Catalytic Stereospecific Allyl-Allyl Cross-Coupling of Internal Allyl Electrophiles with AllylB(pin)

Hai Le, Amanda Batten, and James P. Morken*

Department of Chemistry, Merkert Chemistry Center,
Boston College, Chestnut Hill, MA 02467
morken@bc.edu

Supporting Information

Table of Contents

I. General information:

^{1}H NMR spectra were recorded on a Varian Gemini-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), and coupling constants (Hz). Coupling constants are reported to the nearest 0.5 Hz. ^{13}C NMR spectra were recorded on a Varian Gemini-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, υmax cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High resolution mass spectrometry (ESI) was performed at the Mass Spectrometry Facility, Boston College.

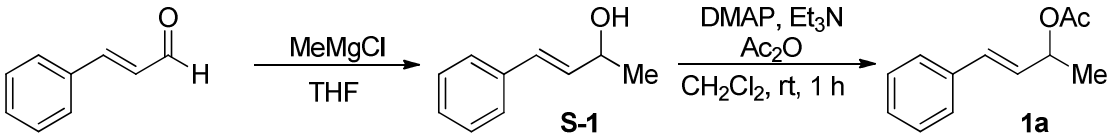
Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230×450 Mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 μm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm), potassium permanganate (KMnO4) in water, ceric ammonium molybdate (CAM) in water, or phosphomolybdic acid (PMA) in ethanol. Analytical chiral gas liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Supelco β-Dex 120 column, or a Supelco Asta Chiraldex B-DM with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Thar SFC equipped with a

Waters 2998 photodiode array detector and an analytical-2-prep column oven with methanol as the modifier. Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 1120 compact chromatograph equipped with gradient pump and variable wavelength detector. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), Toluene (PhMe), and dichloromethane (DCM) were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing through two activated alumina columns after being purged with argon. Triethylamine (TEA) and Ethyl Acetate (EtOAc) were distilled from calcium hydride. Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$**],** bis(cyclopentadienyl)zirconium(IV) dichloride ($ZrCp_2Cl_2$), (*R*)-(−)-5,5′-Bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole ((*R*)-(-)-DTBM-Segphos), 1,2-bis(diphenylphosphino)benzene (dpp-Benzene) were purchased from Strem Chemicals Inc. Allylboronic acid pinacol ester [allylB(pin)] was generously donated by Frontier Scientific. All other reagents were purchased from either Fisher or Aldrich and used without further purification.

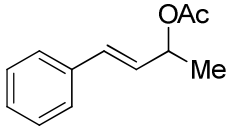
II. Preparation and Characterization of Starting Materials

Synthesis and characterization of (*E*)-4-phenylbut-3-en-2-yl acetate (1a):



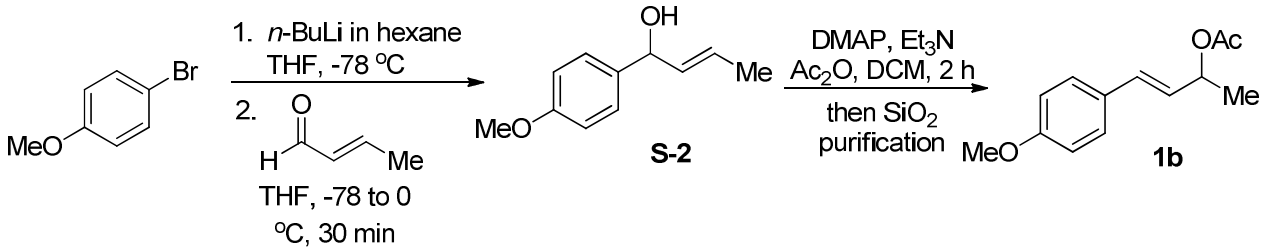
General procedure A: To a flame-dried round-bottomed flask equipped with a stir bar was added 3.0 M methylmagnesium chloride in THF (5.53 mL, 16.5 mmol) and THF (25 mL). The solution was cooled to 0 ºC and cinnamaldehyde (1.88 mL, 14.9 mmol) in THF (5 mL) was added dropwise *via* syringe. The reaction was allowed to stir at 0 ºC for 1 h. The reaction was quenched with water and 0.5 M HCl (aq). The organic layer was separated, and the aq. layer was extracted with ethyl acetate three times. The combined organics were washed with brine, dried with Na_2SO_4, filtered and concentrated *in vacuo.* **S-1** was then acetylated using procedure **B**.

General Procedure B: A 100 mL round-bottomed flask was charged with **S-1** (2.4 g, 9.5 mmol), 4-dimethylaminopyridine (116 mg, 0.95 mmol) and CH_2Cl_2 (20 mL). Triethylamine (2.7 mL, 19 mmol) was added and the reaction stirred for 20 minutes, followed by the addition of acetic anhydride (1.8 mL, 19 mmol). The reaction was capped with a septum, vented with a needle, and was allowed to stir while warming to room temperature for 1 h. The reaction was then quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The organic portions were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified on silica gel (5% Et_2O/pentane) to afford a colorless oil (88 % yield over 2 steps).



(*E*)-4-phenylbut-3-en-2-yl acetate (1a): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.41 (3H, d, *J* = 6.6 Hz), 2.08 (3H, s), 5.53 (1H, quint, *J* = 6.8 Hz), 6.19 (1H, dd, *J* = 15.9, 6.8 Hz), 6.60 (1H, d, 15.9 Hz), 7.23-7.26 (1H, m), 7.29-7.34 (2H, m), 7.36-7.39 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 21.4, 71.0, 126.5, 127.9, 128.8, 131.5, 136.3, 170.3; IR (neat): 2980 (w), 1732 (s), 1370 (m), 1235 (s), 1040 (m), 966 (m), 951 (m), 748 (m), 693 (m) cm^{-1}; HRMS (ESI+) for $C_{13}H_{16}O_2$ [M+H]: calculated: 190.0994, found: 190.1002. R_f = 0.25 in 5% EtOAc/hexane.

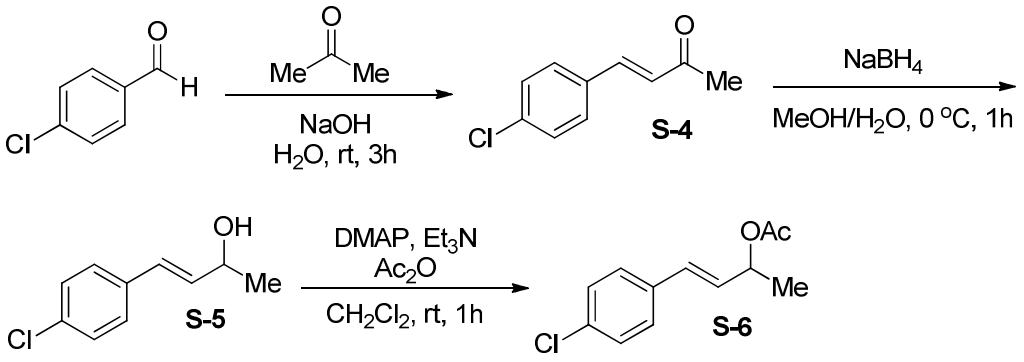
Synthesis and characterization of (*E*)-4-(4-methoxyphenyl)but-3-en-2-yl acetate (1b):



General Procedure C: A flame-dried round-bottomed flask under N_2 was equipped with a stir bar and charged with 4-bromoanisole (0.12 mL, 1 mmol) and THF (4 mL). The solution was cooled to -78 °C before adding 2.5 M *n*-butyllithium in hexane (0.4 mL, 1.0 mmol) dropwise via syringe. The reaction was stirred for 10 minutes before the dropwise addition of crotonaldehyde (0.85 mL, 1.0 mmol) in THF (1 mL). After 10 minutes at -78 °C, the reaction was warmed to room temperature and was allowed to stir for 30 min. The reaction was diluted with ether (10 mL) before quenching with water (5 mL) at 0 °C. The aqueous portion was extracted with ether three times and the organic portions were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo* to afford **S-2**. The alcohol S-2 was then protected following procedure **B**.

After purification on SiO_2, the product rearranged to the corresponding regioisomer. Spectral data is in accordance with literature values.[1]

Synthesis and characterization of (*E*)-4-(4-chlorophenyl)but-3-en-2-yl acetate (1c): [1]

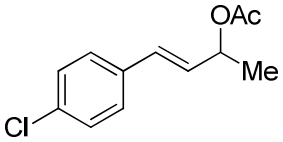


General procedure D:

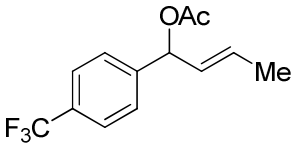
Step 1: A round-bottom flask equipped with a stir bar was charged with 4-chlorobenzaldehyde (0.56 g, 4.0 mmol) and D.I. water (25.5 mL). A suspension of acetone (1.46 mL, 20.0 mmol) and NaOH (0.58 g, 14.4 mmol) in D.I. water (8.5 mL) was added to the reaction. The mixture was stirred at room temperature for 3 h. The reaction was quenched with water and the aqueous layer was extracted with DCM three times. The organic portion was washed with brine, dried with Na_2SO_4, filtered and concentrated *in vacuo*.

Step 2: A round-bottom flask equipped with a stir bar was charged with **S-4** (0.63 g, 2.6 mmol), H_2O (0.5 mL) and MeOH (2 mL). The solution was cooled to 0 ^oC before $NaBH_4$ (113.5 mg, 3 mmol) was added. The reaction was stirred at room temperature for 1 h. The reaction was then diluted with CH_2Cl_2 and washed with brine. The aqueous layer was extracted with CH_2Cl_2 three times. The organic portion was dried over Na_2SO_4, filtered, and concentrated *in vacuo.* The

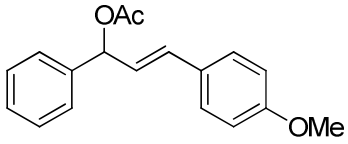
allyl alcohol **S-5** was then protected using general procedure **B**. The crude material was purified on silica gel (5% Et_2O/pentane) to afford a clear colorless oil (60% yield over 2 steps).



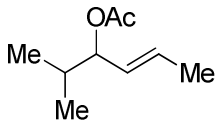
(*E*)-4-(4-chlorophenyl)but-3-en-2-yl acetate (1c): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (3H, d, *J* = 6.5 Hz), 2.07 (3H, s), 5.50 (1H, app dq, *J* = 13.0, 6.6 Hz), 6.16 (1H, dd, *J*= 15.9, 6.6 Hz), 6.55 (1H, d, *J* = 15.9 Hz), 7.26-7.31 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3. 21.3, 701.7, 127.7, 128.7, 129.5, 133.5, 134.8, 170.2; IR (neat): 2981 (w), 1734 (s), 1492 (m), 1371 (m), 1238 (s), 1094 (m), 1042 (m), 1013 (m), 968 (m), 952 (m), 806 (m) cm^{-1}; HRMS (ESI+) for $C_{12}H_{13}ClO_2$ [M+H]: calculated: 224.0604, found: 224.06115. R_f = 0.24 in 5% EtOAc/hexane.



(*E*)-1-(4-(trifluoromethyl)phenyl)but-2-en-1-yl acetate (1d): From commercially available 1-Bromo-4-(trifluoromethyl)benzene, procedure **C** and **B** were followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.73 (3H, d, *J* = 6.4 Hz), 2.11 (3H, s), 5.63 (1H, dd, *J* = 15.2, 6.9 Hz), 5.78 (1H, dq, *J* = 15.2, 6.4 Hz), 6.24 (1H, d, *J* = 6.9 Hz), 7.45 (2H, d, *J* = 8.3 Hz), 7.61 (2H, d, *J* = 8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 143.7, 130.6, 130.0 (q, $^2J_{CF}$ = 32.4 Hz), 128.9, 127.0, 125.4 (q, $^3J_{CF}$ = 3.6 Hz), 124.0 (q, $^1J_{CF}$ = 271.7 Hz), 75.6, 21.2, 17.7; IR (neat): 2921(br), 1737 (s), 1371 (m), 1323 (s), 1227(s), 1164 (s), 1122 (s), 1065 (s), 1016 (s), 962 (s), 831 (m) cm^{-1}; HRMS (ESI+) for $C_{11}H_{10}F_3$ [M-OAc+H]: calculated 199.0735, found: 199.0783. The crude material was purified on silica gel (5% Et_2O/pentane) to afford a colorless yellow oil (86 % yield over 2 steps). R_f = 0.32 in 5% EtOAc/hexane.

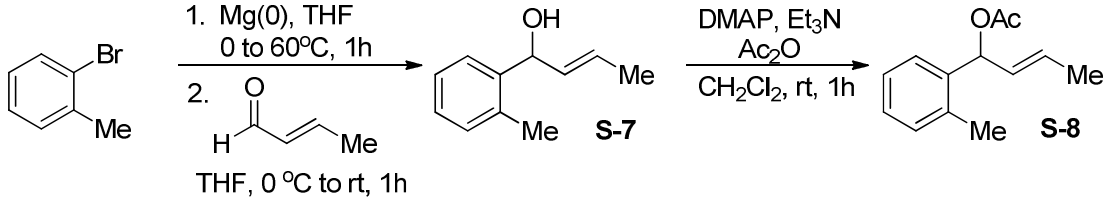


(*E*)-3-(4-methoxyphenyl)-1-phenylallyl acetate (1e): From commercially available 3-(4-methoxyphenyl)-1-phenyl-propenone, general procedure **D,** step 2 was followed. The allyl alcohol was protected using general procedure **B.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.13 (3H, s), 3.81 (3H, s), 6.22 (1H, dd, *J* = 16.1, 7.3 Hz), 6.42 (d, *J* = 7.3 Hz), 6.58 (1H, d, *J* = 16.1 Hz), 6.84 (2H, d, *J* = 8.8 Hz), 7.28-7.44 (7H, m); ^{13}C NMR (125 MHz $CDCl_3$): δ 21.4, 45.9, 55.3, 76.4, 114.0, 125.3, 127.0, 127.9, 128.0, 128.6, 128.9, 132.3, 139.5, 159.6, 170.1; IR (neat): 2934 (br), 1735(s), 1607 (m), 1512 (s), 1455 (w), 1370 (m), 1300 (w), 1233 (s), 1176 (m) cm^{-1}; HRMS (ESI+) for $C_{18}H_{18}O_3$ [M]: calculated: 282.1256, found: 282.1267. The crude material was used without purification (83% yield over 2 steps). R_f = 0.33 in 10% EtOAc/hexane.

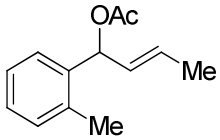


(*E*)-2-methylhex-4-en-3-yl acetate (1f): From commercially available isopropylmagnesium chloride and crotonaldehyde, general procedure **A** and **B** were followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (6H, app. t, *J* = 6.1 Hz), 1.70 (3H, dd, *J* = 6.6, 1.7 Hz), 1.82 (1H, app octet, *J* = 6.9 Hz), 2.04 (3H, s), 4.98 (1H, t, *J* = 7.1 Hz), 5.39 (1H, ddq, *J* = 15.4, 7.8, 1.7 Hz), 5.70 (1H, dq, *J* = 15.4, 6.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.8, 18.0, 18.2, 21.3, 32.0, 79.6, 127.8, 129.9, 170.4; IR (neat): 2963 (m), 2934 (w), 2876 (w), 1735 (s), 1469 (w), 1450 (w), 1371 (m), 1236 (s), 1018 (m), 968 (m) cm^{-1}; HRMS (ESI+) for $C_7H_{13}O_2$ [M -OAc]: calculated: 97.1017, found: 97.1020. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (59% yield over 2 steps). R_f = 0.35 in 5% EtOAc/hexane.

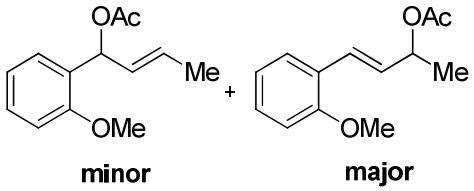
Synthesis and characterization for (*E*)-4-(*o*-tolyl)but-3-en-2-yl acetate (1g):



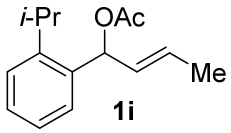
General Procedure E: To a flame-dried round-bottom flask equipped with a stir bar and reflux condenser was added magnesium turnings (280 mg, 11.5 mmol). An additional flame-drying was performed before THF (22 mL) and 2-bromotoluene (1.32 mL, 11 mmol) was added dropwise at 0 ºC. The solution was refluxed at 60 ºC for 1 h, then cooled to 0 ºC before a solution of crotonaldehyde (0.83 mL, 10 mmol) in THF (5 mL) was added dropwise *via* syringe. The reaction was allowed to stir at ambient temperature for 1 h. The reaction was cooled to 0 ºC and quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate three times and the combined organics were washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The allyl alcohol was then protected using general procedure **B**. The crude material was purified on silica gel (5% Et_2O/pentane) to afford **S-8** as a colorless oil (76% yield over 2 steps).



(*E*)-4-(*o*-tolyl)but-3-en-2-yl acetate (1g): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.42 (3H, d, *J* = 6.6 Hz), 2.08 (3H, s), 2.35(3H, s), 5.55 (1H, app q, *J* = 6.6 Hz), 6.07 (1H, dd, *J* = 15.9, 6.8 Hz), 6.82 (1H, d, *J* = 15.8 Hz), 7.13-7.18 (3H, m), 7.41-7.44(1H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.7, 20.5, 21.4, 71.2, 125.6, 126.0, 127.7, 129.5, 130.1, 130.2, 135.4, 135.6, 170.3; IR (neat): 3019 (w), 2979 (w), 2932 (w), 1734 (s), 1486 (w), 1459 (w), 1370 (m), 1234 (s), 1152 (w), 1039 (m), 966 (m), 950 (m), 749 (m) cm^{-1}; HRMS (ESI-) for $C_{13}H_{16}O_2$ [M+H]: calculated: 205.1138, found: 205.0484. R_f = 0.31 in 5% EtOAc/hexane.



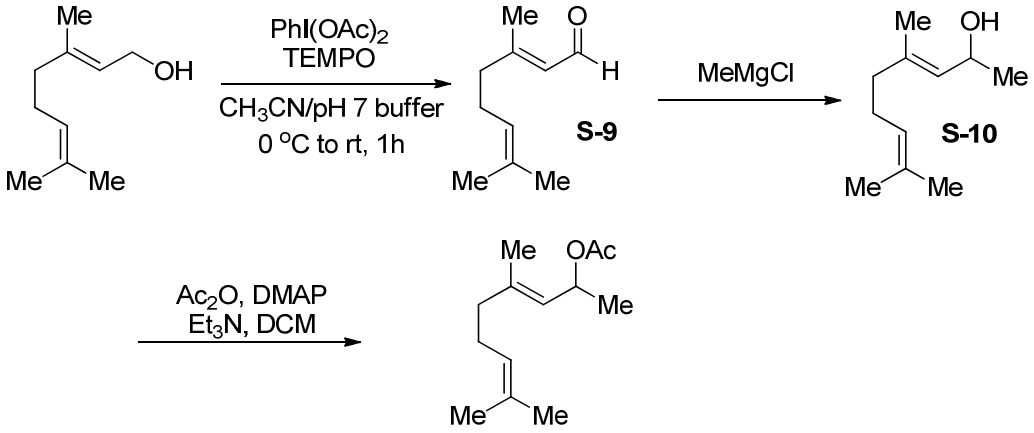
(*E*)-4-(2-methoxyphenyl)but-3-en-2-yl acetate (major – 1h) and (E)-1-(2-methoxyphenyl)but-2-en-1-yl acetate (minor): From commercially available 1-bromo-2-methoxybenzene, general procedure **E** and **B** were followed. The desired starting material isomerized to its regioisomer during silicagel purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.42 (3H, d, *J* = 6.3 Hz, major), 1.69 (3H, d, *J* = 4.9 Hz, minor), 2.07 (3H, s, major), 2.08 (3H, s, minor), 3.84 (3H, s, minor), 3.85 (3H, s, major), 5.54 (1H, dq, *J* = 6.3, 6.3 Hz, major), 5.62-5.76 (2H, m, minor), 6.22 (1H, dd, *J* = 16.1, 6.8 Hz, major), 6.60 (1H, d, *J* = 5.4 Hz, minor), 6.84-6.99 (3H+1H, m, major+minor), 7.20-7.30 (1H+2H, m, major+minor), 7.36 (1H, d, *J* = 7.4 Hz, minor), 7.42 (1H, d, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 20.4, 21.3, 21.4, 55.4, 55.6, 70.7, 71.5, 110.7, 110.8, 120.6, 125.3, 126.5, 127.0, 127.1, 128.2, 128.6, 128.9, 128.9, 129.3, 156.4, 156.9, 169.9, 170.3; IR (neat): 2978 (br), 2937 (br), 2838 (w), 1731 (s), 1598 (m), 1580 (w), 1490 (m), 1463 (m), 1438 (m), 1370 (m), 1232 (s) cm^{-1}; HRMS (ESI+) for $C_{13}H_{16}O_3$ [M +H]: calculated: 220.1099, found: 220.1109. The crude material was purified on silica gel (10% ether/pentane) to afford a clear oil (42%y after 2 steps). R_f = 0.23 in EtOAc/hexane.



(*E*)-1-(2-isopropylphenyl)but-2-en-1-yl acetate (1i): From commercially available 1-bromo-2-isopropylbenzene, procedure **C** and **B** was followed. ^{1}H NMR (500 MHz, $CDCl_3$): 1.20 (3H, d, *J* = 6.8 Hz), 1.27 (3H, d, *J* = 6.9 Hz), 1.70 (3H, d, *J* = 6.3 Hz), 2.08 (3H, s), 3.27 (1H, hept., *J* = 6.8 Hz), 5.60-5.73 (2H, m), 6.54 (1H, d, *J* = 5.8 Hz), 7.18-7.21 (1H, m), 7.28-7.31 (2H, m), 7.37 (1H, d, *J* = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 17.8, 21.4, 23.8, 23.9, 28.6, 72.9, 125.5, 125.9, 127.1, 128.2, 129.4, 129.9, 136.4, 146.3, 170.0; IR (neat): 2963 (m), 2870 (w), 1734 (s), 1368 (m), 1229 (s), 1014 (s), 959 (s), 758 (s); HRMS

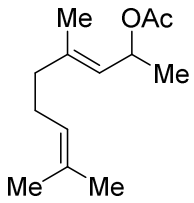
(ESI+) for $C_{15}H_{20}O_2$ [M-OAc]: calculated 173.1325, found 173.1330. The crude material was purified on silica gel (5% Et_2O/pentane) to afford a colorless oil (80% yield over 2 steps). R_f = 0.35 in 5% EtOAc/hexane.

Synthesis and characterization of (*E*)-4,8-dimethylnona-3,7-dien-2-yl acetate (starting material for 4)

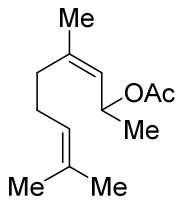


General procedure F: A flame-dried round-bottom flask under N_2 was equipped with a stir bar, and charged with $PhI(OAc)_2$ (44.0 mmol, 14.2 g), TEMPO (4.0 mmol, 270 mg), CH_3CN (34 mL), and aqueous pH 7 buffer (9.6 mL). The solution was cooled to 0 ºC before adding geraniol (40.0 mmol, 6.17 g) *via* syringe. The reaction was allowed to stir while warm to room temperature for 1 h. $Na_2S_2O_3$ was then added. The organic layer was removed and the aqueous layer was extracted with ether three times. The organic portions were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The crude oil was purified on silica gel (10% Et_2O/hexane) to afford a colorless oil (4.9 g, 80% yield).

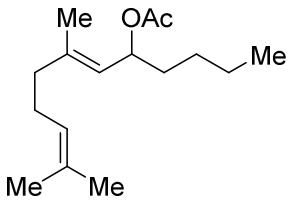
S-9 was subjected to conditions in general procedure **A** and **B** to obtain the desired starting material as a colorless oil (72% yield over 3 steps).



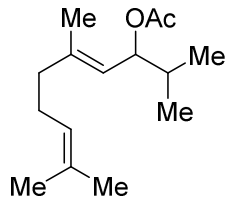
(*E*)-4,8-dimethylnona-3,7-dien-2-yl acetate (starting material for 4): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (3H, d, *J* = 6.4 Hz), 1.60 (3H, s), 1.68 (3H, s), 1.70 (3H, d, *J* = 1.3 Hz), 1.97-2.02 (2H, m), 2.01 (3H, s), 2.04-2.12 (2H, m), 5.07 (1H, br. t, *J* = 6.8 Hz), 5.16 (1H, d, *J* = 8.8 Hz), 5.59 (1H, dq, *J* = 15.1, 6.3 Hz); ^{13}C NMR (125 MHz $CDCl_3$): δ 16.6, 17.6, 20.9, 21.4, 25.6, 26.3, 39.4, 68.1, 123.8, 124.7, 131.7, 139.4, 170.4; IR (neat): 2974 (w), 2929 (w),1732 (m), 1447 (w), 1369 (m), 1240 (s), 1144 (w), 1040 (m), 951 (w) cm^{-1}; HRMS (ESI+) for $C_{11}H_{19}$ [M-OAc]: calculated: 151.1492, found: 151.1482. R_f = 0.65 in 10% EtOAc.



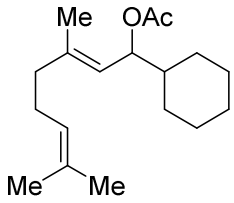
(*Z*)-4,8-dimethylnona-3,7-dien-2-yl acetate (starting material for 5): From commercially available *cis*-3,7-Dimethyl-2,6-octadien-1-ol (Nerol), general procedure **F**, **A**, and **B** were followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (3H, d, *J* = 6.3 Hz), 1.60 (3H, s), 1.67 (3H, s), 1.72 (3H, d, *J* = 1.4 Hz), 2.00 (3H, s), 2.01-2.17 (3H, m), 2.21-2.22 (1H, m), 5.09 (1H, br t, *J* = 6.8 Hz), 5.17 (1H, d, *J* = 9.3 Hz), 5.59 (1H, dq, *J* = 15.4, 6.1 Hz); ^{13}C NMR (125 MHz $CDCl_3$): δ 17.6, 21.2, 21.4, 23.3, 25.7, 26.5, 32.4, 67.8,123.8, 125.4, 132.0, 139.8, 170.3; IR (neat): 2969 (w), 2930 (w),2860 (w), 1734 (m), 1670 (w), 1447 (w), 1369 (m), 1240 (s), 1035 (m), 950 (w) cm^{-1}; HRMS (ESI+) for $C_{11}H_{19}$ [M-OAc]: calculated: 151.1492, found: 151.1534. The crude material was purified on silica gel (2% Et_2O/pentane) to afford a colorless oil (55% yield over 4 steps). R_f = 0.34 in 5% EtOAc/hexane.



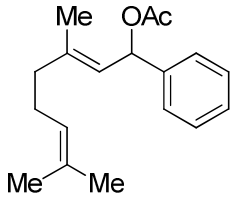
(*E*)-7,11-dimethyldodeca-6,10-dien-5-yl acetate (starting material for 6): From commercially available geraniol, and *n*-butyllithium, **procedure F, A,** and **B** was followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 7.0 Hz), 1.17-1.37 (4H, m), 1.44-1.52 (1H, m), 1.60 (3H, s), 1.60-1.66 (1H, m), 1.68 (3H, s), 1.71 (3H, d, *J* = 1.3 Hz), 1.98-2.20 (2H, m), 2.02 (3H, s), 2.06-2.12 (2H, m), 5.04-5.10 (2H, m), 5.47 (1H, dt, *J* = 9.0, 6.8 Hz); ^{13}C NMR (125 MHz $CDCl_3$): δ 7.0, 9.8, 10.7, 14.4, 15.5, 18.6, 19.2, 20.2, 27.7, 32.5, 64.6, 116.7, 116.9, 124.6, 133.2, 163.4; IR (neat): 2959 (w), 2930 (m), 2860 (w), 1734 (s), 1671 (w), 1443 (w), 1369 (m), 1238 (s) cm^{-1}; HRMS (ESI+) for $C_{14}H_{25}$ [M-OAc]: calculated: 193.1962, found: 193.1963. The crude material was purified on silica gel (2% Et_2O/pentane) to afford a clear oil (79% yield over 3 steps). R_f = 0.53 in 5% EtOAc/hexane.



(*E*)-2,5,9-trimethyldeca-4,8-dien-3-yl acetate (starting material for 7): From commercially available geraniol, and isopropylmagnesium chloride (2M in THF), general procedure **F, A,** and **B** was followed**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (3H, d, *J* = 12.2 Hz), 0.89 (3H, d, *J* = 6.8 Hz), 1.60 (3H, s), 1.67 (3H, s), 1.72 (3H, d, 1.3 Hz), 1.82 (1H, octet, *J* = 6.8 Hz), 2.01-2.04 (2H, m), 2.03 (3H, s), 2.06-2.14 (2H, m), 5.03-5.12 (1H, m), 5.28 (1H, dd, *J* = 9.5, 7.1 Hz); ^{13}C NMR (125 MHz $CDCl_3$): δ 16.9, 17.7, 17.8, 18.3, 21.3, 25.7, 26.3, 32.5, 39.7, 76.0, 122.0, 124.0, 131.6, 140.8, 170.5; IR (neat): 2964 (w), 2928 (w), 1734 (s), 1671 (w), 1446 (w), 1369 (m), 1239 (s), 1017 (m), 972 (m) cm^{-1}; HRMS (ESI+) for $C_{13}H_{23}$ [M-OAc]: calculated: 179.1805, found: 179.1828. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (68% yield over 3 steps). R_f = 0.4 in 5% EtOAc/hexane.

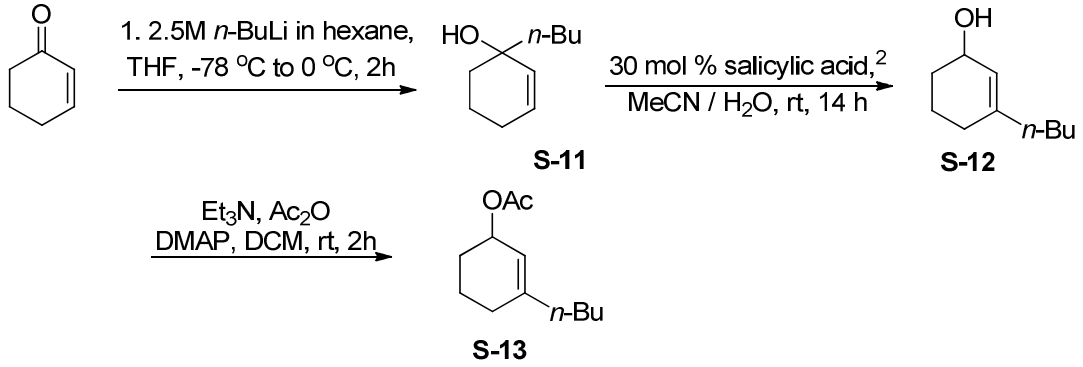


(*E*)-1-cyclohexyl-3,7-dimethylocta-2,6-dien-1-yl acetate (starting material for 8): From commercially available geraniol, and cyclohexylmagnesium chloride (2M in Et_2O), general procedure **F, A,** and **B** was followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86-1.02 (2H, m), 1.07-1.28 (4H, m), 1.44-1.54 (1H, m), 1.60 (3H, s), 1.62-1.69(2H, m), 1.65 (3H, s), 1.69-1.78 (2H, m), 1.70, (3H, s), 1.98-2.06 (2H, m), 2.00 (3H, s), 2.08-2.14 (2H, m), 5.01-5.10 (2H, m), 5.28 (1H, m); ^{13}C NMR (125 MHz $CDCl_3$): δ 16.9, 17.7, 21.3, 25.7, 25.9, 26.0, 26.2, 26.4, 28.3, 28.9, 39.7, 42.2, 75.3, 122.4, 124.0, 131.6, 140.6, 170.5; IR (neat): 2926 (s), 2854 (m), 1734 (s), 1450 (m), 1369 (m), 1240 (s), 1016 (m), 973 (m) cm^{-1}; HRMS (ESI+) for $C_{16}H_{27}$ [M-OAc]: calculated: 219.2113, found: 219.2123. The crude material was used without purification to give a clear oil (77% yield over 3 steps). R_f = 0.5 in 5% EtOAc/hexane.



