Asymmetric Traceless Petasis Borono-Mannich Reactions of Enals: Reductive Transpositions of Allylic Diazenes

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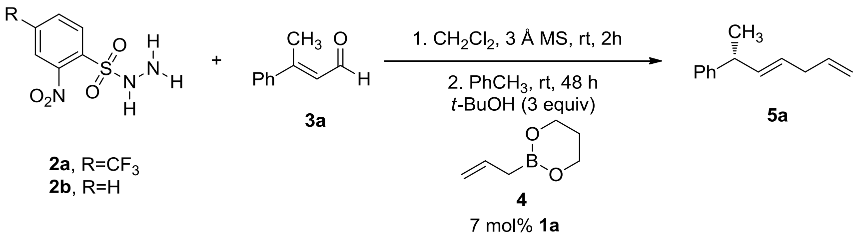
1. General Information.

All ^{1}H NMR and ^{13}C NMR spectra were recorded using Varian Unity Plus 500 MHz spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.). Chemical shifts in ^{1}H NMR spectra are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (app = apparent, br = broad, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts in ^{13}C NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 77.0 ppm). All ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts in ^{19}F NMR spectra are reported in parts per million using 0.05% α, α, α-trifluorotoluene in deuterobenzene as the external standard. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. High-resolution mass spectra were obtained using a Waters Q-TOF mass spectrometer. LC-MS experiments were performed using an Agilent Single-Quad LC/MSD VL with single-quad low resolution (1 decimal place) capable of both ESI positive and negative modes using flow injection analysis. GC-MS experiments were performed using an Agilent GC-MS 6890N equipped with a MS detector up to 800 m/z. The ionization is electron impact (EI) and software is ChemStation. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and were reported as $[\alpha]^{T\,°C}_{D}$ (concentration in grams/100 mL solvent). Chiral HPLC analysis was performed using an Agilent 1100 series HPLC System with a diode array detector. Chiral columns include Chiralcel®OD (Chiral Technologies Inc., 25 cm × 4.6 mm I.D.), Chiralpak®AD-H (Chiral Technologies Inc., 25 cm × 4.6 mm I.D.) and Chiralpak®IA (Chiral Technologies Inc., 25 cm × 4.6 mm I.D.). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Catalyst loadings were calculated with respect to the amount of boronates. All reactions were carried out in oven-dried glassware under an argon or nitrogen atmosphere unless otherwise noted. HPLC grade THF, dichloromethane, Et_2O and toluene were purchased from Fisher and VWR and were purified and dried by passing through as PURE SOLV® solvent purification system (Innovative Technology Inc.). The chiral biphenol catalysts were prepared according to the known literature.[1] Allyl and crotyl boronates were made following disclosed procedures.[2] Hydrazides were synthesized according to published protocols.[3] All other reagents were purchased from commercial suppliers and used without further purification.

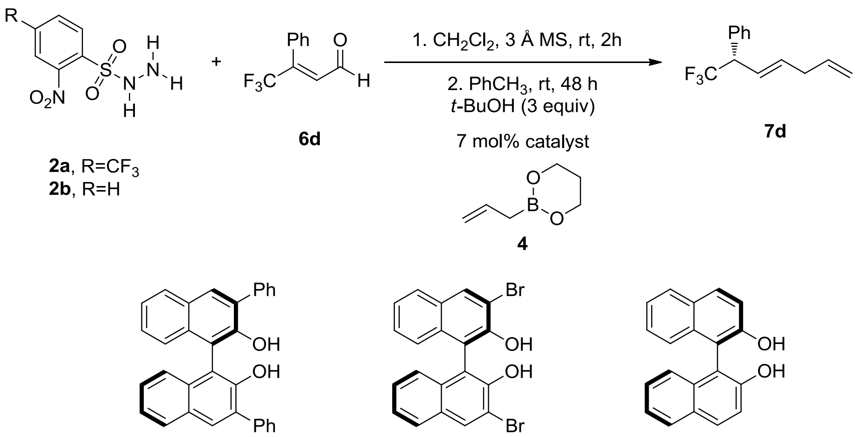
2. Experimental Procedure and Characterization of Products

a. Reaction Optimization



Entry	Variation from the Standard Procedure	Yield(%)[a]	e.r.[b]
1[c]	—	83	98:2
2	Hydrazine **2b** instead of **2a**	15	—
3	Hydrazine **2b** instead of **2a**, 96 h	32	96:4
4	Hydrazine **2b** instead of **2a**, 50 ℃	5	—
5	Hydrazine **2b** instead of **2a**, microwave (10 W, 1 h)	11	96:4
6	10 mol% **1a**	85	98:2
7	3 mol% **1a**	45	90:10
8	No *t*-BuOH	80	81:19

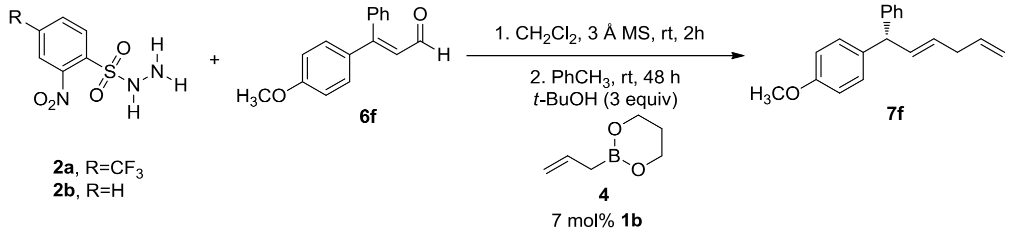
[a] Isolated yield. [b] Determined by chiral HPLC analysis. [c] Reaction condition: aldehyde **3a** (0.4 mmol), hydrazide **2a** (0.4 mmol) and powdered 3 Å molecular sieves (200 mg) were mixed in CH_2Cl_2 (1 mL) at room temperature for 2 h; CH_2Cl_2 was removed; allylboronate **4** (0.6 mmol), 7 mol% catalyst **1a**, *t*-BuOH (1.2 mmol) were added. The reaction was allowed to stir at room temperature for 48 h, after which moment the crude mixture was subjected to purification to afford the 1,4-diene product **5a**.



1a **1b** **1c**

Entry	Hydrazide	Catalyst	Yield(%)[a]	e.r.[b]
1	**2a**	**1a**	10	—
2	**2a**	**1c**	84	78:22
3	**2a**	**1b**	57	91:9
4	**2b**	**1a**	31	50:50
5	**2b**	**1b**	86	92:8
6[c]	**2b**	**1b**	85	97:3

Reaction condition: aldehyde (0.4 mmol), hydrazide (0.4 mmol) and powdered 3 Å molecular sieves (200 mg) were mixed in CH_2Cl_2 (1 mL) at room temperature for 2 h; CH_2Cl_2 was removed; allylboronate (0.6 mmol), catalyst, *t*-BuOH were added. [a] Isolated yield. [b] Determined by chiral HPLC analysis. [c] 5 equivalents of *t*-BuOH were employed under neat conditions.

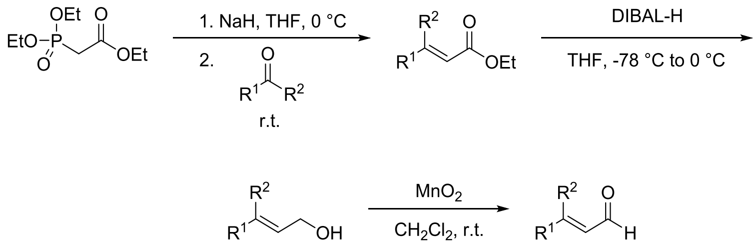


Entry	Variation from the Standard Procedure	Yield(%)[a]	e.r.[b]
1[c]	—	86	98:2
2	Hydrazine **2a** instead of **2b**	45	98:2
3	Catalyst **1a** instead of **1b**	33	50:50
4	40 ℃, 24 h	56	96:4
6	3 mol% **1b**	59	94:6

[a] Isolated yield. [b] Determined by chiral HPLC analysis. [c] Reaction condition: aldehyde **6f** (0.4 mmol), hydrazide **2b** (0.4 mmol) and powdered 3 Å molecular sieves (200 mg) were mixed in CH_2Cl_2 (1 mL) at room temperature for 2 h; CH_2Cl_2 was removed; allylboronate **4** (0.6 mmol), 7 mol% catalyst **1b**, *t*-BuOH (1.2 mmol) were added. The reaction was allowed to stir at room temperature for 48 h, after which moment the crude mixture was subjected to purification to afford the 1,4-diene product **7f**.

b. Synthesis of Enals

β-Aryl-β-alkyl enals were synthesized from the corresponding aryl alkyl ketones by a three-step sequence: Horner-Wadsworth-Emmons olefination/DIBAL-H reduction/MnO_2 oxidation.[4]



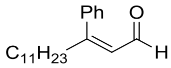
Step 1: To a 100-mL round bottom flask containing NaH (20 mmol, 60% mineral dispersion) and anhydrous THF (40 mL) at 0 ℃ was added triethyl phosphonoacetate (21.5 mmol) dropwise. The reaction mixture was allowed to stir for 30 min at the same temperature, followed by a dropwise addition of a solution of the corresponding ketone (20 mmol, in 20 mL anhydrous THF). The reaction mixture was stirred while being monitored by TLC until the ketone was consumed. Water (40 mL) was slowly added in and the reaction mixture was extracted with EtOAc (3 × 100 mL). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 99/1 → 95/5) to afford the corresponding α,β-unsaturated ester in an isomerically pure form.

Step 2: The unsaturated ester (20 mmol) was dissolved in 40 mL dry THF under argon before being cooled to −78 ℃. DIBAL-H (1.0 M in toluene, 2.4 equiv) was added dropwise over 5 min and the resulting mixture was stirred at −78 ℃ for 30 min. The reaction mixture was then allowed to warm to 0 ℃ and stirred for another 30 min. At the same temperature, the reaction was quenched by a dropwise addition of 2 M aqueous HCl. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 4/1) to afford the corresponding allylic alcohol in an isomerically pure form.

Step 3: To a 100-mL round bottom flask containing the allylic alcohol (10 mmol) obtained above, was added activated MnO_2 (5 equiv) and anhydrous CH_2Cl_2 (25 mL) at room temperature. The reaction mixture was then allowed to stir for at least 24 h, while being monitored by TLC. After complete consumption of the starting material, the reaction mixture was filtered through a pad of celite and rinsed by CH_2Cl_2. The resulting filtrate was concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 99/1 → 95/5) to afford the corresponding β-aryl-β-alkyl enal in an isomerically pure form.

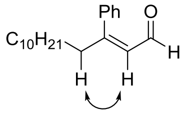
(*E*)-3-Phenylbut-2-enal (**3a**) was synthesized using acetophenone and all spectra were in agreement with reported data.[5] Other β-methyl enals were synthesized in the same manner using corresponding aryl methyl ketones. Geranial was synthesized by direct MnO_2 oxidation of geraniol.[6]

(*E*)-3-Phenylpent-2-enal (**6a**) was synthesized using propiophenone following the three-step synthetic sequence. All spectra were in agreement with reported data.[7]



(*Z*)-3-Phenyltetradec-2-enal (**6b**)

Dodecanophenone was used following the above-mentioned three-step synthetic sequence. (*Z*)-Geometry was determined by NOESY:

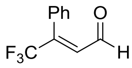


^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (d, J = 8.2 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.29 – 7.22 (m, 2H), 6.10 (d, J = 8.2 Hz, 1H), 2.57 (t, J = 7.5 Hz, 2H), 1.46 – 1.38 (m, 2H), 1.33 – 1.19 (m, 16H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 166.8, 137.8, 128.9, 128.5, 128.4, 128.3, 39.7, 31.9, 29.6, 29.4, 29.3, 29.3, 29.1, 27.4, 22.7, 14.1.

ESIMS found 287.2 (calculated for $[C_{20}H_{31}O]^+$: 287.2)

(*Z*)-4-Methyl-3-phenylpent-2-enal (**6c**) and **(*E*)-4-methyl-3-phenylpent-2-enal** [**(*E*)-8**] were synthesized divergently from isobutyrophenone following the three-step synthetic sequence. All spectra for the corresponding intermediates were in agreement with reported data.[8] The final (*Z*)- and (*E*)-enals can be prepared as single isomers. All spectra were in agreement with reported data.[9]



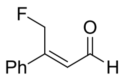
(*E*)-4,4,4-Trifluoro-3-phenylbut-2-enal (**6d**)

2,2,2-Trifluoroacetophenone was used following the above-mentioned three-step synthetic sequence. All spectra for the intermediates [ethyl (*E*)-4,4,4-trifluoro-3-phenylbut-2-enoate and (*E*)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol] were in agreement with reported data.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.55 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.42 – 7.38 (m, 2H), 6.64 (d, *J* = 7.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 147.8 (q, *J* = 31.5 Hz), 130.8, 130.5, 129.9, 128.8, 127.8, 122.7 (q, *J* = 275.0 Hz).

ESIMS found 201.0 (calculated for $[C_{10}H_8F_3O]^+$: 201.0)



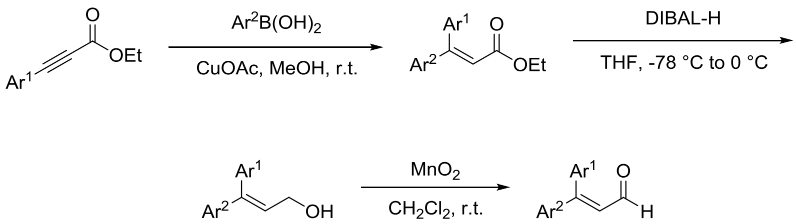
(*Z*)-4-Fluoro-3-phenylbut-2-enal (**6e**)

2-Fluoro-1-phenylethanone[11] was used following the above-mentioned three-step synthetic sequence. All spectra for intermediates [ethyl (*Z*)-4-fluoro-3-phenylbut-2-enoate and (*Z*)-4-fluoro-3-phenylbut-2-en-1-ol] were in agreement with reported data.[12]

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 3H), 6.42 (dd, *J* = 7.2, 1.0 Hz, 1H), 5.73 (d, *J* = 47.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4 (d, *J* = 4.0 Hz), 153.2 (d, *J* = 14.5 Hz), 136.5 (d, *J* = 3.5 Hz), 130.4, 129.6 (d, *J* = 2.9 Hz), 129.0, 126.9, 79.5 (d, *J* = 171.4 Hz).

ESIMS found 165.1 (calculated for $[C_{10}H_{10}FO]^+$: 165.1) β,β-Diaryl enals were synthesized from the corresponding ethyl 3-arylpropiolate and aryl boronic acid by a three-step sequence:[13] Cu-catalyzed conjugate addition[14]/DIBAL-H reduction/MnO_2 oxidation.

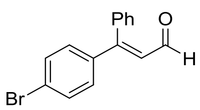


Step 1: In a 100-mL round bottom flask ethyl 3-arylpropiolate (20 mmol, 1 equiv), aryl boronic acid (3 equiv), and CuOAc (2 mol%) were dissolved in 40 mL MeOH. The solution was degassed by three freeze-pump-thaw cycles and then stirred overnight at room temperature. The resulting mixture was filtered off Celite and the solvent was removed under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 95/5) to afford the corresponding α,β-unsaturated ester in an isomerically pure form.

Step 2: The unsaturated ester (15 mmol) was dissolved in 40 mL dry THF under argon before being cooled to −78 ℃. DIBAL-H (1.0 M in toluene, 2.4 equiv) was added dropwise over 5 min and the resulting mixture was stirred at −78 ℃ for 30 min. The reaction mixture was then allowed to warm to 0 ℃ and stirred for another 30 min. At the same temperature, the reaction was quenched by a dropwise addition of 2 M aqueous HCl. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 4/1) to afford the corresponding allylic alcohol in an isomerically pure form.

Step 3: To a 100-mL round bottom flask containing the allylic alcohol (10 mmol) obtained above, was added activated MnO_2 (5 equiv) and anhydrous CH_2Cl_2 (25 mL) at room temperature. The reaction mixture was then allowed to stir for at least 24 h, while being monitored by TLC. After complete consumption of the starting material, the reaction mixture was filtered through a pad of celite and rinsed by CH_2Cl_2. The resulting filtrate was concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 99/1 → 95/5) to afford the corresponding β-branched enal in an isomerically pure form.

(*E*)-3-(4-Methoxyphenyl)-3-phenylacrylaldehyde (**6f**) was synthesized using ethyl phenylpropiolate and 4-methoxyphenylboronic acid. (*E*)-3-(Naphthalen-2-yl)-3-phenylacrylaldehyde (**6j**) was synthesized using ethyl phenylpropiolate and 2-naphthylboronic acid. All spectra for both substrates were in agreement with reported data.[13]



(*E*)-3-(4-Bromophenyl)-3-phenylacrylaldehyde (6g)

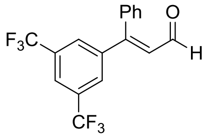
Ethyl phenylpropiolate and 4-bromophenylboronic acid were used following the above-mentioned three-step synthetic sequence.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, J = 7.9 Hz, 1H), 7.56 – 7.39 (m, 5H), 7.32 – 7.25 (m, 2H), 7.25

– 7.17 (m, 2H), 6.56 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 160.8, 138.6, 136.1, 131.9, 130.7, 130.1, 129.7, 128.5, 127.4, 125.1.

ESIMS found 287.0, 289.0 (calculated for $[C_{15}H_{12}BrO]^+$: 287.0)



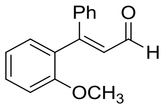
(*E*)-3-(3,5-Bis(trifluoromethyl)phenyl)-3-phenylacrylaldehyde (**6h**)

Ethyl phenylpropiolate and (3,5-bis(trifluoromethyl)phenyl)boronic acid were used following the above-mentioned three-step synthetic sequence.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.7 Hz, 1H), 7.94 (s, 1H), 7.78 (s, 2H), 7.58 – 7.42 (m, 3H), 7.38 – 7.26 (m, 2H), 6.61 (d, *J* = 7.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.5, 158.5, 142.2, 135.0, 132.2 (q, *J* = 33.9 Hz), 130.6, 130.3, 129.3, 128.9, 128.4, 123.6, 122.9 (d, *J* = 272.9 Hz).

ESIMS found 345.1 (calculated for $[C_{17}H_{11}F_6O]^+$: 345.1)



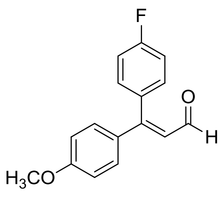
(*E*)-3-(2-Methoxyphenyl)-3-phenylacrylaldehyde (**6i**)

Ethyl phenylpropiolate and 2-methoxyphenylboronic acid were used following the above-mentioned three-step synthetic sequence.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.31 – 7.24 (m, 2H), 7.12 – 7.06 (m, 1H), 6.98 – 6.90 (m, 2H), 6.59 (d, *J* = 8.1 Hz, 1H), 3.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 159.8, 157.6, 138.1, 131.4, 131.1, 130.4, 130.2, 129.5, 129.0, 128.0, 120.5, 111.7, 55.5.

ESIMS found 239.1 (calculated for $[C_{16}H_{15}O_2]^+$: 239.1)



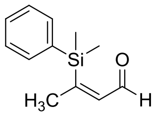
(*Z*)-3-(4-Fluorophenyl)-3-(4-methoxyphenyl)acrylaldehyde (**6k**)

3-(4-Fluorophenyl)propiolaldehyde[13] and 4-methoxyphenylboronic acid were used following the above-mentioned three-step synthetic sequence.

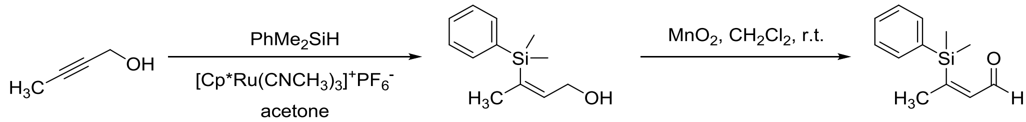
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.16 – 7.10 (m, 2H), 6.91 – 6.85 (m, 2H), 6.54 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 163.3 (d, *J* = 249.9 Hz), 161.8, 160.7, 132.9 (d, *J* = 3.5 Hz), 132.5 (d, *J* = 8.3 Hz), 131.7, 130.3, 125.8, 115.5 (d, *J* = 21.7 Hz), 114.1, 55.4.

ESIMS found 257.1 (calculated for $[C_{16}H_{14}FO_2]^+$: 257.1)



(*Z*)-3-(Dimethyl(phenyl)silyl)but-2-enal (**3g**)



The synthesis of β-silyl enals was adapted from known literature.[15] $[Cp^*Ru(CNCH_3)_3]^+PF_6^-$ (0.2 mol%) was added to a solution of 2-butyn-1-ol (25 mmol) and dimethylphenylsilane (30 mmol) in 25 mL acetone at 0 ℃. The reaction mixture was warmed up to room temperature. After 30 min, the mixture was filtered off a pad of Celite and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexanes/EtOAc (2/1) as eluent to give allylic alcohol product in an isomerically pure form. To a 100-mL round bottom flask containing the allylic alcohol (10 mmol) obtained above, was added activated MnO_2 (5 equiv) and anhydrous CH_2Cl_2 (25 mL) at room temperature. The reaction mixture was then allowed to stir at the same temperature, while being monitored by TLC. After complete consumption of the starting material, the reaction mixture was filtered through a pad of celite and rinsed by CH_2Cl_2. The resulting filtrate was concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc: 95/5) to afford the corresponding (*Z*)-β-silyl enal.

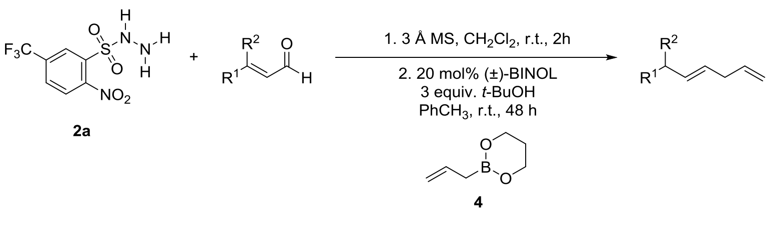
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (d, *J* = 8.6 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.43 – 7.33 (m, 3H), 6.54 (dq, *J* = 8.6, 1.6 Hz, 1H), 2.11 (d, *J* = 1.6 Hz, 3H), 0.54 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 166.9, 142.9, 137.0, 133.6, 129.7, 128.3, 26.7, −0.9.

ESIMS found 205.1 (calculated for $[C_{12}H_{17}OSi]^+$: 205.1).

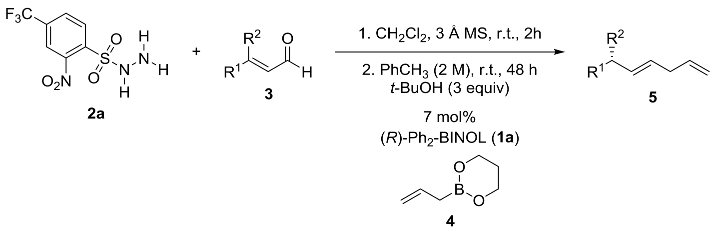
Non-branched enals **13a**-**13f** were commercially available and used without purification. (2*E*,4*E*)-5-Phenylpenta-2,4-dienal (**13g**) and (*E*)-5-phenylpent-2-enal (**13h**) were prepared according to known literature.[16]

c. General Procedure to Prepare Racemic 1,4-Dienes (±)-5, (±)-7



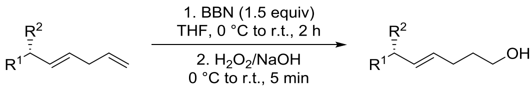
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (0.4 mmol), a β,β-disubstituted enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10-mL reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. Racemic BINOL catalyst (0.12 mmol, 20 mol%), *tert*-butanol (3 equiv, 1.2 mmol) and allylboronate (1.5 equiv, 0.6 mmol) were added and rinsed into the solution with anhydrous toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was then sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

d. General Procedure to Prepare Enantioenriched 1,4-Dienes 5



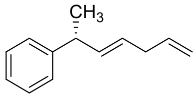
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (0.4 mmol), a β-methyl enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10-mL reaction vial equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (*R*)-Ph_2-BINOL (0.04 mmol, 7 mol%), *tert*-butanol (3 equiv, 1.2 mmol) and allylboronate (1.5 equiv, 0.6 mmol) were added and rinsed into the solution with anhydrous toluene (0.2 mL). The reaction was applied to sonication for 5 min to facilitate dissolution. The vial was then sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

e. General Procedure for Hydroboration/Oxidation of 1.4-Dienes



The 1,4-diene (0.25 mmol) was dissolved in dry THF (0.5 mL) under argon and cooled to 0 ℃. 9-BBN (0.5 M in THF, 1.5 equiv) was added dropwise to the reaction, and the reaction was allowed to warm up to room temperature naturally. After one hour, the reaction was cooled to 0 ℃. 3 M NaOH solution (0.25 mL) was added slowly to the reaction, followed by dropwise addition of H_2O_2 (35% in water, 0.25 mL). The reaction was warmed to room temperature in 5 min. The reaction mixture was transferred to a separatory funnel using Et_2O (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by Et_2O (3 × 5 mL). The combined organic layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel afforded the desired compound.

f. Analytical Data for 1,4-Dienes 5



(*R*,*E*)-Hepta-3,6-dien-2-ylbenzene (5a)

The substrate was run in 0.4 mmol scale following the general procedure and the crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 57 mg, 83%.

e.r.: 98:2.

$[\alpha]_D^{22}$ = –4.2 (c = 1.0, $CHCl_3$).

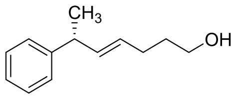
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5a** following the hydroboration/oxidation procedure, tr minor: 36.2 min., tr major: 37.8 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.75:0.25, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 5H), 5.91 – 5.79 (m, 1H), 5.67 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.49 (dt, *J* = 15.4, 6.4 Hz, 1H), 5.09 – 4.97 (ovrlp, 2H), 3.47 (qd, *J* = 7.0, 6.8 Hz, 1H), 2.79 (dd, *J* = 6.4, 6.2 Hz, 2H), 1.37 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 137.2, 136.3, 128.4, 127.2, 126.6, 126.0, 115.0, 42.3, 36.7, 21.5.

GCMS found 172.1 (calculated for $C_{13}H_{16}$: 172.1)

IR (thin film, cm^{-1}): 3026, 2969, 2871, 1493, 1452, 911.



(*R*,*E*)-6-Phenylhept-4-en-1-ol (S5a)

This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.

Yield: 27 mg, 59%

e.r.: 98:2.

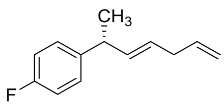
$[\alpha]_D^{22}$ = –7.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 5H), 5.65 (dd, *J* = 15.1, 6.9 Hz, 1H), 5.48 (dt, *J* = 15.1, 6.8 Hz, 1H), 3.65 (td, *J* = 6.2, 6.2 Hz, 2H), 3.43 (qd, *J* = 6.9, 6.9 Hz, 1H), 2.12 (td, *J* = 7.1, 7.1 Hz, 2H), 1.65 (tt, *J* = 6.9, 6.9 Hz, 2H), 1.40 (d, *J* = 6.2, 1H), 1.35 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 135.7, 128.4, 128.3, 127.1, 126.0, 62.5, 42.2, 32.4, 28.8, 21.5.

ESIMS found 213.1 (calculated for $[C_{13}H_{18}ONa]^+$: 213.1)

IR (thin film, cm^{-1}): 3381, 3027, 2962, 2933, 2870, 1493, 1451, 1060, 973.



(*R*,*E*)-1-Fluoro-4-(hepta-3,6-dien-2-yl)benzene (5b)

The substrate was run in 0.4 mmol scale following the general procedure and the crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 57 mg, 75%.

e.r.: 97:3.

[α]$_D^{22}$ = –7.8 (c = 1.0, $CHCl_3$).

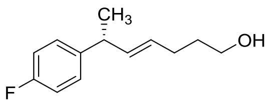
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5b** following the hydroboration/oxidation procedure, tr major: 13.4 min., tr minor: 15.1 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 250 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 2H), 7.03 – 6.94 (m, 2H), 5.84 (ddt, *J* = 16.7, 10.1, 5.9 Hz, 1H), 5.62 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.46 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.07 – 4.97 (ovrlp, 2H), 3.44 (qd, *J* = 7.0, 6.6 Hz, 1H), 2.78 (dd, *J* = 6.8, 5.9 Hz, 2H), 1.34 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.9 Hz), 141.8 (d, *J* = 3.1 Hz), 137.1, 136.1, 128.5 (d, *J* = 7.8 Hz), 126.8, 115.0, 115.0 (d, *J* = 21.0 Hz), 41.5, 36.6, 21.5.

GCMS found 190.1 (calculated for $C_{13}H_{15}F$: 190.1).

IR (thin film, cm^{-1}): 3081, 3005, 2969, 2892, 1638, 1605, 1509, 1223, 1159, 1015, 970, 914.



(*R*,*E*)-6-(4-Fluorophenyl)hept-4-en-1-ol (S5b)

This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.

Yield: 32 mg, 62%.

e.r.: 97:3.

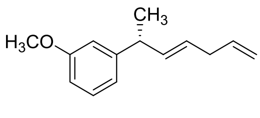
[α]$_D^{22}$ = –7.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 7.01 – 6.93 (m, 2H), 5.60 (dd, *J* = 15.2, 6.9 Hz, 1H), 5.45 (dt, *J* = 15.2, 6.9 Hz, 1H), 3.64 (t, *J* = 5.2 Hz, 2H), 3.41 (qd, *J* = 7.0, 6.9 Hz, 1H), 2.11 (td, *J* = 7.0, 6.9 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.28 (br, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.5 Hz), 141.8 (d, *J* = 3.2 Hz), 135.6, 128.5 (d, *J* = 4.0 Hz), 128.4, 115.0 (d, *J* = 21.0 Hz), 62.5, 41.5, 32.3, 28.8, 21.6.

ESIMS found 231.1 (calculated for $[C_{13}H_{17}FONa]^+$: 231.1).

IR (thin film, cm^{-1}): 3379, 2963, 2873, 1604, 1510, 1223, 1159.



(*R*,*E*)-1-(Hepta-3,6-dien-2-yl)-3-methoxybenzene (5c)

The substrate was run in 0.4 mmol scale following the general procedure and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (150/1) to afford the pure product as a colorless oil.

Yield: 72 mg, 89%.

e.r.: 97:3.

[α]$_D^{22}$ = –4.9 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 24.8 min., tr minor: 26.1 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 0.5 mL/min, 230 nm].

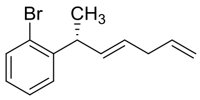
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.80 (s, 1H), 6.76 (d, *J*

= 7.8 Hz, 1H), 5.86 (ddt, J = 16.7, 10.3, 6.4 Hz, 1H), 5.66 (dd, J = 15.5, 6.7 Hz, 1H), 5.56 – 5.46 (m, 1H), 5.10 – 4.98 (ovrlp, 2H), 3.82 (s, 3H), 3.45 (qd, J = 7.1, 6.7 Hz, 1H), 2.80 (dd, J = 6.4, 6.4 Hz, 2H), 1.37 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 148.0, 137.2, 136.1, 129.3, 126.6, 119.6, 115.0, 113.2, 111.0, 55.1, 42.3, 36.6, 21.4.

GCMS found 202.2 (calculated for $C_{14}H_{18}O$: 202.1).

IR (thin film, cm^{-1}): 3081, 3028, 3000, 2965, 2935, 2897, 1601, 1486, 1435, 1262, 1161, 1050.



(*R*,*E*)-1-Bromo-2-(hepta-3,6-dien-2-yl)benzene (5d)

The substrate was run in 0.4 mmol scale following the general procedure and the crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 60 mg, 60%.

e.r.: 96:4.

$[\alpha]_D^{22}$ = +45.5 (c = 1.0, $CHCl_3$).

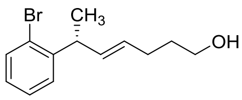
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5d** following the hydroboration/oxidation procedure, tr major: 66.8 min., tr minor: 70.5 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, J = 8.0, 1.2 Hz, 1H), 7.31 – 7.21 (ovrlp, 2H), 7.05 (ddd, J = 8.0, 6.9, 2.1 Hz, 1H), 5.85 (ddt, J = 16.9, 10.1, 6.4 Hz, 1H), 5.64 (dd, J = 15.5, 5.9 Hz, 1H), 5.53 (dt, J = 15.5, 6.4 Hz, 1H), 5.05 (dtd, J = 16.9, 1.6, 1.6 Hz, 1H), 5.00 (ddt, J = 10.1, 1.6, 1.5 Hz, 1H), 3.96 (qd, J = 7.0, 5.7 Hz, 1H), 2.80 (dddd, J = 6.4, 6.4, 1.6, 1.5 Hz, 2H), 1.33 (d, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 137.1, 134.5, 132.8, 128.2, 127.6, 127.5, 127.4, 124.3, 115.1, 40.6, 36.7, 20.3.

GCMS found 250.0, 252.0 (calculated for $C_{13}H_{15}Br$: 250.0).

IR (thin film, cm^{-1}): 3054, 2971, 2872, 1639, 1470, 1439, 1023, 914.



(*R*,*E*)-6-(2-Bromophenyl)hept-4-en-1-ol (S5d)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.

Yield: 44 mg, 82%.

e.r.: 96:4.

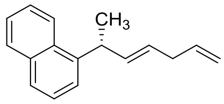
$[\alpha]_D^{22}$ = +45.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.0, 1.3 Hz, 1H), 7.30 – 7.19 (ovrlp, 2H), 7.04 (ddd, J = 8.0, 7.1, 1.9 Hz, 1H), 5.63 (ddt, J = 15.3, 5.9, 1.3 Hz, 1H), 5.50 (dtd, J = 15.3, 6.7, 1.4 Hz, 1H), 3.92 (qdd, J = 7.0, 5.9, 1.3 Hz, 1H), 3.65 (t, J = 6.5 Hz, 2H), 2.16 – 2.09 (m, 2H), 1.71 – 1.60 (m, 2H), 1.31 (d, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 134.0, 132.8, 129.2, 128.1, 127.6, 127.5, 124.3, 62.5, 40.6, 32.3, 28.9, 20.3.

ESIMS found 291.0, 293.0 (calculated for $[C_{13}H_{17}BrONa]^+$: 291.0).

IR (thin film, cm^{-1}): 3340, 2935, 2902, 1470, 1023, 755.



(*R*,*E*)-1-(Hepta-3,6-dien-2-yl)naphthalene (5e)

The substrate was run in 0.4 mmol scale following the general procedure, with the exception that the concentration was 1 M. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 76 mg, 85%.

e.r.: 95:5.

$[\alpha]_D^{22}$ = +48.9 (c = 1.0, $CHCl_3$).

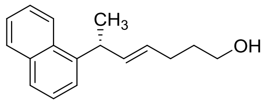
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5e** following the hydroboration/oxidation procedure, tr minor: 27.1 min., tr major: 28.4 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 280 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.41 (ovrlp, 3H), 7.39 (d, *J* = 7.1 Hz, 1H), 5.90 – 5.74 (ovrlp, 2H), 5.54 (dt, *J* = 14.4, 6.5 Hz, 1H), 5.06 – 4.95 (ovrlp, 2H), 4.29 (qd, *J* = 6.9, 6.8 Hz, 1H), 2.79 (dd, *J* = 6.5, 6.4 Hz, 2H), 1.51 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 137.2, 136.0, 133.9, 131.4, 128.9, 127.0, 126.7, 125.7, 125.6, 125.3, 123.6, 123.5, 115.0, 37.0, 36.7, 21.0.

GCMS found 222.1 (calculated for $C_{17}H_{18}$: 222.1).

IR (thin film, cm^{-1}): 3049, 2970, 2931, 1638, 1597, 1511, 1396, 973, 914.



(*R*,*E*)-6-(Naphthalen-1-yl)hept-4-en-1-ol (S5e)

This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.

Yield: 37 mg, 62%.

e.r.: 95:5.

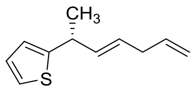
$[\alpha]_D^{22}$ = +32.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.41 (ovrlp, 3H), 7.38 (d, *J* = 6.4 Hz, 1H), 5.79 (dd, *J* = 15.4, 6.5 Hz, 1H), 5.53 (dt, *J* = 15.4, 6.9 Hz, 1H), 4.26 (qd, *J* = 6.9, 6.5 Hz, 1H), 3.63 (td, *J* = 6.4, 5.5 Hz, 2H), 2.13 (dt, *J* = 6.9, 6.8 Hz, 2H), 1.64 (tt, *J* = 6.8, 6.4 Hz, 2H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.23 (t, *J* = 5.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 135.4, 133.9, 131.4, 128.8, 128.8, 126.6, 125.6, 125.6, 125.3, 123.6, 123.4, 62.5, 37.0, 32.4, 28.9, 21.0.

ESIMS found 263.1 (calculated for $[C_{17}H_{19}ONa]^+$: 263.1).

IR (thin film, cm^{-1}): 3367, 3048, 2928, 2869, 1597, 1510, 1451, 1396, 1058, 970.



(*R*,*E*)-2-(Hepta-3,6-dien-2-yl)thiophene (5f)

The substrate was run in 0.4 mmol scale following the general procedure and the crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 52 mg, 73%.

e.r.: 99:1.

$[\alpha]_D^{22}$ = –43.7 (c = 1.0, $CHCl_3$).

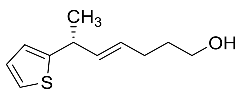
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5f** following the hydroboration/oxidation procedure, tr minor: 59.1 min., tr major: 60.9 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.75:0.25, 0.8 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.4 Hz 1H), 6.81 (d, *J* = 3.4 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.1, 6.3 Hz, 1H), 5.63 (dd, *J* = 15.3, 7.2 Hz, 1H), 5.54 (dt, *J* = 15.3, 6.3 Hz, 1H), 5.09 – 4.98 (ovrlp, 2H), 3.71 (dq, *J* = 7.2, 6.9 Hz, 1H), 2.79 (dd, *J* = 6.3, 6.3 Hz, 2H), 1.43 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 136.9, 135.7, 127.2, 126.6, 123.1, 122.7, 115.1, 38.0, 36.4, 22.3.

GCMS found 178.1 (calculated for $C_{11}H_{14}S$: 178.1).

IR (thin film, cm^{-1}): 2972, 2922, 1637, 1454, 967, 916.



(*R*,*E*)-6-(Thiophen-2-yl)hept-4-en-1-ol (S5f)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (5/1) to afford the pure product as a colorless oil.

Yield: 29 mg, 75%.

e.r.: 99:1.

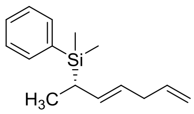
$[\alpha]_D^{22}$ = –29.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.1 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.82 – 6.77 (m, 1H), 5.62 (dd, *J* = 15.3, 7.2 Hz, 1H), 5.53 (dt, *J* = 15.3, 6.7 Hz, 1H), 3.72 – 3.63 (ovrlp, 3H), 2.13 (td, *J* = 7.0, 6.7 Hz, 2H), 1.67 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.41 (d, *J* = 6.9 Hz, 3H), 1.29 (d, *J* = 5.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 135.2, 129.0, 126.6, 123.1, 122.7, 62.4, 38.0, 32.2, 28.6, 22.3.

ESIMS found 197.1 (calculated for $[C_{11}H_{17}OS]^+$: 197.1).

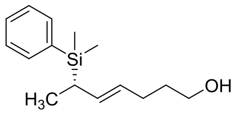
IR (thin film, cm^{-1}): 3409, 2966, 2932, 2870, 1452, 1372, 1234, 1057, 967, 850.



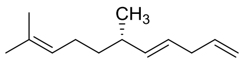
(*S*,*E*)-Hepta-3,6-dien-2-yldimethyl(phenyl)silane (5g)

The substrate was run in 0.4 mmol scale following the general procedure with the exception that 5 equivalents of *t*-BuOH was used under neat conditions. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 81 mg, 88%.
e.r.: 97:3.
[α]$_D^{22}$ = +21.5 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5g** following the hydroboration/oxidation procedure, tr major: 24.6 min., tr minor: 26.6 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.8:0.2, 1.0 mL/min, 210 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.41 – 7.31 (ovrlp, 3H), 5.82 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.48 (dd, *J* = 15.4, 7.5 Hz, 1H), 5.28 – 5.16 (m, 1H), 5.04 – 4.93 (ovrlp, 2H), 2.75 (dd, *J* = 6.5, 6.4 Hz, 2H), 1.80 (dq, *J* = 7.5, 7.2 Hz, 1H), 1.05 (d, *J* = 7.2 Hz, 3H), 0.27 (ovrlp, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 134.1, 133.9, 128.9, 127.6, 124.2, 124.1, 114.4, 37.1, 25.7, 13.8, −4.8, −5.3.
GCMS found 230.1 (calculated for $C_{15}H_{22}Si$: 230.1).
IR (thin film, cm^{-1}): 3071, 3019, 2957, 2903, 2869, 1638, 1428, 1248, 1113, 992.



(*S*,*E*)-6-(Dimethyl(phenyl)silyl)hept-4-en-1-ol (S5g)
This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.
Yield: 49 mg, 79%.
e.r.: 97:3.
[α]$_D^{22}$ = +20.2 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.37 – 7.31 (m, 3H), 5.45 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.25 – 5.15 (m, 1H), 3.61 (td, *J* = 5.8, 5.6 Hz, 2H), 2.07 (td, *J* = 7.0, 7.0 Hz, 2H), 1.76 (dq, *J* = 7.5, 7.3 Hz, 1H), 1.64 – 1.56 (m, 2H), 1.21 (t, *J* = 5.6 Hz, 1H), 1.03 (d, *J* = 7.3 Hz, 3H), 0.25 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 134.0, 133.2, 128.9, 127.6, 126.0, 62.6, 32.8, 29.2, 25.5, 13.9, -4.9, -5.3.
ESIMS found 249.2 (calculated for $[C_{15}H_{25}OSi]^+$: 249.2).
IR (thin film, cm^{-1}): 3306, 3070, 2955, 2868, 1428, 1248, 1113, 972.



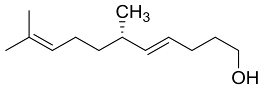
(*S*,*E*)-6,10-Dimethylundeca-1,4,9-triene (5h)
The substrate was run in 0.4 mmol scale following the general procedure and the crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 57 mg, 80%.
e.r.: 85:15.
[α]$_D^{22}$ = +17.1 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S5h** following the hydroboration/oxidation procedure, tr minor: 21.8 min., tr major: 22.8 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99.6:0.4, 0.8 mL/min, 210 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddt, *J* = 16.9, 10.1, 6.3 Hz, 1H), 5.43 – 5.24 (ovrlp, 2H), 5.10 (dddd,

J = 7.2, 5.7, 2.9, 1.5 Hz, 1H), 5.03 (dtd, *J* = 16.9, 1.8, 1.7 Hz, 1H), 4.98 (ddt, *J* = 10.1, 1.7, 1.5 Hz, 1H), 2.74 (t, *J* = 6.3 Hz, 2H), 2.15 – 2.04 (m, 1H), 2.02 – 1.87 (m, 2H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.59 (s, 3H), 1.29 (dt, *J* = 7.5, 7.5 Hz, 2H), 0.97 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 131.1, 125.9, 124.8, 124.7, 114.7, 37.2, 36.7, 36.3, 25.8, 25.7, 20.7, 17.7.

GCMS found 178.2 (calculated for $C_{13}H_{22}$: 178.2).

IR (thin film, cm^{-1}): 2966, 2926, 1639, 1454, 1377, 971, 912.



(*S*,*E*)-6,10-Dimethylundeca-4,9-dien-1-ol (S5h)

This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.

Yield: 32 mg, 65%.

e.r.: 85:15.

$[\alpha]_D^{22}$ = +18.1 (c = 1.0, $CHCl_3$).

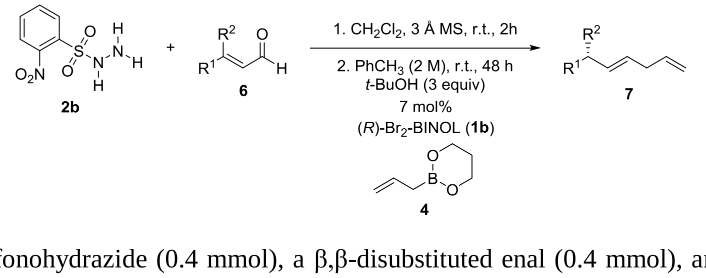
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 – 5.26 (ovrlp, 2H), 5.08 (t, *J* = 7.1 Hz, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.11 – 2.03 (ovrlp, 3H), 1.98 – 1.88 (m, 2H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.68 – 1.58 (m, 2H), 1.58 (s, 3H), 1.37 (br, 1H), 1.27 (dt, *J* = 7.5, 7.5 Hz, 2H), 0.95 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 131.2, 127.7, 124.7, 62.6, 37.2, 36.3, 32.5, 28.9, 25.8, 25.7, 20.8, 17.7.

ESIMS found 197.2 (calculated for $[C_{13}H_{25}O]^+$: 197.2).

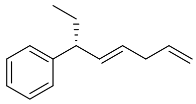
IR (thin film, cm^{-1}): 3349, 2963, 2928, 2869, 1451, 1377, 1058, 969.

g. General Procedure to Prepare Enantioenriched 1,4-Dienes 7



2-Nitrobenzenesulfonohydrazide (0.4 mmol), a β,β-disubstituted enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10-mL reaction vial equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (*R*)-Br_2-BINOL (0.04 mmol, 7 mol%), *tert*-butanol (3 equiv, 1.2 mmol) and allylboronate (1.5 equiv, 0.6 mmol) were added and rinsed into the solution with anhydrous toluene (0.2 mL). The reaction was applied to sonication for 5 min to facilitate dissolution. The vial was then sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

h. Analytical Data for 1,4-Dienes 7



(*R*,*E*)-Octa-4,7-dien-3-ylbenzene (7a)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 56 mg, 75%.

e.r.: 97:3.

[α]$_D^{22}$ = –31.0 (c = 1.0, $CHCl_3$).

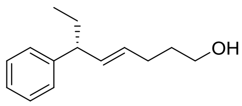
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S7a** following the hydroboration/oxidation procedure, tr minor: 69.1 min., tr major: 72.0 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99:1, 0.4 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.23 – 7.15 (ovrlp, 3H), 5.83 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.60 (dd, *J* = 15.3, 7.6 Hz, 1H), 5.46 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.06 – 4.95 (ovrlp, 2H), 3.12 (dt *J* = 7.6, 7.4 Hz, 1H), 2.77 (dd, *J* = 6.5, 6.4 Hz, 2H), 1.72 (qt, *J* = 7.4, 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 137.2, 135.2, 128.3, 127.5, 127.5, 125.9, 114.9, 50.7, 36.7, 28.9, 12.2.

GCMS found 186.1 (calculated for $C_{14}H_{18}$: 186.1).

IR (thin film, cm^{-1}): 3082, 3028, 2961, 2931, 2874, 1639, 1602, 1493, 1452, 970, 913.



(*R*,*E*)-6-Phenyloct-4-en-1-ol (S7a)

This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (4/1) to afford the pure product as a colorless oil.

Yield: 38 mg, 75%.

e.r.: 97:3.

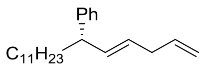
[α]$_D^{22}$ = –38.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (ovrlp, 3H), 5.59 (dd, *J* = 15.3, 7.7 Hz, 1H), 5.45 (dt, *J* = 15.3, 7.0 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.09 (dt, *J* = 7.7, 7.5 Hz, 1H), 2.10 (dt, *J* = 7.0, 7.0 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.67 – 1.59 (m, 2H), 1.26 (br, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 134.6, 129.3, 128.3, 127.5, 125.9, 62.5, 50.7, 32.4, 28.9, 28.9, 12.2.

ESIMS found 205.2 (calculated for $[C_{14}H_{21}O]^+$: 205.2).

IR (thin film, cm^{-1}): 3350, 3027, 2929, 2873, 1601, 1493, 1452, 1054, 968.



(*S*,*E*)-Heptadeca-1,4-dien-6-ylbenzene (7b)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 121 mg, 97%.

e.r.: 96:4.

$[\alpha]_D^{22}$ = +9.8 (c = 1.0, $CHCl_3$).

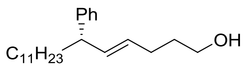
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S7b** following the hydroboration/oxidation procedure, tr major: 45.5 min., tr minor: 48.7 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99.6:0.4, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.22 – 7.15 (ovrlp, 3H), 5.89 – 5.77 (m, 1H), 5.60 (dd, *J* = 15.6, 7.7 Hz, 1H), 5.45 (dt, *J* = 15.6, 6.5 Hz, 1H), 5.07 – 4.95 (ovrlp, 2H), 3.22 (dt, *J* = 7.7, 7.4 Hz, 1H), 2.76 (dd, *J* = 6.5, 6.4 Hz, 2H), 1.68 (dt, *J* = 7.4, 7.2 Hz, 2H), 1.35 – 1.15 (ovrlp, 18H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 137.2, 135.5, 128.3, 127.5, 127.3, 125.9, 114.9, 48.9, 36.7, 36.0, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 27.6, 22.7, 14.1.

GCMS found 312.3 (calculated for $C_{23}H_{36}$: 312.3).

IR (thin film, cm^{-1}): 3082, 3028, 2926, 2854, 1729, 1639, 1494, 1453, 967, 912.



(*S*,*E*)-6-Phenylheptadec-4-en-1-ol (S7b)

This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (4/1) to afford the pure product as a colorless oil.

Yield: 61 mg, 74%.

e.r.: 96:4.

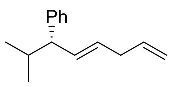
$[\alpha]_D^{22}$ = +14.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.7, 6.7 Hz, 2H), 7.21 – 7.13 (ovrlp, 3H), 5.59 (dd, *J* = 15.1, 7.7 Hz, 1H), 5.44 (dt, *J* = 15.1, 7.0 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.18 (dt, *J* = 7.7, 7.6 Hz, 1H), 2.09 (td, *J* = 7.3, 7.0 Hz, 2H), 1.70 – 1.60 (ovrlp, 4H), 1.33 – 1.15 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 134.9, 129.1, 128.3, 127.4, 125.9, 62.5, 48.9, 36.0, 32.4, 31.9, 29.6 (ovrlp, 2 peaks), 29.6, 29.6, 29.5, 29.3, 28.9, 27.6, 22.7, 14.1.

ESIMS found 331.3 (calculated for $[C_{23}H_{39}O]^+$: 331.3).

IR (thin film, cm^{-1}): 3330, 3062, 3027, 2925, 2854, 1493, 1453, 1060, 969, 759.

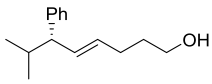


(*S*,*E*)-(2-Methylocta-4,7-dien-3-yl)benzene (7c)

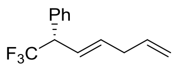
(*Z*)-4-Methyl-3-phenylpent-2-enal (**6c**) was used as the substrate in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 66 mg, 82%.
e.r.: 98:2.
[α]D22 = +52.1 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol following the hydroboration/oxidation procedure, tr minor: 14.3 min., tr major: 15.9 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 230 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.22 – 7.13 (ovrlp, 3H), 5.82 (ddt, *J* = 17.1, 10.1, 6.4 Hz, 1H), 5.65 (dd, *J* = 15.2, 9.0 Hz, 1H), 5.46 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.06 – 4.94 (ovrlp, 2H), 2.87 (dd, *J* = 9.0, 8.8 Hz, 1H), 2.76 (dd, *J* = 6.5, 6.4 Hz, 2H), 1.92 (dqq, *J* = 8.8, 6.7, 6.7 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 137.2, 134.0, 128.3, 128.3, 127.8, 125.8, 114.9, 57.3, 36.7, 33.0, 21.1, 20.8.
GCMS found 200.2 (calculated for $C_{15}H_{20}$: 200.2).
IR (thin film, cm^{-1}): 3084, 3029, 2957, 2867, 1639, 1453, 1385, 970, 913.

The same product afforded by (*E*)-4-methyl-3-phenylpent-2-enal [***(E)*-8**] using (*S*)-Ph_2-BINOL as the catalyst:
Yield: 48 mg, 60%
e.r.: 94:6

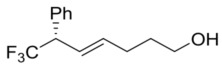


(*S*,*E*)-7-Methyl-6-phenyloct-4-en-1-ol (S7c)
This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.
Yield: 27 mg, 50%.
e.r.: 98:2.
[α]D22 = +39.3 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.21 – 7.11 (ovrlp, 3H), 5.65 (dd, *J* = 15.2, 9.1 Hz, 1H), 5.45 (dt, *J* = 15.2, 6.9 Hz, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.84 (dd, *J* = 9.1, 8.8 Hz, 1H), 2.10 (td, *J* = 7.1, 6.9 Hz, 2H), 1.90 (dqq, *J* = 8.8, 6.6, 6.6 Hz, 1H), 1.68 – 1.58 (m, 2H), 1.30 (br, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.74 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 133.4, 130.2, 128.3, 127.8, 125.8, 62.5, 57.3, 33.0, 32.3, 28.9, 21.1, 20.8.
ESIMS found 219.2 (calculated for $[C_{15}H_{23}O]^+$: 219.2)
IR (thin film, cm^{-1}): 3380, 3027, 2931, 2871, 1451, 701.

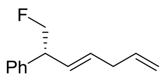


(*S*,*E*)-(1,1,1-Trifluorohepta-3,6-dien-2-yl)benzene (7d)
The substrate was run in 0.4 mmol scale following the general procedure, with the exception that 5 equivalents of *t*-BuOH was used in the absence of toluene. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 75 mg, 83%.
e.r.: 97:3.
[α]$_D^{22}$ = +54.2 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S7d** following the hydroboration/oxidation procedure, tr major: 21.0 min., tr minor: 25.8 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 230 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.30 (ovrlp, 5H), 5.88 – 5.66 (ovrlp, 3H), 5.08 – 5.01 (ovrlp, 2H), 3.98 (qd, *J* = 9.4, 7.4 Hz, 1H), 2.84 (dd, *J* = 6.5, 6.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 135.0 (q, *J* = 1.6 Hz), 134.6, 128.9, 128.7, 128.0, 126.0 (q, *J* = 280.2 Hz), 124.4 (q, *J* = 2.6 Hz), 116.0, 53.2 (q, *J* = 27.6 Hz), 36.4.
GCMS found 226.1 (calculated for $C_{13}H_{13}F_3$: 226.1).
IR (thin film, cm^{-1}): 3069, 3038, 2983, 2902, 1640, 1456, 1255, 1165, 1110, 971, 919.

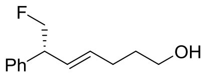


(*S*,*E*)-7,7,7-Trifluoro-6-phenylhept-4-en-1-ol (S7d)
This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (4/1) to afford the pure product as a colorless oil.
Yield: 46 mg, 75%.
e.r.: 97:3.
[α]$_D^{22}$ = +43.9 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (ovrlp, 5H), 5.83 – 5.67 (ovrlp, 2H), 3.94 (qd, *J* = 9.4, 7.6 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.18 (td, *J* = 7.7, 6.3 Hz, 2H), 1.71 – 1.61 (m, 2H), 1.28 (br, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 135.1, 128.8, 128.7, 128.0, 126.0 (q, *J* = 279.8 Hz), 123.8 (q, *J* = 2.3 Hz), 62.2, 53.2 (q, *J* = 27.6 Hz), 31.7, 28.8.
ESIMS found 245.1 (calculated for $[C_{13}H_{16}F_3O]^+$: 245.1).
IR (thin film, cm^{-1}): 3358, 3035, 2936, 1498, 1255, 1163, 1111, 1059.

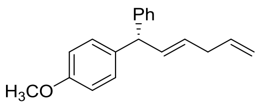


(*R*,*E*)-(1-Fluorohepta-3,6-dien-2-yl)benzene (7e)
The substrate was run in 0.4 mmol scale following the general procedure, with the exception that 5 equivalents of *t*-BuOH was used in the absence of toluene. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 59 mg, 77%.
e.r.: 93:7.
[α]$_D^{22}$ = –28.2 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S7e** following the hydroboration/oxidation procedure, tr minor: 39.7 min., tr major: 42.4 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99:1, 1.0 mL/min, 230 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.29 – 7.21 (ovrlp, 3H), 5.83 (ddt, *J* = 16.6, 10.2, 6.4 Hz, 1H), 5.72 – 5.56 (ovrlp, 2H), 5.08 – 4.98 (ovrlp, 2H), 4.59 (dd, *J* = 47.4, 6.8 Hz, 2H), 3.71 (ddt, *J* = 16.9, 6.8, 6.8 Hz, 1H), 2.81 (dd, *J* = 6.4, 5.7 Hz, 2H).

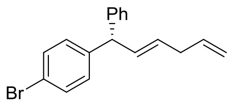
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1 (d, *J* = 5.4 Hz), 136.5, 130.8, 129.6 (d, *J* = 5.4 Hz), 128.6, 128.0, 126.9, 115.4, 85.9 (d, *J* = 174.8 Hz), 49.1 (d, *J* = 19.4 Hz), 36.7.
GCMS found 190.1 (calculated for $C_{13}H_{15}F$: 190.1).
IR (thin film, cm^{-1}): 3081, 3030, 2967, 2898, 1639, 1495, 1454, 1002.



(*R*,*E*)-7-Fluoro-6-phenylhept-4-en-1-ol (S7e)
This product was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.
Yield: 29 mg, 55%.
e.r.: 93:7.
$[\alpha]_D^{22}$ = –28.6 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.28 – 7.19 (ovrlp, 3H), 5.72 – 5.56 (ovrlp, 2H), 4.57 (dd, *J* = 47.3, 6.9 Hz, 2H), 3.74 – 3.60 (ovrlp, 3H), 2.16 (dt, *J* = 7.0, 7.0 Hz, 2H), 1.67 (tt, *J* = 7.0, 6.9 Hz, 2H), 1.25 (t, *J* = 5.4 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1 (d, *J* = 5.5 Hz), 132.6, 129.0 (d, *J* = 5.2 Hz), 128.6, 127.9, 126.9, 85.9 (d, *J* = 174.7 Hz), 62.4, 49.1 (d, *J* = 19.5 Hz), 32.1, 29.0.
ESIMS found 209.1 (calculated for $[C_{13}H_{18}FO]^+$: 209.1).
IR (thin film, cm^{-1}): 3361, 3030, 2936, 1495, 1453, 1007.



(*S*,*E*)-1-Methoxy-4-(1-phenylhexa-2,5-dien-1-yl)benzene (7f)
The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes/EtOAc (100:1) to afford the pure product as a colorless oil.
Yield: 91 mg, 86%.
e.r.: 98:2.
$[\alpha]_D^{22}$ = –4.9 (c = 1.0, $CHCl_3$).
HPLC Analysis, tr major: 16.0 min., tr minor: 18.1 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 1.0 mL/min, 230 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (ovrlp, 3H), 7.16 – 7.08 (m, 2H), 6.90 – 6.83 (m, 2H), 5.95 (dd, *J* = 15.2, 7.5 Hz, 1H), 5.87 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.46 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.10 – 4.99 (ovrlp, 2H), 4.69 (d, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 2.86 (dd, *J* = 6.5, 6.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 144.3, 136.9, 136.2, 134.0, 129.5, 129.5, 128.5, 128.3, 126.2, 115.2, 113.7, 55.2, 53.1, 36.6.
GCMS found 264.2 (calculated for $C_{19}H_{20}O$: 264.2).
IR (thin film, cm^{-1}): 3062, 3027, 2906, 2835, 1610, 1510, 1250, 1178, 1037.



(*S*,*E*)-1-Bromo-4-(1-phenylhexa-2,5-dien-1-yl)benzene (7g)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 109 mg, 87%.

e.r.: 98:2.

$[\alpha]_D^{22}$ = –11.0 (c = 1.0, $CHCl_3$).

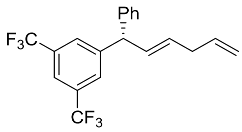
HPLC Analysis, tr major: 15.7 min., tr minor: 16.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 0.5 mL/min, 230 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.34 – 7.26 (m, 2H), 7.25 – 7.18 (m, 1H), 7.19 – 7.13 (m, 2H), 7.09 – 7.02 (m, 2H), 5.95 – 5.78 (ovrlp, 2H), 5.44 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.08 – 4.98 (ovrlp, 2H), 4.67 (d, *J* = 7.4 Hz, 1H), 2.86 – 2.80 (ovrlp, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 143.0, 136.6, 133.1, 131.4, 130.3, 130.3, 128.5, 128.4, 126.4, 120.1, 115.4, 53.3, 36.6.

GCMS found 312.1, 314.1 (calculated for $C_{18}H_{17}Br$: 312.1).

IR (thin film, cm^{-1}): 3062, 3027, 2895, 1638, 1486, 1074, 918.



(*S*,*E*)-1-(1-Phenylhexa-2,5-dien-1-yl)-3,5-bis(trifluoromethyl)benzene (7h)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 129 mg, 87%.

e.r.: 98:2.

$[\alpha]_D^{22}$ = +3.3 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr minor: 28.0 min., tr major: 29.3 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 0.2 mL/min, 210 nm].

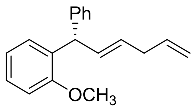
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.67 (s, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.25 (m, 1H), 7.24 – 7.15 (m, 2H), 5.95 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.87 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.54 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.13 – 5.03 (m, 2H), 4.86 (d, *J* = 7.5 Hz, 1H), 2.89 (dd, *J* = 6.5, 6.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 142.0, 136.2, 132.0, 131.7, 131.6 (q, *J* = 28.4 Hz), 128.8, 128.7, 128.4, 127.0, 123.4 ((q, *J* = 272.7 Hz)), 120.6, 115.7, 53.6, 53.6, 36.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ −62.8.

GCMS found 370.1 (calculated for $C_{20}H_{16}F_6$: 370.1).

IR (thin film, cm^{-1}): 3086, 3030, 2898, 1495, 1374, 1278, 1171, 1134, 976.



(*S*,*E*)-1-Methoxy-2-(1-phenylhexa-2,5-dien-1-yl)benzene (7i)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 97 mg, 99%.

e.r.: 98:2.

$[\alpha]_D^{22}$ = +9.9 (c = 1.0, $CHCl_3$).

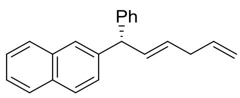
HPLC Analysis, tr major: 25.8 min., tr minor: 28.2 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 0.5 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.26 – 7.14 (ovrlp, 5H), 6.94 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.96 (dd, *J* = 15.2, 7.2 Hz, 1H), 5.86 (ddt, *J* = 16.6, 10.1, 6.1 Hz, 1H), 5.40 (dt, *J* = 15.2, 6.5 Hz, 1H), 5.15 (d, *J* = 7.2 Hz, 1H), 5.08 – 4.97 (ovrlp, 2H), 3.76 (s, 3H), 2.84 (dd, *J* = 6.5, 6.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 144.0, 137.1, 133.4, 132.5, 129.4, 129.2, 128.5, 128.0, 127.4, 125.8, 120.5, 115.1, 110.8, 55.5, 46.6, 36.6.

GCMS found 246.2 (calculated for $C_{19}H_{20}O$: 246.2).

IR (thin film, cm^{-1}): 3061, 3027, 3002, 2936, 2835, 1638, 1491, 1463, 1244, 1107, 1031, 976.



(*S*,*E*)-2-(1-Phenylhexa-2,5-dien-1-yl)naphthalene (7j)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 99 mg, 87%.

e.r.: 95:5.

$[\alpha]_D^{22}$ = +2.3 (c = 1.0, $CHCl_3$).

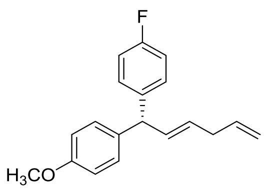
HPLC Analysis, tr major: 16.7 min., tr minor: 29.5 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.76 (ovrlp, 3H), 7.68 (s, 1H), 7.50 – 7.44 (m, 2H), 7.37 – 7.29 (m, 3H), 7.30 – 7.21 (m, 3H), 6.08 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.90 (ddt, *J* = 16.7, 10.3, 6.3 Hz, 1H), 5.59 – 5.49 (m, 1H), 5.13 – 5.00 (m, 2H), 4.92 (d, *J* = 7.4 Hz, 1H), 2.90 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 141.5, 136.8, 133.5, 132.2, 130.1, 128.7, 128.4, 128.0, 127.8, 127.6, 127.3, 126.7, 126.3, 126.0, 125.5, 115.3, 54.1, 36.7.

GCMS found 284.2 (calculated for $C_{22}H_{20}$: 284.2).

IR (thin film, cm^{-1}): 3058, 3026, 2978, 2893, 1637, 1600, 1507, 1493, 975.



(*R*,*E*)-1-Fluoro-4-(1-(4-methoxyphenyl)hexa-2,5-dien-1-yl)benzene (7k)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 96 mg, 85%.

e.r.: 98:2.

$[\alpha]_D^{22}$ = –4.2 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 16.1 min., tr minor: 18.4 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes, 1.0 mL/min, 210 nm].

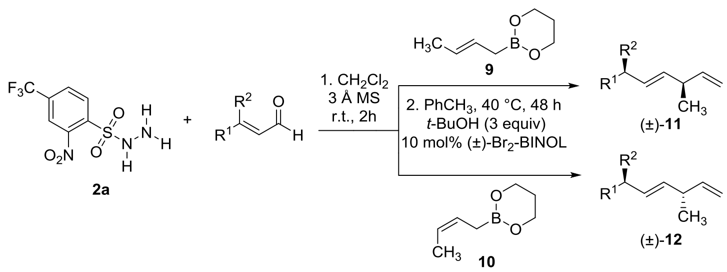
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 2H), 7.12 – 7.06 (m, 2H), 7.02 – 6.94 (m, 2H), 6.89 – 6.83 (m, 2H), 5.95 – 5.80 (ovrlp, 2H), 5.43 (dt, *J* = 15.1, 6.5 Hz, 1H), 5.09 – 4.97 (ovrlp, 2H), 4.66 (d, *J* = 7.3 Hz, 1H), 3.80 (s, 3H), 2.84 (dd, *J* = 6.5, 6.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (d, *J* = 244.3 Hz), 158.1, 140.0 (d, *J* = 3.2 Hz), 136.8, 135.9, 133.8, 129.8 (d, *J* = 7.8 Hz), 129.7, 129.4, 115.3, 115.1 (d, *J* = 21.1 Hz), 113.8, 55.2, 52.3, 36.6.

GCMS found 282.1 (calculated for $C_{19}H_{19}FO$: 282.1).

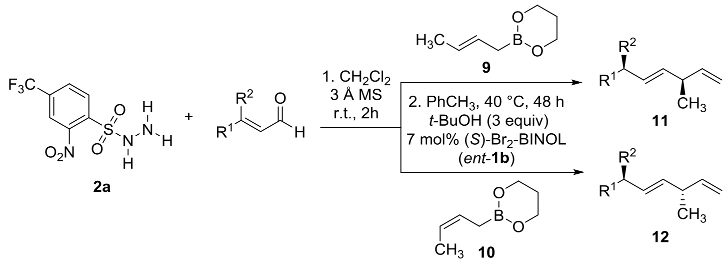
IR (thin film, cm^{-1}): 3031, 3004, 2956, 2901, 2836, 1638, 1608, 1508, 1250, 1179, 1158, 1037.

i. General Procedure to Prepare Racemic 1,4-Dienes (±)-11 and (±)-12



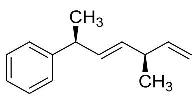
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (0.4 mmol), a β,β-disubstituted enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10-mL reaction vial equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. Racemic Br_2-BINOL catalyst (0.06 mmol, 10 mol%), *tert*-butanol (1.2 mmol) and (*E*)- or (*Z*)-crotylboronate (0.6 mmol) were added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at 40 °C for 48 h, after which time the reaction was cooled to room temperature and the crude mixture was chromatographed on silica gel to afford the desired product.

j. General Procedure to Prepare Enantioenriched 1,4-Dienes 11 and 12



2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (0.4 mmol), a β,β-disubstituted enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10-mL reaction vial equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (*S*)-Br_2-BINOL catalyst (0.04 mmol, 7 mol%), *tert*-butanol (1.2 mmol) and (*E*)- or (*Z*)-crotylboronate (0.6 mmol) were added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at 40 °C for 48 h, after which time the reaction was cooled to room temperature and the crude mixture was chromatographed on silica gel to afford the desired product.

k. Analytical Data for 1,4-Dienes 11 and 12



((2*S*,5*R*,*E*)-5-Methylhepta-3,6-dien-2-yl)benzene (11a)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 44 mg, 59%

e.r.: 98:2

d.r.: 16:1

$[\alpha]_D^{22}$ = –5.2 (c = 1.0, $CHCl_3$).

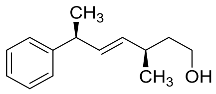
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S11a** following the hydroboration/oxidation procedure, tr minor: 24.6 min., tr major: 29.8 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.5:0.5, 0.8 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.15 (ovrlp, 3H), 5.79 (ddd, *J* = 17.1, 10.3, 6.5 Hz, 1H), 5.61 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.43 (dd, *J* = 15.5, 6.9 Hz, 1H), 4.98 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 10.3 Hz, 1H), 3.44 (qd, *J* = 7.0, 6.9 Hz, 1H), 2.92 – 2.79 (m, 1H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 143.1, 133.9, 132.8, 128.3, 127.2, 125.9, 112.6, 42.1, 40.1, 21.5, 19.9.

GCMS found 186.1 (calculated for $C_{14}H_{18}$: 186.1).

IR (thin film, cm^{-1}): 2962, 2927, 1262, 1100, 807.



(3*R*,6*S*,*E*)-3-Methyl-6-phenylhept-4-en-1-ol (S11a)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.

Yield: 25 mg, 60%.

e.r.: 98:2.

d.r.: 16:1.

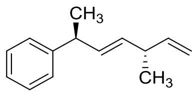
$[\alpha]_D^{22}$ = –17.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.15 (ovrlp, 3H), 5.61 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.35 (dd, *J* = 15.4, 8.1 Hz, 1H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.47 – 3.37 (m, 1H), 2.33 – 2.22 (m, 1H), 1.62 – 1.50 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 134.5, 134.0, 128.4, 127.1, 126.0, 61.4, 42.1, 39.8, 33.9, 21.5, 21.1. (Diastereomer peaks are visible and cannot be separated)

ESIMS found 205.2 (calculated for $[C_{14}H_{21}O]^+$: 205.2)

IR (thin film, cm^{-1}): 3333, 3027, 2962, 2928, 2872, 1493, 1452, 1053, 973.



((2*S*,5*S*,*E*)-5-Methylhepta-3,6-dien-2-yl)benzene (12a)

The substrate was run in 0.4 mmol scale following the general procedure using (*Z*)-crotylboronate. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 40 mg, 54%.

e.r.: >99:1.

d.r.: 9:1.

$[\alpha]_D^{22}$ = +7.5 (c = 1.0, $CHCl_3$).

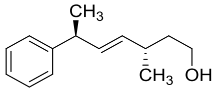
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S12a** following the hydroboration/oxidation procedure, tr major: 26.9 min., tr minor: 32.6 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.5:0.5, 0.8 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.25 – 7.16 (ovrlp, 3H), 5.81 (ddd, *J* = 17.2, 10.4, 6.5 Hz, 1H), 5.62 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.43 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 3.45 (qd, *J* = 6.9, 6.7 Hz, 1H), 2.92 – 2.78 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 143.1, 133.9, 132.8, 128.3, 127.2, 125.9, 112.7, 42.2, 40.2, 21.5, 19.9.

GCMS found 186.1 (calculated for $C_{14}H_{18}$: 186.1).

IR (thin film, cm^{-1}): 2963, 2929, 2872, 1452, 1262, 1097, 1021, 804.



(3*S*,6*S*,*E*)-3-Methyl-6-phenylhept-4-en-1-ol (S12a)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.

Yield: 27 mg, 65%.

e.r.: >99:1.

d.r.: 9:1.

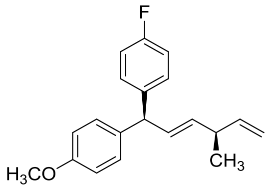
$[\alpha]_D^{22}$ = +35.7 (c = 0.5, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.16 (ovrlp, 3H), 5.61 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.34 (dd, *J* = 15.4, 8.1 Hz, 1H), 3.70 – 3.62 (m, 2H), 3.47 – 3.37 (m, 1H), 2.37 – 2.18 (m, 1H), 1.64 – 1.50 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 134.4, 134.0, 128.4, 127.1, 126.0, 61.4, 42.2, 39.8, 33.8, 21.5, 21.1.

ESIMS found 205.2 (calculated for $[C_{14}H_{21}O]^+$: 205.2)

IR (thin film, cm^{-1}): 3335, 3027, 2962, 2928, 1493, 1053.



1-Fluoro-4-((1*S*,4*R*,*E*)-1-(4-methoxyphenyl)-4-methylhexa-2,5-dien-1-yl)benzene (11b)

The substrate was run in 0.4 mmol scale following the general procedure using (*E*)-crotylboronate. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 73 mg, 62%.

e.r.: 98:2.

d.r.: 15:1.

$[\alpha]_D^{22}$ = –3.9 (c = 1.0, $CHCl_3$).

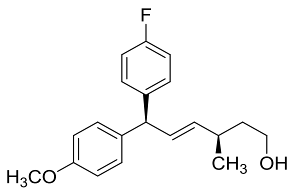
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S11b** following the hydroboration/oxidation procedure, tr minor: 25.6 min., tr major: 27.3 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 250 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 2H), 7.10 – 7.03 (m, 2H), 7.01 – 6.93 (m, 2H), 6.87 – 6.80 (m, 2H), 5.90 – 5.71 (ovrlp, 2H), 5.36 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.03 – 4.88 (ovrlp, 2H), 4.63 (d, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 2.97 – 2.86 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 244.4 Hz), 158.0, 142.7, 140.1 (d, *J* = 3.2 Hz), 136.0, 135.9, 131.6, 129.8 (d, *J* = 7.8 Hz), 129.4, 115.0 (d, *J* = 21.1 Hz), 113.8, 113.0, 55.2, 52.2, 40.2, 19.8.

GCMS found 296.2 (calculated for $C_{20}H_{21}FO$: 296.2).

IR (thin film, cm^{-1}): 3005, 2961, 2930, 2870, 2838, 1606, 1509, 1251, 1178, 1038.



(3*R*,6*S*,*E*)-6-(4-Fluorophenyl)-6-(4-methoxyphenyl)-3-methylhex-4-en-1-ol (S11b)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.

Yield: 35 mg, 56%.

e.r.: 98:2.

d.r.: 15:1.

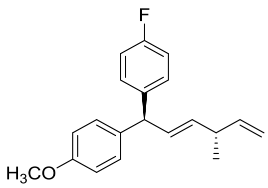
$[\alpha]_D^{22}$ = –19.4 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 – 7.08 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.00 – 6.92 (t, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.85 (dd, *J* = 15.3, 7.4 Hz, 1H), 5.28 (dd, *J* = 15.3, 8.0 Hz, 1H), 4.61 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.42 – 2.32 (m, 1H), 1.74 – 1.45 (m, 2H), 1.03 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 244.4 Hz), 158.0, 140.0 (d, *J* = 3.3 Hz), 137.5, 136.0, 131.5, 129.8 (d, *J* = 7.9 Hz), 129.3, 115.0 (d, *J* = 21.2 Hz), 113.8, 61.3, 55.2, 52.2, 39.7, 33.8, 20.9.

ESIMS found 315.2 (calculated for $[C_{20}H_{24}FO_2]^+$: 315.2)

IR (thin film, cm^{-1}): 3323, 2958, 2929, 2837, 1606, 1508, 1250, 1179, 1038, 977.



1-Fluoro-4-((1*S*,4*S*,*E*)-1-(4-methoxyphenyl)-4-methylhexa-2,5-dien-1-yl)benzene (12b)

The substrate was run in 0.4 mmol scale following the general procedure using (*Z*)-crotylboronate. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 95 mg, 81%.

e.r.: 98:2.

d.r.: 9:1.

