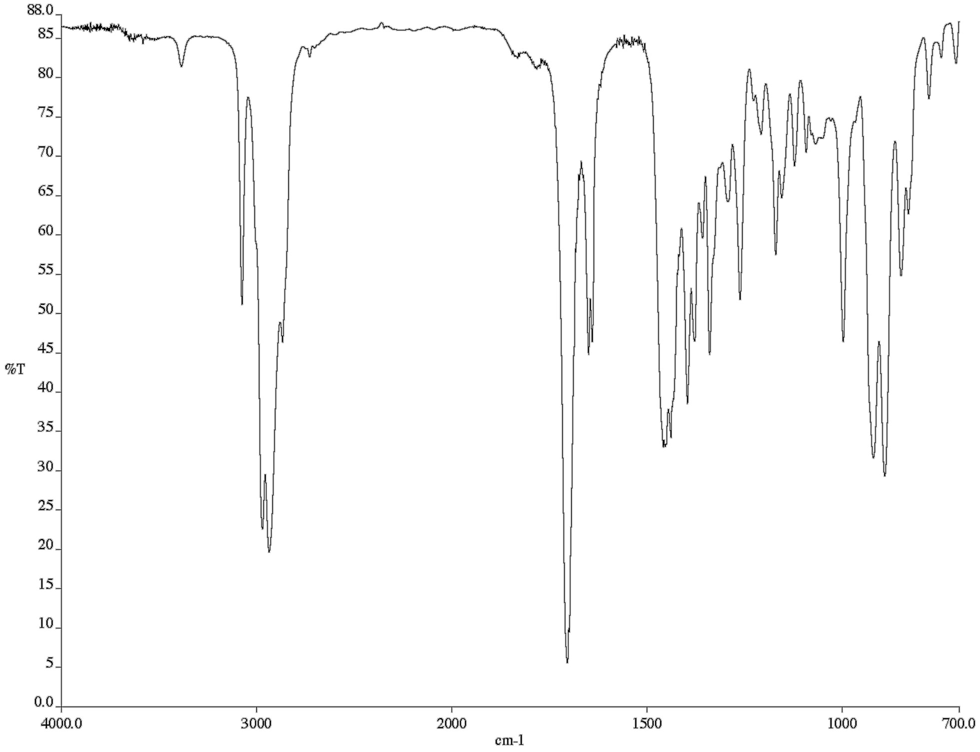


Figure SI-8.2. Infrared spectrum (thin film/NaCl) of compound **23**.

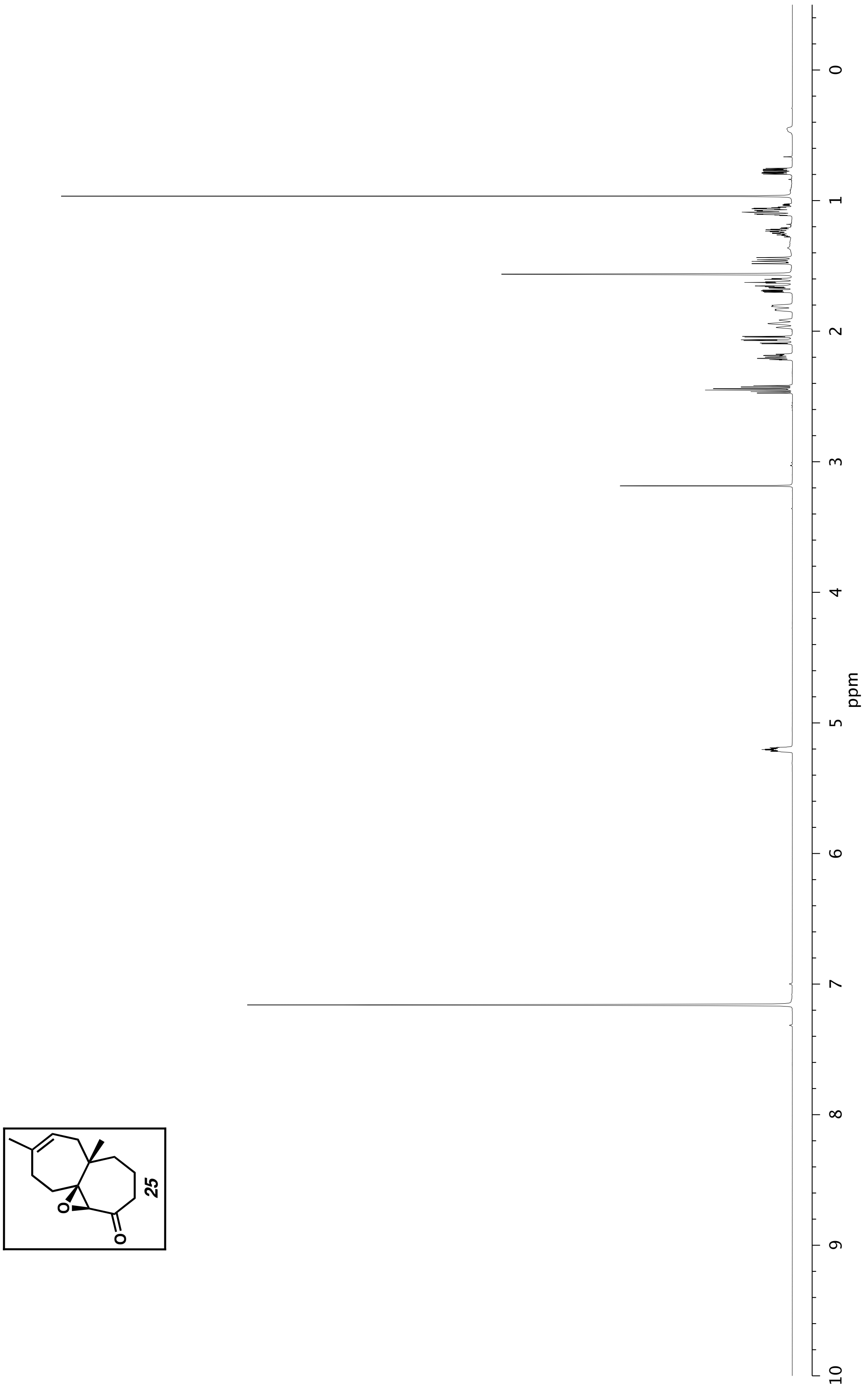


Figure SI-9.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **25**.

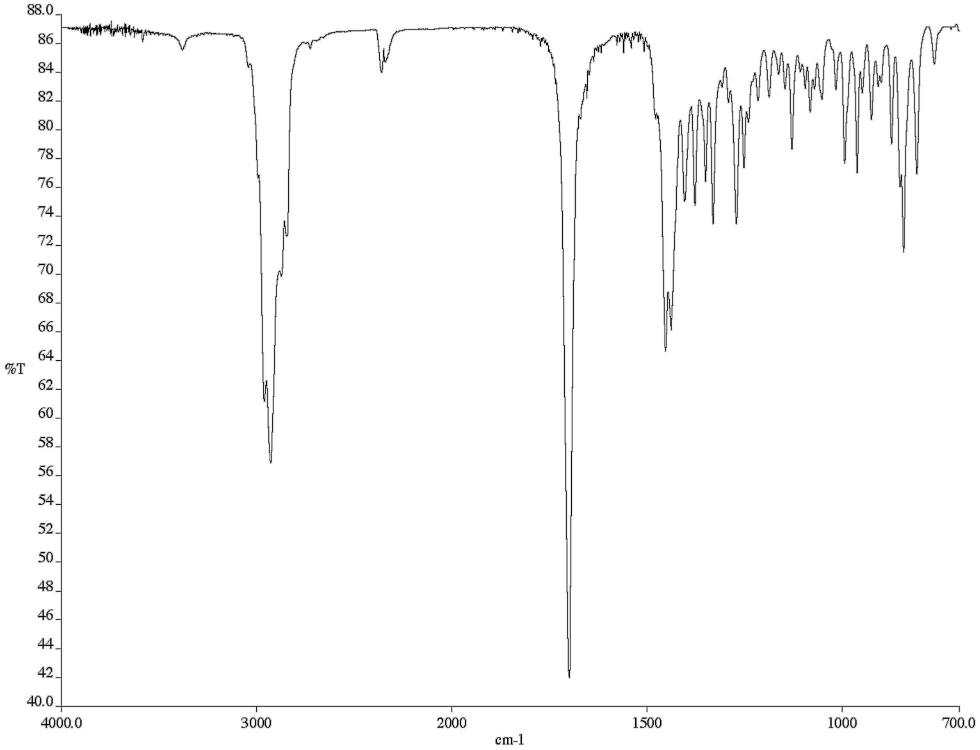


Figure SI-9.2. Infrared spectrum (thin film/NaCl) of compound **25**.

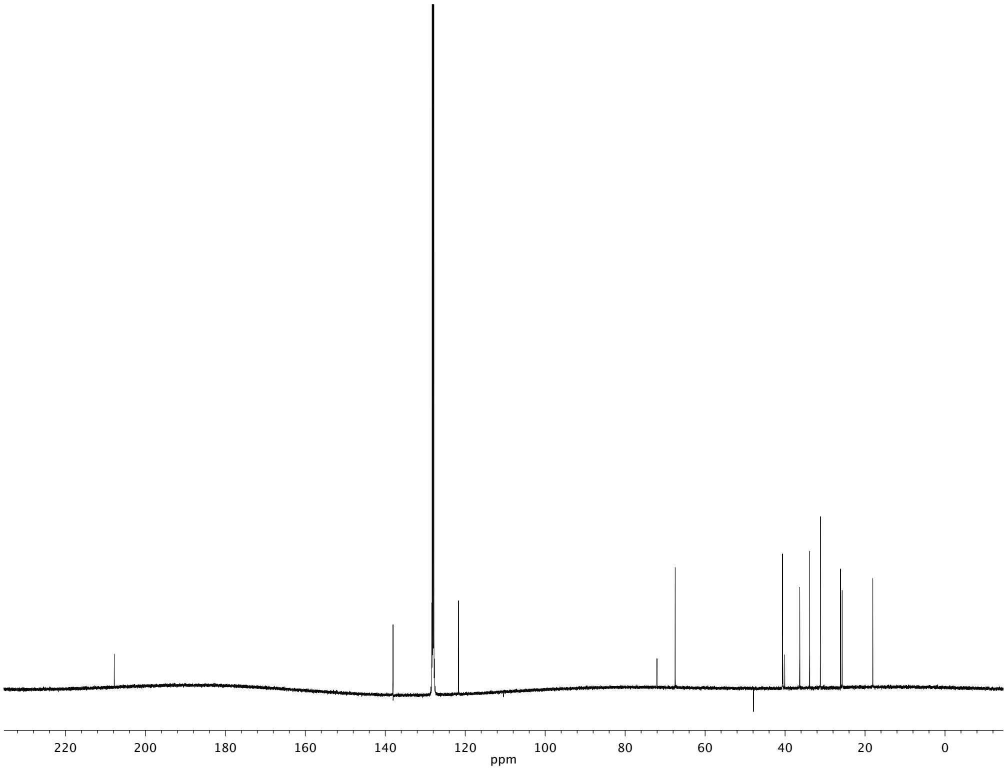
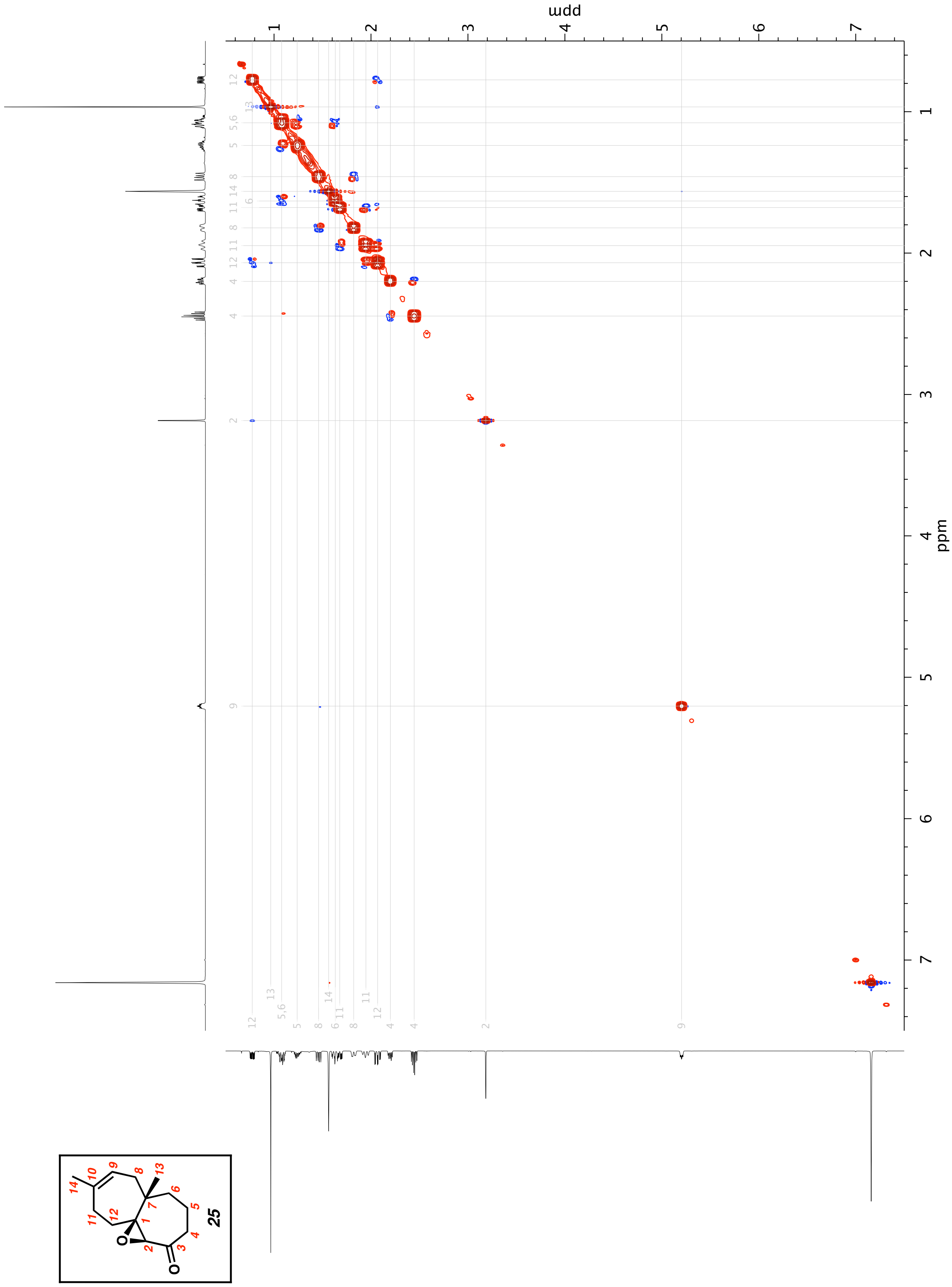


Figure SI-9.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **25**.



25

Figure SI-9.4. NOESY NMR (500 MHz, C_6D_6) of compound **25**.

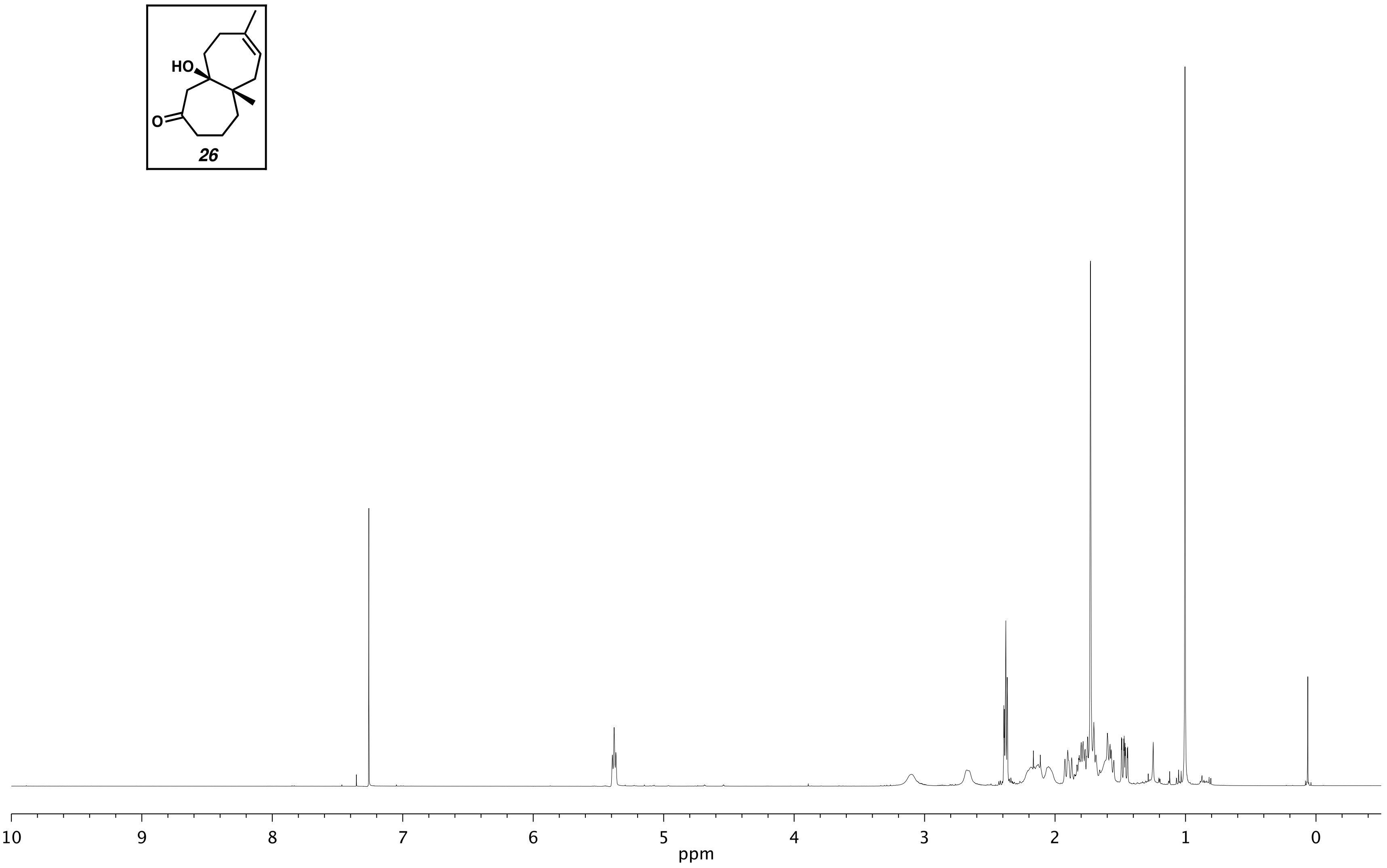


Figure SI-10.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **26**.

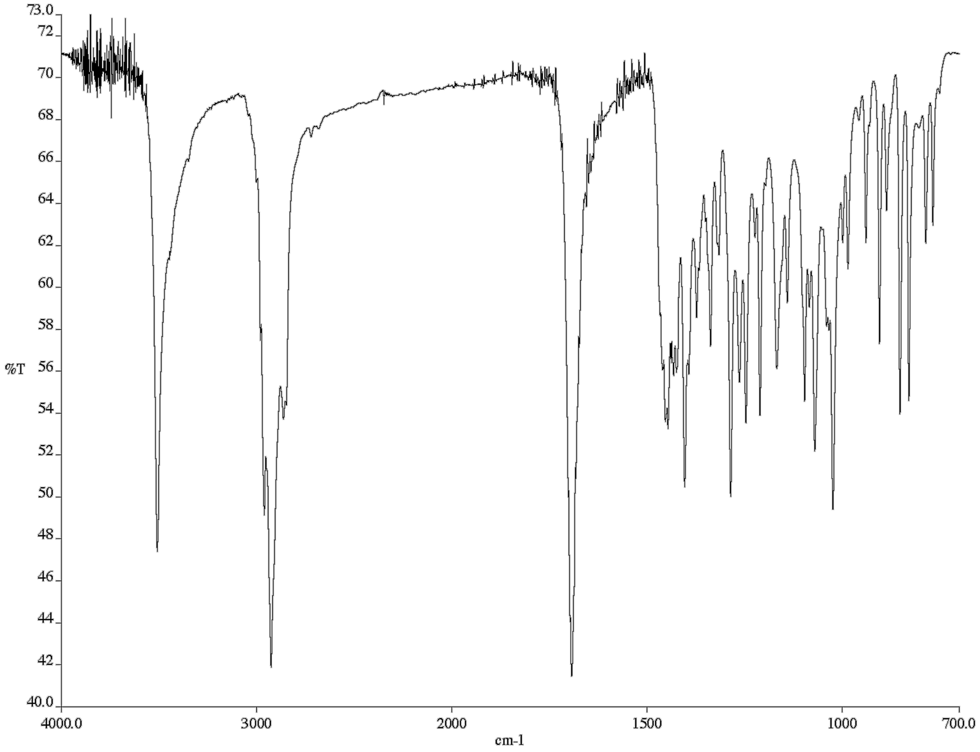


Figure SI-10.2. Infrared spectrum (thin film/NaCl) of compound **26**.

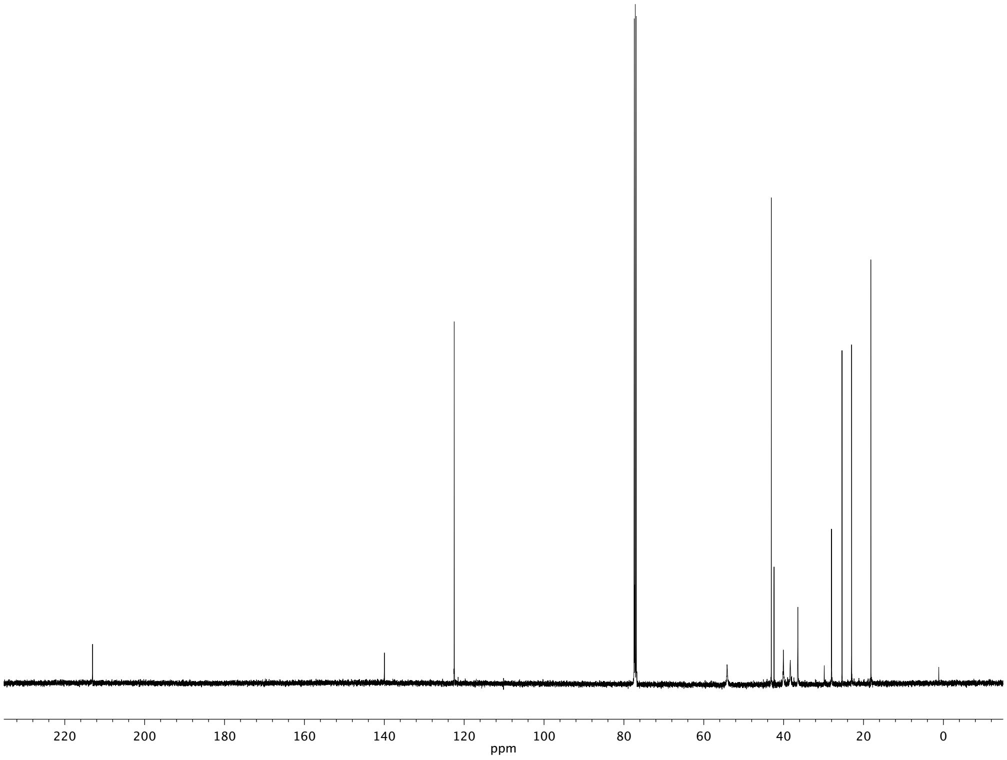


Figure SI-10.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **26**.

