Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Amine-Catalyzed Cyclizations of Tethered a,b-Unsaturated Carbonyl Compounds

Renata Marcia de Figueiredo[a], Roland Fröhlich[b] and Mathias Christmann[a,*]

[a]*Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany*

[b]*University of Münster, Institute of Organic Chemistry, Corrensstraße 40, 48149 Münster Germany*

christmann@oc.rwth-aachen.de

Table of Contents:

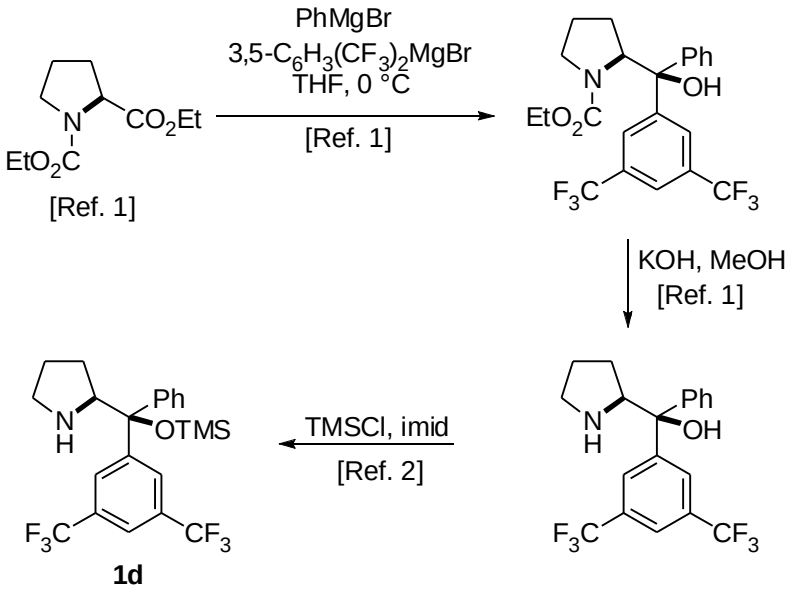
General Experimental

All sensitive reactions were carried out under an argon atmosphere in absolute solvents with syringe and Schlenk techniques in oven-dried glassware. THF was distilled under argon from lead/sodium in the presence of benzophenone. Bulk solvents for chromatography and extraction were distilled prior to use. Reagents were obtained from commercial sources and used without further purification unless otherwise stated. TLC was performed on E. Merck precoated plates (SiO_2 60 F_{254}, layer thickness 0.2 mm), and chromatography was performed with E. Merck SiO_2 60 (0.040–0.063 mm) in the flash mode with a nitrogen pressure of 0.2 bar.

Melting points were determined with a Büchi 510 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300, a Varian Mercury 300, a Varian Inova 400 and a Varian Unity 500 instrument. ^{1}H chemical shifts are reported in delta (d) units in parts per million (ppm) relative to the singlet at 7.26 ppm for *d*-chloroform (residual $CHCl_3$) and the singlet (0.00 ppm) for TMS. ^{13}C Chemical shifts are reported in ppm relative to the central line of the triplet at 77.0 ppm for *d*-chloroform. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; qt, quintet; m, multiplet; and b, broad and combinations thereof. Coupling constants are reported in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer PE 1759 FT instrument; absorptions are given in wave numbers (cm^{-1}). Low resolutions mass spectra were recorded on a Varian MAT 212 S instrument using either electron impact ionisation (EI, 70 eV), or chemical ionisation (CI, CH_4, isobutane or NH_3). High resolution mass spectra were recorded either on a Varian MAT 95 mass spectrometer or on a Micromass LCT Spectrometer (ESI, TOF). Optical rotations were measured with a Perkin-Elmer model 241 polarimeter in a 1-dm cell and the sodium D line (589 nm) at the temperature, solvent, and concentration indicated using solvents of Merck UVASOL-quality. Elemental analyses were performed by the Microanalytical Laboratory of the Institute of Organic Chemistry.

CCDC 668123-668125 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

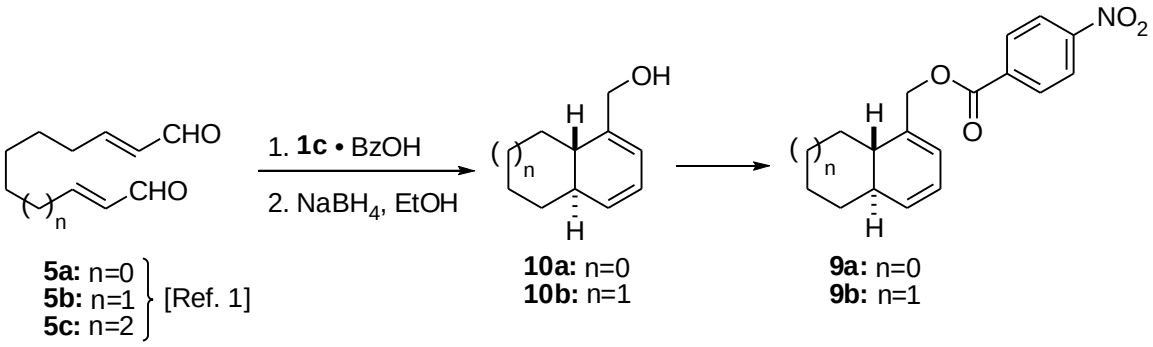
Synthesis of the mixed diarylprolinol TMS ether 1d



[1] J. V. B. Kanth, M. Periasamy, *Tetrahedron* **1993**, *49*, 1527–1532.

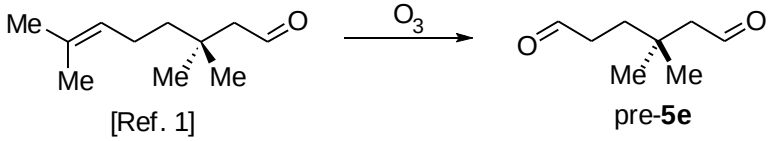
[2] Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem.* **2005**, *117*, 4284–4287; *Angew. Chem. Int. Ed.* **2005**, *44*, 4212–4215.

Synthesis of 10a, 10b, 9a, 9b



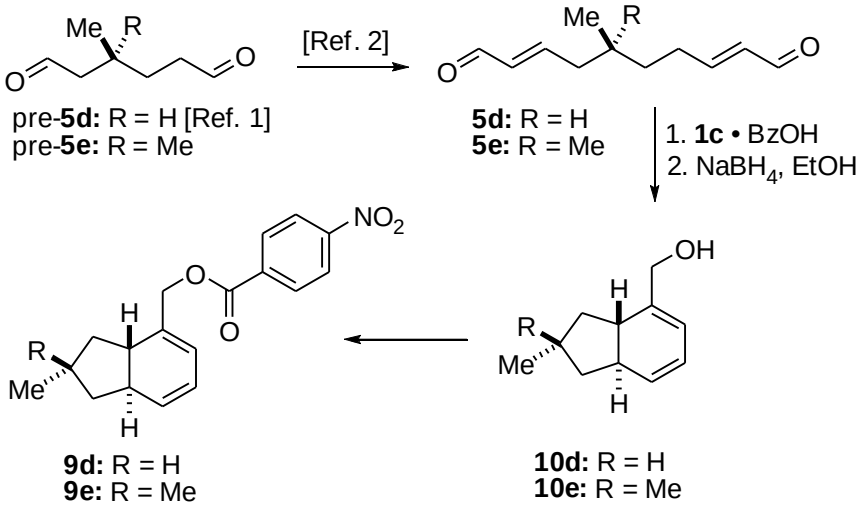
[1] R. M. de Figueiredo, R. Berner, J. Julis, T. Liu, D. Türp, M. Christmann, *J. Org. Chem.* **2007**, *72*, 640–642.

Synthesis of 3,3-Dimethylhexanedial



[1] S. Sakane, K. Maruoka, H. Yamamoto, *Tetrahedron* **1986**, *42*, 2203–2209.

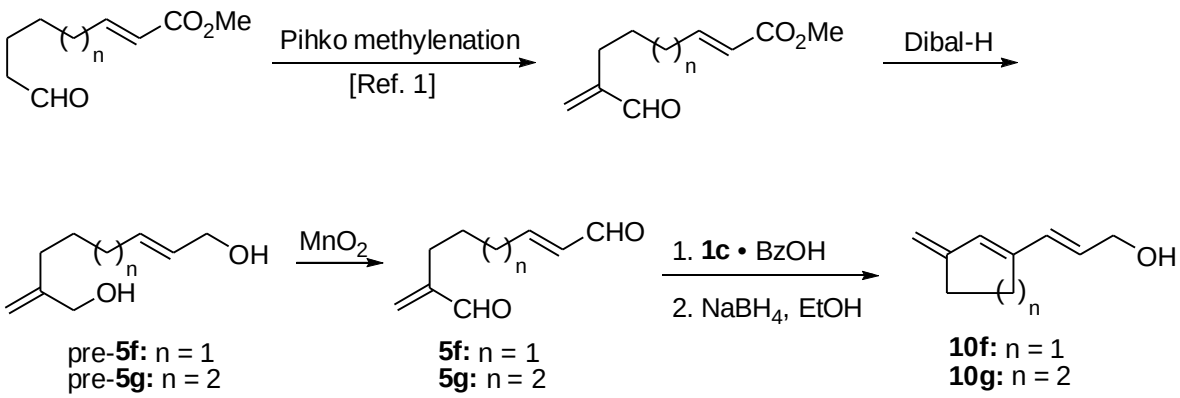
Synthesis of 10d, 10e, 9d, 9e



[1] B. S. Dyer, J. D. Jones, G. D. Ainge, M. Denis, D. S. Larsen, G. F. Painter, *J. Org. Chem.* **2007**, *72*, 3282-3288.

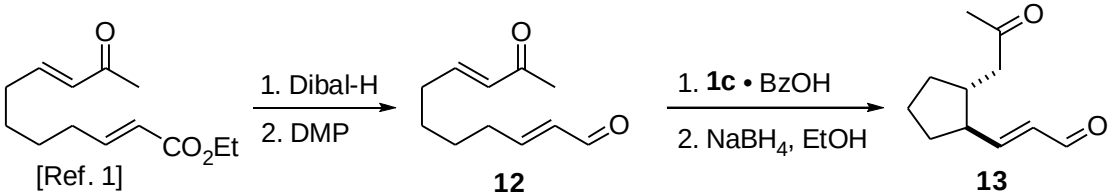
[2] R. M. de Figueiredo, R. Berner, J. Julis, T. Liu, D. Türp, M. Christmann, *J. Org. Chem.* **2007**, *72*, 640–642.

Synthesis of 10f, 10g



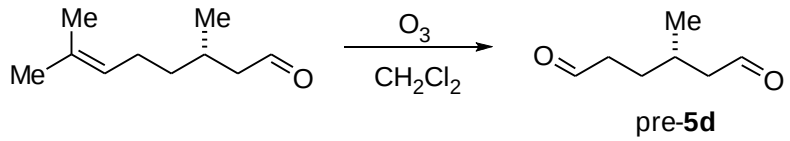
[1] a) A. Erkkilä, P. M. Pihko, *J. Org. Chem.* **2006**, *71*, 2538–2541; b) A. Erkkilä, P. M. Pihko, *Eur. J. Org. Chem.* **2007**, 4205–4216.

Synthesis of 13



[1] G. Pandey, S. Hajra, M. K. Ghorai, K. R. Kumar, J. Am. Chem. Soc. 1997, *119*, 8777–8787.

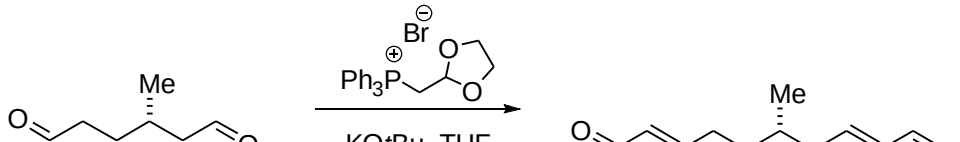
Synthesis of (*S*)-3-methylhexanedial (pre-5d)



pre-**5d**

A solution of the (*S*)-(–)-citronellal (10.0 g, 65.0 mmol, 1 equiv.) in CH_2Cl_2 (300 mL) at –78 °C was purged with ozone until the solution turned blue. Then, SMe_2 (9.60 mL, 130 mmol, 2 equiv.) was added and the reaction mixture was allowed to warm up to room temperature with stirring for 4 h. The reaction was concentrated and the crude residue was purified by chromatography (pentane/Et_2O 1:1) to afford the desired dialdehyde pre-**5d** (7.00 g, 84% yield) as yellowish oil, which was used directly in the following step.

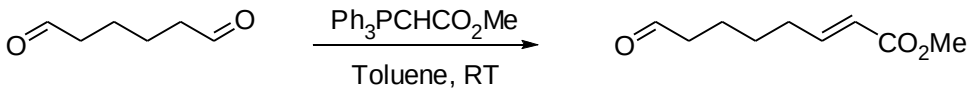
Synthesis of (*S*,2*E*,8*E*)-5-methyldeca-2,8-dienedial (5d)



pre-**5d** **5d**

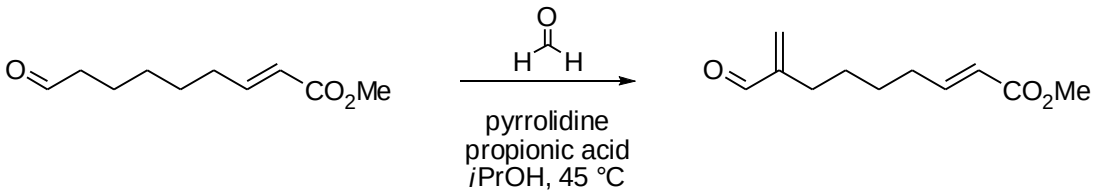
To a stirred suspension of the phosphonium salt (15.0 g, 35.2 mmol, 3.00 equiv.) in THF (210 mL) was added KO*t*Bu in small portions (4.10 g, 36.3 mmol, 3.10 equiv.) at 0 °C under argon. The white suspension becomes deep yellow and after 30 min at this temperature the dialdehyde (1.50 g, 10.5 mmol, 1.00 equiv.) in THF (30 mL) was added dropwise. The mixture was stirred at room temperature for 6 h. Work-up was performed by quenching the reaction mixture with a solution of oxalic acid (40.0 g/400 mL H_2O). The stirring was continued overnight. After extraction with Et_2O (4 x 300 mL) the organic phases were washed twice with a saturated $NaHCO_3$ solution (150 mL). The organic layer was dried (Na_2SO_4) and concentrated. Triphenylphosphine oxide was removed by column chromatography (pentane/Et_2O 3/2) to give the dialdehyde **5d** (1.25 g, 60% yield) as yellowish oil.

Synthesis of (*E*)-methyl 8-oxooct-2-enoate



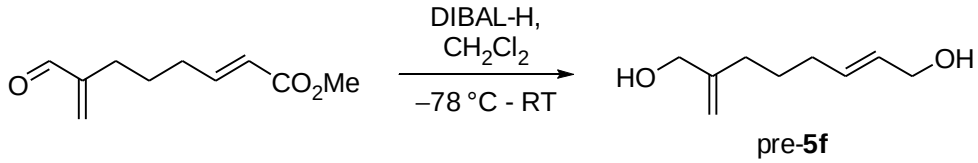
To a suspension of dialdehyde (10.0 g, 87.6 mmol, 1 equiv.) in toluene or CH_2Cl_2 (350 mL) was added the phosphonium ylide (30.0 g, 87.6 mmol, 1 equiv.) at room temperature and the reaction was stirred for 2 days. The mixture was evaporated until half of the solvents and then taken into pentane. The precipitate triphenylphosphine oxide was filtered off and the filtrate evaporated. The crude material was purified by column chromatography (pentane/Et_2O 1:1) to give the desired monoester (7.50 g, 50% yield) as colorless oil.

Synthesis of (*E*)-methyl 8-formylnona-2,8-dienoate



To a mixture of aqueous formaldehyde solution (37% in water, 816 µL, 10.9 mmol, 1 equiv.) and the aldehyde (2.00 g, 10.9 mmol, 1 equiv.) in *i*PrOH (1 mL) was added propionic acid (81.0 µL, 1.09 mmol, 0.10 equiv.) and pyrrolidine (91.0 µL, 1.09 mmol, 0.10 equiv.). The reaction mixture was stirred at 45 °C for 4 h. The reaction was stopped by quenching with a saturated $NaHCO_3$ solution (10 mL) and extracted with CH_2Cl_2 (3x 20 mL). The organic layers were combined, dried (Na_2SO_4) and evaporated. Purification was performed by column chromatography (pentane/Et_2O 3:2) to afford the desired compound (1.70 g, 80% yield) as colorless oil.

Synthesis of (*E*)-7-methyleneoct-2-ene-1,8-diol (pre-5f)

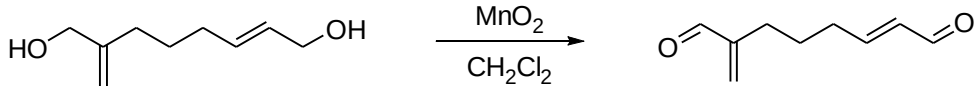


pre-**5f**

To a stirred solution of the starting material (650 mg, 3.57 mmol, 1.00 equiv.) in dry CH_2Cl_2 (27 mL) was added dropwise DIBAL-H (1 N in CH_2Cl_2, 12.9 mL, 12.9 mmol, 3.60 equiv.) at – 78 °C. After 1.5 h at this temperature the reaction was warmed to room temperature and quenched with *i*PrOH (few drops) and water (few drops). Then, silica gel was added and the resulting mixture was stirred for 30 min, diluted with EtOAc and then filtered through a pad

of Celite. The filtrate was concentrated to give a syrup which was purified by chromatography on silica gel (Et_2O) to give the desired diol (480 mg, 86% yield) as colorless oil.

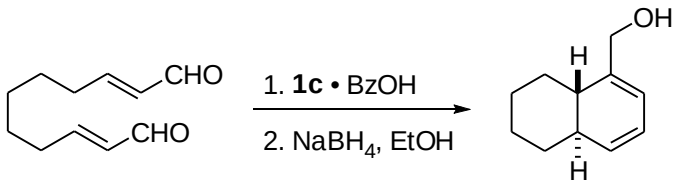
Synthesis of (*E*)-7-methyleneoct-2-enedial (5f)



pre-**5f** **5f**

To a stirred solution of the diol pre-**5f** (480 mg, 3.07 mmol, 1 equiv.) in dry CH_2Cl_2 (45 mL) was added MnO_2 at one portion (6.68 g, 76.9 mmol, 25.0 equiv.) at room temperature. After 18 h of stirring at this temperature, additional MnO_2 (2.00 g was added). After 20 h the reaction was filtered through a pad of Celite (CH_2Cl_2 and EtOAc). The filtrate was evaporated and then purified by chromatography on silica gel (pentane/Et_2O 7:4) to give the dialdehyde **5f** (358 mg, 77% yield) as yellowish oil.

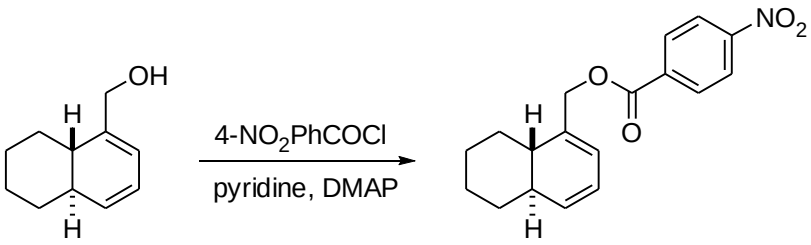
Synthesis of ((4a*R*,8a*S*)-4a,5,6,7,8,8a-hexahydronaphthalen-1-yl)methanol (10b)



5b **10b**

To a solution of catalyst **1c** (397 mg, 1.22 mmol, 0.10 equiv.) and benzoic acid (150 mg, 1.22 mmol, 0.10 equiv.) in toluene (22 mL) was added the dialdehyde **5b** (2.20 g, 12.2 mmol, 1.00 equiv.) at room temperature. The reaction was monitored by TLC and after complete conversion the mixture was purified by column chromatography (pentane/Et_2O 10:1) to give the desired bicyclic aldehyde **8b**. This material was reduced with excess $NaBH_4$ (1.5 equiv.) in ethanol and purified by column chromatography (pentane/EtOAc 5:1 or pentane/Et_2O 3:2) to give alcohol **10b** (1.20 g, 60% yield) as amorphous solid.

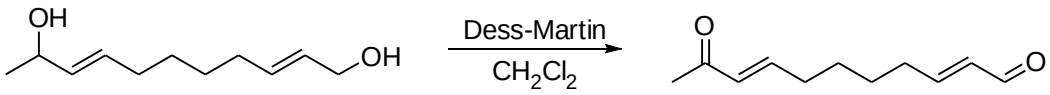
Synthesis of ((3a*S*,7a*R*)-2,3,3a,7a-tetrahydro-1*H*-inden-4-yl)methyl 4-nitrobenzoate (9a)



10b **9b**

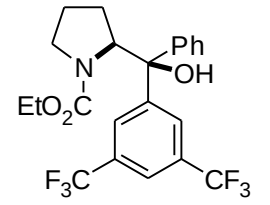
To a solution of **10b** (75 mg, 0.46 mmol, 1.00 equiv.) in pyridine (1 mL) was added 4-nitrobenzoyl chloride (127 mg, 0.69 mmol, 1.50 equiv.) and DMAP (6.1 mg, 0.05 mmol, 0.1 equiv.) at room temperature. After 2 h the reaction was stopped and evaporated. The crude product was purified by column chromatography (pentane/Et_2O 9:1) to yield the bromobenzoate **9b** (114 mg, 80% yield).

Procedure for preparing compound 12:



To a stirred solution of the dialcohol starting material (500 mg, 2.71 mmol, 1.00 equiv.) in dry CH_2Cl_2 (20 mL) was added dropwise Dess-Martin periodinane (15% in CH_2Cl_2, 11.5 mL, 8.14 mmol, 3 equiv.) at room temperature. After 2 h of stirring at this temperature, the reaction was quenched with saturated solution of $NaHCO_3$ and $Na_2S_2O_3$ (20 mL). The organic phase was separated and the aqueous layer washed twice with CH_2Cl_2 (20 mL). After drying (Na_2SO_4), the organic phases were concentrated and the crude was purified by chromatography on silica gel (Et_2O/pentane 3:2) to give the desired dialdehyde (300 mg, 61% yield) as colorless oil.

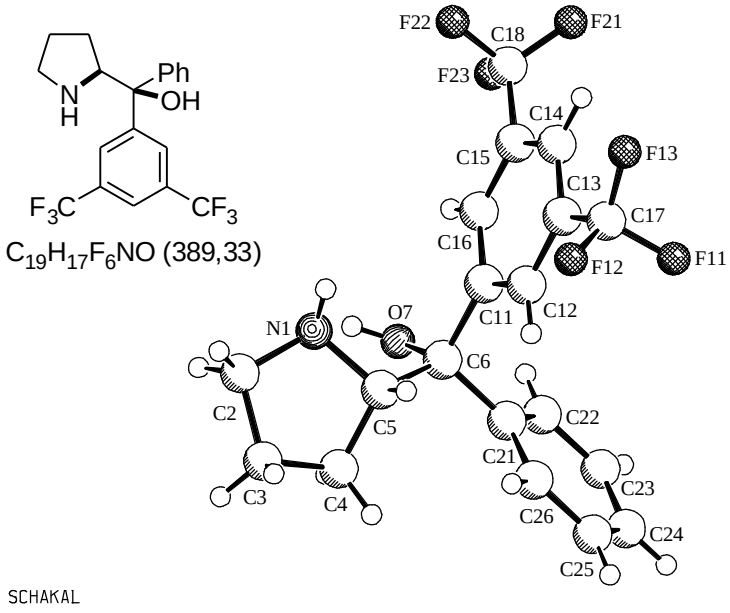
(*S*)-Ethyl-2-((*S*)-(3,5-bis(trifluoromethyl)phenyl)(hydroxy)(phenyl)methyl)pyrrolidine-1-carboxylate



$C_{22}H_{21}F_6NO_3$ (461,40)

colorless solid; R_f 0.55 (pentane/Et_2O 1:1); mp: 130-132 °C; α_D –72.1 (*c* 0.43, $CHCl_3$), ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (bs, 2H), 7.79 (bs, 1H), 7.34 (bs, 5H), 4.88 (dd, *J* = 8.9, 4.0 Hz, 1H), 4.17-4.01 (m, 2H), 3.52-3.44 (m, 1H), 3.09-2.98 (m, 1H), 2.16-2.06 (m, 1H), 1.94-1.86 (m, 1H), 1.62-1.52 (m, 1H), 1.21 (t, *J* = 6.4 Hz, 3H), 0.98 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 149.0, 142.2, 131.0 (q, $J_{C–F}$ = 33.5 Hz, 2C), 128.0 (2C), 127.9, 127.8 (2C), 127.6 (2C), 123.4 (q, $J_{C–F}$ = 273 Hz, 2C), 121.2 (m), 81.2, 65.9, 62.2, 47.8, 29.6, 23.2, 14.5; IR (KBr): 3453, 1670, 1282, 1171, 1121, 700 cm^{-1}; MS (CI): m/z (%) 462 ($[M+H]^+$, 39), 444 ($[M–OH]^+$, 100), 142 (20); Anal calcd for $C_{22}H_{21}F_6NO_3$: C, 57.27; H, 4.59; N, 3.04. Found: C, 57.45; H, 4.67; N, 3.04.

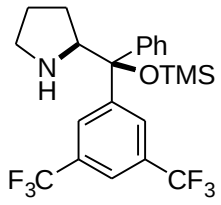
(*S*)-(3,5-Bis(trifluoromethyl)phenyl)(phenyl)((*S*)-pyrrolidin-2-yl)methanol (pre-1d)



$C_{19}H_{17}F_6NO$ (389,33)

colorless solid; R_f 0.4 (EtOAc); mp: 90-91 °C; α_D –43.0 (*c* 0.3, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 2H), 7.71 (s, 1H), 7.52-7.49 (m, 2H), 7.35-7.30 (m, 2H), 7.25-7.20 (m, 1H), 4.86 (bs, 1H), 4.31 (t, *J* = 7.6 Hz, 1H), 3.09-2.97 (m, 2H), 1.80-1.55 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.3, 143.7, 131.4 (q, $J_{C–F}$ = 32.5 Hz, 2C), 128.4 (2C) 127.1, 126.1 (2C), 125.3 (2C), 123.4 (q, $J_{C–F}$ = 273 Hz, 2C), 120.6 (m), 77.0, 64.4, 47.0, 26.7, 25.6; IR (KBr): 3348, 2998, 2886, 1371, 1279, 1135, 705 cm^{-1}; MS (CI): m/z (%) 390 ([M+H]$^+$, 100), 372 ([M–OH]$^+$, 4); Anal calcd for $C_{19}H_{17}F_6NO$: C, 58.61; H, 4.40; N, 3.60. Found: C, 58.87; H, 4.58; N, 3.64.

