Supporting Information

Unlocking Reductive Hydroalkoxylation Cascade for the Stereoselective Synthesis of Cyclic Ethers: Total Synthesis of (±)-Isolaurepan and (±)-*cis*-Lauthisan

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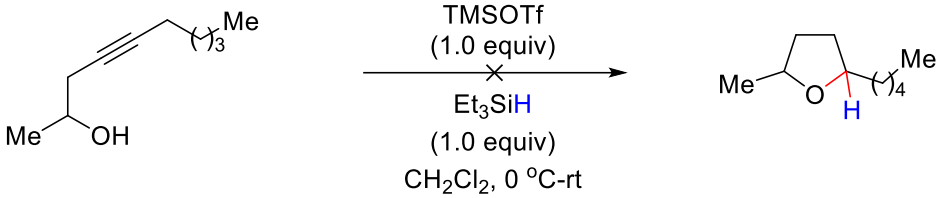
General experimental:

Melting points are recorded using dbk programmable melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.

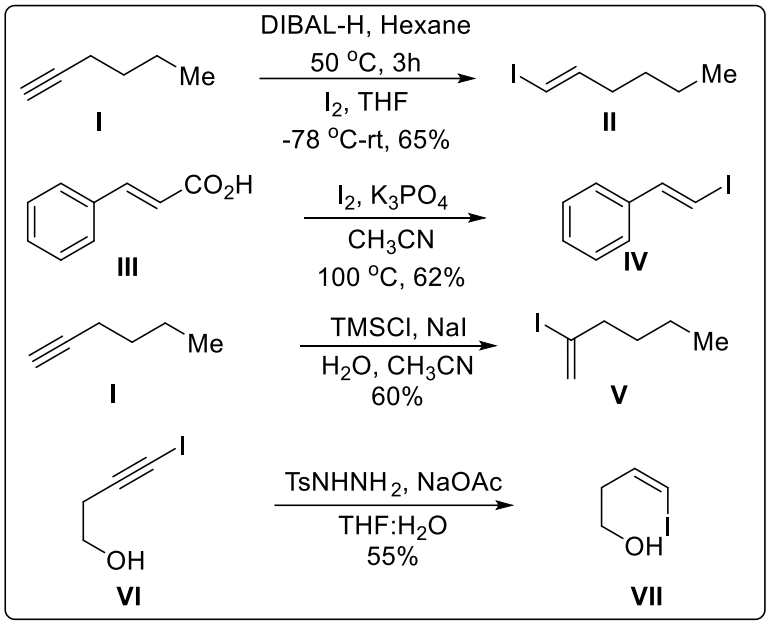
High resolution mass measurements were carried out using Maxis impact (brucker) instrument using direct inlet mode (TOF). X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and Petroleum ether were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain or vanillin strain. All small-scale dry reactions were carried out using standard syringe septum technique. Dry dichloromethane was prepared by refluxing over anhydrous P_2O_5 and distillation on to calcium hydride. Dry DMF was prepared by stirring on CaH and distillation on to molecular sieves. $BF_3{\cdot}OEt_2$, $Cu(OTf)_2$, TMSOTf, TfOH, AgOTf, CuI, and Et_3SiH were obtained from Aldrich. All other Lewis/Bronsted acids, NaH (60% dispersion in mineral oil), benzyl bromide, cyclohexene oxide, cyclopentene oxide, propargyl bromide (80% in toluene), Mg turning, DMP, $[Pd(PPh_3)_2]Cl_2$, PPh_3 are commercial reagents and were used as such without further purification. All other internal enynol was prepared using literature established protocol.[1]

(Note: In the cases where diastereomeric mixture of products was obtained, the isomers could not be separated and data for the major isomer is mentioned. In the cases where *ca*. 1:1 mixture of diastereomers was formed, all the peaks are mentioned.)

Our initial attempt for hydroalkoxylation reduction cascade:

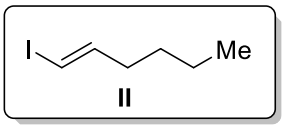


Vinyl iodide synthesis: The vinyl iodides **II-VII** were prepared using a known protocol, and their NMR spectra were matched with those of previously reported compounds.[2]



***(E)-1-iodohex-1-ene* (II):**

To a magnetically stirred solution of hexyne **I** (3.0 g, 36.52 mmol) in hexane (20 mL) at -78 °C was added DIBAL-H (27 mL, 40.17 mmol) and reflux for 3h at 50 °C. Then I_2 (11.3 g, 43.82 mmol) in THF (10 mL) was added drop wise in the reaction mixture at -78 °C and stirred for overnight at rt. The reaction mixture was poured carefully into separatory funnel containing 20% H_2SO_4 and extracted with EtOAc (3 × 15 mL), the combined organic layers were washed twice with aqueous saturated sodium thiosulfate, dried over anhyd. Na_2SO_4 and evaporation of the solvent and purification by silica gel column chromatography using Petroleum ether as eluent to furnish the requisite vinyl iodide **II** (4.8 g, 65%).



Physical appearance: Pale yellow liquid.

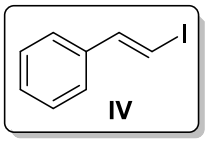
R_f: 0.6 (0.5:9.5, EtOAc:Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54-6.47 (m, 1H), 5.97 (dt, *J* = 14.0, 1.2 Hz, 1H), 2.06 (qd, *J* = 7.2, 1.2 Hz, 2H), 1.42-1.28 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 146.8 (CH), 74.4 (CH), 35.8 (CH_2), 30.6 (CH_2) 22.1 (CH_2), 13.9 (CH_3).

(E)-(2-iodovinyl)benzene) **(IV):**

To a magnetically stirred solution of cinnamic acid **III** (2.0 g, 13.49 mmol) in acetonitrile 50 mL and K_3PO_4 (2.8 g, 13.49 mmol) followed by I_2 (13.7 g, 53.96 mmol) was added successively under nitrogen and reflux at 100 ^oC for overnight under nitrogen atmosphere. The reaction mixture was poured carefully into saturated aqueous $Na_2S_2O_3$ (30 mL) and extracted with EtOAc (3 × 15 mL), the combined organic layers were washed with saturated aqueous Na_2CO_3, dried over anhyd. Na_2SO_4 and evaporation of the solvent and purification by silica gel column chromatography using Petroleum ether as eluent to furnish the requisite vinyl iodide **IV** (1.92 g, 62%).



Physical appearance: Yellow liquid.

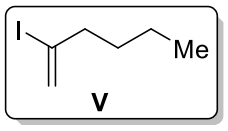
R_f: 0.6 (1:9 ethyl acetate-petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.43 (m, 1H), 7.37-7.32 (m, 5H), 6.86-6.82 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 145.2 (CH), 137.8 (C), 128.9 (2 × CH), 128.6 (CH), 126.2 (2 × CH), 77.2 (CH).

2-iodohex-1-ene **(V):**

To a magnetically stirred solution of NaI (4.38 g, 0.856 mmol) in acetonitrile 15 mL, TMSCl (4.38 g, 29.21 mmol) and H_2O (0.26 mL, 14.61 mmol) was added and the reaction mixture was stirred at room temperature for 10 minutes. Hexyne **I** (2.0 g, 24.36 mmol) was added to the reaction mixture and stirred for 1h. The reaction mixture was poured carefully into water (10 mL) and extracted with EtOAc (3 × 15 mL), the combined organic layers were washed with saturated brine, dried over anhyd. Na_2SO_4 and evaporation of the solvent and purification by silica gel column chromatography using Petroleum ether as eluent to furnish the requisite vinyl iodide **V** (1.5 g, 60%).



Physical appearance: Yellow liquid.

R_f: 0.6 (1:9 ethyl acetate-petroleum ether).

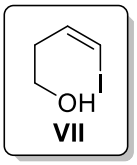
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.00 (s, 1H), 5.67 (s, 1H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.51-1.45 (m, 2H), 1.35-1.28 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 125.2 (CH_2), 112.9 (C), 45.2 (CH_2), 31.3 (CH_2) 21.4 (CH_2), 13.9 (CH_3).

2-iodohex-1-ene **(VII):**

To a magnetically stirred solution of alkynol **VI** (5.0 g, 25.51 mmol) in THF:H_2O (1:1, 100 mL), $TsNHNH_2$ (9.5 g, 51.02 mmol) and NaOAc (6.43, 76.53 mmol) was added successively and reflux for overnight. The reaction was monitored by TLC, quenched with distilled water

(50 mL) at 0 °C upon completion and stirred extra for 5 minutes. The resulting mixture was extracted with EtOAc (3 × 20 mL) and dried over anhyd. Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether as eluent furnished the requisite vinyl iodide **VII** (2.56 g, 55%).



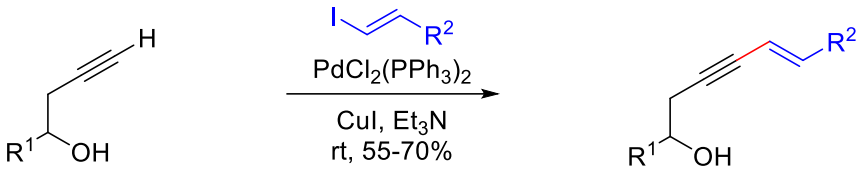
Physical appearance: Colourless liquid.

R_f: 0.2 (2:8 ethyl acetate-petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (d, *J* = 7.5 Hz, 1H), 6.26-6.22 (m, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 3.20-3.15 (m, 1H), 2.37 (q, *J* = 7.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 137.7 (CH), 84.8 (CH), 60.7 (CH_2) 38.0 (CH_2).

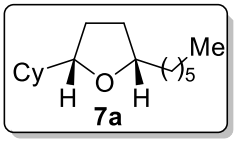
General procedure for Sonogashira Coupling:[1]



To stirred solution of terminal alkynol (1.0 equiv) and vinyl iodide (1.1 equiv) in trimethyl amine (6 ml), $Pd(PPh_3)_2Cl_2$ (0.015 equiv) and CuI (0.02 equiv) was added under N_2 atmosphere. The reaction mixture was allowed to stir overnight, the reaction mixture was quenched with aqueous sat. NH_4Cl (5 mL) and product was extracted with EtOAC (3 × 5 mL) and dried over anhyd. Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished corresponding enynol.

***(2S*,5S*)-2-cyclohexyl-5-hexyltetrahydrofuran* (7a):**

To a magnetically stirred solution of enynol **6a** (60 mg, 0.26 mmol) and Et_3SiH (81.6 µL, 0.51 mmol) in dry CH_2Cl_2 (4 mL), TMSOTf (4.6 µL, 0.03 mmol) was added dropwise at 0 °C. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion, extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhyd. Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-petroleum ether as eluent furnished THF-derivative **7a** (54 mg, 87 %) as mixture of diastereomers (dr-2:1).



Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2926, 2854, 1450, 1377, 1063, 889, 770 cm^{-1}.

Data for the major diastereomer are written:

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (quint, *J* = 6.4 Hz, 1H), 3.48 (q, *J* = 7.2 Hz, 1H), 1.98-1.78 (m, 3H), 1.72-1.69 (m, 2H), 1.65-1.46 (m, 4H), 1.44-1.07 (m, 14H), 1.00-0.89 (m, 2H), 0.86 (t, *J* = 6.8 Hz, 3H).

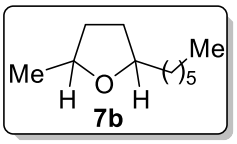
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 83.8 (CH), 79.2 (CH), 43.3 (CH), 36.2 (CH_2), 32.0 (CH_2), 31.1 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 26.7 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{31}O$ 239.2374, found 239.2374.

***(2S*,5R*)-2-hexyl-5-methyltetrahydrofuran* (7b):**

Reaction of enynol **6b** (100 mg, 0.60 mmol) with Et_3SiH (192.7 µL, 1.20 mmol) and TMSOTf (10.9 µL, 0.06 mmol) in dry CH_2Cl_2 (5 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7b** (61 mg, 60 %) as mixture of diastereomers (dr-1:1).

Physical appearance: Colourless liquid.



R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2940, 1466, 1375, 1123, 944, 824, 670 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04 (sext, *J* = 6.0 Hz, 1H), 3.95-3.85 (m, 2H), 3.74 (quint, *J* = 6.8 Hz, 1H), 2.03-1.88 (m, 4H), 1.57-1.46 (m, 2H), 1.45-1.34 (m, 8H), 1.25-1.17 (m, 20H), 0.91-0.83 (m, 6H).

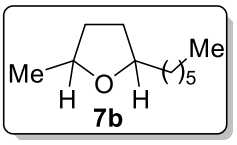
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 79.7 (CH), 78.9 (CH), 75.2 (CH), 74.5 (CH), 36.4 (2 × CH_2), 36.3 (CH_2), 34.1 (CH_2), 32.9 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 31.4 (CH_2), 29.6 (2 × CH_2), 26.3 (2 × CH_2), 22.7 (2 × CH_2), 21.5 (2 × CH_3), 14.2 (2 × CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{11}H_{22}ONa$, 193.1584, found 193.1584.

Gram scale synthesis:

***(2S*,5R*)-2-hexyl-5-methyltetrahydrofuran* (7b):**

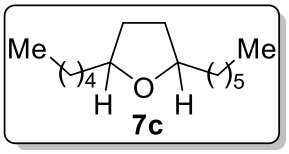
Reaction of enynol **6b** (1.00 gm, 6.017 mmol) with Et_3SiH (1.92 mL, 12.03 mmol) and TMSOTf (326 µL, 1.805 mmol) in dry CH_2Cl_2 (30 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7b** (615 mg, 61 %) as mixture of diastereomers (dr-1:1).



***(2S*,5R*)-2-hexyl-5-pentyltetrahydrofuran* (7c):**

Reaction of enynol **6c** (70 mg, 0.31 mmol) with Et_3SiH (100.3 µL, 0.63 mmol) and TMSOTf (5.6 µL, 0.03 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7c** (60 mg, 85%) as a mixture of diastereomers (dr-1:1).

Physical appearance: Colourless liquid.



R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2930, 2864, 1466, 1374, 1090, 727 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (quint, *J* = 6.4 Hz, 1H), 3.75 (quint, *J* = 6.4 Hz, 3H), 1.99-1.95 (m, 2H), 1.92-1.85 (m, 3H), 1.59-1.53 (m, 5H), 1.47-1.26 (m, 34H), 0.88-0.84 (m, 12H).

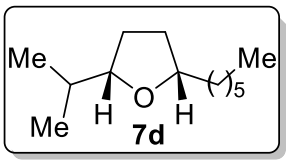
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 79.4 (CH), 78.8 (CH), 36.3 (2 × CH_2), 32.1 (CH_2), 31.2 (2 × CH_2), 29.6 (2 × CH_2), 26.3 (CH_2), 26.1 (CH_2), 22.7 (2 × CH_2), 14.2 (CH_3), 14.1 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. for $C_{15}H_{31}O$, 227.2373, found 227.2373.

***(2S*,5S*)-2-hexyl-5-isopropyltetrahydrofuran* (7d):**

Reaction of enynol **6d** (60 mg, 0.31 mmol) with Et_3SiH (98 μL, 0.628 mmol) and TMSOTf (5.5 μL, 0.031 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7d** (49 mg, 80%) as a mixture of diastereomers (dr-2:1)

Physical appearance: Colourless liquid.



R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2956, 2872, 1467, 1382, 1072, 820, 667 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (quint, *J* = 6.5 Hz, 1H), 3.49 (q, *J* = 7.0 Hz, 1H), 1.94-1.88 (m, 1H), 1.85-1.78 (m, 1H), 1.68-1.47 (m, 3H), 1.46-1.37 (m, 3H), 1.27-1.26 (m, 7H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.87-0.82 (m, 6H).

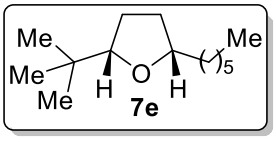
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 84.8 (CH), 79.4 (CH), 36.2 (CH_2), 33.3 (CH), 32.0 (CH_2), 31.3 (CH_2), 29.6 (CH_2), 28.4 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 19.5 (CH_3), 18.5 (CH_3), 14.2 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{13}H_{26}ONa$ 221.1902, found 221.1902.

***(2S*,5S*)-2-(tert-butyl)-5-hexyltetrahydrofuran* (7e):**

Reaction of enynol **6e** (60 mg, 0.29 mmol) with Et_3SiH (91 μL, 0.58 mmol) and TMSOTf (5.2 μL, 0.029 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7e** (52 mg, 85%) as a single *cis* diastereomer (dr ≥19:1).

Physical appearance: Colourless liquid.



R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2929, 2858, 1466, 1362, 1073, 824, 670 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (quint, *J* = 6.4 Hz, 1H), 3.52 (t, *J* = 7.2 Hz, 1H), 1.94-1.85 (m, 1H), 1.76-1.67 (m, 1H), 1.64-1.52 (m, 2H), 1.41-1.35 (m, 2H), 1.31-1.25 (m, 8H), 0.89-0.86 (m, 12H).

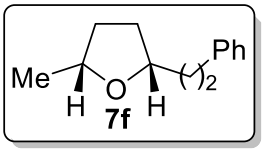
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 87.3 (CH), 79.3 (CH), 36.0 (CH_2), 33.6 (C), 32.0 (CH_2), 31.5 (CH_2), 29.6 (CH_2), 26.2 (2 × CH_2), 26.0 (3 × CH_3), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{14}H_{29}O$ 213.2216, found 213.2216.

***(2R*,5S*)-2-methyl-5-phenethyltetrahydrofuran* (7f):[3]**

Reaction of enynol **6f** (80 mg, 0.43 mmol) with Et_3SiH (68.6 μL, 0.86 mmol) and TMSOTf (7.7 μL, 0.043 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7f** (60 mg, 75%) as a mixture of diastereomers (dr-2:1).

Physical appearance: Colourless liquid.



R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2941, 1717, 1454, 1375, 1088, 884, 750, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.6 Hz, 1H), 7.24-7.17 (m, 4H), 3.98 (sext, *J* = 6.0 Hz, 1H), 3.85 (quint, *J* = 6.4 Hz, 1H), 2.82-2.69 (m, 2H), 2.10-2.02 (m, 1H), 2.01-1.90 (m, 2H), 1.83-1.74 (m, 1H), 1.61-1.48 (m, 2H), 1.28 (t, *J* = 6.0 Hz, 3H).

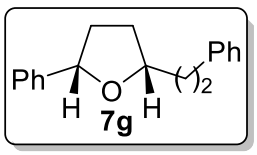
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 142.4 (C), 128.5 (2 × CH), 128.4 (2 × CH), 125.8 (CH), 78.9 (CH), 75.4 (CH), 38.0 (CH_2), 33.0 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 21.6 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{13}H_{19}O$, 191.1433, found 191.1432.

***(2S*,5S*)-2-phenethyl-5-phenyltetrahydrofuran* (7g):[4]**

Reaction of enynol **6g** (50 mg, 0.20 mmol) with Et_3SiH (64 μL, 0.40 mmol) and TMSOTf (3.6 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7g** (36 mg, 70%) as a mixture of diastereomers (dr-1.3:1).

Physical appearance: Colourless liquid.



R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 3020, 2934, 1495, 1453, 1054, 946, 754, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 7.41-7.21 (m, 10H), 4.92 (t, *J* = 7.2 Hz, 1H), 4.08 (quint, *J* = 6.8 Hz, 1H), 2.90-2.72 (m, 2H), 2.39-2.18 (m, 1H), 2.17-2.03 (m, 2H), 1.97-1.90 (m, 2H), 1.75-1.67 (m, 1H).

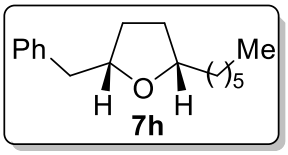
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 144.0 (C), 143.6 (C), 128.6 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.2 (CH), 125.9 (2 × CH), 125.7 (CH), 81.0 (CH), 79.3 (CH), 37.9 (CH_2), 34.6 (CH_2), 32.7 (CH_2), 31.4 (CH_2).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{18}H_{20}ONa$, 275.1408, found 275.1408.

***(2S*,5S*)-2-benzyl-5-hexyltetrahydrofuran* (7h):**

Reaction of enynol **6h** (60 mg, 0.25 mmol) with Et_3SiH (79.2 μL, 0.50 mmol) and TMSOTf (4.4 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7h** (52 mg, 85%) as a mixture of diastereomers (dr-1.3:1).

Physical appearance: Colourless liquid.



7h

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2929, 2860, 1776, 1732, 1455, 1179, 1078, 750, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.27 (m, 2H), 7.24-7.20 (m, 3H), 4.06 (quint, *J* = 6.5 Hz, 1H), 3.83 (quint, *J* = 6.5 Hz, 1H), 2.98 (d, *J* = 6.0 Hz, 1H), 2.73 (d, *J* = 7.5 Hz, 1H), 1.94-1.84 (m, 2H), 1.69-1.56 (m, 2H), 1.49-1.31 (m, 3H), 1.25-1.02 (m, 7H), 0.91-0.89 (m, 3H).

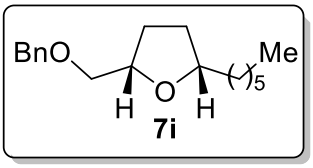
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 139.1 (C), 129.5 (2 × CH), 128.3 (2 × CH), 126.2 (CH), 80.0 (CH), 79.8 (CH), 42.6 (CH_2), 36.4 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 30.6 (CH_2), 29.6 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{17}H_{27}O$, 247.2053, found 247.2053.

***(2S*,5S*)-2-((benzyloxy)methyl)-5-hexyltetrahydrofuran* (7i):**

Reaction of enynol **6i** (100 mg, 0.37 mmol) with Et_3SiH (117.2 μL, 0.73 mmol) and TMSOTf (6.6 μL, 0.04 mmol) in dry CH_2Cl_2 (5 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7i** (86 mg, 85%) as a mixture of diastereomers (dr-1.3:1).

Physical appearance: Colourless liquid.



7i

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2927, 2860, 1454, 1098, 1261, 737, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.32 (m, 4H), 7.29-7.26 (m, 1H), 4.58 (q, *J* = 12.5 Hz, 2H), 4.07 (quint, *J* = 6.0 Hz, 1H), 3.84 (quint, *J* = 6.0 Hz, 1H), 3.51-3.44 (m, 2H), 2.02-1.97 (m, 1H), 1.95-1.89 (m, 1H), 1.70-1.58 (m, 2H), 1.52-1.38 (m, 3H), 1.36-1.29 (m, 7H), 0.89 (t, *J* = 7.0 Hz, 3H).

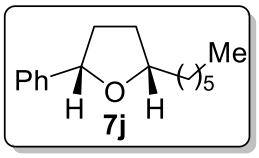
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 138.6 (C), 128.4 (2 × CH), 127.8 (2 × CH), 127.6 (CH), 80.2 (CH), 77.9 (CH), 73.4 (CH_2), 73.2 (CH_2), 36.0 (CH_2), 31.9 (CH_2), 30.9 (CH_2), 29.5 (CH_2), 28.3 (CH_2), 26.3 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{18}H_{28}O_2Na$, 299.1983, found 299.1983.

***(2S*,5S*)-2-hexyl-5-phenyltetrahydrofuran* (7j):**

Reaction of enynol **6j** (50 mg, 0.22 mmol) with Et_3SiH (70.2 μL, 0.44 mmol) and TMSOTf (3.9 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7j** (38 mg, 74%) as a mixture of diastereomers (dr-2.1:1).

Physical appearance: Colourless liquid.



7j

R_f: 0.6 (1:19, EtOAc: Petroleum ether).

IR (neat): 2929, 2861, 1455, 1052, 758, 699 cm^{-1}.

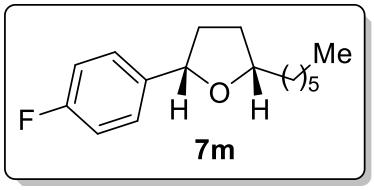
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.25 (m, 5H), 4.89 (t, *J* = 7.5 Hz, 1H), 4.03 (quint, *J* = 6.5 Hz, 1H), 2.32-2.27 (m, 1H), 2.11-2.04 (m, 1H), 1.91-1.74 (m, 2H), 1.68-1.52 (m, 2H), 1.51-1.39 (m, 1H), 1.38-1.29 (m, 7H), 0.92 (t, *J* = 5.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 143.8 (C), 128.3 (2 × CH), 127.2 (CH), 125.9 (2 × CH), 80.9 (CH), 80.2 (CH), 36.2 (CH_2), 34.6 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. for $C_{16}H_{25}O$ 233.1899, found 233.1899.

***(2S*,5S*)-2-(4-fluorophenyl)-5-hexyltetrahydrofuran* (7m):**

Reaction of enynol **6m** (50 mg, 0.20 mmol) with Et_3SiH (64.8 μL, 0.41 mmol) and TMSOTf (3.6 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7m** (25 mg, 50%) as a mixture of diastereomers (dr-1.5:1).



7m

Physical appearance: Yellow liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2947, 2929, 1604, 1466, 1501, 1225, 1051, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 2H), 7.02-6.98 (m, 2H), 4.83 (t, *J* = 7.2 Hz, 1H), 3.99 (quint, *J* = 6.4 Hz, 1H), 2.32-2.22 (m, 1H), 2.17-2.01 (m, 1H), 1.85-1.71 (m, 2H), 1.64-1.39 (m, 4H), 1.39-1.25 (m, 6H), 0.89-0.87 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 162.2 (d, *J* = 245.0 Hz, C), 139.4 (d, *J* = 4.0 Hz, C), 127.6 (d, *J* = 8.0 Hz, 2 × CH), 115.1 (d, *J* = 21.0 Hz, 2 × CH), 80.3 (CH), 79.7 (CH), 36.2 (CH_2), 34.7 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

^{19}F NMR (377 MHz, $CDCl_3$): δ -116.0 (t, *J* = 3.8 Hz).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{24}FO$, 251.1806, found 251.1808.

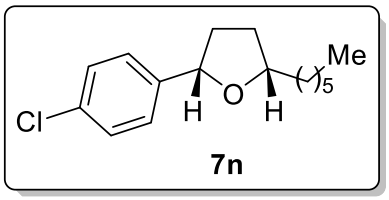
***(2S*,5S*)-2-(4-chlorophenyl)-5-hexyltetrahydrofuran* (7n):**

Reaction of enynol **6n** (50 mg, 0.22 mmol) with Et_3SiH (70.7 µL, 0.44 mmol) and TMSOTf (3.9 µL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7n** (37 mg, 73%) as a mixture of diastereomers (dr-1.6:1).

Physical appearance: Colourless liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2930, 1718, 1594, 1466, 1273, 1092, 1015, 834, 761 cm^{-1}.



7n

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.25 (m, 4H), 4.84 (t, *J* = 7.0 Hz, 1H), 4.00 (quint, *J* = 6.5 Hz, 1H), 2.29-2.25 (m, 1H), 2.12-2.03 (m, 1H), 1.80-1.45 (m, 2H), 1.39-1.26 (m, 4H), 0.91-0.86 (m, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 142.3 (C), 132.7 (C), 128.5 (2 × CH), 127.3 (2 × CH), 80.4 (CH), 80.1 (CH), 36.1 (CH_2), 34.6 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{24}OCl$, 267.1499, found 267.1499.

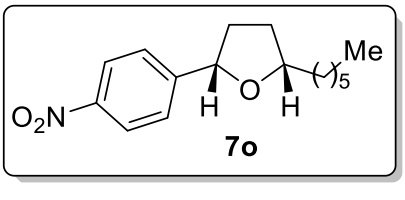
***(2S*,5S*)-2-hexyl-5-(4-nitrophenyl)tetrahydrofuran* (7o):**

Reaction of enynol **6o** (50 mg, 0.22 mmol) with Et_3SiH (70.9 µL, 0.44 mmol) and TMSOTf (3.9 µL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7o** (38 mg, 76%) as a mixture of diastereomers (dr-1.7:1).

Physical appearance: Colourless liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2930, 2850, 1723, 1604, 1522, 1465, 1350, 1064, 853, 750 cm^{-1}.



7o

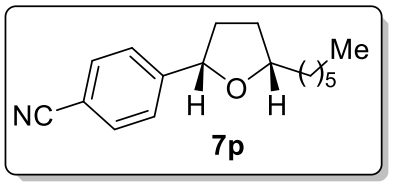
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 4.96 (t, *J* = 6.8 Hz, 1H), 4.09 (quint, *J* = 6.8 Hz, 1H), 2.81-2.32 (m, 1H), 2.10-2.07 (m, 1H), 1.83-1.53 (m, 5H), 1.39-1.24 (m, 7H), 0.91-0.86 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 152.1 (C), 147.2 (C), 126.5 (2 × CH), 123.7 (2 × CH), 80.0 (CH), 79.8 (CH), 36.1 (CH_2), 34.7 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 29.5 (CH_2), 26.4 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{16}H_{23}NO_3Na$, 300.1579, found 300.1579.

***4-((2S*,5S*)-5-hexyltetrahydrofuran-2-yl)benzonitrile* (7p):**

Reaction of enynol **6p** (50 mg, 0.20 mmol) with Et_3SiH (63 μL, 0.39 mmol) and TMSOTf (3.57 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7p** (39 mg, 78%) as a mixture of diastereomers (dr-1.7:1).



7p

Physical appearance: Yellow liquid.

R_f: 0.65 (1:9, EtOAc: Petroleum ether).

IR (neat): 2960, 2929, 2857, 2227, 1464, 1065, 833, 756 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.90 (t, *J* = 7.0 Hz, 1H), 4.03 (quint, *J* = 7.0 Hz, 1H), 2.37-2.30 (m, 1H), 2.11-2.03 (m, 1H), 1.78-1.66 (m, 2H), 1.62-1.41(m, 2H), 1.35-1.30 (m, 8H), 0.89 (t, *J* = 6.5 Hz, 3H).

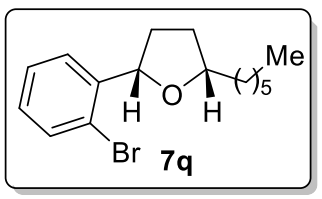
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 149.5 (C), 132.2 (2 × CH), 126.4 (2 × CH), 119.1 (C), 110.8 (C), 80.7 (CH), 79.9 (CH), 36.0 (CH_2), 34.6 (CH_2), 31.9 (CH_2), 31.3 (CH_2), 29.5 (CH_2), 26.3 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{17}H_{24}NO$ 258.1852, found 258.1851.

***(2S*,5S*)-2-(2-bromophenyl)-5-hexyltetrahydrofuran* (7q):**

Reaction of enynol **6q** (60 mg, 0.20 mmol) with Et_3SiH (62.3 μL, 0.39 mmol) and TMSOTf (4.3 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7q** (46 mg, 75%) as a mixture of diastereomers (dr-1.5:1).

Physical appearance: Yellow liquid.



7q

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2929, 1716, 1466, 1273, 1051, 755, 670 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.30 (td, *J* = 7.2, 1.2 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.15 (t, *J* = 6.8 Hz, 1H), 4.02 (quint, *J* = 6.4 Hz, 1H), 2.55-2.48 (m, 1H), 2.08-2.01 (m, 1H), 1.84-1.77 (m, 3H), 1.71-1.51 (m, 2H), 1.51-1.33 (m, 7H), 0.93-0.89 (m, 3H).

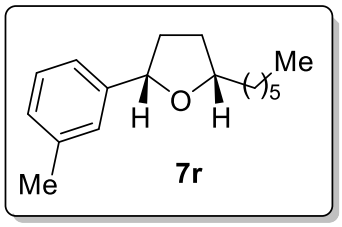
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.4 (C), 132.5 (CH), 128.4 (CH), 127.5 (CH), 127.1 (CH), 121.5 (C), 80.5 (CH), 79.7 (CH), 35.9 (CH_2), 33.4 (CH_2), 32.0 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 26.5 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. for $C_{16}H_{23}BrNa$, 333.0825, found 333.0825.

***(2S*,5S*)-2-hexyl-5-(m-tolyl)tetrahydrofuran* (7r):**

Reaction of enynol **6r** (50 mg, 0.20 mmol) with Et_3SiH (64.8 µL, 0.40 mmol) and TMSOTf (3.7 µL, 0.20 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7r** (26 mg, 52%) as a mixture of diastereomers (dr-1.5:1).

Physical appearance: Colourless liquid.



7r

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2956, 2927, 2856, 1463, 1063, 885, 784, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.17 - 7.12 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 4.83 (t, *J* = 7.2 Hz, 1H), 4.00 (quint, *J* = 6.8 Hz, 1H), 2.35 (s, 3H), 2.32-2.23 (m, 1H), 2.10-2.01 (m, 1H), 1.84-1.76 (m, 2H), 1.67-1.59 (m, 1H), 1.49-1.37 (m, 1H), 1.36-1.27 (m, 8H), 0.92-0.89 (m, 3H).

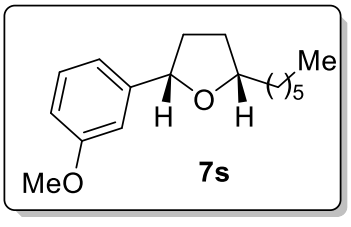
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.6 (C), 137.9 (C), 128.3 (CH), 128.0 (CH), 126.7 (CH), 123.1 (CH), 80.9 (CH), 80.2 (CH), 36.2 (CH_2), 34.5 (CH_2), 32.0 (CH_2), 31.5 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 22.8 (CH_2), 21.6 (CH_3), 14.2 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. for $C_{17}H_{27}O$ 247.2056, found 247.2051.

***(2S*,5S*)-2-hexyl-5-(3-methoxyphenyl)tetrahydrofuran* (7s):**

Reaction of enynol **6s** (50 mg, 0.19 mmol) with Et_3SiH (62 µL, 0.39 mmol) and TMSOTf (3.5 µL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7s** (23 mg, 55%) as a mixture of diastereomers (dr-1.5:1).

Physical appearance: Colourless liquid.



7s

R_f: 0.65 (1:9, EtOAc: Petroleum ether).

IR (neat): 2933, 2870, 1612, 1491, 1261, 1049, 774 cm^{-1}.

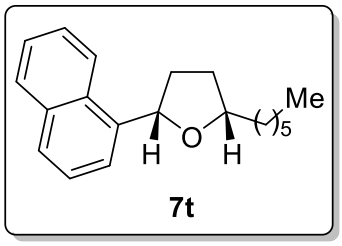
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (t, *J* = 8.0 Hz, 1H), 6.94-6.91 (m, 2H), 6.80-6.78 (m, 1H), 4.87 (t, *J* = 7.0 Hz, 1H), 4.02 (quint, *J* = 7.0 Hz, 1H), 3.82 (s, 3H), 2.32-2.25 (m, 1H), 2.07-2.02 (m, 1H), 1.87-1.73 (m, 1H), 1.68-1.58 (m, 2H), 1.57-1.40 (m, 1H), 1.37-1.27 (m, 8H), 0.90 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 159.7 (C), 145.6 (C), 129.4 (CH), 118.3 (CH), 112.5 (CH), 111.5 (CH), 80.7 (CH), 80.3 (CH), 55.3 (CH_3), 36.2 (CH_2), 34.6 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{17}H_{27}O_2$ 263.2006, found 263.1999.

***(2S*,5S*)-2-hexyl-5-(naphthalen-1-yl)tetrahydrofuran* (7t):**

Reaction of enynol **6t** (50 mg, 0.18 mmol) with Et_3SiH (57.4 μL, 0.35 mmol) and TMSOTf (3.24 μL, 0.02 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7t** (25 mg, 50%) as a mixture of diastereomers (dr-1.3:1).



7t

Physical appearance: Yellow liquid.

R_f: 0.7 (1:9, EtOAc: Petroleum ether).

IR (neat): 2925, 2848, 1599, 1217, 1069, 776, 698 cm^{-1}.

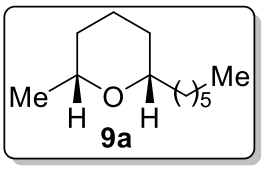
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99-7.97 (m, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.77-7.74 (m, 2H), 7.52-7.46 (m, 3H), 5.63 (t, *J* = 7.0 Hz, 1H), 4.12 (quint, *J* = 6.0 Hz, 1H), 2.60-2.53 (m, 1H), 2.16-2.09 (m, 1H), 1.97-1.87 (m, 2H), 1.79-1.64 (m, 2H), 1.61-1.51 (m, 1H), 1.48-1.35 (m, 7H), 0.93 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 139.7 (C), 133.8 (C), 130.4 (C), 128.9 (CH), 127.4 (CH), 125.8 (CH), 125.7 (CH), 125.4 (CH), 123.5 (CH), 122.3 (CH), 80.4 (CH), 77.9 (CH), 36.0 (CH_2), 34.0 (CH_2), 32.0 (CH_2), 31.5 (CH_2), 29.6 (CH_2), 26.6 (CH_2), 22.8 (CH_2), 14.3 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for 283.2056, found 283.2054.

***(2S*,6R*)-2-hexyl-6-methyltetrahydro-2H-pyran* (9a):**

Reaction of enynol **8a** (60 mg, 0.33 mmol) with Et_3SiH (106.2 μL, 0.40 mmol) and TMSOTf (60.1 μL, 0.33 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9a** (40 mg, 65%) as single diastereomer.



9a

Physical appearance: Yellow liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2928, 1466, 1217, 1040, 770, 591 cm^{-1}.

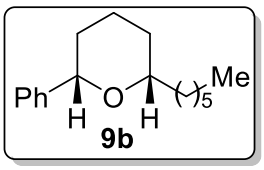
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42-3.36 (m, 1H), 3.26-3.21 (m, 1H), 1.80-1.76 (m, 1H), 1.56-1.44 (m, 4H), 1.37-1.35 (m, 2H), 1.28-1.26 (m, 9H), 1.15 (d, *J* = 4.8 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 78.1 (CH), 73.9 (CH), 36.8 (CH_2), 33.6 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 25.8 (CH_2), 23.9 (CH_2), 22.8 (CH_2), 22.4 (CH_3), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{12}H_{25}O$, 185.1889, found 185.1889.

***(2S*,6S*)-2-hexyl-6-phenyltetrahydro-2H-pyran* (9b):**

Reaction of enynol **8b** (70 mg, 0.29 mmol) with Et_3SiH (92.5 μL, 0.58 mmol) and TMSOTf (52.2 μL, 0.29 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9b** (35 mg, 50 %) as a single diastereomer.



Physical appearance: Yellow liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2932, 2859, 1717, 1451, 1315, 1275, 1111, 1027, 758 cm^{-1}.

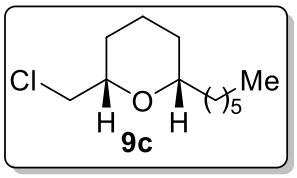
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.31 (m, 4H), 7.26-7.22 (m, 1H), 4.36 (dd, *J* = 11.2, 2.0 Hz, 1H) 3.47 (quint, *J* = 4.8 Hz, 1H), 1.98-1.91 (m, 1H), 1.87-1.84 (m, 1H), 1.70-1.60 (m, 3H), 1.54-1.41 (m, 3H), 1.31-1.30 (m, 8H), 0.89 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.9 (C), 128.3 (2 × CH), 127.1 (CH), 126.0 (2 × CH), 79.7 (CH), 78.5 (CH), 36.7 (CH_2), 33.8 (CH_2), 32.0 (CH_2), 31.3 (CH_2), 29.6 (CH_2), 25.6 (CH_2), 24.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{17}H_{27}O$, 247.2057, found 247.2057.

***(2S*,6S*)-2-(chloromethyl)-6-hexyltetrahydro-2H-pyran* (9c):**

Reaction of enynol **8c** (60 mg, 0.28 mmol) with Et_3SiH (89.2 μL, 0.56 mmol) and TMSOTf (50.4 μL, 0.28 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9c** (36 mg, 60%) as a single diastereomer.



Physical appearance: Colourless liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2934, 1440, 1664, 1466, 824, 777, 670 cm^{-1}.

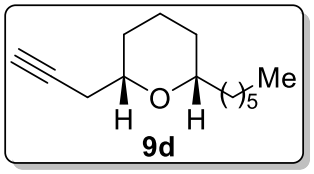
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.53-3.47 (m, 2H), 3.45-3.40 (m, 1H), 3.31-3.27 (m, 1H), 1.89-1.84 (m, 1H), 1.73-1.71 (m, 1H), 1.61-1.60 (m, 1H), 1.57-1.46 (m, 2H), 1.41-1.36 (m, 2H), 1.28-1.22 (m, 8H), 1.21-1.13 (m, 1H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 78.5 (CH), 77.6 (CH), 47.7 (CH_2), 36.5 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 25.6 (CH_2), 23.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{12}H_{23}ClNaO$, 241.1346, found 241.1346.

***(2S*,6S*)-2-hexyl-6-(prop-2-yn-1-yl)tetrahydro-2H-pyran* (9d):**

Reaction of enynol **8d** (60 mg, 0.29 mmol) with Et_3SiH (93.7 μL, 0.587 mmol) and TMSOTf (53.0 μL, 0.29 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9d** (40 mg, 66%) as a single diastereomer.



9d

Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2933, 2857, 2349, 1456, 1373, 1071, 637 cm^{-1}.

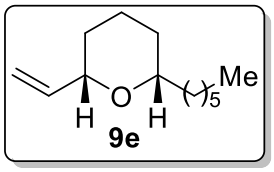
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.47-3.40 (m, 1H), 3.30-3.24 (m, 1H), 2.49-2.43 (m, 1H), 2.31-2.24 (m, 1H), 1.98 (t, *J* = 2.8 Hz, 1H), 1.87-1.80 (m, 2H), 1.59-1.43 (m, 4H), 1.39-1.33 (m, 2H), 1.27-1.23 (m, 6H), 1.22-1.10 (m, 2H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 81.5 (C), 78.4 (CH), 76.2 (CH), 69.7 (CH), 36.6 (CH_2), 32.0 (CH_2), 31.4 (CH_2), 31.0 (CH_2), 29.5 (CH_2), 26.4 (CH_2), 25.7 (CH_2), 23.6 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{14}H_{25}O$, 209.1900, found 209.1900.

***(2S*,6S*)-2-hexyl-6-vinyltetrahydro-2H-pyran* (9e):**

Reaction of enynol **8e** (50 mg, 0.26 mmol) with Et_3SiH (83.0 μL, 0.52 mmol) and TMSOTf (46.9 μL, 0.26 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9e** (31 mg, 62%) as a single diastereomer.



9e

Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2930, 2871, 1736, 1464, 1281, 1134, 972, 712, 670 cm^{-1}.

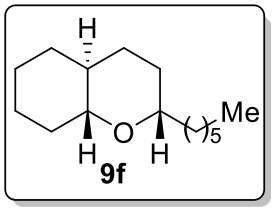
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87 (ddd, *J* = 16.8, 10.8, 5.6 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H), 3.80 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.31 (quint, *J* = 5.6 Hz, 1H), 1.86-1.81 (m, 1H), 1.64-1.47 (m, 5H), 1.41-1.40 (m, 2H), 1.31-1.14 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 139.9 (CH), 114.4 (CH_2), 78.4 (CH), 78.0 (CH), 36.7 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 31.4 (CH_2), 29.6 (CH_2), 25.7 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{13}H_{24}ONa$, 219.1746, found 219.1746.

***((2S*,4aS*,8aR*)-2-hexyloctahydro-2H-chromene* (9f):**

Reaction of enynol **8f** (50 mg, 0.23 mmol) with Et_3SiH (72.0 µL, 0.45 mmol) and TMSOTf (41.1 µL, 0.23 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9f** (35 mg, 70%) as a single diastereomer.



Physical appearance: Yellow liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2928, 2856, 1452, 1373, 1112, 1088, 830, 670 cm^{-1}.

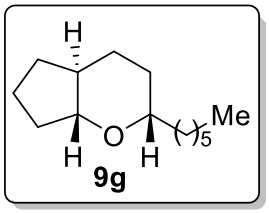
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.26 (quint, *J* = 5.5 Hz, 1H), 2.88 (td, *J* = 9.5, 4.0 Hz, 1H), 1.88-1.85 (m, 1H), 1.76-1.75 (m, 1H), 1.70-1.67 (m, 1H), 1.62-1.51 (m, 3H), 1.50-1.49 (m, 1H), 1.38-1.32 (m, 2H), 1.30-1.21 (m, 11H), 1.18-1.11 (m, 2H), 0.96-0.92 (m, 1H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 82.0 (CH), 78.1 (CH), 42.0 (CH), 36.7 (CH_2), 32.8 (CH_2), 32.4 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.2 (CH_2), 29.6 (CH_2), 26.0 (CH_2), 25.8 (CH_2), 25.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. for $C_{15}H_{29}O$, 225.2214, found 225.2214.

***(2S*,4aS*,7aR*)-2-hexyloctahydrocyclopenta[b]pyran* (9g):**

Reaction of enynol **8g** (100 mg, 0.48 mmol) with Et_3SiH (154.8 µL, 0.97 mmol) and TMSOTf (87.6 µL, 0.48 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9g** (65 mg, 65%) as a single diastereomer.



Physical appearance: Yellow liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2930, 2850, 1455, 1342, 1114, 824, 670 cm^{-1}.

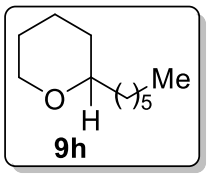
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.34 (quint, *J* = 4.0 Hz, 1H), 3.05 (td, *J* = 10.0, 7.0 Hz, 1H), 1.94-1.85 (m, 2H), 1.72-1.54 (m, 5H), 1.51-1.39 (m, 3H), 1.30-1.19 (m, 10H), 1.10-1.03 (m, 1H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 84.5 (CH), 79.0 (CH), 43.5 (CH), 36.4 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 25.9 (CH_2), 22.8 (CH_2), 19.3 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. for $C_{14}H_{27}O$, 211.2058, found 211.2058.

