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Supporting Information

Total Syntheses of Cyanthiwigins B, F, and G

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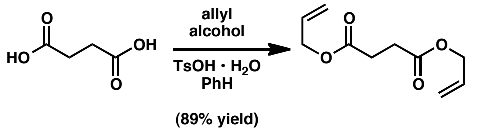
Materials and Methods

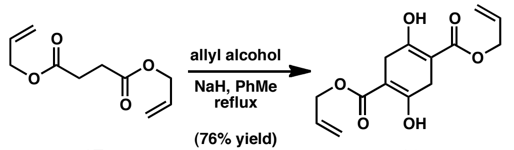
All reactions were performed at ambient temperature (22 °C) unless otherwise noted. Reactions requiring external heat were modulated to the specified temperatures indicated by using an IKAmag temperature controller. All reactions were performed in glassware flame dried under vacuum and allowed to cool under nitrogen or argon. Solvents were dried by passage over a column of activated alumina with an overpressure of argon gas. Tetrahydrofuran was distilled directly over benzophenone and sodium, or else was dried by passage over a column of activated alumina with an overpressure of argon gas. Grubbs' ruthenium catalysts **52** and **55** were donated by Materia Inc. and used without further purification. (*S*)-*t*-BuPHOX (**43**),[1,2] enol stannane **50**,[3] 4-iodo-2-methyl-1-butene (**54**),[4] and vinyl boronate ester **56**[5] were prepared according to known methods. All other chemicals and reagents were used as received. Compounds purified by flash chromatography utilized ICN silica gel (particle size 0.032–0.063 mm) or SiliCycle® Silia*Flash*® P60 Academic Silica Gel (particle size 40–63 μm; pore diameter 60 Å). Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized by UV, *p*-anisaldehyde, or alkaline permanganate staining. NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR), Varian Inova 500 (at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR), or Varian Inova 600 (at 600 MHz for ^{1}H NMR only) instrument, and are reported relative to residual $CHCl_3$ (δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR) or C_6H_6 (δ 7.16 for ^{1}H NMR, δ 128.06 for ^{13}C NMR). The following format is used for the reporting of ^{1}H NMR data: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Spectrum Paragon 1000 spectrometer, and data are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from the Caltech Mass Spectral Facility, or else were acquired using an Agilent 6200 Series TOF mass spectrometer with an Agilent G1978A Multimode source in ESI, APCI, or MM (ESI/APCI) ionization mode. Analytical chiral gas chromatography was performed with an Agilent 6850 GC using a G-TA (30 m x 0.25 mm) column (1.0 mL/min carrier gas flow). Analytical achiral gas chromatography was performed with an Agilent 6850 GC using a DB-WAX (30 x 0.25 mm) column (1.0 mL/min carrier gas flow). Preparatory reverse-phase HPLC was performed on a Waters HPLC with Waters Delta-Pak 2 x 100 mm, 15 μm column equipped with a guard, employing a flow rate of 1 mL/min and a variable gradient of acetonitrile and water as eluent. HPLC visualization was performed by collecting 1 mL fractions after initial injection and analyzing each fraction via TLC. Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm using a 100 mm path-length cell.

Experimental Procedures



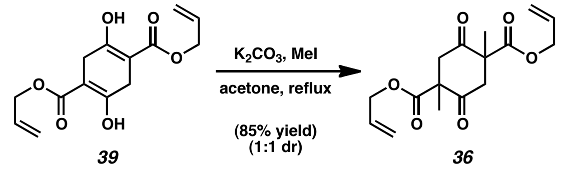
38 37

Diallyl succinate (37). To a solution of succinic acid (**38**, 40.0 g, 338.7 mmol) in benzene (300 mL) was added TsOH • H_2O (0.21 g, 1.2 mmol, 0.003 equiv). After brief mixing, allyl alcohol (70 mL, 1.01 mol, 3.00 equiv) was added to the reaction, and the flask was fitted with a Dean–Stark trap and reflux condenser under nitrogen. The reaction was heated to 105 °C and allowed to reflux over 12 h. After collection of 13 mL H_2O from the Dean–Stark trap, the reaction was allowed to cool to room temperature and was quenched by slow treatment with saturated $NaHCO_{3(aq)}$ until gas evolution halted. The phases were separated, and the organic layer was washed with saturated $NaHCO_{3(aq)}$ (2 x 40 mL) and brine (2 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and solvent was removed in vacuo. The resulting colorless oil was dried under high vacuum to afford diallyl succinate (**37**, 59.8 g, 89% yield). This material was carried into the next step without further purification: R_f = 0.35 (10:90 Et_2O/pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, J = 17.3, 10.5, 5.6 Hz, 2H), 5.31 (ddt, J = 17.0, 1.6, 1.3 Hz, 2H), 5.23 (ddt, J = 10.4, 1.3, 1.1 Hz, 2H), 4.60 (ddd, J = 5.9, 1.3, 1.3 Hz, 4H), 2.67 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 132.1, 118.5, 65.5, 29.2; IR (Neat film, NaCl) 3086, 2942, 1738, 1649, 1413, 1377, 1271, 1157, 990, 932 cm^{-1}; HRMS (EI) m/z calc'd for $C_{10}H_{14}O_4$ $[M]^+$: 198.0892, found 198.0888.

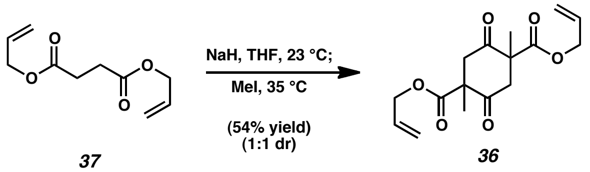


37 39

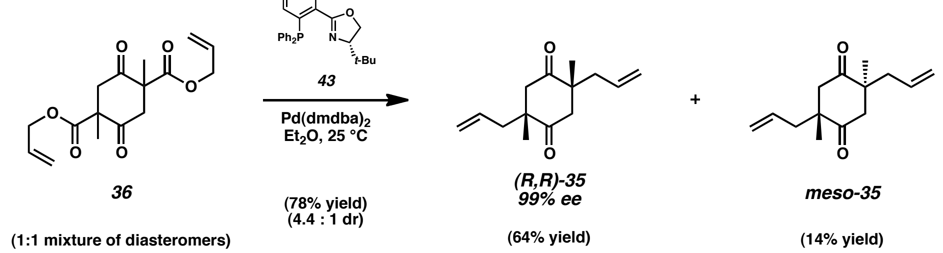
Diallyl succinylsuccinate (39).[6] To a flame dried flask under argon was added NaH (60% in mineral oil, 25.0 g, 630.6 mmol, 2.50 equiv) and toluene (125 mL). To this was added, dropwise, neat allyl alcohol (4.14 mL, 70.6 mmol, 0.28 equiv) with vigorous stirring. After gas evolution had ceased, neat diallyl succinate (**37**, 50.0 g, 252.2 mmol, 1.00 equiv) was added dropwise, and the reaction was heated to 95 °C. The reaction flask was fitted with a reflux condenser, and reaction was allowed to proceed over 10 h. After ca. 15 min, an additional portion of toluene (125.0 mL) was added to the reaction to ensure fluidity of the mixture. Once the reaction had completed by TLC, the flask was cooled to room temperature, and the solvent was removed in vacuo. The crude solid was immediately suspended in CH_2Cl_2, and then acidified by addition of 2 N $HCl_{(aq)}$ (350 mL). The biphasic mixture was allowed to stir over 2 h, after which time all solids had dissolved. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and solvent was removed in vacuo to yield a crude orange solid. The crude residue was recrystallized twice from a mixture of petroleum ether and acetone to afford diallyl succinylsuccinate (**39**) as a flaky white solid (26.9 g, 76% yield): R_f = 0.6 (15:85 ethyl acetate/hexane) ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.11 (s, 2H), 5.95 (dddd, *J* = 17.1, 10.7, 5.7, 5.7 Hz, 2H), 5.35 (ddt, *J* = 17.3, 1.6, 1.3 Hz, 2H), 5.27 (ddt, *J* = 10.4, 1.3, 1.3 Hz, 2H), 4.69 (ddd, *J* = 5.3, 1.3, 1.3 Hz, 4H), 3.22 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 168.8, 131.7, 118.4, 93.1, 65.2, 28.5; IR (Neat film, NaCl) 1666, 1647, 1684, 1451, 1389, 1329, 1219, 1204, 1133, 1061, 961, 843, 783 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{16}O_6$ $[M]^+$: 280.0947, found 280.0948.



Bis(β-ketoester) 36. Prior to use in the reaction, acetone was dried by stirring it over anhydrous calcium sulfate, and then was passing the solvent over a short plug of silica. Potassium carbonate (5.80 g, 43.9 mmol, 4.10 equiv) and diallyl succinylsuccinate (**39**, 3.00 g, 10.7 mmol, 1.00 equiv) were suspended in acetone (21.3 mL). After addition of solvent to the solids, the reaction mixture was fitted with a reflux condenser and then was heated to 50 °C. To this mixture was added methyl iodide (3.40 mL, 54.5 mmol, 5.10 equiv). The reaction was stirred vigorously to ensure completion. (Note: If reaction is not stirred, or if stirring is not efficient, potassium carbonate will collect into a solid aggregate and the reaction will halt. Breaking up these solid collections with a spatula is typically enough to reinitiate reaction, though in some cases additional methyl iodide may be required.) After 6 h, the reaction was allowed to cool and then was passed through filter paper. The remaining solids were washed with additional CH_2Cl_2 to ensure complete solvation of any precipitated product trapped within the potassium carbonate. The collected organic layers were combined and concentrated to yield an amorphous semi-solid, which was purified over silica gel using 15% → 20% ethyl acetate in hexanes as eluent. Compound **36** was afforded as two diastereomers in a 1 : 1 ratio. The less polar diastereomer (by TLC analysis with 20% ethyl acetate in hexane) was obtained as a white, fluffy solid, and the more polar diastereomer was obtained as a thick, yellow oil (1.4 g for each diastereomer, 2.8 g for combined diastereomers, 85% yield). **Diastereomer A**: R_f = 0.30 (20:80 ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (dddd, *J* = 17.3, 10.4, 5.8, 5.8 Hz, 2H), 5.30 (app dq, *J* = 17.3, 1.3 Hz, 2H), δ 5.26 (app dq, *J* = 10.4, 1.3 Hz, 2H), δ 4.60 (app ddd, *J* = 5.9, 1.3, 1.3 Hz, 4H), δ 3.14 (d, *J* = 15.2 Hz, 2H), δ 2.80 (d, *J* = 15.2 Hz, 2H), δ 1.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 170.6, 131.0, 119.7, 66.8, 57.6, 48.1, 20.8; IR (Neat film, NaCl) 2988, 2940, 1749, 1708, 1420, 1375, 1281, 1227, 1132, 1076, 911, 809, 744 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O_6$ [M$^+$]: 308.1260, found 308.1263. **Diastereomer B**: R_f = 0.20 (20:80 ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 17.1, 10.4, 5.7, 5.7 Hz, 2H), δ 5.31 (app dq, *J* = 17.2, 1.5 Hz, 2H), δ 5.27 (app dq, *J* = 10.3, 1.5, 2H), δ 4.62 (app ddd, *J* = 5.4, 1.5, 1.5 Hz, 4H), δ 3.47 (d, *J* = 15.6 Hz, 2H), δ 2.63 (d, *J* = 15.9 Hz, 2H), δ 1.46 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 169.9, 131.1, 119.1, 66.7, 56.6, 47.1, 21.5; IR (Neat film, NaCl) 3088, 2984, 2940, 1747, 1722, 1649, 1454, 1422, 1381, 1275, 1233, 1196, 1110, 984, 934 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O_6$ [M$^+$]: 308.1260, found 308.1263.

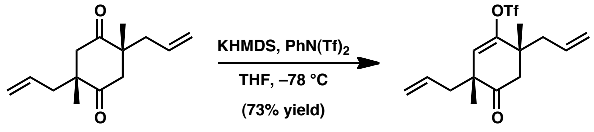


Alternative preparation of bis(β-ketoester) 36.[7] A flame dried round bottom flask was charged with NaH (60% in mineral oil, 4.44 g, 111.0 mmol, 2.2 equiv). The flask was briefly vacuum purged, and then was backfilled with argon. The solid NaH was then suspended in freshly distilled (or freshly dispensed) THF (40 mL). The resulting suspension was cooled to 0 °C in an ice water bath. After cooling, the NaH slurry was treated with a THF solution (20 mL) of diallyl succinate (**37**, 10.0 g, 50.4 mmol) added via cannula. The reaction was allowed to gradually warm to room temperature overnight (12 h). The next morning the reaction was heated to 40 °C to encourage completion of the Claisen condensation/Dieckmann cyclization process. After 24 h at this temperature, TLC analysis revealed total consumption of diallyl succinate (**37**). The reaction was cooled to 35 °C, and then a single portion of MeI (8.16 mL, 131.2 mmol, 2.6 equiv) was introduced via syringe. After an additional 12 h at 35 °C, the reaction was quenched with saturated $NH_4Cl_{(aq)}$ (40 mL). The organic layer was separated from the aqueous layer, and the aqueous layer was extracted with CH_2Cl_2 (3 x 40 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, and filtered. The crude material obtained upon removal of solvent in vacuo was further purified via column chromatography over silica using 15% → 20% ethyl acetate in hexanes as eluent. Compound **36** was afforded as two diastereomers in a 1 : 1 ratio, again as both a white solid and a clear oil (2.1 g for each diastereomer, 4.2 g for combined diastereomers, 54% yield). All spectroscopic data was identical to that reported above.



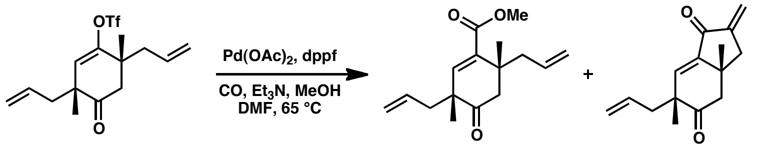
Diketone 35. A flame dried round bottom flask cooled under argon was charged with bis(3,5-dimethoxydibenzylideneacetone)palladium(0) ($Pd(dmdba)_2$, 0.268 g, 0.330 mmol, 0.05 equiv) and (*S*)-*t*-BuPHOX (**193**) (0.140 g, 0.362 mmol, 0.055 equiv). The flask was purged under vacuum briefly, and then backfilled with argon. The solids were dissolved in Et_2O (500 mL), and the resulting solution was stirred at 25 °C for 30 min. After precomplexation, neat **36** (2.00 g, 6.59 mmol, 1.00 equiv) was added to the reaction. The solution was stirred vigorously at 25 °C for 10 h (Note: continual stirring is necessary due to the apparent low solubility of $Pd(dmdba)_2$ in Et_2O.), after which time the solvent was removed in vacuo. The crude oil was purified over silica gel using 3% ethyl acetate in hexanes as eluent to afford **35** as a colorless oil (1.07 g, 78% yield, 4.4 : 1 dr, 99% *ee*): R_f = 0.7 (15:85 ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (dddd, *J* = 18.3, 10.2, 6.9, 6.9 Hz, 2H), 5.17–5.09 (comp. m, 3H), 5.07–5.04 (m, 1H), 2.82 (d, *J* = 14.7 Hz, 2H), 2.38 (d, *J* = 15 Hz, 2H), 2.34 (app ddt, *J* = 13.2, 6.9, 1.0 Hz, 2H), 2.09 (app ddt, *J* = 13.5, 7.8, 0.9 Hz, 2H), 1.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 132.4, 120.0, 49.4, 48.4, 43.8, 24.3; IR (Neat film, NaCl) 3078, 2978, 1712, 1640, 1458, 1378, 1252, 1129, 1101, 998, 921 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{20}O_2$ $[M]^+$: 220.1463, found 220.1466; $[\alpha]^{25}_D$ –163.1 (*c* 0.52, CH_2Cl_2). Chiral GC assay (GTA column): 100 °C isothermal method over 90 min. Retention times: 67.7 min (Major enantiomer, C_2 diastereomer, 81.7%), 74.1 min (Minor

enantiomer, C_2 diastereomer, 0.6%), 77.4 min (*meso* diastereomer, 17.6%). Achiral GC assay (DB-Wax column): 100 °C isotherm over 2.0 min, ramp 5 °C/min to 190 °C, then 190 °C isotherm for 10.0 min. Retention times: 18.5 min (C_2 diastereomer, 81.0%), 18.7 min (*meso* diastereomer, 19.0%).



35 *44*

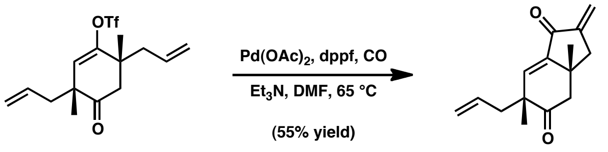
Triflate 44. A flask was charged with potassium bis(trimethylsilyl)amide (1.49 g, 7.49 mmol, 1.10 equiv) in the glovebox, and then was transferred to a manifold line outside of the glovebox under argon. The solids were dissolved in THF (180 mL), and the resulting solution was stirred while being cooled to –78 °C. To this alkaline solution was added, dropwise, neat diketone **35** (1.50 g, 6.80 mmol, 1.00 equiv). The solution immediately turned yellow, and viscosity increased. Deprotonation was allowed over 30 min, after which time the anionic solution was transferred by cannula into a solution of *N*-phenyl bis(trifluoromethane)sulfonimide (2.91 g, 8.17 mmol, 1.20 equiv) in THF (60 mL) at –78 °C. Reaction was allowed to proceed at this temperature over 6 h, after which time the mixture was brought to room temperature. The anionic reaction was quenched with brine (100 mL). The phases were separated, and the aqueous layer was extracted with diethyl ether (3 x 100 mL) and ethyl acetate (1 x 100 mL). The combined organic layers were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude oil obtained was loaded onto a silica gel column and eluted with 2% Et_2O in pentane. This afforded triflate **44** as a colorless oil (1.75 g, 73% yield). R_f = 0.40 (5:95 ethyl acetate/hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 5.77–5.58 (comp. m, 2H), 5.63 (s, 1H), 5.22–5.03 (comp. m, 4H), 2.71 (d, *J* = 14.3 Hz, 1H), 2.40 (d, *J* = 14.4 Hz, 1H), 2.49–2.30 (comp. m, 2H), 2.24 (app ddt, *J* = 13.5, 6.9, 1.3 Hz, 1H), 2.09 (app ddt, *J* = 13.8, 8.24, 1.2 Hz, 1H), 1.22 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 152.0, 132.6, 132.1, 122.9, 120.6, 119.7, 49.2, 48.9, 43.8, 43.0, 42.1, 25.2, 24.6; IR (Neat film, NaCl) 3081, 2980, 2934, 1721, 1673, 1641, 1457, 1416, 1214, 1141, 1010, 923.6, 895.2, 836.2 cm^{-1}; HRMS *m/z* calc'd for $C_{15}H_{19}O_4SF_3$ [M^+]: 352.0956, found 352.0949; $[\alpha]^{25}_D$ –6.5 (*c* 1.15, CH_2Cl_2).



44 ***45*** ***46***

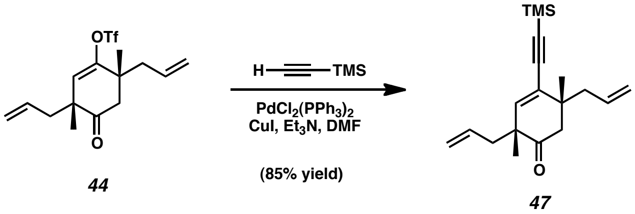
(64% yield) (1% yield)

Enoate 45. A flame dried round bottom flask was charged with Pd(OAc)$_2$ (0.089 g, 0.397 mmol, 0.07 equiv) and dppf (0.315 g, 0.568 mmol, 0.10 equiv). The solids were briefly vacuum purged, and then the flask was backfilled with nitrogen. To the palladium and ligand were added, in sequence, DMF (67 ml), MeOH (4.6 mL), triflate **44** (2.01 g, 5.68 mmol, 1.00 equiv), and triethyl amine (2.37 mL, 17.0 mmol, 3.00 equiv). The resulting solution was sparged for 10 min with an overpressure of carbon monoxide. After this time had elapsed, the reaction was fitted with a double-walled balloon of carbon monoxide to preserve gas overpressure, and then was heated to 65 °C for 10 h. Once the reaction had completed by TLC analysis, a majority of the DMF solvent was removed in vacuo. The crude residue obtained was dissolved in CH$_2$Cl$_2$ (50 mL) and was washed with brine (30 mL). The layers were separated, and the aqueous layer was thereafter extracted with CH$_2$Cl$_2$ (4 x 30 mL). Combined organics were washed with brine (50 mL), then were dried over MgSO$_4$ and filtered. The crude product was purified via chromatography over silica gel, using 2% → 3% → 4% → 5% ethyl acetate in hexanes, followed by 100% diethyl ether, as eluent. This afforded enoate **45** (848 mg, 54% yield) and dienone **46** (17.0 mg, 1% yield), both as clear oils: Data for enoate **45** was observed as follows: $R_f = 0.30$ (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.57 (s, 1H), 5.70–5.58 (m, 2H), 5.09–4.99 (m, 4H), 3.75 (s, 3H), 2.69 (dd, J = 13.9, 6.3 Hz, 2H), 2.36 (app ddt, J = 13.6, 8.1, 0.9 Hz, 1H), 2.26 (app ddt, J = 13.7, 6.9, 1.2 Hz, 1H), 2.15 (dd, J = 13.9, 7.3 Hz, 2H), 1.23 (s, 3H), 1.16, (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 212.5, 167.1, 144.8, 136.4, 134.1, 132.9, 119.1, 119.0, 51.8, 50.1, 49.0, 44.2, 43.9, 41.9, 27.5, 23.3; IR (Neat film, NaCl) 3077, 29.54, 2871, 1717, 1639, 1436, 1326, 1244, 1063, 995, 920 cm^{-1}; HRMS *m/z* calc'd for C$_{16}$H$_{22}$O$_3$ [M+H]: 263.1642, found 263.1649; $[\alpha]^{25}_{D}$ –85.9 (*c* 0.62, CH$_2$Cl$_2$).



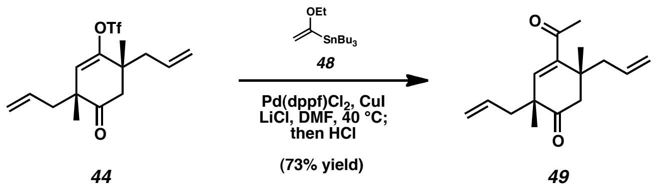
44 ***46***

Dieneone 46. A flame dried round bottom flask was charged with Pd(OAc)$_2$ (10.0 mg, 45.0 μmol, 0.07 equiv) and dppf (31.0 mg, 56.0 μmol, 0.10 equiv). The solids were briefly vacuum purged, and then the flask was backfilled with nitrogen. To the palladium and ligand were added, in sequence, DMF (5.5 ml), triflate **44** (200 mg, 0.568 mmol, 1.0 equiv), and triethyl amine (237 μL, 1.70 mmol, 3.0 equiv). The resulting solution was sparged for 15 min with an overpressure of carbon monoxide. After this time had elapsed, the reaction was fitted with a double-walled balloon of carbon monoxide to preserve gas overpressure, and then was heated to 65 °C for 3 h. Once the reaction had completed by TLC analysis, a majority of the DMF solvent was removed in vacuo. The crude residue obtained was dissolved in ethyl acetate (50 mL) and was washed with brine (30 mL). The layers were separated, and the aqueous layer was thereafter extracted with ethyl acetate (4 x 30 mL). The combined organics were washed with brine (30 mL), then were dried over $MgSO_4$ and filtered. The crude product was purified via chromatography over silica gel, using 2% → 3% ethyl acetate in hexanes, followed by 100% diethyl ether, as eluent. This afforded dieneone **46** as a clear oil (67 mg, 55% yield): R_f = 0.30 (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.19 (ddd, *J* = 3.4, 1.6, 0.9 Hz, 1H), 5.62 (dddd, *J* = 16.8, 10.1, 8.5, 6.6 Hz, 1H), 5.52–5.49 (m, 1H), 5.05 (dddd, *J* = 16.9, 4.5, 2.3, 1.2 Hz, 2H), 2.69 (app dt, *J* = 15.8, 1.6 Hz, 1H), 2.64 (d, *J* = 13.8 Hz, 1H), 2.57 (app dt, *J* = 15.9, 3.1 Hz, 1H), 2.46 (dd, *J* = 13.8, 0.6 Hz, 1H), 2.37 (app ddt, *J* = 13.5, 8.5, 1.0 Hz, 1H), 2.27 (app ddt, *J* = 13.5, 6.5, 1.5 Hz, 1H), 1.24 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.2, 192.9, 144.9, 144.3, 137.9, 132.7, 120.3, 119.4, 52.4, 48.8, 45.6, 43.1, 39.7, 27.9, 23.2; IR (Neat film, NaCl) 2958, 2929, 1711, 1657, 1639, 1454, 1437, 1399, 1378, 1259, 1156, 1131, 929 cm^{-1}; HRMS *m/z* calc'd for $C_{15}H_{18}O_2$ [M$^+$]: 230.1307, found 230.1313; $[\alpha]^{25}_D$ –130.8 (*c* 0.50, CH_2Cl_2).



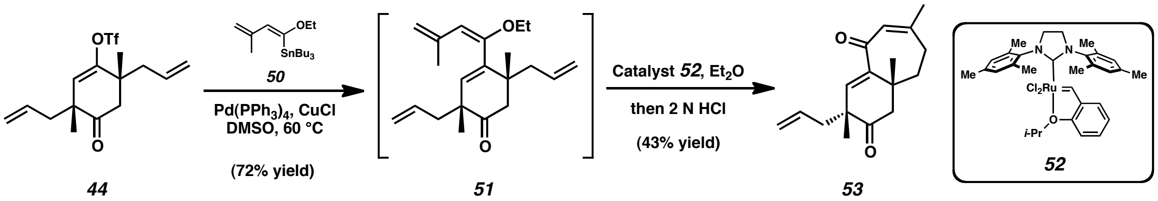
Enyne 47. To a flame dried flask was added $PdCl_2(PPh_3)_2$ (59 mg, 85.0 μmol, 0.1 equiv) and CuI (10 mg, 52.0 μmol, 0.05 equiv). These solids were briefly vacuum purged, and then the flask was backfilled with nitrogen. The metal salts were thereafter dissolved in DMF (5.1 mL), and treated with triethyl amine (356 μL, 2.55 mmol, 3.00 equiv), triflate **44** (300 mg, 0.851 mmol, 1.00 equiv), and (trimethylsilyl)acetylene (241 μL, 1.70 mmol, 2.0 equiv). The resulting solution was stirred at room temperature for 4 h, after which time the reaction had completed. The reaction was quenched by the

addition of brine (10 mL), followed by extraction with diethyl ether (4 x 20 mL). The combined organics were washed with brine (10 mL), then were dried over $MgSO_4$ and filtered. The crude material isolated was purified silica gel chromatography using 2% ethyl acetate in hexanes as eluent. Enyne **47** was isolated as a clear oil (218 mg, 85% yield): $R_f = 0.50$ (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (s, 1H), 5.80 (dddd, *J* = 16.6, 10.1, 8.4, 6.3 Hz, 1H), 5.66 (dddd, *J* = 17.0, 10.2, 8.1, 6.9 Hz, 1H), 5.14–5.01 (comp. m, 4H), 2.60 (d, *J* = 13.9 Hz, 1H), 2.43 (app ddt, *J* = 13.7, 6.3, 1.3 Hz, 1H), 2.31 (app ddt, *J* = 13.7, 8.1, 1.0 Hz, 1H), 2.20 (app ddt, *J* = 13.6, 6.9, 1.3 Hz, 1H), 2.19 (d, *J* = 13.9 Hz, 1H), 2.03 (app ddt, *J* = 13.7, 8.4, 1.0 Hz, 1H), 1.12 (s, 3H), 1.10 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 141.2, 134.3, 133.3, 128.5, 118.9, 118.8, 103.2, 95.8, 49.3, 48.5, 45.3, 44.5, 42.5, 27.5, 23.6, 0.1; IR (Neat film, NaCl) 3077, 2962, 2144, 1717, 1638, 1457, 1375, 1250, 1147, 996, 843 cm^{-1}; HRMS *m/z* calc'd for $C_{19}H_{28}OSi$ [M+H]: 301.1982, found 301.1980; $[\alpha]^{25}_D$ –88.3 (*c* 0.33, CH_2Cl_2).



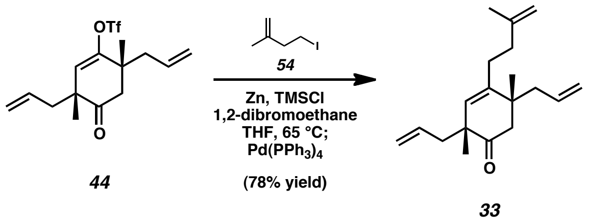
Enone 49. To a flame dried round bottom flask under argon was added Pd(dppf)Cl_2 (116 mg, 0.142 mmol, 0.10 equiv), CuI (27 mg, 0.142 mmol, 0.10 equiv), and LiCl (319 mg, 7.52 mmol, 5.3 equiv). These solids were briefly vacuum purged before being backfilled with argon, and then were dissolved in DMF (20 mL). The resulting solution was then treated with triflate **44** (500 mg, 1.42 mmol, 1.0 equiv) and tributylethoxyvinyl stannane (**48**, 623 µL, 1.84 mmol, 1.3 equiv). Subsequent to the addition of all reagents, the reaction was freeze-pump-thawed, and then was heated to 40 °C. After 9 h at 40 °C, the reaction was cooled to room temperature and diluted with brine (40 mL). The resulting solution was extracted with diethyl ether (3 x 40 mL), and the combined organic layers were washed with additional brine (2 x 30 mL). The combined aqueous layers were thereafter back-extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers from all extractions were dried over $MgSO_4$, filtered, and solvent was removed in vacuo. The crude material obtained after removal of solvent was then redissolved in CH_2Cl_2 (40 mL) and stirred with 2 N $HCl_{(aq)}$ (20 mL) for 2 h. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material obtained was purified via silica gel chromatography using 2% → 3% ethyl acetate in hexanes as eluent. This afforded enone **49** as a clear

oil (255 mg, 73%): $R_f = 0.50$ (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (s, 1H), 5.68 (dddd, *J* = 16.9, 10.1, 8.2, 6.9 Hz, 1H), 5.57 (app dt, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.13–4.96 (m, 4H), 2.75 (app ddt, *J* = 13.5, 7.0, 1.0 Hz, 1H), 2.69 (d, *J* = 13.8 Hz, 1H), 2.39 (app ddt, *J* = 13.6, 8.2, 0.8 Hz, 1H), 2.32 (s, 3H), 2.29 (app ddt, *J* = 13.5, 6.8, 1.3 Hz, 1H), 2.12 (d, *J* = 13.9 Hz, 1H), 2.03 (app ddt, *J* = 13.8, 7.6, 1.2 Hz, 1H), 1.22 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 199.8, 145.1, 145.0, 134.3, 132.8, 119.3, 118.9, 50.5, 49.1, 44.5, 43.4, 42.7, 28.1, 27.7, 23.2; IR (Neat film, NaCl) 3077, 2977, 2930, 2869, 1717, 1676, 1637, 1540, 1457, 1365, 1235, 995, 919 cm^{-1}; HRMS *m/z* calc'd for $C_{16}H_{22}O_2$ [M+H]: 247.1693, found 247.1699; $[\alpha]^{25}_D$ –60.4 (*c* 0.33, CH_2Cl_2).

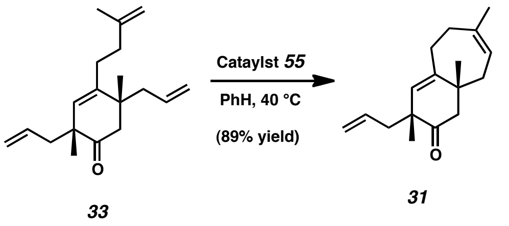


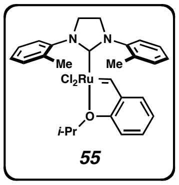
Enone 53. To a round bottom flask was added LiCl (64 mg, 1.50 mmol, 6.0 equiv). This flask was flame dried, backfilled with argon, and then was transferred to the glovebox. Once inside the glovebox, $Pd(PPh_3)_4$ (29 mg, 25.0 μmol, 0.1 equiv) and CuCl (124 mg, 1.25 mmol, 5.0 equiv) were added to the flask. The flask was removed from the glovebox and was transferred to a manifold line. The solids were briefly purged under vacuum, then were backfilled with argon. Afterwards, the solids were dissolved in DMSO (2.0 mL), resulting in an immediate black solution. The flask was wrapped with aluminium foil to shield from light, and then triflate **44** (88 mg, 0.250 mmol, 1.0 equiv) and enol stannane **50** (120 mg, 0.300 mmol, 1.2 equiv) were added. The solution was freeze-pump-thawed thrice, and then was heated to 60 °C. After 24 h, the reaction was cooled to room temperature and diluted with brine (4 mL). To this mixture was added ethyl acetate (5 mL), and the phases were separated. The ethyl acetate layer was separated, then was washed with brine (5 mL) and saturated $NH_4Cl_{(aq)}$ (2 x 20 mL). Combined aqueous layers were extracted with ethyl acetate (3 x 30 mL), and the resulting combined organic layers were washed with brine (40 mL). After washing, the organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material obtained was purified via chromatography over silica gel, using 1% → 2% → 5% diethyl ether in pentane. This afforded crude enol ether **51** as a clear oil. This material was carried directly into the next reaction without further purification or characterization, due to tautomeric instability.

To a flame dried flask under argon was added crude **51** from the previous reaction sequence. This oil was dissolved in acetonitrile and azeotroped three times, and then was dried briefly under vacuum to remove residual solvent. The residue obtained was dissolved in diethyl ether, and then was treated with the Grubbs–Hoveyda second-generation catalyst (**52**, 18 mg, 21.0 μmol, 0.05 equiv). The reaction was heated to 30 °C for 30 min, and then was cooled to room temperature and quenched with saturated $NaHCO_{3(aq)}$. The phases were separated, and the aqueous layer was extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine (30 mL), then were dried over $MgSO_4$ and filtered. In order to prevent purification difficulties resulting from partial decomposition of the enol ether moiety on silica, the enol ether was pre-emptively cleaved to reveal the ketone. The crude product oil was redissolved in diethyl ether (25 mL) and was stirred with 2 N $HCl_{(aq)}$ (25 mL) for 30 min. The phases were separated, and the aqueous layer was extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine (30 mL), then were dried over $MgSO_4$ and filtered. After concentrating in vacuo, the crude residue obtained was purified via chromatography over silica gel using 50% benzene in hexanes as eluent. This afforded bicyclic enone **53** as a clear oil, and as a mixture of diastereomers (19.7 mg, 30% yield). **Diastereomer A**: $R_f = 0.30$ (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 (s, 1H), 6.06 (dd, *J* = 2.3, 1.2 Hz, 1H), 5.66 (dddd, *J* = 17.0, 10.2, 8.2, 6.8 Hz, 1H), 5.08–5.00 (comp. m, 2H), 2.57 (dd, *J* = 13.7, 0.6 Hz, 1H), 2.49 (dddd, *J* = 7.1, 3.3, 1.3, 0.8 Hz, 1H), 2.45 (dddd, *J* = 7.0, 3.2, 1.2, 0.8 Hz, 1H), 2.39 (app ddt, *J* = 13.6, 8.2, 0.9 Hz, 1H), 2.25 (d, 13.7 Hz, 1H), 2.24 (app ddt, *J* = 13.5, 6.8, 1.2 Hz, 1H), 1.97 (app t, *J* = 0.5 Hz, 3H), 1.89 (ddd, *J* = 14.4, 9.5, 3.4 Hz, 1H), 1.69 (ddd, *J* = 14.4, 7.1, 3.7 Hz, 1H), 1.21 (s, 3H), 1.12 (app d, *J* = 0.6 Hz. 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 193.1, 157.9, 146.5, 140.3, 133.2, 129.9, 119.0, 52.9, 49.1, 44.9, 39.2, 38.6, 32.8, 27.2, 26.4, 23.4; IR (Neat film, NaCl) 2964, 2929, 1716, 1648, 1593, 1456, 1436, 1418, 1375, 1266 cm^{-1}. HRMS *m/z* calc'd for $C_{17}H_{22}O_2$ [M+H]: 259.1693, found 259.1694; $[\alpha]^{25}_D$ –112.6 (*c* 0.28, CH_2Cl_2). **Diastereomer B**: $R_f = 0.25$ (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (s, 3H), 6.06 (dd, *J* = 2.4, 1.2, Hz, 1H), 5.66 (dddd, *J* = 17.2, 10.1, 7.8, 7.2 Hz, 1H), 5.08–5.02 (comp. m, 2H), 2.67 (dd, *J* = 13.5, 0.6 Hz, 1H), 2.54 (app ddt, 13.6, 7.9, 1.0 Hz, 1H), 2.47–2.34 (comp. m, 2H), 2.26 (app ddt, *J* = 13.6, 7.1, 1.2 Hz, 1H), 2.20 (d, *J* = 13.5 Hz, 1H), 1.96 (d, *J* = 1.1 Hz, 2H), 1.91 (ddd, *J* = 14.3, 9.5, 3.9 Hz, 1H), 1.68 (ddd, *J* = 14.4, 6.5, 4.1 Hz, 1H), 1.21 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 192.8, 157.2, 146.2, 140.3, 133.5, 129.9, 119.0, 51.9, 49.2, 41.9, 39.4, 38.5, 33.1, 27.1, 25.9, 25.5; IR (Neat film, NaCl) 2927, 1715, 1647, 1591, 1451, 1378, 1270, 1034, 919 cm^{-1}; HRMS *m/z* calc'd for $C_{17}H_{22}O_2$ [M+H]: 259.1693, found 259.1700; $[\alpha]^{25}_D$ –35.6 (*c* 0.28, CH_2Cl_2).

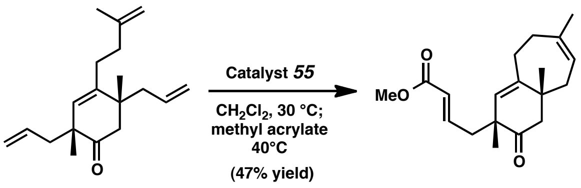


Tetraene 33. To a flame dried Schlenk flask backfilled with argon was added powdered Zn metal (3.20 g, 48.9 mmol, 7.5 equiv). After a brief vacuum purge and argon backfill, the metal was suspended in THF (45 mL). To this suspension was cannula transferred a prepared solution of 1,2-dibromoethane (0.675 mL, 7.83 mmol, 1.2 equiv) and trimethylsilyl chloride (0.271 mL, 2.13 mmol, 0.33 equiv) in THF (22.5 mL). The reaction vessel was sealed, then heated to 65 °C for 15 min. After this time had elapsed, the reaction was cooled to room temperature, and a solution of 4-iodo-2-methyl-1-butene (**54**, 1.92 g, 9.79 mmol, 1.5 equiv) in THF (22.5 mL) was cannula transferred into the suspension of activated Zn metal. The reaction vessel was sealed once again, and then was heated to 65 °C for 2 h. After this time had elapsed, the reaction was cooled to room temperature, and a prepared solution of triflate **44** (2.3 g, 6.53 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (0.377g, 0.33 mmol, 0.05 equiv) in THF (45 mL) was added to the alkyl zinc solution via cannula. The reaction was sealed and heated to 65 °C for 3 h. After reaction had completed by TLC, it was cooled to room temperature and filtered over a Celite pad with copious washing with Et_2O. The filtrate then was diluted with brine and extracted with Et_2O (4 x 100 mL). The combined organic layers were washed with brine (40 mL), followed by saturated $Na_2S_2O_{3(aq)}$ (40 mL) to removed colored impurities. The washed organic layers were dried over $MgSO_4$, filtered, and then solvent was removed in vacuo. The crude material obtained was then purified over silica gel using 0.5% → 1.0% → 1.5% → 3.0% Et_2O in petroleum ether as eluent. This afforded tetraene **33** as a colorless oil (1.40 g, 78%): $R_f = 0.50$ (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77–5.61 (comp. m, 2H), 5.20 (s, 1H), 5.10–4.97 (comp. m, 4H), 4.74 (d, J = 8.8 Hz, 2H), 2.56 (d, J = 13.5 Hz, 1H), 2.40–2.13 (comp. m, 8H), 2.05–1.98 (m, 1H), 1.77 (s, 3H), 1.09 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) d 214.4, 145.5, 142.5, 134.1, 134.0, 128.6, 118.6, 117.9, 110.1, 49.5, 48.7, 44.4, 44.3, 43.2, 36.5, 28.6, 26.5, 24.7, 22.7; IR (Neat film, NaCl) 3076, 2996, 2928, 2360, 1715, 1639, 1455, 1376, 1320, 1298, 1261, 1229, 1138, 1093, 996, 916, 887 cm^{-1}; HRMS (EI) m/z calc'd for $C_{19}H_{28}O$ [M^+]: 272.2140, found 272.2138; $[\alpha]^{25}_{D}$ –72.4 (c 0.22, CH_2Cl_2).



