Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of Enantioenriched γ-Quaternary Cycloheptenones Using a Combined Allylic Alkylation/Stork–Danheiser Approach: Preparation of Mono-, Bi-, and Tricyclic Systems

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Supporting Information

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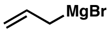
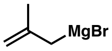
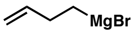
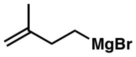
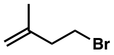
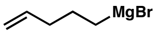
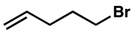
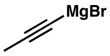
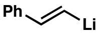
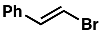
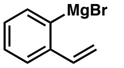
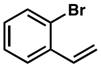
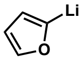
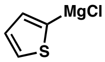
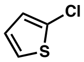
Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC). Solvents were dried by passage through an activated alumina column under argon.[i] Brine solutions are saturated aqueous solutions of sodium chloride. Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Vinylogous ester **9** and **18** were prepared following our previous literature procedures.[ii] Reaction temperatures were controlled by an IKAmag temperature modulator. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. ICN silica gel (particle size 0.032-0.0653 mm) was used for flash chromatography. Automated flash column chromatography was performed on a Teledyne Isco CombiFlash R_f system. ^1H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm) or benzene-d_6 (δ 7.16 ppm). ^{13}C NMR spectra are recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and are reported relative to $CDCl_3$ (δ 77.16 ppm) or benzene-d_6 (δ 128.06 ppm). Variable temperature NMR experiments were performed on a Varian Inova 500 MHz spectrometer and are reported relative to residual DMSO (δ 2.50 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, dm = doublet of multiplets, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent, *ee*). High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility (EI+) or Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

List of Abbreviations. The following abbreviation is used in experimental procedures:

µwaves = microwave irradiation

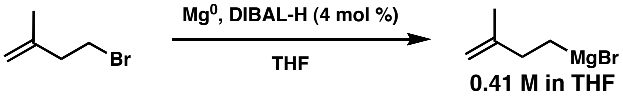
Procedures for the Formation of Grignard and Organolithium Reagents

Table SI-1. Purchase/Production of Grignard and Organolithium Reagents

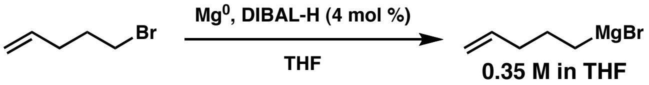
entry	Grignard/ organolithium reagent	molarity (M)	obtained from
1		0.86 M in Et$_2$O	Sigma-Aldrich
2		0.39 M in THF	Sigma-Aldrich
3		0.44 M in THF	Sigma-Aldrich
4		0.41 M in THF	
5		0.35 M in THF	
6		0.25 M in THF	Sigma-Aldrich
7		n/a[b]	
8		0.40 M in THF	
9		n/a[b]	
10		0.44 M in THF	

[a] Titrated using method of Love (see ref. i). [b] Not titrated.

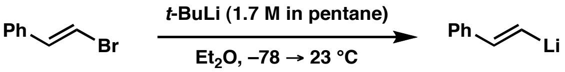
Table SI-1. Grignard and organolithium reagents were purchased from Sigma-Aldrich or prepared according to procedures listed below. Reagents were titrated using the method of Love.[iii]



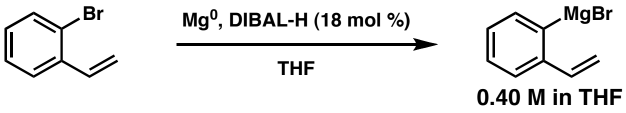
(3-Methylbut-3-enyl)magnesium bromide (Table SI-1, entry 4). A 250 mL Schlenk bomb (14/20 joint off of a 12 mm Kontes valve) equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. Once cool, magnesium metal (2.04 g, 83.79 mmol, 2.50 equiv) was added. After three argon backfilling cycles, the flask was charged with THF (50 mL, 0.7 M) and neat DIBAL-H[iv] (150 µL, 1.29 mmol, 4 mol %) and stirring was initiated. The stirring was stopped after 10 min and 4-bromo-2-methylbut-1-ene[v] (5.00 g, 33.57 mmol, 1.00 equiv) was added via syringe with the needle in the solution directly above the magnesium. The mixture was heated to reflux, sealed by closing the Schlenk valve, and stirred vigorously. The flask was occasionally heated back to reflux and then allowed to cool to room temperature (23 °C). The reaction color became amber over time. After 30 min, an aliquot was removed and titrated following the procedure of Love (0.41 M in THF).[iii] See page SI 9 for use of this reagent.



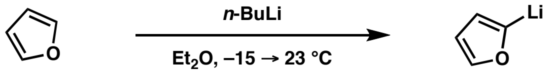
Pent-4-enylmagnesium bromide (Table SI-1, entry 5). A 250 mL Schlenk bomb (14/20 joint off of a 12 mm Kontes valve) equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. Once cool, magnesium metal (614.4 mg, 25.27 mmol, 2.53 equiv) was added. After three argon backfilling cycles, the flask was charged with THF (20 mL, 0.5 M) and neat DIBAL-H[iv] (50 µL, 0.43 mmol, 4 mol %) and stirring was initiated. The stirring was stopped after 10 min and 5-bromopent-1-ene (1.18 mL, 9.98 mmol, 1.00 equiv) was added via a syringe with the needle in the solution directly above the magnesium. The mixture was heated to reflux, sealed by closing the Schlenk valve, and stirred vigorously. The flask was occasionally heated back to reflux and then allowed to cool to room temperature (23 °C). The reaction color became amber over time. After 30 min, an aliquot was removed and titrated following the procedure of Love (0.35 M in THF).[iii] See page SI 10 for use of this reagent.



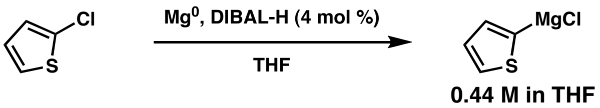
(*E*)-Styryllithium (Table SI-1, entry 7). See page SI 10 for the synthesis and use of this reagent.



(2-vinylphenyl)magnesium bromide (Table SI-1, entry 8). A 250 mL Schlenk round-bottom flask (14/20 joint off of a 12 mm Kontes valve) equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. Once cool, magnesium metal (491.3 mg, 20.21 mmol, 2.53 equiv) was added. After three argon backfilling cycles, the flask was charged with THF (16 mL, 0.5 M) and neat DIBAL-H[iv] (170 µL, 1.46 mmol, 18 mol %) and stirring was initiated. The stirring was stopped after 10 min and *o*-bromostyrene (1.00 mL, 7.98 mmol, 1.00 equiv) was added with the needle in the solution directly above the magnesium. The mixture was heated to reflux, sealed by closing the Schlenk valve, and stirred vigorously. The flask was occasionally heated back to reflux and then allowed to cool to room temperature (23 °C). The reaction became amber over time. After 2 h, a small portion of the reaction was removed and titrated following the procedure of Love.[iii] See page SI 12 for use of this reagent.

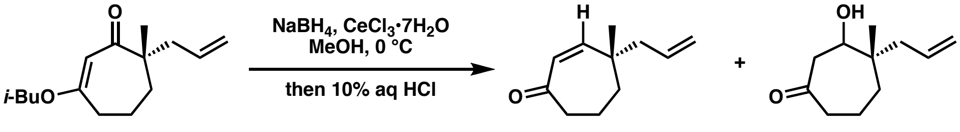


Furan-2-yllithium (Table SI-1, entry 9). Prepared following a procedure similar to Sauers and Hagedorn.[vi] See page SI 13 for the synthesis and use of this reagent.



Thiophen-2-ylmagnesium chloride (Table SI-1, entry 10). A two neck 50 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum on one neck and a water condenser on the other neck, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, magnesium metal (635.0 mg, 26.12 mmol, 2.60 equiv) was added. After two argon backfilling cycles, the flask was charged with THF (20 mL) and neat DIBAL-H[iv] (50 μL, 0.43 mmol, 4 mol %) and stirring was initiated. The stirring was stopped after 10 min and 2-chlorothiophene (930 μL, 10.04 mmol, 1.00 equiv) was added via a syringe with the needle in the solution directly above the magnesium. The mixture was heated to reflux. A small piece of I_2 (size of a spatula tip) dissolved in THF (1 mL) was cannula-transferred into the mixture after 12 h and 13.5 h. The flask was allowed to cool to room temperature (23 °C). After 15 h, an aliquot was removed and titrated following the procedure of Love (0.44 M in THF).[iii] See page SI 14 for use this reagent.

Procedures for the Synthesis of Cycloheptenones 1



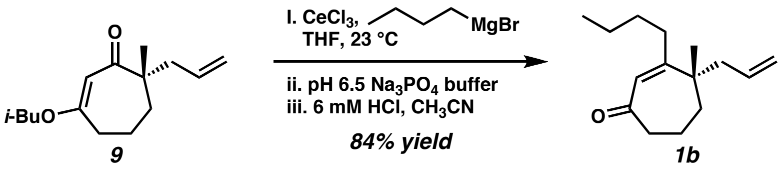
9 *1a* *14a*

82% yield

1% yield
3.5:1 dr

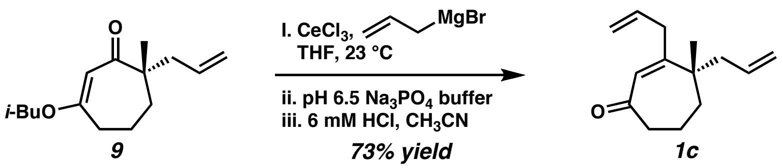
Cycloheptenone 1a and β-Hydroxyketone 14a. A 100 mL round-bottom flask with magnetic stir bar was charged with vinylogous ester **9** (186.8 mg, 0.79 mmol, 1.00 equiv) and anhydrous MeOH (14 mL). The solution was cooled to 0 °C. $CeCl_3 \cdot 7H_2O$ (294.5 mg, 0.79 mmol, 1.56 equiv) was added in one portion and the mixture was stirred for 5 min. Portionwise addition of $NaBH_4$ (89.7 mg, 2.37 mmol, 3.00 equiv) at 0 °C led to the evolution of gas and a turbid solution that became clearer after several minutes.

TLC analysis indicated that no starting material remained after 2 min. Consequently, the reaction was quenched by dropwise addition of 10% aq. HCl (2 mL) at 0 °C. After an additional 10 min of stirring, the reaction was diluted with CH_2Cl_2 (60 mL) and H_2O (2 mL). The layers were separated. The aqueous layer was extracted with CH_2Cl_2 (6 x 5 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (2 x 5 mL) and brine (2 x 5 mL), dried over Na_2SO_4, filtered, and evaporated to give a pale yellow oil. The crude mixture was purified using flash chromatography (SiO_2, 2 x 25 cm, 20:1→15:1→3:1 hexanes:EtOAc) to afford volatile enone **1a** (106.9 mg, 0.645 mmol, 82% yield) as a pale yellow oil and β-hydroxyketone **14a** as a mixture of diastereomers (1.4 mg, 0.0077 mmol, 1% yield, 3.5:1 dr) as a colorless oil. Characterization data is identical to previously reported data.[ii]



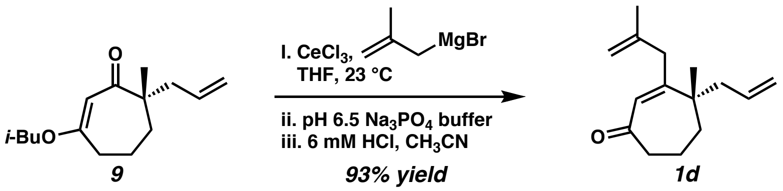
Cycloheptenone 1b. A 50 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (260.8 mg, 1.06 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (8.5 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of *n*-butylmagnesium bromide (680 µL, 1.87 M in THF, 1.27 mmol, 3.00 equiv) was added and the mixture turned grey. After 30 min of stirring, vinylogous ester **9** (100.0 mg, 0.42 mmol, 1.00 equiv) was added neat from a Hamilton syringe and the needle was rinsed with a small portion of THF (2 mL; total THF added = 10.5 mL, 0.04 M). The color of the slurry initially transitioned to yellow with the vinylogous ester addition before turning back to grey.

TLC analysis indicated that no starting material remained after 15 min. After an additional 10 min of stirring, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (8 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (125 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (1.0 mL), and 6 mM aq. HCl (1.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 5 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (100 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1b** (82.4 mg, 0.35 mmol, 84% yield) as a pale yellow oil. Characterization data is identical to previously reported data.[ii]



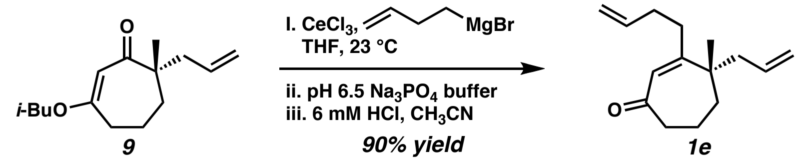
Cycloheptenone 1c. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.3 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of allylmagnesium bromide (3.49 mL, 0.86 M in Et_2O, 3.00 mmol, 3.00 equiv) was added and the mixture turned initially orange and red over time. After 30 min of stirring, vinylogous ester **9** (236.6 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M). The mixture faded back to orange with the addition.

TLC analysis indicated that no starting material remained after 5 min. After an additional 10 min of stirring, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (20 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (250 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (2.0 mL), and 6 mM aq. HCl (2.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 30 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1c** (148.6 mg, 0.73 mmol, 73% yield) as a pale yellow oil; R_f = 0.68 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.75 (dddd, *J* = 16.9, 10.1, 6.8, 6.8 Hz, 1H), 5.64 (dddd, *J* = 17.0, 10.3, 7.8, 6.8 Hz, 1H), 5.14–5.00 (m, 4H), 2.96–2.84 (m, 2H), 2.62–2.54 (m, 2H), 2.38 (dddd, *J* = 14.2, 6.8, 1.3, 1.3 Hz, 1H), 2.10 (dddd, *J* = 14.2, 7.8, 1.1, 1.1 Hz, 1H), 1.84–1.76 (m, 3H), 1.67–1.57 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 160.3, 136.0, 134.0, 130.0, 118.3, 117.9, 45.5, 45.2, 44.4, 38.8, 38.5, 25.7, 17.6; IR (Neat Film NaCl) 3077, 2976, 2939, 2872, 1654, 1612, 1458, 1412, 1380. 1342, 1290, 1250, 1217, 1177, 1106, 996, 916 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{14}H_{21}O$ $[M+H]^+$: 205.1587; found 205.1587; $[\alpha]_D^{25.0}$ –34.64 (*c* 1.55, $CHCl_3$, 88% ee).



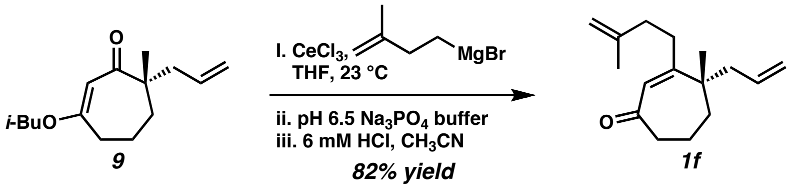
Cycloheptenone 1d. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of (2-methylallyl)magnesium bromide (7.7 mL, 0.39 M in THF, 3.00 mmol, 3.00 equiv) was added and the mixture turned initially yellow and eventually orange with time. After 30 min of stirring, vinylogous ester **9** (236.2 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M).

TLC analysis indicated that no starting material remained after 5 min. After an additional 15 min of stirring, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (20 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (150 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (2.0 mL), and 6 mM aq. HCl (2.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 30 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1d** (202.9 mg, 0.93 mmol, 93% yield) as a pale yellow oil; R_f = 0.65 (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.89 (s, 1H), 5.65 (dddd, *J* = 16.9, 10.3, 7.8, 6.8 Hz, 1H), 5.09–5.01 (m, 2H), 4.94–4.91 (m, 1H), 4.78 (dd, *J* = 1.9, 0.9 Hz, 1H), 2.85 (q, *J* = 16.2 Hz, 2H), 2.63–2.55 (m, 2H), 2.37 (dddd, *J* = 14.1, 6.8, 1.3, 1.3 Hz, 1H), 2.10 (dddd, *J* = 14.2, 7.8, 1.1, 1.1 Hz, 1H), 1.85–1.75 (m, 3H), 1.68 (s, 3H), 1.66–1.59 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 159.1, 142.8, 134.0, 129.5, 118.3, 115.2, 45.4, 45.0, 44.4, 42.7, 38.8, 25.6, 22.2, 17.6; IR (Neat Film NaCl) 3075, 2970, 2939, 2872, 1661, 1652, 1612, 1455, 1376, 1342, 1309, 1249, 1218, 996, 914, 893 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{15}H_{23}O$ $[M+H]^+$: 219.1743; found 219.1740; $[\alpha]_D^{25.0}$ –35.09 (*c* 0.95, $CHCl_3$, 88% ee).



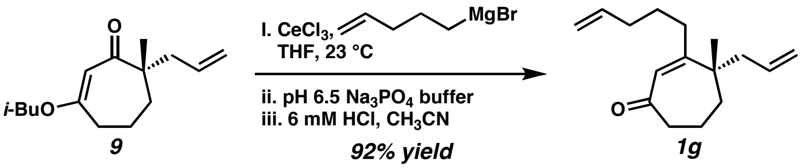
Cycloheptenone 1e. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting white mixture was stirred, a solution of but-3-enylmagnesium bromide (6.82 mL, 0.44 M in THF, 3.00 mmol, 3.00 equiv) was added, generating a thick grey slurry. After 30 min of stirring, vinylogous ester **9** (236.4 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M).

After 20 min, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (20 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organic (150 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (2.0 mL), and 6 mM aq. HCl (2.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 5 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (80 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5%→10% EtOAc in hexanes) to afford cycloheptenone **1e** (196.6 mg, 0.90 mmol, 90% yield) as a yellow oil; R_f = 0.67 (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.86–5.77 (m, 1H), 5.63 (dddd, *J* = 16.9, 10.3, 7.8, 6.8 Hz, 1H), 5.08–4.96 (m, 4H), 2.59–2.54 (m, 2H), 2.36 (dddd, *J* = 14.1, 6.7, 1.3, 1.3 Hz, 1H), 2.28–2.17 (m, 4H), 2.08 (dddd, *J* = 14.1, 7.9, 2.1, 1.0 Hz, 1H), 1.83–1.73 (m, 3H), 1.65–1.57 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 161.6, 137.7, 134.0, 128.9, 118.2, 115.4, 45.7, 45.2, 44.3, 38.7, 34.0, 33.4, 25.7, 17.6; IR (Neat Film NaCl) 3076, 2975, 2938, 2872, 1652, 1611, 1465, 1452, 1415, 1379, 1342, 1263, 1218, 1177, 1109, 1069, 996, 914, 877, 841, 764, 714 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{15}H_{23}O$ [M+H]$^+$: 219.1743; found 219.1742; $[\alpha]_D^{25.0}$ –34.11 (*c* 1.21, $CHCl_3$, 88% ee).



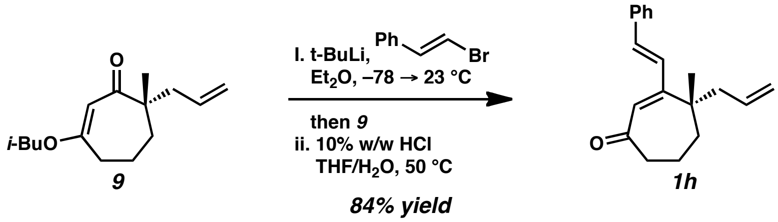
Cycloheptenone 1f. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of (3-methylbut-3-enyl)magnesium bromide (7.3 mL, 0.41 M in THF, 2.99 mmol, 2.99 equiv) was added and the mixture turned yellow. After 30 min of stirring, vinylogous ester **9** (236.4 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M).

TLC analysis indicated that no starting material remained after 5 min. After an additional 10 min of stirring, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (20 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organic (150 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (2.0 mL), and 6 mM aq. HCl (2.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 5 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1f** (191.1 mg, 0.82 mmol, 82% yield) as a clear colorless oil; $R_f = 0.69$ (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (s, 1H), 5.64 (dddd, *J* = 16.9, 10.3, 7.8, 6.8 Hz, 1H), 5.09–4.99 (m, 2H), 4.77–4.73 (m, 1H), 4.72–4.69 (m, 1H), 2.59–2.56 (m, 2H), 2.38 (dddd, *J* = 14.1, 6.7, 1.3, 1.3 Hz, 1H), 2.31–2.14 (m, 4H), 2.10 (dddd, *J* = 14.1, 7.8, 1.1, 1.1 Hz, 1H), 1.83–1.75 (m, 3H), 1.75–1.74 (m, 3H), 1.66–1.57 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 162.1, 145.1, 134.0, 129.0, 118.3, 110.6, 45.8, 45.3, 44.3, 38.8, 38.3, 32.5, 25.7, 22.7, 17.6; IR (Neat Film NaCl) 3075, 2968, 2938, 2873, 1652, 1611, 1455, 1415, 1377, 1342, 1262, 1218, 1181, 1109, 1069, 996, 915, 887 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{16}H_{25}O$ [M+H]$^+$: 233.1900; found 233.1896; $[\alpha]_D^{25.0}$ –32.57 (*c* 1.32, $CHCl_3$, 88% ee).



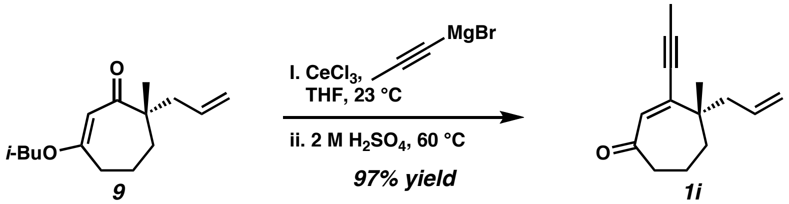
Cycloheptenone 1g. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of pent-4-enylmagnesium bromide (8.6 mL, 0.35 M in THF, 3.01 mmol, 3.01 equiv) was added and the mixture turned grey. After 30 min of stirring, vinylogous ester **9** (236.3 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M).

TLC analysis indicated that no starting material remained after 5 min. After an additional 10 min of stirring, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (20 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organic (150 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (2.0 mL), and 6 mM aq. HCl (2.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 30 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→1%→2%→5% EtOAc in hexanes) to afford cycloheptenone **1g** (214.2 mg, 0.92 mmol, 92% yield) as a clear colorless oil; $R_f = 0.65$ (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.79 (dddd, J = 16.9, 10.2, 6.7, 6.7 Hz, 1H), 5.67–5.57 (m, 1H), 5.07–4.96 (m, 4H), 2.60–2.53 (m, 2H), 2.35 (dddd, J = 14.1, 6.7, 2.5, 1.2 Hz, 1H), 2.20–2.04 (m, 5H), 1.83–1.73 (m, 3H), 1.66–1.53 (m, 3H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 162.6, 138.2, 134.1, 128.8, 118.2, 115.3, 45.7, 45.2, 44.3, 38.7, 33.8, 33.5, 29.3, 25.7, 17.6; IR (Neat Film NaCl) 3076, 2975, 2937, 2870, 1652, 1611, 1456, 1415, 1380, 1343, 1257, 1218, 1179, 1110, 1071, 994, 913 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{16}H_{25}O$ $[M+H]^+$: 233.1900; found 233.1900; $[\alpha]_D^{25.0}$ –34.96 (*c* 1.46, $CHCl_3$, 88% ee).



Cycloheptenone 1h. A flame-dried round-bottom flask equipped with a magnetic stir bar and fitted with a rubber septum was connected to a Schlenk manifold. The flask was charged with (*E*)-β-bromostyrene (1.5 mL, 11.69 mmol, 1.98 equiv) and Et_2O (13 mL) and lowered into a dry ice/acetone bath (–78 °C). After dropwise addition of *t*-butyllithium (13.5 mL, 1.7 M in pentane, 22.95 mmol, 3.88 equiv), the solution was stirred for 2 hours (at –78 °C), warmed to room temperature (30 min stir at 23 °C), and placed back into the dry ice/acetone bath. Vinylogous ester **9** (1.40 g, 5.92 mmol, 1.00 equiv) was transferred to the round-bottom flask by two Et_2O rinses (2 x 3 mL, total Et_2O added = 19 mL, 0.3 M). The flask was stirred at –78 °C for 25 min before being transferred to an ice/water bath (0 °C).

TLC analysis indicated that no starting material remained after 2 h. Consequently, the reaction was quenched with 10% w/w aq. HCl (10 mL). After 20 min of stirring, the mixture was transferred to a separatory funnel where the aqueous phase was extracted three times with Et_2O. The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. A round-bottom flask was charged with the crude oil, THF (20 mL), and 10% w/w aq. HCl (0.5 mL) and lowered into a preheated oil bath (50 °C). After 2 h, the reaction allowed to cool to room temperature, concentrated under reduced pressure, diluted with water (10 mL) and Et_2O (20 mL), and transferred to a separatory funnel where the aqueous layer was extracted twice with Et_2O (2 x 20 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 23 cm, 20:1→15:1→10:1 hexanes:EtOAc) to afford cycloheptenone **1h** (1.33 g, 4.99 mmol, 84% yield) as a yellow oil; $R_f = 0.67$ (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 6.90 (s, 2H), 6.30 (s, 1H), 5.67 (dddd, *J* = 16.8, 10.3, 8.1, 6.5 Hz, 1H), 5.09–5.02 (m, 2H), 2.71–2.57 (m, 2H), 2.46 (dddd, *J* = 14.1, 6.5, 1.3, 1.3 Hz, 1H), 2.14 (dddd, *J* = 14.1, 8.1, 1.1, 1.1 Hz, 1H), 1.92–1.79 (m, 3H), 1.72–1.64 (m, 1H), 1.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 158.5, 136.7, 133.9, 133.3, 129.2, 128.9, 128.5, 127.1, 127.1, 118.4, 46.2, 44.5, 44.4, 38.7, 26.8, 17.6; IR (Neat Film NaCl) 3075, 3059, 3002, 2966, 2936, 2869, 1640, 1581, 1573, 1495, 1449, 1414, 1379. 1343, 1303, 12.77, 1250, 1217, 1178, 1109, 1082, 1028, 996, 963, 916, 839, 799, 752, 718 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{19}H_{23}O$ $[M+H]^+$: 267.1743; found 267.1755; $[\alpha]_D^{25.0}$ –44.99 (*c* 0.81, $CHCl_3$, 88% ee).

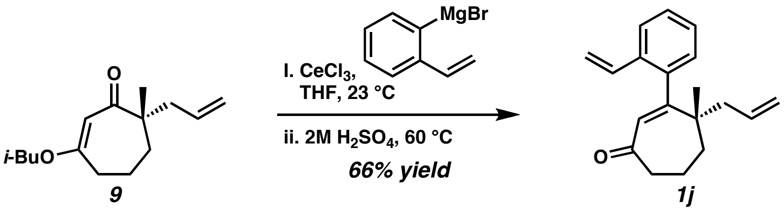


9 **1i**

Cycloheptenone 1i. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of prop-1-ynylmagnesium bromide (12 mL, 0.25 M in THF, 3.00 mmol, 3.00 equiv) was added and the mixture turned yellow. After 30 min of stirring, vinylogous ester **9** (236.4 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M). The slurry maintained the yellow color with the addition.

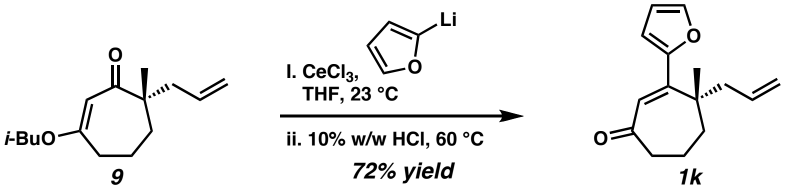
TLC analysis indicated that no starting material remained after 5 min. After an additional

10 min of stirring, the reaction was quenched with 2 M H_2SO_4 (5 mL) and lowered into a preheated oil bath (60 °C). A white precipitate formed within several minutes. After 12 h, the yellow suspension was removed from the bath, cooled to room temperature (23 °C), treated with sat. aq. $NaHCO_3$ solution (50 mL), and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (175 mL) were rinsed once with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1i** (195.4 mg, 0.97 mmol, 97% yield) as a yellow oil; R_f = 0.65 (30% EtoAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (s, 1H), 5.70 (dddd, *J* = 16.8, 10.5, 8.2, 6.6 Hz, 1H), 5.10–5.01 (m, 2H), 2.65–2.49 (m, 3H), 2.16 (dddd, *J* = 13.8, 8.2, 1.0, 1.0 Hz, 1H), 2.01 (s, 3H), 1.83–1.75 (m, 3H), 1.66–1.59 (m, 1H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 145.6, 135.0, 134.3, 118.3, 92.9, 80.7, 46.5, 45.4, 44.6, 37.3, 27.0, 17.6, 4.7; IR (Neat Film NaCl) 3076, 2969, 2937, 2219, 1652, 1580, 1455, 1415, 1377, 1346, 1255, 1225, 1184, 1110, 998, 916, 893, 866, 813, 784, 716 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{14}H_{19}O$ [M+H]$^+$: 203.1430; found 203.1428; $[\alpha]_D^{25.0}$ –49.25 (*c* 1.21, $CHCl_3$, 88% ee).



Cycloheptenone 1j. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (4 cycles, 1 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.4 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of (2-vinylphenyl)magnesium bromide (7.5 mL, 0.40 M in THF, 3.00 mmol, 3.00 equiv) was added and the mixture turned yellow and green over time. After 30 min of stirring, vinylogous ester **9** (236.3 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M). The reaction color returned to yellow with addition of vinylogous ester **9**.

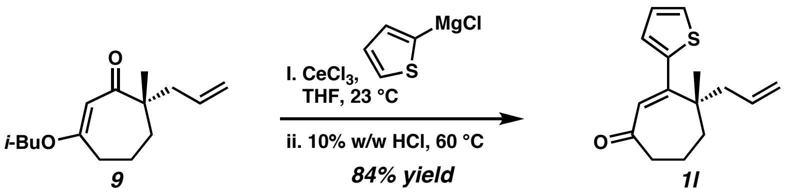
TLC analysis indicated that no starting material remained after 40 min. After an additional 30 min of stirring, the reaction was quenched with 2 M H_2SO_4 (5 mL) and lowered into a preheated oil bath (60 °C). A grey precipitate formed within several minutes. After 26 h, the yellow suspension was removed from the bath, cooled to room temperature (23 °C), treated with sat. aq. $NaHCO_3$ solution (50 mL), and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (175 mL) were rinsed once with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified first by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) and then by flash chromatography using a Teledyne Isco CombiFlash R_f system (SiO_2, 12 g loading cartridge, 40 g column, multi-step gradient, hold 0% [2 min]→ramp to 85% [17 min]→hold 85% CH_2Cl_2 in hexanes [2.5 min]→ramp to 100% [3 min]→hold 100% CH_2Cl_2 [5 min]) to afford cycloheptenone **1j** (176.7 mg, 0.66 mmol, 66% yield) as a pale yellow oil; R_f = 0.74 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) mixture of two atropisomers isomers (1.9 : 1 ratio), see **Figure SI-8A** ^{1}H NMR (in $CDCl_3$) and **Figure SI-8B** for variable temperature ^{1}H NMR data (in DMSO-d_6 at 25, 50, 75, and 100 °C); IR (Neat Film NaCl) 3060, 3007, 2973, 2936, 2936, 1669, 1626, 1604, 1594, 1476, 1464, 1443, 1413, 1379, 1356, 1338, 1307, 1281, 1251, 1214, 1177, 1136, 1109, 1095, 1057, 1020, 996, 915, 864, 818, 769, 743 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{19}H_{23}O$ $[M+H]^+$: 267.1743; found 267.1751.



Cycloheptenone 1k. A 100 and 25 mL round-bottom flask each equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold were flame-dried three times, backfilling with argon after each drying cycle. The hot 100 mL flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold.

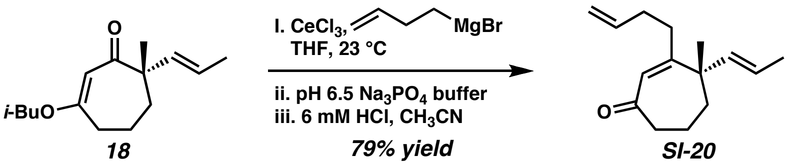
Once cool, the 25 mL flask was charged with furan[vii] (230 μL, 3.16 mmol, 1.05 equiv) and Et_2O (3 mL, 1 M) and lowered into an ethylene glycol/dry ice bath (–15 °C). To the cooled solution was added *n*-BuLi (1.42 mL, 2.12 M in hexanes, 3.01 mmol, 1.00 equiv) dropwise and the flask was warmed to room temperature (23 °C). The reaction became cloudy and white with time. After 1h, a portion of THF (13 mL) was added to the 100 mL flask before the contents of the 25 mL flask were cannula-transferred to the 100 mL flask. After 30 min of stirring, vinylogous ester **9** (236.4 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the 100 mL flask from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M).

After 35 min, the reaction was quenched with 10% w/w aq. HCl (5 mL) and lowered into a preheated oil bath (60 °C). After 17 h, the solution was removed from the bath, cooled to room temperature (23 °C), treated with sat. aq. $NaHCO_3$ solution (50 mL), and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (250 mL) were rinsed once with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1k** (164.7 mg, 0.72 mmol, 72% yield) as a yellow oil; R_f = 0.70 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 1.8, 0.6 Hz, 1H), 6.56 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.43 (s, 1H), 6.41 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.65 (dddd, *J* = 16.9, 10.2, 8.1, 6.6 Hz, 1H), 5.01 (dddd, *J* = 10.2, 2.0, 0.9, 0.9 Hz, 1H), 4.97 (dddd, *J* = 16.9, 2.3, 1.4, 1.4 Hz, 1H), 2.71–2.60 (m, 3H), 2.24 (dddd, *J* = 14.1, 8.1, 1.1, 1.1 Hz, 1H), 1.97–1.81 (m, 3H), 1.72–1.64 (m, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 155.3, 149.2, 142.9, 134.3, 129.3, 118.1, 111.4, 111.2, 45.9, 44.7, 44.3, 39.8, 26.3, 17.4; IR (Neat Film NaCl) 3118, 3075, 2941, 2871, 1661, 1652, 1645, 1581, 1557, 1455, 1415, 1380, 1341, 1258, 1215, 1173, 1152, 1106, 1080, 1029, 997, 956, 917, 898, 886, 858, 812, 742 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380; found 231.1374; $[\alpha]_D^{25.0}$ –26.90 (*c* 1.18, $CHCl_3$, 88% ee).



Cycloheptenone 1l. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (3 cycles, 5 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (616.2 mg, 2.50 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (13 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of thiophen-2-ylmagnesium chloride (6.8 mL, 0.44 M in THF, 2.99 mmol, 2.99 equiv) was added and the mixture turned dark grey. After 30 min of stirring, vinylogous ester **9** (236.4 mg, 1.00 mmol, 1.00 equiv) was cannula-transferred to the slurry from a flame-dried 10 mL conical flask using several THF rinses (3 x 4 mL; total THF added = 25 mL, 0.04 M).

TLC analysis indicated that no starting material remained after 25 min. After an additional 5 min of stirring, the reaction was quenched with 10% w/w aq. HCl (5 mL) and lowered into a preheated oil bath (60 °C). After 20 h, additional 10% w/w aq. HCl (5 mL) was added. After 26 h, the yellow solution was removed from the bath, cooled to room temperature (23 °C), treated with sat. aq. $NaHCO_3$ solution (25 mL), and transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (150 mL) were rinsed once with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **1l** (206.1 mg, 0.84 mmol, 84% yield) as a yellow/orange oil; R_f = 0.70 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.00–6.95 (m, 2H), 6.17 (s, 1H), 5.69 (dddd, *J* = 16.7, 10.2, 8.1, 6.4 Hz, 1H), 5.06 (dddd, *J* = 10.2, 2.0, 1.0, 1.0 Hz, 1H), 5.01 (ddd, *J* = 16.9, 3.4, 1.5 Hz, 1H), 2.74–2.59 (m, 2H), 2.50 (dddd, *J* = 14.1, 6.4, 1.4, 1.4 Hz, 1H), 2.12 (dddd, *J* = 14.1, 8.1, 1.1, 1.1 Hz, 1H), 1.96–1.84 (m, 3H), 1.77–1.68 (m, 1H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 154.6, 143.8, 134.0, 133.7, 127.0, 126.7, 125.5, 118.5, 45.6, 45.1, 44.2, 38.8, 26.4, 17.7; IR (Neat Film NaCl) 3103, 3075, 2964, 2938, 2871, 1671, 1655, 1590, 1519, 1454, 1438, 1415, 1378, 1341, 1251, 1234, 1218, 1178, 1134, 1107, 1077, 1045, 996, 917, 849, 836, 761, 708 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{15}H_{19}OS$ $[M+H]^+$: 247.1151; found 247.1152; $[\alpha]_D^{25.0}$ –3.65 (*c* 1.31, $CHCl_3$, 88% ee).

