# ELECTRONIC SUPPLEMENTARY INFORMATION

## A Novel Catalytic Asymmetric Route towards Skipped Dienes with a Methyl-Substituted Central Stereogenic Carbon

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## *Table of Contents*

## General Techniques

Starting materials were purchased from Aldrich, Alpha Aesar or Acros and used as received unless stated otherwise. All solvents were reagent grade and, if necessary, dried and distilled prior to use. All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Column chromatography was performed on silica gel (Aldrich 60, 230-400 mesh). TLC was performed on silica gel 60/Kieselguhr $F_{254}$.

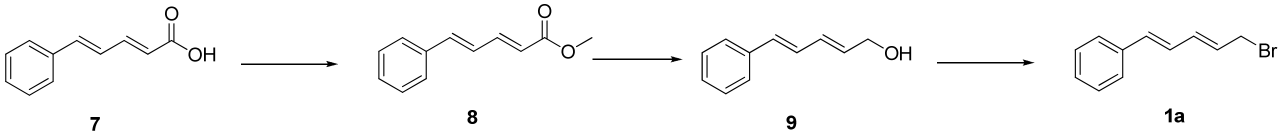
$^1$H and $^{13}$C NMR spectra were recorded on a Varian VXR300 (299.97 MHz for $^1$H, 75.48 MHz for $^{13}$C) or a Varian AMX400 (399.93 MHz for $^1$H, 100.59 MHz for $^{13}$C) spectrometer in $CDCl_3$ unless stated otherwise. Chemical shifts are reported in δ values (ppm) relative to the residual solvent peak ($CDCl_3$, $^1$H = 7.24, $^{13}$C = 77.0). Carbon assignments are based on $^{13}$C and APT $^{13}$C experiments. Splitting patterns are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

High resolution mass spectra (HRMS) were recorded on an AEI-MS-902 and FTMS orbitrap (Thermo Fisher Scientific) mass spectrometer. Optical rotations were measured on a *Schmidt+ Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector (Chiralcel OD-H, 250*4.6, 10 µm) or by capillary GC analysis (HP 6890, CP-Chiralsil-Dex-CB column (25 m * 0.25 mm)) using a flame ionization detector.

Racemic products were synthesized by reaction of the allyl bromide and the corresponding organomagnesium reagent at –80 °C in dry dichloromethane in the presence of $CuBr{\bullet}SMe_2$ (10 mol%) and $PPh_3$ (20 mol%).

## Synthesis of allylic bromides

### Synthesis of ((1*E*,3*E*)-5-bromopenta-1,3-dienyl)benzene (1a)[1]



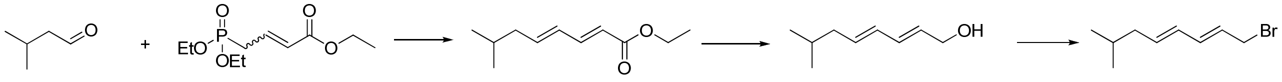
**(2*E*,4*E*)-Methyl 5-phenylpenta-2,4-dienoate (8)**. To a stirred solution of 5-phenylpenta-2,4-dienoic acid **7** (3.91 g, 22.4 mmol) in 50 mL of methanol was added HCl (20 ml, 60 mmol, 3M in methanol) at room temperature. The solution was stirred for 16 h, concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give **8**[1] as a white solid (4.07 g, 97% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.21 (m, 6H), 6.87 – 6.73 (m, 2H), 5.93 (d, *J* = 15.3 Hz, 1H), 3.70 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.5, 144.8, 140.5, 136.0, 129.0, 128.8, 127.2, 126.2, 120.8, 51.6.

**(2*E*,4*E*)-5-Phenylpenta-2,4-dien-1-ol (9).** To a stirred solution of the methyl ester **8** (4.0 g, 21.2 mmol) in 50 mL of dry DCM was added DIBAL-H (63.8 ml, 1 M in DCM, 63.8 mmol, 3 eq) over 0.5 h at –78 °C. The reaction mixture was stirred for 4 h when TLC showed full conversion. The mixture was quenched with 60 mL of saturated aqueous Rochelle salt (potassium sodium tartrate) and stirred for 30 min. The phases were separated and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic phases were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/ether = 4/1) to give **9**[1] as a white solid (3.0 g, 88% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.05 (m, 5H), 6.72 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.36 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.90 (dt, *J* = 15.1, 5.9 Hz, 1H), 4.19 (d, *J* = 5.9 Hz, 2H), 1.31 (br, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 137.1, 132.8, 132.4, 131.6, 128.6, 128.1, 127.6, 126.4, 63.5.

**((1*E*,3*E*)-5-Bromopenta-1,3-dienyl)benzene (1a).** To a stirred solution of NBS (4.17 g, 23.4 mmol, 1.3 eq) in DCM (40 mL) at –20 °C was added $Me_2S$ (0.98 g, 1.2 mL, 28.9 mmol, 1.83 eq) slowly over 5 min. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **9** (2.5 g, 15.6 mmol) in 10 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous $NH_4Cl$ solution (50 mL) when TLC showed full conversion and after the mixture was warmed up to room temperature, the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over $Na_2SO_4$, filtered and concentrated to give crude **1a** as a white solid (2.83 g, 81%) which was used in the next step (asymmetric allylic alkylation) immediately due to instability.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.54 – 7.15 (m, 5H), 6.77 (dd, $J$ = 15.6, 10.4 Hz, 1H), 6.60 (d, $J$ = 15.6 Hz, 1H), 6.46 (dd, $J$ = 14.8, 10.4 Hz, 1H), 6.08 – 5.90 (m, 1H), 4.11 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.7, 135.2, 134.5, 128.9, 128.7, 128.0, 127.3, 126.6, 33.4.

## Synthesis of (2*E*,4*E*)-1-bromo-7-methylocta-2,4-diene (1b)



10 11 12 13 1b

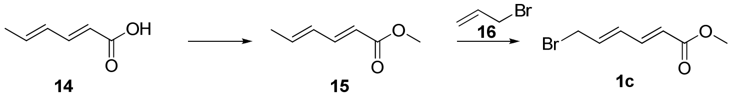
**(2*E*,4*E*)-Ethyl 7-methylocta-2,4-dienoate (12).** To a stirred solution of compound **11** (mixture of E/Z isomers, 5.0 g, 20 mmol) in 30 mL of dry THF was added LiHDMS (20 mL, 20 mmol, 1M in THF) at –78 °C under nitrogen. The mixture was stirred for about 30 min when a THF solution (5 mL) of aldehyde **10** (1.72 g, 20 mmol, 1 eq) was added dropwise over 10 min. The resulting solution was stirred overnight and quenched with a saturated aqueous NH$_4$Cl solution (50 mL) at –78 °C. The mixture was warmed up to room temperature and the layers were separated. The aqueous layer was washed with ether (3 x 30 mL) and the organic layers were dried over Na$_2$SO$_4$, filtered and concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give **12**[2] as a colorless oil (2.3 g, 62% yield). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.25 – 7.12 (m, 1H), 6.17 – 5.94 (m, 2H), 5.72 (d, $J$ = 15.5 Hz, 1H), 4.13 (q, $J$ = 7.1 Hz, 2H), 2.01 – 1.97 (m, 2H), 1.66 – 1.63 (m, 1H), 1.23 (t, $J$ = 7.1 Hz, 3H), 0.84 (d, $J$ = 6.7 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.3, 145.0, 143.5, 129.4, 119.2, 60.2, 42.3, 28.3, 22.3, 14.3.

**(2*E*,4*E*)-7-Methylocta-2,4-dien-1-ol (13).** To a stirred solution of the ethyl ester **12** (2.0 g, 11 mmol) in 30 mL of dry DCM was added DIBAL-H (33 ml, 1 M in DCM, 33 mmol, 3 eq) over 0.5 h at –78 °C. The reaction mixture was stirred for 4 h when TLC showed full conversion. The reaction mixture was quenched with 30 mL saturated aqueous Rochelle salt (potassium sodium tartrate) and stirred for 30 min. The phases were separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic phases were dried over Na$_2$SO$_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/ether = 4/1) to give **13**[1] as a colorless oil (1.5 g, 95% yield). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 6.23 (dd, $J$ = 15.1, 10.4 Hz, 1H), 6.03 (dd, $J$ = 15.1, 10.4 Hz, 1H), 5.81 – 5.63 (m, 2H), 4.16 (dd, $J$ = 6.1, 0.9 Hz, 2H), 2.02 – 1.92 (m, 2H), 1.65 – 1.62 (m, 1H), 1.38 (br, 1H), 0.89 (d, $J$ = 6.7 Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.5, 132.1, 130.4, 129.3, 63.5, 42.0, 28.5, 22.3. HRMS (APCI+) calculated for $C_9H_{15}[M–OH]^+$: 123.1174, found: 123.1116.

**(2*E*,4*E*)-1-Bromo-7-methylocta-2,4-diene (1b).** To a stirred solution of NBS (1.07 g, 6 mmol, 1.3 eq) in DCM (20 mL) at –20 °C was slowly added Me$_2$S (460 mg, 0.54 mL, 7.4 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **13** (560 mg, 4 mmol) in 10 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous $NH_4Cl$ solution (50 mL) when TLC showed full conversion and after the mixture was warmed up to room temperature, the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over $Na_2SO_4$, filtered and the solvent was concentrated to give crude **1b** as colorless oil (0.69 g, 85%) used in the next step immediately due to instability.

$^1$H NMR (400 MHz, $CDCl_3$) δ 6.32 – 6.07 (m, 1H), 5.99 – 5.88 (m, 1H), 5.78 – 5.63 (m, 2H), 4.02 – 3.85 (m, 2H), 1.96 – 1.87 (m, 2H), 1.60 – 1.57 (m, 1H), 0.82 (d, *J* = 6.7 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 136.5, 135.4, 129.8, 126.1, 42.0, 33.9, 28.4, 22.3.

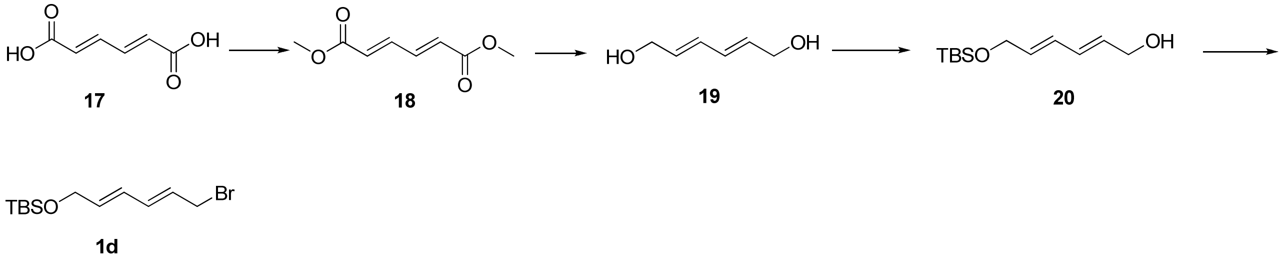
## Synthesis of (2*E*,4*E*)-methyl 6-bromohexa-2,4-dienoate (1c)[3]



**(2*E*,4*E*)-Methyl hexa-2,4-dienoate (15).** To a stirred solution of acid **14** (4 g, 36 mmol, 1 eq) in 50 mL of methanol was added HCl (24 mL, 72 mmol, 3M in methanol, 2 eq) at room temperature. The resulting solution was stirred for 16 h, concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give **15**[4] as colorless oil (4.22 g, 93% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.10 (m, 1H), 6.19 – 5.98 (m, 2H), 5.71 (d, *J* = 15.4 Hz, 1H), 3.67 (s, 3H), 1.78 (d, *J* = 5.6 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.8, 145.2, 139.4, 129.7, 118.5, 51.4, 18.6.

**(2*E*,4*E*)-Methyl 6-bromohexa-2,4-dienoate (1c).** To a solution of methyl sorbate **15** (1.0 g, 8 mmol) and allyl bromide **16** (4.84 g, 40 mmol, 5 eq) in 80 mL of $CH_2Cl_2$ (*c* = 0.1 M) was added the Hoveyda-Grubbs-II catalyst ($C_{11}H_{38}Cl_2N_2ORu$, 50 mg, 0.08 mmol, 0.01 equiv) at room temperature. After stirring for 24 h, silica was added to the reaction mixture and after evaporation of the solvent, the pad of silica was loaded on top of a silica gel column and the product was quickly purified by a flash chromatography (eluent pentane/ether = 4/1) to give **1c** as a colorless oil (483 mg, 30% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 1H), 6.39 (dd, *J* = 15.0, 10.9 Hz, 1H), 6.24 (dd, *J* = 15.4, 10.9 Hz, 1H), 5.94 (d, *J* = 15.4 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.75 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.9, 142.8, 136.7, 131.8, 122.7, 51.7, 31.2.

## Synthesis of ((2*E*,4*E*)-6-bromohexa-2,4-dienyloxy)(*tert*-butyl) dimethylsilane (1d)



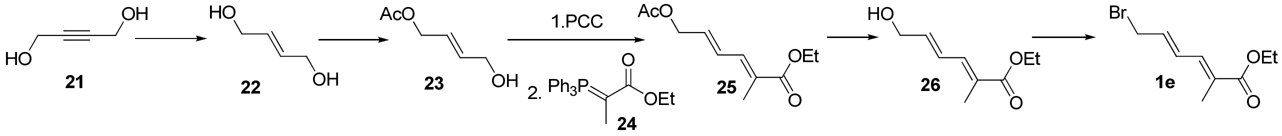
**(2*E*,4*E*)-Dimethyl hexa-2,4-dienedioate (18).** To a stirred solution of acid **17** (4.0 g, 28.1 mmol) in 50 mL of methanol was added HCl (19 mL, 57 mmol, 3M in methanol, 2 eq) at room temperature. The resulting solution was stirred for 16 h, concentrated and purified by crystallization from ether to give **18**[5] as a white solid (4.13 g, 86% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 2H), 6.21 – 6.07 (m, 2H), 3.72 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.3, 140.9, 128.0, 51.9.

**(2*E*,4*E*)-Hexa-2,4-diene-1,6-diol (19).** To a stirred solution of the methyl ester **18** (1.0 g, 5.94 mmol) in 30 mL of dry DCM was added DIBAL-H (36 ml, 1 M in DCM, 36 mmol, 6 eq) over 0.5 h at –78 °C. The reaction mixture was stirred for 8 h when TLC showed full conversion. The reaction mixture was quenched with 30 mL saturated aqueous Rochelle salt (potassium sodium tartrate) followed by stirring for 30 min. The phases were separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic phases were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 2/1) to give **19**[6] as a white solid (560 mg, 83% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.30 – 6.08 (m, 2H), 5.91 – 5.66 (m, 2H), 4.14 (t, *J* = 5.4 Hz, 4H), 1.29 (t, *J* = 5.4 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 132.4, 130.4, 63.2.

**(2*E*,4*E*)-6-((*tert*-Butyldimethylsilyl)oxy)hexa-2,4-dien-1-ol (20).** To a solution of **19** (300 mg, 2.63 mmol) in dry dichloromethane (20 mL) was added imidazole (269 mg, 3.95 mmol, 1.5 eq) followed by *tert*-butyl-dimethylsilyl chloride (436 mg, 2.89 mmol, 1.1 eq), and the resulting white suspension was stirred at room temperature for 12 h. The reaction mixture was quenched with 20 mL of water and extracted with ether (3 x 20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 4/1) to give **20**[7] as a colorless oil (319 mg, 53%). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.24 – 6.11 (m, 2H), 5.81 – 5.65 (m, 2H), 4.15 (d, *J* = 4.5 Hz, 2H), 4.11 (t, *J* = 5.6 Hz, 2H), 1.50 (br, 1H), 0.84 (s, 9H), 0.00 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 133.3, 131.4, 131.0, 128.8, 63.4, 63.3, 25.9, 18.4, –5.2.

**((2*E*,4*E*)-6-Bromohexa-2,4-dienyloxy)(*tert*-butyl) dimethylsilane (1d).** To a stirred solution of NBS (267 mg, 1.5 mmol, 1.5 eq) in DCM (20 mL) at –20 °C was slowly added $Me_2S$ (115 mg, 0.14 mL, 1.85 mmol, 1.85 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **20** (228 mg, 1 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous $NH_4Cl$ solution (20 mL) when TLC showed full conversion and subsequently the mixture was warmed up to room temperature and the layers separated. The organic layer was washed with water (3 x 10 mL), dried over $Na_2SO_4$, filtered and concentrated to give the crude **1d** as colorless oil (248 mg, 85%) immediately used in the next step due to instability. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.29 – 6.10 (m, 2H), 5.77 (m, 2H), 4.16 (dd, *J* = 5.0, 1.1 Hz, 2H), 3.96 (d, *J* = 7.9 Hz, 2H), 0.84 (s, 9H), 0.00 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.4, 127.9, 127.9, 63.1, 33.3, 25.9, 18.1, –5.3.

## Synthesis of (2*E*,4*E*)-ethyl 6-bromo-2-methylhexa-2,4-dienoate (1e)



**(*E*)-But-2-ene-1,4-diol (22).** To a stirred solution of diol **21** (2.6 g, 30 mmol) in dry THF (40 mL) was added solid $LiAlH_4$ (1.44 g, 36 mmol, 1.2 eq) at 0 °C under nitrogen. The mixture was heated to reflux for 4 h, followed by quenching with a saturated aqueous $NH_4Cl$ solution (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and the phases were separated. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 1/1) to give **22**[8] as colourless oil (660 mg, 20% yield, soluble in water). $^1$H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.79 (m, 2H), 4.17 – 4.05 (m, 4H), 1.38 (br, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 130.5, 62.9.

**(*E*)-4-Hydroxybut-2-en-1-yl acetate (23).** To a stirred solution of but-2-ene-1,4-diol **22** (1.0 g, 11 mmol) in dry THF (20 mL) was added solid NaH (440 mg, 60% in mineral oil, 11 mmol, 1 eq) at 0 °C. The mixture was stirred at room temperature for 1 h followed by the addition of a THF solution (5 mL) of acetyl chloride (863 mg, 0.81 mL, 1 eq). The reaction mixture was stirred for 3 h after which time TLC (diethyl ether) showed a mixture of starting compound, monoacetate and diacetate. $H_2O$ (10 mL) was added, and the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic phases were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 4/1) to give **23**[9] as colourless oil (930 mg, 65% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.81 (m, 1H), 5.80 – 5.73 (m, 1H), 4.52 (dd, *J* = 5.8, 1.2 Hz, 2H), 4.12 (dd, *J* = 5.0, 1.2 Hz, 2H), 2.01 (s, 3H), 1.63 (br, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.6, 133.5, 125.1, 64.2, 62.7, 20.9.

**(2*E*,4*E*)-Ethyl 6-acetoxy-2-methylhexa-2,4-dienoate (25).** 4-Acetoxy- 2-buten-1-ol **23** (0.91 g, 7 mmol) was added to a suspension of pyridinium chlorochromate (1.81 g, 8.4 mmol) in 20 mL of DCM at 0 °C. The mixture was stirred at room temperature until TLC showed full conversion. The solids were removed by flash chromatography, washed with diethyl ether and the organic solvents were removed in vacuo to give 4-acetoxy-crotonaldehyde used immediately in the next step.

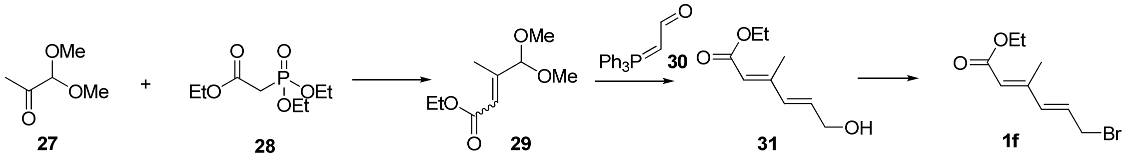
The aldehyde was dissolved in 10 mL of DCM followed by the addition of phosphorane **24** (2.54 g, 7.0 mmol) at room temperature. The solution was stirred for 30 min until TLC showed full conversion. The solvent was removed in vacuo. The product was purified by flash chromatography (eluent pentane/ether = 4/1) to give **25**[9] as colourless oil (945 mg, 64% yield over 2 steps). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 11.4 Hz, 1H), 6.58 – 6.45 (m, 1H), 6.02 (dt, *J* = 15.2, 6.1 Hz, 1H), 4.62 (d, *J* = 6.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.88 (d, *J* = 0.7 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

**(2*E*,4*E*)-Ethyl 6-hydroxy-2-methylhexa-2,4-dienoate (26).** $K_2CO_3$ (1.23 g, 8.9 mmol) was added to a solution of **25** (945 mg, 4.45 mmol) in 15 mL of ethanol at room temperature. The resulting mixture was stirred about 2 h when TLC showed full conversion. The reaction was quenched with an aqueous saturated NaCl solution (20 mL). The phases were separated and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 4/1) to give **26**[9] as colourless oil (707 mg, 93% yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 11.4 Hz, 1H), 6.53 (dd, *J* = 15.2, 11.4 Hz, 1H), 6.11 (dt, *J* = 15.2, 5.2 Hz, 1H), 4.28 – 4.20 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.89 (d, *J* = 0.7 Hz, 3H), 1.45 (br, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.4, 139.2, 137.1, 127.8, 125.7, 63.1, 60.6, 14.3, 12.7.