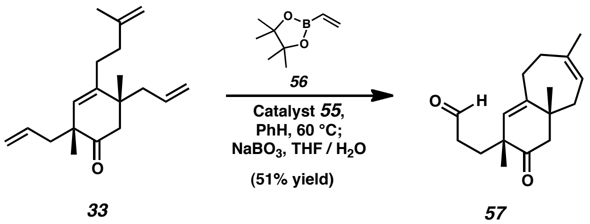


Bicyclic triolefin 31. To a flame dried flask was added tetraolefin **33** (160 mg, 588 mmol, 1.00 equiv). This oil was dissolved in benzene (5 mL), and then azeotroped from this solvent. This process was repeated three times, and then the resulting residue was dissolved in benzene (28 mL) and sparged with argon for 30 min. After the sparge time had elapsed, a single portion of Grubbs–Hoveyda catalyst **55** (34.0 mg, 59.0 μmol, 0.10 equiv) was added to the solution. The reaction was then heated to 40 °C. (Note: tetraolefin **33** and bicyclic triolefin **31** are difficult to separate by TLC in a wide variety of solvent systems, and frequently are seen to co-spot. In order to afford more efficient separation via TLC, the use of silver nitrate treated silica gel TLC plates is very effective.) After 20 min at 40 °C, the reaction had completed by TLC, and so was quenched via the addition of ethyl vinyl ether (20 mL). The solvents were removed in vacuo, and the resulting crude mixture was purified via chromatography over silica gel using 0.5% → 1.0% → 1.5% → 3.0% Et_2O in petroleum ether as eluent. This afforded bicyclic triene **31** as a colorless oil (128 mg, 89% yield): R_f= 0.50 (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (dddd, *J* = 16.8, 10.2, 8.4, 6.5 Hz, 1H), 5.33 (dddd, *J* = 6.9, 5.4, 2.9, 1.5 Hz, 1H), 5.19 (s, 1H), 5.01–4.93 (comp. m, 2H), 2.73 (dd, *J* = 13.4, 0.6 Hz, 1H), 2.53 (dddd, *J* = 13.2, 11.7, 5.3, 0.6 Hz, 1H), 2.45–2.39 (m, 2H), 2.22–2.17 (m, 1H), 2.22 (app ddt, *J* = 13.5, 8.4, 0.9 Hz, 1H), 2.11–2.03 (m, 2H), 2.11 (app ddt, *J* = 13.5, 6.5, 1.4 Hz, 1H), 2.03 (d, *J* = 13.5 Hz, 1H), 1.65 (s, 3H), 1.10 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.6, 145.3, 138.5, 134.0, 129.2, 120.2, 117.8, 51.7, 49.0, 46.3, 44.9, 37.4, 29.5, 28.1, 25.8, 23.7; IR (Neat film, NaCl) 3076, 2961, 2927, 1711, 1639, 1452, 1372, 1225, 1163, 997, 916 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O$ [M^+]: 244.1827, found 244.1821; $[\alpha]^{25}_{D}$ –96.7 (*c* 1.33, CH_2Cl_2).

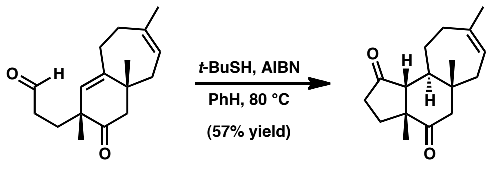


33 **58**

Enoate 58. To a flame dried flask under argon was added tetraolefin **33** (49.0 mg, 0.180 mmol, 1.00 equiv). This material was dissolved in benzene and azeotroped thrice, then briefly dried under high vacuum to remove residual solvent. The flask was then charged with Grubbs–Hoveyda catalyst **55** (7.0 mg, 9.0 μmol, 0.05 equiv) and CH_2Cl_2 (12 mL) and was heated to 30 °C. The reaction was allowed to stir at this temperature for 20 min, after which time TLC analysis showed complete conversion of the starting material to the ring-closed product. After 20 min had elapsed the reaction was treated with methyl acrylate (243 μL, 2.70 mmol, 15 equiv) in a single portion, and the heat was increased to 40 °C. After 4 h, the reaction was quenched via the addition of water (20 mL). The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material obtained was purified via chromatography over silica gel using 3% → 5% ethyl acetate in hexanes as eluent. This afforded enoate **58** as a colorless oil (25.0 mg, 47% yield): R_f = 0.10 (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (ddd, *J* = 15.7, 8.7, 7.1 Hz, 1H), 5.75 (app dt, *J* = 15.7, 1.3 Hz, 1H), 5.33 (dddd, *J* = 7.1, 5.6, 3.0, 1.5 Hz, 1H), 3.70 (s, 3H), 2.65 (dd, *J* = 13.6, 0.7 Hz, 1H), (2.58–2.51 (m, 1H), 2.47–2.41 (comp. m, 2H), 2.39 (dd, *J* = 8.7, 1.2 Hz, 1H), 2.37 (dd, *J* = 8.7, 1.2 Hz, 1H), 2.22 (ddd, *J* = 13.6, 7.1, 1.6 Hz, 2H), 2.12–2.02 (m, 2H), 1.68–1.62 (m, 2H), 1.66 (s, 3H), 1.15 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.9, 166.5, 146.6, 144.3, 138.6, 128.2, 123.9, 119.9, 51.4, 49.6, 48.8, 44.8, 44.3, 37.5, 37.4, 29.5, 28.0, 25.8, 24.2; IR (Neat film, NaCl) 2954, 2879, 1725, 1657, 1436, 1374, 1332, 1271, 1200, 1151, 1039, 987, 851, 825 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{19}H_{26}O_3$ [M$^+$]: 302.1882, found 302.1881; $[\alpha]^{25}_{D}$ –106.4 (*c* 1.09, CH_2Cl_2).

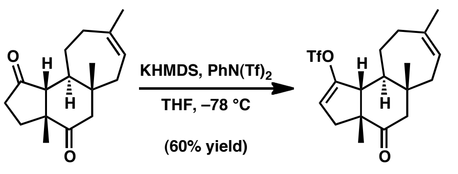


Bicyclic aldehyde 57. The following reaction was preformed in a glovebox under an atmosphere of nitrogen. To a flame dried flask was added tetraene **33** (100 mg, 0.37 mmol, 1.00 equiv) and PhH (10 mL). The solution was treated with Grubbs–Hoveyda catalyst **55** (23.0 mg, 37.0 μmol, 0.10 equiv) and was heated to 40 °C for 30 min. After this time had elapsed vinyl boronate ester **56**[5] (283 mg, 1.84 mmol, 5.0 equiv) was added via syringe and the temperature was maintained at 40 °C for 20 h. The reaction was then cooled to –20 °C briefly and treated with ethyl vinyl ether (ca. 200 μL) to quench the remaining catalyst. At this stage, the reaction was removed from the glovebox. Solvent was removed in vacuo, and the crude mixture was passed over a short plug of silica gel using 20% ethyl acetate in hexanes as eluent to remove all remaining catalyst and various ruthenium byproducts. The oil obtained was then redissolved in THF (10 mL) and treated with water (10 mL). A single portion of $NaBO_3{\bullet}H_2O$ (220 mg, 2.20 mmol, 6.00 equiv) was added, and the reaction was allowed to stir for 1 h. After complete consumption of the boronate was observed via TLC, the phases were separated, and the aqueous phase was extracted with ethyl acetate (4 x 20 mL). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified over silica gel using 5.0% → 7.5% ethyl acetate in hexanes as eluent to afford bicyclic aldehyde **57** as a colorless oil (48.0 mg, 51% yield): $R_f = 0.20$ (10:90 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (app t, J = 1.3 Hz, 1H), 5.38–5.31 (m, 1H), 5.15 (s, 1H), 2.70 (d, J = 13.6 Hz, 1H), 2.59–2.32 (comp. m, 5H), 2.12 (d, J = 13.8 Hz, 1H), 2.24–2.04 (comp. m, 2 H), 1.89–1.64 (comp. m, 3 H), 1.67 (s, 3H), 1.12 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.5, 201.6, 146.4, 138.7, 129.0, 120.1, 51.6, 47.7, 39.9, 37.6, 37.2, 33.1, 29.6, 27.8, 25.9, 23.9; IR (Neat film, NaCl) 2960, 2927, 2360, 2341, 1711–1710 (overlapping peaks), 1452, 1374, 1296, 1163 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O_2$ [M$^+$]: 260.1776, found 260.1784; $[\alpha]^{25}_D$ –83.5 (*c* 1.09, CH_2Cl_2).



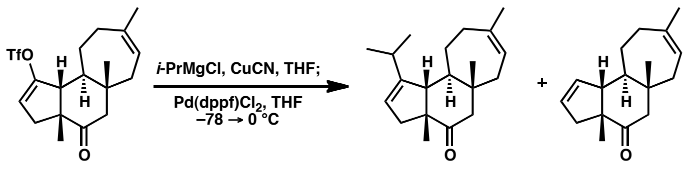
57 *63*

Tricyclic diketone 63. To a flame dried Schlenk flask was added bicyclic aldehyde **57** (600 mg, 2.32 mmol, 1.0 equiv). Dry PhH (5 mL) was added, then evaporated under vacuum. This azeotropic drying procedure was repeated two additional times, and the resulting material was then dried under high vacuum and backfilled with argon. To this was added *t*-butyl thiol (0.78 mL, 6.91 mmol, 3.0 equiv), AIBN (568 mg, 3.46 mmol, 1.5 equiv), and PhH (20 mL). The reaction was freeze-pump-thawed thrice, and afterward was backfilled with argon. The reaction vessel was sealed and the reaction was heated to 80 °C and allowed to react over 22 h. After this time, the reaction was cooled to room temperature and solvent was removed in vacuo. The crude material was purified over silica gel using a gradient of 5.0% → 7.5% → 10.0% ethyl acetate in hexanes as eluent to afford tricyclic diketone **57** as an amorphous solid (342 mg, 57% yield). An analytically pure sample was prepared via reverse-phase HPLC purification using 30% acetonitrile in water. X-ray diffraction samples were grown via diffusion crystallization of the amorphous solid from acetonitrile and water. R_f = 0.40 (10:90 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (ddq, *J* = 5.13, 5.13, 1.71 Hz, 1 H), 2.65 (d, *J* = 14.5 Hz, 1H), 2.55–2.49 (m, 1H), 2.41–2.28 (m, 2H), 2.27–2.21 (m, 1H), 2.20–2.12 (m, 1H), 2.02 (d, *J* = 14.5 Hz, 1H), 2.01–1.93 (m, 2H), 1.89 (dd, *J* = 12.2, 1.2 Hz, 1H), 1.83–1.72 (m, 3H), 1.74 (s, 3H), 1.09 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 218.0, 212.8, 142.6, 121.0, 63.2, 52.6, 51.0, 47.8, 42.3, 40.1, 34.4, 32.4, 31.4, 25.4, 24.1, 21.7, 17.3; IR (Neat film, NaCl) 2961, 2926, 2868, 1735, 1705, 1576, 1453, 1380, 1149 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O_2$ [M$^+$]: 260.1777, found 260.1776; $[\alpha]^{25}_D$ –158.6 (*c* 0.925, CH_2Cl_2); mp 94–96 °C.



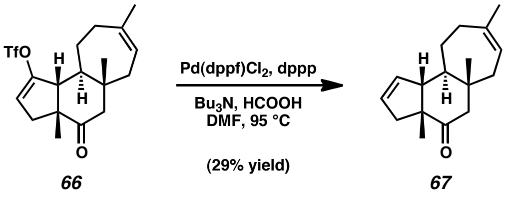
63 *66*

Tricyclic triflate 66. To a flame dried flask under argon was added tricyclic diketone **63** (250 mg, 0.960 mmol, 1.0 equiv). Dry PhH (5 mL) was added, then evaporated under vacuum. This azeotropic drying procedure was repeated two additional times, and the resulting material was then dried under high vacuum briefly, then dissolved in THF (10 mL). A separate flame dried flask under argon was charged with potassium bis(trimethylsilyl)amide (211 mg, 1.06 mmol, 1.1 equiv) and THF (10 mL). The flask containing diketone **63** was cooled to –78 °C, and the basic solution was cannula transferred into the cooled solution containing the substrate diketone via a positive pressure of argon. Deprotonation was allowed over 30 min. After this time had elapsed, a solution of *N*-phenyl bis(trifluoromethane)sulfonimide (395 mg, 1.10 mmol, 1.15 equiv) in THF (10 mL) was cannula transferred to the anionic solution under a positive pressure of argon. After 3 h, the reaction was quenched via addition of a solution of saturated NaHCO$_{3\ (aq)}$. The phases were separated, and the aqueous layer was extracted with Et$_2$O (3 x 30 mL). The combined organic layers were washed, sequentially, with 2 N NaOH$_{(aq)}$ (30 mL), 2 N HCl$_{(aq)}$ (30 mL), and brine (2 x 30 mL). The organic layers were then dried over MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude material was purified over silica gel using 0.5% → 1.0% ethyl acetate in hexanes as eluent to afford triflate **66** as a white solid (226 mg, 60% yield): R$_f$ = 0.45 (10:90 ethyl acetate/hexane); ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 5.16 (ddq, *J* = 5.1, 1.7, 1.7 Hz, 1H), 5.08 (dd, *J* = 3.0, 2.0 Hz, 1H), 2.07 (dd, *J* = 10.7, 2.2 Hz, 1H), 2.02 (br. t, *J* = 13.3 Hz, 1 H), 1.94–1.86 (m, 3H), 1.90 (s, 1H), 1.85 – 1.79 (m, 1H), 1.74 (app ddt, *J* = 14.8, 6.8, 1.5 Hz, 1H), 1.59 (s, 3H), 1.57 (d, *J* = 3.4 Hz, 1H), 1.54 (d, *J* = 3.4 Hz, 1H), 1.38–1.31 (m, 1H), 1.35 (dd, *J* = 14.4, 8.5 Hz, 1H), 1.23 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 209.8, 153.2, 141.9, 121.4, 116.0, 57.6, 54.1, 54.0, 51.2, 41.6, 38.1, 36.5, 32.5, 26.2, 25.0, 23.6, 16.8; IR (Neat film, NaCl) 2932, 1709, 1656, 1423, 1382, 1245, 1211, 1141, 1097, 927 cm^{-1}; HRMS (EI) *m/z* calc'd for C$_{17}$H$_{23}$F$_3$O$_4$S [M$^+$]: 392.1269, found 392.1273; $[\alpha]^{25}_D$ –101.9 (*c* 0.63, CH$_2$Cl$_2$).

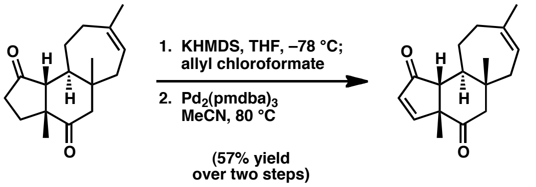


66 *Cyanthiwigin F (6)* (41% yield) *67* (23% yield)

Cyanthiwigin F (6). To a flame dried 1 dram vial under argon was added CuCN (3.8 mg, 40.0 μmol, 1.5 equiv), followed by 0.5 mL of THF. This suspension was cooled to –78 °C, and to this was dropwise added *i*-PrMgCl (40 μL, 1.91 M solution in THF, 80.0 μmol, 3.00 equiv). After complete addition, the reaction was warmed to 0 °C and allowed to remain at this temperature until a homogeneous pale pink solution was obtained (~10 min). A separate solution was then prepared, consisting of Pd(dppf)Cl$_2$ (3.0 mg, 5.0 μmol, 0.15 equiv) and triflate species **66** (10.0 mg, 25.0 μmol, 1.00 equiv) dissolved in 0.5 mL of THF. The solution containing **66** was treated with the organocuprate solution via dropwise cannula addition at 0 °C. This was allowed to react at 0 °C for 3 h, after which time the reaction was quenched with a 1 : 1 mixture of saturated $NH_4Cl_{(aq)}$ and $NH_4OH_{(aq)}$ (1 mL). The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified over silica gel using 1% Et_2O in petroleum ether as eluent to afford colorless crystals (4.4 mg, 63% yield, 1.8 : 1 mixture of **6** : **67**). An analytically pure sample of **6** was prepared via reverse-phase HPLC purification using a gradient of 15% → 30% acetonitrile in water. R_f = 0.30 (5:95 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (app q, *J* = 1.6 Hz, 1H), 5.34 (ddq, *J* = 5.1, 1.5, 1.5 Hz, 1H), 2.60 (d, *J* = 16.1 Hz, 1H), 2.50 (d, *J* = 13.7 Hz, 1H), 2.47 (app t, *J* = 6.4 Hz, 1H), 2.24 (app t, *J* = 13.3 Hz, 1H), 2.19–2.17 (m, 1H), 2.15 (d, *J* = 10.3 Hz, 1 H), 1.99 (app ddt, *J* = 14.6, 6.8, 1.5 Hz, 1H), 1.98 (d, *J* = 14.1 Hz, 1H), 1.89 (dd, *J* = 16.1, 2.4 Hz, 1H), 1.84 (app ddt, *J* = 14.2, 6.8, 2.5 Hz, 1H), 1.74 (s, 3H), 1.73 (app dd, *J* = 14.6, 8.3 Hz, 1H), 1.61 (dt, *J* = 11.0, 2.9 Hz, 1H), 1.25 (m, 1H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.09 (s, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.5, 156.5, 141.8, 121.4, 119.9, 59.8, 55.2, 54.7, 54.3, 42.7, 42.2, 37.8, 33.2, 30.3, 26.4, 25.1, 22.8, 22.4, 21.6, 17.3; IR (Neat film, NaCl) 2961, 2924, 1703, 1444, 1380, 1294, 1144, 912, 858, 810 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{20}H_{30}O_2$ [M$^+$]: 286.2297, found 286.2292; $[\alpha]^{25}_D$ –125.4 (*c* 0.025, MeOH).



Reduction byproduct 67. This material was obtained as a side product from the cross-coupling attempts to synthesize cyanthiwigin F (**6**), presumably as a result of reduction of the triflate moiety of **66**. Compound **67** was later synthesized directly by the following method: To a flame dried vial containing 22 mg of **66** (22 mg, 56.0 μmol, 1.00 equiv) was added dppp (7.0 mg, 17.0 μmol, 0.30 equiv) and PdCl$_2$(dppf) (5.0 mg, 6.83 μmol, 0.12 equiv). The solids were dissolved in DMF (0.5 mL), and the resulting solution was treated with 114 of Bu_3N (114 μL, 0.479 μmol, 0.009 equiv) and 11 of formic acid (11 μL, 0.292 μmol, 0.005 equiv) (Note: Upon addition of the formic acid, the reaction evolves white smoke). The reaction mixture was heated to 95 °C for 4 h, after which time all of the starting triflate was observed to be consumed by TLC. The reaction was quenched by the addition of brine (1 mL), followed by dilution with Et_2O (2 mL). The aqueous and organic phases were separated, and the aqueous phase was thereafter extracted with Et_2O (3 x 10 mL). The combined organic phases were washed with 2 N $HCl_{(aq)}$ (5 mL) to remove any residual amine, then washed with brine (3 mL). The collected organic phases were dried over $MgSO_4$, filtered, and then concentrated in vacuo. The resulting crude material was purified over silica gel using 2% Et_2O in petroleum ether to afford **67** as a white solid (4.0 mg, 29% yield): R_f = 0.30 (5:95 ethyl acetate/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00–5.94 (m, 1H), 5.72–5.68 (m, 1H), 5.39–5.30 (m, 1H), 2.55 (ddd, *J* = 16.6, 4.4, 2.2 Hz, 1H), 2.39 (d, *J* = 14.9 Hz, 1H), 2.23 (t, *J* = 13.5 Hz, 1H), 2.18–2.12 (comp. m, 1H), 2.08 (dd, *J* = 2.7, 1.1 Hz, 1H), 2.03 (dd, *J* = 2.7, 1.2 Hz, 1H), 2.02 (d, *J* = 14.7 Hz, 1H), 2.01 (dddd, *J* = 14.6, 6.9, 1.5, 1.5 Hz 1H), 1.99 (d, *J* = 14.6 Hz, 1H), 1.97–1.94 (m, 1H), 1.75 (s, 3H), 1.61 (s, 1H), 1.43–1.35 (m, 1H), 1.12 (s, 3H), 0.7 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.7, 142.0, 134.9, 128.0, 121.5, 59.4, 55.8, 54.9, 51.9, 43.8, 41.9, 37.5, 33.1, 26.6, 25.3, 23.8, 16.8; IR (Neat film, NaCl) 2961, 2927, 1702, 1559, 1441, 1380, 1293, 1257, 1140, 856, 726 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O$ [M$^+$]: 244.1827, found 244.1821; $[\alpha]^{25}_{D}$ –238.4 (*c* 0.02, MeOH).

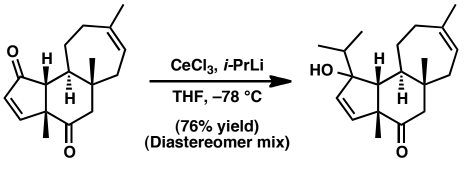


63 *69*

Tricyclic Enone 69. A flame dried vial charged with tricyclic diketone **63** (22 mg, 77.0 μmol, 1.00 equiv), and this material was thereafter dissolved in THF (200 μL). A separate flame dried vial was backfilled with argon and cycled into a glovebox. Once inside, this vessel was charged with KHMDS (19 mg, 95.0 μmol, 1.30 equiv), and then was removed from the glovebox. Once placed on a manifold line, the KHMDS was dissolved in THF (200 μL). Both solutions were cooled to –78 °C, and then the KHMDS solution was added dropwise to the solution of diketone **63**. The mixed solutions were allowed to deprotonate at –78 °C for 30 min, after which time allyl chloroformate (10 μL, 92.0 μmol, 1.20 equiv) was added. This was allowed to react for a further 2.5 h at –78 °C. Once this time had elapsed, the reaction was warmed slowly to room temperature, and then was quenched with an excess of saturated

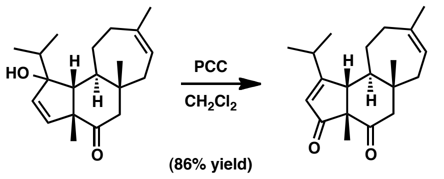
$NH_4Cl_{(aq)}$. The phases were separated, and the aqueous layer was extracted with diethyl ether (4 x 10 mL). The combined organic layers were washed with brine (5 mL), then dried over $MgSO_4$, filtered, and concentrated. The crude material obtained was briefly passed over a plug of silica gel using 3% ethyl acetate in hexanes as eluent. The material obtained from this rapid purification was used directly in the next reaction without further characterization.

The material obtained from the silica plug above (ca. 16.6 mg) was transferred to a flame dried vial under argon, and then was azeotroped thrice from acetonitrile. The material was briefly dried under high vacuum, and then $Pd_2(pmdba)_3$ (2.8 mg, 2.0 μmol, 0.05 equiv) and acetonitrile (250 μL) were added. The reaction vial was sealed, and then the reaction was heated to 80 °C. After 2 h, the vial was cooled to room temperature, and solvent was removed in vacuo. The crude material obtained was purified via chromatography over silica using 5% ethyl acetate in hexanes as eluent. This afforded enone **69** as a colorless oil (11 mg, 57% yield): $R_f = 0.60$ (10:90 ethyl acetate/hexane); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 5.5 Hz, 1H), 6.09 (d, J = 5.5 Hz, 1H), 5.33 (dddd, J = 8.7, 5.2, 3.6, 1.7 Hz, 1H), 2.37 (app ddt, J = 14.3, 6.8, 2.2 Hz, 1H), 2.27–2.14 (m, 2H) 2.21 (dd, J = 15.7, 0.7 Hz, 1H), 2.15 (d, J = 15.7 Hz, 1H), 2.04 (d, J = 11.0 Hz, 1H), 2.03 (app ddt, J = 15.0, 6.7, 1.5 Hz, 1H) 1.75 (s, 3H), 1.77–1.67 (m, 1H), 1.35 (s, 3H), 1.27 (app dtd, J = 13.9, 12.1, 1.7 Hz, 1H), 1.21 (d, J = 15.1 Hz, 1H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.7, 210.6, 165.9, 142.7, 131.4, 120.7, 59.1, 56.8, 55.5, 51.7, 41.7, 38.4, 32.9, 26.9, 26.0, 25.3, 17.9; IR (Neat film, NaCl) 2963, 2925, 2867, 1703, 1590, 1444, 1381, 1331, 1255, 1227, 1184, 1070, 996 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{17}H_{22}O_2$ $[M^+]$: 258.1620, found 258.1622; $[\alpha]^{25}_D$ –210.9 (*c* 0.97, CH_2Cl_2).



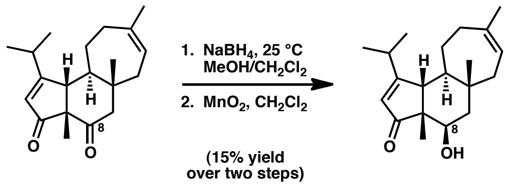
69 *70*

Allylic alcohol 70. To a flame dried vial was added enone **69** (29 mg, 0.112 mmol, 1.00 equiv). This material was briefly vacuum purged, and then was backfilled with argon. The vial was cycled into the glovebox, where it was charged with $CeCl_3$ (31 mg, 0.118 mmol, 1.05 equiv). The vial was then removed from the glovebox, placed under a manifold line, charged with THF (1.1 mL), and cooled to –78 °C. After reaching the desired temperature, isopropyl lithium (200 μL, 0.7 M in hexanes, 0.135 mmol, 1.20 equiv) was added to the suspension dropwise at –78 °C. The reaction was allowed to reach room temperature slowly by warming in the bath overnight. The reaction looked incomplete the next morning, and so was allowed to continue for an additional 14 h (total 22 h). The reaction was thereafter quenched with saturated $NH_4Cl_{(aq)}$ (2 mL). The phases were separated, and the aqueous layer was extracted with diethyl ether (4 x 5 mL). The combined organics were washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material obtained was purified via chromatography over silica gel using 7% → 8% → 9% ethyl acetate in hexanes as eluent. This afforded allylic alcohol **70** as a clear oil (26 mg, isolated as two diastereomers, 76% combined yield). **Diastereomer A**: R_f = 0.40 (20:80 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (d, *J* = 5.6 Hz, 1H), 5.54 (d, *J* = 5.6 Hz, 1H), 5.33 (dddd, *J* = 8.6, 5.1, 3.4, 1.6 Hz, 1H), 2.27 (dd, *J* = 15.4, 0.9 Hz, 1H), 2.25 (m, 1H) 2.06 (d, *J* = 15.4 Hz, 1H), 2.00 (app ddt, *J* = 14.9, 6.6, 1.5 Hz, 1H), 1.99 (d, *J* = 10.6 Hz, 2H), 1.91 (app ddt, *J* = 13.6, 6.6, 2.1 Hz, 1H), 1.85 (app dt, *J* = 10.6, 2.1 Hz, 1H), 1.81–1.73 (comp. m, 3H), 1.75 (s, 3H), 1.30 (s, 3H), 1.11 (dddd, *J* = 13.6, 12.1, 10.6, 1.6 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.6, 142.3, 137.3, 36.2, 121.2, 90.3, 59.9, 57.2, 55.1, 49.5, 42.9, 39.0, 36.6, 33.6, 28.5, 26.9, 25.5, 18.7, 18.2, 18.0; IR (Neat film, NaCl) 3494, 2968, 2923, 1694, 1456, 1382, 1286, 1249, 1137, 1110, 979 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{30}O_2$ [M$^+$]: 302.2246, found 302.2248; $[\alpha]^{25}_{D}$ –89.3 (*c* 0.72, CH_2Cl_2). **Diastereomer B**: R_f = 0.20 (20:80 ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (d, *J* = 5.8 Hz, 1H), 5.62 (d, *J* = 5.8 Hz, 1H), 5.38–5.33 (m, 1H), 2.30 (d, *J* = 18.1 Hz, 1H), 2.27–2.20 (m, 2H), 2.10 (dd, *J* = 18.1, 0.5 Hz, 2H), 2.01 (d, *J* = 10.7, 2H), 1.86 (dd, *J* = 14.5, 8.9 Hz, 2H), 1.81–1.75 (m, 2H), 1.77 (s, 3H), 1.47 (s, 3H) 1.41–1.34 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.05 (s, 3H), 0.71 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 138.5, 121.8, 92.5, 62.8, 59.3, 54.3, 48.9, 44.4, 36.2, 33.6, 31.5, 30.3, 29.3, 25.9, 21.0, 19.9, 18.5; IR (Neat film, NaCl) 3472, 2963, 2925, 1698, 1449, 1382, 1287, 1246, 1012, 980, 795 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{30}O_2$ [M$^+$]: 302.2246, found 302.2249; $[\alpha]^{25}_{D}$ –67.3 (*c* 0.16, CH_2Cl_2).



70 Cyanthiwigin B (2)

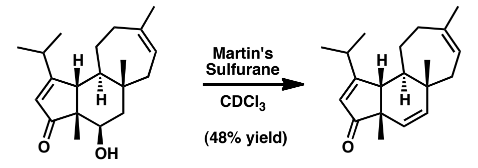
Cyanthiwigin B (2). To a flame dried vial was added allylic alcohol **70** (8.2 mg, 27.0 μmol, 1.00 equiv). This was dissolved in CH_2Cl_2 (275 μL), and then was treated with PCC (23 mg, 108.0 μmol, 4.00 equiv). This reaction was allowed to stir at room temperature for 14 h, and then was diluted with diethyl ether (1 mL) and passed over a plug of celite. The celite pad was washed with additional diethyl ether (5 mL), and the collected organic solvents were concentrated to dryness. The residue obtained was purified over silica gel using 6.5% ethyl acetate in hexanes as eluent. This afforded cyanthiwigin B (**2**) as a white solid (7.0 mg, 86% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (s, 1H), 5.30–5.25 (m, 1H), 2.73 (app dt, *J* = 13.5, 6.7 Hz, 1H), 2.54 (d, *J* = 9.2 Hz, 1H), 2.20–2.12 (m, 1H), 2.10 (s, 1H), 2.09 (dd, *J* = 13.6, 0.7 Hz, 1H), 2.02 (app ddt, *J* = 15.1, 6.5, 1.6 Hz, 1H), 2.00 (d, *J* = 13.7 Hz, 1H), 1.81 (app ddt, *J* = 14.2, 6.6, 2.0 Hz, 1H), 1.71 (dd, *J* = 14.8, 8.7 Hz, 1H), 1.69 (s, 3H), 1.56 (ddd, *J* = 11.4, 9.3, 2.2 Hz, 1H), 1.47–1.39 (m, 1H), 1.24 (s, 3H), 1.23 (d, *J* = 6.5 Hz, 3H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 141.4, 123.2, 121.7, 63.7, 58.9, 56.8, 56.2, 42.6, 39.1, 33.7, 31.4, 31.2, 28.5, 25.8, 25.2, 21.9, 21.4, 18.3; IR (Neat film, NaCl) 2920, 1723, 1693, 1602, 1452, 1261, 1161, 866 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{28}O_2$ [M^+]: 300.2089, found 300.2093. $[\alpha]^{24}_D$ –215.2 (*c* 0.84, CH_2Cl_2), $[\alpha]^{25}_D$ –195.7 (*c* 0.84, MeOH).



Cyanthiwigin B (2) 8-epi-Cyanthiwigin E (71)

8-*epi*-Cyanthiwigin E (71). To a flame dried vial was added cyanthiwigin B (**2**, 7.2 mg, 24.0 μmol, 1.00 equiv). The solids were dissolved in a 1 : 1 mixture of CH_2Cl_2 and methanol (1.0 mL). In a separate flame dried vial, $NaBH_4$ (23 mg) was dissolved in 1 : 1 mixture of CH_2Cl_2 and methanol (2.0 mL). Both solutions were cooled to –78 °C, and then a portion of the $NaBH_4$ solution (100 μL, 1.1 mg, 30.0 μmol, 1.20 equiv) was added to the solution of cyanthiwigin B (**2**). After 1 h, no conversion was observed, and so an additional portion of the $NaBH_4$ solution was added (100 μL, 1.1 mg, 30.0 μmol, 1.2 equiv). After no conversion was observed over an additional 2.5 h period, an additional portion of the $NaBH_4$ solution was added (200 μL, 2.2 mg, 60.0 μmol, 2.40 equiv) and the temperature of reaction was warmed to –45 °C. The reaction was thereafter allowed to progress overnight. After an additional 8 h of reaction, conversion was still incomplete, and so reaction was pushed to completion by the addition of solid $NaBH_4$ (4.0 mg, 106.0 μmol, 4.40 equiv). The reaction was allowed to stir for 3 h, and then was quenched with acetone (1 mL) and 2 N $NaOH_{(aq)}$ (5 mL). The phases were separated, and the organic layer was washed immediately with brine (5 mL), and then dried over Na_2SO_4. The reaction was filtered and the solvent was removed in vacuo. The crude material obtained was purified over silica using 20% → 30% ethyl acetate in hexanes as eluent. Repurification was then executed using 7% → 10% → 20% → 50% ethyl acetate in hexanes as eluent. The material obtained as a white solid was difficult to characterize, and so was taken directly into the next reaction.

The white solid obtained above (ca. 2.2 mg) and MnO_2 (9.0 mg, 108.0 μmol, 15.0 equiv) were added to a flame dried vial. These solids were suspended in CH_2Cl_2 (0.5 mL), and were allowed to stir at room temperature for 15 h. The reaction was then passed over a plug of celite, and the plug was washed with ethyl acetate (15 mL). The solvent was removed in vacuo, and the crude material was purified via chromatography over silica using 6% ethyl acetate in hexanes as eluent. The material obtained was then repurified over silica using 4% ethyl acetate in hexanes as eluent. This afforded 8-*epi*-cyanthiwigin E (**71**) as a white solid (1.1 mg, 15% over two steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.40–5.35 (m, 1H), 4.15 (ddd, *J* = 11.3, 5.0, 2.2 Hz, 1H), 2.63 (app dt, *J* = 13.6, 6.9, 1H), 2.53 (d, *J* = 2.2 Hz, 1H), 2.45 (d, *J* = 10.8 Hz, 1H), 2.29–2.20 (m, 1H), 2.12–2.04 (m, 1H), 1.98 (app ddt, *J* = 15.0, 6.3, 1.6 Hz, 1H), 1.89 (dd, *J* = 14.8, 8.8 Hz, 1H), 1.71 (s, 3H), 1.63 (dd, *J* = 13.8, 11.3 Hz, 1H), 1.57 (d, *J* = 5.1 Hz, 1H), 1.43–1.28 (comp. m, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.9 Hz, 3H), 1.10 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.9, 193.9, 139.4, 125.4, 123.1, 77.4, 67.4, 56.6, 55.3, 55.0, 44.8, 44.4, 35.2, 34.2, 33.5, 25.7, 25.3, 23.3, 22.1, 20.4, 19.6; IR (Neat film, NaCl) 3429, 2963, 2918, 1684, 1602, 1444, 1367, 1270, 1002 cm^{-1}; HRMS (MM: ESI-APCI) *m/z* calc'd for $C_{20}H_{30}O_2$ [M$^+$]: 302.2246, found 302.2248; $[\alpha]^{23}_{D}$ –7.19 (*c* 0.16, MeOH).



8-epi-Cyanthiwigin E (71) *Cyanthiwigin G (7)*

Cyanthiwigin G (7). To a flame dried vial was added *epi*-8-cyanthiwigin E (**71**, 1.1 mg, 4.0 μmol, 1.00 equiv). This vial was then cycled into the glovebox directly, and then was treated with Martin's sulfurane (6.2 mg, 9.0 μmol, 2.50 equiv). The vial was removed from the glovebox and transferred to a manifold line, where it was then charged with $CDCl_3$ (250 μL) and allowed to react at room temperature for 5 h. After this time had elapsed, the reaction was directly loaded onto a silica gel column and purified via chromatography using 3% ethyl acetate in hexanes as eluent. This afforded cyanthiwigin G (**7**) as a white solid (0.5 mg, 48% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (d, *J* = 0.9 Hz, 1H), 5.69 (d, *J* = 9.9 Hz, 1H), 5.54 (d, *J* = 9.9 Hz, 1H), 5.39–5.35 (m, 1H), 2.75–2.67 (m, 1H), 2.48 (d, *J* = 10.4, 1H), 2.22–2.12 (comp. m, 2H), 1.96 (app ddt, *J* = 14.7, 6.7, 1.4 Hz, 1H), 1.89 (dd, *J* = 14.5, 8.6 Hz, 1H), 1.74 (s, 3H), 1.77–1.67 (m, 1H), 1.36–1.29 (comp. m, 2H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.15 (s, 3H), 1.13 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.5, 192.1, 141.4, 140.9, 127.3, 124.4, 122.2, 58.2, 55.3, 53.8, 41.5, 37.6, 33.7, 33.4, 30.5, 28.4, 26.1, 25.2, 23.2, 20.3, 19.8; IR (Neat film, NaCl) 2962, 2921, 1706, 1601, 1444, 1366, 1261, 1156, 1091, 863, 761 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{20}H_{29}O$ [M+H]: 285.2218, found 285.2221; $[\alpha]^{25}_{D}$ –12.35 (*c* 0.10, MeOH).

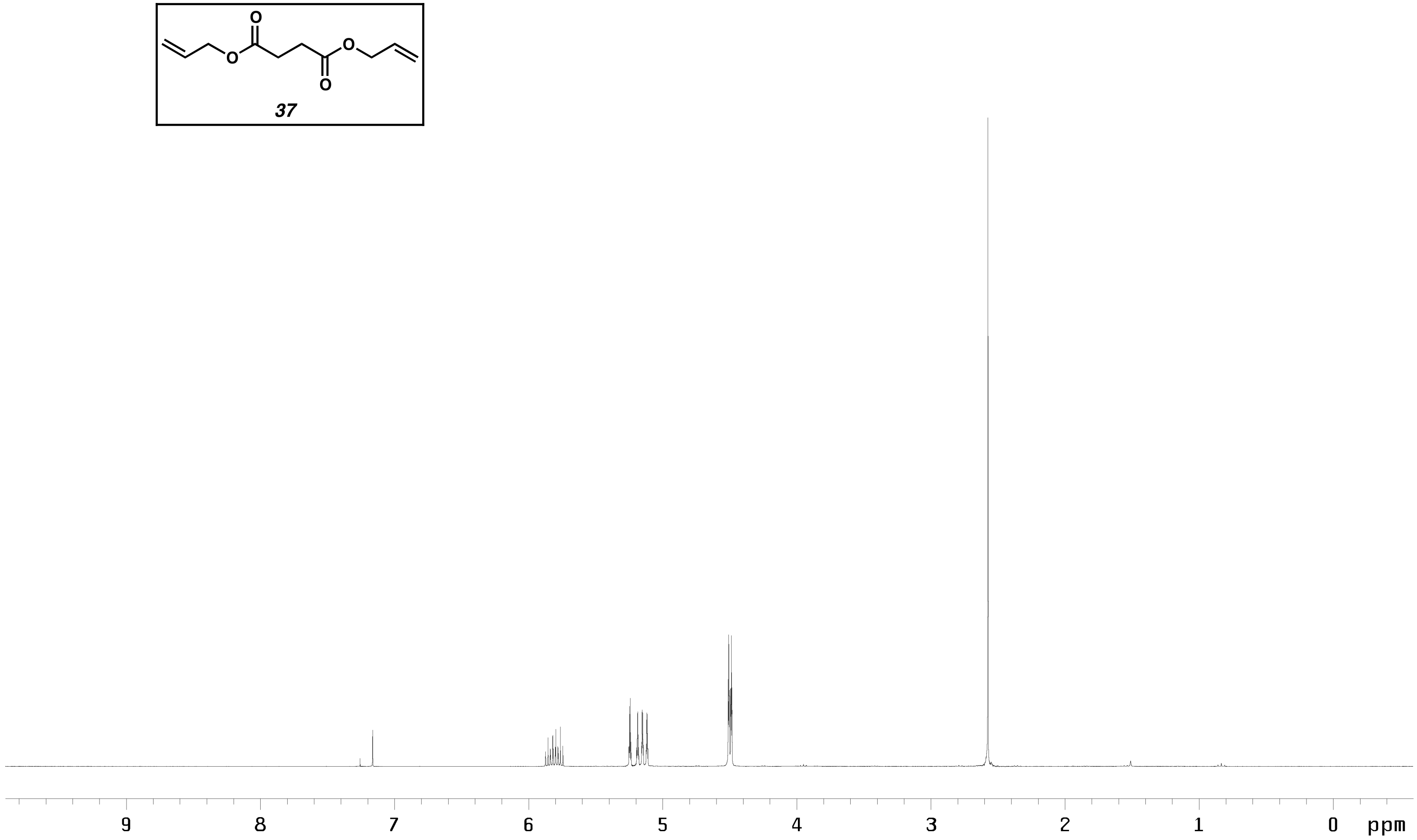


Figure S.1 ^{1}H NMR (300 MHz, $CDCl_3$) of diallyl succinate (3**7**).

