Enantioselective Synthesis of Allenes by Catalytic Traceless Petasis Reactions

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Supporting Information

1. General Information.

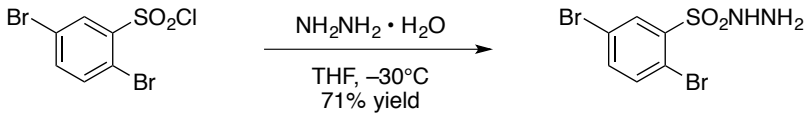
All ^{1}H NMR and ^{13}C NMR spectra were recorded using Varian Unity Plus 500 or 400 MHz spectrometer at ambient temperature in $CDCl_3$ (Cambridge Isotope Laboratories, Inc.). Chemical shifts in ^{1}H NMR spectra are reported in parts per million from tetramethylsilane with the solvent resonance as 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 $[\alpha]^{T\ ^{\circ}C}_{D}$ (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., 25cm×4.6mm I.D.), Chiralpak®AD-H (Chiral Technologies Inc., 25cm × 4.6 mm I.D.) and Chiralpak®IA-H (Chiral Technologies Inc., 25cm × 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.). Triethyl borate was distilled over CaH_2 before use in the preparation of alkynyl boronates. Mesitylene was dried by and stored with 3 Å molecular sieves beads. The previously reported chiral biphenol catalysts were prepared according to known literature procedures.[1] All other reagents were purchased from commercial suppliers and used without further purification.

2. Experimental Procedures

a. Synthesis of Hydrazides

2-Nitrobenzenesulfonylhydrazide (NBSH, **20**) was synthesized according to the procedure reported by Myers and coworkers.[2]



8

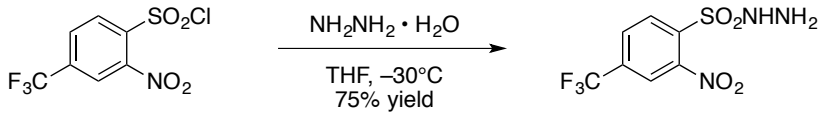
2,5-Dibromobenzenesulfonohydrazide (8)

Hydrazine monohydrate (6.1 mL, 125 mol, 2.5 eq) was added dropwise to a solution of 2,5-dibromobenzenesulfonyl chloride (16.7 g, 50 mmol, 1 eq) in THF (20 mL) at –30 °C under an argon atmosphere. During the addition a white precipitate of hydrazine hydrochloride was deposited. After stirring at –30 °C for 1 h, EtOAc (30 mL, 23 °C) was added to the cold reaction solution and the mixture was washed repeatedly with ice-cold 10% aqueous sodium chloride solution (5 × 100 mL). The organic layer was dried over sodium sulfate at 0 °C and then was added slowly to a stirring solution of hexanes (500 ml) at 23 °C over 5 min. 2,5-Dibromobenzenesulfonohydrazide precipitated within 10 min as an off-white solid and was collected by vacuum filtration. The filter cake was washed with hexanes (2 × 20 mL, 23 °C) and then recrystallized by dichloromethane to afford an off-white crystal (11.7 g, 71% yield). The hydrazide was stored at –8 °C without exposure to light.

Caution: During the reaction one equivalent of hydrazine hydrochloride was generated as a white precipitate. Stirring might be impeded and the rate of stirring should be adjusted. Hydrazine hydrochloride is extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion or inhalation. After the aqueous work-up it remained in the water layer, which should be disposed to a separate container as a hazardous waste.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (br, 1H), 8.04 (d, J = 2.4 Hz, 1H), 7.79 – 7.68 (m, 2H), 4.43 (br, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 140.0, 137.5, 137.0, 134.4, 121.1, 119.2.



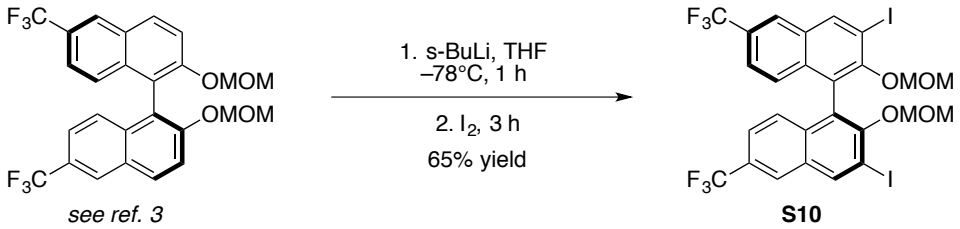
17

2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (17)

Hydrazine monohydrate (6.1 mL, 125 mol, 2.5 eq) was added dropwise to a solution of 2-nitro-4-(trifluoromethyl)benzenesulfonyl chloride (14.5 g, 50 mmol, 1 eq) in THF (20 mL) at –30 °C under an argon atmosphere. During the addition a white precipitate of hydrazine hydrochloride was deposited. After stirring at –30 °C for 30 min, EtOAc (30 mL, 23 °C) was added to the cold reaction solution and the mixture was washed repeatedly with ice-cold 10% aqueous sodium chloride solution (5 × 100 mL). The organic layer was dried over sodium sulfate at 0 °C and then was added slowly to a stirring solution of hexanes (500 ml) at 23 °C over 5 min. 2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide precipitated within 10 min as a yellow solid and was collected by vacuum filtration. The filter cake was washed with hexanes (2 × 20 mL, 23 °C) and then recrystallized by dichloromethane to afford a pale white solid (10.7 g, 75% yield). The

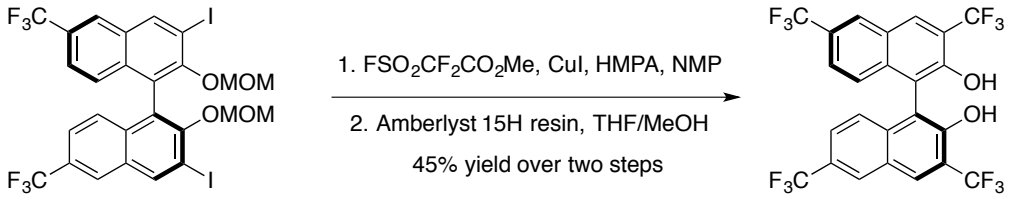
hydrazide was stored at –8 °C without exposure to light.
Caution: During the reaction one equivalent of hydrazine hydrochloride was generated as a white precipitate. Stirring might be impeded and the rate of stirring should be adjusted. Hydrazine hydrochloride is extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion or inhalation. After the aqueous work-up it remained in the water layer, which should be disposed to a separate container as a hazardous waste.
^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 8.26 (d, J = 8.2 Hz, 1H), 8.22 (q, J = 1.0 Hz, 1H), 8.13 (dq, J = 8.3, 1.0 Hz, 1H), 7.15 (br, 1H), 2.74 (br, 2H).
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 148.7, 135.0 (q, J = 34.5 Hz), 133.9, 133.5, 129.3 (q, J = 3.8 Hz), 122.5 (q, J = 272.7 Hz), 122.3 (q, J = 4.0 Hz).
^{19}F NMR (470 MHz, Acetonitrile-d_3) δ –63.9.

b. Synthesis of (*S*)-(CF_3)$_4$-BINOL (10)



see ref. 3 **S10**

(*S*)-3,3'-Diiodo-2,2'-bis(methoxymethoxy)-6,6'-bis(trifluoromethyl)-1,1'-binaphthalene (S10)
To a solution of (*S*)-2,2'-bis(methoxymethyloxy)-6,6'-bis(trifluoromethyl)-1,1'-binaphthyl[3] (3.17 g, 5.19 mmol) in dry THF (60 mL) was added a hexane-cyclohexane solution of *s*-butyllithium (1.02 M, 20.8 mL, 21.2 mmol) at –78 °C under argon and the resulting mixture was stirred for 1 h at the same temperature. Iodine (7.92 g, 31.2 mmol) in dry THF (25 mL) was then added by a cannula and the reaction mixture was stirred for an additional 3 h at the same temperature. The reaction was quenched with water and diluted with EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined and treated with aqueous 10% Na_2SO_3 to destroy excess iodine, and washed with brine, and dried over anhydrous sodium sulfate. After filtration and concentration under reduced pressure, the crude product was purified by silica gel column chromatography (hexanes/EtOAc: 50/1) to afford (*S*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-6,6'-bis(trifluoromethyl)-1,1'-binaphthalene as an amorphous oil in 65% yield.
$[\alpha]_D^{22}$= +3.1 (c=1.1, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 2H), 8.11 (s, 2H), 7.48 (d, J = 8.9 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 4.91 – 4.71 (m, 4H), 2.55 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 141.1, 134.9, 130.8, 127.9 (q, J = 32.6 Hz), 127.5, 125.8, 125.0, 124.5 (q, J = 4.5 Hz), 122.9 (q, J = 3.2 Hz), 99.8, 94.2, 56.5.
^{19}F NMR (470 MHz, $CDCl_3$) δ -62.5.
ESI-MS found 762.9 (calculated for $[C_{26}H_{19}F_6I_2O_4]^+$: 762.9)
IR (thin film, cm^{-1}): 3015, 2948, 2902, 2827, 1570, 1328, 1164, 1069, 957.



S10 **10**

(*S*)-3,3',6,6'-Tetrakis(trifluoromethyl)-[1,1'-binaphthalene]-2,2'-diol (10)

A mixture of (*S*)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-6,6'-bis(trifluoromethyl)-1,1'-binaphthalene (**S10**) (0.56g, 1 mmol) and $FSO_2CF_2CO_2Me$ (0.51 ml, 4 mmol), CuI (0.46 g, 2.4 mmol), HMPA (0.70 ml, 4 mmol) in NMP (20 mL) was stirred under argon atmosphere at 80 °C and monitored by TLC. When the starting material vanished, the reaction was cooled to room temperature and diluted with dichloromethane (50 mL). The solution was washed with water (3 X 100 mL), dried over sodium sulfate, and concentrated to afford a syrup. The crude product was then dissolved in THF/MeOH (1:1, 25 ml/ 25 ml) mixture. 1 gram of Amberlyst 15 was added and the mixture was heated to 50 °C for 3 h. The Amberlyst powder was filtered off and the filtrate was concentrated and subjected to column chromatography (hexanes/EtOAc: 50/1) to directly afford the deprotected product as a light yellow solid (45% yield over two steps).

$[\alpha]_D^{22}$= +4.0 (c=1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 2H), 8.34 (s, 2H), 7.63 (d, *J* = 9.0, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 5.53 (s, 2H).

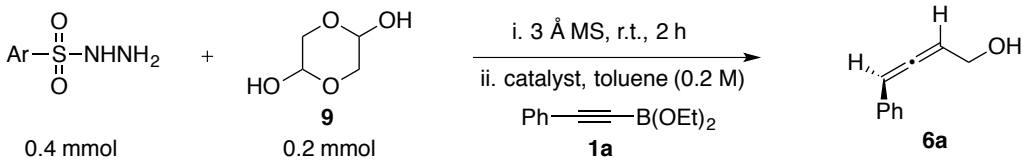
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 136.1, 131.4 (q, *J* = 5.4 Hz), 127.9 (q, *J* = 33.0 Hz), 127.4 (q, *J* = 4.3 Hz), 126.7, 125.9 (q, *J* = 3.0 Hz), 124.9, 124.4 (q, *J* = 119.0 Hz), 122.2 (q, *J* = 119.8 Hz), 120.4 (q, *J* = 31.9 Hz), 112.3.

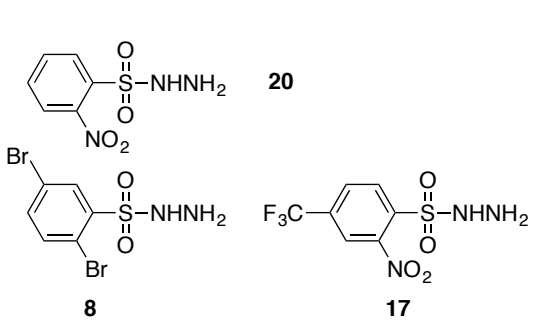
^{19}F NMR (470 MHz, $CDCl_3$) δ -62.6, -62.7.

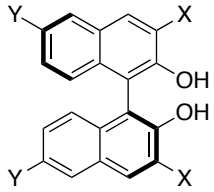
ESI-MS found 557.0 (calculated for $[C_{24}H_9F_{12}O_2]^-$: 557.0)

IR (thin film, cm^{-1}): 3549, 1639, 1467, 1338, 1144.

Table S1: Optimization of Asymmetric Petasis Alkynylations





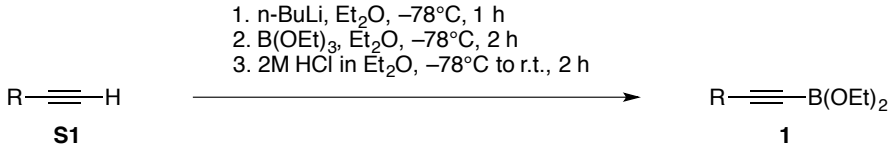


C1, X = CF_3, Y = H
C2, X = CH_3, Y = H
C3, X = Br, Y = H
C4, X = CF_3, Y = Br
10, X = CF_3, Y = CF_3
19, X = Ph, Y = H

Entry	Catalyst (mol%)	Hydrazide	Temperature/Time	Yield	e.r.
1	**C1** (15 mol%)	**20**	0 °C /24 h	85%	86:14
2	**C2** (15 mol%)	**20**	0 °C /24 h	20%	85:15
3	**C3** (15 mol%)	**20**	0 °C /24 h	75%	70:30
4	**19** (15 mol%)	**20**	0 °C /24 h	70%	73:27
5	**10** (15 mol%)	**20**	0 °C /24 h	85%	87:13
6	**C1** (15 mol%)	**20**	–10 °C /48 h	20%	88:12
7	**10** (15 mol%)	**20**	–10 °C /48 h	50%	90:10
8	**C1** (15 mol%)	**8**	0 °C /48 h	68%	88:12
9	**C1** (15 mol%)	**17**	0 °C /24 h	83%	58:42
10	**10** (15 mol%)	**8**	0 °C /48 h	83%	92:8
11	**10** (10 mol%)	**8**	0 °C /48 h	85%	92:8
12	**C4** (10 mol%)	**8**	0 °C /48 h	51%	85:15
13[a]	**10** (10 mol%)	**8**	0 °C /48 h	85%	93:7

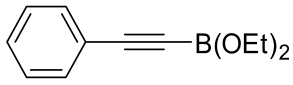
[a] $PhCH_3$/Mesitylene=1:1

c. General Procedure for Synthesis of Acyclic Alkynyl Boronates



S1 **1**

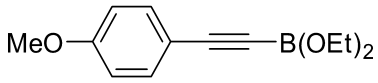
Acyclic alkynyl boronates were synthesized in a modified procedure based on the published method.[4] To flask A charged with argon was added 25 mL diethyl ether and alkyne (15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The boronates were allowed to be stored for up to 2 weeks and were used directly without further purification.



Diethyl (phenylethynyl)boronate (1a/14)

To a flask A charged with argon was added diethyl ether (25 mL) and phenyl acetylene (1.65 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (phenylethynyl)boronate (**1a/14**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

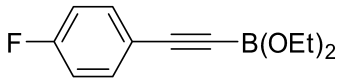
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.37 – 7.29 (m, 3H), 4.09 (q, J = 7.1 Hz, 4H), 1.28 (t, J = 7.1 Hz, 6H).



Diethyl ((4-methoxyphenyl)ethynyl)boronate (1b)

To a flask A charged with argon was added 25 mL diethyl ether and 4-ethynylanisole (1.95 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl ((4-methoxyphenyl)ethynyl)boronate (**1b**) was allowed to be stored for up to 1 week and used directly without further purifications.

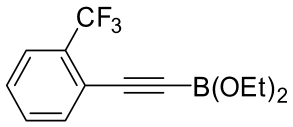
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 2H), 7.02 (d, J = 8.5, 2H), 4.39 – 4.25 (m, 4H), 3.92 (s, 3H), 1.52 (t, J = 7.6 Hz, 6H).



Diethyl ((4-fluorophenyl)ethynyl)boronate (1c)

To a flask A charged with argon was added 25 mL diethyl ether and 1-ethynyl-4-fluorobenzene (1.72 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl ((4-fluorophenyl)ethynyl)boronate (**1c**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

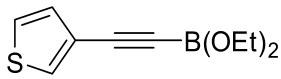
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.58 (m, 2H), 7.18 (d, J = 7.4 Hz, 2H), 4.33 (q, J = 7.1 Hz, 4H), 1.51 (t, J = 7.1 Hz, 6H).



Diethyl ((2-(trifluoromethyl)phenyl)ethynyl)boronate (1d)

To a flask A charged with argon was added 25 mL diethyl ether and 1-ethynyl-2-trifluoromethylbenzene (2.09 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl ((2-(trifluoromethyl)phenyl)ethynyl)boronate (**1d**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

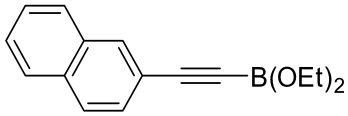
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.70 (m, 2H), 7.64 – 7.54 (m, 1H), 7.53 (dd, *J* = 7.5, 7.5 Hz, 1H), 4.29 (q, *J* = 7.0 Hz, 4H), 1.42 (t, *J* = 7.0 Hz, 6H).



Diethyl (thiophen-3-ylethynyl)boronate (1e)

To a flask A charged with argon was added 25 mL diethyl ether and 3-ethynylthiophene (1.48 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (thiophen-3-ylethynyl)boronate (**1e**) was allowed to be stored for up to 1 week and used directly without further purifications.

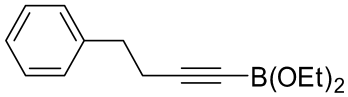
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.60 (m, 1H), 7.50 – 7.40 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 4H), 1.39 (t, *J* = 7.1 Hz, 6H).