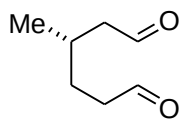
(*S*)-2-((*S*)-(3,5-Bis(trifluoromethyl)phenyl)(phenyl)(trimethylsilyloxy)methyl)pyrrolidine (1d)



$C_{22}H_{25}F_6NOSi$ (461,52)

colorless solid; mp: 35-36 °C; α_D +9.5 (*c* 0.43, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 2H), 7.77 (s, 1H), 7.33-7.25 (m, 5H), 4.23 (dd, *J* = 7.9, 6.7 Hz, 1H), 2.85 (dt, *J* = 7.9, 6.7 Hz, 1H), 2.60-2.55 (m, 1H), 1.81-1.73 (m, 1H), 1.75-1.61 (bs, 1H), 1.55-1.47 (m, 1H), 1.47-1.38 (m, 1H), 1.10-1.00 (m, 1H), -0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.0, 144.7, 129.9 (q, $J_{C–F}$ = 273 Hz, 2C), 128.9 (2C), 128.3 (2C), 128.2 (2C), 127.8, 123.6 (q, $J_{C–F}$ = 32.6 Hz, 2C), 120.5 (m), 82.9, 64.2, 47.1, 27.4, 25.4, 1.8 (3C); IR (neat): 2961, 1279, 1172, 1134, 887, 843 cm^{-1}; MS (CI): m/z (%) 462 ([M+H]$^+$, 100), 372 ([M–OTMS]$^+$, 3); Anal calcd for $C_{19}H_{17}F_6NO$: C, 57.25; H, 5.46; N, 3.03. Found: C, 57.46; H, 5.39; N, 3.48.

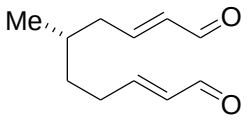
(*S*)-3-Methylhexanedial (pre-5d)



$C_7H_{12}O_2$ (128,17)

Colorless oil; R_f 0.25 (pentane/Et_2O 1:1); α_D +2.6 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.5 Hz, 1H), 9.73 (t, *J* = 1.9 Hz, 1H), 2.52-2.41 (m, 2H), 2.40 (ddd, *J* = 16.5, 5.8, 1.8 Hz, 1H), 2.27 (ddd, *J* = 16.5, 7.6, 2.3 Hz, 1H), 2.11-2.02 (m, 1H), 1.73-1.64 (m, 1H), 1.55-1.46 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 201.9, 50.7, 41.4, 28.5, 27.4, 19.5; IR ($CHCl_3$): 2955, 2726, 1722, 1460, 1379 cm^{-1}; MS (CI): m/z (%) 128 (M^+, 8), 127 ($[M-H]^-$, 100), 99 (15), 81 (50).

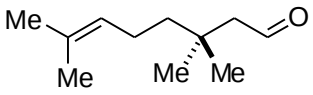
(*S*,2*E*,8*E*)-5-Methyldeca-2,8-dienedial (5d)



$C_{11}H_{16}O_2$ (180,24)

Colorless oil; R_f 0.20 (pentane/Et_2O 3:2); α_D +0.4 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 9.51 (d, *J* = 4.7 Hz, 1H), 9.49 (d, J = 4.4 Hz, 1H), 6.86-6.75 (m, 2H), 6.15-6.07 (m, 2H), 2.46-2.26 (m, 3H), 2.25-2.16 (m, 1H), 1.80-1.68 (m, 1H), 1.62-1.52 (m, 1H), 1.45-1.34 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 193.5, 157.7, 156.3, 134.3, 133.0, 39.9, 34.6, 32.1, 30.2, 19.3; IR ($CHCl_3$): 2924, 2816, 1689,1146, 978 cm^{-1}; MS (EI): m/z (%) 179 ($[M-H]^+$, 1), 151 ($[M-CHO]^+$, 14), 95 (37), 81 (36), 70 (66), 55 (100); HRMS calcd for $C_{10}H_{15}O$ ($[M-CHO]^+$), 151.11229, Found: 151.11229.

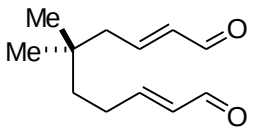
3,3,7-Trimethyloct-6-enal



$C_{11}H_{20}O$ (168,28)

Colorless oil; R_f 0.61 (pentane/Et_2O 10:1); ^1H NMR (300 MHz, $CDCl_3$): δ 9.84 (t, *J* = 3.2 Hz, 1H), 5.11-5.05 (m, 1H), 2.26 (d, *J* = 3.2 Hz, 2H), 2.01-1.90 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.38-1.30 (m, 2H), 1.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.6, 131.5, 124.3, 54.7, 42.7, 33.5, 27.4 (2C), 25.6, 22.7, 17.5; ; IR ($CHCl_3$): 2961, 1722, 1465, 1376, 758 cm^{-1}; MS (EI): m/z (%) 168 (M^+, 15), 135 (29), 123 (29), 109 (72), 83 (55), 55 (59); HRMS calcd for $C_{11}H_{20}O$ (M^+), 168.15141, Found: 168.15141.

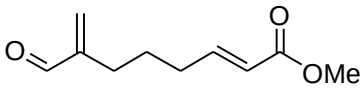
(2*E*,8*E*)-5,5-Dimethyldeca-2,8-dienedial (5e)



$C_{12}H_{18}O_2$ (194,27)

Colorless oil; R_f 0.28 (pentane/Et_2O 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): 9.46-9.36 (m, 2H), 6.84-6.71 (m, 2H), 6.08-5.96 (m, 2H), 2.29-2.14 (m, 4H), 1.40-1.31 (m, 2H), 0.89 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 193.4, 158.4, 154.8, 135.1, 132.5, 44.8, 39.7, 33.8, 27.3, 26.5 (2C); IR ($CHCl_3$): 2959, 2926, 2871, 2818, 1688, 1637, 1469, 1160, 1118, 978, 756 cm^{-1}; MS (EI): m/z (%) 195 ([M+H]$^+$, 6), 125 (62), 107 (42), 81 (47), 70 (67), 67 (40), 55 (100). HRMS calcd for $C_{12}H_{18}O_2$ ([M]$^+$), 194.1307, Found: 194.1307.

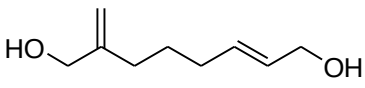
(*E*)-Methyl-7-formylocta-2,7-dienoate



$C_{10}H_{14}O_3$ (182,22)

Colorless oil; R_f 0.59 (pentane/Et_2O 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s,1H), 6.01 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.23 (s, 1H), 6.00 (s, 1H), 5.80 (dt, *J* = 15.7, 1.6 Hz, 1H), 3.68 (s, 3H), 2.28-2.15 (m, 4H), 1.64-1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 166.7, 149.4, 148.4, 134.2, 121.3, 51.4, 31.7, 27.3, 26.1; IR ($CHCl_3$): 2947, 1722, 1657, 1437 cm^{-1}; MS (EI): m/z (%) 183 ([M+H]$^+$, 5), 154 ([M-CHO]$^+$, 3), 150 (39), 122 (54), 113 (94), 81 (100), 53 (58); HRMS calcd for $C_{10}H_{15}O_3$ ([M+H]$^+$), 183.10212, Found: 183.10212.

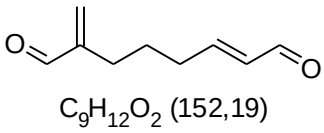
(*E*)-7-Methyleneoct-2-ene-1,8-diol (pre-5f)



$C_9H_{16}O_2$ (156,22)

Colorless oil; R_f 0.32 (Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73-5.59 (m, 2H), 5.02 (s, 1H), 4.86 (s, 1H), 4.09-4.04 (m, 2H), 2.10-2.03 (m, 4H), 1.78 (bs, 1H), 1.65 (bs, 1H), 1.60-1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 132.6, 129.3, 109.4, 65.8, 63.7, 32.3, 31.9, 27.1; IR ($CHCl_3$): 3340, 2928, 2859, 1440, 1008, 971, 898 cm^{-1}; MS (EI): m/z (%) 125 (22), 121 (21), 107 (46), 79 (100), 67 (80), 55 (96).

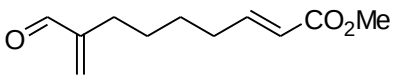
(*E*)-7-Methyleneoct-2-enedial (5f)



$C_9H_{12}O_2$ (152,19)

Colorless oil; R_f 0.65 (Et_2O);^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 9.48 (d, *J* = 8.0 Hz, 1H), 6.82 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.26 (s, 1H), 6.10 (ddt, *J* = 15.7, 8.0, 1.4 Hz, 1H), 6.03 (s, 1H), 2.38-2.25 (m, 4H), 1.71-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 193.7, 157.5, 149.2, 134.4, 133.2, 32.2, 27.4, 26.1; IR ($CHCl_3$): 2823, 1689, 1637, 1442, 1125, 972 cm^{-1}; MS (EI): m/z (%) 153 ([M+H]$^+$, 1), 123 (21), 95 (33), 83 (100), 55 (96); HRMS calcd for $C_9H_{13}O_2$ ([M+H]$^+$), 153.09156, Found: 153.09156.

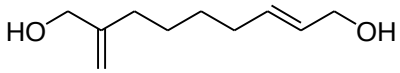
(*E*)-methyl 8-formylnona-2,8-dienoate



$C_{11}H_{16}O_3$ (196,24)

Colorless oil; R_f 0.59 (pentane/Et_2O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.52 (s, 1H), 6.93 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.23 (s, 1H), 5.99 (s, 1H), 5.80 (d, *J* = 15.4 Hz, 1H), 3.71 (s, 3H), 2.28-2.16 (m, 4H), 1.51-1.43 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.4, 166.9, 149.8, 149.0, 134.0, 121.0, 51.4, 31.9, 27.7, 27.6, 27.3; IR (capillary): 2940, 2860, 1723, 1693, 1657, 1437, 1273, 1199, 717 cm^{-1}; MS (CI): m/z (%) 197.1 ([M+H]$^+$, 9), 165 (100), 137 (11); Anal calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22; Found: C, 67.21; H, 8.05.

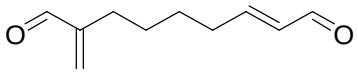
(*E*)-8-Methylenenon-2-ene-1,9-diol (pre-5g)



$C_{10}H_{18}O_2$ (170,25)

Colorless oil; R_f 0.55 (Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73-5.57 (m, 2H), 5.00 (s, 1H), 4.85 (s, 1H), 4.09-4.03 (m, 4H), 2.10-2.02 (m, 4H), 1.75 (bs, 2H), 1.51-1.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 132.9, 129.0, 109.2, 65.8, 63.7, 32.8, 32.0, 28.8, 27.2; IR ($CHCl_3$): 3336, 2927, 2857, 1452, 1085, 1014, 972, 897 cm^{-1}; MS (CI): m/z (%) 153 ([M-H_2O]$^+$, 6), 135 ([M-2H_2O+H]$^+$, 100).

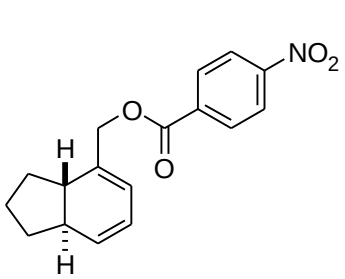
(E)-8-Methylenenon-2-enedial (5g)

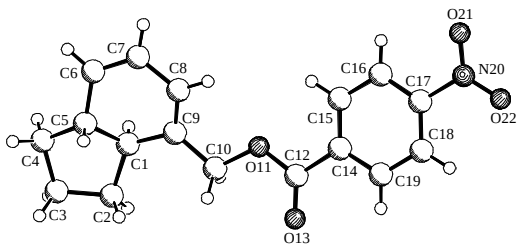


$C_{10}H_{14}O_2$ (166,22)

Colorless oil; R_f 0.60 (pentane/Et_2O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.53 (s, 1H), 9.49 (d, *J* = 7.9 Hz, 1H), 6.83 (dt, *J* = 15.6, 7.9, 1.5 Hz, 1H), 6.23 (s, 1H), 6.10 (ddt, *J* = 15.6, 7.9, 1.5 Hz, 1H), 6.01 (s, 1H), 2.39-2.32 (m, 2H), 2.27 (t, *J* = 7.3 Hz, 2H), 1.57-1.46 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.6, 194.0, 158.2, 149.8, 134.3, 133.1, 32.4, 27.5, 27.4, 27.3; IR ($CHCl_3$): 2935, 1689, 1636, 1125, 973, 953 cm^{-1}; MS (EI): m/z (%) 137 ([M-CHO]$^+$, 13), 96 (51), 95 (58), 83 (46), 79 (38), 70 (100), 54 (80); HRMS calcd for $C_9H_{13}O$ ([M-CHO]$^+$), 137.09664, Found: 137.09664.

((3a*S*,7a*R*)-2,3,3a,7a-Tetrahydro-1*H*-inden-4-yl)methyl 4-nitrobenzoate (9a)





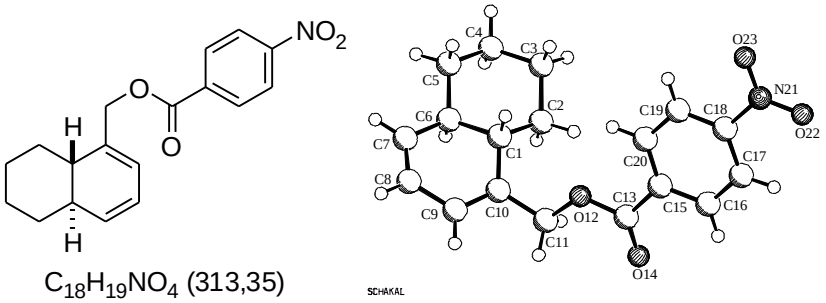
$C_{17}H_{17}NO_4$ (299,32)

SCHAKAL

Yellow crystals; mp: 86-88 °C; R_f 0.48 (pentane/Et_2O 9:1); α_D –22.4 (*c* 1.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.2 Hz, 2H), 8.22 (d, *J* = 9.2 Hz, 2H), 6.14 (d, *J* = 9.2

Hz, 1H), 6.06-6.03 (m, 1H), 5.98 (ddd, *J* = 9.2, 4.9, 2.4 Hz, 1H), 5.00-4.98 (m, 2H), 2.27-2.15 (m, 2H), 1.92-1.75 (m, 4H), 1.50-1.35 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 150.5, 137.4, 135.6, 133.1, 130.7 (2C), 125.1, 124.4, 123.6 (2C), 67.1, 44.5, 44.3, 26.4, 25.2, 22.8; IR (KBr): 2943, 2865, 1723, 1602, 1524, 1344, 1270, 1105 cm^{-1}; MS (EI): m/z (%) 299 (M^+, 2), 132 (75), 117 (100), 91 (32); HRMS calcd for $C_{17}H_{17}NO_4$ (M^+), 299.11576, Found: 299.11556.

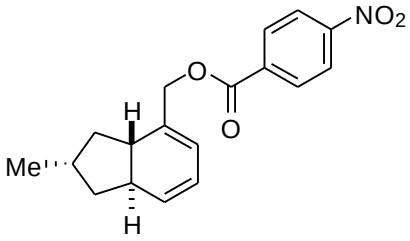
((4a*R*,8a*S*)-4a,5,6,7,8,8a-Hexahydronaphthalen-1-yl)methyl 4-nitrobenzoate (9b)



$C_{18}H_{19}NO_4$ (313,35)

Yellow crystals; mp: 70-72 °C; R_f 0.53 (pentane/Et_2O 9:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31-8.28 (m, 2H), 8.23-8.19 (m, 2H), 6.08-6.04 (m, 1H), 5.92 (ddd, *J* = 9.5, 5.2, 2.8 Hz, 1H), 5.69 (d, *J* = 9.5 Hz, 1H), 4.96-4.88 (m, 2H), 2.20-2.02 (m, 3H), 1.90-1.75 (m, 3H), 1.39-1.24 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 150.5, 135.7, 135.5, 134.8, 130.7 (2C), 125.1, 123.6 (2C), 123.2, 66.9, 41.3, 40.6, 32.5, 29.0, 26.7, 26.5; IR ($CHCl_3$): 2926, 2852, 2803, 1724, 1604, 1528, 1346, 1271, 1102, 717 cm^{-1}; MS (EI): m/z (%) 313 (M^+, 3), 146 (100), 131 (75), 118 (43), 103 (35), 91 (42); HRMS calcd for $C_{17}H_{17}NO_4$ (M^+), 313.13141, Found: 313.13141.

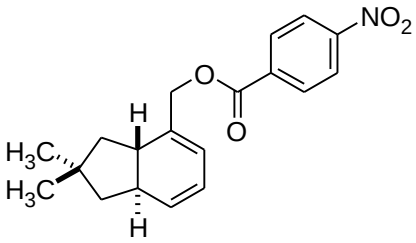
((2*S*,3a*S*,7a*R*)-2-Methyl-2,3,3a,7a-tetrahydro-1*H*-inden-4-yl)methyl 4-nitrobenzoate (9d)



$C_{18}H_{19}NO_4$ (313,35)

Yellow solid; R_f 0.59 (pentane/Et_2O 9:1); α_D –10.5 (*c* 1.07, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.2 Hz, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 6.10 (d, *J* = 9.2 Hz, 6.05-6.02 (m, 1H), 5.97 (ddd, *J* = 7.9, 5.2, 3.1 Hz, 1H), 4.97 (d, *J* = 13.1 Hz, 1H), 4.93 (d, *J* = 13.1 Hz, 1H), 2.41-2.20 (m, 3H), 2.13-2.06 (m, 1H), 1.70 (ddd, *J* = 12.5, 11.6, 10.4 Hz, 1H), 1.35 (ddd, *J* = 12.5, 7.6, 3.1 Hz, 1H), 1.05 (ddd, *J* = 11.6, 11.6, 8.2 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 150.6, 137.5, 135.7, 133.1, 130.7 (2C), 125.0, 124.3, 123.6 (2C), 67.0, 45.0, 42.6, 35.4, 34.6, 31.8, 23.2; IR ($CHCl_3$): 2951, 1726, 1529, 1348, 1271, 1103, 717 cm^{-1}; MS (EI): m/z (%) 313 (M^+, 1), 146 (71), 131 (100), 104 (48), 91 (41); HRMS calcd for $C_{18}H_{19}NO_4$ (M^+), 313.13141, Found: 313.13141.

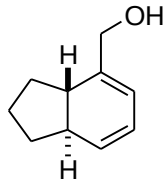
((3a*S*,7a*R*)-2,2-Dimethyl-2,3,3a,7a-tetrahydro-1*H*-inden-4-yl)methyl 4-nitrobenzoate (9e)



$C_{19}H_{21}NO_4$ (327,37)

Yellow solid; R_f 0.53 (pentane/Et_2O 9:1); α_D –32.7 (*c* 1.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.2 Hz, 2H), 8.22 (d, *J* = 9.2 Hz, 2H), 6.06 (d, *J* = 9.2 Hz, 1H), 6.04-6.01 (m, 1H), 5.96 (ddd, *J* = 9.2, 4.9, 2.1 Hz, 1H), 4.92 (s, 1H), 2.42-2.37 (m, 2H), 1.70-1.62 (m, 2H), 1.38-1.27 (m, 2H), 1.07 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 150.6, 137.3, 135.6, 132.9, 130.7 (2C), 125.1, 124.1, 123.6 (2C), 66.9, 43.73, 43.71, 43.0, 41.6, 38.0, 32.2, 32.1; IR ($CHCl_3$): 2948, 2863, 1767, 1530, 1348, 1104, 717 cm^{-1}; MS (EI): m/z (%) 327 (M^+, 1), 160 (65), 145 (100), 104 (38), 91 (23); HRMS calcd for $C_{19}H_{21}NO_4$ (M^+), 327.14706, Found: 327.14706.

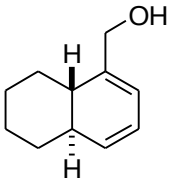
((3a*S*,7a*R*)-2,3,3a,7a-Tetrahydro-1*H*-inden-4-yl)methanol (10a)



$C_{10}H_{14}O$ (150,22)

Colorless oil; R_f 0.33 (pentane/EtOAc 5:1); α_D −58.1 (*c* 1.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.05 (d, *J* = 9.2 Hz, 1H), 5.98-5.94 (m, 1H), 5.92-5.89 (m, 1H), 4.28-4.18 (m, 2H), 2.18-2.03 (m, 2H), 1.90-1.73 (m, 4H), 1.64 (bs, 1H), 1.41-1.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 131.6, 125.4, 120.2, 64.2, 44.5, 44.2, 26.4, 24.9, 22.8; IR ($CHCl_3$): 3357, 3029, 2952, 2868, 2806, 1455, 1203, 1094, 1053, 1003, 705 cm^{-1}; MS (EI): m/z (%) 150 (M^+, 31), 119 (64), 117 (30), 91 (100); HRMS calcd for $C_{10}H_{14}O$ (M^+), 150.10447, Found: 150.10446.

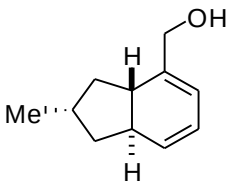
((4a*R*,8a*S*)-4a,5,6,7,8,8a-Hexahydronaphthalen-1-yl)methanol (10b)



$C_{11}H_{16}O$ (164,24)

Colorless oil; R_f 0.33 (pentane/EtOAc 5:1); α_D −97.7 (*c* 0.87, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95-5.87 (m, 2H), 5.60 (d, *J* = 9.2 Hz, 1H), 4.25-4.14 (m, 2H), 2.15-1.95 (m, 3H), 1.87-1.73 (m, 3H), 1.36-1.17 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7, 133.4, 123.4, 120.8, 64.0, 41.2, 40.6, 32.6, 28.7, 26.6, 26.5; IR ($CHCl_3$): 3335, 3028, 2923, 2852, 2800, 1446, 1061, 1034, 988, 757, 706 cm^{-1}; MS (EI): m/z (%) 164 (M^+, 31), 133 (26), 121 (17), 107 (23), 91 (100), 79 (15); HRMS calcd for $C_{11}H_{16}O$ (M^+), 164.12012, Found: 164.12012.

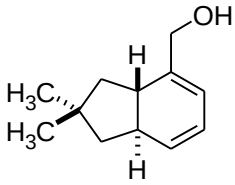
((2*S*,3a*S*,7a*R*)-2-Methyl-2,3,3a,7a-tetrahydro-1*H*-inden-4-yl)methanol (10d)



$C_{11}H_{16}O$ (164,24)

Colorless oil; R_f 0.36 (pentane/Et_2O 3:2); diastereomeric mixture (~ 2:1); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 131.6, 125.3, 120.1, 64.1, 45.1, 42.7, 35.2, 34.6, 31.8, 23.2; IR ($CHCl_3$): 3329, 2950, 2865, 2811, 1454, 1054, 997, 704 cm^{-1}; MS (EI): m/z (%) 164 (M^+, 31), 133 (46), 131 (28), 91 (100); HRMS calcd for $C_{11}H_{16}O$ (M^+), 164.12012, Found: 164.12012.

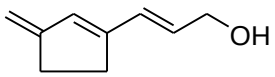
((3a*S*,7a*R*)-2,2-Dimethyl-2,3,3a,7a-tetrahydro-1*H*-inden-4-yl)methanol (10e)



$C_{12}H_{18}O$ (178,27)

Colorless oil; R_f 0.33 (pentane/Et_2O 3:2); α_D – 101.8 (*c* 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 6.01-5.89 (m, 3H), 4.22 (d, *J* = 14.3 Hz, 1H), 4.17 (d, *J* = 14.3 Hz, 1H), 2.38-2.24 (m, 2H), 1.70-1.59 (m, 2H), 1.41 (bs, 1H), 1.33-1.25 (m, 2H), 1.064 (s, 3H), 1.057 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 131.6, 125.3, 120.1, 64.2, 43.82, 43.77, 43.1, 41.4, 37.9, 32.2, 32.1; IR ($CHCl_3$): 3311, 3032, 2945, 2863, 2810, 1456, 1365, 1053, 704 cm^{-1}; MS (EI): m/z (%) 178 (M^+, 33), 147 (51), 105 (35), 91 (100), 83 (43), 57 (26); HRMS calcd for $C_{12}H_{18}O$ (M^+), 178.13577, Found: 178.13577.

(*E*)-3-(3-Methylenecyclopent-1-enyl)prop-2-en-1-ol (10f)

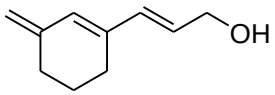


$C_9H_{12}O$ (136,19)

Yellowish solid; R_f 0.40 (pentane/Et_2O 1:1); ^1H NMR (500 MHz, $CDCl_3$): δ 6.53 (d, *J* = 15.9 Hz, 1H), 6.12 (s, 1H), 5.86 (dt, *J* = 15.8, 5.8 Hz, 1H), 4.89 (s, 1H), 4.77 (s, 1H), 4.25 (d, *J* =

5.8 Hz, 2H), 2.64-2.55 (m, 4H), 1.61 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7, 148.8, 133.6, 130.8, 127.8, 103.3, 63.5, 30.5, 29.2 IR (KBr): 3889, 2922, 2859, 1643, 1613, 1452, 1095, 1007, 965, 856 cm^{-1}; MS (EI): m/z (%) 136 (M^+, 100), 117 (45), 91 (81), 83 (77), 79 (61), 77 (42); HRMS calcd for $C_9H_{12}O$ (M^+), 136.08882, Found: 136.08882.

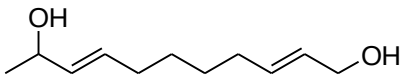
(*E*)-3-(3-Methylenecyclohex-1-enyl)prop-2-en-1-ol (10g)



$C_{10}H_{14}O$ (150,22)

Colorless oil; R_f 0.49 (pentane/Et_2O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.28 (d, J = 15.9 Hz, 1H), 6.15 (s, 1H), 5.86 (dt, J = 15.6, 5.1 Hz, 1H), 4.86 (s, 1H), 4.83 (s, 1H), 4.22 (d, J = 5.8 Hz, 2H), 2.35-2.30 (m, 2H), 2.23 (t, J = 5.8 Hz, 2H), 1.78-1.71 (m, 2H), 1.69 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 137.5, 134.2, 130.7, 127.3, 111.9, 63.8, 30.5, 24.5, 22.5; IR ($CHCl_3$): 3381, 3330, 2932, 2863, 1436, 1006, 966, 889 cm^{-1}; MS (EI): m/z (%) 150 (M^+, 100), 117 (53), 106 (47), 91 (98), 79 (55); HRMS calcd for $C_{10}H_{14}O$ (M^+), 150.10447, Found: 150.10447.

