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SUPPORTING INFORMATION

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Title: Enantioselective Synthesis of Caprolactam and Enone Precursors to the Heterocyclic DEFG Ring System of Zoanthenol

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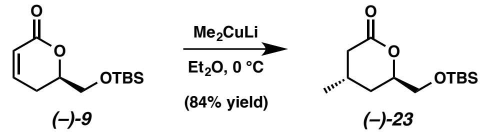
Materials and Methods

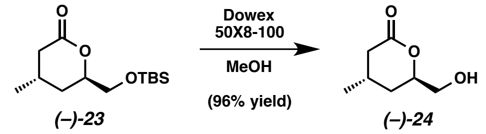
Unless stated otherwise, reactions were conducted in flame-dried glassware using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All reactions were conducted under an inert atmosphere of dry nitrogen or argon, unless otherwise stated. All commercially obtained reagents were used as received. When required, commercial reagents were purified following the guidelines of Perrin and Armarego.[1] Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, ceric ammonium molybdate, and potassium permanganate staining. ICN silica gel (particle size 0.032–0.063 mm) was used for flash chromatography using the method described by Still.[2]

^{1}H NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz), a Varian Inova 500 (at 500 MHz), and are reported relative to residual protio solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 75 MHz) and are reported relative to residual protio solvent signals. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-1010 polarimeter (Na lamp, 589 nm). HPLC analysis was performed on a Hewlet-Packard 1100 Series HPLC (UV detector at 245 nm) equipped with the following Chiralcel columns: OD-H (25 cm), OD guard (5 cm), AD (25 cm), OJ (25 cm) and OB-H (25 cm). High resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility.

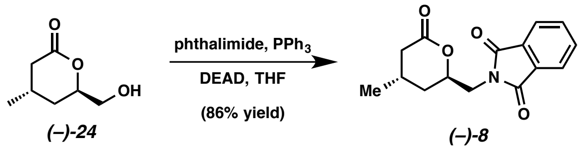
Preparative Procedures



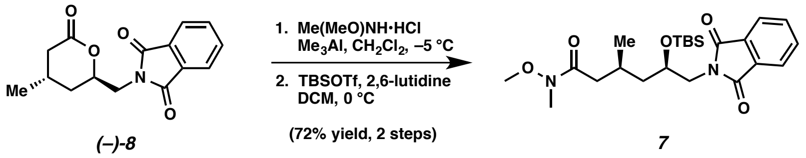
β-Me, δ-Lactone (–)-23. MeLi (1.3 M in ether, 5.8 mL, 7.56 mmol) was added to a stirring slurry of CuI (714 mg, 3.89 mmol) in diethyl ether cooled to –78 °C. The vessel was warmed to 0 °C for 15 min, then cooled again to –78 °C. A solution of the α,β-unsaturated lactone **(–)-9** (471 mg, 1.95 mmol) in diethyl ether (4 mL) was then carefully added along the cooled inner walls of the reaction flask. After 1 h, the reaction mixture was quenched by the slow addition of saturated aq ammonium chloride (15 mL) at –78 °C. The reaction flask was gradually warmed to ambient temperature for 30 min, then diluted with ether (30 mL). The biphasic mixture was transferred to a separatory funnel and shaken vigorously to dissolve solids. The organic layer was washed with saturated aq ammonium chloride (2 x 20 mL), then brine (1 x 10 mL), dried over magnesium sulfate and concentrated. The resulting material was purified by flash chromatography over silica gel (25% EtOAc:hexane eluent) to yield δ-lactone **(–)-23** (422 mg, 84% yield, R_f 0.20 in 25% EtOAc:hexane) as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 4.47-4.40 (m, 1H), 3.70-3.73 (m, 2H), 2.55 (dd, *J*=16.3, 5.1 Hz, 1H), 2.18-2.29 (m, 1H), 2.12 (dd, *J*=16.4, 8.9 Hz, 1H), 1.90-1.99 (m, 1H), 1.52-1.60 (m, 1H), 1.05 (d, *J*=6.6 Hz, 3H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 77.8, 65.1, 38.1, 31.7, 26.2, 24.1, 21.4, 18.6, 5.00; IR (neat) 1743 cm^{-1}; HRMS (FAB^+) *m/z* calc'd for $[C_{13}H_{26}O_3Si]^+$: 201.0947, found 201.0950; $[\alpha]_D^{20}$ –25.027° (c=1, $CDCl_3$).



Alcohol (–)-24. Lactone **(–)-23** (100 mg, 0.39 mmol) was dissolved in methanol (5.0 mL) and added to a reaction flask equipped with Dowex 50X8-100 cation exchange resin (1.0 g). The mixture was stirred at ambient temperature for 3 h, then filtered. The resin was washed with methanol (2 x 5 mL) and the combined organics were concentrated. The crude material was dried overnight under high vacuum to yield the alcohol **(–)-24** (53 mg, 96% yield, R_f 0.18 in 80% EtOAc:hexane) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.47-4.52 (m, 1H), 3.75 (dd, *J*=12.3, 3.6 Hz, 1H), 3.66 (dd, *J*=12.1, 5.8 Hz, 1H), 2.69 (br s, 1H), 2.53-2.58 (m, 1H), 2.13-2.23 (m, 2H), 1.88-1.97 (m, 1H), 1.49-1.57 (m, 1H), 1.08 (d, *J*=6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 78.2, 65.1, 37.8, 31.1, 24.3, 21.4; IR (neat) 1722.4 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_7H_{12}O_3]^+$: 144.0786, found 144.0787; $[\alpha]_D^{20}$ –162.147° (c=1, $CDCl_3$).



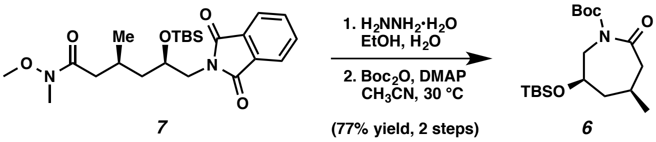
Phthalimide (–)-8. To a stirred solution of alcohol **(–)-24** (1.48 g, 10.28 mmol) in tetrahydrofuran (30 mL) was added triphenyl phosphine (2.83 g 10.79 mmol), then phthalimide (1.59 g, 10.76 mmol). Once all reagents had dissolved, the reaction mixture was cooled to 0 °C and DEAD (1.707 mL, 10.79 mmol) was added dropwise to the stirred solution. The reaction flask was then warmed to 30 °C for 12 h, then concentrated. The concentrated reaction mixture was flashed over silica (4:1 hexanes/EtOAc eluent). The resulting solid was recrystalized from dichloromethane to provide phthalimide **(–)-8** (2.42 g, 86% yield, R_f 0.16 in 40% EtOAc:hexane) as a white solid: m.p. 118-120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.88 (m, 2H), 7.71-7.76 (m, 2H), 4.74-4.83 (m, 1H), 4.04 (dd, *J*=15.0, 8.3 Hz, 1H), 3.78 (dd, *J*=15.0, 5.5 Hz, 1H), 2.63 (dd, *J*=16.6, 5.4 Hz, 1H), 2.28 (m, 1H), 2.16 (dd, *J*=16.5, 9.1 Hz, 1H), 1.86 (m, 1H), 1.66 (m, 1H), 1.09 (d, *J*=6.9 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 170.9, 168.1, 134.4, 132.0, 123.7, 74.1, 41.9, 37.9, 32.8, 24.0, 21.5; IR (neat) 1773.9, 1715.8 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{15}H_{16}NO_4]^+$: 274.1079, found 274.1076; $[\alpha]_D^{20}$ –68.6255° (c=1, $CDCl_3$).



Weinreb Amide (–)-7. Trimethylaluminum (2.0 M in toluene, 10.32 mL, 20.64 mmol) was slowly added to a stirred solution of *N,O*-dimethylhydroxylamine hydrochloride (2.01 g, 16.80 mmol) in dichloromethane (40 mL) cooled to –10 °C The solution was stirred for 20 min before the dropwise addition of the Mitusunobu adduct **(–)-8** (2.26 g, 8.23 mmol) in dichloromethane (10 mL). The reaction temperature was maintained at –10 °C for 30 min before the addition of saturated sodium bicarbonate (20 mL). The reaction mixture was then allowed to warm to room temperature. The crude reaction mixture was diluted with dichloromethane (30 mL) and brine (20 mL) to dissipate emulsions during extraction. The crude was transferred to a separatory funnel and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 30 mL). The combined organic layers were washed with brine (1 x 30 mL), then dried and concentrated to a volume of 10 mL over a rotovap bath temperature of 15 °C.

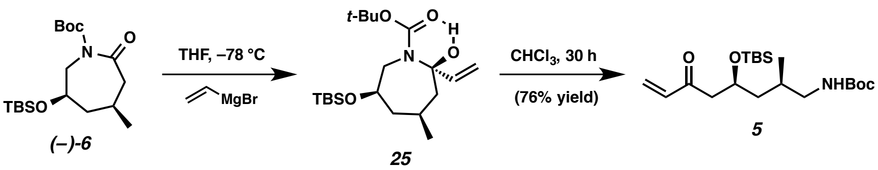
The crude amide was diluted with dichloromethane (20 mL) and cooled to 0 °C. To the cooled, stirred solution was added TBSOTf (3.79 mL, 16.51 mmol) followed by 2,6-lutidine (1.442 mL, 12.38 mmol). The solution was maintained at 0 °C for 20 min, then quenched by addition of saturated ammonium chloride (20 mL). The biphasic mixture was allowed to warm to room temperature while stirring vigorously, then transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organics were washed with saturated sodium bicarbonate solution (1 x 15 mL) and water (1 x 15 mL), then dried over magnesium sulfate and concentrated. The resulting crude product was flashed over silica gel (20% EtOAc:hexanes eluent) to provide Weinreb amide **(–)-7** (2.58g, 72% yield, R_f 0.30 in 40% EtOAc:hexane) as an oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.82 (dd, *J*=5.4, 3.1 Hz, 2H), 7.70 (dd, *J*=5.6, 2.9 Hz, 2H), 4.05-4.14 (m, 1H), 3.68-3.78 (m, 2H), 3.65 (s, 3H), 3.14 (s, 3H), 2.38-2.45 (m, 1H), 2.18-2.29 (m, 1H), 1.51-1.60 (m, 1H), 1.38-1.47 (m, 1H), 1.03 (d, *J*=6.3 Hz, 3H), 0.76 (s, 9H), –0.01 (s, 3H),

–0.20 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 168.5, 134.1, 132.3, 123.3, 68.3, 61.5, 44.0, 43.7, 39.7, 32.3, 26.9, 26.0, 20.8, 18.1, –4.3, –4.4; IR (neat) 3473.5, 2955.4, 2857.3, 1774.2, 1714.5, 1660.3 cm^{-1}; HRMS *m/z* calc'd for $[C_{23}H_{37}N_2O_5Si]^+$: 449.2472, found 449.2470; $[\alpha]_D^{20}$ –29.7° (*c*=1, $CDCl_3$).



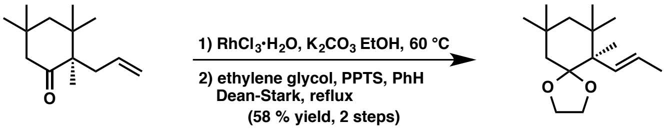
Caprolactam SI-1. To a solution of (–)-**7** (2.848 g, 6.55 mmol) in absolute ethanol was added hydrazine monohydrate (1.75 mL, 32.77 mmol) and deionized water (0.39 mL). The solution was heated to 90 °C for 4 h. The reaction was then cooled in an ice bath and the thick cottony solids were filtered. The filtrate was then concentrated to a solid. The crude solid was taken up in EtOAc (50 mL), cooled in an ice bath, and filtered over a pad of Celite, rinsing with portions of EtOAc (2 x 20 mL). The organics were then dried over sodium sulfate and concentrated. The crude solid was subjected to chromatography over silica gel (30% EtOAc:hexane eluent) to yield the unprotected caprolactam **(–)-SI-1** (1.633g, 81% yield, R_f 0.22 in 50% EtOAc:hexane) as a white solid: m.p. 79–81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27 (br s, 1H), 3.56-3.65 (m, 1H), 3.18-3.28 (m, 1H), 3.01-3.10 (m, 1H), 2.38 (dd, *J*=13.7, 11.0 Hz, 1H), 2.25 (dd, *J*=12.1, 1.7 Hz, 1H), 1.96-2.04 (m, 1H), 1.83-1.93 (m, 1H), 1.36 (q, *J*=11.8 Hz, 1H), 1.04 (d, *J*=6.9 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 177.3, 71.0, 49.7, 48.9, 44.2, 28.6, 26.1, 24.8, 18.4, –4.2, –4.4; IR (neat) 3239.9, 2929.8, 2857.6, 1673.1 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{13}H_{28}NO_2Si]^+$: 242.1576, found 242.1576; $[\alpha]_D^{20}$ –15.0° (c=1, $CDCl_3$).

***N*-Boc-caprolactam** (–)-**6**. To a solution of **SI-1** (853 mg, 3.313 mmol) in acetonitrile (40 ml) was added *t*-butyl carbonate anhydride (1.81 g, 8.28 mmol). After the *t*-butyl carbonate anhydride had completely dissolved, *N*,*N*-dimethylamino pyridine (1.01 g, 8.28 mmol) was added in several small portions. The resulting dark-brown solution was stirred for 10 min at ambient temperature, then warmed to 35 °C. After 5 hours, the reaction was quenched by addition of water (20 mL). The mixture was transferred to a separatory funnel and extracted with EtOAc (4 x 30 mL). The combined organics were washed with brine (1 x 30 mL), dried over sodium sulfate, and concentrated to give a brown waxy solid, which was purified by flash chromatography over silica (10% EtOAc:hexane) to provide *N*-Boc-caprolactam (–)-**6** (1.314 g, 95% yield, R_f 0.22 in 10% EtOAc:hexane) as a waxy solid: m.p. 77–78°; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 (dt, *J*=14.8, 1.8 Hz, 1H), 3.63 (tdd, *J*=22.0, 4.9, 2.2 Hz, 1H), 3.33 (dd, *J*=15.0, 9.5 Hz, 1H), 2.56 (dd, *J*=14.1, 10.9 Hz, 1H), 2.41 (d, *J*=14.3 Hz, 1H), 1.96-2.03 (m, 1H), 1.87-1.94 (m, 1H), 1.51 (s, 9H), 1.27-1.39 (m, 1H), 1.04 (d, *J*=6.6 Hz, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.1, 152.5, 83.4, 70.4, 52.4, 47.7, 47.0, 28.4, 28.1, 26.1, 24.5, 18.4, 4.3, 4.4; IR (neat) 2932.4, 1710.2, 1645.1 cm^{-1}; HRMS *m/z* calc'd for $[C_{18}H_{36}NO_4Si]^+$: 358.2414, found 358.2426; $[\alpha]_D^{20}$ –48.0° (c=1, $CDCl_3$).



Enone 5. To a stirred solution of (±)-*N*-Boc-caprolactam **6** (1.0 g, 2.79 mmol, 1.00 equiv) in THF (10 mL) at −78 °C was added a 1.0 M solution of vinyl magnesium bromide (3.35 mL, 3.35 mmol, 1.2 equiv) dropwise. The solution was stirred at −78 °C for 1 h then quenched with saturated NH_4Cl (5 mL) at −78 °C. The mixture was allowed to warm to ambient temperature then diluted with H_2O (10 mL) and Et_2O (20 mL). The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with water then brine and dried over Na_2SO_4 and concentrated to give a crude oil, which was purified by flash chromatography (10% EtOAc/Hexanes) to provide a mixture of **25** and **5**. A solution of the purified product mixture in $CHCl_3$ (0.15 M) was allowed to stand at ambient temperature for 30 h before concentrating to afford enone **5** (818 mg, 2.121 mmol, 76% yield) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (dd, J = 17.6, 10.2 Hz, 1H), 6.20 (dd, *J* = 17.6, 1.5 Hz, 1H), 5.80 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.78 (bm, 1H), 3.81 (m, 1H), 3.29 (bm, 1H), 3.01 (dt, *J* = 13.8, 6.1 Hz, 1H), 2.57 (dd, *J* = 15.8, 5.6 Hz, 1H), 2.39 (dd, *J* = 15.8, 7.9 Hz, 1H), 2.13 (m, 1H), 1.52– 1.28 (m, 2H), 1.44 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.87 (s, 9H), 0.06 (d, *J* = 3.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

200.1, 156.0, 136.7, 128.0, 69.5, 47.3, 45.8, 42.3, 28.4, 26.0, 25.8, 20.3, 18.0, −4.6 Hz; IR (Neat film NaCl) 3379, 2957, 2930, 2858, 1714, 1705, 1505, 1366, 1253, 1173, 836, 776 cm^{-1}; HRMS (FAB$^+$) $[M+H]^+$ *m/z* calc'd for $[C_{20}H_{39}NO_4Si+H]^+$: 386.2727, found 386.2713.

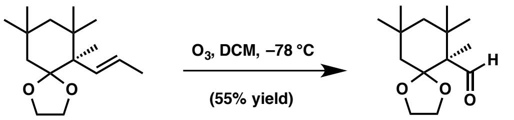


26
(85% ee)

(+)-27

Ketal (+)-27. To a solution of allyl ketone **26** (905 mg, 4.35 mmol, 1.00 equiv) in EtOH (45 mL) in a sealable Schlenk flask (100 mL) was added K_2CO_3 (601 mg, 4.35 mmol, 1.00 equiv) and $RhCl_3{\bullet}H_2O$ (49.4 mg, 0.218 mmol, 0.05 equiv). The reaction mixture was sparged with Ar for 10 min, sealed and heated to 60 °C for 12 h. After cooling to ambient temperature, the reaction mixture was filtered, washed with EtOH, concentrated, and purified by flash chromatography on silica gel (7.5 to 10% Et_2O in pentane) to give the isomerized ketone **SI-2** (759 mg, 84% yield of a 10:1 mixture containing allyl ketone **26** as the minor component) as an amorphous solid. R_f 0.67, 0.46 (25% Et_2O in hexanes, 5% Et_2O in hexanes developed twice); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dq, J = 1.8, 15.5 Hz, 1H), 5.42 (dq, J = 15.3, 6.3 Hz, 1H), 2.53 (d, J = 13.2 Hz, 1H), 2.11 (dd, J = 13.5, 1.8 Hz, 1H), 1.85 (d, J = 14.4 Hz, 1H), 1.71 (dd, J = 6.5, 1.7 Hz, 3H), 1.42 (dd, J = 14.4, 1.8 Hz, 1H), 1.09 (s, 3H), 1.04 (s, 3H), 1.01 (s, 3H), 0.90 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 132.5, 126.2, 56.4, 50.7, 49.6, 40.6, 35.4, 33.7, 30.2, 26.9, 26.8, 18.6, 15.6; IR (Neat film NaCl) 2957, 1707, 1458, 1391, 1370, 1283, 977 cm^{-1}; HRMS (EI) $[M]^+$ calc'd for $[C_{14}H_{24}O]^+$: *m/z* 208.1827, found 208.1820; $[\alpha]_D^{25}$ −59.07 (*c* 1.04, $CHCl_3$, 85% ee).