(*E*)-3,7-dimethyl-1-phenylocta-2,6-dien-1-yl acetate (starting material for 9): From commercially available geraniol, general procedure **F, C,** and then **B** was followed**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.57 (3H, s), 1.65 (3H, s), 1.81 (3H, s), 2.03-2.11 (4H, m), 2.09 (3H, s), 5.02-5.06 (1H, s), 5.40 (1H, d, *J* = 8.8 Hz), 6.53 (1H, d, *J* = 8.8 Hz), 7.25-7.30 (1H, m), 7.34 (4H, d, *J* = 4.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.9, 17.6, 21.3, 25.6, 26.2, 39.5, 72.7, 123.3, 1213.7, 126.5, 127.6, 128.4, 131.8, 140.4, 140.7, 170.2; IR (neat): 2966 (w), 1734 (s), 1369 (m), 1230 (s), 1016, (m), 960 (m), 745 (m), 671 (s); HRMS (ESI+) for $C_{16}H_{22}$ $[M\text{-}OAc]^+$: calculated: 214.1722, found: 214.1802. The crude material was purified on silica gel (5% ether/hexane) to afford a colorless oil (55% yield). R_f = 0.29 in 5% ether/hexane.

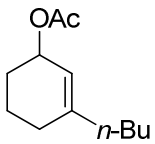
Synthesis and characterization of 3-butylcyclohex-2-en-1-yl acetate (starting material for 10):



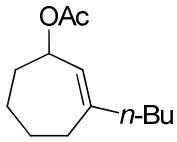
General procedure G:

Step 1: To a flame-dried round-bottomed flask charged with magnetic stir bar, under positive N_2 atmosphere was added by 8 mL THF. The flask was cooled to -78 ^oC, and 2.4 mL *n*-BuLi (2.54 M in hexane) was added dropwise. Cyclohexenone (0.49 mL, 5.0 mmol in 2 mL THF) was slowly added to the mixture. The flasked was warmed to 0 ^oC and allowed to stir for 2 hours. The reaction was then quenched with H_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O three times. The organics were combined and condensed *in vacuo* to afford **S-11**. The crude oil of **S-11** was used in the next step without further purification.

Step 2: [2] To a round-bottomed flask charged with stir bar and the crude oil of **S-11** was added MeCN (25 mL) and H_2O (D.I., 5 mL), followed by salicylic acid (210 mg, 1.5 mmol). The flask was capped and allowed to stir overnight. Saturated $NaHCO_3$ was added to the reaction mixture, the organic layer was separated and the aqueous layer was extracted with Et_2O three times. The combined organics were concentrated *in vacuo* to afford **S-12** as a light, yellow oil. The crude oil of **S-12** was subjected directly to acetylation conditions (general procedure **B**).

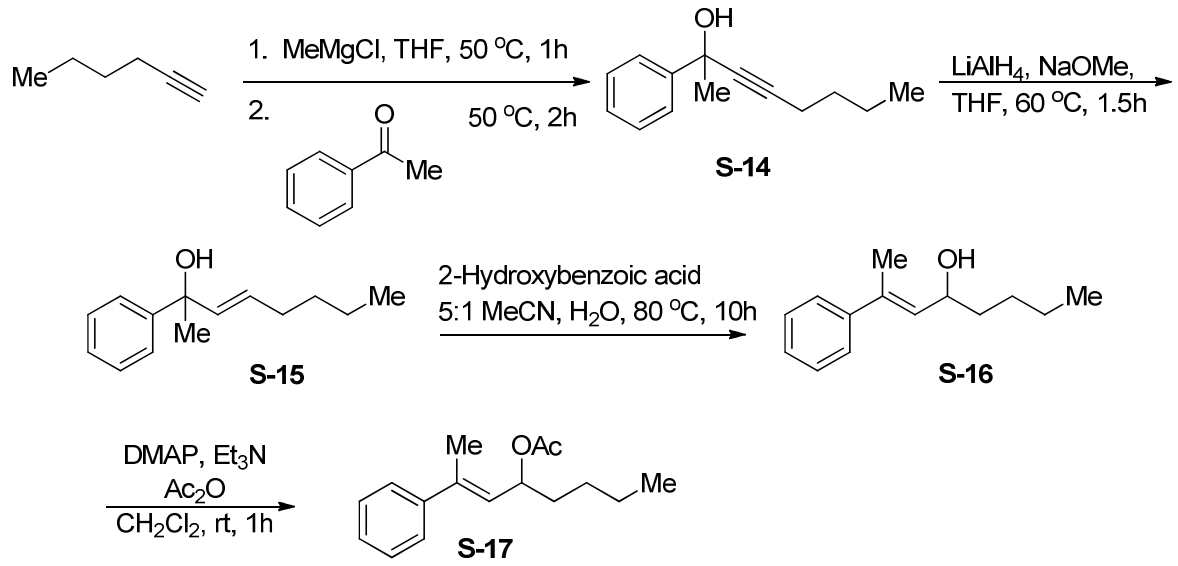


3-butylcyclohex-2-en-1-yl acetate (starting material for 10): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.8 Hz), 1.29 (2H, tq, *J* = 14.7, 7.4 Hz), 1.36-1.42 (2H, m), 1.54-1.80 (4H, m), 1.88-195 (1H, m), 1.97-2.00 (3H, m), 2.04 (3H, s), 5.27 (1H, br s), 5.44 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 19.1, 21.5, 22.4, 28.3, 28.4, 29.6, 37.3, 68.9, 119.3, 144.9, 170.9; IR (neat): 2930 (s), 1730 (s), 1369 (m), 1234 (s), 1057 (m), 909 (m); HRMS (ESI+) for $C_{10}H_{17}$ [M-OAc]$^{+}$: calculated: 137.1325, found: 137.1369. The crude material was purified on silica gel (5% ether/hexane) to afford a colorless oil (78% yield over 3 steps). R_f = 0.33 in 5% ether/hexane.



3-butylcyclohept-2-en-1-yl acetate (starting material for 11): Starting from cycloheptenone, general procedure **G** was followed; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 7.1 Hz), 1.25-1.39 (6H, m), 1.59-1.71 (4H, m), 1.78-1.82 (1H, m), 1.88-1.93 (1H, m), 1.94-1.99 (2H, m), 2.05 (3H, s), 2.03-2.18 (2H, m), 5.35-5.40 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 21.4, 22.3, 26.0, 27.1, 29.8, 32.4, 32.9, 39.8, 74.0, 127.1, 143.9, 170.4; IR (neat): 2926 (m), 1734 (s), 1367 (m), 1237 (s), 1024 (m), 840 (w); HRMS (ESI+) for $C_{11}H_{20}$ [M-OAc]$^{+}$: calculated: 152.1565, found: 152.1593. The crude material was purified on silica gel (5% ether/hexane) to afford a colorless oil. R_f = 0.24 in 5% ether/hexane.

Synthesis and chacracterization of (*E*)-2-phenyloct-2-en-4-yl acetate (starting material for 12):

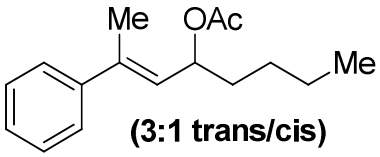


General Procedure H:

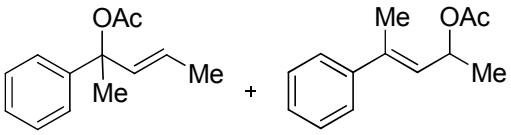
Step 1:[3] A flame-dried 2-neck round-bottom flask equipped with a reflux condenser, stir bar, and rubber septum was charged with THF (4 mL), methylmagnesium chloride (2.16 mL, 4.8 mmol, 2.2 M in THF) and 1-hexyne (0.55 mL, 4.8 mmol). The reaction was heated to 50 °C for 1 h, at which point the reaction was cooled to room temperature, and aceteophenone (0.47 mL, 4.0 mmol) was added dropwise *via* syringe. The reaction was warmed to 50 °C, and was allowed to stir for an additional 2 h. The solution was then cooled to room temperature and quenched with saturated aqueous ammonium chloride (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The organic portions were combined and washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*.

Step 2: Literature procedure was followed to reduce the alkyne and obtain **S-15**. [1]

The allylic alcohol **S-15** was subjected to conditions in procedure **G** (step 2) and procedure **B** to afford the desired allylic acetate **S-17**.



(*E*) & (*Z*)-2-phenyloct-2-en-4-yl acetate: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.77 (3H, t, *J* = 7.0 Hz, *cis*), 0.86 (3H, t, *J* = 7.0 Hz, *trans*), 1.06-1.19 (m), 1.20-1.34 (m), 1.36-1.48 (m), 1.52-1.60 (m), 1.66-1.74 (m), 1.93 (3H, s, *cis*), 1.99 (3H *trans* + 3H *cis*, s), 2.09 (3H, s, *trans*), 5.14 (1H, dt, *J* = 9.3, 6.6 Hz, *cis*), 5.36 (1H, dd, *J* = 9.3, 1.5 Hz, *cis*), 5.56-5.64 (2H, m, *trans*), 7.11-7.15 (m), 7.18-7.22 (m), 7.24-7.30 (m), 7.32-7.36 (m); ^{13}C NMR (125 MHz $CDCl_3$): δ 13.9, 14.0, 16.5, 21.3, 22.4, 22.6, 26.0, 27.1, 27.2, 34.6, 34.7, 71.7, 72.6, 125.9, 125.9, 126.6, 127.0, 127.3, 127.5, 128.2, 128.2, 138.7, 141.0, 141.1, 142.8, 170.1, 170.5; IR (neat): 2957 (w), 2932 (w), 2861 (w), 1732 (s), 1494 (w), 1445 (w), 1369 (m), 1235 (s), 1016 (m), 950(m) cm^{-1}; HRMS (ESI+) for $C_{14}H_{19}$ [M-OAc]: calculated:187.1418, found:187.1491. The crude material was purified on silica gel (10% ether/hexane) to afford a clear oil (24% yield over 4 steps). R_f = 0.33 in 5% EtOAc/hexane.

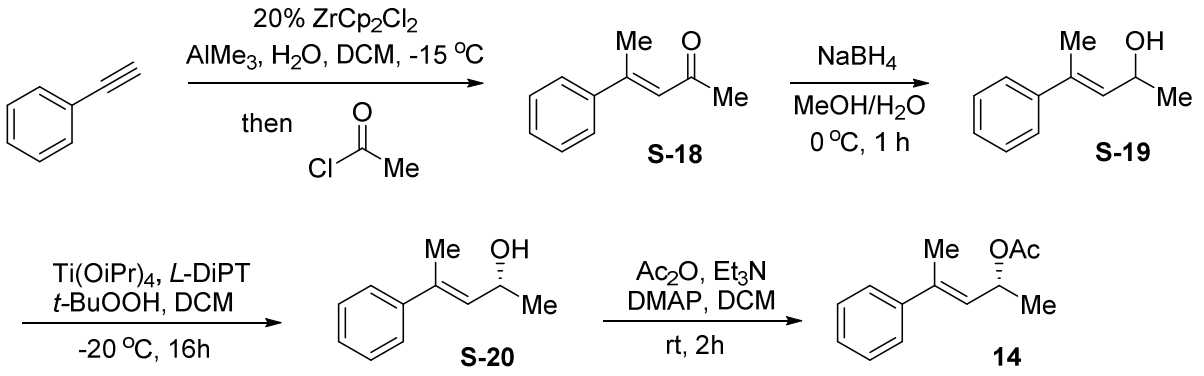


(*E*)-2-phenylpent-3-en-2-yl acetate (major) & (*E*)-4-phenylpent-3-en-2-yl acetate (minor) (starting material for 13): From commercially available (*E*)-pent-3-en-2-one, procedure **A** and **B** was followed. ^{1}H NMR (500 MHz, $CDCl_3$):1.37 (3H, d, *J* = 6.3 Hz, minor), 1.75 (3H, dd, *J* = 6.4, 1.9 Hz, major), 1.85 (3H, s, major), 2.05 (3H, s, minor), 2.06 (3H, s, major), 2.12 (3H, d, *J* = 1.5 Hz, minor), 5.67 (1H, app dq, *J* = 19.5, 6.4 Hz, major), 5.72-5.79 (2H, m, minor), 5.99 (1H, ddd, J = 15.1, 2.9, 1.4 Hz, major), 7.22-7.28 (1H major + 1 H minor, m), 7.31-7.36 (3H major + 3H

minor), 7.39-7.41 (1H major + 1H minor, m); ^{13}C NMR (125 MHz, $CDCl_3$): 16.3, 17.9, 20.8, 21.4, 22.3, 26.2, 68.3, 83.2, 125.1, 125.9, 126.2, 126.9, 127.0, 127.1, 127.3, 127.4, 127.5, 128.1, 128.2, 128.3, 134.6, 137.9, 142.7, 144.6, 169.4, 170.4; IR (neat): 3026 (w), 2935 (w), 1736 (s), 1494 (m), 1240 (s), 1119 (m), 913 (m), 760 (m), 699 (m); HRMS (ESI+) for $C_{13}H_{16}O_2$ [M-OAc]: calculated 145.1012, found 145.1003. The crude material was purified on silica gel (5% Et_2O/Pentane) to afford a colorless oil (30% yield over 2 steps). R_f = 0.38 in 5% EtOAc/hexane.

Synthesis of enantioenriched starting materials:

Synthesis and characterization of (*E*)-4-phenylpent-3-en-2-yl acetate (13)



General Procedure I:

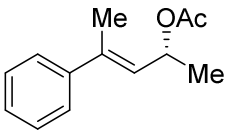
Step 1: Starting from phenylacetylene, literature procedure was followed.[4]

Step 2: General procedure **D**, step 2 was followed.

Step 3:[5] A flame dried round bottom flask equipped with a stir bar was charged with **S-19** (1.2 g, 7.6 mmol), *L*-(-)-DIPT (1.92 mL, 9.2 mmol), and CH_2Cl_2 (76 mL). The mixture was cooled to -20 °C and Ti(O*i*-Pr)$_4$ (2.26 mL, 7.6 mmol) was added. The solution stirred for 30 minutes, then

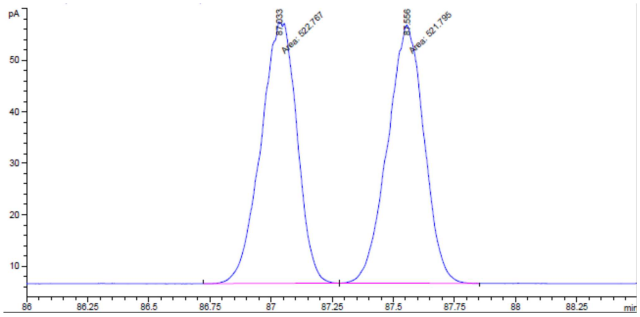
5.5 M. *t*-BuO_2H in decane (0.84 mL, 4.6 mmol) was added slowly *via* syringe. The reaction was stirred for 16 h. The reaction was then quenched with a cold solution of citric acid (6 g) and $FeSO_4 \cdot 7H_2O$ (16 g) in 50 mL D.I. H_2O and was stirred vigorously at room temperature, until the solution was clear. The organic layer was set aside and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic fractions were concentrated *in vacuo*, and the crude residue was dissolved in diethyl ether (50 mL). To this solution was added a solution of NaOH (20 g) and NaCl (3 g) in H_2O (50 mL) at 0 ^oC. The mixture stirred at 0 ^oC for 1 h before the addition of H_2O (25 mL). The organic layer was removed and the aqueous layer was extracted with ethylacetate three times. The organic portions were combined, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified on silica gel to afford the enantioenriched alcohol.

Step 4: General procedure **B** was followed to obtain the desired starting material **14**.

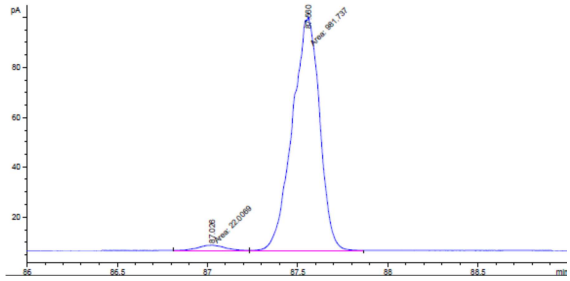


(*E*)-4-phenylpent-3-en-2-yl acetate (14): Spectral data is in accordance with literature values.[7]

Analysis of stereo chemistry: The enantiopurity was determined using chiral GLC (Chiral β-dex, Supelco, 60 ^{o}C for 5 minutes, ramp 1 ^{o}C / min to 140 ^{o}C, hold at 140 ^{o}C for 20 minutes, 20 psi, sr = 35:1). The absolute stereochemistry was determined by analogy to reported literature.[5]



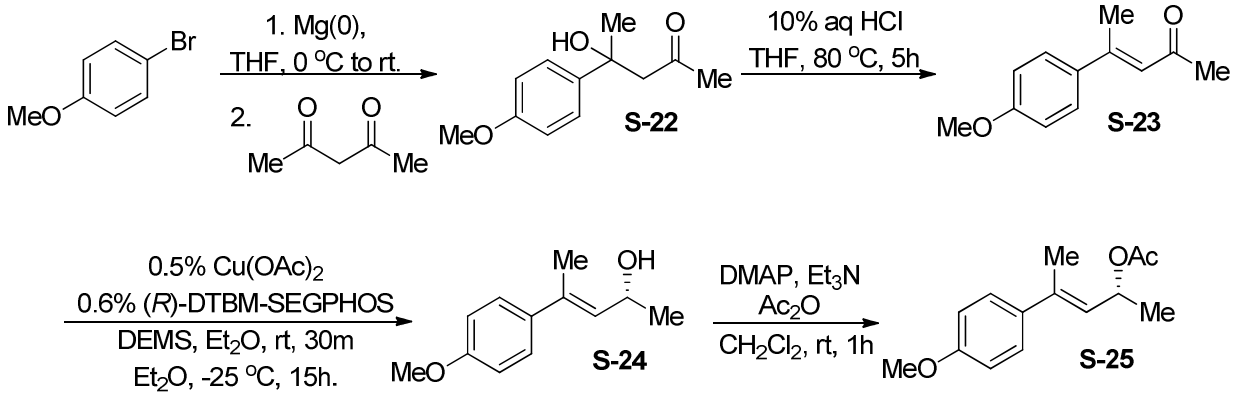
Racemic



Reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	87.026	MM	0.1676	22.00691	2.18899	2.19248
2	87.560	MM	0.1748	981.73694	93.59392	97.80752
Totals :				1003.74385	95.78291	

Synthesis and characterization of (*E*)-4-(4-methoxyphenyl)pent-3-en-2-yl acetate (starting material for 16):



General procedure K:

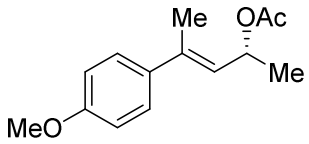
Step 1: Starting with 4-bromoanisole, **S-22** was obtained following literature procedure.[6]

Step 2: Adapted from literature procedure.[6] A round-bottomed flask was equipped with a stir bar and reflux condenser. The flask was charged with **S-22** (3.94 g, 16 mmol), THF (48 mL) and 10% HCl in H_2O (16 mL). The reaction was stirred at 80 ^oC for 1 h. The reaction was then diluted with H_2O and extracted with ethyl acetate three times. The organic portion was washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified on column chromatography (SiO_2, 20% EtOAc/hex) to afford ketone **S-23** as a white solid.

Step 3:[7] In the dry-box, an oven-dried 2-dram vial equipped with a stir bar was charged with anhydrous $Cu(OAc)_2$ (4.63 mg, 0.026 mmol) and (*R*)-DTBM-SEGPHOS (30.08 mg, 0.026 mmol). The vial was capped with a rubber septum and brought out of the box. At room temperature, dry ethyl ether (2 mL) and diethoxymethyl silane (2.45 mL, 15.3 mmol) were added under N_2. After stirring for 10 min, the reaction mixture was cooled to -25 ^oC. A solution of **S-23** (0.82 g, 5.1 mmol) in dry ethyl ether (1 mL) was added slowly *via* syringe. The mixture was

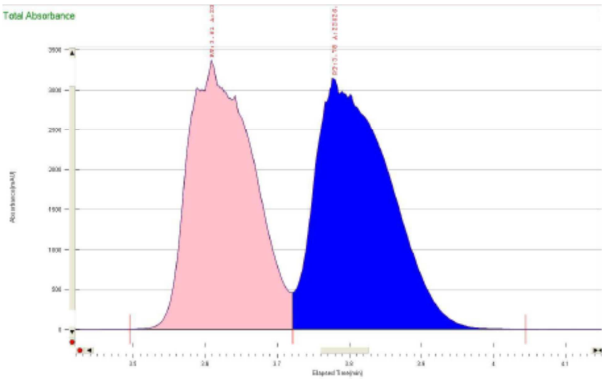
stirred for 15 h at -25 ^{o}C. To the mixture was added 1.0 M TBAF in THF (15.3 mL) and the reaction was stirred for an additional 1 h. MeOH (10 mL) was then added, and the reaction was warmed to room temperature, concentrated *in vacuo*, and filtered through a short SiO_2 plug. The crude material was then purified using column chromatography (SiO_2, 20% ethylacetate/hexane) to afford clean **S-24** as a colorless oil (814.2 mg, 83% yield).

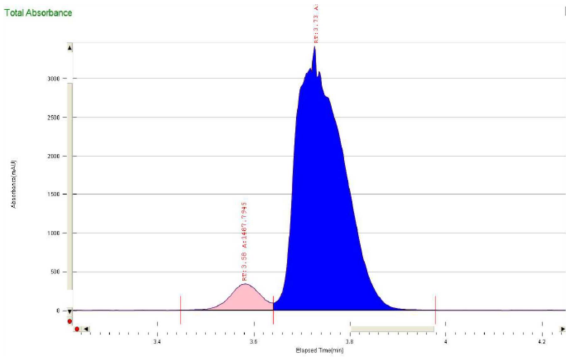
Step 4: General procedure **B** was followed to obtain the desired starting material.



(E)-4-(4-methoxyphenyl)pent-3-en-2-yl acetate (S-25): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (3H, d, *J* = 6.3 Hz), 2.05 (3H,s), 2.10 (3H, s), 3.81 (3H, s), 5.67 (1H, d, *J* = 8.8 Hz), 5.76 (1H, dq, *J* = 8.8, 6.3 Hz), 6.86 (2H, d, *J* = 8.8 Hz), 7.34 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3, 20.9, 21.4, 55.3, 68.4, 113.6, 125.9, 126.9, 135.1, 137.3, 159.1, 170.4; IR (neat): 2977(br), 2932 (br), 2837 (w), 1732 (m), 1607 (w), 1513 (m), 1444 (w), 1370 (w), 1289 (w), 1242 (s), 1181 (w), 1036 (m) cm^{-1}; HRMS (ESI+) for $C_{14}H_{19}O_3$ [M+H]: calculated: 235.1334, found: 235.1321. The crude material was purified on silica gel (7% ether/pentane) to afford a corlorless oil (15% yield over 4 steps). R_f = 0.12 in 5% EtOAc/hexane.

Analysis of stereo chemistry: The enantiopurity was determined on alohol **S-24** using chiral SFC (OJ-H, Chiralpak, 3mL/min, 4% isopropanol, 100 bar, 35 ^{o}C). The absolute stereochemistry was determined by analogy to reported literature.[7]



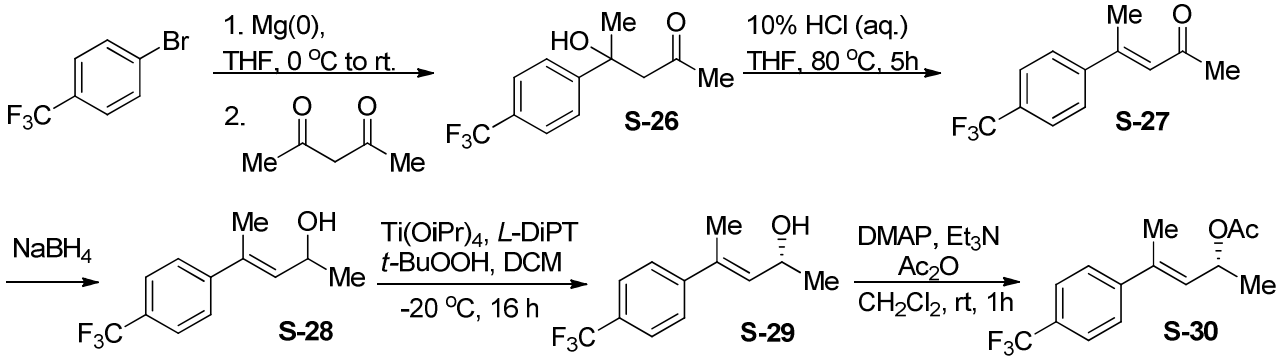


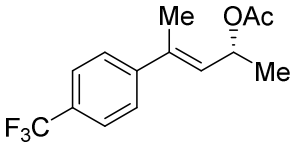
Racemic

Reaction product

Peak No	% Area	Area	RT (min)
1	6.1967	1487.7945	3.58
2	93.8033	22521.5346	3.73
Total:	100	24009.3291	

Synthesis and characterization of (*E*)-4-(4-(trifluoromethyl)phenyl)pent-3-en-2-yl acetate (starting material for 17):

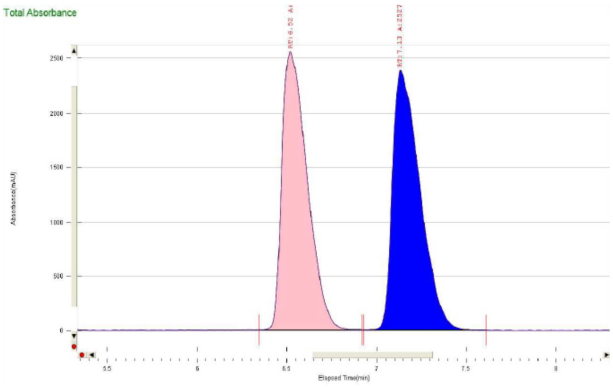




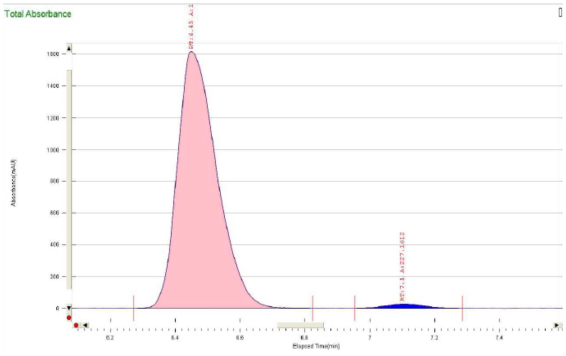
(*E*)-4-(4-(trifluoromethyl)phenyl)pent-3-en-2-yl acetate (S-30): From commercially available 4-bromobenzotrifluoride, procedure **K**, step 1 and 2 was followed, then procedure **I** step 3 and 4 and procedure **B** was followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.40 (3H, d, *J* = 5.9 Hz), 2.05 (3H, s), 2.14 (3H, d, *J* = 1.5 Hz), 5.73-5.80 (2H, m), 7.43 (2H, d, *J* = 8.3 Hz), 7.57 (2H, d, *J* = 8.3 Hz); (125 MHz,

$CDCl_3$): δ 16.3, 20.6, 21.3, 68.1, 123.1, 125.1, 125.2, 125.3, 125.4, 126.2, 129.4 (q, $^2J_{CF}$ = 32.4 Hz), 136.7, 146.2, 170.4; IR (neat): 2979 (br), 1738 (m), 1616 (w), 1371 (w), 1326 (s), 1240 (m), 1165 (m), 1124 (m), 1072 (m), 1042 (w), 1014 (w), 946 (w) cm^{-1}; HRMS (ESI+) for $C_{14}H_{15}F_3O_2$ [M+H]: calculated: 273.1102, found: 273.1099. The crude material was purified on silica gel (10% ether/pentane) to afford a colorless oil. R_f = 0.22 in 5% EtOAc/hexane.

Analysis of stereo chemistry: The enantiopurity was determined on alohol **S-29** using chiral SFC (OD-H, Chiralpak, 3mL/min, 3% Isopropanol, 100 bar, 35 ^oC). The absolute stereochemistry was determined by analogy to reported literature.[5]



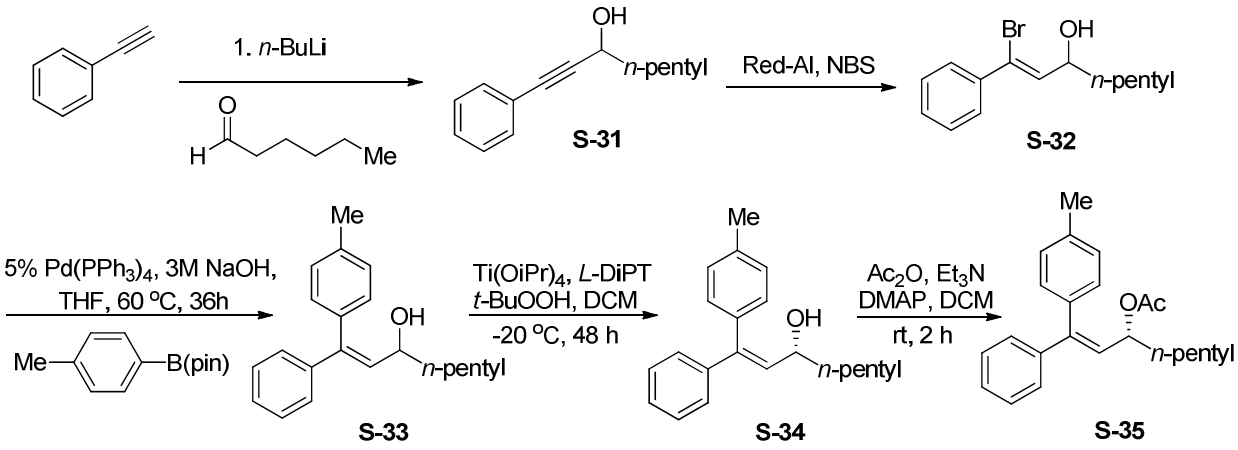
Racemic



Reaction product

Peak No	% Area	Area	RT (min)
1	98.3578	13605.9216	6.45
2	1.6422	227.1612	7.1
Total:	100	13833.0828	

Synthesis and characterization for (*R*, *Z*)-1-phenyl-1-(*p*-tolyl)hept-1-en-3-yl acetate (starting material for 18)



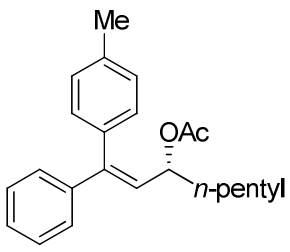
Step 1: To a flame-dried round bottom flask under possitive N_2 pressure was added 2.5M *n*-BuLi (3 mL, 24 mmol), followed by THF (30 mL). The flask was cooled to -78 ^oC and phenyl acetylene (2.2 mL, 20 mmol) in 5 mL THF was added dropwise. After 15 minutes, hexanal (3 mL, 24 mmol) in 5 mL THF was added dropwise via syringe. The reaction was stirred for 1 h at room temperature. The reaction was then worked up by slow addition of H_2O at 0 ^oC. The reaction mixture was then transfered to a separatory funnel; and the organic layer was seperated. The aqueous layer was extracted with ethylacetate 3 times. The organics were combined and condensed *in vacuo*. The crude material was purified on silica gel to afford the desired propargyl alcohol **S-31** as a colorless oil (3.5 g, 80% yield).