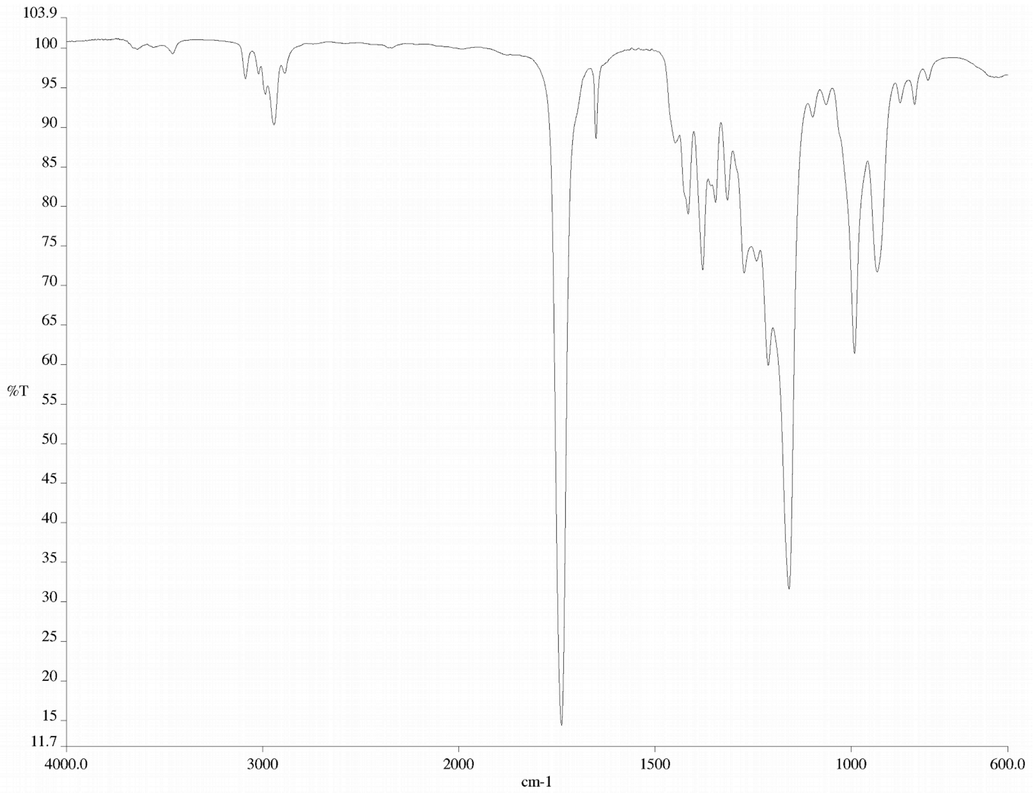


Figure S.2 Infrared spectrum (thin film/NaCl) of diallyl succinate (**37**).

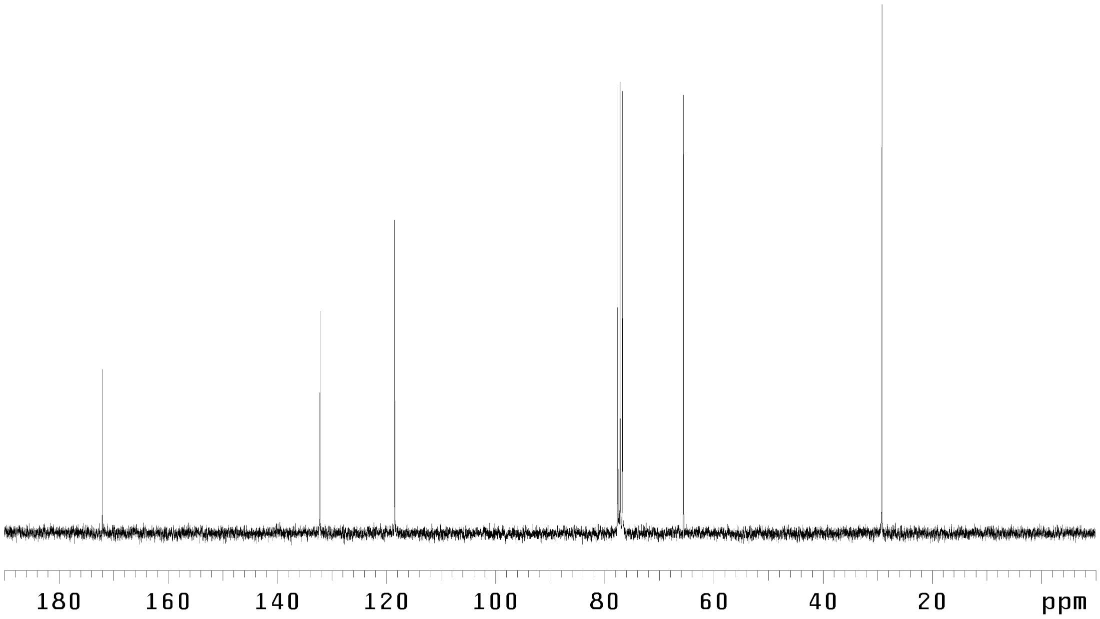


Figure S.3 ^{13}C NMR (75 MHz, CDCl$_3$) of diallyl succinate (**37**).

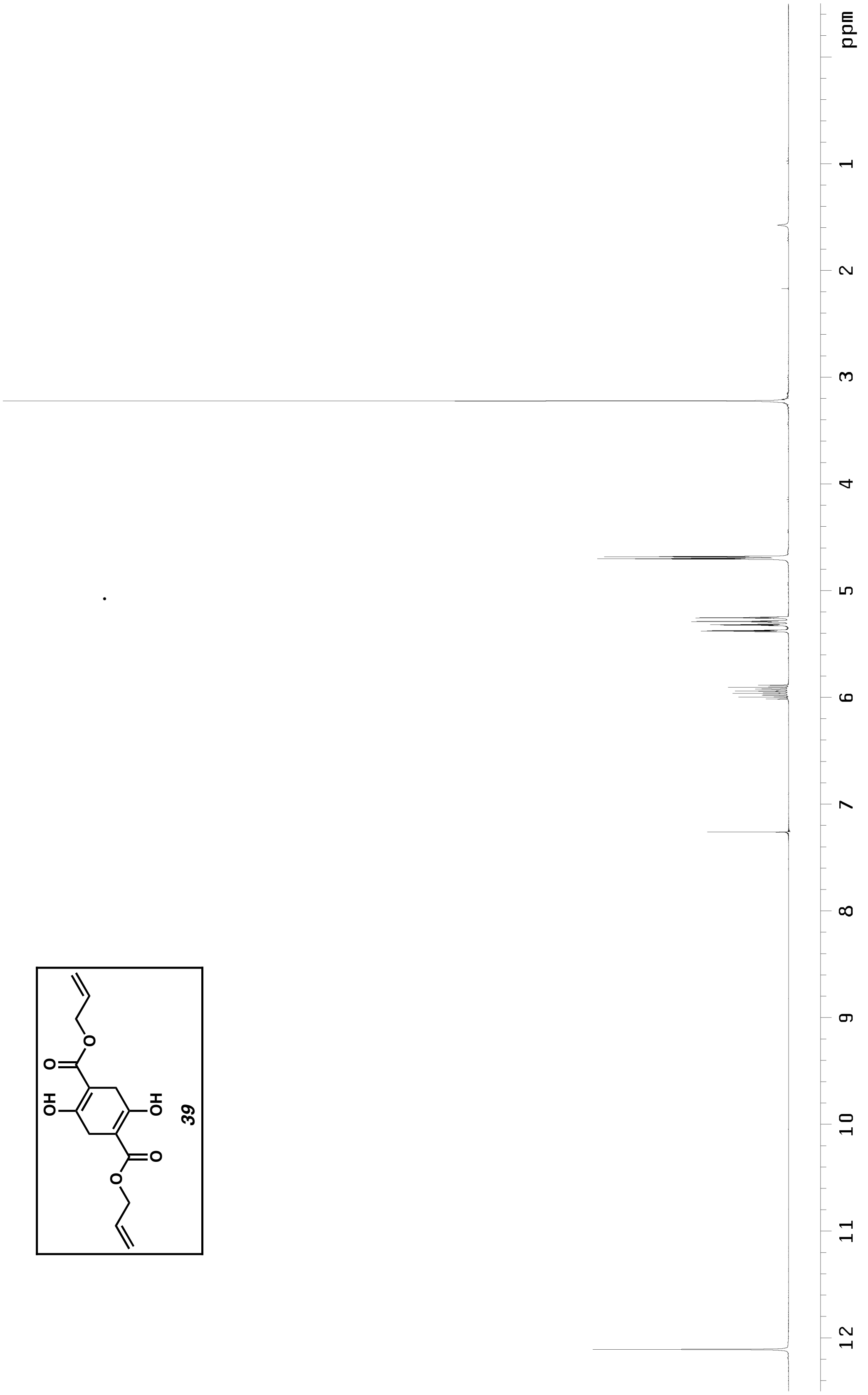


Figure S.4 ^{1}H NMR (300 MHz, CDCl$_3$) of diallyl succinyl succinate (**39**).

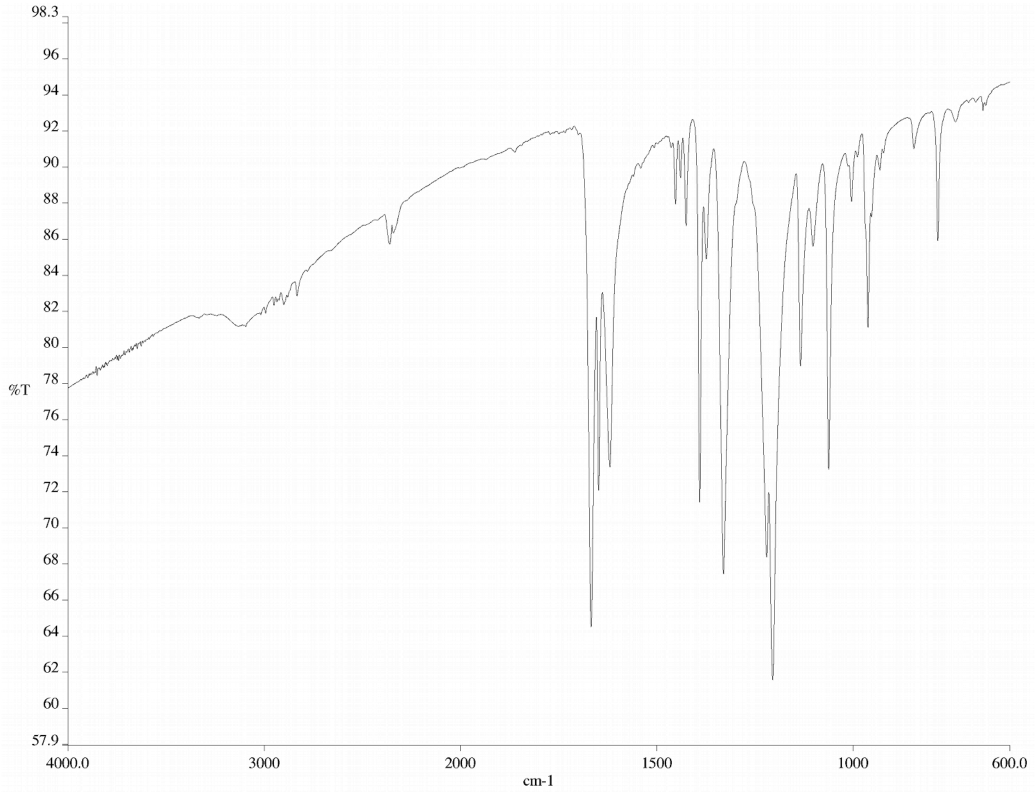


Figure S.5 Infrared spectrum (thin film/NaCl) of diallyl succinyl succinate (**39**).

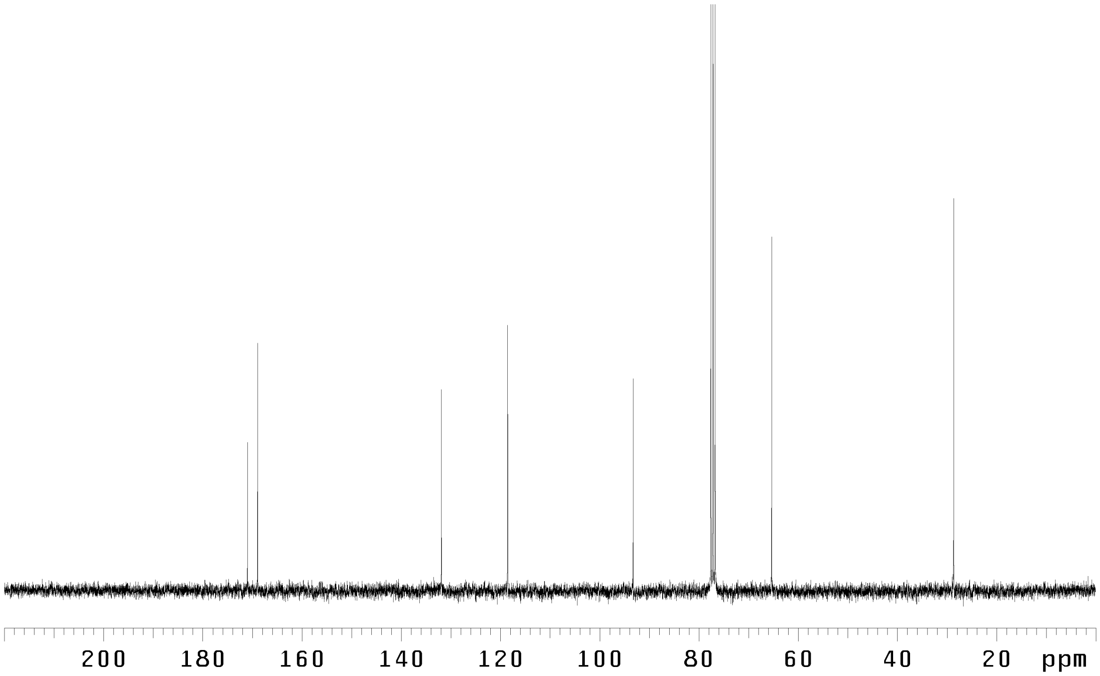


Figure S.6 ^{13}C NMR (75 MHz, $CDCl_3$) of diallyl succinyl succinate (**39**).

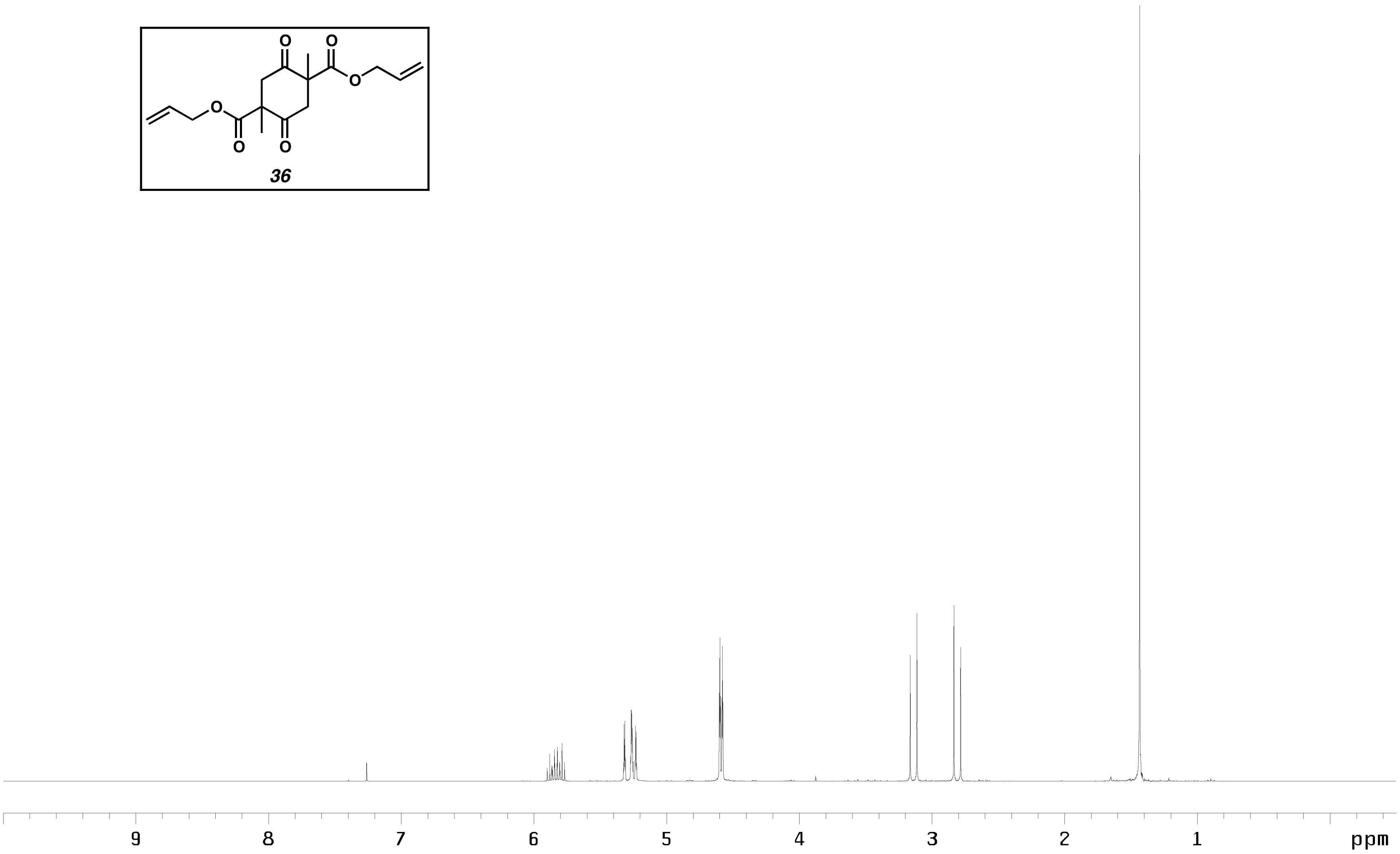


Figure S.7 ^{1}H NMR (300 MHz, $CDCl_3$) of bis(β-ketoester) **36**.

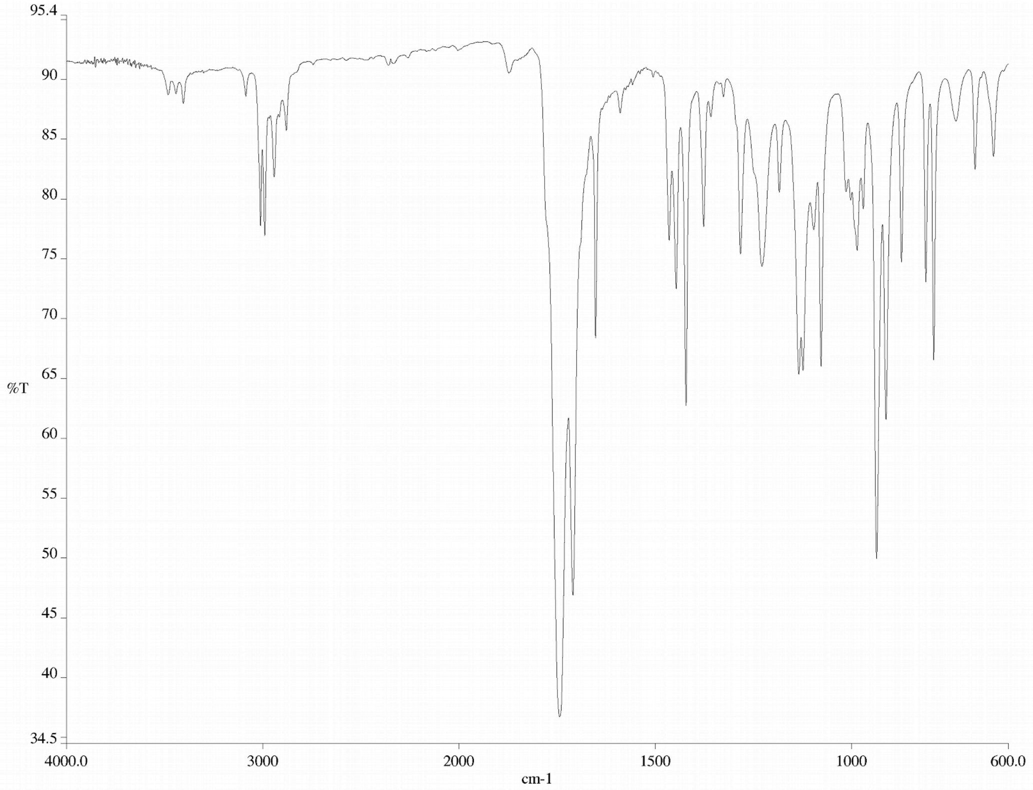


Figure S.8 Infrared spectrum (thin film/NaCl) of bis(β-ketoester) **36**.

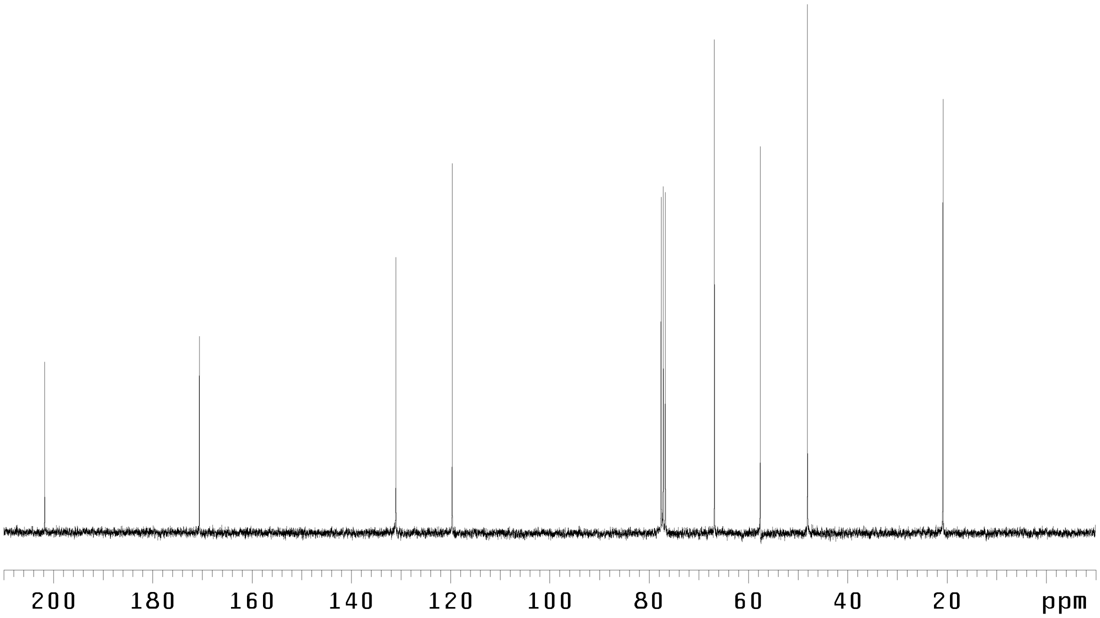


Figure S.9 ^{13}C NMR (75 MHz, CDCl$_3$) of bis(β-ketoester) **36**.

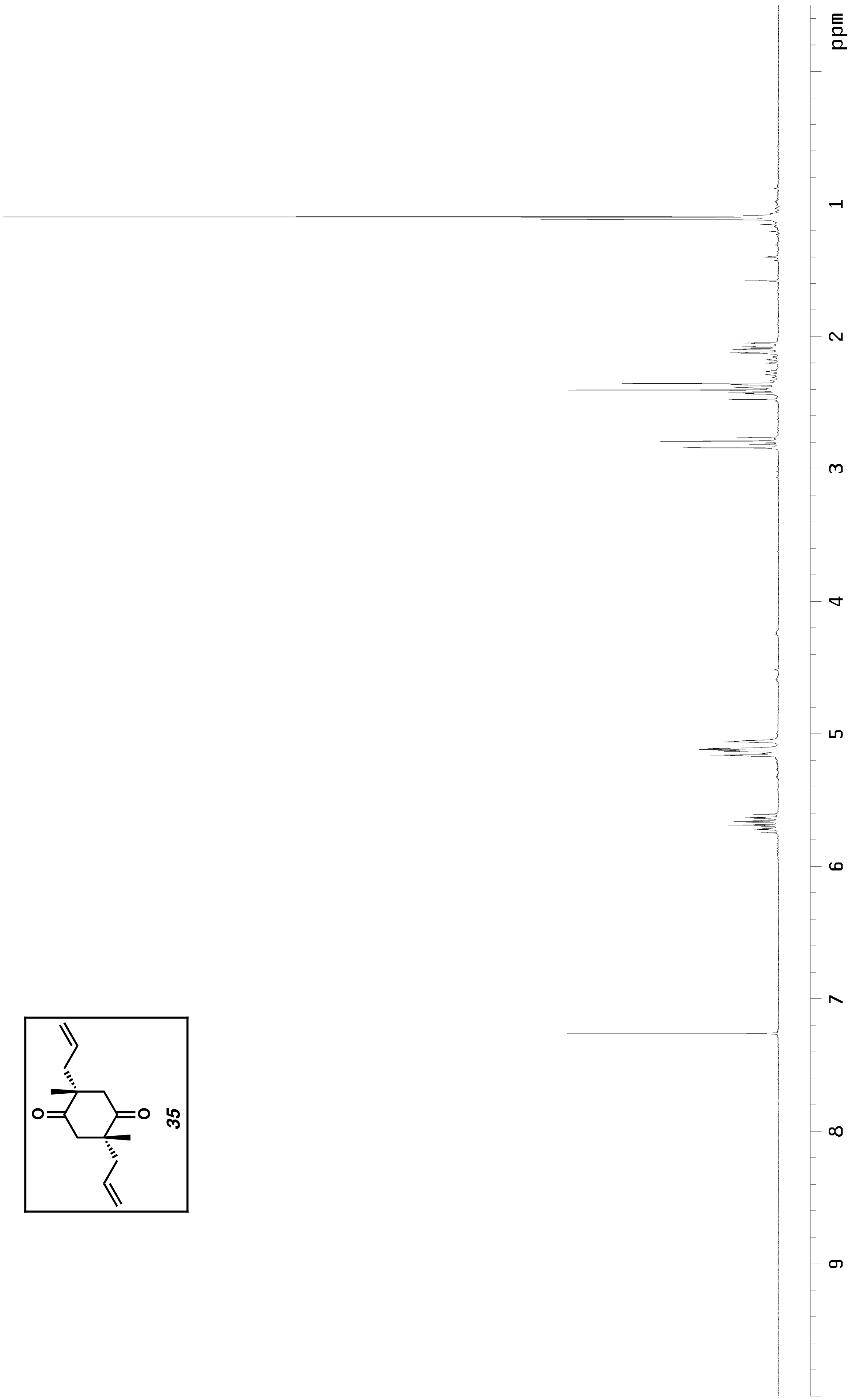


Figure S.10 ^{1}H NMR (300 MHz, CDCl$_3$) of diketone **35**.

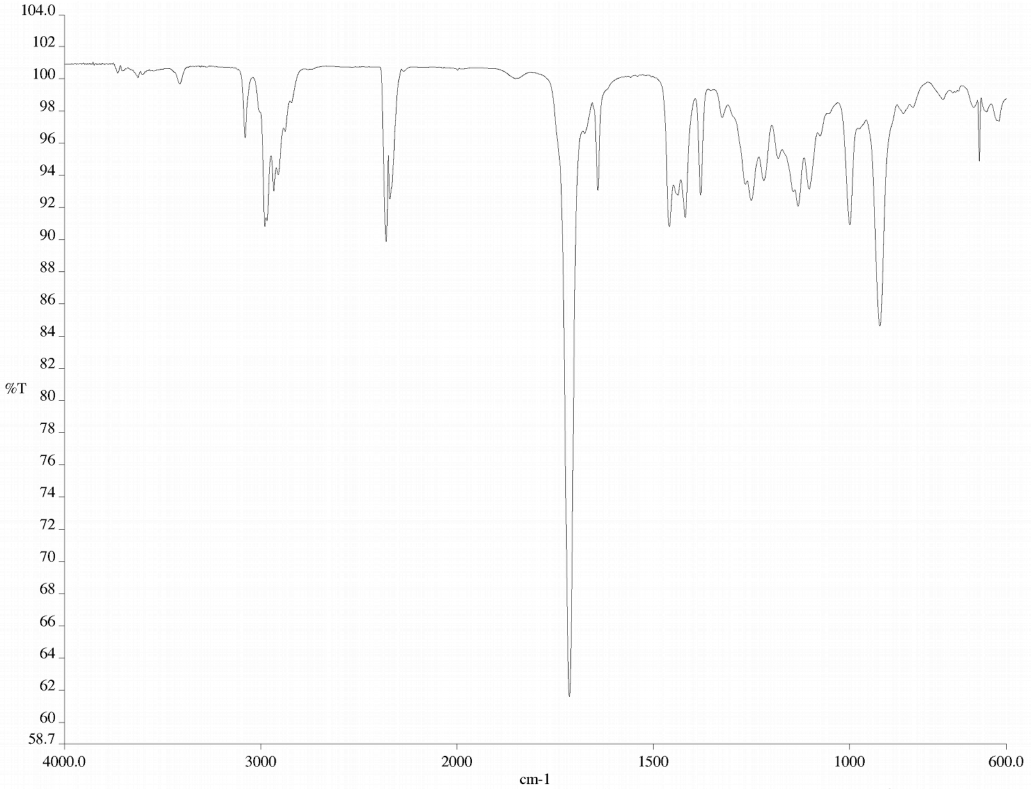


Figure S.11 Infrared spectrum (thin film/NaCl) of diketone **35**.

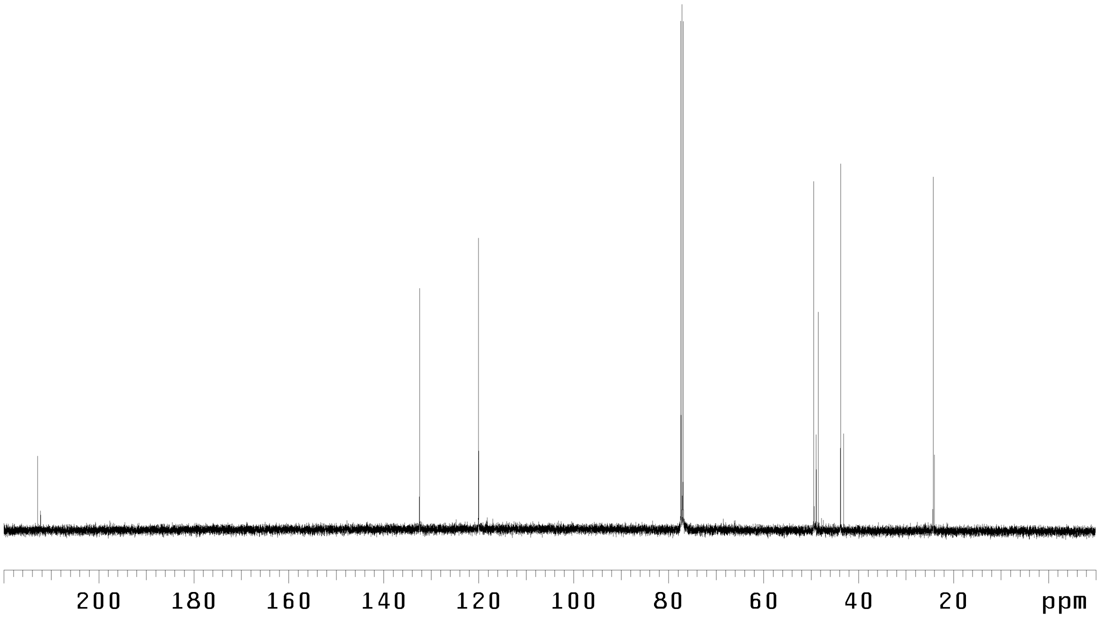


Figure S.12 ^{13}C NMR (125 MHz, CDCl$_3$) of diketone **35**.

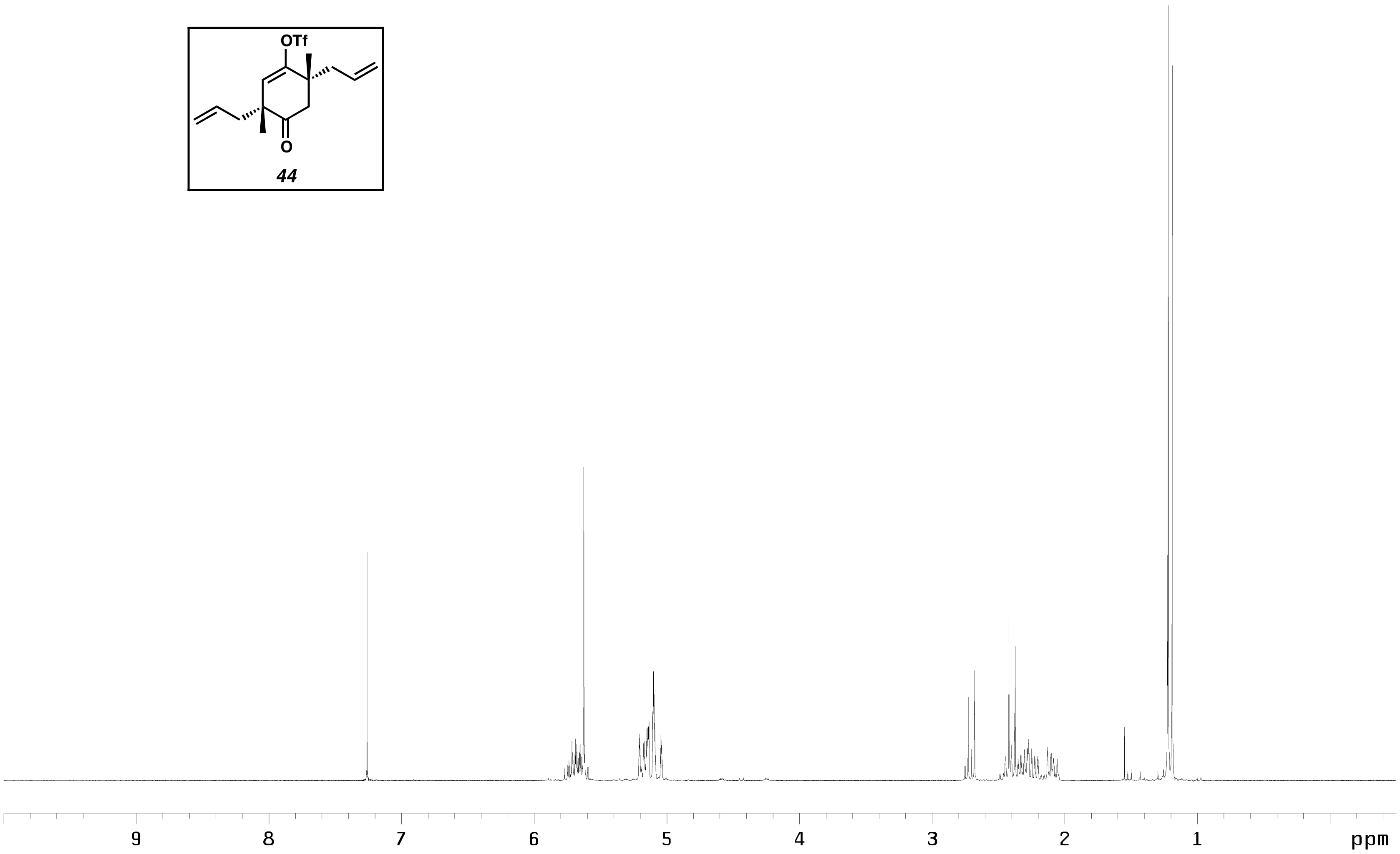


Figure S.13 ^{1}H NMR (300 MHz, $CDCl_3$) of triflate **44**.

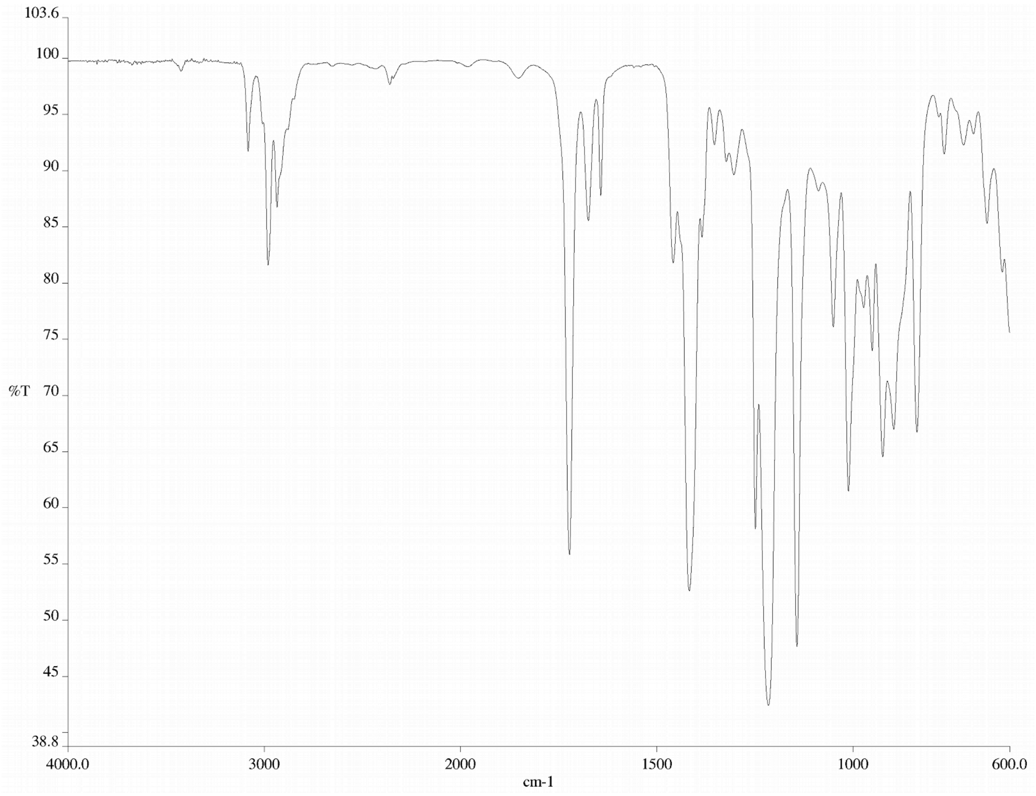


Figure S.14 Infrared spectrum (thin film/NaCl) of trilfate **44**.