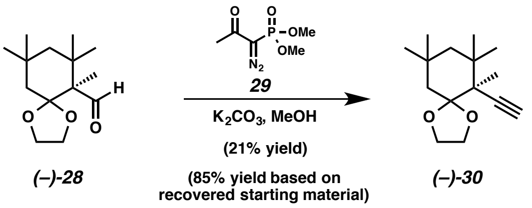
A solution of the vinyl ketone **SI-2** (700 mg, 3.36 mmol, 1.00 equiv), ethylene glycol (1.30 mL, 23.5 mmol, 7.00 equiv), and pyridinium *p*-toluenesulfonate (211 mg, 0.84 mmol, 0.25 equiv) in benzene (70 mL) was fitted with a Dean-Stark apparatus and refluxed at 100 °C for 30 h. The reaction mixture was cooled to ambient temperature, diluted with saturated aqueous $NaHCO_3$ (40 mL), and extracted with PhH (3x30 mL). The combined organics were washed with brine (20 mL), dried (Na_2SO_4), concentrated, and purified by flash chromatography on silica gel (1 to 2% Et_2O in hexane) to give acetal **(+)-27** (585 mg, 70% yield) as an oil: R_f 0.61, 0.67 (5% Et_2O in hexanes developed twice, 25% Et_2O in hexanes); ^{1}H NMR (300 MHz, CDCl3) δ 5.74 (dq, J = 15.8, 1.5 Hz, 1H), 5.44 (dq, J = 15.8, 6.3 Hz, 1H), 3.92–3.78 (m, 4H), 1.72 (dd, J = 6.5, 1.7 Hz, 3H), 1.52 (s, 2H), 1.37 (d, J = 14.1 Hz, 1H), 1.30 (d, J = 14.1 Hz, 1H), 1.03 (s, 6H), 1.02 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.7, 124.3, 113.8, 64.6, 64.4, 49.8, 48.6, 42.2, 38.0, 32.3, 32.0, 31.5, 28.3, 27.7, 18.7, 14.2; IR (Neat film NaCl) 2952, 1455, 1388, 1225, 1146, 1124, 1078, 981 cm^{-1}; HRMS (EI) $[M]^+$ calc'd for $[C_{16}H_{28}O]^+$: m/z 252.2089, found 252.2090; $[\alpha]_D^{24}$ +1.51 (c 1.11, $CHCl_3$, 85% ee).



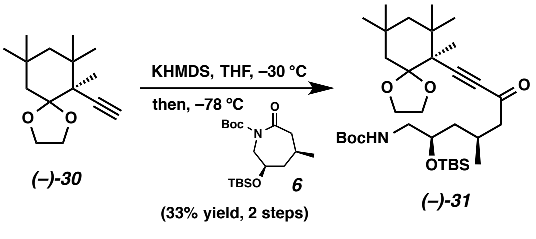
(+)-27

(–)-28

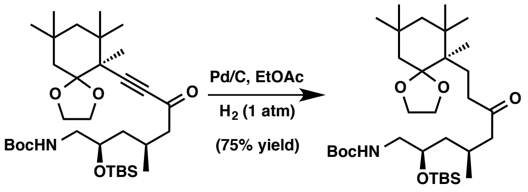
Aldehyde (+)-27. Through a cooled (–78 °C) solution of acetal **(+)-27** (252 mg, 1.00 mmol, 1.00 equiv) in CH_2Cl_2 (25 mL) was bubbled a stream of ozone until the reaction mixture turned blue. The reaction mixture was quenched with dimethyl sulfide (0.20 mL), allowed to warm to ambient temperature, concentrated to an oil, and purified by flash chromatography on silica gel (2.5 to 10% Et2O in hexane) to give aldehyde **(–)-28** (132 mg, 55% yield) as an oil: R_f 0.41, 0.29 (25% Et_2O in hexanes, 5% Et_2O in hexanes developed twice); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (s, 1H), 3.98–3.85 (m, 4H), 1.69 (d, J = 14.4 Hz, 3H), 1.57 (dd, J = 14.4, 1.2 Hz, 1H), 1.50 (d, J = 14.4 Hz, 1H), 1.37 (dd, J = 14.4, 1.2 Hz, 1H), 1.08 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.2, 112.1, 64.5, 64.3, 58.0, 50.3, 43.0, 38.1, 32.9, 31.6, 30.6, 27.8, 27.7, 11.1; IR (Neat film NaCl) 2954, 2899, 1722, 1241, 1110, 1075, 964 cm^{-1}; HRMS (EI) $[M]^+$ calc'd for $[C_{14}H_{24}O_3]^+$: m/z 240.1726, found 240.1720; $[\alpha]_D^{24}$ –39.53 (c 0.385, $CHCl_3$, 85% ee).



Alkyne (–)-30. To a solution of aldehyde **(–)-28** (75.0 mg, 0.312 mmol, 1.00 equiv), and K_2CO_3 (108 mg, 0.780 mmol, 2.50 equiv) in MeOH (3.10 mL) was added diazoketone **29** (89.9 mg, 0.468 mmol, 1.5 equiv). After 1 h, an additional portion of K_2CO_3 (214 mg, 1.56 mmol, 5.00 equiv) and of diazoketone **29** (150 mg, 0.780 mmol, 2.5 equiv) were added. After a further 4 h, a final portion of K_2CO_3 (200 mg, 1.45 mmol, 4.65 equiv) and of diazoketone **29** (200 mg, 1.05 mmol, 3.37 equiv) were added. After stirring for 20 h, the reaction mixture was diluted with H_2O (10 mL), extracted with CH_2Cl_2 (8 x 5 mL), dried ($MgSO_4$), concentrated, and purified by flash chromatography on silica gel (1 to 7% Et2O in hexanes) to give recovered aldehyde **(–)-28** (55.6 mg, 74% yeld) and alkyne **(–)-30** (15.5 mg, 21% yield, 85% yield based on recovered aldehyde **(–)-28**) as an oil: R_f 0.40 (5% Et_2O in hexanes developed twice); ^1H NMR (300 MHz, C_6D_6) δ 3.62–3.40 (m, 4H), 2.01 (d, J = 14.1 Hz, 1H), 1.93 (s, 1H), 1.72 (d, J = 14.1 Hz, 1H), 1.47 (dd, J = 13.8, 1.8 Hz, 1H), 1.36 (s, 3H), 1.34 (s, 3H), 1.22 (s, 3H), 1.17 (dd, J = 14.3, 1.7 Hz, 1H), 1.10 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.5, 89.1, 76.6, 70.7, 65.5, 64.2, 49.8, 47.3, 42.5, 38.0, 34.6, 31.4, 29.8, 28.8, 24.9, 16.2; IR (Neat film NaCl) 3309, 2954, 2911, 2111, 1454, 1390, 1367, 1235, 1148, 1088, 1073, 984 cm^{-1}; HRMS (EI) $[M]^+$ calc'd for $[C_{15}H_{24}O_2]^+$: *m/z* 236.1776, found 236.1786; $[\alpha]_D^{26}$ –20.35 (*c* 1.25, CH_2Cl_2, 85% ee).



Ynone (–)-31. To a cooled (–30 °C) solution of KHMDS (24.1 mg, 0.121 mmol, 2.20 equiv) in THF (1.00 mL) was added alkyne (–)-**30** (13.0 mg, 0.055 mmol, 1.00 equiv) in THF (1.00 mL). The solution was maintained for 30 min each at –30 °C, 0 °C, and 22 °C. The alkyne anion was cooled to –78 °C, and caprolactam **6** (23.6 mg, 0.066 mmol, 1.2 equiv) in THF (1.00 mL) was added. After 1 h, additional KHMDS (12.0 mg, 0.061 mmol, 1.10 equiv) in THF (0.50 mL) was added. After a further 5 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (0.50 mL), diluted with H_2O (2 mL), brine (4 mL), and Et_2O (4 mL), and extracted with Et_2O (6 x 4 mL) and CH_2Cl_2 (2 x 2 mL). The combined organics were dried (Na_2SO_4), and concentrated to an oil, which was purified by flash chromatography on silica gel (2.5 to 15% EtOAc in hexanes) to give ynone **(–)-31** (10.9 mg, 33% yield) as an oil: R_f 0.24, 0.50 (10% EtOAc in hexanes developed twice, 20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.07–4.02 (m, 1H), 4.00–3.94 (m, 3H), 3.84 (bs, 1H), 3.38–3.30 (m, 1H), 2.97 (dt, J = 14.5, 6.0 Hz, 1H), 2.58 (dd, J = 15.5, 5.5 Hz, 1H), 2.38 (dd, J = 15.5, 8.0 Hz, 1H), 2.26–2.16 (m, 1H), 1.76 (d, J = 14.0 Hz, 1H), 1.62–1.44 (comp. m, 4H), 1.46 (s, 9H), 1.40–1.30 (m, 1H), 1.26 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 1.07 (s, 3H), 1.01 (s, 3H), 1.00 (s, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.2, 155.9, 112.1, 98.7, 83.7, 79.1, 69.4, 65.5, 64.6, 53.2, 49.8, 48.1, 45.9, 43.0, 42.2, 38.7, 33.8, 31.4, 29.7, 29.6, 28.4, 28.0, 26.3, 25.9, 25.6, 20.2, 18.0, –4.5, –4.6; IR (Neat film NaCl) 3383, 2955, 2930, 2208, 1716, 1673, 1504, 1391, 1366, 1252, 1171, 1090, 836 cm^{-1}; HRMS (FAB$^+$) $[M+H]^+$ calc'd for $[C_{33}H_{59}NO_6Si+H]^+$: m/z 594.4190, found 594.4208; $[\alpha]_D^{26}$ –36.12 (c 0.545, EtOAc).



(–)-31 (+)-32

Ketone 32. To a solution of ynone **(–)-31** (10.9 mg, 18.3 μmol, 1.00 equiv) in EtOAc (6 mL) was added 10% Pd/C (4.0 mg), and the reaction mixture was sparged with H2 (5 min). After 18 h of vigorous stirring under an atmosphere of H_2 (balloon), the reaction mixture was concentrated, and purified by flash chromatography on silica gel (5 to 10% EtOAc in hexanes). NMR analysis of the chromatographed product indicated the presence of some partially hydrogenated material. A solution of this material in EtOAc (5 mL) was treated again with 10% Pd/C (5.0 mg) under an atmosphere of H_2 (balloon) for 4 h.

The reaction mixture was concentrated to an oil and purified by flash chromatography on silica gel (5 to 10% EtOAc in hexanes) to give ketone **(+)-32** (8.2 mg, 75% yield) as an oil: R_f 0.53 (20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (s, 1H), 3.96 (app. t, *J* = 6.8 Hz, 1H), 3.83 (app. q, *J* = 7.0 Hz, 1H), 3.79 (bs, 1H), 3.74 (app. q, *J* = 7.0 Hz, 1H), 3.34–3.26 (m, 1H), 2.98 (dt, *J* = 13.5, 6.5 Hz, 1H), 2.60–2.50 (m, 1H), 2.48–2.36 (m 2H), 2.20 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.12–2.02 (m, 1H), 2.00– 1.92 (m, 1H), 1.56–1.24 (comp. m, 9H), 1.44 (s, 9H), 1.15 (d, *J* = 14.0 Hz, 1H), 1.11 (s, 3H), 1.05 (s, 3H), 0.96 (s, 3H), 0.92-0.89 (m, 6H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 156.2, 115.2, 79.3, 69.8, 64.9, 62.6, 50.6, 50.5, 46.2, 44.2, 42.7, 41.4, 40.9, 39.1, 34.7, 31.5, 30.0, 29.4, 28.7, 28.3, 26.8, 26.1, 26.0, 24.4, 20.6, 18.3, 16.8, –4.3; IR (Neat film NaCl) 3391, 2953, 2930, 1714, 1503, 1366, 1253, 1173, 1076, 836, 776 cm-1; HRMS (FAB$^+$) $[M+H]^+$ calc'd for $[C_{33}H_{63}NO_6Si+H]^+$: *m/z* 598.4503, found 598.4489; $[\alpha]_D^{26}$ +9.33 (*c* 0.105, CH_2Cl_2).

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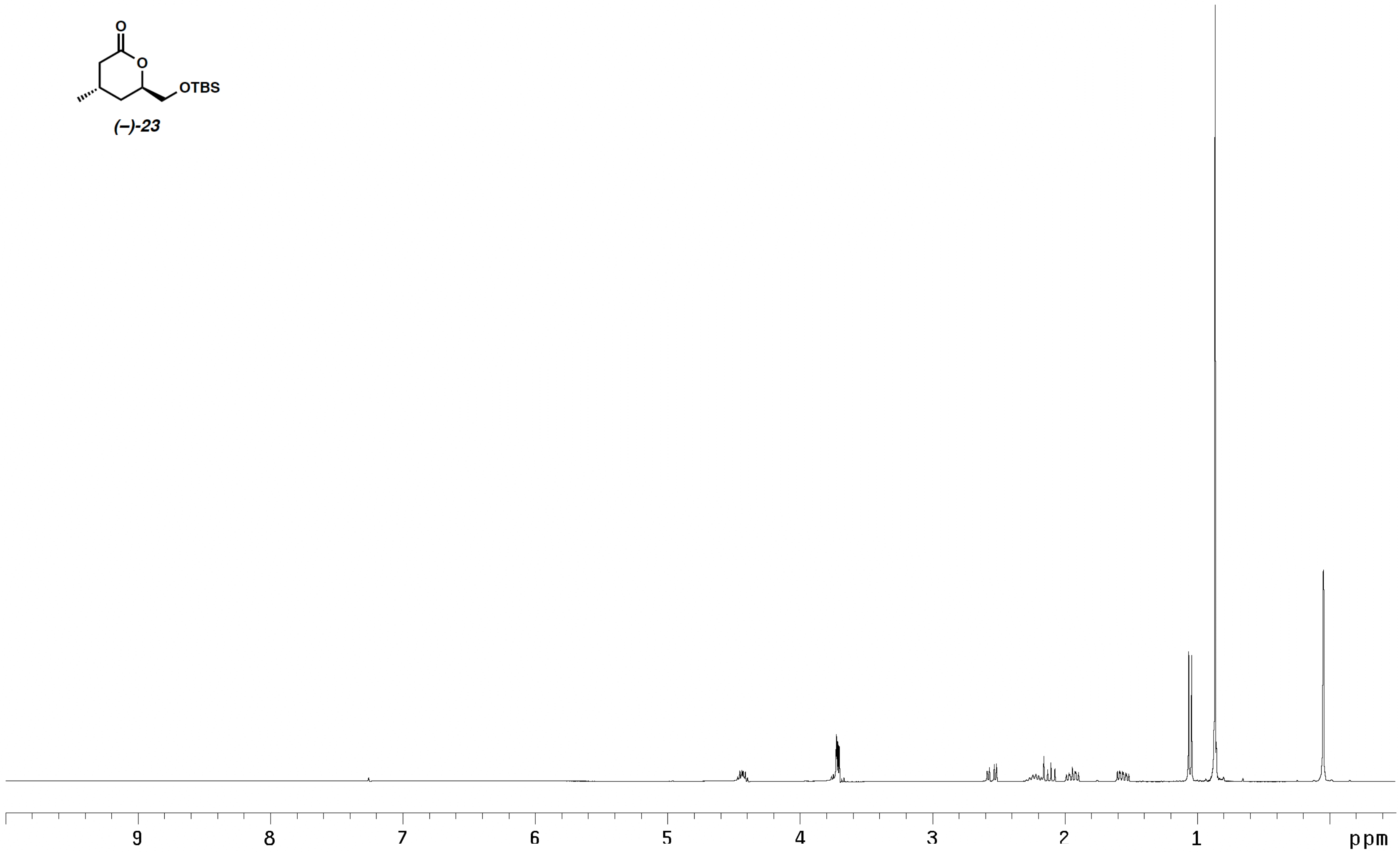
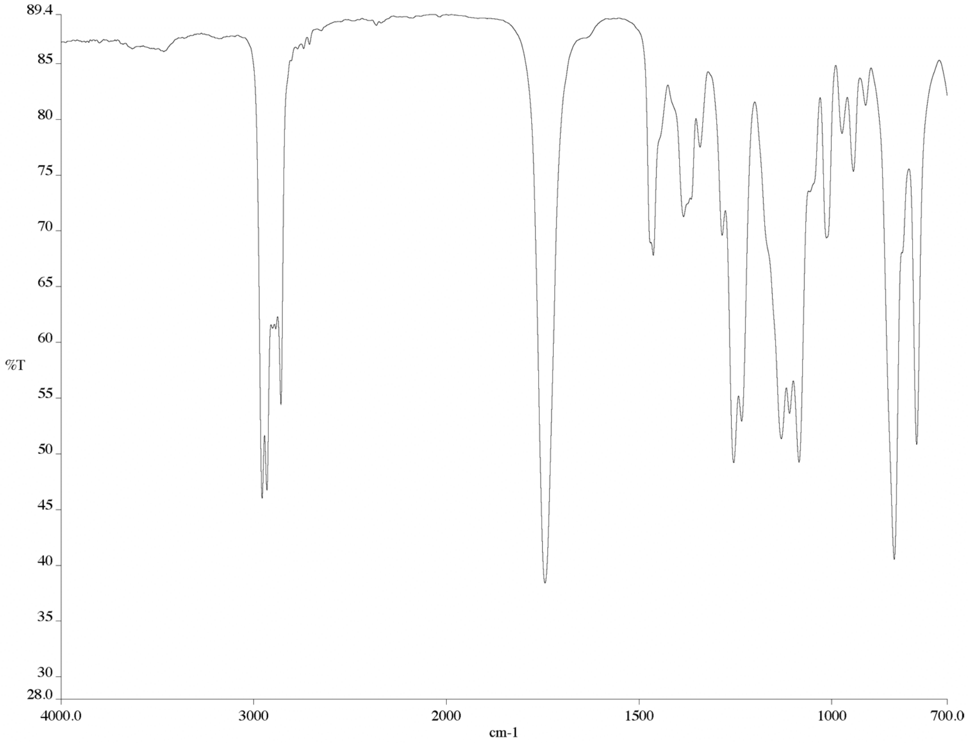
(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd ed., Pergamon Press, Oxford, 1988.