**(2*E*,4*E*)-Ethyl 6-bromo-2-methylhexa-2,4-dienoate (1e).** To a stirred solution of NBS (470 mg, 2.64 mmol, 1.3 eq) in DCM (20 mL) at –20 °C was slowly added $Me_2S$ (197 mg, 0.23 mL, 3.17 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **26** (300 mg, 1.76 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous $NH_4Cl$ solution (50 mL) when TLC showed full conversion and after the mixture was warmed to room temperature, the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over $Na_2SO_4$, filtered and concentrated to give the crude **1e** as colorless oil (323 mg, 79%) used in the next step immediately due to instability. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 11.4, 0.9

Hz, 1H), 6.59 – 6.44 (m, 1H), 6.13 (dt, *J* = 15.4, 7.8 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.01 (d, *J* = 7.8 Hz, 2H), 1.90 (d, *J* = 1.3 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.9, 136.0, 135.1, 129.6, 129.5, 60.8, 32.0, 14.3, 12.8.

### Synthesis of (2*E*,4*E*)-ethyl 6-bromo-3-methylhexa-2,4-dienoate (1f)



**Ethyl 4,4-dimethoxy-3-methylbut-2-enoate (29).** A mixture of 1,1-dimethoxyacetone **27** (5.91 g, 50 mmol) and ethyl 2-(diethoxyphosphoryl)acetate **28** (13.45 g, 60 mmol) was added dropwise to a suspension of $K_2CO_3$ (17.28 g) in 10 mL of water at room temperature. The reaction mixture was stirred for 16 h. The insoluble material was then removed by filtration and washed with ether. The organic phase was separated and washed with brine (50 mL). The organic layer was dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/ether) to give product **29**[10] as colorless oil (8.0 g, 85%, mixture of E and Z acetal esters).

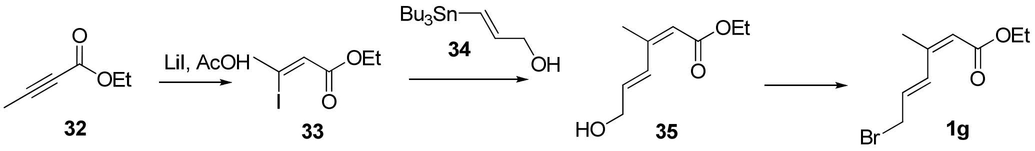
**(2*E*,4*E*)-Ethyl 6-hydroxy-3-methylhexa-2,4-dienoate (31).** HCl (3 N, 3.5 mL of an aq. solution) was added dropwise to a stirred solution of the above obtained esters **29** (2.0 g, 10.6 mmol) in 15 mL DCM at 0 °C. The resulting mixture was stirred for 2 h. The organic layer was separated and washed with a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (20 mL), dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by vacuum distillation to yield the aldehyde which was used directly for the next step.

Compound **30** (3.2 g, 10.6 mmol) was added to a stirred solution of the aldehyde in DCM (10 mL) at room temperature. The reaction mixture was stirred for 15 h and subsequently concentrated. The resulting mixture was dissolved in pentane and the solids were filtered. The solution was concentrated to give the crude aldehyde which was used in the next step.

A solution of the aldehyde in 5 mL of ethanol was added to a solution of sodium borohydride (1.0 g, 25 mmol) in EtOH/$H_2O$ (1:1, 20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 20 min followed by quenching with aqueous saturated NaCl. The aqueous layer was separated and extracted with $Et_2O$ (5 x 20 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, concentrated and purified by flash chromatography (eluent pentane/ether = 1/1) to give product **31**[11] as colorless oil (0.87 g, 50% yield over three steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.26 (d, *J* = 15.8 Hz, 1H), 6.17 (m, 1H), 5.71 (s, 1H), 4.24 (d, *J* = 5.2 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.51 (br, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.0, 151.3, 134.3, 133.8, 119.7, 63.1, 59.8, 14.3, 13.8.

**(2*E*,4*E*)-Ethyl 6-bromo-3-methylhexa-2,4-dienoate (1f).** To a stirred solution of NBS (470 mg, 2.64 mmol, 1.3 eq) in DCM (20 mL) at –20 °C was slowly added $Me_2S$ (197 mg, 0.23 mL, 3.17 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **31** (300 mg, 1.76 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous $NH_4Cl$ solution (50 mL) when TLC showed full conversion and subsequently the mixture was warmed up to room temperature and the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over $Na_2SO_4$, filtered and concentrated to give the crude **1f** as colorless oil (354 mg, 86%) used in the next step immediately due to instability. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.29 – 6.13 (m, 2H), 5.73 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.99 (d, *J* = 7.1 Hz, 2H), 2.20 (d, *J* = 1.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.6, 150.3, 137.6, 130.7, 121.1, 59.9, 32.0, 14.3, 13.8.

## Synthesis of (2*Z*,4*E*)-ethyl 6-bromo-3-methylhexa-2,4-dienoate (1g)



**(*Z*)-Ethyl 3-iodobut-2-enoate (33).** To a mixture of ethyl but-2-ynoate **32** (2.34 g, 20 mmol) and lithium iodide (4.4 g, 32 mmol, 1.6 eq) was added acetic acid (6 mL) at room temperature. The reaction mixture was heated to 70 °C and stirred for 16 h followed by dilution with ether (50 mL). The organic phase was washed with water (20 mL), saturated aqueous $NaHCO_3$ (20 mL), and saturated aqueous $Na_2S_2O_3$ (20 mL), dried over $Na_2SO_4$, filtered and concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give product **33**[12] as a colorless oil (2.1 g, 88% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.29 (q, *J* = 1.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.73 (d, *J* = 1.4 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

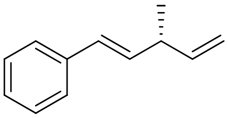
**(2*Z*,4*E*)-Ethyl 6-hydroxy-3-methylhexa-2,4-dienoate (35).** A solution of $Pd_2(dba)_3$ (45 mg, 0.005 mmol) in 20 mL of NMP was treated with triphenyl arsine (59 mg, 0.2 mmol) at room temperature. The solution was stirred for 10 min followed by the addition of a solution of iodide **33** (466 mg, 1.94 mmol) in 5 mL of NMP. The solution was further stirred for 10 min followed by the addition of a solution of stannane **34**[13] (674 mg, 1.94 mmol) in 5 mL of NMP. The reaction mixture was stirred for 16 h followed by quenching with saturated aqueous potassium fluoride solution (20 mL). The reaction mixture was diluted with diethyl ether (20 mL). The organic layer was separated and washed with saturated aqueous potassium fluoride solution (10 mL), dried over $Na_2SO_4$, filtered and concentrated. The product was purified by column chromatography (eluent pentane/ether = 2/1) to give **35** as a colourless oil (252 mg, 76%). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 16.0, 0.7 Hz, 1H), 6.23 (dt, *J* = 16.0, 5.6 Hz, 1H), 5.71 (s, 1H), 4.32 (td, *J* = 5.6, 1.4 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.02 (d, *J* = 1.3 Hz, 3H), 1.63 (br, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.2, 150.0, 135.8, 127.8, 117.9, 63.6, 59.8, 21.0, 14.3. HRMS (APCI+) calculated for $C_9H_{13}O_2[M{-}OH]^+$:153.0910, found:153.0909.

**(2*Z*,4*E*)-Ethyl 6-bromo-3-methylhexa-2,4-dienoate (1g).** To a stirred solution of NBS (313 mg, 1.76 mmol, 1.3 eq) in DCM (20 mL) at –20 °C was slowly added $Me_2S$ (132 mg, 0.16 mL, 2.12 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **35** (200 mg, 1.18 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous $NH_4Cl$ solution (50 mL) after TLC showed full conversion and subsequently the mixture was warmed up to room temperature and the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated to give the crude **1g** as colorless oil (214 mg, 78%) used in the next step immediately due to instability. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 15.6, 0.9 Hz, 1H), 6.23 (dt, *J* = 15.6, 7.8 Hz, 1H), 5.72 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.10 (dd, *J* = 7.8, 0.9 Hz, 2H), 2.00 (d, *J* = 1.3 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 165.9, 149.0, 132.0, 131.1, 119.2, 59.9, 32.6, 20.8, 14.3.

## General procedure for the copper-catalyzed allylic alkylation of an allylic bromide with organomagnesium reagents

A Schlenk tube equipped with septum and stirring bar was charged with CuBr•SMe$_2$ (0.0125 mmol, 2.6 mg, 5 mol%) and the appropriate ligand (0.015 mmol, 6 mol%). Dry dichloromethane (3 mL) was added and the solution was stirred under nitrogen at room temperature for 15 min and cooled to –80 °C. Then, the corresponding organomagnesium reagent (0.3 mmol, 1.2 eq) was added under nitrogen. Allylic bromide (0.25 mmol) was dissolved in 1 mL of DCM and added dropwise to the reaction mixture over 1 h using a syringe pump. The reaction was quenched after overnight with a saturated aqueous NH$_4$Cl solution (2 mL) and the mixture was warmed up to room temperature, diluted with ether and the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 5 mL) and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and carefully concentrated (note: several products are highly volatile). The crude product was purified by flash chromatography on silica gel using different mixtures of n-pentane: Et$_2$O as the eluent.

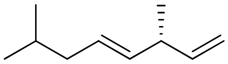
**Note**: Gas chromatography analysis was carried out to determine the S$_N$2':S$_N$2 ratio's and ee's on a sample obtained after aqueous extraction with dichloromethane, which has been passed through a short plug of silica gel to remove transition metal residues.



**(*R*,*E*)-(3-Methylpenta-1,4-dienyl)benzene (2a)**

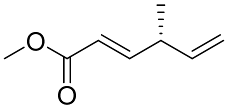
The title compound was prepared from **1a** (55 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO$_2$, Pentane) afforded product (26 mg, 66% yield, 99% *ee*) as a colourless oil as a mixture of two regioisomers **2a**/**3a** (S$_N$2'/S$_N$2) in 95:5 ratio (determined by $^1$H NMR at 20 °C and GC). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.14 (m, 5H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.88 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.05 (m, 2H), 3.11 – 2.99 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.4, 137.6, 134.3, 128.6, 128.5, 127.0, 126.1, 113.3, 40.6, 19.8. HRMS (APCI+) calculated for C$_{12}$H$_{15}$:159.1168, found: 159.1157. $[\alpha]_D^{20}$ = –56.5 (c = 2.3, CHCl$_3$), [Lit. [14] (*S* isomer, er = 96:4) $[\alpha]_D^{20}$ = +55 (c = 0.87, CHCl$_3$)]. Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 80 ºC for 80 min, then 1°C/min to 140°C (hold for 5 min), then 10°C/min to 180°C (final temp), retention times (min.): 25.8 (major) and 26.9 (minor); retention time **3a**: 72.0 min.

In analogy to this result, the absolute configuration of the other products is assumed to be (***R***).



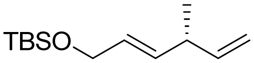
### (***R***,***E***)-3,7-Dimethylocta-1,4-diene (2b)

The title compound was prepared from **1b** (50 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography ($SiO_2$, Pentane) afforded product (11 mg, 32% yield, 99% *ee*) as a colourless oil as a mixture of two regioisomers **2b**/**3b** ($S_N2'/S_N2$) in 96:4 ratio (determined by $^1H$ NMR at 20 °C and GC). $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.66 (m, 1H), 5.38 – 5.23 (m, 2H), 4.97 – 4.81 (m, 2H), 2.77 – 2.73 (m, 1H), 1.82 (dd, *J* = 9.7, 3.6 Hz, 2H), 1.55 – 1.50 (m, 1H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 6H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 143.4, 135.0, 128.0, 112.4, 41.9, 40.3, 28.4, 22.2, 20.0. HRMS (APCI+) calculated for $C_7H_{11}$ [M–*iso*-propyl]$^+$: 95.0861, found: 95.0814. $[\alpha]_D^{20}$ = +4.8 (c = 0.25, $CHCl_3$). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 ºC for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min.): 15.1 (major) and 15.5 (minor); retention time **3b**: 34.6 min.



### (***R***,***E***)-Methyl 4-methylhexa-2,5-dienoate (2c)[15]

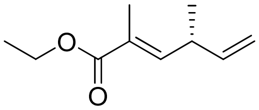
The title compound was prepared from **1c** (51 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ = 10/1) afforded product (15 mg, 43% yield, 97% *ee*) as a colorless oil as a mixture of two regioisomers **2c**/**3c** ($S_N2'/S_N2$) in 94:6 ratio (determined by $^1H$ NMR at 20 °C and GC). $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.79 – 5.63 (m, 2H), 5.05 – 4.94 (m, 2H), 3.66 (s, 3H), 3.02 – 2.87 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 167.1, 152.1, 140.0, 119.7, 114.8, 51.4, 40.0, 18.8. $[\alpha]_D^{20}$ = –20 (c = 0.65, $CHCl_3$). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 ºC for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min.): 35.9 (major) and 37.6 (minor); retention time **3c**: 64.0 min.



### (***R***,***E***)-***tert***-Butyldimethyl(4-methylhexa-2,5-dienyloxy)silane (2d)

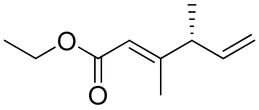
The title compound was prepared from **1d** (73 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ = 10/1) afforded product (52 mg, 92% yield, 99% *ee*) as a colorless oil as a mixture of two regioisomers **2d**/**3d** ($S_N2'/S_N2$) in 91:9 ratio (determined by $^1H$ NMR at 20 °C and GC). $^1H$ NMR (400

MHz, $CDCl_3$) δ 5.72 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.58 – 5.39 (m, 2H), 4.91 (m, 2H), 4.08 (dt, *J* = 4.7, 1.0 Hz, 2H), 2.87 – 2.72 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.6, 134.5, 128.2, 112.9, 64.0, 39.9, 26.0, 19.6, 18.4, –5.1. HRMS (ESI+) calculated for $C_{13}H_{27}OSi$:227.1826, found: 227.1820. $[\alpha]_D^{20}$ = –4.4 (c = 2.5, $CHCl_3$). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 80 ºC for 80 min, then 1°C/min to 140°C (hold for 5 min), then 10°C/min to 180°C (final temp), retention times (min.): 23.6 (major) and 24.4 (minor); retention time **3d**: 48.2 min.



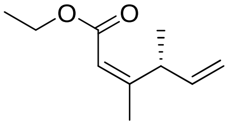
**(*R*,*E*)-Ethyl 2,4-dimethylhexa-2,5-dienoate (2e)**

The title compound was prepared from **1e** (58 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ = 10/1) afforded product (38 mg, 90% yield, 98% *ee*) as a colorless oil as a mixture of two regioisomers **2e**/**3e** ($S_N2$'/$S_N2$) in 97:3 ratio (determined by $^1$H NMR at 20 °C and GC). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.51 (dd, *J* = 9.6, 1.4 Hz, 1H), 5.69 (ddd, *J* = 16.6, 10.3, 6.4 Hz, 1H), 5.02 – 4.87 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.16 – 3.10 (m, 1H), 1.79 (d, *J* = 1.3 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.3, 144.5, 140.6, 127.0, 113.7, 60.5, 37.0, 19.7, 14.3, 12.4. HRMS (APCI+) calculated for $C_{10}H_{17}O_2$:169.1223, found: 169.1219. $[\alpha]_D^{20}$ = –2.8 (c = 1.85, $CHCl_3$). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 ºC for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min.): 54.6 (major) and 55.8 (minor); retention time **3e**: 86.3 min.



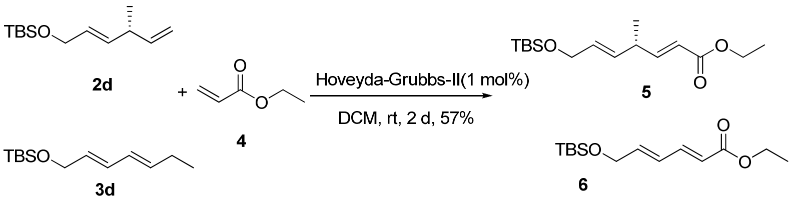
**(*R*,*E*)-Ethyl 3,4-dimethylhexa-2,5-dienoate (2f)**

The title compound was prepared from **1f** (58 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ = 10/1) afforded product (31 mg, 74% yield, 98% *ee*) as a colorless oil as a mixture of two regioisomers **2f**/**3f** ($S_N2$'/$S_N2$) in 95:5 ratio (determined by $^1$H NMR at 20 °C and GC). $^1$H NMR (400 MHz, $CDCl_3$) δ 5.75 – 5.60 (m, 2H), 5.05 – 4.96 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.89 – 2.77 (m, 1H), 2.05 (d, *J* = 1.3 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 167.0, 162.2, 140.3, 115.2, 115.0, 59.6, 47.2, 17.8, 16.8, 14.3. HRMS (APCI+) calculated for $C_{10}H_{17}O_2$:169.1223, found: 169.1220. $[\alpha]_D^{20}$ = +19.0 (c = 0.6, $CHCl_3$). Enantiomeric excess was determined by HPLC analysis (Chiralpak OD-H: 0.5 mL/min, n-heptane, 40 °C isotherm, 214 nm), retention times: 54.2 min (major), 57.9 min (minor).



**(*R*,*Z*)-Ethyl 3,4-dimethylhexa-2,5-dienoate (2g)**
The title compound was prepared from **1g** (58 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography ($SiO_2$, Pentane/$Et_2O$ = 10/1) afforded product (32 mg, 74% yield with trace of ether, 99% *ee*) as a colorless oil as a mixture of two regioisomers **2g**/**3g** ($S_N2'$/$S_N2$) in 96:4 ratio (determined by $^1$H NMR at 20 °C and GC). $^1$H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddd, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.58 (s, 1H), 5.10 – 4.92 (m, 2H), 4.63 – 4.50 (m, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.71 (d, *J* = 1.0 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.1, 162.0, 140.4, 116.1, 114.3, 59.5, 37.9, 20.0, 17.1, 14.3. HRMS (APCI+) calculated for $C_{10}H_{17}O_2$:169.1223, found: 169.1222. $[\alpha]_D^{20}$ = +130.1 (c = 1.5, $CH_2Cl_2$). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 ºC for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min): 56.1 (major) and 56.5 (minor); retention time **3g**: 80.6 min.

### Cross metathesis between 2d and 4



**(*S*,2*E*,5*E*)-Ethyl 7-((*tert*-butyldimethylsilyl)oxy)-4-methylhepta-2,5-dienoate (5).** To a stirred solution of compound **2d/3d** (20 mg, 0.088 mmol, 91/9) in 4 mL of dry DCM was added ethyl acrylate **4** (9 mg, 0.09 mmol) and Hoveyda–Grubbs second-generation catalyst[16] (0.6 mg, 0.00088 mmol, 1 mol%) under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 2 d and the product was purified by flash chromatography (pentane/$Et_2O$ = 10/1) to give **5** as a colorless oil (15 mg, 57%) which was contaminated by trace of compound **6**. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.84 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.72 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.55 – 5.44 (m, 2H), 4.14 – 4.07 (m, 4H), 2.99 – 2.94 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.8, 152.1, 132.0, 129.8, 119.9, 63.6, 60.2, 38.7, 26.0, 19.1, 18.4, 14.3, -5.2. HRMS (APCI+) calculated for $C_{16}H_{31}O_3Si$:299.2042, found: 299.2037. $[\alpha]_D^{20}$ = +8.2 (c = 0.7, $CH_2Cl_2$).