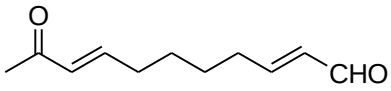
(±)-(2*E*,8*E*)-Undeca-2,8-diene-1,10-diol (pre-12)



$C_{11}H_{20}O_2$ (184,28)

Colorless oil; R_f 0.35 (Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75-5.55 (m, 3H), 5.49 (ddt, *J* = 15.3, 6.4, 1.2 Hz, 1H), 4.28-4.21 (m, 1H), 4.07 (d, *J* = 4.9 Hz, 2H), 2.07-1.97 (m, 4H), 1.62 (bs, 1H), 1.55 (bs, 1H), 1.42-1.33 (m, 4H), 1.24 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 133.1, 130.7, 129.0, 68.9, 63.7, 32.0, 31.9, 28.6, 28.5, 23.4; IR (capillary): 3348, 2970, 2926, 2855, 1453, 1063, 1005, 971 cm^{-1}; MS (CI): m/z (%) 167 ($[M\text{-}H_2O]^+$, 4), 150 ($[M\text{-}2H_2O]^+$, 12), 149 ($[M\text{-}2H_2O\text{-}H]^+$, 100).

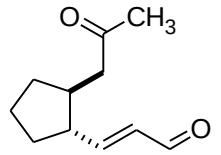
(2*E*,8*E*)-10-Oxoundeca-2,8-dienal (12)



$C_{11}H_{16}O_2$ (180,24)

Colorless oil; R_f 0.19 (pentane/Et_2O 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.50 (d, *J* = 7.9 Hz, 1H), 6.81 (dt, *J* = 15.6, 6.7 Hz, 1H), 6.77 (dt, *J* = 15.9, 7.0 Hz, 1H), 6.11 (ddt, *J* = 15.6, 7.9, 1.5 Hz, 1H), 6.07 (dt, *J* = 15.9, 1.5 Hz), 2.49-2.32 (m, 2H), 2.29-2.22 (m, 2H), 2.24 (s, 3H), 1.60-1.50 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 193.9, 157.9, 147.4, 133.2, 131.5, 32.4, 32.0, 27.5, 27.3, 26.9; IR (capillary): 2932, 1688, 1630, 1362, 1255, 1160, 979 cm^{-1}; MS (EI): m/z (%) 181 ($[M+H]^+$, 1), 165 ($[M-CH_3]^+$, 2), 151 ($[M-CHO]^+$, 32), 137 ($[M-C_2H_3O]^+$, 68); HRMS calcd for $C_{10}H_{13}O_2$ ($[M-CH_3]^+$), 165.09155, Found: 165.09155.

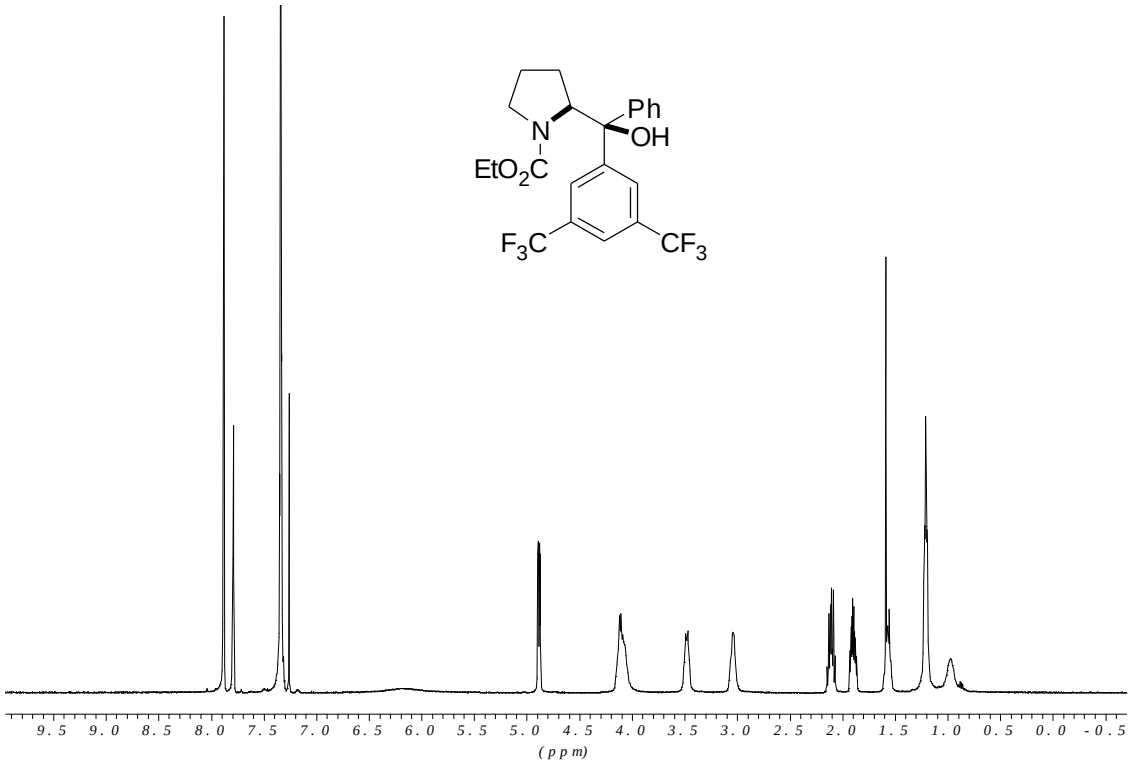
(*E*)-3-((1*R*,2*S*)-2-(2-Oxopropyl)cyclopentyl)acrylaldehyde (13)

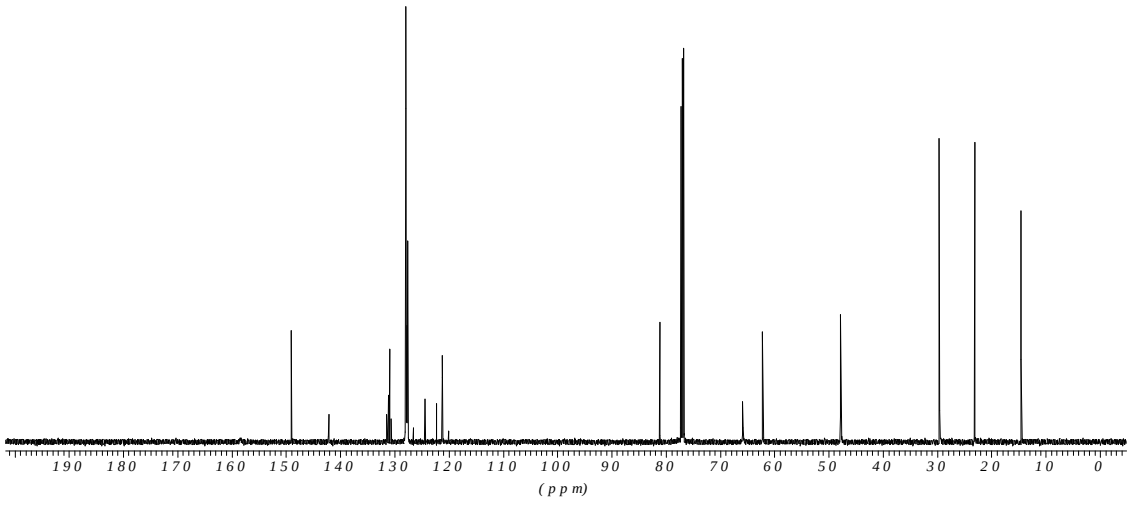


$C_{11}H_{16}O_2$ (180,24)

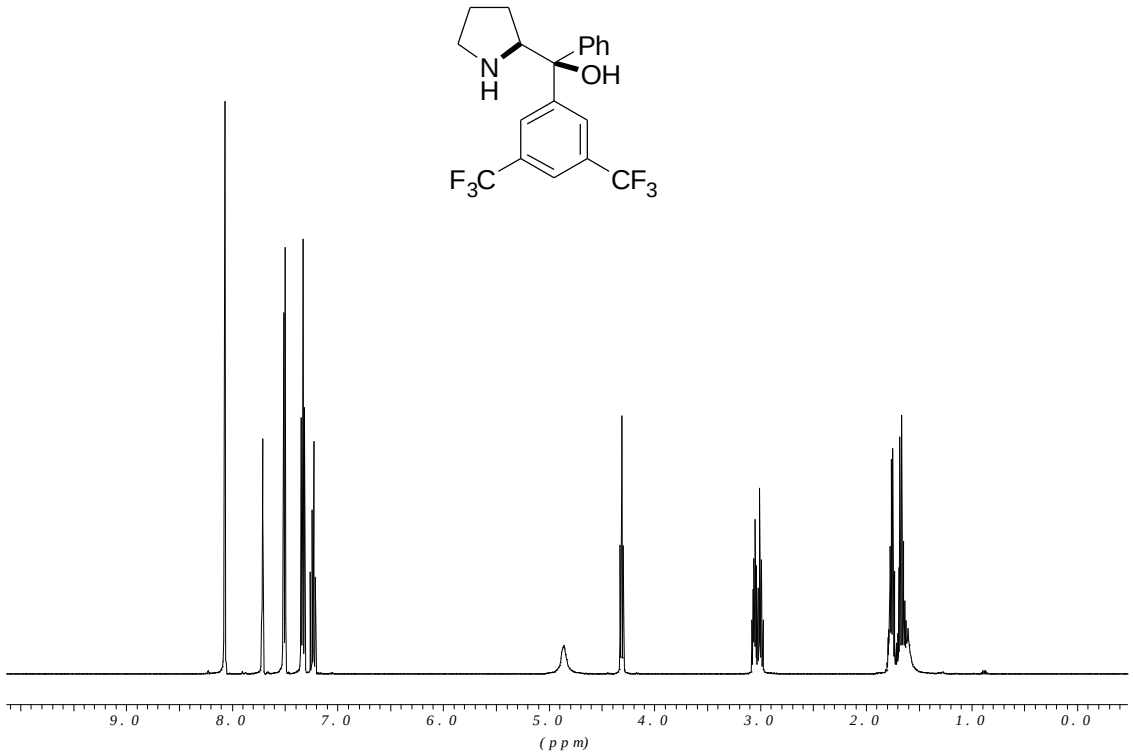
Colorless oil; R_f 0.27 (pentane/Et_2O 1:1); α_D +19.2 (*c* 0.60, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.50 (d, *J* = 7.6 Hz, 1H), 6.72 (dd, *J* = 15.6, 8.9 Hz, 1H), 6.07 (ddd, *J* = 15.6, 7.9, 0.6 Hz, 1H), 2.55 (dd, *J* = 16.8, 8.9 Hz, 1H), 2.36 (dd, *J* = 16.8, 8.9 Hz, 1H), 2.33-2.25 (m, 1H), 2.20-2.11 (m, 1H), 2.12 (s, 3H), 2.11-2.03 (m, 1H), 1.99-1.91 (m, 1H), 1.80-1.65 (m, 2H), 1.59-1.50 (m, 1H), 1.28-1.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.0, 193.9, 161.4, 132.4, 49.8, 47.8, 41.5, 32.4, 32.3, 30.4, 23.8; IR ($CHCl_3$): 2954, 2872, 1688 cm^{-1}; MS (EI): m/z (%) 136 ($[M-CH_3-CHO]^+$, 100).

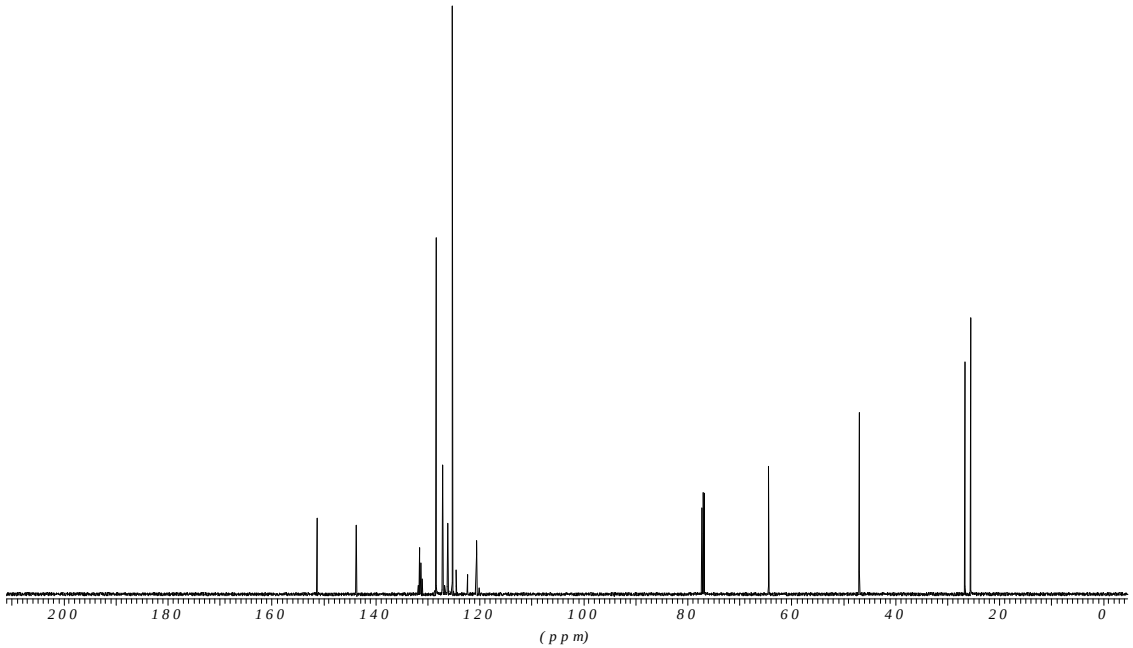
Catalyst precursor



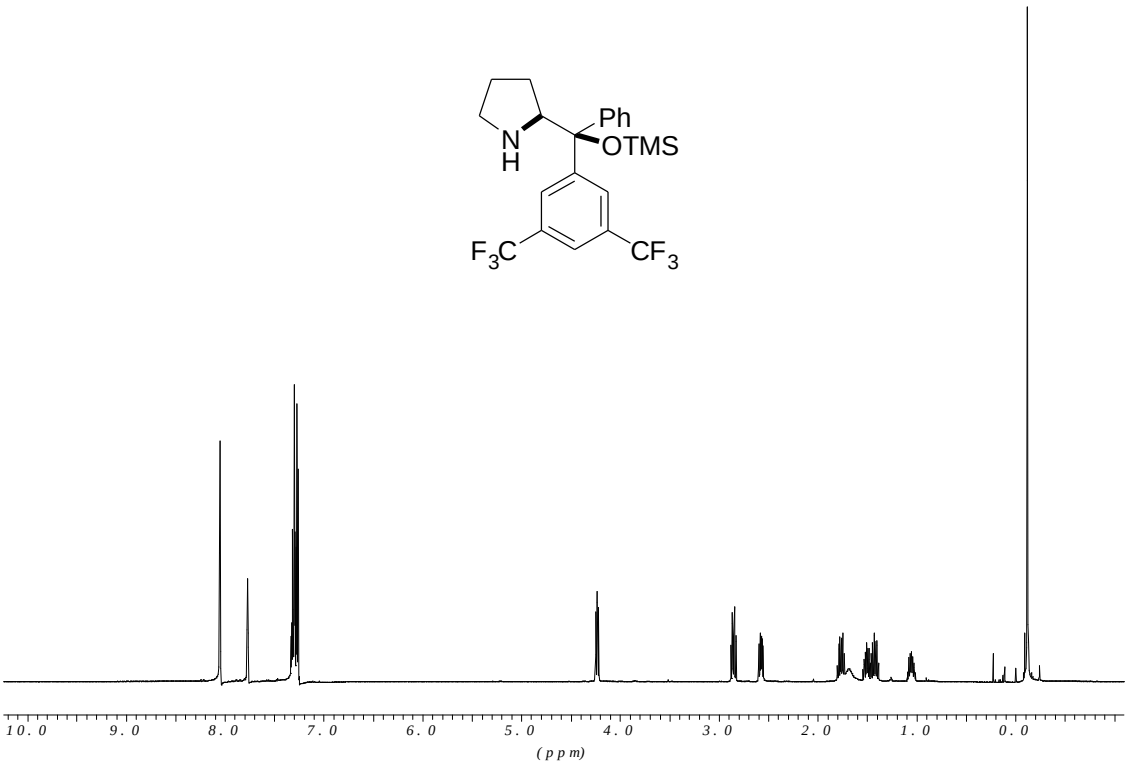


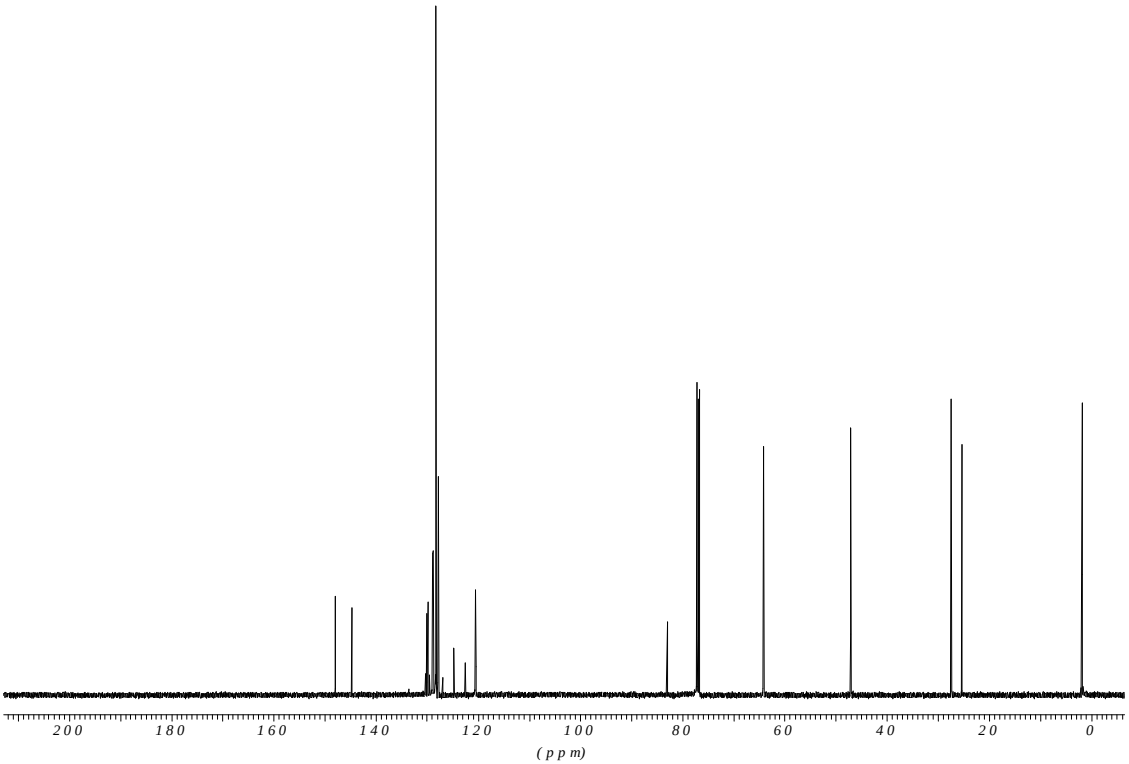
pre-1d


Ph
OH
N
H
F3C
CF3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

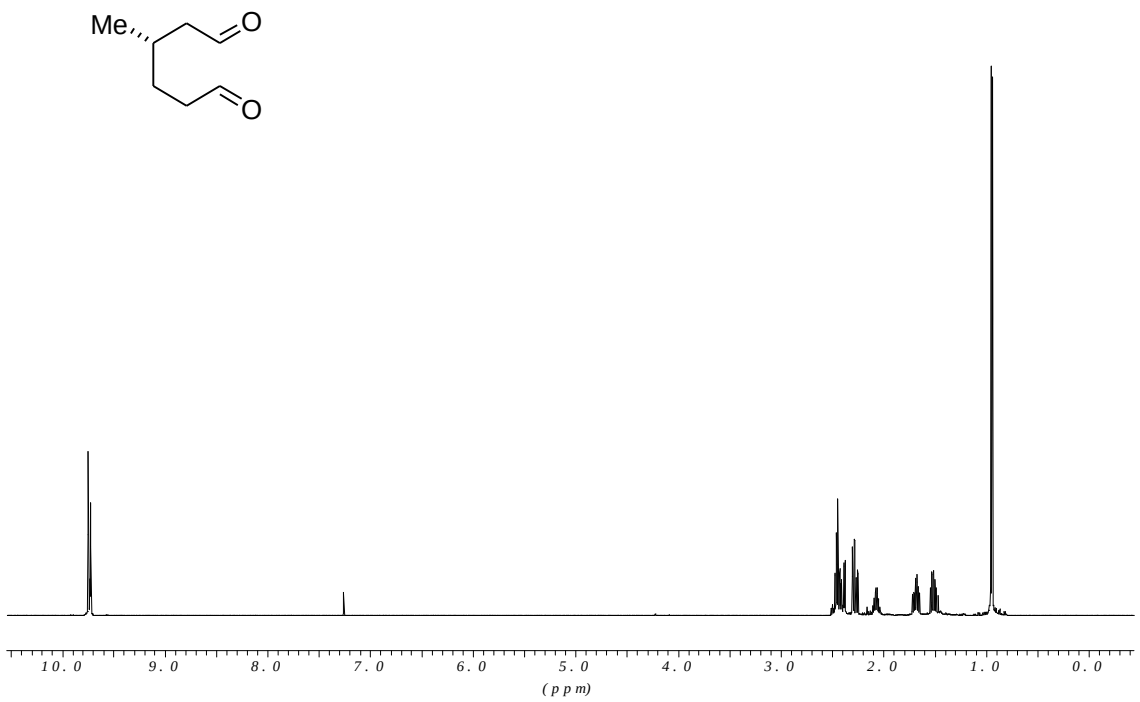

200
180
160
140
120
100
80
60
40
20
0
(ppm)

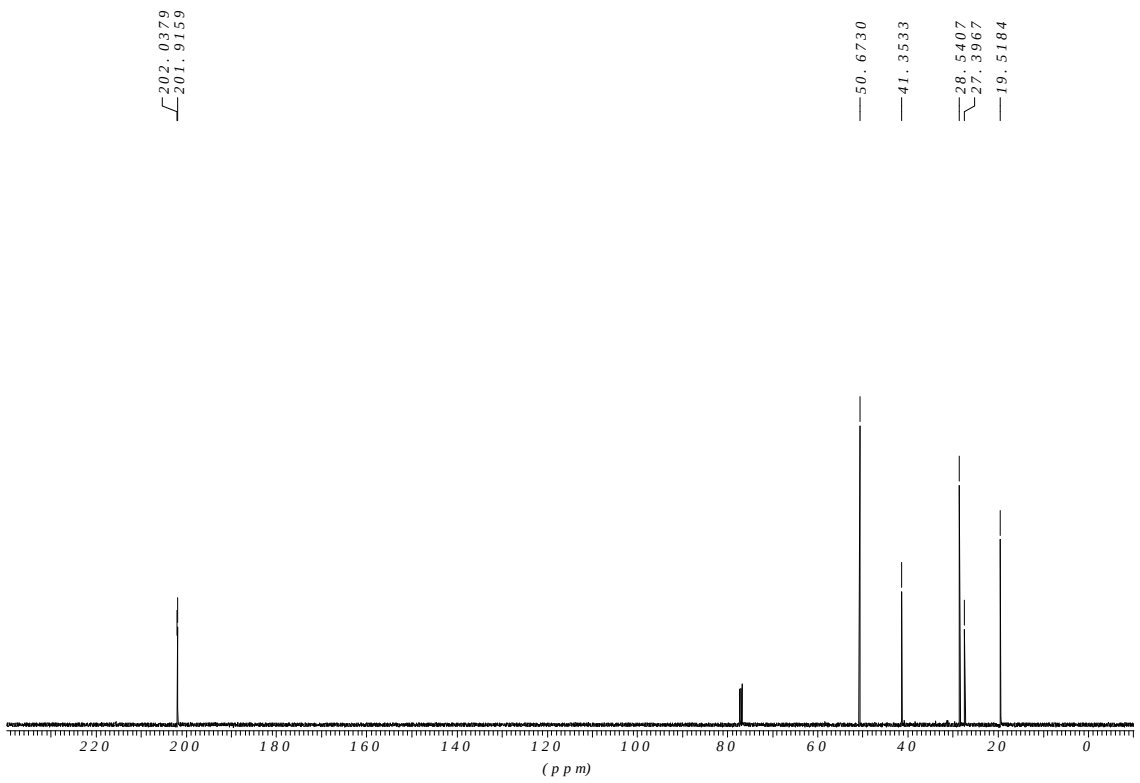
1d


Ph
OTMS
N
H
F3C
CF3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

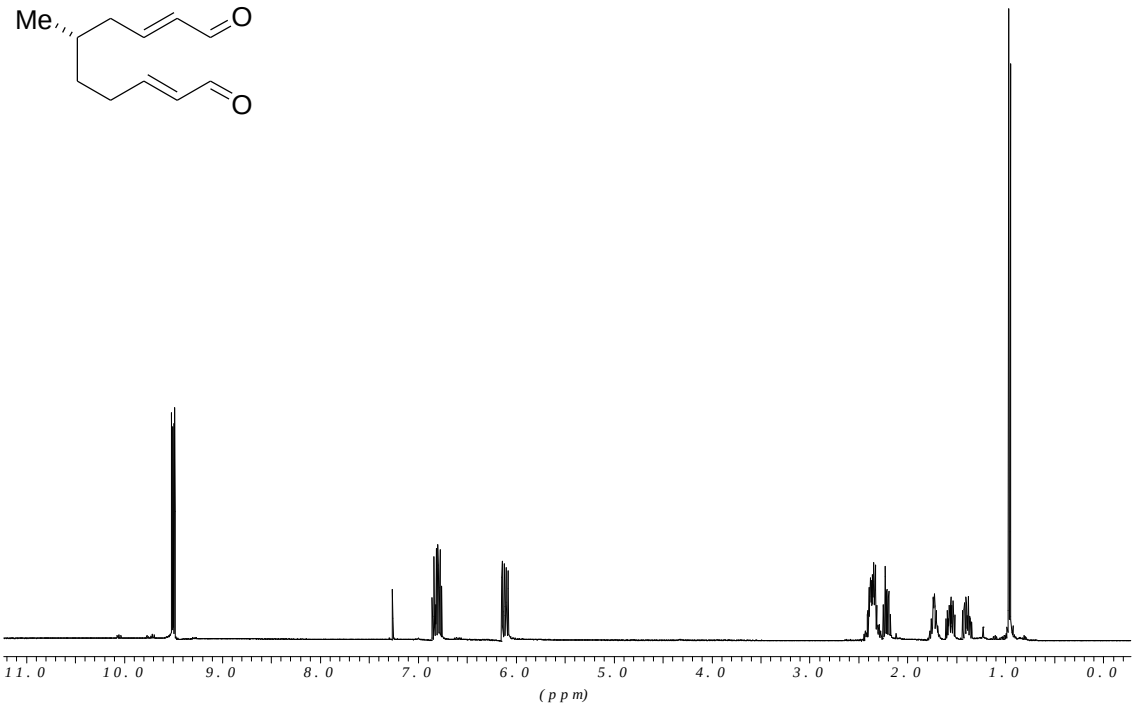

200
180
160
140
120
100
80
60
40
20
0
(ppm)