(2) Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

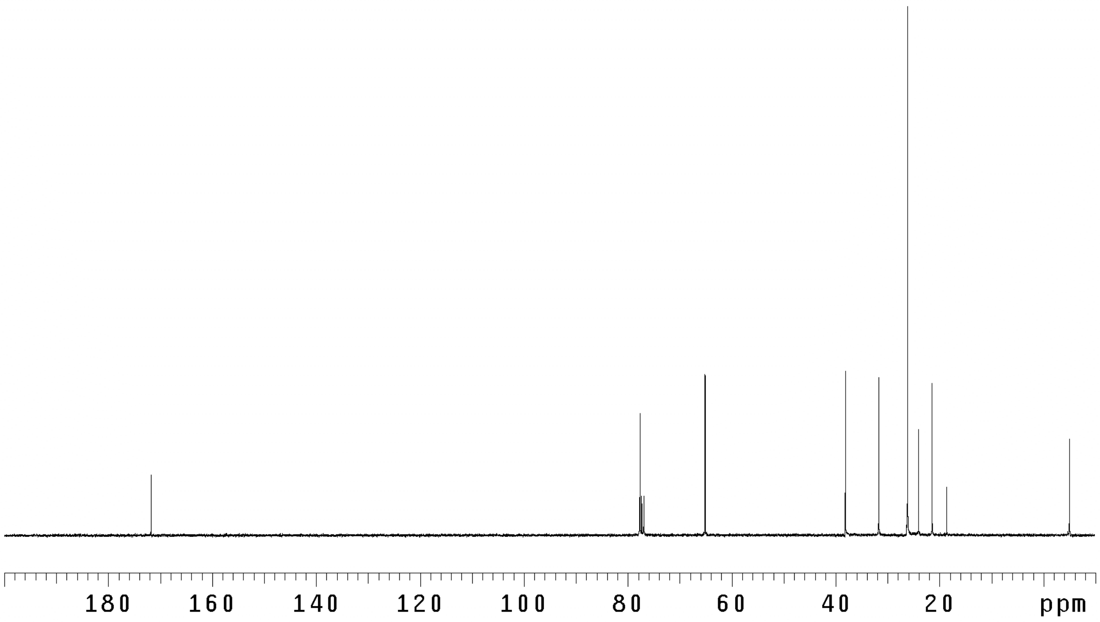
Spectra



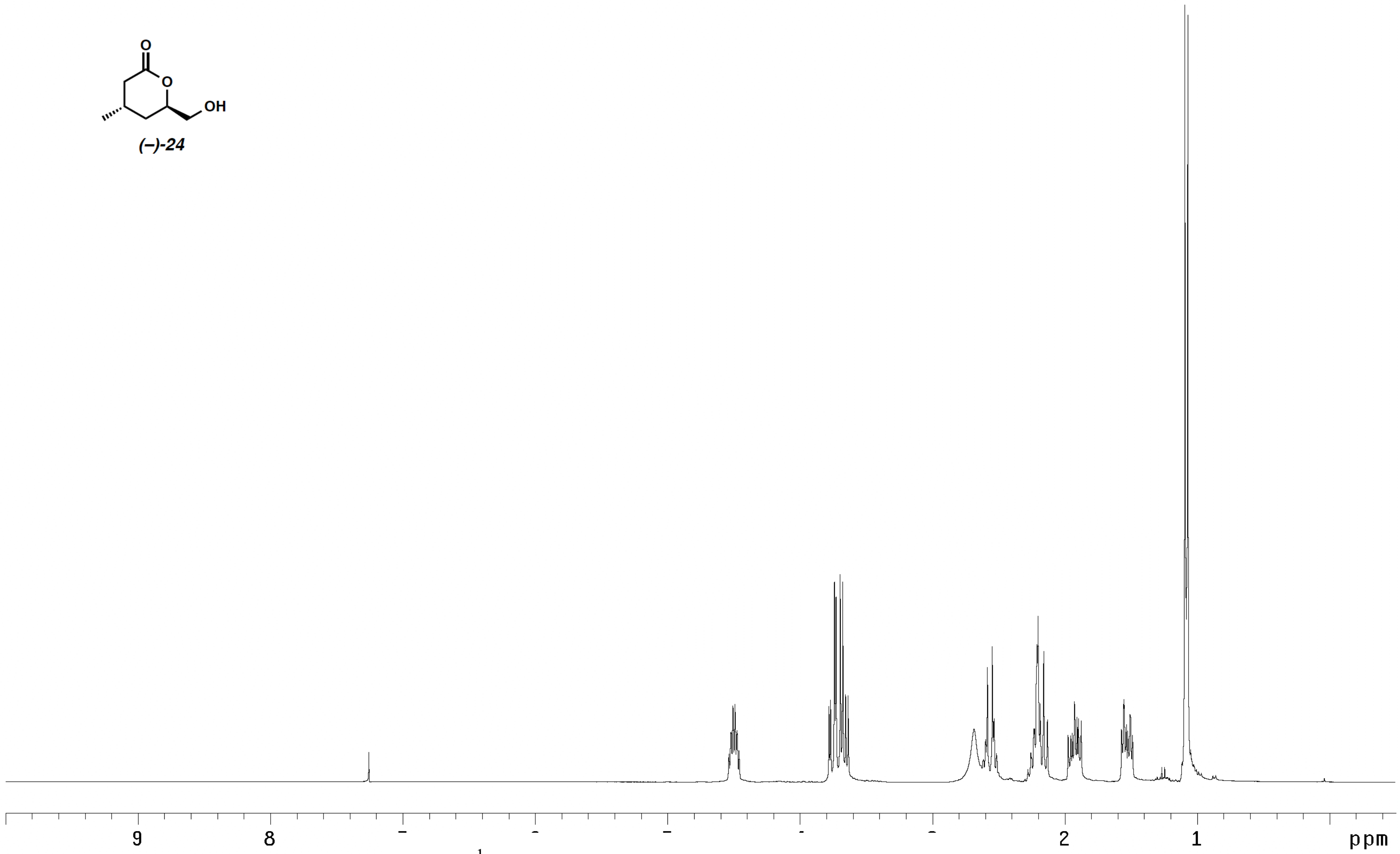
^{1}HNMR (300 MHz, CDCl$_3$) of compound **23**.



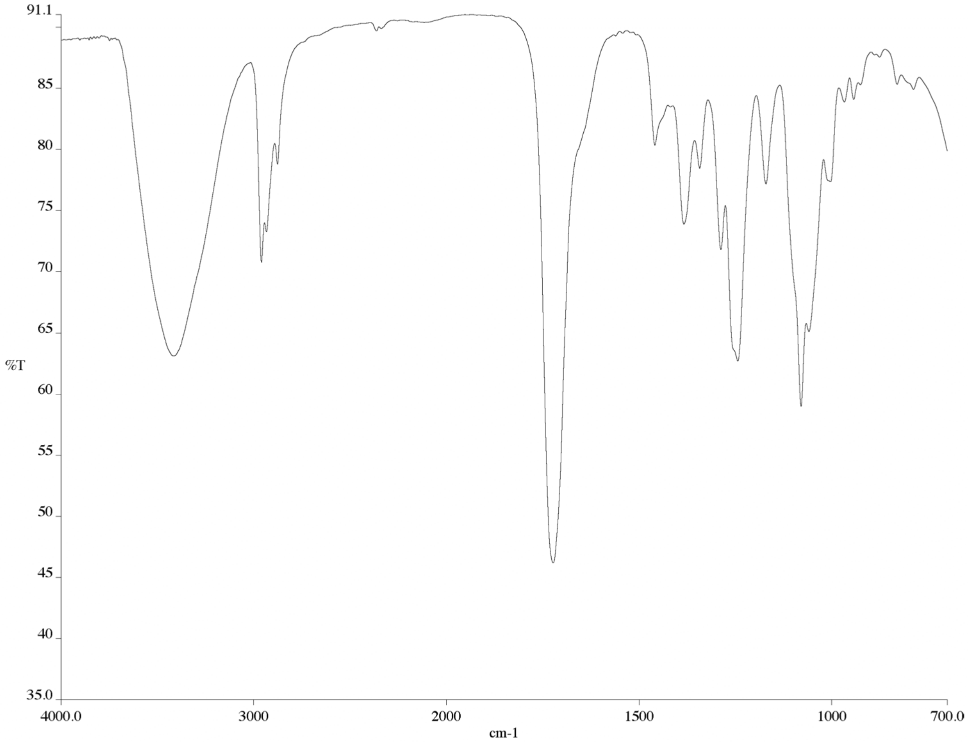
Infrared spectrum (thin film/NaCl) of compound **23**.



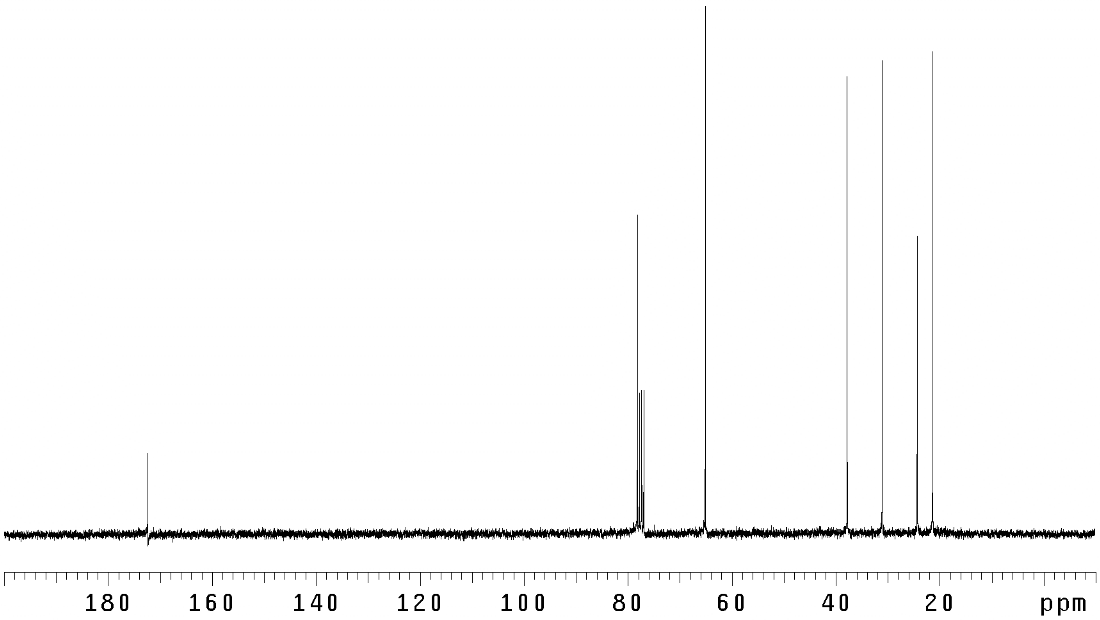
^{13}CNMR (125 MHz, $CDCl_3$) of compound **23**.



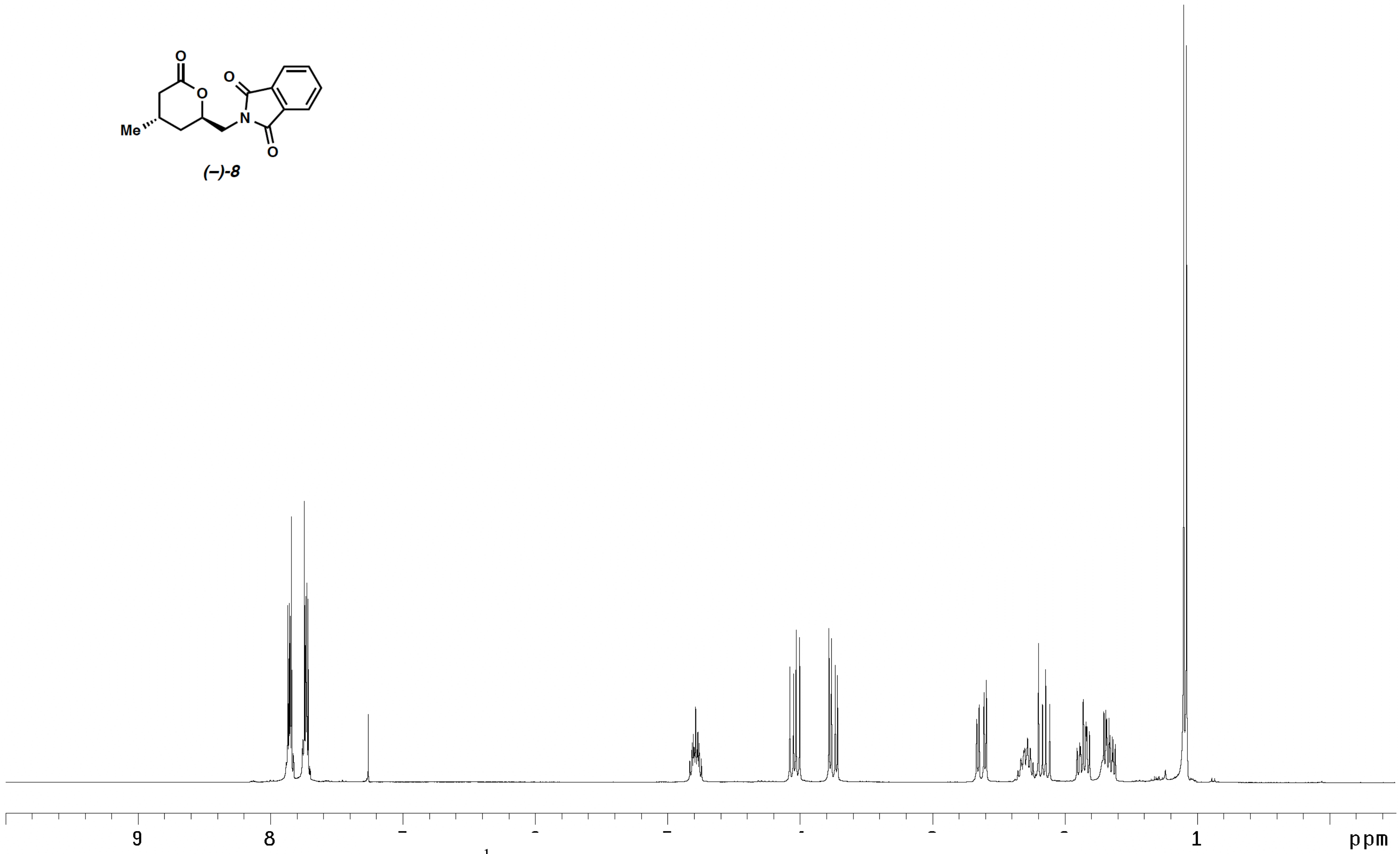
^{1}HNMR (300 MHz, $CDCl_3$) of compound **24**.



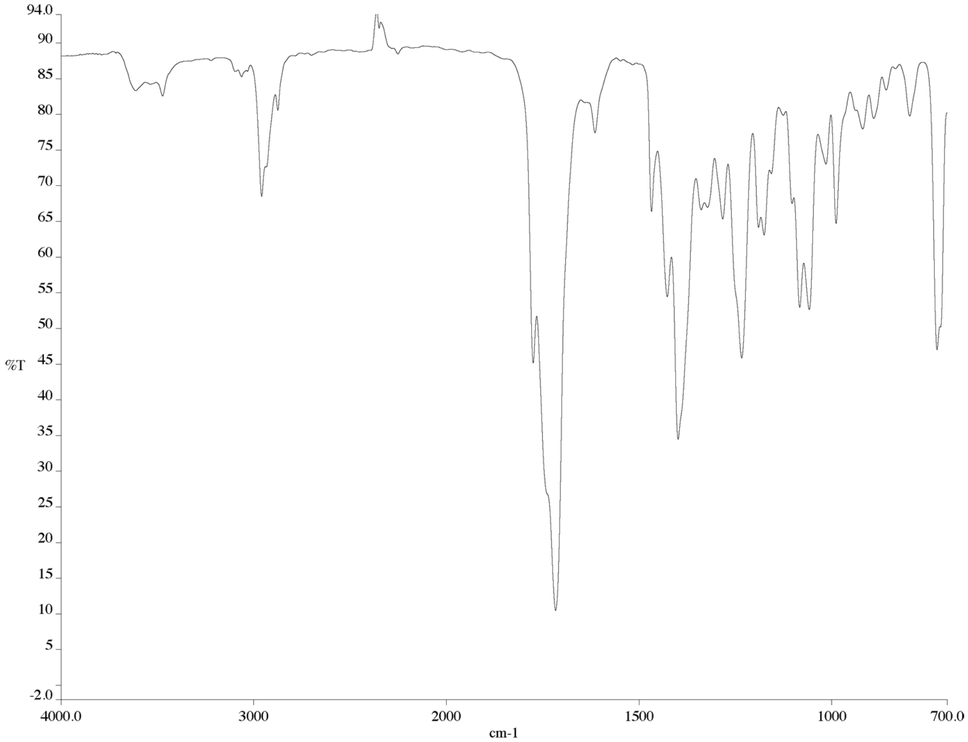
Infrared spectrum (thin film/NaCl) of compound **24**.