Step 2: To a dried round-bottomed flask under positive N_2 pressure was added Red-Al (3.93 mL, 65 wt % in Tol), followed by 30 mL of dried Et_2O. The reaction was cooled to 0 ^oC, then **S-31** in 10 mL Et_2O was added dropwise via syringe. The reaction was stirred for 4 h at room temperature, then freshly D.I. ethylacetate (1 mL, 10 mmol) was added dropwise at 0 ^oC. The

reaction was then cooled to -78 ^{o}C and NBS (2.7 g, 15 mmol) was added at once. The reaction was then warmed to room temperature and allowed to stir overnight. Saturated aqueous $Na_2S_2O_3$ was added to the mixture at 0 ^{o}C. The organic layer was seperated and the aqueous layer was extracted with ethyl acetate three times. The combined organics were then condensed *in vacuo* and purified using column chromatography (SiO_2, 10% EtOAc/hex) to afford the desired product (2.3 g, 80 % yield).

Step 3: Inbox, to a 3-neck round-bottomed flask charged with stir bar was added $Pd(PPh_3)_4$ (290 mg, 0.25 mmol), **S-32** (1.4 g, 5.0 mmol), and 4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane. The flask was capped and brought out of the dry box. A previously oven-dried reflux condenser was added, and the entire system was put under possitive N_2 pressure. 10 mL THF and 3mL of 3M aqueous NaOH was added to the reaction via syringe. The reaction was heated to 60 ^{o}C for 48 h. The reaction was then cooled to room temperature, and diluted with H_2O and Et_2O. The organic layer was seperated and the aqueous layer was extracted three times with Et_2O. The combined organics was then condensed *in vacuo* and purified using column chromatography (SiO_2, 10% EtOAc/hex) to afford the desired product (1.0 g, 63% yield).

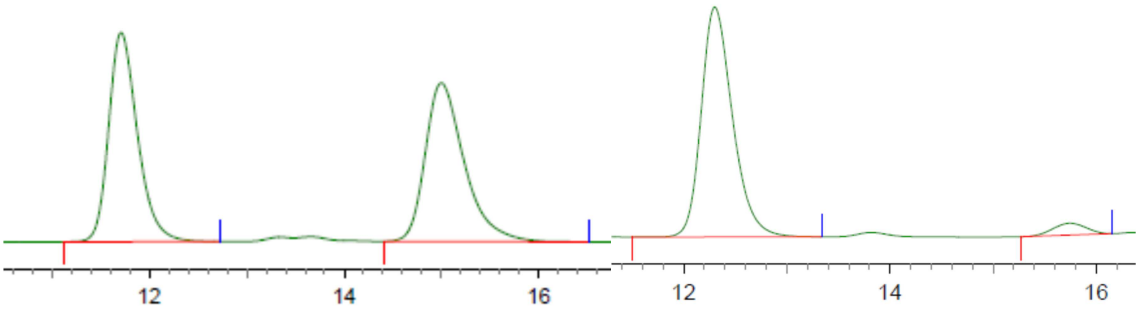
Step 4 and 5 was carried out following general procedure **I**, step 4 and general procedure **B** to afforded the desired starting material.



(*R*, *Z*)-1-phenyl-1-(*p*-tolyl)hept-1-en-3-yl acetate (Starting material for 18): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.83 (3H, *t*, *J* = 9.7, 7.3 Hz), 1.13-1.30 (6H, m), 1.54-1.61 (1H, m), 1.66-1.71 (1H, m), 2.02 (3H, s), 2.38 (3H, s), 5.35 (1H, dt, *J* = 13.2, 6.8 Hz), 5.97 (1H, d, *J* = 9.2 Hz), 7.10 (2H, d, *J* = 8.4 Hz), 7.19 (2H, d, *J* = 7.3 Hz), 7.22-7.29 (5H, m); ^{13}C NMR (125 MHz,

$CDCl_3$): δ 13.9, 21.2, 21.3, 22.5, 24.7, 31.5, 35.0, 72.9, 127.0, 127.4, 127.6, 128.1, 128.9, 129.4, 136.1, 137.1, 141.9, 144.5, 170.1; IR (neat): 2928 (m), 1733 (s), 1367 (m), 1234 (s), 1016 (m), 821 (m), 763 (s), 696 (s). HRMS (ESI+) for $C_{21}H_{26}$ $[M\text{-}OAc]^+$: calculated:278.2035, found: 278.1996. $[\alpha]^{20}_D$ = -3.546 (*c* = 3.654, $CHCl_3$)The crude material was purified on silica gel (5% ether/hexane) to afford a colorless oil. R_f = 0.24 in 5% ether/hexane.

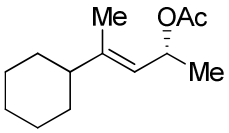
Analysis of stereo chemistry: The enantiopurity was determined on alohol **S-34** using chiral HPLC (AD-H, Chiralpak, 1.0 mL/min, 1% isopropanol/hexane, 254 nm). The absolute stereochemistry was determined by analogy to reported literature.[5]



Racemic Reaction product

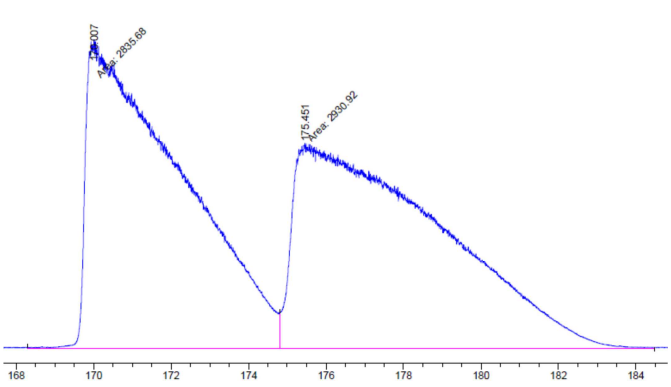
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
12.300	953877701	94.79	44950119	95.11
15.747	52453552	5.21	2312137	4.89
Totals	1006331253	100.00	47262256	100.00

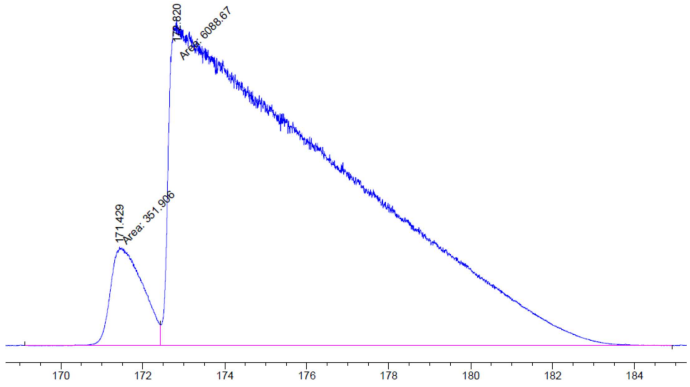


(*R*, *E*)-4-cyclohexylpent-3-en-2-yl acetate (staring material for 19): starting from cyclohexylacetylene, general procedure **I** was followed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08-1.31 (5H, m), 1.25 (3H, d, *J* = 6.3 Hz), 1.63-1.72 (3H, m), 1.73-1.86 (3H, m), 1.66 (3H, s), 2.01 (3H, s), 5.14 (1H, d, *J* = 6.0 Hz), 5.60 (1H, app dq, *J* = 16.5, 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.0, 20.1, 21.5, 26.3, 26.5, 26.6, 31.6, 31.7, 47.0, 68.2, 122.7, 144.6, 170.4; IR (neat): 2852 (m), 1735, (s), 1448 (m), 1368 (m), 1240 (s), 1041 (m), 852 (m); HRMS (ESI+) for $C_{11}H_{19}$ $[M\text{-}OAc]^+$: calculated: 151.1481, found: 151.1565; $[\alpha]^{20}_D$ = 19.051 (*c* = 2.150, $CHCl_3$)

Analysis of stereo chemistry: The enantiopurity was determined using chiral GLC (Chiral β-dex, Supelco, 90 ^{o}C for 150 minutes, 20 psi, sr = 35:1). The absolute stereochemistry was determined by analogy to reported literature.[5]

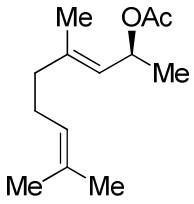


Racemic



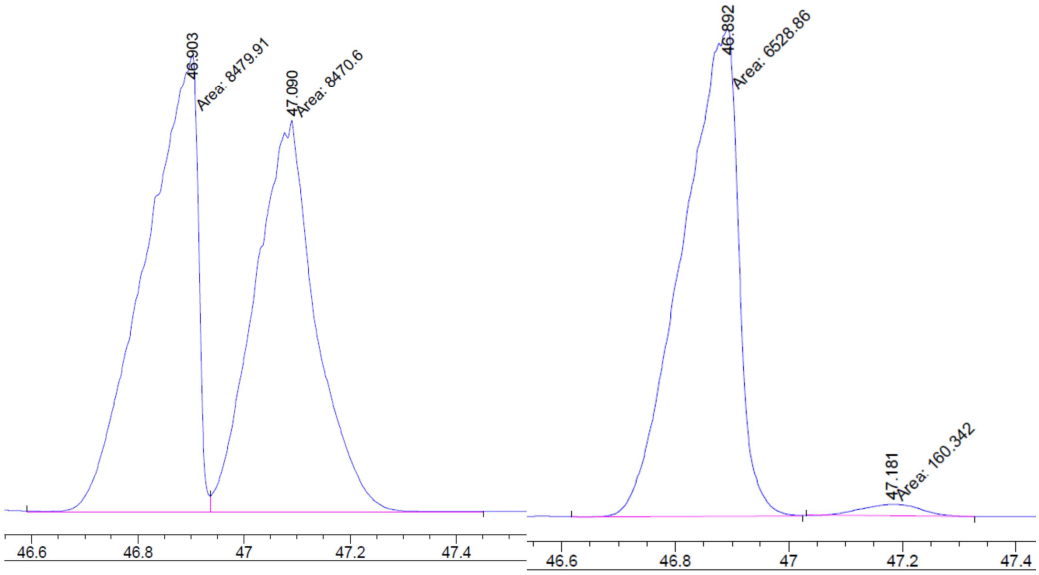
Reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	171.429	MF	0.9040	351.90646	6.48791	5.46390
2	172.820	FM	4.7795	6088.67041	21.23188	94.53610
Totals :				6440.57687	27.71979	



(*S, E*)-4,8-dimethylnona-3,7-dien-2-yl acetate (starting material for 20): Starting from geraniol and *D*-DIPT, the desired compound was synthesized using literature procedure.[5]

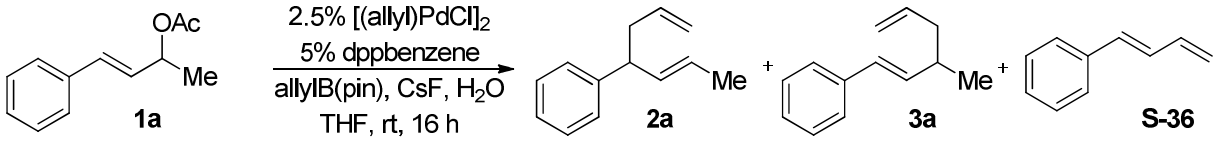
Analysis of stereo chemistry: The enantiopurity was determined using chiral GLC (Chiral β-dex, Supelco, 60 ^{o}C for 10 minutes, ramp 2 ^{o}C/min to 180 ^{o}C, 20 psi, sr = 35:1). The absolute stereochemistry was determined by analogy to reported literature.[5]



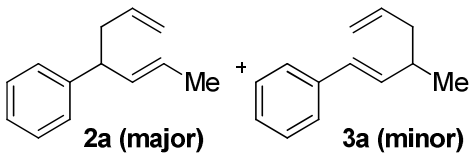
Racemic Reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.892	MM	0.1148	6528.85547	947.90997	97.60297
2	47.181	MM	0.1187	160.34241	22.51488	2.39703
Totals :				6689.19788	970.42485	

III. Synthesis and Characterization of the Allyl-Allyl Coupling Products

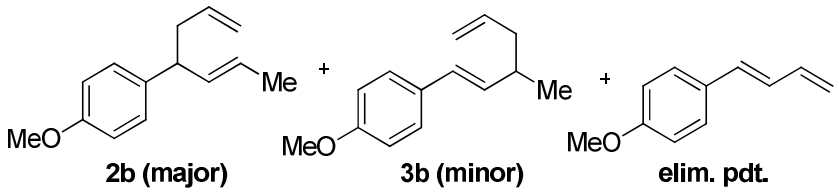


General procedure L: In the dry-box, an oven dried 2-dram vial equipped with a stir bar was charged with (η^3-allylPdCl)$_2$ (1.4 mg, 0.0038 mmol), dppbenzene (4.6 mg, 0.0075 mmol), and THF (0.25 mL). The resulting solution was allowed to stir at room temperature for 5 min. At this time, the vial was sequentially charged with **1a** (37.2 mg, 0.15 mmol), allylB(pin) (75.6 mg, 0.45 mmol), CsF (228 mg, 1.5 mmol), and THF (0.75 mL). The vial was tightly capped with a rubber septum, removed from the dry-box, and placed under a positive pressure of N_2. Degassed H_2O was then added (40 µL) *via* a glass syringe. The rubber septum was rapidly exchanged with a polypropylene cap, sealed with tape, and the reaction was allowed to stir at room temperature for 16 h. The slurry was diluted with water, the organic layer was separated and the aqueous layer was extracted three times with Et_2O. The organic portion was dried with Na_2SO_4 filtered, and concentrated under reduced pressure. The crude material was purified by silica gel chromatography (100% pentane) to yield a 6:2:1 mixture of **2a**, **2b**, and elimination product **S-36**. The combined yield of **2a** and **2b** was calculated to be 88%. **S-36** can be removed by treating the mixture with maleic anhydride (30mg, 0.3 mmol) in THF at 60 ^oC for 3 h.



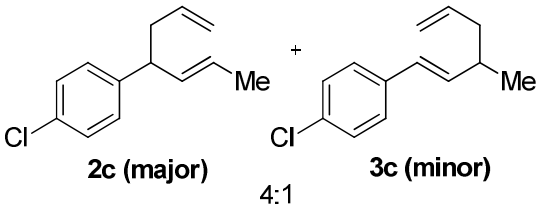
(*E*)-hepta-1,5-dien-4-ylbenzene (2a, major) & (*E*)-(3-methylhexa-1,5-dien-1-yl)benzene (3a, minor): ^1H NMR (500 MHz, $CDCl_3$): δ 1.11 (3H, d, *J* = 6.8 Hz, minor), 1.66 (3H, d, *J* = 5.6 Hz, major), 2.10-2.26 (2H, m, minor), 2.36-2.54 (2H+1H, m,

major+minor), 3.70 (1H, q, *J* = 8.3 Hz, major), 4.95-5.09 (2H+2H, m, major+minor), 5.50-5.61(2H, m, major), 5.70-5.87(1H+1H, m, major+minor), 6.16 (1H, dd, *J* = 15.9, 7.3 Hz, minor), 6.37 (1H, d, *J* = 15.9 Hz, minor), 7.17-7.38 (5H + 5H, m, major + minor); ^{13}C NMR (125 MHz $CDCl_3$): δ 13.2, 19.9, 36.9, 41.1, 41.4, 43.0, 115.9,116.0, 124.0, 126.0, 126.0, 126.8, 127.3, 128.2, 128.4, 128.5, 133.8, 136.0,136.7, 137.0, 137.8, 144.9); IR (neat): 3077(m), 3026 (m), 2976 (m), 2922 (m), 1640 (m), 1600 (w), 1493(m), 1451 (m), 1072 (w), 1030 (w), 994(s) cm^{-1}; HRMS (ESI+) for $C_{13}H_{17}$ [M +H]: calculated: 173.1330, found: 173.1333. The crude material was purified on silica gel (100% pentane) to afford a colorless oil. R_f = 0.81 in 5% EtOAc/hexane.

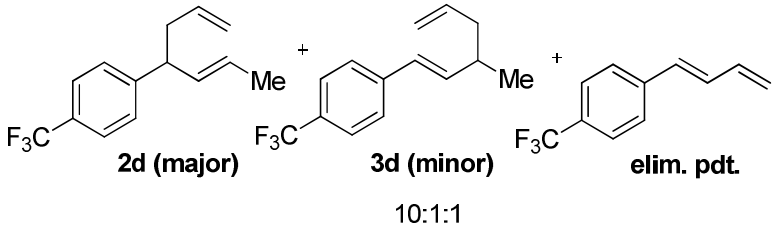


(*E*)-1-(hepta-1,5-dien-4-yl)-4-methoxybenzene (2b, major) & (*E*)-1-methoxy-4-(3-methylhexa-1,5-dien-1-yl)benzene (3b, minor): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09 (3H, d, *J* = 6.8 Hz, minor), 1.65 (3H, d, *J* = 4.9 Hz, major), 2.06-2.24 (2H, m, minor), 2.33-2.49 (2H, m, major), 2.82-2.89 (1H, m, minor), 3.65 (1H, td, *J* = 8.3, 6.6 Hz, major), 3.79 (3H, s, major), 3.81 (3H, s, minor), 3.82 (3H, s, elim. pdt.), 4.95-5.06 (2H minor + 2H elim. pdt., m), 4.97 (1H, d, *J* = 10.3 Hz, major), 5.03 (1H, d, *J* = 17.1 Hz, major), 5.47-5.57 (2H, m, major), 5.74 (1H, ddt, *J* = 17.1, 10.3, 6.8 Hz, major), 5.82 (1H, ddt, *J* = 17.1, 9.8, 7.3 Hz, minor), 6.01 (1H, dd, *J* = 15.6, 7.3 Hz, minor), 6.29-6.32 (1H, m, elim. pdt.), 6.82-6.88 (2H major + 2H minor, m), 7.11-7.16 (2H major + 2H elim. pdt., m), 7.21 (2H elim. pdt., m), 7.29 (2H minor, m); ^{13}C NMR (125 MHz $CDCl_3$): δ 13.1, 41.2, 42.1, 55.2, 113.8, 115.8, 123.7,

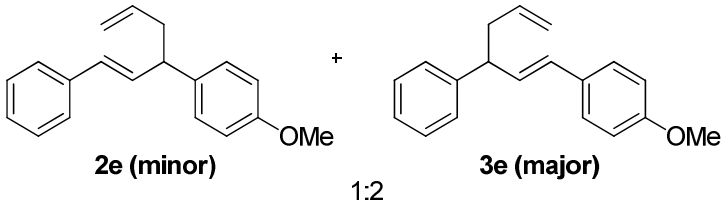
128.2, 134.1, 136.8, 137.1, 157.8; IR (neat): 3074 (w), 3007 (w), 2914 (w), 2835 (w), 1609(w), 1510 (s), 1463 (w), 1441 (w), 1302 (w), 1247 (s), 1177 (m), 996 (m) cm^{-1}; HRMS (ESI+) for $C_{14}H_{18}O_1$ [M +H]: calculated: 203.1435, found: 203.1443. The crude material was purified on silica gel (1% ether/pentane) to afford a colorless oil (22mg, 70% combined yield for **2b** and **3b**). R_f = 0.52 in 5% ether/hex



(*E*)-1-chloro-4-(hepta-1,5-dien-4-yl)benzene (2c, major) & (*E*)-1-chloro-4-(3-methylhexa-1,5-dien-1-yl)benzene (3c, minor): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11 (3H, d, *J* = 6.8 Hz, minor), 1.65 (3H, d, *J* = 5.3 Hz, major), 2.09-2.23 (2H, m, minor), 2.34-2.49 (2H + 1H, m, major+minor), 3.67 (1H, q, *J* = 7.5 Hz, major), 4.99 (1H, d, *J* = 10.3 Hz, major), 5.03 (1H, d, *J* = 17.1 Hz, major), 4.96-5.08 (2H, m, minor),5.49-5.47 (2H, m, major), 5.71 (1H, ddt, *J* = 17.2, 10.3, 6.9 Hz, major), 5.81 (1H, ddt, *J* = 17.1, 10.1, 7.1 Hz, minor), 6.14 (1H, dd, *J* = 15.9, 7.5 Hz, minor), 6.32 (1H, d, *J* = 15.6 Hz, minor), 7.10-7.30 (4H major + 4H minor, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.2, 19.8, 36.9,41.1, 41.3, 42.4, 116.1, 116.3, 124.5,127.1, 127.2, 128.5, 128.6, 128.7, 131.6, 133.3, 136.2, 136.8, 143.4; IR (neat): 3077(w), 3013 (w), 2977 (w), 2922 (w), 1640 (w), 1491 (s), 1439 (m), 1371 (w), 1092 (s), 1014 (s), 994 (m), 967 (m), 913(s) cm^{-1}; HRMS (ESI+) for $C_{13}H_{15}Cl$ [M +H]: calculated: 207.0948, found: 207.0941. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (28mg, 92% combined yield for **2c** and **3c**). R_f = 0.93 in 5% EtOAc/hexane.

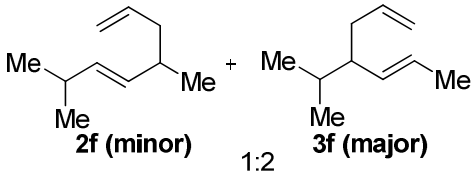


(*E*)-1-(hepta-1,5-dien-4-yl)-4-(trifluoromethyl)benzene (2d, major) & (*E*)-1-(3-methylhexa-1,5-dien-1-yl)-4-(trifluoromethyl)benzene (3d, minor) & (E)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (elim. pdt.): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.11 (3H, d, *J* = 6.9 Hz, elim. pdt.), 1.64 (3H, d, *J* = 5.4 Hz, major), 1.68 (3H, d, *J* = 6.4 Hz, minor), 2.11-2.25 (1H, m, minor), 2.37-2.52 (2H+1H, m, major + minor), 3.14 (1H, ap. t, *J* = 8.0 Hz, minor), 3.67 (1H, q, *J* = 7.4 Hz, major), 4.94-5.08 (6H, m, major + minor + elim. pdt.), 5.46 (1H, dq, *J* = 15.6, 6.4 Hz, minor), 5.51-5.62 (2H+1H, m, major + minor), 5.64-5.75 (2H, m, major + minor), 5.75-5.85 (1H, m, elim. pdt.), 6.25 (1H, dd, *J* = 16.1, 7.8 Hz, elim. pdt.), 6.39(1H, d, *J* = 15.7 Hz, elim. pdt.); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.2, 14.0, 17.9, 19.7, 22.3, 29.7, 34.1, 36.9, 40.1, 40.9, 41.2, 42.9, 48.6, 116.2, 116.4, 116.5, 119.4, 125.0, 125.2, 125.3 (q, $^{3}J_{CF}$ = 3.8 Hz), 126.1, 126.5, 127.1, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 132.8, 133.5, 135.9, 136.2, 136.6, 138.8, 149.0; IR (neat): 3026 (w), 2917 (w), 1639 (w), 1598 (w), 1493 (m), 1445 (m), 1375 (w), 973 (s), 912 (s) cm^{-1}; HRMS (ESI+) for $C_{14}H_{15}F_3$ [M +H]: calculated: 241.1204, found: 241.1197. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (17.4mg, 50% combined yield for **2d** and **3d**). R_f = 0.8 in 5% ether/hexane



2e (minor) 1:2 3e (major)

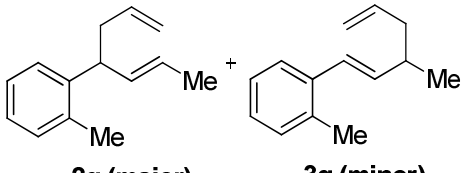
(*E*)-1-methoxy-4-(1-phenylhexa-1,5-dien-3-yl)benzene (2e, minor) & (*E*)-1-methoxy-4-(3-phenylhexa-1,5-dien-1-yl)benzene (3e, major): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.54-2.62 (2H major + 2H minor, m), 3.50 (1H major + 1H minor, app dt, J = 14.7, 7.3 Hz), 3.79 (3H major, s), 3.80 (3H minor, s), 4.98 (1H major + 1H minor, d, *J* = 10.4 Hz), 5.05 (1H major + 1 H minor, d = 17.1 Hz), 5.72-5.82 (1H major + 1H minor, m), 6.22 (1H major, dd, *J* = 15.7, 7.3 Hz), 6.31-6.38 (1H major + 2H minor, m), 6.83 (2H major, d, *J* = 8.3 Hz), 6.87 (2H minor, d, *J* = 8.8 Hz), 7.16-7.36 (7H major + 7H minor, m); ^{13}C NMR (150 MHz, $CDCl_3$): δ 40.2, 40.3, 48.1, 49.0, 55.2, 55.3, 113.9, 116.3, 126.2, 126.3, 127.1, 127.3, 127.4, 127.8, 128.2, 128.5, 128.6, 128.7, 129.2, 129.5, 129.9, 130.3, 131.4, 133.9, 135.9, 136.7, 137.5, 144.1, 158.1, 158.9; IR (neat): 3001 (w), 1639 (m), 1510 (s), 1463 (m), 1247 (s), 1175 (m), 1035 (m), 993 (m), 699 (m); HRMS (ESI+) for $C_{19}H_{20}O$ $[M+H]^+$: calculated: 265.1592, found: 265.1580. The crude material was purified on silica gel (2% ether/pentane) to afford a clear oil (29 mg, 75% combined yield for **2e** and **3e**). R_f = 0.5 in 2% ether/hexane.



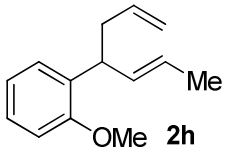
2f (minor) 1:2 3f (major)

(*E*)-4,7-dimethylocta-1,5-diene (2f, minor) and (*E*)-4-isopropylhepta-1,5-diene (3f, major): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (3H, d, *J* = 6.8 Hz, major), 0.89 (3H, d, *J* = 6.8 Hz, major), 0.92-0.98 (3H, m, minor), 0.94 (6H, d, *J* = 6.4 Hz, minor), 1.58 (3H, dd, *J* = 6.8, 2.0 Hz, major), 1.61 (1H, m, major), 1.98 (2H, m, major), 2.04-2.30 (4H, m, major+minor), 2.48-2.62 (2H, m, minor), 4.91-5.05 (4H, m, major+minor), 5.12 (1H, d, *J* = 10.2 Hz, minor), 5.17 (1H, t, *J* = 10.8 Hz, major), 5.53 (1H, dq, *J*

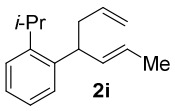
= 10.3 Hz, 6.8 Hz, major), 5.70-5.81 (1H major + 1 H minor, m); ^{13}C NMR (125 MHz $CDCl_3$): δ 13.3, 18.7, 20.7, 21.1, 23.3, 23.5, 26.8, 31.7, 32.0, 37.4, 41.9, 42.8, 115.0, 115.4, 124.3, 132.8, 133.0, 136.2, 137.4, 137.9; IR (neat): 2960 (w), 2923 (br), 1465 (w), 1384 (w), 903 (s), 724 (s), 650 (m) cm^{-1}; HRMS (ESI+) for $C_{10}H_{17}$ [M-H]: calculated: 137.1330, found: 137.1328. The crude material was purified on silica gel (100% pentane) to afford a colorless oil. R_f = 0.49 in 5% EtOAc/hexane.



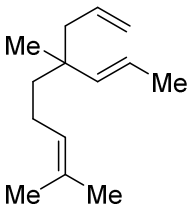
(*E*)-1-(hepta-1,5-dien-4-yl)-2-methylbenzene (2g) & (*E*)-1-methyl-2-(3-methylhexa-1,5-dien-1-yl)benzene (3g): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (3H, d, *J* = 6.6 Hz, minor), 1.66 (3H, d, *J* = 4.9 Hz, major), 2.12-2.26 (2H, m, minor), 2.34 (3H, s, minor), 2.36 (3H, s, major), 2.38-2.49 (2H, m, major), 3.84-3.93 (1H, m, major), 4.96-5.08 (2H major + 2H minor, m), 5.48-5.56 (2H, m, major), 5.76 (1H, ddt, 17.1, 10.3, 7.1 Hz, major), 5.83 (1H, ddt, *J* = 17.1, 10.0, 7.1 Hz, minor), 6.10 (1H, dd, *J* = 15.7, 7.6 Hz, minor), 6.55 (1H, d, *J* = 15.9 Hz, minor), 7.06-7.20 (m, major and minor), 7.23 (1H, d, *J* = 7.8 Hz, major), 7.41 (1H, d, *J* = 7.1 Hz minor); ^{13}C NMR (125 MHz, $CDCl_3$): δ major (143.2, 136.9, 135.4, 133.8, 130.3, 126.3, 126.2, 125.7, 123.9, 115.9, 40.7, 38.7, 19.7, 13.3) minor (137.5, 137.0, 135.0, 130.1, 126.7, 126.1, 126.0, 125.5, 115.9, 41.5, 37.2, 20.1, 19.8); IR (neat): 3074 (m), 3017 (m), 2975 (m), 2860 (m), 1640 (m), 1603 (w), 1488 (m), 1461 (m), 1440 (m), 912 (s), 751(s), 726 (s) cm^{-1}; HRMS (ESI+) for $C_{14}H_{18}$ [M +H]: calculated: 187.1482, found: 187.1487. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (26 mg, 94 % combined yield for **2g** and **3g**). R_f = 0.71 in 5% EtOAc/hexane.