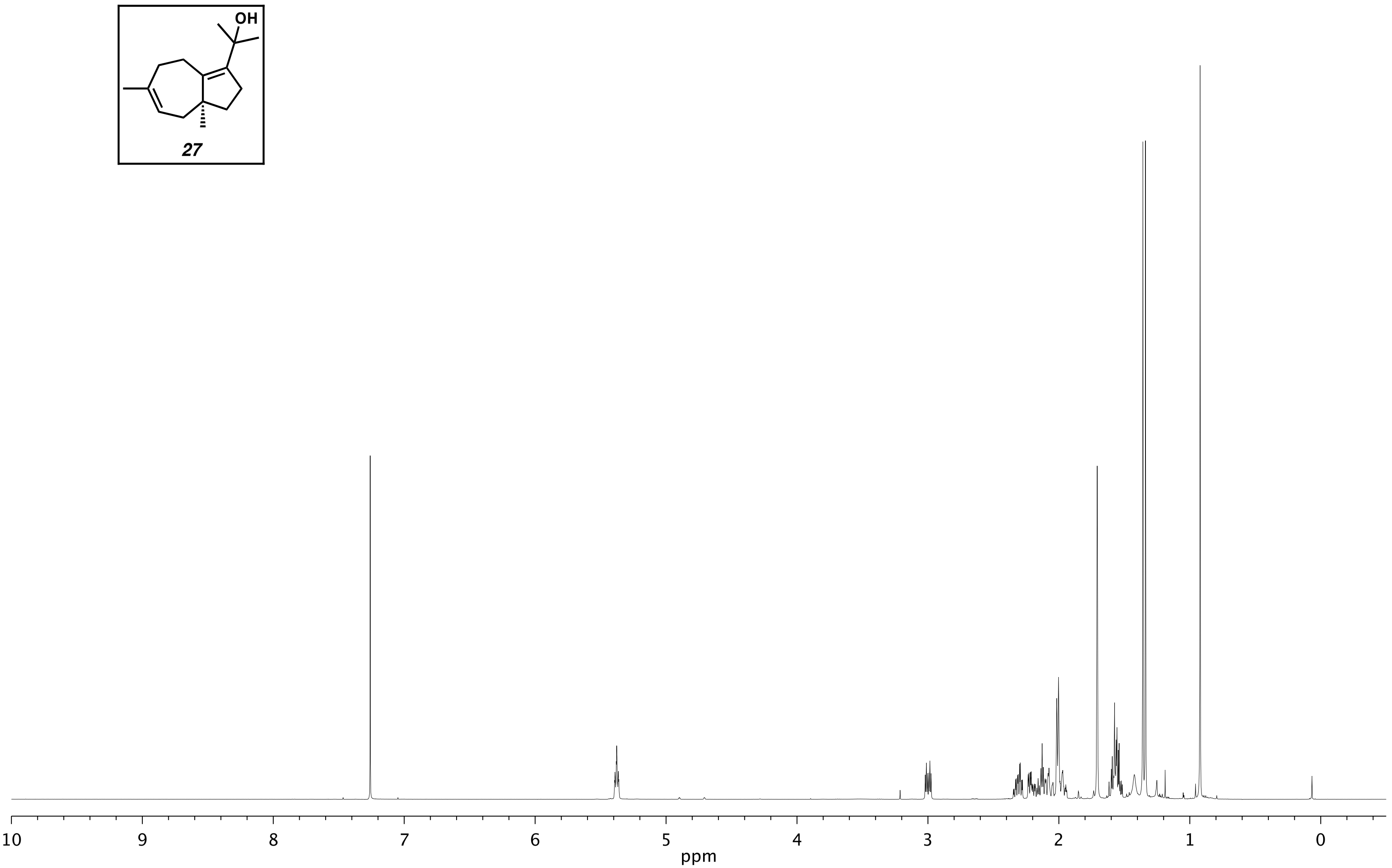


Figure SI-11.1. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **27**.

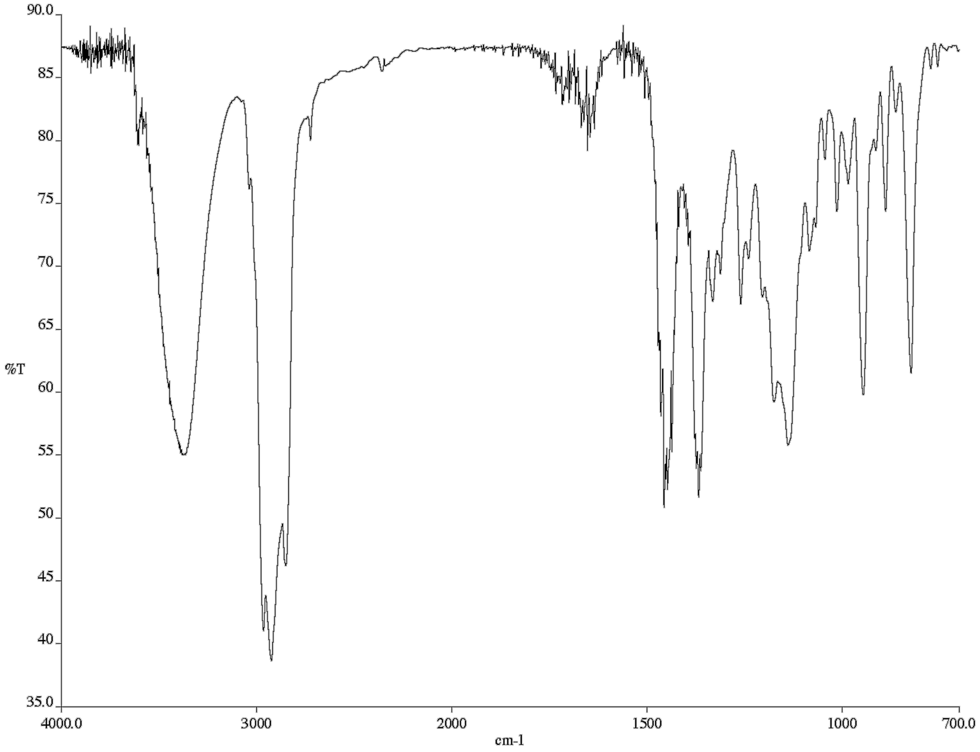


Figure SI-11.2. Infrared spectrum (thin film/NaCl) of compound **27**.

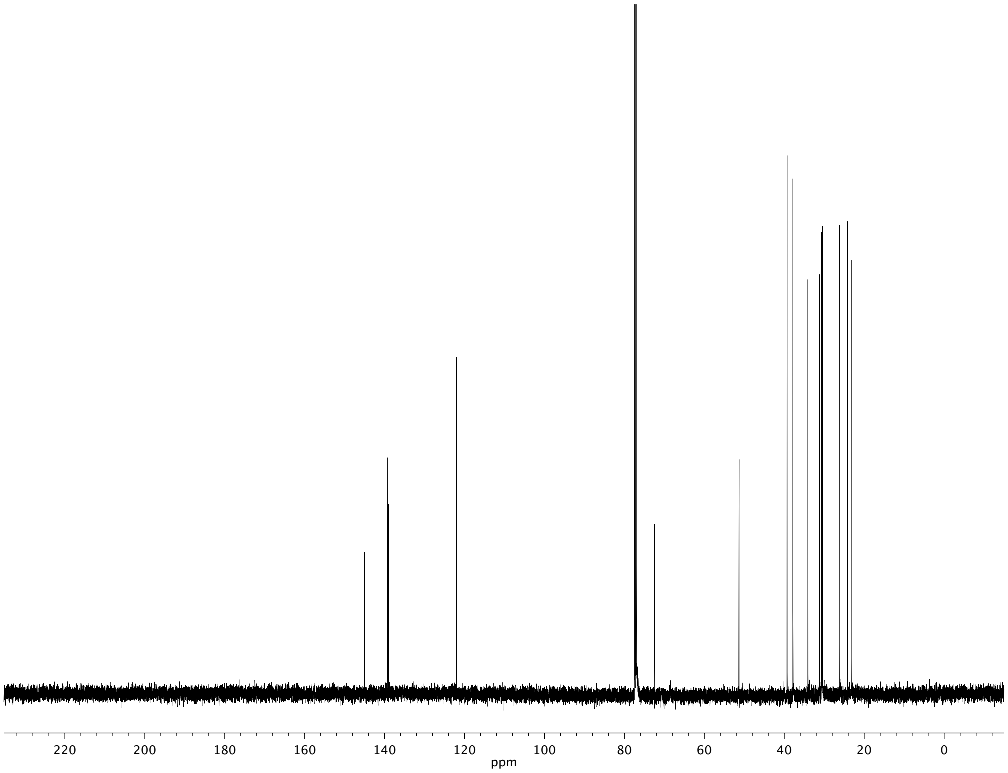


Figure SI-11.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **27**.

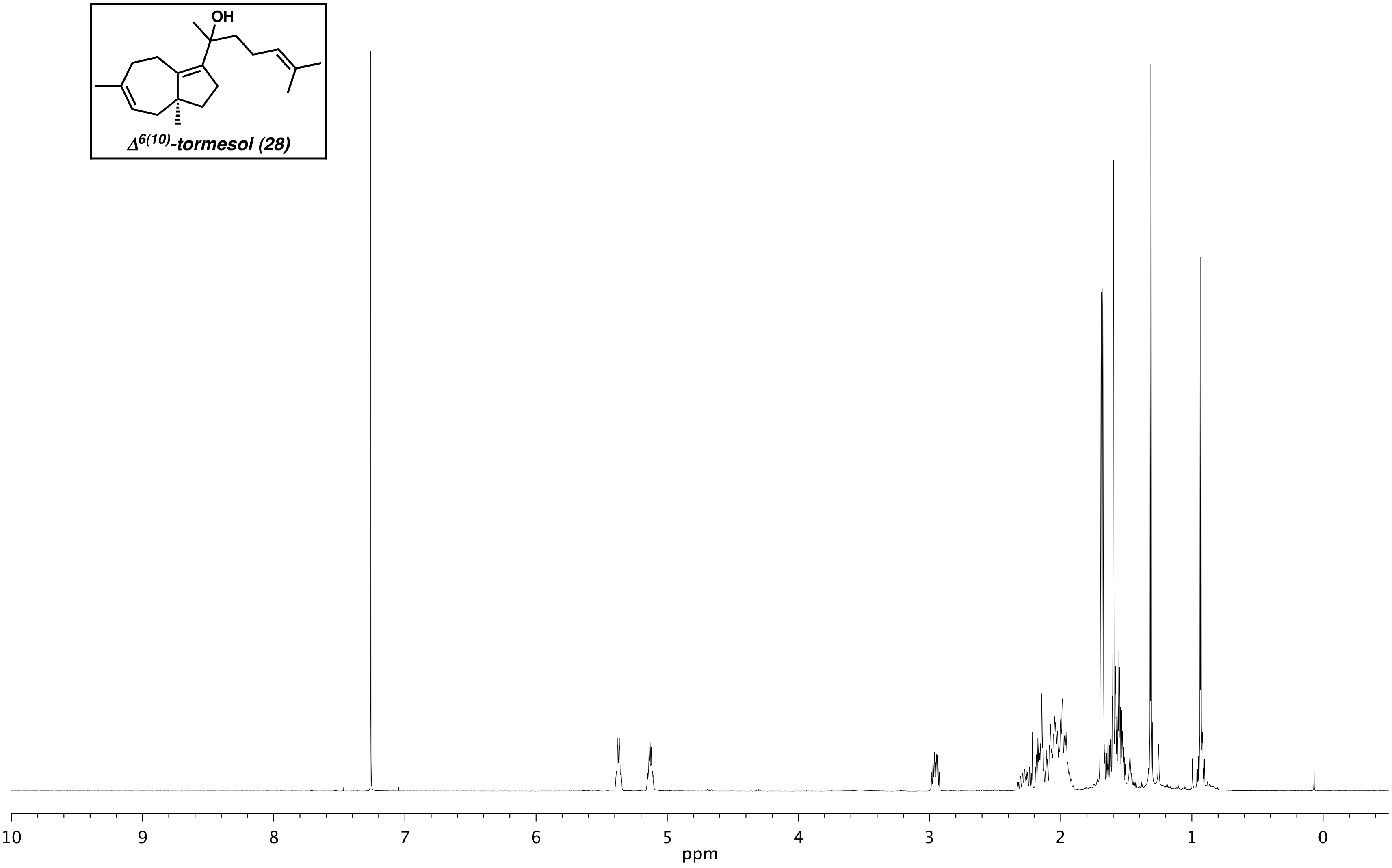


Figure SI-12.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **28**.

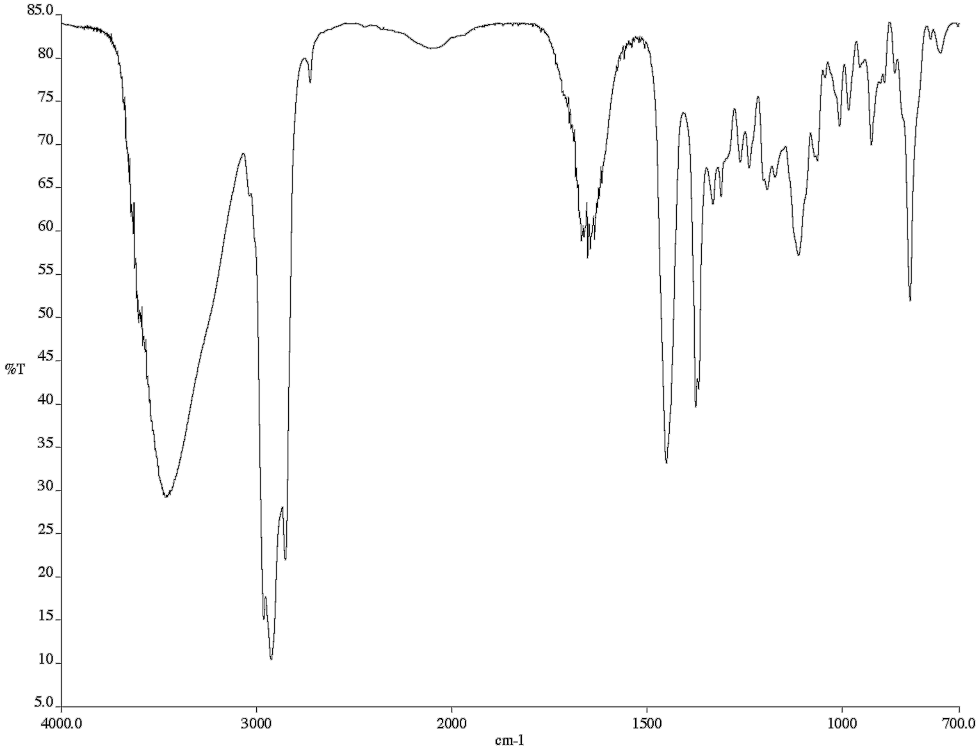


Figure SI-12.2. Infrared spectrum (thin film/NaCl) of compound **28**.

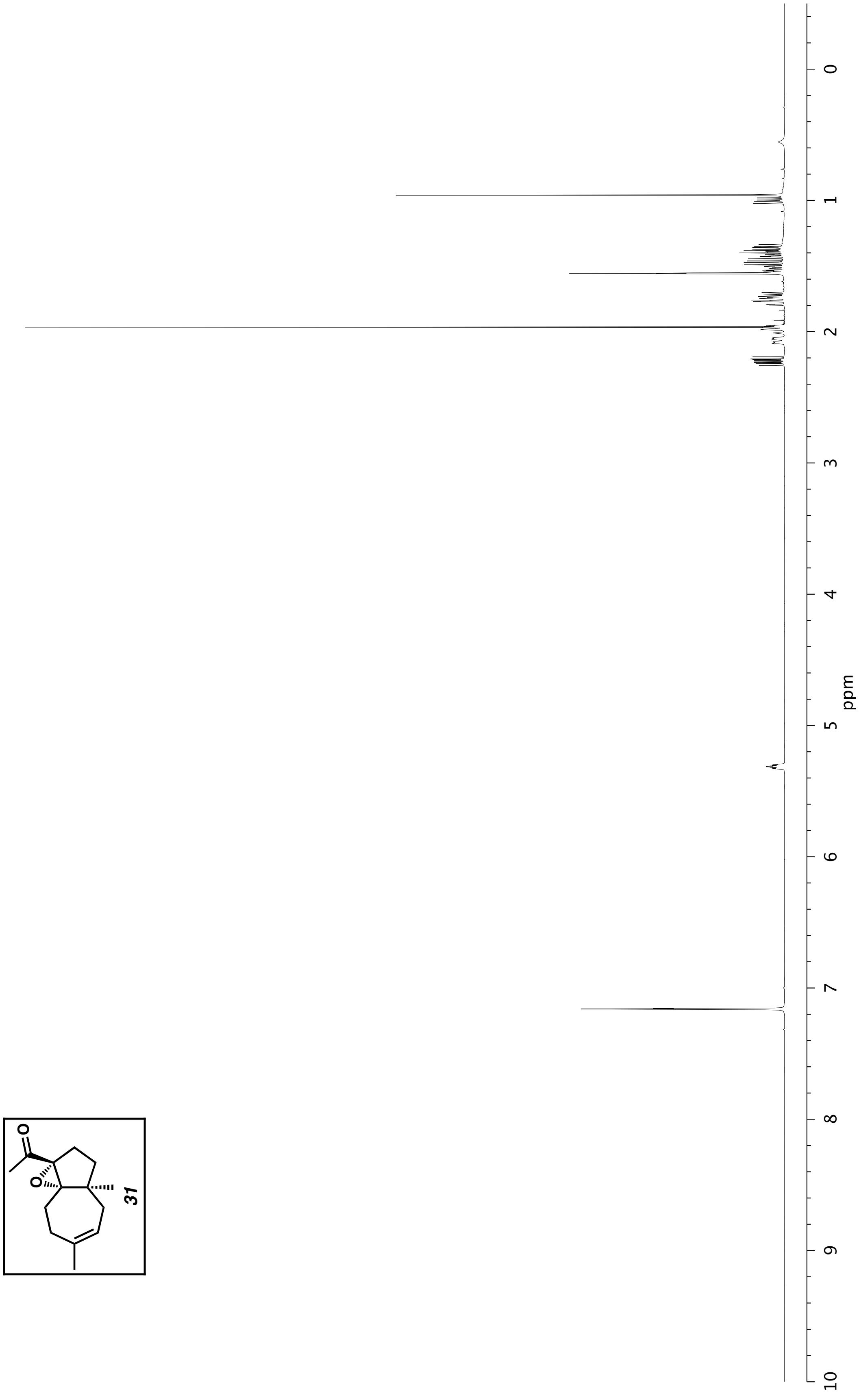


Figure SI-13.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **31**.

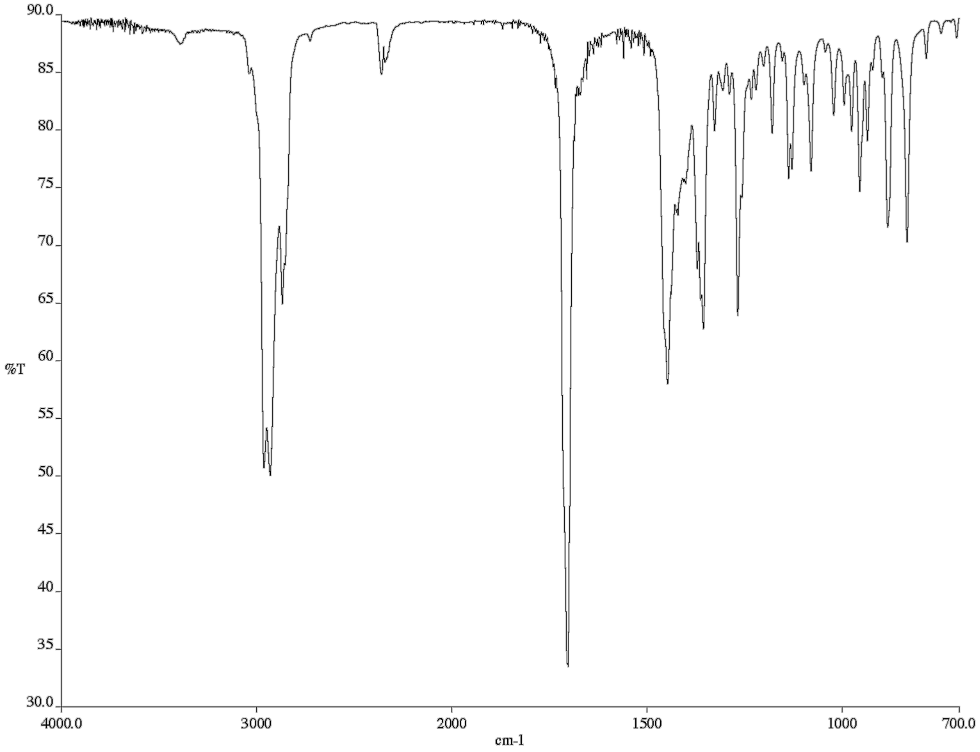


Figure SI-13.2. Infrared spectrum (thin film/NaCl) of compound **31**.

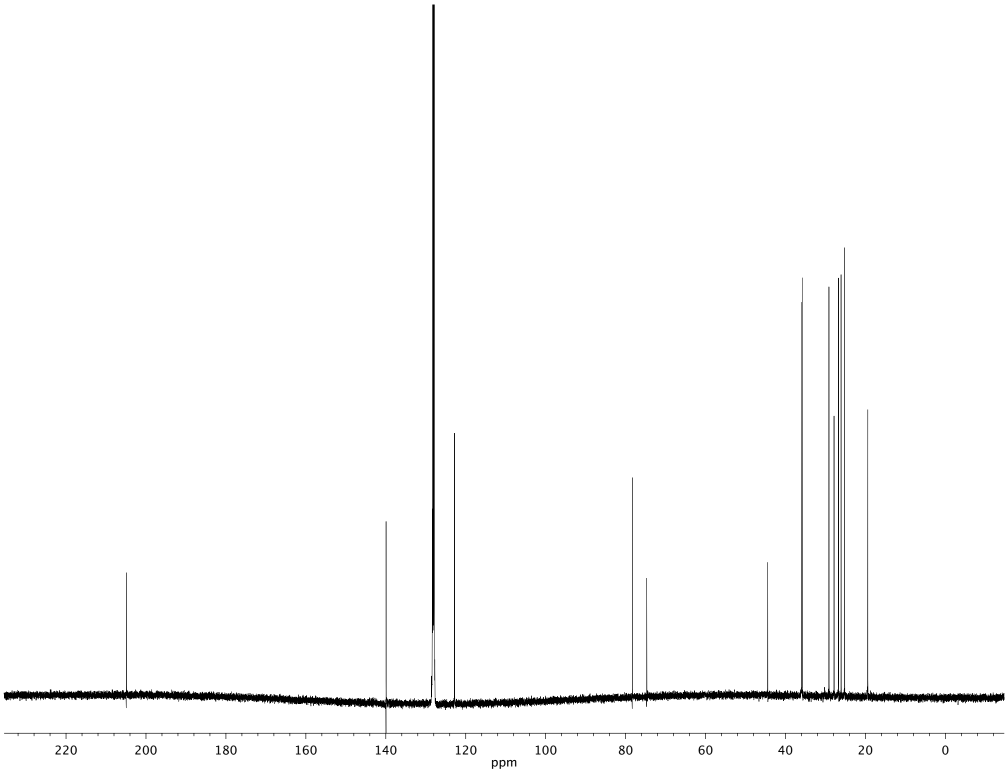


Figure SI-13.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **31**.