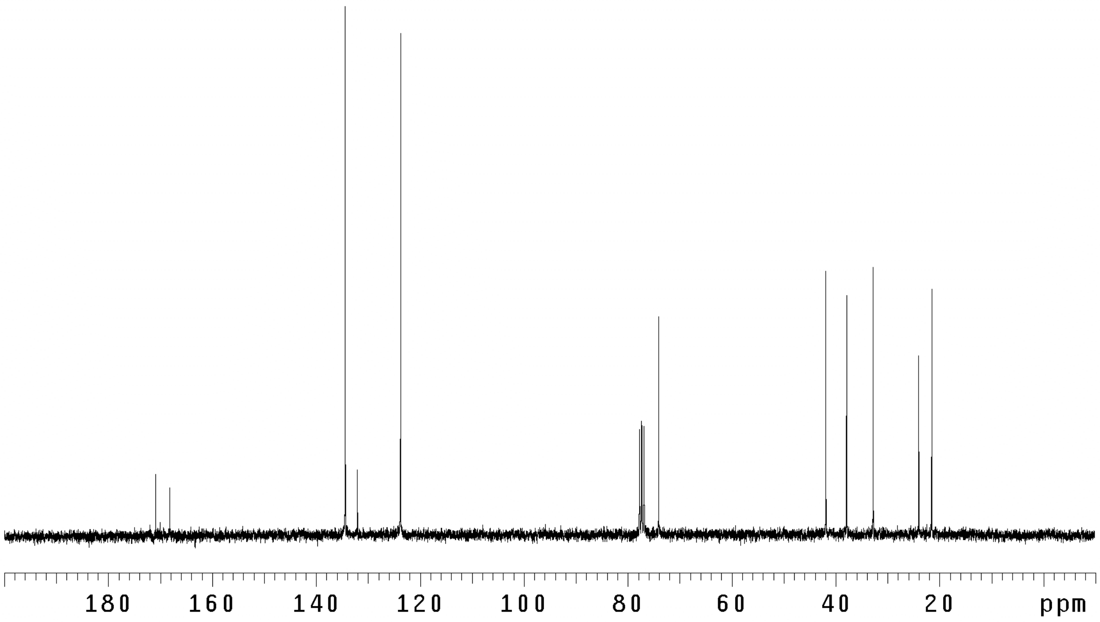
^{13}CNMR (125 MHz, $CDCl_3$) of compound **24**.



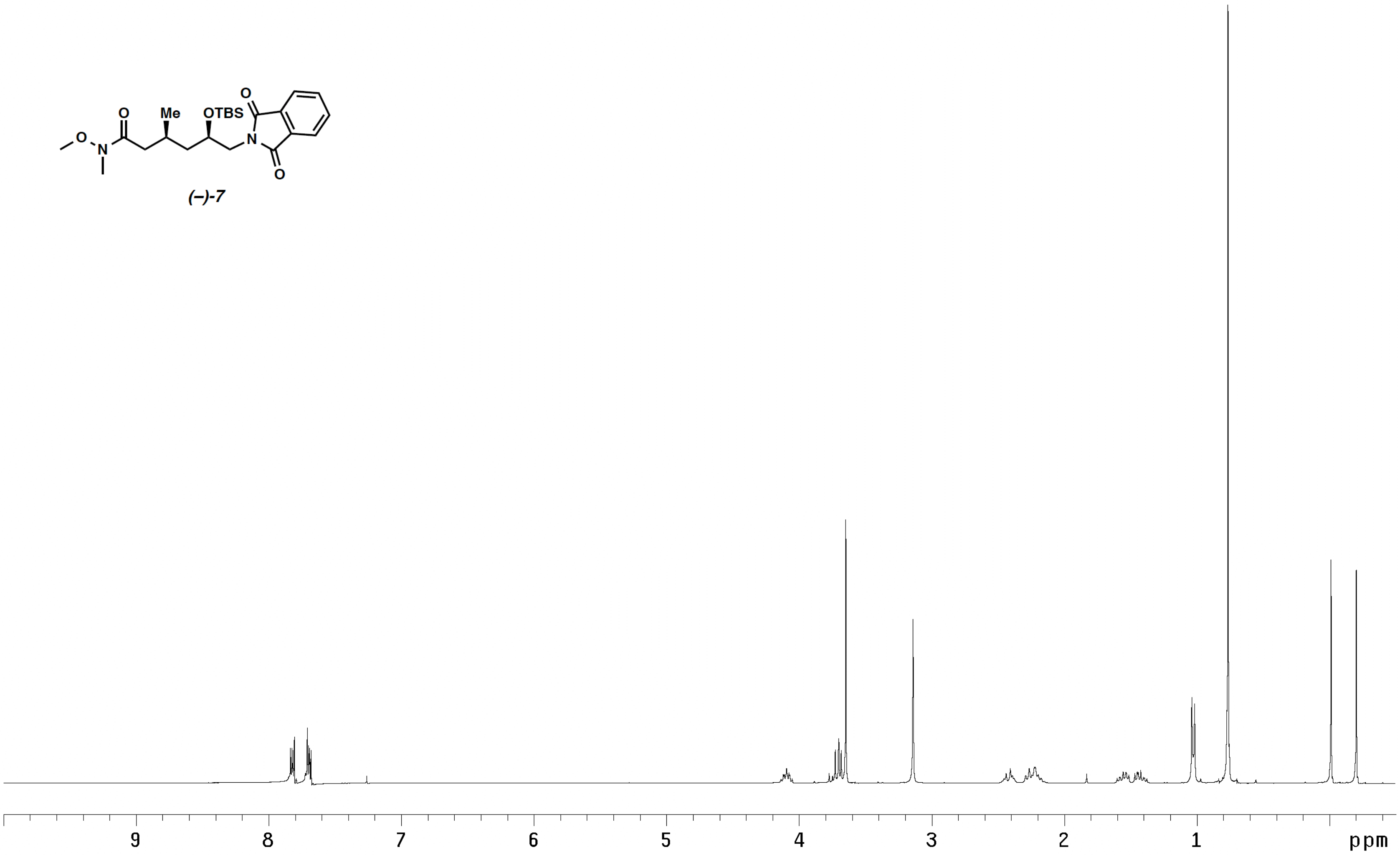
^{1}HNMR (300 MHz, $CDCl_3$) of compound **8**.



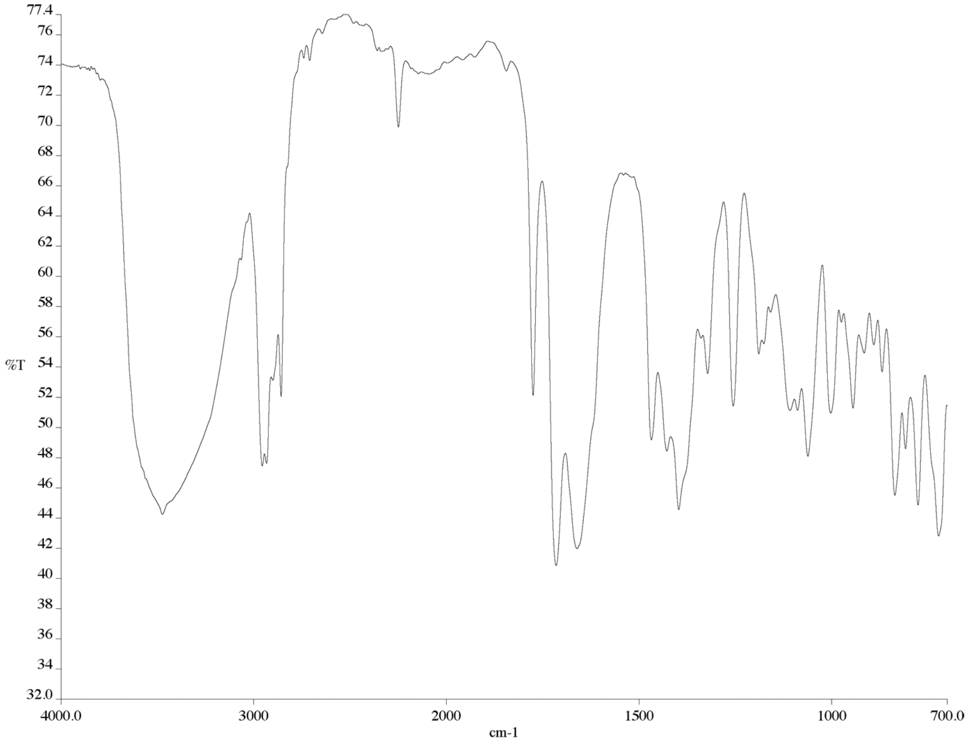
Infrared spectrum (thin film/NaCl) of compound **8**.



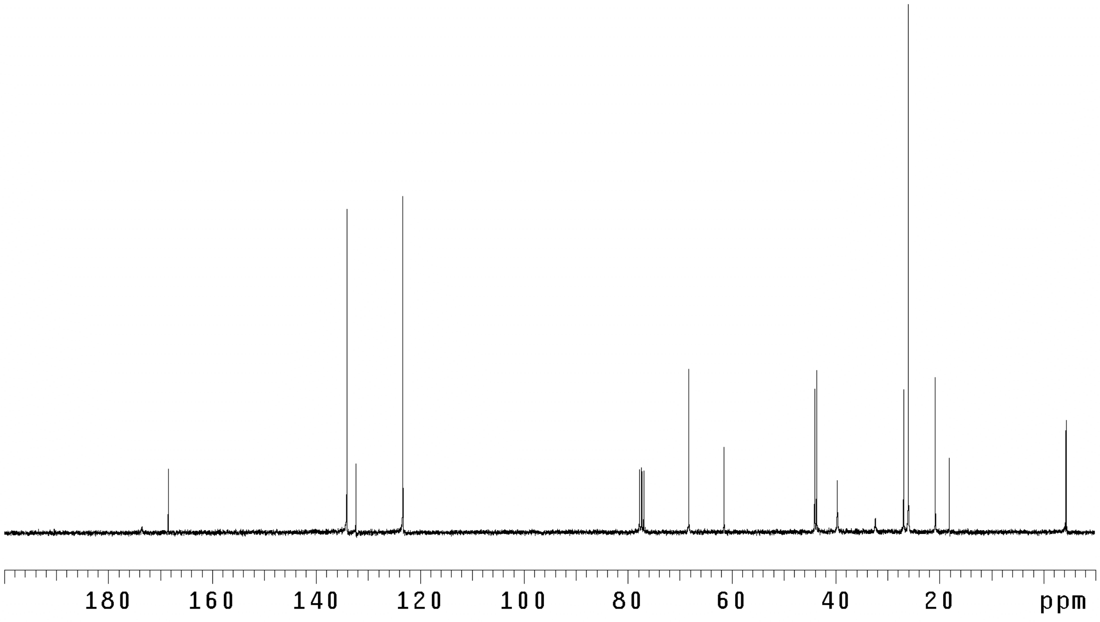
^{13}CNMR (125 MHz, CDCl$_3$) of compound **8**.



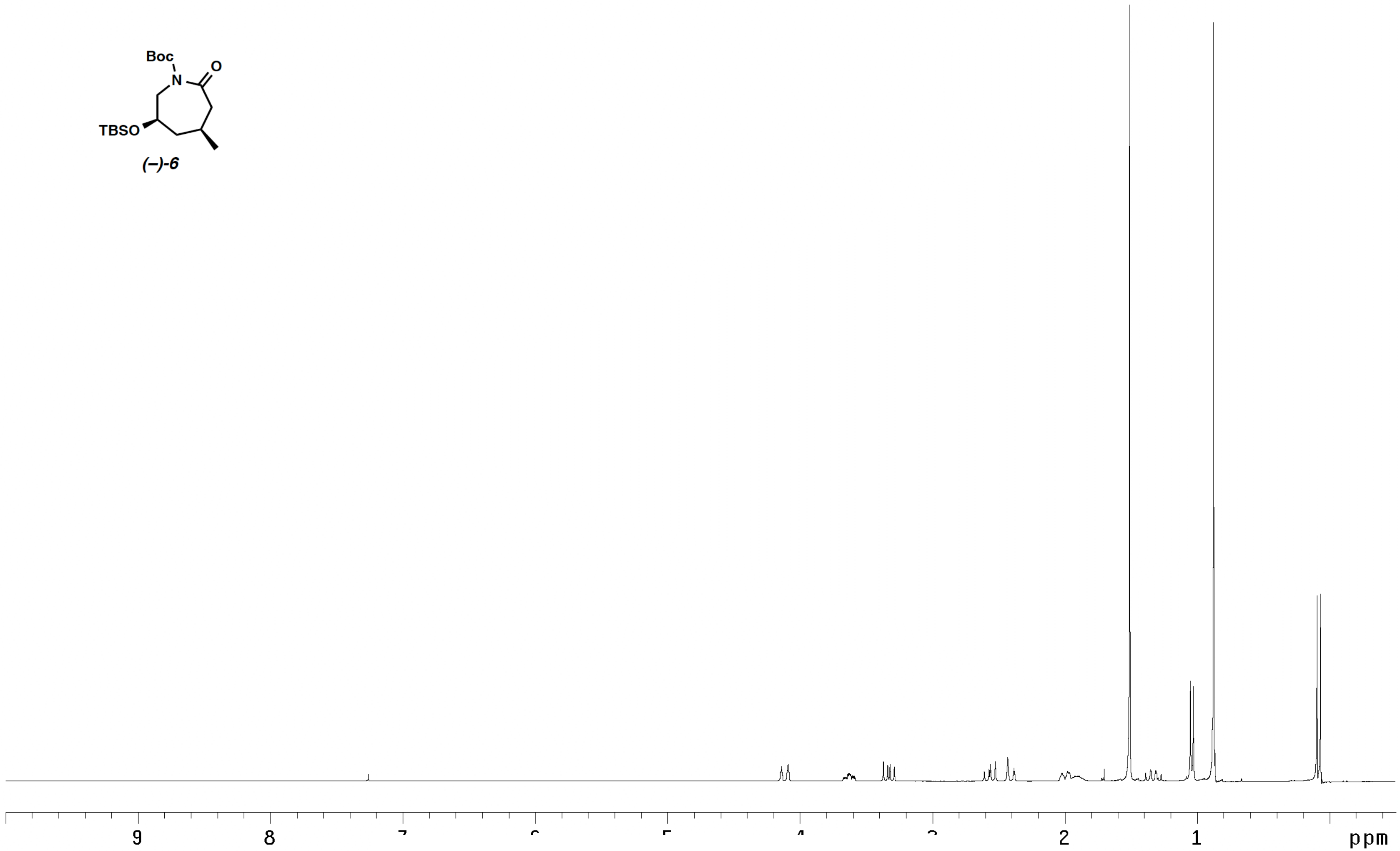
^{1}HNMR (300 MHz, $CDCl_3$) of compound **7**.



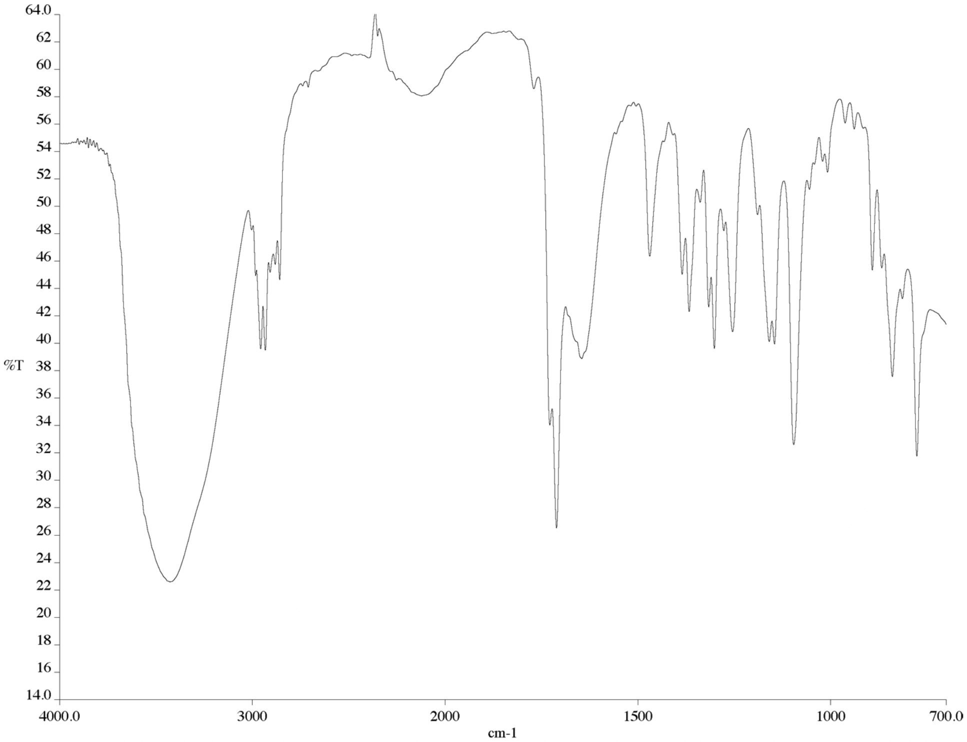
Infrared spectrum (thin film/NaCl) of compound **7**.



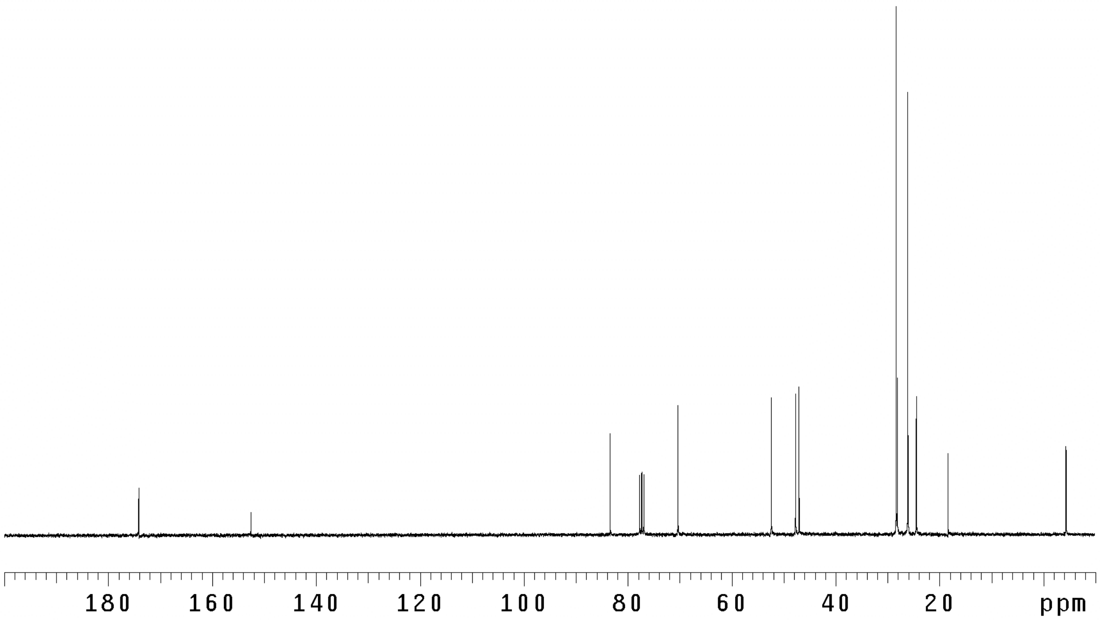
^{13}CNMR (125 MHz, $CDCl_3$) of compound **7**.