Diethyl (naphthalen-2-ylethynyl)boronate (1f)

To a flask A charged with argon was added 25 mL diethyl ether and 2-ethynylnaphthalene (2.13 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (naphthalen-2-ylethynyl)boronate (**1f**) was allowed to be stored for up to 1 week and used directly without further purifications.

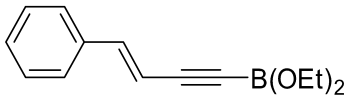
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 4H), 7.83 – 7.74 (m, 1H), 7.72 – 7.63 (m, 2H), 4.38 (q, J = 7.2 Hz, 4H), 1.54 (t, J = 7.2 Hz, 6H).



Diethyl (4-phenylbut-1-yn-1-yl)boronate (1g)

To a flask A charged with argon was added 25 mL diethyl ether and (3-butynyl)benzene (1.95 g, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (4-phenylbut-1-yn-1-yl)boronate (**1g**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 5H), 4.31 – 4.15 (m, 4H), 3.14 – 3.06 (m, 2H), 2.88 – 2.74 (m, 2H), 1.55 – 1.31 (m, 6H).

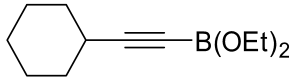


Diethyl (*E*)-(4-phenylbut-3-en-1-yn-1-yl)boronate (1h)

(*E*)-but-1-en-3-yn-1-ylbenzene (**S6h**) was synthesized according to disclosed procedure.[5]

To a flask A charged with argon was added 25 mL diethyl ether and (*E*)-but-1-en-3-yn-1-ylbenzene (1.92 g, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (*E*)-(4-phenylbut-3-en-1-yn-1-yl)boronate (**1h**) was allowed to be stored for up to 1 week and used directly without further purifications.

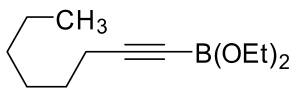
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.56 (m, 4H), 7.38 – 7.30 (m, 1H), 6.47 (d, J = 16.2 Hz, 1H), 6.37 (d, J = 16.2, 1H), 4.31 (q, J = 7.2 Hz, 4H), 1.48 (t, J = 7.2 Hz, 6H).



Diethyl (cyclohexylethynyl)boronate (1i)

To a flask A charged with argon was added 25 mL diethyl ether and cyclohexylacetylene (1.96 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (cyclohexylethynyl)boronate (**1i**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

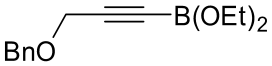
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 – 4.10 (m, 4H), 2.83 – 2.62 (m, 1H), 2.10 – 1.85 (m, 5H), 1.80 – 1.60 (m, 5H), 1.50 – 1.28 (m, 6H).



Diethyl oct-1-yn-1-ylboronate (1j)

To a flask A charged with argon was added 25 mL diethyl ether and 1-octyne (2.21 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl oct-1-yn-1-ylboronate (**1j**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

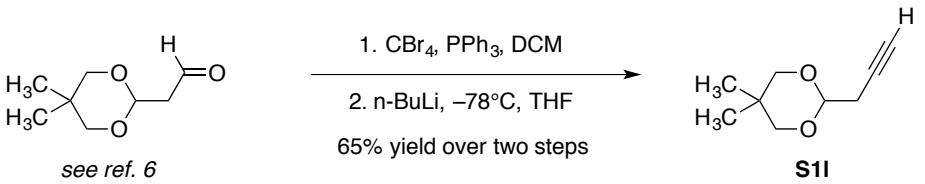
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 – 4.17 (m, 4H), 1.87 – 1.72 (m, 4H), 1.72 – 1.60 (m, 4H), 1.53 – 1.39 (m, 8H), 1.16 (m, 3H).



Diethyl (3-(benzyloxy)prop-1-yn-1-yl)boronate (1k)

To a flask A charged with argon was added 25 mL diethyl ether and propargyl benzyl ether (2.19 g, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (3-(benzyloxy)prop-1-yn-1-yl)boronate (**1k**) was allowed to be stored for up to 2 weeks and used directly without further purifications.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 5H), 4.89 – 4.77 (m, 2H), 4.48 – 4.34 (m, 2H), 4.28 (q, J = 7.2 Hz, 4H), 1.55 – 1.35 (m, 6H).

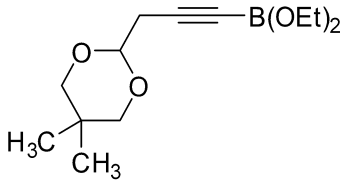


5,5-Dimethyl-2-(prop-2-yn-1-yl)-1,3-dioxane (S1l)

To a stirred solution of carbon tetrabromide (6.6 g, 20 mmol) in dichloromethane (100 mL) was added triphenylphosphine (7.9 g, 30 mmol) in dichloromethane (50 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, before a solution of 2-(5,5-dimethyl-1,3-dioxan-2-yl)acetaldehyde[6] (1.6 g, 10 mmol) in anhydrous dichloromethane (5 mL) was added. The resulting mixture was stirred for 1 h at 0 °C before an addition of H_2O (40 mL) to partition the organic layer. The resulting mixture was extracted with dichloromethane (3 X 50 mL); the combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was dissolved in 5 ml dichloromethane and filtered through a silica gel column by hexane/ether (10:1, 500 ml) to afford 2-(3,3-dibromoallyl)-5,5-dimethyl-1,3-dioxane as a yellow solid, which was used in the next step without further purification. To a stirred solution of 2-(3,3-dibromoallyl)-5,5-dimethyl-1,3-dioxane (3.1 g, 10 mmol) in THF (30 mL) was added nBuLi (15.6 mL, 1.6 M in hexane, 25 mmol) dropwise at –78 °C for 30 min. The resulting solution was stirred for 30 min at –78 °C, before it was quenched with aqueous sat. NH_4Cl (5 mL) at –78 °C. The aqueous layer was extracted with EtOAc (3 X 50 mL). The organic layer was washed with brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was eluted through a silica column by hexanes/EtOAc (10:1) to afford compound 5,5-dimethyl-2-(prop-2-yn-1-yl)-1,3-dioxane (**S1l**) (1.0 g, 65 % over two steps) as a colorless liquid.

^{1}H NMR (500 MHz, C_6D_6) δ 4.35 (t, *J* = 5.1 Hz, 1H), 3.31 (d, *J* = 11.2, 2H), 3.02 (d, *J* = 10.7, 2H), 2.45 (dd, *J* = 5.1, 2.7 Hz, 2H), 1.83 (t, *J* = 2.7 Hz, 1H), 1.01 (s, 3H), 0.25 (s, 3H).

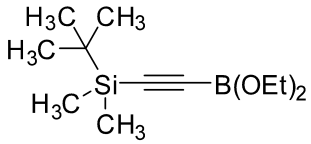
^{13}C NMR (126 MHz, C_6D_6) δ 99.6, 79.2, 76.5, 70.1, 29.4, 25.5, 22.6, 21.1.



Diethyl (3-(5,5-dimethyl-1,3-dioxan-2-yl)prop-1-yn-1-yl)boronate (1l)

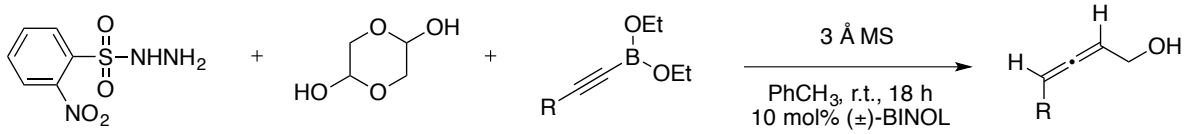
To a flask A charged with argon was added 10 mL diethyl ether and 5,5-dimethyl-2-(prop-2-yn-1-yl)-1,3-dioxane (**S1l**) (0.77 g, 5 mmol, 1 eq, *vide infra*). Solution was cooled to –78 °C and to it was added nBuLi (3.1 mL, 5 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 20 mL diethyl ether and freshly distilled triethyl borate (0.85 mL, 5 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (2.5 mL, 2 M solution sure-sealed in diethyl ether, 5 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to

less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (3-(5,5-dimethyl-1,3-dioxan-2-yl)prop-1-yn-1-yl)boronate (**1l**) was allowed to be stored for up to 1 week and used directly without further purifications.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (t, *J* = 5.3 Hz, 1H), 4.30 – 4.15 (m, 4H), 3.87 – 3.73 (m, 2H), 3.61 (d, *J* = 10.8 Hz, 2H), 1.43 (ovrlp, 9H), 0.88 (s, 3H).



Diethyl ((tert-butyldimethylsilyl)ethynyl)boronate (1m)
To a flask A charged with argon was added 25 mL diethyl ether and (*tert*-butyldimethylsilyl)acetylene (2.80 g, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl ((tert-butyldimethylsilyl)ethynyl)boronate (**1m**) was allowed to be stored for up to 2 weeks and used directly without further purifications.
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 (q, *J* = 7.6 Hz, 4H), 1.52 – 1.33 (m, 6H), 1.16 (s, 9H), 0.36 (s, 6H).

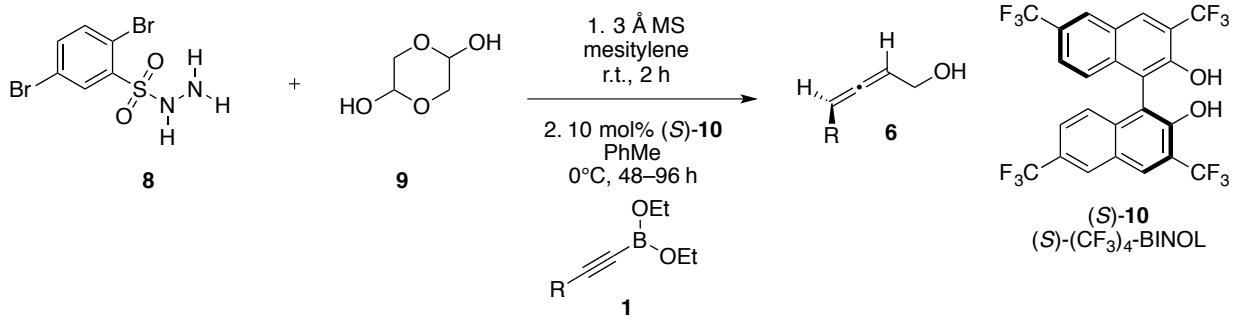
d. General Procedure for Racemic Petasis Alkynylations



20 **9** **1** **6**

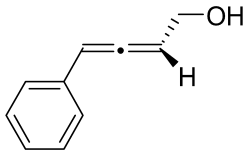
2-Nitrobenzenesulfonohydrazide **20** (87 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Racemic BINOL catalyst (15 mg, 0.052 mmol) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was stirred for 5 min, at which moment to it was subjected the alkynyl boronate (0.52 mmol, stored as 1 M solution in toluene). The reaction was stirred at room temperature for 18 h. The racemic allenyl alcohol products were isolated directly by silica gel chromatography.

e. General Procedure for Asymmetric Petasis Alkynylations



2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C for 10 min under argon, at which moment to it was subjected the alkynyl boronate (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at 0 °C for 48 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 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 Allenyl Alcohols



(*S*)-4-Phenylbuta-2,3-dien-1-ol (6a)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1a** (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

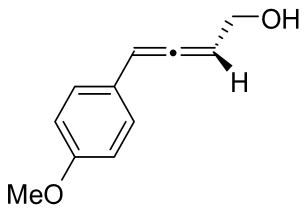
Yield: 50 mg, 85%.

e.r.: 93:7.

$[\alpha]_D^{22}$ = +103.0 (c = 0.49, CH_3CN). In lit:[7] $[\alpha]_D^{22}$ = +105.9 (c = 0.49, CH_3CN). The absolute stereochemistry was assigned as (*S*).

HPLC Analysis, tr major: 43.7 min., tr minor: 46.9 min., [Chiralpak®AD-H column, 24cm × 4.6 mm I.D., Hexanes:iPrOH = 98:2, 0.5 mL/min, 250 nm].

All spectra were in agreement with reported data.[7]



(*S*)-4-(4-Methoxyphenyl)buta-2,3-dien-1-ol (6b)

2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (58 mg, 0.104 mmol, 20 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to –10 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate **1b** (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at –10 °C for 48 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

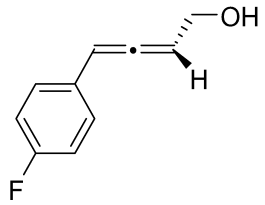
Yield: 56 mg, 80%.

e.r.: 91:9.

$[\alpha]_D^{22}$ = +27.1 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 39.5 min., tr minor: 42.9 min., [Chiralpak®AD-H column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1 mL/min, 250 nm].

The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.[8]



(*S*)-4-(4-Fluorophenyl)buta-2,3-dien-1-ol (6c)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1c** (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

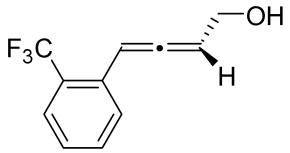
Yield: 51 mg, 78%.

e.r.: 93:7.

$[\alpha]_D^{22}$ = +53.8 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 30.6 min., tr minor: 31.7 min., [Chiralpak®IA-H column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 0.8 mL/min, 254 nm].

The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.[8]



(*S*)-4-(2-(Trifluoromethyl)phenyl)buta-2,3-dien-1-ol (6d)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1d** (0.52 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (10:1) to afford the pure product as a colorless oil.

Yield: 61 mg, 71%

e.r.: 93:7

$[\alpha]_D^{22}$ = +72.6 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr minor: 43.4 min., tr major: 45.7 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 99.6:0.4, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.47 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.30 (dd, *J* = 7.7, 7.7 Hz, 1H), 6.69 (dddd, *J* = 6.0, 4.3, 2.0, 2.0 Hz, 1H), 5.84 (ddd, *J* = 6.1, 6.1, 6.0 Hz, 1H), 4.34 – 4.24 (m, 2H).

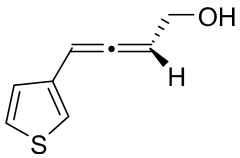
^{13}C NMR (126 MHz, $CDCl_3$) δ 205.5, 132.4 (q, $^4J_{C\text{-}F}$ = 1.3 Hz), 131.8, 128.7, 127.0, 126.2 (q, $^1J_{C\text{-}F}$ = 239.4 Hz), 126.8 (q, $^2J_{C\text{-}F}$ = 30.5 Hz), 126.0 (q, $^3J_{C\text{-}F}$ = 5.6 Hz), 95.9, 93.3 (q, $^4J_{C\text{-}F}$ = 2.7 Hz), 60.1

^{19}F NMR (470 MHz, $CDCl_3$) δ –59.5.

HRMS found 215.0690 (calculated for $[C_{11}H_{10}F_3O]^+$: 215.0684)

IR (thin film, cm^{-1}): 3377, 3082, 2940, 1955, 1731, 1495, 1316, 1162, 1121, 1060, 766.

The absolute stereochemistry was assigned by analogy.



(*S*)-4-(Thiophen-3-yl)buta-2,3-dien-1-ol (6e)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1e** (0.52 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (6:1) to afford the pure product as a colorless oil.

Yield: 43 mg, 70%

e.r.: 92:8

$[\alpha]_D^{22}$ = +116.4 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr minor: 21.4 min., tr major: 23.9 min., [Chiralpak®IA-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1 mL/min, 254 nm].

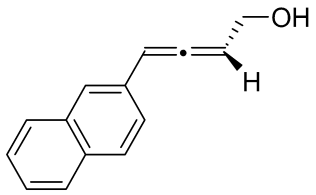
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (ddd, *J* = 5.1, 3.0, 0.6 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.07 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.40 (ddd, *J* = 6.4, 3.0, 2.9 Hz, 1H), 5.73 (ddd, *J* = 6.4, 5.8, 5.8, 1H), 4.28 – 4.20 (m, 2H), 1.54 (t, *J* = 6.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.5, 135.0, 126.2, 126.1, 121.3, 95.1, 91.8, 60.4.

HRMS found 153.0370 (calculated for $[C_8H_9OS]^+$: 153.0374)

IR (thin film, cm^{-1}): 3381, 3104, 2926, 1952, 1435, 1333, 1234, 1015, 789.

The absolute stereochemistry was assigned by analogy.



(*S*)-4-(Naphthalen-2-yl)buta-2,3-dien-1-ol (6f)

2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C for 10 min, at which moment to it was subjected the alkynyl boronate **1f** (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

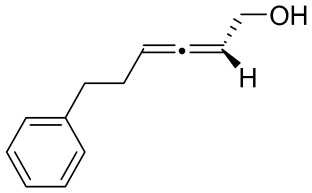
Yield: 67 mg, 85%.

e.r.: 90:10.

$[\alpha]_D^{22}$ = +116.8 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 40.5 min., tr minor: 47.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1.0 mL/min, 254 nm].

The absolute stereochemistry was assigned by analogy. All spectra agreed with reported data.[8]



(*S*)-6-Phenylhexa-2,3-dien-1-ol (6g)

2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate **1g** (0.52 mmol, 1 M solutions in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

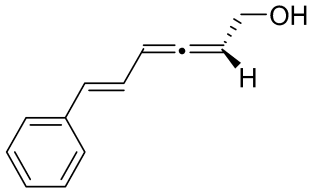
Yield: 54 mg, 72%.

e.r.: 92:8.

$[\alpha]_D^{22}$ = +10.5 (c = 1.0, $CHCl_3$). In lit for (*R*)-6-phenylhexa-2,3-dien-1-ol:[9] $[\alpha]_D^{20}$ = –38.7 (c = 1.05, $CHCl_3$, 96% ee).

HPLC Analysis, tr minor: 27.6 min., tr major: 44.8 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 0.8 mL/min, 210 nm].