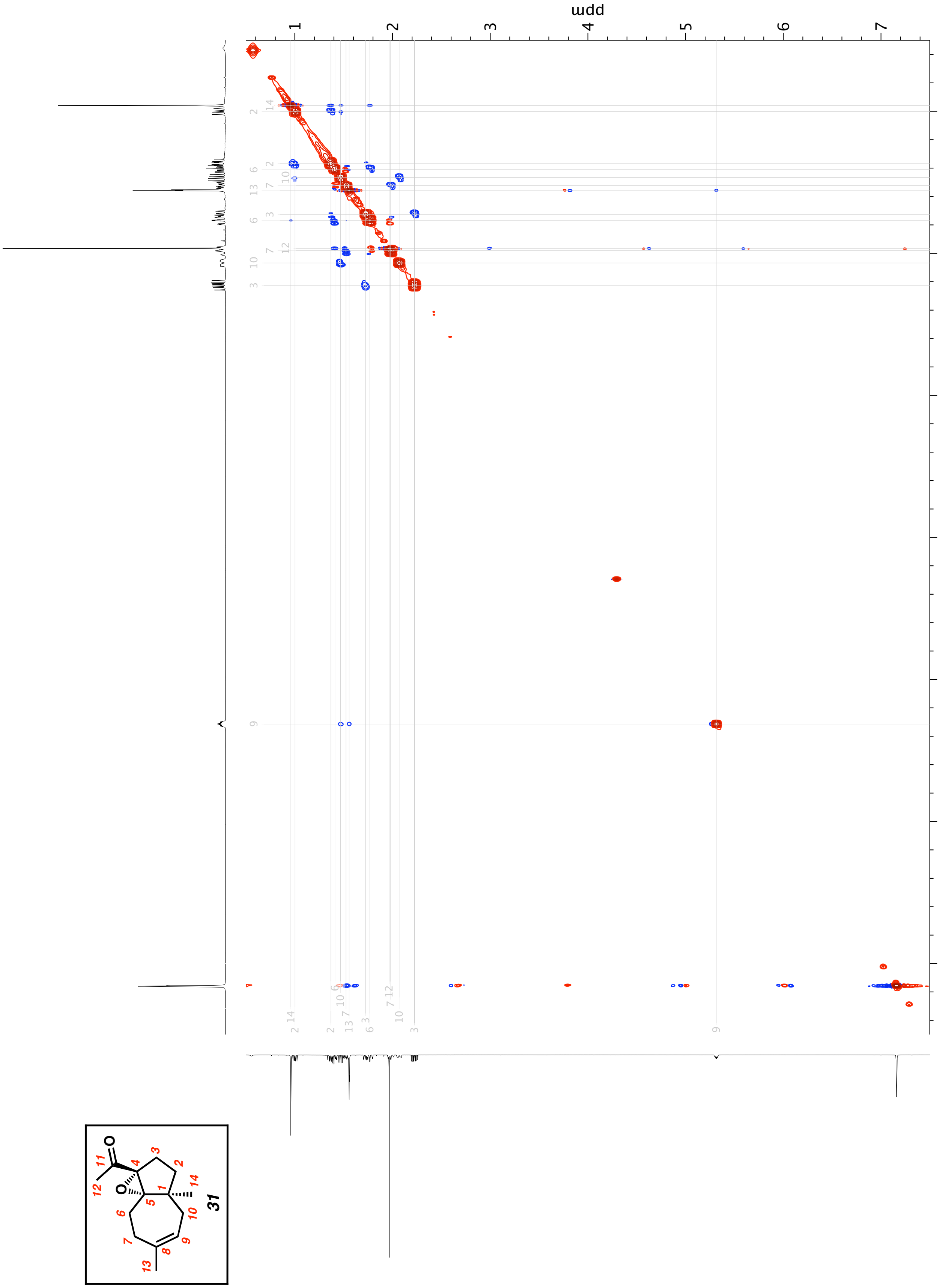


Figure SI-13.4. NOESY NMR (500 MHz, C_6D_6) of compound **31**.

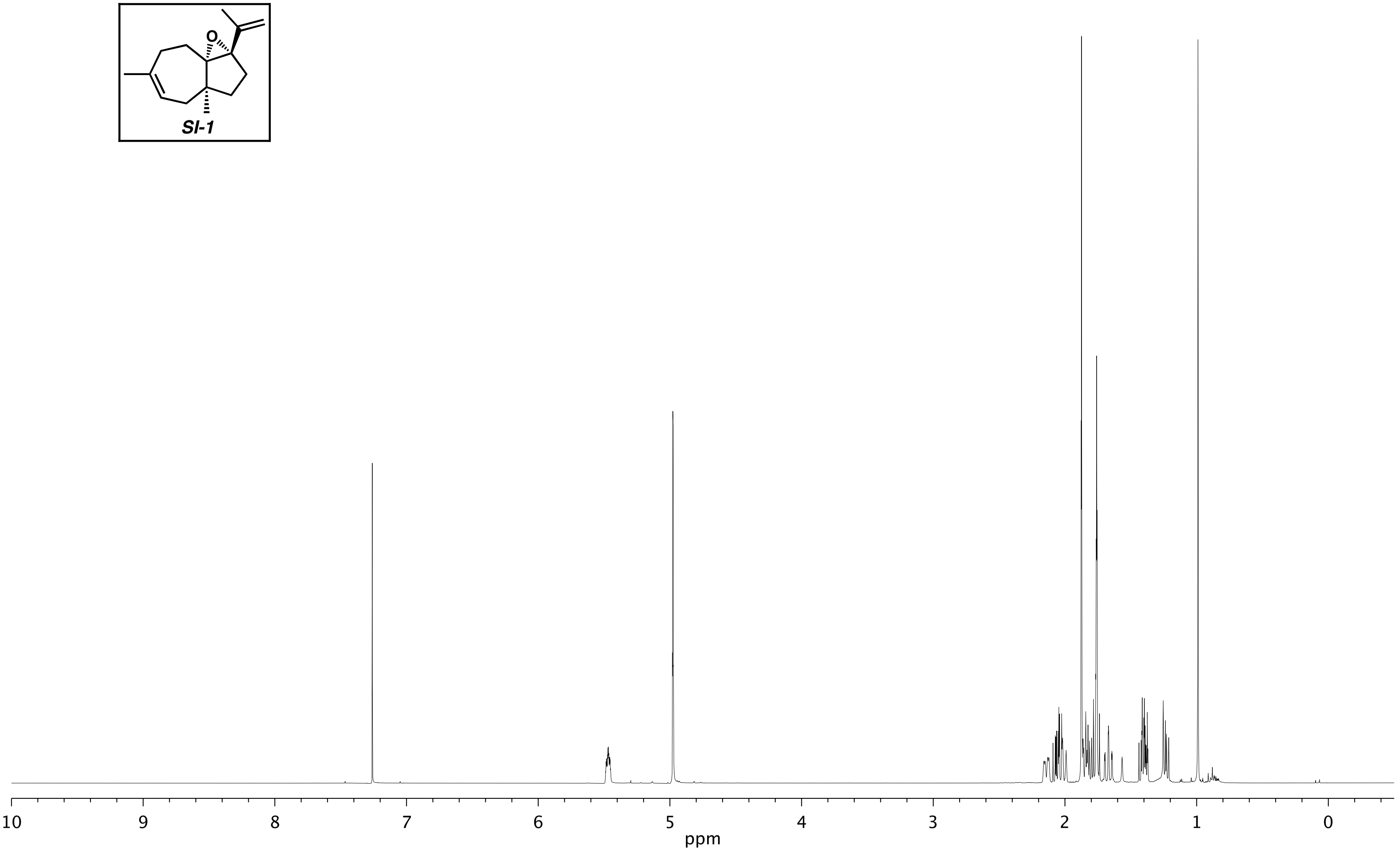


Figure SI-14.1. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI-1**.

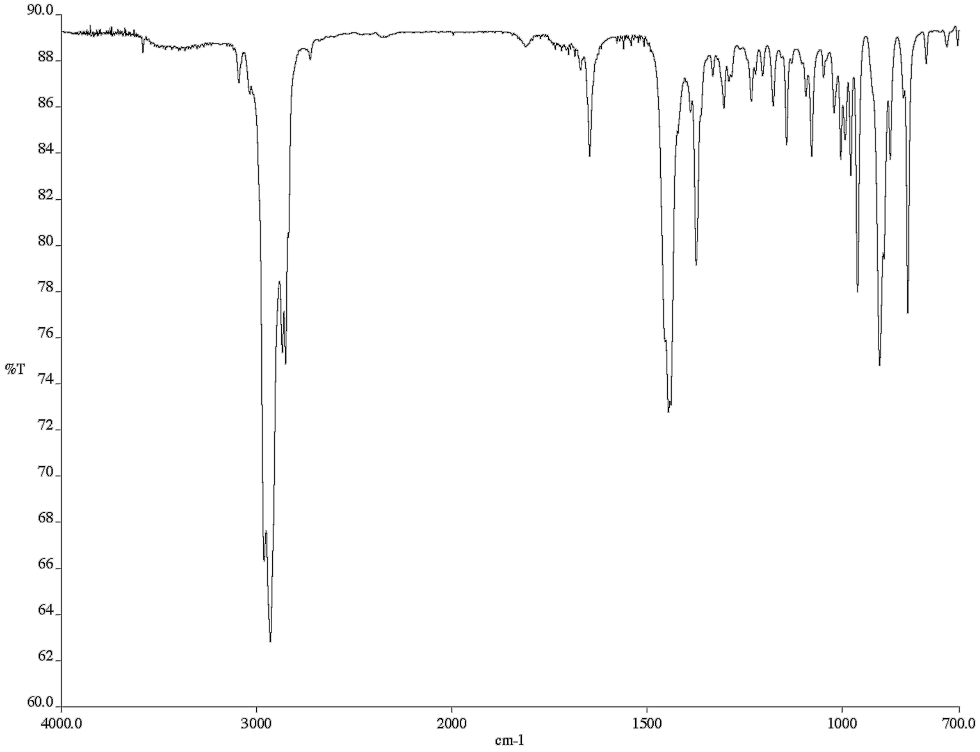


Figure SI-14.2. Infrared spectrum (thin film/NaCl) of compound **SI-1**.

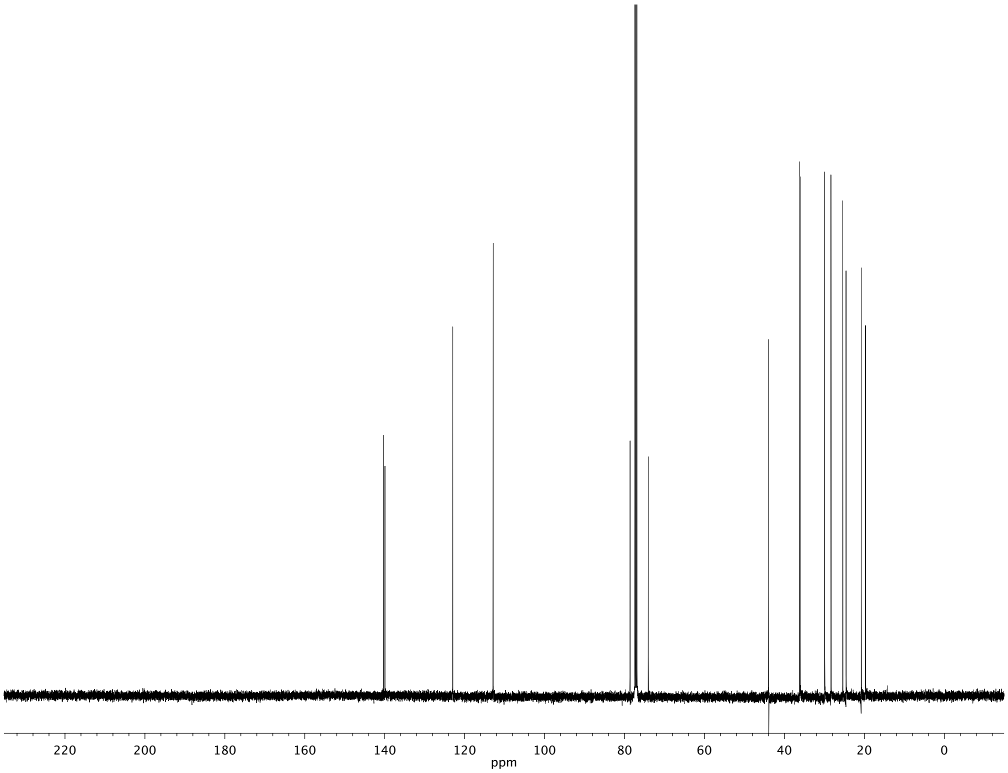


Figure SI-14.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **SI-1**.

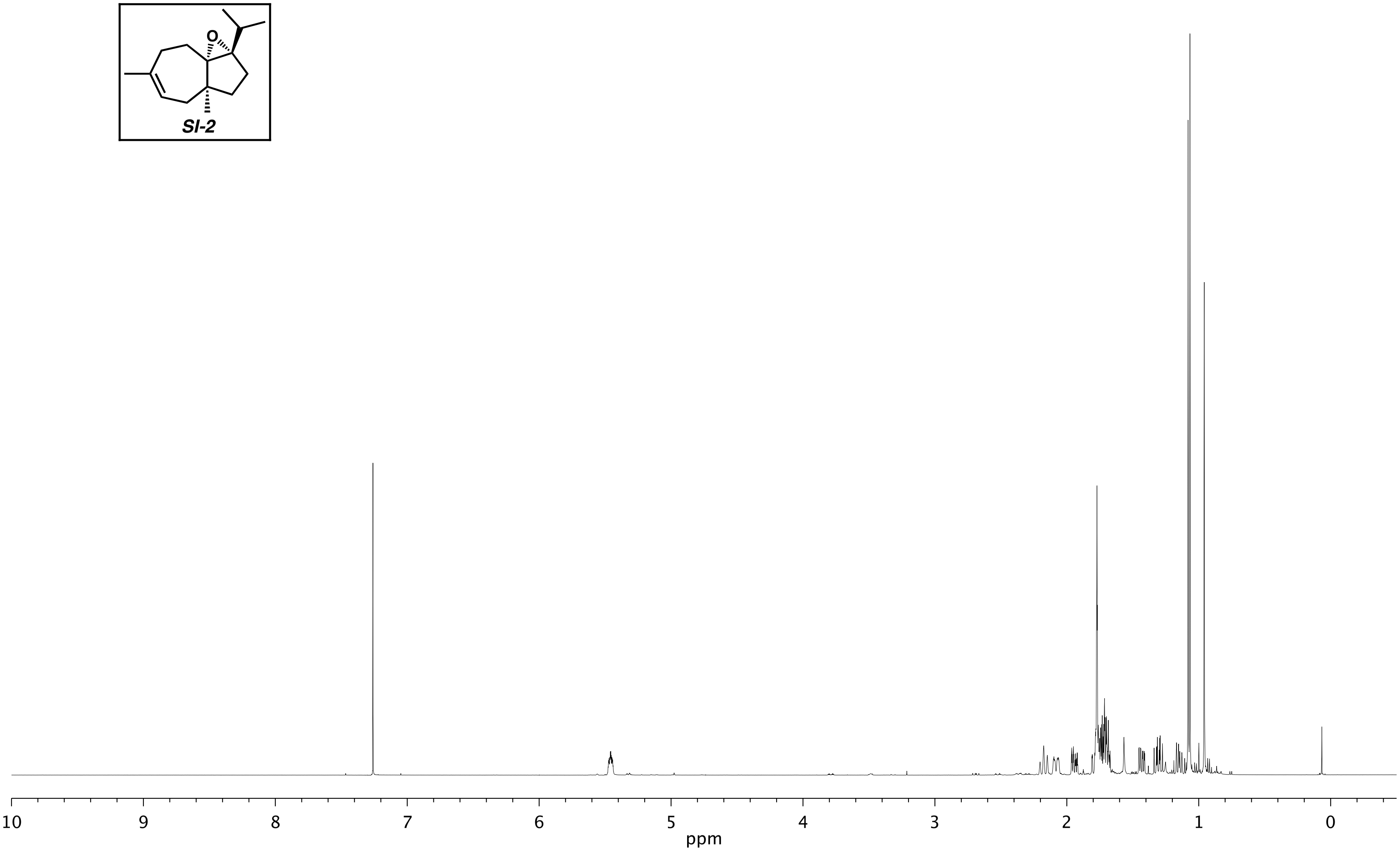


Figure SI-15.1. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI-2**.

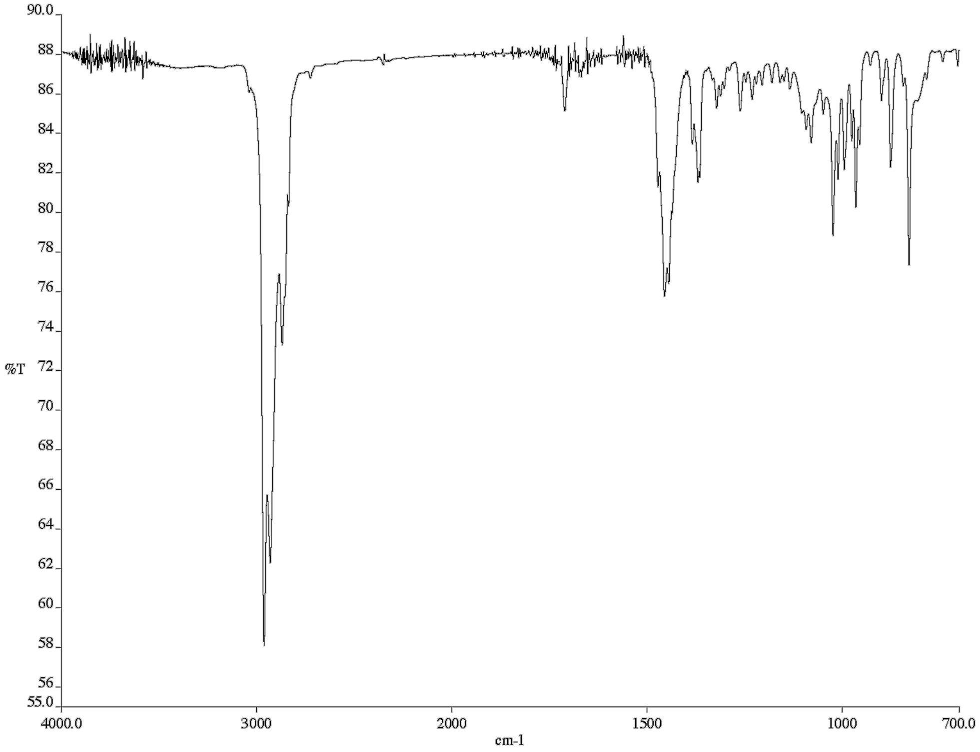


Figure SI-15.2. Infrared spectrum (thin film/NaCl) of compound **SI-2**.

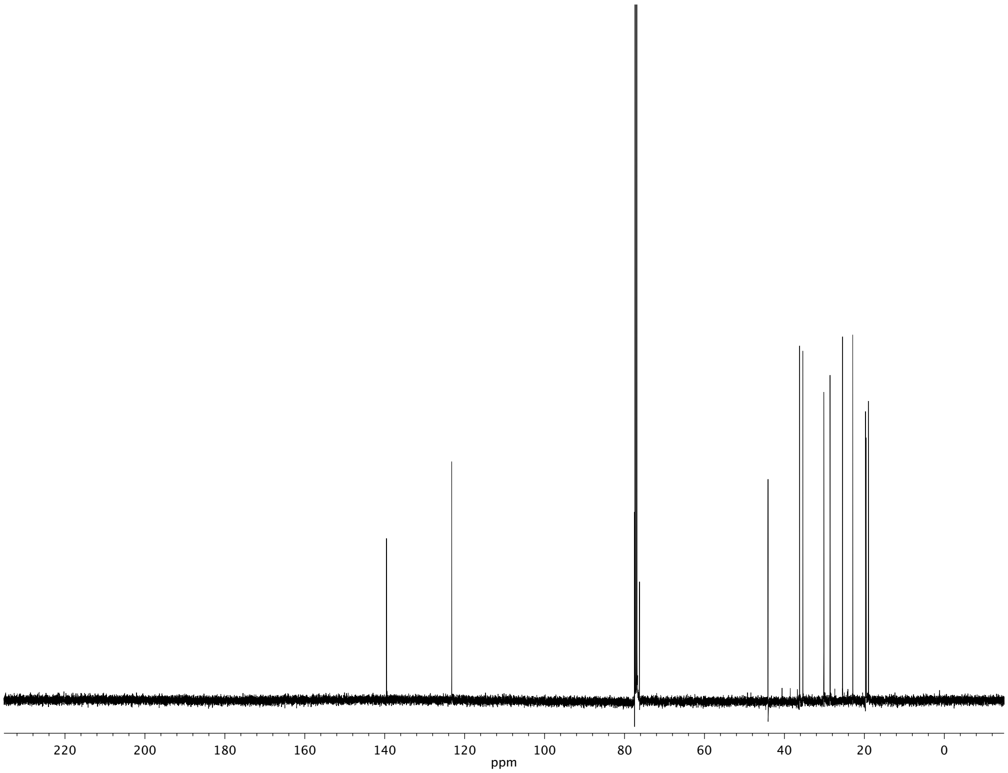


Figure SI-15.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **SI-2**.