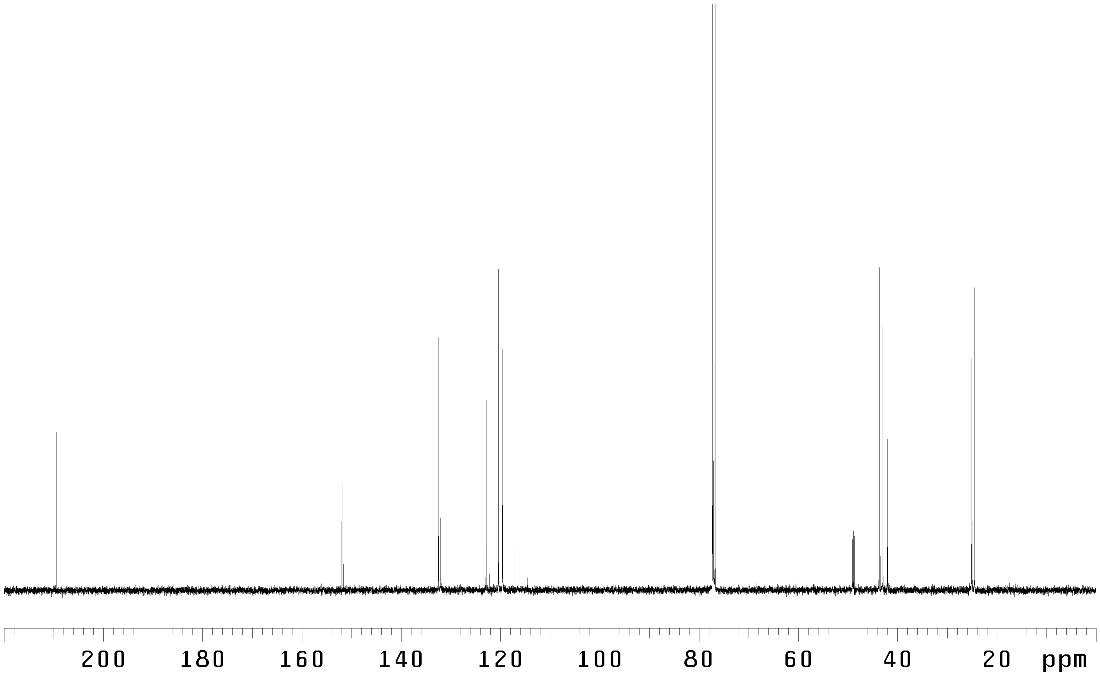


Figure S.15 ^{13}C NMR (125 MHz, CDCl$_3$) of triflate **44**.

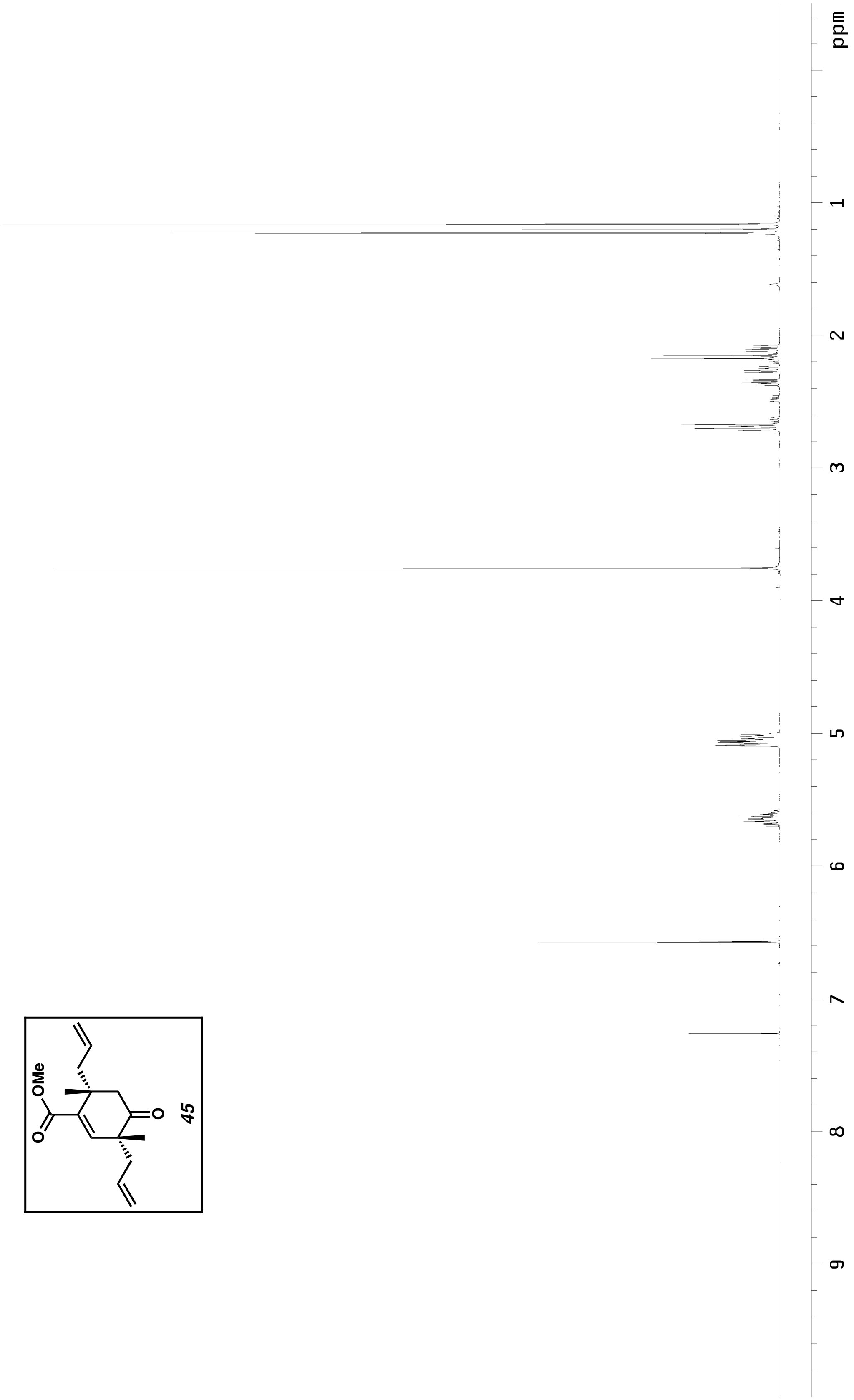


Figure S.16 ^{1}H NMR (500 MHz, CDCl$_3$) of enoate **45**.

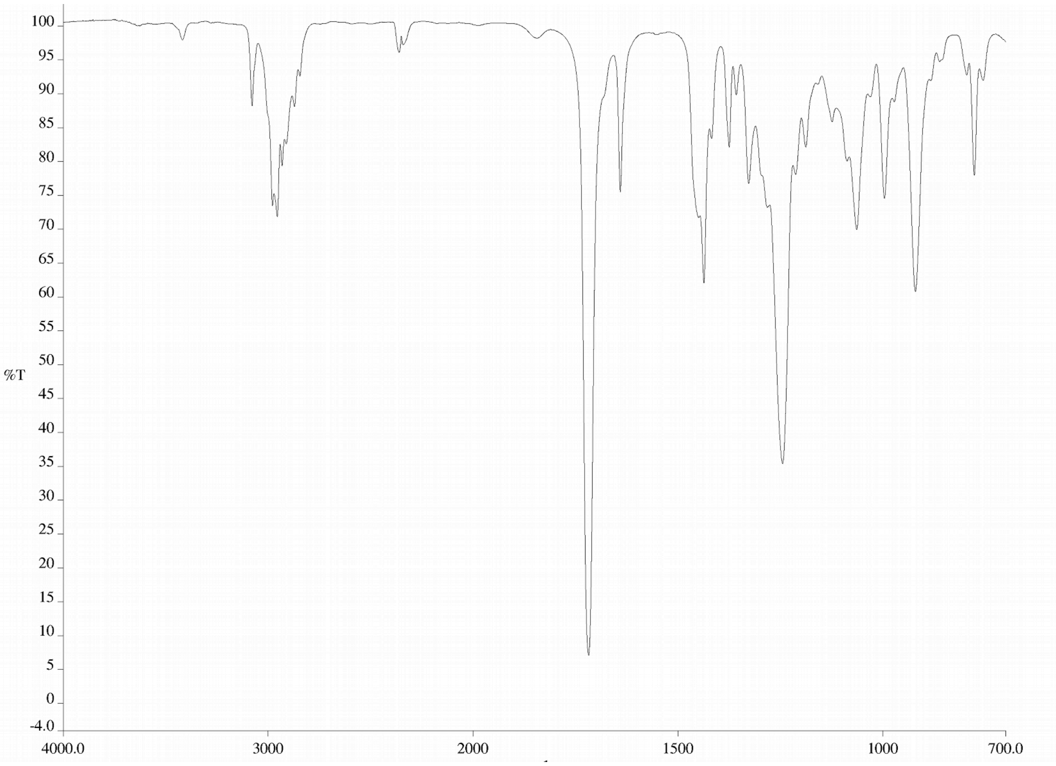


Figure S.17 Infrared spectrum (thin film/NaCl) of enoate **45**.

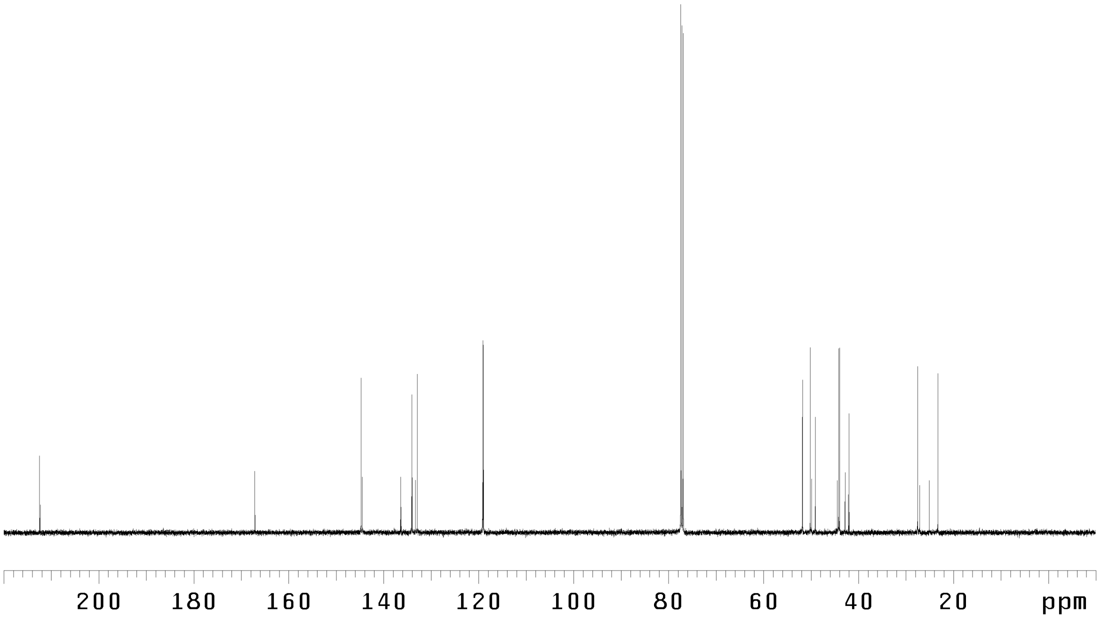


Figure S.18 ^{13}C NMR (125 MHz, CDCl$_3$) of enoate **45**.

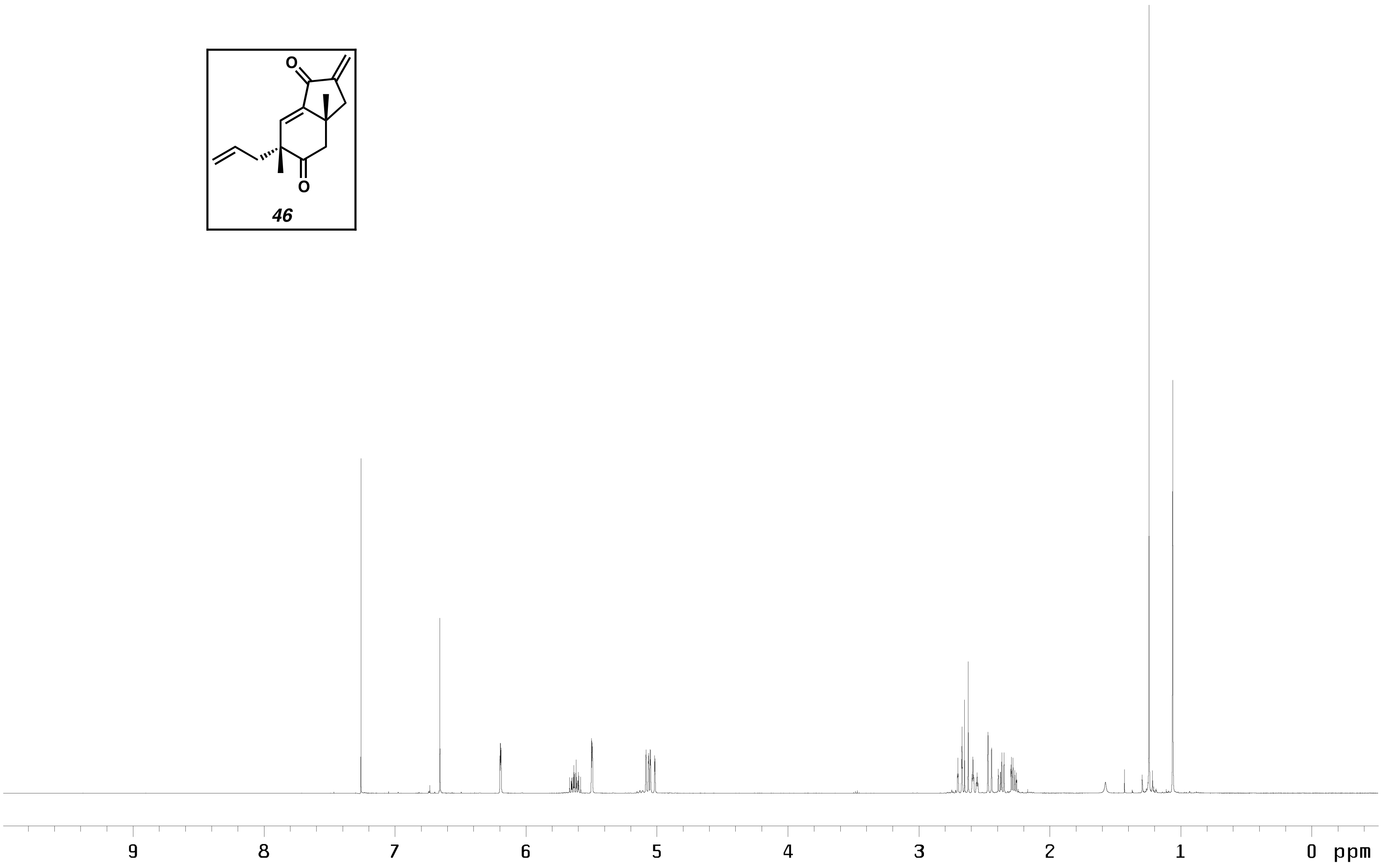


Figure S.19 ^{1}H NMR (500 MHz, $CDCl_3$) of cyclopentadienone **46**.

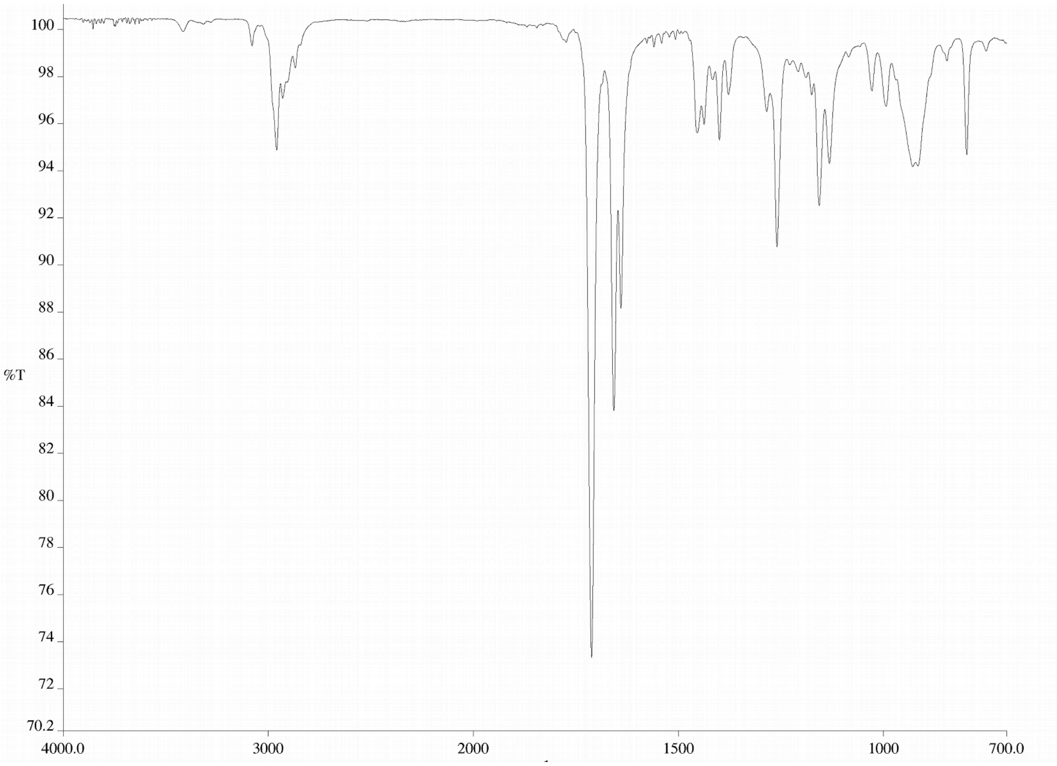


Figure S.20 Infrared spectrum (thin film/NaCl) of cyclopentadienone **46**.

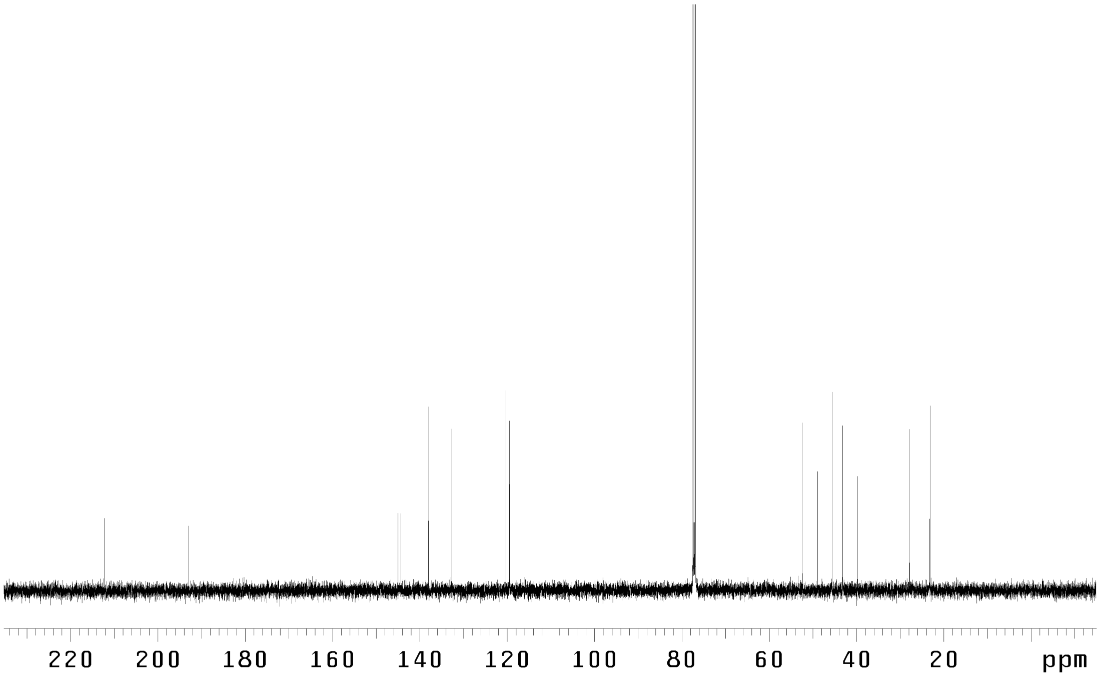


Figure S.21 ^{13}C NMR (125 MHz, $CDCl_3$) of cyclopentadienone **46**.

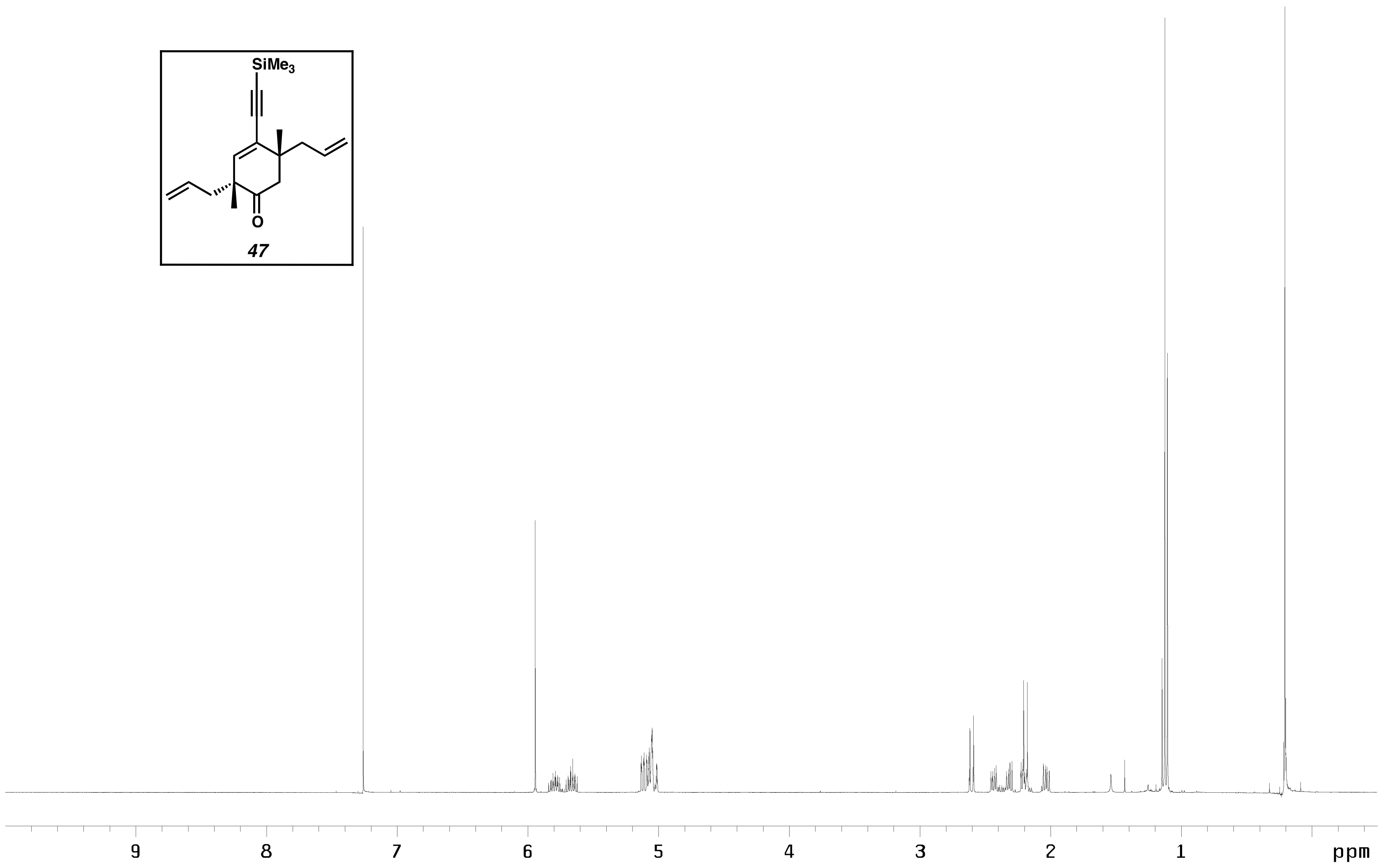


Figure S.22 ^{1}H NMR (500 MHz, CDCl$_3$) of alkyne **47**.

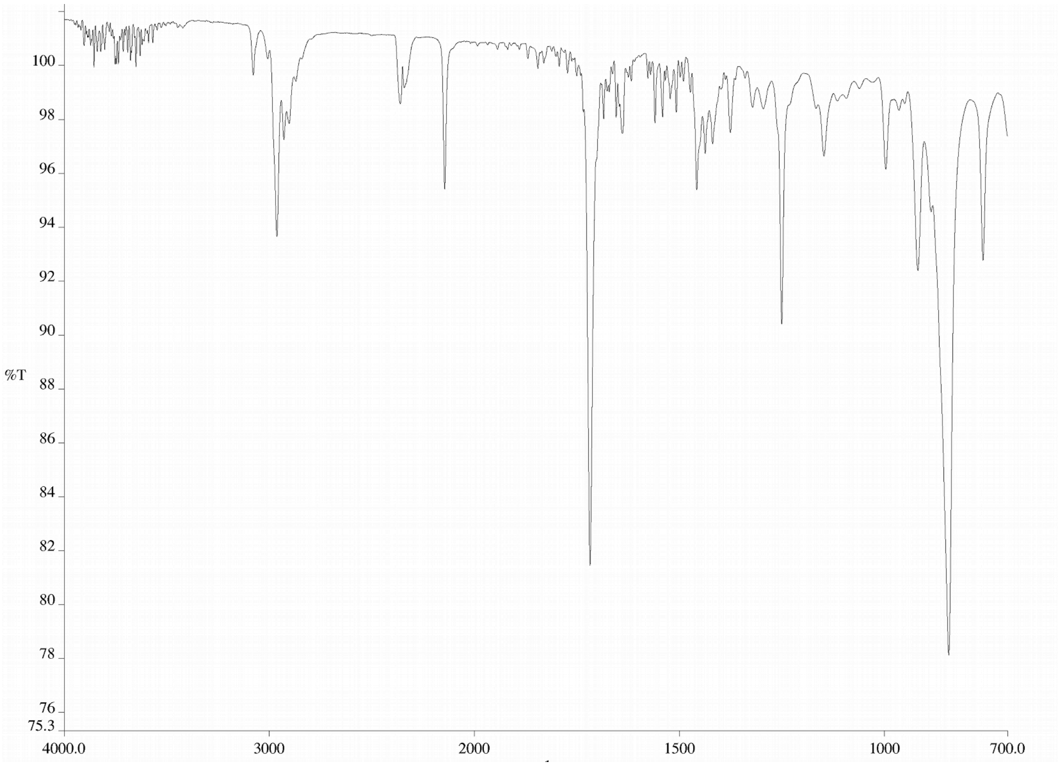


Figure S.23 Infrared spectrum (thin film/NaCl) of alkyne **49**.

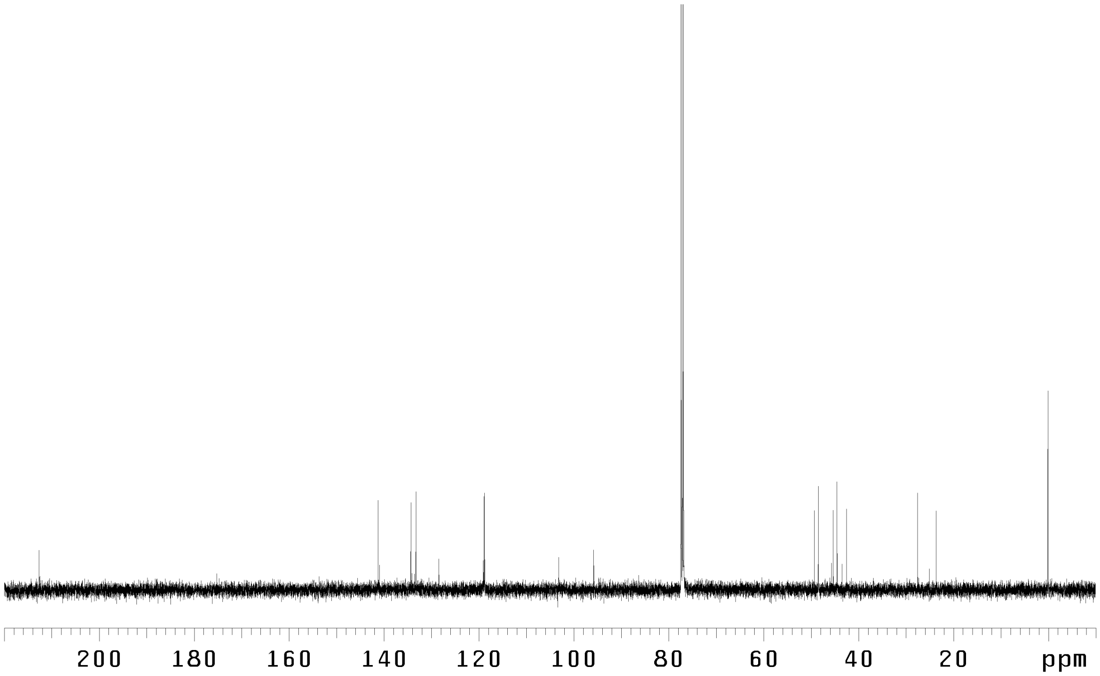


Figure S.24 ^{13}C NMR (500 MHz, CDCl$_3$) of alkyne **49**.

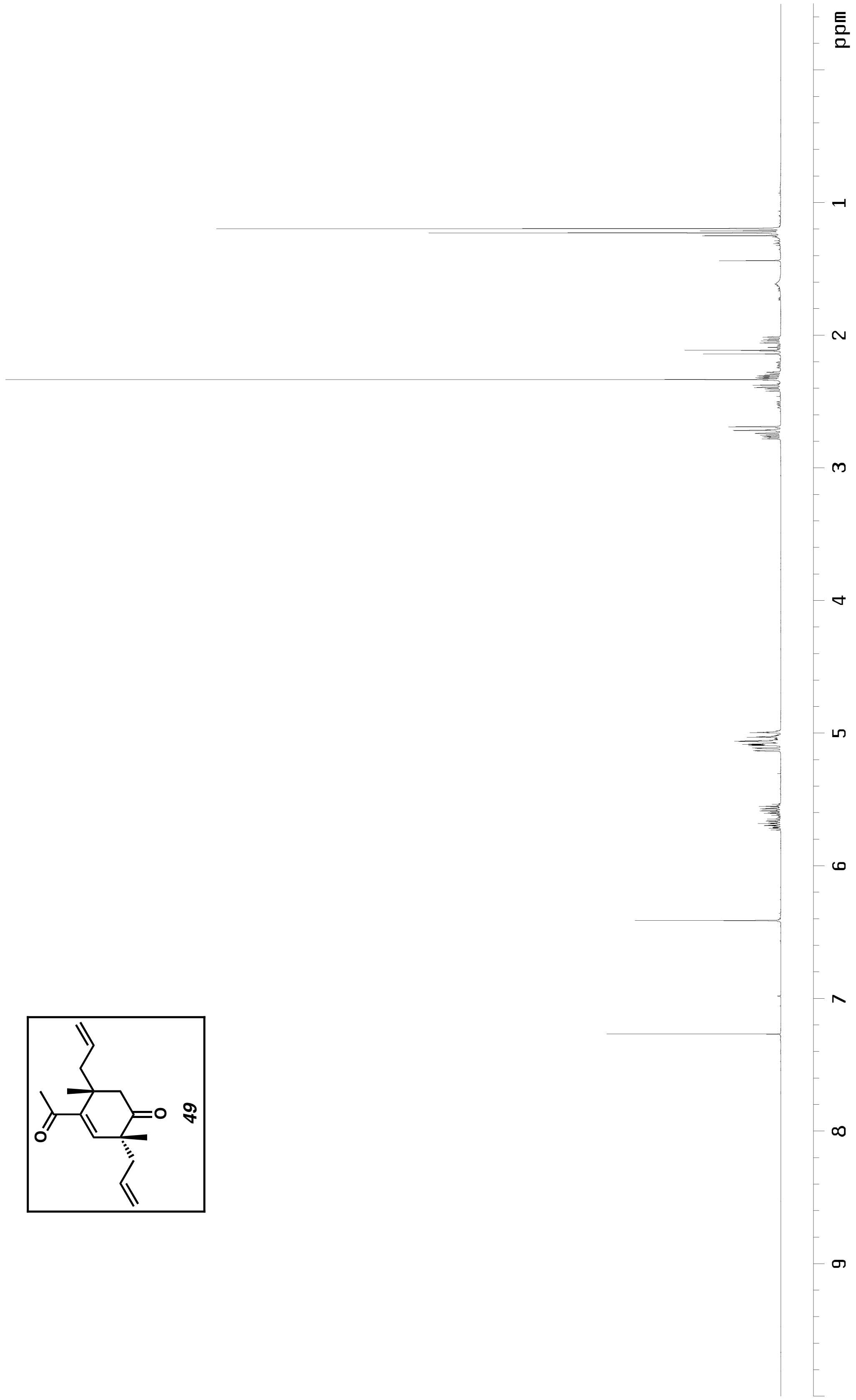


Figure S.25 ^{1}H NMR (500 MHz, $CDCl_3$) of ketone **49**.

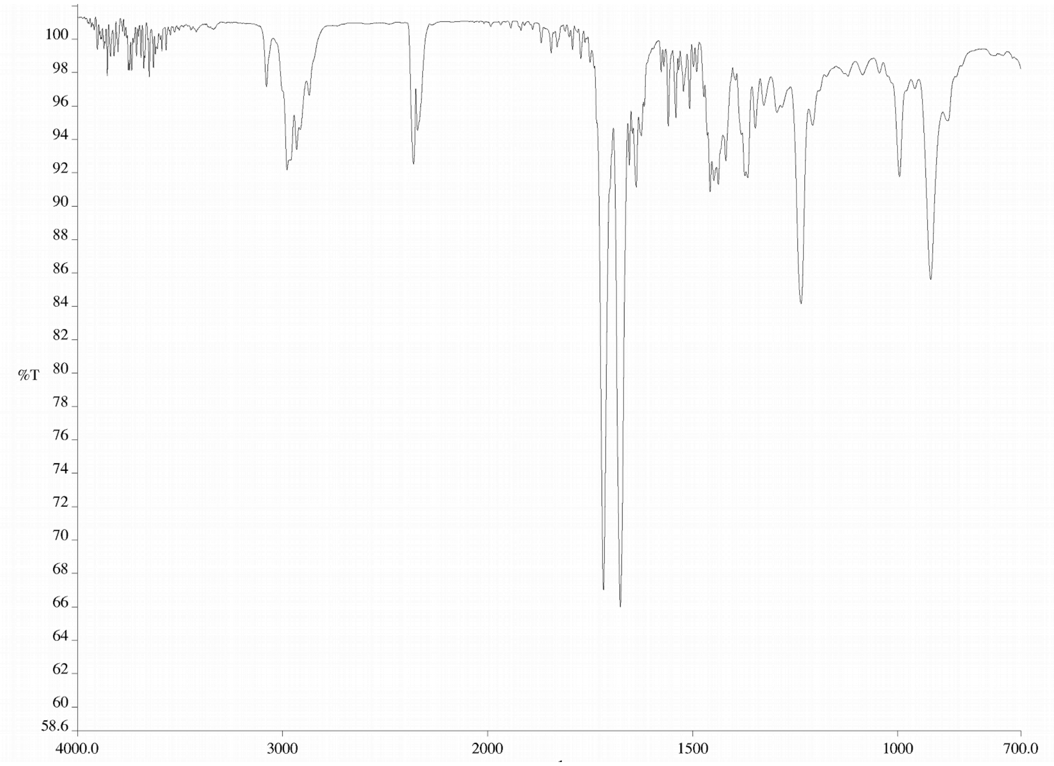


Figure S.26 Infrared spectrum (thin film/NaCl) of ketone **49**.

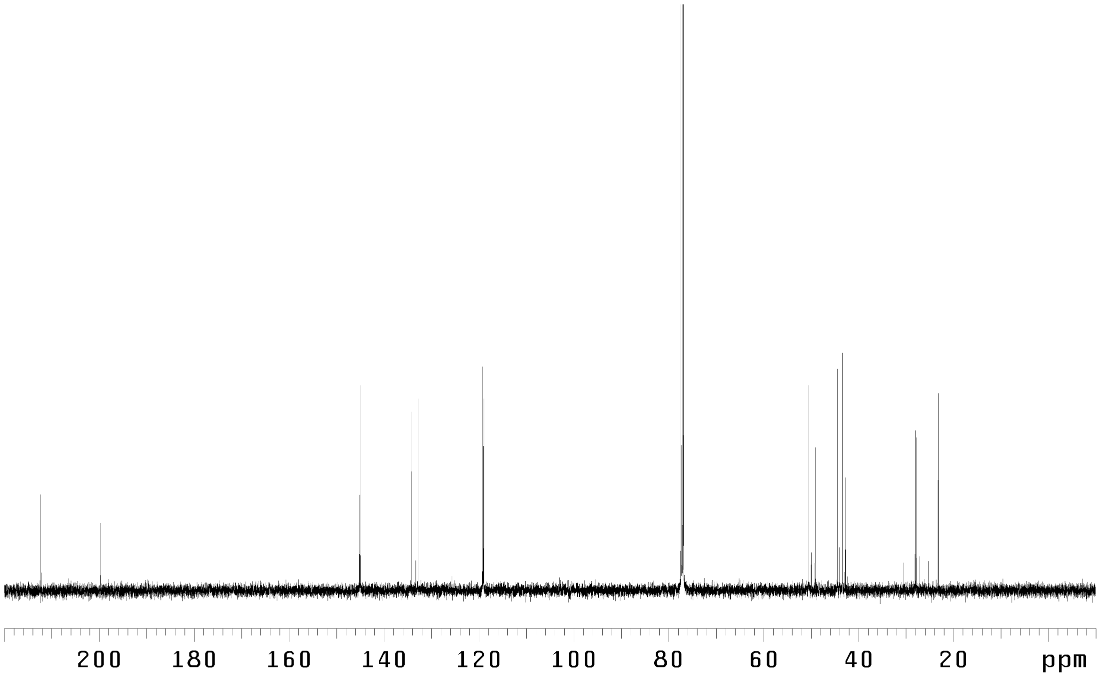


Figure S.27 ^{13}C NMR (125 MHz, CDCl$_3$) of ketone **49**.