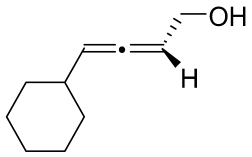
All spectra were in agreement with reported data.[9]



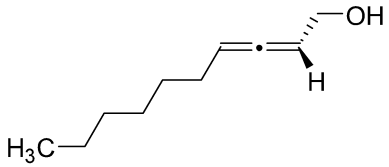
(*S*,*E*)-6-Phenylhexa-2,3,5-trien-1-ol (6h)

2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate **1h** (0.52 mmol, 1 M solutions in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic

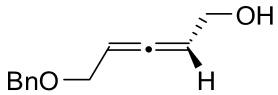
layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.
Yield: 49 mg, 71%.
e.r.: 90:10.
$[\alpha]_D^{22}$ = +29.2 (c = 1.0, $CHCl_3$).
HPLC Analysis, tr minor: 43.4 min., tr major: 54.0 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1.0 mL/min, 254 nm].
The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.[10]



(*S*)-4-Cyclohexylbuta-2,3-dien-1-ol (6i)
Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1i** (0.52 mmol) according to the General Procedure, but for 72 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.
Yield: 38 mg, 63%.
e.r.: 90:10.
$[\alpha]_D^{22}$ = +80.5 (c = 1.0, $CHCl_3$). In lit:[9] $[\alpha]_D^{21}$ = +100.9 (c = 1.04, $CHCl_3$, 99% ee).
HPLC Analysis, tr minor: 19.0 min., tr major: 19.8 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 99:1, 1.0 mL/min, 230 nm].
All spectra were in agreement with reported data.[9]



(*S*)-Deca-2,3-dien-1-ol (6j)
Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1j** (0.52 mmol) according to the General Procedure but for 96 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.
Yield: 45 mg, 73%.
e.r.: 90:10.
$[\alpha]_D^{22}$ = +60.7 (c = 1.0, $CHCl_3$). In lit for (*R*)-deca-2,3-dien-1-ol:[11] $[\alpha]_D^{20}$ = –72.5 (c = 1.02, $CHCl_3$, 94% ee).
HPLC Analysis, tr minor: 18.3 min., tr major: 19.5 min., [Chiralpak®IA-H column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 99.6:0.4, 1 mL/min, 210 nm].
All spectra were in agreement with reported data.[11]



(*S*)-5-(Benzyloxy)penta-2,3-dien-1-ol (6k)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1k** (0.52 mmol) according to the General Procedure but for 96 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

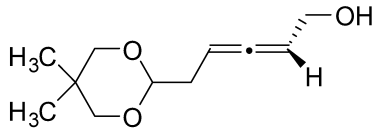
Yield: 46 mg, 60%.

e.r.: 90:10.

$[\alpha]_D^{22}$ = +33.2 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr minor: 37.1 min., tr major: 39.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: EtOH = 99:1, 1.0 mL/min, 250 nm].

The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.[8]



(*S*)-5-(5,5-Dimethyl-1,3-dioxan-2-yl)penta-2,3-dien-1-ol (6l)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1l** (0.52 mmol) according to the General Procedure but for 72 hours. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (10:1) to afford the pure product as a colorless oil.

Yield: 56 mg, 70%

e.r.: 85:15

$[\alpha]_D^{22}$ = –19.6 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 13.0 min., tr minor: 13.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 97:3, 1.0 mL/min, 210 nm].

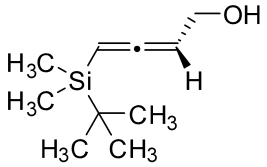
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 – 5.31 (m, 2H), 4.51 (dd, *J* = 4.8, 4.8 Hz, 1H), 4.13 – 4.07 (m, 2H), 3.61 (d, *J* = 11.0 Hz, 2H), 3.43 (d, *J* = 10.9 Hz, 2H), 2.39 – 2.35 (m, 2H), 2.19 (t, *J* = 5.9 Hz, 1H), 1.18 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.6, 100.8, 92.4, 89.2, 77.2, 77.1, 59.5, 34.4, 30.1, 22.9, 21.7.

ESI-MS found 199.1 (calculated for $[C_{11}H_{19}O_3]^+$: 199.1)

IR (thin film, cm^{-1}): 3370, 2956, 2849, 1969, 1472, 1392, 1131, 1090, 1020.

The absolute stereochemistry was assigned by analogy.



(*S*)-4-(*tert*-Butyldimethylsilyl)buta-2,3-dien-1-ol (6m)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **1m** (0.52 mmol) according to the General Procedure, but for 96 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

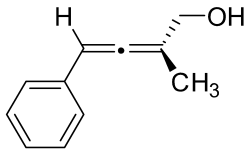
Yield: 46 mg, 62%.

e.r.: 95:5.

$[\alpha]_D^{22}$ = +116.9 (c = 1.0, $CHCl_3$).

HPLC Analysis, tr major: 14.9 min., tr minor: 16.8 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes: EtOH = 99.6:0.4, 1.0 mL/min, 210 nm].

The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.[12]



(*S*)-2-Methyl-4-phenylbuta-2,3-dien-1-ol (6n)

2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), hydroxyacetone (**11**) (30 mg, 0.4 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate **1a** (0.52 mmol, 1 M solutions in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

Yield: 58 mg, 91%.

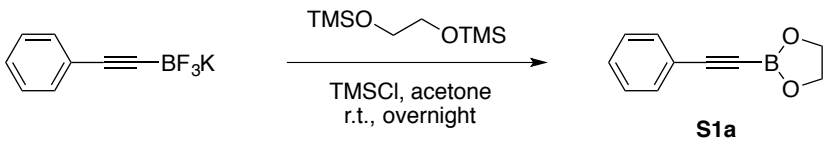
e.r.: 90:10.

$[\alpha]_D^{22}$ = +9.8 (c = 1.0, $CHCl_3$). In lit for (*R*)-2-methyl-4-phenylbuta-2,3-dien-1-ol:[13] $[\alpha]_D^{20}$ = –10.9 (c = 0.5, $CHCl_3$, 99% ee).

HPLC Analysis, tr major: 14.3 min., tr minor: 15.7 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: EtOH = 98:2, 1.0 mL/min, 210 nm].

All spectra were in agreement with reported data.[13]

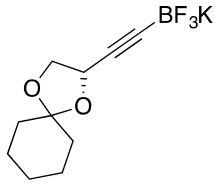
g. General procedure for Synthesis of Cyclic Alkynyl Boronates



S1a

Cyclic alkynyl boronates were synthesized according to the modified procedure by Yamamoto.[14] To a solution of the potassium trifluoro(phenylethynyl)borate (2.07 g, 10.0 mmol) and 2,2,7,7-tetramethyl-3,6-dioxa-2,7-disilaoctane[15] (2.06 g, 10.0 mmol) in dry acetone (10 mL) was added chlorotrimethylsilane (2.17 g, 20.0 mmol) at room temperature, and the solution was stirred overnight. The precipitates were removed by filtration under N_2 atmosphere, and the filtrate was concentrated. The crude oil was purified by a quick neutral alumina column by hexanes and the resulting 2-(phenylethynyl)-1,3,2-dioxaborolane **S1a** solution was concentrated and stored as 1 M solution in toluene.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.41 – 7.34 (m, 1H), 7.36 – 7.29 (m, 2H), 4.32 (s, 4H).



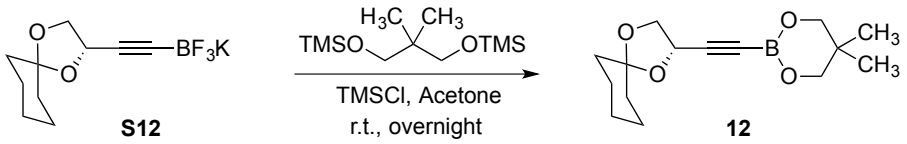
Potassium *(S)*-((1,4-dioxaspiro[4.5]decan-2-yl)ethynyl)trifluoroborate (S12)

The title trifluoroborate salt was synthesized according to the procedure reported by Thomson and coworkers.[8] To a solution of (S)-2-ethynyl-1,4-dioxaspiro[4.5]decane[16] (4.00 g, 24.1 mmol) in dry THF (75 mL) at –78 °C under N_2 atmosphere was added *n*-BuLi (13.75 mL, 24.1 mmol, 1.75 M in hexanes) dropwise over 10 minutes. After stirring at –78 °C for 1 h, triisopropyl borate (8.33 mL, 36.1 mmol) was quickly added by syringe. The reaction was maintained at –78 °C for 10 minutes, and removed from the bath and allowed to warm up to room temperature over 2 h. The reaction was then cooled to 0 °C and dry MeOH (25 mL) was then added by syringe, followed by a slurry of potassium hydrogen difluoride (KHF_2) (11.28 g, 144.4 mmol) in H_2O (60 mL + 2 x 5 mL rinses) via addition funnel. The reaction was then allowed to warm to room temperature over 1.5 h. The solvent was removed under reduced pressure, and the resulting suspension was allowed to dry over high vacuum overnight. The residual solids were broken up using a spatula and dissolved in 75 mL of acetone. The resulting mixture was placed on a rotary evaporator and rotated rapidly at atmospheric pressure with the bath set at 45 °C for 45 minutes. The mixture was decanted over Celite® under vacuum, and the residual solids were once again taken up in 75 mL of acetone and the mixture was heated at 45 °C for 15 minutes. The mixture was filtered over Celite®, washing with acetone. The filtrate was concentrated to ~ 10 mL, and Et_2O (100 mL) was added, causing a gel to crash out. The flask was chilled in the freezer at –30 °C for 6 h, and the gel was collected by vacuum filtration using a medium gauge fritted filter, then further dried over high vacuum overnight to afford **S12** (2.51 g, 9.22 mmol, 38%) as an off-white solid that contained minor impurities and cannot be further purified.

mp (decomp) 327 °C

$[\alpha]_D^{22}$ = +268.5 (c = 0.94, CH_3CN).

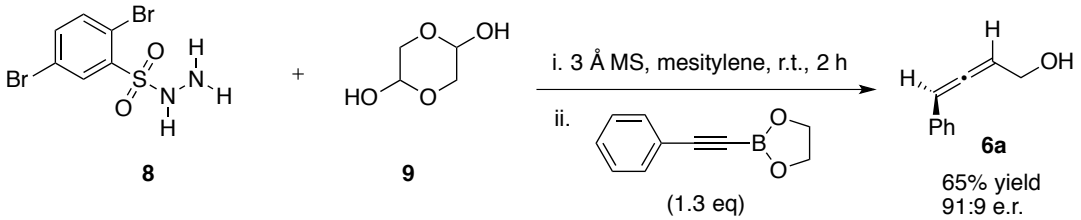
^{1}H NMR (500 MHz, DMSO-d_6) δ 4.58 (dd, J = 7.5, 6.1 Hz, 1H), 4.05 (dd, J = 7.5, 6.1 Hz, 1H), 3.60 (dd, J = 7.5, 7.5 Hz, 1H), 1.65 – 1.48 (m, 8H), 1.40 – 1.34 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) (relaxation time d_1 = 3 seconds, increasing to d_1 = 7 seconds does not reveal clear signal for the second acetylenic carbon atom) δ 109.0, 69.2, 65.5, 35.6, 35.1, 24.6, 23.5.
^{11}B NMR (128.4 MHz, DMSO-d_6) δ –2.10.
^{19}F NMR (376.5 MHz, DMSO-d_6) δ –127.3.
ESI-HRMS found 233.1054 (calculated for $C_{10}H_{13}BF_3O_2$ [M–K]$^-$: 233.1075.)
IR (thin film, cm^{-1}): 2935, 2861, 1449, 1365, 1345, 1279, 1236, 979.



S12 **12**

***(S)*-2-((1,4-Dioxaspiro[4.5]decan-2-yl)ethynyl)-5,5-dimethyl-1,3-2-dioxaborinane (12)**
To a flame-dried round bottom flask equipped with a stir bar was added potassium trifluoroborate **S12** (1.00 g, 3.67 mmol) and dry acetone (3.70 mL). 1,3-Bis(trimethylsilyloxy)-2,2-dimethylpropane[17] (1.10 mL, 3.67 mmol) was then added quickly, followed by trimethyl silyl chloride (0.933 mL, 7.35 mmol). The reaction was allowed to stir at room temperature for 24 h, at which time it was filtered over a pad of neutral alumina, washing with hexanes. The filtrate was then concentrated to afford the title compound (0.762 g) with some impurities as a yellow oil. It was then stored as a 1M solution in toluene.
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 4.71 (td, J = 6.3, 2.1 Hz, 1H), 4.17 (ddd, J = 8.0, 6.1, 0.6 Hz, 1H), 3.94 (dddd, J = 8.0, 6.2, 4.8, 0.6 Hz, 1H), 3.59 (d, J = 0.6 Hz, 3H), 3.50 (dd, J = 1.8, 0.6 Hz, 1H), 1.77 – 1.54 (m, 10 H), 0.95 (d, J = 0.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) *δ* 111.2, 81.6, 73.7, 72.0, 69.8, 69.5, 64.9, 35.6, 35.4, 25.0, 23.9, 22.8, 22.6, 21.8.
^{11}B NMR (128.4 MHz, $CDCl_3$) *δ* 31.57.

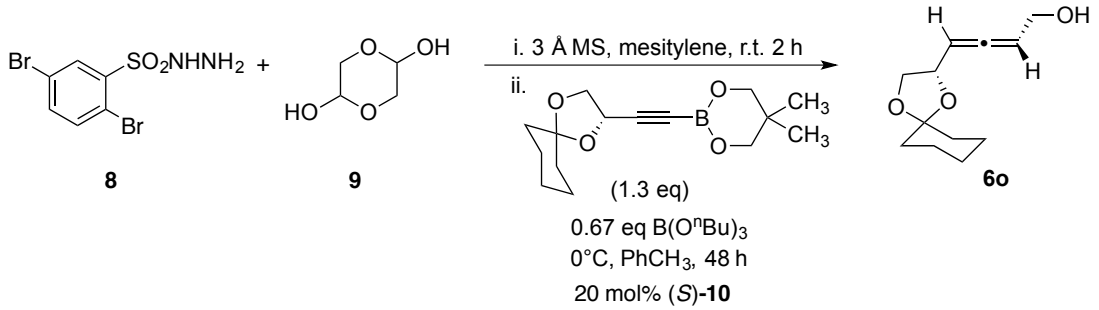
h. General Procedure for Petasis Reactions Using Cyclic Alkynyl Boronates



8 **9** (1.3 eq) **6a**
65% yield
91:9 e.r.

2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (58 mg, 0.104 mmol, 20 mol%) was added and rinsed into the solution with tributyl borate (60 mg, 0.26 mmol) and dry toluene (0.48 mL). The mixture was cooled to

4 °C for 10 min, at which moment to it was subjected 2-(phenylethynyl)-1,3,2-dioxaborolane **S1a** (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at 4 °C for 46 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 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 **6a** in 91:9 e.r. and 65% yield.



(*S*)-4-((*S*)-1,4-Dioxaspiro[4.5]decan-2-yl)buta-2,3-dien-1-ol (6o)

Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **12** (0.52 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (19:1) to afford the pure product as a colorless oil. The single diastereomer can be isolated by the same chromatography conditions using silver-impregnated ($AgNO_3$) silica gel.

Yield: 56 mg, 68%

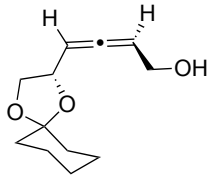
$[\alpha]_D^{24}$ = +35.8 (c = 2.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (qd, J = 6.0, 1.6 Hz, 1H), 5.37 (tt, J = 6.1, 2.8 Hz, 1H), 4.59 (ddd, J = 6.4, 6.4, 1.6 Hz, 1H), 4.18 (dd, J = 6.0, 2.8, 2H), 4.12 (dd, J = 8.3, 6.1 Hz, 1H), 3.70 (dd, J = 8.2, 6.7 Hz, 1H), 1.75 – 1.53 (m, 11H), 1.48 – 1.32 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.6, 110.2, 94.0, 94.0, 73.9, 73.8, 69.1, 60.2, 36.3, 35.3, 25.1, 23.9, 23.8.

HRMS (EI) found 210.1248 (calculated for $C_{12}H_{18}O_3$: 210.1256.)

IR (thin film, cm^{-1}): 3399, 2934, 2861, 1966, 1448, 1366, 1279, 1162, 1096, 1018.



***(R)*-4-((*S*)-1,4-Dioxaspiro[4.5]decan-2-yl)buta-2,3-dien-1-ol (6p)**

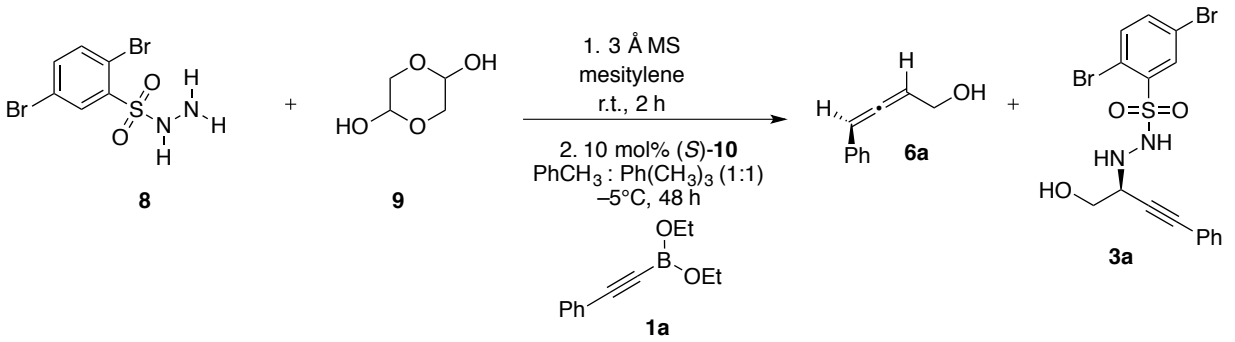
Prepared from glycolaldehyde dimer **9** (0.2 mmol) and the corresponding alkynyl boronate **12** (0.52 mmol) according to the General Procedure, using (*R*)-**10** catalyst. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (19:1) to afford the pure product as a colorless oil. The single diastereomer can be isolated by the same chromatography conditions using silver-impregnated ($AgNO_3$) silica gel.