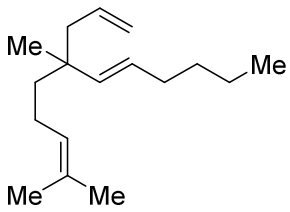
(*E*)-1-(hepta-1,5-dien-4-yl)-2-methoxybenzene (2h): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (3H, d, *J* = 6.8 Hz), 2.38 (1H, app dt, *J* = 14.2, 7.3 Hz), 2.46 (1H, app dt, *J* = 13.7, 5.9 Hz), 3.84 (3H, s), 4.13 (1H, app q, *J* = 6.3 Hz), 4.94 (1H, d, *J* = 10.2 Hz), 5.00 (1H, d, *J* = 17.1 Hz), 5.46-5.53 (1H, m), 5.56-5.61 (1H, m), 5.76 (1H, ddt, *J* = 17.1, 10.2, 6.9 Hz), 6.86 (1H, d, *J* = 8.1 Hz), 6.91 (1H, t, *J* = 7.5), 7.14-7.21 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.2, 36.1, 40.0, 55.4, 120.6, 124.1, 126.8, 127.7, 133.3, 133.6, 137.2, 156.8; IR (neat): 3073 (w), 3007 (w), 2918 (w), 2835 (w), 1639 (w), 1599 (w), 1490 (s), 1463 (m), 1438 (m), 1238 (s), 1031 (m), 808 (s) cm^{-1}; HRMS (ESI+) for $C_{14}H_{18}O_1$ [M+H]: calculated: 203.1429, found: 203.1436. The crude material was purified on silica gel (2% ether in pentane) to afford a clear oil (21 mg, 70% yield for **2h**). R_f = 0.74 in 5% EtOAc/hexane.



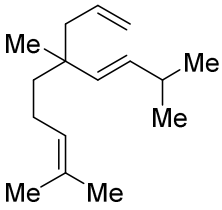
(*E*)-1-(hepta-1,5-dien-4-yl)-2-isopropylbenzene (2i): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): 1.22 (3H, d, *J* = 7.0 Hz), 1.27 (3H, d, *J* = 7.0 Hz), 1.64 (3H, dd, *J* = 6.9, 1.8 Hz), 2.35-2.45 (2H, m), 3.29 (1H, hept., *J* = 6.9 Hz), 4.03 (1H, ddd, *J* = 17.6, 8.8, 6.3 Hz), 4.97 (1H, app dq, *J* = 9.9, 1.1 Hz), 5.04 (1H, app dq, *J* = 7.3, 1.5 Hz), 5.46-5.52 (1H, m), 5.54-6.00 (1H, m), 5.76 (1H, app ddt, *J* = 24.2, 17.3, 10.3, 7.0 Hz), 7.13-7.19 (2H, m), 7.22-7.27 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$): 24.0, 24.1, 28.3, 30.3, 34.2, 37.8, 41.7, 115.8, 123.7, 125.2, 125.8, 126.0, 126.7, 134.4, 136.9, 145.9; IR (neat): 3015.2 (s), 1639 (w), 1487 (m), 1445 (m), 1400 (w), 1034 (m), 911 (s), 754 (s), 710 (s); HRMS (ESI+) for $C_{16}H_{22}$ [M+H]: calculated 215.1800, found 215.1808. The crude material was purified on silica gel (pentane) to afford a colorless oil (78% yield). R_f = 0.80 in hexane.



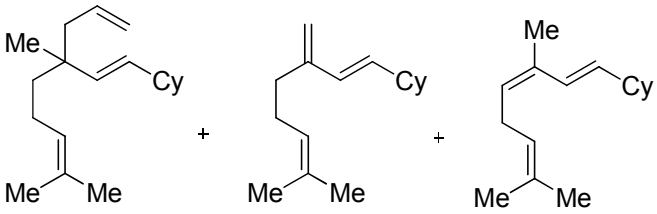
(*E*)-4,8-dimethyl-4-(prop-1-en-1-yl)nona-1,7-diene (4): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (3H, s), 1.24-1.29 (2H, m), 1.58 (3H, s), 1.68 (3H, s), 1.69 (3H, s), 1.88 (2H, app dt, *J* = 15.9, 7.3 Hz), 1.99-2.08 (2H, m), 4.90 (1H, d, *J* = 17.6 Hz), 5.00 (1H, s), 5.08 (1H, t, *J* = 7.3 Hz), 5.27-5.37 (2H, m), 5.76 (1H, ddt, *J* = 18.1, 11.0, 7.6 Hz); ^{13}C NMR (125 MHz $CDCl_3$): δ 17.5, 18.2, 22.8, 23.5, 25.7, 38.6, 40.9, 45.7, 116.5, 121.8, 125.1, 130.8, 135.7, 139.5; IR (neat): 2964 (m), 2916 (m), 2856 (m), 1639 (w), 1450 (m), 1439 (m), 1377 (m), 995 (m), 972 (s), 911 (s) cm^{-1}; HRMS (ESI+) for $C_{14}H_{25}$ [M+H]: calculated: 193.1956, found: 193.1948. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (23 mg, 80% yield). R_f = 0.89 in 5% EtOac/hexane.



(*E*)-6-allyl-2,6-dimethyldodeca-2,7-diene (6): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.8 Hz), 0.94 (3H, s), 1.20-1.38 (6H, m), 1.58 (3H, s), 1.67 (3H, s), 1.87 (2H, app dt, *J* = 16.3, 7.8 Hz), 1.98-2.90 (4H, m), 2.22-2.31 (1H, m), 4.98 (1H, d, *J* = 5.4 Hz), 4.99 (1H, s), 5.09 (1H, t, *J* = 7.3 Hz), 5.24-5.34 (2H, m), 5.75 (1H, ddt, *J* = 16.1,10.7, 7.3); ^{13}C NMR (125 MHz $CDCl_3$): δ 13.9, 17.5, 22.1, 22.9, 23.4, 25.7, 32.0, 32.5, 38.5, 41.0, 45.8, 116.5, 125.2, 127.6, 130.9, 135.7, 138.3; IR (neat): 2959 (s), 2924 (s), 2872 (m), 2856 (m), 1639 (s), 1457 (m), 1377 (m), 995 (m), 974 (s) 911 (s) cm^{-1}; HRMS (ESI+) for $C_{17}H_{31}$ [M+H]: calculated: 235.2426, found: 235.2430. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (28 mg, 79% yield). R_f = 0.87in 5% EtOAc/hexane.



(*E*)-6-allyl-2,6,9-trimethyldeca-2,7-diene (7): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (3H, s), 0.97 (6H, d, *J* = 6.6 Hz), 1.20-1.32 (2H, m), 1.59 (3H, s), 1.68 (3H, s), 1.87 (2H, app dt, *J* = 16.4, 7.6 Hz), 2.03 (2H, m), 2.22-2.31 (1H, m), 4.98 (1H, d, *J* = 8.3 Hz), 5.00 (1H, s), 5.08-5.12 (1H, m), 5.24-5.26 (2H, m), 5.69-5.79 (1H, m); ^{13}C NMR (125 MHz $CDCl_3$): δ 17.5, 22.8, 23.0, 23.0, 23.4, 25.7, 31.4, 38.2, 41.0, 45.8, 116.4, 125.2, 130.9, 134.9, 135.2, 135.7; IR (neat): 2960 (s), 2923 (m), 2867 (m), 1638 (w), 1509 (m), 1377 (m), 1102 (w), 995 (m), 974 (s), 911 (s) cm^{-1}; HRMS (ESI+) for $C_{16}H_{29}$ [M+H]: calculated: 221.2269, found: 221.2278. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (21 mg, 63% yield). R_f = 0.9 in 5% EtOAc/hexane.

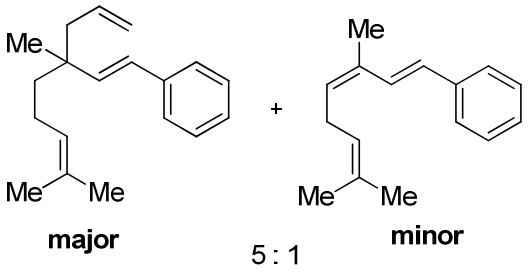


8 **S-37** **S-38**

6:2:1

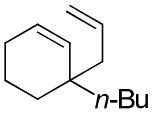
(*E*)-(3-allyl-3,7-dimethylocta-1,6-dien-1-yl)cyclohexane (8); (*E*)-(7-methyl-3-methyleneocta-1,6-dien-1-yl)cyclohexane (S-37); ((1*E*, 3*Z*)-3,7-dimethylocta-1,3,6-trien-1-yl)cyclohexane (S-38): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (**8**, 3H, s), 1.05-1.21 (**8** + **S-37** + **S-38**, m), 1.22-1.34 (**8** + **S-37** + **S-38**, m), 1.58 (**8**, 3H, s), 1.61 (**S-37**, 3H, s), 1.63-1.78 (**8** + **S-37** + **S-38**, m), 1.79 (**S-38**, 3H, s), 1.83-1.96 (**8** + **S-37** + **S-38**, m), 1.97-2.09 (**8**, 2H, m), 2.12-2.24 (2H **S-37** + 1H **S-38**, m), 2.84 (**S-38**, 2H, br t, *J* = 7.4 Hz), 4.86 (**S-37**, 1H, s), 4.90 (**S-37**, 1H, s), 4.97 (**8**, 1H, d, *J* = 6.3 Hz), 4.99 (**8**, 1H, s), 5.06-5.14 (**8**, 1H, m), 5.14-5.18 (**S-37**, 1H, m), 5.19-5.23 (**S-38**, 1H, m), 5.24 (**S-37**, 1H, d, *J* = 5.9 Hz),

5.25 (**8**, 1H, s), 5.62 (**S-38**, 1H, dd, *J* = 15.1, 6.8 Hz), 5.64 (**S-37**, 1H, dd, *J* = 15.7, 6.9 Hz), 5.72-5.79 (**8**, 1H, m), 6.02 (**S-37**, 1H, d, *J* = 15.7 Hz), 6.42 (**8**, 1H, d, *J* = 15.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.5, 17.7, 20.6, 22.9, 23.4, 25.7, 26.0, 26.1, 26.1, 26.2, 26.2, 26.4, 27.0, 29.7, 32.3, 33.2, 33.5, 33.5, 38.3, 41.0, 41.4, 45.9, 113.1, 116.4, 122.9, 124.4, 125.2, 127.2, 129.3, 130.9, 131.7,131.9, 133.6, 135.7, 136.7; IR (neat): 3073 (w), 2962 (m), 2921 (s), 2851 (s), 1679 (br), 1639 (w), 1448 (s), 1377 (m), 1259 (w), 1103 (br), 995 (m), 971 (s), 910 (s) cm^{-1}; HRMS (ESI+) for $C_{19}H_{33}$ [M +H]: calculated: 261.2582, found: 261.2589. The crude material was purified on silica gel eluted with (100% pentane) to afford a colorless oil (30 mg, 77% yield for **8**). R_f = 0.94 in 5% EtOAc/hexane.

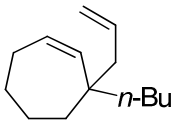


(*E*)-(3-allyl-3,7-dimethylocta-1,6-dien-1-yl)benzene (9) & ((1*E*,3*Z*)-3,7-dimethylocta-1,3,6-trien-1-yl)benzene: Prepared using general procedure **L** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09 (3H major, s), 1.36-1.46 (2H major, m), 1.58 (3H major, s), 1.67 (3H major, s), 1.69 (3H minor, s), 1.72 (3H minor, s), 1.89-1.99 (2H major, m), 1.94 (3H minor, s), 2.15 (1H major, dd, *J* = 13.2, 5.4 Hz), 2.20 (1H major, dd, *J* = 13.2, 5.4 Hz), 2.97 (2H minor, br t, *J* = 6.9 Hz), 5.02 (1H major, s), 5.06 (1H major, d, *J* = 8.3 Hz), 5.07-5.12 (1H major, m), 5.13-5.18 (1H minor, m), 5.43 (1H minor, br t, *J* = 7.3 Hz), 5.75-5.83 (1H major, m), 6.16 (1H major, d, *J* = 16.2 Hz), 6.28 (1H major, d, *J* = 16.6 Hz), 6.56 (1H minor, d, *J* = 16.1 Hz), 7.17-7.23 (1 H major + 1 H minor, m), 7.28-7.33 (2 H major, m), 7.35-7.38 (2 H major + 2 H minor, m), 7.44 (2H minor, d, *J* = 7.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.6, 17.8, 20.5, 23.0, 23.3, 25.7, 26.7, 30.3, 39.2, 41.0, 45.7, 117.0, 122.5, 124.8, 125.9, 126.0, 126.4, 126.8,

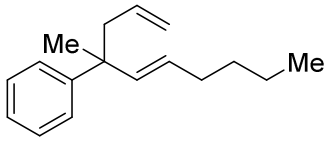
127.0, 127.2, 128.3, 128.5, 128.6, 130.4, 131.2, 135.2, 138.0, 139.1, 145.5; IR (neat): 2966 (m), 1718 (w), 1493 (s), 1377 (s), 1027 (s), 912 (s), 747 (s), 694 (s); HRMS (ESI+) for $C_{19}H_{26}$ [M +H]$^+$ (major): calculated: 253.1944, found: 253.1956. The crude material was purified on silica gel (pentane) to afford a colorless oil (21 mg, 55% yield for **9**). R_f = 0.80 in pentane.



3-allyl-3-butylcyclohex-1-ene (10): Prepared using general procedure **L**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.9 Hz), 1.19-1.37 (6H, m), 1.41-1.46 (2H, m), 1.58-1.62 (2H, m), 1.93 (2H, dddd, *J* = 10.3, 6.4, 4.0, 2.5 Hz), 2.05 (2H, d, *J* = 7.8 Hz), 4.97-5.00 (1H, m), 5.01-5.03 (1H, m); 5.42 (1H, d , *J* = 10.3 Hz), 5.64 (1H, dt, *J* = 9.8, 3.5 Hz), 5.77 (1H, dddd, J = 17.6, 16.6, 10.3, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 14.1, 19.0, 22.7, 23.6, 25.1, 32.1, 32.3, 39.6, 44.3, 116.6, 126.1, 135.5, 135.6; IR (neat): 2923 (s), 1638 (m), 1455 (s), 1377 (w), 994 (m), 911 (s), 689 (w); HRMS (ESI+) for $C_{13}H_{22}$ [M+H]$^+$: calculated: 179.1755, found: 179.1693. The crude material was purified on silica gel (pentane) to afford a colorless oil (16 mg, 59% yield). R_f = 0.89 in pentane.



3-allyl-3-butylcyclohept-1-ene (11): Prepared using general procedure **L**, ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (3H, t, *J* = 6.8 Hz), 1.18-1.39 (6H, m), 1.41-1.60 (4H, m) 1.62-1.77 (2H, m), 2.08-2.18 (4H, m), 4.99-5.02 (2H, m), 5.40 (1H, d, *J* = 11.7 Hz), 5.63 (1H, dt, *J* = 11.8, 5.9 Hz), 5.76-5.84 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 23.6, 24.8, 25.9, 28.2, 29.7, 35.7, 39.0, 42.5, 44.2, 116.7, 129.2, 135.7, 140.1; IR (neat): 2923 (s), 1670 (m), 1457 (m), 1377 (w), 995 (w), 912 (m), 727 (w); HRMS (ESI+) for $C_{14}H_{24}$ [M+H]$^+$: calculated: 193.1956, found: 193.1948. The crude material was purified on silica gel (pentane) to afford a colorless oil (21.9 mg, 78% yield). R_f = 0.88 in pentane.



(*E*)-(4-methyldeca-1,5-dien-4-yl)benzene (12): Prepared using general procedure **L**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (3H, t, *J* = 7.0 Hz), 1.29-1.42 (7H, m), 2.07 (2H, dd, *J* = 7.0 Hz), 2.46-2.56 (2H, m), 4.94 (H, d, *J* = 9.5 Hz), 5.01 (H, d, *J* = 17.9 Hz), 5.43 (1H, app dt, *J* = 13.4, 6.8 Hz), 5.56-5.66 (2H, m), 7.16-7.20 (1H, m), 7.28-7.35 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 25.6, 31.8, 32.5, 43.2, 46.2, 116.9, 125.7, 126.7, 128.0, 135.5, 148.0; IR (neat): 3075 (w), 2959 (s), 2925 (s), 1639 (w), 1599 (w), 1494 (m), 1458 (m), 1444 (m), 1374 (m), 975 (m), 912 (s), 762 (s), 698 (s) cm^{-1}; HRMS (ESI+) for $C_{17}H_{25}$ [M+H]: calculated: 229.1956, found: 229.1948. The crude material was purified on SiO_2 eluted with (100% pentane) to afford a colorless oil (30 mg, 86% yield). R_f = 0.8 in 5% EtOAc/hexane.

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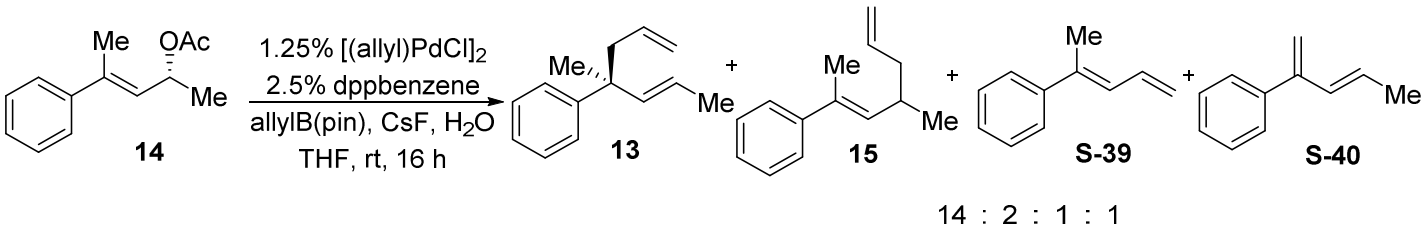
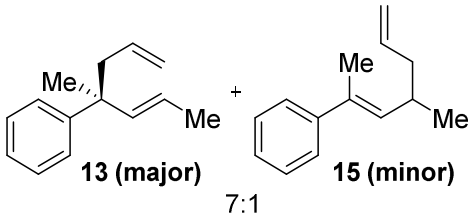


General procedure M: In the dry-box, (η^3-allylPdCl)$_2$ in solution of THF (25.5 µL, 0.00188 mmol) and dppbenzene in solution of THF (43 µL, 0.00375 mmol) was added to an oven dried 2-dram vial equipped with a stir bar. The resulting solution was allowed to stir at room temperature for 5 min. At this time, the vial was sequentially charged with **14** (24.3 mg, 0.15 mmol), allylB(pin) (75.6 mg, 0.45 mmol), CsF (228 mg, 1.5 mmol), and THF (0.75 mL). The vial was tightly capped with a rubber septum, removed from the dry-box, and placed under a positive pressure of N_2. Degassed, D.I. water was then added (40 µL) *via* a micro syringe. The

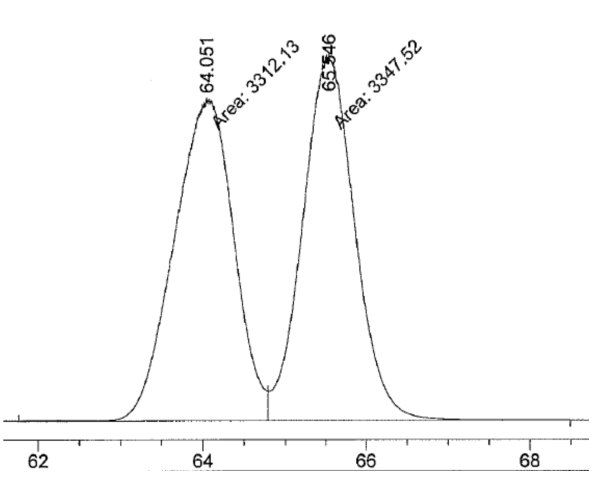
rubber septum was rapidly exchanged with a polypropylene cap, sealed with electrical tape, and the reaction was allowed to stir at room temperature for 16 h. The slurry was then diluted with water, the organic layer was separated and the aqueous layer was extracted three times with Et_2O. The organic portion was combined and dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by silica gel chromatography (100% pentane) to yield a mixture of 14:2:1:1 of **13**, **15**, **S-39**, **S-38**, respectively. The combined yield of **13** and **15** was calculated to be 70% yield (19.5 mg). **S-39** and **S-38** can be removed by treating the mixture with maleic anhydride (30 mg, 0.3 mmol) in THF at 60 ^oC for 3 h.



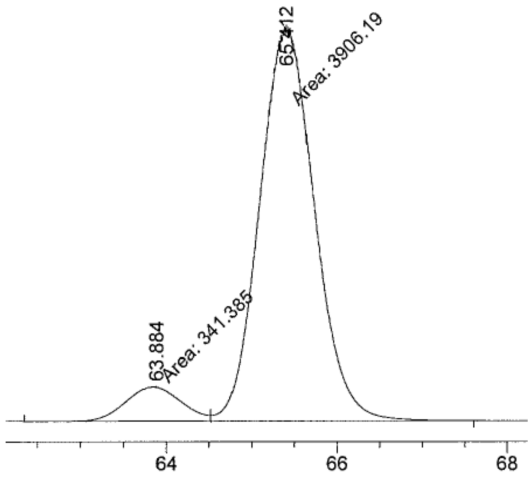
(*E*)-(4-methylhepta-1,5-dien-4-yl)benzene (13, major) & (*E*)-(4-methylhepta-2,6-dien-2-yl)benzene (15, minor): Prepared using general procedure **M**. ^1H NMR (500 MHz, $CDCl_3$): δ 1.05 (3H, d, *J* = 6.8 Hz, minor), 1.34 (3H, s, major), 1.73 (3H, dd, *J* = 6.9, 2.0 Hz, major), 2.04 (3H, d, *J* = 1.5 Hz), 2.11-2.16 (2H, m, minor), 2.44-2.57 (2H major + 1H minor, m), 2.57-2.69 (1H, m, minor), 4.94-5.07 (2H major + 2H minor, m), 5.44 (1H, dq, *J* = 15.7, 6.4 Hz), 5.56-5.64 (2H, m, major+minor), 5.67 (1H, dq, *J* = 15.2, 1.5 Hz, major), 5.82 (1H, ddt, *J* = 17.1, 10.3, 7.3 Hz, minor), 7.16-7.40 (8H, m, major+minor); ^{13}C NMR (125 MHz, $CDCl_3$): δ major: 16.0, 18.1, 20.5, 25.5, 33.2, 41.8, 43.2, 46.1, 115.7, 117.0, 122.3, 125.7, 125.9, 126.5, 126.7, 128.0, 128.1, 133.5, 134.3, 135.4, 137.2, 139.6, 144.0, 147.9; IR (neat): 3075 (w), 3058 (w), 3026 (w), 2966 (m), 2916 (m), 2856 (w), 1639 (w), 1598 (w), 1494 (m), 1445 (m), 1375 (m), 1028 (w), 995 (m), 971 (m) cm^{-1}; HRMS (ESI+) for $C_{14}H_{19}$ [M+H]: calculated: 187.1487, found: 187.1478. The crude material was

purified on silica gel (100% pentane) to afford a colorless oil (19.5 mg, 70% combined yield). R_f = 0.78 in 5% EtOAc/hexane.

Analysis of stereo chemistry: The enantiomer ratio of **13** was determined using chiral GLC (CD-BDM, Supelco, 80 ^{o}C for 70 minutes, 15 psi, sr = 35:1). The absolute stereo chemistry was determined by analogy to **16**.

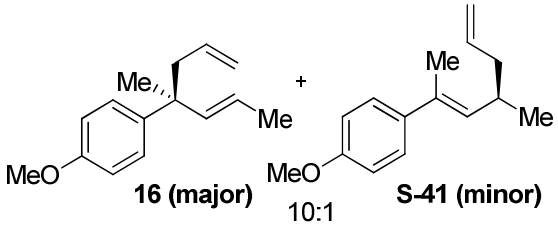


Racemic



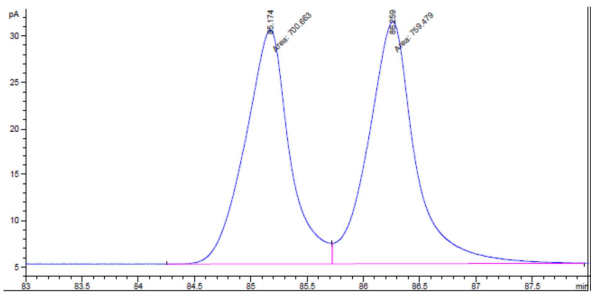
Reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	63.884	MF	0.7383	341.38510	7.70674	8.03718
2	65.412	FM	0.7424	3906.18921	87.69042	91.96282

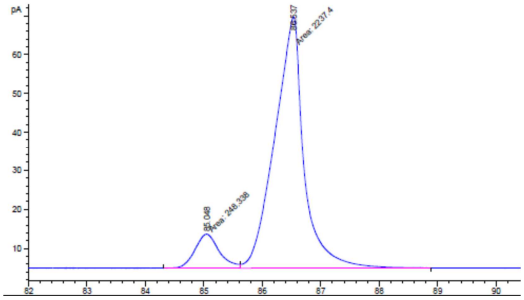


(*E*)-1-methoxy-4-(4-methylhepta-1,5-dien-4-yl)benzene (16, major) & (*R*,*E*)-1-methoxy-4-(4-methylhepta-2,6-dien-2-yl)benzene (S-41, minor): Prepared using general procedure **M**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05 (3H, d, *J*= 6.8 Hz, minor), 1.33 (3H, s, major), 1.73 (3H, dd, *J* = 6.3, 2.0 Hz, major), 2.03 (3H, d, *J* = 1.5 Hz, minor), 2.42-2.55 (2H major + 2H minor, m), 2.58-2.67 (1H, m, minor), 3.81 (3H, s, major), 3.82 (3H, s, minor), 4.94-5.08 (2H major + 2H minor, m), 5.44 (1H, dq, *J* = 15.6, 6.3 Hz, major), 5.52 (1H, d, *J* = 9.3 Hz, minor), 5.56-5.68 (2H, m, major), 5.82 (1H, ddt, *J* = 17.1, 9.8, 6.8 Hz, minor), 6.83-6.88 (2H, m, minor), 6.86 (2H, d, *J* = 8.8 Hz, major), 7.25 (2H, d, *J* = 8.8 Hz), 7.34 (2H, d, *J* = 8.8 Hz, minor); ^{13}C NMR (125 MHz, $CDCl_3$): δ major: 16.1, 18.1, 20.5, 25.6, 33.1, 41.9, 42.6, 46.2, 55.2, 55.3, 113.3, 113.5, 115.6, 116.9, 122.0, 126.7, 127.6, 127.4, 129.4, 132.8, 135.5, 137.3, 139.9, 140.0, 157.5; IR (neat): 3138 (w), 3001 (m), 2962 (m), 2834 (w), 1638 (w), 1609 (m), 1580 (w), 1511 (s), 1463 (m), 1441 (m), 1374 (w), 1293 (m), 1248 (s), 1182 (m), 1035 (m) cm^{-1}; HRMS (ESI+) for $C_{15}H_{21}O_1$ [M+H]: calculated: 217.1592, found: 217.1591. The crude material was purified on silica gel (100% pentane) to afford a colorless oil (22.7 mg, 86% combined yield). R_f = 0.33 in 5% EtOAc/hexane.

Analysis of stereo chemistry: The enantiomer ratio of **16** was determined using chiral GLC (CD-BDM, Supelco, 80 ^{o}C, ramp 0.5 ^{o}C/min to 115 ^{o}C, hold at 115 ^{o}C for 30 minutes, 20 psi, sr = 35:1).



Racemic

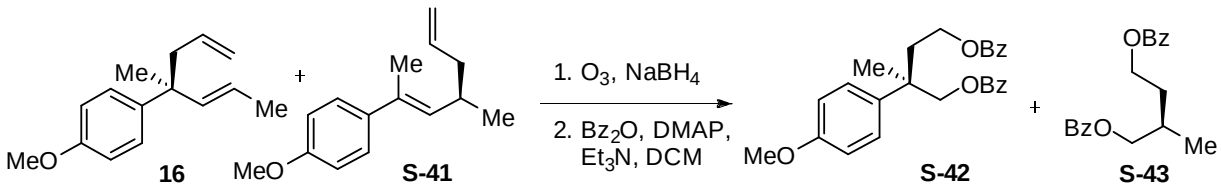


Reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	85.048	MF	0.4782	248.33794	8.65465	9.99050
2	86.537	FM	0.5764	2237.40283	64.69248	90.00950
Totals :				2485.74077	73.34713	

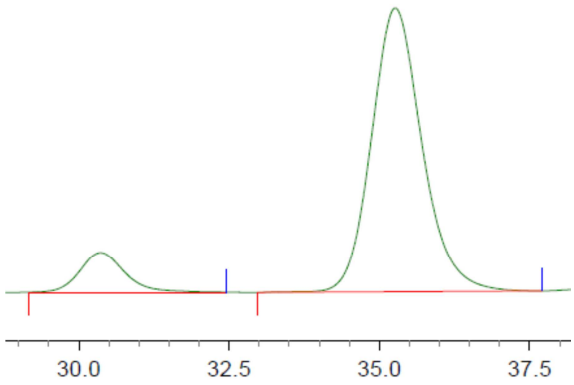
Proof of stereo chemistry:

Mixture of **16** and **S-41** was treated with ozonolysis/reduction contitions, followed by alcohol protection with benzyl group to obtain **S-42** and **S-43**, which can be easily separated.



Absolute stereochemistry of **16** was determined by comparing the HPLC chromatogram of **S-42** with that of compound reported previously.[8]

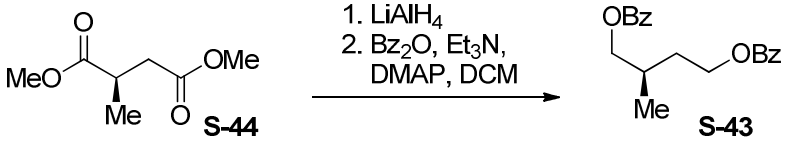
Chiral HPLC: AD-H, Chiralpak, 1.0 mL/min, 2% isopropanol/hex, 254 nm



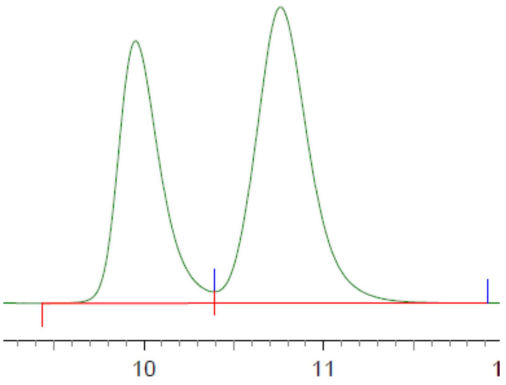
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
30.363	7602484	11.13	145838	12.39
35.263	60721550	88.87	1030928	87.61
Totals	68324034	100.00	1176766	100.00

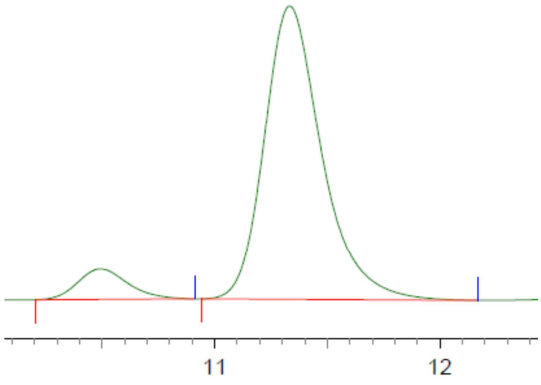
Absolute stereochemistry of the minor isomer **S-41** was determined by comparing with authentic sample of dimethyl (*R*)-(+)-methylsuccinate (**S-44**) via intermediate **S-43**.