$[\alpha]_D^{22}$ = +18.3 (c = 1.0, $CHCl_3$).

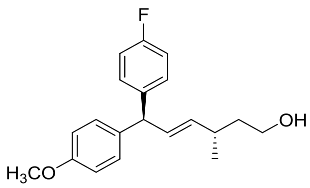
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S12b** following the hydroboration/oxidation procedure, tr major: 30.4 min., tr minor: 33.6 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 250 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.01 – 6.94 (m, 2H), 6.89 – 6.82 (m, 2H), 5.90 – 5.72 (ovrlp, 2H), 5.37 (dd, *J* = 15.4, 6.8 Hz, 1H), 5.04 – 4.90 (ovrlp, 2H), 4.64 (d, *J* = 7.3 Hz, 1H), 3.80 (s, 3H), 2.97 – 2.86 (m, 1H), 1.12 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 244.2 Hz), 158.1, 142.7, 140.1 (d, *J* = 3.2 Hz), 136.0, 135.9, 131.6, 129.8 (d, *J* = 7.8 Hz), 129.4, 115.0 (d, *J* = 21.1 Hz), 113.8, 113.0, 55.2, 52.2, 40.2, 19.8.

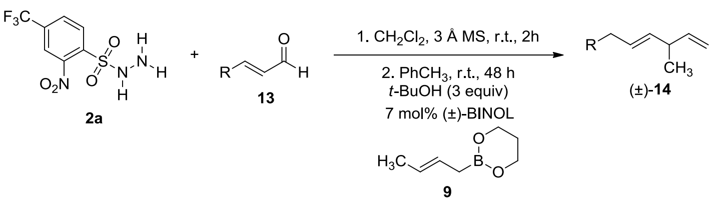
GCMS found 296.2 (calculated for $C_{20}H_{21}FO$: 296.2).

IR (thin film, cm^{-1}): 3005, 2961, 2930, 2839, 1606, 1509, 1251, 1038.



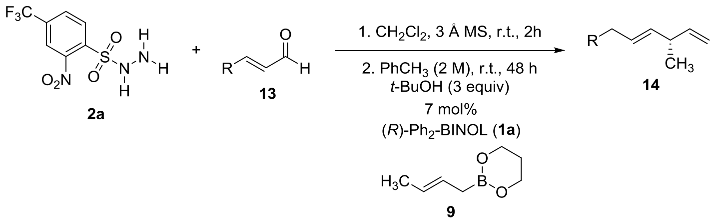
(3*S*,6*S*,*E*)-6-(4-Fluorophenyl)-6-(4-methoxyphenyl)-3-methylhex-4-en-1-ol (S12b)
This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.
Yield: 44 mg, 70%.
e.r.: 98:2.
d.r.: 9:1.
$[\alpha]_D^{22}$ = +18.3 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 2H), 7.09 – 7.02 (m, 2H), 7.01 – 6.92 (m, 2H), 6.87 – 6.80 (m, 2H), 5.85 (dd, *J* = 15.3, 7.4 Hz, 1H), 5.28 (dd, *J* = 15.3, 8.1 Hz, 1H), 4.61 (d, *J* = 7.4 Hz, 1H), 3.79 (s, 3H), 3.64 (td, *J* = 6.6, 2.8 Hz, 2H), 2.43 – 2.24 (m, 1H), 1.65 – 1.47 (m, 2H), 1.22 (br, 1H), 1.03 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 244.4 Hz), 158.0, 140.0 (d, *J* = 3.0 Hz), 137.5, 135.9, 131.5, 129.8 (d, *J* = 7.8 Hz), 129.3, 115.1 (d, *J* = 21.3 Hz) 113.8, 61.3, 55.2, 52.2, 39.7, 33.8, 20.9.
ESIMS found 315.2 (calculated for $[C_{20}H_{24}FO_2]^+$: 315.2)
IR (thin film, cm^{-1}): 3330, 2958, 2929, 2837, 1606, 1508, 1250, 1179, 1038.

l. General Procedure to Prepare Racemic 1,4-Dienes (±)-14



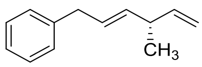
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (0.4 mmol), a non-branched enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. Racemic BINOL (0.06 mmol, 10 mol%), *tert*-butanol (3 equiv, 1.2 mmol) and (*E*)-crotylboronate (1.5 equiv, 0.6 mmol) were added and rinsed into the solution with anhydrous toluene (0.2 mL). The reaction was applied to sonication for 5 min to facilitate dissolution. The vial was then sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

m. General Procedure to Prepare Enantioenriched 1,4-Dienes 14



2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (0.4 mmol), a non-branched enal (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (*R*)-Ph_2-BINOL (0.04 mmol, 7 mol%), *tert*-butanol (3 equiv, 1.2 mmol) and (*E*)-crotylboronate (1.5 equiv, 0.6 mmol) were added and rinsed into the solution with anhydrous toluene (0.2 mL). The reaction was applied to sonication for 5 min to facilitate dissolution. The vial was then sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

n. Analytical Data for 1,4-Dienes 14



(*S*,*E*)-(4-Methylhexa-2,5-dien-1-yl)benzene (14a)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 59 mg, 85%.

e.r.: 97:3.

$[\alpha]_D^{22}$ = +10.2 (c = 1.0, $CHCl_3$).

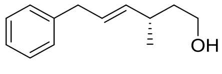
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14a** following the hydroboration/oxidation procedure, tr major: 22.5 min., tr minor: 24.8 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.5:0.5, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 2H), 7.24 – 7.14 (ovrlp, 3H), 5.81 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.64 – 5.54 (m, 1H), 5.49 (dd, *J* = 15.4, 6.6 Hz, 1H), 5.06 – 4.90 (ovrlp, 2H), 3.36 (d, *J* = 6.6 Hz, 2H), 2.92 – 2.83 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 140.9, 135.5, 128.5, 128.3, 127.8, 125.9, 112.7, 40.2, 39.0, 19.9.

GCMS found 172.1 (calculated for $C_{13}H_{16}$: 172.1).

IR (thin film, cm^{-1}): 3084, 3064, 3028, 2966, 2927, 2871, 1636, 1604, 1495, 1453, 1217, 971.



(*S*,*E*)-3-Methyl-6-phenylhex-4-en-1-ol (S14a)

This product was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc: 3/1 to afford the pure product as a colorless oil.

Yield: 46 mg, 80%.

e.r.: 97:3.

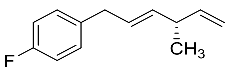
$[\alpha]_D^{22}$ = +24.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.14 (ovrlp, 3H), 5.59 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.41 (dd, *J* = 15.0, 8.0 Hz, 1H), 3.70 – 3.62 (m, 2H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.36 – 2.24 (m, 1H), 1.66 – 1.46 (m, 2H), 1.28 (t, *J* = 5.4 Hz, 1H), 1.03 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 137.3, 128.4, 128.4, 127.8, 125.9, 61.4, 39.8, 39.0, 33.8, 21.0.

ESIMS found 191.1 (calculated for $[C_{13}H_{19}O]^+$: 191.1)

IR (thin film, cm-1): 3339, 3027, 2959, 2926, 1603, 1495, 1453, 1375, 1218, 1056, 972.



(*S*,*E*)-1-Fluoro-4-(4-methylhexa-2,5-dien-1-yl)benzene (14b)

The substrate was run in 0.4 mmol scale following the general procedure but at 50 ℃ in 24 h. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 49 mg, 65%.

e.r.: 97:3.

$[\alpha]_D^{22}$ = +9.2 (c = 1.0, $CHCl_3$).

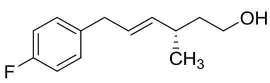
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14b** following the hydroboration/oxidation procedure, tr major: 40.3 min., tr minor: 44.2 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99.6:0.4, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.04 (m, 2H), 7.01 – 6.93(m, 2H), 5.81 (ddd, *J* = 16.9, 10.3, 7.1 Hz, 1H), 5.59 – 5.51 (m, 1H), 5.47 (dd, *J* = 15.3, 6.5 Hz, 1H), 5.07 – 4.87 (ovrlp, 2H), 3.32 (d, *J* = 6.4 Hz, 2H), 2.95 – 2.72 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 243.5 Hz), 142.9, 136.4 (d, *J* = 3.2 Hz), 135.7, 129.8 (d, *J* = 7.8 Hz), 127.7, 115.0 (d, *J* = 21.1 Hz), 112.8, 40.2, 38.1, 19.9.

GCMS found 190.1 (calculated for $C_{13}H_{15}F$: 190.1).

IR (thin film, cm^{-1}): 3080, 2968, 2929, 1605, 1509, 1223, 1157, 972.



(*S*,*E*)-6-(4-Fluorophenyl)-3-methylhex-4-en-1-ol (S14b)

This product was prepared following the general hydroboration/oxidation procedure in 0.15 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc: 3/1 to afford the pure product as a colorless oil.

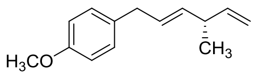
Yield: 22 mg, 70%.

e.r.: 97:3.

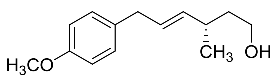
$[\alpha]_D^{22}$ = +25.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 2H), 7.01 – 6.92 (m, 2H), 5.55 (dt, *J* = 14.5, 6.7 Hz, 1H), 5.38 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.65 (t, *J* = 7.2 Hz, 2H), 3.29 (d, *J* = 6.7 Hz, 2H), 2.36 – 2.25 (m, 1H), 1.62 – 1.53 (m, 2H), 1.31 (br, 1H), 1.02 (d, *J* = 6.7 Hz, 3H).

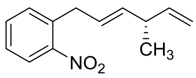
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 243.5 Hz), 137.4, 136.4 (d, *J* = 3.2 Hz), 129.7 (d, *J* = 7.8 Hz), 127.7, 115.1 (d, *J* = 21.2 Hz), 61.3, 39.7, 38.1, 33.7, 21.0.
^{19}**F NMR** (470 MHz, $CDCl_3$) δ –117.7 (ddd, *J* = 14.3, 9.0, 5.5 Hz).
ESIMS found 209.1 (calculated for $[C_{13}H_{18}FO]^+$:209.1)
IR (thin film, cm-1): 3384, 2960, 2931, 1601, 1509, 1222, 1157, 1058, 974.



(*S*,*E*)-1-Methoxy-4-(4-methylhexa-2,5-dien-1-yl)benzene (14c)
The substrate was run in 0.4 mmol scale following the general procedure but at 50 ℃ in 24 h. The crude mixture after the reaction was purified by flash column chromatography with hexanes/EtOAc: 50/1 to afford the pure product as a colorless oil.
Yield: 65 mg, 81%.
e.r.: 98:2.
$[\alpha]_D^{22}$ = +5.7 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14c** following the hydroboration/oxidation procedure, tr major: 31.8 min., tr minor: 34.5 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99:1, 1.0 mL/min, 210 nm].
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.81 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.57 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.46 (dd, *J* = 15.4, 6.7 Hz, 1H), 5.10 – 4.90 (ovrlp, 2H), 3.80 (s, 3H), 3.30 (d, *J* = 6.6 Hz, 2H), 2.91 – 2.82 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 3H).
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 157.9, 143.0, 135.2, 132.9, 129.4, 128.2, 113.8, 112.7, 55.2, 40.2, 38.1, 19.9
GCMS found 202.1 (calculated for $C_{14}H_{18}O$: 202.1).
IR (thin film, cm^{-1}): 3081, 2965, 2934, 2906, 2835, 1612, 1512, 1325, 1247, 1177, 1039.



(*S*,*E*)-6-(4-Methoxyphenyl)-3-methylhex-4-en-1-ol (S14c)
This product was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.
Yield: 50 mg, 75%.
e.r.: 98:2.
$[\alpha]_D^{22}$ = +17.8 (c = 1.0, $CHCl_3$).
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.11 – 7.03 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.56 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.37 (dd, *J* = 15.2, 8.0 Hz, 1H), 3.79 (s, 3H), 3.69 – 3.60 (m, 2H), 3.27 (d, *J* = 6.8 Hz, 2H), 2.35 – 2.23 (m, 1H), 1.62 – 1.46 (m, 2H), 1.31 – 1.19 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H).
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 157.9, 136.9, 132.9, 129.3, 128.2, 113.8, 61.4, 55.3, 39.8, 38.0, 33.8, 21.0.
ESIMS found 221.1 (calculated for $[C_{14}H_{21}O_2]^+$: 221.1)
IR (thin film, cm-1): 3382, 3015, 2929, 1512, 1216, 1039, 755.



(*S*,*E*)-1-(4-Methylhexa-2,5-dien-1-yl)-2-nitrobenzene (14d)

The substrate was run in 0.4 mmol scale following the general procedure but at 50 ℃ in 24 h. The crude mixture after the reaction was purified by flash column chromatography with hexanes:EtOAc (50:1) to afford the pure product as a colorless oil.

Yield: 69 mg, 79%.

e.r.: 98:2.

$[\alpha]_D^{22}$ = +5.2 (c = 1.0, $CHCl_3$).

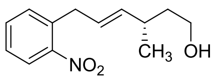
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14d** following the hydroboration/oxidation procedure, tr minor: 47.0 min., tr major: 57.0 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 98:2, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 8.5, 7.5 Hz, 1H), 7.40 – 7.30 (ovrlp, 2H), 5.77 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.55 (dt, *J* = 15.3, 6.2 Hz, 1H), 5.49 (dd, *J* = 15.3, 6.5 Hz, 1H), 5.04 – 4.90 (ovrlp, 2H), 3.63 (d, *J* = 6.2 Hz, 2H), 2.92 – 2.77 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 142.6, 137.0, 135.6, 132.9, 131.7, 127.1, 125.4, 124.5, 113.0, 40.2, 35.8, 19.7.

GCMS found 217.1 (calculated for $C_{13}H_{15}NO_2$: 217.1).

IR (thin film, cm^{-1}): 3070, 2962, 2929, 2864, 1698, 1528, 1353, 1128, 916.



(*S*,*E*)-3-Methyl-6-(2-nitrophenyl)hex-4-en-1-ol (S14d)

This product was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.

Yield: 45 mg, 64%.

e.r.: 98:2.

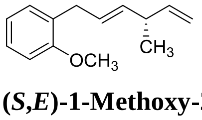
$[\alpha]_D^{22}$ = +18.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 1H), 7.56 – 7.46 (m, 1H), 7.38 – 7.33 (ovrlp, 2H), 5.55 (dtd, *J* = 15.3, 6.5, 0.9 Hz, 1H), 5.39 (ddt, *J* = 15.3, 8.1, 1.4 Hz, 1H), 3.74 – 3.45 (ovrlp, 4H), 2.38 – 2.17 (m, 1H), 1.66 – 1.45 (m, 2H), 1.25 (t, *J* = 5.1 Hz, 1H), 1.00 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 138.6, 135.5, 132.9, 131.7, 127.2, 125.3, 124.6, 61.2, 39.6, 35.8, 33.8, 20.8.

ESIMS found 236.1 (calculated for $[C_{13}H_{18}NO_3]^+$: 236.1)

IR (thin film, cm-1): 3357, 2960, 2926, 2873, 1610, 1526, 1448, 1352, 1057, 975, 858.



(*S*,*E*)-1-Methoxy-2-(4-methylhexa-2,5-dien-1-yl)benzene (14e)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes:EtOAc (100:1) to afford the pure product as a colorless oil.

Yield: 65 mg, 81%.

e.r.: 99:1.

[α]$_D^{22}$ = +7.9 (c = 1.0, $CHCl_3$).

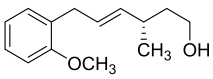
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14e** following the hydroboration/oxidation procedure, tr major: 31.9 min., tr minor: 34.7 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99.5:0.5, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.91 (dd, *J* = 7.6, 7.4 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 5.81 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.59 (dt, *J* = 14.8, 6.7 Hz, 1H), 5.46 (dd, *J* = 14.8, 6.8 Hz, 1H), 5.04 – 4.90 (ovrlp, 2H). 3.83 (s, 3H), 3.35 (d, *J* = 6.7 Hz, 2H), 2.92 – 2.79 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 143.2, 135.1, 129.6, 129.4, 127.2, 127.1, 120.4, 112.5, 110.3, 55.3, 40.2, 32.9, 19.9.

GCMS found 202.1 (calculated for $C_{14}H_{18}O$: 202.1).

IR (thin film, cm^{-1}): 3076, 2961, 2836, 1601, 1493, 1465, 1244, 1111, 1033.



(*S*,*E*)-6-(2-Methoxyphenyl)-3-methylhex-4-en-1-ol (S14e)

This product was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (3/1) to afford the pure product as a colorless oil.

Yield: 48 mg, 72%.

e.r.: 99:1.

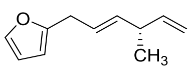
[α]$_D^{22}$ = +15.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 7.6, 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.59 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.36 (dd, *J* = 15.8, 8.2 Hz, 1H), 3.82 (s, 3H), 3.67 – 3.61 (m, 2H), 3.32 (d, *J* = 6.6 Hz, 2H), 2.33 – 2.22 (m, 1H), 1.66 – 1.45 (m, 2H), 1.41 (br, 1H), 1.00 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 136.8, 129.6, 129.2, 127.3, 127.2, 120.5, 110.3, 61.6, 55.3, 39.9, 34.4, 33.1, 21.1.

ESIMS found 221.1 (calculated for $[C_{14}H_{21}O_2]^+$: 221.1)

IR (thin film, cm-1): 3384, 2930, 2835, 1601, 1493, 1464, 1244, 1051.



(*S*,*E*)-2-(4-Methylhexa-2,5-dien-1-yl)furan (14f)

The substrate was run in 0.4 mmol scale following the general procedure. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

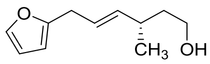
Yield: 47 mg, 73%.

e.r.: 99:1.

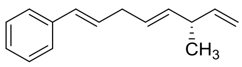
[α]$_D^{22}$ = +6.4 (c = 1.0, $CHCl_3$).

HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14f** following the hydroboration/oxidation procedure, tr major: 18.5 min., tr minor: 20.8 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., hexanes:EtOH = 99:1, 1.0 mL/min, 210 nm].

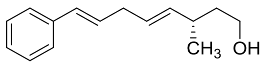
¹H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 1.9 Hz, 1H), 6.29 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.00 (d, *J* = 3.0 Hz, 1H), 5.80 (ddd, *J* = 17.2, 10.3, 6.5 Hz, 1H), 5.60 – 5.45 (ovrlp, 2H), 5.08 – 4.92 (ovrlp, 2H), 3.35 (d, *J* = 4.4 Hz, 2H), 2.97 – 2.79 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 3H).
¹³C NMR (126 MHz, $CDCl_3$) δ 154.7, 142.7, 141.1, 136.5, 124.3, 112.9, 110.2, 105.1, 40.1, 31.4, 19.7.
GCMS found 162.1 (calculated for $C_{11}H_{14}O$: 162.1).
IR (thin film, cm^{-1}): 3083, 2968, 2930, 1596, 1507, 1456, 1147, 1009, 970.



(*S*,*E*)-6-(Furan-2-yl)-3-methylhex-4-en-1-ol (S14f)
This product was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.
Yield: 33 mg, 61%.
e.r.: 99:1.
$[\alpha]_D^{22}$ = +13.4 (c = 1.0, $CHCl_3$).
¹H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 6.28 (dd, *J* = 3.0, 1.9 Hz, 1H), 5.98 (d, *J* = 3.0 Hz, 1H), 5.55 (dt, *J* = 15.4, 6.5 Hz, 1H), 5.45 (dd, *J* = 15.4, 7.9 Hz, 1H), 3.66 (t, *J* = 6.0 Hz, 2H), 3.33 (d, *J* = 6.5 Hz, 2H), 2.36 – 2.26 (m, 1H), 1.65 – 1.45 (m, 2H), 1.32 (br, 1H), 1.02 (d, *J* = 6.8 Hz, 3H).
¹³C NMR (126 MHz, $CDCl_3$) δ 154.6, 141.1, 138.3, 124.2, 110.2, 105.1, 61.3, 39.7, 33.9, 31.4, 20.8.
ESIMS found 181.1 (calculated for $[C_{11}H_{17}O_2]^+$: 181.1)
IR (thin film, cm-1): 3353, 2956, 2930, 2450, 1507, 1057, 1008, 971.



((*S*,1*E*,4*E*)-6-Methylocta-1,4,7-trien-1-yl)benzene (14g)
The substrate was run in 0.4 mmol scale following the general procedure but with 14 mol% catalyst. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 43 mg, 54%.
e.r.: 98:2.
$[\alpha]_D^{22}$ = +4.2 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14g** following the hydroboration/oxidation procedure, tr major: 30.1 min., tr minor: 33.6 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99:1, 1.0 mL/min, 230 nm].
¹H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (dd, *J* = 7.9, 7.7 Hz, 2H), 7.24 – 7.17 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.0 Hz, 1H), 5.82 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.53 – 5.47 (ovrlp, 2H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.97 (d, *J* = 10.3 Hz, 1H), 2.93 (dd, *J* = 6.0, 5.4 Hz, 2H), 2.91 – 2.83 (m, 1H), 1.12 (d, *J* = 6.9 Hz, 3H).
¹³C NMR (126 MHz, $CDCl_3$) δ 143.0, 137.7, 135.4, 130.4, 129.1, 128.5, 126.9, 126.7, 126.0, 112.7, 40.3, 35.9, 19.9.
GCMS found 198.1 (calculated for $C_{15}H_{18}$: 198.1).
IR (thin film, cm^{-1}): 3060, 3026, 2966, 2928, 1636, 1495, 1450, 966, 913.



(*S*,4*E*,7*E*)-3-Methyl-8-phenylocta-4,7-dien-1-ol (S14g)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.

Yield: 32 mg, 75%.

e.r.: 98:2.

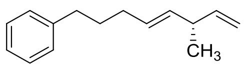
$[\alpha]_D^{22}$ = +13.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 16.0, 6.6 Hz, 1H), 5.51 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.39 (dd, *J* = 15.3, 7.8 Hz, 1H), 3.71 – 3.63 (m, 2H), 2.90 (dd, *J* = 6.6, 6.5 Hz, 2H), 2.38 – 2.23 (m, 1H), 1.65 – 1.53 (m, 2H), 1.25 (br, 1H), 1.02 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 137.2, 130.4, 129.0, 128.5, 126.9, 126.7, 126.0, 61.4, 39.7, 35.8, 33.9, 21.0.

ESIMS found 217.2 (calculated for $[C_{15}H_{21}O]^+$: 217.2)

IR (thin film, cm-1): 3327, 3027, 2928, 1495, 1450, 1056, 969, 755.



(*S*,*E*)-(6-Methylocta-4,7-dien-1-yl)benzene (14h)

The substrate was run in 0.4 mmol scale following the general procedure but with 14 mol% of 3,3'-Br_2-BINOL catalyst. The crude mixture after the reaction was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 43 mg, 54%.

e.r.: 99:1.

$[\alpha]_D^{22}$ = +6.4 (c = 1.0, $CHCl_3$).

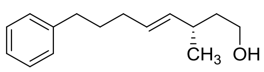
HPLC Analysis, this compound was converted to the corresponding terminal alcohol **S14h** following the hydroboration/oxidation procedure, tr major: 30.1 min., tr minor: 33.6 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., hexanes:*i*-PrOH = 99.6:0.4, 1.0 mL/min, 250 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.15 (ovrlp, 3H), 5.81 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.50 – 5.34 (ovrlp, 2H), 5.09 – 4.91 (ovrlp, 2H), 2.88 – 2.79 (m, 1H), 2.66 – 2.59 (m, 2H), 2.06 (td, *J* = 7.5, 5.7 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.10 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 142.6, 134.5, 128.8, 128.4, 128.2, 125.6, 112.5, 40.3, 35.3, 32.1, 31.2, 20.0.

GCMS found 200.2 (calculated for $C_{15}H_{20}$: 200.2).

IR (thin film, cm^{-1}): 3084, 3027, 2966, 2931, 2858, 1626, 1497, 1454, 970.

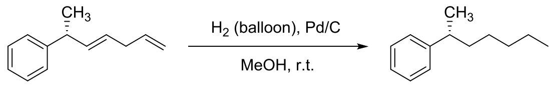


(*S*,*E*)-3-Methyl-8-phenyloct-4-en-1-ol (S14h)

This product was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (3:1) to afford the pure product as a colorless oil.

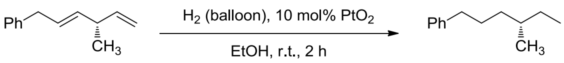
Yield: 30 mg, 68%.
e.r.: 99:1.
$[\alpha]_D^{22}$ = +18.7 (c = 1.0, $CHCl_3$).
^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.13 (ovrlp, 3H), 5.44 (dt, *J* = 15.2, 6.7 Hz, 1H), 5.30 (dd, *J* = 15.2, 8.0 Hz, 1H), 3.65 (t, *J* = 6.7 Hz, 2H), 2.64 – 2.57 (m, 2H), 2.32 – 2.19 (m, 1H), 2.03 (td, *J* = 6.8, 6.7 Hz, 2H), 1.68 (tt, *J* = 9.3, 6.8 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.28 (br, 1H), 1.00 (d, *J* = 6.8 Hz, 3H).
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 142.5, 136.2, 128.8, 128.4, 128.2, 125.6, 61.4, 39.8, 35.3, 34.0, 32.0, 31.3, 21.2.
ESIMS found 219.2 (calculated for $[C_{15}H_{22}O]^+$: 219.2)
IR (thin film, cm-1): 3346, 3027, 2928, 2857, 1496, 1454, 1053, 971.

o. Absolute Stereochemistry Determination for 1,4-Dienes



5a **15**

A 10-mL reaction vial equipped with a magnetic stir bar was charged with enantioenriched 1,4-diene (0.3 mmol). MeOH (3 mL), Pd/C (5 mg) were successively added to the vial. The reaction mixture was purged by hydrogen gas from a balloon for 10 min, after which time the balloon was refilled with hydrogen and the reaction was allowed to stir under the H_2 atmosphere for 12 h at room temperature. The reaction mixture was filtered by a short pad of Celite, and condensed *in vacuo*. Chromatography on silica gel eluted by hexanes afforded the desired reduced product **15**.
Yield: 43 mg, 81%.
$[\alpha]_D^{22}$ = –12.7 (c=1.0, CCl_4). In lit:[17] $[\alpha]_D^{22}$ = –10 (CCl_4).
All spectra were in agreement with reported data.[18]



14a **16**

A 10-mL reaction vial equipped with a magnet stir bar was charged with enantioenriched 1,4-diene (0.3 mmol). EtOH (3 mL), PtO_2 (10 mol%) were succesively added to the vial. The reaction mixture was purged by hydrogen gas from a balloon for 10 min, after which time the balloon was refilled with hydrogen and the reaction was allowed to stir under the H_2 atmosphere for 2 h at room temperature. The reaction mixture was filtered by a short pad of celite, and condensed *in vacuo*. Chromatography on silica gel eluted by hexanes afforded the desired reduced product **16**.
Yield: 26 mg, 50%.
$[\alpha]_D^{22}$ = +6.3 (c=1.0, $CHCl_3$). In lit:[19] $[\alpha]_D^{22}$ = +3.95 (neat).
All spectra were in agreement with reported data.[19]

3. References

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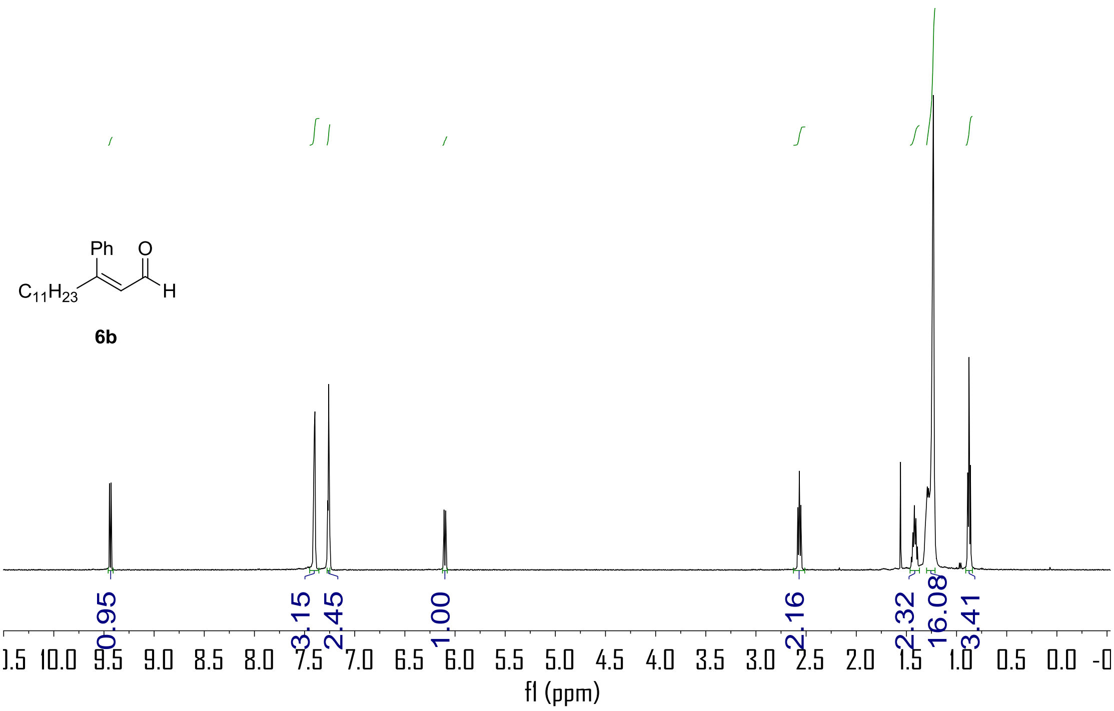
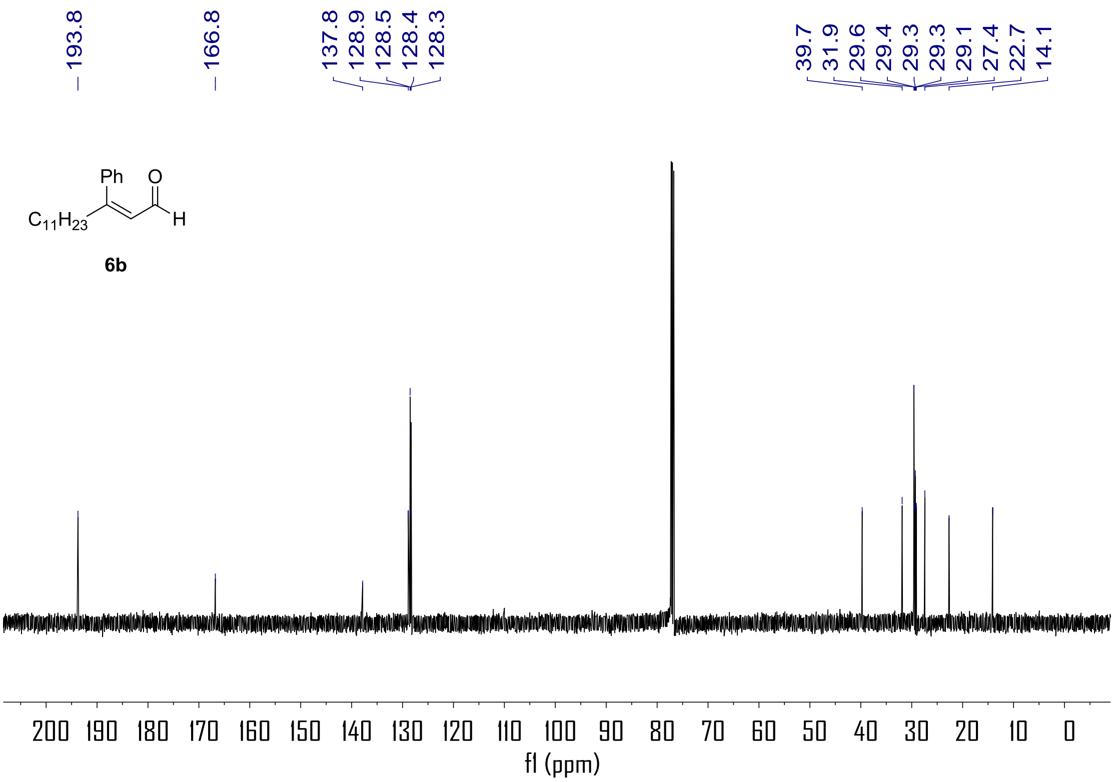
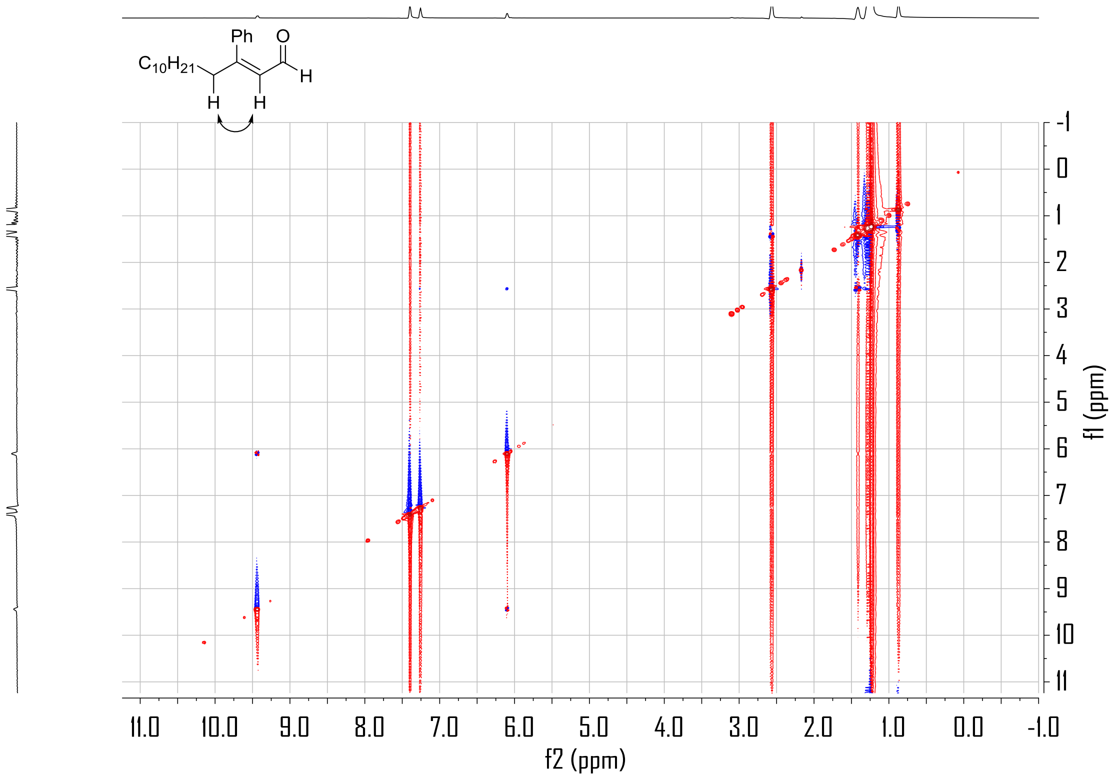
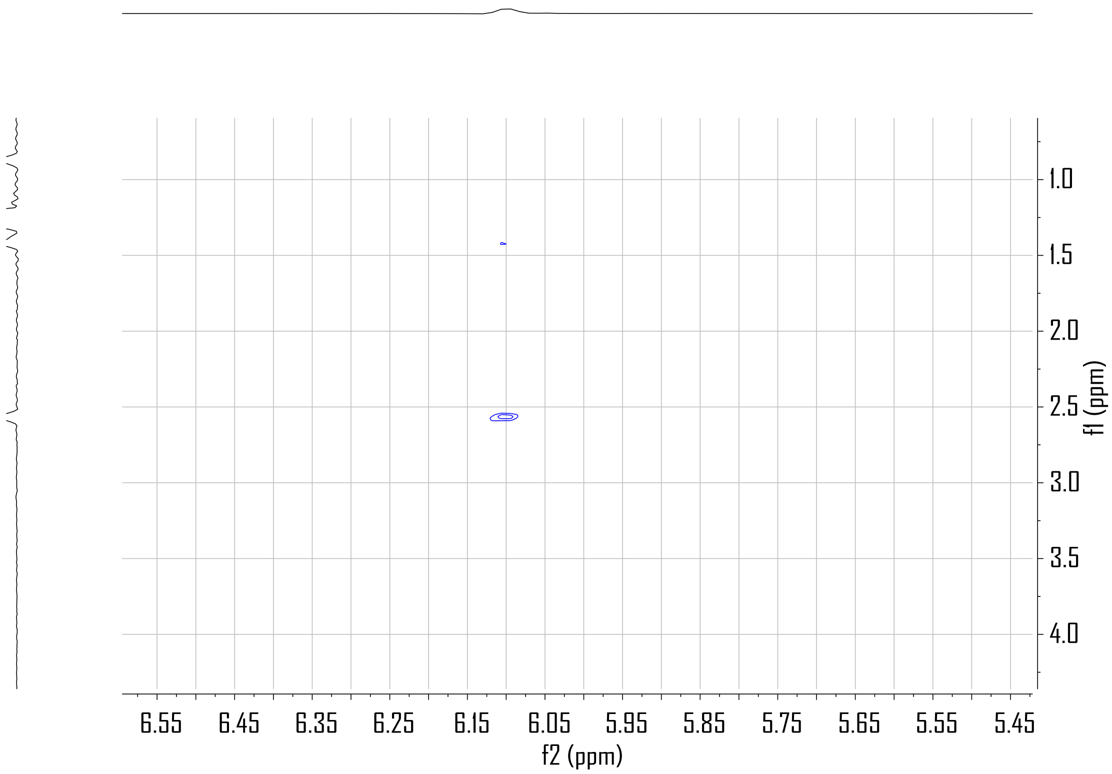
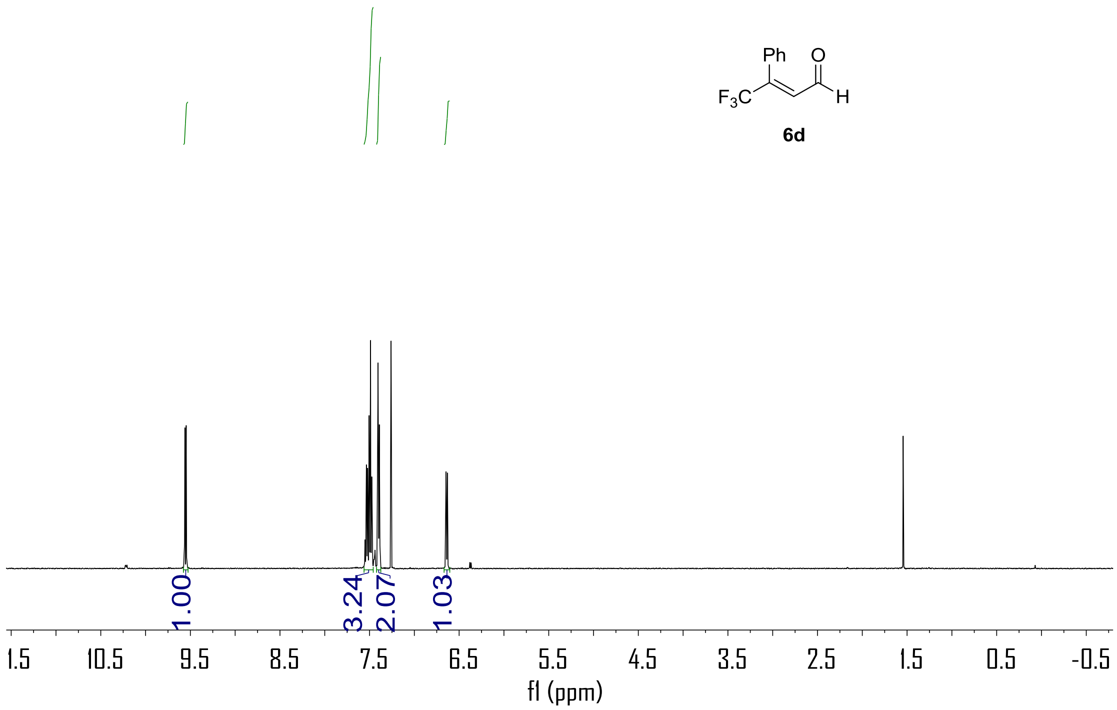
4. NMR Spectra

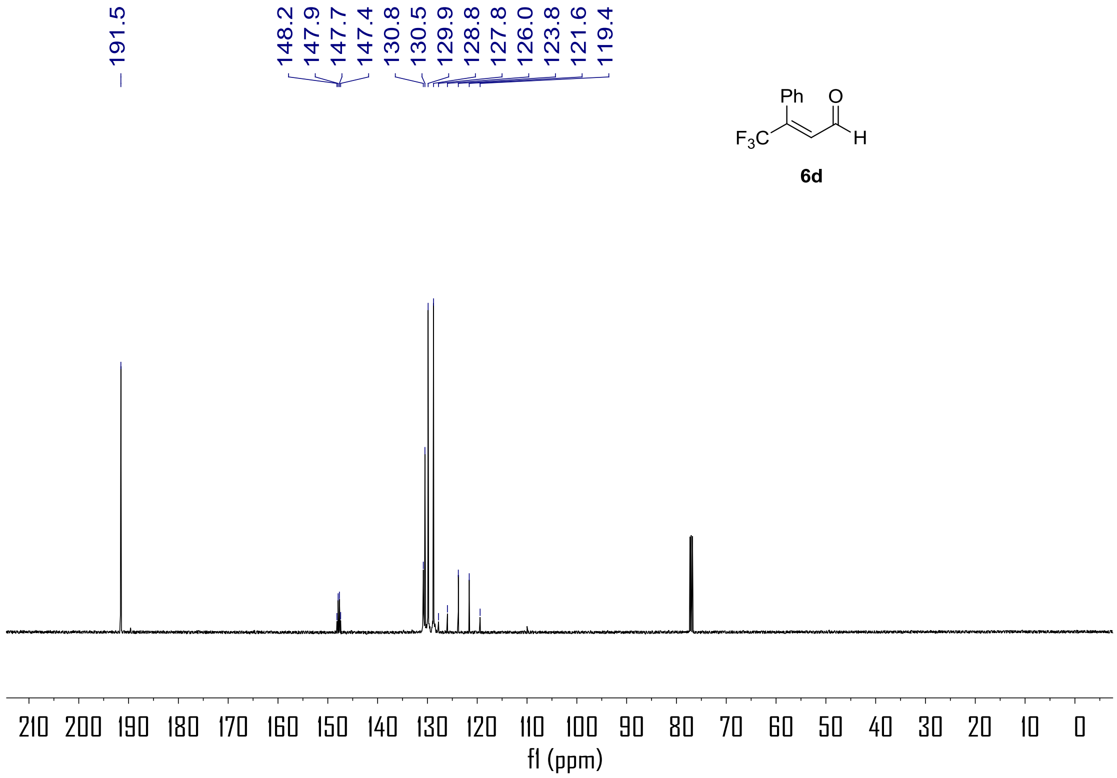


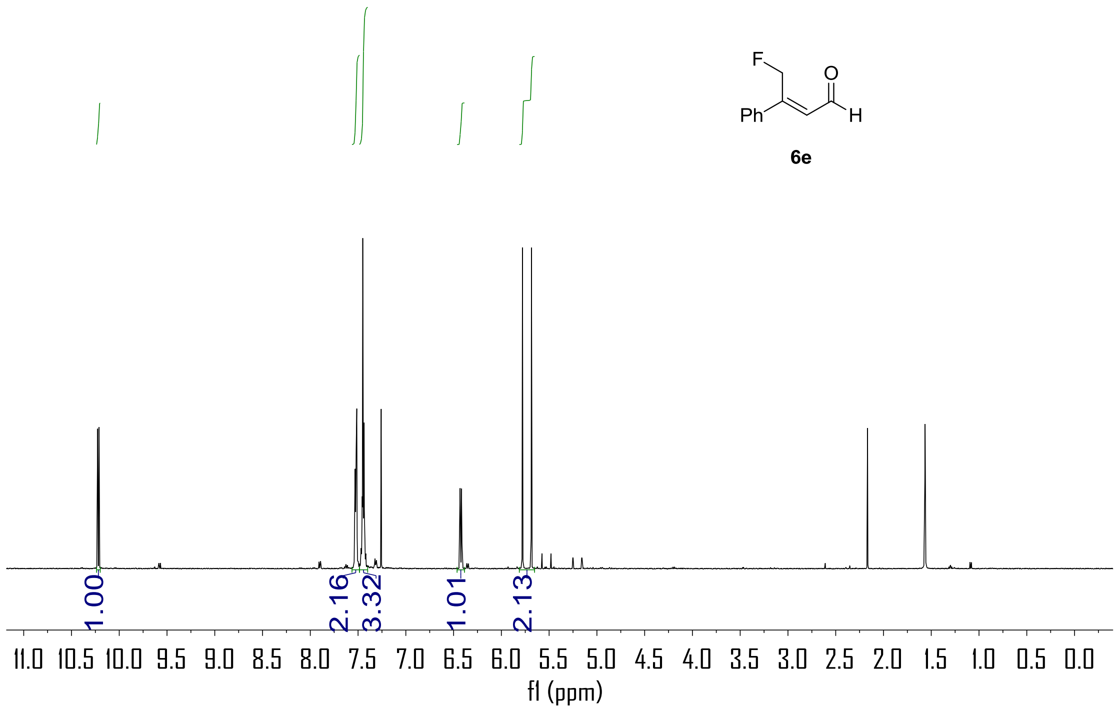


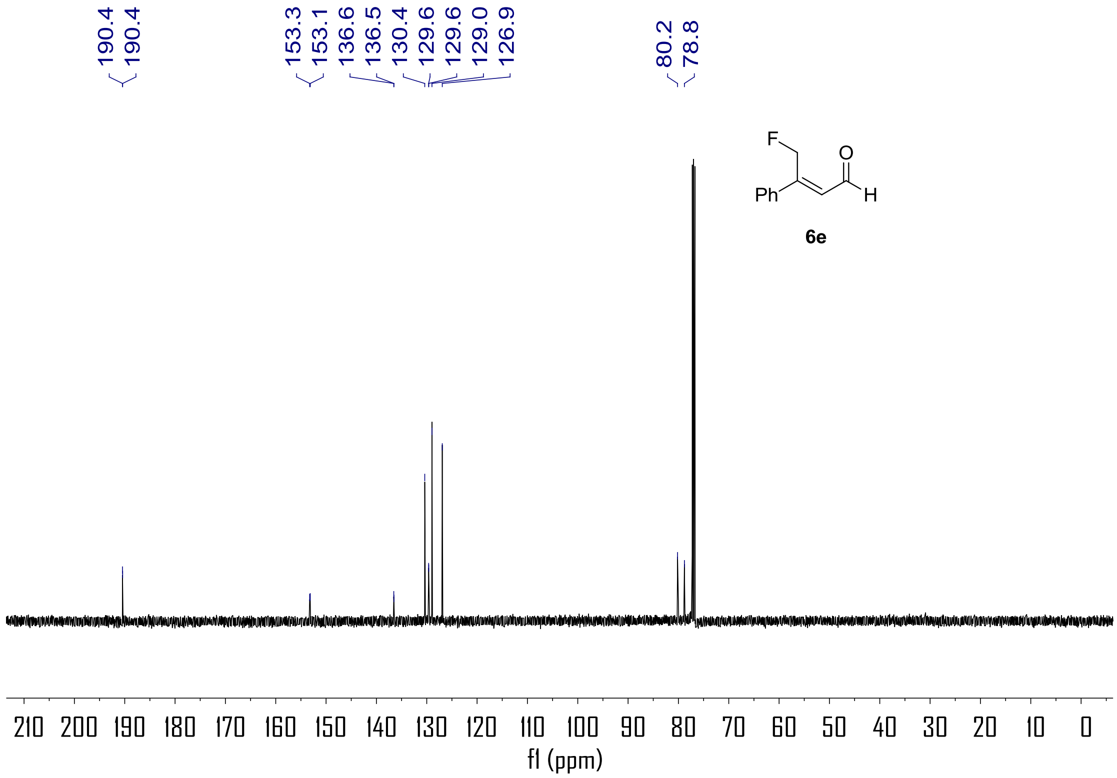

Ph
O
$C_{10}H_{21}$
H
H
H
f2 (ppm)
f1 (ppm)

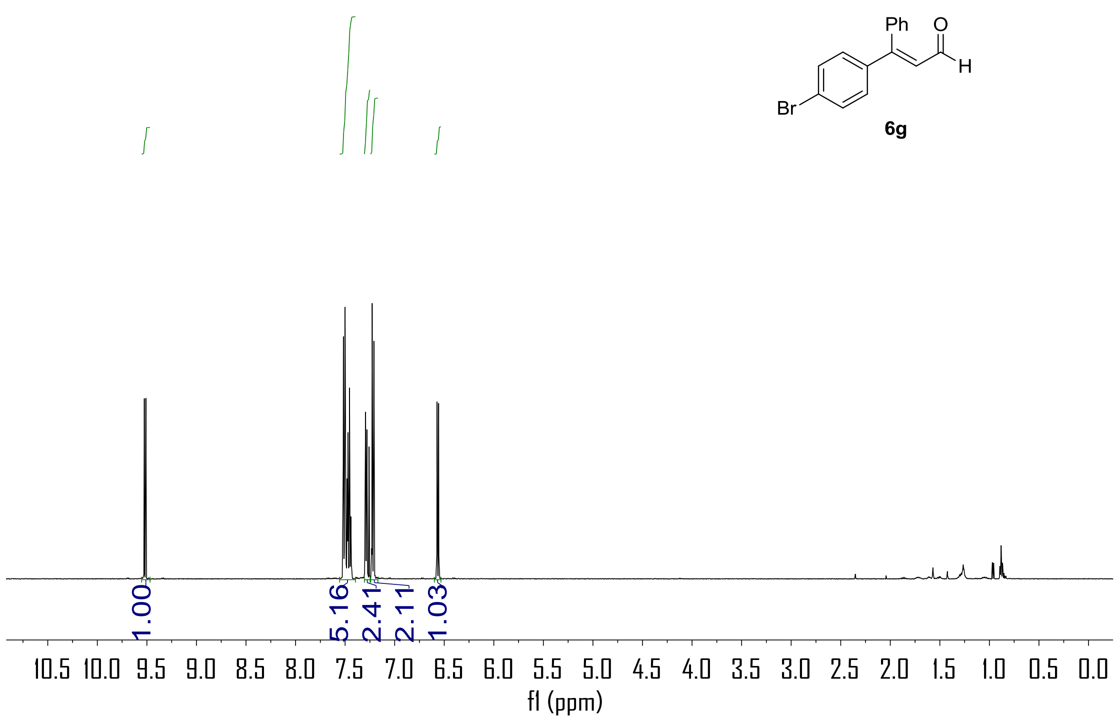

f2 (ppm)
f1 (ppm)

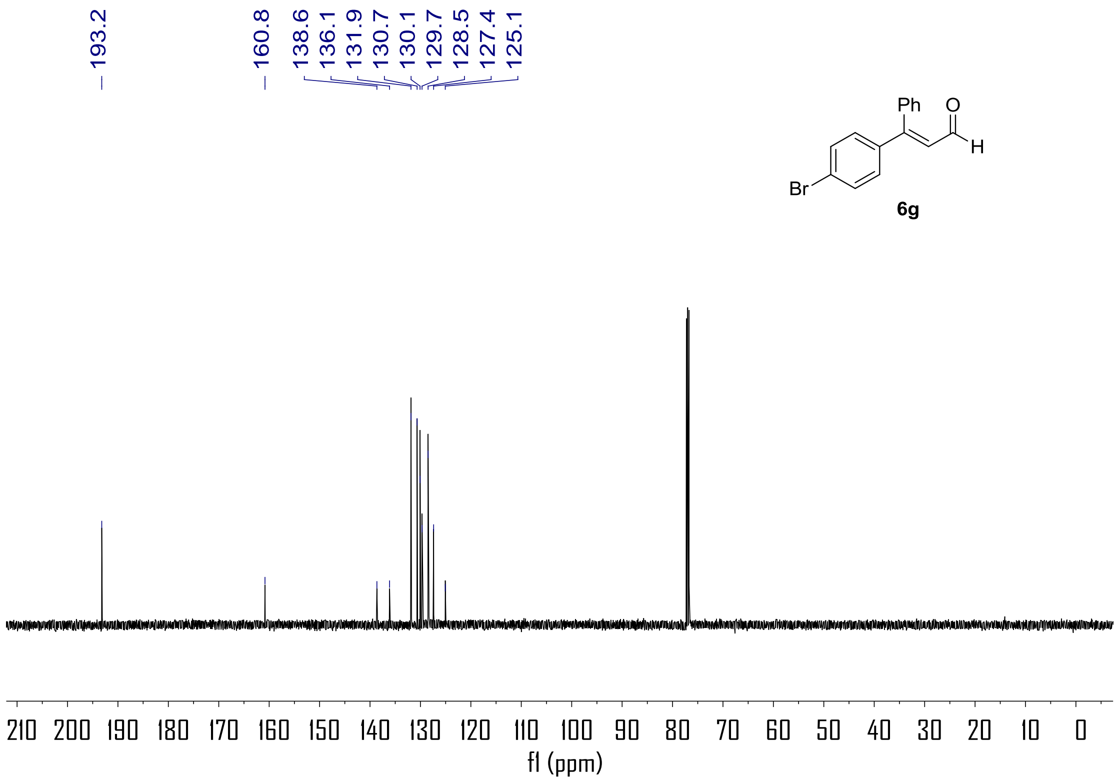


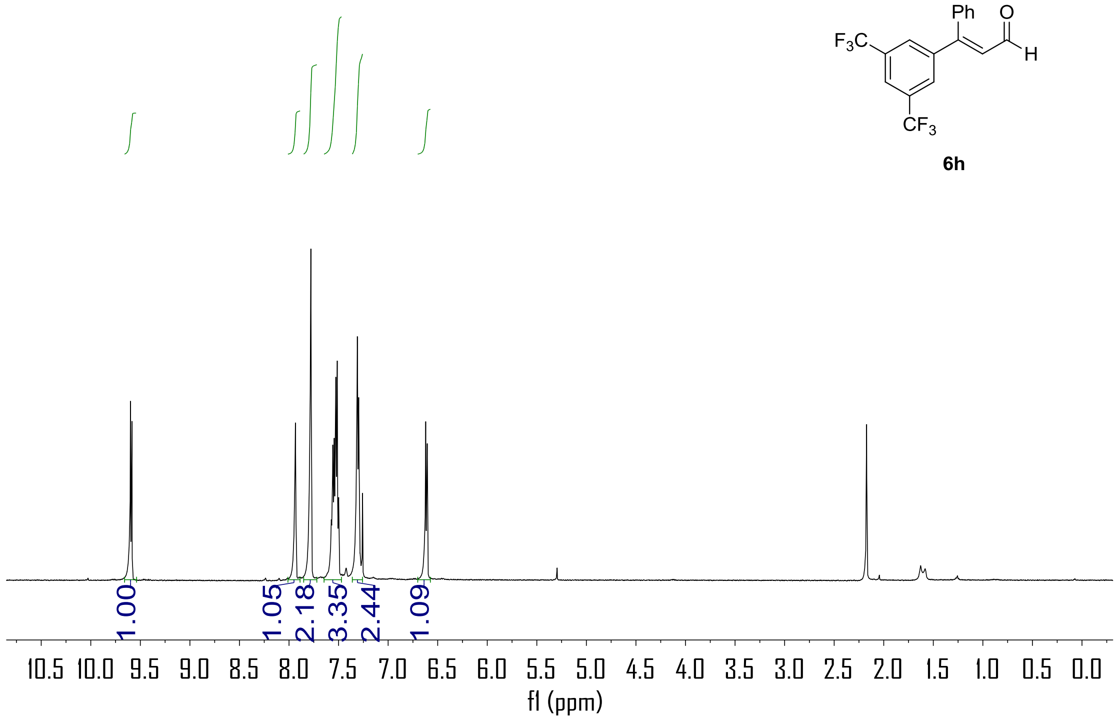


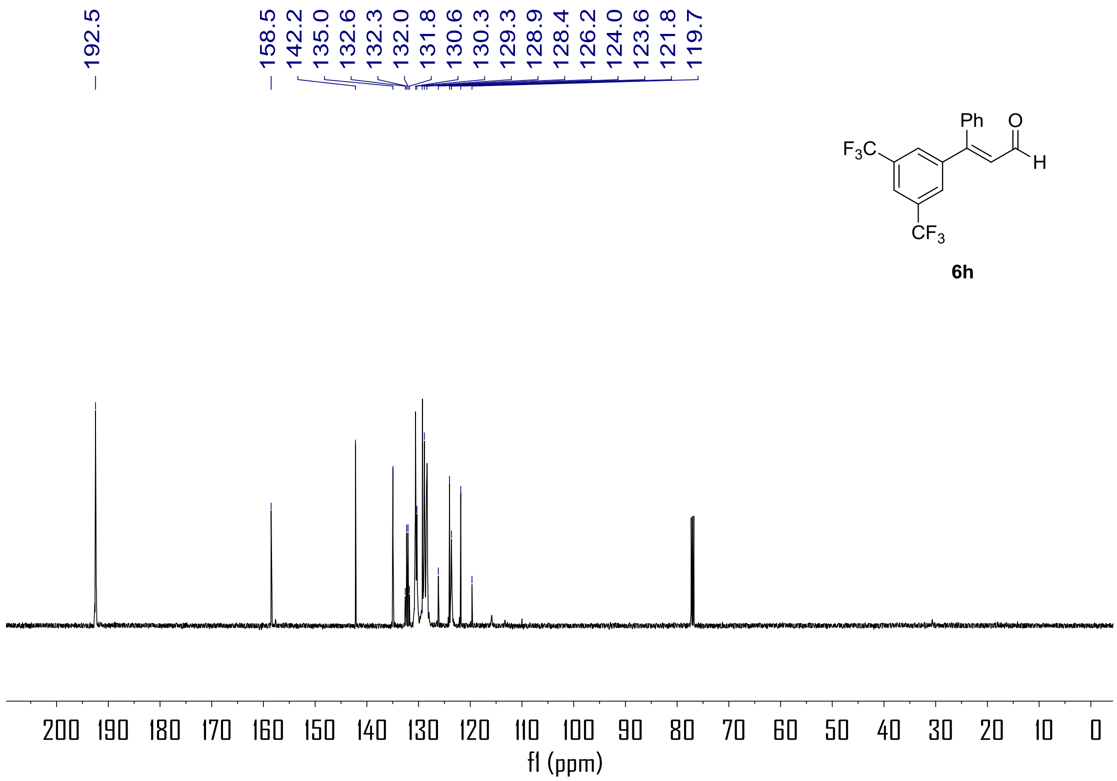

F
O
Ph
H
6e
1.00
2.16
3.32
1.01
2.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

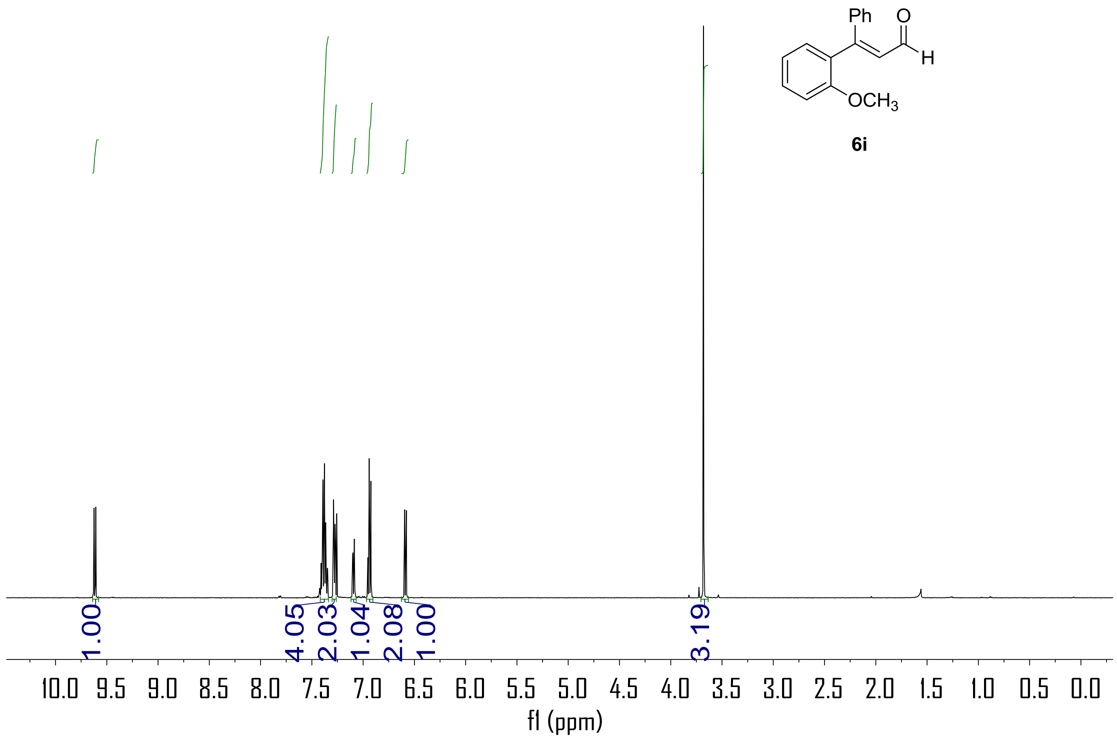

190.4
190.4
153.3
153.1
136.6
136.5
130.4
129.6
129.6
129.0
126.9
80.2
78.8
F
O
Ph
H
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
H
Br
6g
1.00
5.16
2.41
2.11
1.03
10.5 10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

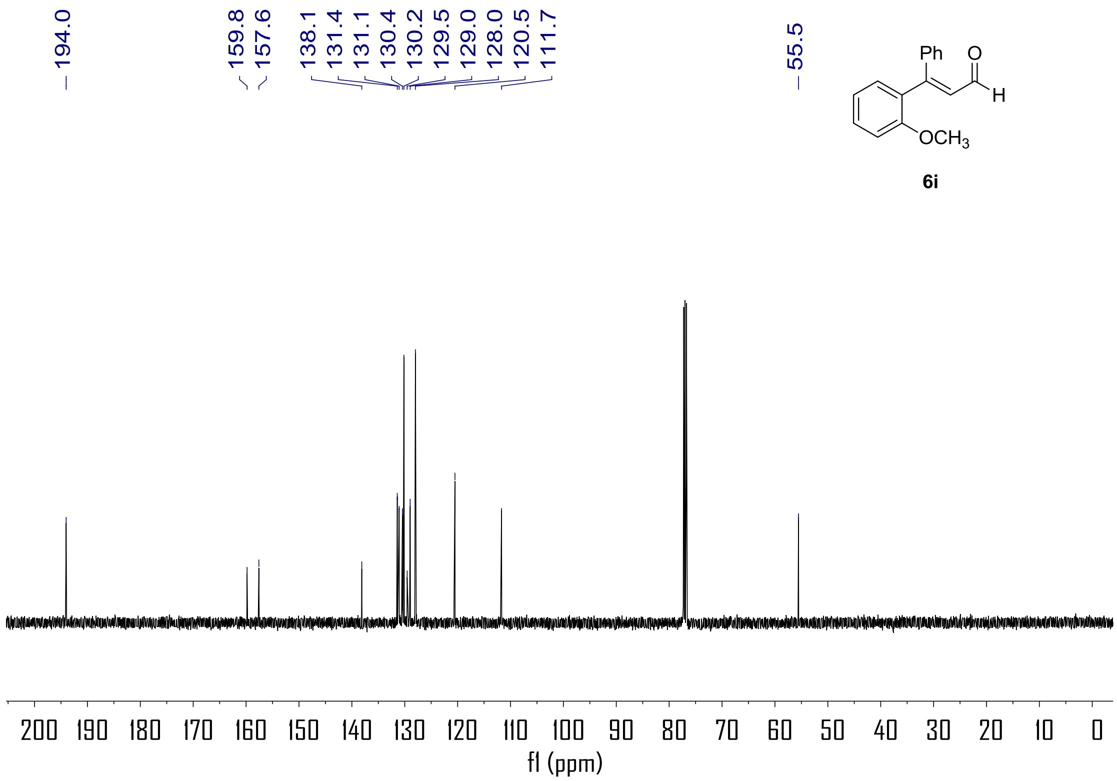

193.2
160.8
138.6
136.1
131.9
130.7
130.1
129.7
128.5
127.4
125.1
Ph
O
H
Br
6g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
O
F3C
H
CF3
6h
1.00
1.05
2.18
3.35
2.44
1.09
10.5 10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

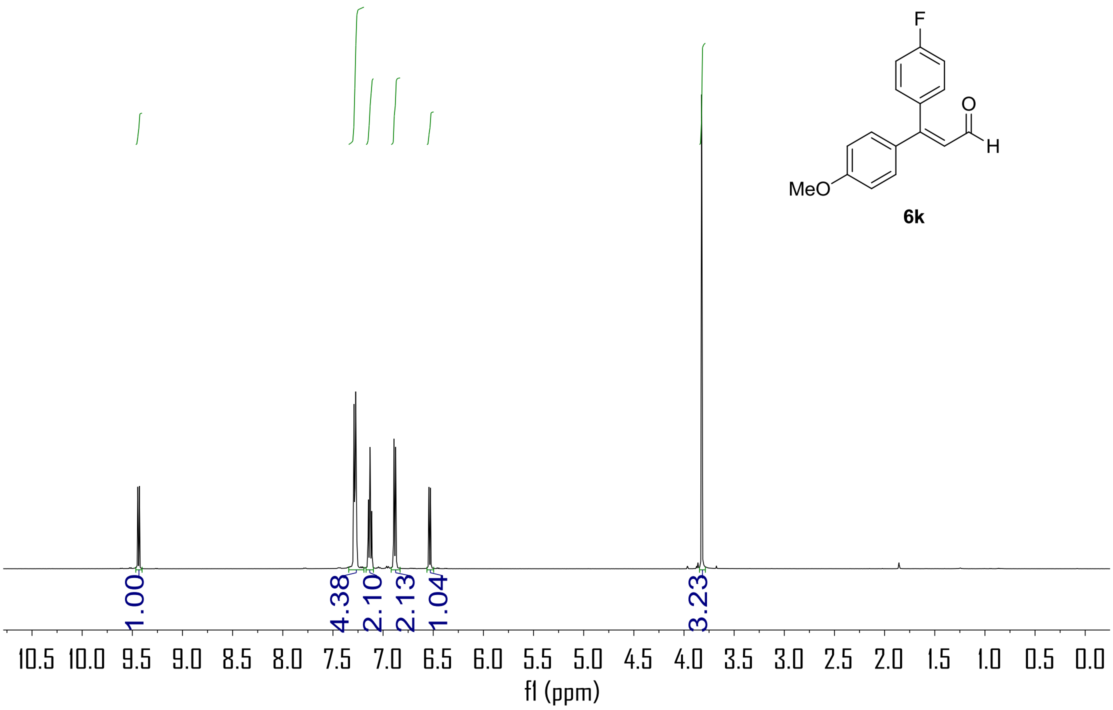

192.5
158.5
142.2
135.0
132.6
132.3
132.0
131.8
130.6
130.3
129.3
128.9
128.4
126.2
124.0
123.6
121.8
119.7
Ph
O
F3C
H
CF3
6h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



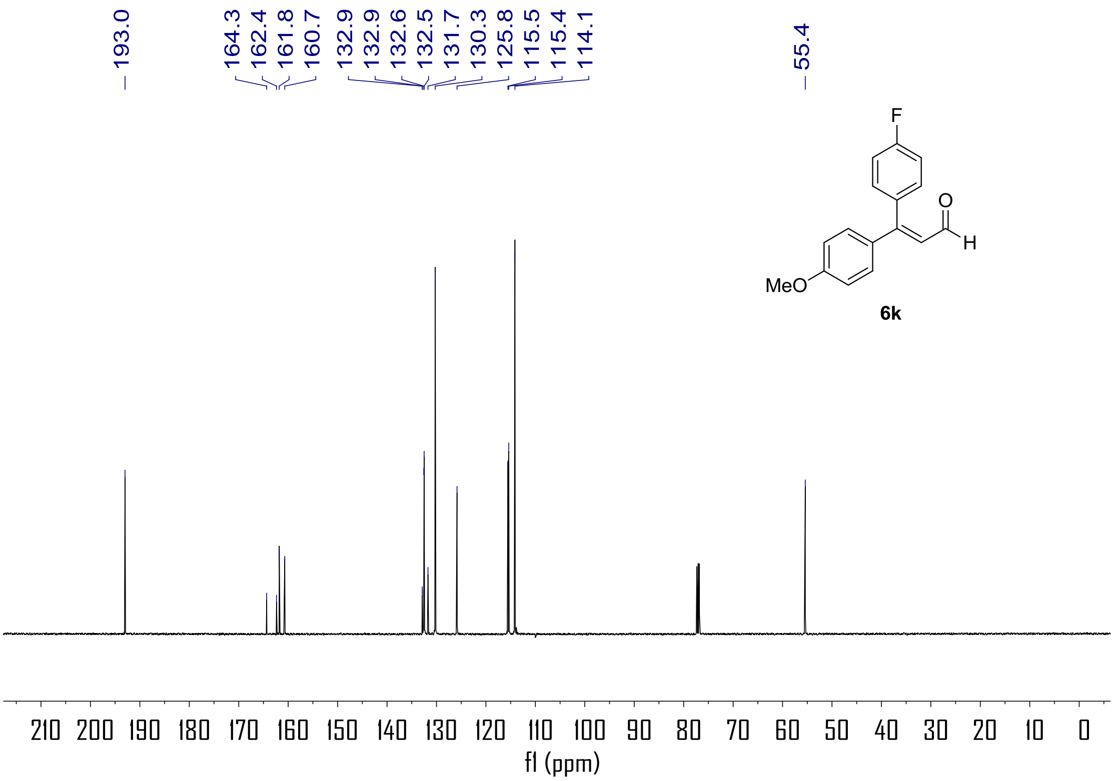
Ph
O
H
OCH3
6i
1.00
4.05
2.03
1.04
2.08
1.00
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



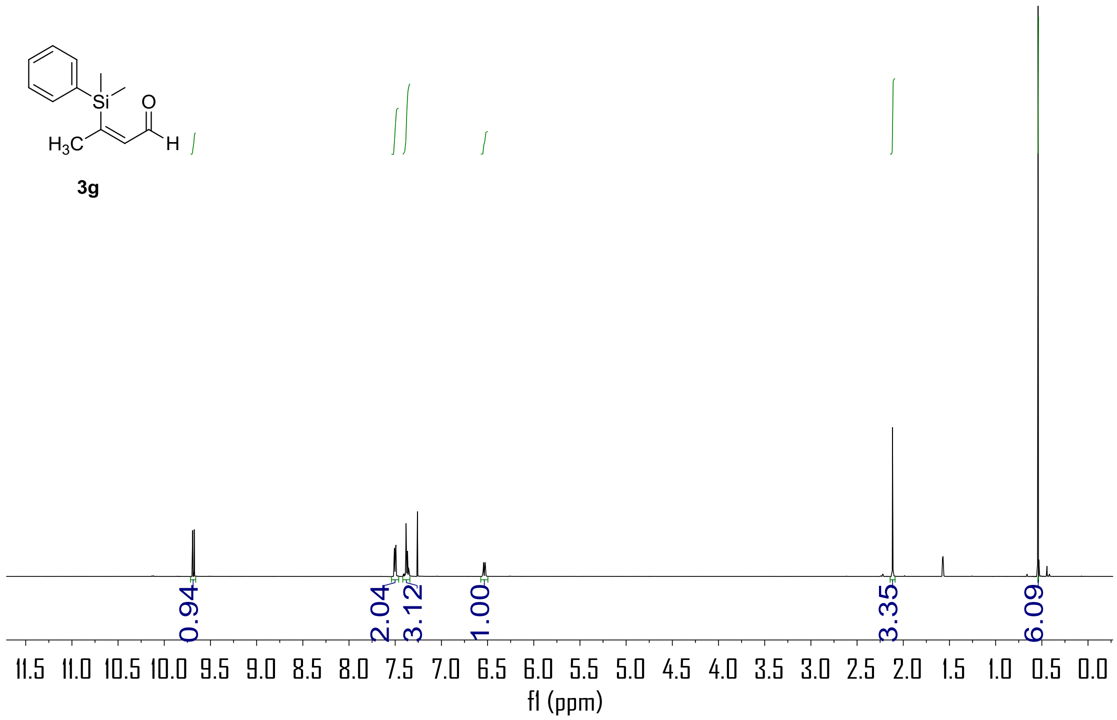
194.0
159.8
157.6
138.1
131.4
131.1
130.4
130.2
129.5
129.0
128.0
120.5
111.7
55.5
Ph
O
H
OCH3
6i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

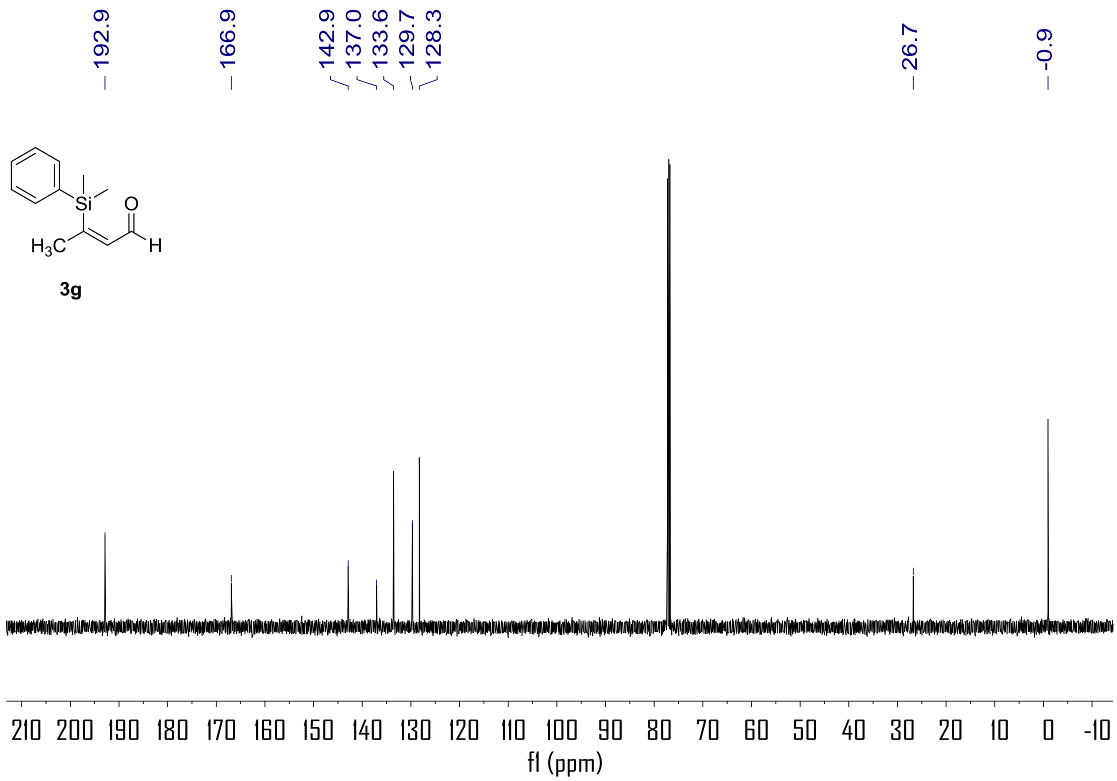


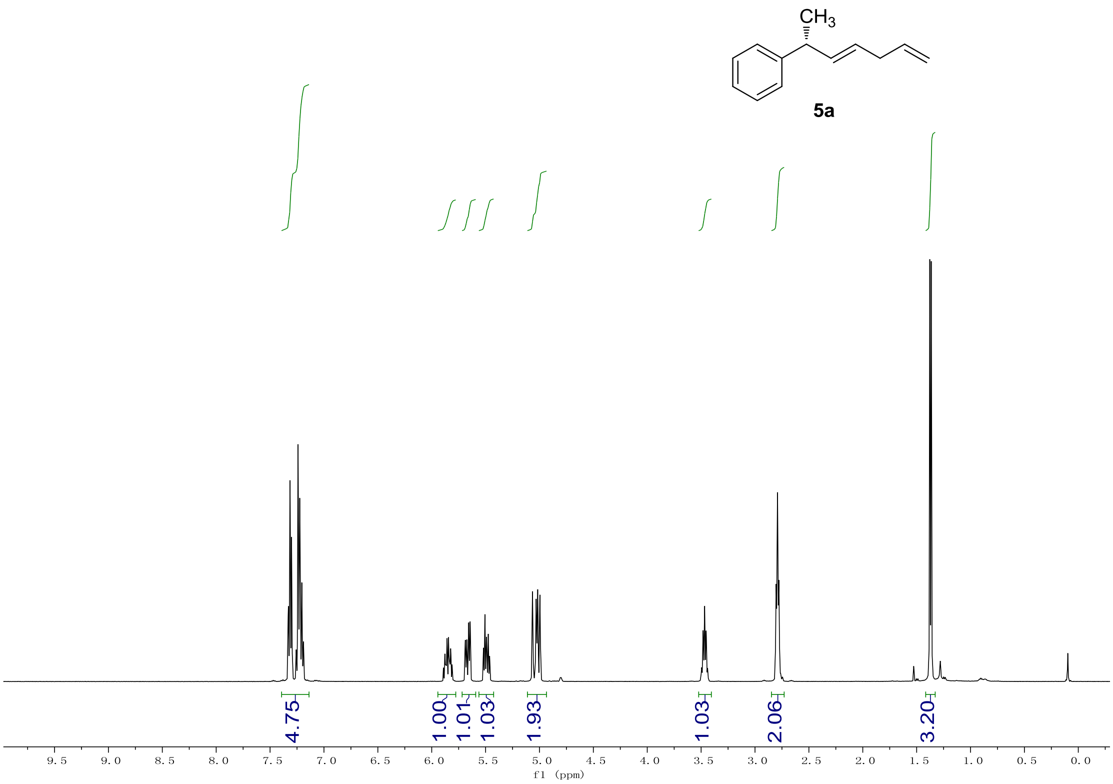
F
O
H
MeO
6k
1.00
4.38
2.10
2.13
1.04
3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