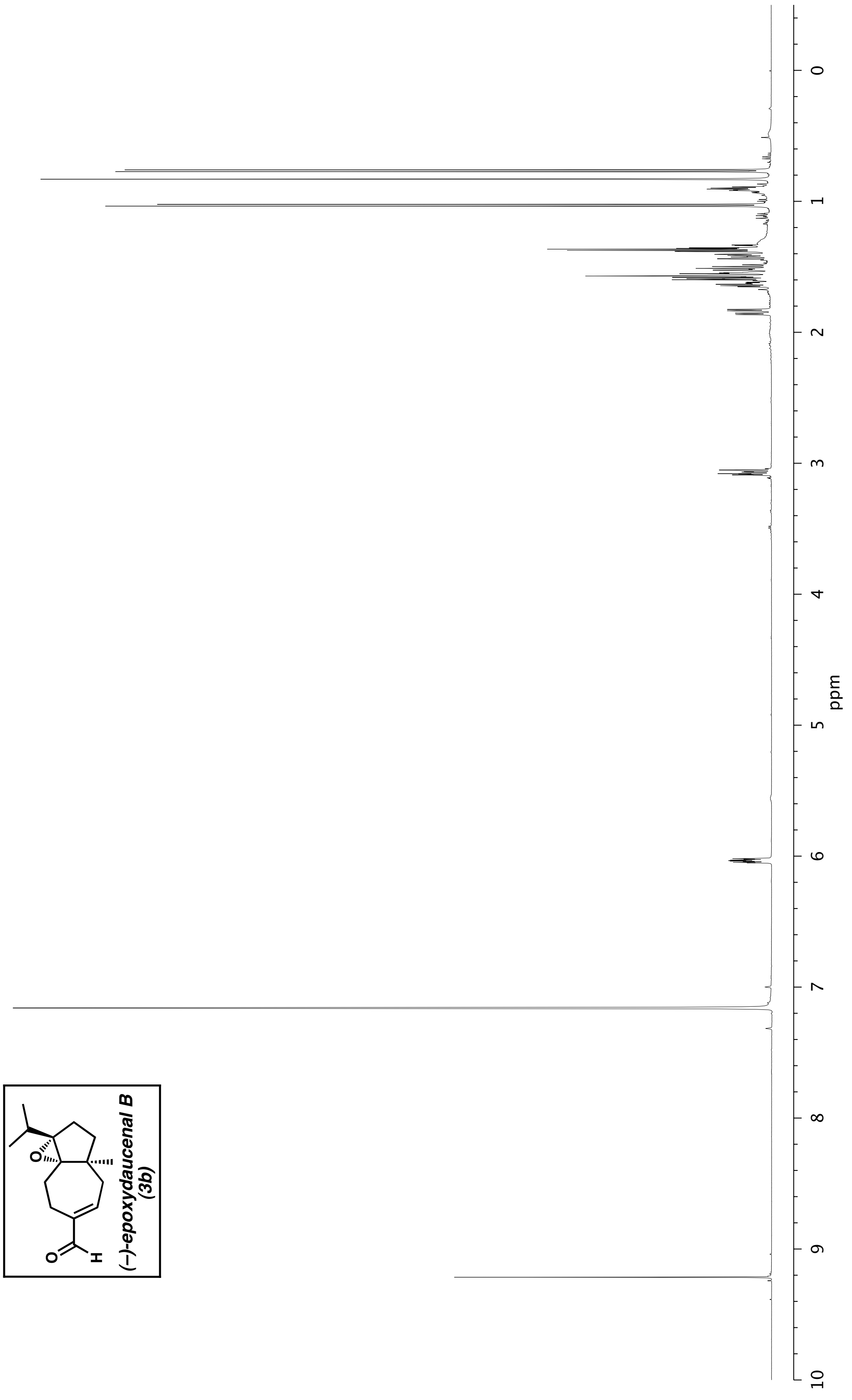


Figure SI-16.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **3b**.

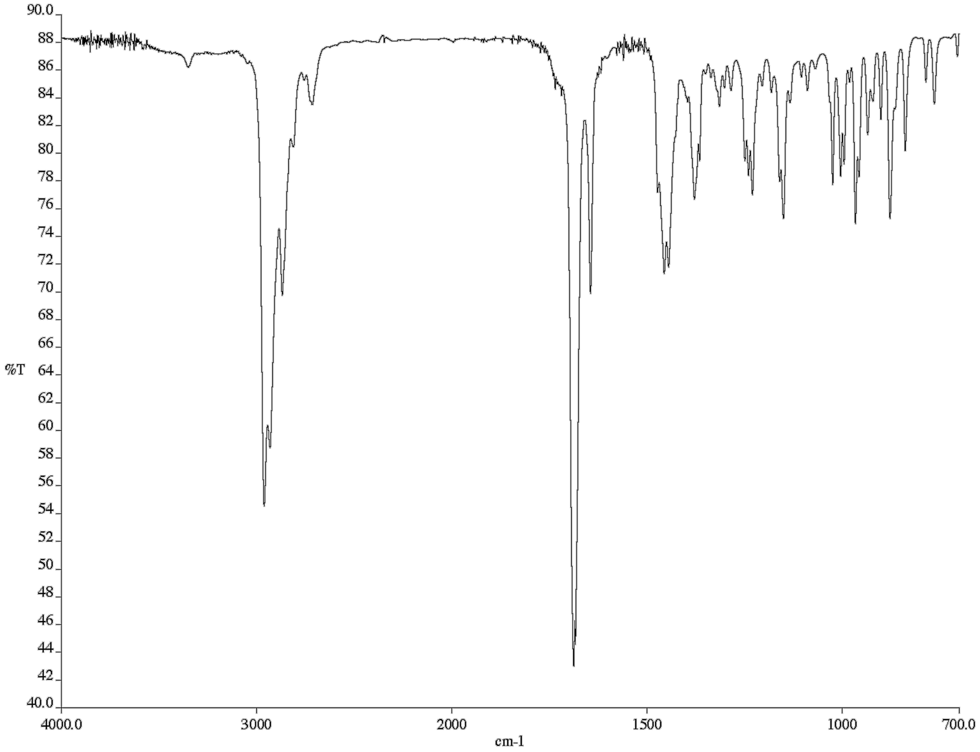


Figure SI-16.2. Infrared spectrum (thin film/NaCl) of compound **3b**.

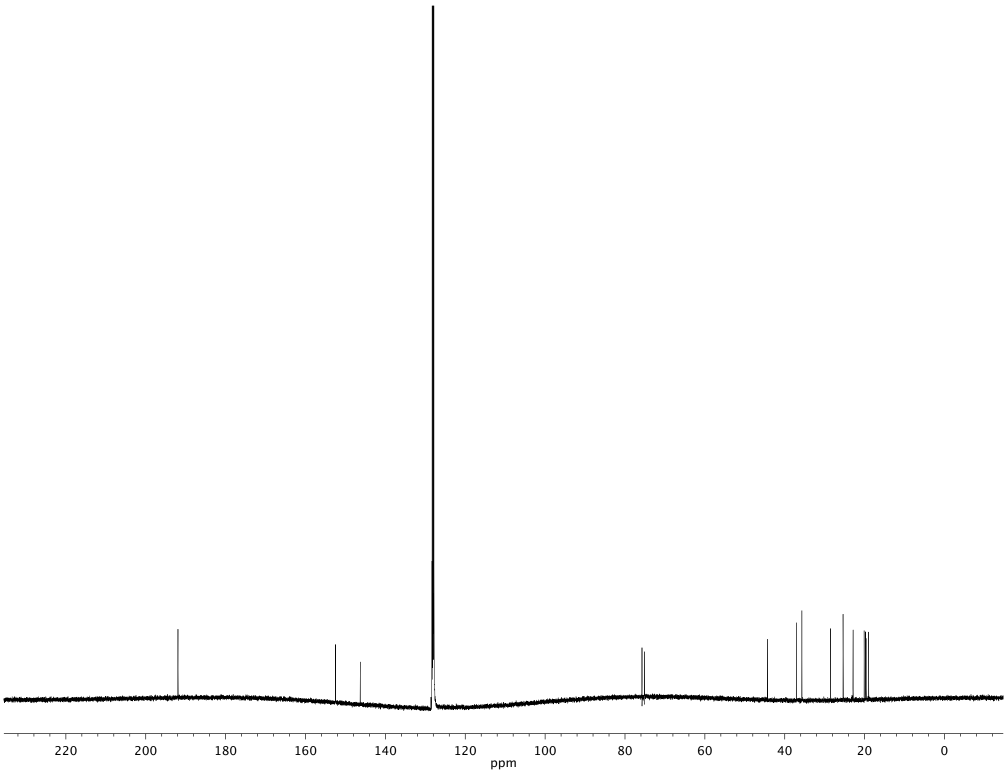


Figure SI-16.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **3b**.

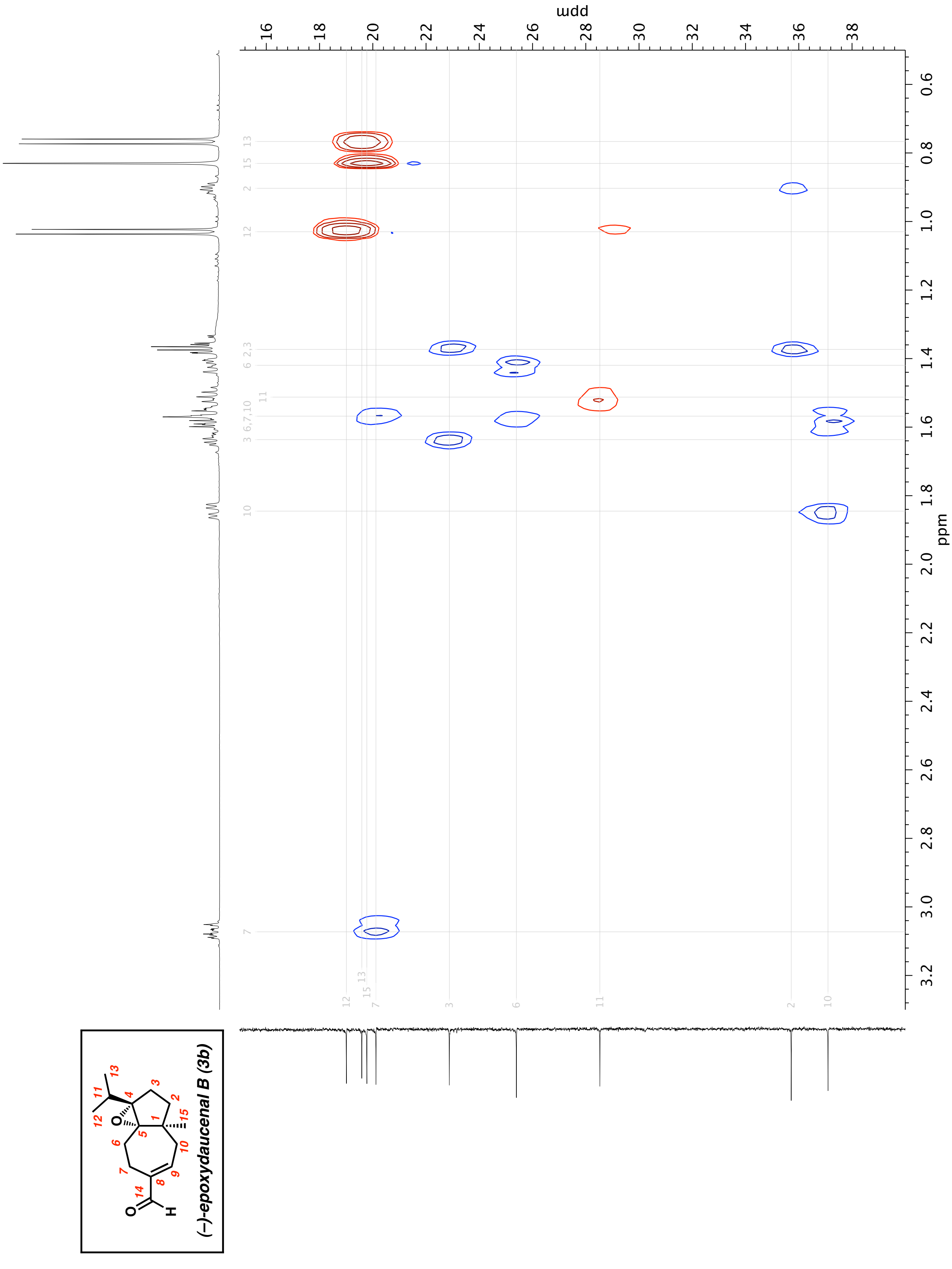


Figure SI-16.4. HSQC NMR (400 MHz, C_6D_6) of compound **3b**.

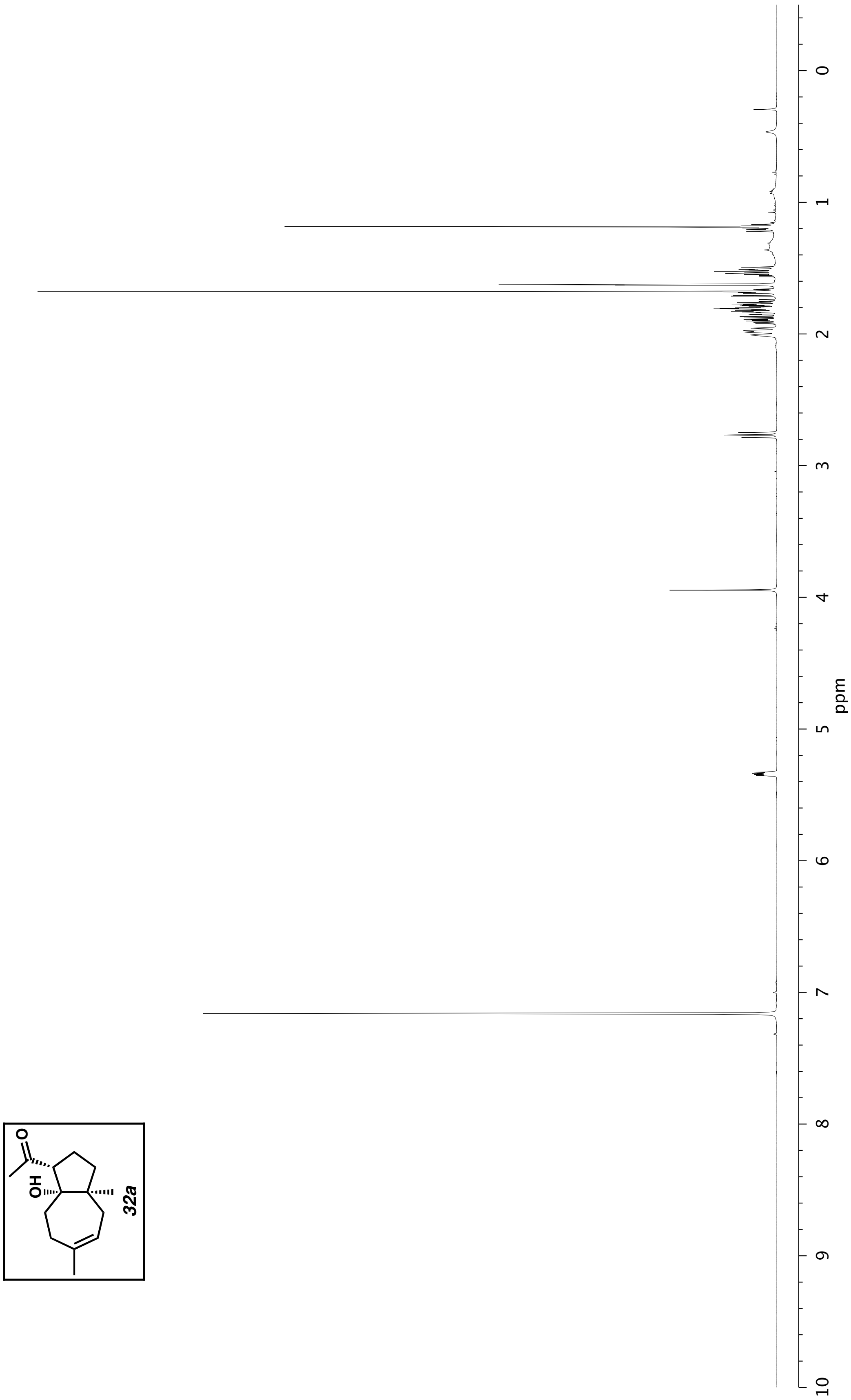


Figure SI-17.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **32a**.

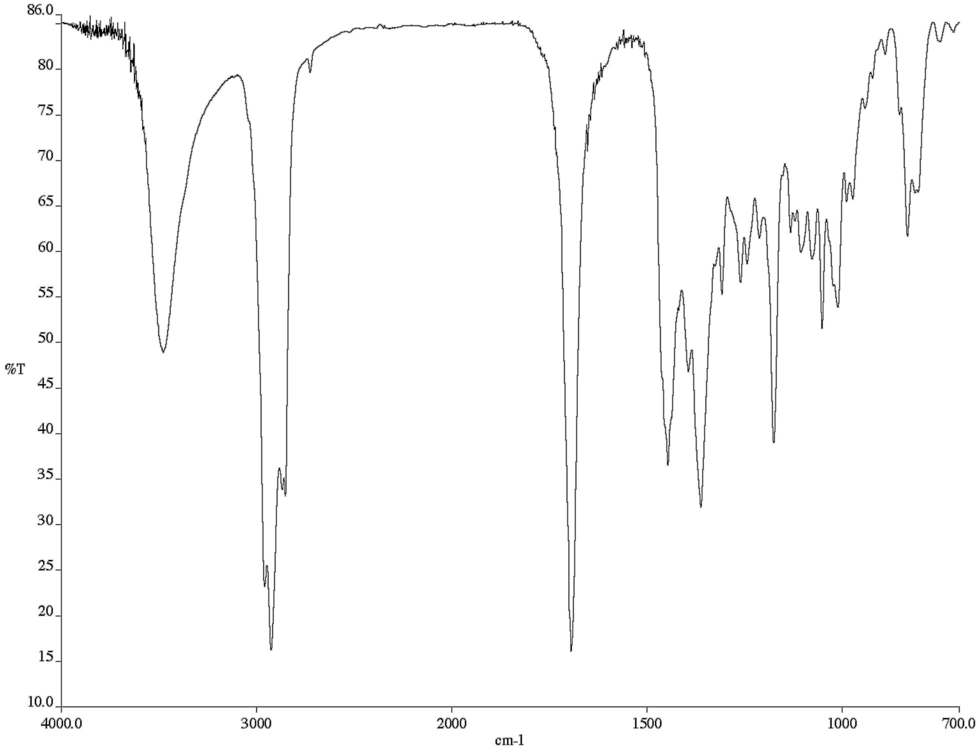


Figure SI-17.2. Infrared spectrum (thin film/NaCl) of compound **32a**.

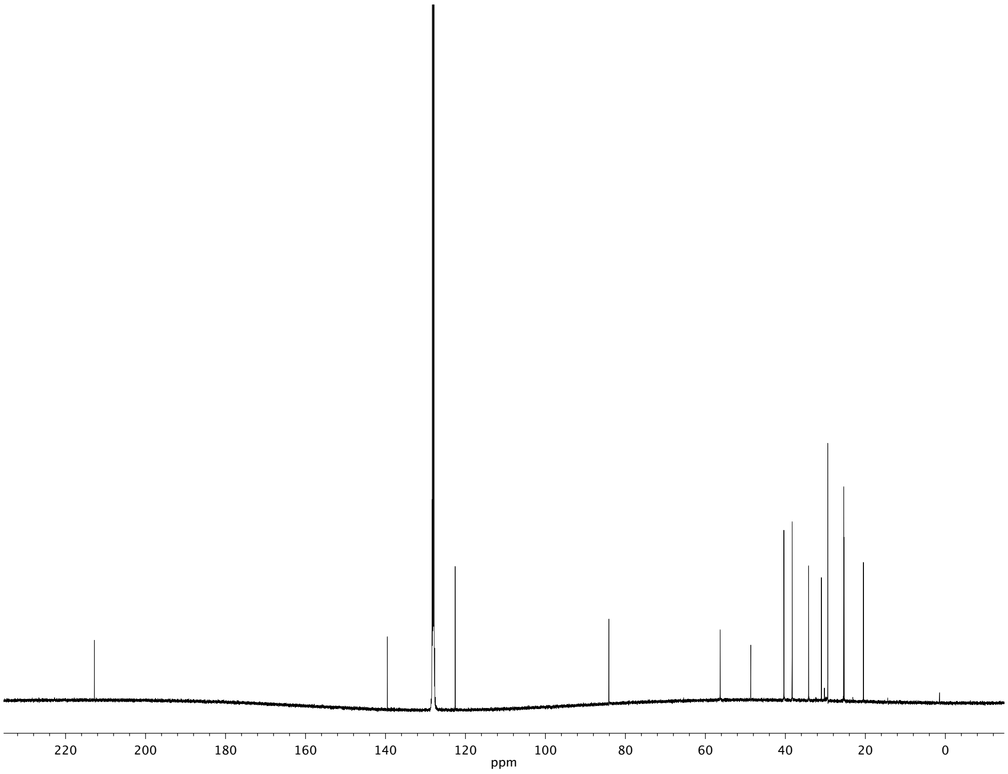


Figure SI-17.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **32a**.

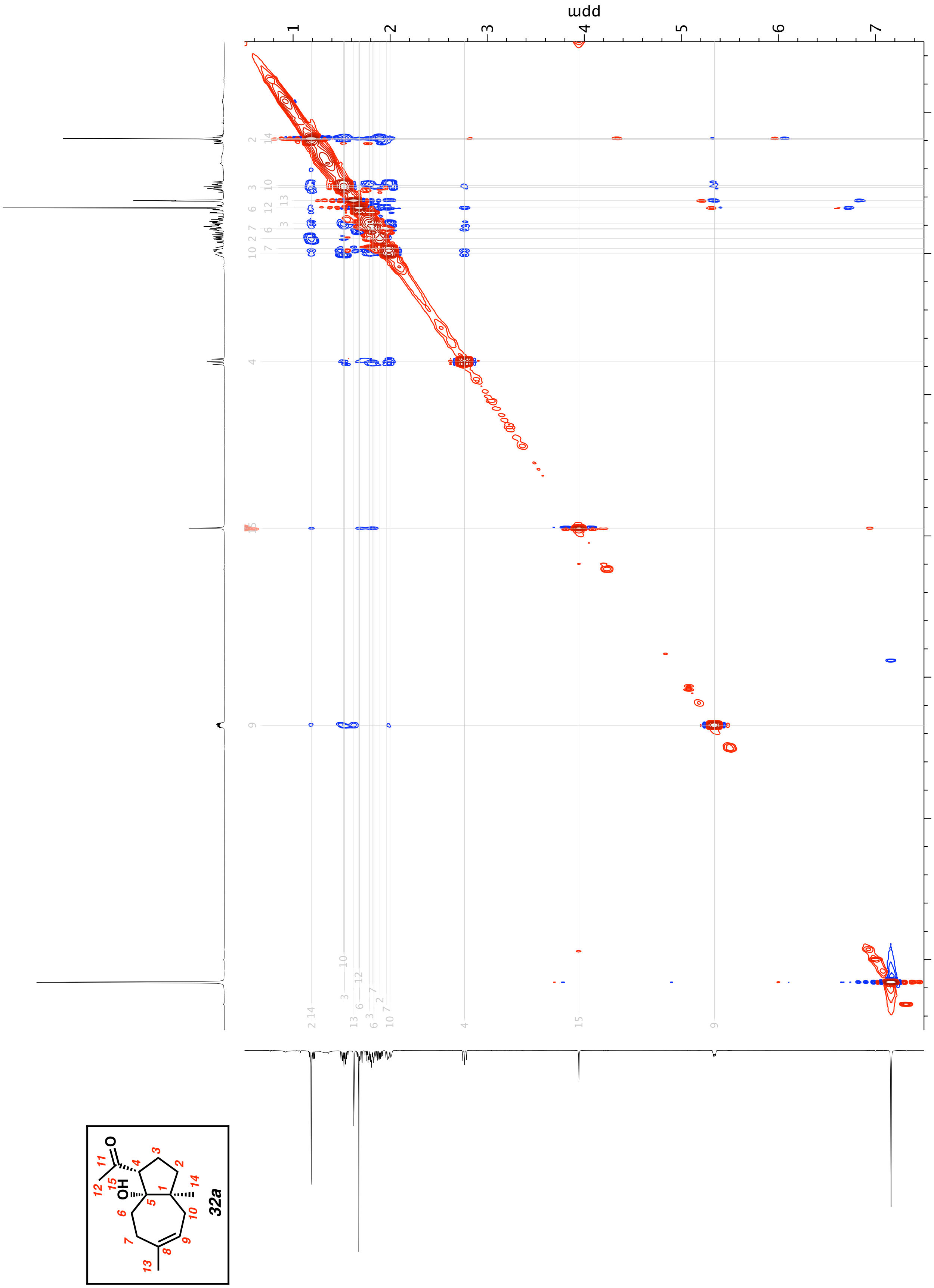


Figure SI-17.4. NOESY NMR (500 MHz, C_6D_6) of compound **32a**.