***2-hexyltetrahydro-2H-pyran* (9h):**

Reaction of enynol **8h** (60 mg, 0.36 mmol) with Et_3SiH (115.3 μL, 0.72 mmol) and TMSOTf (65.2 μL, 0.36 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9h** (42 mg, 71%).



9h

Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2928, 2883, 1652, 1518, 1461, 1046, 826, 709, 604 cm^{-1}.

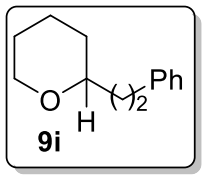
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.94 (d, *J* = 11.0 Hz, 1H), 3.39 (t, *J* = 11.0 Hz, 1H), 3.24-3.18 (m, 1H), 1.79 (d, *J* = 11.5 Hz, 1H), 1.55 (t, *J* = 7.0 Hz, 2H), 1.48-1.41 (m, 3H), 1.37-1.31 (m, 2H), 1.26-1.21 (m, 8H), 0.86 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 78.1 (CH), 68.6 (CH_2), 36.8 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 29.6 (CH_2), 26.4 (CH_2), 25.6 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{11}H_{23}O$ 171.1742, found 171.1742.

***2-phenethyltetrahydro-2H-pyran* (9i):**

Reaction of enynol **8i** (32 mg, 0.17 mmol) with Et_3SiH (55.0 μL, 0.34 mmol) and TMSOTf (31.0 μL, 0.17 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9i** (18 mg, 55%) yield.



9i

Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2934, 2857, 1463, 1254, 1217, 1100, 832, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.21-7.16 (m, 3H), 4.01 (dt, *J* = 9.2, 2.0 Hz, 1H), 3.42 (td, *J* = 7.6, 2.4 Hz, 1H), 3.28-3.21 (m, 1H), 2.81-2.74 (m, 1H), 2.69-2.62 (m, 1H), 1.87-1.77 (m, 2H), 1.72-1.63 (m, 1H), 1.61-1.41 (m, 4H), 1.35-1.25 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 142.6 (C), 128.6 (2 × CH), 128.4 (2 × CH), 125.8 (CH), 77.1 (CH), 68.6 (CH_2), 38.4 (CH_2), 32.1 (CH_2), 31.9 (CH_2), 29.4 (CH_2), 23.7 (CH_2).

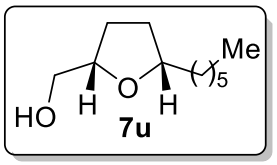
HRMS (ESI, M+H$^+$): m/z calcd. for $C_{13}H_{19}O$, 191.1430, found 191.1430.

***((2S*,5S*)-5-hexyltetrahydrofuran-2-yl)methanol* (7u):[5]**

Reaction of enynol **6u** (60 mg, 0.33 mmol) with Et_3SiH ((105.1 μL, 0.66 mmol) and TMSOTf (59.4 μL, 0.33 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7u** (53 mg, 88%) as a mixture of diastereomers (dr-2.3:1).

Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).



IR (neat): 3381, 2930, 2721, 1217, 771, 670 cm^{-1}.

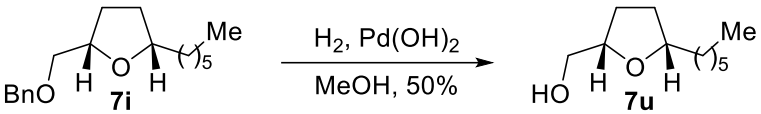
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98-3.92 (m, 1H), 3.82 (quint, *J* = 6.4 Hz, 1H), 3.64-3.58 (m, 1H), 3.47-3.42 (m, 1H), 2.53 (bs, 1H), 2.01-1.80 (m, 2H), 1.69-1.51 (m, 2H), 1.50-1.32 (m, 3H), 1.31-1.24 (m, 7H), 0.84 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 80.3 (CH), 79.4 (CH), 65.3 (CH_2), 36.0 (CH_2), 31.9 (CH_2), 31.4 (CH_2), 29.5 (CH_2), 27.1 (CH_2), 26.3 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{11}H_{23}O_2$, 187.1700, found 187.1700.

Procedure for benzyl deprotection:

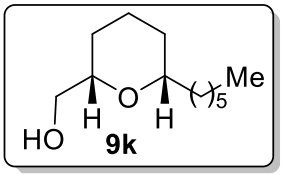
***((2S*,5S*)-5-hexyltetrahydrofuran-2-yl)methanol* (7u):**



After two vacuum/H_2 cycles to replace air inside the reaction mixture with hydrogen, the 2-((benzyloxy)methyl)-5-hexyltetrahydrofuran **7i** (45 mg, 0.163 mmol) and $Pd(OH)_2$/C (4.5 mg,) in methanol (3 mL) was vigorously stirred at rt under ordinary hydrogen pressure (balloon). The reaction mixture was stirred at rt until starting material was consumed (TLC control). The reaction mixture was filtered over celite bed, followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THF-derivative **7u** (15 mg, 50%) as a mixture of diastereomers (dr-1.3:1).

***((2S*,6S*)-6-hexyltetrahydro-2H-pyran-2-yl)methanol* (9k):[6]**

Reaction of enynol **8k** (60 mg, 0.30 mmol) with Et_3SiH ((97.6 μL, 0.61 mmol) and TMSOTf (55.2 μL, 0.30 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **9k** (40 mg, 67%) as a single diastereomer.



Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 3423, 2930, 2858, 1463, 1377, 1261, 1091, 1049, 824, 670 cm^{-1}.

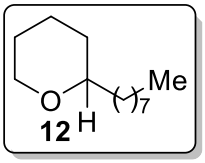
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.55-3.53 (m, 1H), 3.50-3.40 (m, 2H), 3.31-3.26 (m, 1H), 2.33 (bs, 1H), 1.84-1.81 (m, 1H), 1.59-1.58 (m, 1H), 1.53-1.43 (m, 3H), 1.38-1.32 (m, 2H), 1.28-1.22 (m, 8H), 1.21-1.11 (m, 1H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 78.1 (CH), 76.9 (CH), 66.4 (CH_2), 36.6 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 29.5 (CH_2), 27.4 (CH_2), 25.6 (CH_2), 23.3 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{12}H_{25}O_2$, 201.1851, found 201.1850.

***2-octyltetrahydro-2H-pyran* (12):**[7]

Reaction of enynol **11** (50 mg, 0.26 mmol) with Et_3SiH (82.4 μL, 0.51 mmol) and TMSOTf (46.4 μL, 0.26 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **12** (38 mg, 75%).



Physical appearance: Colourless liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2927, 2854, 1464, 1134, 1091, 846, 757 cm^{-1}.

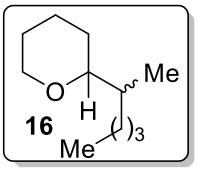
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98-3.93 (m, 1H), 3.40 (td, *J* = 11.2, 2.4 Hz, 1H), 3.24-3.18 (m, 1H), 1.82-1.77 (m, 1H), 1.60-1.52 (m, 2H), 1.50-1.43 (m, 3H), 1.41-1.30 (m, 1H), 1.25-1.18 (m, 13H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 78.1 (CH), 68.6 (CH_2), 36.8 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 26.4 (CH_2), 25.7 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{13}H_{27}O$ 199.2057, found 199.2057.

***2-(hexan-2-yl)tetrahydro-2H-pyran* (16):**

Reaction of enynol **15** (80 mg, 0.48 mmol) with Et_3SiH (154.2 μL, 0.96 mmol) and TMSOTf (87 μL, 0.48 mmol) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the THP-derivative **16** (56 mg, 70%, dr-1:1).



Physical appearance: Colourless liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2955, 2927, 2859, 1459, 1377, 1091, 1066, 757 cm^{-1}.

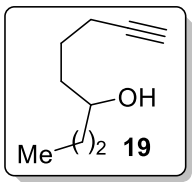
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99-3.82 (m, 4H), 3.72-3.66 (m, 2H), 1.99-1.90 (m, 3H), 1.88-1.78 (m, 4H), 1.58-1.49 (m, 3H), 1.45-1.34 (m, 4H), 1.28-1.53 (m, 12H), 0.89-0.85 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 77.9 (CH), 77.4 (CH), 67.6 (2 × CH_2), 43.4 (CH_2), 43.2 (CH_2), 37.5 (CH_2), 36.9 (CH_2), 32.2 (CH_2), 31.8 (CH_2), 30.7 (CH), 30.4 (CH), 29.3 (2 × CH_2), 25.8 (CH_2), 25.7 (CH_2), 23.1 (2 × CH_2), 20.2 (CH_3), 19.6 (CH_3), 14.3 (2 × CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{11}H_{23}O$ 171.1731, found 171.1731.

***Non-8-yn-4-ol* (19):**

The stirred suspension of magnesium turnings (625 mg, 26.04 mmol) in dry Et_2O (20 mL) with mercury(II) chloride (84 mg, 0.31 mmol) and a pinch of I_2 was cooled to 0 °C. To the reaction mixture 1-bromopropane (0.95 mL, 10.41 mmol) was added drop wise. The mixture was stirred at 0 °C for 1 h and then warmed to room temperature and stirred for 1 h. Then to a solution of aldehyde **18** (500 mg, 5.20 mmol, 1 equiv) in ether (10 mL), propane magnesium bromide in ether (prepared as above) was slowly added at -78 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched at 0 °C with saturated aqueous NH_4Cl solution (20 mL) carefully as it is exothermic, extracted with Et_2O (3 × 30 mL). The combined extracts were washed with brine (30 mL), dried over anh. Na_2SO_4 and concentrated, followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the corresponding alkynol **19** (550 mg, 74%) and NMR spectra were matched with previously reported data.[8a]



Physical appearance: Pale yellow liquid.

R_f: 0.5 (2:8, EtOAc: Petroleum ether).

IR (neat): 3410, 2930, 2874, 1452, 1048, 757, 666 cm^{-1}.

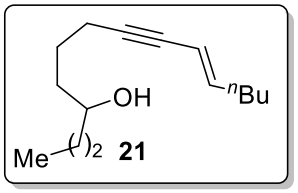
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.56-3.55 (m, 1H), 2.17-1.91 (m, 3H), 1.91 (s, 1H) 1.66-1.51 (m, 4H), 1.47-1.14 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 84.5 (C), 71.1 (CH), 68.5 (CH), 39.7 (CH_2), 36.4 (CH_2), 24.6 (CH_2), 18.8 (CH_2), 18.4 (CH_2), 14.1 (CH_3).

***(E)-pentadec-10-en-8-yn-4-ol* (21):**

To a magnetically stirred solution of alkynol **19** (230 mg, 1.64 mmol) and vinyl iodide **20** (361 mg, 1.72 mmol) in Et_3N (6 mL), $Pd(PPh_3)_2Cl_2$ (17.2 mg, 0.024 mmol) and CuI (6.2 mg, 0.032 mmol) was added and the reaction mixture was stirred at room temperature for overnight under nitrogen atmosphere. Reaction was monitored by TLC and the Et_3N was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether as eluent to furnish requisite enynol **21** (258 mg, 70%).

Physical appearance: Yellow liquid.



R_f: 0.4 (2:8, EtOAc: Petroleum ether).

IR (neat): 3460, 2957, 2934, 2873, 2352, 1457, 1251, 1120, 1015, 758 cm^{-1}.

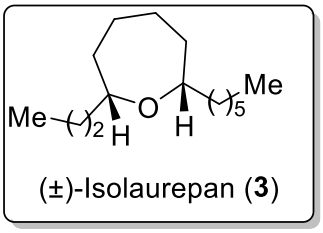
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05-5.97 (m, 1H), 5.44-5.38 (m, 1H), 3.62 (bs, 1H), 2.31-2.28 (m, 2H), 2.08-2.05 (m, 2H), 1.67-1.63 (m, 1H), 1.60-1.53 (m, 2H), 1.51-1.37 (m, 4H), 1.34-1.27 (m, 5H), 0.91-0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.6 (CH), 109.8 (CH), 88.3 (C), 79.7 (C), 71.4 (CH), 39.8 (CH_2), 36.7 (CH_2), 32.7 (CH_2), 31.0 (CH_2), 25.1 (CH_2), 22.2 (CH_2), 19.5 (CH_2), 18.9 (CH_2), 14.2 (CH_3), 14.0 (CH_3).

HRMS (ESI, M+H$^+$): m/z calculated for $C_{15}H_{27}O$ 223.2056, found 223.2056.

***(±)-Isolaurepan* (3):** [8]

Reaction of enynol **21** (50 mg, 0.19 mmol) with Et_3SiH (124 μL, 0.77 mmol) and TMSOTf (52 μL, 0.29) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the (±)-isolaurepan (**3**) (35 mg, 70%) as a mixture of diastereomers (dr-1.5:1).



Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 2923, 1742, 1507, 1374, 1017, 576 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.41-3.33 (m, 2H), 1.77-1.61 (m, 4H), 1.56-1.43 (m, 8H), 1.34-1.27 (m, 10H), 0.91-0.86 (m, 6H).

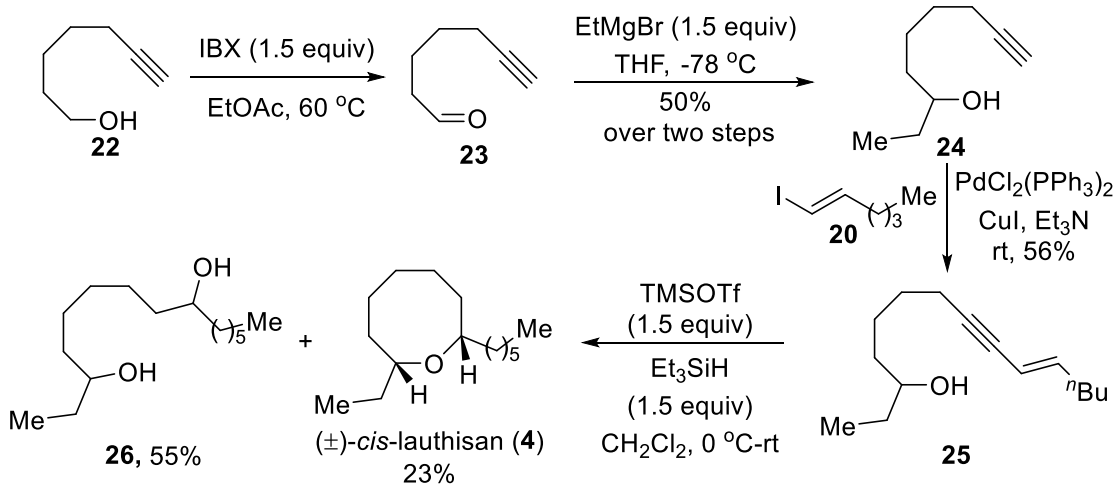
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 80.5 (CH), 80.2 (CH), 39.8 (CH_2), 37.6 (CH_2), 37.1 (CH_2), 37.0 (CH_2), 32.0 (CH_2), 29.5 (CH_2), 26.4 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 22.8 (CH_2), 19.6 (CH_2), 14.2 (2 × CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{31}O$ 227.2374, found 227.2373.

Comparison of (±)-Isolaurepan (3) ^{13}C NMR peaks with previously reported ^{13}C NMR[8]

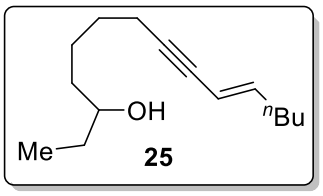
This work, (δ ^{13}C [ppm], 100 MHz, $CDCl_3$)	Previously reported, [8] (δ ^{13}C [ppm], 125 MHz, $CDCl_3$)	Δδ [ppm]
80.48	80.3	0.18
80.19	80.0	0.19
39.78	39.6	0.18
37.59	37.4	0.19
37.07	36.92	0.15
37.02	36.87	0.15
32.04	31.9	0.14
29.48	29.3	0.18
26.42	26.3	0.12
25.49	25.33	0.16
25.46	25.29	0.17
22.79	22.6	0.19
19.62	19.5	0.12
14.24	14.11	0.13
14.24	14.10	0.14

Total synthesis of (±)-*cis*-lauthisan (4):



***(E)-pentadec-10-en-8-yn-3-ol* (25):**

To a magnetically stirred solution of alkynol **24** (950 mg, 6.779 mmol) and vinyl iodide **20** (1.56 gm, 7.45 mmol) in Et_3N (15 mL), $Pd(PPh_3)_2Cl_2$ (71.2 mg, 0.102 mmol) and CuI (25.7 mg, 0.136 mmol) was added and the reaction mixture was stirred at room temperature for overnight under nitrogen atmosphere. Reaction was monitored by TLC and the Et_3N was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using EtOAc: Petroleum ether as eluent to furnish requisite enynol **25** (850 mg, 56%).



Physical appearance: Yellow liquid.

R_f: 0.4 (2:8, EtOAc: Petroleum ether).

IR (neat): 3459, 2955, 2927, 2234, 1728, 1457, 1251, 970, 761 cm^{-1}.

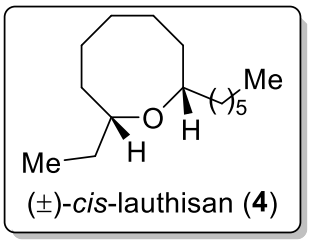
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.43 (dt, *J* = 16.0, 1.6 Hz, 1H), 3.55-3.50 (m, 1H), 2.30-2.28 (m, 2H), 2.09-2.03 (m, 2H), 1.56-1.40 (m, 9H), 1.39-1.24 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.6 (CH), 109.8 (CH), 88.5 (C), 79.5 (C), 73.3 (CH), 36.5 (CH_2), 32.8 (CH_2), 31.1 (CH_2), 30.3 (CH_2), 29.0 (CH_2), 25.1 (CH_2), 22.3 (CH_2), 19.5 (CH_2), 14.0 (CH_3), 10.0 (CH_3).

HRMS (ESI, M+H$^+$): m/z calculated for $C_{15}H_{27}O$ 223.2059, found 223.2059.

***(±)-cis-lauthisan* (4):[9]**

Reaction of enynol **25** (30 mg, 0.14 mmol) with Et_3SiH (86.4 μL, 0.54 mmol) and TMSOTf (36.5 μL, 0.20) in dry CH_2Cl_2 (4 mL) as described for the THF-derivative **7a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the *cis*-lauthisan (**4**) (7 mg, 23%) as a single diastereomers and hydrolysed product **26** (19 mg, 55%).



Physical appearance: Colourless liquid.

R_f: 0.5 (1:9, EtOAc: Petroleum ether).

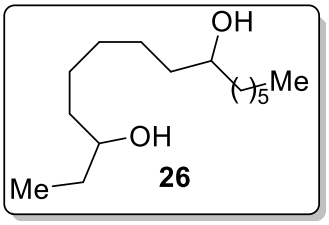
IR (neat): 2955**,** 2924, 2853, 1456, 1363, 1136, 768 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.45-3.30 (m, 2H), 1.77-1.60 (m, 6H), 1.53-1.50 (m, 2H), 1.43-1.36 (m, 6H), 1.27-1.25 (m, 8H), 0.94-0.86 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 81.2 (CH), 79.8 (CH), 37.2 (CH_2), 33.7 (CH_2), 33.5 (CH_2), 32.0 (CH_2), 29.9 (CH_2), 29.6 (CH_2), 27.2 (CH_2), 26.4 (CH_2), 24.2 (2 × CH_2), 22.8 (CH_2), 14.2 (CH_3), 10.0 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{31}O$ 227.2375, found 227.2375.

Pentadecane-3,9-diol **(26):**



Physical appearance: Colourless liquid.

R$_f$: 0.5 (1:9, EtOAc: Petroleum ether).

IR (neat): 3345, 2924, 2853, 1730, 1456, 1136, 986, 824, 768, 670 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.59-3.49 (m, 2H), 1.67-1.25 (m, 24H), 0.96-0.86 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 73.5 (CH), 72.1 (CH), 37.7 (CH_2), 37.5 (CH_2), 37.0 (CH_2), 32.0 (CH_2), 30.3 (CH_2), 29.9 (CH_2), 29.5 (CH_2), 25.8 (3 × CH_2), 22.8 (CH_2), 14.3 (CH_3), 11.0 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{33}O_2$ 245.2447, found 245.2447.

Comparison of (±)-*cis*-lauthisan (4): ^{13}C NMR peaks with previously reported ^{13}C NMR[9]

This work, (δ ^{13}C [ppm], 125 MHz, $CDCl_3$)	Previously reported, [9] (δ ^{13}C [ppm], 75 MHz, $CDCl_3$)	Δδ [ppm]
81.22	81.06	0.16
79.78	79.61	0.17
37.17	37.01	0.16
33.73	33.57	0.16
33.46	33.29	0.17
32.05	31.90	0.15
29.92	29.76	0.16
29.63	29.48	0.15
27.22	27.06	0.16
26.45	26.29	0.16
24.16	23.99	0.17
22.80	22.64	0.16
14.26	14.11	0.15
11.03	10.88	0.15

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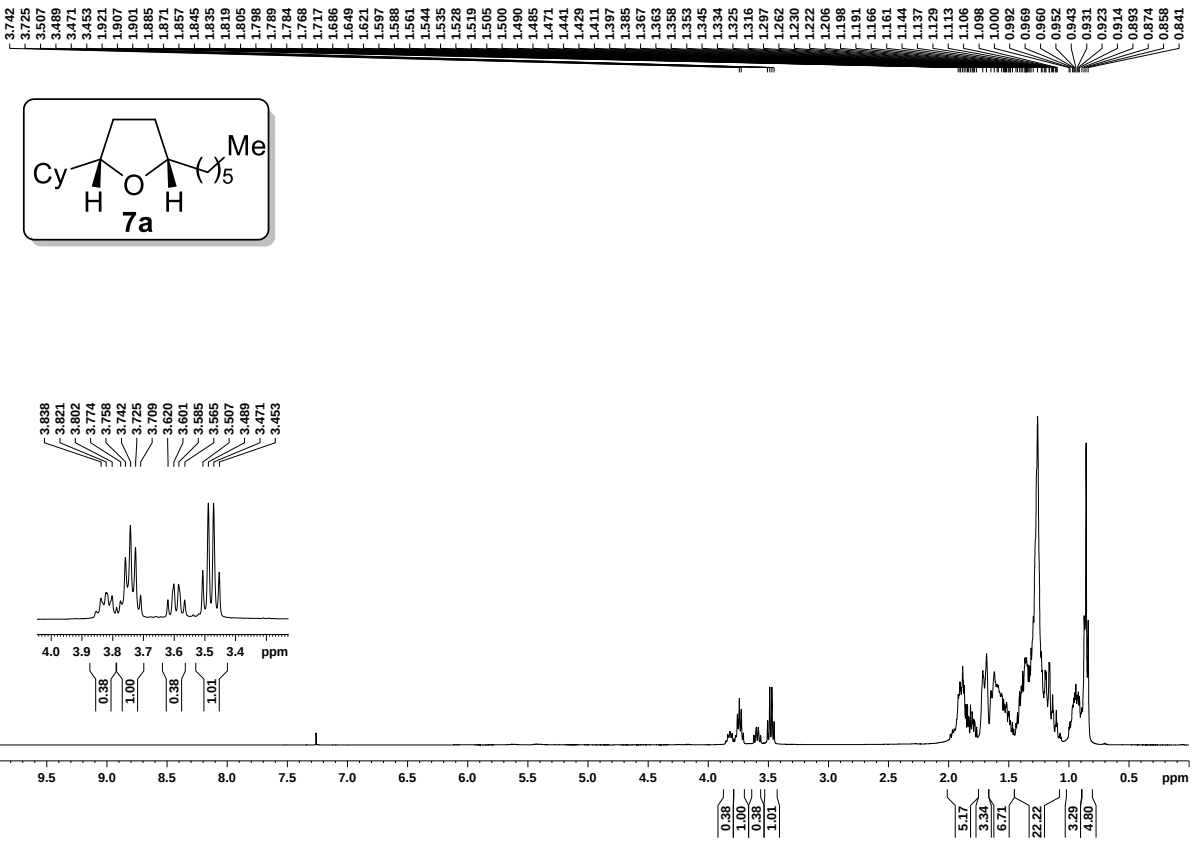
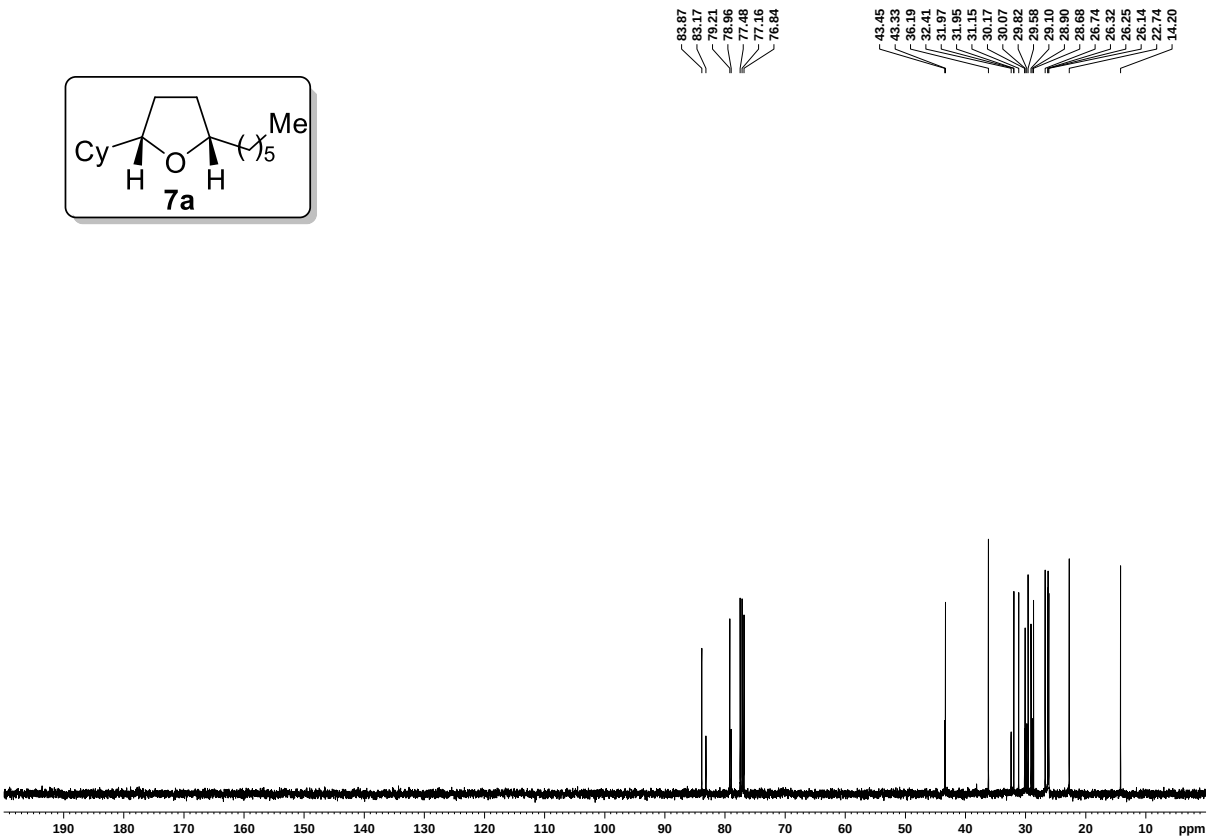
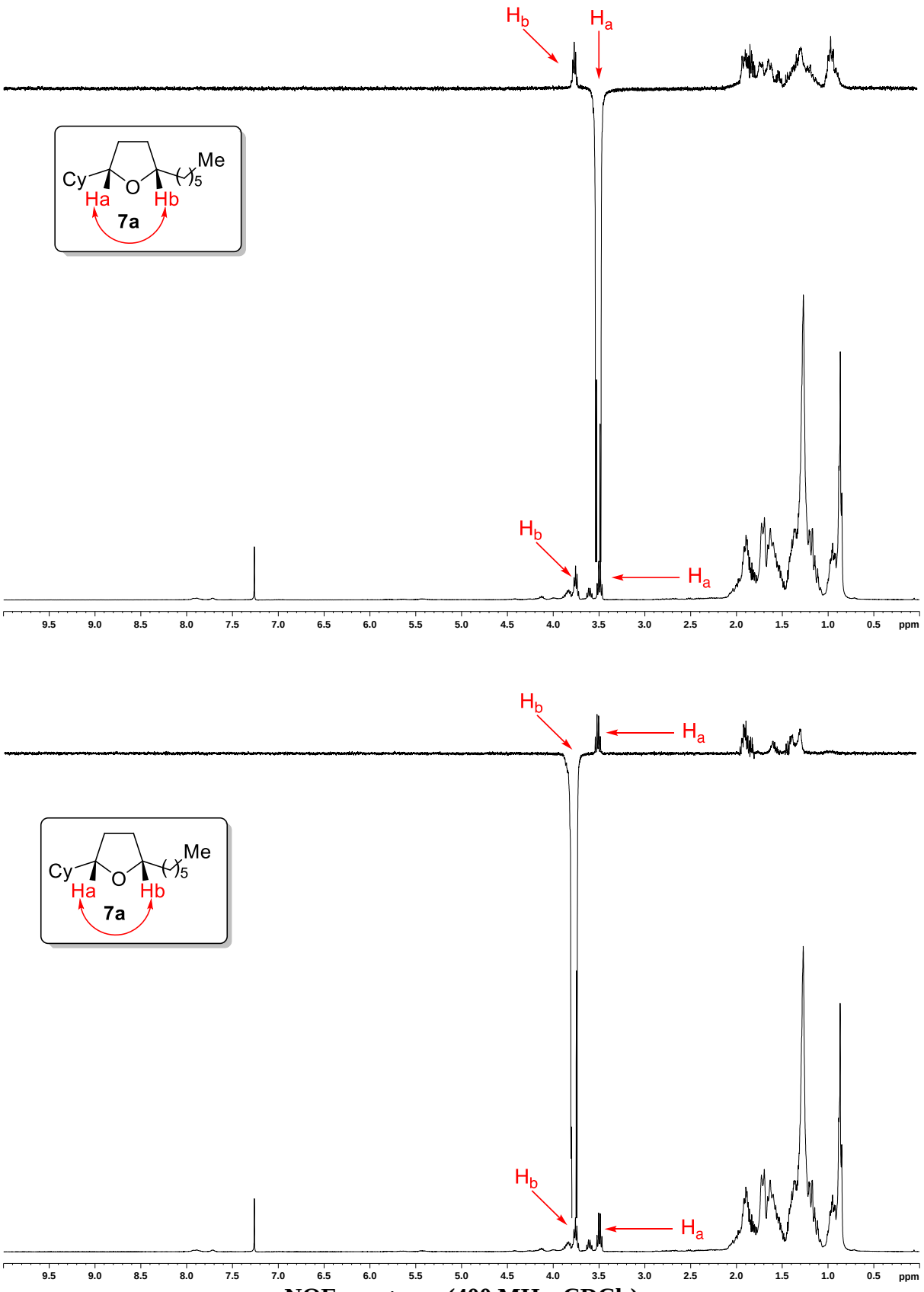


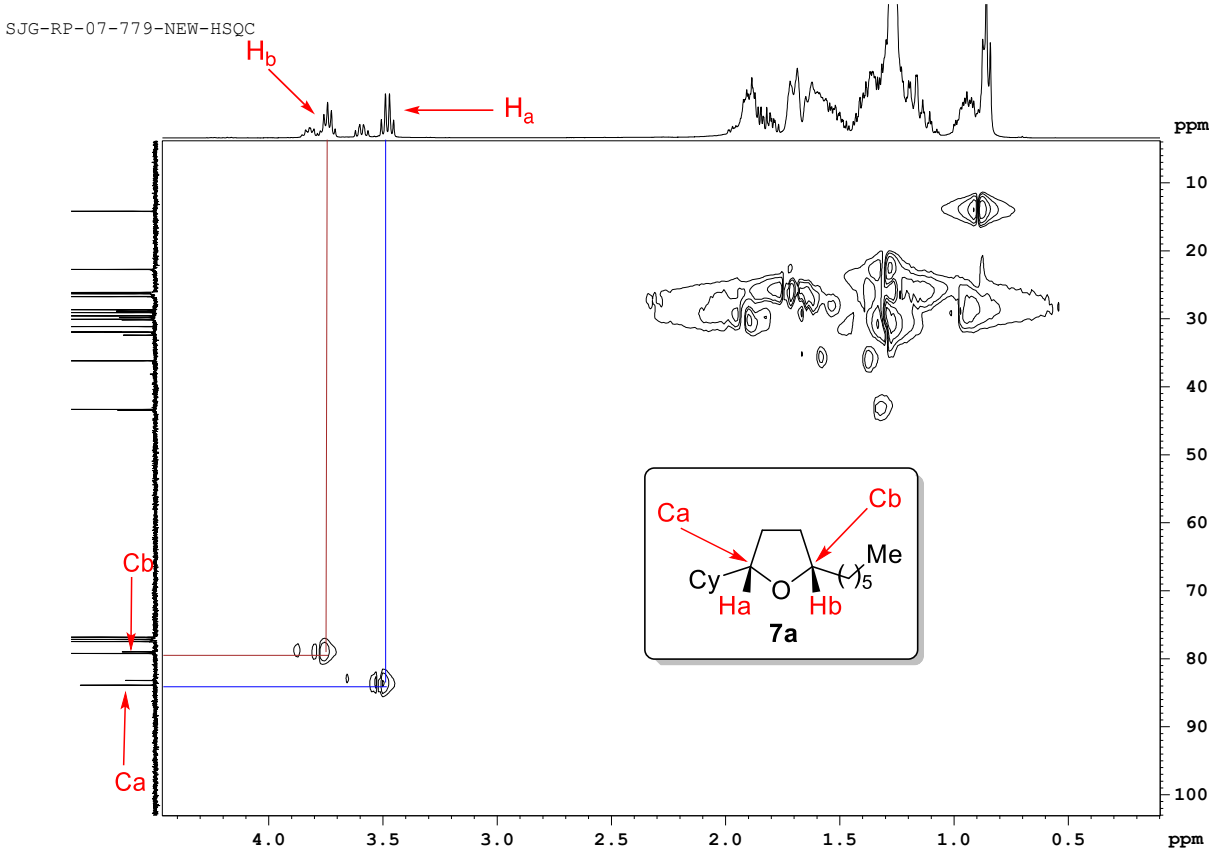
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



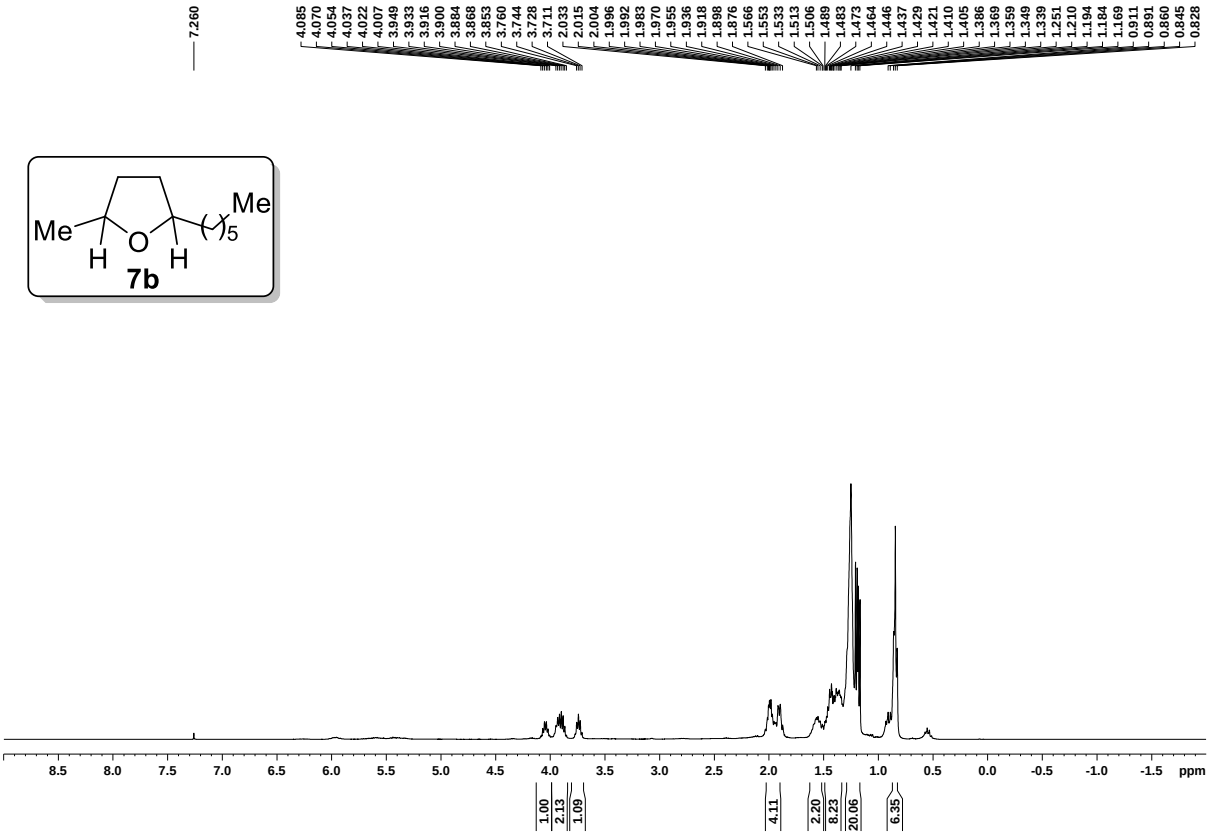
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



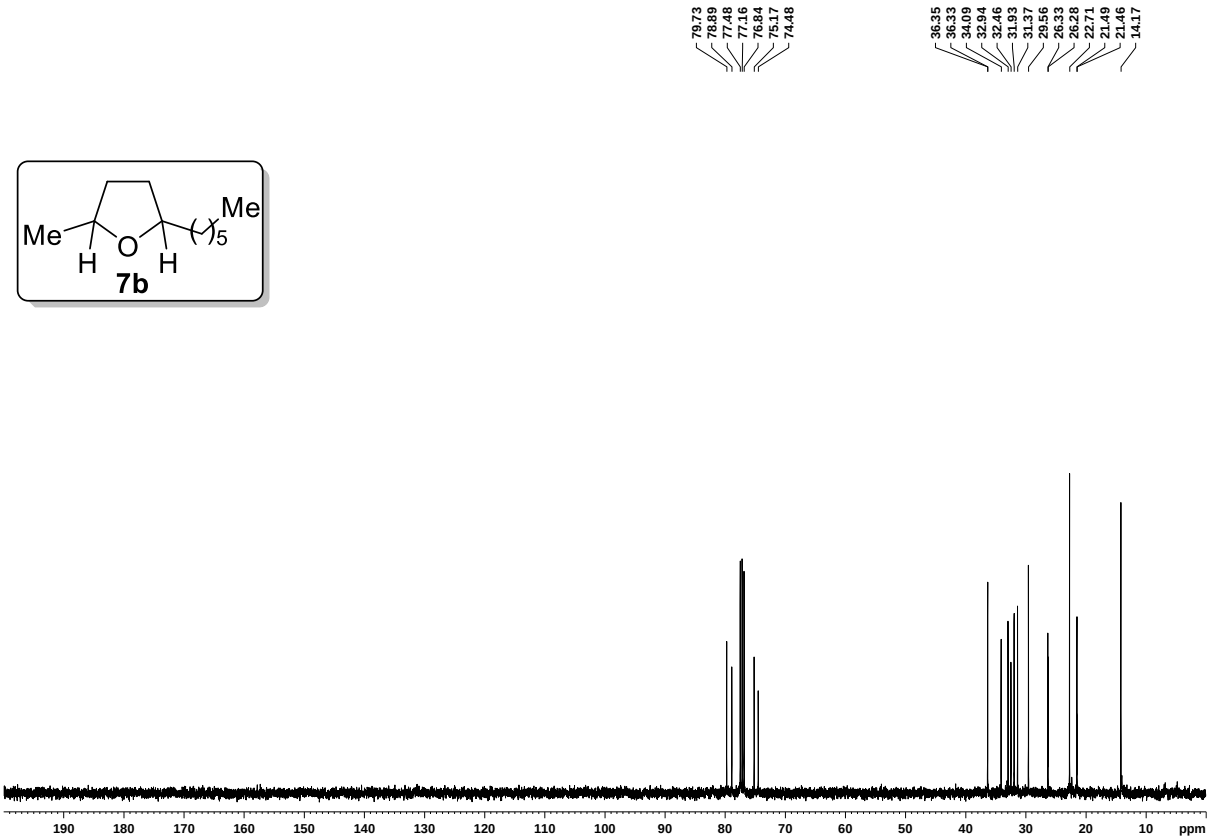
NOE spectrum (400 MHz, $CDCl_3$)



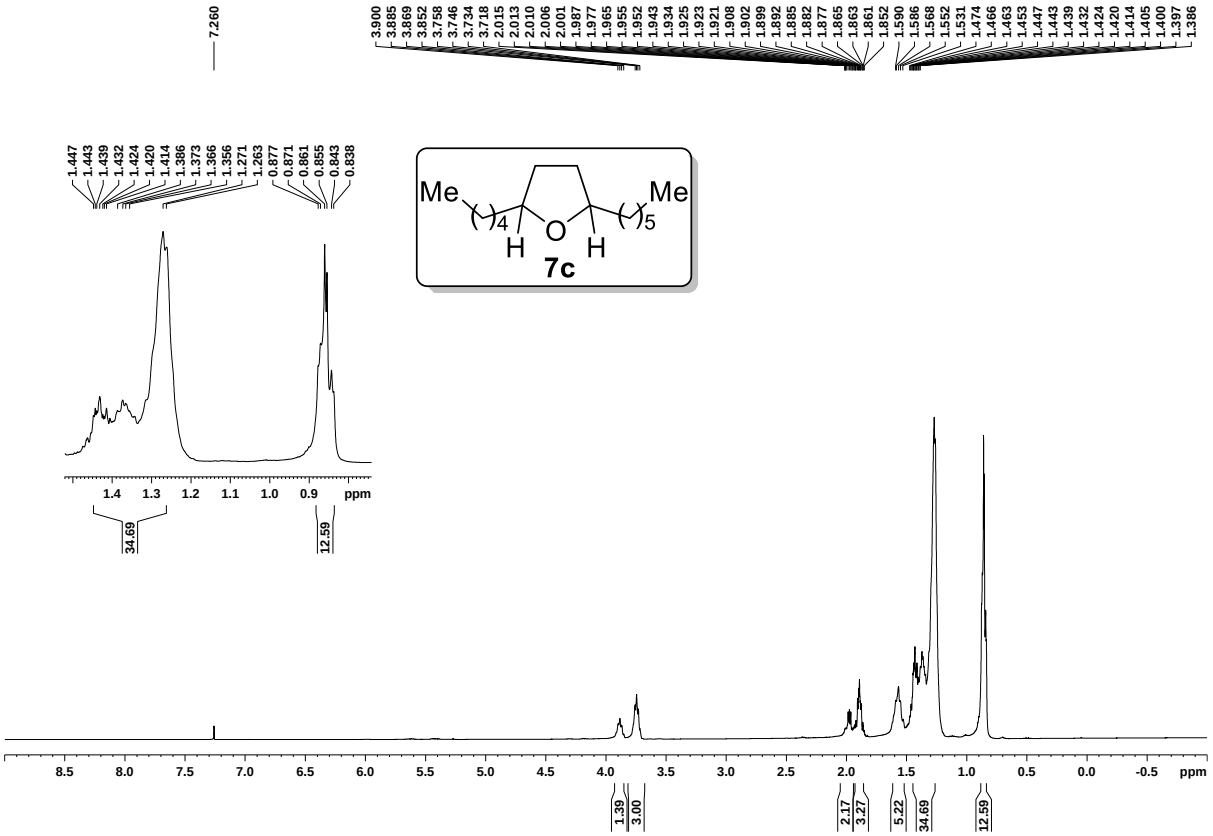
HSQC, spectrum (400 MHz, $CDCl_3$)



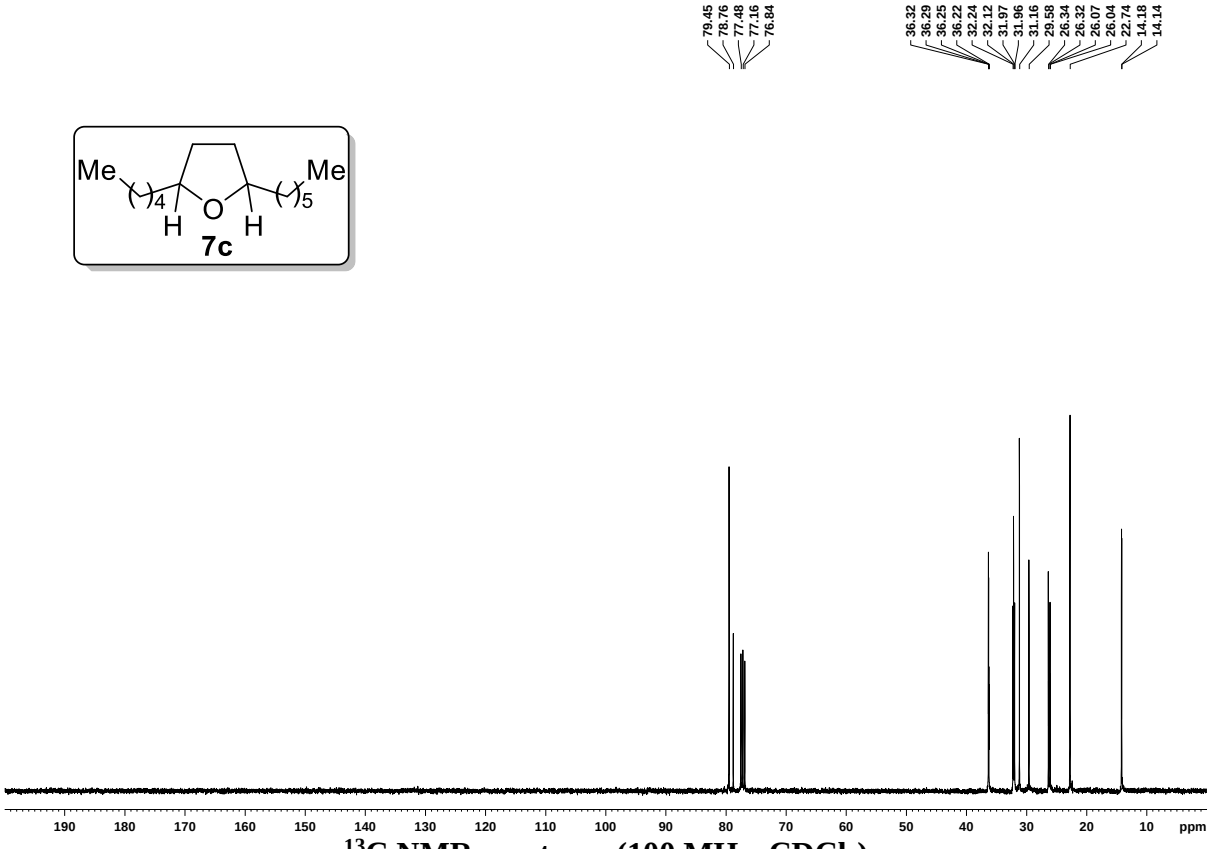
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