Yield: 60 mg, 71%

$[\alpha]_D^{24}$ = +16.5 (c = 1.3, $CHCl_3$).

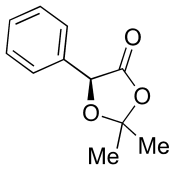
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52 (qd, J = 6.1, 1.5 Hz, 1H), 5.36 (tt, J = 6.2, 2.9 Hz, 1H), 4.59 (ddd, J = 6.3, 6.1, 1.2 Hz, 1H), 4.14 (dd, J = 5.9, 2.8 Hz, 2H), 4.09 (dd, J = 8.2, 6.1 Hz, 1H), 3.74 (dd, J = 8.3, 6.3 Hz, 1H), 1.79 – 1.48 (m, 9H), 1.45 – 1.32 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 203.6, 110.3, 94.3, 93.8, 73.7, 73.7, 68.8, 60.1, 36.4, 35.3, 25.0, 23.9, 23.8.

h. Isolation of the Propargylic Intermediate 3a



2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), glycolaldehyde dimer **9** (24 mg, 0.2 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (29 mg, 0.104 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to –5 °C for 20 min, at which moment to it was subjected alkynyl boronate **1a** (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at the same temperature for 48 h, at which moment the reaction mixture was subjected to flash column chromatography on silica gel using pentane/Et_2O (10:1 to 1:2) to afford allenol product **6a** and intermediate **3a**. **3a** was condensed by a high-vac pump without allowing the temperature to exceed 10 □.
^{1}H NMR (500 MHz, $CDCl_3$) 8.32 (s, 1H), 7.64 – 7.53 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 6.81 (s, 1H), 3.95 – 3.87 (m, 2H), 3.72 (par obsc, 1H), 2.82 (br, 1H).
Note: this compound is not stable and its spectra contain solvent peaks.
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 137.4, 136.3, 135.6, 131.9, 129.0, 128.4, 122.1, 121.7, 118.2, 87.0, 83.7, 61.7, 54.7.
ESI-MS found 472.9, 474.9, 476.9 (calculated for **3a** $[C_{16}H_{15}Br_2N_2O_3S]^+$: 474.9)

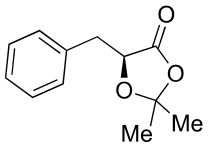
i. Synthesis of α-Hydroxy Lactones (S13)



(*S*)-2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-one (S13a)

To a flame-dried round bottom flask equipped with a stir bar was added S-(+)-mandelic acid (3.00 g, 19.7 mmol) and acetone (30 mL). 2,2-dimethoxypropane (7.19 g, 69.0 mmol) was then added, followed by p-toluenesulfonic acid (0.150 g, 0.789 mmol). The reaction was allowed to stir at room temperature for 14 h. The solvent was then evaporated under reduced pressure, and the residue was taken up in EtOAc (40 mL) and transferred to a separatory funnel, where it was washed with 25 mL of sat. $NaHCO_3$ and 35 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated to afford the title compound (3.60 g, 18.7 mmol, 95%) as a white solid that required no further purification. Spectral data matched those previously reported in the literature.[18]

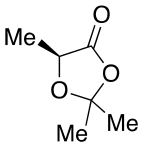
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 5H), 5.39 (s, 1H), 1.73 (s, 3H), 1.68 (s, 3H).



(*S*)-5-Benzyl-2,2-dimethyl-1,3-dioxolan-4-one (S13b)

To a flame-dried round bottom flask equipped with a stir bar was added L-(–)-3-phenyllactic acid (3.00 g, 18.1 mmol) and acetone (30 mL). 2,2-dimethoxypropane (6.58 g, 63.2 mmol) was then added, followed by p-toluenesulfonic acid (0.137 g, 0.722 mmol). The reaction was allowed to stir at room temperature for 18 h. The solvent was then evaporated under reduced pressure, and the residue was taken up in EtOAc (40 mL) and transferred to a separatory funnel, where it was washed with 25 mL of sat. $NaHCO_3$ and 25 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated to afford the title compound (3.63 g, 17.6 mmol, 98%) as a clear and colorless liquid that solidified into a white solid upon refrigeration. Spectral data matched those previously reported in the literature.[19]

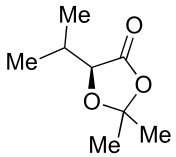
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 4.66 (dd, J = 6.6, 4.1 Hz, 1H), 3.20 (dd, J = 14.5, 4.1 Hz, 1H), 3.05 (dd, J = 14.5, 6.5 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H).



(*S*)-2,2,5-Trimethyl-1,3-dioxolan-4-one (S13c)

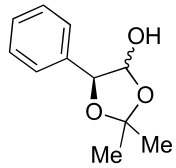
To a flame-dried round bottom flask equipped with a stir bar was added L–(+)–lactic acid (5.00 g, 55.5 mmol) and anhydrous benzene (35 mL). 2,2-dimethoxypropane (10.2 mL, 83.3 mmol) was then added, and the reaction was allowed to stir under reflux with a Dean-Stark apparatus for 4 h with azeotropic removal of methanol. The reaction was then concentrated to afford the title compound (4.05 g, 31.1 mmol, 56%) as a clear and colorless oil that required no further purification.

$[\alpha]_D^{22}$ = +42.9 (c = 1.0, $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (q, J = 6.8 Hz, 1H), 1.61 (s, 3H), 1.58 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 110.3, 70.4, 27.4, 25.6, 17.4.
HRMS (ESI) found 131.0708. (Calculated for $C_6H_{10}O_3$ $[M+H]^+$ 131.0706.)
IR (neat, cm^{-1}): 2992, 2941, 2876, 1799, 1447, 1346, 1267, 1146, 1126, 1051, 935, 844.

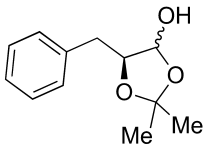


(*S*)-5-Isopropyl-2,2-dimethyl-1,3-dioxolan-4-one (S13d)
To a flame-dried round bottom flask equipped with a stir bar was added (S)-(+)-2-hydroxy-3-methyl-butyric acid (2.30 g, 19.5 mmol) and acetone (50 mL). 2,2-dimethoxypropane (7.10 g, 68.1 mmol) was then added, followed by p-toluenesulfonic acid (0.129 g, 0.677 mmol). The reaction was allowed to stir at room temperature for 18 h. The solvent was then evaporated under reduced pressure, and the residue was taken up in EtOAc (100 mL) and transferred to a separatory funnel, where it was washed with 50 mL of sat. $NaHCO_3$ and 50 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated to afford the title compound (2.82 g, 17.8 mmol, 92%) as a pale yellow liquid. Spectral data matched those previously reported in the literature.[19]
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (d, J = 3.9 Hz, 1H), 2.20 – 2.09 (m, 1H), 1.60 (s, 3H), 1.53 (s, 3H), 1.07 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H).

j. Synthesis of α-Hydroxy Lactols (13)



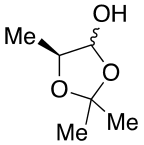
(5*S*)-2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-ol (13a)
To a flame-dried round bottom flask equipped with a stir bar was added the acetonide **S13a** (1.26 g, 6.57 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (10.95 mL, 10.95 mmol, 1.0 M in hexanes) was then added dropwise. The mixture was allowed to stir at –78°C for 50 minutes, at which time 15 mL of 1M HCl was added carefully to quench the reaction. The cooling bath was removed, and the flask was allowed to warm slowly to room temperature. After the clear formation of two layers, the mixture was transferred to a separatory funnel using EtOAc (25 mL) and water (10 mL). The layers were separated, and the aqueous layer was extracted with 3 x 25 mL of EtOAc. The combined organic layers were filtered through a pad of silica gel, washing with EtOAc, then were dried over $MgSO_4$ and concentrated to afford the title compound (1.19 g, 6.13 mmol, 93%) as a clear and colorless oil that was directly used in the next step without further purification.
^{1}H NMR (500 MHz, CDCl3) δ 7.42 – 7.29 (m, 5H), 5.32 (t, *J* = 3.9 Hz, 1H), 4.99 (d, *J* = 3.7 Hz, 1H), 2.94 (br s, 1H), 1.64 (s, 3H), 1.59 (s, 3H), major diastereomer.



(5*S*)-5-Benzyl-2,2-dimethyl-1,3-dioxolan-4-ol (13b)

To a flame-dried round bottom flask equipped with a stir bar was added the acetonide **S13b** (1.50 g, 7.27 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (6.86 mL, 10.2 mmol, 25 wt% in toluene) was then added dropwise. The mixture was allowed to stir at –78°C for 60 minutes, at which time 6 mL of 3M HCl was added carefully to quench the reaction. The cooling bath was removed, and the flask was allowed to warm slowly to room temperature. After the clear formation of two layers, the mixture was transferred to a separatory funnel using EtOAc (25 mL) and water (10 mL). The layers were separated, and the aqueous layer was extracted with 3 x 25 mL of EtOAc. The combined organic layers were filtered through a pad of silica gel, washing with EtOAc, then were dried over $MgSO_4$ and concentrated to afford the title compound (1.28 g, 6.15 mmol, 85%) as a clear and colorless oil that was directly used in the next step without further purification.

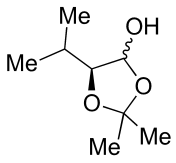
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 5H), 5.11 (dd, J = 4.0, 3.0 Hz, 1H), 4.28 (td, J = 6.7, 3.0 Hz, 1H), 3.04 (dd, J = 7.0, 1.2 Hz, 1H), 2.97 (dd, J = 14.0, 7.0 Hz, 1H0, 2.89 (dd, J = 14.0, 6.5 Hz, 1H), 1.52 (s, 3H), 1.46 (s, 3H), major diastereomer.



(5*S*)-2,2,5-Trimethyl-1,3-dioxolan-4-ol (13c)

To a flame-dried round bottom flask equipped with a stir bar was added the acetonide **S13c** (0.335 g, 2.57 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (2.08 mL, 3.09 mmol, 25 wt% in toluene) was then added dropwise. The mixture was allowed to stir at –78°C for 60 minutes, at which time 5 mL of anhydrous MeOH was added carefully to quench the reaction. The flask was allowed to warm to room temperature, and a saturated solution of Rochelle's salt (10 mL) was then added, causing a gel to form immediately. This gel was filtered over Celite® to form a biphasic solution that was transferred to a separatory funnel with the aid of EtOAc (10 mL). The layers were separated, and the aq. Layer was extracted with 50 mL of EtOAc. The combined organic layers were washed with 50 mL of sat. $NaHCO_3$ followed by 50 mL of brine, then dried over $MgSO_4$ and concentrated to afford the title compound (68 mg, 0.51 mmol, 20%) that was directly used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.21 (t, J = 3.7 Hz, 1H), 3.72 (dd, J = 7.1, 3.4 Hz, 1H), 2.90 (br s, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 0.98 (d, J = 6.7 Hz, 3H), major diastereomer.

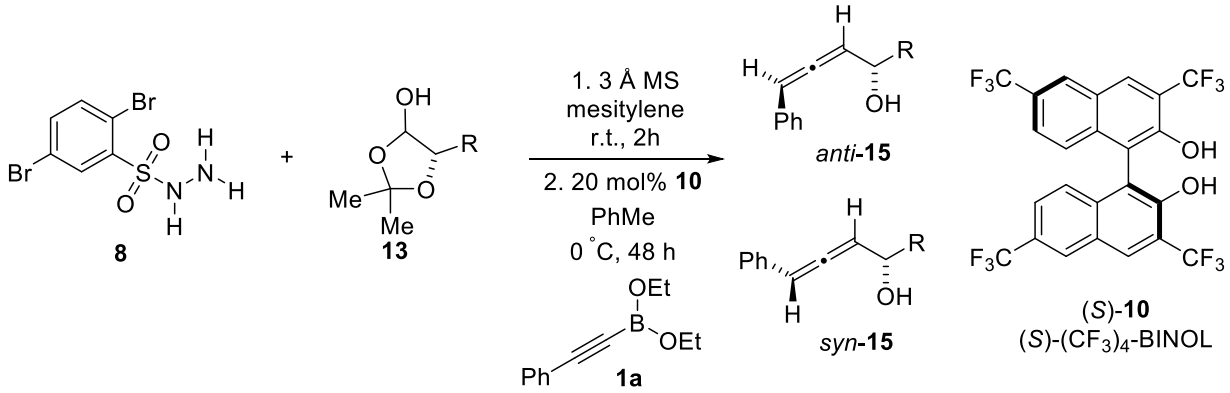


(5*S*)-5-Isopropyl-2,2-dimethyl-1,3-dioxolan-4-ol (13d)

To a flame-dried round bottom flask equipped with a stir bar was added the acetonide **S13d** (1.00 g, 6.32 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (5.05 mL, 7.59 mmol, 25 wt% in toluene) was then added dropwise. The mixture was allowed to stir at –78°C for 60 minutes, at which time 15 mL of 1M HCl was added carefully to quench the reaction. The cooling bath was removed, and the flask was allowed to warm slowly to room temperature for 1h. After the clear formation of two layers, the mixture was transferred to a separatory funnel using EtOAc (25 mL) and water (10 mL). The layers were separated, and the aqueous layer was extracted with 3 x 25 mL of EtOAc. The combined organic layers were filtered through a pad of silica gel, washing with EtOAc, then were dried over $MgSO_4$ and concentrated to afford the title compound (0.785 g, 4.90 mmol, 78%) as a clear and colorless oil that was directly used in the next step without further purification.

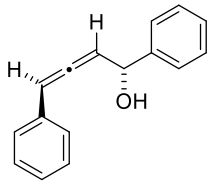
^{1}H NMR (500 MHz, CDCl3) δ 5.11 (dd, *J* = 4.3, 3.5 Hz, 1H), 4.14 (dqd, *J* = 19.2, 6.3, 3.4 Hz, 1H), 2.73 (dd, J = 4.4, 0.9 Hz, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 1.32 (d, J = 6.5 Hz, 6H), major diastereoisomer.

k. General Procedure for Diastereoselective Petasis Alkynylations



2,5-Dibromobenzenesulfonohydrazide **8** (132 mg, 0.4 mmol), α-hydroxy lactol **13** (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (250 mg) were added to a 4 dram flame-dried reaction vial equipped with a magnetic stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (*S*)-$(CF_3)_4$-BINOL catalyst **10** (44 mg, 0.078 mmol, 15 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C for 10 min under nitrogen, at which time the alkynyl boronate **1a** (0.52 mmol, 1 M solution in toluene) was added. The reaction was allowed to stir at 0 °C for 48 h and then quenched by 1 ml aqueous 10% NaOH solution. The reaction was then diluted with 5 mL Et_2O and transferred to a separatory funnel with the aid of additional NaOH (5 mL). The layers were separated, and the aqueous layer was extracted with 3 x 5 mL Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography on silica gel afforded the desired compound.

l. Analytical Data for Allenyl Alcohols



(1*R*, 3*S*)-1,4-Diphenylbuta-2,3-dien-1-ol (*anti*-15a)

Prepared from the corresponding α-hydroxy lactol **13a** (0.4 mmol) and alkynyl boronate **1a** (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (9:1) to afford the pure product as a pale yellow oil.

Yield: 80 mg, 90%.

d.r.: 20:1.

$[\alpha]_D^{22}$ = +158.9 (c = 1.0, $CHCl_3$). In lit:[20] $[\alpha]_D^{22}$ = +168.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.12 (m, 6H), 6.31 (dd, J = 6.4, 2.2 Hz, 1H), 5.81 (app t, J = 6.4 Hz, 1H), 5.31 (dd, J = 6.4, 2.3 Hz, 1H), 2.10 (br s, 1H).

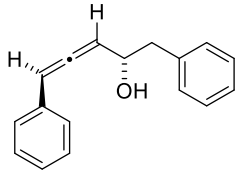
^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 142.8, 133.6, 128.7, 128.6, 127.9, 126.9, 126.0, 100.0, 97.9, 72.4.

All spectra were in agreement with reported data.[20] Thus, the major diastereomer was assigned as *anti*-**15a**.

Carrying out the reaction under identical conditions with catalyst (*R*)-**10** afforded the title compound (0.040 g, 0.17 mmol, 45%, 1.2 : 1 d.r.) as a pale yellow oil. The minor *syn*-**15a** isomer was not separable from its *anti*-**15a** isomer through chromatography. The following signals are discernible:

^{1}H NMR (500 MHz, $CDCl_3$) *δ* 5.27 (dd, J = 6.4, 2.3 Hz, 1H)

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 203.5, 142.7, 127.8, 126.0, 99.9, 97.9, 72.1.



(2*S*, 4*S*)-1,5-Diphenylpenta-3,4-dien-2-ol (*anti*-15b)

Prepared from the corresponding α-hydroxy lactol **13b** (0.4 mmol) and alkynyl boronate **1a** (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.

Yield: 77 mg, 85%.

d.r.: 20:1.

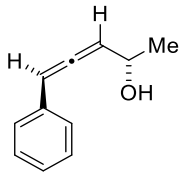
$[\alpha]_D^{22}$ = –343.9 (c = 0.5, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.10 (m, 8H), 7.08 – 7.05 (m, 2H), 6.26 (d, J = 6.4, 1.9 Hz, 1H), 5.69 (app t, J = 6.5 Hz, 1H), 4.53 (m, 1H), 3.02 (dd, J = 13.4, 7.0 Hz, 1H), 2.94 (dd, J = 13.5, 6.5 Hz, 1H), 1.86 (d, J = 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) *δ* 204.0, 137.5, 133.6, 129.7, 128.6, 127.1, 126.8, 126.6, 98.6, 97.1,

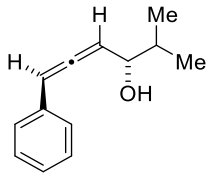
71.4, 44.1.
The spectral data matched those of an authentic sample previously reported in the literature.[8] Thus, the major diastereomer was assigned *anti*-**15b**.