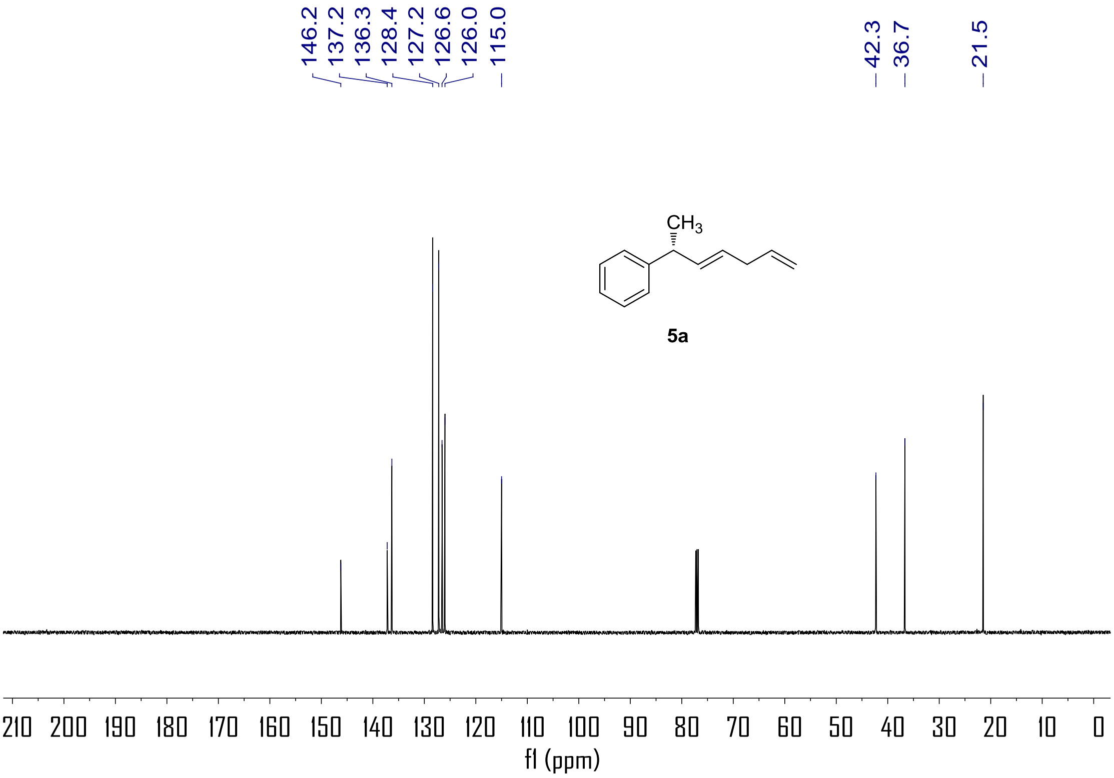


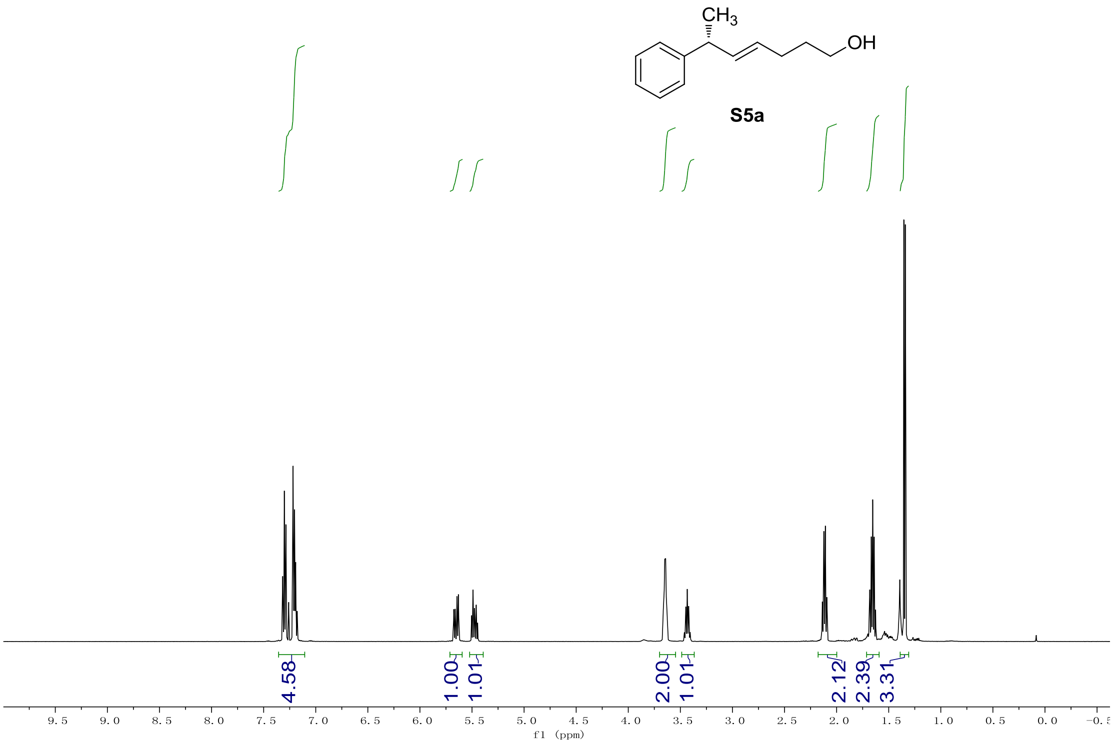
193.0
164.3
162.4
161.8
160.7
132.9
132.9
132.6
132.5
131.7
130.3
125.8
115.5
115.4
114.1
55.4
F
O
H
MeO
6k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

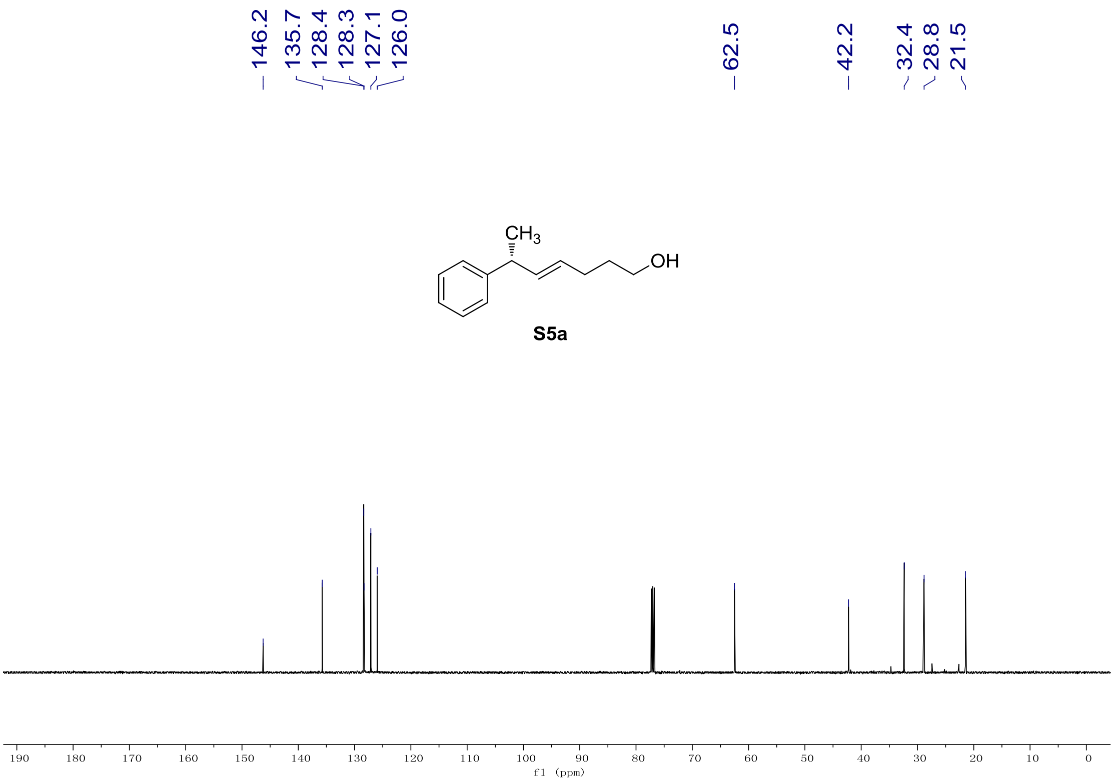

O
Si
H3C
H
3g
0.94
2.04
3.12
1.00
3.35
6.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

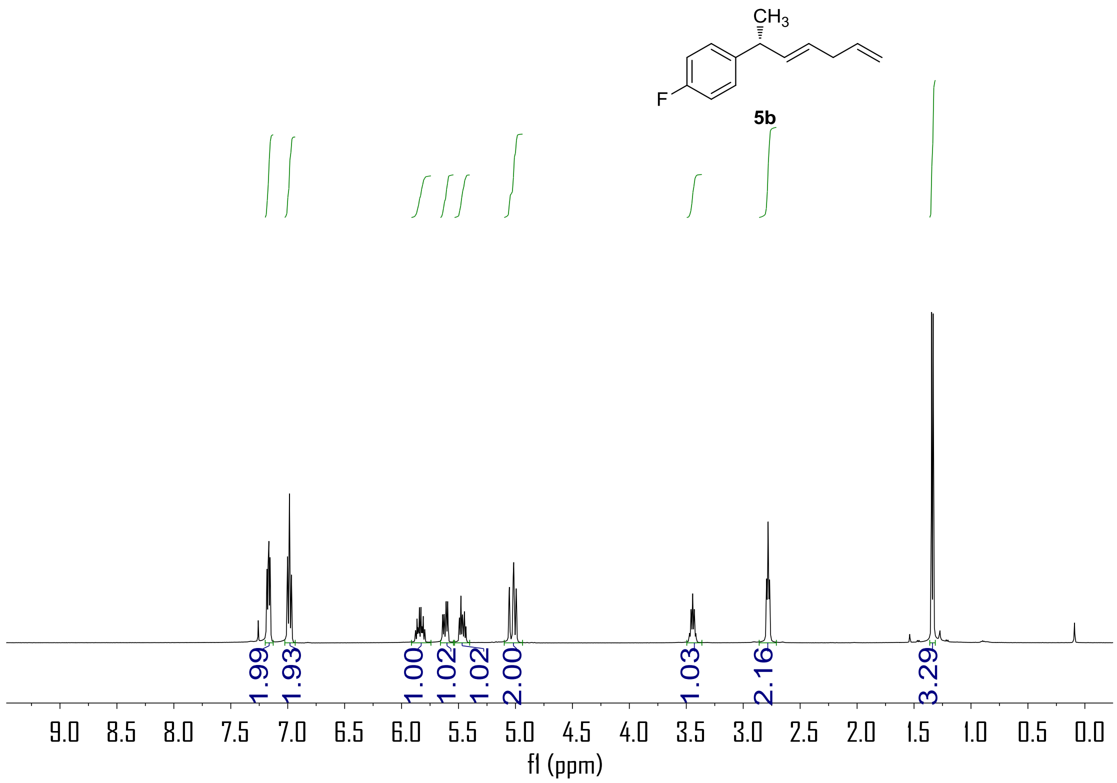

192.9
166.9
142.9
137.0
133.6
129.7
128.3
26.7
-0.9
O
Si
H3C
H
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

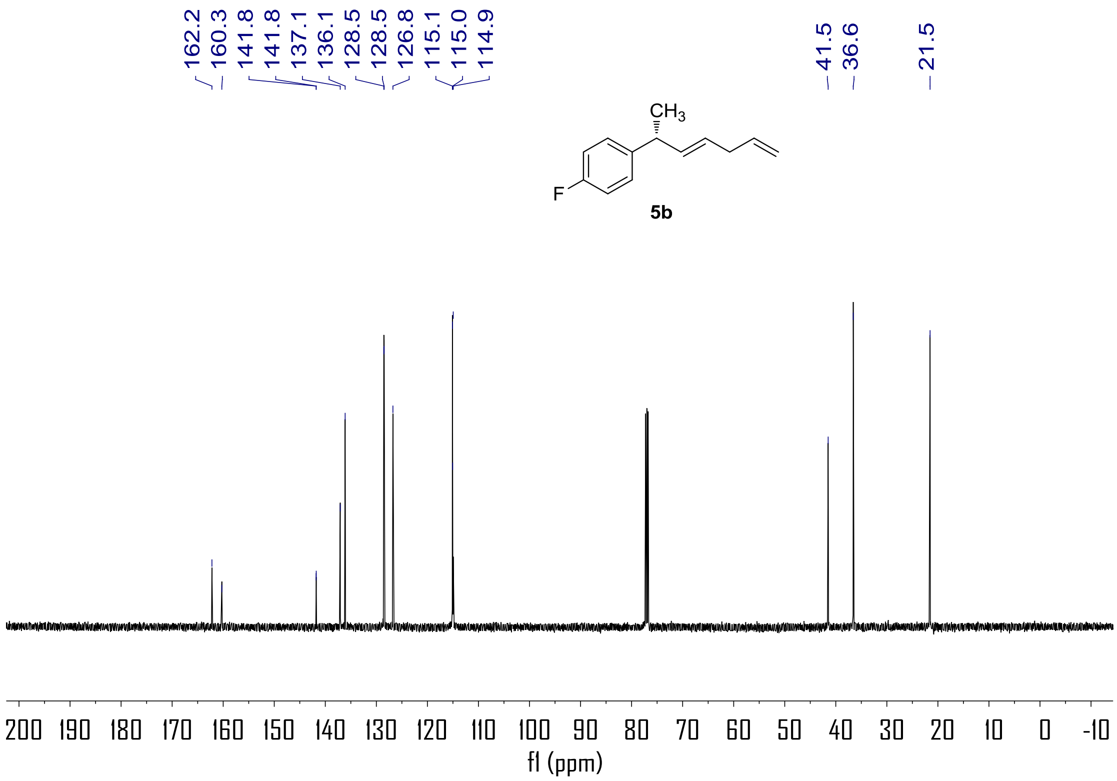

5a
4.75
1.00
1.01
1.03
1.93
1.03
2.06
3.20
f1 (ppm)

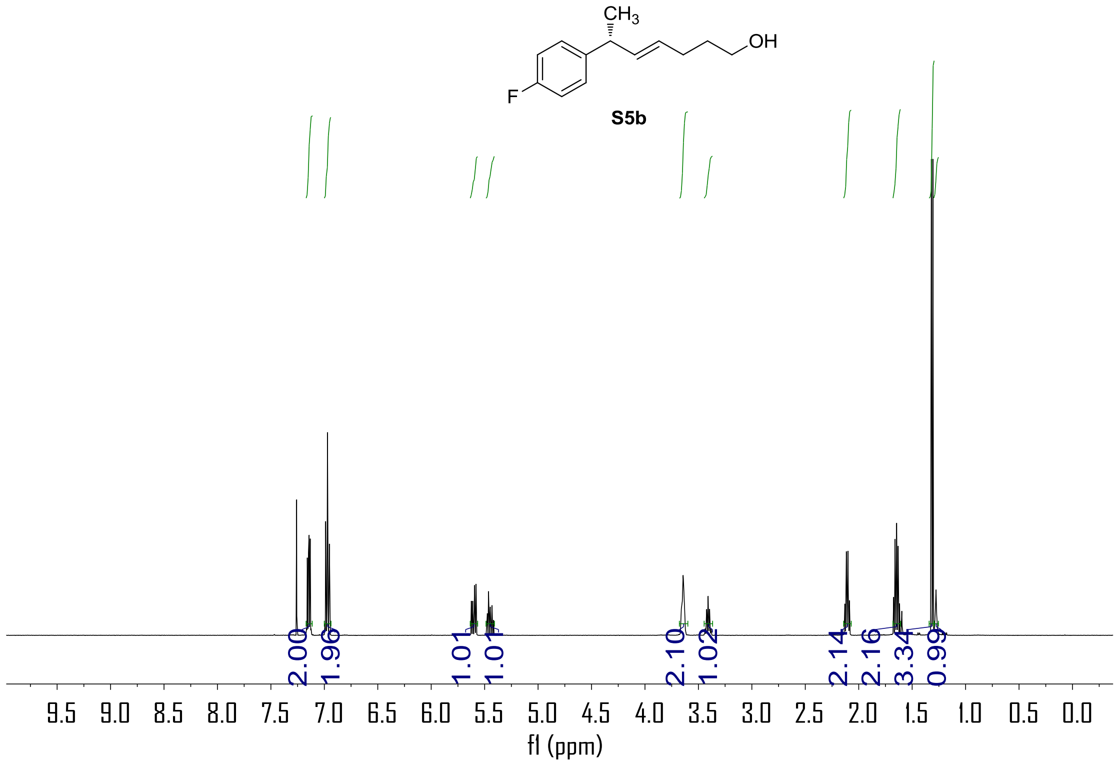

146.2
137.2
136.3
128.4
127.2
126.6
126.0
115.0
42.3
36.7
21.5
5a
f1 (ppm)


CH3
OH
S5a
4.58
1.00
1.01
2.00
1.01
2.12
2.39
3.31
f1 (ppm)

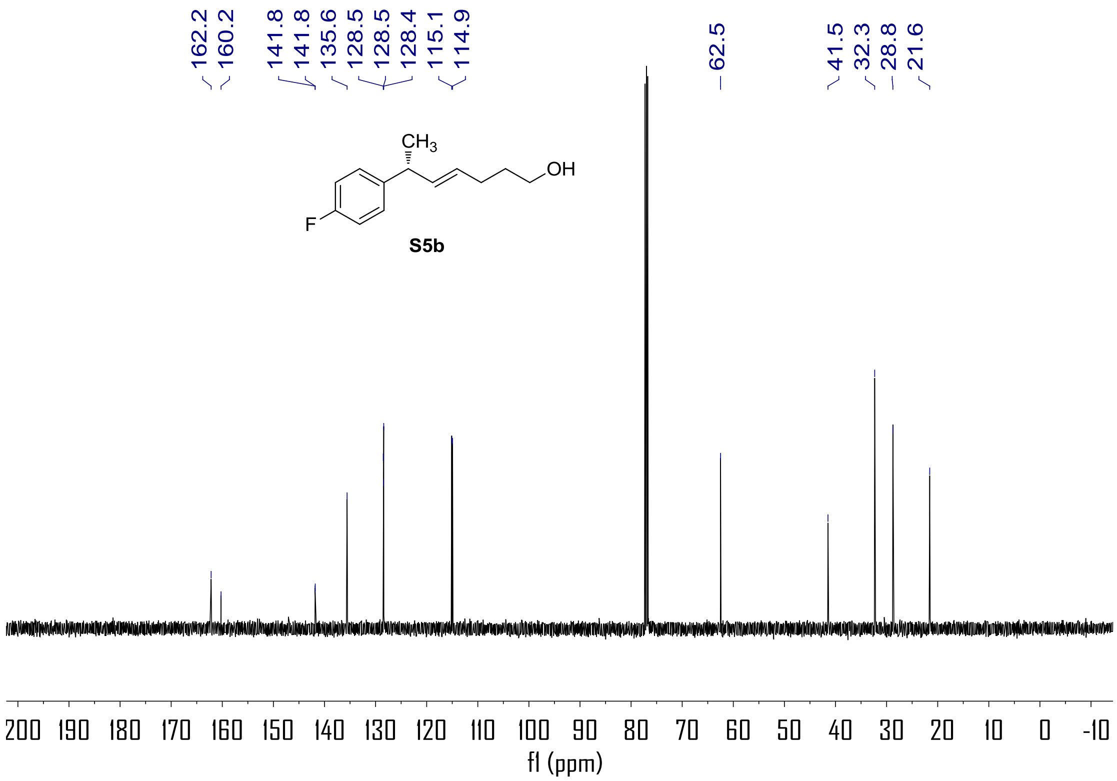

146.2
135.7
128.4
128.3
127.1
126.0
62.5
42.2
32.4
28.8
21.5
CH3
OH
S5a
f1 (ppm)


CH3
F
5b
1.99
1.93
1.00
1.02
1.02
2.00
1.03
2.16
3.29
9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

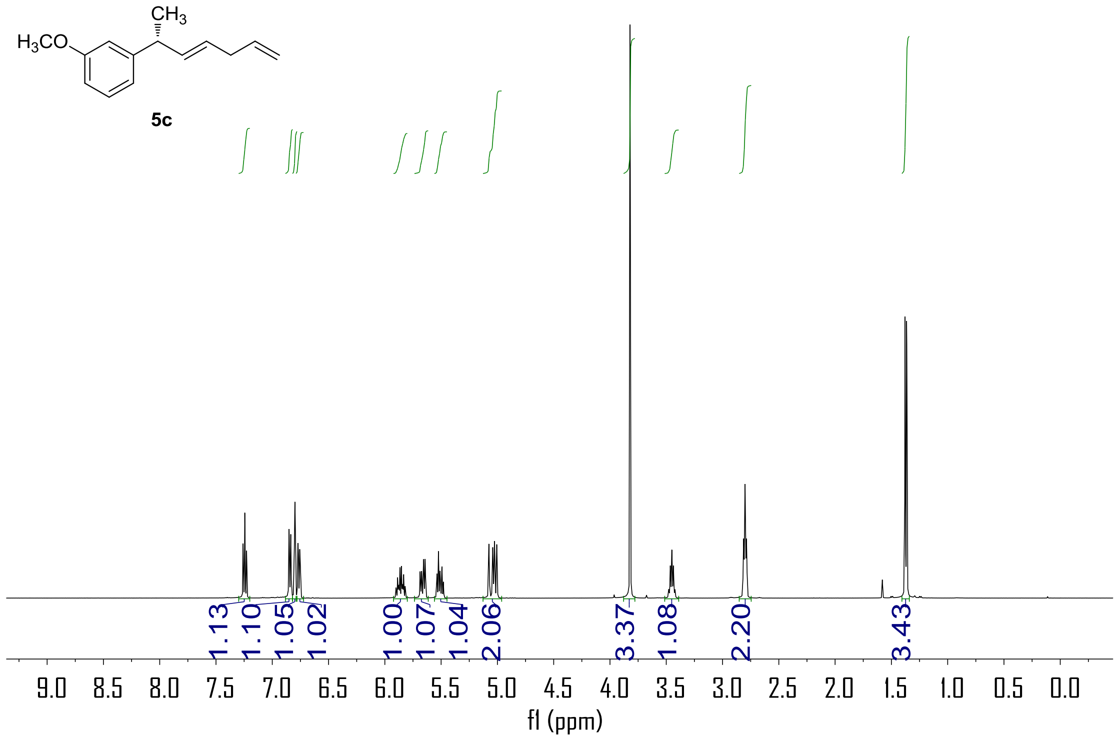

162.2
160.3
141.8
141.8
137.1
136.1
128.5
128.5
126.8
115.1
115.0
114.9
41.5
36.6
21.5
CH3
F
5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



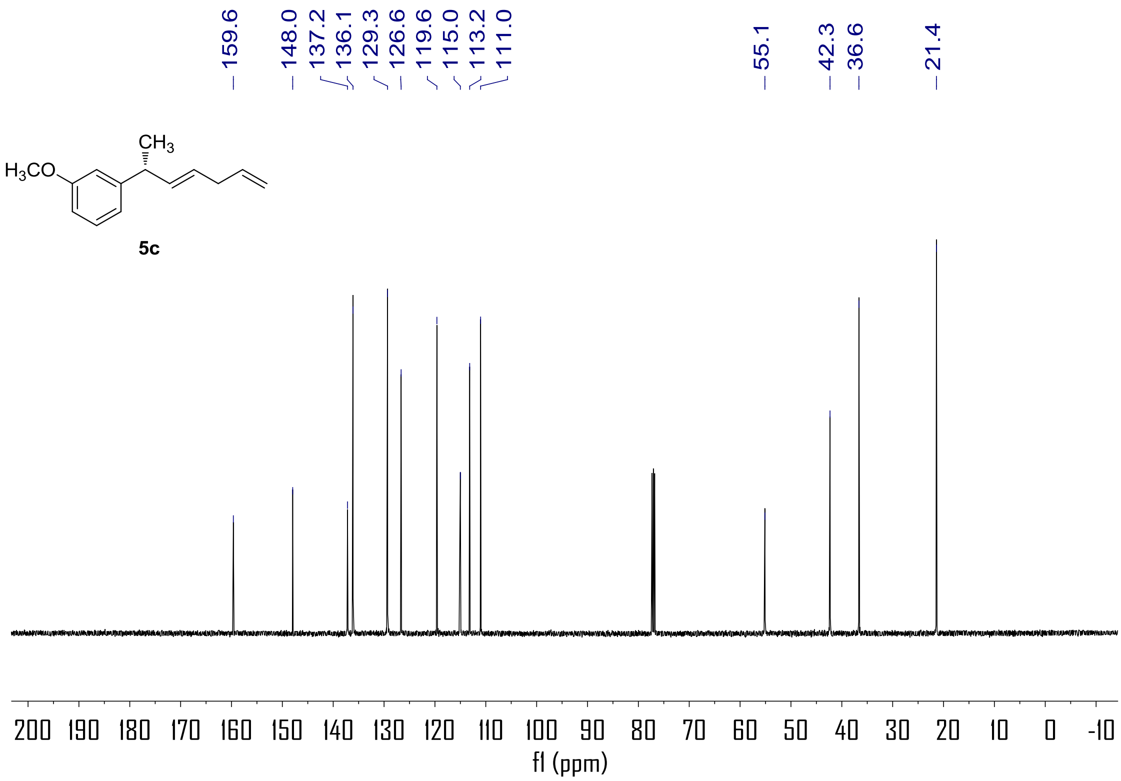
CH3
OH
F
S5b
2.00
1.96
1.01
1.01
2.10
1.02
2.14
2.16
3.34
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



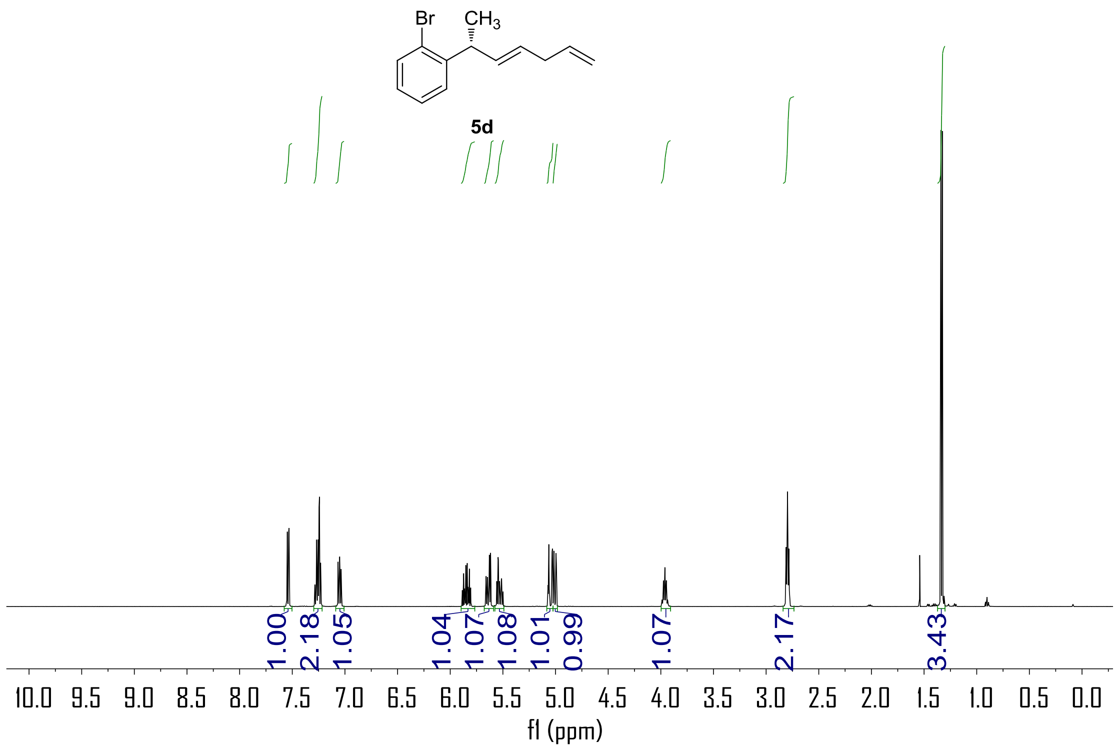
162.2
160.2
141.8
141.8
135.6
128.5
128.5
128.4
115.1
114.9
62.5
41.5
32.3
28.8
21.6
CH3
OH
F
S5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

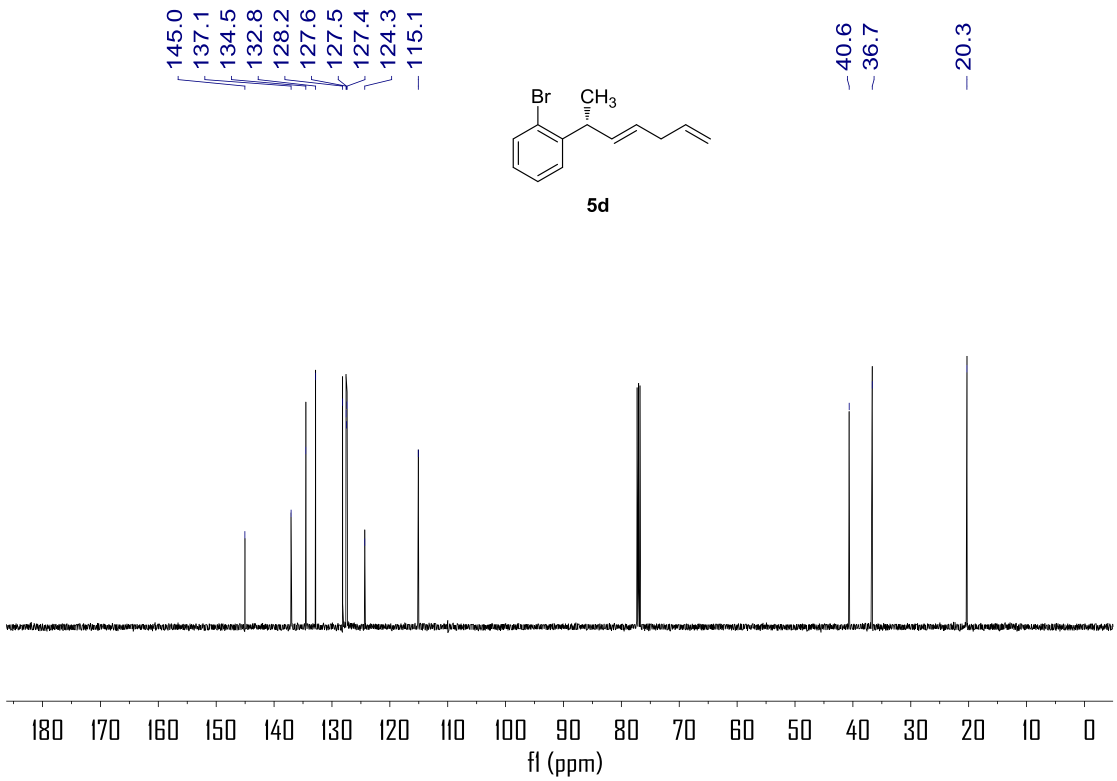


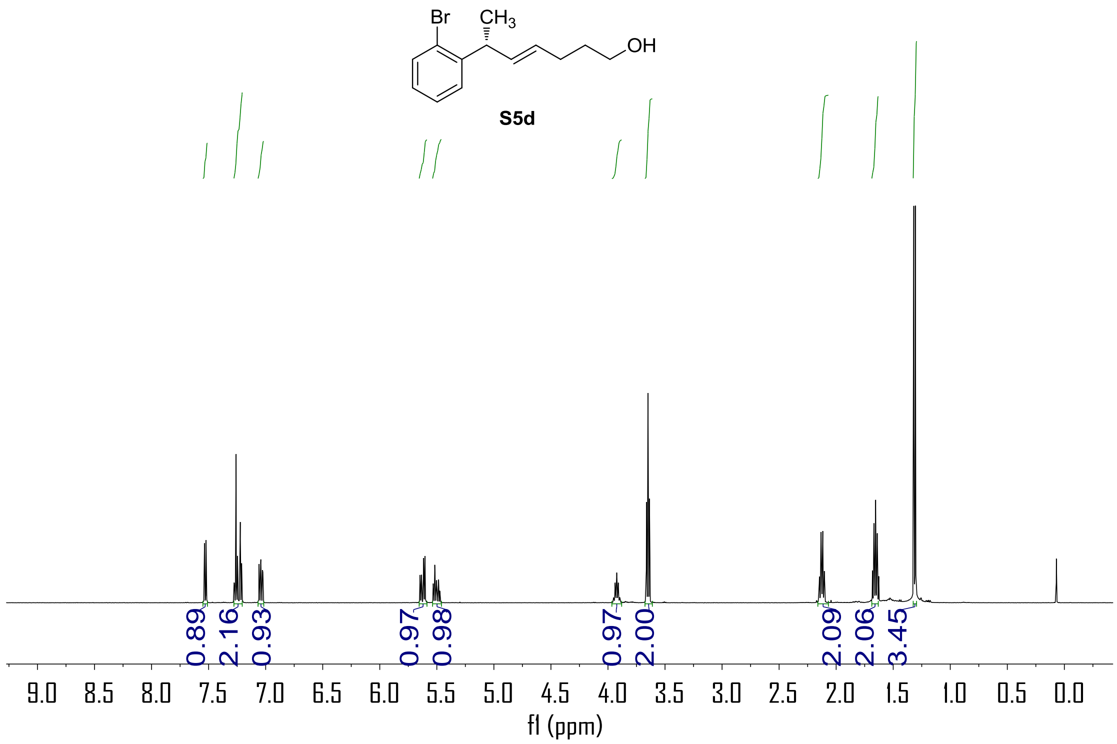
CH3
H3CO
5c
1.13
1.10
1.05
1.02
1.00
1.07
1.04
2.06
3.37
1.08
2.20
3.43
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

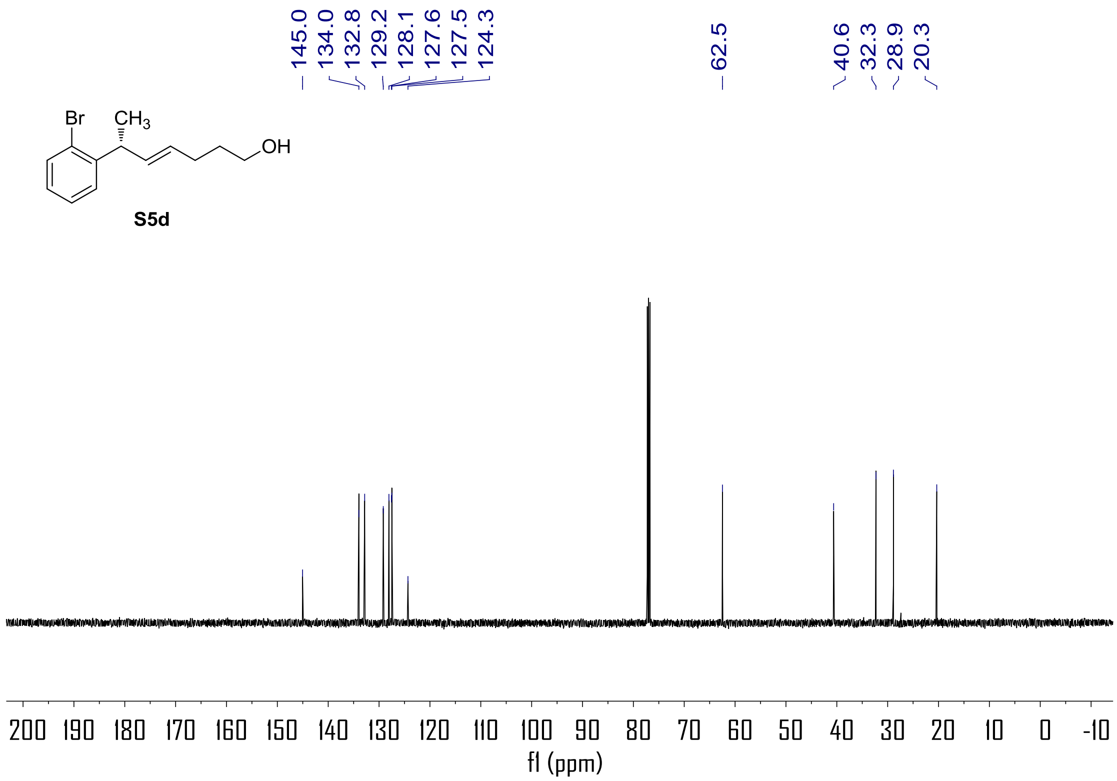


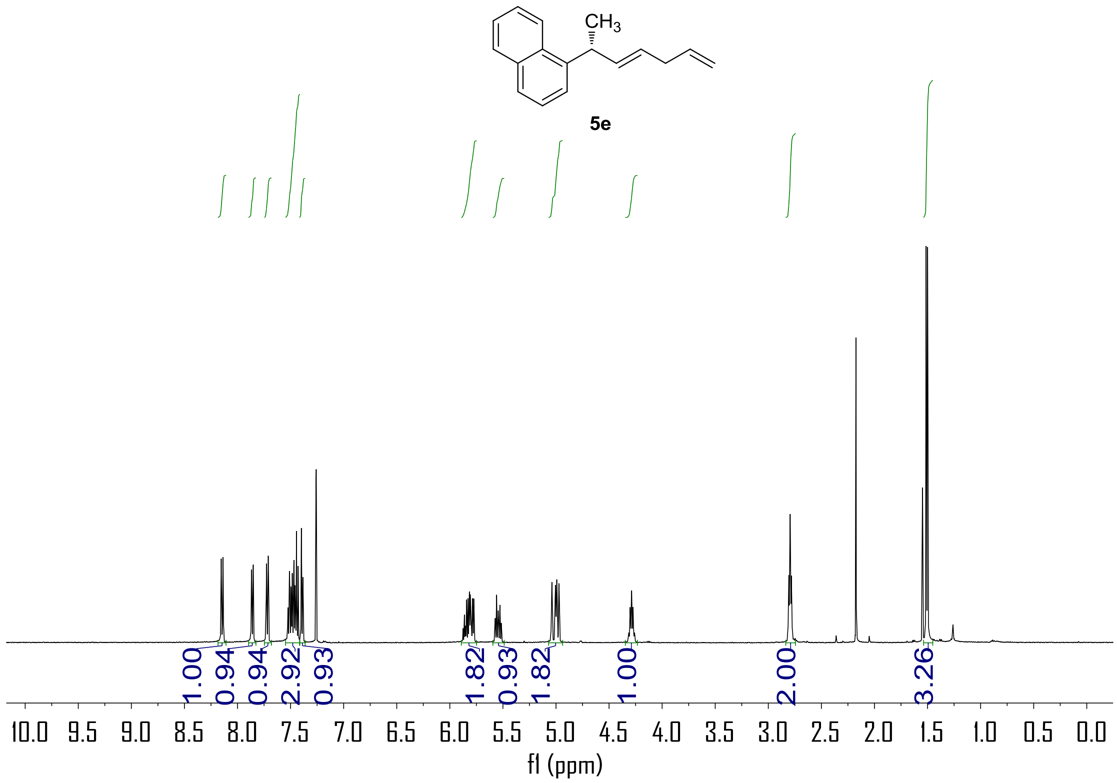
159.6
148.0
137.2
136.1
129.3
126.6
119.6
115.0
113.2
111.0
55.1
42.3
36.6
21.4
CH3
H3CO
5c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

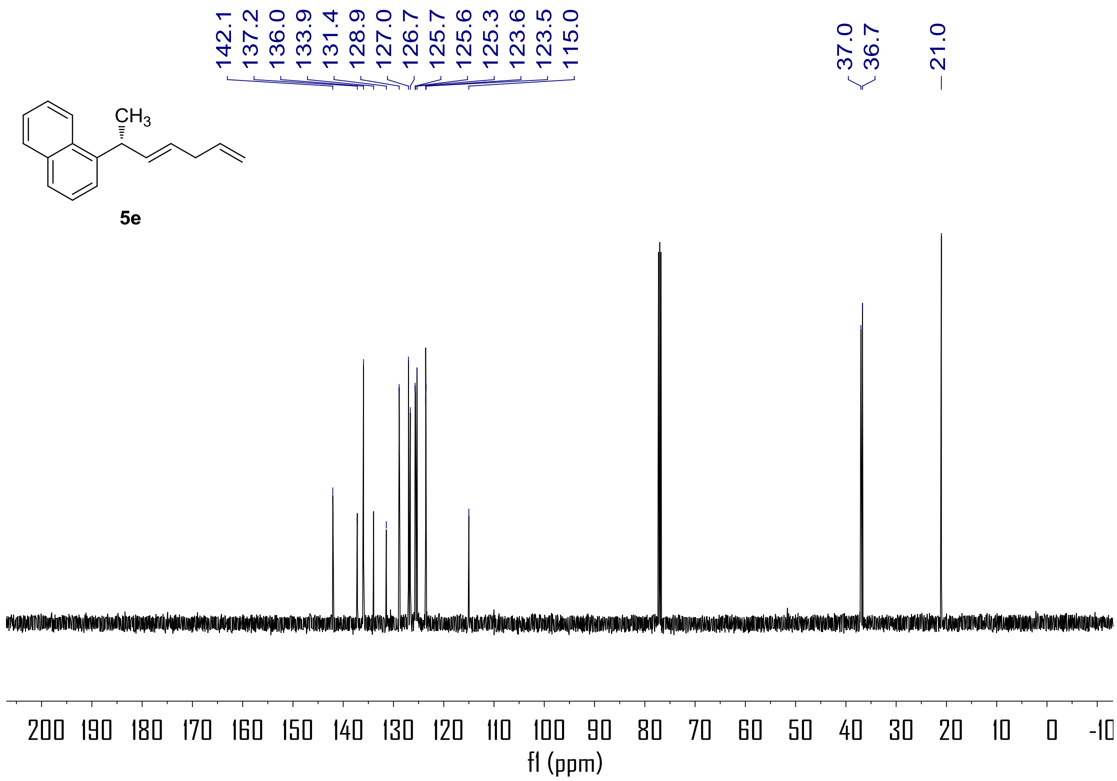

Br
CH3
5d
1.00
2.18
1.05
1.04
1.07
1.08
1.01
0.99
1.07
2.17
3.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

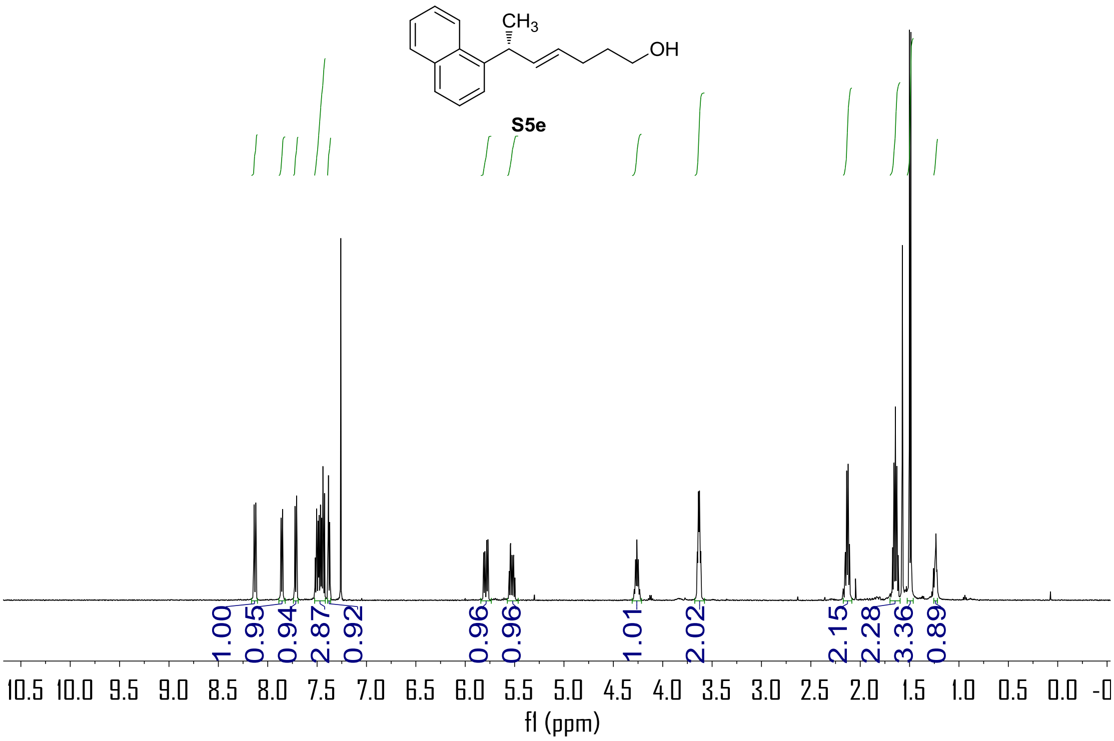

145.0
137.1
134.5
132.8
128.2
127.6
127.5
127.4
124.3
115.1
40.6
36.7
20.3
Br
CH3
5d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
CH3
OH
S5d
0.89
2.16
0.93
0.97
0.98
0.97
2.00
2.09
2.06
3.45
9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

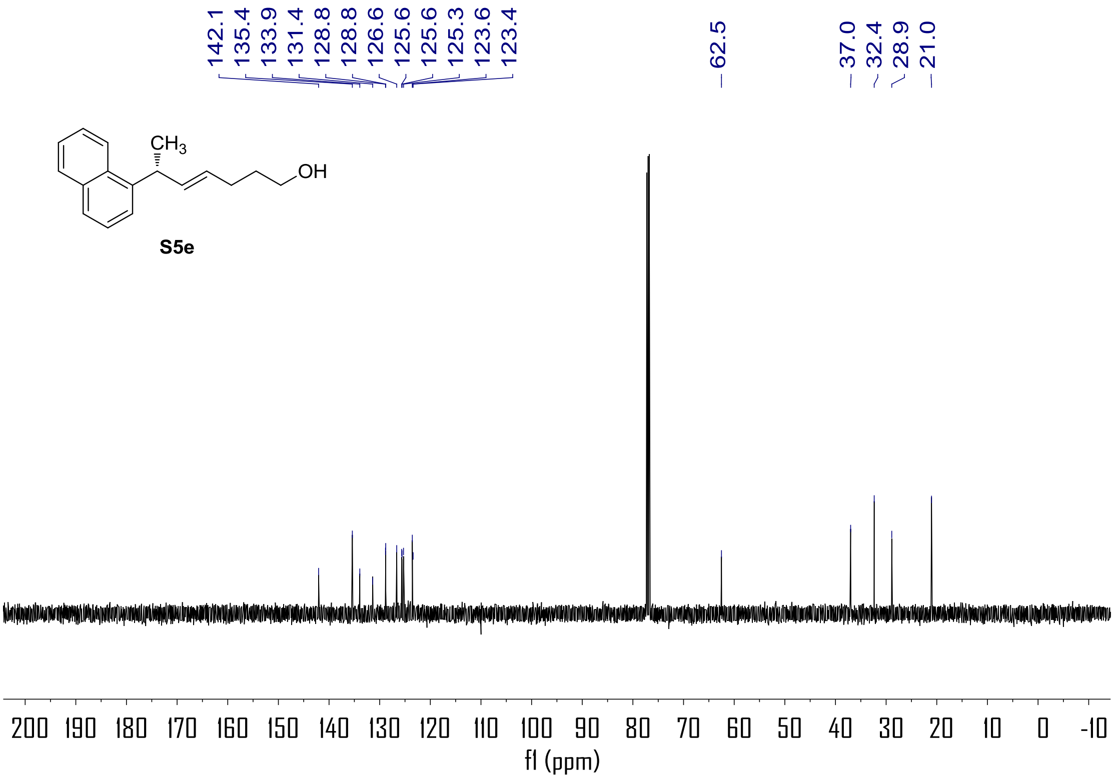

145.0
134.0
132.8
129.2
128.1
127.6
127.5
124.3
62.5
40.6
32.3
28.9
20.3
Br
CH3
OH
S5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CH3
5e
1.00
0.94
0.94
2.92
0.93
1.82
0.93
1.82
1.00
2.00
3.26
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

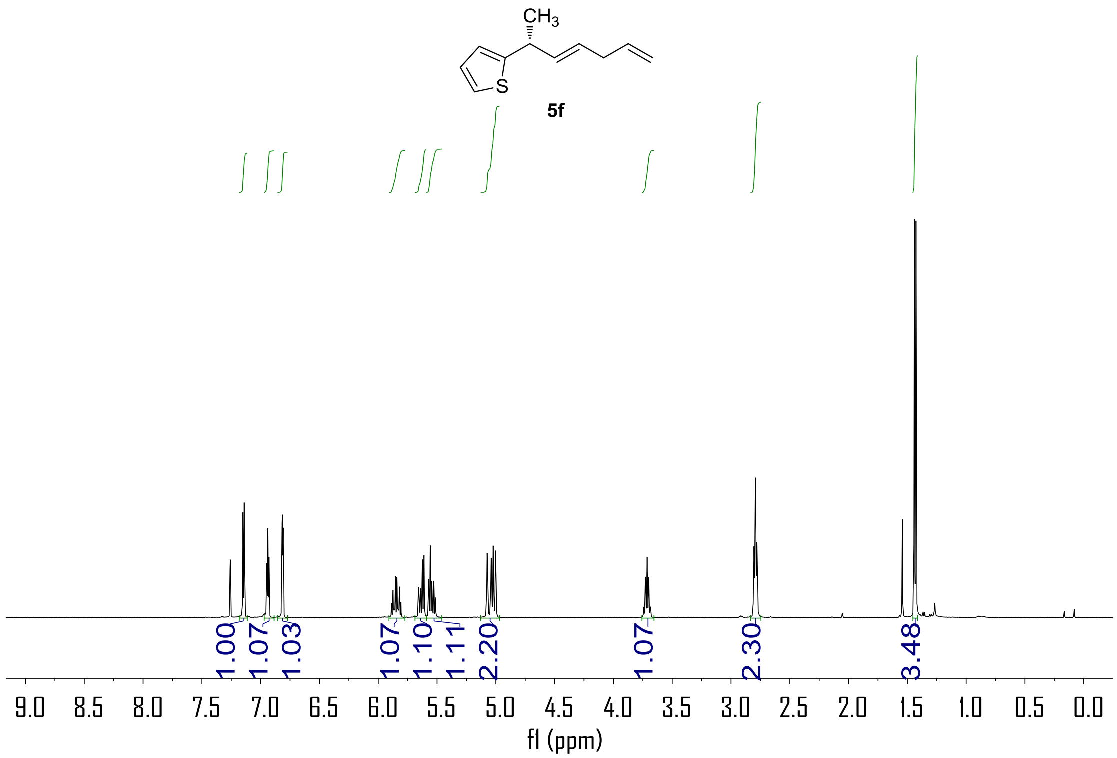

142.1
137.2
136.0
133.9
131.4
128.9
127.0
126.7
125.7
125.6
125.3
123.6
123.5
115.0
37.0
36.7
21.0
CH3
5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



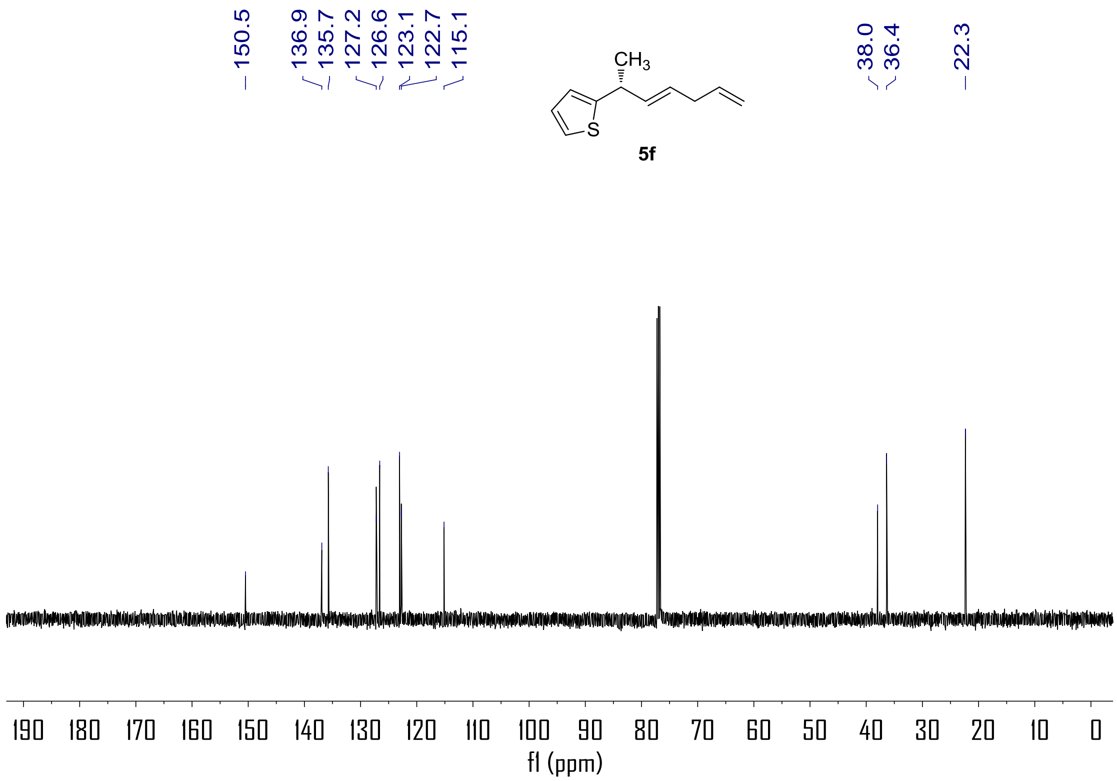
CH3
OH
S5e
1.00
0.95
0.94
2.87
0.92
0.96
0.96
1.01
2.02
2.15
2.28
3.36
0.89
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)



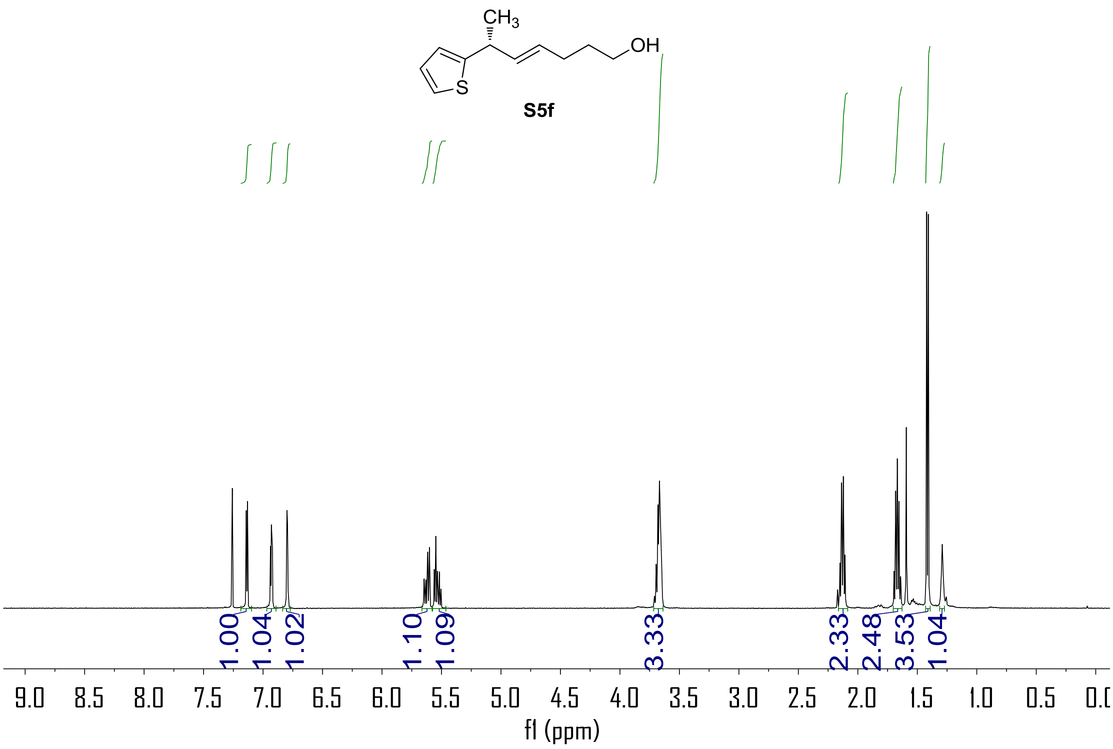
142.1
135.4
133.9
131.4
128.8
128.8
126.6
125.6
125.6
125.3
123.6
123.4
62.5
37.0
32.4
28.9
21.0
CH3
OH
S5e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

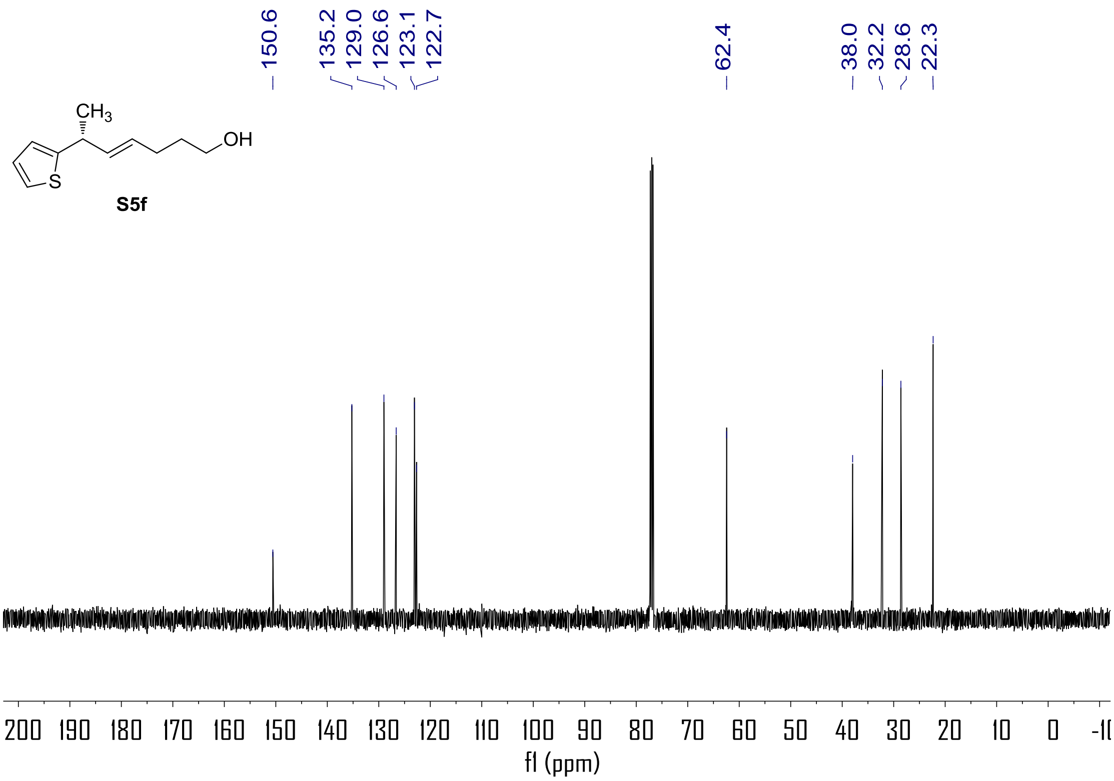


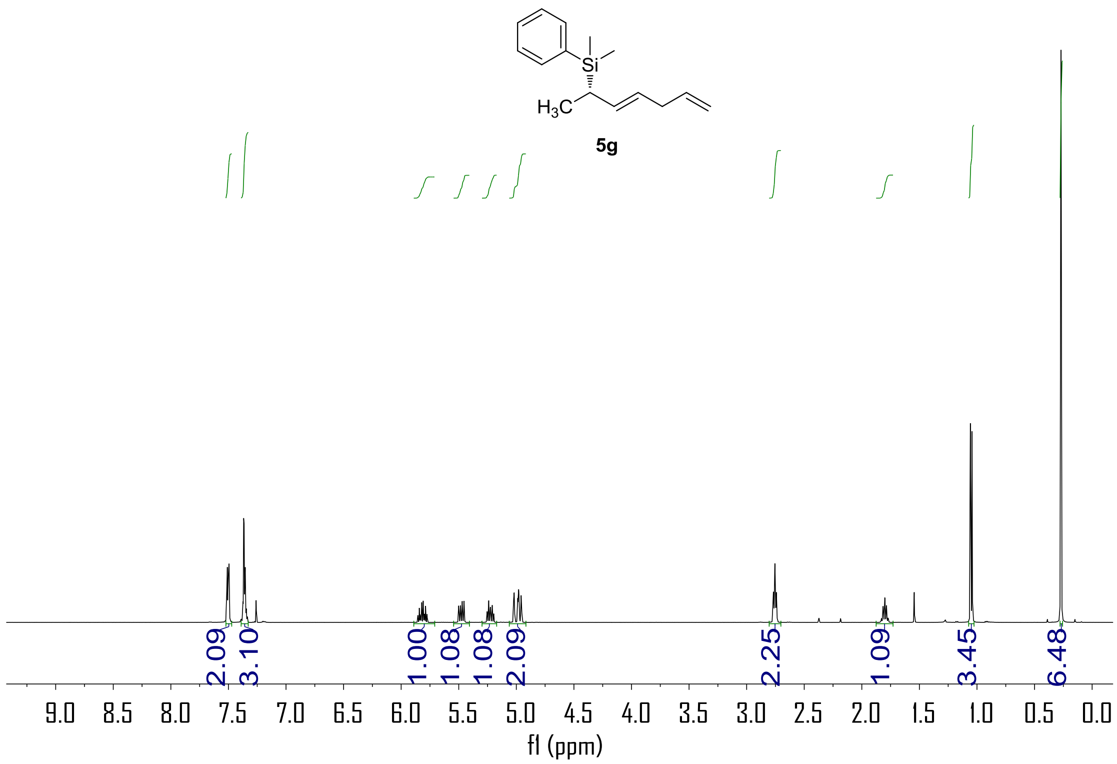
CH3
S
5f
1.00
1.07
1.03
1.07
1.10
1.11
2.20
1.07
2.30
3.48
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

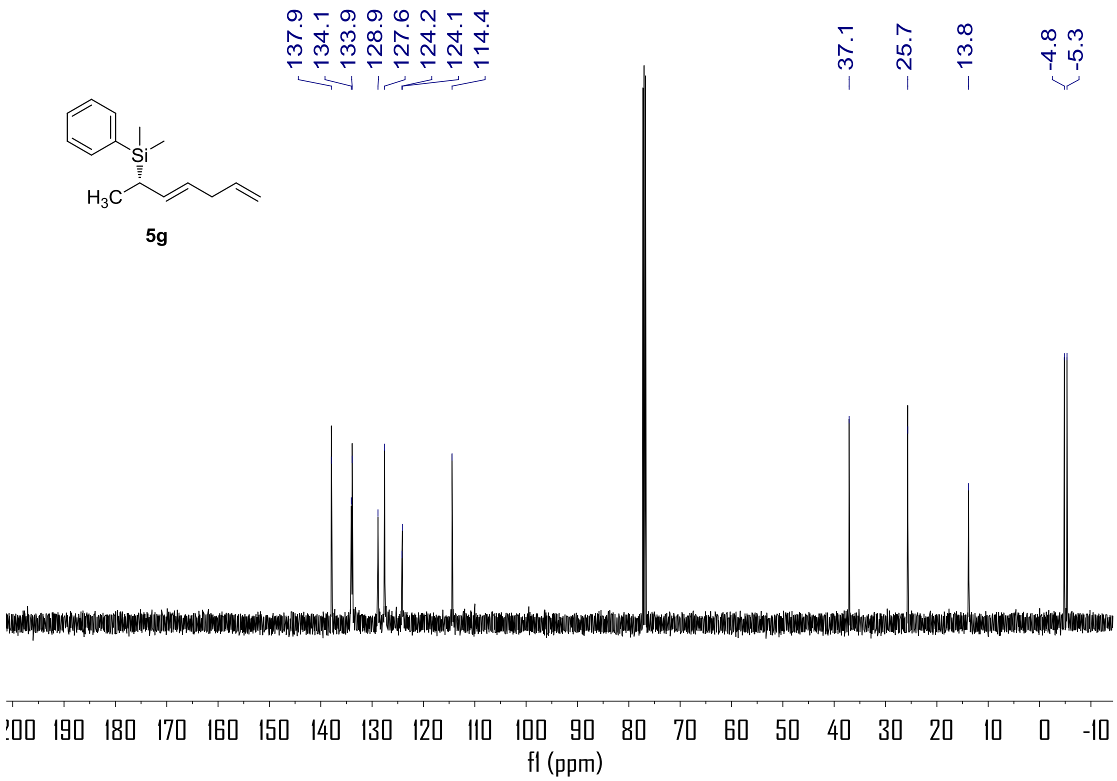


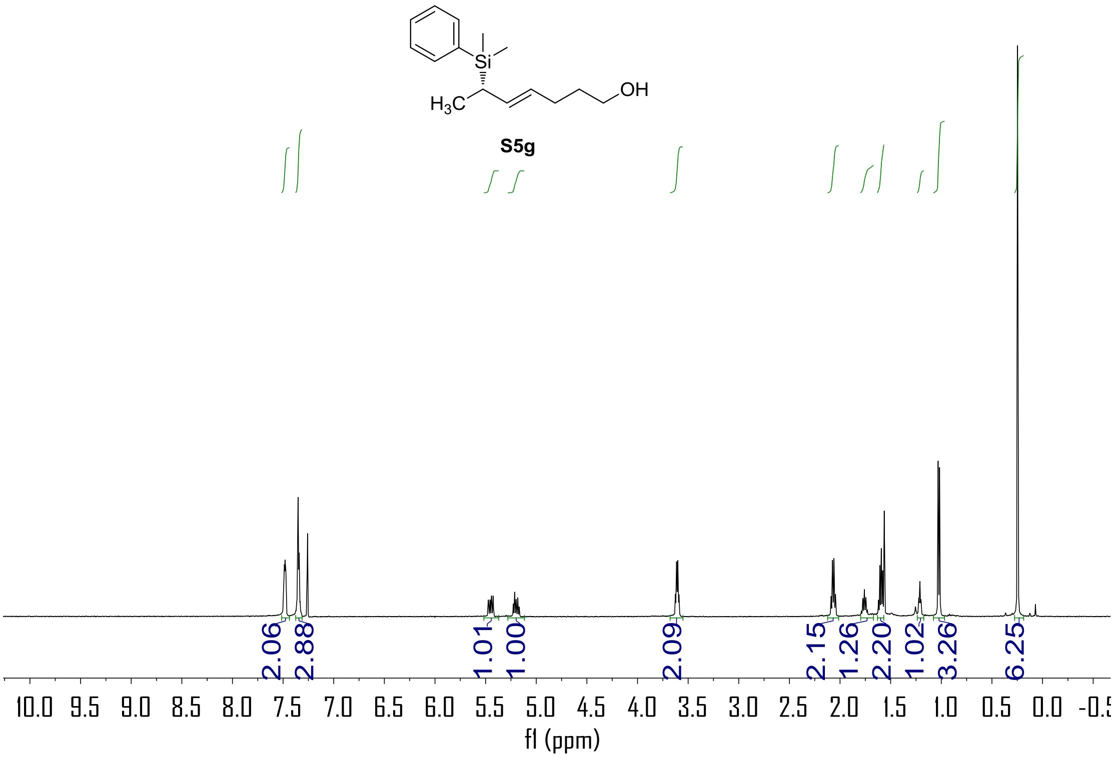
150.5
136.9
135.7
127.2
126.6
123.1
122.7
115.1
CH3
S
5f
38.0
36.4
22.3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
OH
S
S5f
1.00
1.04
1.02
1.10
1.09
3.33
2.33
2.48
3.53
1.04
9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

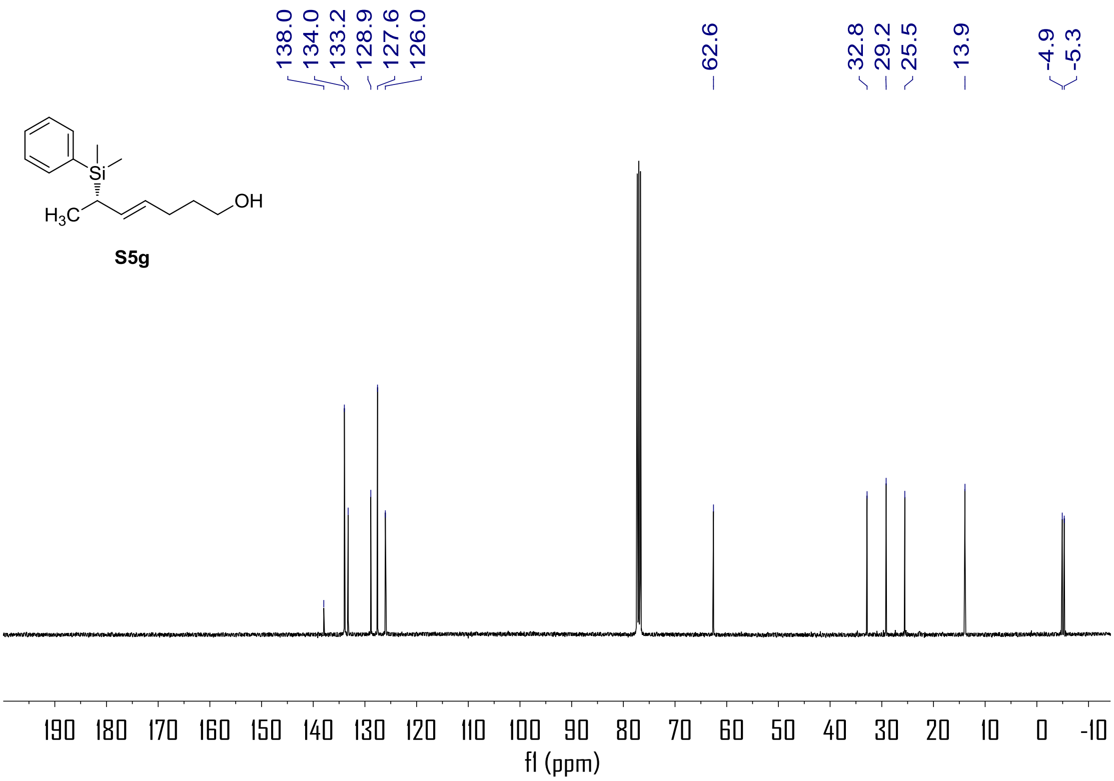

150.6
135.2
129.0
126.6
123.1
122.7
62.4
38.0
32.2
28.6
22.3
CH3
OH
S
S5f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Si
H3C
5g
2.09
3.10
1.00
1.08
1.08
2.09
2.25
1.09
3.45
6.48
9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

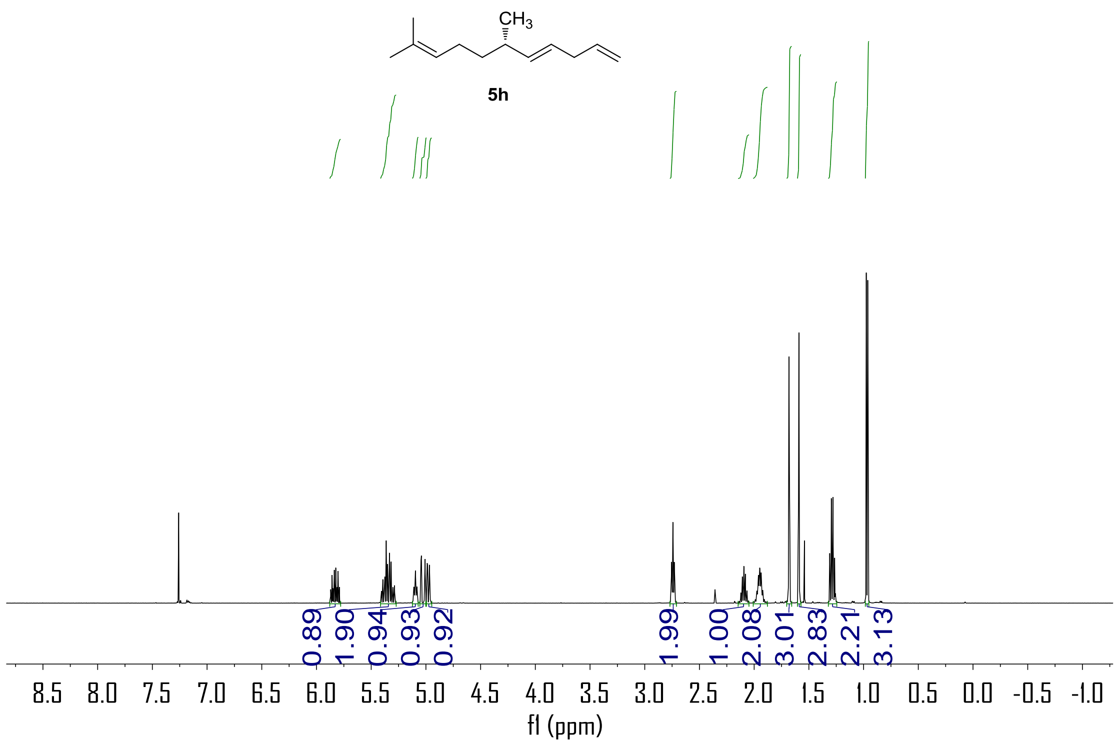

137.9
134.1
133.9
128.9
127.6
124.2
124.1
114.4
37.1
25.7
13.8
-4.8
-5.3
Si
H3C
5g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