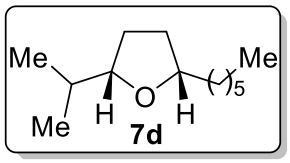
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

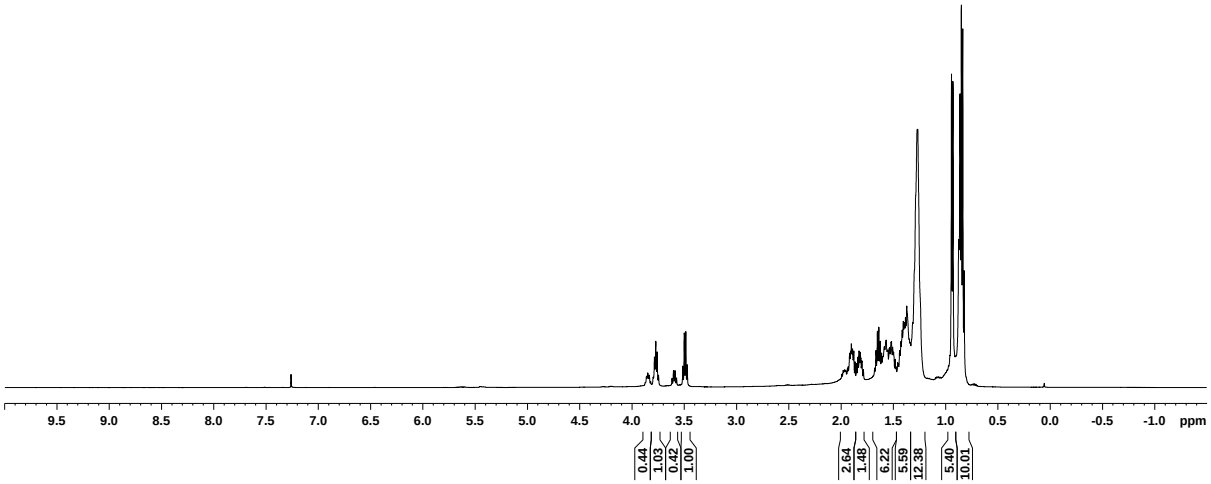


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

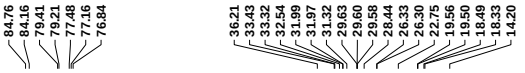


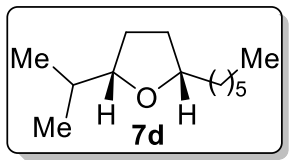
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

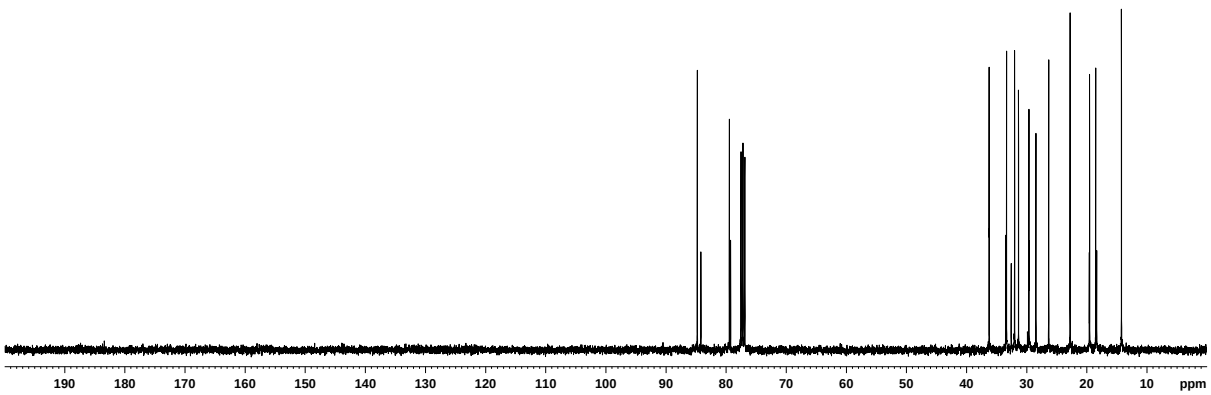




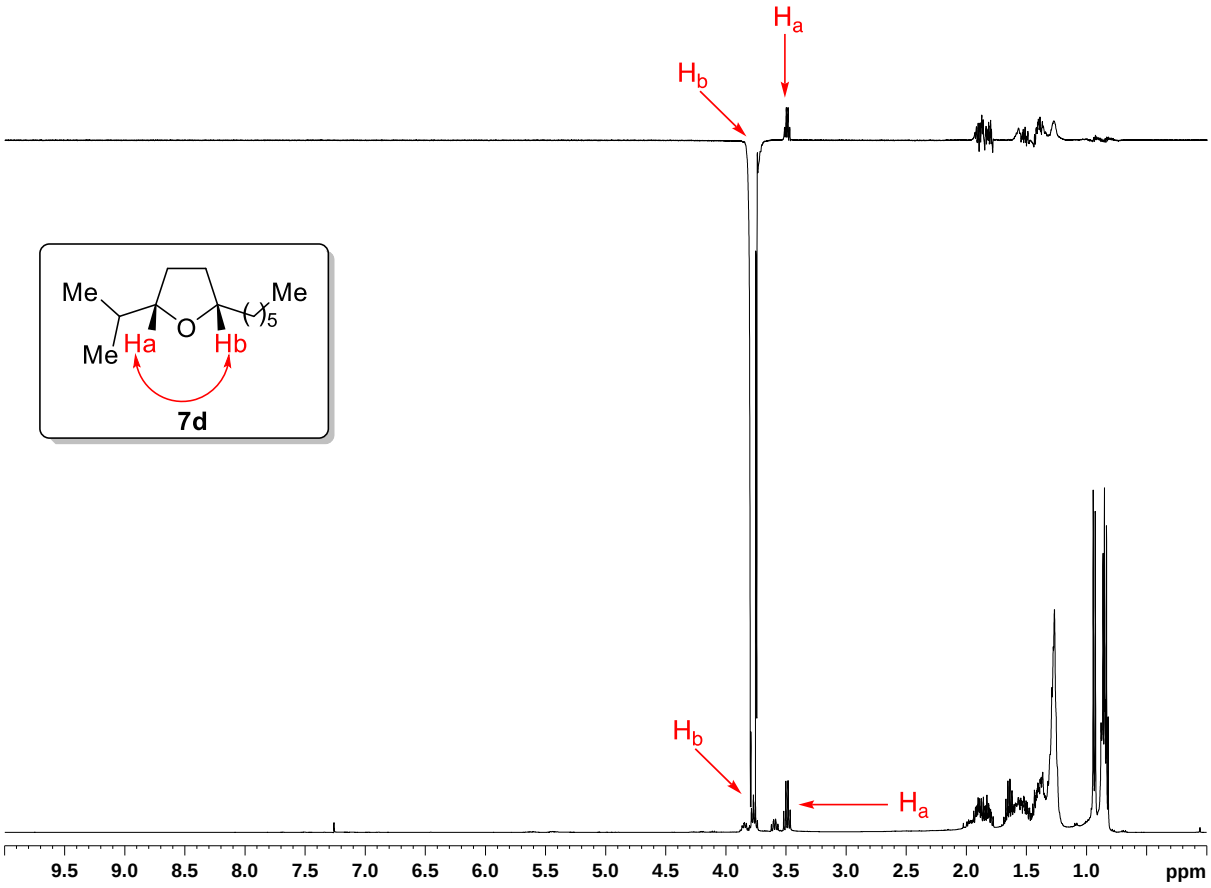
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

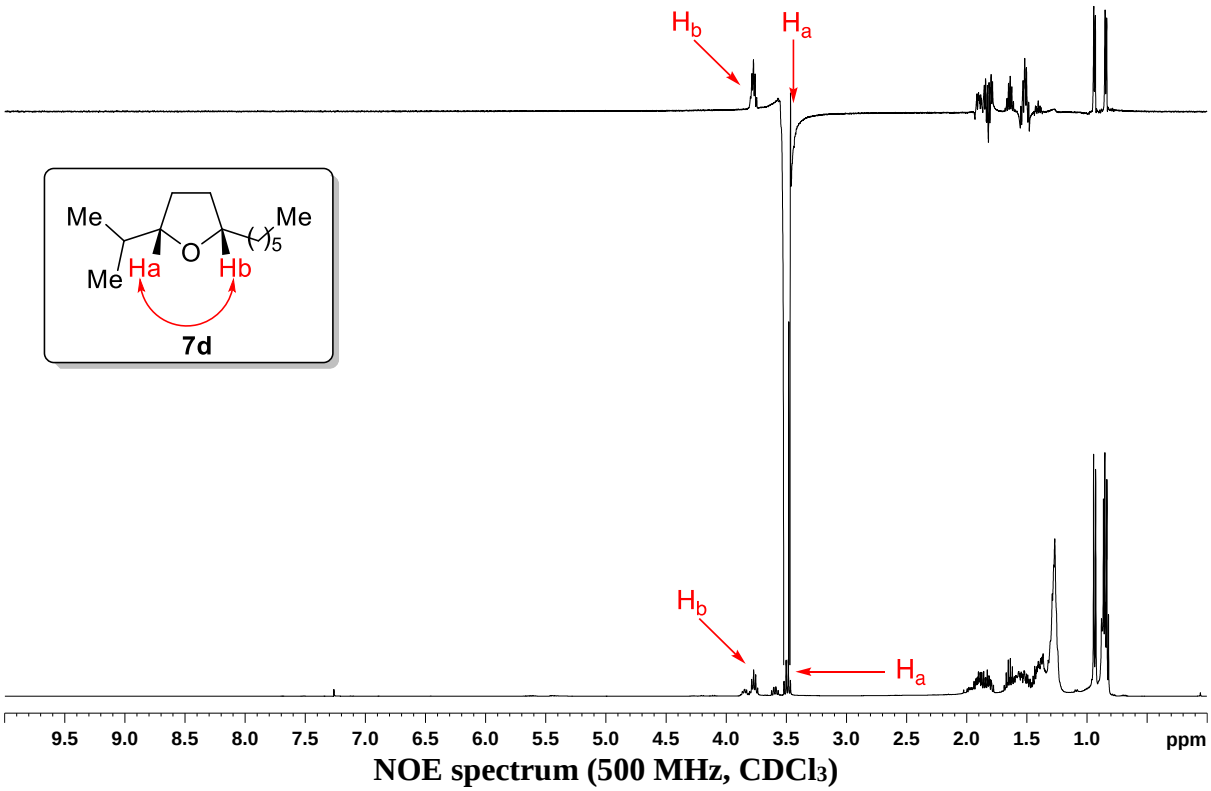




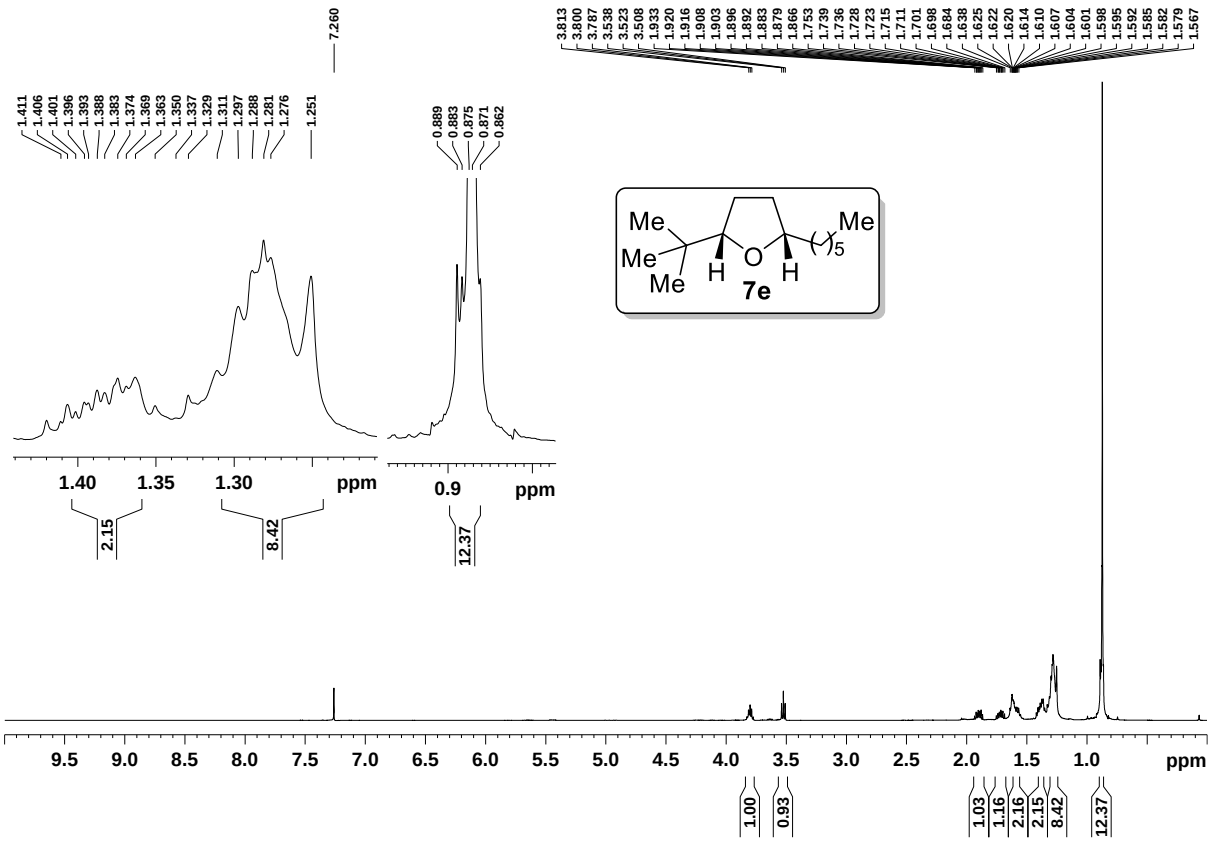


^{13}C NMR spectrum (125 MHz, $CDCl_3$)

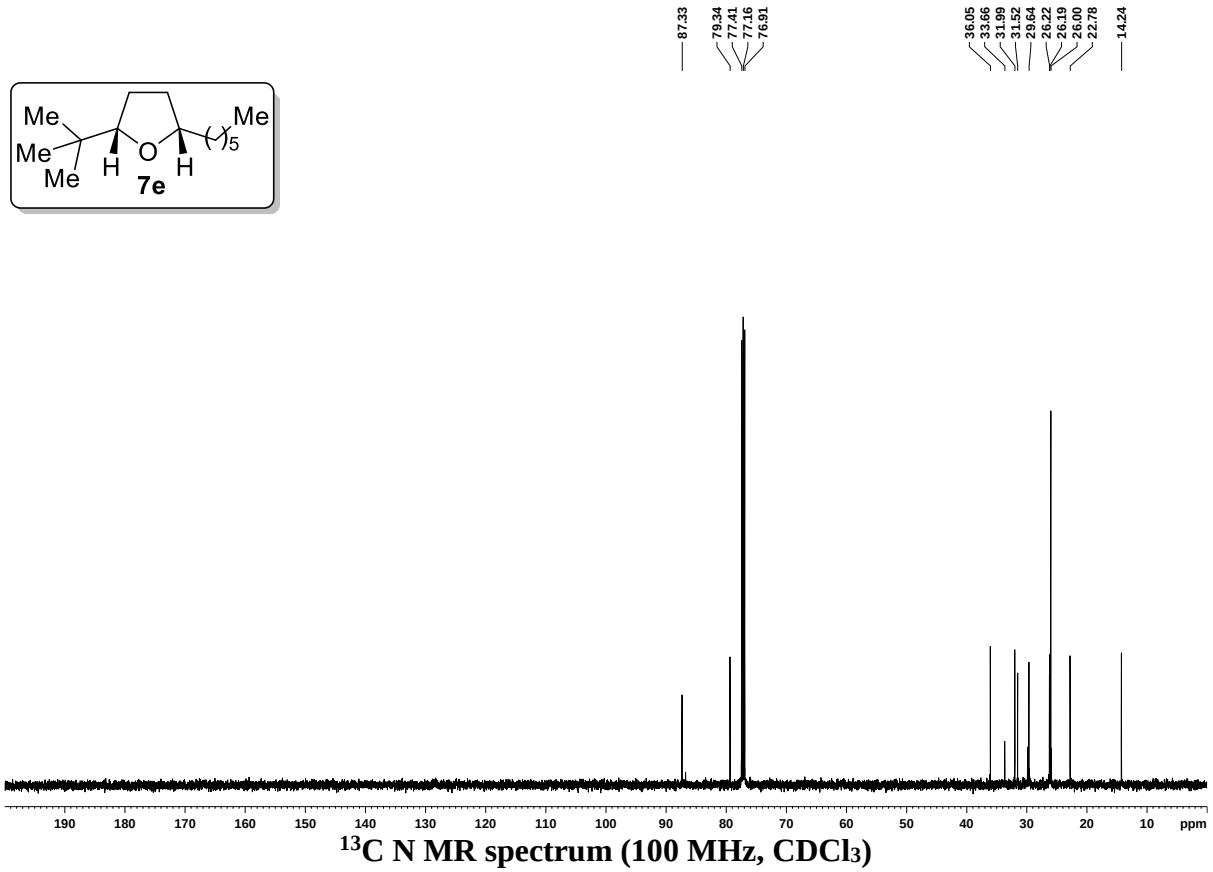




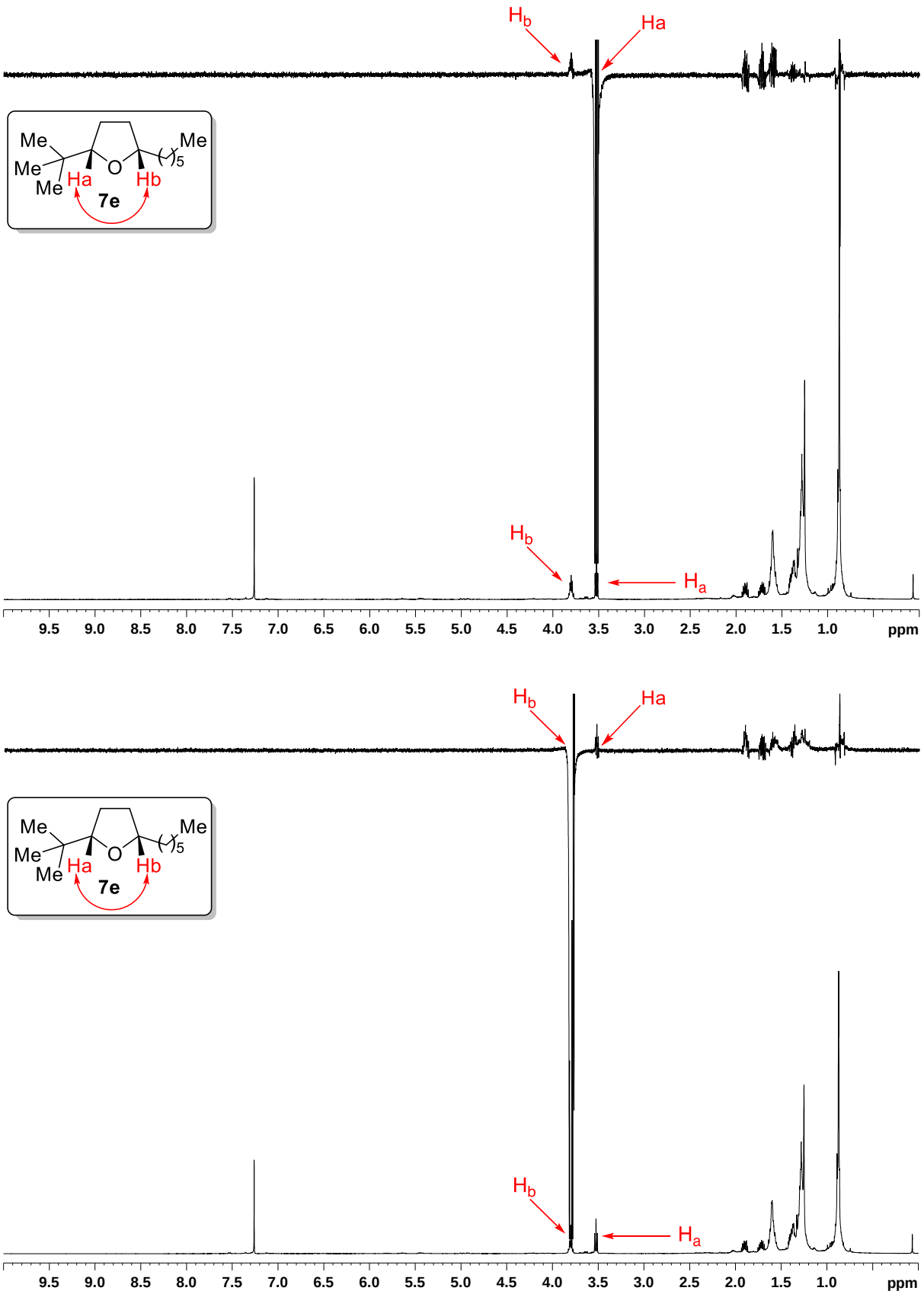
NOE spectrum (500 MHz, $CDCl_3$)



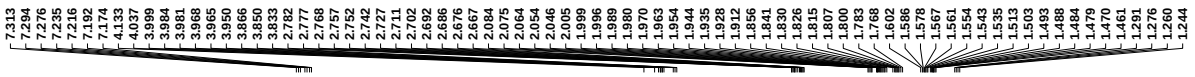
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

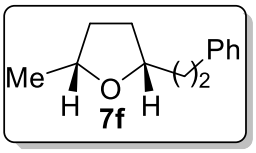


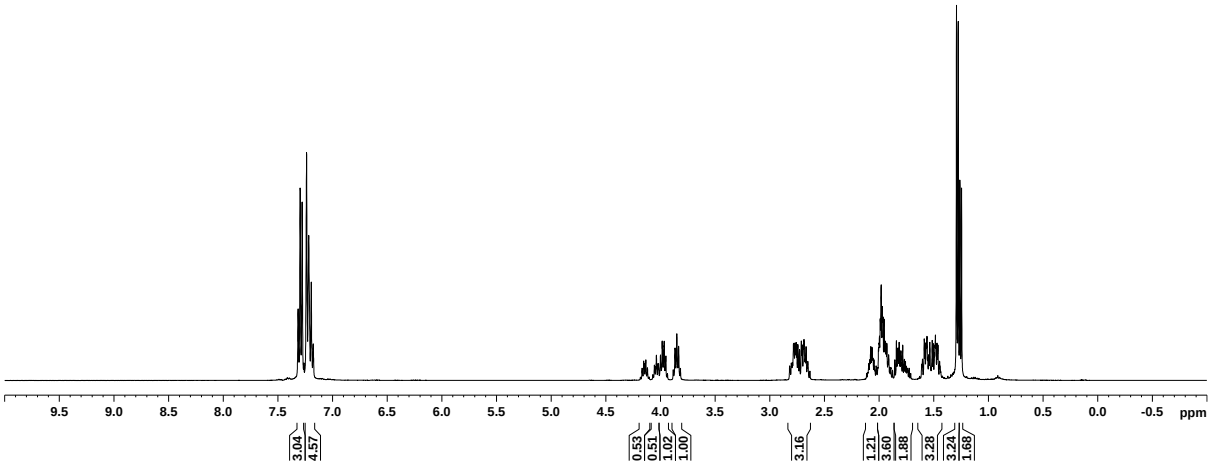
^{13}C N MR spectrum (100 MHz, $CDCl_3$)



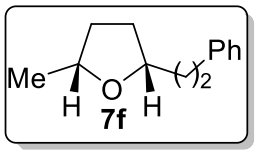
NOE spectrum (400 MHz, $CDCl_3$)

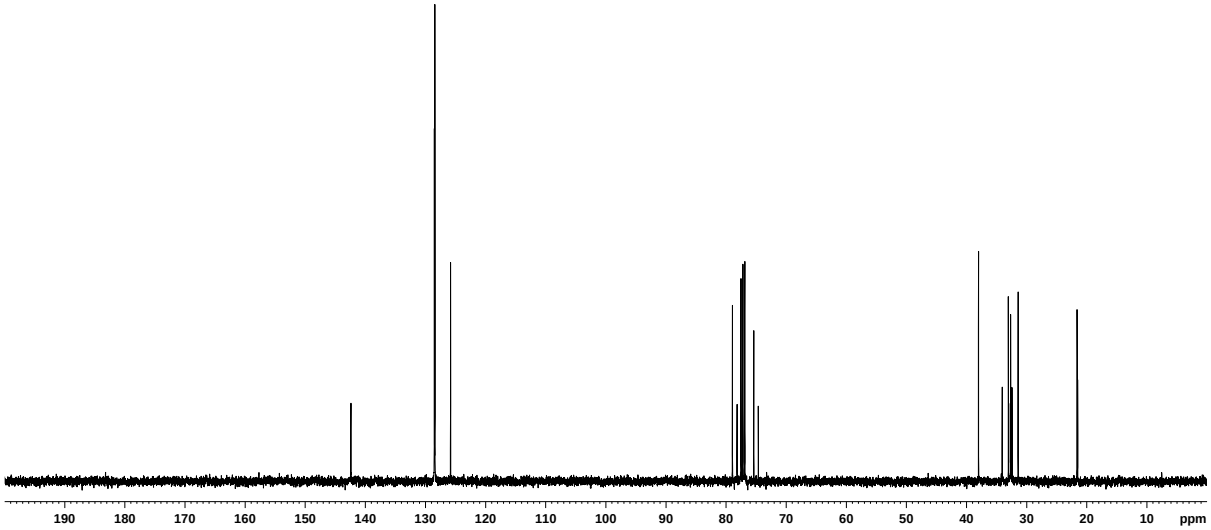




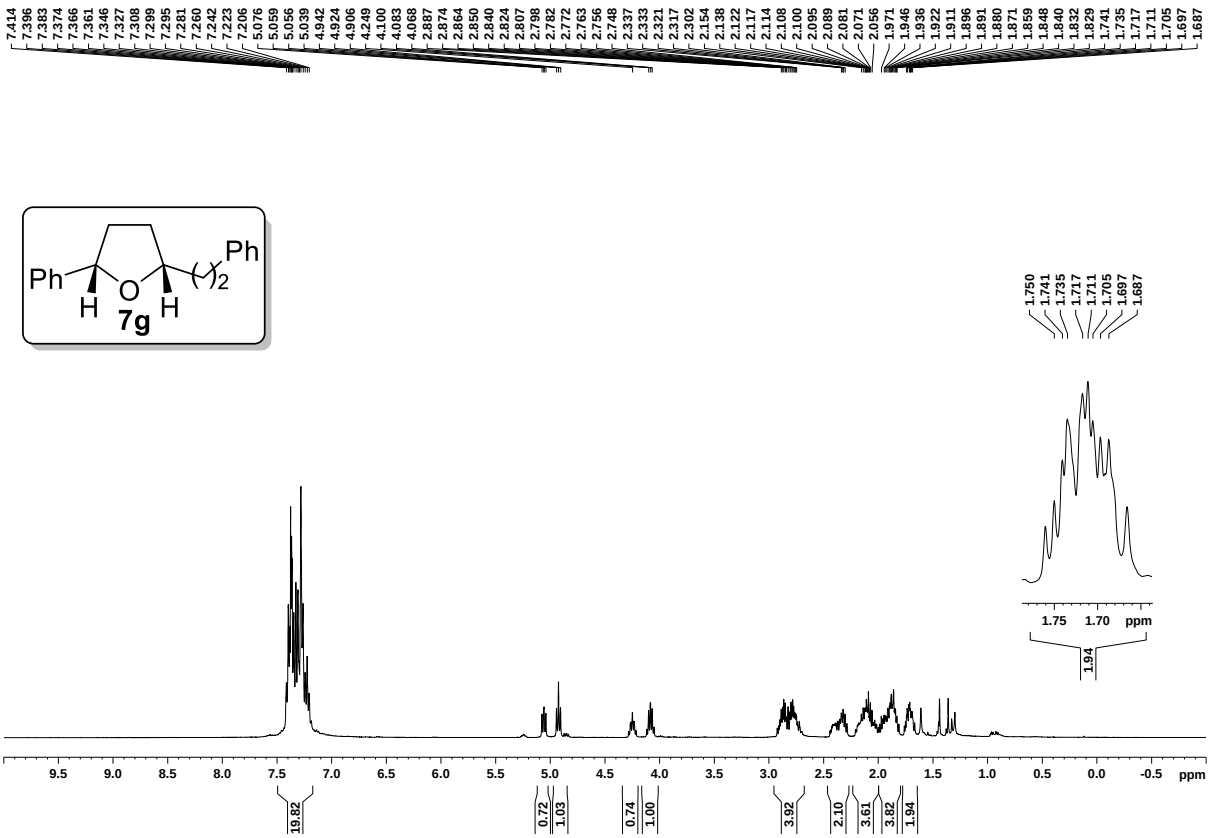


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

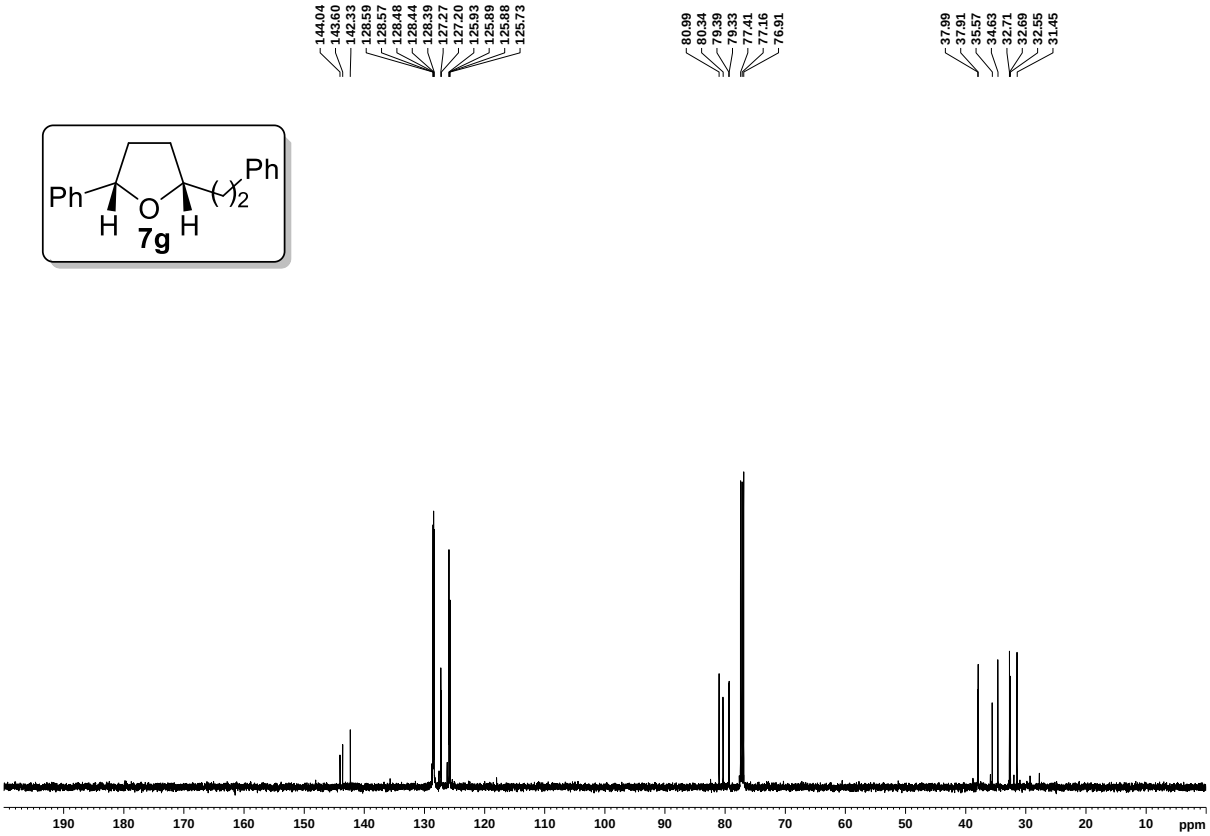




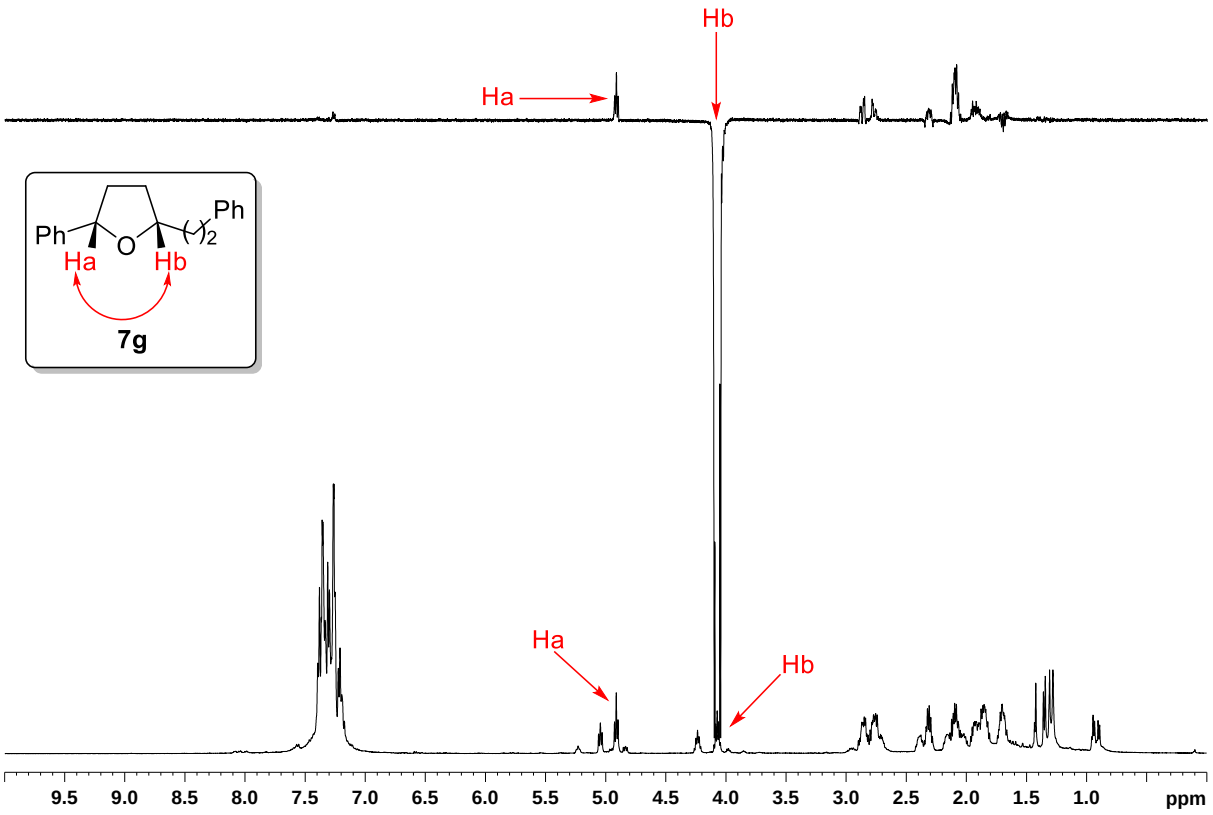
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

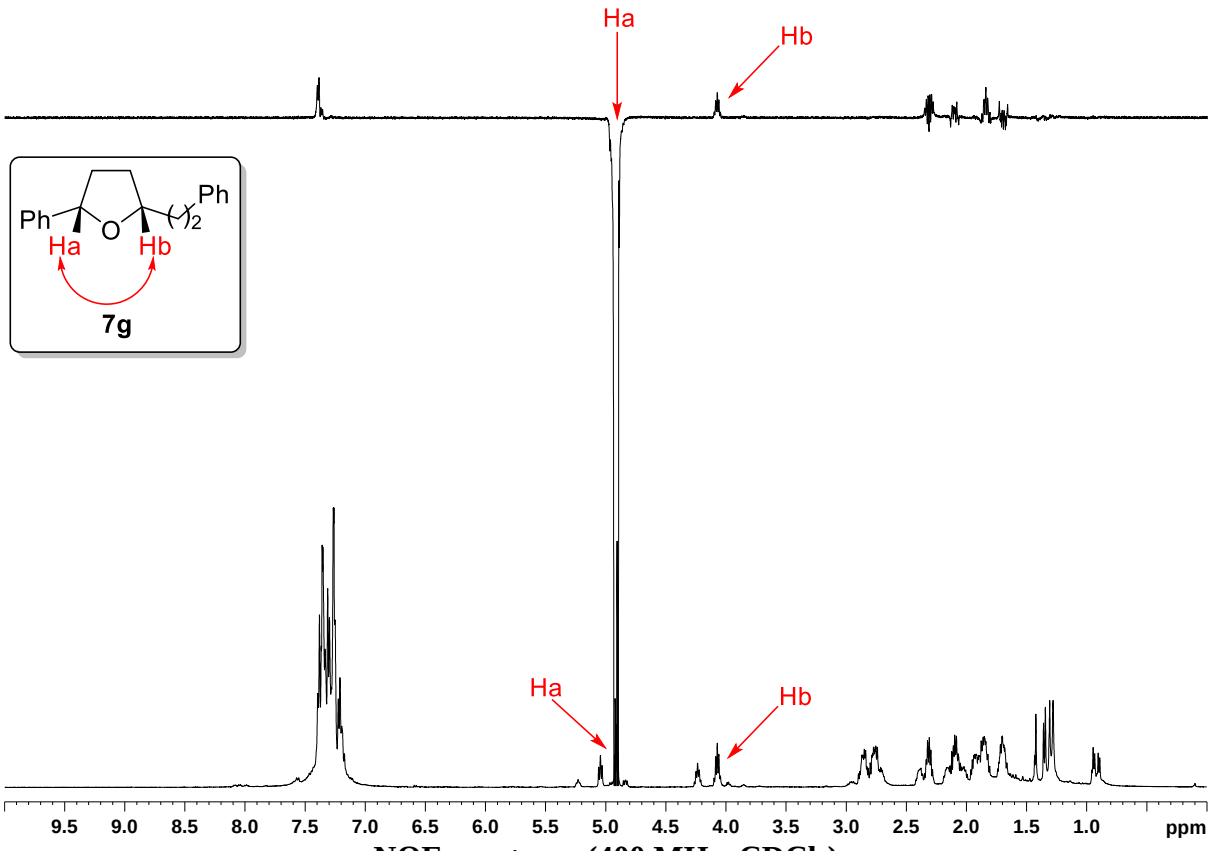


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

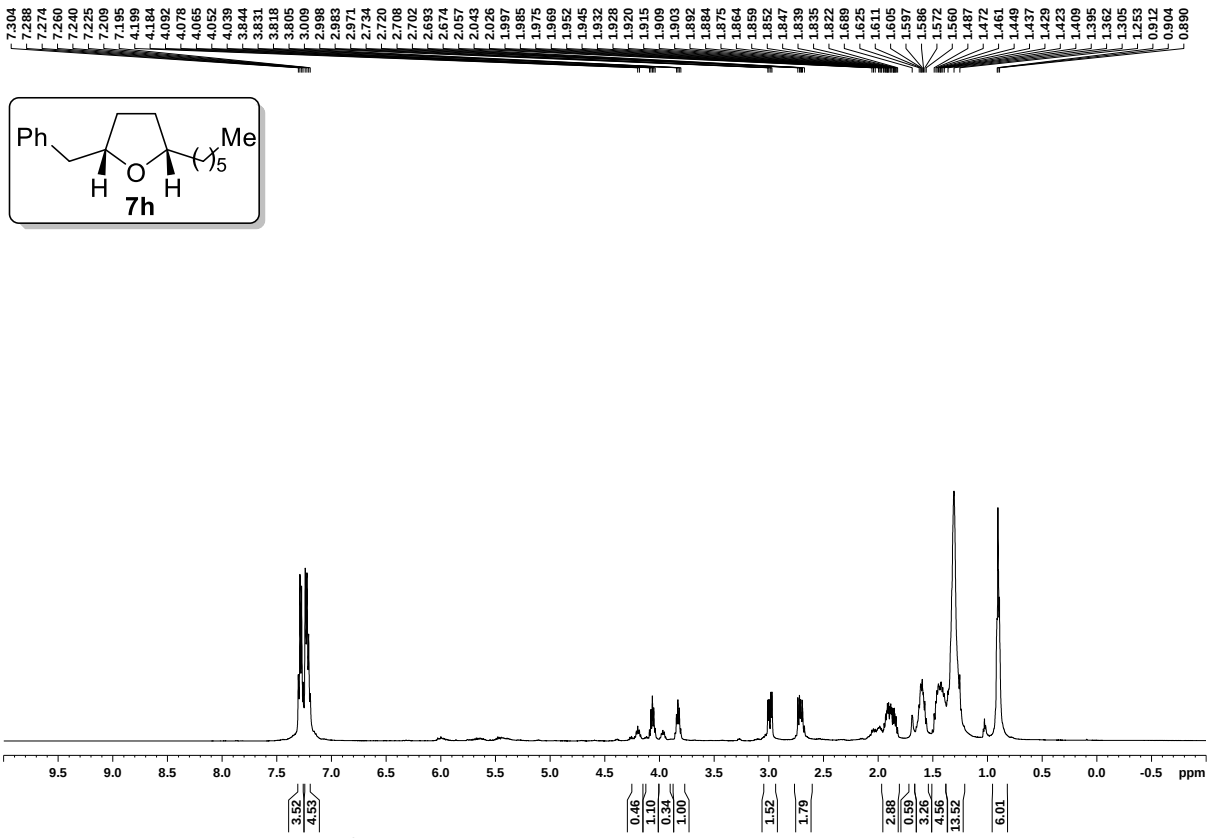


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

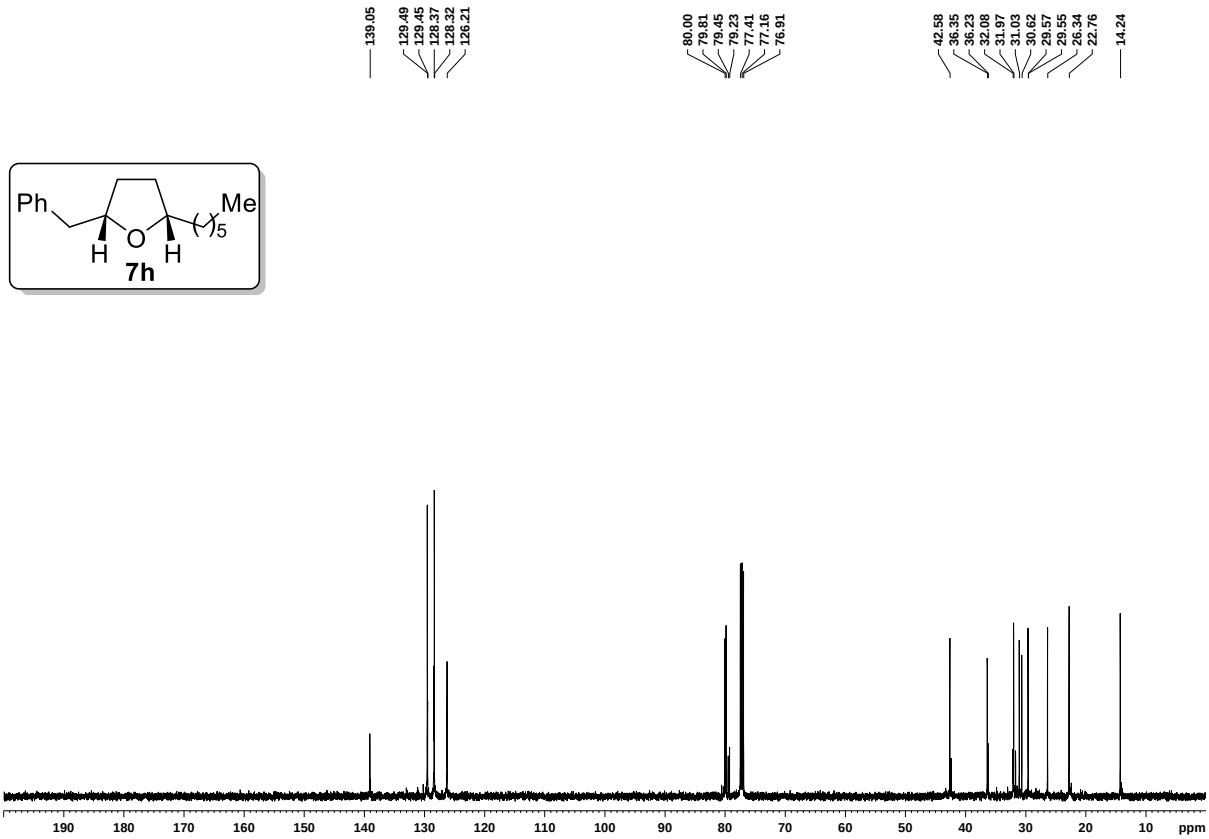




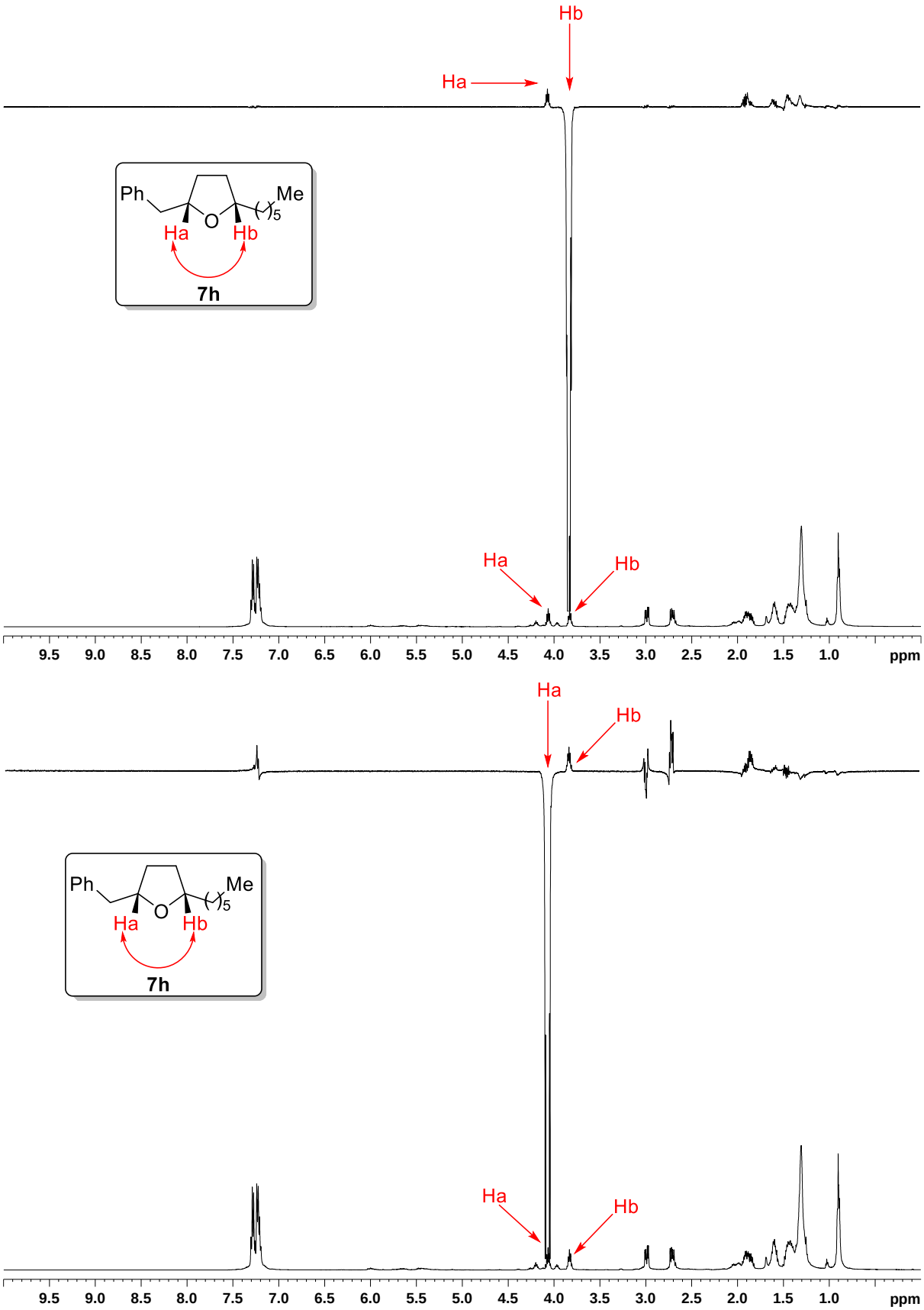
NOE spectrum (400 MHz, $CDCl_3$)