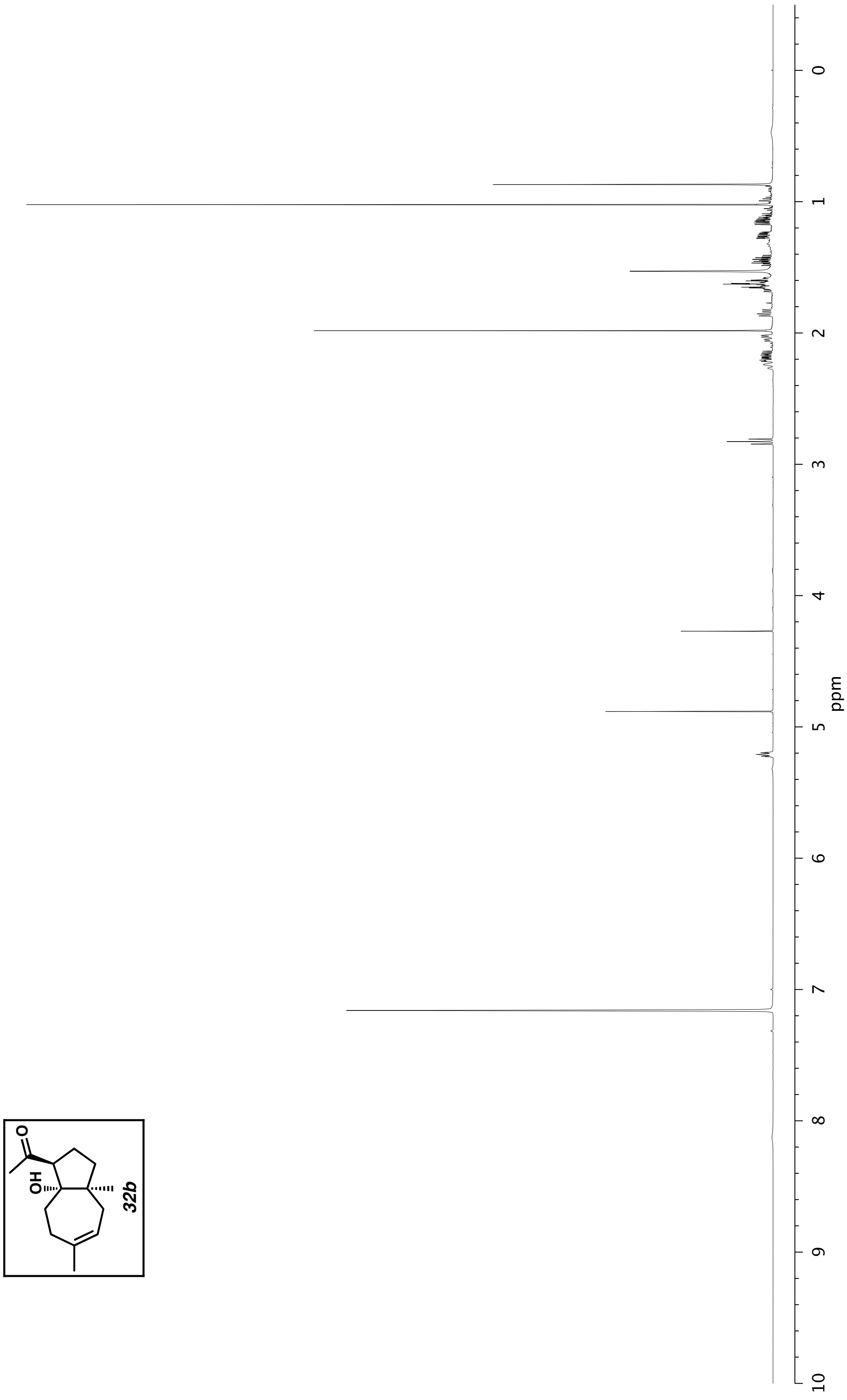


Figure SI-18.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **32b**.

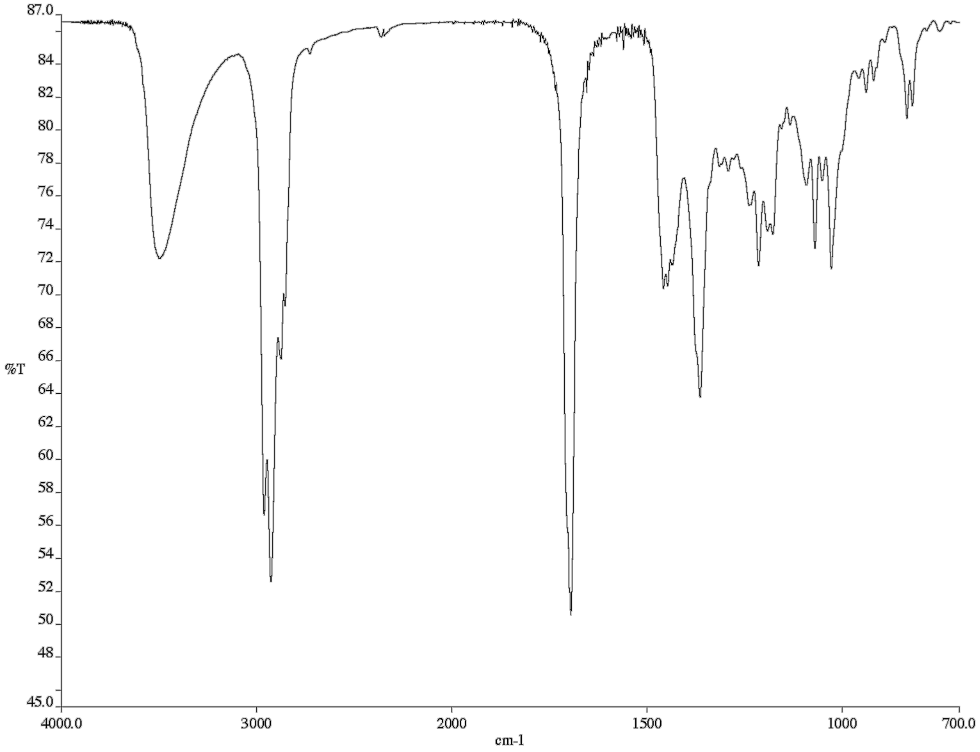


Figure SI-18.2. Infrared spectrum (thin film/NaCl) of compound **32b**.

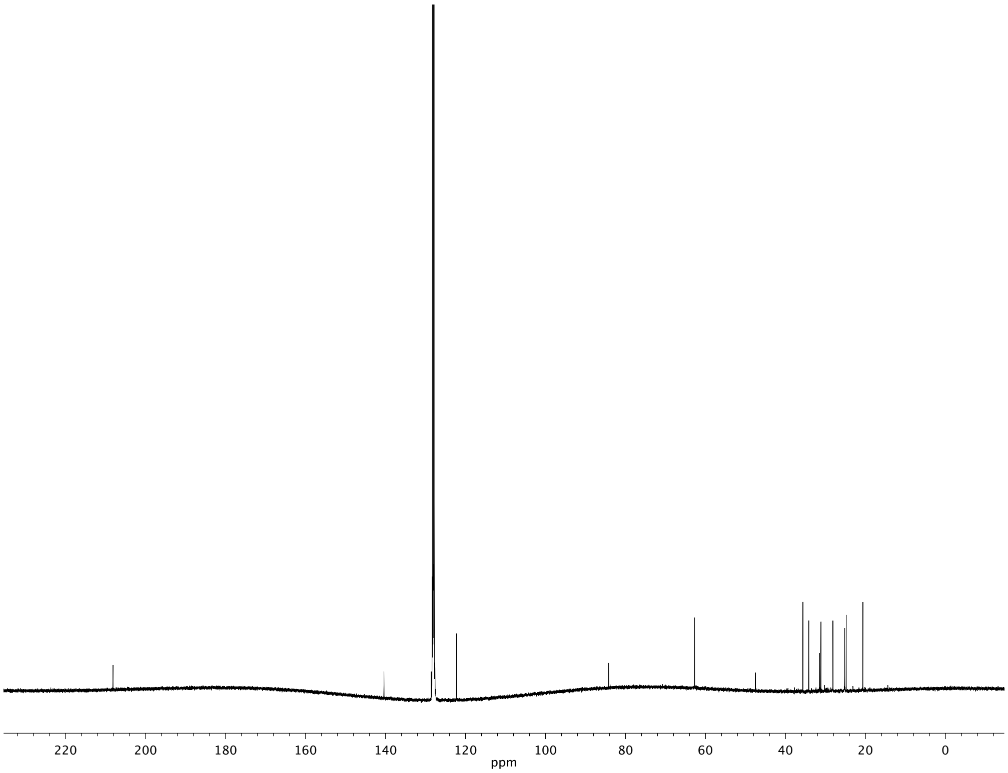


Figure SI-18.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **32b**.

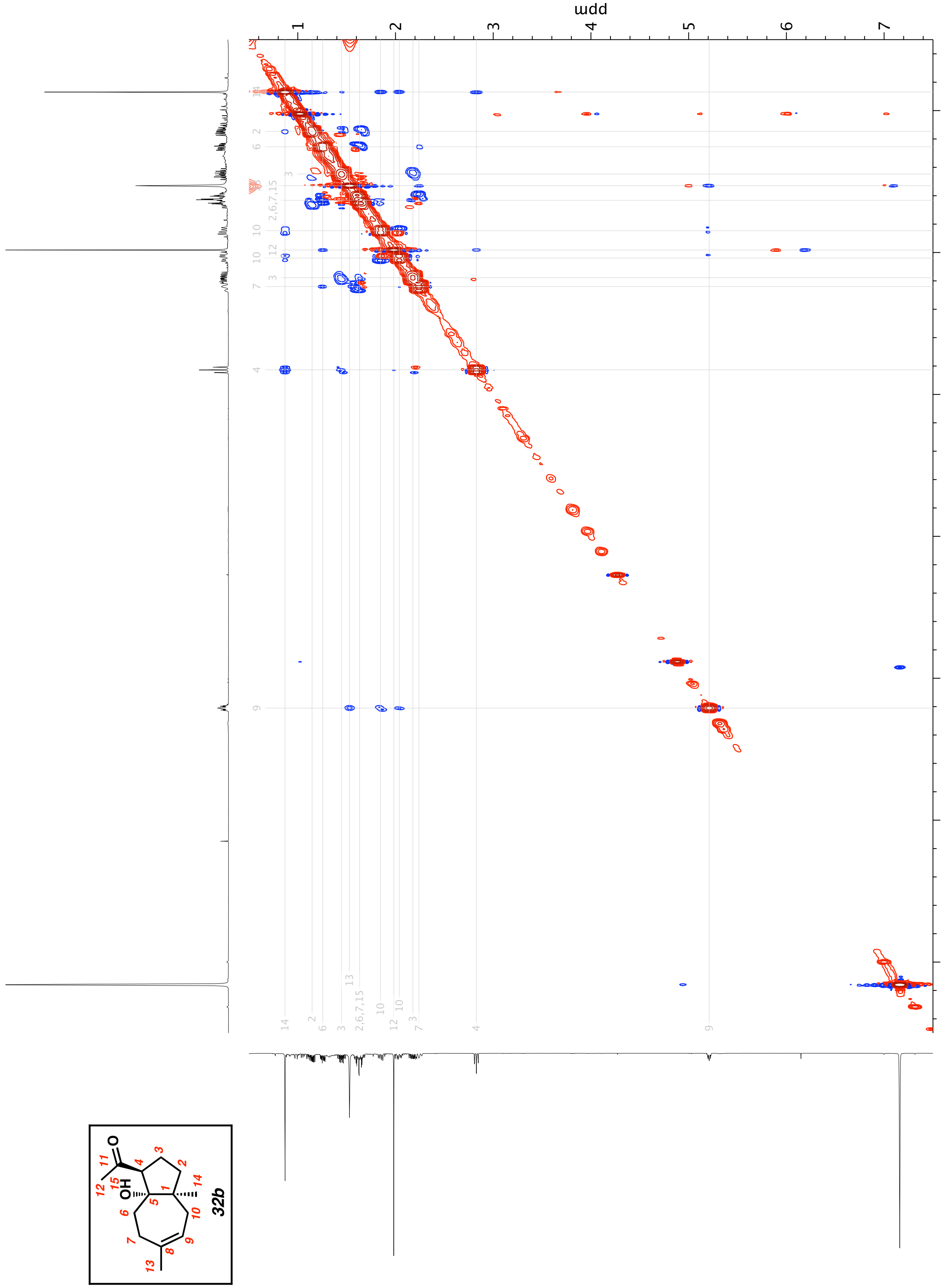


Figure SI-18.4. NOESY NMR (500 MHz, C_6D_6) of compound **32b**.

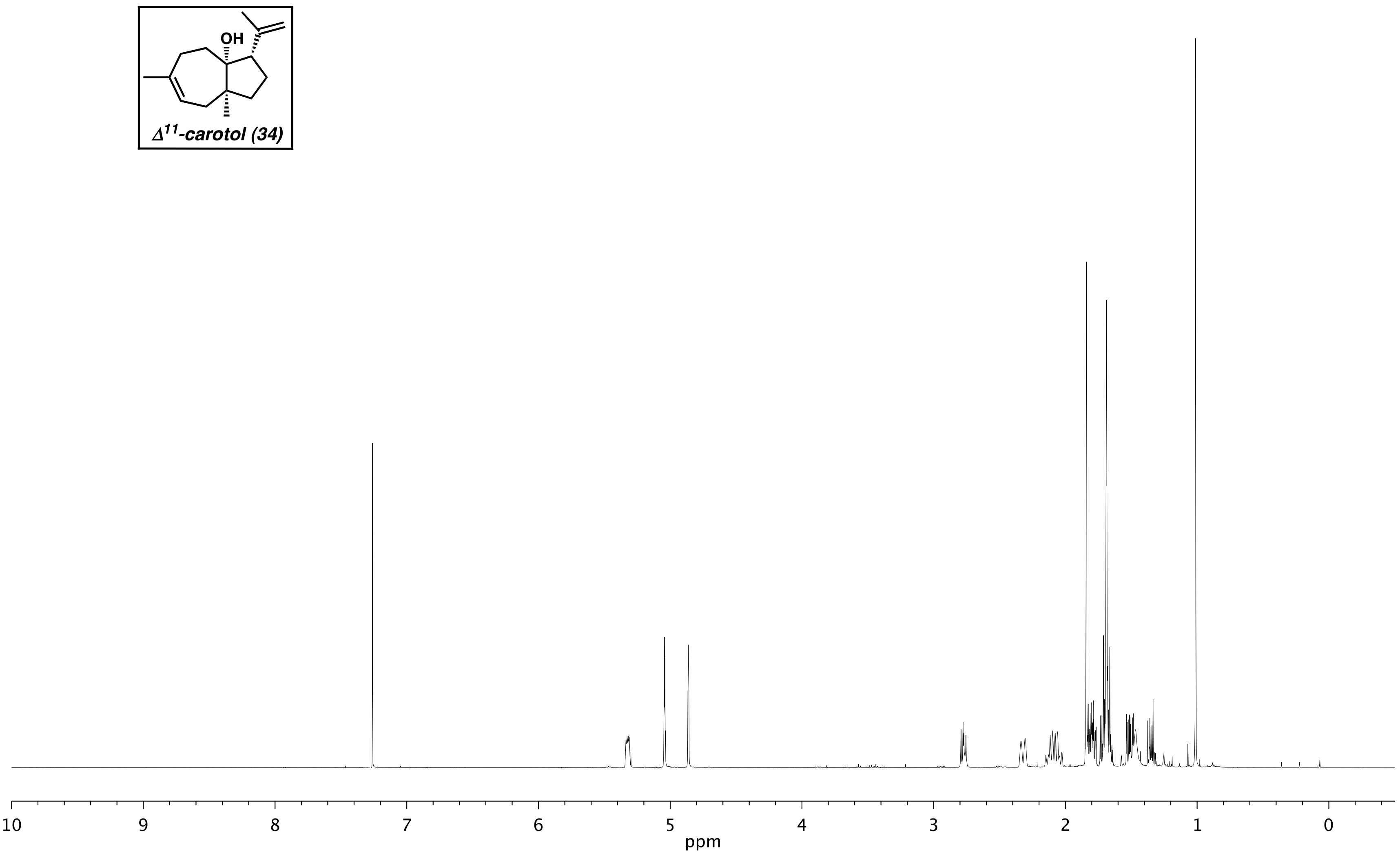


Figure SI-19.1. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **34**.

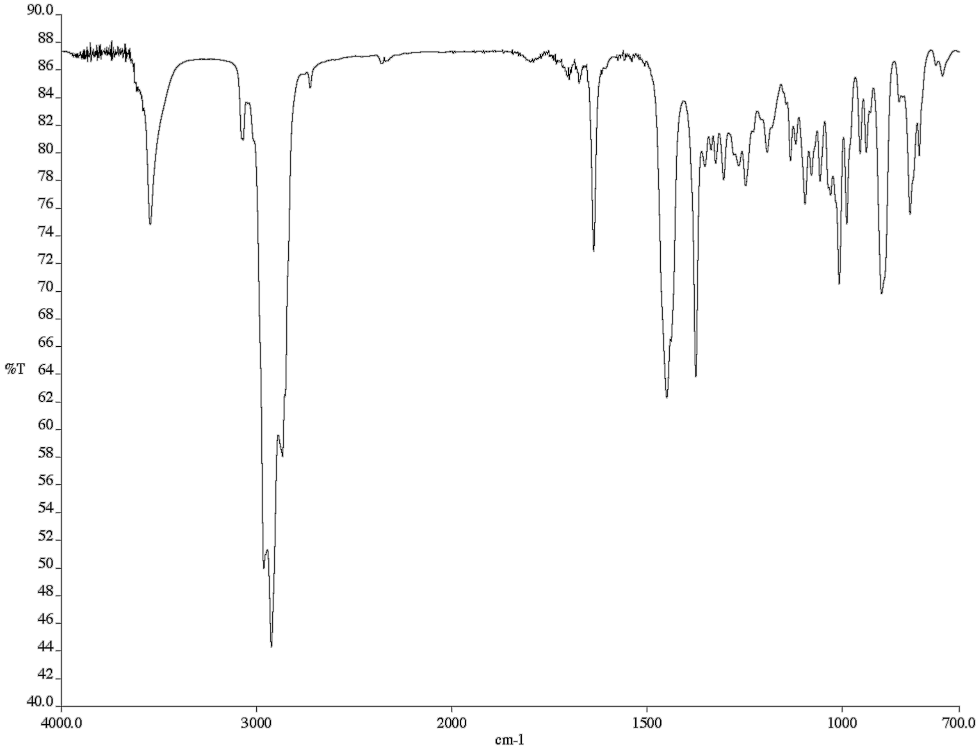


Figure SI-19.2. Infrared spectrum (thin film/NaCl) of compound **34**.

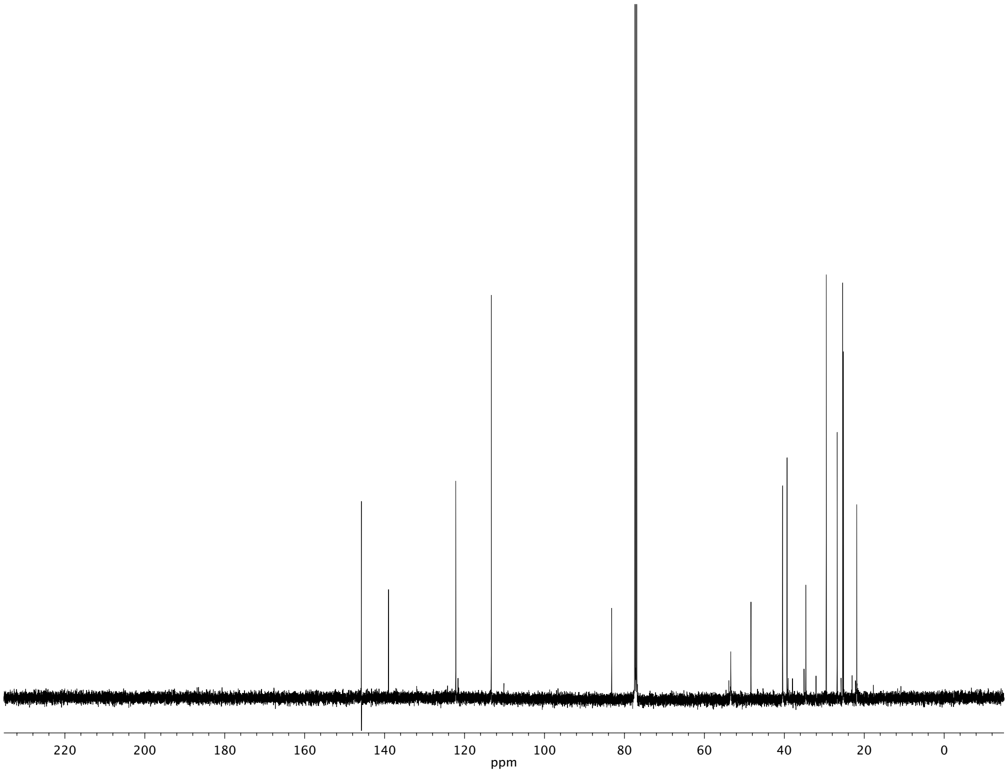


Figure SI-19.3. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **34**.