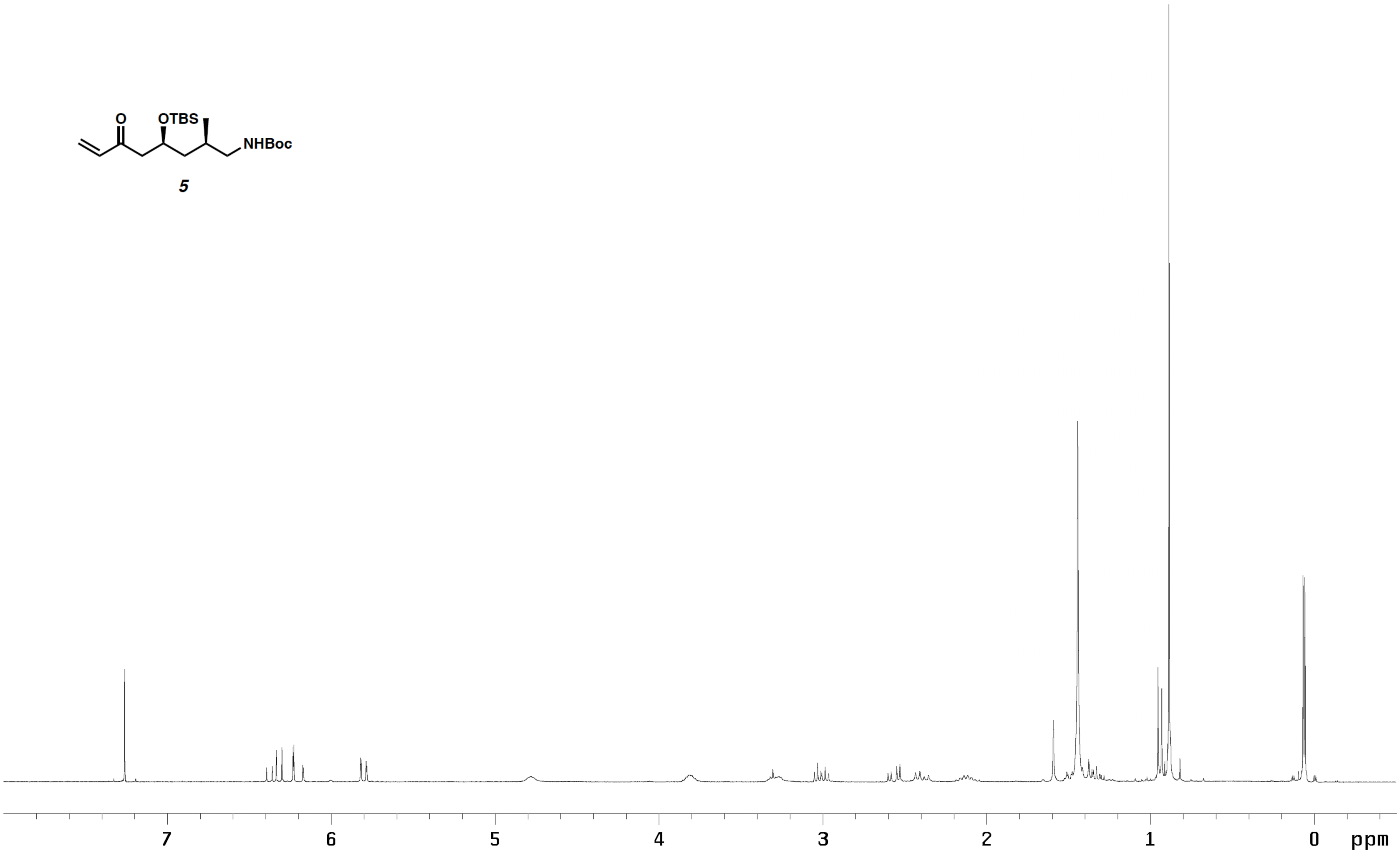
^{1}HNMR (300 MHz, CDCl$_3$) of compound **6**.



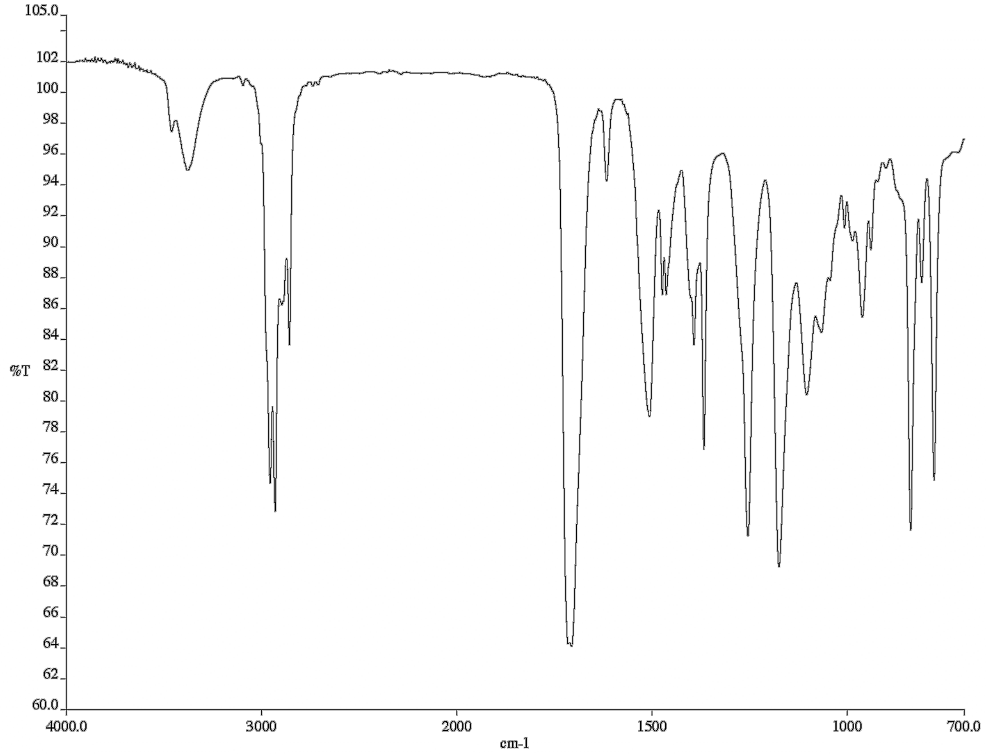
Infrared spectrum (thin film/NaCl) of compound **6**.



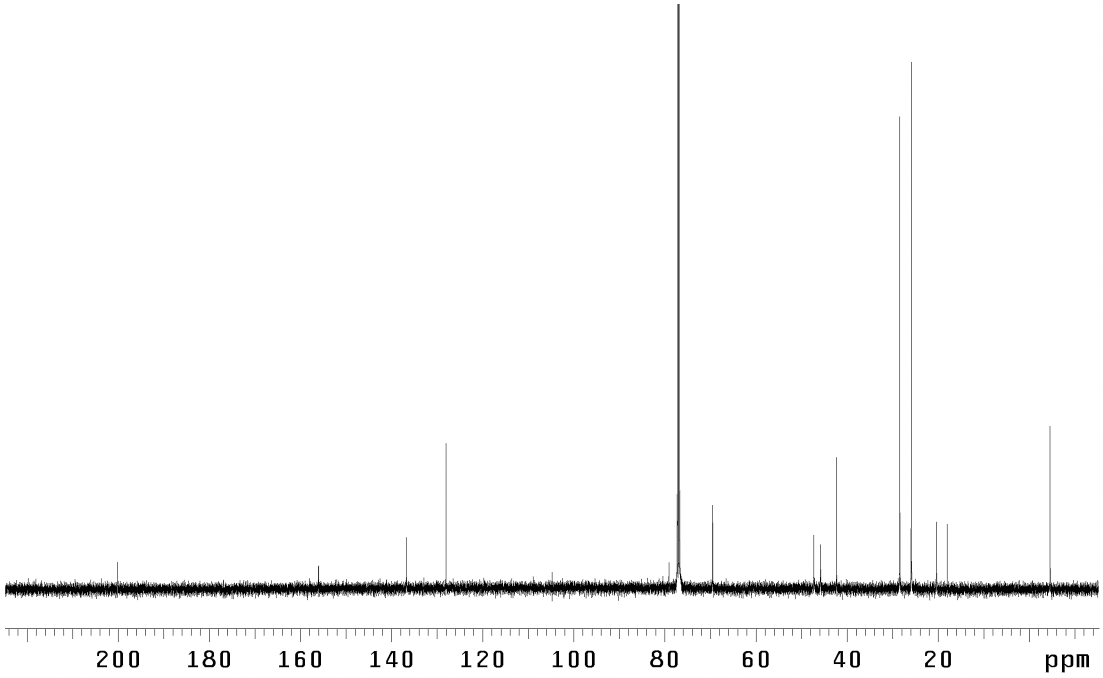
^{13}CNMR (125 MHz, CDCl$_3$) of compound **6**.



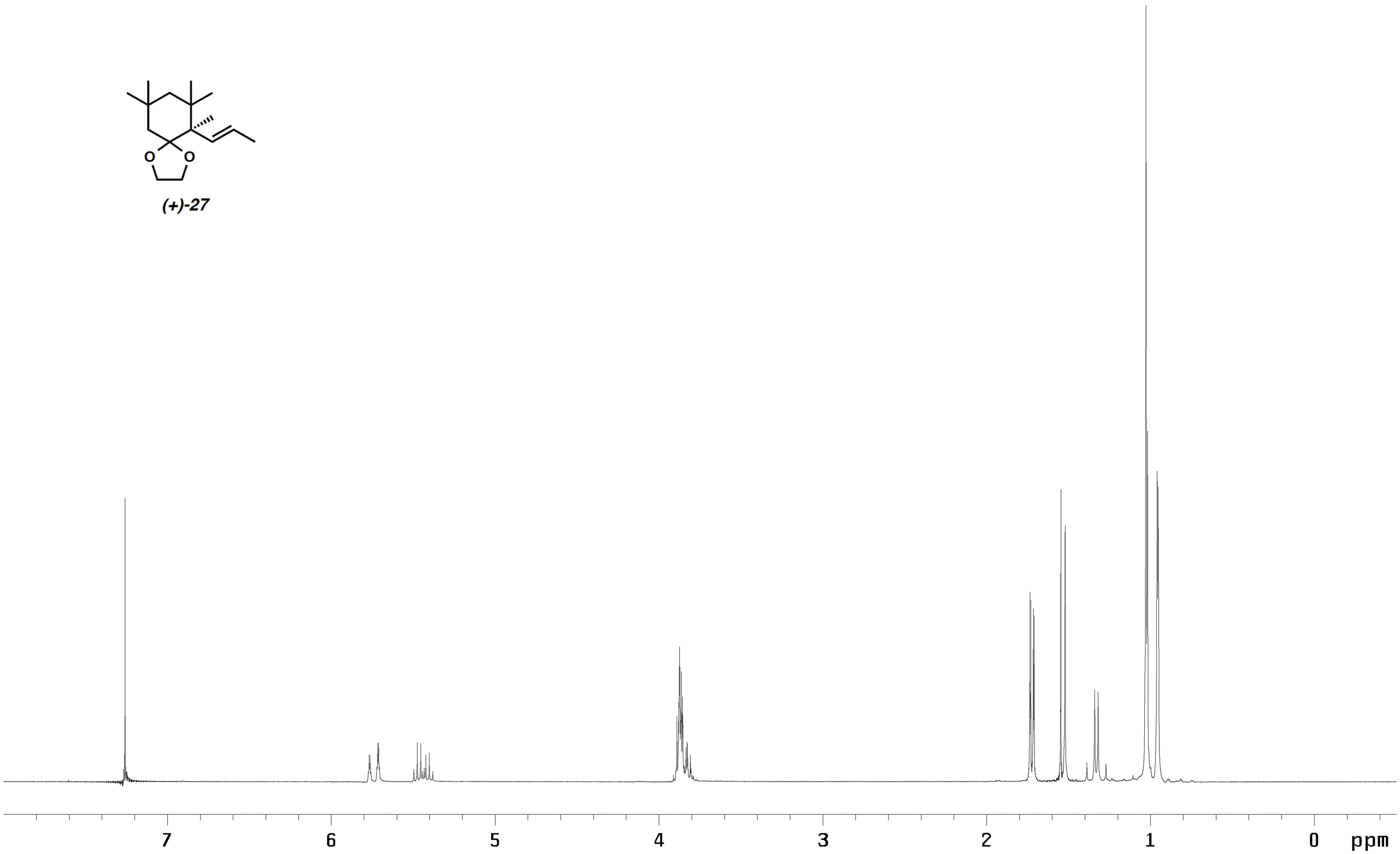
^{1}H NMR (500 MHz, CDCl$_3$) of compound **5**.



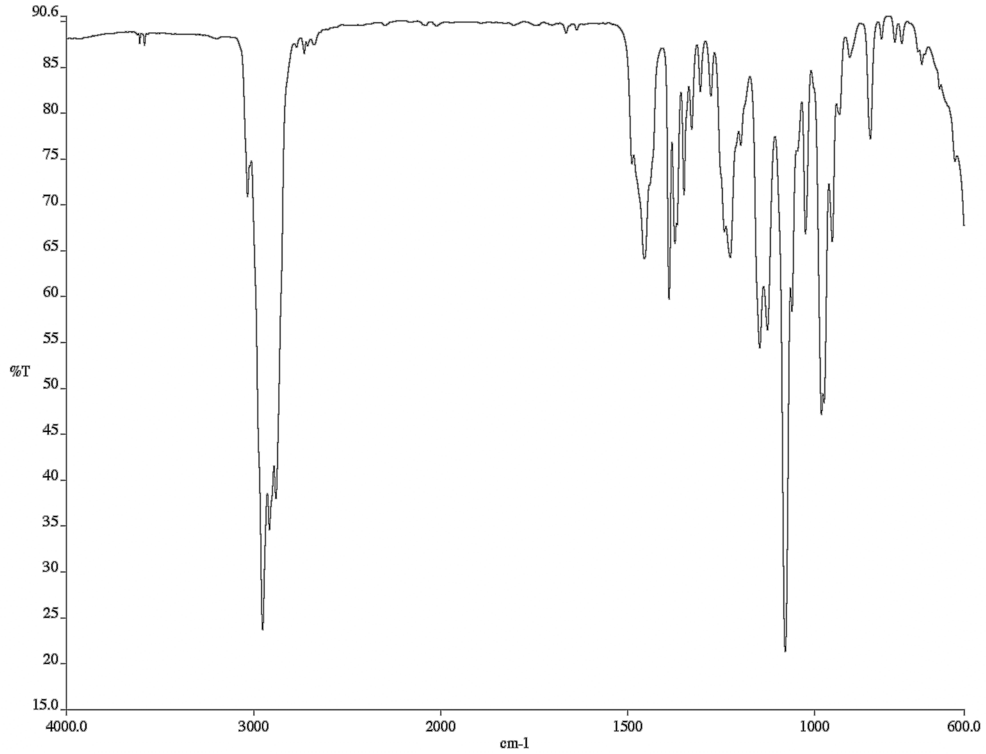
Infrared spectrum (thin film/NaCl) of compound **5**.



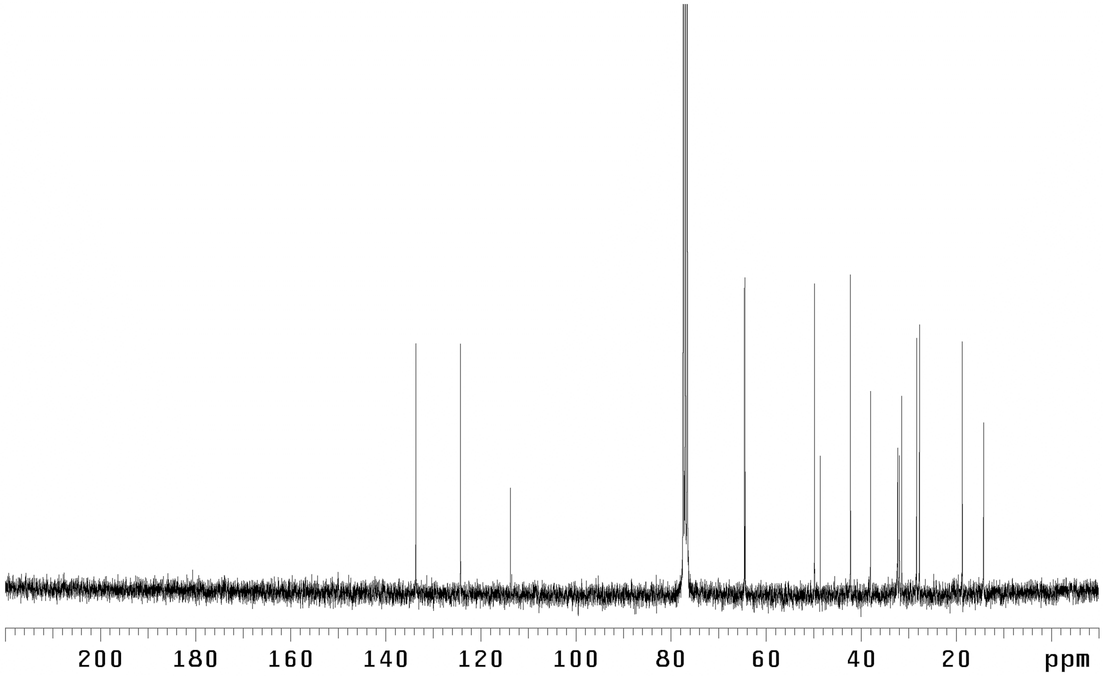
^{13}C NMR (125 MHz, CDCl$_3$) of compound **5**.