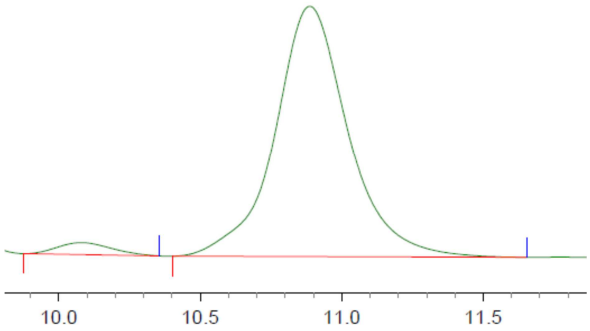
Chiral HPLD: AD-H, Chiralpak, 1.0 ml/min, 1% isopropanol/hex, 254 nm.



Racemic S-43 from racemic S-44



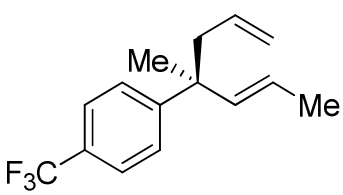
S-43 from authentic S-44



S-43 derived from S-41

VWD: Signal A,
254 nm Results

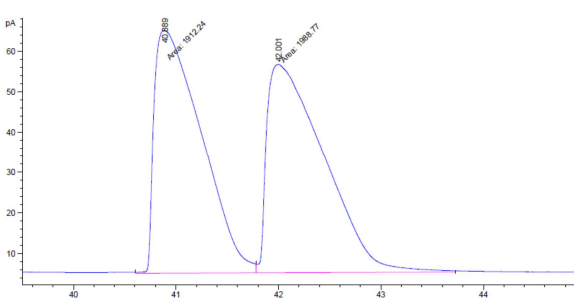
Retention Time	Area	Area %	Height	Height %
10.080	424634	3.37	32151	4.54
10.887	12193245	96.63	675793	95.46
Totals	12617879	100.00	707944	100.00



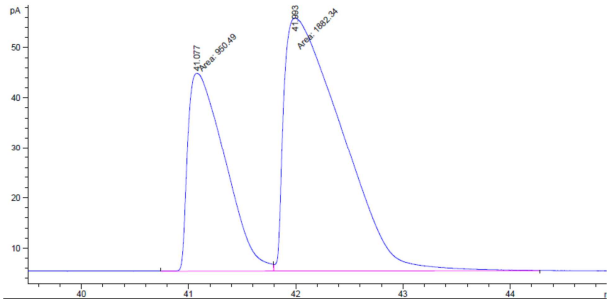
(*E*)-1-(4-methylhepta-1,5-dien-4-yl)-4-(trifluoromethyl)benzene (17): Prepared using general procedure **M**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (3H, s), 1.73 (3H, dd, *J* = 6.8, 2.0 Hz), 2.45-2.57 (1H, m), 4.86-5.04 (2H, m), 5.46 (1H, dq, *J* = 15.6, 6.3 Hz), 5.56 (1H, ddt, *J* = 17.1, 9.8, 6.3

Hz), 5.64 (1H, d, J = 15.6 Hz), 7.42 (2H, d, J= 8.3 Hz), 7.54 (2H, d, J = 8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.1, 25.4, 43.4, 46.0, 117.6, 123.2, 124.7, 124.8, 124.9, 127.1, 127.5 (p, $^1J_{CF}$ = 32.3 Hz), 134.6, 138.7, 152.0; IR (neat): 2922 (w), 1640 (w), 1617 (w), 1451 (w), 1410 (w), 1326 (s), 1165 (m), 1124 (s), 1071(m), 1016 (m) cm^{-1}; HRMS (ESI+) for $C_{15}H_{18}F_3$ [M+H]: calculated: 255.13606, found: 255.13573. The crude material was purified on silica gel (100% pentane) to afford a clolorless oil (27mg, 69% yield). R_f = 0.8 in 5% EtOAc/hexane.

Analysis of stereo chemistry: The enantiomer ratio of **17** was determined using chiral GLC (CD-BDM, Supelco, 80 ^{o}C, ramp 0.5 ^{o}C/min to 110 ^{o}C, hold at 110 ^{o}C for 10 minutes, 20 psi, sr = 35:1). Absolute stereochemistry was determined by analogy to **16**.

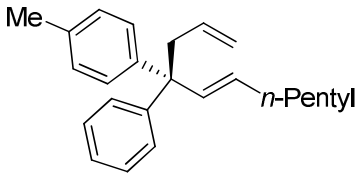


Racemic



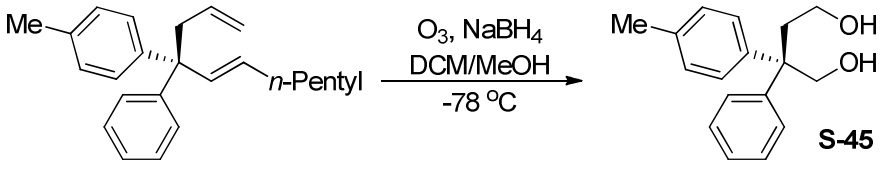
Reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	41.077	MF	0.4012	950.49042	39.48108	33.55262
2	41.993	FM	0.6216	1882.34460	50.47442	66.44738
Totals :				2832.83502	89.95550	

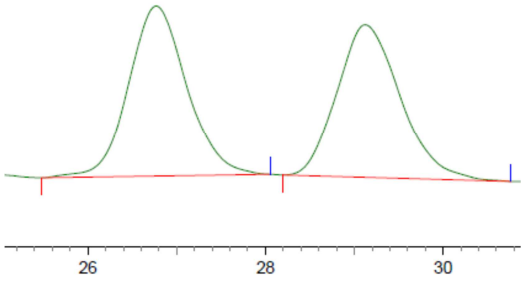


(*R, E*)-1-methyl-4-(4-phenylundeca-1,5-dien-4-yl)benzene (18): Prepared using general procedure **M.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (3H, t, *J* = 6.9 Hz), 1.41-1.56 (6H, m), 2.25 (2H, app dq, *J* = 7.3 Hz), 2.51 (3H, s), 3.21 (2H, d, *J* = 6.9 Hz), 5.14 (1H, d, *J* = 18.6 Hz), 5.27 (1H, dt, *J* = 15.7, 6.9 Hz), 5.77 (1H, app ddt, *J* = 24.0, 13.7, 10.3, 6.9 Hz), 6.20 (1H, dd, *J* = 15.7, 1.0 Hz), 7.23-7.28 (4H, m), 7.34-7.39 (3H, m), 7.43-7.47 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 20.9, 22.5, 29.1, 30.3, 31.4, 32.8, 44.6, 52.2, 117.2, 125.8, 127.7, 128.5, 128.6, 128.8, 130.9, 135.3, 135.5, 136.6, 144.1, 147.3; IR (neat): 2955 (s), 1510 (m), 1493 (m), 1444 (s), 938 (m), 912 (m), 816 (m), 764 (m), 699 (s); HRMS (ESI+) for $C_{24}H_{30}$ $[M+H]^+$: calculated: 319.2381, found: 319.2440. $[\alpha]^{20}_D$ = 0.543 (*c* = 3.315, $CHCl_3$). The crude material was purified on silica gel (pentane) to afford a colorless oil (45mg, 95% yield). R_f = 0.56 in pentane.

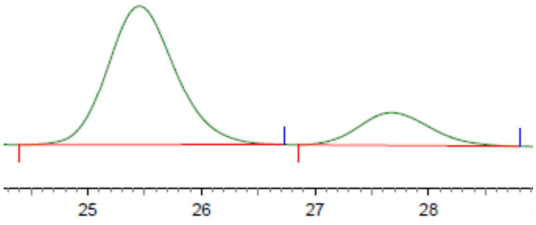
Analysis of stereo chemistry: The titled compound was ozonolyzed to the corresponding 1,4-diol as described in the sequence below. The analogous racemic material was prepared via the same route, using racemic **S-35**.



The enantiopurity was determined on diol **S-45** using chiral HPLC (AD-H, Chiraldex, 1.0 mL/min, 5% isopropanol/hexane, 254 nm). The absolute stereochemistry was determined by analogy to **16**.



Racemic



Reaction Product

VWD: Signal A,
254 nm Results

Retention Time	Area	Area %	Height	Height %
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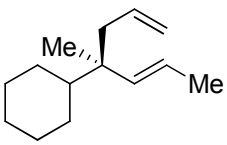
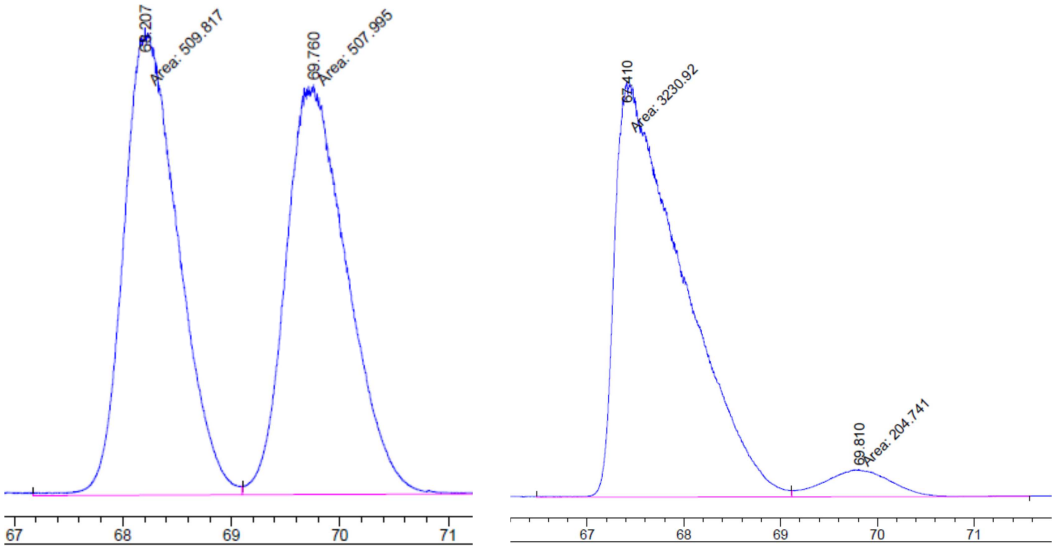
27.670	2157473	19.84	48804	19.00
Totals				
	10871898	100.00	256927	100.00



(*R*, *E*)-(4-methylhepta-1,5-dien-4-yl)cyclohexane (19): Prepared using general procedure **M**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (3H, s), 0.87-0.97 (4H, m), 1.06-1.19 (5H, m), 1.62-1.76 (3H, m), 1.68 (3H, dd, *J* = 5.8, 1.5 Hz), 2.06 (2H, d, *J* = 7.3 Hz), 4.96 (1H, d, *J* = 7.8 Hz), 4.99 (1H, s), 5.22-5.30 (1H, m), 5.32 (1H, d, *J* = 17.1 Hz), 5.75 (1H, dddd, *J* = 18.1, 16.6, 10.8, 7.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.2, 20.1, 26.8, 27.1, 27.2, 27.7, 29.7, 41.2, 43.7, 46.2, 116.2, 122.1, 136.1, 138.7 ; IR (neat): 2921 (s), 1638 (w), 1449 (m), 1377 (m), 995 (w), 974 (s), 908 (s); HRMS (ESI+) for $C_{14}H_{24}$ $[M+H]^+$: calculated: 193.1956, found: 193.1962; $[\alpha]^{20}_D$ = 5.881 (*c* = 0.136, $CHCl_3$).The crude

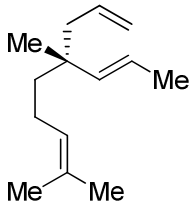
material was purified on silica gel (pentane) to afford a clear oil (49% yield). R_f = 0.85 in pentane.

Analysis of stereo chemistry: The analogous racemic material was prepared via the same route, using the corresponding racemic acetate**.** The enantiopurity was determined using chiral GLC (Chiral β-dex, Supelco, 85 ^{o}C for 100 minutes, 20 psi, sr = 35:1). The absolute stereochemistry was determined by analogy to **16**.



Racemic Reaction product

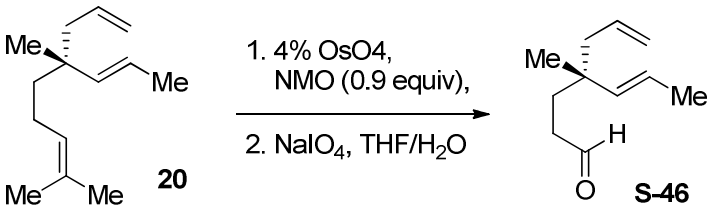
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	67.410	MF	0.8151	3230.91870	66.06355	94.04072
2	69.810	FM	0.7947	204.74057	4.29393	5.95928
Totals :				3435.65927	70.35748	



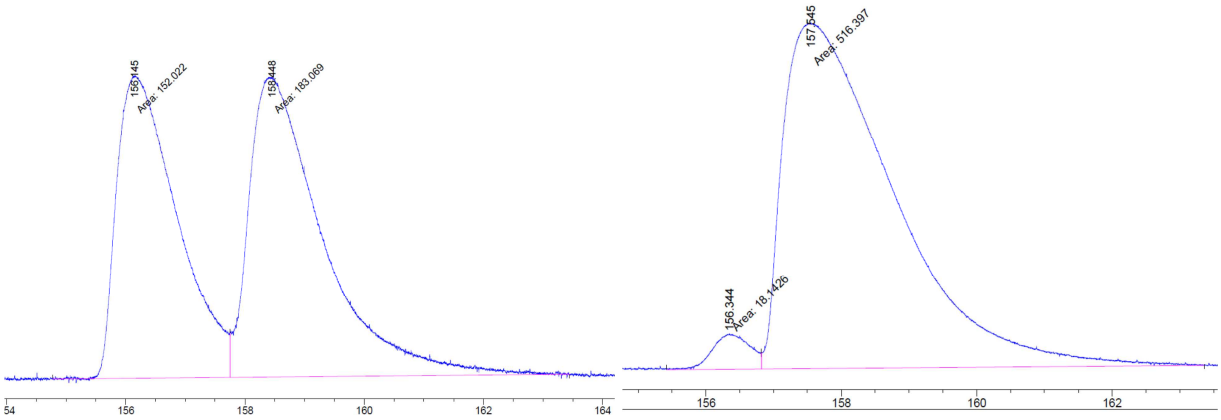
(*R*,*E*)-4,8-dimethyl-4-(prop-1-en-1-yl)nona-1,7-diene (**20**): Prepared using general procedure **M**. All spectral information match with the analogous racemic product **4**. The crude material was purified on silica gel (pentane) to afford a colorless oil (14 mg, 50% yield). R_f = 0.90 in pentane.

Analysis of stereochemistry:

Product **20** was treated with catalytic OsO_4, and NMO followed by $NaIO_4$ diol cleavage to afford **S-46** for GLC analysis. The analogous racemic material was prepared from racemic product **4**. The absolute stereochemistry was determined by analogy to **16**.



Chiral GLC (CD-BDM, Supelco, 40 ^{o}C, ramp 0.15 ^{o}C to 90 ^{o}C, 90 ^{o}C for 30 minutes, 20 psi, sr: 35:1)



Racemic **S-46** **S-46** from reaction product

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	156.344	MF	0.6451	18.14260	4.68757e-1	3.39406
2	157.545	FM	1.8869	516.39673	4.56115	96.60594
Totals :				534.53933	5.02991	

References:

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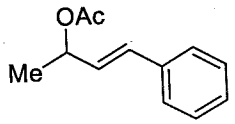
7. Voigtritter, K. R.; Isley, N. A.; Moser, R.; Aue, H. D.; Lipshutz, B. H. *Tetrahedron* **2012**, *68*, 3410
8. Zhang, P.; Le, H.; Kyne, R. E.; Morken J. P. *J. Am. Chem. Soc.* **2011**, *133*, 9716

IV. ^{1}H NMR and ^{13}C NMR spectra for characterized compounds



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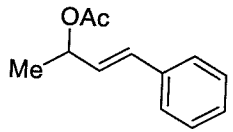

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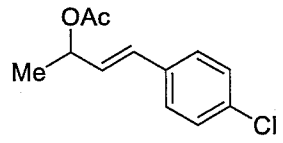

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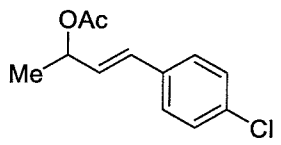

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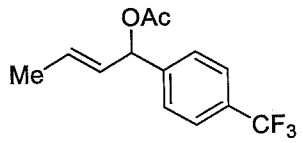

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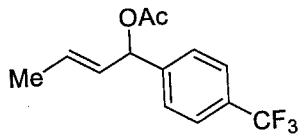

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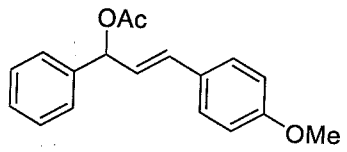

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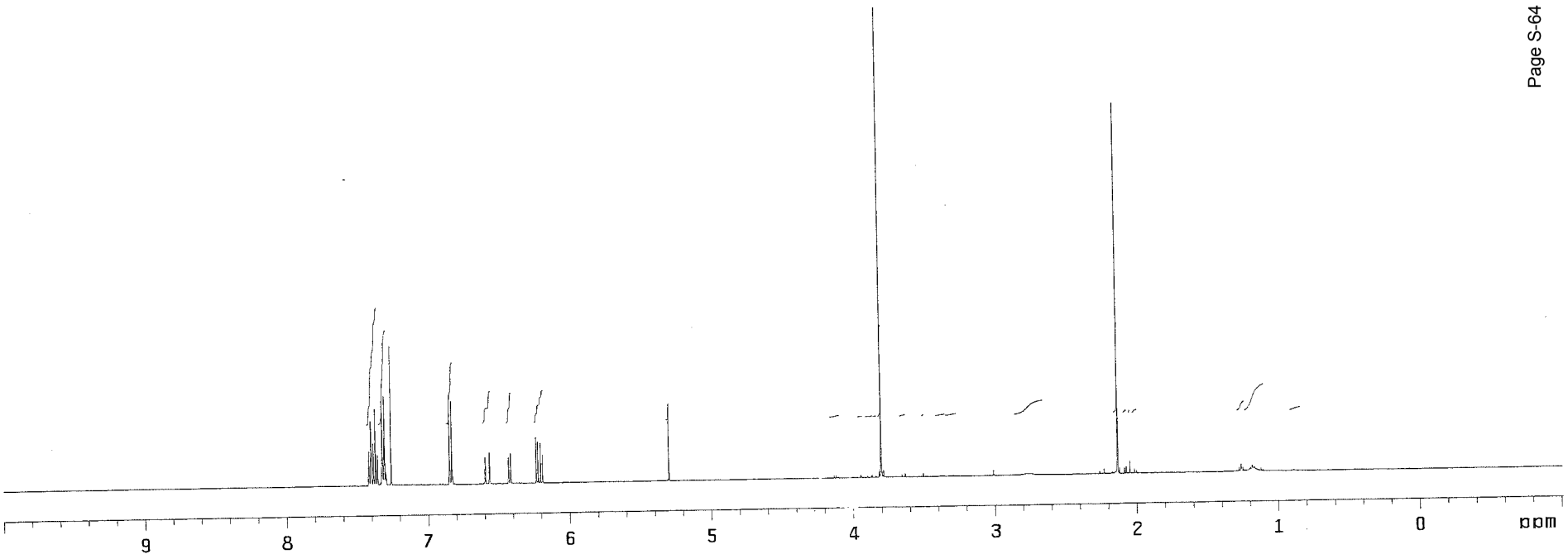

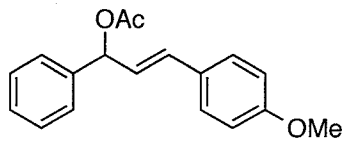

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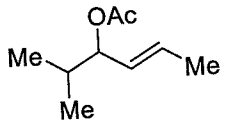

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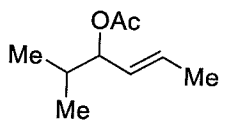

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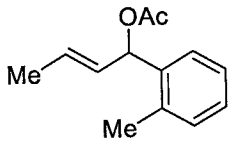

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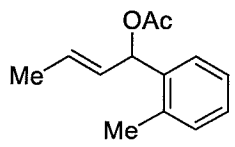

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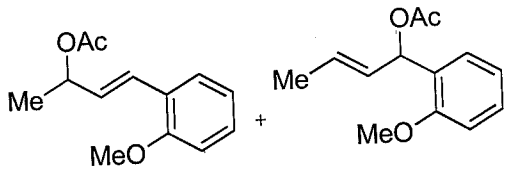
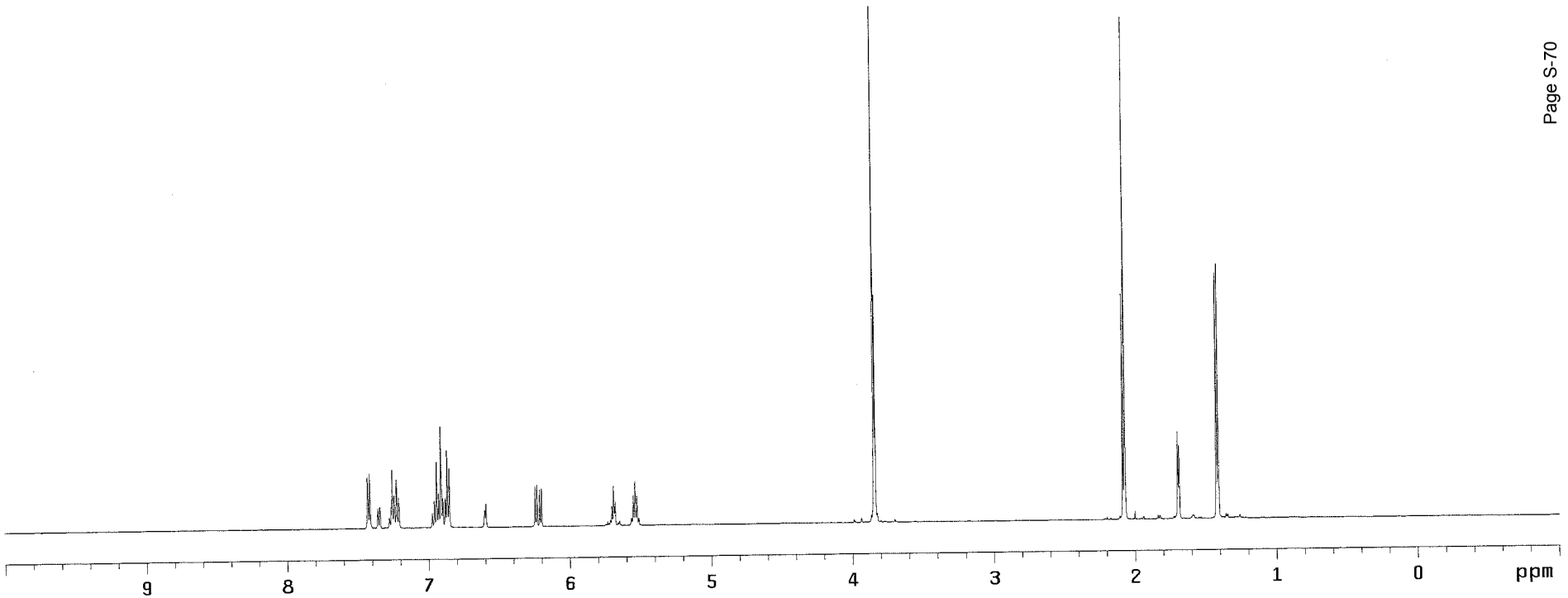
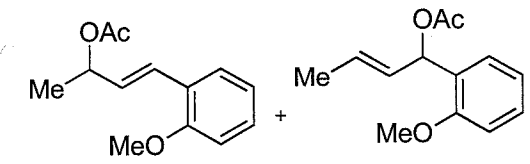


1h **major** 3:1 **minor**





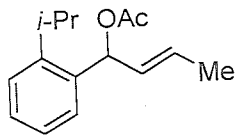
major

+

minor

3:1

1h



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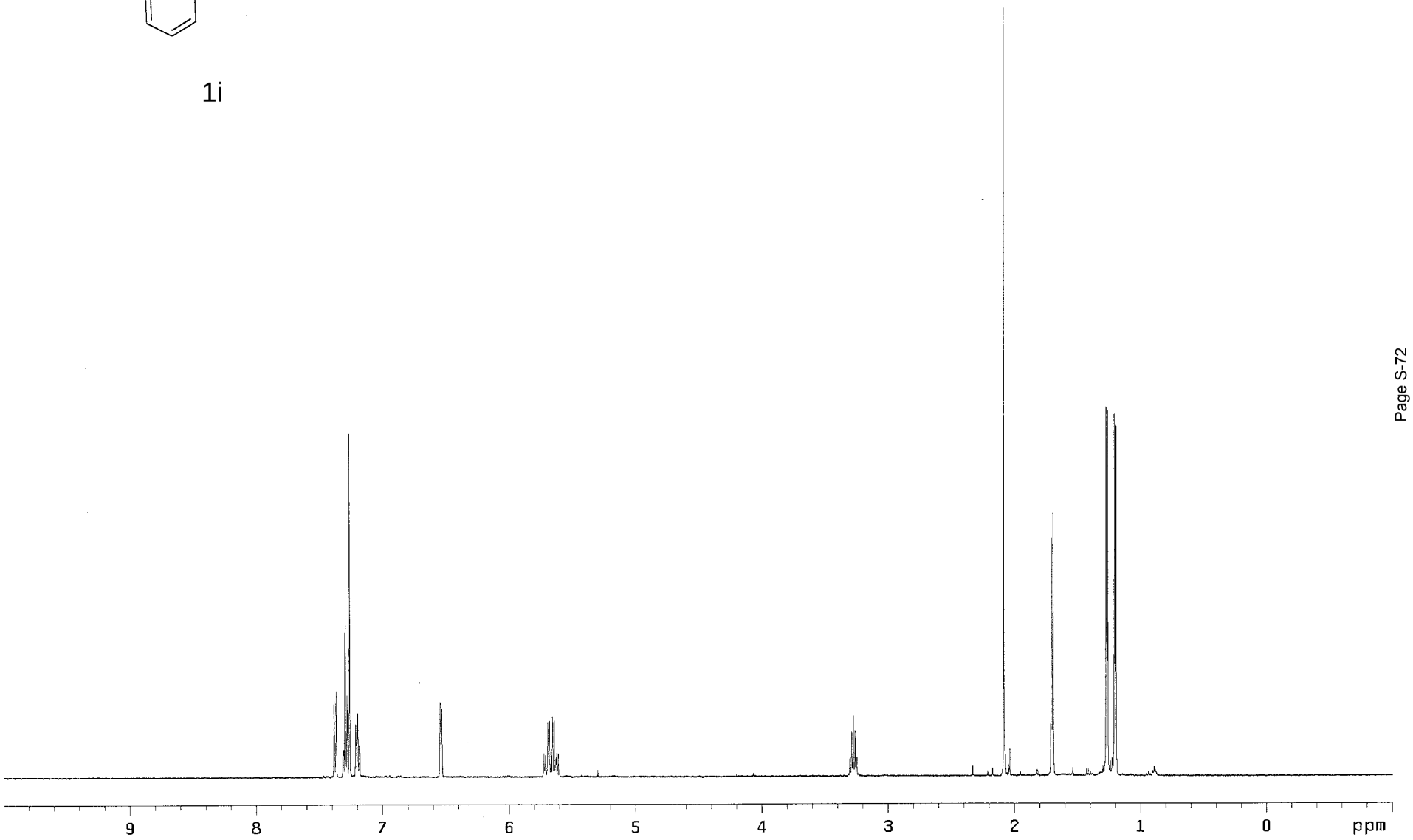

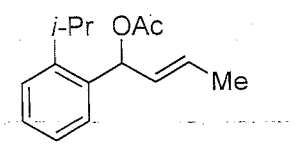

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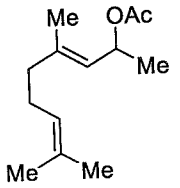

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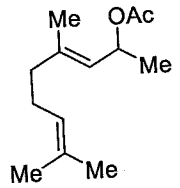

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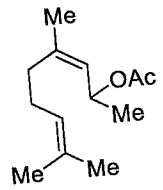

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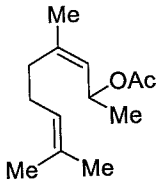

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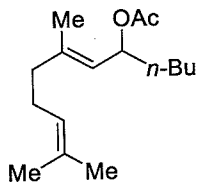

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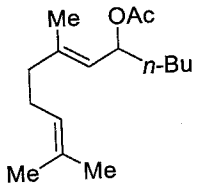