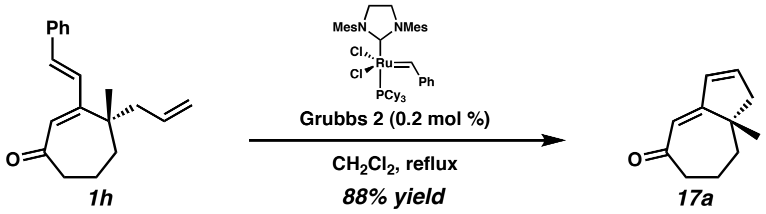


Cycloheptenone SI-20. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a rubber septum, and connected to a Schlenk manifold was flame-dried three times, backfilling with argon after each drying cycle. The hot flask was placed into a glove box antechamber, which was evacuated/backfilled with N_2 (4 cycles, 1 min evacuation per cycle) before the flask was brought into the glove box. The flask was loaded with anhydrous cerium chloride (591.6 mg, 2.40 mmol, 2.50 equiv), refitted with the septum, removed from the glove box, and reconnected to the argon-filled Schlenk manifold. A portion of THF (12 mL) was added, rinsing the cerium chloride to the bottom of the flask. As the resulting thick white slurry was stirred, a solution of but-3-enylmagnesium bromide (6.55 mL, 0.44 M in THF, 2.88 mmol, 3.00 equiv) was added and the mixture turned pale yellow. After 40 min of stirring, vinylogous ester **18** (226.9 mg, 0.96 mmol, 1.00 equiv) was cannula-transferred to the slurry from a 20 mL scintillation vial using several THF rinses (3 x 4 mL; total THF added = 24 mL, 0.04 M).

TLC analysis indicated that no starting material remained after 5 min. After an additional 10 min, the reaction was quenched with pH 6.5 Na_3PO_4 buffer (20 mL). A thick grey emulsion formed. The mixture was transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organic (125 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was transferred to a 20 mL scintillation vial and concentrated under reduced pressure. A stir bar, CH_3CN (2.0 mL), and 6 mM aq. HCl (2.0 mL) were added to the vial. The resulting cloudy solution was stirred vigorously for 5 min before being transferred to a separatory funnel where the aqueous phase was extracted four times with Et_2O. The combined organics (75 mL) were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 30.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **SI-20** (165.0 mg, 0.76 mmol, 79% yield) as a pale yellow oil; $R_f = 0.74$ (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.83–5.74 (m, 1H), 5.43–5.32 (m, 2H), 5.02 (dm, $J = 17.2$ Hz, 1H), 4.97 (dm, $J = 10.2$ Hz, 1H), 2.66–2.50 (m, 2H), 2.27–2.12 (m, 4H), 1.84–1.71 (m, 4H), 1.69 (dd, $J = 4.8, 0.7$ Hz, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 161.7, 137.8, 137.2, 129.3, 124.4, 115.2, 48.6, 44.1, 41.3, 34.8, 34.1, 26.0, 18.2, 18.0; IR (Neat Film NaCl) 3077, 2962, 2937, 2874, 2856, 1650, 1614, 1451, 1414, 1378, 1342, 1273, 1251, 1224, 1198, 1126, 1069, 974, 911 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{15}H_{23}O$ $[M+H]^+$: 219.1743; found 219.1741; $[\alpha]_D^{20.0}$ 123.43 (*c* 1.10, $CHCl_3$, 88% ee).

Procedures for the Preparation of Enone Derivatives

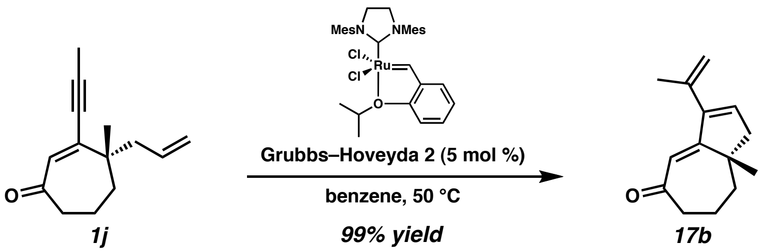
Ring Closing Metatheses to Generate Bi- and Tricyclic Structures 17



Enone 17a. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **1h** (452.8 mg, 1.70 mmol, 1.00 equiv) and dichloromethane (60 mL, 0.03 M) and the resulting solution was sparged with Ar. After 30 min of degassing, Grubbs 2nd generation catalyst (3.4 mg, 0.0040 mmol, 0.2 mol %) was added to the flask. The solution color turned pale red with addition of catalyst. The flask was lowered into a preheated oil bath (50 °C).

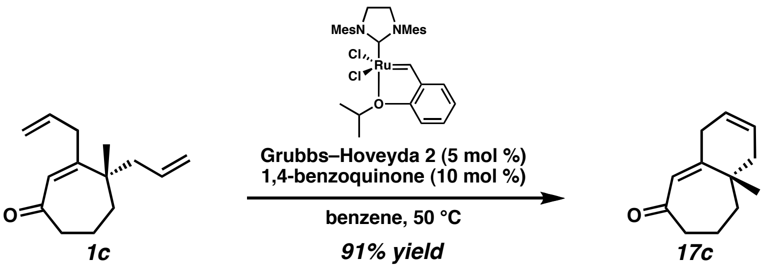
The flask was removed from oil bath after 1 h, cooled to room temperature (23 °C), and charged with DMSO (50 μL) and silica gel (70 mg). The resulting mixture was concentrated the reaction under reduced pressure and purified by flash chromatography (SiO_2, 2 x 17 cm, 15:1

hexanes:EtOAc) to afford cycloheptenone **17a** (242.9 mg, 1.50 mmol, 88% yield) as a yellow oil; R_f = 0.52 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35–6.32 (m, 1H), 6.14 (dddd, *J* = 5.6, 2.5, 1.7, 0.7 Hz, 1H), 5.87 (app s, 1H), 2.70 (dddt, *J* = 15.1, 6.4, 3.5, 0.9 Hz, 1H), 2.59–2.51 (m, 2H), 2.41 (ddd, *J* = 17.9, 2.9, 1.6 Hz, 1H), 2.11–2.02 (m, 1H), 2.00–1.82 (m, 3H), 1.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 169.2, 142.7, 134.4, 121.7, 51.6, 46.7, 45.1, 37.9, 29.7, 21.2; IR (Neat Film NaCl) 3056, 2930, 2867, 2841, 1651, 1615, 1580, 1449, 1372, 1352, 1293, 1261, 1211, 1190, 1159, 1080, 968, 951, 862, 844, 801, 811, 723 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{11}H_{15}O$ $[M+H]^+$: 163.1117; found 163.1120; $[\alpha]_D^{26.0}$ –48.88 (*c* 1.83, $CHCl_3$, 88% ee).



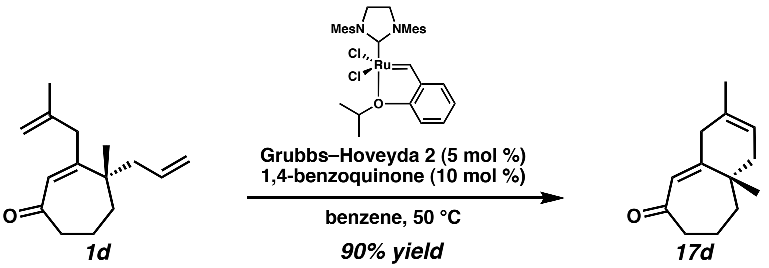
Enone 17b. A two neck 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with rubber septa and a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **1j** (50.0 mg, 0.25 mmol, 1.00 equiv) and backfilled with argon. Benzene (1 h argon sparge before use, 39 mL) was added to the flask, followed by Grubbs–Hoveyda 2nd generation catalyst (7.8 mg, 0.012 mmol, 5 mol %). The solution color turned pale green with addition of catalyst. The flask was rinsed with more benzene (10 mL; total benzene added = 49 mL, 0.005 M) and lowered into a preheated oil bath (50 °C).

TLC analysis indicated no starting material remained after 3 h. Consequently, the reaction was removed from oil bath, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (1 mL). The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 2 x 28.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17b** (50 mg, 0.25 mmol, 99% yield) as a yellow oil; R_f = 0.64 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 (t, *J* = 2.8 Hz, 1H), 6.02 (s, 1H), 5.13–5.11 (m, 1H), 4.97 (s, 1H), 2.76 (ddd, *J* = 14.7, 6.7, 4.7 Hz, 1H), 2.56 (ddd, *J* = 14.7, 9.8, 5.1 Hz, 1H), 2.48 (dd, *J* = 17.8, 2.0 Hz, 1H), 2.33 (dd, *J* = 17.8, 3.1 Hz, 1H), 2.09–1.99 (m, 1H), 1.94 (dd, *J* = 9.9, 4.0 Hz, 2H), 1.91–1.89 (m, 3H), 1.89–1.83 (m, 1H), 1.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 167.2, 146.8, 138.4, 137.5, 122.0, 115.9, 49.5, 48.3, 45.0, 38.2, 28.4, 23.1, 20.9; IR (Neat Film NaCl) 3084, 3052, 2918, 2868, 2845, 1652, 1607, 1450, 1374, 1352, 1311, 1290, 1259, 1210, 1190, 1164, 1117, 1082, 1004, 982, 944, 898, 881, 848, 811, 771, 746 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{14}H_{19}O$ $[M+H]^+$: 203.1430; found 203.11428; $[\alpha]_D^{25.0}$ –55.41 (*c* 1.61, $CHCl_3$, 88% ee).



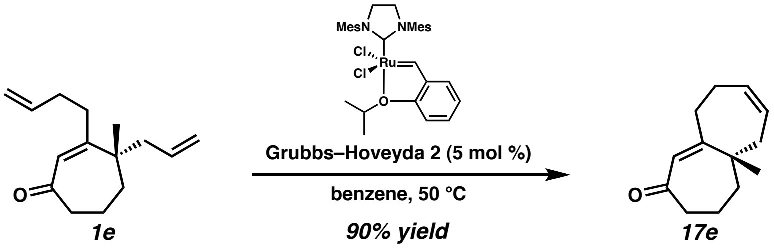
Enone 17c. A 250 mL round-bottom flask equipped with a magnetic stir bar, fitted with a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, cycloheptenone **1c** (174.6 mg, 0.85 mmol, 1.00 equiv) was cannula-transferred from a 20 mL scintillation vial to the 250 mL flask using several benzene rinses (1.5 h argon sparge before use, 5 x 4 mL). Additional benzene (141 mL) was added to the flask followed by 1,4-benzoquinone (9.2 mg, 0.085 mmol, 10 mol %) and Grubbs–Hoveyda 2nd generation catalyst (26.8 mg, 0.043 mmol, 5 mol %). The solution color turned pale green with addition of catalyst. The flask was rinsed with more benzene (10 mL; total benzene added = 171 mL, 0.005 M) and lowered into a preheated oil bath (50 °C).

The reaction was removed from oil bath after 2.5 h, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (2 mL). The reaction color turned dark green with the ethyl vinyl ether addition. The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 3 x 25 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17c** (47.7 mg, 0.27 mmol, 91% yield) as a yellow oil; R_f = 0.58 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, benzene-d_6) δ 5.95 (d, *J* = 2.1 Hz, 1H), 5.46–5.41 (m, 1H), 5.34 (ddddd, *J* = 9.9, 4.4, 2.8, 2.8, 1.0 Hz, 1H), 2.72 (dm, *J* = 20.2 Hz, 1H), 2.44–2.33 (m, 2H), 2.27 (dm, *J* = 20.2 Hz, 1H), 1.97 (dm, *J* = 17.6 Hz, 1H), 1.44 (ddd, *J* = 17.5, 5.2, 0.9 Hz, 1H), 1.33–1.19 (m, 4H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, benzene-d_6) δ 202.2, 156.0, 127.2, 125.1, 125.0, 44.3, 41.8, 41.4, 41.2, 36.3, 26.1, 17.6; IR (Neat Film NaCl) 3274, 3029, 2933, 2833, 1720, 1650, 1619, 1452, 1420, 1381, 1345, 1306, 1264, 1239, 1219, 1185, 1125, 1105, 1082, 1004, 976, 952, 938, 924, 892, 884, 871, 836, 775, 733 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{12}H_{17}O$ $[M+H]^+$: 177.1274; found 177.1277; $[\alpha]_D^{25.0}$ –49.94 (*c* 0.86, $CHCl_3$, 88% ee).



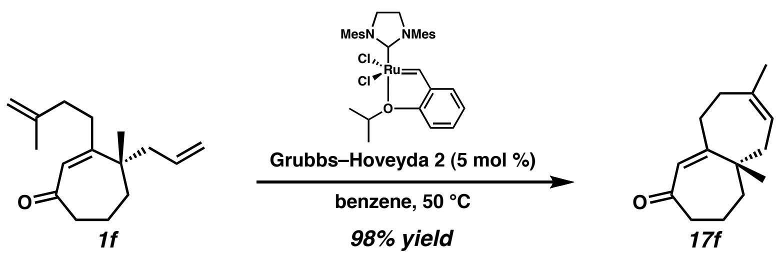
Enone 17d. A three neck 100 mL round-bottom flask equipped with a magnetic stir bar and fitted with rubber septa and a water condenser was connected to a Schlenk manifold (through the condenser). The flask was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **1d** (50.0 mg, 0.23 mmol, 1.00 equiv), benzene (1 h argon sparge before use, 46 mL, 0.005 M), 1,4-benzoquinone (2.5 mg, 0.023 mmol, 10 mol %), and Grubbs–Hoveyda 2nd generation catalyst (7.2 mg, 0.011 mmol, 5 mol %). The solution color turned pale green with addition of catalyst. The flask was lowered into a preheated oil bath (50 °C).

The reaction was removed from oil bath after 1 h, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (1.5 mL). The reaction color turned dark green with the ethyl vinyl ether addition. The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 2 x 28 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17d** (39.0 mg, 0.21 mmol, 90% yield) as a yellow oil; R_f = 0.56 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (d, *J* = 2.0 Hz, 1H), 5.38–5.34 (m, 1H), 3.06 (dm, *J* = 19.7 Hz, 1H), 2.63–2.49 (m, 3H), 2.28 (dm, *J* = 17.2 Hz, 1H), 1.85 (dd, *J* = 17.2, 5.3 Hz, 1H), 1.81–1.75 (m, 2H), 1.74–1.65 (m, 2H), 1.68 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 159.4, 131.8, 126.3, 119.5, 44.3, 41.6, 41.5, 41.3, 41.3, 26.6, 22.5, 17.6; IR (Neat Film NaCl) 3273, 3017, 2963, 2930, 1720, 1656, 1651, 1645, 1619, 1616, 1450, 1418, 1378, 1363, 1345, 1268, 1239, 1220, 1191, 1151, 1134, 1104, 1072, 1038, 989, 972, 962, 944, 931, 897, 877, 854, 827, 784, 732 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{13}H_{19}O$ $[M+H]^+$: 191.1430; found 191.1436; $[\alpha]_D^{25.0}$ 9.09 (*c* 0.86, $CHCl_3$, 88% ee).



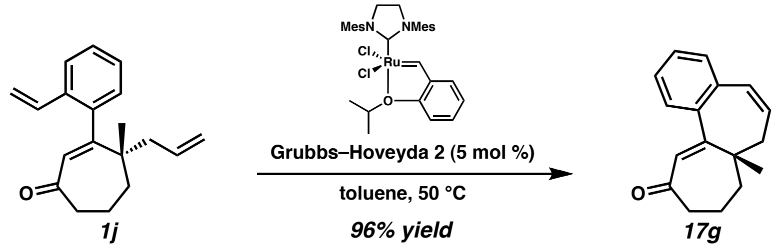
Enone 17e. A two neck 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with rubber septa and a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **1e** (50.0 mg, 0.23 mmol, 1.00 equiv), Grubbs–Hoveyda 2nd generation catalyst (7.2 mg, 0.011 mmol, 5 mol %), benzene (1 h argon sparge before use, 46 mL, 0.005 M). The solution color turned pale green with addition of catalyst. The flask was lowered into a preheated oil bath (50 °C).

TLC analysis indicated no starting material remained after 15 min. Consequently, the reaction was removed from the oil bath, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (1 mL). The reaction color turned amber with the ethyl vinyl ether addition. The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 2 x 27.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17e** (39.4 mg, 0.21 mmol, 90% yield) as a yellow oil; R_f = 0.58 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 1H), 5.65–5.58 (m, 1H), 5.54–5.49 (m, 1H), 2.81–2.74 (m, 1H), 2.66–2.59 (m, 2H), 2.56–2.46 (m, 2H), 2.24–2.13 (m, 2H), 2.07 (ddd, *J* = 14.1, 11.1, 3.1 Hz, 1H), 1.93 (ddddd, *J* = 14.1, 11.0, 9.3, 4.8, 2.9 Hz, 1H), 1.85–1.79 (m, 1H), 1.76 (dd, *J* = 14.9, 7.9 Hz, 1H), 1.66 (ddd, *J* = 14.0, 6.9, 2.8 Hz, 1H), 1.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 165.3, 129.9, 129.7, 126.2, 47.8, 43.9, 40.7, 40.3, 34.5, 32.2, 27.8, 19.6; IR (Neat Film NaCl) 3287, 3017, 2930, 2833, 1652, 1616, 1481, 1450, 1380, 1352, 1342, 1291, 1279, 1262, 1243, 1224, 1204, 1184, 1162, 1084, 1075, 1047, 1021, 984, 963, 921, 896, 877, 846, 834, 788, 755 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{13}H_{19}O$ $[M+H]^+$: 191.1430; found 191.1430; $[\alpha]_D^{25.0}$ –92.01 (*c* 0.82, $CHCl_3$, 88% ee).



Enone 17f. A two neck 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with rubber septa and a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **1f** (50.0 mg, 0.22 mmol, 1.00 equiv) and backfilled with argon. Benzene (1 h argon sparge before use, 33 mL) was added to the flask, followed by Grubbs–Hoveyda 2nd generation catalyst (6.7 mg, 0.011 mmol, 5 mol %). The solution color turned pale green with addition of catalyst. The flask was rinsed with more benzene (10 mL; total benzene added = 43 mL, 0.005 M) and lowered into a preheated oil bath (50 °C).

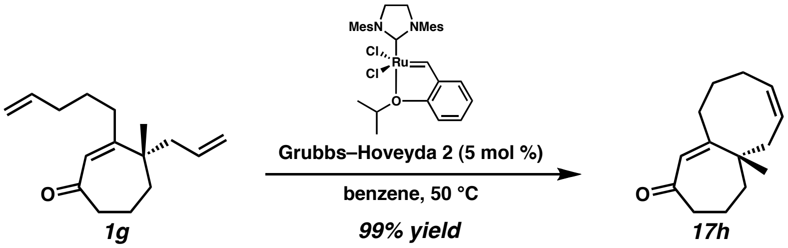
TLC analysis indicated no starting material remained after 30 min. After an additional 10 min of stirring, the reaction was removed from the oil bath, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (1 mL). The reaction color turned dark brown with the ethyl vinyl ether addition. The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 2 x 28.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17f** (43.2 mg, 0.21 mmol, 98% yield) as a clear colorless oil; $R_f = 0.63$ (30% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 1H), 5.41–5.34 (m, 1H), 2.79 (td, J = 12.3, 5.3 Hz, 1H), 2.66–2.55 (m, 2H), 2.54–2.42 (m, 2H), 2.19 (ddd, J = 12.5, 6.0, 3.3 Hz, 1H), 2.14–2.02 (m, 2H), 1.98–1.88 (m, 1H), 1.85–1.76 (m, 1H), 1.71–1.63 (m, 2H), 1.62 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.9, 165.8, 136.9, 129.5, 120.7, 47.7, 43.9, 40.6, 40.2, 36.9, 34.3, 27.5, 25.3, 19.7; IR (Neat Film NaCl) 3300, 3014, 2928, 2828, 1657, 1617, 1480, 1450, 1379, 1353, 1342, 1292, 1259, 1216, 1171, 1131, 1106, 1082, 1050, 1009, 982, 962, 916, 897, 874, 833, 814, 795, 765 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{14}H_{21}O_2$ $[M+H]^+$: 205.1587; found 205.1582; $[\alpha]_D^{25.0}$ –73.66 (c 0.95, $CHCl_3$, 88% ee).



Enone 17g. A three neck 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with rubber septa and a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, cycloheptenone **1j** (65.8 mg, 0.25 mmol, 1.00 equiv) was cannula-transferred from a 20 mL scintillation vial to the 100 mL flask using several toluene rinses (1.5 h argon sparge before use, 5 x 4 mL). Additional toluene (20 mL) was added to the flask followed by Grubbs–Hoveyda 2nd generation catalyst (7.7 mg, 0.012 mmol, 5 mol %). The solution color turned pale green with

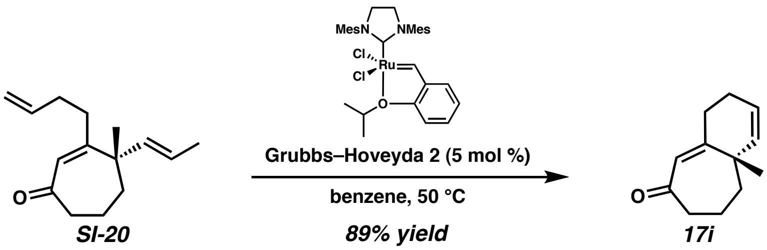
addition of catalyst. The flask was rinsed with more toluene (9 mL; total toluene added = 49 mL, 0.005 M) and lowered into a preheated oil bath (50 °C).

The reaction was removed from the oil bath after 6.5 h, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (0.5 mL). The reaction color turned dark brown with the ethyl vinyl ether addition. The reaction was filtered through a short silica gel plug rinsing with EtOAc and concentrated under reduced pressure. The crude oil was purified by flash chromatography (SiO_2, 2 x 24.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17g** (56.7 mg, 0.23 mmol, 96% yield) as a yellow oil; R_f = 0.64 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 1H), 7.22–7.19 (m, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.53 (dm, *J* = 11.1 Hz, 1H), 6.03 (dt, *J* = 11.2, 6.0 Hz, 1H), 5.82 (s, 1H), 2.71–2.60 (m, 2H), 2.30 (ddd, *J* = 15.6, 5.8, 0.8 Hz, 1H), 2.21 (ddd, *J* = 15.6, 6.3, 1.8 Hz, 1H), 2.15 (ddd, *J* = 13.9, 7.5, 4.5 Hz, 1H), 2.01–1.85 (m, 3H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 162.5, 142.5, 135.5, 132.0, 130.8, 130.0, 128.8, 128.8, 127.9, 127.3, 50.6, 44.2, 42.4, 40.1, 27.8, 19.3; IR (Neat Film NaCl) 3057, 3017, 2933, 2870, 1718, 1665, 1601, 1481, 1445, 1417, 1383, 1354, 1340, 1286, 1258, 1228, 1180, 1125, 996, 984, 936, 890, 828, 780, 757 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{17}H_{19}O$ $[M+H]^+$: 239.1430; found 239.1432; $[\alpha]_D^{20.0}$ –86.75 (*c* 0.70, $CHCl_3$, 88% ee).



Enone 17h. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **1g** (50.0 mg, 0.22 mmol, 1.00 equiv) and backfilled with argon twice. Benzene (1 h argon sparge before use, 43 mL, 0.005 M) was added to the flask, followed by Grubbs–Hoveyda 2nd generation catalyst (6.7 mg, 0.011 mmol, 5 mol %). The solution color turned pale green with addition of catalyst. The flask was lowered into a preheated oil bath (50 °C).

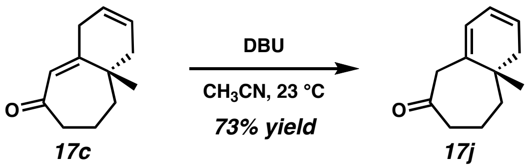
The reaction was removed from the oil bath after 30 min, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (1 mL). The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified twice by flash chromatography (SiO_2, both columns 2 x 28 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17h** (43.5 mg, 0.21 mmol, 99% yield) as a yellow oil; R_f = 0.56 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77–5.70 (m, 1H), 5.65 (tdt, *J* = 10.4, 6.4, 1.3 Hz, 1H), 2.68–2.55 (m, 2H), 2.54–2.44 (m, 1H), 2.30–2.24 (m, 2H), 2.24–2.15 (m, 1H), 2.13–2.04 (m, 1H), 1.94–1.69 (m, 7H), 1.52–1.41 (m, 1H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.2, 165.6, 132.2, 131.9, 128.5, 49.0, 44.2, 39.8, 39.5, 35.5, 31.1, 27.0, 26.5, 17.8; IR (Neat Film NaCl) 3018, 2928, 2859, 1645, 1608, 1468, 1448, 1411, 1380, 1343, 1327, 1279, 1253, 1214, 1178, 1131, 1102, 1088, 1051, 1015, 987, 965, 937, 920, 899, 880, 845, 796, 777, 747 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{14}H_{21}O$ $[M+H]^+$: 205.1587; found 205.1587; $[\alpha]_D^{25.0}$ –141.99 (*c* 1.01, $CHCl_3$, 88% ee).



Enone 17i. A 100 mL round-bottom flask equipped with a magnetic stir bar, fitted with a water condenser, and connected to a Schlenk manifold (through the condenser) was flame-dried three times, backfilling with argon after each drying cycle. Once cool, the flask was loaded with neat cycloheptenone **SI-20** (50.0 mg, 0.23 mmol, 1.00 equiv) and backfilled with argon twice. Benzene (1 h argon sparge before use, 44 mL) was added to the flask, followed by Grubbs–Hoveyda 2nd generation catalyst (7.2 mg, 0.011 mmol, 5 mol %). The flask was rinsed with more benzene (2 mL; total benzene added = 46 mL, 0.005 M) and lowered into a preheated oil bath (50 °C). The solution color turned pale green with addition of catalyst and amber over time.

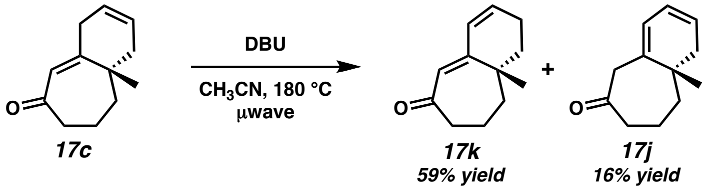
The reaction was removed from the oil bath after 50 min, cooled to room temperature (23 °C), and quenched with ethyl vinyl ether (0.5 mL). The reaction was filtered through a short silica gel plug rinsing with Et_2O and concentrated under reduced pressure. The crude oil was purified twice by flash chromatography (SiO_2, both columns 2 x 27.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford cycloheptenone **17i** (35.8 mg, 0.23 mmol, 89% yield, 70% yield from vinylogous ester **18**) as a pale yellow oil; R_f = 0.62 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (s, 1H), 5.72–5.67 (m, 1H), 5.28 (dd, *J* = 9.7, 2.4 Hz, 1H), 2.71–2.64 (m, 1H), 2.62–2.54 (m, 1H), 2.53–2.46 (m, 1H), 2.31–2.11 (m, 3H), 1.92–1.74 (m, 3H), 1.70 (ddd, *J* = 14.0, 6.6, 2.4 Hz, 1H), 1.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.5, 161.3, 137.8, 126.9, 125.3, 44.6, 43.6, 40.6, 33.8, 28.1, 27.7, 18.6; IR (Neat Film NaCl) 3019, 2934, 2866, 2845, 1665, 1653, 1621, 1450, 1414, 1350, 1309, 1281, 1258, 1217, 1181, 1171, 1132, 1087, 1074, 1024, 1013, 973, 938, 902, 881, 865, 783, 767, 716 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{12}H_{17}O$ $[M+H]^+$: 177.1274; found 177.1274; $[\alpha]_D^{20.0}$ –188.35 (*c* 0.72, $CHCl_3$, 88% ee).

Preparation of Other Cycloheptenone Derivatives



Diene 17j. A 20 mL scintillation vial containing enone **17c** (31.5 mg, 0.18 mmol, 1.00 equiv) was equipped with a stir bar and sealed with a screw cap containing a Teflon septum. The vial was connected to a Schlenk manifold and backfilled with argon three times. Acetonitrile (1.8 mL, 0.1 M) was added to the vial followed by DBU (30 μL, 0.20 mmol, 1.12 equiv). The solution was stirred at room temperature (23 °C) until no starting material remained by TLC analysis (4 h). The reaction was passed through a short silica gel plug, rinsed with water, dried over $MgSO_4$, filtered through another short silica gel plug, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (SiO_2, 1 x 28.5 cm, 100% hexanes→2%→5% EtOAc in hexanes) to afford diene **17j** (23.1 mg, 0.13 mmol, 73%

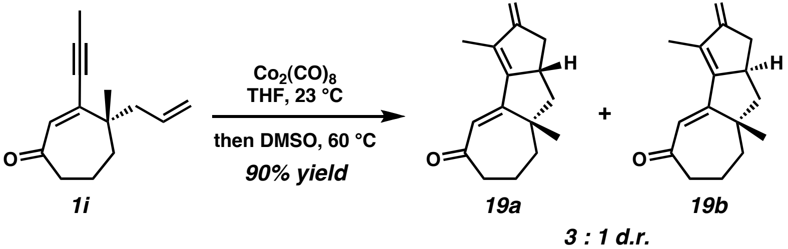
yield) as a pale yellow oil; R_f = 0.63 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 9.0, 5.3, 1.7 Hz, 1H), 5.79–5.73 (m, 2H), 3.27 (d, *J* = 16.3 Hz, 1H), 2.93 (d, *J* = 16.3 Hz, 1H), 2.73 (ddd, *J* = 12.4, 10.0, 4.7 Hz, 1H), 2.33–2.23 (m, 2H), 2.08–2.00 (m, 1H), 1.89–1.67 (m, 3H), 1.49–1.41 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 138.6, 125.4, 123.9, 123.6, 49.5, 42.7, 37.6, 37.5, 36.5, 24.1, 20.9; IR (Neat Film NaCl) 3039, 2929, 2865, 2817, 1708, 1645, 1587, 1453, 1424, 1403, 1371, 1356, 1319, 1286, 1263, 1235, 1211, 1143, 1105, 1082, 1039, 987, 969, 940, 925, 851, 817, 761, 704 cm^{-1}; HRMS (GC-EI+) calc'd for $C_{12}H_{16}O$ $[M+\cdot]^+$: 176.1201; found 176.1219; $[\alpha]_D^{25.0}$ –205.54 (*c* 0.71, $CHCl_3$, 88% ee).



Diene 17k and Diene 17j. A 2.0–5.0 mL μwave vial fitted with a stir bar and sealed with a screw cap containing a Teflon septum was flame-dried three times, backfilling with argon after each drying cycle. Once cool, diene **17c** (66.7 mg, 0.38 mmol, 1.00 equiv) was cannula-transferred to the vial with several acetonitrile rinses (4 x 1 mL, 0.09 M) and the flask was charged with DBU (66 μL, 0.44 mmol, 1.17 equiv). The pale yellow solution was subjected to microwave irradiation in a Biotage Initiator microwave reactor (temperature: 180 °C, sensitivity: normal). After 5 h of irradiation, the crimp cap was removed and the reaction was filtered through a silica gel plug. The resulting solution was concentrated under reduced pressure and purified by flash chromatography (SiO_2, 2 x 29 cm, 100% hexanes→10%→30%→50%→80% CH_2Cl_2 in hexanes) to yield diene **17k** (39.5 mg, 0.22 mmol, 59% yield) as a yellow oil and diene **17j** (10.4 mg, 0.059 mmol, 16% yield) as a pale yellow oil.

Diene **17j** is identical to the characterization data described above.

Diene **17k**: R_f = 0.56 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13–6.07 (m, 1H), 6.02 (dd, *J* = 9.9, 2.8 Hz, 1H), 5.76 (s, 1H), 2.75 (dddt, *J* = 15.6, 6.6, 5.0, 0.9 Hz, 1H), 2.52 (ddd, *J* = 15.4, 9.5, 5.6 Hz, 1H), 2.38–2.27 (m, 1H), 2.19 (dtt, *J* = 19.3, 5.6, 1.3 Hz, 1H), 2.05–1.93 (m, 1H), 1.87–1.77 (m, 2H), 1.74–1.62 (m, 2H), 1.44 (ddt, *J* = 13.2, 5.4, 1.5 Hz, 1H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.1, 156.2, 135.1, 131.4, 129.1, 44.6, 42.2, 38.9, 37.6, 23.1, 22.9, 18.8; IR (Neat Film NaCl) 3026, 2967, 2922, 2868, 2849, 1650, 1621, 1583, 1449, 1428, 1383, 1353, 1338, 1284, 1244, 1225, 1207, 1173, 1163, 1130, 1114, 1090, 1077, 1023, 978, 954, 935, 911, 881, 866, 840, 777, 727 cm^{-1}; HRMS (MM: ESI–APCI+) calc'd for $C_{12}H_{17}O$ $[M+H]^+$: 177.1274; found 177.1278; $[a]_D^{25.0}$ –298.04 (*c* 1.24, $CHCl_3$, 88% ee).



Enones 19a and 19b. A 20 mL scintillation vial containing cycloheptenone **1i** (185.6 mg, 0.92 mmol, 1.00 equiv) was equipped with a stir bar and sealed with a screw cap containing a Teflon septum. The vial was connected to a Schlenk manifold and backfilled with argon three times.

The vial was charged with THF (5.0 mL, 0.2 M) and dicobalt octacarbonyl (388.5 mg, 1.14 mmol, 1.24 equiv), generating a dark brown solution. After 12 h of stirring at room temperature (23 °C), DMSO (380 μL, 5.35 mmol, 5.83 equiv) was added and the vial was lowered into a preheated oil bath (60 °C). Reaction turned dark red over time. The vial was removed from the oil bath after 14 h and cooled to room temperature. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography using a Teledyne Isco CombiFlash R_f system (SiO_2, 25 g loading cartridge, 40 g column, multi-step gradient, hold 0% [5 min]→ramp to 5% [5 min]→hold 5% [50 min]→ramp to 10% [5 min]→hold 10% [15 min]→ramp to 15% [1 min]→hold 15% [7 min]→ramp to 20% [1 min]→hold 20% EtOAc in hexanes [27 min]) to afford a 3:1 diastereomeric mixture of cycloheptenones **19a**:**19b** (190.2 mg, 0.83 mmol, 90% yield). Analytically pure samples of **19a** and **19b** could be obtained using the above column conditions.

Major diasteriomer (19a): yellow oil that solidified upon cooling; R_f = 0.32 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.38 (s, 1H), 3.21–3.12 (m, 1H), 2.81–2.75 (m, 1H), 2.75 (dd, *J* = 17.8, 6.3 Hz, 1H), 2.62 (ddd, *J* = 14.0, 11.4, 4.6 Hz, 1H), 2.19–2.09 (m, 1H), 2.11 (dd, *J* = 17.8, 3.7 Hz, 1H), 2.01 (dd, *J* = 11.6, 6.9 Hz, 1H), 1.99–1.90 (m, 2H), 1.89 (d, *J* = 2.6 Hz, 3H), 1.88–1.81 (m, 1H), 1.32 (s, 3H), 1.28 (t, *J* = 11.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 204.8, 172.4, 155.0, 135.6, 128.8, 50.9, 47.2, 45.6, 42.3, 40.5, 39.5, 26.8, 20.9, 9.0; For NOESY correlation data, see **Figure SI-23B**; IR (Neat Film NaCl) 2945, 2917, 2867, 1701, 1662, 1446, 1375, 1332, 1304, 1258, 1219, 1196, 1148, 1099, 1054, 978, 945, 895, 869, 852, 830, 802, 706 cm^{-1}; HRMS (GC-EI+) calc'd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380; found 231.1381; $[\alpha]_D^{20.0}$ 150.77 (*c* 1.01, $CHCl_3$, 88% ee).