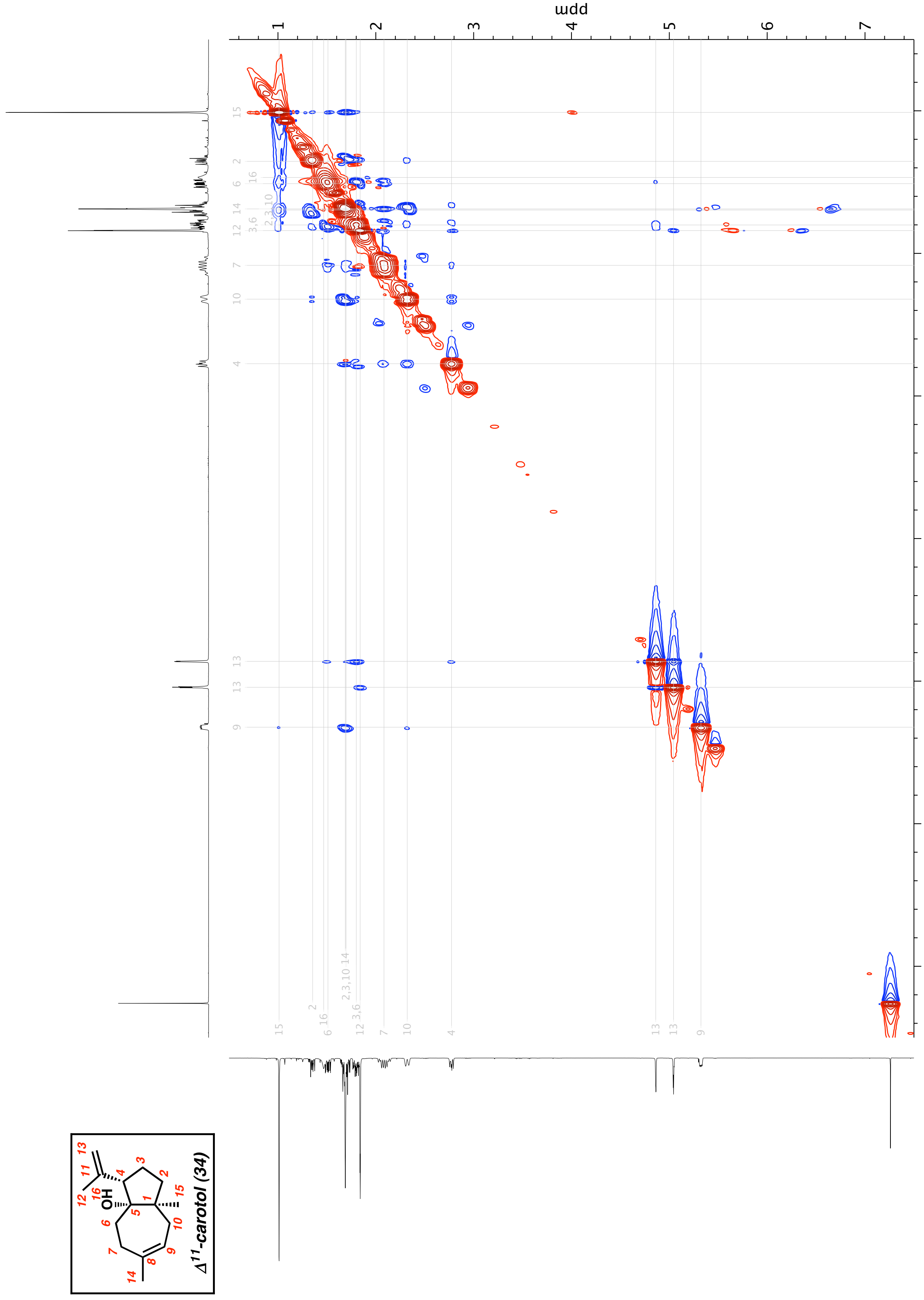


Figure SI-19.4. NOESY NMR (500 MHz, $CDCl_3$) of compound **34**.

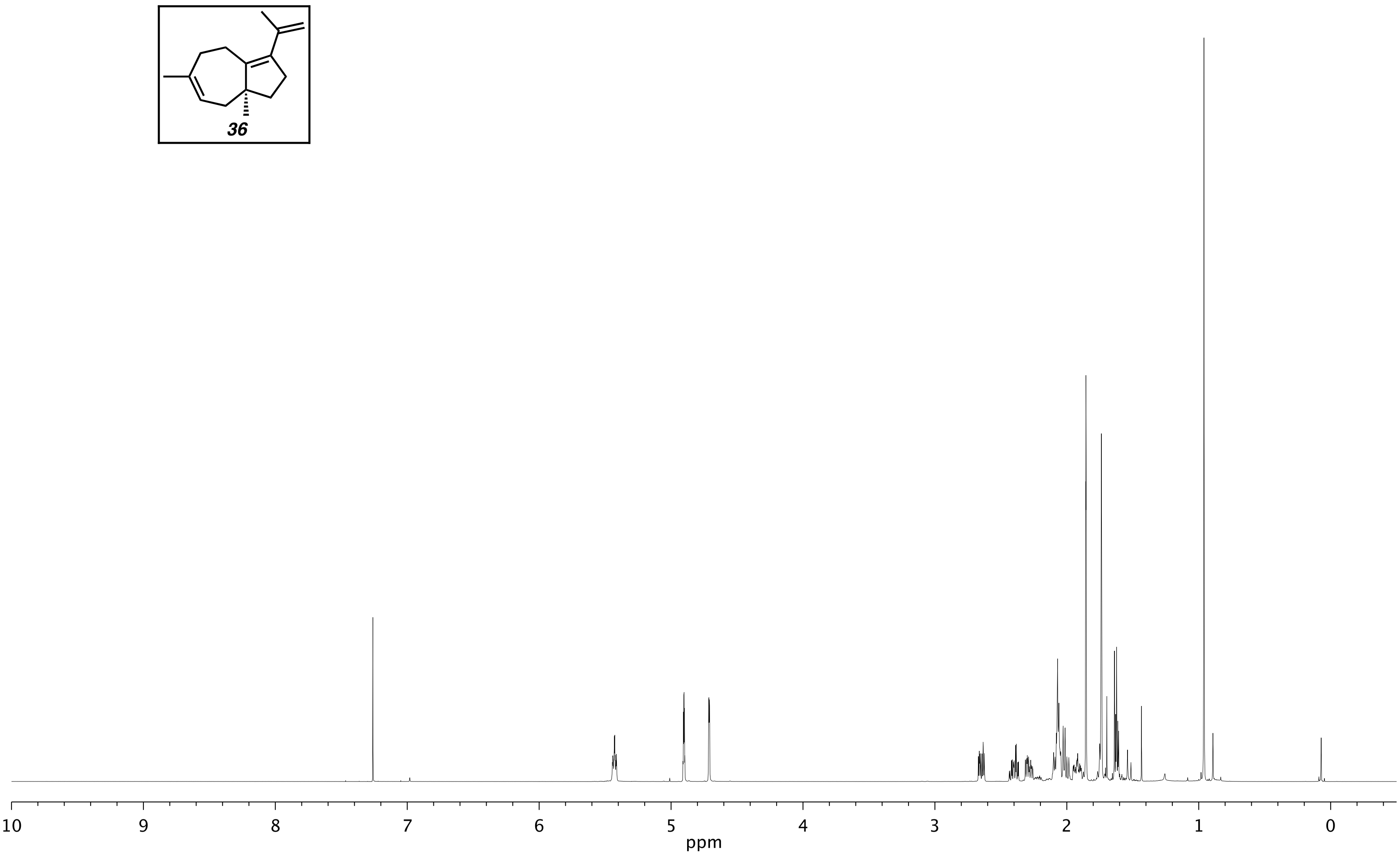


Figure SI-20.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **36**.

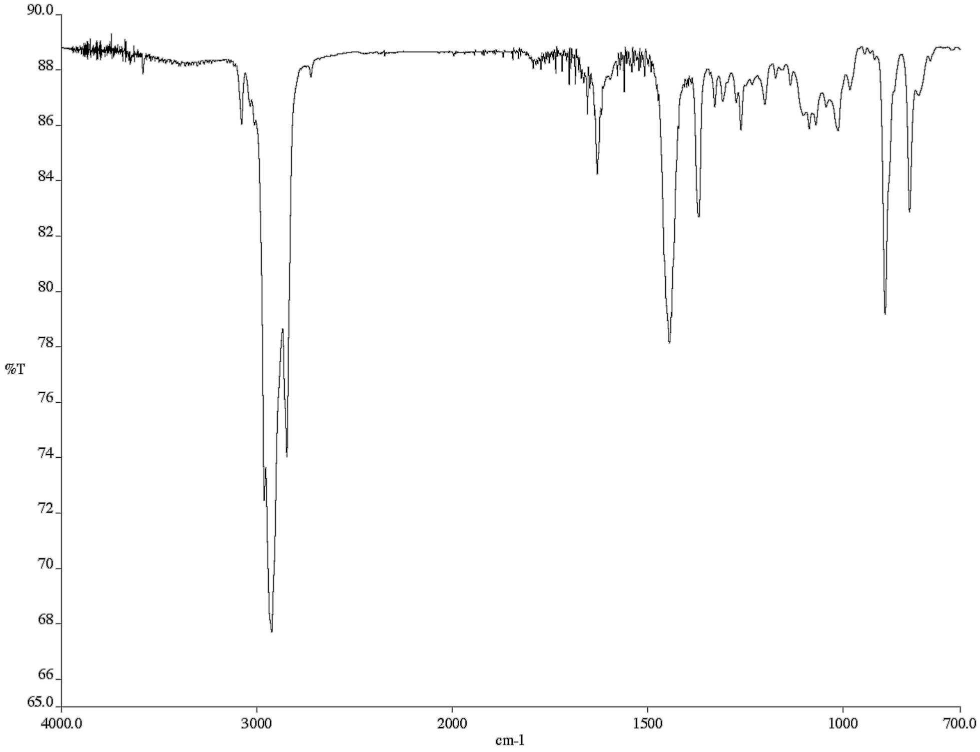


Figure SI-20.2. Infrared spectrum (thin film/NaCl) of compound **36**.

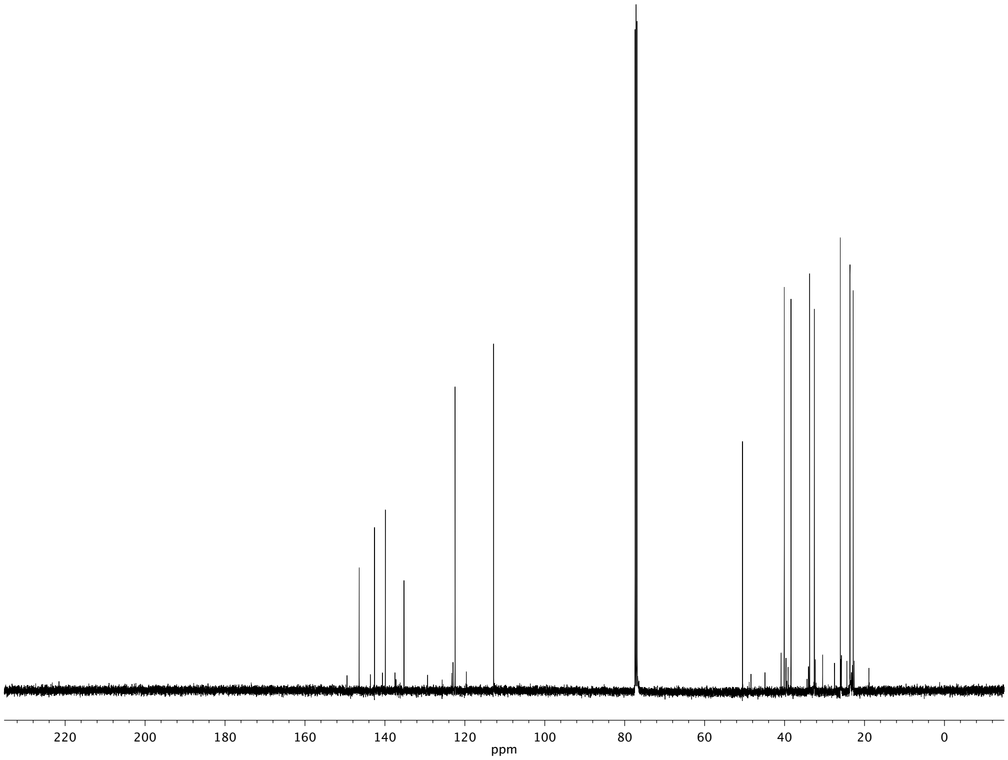


Figure SI-20.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **36**.

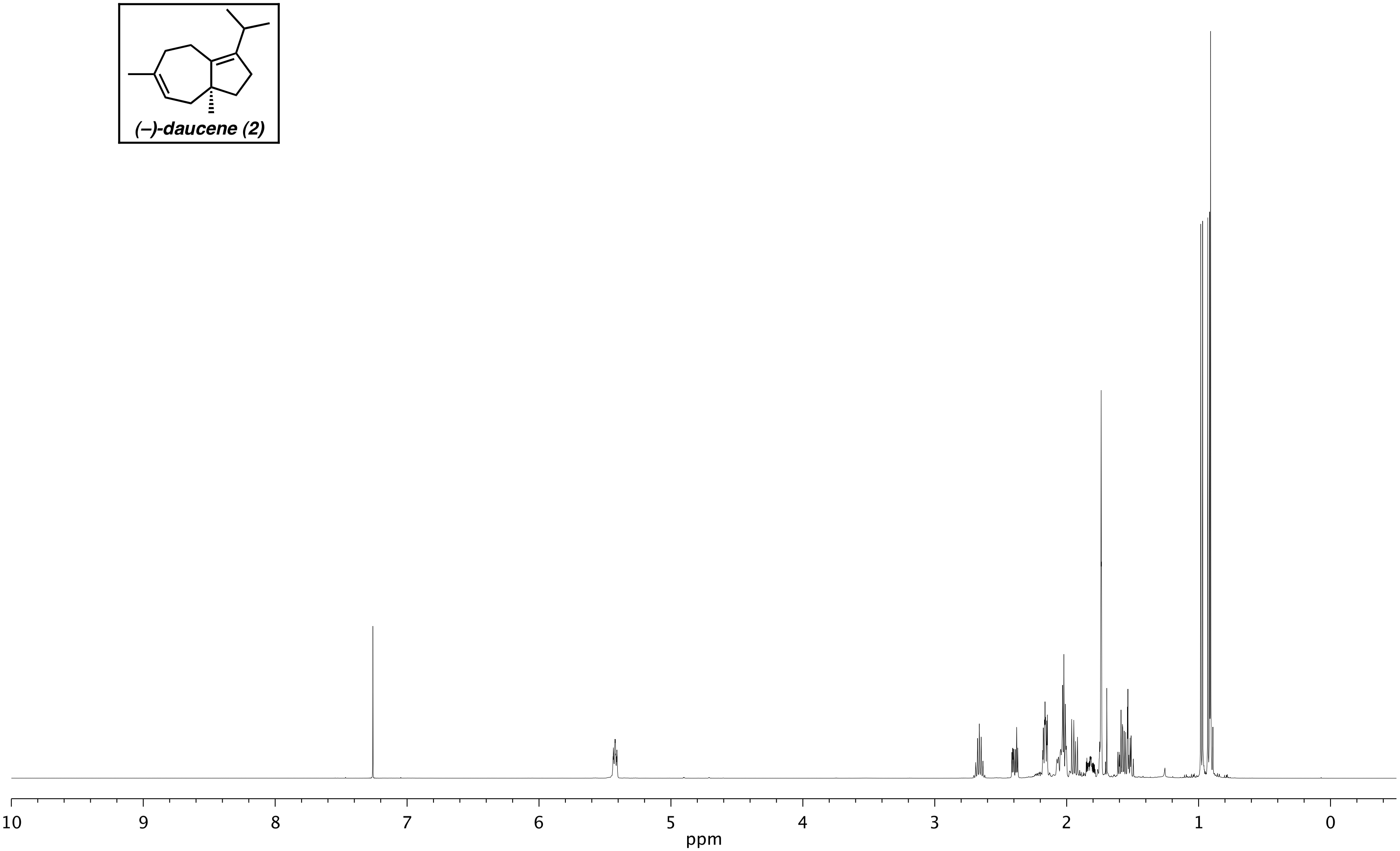


Figure SI-21.1. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **2**.

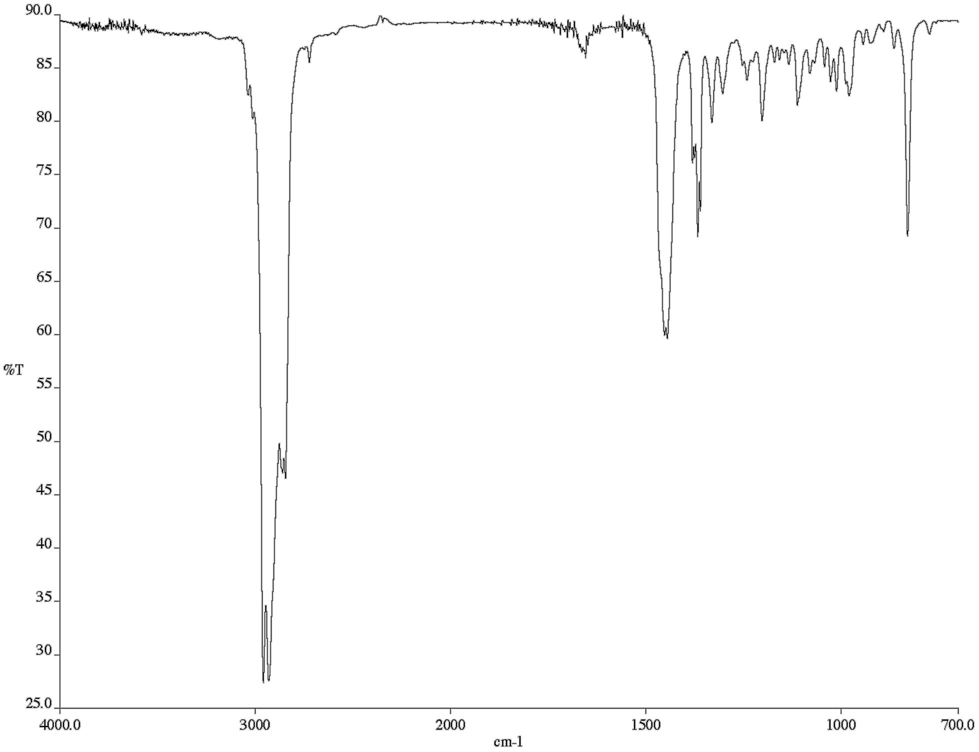


Figure SI-21.2. Infrared spectrum (thin film/NaCl) of compound **2**.

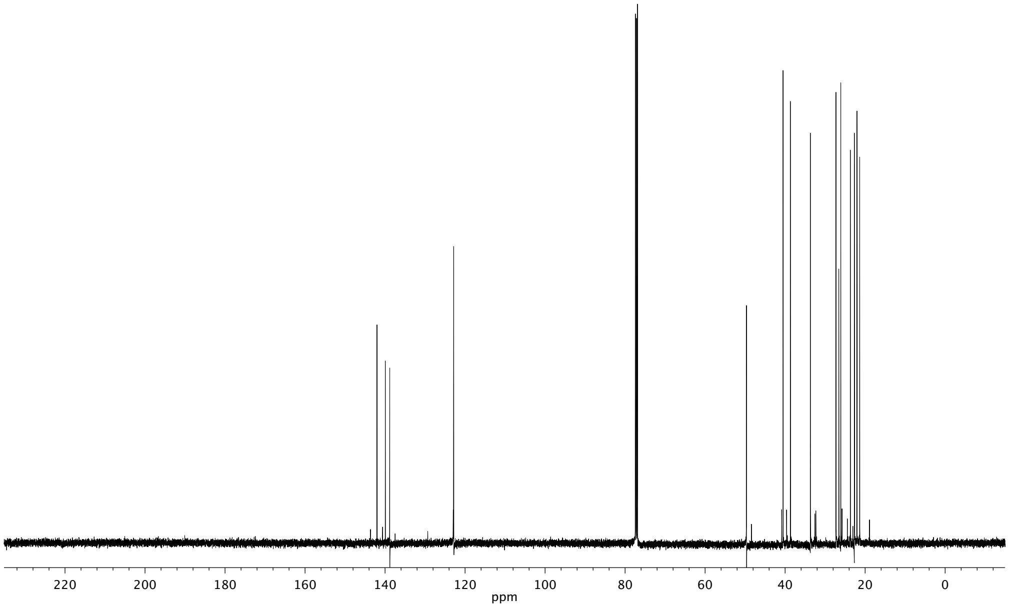


Figure SI-21.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **2**.

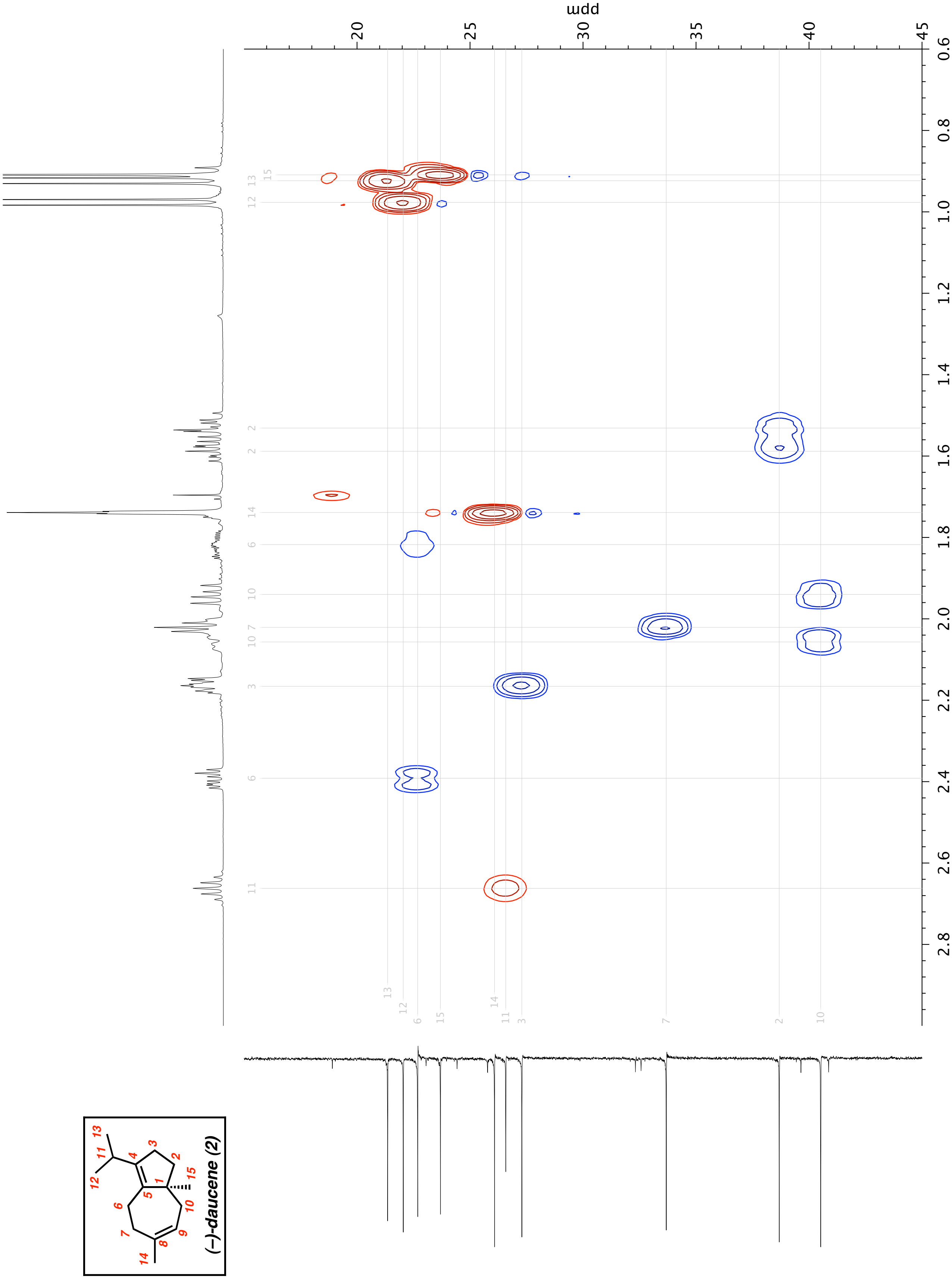


Figure SI-21.4. HSQC NMR (500 MHz, $CDCl_3$) of compound **2**.