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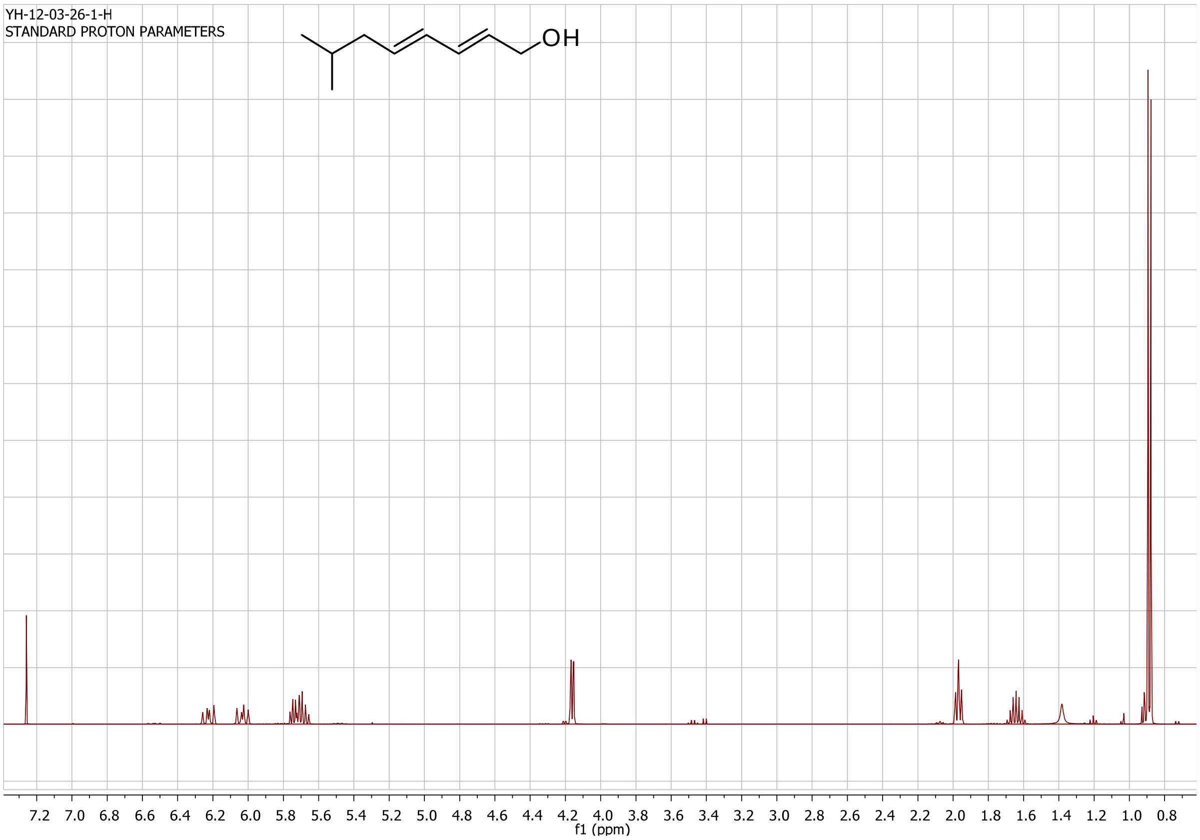
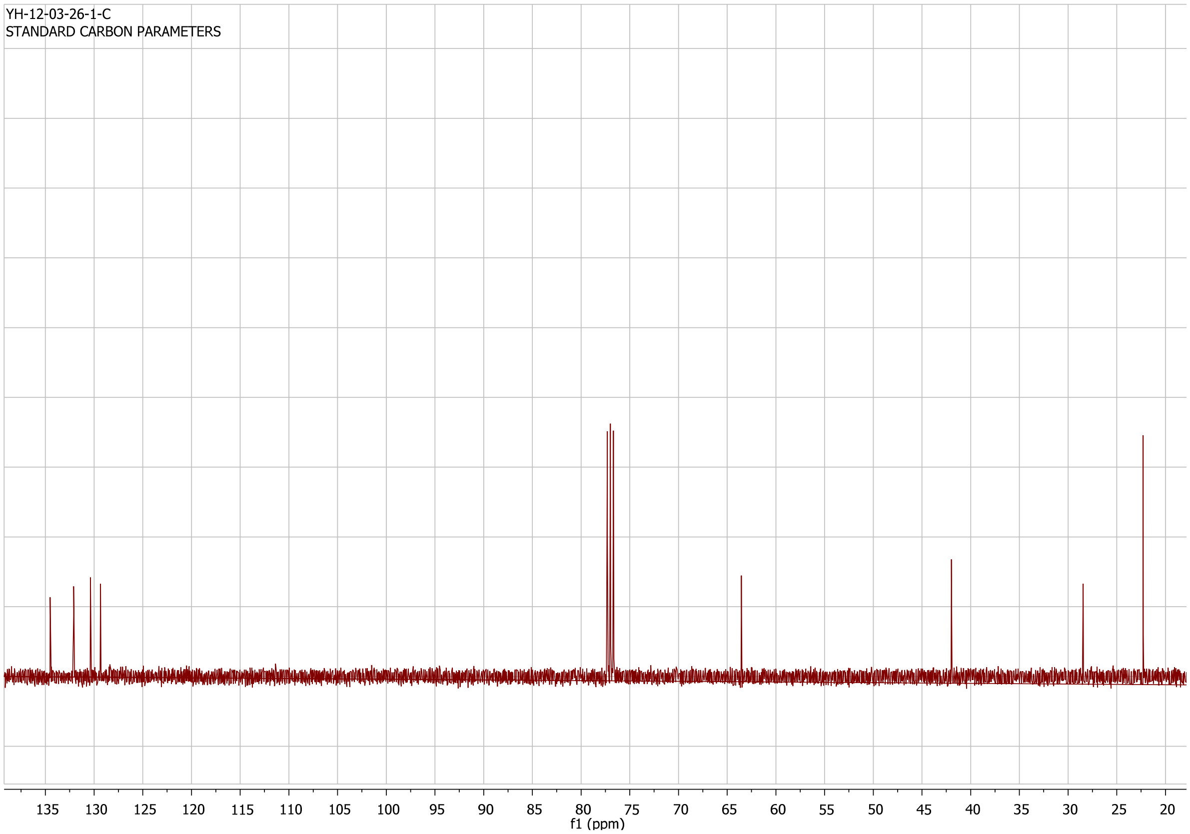
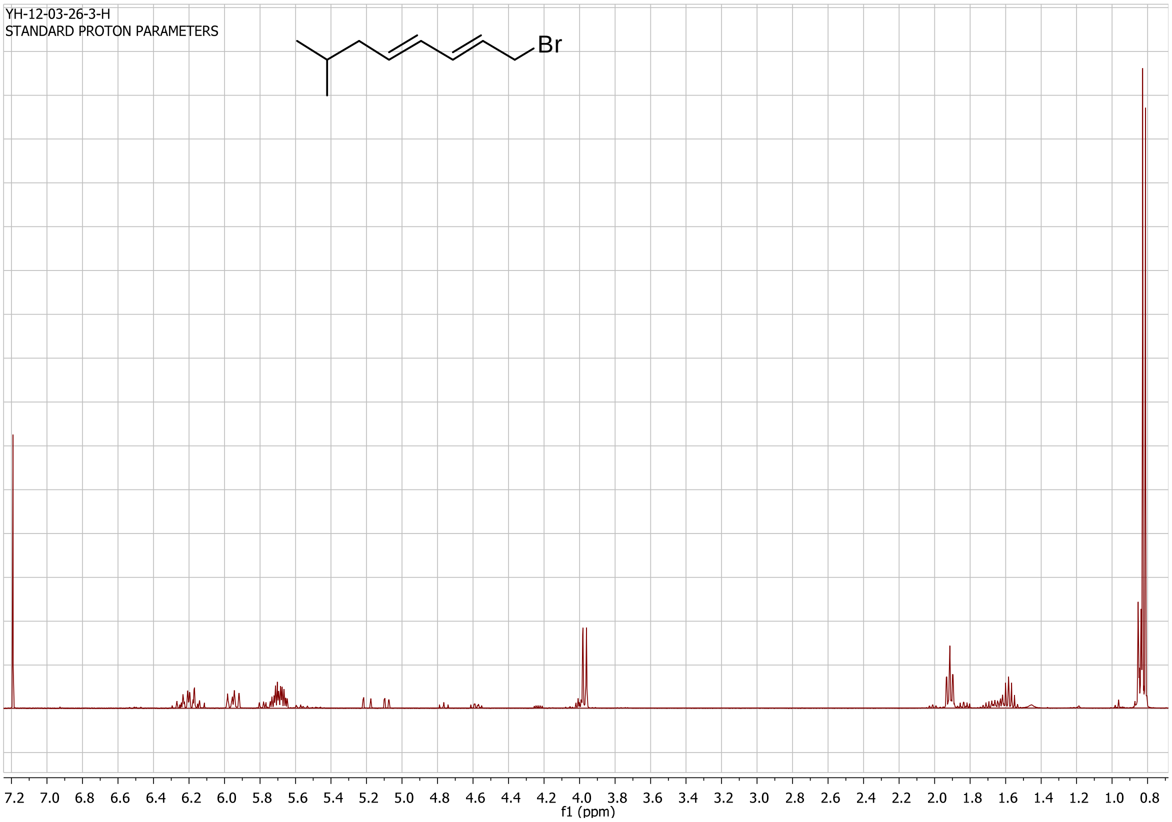
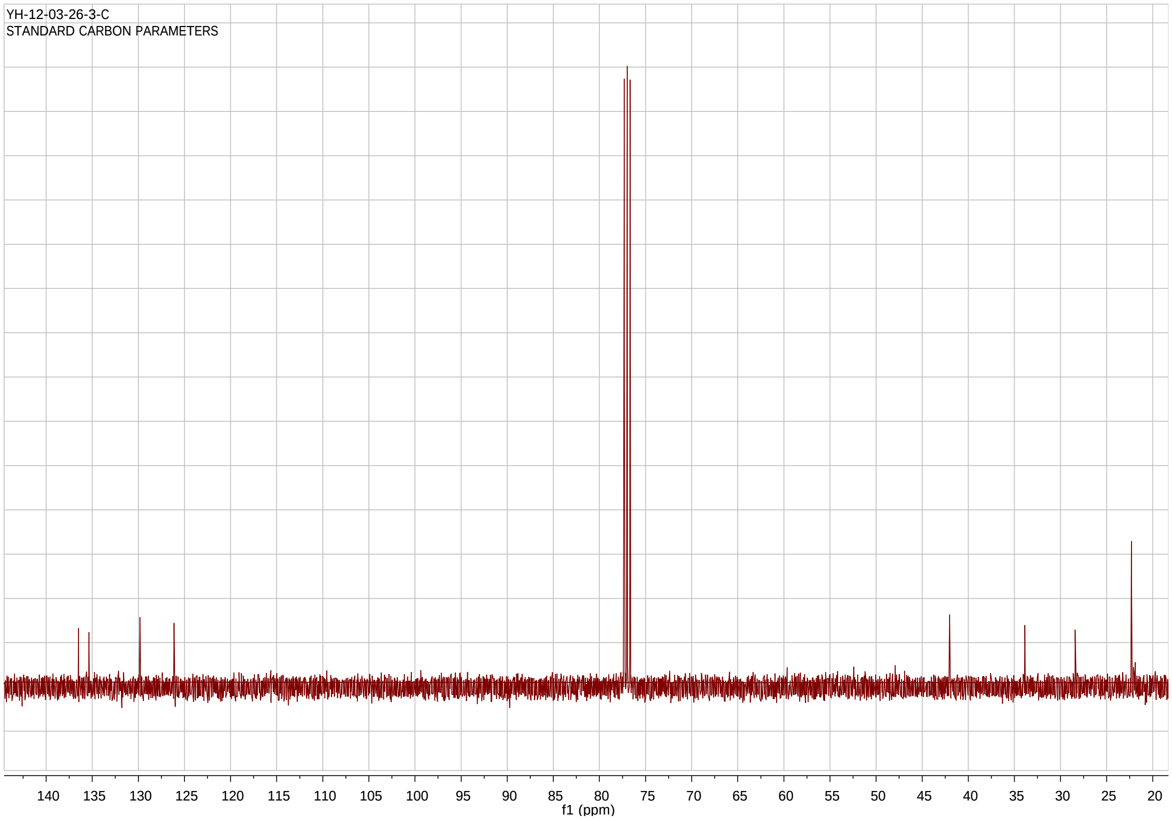
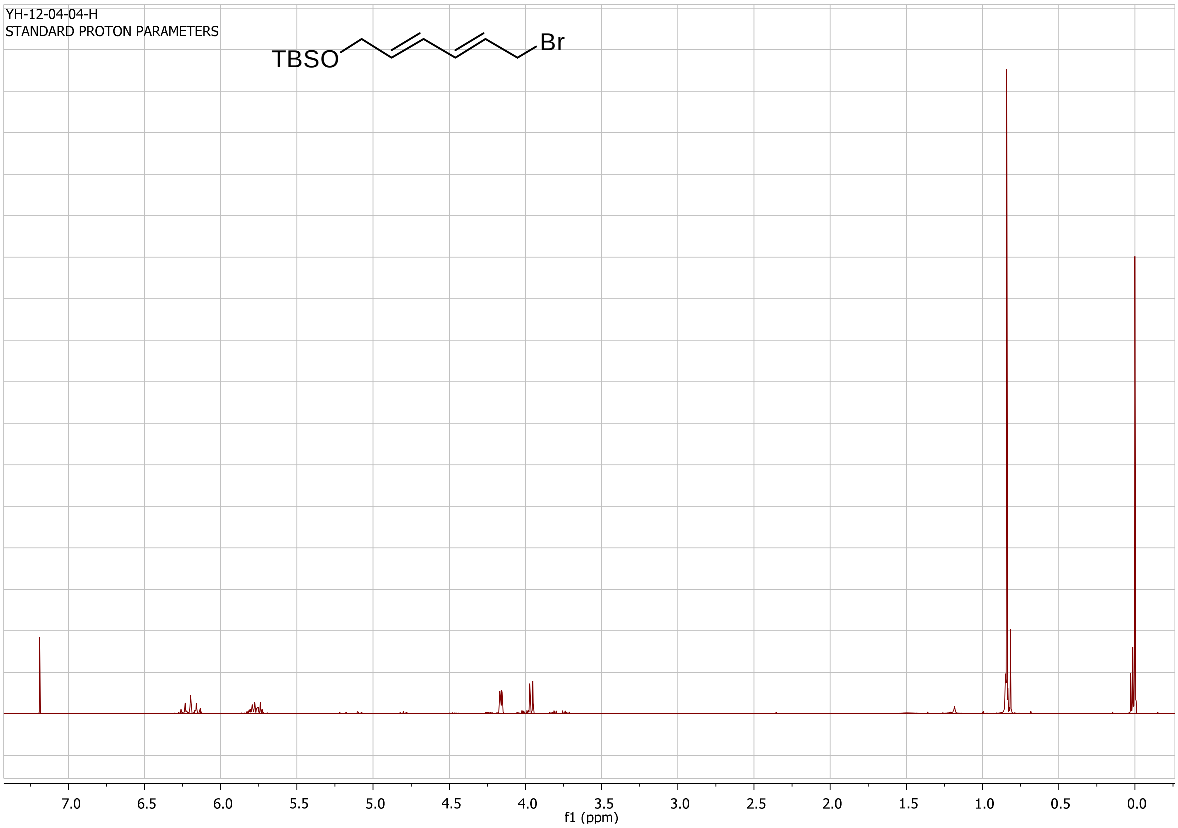
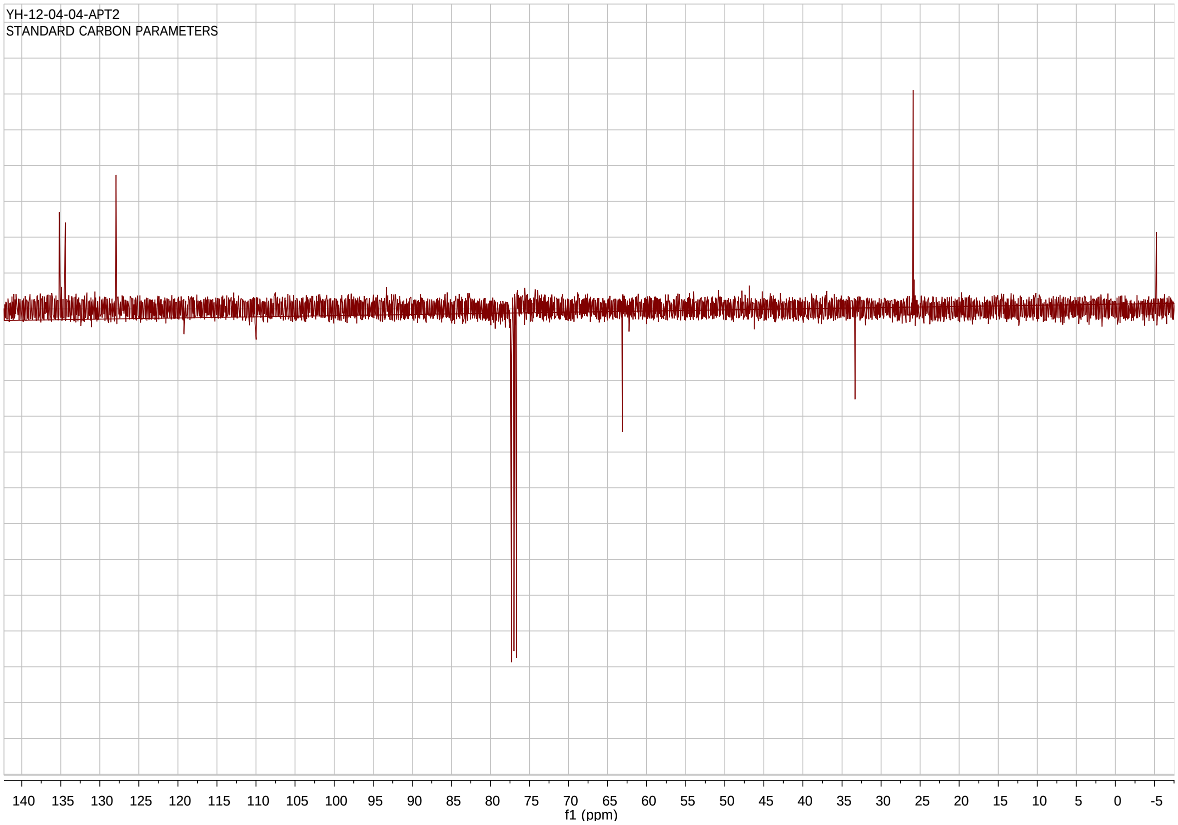

YH-12-03-26-1-H
STANDARD PROTON PARAMETERS
OH
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)

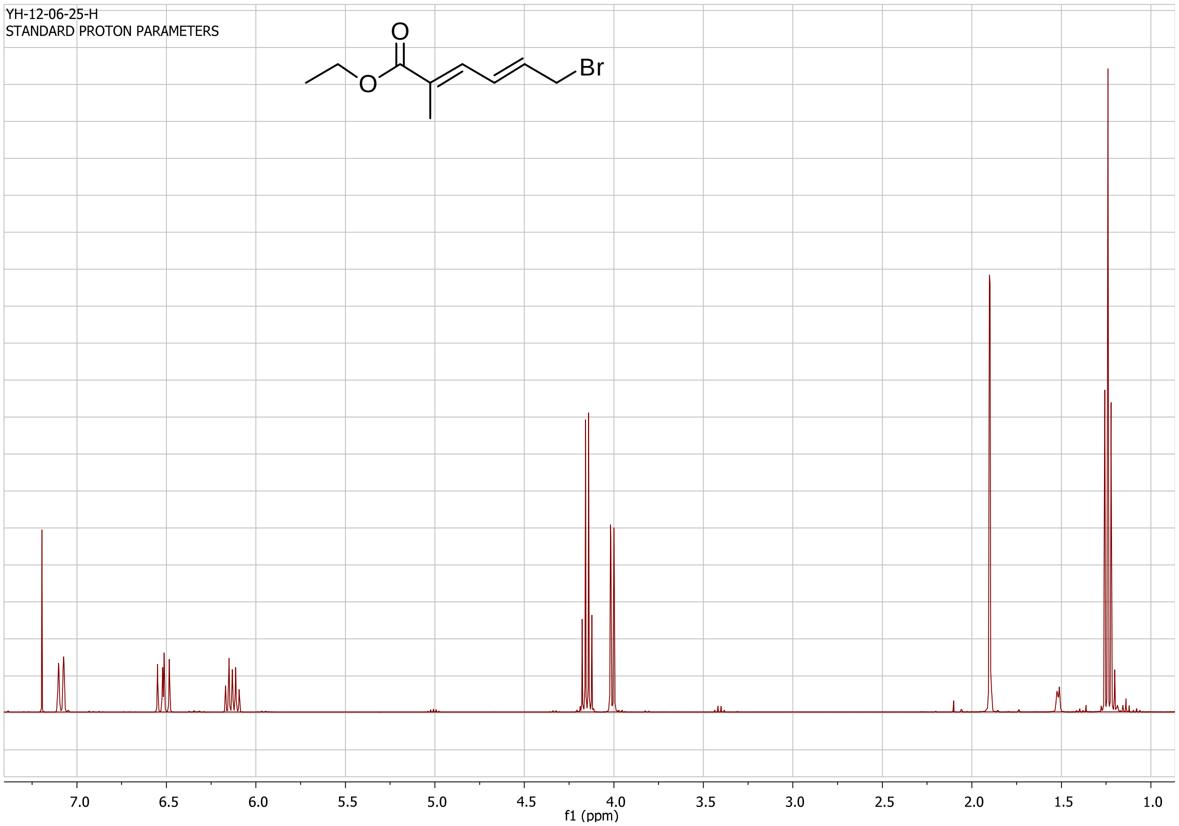

YH-12-03-26-1-C
STANDARD CARBON PARAMETERS
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