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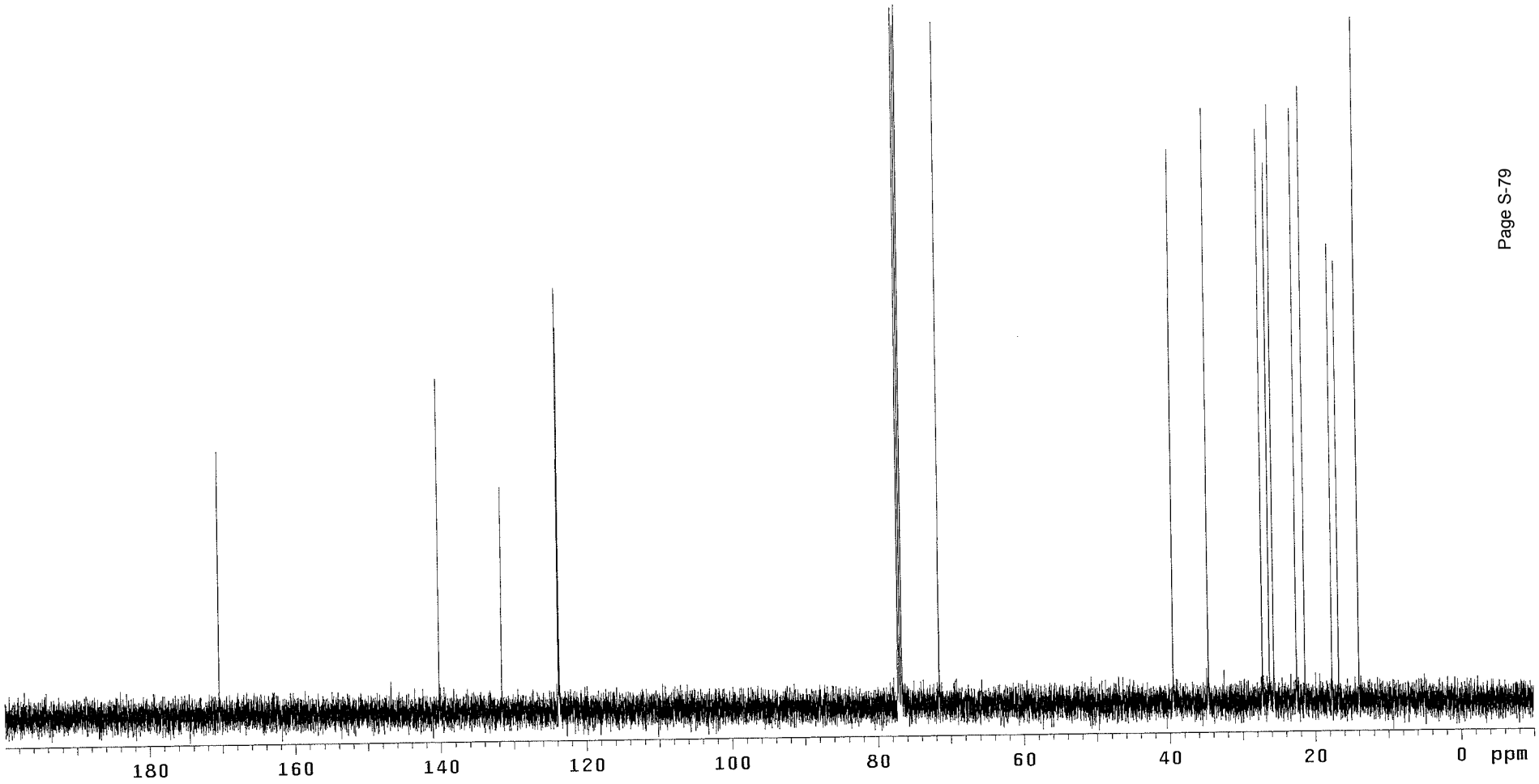

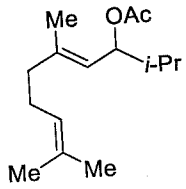

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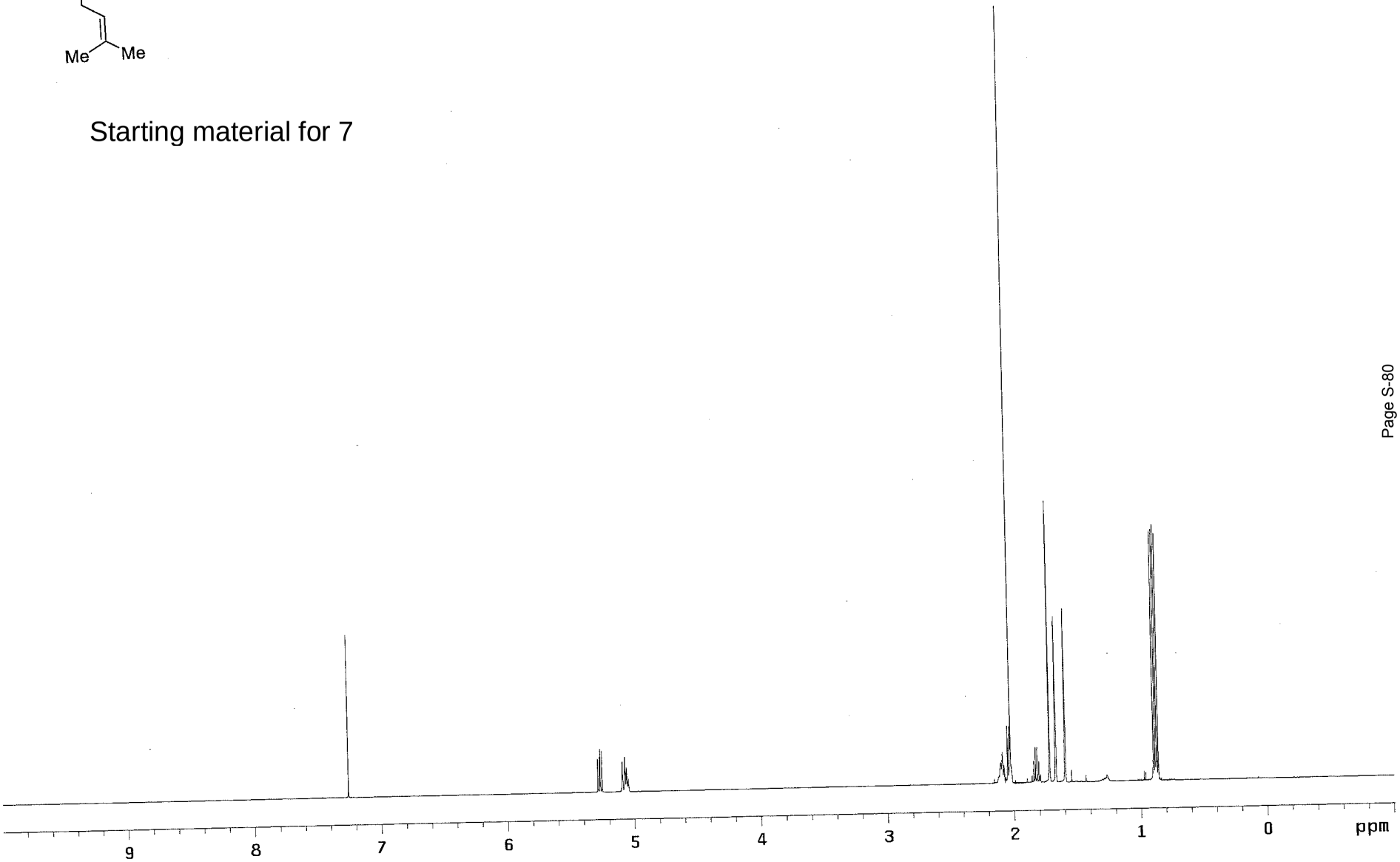
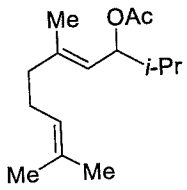
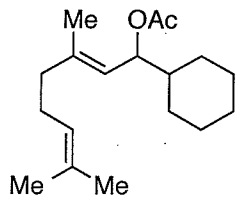
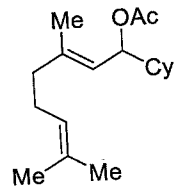




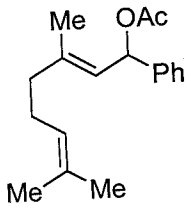
Starting material for 7



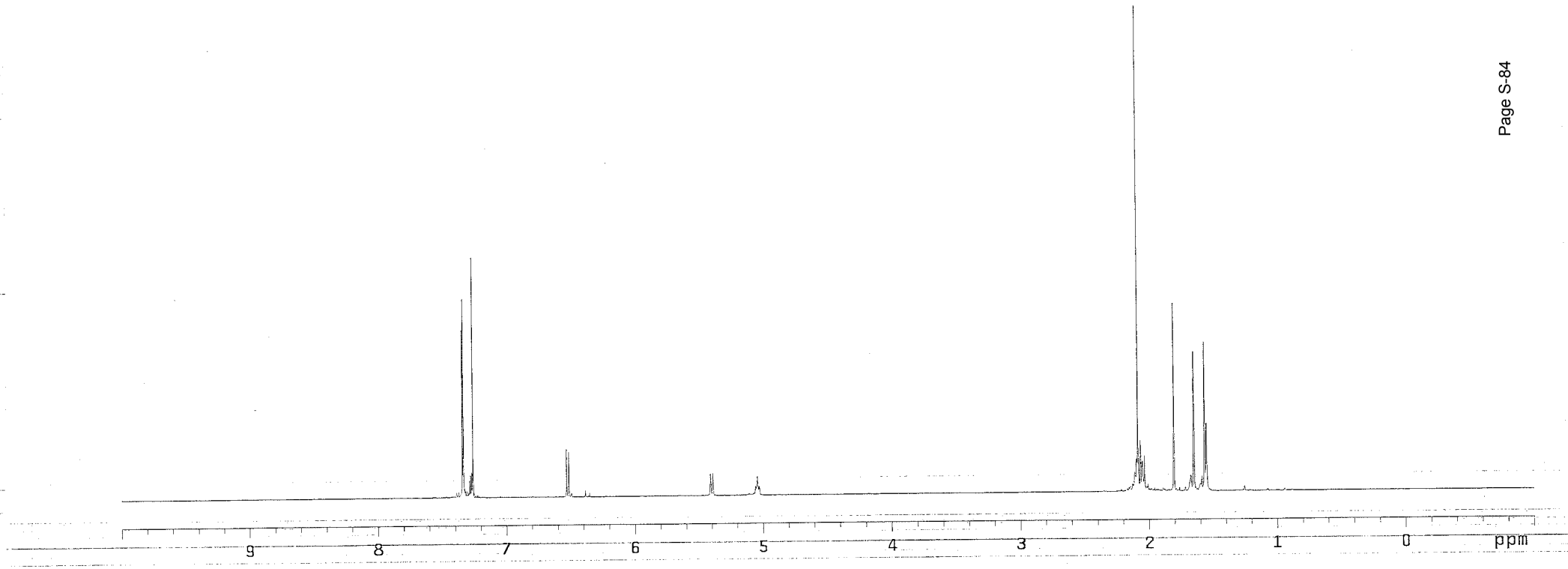
Starting material for 8

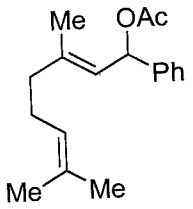


Starting material for 8

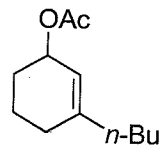


Starting material for 9

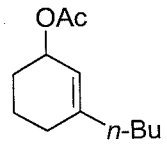




Starting material for 9



Starting material for 10



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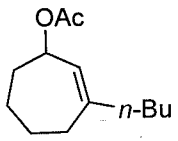
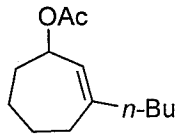
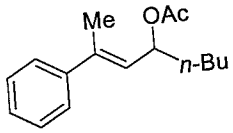


Starting material for 11



Starting material for 11



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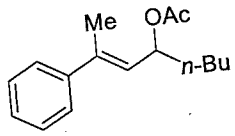
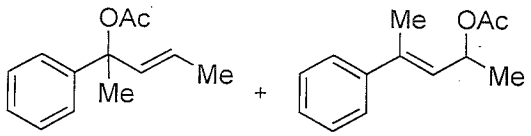


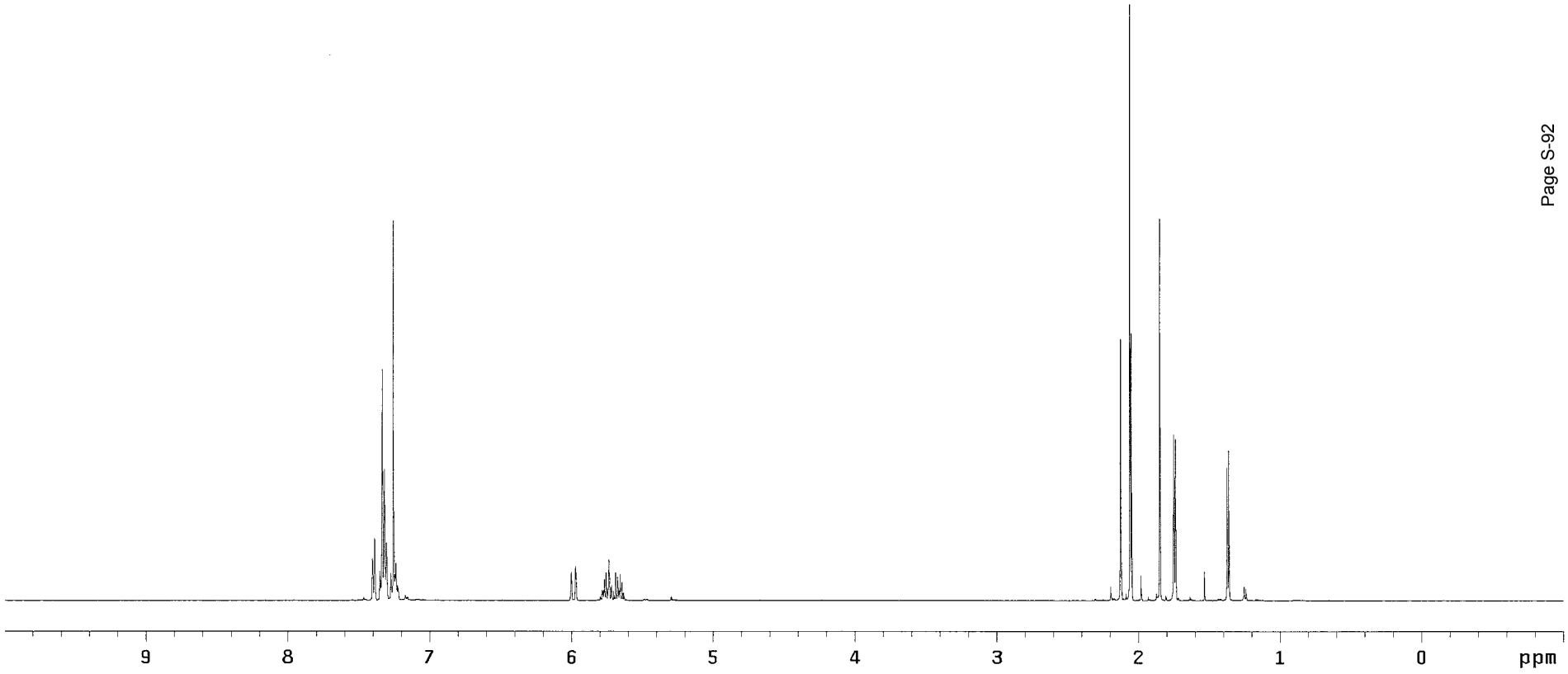
Starting material for 12

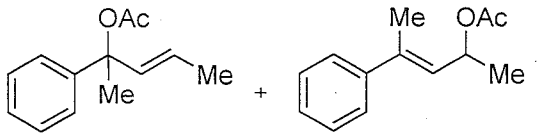


major **minor**

1.4 : 1

Starting material for 13

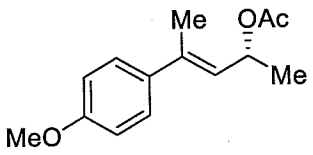




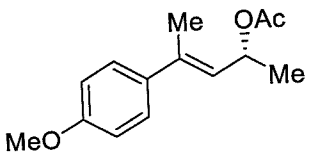
major **minor**

1.4 : 1

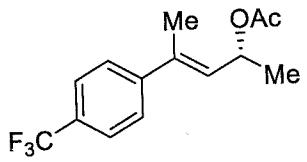
Starting material for 13



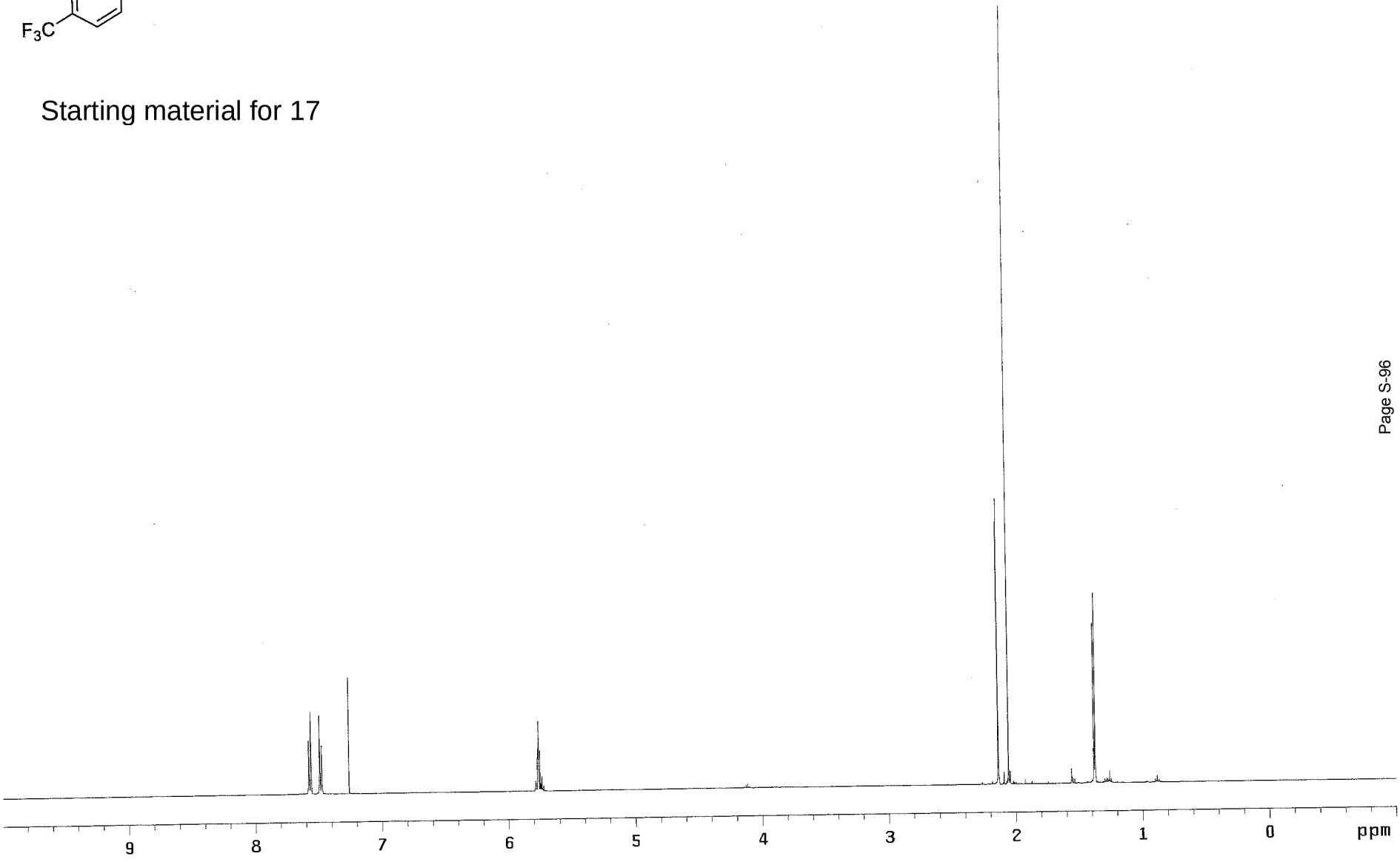
Starting material for 16

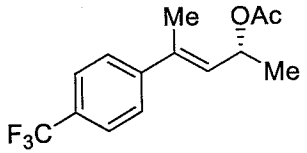


Starting material for 16

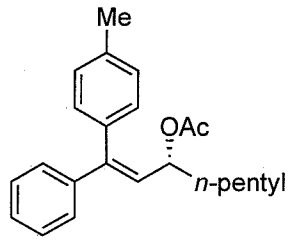


Starting material for 17

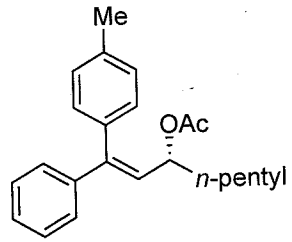




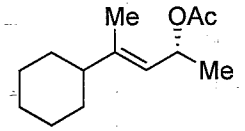
Starting material for 17



Starting material for 18



Starting material for 18



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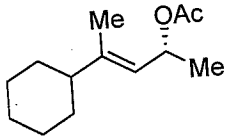
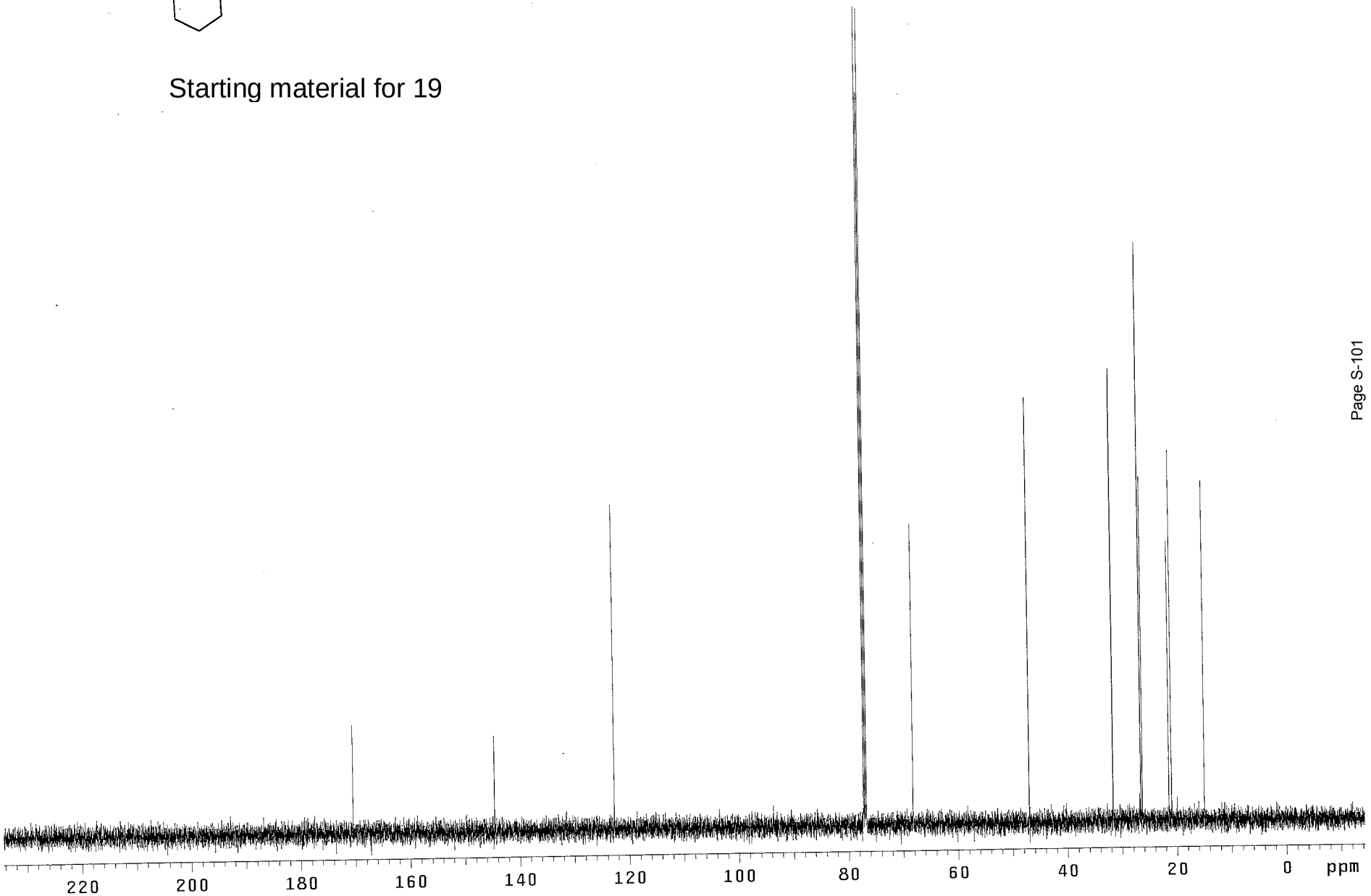
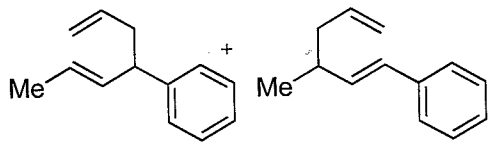