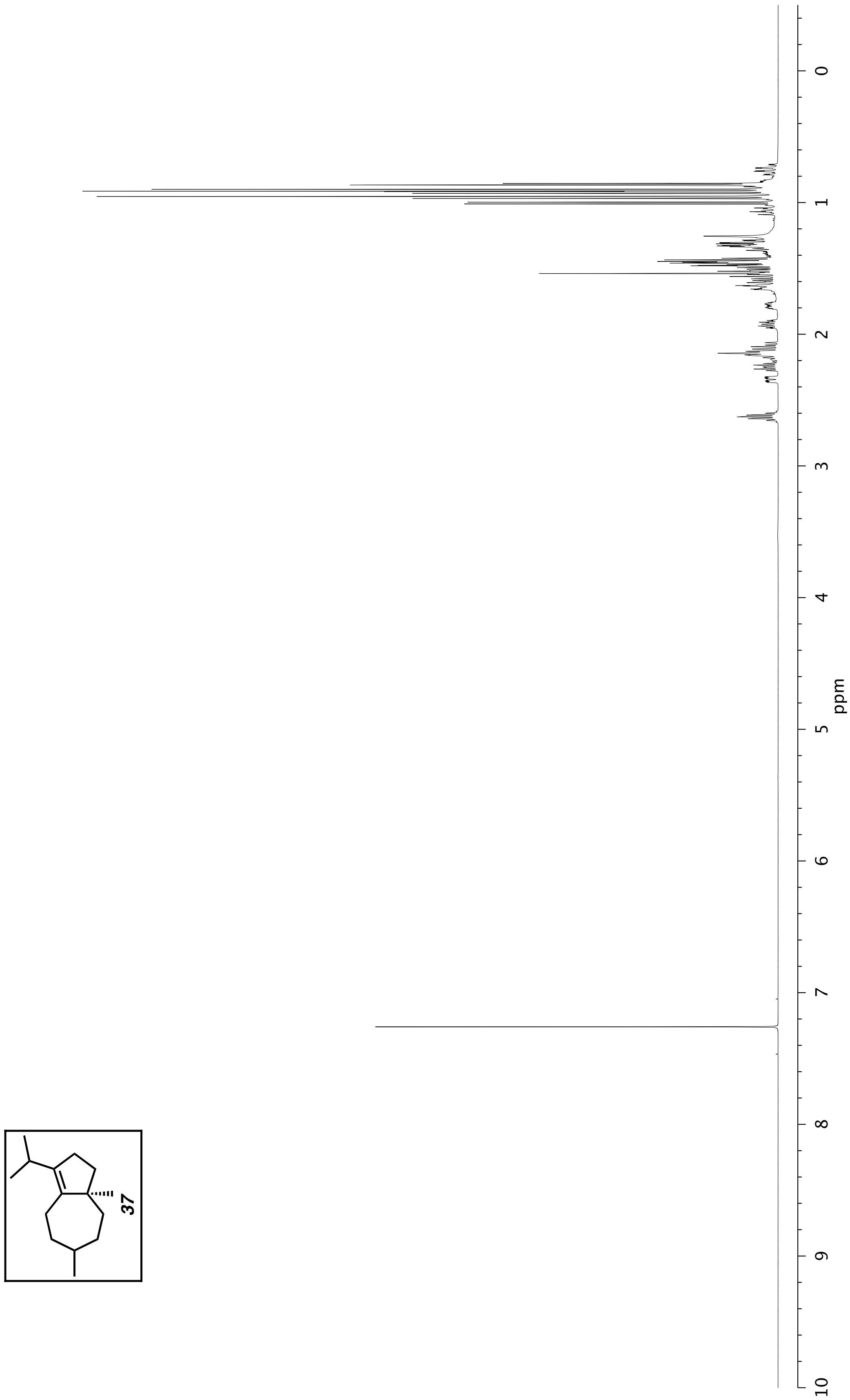


Figure SI-22.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **37**.

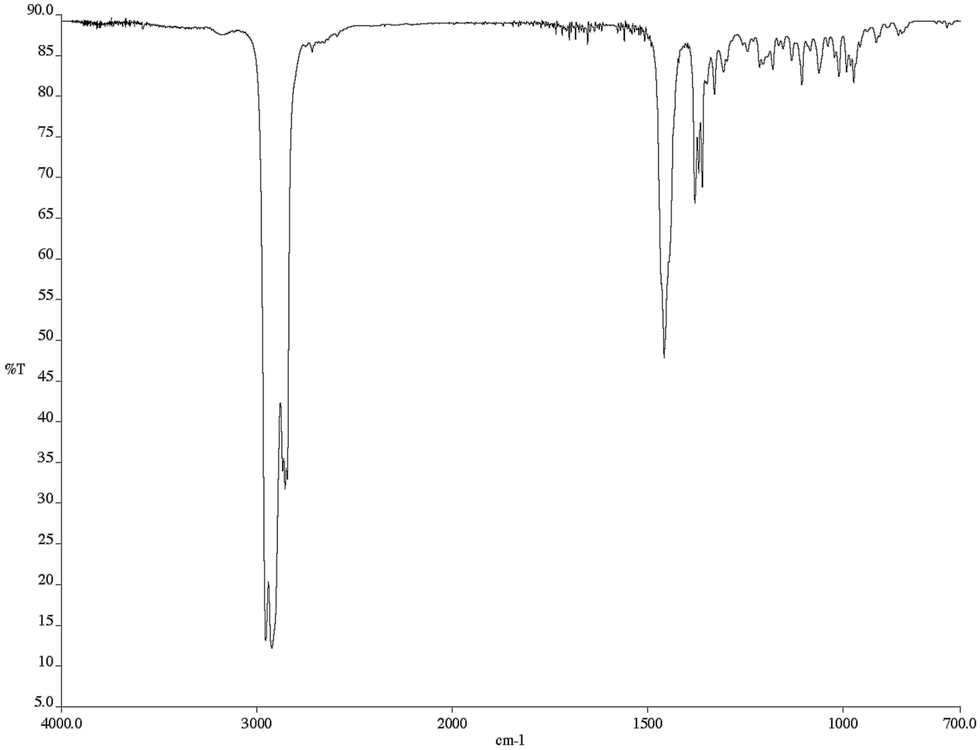


Figure SI-22.2. Infrared spectrum (thin film/NaCl) of compound **37**.

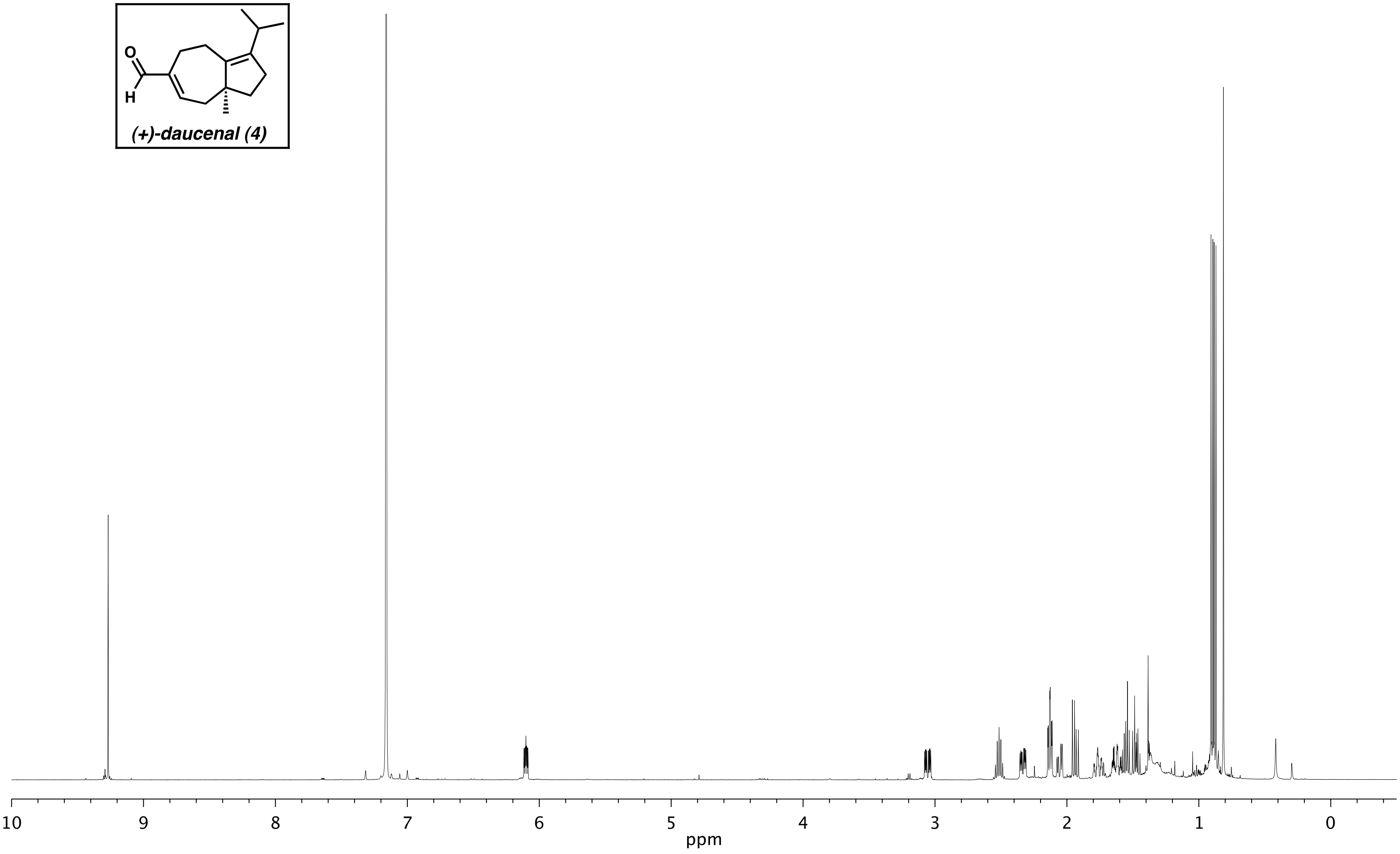


Figure SI-23.1. ^{1}H NMR (500 MHz, C_6D_6) of compound **4**.

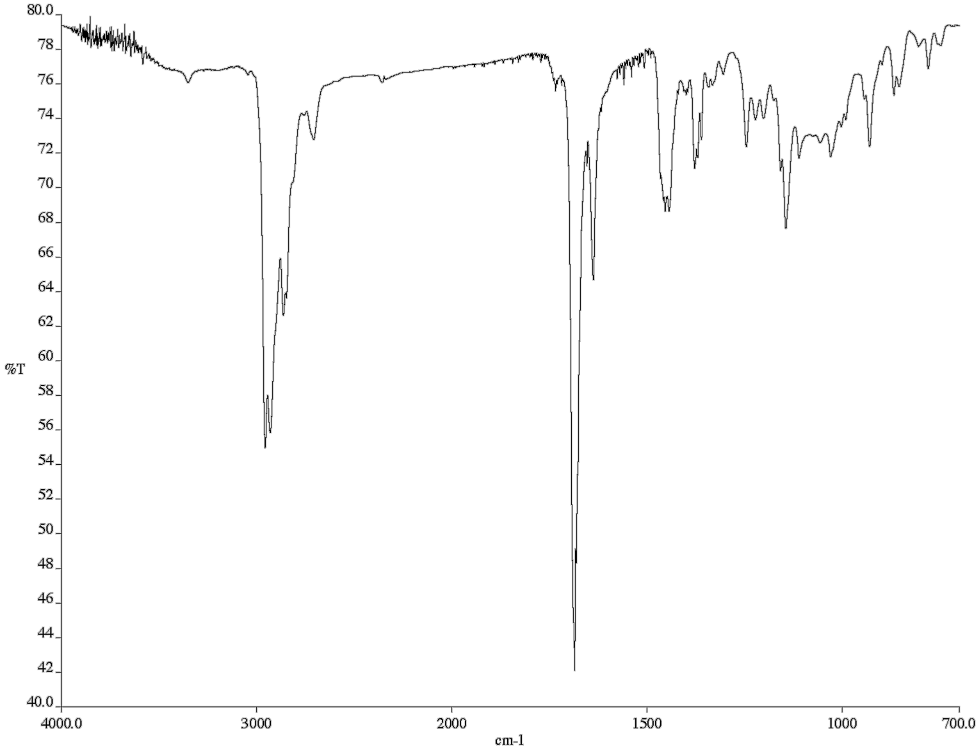


Figure SI-23.2. Infrared spectrum (thin film/NaCl) of compound **4**.

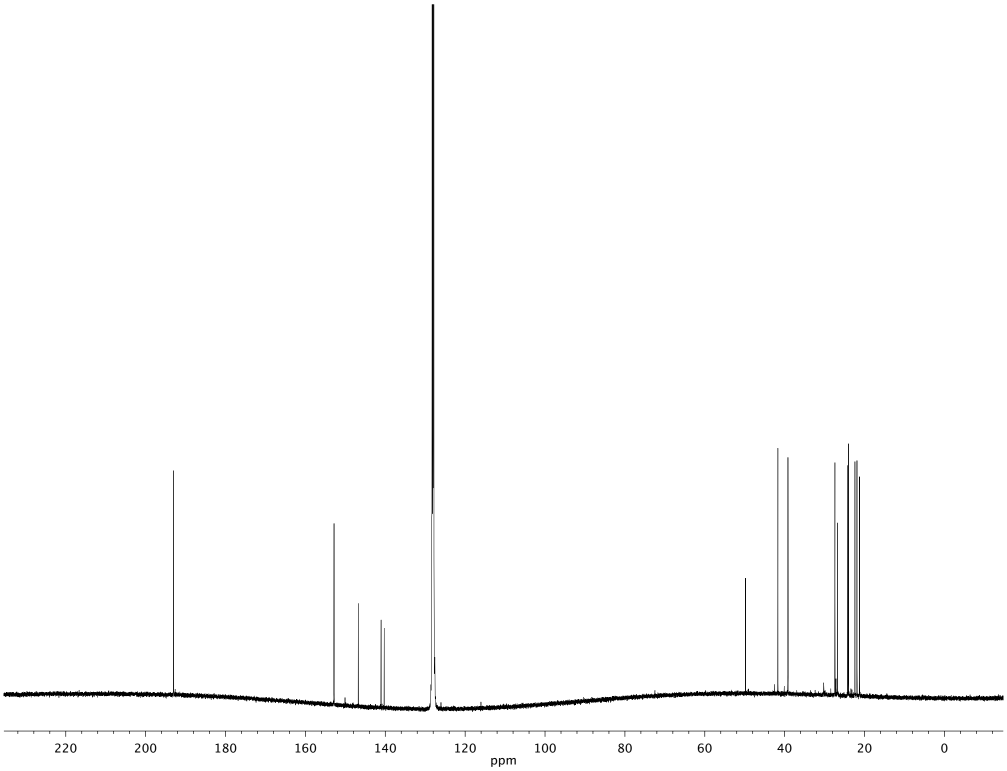
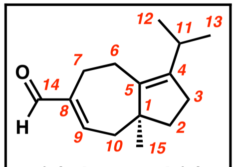


Figure SI-23.3. ^{13}C NMR (125 MHz, C_6D_6) of compound **4**.



(+)-daucenal (4)

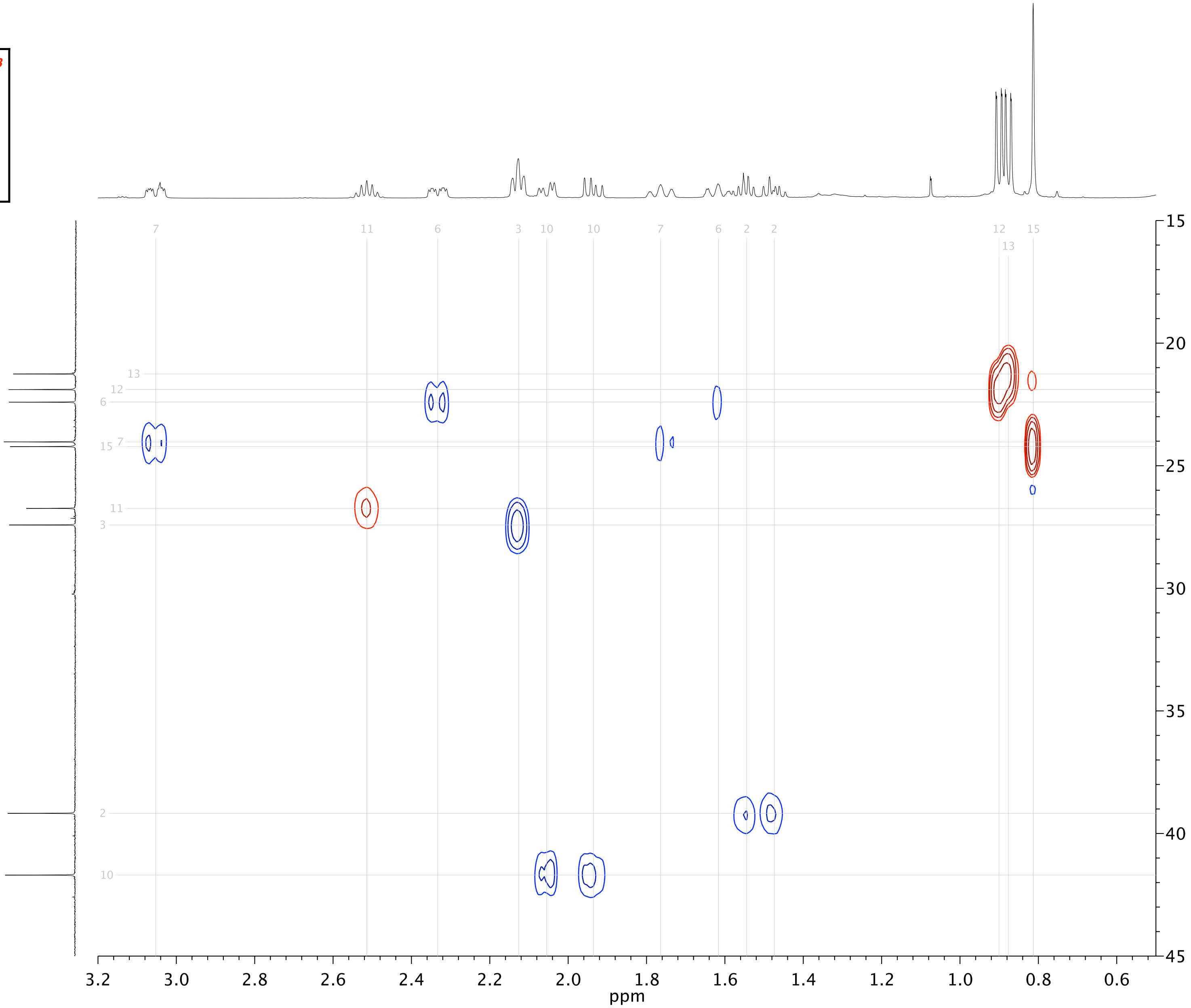


Figure SI-23.4. HSQC NMR (500 MHz, C_6D_6) of compound **4**.

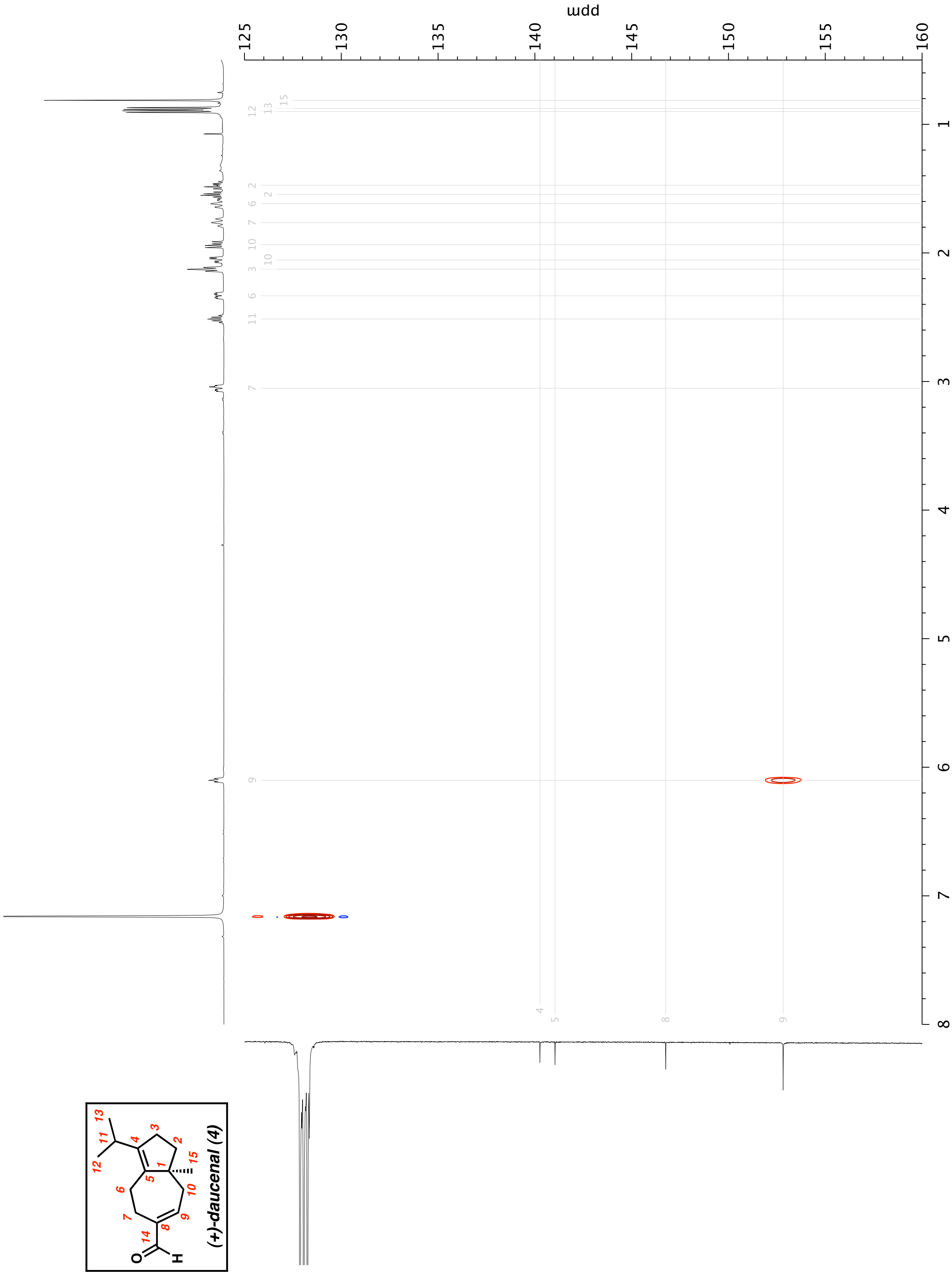


Figure SI-23.5. HSQC NMR (500 MHz, C_6D_6) of compound **4**.