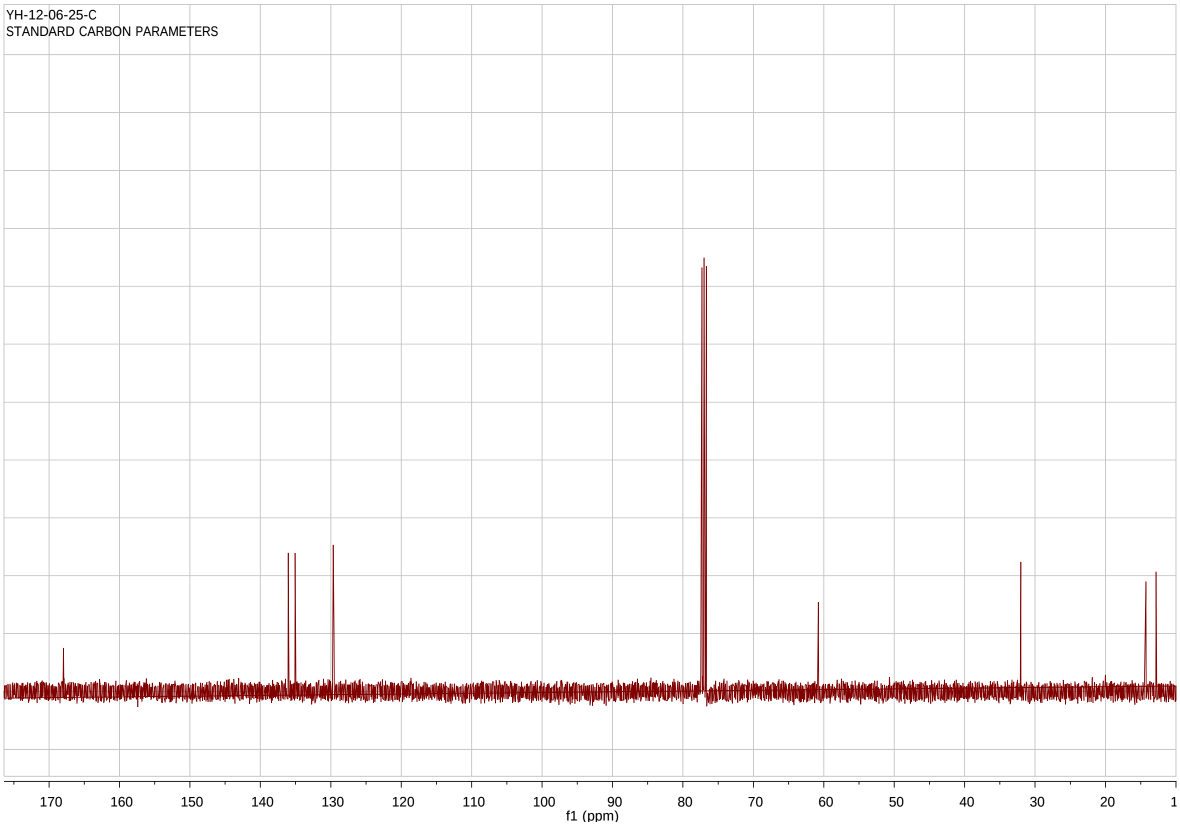

YH-12-03-26-3-H
STANDARD PROTON PARAMETERS
Br
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8
f1 (ppm)

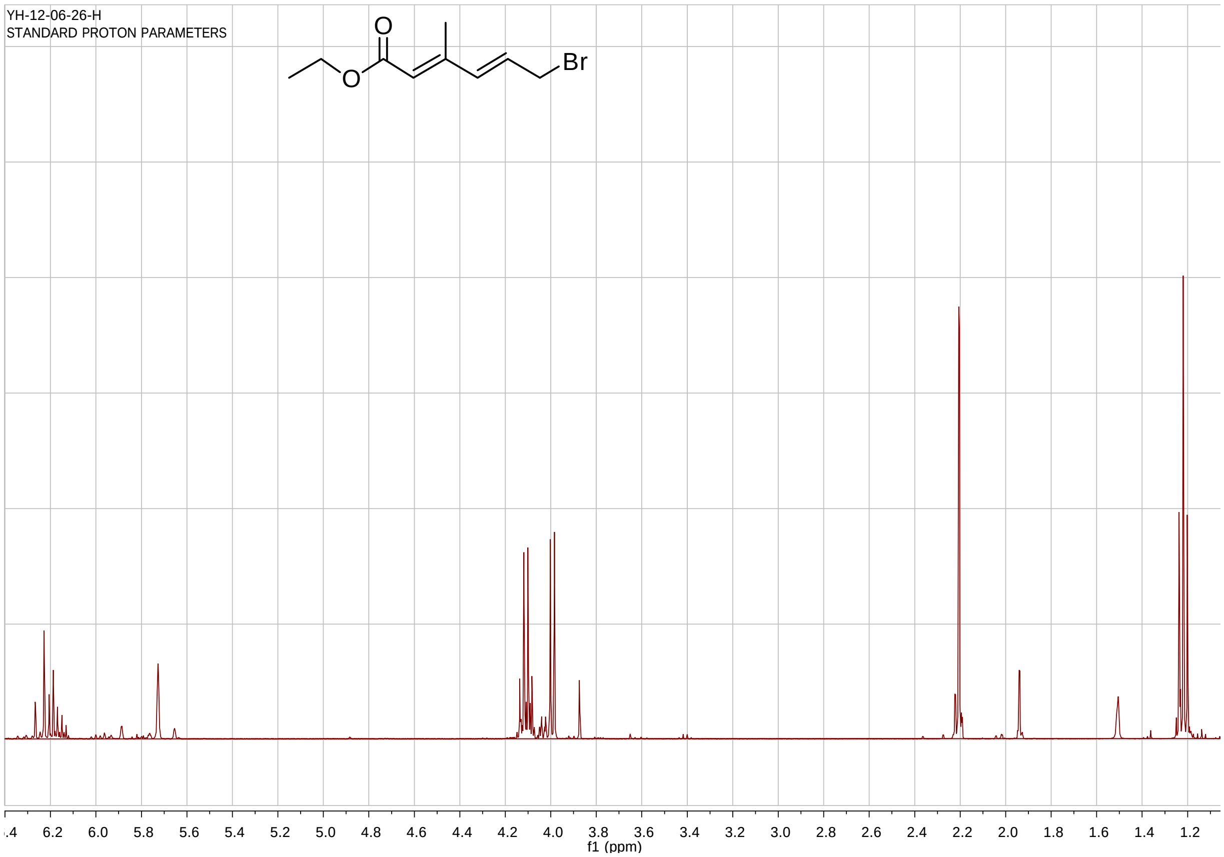

YH-12-03-26-3-C
STANDARD CARBON PARAMETERS
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

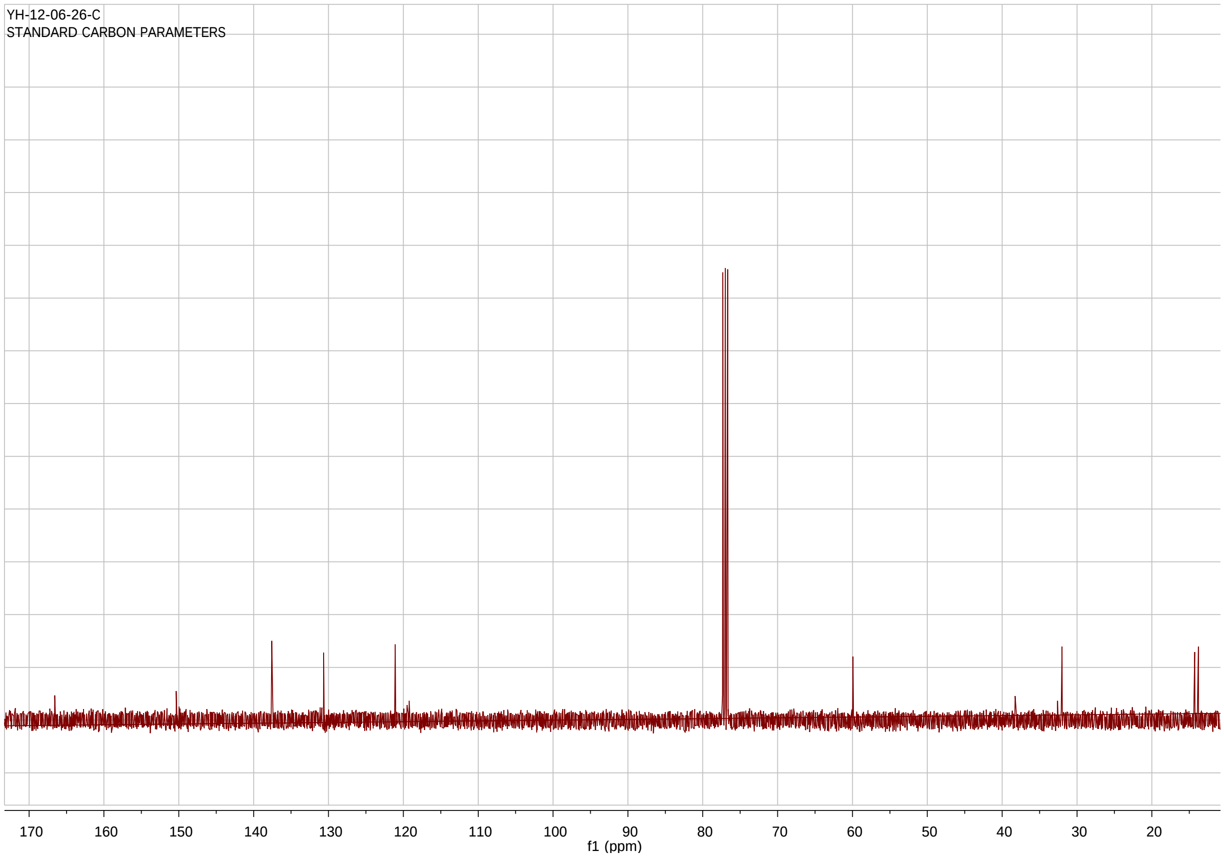

YH-12-04-04-H
STANDARD PROTON PARAMETERS
TBSO
Br
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

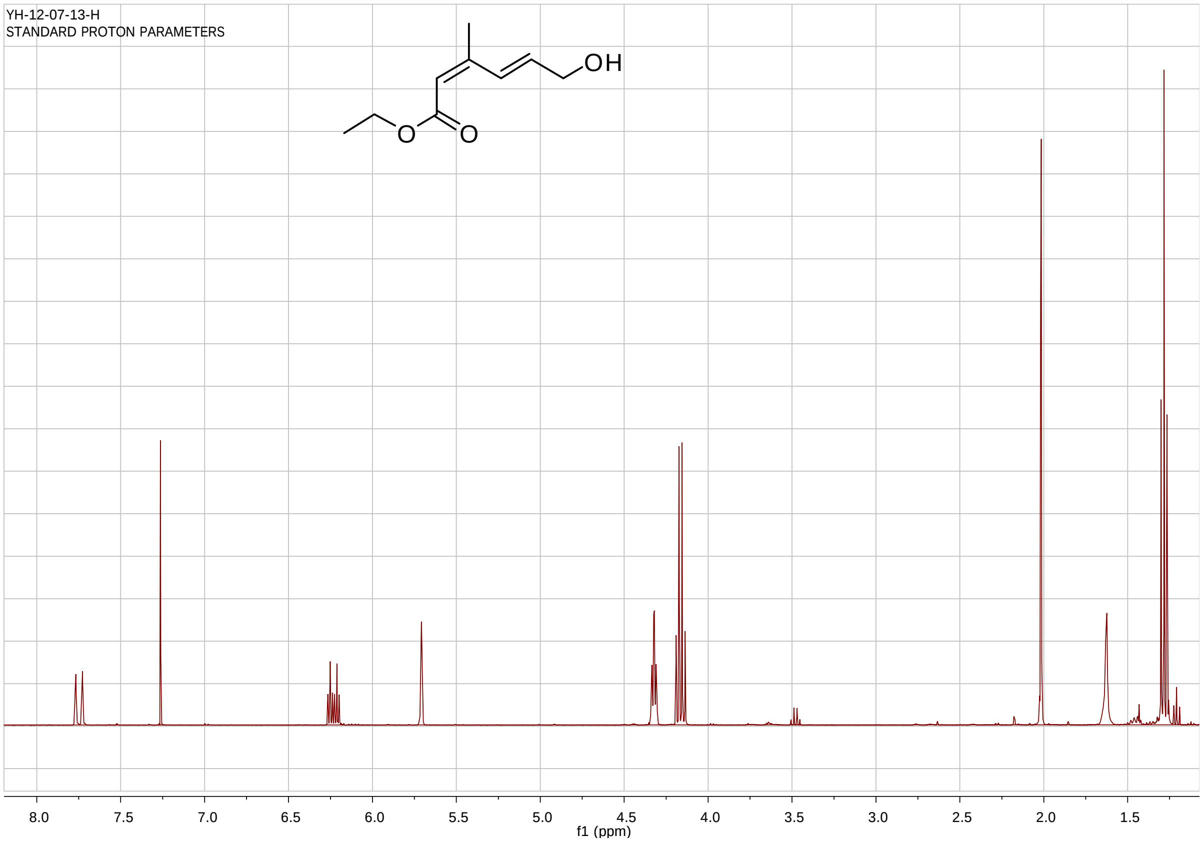

YH-12-04-04-APT2
STANDARD CARBON PARAMETERS
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)

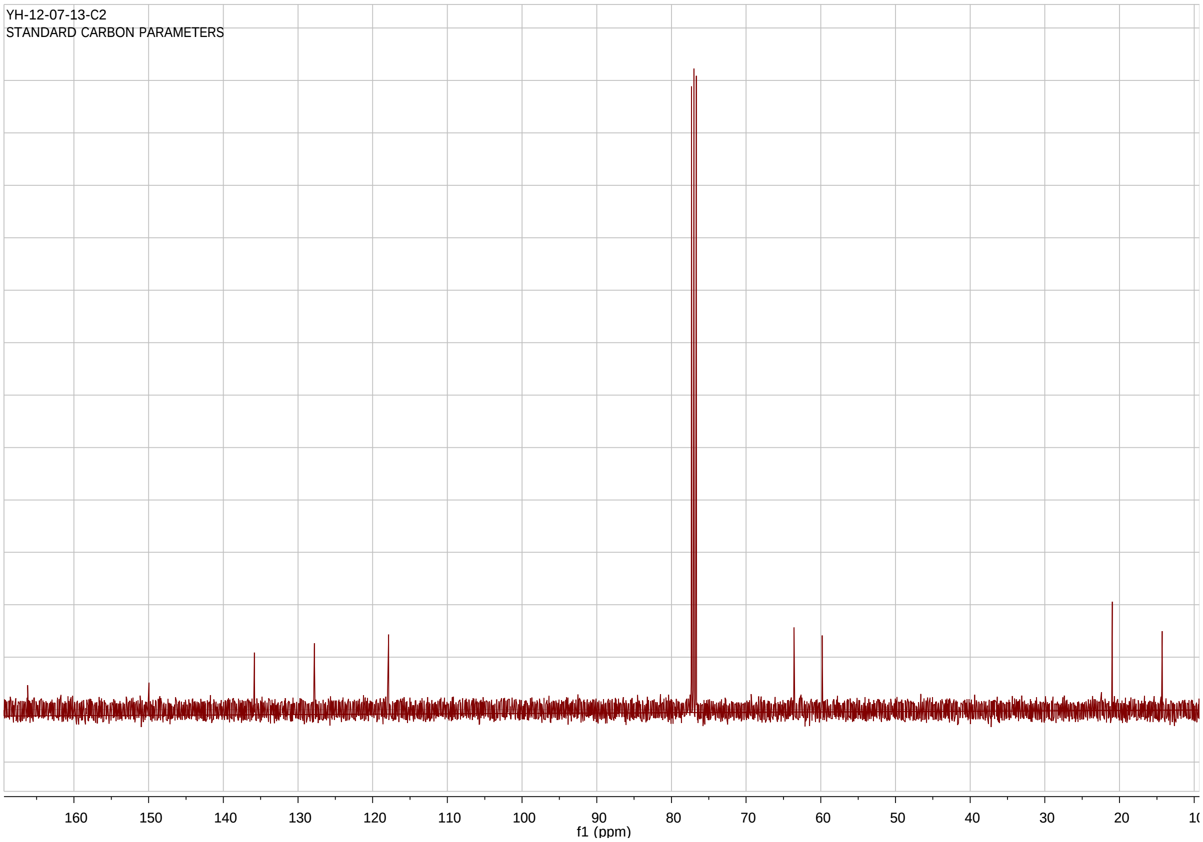

YH-12-06-25-H
STANDARD PROTON PARAMETERS
O
O
Br
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

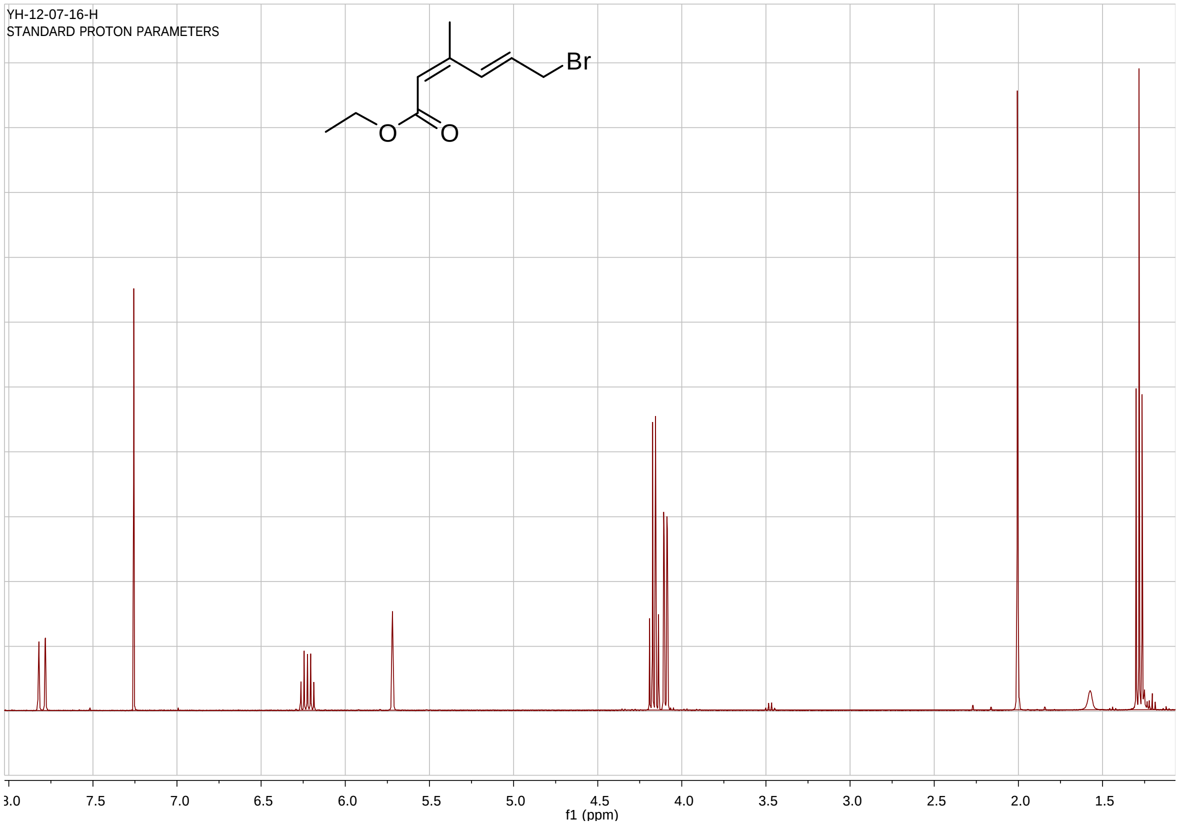

YH-12-06-25-C
STANDARD CARBON PARAMETERS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)

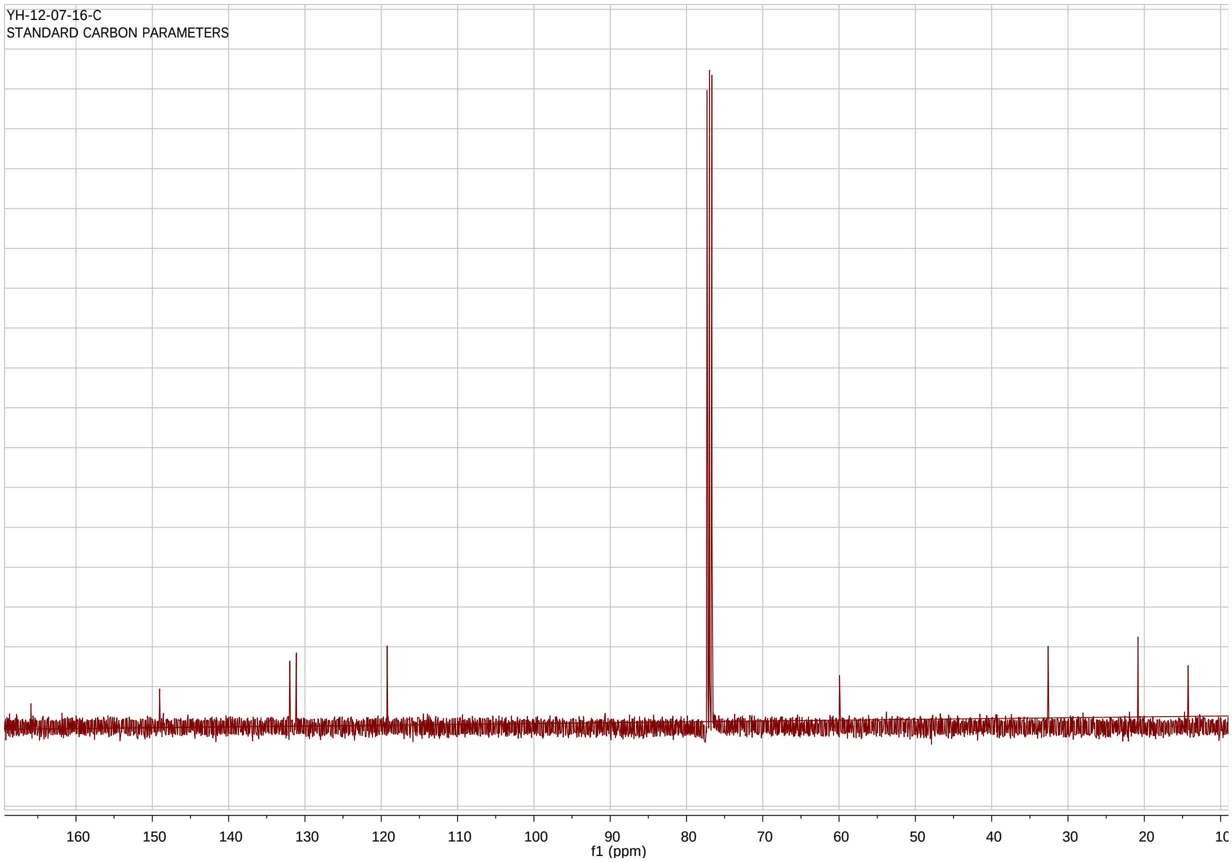

YH-12-06-26-H
STANDARD PROTON PARAMETERS
O
O
Br
.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f1 (ppm)