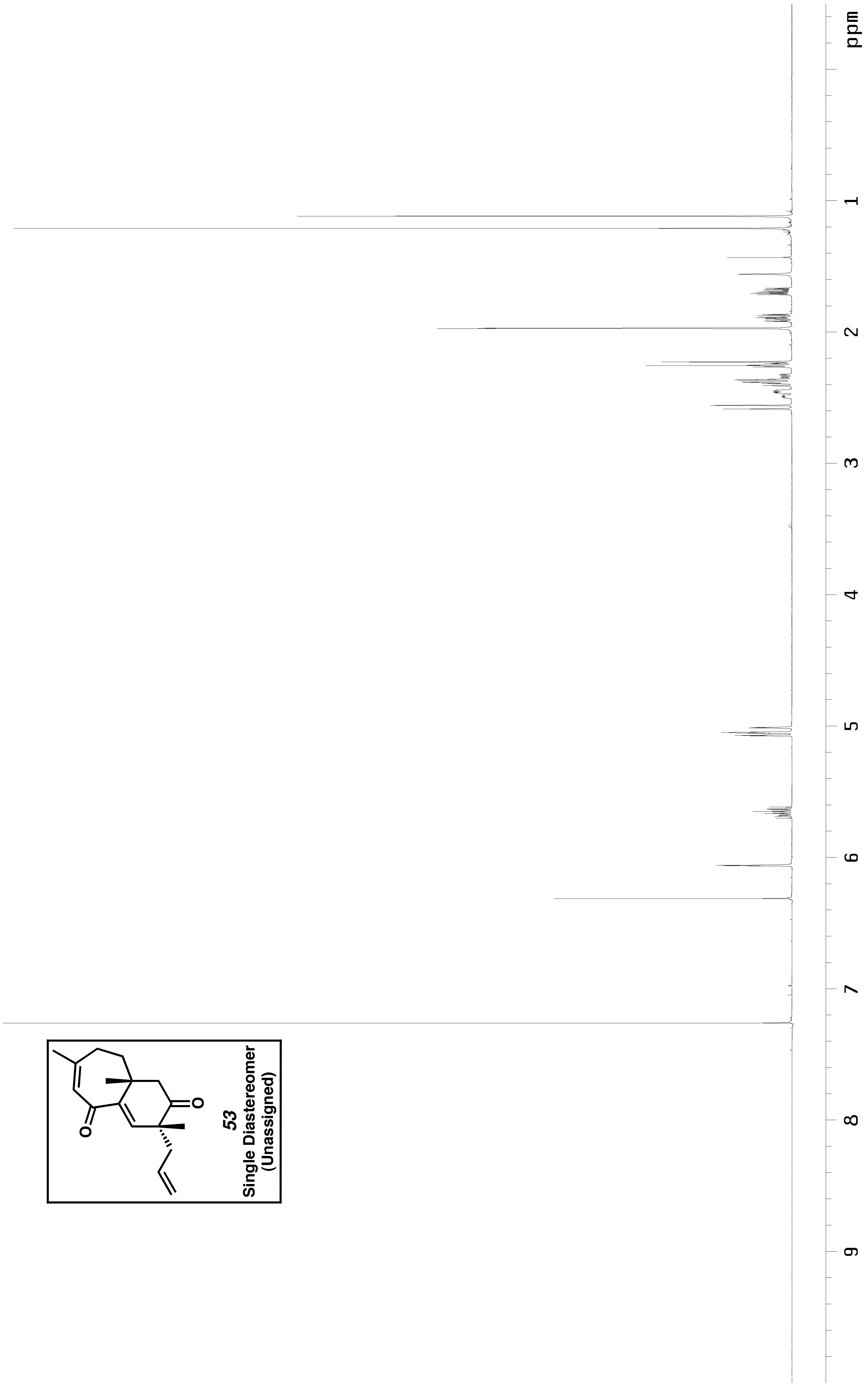


Figure S.28 ^{1}H NMR (500 MHz, $CDCl_3$) of bicyclic enone **53(A)**.

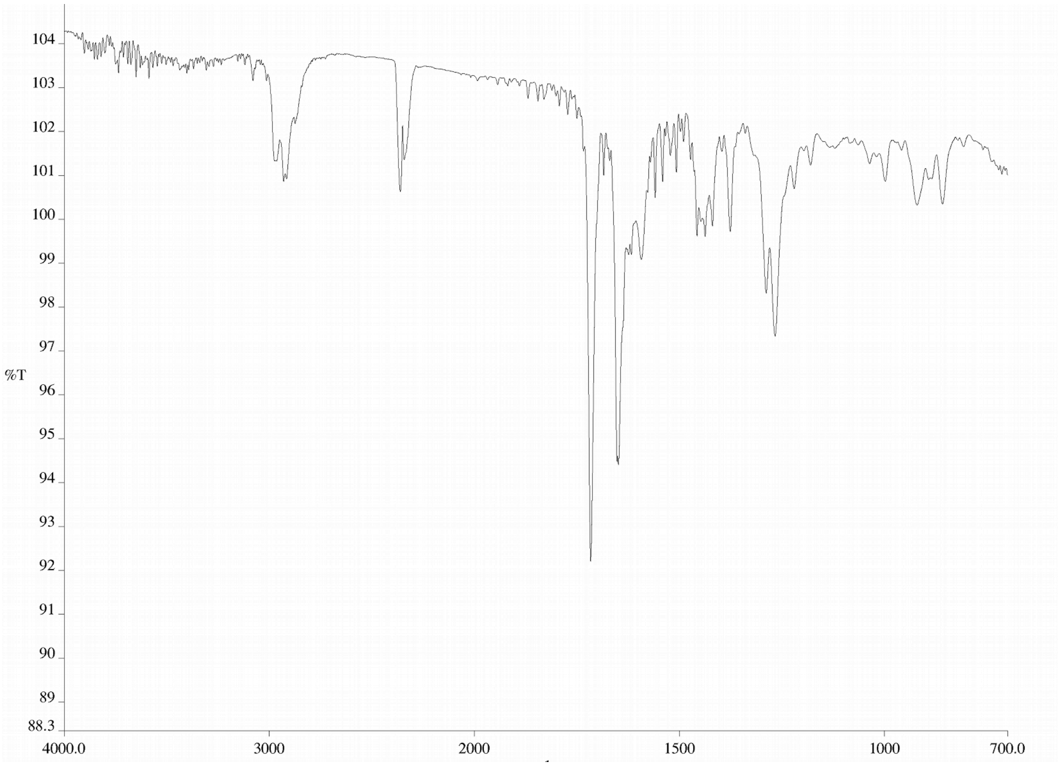


Figure S.29 Infrared spectrum (thin film/NaCl) of bicyclic enone **53(A)**.

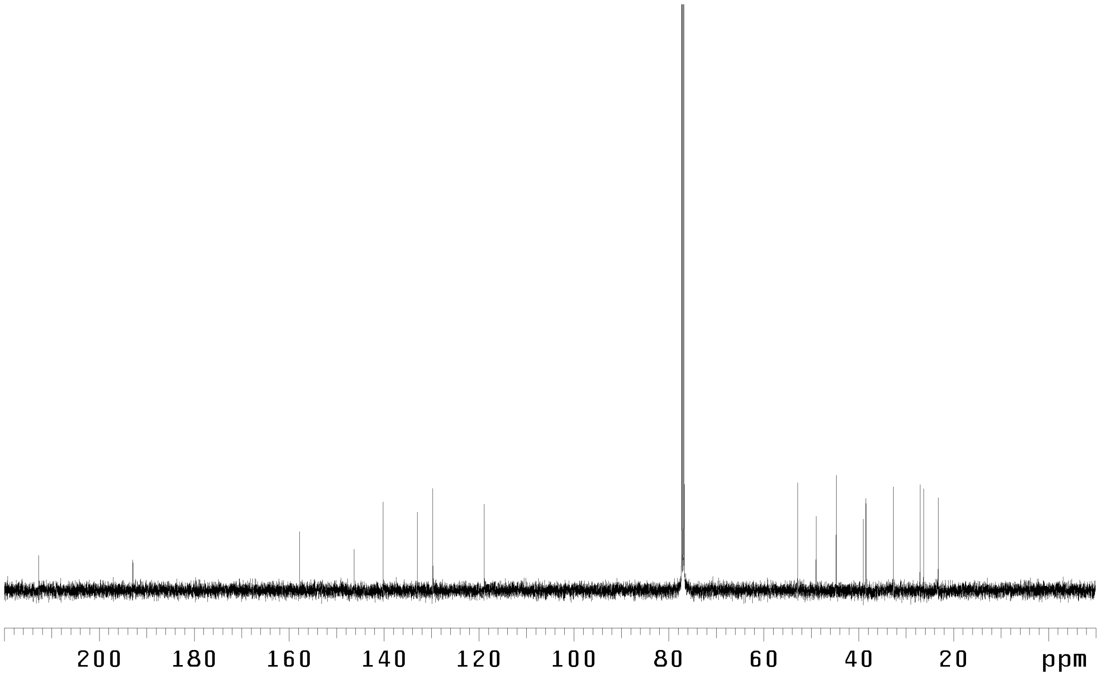


Figure S.30 ^{13}C NMR (125 MHz, CDCl$_3$) of bicyclic enone **53(A)**.

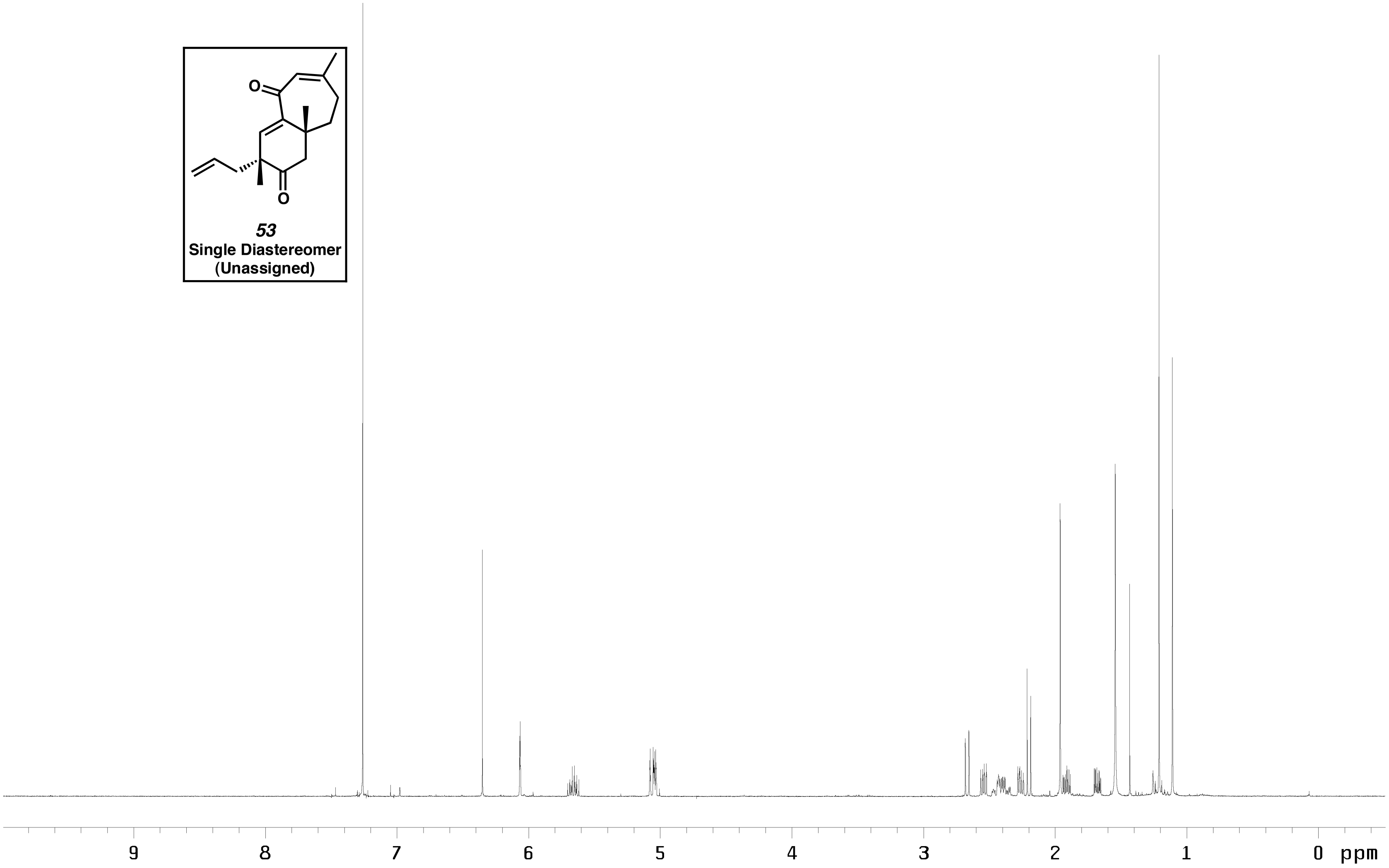


Figure S.31 ^{1}H NMR (500 MHz, $CDCl_3$) of bicyclic enone **204(B)**.

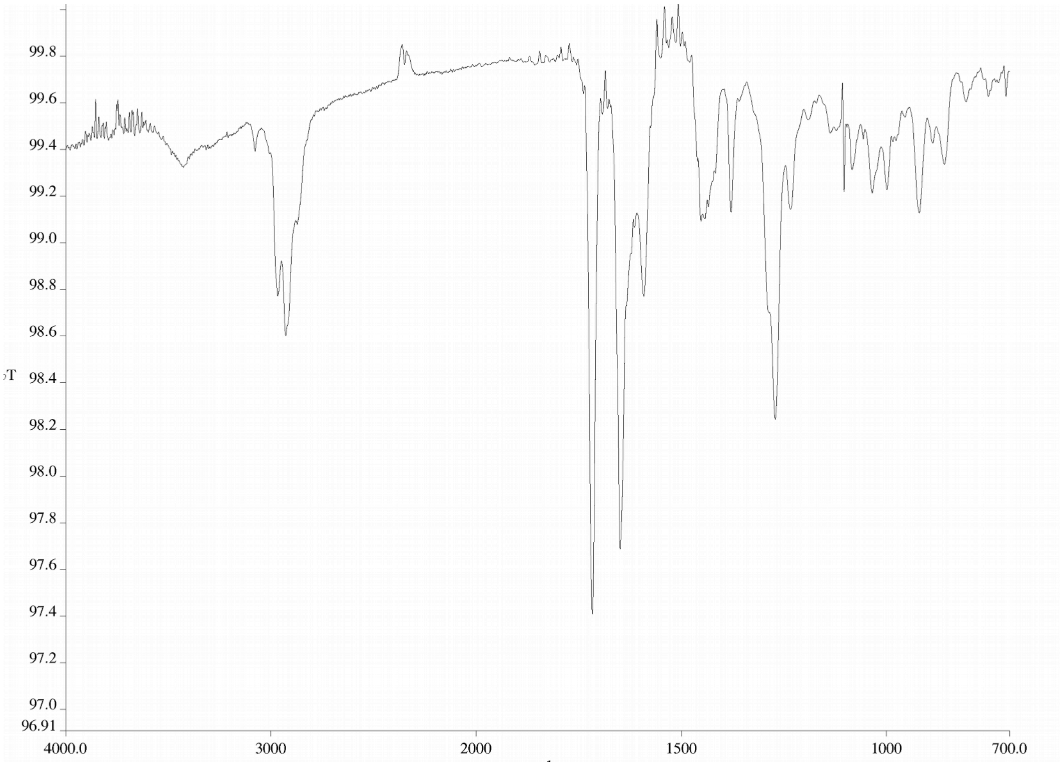


Figure S.32 Infrared spectrum (thin film/NaCl) of bicyclic enone **53(B)**.

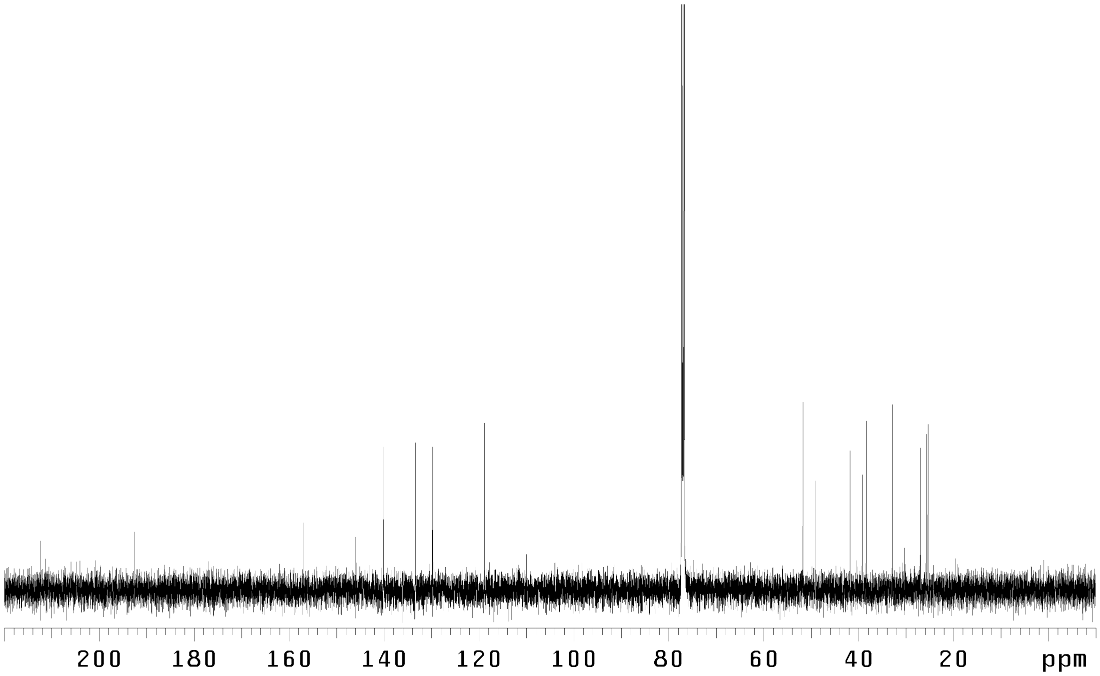


Figure S.33 ^{13}C NMR (125 MHz, CDCl$_3$) of bicyclic enone **53(B)**.

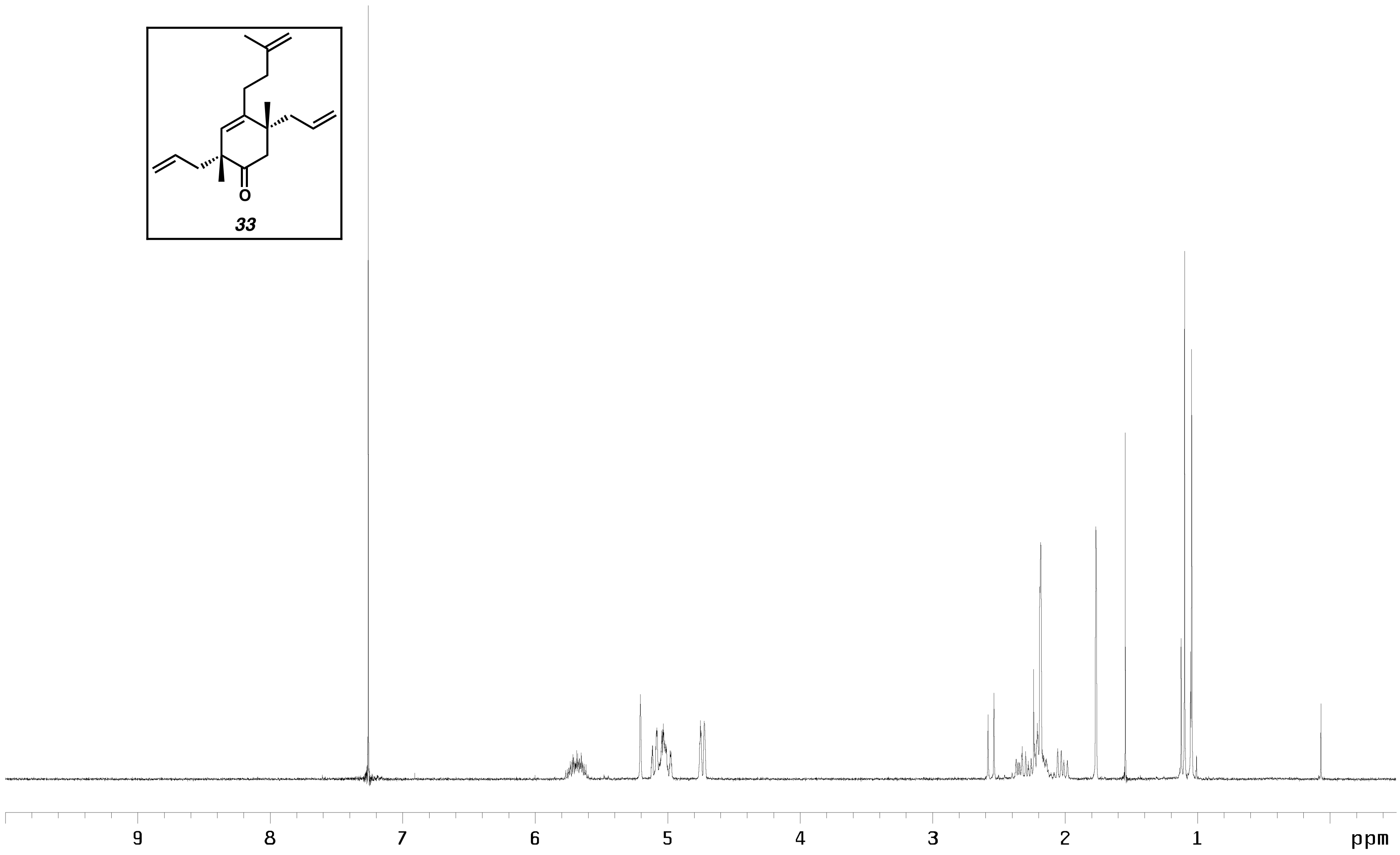


Figure S.34 ^{1}H NMR (300 MHz, $CDCl_3$) of tetraolefin **33**.

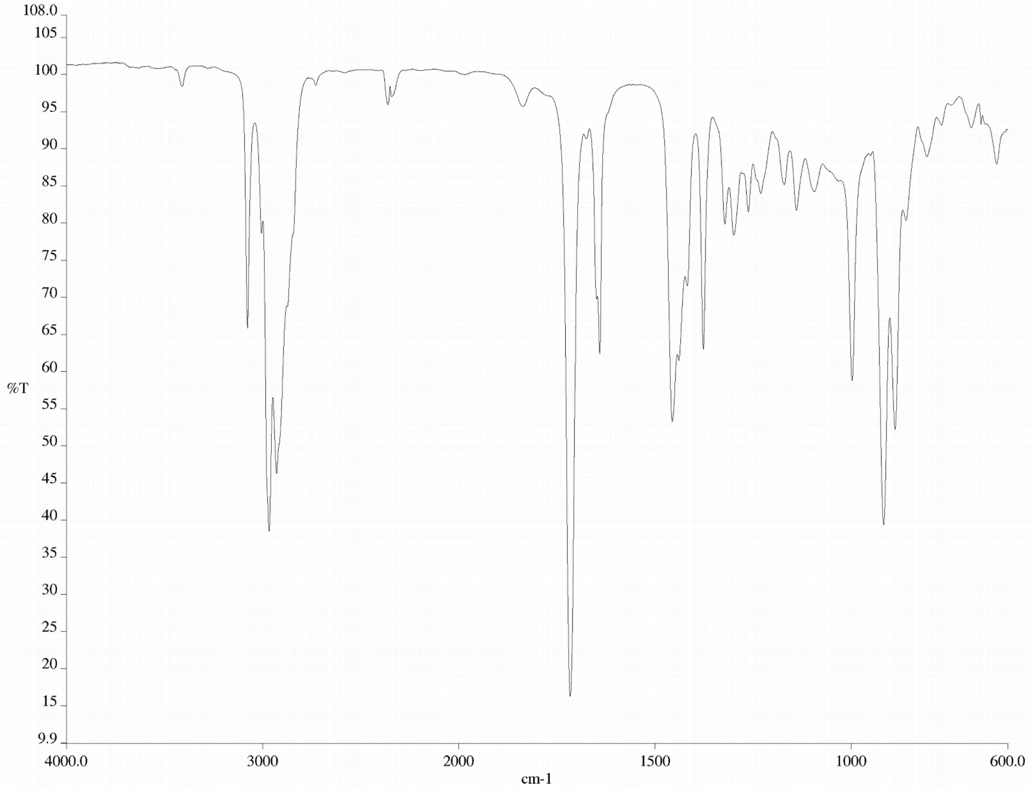


Figure S.35 Infrared spectrum (thin film/NaCl) of tetraolefin **33**.

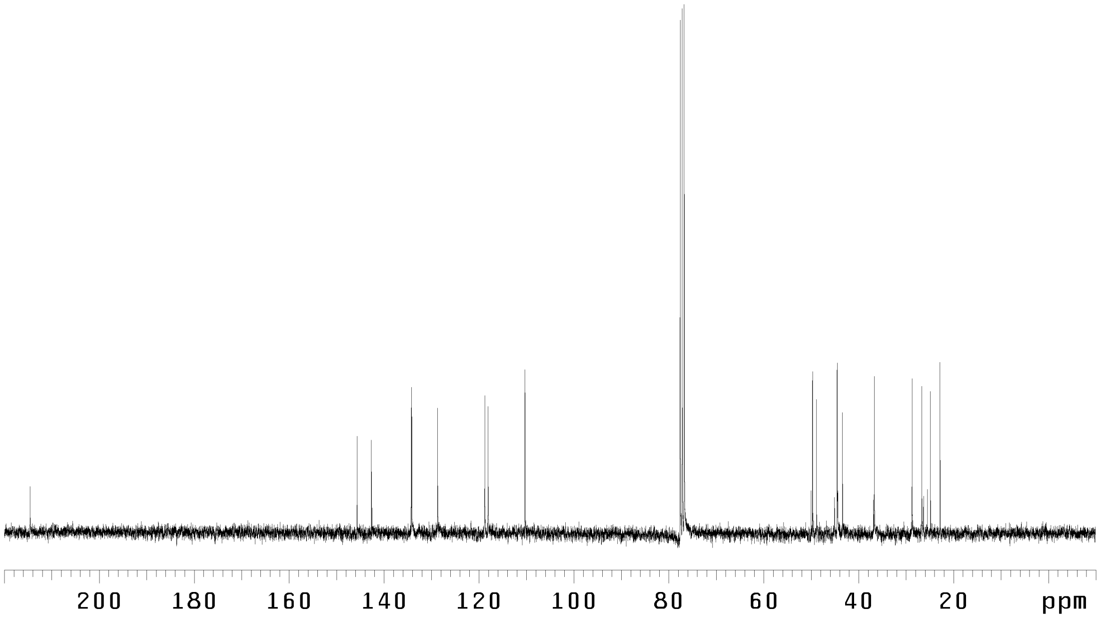


Figure S.36 ^{13}C NMR (75 MHz, CDCl$_3$) of tetraolefin **33**.

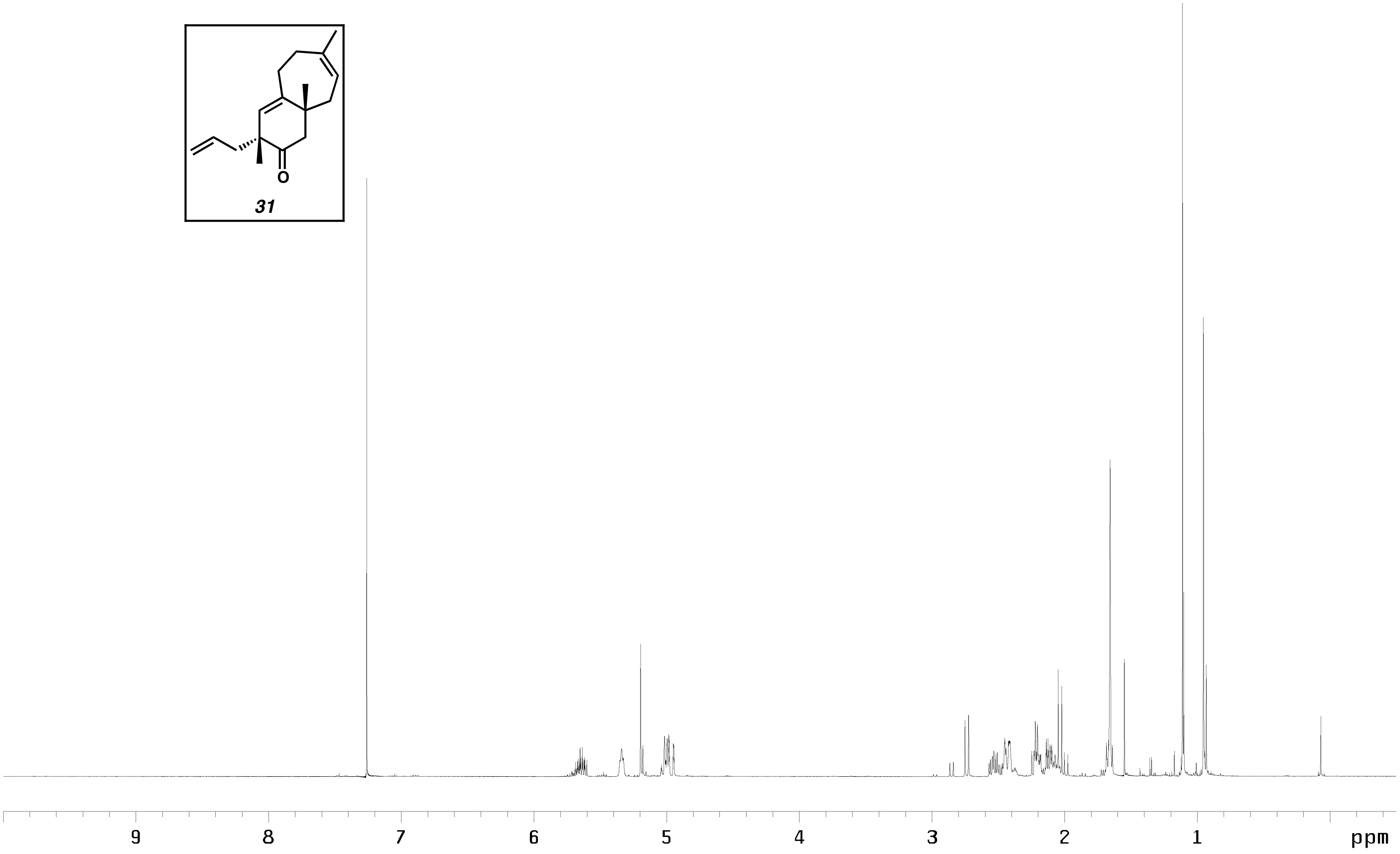


Figure S.37 ^{1}H NMR (500 MHz, CDCl$_3$) of bicyclic ketone **31**.

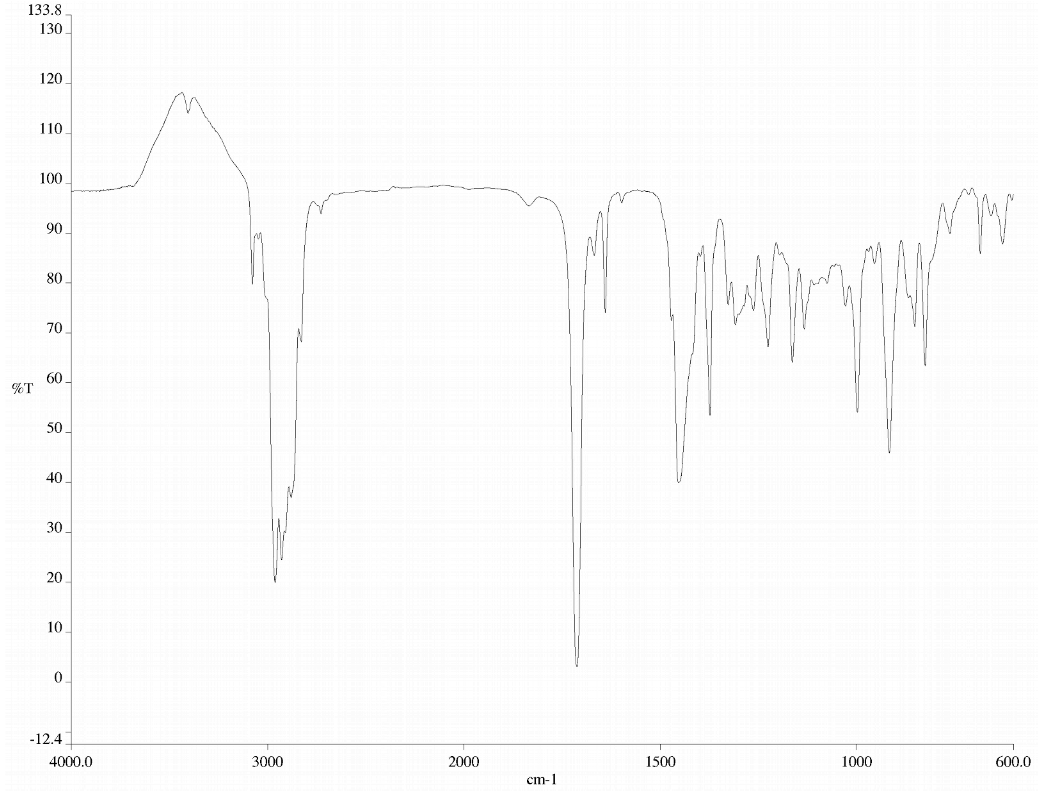


Figure S.38 Infrared spectrum (thin film/NaCl) of bicyclic ketone **31**.

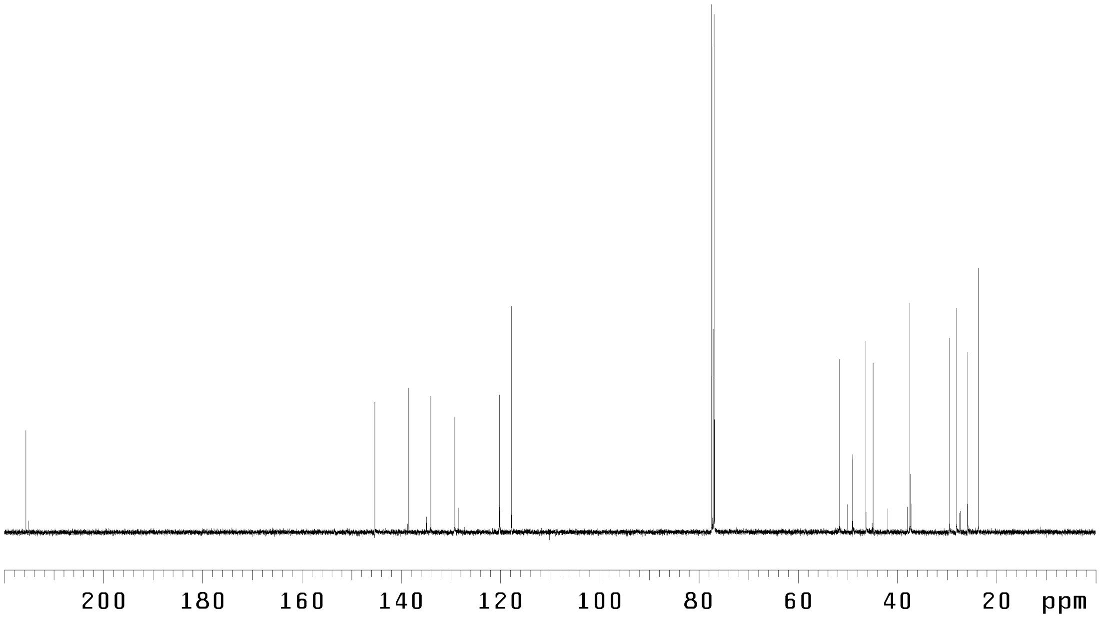


Figure S.39 ^{13}C NMR (125 MHz, CDCl$_3$) of bicyclic ketone **31**.

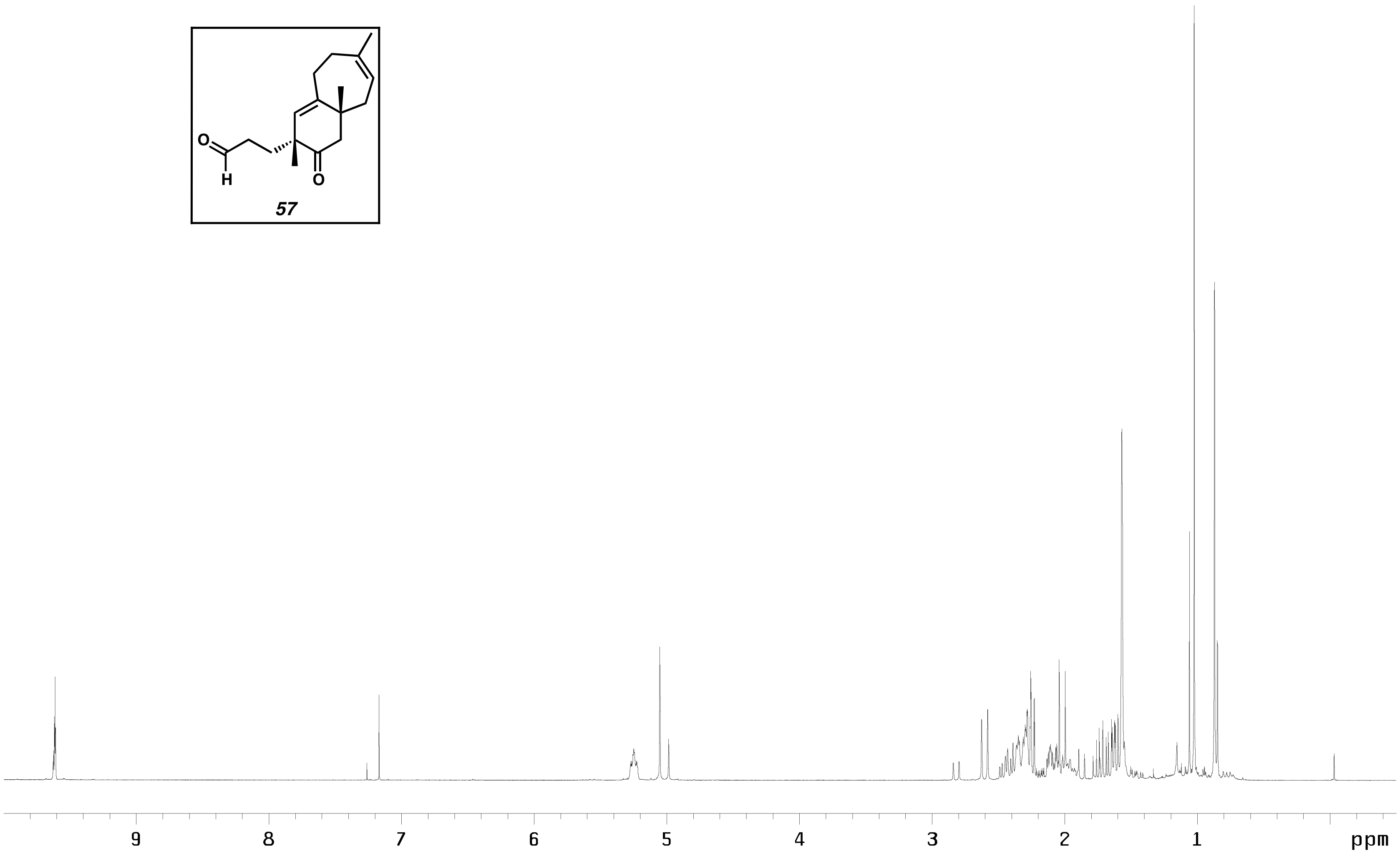


Figure S.40 ^{1}H NMR (300 MHz, $CDCl_3$) of bicyclic aldehyde **57**.

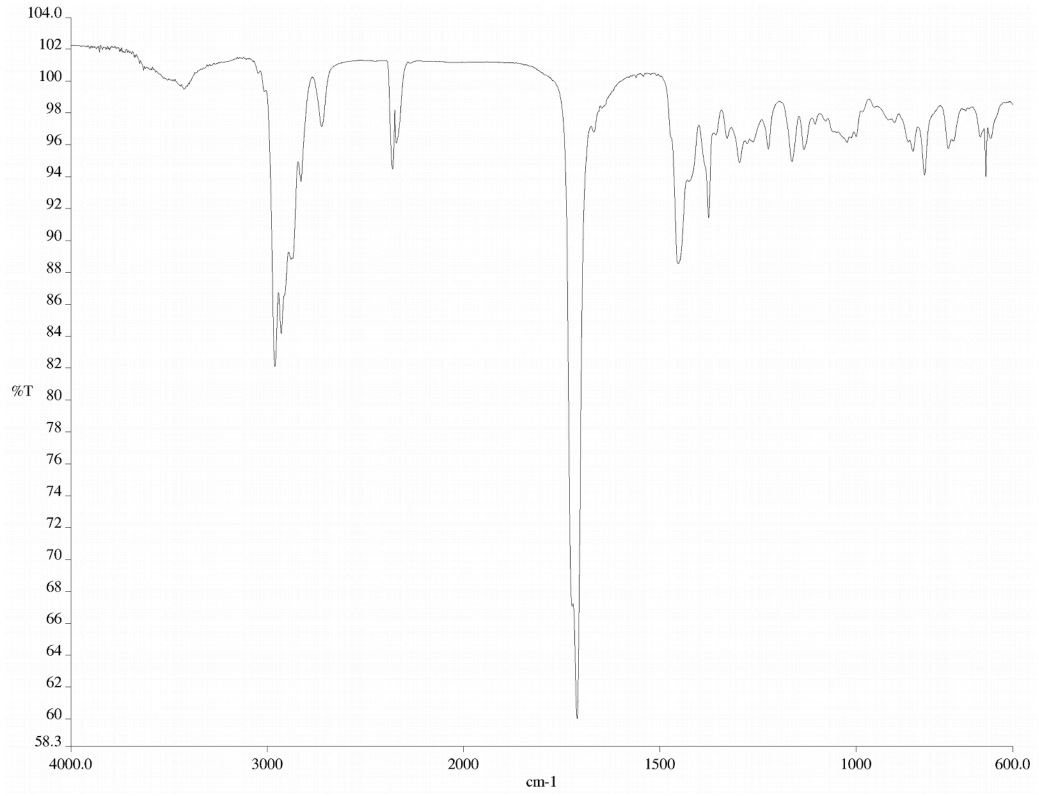


Figure S.41 Infrared spectrum (thin film/NaCl) of bicyclic aldehyde **57**.