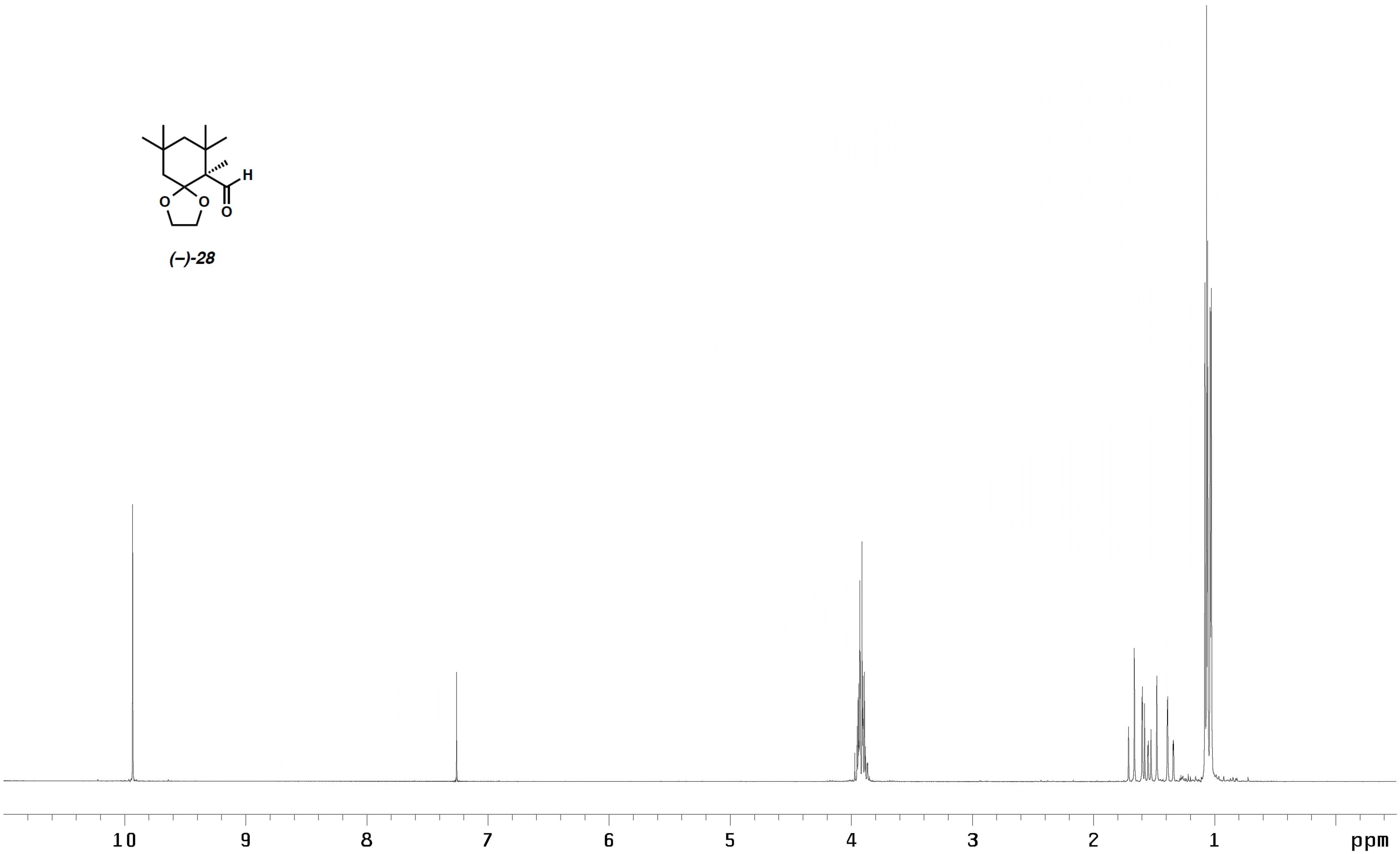
^{1}H NMR (300 MHz, CDCl$_3$) of compound **27**.



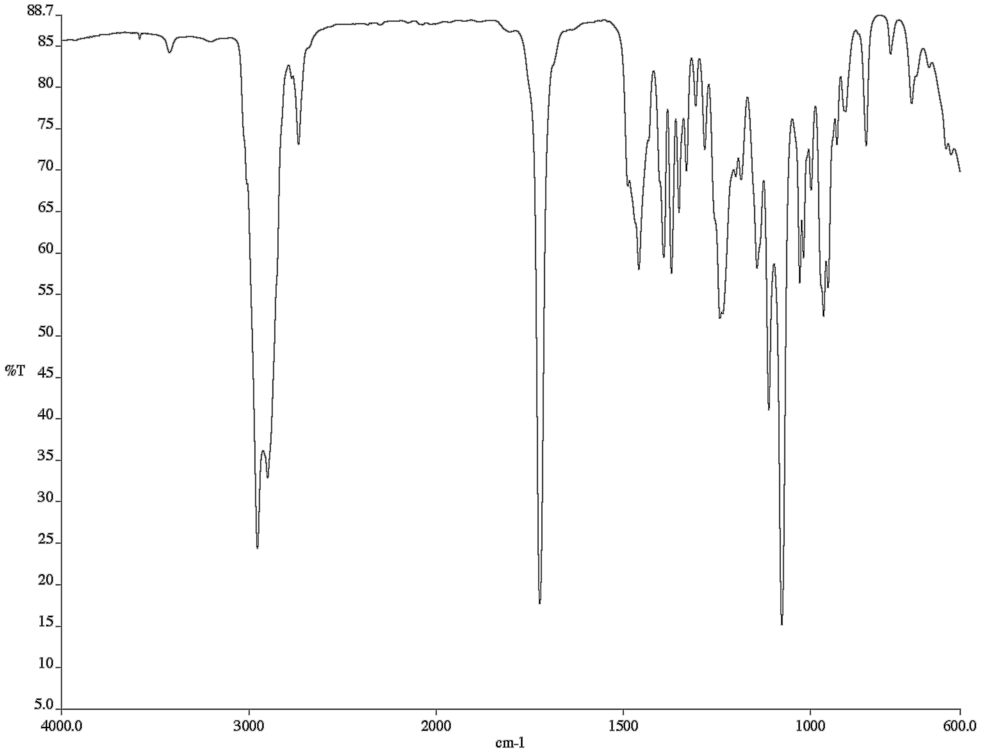
Infrared spectrum (thin film/NaCl) of compound **27**.



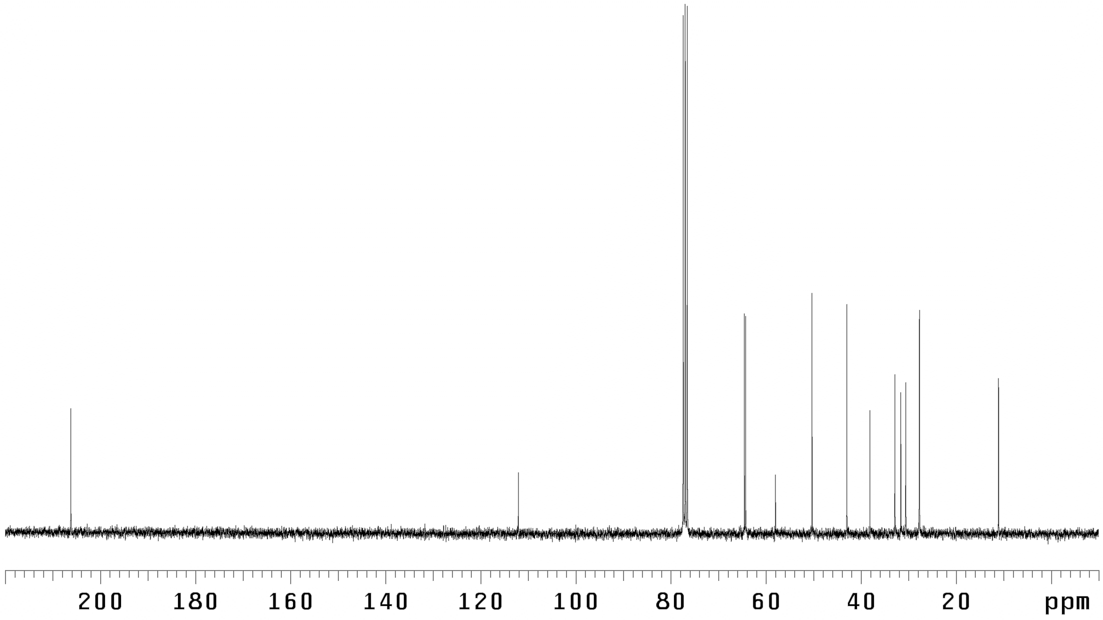
^{13}C NMR (75 MHz, $CDCl_3$) of compound **27**.



^{1}H NMR (300 MHz, CDCl$_3$) of compound **28**.



Infrared spectrum (thin film/NaCl) of compound **28**.



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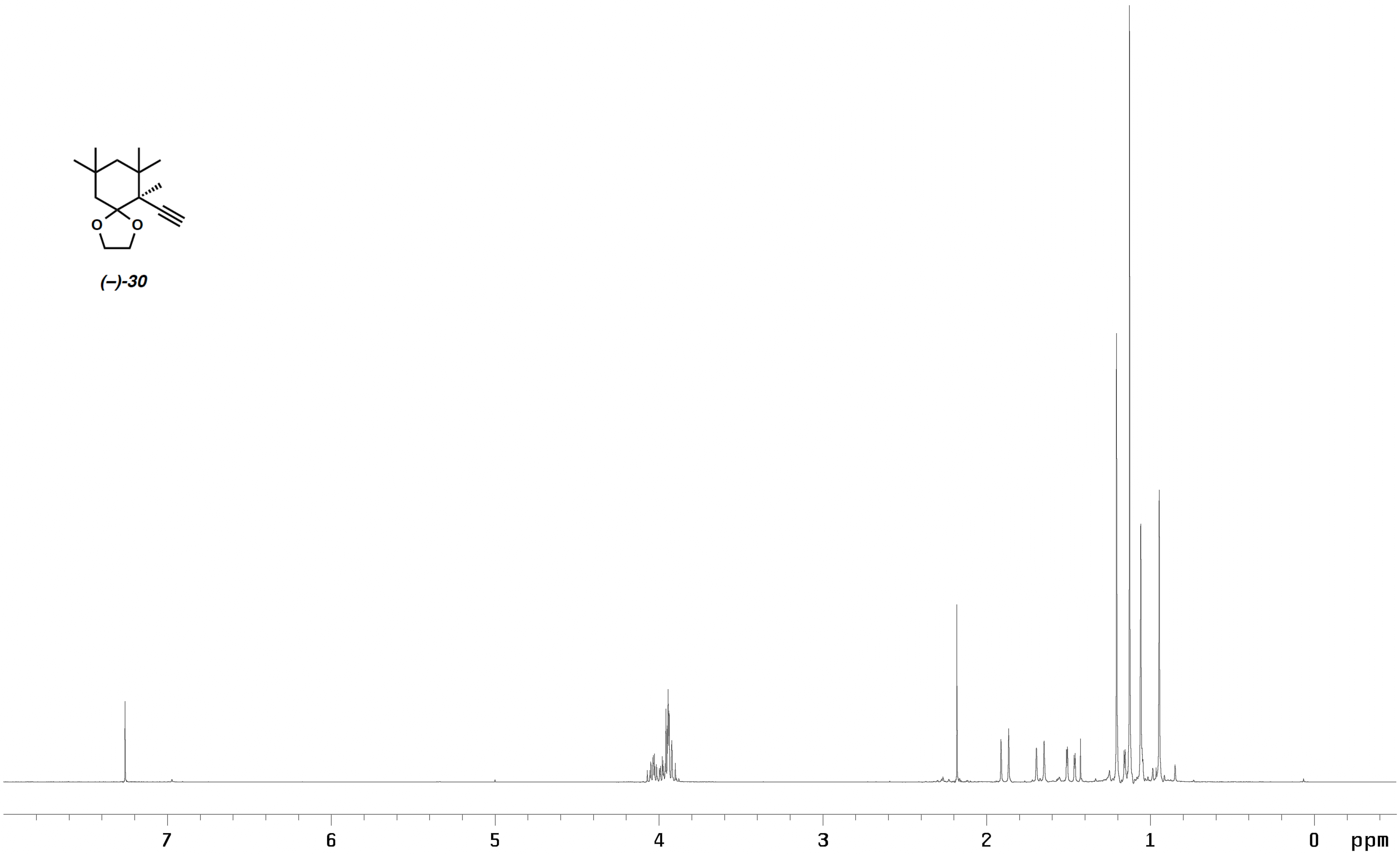

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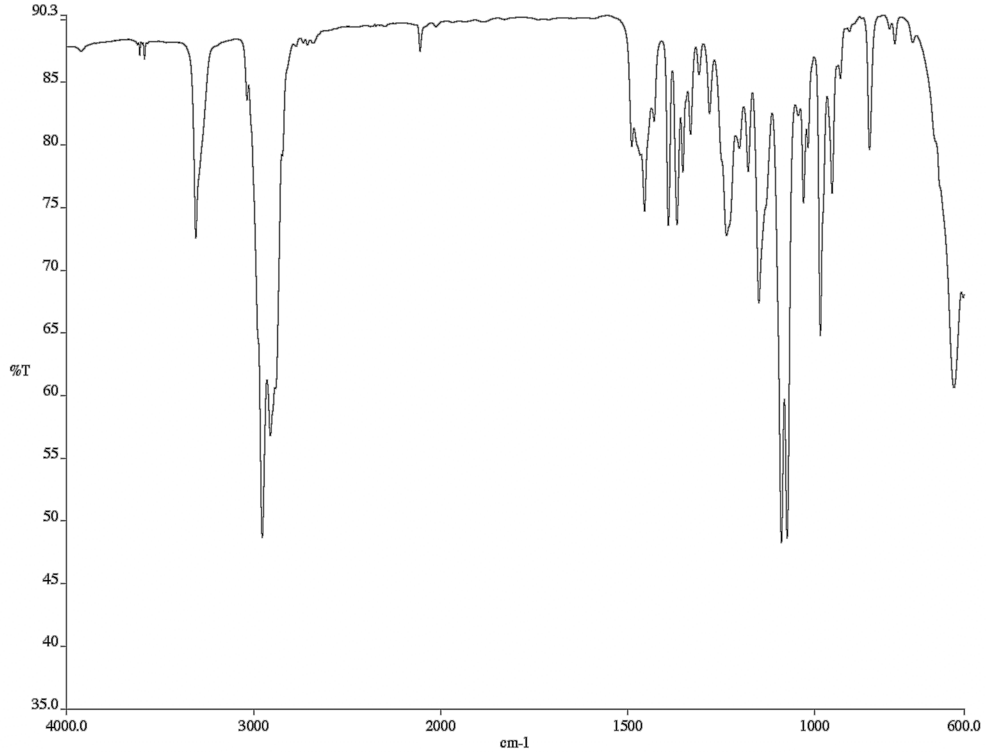
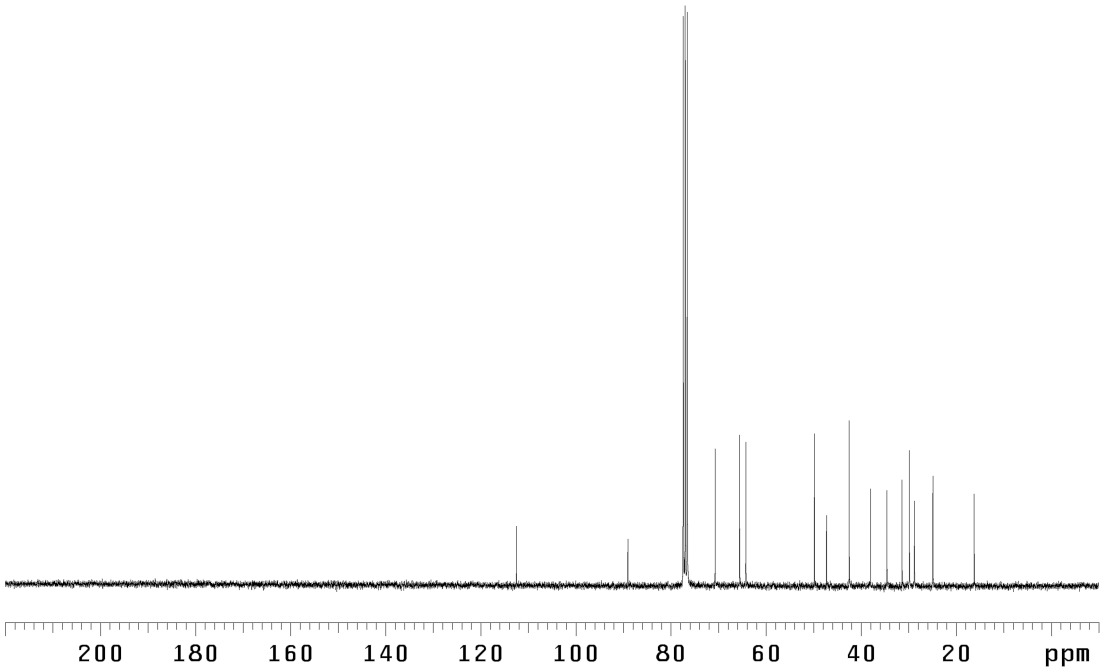
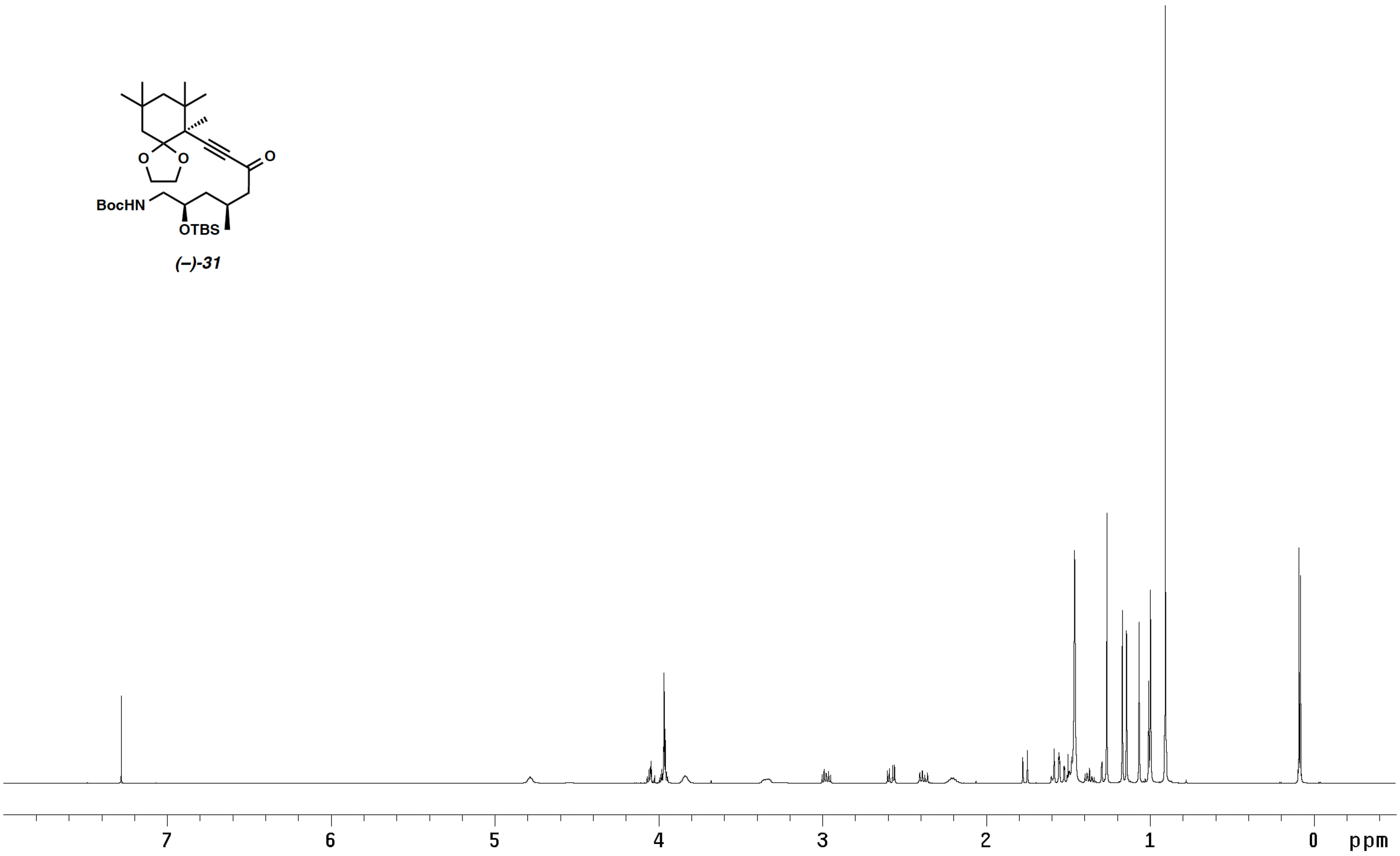