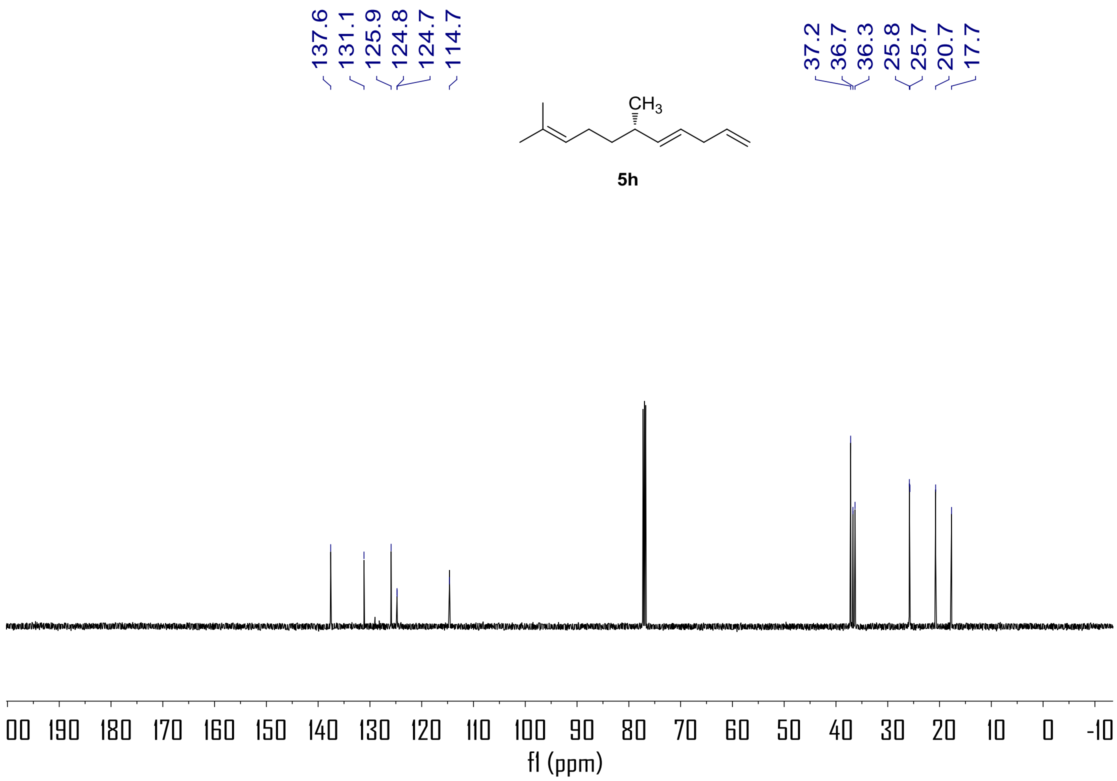


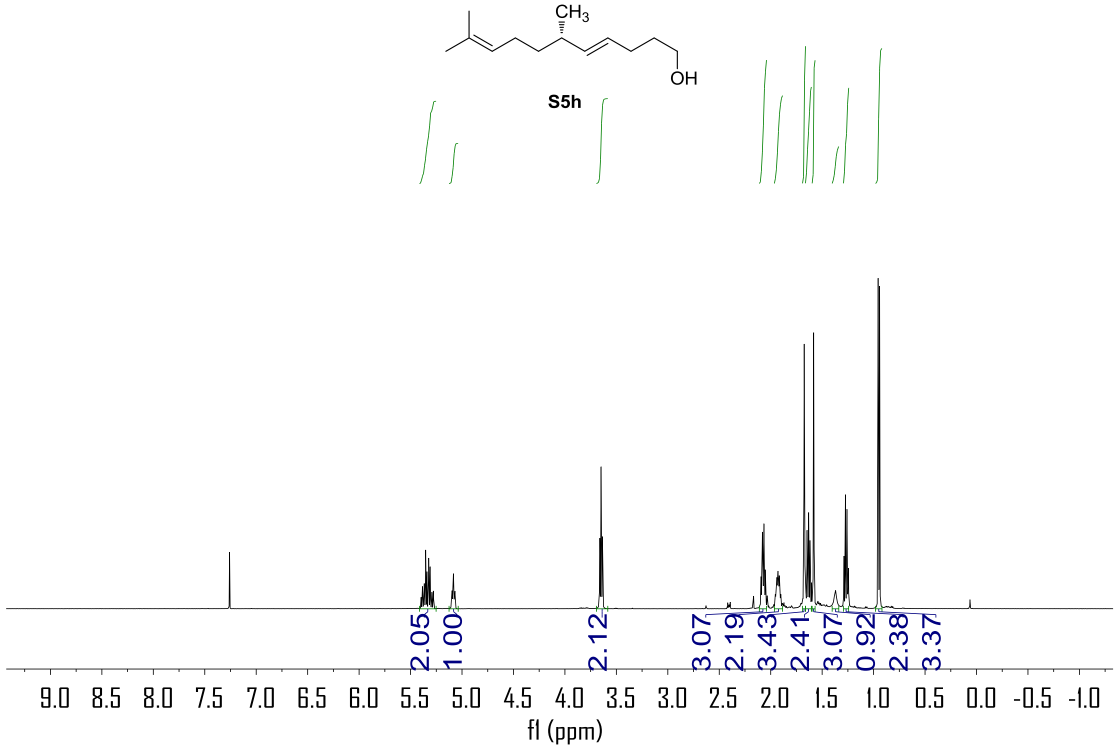
OH
H_3C
Si
S5g
2.06
2.88
1.01
1.00
2.09
2.15
1.26
2.20
1.02
3.26
6.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

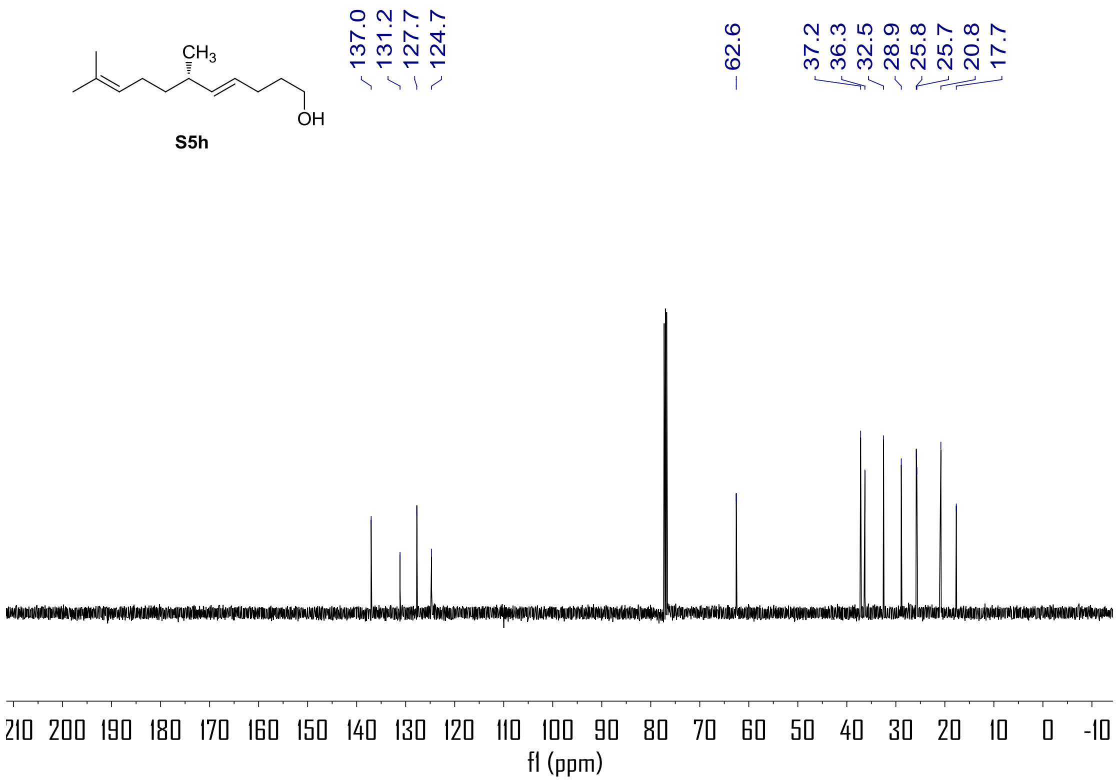


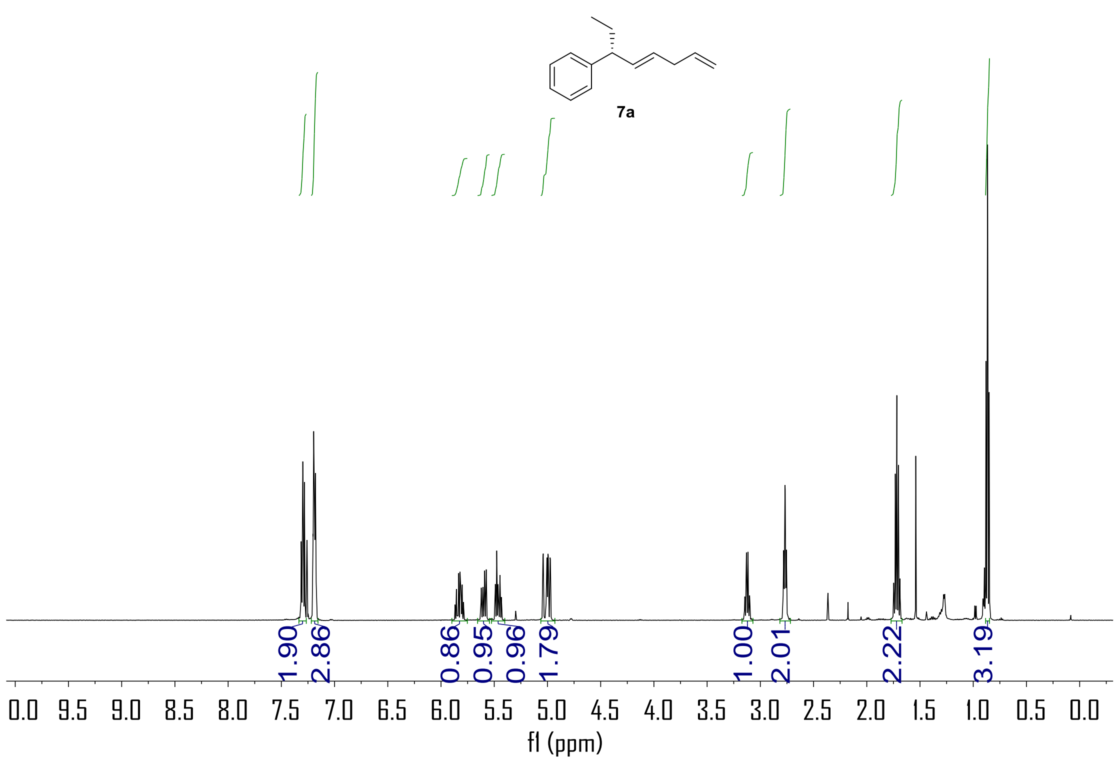
138.0
134.0
133.2
128.9
127.6
126.0
62.6
32.8
29.2
25.5
13.9
-4.9
-5.3
OH
H_3C
Si
S5g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

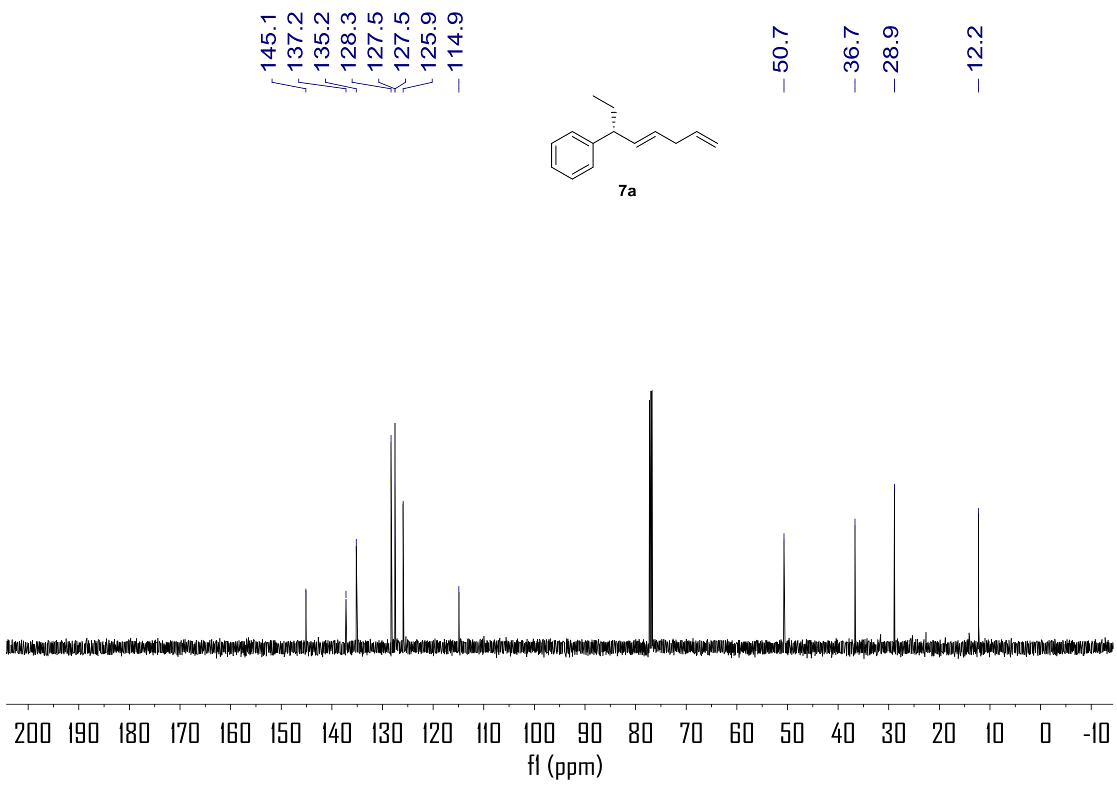

CH3
5h
0.89
1.90
0.94
0.93
0.92
1.99
1.00
2.08
3.01
2.83
2.21
3.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

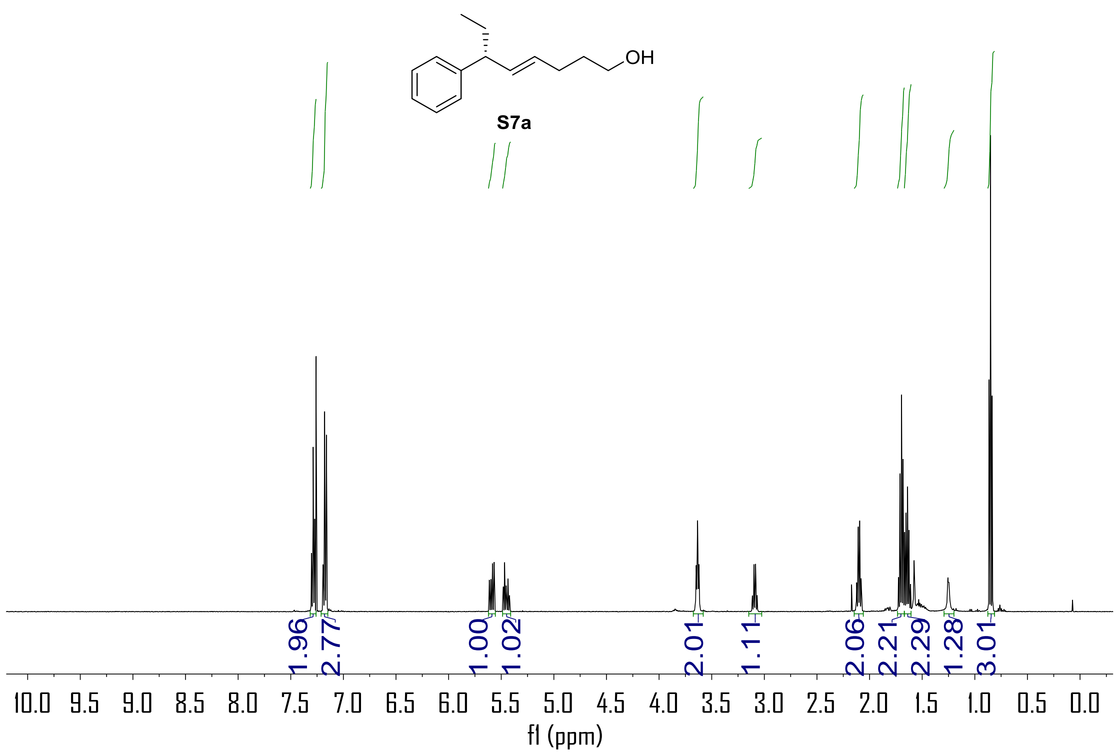

137.6
131.1
125.9
124.8
124.7
114.7
37.2
36.7
36.3
25.8
25.7
20.7
17.7
CH3
5h
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

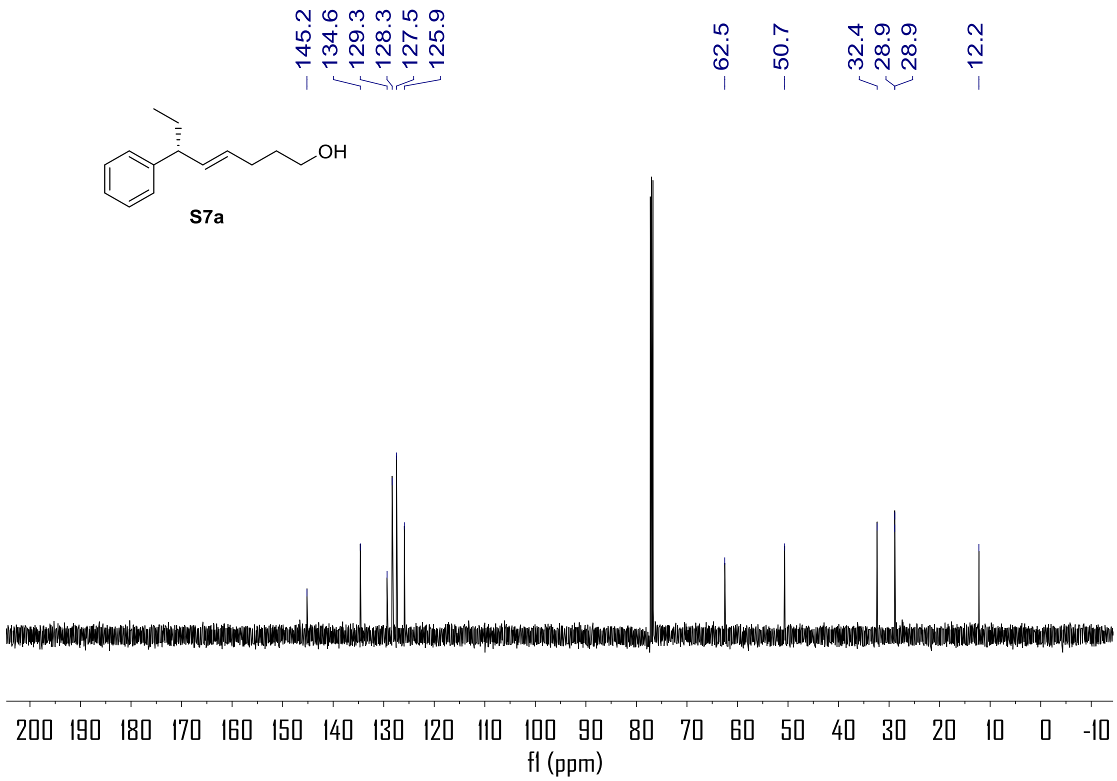

CH3
OH
S5h
2.05
1.00
2.12
3.07
2.19
3.43
2.41
3.07
0.92
2.38
3.37
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

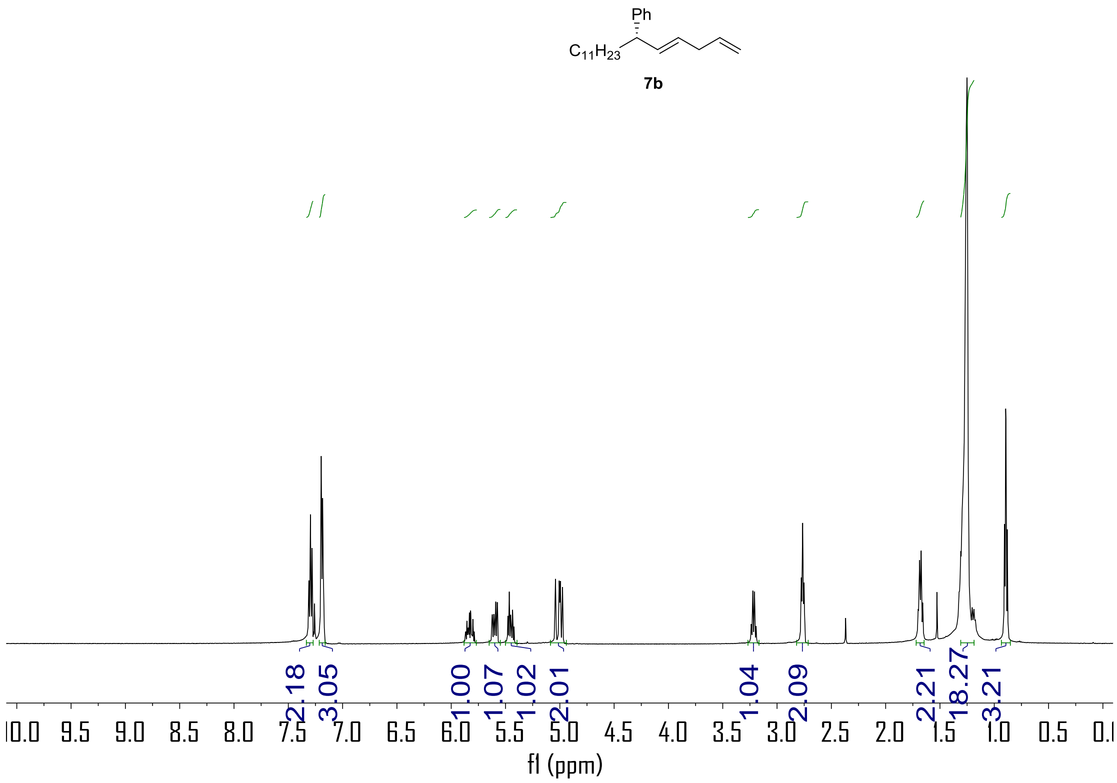

137.0
131.2
127.7
124.7
62.6
37.2
36.3
32.5
28.9
25.8
25.7
20.8
17.7
CH3
OH
S5h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

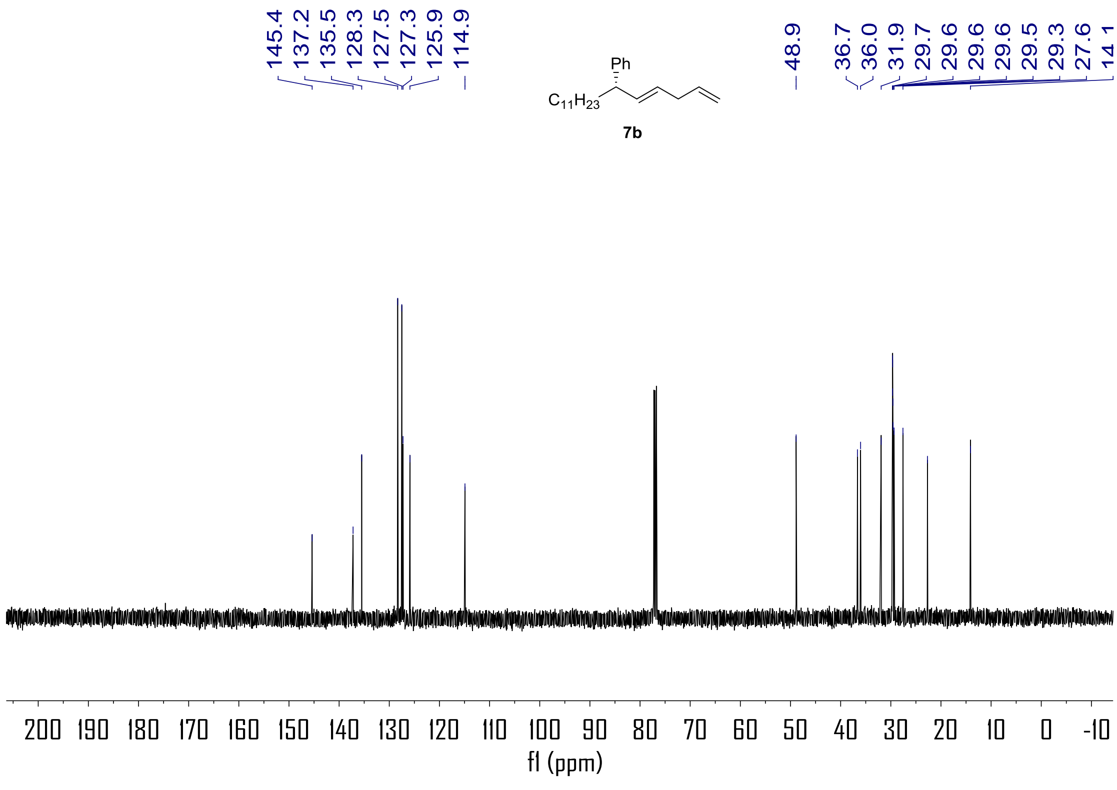

7a
1.90
2.86
0.86
0.95
0.96
1.79
1.00
2.01
2.22
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

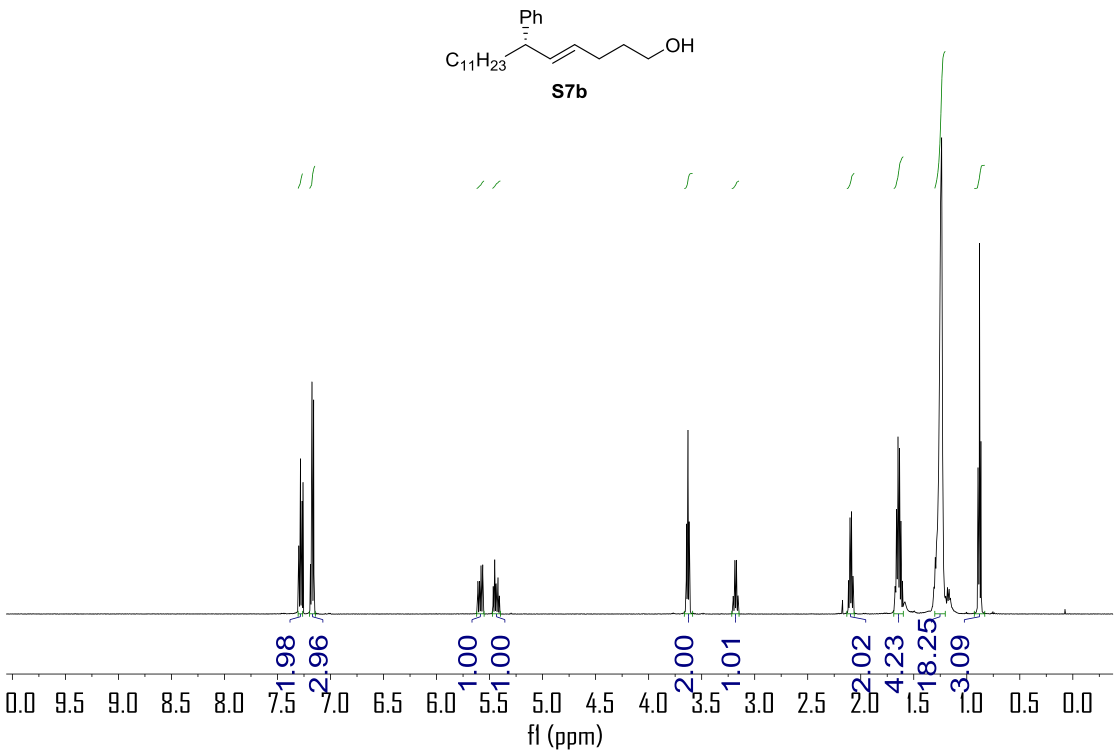

145.1
137.2
135.2
128.3
127.5
127.5
125.9
114.9
50.7
36.7
28.9
12.2
7a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

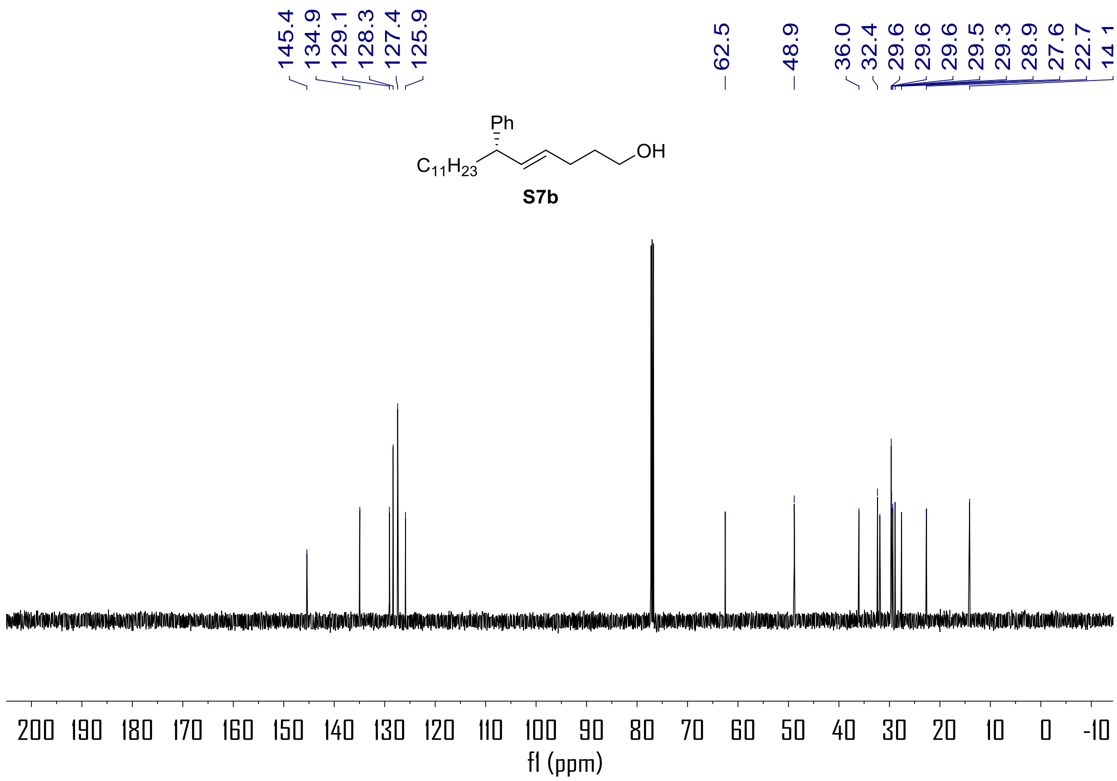

OH
S7a
1.96
2.77
1.00
1.02
2.01
1.11
2.06
2.21
2.29
1.28
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

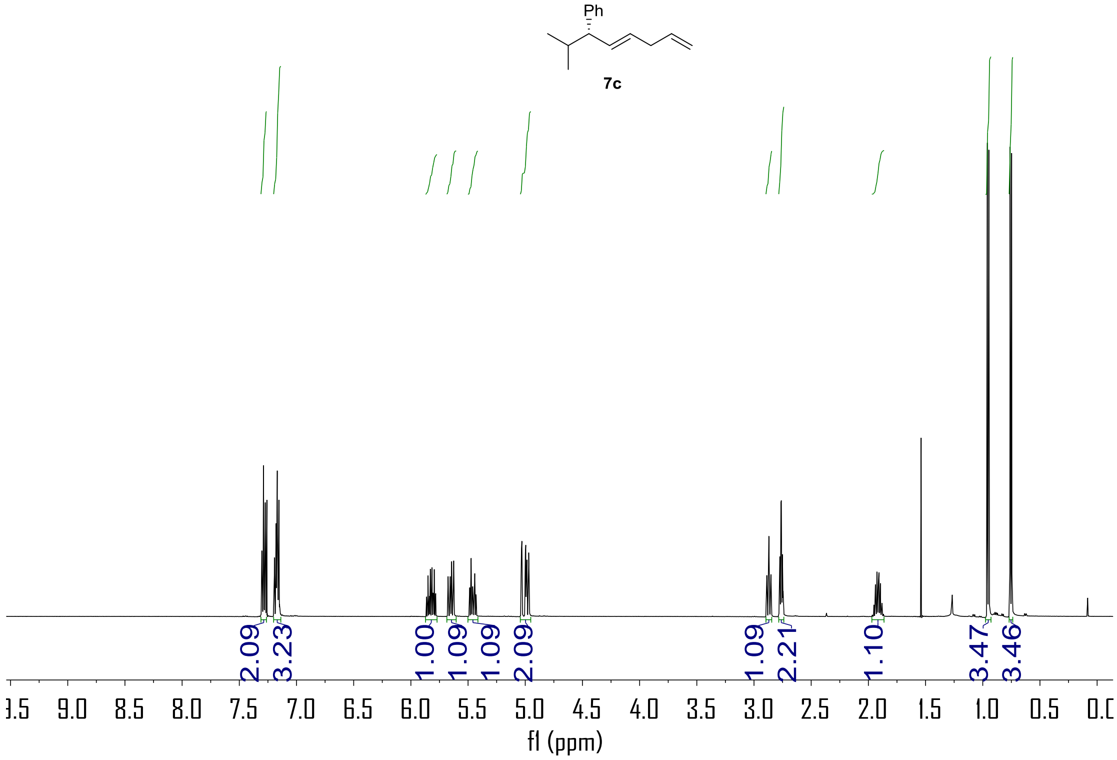

145.2
134.6
129.3
128.3
127.5
125.9
62.5
50.7
32.4
28.9
28.9
12.2
OH
S7a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
$C_{11}H_{23}$
7b
2.18
3.05
1.00
1.07
1.02
2.01
1.04
2.09
2.21
18.27
3.21
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

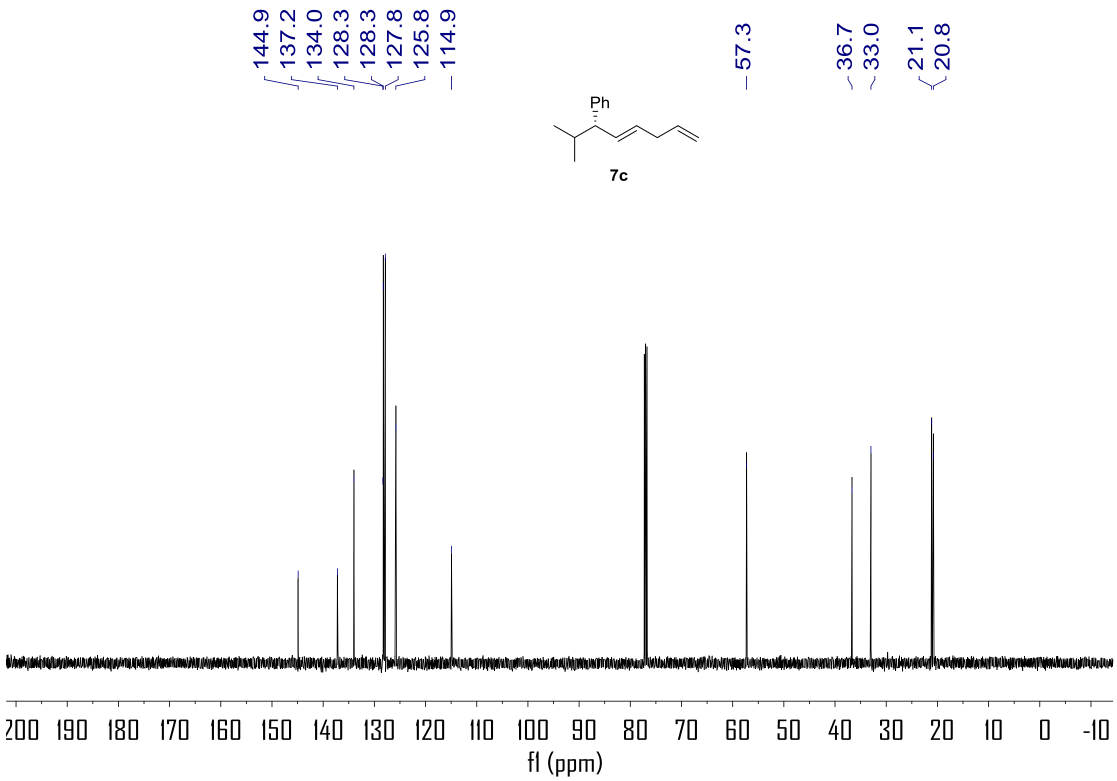

145.4
137.2
135.5
128.3
127.5
127.3
125.9
114.9
Ph
$C_{11}H_{23}$
7b
48.9
36.7
36.0
31.9
29.7
29.6
29.6
29.6
29.5
29.3
27.6
14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
C11H23
OH
S7b
1.98
2.96
1.00
1.00
2.00
1.01
2.02
4.23
18.25
3.09
f1 (ppm)

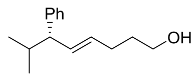

145.4
134.9
129.1
128.3
127.4
125.9
62.5
48.9
36.0
32.4
29.6
29.6
29.6
29.5
29.3
28.9
27.6
22.7
14.1
Ph
C11H23
OH
S7b
f1 (ppm)



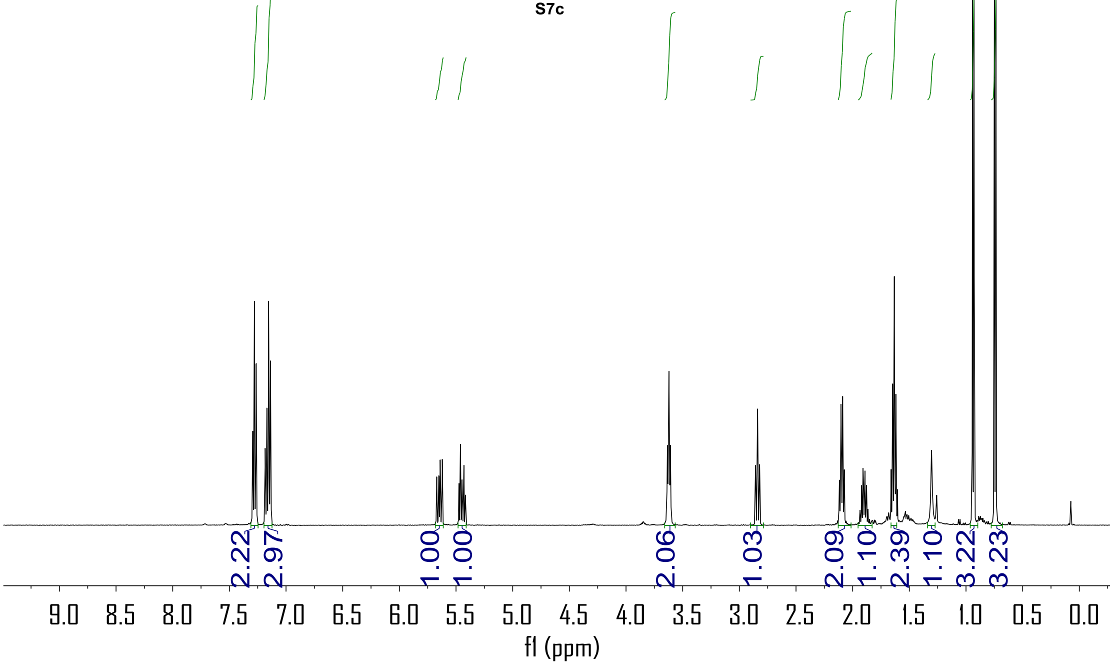
Ph
7c
2.09
3.23
1.00
1.09
1.09
2.09
1.09
2.21
1.10
3.47
3.46
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

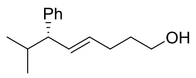


144.9
137.2
134.0
128.3
128.3
127.8
125.8
114.9
57.3
36.7
33.0
21.1
20.8
Ph
7c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

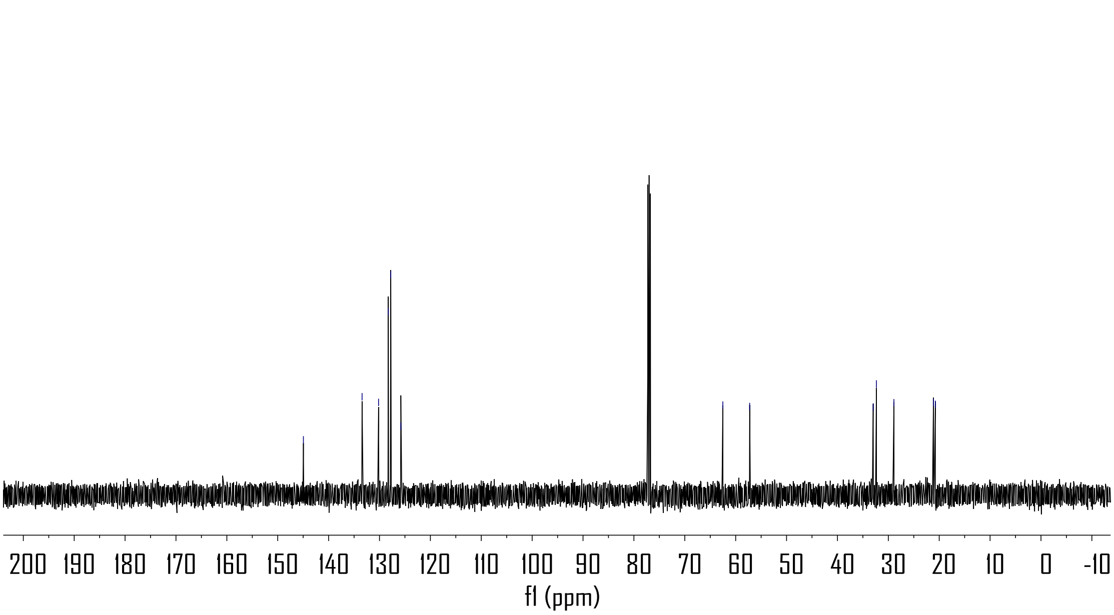

Ph
OH

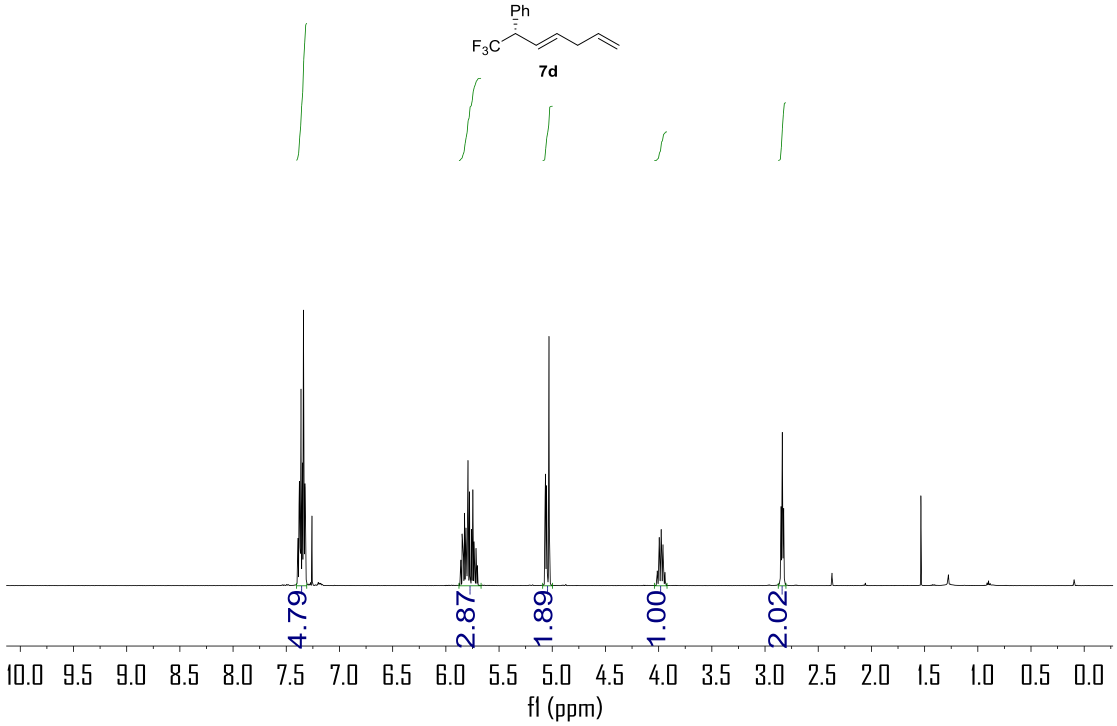
S7c

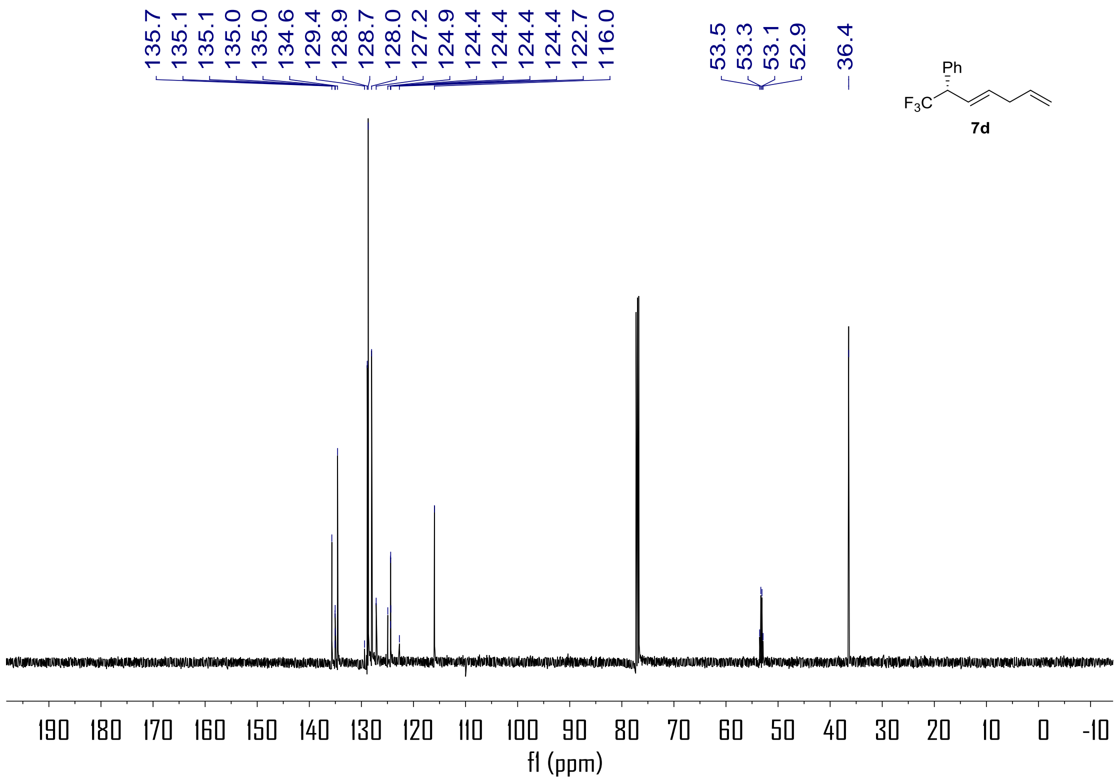

2.22
2.97
1.00
1.00
2.06
1.03
2.09
1.10
2.39
1.10
3.22
3.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

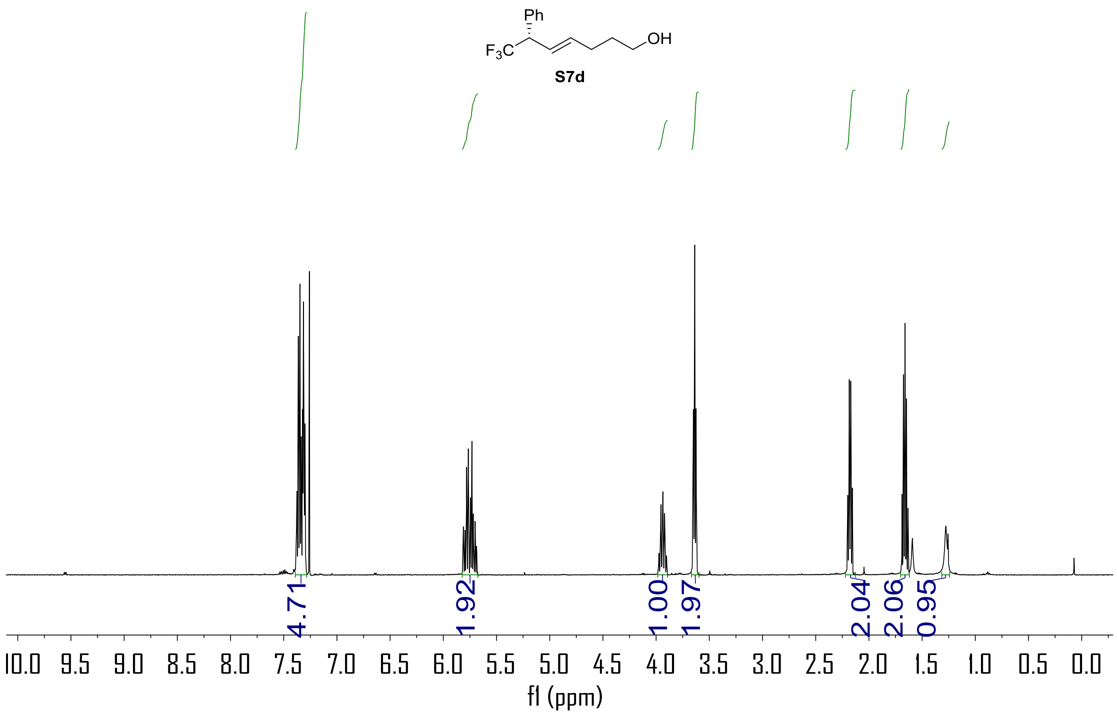

Ph
OH

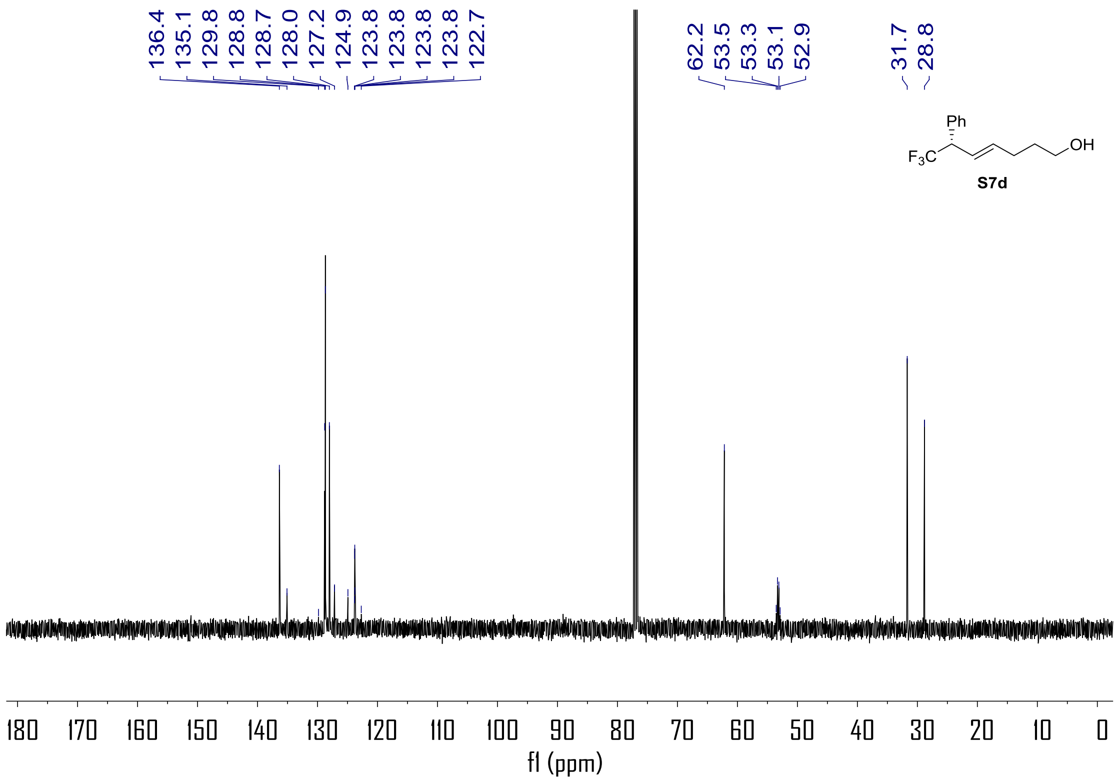
S7c

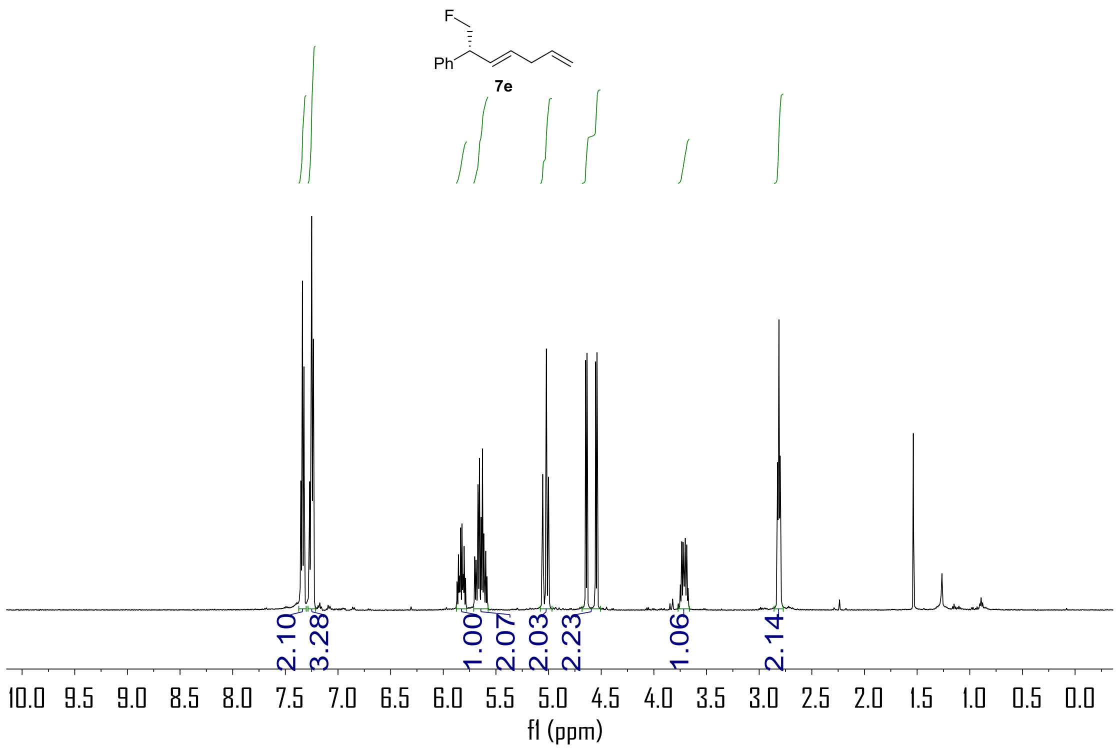

145.0
133.4
130.2
128.3
127.8
125.8
62.5
57.3
33.0
32.3
28.9
21.1
20.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

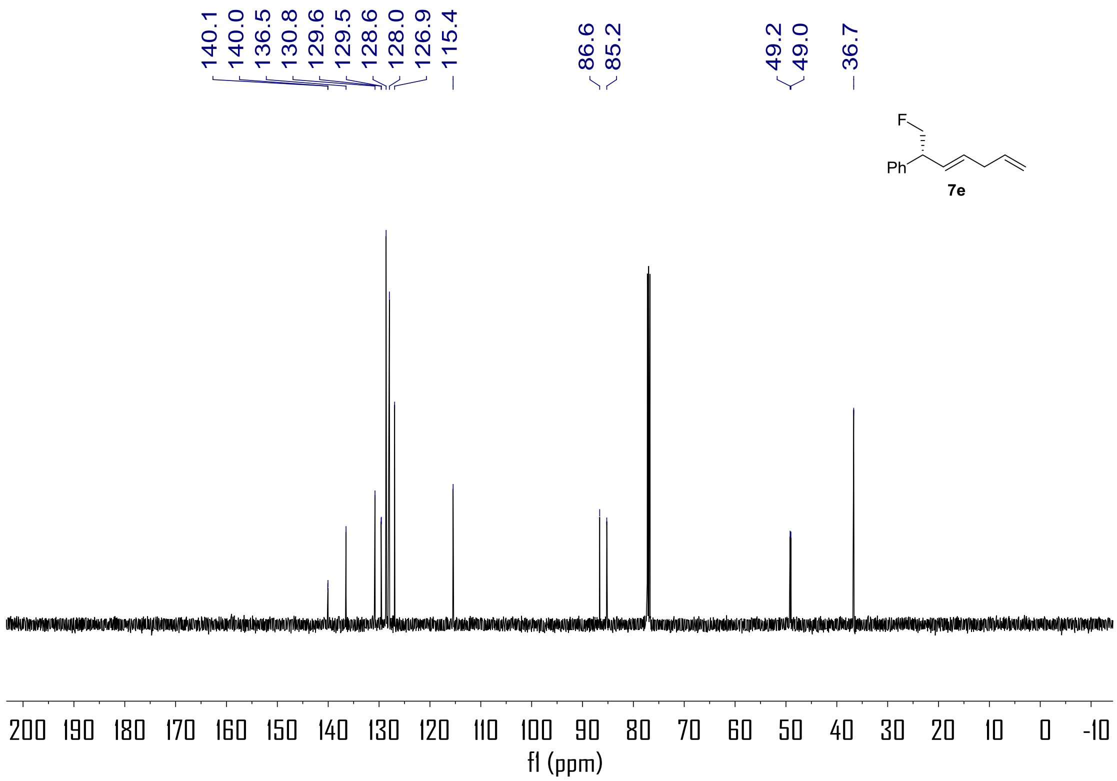

Ph
F3C
7d
4.79
2.87
1.89
1.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

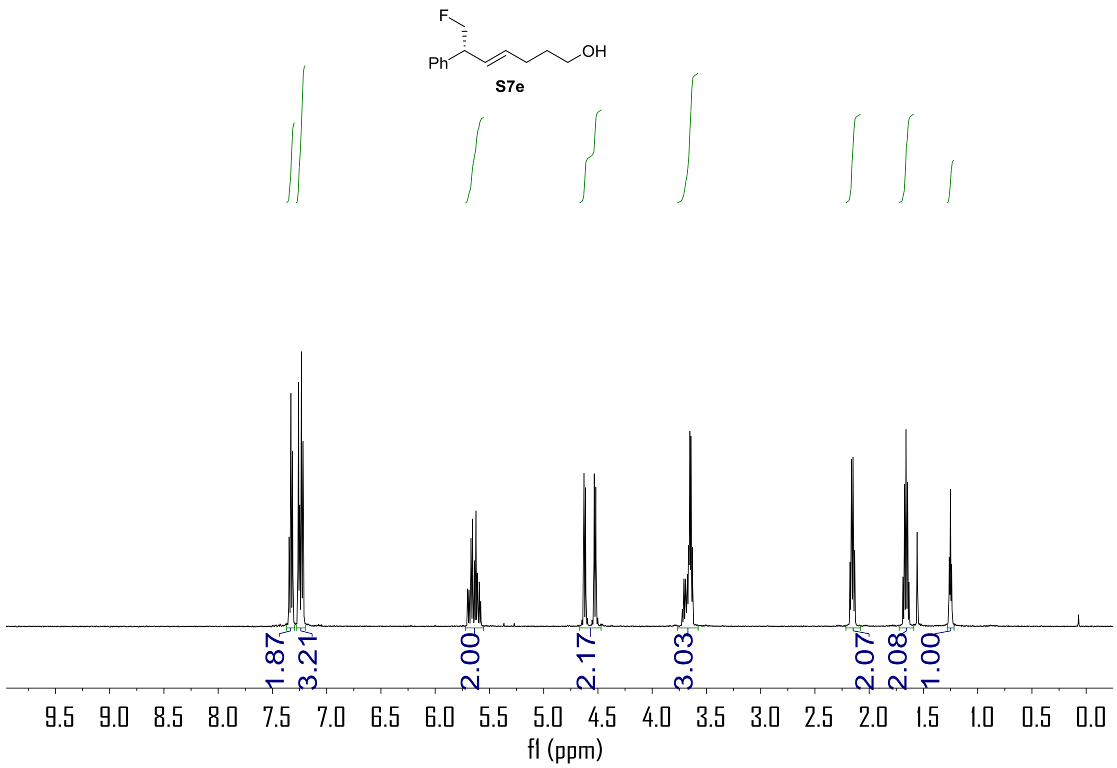

135.7
135.1
135.1
135.0
135.0
134.6
129.4
128.9
128.7
128.0
127.2
124.9
124.4
124.4
124.4
124.4
122.7
116.0
53.5
53.3
53.1
52.9
36.4
Ph
F3C
7d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

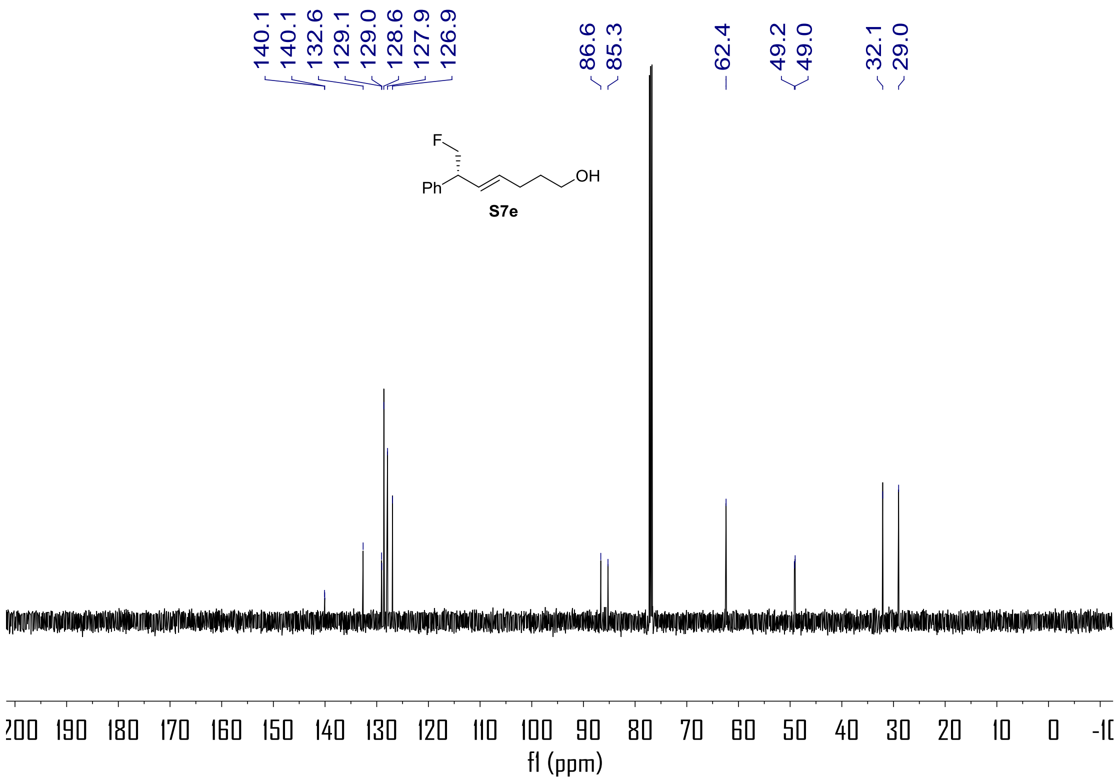

Ph
F_3C
OH
S7d
4.71
1.92
1.00
1.97
2.04
2.06
0.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

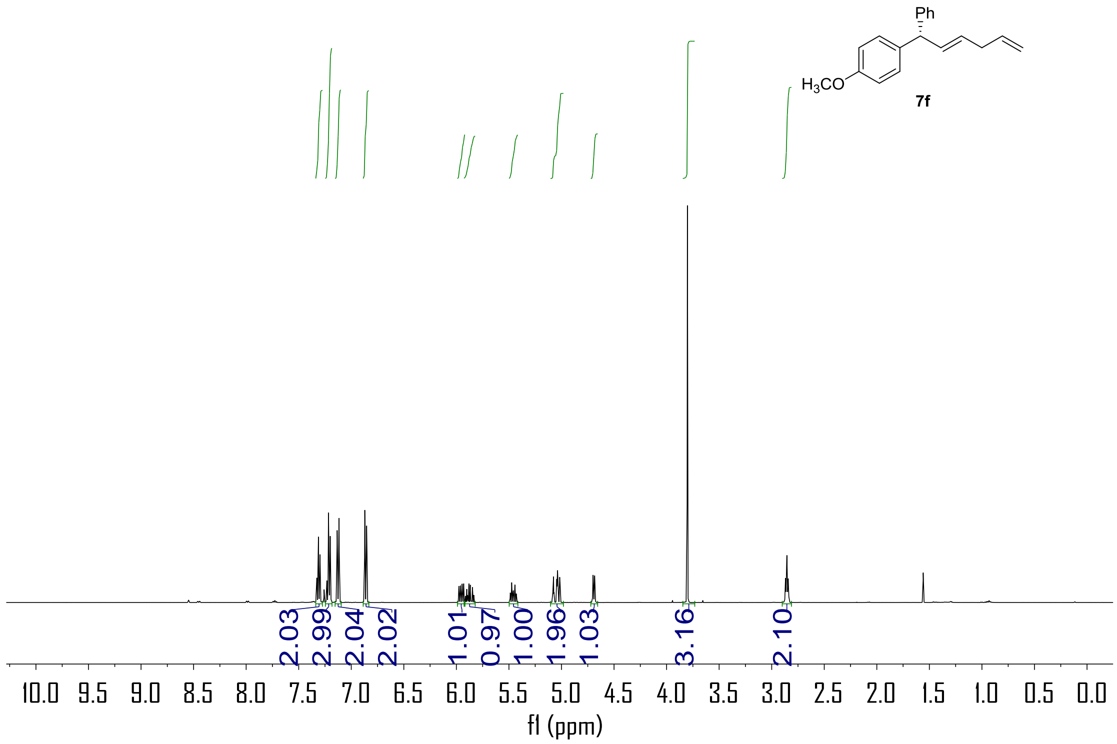

136.4
135.1
129.8
128.8
128.7
128.0
127.2
124.9
123.8
123.8
123.8
123.8
122.7
62.2
53.5
53.3
53.1
52.9
31.7
28.8
Ph
F_3C
OH
S7d
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

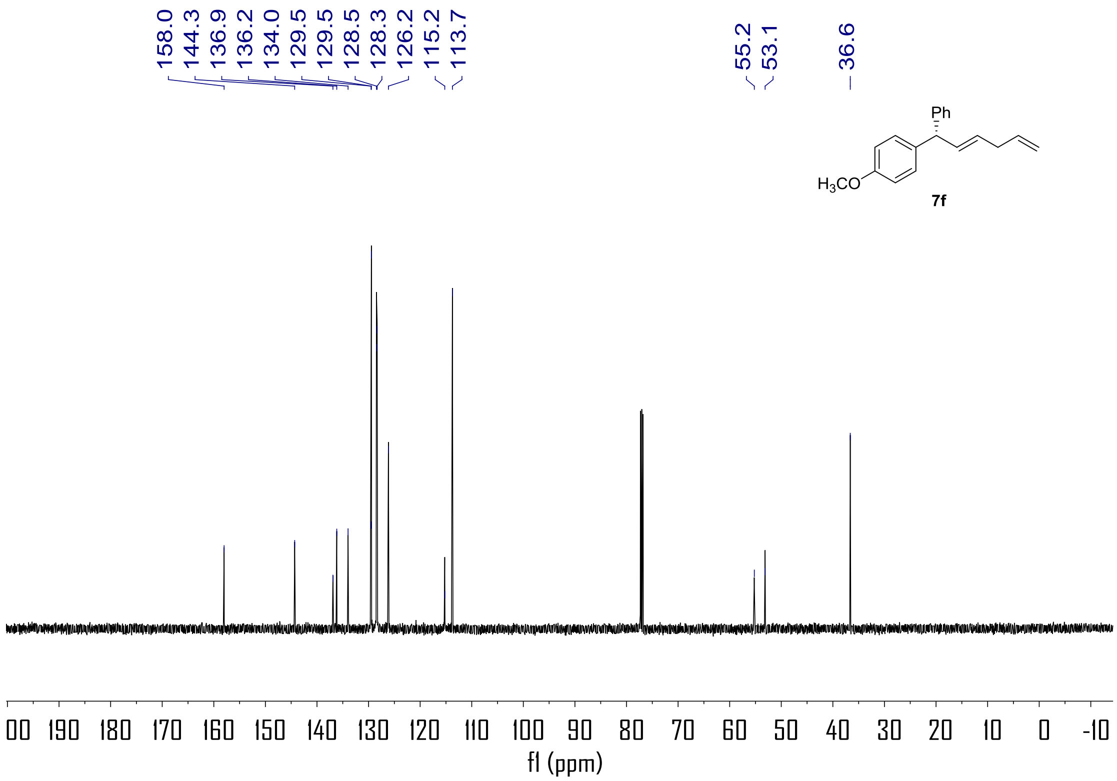

F
Ph
7e
2.10
3.28
1.00
2.07
2.03
2.23
1.06
2.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

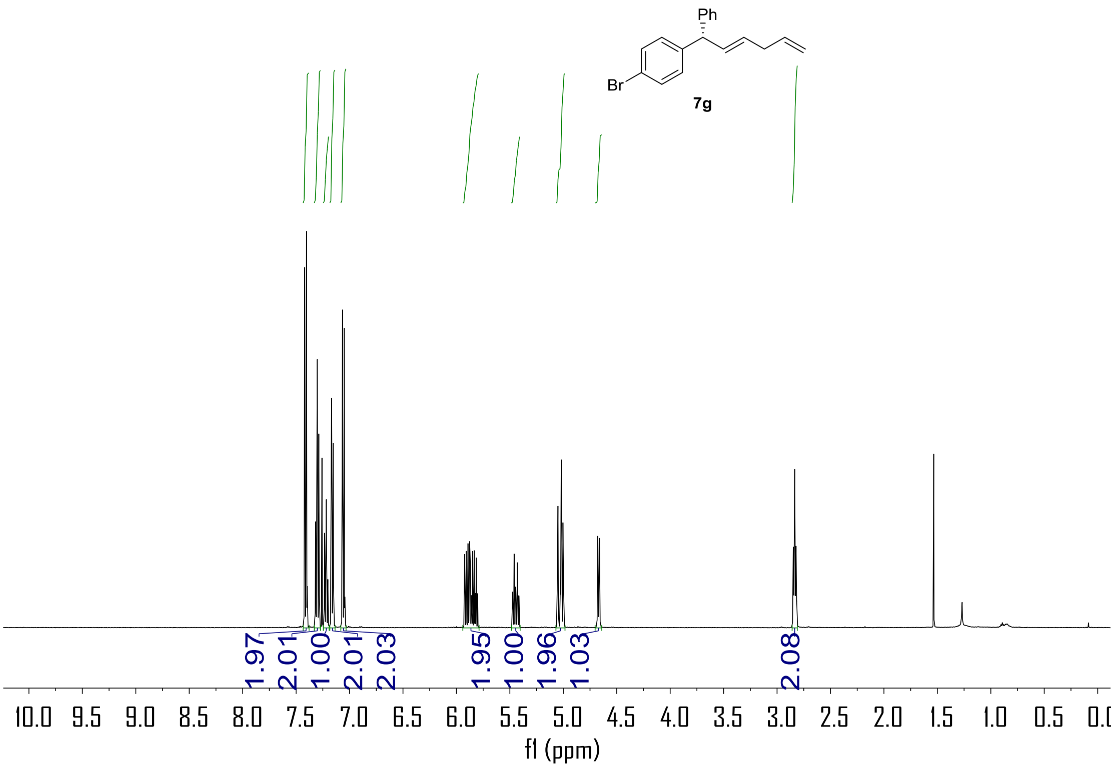

140.1
140.0
136.5
130.8
129.6
129.5
128.6
128.0
126.9
115.4
86.6
85.2
49.2
49.0
36.7
F
Ph
7e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

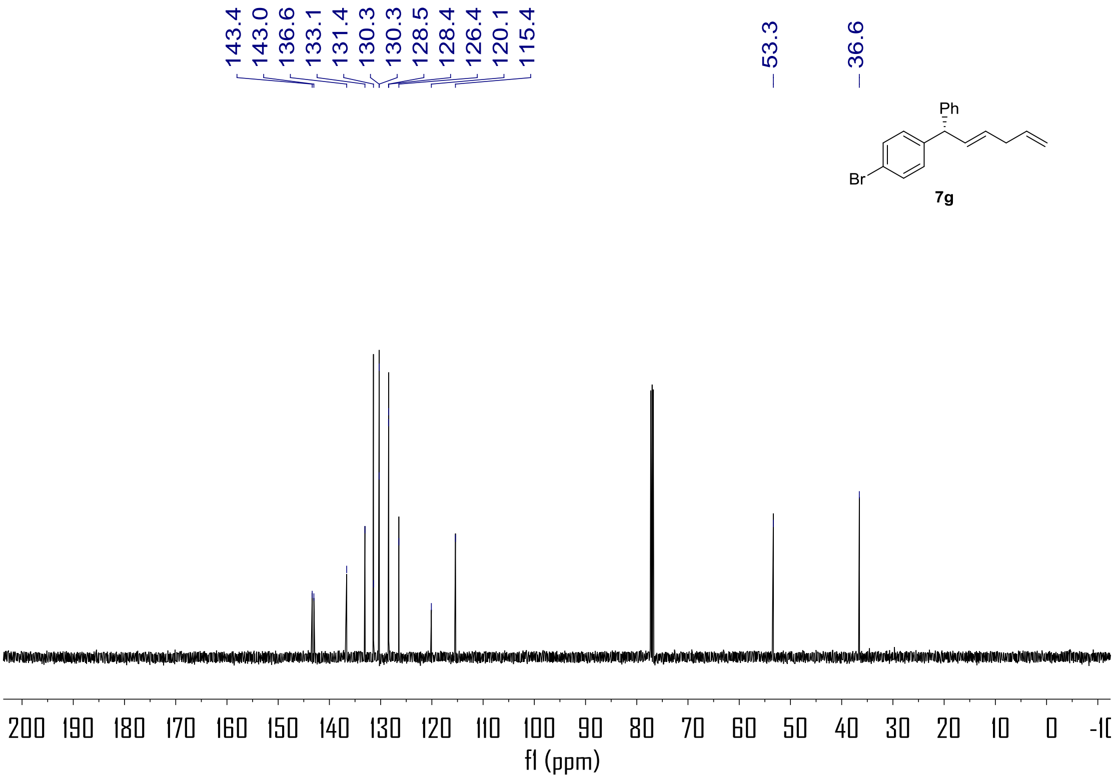

F
Ph
OH
S7e
1.87
3.21
2.00
2.17
3.03
2.07
2.08
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