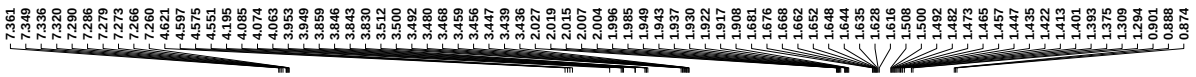
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

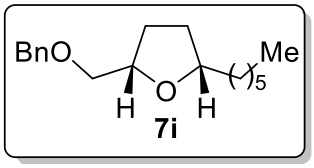


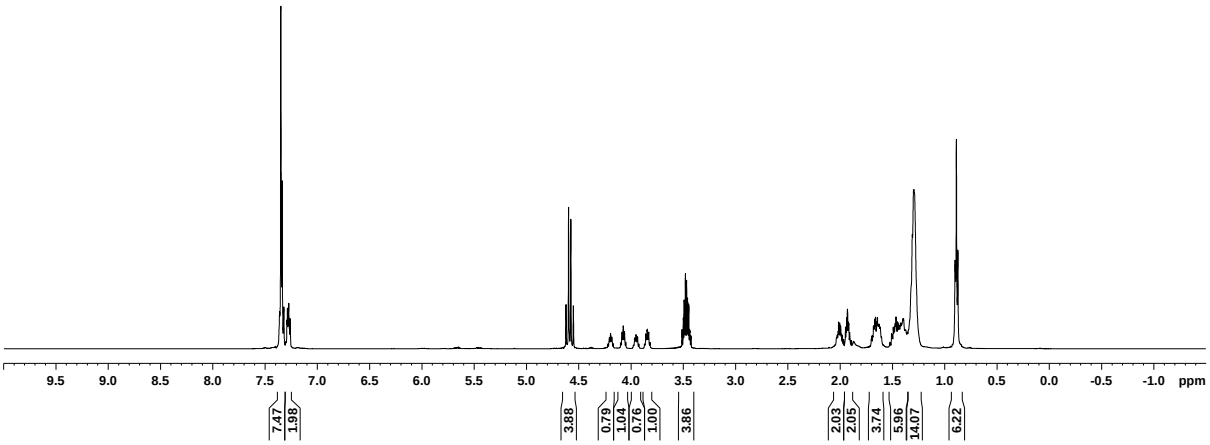
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



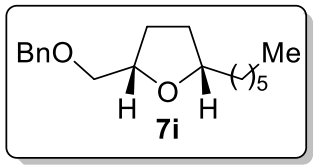
NOE spectrum (500 MHz, $CDCl_3$)

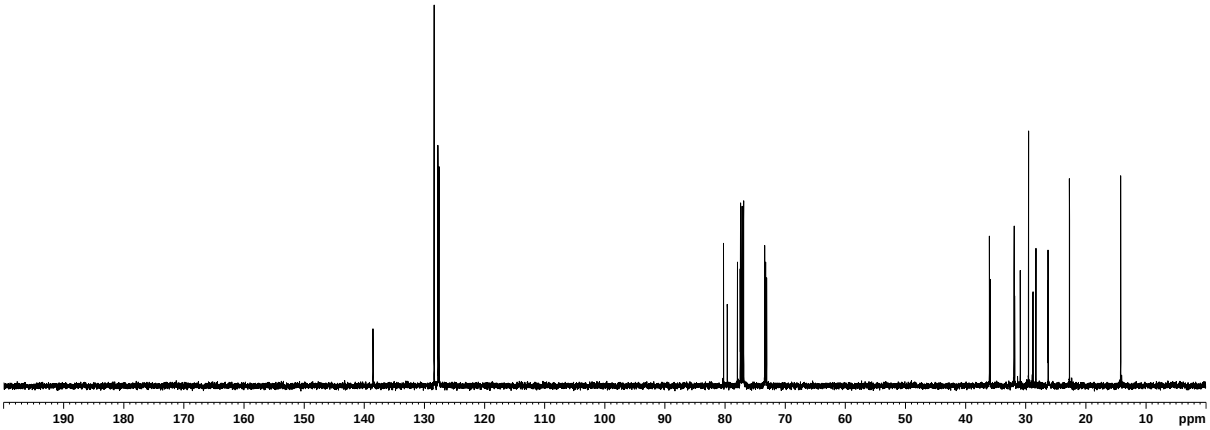




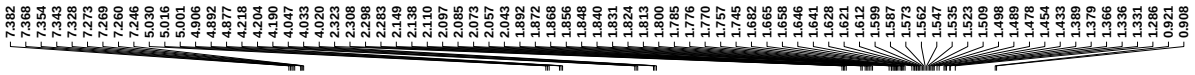


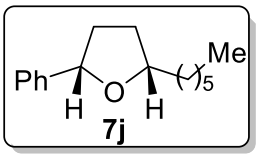
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

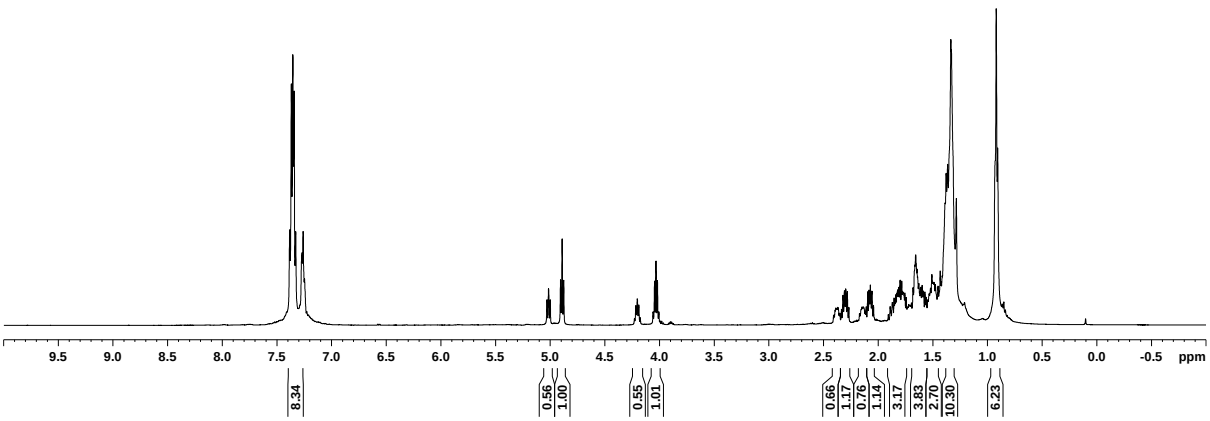




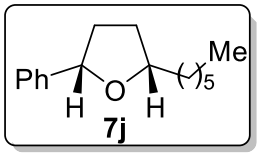
^{13}C NMR spectrum (125 MHz, $CDCl_3$)

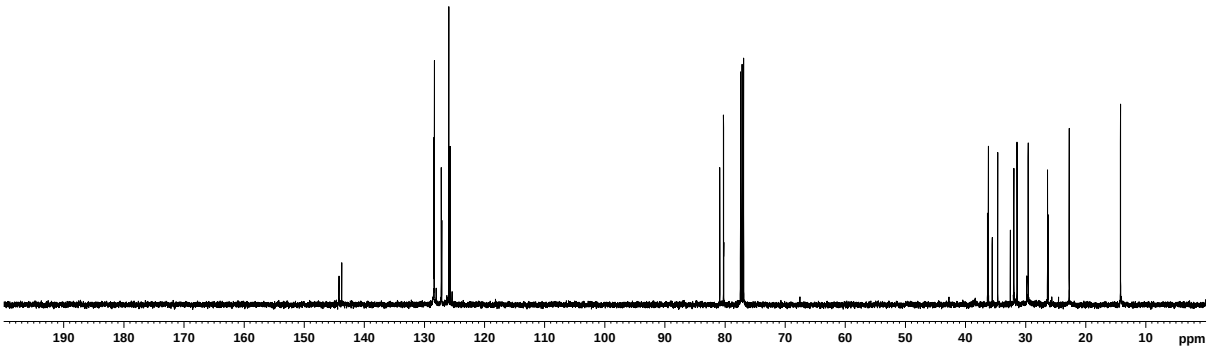




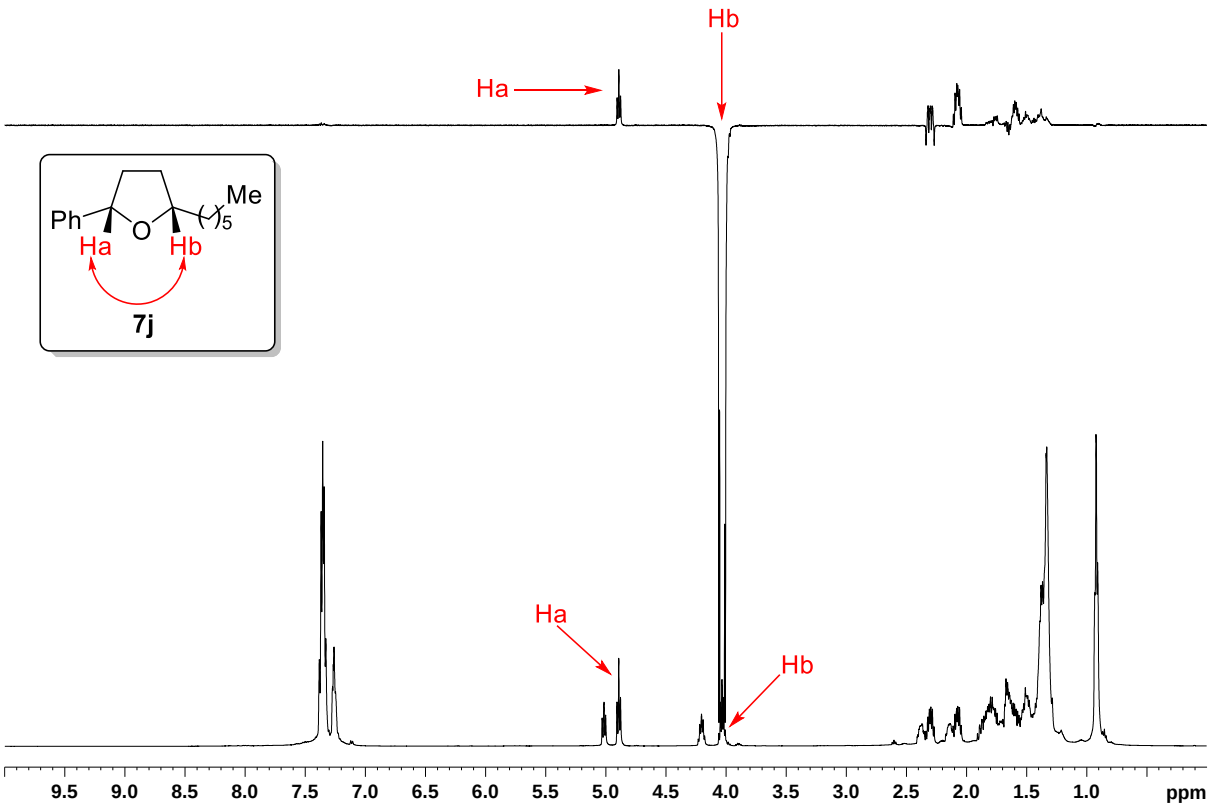


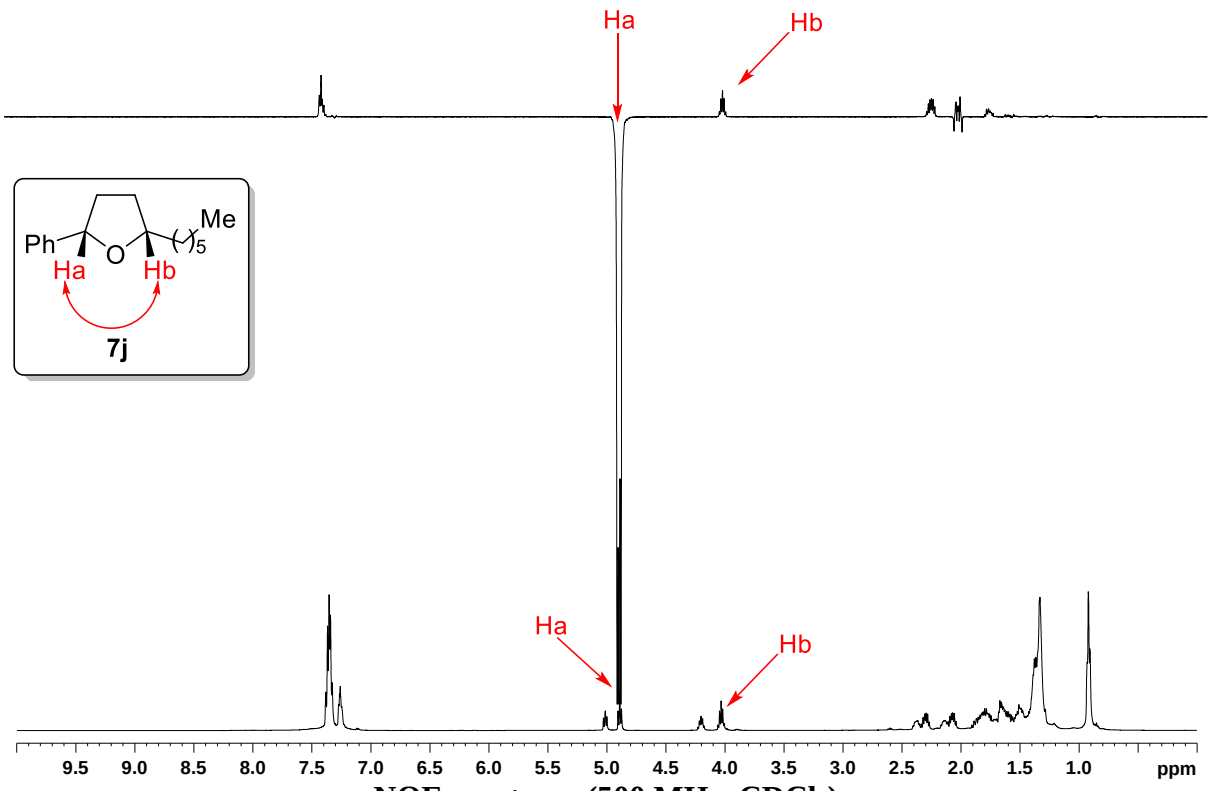
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



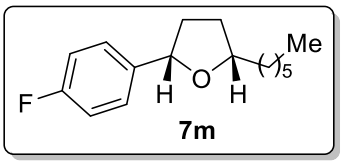


^{13}C NMR spectrum (125 MHz, $CDCl_3$)

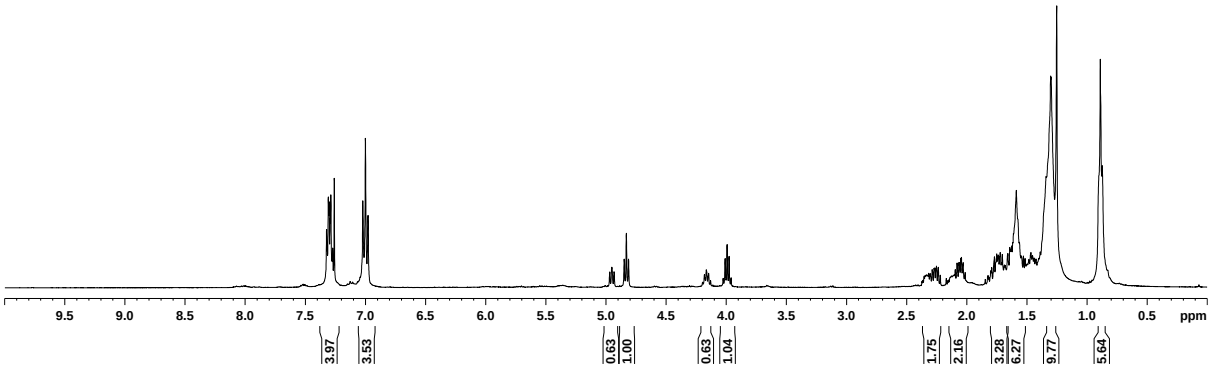




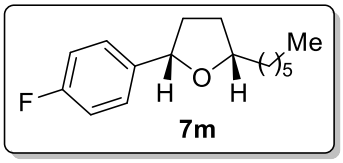
NOE spectrum (500 MHz, $CDCl_3$)



7m

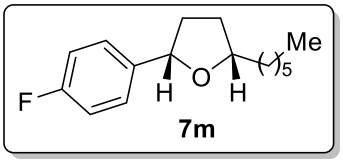


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

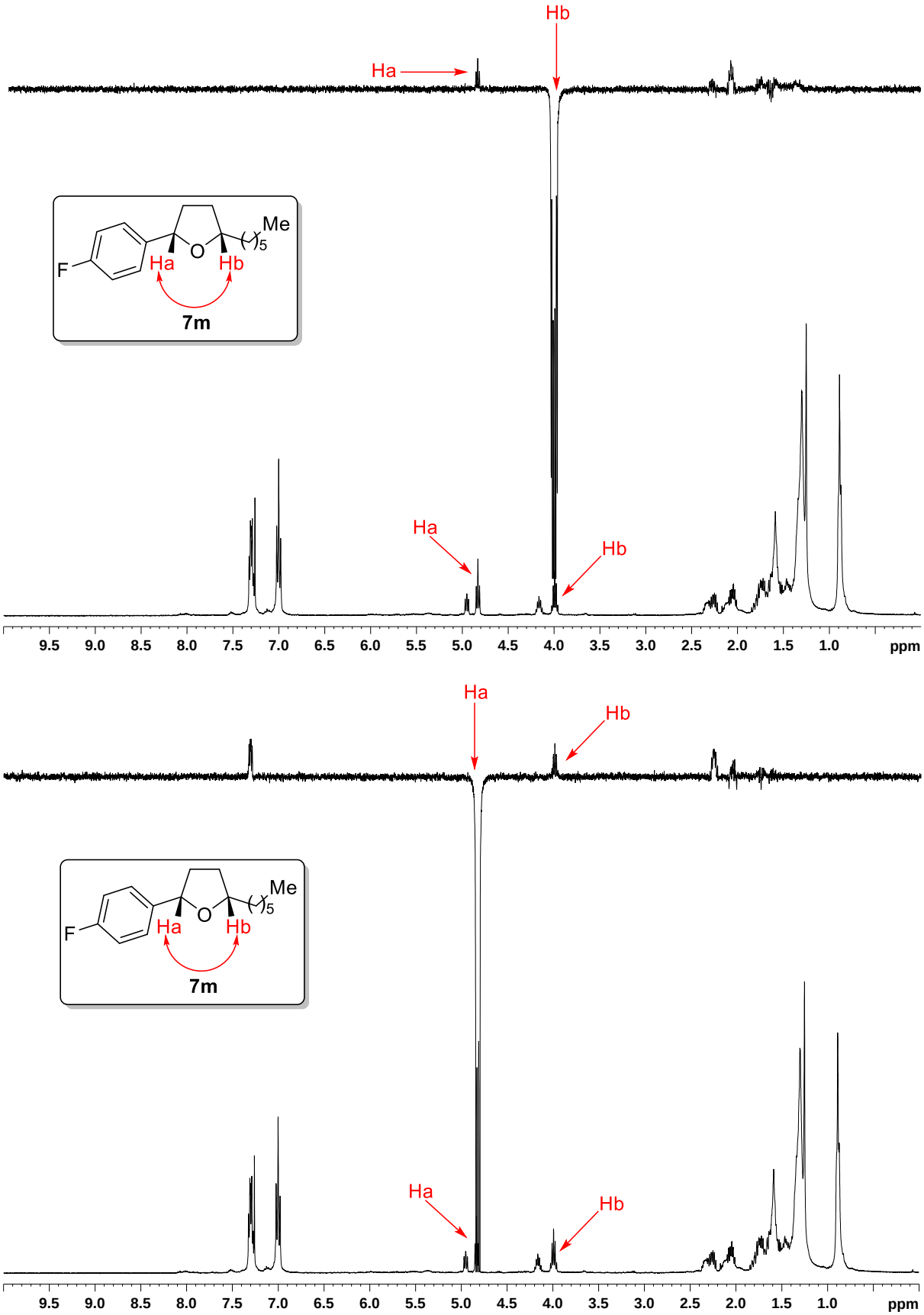


7m

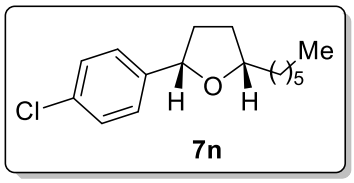
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



^{19}F NMR spectrum (377 MHz, $CDCl_3$)



NOE spectrum (400 MHz, $CDCl_3$)



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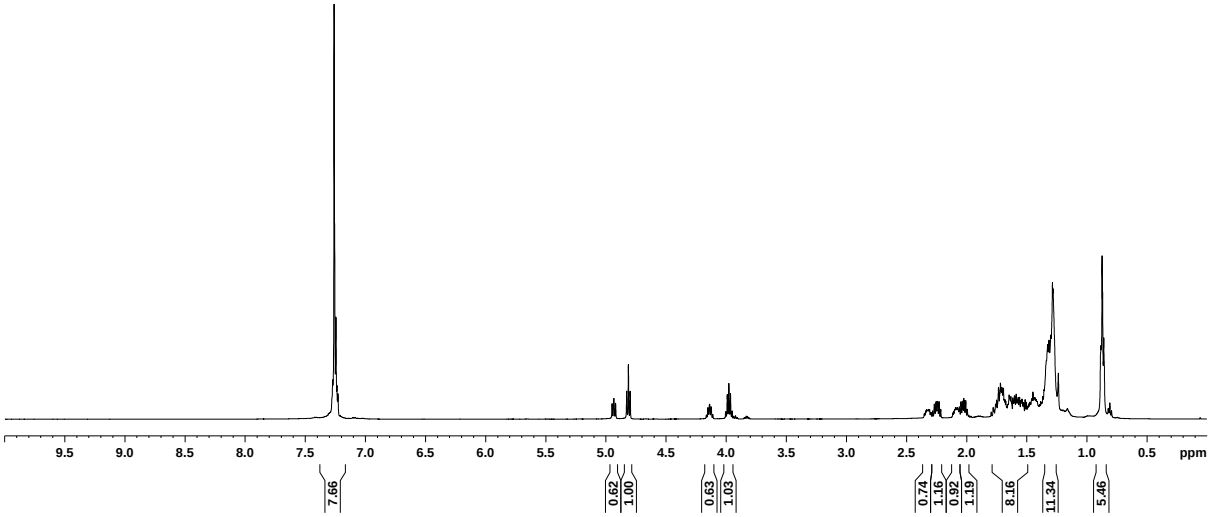
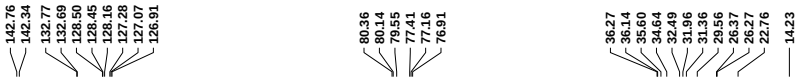
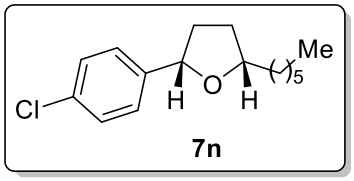


^{1}H NMR spectrum (500 MHz, $CDCl_3$)





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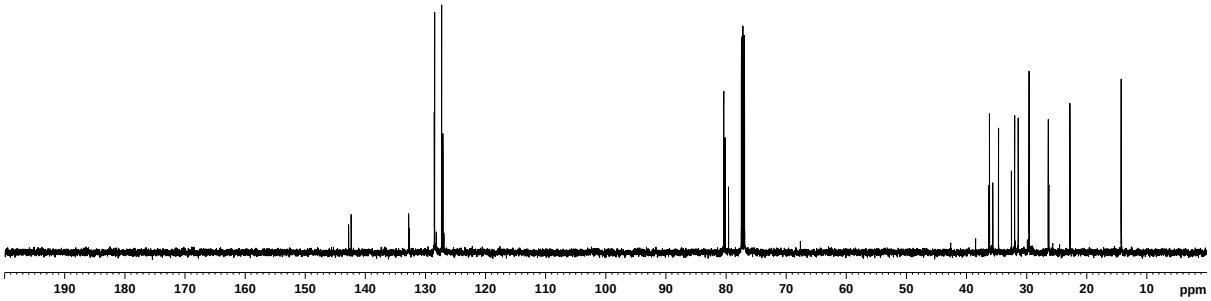
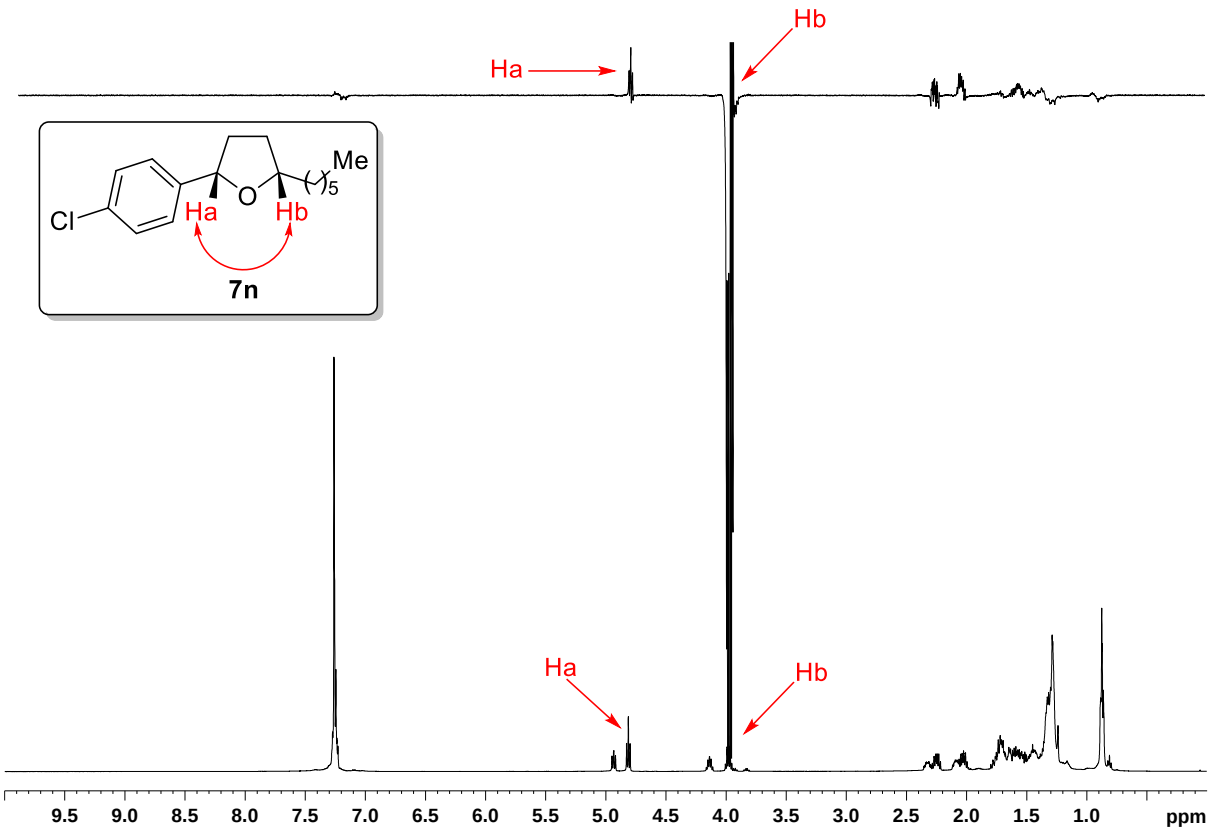
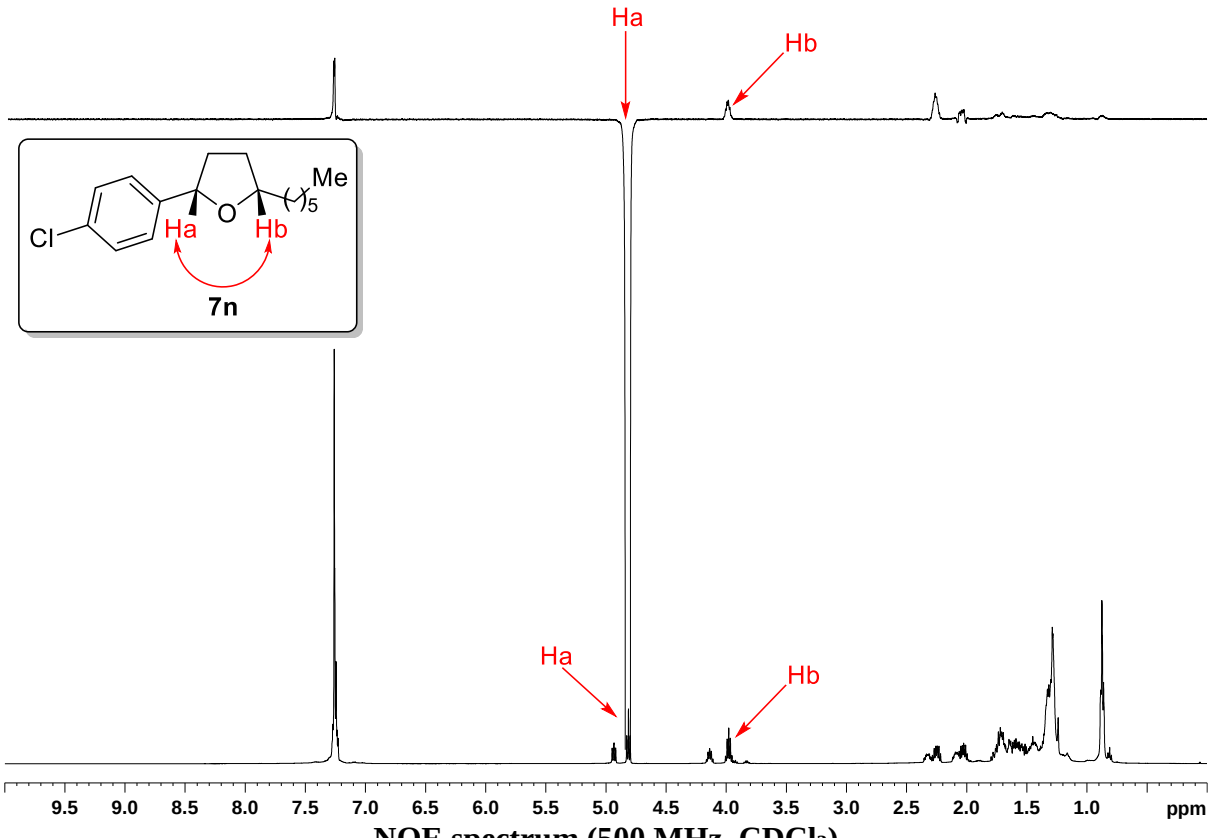
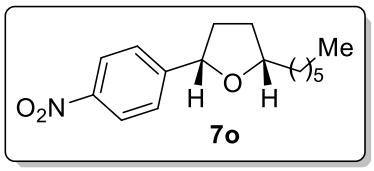


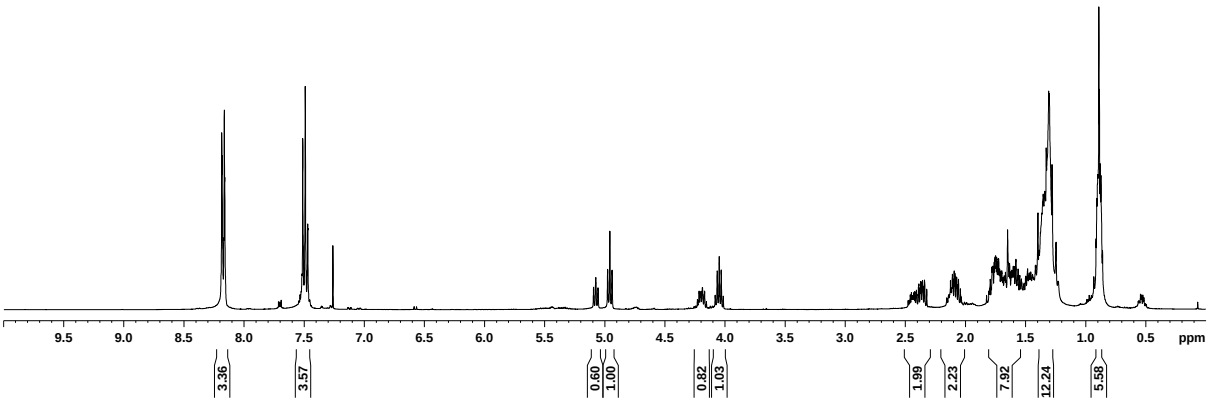
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



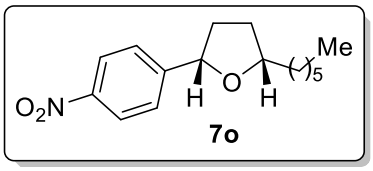


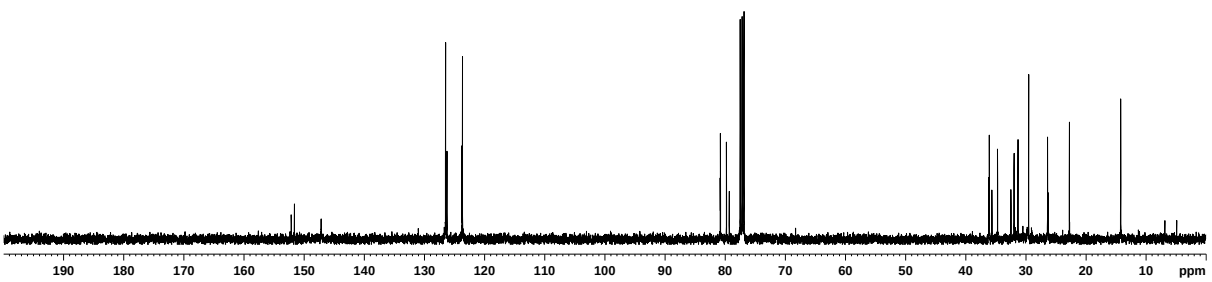
NOE spectrum (500 MHz, $CDCl_3$)



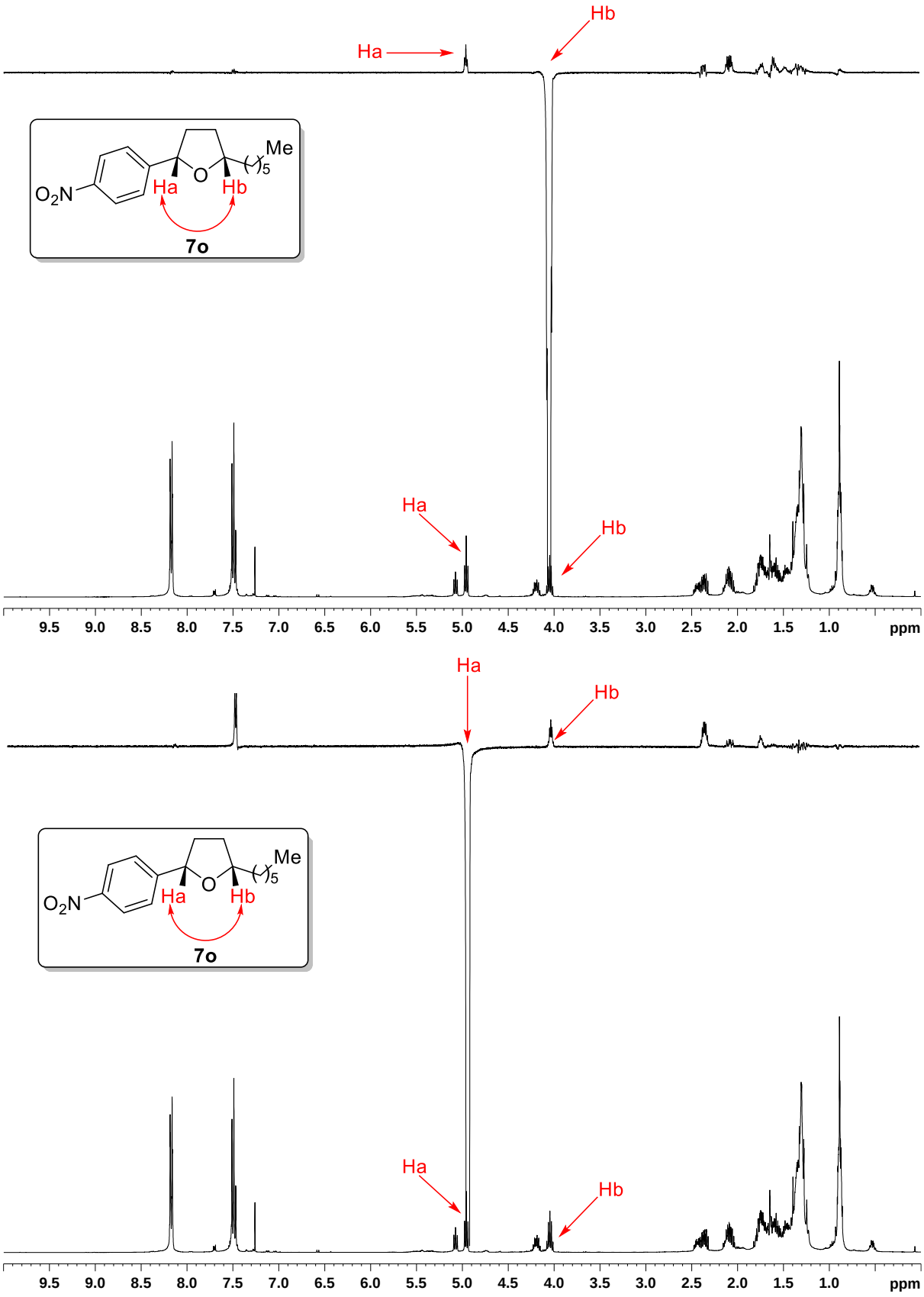


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

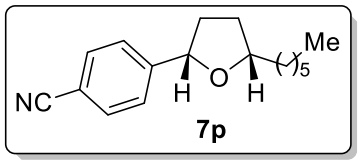




^{13}C NMR spectrum (100 MHz, $CDCl_3$)



NOE spectrum (400 MHz, $CDCl_3$)



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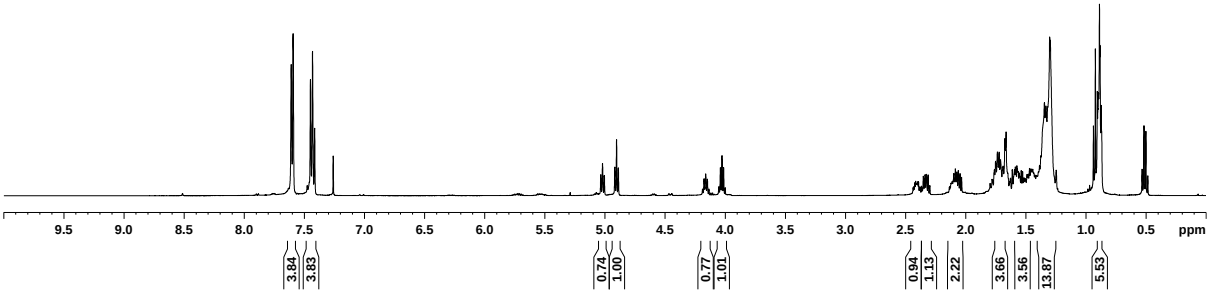
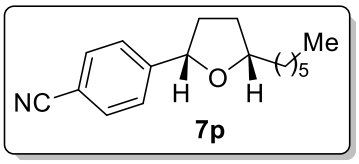