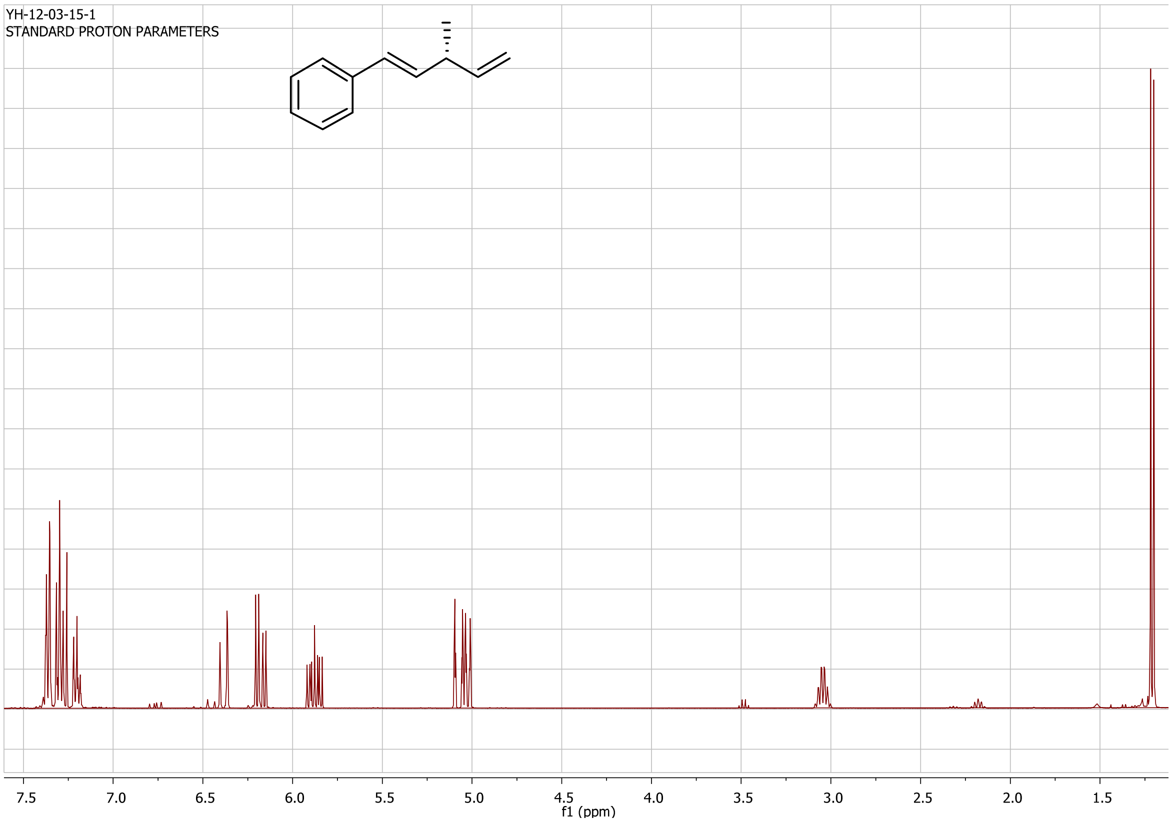

YH-12-06-26-C
STANDARD CARBON PARAMETERS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

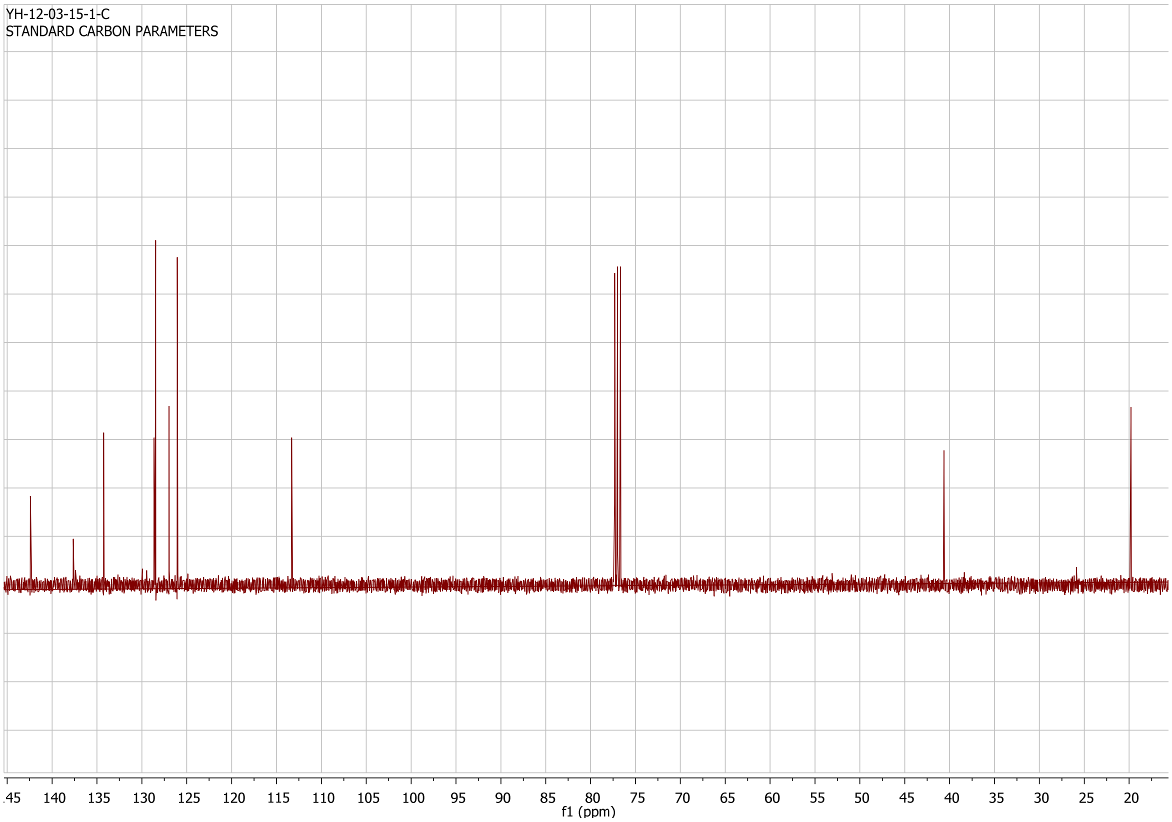

YH-12-07-13-H
STANDARD PROTON PARAMETERS
OH
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

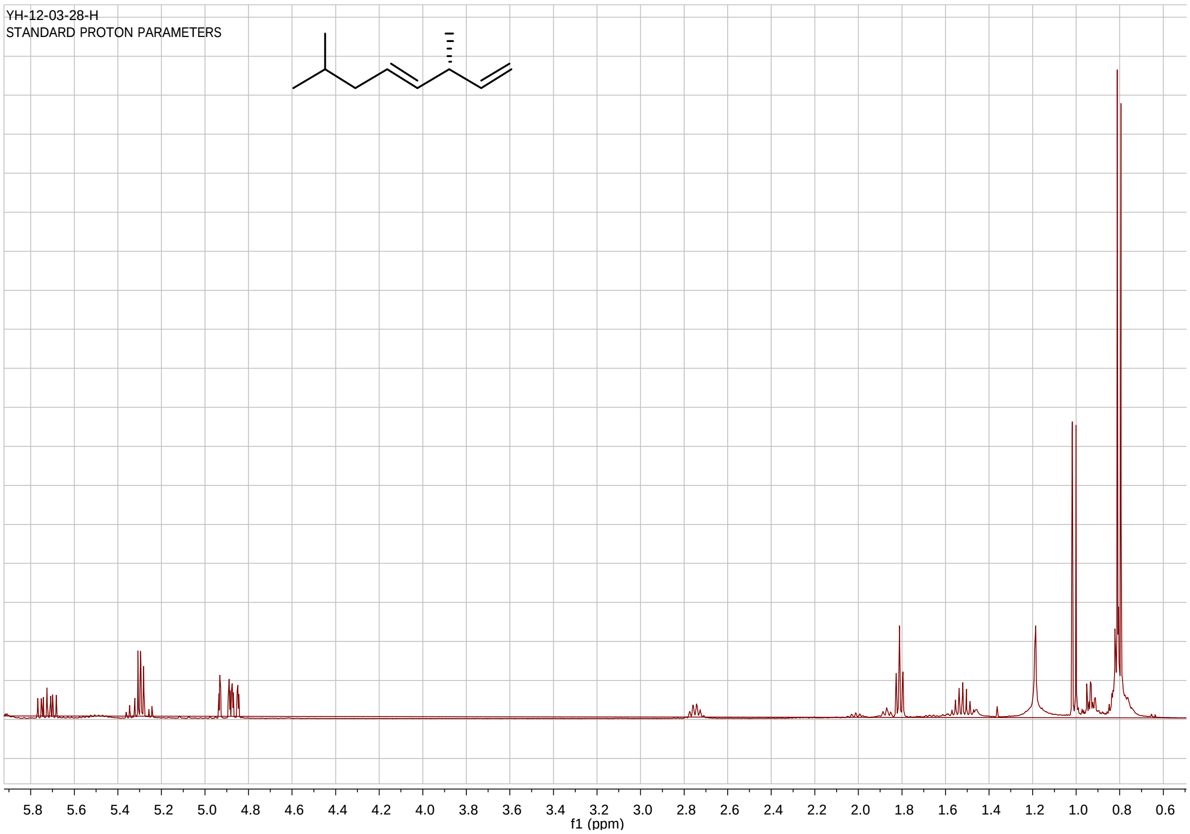

YH-12-07-13-C2
STANDARD CARBON PARAMETERS
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

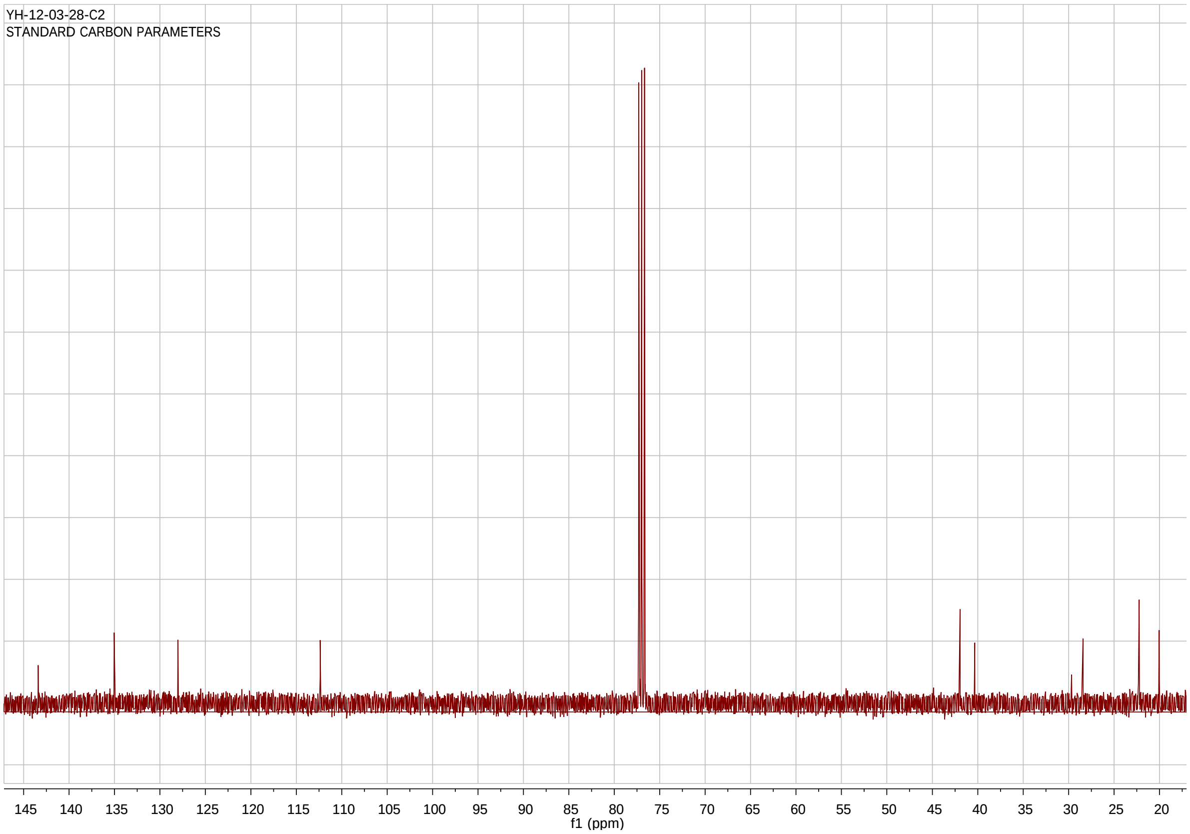

YH-12-07-16-H
STANDARD PROTON PARAMETERS
Br
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

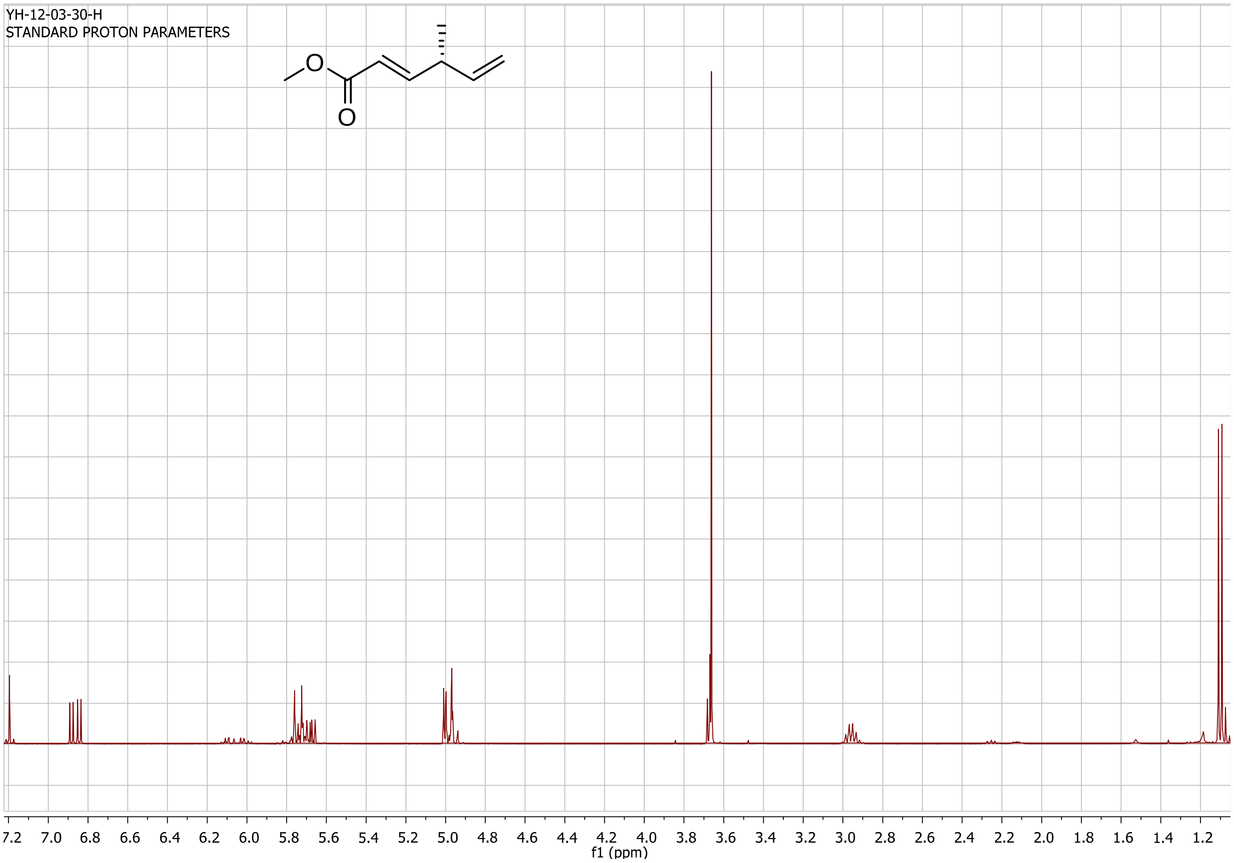

YH-12-07-16-C
STANDARD CARBON PARAMETERS
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

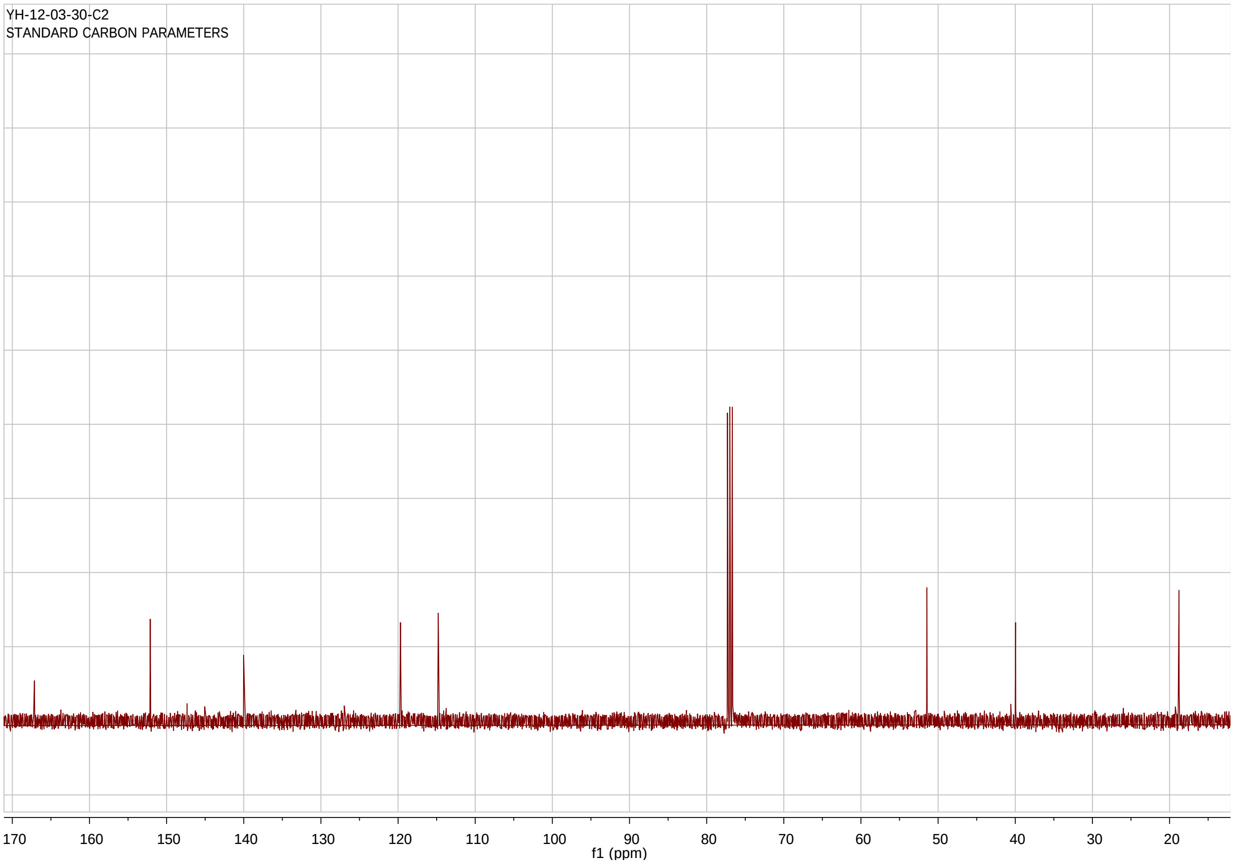

YH-12-03-15-1
STANDARD PROTON PARAMETERS
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