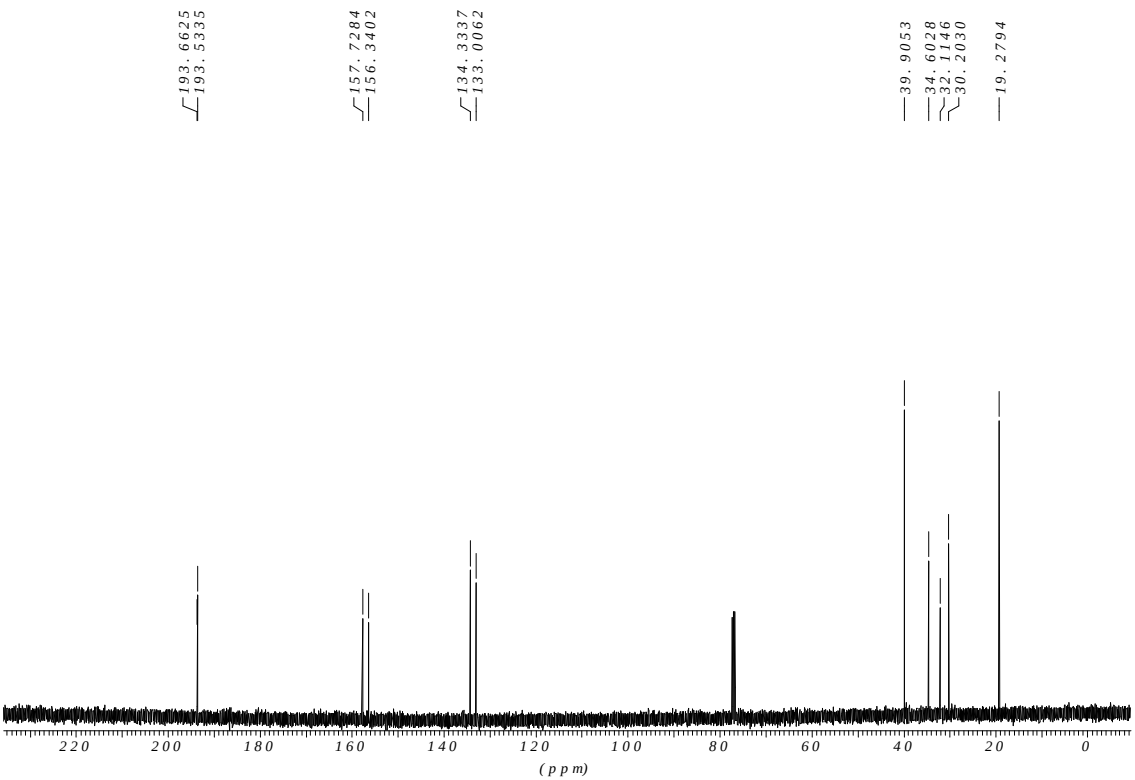
pre-5d


Me
O
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

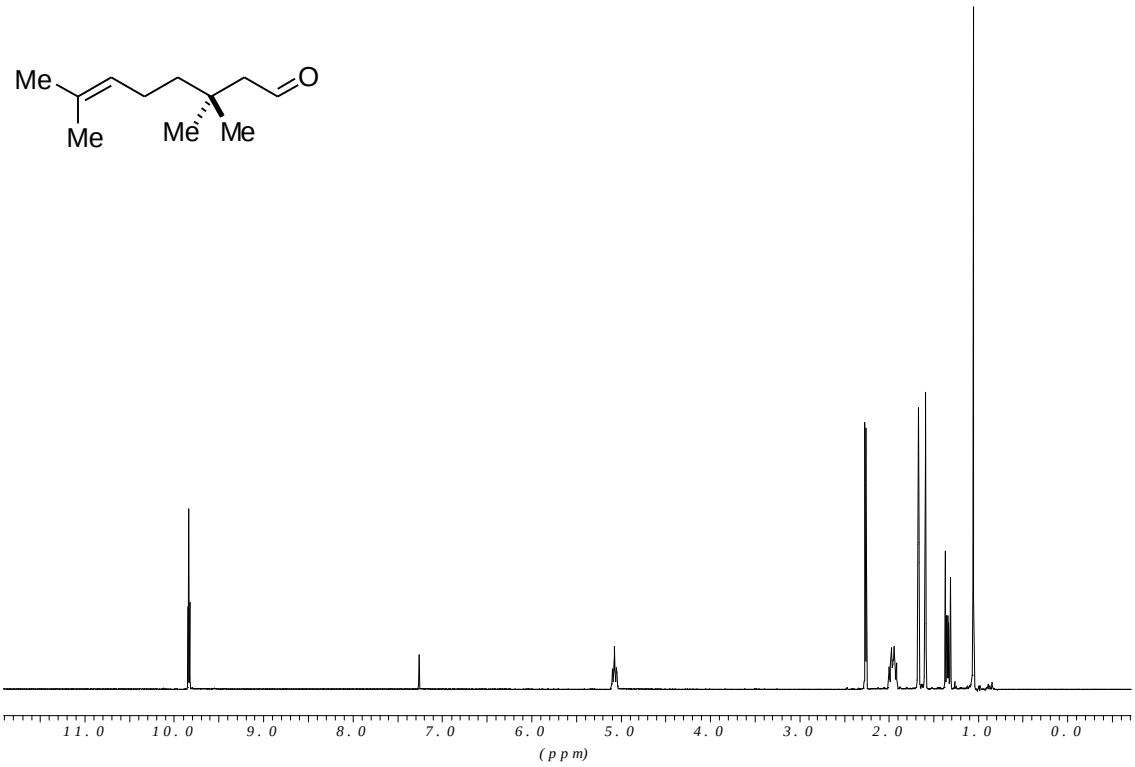

202.0379
201.9159
50.6730
41.3533
28.5407
27.3967
19.5184
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

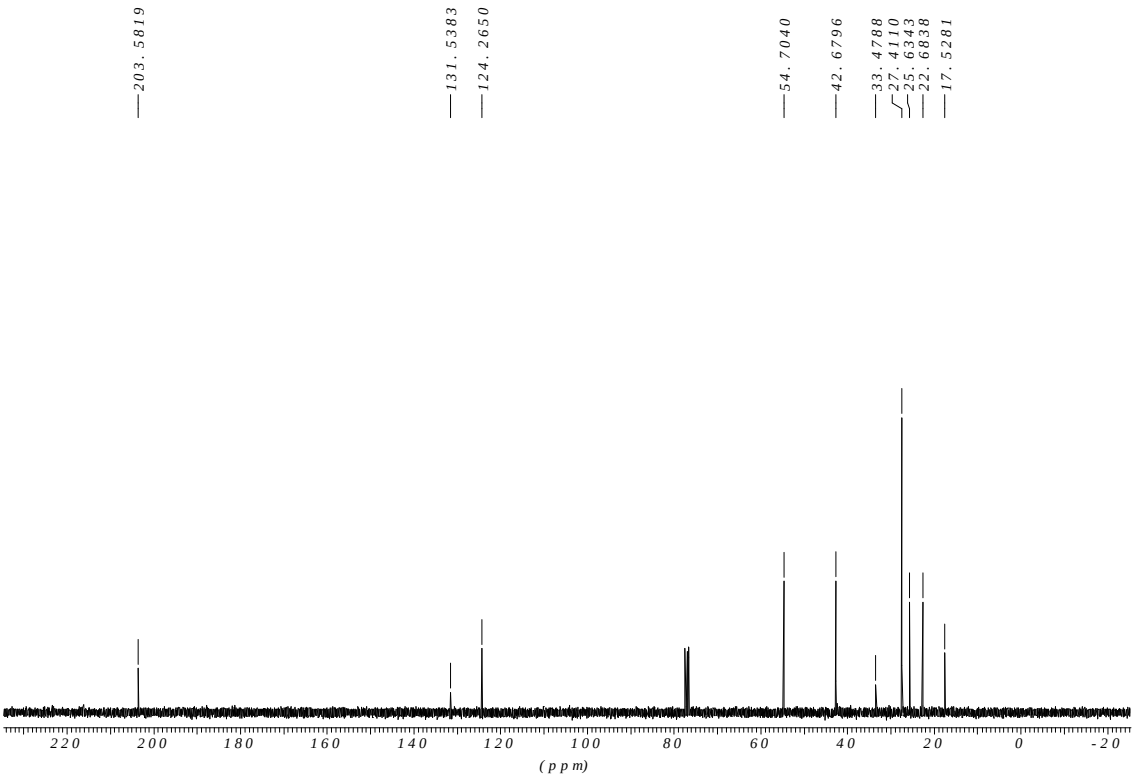
5d


Me
O
O
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

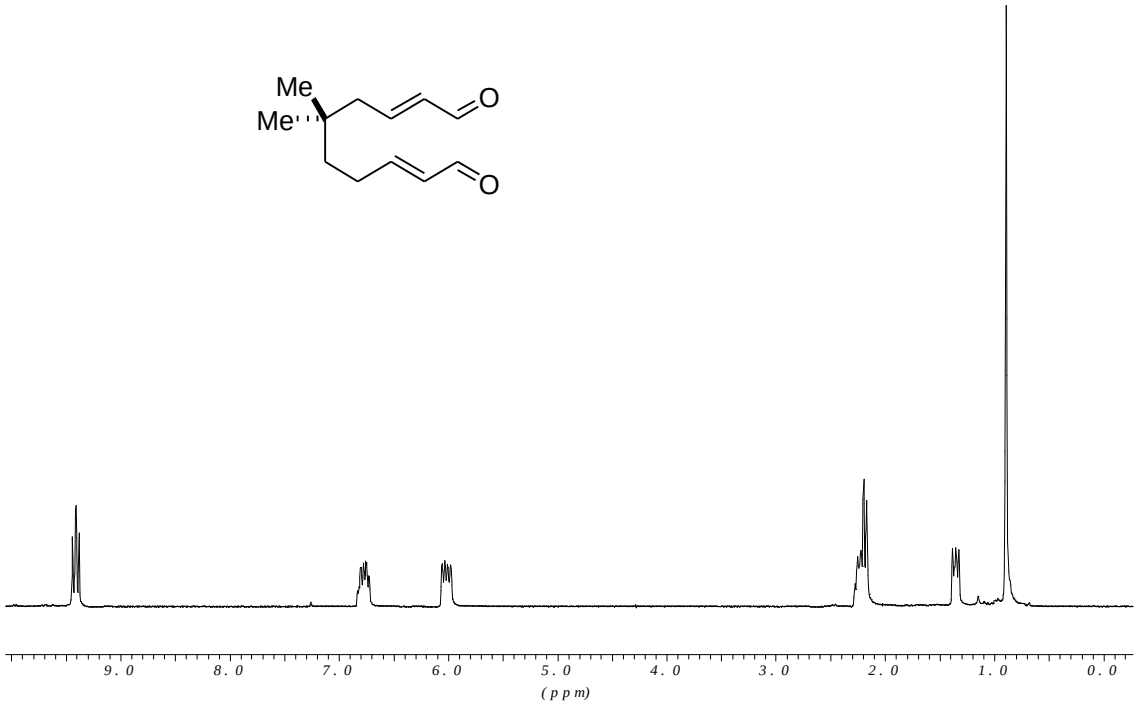

193.6625
193.5335
157.7284
156.3402
134.3337
133.0062
39.9053
34.6028
32.1146
30.2030
19.2794
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

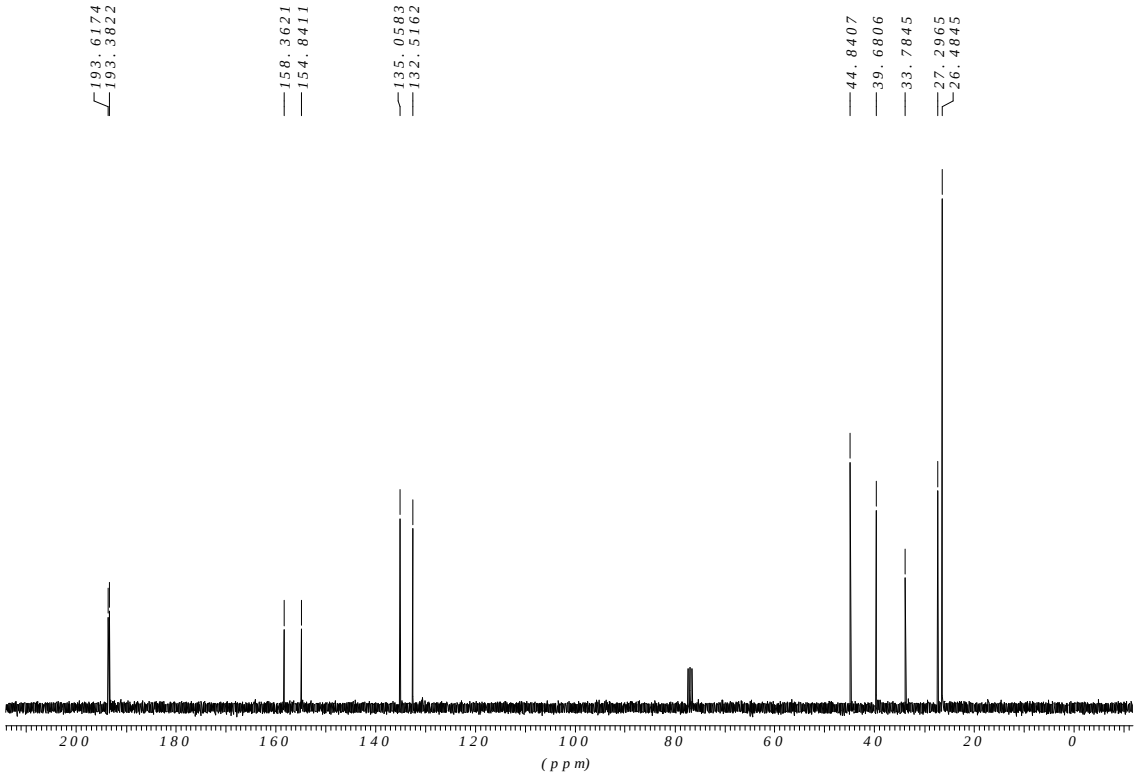
3,3,7-Trimethyloct-6-enal



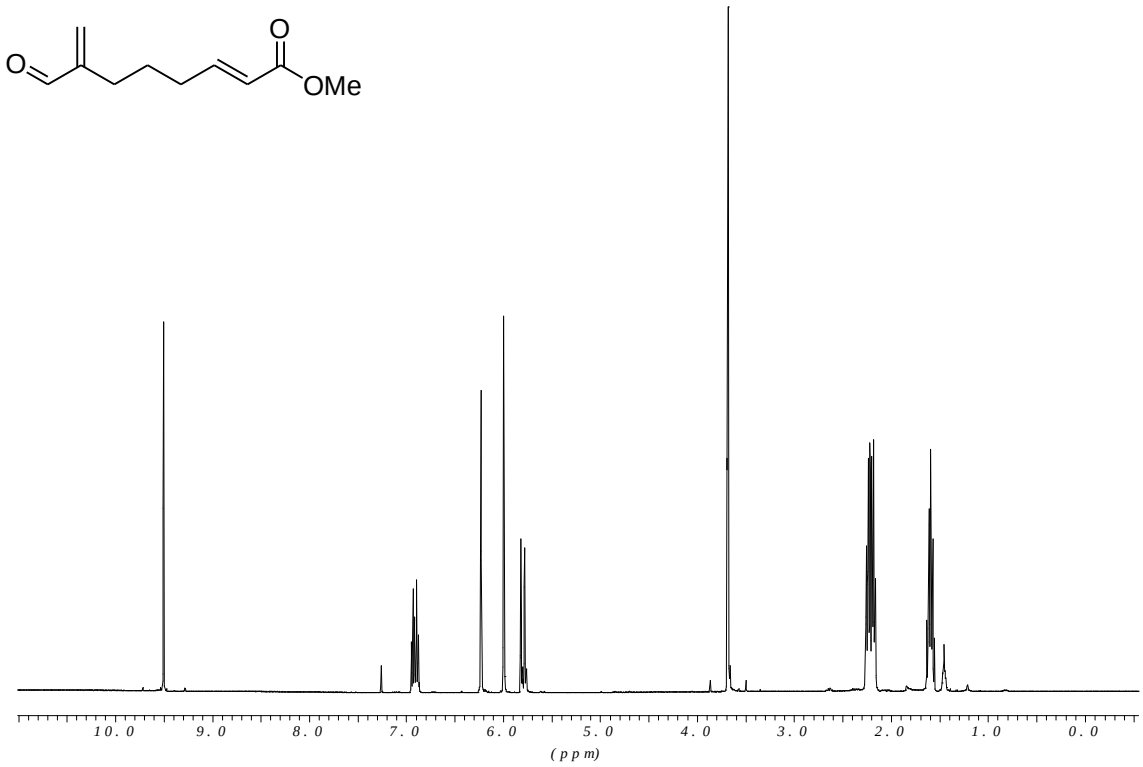


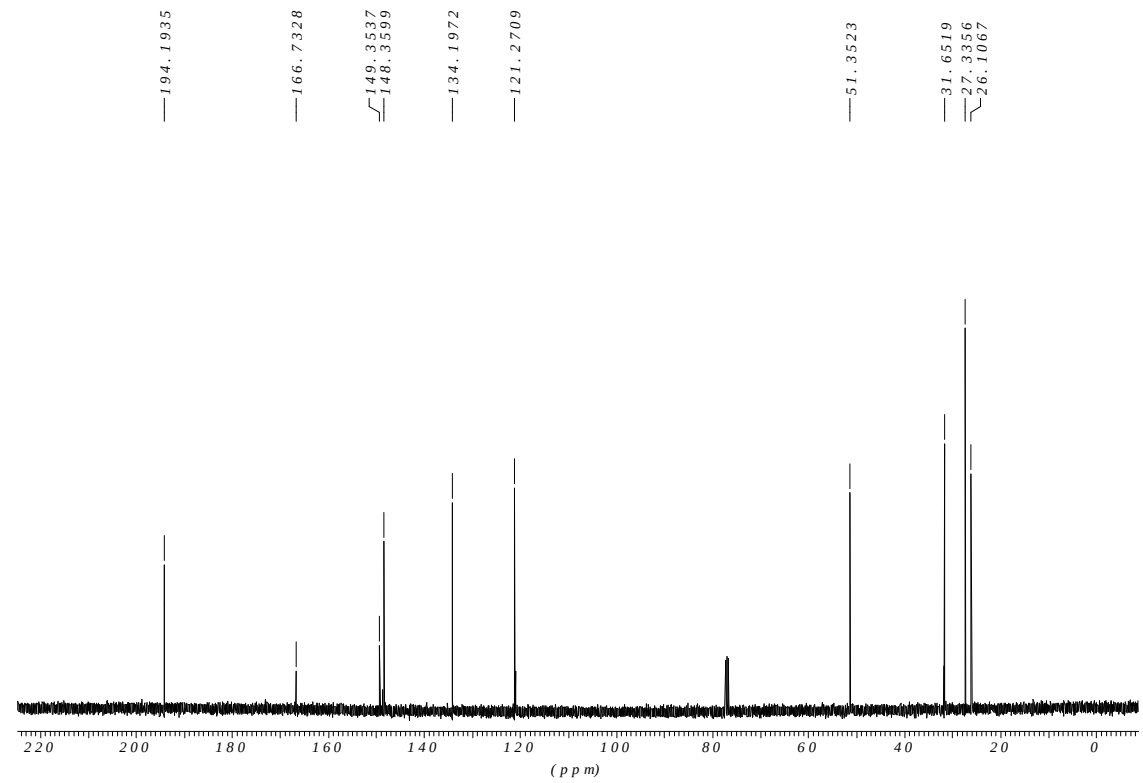
5e


Me
Me
O
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

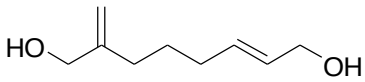

193.6174
193.3822
158.3621
154.8411
135.0583
132.5162
44.8407
39.6806
33.7845
27.2965
26.4845
200
180
160
140
120
100
80
60
40
20
0
(ppm)