Minor diasteriomer (19b): orange oil that solidified upon cooling; R_f = 0.25 (30% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (s, 1H), 3.09–2.98 (m, 1H), 2.70 (dd, *J* = 18.1, 6.4 Hz, 1H), 2.71–2.64 (m, 1H), 2.63–2.56 (m, 1H), 2.16 (dd, *J* = 12.5, 8.5 Hz, 1H), 2.11 (dd, *J* = 18.1, 3.3 Hz, 1H), 2.12–1.96 (m, 2H), 1.95–1.87 (m, 2H), 1.87 (d, *J* = 2.5 Hz, 3H), 1.28 (dd, *J* = 12.4, 11.6 Hz, 1H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.7, 206.4, 173.0, 154.6, 133.7, 127.4, 48.9, 48.3, 42.4, 42.3, 41.3, 37.5, 31.9, 22.2, 8.5; For NOESY correlation data, see **Figure SI-24B**; IR (Neat Film NaCl) 2928, 2867, 1703, 1668, 1453, 1410, 1377, 1305, 1285, 1236, 1208, 1157, 1094, 1054, 996, 949, 891, 874, 859, 791, 720 cm^{-1}; HRMS (GC-EI+) calc'd for $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1380; found 231.1372; $[\alpha]_D^{20.0}$ –407.06 (*c* 1.65, $CHCl_3$, 88% ee).

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[i] Pangborn, A. M.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[ii] Hong, A. Y.; Krout, M. R.; Jensen, T.; Bennett, N. B.; Harned, A. M.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 2756–2760.

[iii] Love, B. E.; Jones, E. G. *J. Org. Chem.* **1999**, *64*, 3755–3756.

[iv] DIBAL-H is used to activate the magnesium. See: Tilstam, U.; Weinmann, H. *Org. Proc. Res. Dev.* **2002**, *6*, 906–910.

[v] Produced from the corresponding alcohol. See: Berkowitz, W. F.; Wu, Y. *J. Org. Chem.* **1997**, *62*, 1536–1539.

[vi] Sauers, R. R.; Hagedorn, A. A., III; Van Arnum, S. D.; Gomez, R. P.; Moquin, R. V. *J. Org. Chem.* **1987**, *52*, 5501–5505.

[vii] Furan was distilled over KOH and hydroquinone prior to use.

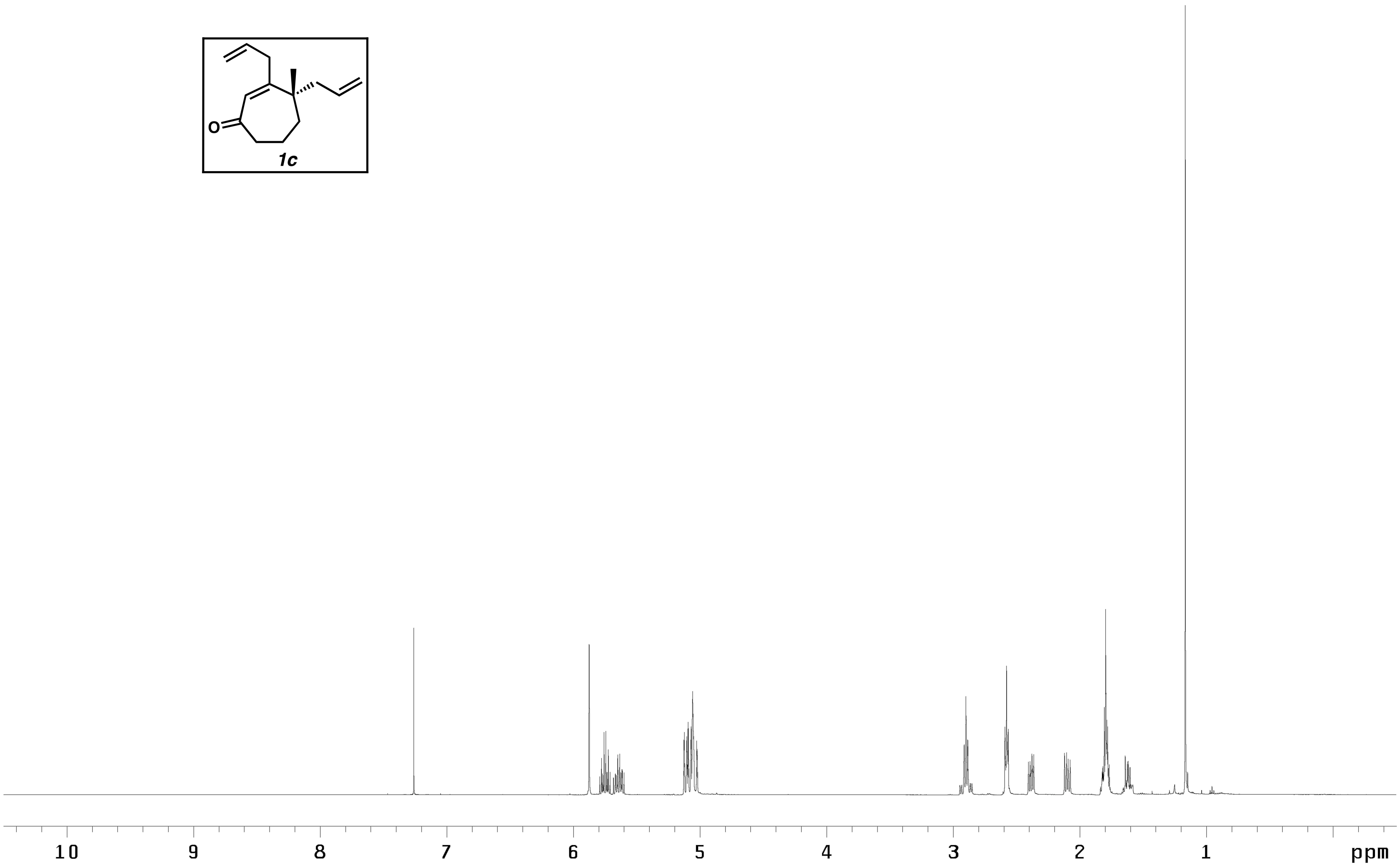


Figure SI-1A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **1c**.

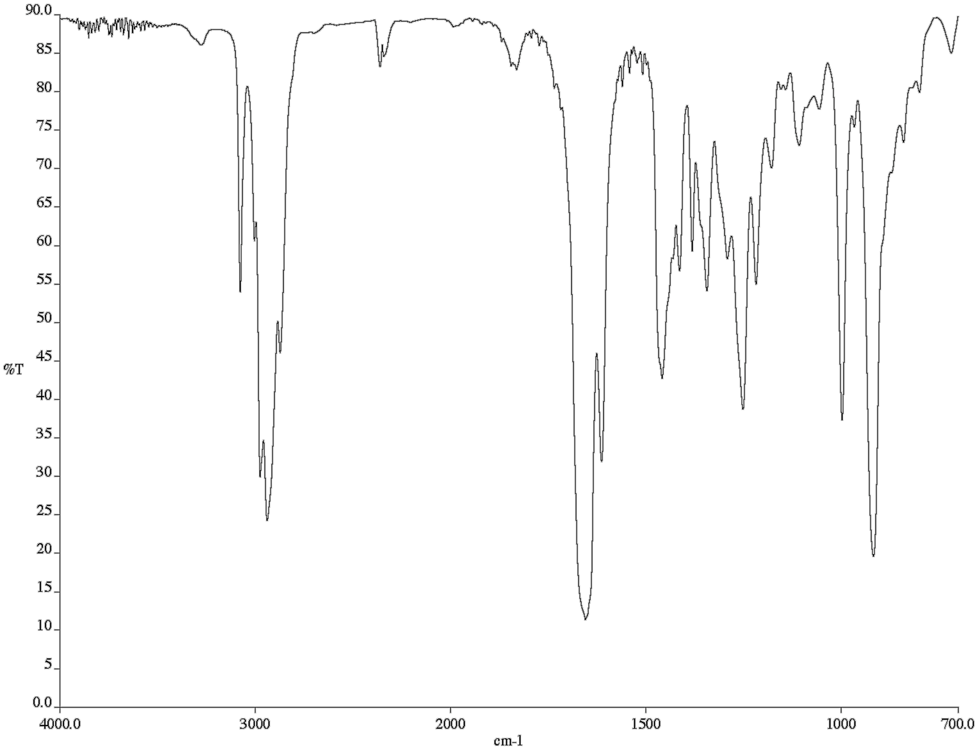


Figure SI-1B. Infrared spectrum (thin film/NaCl) of compound **1c**.

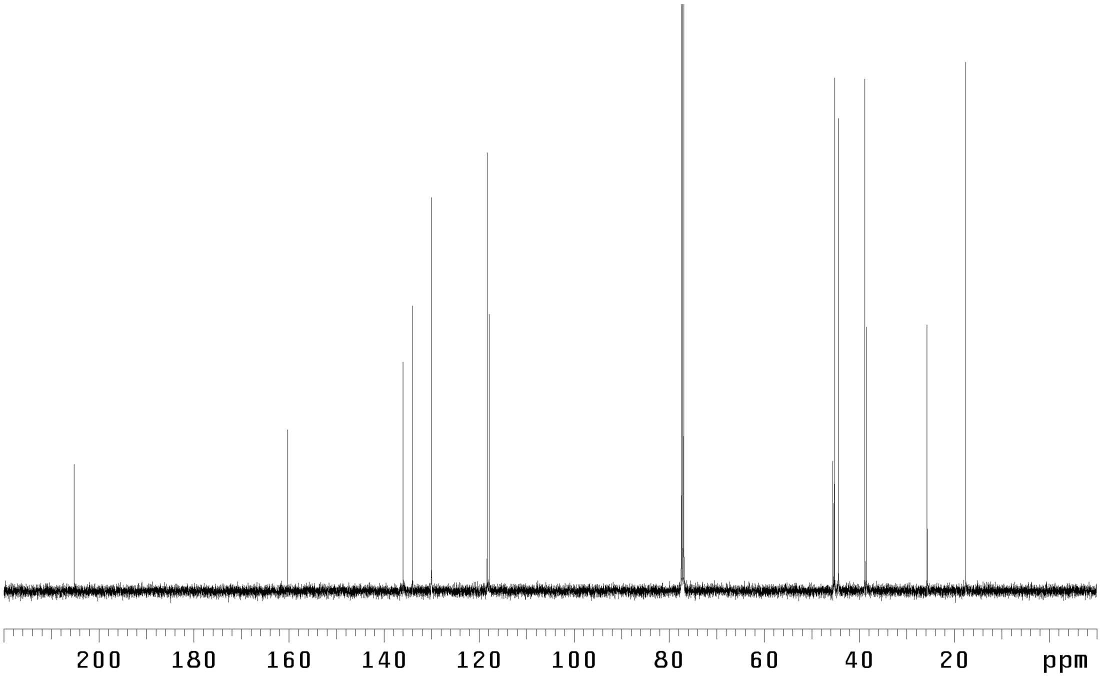


Figure SI-1C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **1c**.

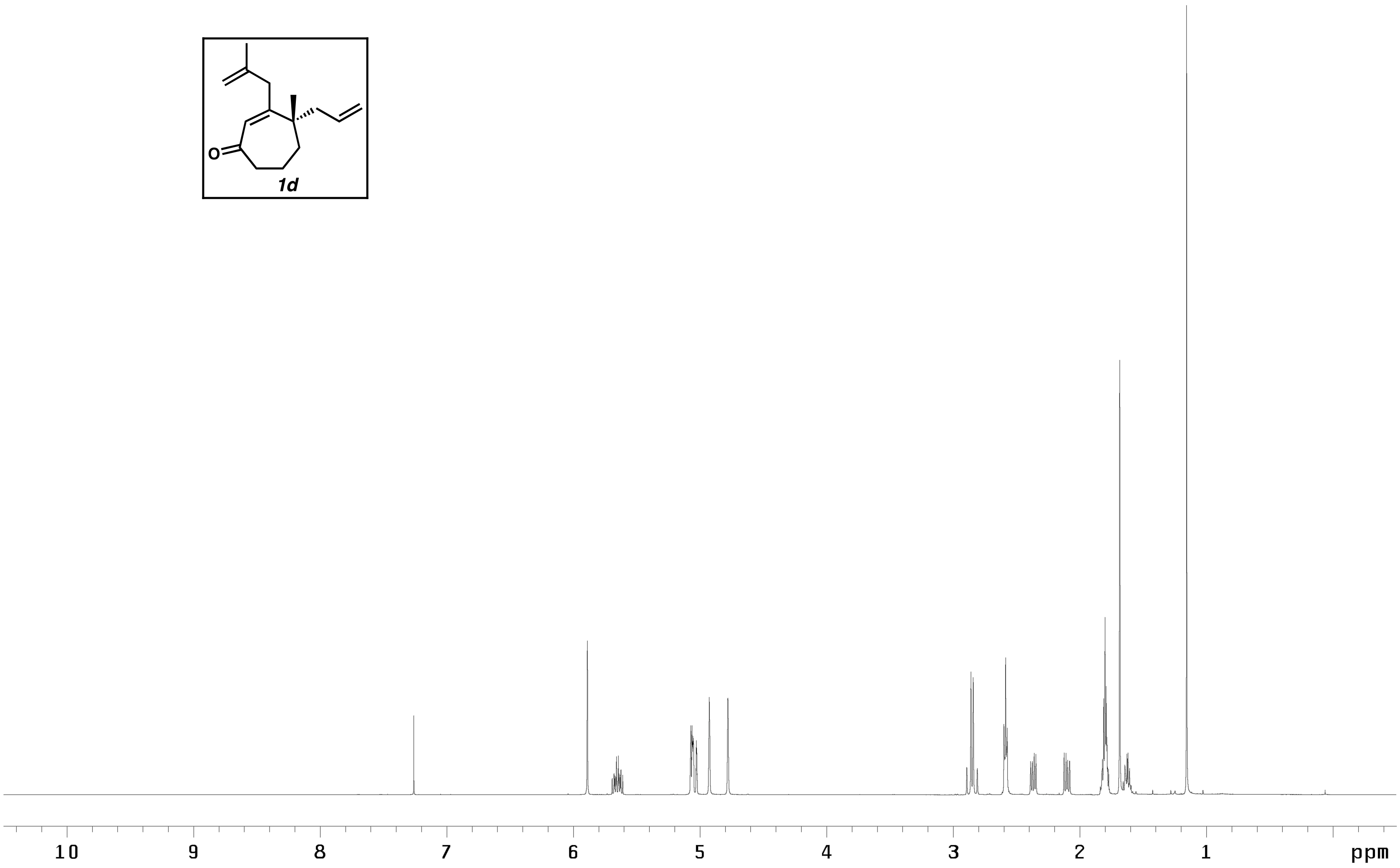


Figure SI-2A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1d**.

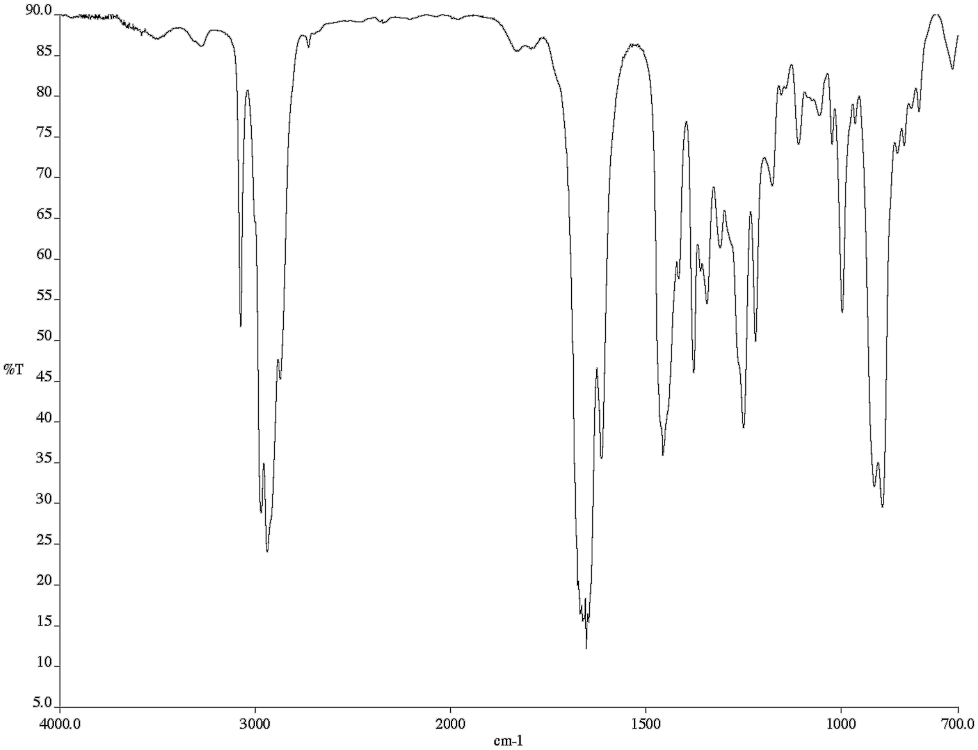


Figure SI-2B. Infrared spectrum (thin film/NaCl) of compound **1d**.

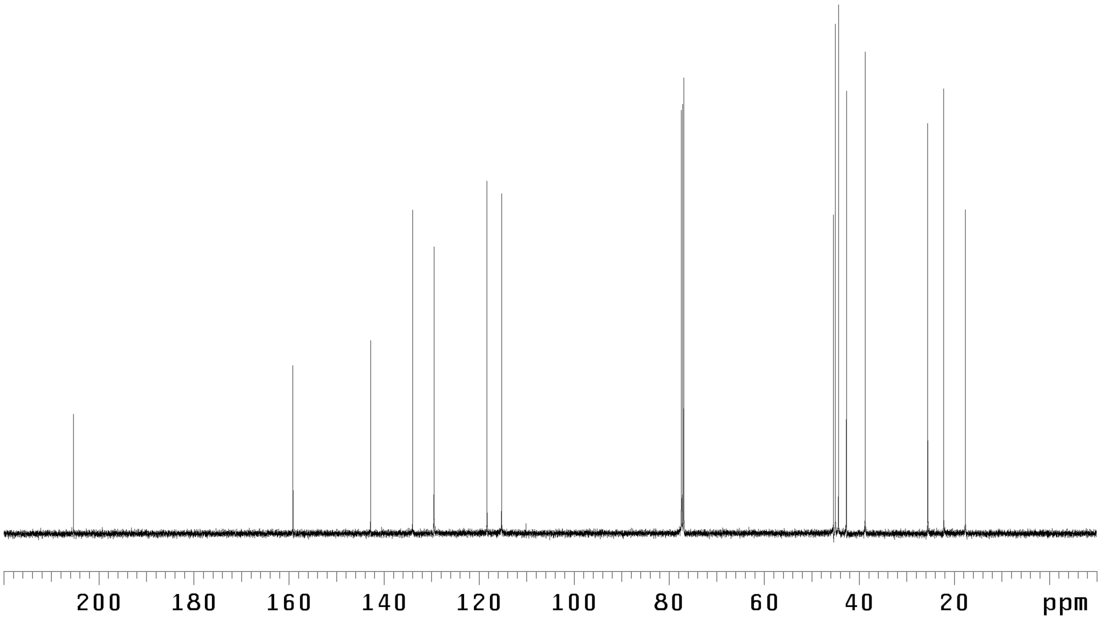


Figure SI-2C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **1d**.

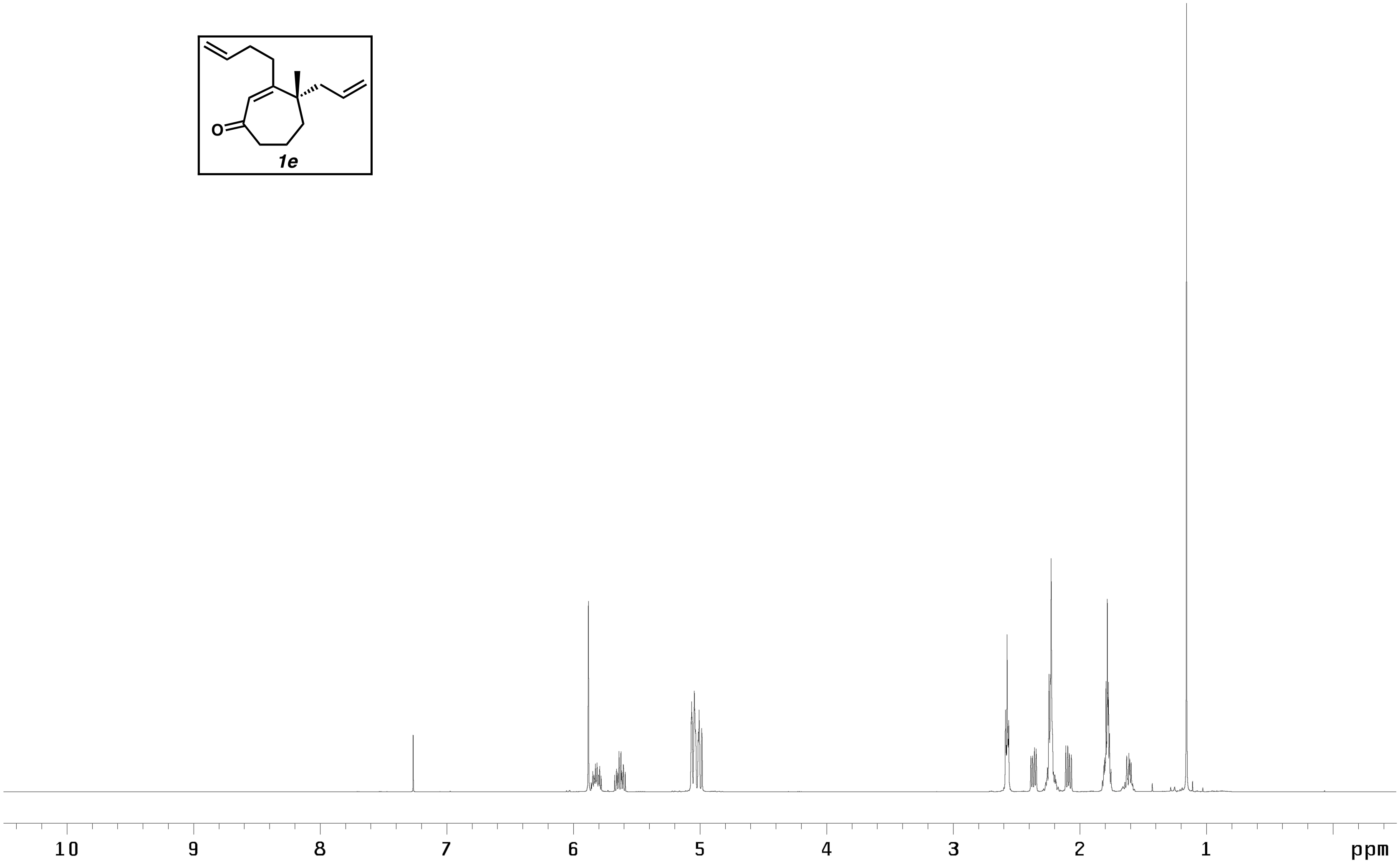


Figure SI-3A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **1e**.

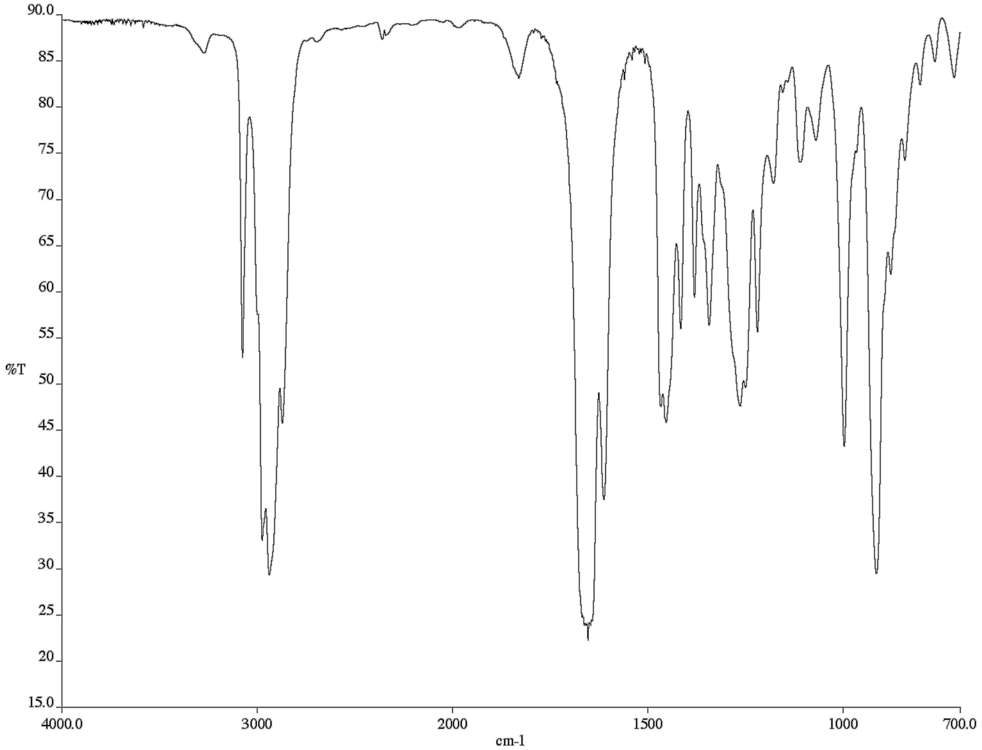


Figure SI-3B. Infrared spectrum (thin film/NaCl) of compound **1e**.

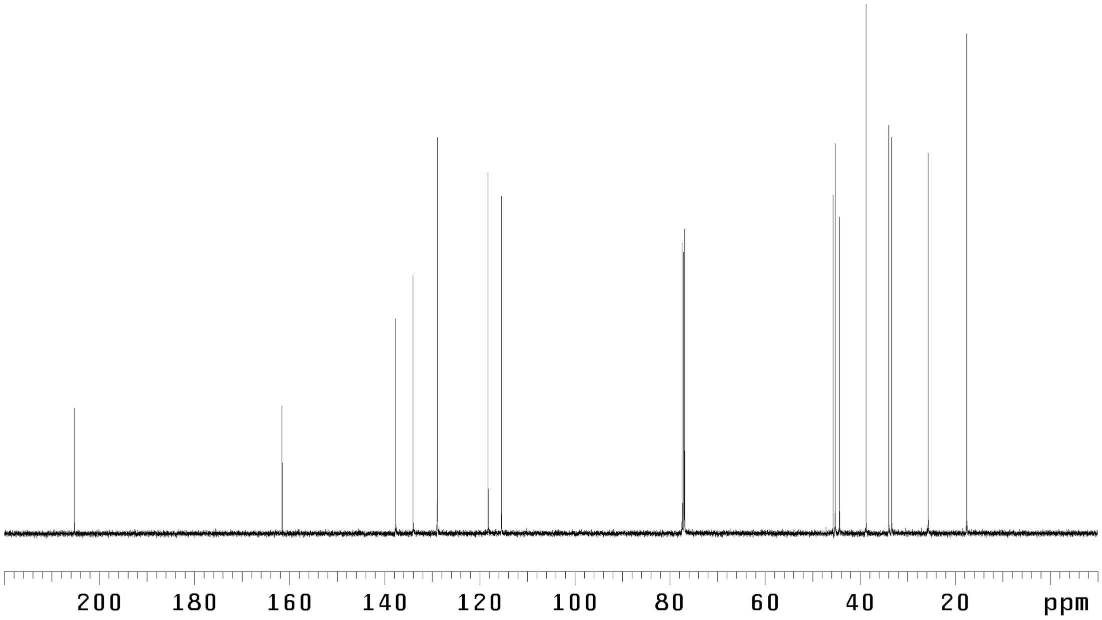


Figure SI-3C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **1e**.

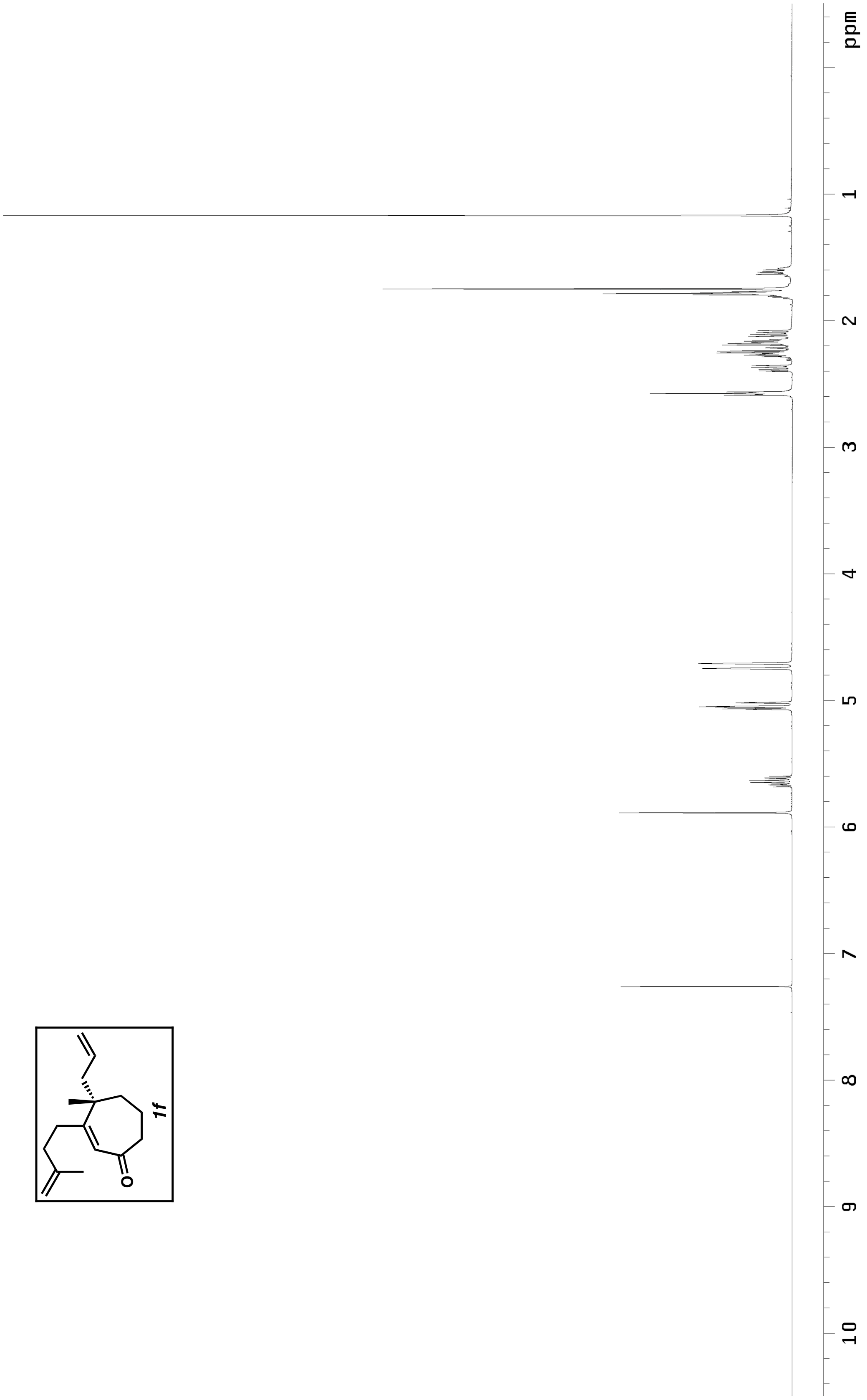


Figure SI-4A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **1f**.

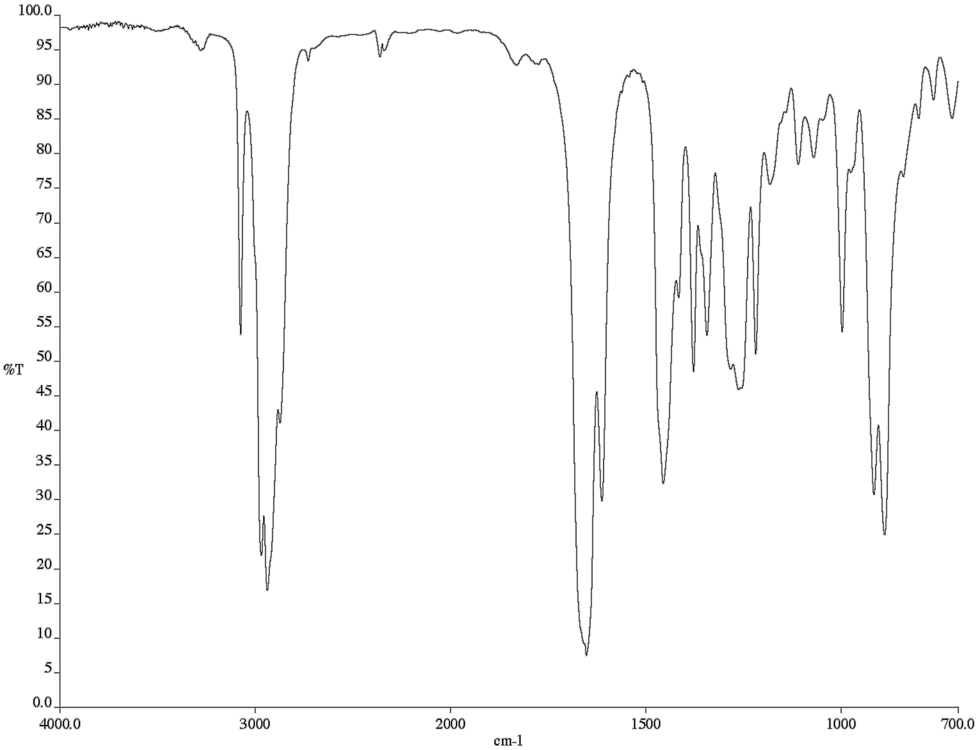


Figure SI-4B. Infrared spectrum (thin film/NaCl) of compound **1f**.

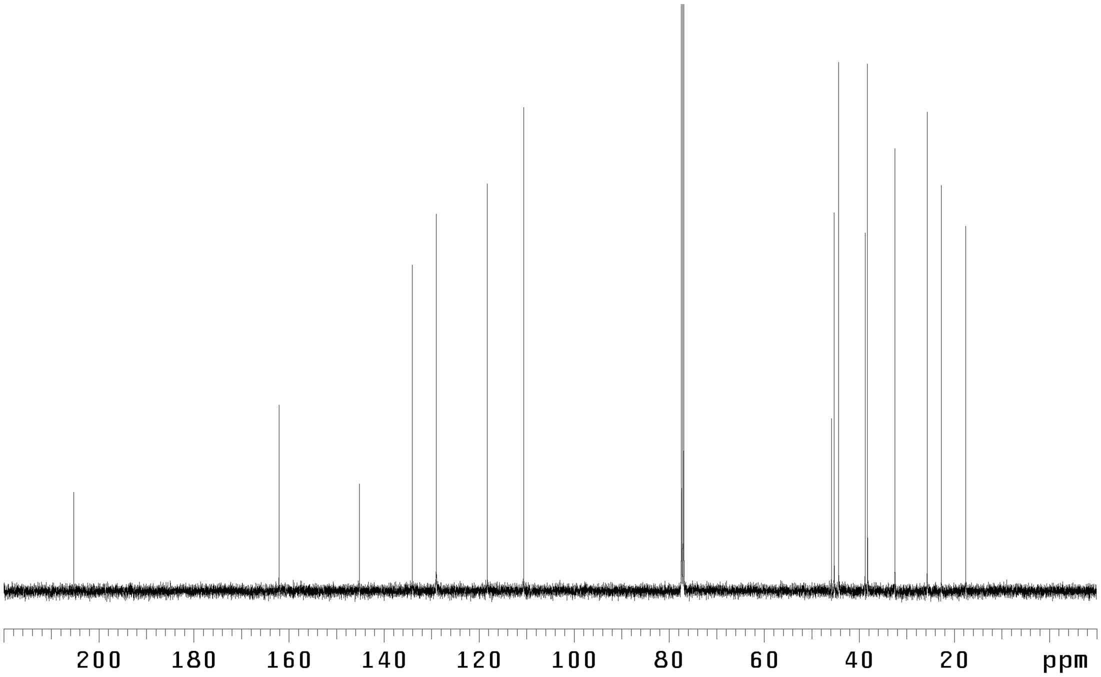


Figure SI-4C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **1f**.