Carrying out the reaction under identical conditions with catalyst (*R*)-**10** afforded the title compound (0.044 g, 0.187 mmol, 47%, 1.1 : 1 d.r.) as a clear and colorless oil. Partial separation of the minor *syn*-**15b** isomer was possible under the chromatography conditions. The spectral data matched those of an authentic sample previously reported in the literature.[8]
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 2H); 7.26 (m, 5H), 7.19 (m, 1H), 7.12 (m, 2H), 6.29 (dd, J = 6.4, 2.9 Hz, 1H), 5.73 (app t, J = 5.8 Hz, 1H), 4.53 (m, 1H), 3.01 (dd, J = 13.6, 5.2 Hz, 1H), 2.91 (dd, J = 13.7, 6.9 Hz, 1H), 1.87 (d, J = 4.8 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 137.3, 133.6, 129.8, 128.6, 128.5, 127.2, 126.8, 126.6, 99.2, 98.0, 70.0, 43.8.



(2*S*,4*S*)-5-Phenylpenta-3,4-dien-2-ol (*anti*-15c)
Prepared from the corresponding α-hydroxy lactol **13c** (0.2 mmol) and alkynyl boronate **1a** (0.26 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.
Yield: 24.6 mg, 76%.
d.r.: 6:1.
$[\alpha]_D^{22}$ = +70.7 (c = 0.15, $CHCl_3$).
^{1}H NMR (500 MHz, C_6D_6) δ 7.51 – 7.48 (m, 1H), 7.22 (dd, J = 8.0, 1.4 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.05 –6.93 (m, 2H), 6.14 (dd, J = 6.4, 2.5 Hz, 1H), 5.49 (app t, J = 6.0 Hz, 1H), 4.17 (app pd, J = 6.1, 2.4 Hz, 1H), 1.35 (br s, 1H), 1.15 (d, J = 6.3 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 203.4, 129.6, 129.0, 127.4, 127.1, 101.5, 97.5, 23.8.
This compound was previously reported in the literature.[21]

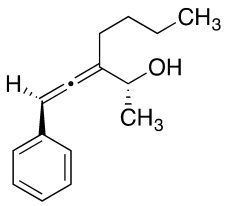
Carrying out the reaction under identical conditions with catalyst (*R*)-**10** afforded the title compound (12.2 mg, 0.076 mmol, 36%, 1 : 1.4 d.r.) as a clear and colorless oil. Partial separation of the *syn*-**15c** isomer was not possible under the chromatography conditions. The following peaks are discernible:
^{13}C NMR (125 MHz, C_6D_6) δ 203.5, 130.4, 128.9, 101.4, 97.6, 23.1.



(3*S*,5*S*)-2-Methyl-6-phenylhexa-4,5-dien-3-ol (*anti*-15d)
Prepared from the corresponding α-hydroxy lactol **13d** (0.4 mmol) and alkynyl boronate **1a** (0.52

mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.
Yield: 59 mg, 78%.
d.r.: 12:1.
$[\alpha]_D^{22}$ = +7.1 (c = 0.25, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 4H), 7.22 (app h, J = 4.0 Hz, 1H), 6.34 (dd, J = 6.5, 2.7 Hz, 1H), 5.68 (app t, J = 6.1 Hz, 1H), 4.07 (td, J = 5.6, 2.7 Hz, 1H), 1.86 (dq, J = 13.0, 6.5, 6.1 Hz, 1H), 1.72 (br s, 1H), 1.01 (d, J = 6.8 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 203.5, 134.0, 128.7, 127.2, 126.8, 98.1, 97.6, 74.6, 34.3, 18.2, 17.7.
HRMS (ESI) found 188.1208 (calculated for $C_{13}H_{16}O$ $[M]^+$: 188.1201.)
IR (neat, cm^{-1}): 3410, 2961, 2926, 2873, 1951, 1598, 1459, 1386, 1261, 1168, 1027.

Carrying out the reaction under identical conditions with catalyst (*R*)-**10** afforded the title compound (0.035 g, 0.187 mmol, 47%, 1.2 : 1 d.r.) as a clear and colorless oil. Partial separation of the minor *syn*-**15d** isomer was possible under the chromatography conditions.
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.31 – 7.29 (m, 4H), 7.22 (app h, J = 4.0 Hz, 1H), 6.32 (dd, J = 6.4, 2.1 Hz, 1H), 5.66 (app t, J = 6.4 Hz, 1H), 4.07 (td, J = 5.6, 2.7 Hz, 1H), 1.86 (dq, J = 13.0, 6.5, 6.1 Hz, 1H), 1.69 (br s, 1H), 1.02 (d, J = 6.8 Hz, 6H)
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0, 134.0, 128.7, 127.2, 126.8, 97.7, 97.0, 75.2, 34.2, 18.3, 17.9.



(*S*)-3-((*S*)-2-Phenylvinylidene)heptan-2-ol (*anti*-15e)
Prepared from the corresponding α-hydroxy ketone **16** (0.4 mmol) and alkynyl boronate **1a** (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (9:1) to afford the pure product as a clear and colorless oil.
Yield: 61 mg, 70%.
d.r.: 20:1.
$[\alpha]_D^{22}$ = –23.1 (c = 1.5, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 4H), 7.17 (ddd, J = 6.1, 2.7 Hz, 1H), 6.30 (app q, J = 3.0 Hz, 1H), 4.32 (ddt, J = 10.0, 6.4, 3.2 Hz, 1H), 2.12 (ddt, J = 7.8, 5.7, 3.0 Hz, 2H), 1.59 (d, J = 5.4 Hz, 1H), 1.45 (ddt, J = 13.2, 8.5, 6.6 Hz, 2H), 1.39 – 1.30 (m, 2H), 1.34 (d, J = 6.3 Hz, 3H), 0.84 (t, J = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 135.0, 128.6, 126.9, 126.5, 114.4, 98.7, 68.5, 30.0, 28.5, 22.6, 22.5, 13.9.
HRMS (ESI) found 216.1506 (calculated for $C_{15}H_{20}O$ $[M]^+$: 216.1514.
IR (neat, cm^{-1}): 3384, 2959, 2929, 2873, 2858, 1952, 1598, 1496, 1460, 1377, 1216, 1081.

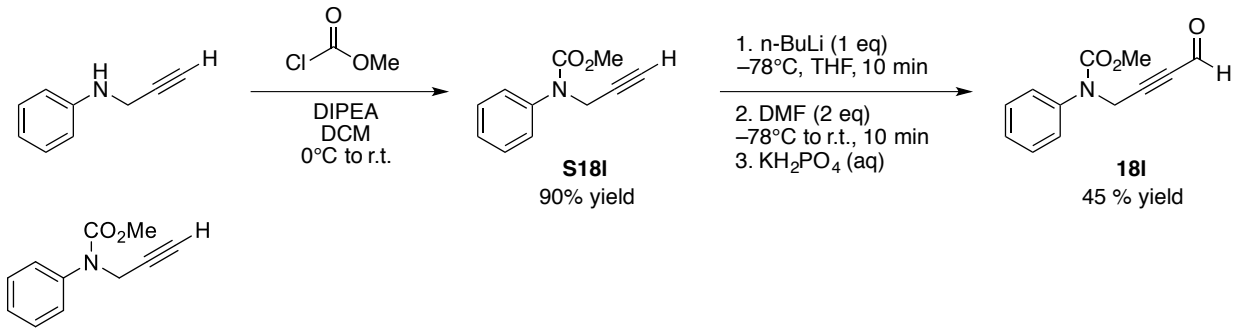
Carrying out the reaction under identical conditions with catalyst (*R*)-**10** afforded the title

compound (50 mg, 0.23 mmol, 58%, 9 : 1 d.r.) as a clear and colorless oil. Partial separation of the *syn*-**15e** isomer was not possible under the chromatography conditions. The following peaks are discernible:
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 (app q, J = 3.0 Hz, 1H), 4.27 (ddt, J = 10.0, 6.4, 3.2 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 135.1, 99.0, 68.5, 30.2, 29.1, 22.9, 21.2, 14.4.

m. Synthesis of Ynals (18)

Ynal **18a** was purchased from Santa Cruz biotechnology and used as received. **18b**,[22] **18c**,[22] **18d**,[23] **18e**,[24] **18f**,[25] **18g**,[26] **18h**,[27] **18i**,[28] **18j**,[29] **18k**,[30] **18m**,[30] **18n**[23] were synthesized following the disclosed literature procedure. Hept-2-ynal in Table 4 was also synthesized in the same manner.[23]

n. Synthesis of 18l

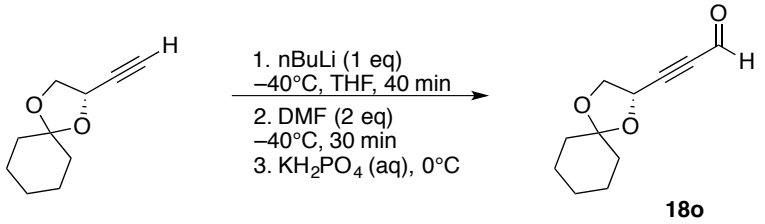


Methyl phenyl(prop-2-yn-1-yl)carbamate (S18l)
To the solution of *N*-(prop-2-yn-1-yl)aniline[31] (2.2 g, 17 mmol, 1.0 eq) in dichloromethane (35 ml) was added DIPEA (*N*,*N*-diisopropylethylamine) (4.4 ml, 1.5 eq) and methyl chloroformate (1.4 ml, 1.1 eq) at 0 °C. The reaction was allowed to warm up to room temperature and stir for overnight, after which moment the mixture was diluted with dichloromethane, washed with 1 M HCl solution and extracted with dichloromethane (3 X 100 ml). The combined organic layer was then washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered and concentrated to give a residue, which was purified by flash chromatography with hexanes/EtOAc (10:1) to afford methyl phenyl(prop-2-yn-1-yl)carbamate (**S18l**) as a light yellow liquid in 90% yield (2.9 g).
^{1}H NMR (500 MHz, $CDCl_3$) 7.40 – 7.28 (m, 4H), 7.30 – 7.22 (m, 1H), 4.39 (d, *J* = 2.5 Hz, 2H), 3.70 (s, 3H), 2.27 (t, *J* = 2.5 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 141.4, 129.0, 127.1, 126.7, 79.5, 72.3, 53.2, 40.2.

Methyl (4-oxobut-2-yn-1-yl)(phenyl)carbamate (18l)
Dry THF (25 ml) and methyl phenyl(prop-2-yn-1-yl)carbamate (**S18l**) (1.9 g, 10 mmol, 1.0 eq) were added to an oven dried nitrogen purged flask. The flask was cooled to –78 °C using a dry ice-acetone cold bath. Next, *n*-butyllithium (6.3 mL, 1.6 M in hexanes, 1.0 eq) was added dropwise to the flask and allowed to stir for 10 minutes at the same temperature. To the flask, dry

dimethylformamide (DMF) (1.5 mL, 2.0 eq) was then slowly added. The reaction temperature was allowed to warm to room temperature in 10 min. The reaction was then poured into a vigorously stiired biphasic solution prepared from a 10% aqueous solution of KH_2PO_4 (100 ml) and Et_2O (80 ml) at 0 °C. The organic layer was washed with water (2 X 100 ml). The combined aqueous layers were then extracted with Et_2O (200 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrate. The residue was purified by flash chromatography on silica gel using hexanes/EtOAc (8:1) to afford methyl (4-oxobut-2-yn-1-yl)(phenyl)carbamate (**18l**) in 45% yield (1.0 g) as a light yellow liquid.
^{1}H NMR (500 MHz, $CDCl_3$) 9.18 (s, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.24 (m, 3H), 4.61 (s, 2H), 3.73 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 155.5, 140.9, 129.3, 127.5, 126.7, 92.0, 83.3, 53.5, 40.6.

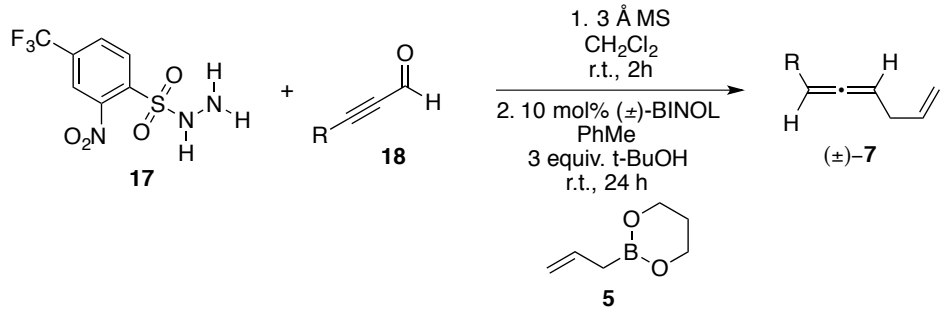
o. Synthesis of 18o



18o

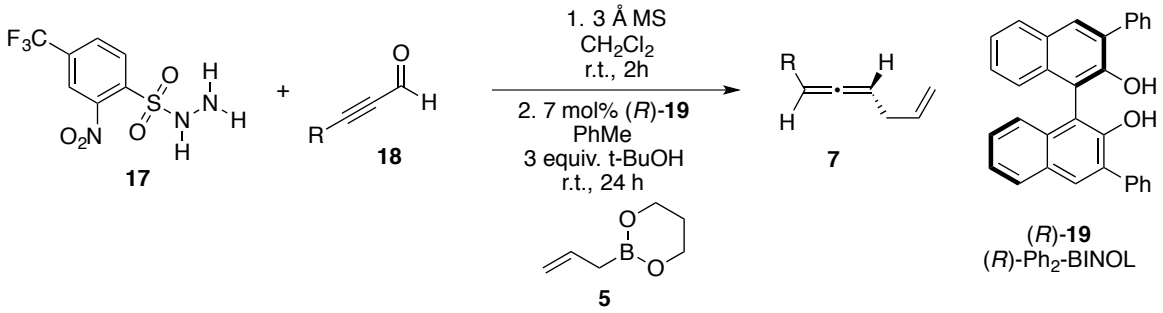
(*S*)-3-(1,4-dioxaspiro[4.5[decan-2-yl)propiolaldehyde (18o)
To a solution of (*S*)-2-ethynyl-1-4,-dioxaspiro[4.5]decane (1.00 g, 6.02 mmol, 1.0 eq) in dry THF (16.5 mL) at –40°C under N_2 atmosphere was added *n*-BuLi (2.4 mL, 6.02 mmol, 2.50 M in hexanes, 1.0 eq) dropwise over 3 minutes. The reaction was maintained at –40°C for 40 minutes, at which point *N,N*-dimethyl formamide (0.93 mL, 12.04 mmol, 2 eq) was added, and the reaction was allowed to stir at the same temperature for an additional 30 minutes. The solution was then poured into an Erlenmeyer flask containing a stirring mixture of KH_2PO_4 (0.90 g, 6.62 mmol, 1.1 eq), Et_2O (66 mL) and H_2O (66 mL) at 0°C. After stirring for 5 min at that temperature, the mixture was transferred to a separatory funnel with the aid of Et_2O and H_2O (10 mL each). The layers were separated, and the organic layer was washed with H_2O (30 mL), dried over anhydrous $MgSO_4$, and concentrated. The crude residue was purified by silica gel chromatography with hexanes/EtOAc (19:1) to afford the title compound (1.04 g, 5.35 mmol, 89%) as a pale yellow oil.
$[\alpha]_D^{22}$ = +48.5 (c = 1.1, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (d, J = 0.7 Hz, 1H), 4.89 (ddd, J = 6.5, 5.4 0.6 Hz, 1H), 4.22 (dd, J = 8.3, 6.6 Hz, 1H), 4.05 (dd, J = 8.3, 5.4 Hz, 1H), 1.69 – 1.58 (m, 8H), 1.47 – 1.35 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 112.0, 93.4, 83.9, 68.9, 64.7, 35.6, 35.1, 24.9, 23.8, 23.8.
ESI-HRMS found 194.0952 (calculated for $[C_{11}H_{14}O_3]^+$: 194.0943.)
IR (neat, cm^{-1}): 2935, 2861, 2262, 1713, 1449, 1366, 1333, 1160, 1094.

p. General Procedure for Racemic Allylation



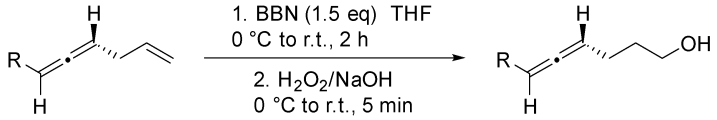
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide **17** (114 mg, 0.4 mmol), ynal **18** (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was 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 (17 mg, 0.06 mmol, 10 mol%), *tert*-butanol (89 mg, 1.2 mmol) and allylboronate **5**[32] (76 mg, 0.6 mmol) was 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 room temperature for 24 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

q. General Procedure for Asymmetric Allylation



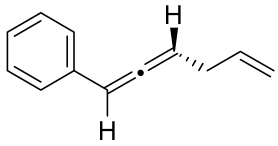
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide **17** (114 mg, 0.4 mmol), ynal **18** (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL oven dried reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture 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. (*R*)-Ph_2-BINOL catalyst **19** (18 mg, 0.04 mmol, 7 mol%), *tert*-butanol (89 mg, 1.2 mmol) and allylboronate **5** (76 mg, 0.6 mmol) was 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 room temperature for 24 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

r. General Procedure for Hydroboration/Oxidation

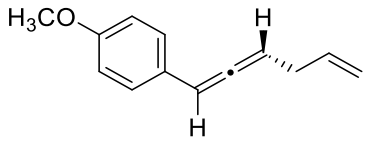


The allyl allene (0.3 mmol) was dissolved in dry THF (0.4 ml) under argon and cooled to 0 °C. 9-BBN (0.5 M in THF, 0.45 ml, 1.5 eq) was added dropwise to the reaction, and the reaction was allowed to warm up to room temperature naturally. After one hour, the reaction was cooled to 0 °C. 3 M NaOH solution (0.1 ml) was added slowly to the reaction, followed by dropwise addition of H_2O_2 (35% in water, 0.3 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 X 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.

s. Analytical Data for Allyl Allenes

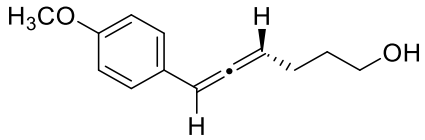


(*R*)-(Hexa-1,2,5-trien-1-yl)benzene (7a)
Prepared from the corresponding ynal **18a** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 52 mg, 83%
e.r.: 99:1
$[\alpha]_D^{22}$ = –227.6 (c = 1.0, $CHCl_3$). Absolute stereochemistry as assigned by Lowe's rule.[33]
HPLC Analysis, tr major: 6.1 min., tr minor: 6.7 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes, 1 mL/min, 250 nm].
All spectra were in agreement with reported data.[34]

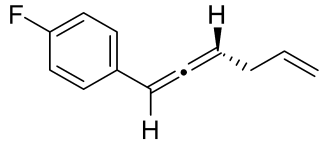


(*R*)-1-(Hexa-1,2,5-trien-1-yl)-4-methoxybenzene (7b)
Prepared from the corresponding ynal **18b** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (50:1) to afford the pure product as a colorless oil.
Yield: 66 mg, 88%
e.r.: 98:2
$[\alpha]_D^{22}$ = –248.7 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding alcohol **S7b** following the hydroboration/oxidation procedure, tr major: 21.9 min., tr minor: 33.0 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 97:3, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.13 (ddd, *J* = 6.0, 2.9, 2.9 Hz, 1H), 5.97 – 5.85 (m, 1H), 5.56 (ddd, *J* = 6.7, 6.7, 6.7 Hz, 1H), 5.15 (dddd, *J* = 17.1, 1.6, 1.6, 1.6 Hz, 1H), 5.05 (dddd, *J* = 10.2, 1.6, 1.5, 1.5 Hz, 1H), 3.80 (s, 3H), 2.91 – 2.85 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 158.6, 136.3, 127.7, 127.0, 115.5, 114.1, 94.4, 93.0, 55.3, 33.3.
GCMS found 186.1 (calculated for $C_{13}H_{14}O$: 186.1)
IR (thin film, cm^{-1}): 3072, 3005, 2935, 2836, 1608, 1511, 1303, 1172, 1035, 833.