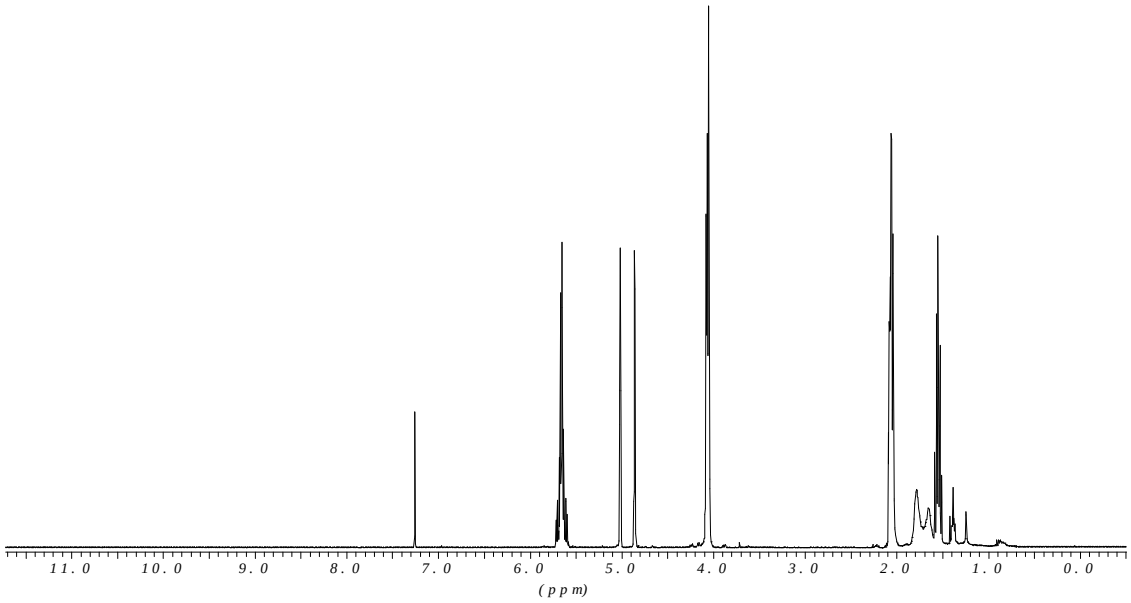
(*E*)-Methyl 7-formylocta-2,7-dienoate

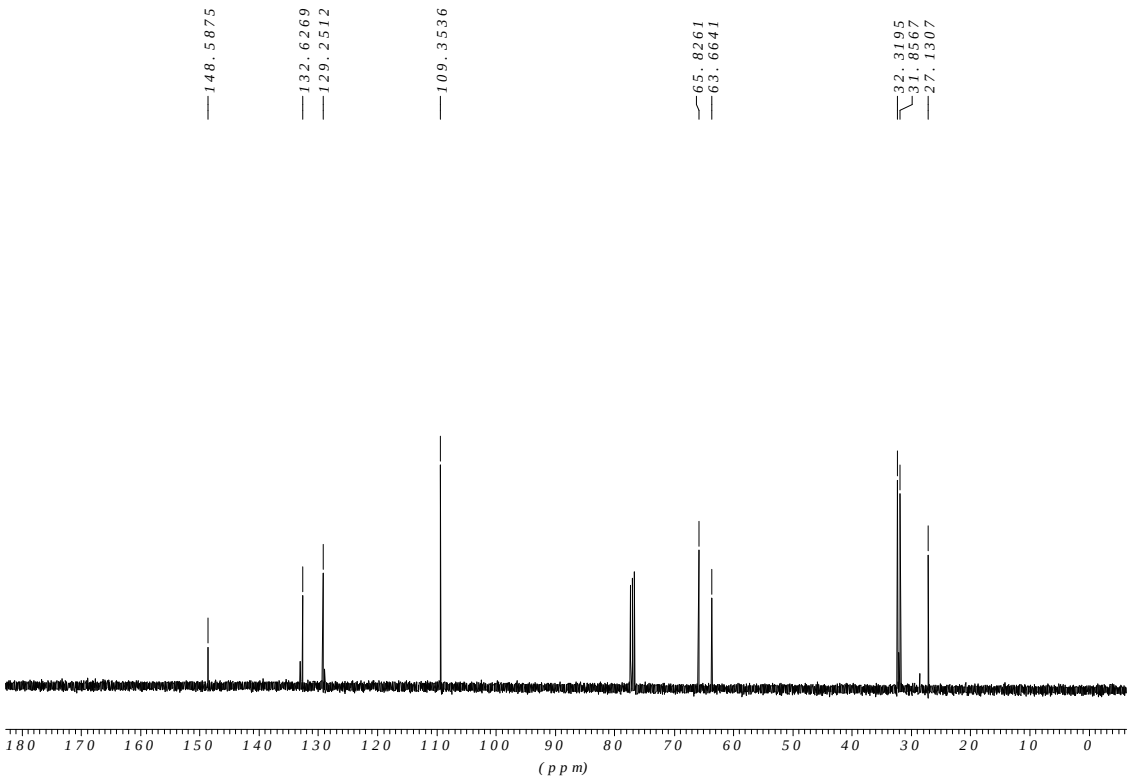




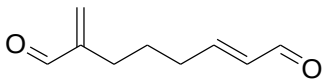
pre-5f

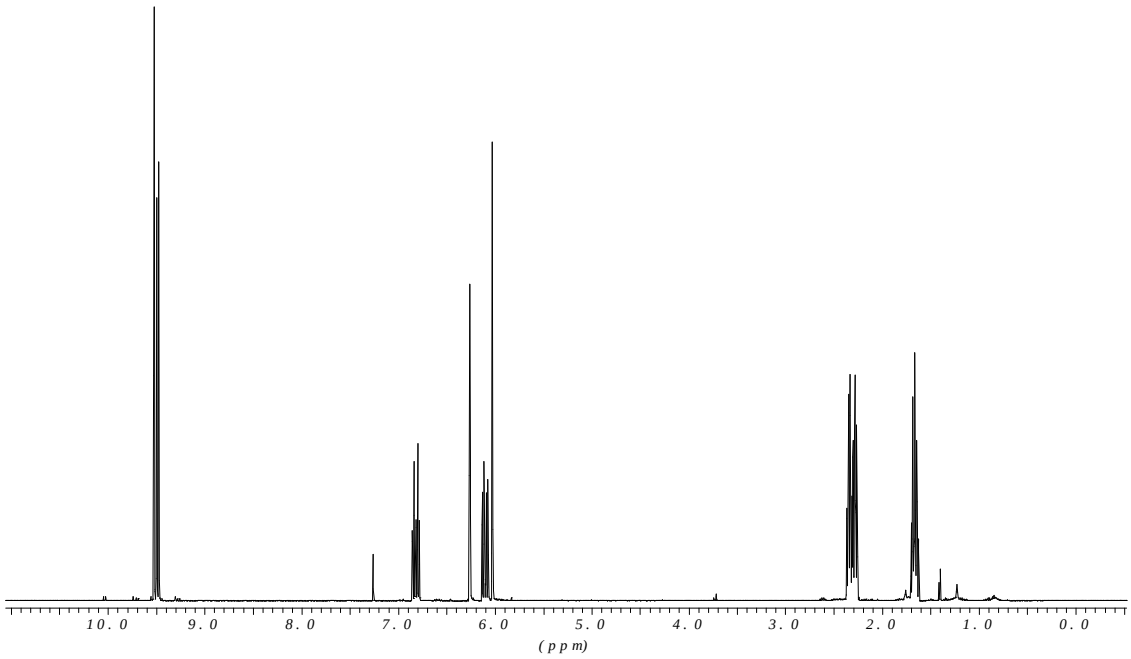

HO
OH

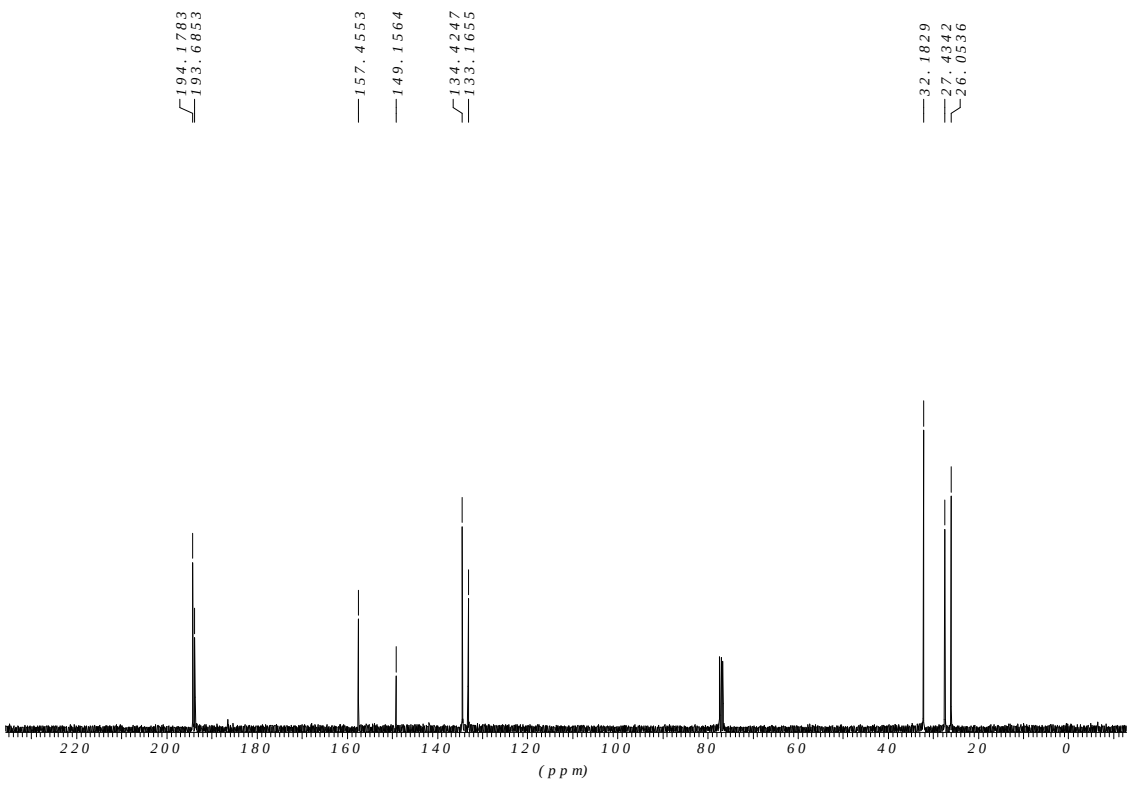

11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


148.5875
132.6269
129.2512
109.3536
65.8261
63.6641
32.3195
31.8567
27.1307
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

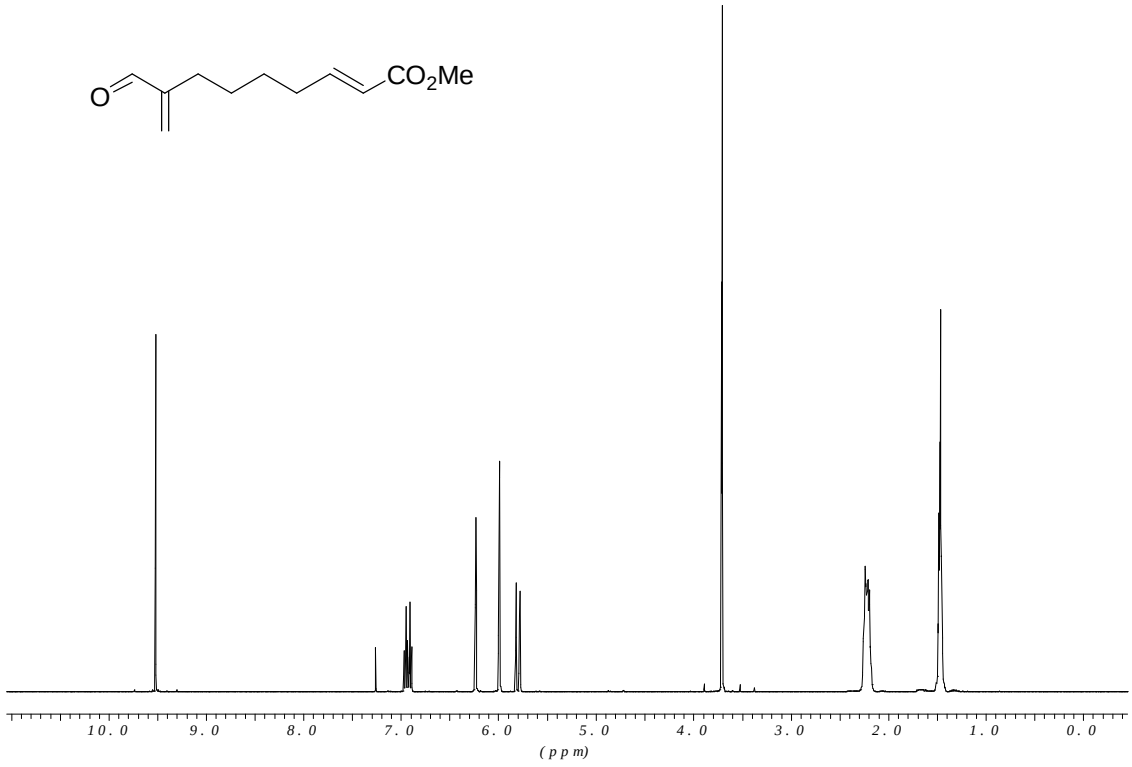
5f

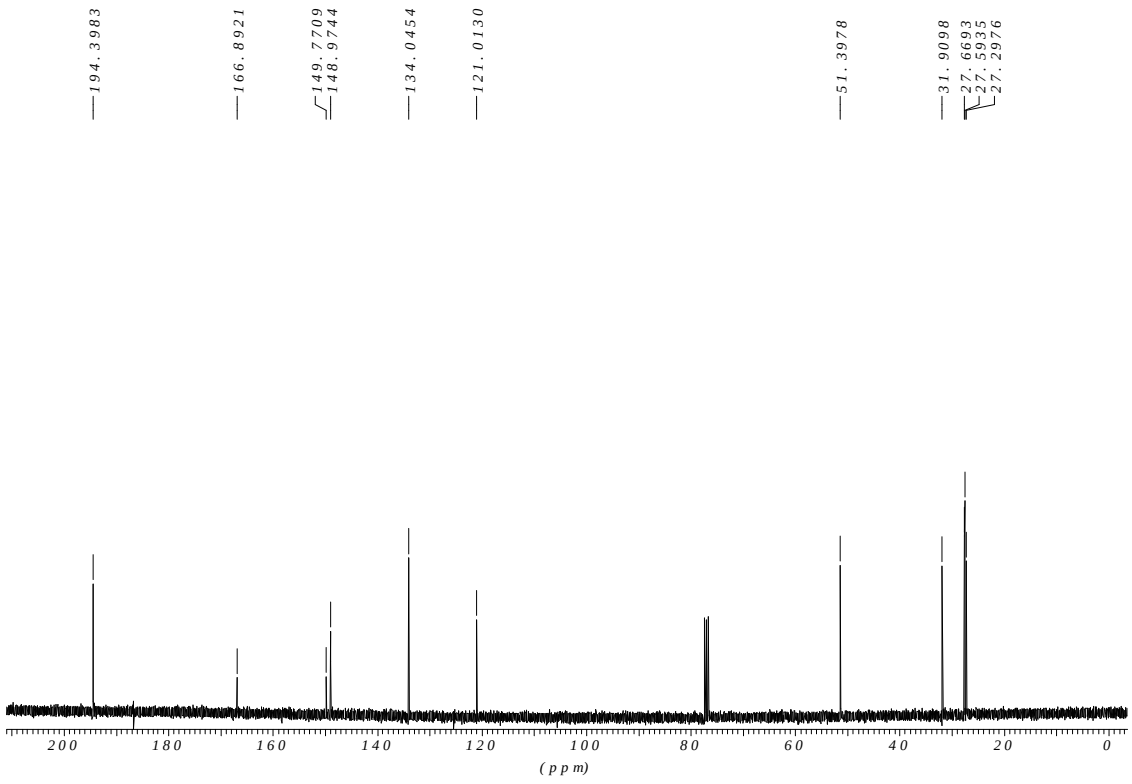

O
O


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

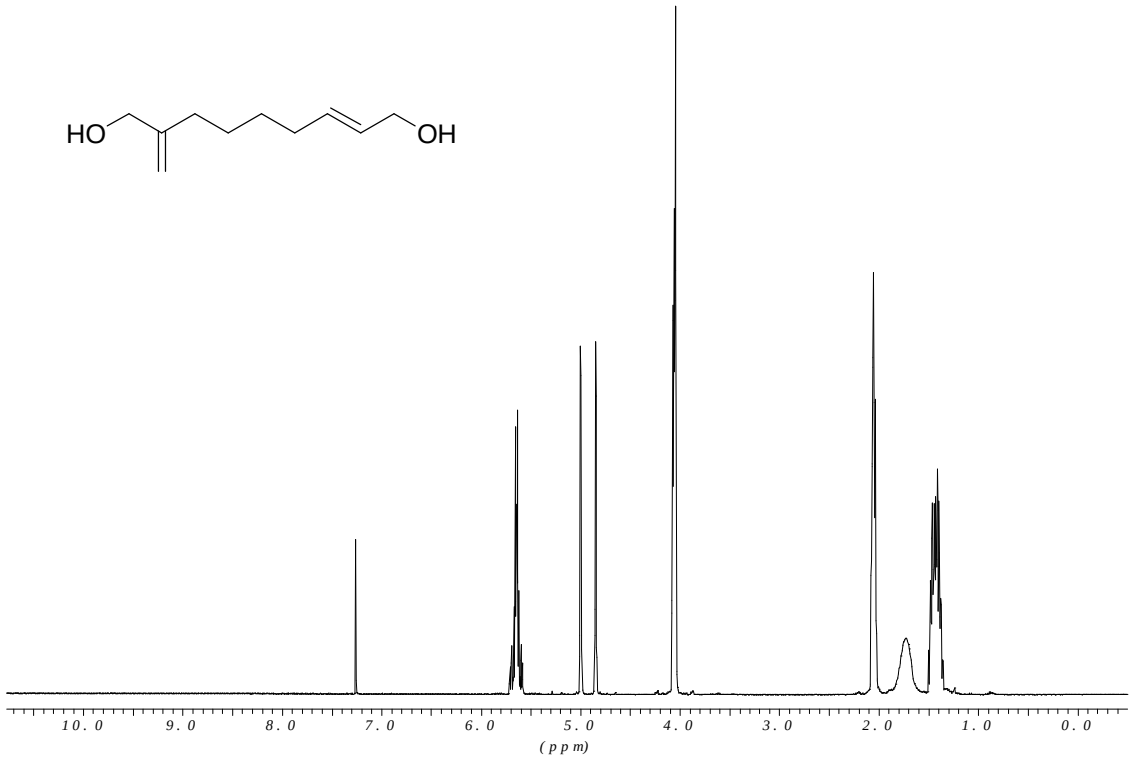

194.1783
193.6853
157.4553
149.1564
134.4247
133.1655
32.1829
27.4342
26.0536
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

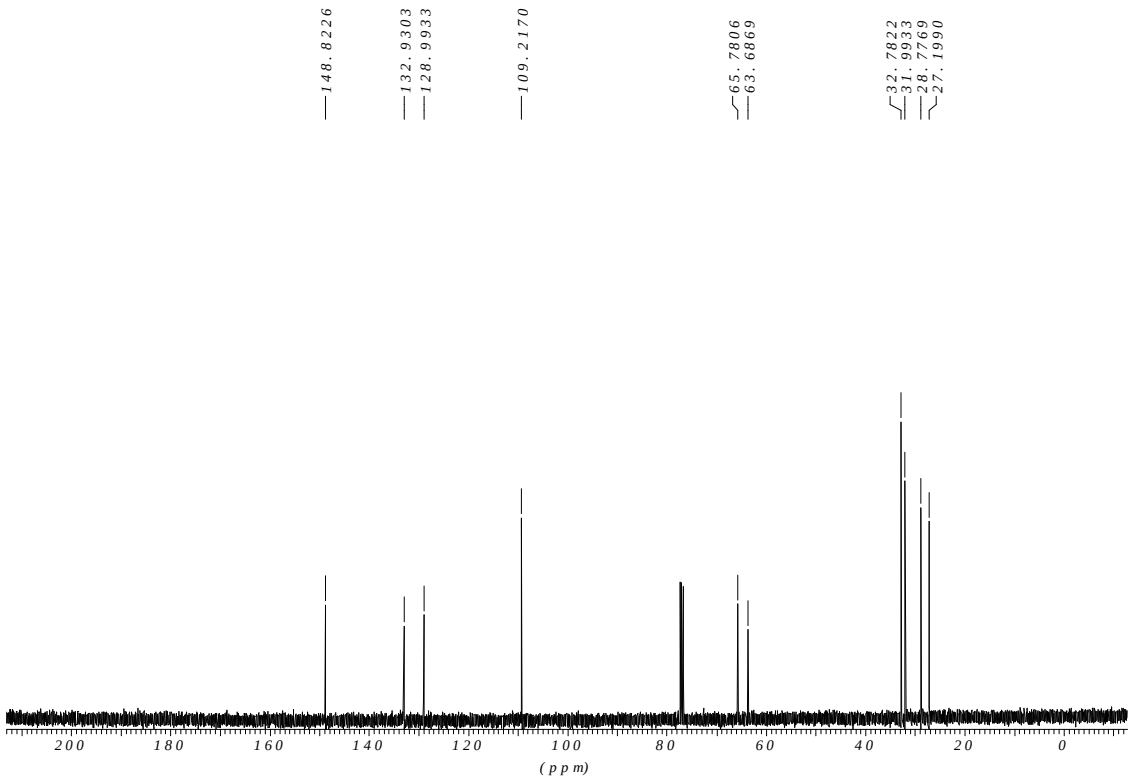
(*E*)-Methyl 8-formylnona-2,8-dienoate



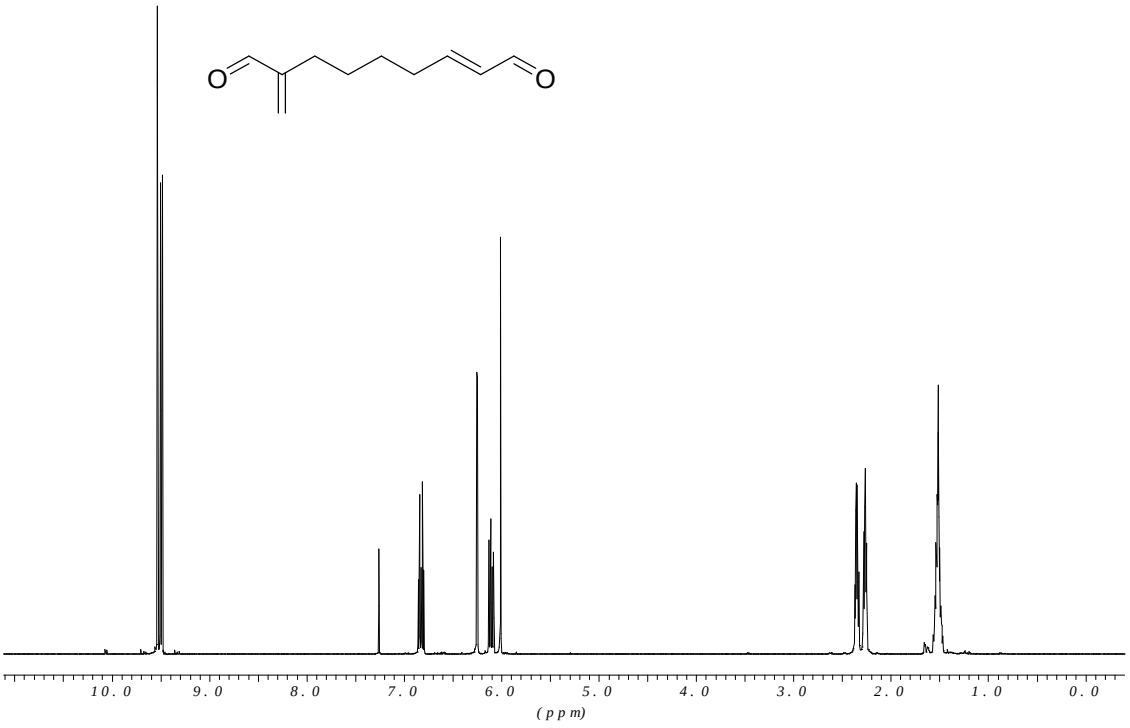


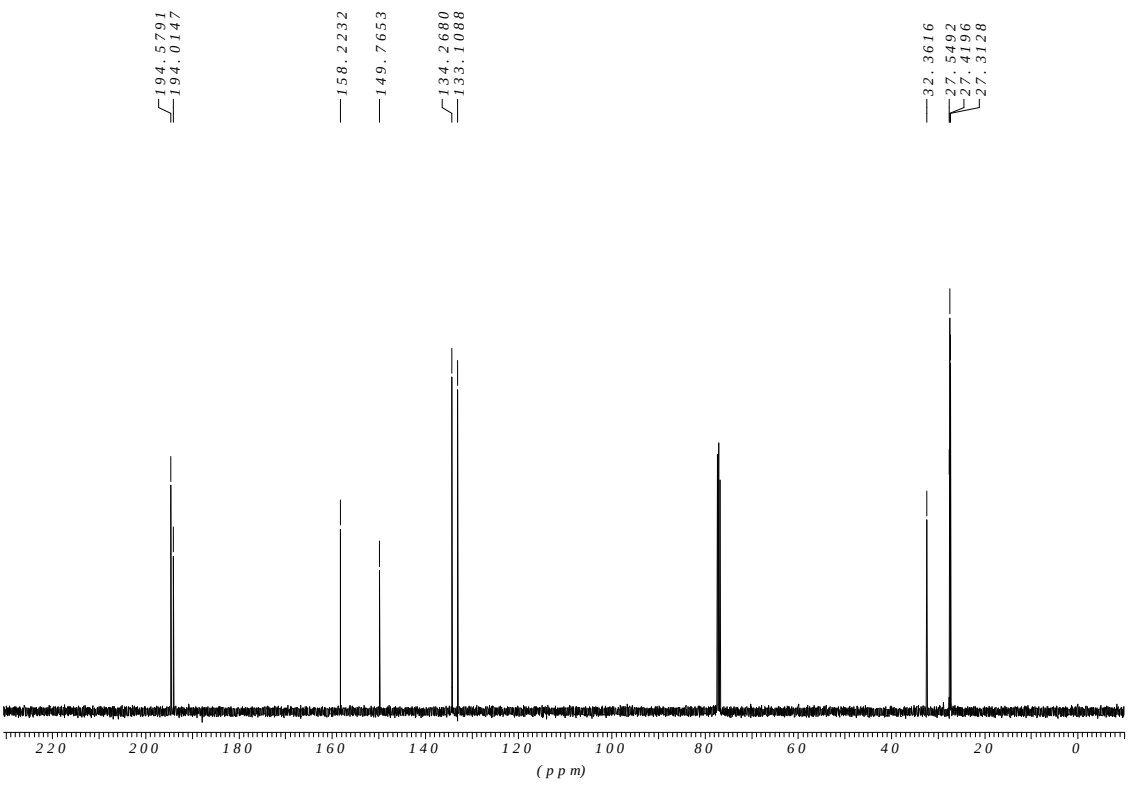
pre-5g


HO
OH
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

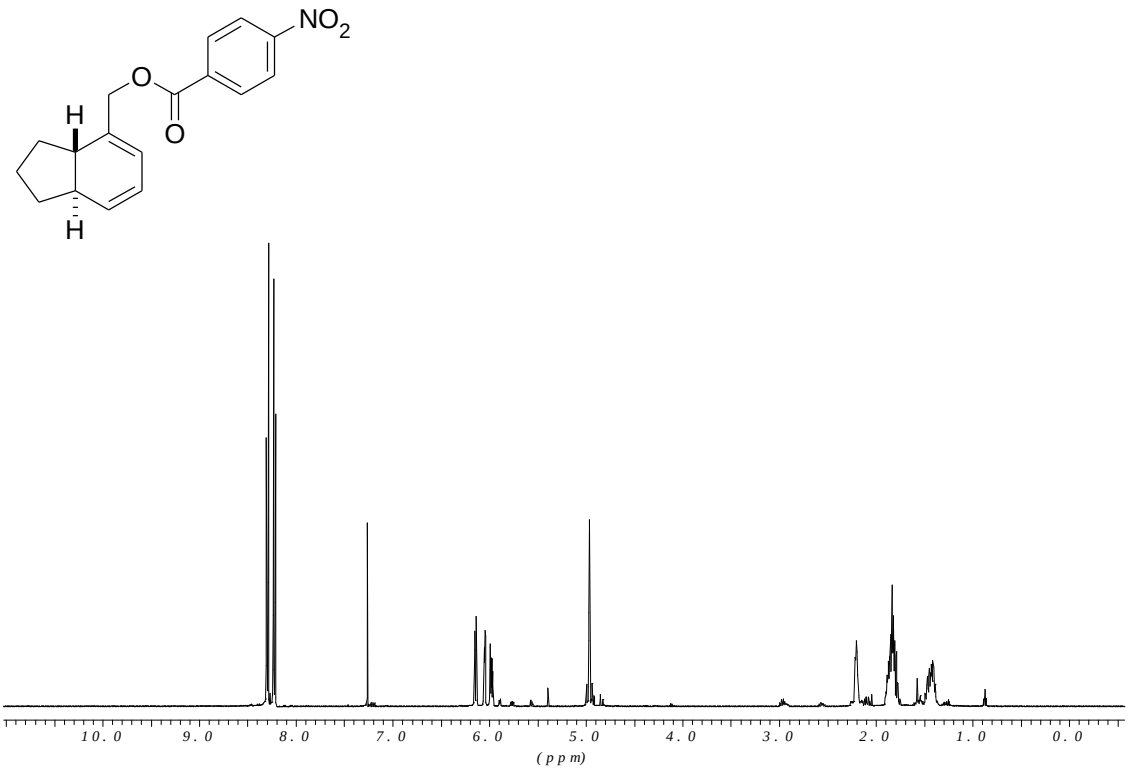

148.8226
132.9303
128.9933
109.2170
65.7806
63.6869
32.7822
31.9933
28.7769
27.1990
200
180
160
140
120
100
80
60
40
20
0
(ppm)