^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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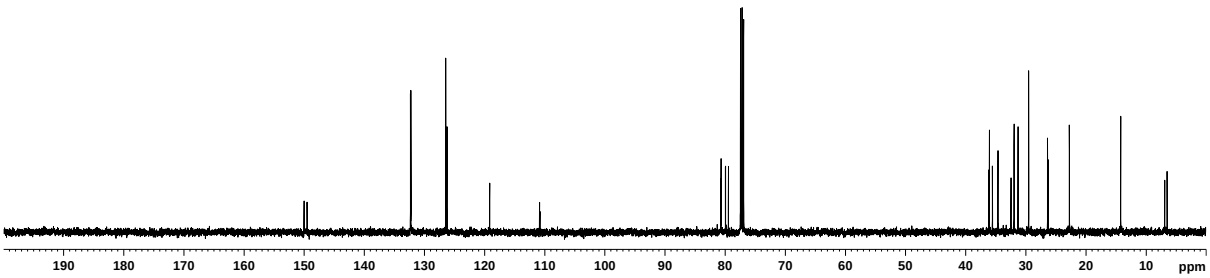
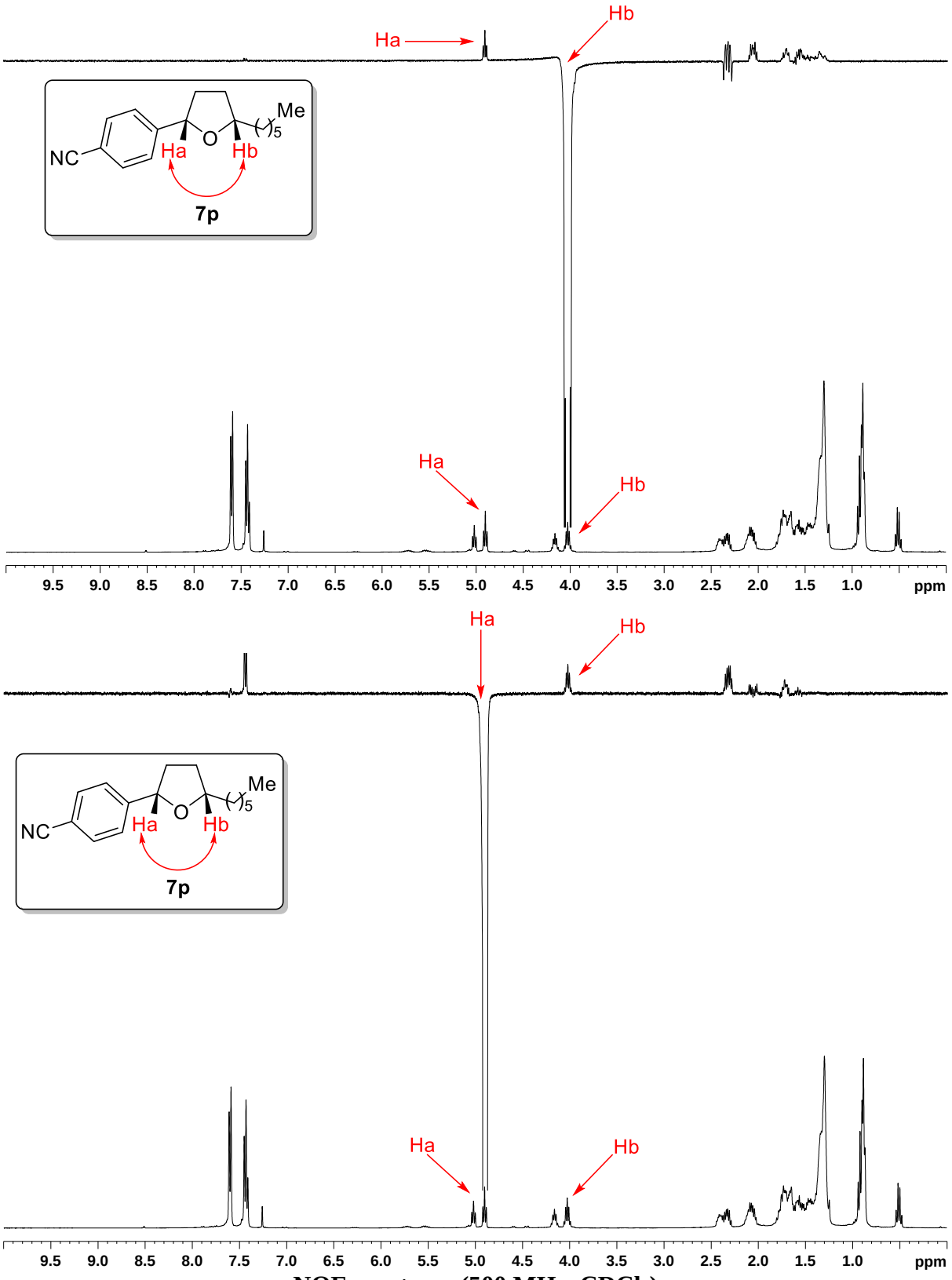
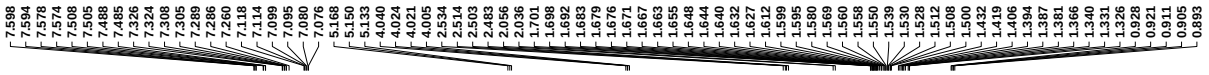
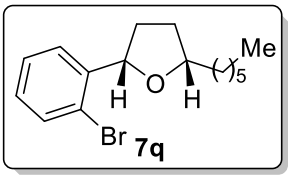


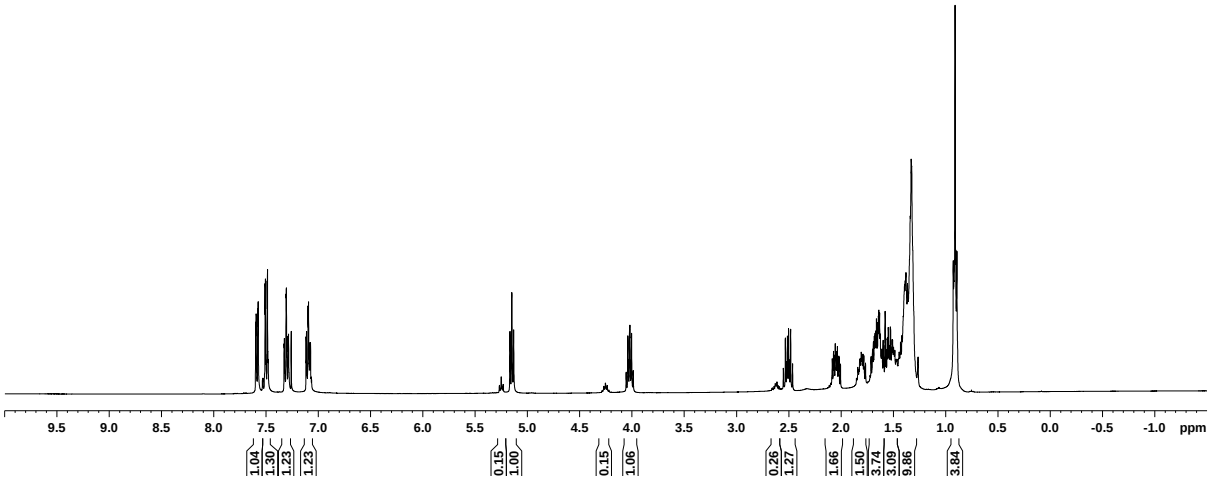
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



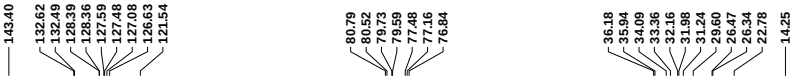
NOE spectrum (500 MHz, $CDCl_3$)

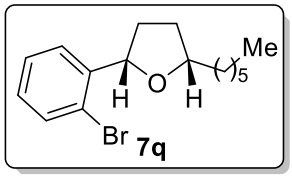


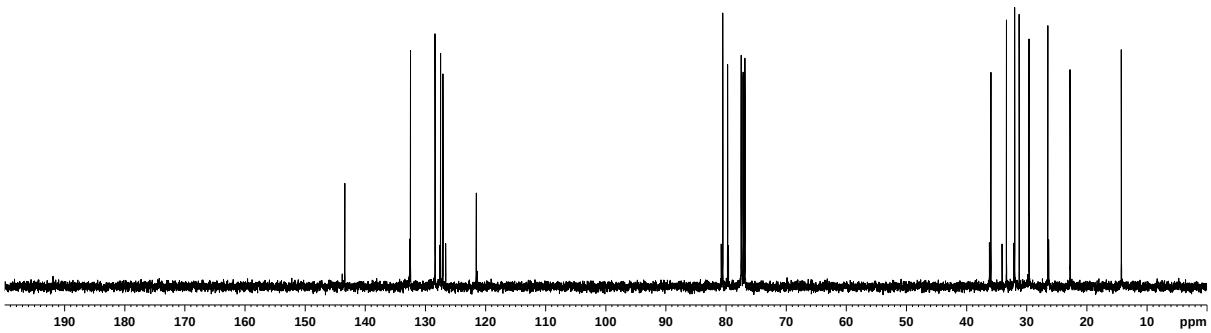




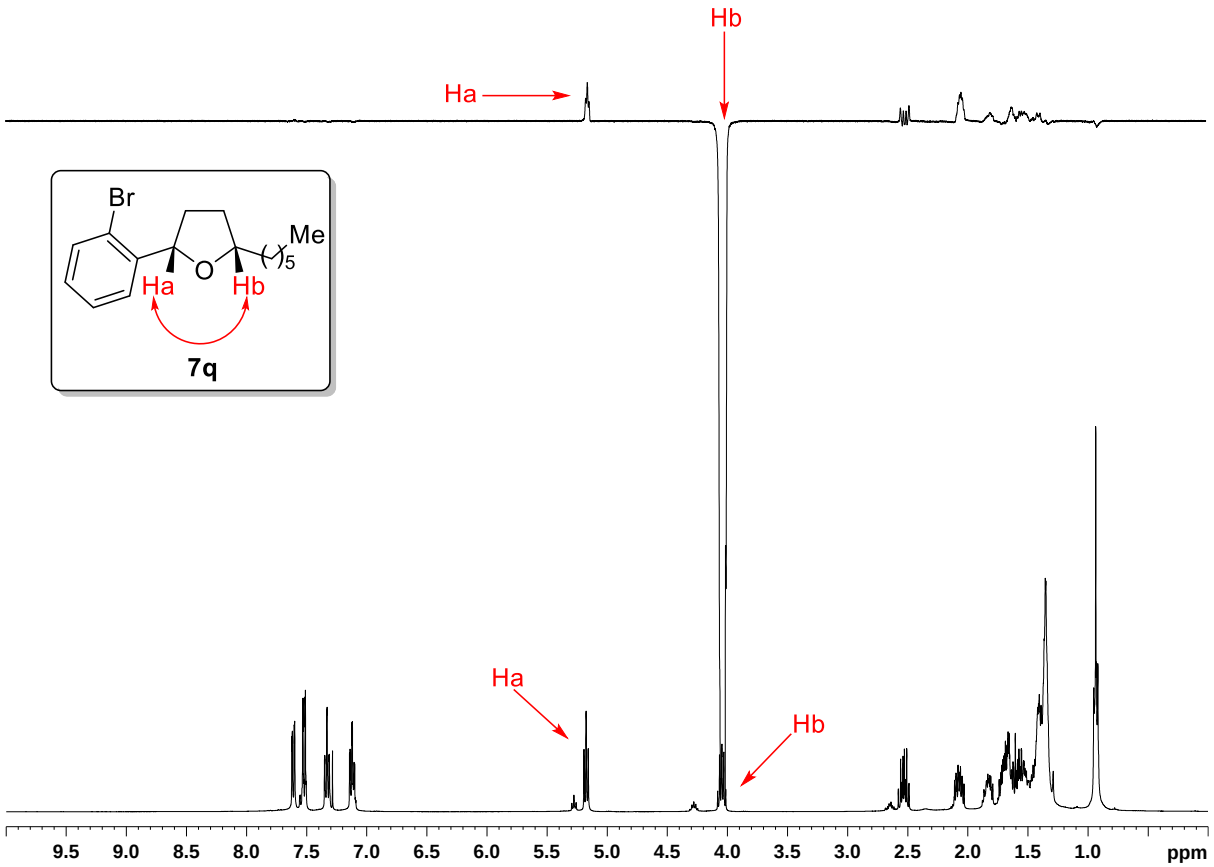
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

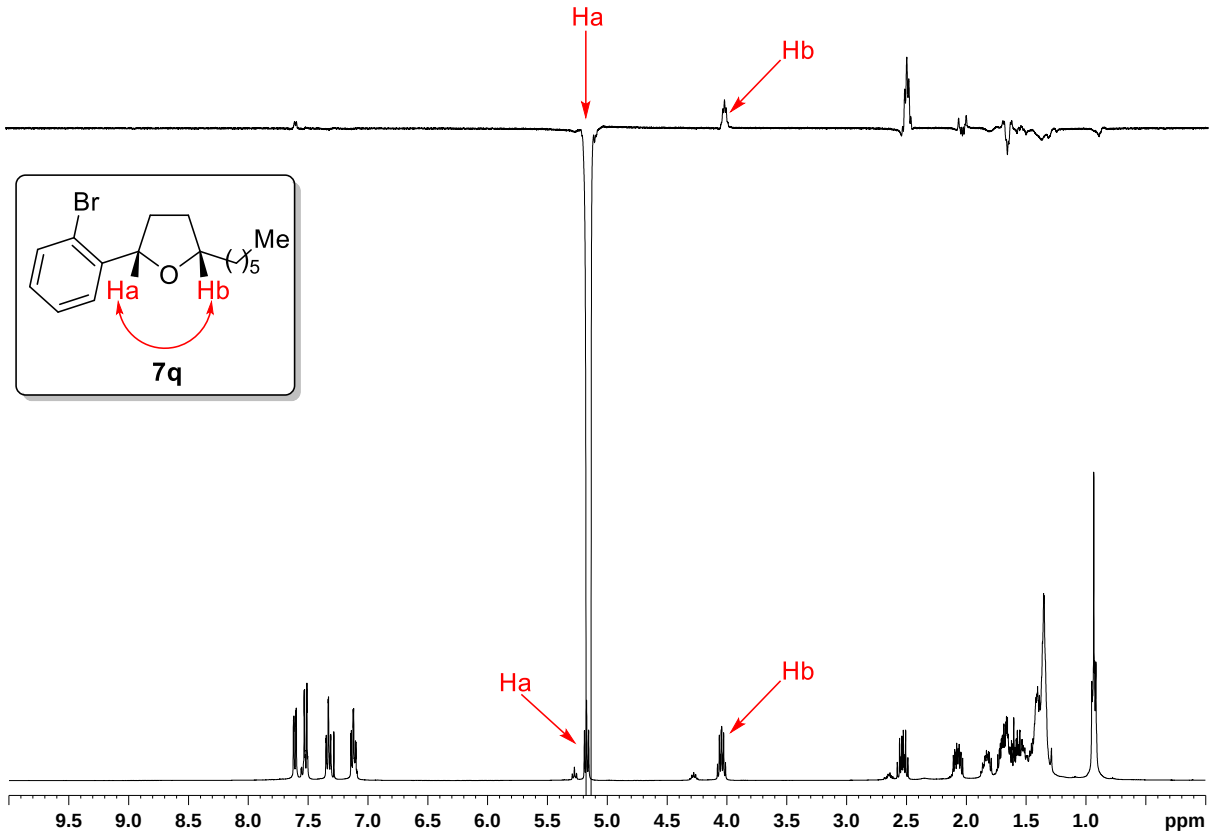




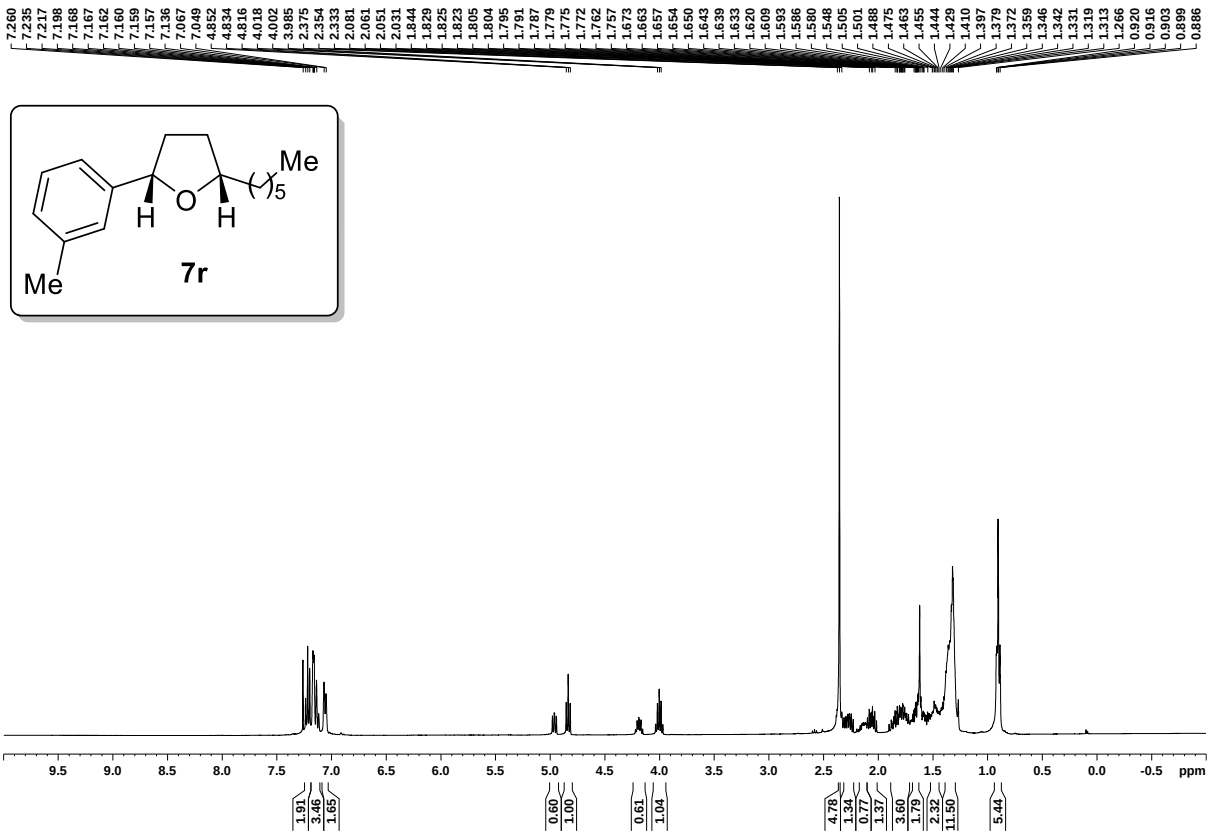


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

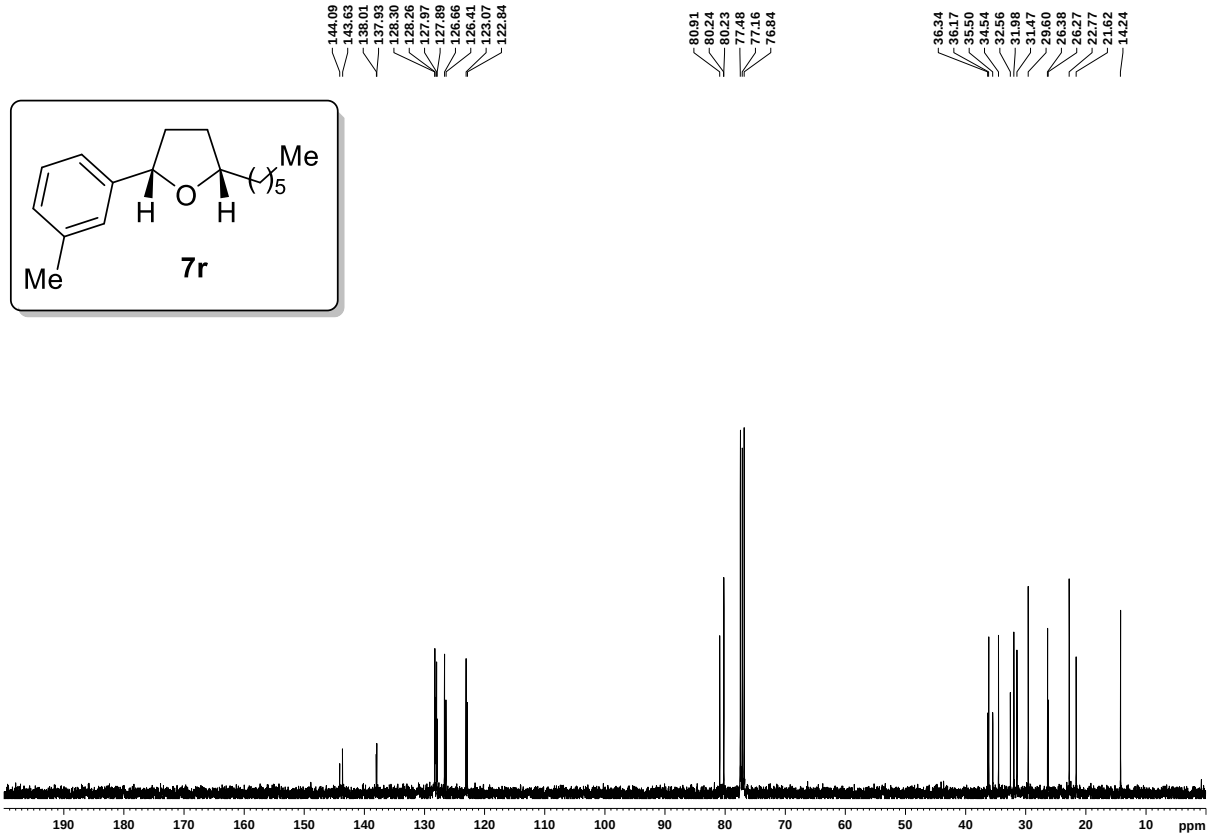




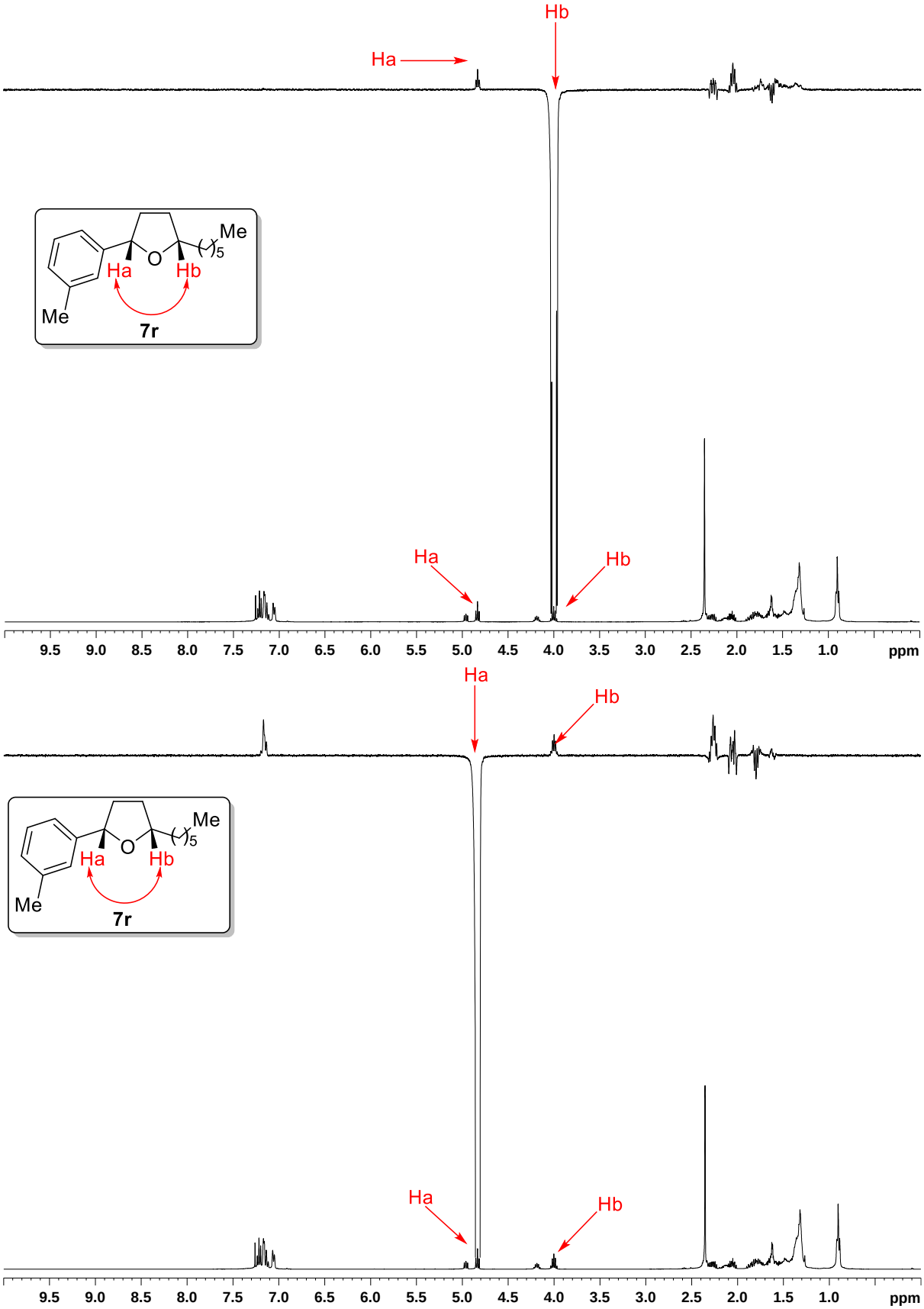
NOE spectrum (400 MHz, $CDCl_3$)



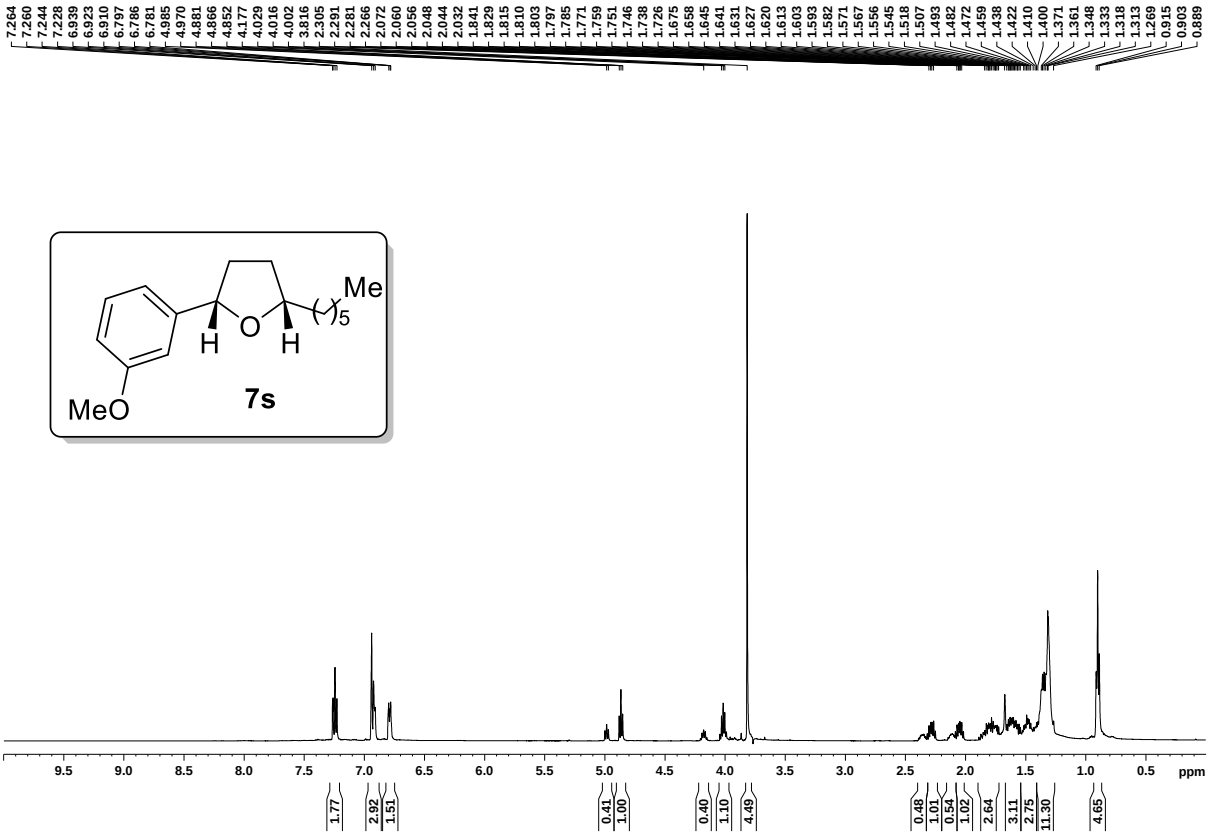
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



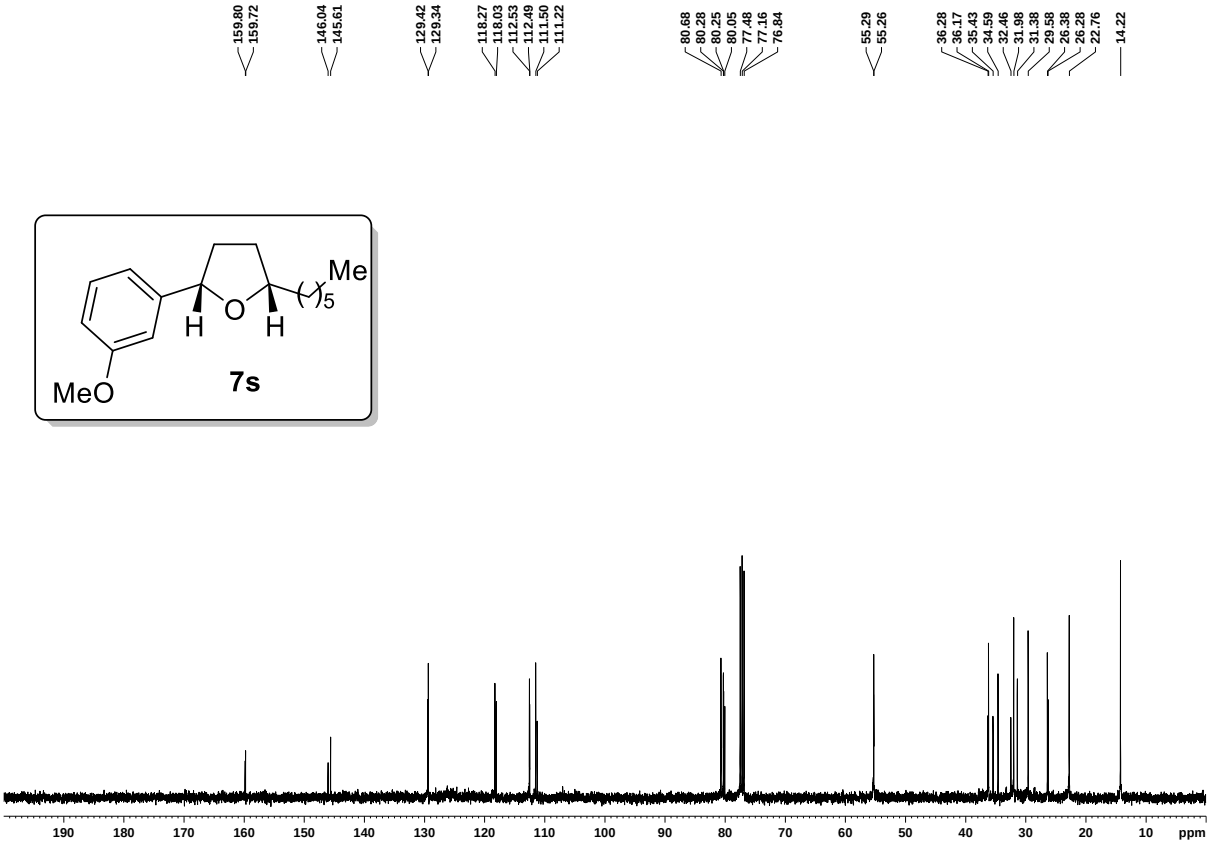
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



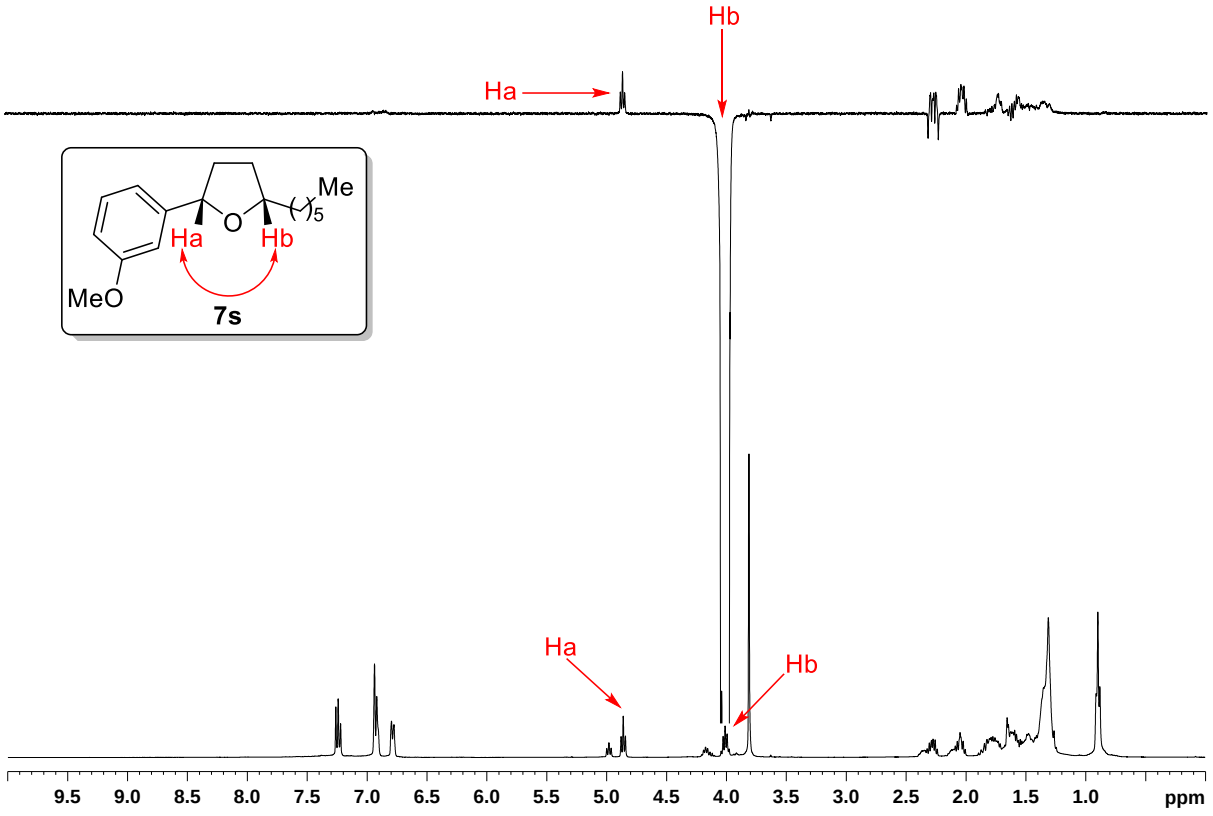
NOE spectrum (400 MHz, $CDCl_3$)

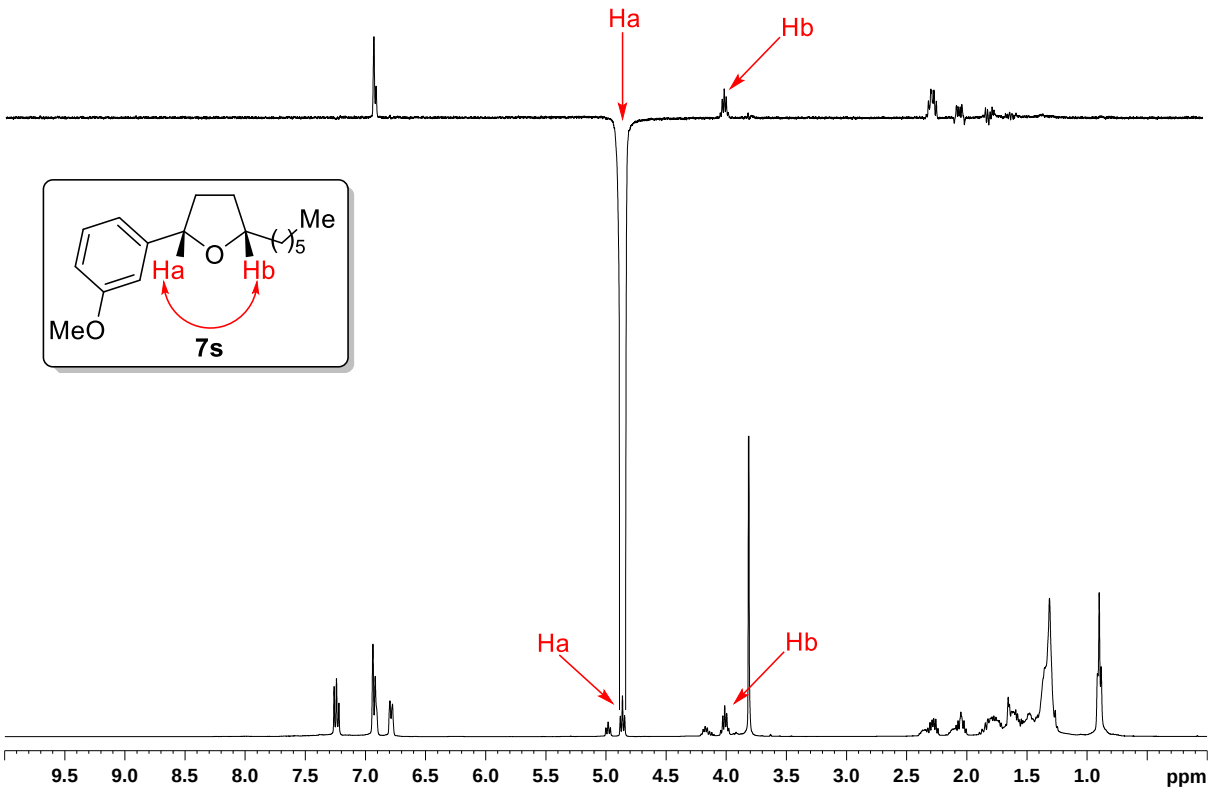


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

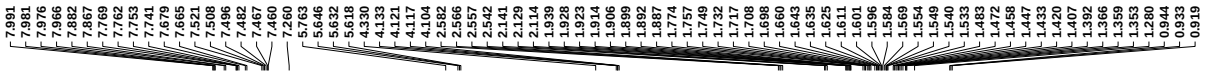


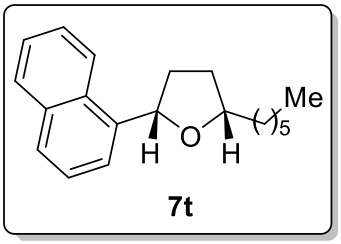
^{13}C NMR spectrum (125 MHz, $CDCl_3$)





NOE spectrum (500 MHz, $CDCl_3$)





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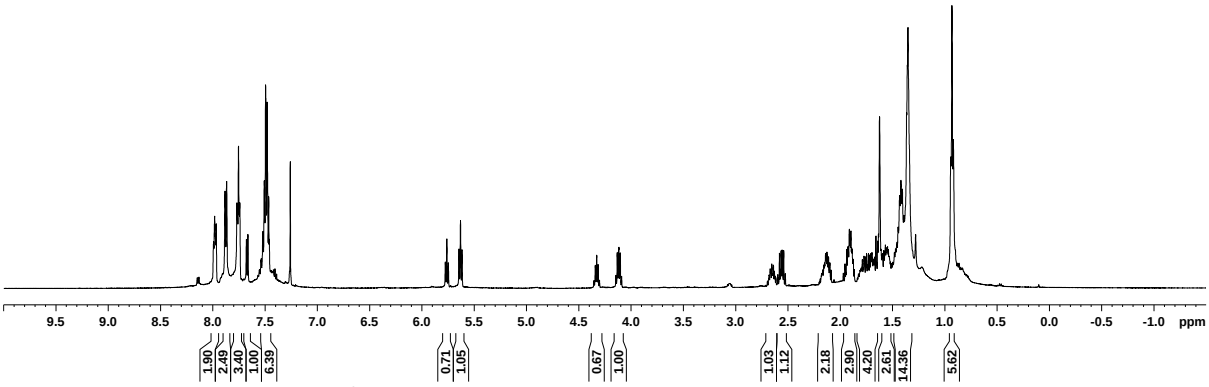
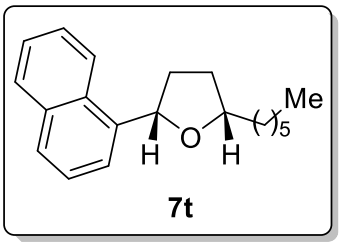


^{1}H NMR spectrum (500 MHz, $CDCl_3$)



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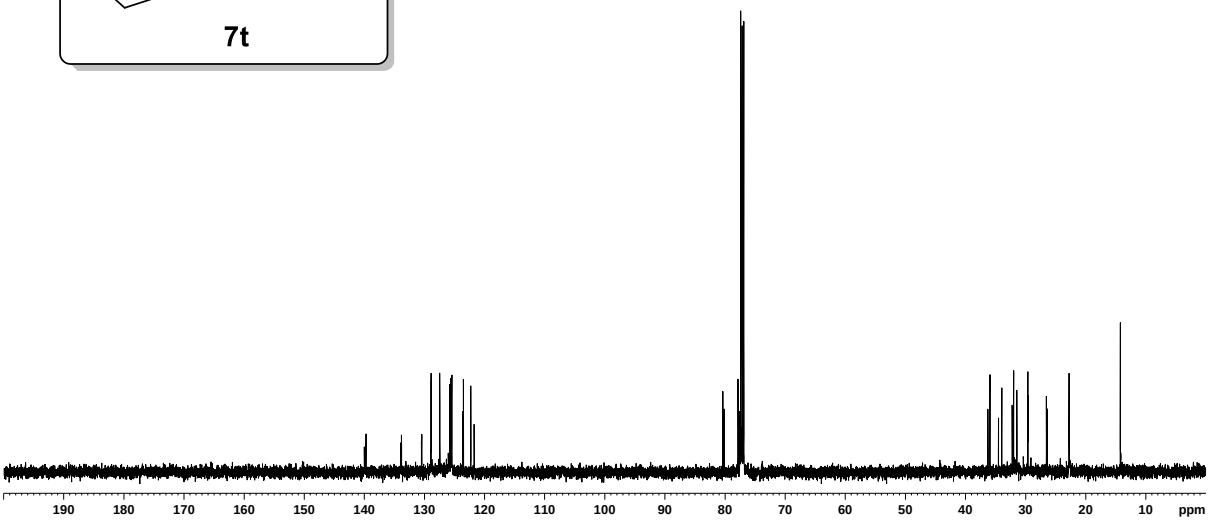
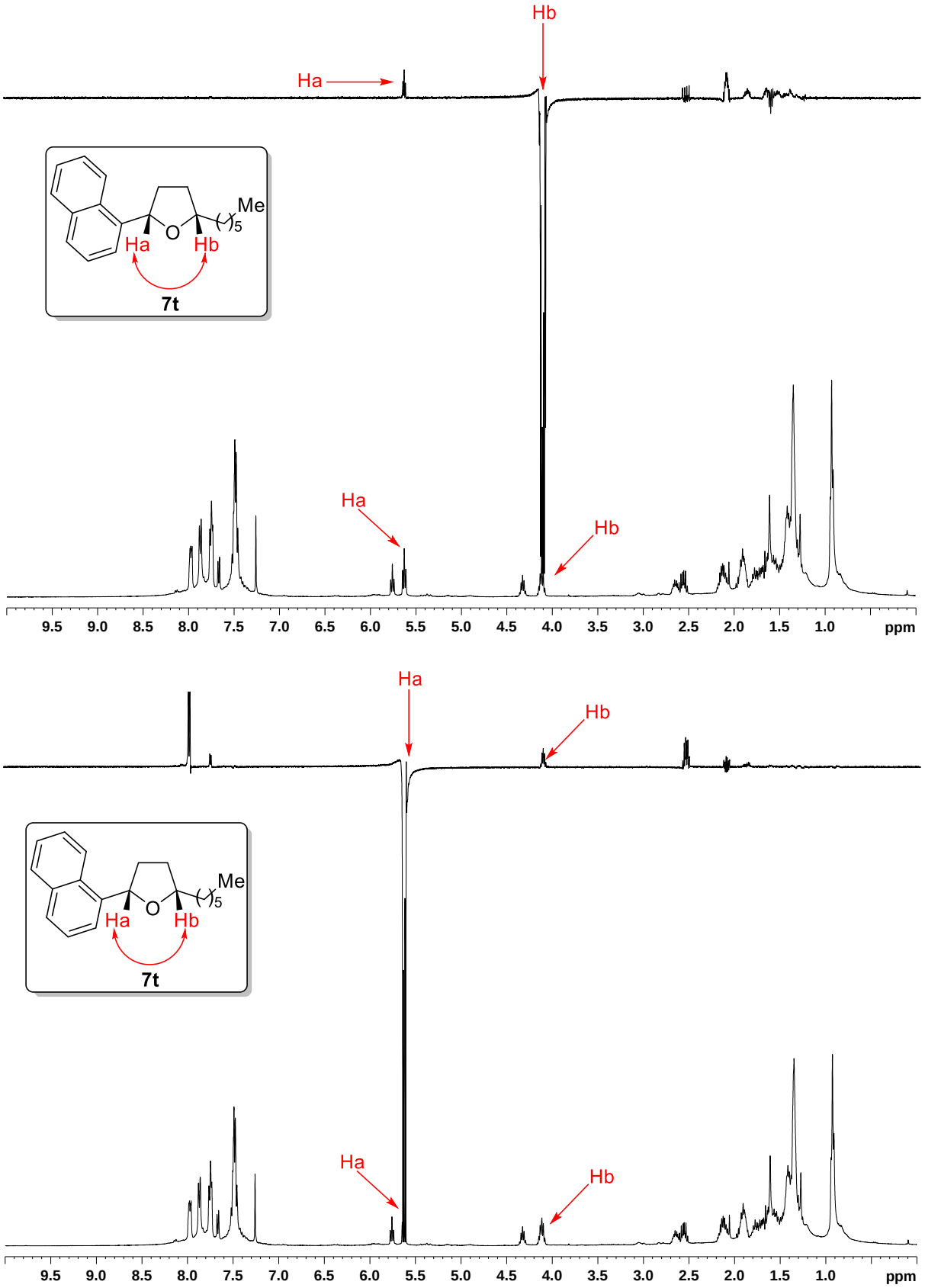
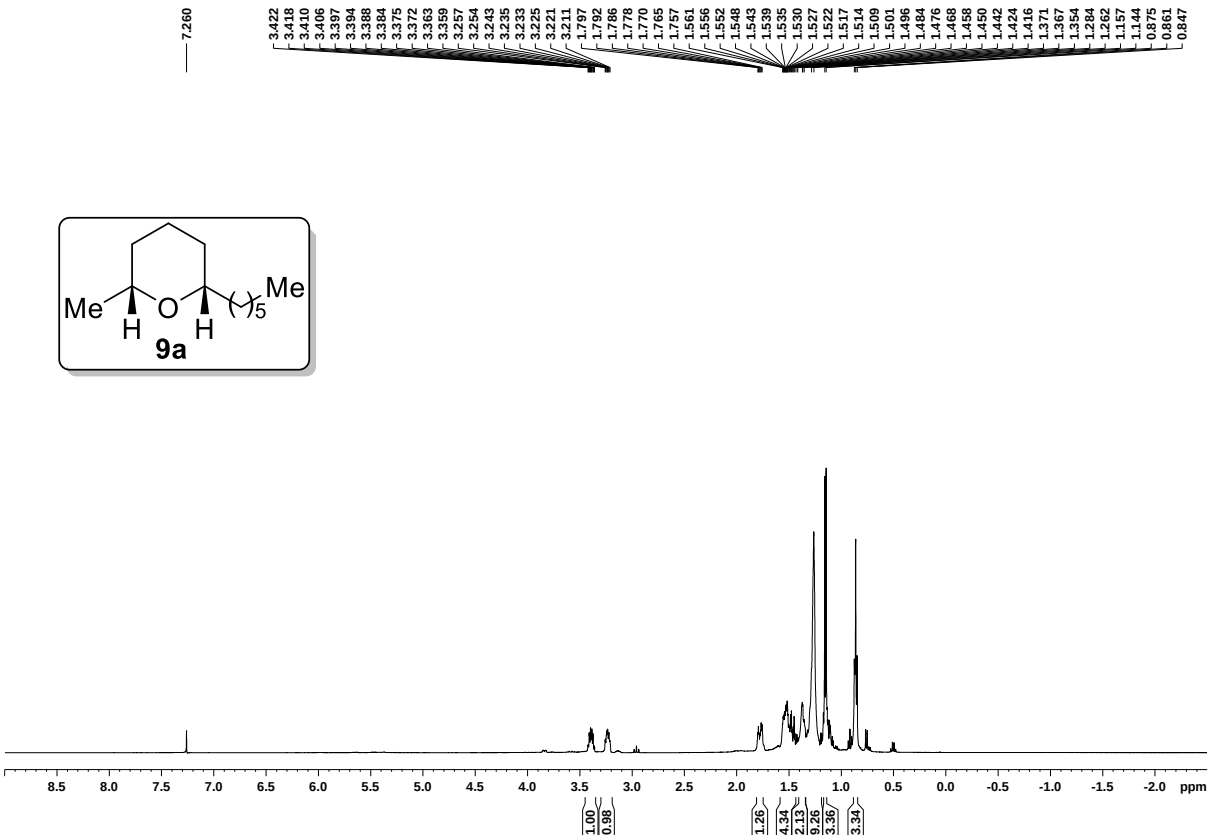