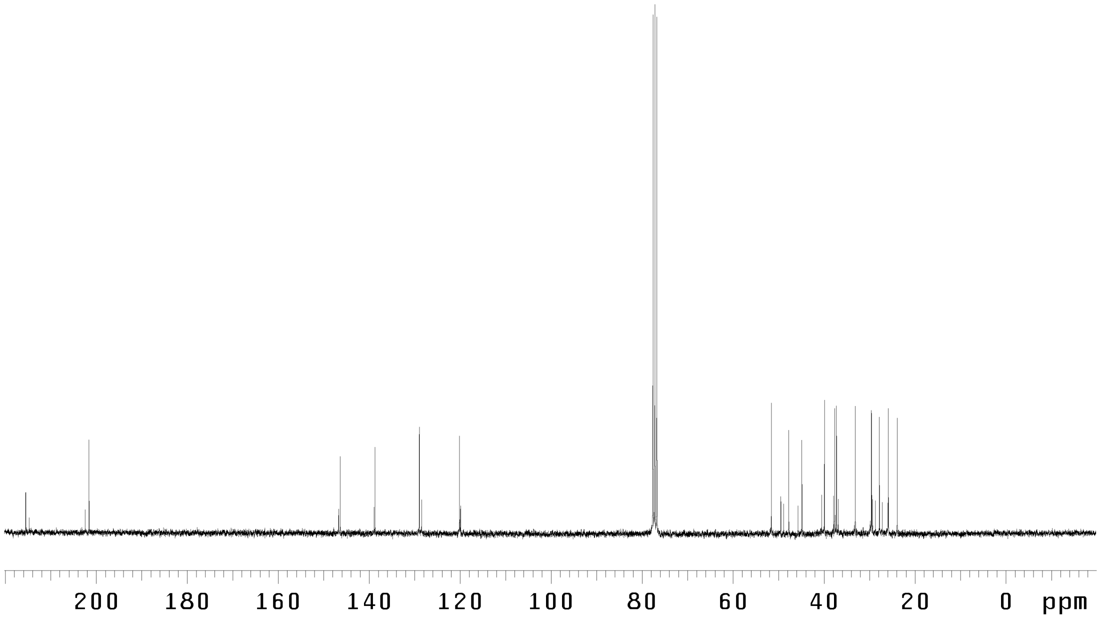


Figure S.42 ^{13}C NMR (75 MHz, CDCl$_3$) of bicyclic aldehyde **57**.

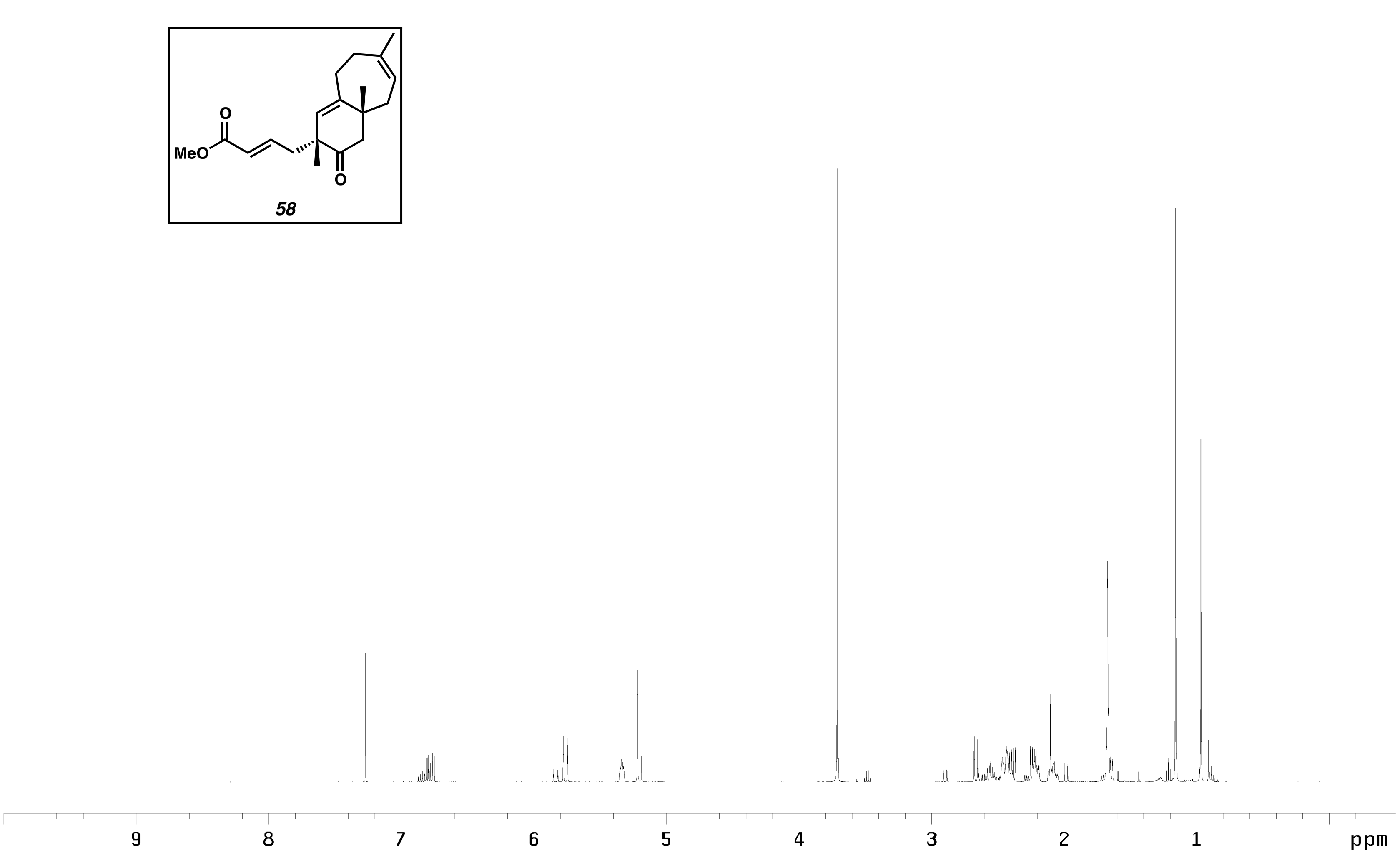


Figure S.43 ^{1}H NMR (500 MHz, $CDCl_3$) of bicyclic enoate **58**.

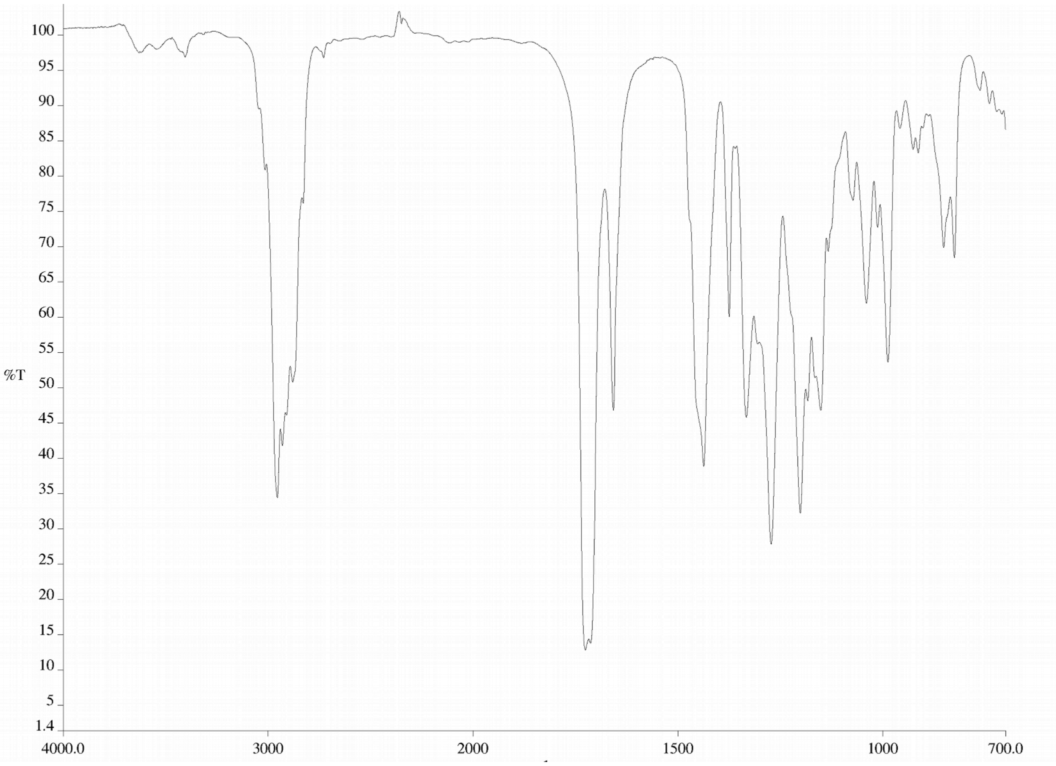


Figure S.44 Infrared spectrum (thin film/NaCl) of bicyclic enoate **58**.

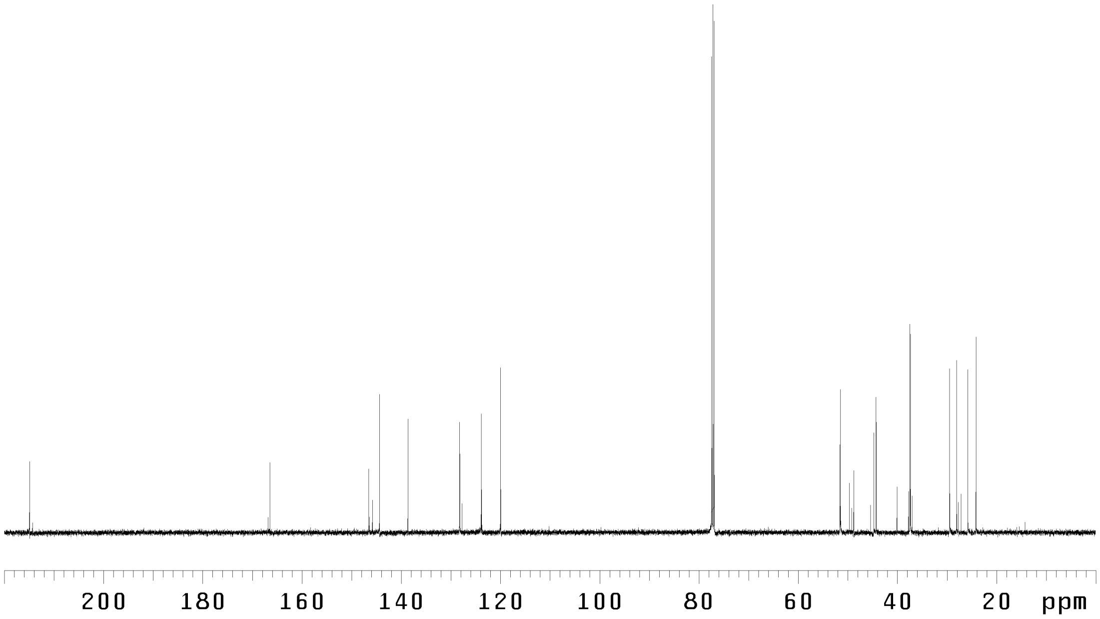


Figure S.45 ^{13}C NMR (125 MHz, CDCl$_3$) of bicyclic enoate **58**.

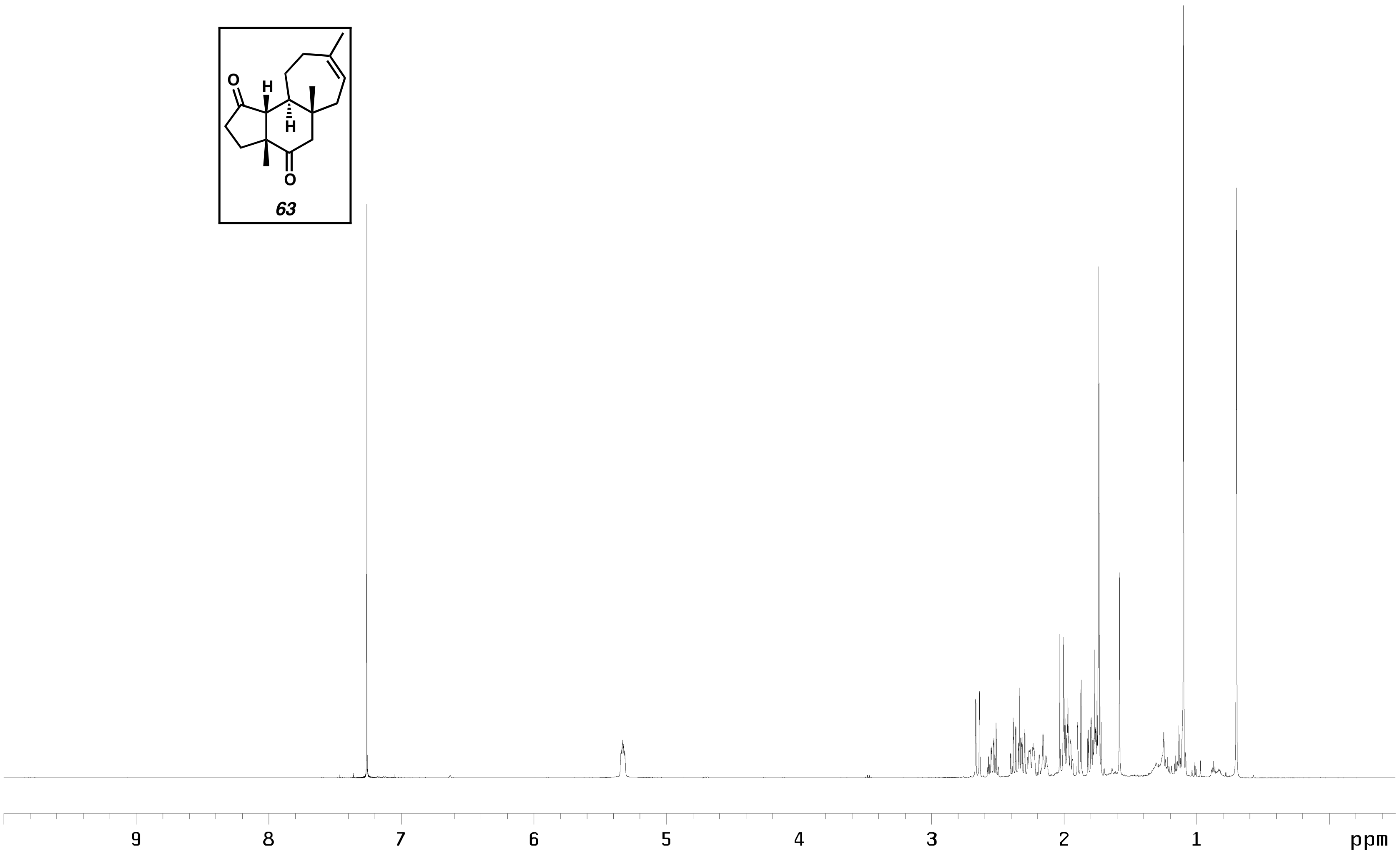


Figure S.46 ^{1}H NMR (500 MHz, $CDCl_3$) of tricyclic diketone **63**.

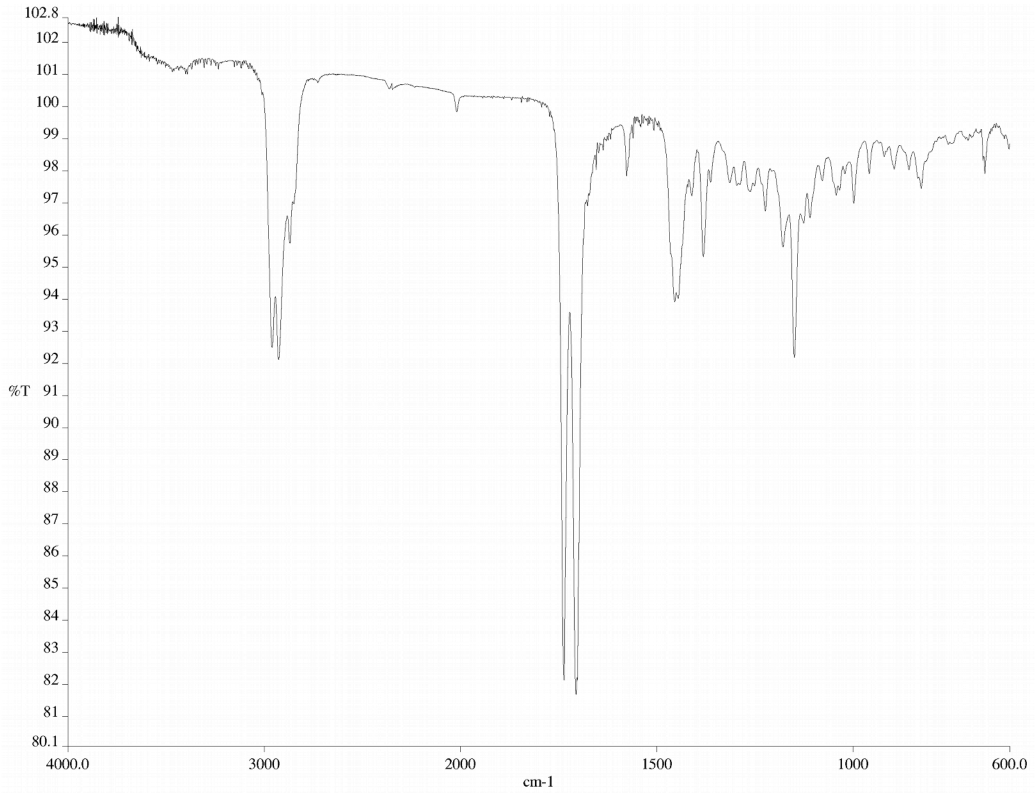


Figure S.47 Infrared spectrum (thin film/NaCl) of tricyclic diketone **63**.

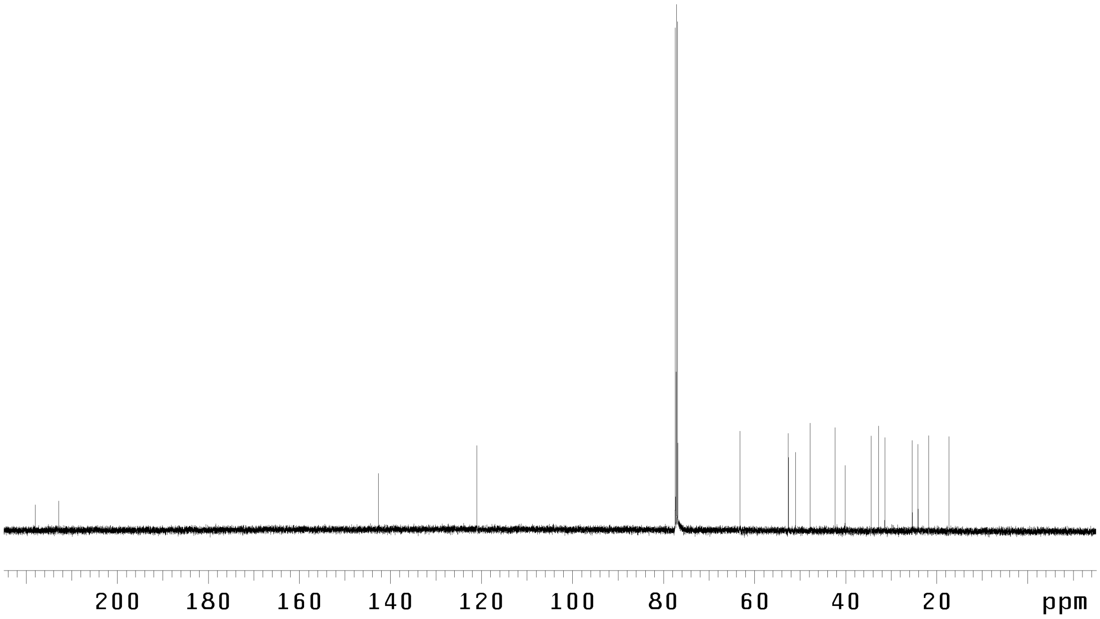


Figure S.48 ^{13}C NMR (125 MHz, CDCl$_3$) of tricyclic diketone **63**.

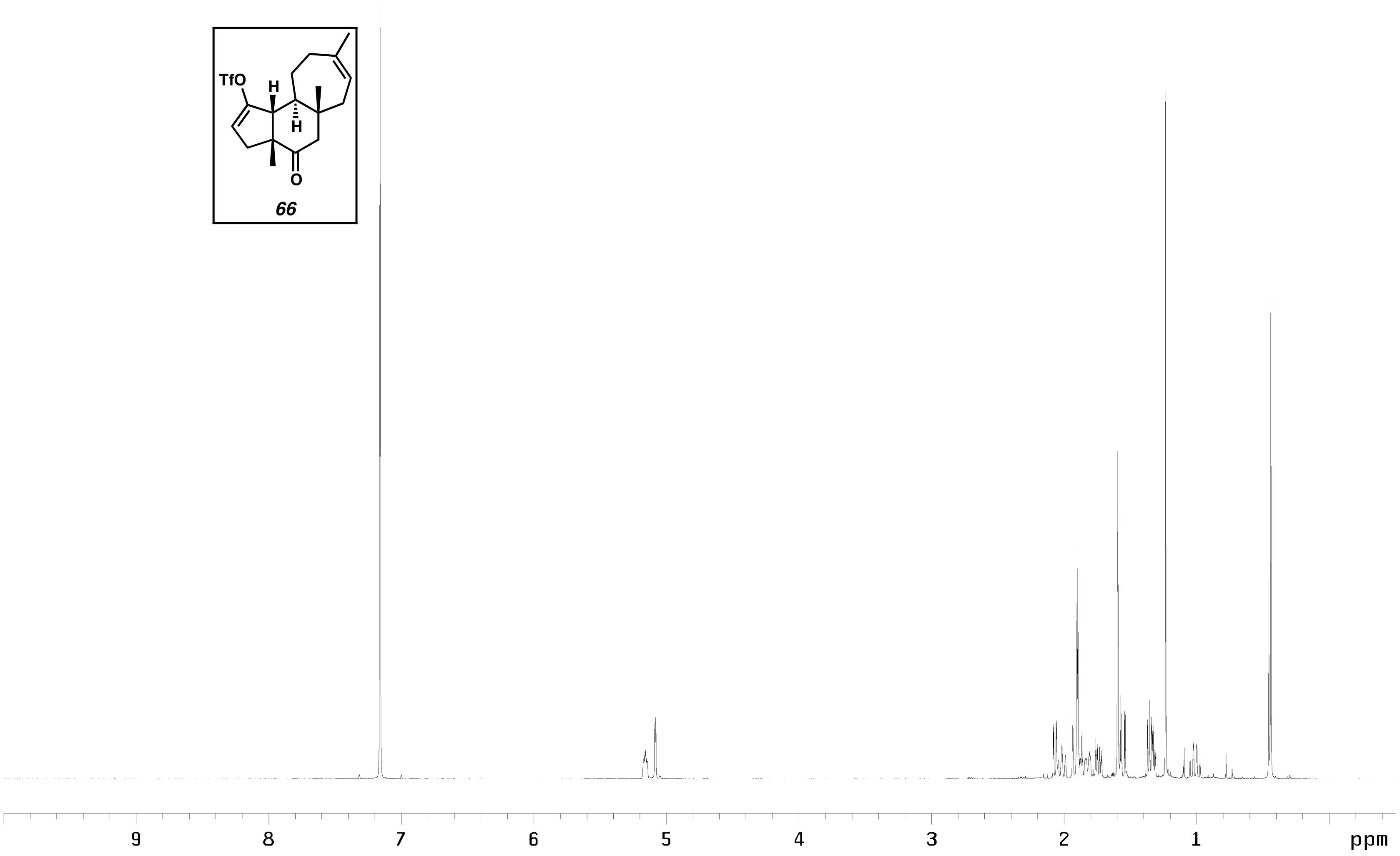


Figure S.49 ^{1}H NMR (500 MHz, C_6D_6) of tricyclic triflate **66**.

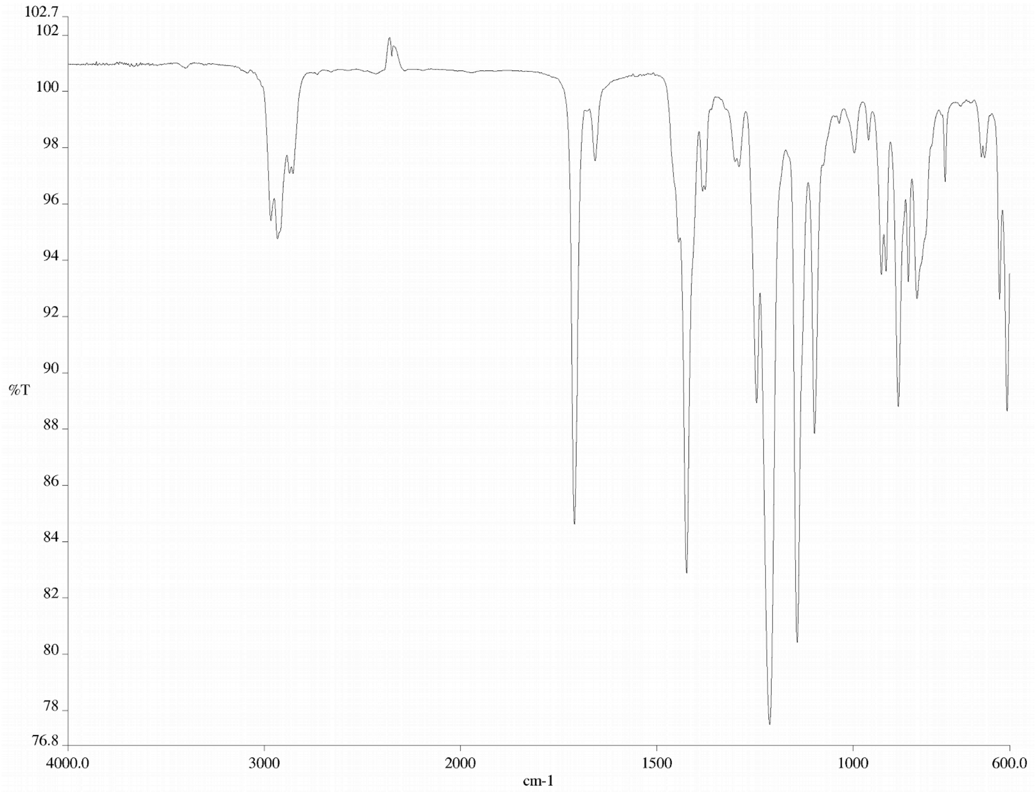


Figure S.50 Infrared spectrum (thin film/NaCl) of tricyclic triflate **66**.

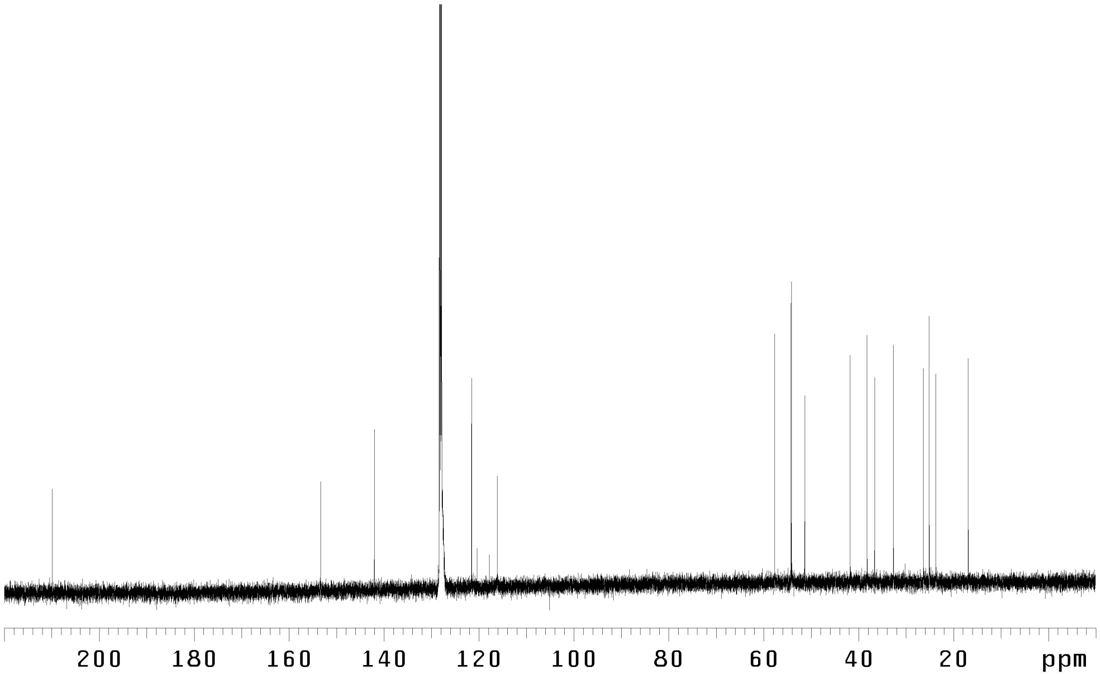


Figure S.51 ^{13}C NMR (125 MHz, C_6D_6) of tricyclic triflate **66**.

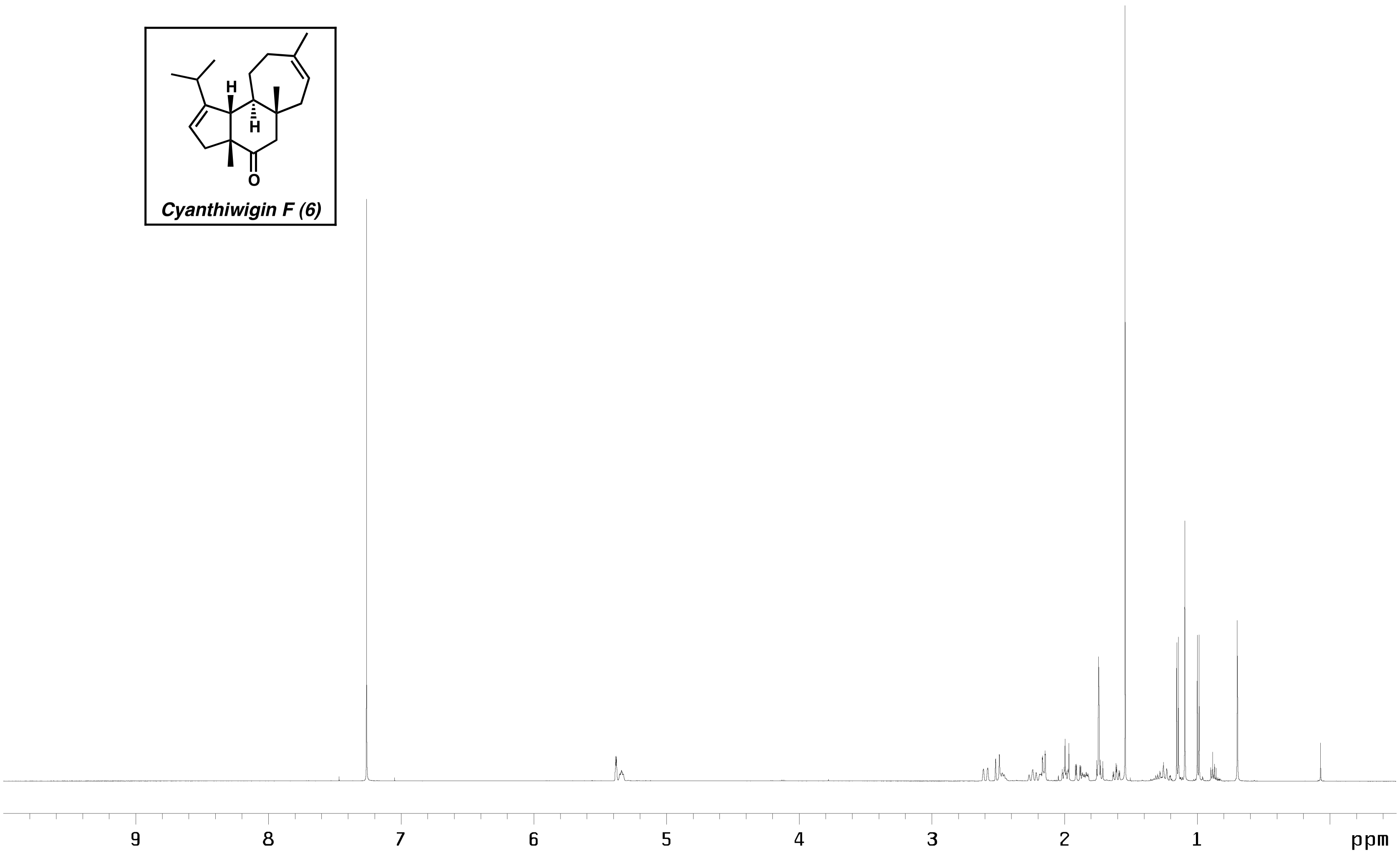


Figure S.52 ^{1}H NMR (500 MHz, CDCl$_3$) of cyanthiwigin F (**6**).

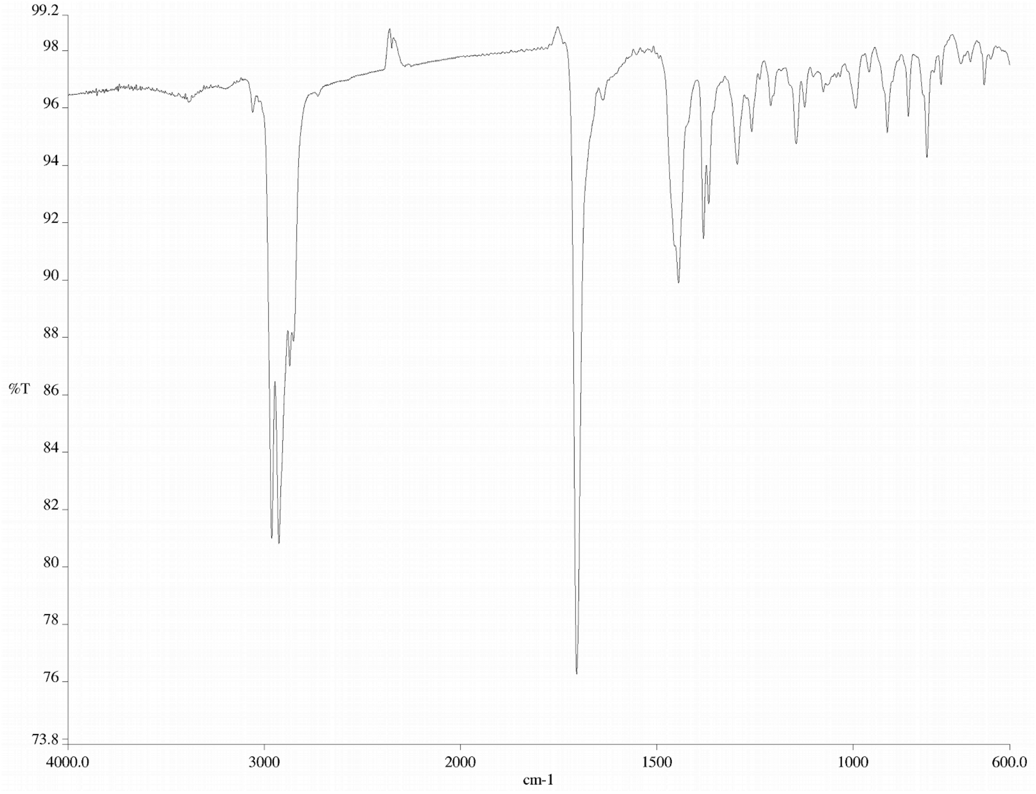


Figure S.53 Infrared spectrum (thin film/NaCl) of cyanthiwigin F (**6**).

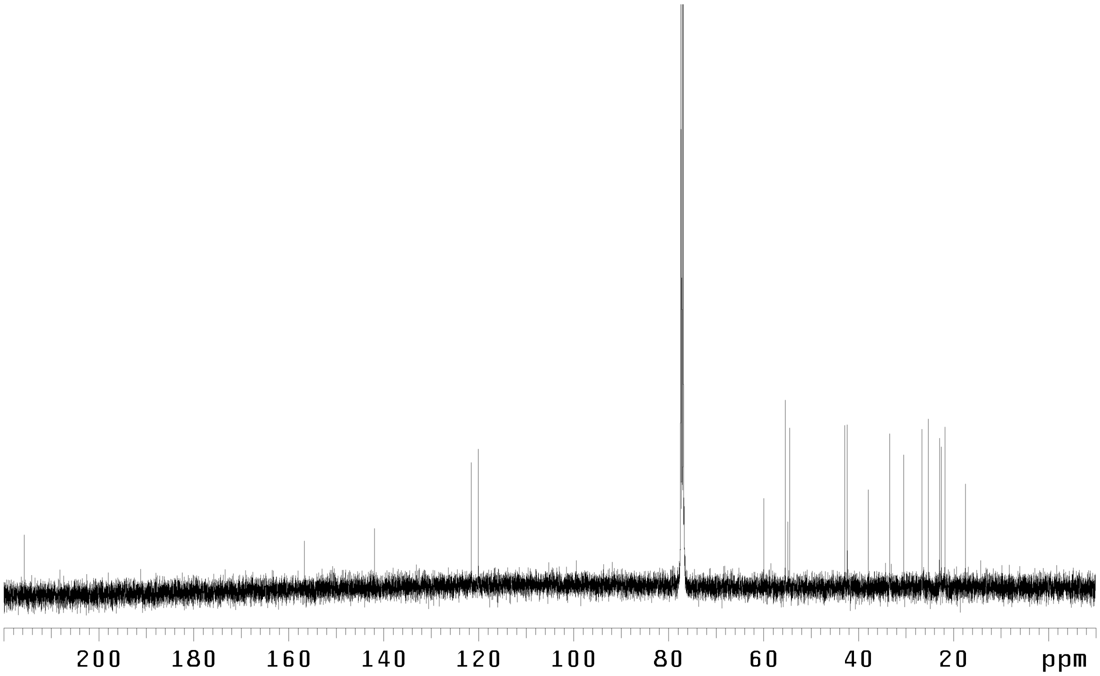


Figure S.54 ^{13}C NMR (125 MHz, CDCl$_3$) of cyanthiwigin F (**6**).