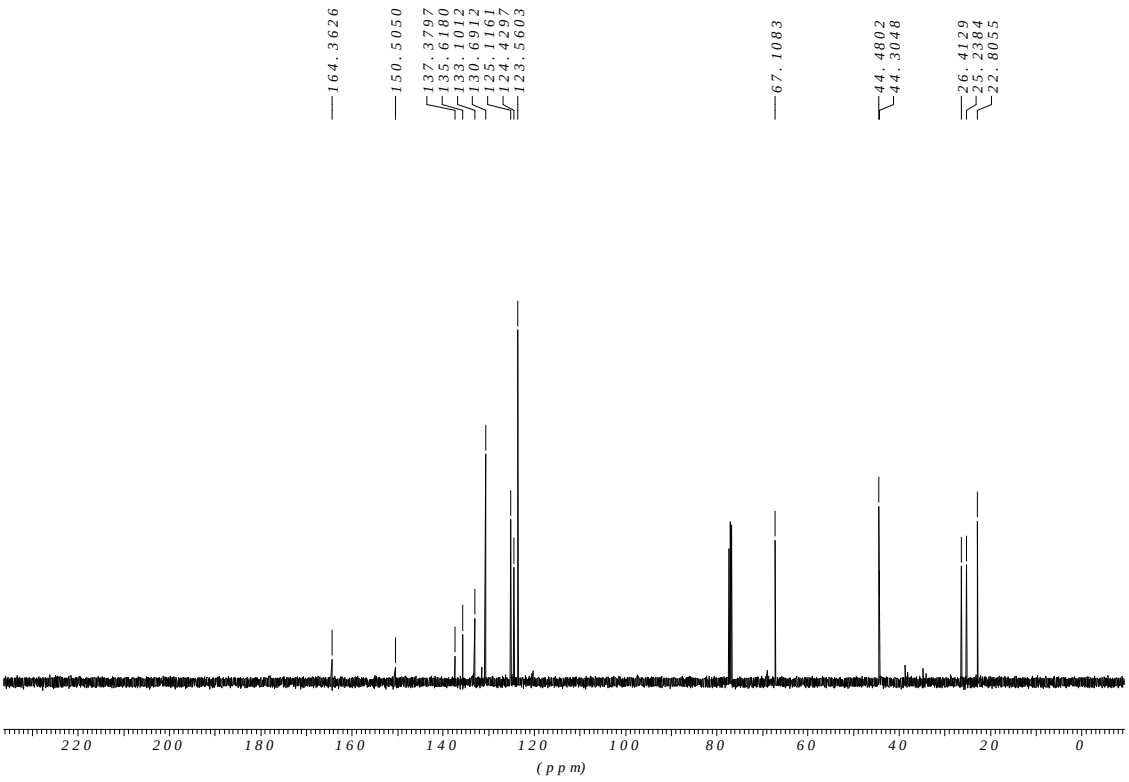
5g


O
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

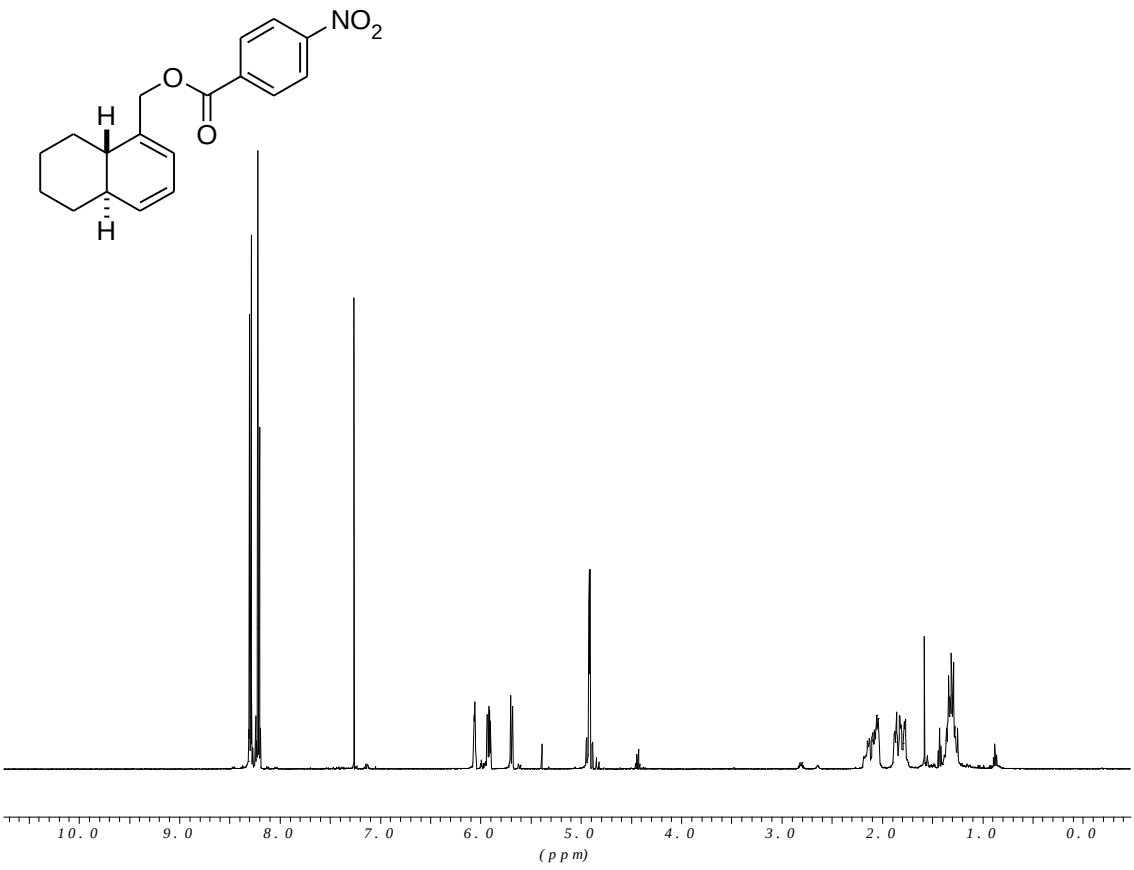

194.5791
194.0147
158.2232
149.7653
134.2680
133.1088
32.3616
27.5492
27.4196
27.3128
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

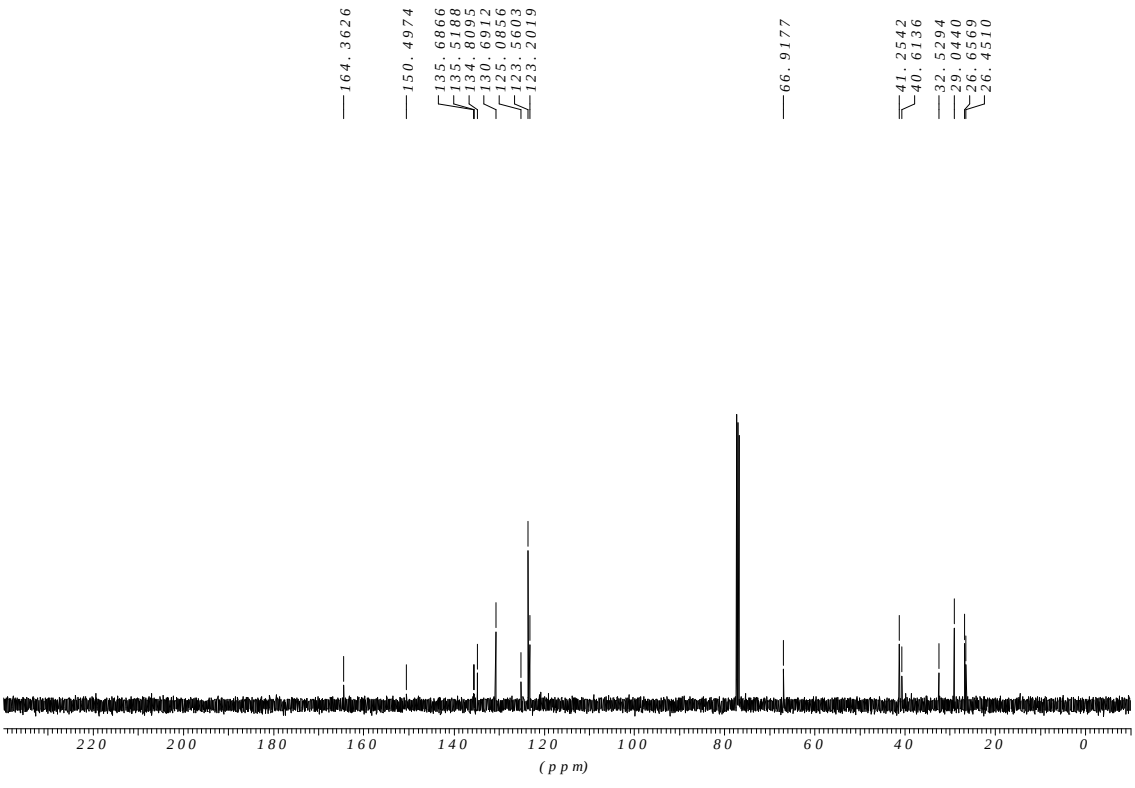
9a


NO2
O
O
H
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

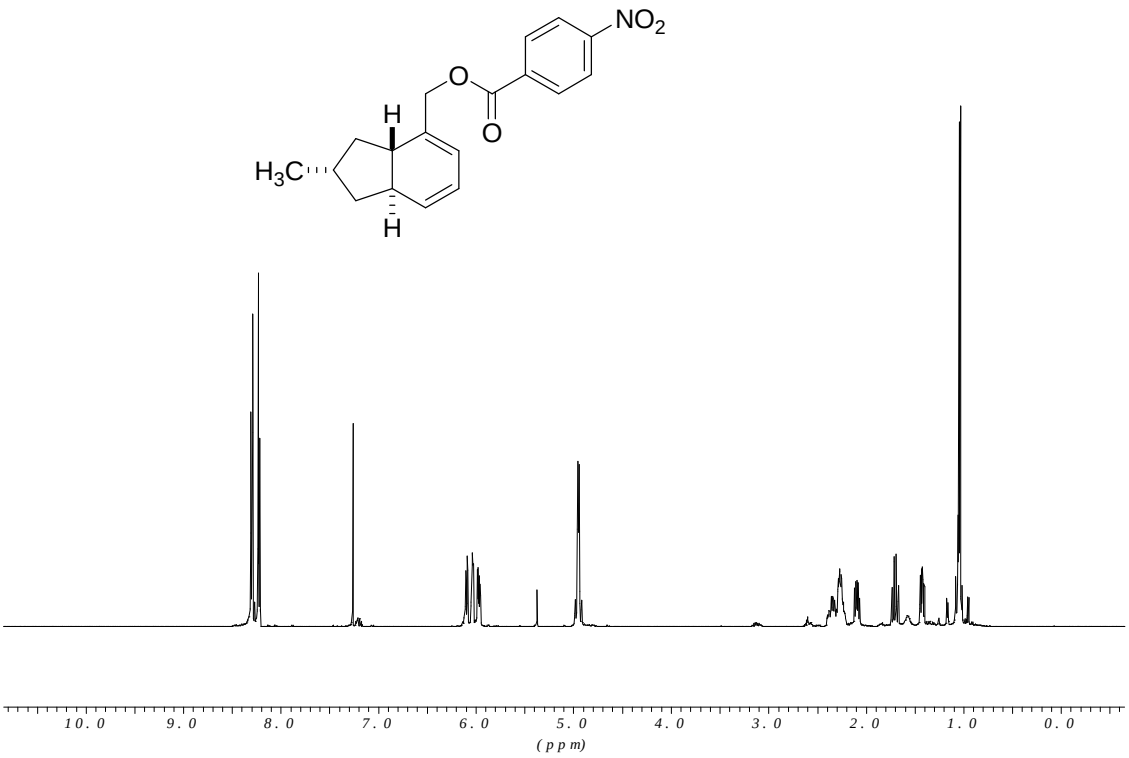

164.3626
150.5050
137.3797
135.6180
133.1012
130.6912
125.1161
124.4297
123.5603
67.1083
44.4802
44.3048
26.4129
25.2384
22.8055
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

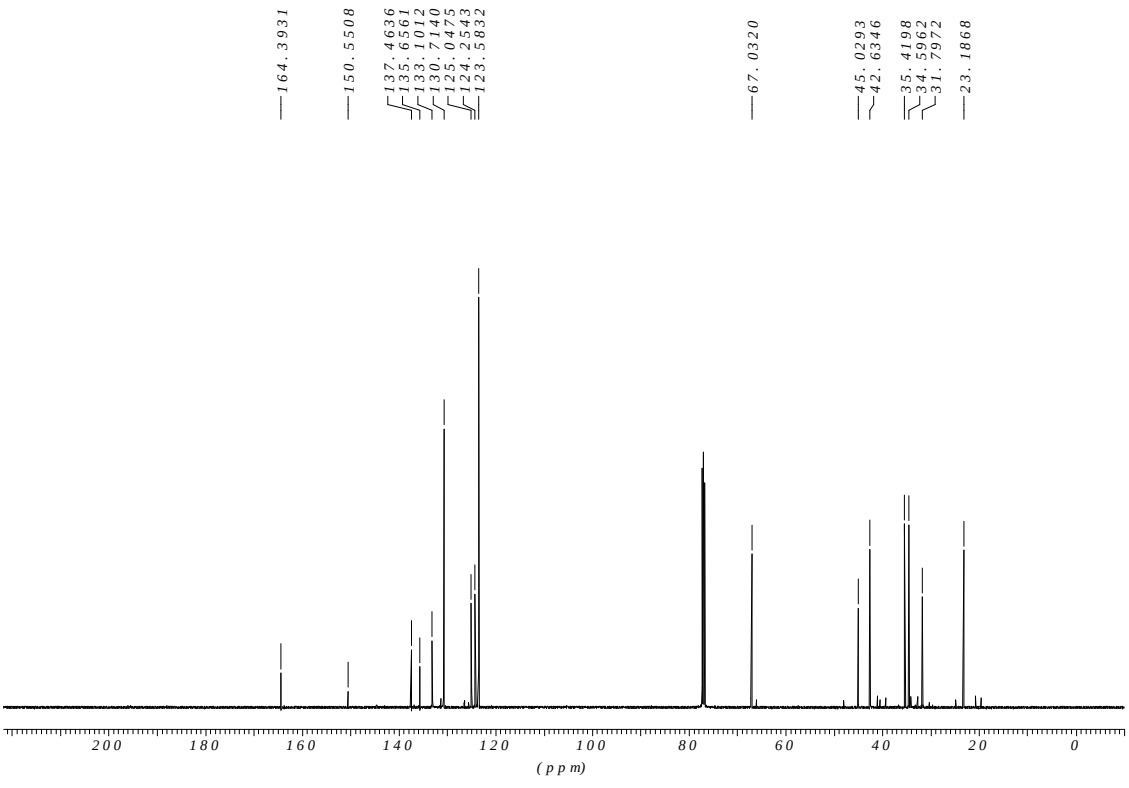
9b


NO2
O
O
H
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

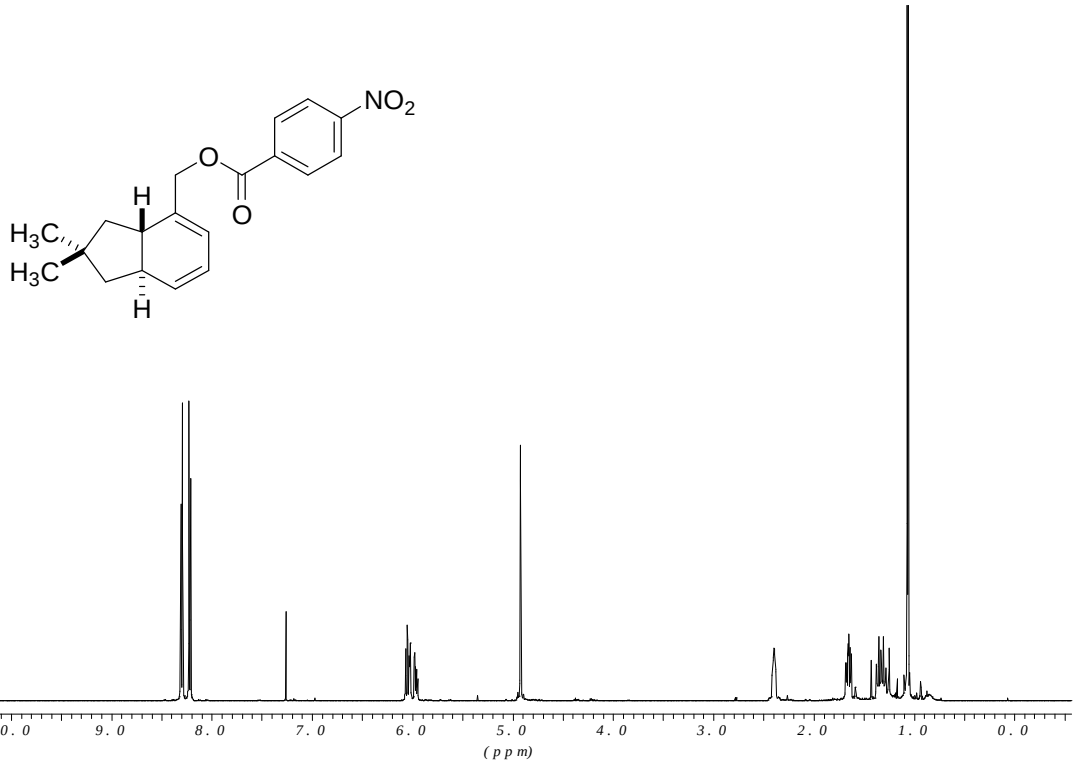

164.3626
150.4974
135.6866
135.5188
134.8095
130.6912
125.0856
123.5603
123.2019
66.9177
41.2542
40.6136
32.5294
29.0440
26.6569
26.4510
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

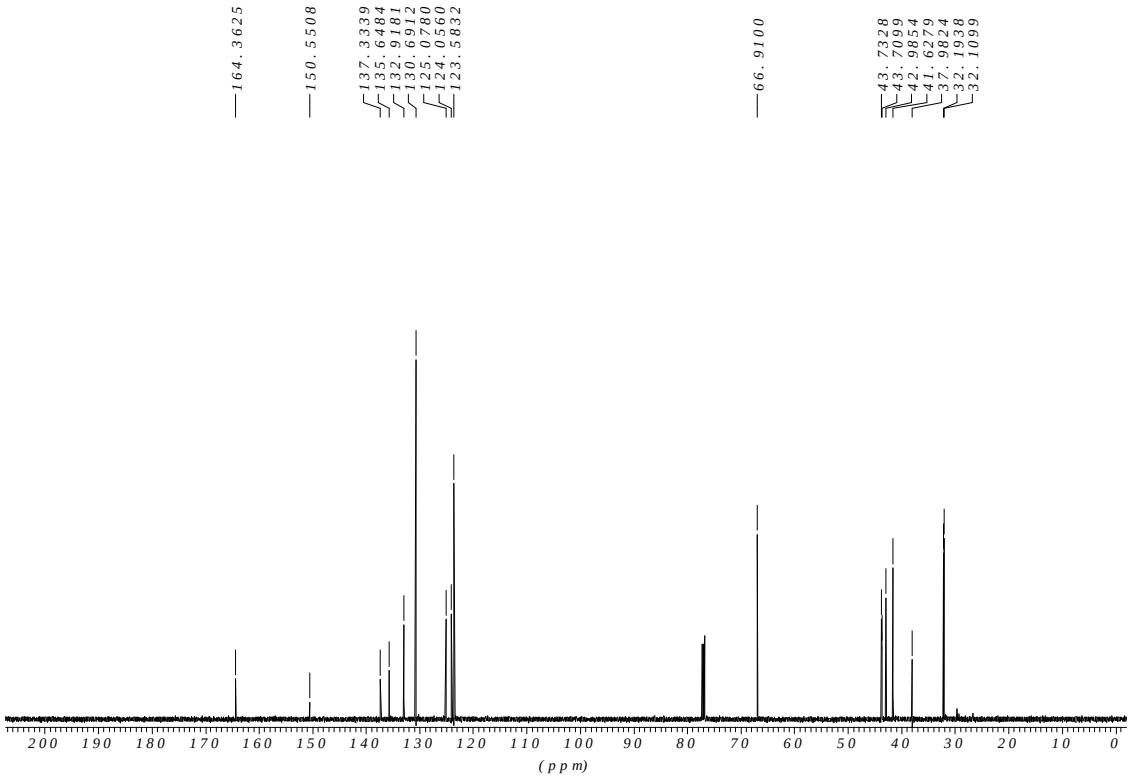
9d


NO2
O
O
H
H3C
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

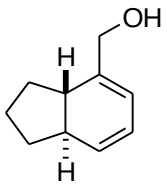

164.3931
150.5508
137.4636
135.6561
133.1012
130.7140
125.0475
124.2543
123.5832
67.0320
45.0293
42.6346
35.4198
34.5962
31.7972
23.1868
200
180
160
140
120
100
80
60
40
20
0
(ppm)

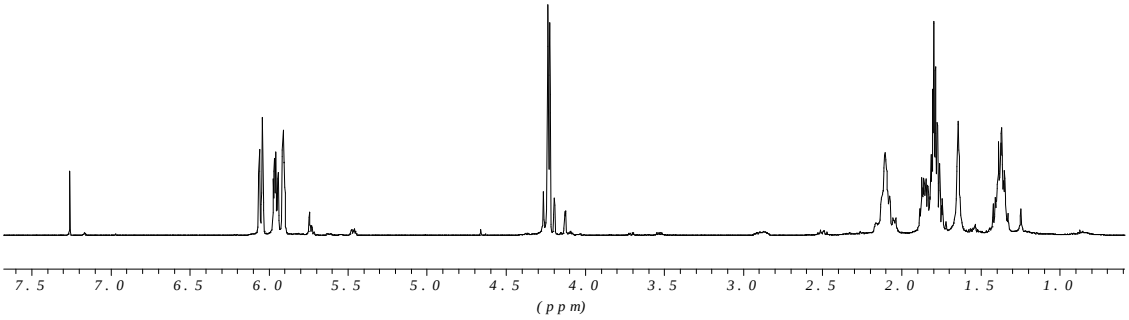
9e

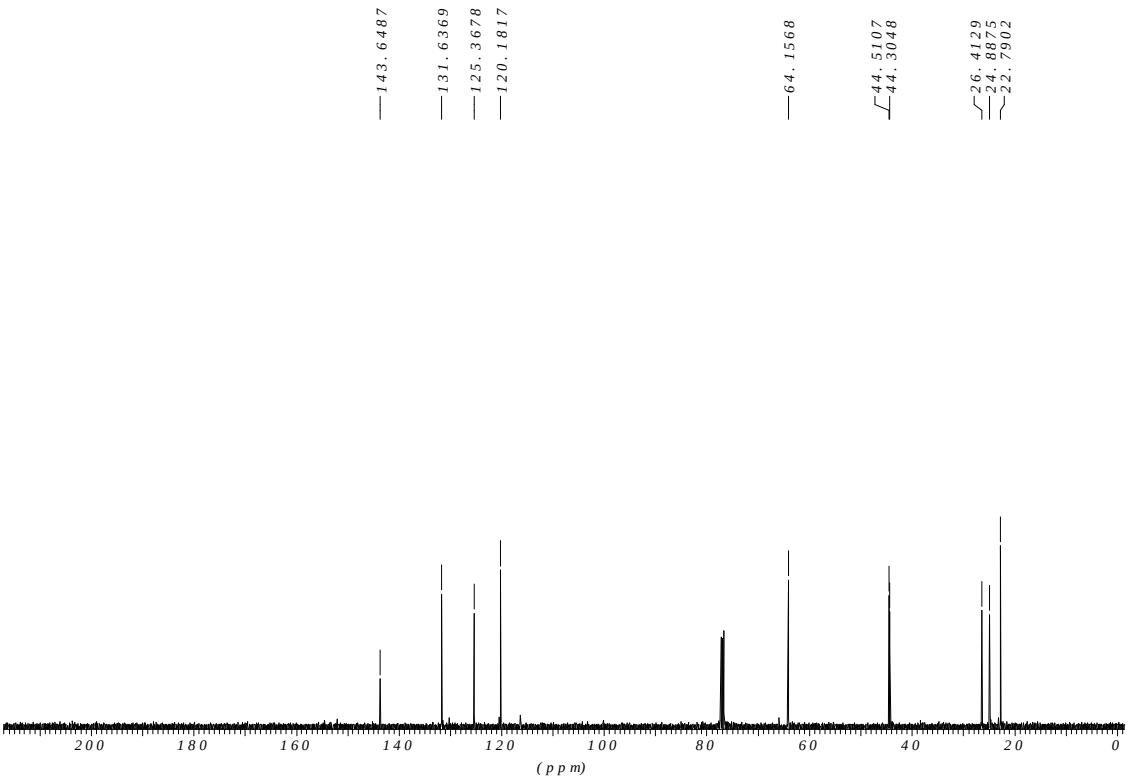

NO2
O
O
H
H3C
H3C
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


164.3625
150.5508
137.3339
135.6484
132.9181
130.6912
125.0780
124.0560
123.5832
66.9100
43.7328
43.7099
42.9854
41.6279
37.9824
32.1938
32.1099
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

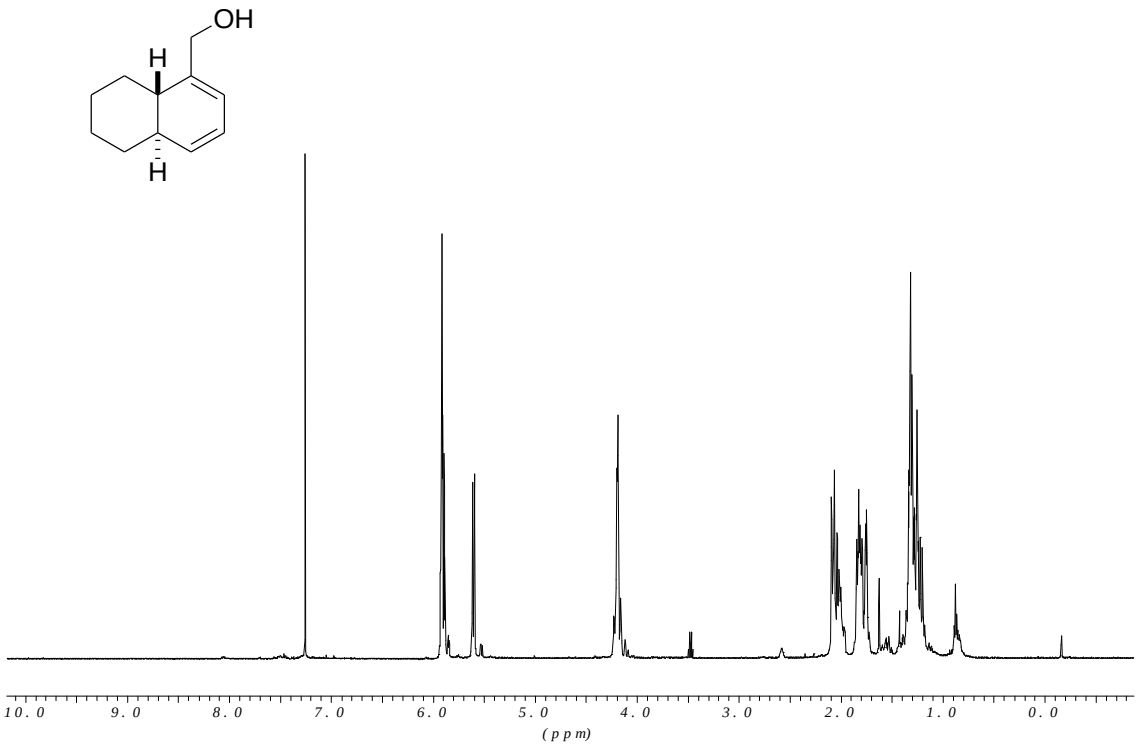
10a

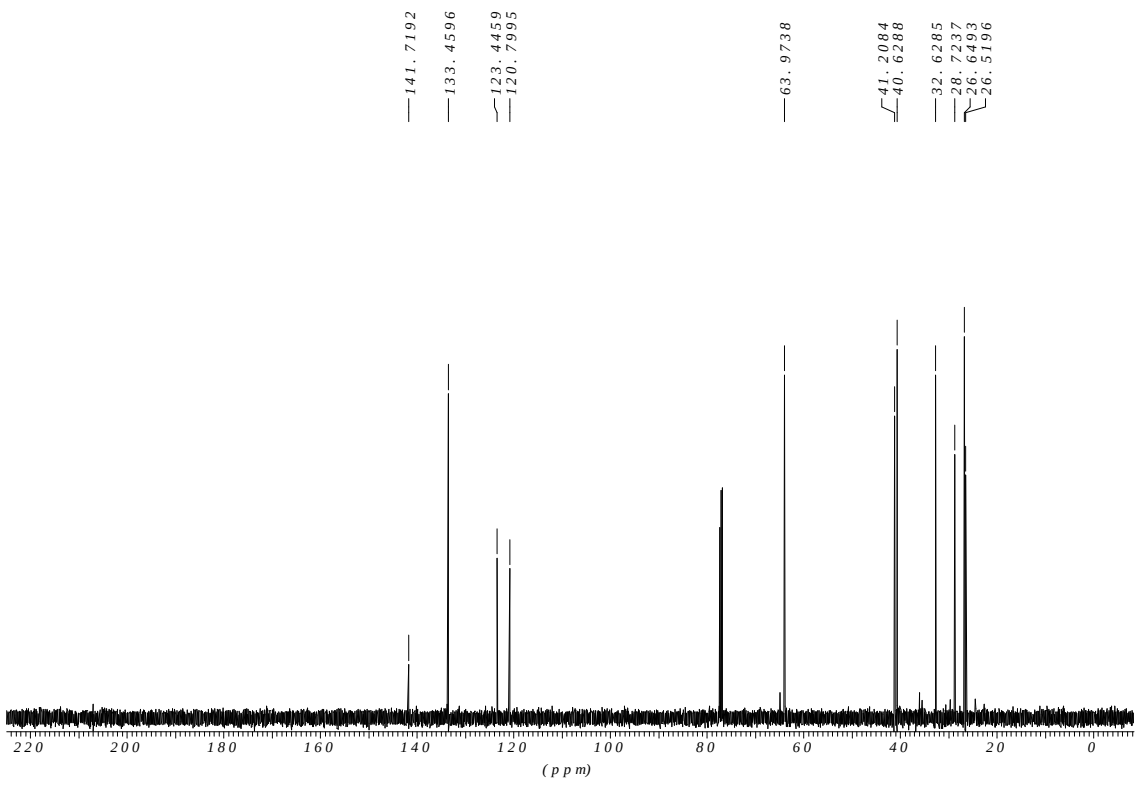

OH
H
H


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

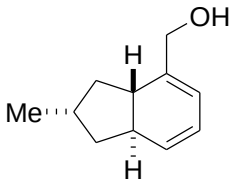

143.6487
131.6369
125.3678
120.1817
64.1568
44.5107
44.3048
26.4129
24.8875
22.7902
200
180
160
140
120
100
80
60
40
20
0
(ppm)