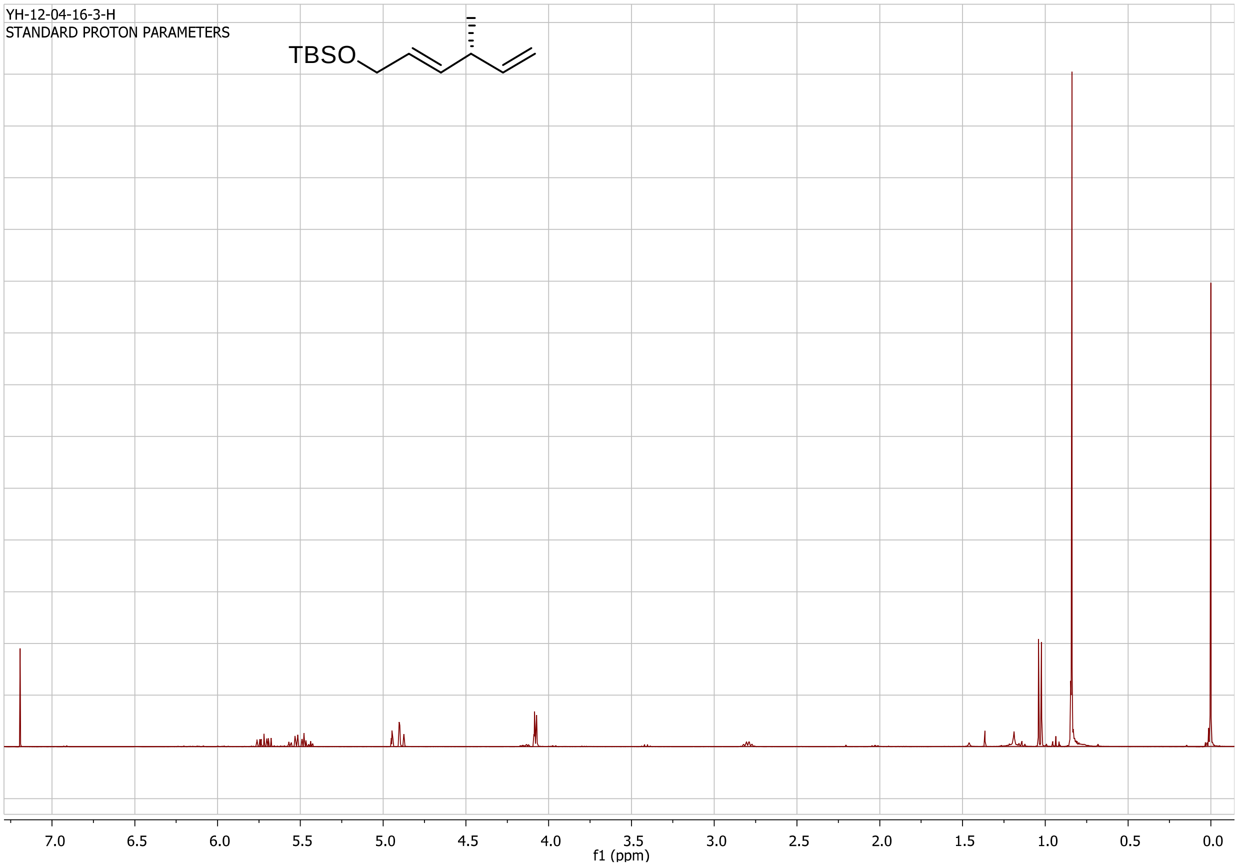

YH-12-03-15-1-C
STANDARD CARBON PARAMETERS
45
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

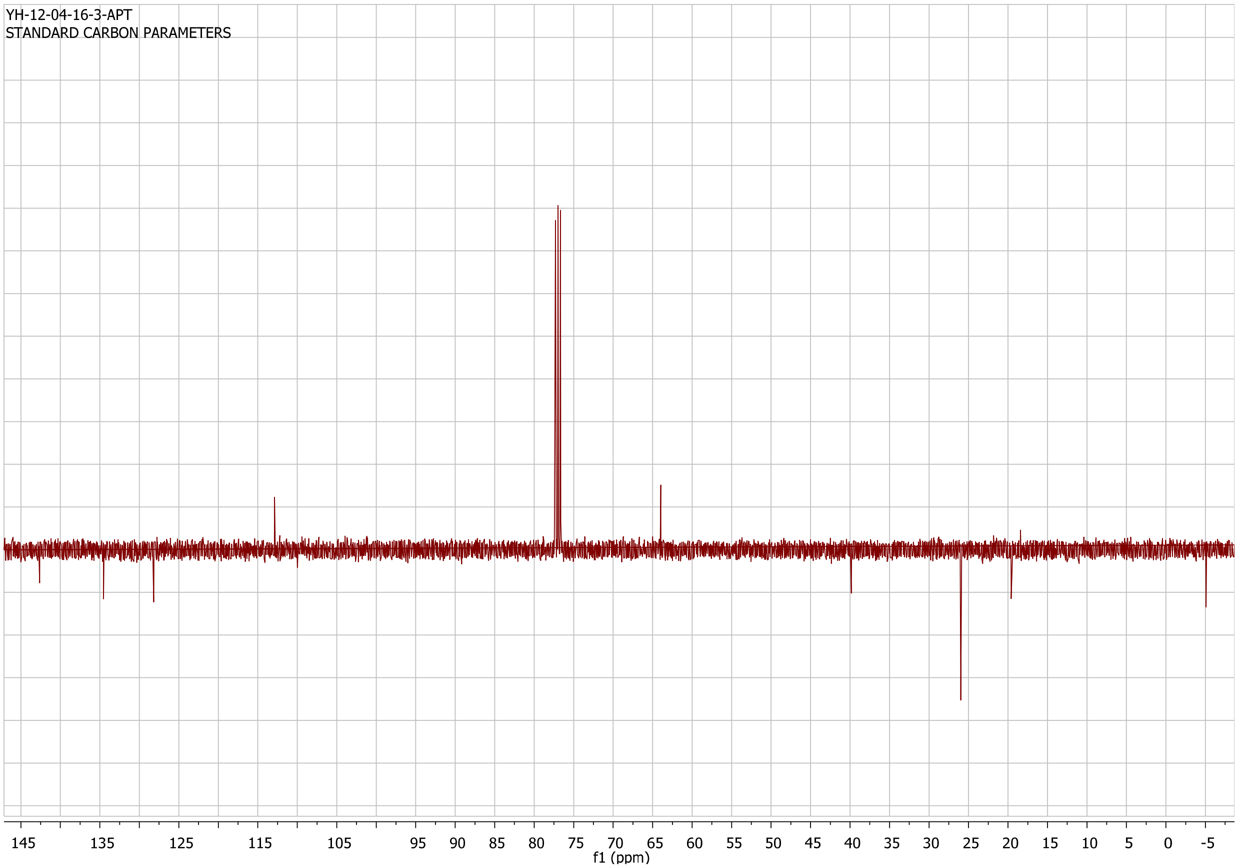

YH-12-03-28-H
STANDARD PROTON PARAMETERS
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f1 (ppm)

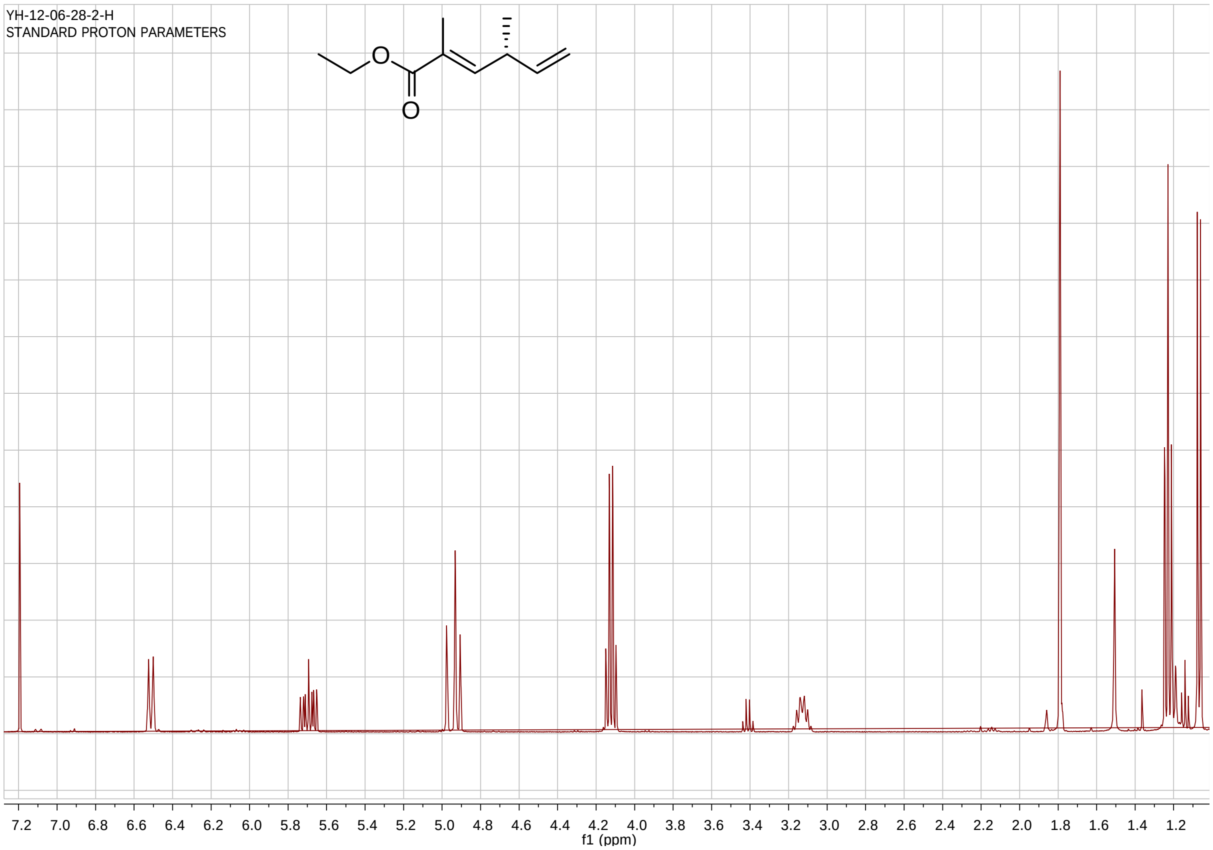

YH-12-03-28-C2
STANDARD CARBON PARAMETERS
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

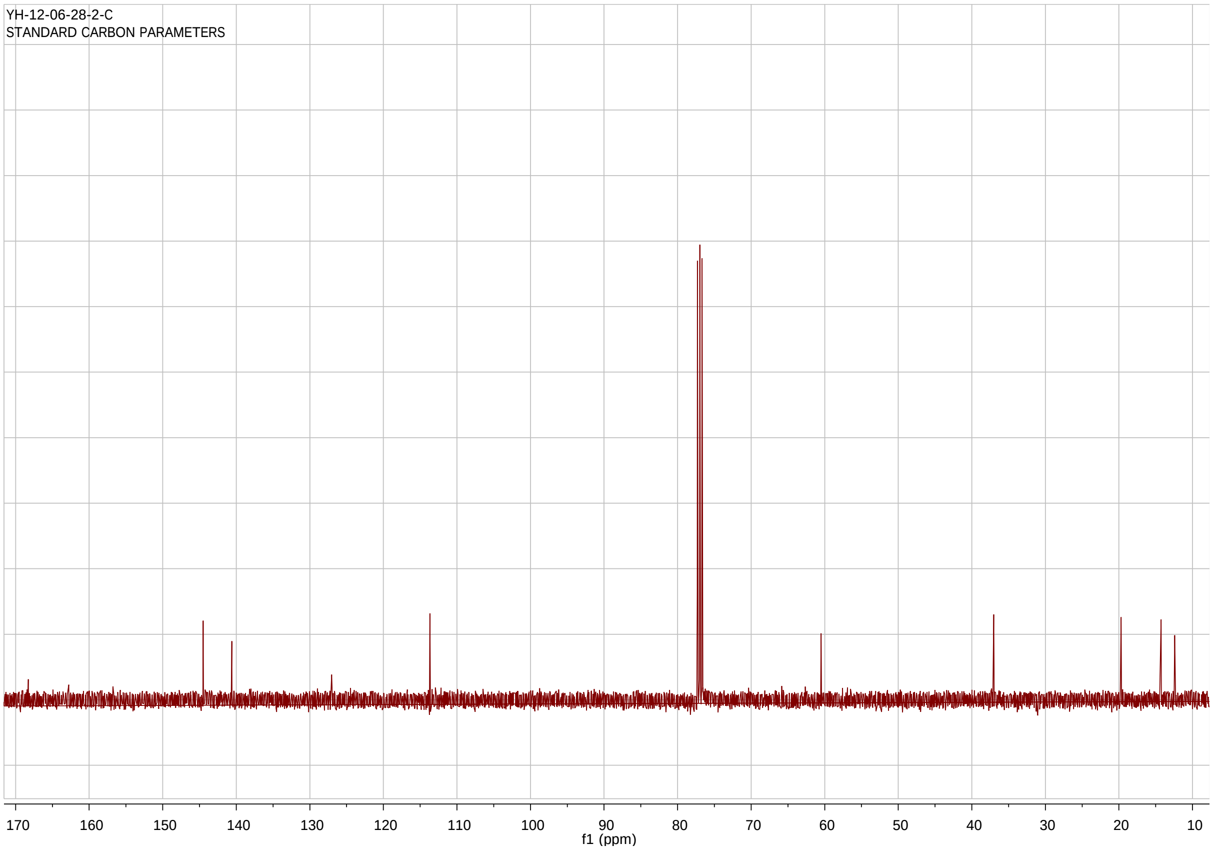

YH-12-03-30-H
STANDARD PROTON PARAMETERS
O
O
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f1 (ppm)

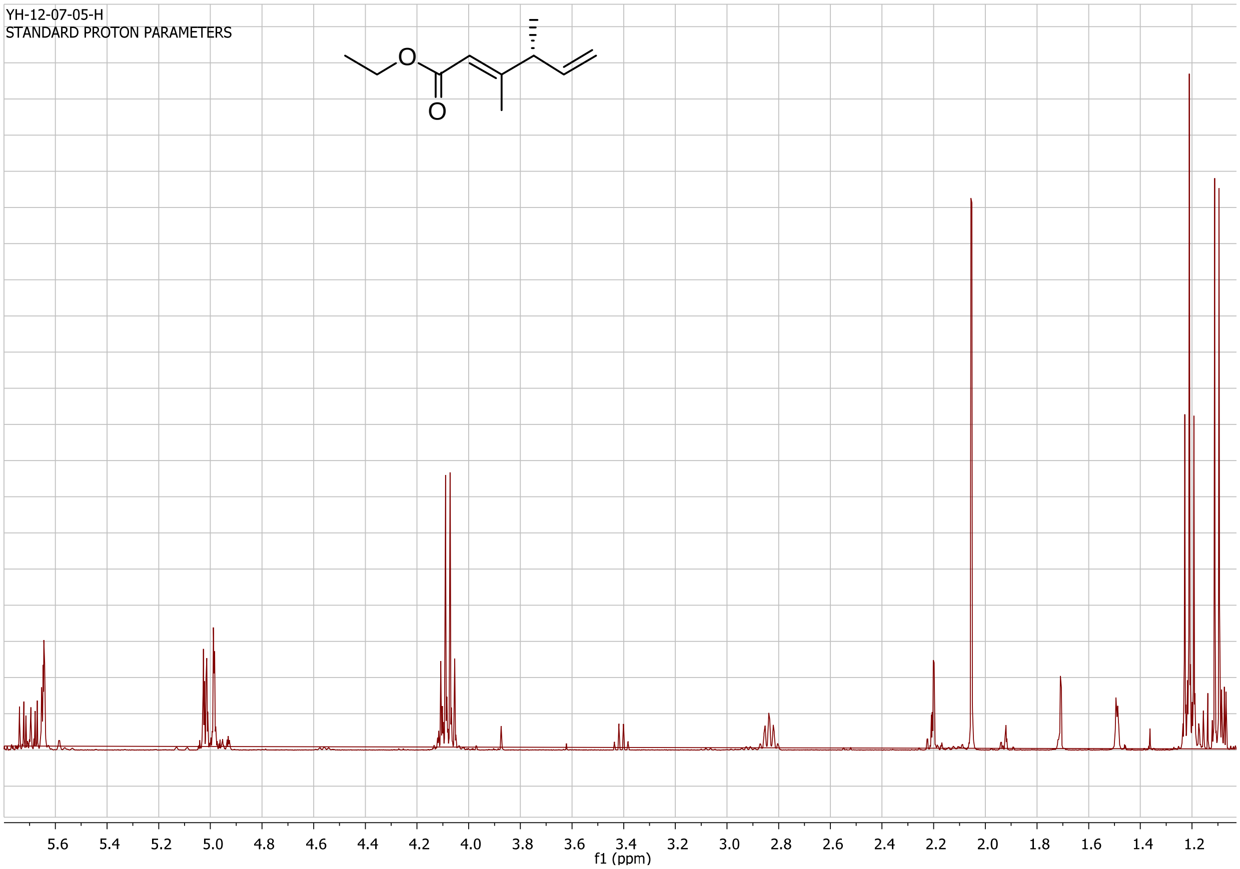

YH-12-03-30-C2
STANDARD CARBON PARAMETERS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

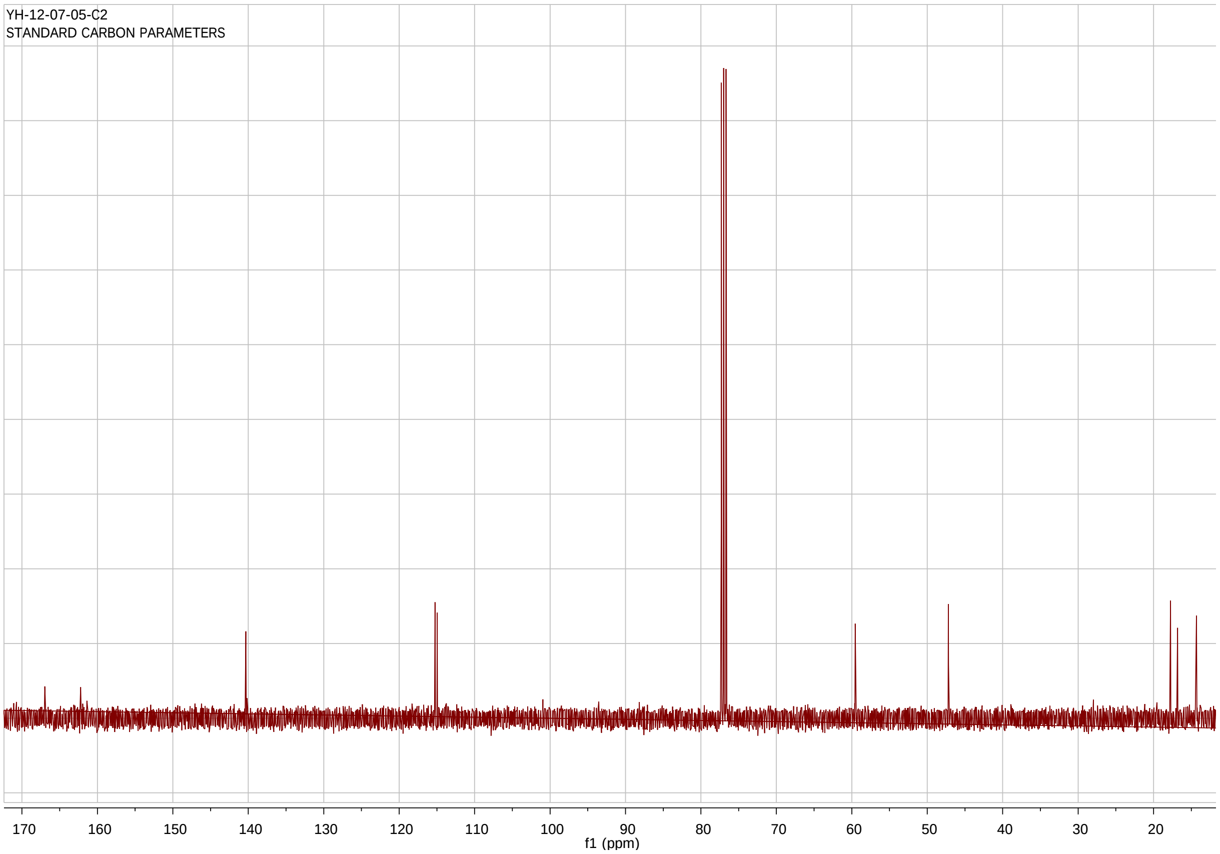

YH-12-04-16-3-H
STANDARD PROTON PARAMETERS
TBSO
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