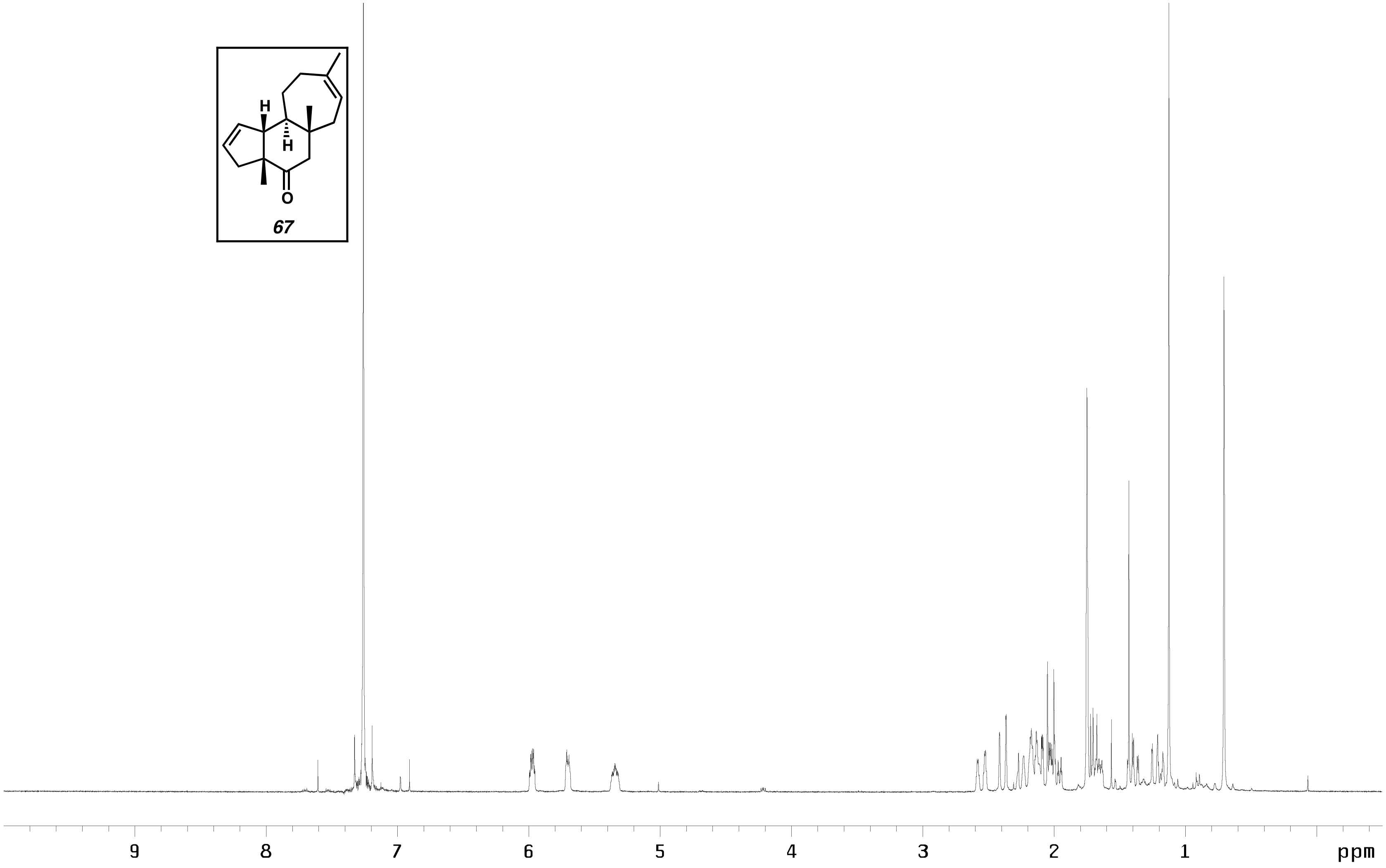


Figure S.55 ^{1}H NMR (500 MHz, $CDCl_3$) of tricyclic ketone **67**.

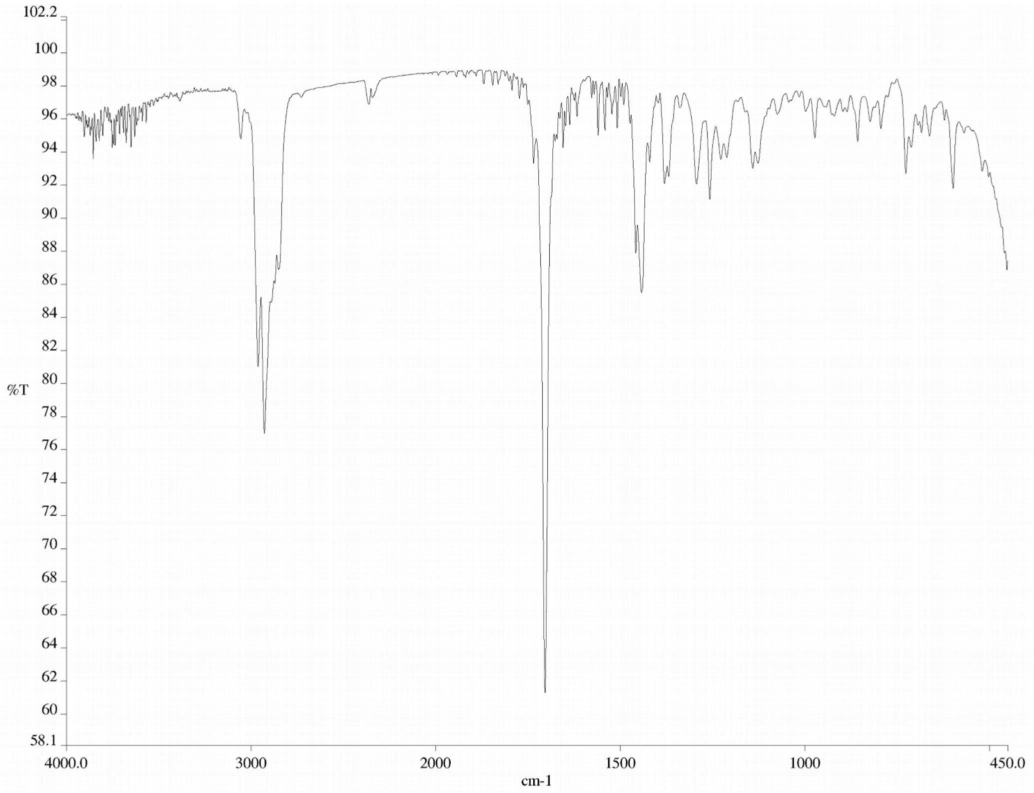


Figure S.56 Infrared spectrum (thin film/NaCl) of tricyclic ketone **67**.

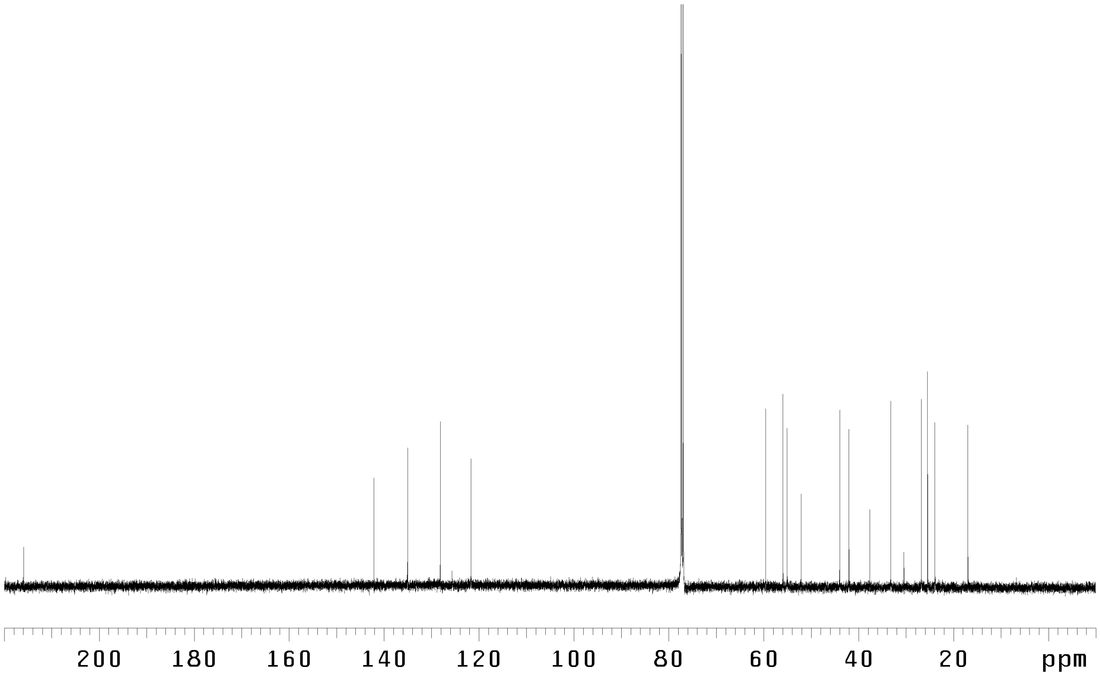


Figure S.57 ^{13}C NMR (125 MHz, $CDCl_3$) of tricyclic ketone **67**.

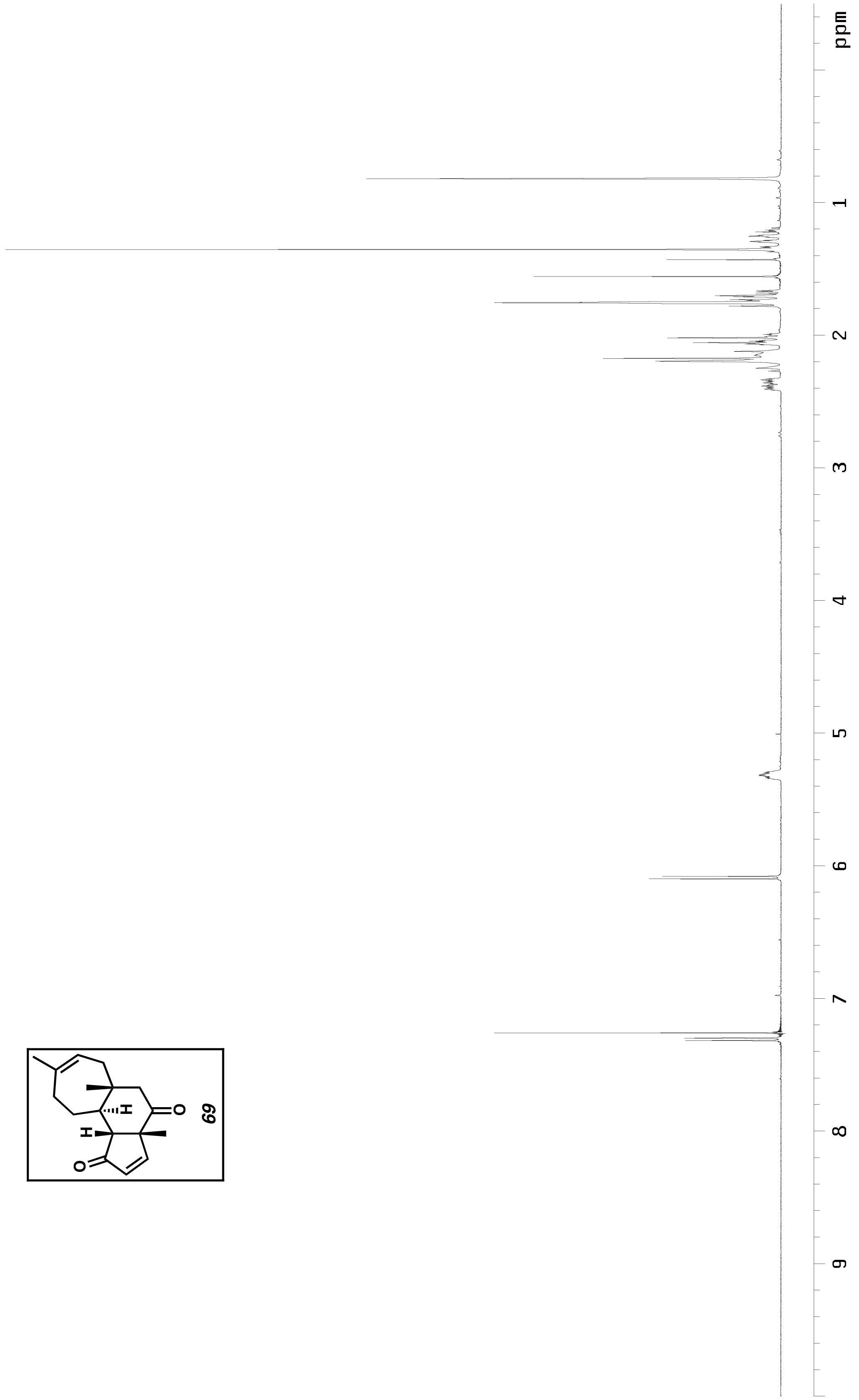


Figure S.58 ^{1}H NMR (500 MHz, CDCl$_3$) of tricyclic enone **69**.

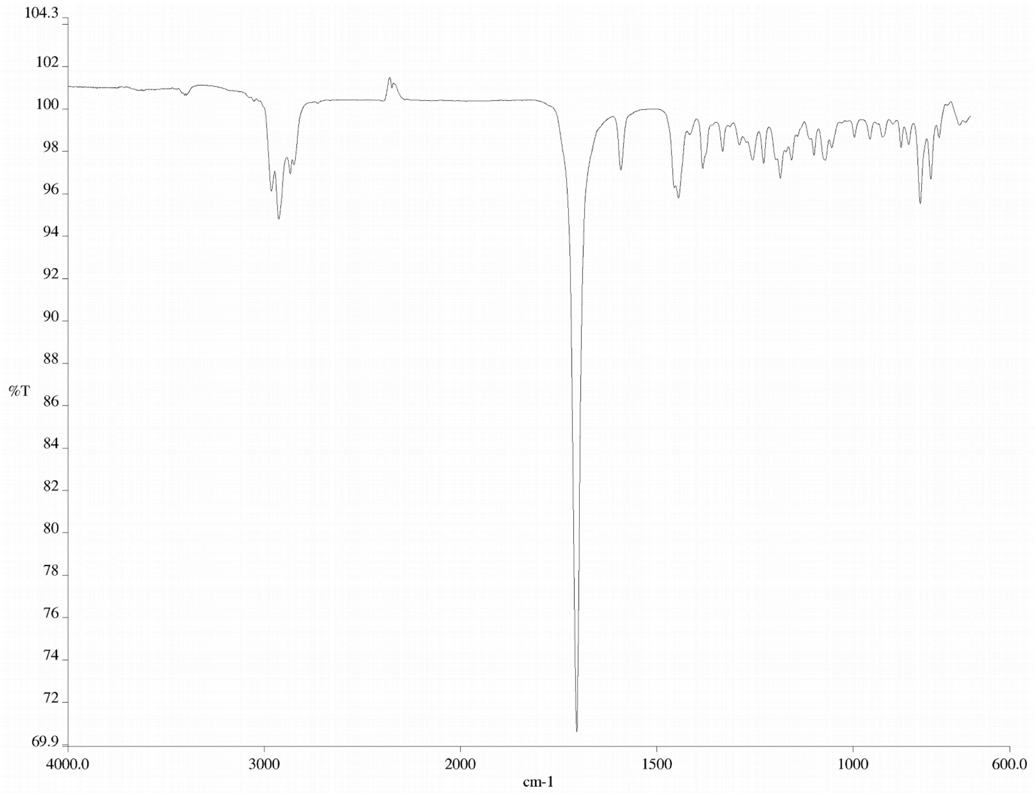


Figure S.59 Infrared spectrum (thin film/NaCl) of tricyclic enone **69**.

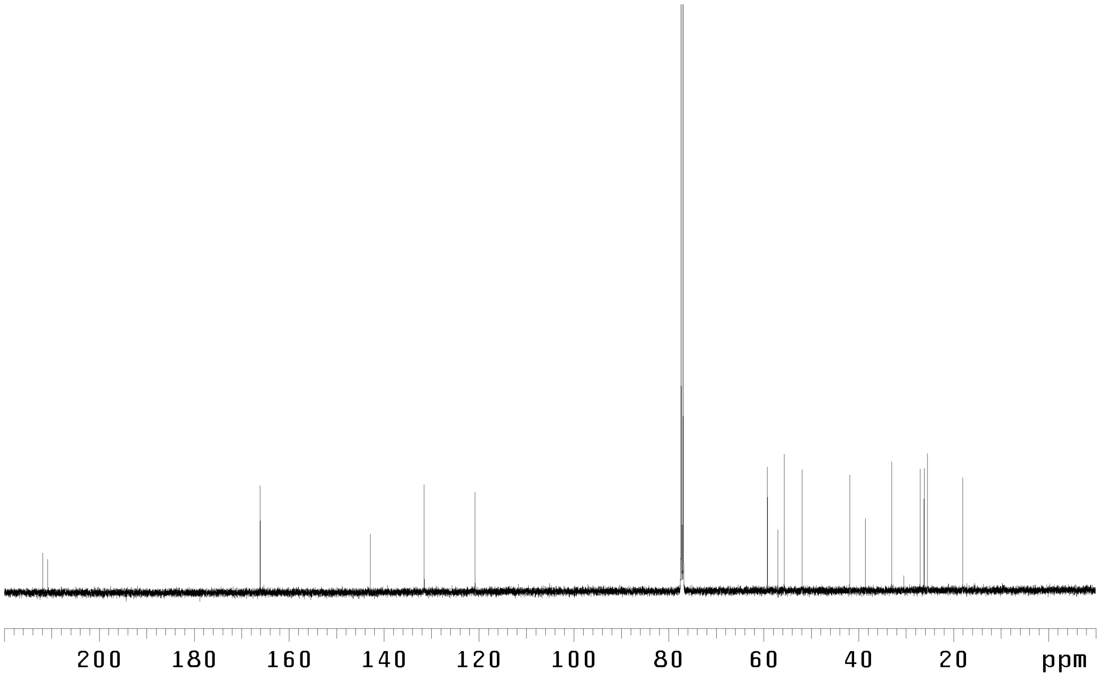


Figure S.60 ^{13}C NMR (125 MHz, CDCl$_3$) of tricyclic enone **69**.

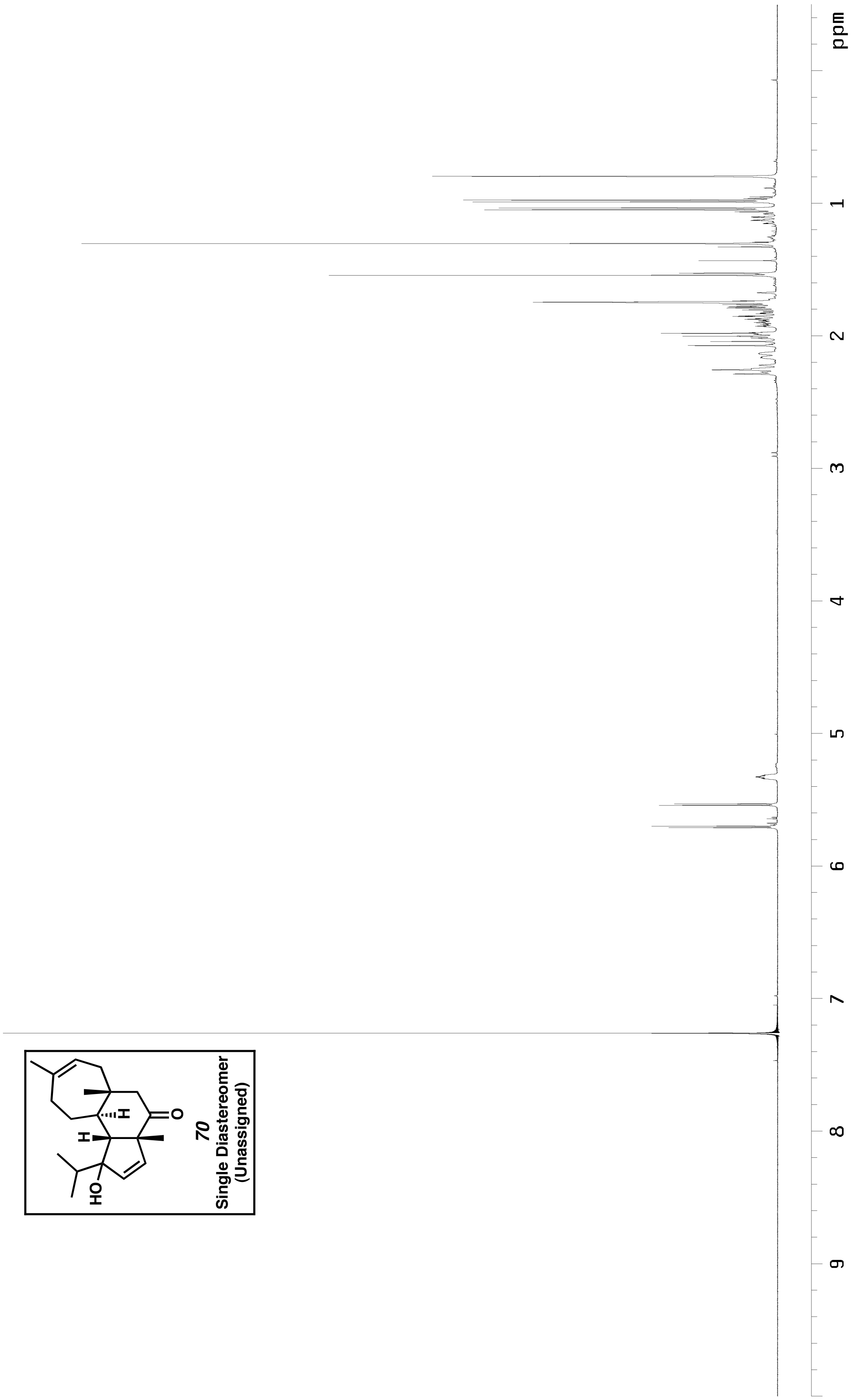


Figure S.61 ^{1}H NMR (500 MHz, CDCl$_3$) of allylic alcohol **70(A)**.

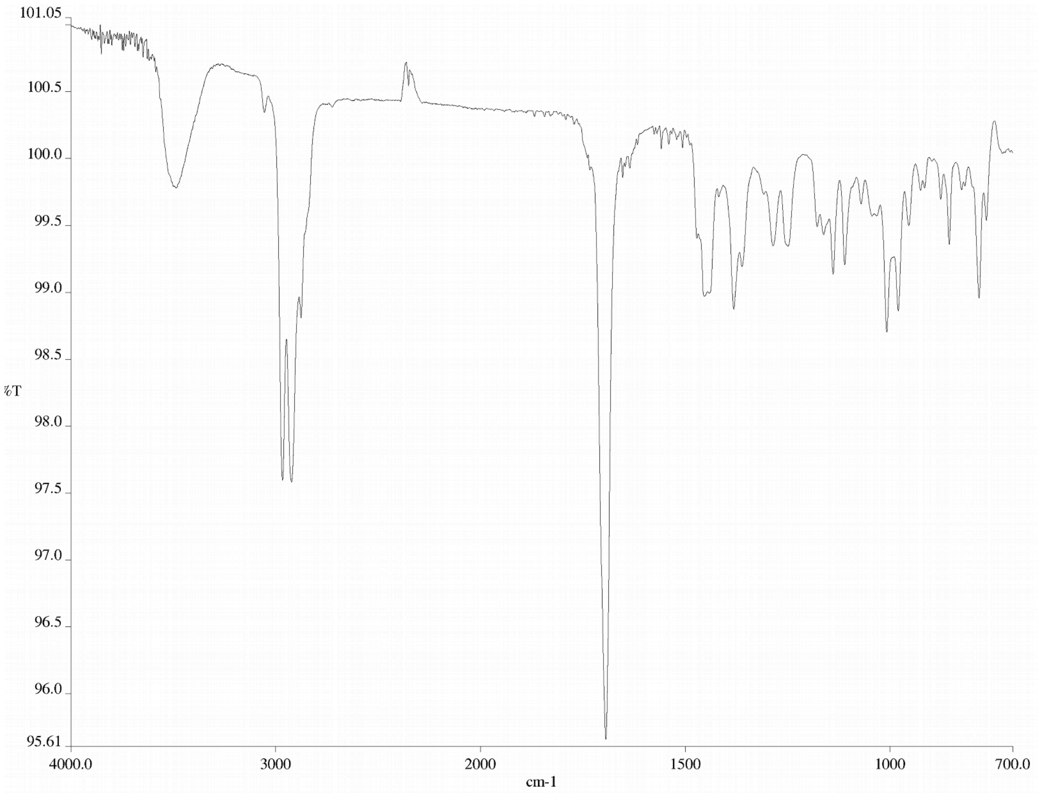


Figure S.62 Infrared spectrum (thin film/NaCl) of allylic alcohol **70(A)**.

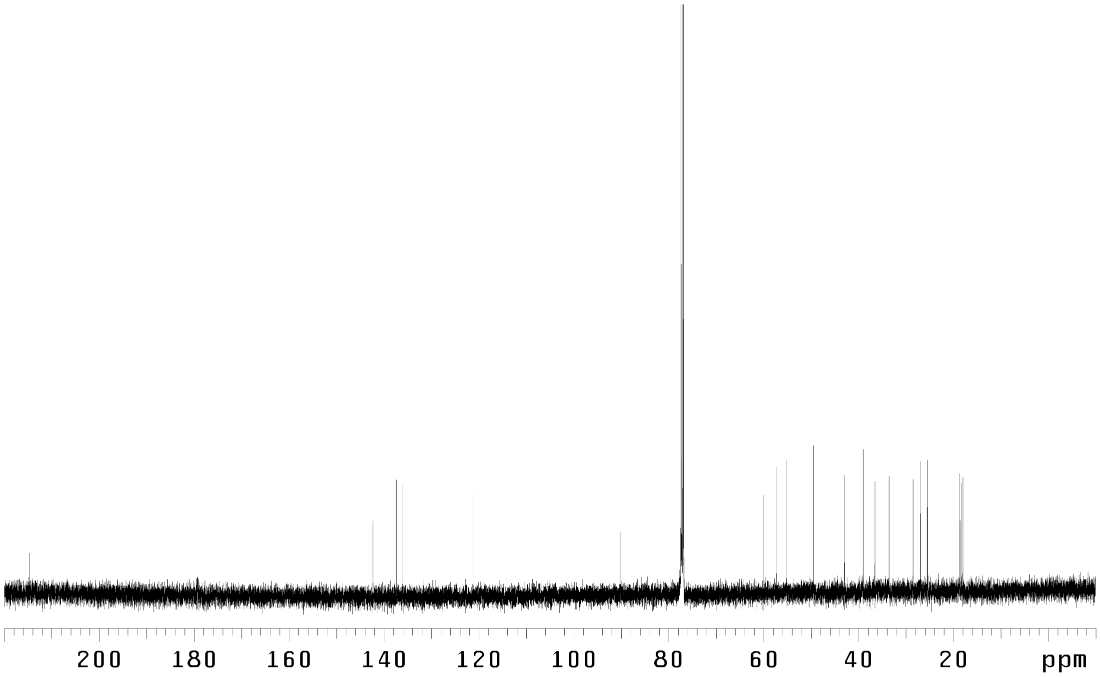


Figure S.63 ^{13}C NMR (125 MHz, CDCl$_3$) of allylic alcohol **70(A)**.

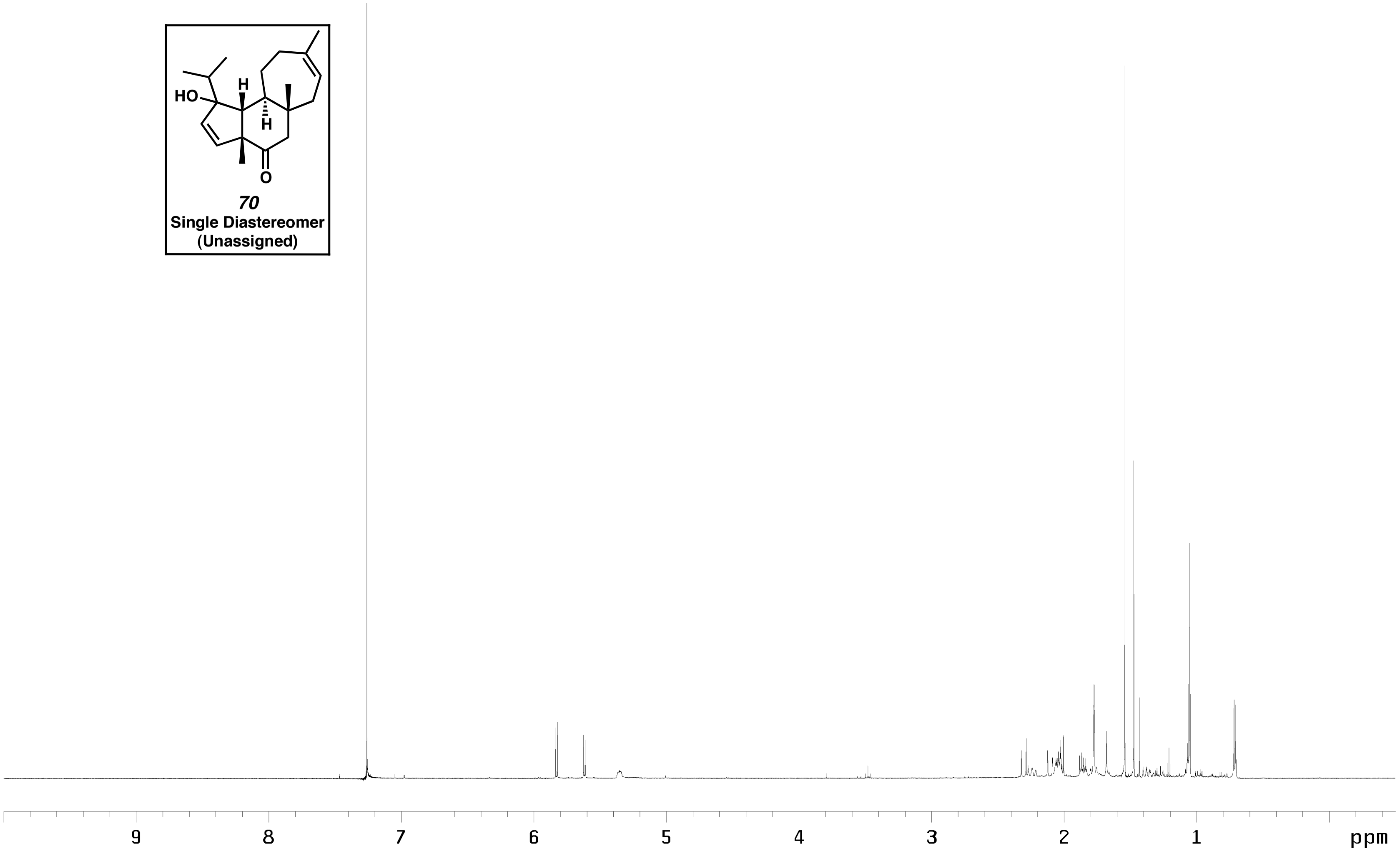


Figure S.64 ^{1}H NMR (500 MHz, $CDCl_3$) of allylic alcohol **70(B)**.

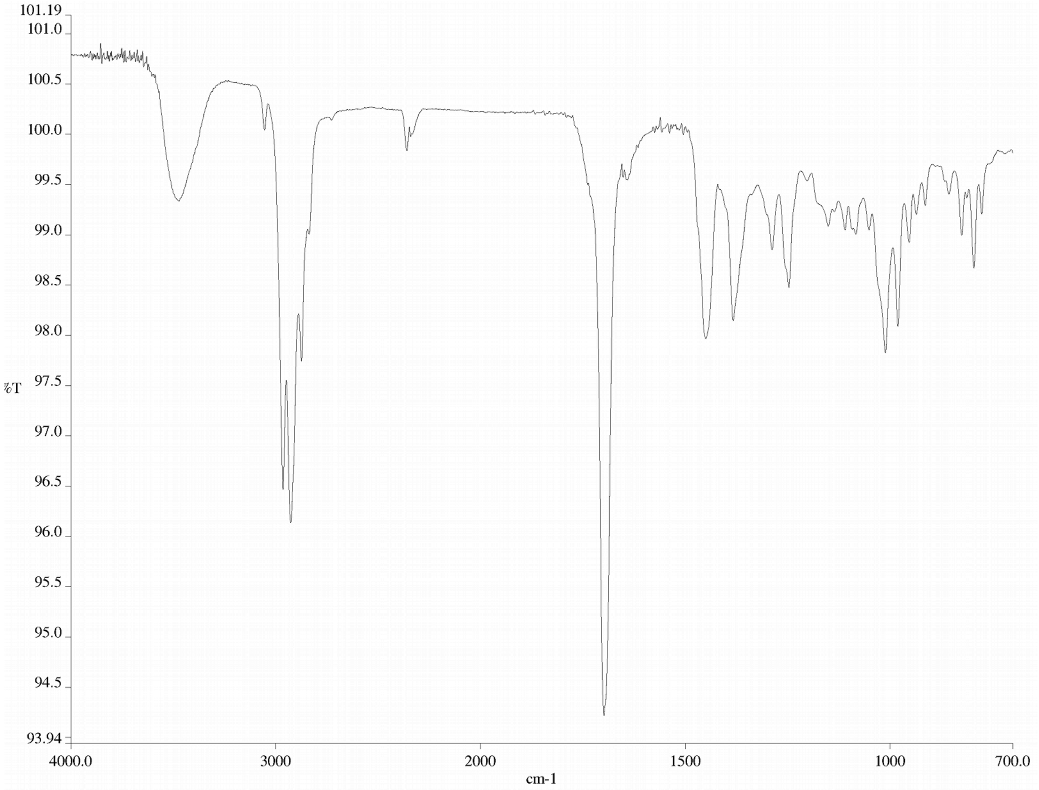


Figure S.65 Infrared spectrum (thin film/NaCl) of allylic alcohol **70(B)**.

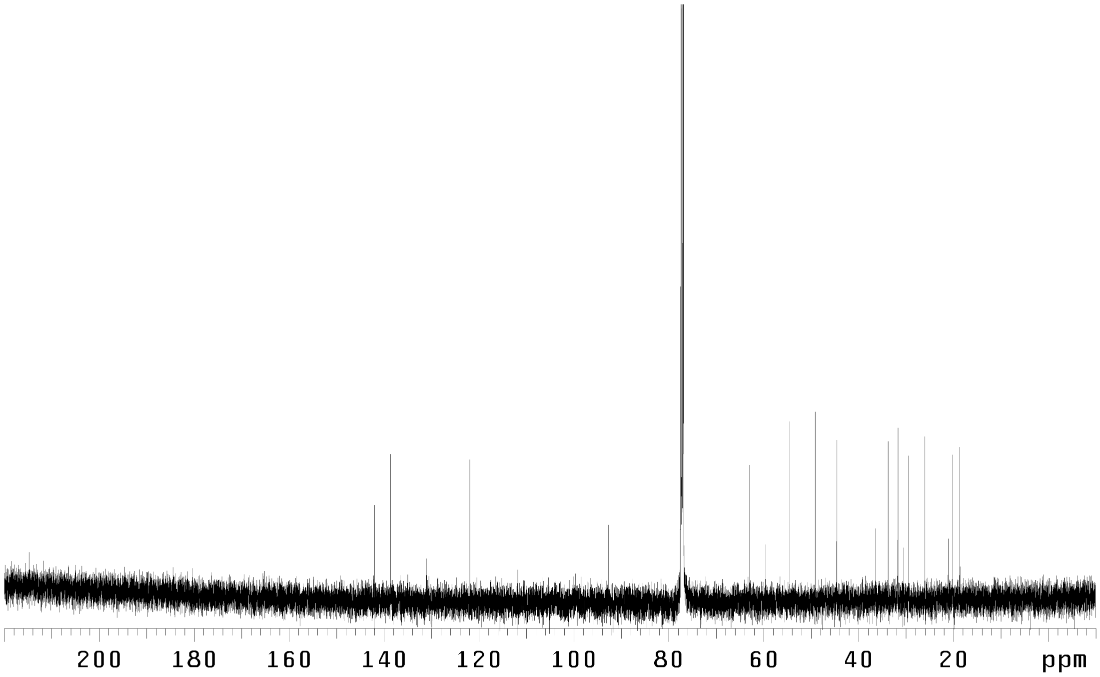


Figure S.66 ^{13}C NMR (125 MHz, $CDCl_3$) of allylic alcohol **70(B)**.

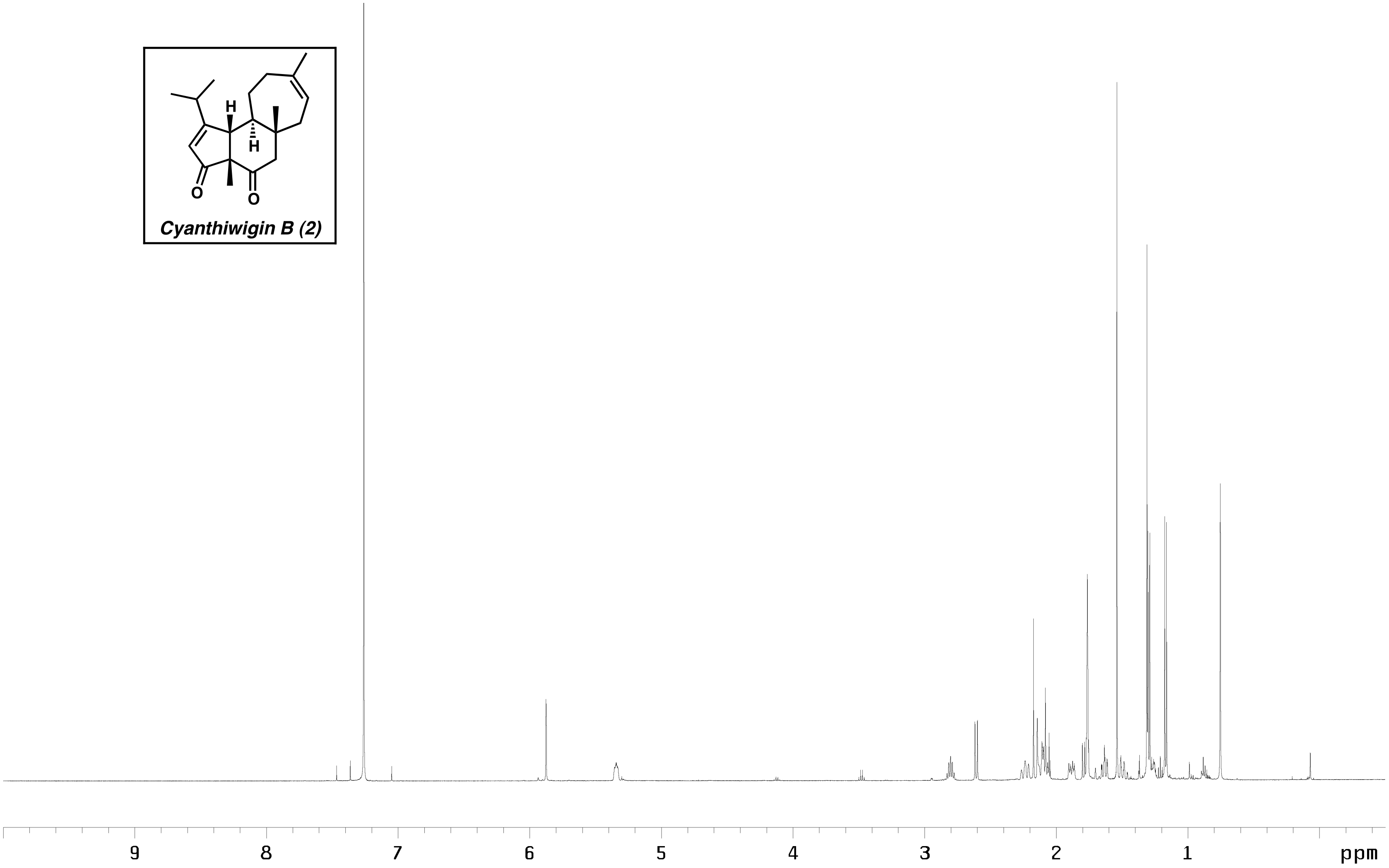


Figure S.67 ^{1}H NMR (125 MHz, CDCl$_3$) of cyanthiwigin B (**2**).