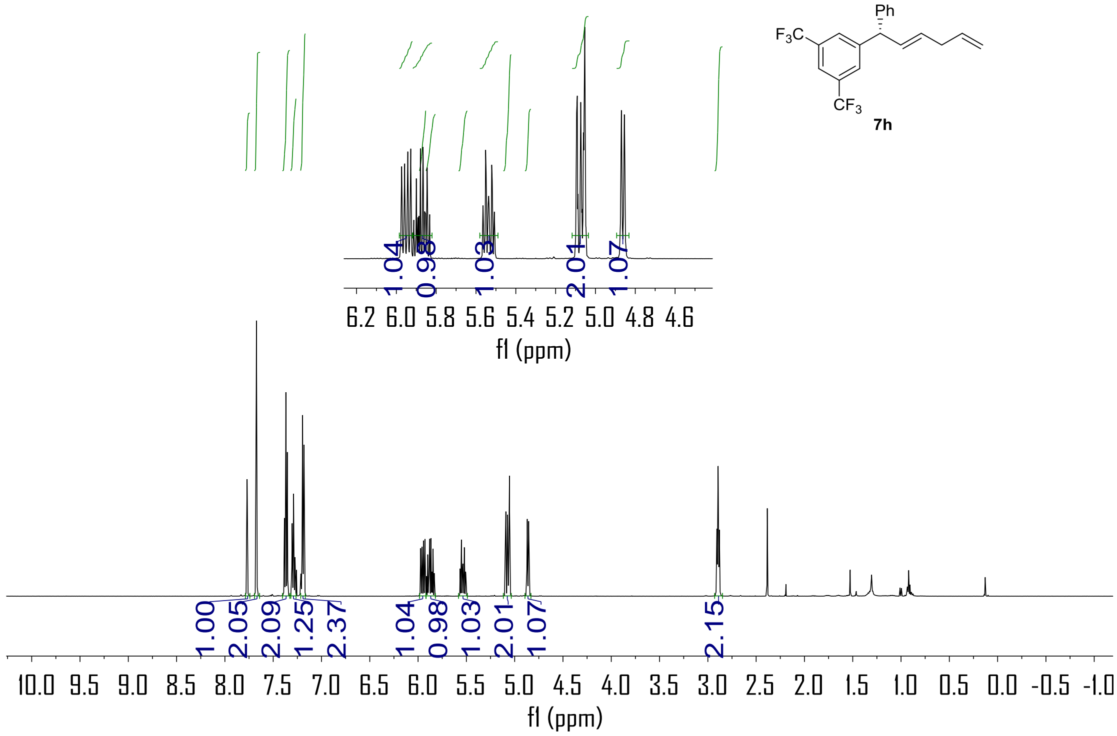

140.1
140.1
132.6
129.1
129.0
128.6
127.9
126.9
86.6
85.3
62.4
49.2
49.0
32.1
29.0
F
Ph
OH
S7e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

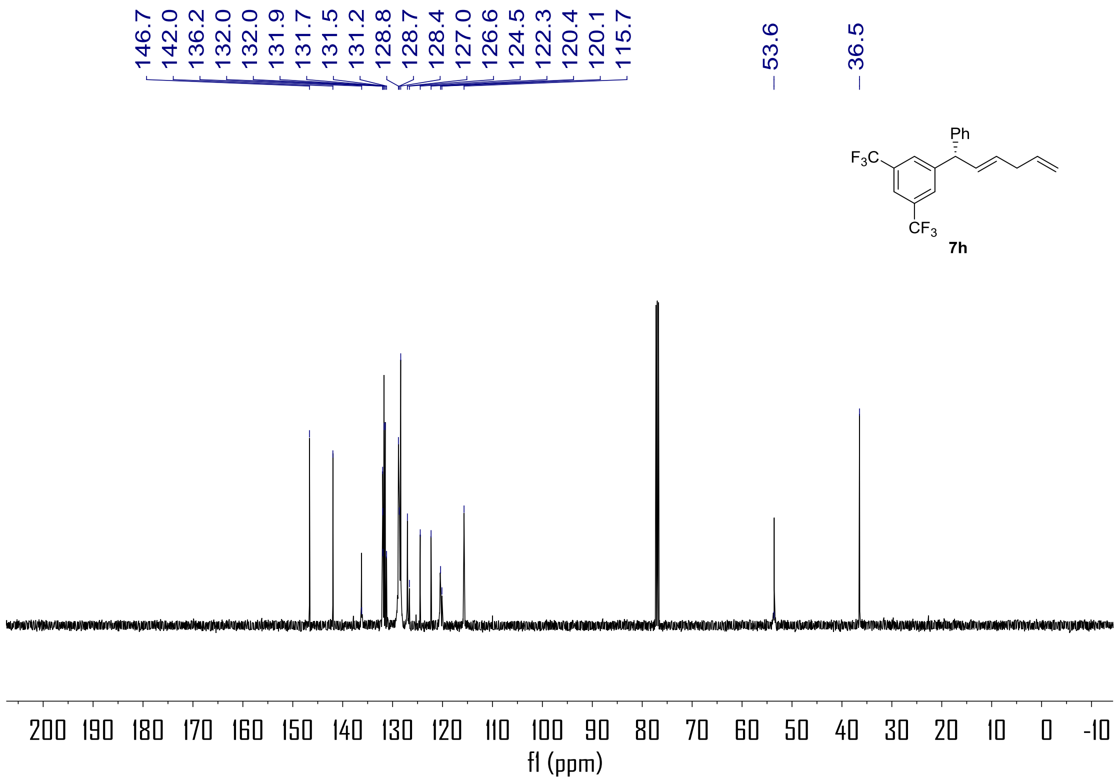

Ph
H3CO
7f
2.03
2.99
2.04
2.02
1.01
0.97
1.00
1.96
1.03
3.16
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

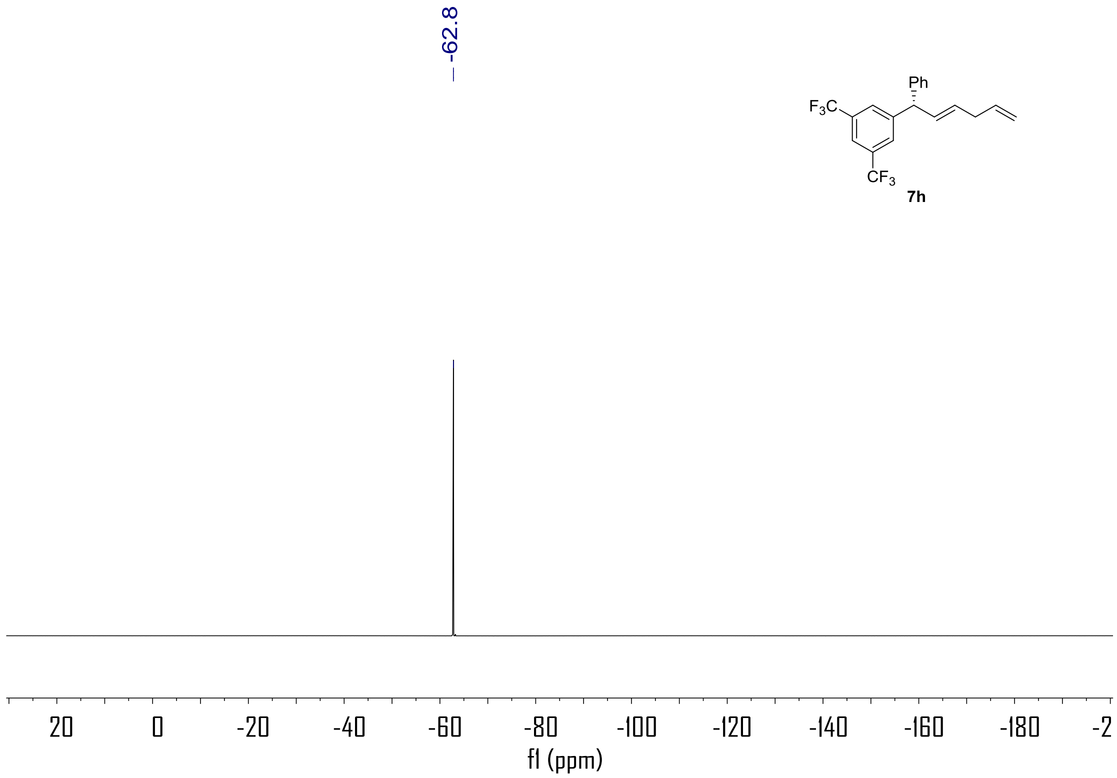

158.0
144.3
136.9
136.2
134.0
129.5
129.5
128.5
128.3
126.2
115.2
113.7
55.2
53.1
36.6
Ph
H3CO
7f
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Br
7g
1.97
2.01
1.00
2.01
2.03
1.95
1.00
1.96
1.03
2.08
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

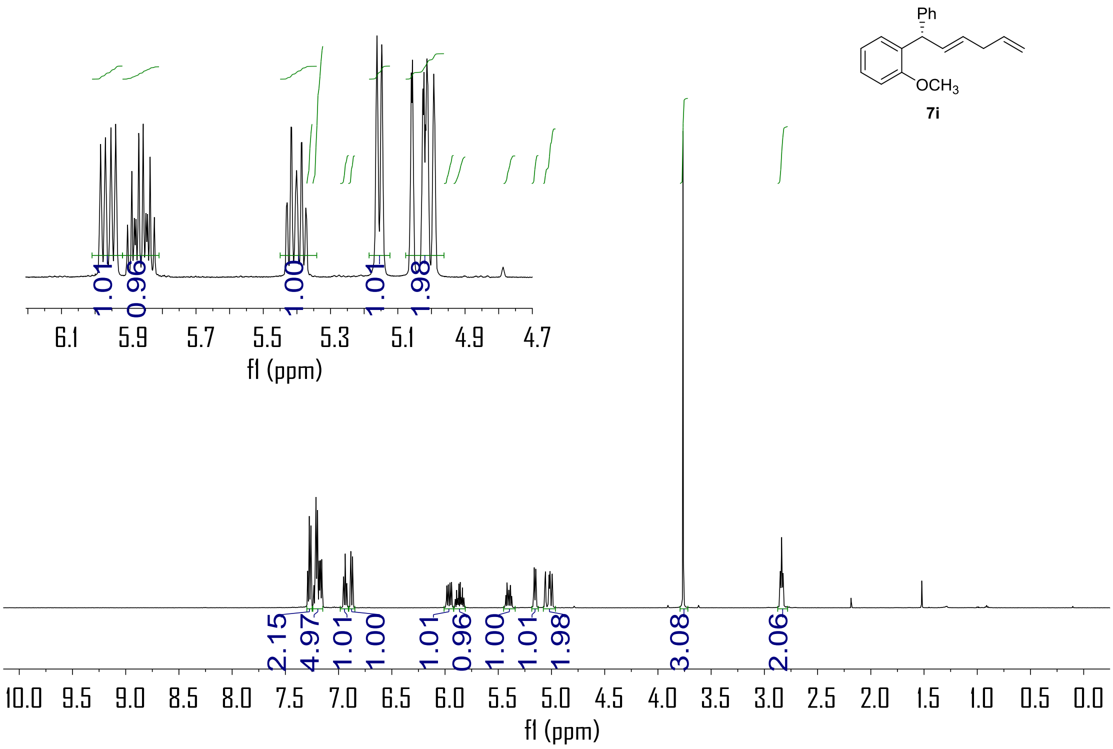

143.4
143.0
136.6
133.1
131.4
130.3
130.3
128.5
128.4
126.4
120.1
115.4
53.3
36.6
Ph
Br
7g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

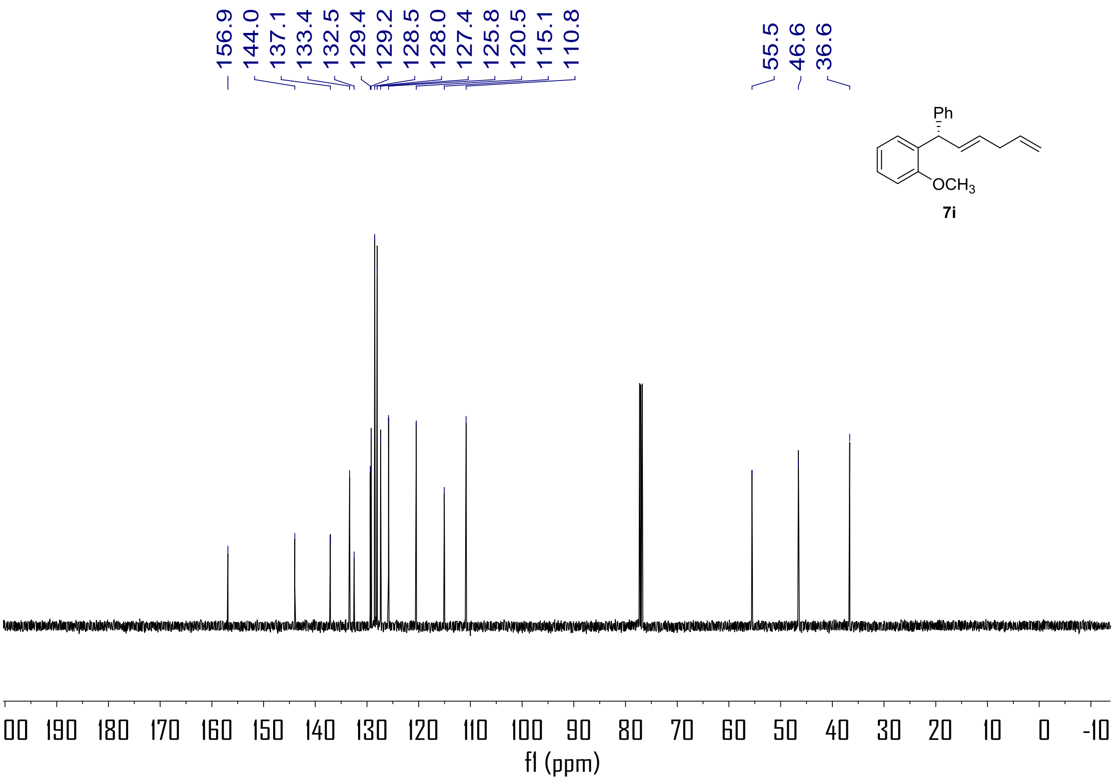

Ph
F3C
CF3
7h
1.04
0.98
1.03
2.01
1.07
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6
f1 (ppm)
1.00
2.05
2.09
1.25
2.37
1.04
0.98
1.03
2.01
1.07
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

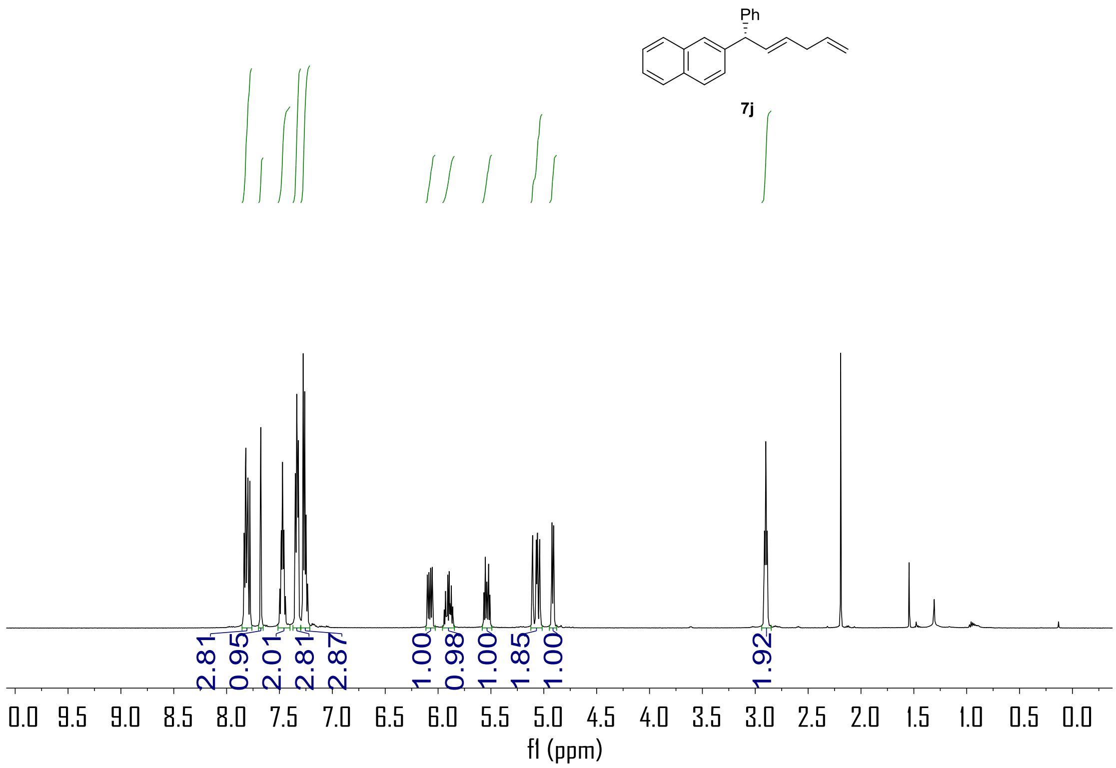

146.7
142.0
136.2
132.0
132.0
131.9
131.7
131.5
131.2
128.8
128.7
128.4
127.0
126.6
124.5
122.3
120.4
120.1
115.7
53.6
36.5
Ph
F3C
CF3
7h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

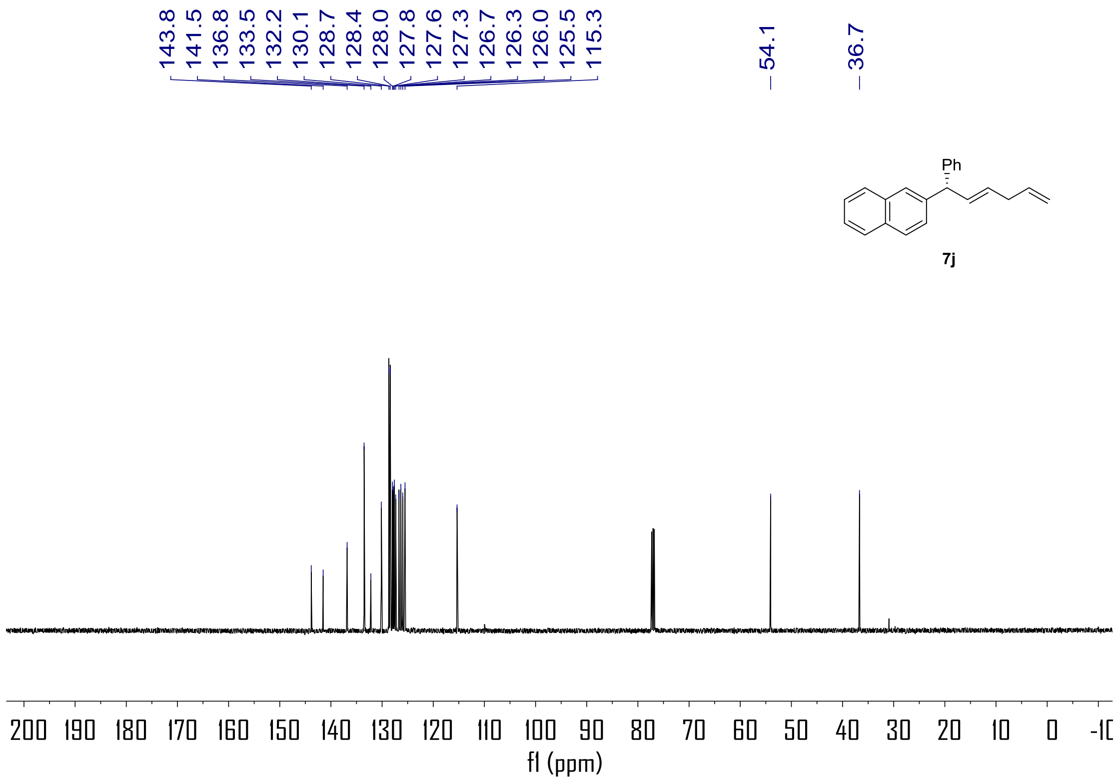


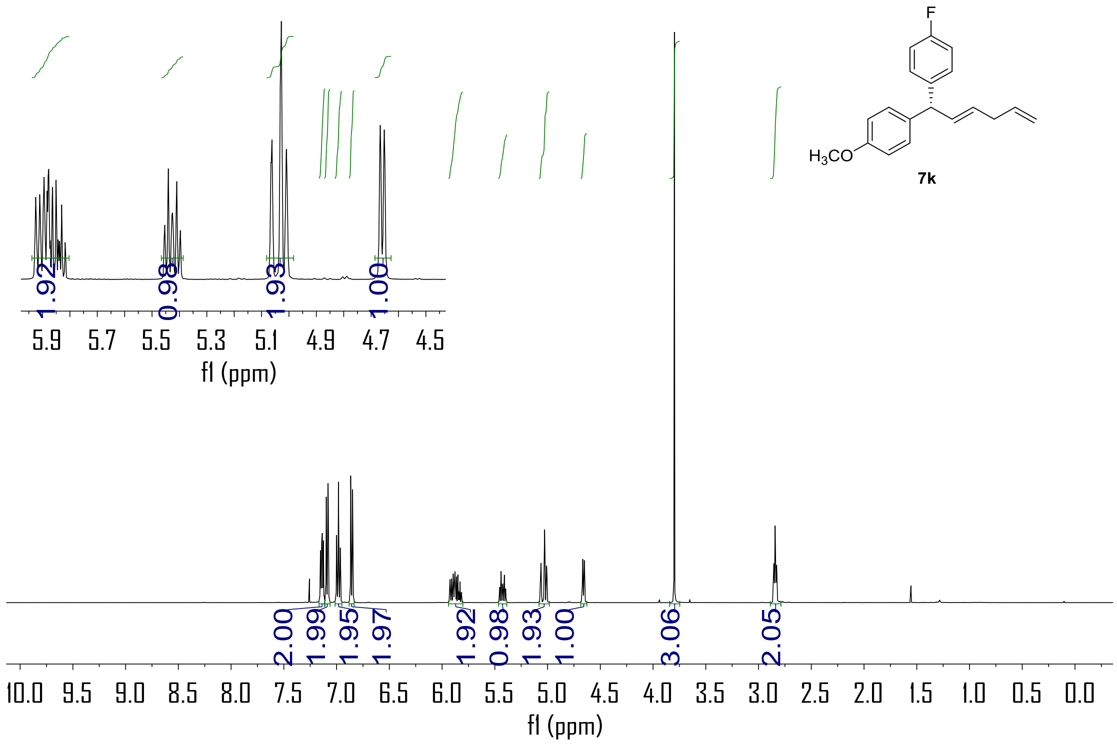
-62.8
Ph
F3C
CF3
7h
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

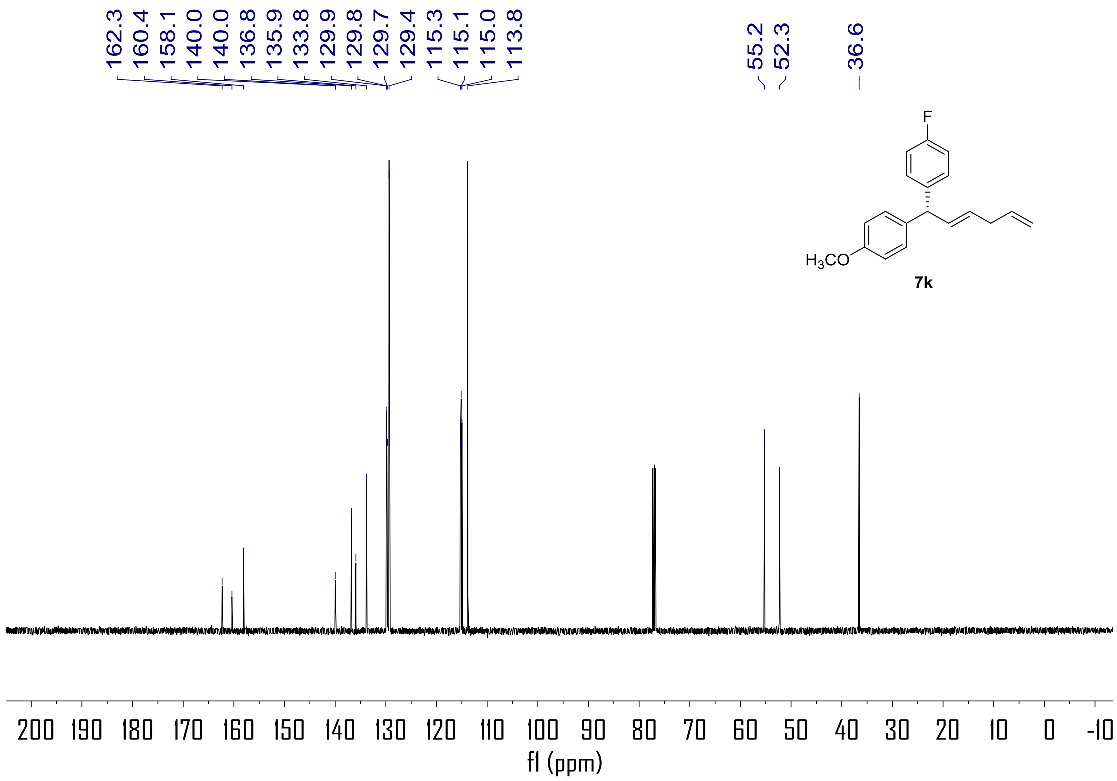

Ph
OCH3
7i
1.01
0.96
1.00
1.01
1.98
6.1 5.9 5.7 5.5 5.3 5.1 4.9 4.7
f1 (ppm)
2.15
4.97
1.01
1.00
1.01
0.96
1.00
1.01
1.98
3.08
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

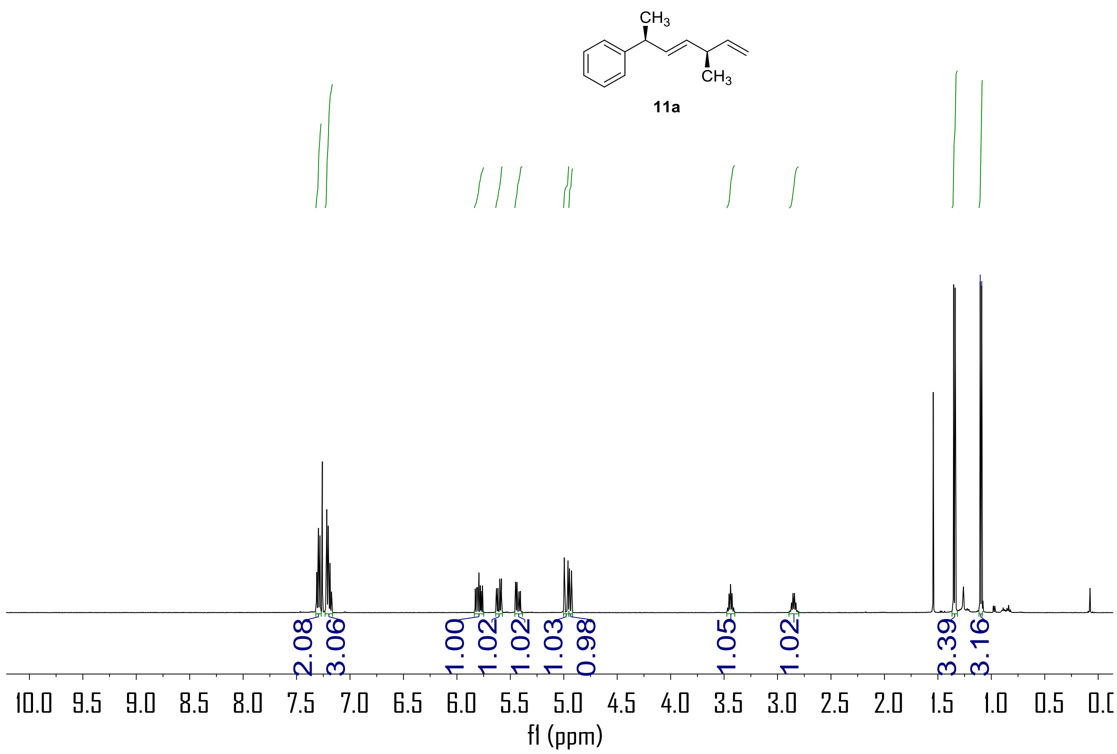

156.9
144.0
137.1
133.4
132.5
129.4
129.2
128.5
128.0
127.4
125.8
120.5
115.1
110.8
55.5
46.6
36.6
Ph
OCH3
7i
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

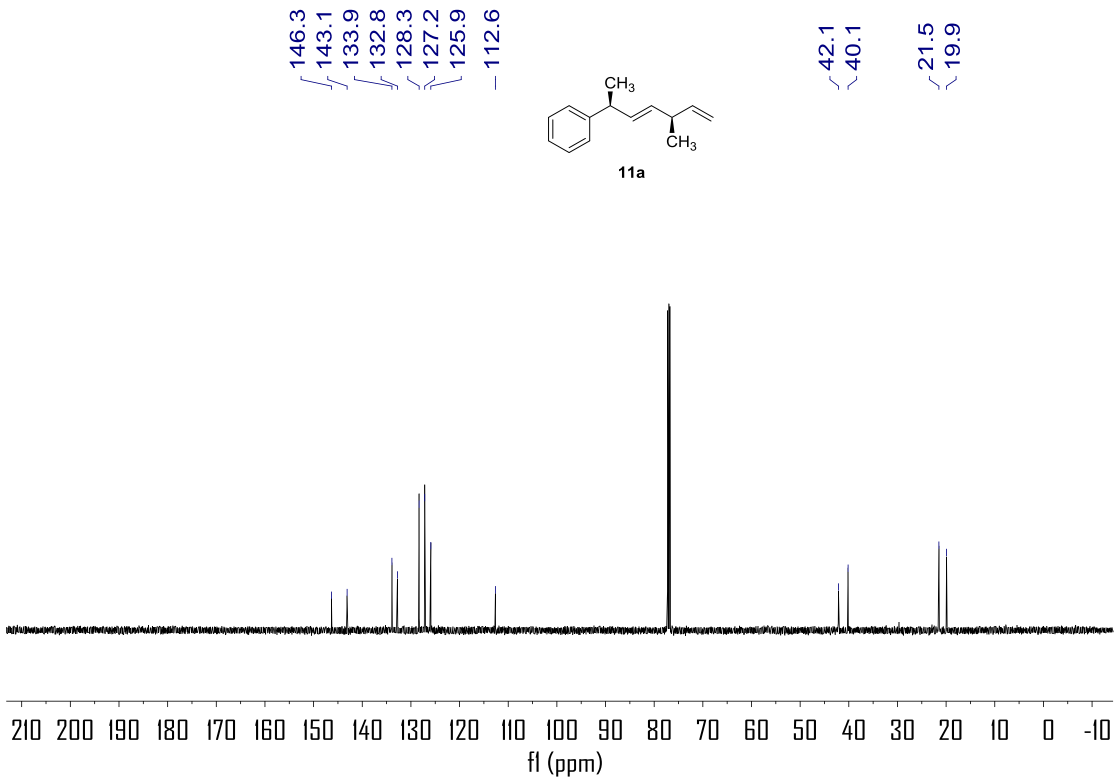

Ph
7j
2.81
0.95
2.01
2.81
2.87
1.00
0.98
1.00
1.85
1.00
1.92
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

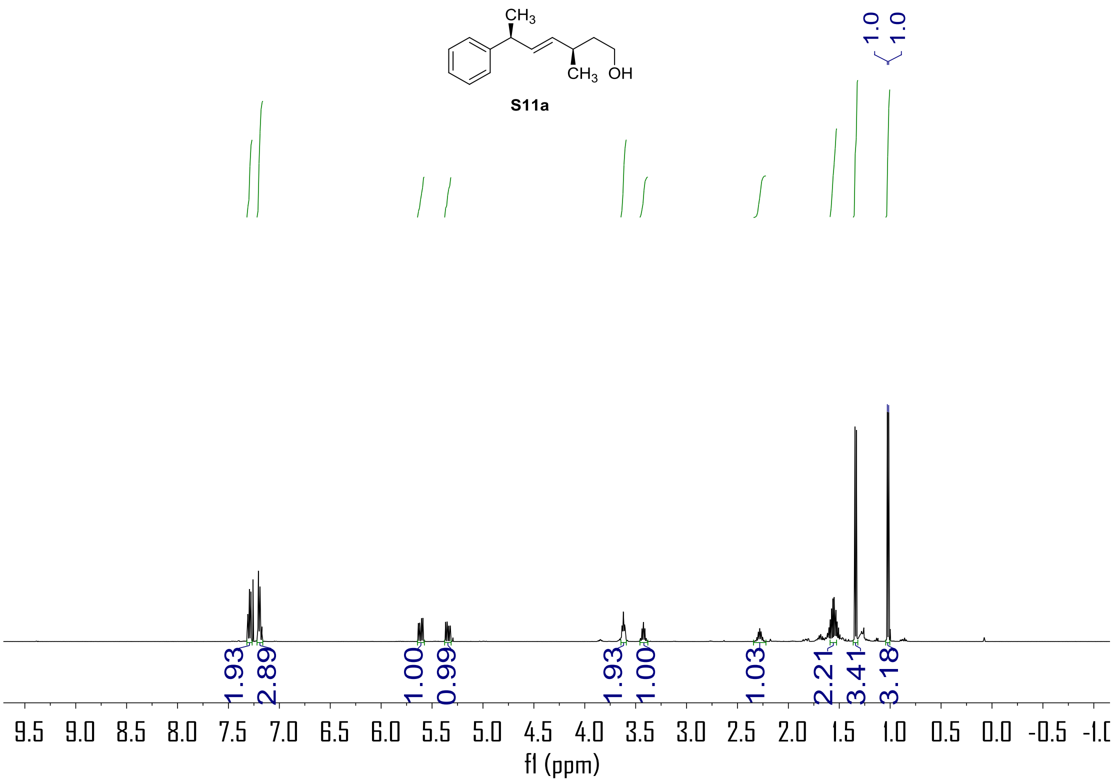

143.8
141.5
136.8
133.5
132.2
130.1
128.7
128.4
128.0
127.8
127.6
127.3
126.7
126.3
126.0
125.5
115.3
54.1
36.7
Ph
7j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1.92
0.98
1.93
1.00
5.9 5.7 5.5 5.3 5.1 4.9 4.7 4.5
f1 (ppm)
2.00
1.99
1.95
1.97
1.92
0.98
1.93
1.00
3.06
2.05
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)
F
H3CO
7k

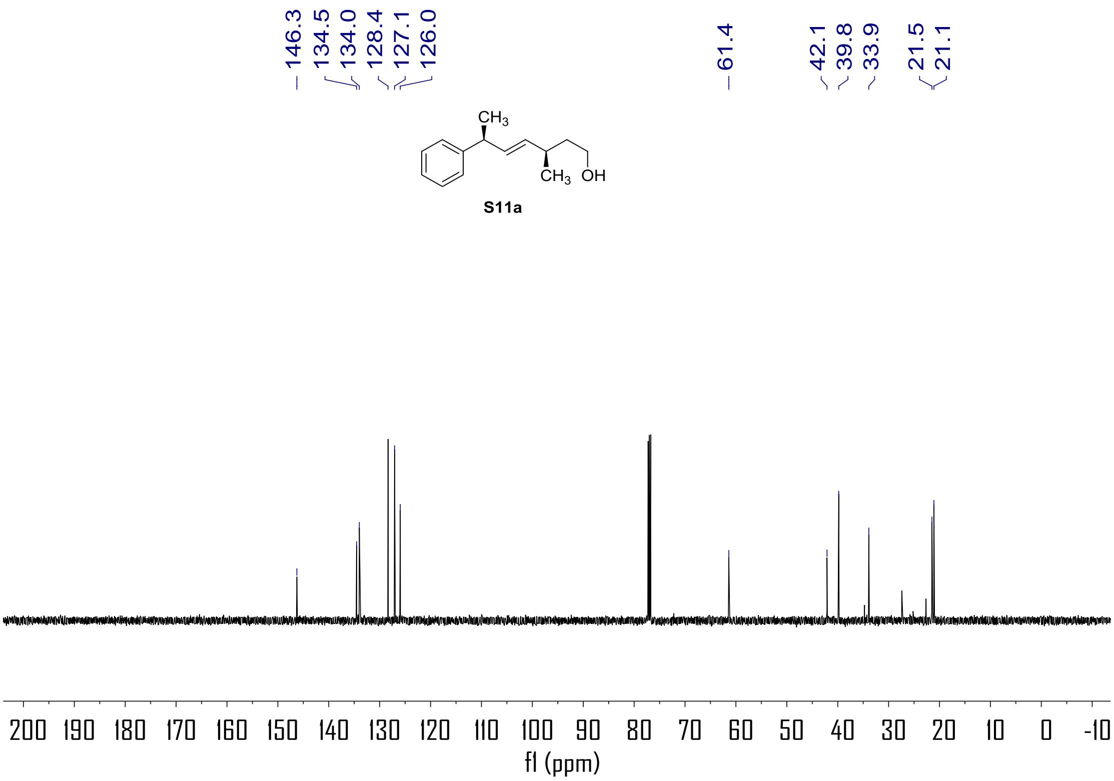

162.3
160.4
158.1
140.0
140.0
136.8
135.9
133.8
129.9
129.8
129.7
129.4
115.3
115.1
115.0
113.8
55.2
52.3
36.6
F
H3CO
7k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CH3
CH3
11a
2.08
3.06
1.00
1.02
1.02
1.03
0.98
1.05
1.02
3.39
3.16
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

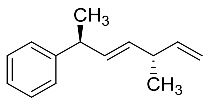

146.3
143.1
133.9
132.8
128.3
127.2
125.9
112.6
42.1
40.1
21.5
19.9
CH3
CH3
11a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



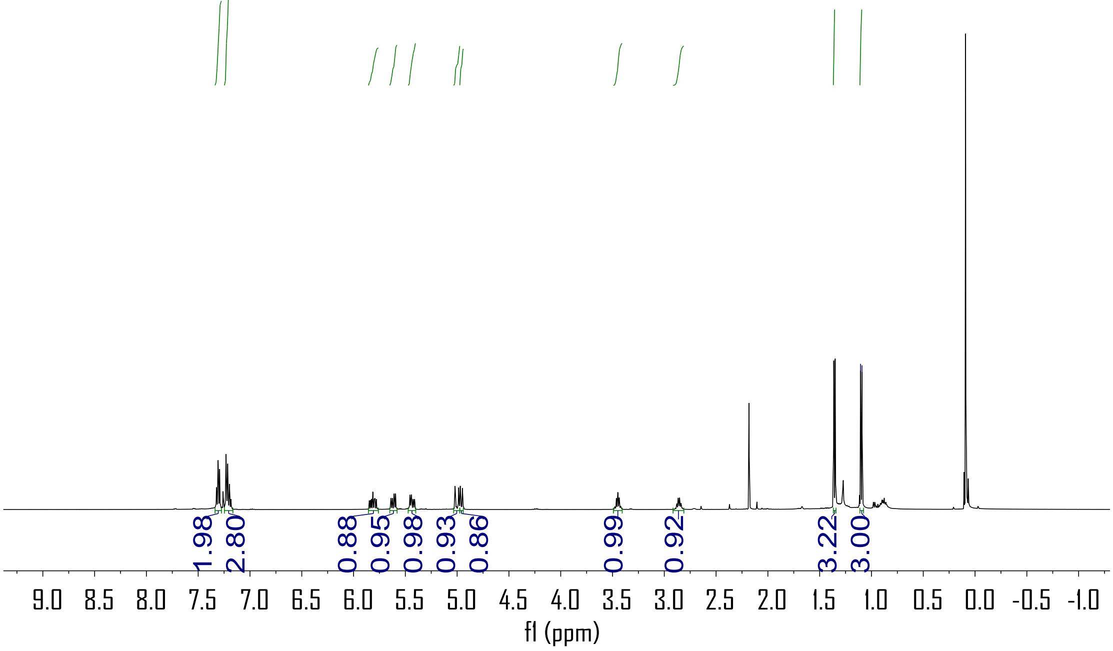
CH3
CH3 OH
S11a
1.0
1.0
1.93
2.89
1.00
0.99
1.93
1.00
1.03
2.21
3.41
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



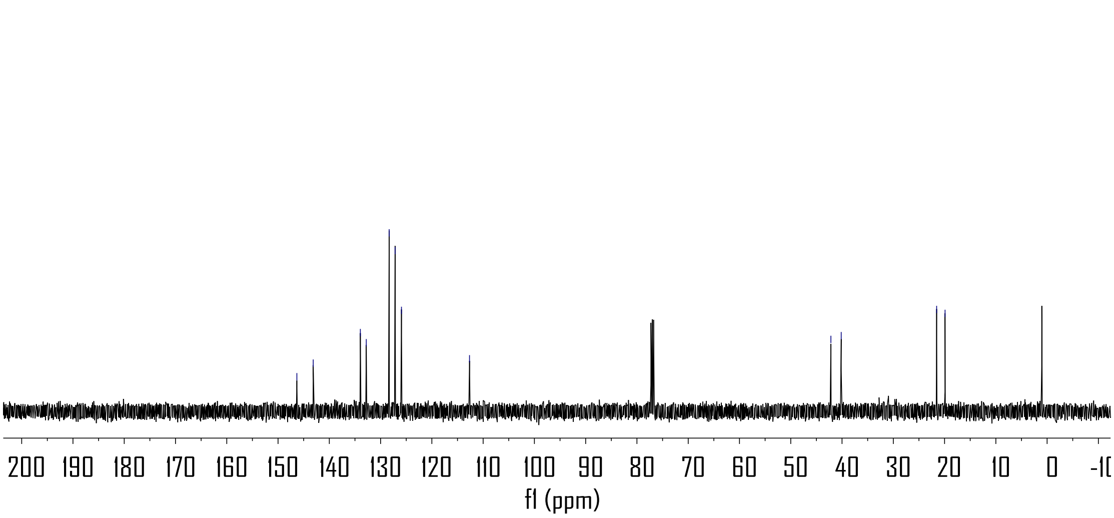
146.3
134.5
134.0
128.4
127.1
126.0
61.4
42.1
39.8
33.9
21.5
21.1
CH3
CH3 OH
S11a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



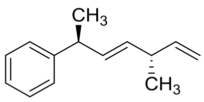
12a



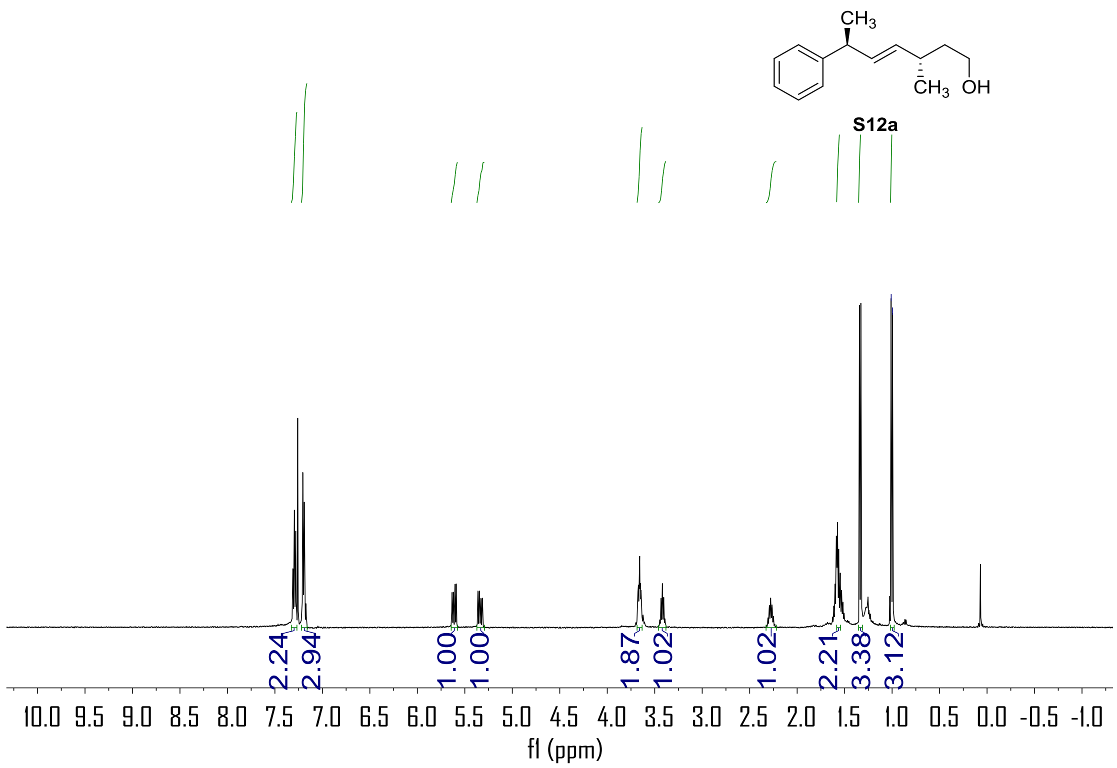
1.98
2.80
0.88
0.95
0.98
0.93
0.86
0.99
0.92
3.22
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

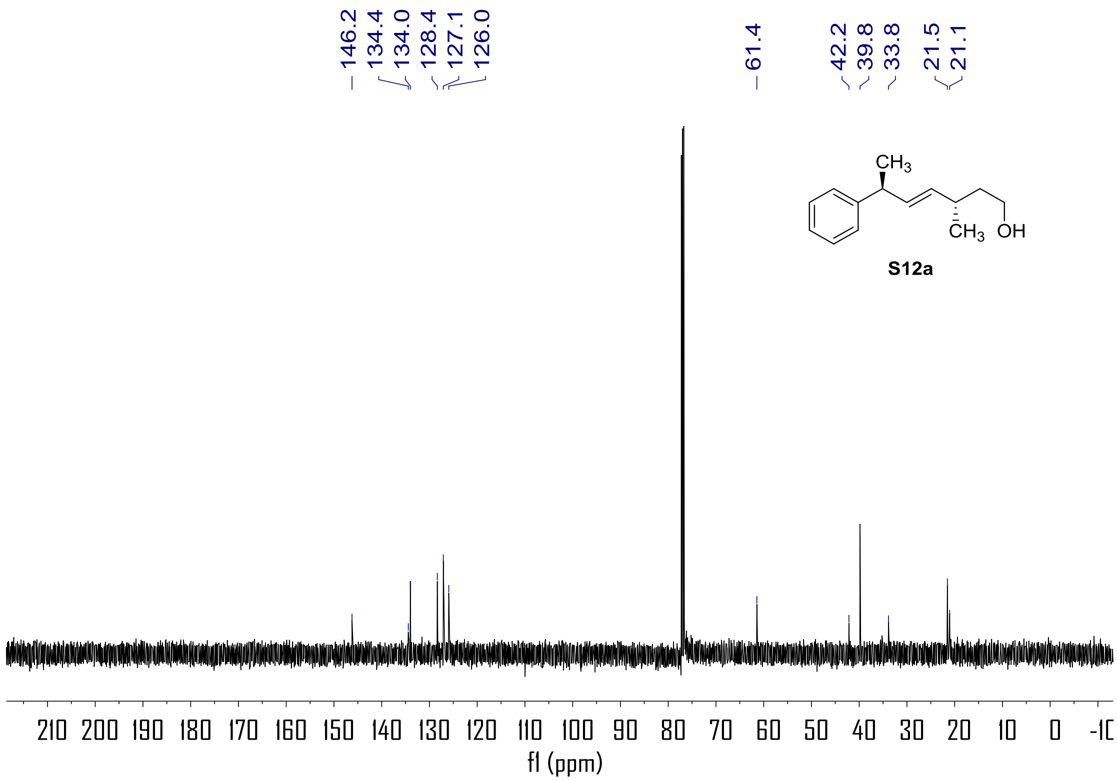


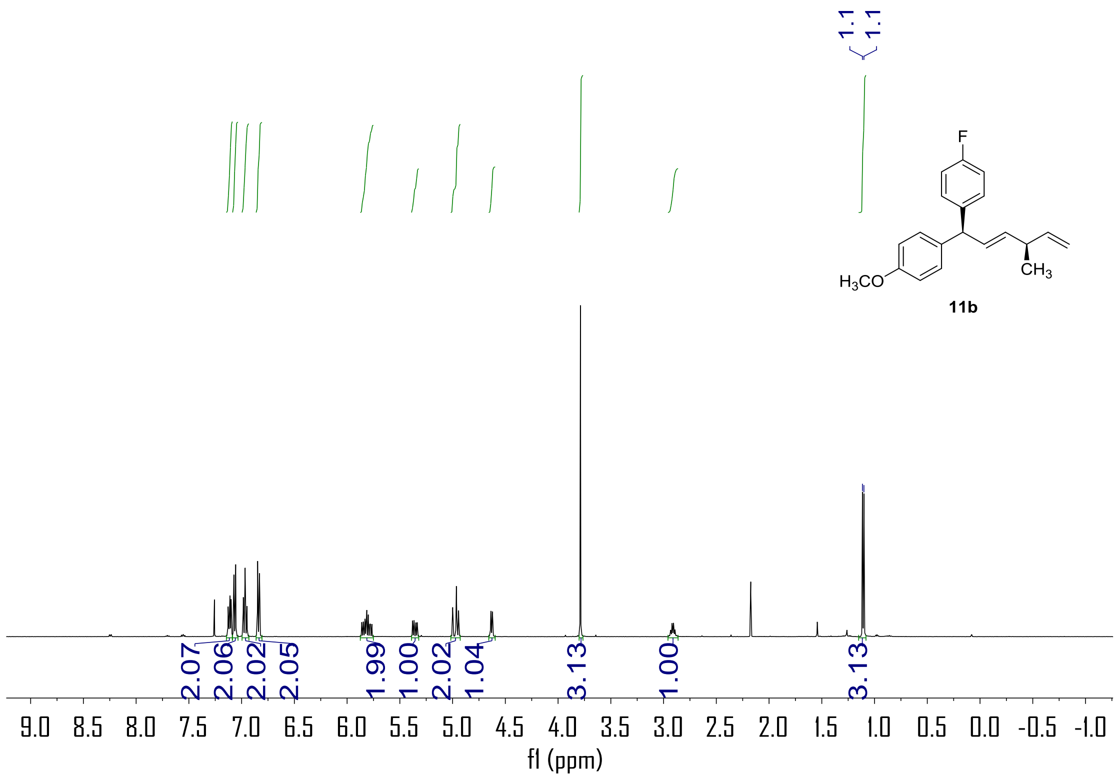
146.3
143.1
133.9
132.8
128.3
127.2
125.9
112.7
42.2
40.2
21.5
19.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



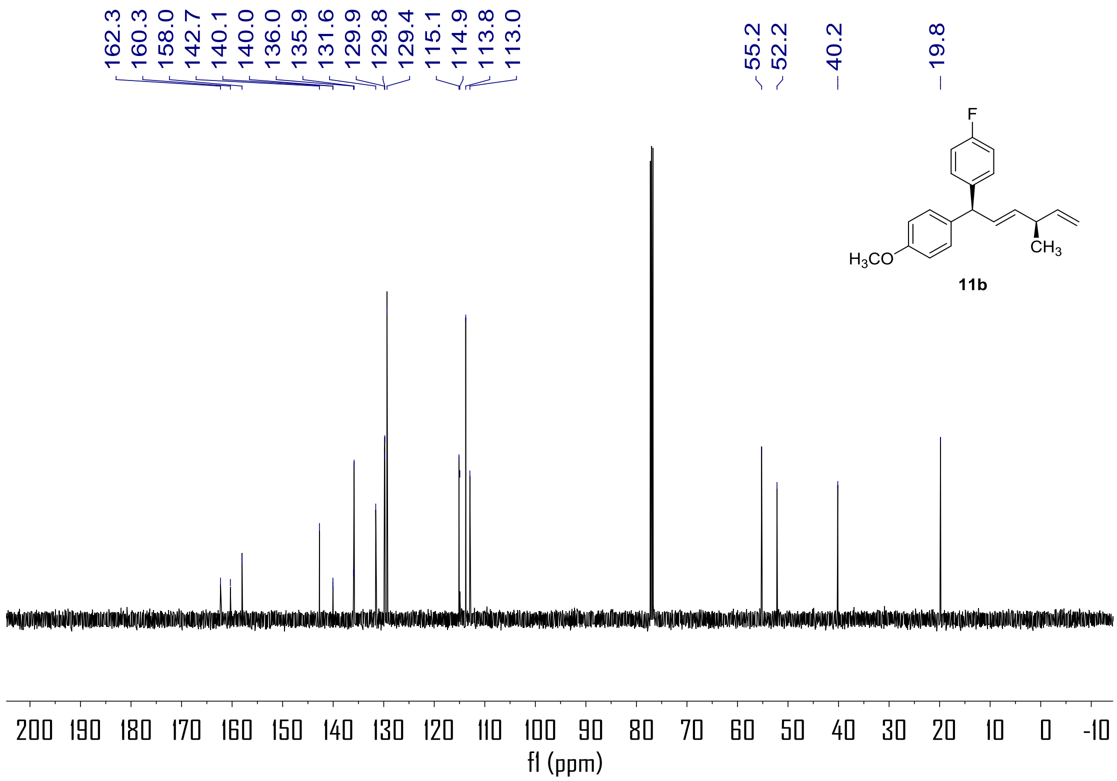
12a


CH3
CH3 OH
S12a
2.24
2.94
1.00
1.00
1.87
1.02
1.02
2.21
3.38
3.12
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

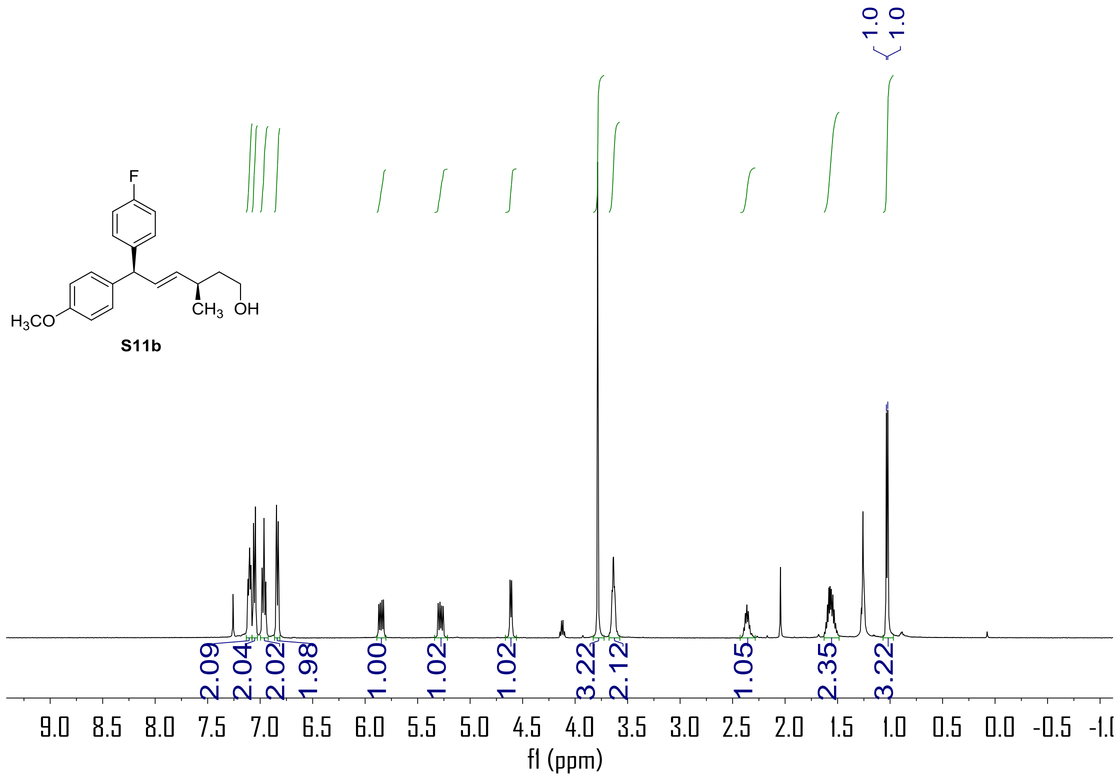

146.2
134.4
134.0
128.4
127.1
126.0
61.4
42.2
39.8
33.8
21.5
21.1
CH3
CH3 OH
S12a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

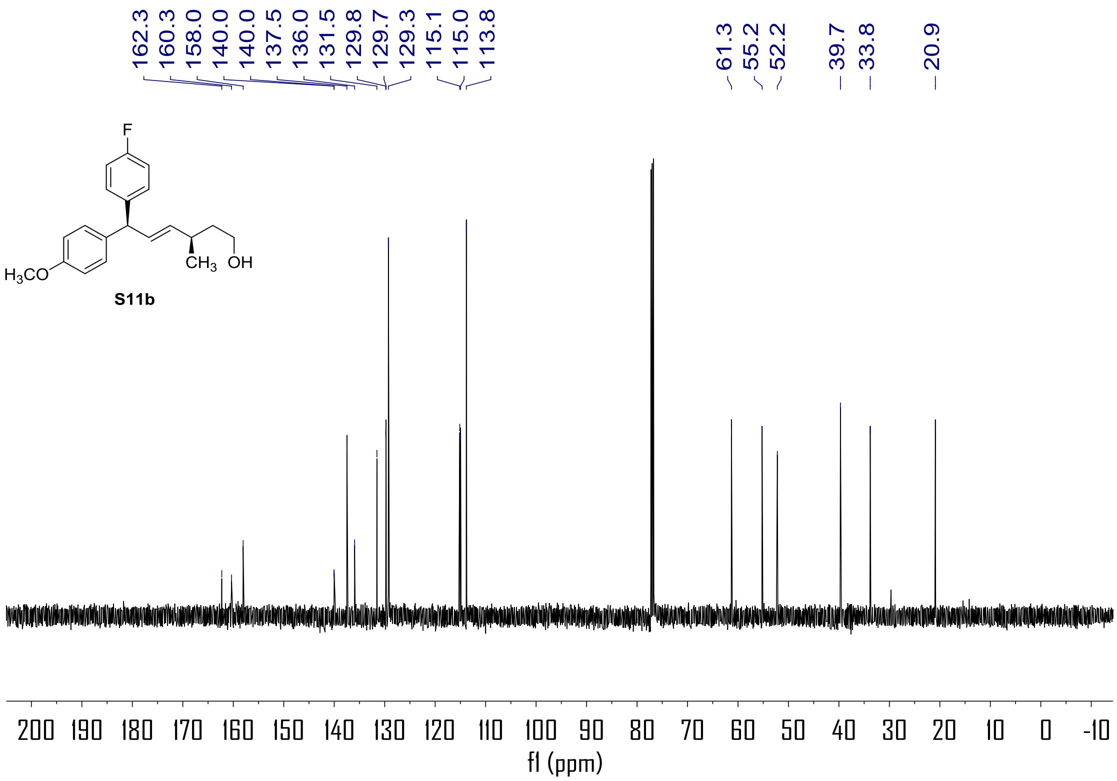


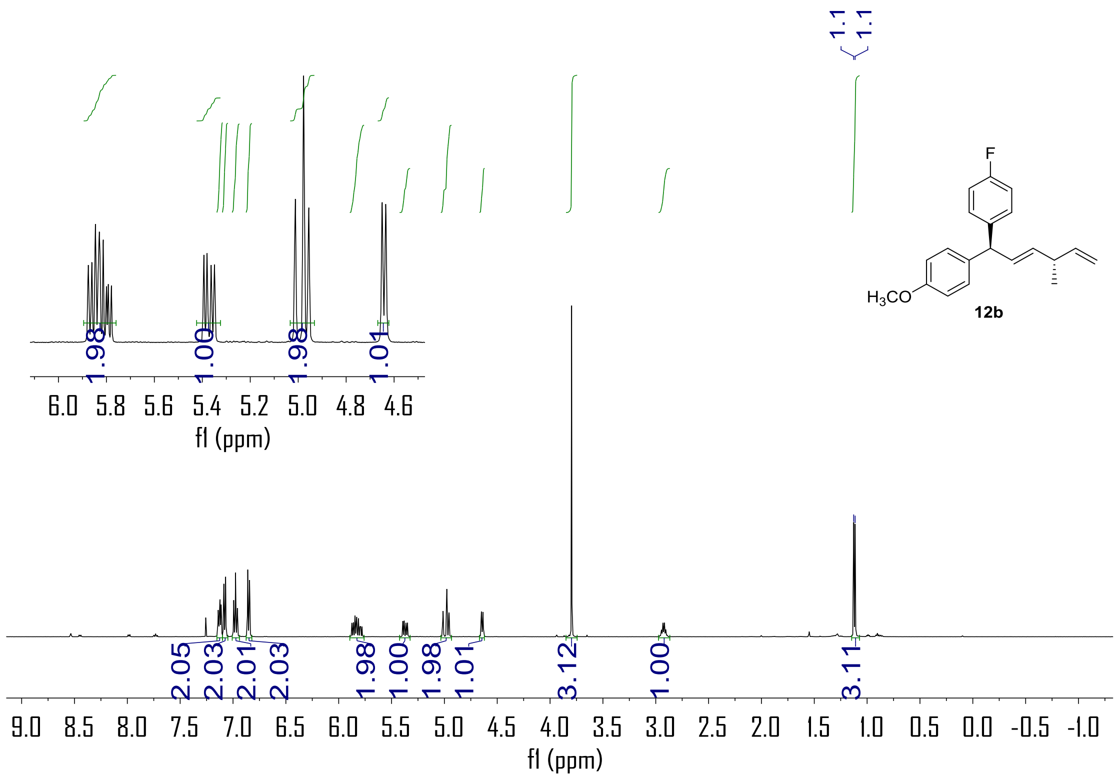
1.1
1.1
H3CO
CH3
F
11b
2.07
2.06
2.02
2.05
1.99
1.00
2.02
1.04
3.13
1.00
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

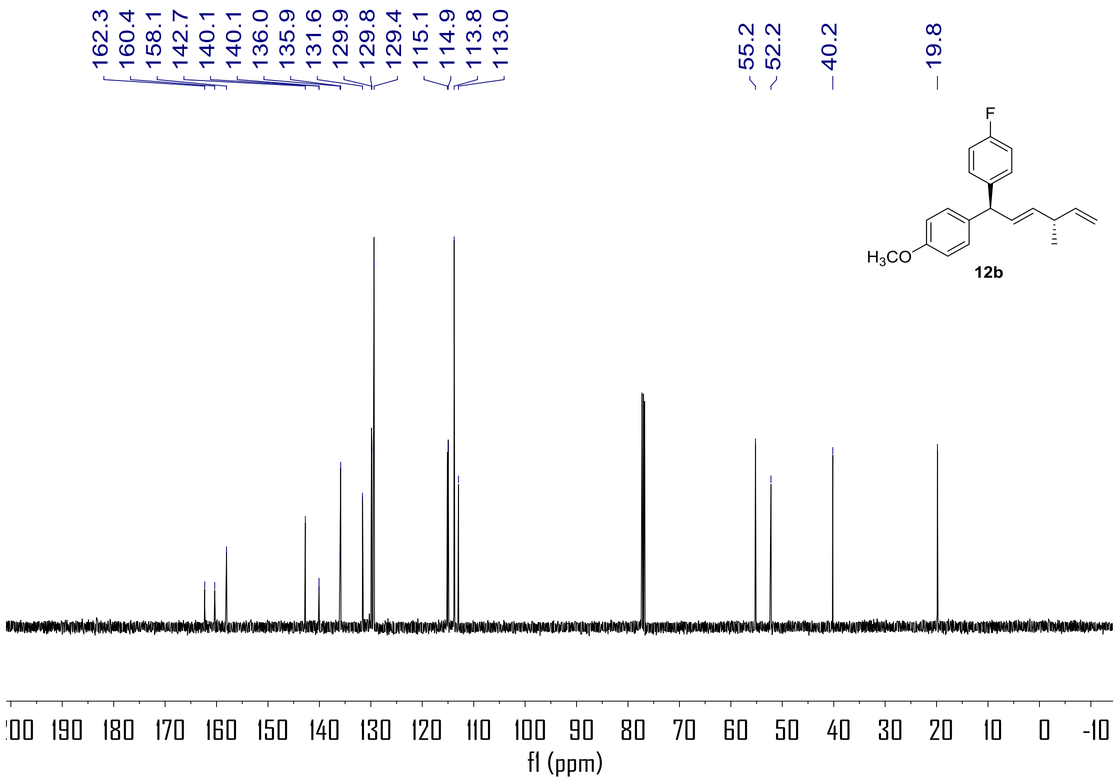


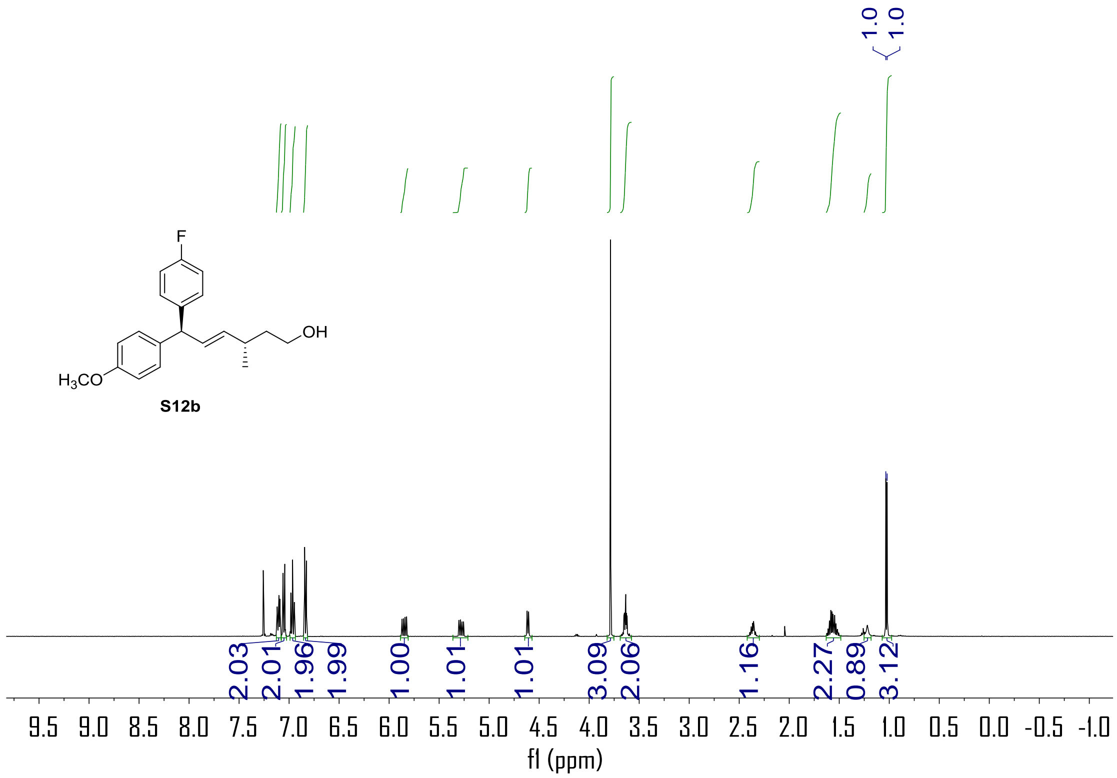
162.3
160.3
158.0
142.7
140.1
140.0
136.0
135.9
131.6
129.9
129.8
129.4
115.1
114.9
113.8
113.0
55.2
52.2
40.2
19.8
F
H3CO
CH3
11b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

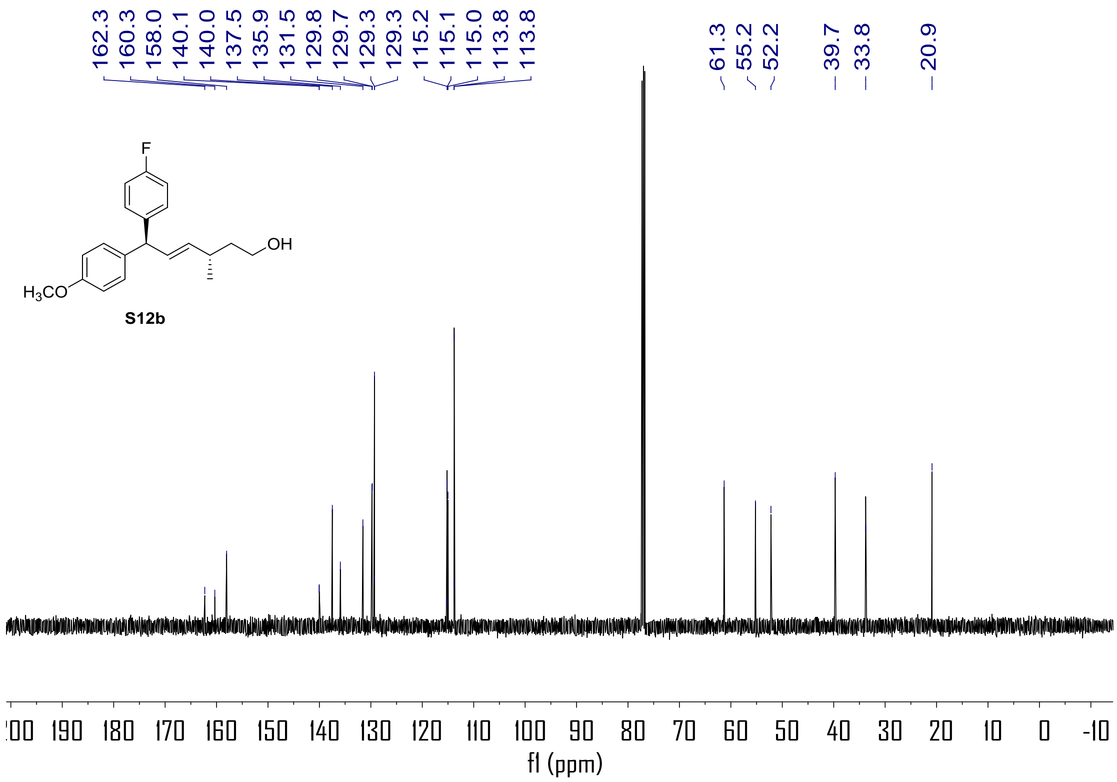

F
H3CO
CH3
OH
S11b
1.0
1.0
2.09
2.04
2.02
1.98
1.00
1.02
1.02
3.22
2.12
1.05
2.35
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

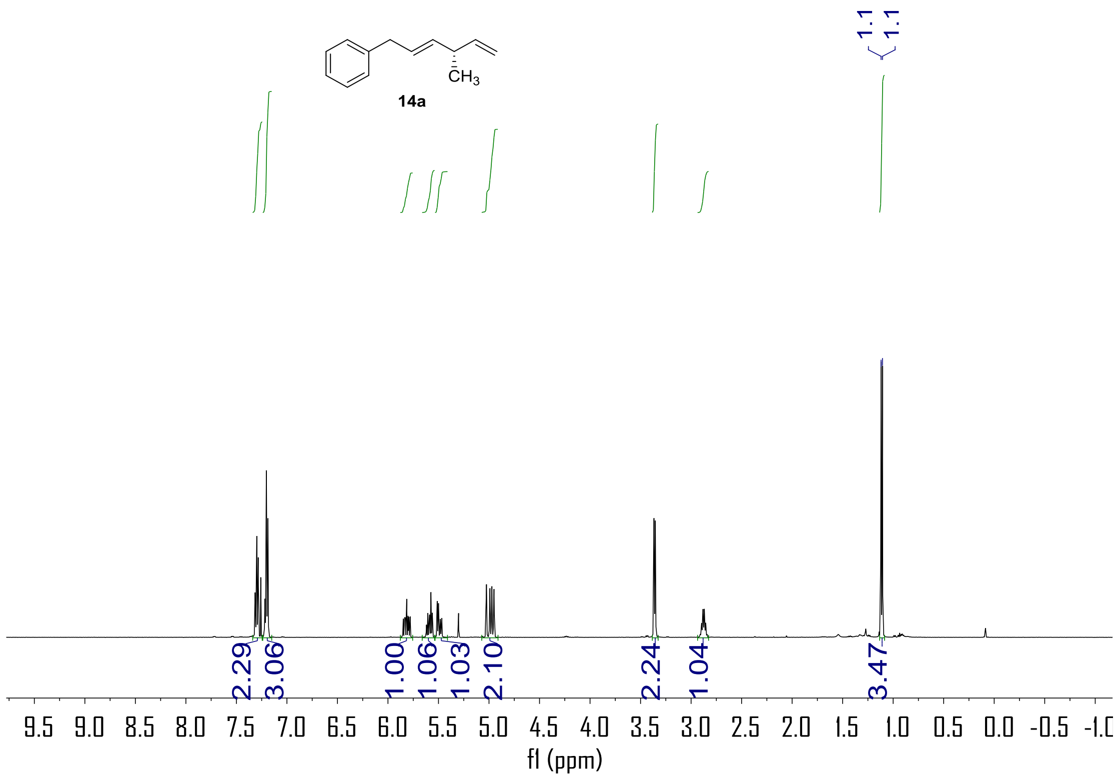

162.3
160.3
158.0
140.0
140.0
137.5
136.0
131.5
129.8
129.7
129.3
115.1
115.0
113.8
61.3
55.2
52.2
39.7
33.8
20.9
F
H3CO
CH3
OH
S11b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