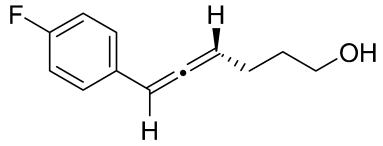


(*R*)-6-(4-Methoxyphenyl)-hexa-4,5-dien-1-ol (S7b)
S7b was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (5:1) to afford the pure product as a colorless oil.
Yield: 17 mg, 42%
e.r.: 98:2
$[\alpha]_D^{22}$ = –66.0 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.12 (ddd, *J* = 6.3, 3.1, 3.1 Hz, 1H), 5.58 (ddd, *J* = 6.5, 6.5, 6.5 Hz, 1H), 3.80 (s, 3H), 3.72 (t, *J* = 6.5 Hz, 2H), 2.21 (dddd, *J* = 12.8, 6.5, 3.1, 1.7 Hz, 2H), 1.76 (ddt, *J* = 9.5, 7.8, 6.5 Hz, 2H), 1.25 (br, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.5, 127.6, 127.1, 114.1, 113.9, 94.5, 94.3, 62.4, 55.3, 31.9, 25.1.
HRMS found 205.1239 (calculated for $[C_{13}H_{17}O_2]^+$: 205.1229)
IR (thin film, cm^{-1}): 3412, 2989, 2934, 2875, 1605, 1512, 1467, 1249, 1172, 1034, 836.

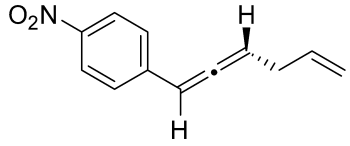


(*R*)-1-Fluoro-4-(hexa-1,2,5-trien-1-yl)benzene (7c)
Prepared from the corresponding ynal **18c** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (200:1) to afford the pure product as a colorless oil.
Yield: 61 mg, 87%
e.r.: 99:1
$[\alpha]_D^{22}$ = –246.6 (c = 1.0, $CHCl_3$).
HPLC Analysis, this compound was converted to the corresponding alcohol **S7c** following the hydroboration/oxidation procedure, tr major: 18.4 min., tr minor: 20.3 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1.0 mL/min, 254 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.03 – 6.94 (m, 2H), 6.14 (ddd, *J* = 6.2, 2.9, 2.9 Hz, 1H), 5.90 (dddd, *J* = 16.7, 10.2, 6.4, 6.4 Hz, 1H), 5.59 (ddd, *J* = 6.7, 6.7, 6.7 Hz, 1H), 5.15 (dddd, *J* = 17.0, 1.7, 1.7, 1.6 Hz, 1H), 5.06 (dddd, *J* = 10.2, 1.6, 1.5, 1.5 Hz, 1H), 2.92 – 2.85 (m, 2H).

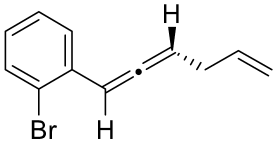
^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3 (d, *J* = 2.4 Hz), 162.8, 160.8, 136.0, 130.7 (d, *J* = 3.3 Hz), 128.0 (d, *J* = 7.8 Hz), 115.6 (d, *J* = 19.4 Hz), 115.5 (d, *J* = 21.7 Hz), 93.7 (d, *J* = 84.3 Hz), 33.1.
^{19}F NMR (470 MHz, $CDCl_3$) δ –115.7 (ddd, *J* = 14.2, 9.1, 5.6 Hz).
GCMS found 174.1 (calculated for $C_{12}H_{11}F$: 174.1)
IR (thin film, cm^{-1}): 3062, 2976, 2918, 1950, 1640, 1604, 1508, 1229, 1156, 837.



(*R*)-6-(4-Fluorophenyl)-hexa-4,5-dien-1-ol (S7c)
S7c 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 (4:1) to afford the pure product as a colorless oil.
Yield: 20 mg, 35%
$[\alpha]_D^{22}$ = –117.4 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.01 – 6.95 (m, 2H), 6.12 (ddd, *J* = 6.5, 3.1, 3.1 Hz, 1H), 5.61 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H), 3.76 – 3.67 (m, 2H), 2.22 (td, *J* = 7.2, 3.1 Hz, 2H), 1.81 – 1.70 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 162.8, 160.8, 130.8, 127.9 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.7 Hz), 94.4 (d, *J* = 68.0 Hz), 62.3, 31.8, 24.9.
^{19}F NMR (470 MHz, $CDCl_3$) δ –115.8 (ddd, *J* = 13.9, 8.9, 5.5 Hz).
ESI-MS found 175.1, 193.1 (calculated for $[C_{12}H_{14}FO]^+$: 193.1)
IR (thin film, cm^{-1}): 3360, 3045, 2937, 1951, 1604, 1508, 1226, 1156, 840.



(*R*)-1-(Hexa-1,2,5-trien-1-yl)-4-nitrobenzene (7d)
Prepared from the corresponding ynal **18d** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:1) to afford the pure product as a yellow oil.
Yield: 70 mg, 87%
e.r.: 98:2
$[\alpha]_D^{22}$ = –318.4 (c = 1.0, $CHCl_3$).
HPLC Analysis, tr minor: 14.8 min., tr major: 16.3 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 230 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.26 – 6.20 (m, 1H), 5.89 (dddd, *J* = 16.7, 10.2, 6.4, 6.4 Hz, 1H), 5.71 (ddd, *J* = 6.7, 6.7, 6.7 Hz, 1H), 5.17 (dddd, *J* = 17.1, 1.5, 1.4, 1.4 Hz, 1H), 5.09 (dddd, *J* = 10.1, 1.5, 1.4, 1.4 Hz, 1H), 2.96 – 2.89 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.4, 146.4, 142.2, 135.4, 127.0, 124.0, 116.2, 94.2, 32.6.
GCMS found 201.1 (calculated for $C_{12}H_{11}NO_2$: 201.1)
IR (thin film, cm^{-1}): 3078, 2979, 2843, 1949, 1640, 1595, 1516, 1494, 1342, 1110, 874.



(*R*)-1-Bromo-2-(hexa-1,2,5-trien-1-yl)benzene (7e)

Prepared from the corresponding ynal **18e** (0.26 mmol) and allyl boronate **5** (0.4 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:1) to afford the pure product as a colorless oil.

Yield: 35 mg, 60%

e.r.: 99:1

$[\alpha]_D^{22}$ = –148.4 (c = 1.0, $CHCl_3$).

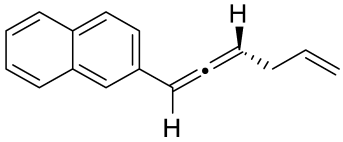
HPLC Analysis, tr major: 7.4 min., tr minor: 9.3 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes, 1 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.04 (ddd, *J* = 8.0, 7.7, 1.7 Hz, 1H), 6.62 (ddd, *J* = 6.4, 2.9, 2.9 Hz, 1H), 5.91 (dddd, *J* = 16.9, 10.1, 6.4, 6.4 Hz, 1H), 5.63 (ddd, *J* = 6.7, 6.4, 6.4 Hz, 1H), 5.17 (dddd, *J* = 16.9, 1.7, 1.7, 1.6 Hz, 1H), 5.08 (dddd, *J* = 10.1, 1.6, 1.4, 1.4 Hz, 1H), 2.96 – 2.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.5, 135.9, 134.2, 132.9, 128.3, 128.1, 127.4, 122.4, 115.8, 94.1, 93.3, 32.9.

GCMS found 234.1, 236.1 (calculated for $C_{12}H_{11}Br$: 234.0)

IR (thin film, cm^{-1}): 3078, 2928, 1953, 1600, 1563, 1474, 1439, 1022, 917.



(*R*)-2-(-Hexa-1,2,5-trien-1-yl)naphthalene (7f)

Prepared from the corresponding ynal **18f** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 73 mg, 89%

e.r.: 98:2

$[\alpha]_D^{22}$ = –236.4 (c = 1.0, $CHCl_3$).

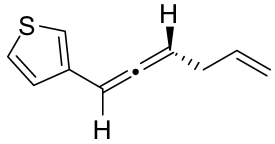
HPLC Analysis, tr major: 16.1 min., tr minor: 16.9 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes, 1.0 mL/min, 250 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 3H), 7.66 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.49 – 7.39 (m, 2H), 6.36 (ddd, *J* = 6.1, 2.9, 2.9 Hz, 1H), 5.95 (dddd, *J* = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.67 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H), 5.20 (dddd, *J* = 17.1, 1.7, 1.7, 1.6 Hz, 1H), 5.09 (dddd, *J* = 10.1, 1.6, 1.5, 1.5 Hz, 1H), 2.98 – 2.91 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.1, 136.1, 133.7, 132.6, 132.3, 128.2, 127.7, 127.7, 126.2, 125.5, 125.4, 124.6, 115.7, 95.4, 93.4, 33.2.

GCMS found 206.1 (calculated for $C_{16}H_{14}$: 206.1)

IR (thin film, cm^{-1}): 3056, 2978, 1947, 1639, 1599, 1509, 895, 819, 754.



(*R*)-3-(-Hexa-1,2,5-trien-1-yl)thiophene (7g)

Prepared from the corresponding ynal **18g** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 56 mg, 87%

e.r.: 99:1

$[\alpha]_D^{22}$ = –267.4 (c = 1.0, $CHCl_3$).

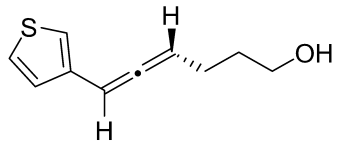
HPLC Analysis, this compound was converted to the corresponding alcohol **S7g** following the hydroboration/oxidation procedure, tr major: 44.6 min., tr minor: 50.0 min., [Chiralpak® AD-H column, 24 cm × 4.6 mm I.D., Hexanes: EtOH=99:1, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.09 – 7.04 (m, 2H), 6.24 (ddd, *J* = 6.1, 2.7, 2.7 Hz, 1H), 5.90 (dddd, *J* = 16.6, 10.9, 6.5, 6.5 Hz, 1H), 5.52 (ddd, *J* = 6.7, 6.7, 6.7 Hz, 1H), 5.15 (dd, *J* = 17.2, 2.2 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 2.91 – 2.84 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.8, 136.2, 136.1, 126.3, 125.8, 120.4, 115.6, 92.3, 89.6, 33.2.

GCMS found 162.1 (calculated for $C_{10}H_{10}S$: 162.1)

IR (thin film, cm^{-1}): 3079, 2978, 2911, 1952, 1791, 1639, 1435, 1258, 993, 787.



(*R*)-6-(Thiophen-3-yl)-hexa-4,5-dien-1-ol (S7g)

S7g 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 (5:1) to afford the pure product as a colorless oil.

Yield: 32 mg, 59%

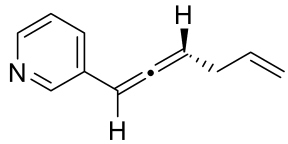
$[\alpha]_D^{22}$ = –183.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.08 – 7.03 (m, 2H), 6.22 (ddd, *J* = 6.3, 3.1, 3.1 Hz, 1H), 5.54 (ddd, *J* = 6.5, 6.5, 6.5 Hz, 1H), 3.71 (t, *J* = 6.5 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.80 – 1.70 (m, 2H), 1.39 (br, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.4, 136.2, 126.2, 125.8, 120.4, 93.6, 89.7, 62.3, 31.8, 25.0.

ESI-MS found 181.1 (calculated for $[C_{10}H_{13}OS]^+$: 181.1)

IR (thin film, cm^{-1}): 3463, 3056, 2944, 1951, 1057, 788.



(*R*)-3-(Hexa-1,2,5-trien-1-yl)pyridine (7h)

2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide **17** (114 mg, 0.4 mmol), 3-(pyridin-3-yl)propiolaldehyde **18h** (52 mg, 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 (0.5

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 catalyst **19** (36 mg, 0.08 mmol, 7 mol%), *tert*-butanol (89 mg, 1.2 mmol) and allylboronate **5** (152 mg, 1.2 mmol) was 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 room temperature for 24 h, at which time the crude mixture was chromatographed on silica gel with hexanes/EtOAc (50:1) to afford the pure product as a brown oil.

Yield: 17 mg, 27%.

e.r.: 98:2

$[\alpha]_D^{22}$ = –222.4 (c = 1.0, $CHCl_3$).

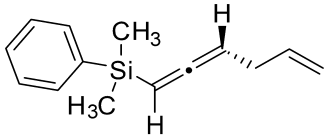
HPLC Analysis, tr minor: 11.0 min., tr major: 11.5 min., [Chiralpak®IA-H column, 24 cm × 4.6 mm I.D., Hexanes:EtOH=99:1, 1 mL/min, 250 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.41 (d, *J* = 4.6 Hz, 1H), 7.58 (ddd, *J* = 7.9, 1.9, 1.9 Hz, 1H), 7.21 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.14 (ddd, *J* = 6.1, 2.9, 2.9 Hz, 1H), 5.89 (dddd, *J* = 16.7, 10.1, 6.4, 6.4 Hz, 1H), 5.65 (ddd, *J* = 6.8, 6.8, 6.8 Hz, 1H), 5.15 (dddd, *J* = 17.0, 1.6, 1,6, 1.5 Hz, 1H), 5.07 (dddd, *J* = 10.1, 1.5, 1.4, 1.4 Hz, 1H), 2.93 – 2.87 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.0, 148.2, 147.9, 135.7, 133.4, 130.7, 123.4, 116.0, 93.9, 91.8, 32.8.

HRMS found 158.0979 (calculated for $[C_{11}H_{12}N]^+$: 158.0970)

IR (thin film, cm^{-1}): 3057, 2982, 1951, 1640, 1571, 1481, 1431, 1025, 916, 810, 748.



(*R*)-(Hexa-1,2,5-trien-1-yl)dimethyl(phenyl)silane (7i)

Prepared from the corresponding ynal **18i** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 62 mg, 73%

e.r.: 98:2

$[\alpha]_D^{22}$ = –50.0 (c = 1.0, $CHCl_3$).

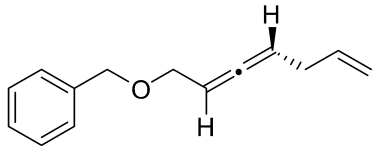
HPLC Analysis, tr major: 9.9 min., tr minor: 10.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes, 0.5 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.40 – 7.32 (m, 3H), 5.82 (dddd, *J* = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.13 – 5.03 (m, 2H), 5.00 (dddd, *J* = 10.1, 1.5, 1.5, 1.5 Hz, 1H), 4.86 (ddd, *J* = 6.9, 6.9, 6.9 Hz, 1H), 2.77 – 2.71 (m, 2H), 0.38 – 0.34 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 138.5, 136.9, 133.7, 129.1, 127.7, 115.0, 82.1, 81.5, 32.3, -2.2, -2.3.

GCMS found 214.1 (calculated for $C_{14}H_{18}Si$: 214.1).

IR (thin film, cm^{-1}): 3069, 3001, 2961, 2905, 1940, 1642, 1428, 1249, 1114, 816.



(*R*)-(((Hepta-2,3,6-trien-1-yl)oxy)methyl)benzene (7j)

Prepared from the corresponding ynal **18j** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (50:1) to afford the pure product as a colorless oil.

Yield: 72 mg, 90%

e.r.: 98:2

$[\alpha]_D^{22}$ = –58.6 (c = 1.0, $CHCl_3$).