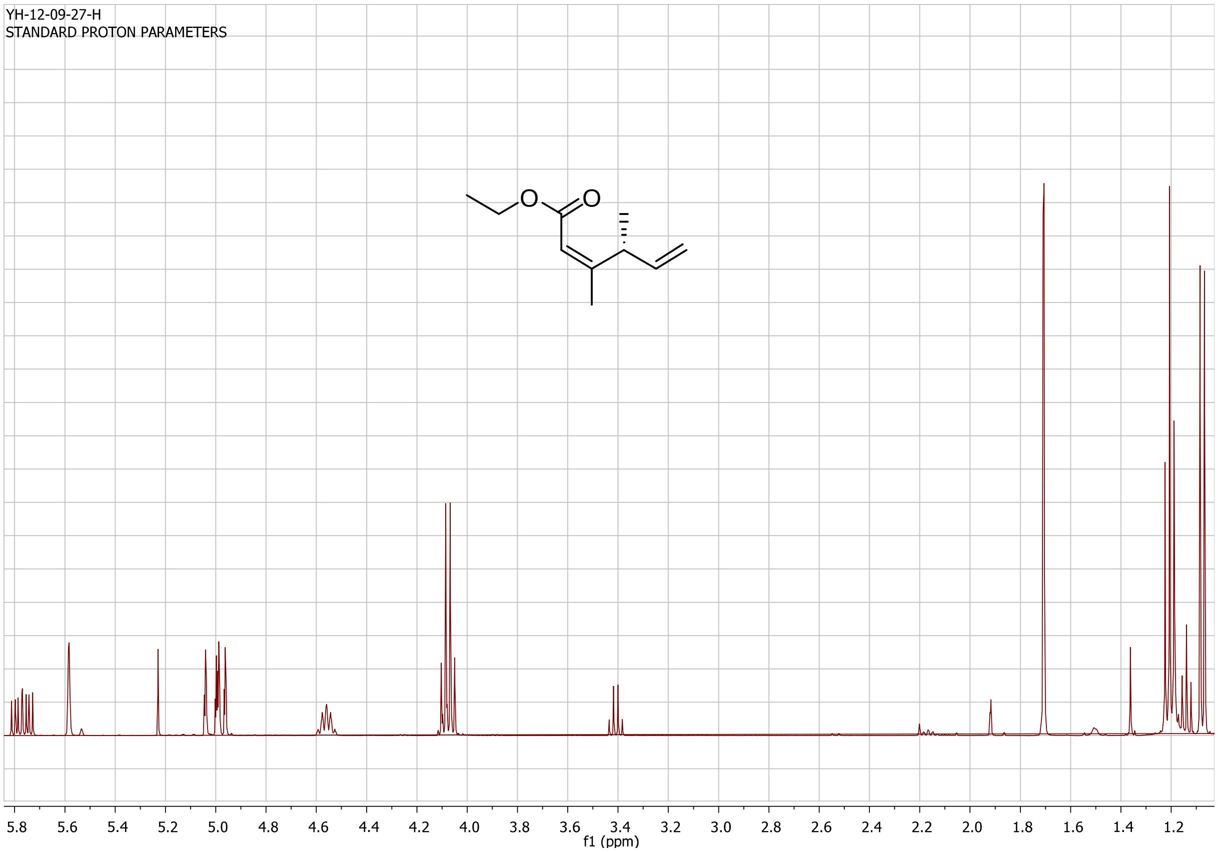

YH-12-04-16-3-APT
STANDARD CARBON PARAMETERS
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)

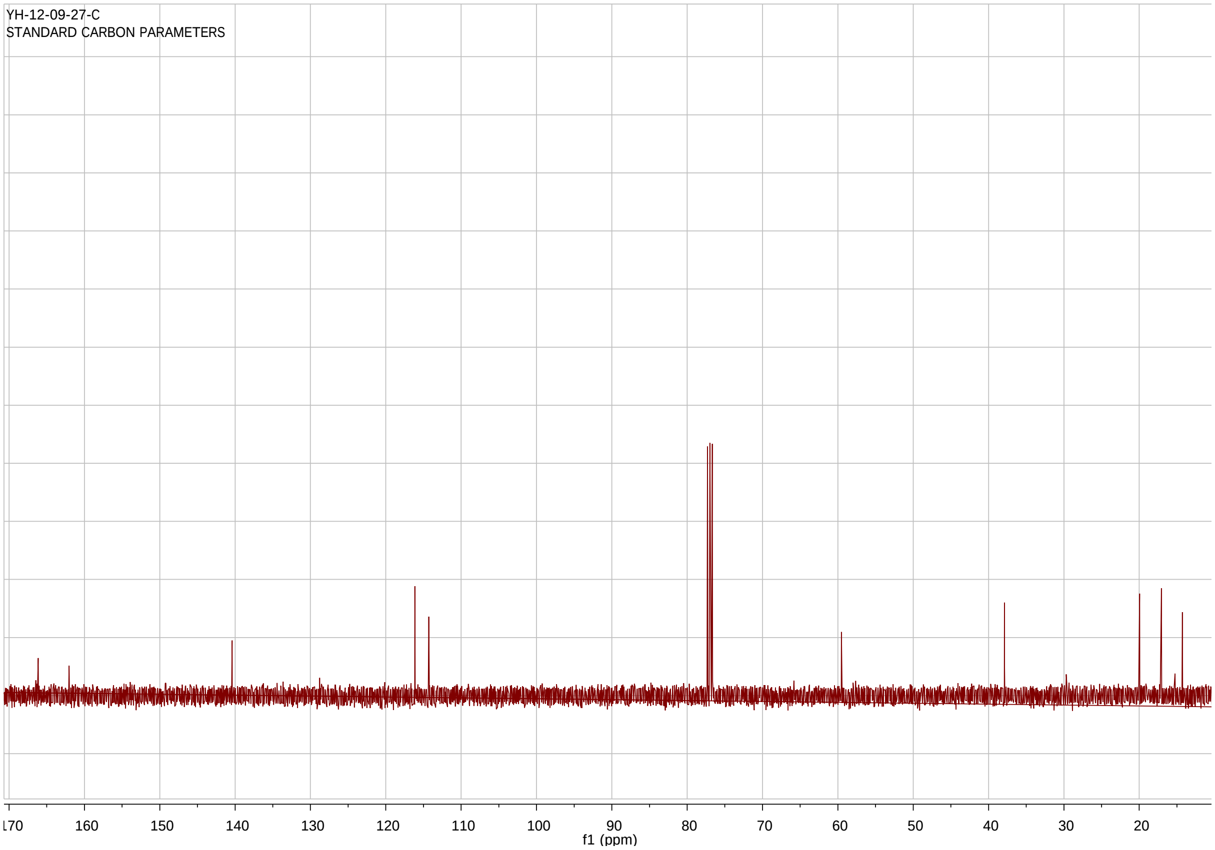

YH-12-06-28-2-H
STANDARD PROTON PARAMETERS
O
O
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)

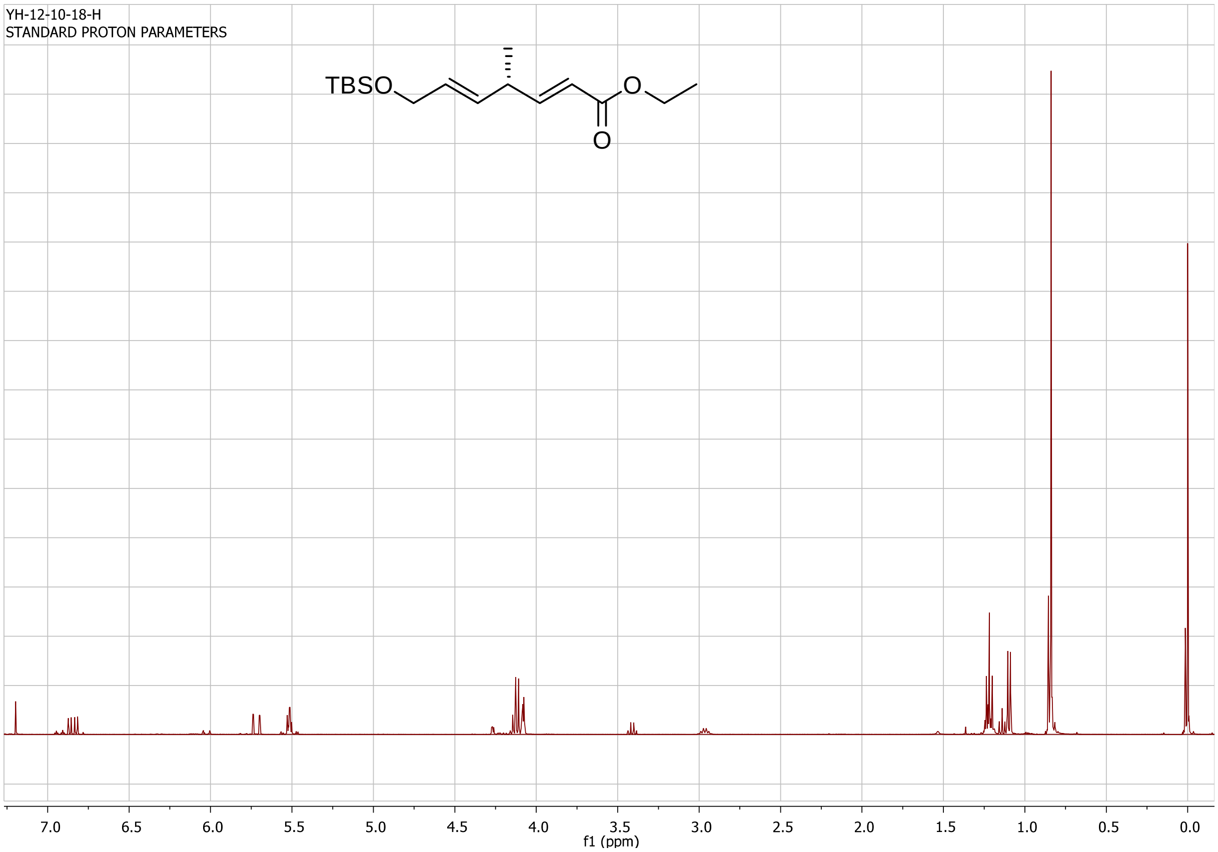

YH-12-06-28-2-C
STANDARD CARBON PARAMETERS
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

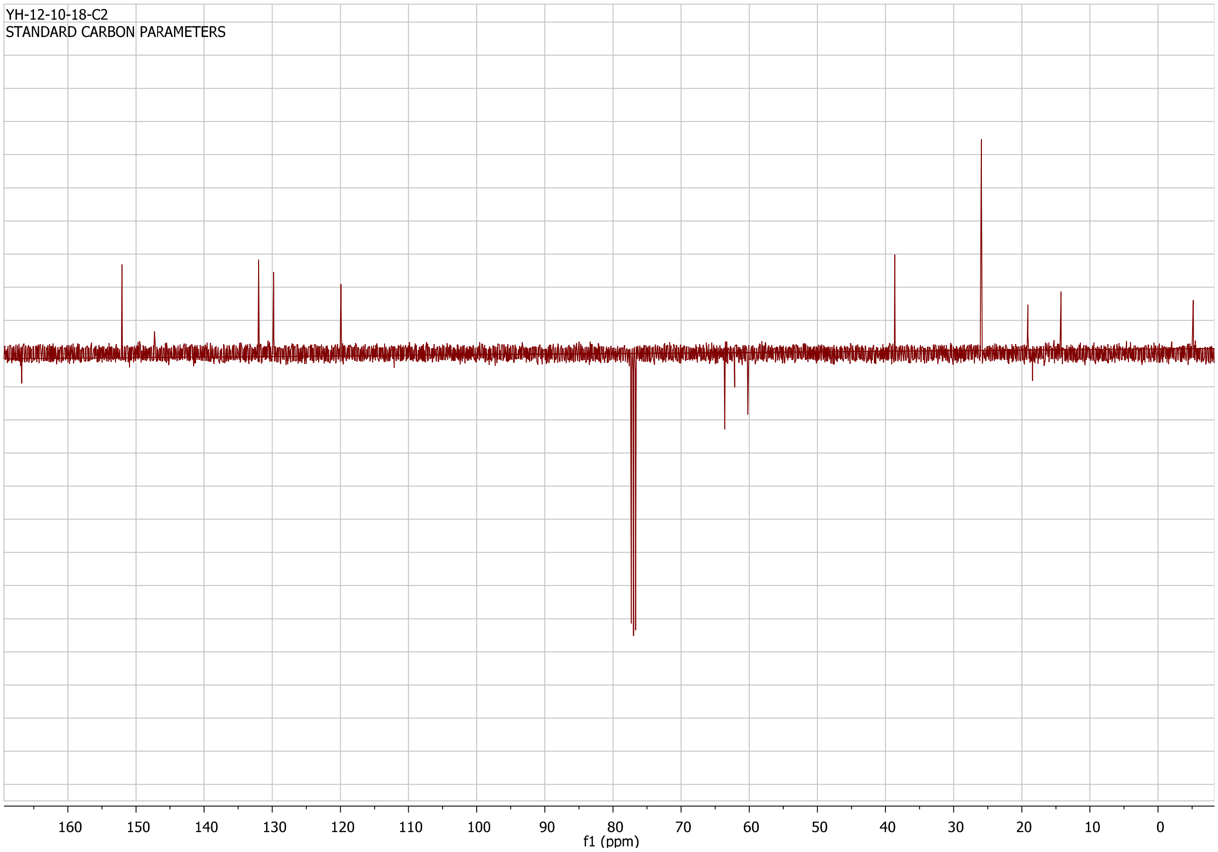

YH-12-07-05-H
STANDARD PROTON PARAMETERS
O
O
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f1 (ppm)


YH-12-07-05-C2
STANDARD CARBON PARAMETERS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

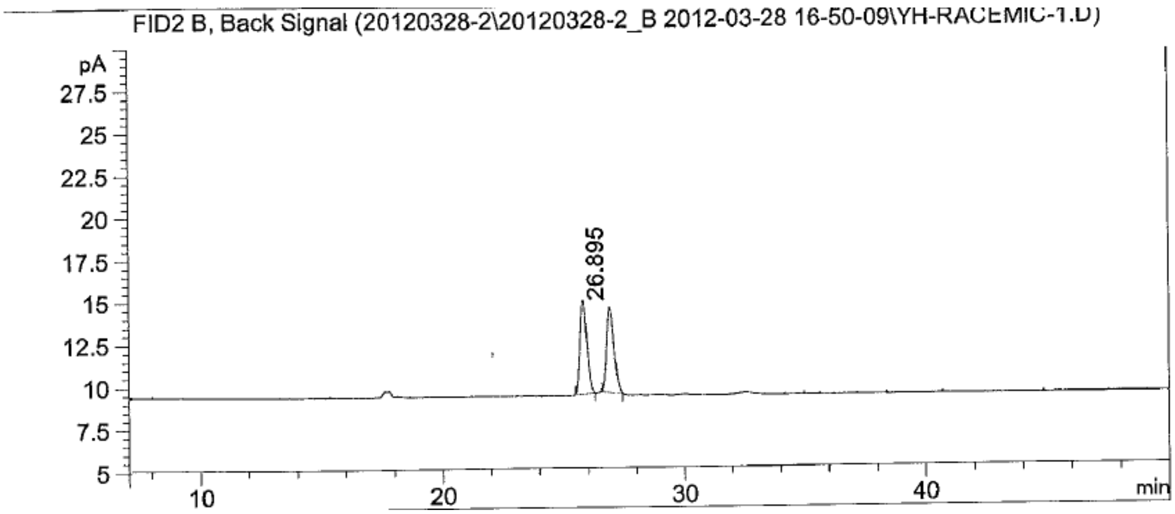

YH-12-09-27-H
STANDARD PROTON PARAMETERS
O
O
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f1 (ppm)


YH-12-09-27-C
STANDARD CARBON PARAMETERS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


YH-12-10-18-H
STANDARD PROTON PARAMETERS
TBSO
O
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

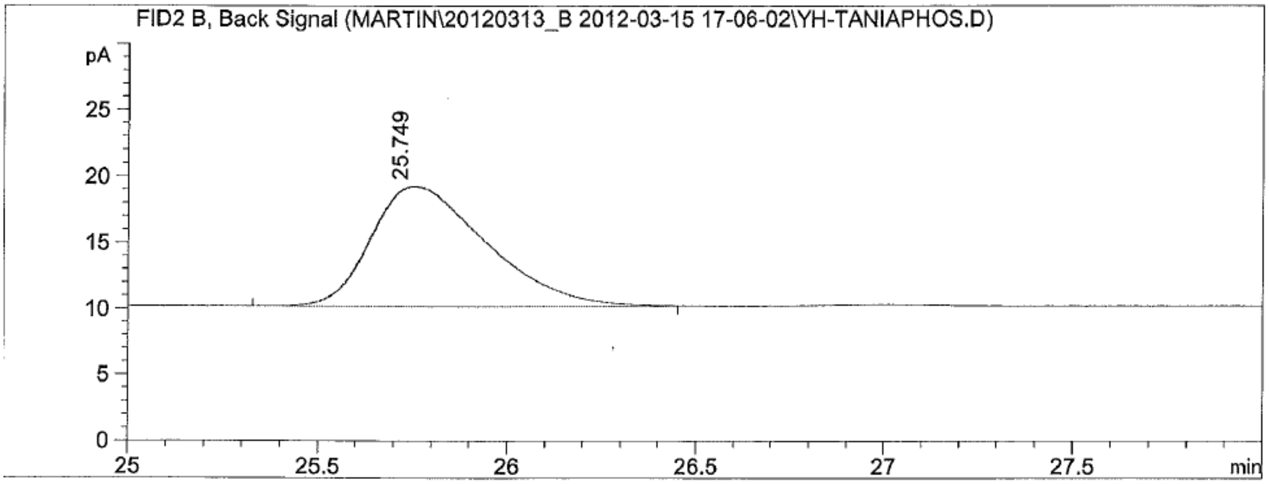

YH-12-10-18-C2
STANDARD CARBON PARAMETERS
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Racemic **2a**:



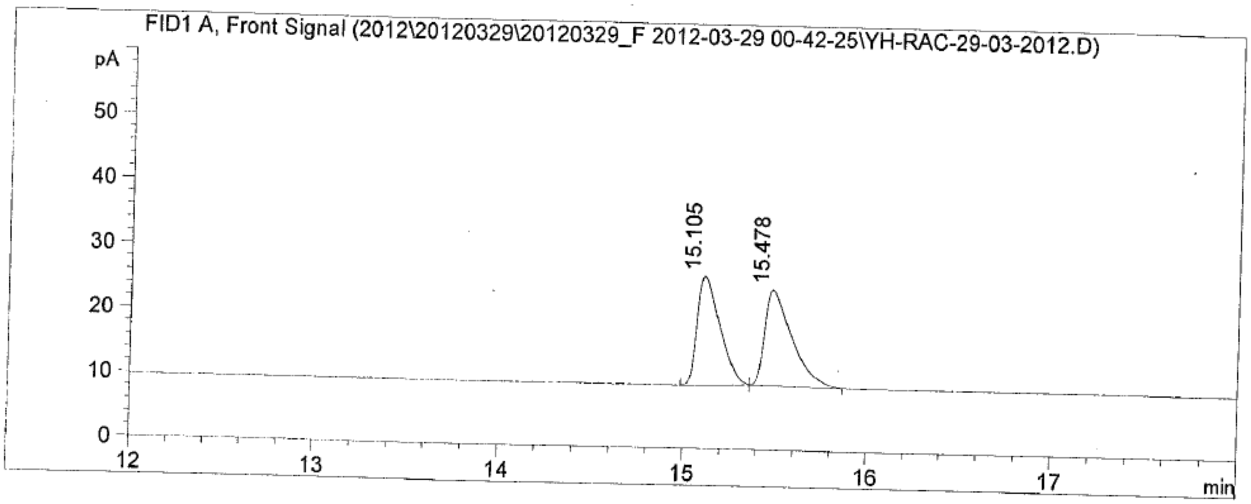
```
  #     Meas.RT Main Pe    Main Pe
 ------------------------ --------
      1  25.802  50.304    108.954
      2  26.895  49.696    107.637

 ------------------------ --------
```

Optically active **2a**:



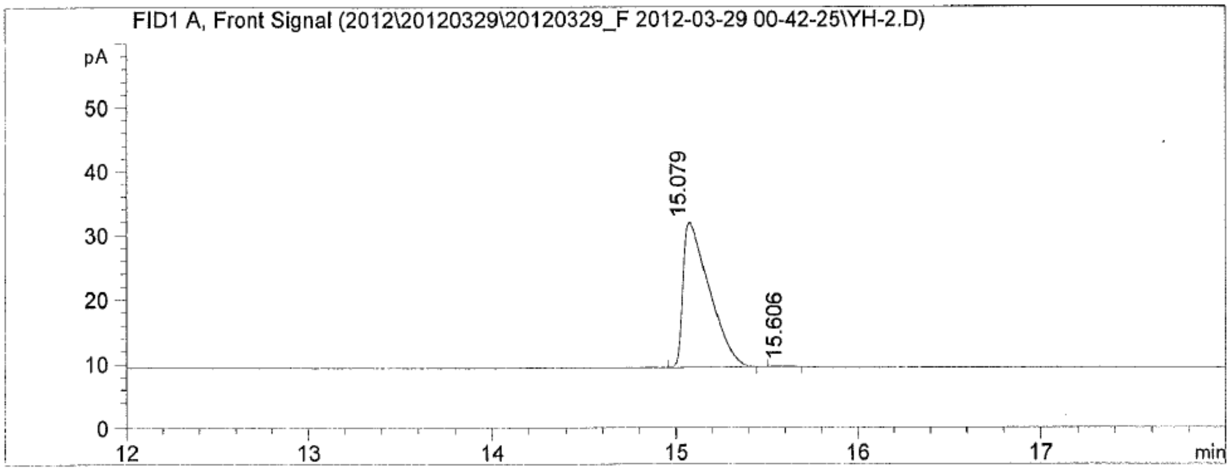
```
  #     Meas.RT Main Pe    Main Pe
 ------------------------ --------

      2  25.749 100.000    194.255
 ------------------------ --------
```