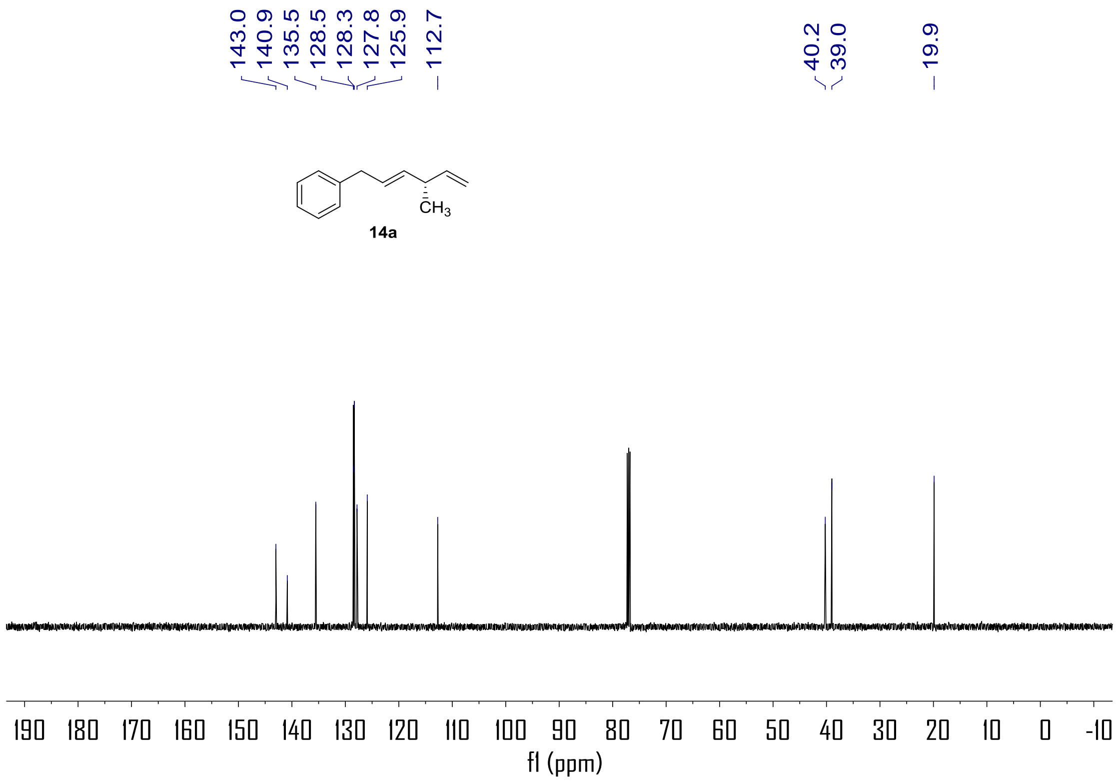




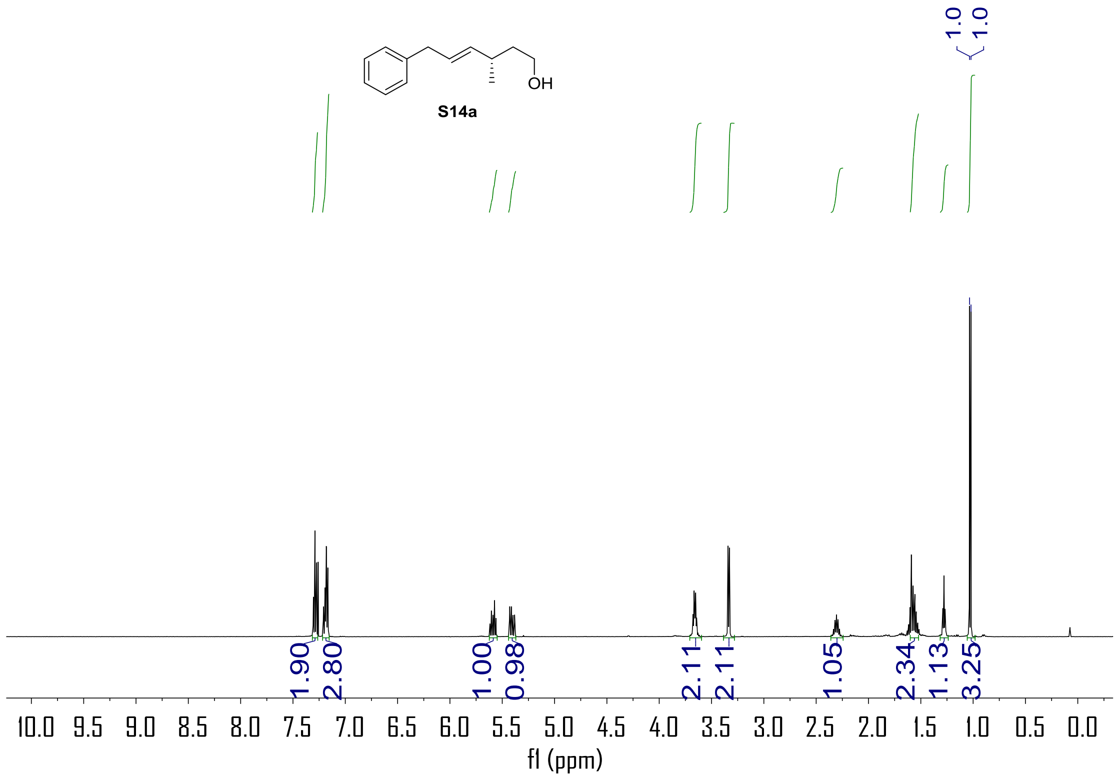


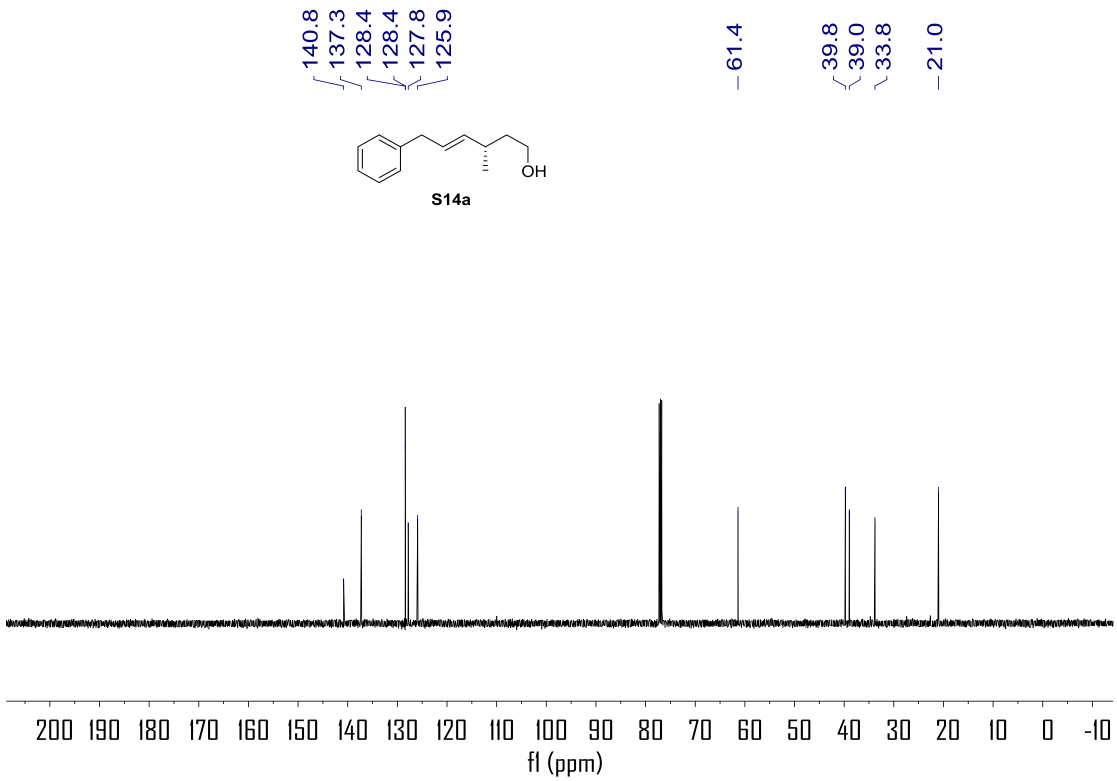


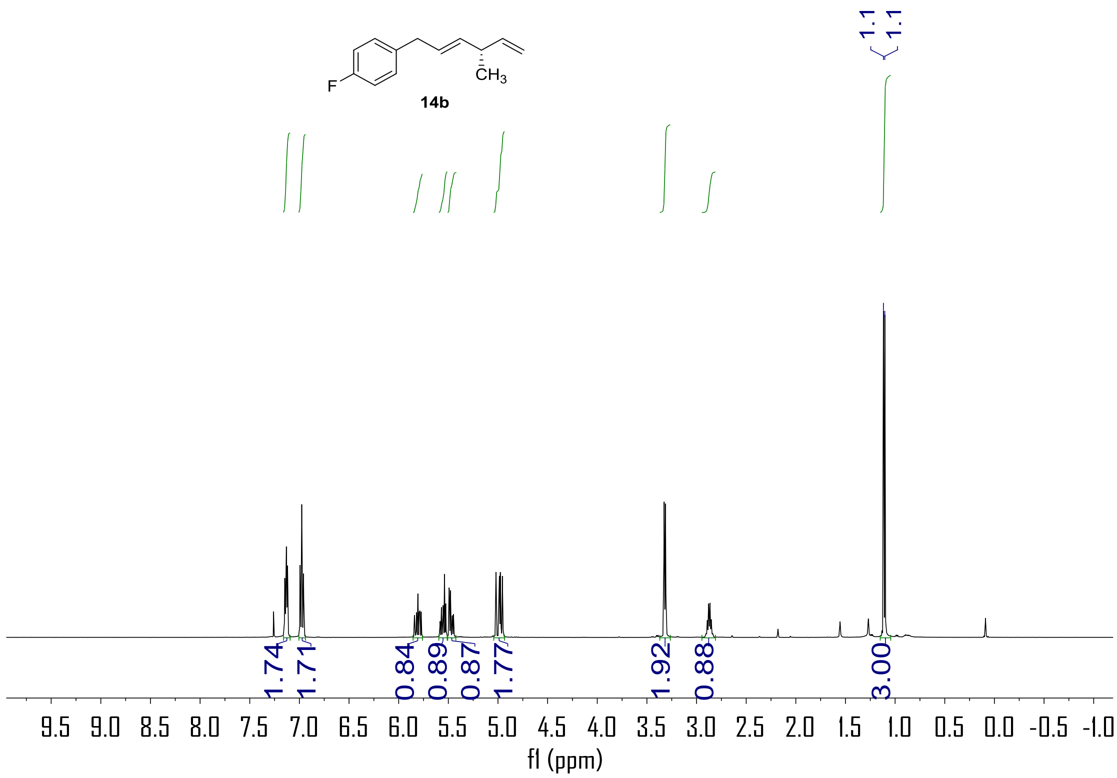
14a
1.1
1.1
2.29
3.06
1.00
1.06
1.03
2.10
2.24
1.04
3.47
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



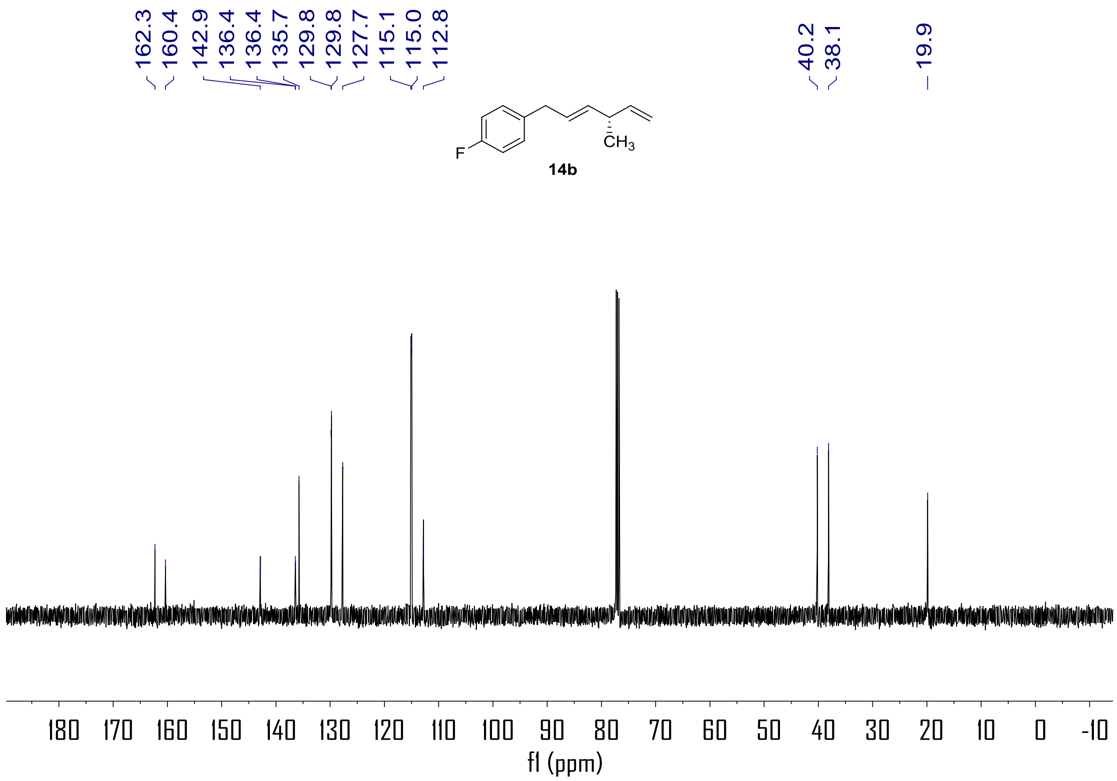
143.0
140.9
135.5
128.5
128.3
127.8
125.9
112.7
40.2
39.0
19.9
14a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
S14a
1.0
1.0
1.90
2.80
1.00
0.98
2.11
2.11
1.05
2.34
1.13
3.25
10.0 9.5 9.0 8.5 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 1.0 0.5 0.0
f1 (ppm)

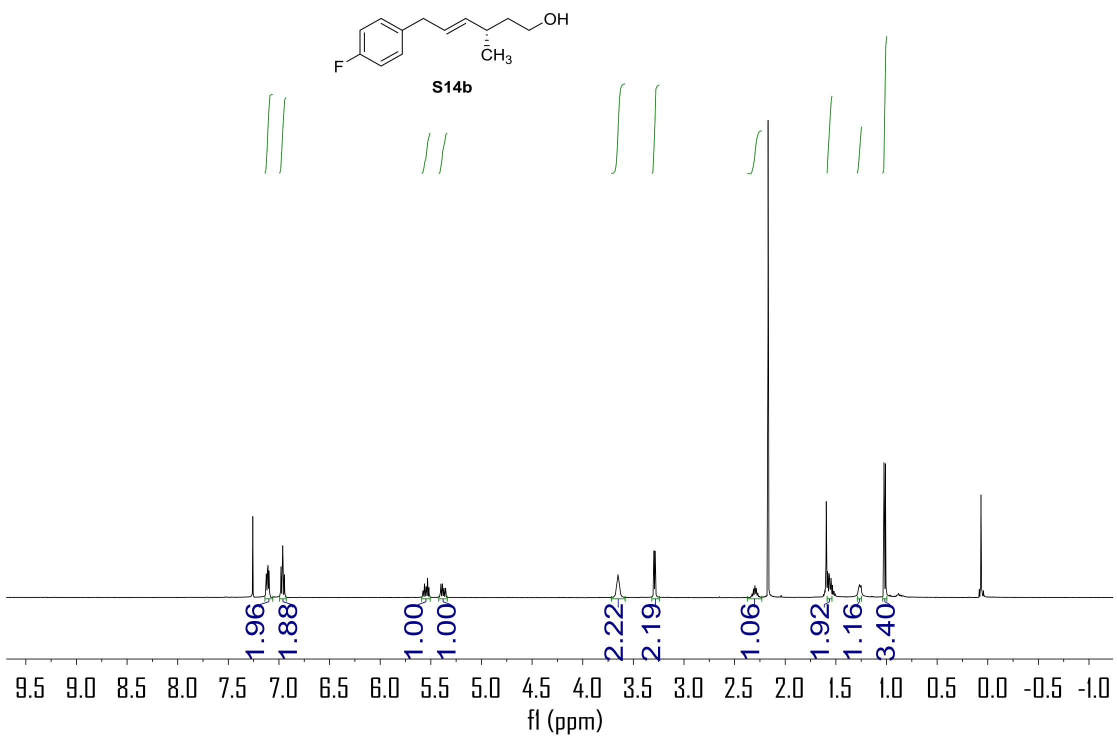

140.8
137.3
128.4
128.4
127.8
125.9
61.4
39.8
39.0
33.8
21.0
OH
S14a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

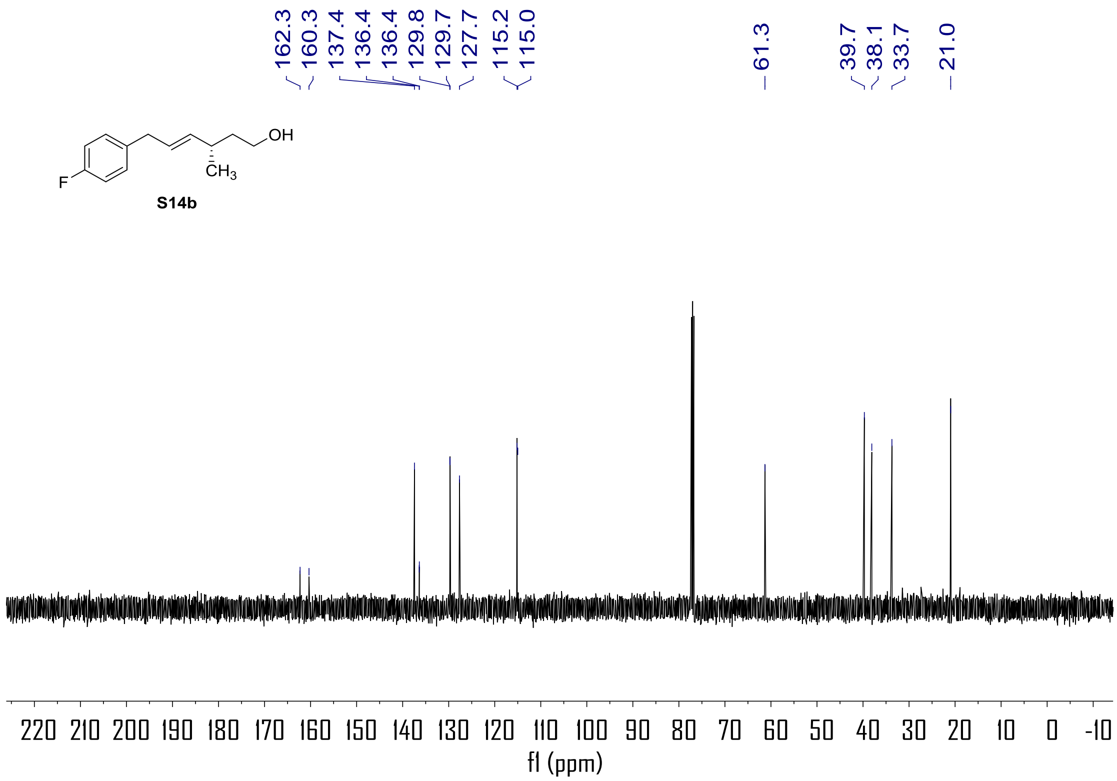


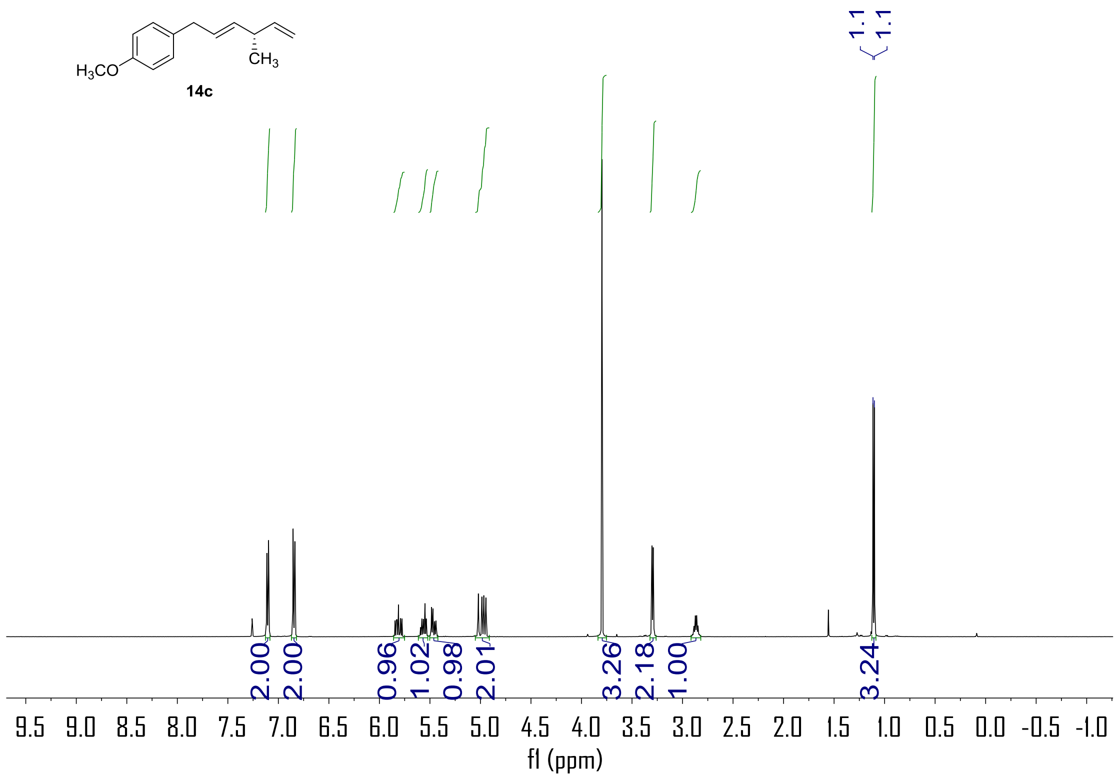
1.1
1.1
F
CH3
14b
1.74
1.71
0.84
0.89
0.87
1.77
1.92
0.88
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

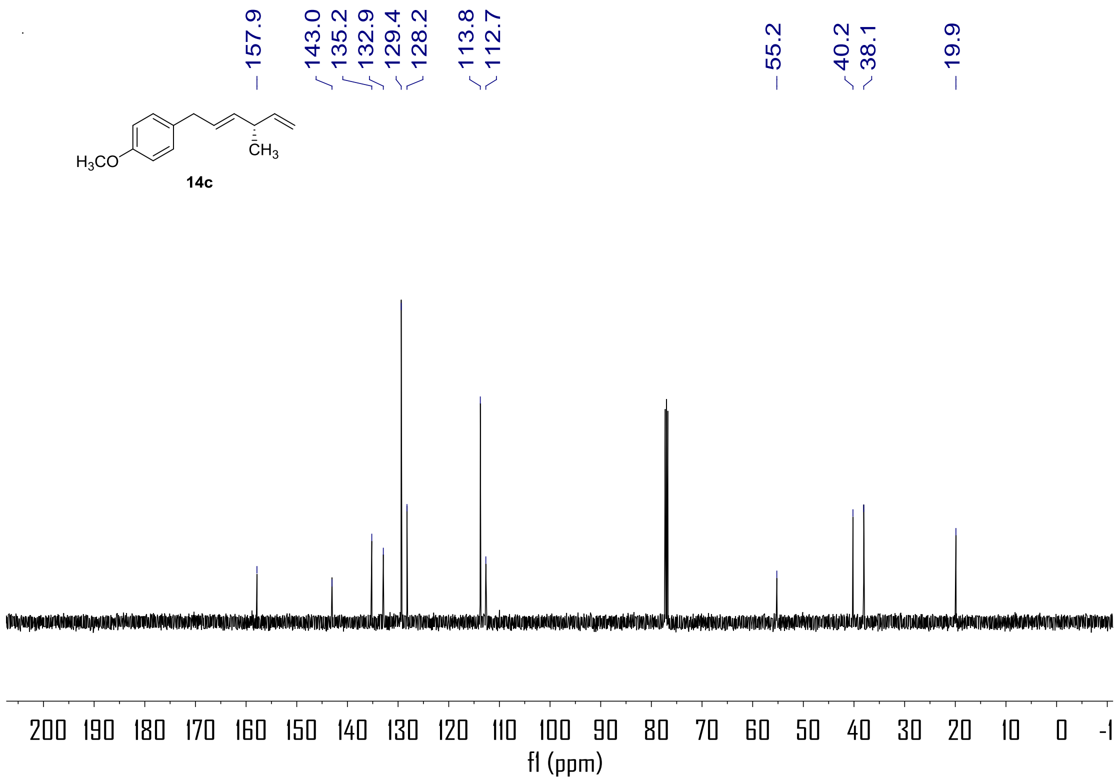


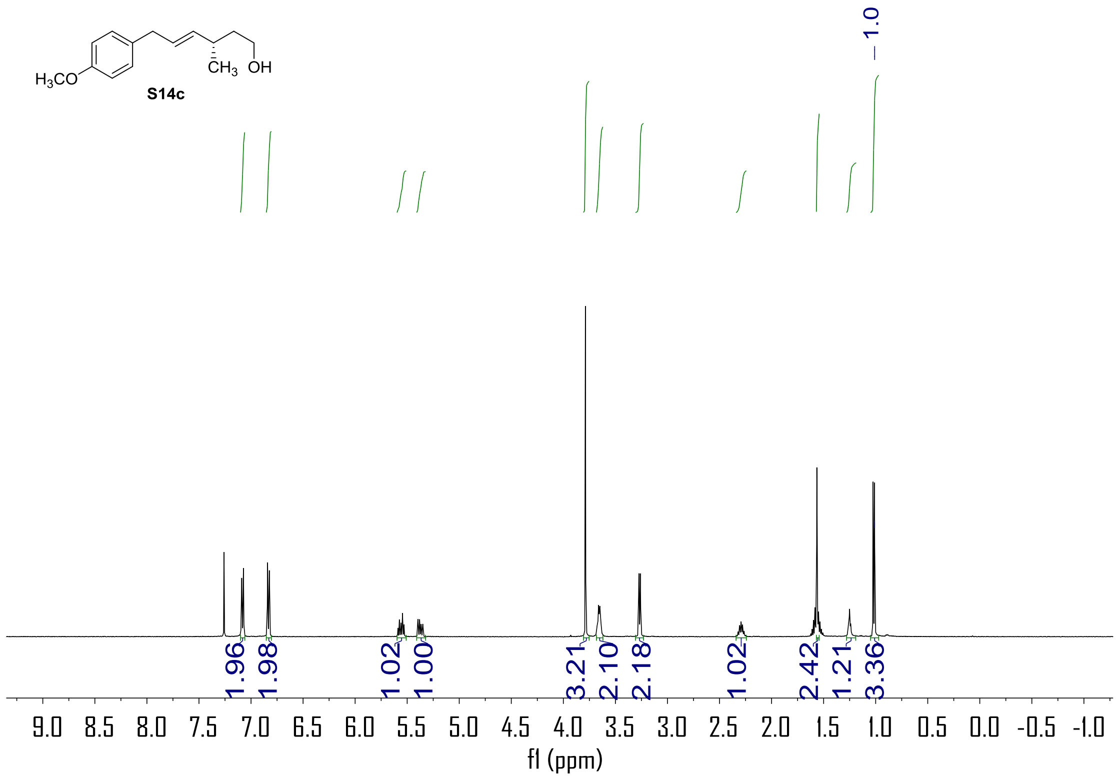
162.3
160.4
142.9
136.4
136.4
135.7
129.8
129.8
127.7
115.1
115.0
112.8
40.2
38.1
19.9
F
CH3
14b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

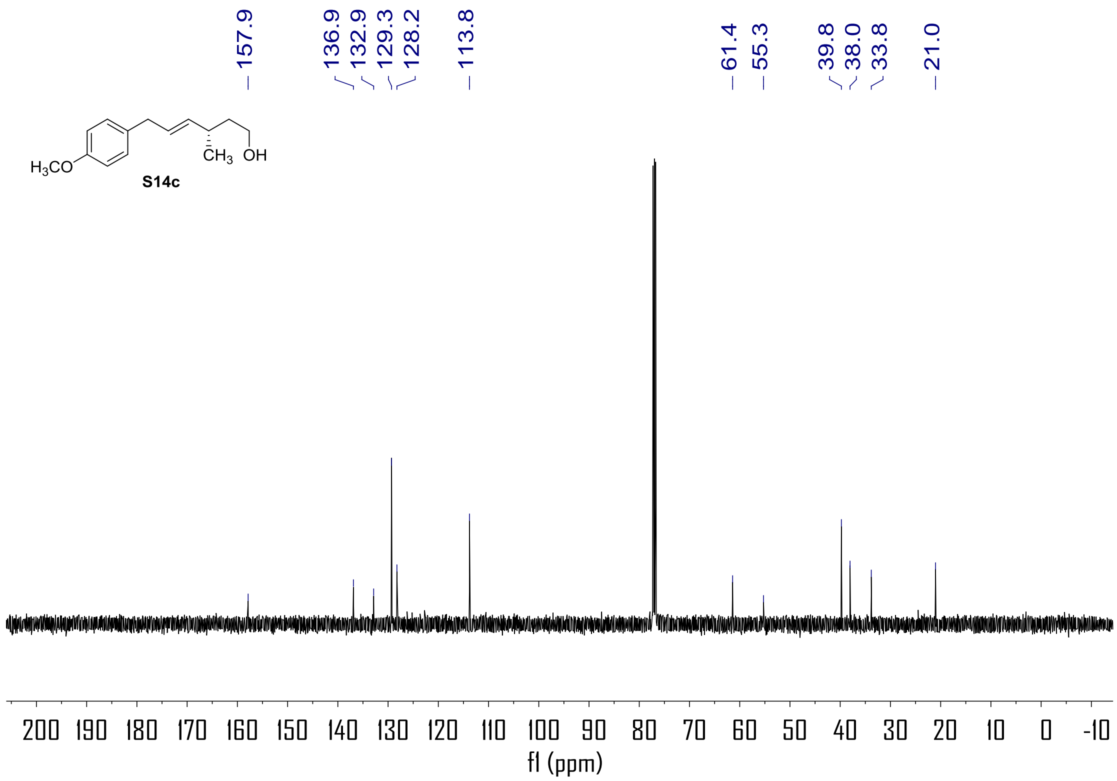

OH
F
CH3
S14b
1.96
1.88
1.00
1.00
2.22
2.19
1.06
1.92
1.16
3.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

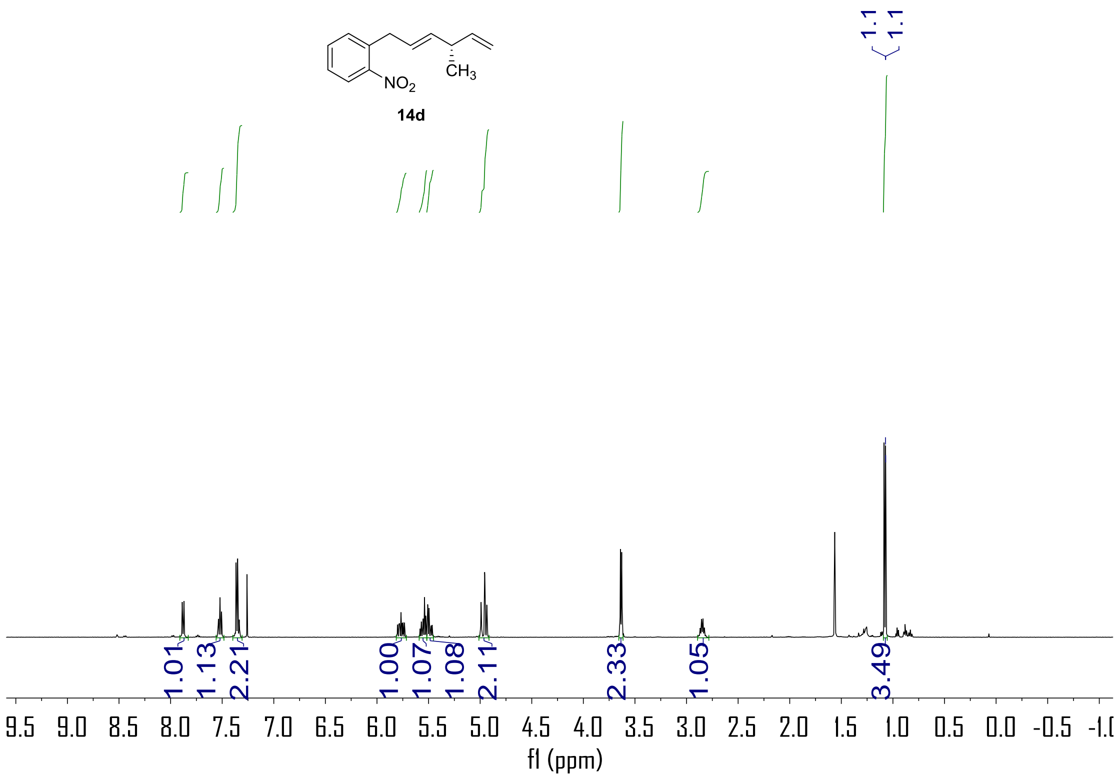

162.3
160.3
137.4
136.4
136.4
129.8
129.7
127.7
115.2
115.0
61.3
39.7
38.1
33.7
21.0
OH
F
CH3
S14b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


14c
1.1
1.1
2.00
2.00
0.96
1.02
0.98
2.01
3.26
2.18
1.00
3.24
9.5 9.0 8.5 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 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

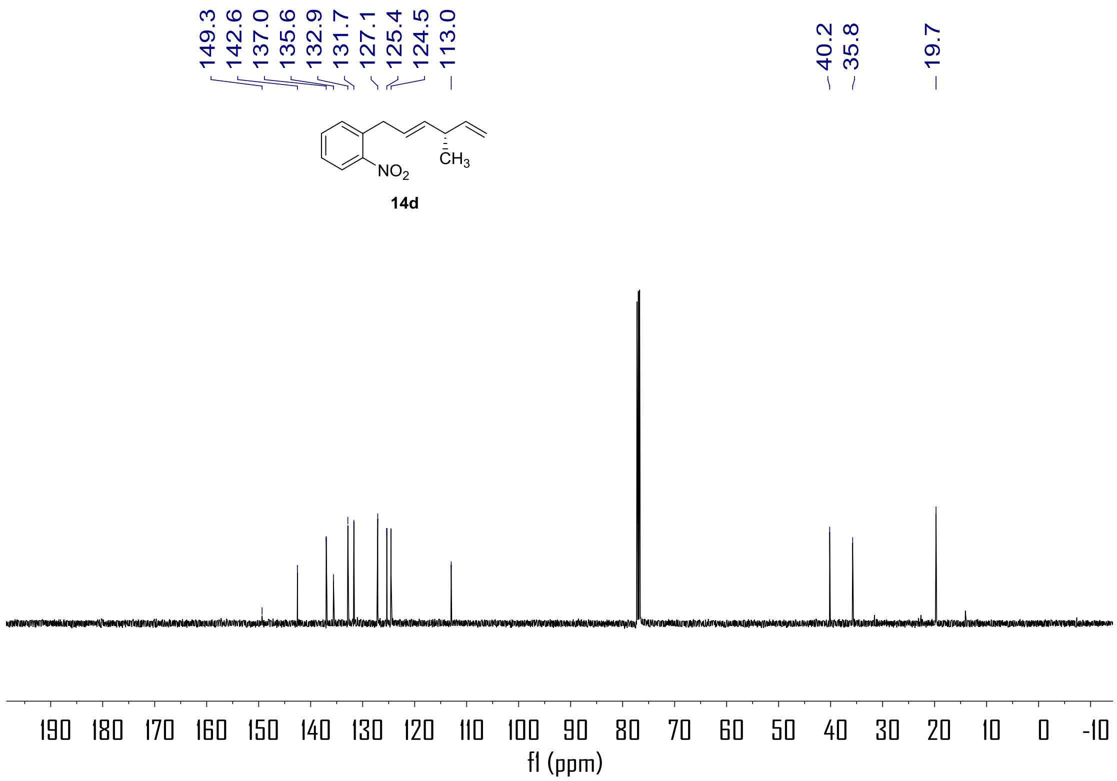

157.9
143.0
135.2
132.9
129.4
128.2
113.8
112.7
55.2
40.2
38.1
19.9
14c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


H3CO
CH3 OH
S14c
1.0
1.96 1.98 1.02 1.00 3.21 2.10 2.18 1.02 2.42 1.21 3.36
9.0 8.5 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 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

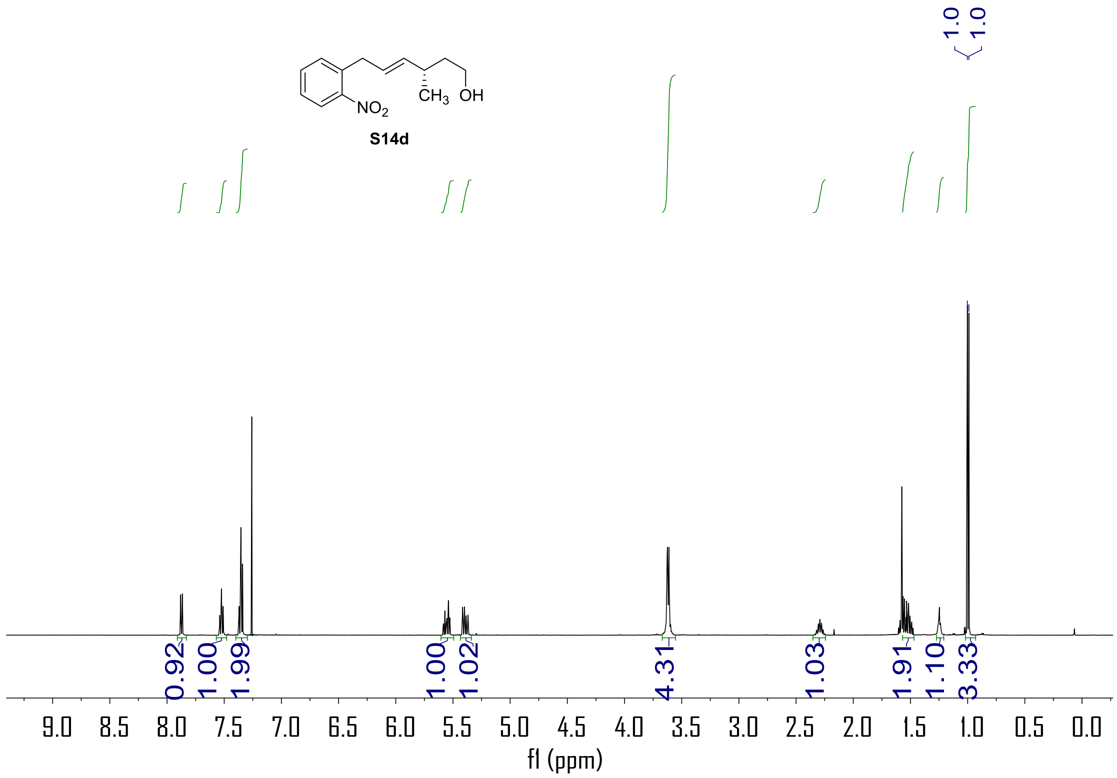

157.9
136.9 132.9 129.3 128.2
113.8
61.4 55.3
39.8 38.0 33.8
21.0
H3CO
CH3 OH
S14c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



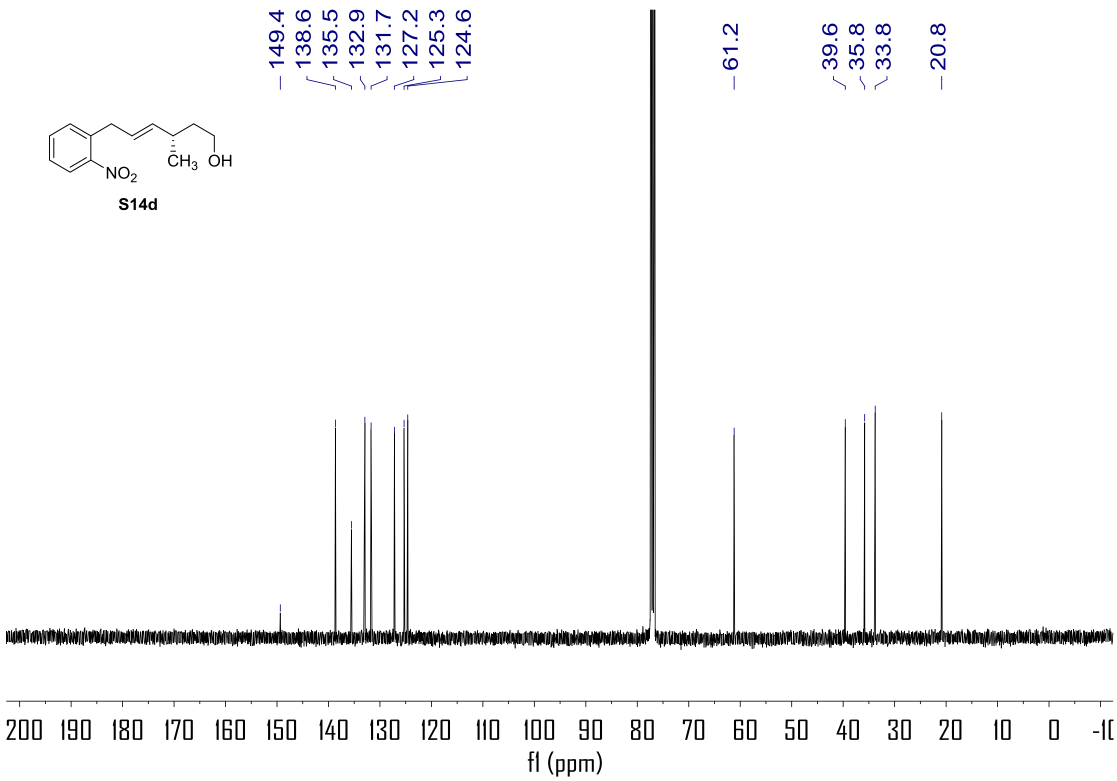
NO2
CH3
14d
1.1
1.1
1.01
1.13
2.21
1.00
1.07
1.08
2.11
2.33
1.05
3.49
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



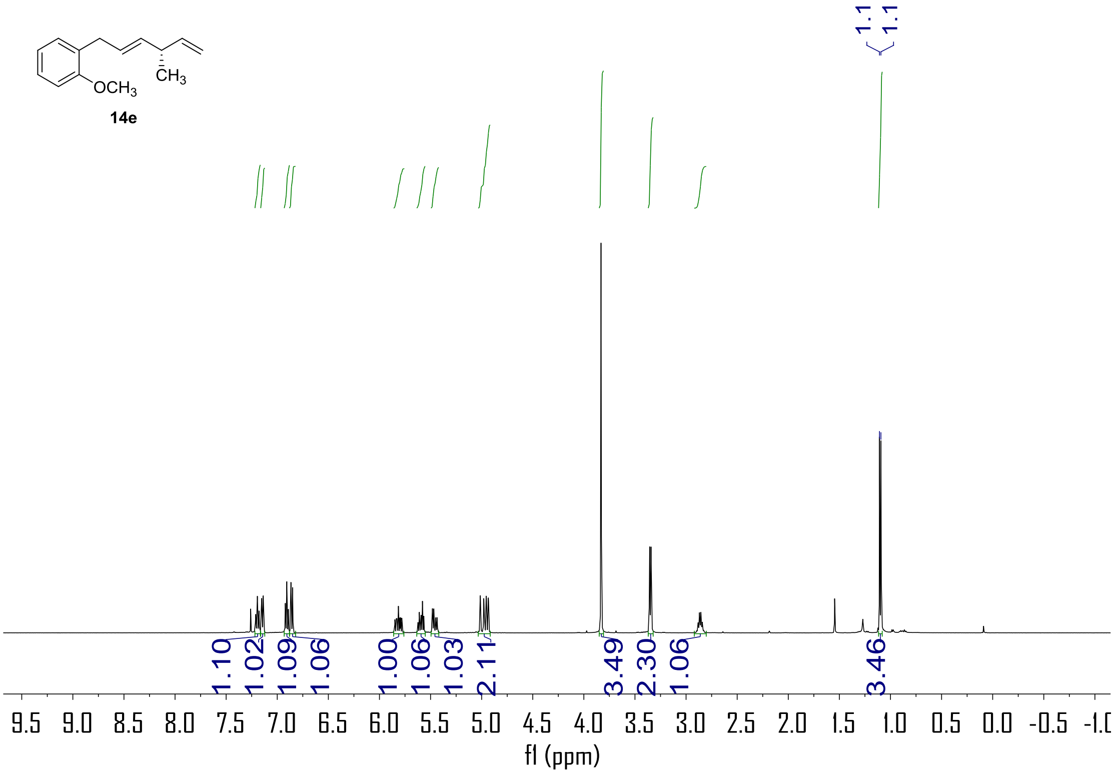
149.3
142.6
137.0
135.6
132.9
131.7
127.1
125.4
124.5
113.0
40.2
35.8
19.7
NO2
CH3
14d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

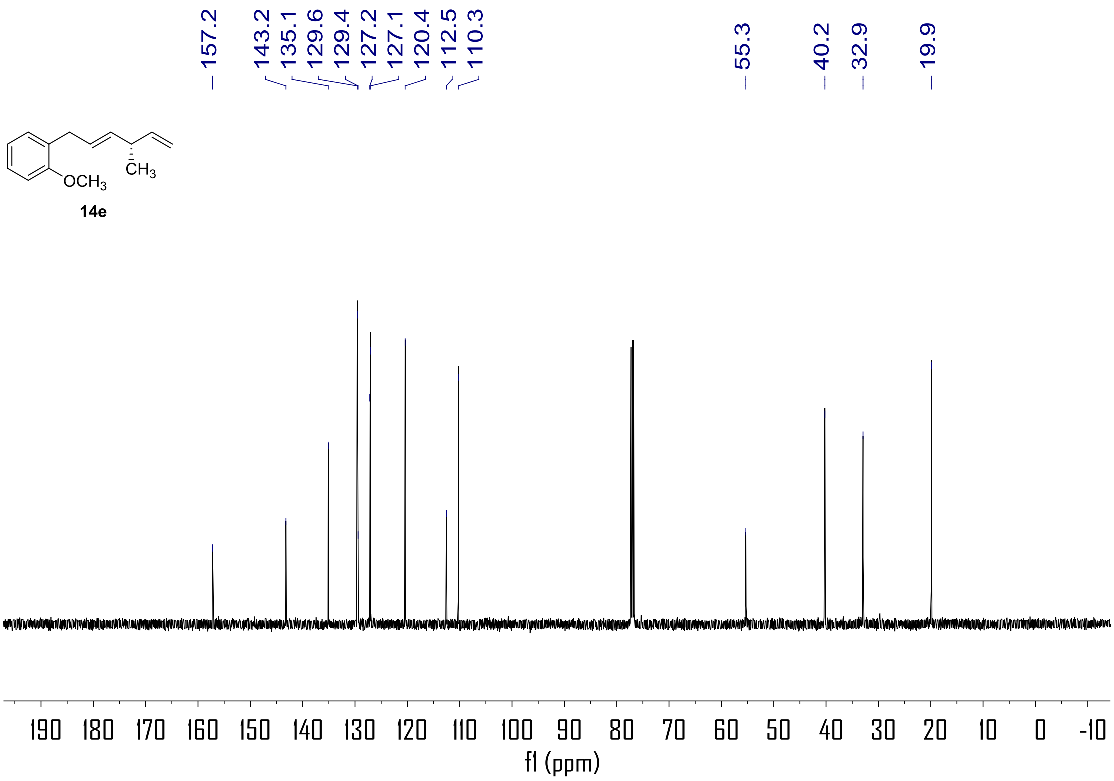


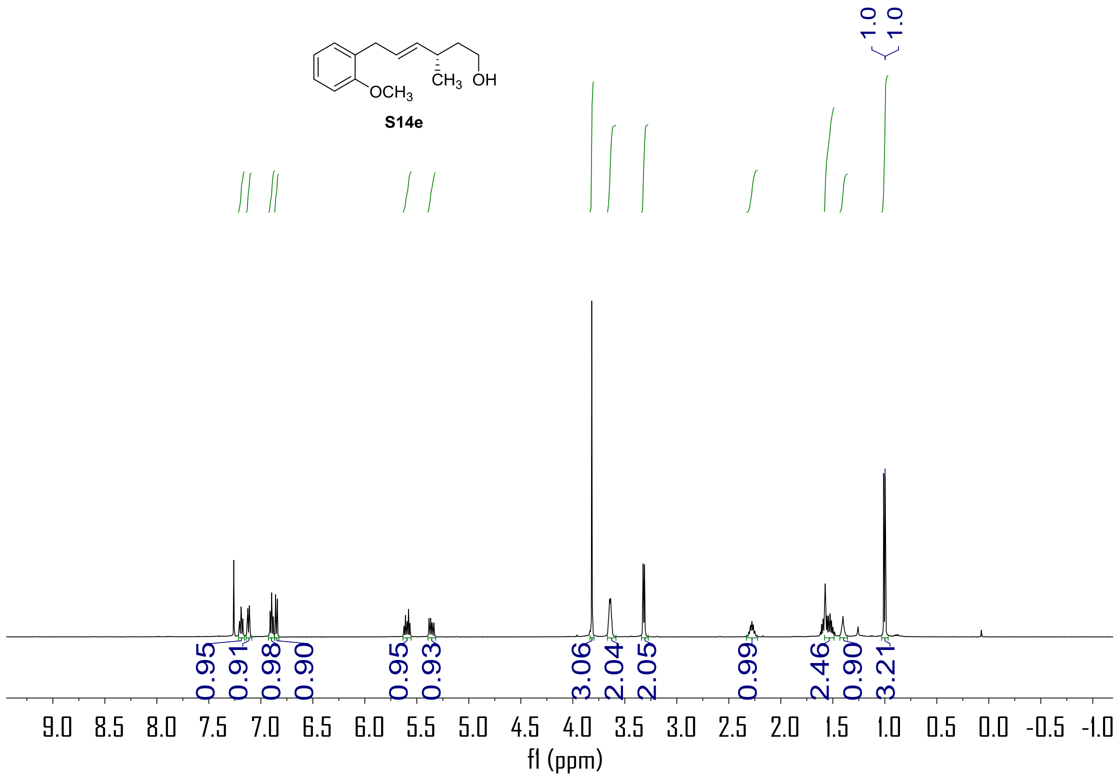
NO2
CH3
OH
S14d
1.0
1.0
0.92
1.00
1.99
1.00
1.02
4.31
1.03
1.91
1.10
3.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

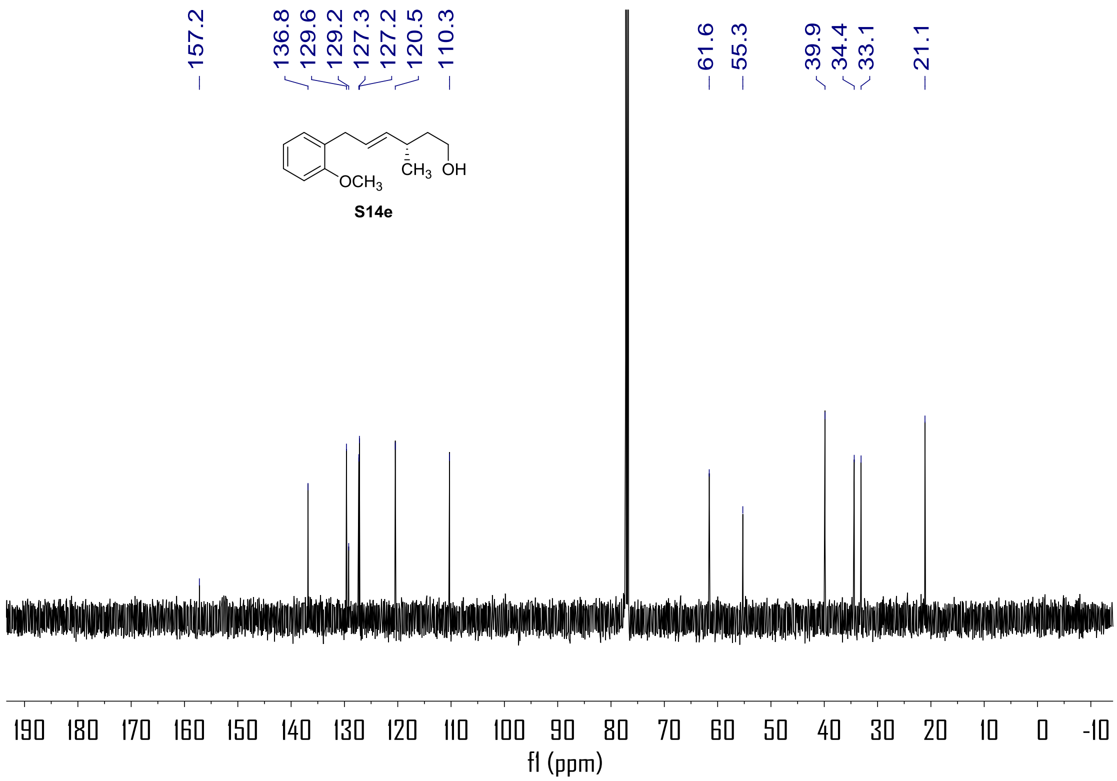


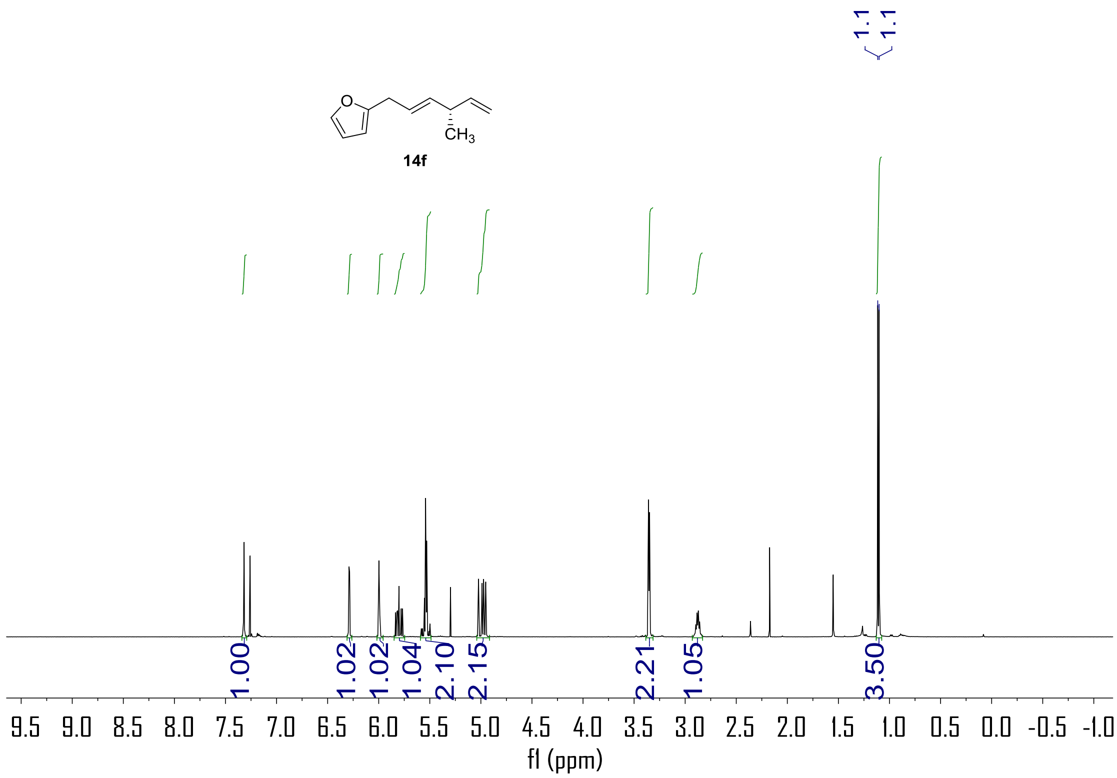
149.4
138.6
135.5
132.9
131.7
127.2
125.3
124.6
61.2
39.6
35.8
33.8
20.8
NO2
CH3
OH
S14d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

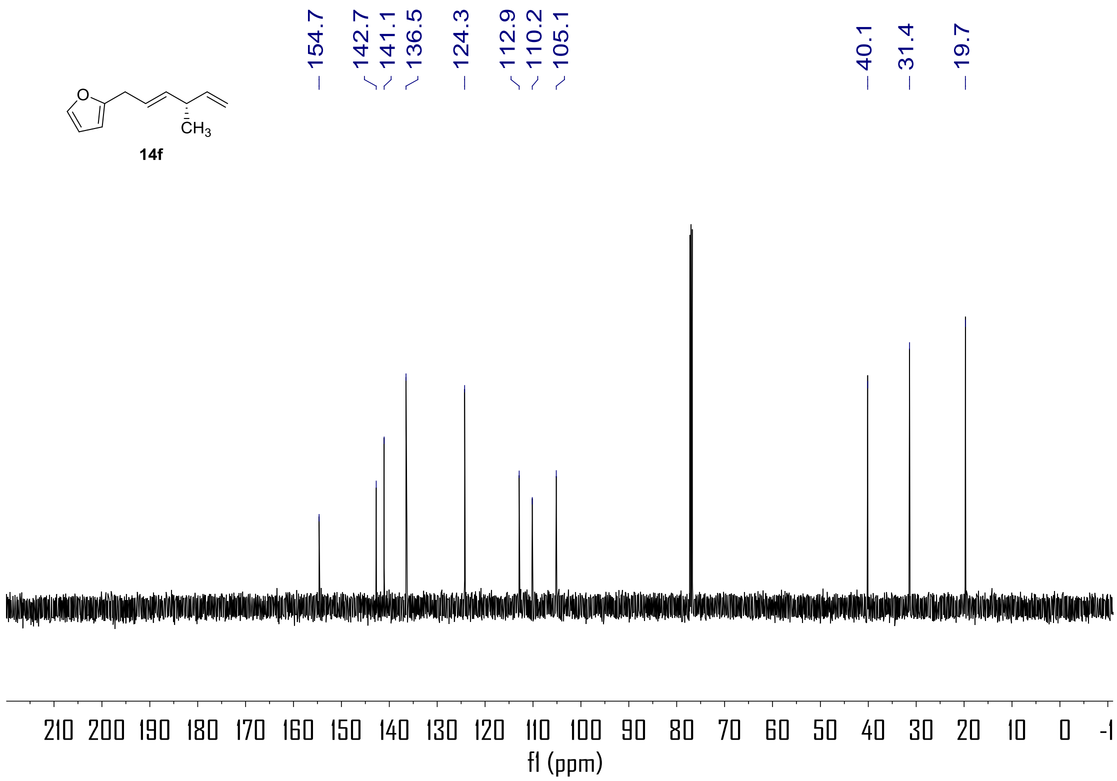

OCH3
CH3
14e
1.1
1.1
1.10
1.02
1.09
1.06
1.00
1.06
1.03
2.11
3.49
2.30
1.06
3.46
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

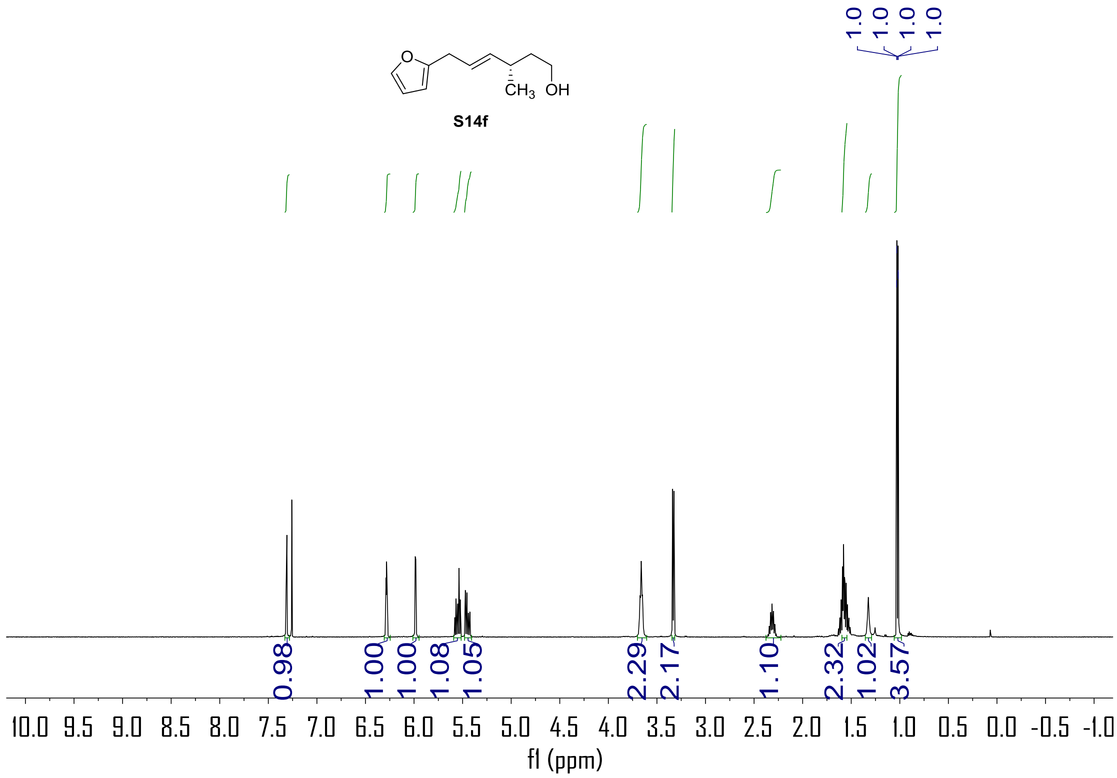

157.2
143.2
135.1
129.6
129.4
127.2
127.1
120.4
112.5
110.3
55.3
40.2
32.9
19.9
OCH3
CH3
14e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



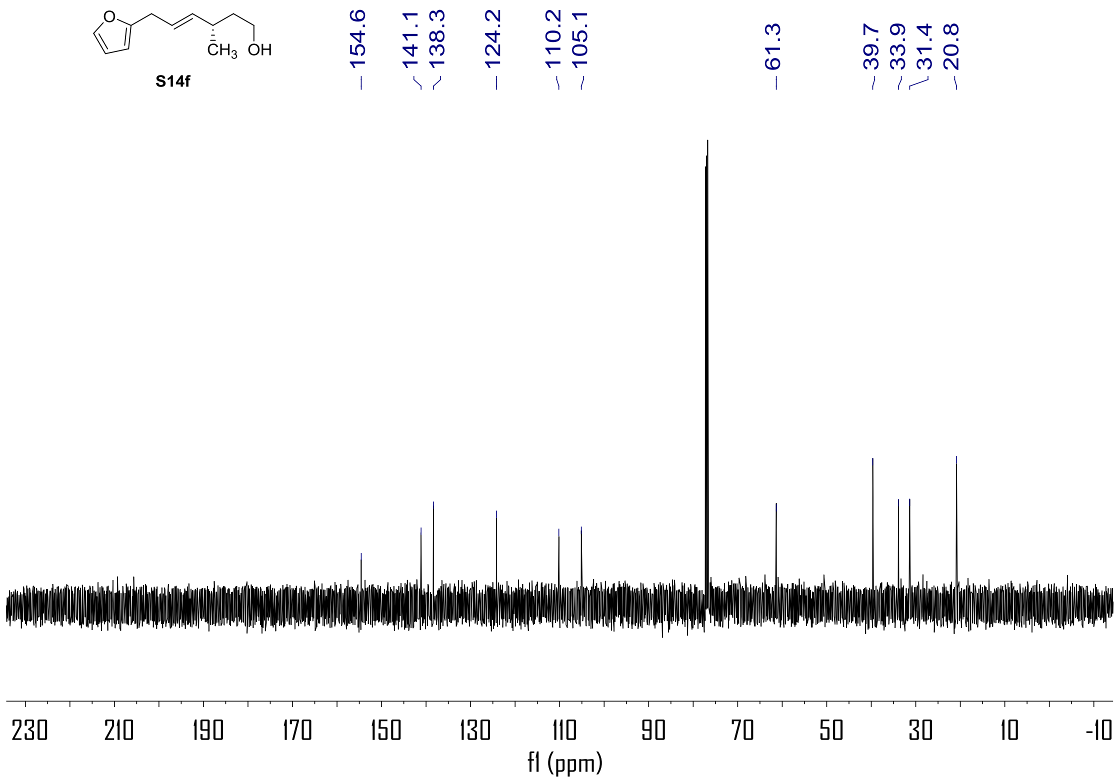



14f
1.1
1.1
1.00
1.02
1.02
1.04
2.10
2.15
2.21
1.05
3.50
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

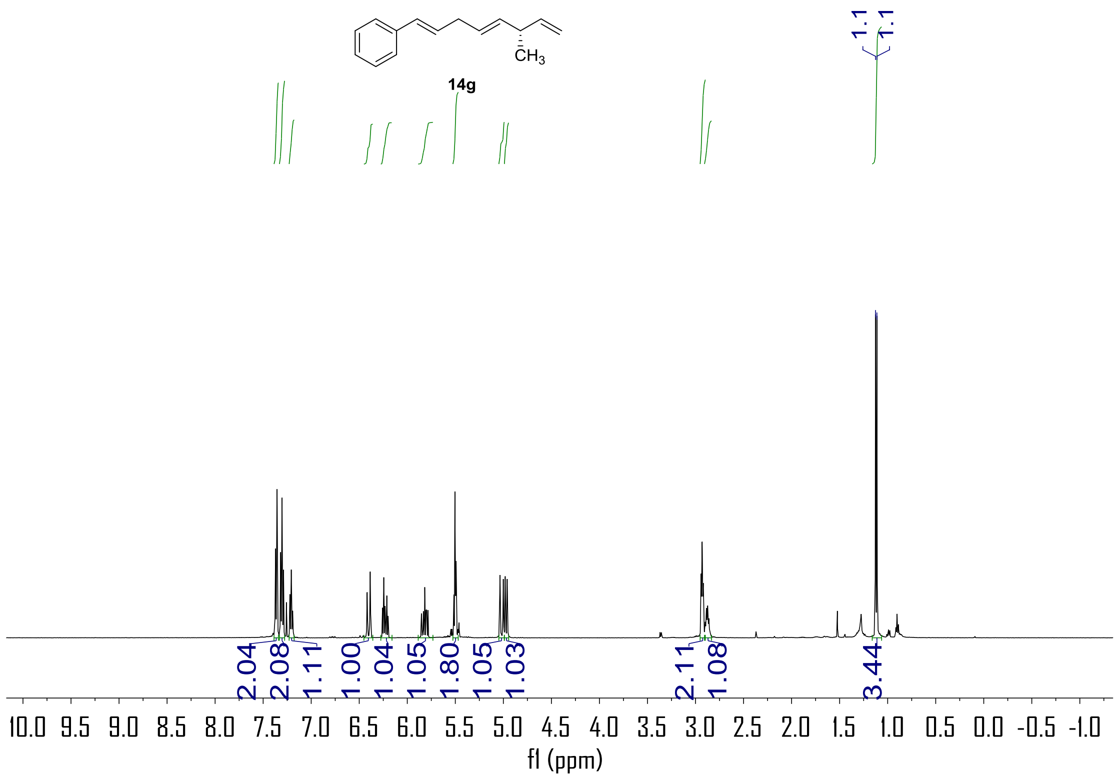

14f
154.7
142.7
141.1
136.5
124.3
112.9
110.2
105.1
40.1
31.4
19.7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



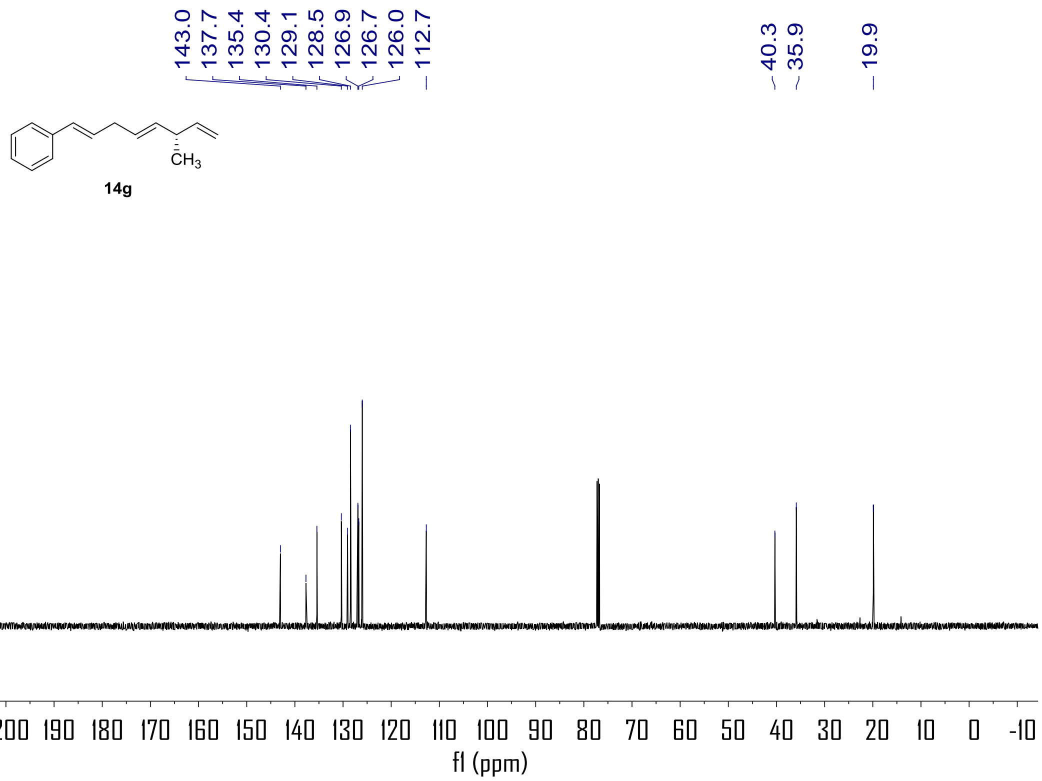
S14f
1.0
1.0
1.0
1.0
0.98
1.00
1.00
1.08
1.05
2.29
2.17
1.10
2.32
1.02
3.57
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



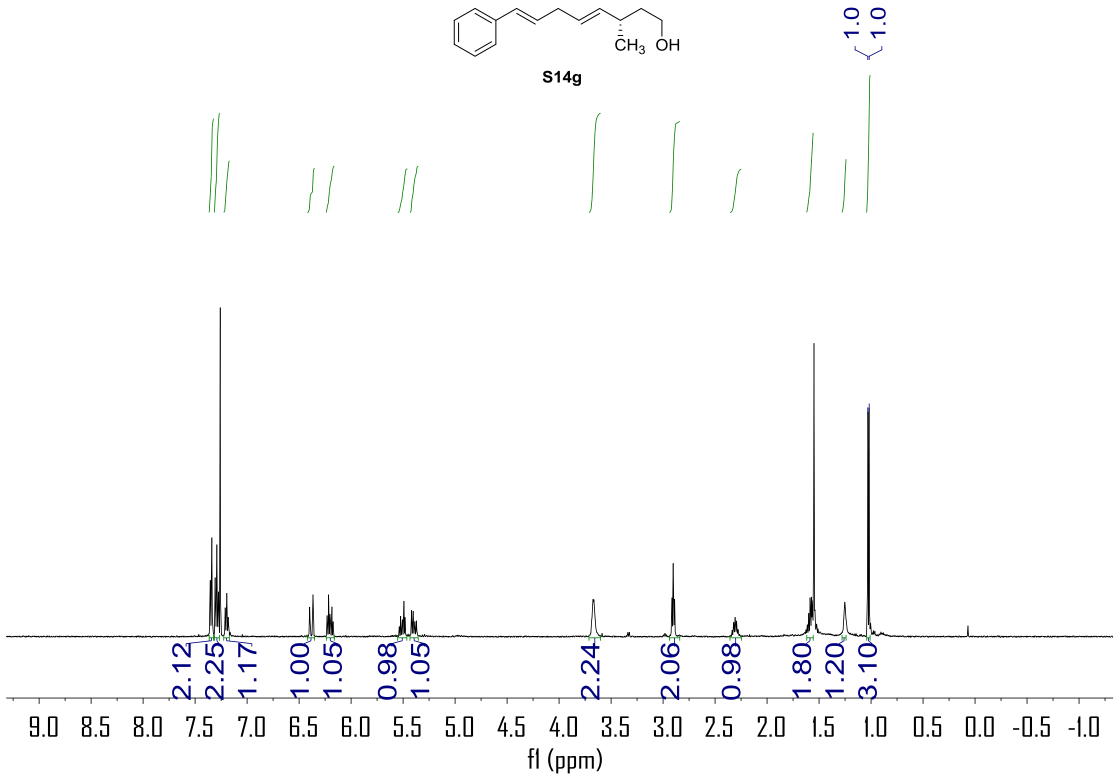
S14f
154.6
141.1
138.3
124.2
110.2
105.1
61.3
39.7
33.9
31.4
20.8
230 210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)

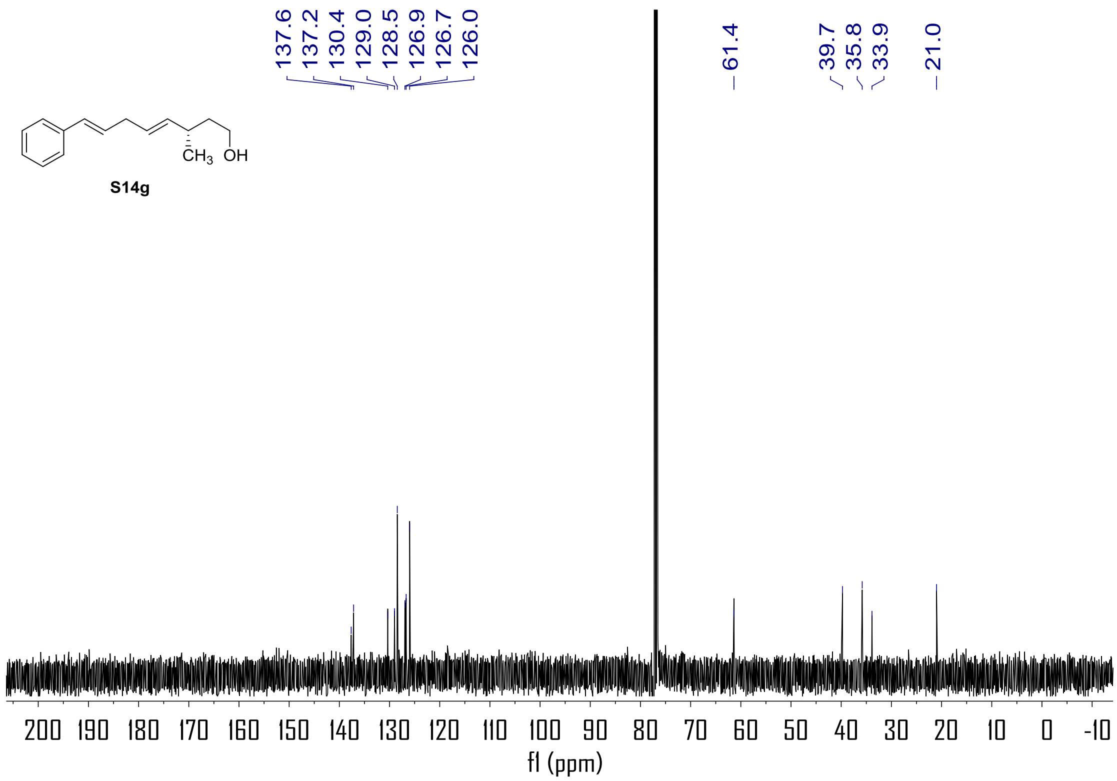


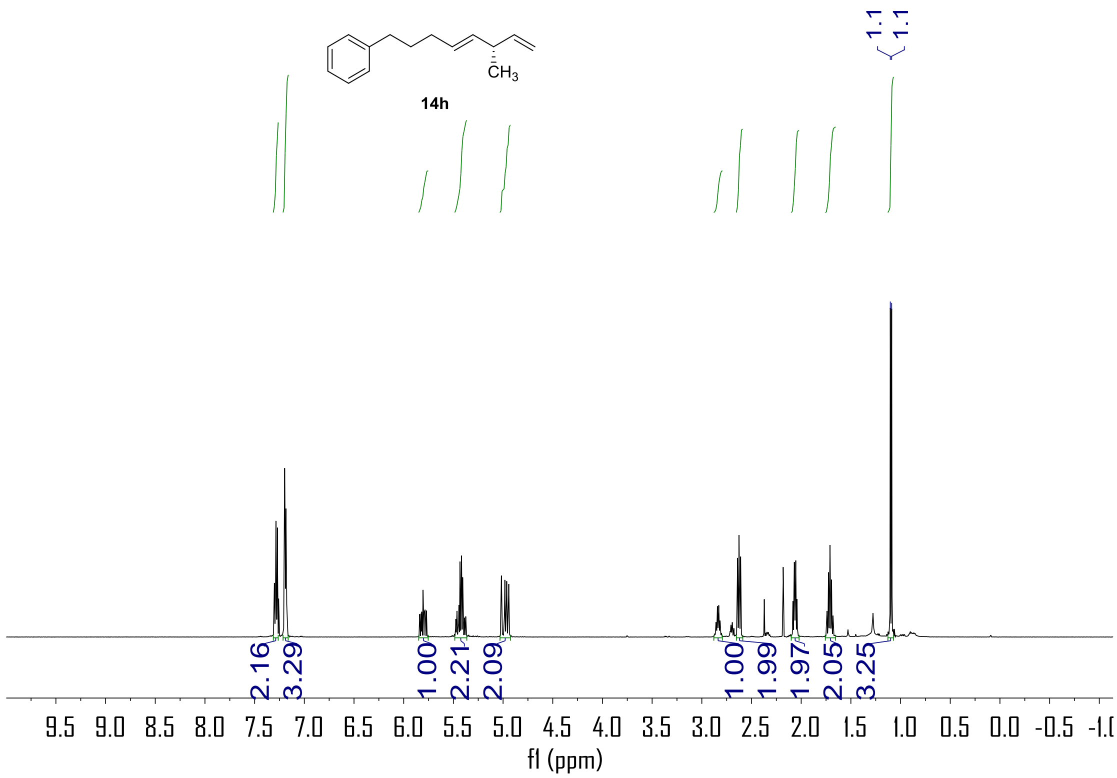
14g
CH3
1.1
1.1
2.04
2.08
1.11
1.00
1.04
1.05
1.80
1.05
1.03
2.11
1.08
3.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