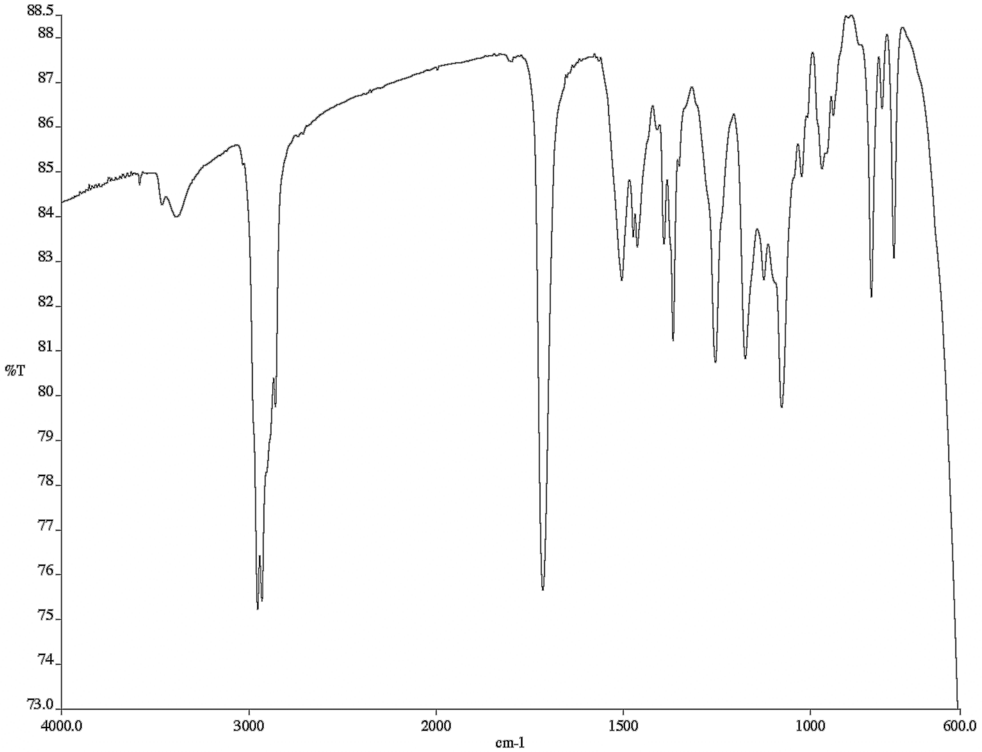
Infrared spectrum (thin film/NaCl) of compound **30**.



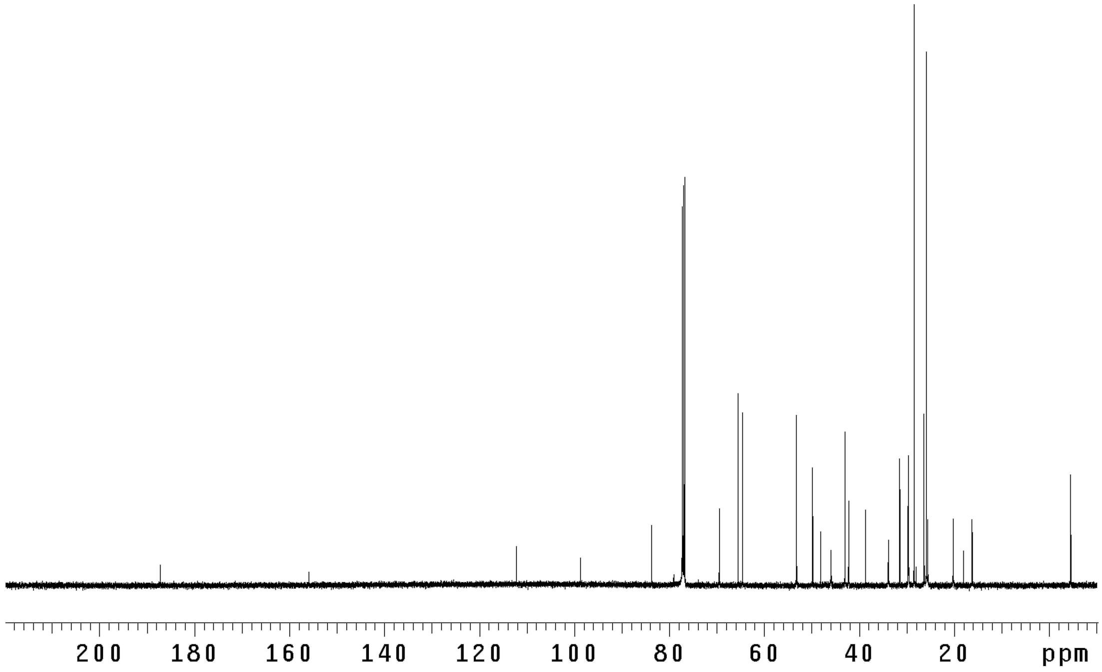
^{13}C NMR (75 MHz, $CDCl_3$) of compound **30**.



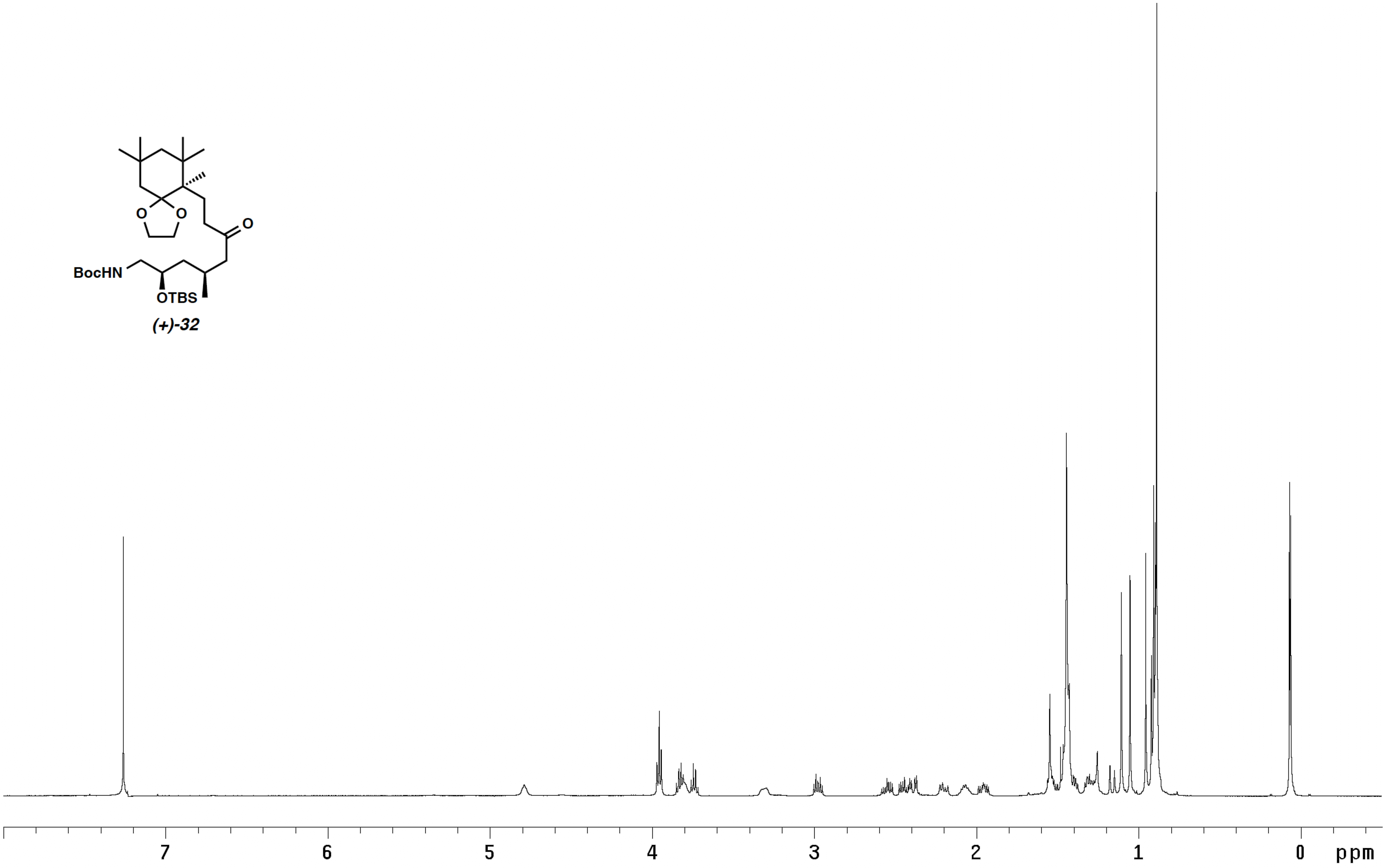
^{1}H NMR (500 MHz, CDCl$_3$) of compound **31**.



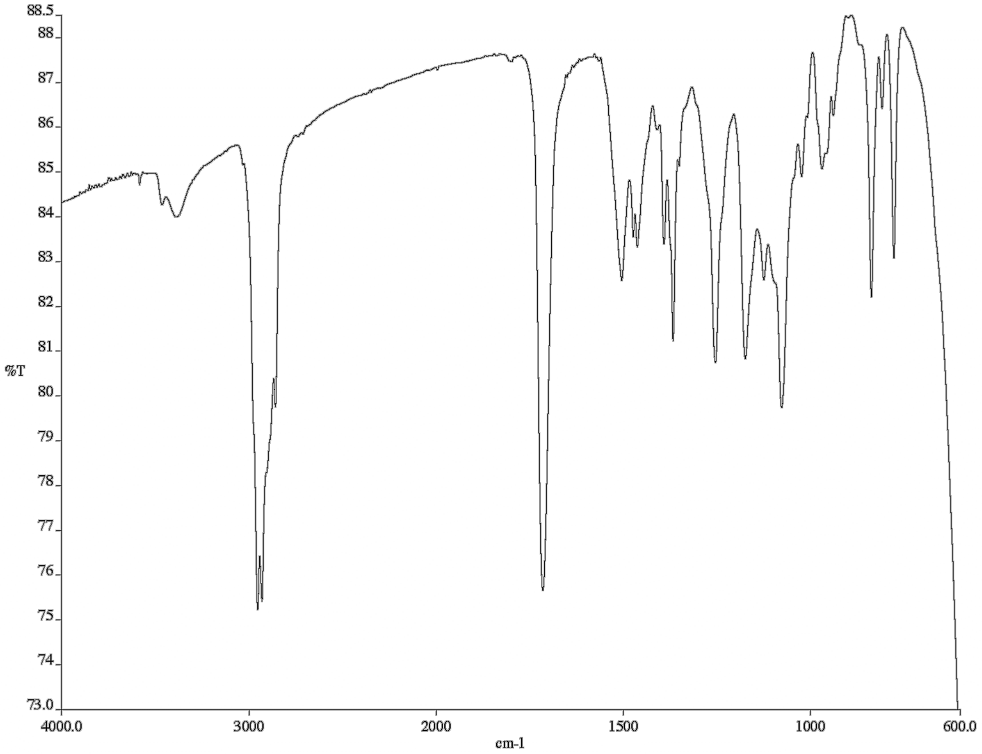
Infrared spectrum (thin film/NaCl) of compound **31**.



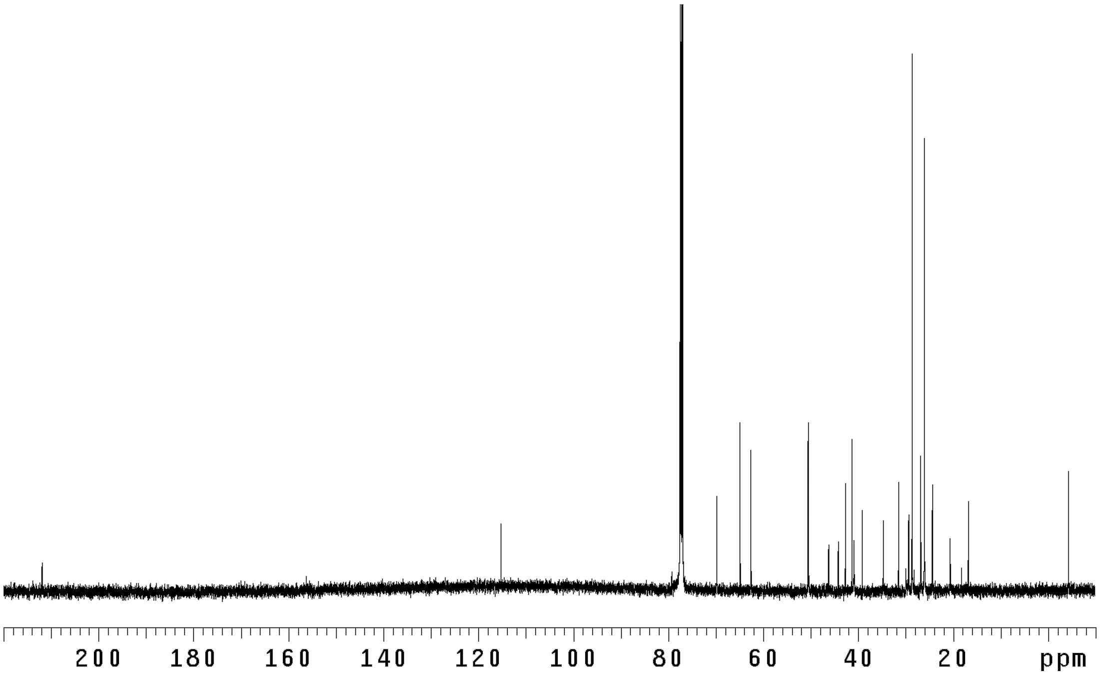
^{13}C NMR (125 MHz, $CDCl_3$) of compound **31**.



^{1}H NMR (500 MHz, CDCl$_3$) of compound **32**.



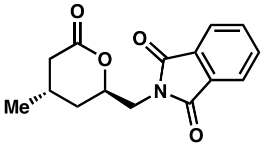
Infrared spectrum (thin film/NaCl) of compound **32**.



^{13}C NMR (125 MHz, CDCl$_3$) of compound **32**.

X-Ray Crystallographic Data

2-(((2*R*,4*S*)-4-methyl-6-oxotetrahydro-2*H*-pyran-2-yl)methyl)-isoindoline-1,3-dione (8)



Contents

Table 1.	Crystal data
Figures	Figures for publication
Table 2.	Atomic coordinates
Table 3.	Selected bond distances and angles
Table 4.	Full bond distances and angles (for deposit)
Table 5.	Anisotropic displacement parameters

Table 1. Crystal data and structure refinement for JTB01 (CCDC 181862).

Empirical formula	$C_{15}H_{15}NO_4$
Formula weight	273.28
Crystallization solvent	Heptane/ethylacetate
Crystal habit	Tabular
Crystal size	0.53 x 0.30 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker P4
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 7982 reflections used in lattice determination	2.33 to 27.55°
Unit cell dimensions	a = 7.0241(7) Å b = 19.2892(19) Å β= 109.578(2)° c = 10.3911(10) Å
Volume	1326.5(2) Å^3
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.368 Mg/m^3
F(000)	576
Data collection program	Bruker SMART v5.054
θ range for data collection	2.11 to 27.89°
Completeness to θ = 27.89°	94.1 %
Index ranges	-9 ≤ h ≤ 8, -25 ≤ k ≤ 25, -13 ≤ l ≤ 13
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	18272
Independent reflections	2992 [R_{int}= 0.0434]
Absorption coefficient	0.100 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9764 and 0.9489

Table 1 (cont.)