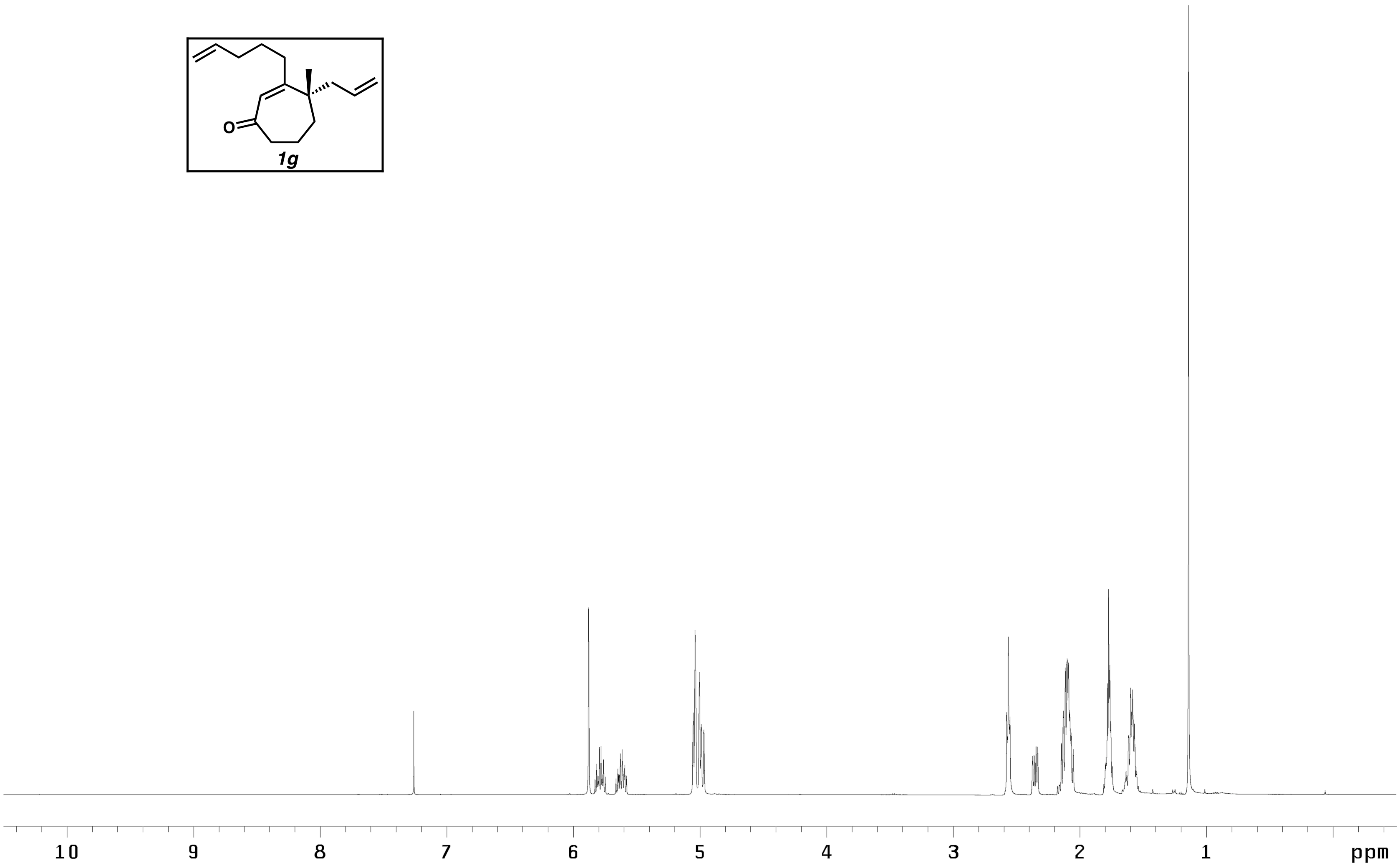


Figure SI-5A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1g**.

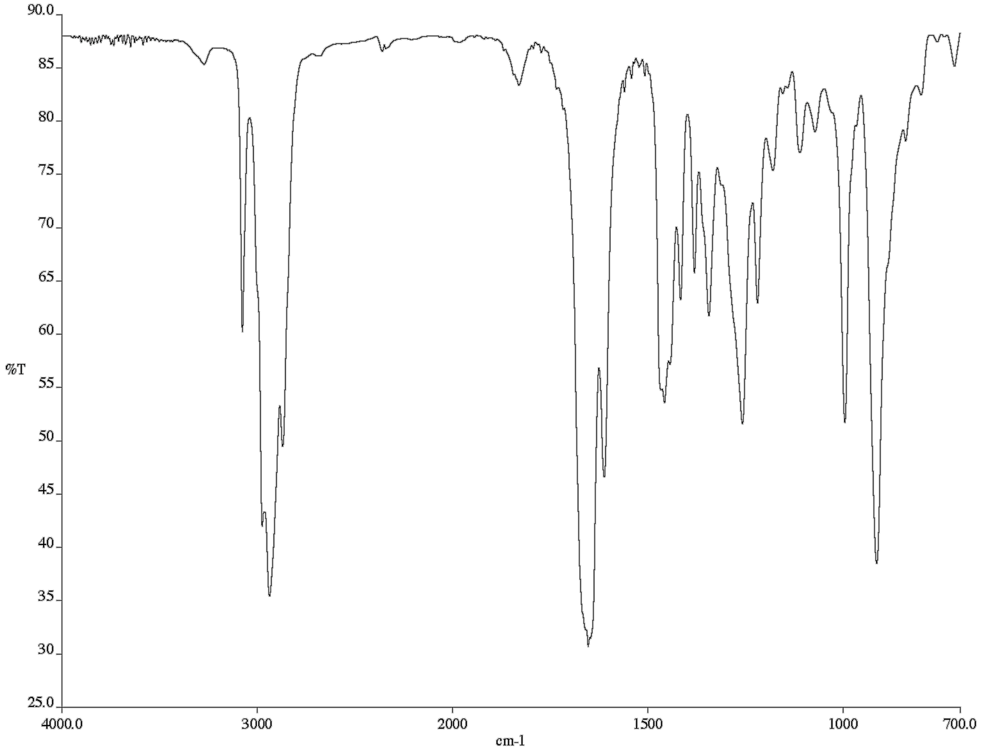


Figure SI-5B. Infrared spectrum (thin film/NaCl) of compound **1g**.

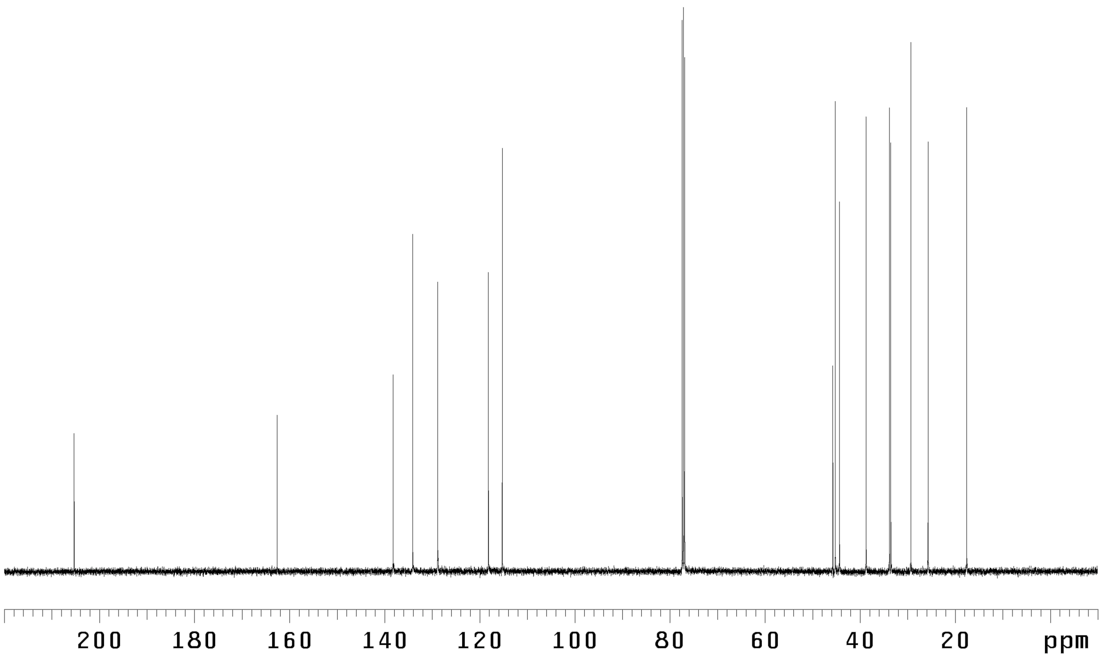


Figure SI-5C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **1g**.

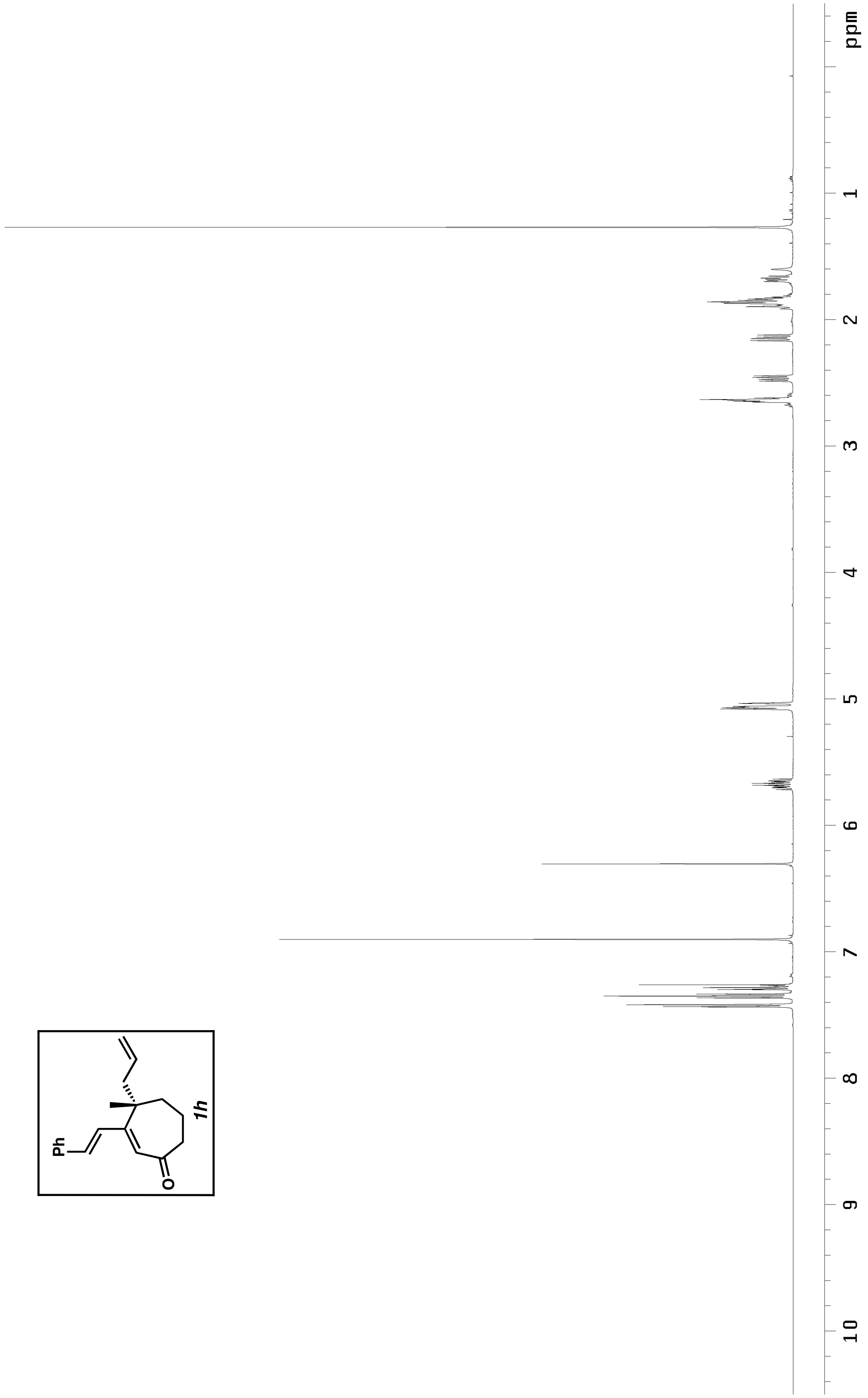


Figure SI-6A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1h**.

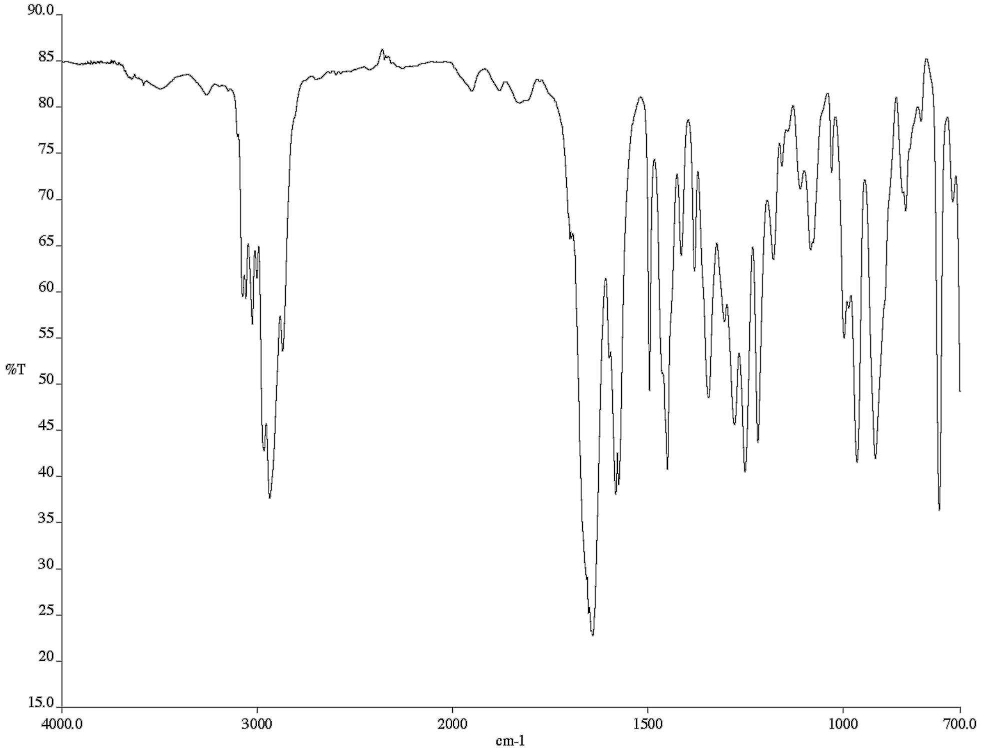


Figure SI-6B. Infrared spectrum (thin film/NaCl) of compound **1h**.

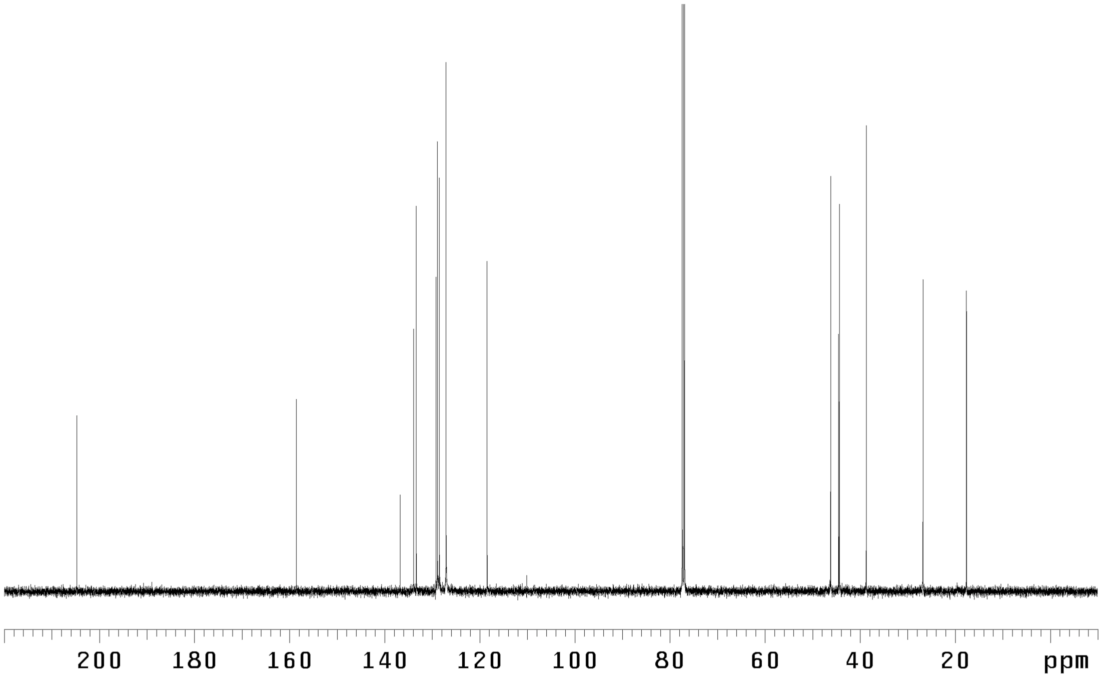


Figure SI-6C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **1h**.

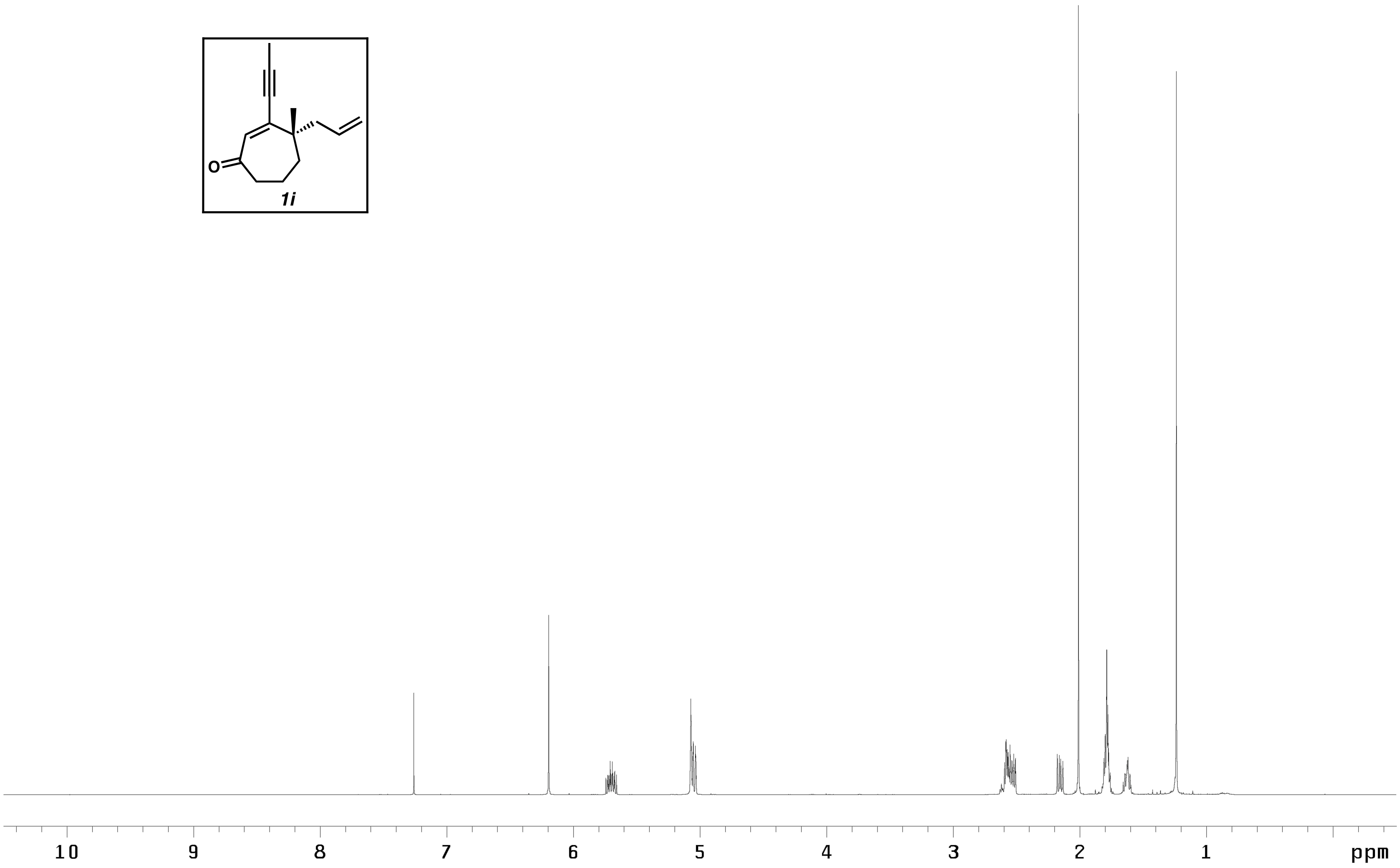


Figure SI-7A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1i**.

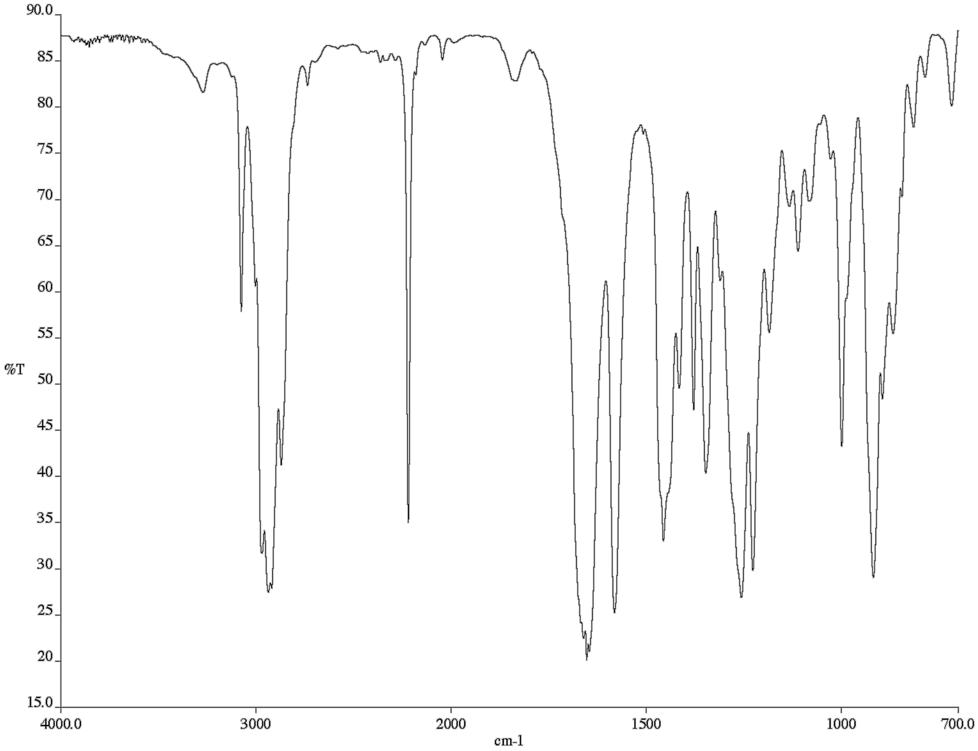


Figure SI-7B. Infrared spectrum (thin film/NaCl) of compound **1i**.

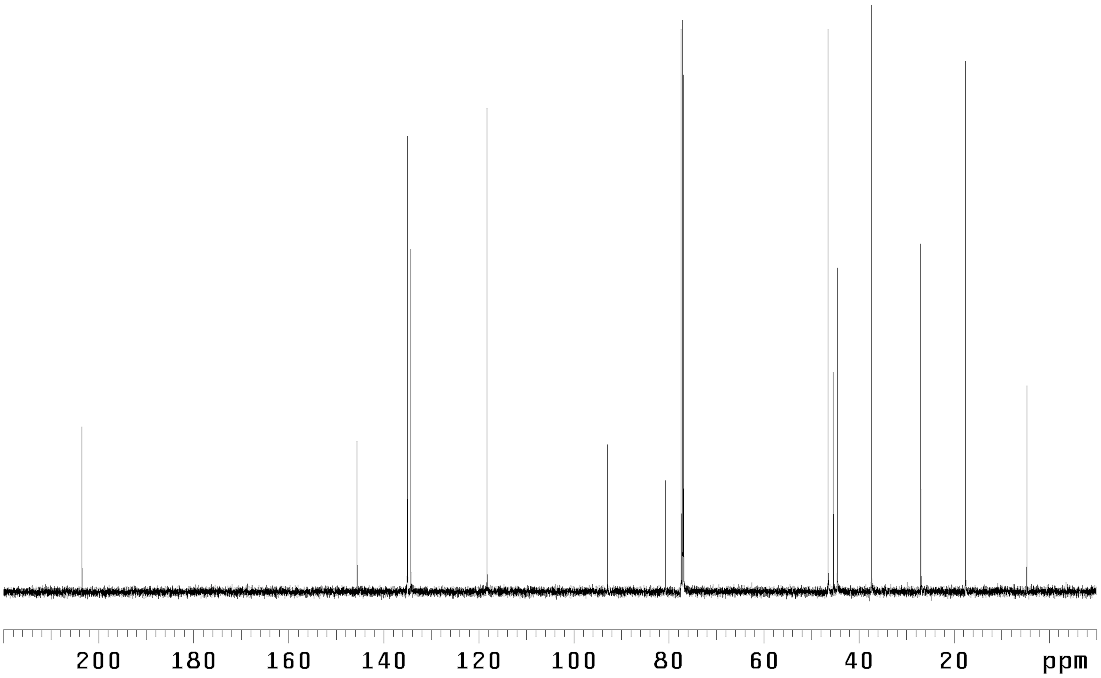


Figure SI-7C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **1i**.

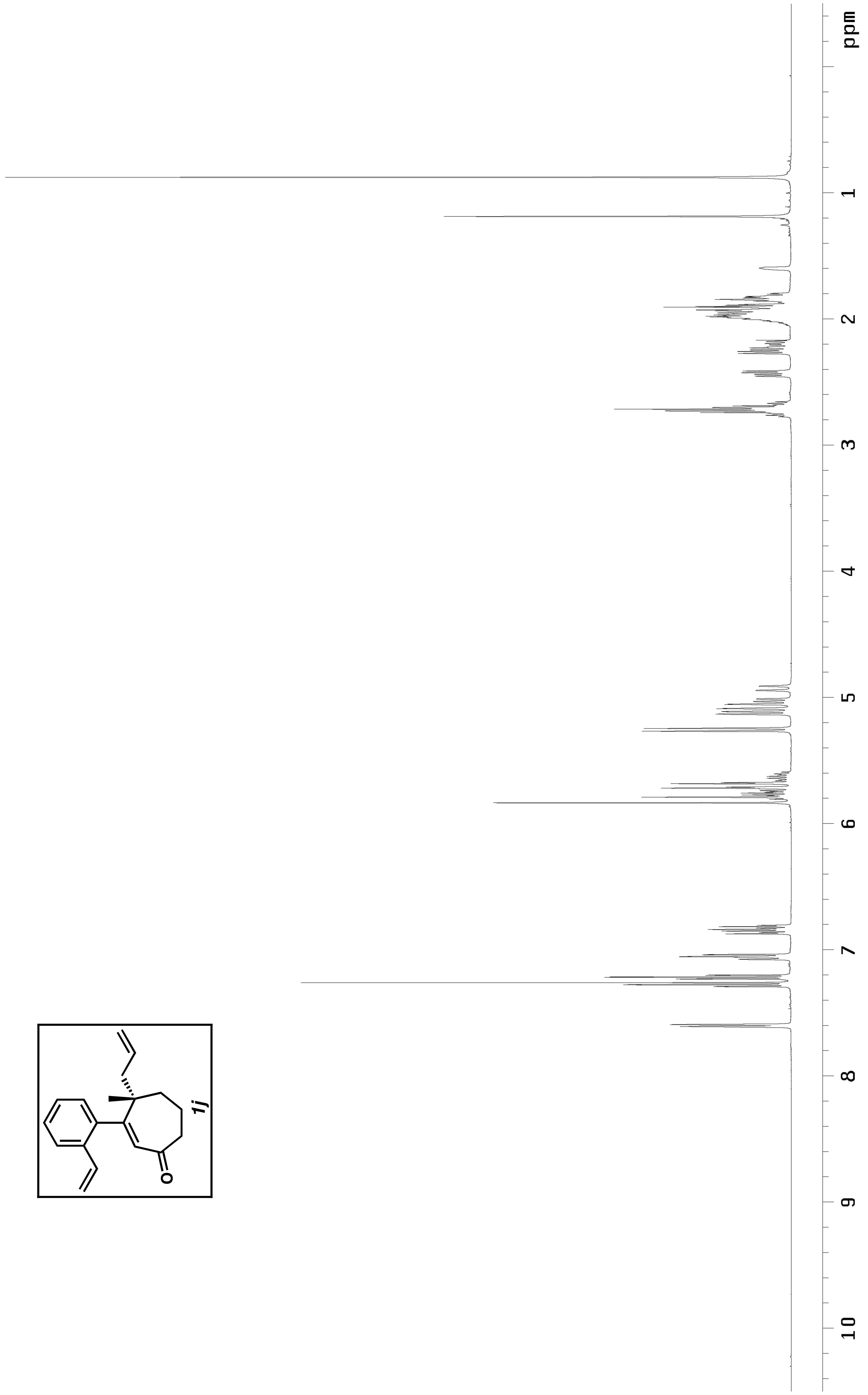


Figure SI-8A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **1j**.

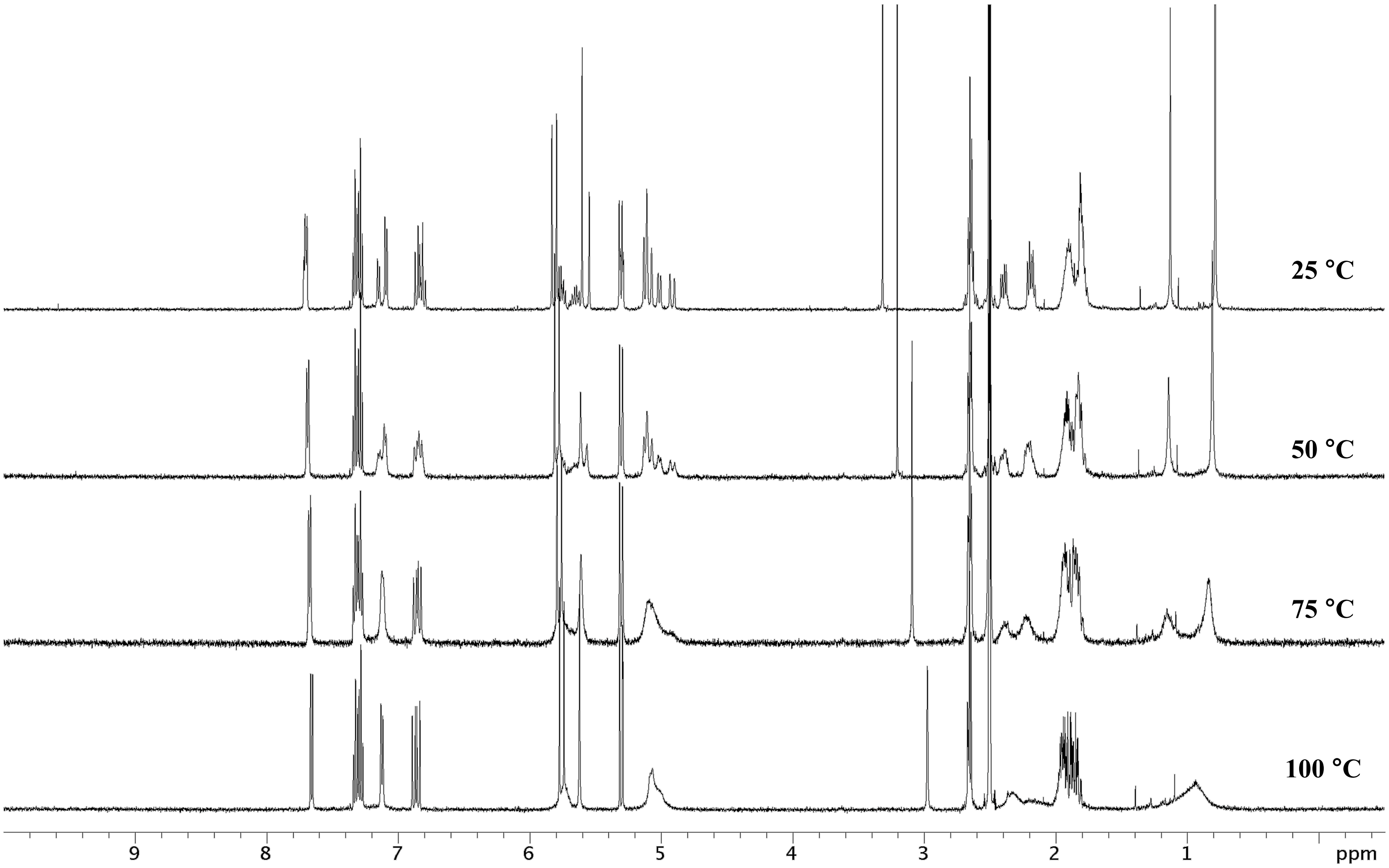


Figure SI-8B. Variable Temperature ^{1}H NMR (500 MHz, DMSO-d_6) of compound **1j**.

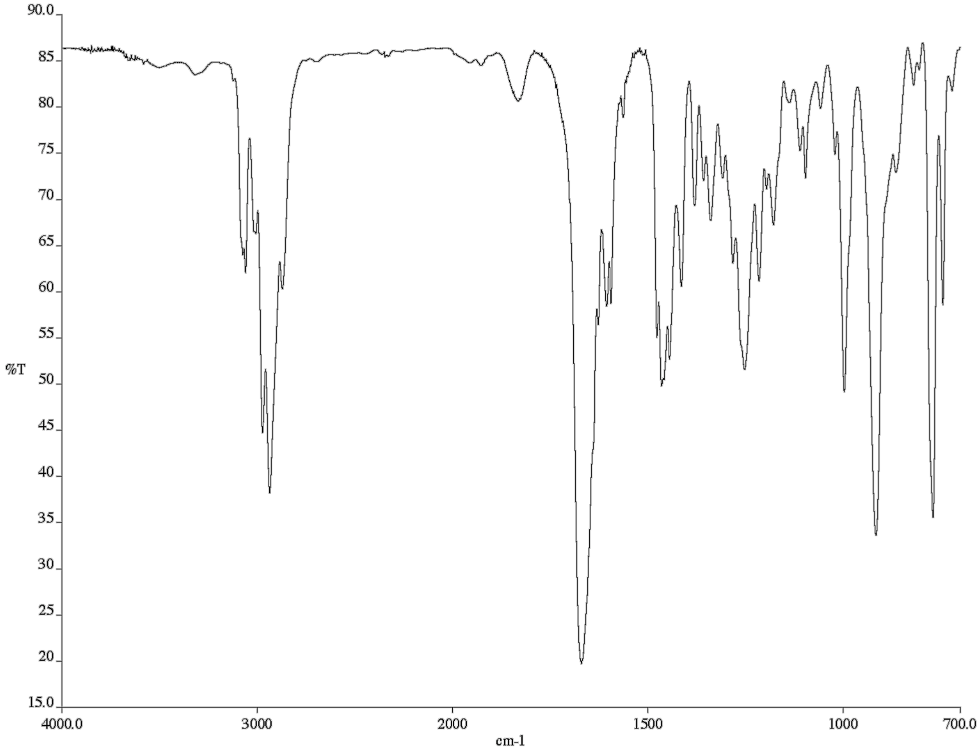


Figure SI-8C. Infrared spectrum (thin film/NaCl) of compound **1j**.

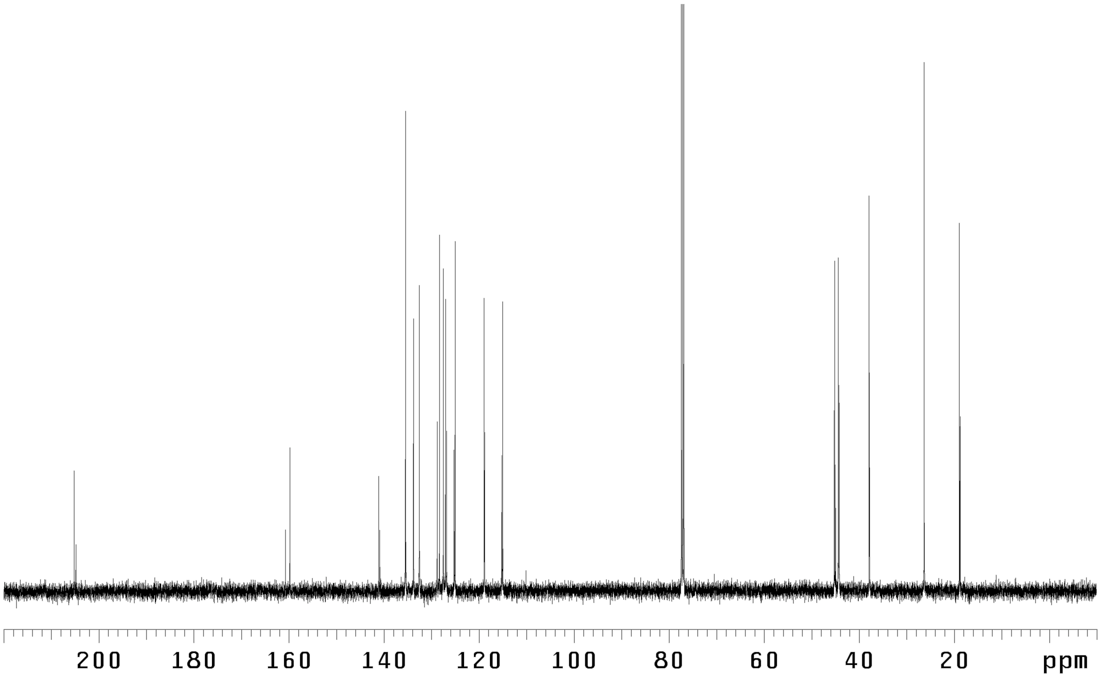


Figure SI-8D. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **1j**.