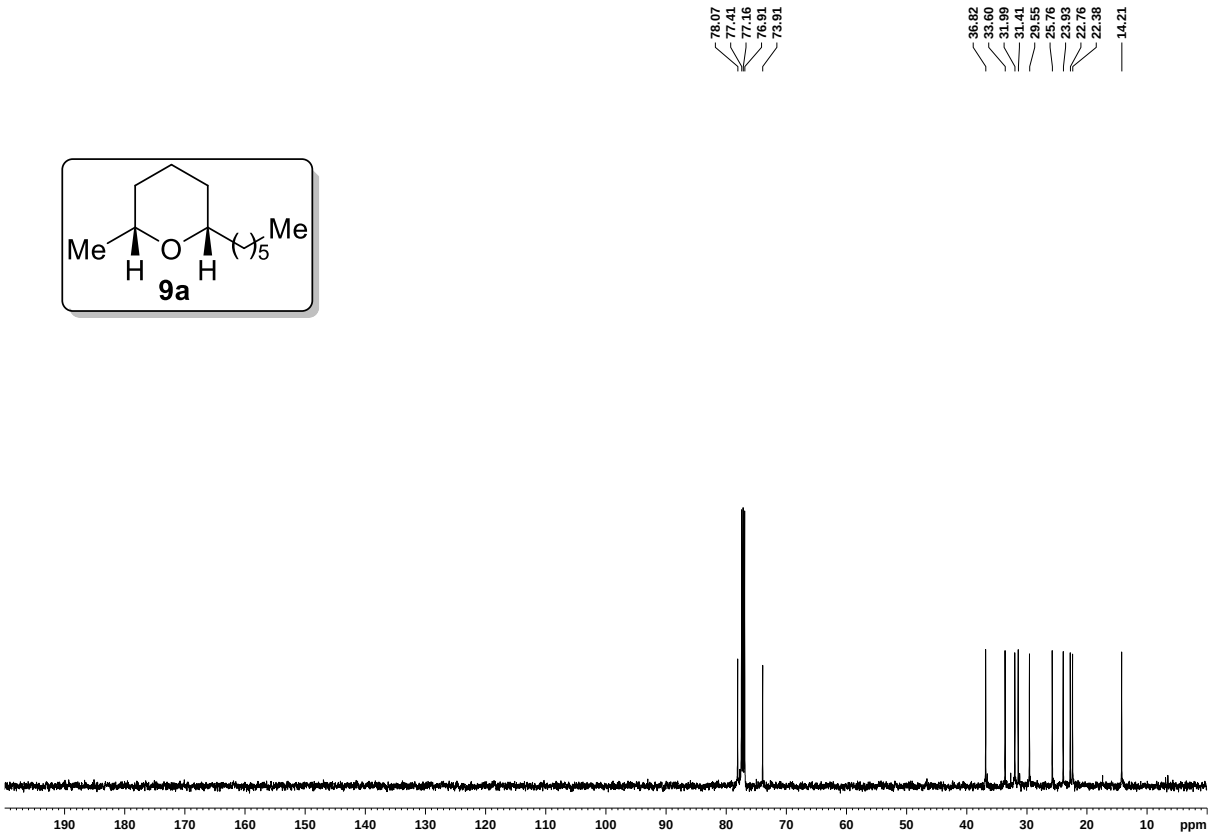
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



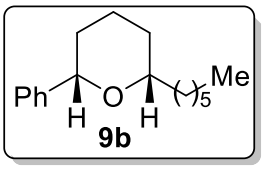
NOE spectrum (500 MHz, $CDCl_3$)

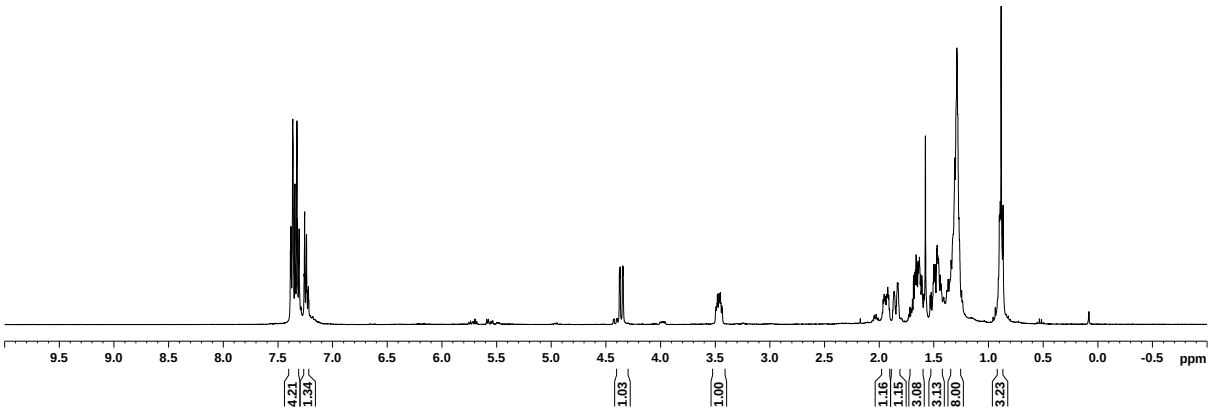


^{1}H NMR spectrum (400 MHz, $CDCl_3$)

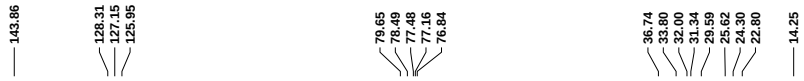


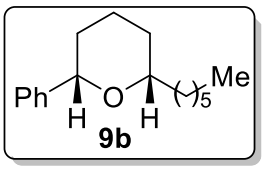
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

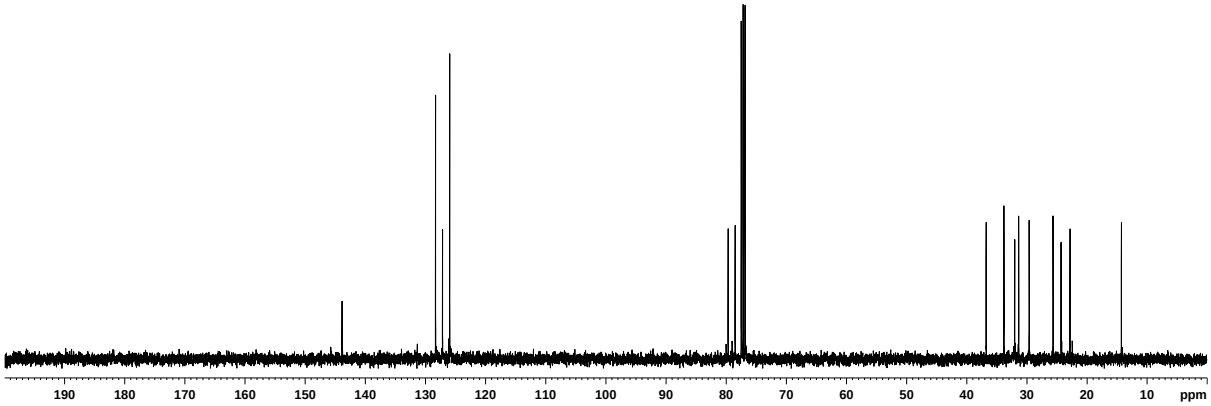




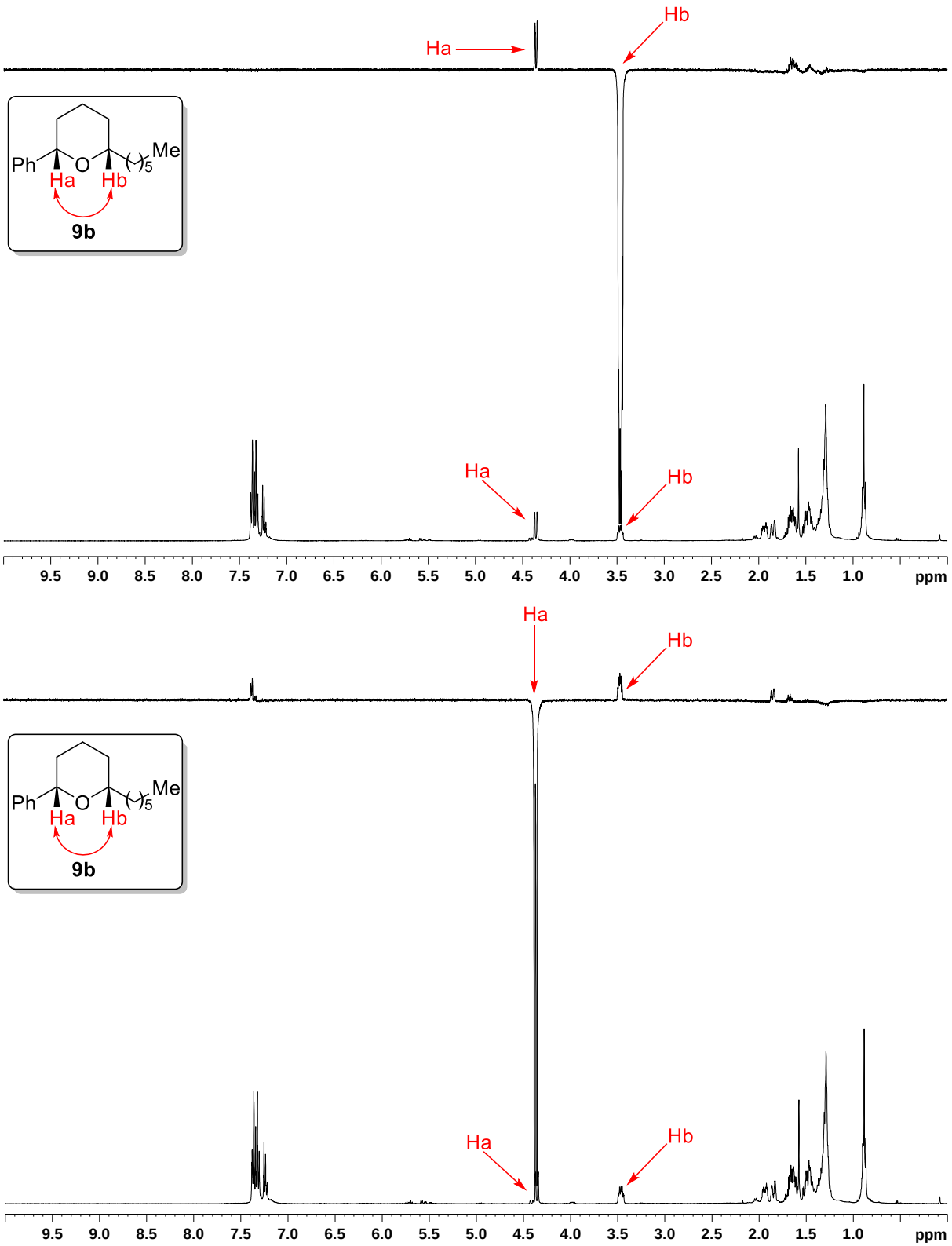
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



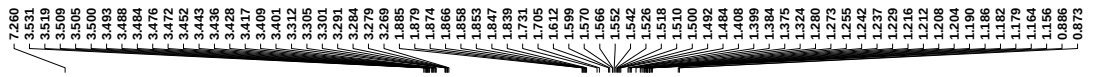


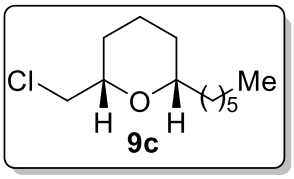


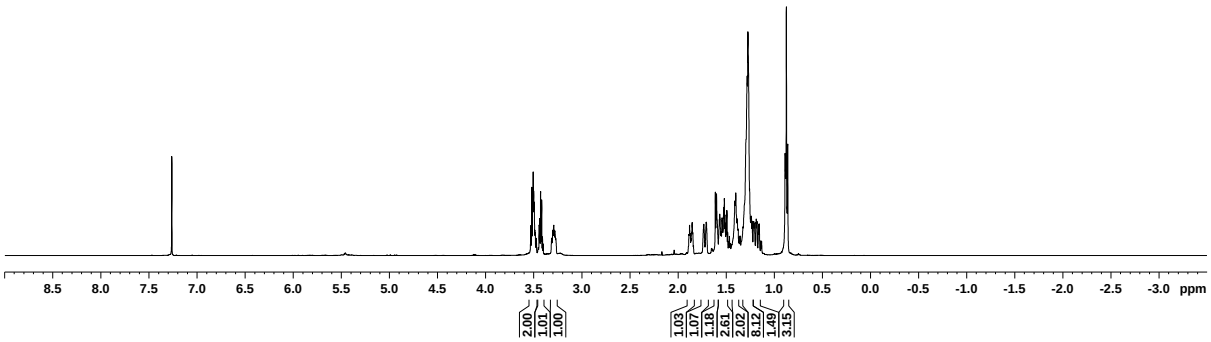
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



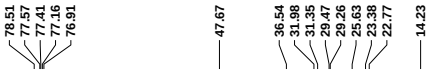
NOE spectrum (400 MHz, $CDCl_3$)

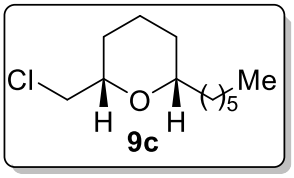


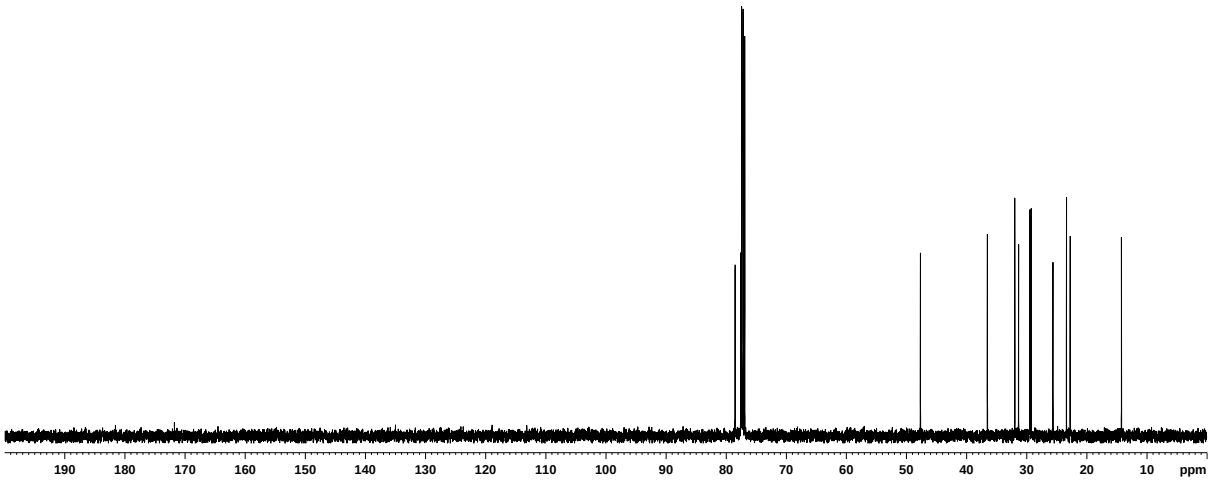




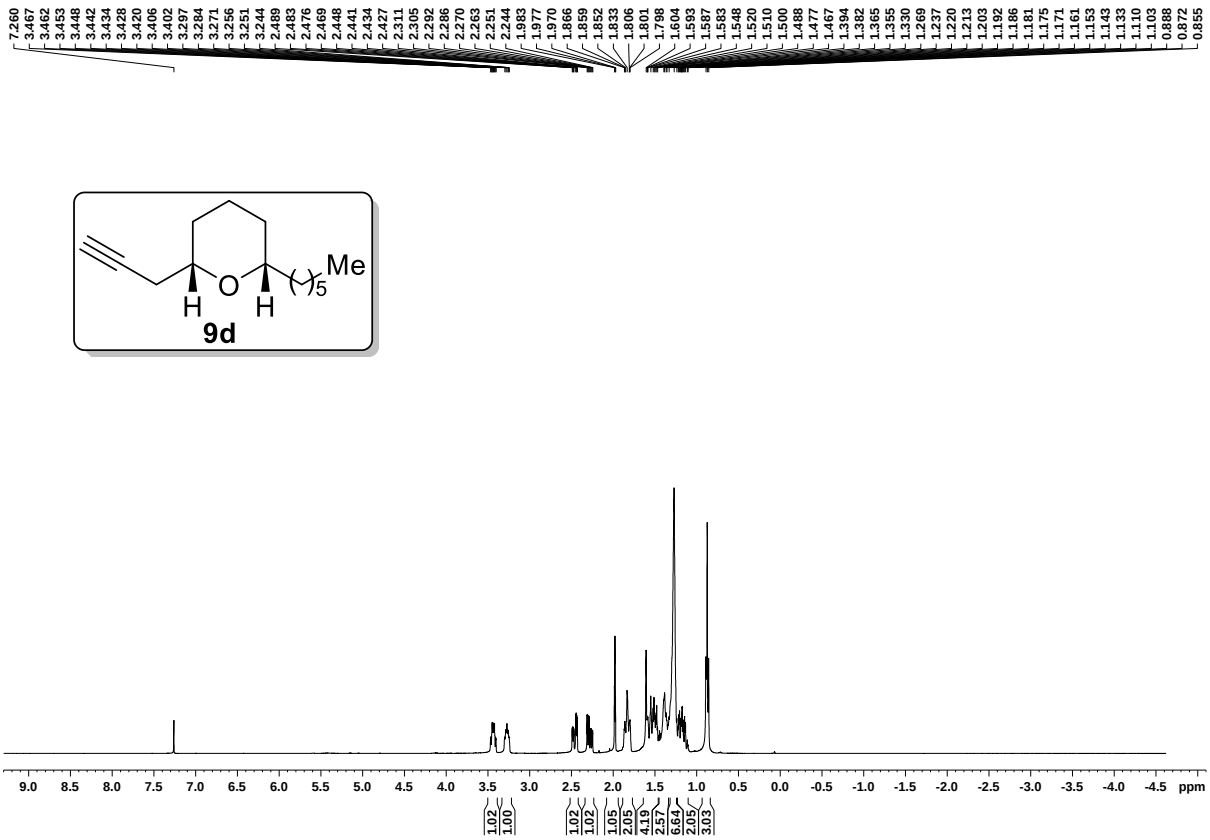
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



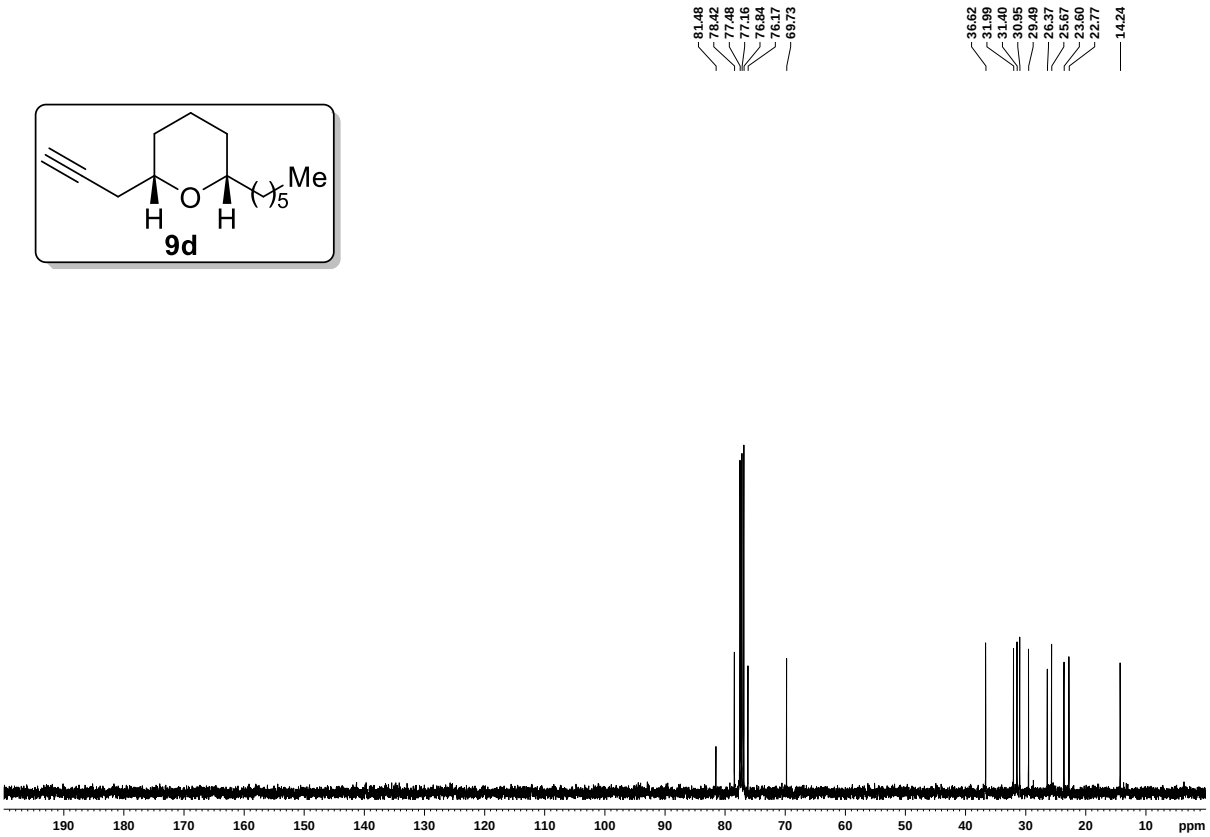




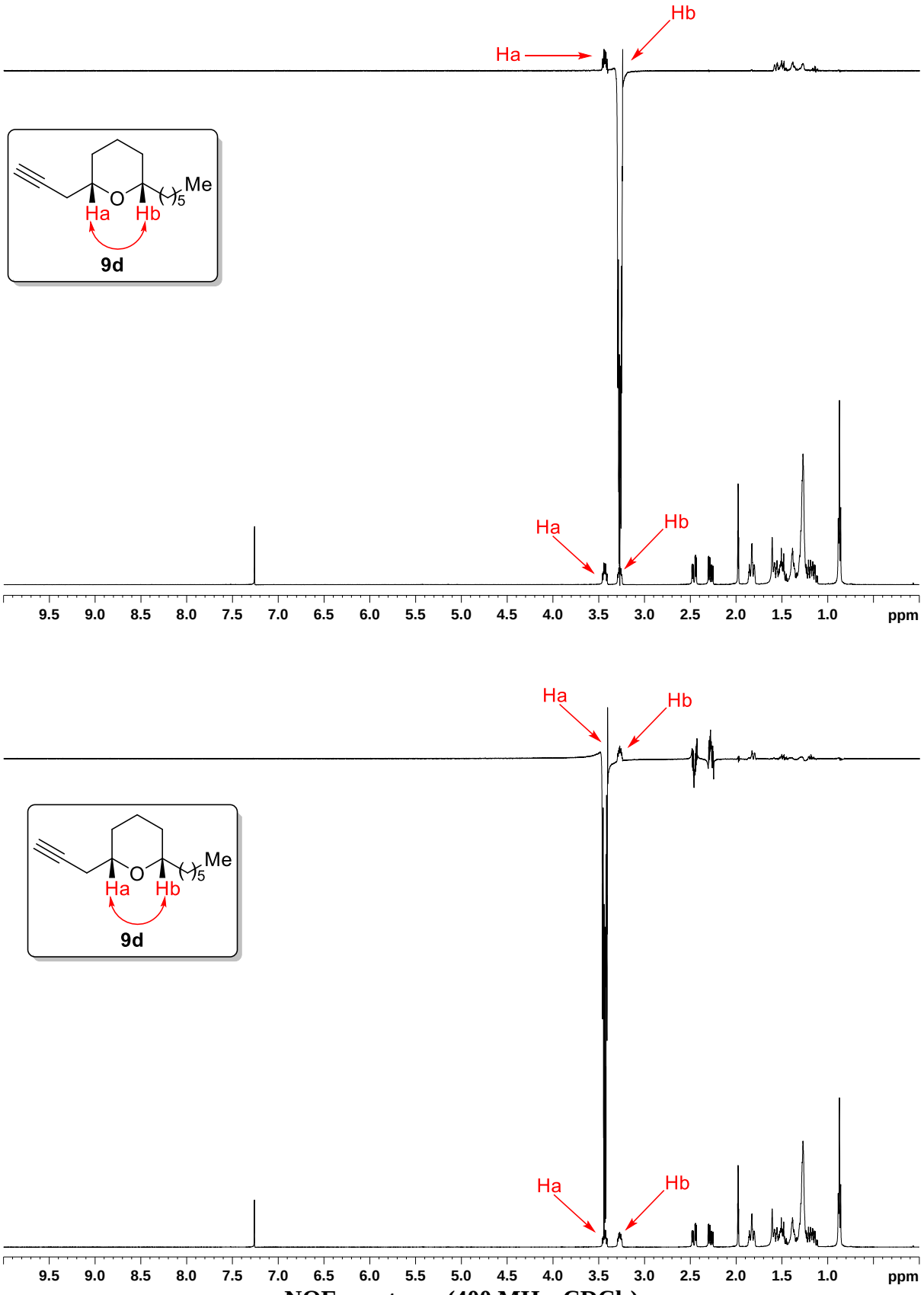
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



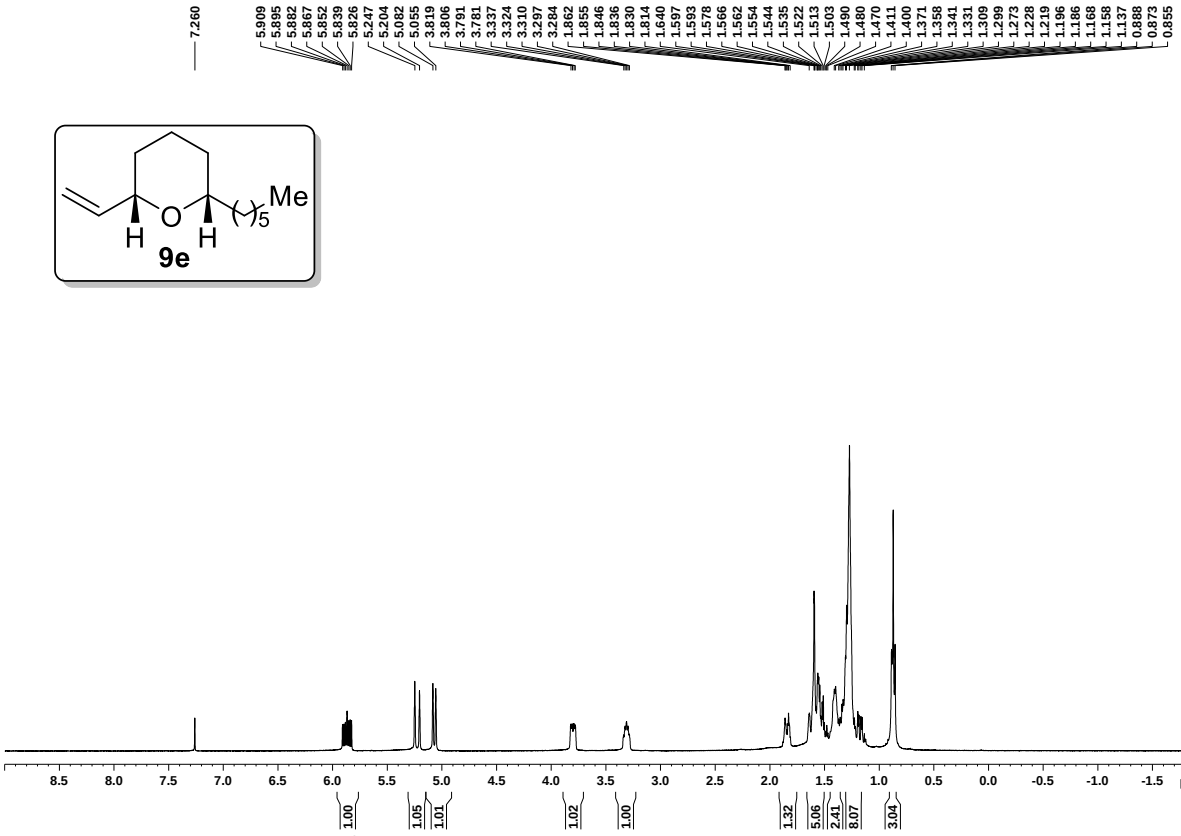
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



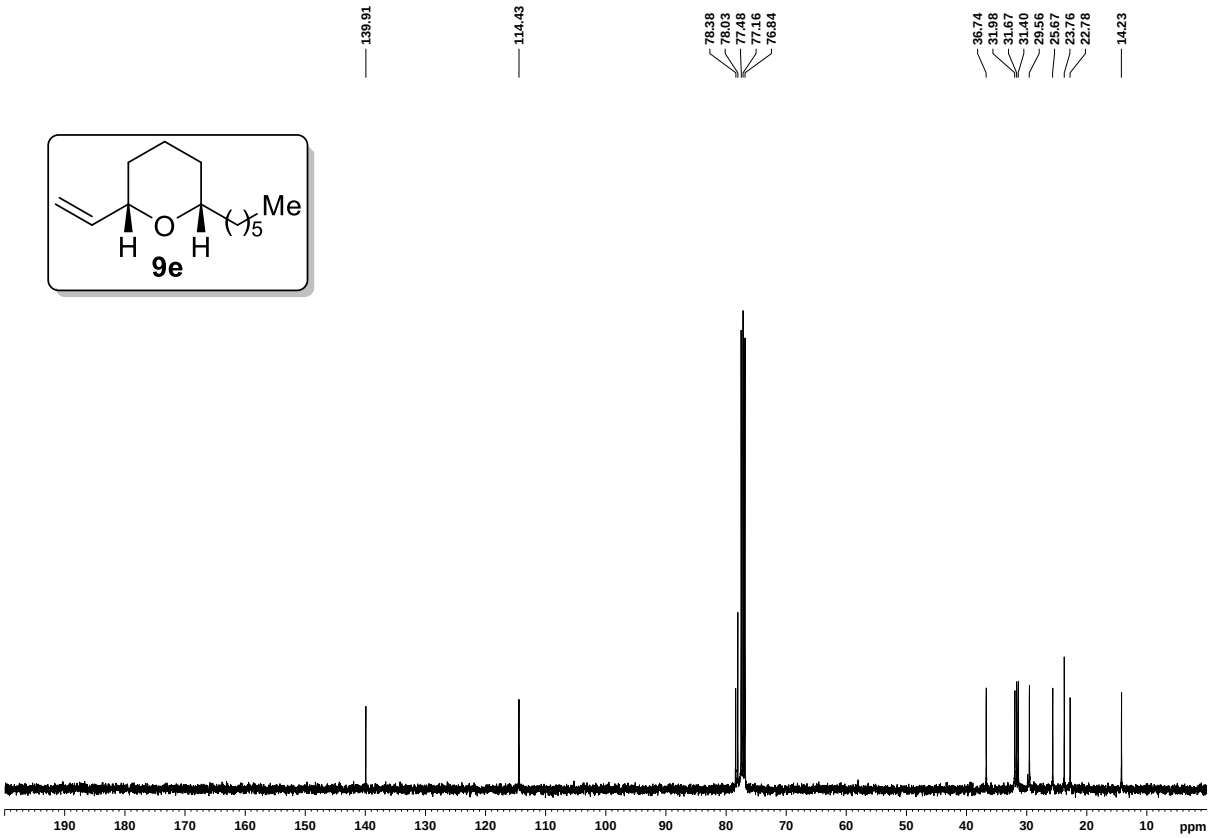
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



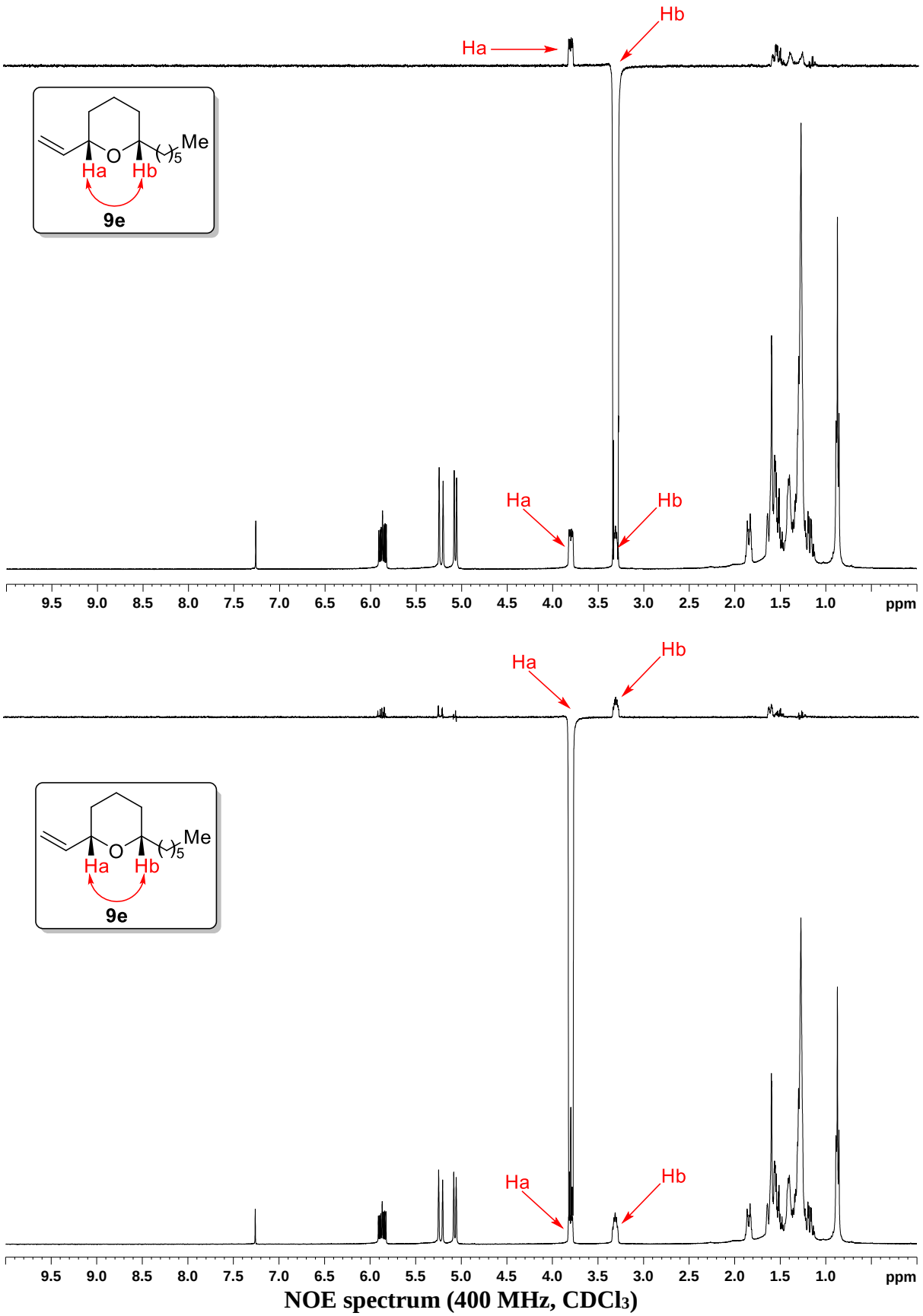
NOE spectrum (400 MHz, $CDCl_3$)



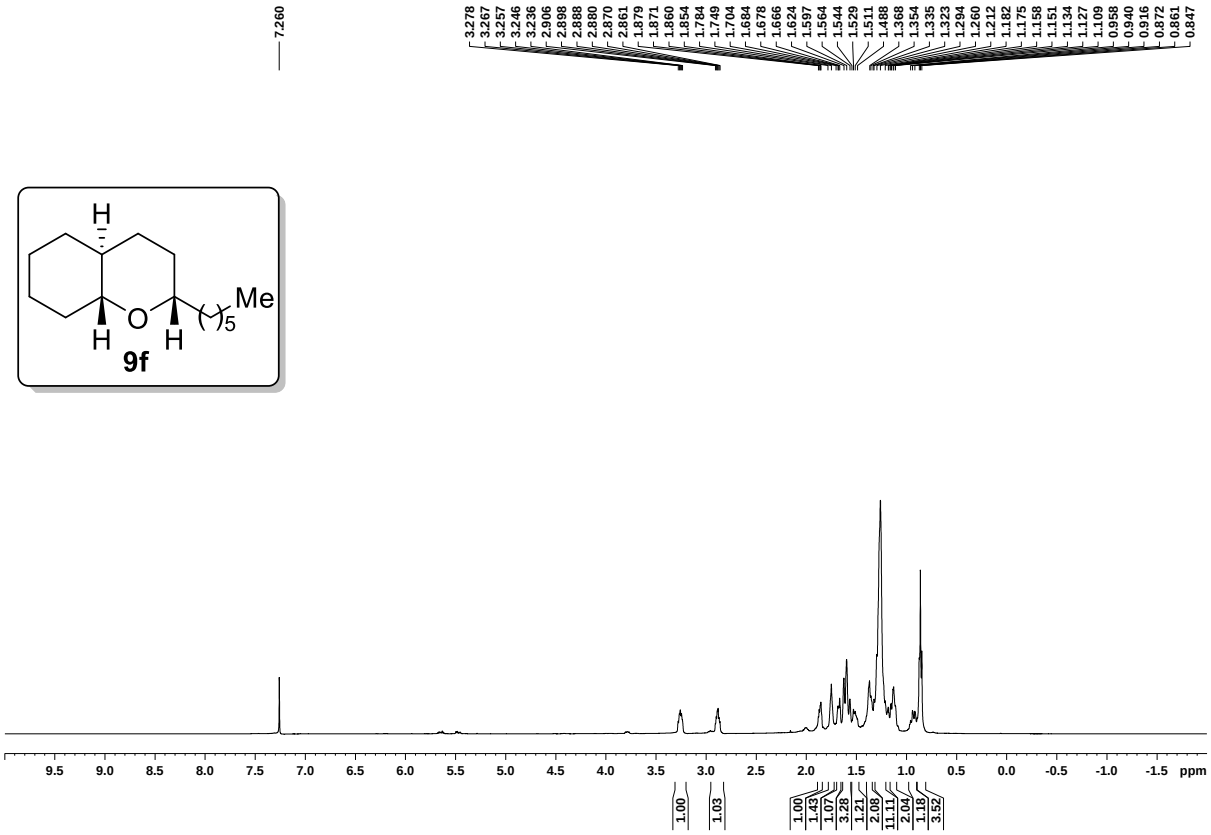
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



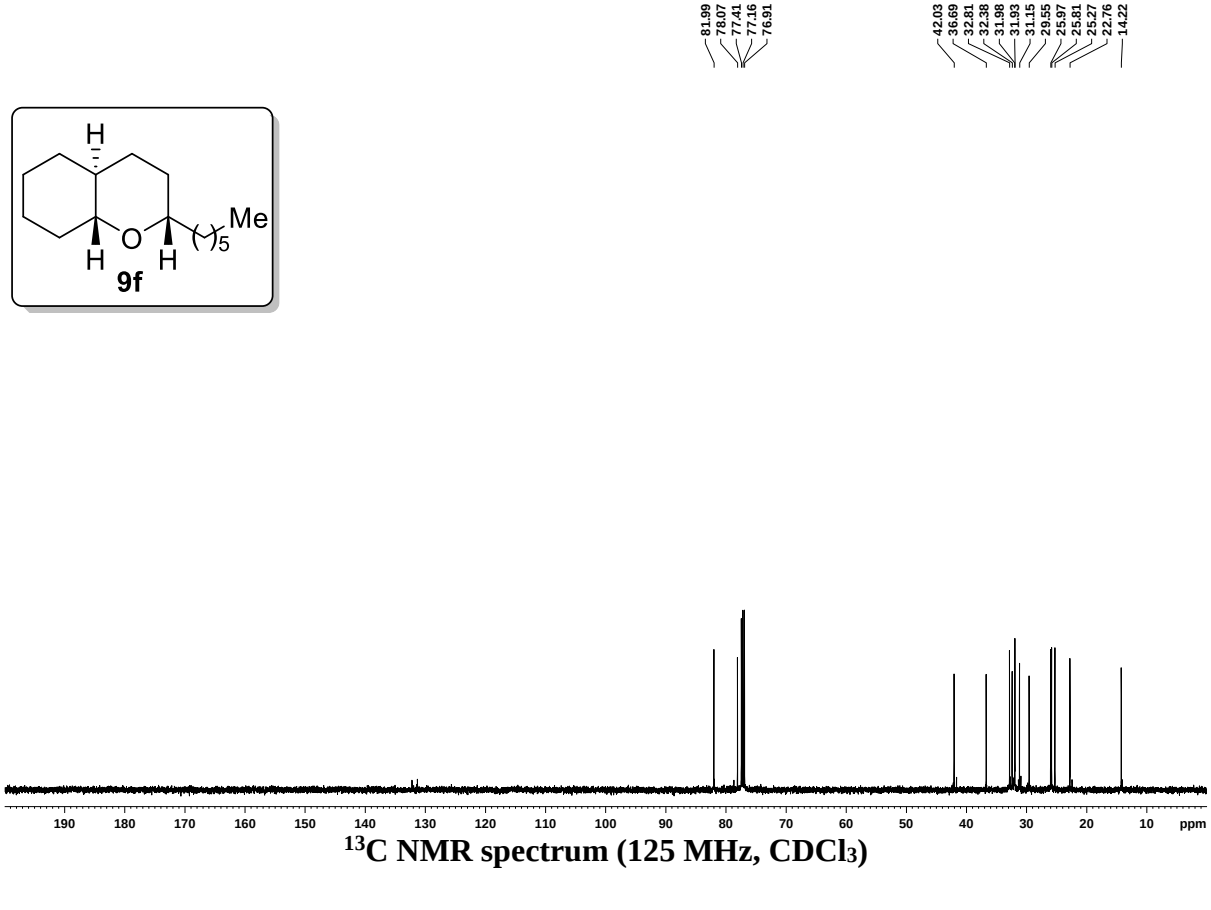
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