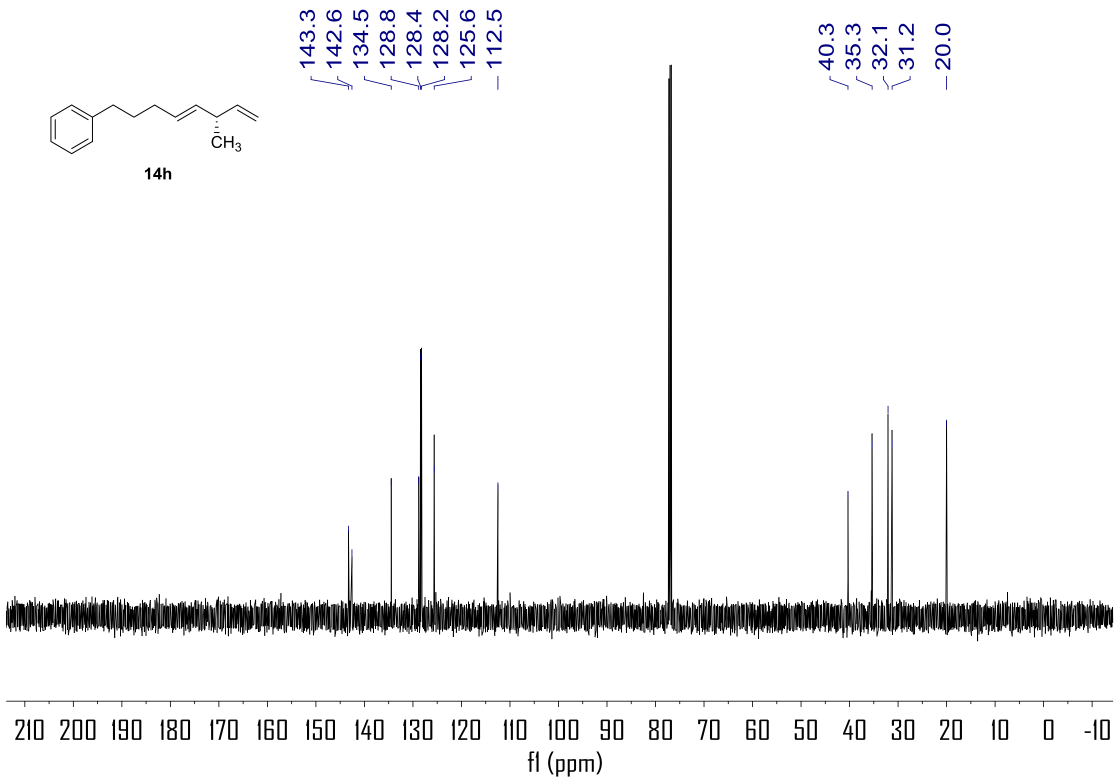


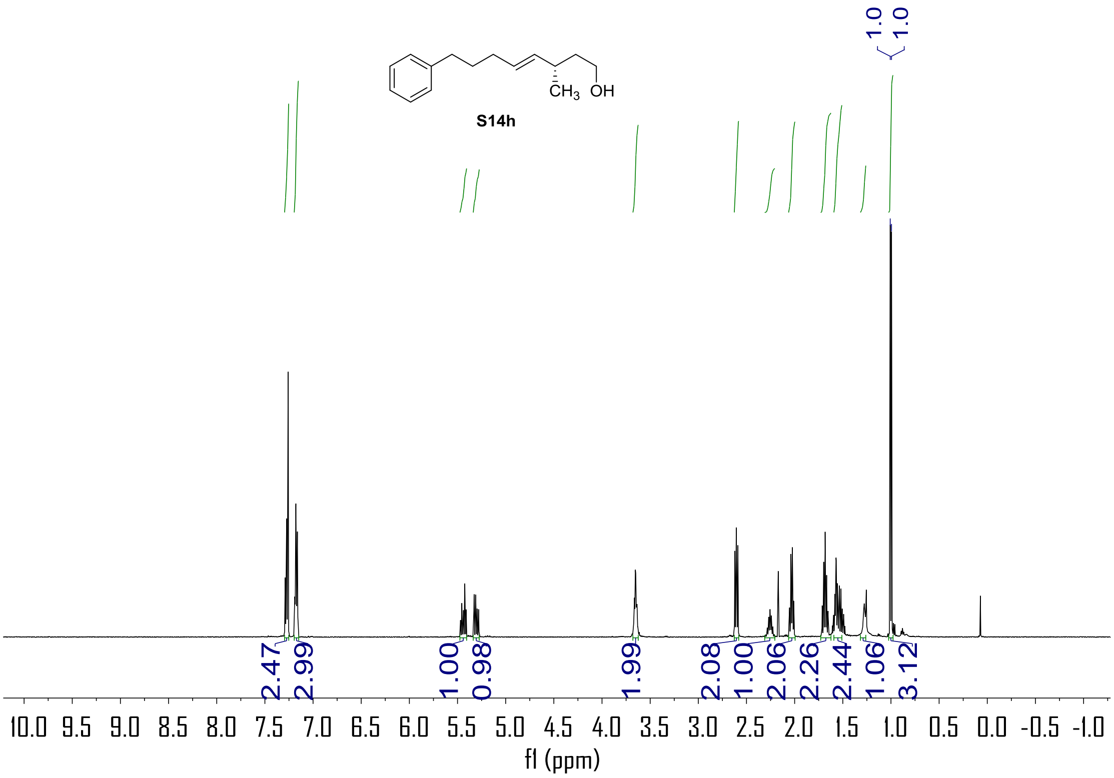
143.0
137.7
135.4
130.4
129.1
128.5
126.9
126.7
126.0
112.7
40.3
35.9
19.9
CH3
14g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CH3 OH
S14g
1.0
1.0
2.12
2.25
1.17
1.00
1.05
0.98
1.05
2.24
2.06
0.98
1.80
1.20
3.10
9.0 8.5 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 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

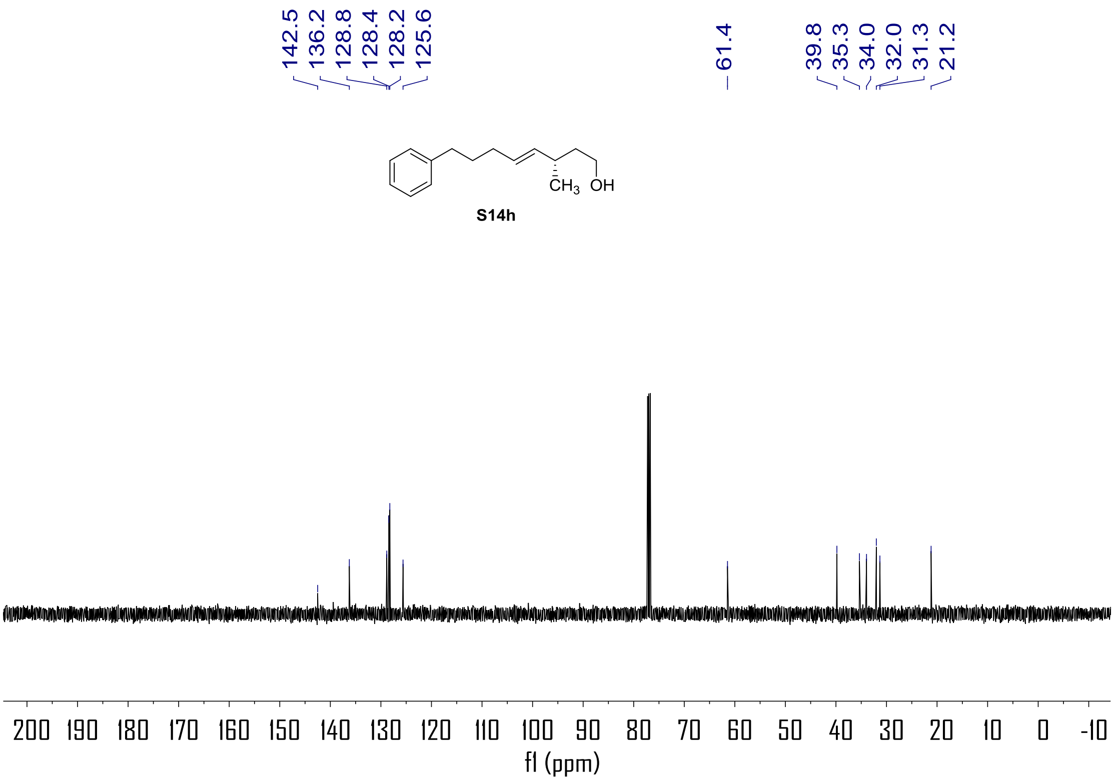

137.6
137.2
130.4
129.0
128.5
126.9
126.7
126.0
61.4
39.7
35.8
33.9
21.0
CH3 OH
S14g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


14h
CH3
1.1
1.1
2.16
3.29
1.00
2.21
2.09
1.00
1.99
1.97
2.05
3.25
9.5 9.0 8.5 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 1.0 0.5 0.0 -0.5
f1 (ppm)


14h
CH3
143.3
142.6
134.5
128.8
128.4
128.2
125.6
112.5
40.3
35.3
32.1
31.2
20.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

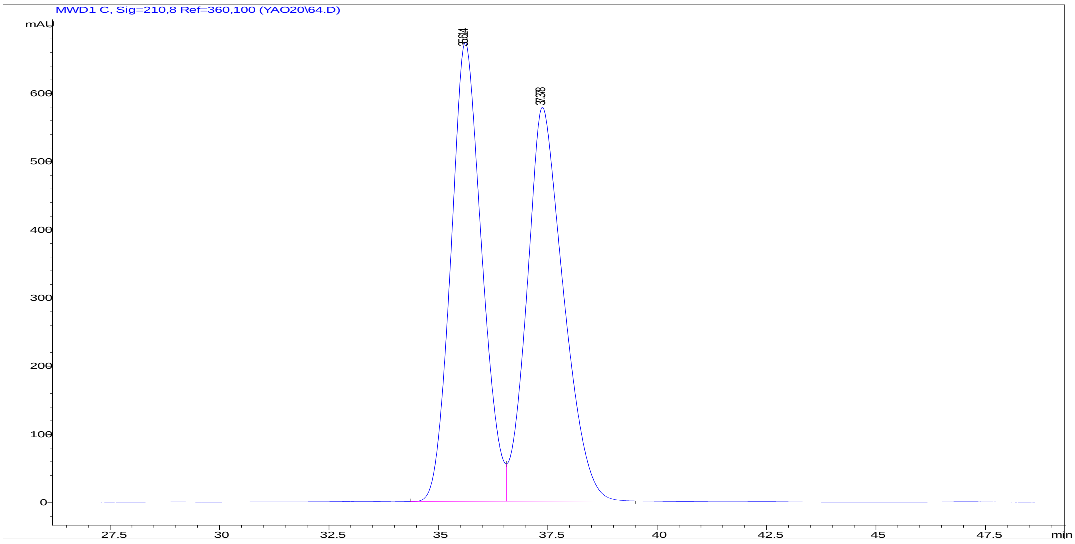


CH3 OH
S14h
1.0
1.0
2.47
2.99
1.00
0.98
1.99
2.08
1.00
2.06
2.26
2.44
1.06
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



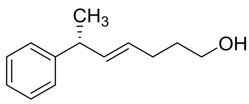
142.5
136.2
128.8
128.4
128.2
125.6
61.4
39.8
35.3
34.0
32.0
31.3
21.2
CH3 OH
S14h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5. HPLC Traces

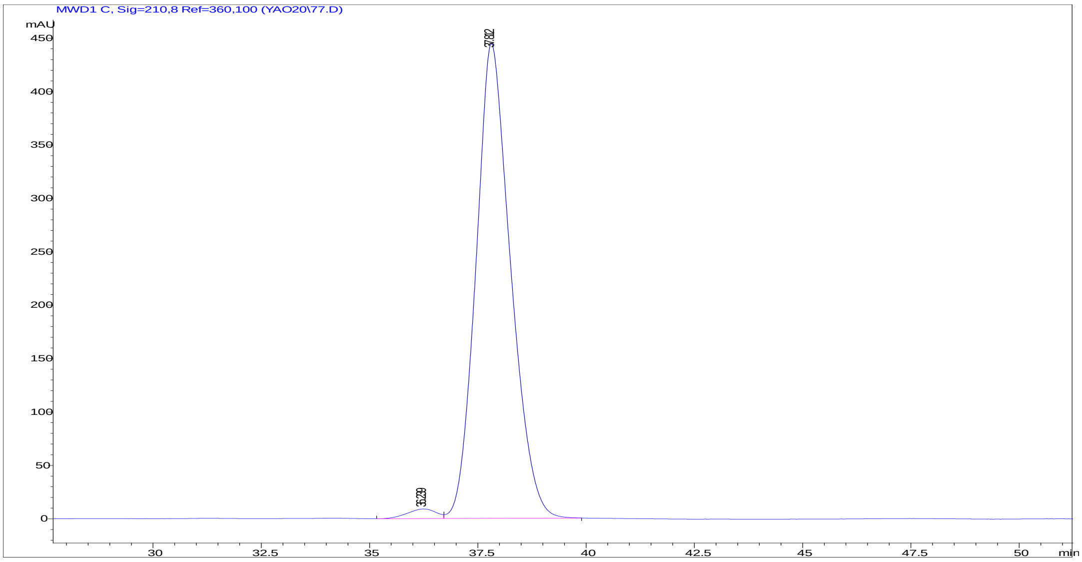


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.614	VV	0.7320	3.31146e4	673.01642	49.6825
2	37.378	VB	0.8454	3.35379e4	577.60913	50.3175
Totals :				6.66525e4	1250.62555	

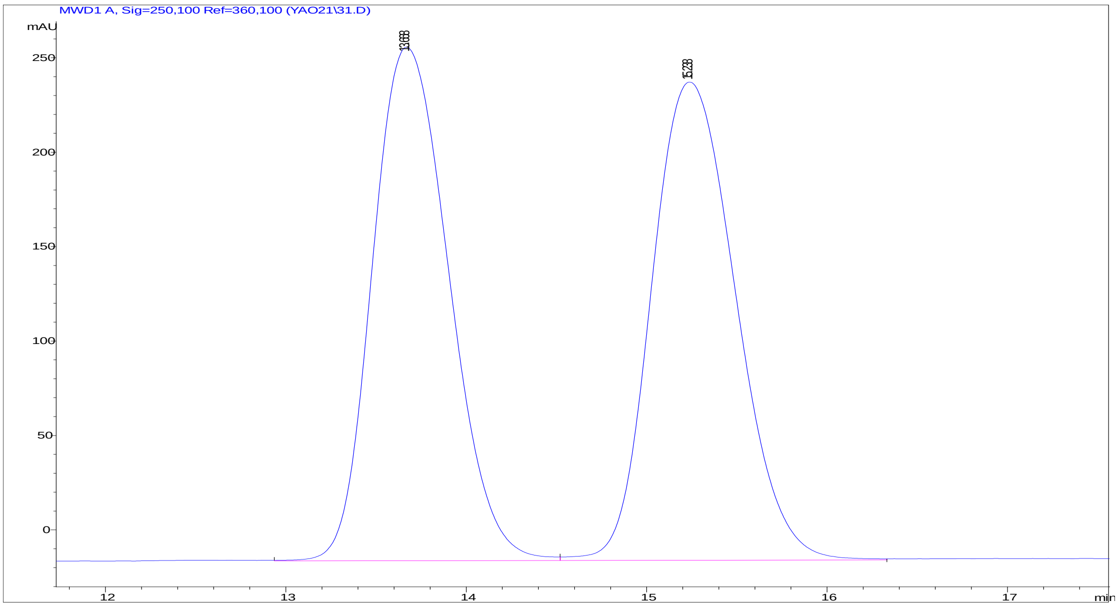


S5a



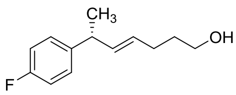
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.239	PV	0.5653	417.83636	9.03895	1.6603
2	37.812	VB	0.8195	2.47491e4	444.58871	98.3397
Totals :				2.51669e4	453.62767	

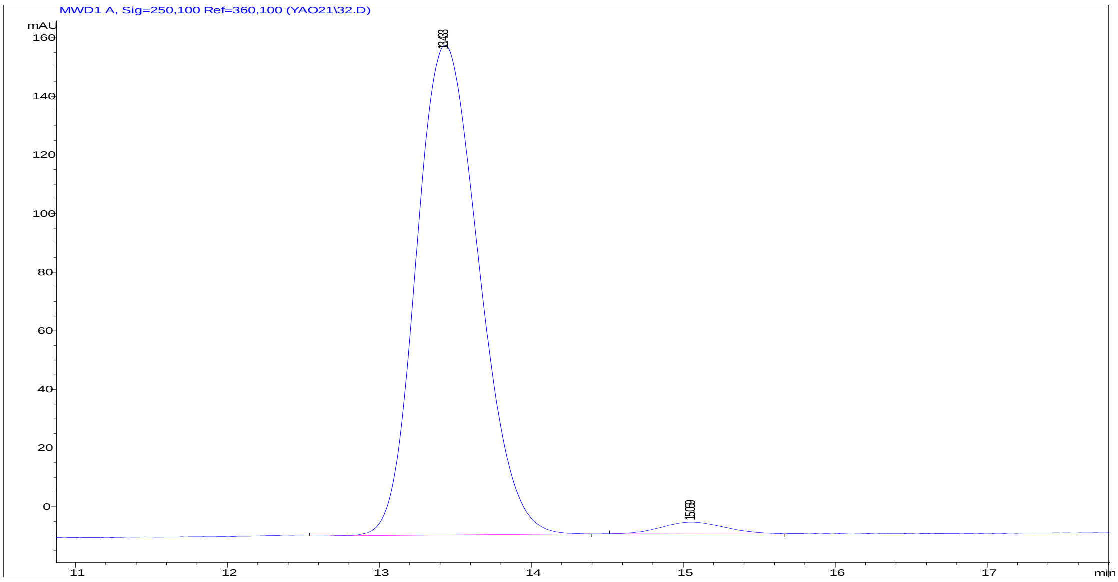


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.668	VV	0.4636	8011.33447	271.99335	49.4931
2	15.238	VV	0.5146	8175.44287	253.24960	50.5069
Totals :				1.61868e4	525.24295	

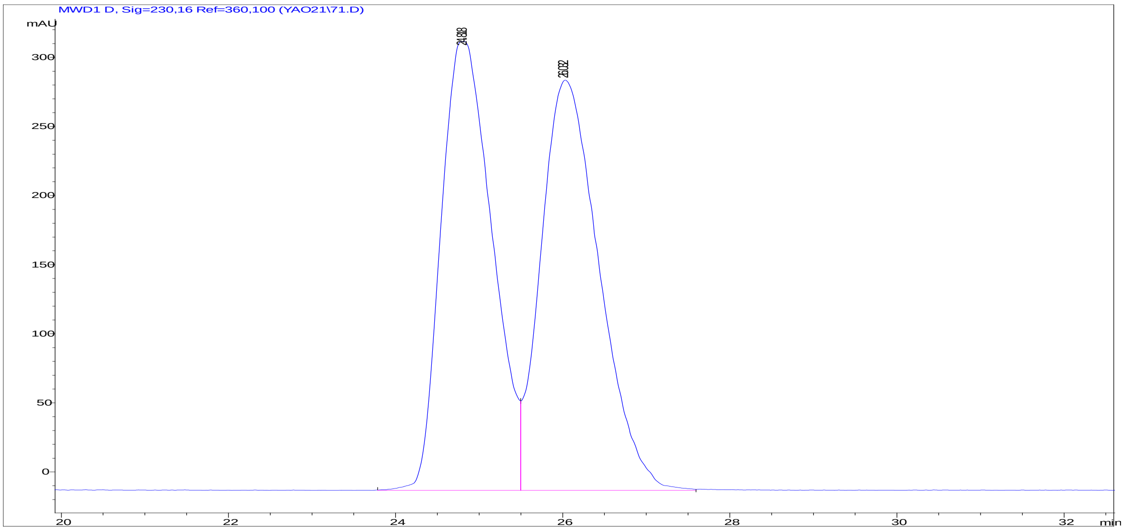


S5b

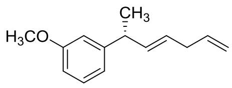


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.433	VB	0.4560	4784.17969	167.10588	97.6175
2	15.059	BV	0.3609	116.76463	3.97317	2.3825
Totals :				4900.94432	171.07905	

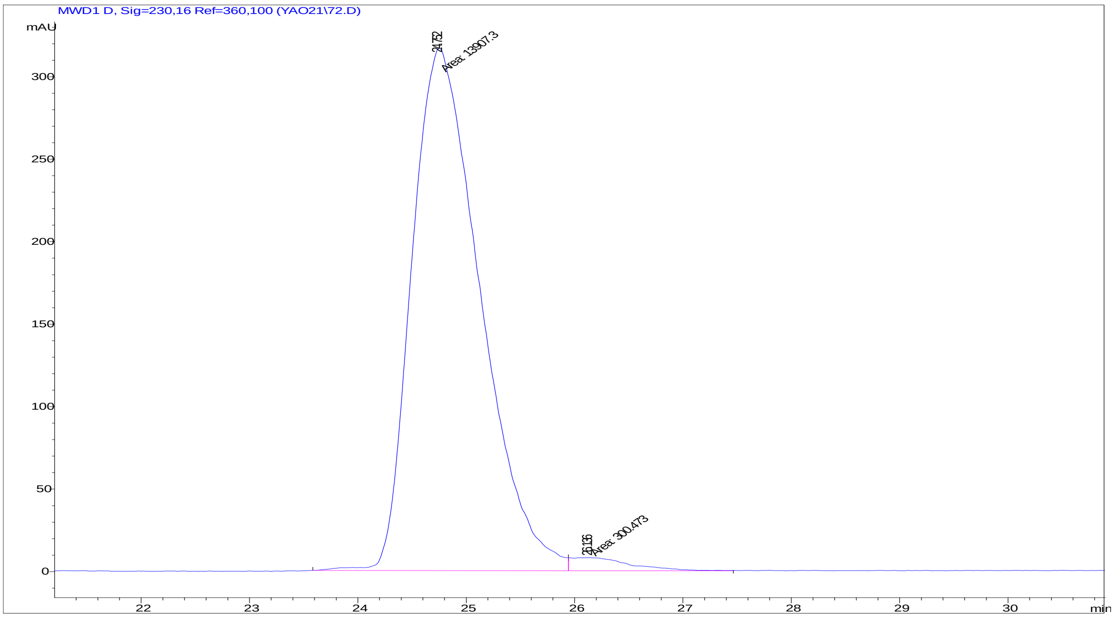


Signal 4: MWD1 D, Sig=230,16 Ref=360,100



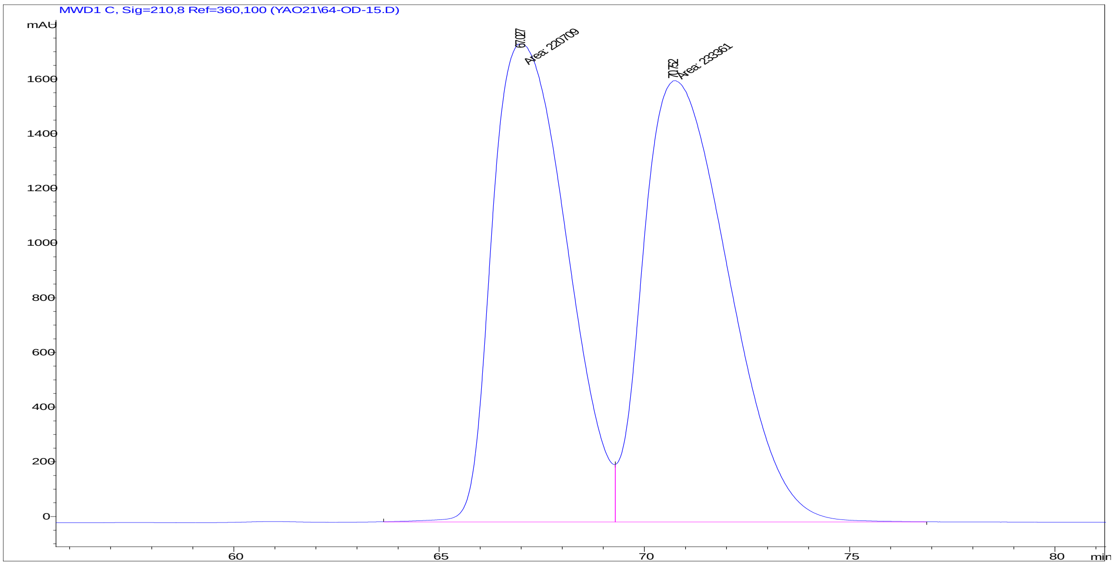
S5c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.818	VV	0.5269	1.38403e4	324.92722	48.9535
2	26.032	VV	0.6450	1.44320e4	296.96225	51.0465
Totals :				2.82723e4	621.88947	



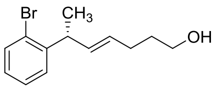
Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.752	MF	0.7313	1.39073e4	316.96719	97.8852
2	26.136	FM	0.6289	300.47311	7.96334	2.1148
Totals :				1.42078e4	324.93053	

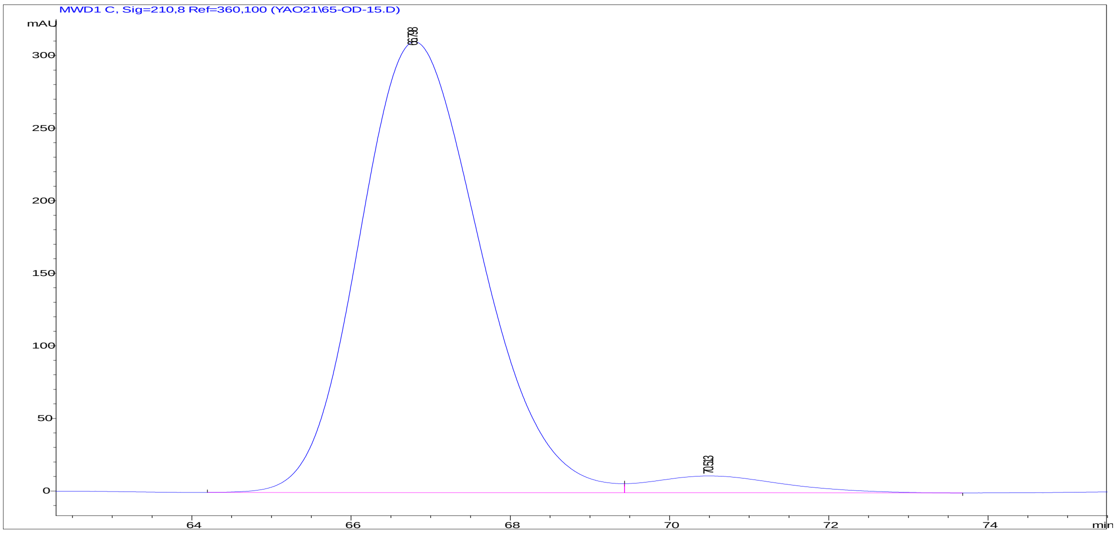


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.027	MF	2.1039	2.20709e5	1748.44641	48.6068
2	70.752	FM	2.4098	2.33361e5	1613.98328	51.3932
Totals :				4.54071e5	3362.42969	

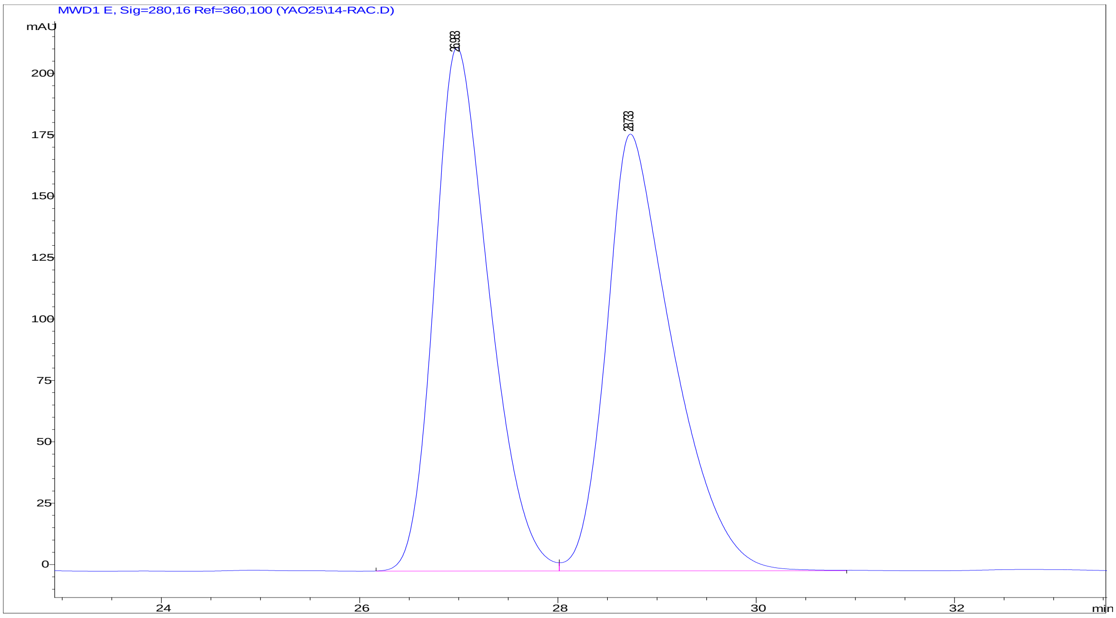


S5d

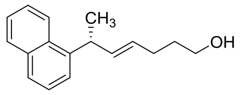


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	66.798	BV	1.5778	3.27920e4	310.58850	96.0518
2	70.513	VP	1.3675	1347.89758	11.63566	3.9482
Totals :				3.41399e4	322.22416	

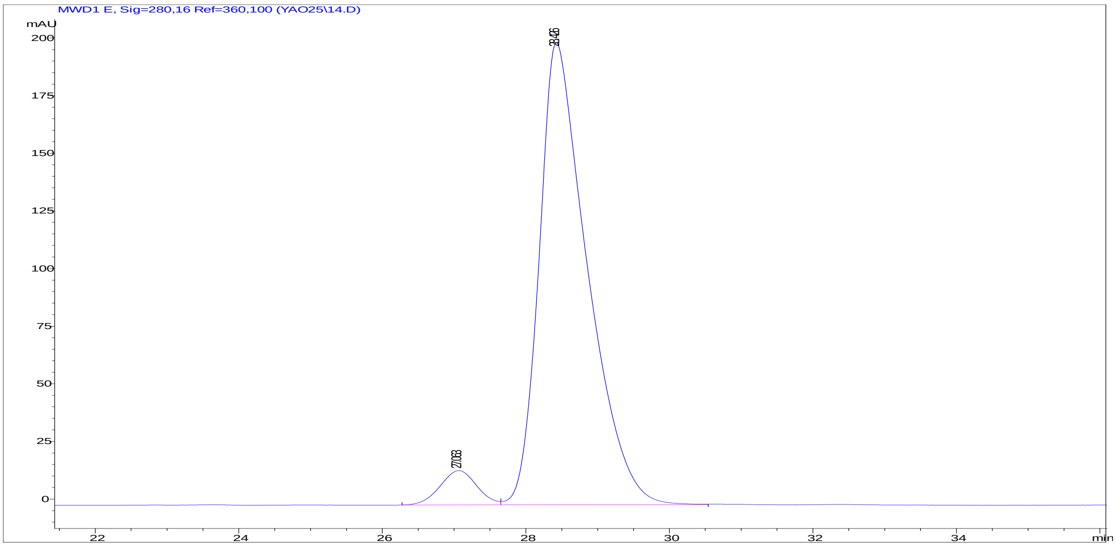


Signal 5: MWD1 E, Sig=280,16 Ref=360,100



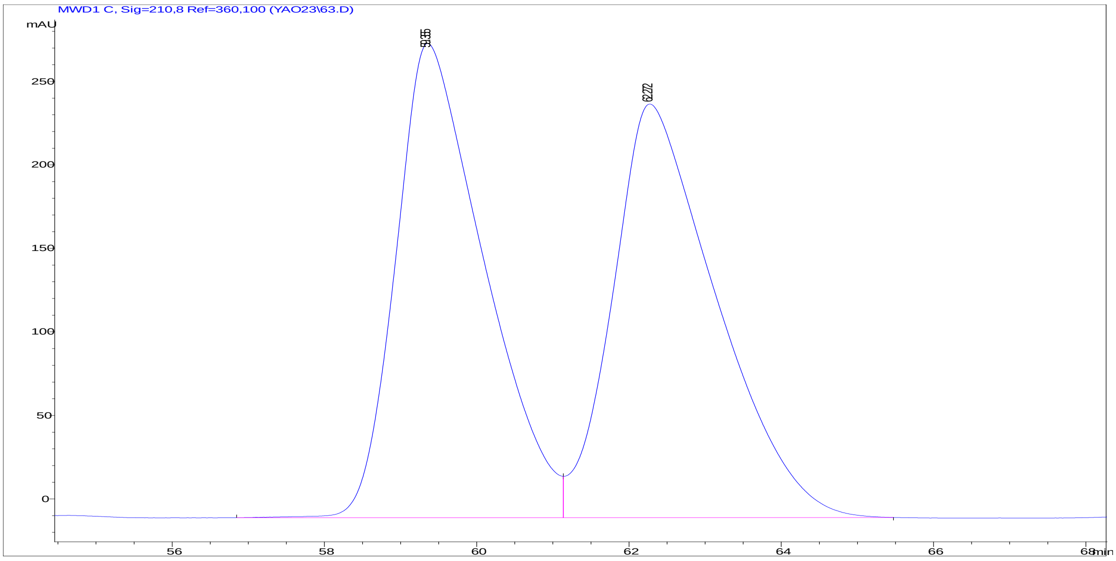
S5e

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.983	BV	0.5861	8218.89355	213.05386	49.7787
2	28.733	VB	0.6799	8291.97168	177.85040	50.2213
Totals :				1.65109e4	390.90427	



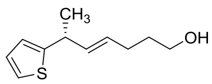
Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.063	BV	0.5601	531.11029	14.89005	5.3756
2	28.426	VB	0.6722	9348.90430	200.42754	94.6244
Totals :				9880.01459	215.31758	

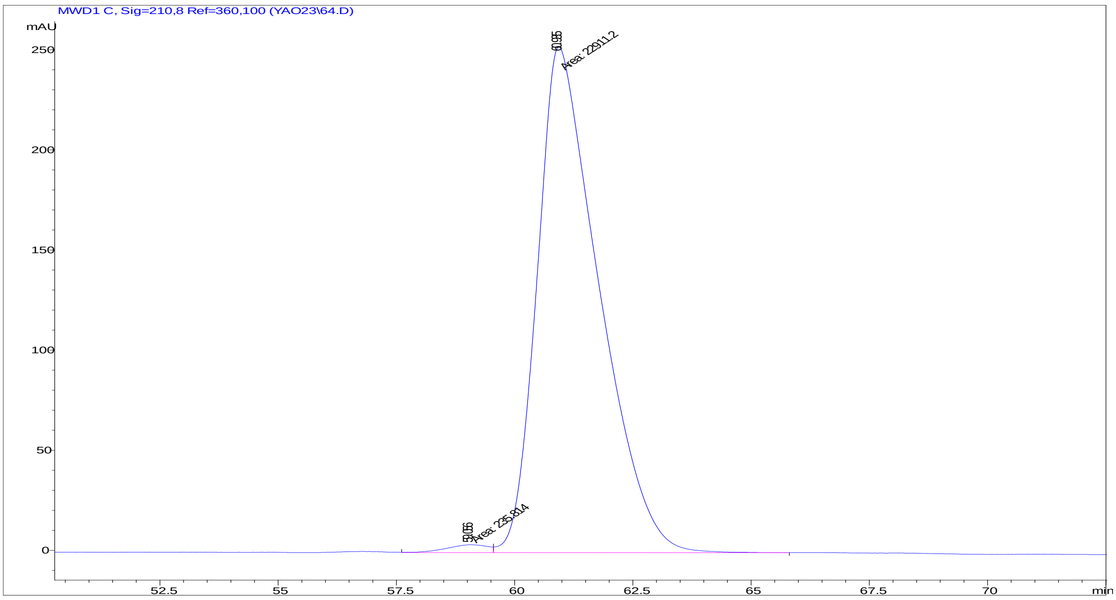


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.355	BV	1.1217	2.29247e4	284.00952	49.4731
2	62.272	VB	1.2949	2.34129e4	247.65938	50.5269
Totals :				4.63376e4	531.66890	

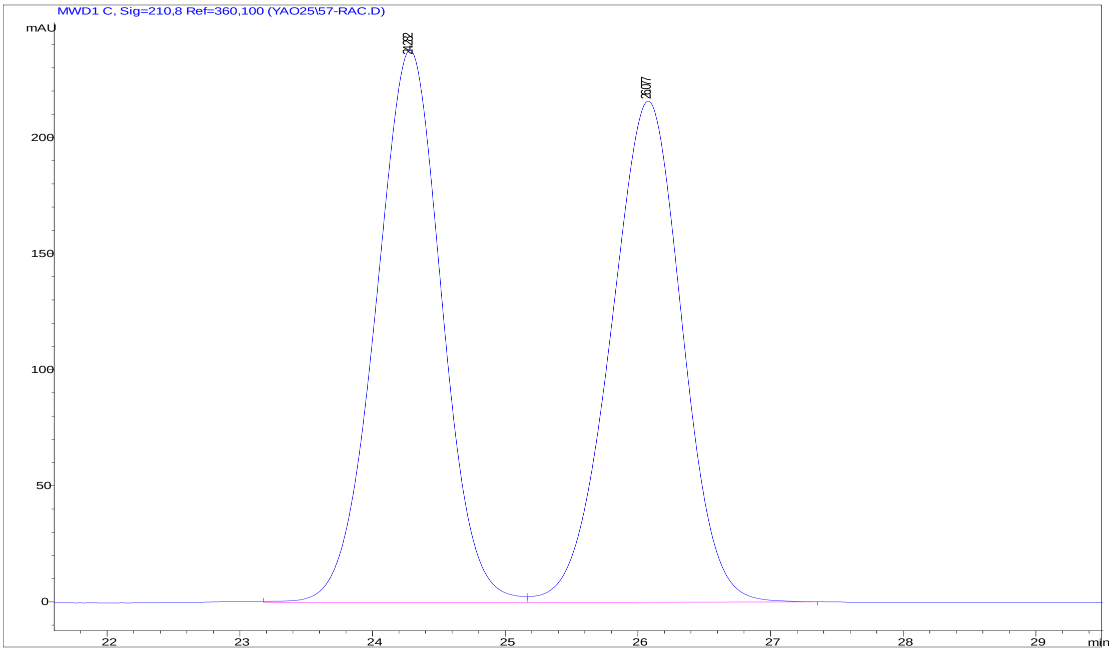


S5f

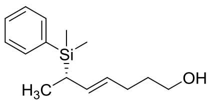


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	59.056	MF	1.0089	235.81412	3.89539	1.0188
2	60.935	FM	1.5116	2.29112e4	252.61760	98.9812
Totals :				2.31470e4	256.51299	

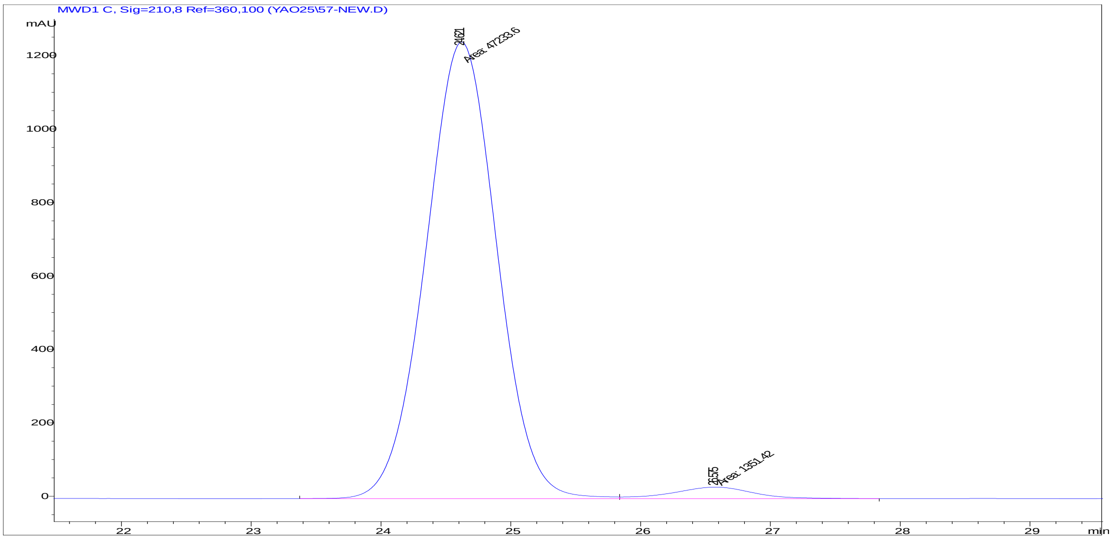


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



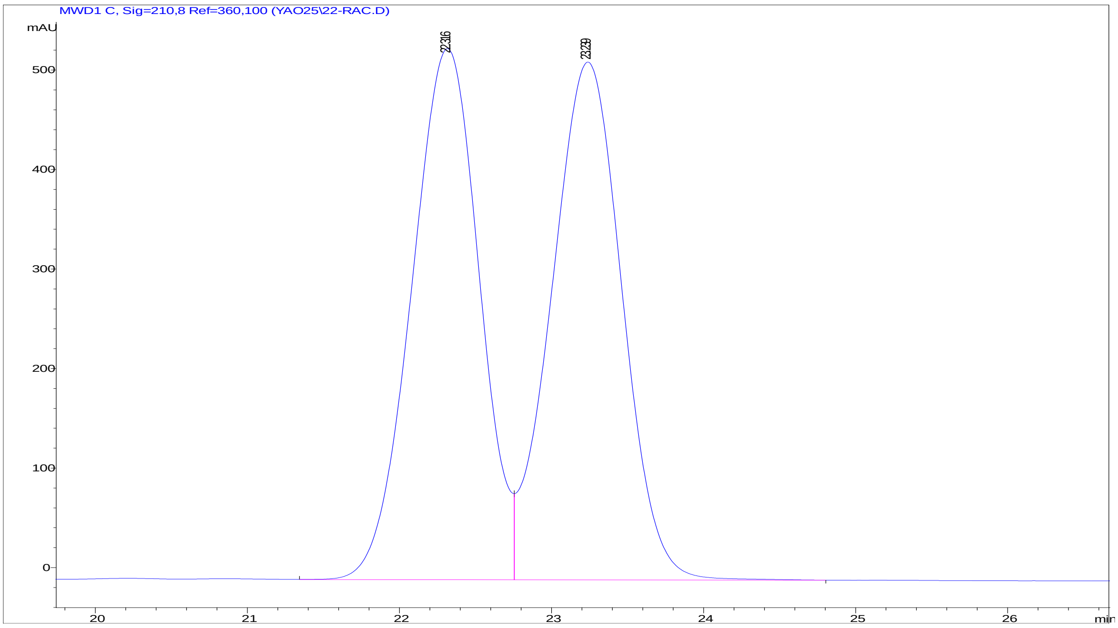
S5g

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.282	VV	0.5306	8250.25684	237.91258	50.5113
2	26.077	VB	0.5771	8083.23828	215.76483	49.4887
Totals :				1.63335e4	453.67741	

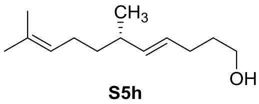


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.621	MF	0.6330	4.72336e4	1243.59985	97.2184
2	26.575	FM	0.7150	1351.42358	31.50056	2.7816
Totals :				4.85850e4	1275.10042	

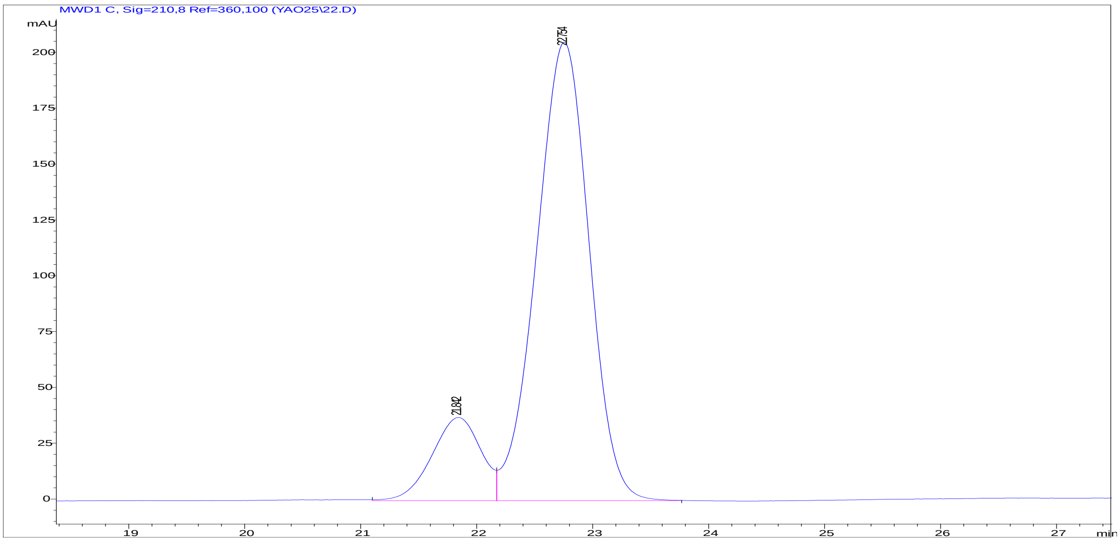


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



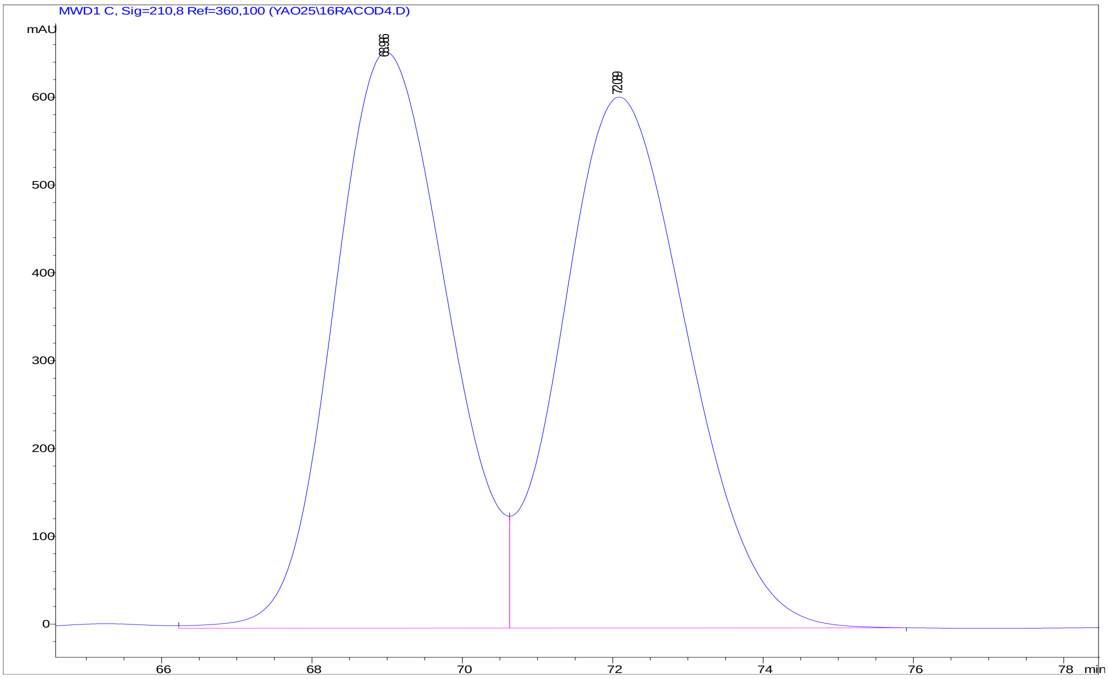
S5h

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.316	VV	0.4838	1.65538e4	533.80267	49.5973
2	23.239	VB	0.5031	1.68226e4	520.44165	50.4027
Totals :				3.33764e4	1054.24432	



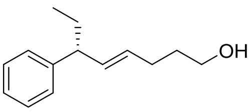
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.842	BV	0.4522	1098.66541	37.23779	14.4806
2	22.754	VB	0.4888	6488.46289	205.26900	85.5194
Totals :				7587.12830	242.50679	

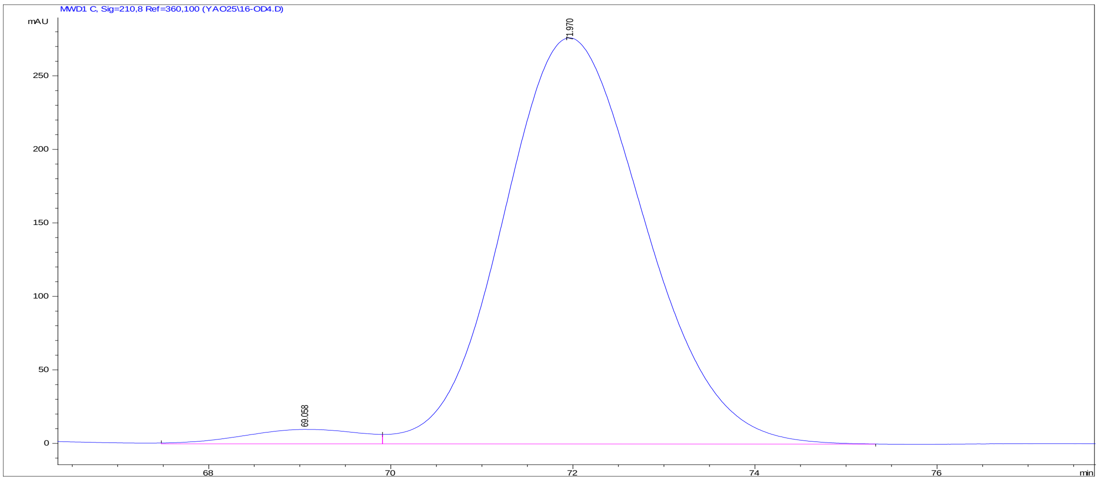


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.986	VV	1.5006	6.90719e4	655.91278	49.5156
2	72.089	VB	1.6371	7.04232e4	604.50391	50.4844
Totals :				1.39495e5	1260.41669	

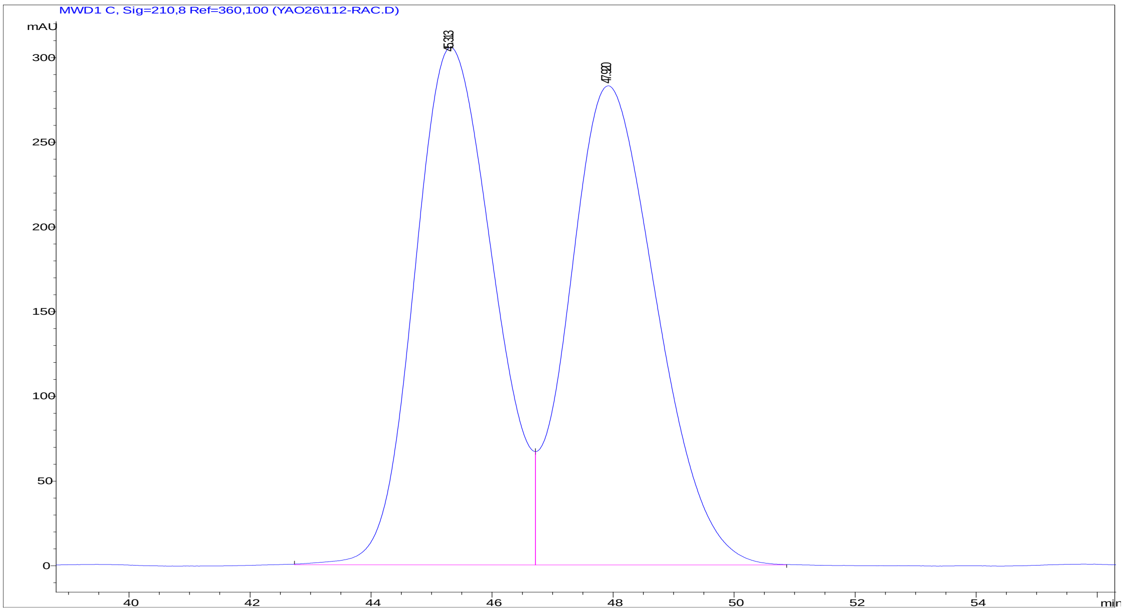


S7a



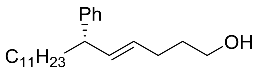
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.058	VV	1.0629	885.67426	9.87016	2.8794
2	71.970	VB	1.5496	2.98730e4	276.24344	97.1206
Totals :				3.07587e4	286.11360	

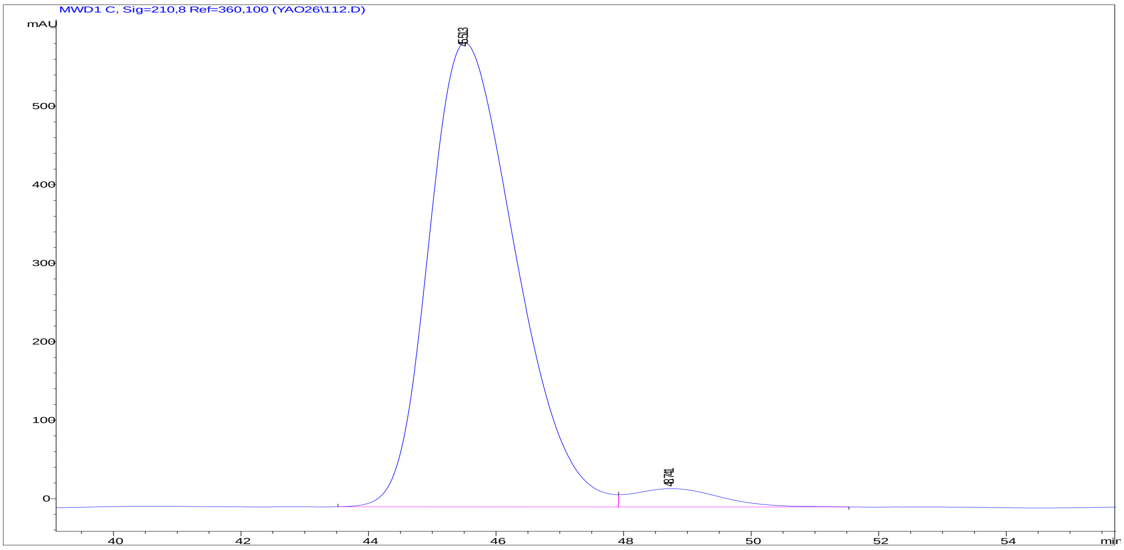


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.313	BV	1.4058	2.78060e4	305.52203	49.4240
2	47.920	VB	1.5457	2.84541e4	282.82498	50.5760
Totals :				5.62601e4	588.34702	

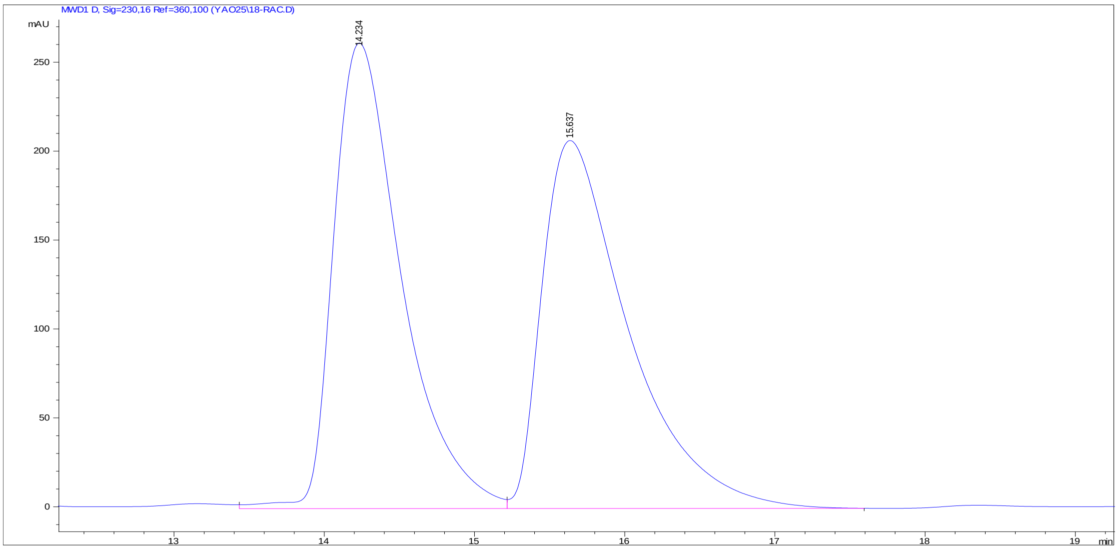


S7b

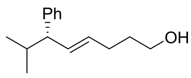


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.513	BV	1.4321	5.59715e4	591.44849	96.1317
2	48.741	VB	1.2217	2252.27173	23.34252	3.8683
Totals :				5.82237e4	614.79101	

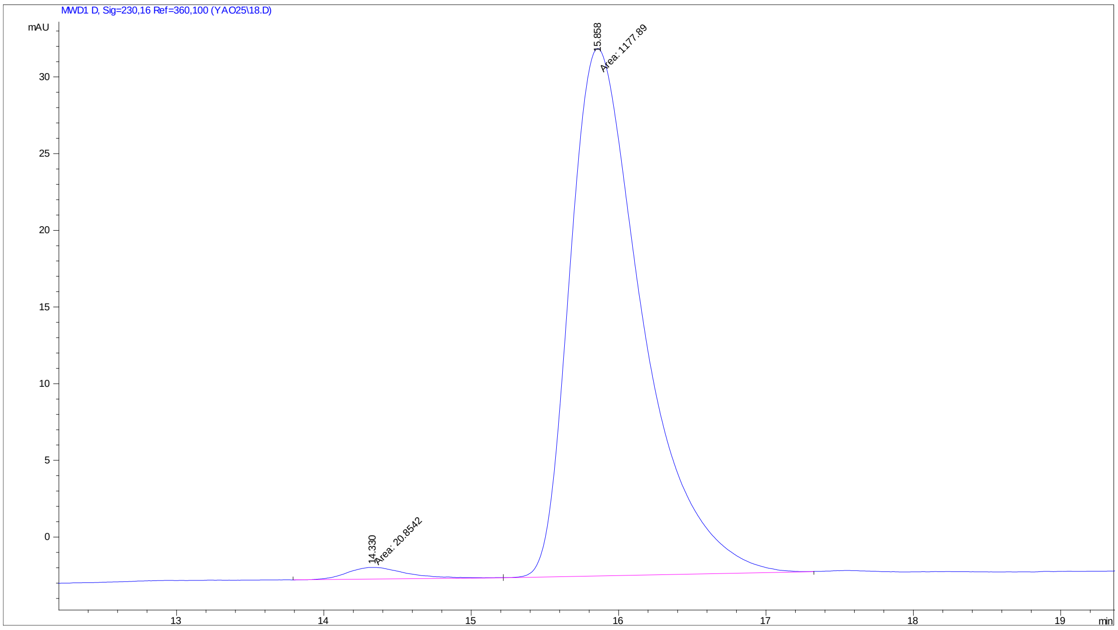


Signal 4: MWD1 D, Sig=230,16 Ref=360,100



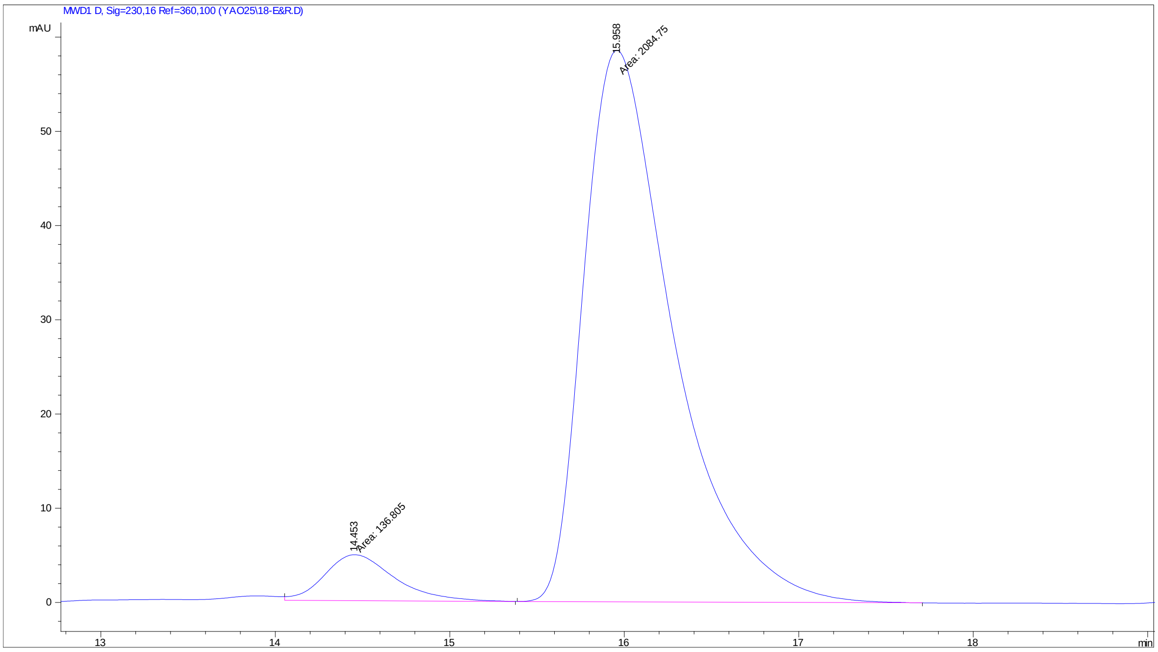
S7c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.234	VV	0.4815	8247.66797	261.84363	49.9225
2	15.637	VB	0.6005	8273.28223	206.90852	50.0775
Totals :				1.65210e4	468.75215	

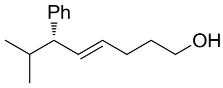


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.330	MM	0.4581	20.85415	7.58792e-1	1.7397
2	15.858	MM	0.5708	1177.88574	34.39566	98.2603
Totals :				1198.73990	35.15445	

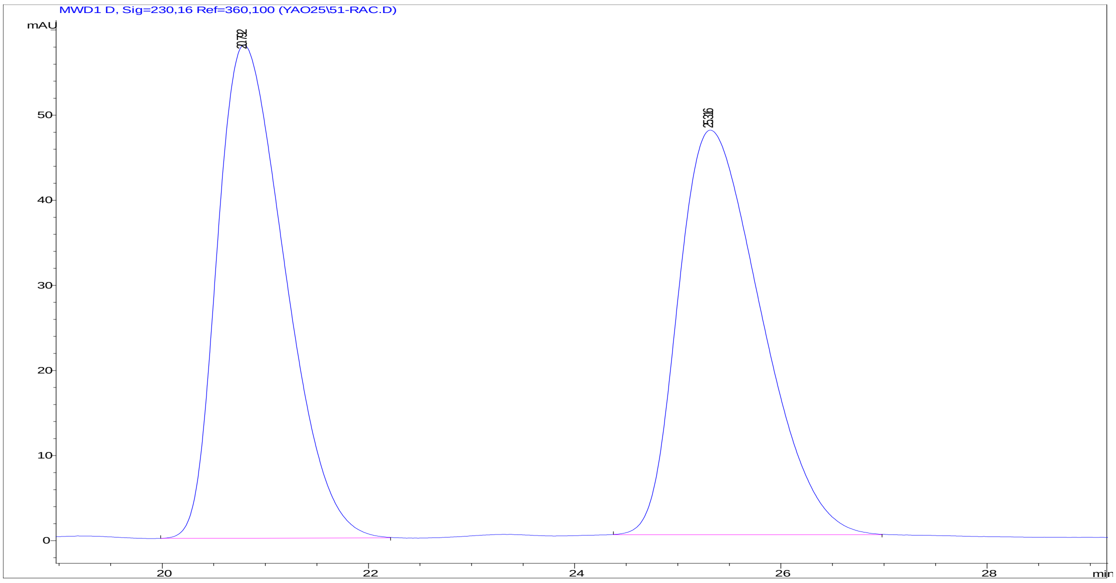


Signal 4: MWD1 D, Sig=230,16 Ref=360,100



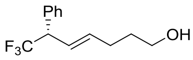
S7c
from **(*E*)-8**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.453	MM	0.4676	136.80518	4.87605	6.1581
2	15.958	MM	0.5935	2084.75269	58.54684	93.8419
Totals :				2221.55786	63.42290	

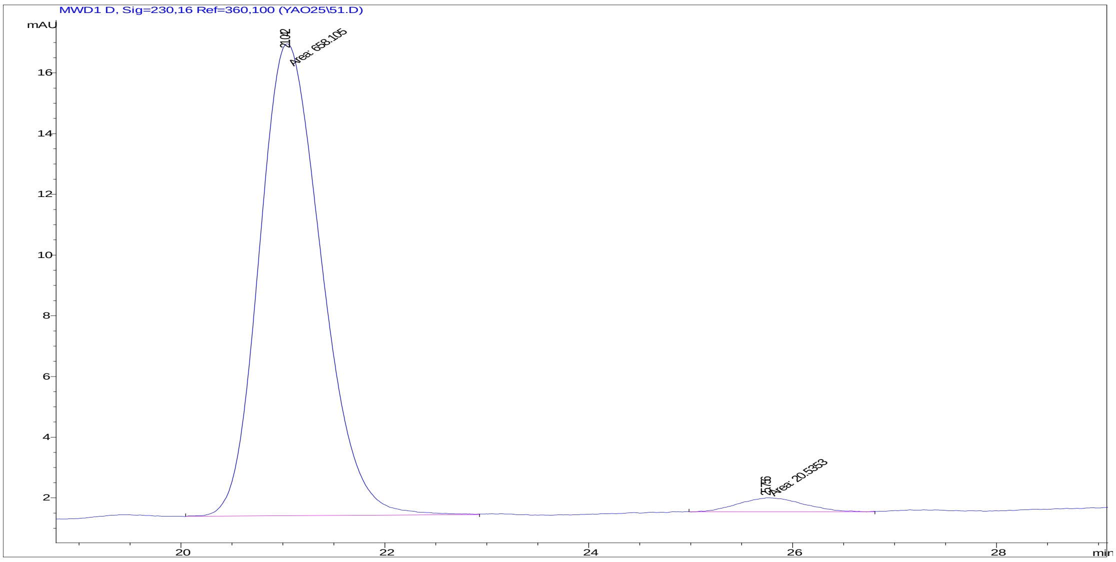


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.792	BB	0.7163	2644.68457	57.96334	49.9100
2	25.316	BB	0.8713	2654.22095	47.54547	50.0900
Totals :				5298.90552	105.50880	

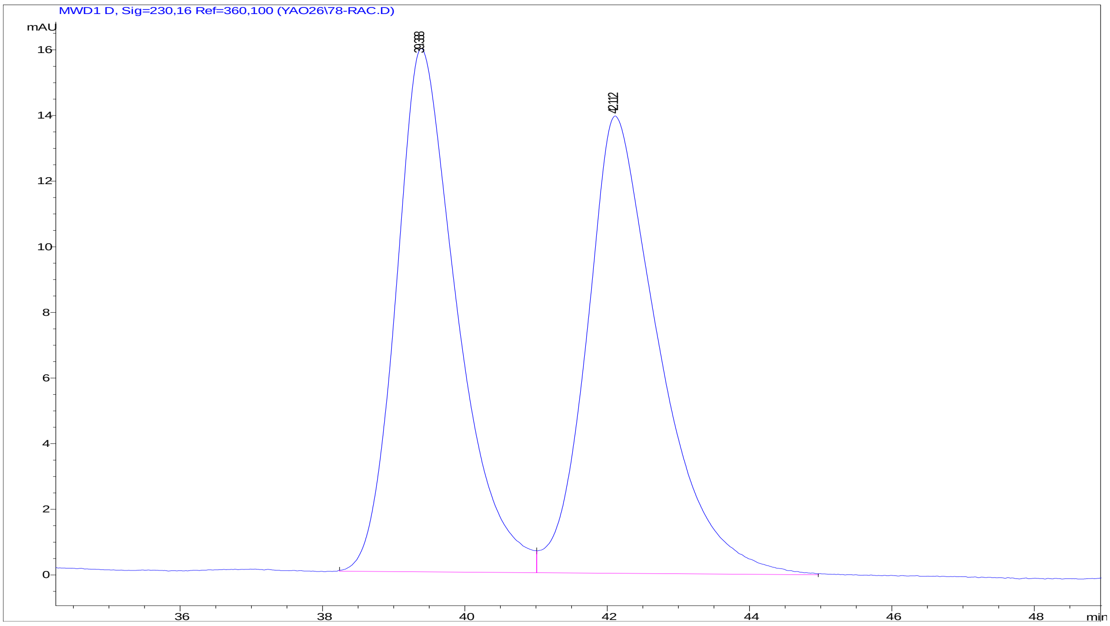


S7d



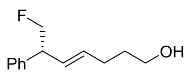
Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.042	MM	0.7056	658.10541	15.54498	96.9741
2	25.756	MM	0.7391	20.53532	4.63092e-1	3.0259
Totals :				678.64072	16.00807	

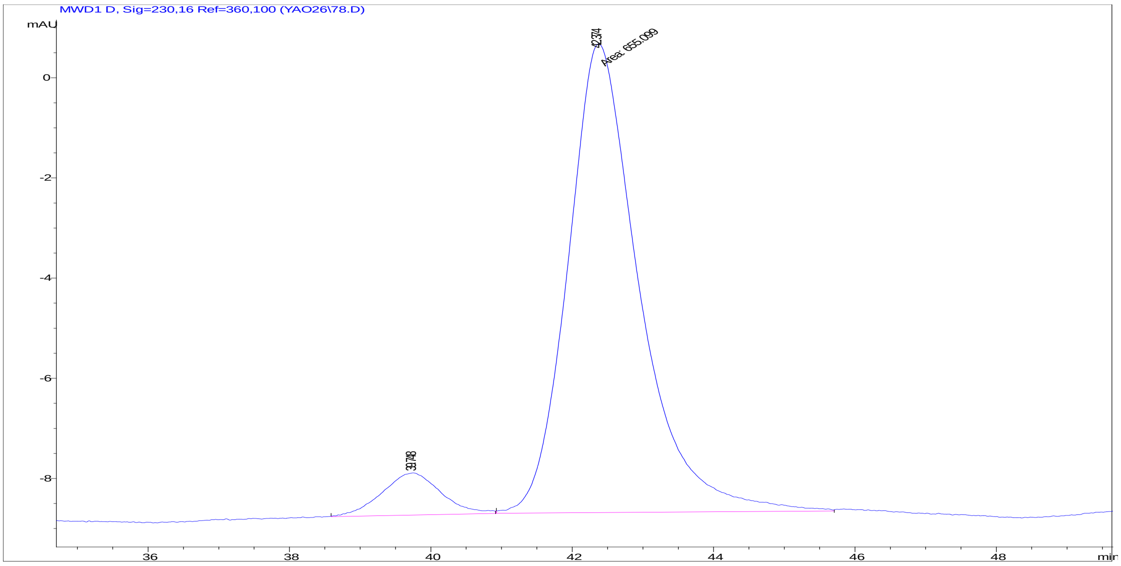


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.388	BV	0.8674	950.57697	15.94785	49.1595
2	42.112	VB	0.9914	983.08289	13.92924	50.8405
Totals :				1933.65985	29.87709	

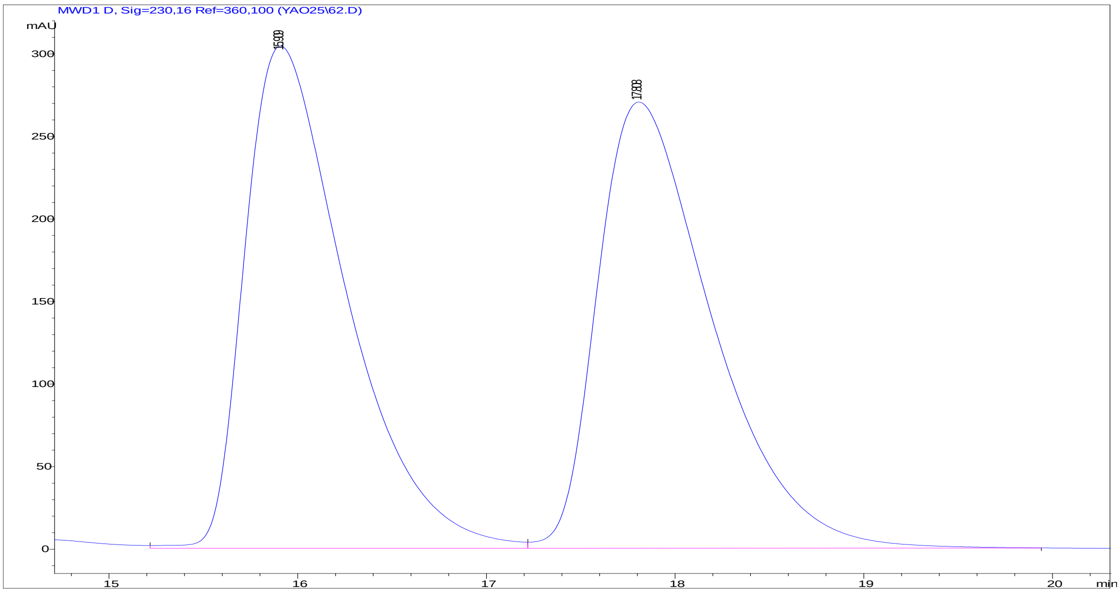


S7e



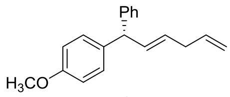
Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.748	BV	0.8130	48.92134	8.43062e-1	6.9489
2	42.374	MM	1.1663	655.09906	9.36190	93.0511
Totals :				704.02040	10.20496	

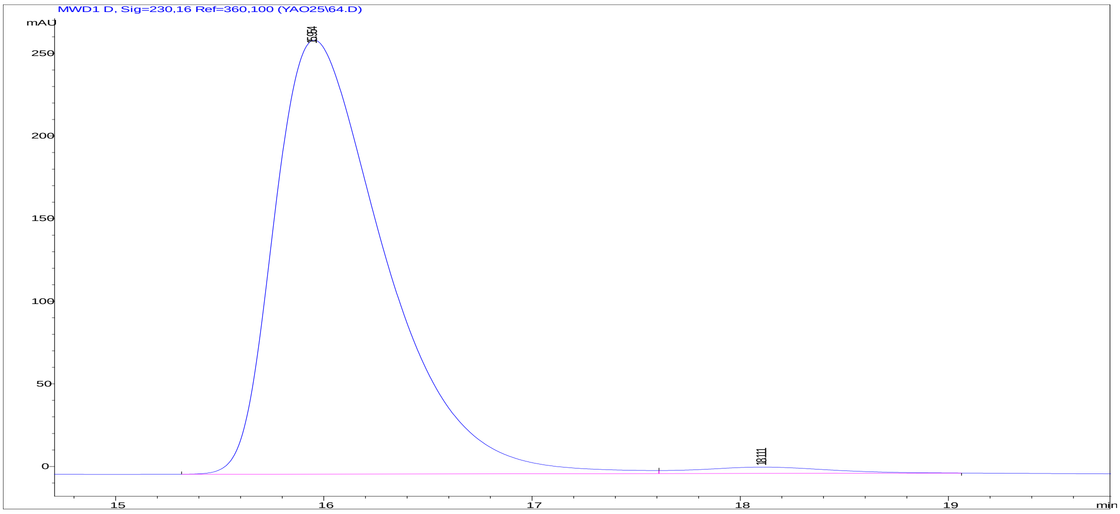


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.909	VV	0.5689	1.13955e4	304.32529	49.9911
2	17.808	VB	0.6461	1.13996e4	270.25388	50.0089
Totals :				2.27951e4	574.57916	