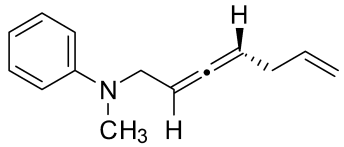
HPLC Analysis, tr major: 14.9 min., tr minor: 15.8 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 0.8 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.34 – 7.27 (m, 1H), 5.87 (dddd, *J* = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.35 – 5.21 (m, 2H), 5.12 (dddd, *J* = 17.1, 1.7, 1.7, 1.6 Hz, 1H), 5.06 (dddd, *J* = 10.1, 1.6, 1.5, 1.5 Hz, 1H), 4.55 (d, *J* = 2.2 Hz, 2H), 4.13 – 4.02 (m, 2H), 2.84 – 2.79 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.4, 138.2, 136.2, 128.4, 127.8, 127.6, 115.5, 90.0, 88.9, 71.6, 68.4, 32.9.

GCMS found 200.1 (calculated for $C_{14}H_{16}O$: 200.1)

IR (thin film, cm^{-1}): 3064, 3030, 2978, 2857, 1964, 1640, 1496, 1454, 1351, 1095, 1029, 915, 736.



(*R*)-*N*-(Hepta-2,3,6-trien-1-yl)-*N*-methylaniline (7k)

Prepared from the corresponding ynal **18k** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure, but for 40 hours. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:5) to afford the pure product as a brown oil.

Yield: 40 mg, 50%

e.r.: 99:1

$[\alpha]_D^{22}$ = +3.5 (c = 1.0, $CHCl_3$).

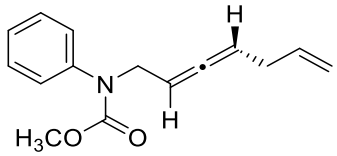
HPLC Analysis, tr minor: 8.8 min., tr major: 9.2 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes, 1.0 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 5.77 (dddd, *J* = 16.7, 10.1, 6.4, 6.4 Hz, 1H), 5.19 – 5.11 (m, 2H), 5.10 – 4.94 (m, 2H), 4.05 – 3.87 (m, 2H), 2.95 (s, 3H), 2.73 – 2.67 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.0, 149.1, 136.3, 129.0, 116.6, 115.3, 112.9, 90.4, 87.2, 51.9, 38.1, 33.1.

HRMS found 200.1433 (calculated for $[C_{14}H_{18}N]^+$: 200.1439)

IR (thin film, cm^{-1}): 3006, 2979, 2908, 1965, 1600, 1506, 1342, 748.



(*R*)-Methyl(hepta-2,3,6-trien-1-yl)(phenyl)carbamate (7l)

Prepared from the corresponding ynal **18l** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure, but for 40 hours. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:5) to afford the pure product as a colorless oil.

Yield: 83 mg, 85%

e.r.: 99:1

$[\alpha]_D^{22}$ = –23.2 (c = 1.0, $CHCl_3$).

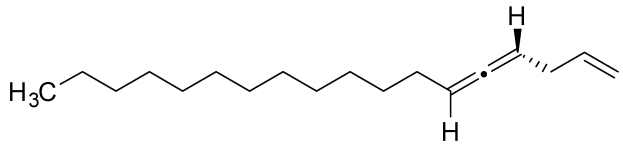
HPLC Analysis, tr major: 45.5 min., tr minor: 49.7 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 5.71 (dddd, *J* = 16.9, 10.1, 6.4, 6.4 Hz, 1H), 5.27 – 5.21 (m, 1H), 5.17 (ddddd, *J* = 6.6, 6.6, 6.6, 2.6, 2.6 Hz, 1H), 5.02 (dddd, *J* = 16.9, 1.7, 1.7, 1.6 Hz, 1H), 4.97 (dddd, *J* = 10.1, 1.6, 1.5, 1.5 Hz, 1H), 4.33 (ddd, *J* = 15.2, 5.9, 2.8 Hz, 1H), 4.16 (ddd, *J* = 15.2, 6.5, 2.5 Hz, 1H), 2.68 – 2.63 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 155.8, 136.1, 128.8, 126.9, 126.5, 115.4, 110.0, 91.0, 88.3, 52.9, 49.9, 32.9.

HRMS found 244.1338 (calculated for $[C_{15}H_{18}NO_2]^+$: 244.1331)

IR (thin film, cm^{-1}): 3292, 2958, 1700, 1596, 1497, 1446, 1381, 1280, 1218.



(*R*)-Octadeca-1,4,5-triene (7m)

Prepared from the corresponding ynal **18m** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 97 mg, 98%

e.r.: 98:2

$[\alpha]_D^{22}$ = –39.5 (c = 1.0, $CHCl_3$).

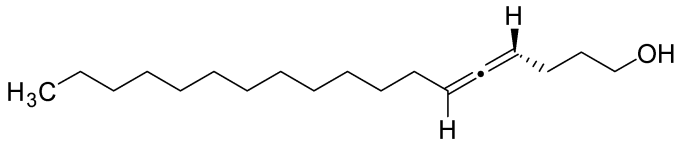
HPLC Analysis, this compound was converted to the corresponding alcohol **S7m** following the hydroboration/oxidation procedure, tr minor: 28.3 min., tr major: 30.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (dddd, *J* = 16.7, 10.5, 6.3, 6.3 Hz, 1H), 5.16 – 5.03 (m, 3H), 5.01 (ddd, *J* = 10.3, 1.7, 1.7 Hz, 1H), 2.77 – 2.71 (m, 2H), 2.02 – 1.92 (m, 2H), 1.43 – 1.36 (m, 2H), 1.36– 1.18 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.2, 136.8, 115.0, 91.4, 88.9, 33.5, 31.9, 29.7, 29.7, 29.7, 29.5, 29.4, 29.1, 29.1, 28.8, 22.7, 14.1.

GCMS found 248.3 (calculated for $C_{18}H_{32}$: 248.3)

IR (thin film, cm^{-1}): 3082, 2956, 2854, 1963, 1641, 1467, 1261, 991, 912, 870.



(*R*)-Octadeca-4,5-dien-1-ol (S7m)

S7m 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 (100:10) to afford the pure product as a colorless oil.

Yield: 58 mg, 72%

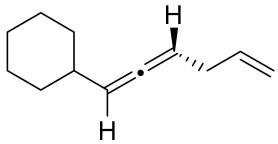
$[\alpha]_D^{22}$ = –41.2 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 – 5.06 (m, 2H), 3.69 (dt, *J* = 6.1, 6.1 Hz, 2H), 2.11 – 2.04 (m, 2H), 2.02 – 1.91 (m, 2H), 1.69 (tt, *J* = 6.9, 6.9 Hz, 1H), 1.41 – 1.35 (m, 2H), 1.26 (m, 18H), 1.35 – 1.15 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 91.6, 90.1, 62.4, 32.0, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 25.2, 22.7, 14.1.

ESIMS found 267.3 (calculated for $[C_{18}H_{35}O]^+$: 267.3)

IR (thin film, cm^{-1}): 2952, 2924, 2854, 2200, 1964, 1467, 1059, 883.



(*R*)-(Hexa-1,2,5-trien-1-yl)cyclohexane (7n)

Prepared from the corresponding ynal **18n** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 40 mg, 62%

e.r.: 99:1

$[\alpha]_D^{22}$ = –57.0 (c = 1.0, $CHCl_3$).

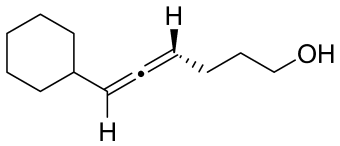
HPLC Analysis, this compound was converted to the corresponding alcohol **S7n** following the hydroboration/oxidation procedure, tr minor: 40.4 min., tr major: 53.8 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (dddd, *J* = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.16 – 5.03 (m, 3H), 5.00 (dddd, *J* = 10.1, 1.5, 1.5, 1.5 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.00 – 1.90 (m, 1H), 1.74 – 1.57 (m, 4H), 1.33 – 1.06 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 136.8, 115.0, 97.5, 89.8, 37.1, 33.6, 33.1, 33.0, 26.2, 26.0, 26.0.

GCMS found 162.1 (calculated for $C_{12}H_{18}$: 162.1)

IR (thin film, cm^{-1}): 3078, 2925, 2853, 1960, 1640, 1449, 1261, 992, 913, 761.



(*R*)-6-Cyclohexyl-hexa-4,5-dien-1-ol (S7n)

S7n 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 (100:10) to afford the pure product as a colorless oil.

Yield: 27 mg, 59%

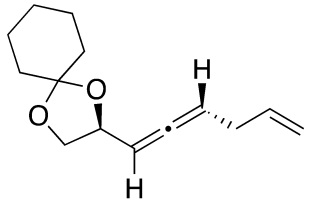
$[\alpha]_D^{22}$ = –37.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.05 – 5.29 (m, 2H), 3.68 (tt, *J* = 6.3, 2.9 Hz, 2H), 2.06 (tdd, *J* = 6.8, 5.4, 2.0 Hz, 2H), 1.94 (m, 1H), 1.75 – 1.60 (m, 8H), 1.21 – 1.10 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 97.6, 91.1, 62.4, 37.2, 33.1, 33.1, 32.0, 26.2, 26.0, 25.3.

ESIMS found 181.2 (calculated for $[C_{12}H_{21}O]^+$: 181.2)

IR (thin film, cm^{-1}): 2923, 2850, 1469, 1053.



***(S)*-2-((*R*)-Hexa-1,2-5-trien-1-yl)-1,4-dioxaspiro[4.5]decane (7o)**

Prepared from the corresponding ynal **18o** (0.4 mmol) and allyl boronate **5** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a pale yellow oil.

Yield: 70 mg, 79%

e.r.: 98:2

$[\alpha]_D^{22}$ = +69.0 (c = 1.0, $CHCl_3$).

HPLC Analysis tr major: 4.25 min., tr minor: 6.69 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 99.0 : 1.0, 1.0 mL/min, 250 nm].

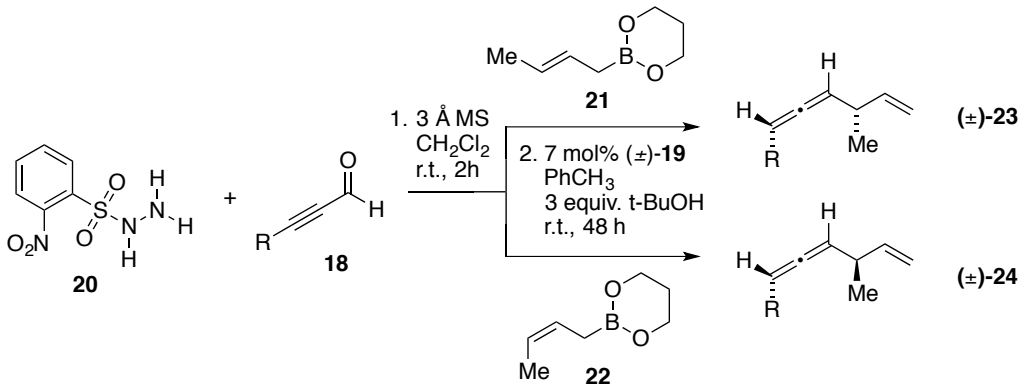
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.31 (qd, J = 6.8, 1.4 Hz, 1H), 5.21 (ddt, J = 7.5, 6.0, 2.9 Hz, 1H), 5.08 (dq, J = 17.1, 1.7 Hz, 1H), 5.03 (dq, J = 10.1, 1.5 Hz, 1H), 4.55 (tdd, J = 7.4, 6.1, 1.4 Hz, 1H), 4.09 (dd, J = 8.2, 6.1 Hz, 1H) 3.69 (dd, J = 8.2, 7.0 Hz, 1H), 2.76 (tdt, J = 6.6, 2.9, 1.5 Hz, 2H), 1.68 – 1.55 (m, 8H), 1.45 – 1.34 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 135.9, 115.6, 110.0, 91.5, 91.4, 74.4, 69.3, 36.4, 35.4, 32.7, 25.1, 23.9, 23.9.

HRMS (EI) found 221.1467 (calculated for $C_{14}H_{20}O_2$ $[M+H]^+$ 221.1463)

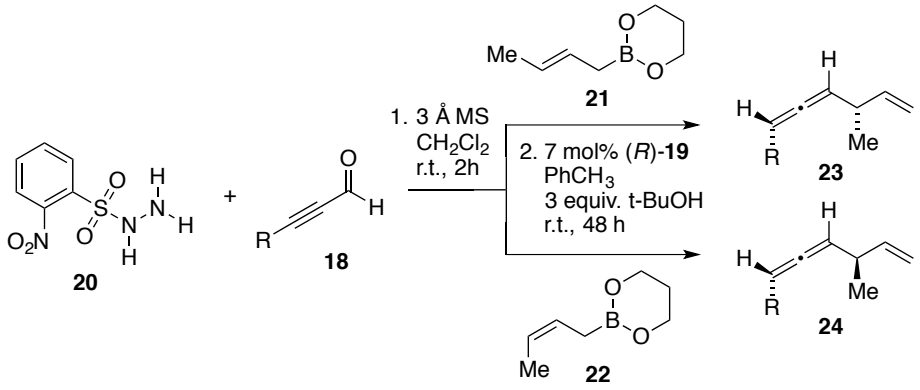
IR (thin film, cm^{-1}): 2936, 2862, 2002, 1586, 1586, 1448, 1366, 1278, 1162, 1099, 1041.

t. General Procedure for Racemic Crotylations



2-Nitrobenzenesulfonohydrazide **20** (87 mg, 0.4 mmol), ynal **18** (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 Ph_2-BINOL catalyst **19** (18 mg, 0.04 mmol, 7 mol%), *tert*-butanol (89 mg, 1.2 mmol) and crotylboronate[32] **21** or **22** (84 mg, 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 room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

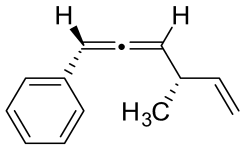
u. General Procedure for Asymmetric Crotylations



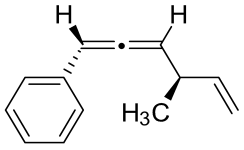
2-Nitrobenzenesulfonohydrazide **20** (87 mg, 0.4 mmol), ynal **18** (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature 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. (*R*)-Ph_2-BINOL catalyst **19** (18 mg, 0.04 mmol, 7 mol%), *tert*-butanol (89 mg, 1.2 mmol) and crotylboronate **21** or **22** (84 mg, 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 room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to

afford the desired product.

v. Analytical Data for Crotyl Allenes

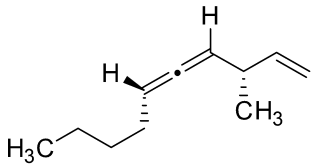


(R_a, *S*)-(4-Methyl-hexa-1,2,5-trien-1-yl)benzene (23a)
Prepared from the corresponding ynal **18a** (0.4 mmol) and crotyl boronate **21** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 53 mg, 78%
e.r.: 98:2. **d.r.**: >20:1.
$[\alpha]_D^{22}$ = –163.4 (c = 1.0, $CHCl_3$).
HPLC Analysis, tr major: 6.2 min., tr minor: 6.6 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 800:1, 1.0 mL/min, 254 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 4H), 7.23 – 7.17 (m, 1H), 6.23 (dd, *J* = 6.4, 2.9 Hz, 1H), 5.90 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.62 (dd, *J* = 6.4, 6.3 Hz, 1H), 5.13 (ddd, *J* = 17.2, 1.5, 1.4 Hz, 1H), 5.03 (ddd, *J* = 10.2, 1.4, 1.3 Hz, 1H), 3.07 – 2.97 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3, 142.4, 134.9, 128.6, 126.8, 126.5, 113.3, 99.5, 96.0, 37.5, 19.8.
GCMS found 170.1 (calculated for $C_{13}H_{14}$: 170.1)
IR (thin film, cm^{-1}): 3084, 3030, 2970, 2930, 1950, 1495, 1458, 915, 776.



(R_a, *R*)-(4-Methyl-hexa-1,2,5-trien-1-yl)benzene (24a)
Prepared from the corresponding ynal **18a** (0.4 mmol) and crotyl boronate **22** (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 36 mg, 53%
e.r.: 98:2
$[\alpha]_D^{22}$ = –120.8 (c = 1.0, $CHCl_3$).
HPLC Analysis, tr major: 27.7 min., tr minor: 30.0 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 800:1, 0.2 mL/min, 254 nm].
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 6.23 (dd, *J* = 6.4, 2.8 Hz, 1H), 5.90 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.62 (dd, *J* = 6.4, 6.3 Hz, 1H), 5.14 (ddd, *J* = 17.1, 1.5, 1.5 Hz, 1H), 5.03 (ddd, *J* = 10.2, 1.3, 1.3 Hz, 1H), 3.11 – 2.97 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3, 142.4, 134.9, 128.6, 126.8, 126.6, 113.3, 99.5, 96.0, 37.5, 19.8.
GCMS found 170.1 (calculated for $C_{13}H_{14}$: 170.1)

IR (thin film, cm^{-1}): 3065, 3032, 2973, 1726, 1495, 1262, 919, 698.



(R_a, *S*)-3-Methyl-deca-1,4,5-triene (23b)

Prepared from the corresponding ynal **36** (0.5 mmol) and crotyl boronate **21** (0.75 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 57 mg, 76%

e.r.: 99:1

$[\alpha]_D^{22}$ = +34.1 (c = 1.0, $CHCl_3$).

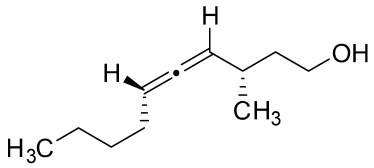
HPLC Analysis, this compound was converted to the corresponding alcohol **23bS1** following the hydroboration/oxidation procedure, tr major: 28.3 min., tr minor: 33.7 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.18 (dddd, *J* = 6.5, 6.5, 6.4, 2.9 Hz, 1H), 5.10 (dddd, *J* = 6.4, 6.2, 3.0, 3.0 Hz, 1H), 5.04 (ddd, *J* = 17.1, 1.7, 1.6 Hz, 1H), 4.96 (ddd, *J* = 10.2, 1.7, 1.1 Hz, 1H), 2.90 – 2.78 (m, 1H), 2.00 (dtd, *J* = 7.4, 6.6, 3.0 Hz, 2H), 1.45 – 1.30 (m, 4H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.95 – 0.85 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 143.0, 112.6, 95.4, 92.5, 37.3, 31.3, 28.6, 22.2, 19.7, 13.9.