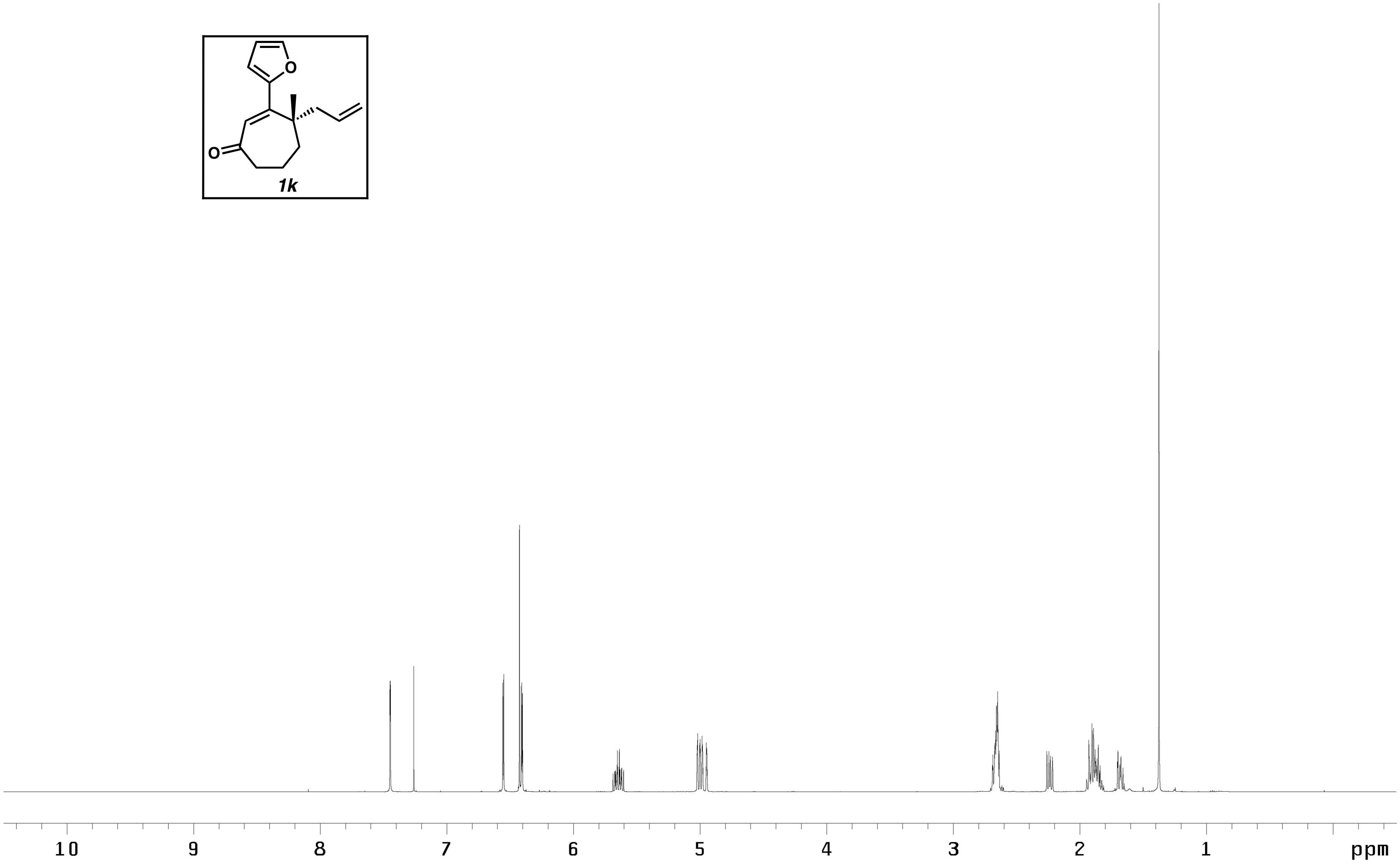


Figure SI-9A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1k**.

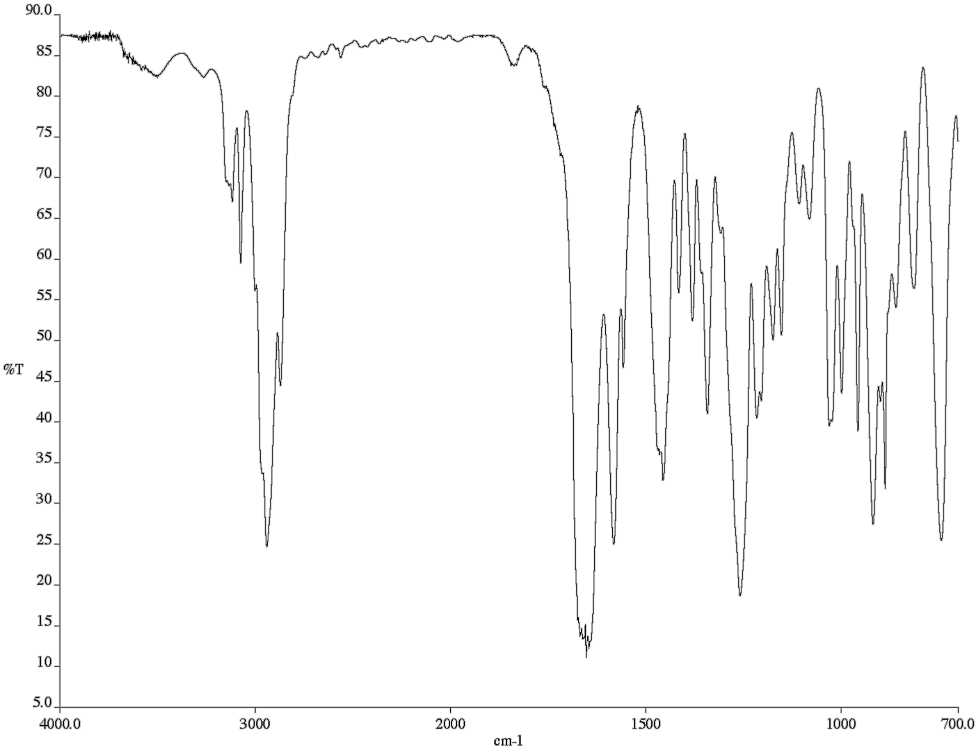


Figure SI-9B. Infrared spectrum (thin film/NaCl) of compound **1k**.

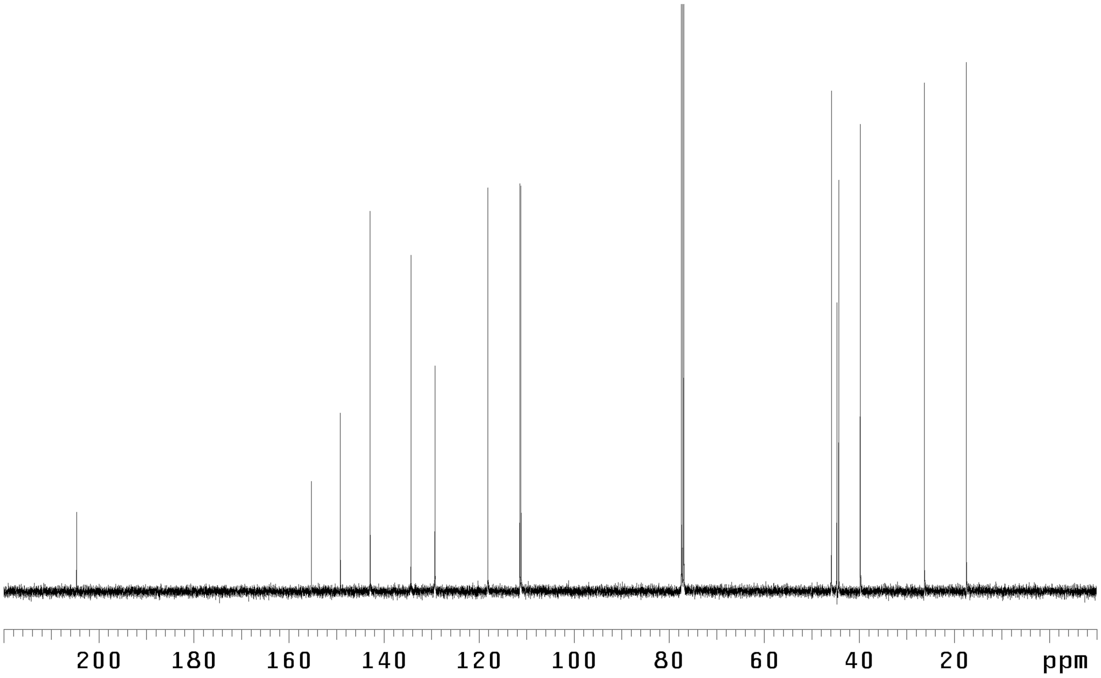


Figure SI-9C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **1k**.

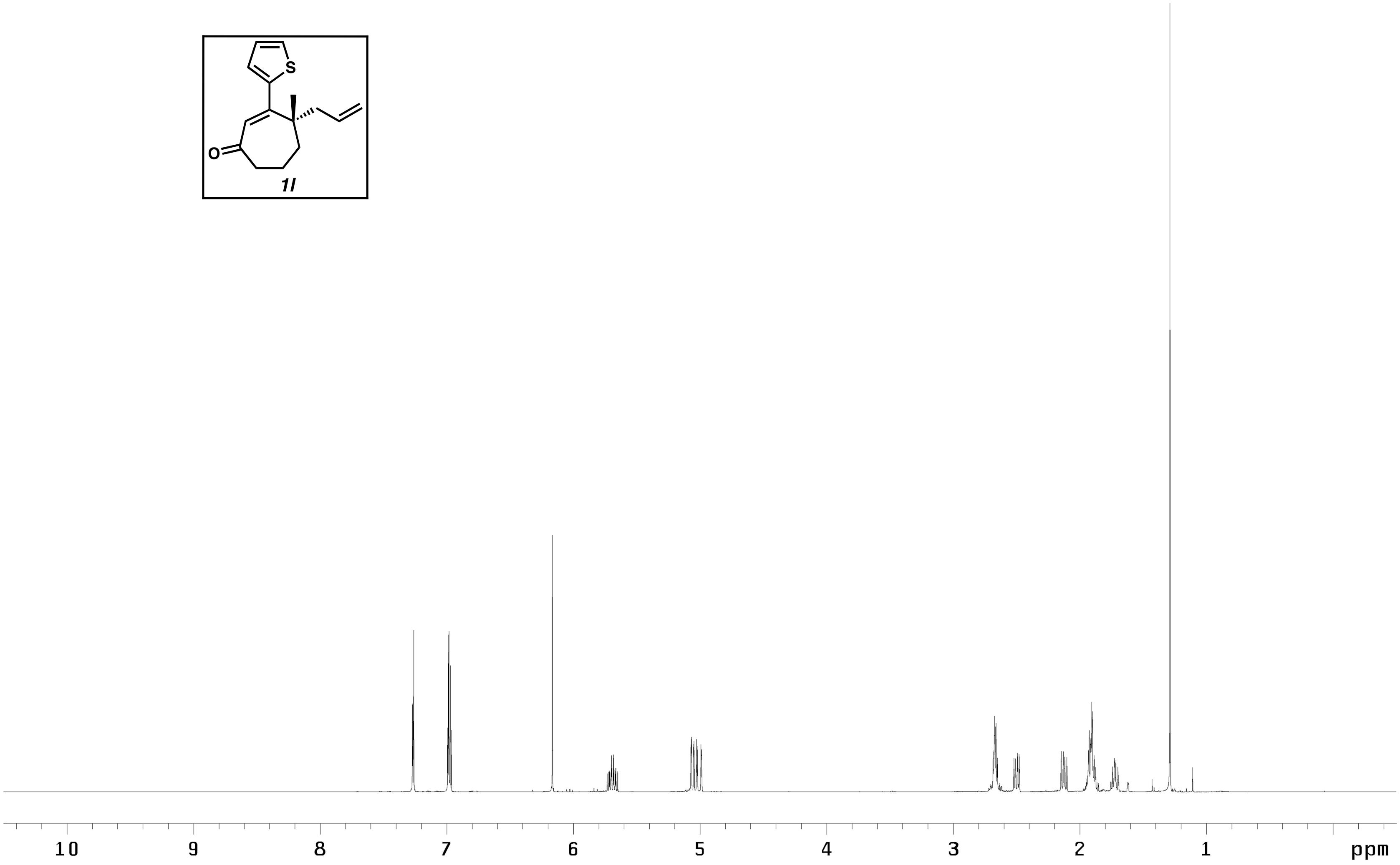


Figure SI-10A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **1l**.

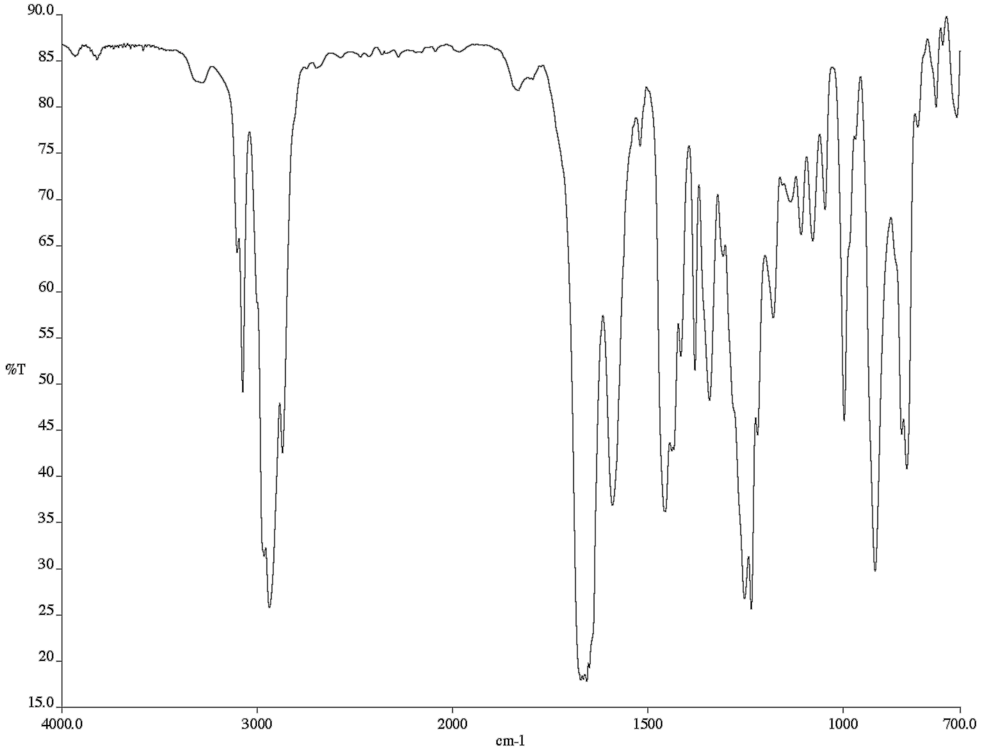


Figure SI-10B. Infrared spectrum (thin film/NaCl) of compound **1l**.

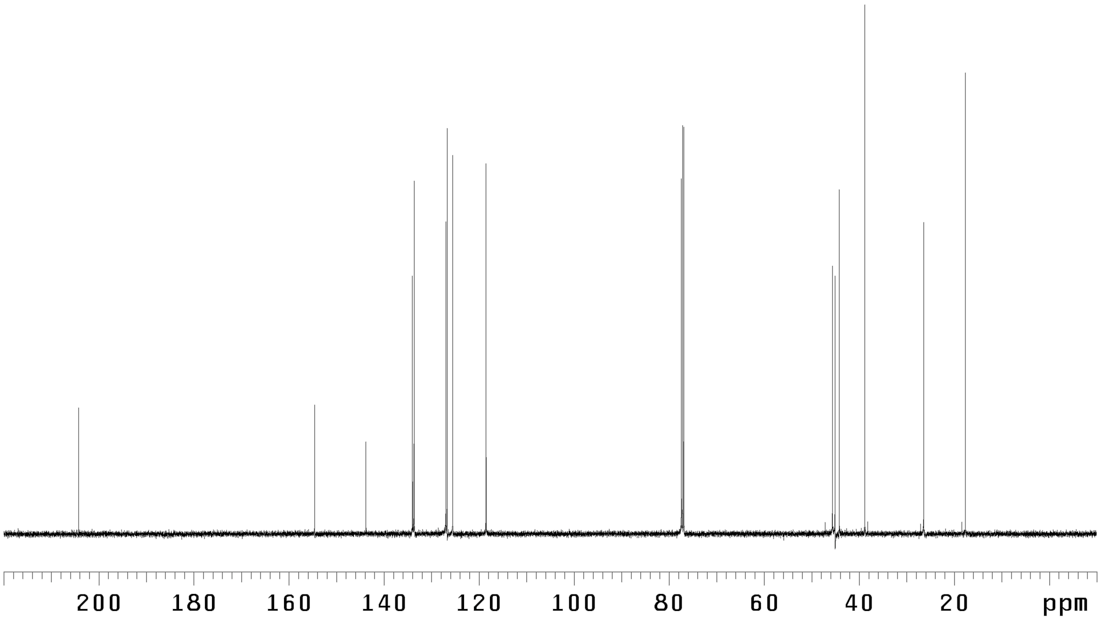


Figure SI-10C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **1l**.

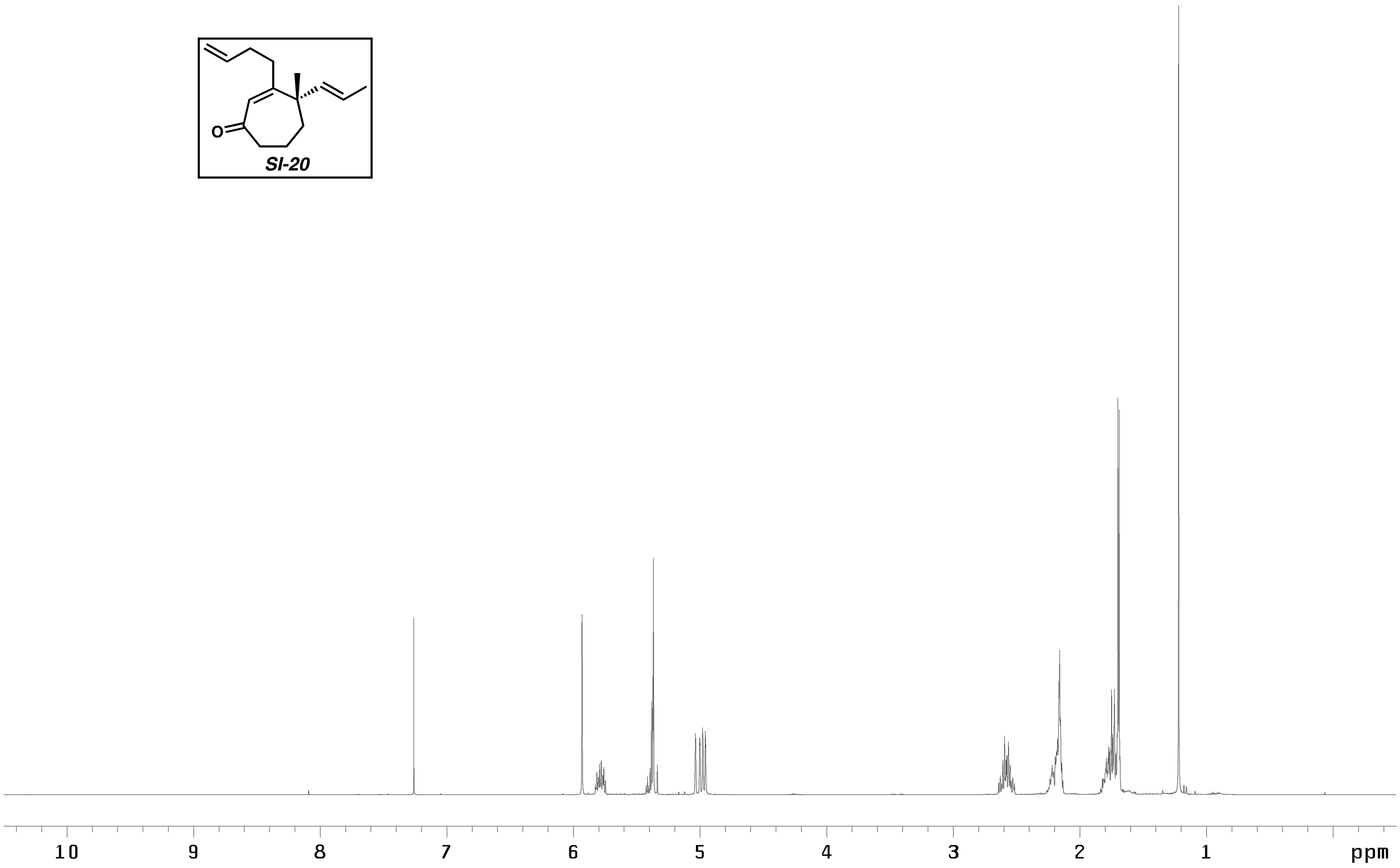


Figure SI-11A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI-20**.

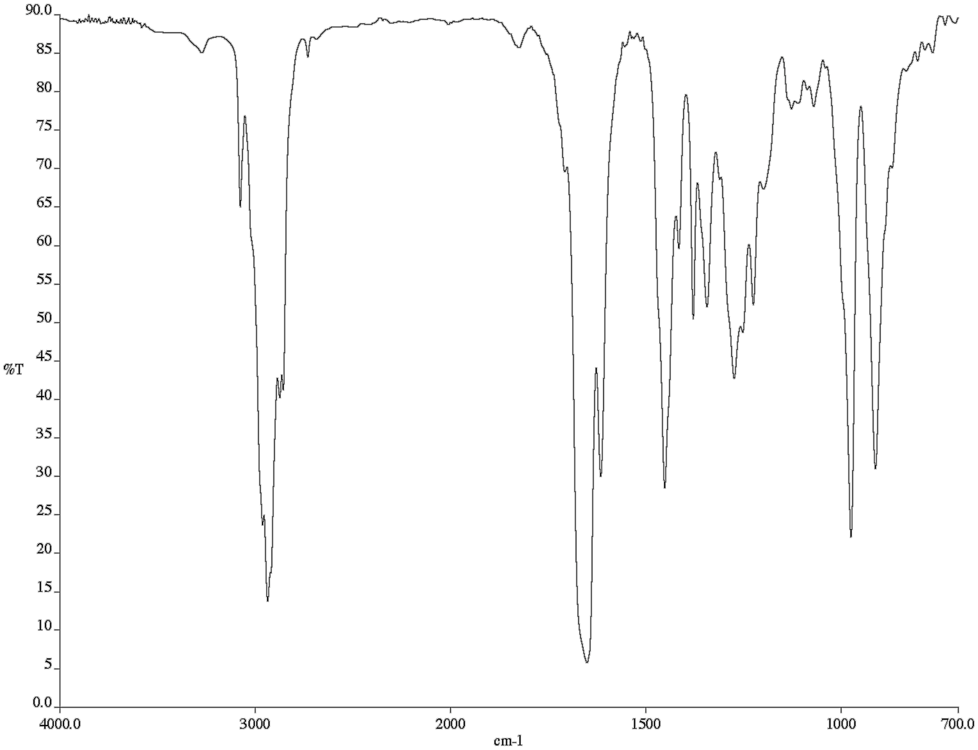


Figure SI-11B. Infrared spectrum (thin film/NaCl) of compound **SI-20**.

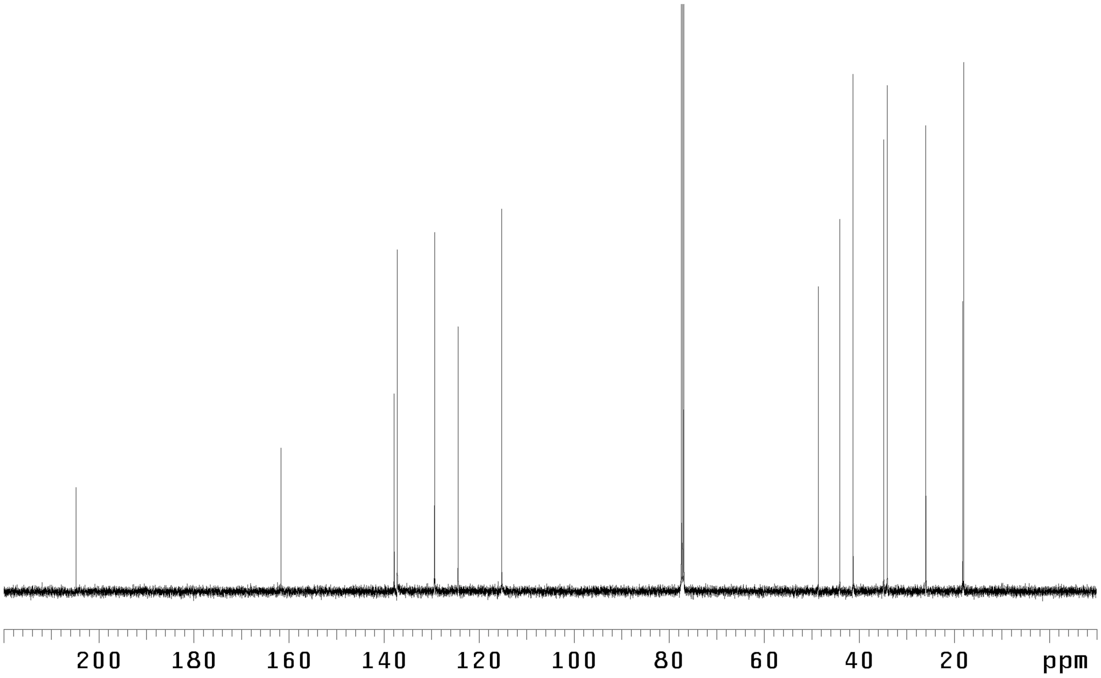


Figure SI-11C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **SI-20**.

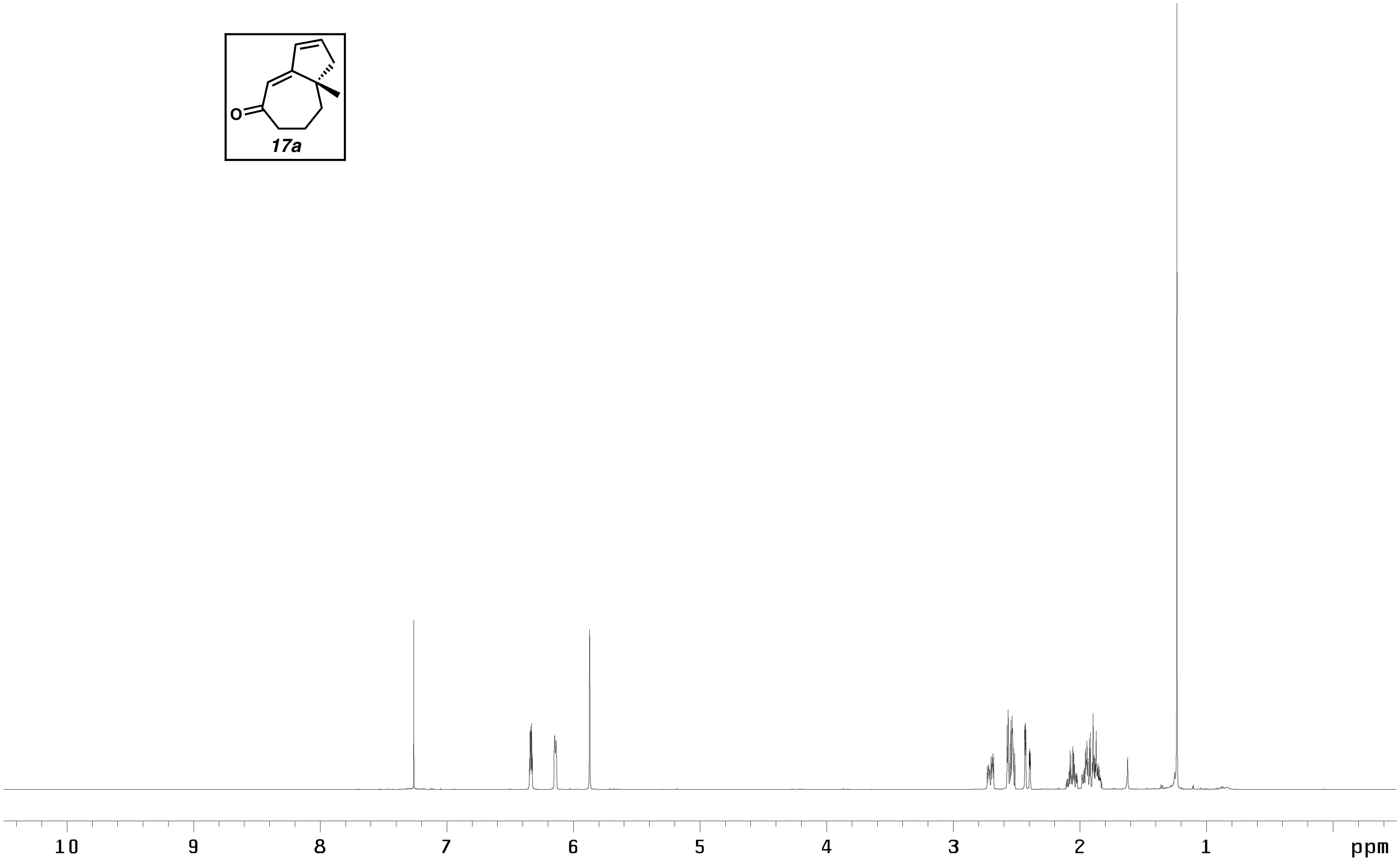


Figure SI-12A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17a**.

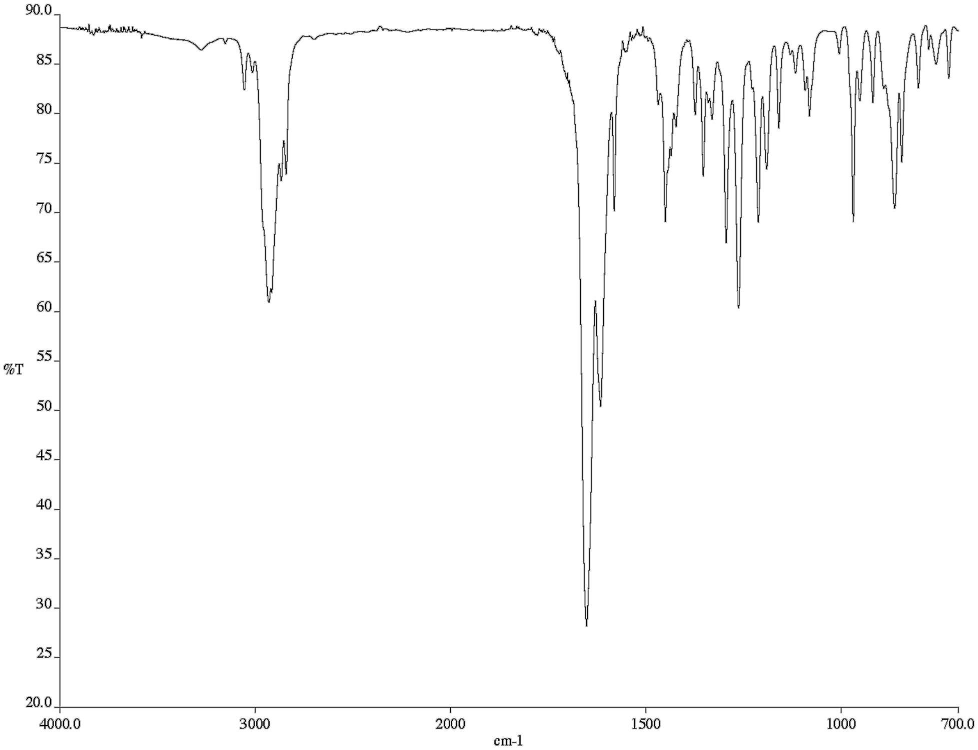


Figure SI-12B. Infrared spectrum (thin film/NaCl) of compound **17a**.

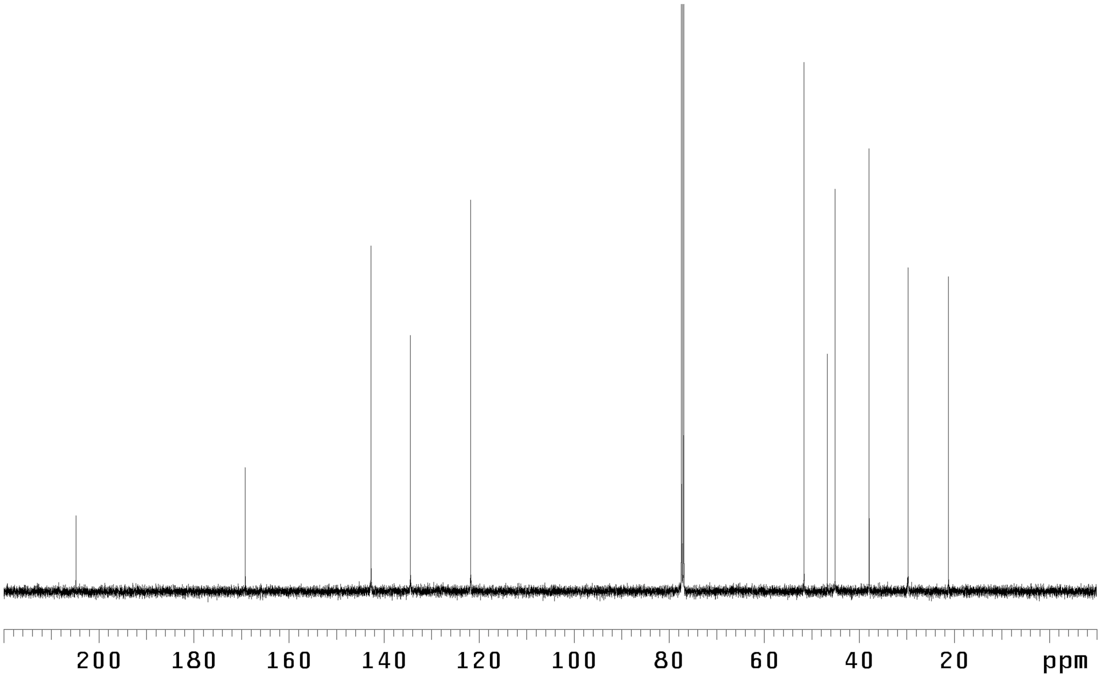


Figure SI-12C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **17a**.