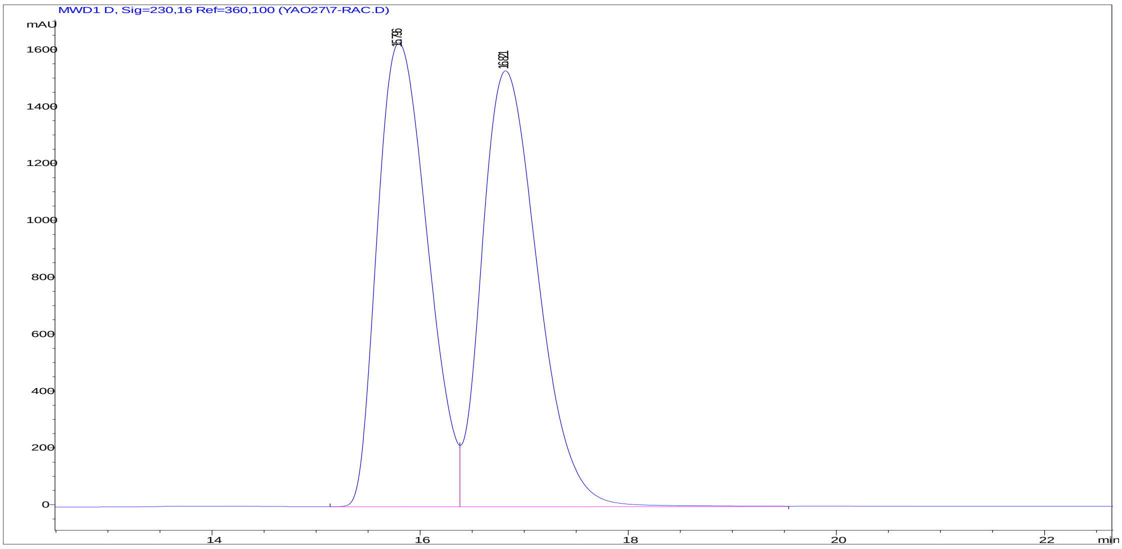


7f



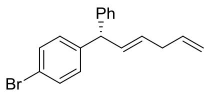
Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.954	BB	0.5645	9693.57422	262.69174	98.2585
2	18.111	BB	0.5862	171.80400	3.85338	1.7415
Totals :				9865.37822	266.54512	

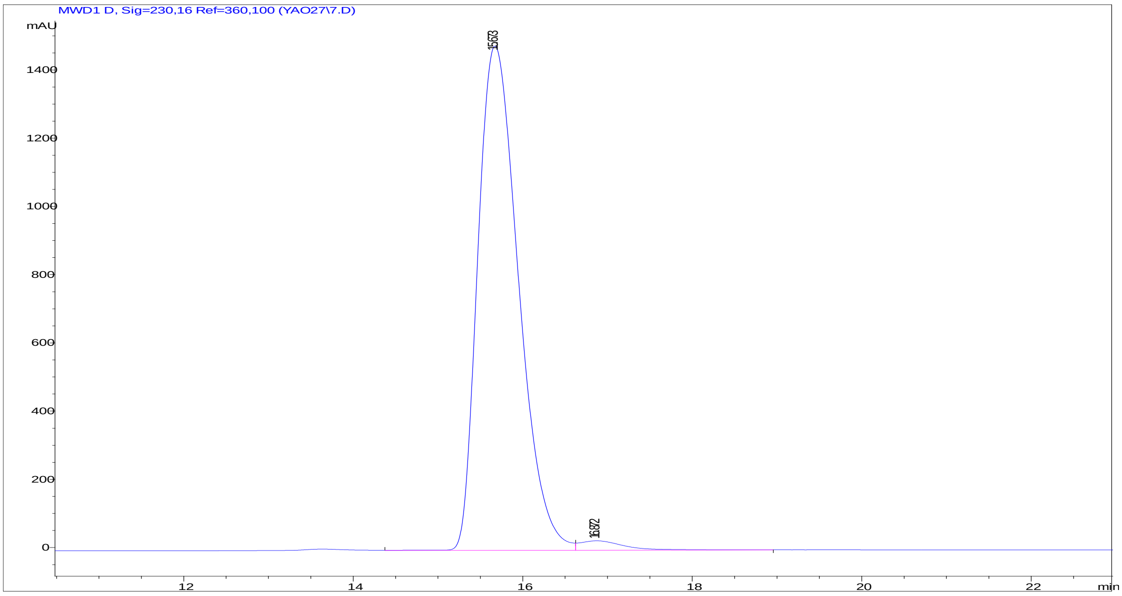


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.796	VV	0.5317	5.47482e4	1630.75940	48.8053
2	16.821	VV	0.5813	5.74284e4	1532.09973	51.1947
Totals :				1.12177e5	3162.85913	

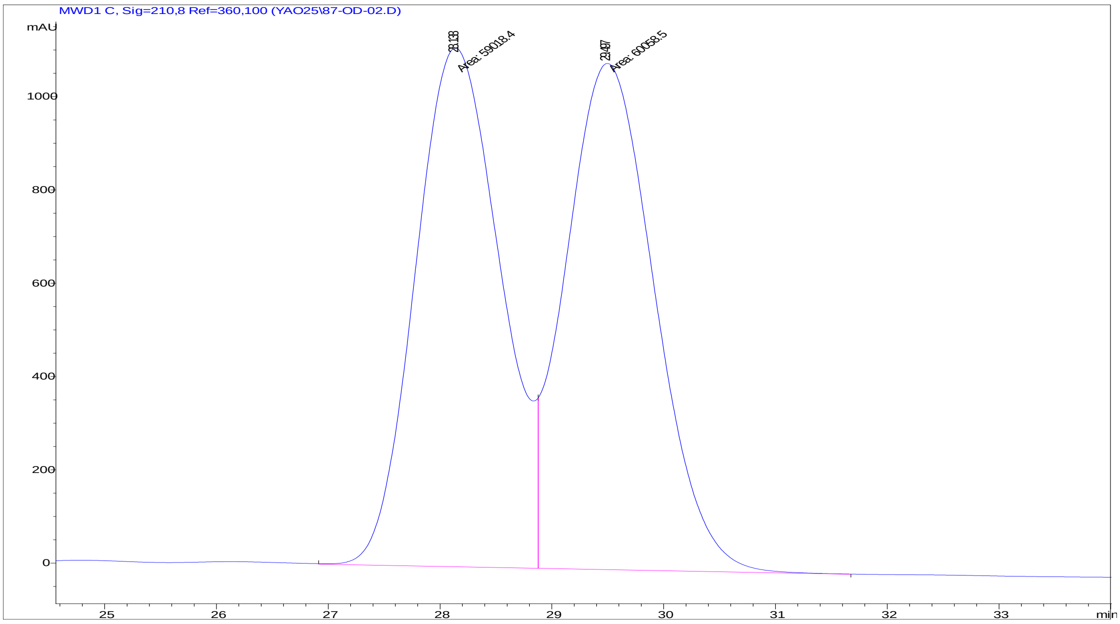


7g

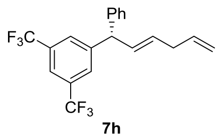


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

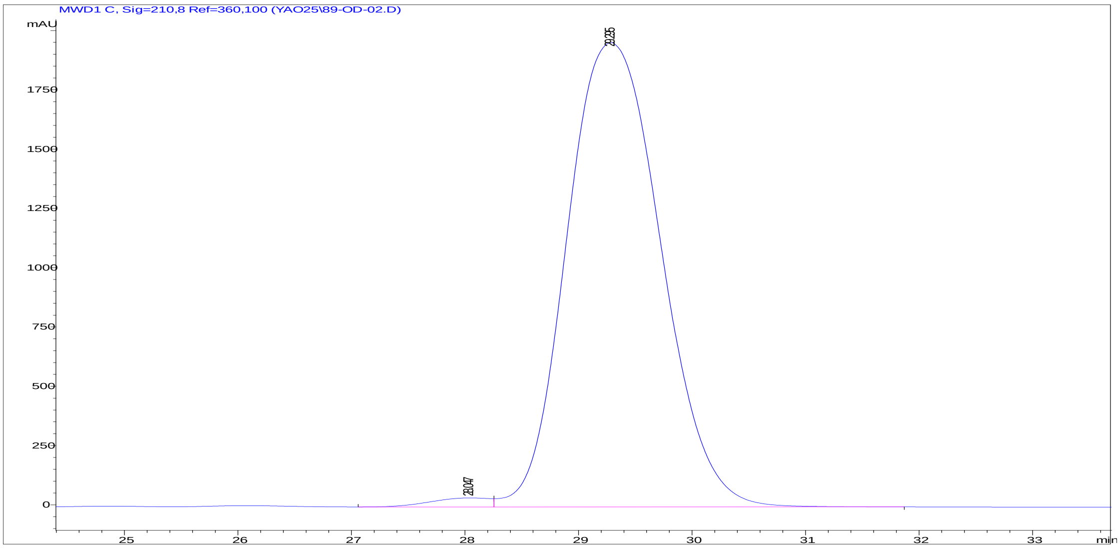
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.673	VV	0.5279	4.91434e4	1478.21790	97.9808
2	16.872	VB	0.5417	1012.75592	27.49878	2.0192
Totals :				5.01562e4	1505.71668	



Signal 3: MWD1 C, Sig=210,8 Ref=360,100

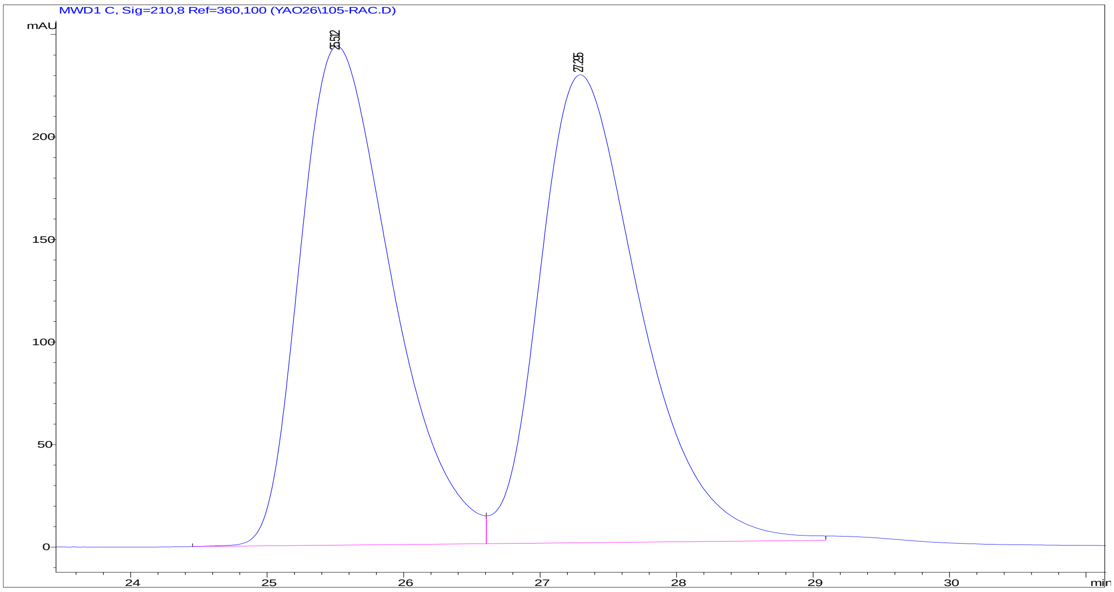


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.138	MF	0.8848	5.90184e4	1111.71680	49.5633
2	29.497	FM	0.9226	6.00585e4	1084.94263	50.4367
Totals :				1.19077e5	2196.65942	



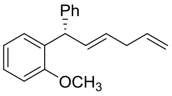
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.047	VV	0.5453	1378.86389	38.18208	1.2103
2	29.295	VB	0.7928	1.12545e5	1957.37463	98.7897
Totals :				1.13923e5	1995.55671	

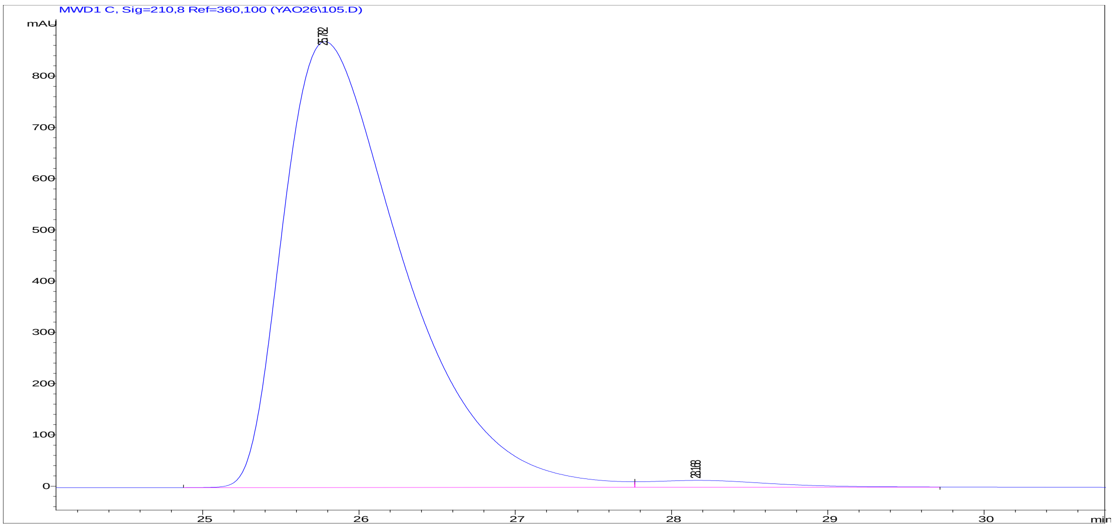


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.512	PV	0.7287	1.13656e4	243.43730	49.4575
2	27.295	VB	0.7619	1.16149e4	228.17755	50.5425
Totals :				2.29805e4	471.61485	

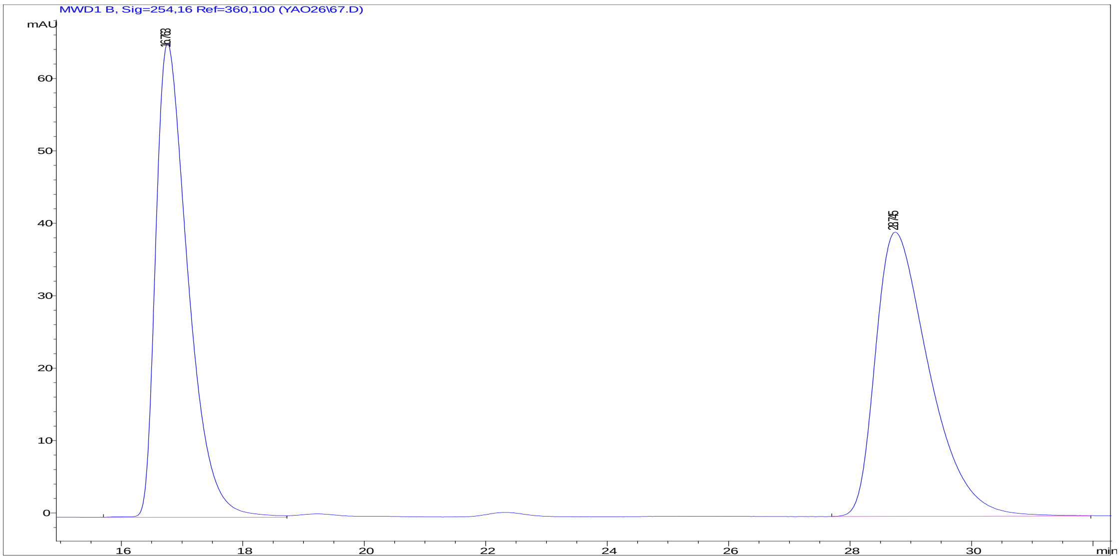


7i



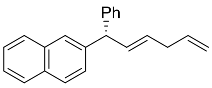
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.782	BV	0.8096	4.63662e4	870.23834	98.4141
2	28.168	VB	0.7607	747.16693	13.52102	1.5859
Totals :				4.71133e4	883.75936	

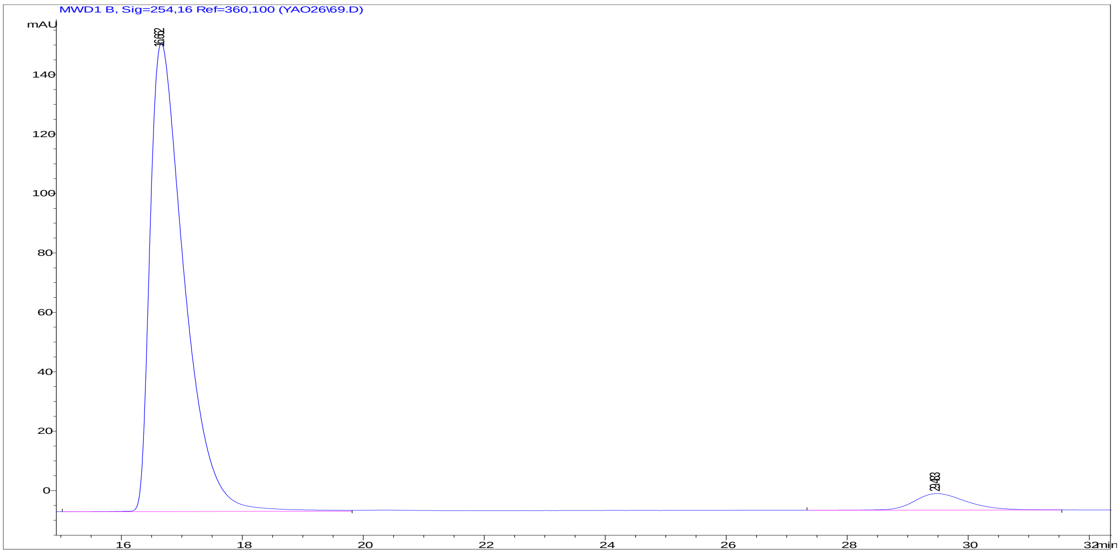


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.763	BV	0.5672	2418.63281	65.43732	50.0862
2	28.745	PB	0.9409	2410.30298	39.22664	49.9138
Totals :				4828.93579	104.66396	

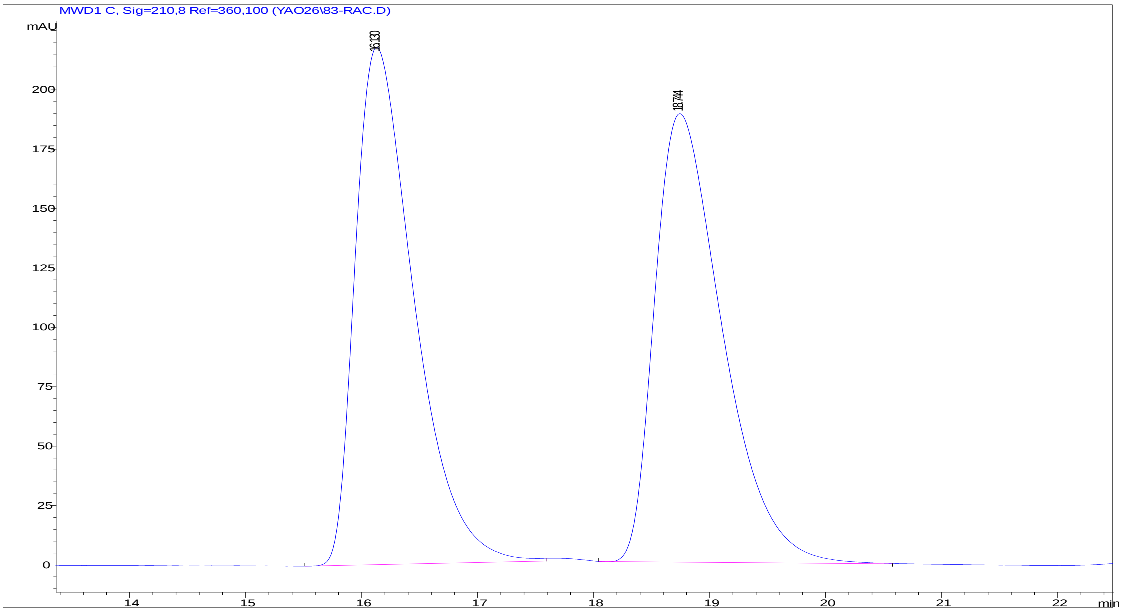


7j



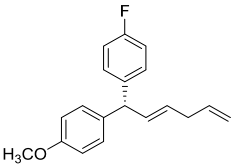
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.662	VB	0.5941	6193.04150	157.71408	94.9054
2	29.483	PB	0.9116	332.44989	5.54438	5.0946
Totals :				6525.49139	163.25846	

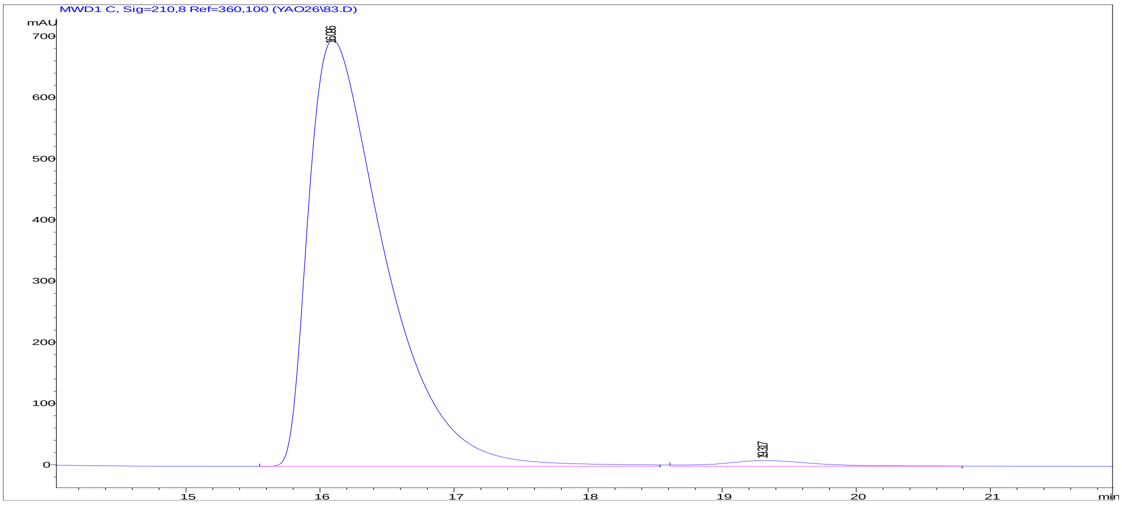


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.130	PB	0.5438	7686.93652	217.77892	50.1411
2	18.744	PB	0.6244	7643.66895	188.75621	49.8589
Totals :				1.53306e4	406.53513	

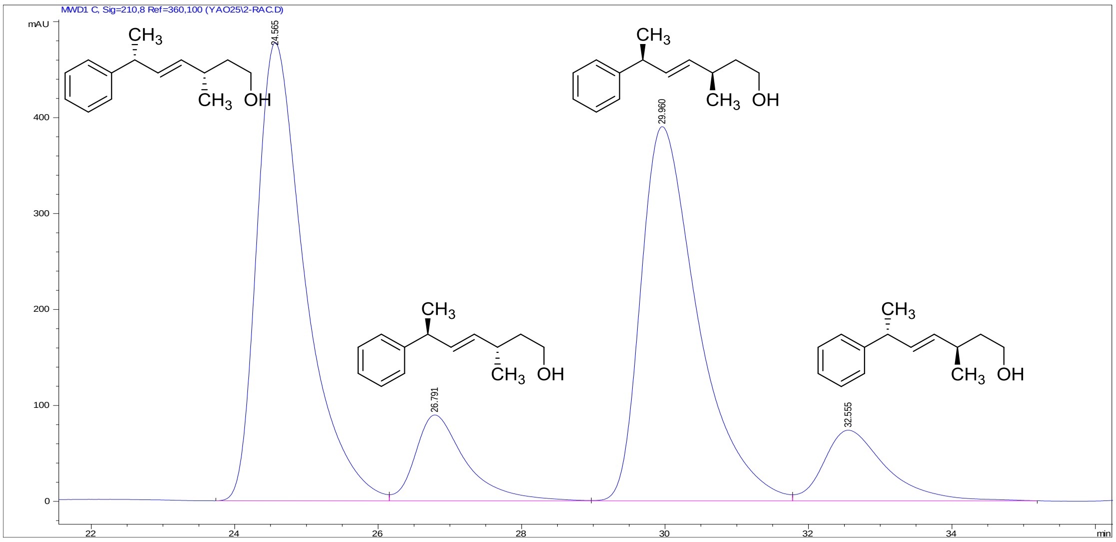


7k



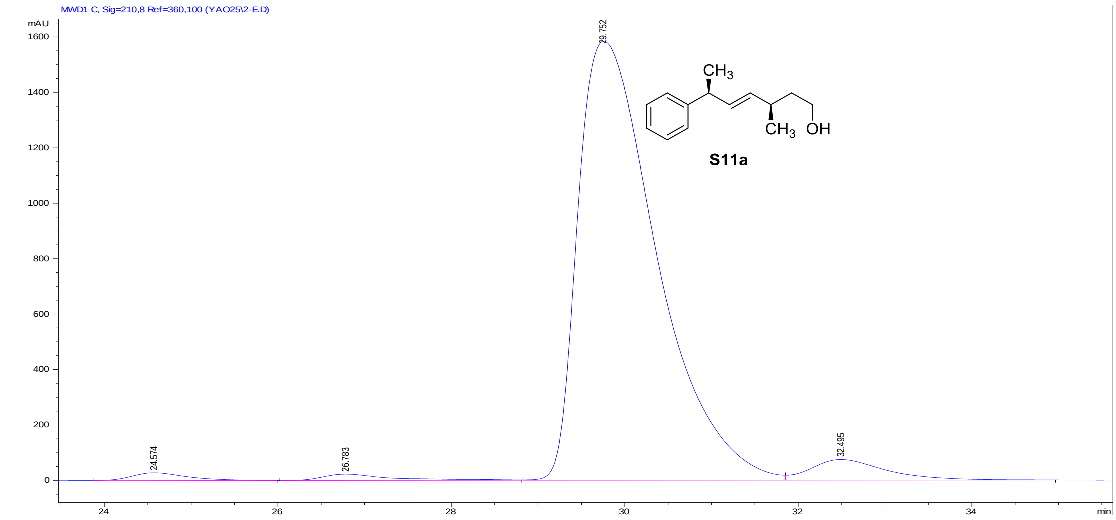
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.096	PB	0.5961	2.74944e4	697.13684	98.4468
2	19.317	BB	0.6573	433.77316	9.28090	1.5532
Totals :				2.79281e4	706.41774	



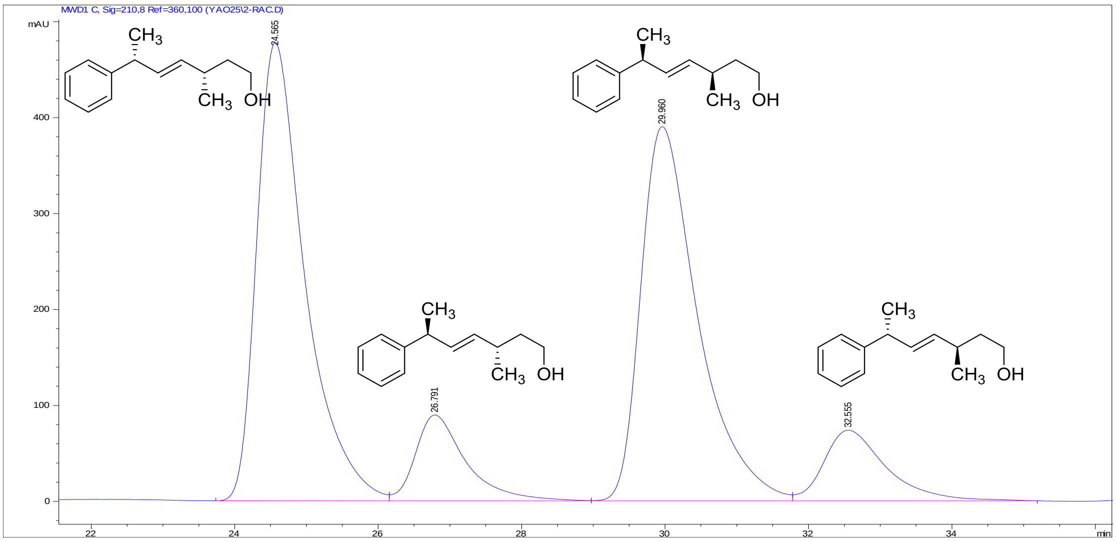
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.565	PV	0.6994	2.23288e4	477.60526	42.3377
2	26.791	VV	0.7242	4372.46973	89.47145	8.2907
3	29.960	VV	0.8294	2.15734e4	389.99411	40.9053
4	32.555	VB	0.8933	4465.14648	73.65461	8.4664
Totals :				5.27398e4	1030.72543	



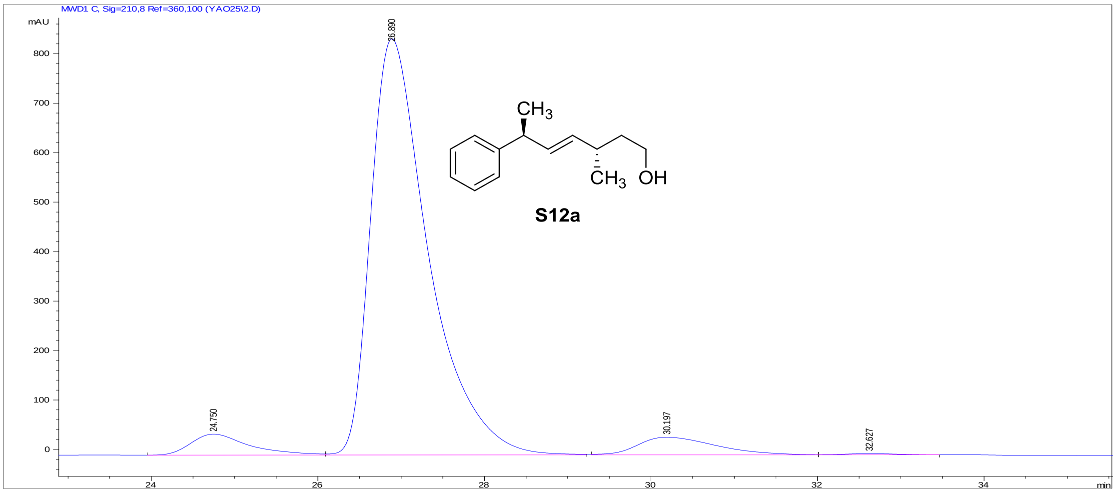
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.574	PB	0.6512	1201.75940	27.53548	1.1228
2	26.783	PB	0.7932	1297.54919	22.82468	1.2123
3	29.752	BV	0.9605	1.00058e5	1584.97046	93.4847
4	32.495	VB	0.8869	4474.07861	74.47469	4.1802
Totals :				1.07031e5	1709.80531	



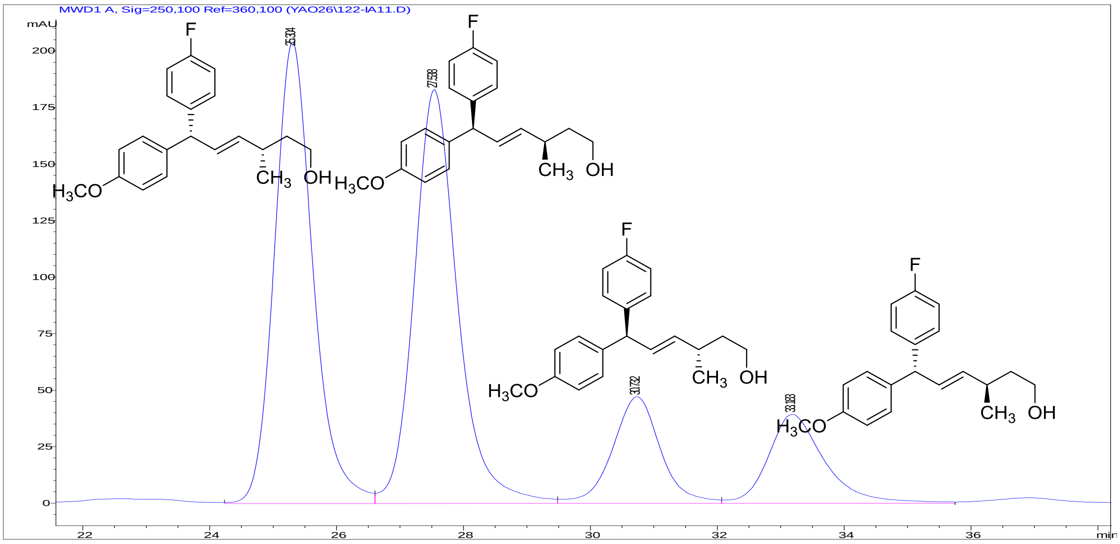
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.565	PV	0.6994	2.23288e4	477.60526	42.3377
2	26.791	VV	0.7242	4372.46973	89.47145	8.2907
3	29.960	VV	0.8294	2.15734e4	389.99411	40.9053
4	32.555	VB	0.8933	4465.14648	73.65461	8.4664
Totals :				5.27398e4	1030.72543	



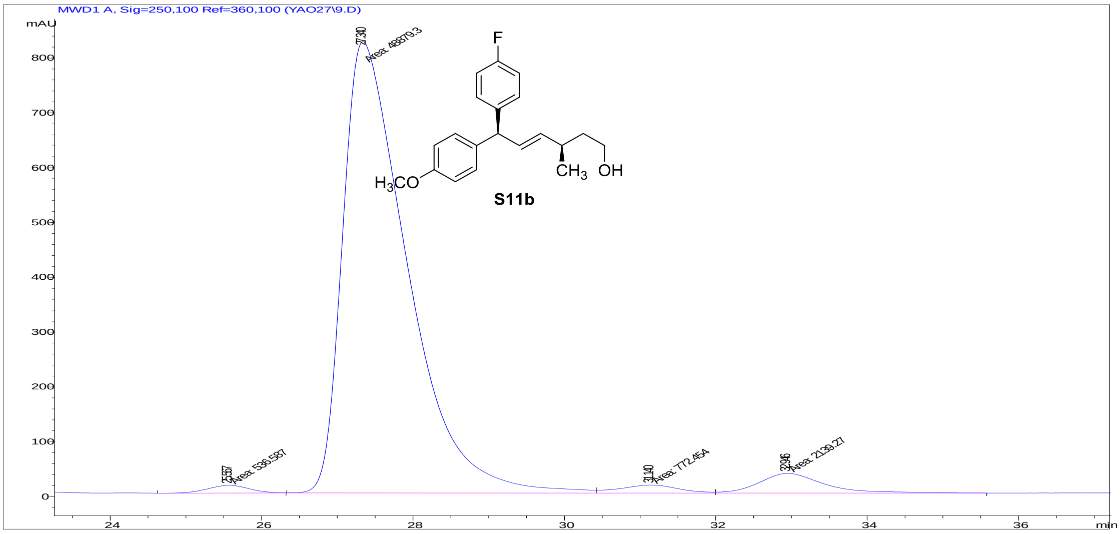
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.750	PV	0.7090	2054.13745	42.41430	4.5667
2	26.890	VB	0.7271	4.04784e4	841.63153	89.9912
3	30.197	BB	0.9230	2336.17407	35.81300	5.1938
4	32.627	BP	0.5309	111.70631	2.49227	0.2483
Totals :				4.49804e4	922.35110	



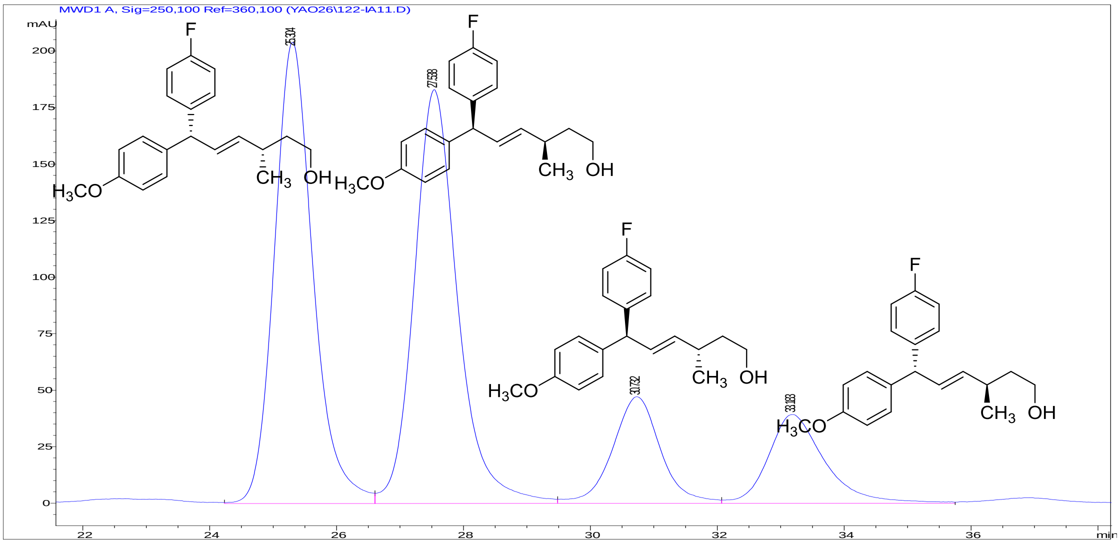
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.304	VV	0.6478	8664.09473	203.87277	38.8938
2	27.538	VV	0.7154	8708.48730	182.93141	39.0931
3	30.732	VV	0.8044	2475.82837	47.16716	11.1142
4	33.183	VV	0.9135	2427.89258	39.25925	10.8990
Totals :				2.22763e4	473.23060	



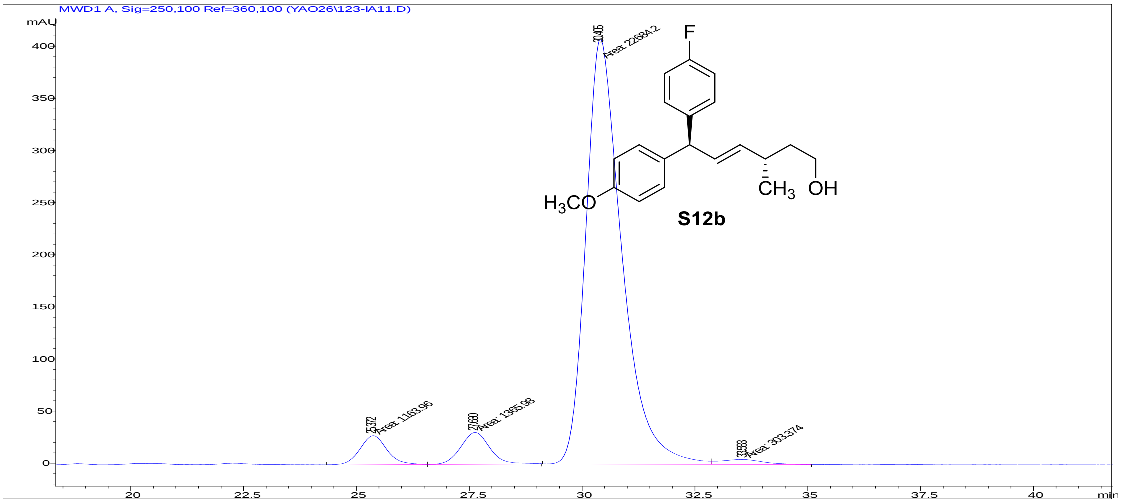
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.567	MM	0.6311	536.58716	14.17014	1.0254
2	27.340	MF	0.9890	4.88793e4	823.71497	93.4102
3	31.140	MF	0.8844	772.45441	14.55666	1.4762
4	32.946	FM	0.9953	2139.26880	35.82443	4.0882
Totals :				5.23276e4	888.26619	



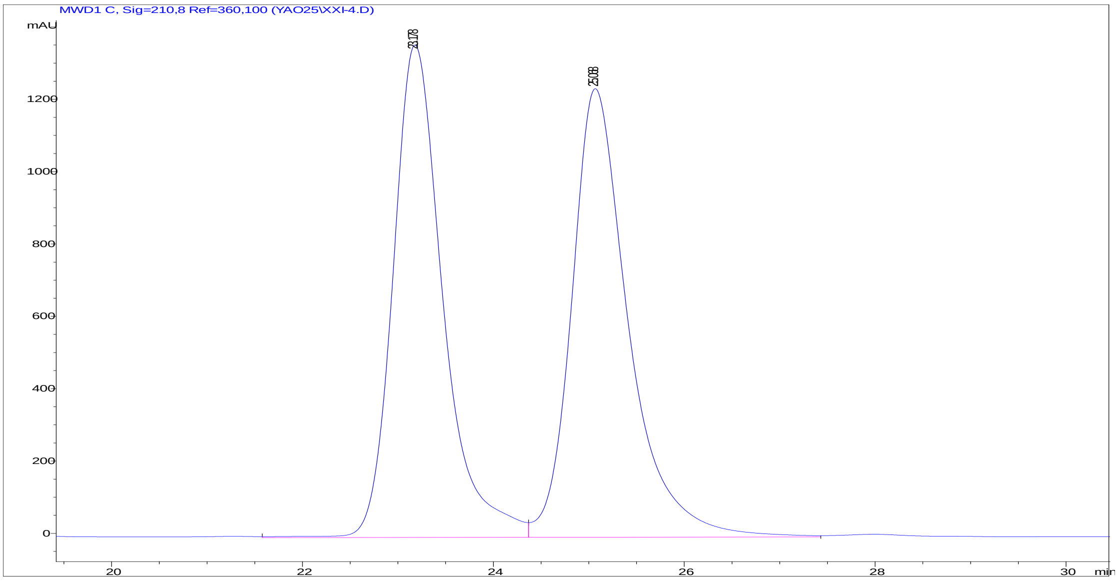
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.304	VV	0.6478	8664.09473	203.87277	38.8938
2	27.538	VV	0.7154	8708.48730	182.93141	39.0931
3	30.732	VV	0.8044	2475.82837	47.16716	11.1142
4	33.183	VV	0.9135	2427.89258	39.25925	10.8990
Totals :				2.22763e4	473.23060	

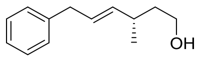


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.372	MM	0.6946	1163.96326	27.92997	4.5614
2	27.630	MM	0.7468	1365.98254	30.48323	5.3531
3	30.405	MF	0.9271	2.26842e4	407.79678	88.8966
4	33.583	FM	1.0621	303.37387	4.76062	1.1889
Totals :				2.55175e4	470.97060	

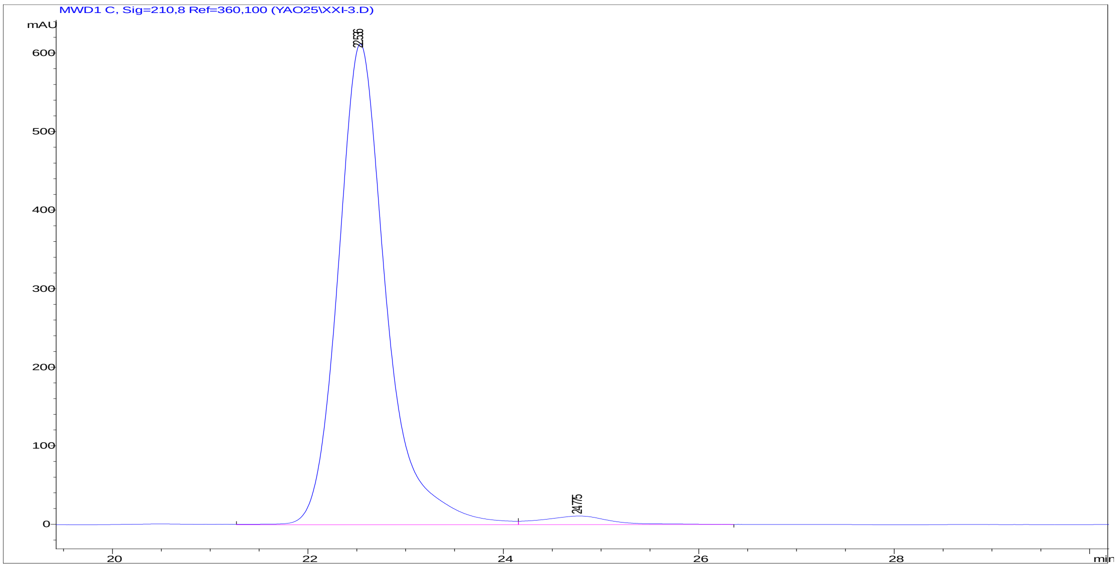


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



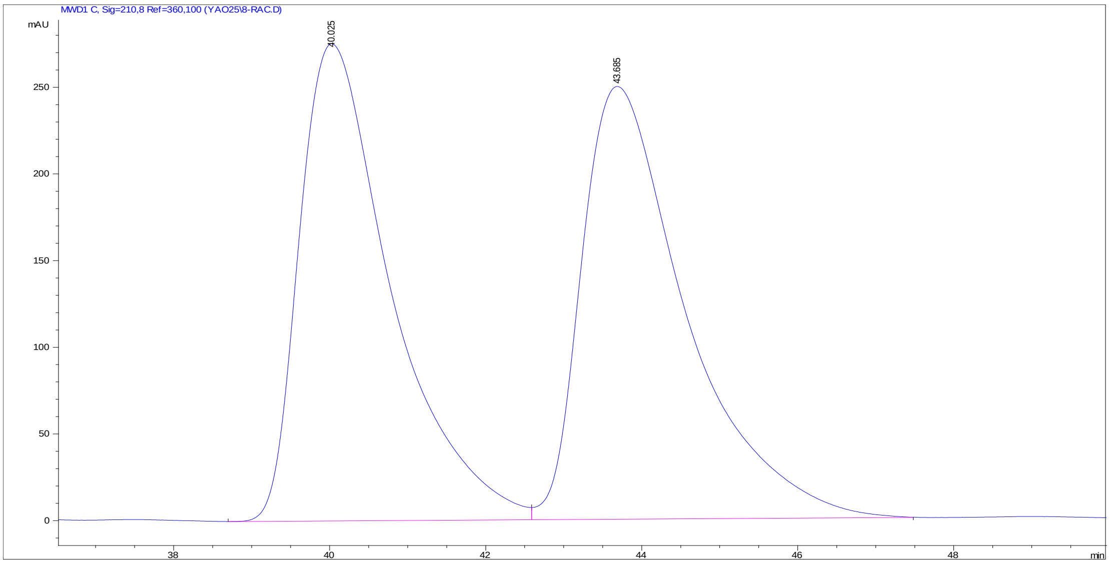
S14a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.178	VV	0.5499	4.94659e4	1361.50232	49.1396
2	25.068	VB	0.6137	5.11982e4	1240.06226	50.8604
Totals :				1.00664e5	2601.56458	



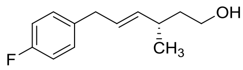
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.536	BV	0.5116	2.09649e4	612.05121	97.5614
2	24.775	VV	0.5973	524.03821	10.93197	2.4386
Totals :				2.14890e4	622.98318	

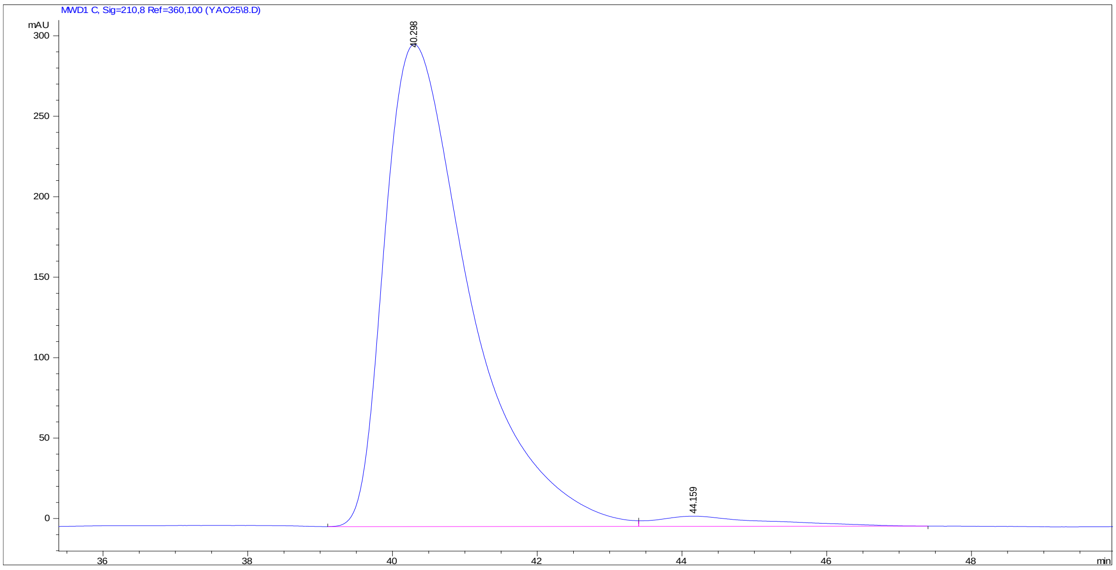


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.025	PV	1.2239	2.25071e4	275.27460	49.2940
2	43.685	VB	1.3760	2.31518e4	249.64015	50.7060
Totals :				4.56589e4	524.91475	

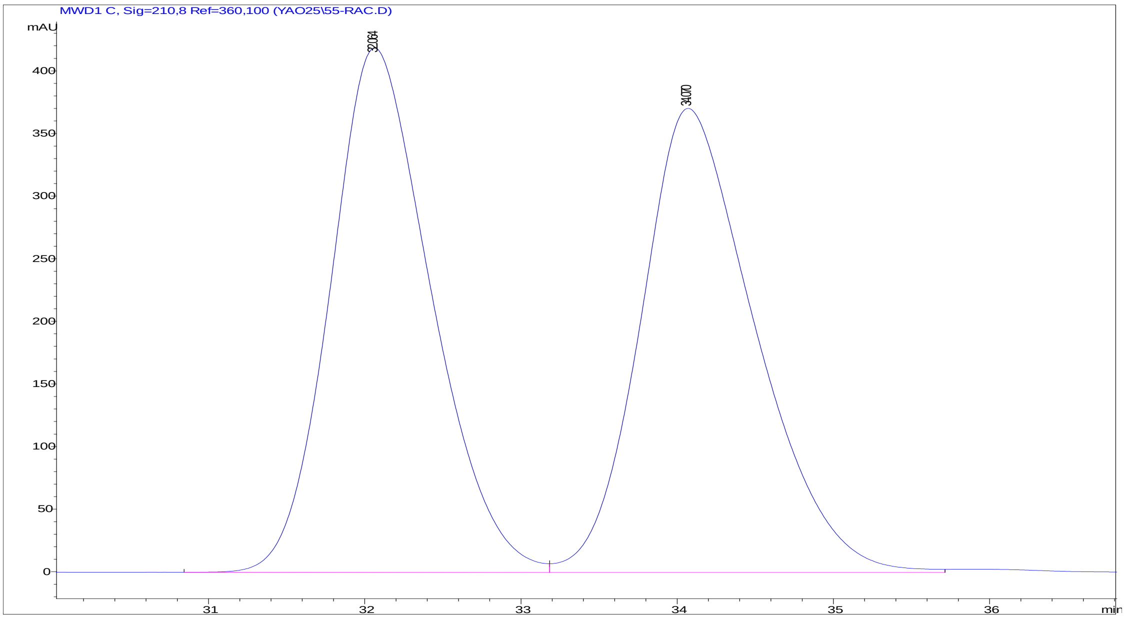


S14b



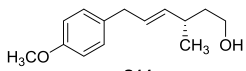
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.298	PV	1.2228	2.45793e4	299.69809	97.2982
2	44.159	VV	1.2648	682.52643	6.33566	2.7018
Totals :				2.52618e4	306.03375	

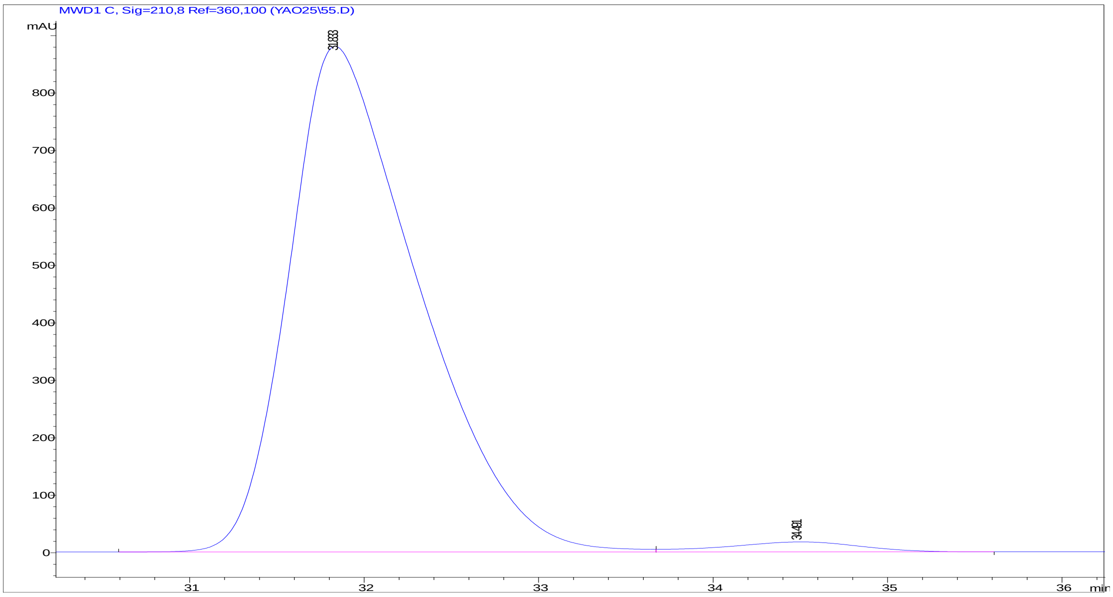


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.064	VV	0.6805	1.87636e4	418.94101	49.8345
2	34.070	VB	0.7466	1.88883e4	370.62140	50.1655
Totals :				3.76519e4	789.56241	

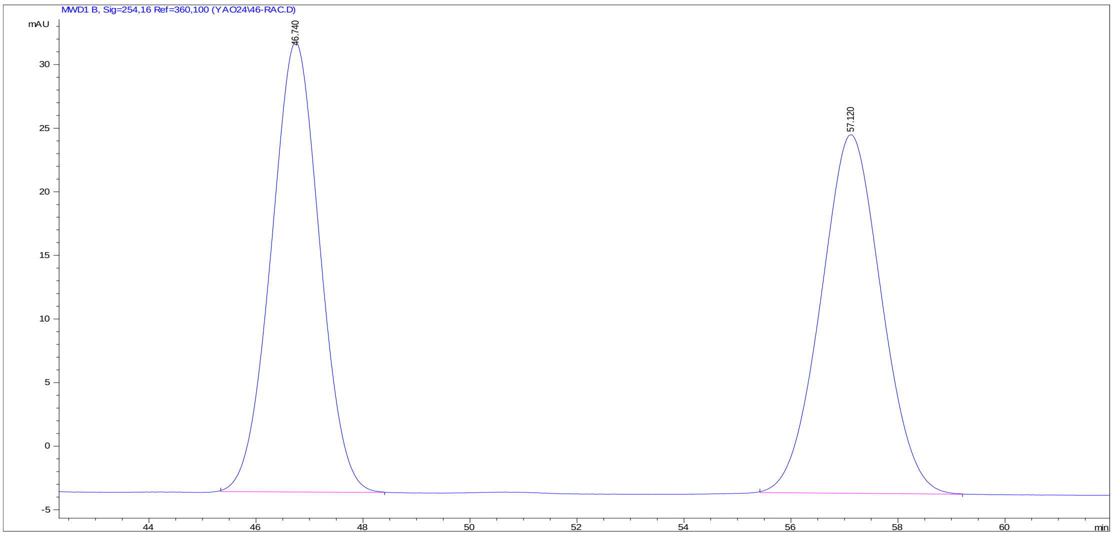


S14c



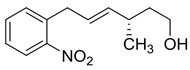
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.833	PV	0.7257	4.53907e4	880.13147	98.0111
2	34.491	VP	0.6548	921.07812	17.36454	1.9889
Totals :				4.63118e4	897.49601	

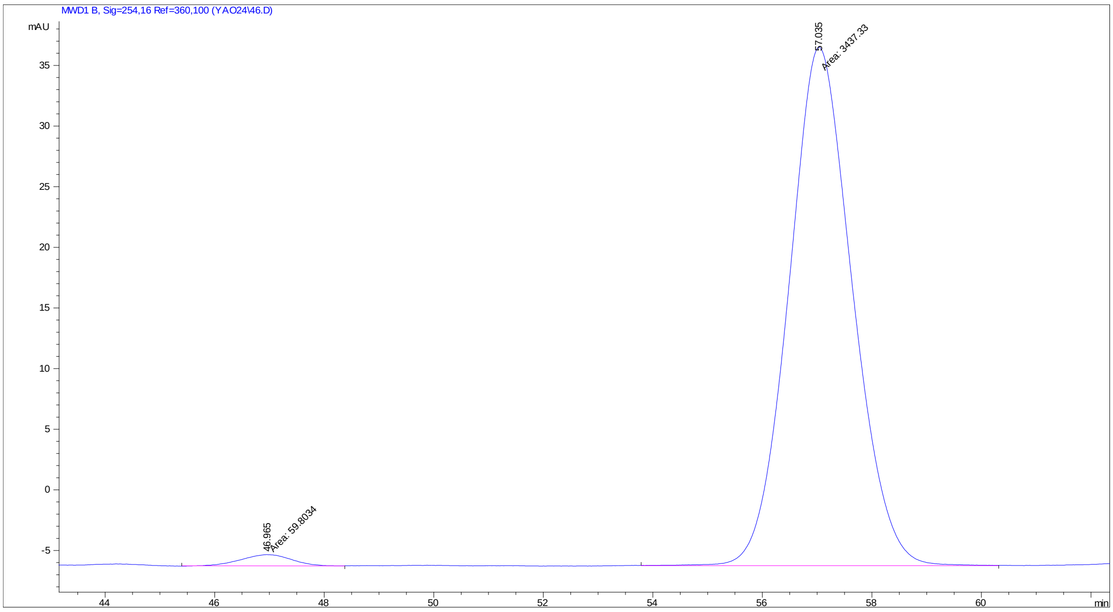


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.740	BB	0.9423	2225.61890	35.35958	50.0586
2	57.120	BB	1.1511	2220.40747	28.18368	49.9414
Totals :				4446.02637	63.54325	

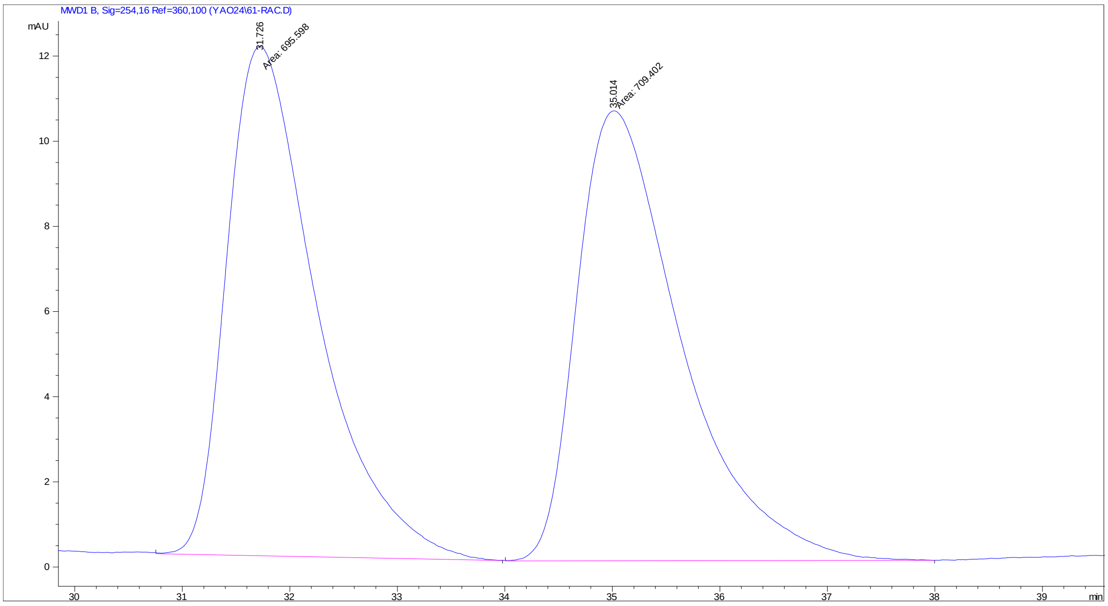


S14d



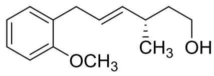
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.965	MM	1.0778	59.80341	9.24772e-1	1.7101
2	57.035	MM	1.3404	3437.32666	42.73948	98.2899
Totals :				3497.13007	43.66425	

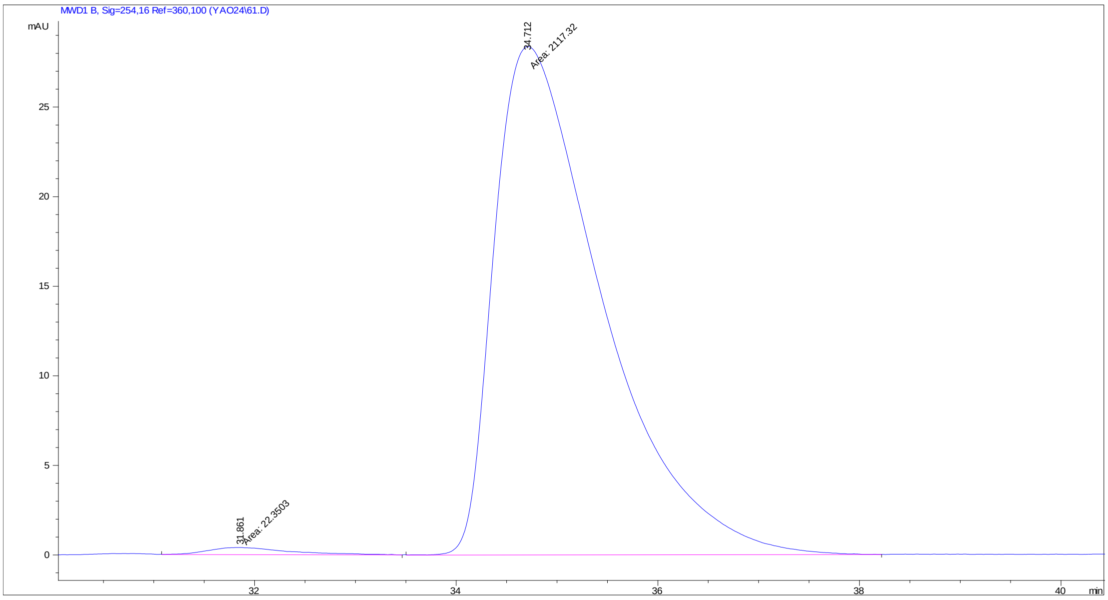


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.726	MM	0.9696	695.59833	11.95682	49.5088
2	35.014	MM	1.1188	709.40228	10.56825	50.4912
Totals :				1405.00061	22.52507	

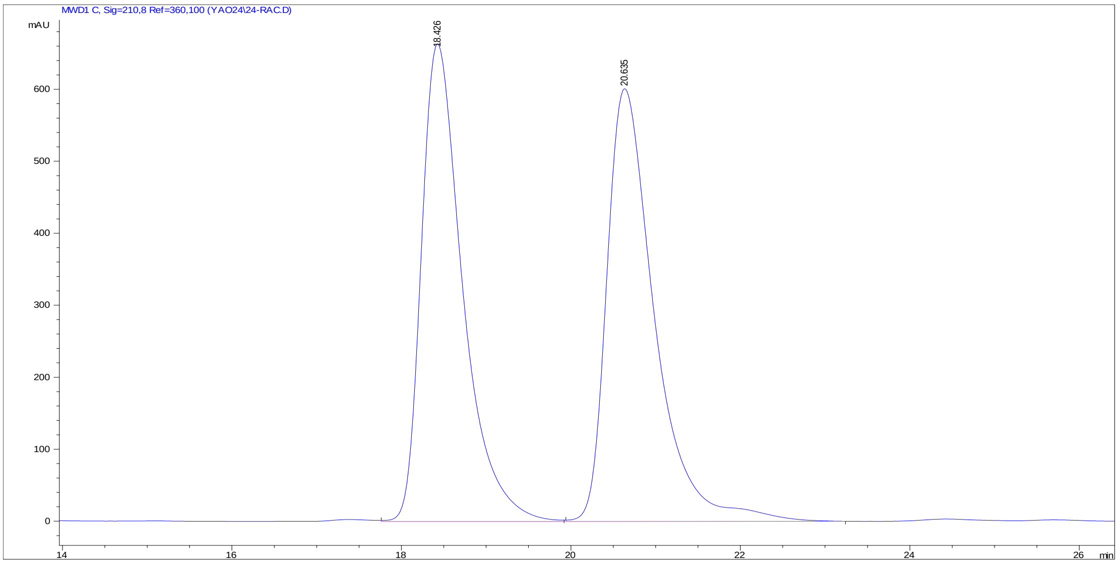


S14e



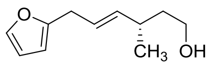
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.861	MM	0.9387	22.35028	3.96818e-1	1.0446
2	34.712	MM	1.2437	2117.32495	28.37493	98.9554
Totals :				2139.67523	28.77175	

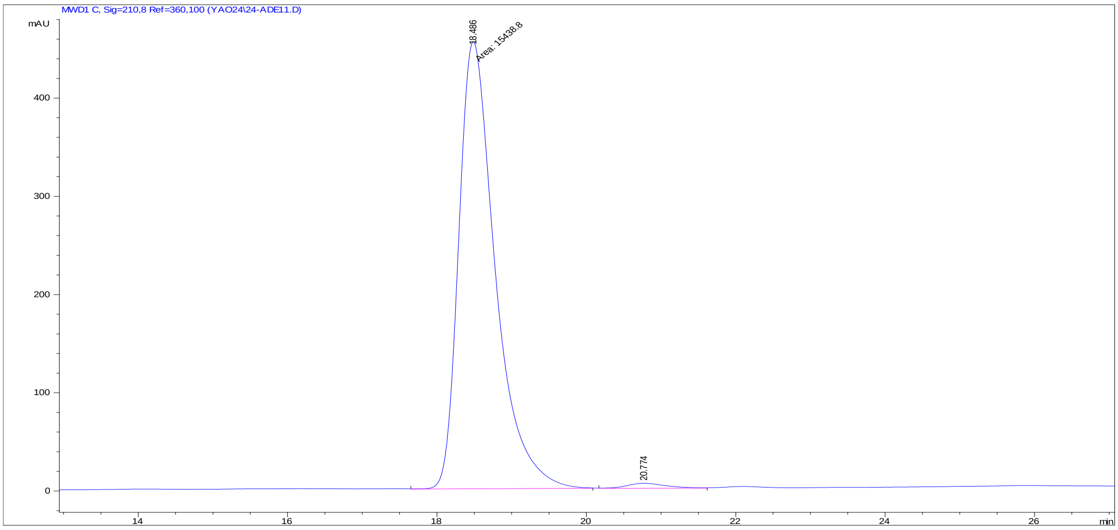


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.426	VB	0.5125	2.24316e4	663.37885	48.8792
2	20.635	BB	0.5914	2.34603e4	601.00964	51.1208
Totals :				4.58919e4	1264.38849	

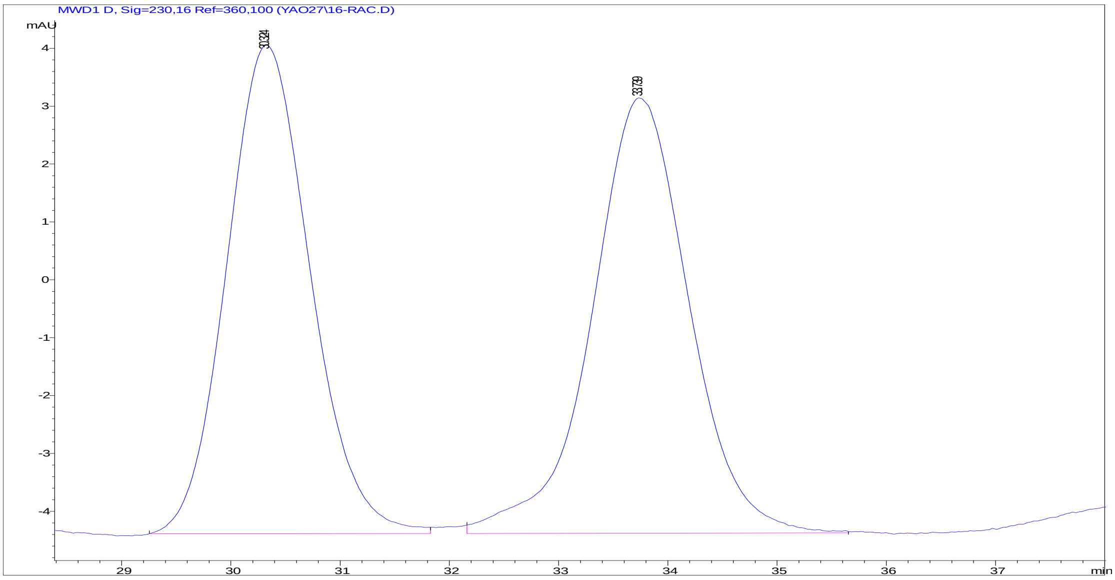


S14f



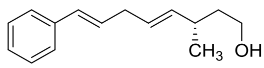
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.486	MM	0.5652	1.54388e4	455.29068	98.8576
2	20.774	BV	0.4471	178.40811	5.01487	1.1424
Totals :				1.56172e4	460.30555	

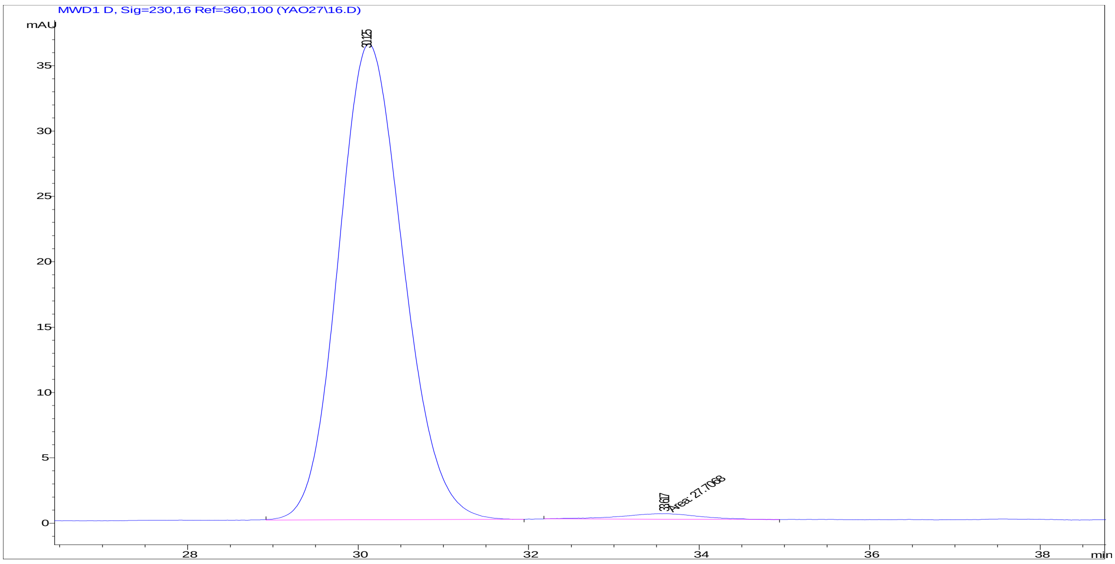


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.324	BB	0.8268	447.94687	8.44604	49.0595
2	33.739	BB	0.9456	465.12256	7.52049	50.9405
Totals :				913.06943	15.96653	

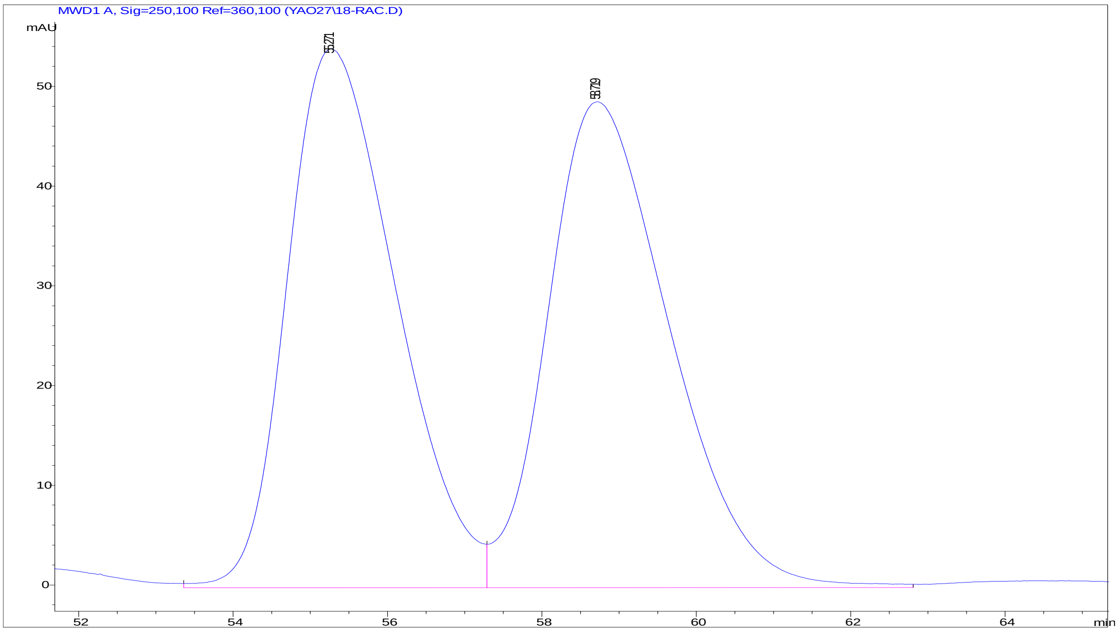


S14g

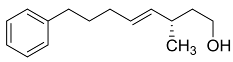


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.125	BP	0.8264	1929.18689	36.39350	98.5841
2	33.617	MM	1.0722	27.70685	4.30694e-1	1.4159
Totals :				1956.89374	36.82420	

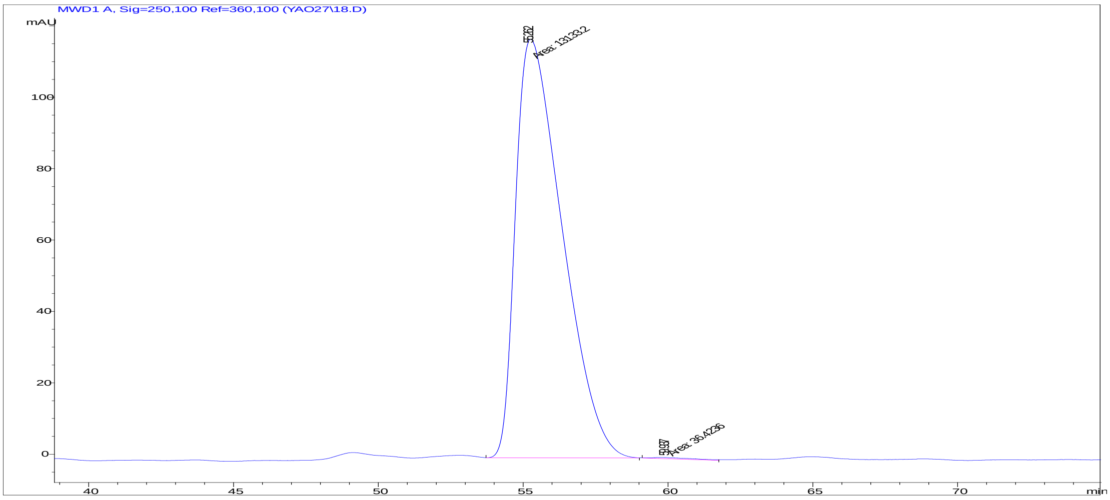


Signal 1: MWD1 A, Sig=250,100 Ref=360,100



S14h

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.271	VV	1.5107	5292.55957	54.03773	49.7665
2	58.719	VB	1.6635	5342.23438	48.71211	50.2335
Totals :				1.06348e4	102.74984	



Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.262	MM	1.8660	1.31332e4	117.30078	99.7234
2	59.937	MM	1.7549	36.42359	3.45926e-1	0.2766
Totals :				1.31696e4	117.64671	