10b

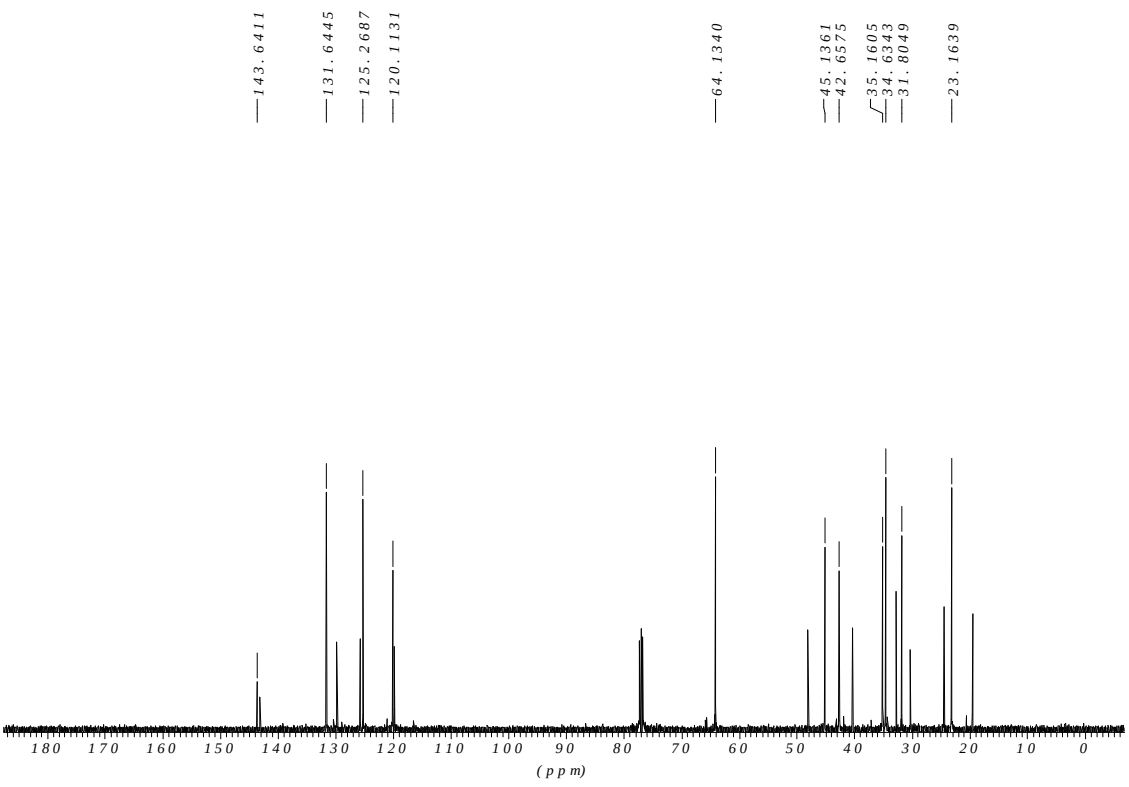

OH
H
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


141.7192
133.4596
123.4459
120.7995
63.9738
41.2084
40.6288
32.6285
28.7237
26.6493
26.5196
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

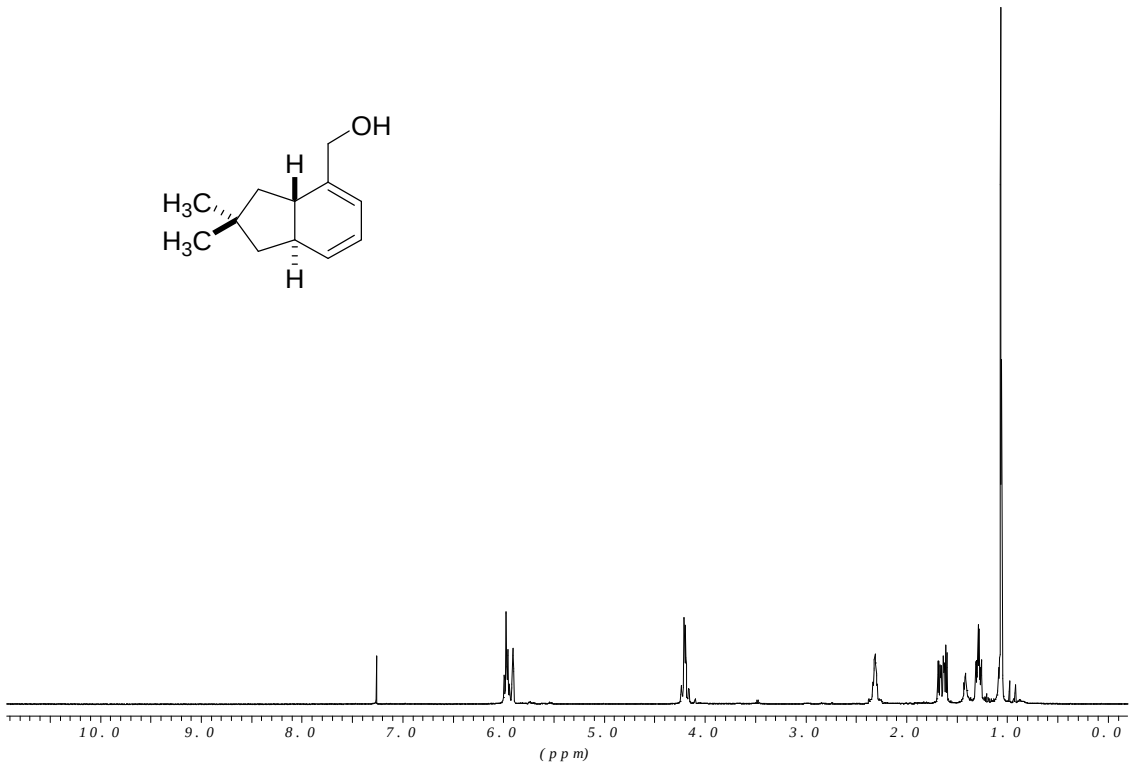
10d

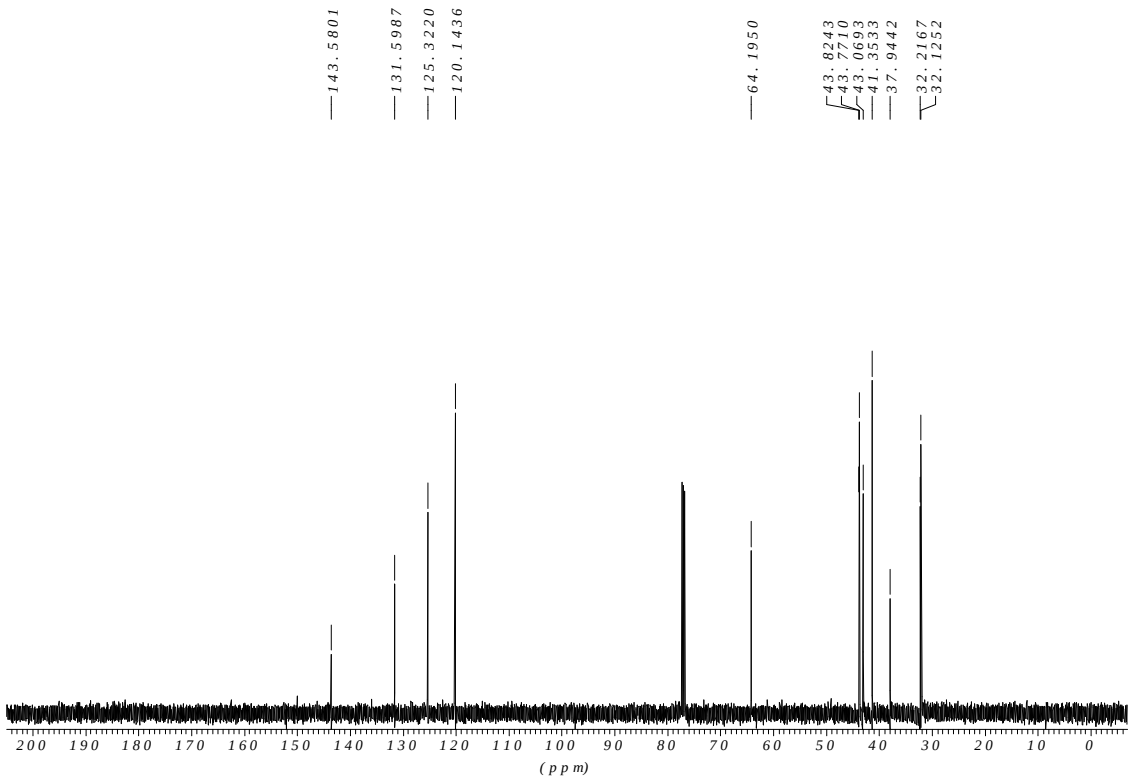

OH
H
Me
H

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

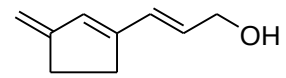

143.6411
131.6445
125.2687
120.1131
64.1340
45.1361
42.6575
35.1605
34.6343
31.8049
23.1639
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

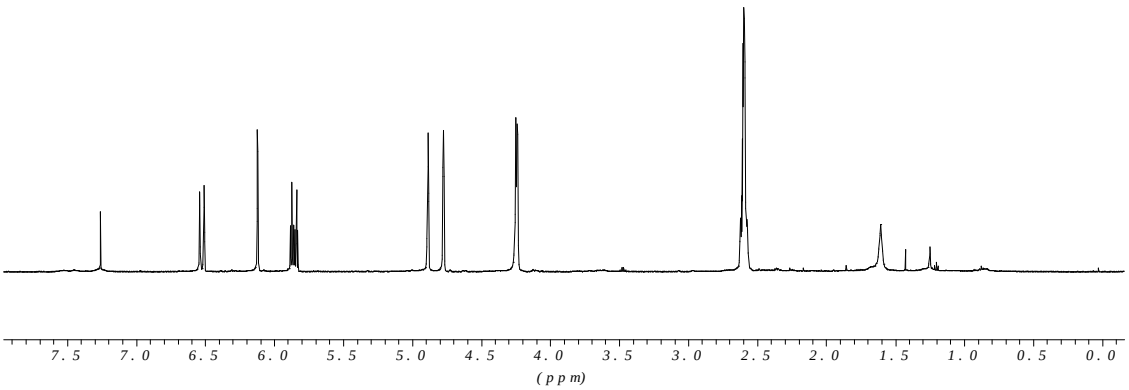
10e

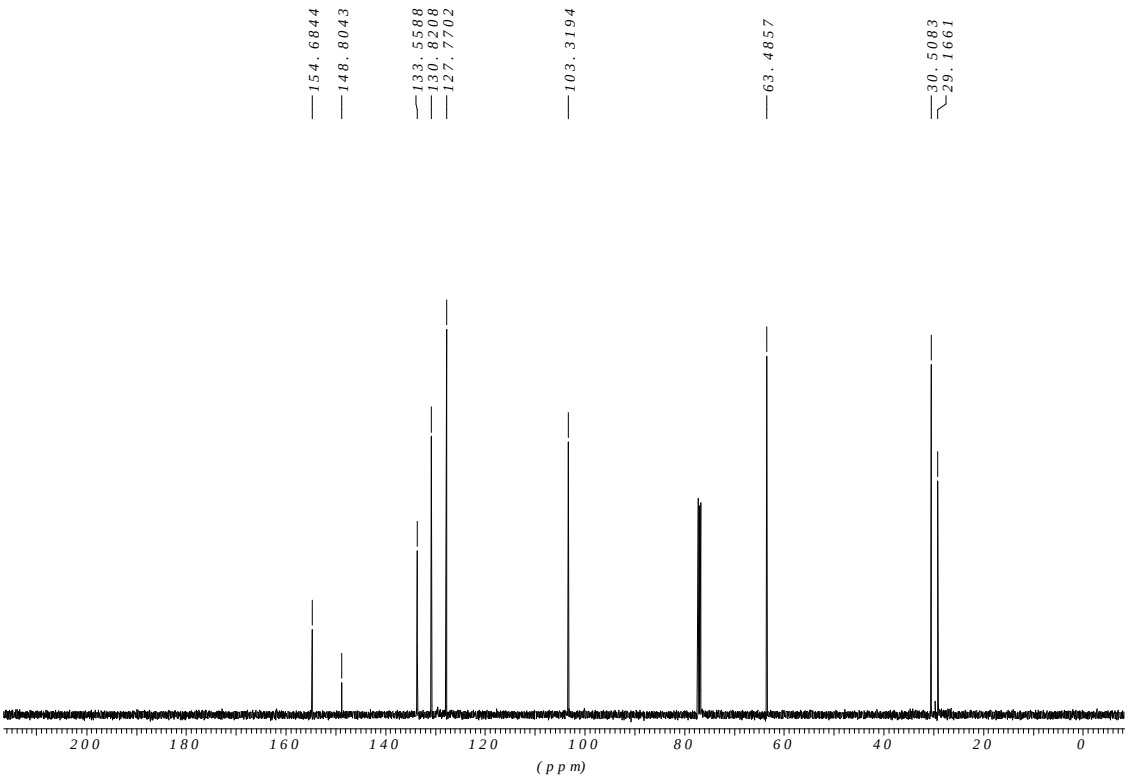

OH
H
H3C
H3C
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


143.5801
131.5987
125.3220
120.1436
64.1950
43.8243
43.7710
43.0693
41.3533
37.9442
32.2167
32.1252
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

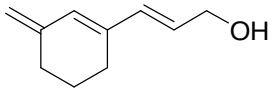
10f

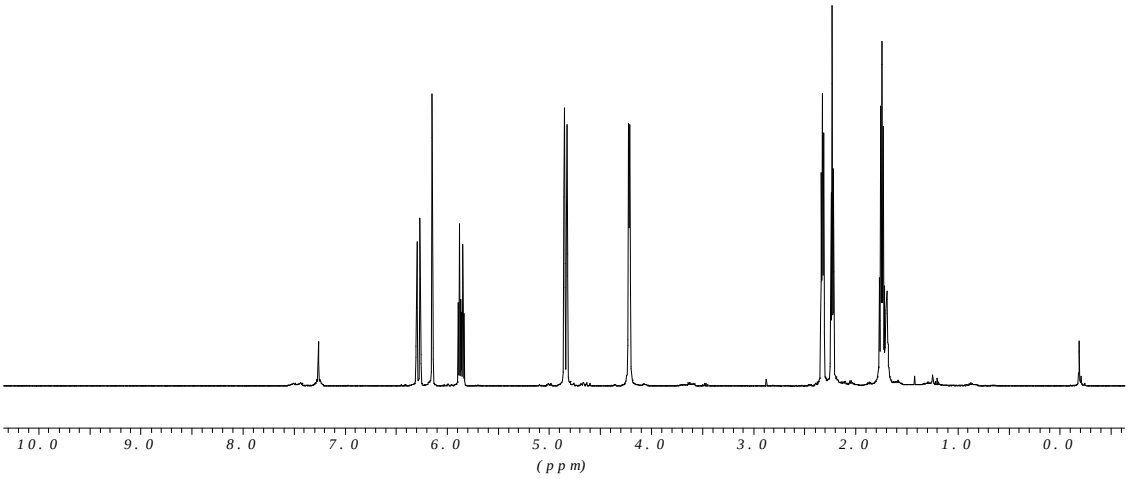

OH

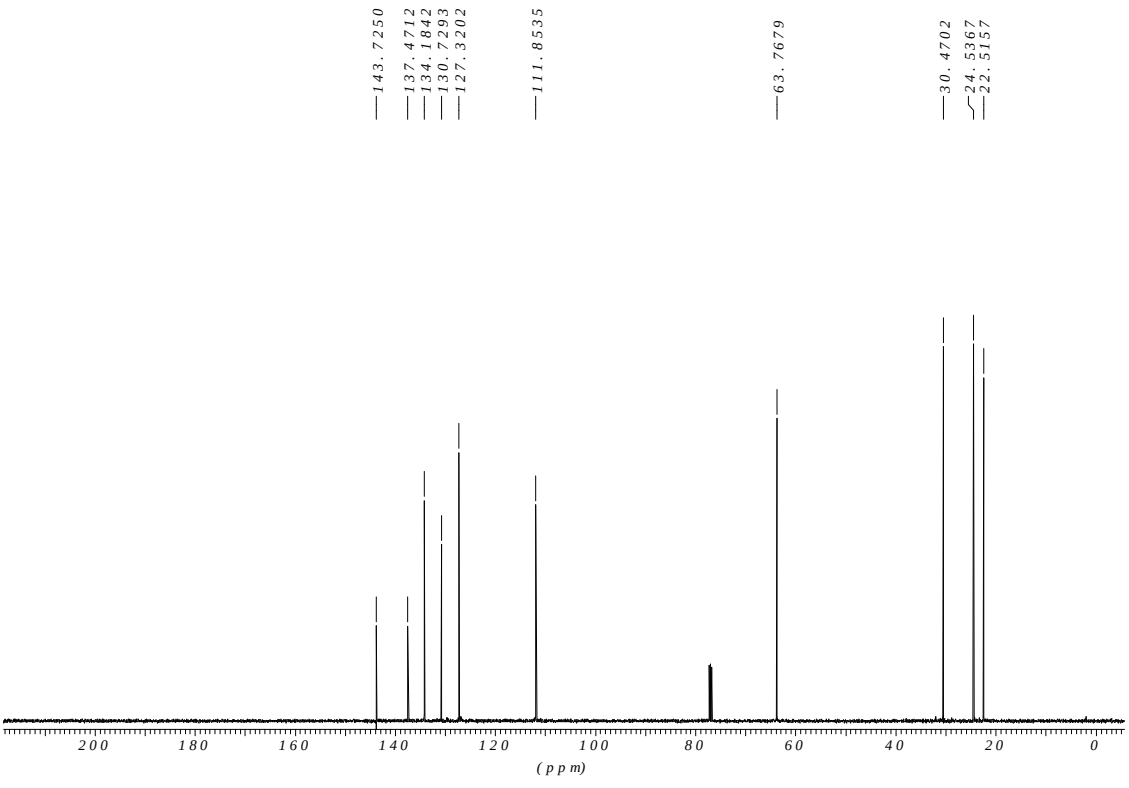

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


154.6844
148.8043
133.5588
130.8208
127.7702
103.3194
63.4857
30.5083
29.1661
200
180
160
140
120
100
80
60
40
20
0
(ppm)

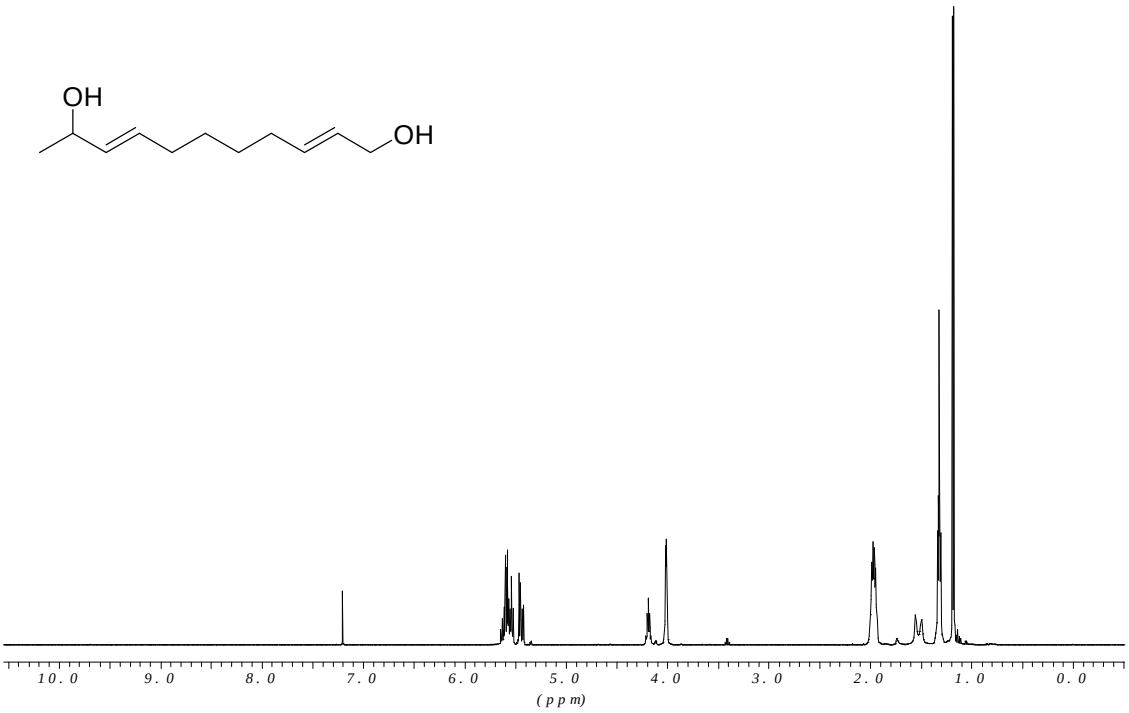
10g

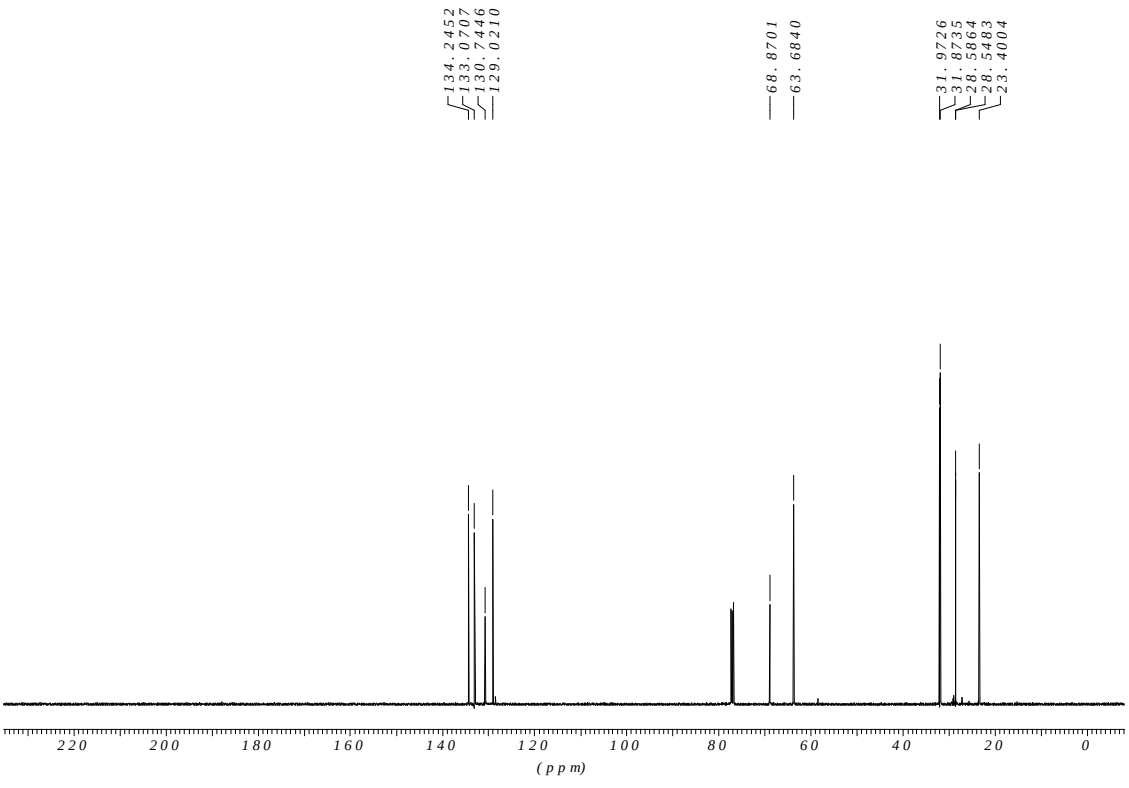

OH


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

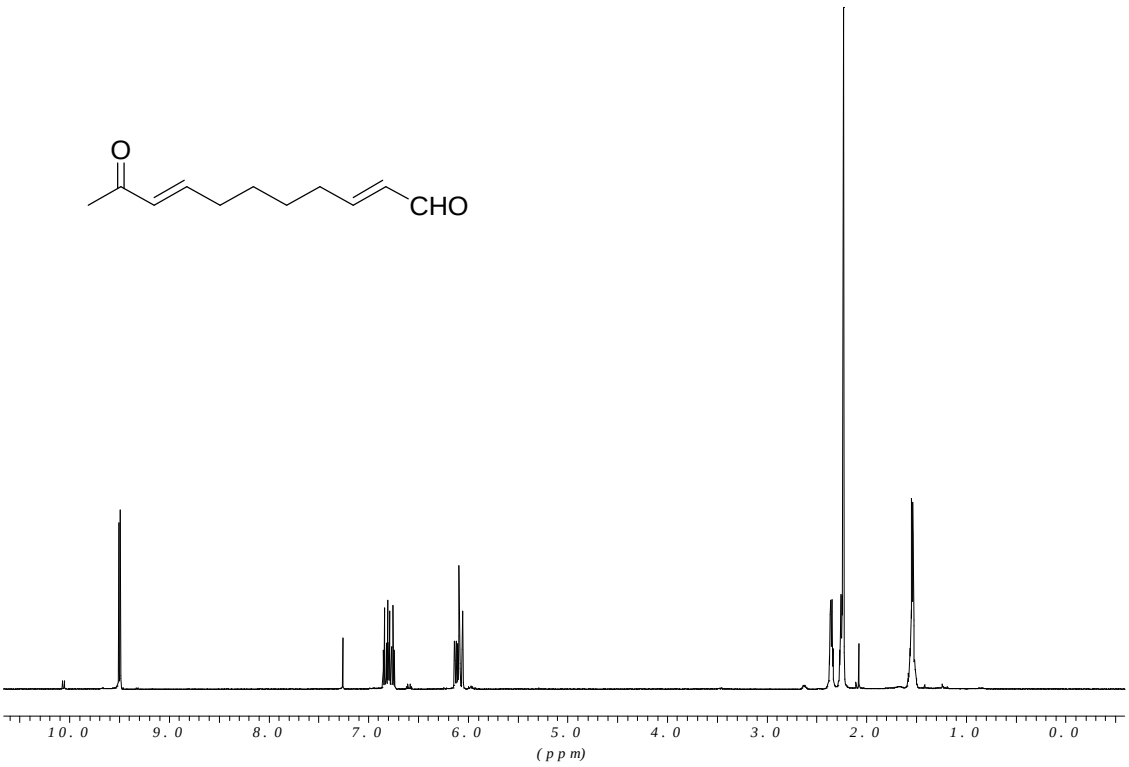

143.7250
137.4712
134.1842
130.7293
127.3202
111.8535
63.7679
30.4702
24.5367
22.5157
200
180
160
140
120
100
80
60
40
20
0
(ppm)