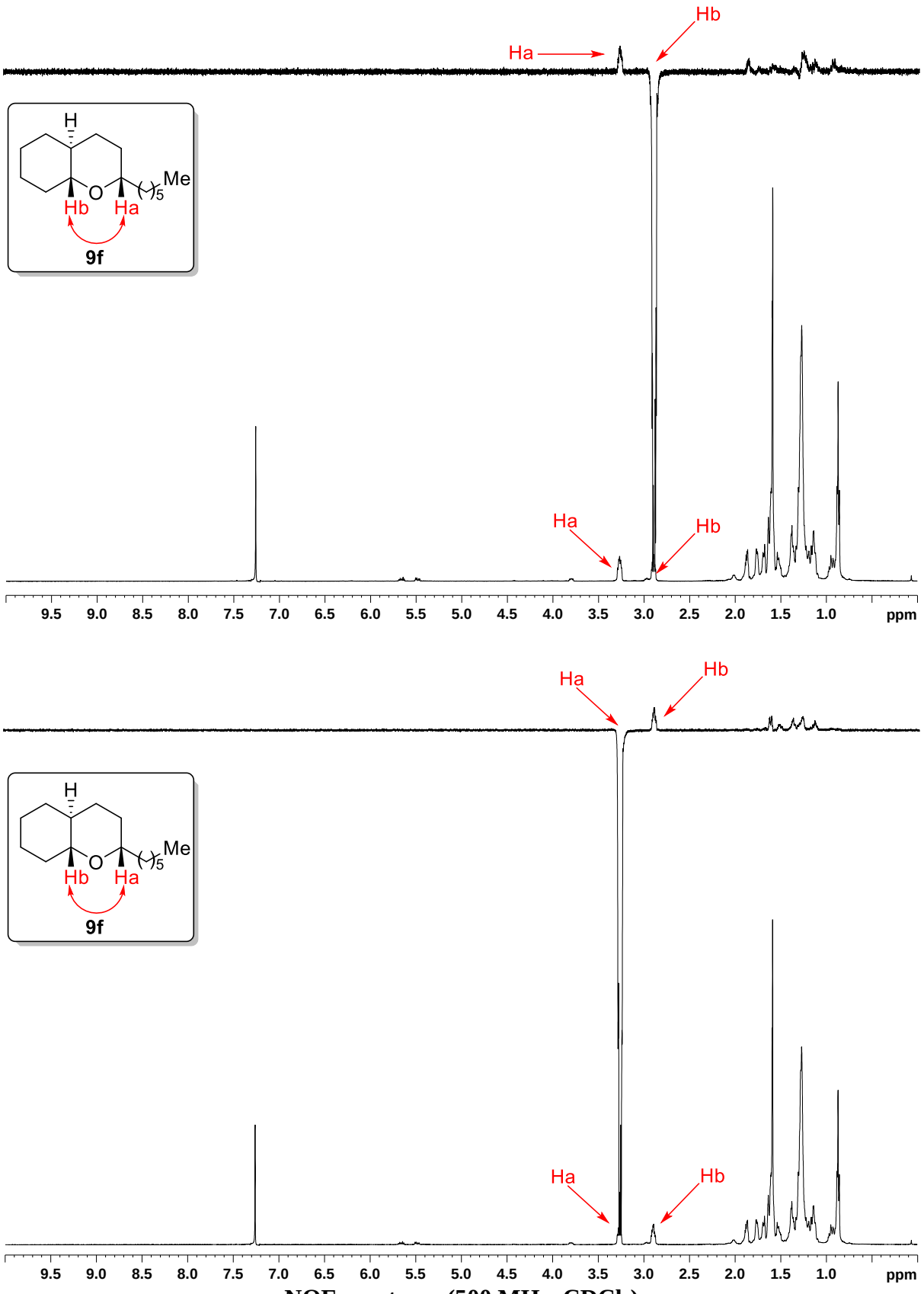
NOE spectrum (400 MHz, $CDCl_3$)



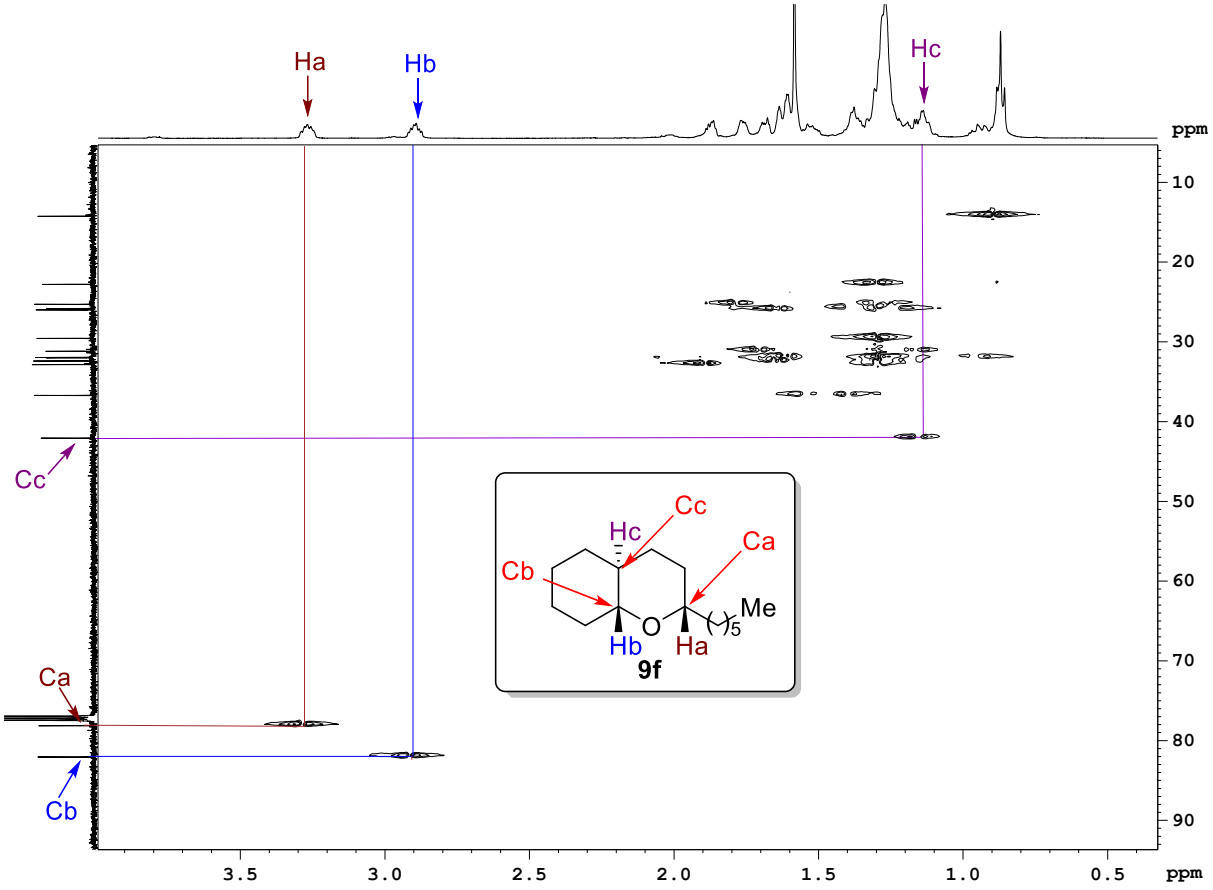
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



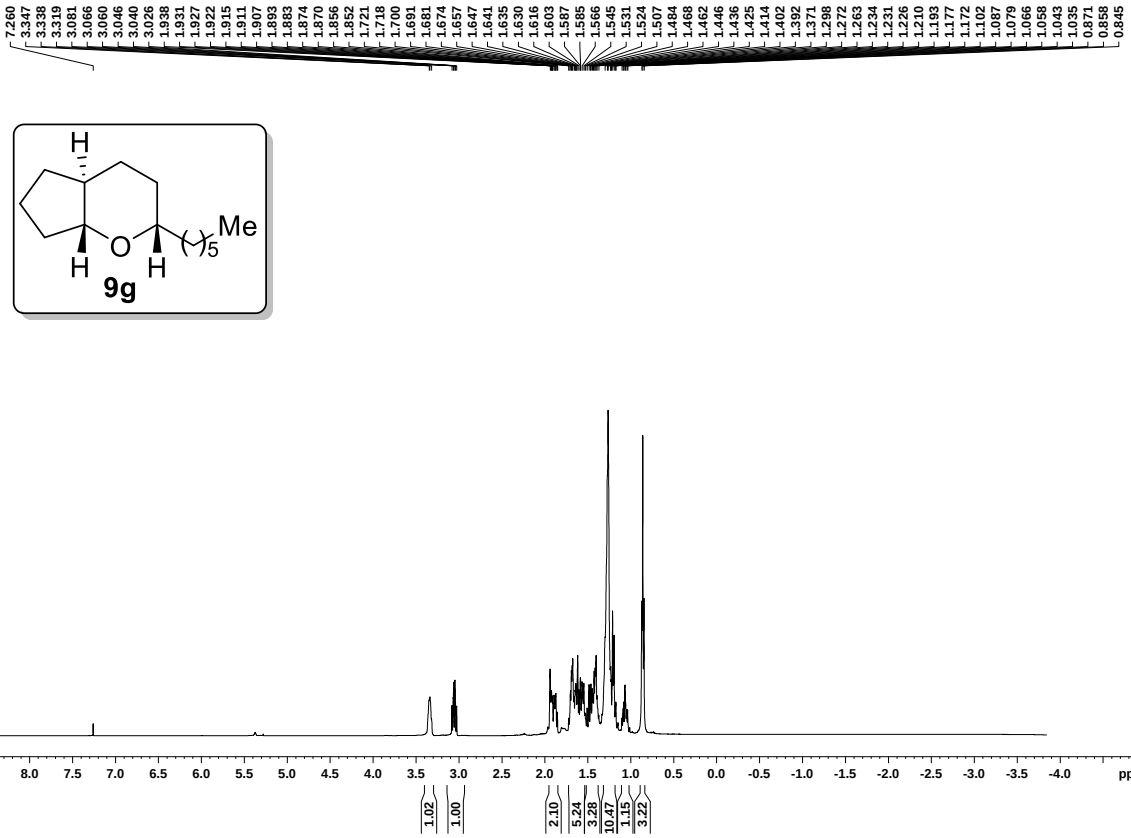
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



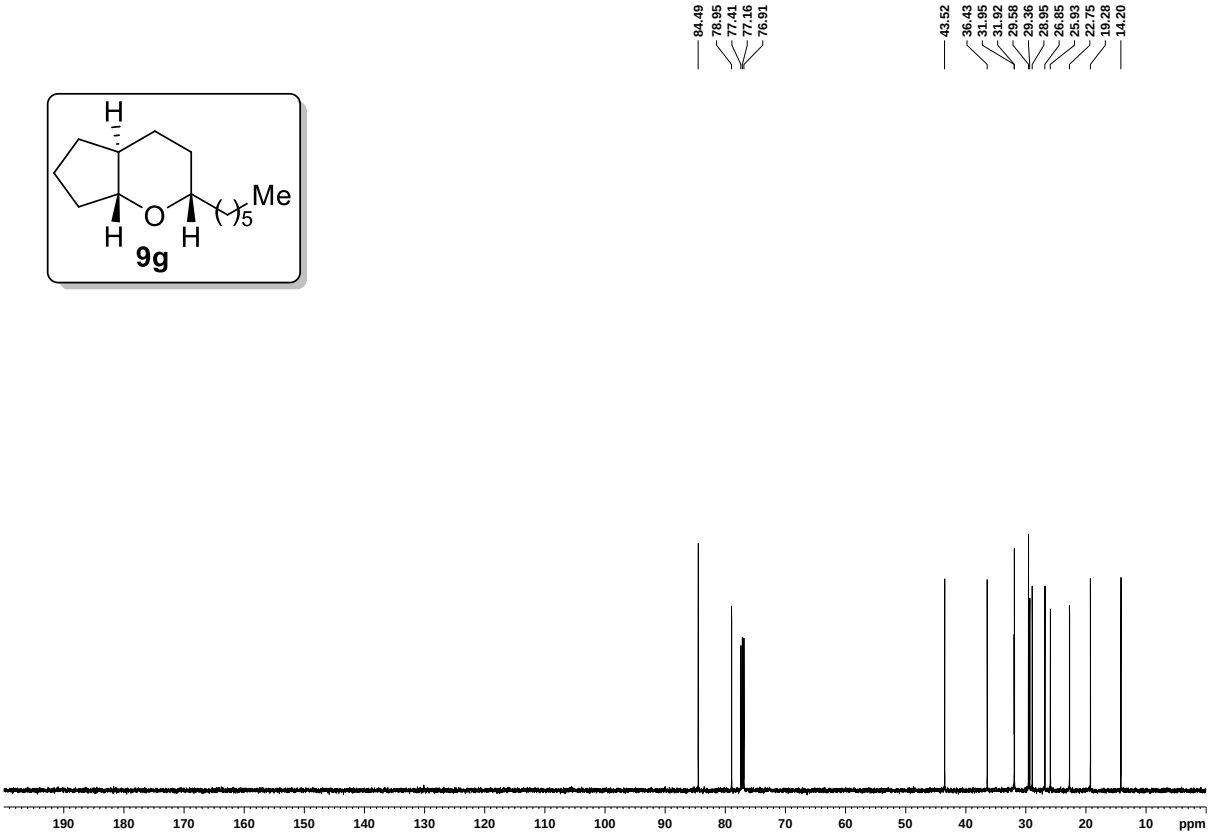
NOE spectrum (500 MHz, $CDCl_3$)



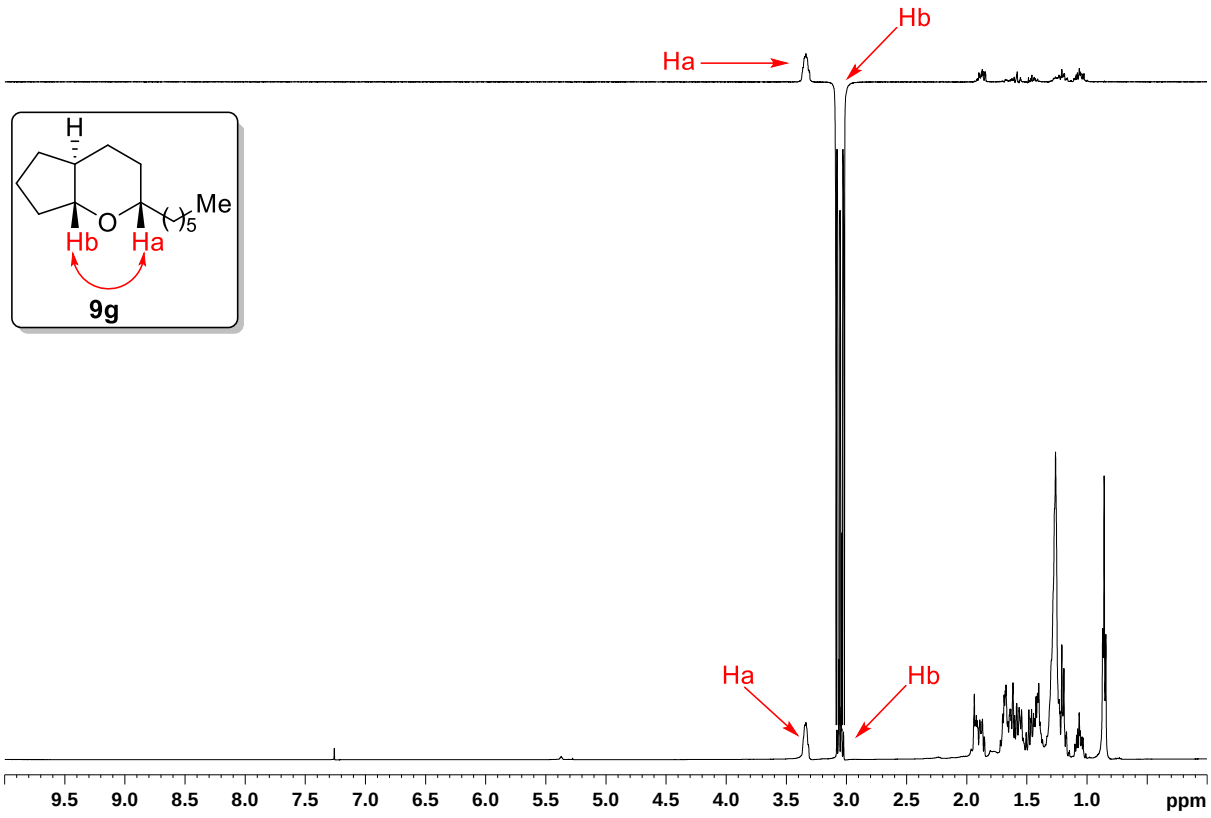
HSQC, spectrum (500 MHz, $CDCl_3$)

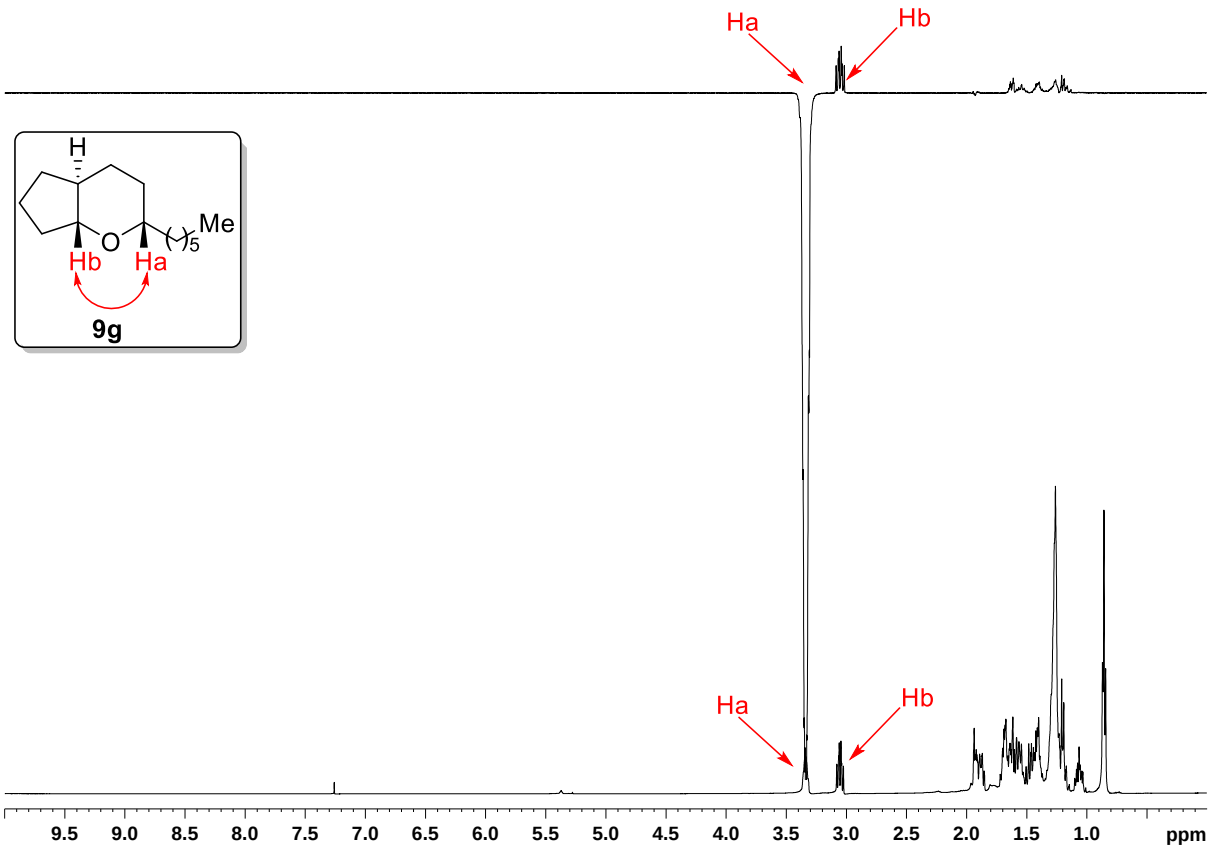


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

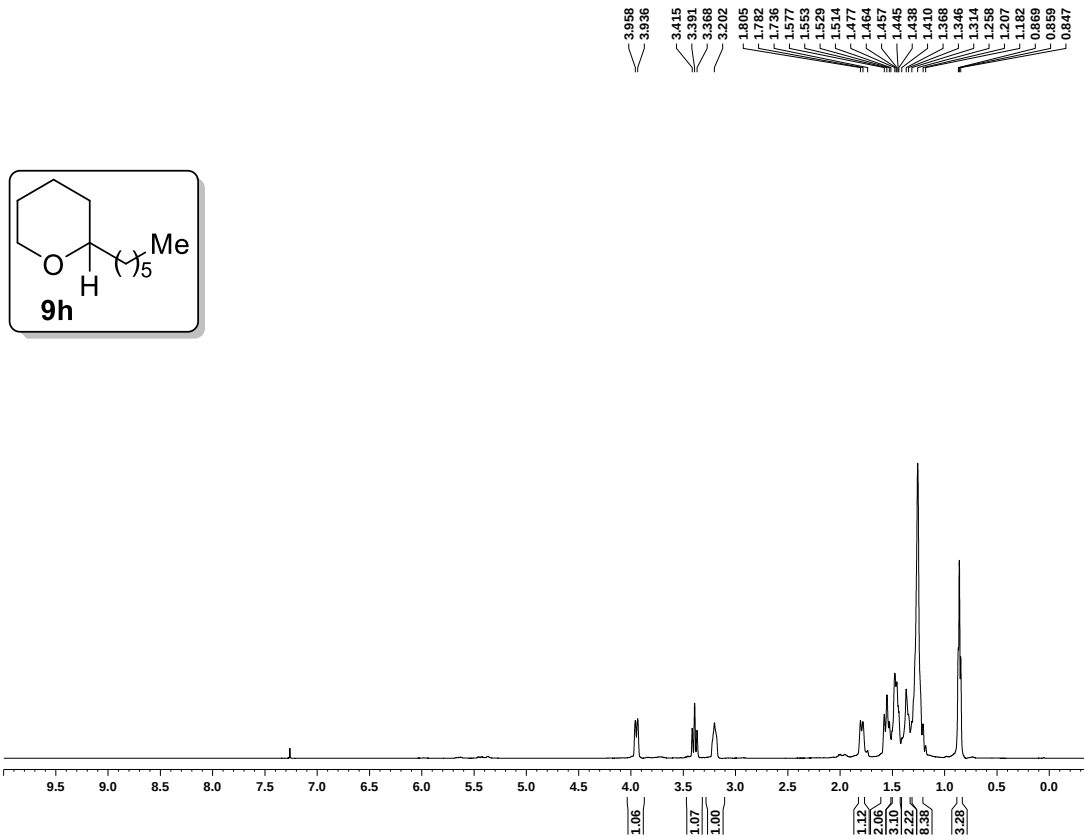


^{13}C NMR spectrum (125 MHz, $CDCl_3$)

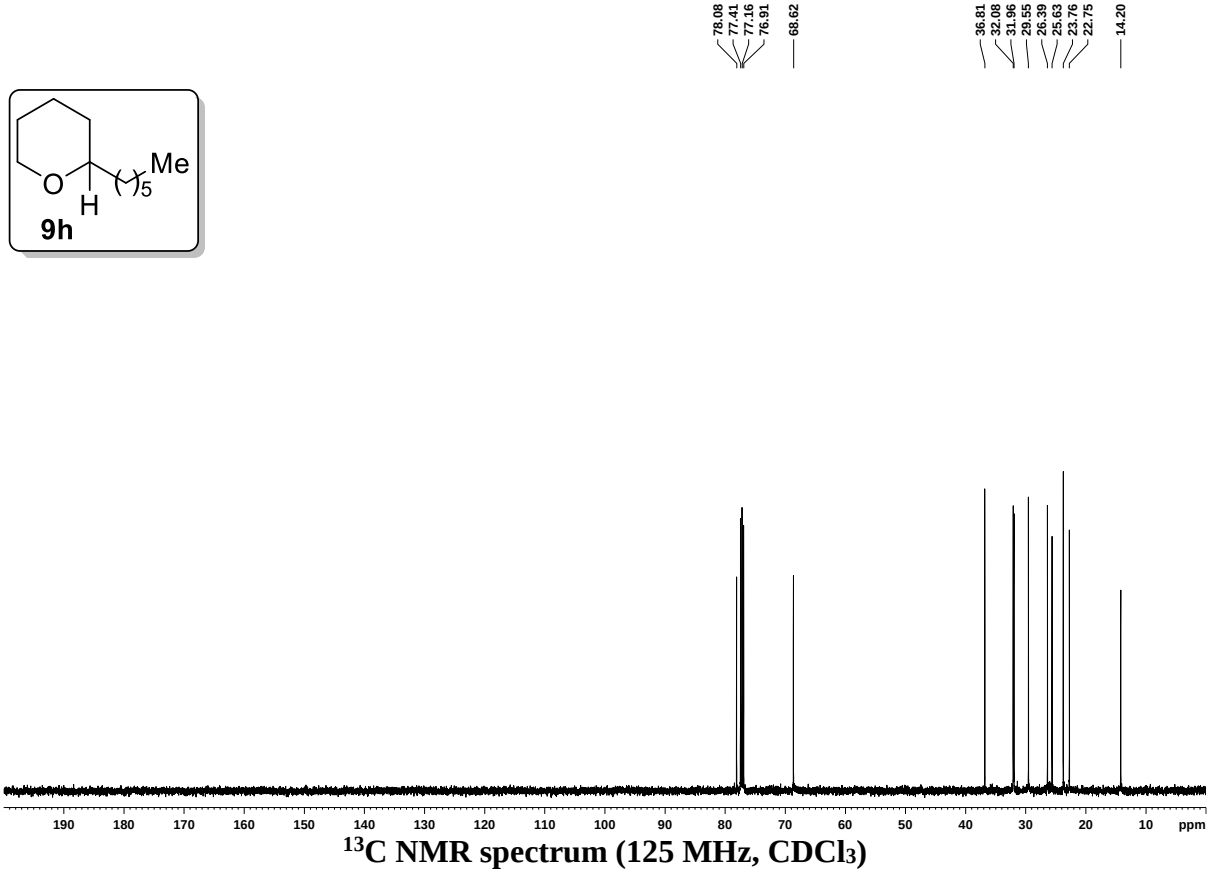




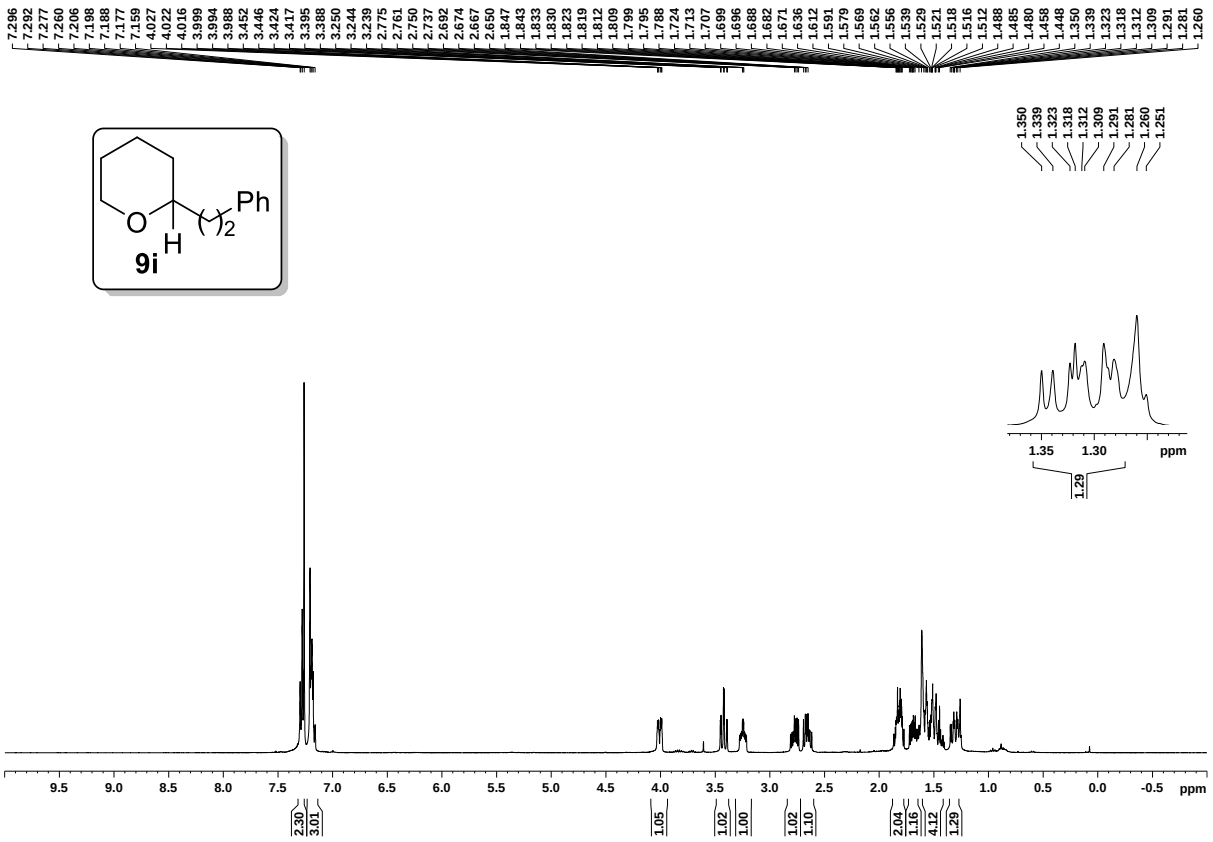
NOE spectrum (500 MHz, $CDCl_3$)



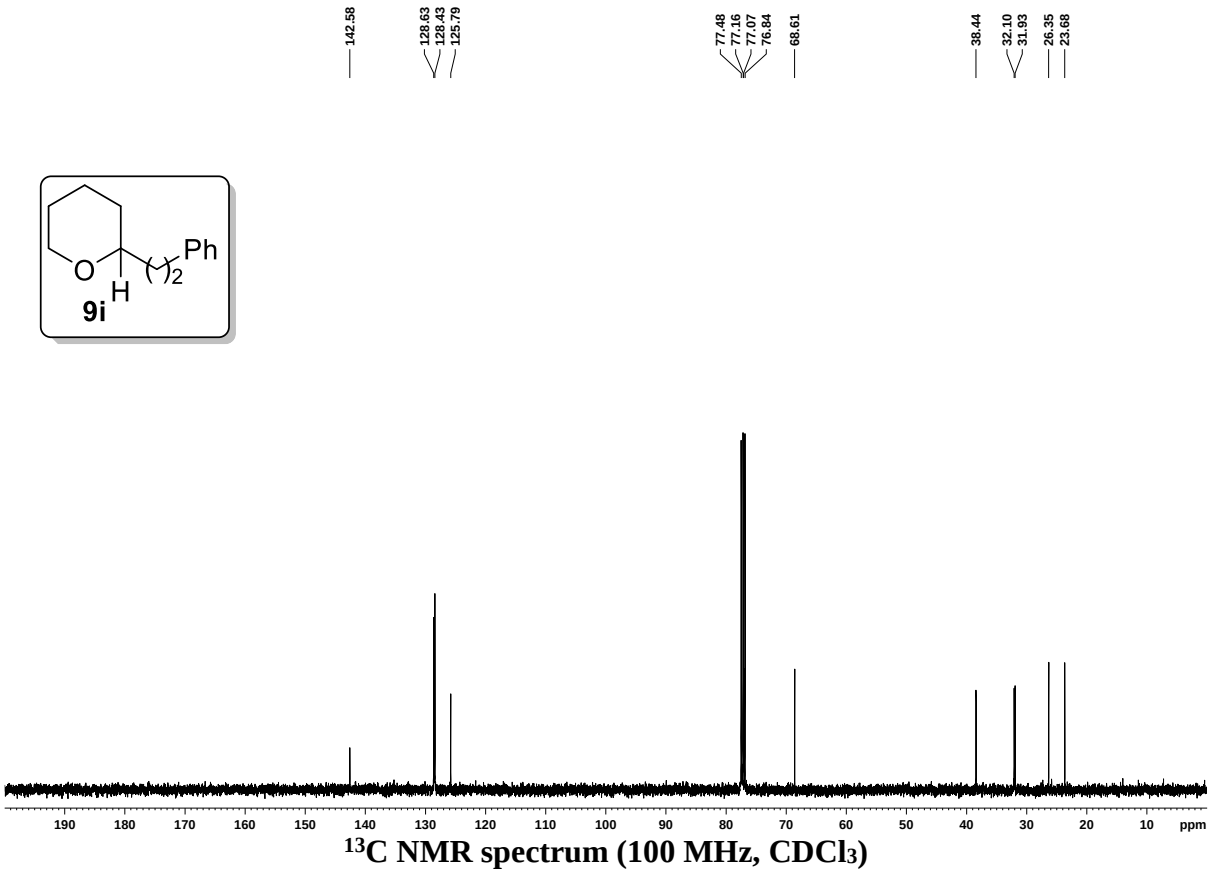
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



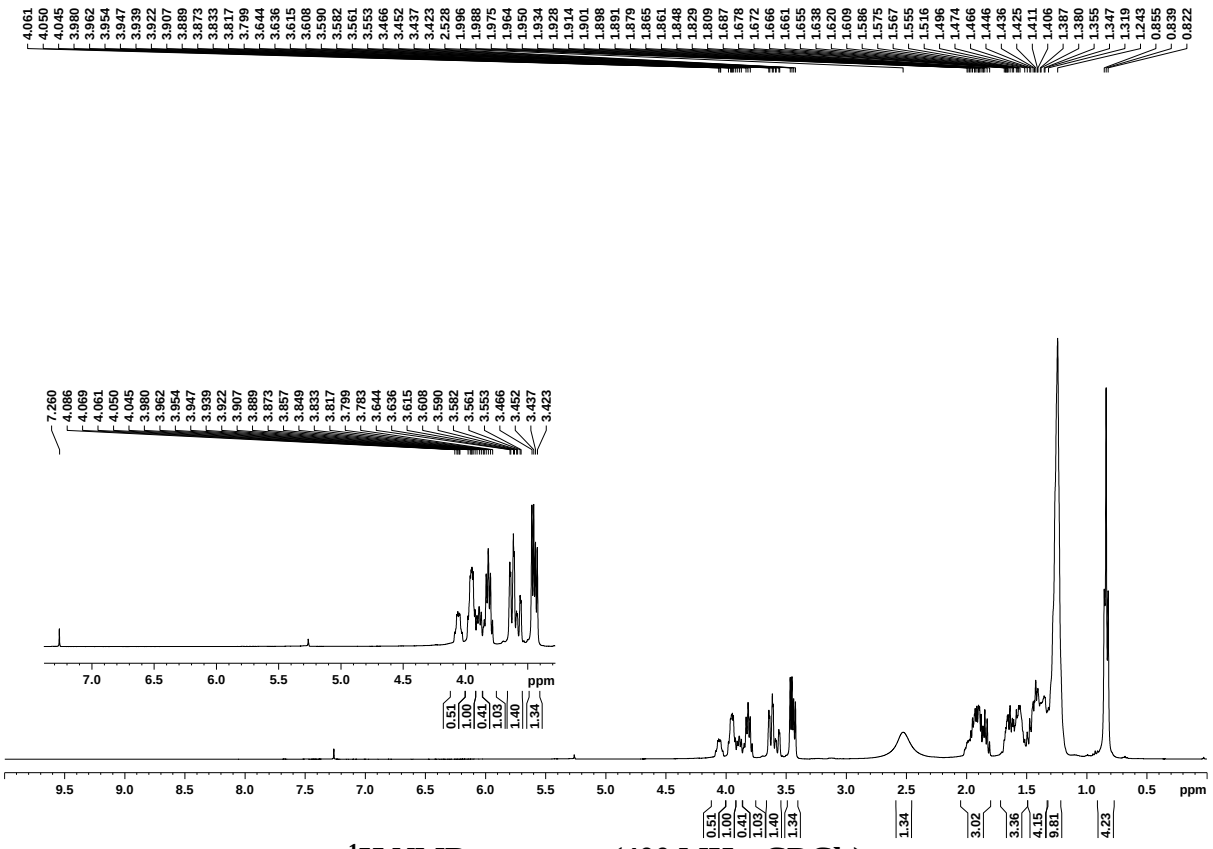
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



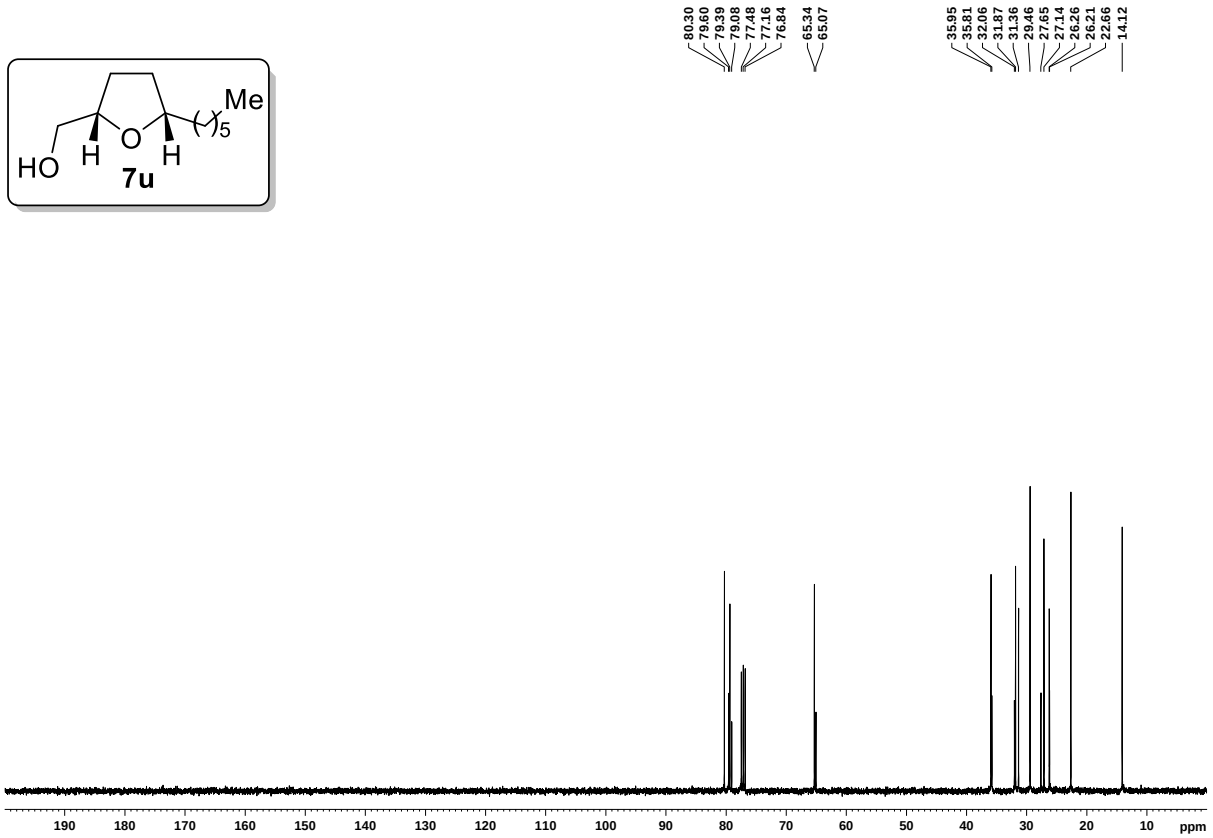
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



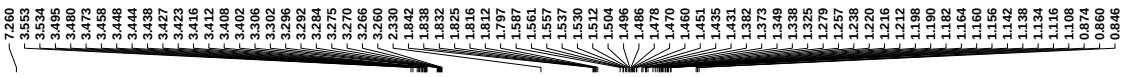
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

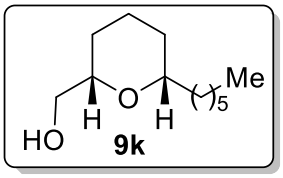


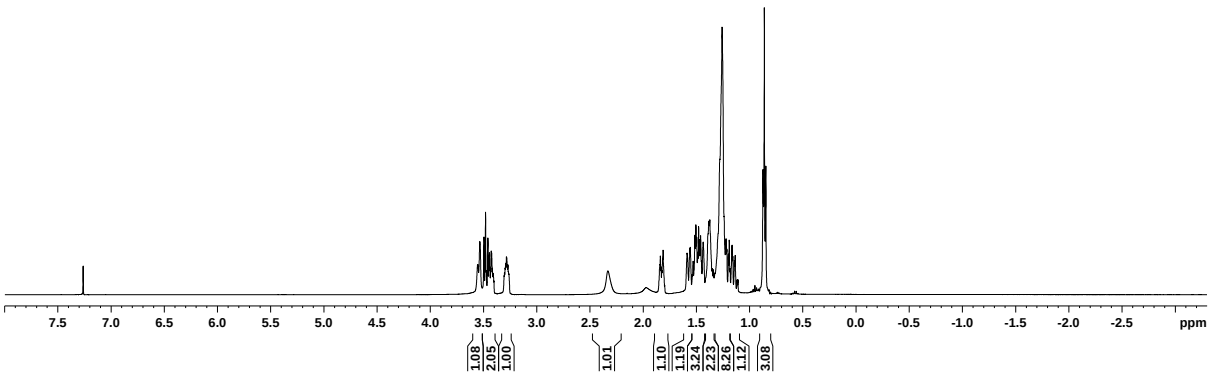
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



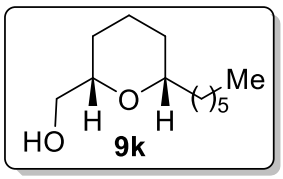
^{13}C NMR spectrum (100 MHz, $CDCl_3$)

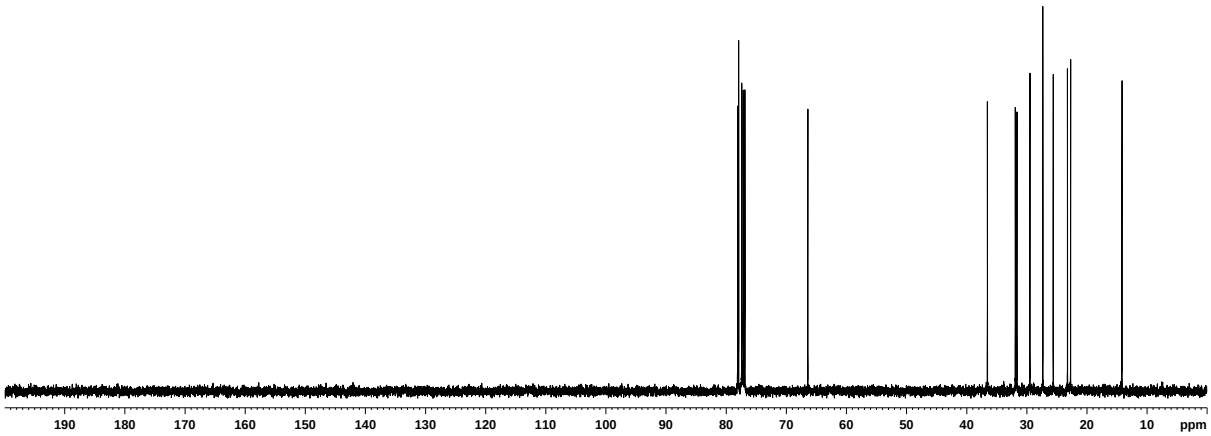




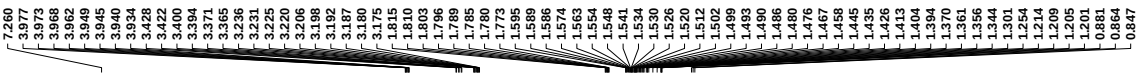


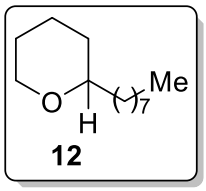
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

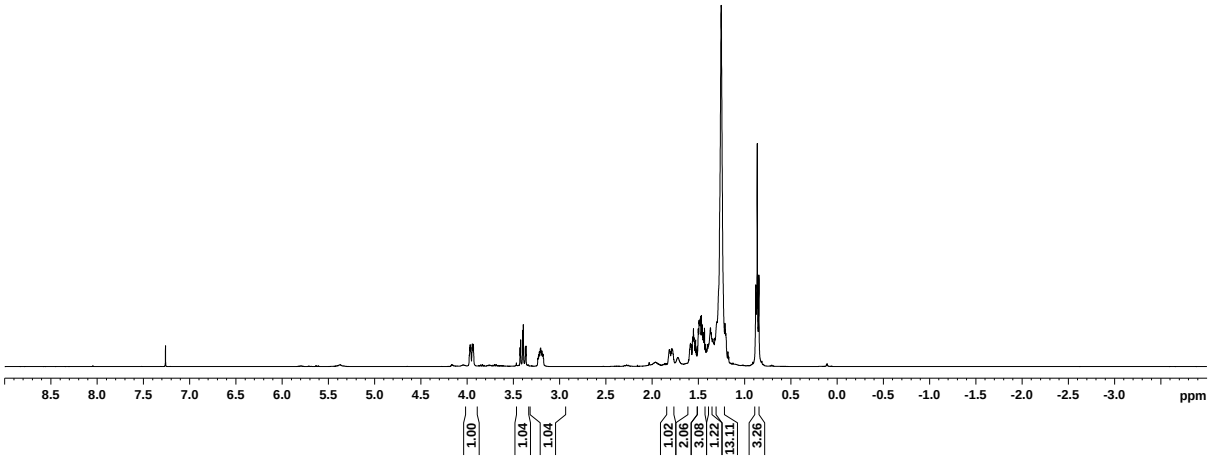




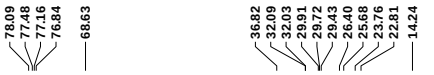
^{13}C NMR spectrum (125 MHz, $CDCl_3$)