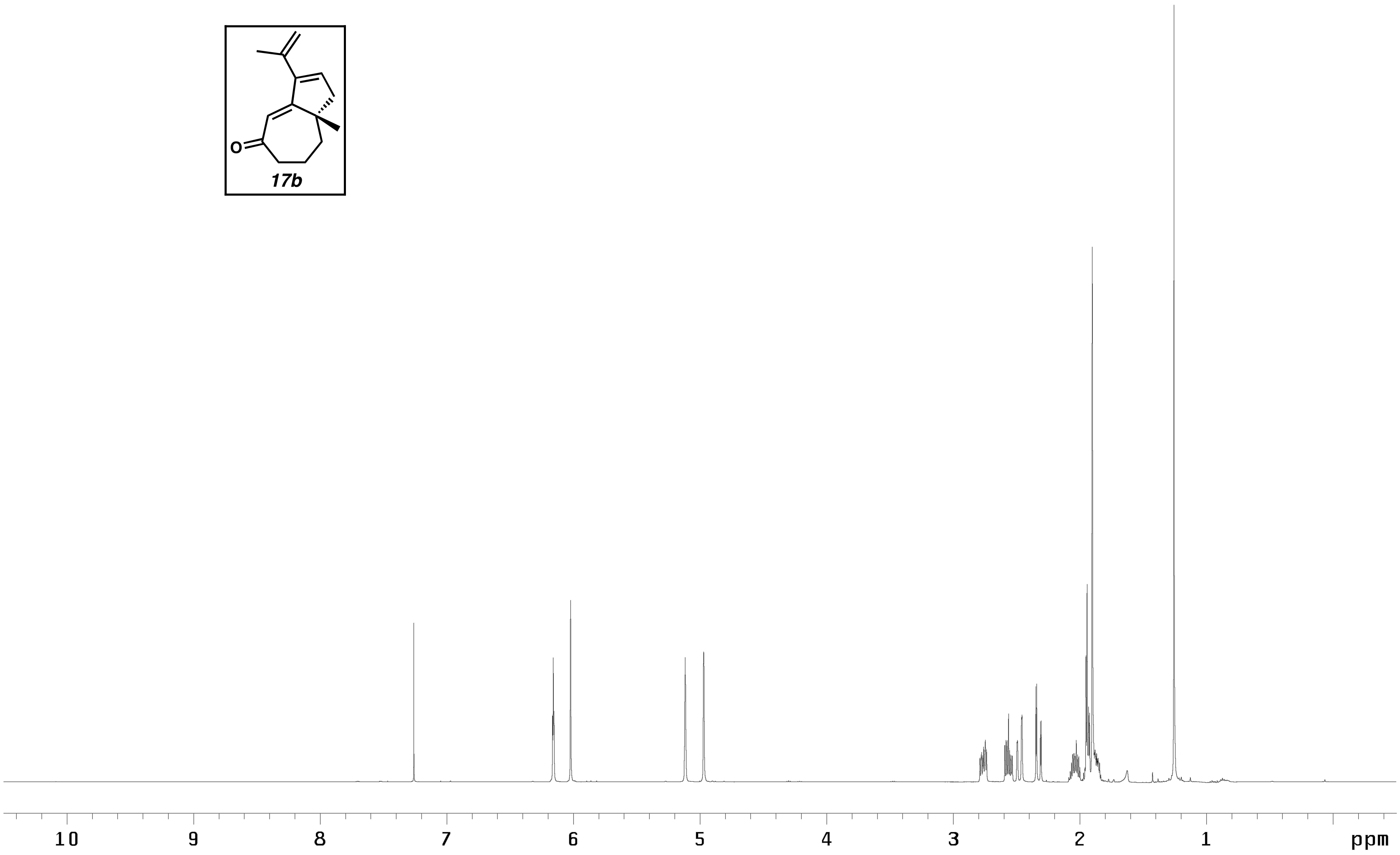


Figure SI-13A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17b**.

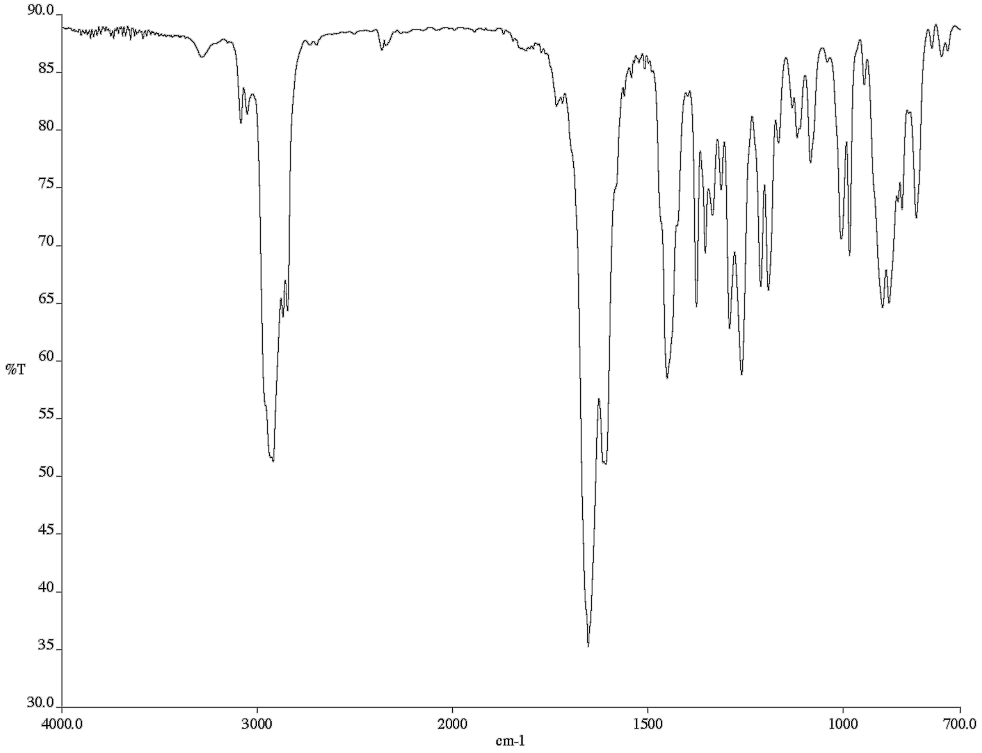


Figure SI-13B. Infrared spectrum (thin film/NaCl) of compound **17b**.

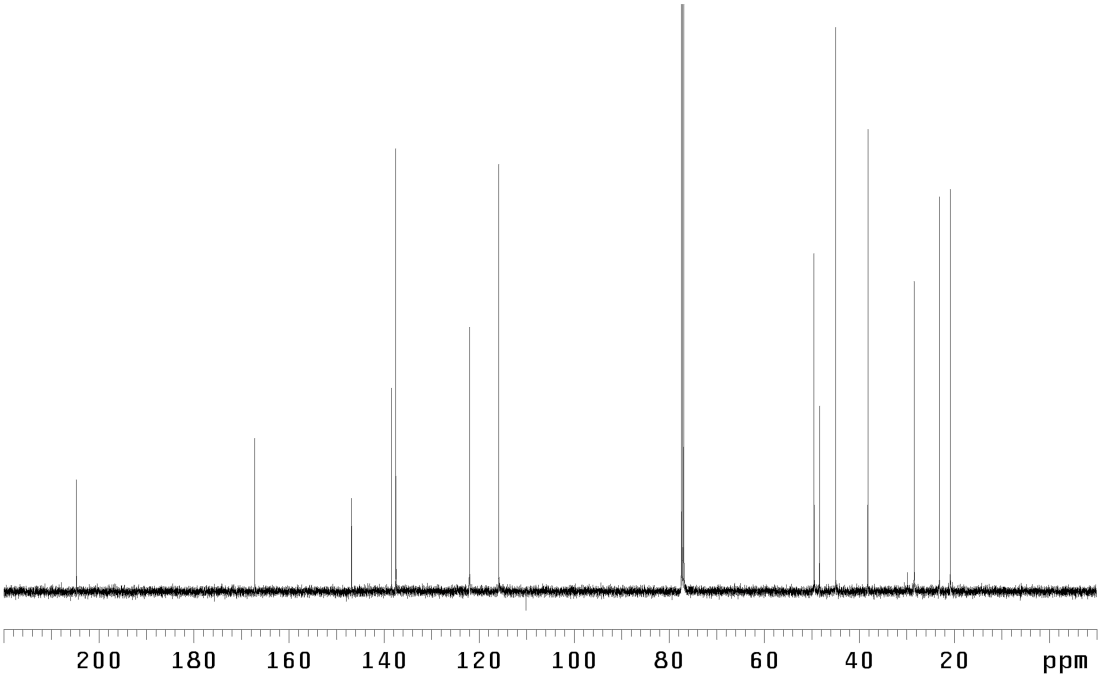


Figure SI-13C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17b**.

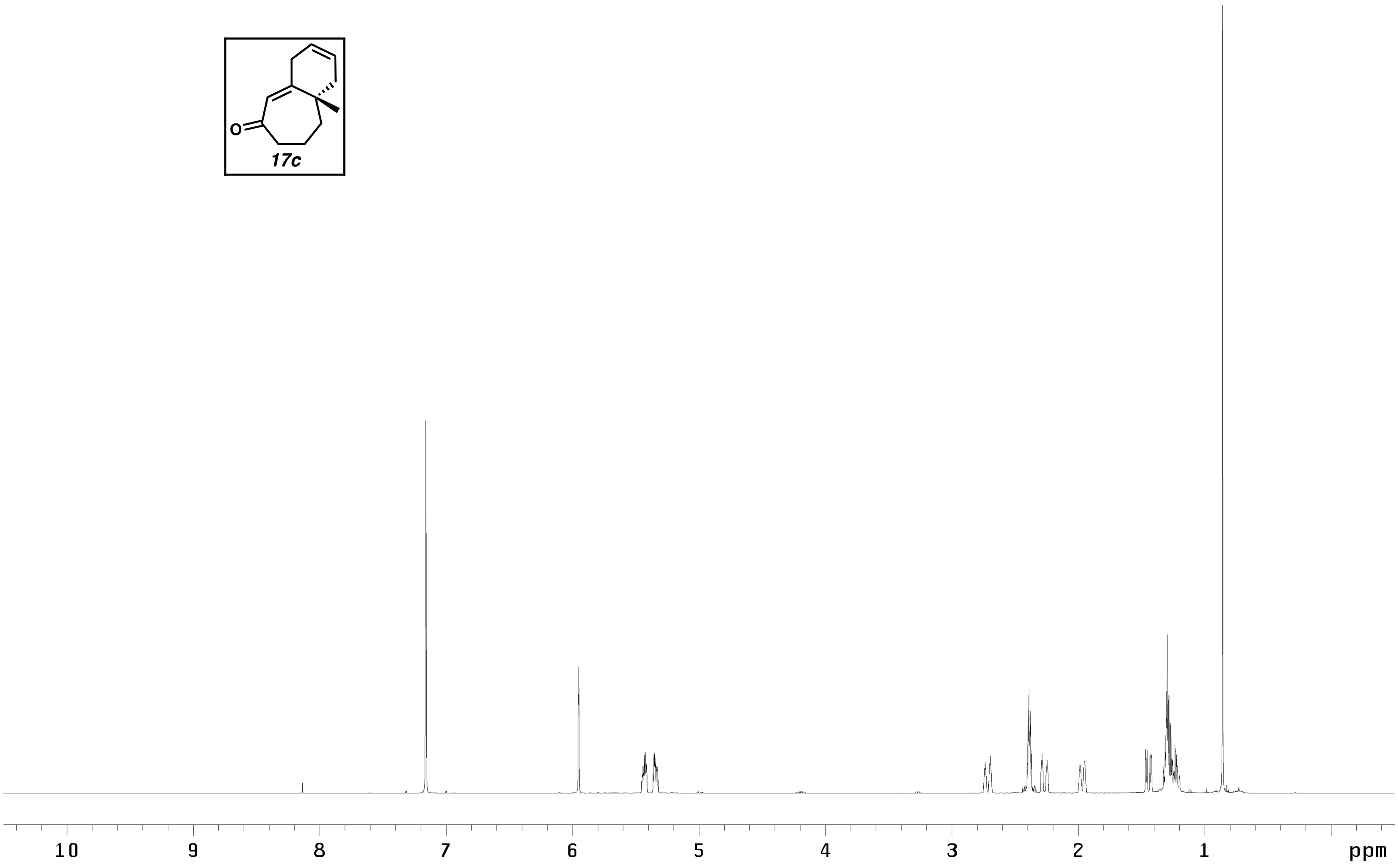


Figure SI-14A. ^{1}H NMR (500 MHz, C_6D_6) of compound **17c**.

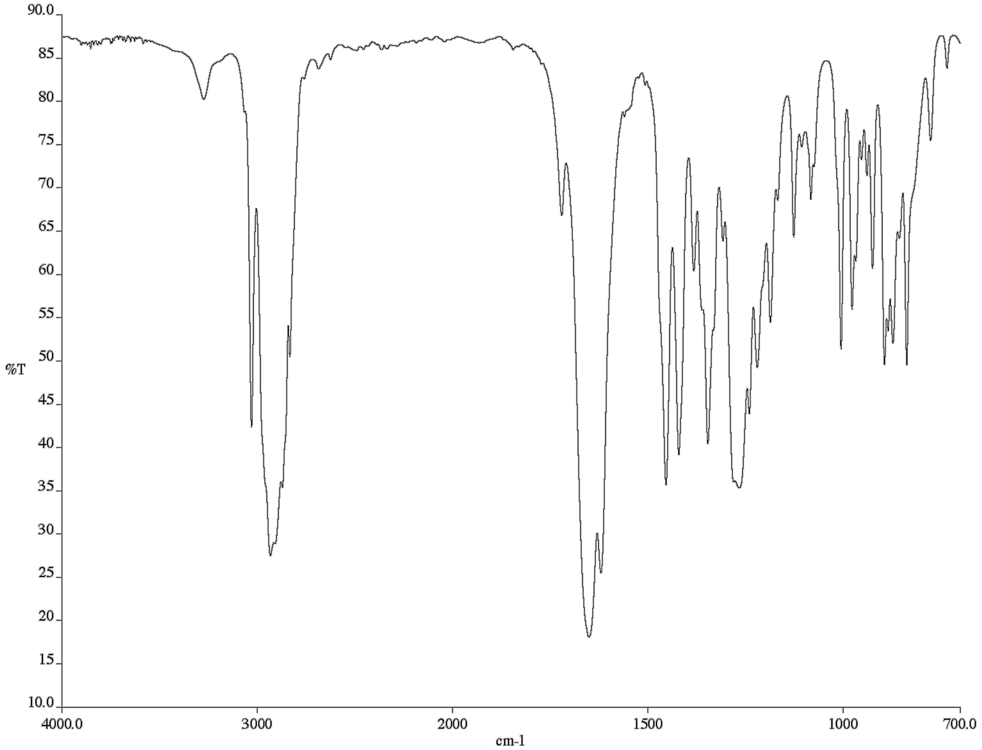


Figure SI-14B. Infrared spectrum (thin film/NaCl) of compound **17c**.

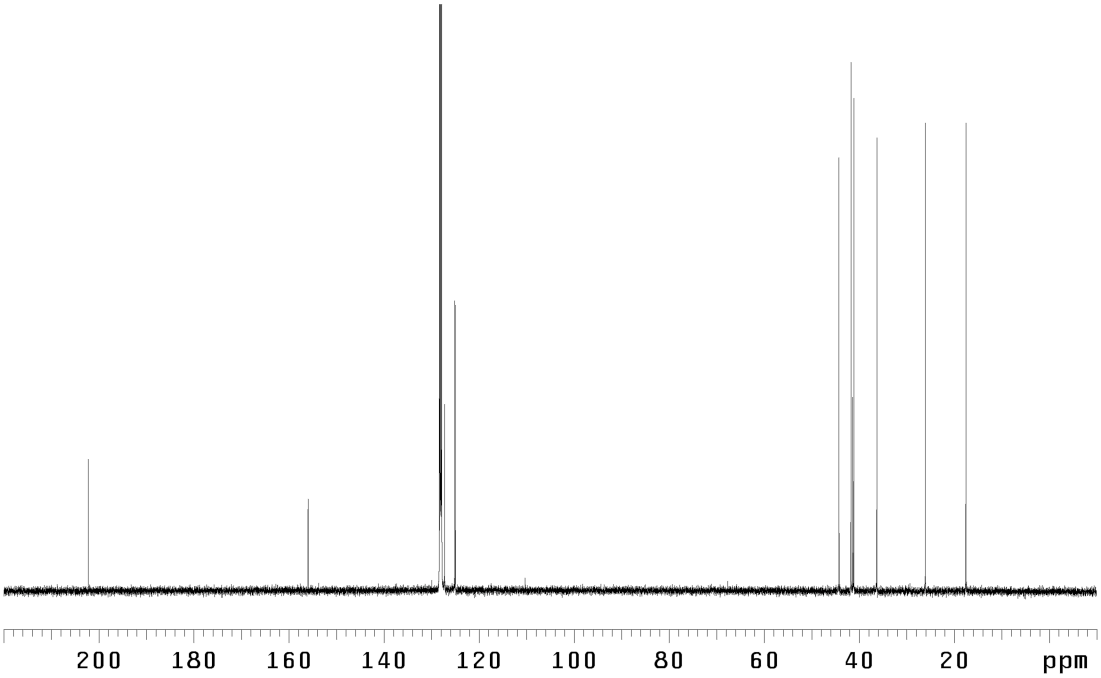


Figure SI-14C. ^{13}C NMR (125 MHz, C_6D_6) of compound **17c**.

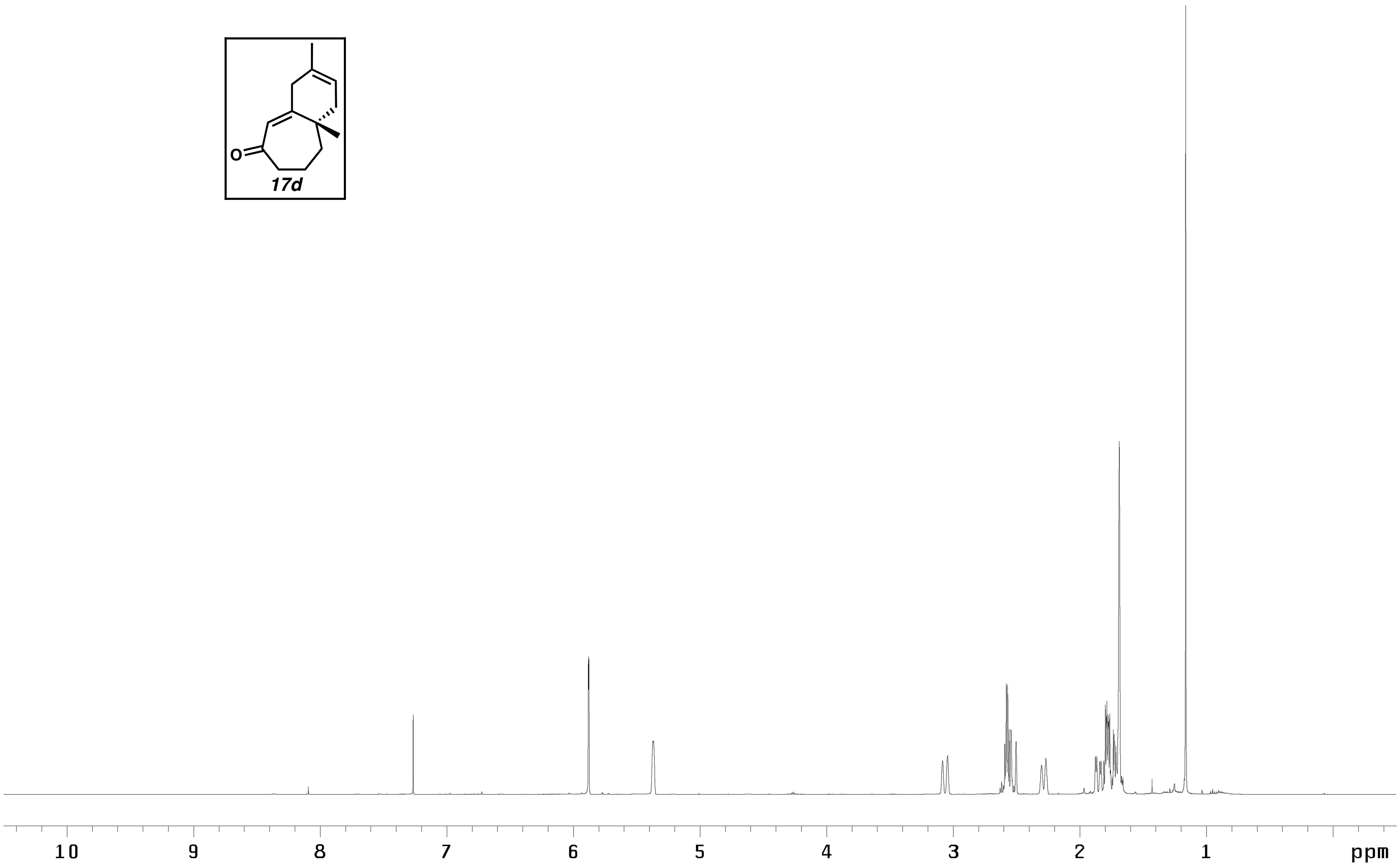


Figure SI-15A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17d**.

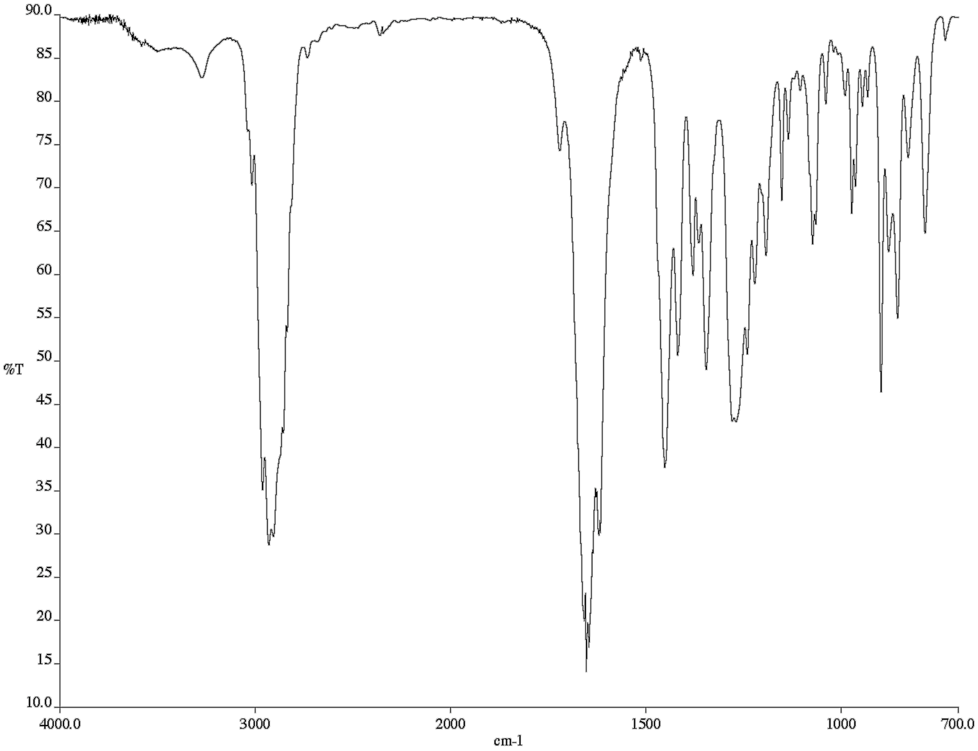


Figure SI-15B. Infrared spectrum (thin film/NaCl) of compound **17d**.

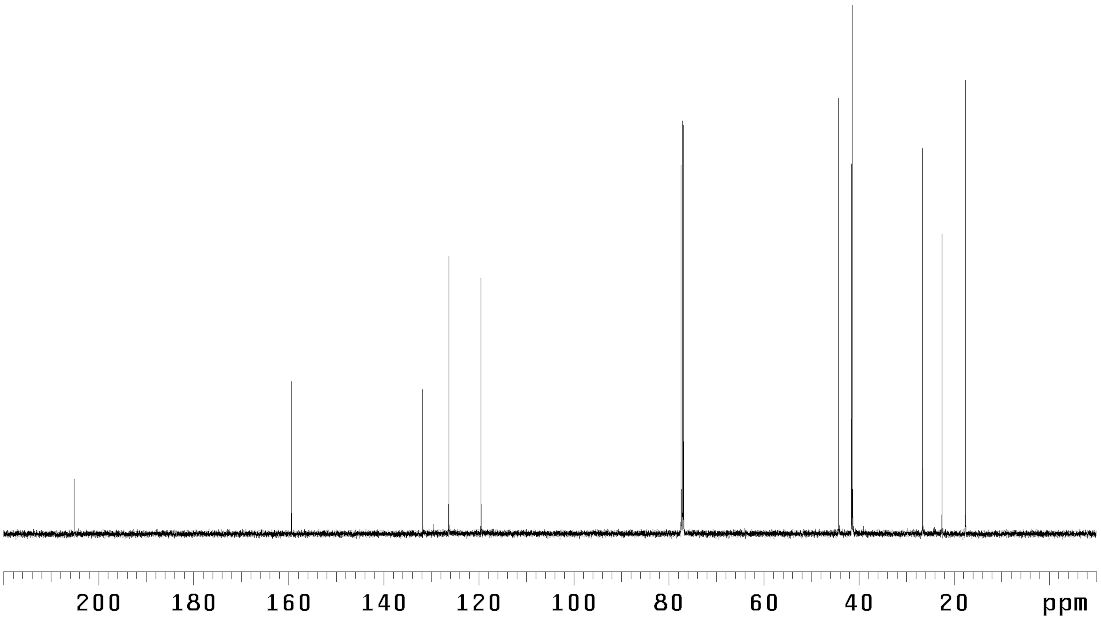


Figure SI-15C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17d**.

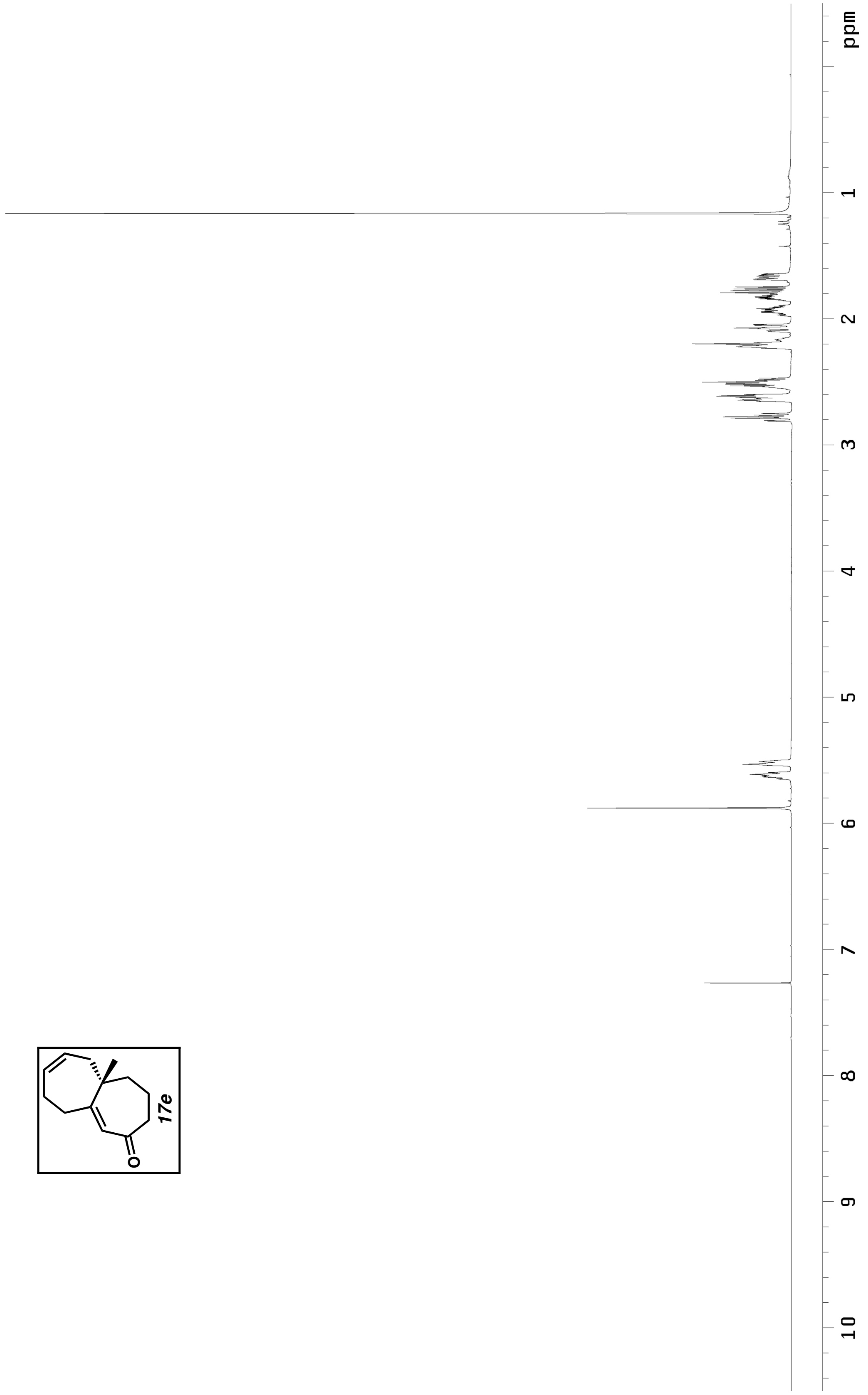


Figure SI-16A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **17e**.

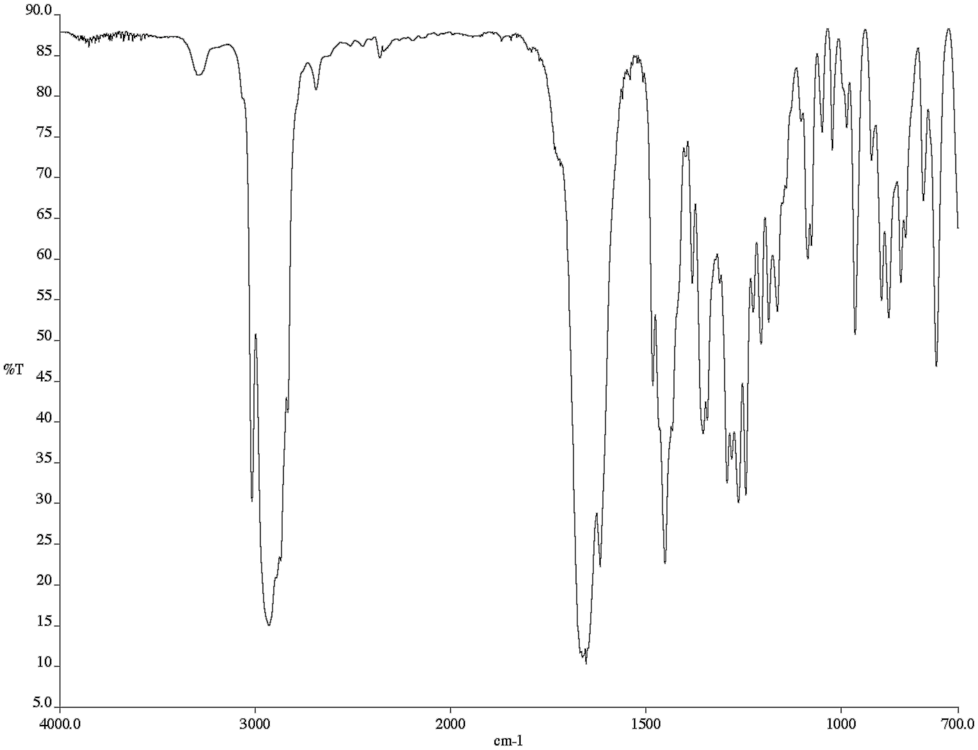


Figure SI-16B. Infrared spectrum (thin film/NaCl) of compound **17e**.

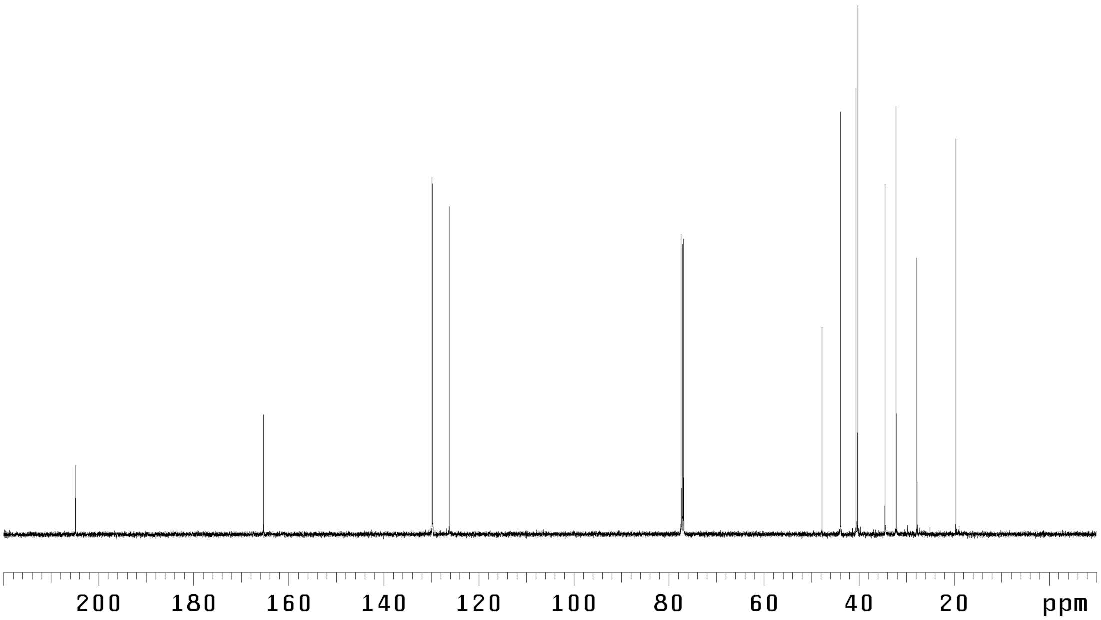


Figure SI-16C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17e**.

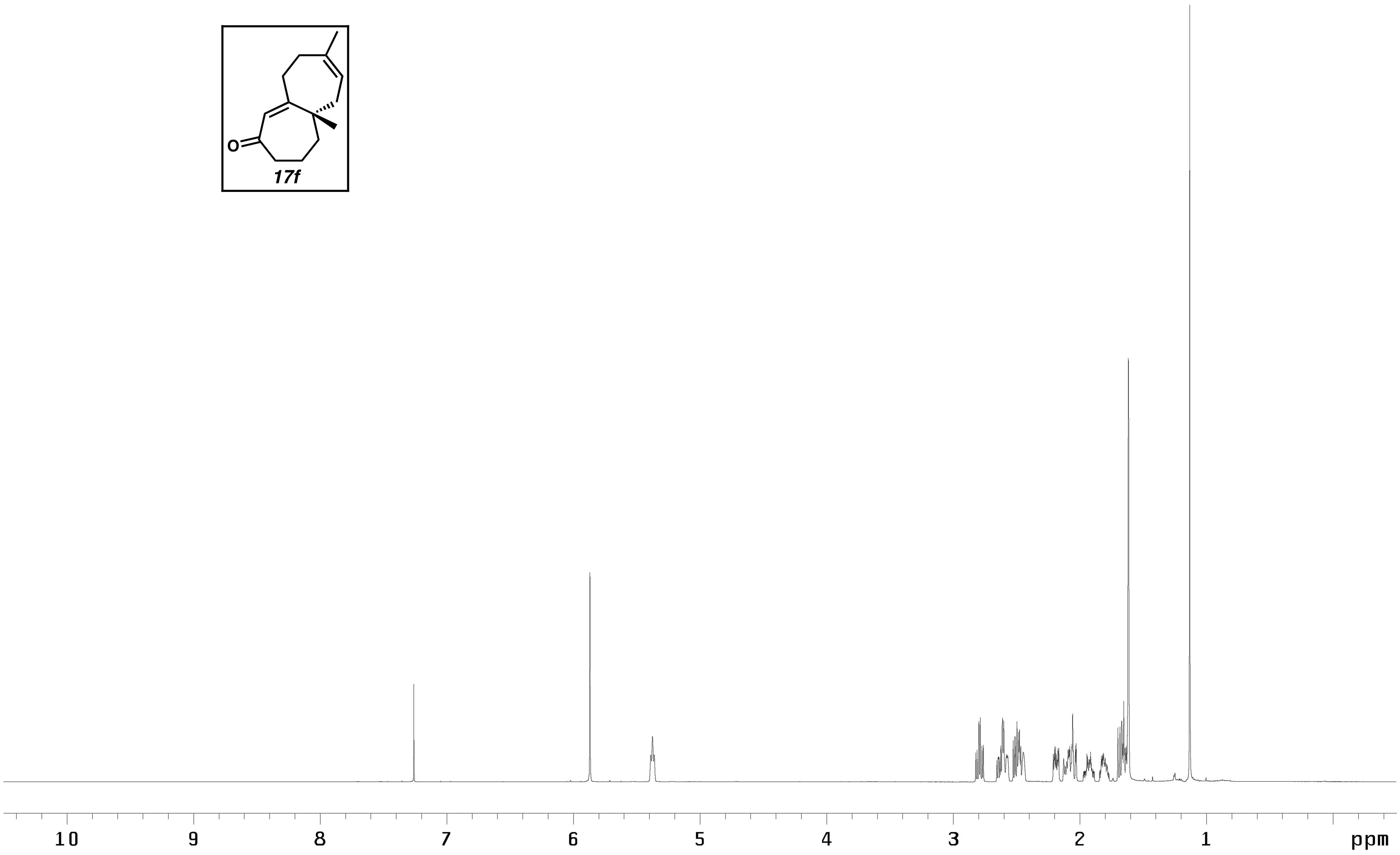


Figure SI-17A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **17f**.