Racemic **2b**:



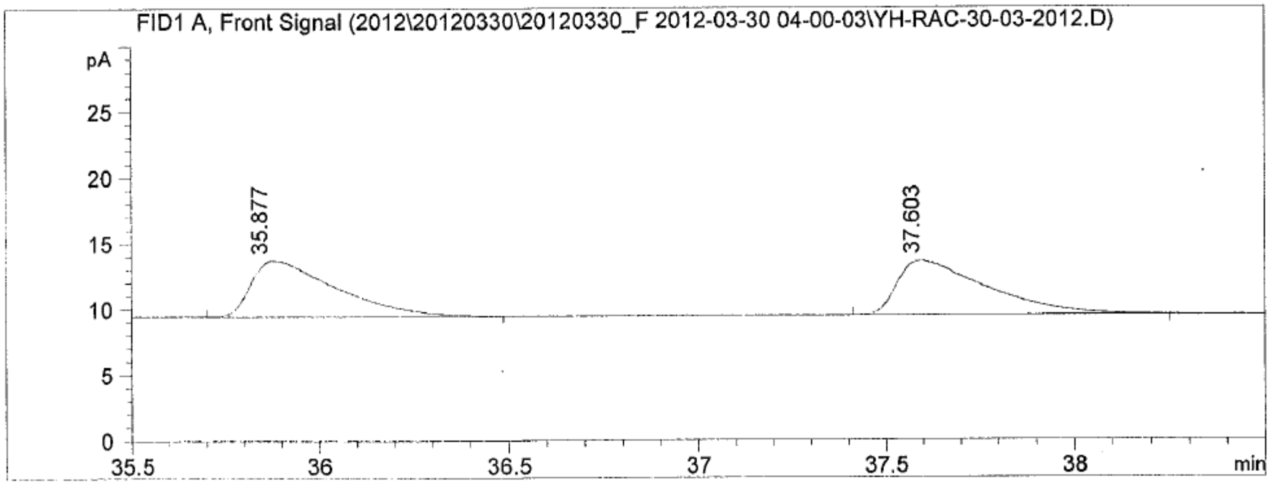
```
Main Pe Main Pe Meas.RT
-----------------------
 48.601 144.036  15.105
 51.399 152.330  15.478
-----------------------
```

Optically active **2b**:



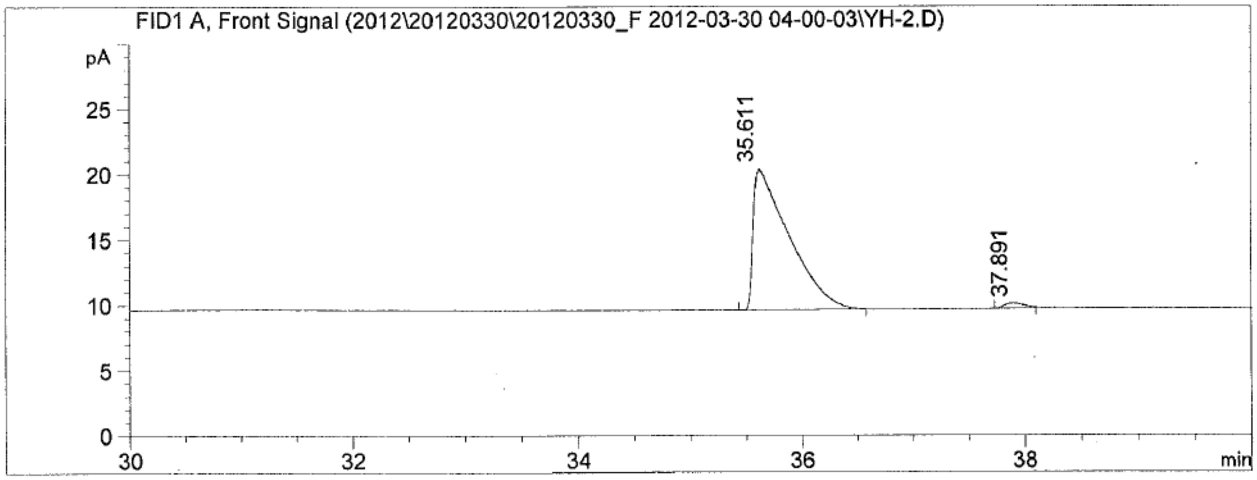
```
Main Pe Main Pe Meas.RT
-----------------------
 99.434 224.444  15.079
  0.566   1.278  15.606
-----------------------
```

Racemic **2c**:



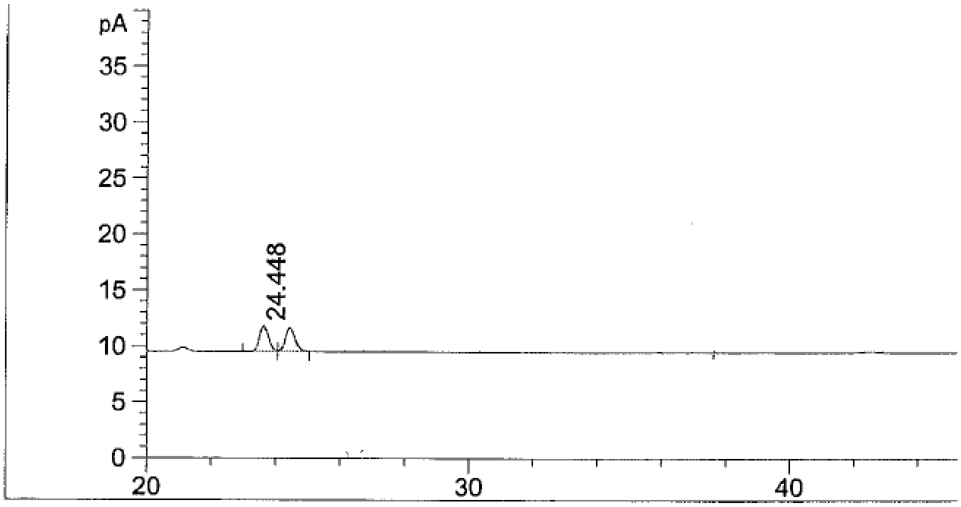
```
Main Pe Main Pe Meas.RT
------------------------
 50.012  66.953  35.877
 49.988  66.922  37.603
------------------------
```

Optically active **2c**:



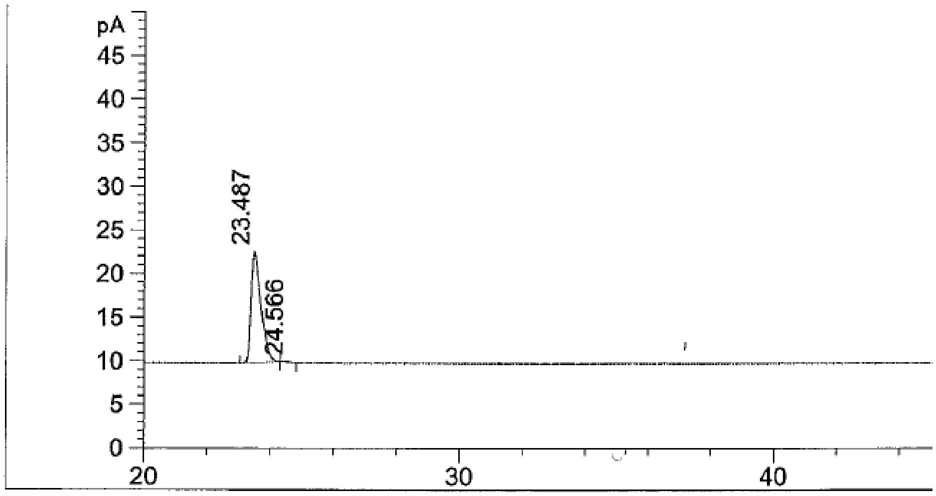
```
Main Pe Main Pe Meas.RT
-----------------------
 98.262 238.634  35.611
  1.738   4.220  37.891
-----------------------
```

Racemic **2d**:



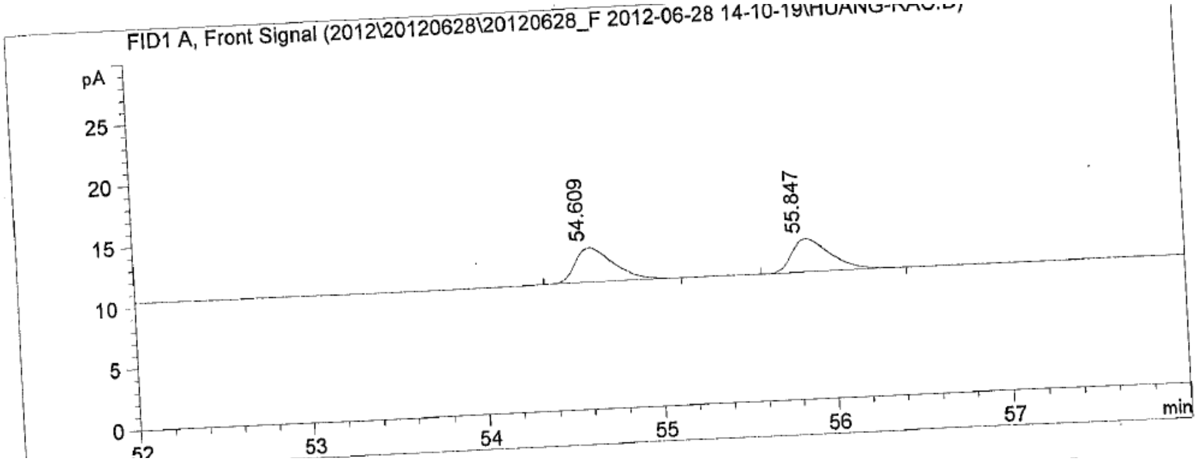
```
#     Meas.RT Main Pe Main Pe
--------------------------------
        1 23.631  50.167  44.902
        2 24.448  49.833  44.603
--------------------------------
```

Optically active **2d**:



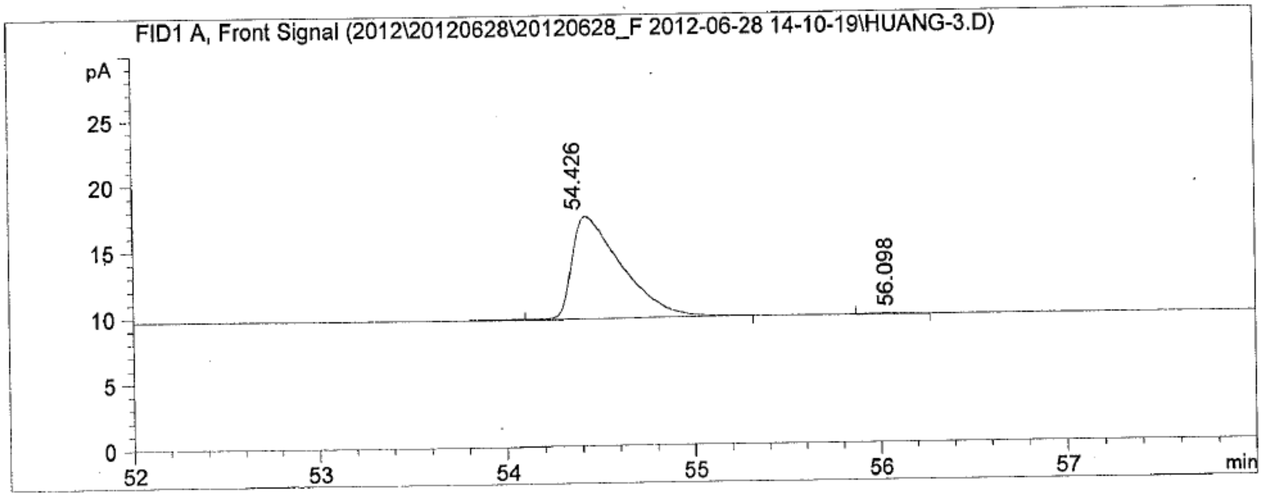
```
#     Meas.RT Main Pe Main Pe
--------------------------------
        1 23.587  99.319 161.959
        2 24.434   0.681   1.111

--------------------------------
```

Racemic **2e**:



| Main Pe | Main Pe | Meas.RT |
|---|---|---|
| 50.519 | 42.732 | 54.609 |
| 49.481 | 41.854 | 55.847 |

Optically active **2e**:

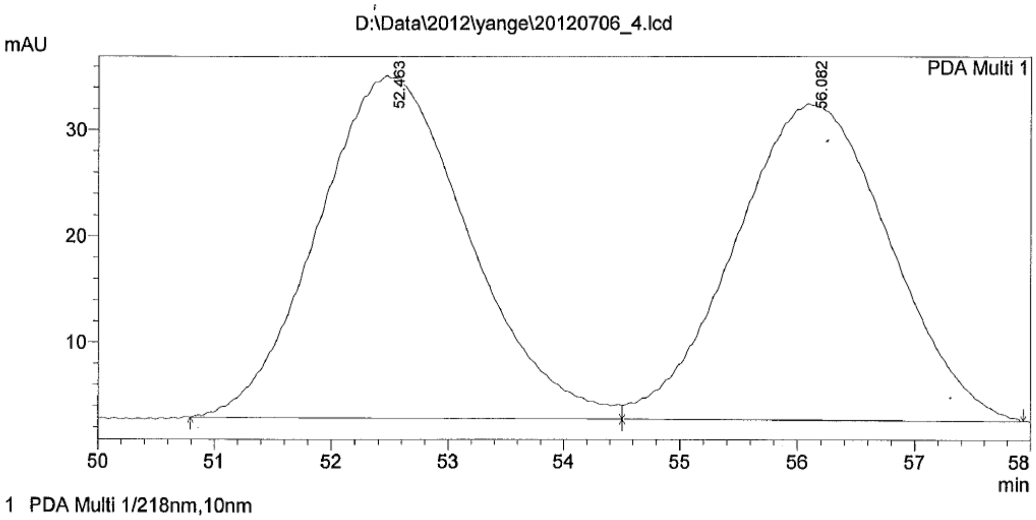


| Main Pe | Main Pe | Meas.RT |
|---|---|---|
| 98.768 | 141.958 | 54.426 |
| 1.232 | 1.771 | 56.098 |

Racemic **2f**:

---

**<Chromatogram>**



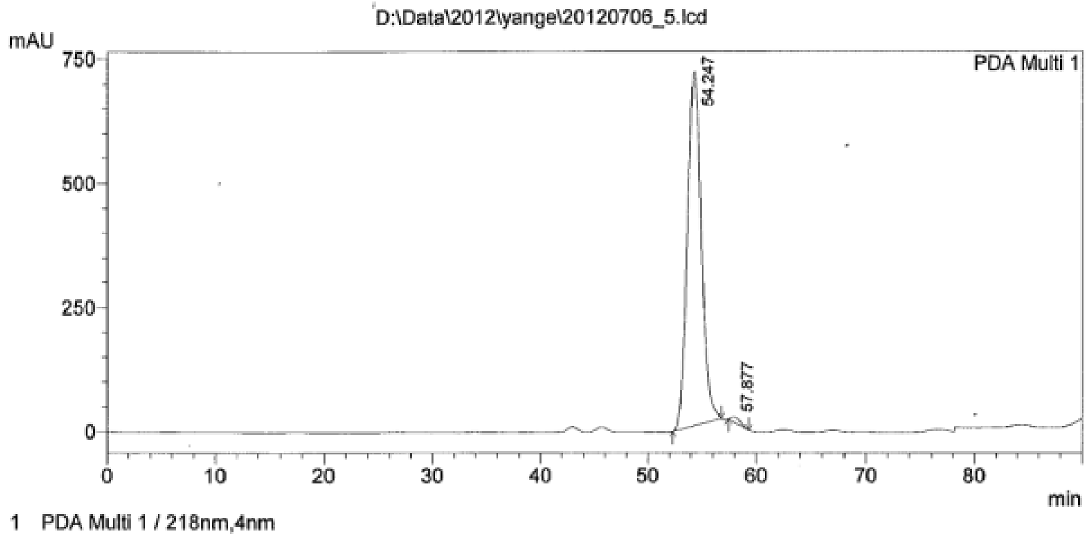
PeakTable

PDA Ch1 218nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 52.463 | 2905953 | 32265 | 51.614 | 52.002 |
| 2 | 56.082 | 2724247 | 29782 | 48.386 | 47.998 |
| Total | | 5630200 | 62047 | 100.000 | 100.000 |

Optically active **2f**:

**<Chromatogram>**

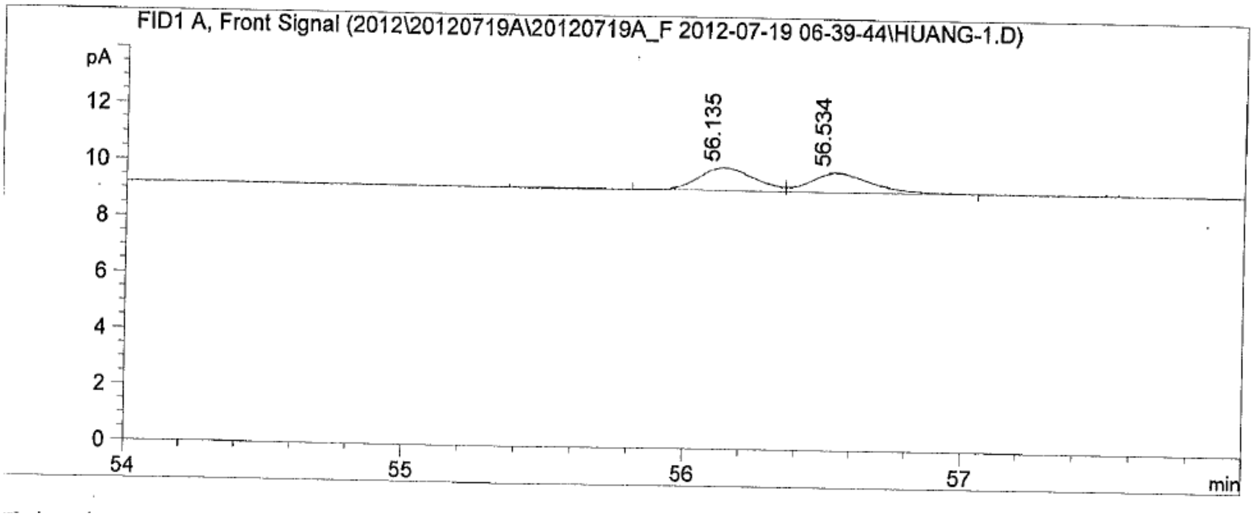


PeakTable

PDA Ch1 218nm

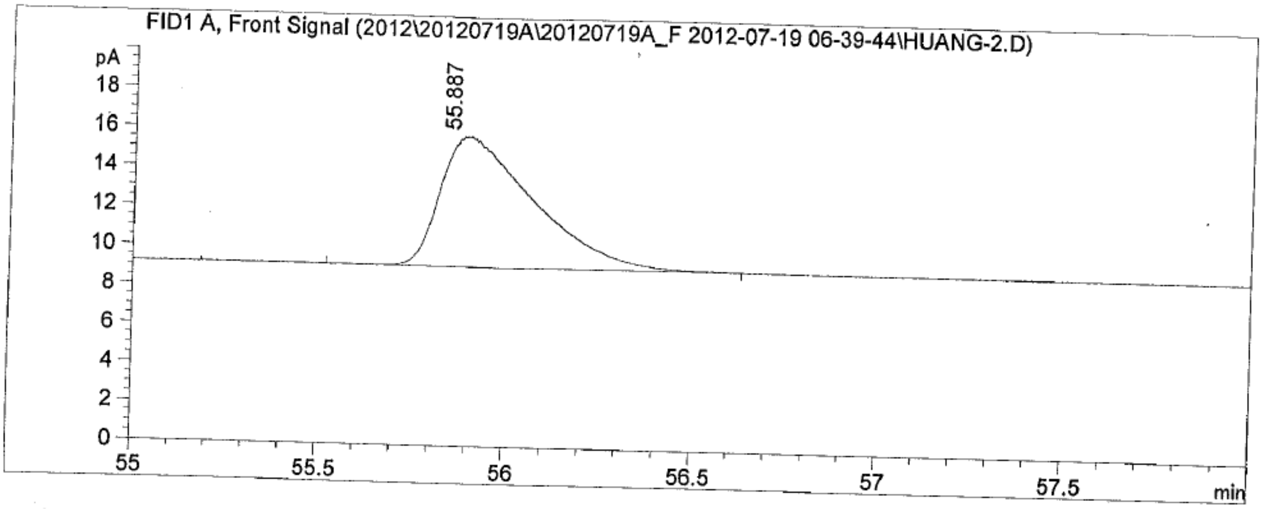
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 54.247 | 63652700 | 712033 | 98.969 | 98.596 |
| 2 | 57.877 | 663420 | 10142 | 1.031 | 1.404 |
| Total | | 64316119 | 722175 | 100.000 | 100.000 |

Racemic **2g**:



```
Main Pe Main Pe Meas.RT
-----------------------
 50.647  11.023  56.135
 49.353  10.741  56.534
-----------------------
```

Optically active **2g**:



```
Main Pe Main Pe Meas.RT
-----------------------
100.000 114.034  55.887
-----------------------
```