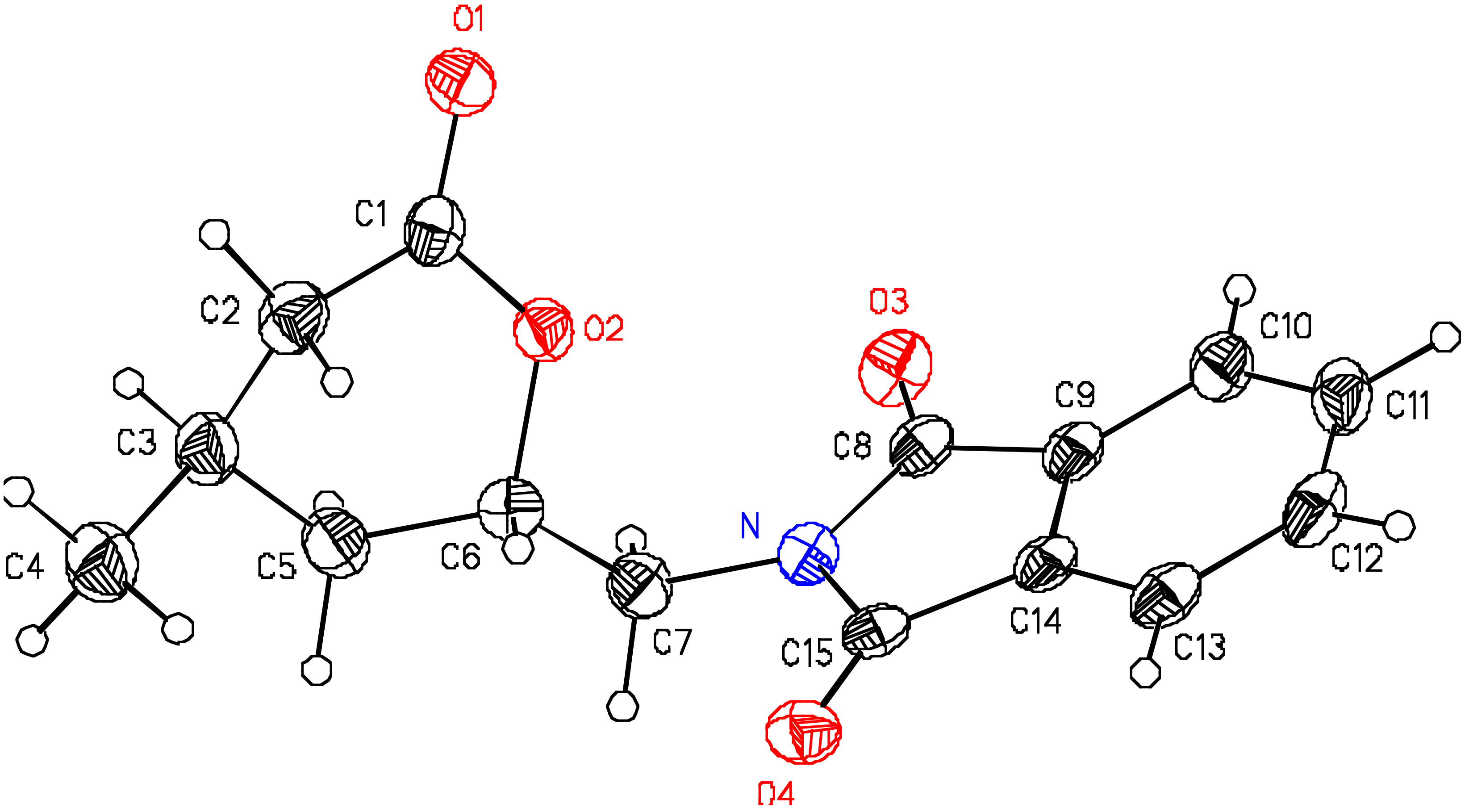
Structure Solution and Refinement

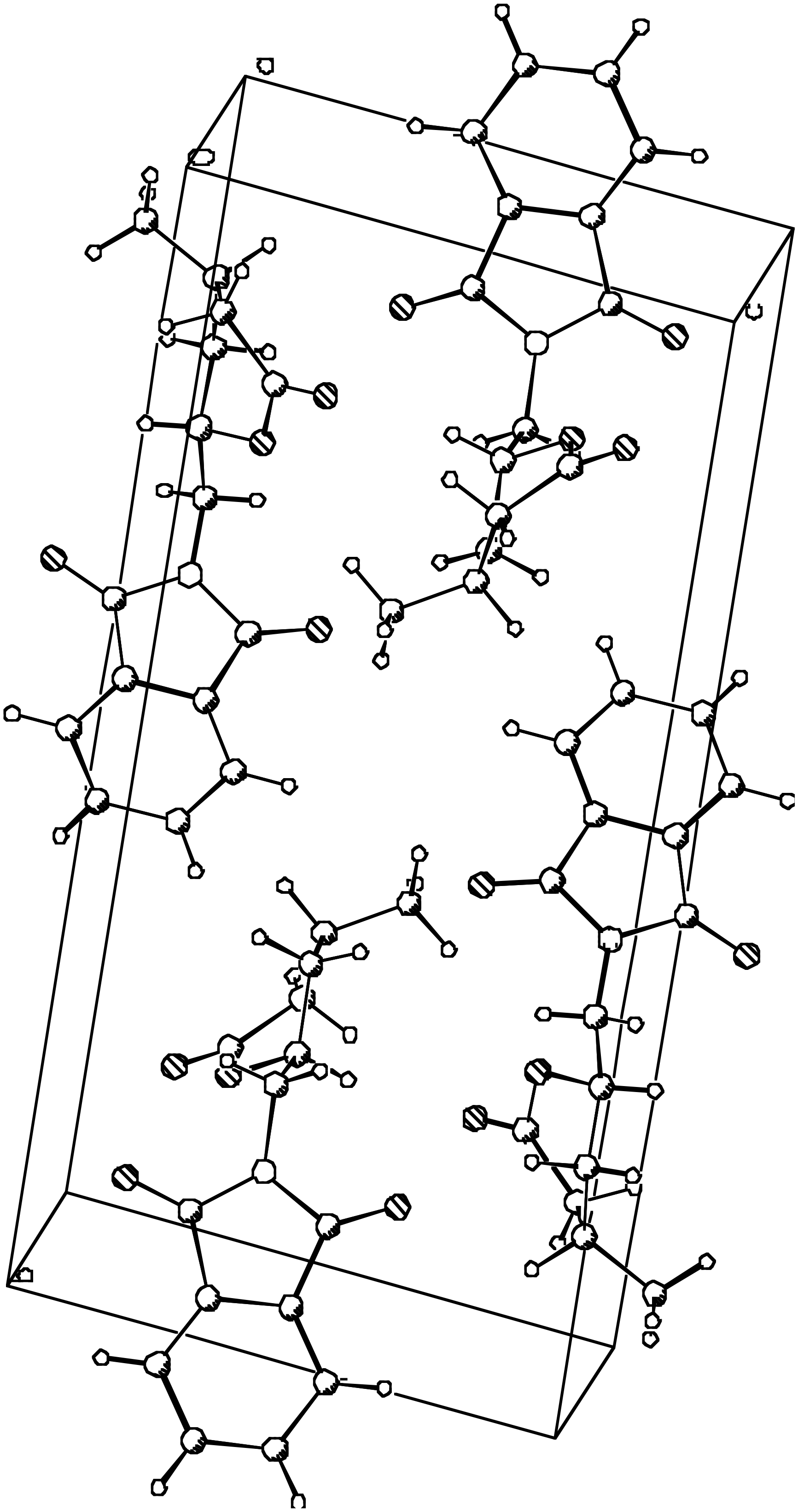
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2992 / 0 / 241
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	2.274
Final R indices [$I>2\sigma(I)$, 2323 reflections]	R1 = 0.0428, *w*R2 = 0.0682
R indices (all data)	R1 = 0.0579, *w*R2 = 0.0692
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
Largest diff. peak and hole	0.298 and -0.245 e.Å^{-3}

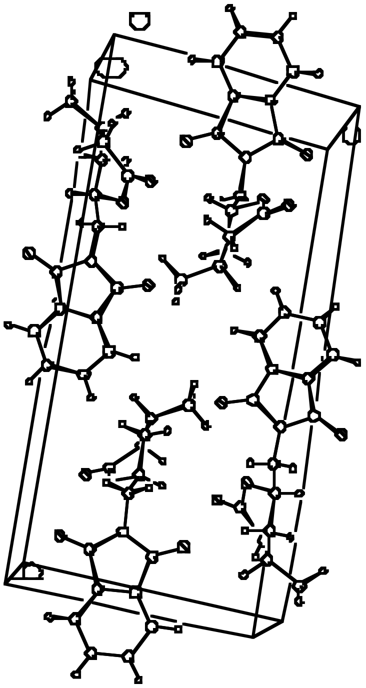
Special Refinement Details

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 $F^2 > 2s(F^2)$ 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.


O1
C1
C2
O2
C3
C4
C5
C6
C7
N
O3
C8
C9
C10
C11
C12
C13
C14
C15
O4





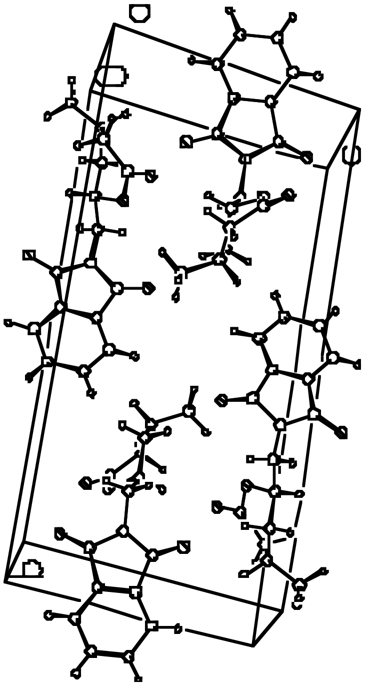


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for JTB01 (CCDC 181862). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	8436(1)	2407(1)	2404(1)	32(1)
O(2)	5191(1)	2656(1)	1692(1)	27(1)
O(3)	3360(1)	3947(1)	3345(1)	33(1)
O(4)	1021(1)	3763(1)	-1307(1)	33(1)
N	2145(2)	3677(1)	1039(1)	24(1)
C(1)	6761(2)	2271(1)	1623(1)	26(1)
C(2)	6257(2)	1726(1)	544(2)	34(1)
C(3)	4416(2)	1280(1)	485(2)	34(1)
C(4)	3661(3)	892(1)	-851(2)	43(1)
C(5)	2781(2)	1731(1)	758(2)	32(1)
C(6)	3201(2)	2493(1)	708(2)	27(1)
C(7)	1738(2)	2943(1)	1113(2)	28(1)
C(8)	2953(2)	4115(1)	2163(1)	25(1)
C(9)	3146(2)	4805(1)	1580(1)	24(1)
C(10)	3904(2)	5421(1)	2214(2)	30(1)
C(11)	3914(2)	5986(1)	1383(2)	34(1)
C(12)	3170(2)	5931(1)	-26(2)	32(1)
C(13)	2400(2)	5310(1)	-662(2)	29(1)
C(14)	2416(2)	4750(1)	168(1)	23(1)
C(15)	1753(2)	4027(1)	-194(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for JTB01 (CCDC 181862).

O(1)-C(1)	1.2131(16)	C(4)-C(3)-C(5)	113.28(14)
O(2)-C(1)	1.3515(15)	C(2)-C(3)-C(5)	110.22(12)
O(2)-C(6)	1.4634(16)	C(4)-C(3)-H(3)	108.4(7)
O(3)-C(8)	1.2081(14)	C(2)-C(3)-H(3)	106.2(7)
O(4)-C(15)	1.2093(15)	C(5)-C(3)-H(3)	108.2(7)
N-C(15)	1.3913(16)	C(3)-C(4)-H(4A)	110.1(8)
N-C(8)	1.3973(16)	C(3)-C(4)-H(4B)	107.8(7)
N-C(7)	1.4525(17)	H(4A)-C(4)-H(4B)	108.8(11)
C(1)-C(2)	1.4899(19)	C(3)-C(4)-H(4C)	108.8(9)
C(2)-C(3)	1.537(2)	H(4A)-C(4)-H(4C)	109.4(12)
C(2)-H(2A)	0.976(14)	H(4B)-C(4)-H(4C)	111.9(12)
C(2)-H(2B)	0.995(14)	C(6)-C(5)-C(3)	112.23(12)
C(3)-C(4)	1.509(2)	C(6)-C(5)-H(5A)	107.5(8)
C(3)-C(5)	1.541(2)	C(3)-C(5)-H(5A)	111.4(7)
C(3)-H(3)	1.036(13)	C(6)-C(5)-H(5B)	106.7(7)
C(4)-H(4A)	1.057(16)	C(3)-C(5)-H(5B)	111.0(7)
C(4)-H(4B)	1.060(14)	H(5A)-C(5)-H(5B)	107.7(11)
C(4)-H(4C)	1.026(17)	O(2)-C(6)-C(5)	109.82(11)
C(5)-C(6)	1.5024(19)	O(2)-C(6)-C(7)	105.13(11)
C(5)-H(5A)	1.037(15)	C(5)-C(6)-C(7)	113.12(12)
C(5)-H(5B)	1.052(13)	O(2)-C(6)-H(6)	108.5(7)
C(6)-C(7)	1.5088(19)	C(5)-C(6)-H(6)	106.2(7)
C(6)-H(6)	1.018(12)	C(7)-C(6)-H(6)	114.0(7)
C(7)-H(7A)	0.943(13)	N-C(7)-C(6)	112.46(11)
C(7)-H(7B)	0.984(13)	N-C(7)-H(7A)	107.1(8)
C(8)-C(9)	1.4882(18)	C(6)-C(7)-H(7A)	110.3(8)
C(9)-C(10)	1.3757(19)	N-C(7)-H(7B)	108.1(7)
C(9)-C(14)	1.3866(18)	C(6)-C(7)-H(7B)	109.0(7)
C(10)-C(11)	1.391(2)	H(7A)-C(7)-H(7B)	109.9(11)
C(10)-H(10)	0.952(13)	O(3)-C(8)-N	125.45(12)
C(11)-C(12)	1.384(2)	O(3)-C(8)-C(9)	129.04(13)
C(11)-H(11)	0.959(13)	N-C(8)-C(9)	105.50(11)
C(12)-C(13)	1.387(2)	C(10)-C(9)-C(14)	121.29(13)
C(12)-H(12)	0.960(13)	C(10)-C(9)-C(8)	130.66(13)
C(13)-C(14)	1.3795(18)	C(14)-C(9)-C(8)	108.04(12)
C(13)-H(13)	0.975(12)	C(9)-C(10)-C(11)	117.42(14)
C(14)-C(15)	1.4788(18)	C(9)-C(10)-H(10)	121.0(8)
C(1)-O(2)-C(6)	116.71(10)	C(11)-C(10)-H(10)	121.5(8)
C(15)-N-C(8)	112.13(11)	C(12)-C(11)-C(10)	121.18(15)
C(15)-N-C(7)	122.64(12)	C(12)-C(11)-H(11)	119.5(8)
C(8)-N-C(7)	125.22(11)	C(10)-C(11)-H(11)	119.4(8)
O(1)-C(1)-O(2)	118.14(12)	C(11)-C(12)-C(13)	121.26(14)
O(1)-C(1)-C(2)	126.02(13)	C(11)-C(12)-H(12)	119.4(8)
O(2)-C(1)-C(2)	115.82(13)	C(13)-C(12)-H(12)	119.3(8)
C(1)-C(2)-C(3)	114.18(12)	C(14)-C(13)-C(12)	117.24(14)
C(1)-C(2)-H(2A)	108.5(8)	C(14)-C(13)-H(13)	121.7(7)
C(3)-C(2)-H(2A)	111.5(8)	C(12)-C(13)-H(13)	121.0(7)
C(1)-C(2)-H(2B)	108.7(8)	C(13)-C(14)-C(9)	121.60(13)
C(3)-C(2)-H(2B)	104.4(9)	C(13)-C(14)-C(15)	130.02(13)
H(2A)-C(2)-H(2B)	109.3(11)	C(9)-C(14)-C(15)	108.37(12)
C(4)-C(3)-C(2)	110.27(13)	O(4)-C(15)-N	124.54(12)

O(4)-C(15)-C(14)	129.54(13)

N-C(15)-C(14)	105.92(11

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for JTB01 (CCDC 181862). 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)	274(6)	301(6)	372(6)	0(5)	108(5)	-30(5)
O(2)	247(5)	231(5)	327(6)	-18(4)	110(5)	-13(4)
O(3)	397(6)	350(6)	256(6)	42(5)	142(5)	51(5)
O(4)	305(6)	376(6)	264(6)	-5(5)	49(5)	1(5)
N	238(6)	239(6)	253(6)	23(5)	105(5)	11(5)
C(1)	314(9)	227(8)	272(8)	59(6)	135(7)	3(7)
C(2)	357(10)	350(9)	318(9)	-33(7)	139(8)	68(7)
C(3)	407(10)	279(8)	295(9)	-32(7)	87(7)	23(7)
C(4)	496(12)	372(10)	376(11)	-71(8)	92(9)	19(9)
C(5)	340(10)	286(9)	315(9)	-21(7)	91(8)	-36(7)
C(6)	257(8)	290(8)	271(8)	0(7)	81(7)	0(6)
C(7)	275(9)	268(8)	313(9)	22(7)	120(7)	-29(7)
C(8)	217(8)	285(8)	267(8)	21(6)	118(6)	56(6)
C(9)	194(7)	256(8)	293(8)	29(6)	121(6)	52(6)
C(10)	280(8)	285(8)	355(9)	-38(7)	136(7)	40(7)
C(11)	293(9)	245(8)	537(11)	-35(8)	210(8)	13(7)
C(12)	290(9)	260(8)	493(11)	125(8)	225(8)	79(7)
C(13)	235(8)	337(9)	319(9)	85(7)	141(7)	69(7)
C(14)	158(7)	270(8)	295(8)	34(6)	107(6)	49(6)
C(15)	157(7)	307(8)	266(8)	30(7)	79(6)	36(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for JTB01 (CCDC 181862).

	x	y	z	U_{iso}
H(2A)	7460(20)	1442(7)	672(13)	36(4)
H(2B)	5870(20)	1955(8)	-365(15)	46(5)
H(3)	4920(20)	922(7)	1269(13)	38(4)
H(4A)	4850(20)	602(8)	-998(14)	54(5)
H(4B)	2520(20)	546(7)	-800(13)	41(4)
H(4C)	3130(20)	1243(9)	-1632(16)	64(5)
H(5A)	1360(20)	1636(7)	47(14)	42(4)
H(5B)	2700(20)	1631(7)	1732(14)	37(4)
H(6)	3229(18)	2588(6)	-250(13)	22(3)
H(7A)	1826(19)	2848(6)	2021(14)	29(4)
H(7B)	360(20)	2850(6)	493(13)	27(4)
H(10)	4410(20)	5457(6)	3184(14)	29(4)
H(11)	4470(20)	6418(7)	1795(13)	31(4)
H(12)	3220(20)	6327(7)	-574(13)	33(4)
H(13)	1905(18)	5270(6)	-1655(13)	24(4)