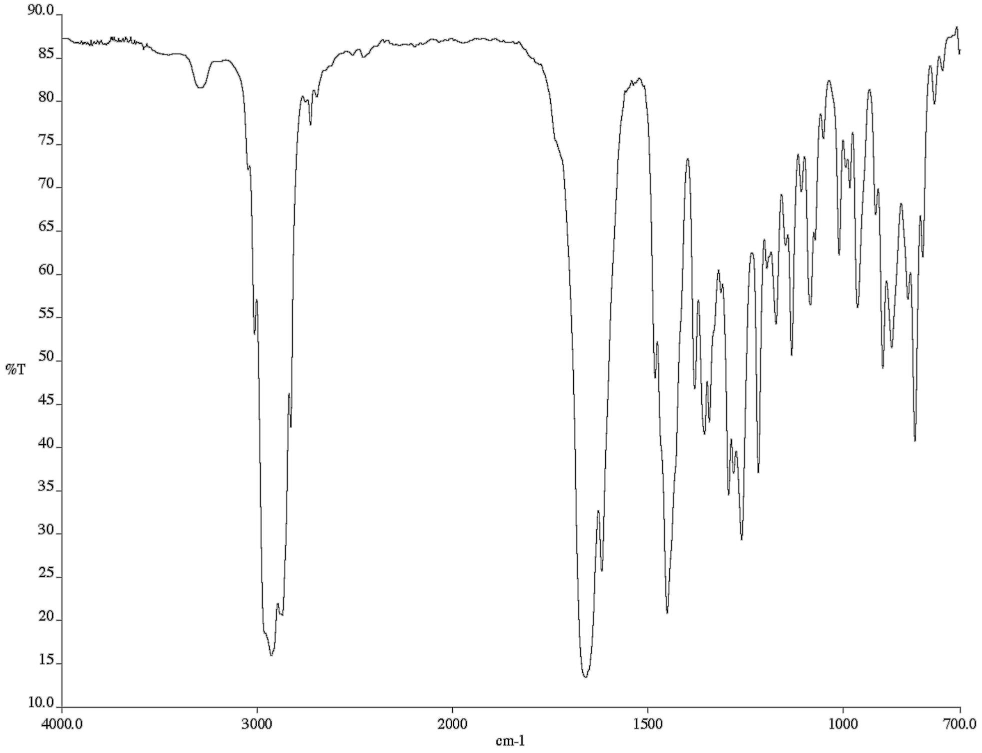


Figure SI-17B. Infrared spectrum (thin film/NaCl) of compound **17f**.

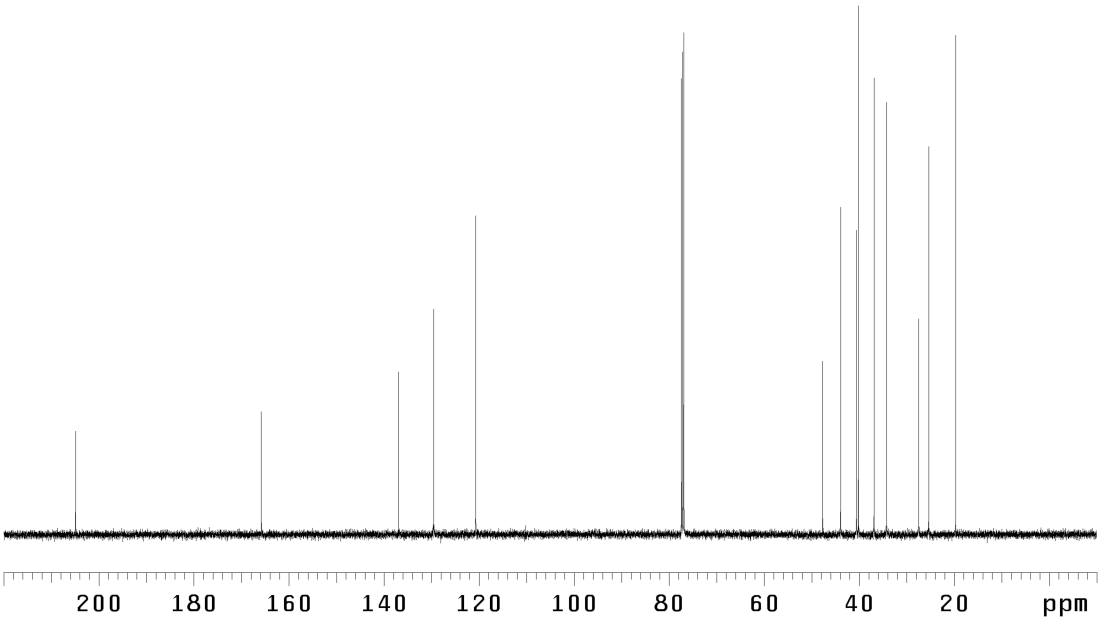


Figure SI-17C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17f**.

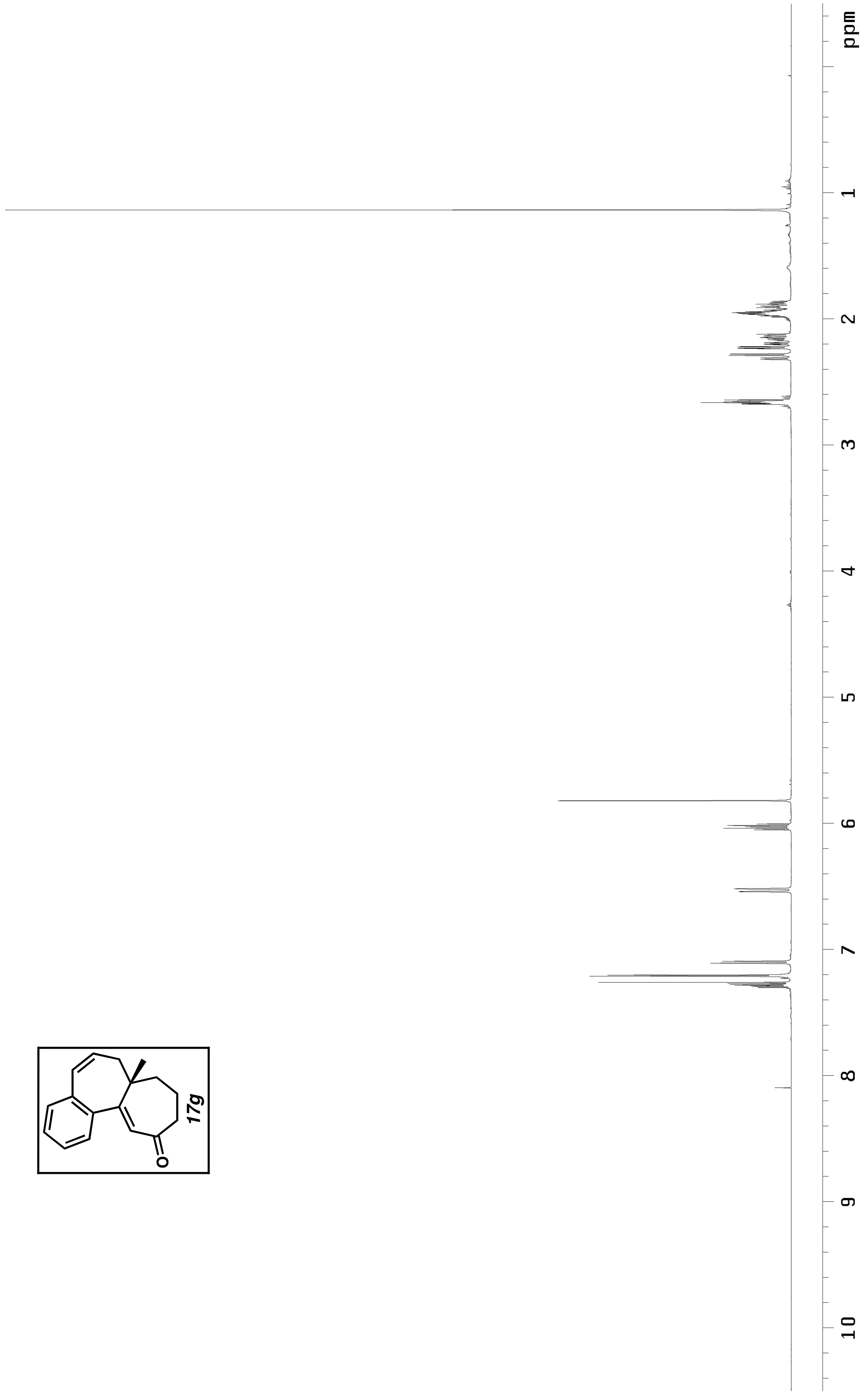


Figure SI-18A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17g**.

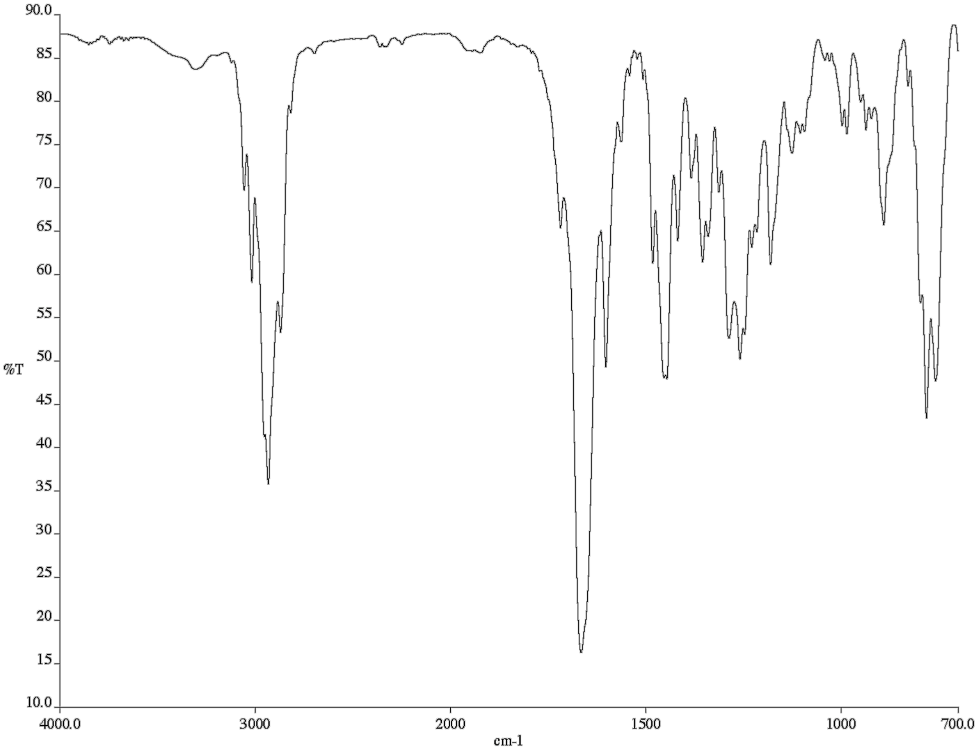


Figure SI-18B. Infrared spectrum (thin film/NaCl) of compound **17g**.

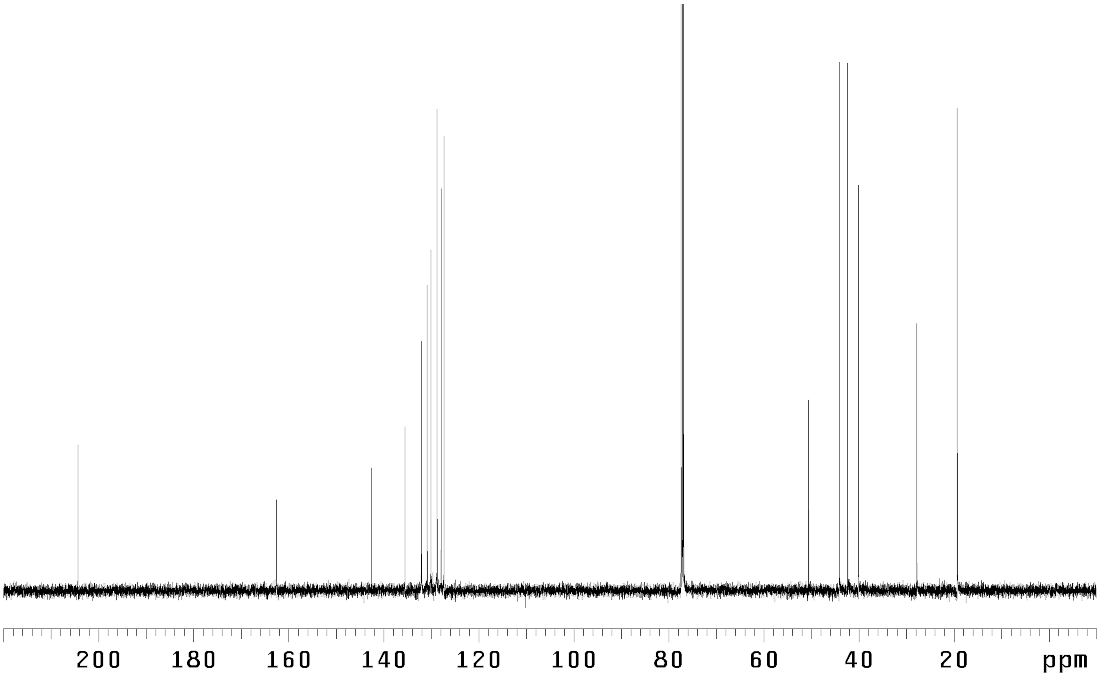


Figure SI-18C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **17g**.

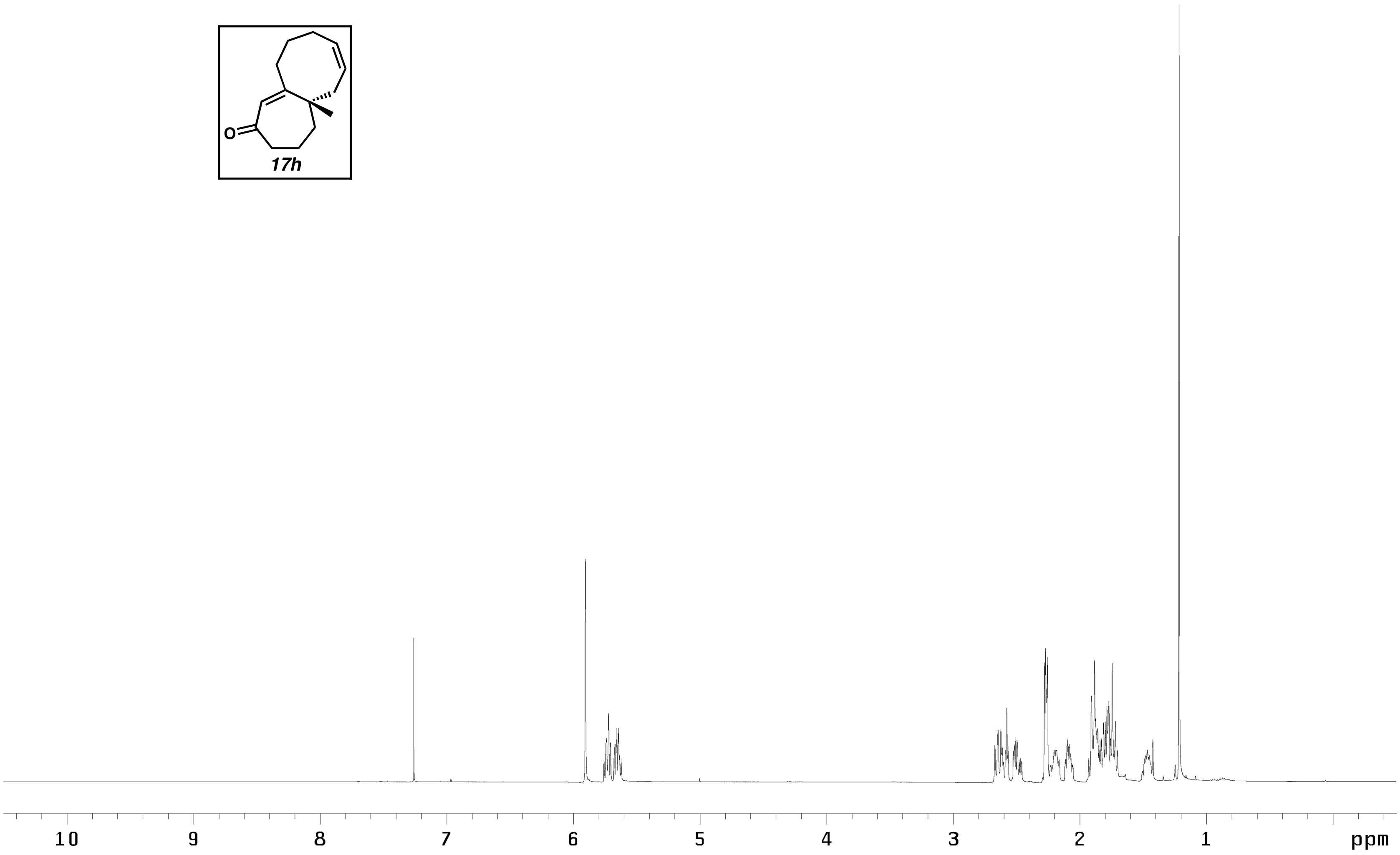


Figure SI-19A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17h**.

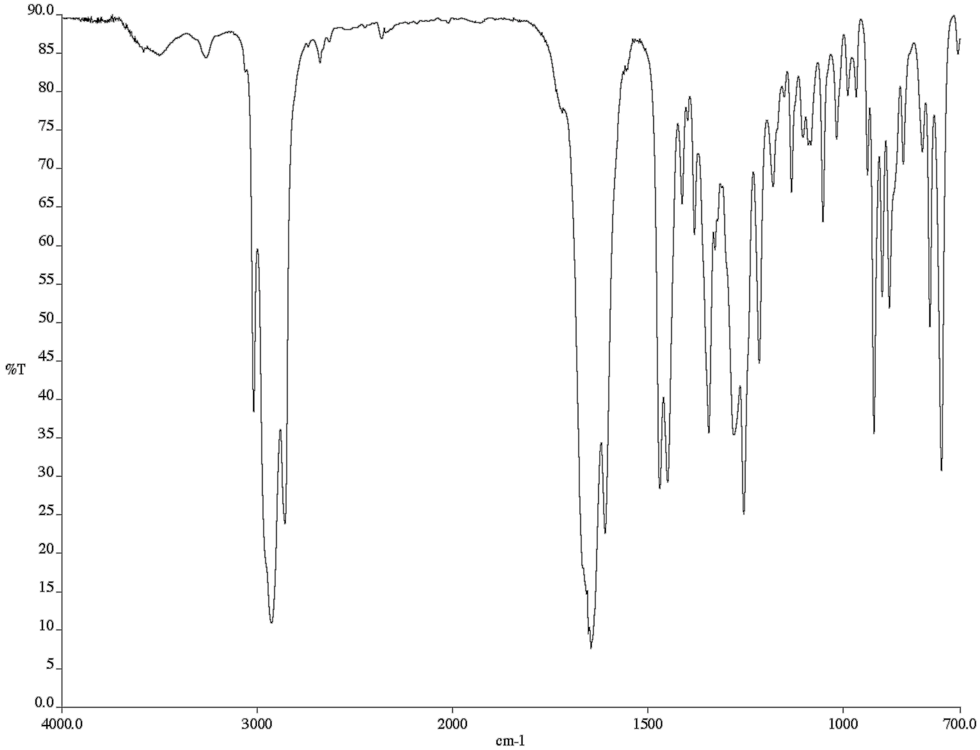


Figure SI-19B. Infrared spectrum (thin film/NaCl) of compound **17h**.

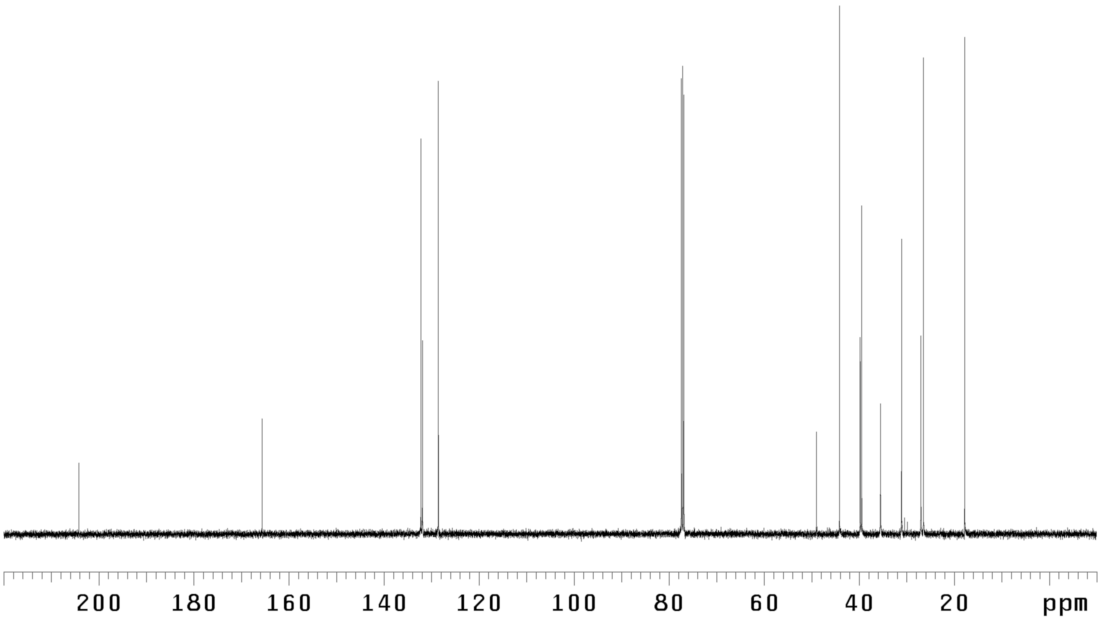


Figure SI-19C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17h**.

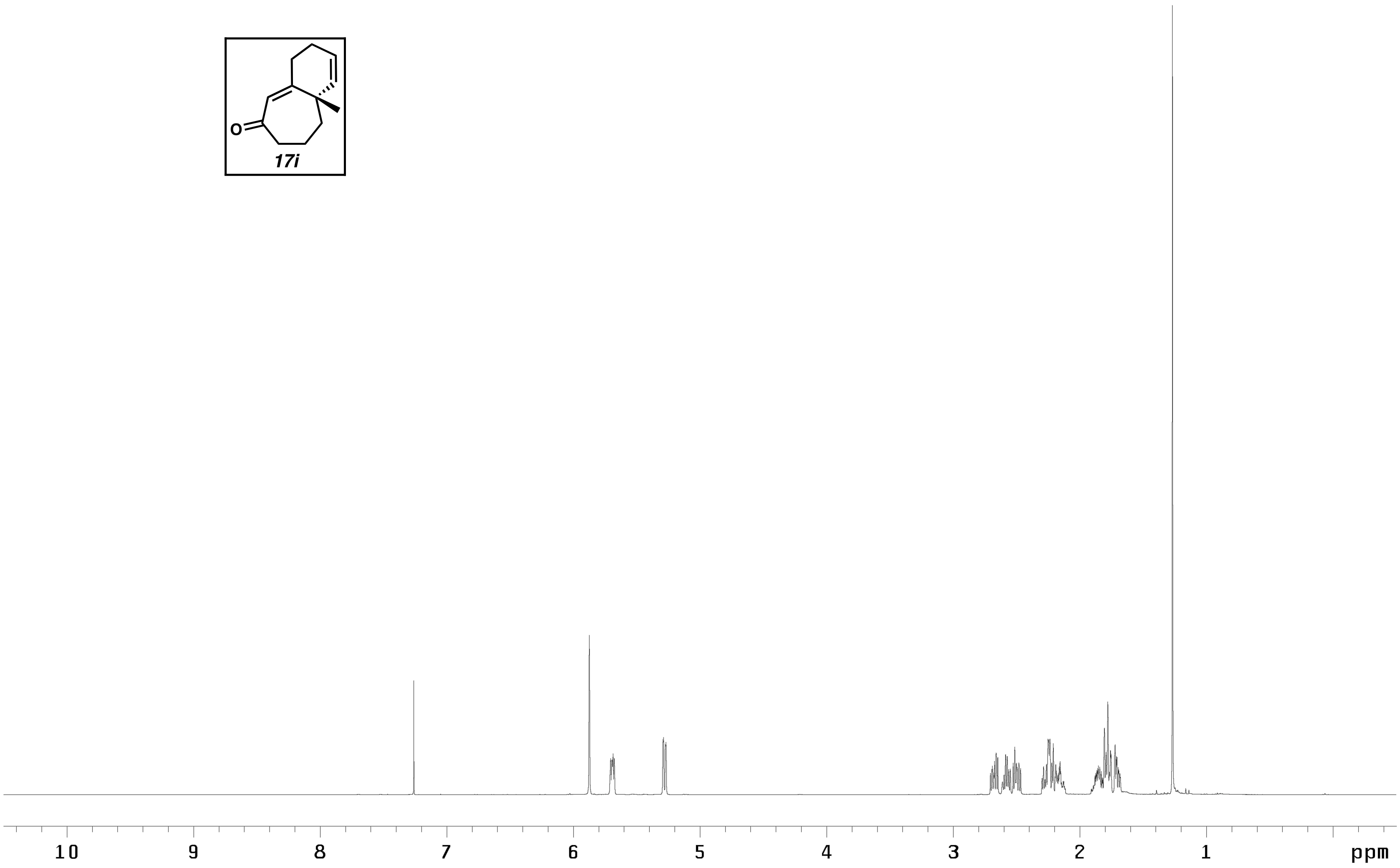


Figure SI-20A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17i**.

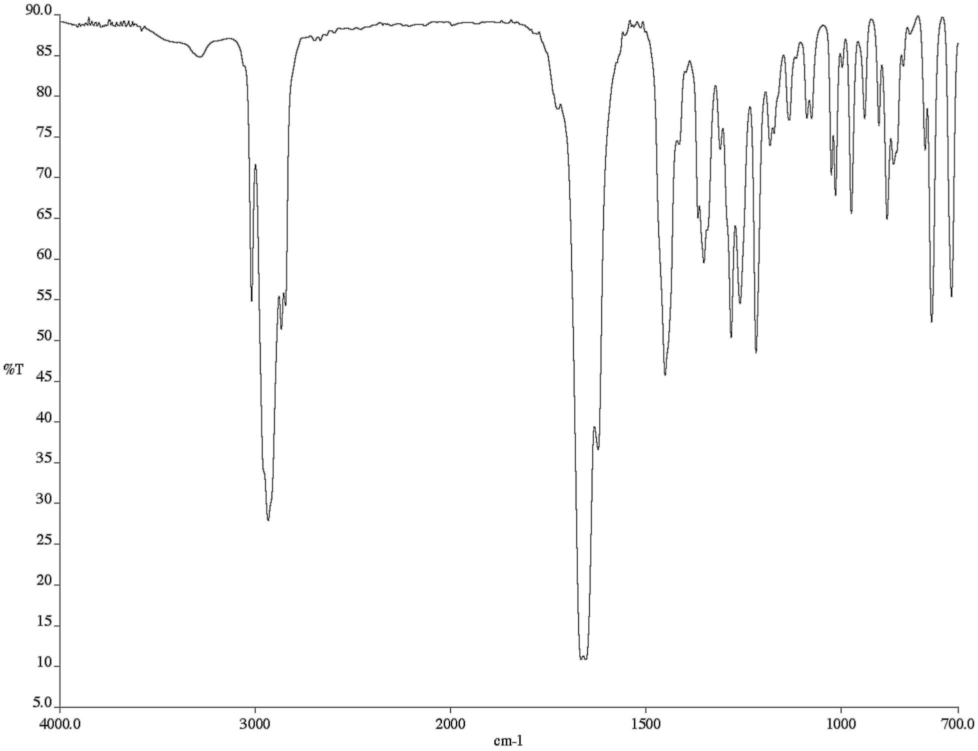


Figure SI-20B. Infrared spectrum (thin film/NaCl) of compound **17i**.

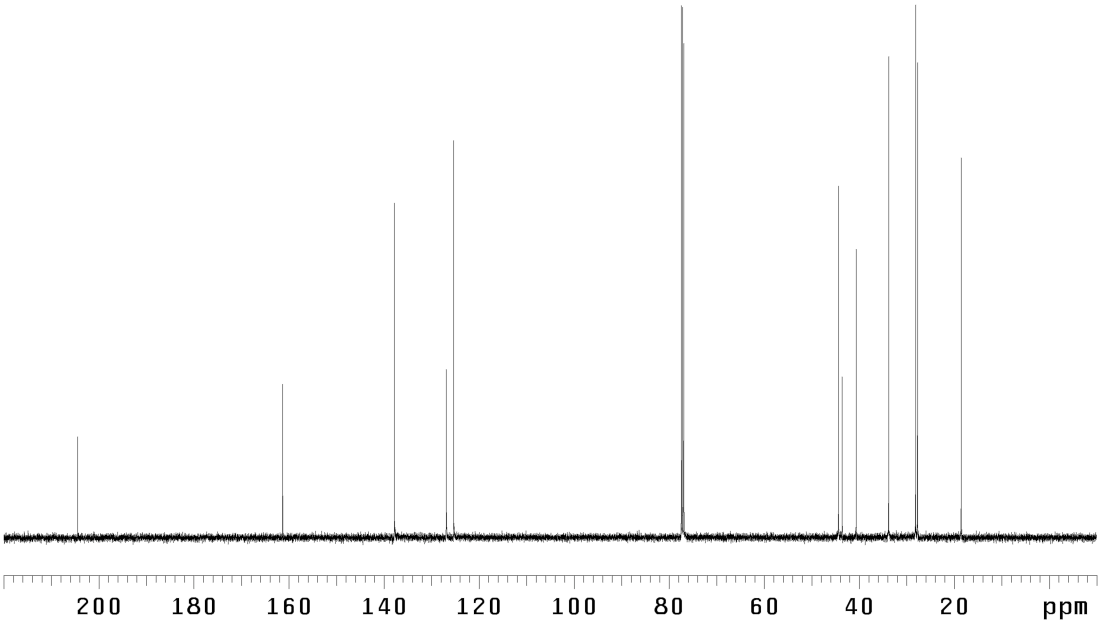


Figure SI-20C. ^{13}C NMR (125 MHz, $CDCl_3$) of compound **17i**.

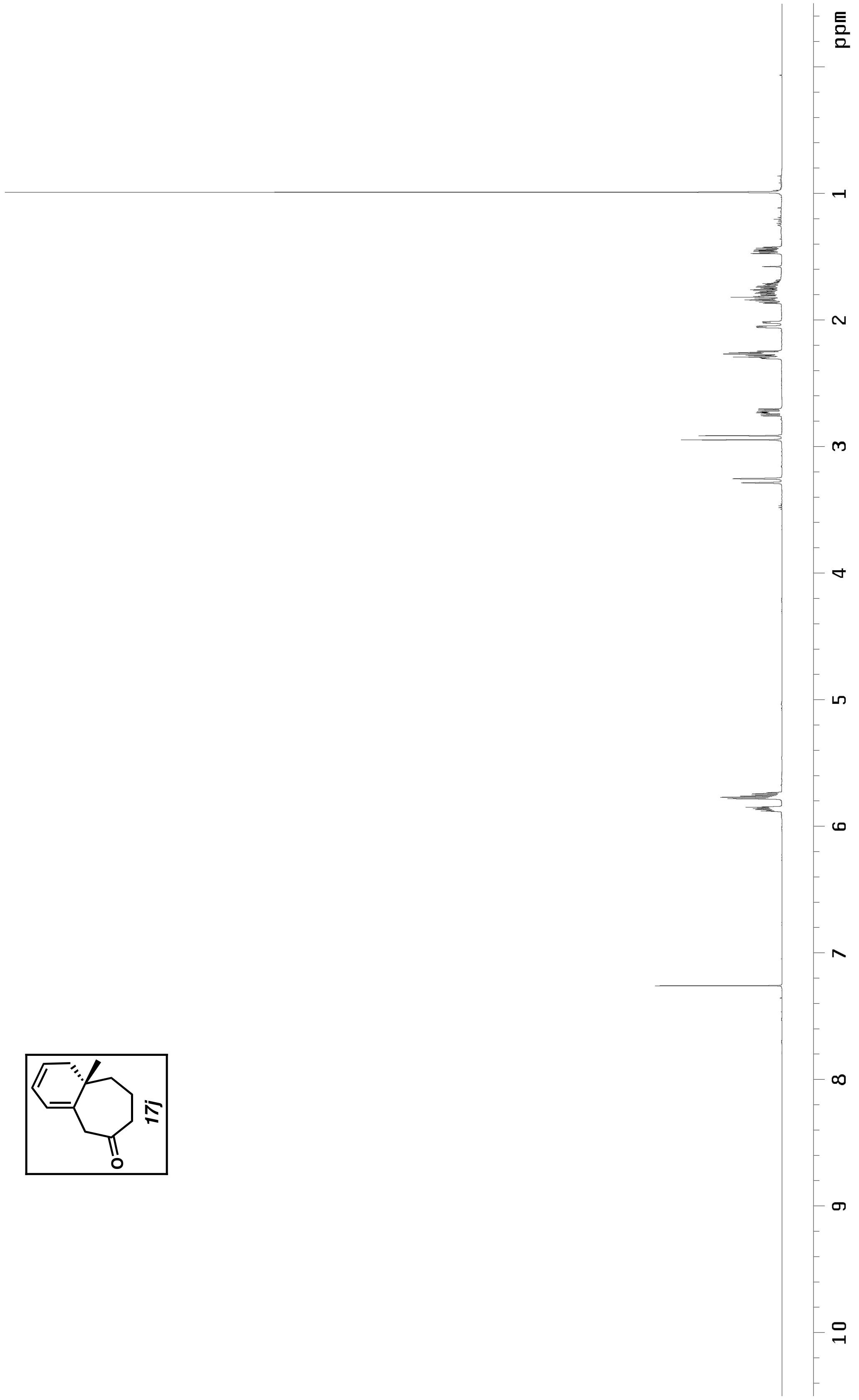


Figure SI-21A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17j**.

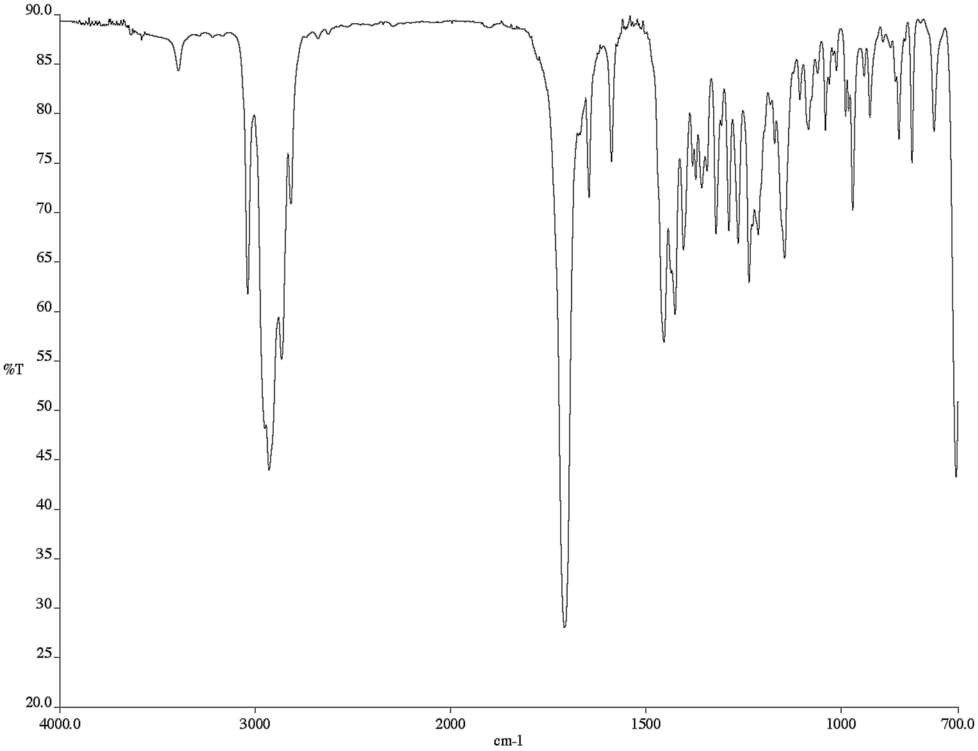


Figure SI-21B. Infrared spectrum (thin film/NaCl) of compound **17j**.