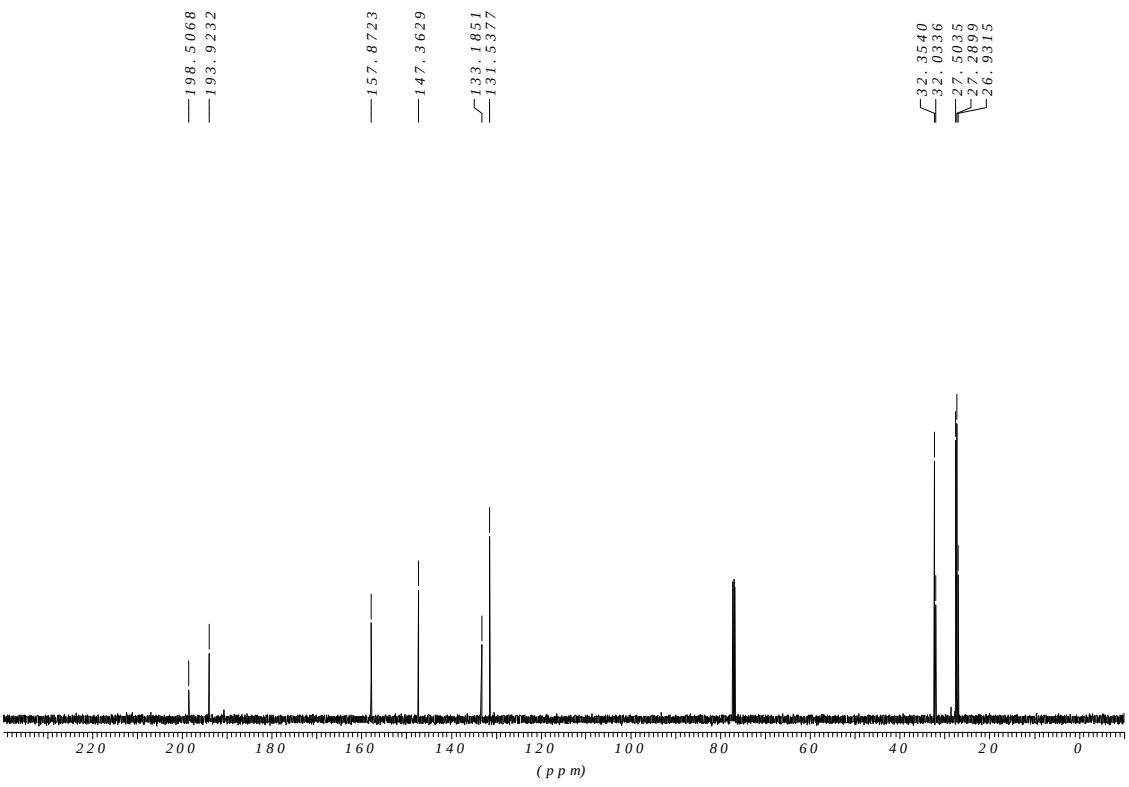
pre-12


OH
OH
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

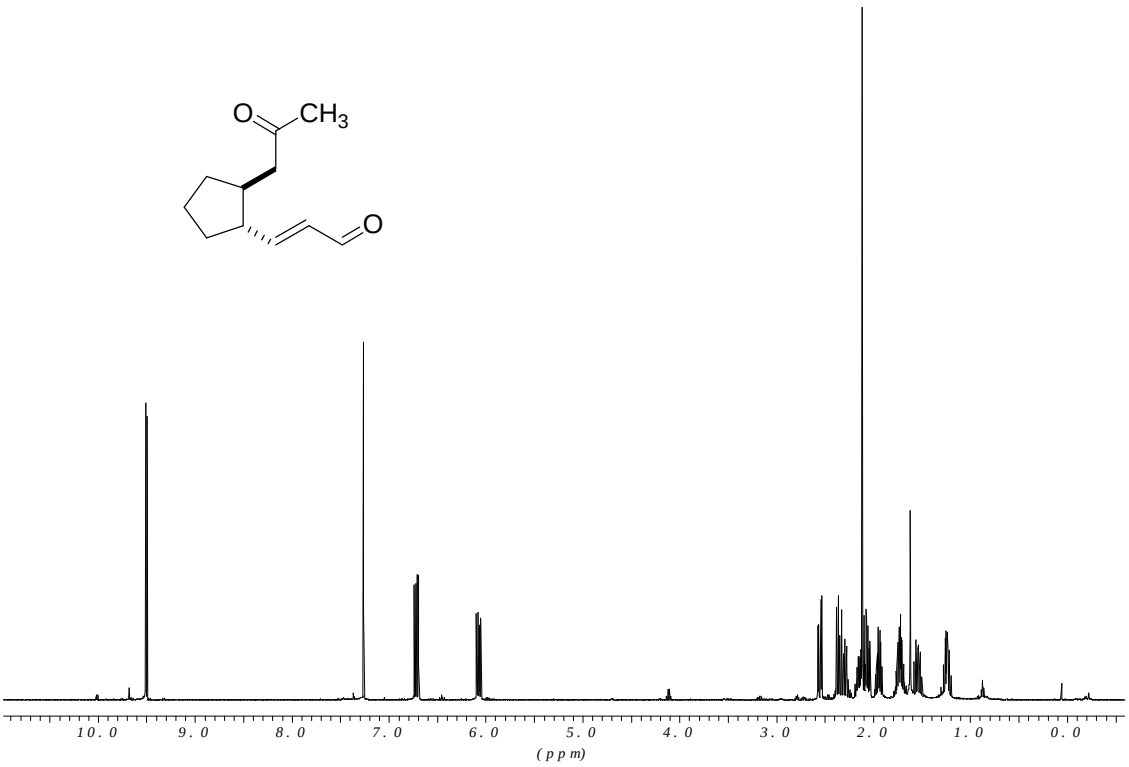

134.2452
133.0707
130.7446
129.0210
68.8701
63.6840
31.9726
31.8735
28.5864
28.5483
23.4004
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

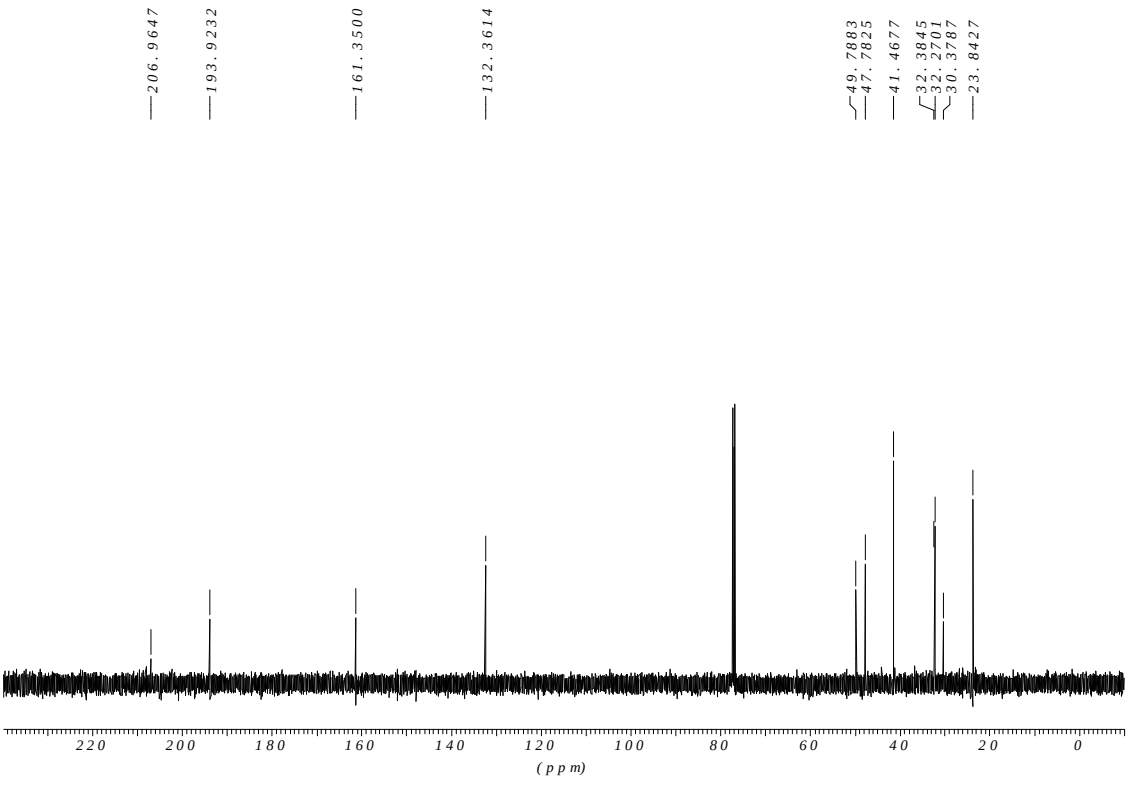
12


O
CHO
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

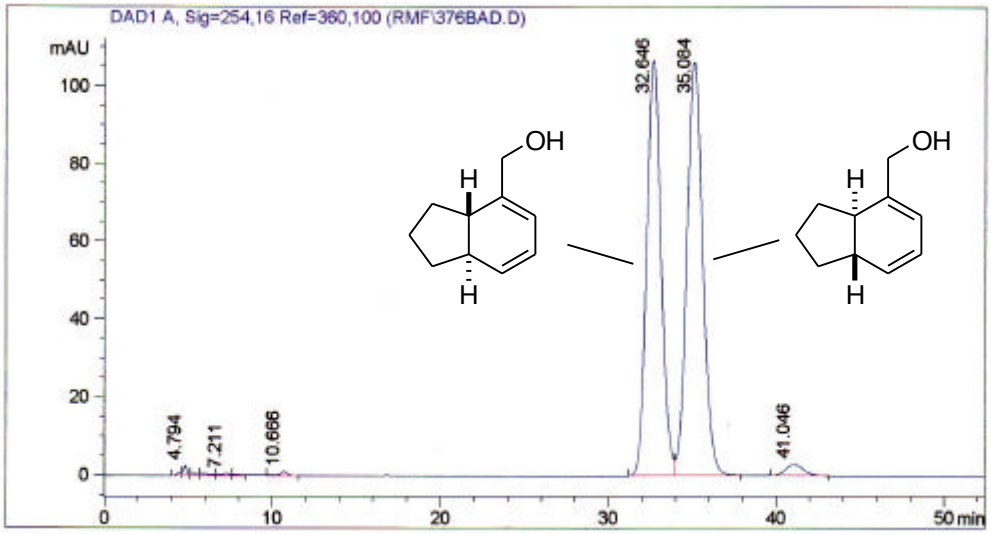

198.5068
193.9232
157.8723
147.3629
133.1851
131.5377
32.3540
32.0336
27.5035
27.2899
26.9315
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

13


O
CH3
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

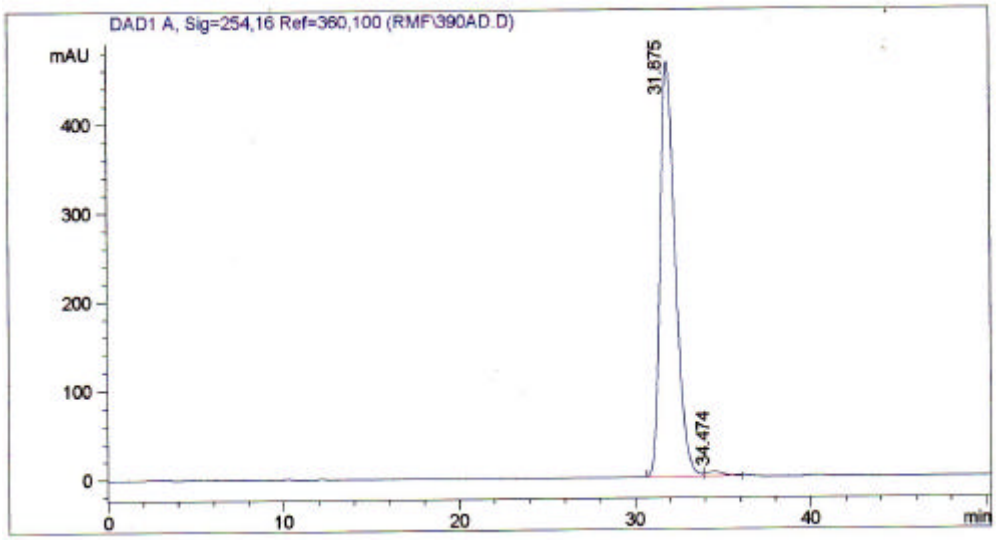

206.9647
193.9232
161.3500
132.3614
49.7883
47.7825
41.4677
32.3845
32.2701
30.3787
23.8427
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

Racemate (±)-**10a**:



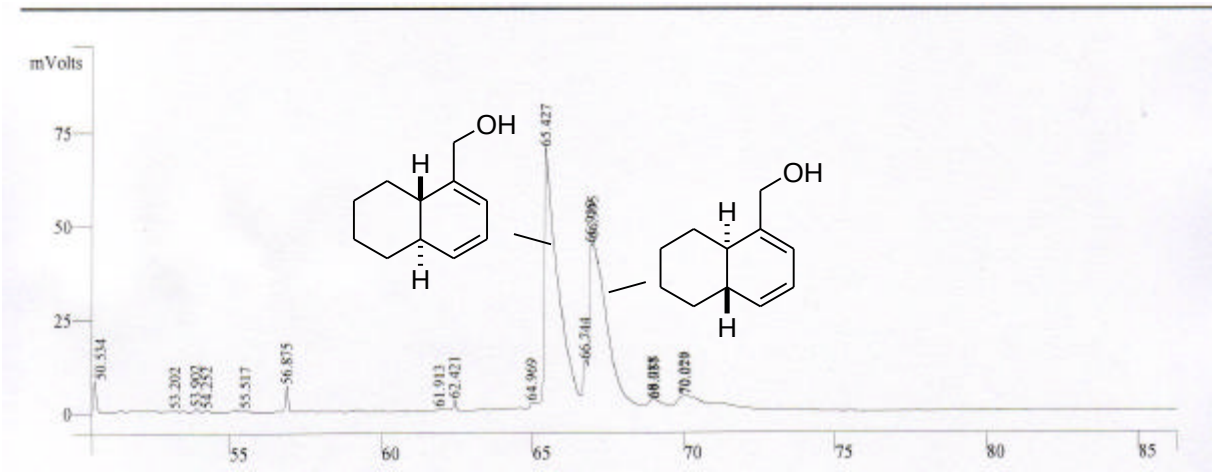
HPLC (DAICELAD.M (250 x 4.6 mm); n-heptane/isopropanol 99:1; 0.7 mL/min.

Enriched sample:



HPLC (DAICELAD.M (250 x 4.6 mm); n-heptane/isopropanol 99:1; 0.7 mL/min.

Racemate (±)-**10b**:



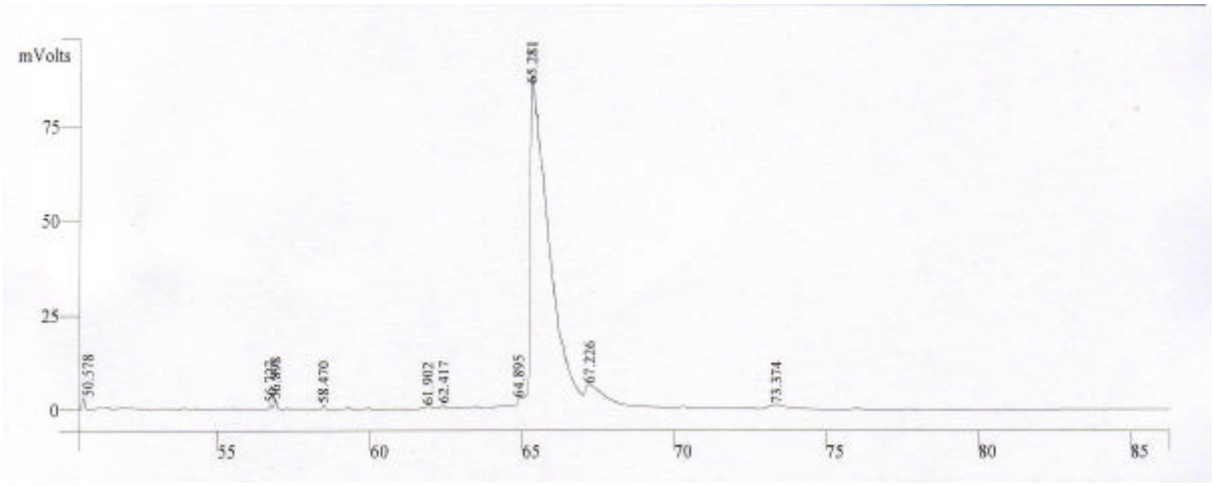
GC

Temp.-Progr.: 60-15iso-1-80-2-180-100iso 11,6 PSI H2

Channel Front: CP-Chirasil-dex CB 25 m x 0,25 mm ID

Channel Middel : Lipodex E 25 m x 0,25 mm ID

Enriched sample:



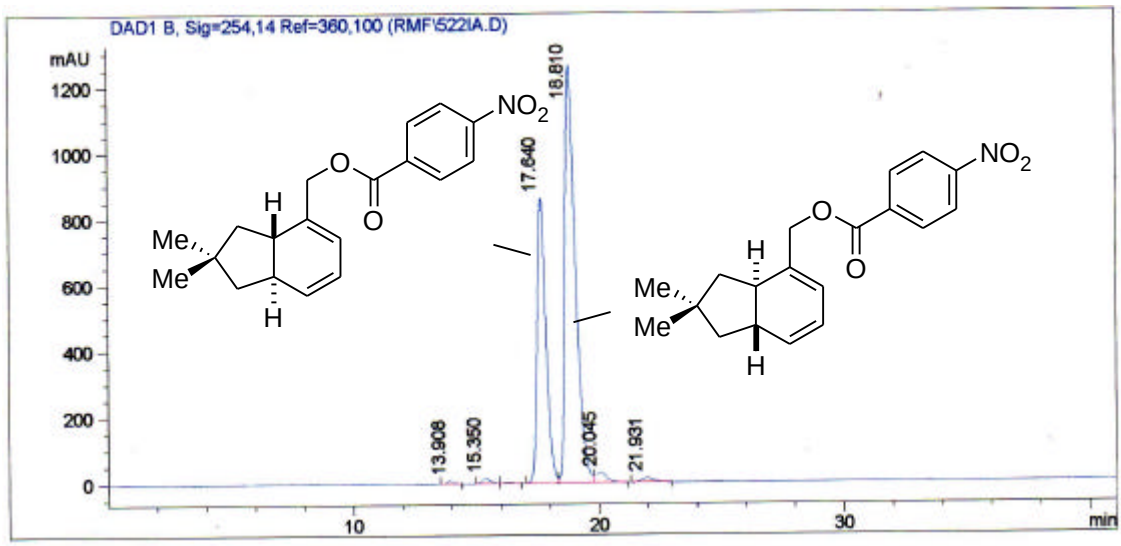
GC

Temp.-Progr.: 60-15iso-1-80-2-180-100iso 11,6 PSI H2

Channel Front: CP-Chirasil-dex CB 25 m x 0,25 mm ID

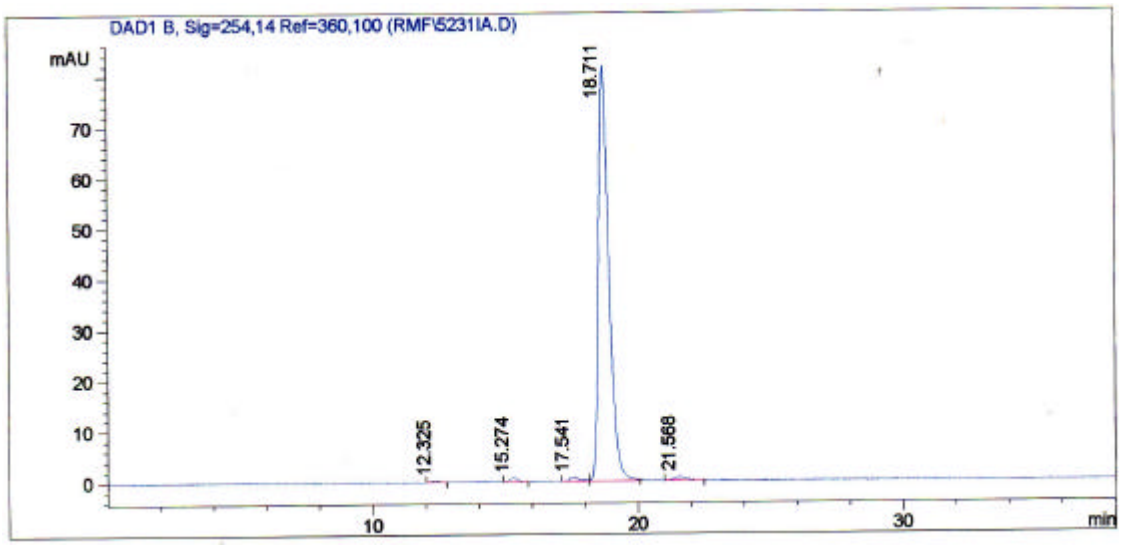
Channel Middel : Lipodex E 25 m x 0,25 mm ID

Scalemic mixture **9d**:



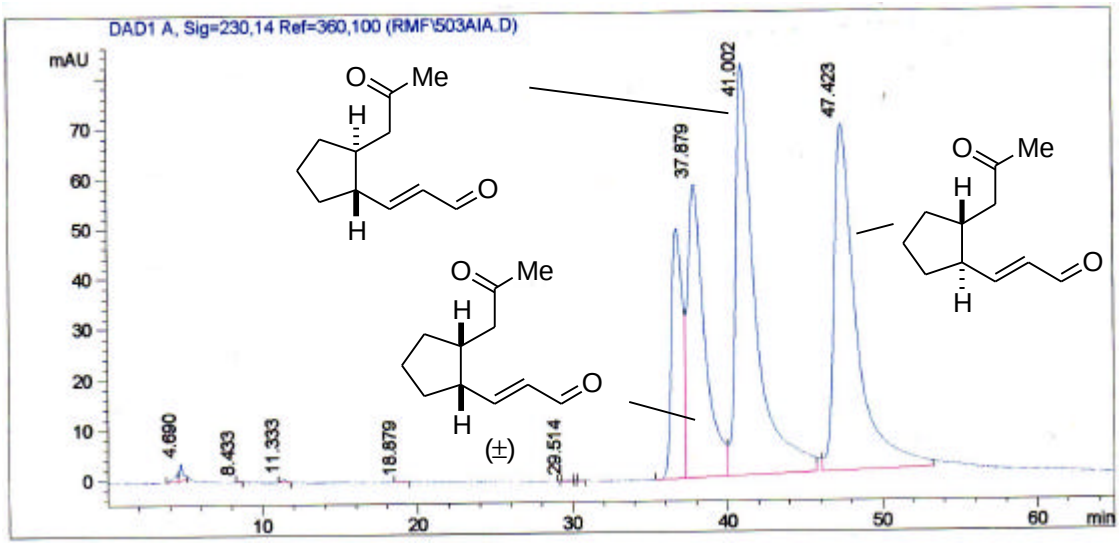
HPLC (DAICELIA.M (250 x 4.6 mm) 10 μ; n-heptane/isopropanol 99:1; 0.5 mL/min.

Enriched sample:



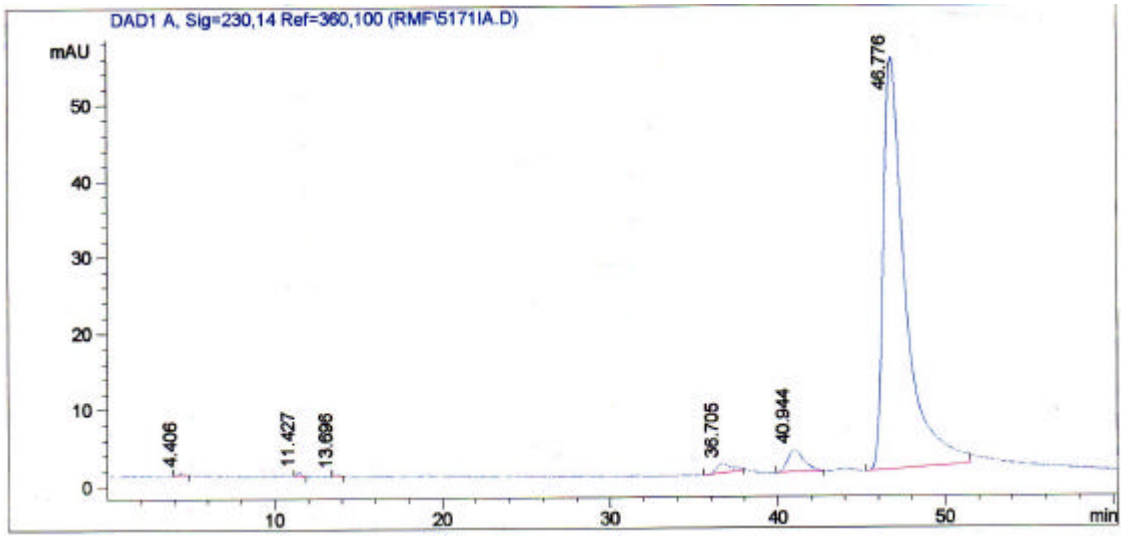
HPLC (DAICELIA.M (250 x 4.6 mm) 10 μ; n-heptane/isopropanol 99:1; 0.5 mL/min.

Racemate (±)-**13**:



HPLC (DAICELIA.M (250 x 4.6 mm) 10 µ; n-heptane/isopropanol 99:1; 0.7 mL/min.

Enriched sample (diastereomerically and enantiomerically):



HPLC (DAICELIA.M (250 x 4.6 mm) 10 µ; n-heptane/isopropanol 99:1; 0.7 mL/min.