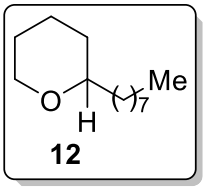


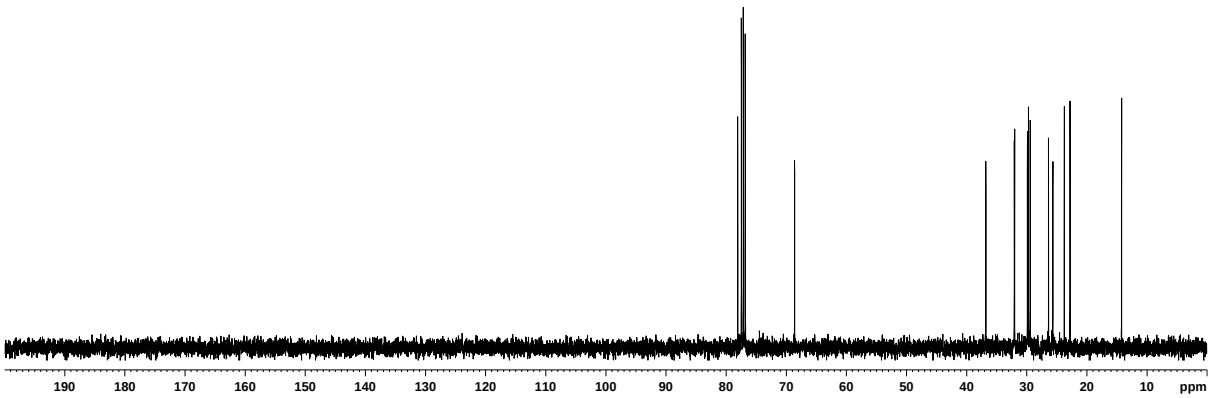




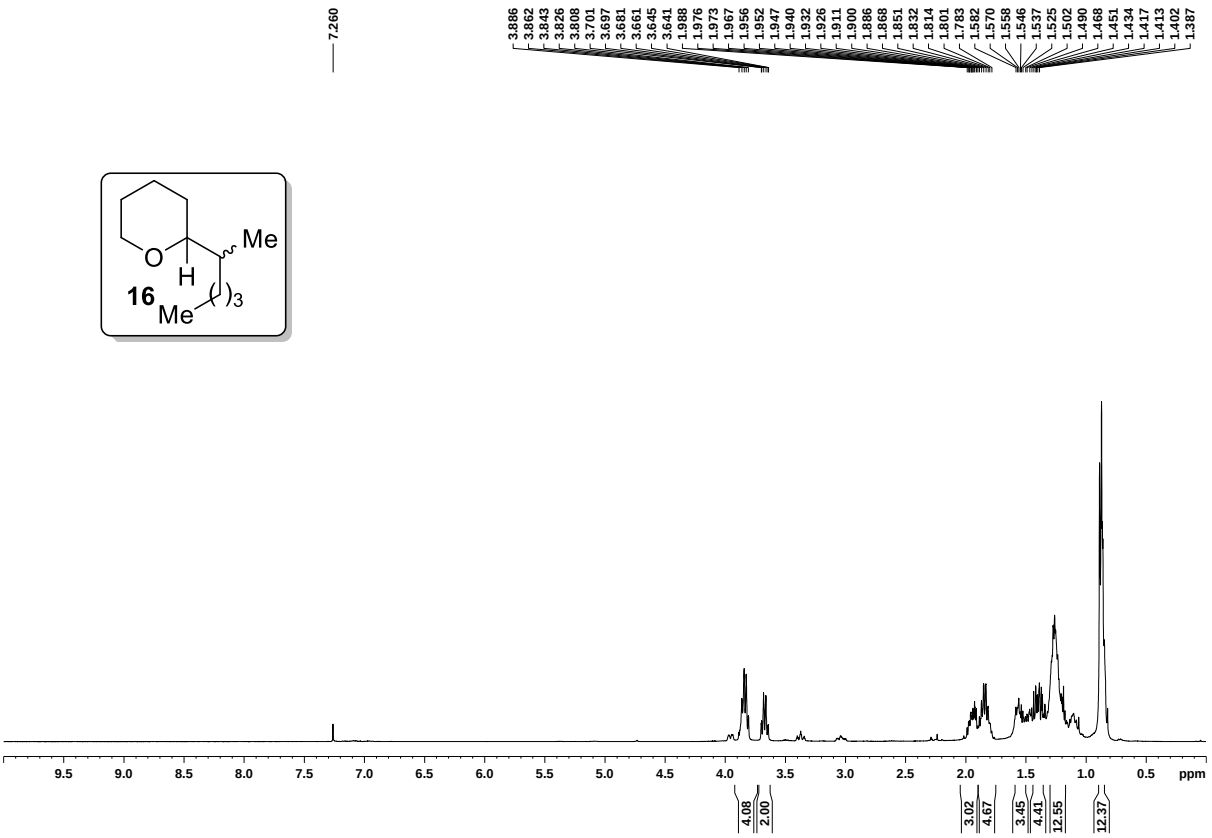
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



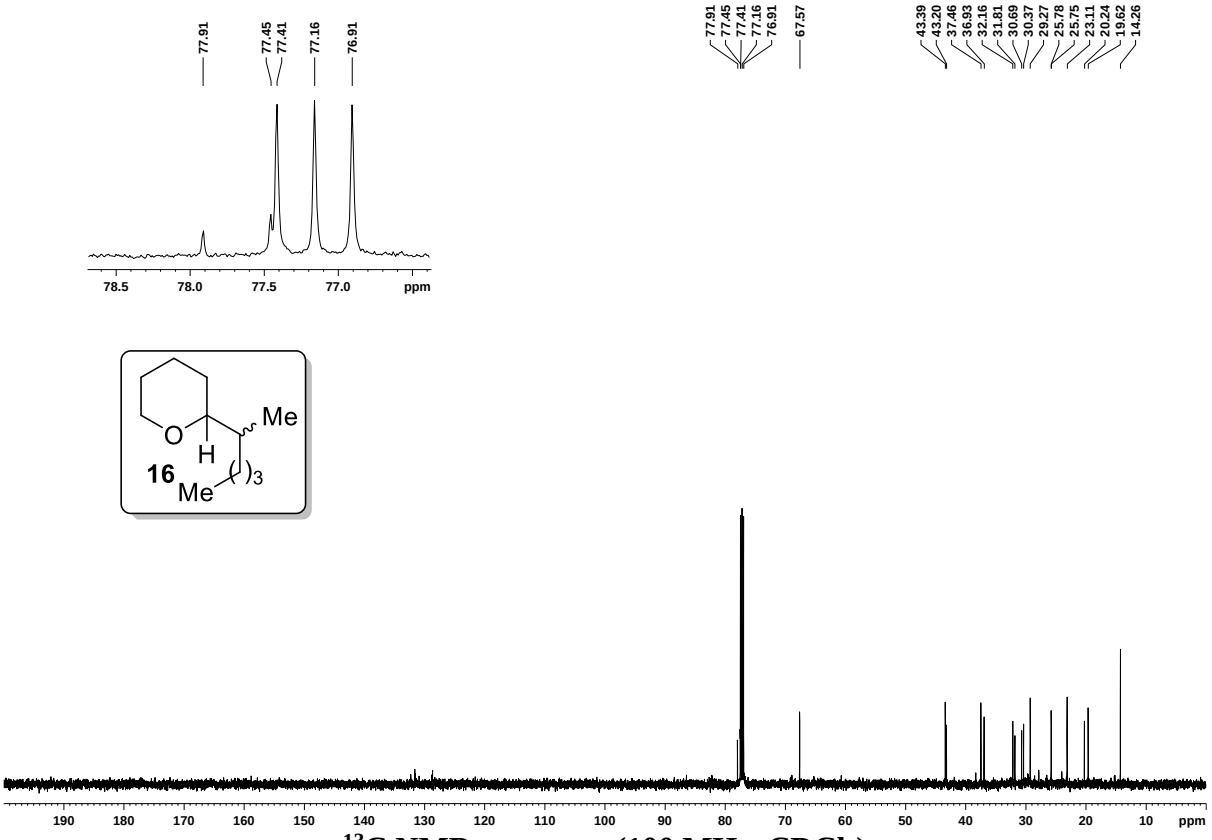




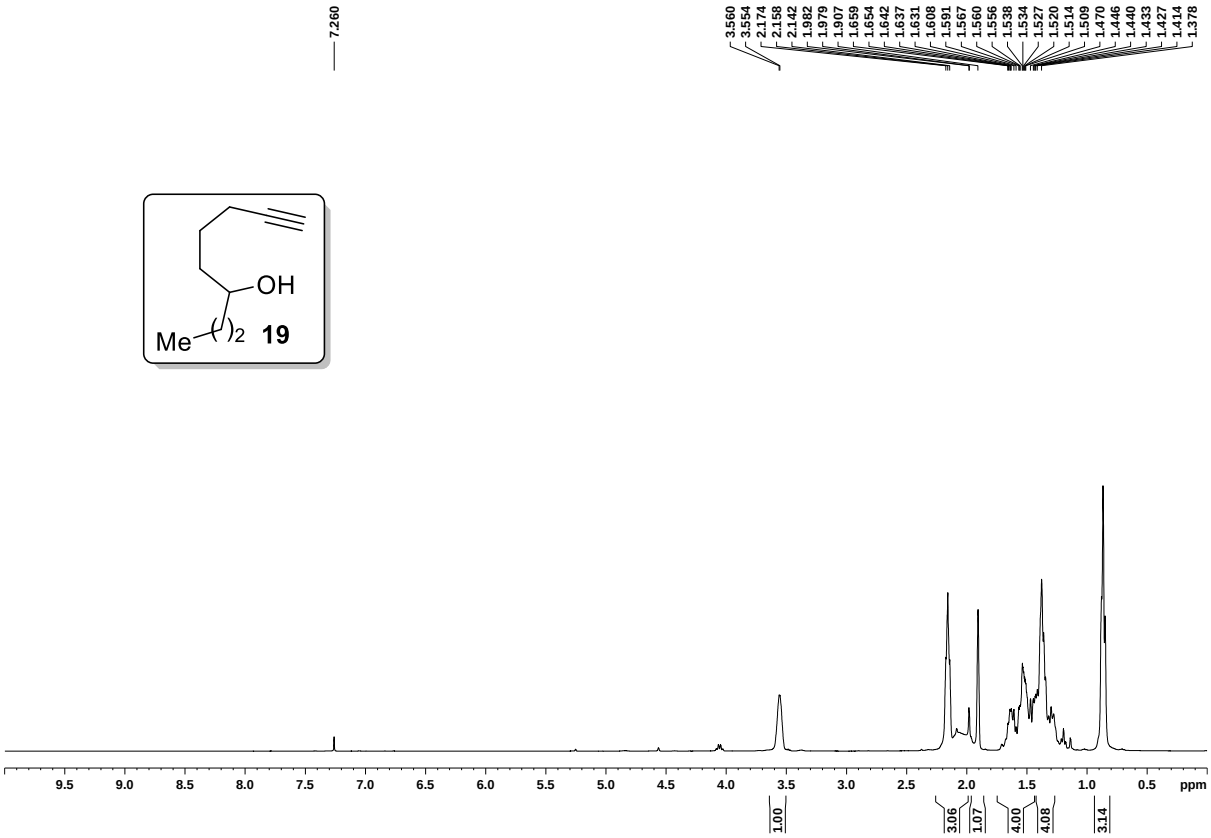
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



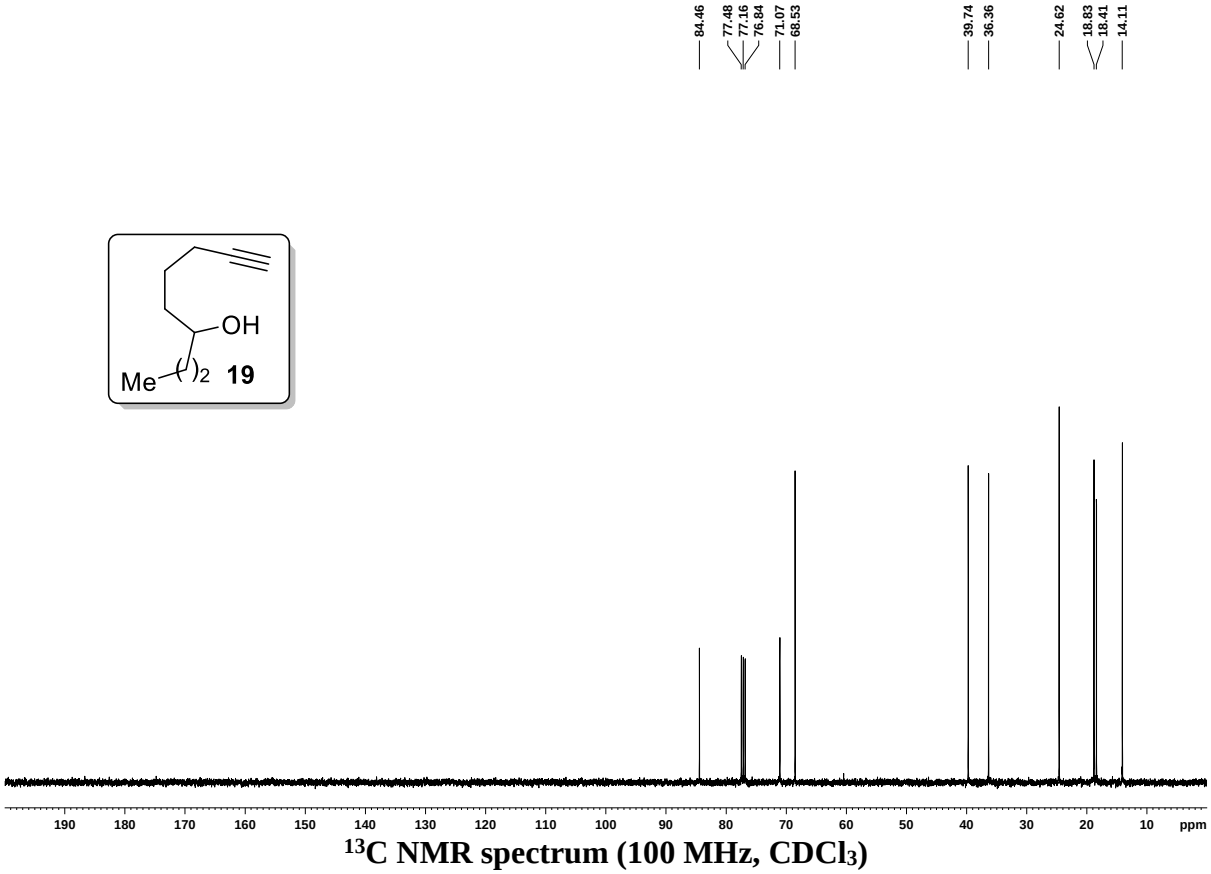
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



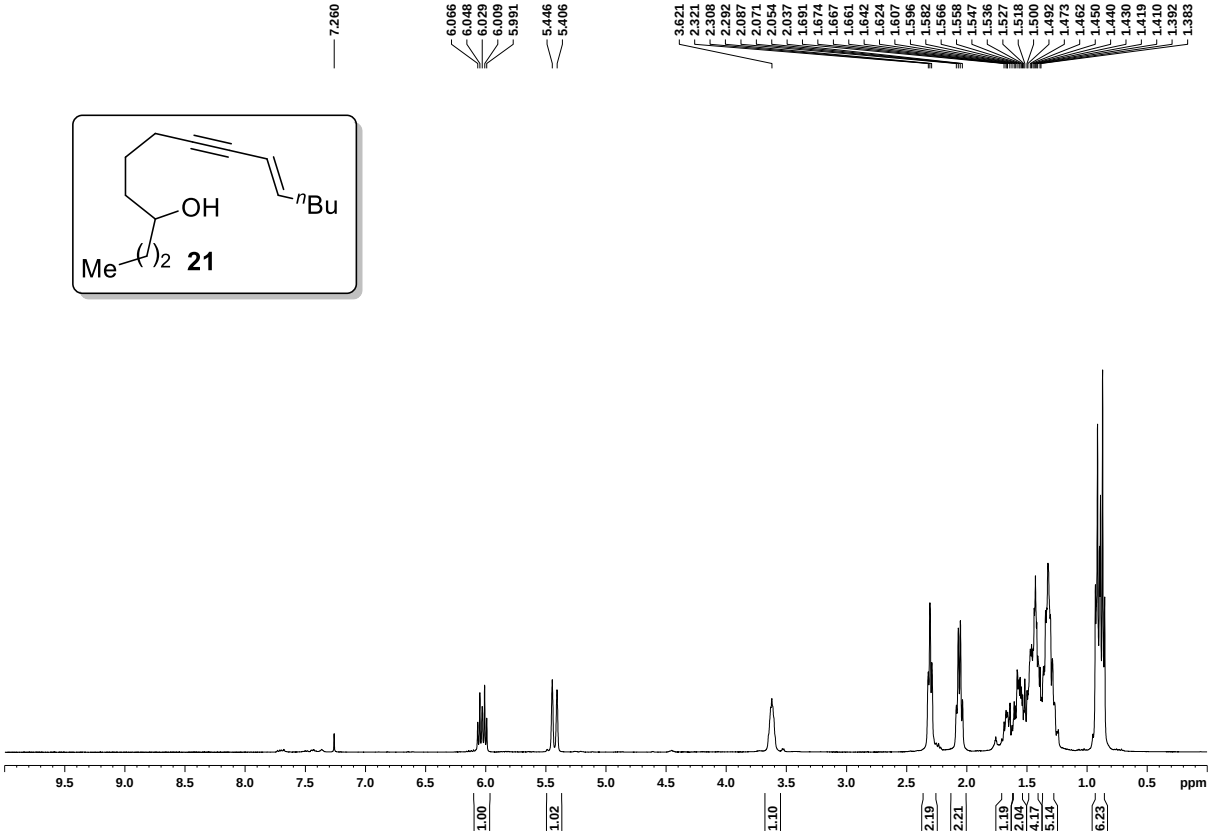
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



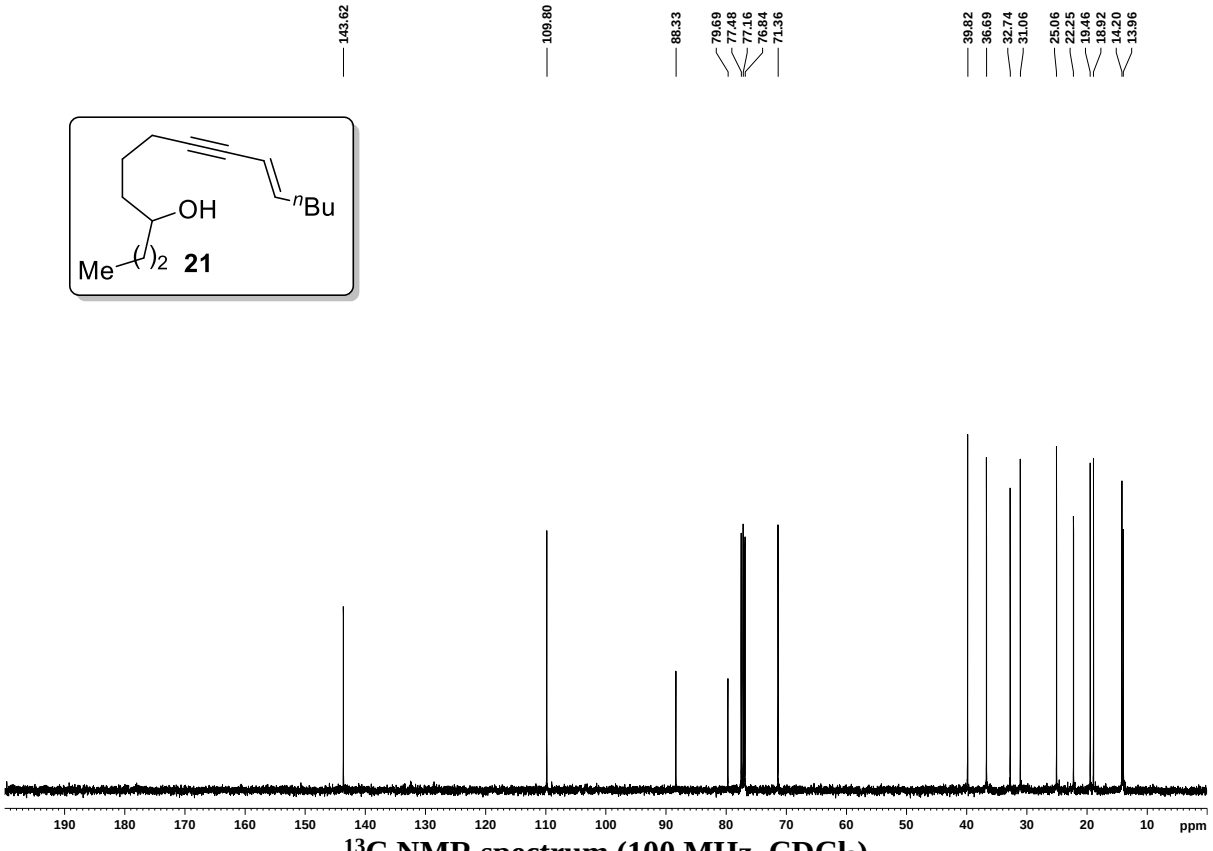
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



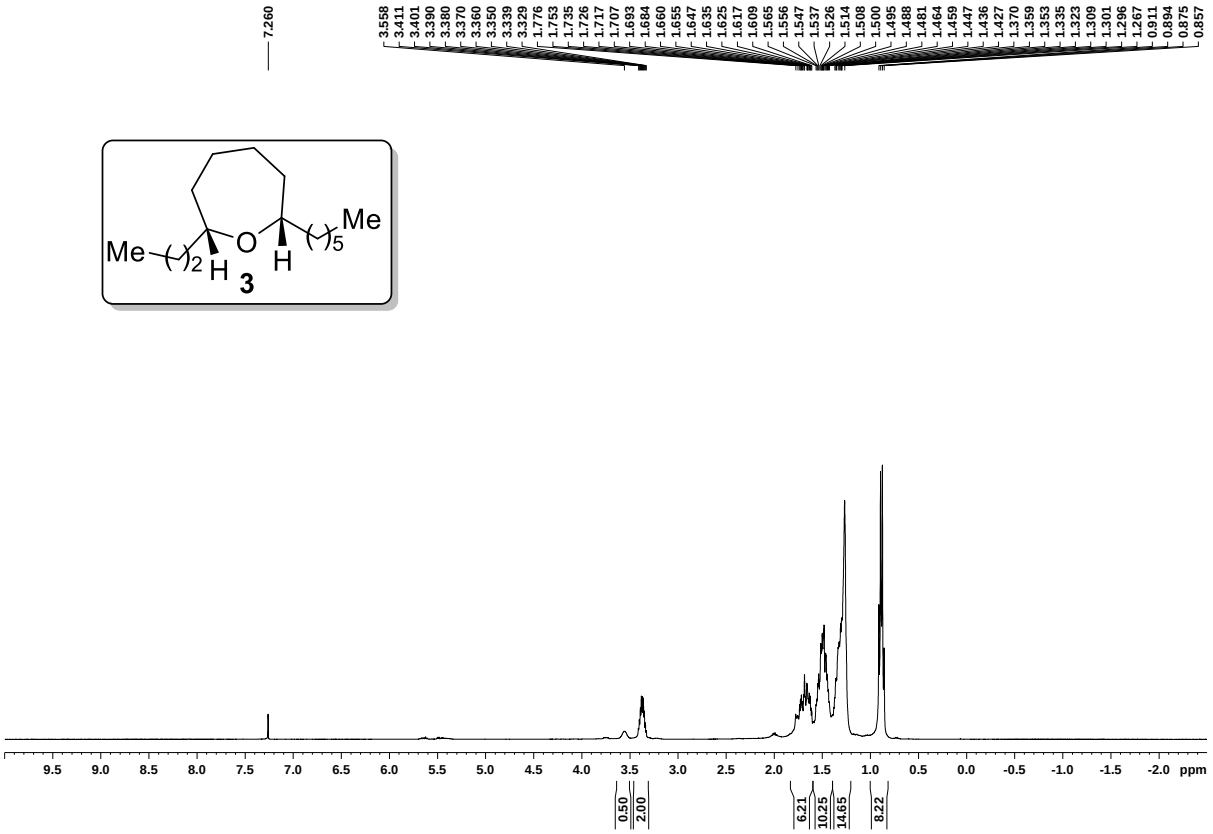
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



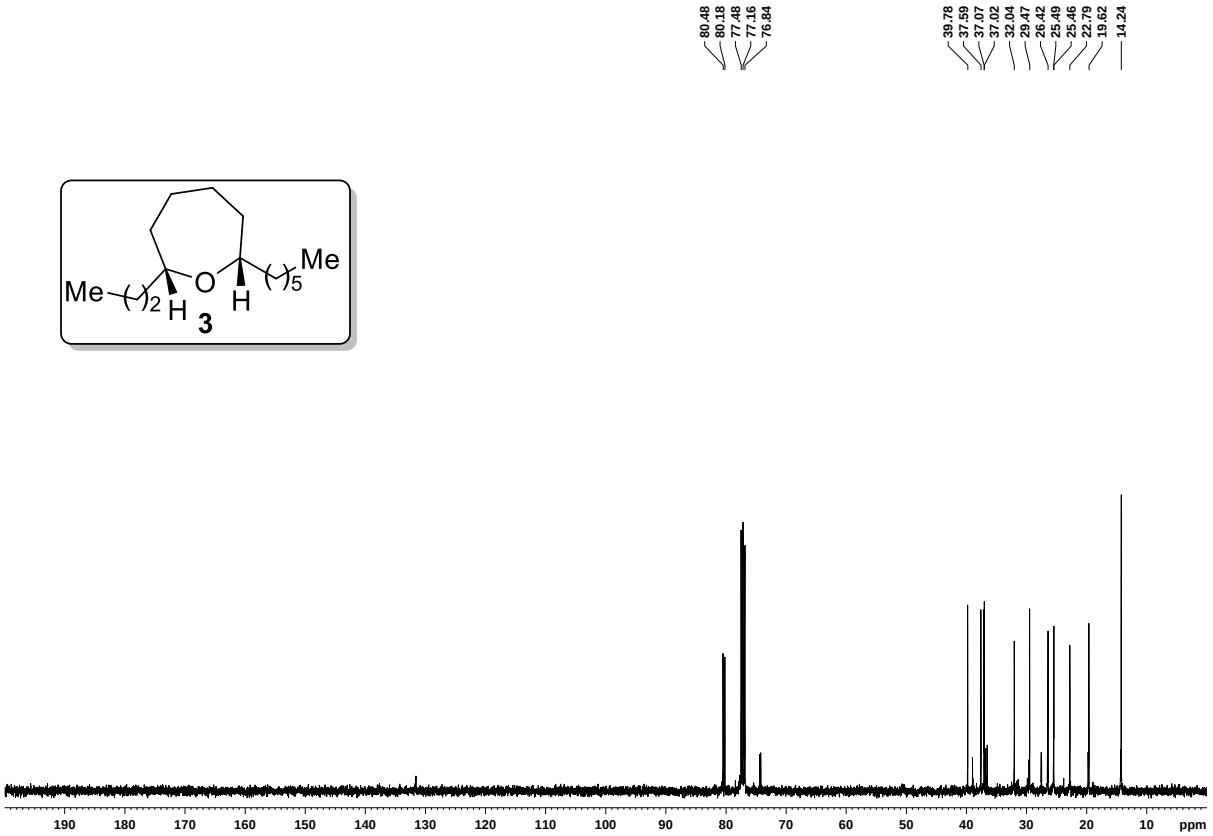
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



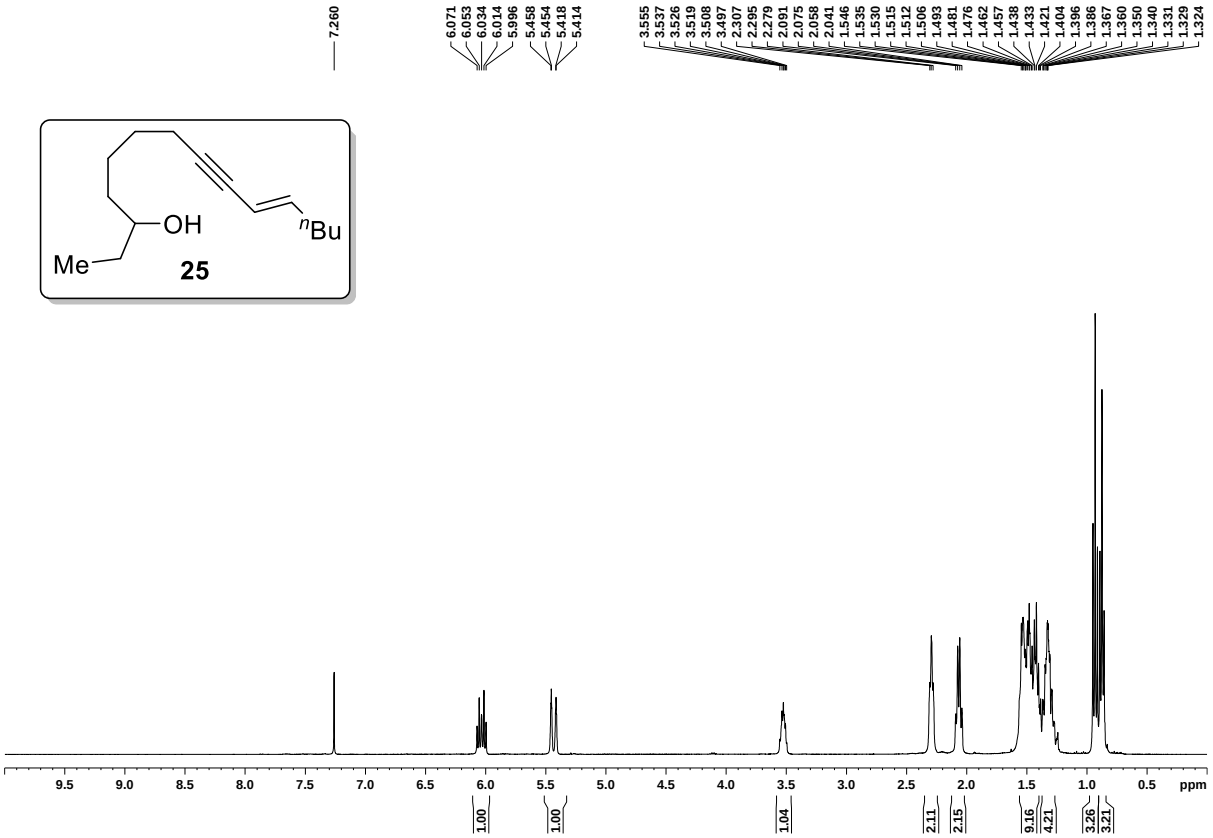
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



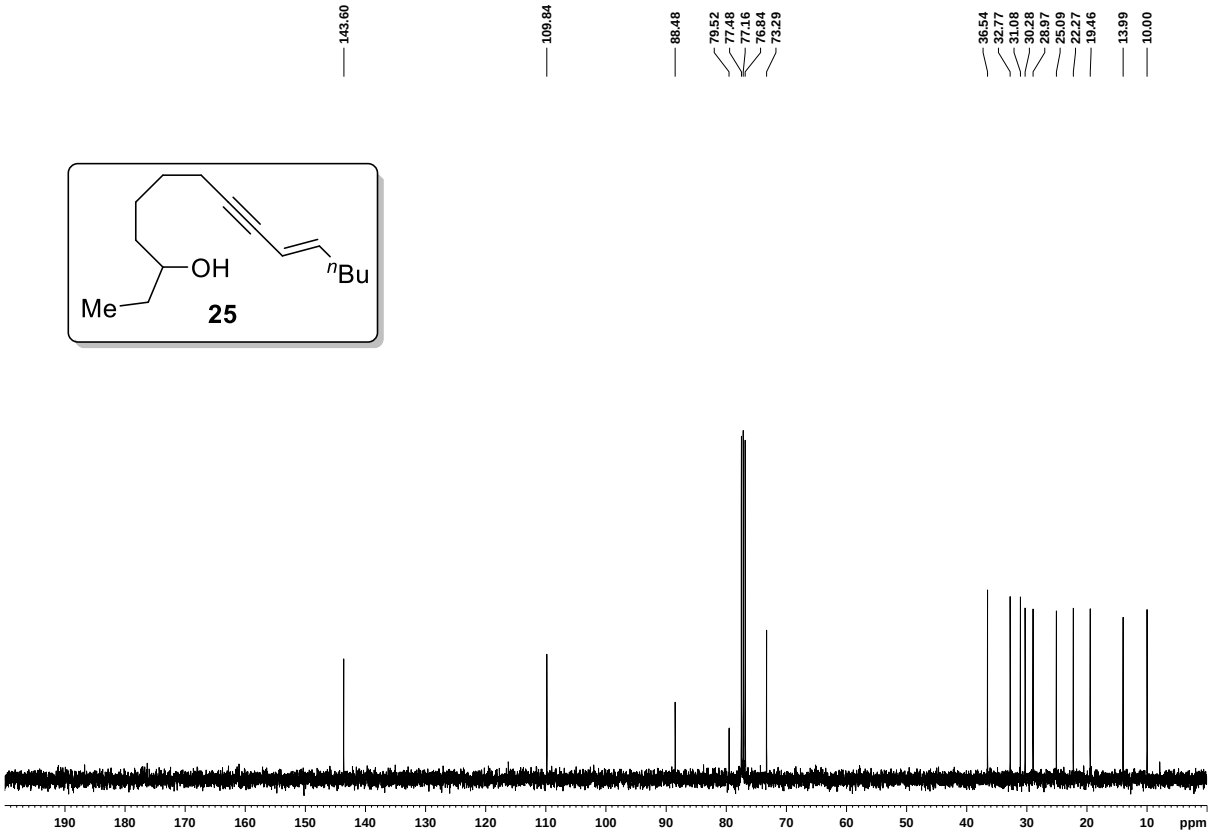
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



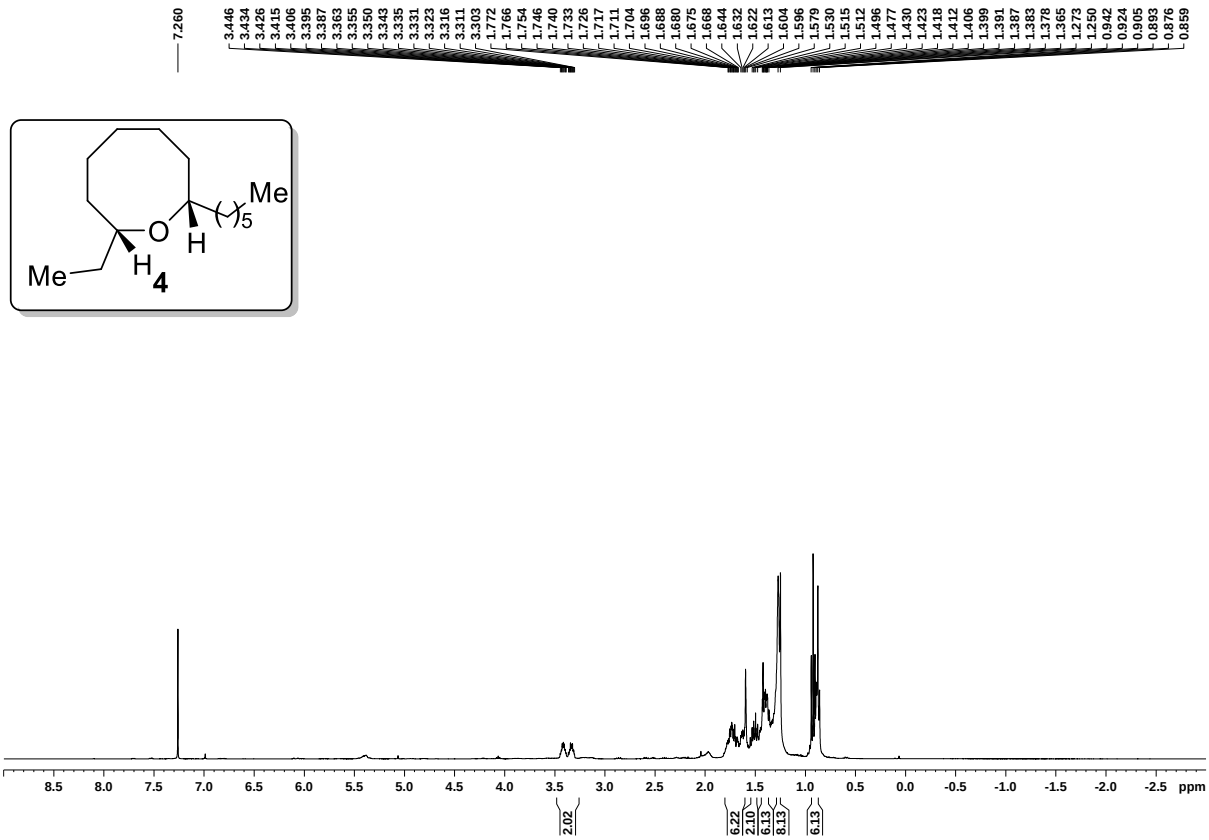
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



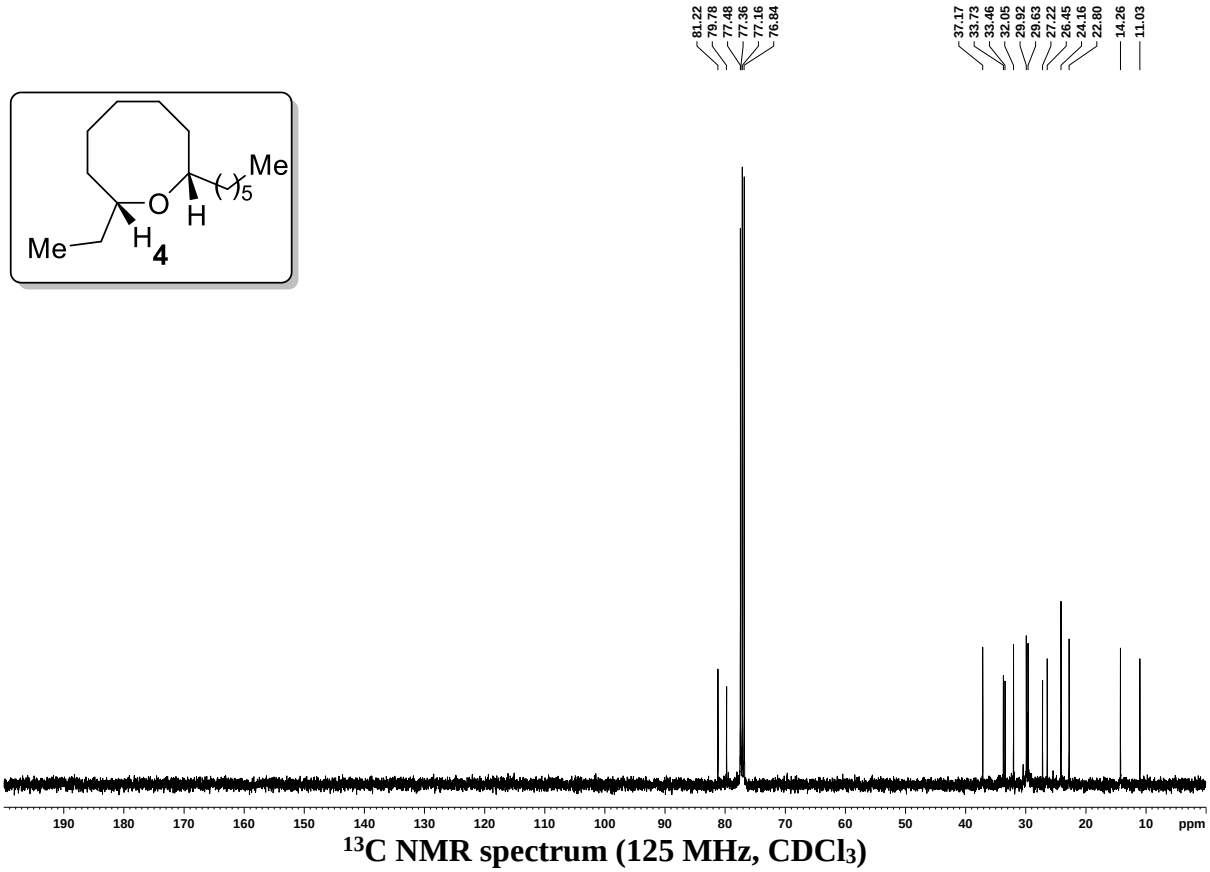
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



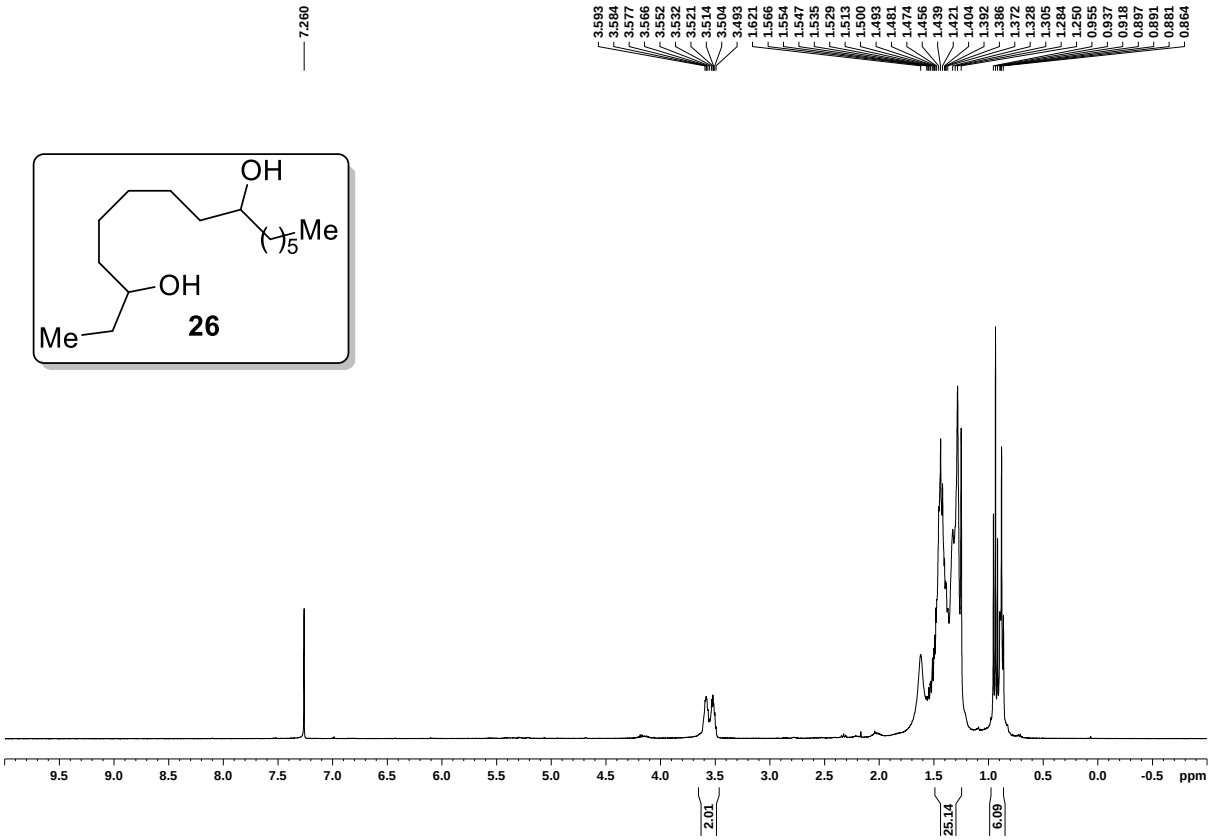
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



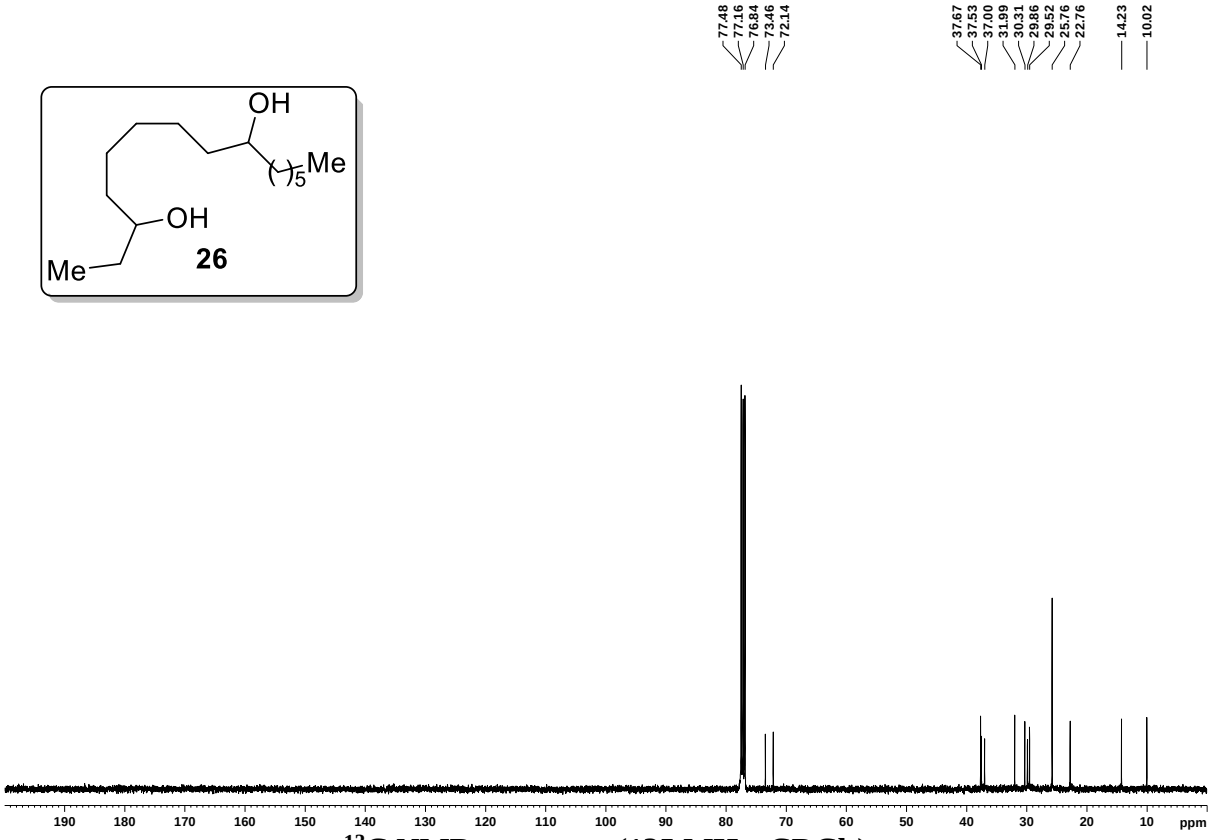
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR spectrum (125 MHz, $CDCl_3$)



^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{13}C NMR spectrum (125 MHz, $CDCl_3$)