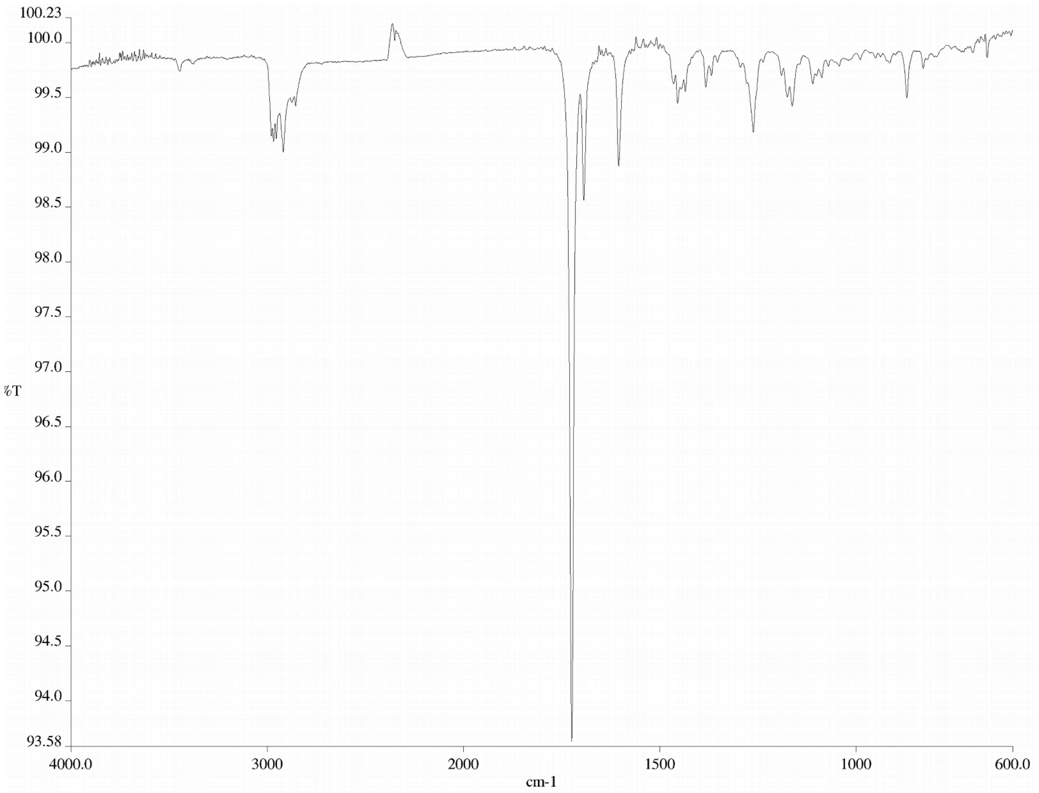


Figure S.68 Infrared spectrum (thin film/NaCl) of cyanthiwigin B (**2**).

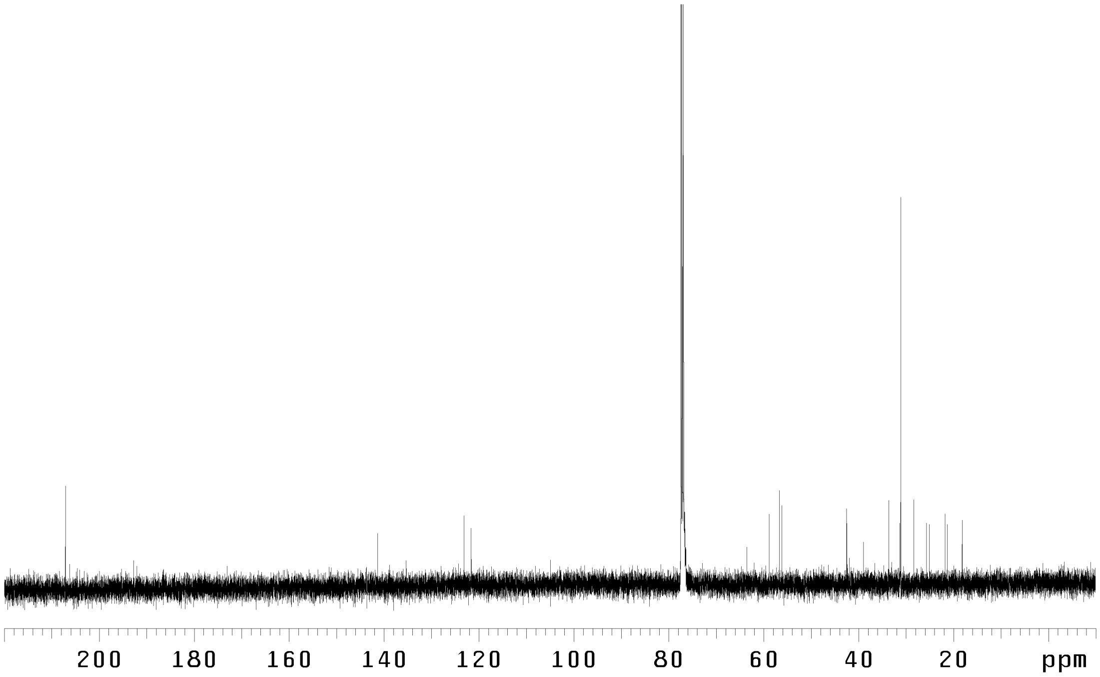


Figure S.69 ^{13}C NMR (125 MHz, CDCl$_3$) of cyanthiwigin B (**2**).

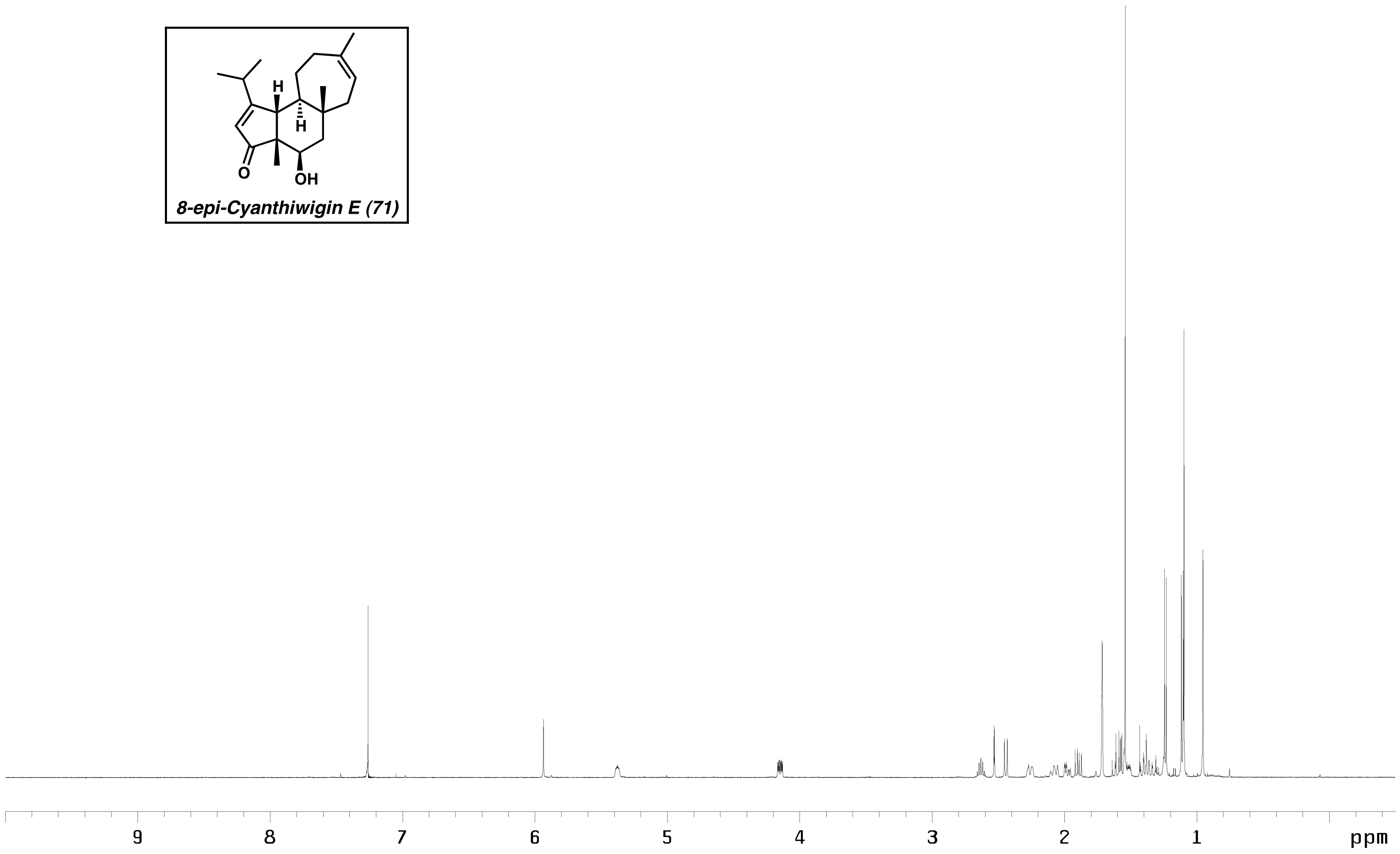


Figure S.70 ^{1}H NMR (500 MHz, $CDCl_3$) of 8-*epi*-cyanthiwigin E (71).

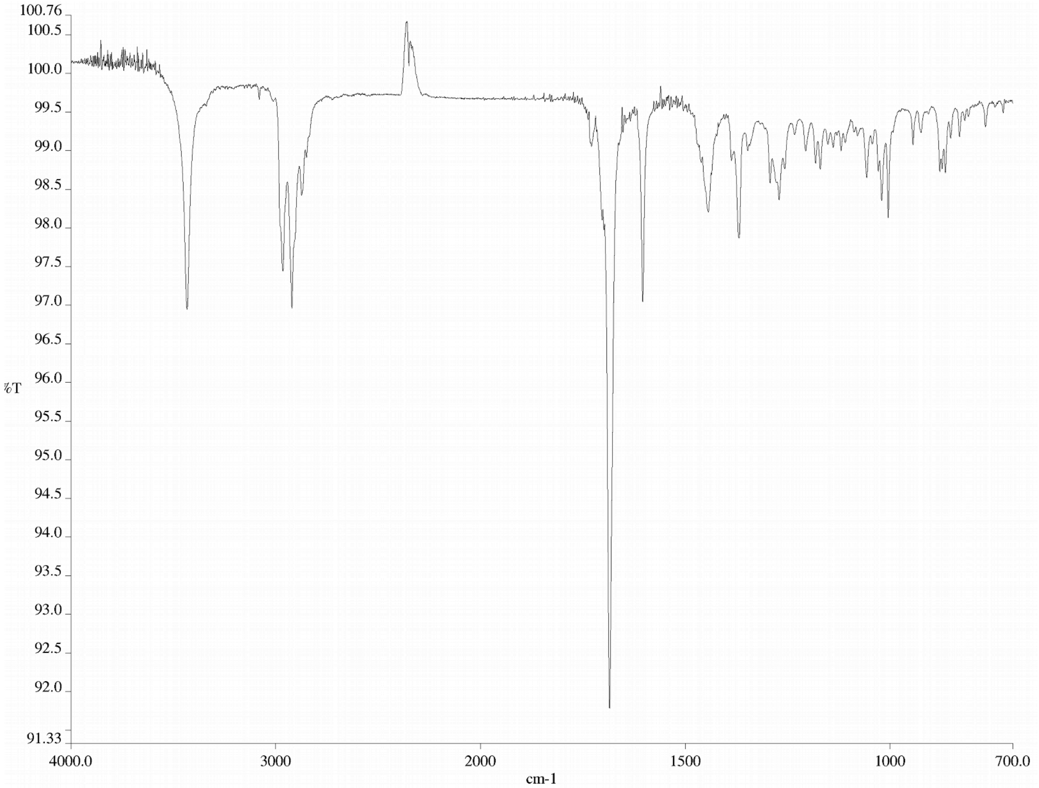


Figure S.71 Infrared spectrum (thin film/NaCl) of 8-*epi*-cyanthiwigin E (**71**).

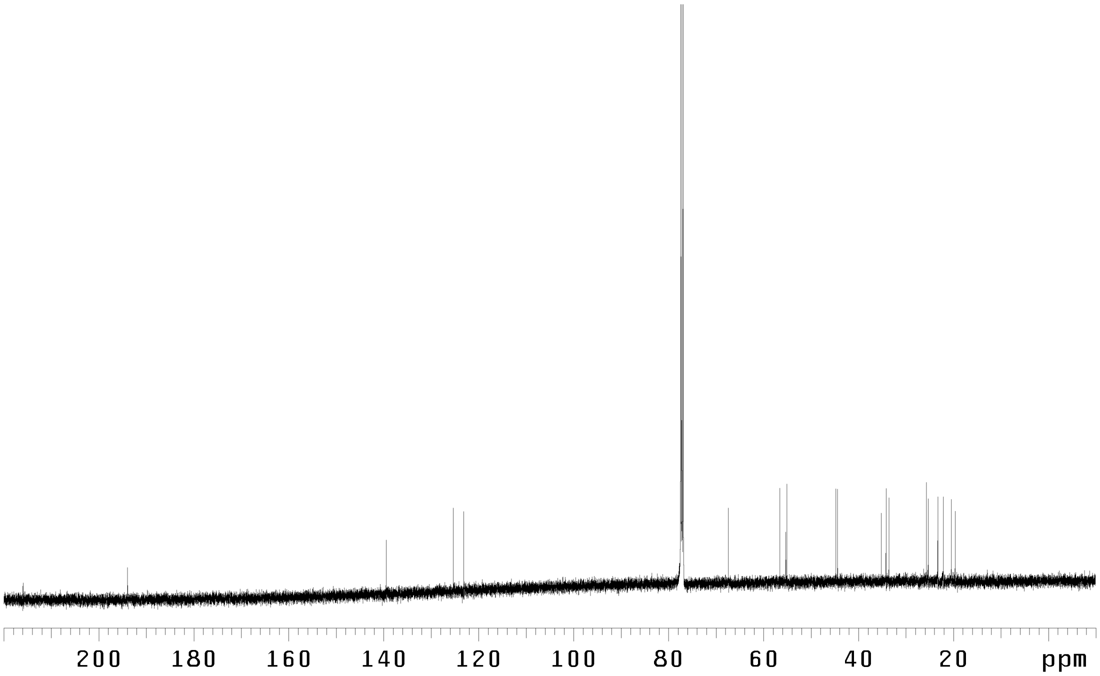


Figure S.72 ^{13}C NMR (125 MHz, CDCl$_3$) of 8-*epi*-cyanthiwigin E (**71**).

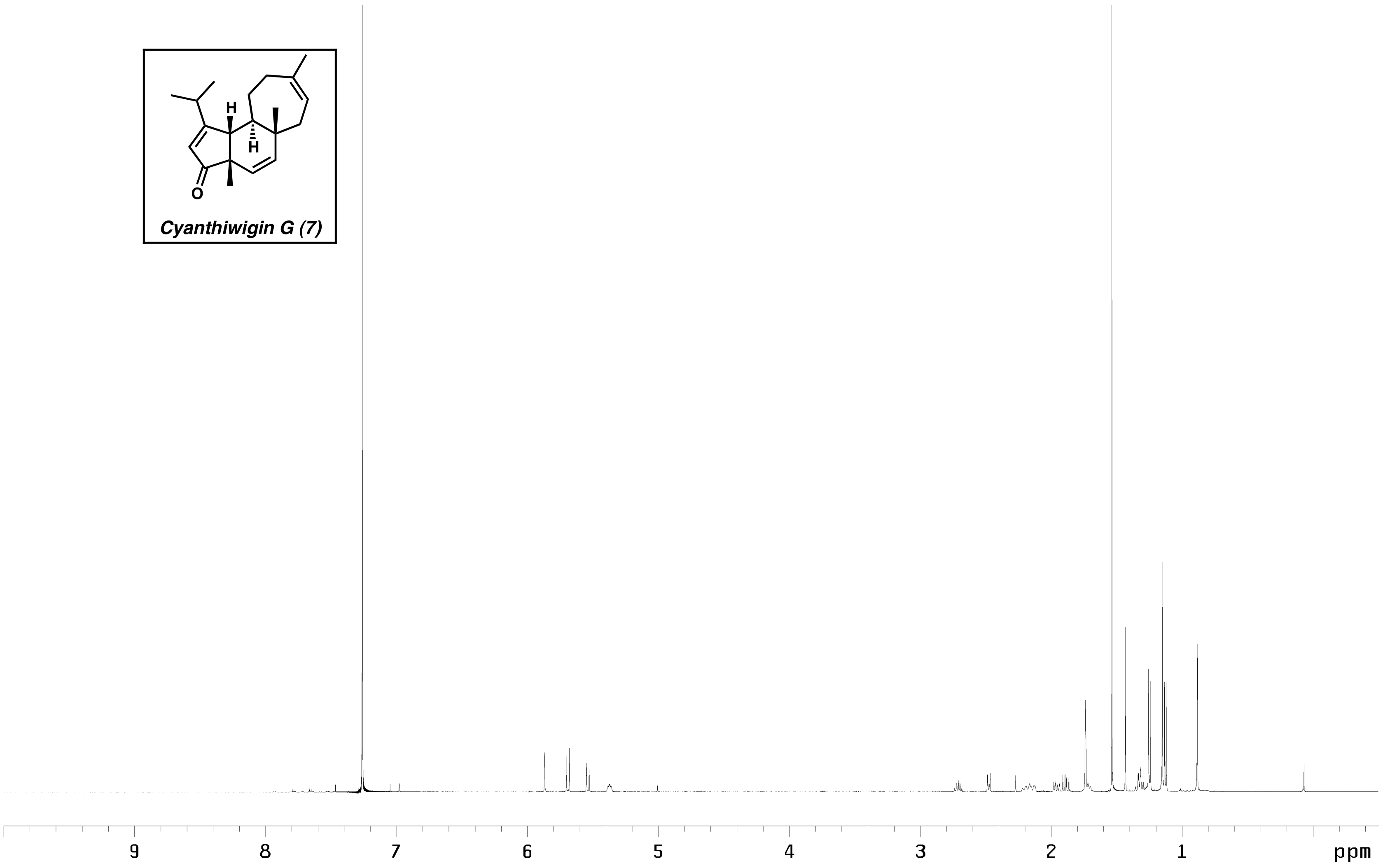


Figure S.73 ^{1}H NMR (500 MHz, CDCl$_3$) of cyanthiwigin G (**7**).

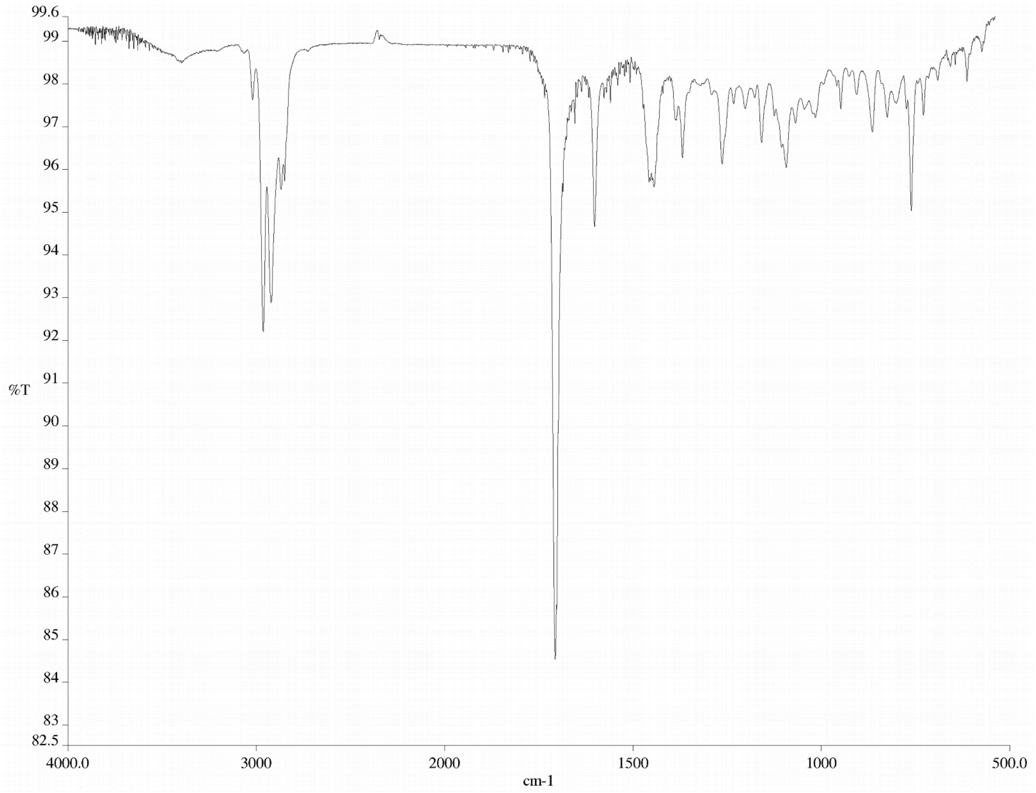


Figure S.74 Infrared spectrum (thin film/NaCl) of cyanthiwigin G (**7**).

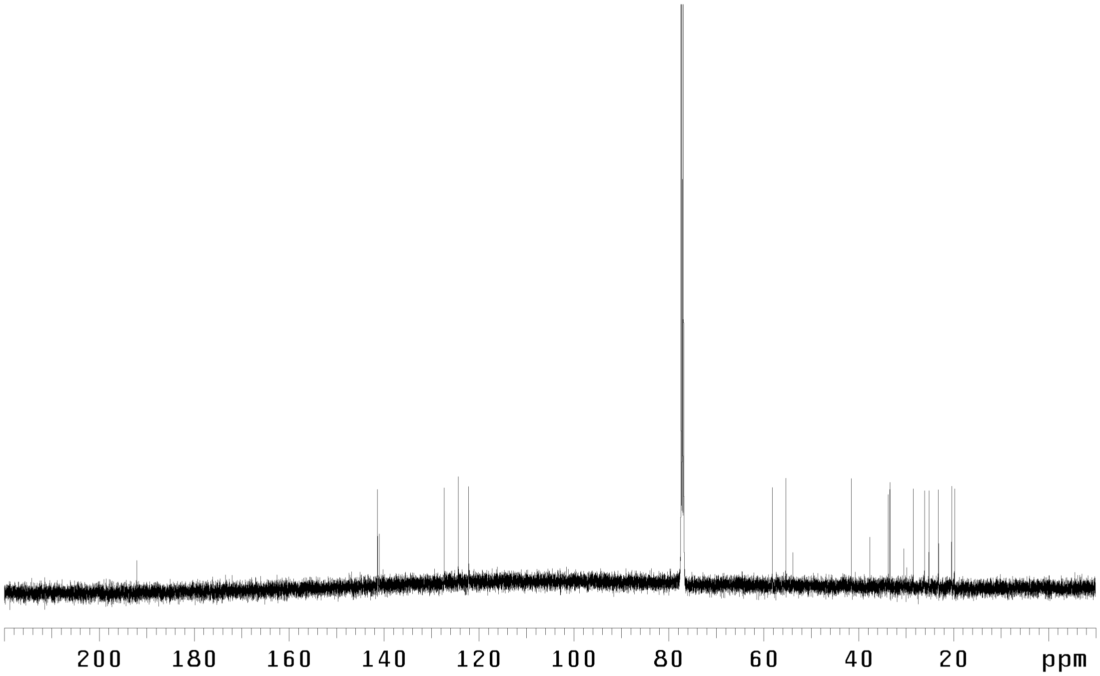


Figure S.75 ^{13}C NMR (125 MHz, $CDCl_3$) of cyanthiwigin G (**7**).

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(5) For development and synthetic application of the vinyl boronate cross-metathesis, See: (a) Morrill, C.; Funk, T. W.; Grubbs, R. H. *Tetrahedron Lett.* **2004**, *45*, 7733–7736. (b) Morrill, C.; Grubbs, R. H. *J. Org. Chem.* **2003**, *68*, 6031–6034. (c) Njardarson, J. T.; Biswas, K.; Danishefsky, S. J. *Chem. Commun.* **2002**, 2759–2761.

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(7) Conditions for this optimized procedure were adapted from a Dieckmann reaction previously published by our group in *Organic Syntheses*. See: Mohr, J. T.; Krout, M. R.; Stoltz, B. M. *Org. Synth.* **2009**, *86*, 194–211.

Table S.1 Crystal data and structure refinement for tricyclic diketone **214** (CCDC 664430).

Empirical formula	$C_{17}H_{24}O_2$
Formula weight	260.36
Crystallization Solvent	Water/acetonitrile
Crystal Habit	Fragment
Crystal size	0.39 x 0.28 x 0.09 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	1.54178 Å CuKα
Data Collection Temperature	100(2) K
θ range for 5024 reflections used in lattice determination	4.12 to 65.79°
Unit cell dimensions	a = 7.4937(2) Å b = 9.0345(2) Å c = 21.4487(5) Å
Volume	1452.12(6) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.191 Mg/m^3
F(000)	568
Data collection program	Bruker SMART v5.630
θ range for data collection	4.12 to 65.79°
Completeness to θ = 65.79°	96.1 %
Index ranges	$-7 \le h \le 8$, $-10 \le k \le 8$, $-21 \le l \le 24$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	7914
Independent reflections	2344 [R_{int}= 0.0753]
Absorption coefficient	0.593 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9486 and 0.8017

Table S.1 (cont.)

Structure solution and Refinement

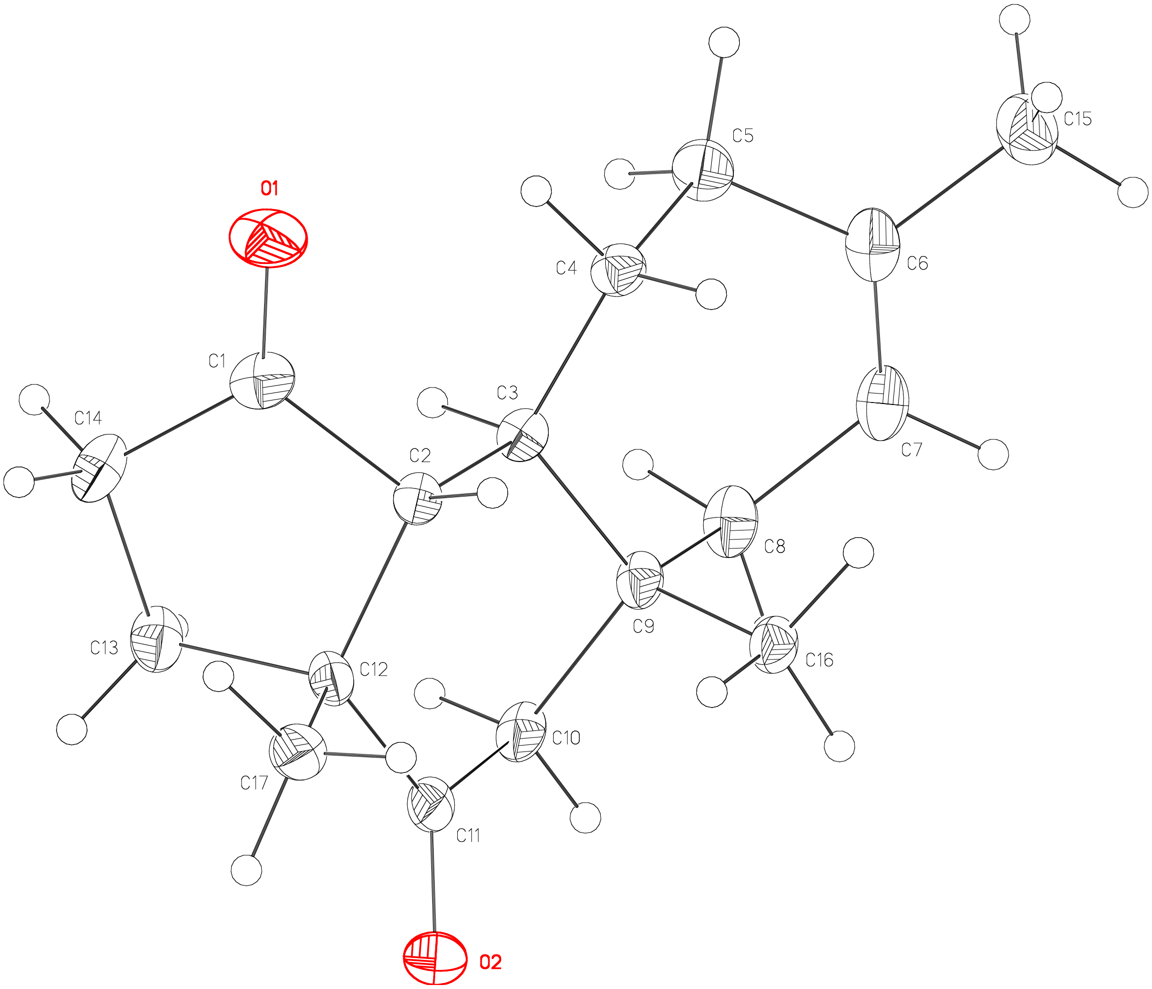
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2344 / 0 / 268
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.394
Final R indices [$I>2\sigma(I)$, 2083 reflections]	R1 = 0.0335, *w*R2 = 0.0669
R indices (all data)	R1 = 0.0391, *w*R2 = 0.0686
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	0.2(2)
Largest diff. peak and hole	0.142 and -0.155 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Figure S.76 ORTEP drawing of tricyclic diketone **63** (shown with 50% probability ellipsoids) (CCDC 664430)



Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 664430.

Table S.2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for diketone **63** (CCDC 664430). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	8369(2)	2053(2)	7466(1)	32(1)
O(2)	13478(2)	3487(2)	5446(1)	29(1)
C(1)	9211(2)	2001(2)	6981(1)	21(1)
C(2)	10059(2)	3336(2)	6653(1)	15(1)
C(3)	8595(2)	4237(2)	6306(1)	15(1)
C(4)	7465(3)	5062(2)	6791(1)	18(1)
C(5)	5740(3)	5787(2)	6542(1)	25(1)
C(6)	6041(2)	7246(2)	6214(1)	23(1)
C(7)	7053(3)	7331(2)	5712(1)	24(1)
C(8)	7949(3)	6025(2)	5407(1)	22(1)
C(9)	9420(3)	5246(2)	5792(1)	17(1)
C(10)	10444(3)	4224(2)	5340(1)	20(1)
C(11)	11962(2)	3449(2)	5658(1)	20(1)
C(12)	11518(2)	2593(2)	6244(1)	17(1)
C(13)	10651(3)	1092(2)	6049(1)	22(1)
C(14)	9615(3)	599(2)	6620(1)	24(1)
C(15)	5143(3)	8573(3)	6497(1)	30(1)
C(16)	10728(3)	6397(2)	6053(1)	19(1)
C(17)	13190(3)	2308(2)	6637(1)	23(1)

Table S.3 Bond lengths [Å] and angles [°] for diketone **63** (CCDC 664430)

O(1)-C(1)	1.219(2)	C(1)-C(2)-C(3)	109.78(14)
O(2)-C(11)	1.224(2)	C(12)-C(2)-C(3)	116.84(14)
C(1)-C(14)	1.514(3)	C(1)-C(2)-H(2)	108.8(9)
C(1)-C(2)	1.533(2)	C(12)-C(2)-H(2)	111.2(9)
C(2)-C(12)	1.554(2)	C(3)-C(2)-H(2)	107.8(9)
C(2)-C(3)	1.556(2)	C(4)-C(3)-C(2)	108.61(14)
C(2)-H(2)	0.972(16)	C(4)-C(3)-C(9)	114.51(15)
C(3)-C(4)	1.534(3)	C(2)-C(3)-C(9)	111.44(14)
C(3)-C(9)	1.559(2)	C(4)-C(3)-H(3)	107.6(9)
C(3)-H(3)	1.050(16)	C(2)-C(3)-H(3)	106.6(9)
C(4)-C(5)	1.544(3)	C(9)-C(3)-H(3)	107.7(8)
C(4)-H(4A)	1.008(19)	C(3)-C(4)-C(5)	115.75(16)
C(4)-H(4B)	0.995(18)	C(3)-C(4)-H(4A)	111.3(11)
C(5)-C(6)	1.511(3)	C(5)-C(4)-H(4A)	107.4(11)
C(5)-H(5A)	0.994(19)	C(3)-C(4)-H(4B)	108.6(10)
C(5)-H(5B)	1.06(2)	C(5)-C(4)-H(4B)	107.8(10)
C(6)-C(7)	1.320(3)	H(4A)-C(4)-H(4B)	105.5(14)
C(6)-C(15)	1.503(3)	C(6)-C(5)-C(4)	113.95(17)
C(7)-C(8)	1.507(3)	C(6)-C(5)-H(5A)	109.1(11)
C(7)-H(7)	0.99(2)	C(4)-C(5)-H(5A)	106.3(11)
C(8)-C(9)	1.547(3)	C(6)-C(5)-H(5B)	108.4(12)
C(8)-H(8A)	1.046(19)	C(4)-C(5)-H(5B)	107.8(11)
C(8)-H(8B)	1.013(19)	H(5A)-C(5)-H(5B)	111.3(15)
C(9)-C(16)	1.535(2)	C(7)-C(6)-C(15)	122.73(18)
C(9)-C(10)	1.543(2)	C(7)-C(6)-C(5)	121.05(18)
C(10)-C(11)	1.500(3)	C(15)-C(6)-C(5)	116.21(18)
C(10)-H(10A)	1.008(19)	C(6)-C(7)-C(8)	124.41(19)
C(10)-H(10B)	0.94(2)	C(6)-C(7)-H(7)	121.8(11)
C(11)-C(12)	1.514(2)	C(8)-C(7)-H(7)	113.8(11)
C(12)-C(17)	1.532(3)	C(7)-C(8)-C(9)	116.25(16)
C(12)-C(13)	1.561(3)	C(7)-C(8)-H(8A)	109.8(11)
C(13)-C(14)	1.518(3)	C(9)-C(8)-H(8A)	108.7(11)
C(13)-H(13A)	0.966(18)	C(7)-C(8)-H(8B)	110.5(10)
C(13)-H(13B)	0.973(19)	C(9)-C(8)-H(8B)	105.5(10)
C(14)-H(14A)	0.99(2)	H(8A)-C(8)-H(8B)	105.5(15)
C(14)-H(14B)	1.00(2)	C(16)-C(9)-C(10)	108.47(16)
C(15)-H(15A)	1.00(2)	C(16)-C(9)-C(8)	109.99(15)
C(15)-H(15B)	1.01(2)	C(10)-C(9)-C(8)	106.98(15)
C(15)-H(15C)	0.96(2)	C(16)-C(9)-C(3)	112.96(14)
C(16)-H(16A)	1.03(2)	C(10)-C(9)-C(3)	106.99(14)
C(16)-H(16B)	1.000(19)	C(8)-C(9)-C(3)	111.19(15)
C(16)-H(16C)	1.036(19)	C(11)-C(10)-C(9)	111.79(15)
C(17)-H(17A)	1.00(2)	C(11)-C(10)-H(10A)	107.4(10)
C(17)-H(17B)	1.01(2)	C(9)-C(10)-H(10A)	110.6(10)
C(17)-H(17C)	0.95(2)	C(11)-C(10)-H(10B)	110.2(12)
		C(9)-C(10)-H(10B)	109.6(12)
O(1)-C(1)-C(14)	124.84(18)	H(10A)-C(10)-H(10B)	107.0(15)
O(1)-C(1)-C(2)	125.15(17)	O(2)-C(11)-C(10)	121.45(17)
C(14)-C(1)-C(2)	109.99(15)	O(2)-C(11)-C(12)	121.84(17)
C(1)-C(2)-C(12)	102.14(14)	C(10)-C(11)-C(12)	116.70(15)

C(11)-C(12)-C(17)	111.27(16)	C(6)-C(15)-H(15B)	110.4(12)
C(11)-C(12)-C(2)	113.80(14)	H(15A)-C(15)-H(15B)	106.7(18)
C(17)-C(12)-C(2)	109.74(15)	C(6)-C(15)-H(15C)	114.4(14)
C(11)-C(12)-C(13)	108.17(14)	H(15A)-C(15)-H(15C)	112.7(19)
C(17)-C(12)-C(13)	110.00(16)	H(15B)-C(15)-H(15C)	102.7(17)
C(2)-C(12)-C(13)	103.55(15)	C(9)-C(16)-H(16A)	109.4(11)
C(14)-C(13)-C(12)	104.54(15)	C(9)-C(16)-H(16B)	111.8(11)
C(14)-C(13)-H(13A)	110.1(10)	H(16A)-C(16)-H(16B)	111.5(15)
C(12)-C(13)-H(13A)	110.7(11)	C(9)-C(16)-H(16C)	107.7(10)
C(14)-C(13)-H(13B)	111.8(11)	H(16A)-C(16)-H(16C)	107.4(15)
C(12)-C(13)-H(13B)	112.1(12)	H(16B)-C(16)-H(16C)	108.8(14)
H(13A)-C(13)-H(13B)	107.6(15)	C(12)-C(17)-H(17A)	110.3(11)
C(1)-C(14)-C(13)	105.56(16)	C(12)-C(17)-H(17B)	112.1(12)
C(1)-C(14)-H(14A)	113.1(12)	H(17A)-C(17)-H(17B)	108.9(16)
C(13)-C(14)-H(14A)	111.2(12)	C(12)-C(17)-H(17C)	111.9(11)
C(1)-C(14)-H(14B)	109.3(12)	H(17A)-C(17)-H(17C)	109.2(16)
C(13)-C(14)-H(14B)	112.8(12)	H(17B)-C(17)-H(17C)	104.2(15)
H(14A)-C(14)-H(14B)	105.1(17)		
C(6)-C(15)-H(15A)	109.6(13)		

Table S.4 Anisotropic displacement parameters ($Å^2$x 10^4) for diketone **63** (CCDC 664430). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	372(9)	382(9)	203(8)	136(6)	113(6)	108(7)
O(2)	332(8)	252(8)	275(8)	-7(6)	149(6)	2(7)
C(1)	202(11)	268(11)	149(10)	90(8)	-25(8)	30(8)
C(2)	203(10)	152(10)	94(10)	-6(7)	-6(7)	-11(7)
C(3)	175(10)	170(10)	115(10)	12(7)	-25(7)	-14(8)
C(4)	183(11)	195(11)	170(11)	27(9)	1(8)	1(8)
C(5)	173(11)	242(12)	320(13)	9(9)	-27(10)	14(9)
C(6)	199(12)	187(10)	317(12)	2(9)	-117(9)	9(8)
C(7)	306(12)	175(11)	231(12)	53(8)	-85(9)	15(9)
C(8)	312(11)	188(11)	165(11)	37(8)	-69(9)	3(9)
C(9)	252(11)	141(10)	124(10)	15(7)	-2(8)	-2(8)
C(10)	332(12)	160(11)	98(10)	17(8)	33(8)	-30(9)
C(11)	296(12)	142(11)	163(11)	-59(7)	66(8)	-34(8)
C(12)	211(11)	130(10)	157(10)	1(7)	5(7)	26(7)
C(13)	340(12)	174(11)	160(11)	-5(8)	4(9)	-7(9)
C(14)	308(13)	197(11)	213(12)	38(8)	-22(9)	-82(9)
C(15)	233(12)	241(12)	421(15)	3(11)	-34(10)	51(9)
C(16)	244(11)	150(10)	178(11)	-20(8)	16(8)	-29(9)
C(17)	212(12)	212(12)	262(12)	30(9)	28(9)	30(9)

Table S.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for diketone **214** (CCDC 664430)

	x	y	z	U_{iso}
H(2)	10590(20)	3978(18)	6967(7)	5(4)
H(3)	7760(20)	3463(18)	6085(7)	7(4)
H(7)	7290(20)	8280(20)	5503(9)	29(5)
H(4A)	8180(20)	5860(20)	7005(8)	21(5)
H(5A)	5210(20)	5070(20)	6242(9)	24(5)
H(8A)	8490(30)	6340(20)	4977(9)	33(5)
H(10A)	9630(20)	3440(20)	5166(8)	22(5)
H(13A)	9850(20)	1230(20)	5701(9)	19(5)
H(14A)	8530(30)	40(20)	6501(9)	33(6)
H(15A)	5460(30)	9480(30)	6252(10)	46(7)
H(16A)	11750(30)	5860(20)	6279(9)	31(6)
H(17A)	14160(30)	1860(20)	6372(9)	30(5)
H(4B)	7120(20)	4350(20)	7125(8)	16(5)
H(5B)	4880(30)	5970(20)	6926(10)	41(6)
H(8B)	7040(20)	5230(20)	5307(8)	17(5)
H(10B)	10870(20)	4780(20)	5001(9)	26(5)
H(13B)	11540(30)	360(20)	5925(9)	24(6)
H(14B)	10310(30)	-90(20)	6890(10)	36(6)
H(15B)	5590(30)	8740(20)	6937(9)	34(6)
H(16B)	10120(20)	7120(20)	6333(8)	26(5)
H(17B)	12940(30)	1620(20)	7000(9)	37(6)
H(15C)	3890(30)	8470(30)	6556(10)	43(6)
H(16C)	11280(20)	6960(20)	5679(9)	22(5)
H(17C)	13620(20)	3190(20)	6827(8)	17(5)