Starting material for 19

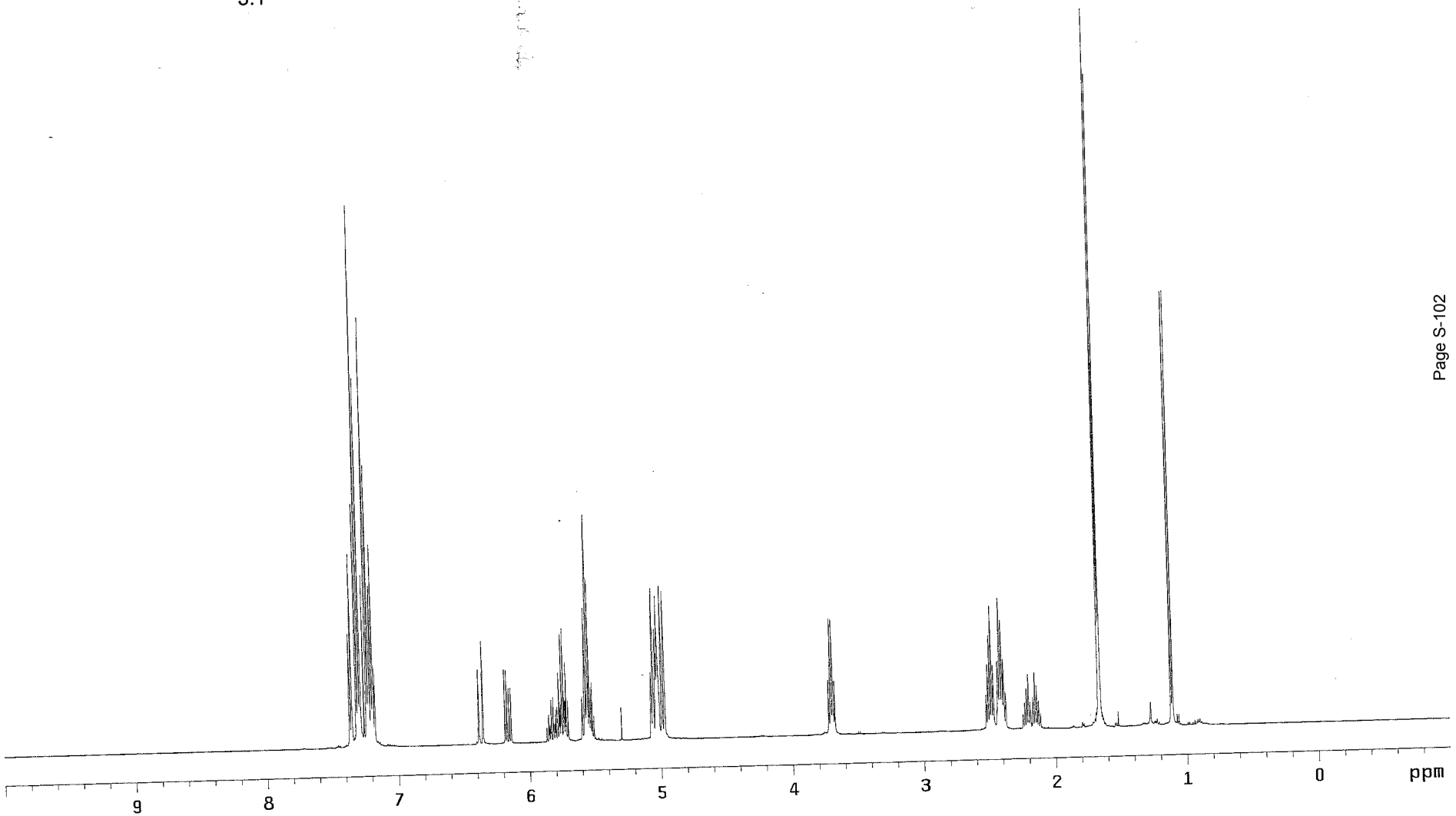


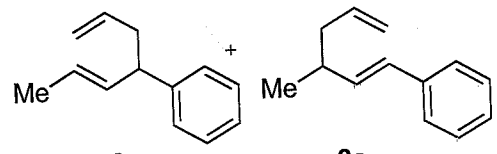


2a

3a

3:1

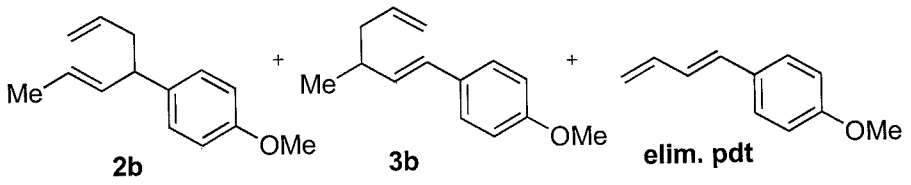




2a

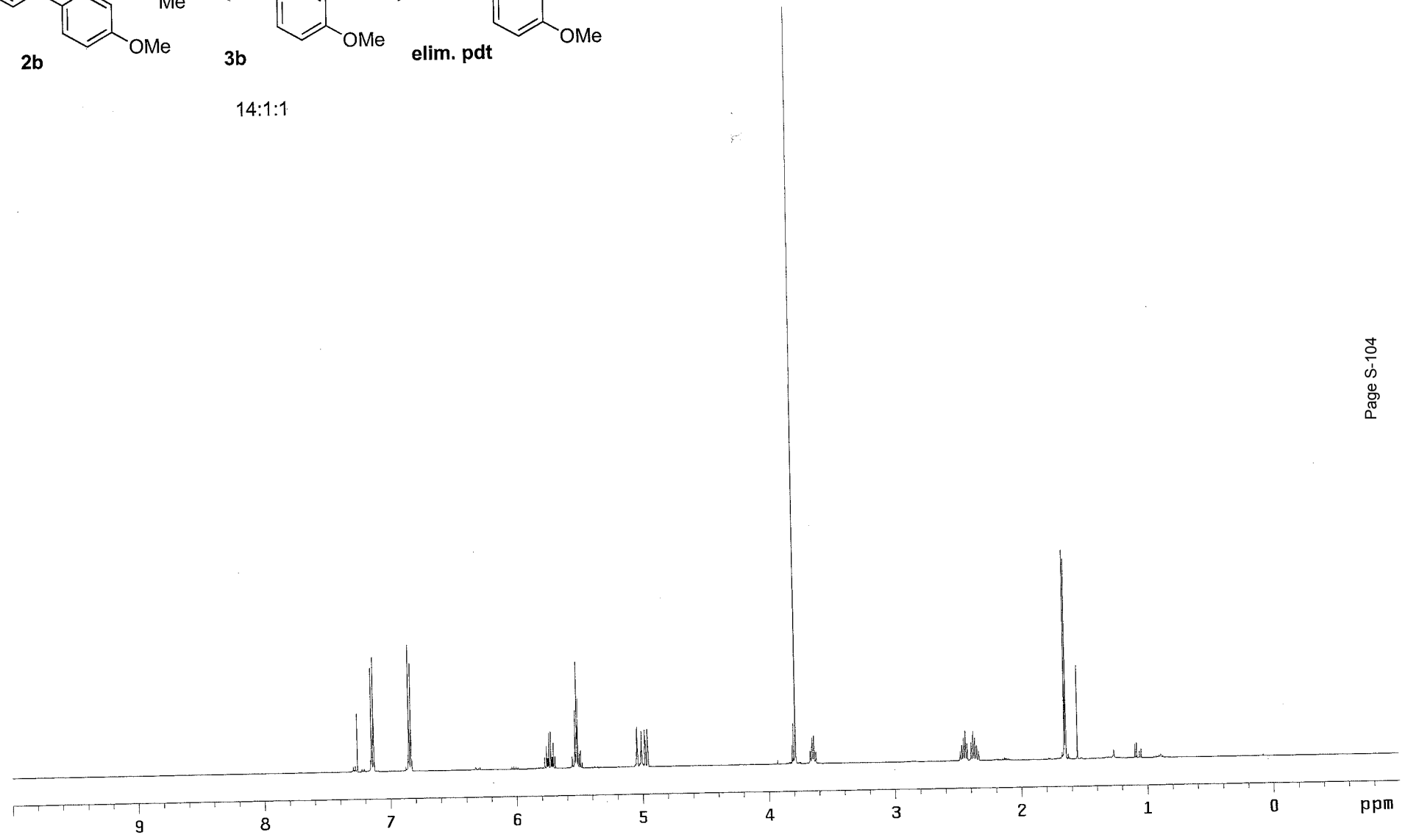
3:1

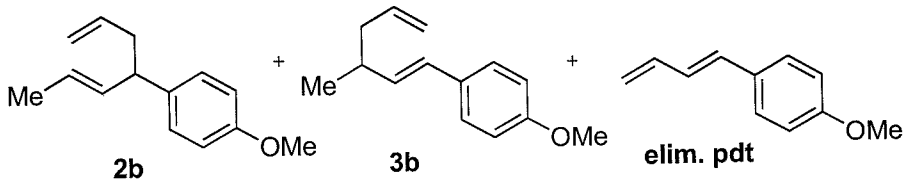
3a



2b + **3b** + **elim. pdt**

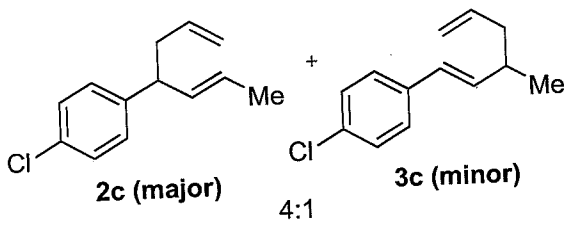
14:1:1



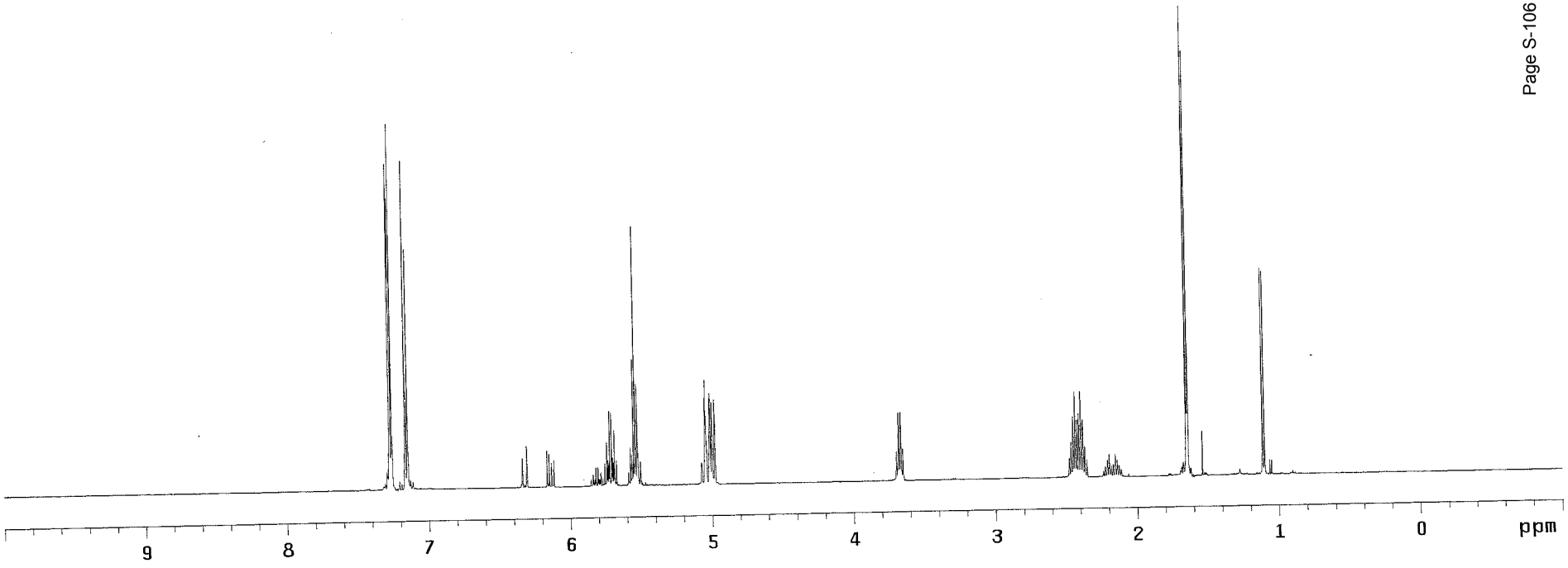


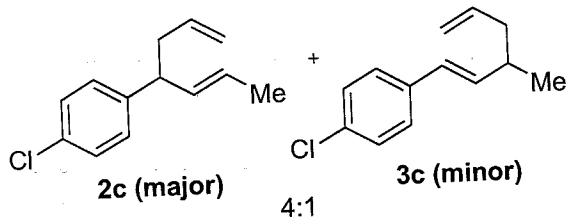
2b **3b** **elim. pdt**

14:1:1



2c (major) 4:1 **3c (minor)**



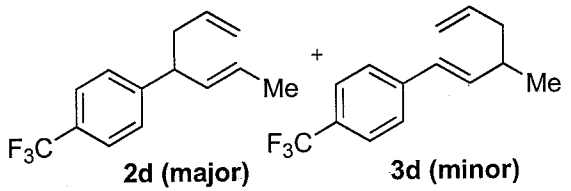


2c (major)

+

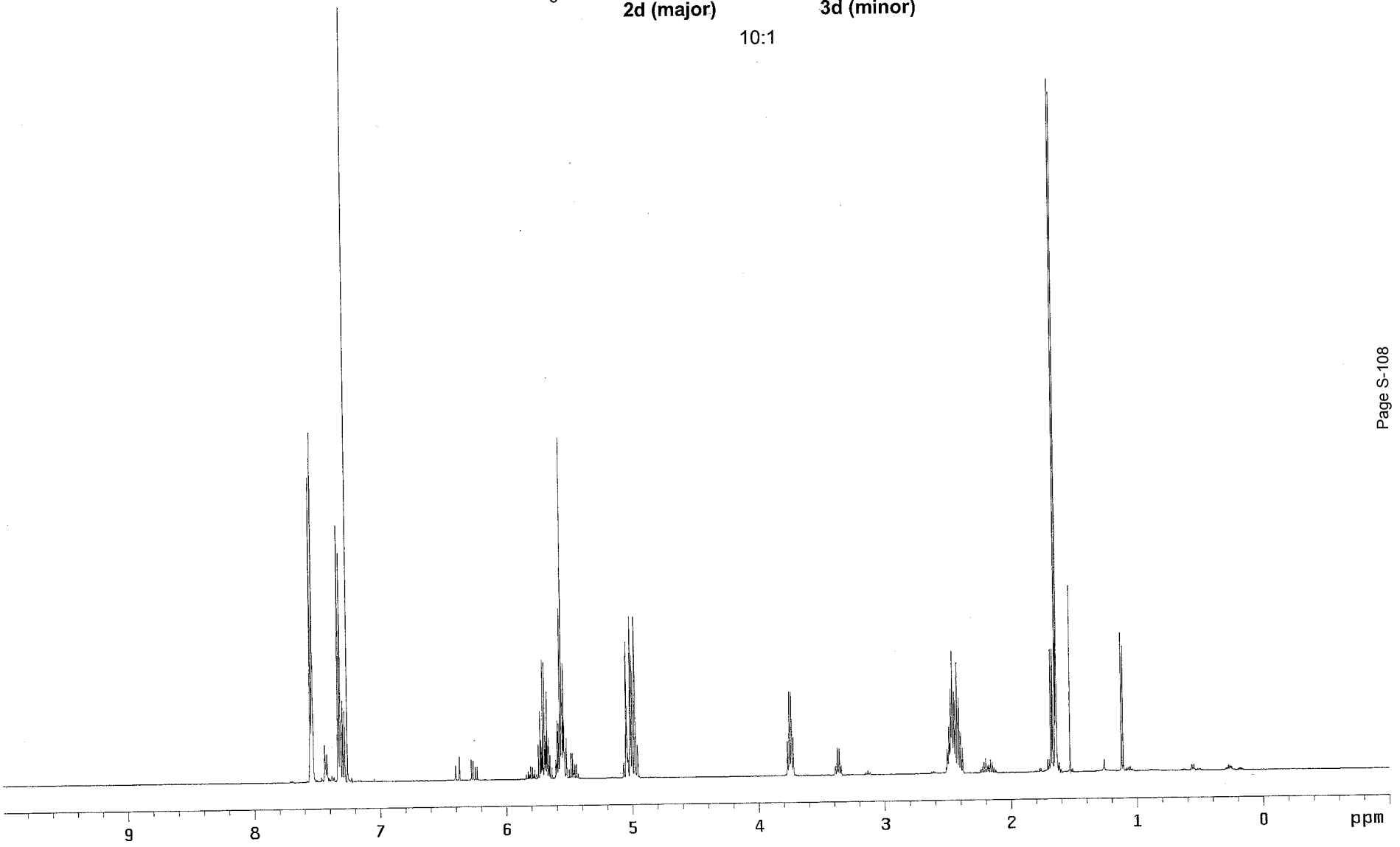
3c (minor)

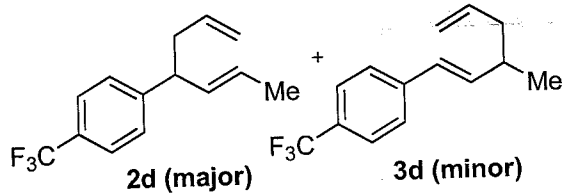
4:1



2d (major) + **3d (minor)**

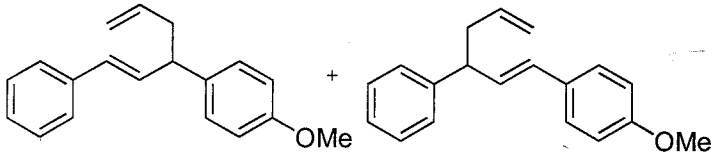
10:1



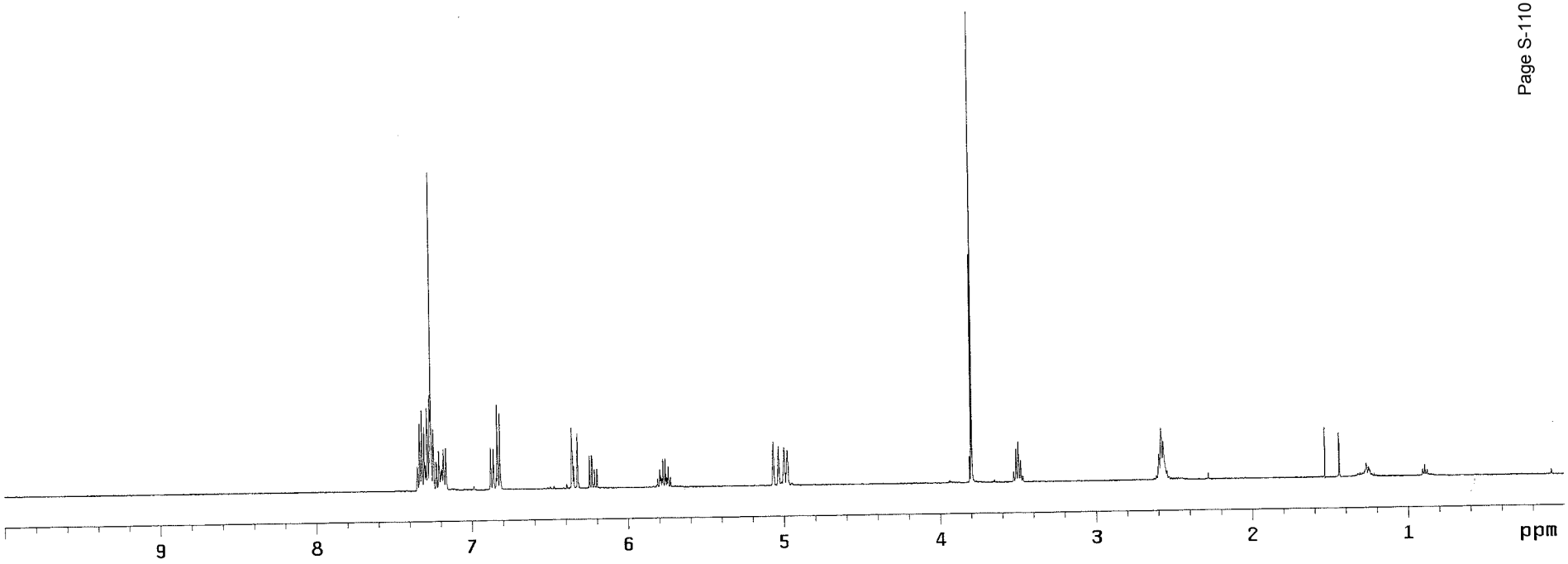


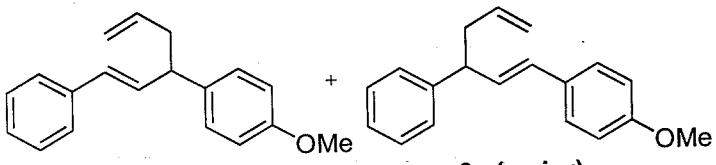
2d (major) **3d (minor)**

10:1



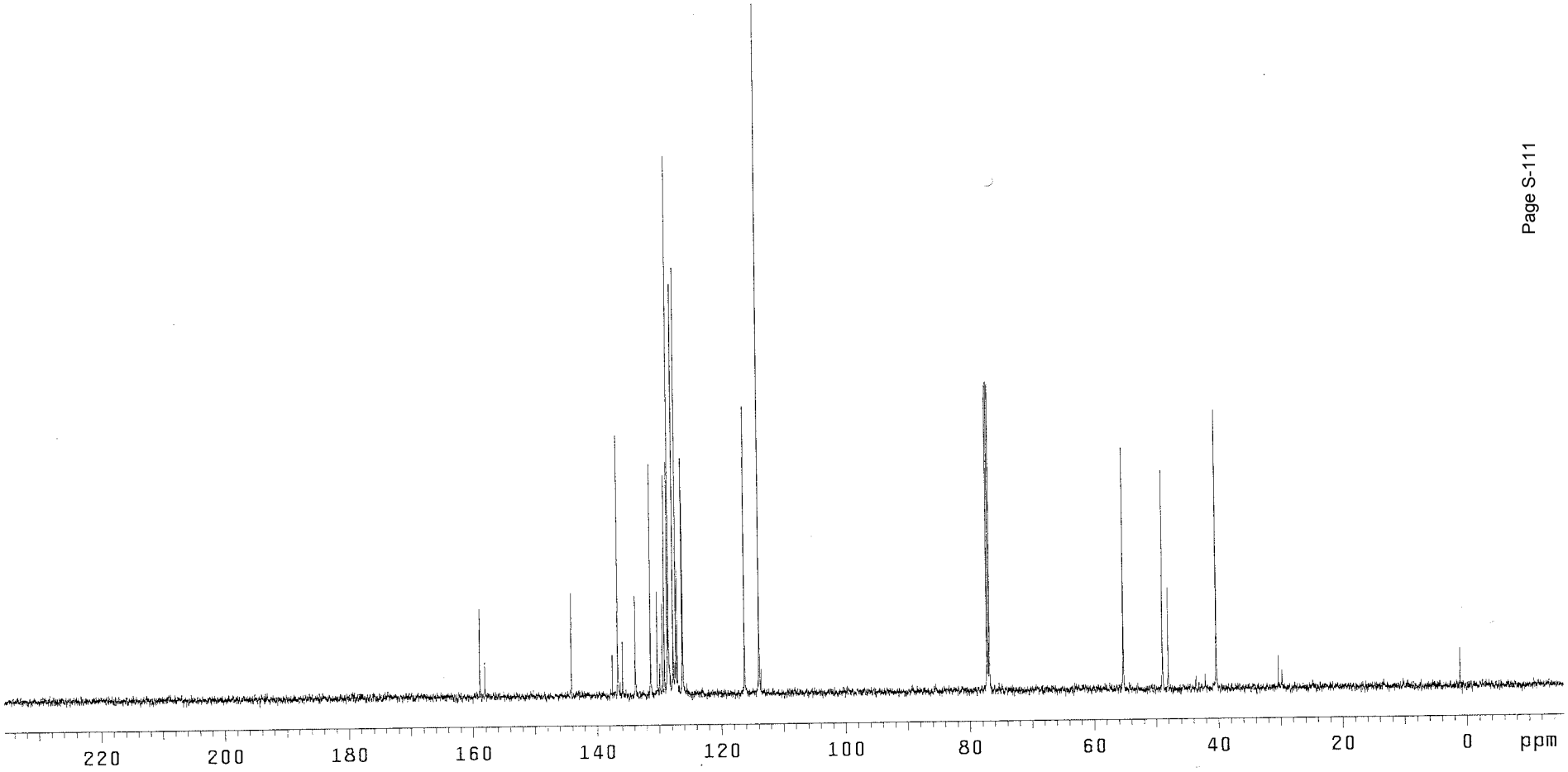
2e (minor) 1:2 **3e (major)**

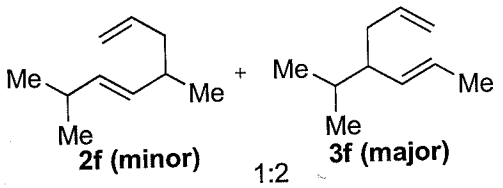


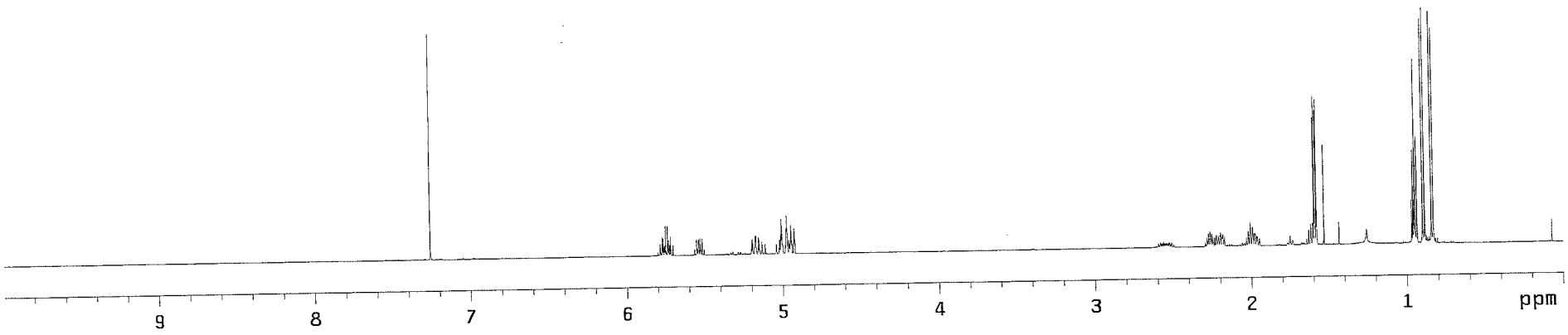


2e (minor) + **3e (major)**

1:2




Me
Me
Me
2f (minor)
+
Me
Me
Me
3f (major)
1:2


9
8
7
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5
4
3
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1
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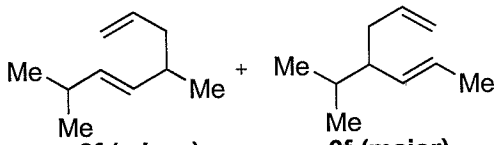
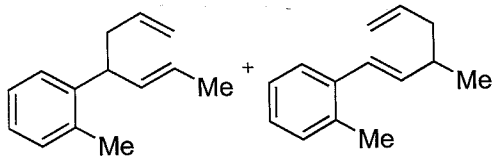


2f (minor)

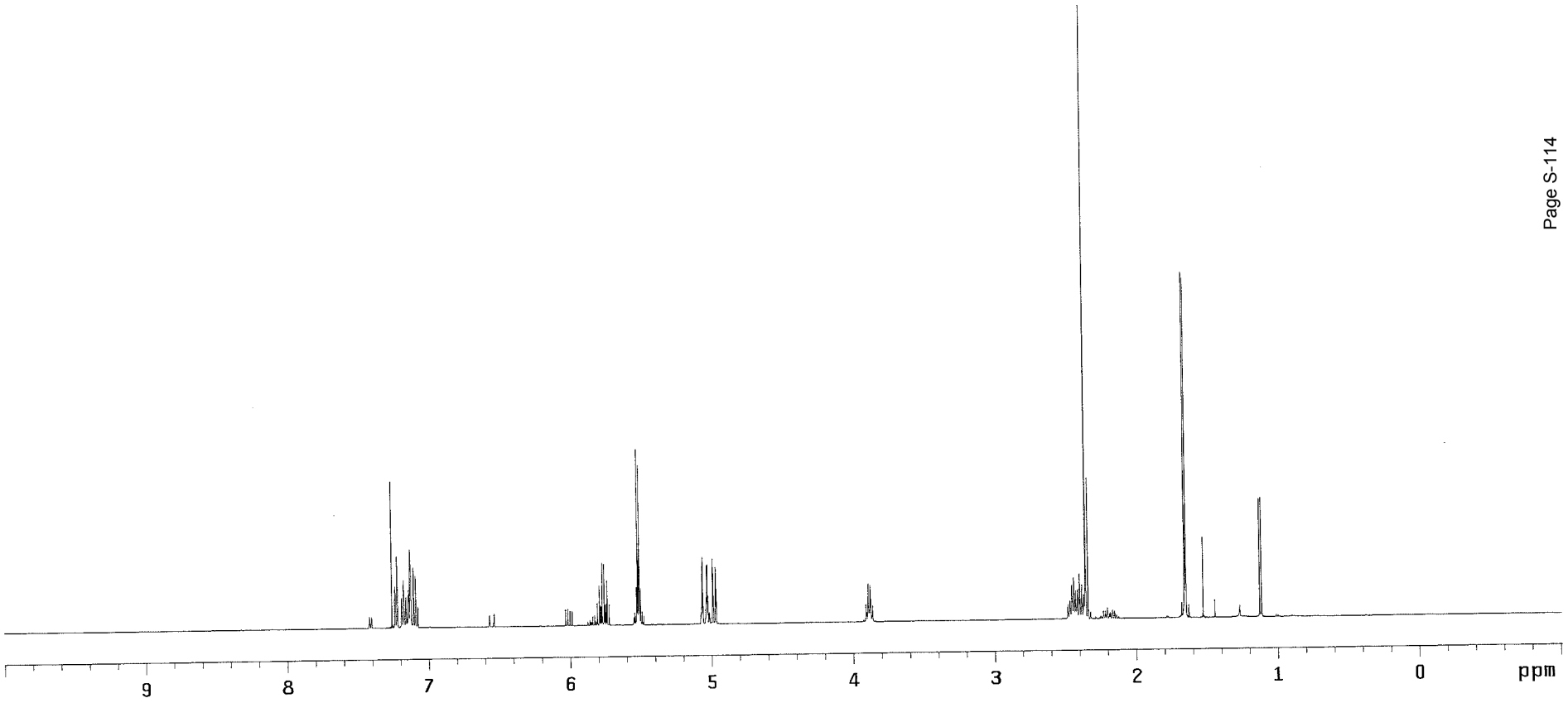
+

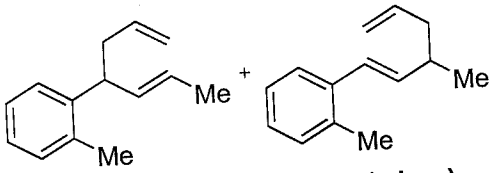
3f (major)

1:2



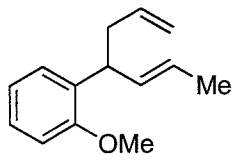
2g (major) 7:1 **3g (minor)**



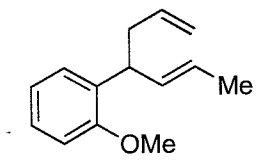


2g (major) 7:1

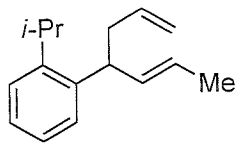
3g (minor)



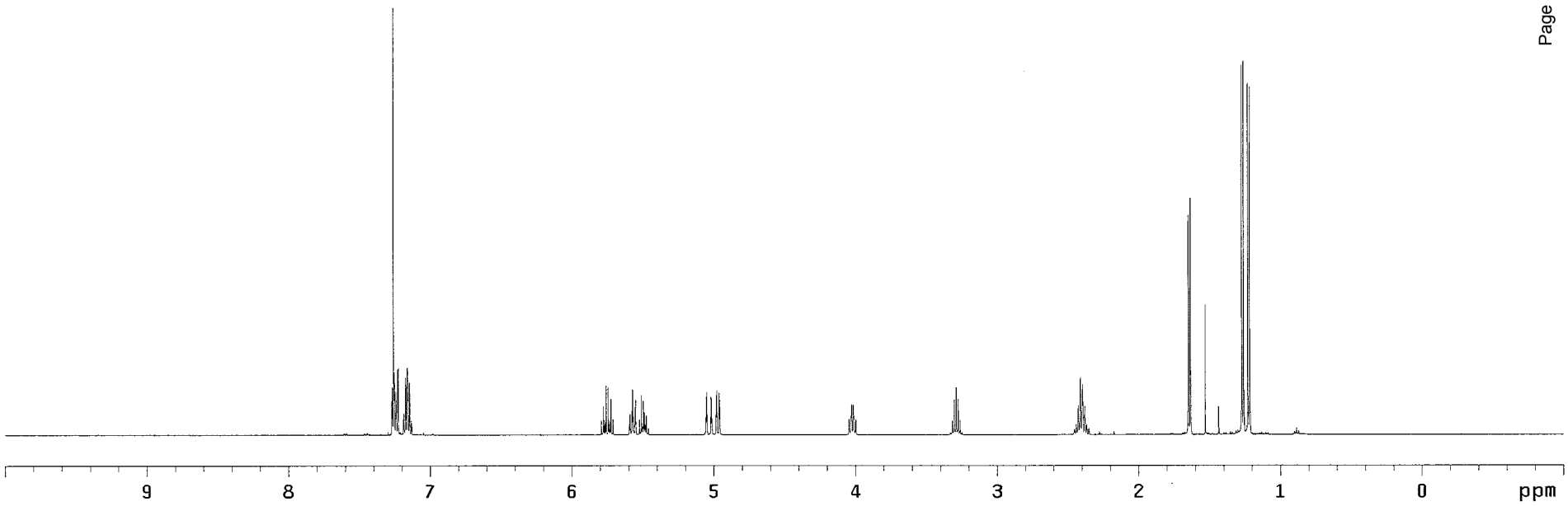
2h

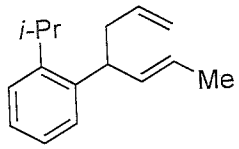


2h

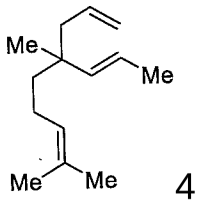


2i





2i



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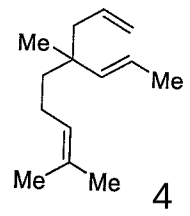
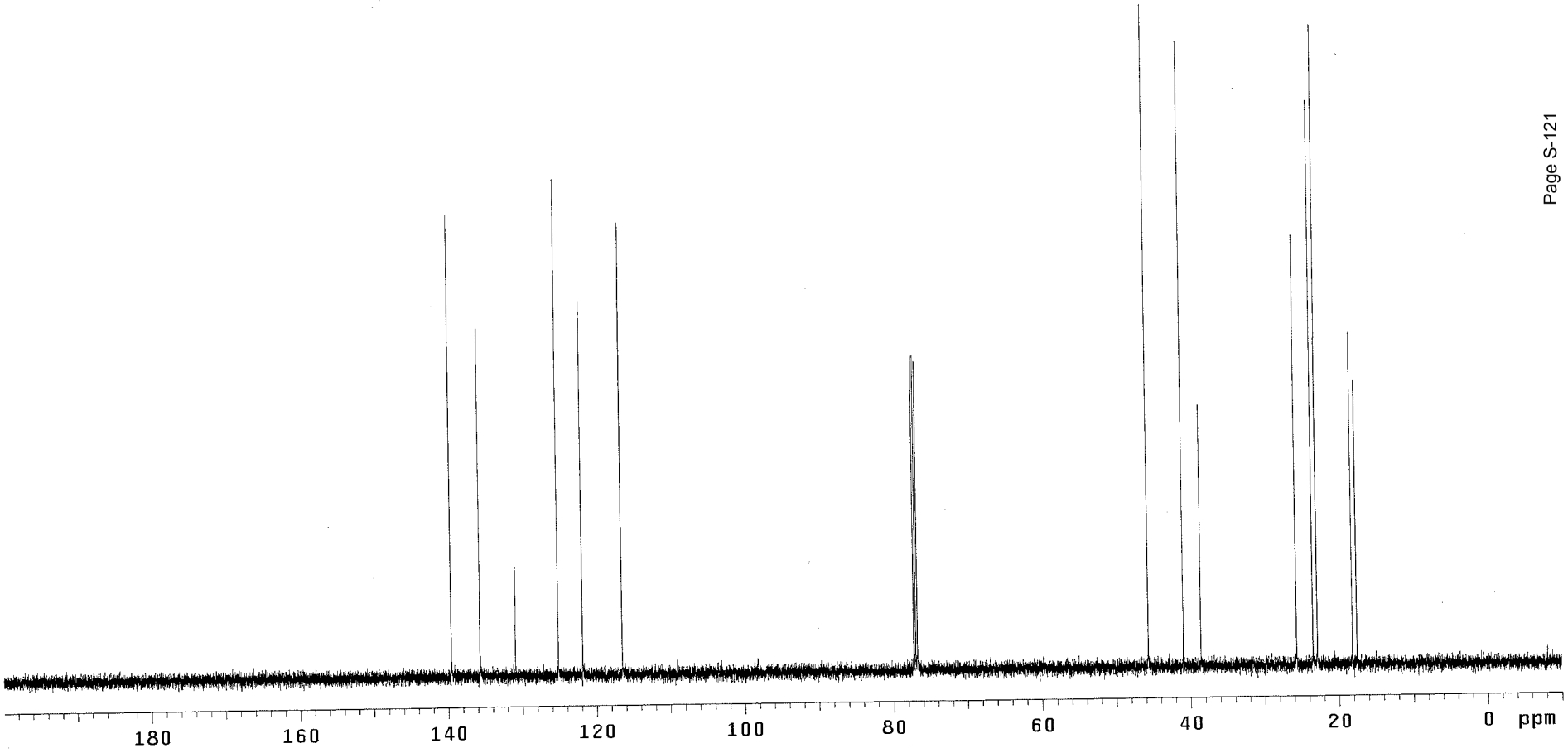
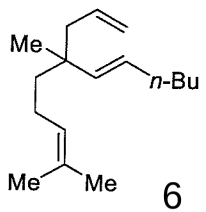