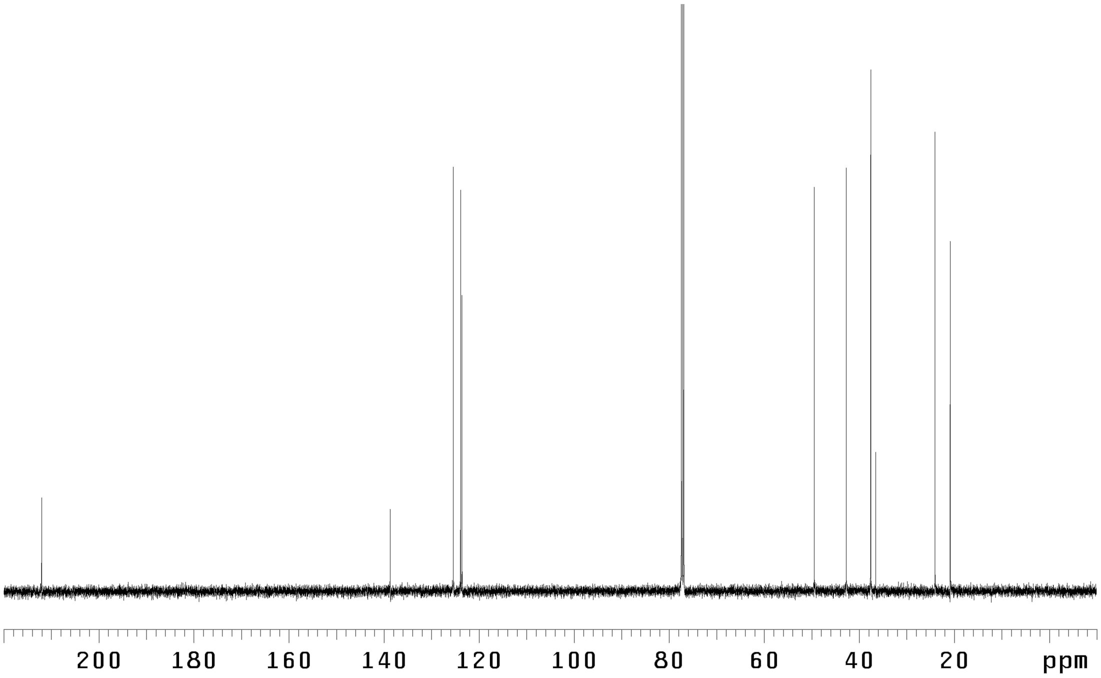


Figure SI-21C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17j**.

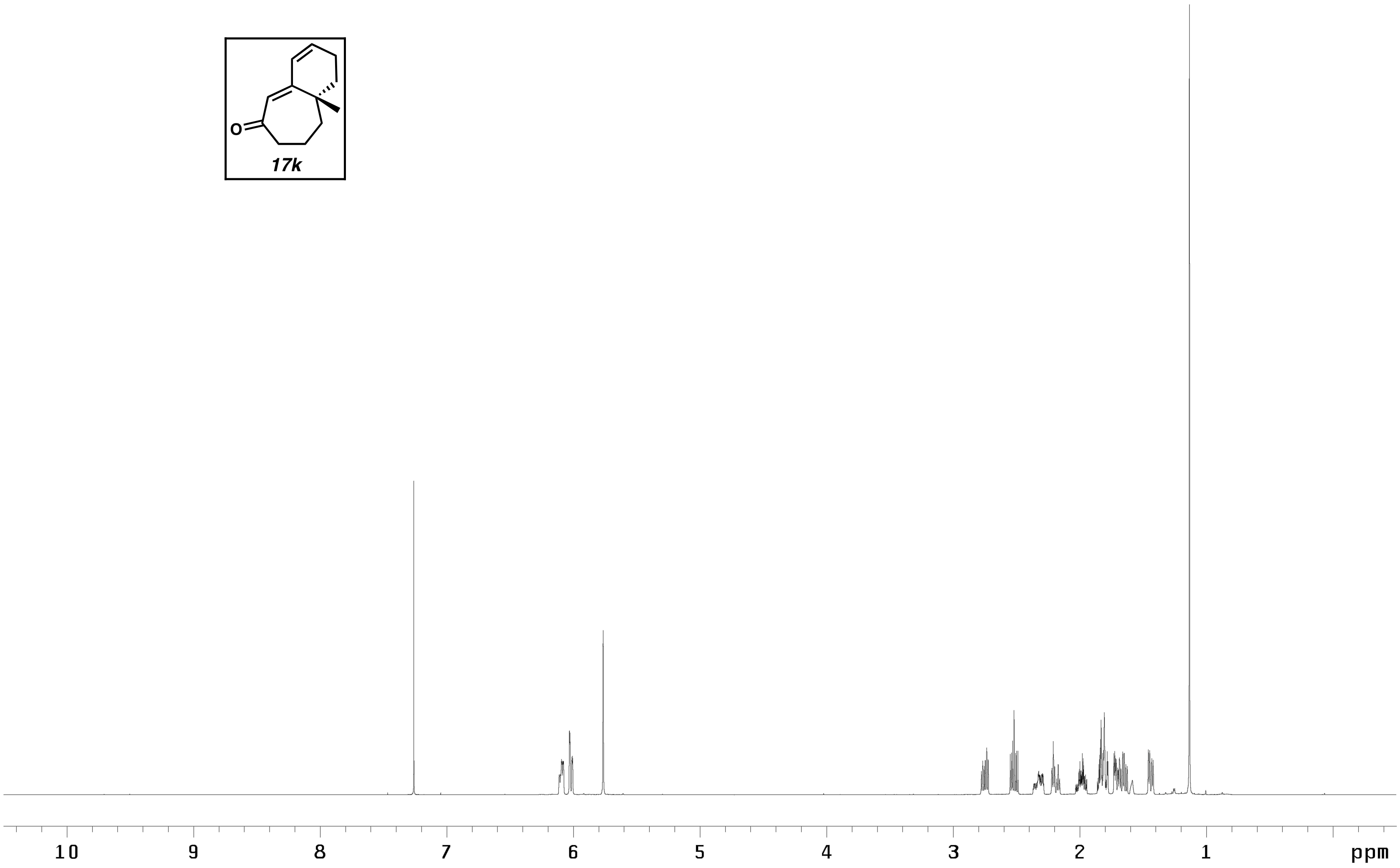


Figure SI-22A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **17k**.

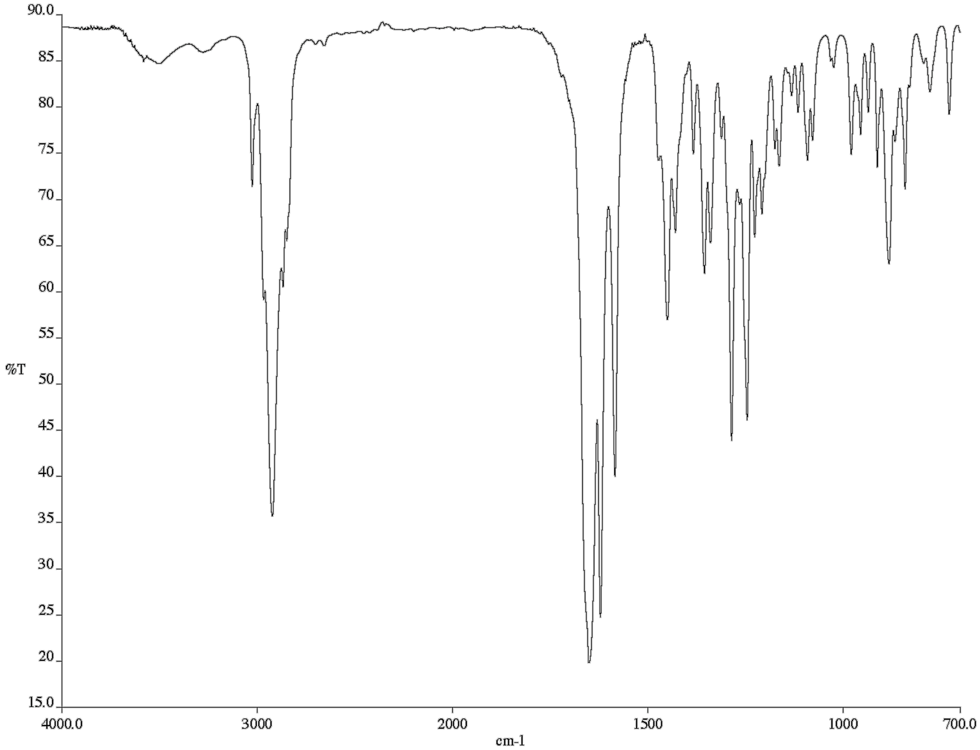


Figure SI-22B. Infrared spectrum (thin film/NaCl) of compound **17k**.

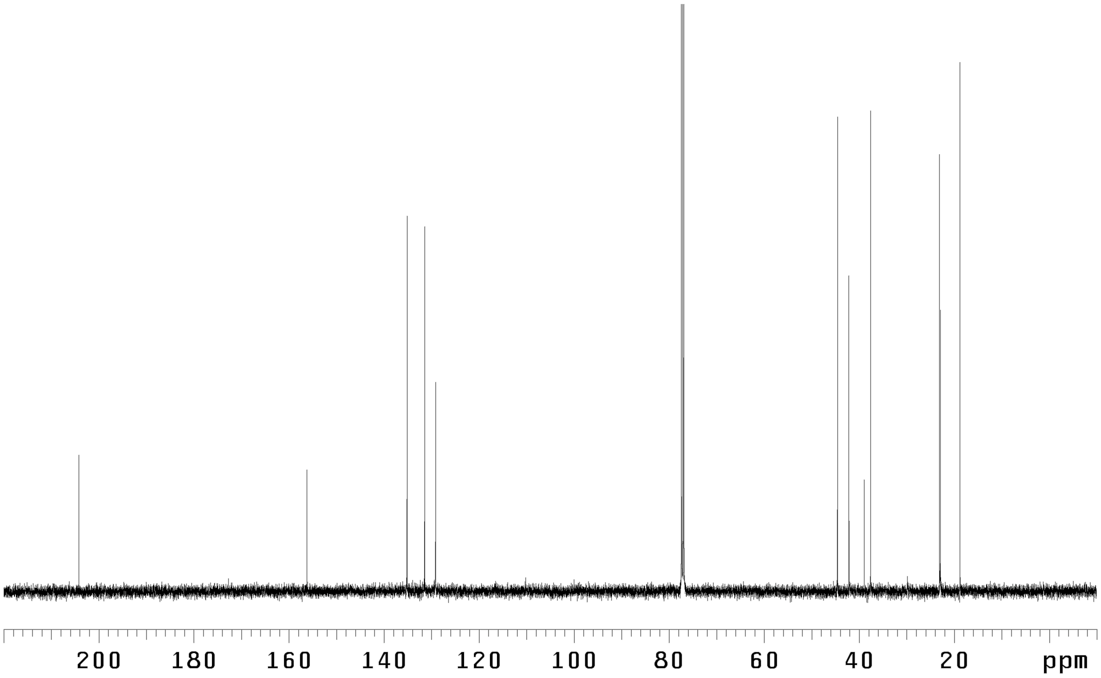


Figure SI-22C. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **17k**.

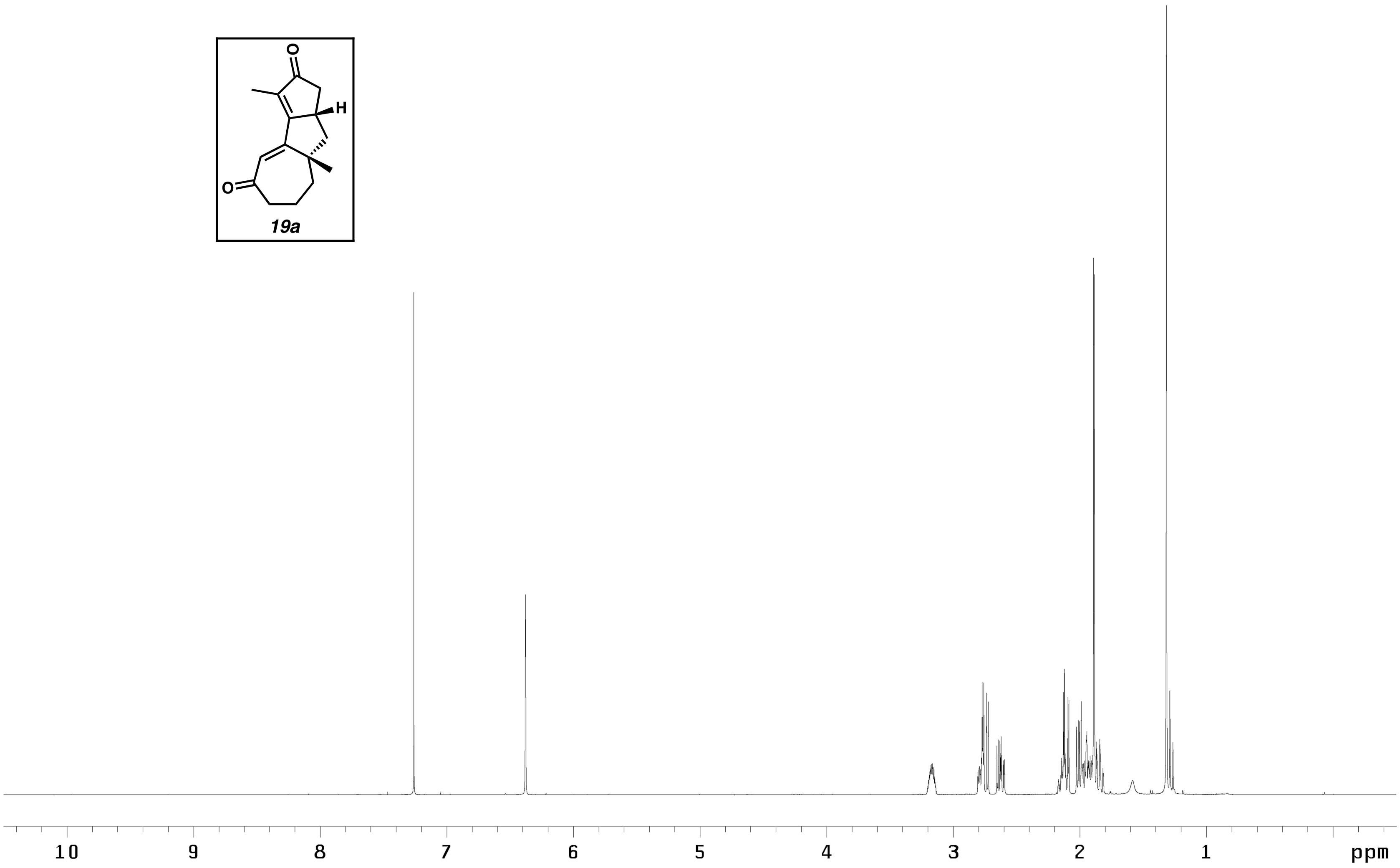
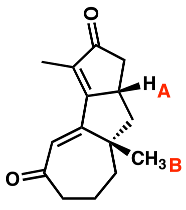


Figure SI-23A. ^{1}H NMR (500 MHz, $CDCl_3$) of compound **19a**.



19a

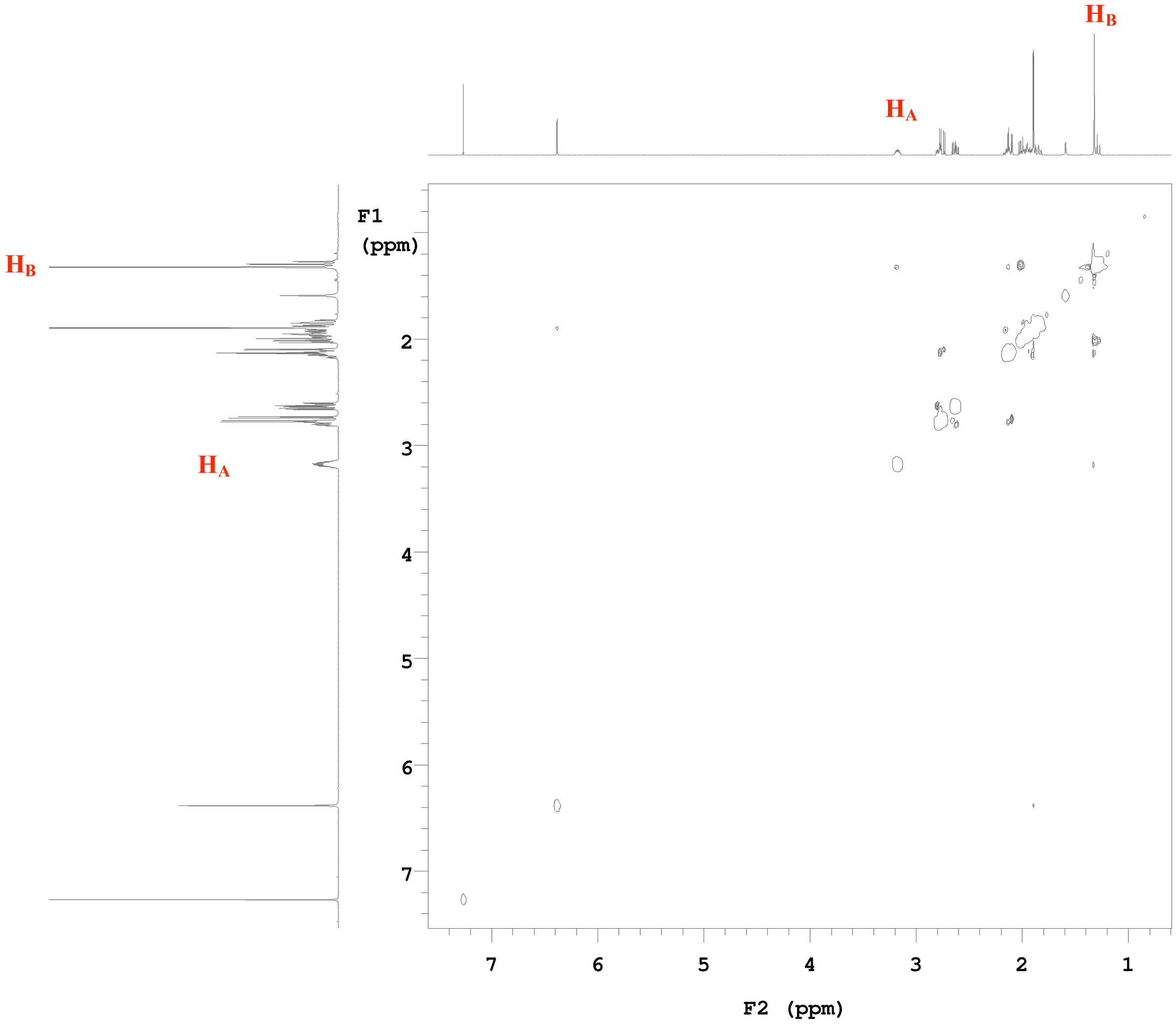


Figure SI-23B. NOESY (500 MHz, $CDCl_3$) of compound **19a**.

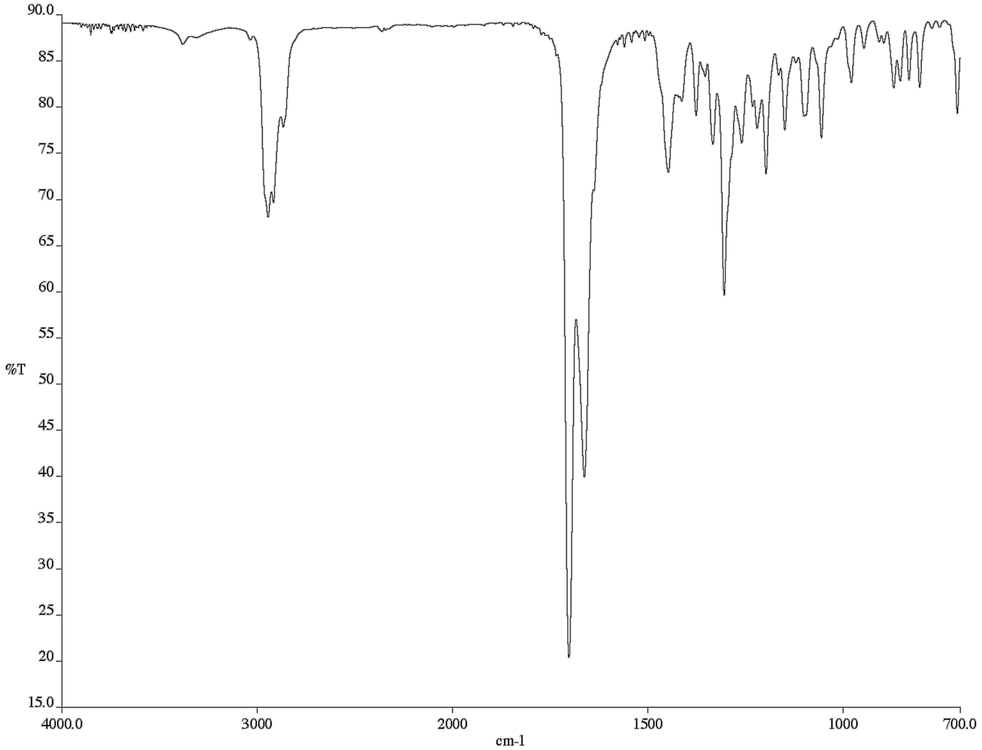


Figure SI-23C. Infrared spectrum (thin film/NaCl) of compound **19a**.

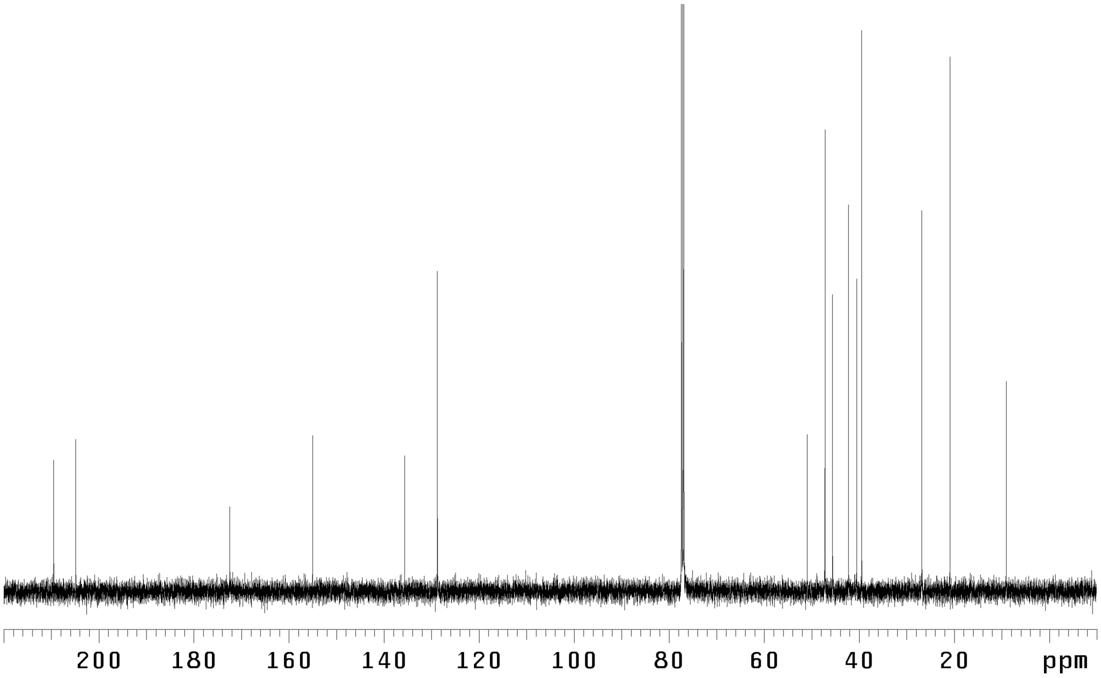


Figure SI-23D. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **19a**.

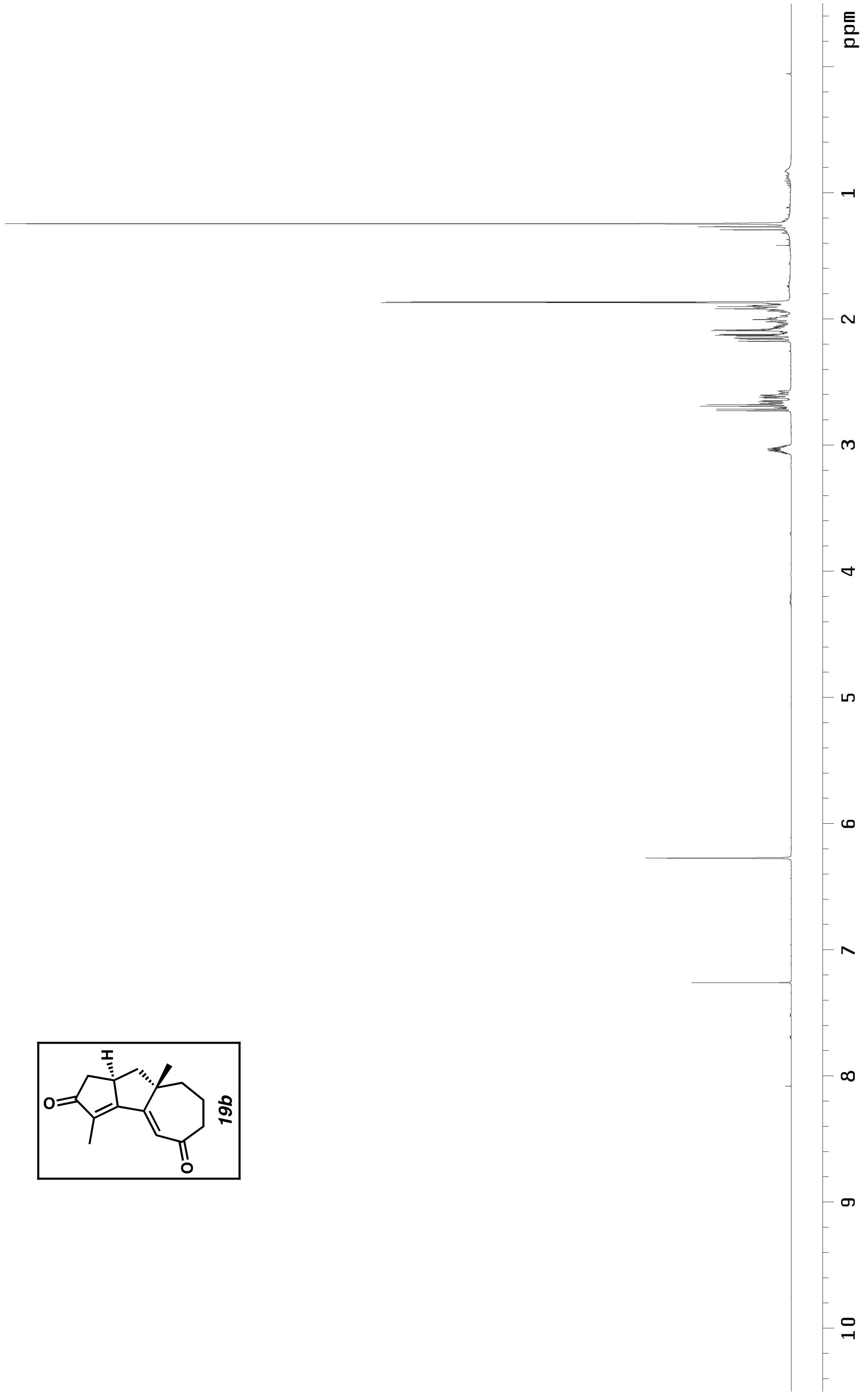


Figure SI-24A. ^{1}H NMR (500 MHz, CDCl$_3$) of compound **19b**.

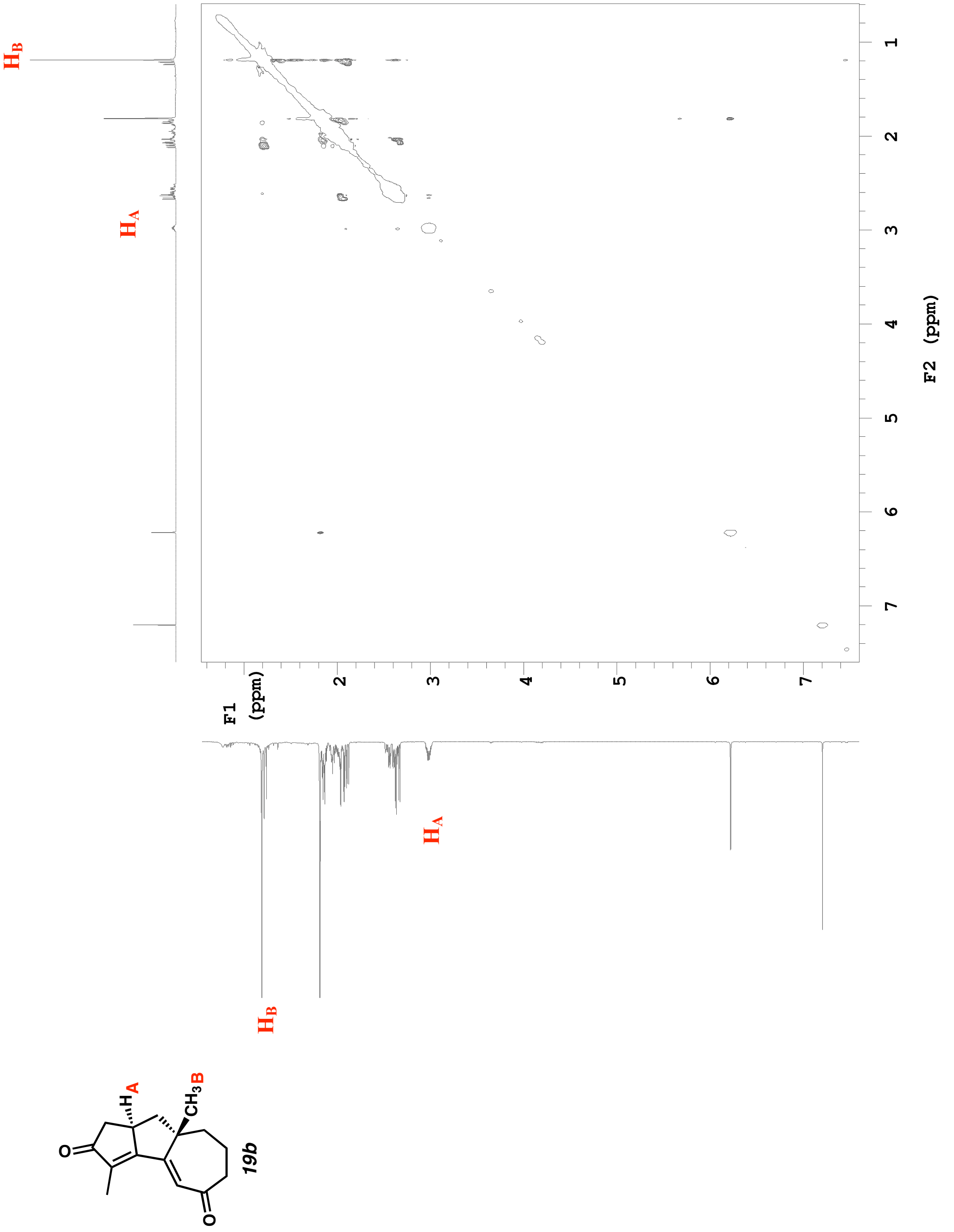


Figure SI-24B. NOESY (500 MHz, CDCl$_3$) of compound **19b**.

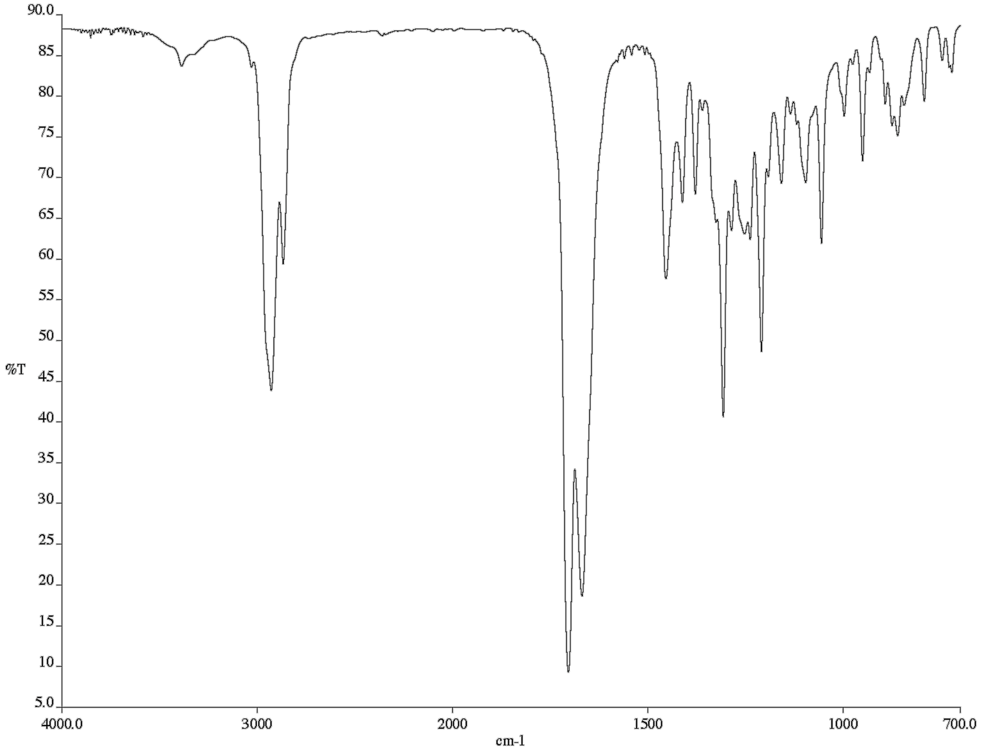


Figure SI-24C. Infrared spectrum (thin film/NaCl) of compound **19b**.

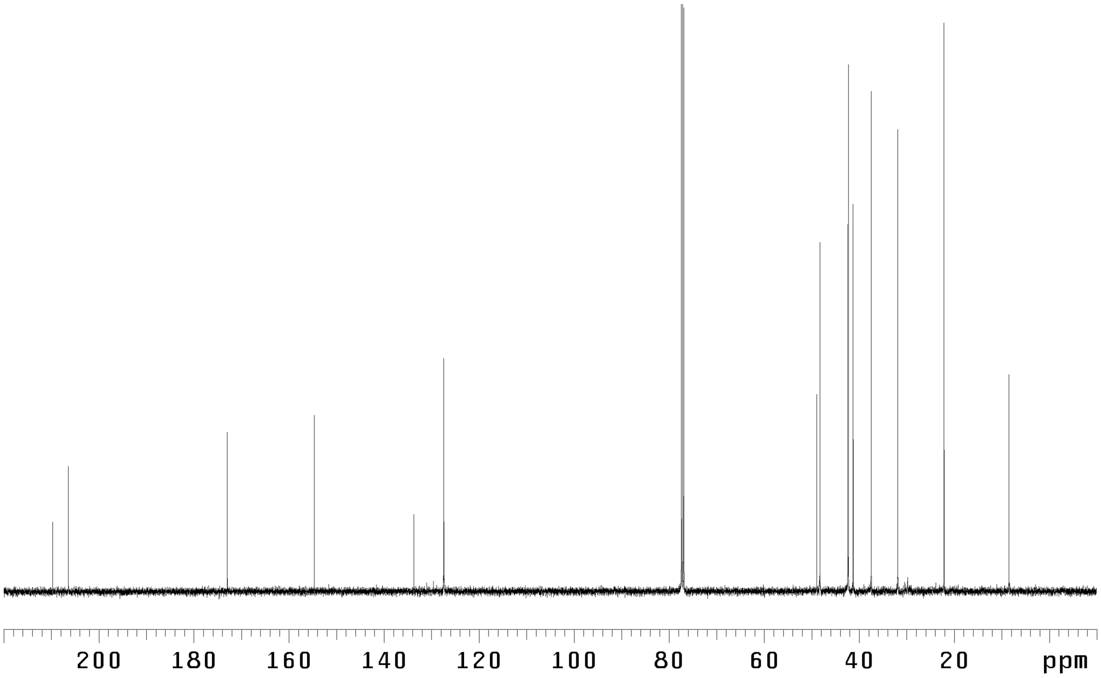


Figure SI-24D. ^{13}C NMR (125 MHz, CDCl$_3$) of compound **19b**.