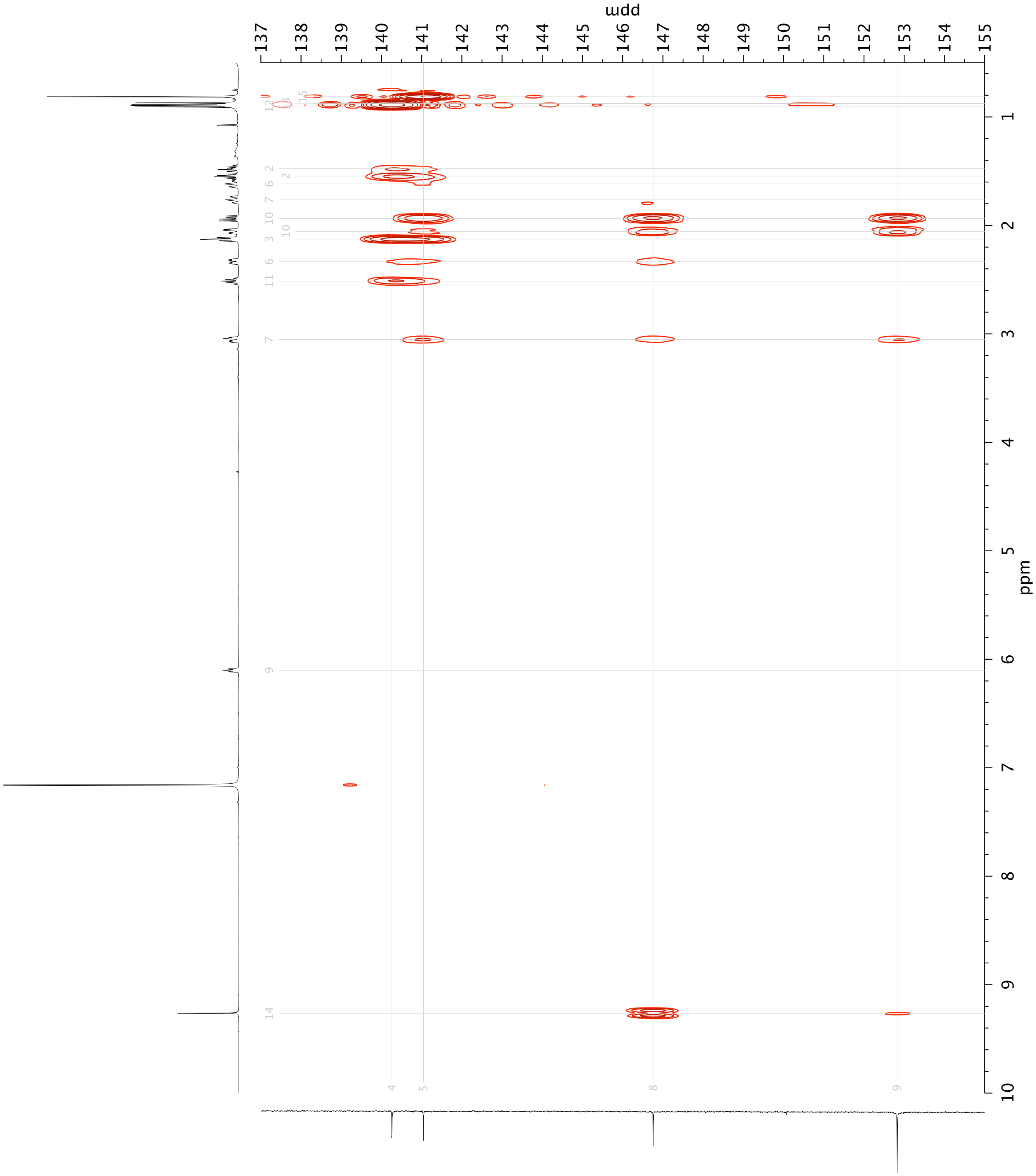
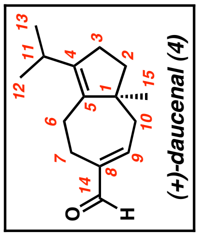


Figure SI-23.6. HMBC NMR (500 MHz, C_6D_6) of compound **4**.



(+)-daucenal (4)

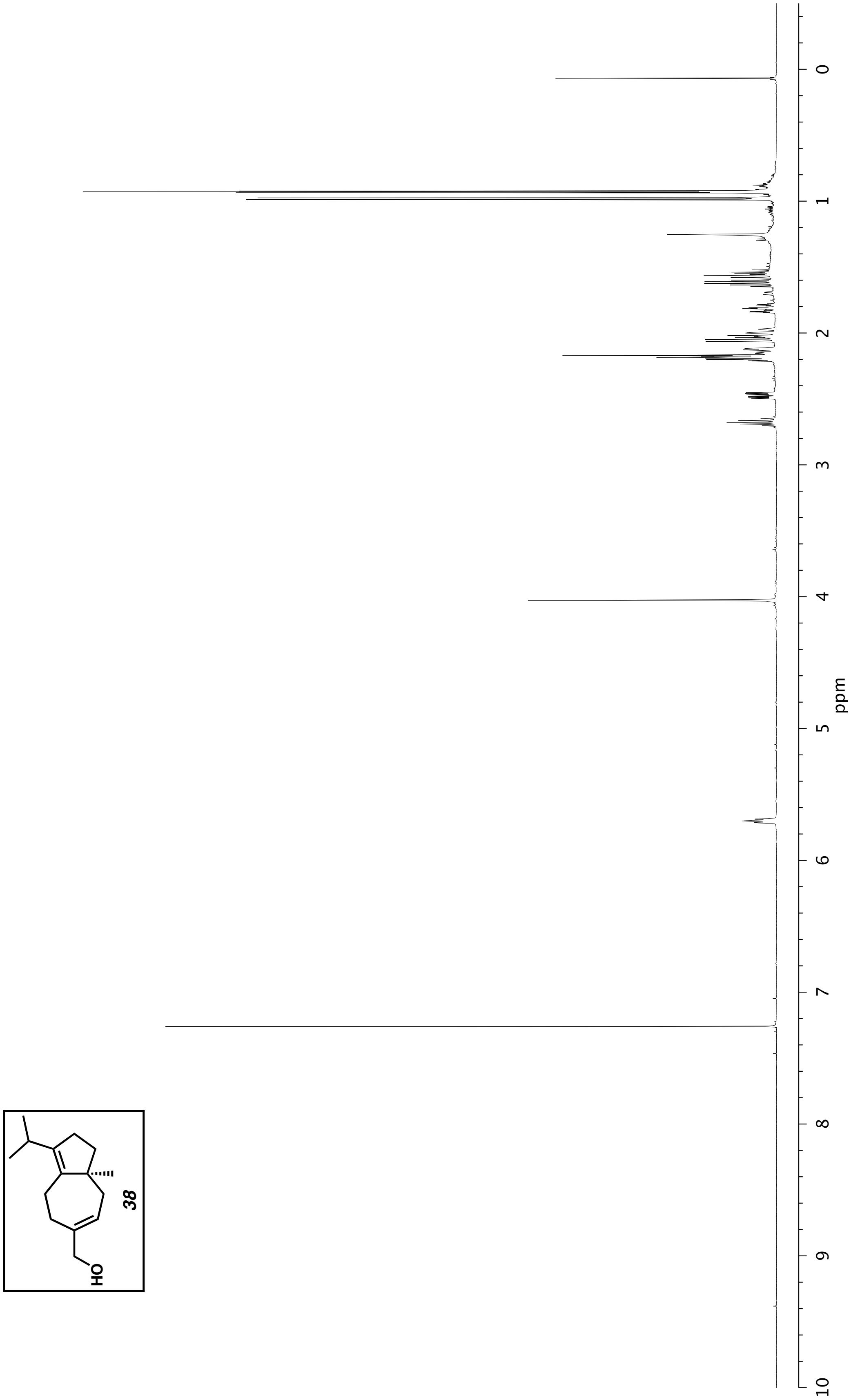


Figure SI-24.1. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **38**.

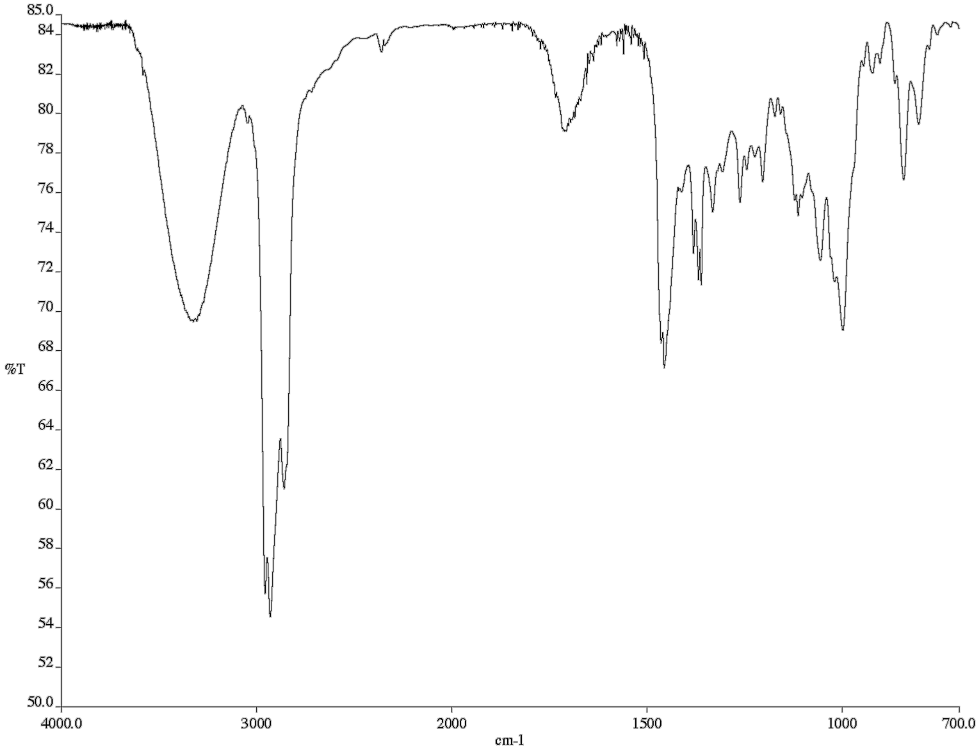


Figure SI-24.2. Infrared spectrum (thin film/NaCl) of compound **38**.

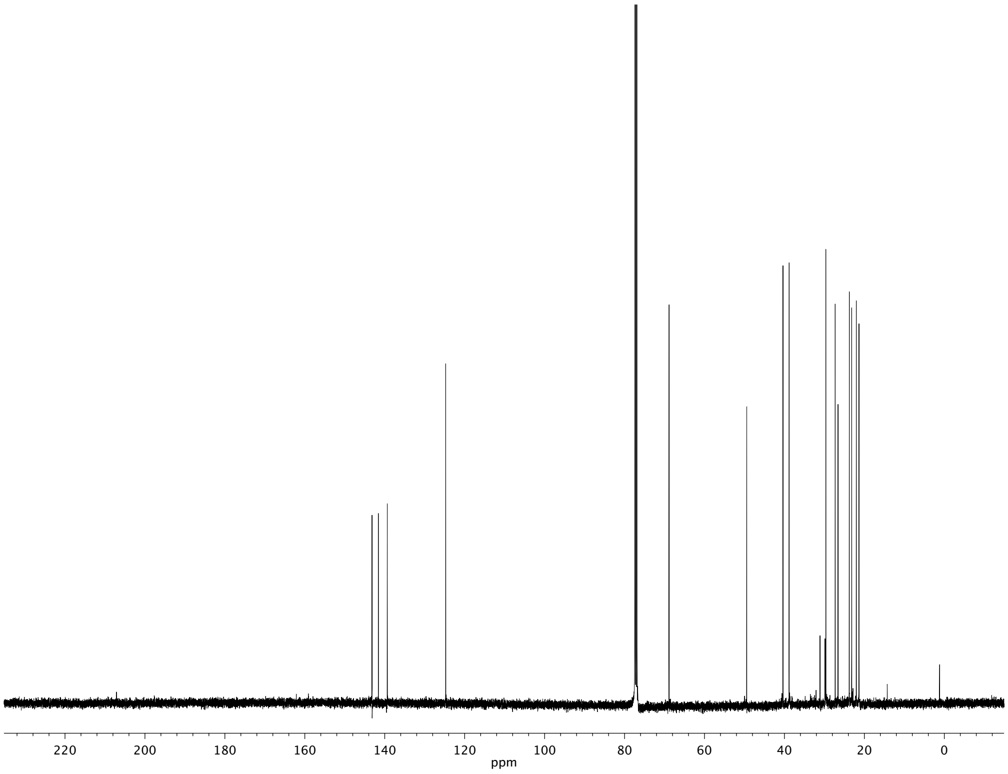
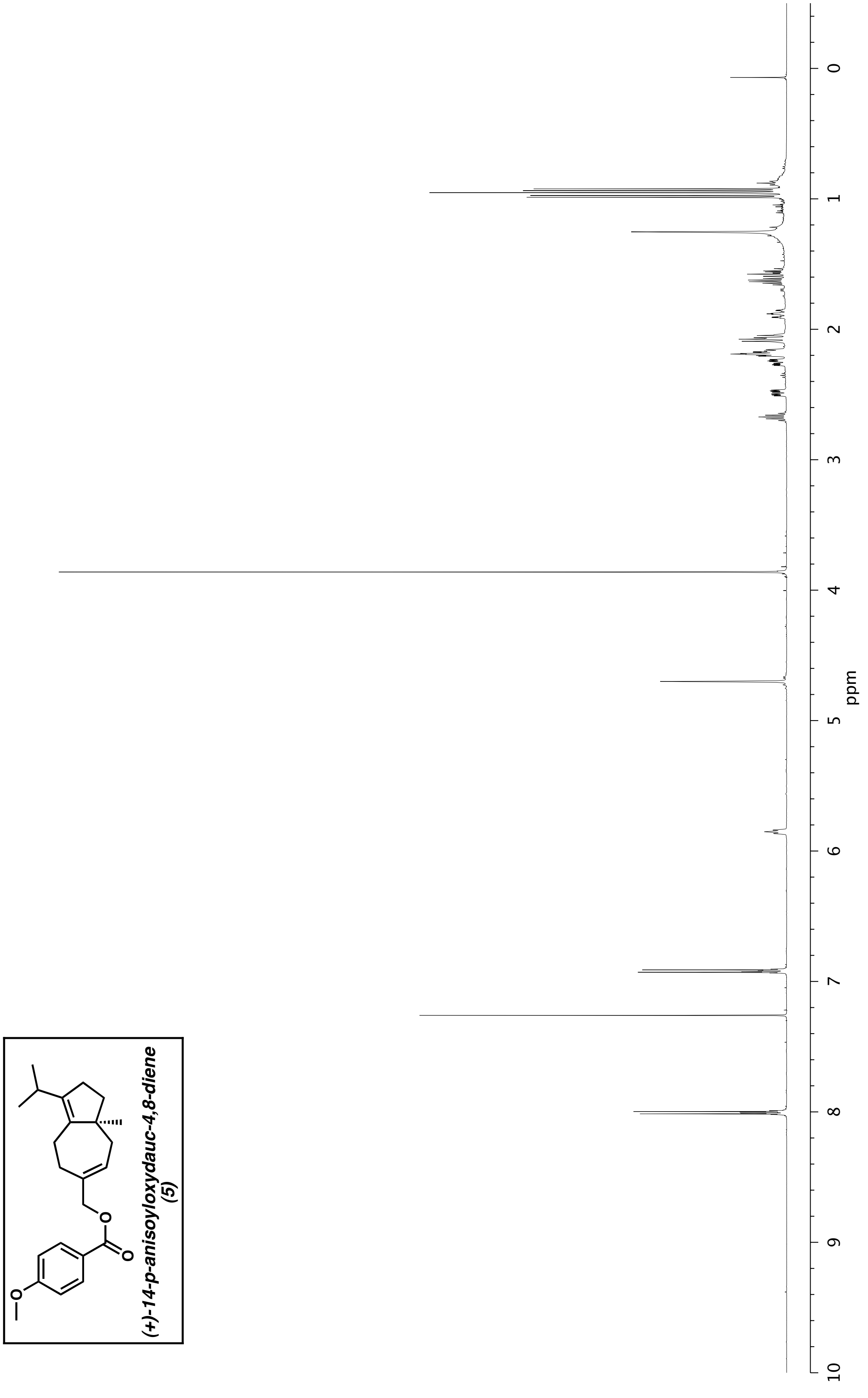


Figure SI-24.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **38**.



(+)-14-*p*-anisoyloxydauc-4,8-diene
(5)

Figure SI-25.1. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**.

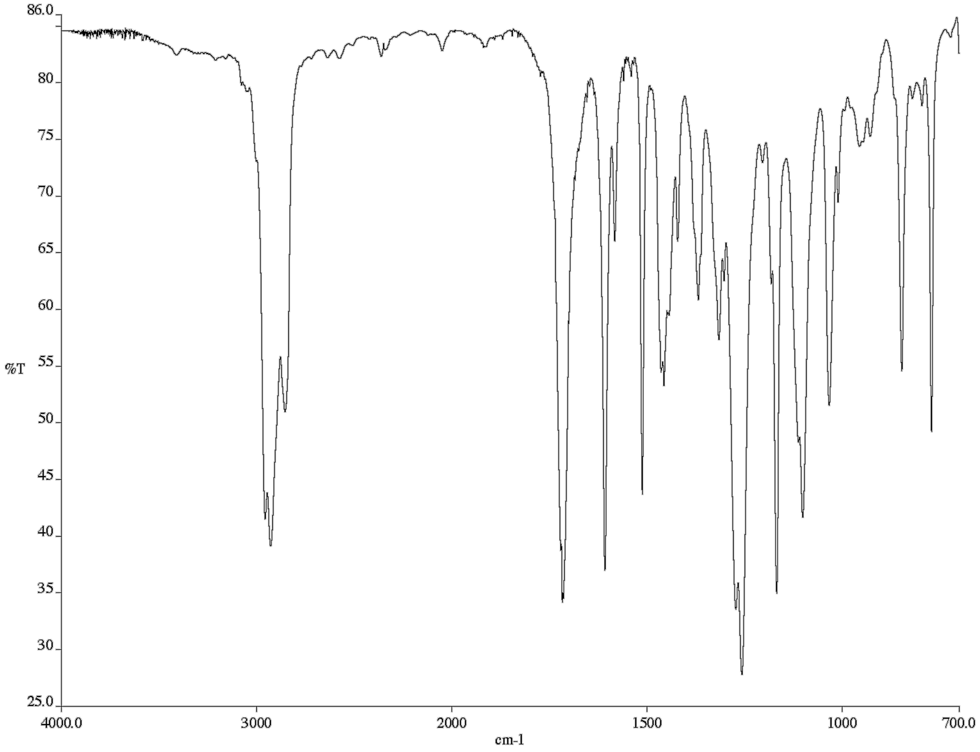


Figure SI-25.2. Infrared spectrum (thin film/NaCl) of compound **5**.

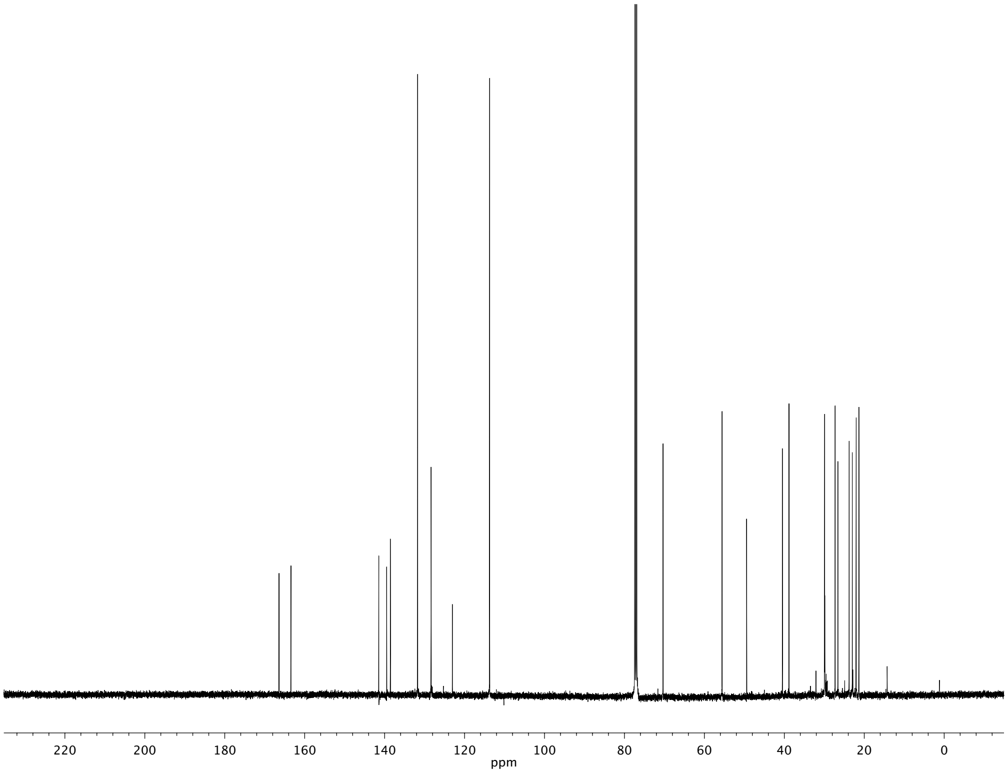


Figure SI-25.3. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **5**.