4





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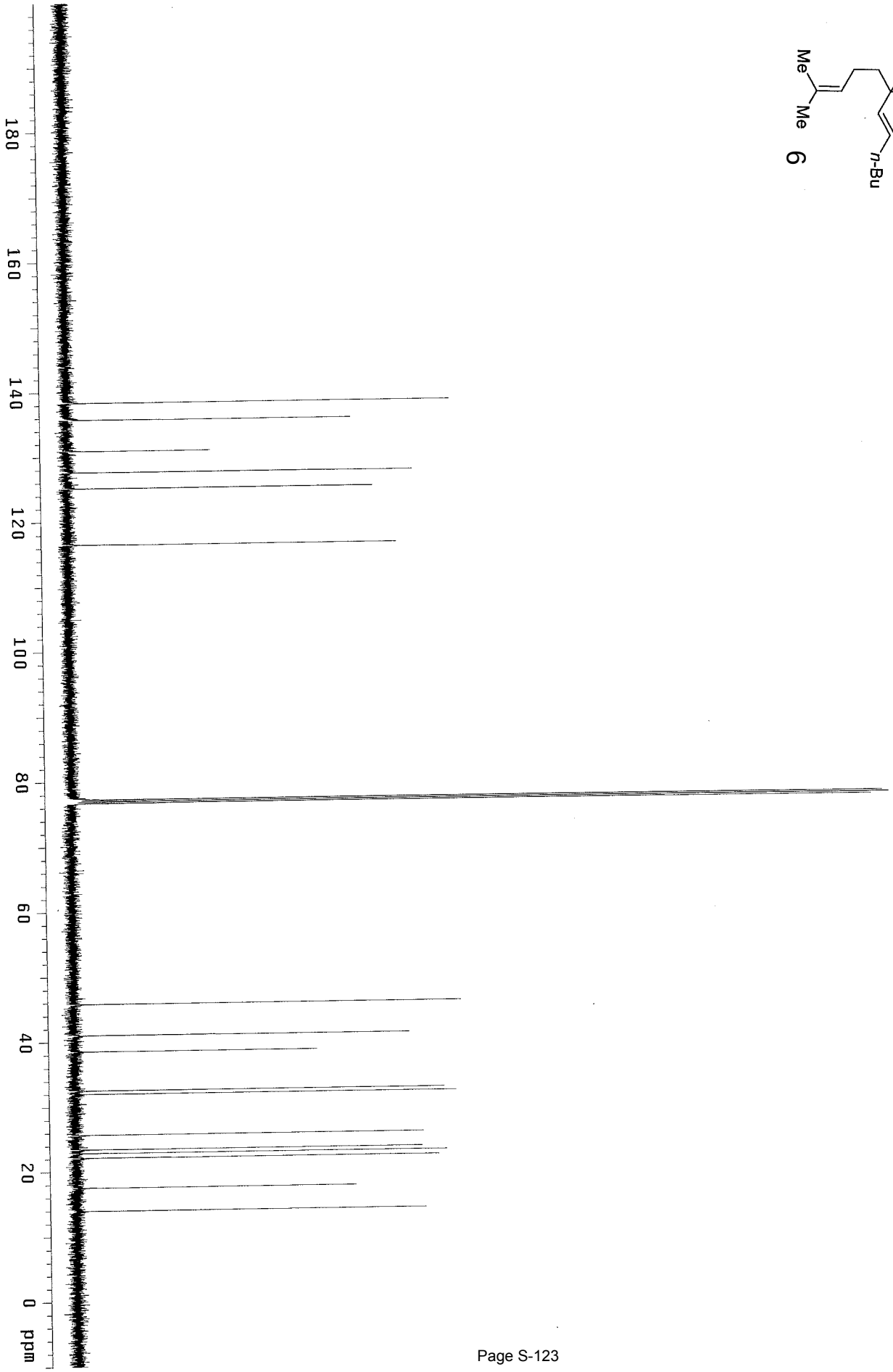
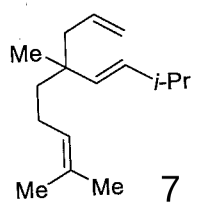


6



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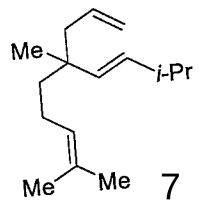

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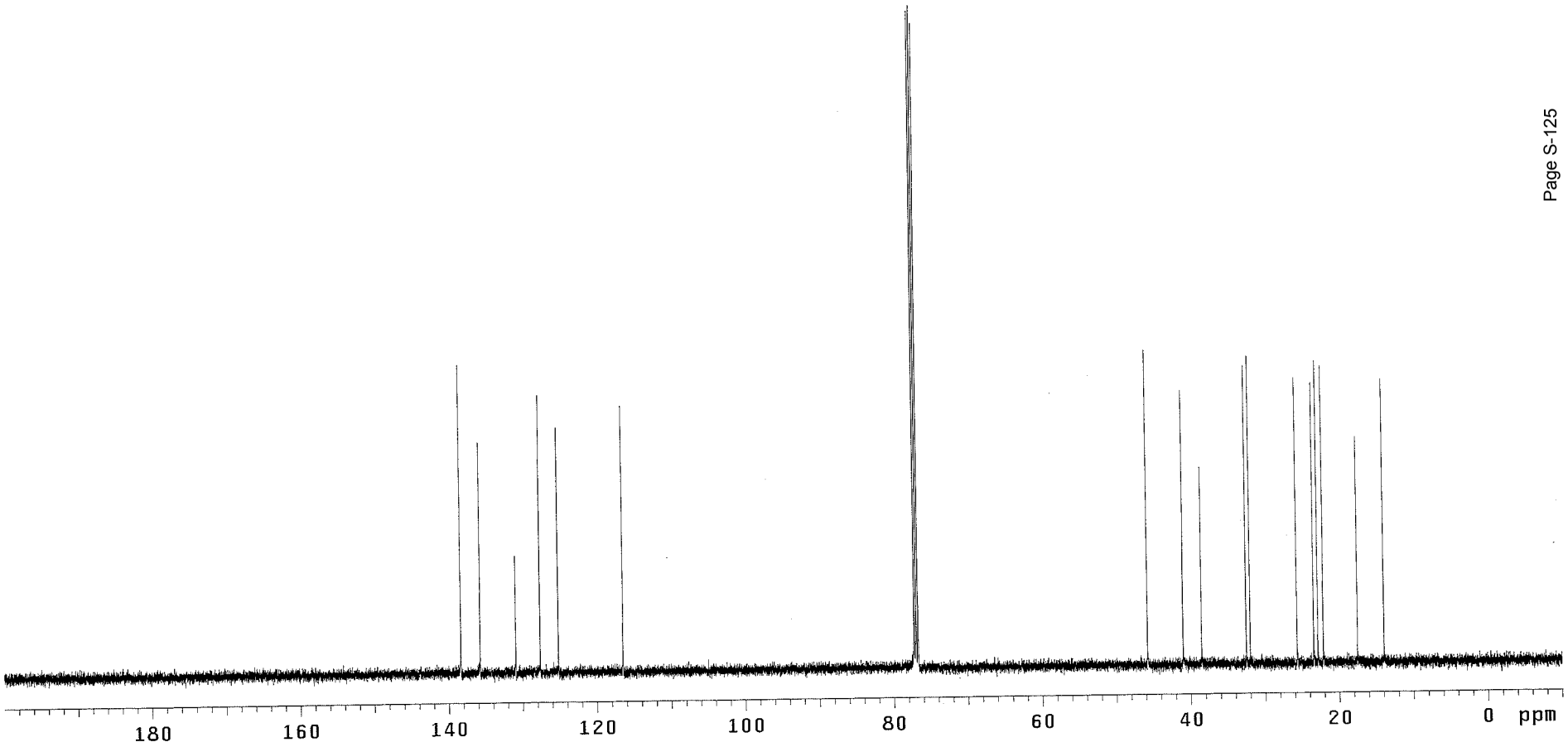
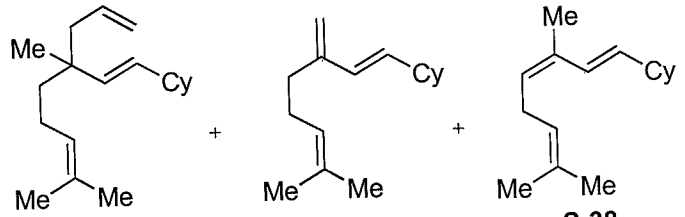
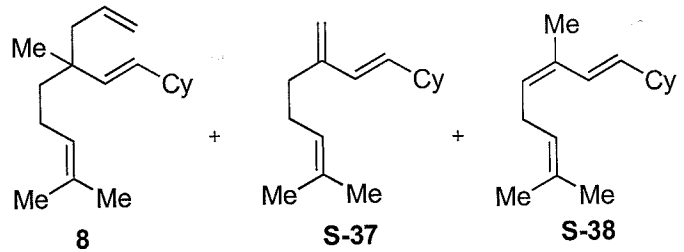




8 **S-37** **S-38**

6:2:1



8 **S-37** **S-38**

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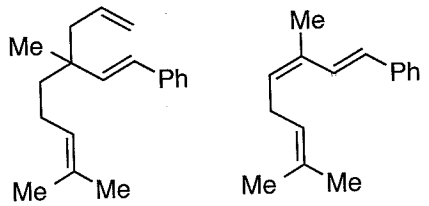
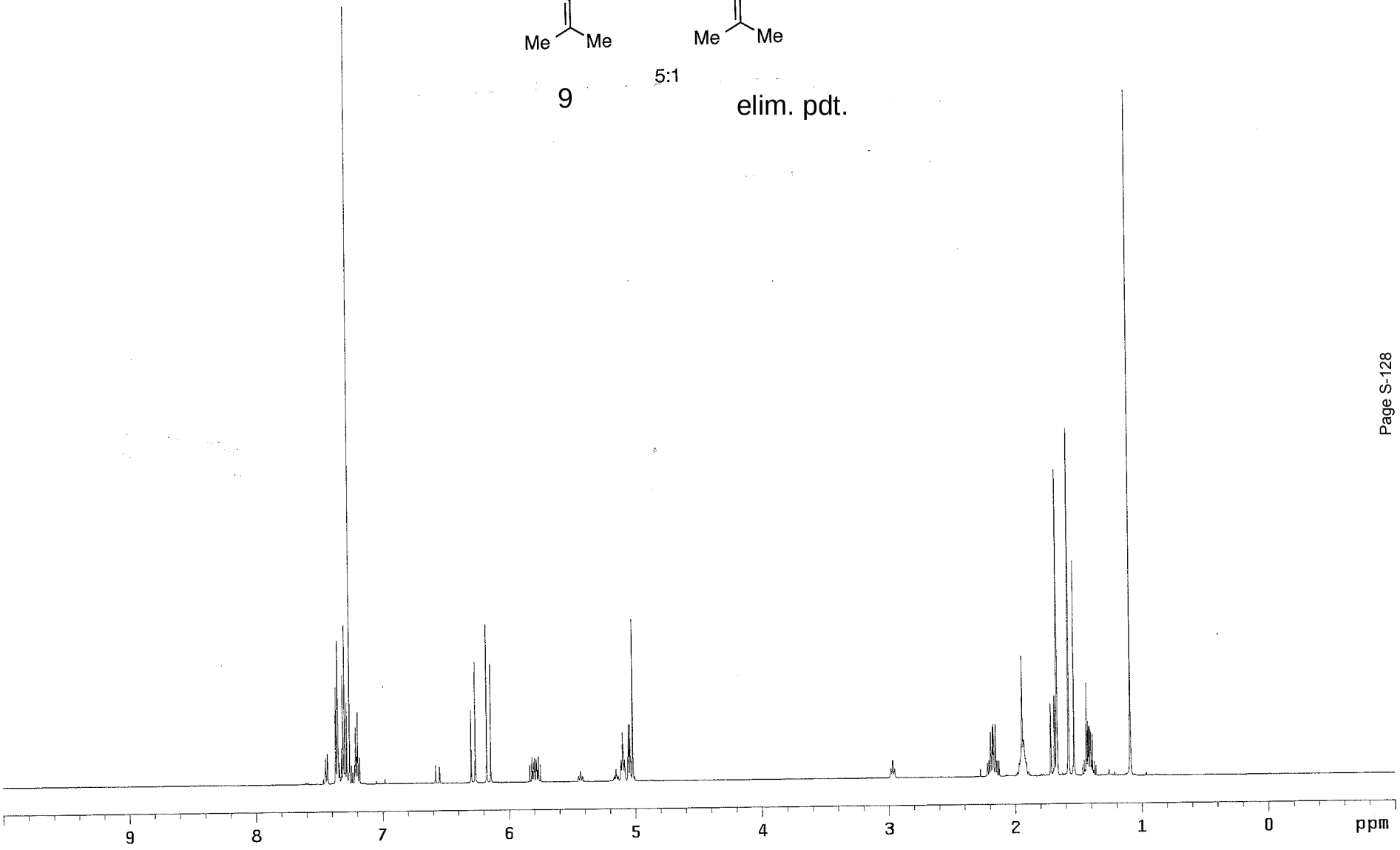
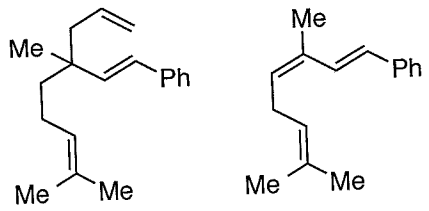


5:1

9

elim. pdt.





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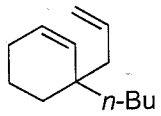

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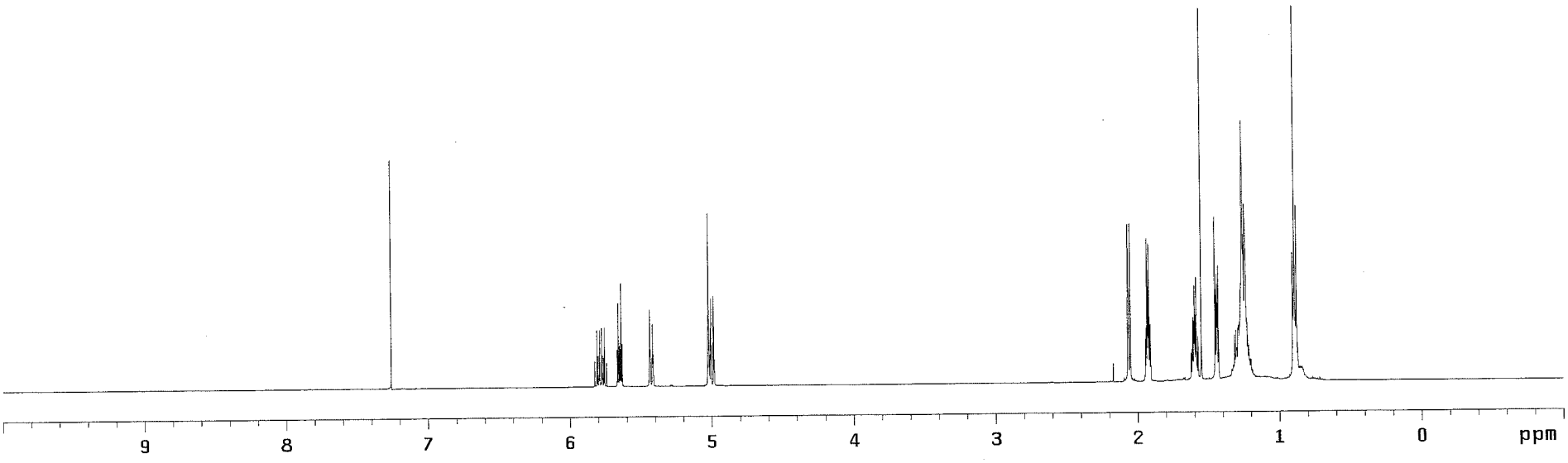

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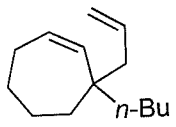

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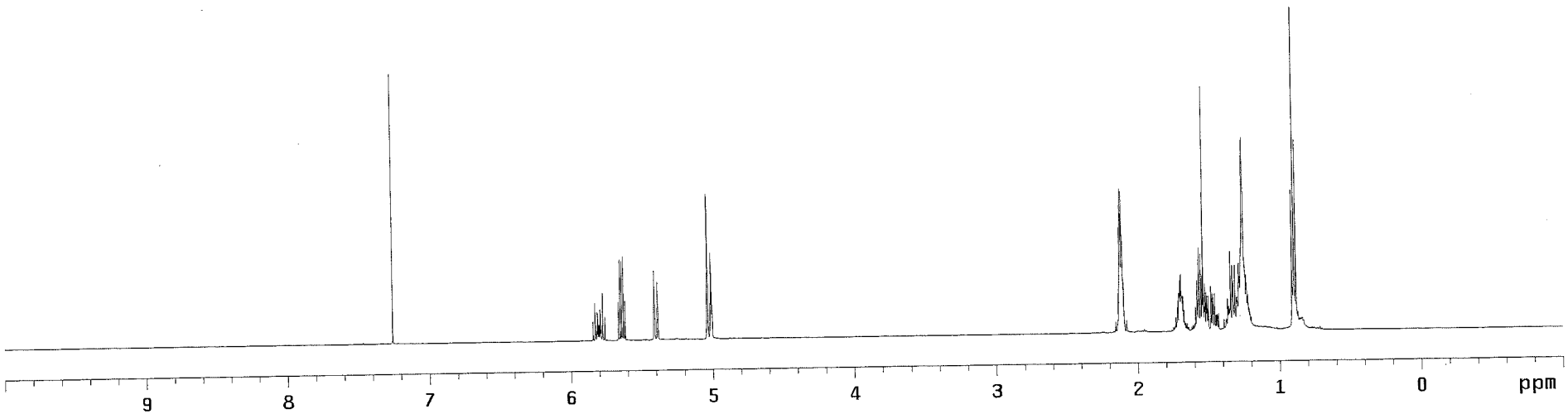

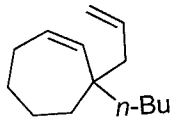

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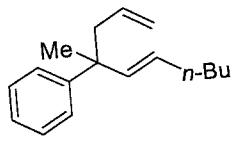

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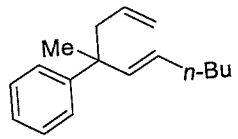

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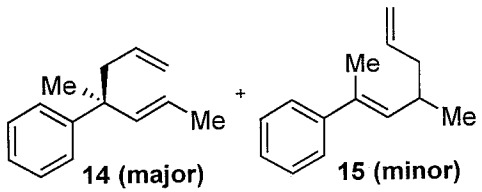
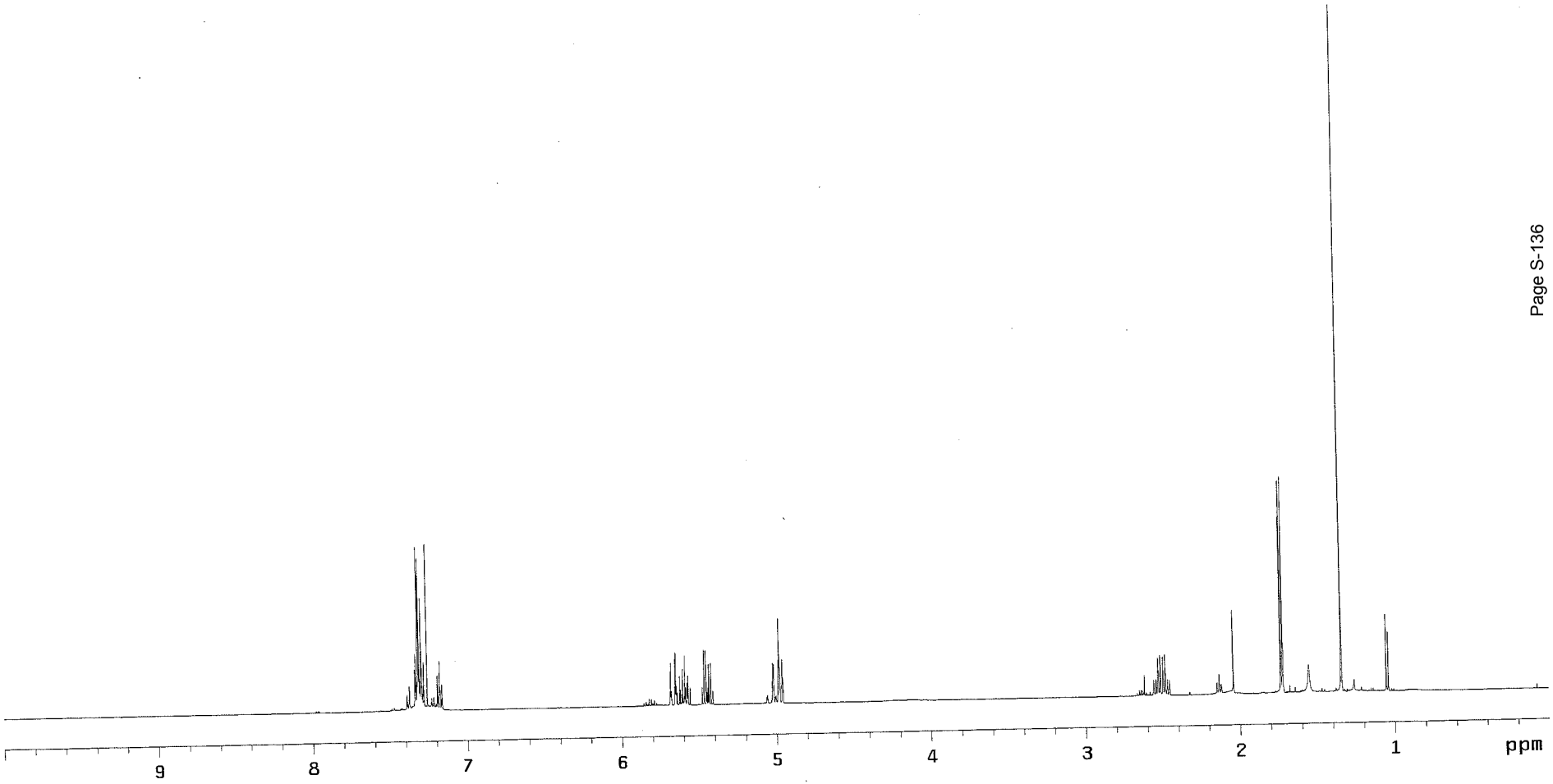


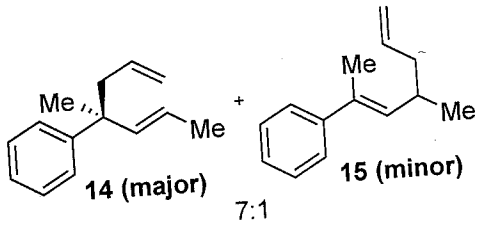
14 (major)

+

15 (minor)

7:1




Me
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15 (minor)
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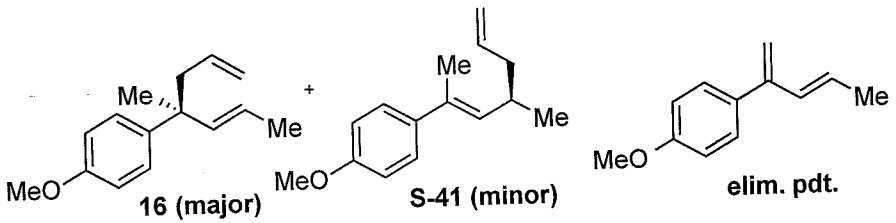

16 (major) **S-41 (minor)** **elim. pdt.**

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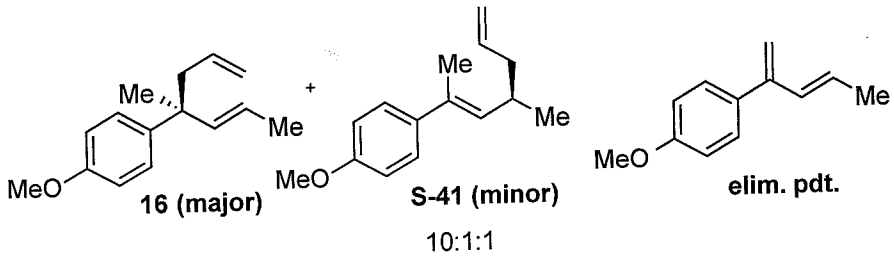

16 (major) **S-41 (minor)** **elim. pdt.**

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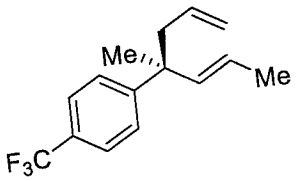

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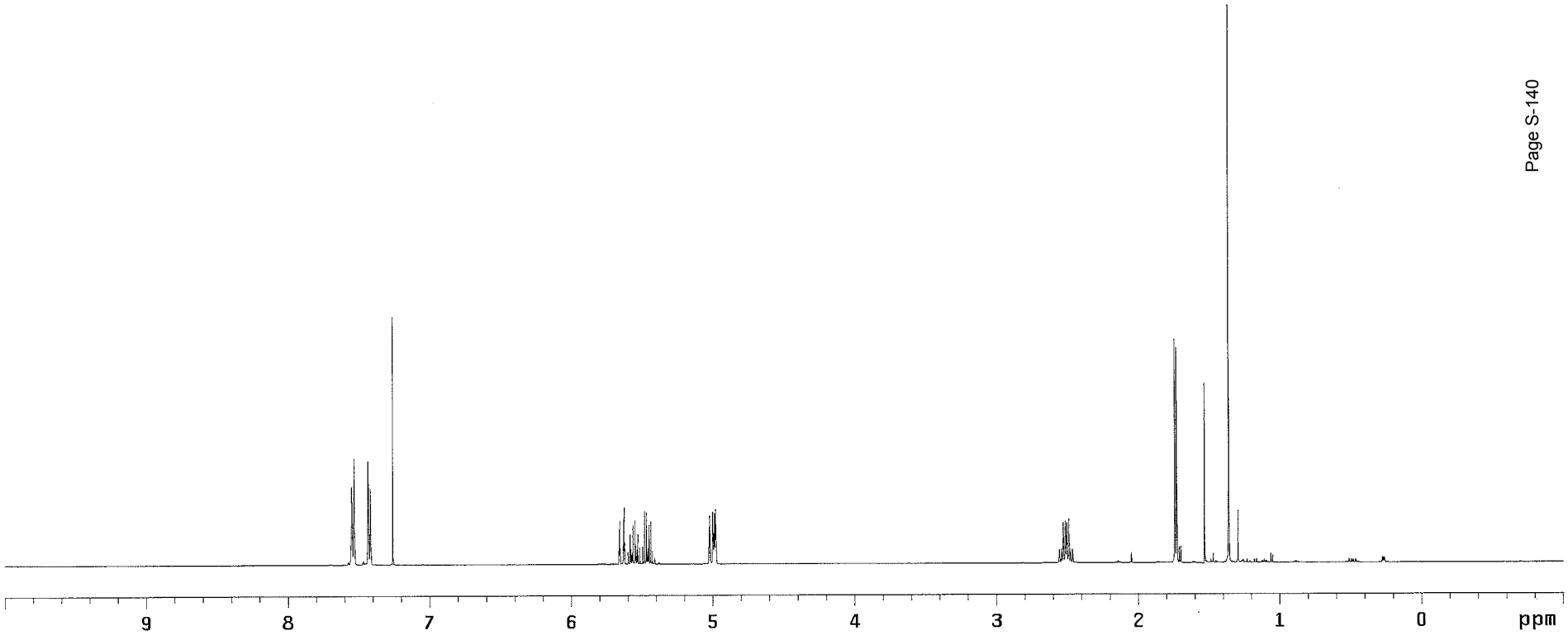

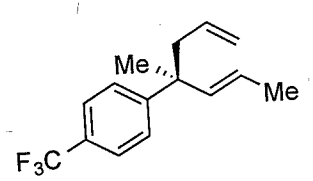

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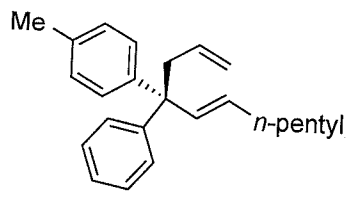

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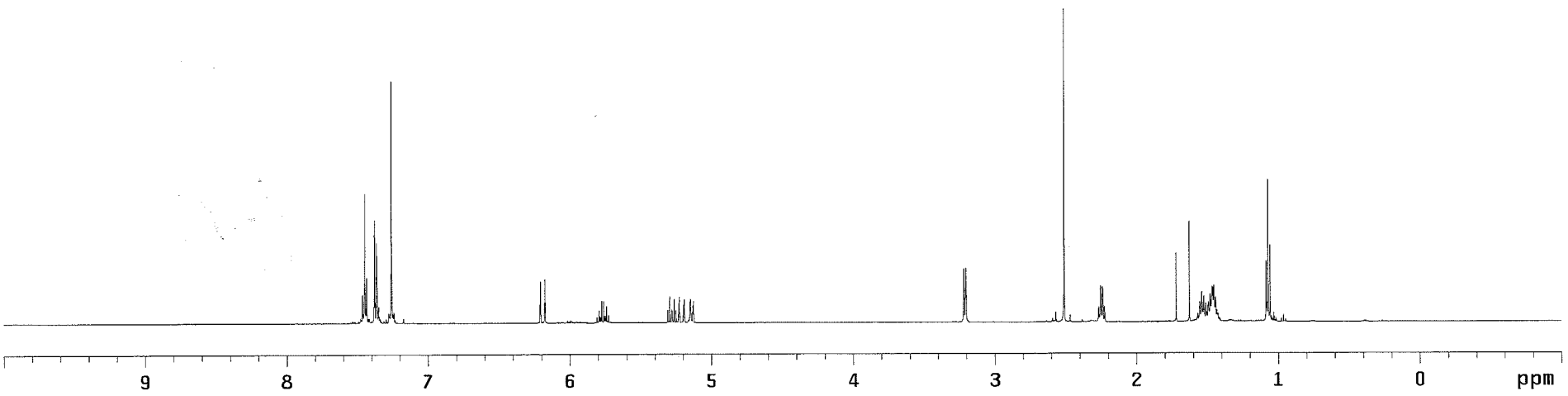

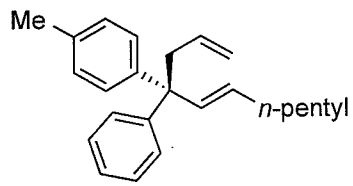

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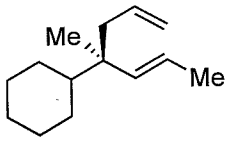

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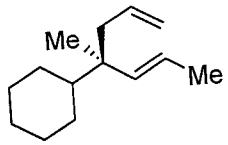

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