GCMS found 150.1 (calculated for $C_{11}H_{18}$: 150.1)

IR (thin film, cm^{-1}): 2960, 2872, 1683, 1590, 1456, 917, 875.



(R_a, *S*)-3-Methyl-deca-4,5-dien-1-ol (23bS1)

The substrate was run in 0.2 mmol scale following the hydroboration/oxidation procedure and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (8:1) to afford the pure product as a colorless oil.

Yield: 19 mg, 56%

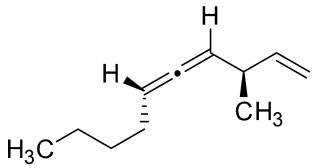
$[\alpha]_D^{22}$ = –15.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (dddd, *J* = 6.6, 6.6, 6.5, 2.5 Hz, 1H), 5.04 (dddd, *J* = 6.4, 6.3, 3.0, 3.0 Hz, 1H), 3.70 (t, *J* = 6.5 Hz, 2H), 2.33 – 2.23 (m, 1H), 2.02 – 1.94 (m, 2H), 1.64 – 1.55 (m, 2H), 1.40 – 1.31 (m, 4H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 96.4, 92.1, 61.2, 39.8, 31.3, 30.4, 28.7, 22.2, 20.7, 13.9.

HRMS found 169.1593 (calculated for $[C_{11}H_{21}O]^+$: 169.1592)

IR (thin film, cm^{-1}): 3370,2958, 2929, 2871, 1459, 1369, 1261. 1203, 1170, 1049, 874, 834, 755.



(R_a, *R*)-3-Methyl-deca-1,4,5-triene (24b)

Prepared from the corresponding ynal **36** (1.0 mmol) and crotyl boronate **22** (1.5 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 100 mg, 67%

e.r.: 99:1

$[\alpha]_D^{22}$ = –124.4 (c = 1.0, $CHCl_3$).

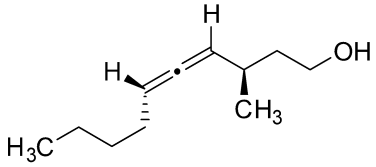
HPLC Analysis, this compound was converted to the corresponding alcohol **37** following the hydroboration/oxidation procedure, tr major: 32.3 min., tr minor: 39.7 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =99.9:0.1, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.2, 10.2, 6.7 Hz, 1H), 5.17 (dddd, *J* = 6.5, 6.5, 6.5, 2.8 Hz, 1H), 5.13 – 5.08 (m, 1H), 5.04 (ddd, *J* = 17.2, 1.7, 1.6 Hz, 1H), 4.96 (ddd, *J* = 10.2, 1.7, 1.2 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.04 –1.97 (m, 2H), 1.48 – 1.29 (m, 4H), 1.11 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 142.9, 112.6, 95.3, 92.5, 37.2, 31.3, 28.6, 22.1, 19.7, 13.9.

GCMS found 150.1 (calculated for $C_{11}H_{18}$: 150.1)

IR (thin film, cm^{-1}): 2959, 2928, 2872, 1683, 1590, 1456, 917, 875, 760.



(R_a, *R*)-3-Methyl-deca-4,5-dien-1-ol (37)

The substrate was run in 0.67 mmol scale following the general procedure of hydroboration/oxidation and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

Yield: 70 mg, 62%

$[\alpha]_D^{22}$ = –71.0 (c = 1.0, $CHCl_3$).

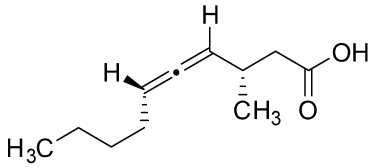
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 (dddd, *J* = 6.6, 6.6, 6.6, 2.4 Hz, 1H), 5.05 (dt, *J* = 6.5, 3.1 Hz, 1H), 3.71 (td, *J* = 6.4, 3.5 Hz, 2H), 2.33 – 2.22 (m, 1H), 2.03 – 1.94 (m, 2H), 1.63 – 1.55 (m, 2H), 1.42 – 1.31 (m, 4H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 96.4, 92.2, 61.3, 39.7, 31.4, 30.5, 28.8, 22.2, 20.8, 13.9.

HRMS found 169.1586 (calculated for $[C_{11}H_{21}O]^+$: 169.1592)

IR (thin film, cm^{-1}): 3353, 2958, 2929, 2872, 1961, 1457, 1053.

w. Stereochemistry Determination of Crotyl Allenes



(*R*$_a$, *S*)-3-Methyldeca-4,5-dienoic acid (23bS2)

(*R*$_a$, *S*)-3-methyl-deca-4,5-dien-1-ol (**23bS1**) (73 mg, 0.4 mmol) was dissolved in 3 ml acetone and cooled to –20 °C. Jones reagent (2.5 equiv), prepared from CrO_3 (100 mg, 1.0 mmol), concentrated H_2SO_4 (0.09 ml, 1.6 mmol), and water (0.4 ml), was added slowly to the reaction and the reaction was allowed to warm to 0 °C in 2 h before quenched by addition of 1 ml *i*-PrOH, and the mixture was filtered and concentrated down to 1 ml. The residue was then purified by flash column chromatography with hexanes:EtOAc (8:1) to afford the pure product as a colorless oil.

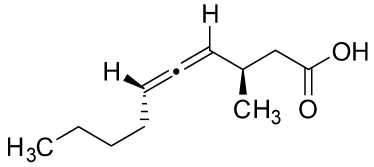
Yield: 39 mg, 53%

$[\alpha]_D^{22}$ = –50.9 (c = 1.0, $CHCl_3$). In lit:[35] its enantiomer (*S*$_a$, *R*)-3-methyldeca-4,5-dienoic acid **$[\alpha]_D^{22}$** = +45 (c = 1.0, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 – 5.11 (m, 2H), 2.71 – 2.61 (m, 1H), 2.46 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.30 (dd, *J* = 15.6, 7.4 Hz, 1H), 2.02 – 1.93 (m, 2H), 1.41 – 1.28 (m, 4H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.4, 178.2, 95.5, 93.4, 40.9, 31.3, 29.7, 28.6, 22.2, 20.2, 13.9.

Analytical data for this compound matched that of the previously reported values and therefore confirmed the stereochemistry.[35]



(*R*$_a$, *R*)-3-Methyldeca-4,5-dienoic acid (38)

(*R*$_a$, *R*)- 3-Methyl-deca-4,5-dien-1-ol (**37**) (73 mg, 0.4 mmol) was dissolved in 3 ml acetone and cooled to 0 °C. Jones reagent (2.5 equiv), prepared from CrO_3 (100 mg, 1.0 mmol), concentrated H_2SO_4 (0.09 ml, 1.6 mmol), and water (0.4 ml), was added slowly to the reaction and the reaction remained at the same temperature for 2 h before quenched by addition of 1 ml *i*-PrOH, and the mixture was filtered and concentrated down to 1 ml. The residue was then purified by flash column chromatography with hexanes:EtOAc (8:1) to afford the pure product as a colorless oil.

Yield: 41 mg, 56%

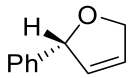
$[\alpha]_D^{22}$ = –80.5 (c = 1.34, $CHCl_3$). In lit:[35] **$[\alpha]_D^{22}$** = –74.9 (c = 1.34, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24 – 5.08 (m, 2H), 2.71 – 2.58 (m, 1H), 2.45 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.29 (dd, *J* = 15.6, 7.4 Hz, 1H), 2.02 – 1.94 (m, 2H), 1.43 – 1.28 (m, 4H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.4, 177.5, 95.5, 93.4, 40.8, 31.3, 29.8, 28.6, 22.2, 20.3, 13.9.

Analytical data for this compound matched that of the previously reported values and therefore confirmed the stereochemistry.[35]

x. Cyclization of Enantioenriched Allenols



(*R*)-2-Phenyl-2,5-dihydrofuran (25)

(*S*)-4-Phenylbuta-2,3-dien-1-ol (**6a**) (44 mg, 0.3 mmol, 92:8 e.r.) was dissolved in 3 ml hot pentane. Silver nitrate on silica gel (51 mg, 10% wt, 0.1 eq) was added in and the reaction flask was wrapped with aluminum foil and allowed to stir for 26 hours at room temperature. After the allenol was consumed (as monitored by TLC), the reaction mixture was subjected directly to column chromatography on silica gel eluting with hexanes to afford the cyclized product **25** as a colorless oil.

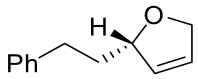
Yield: 35 mg, 79%.

e.r.: 92:8.

$[\alpha]_D^{22}$ = +111.8 (c = 0.42, $CHCl_3$). In lit[36]: $[\alpha]_D^{22}$ = +248 (c = 0.59, $CHCl_3$, 93% ee).

HPLC Analysis, tr minor: 12.9 min., tr major: 17.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 99.95:0.05, 1.0 mL/min, 210 nm].

All spectra were in agreement with reported data.[37]



(*S*)-2-Phenethyl-2,5-dihydrofuran (26)

(*S*)-6-Phenylhexa-2,3-dien-1-ol (**6g**) (52 mg, 0.3 mmol, 92:8 e.r.) was dissolved in a mixture of acetone/water (1.2 ml/0.8 ml). Silver nitrate (10 mg, 0.2 eq) was added in and the reaction flask was wrapped with aluminum foil and allowed to stir for 48 hours at room temperature. After the allenol was consumed (as monitored by TLC), the solvent was removed under reduced pressure and the crude reaction mixture was subjected to column chromatography using hexanes to give cyclized product **26** as a colorless oil.

Yield: 35 mg, 67%.

e.r.: 92:8.

$[\alpha]_D^{22}$ = +74.6 (c = 1.0, $CHCl_3$).

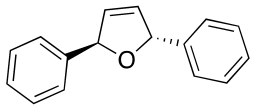
HPLC Analysis, tr minor: 11.5 min., tr major: 12.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 99.9:0.1, 0.8 mL/min, 254 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 2H), 7.24 – 7.09 (m, 3H), 5.91 (ddt, *J* = 6.0, 1.8, 1.8 Hz, 1H), 5.79 (dtd, *J* = 6.0, 2.4, 1.4 Hz, 1H), 4.90 – 4.83 (m, 1H), 4.76 – 4.57 (m, 2H), 2.78 – 2.61 (m, 2H), 1.95 – 1.79 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 129.5, 128.4, 128.3, 126.7, 125.7, 85.4, 75.1, 37.7, 31.5.

ESIMS found 175.1 (calculated for $[C_{12}H_{15}O]^+$: 175.1)

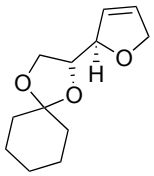
IR (thin film, cm^{-1}): 3081, 3061, 3027, 2924, 2848, 1603, 1496, 1454, 1354, 1079, 1018.



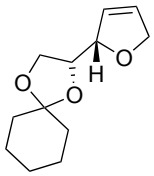
(2*R*, 5*R*)-2,5-Piphenyl-2,5-dihydrofuran (S19)

To a solution of $AuCl_3$ (0.6 mg, 0.0020 mmol) in THF (0.5 mL) in a flame-dried vial equipped with a magnetic stir bar was added a solution of the allenol (*anti*-**15a**) (33 mg, 0.15 mmol) in THF (1 mL) via cannula, followed by a 1 mL rinse. The reaction was allowed to stir at r.t. for 4 h,

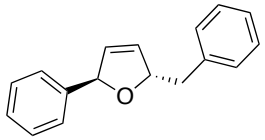
at which time TLC indicated full consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with hexanes (39 : 1) to afford the title compound as a pale yellow oil.
Yield: 23 mg, 70%.
$[\alpha]_D^{22}$ = +382.2 (c = 0.48, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 7H), 7.20 – 7.05 (m, 3H), 5.93 (app d, J = 2.4 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 130.3, 128.6, 127.9, 126.5, 88.3.
HRMS (ESI) found 223.1116 (calculated for $[C_{16}H_{14}O+ H]^+$: 223.1123)
IR (thin film, cm^{-1}): 3084, 3062, 3029, 2922, 2851, 1601, 1493.



(*R*)-2-((*R*)-2,5-Dihydrofuran-2-yl)-1,4-dioxaspiro[4.5]decane (27)
To a solution of $AuCl_3$ (0.6 mg, 0.0020 mmol) in THF (0.5 mL) in a flame-dried vial equipped with a magnetic stir bar was added a solution of the allenol **11o** (30 mg, 0.14 mmol) in THF (1 mL) via cannula, followed by a 1 mL rinse. The reaction was allowed to stir at r.t. for 2 h, at which time TLC indicated full consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with hexanes (39 : 1) to afford the title compound as a pale yellow oil and a single diastereomer.
Yield: 19 mg, 64%.
$[\alpha]_D^{24}$ = +41.3 (c = 0.40, CH_2Cl_3). In lit[38]: **$[\alpha]_D^{24}$** = +51 (c = 0.9, CH_2Cl_2).
All spectra were in agreement with reported data.[38]



(*R*)-2-((*S*)-2,5-Dihydrofuran-2-yl)-1,4-dioxaspiro[4.5]decane (28)
To a solution of $AuCl_3$ (0.6 mg, 0.0020 mmol) in THF (0.5 mL) in a flame-dried vial equipped with a magnetic stir bar was added a solution of the allenol **11p** (30 mg, 0.14 mmol) in THF (1 mL) via cannula, followed by a 1 mL rinse. The reaction was allowed to stir at r.t. for 2 h, at which time TLC indicated full consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with hexanes (39 : 1) to afford the title compound as a pale yellow oil and a single diastereomer.
Yield: 18 mg, 59%.
$[\alpha]_D^{24}$ = +26.1 (c = 0.40, CH_2Cl_3).
All spectra were in agreement with reported data.[38]



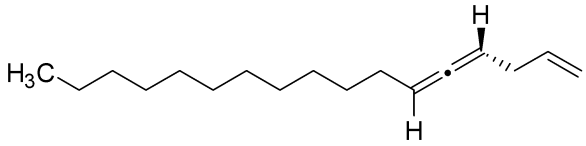
(2*S*, 5*R*)-2-Benzyl-5-phenyl-2,5-dihydrofuran (29)

A solution of the allenol *anti*-**15b** (0.046 g, 0.19 mmol) in THF (2.0 mL) was added by cannula to a solution of $AuCl_3$ (~0.6 mg, 0.002 mmol) in THF (0.5 mL). The reaction was allowed to stir at room temperature over 2h, at which time TLC indicated full consumption of the starting material. The reaction was then concentrated under reduced pressure, and the residue was purified by flash column chromatography with 0% → 2% EtOAc/Hexanes to afford the title compound as a clear and colorless oil.

Yield: (0.027 g, 0.16 mmol, 59%) as a clear oil.

All spectra were in agreement with reported data.[8]

y. Synthesis of Laballenic Acid



(*R*)-Heptadeca-1,4,5-triene (31)

Prepared from the corresponding ynal **30** (2.0 mmol) and allyl boronate **5** (3.0 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 399 mg, 85%

e.r.: 99:1

$[\alpha]_D^{22}$ = –38.3 (c = 1.0, $CHCl_3$).

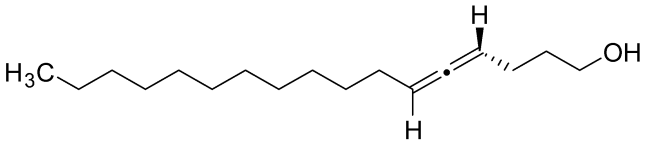
HPLC Analysis, this compound was converted to the corresponding alcohol (see below) following the hydroboration/oxidation procedure, tr minor: 32.5 min., tr major: 34.3 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (dddd, *J* = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.16 – 5.04 (m, 3H), 5.01 (ddd, *J* = 10.1, 1.5, 1.5 Hz, 1H), 2.80 – 2.71 (m, 2H), 2.03 – 1.92 (m, 2H), 1.46 – 1.35 (m, 2H), 1.35 – 1.19 (m, 16H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.2, 136.8, 115.0, 91.5, 88.9, 33.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 29.1, 28.8, 22.7, 14.1.

GCMS found 234.2 (calculated for $C_{17}H_{30}$: 234.2)

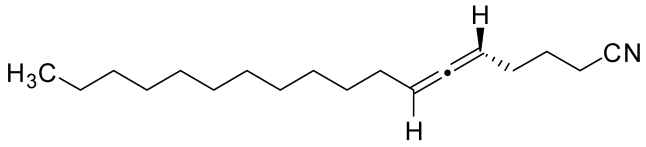
IR (thin film, cm^{-1}): 2956, 2926, 2854.



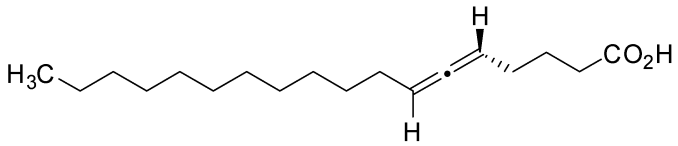
(*R*)-Heptadeca-4,5-dien-1-ol (32)

The product was prepared on a 1.0 mmol scale following the general procedure for hydroboration/oxidation and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (100:5) to afford the pure product as a colorless oil.

Yield: 189 mg, 75%
$[\alpha]_D^{22}$ = –43.7 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 – 5.07 (m, 2H), 3.74 – 3.62 (m, 2H), 2.12 – 2.03 (m, 2H), 2.01 – 1.93 (m, 2H), 1.69 (tt, *J* = 7.3, 6.5 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.33 – 1.21 (m, 16H), 0.91 – 0.85 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 91.6, 90.1, 62.4, 32.0, 31.9, 29.7, 29.7, 29.5, 29.3, 29.2, 29.1, 25.2, 22.7, 14.1.
ESIMS found 253.2 (calculated for $[C_{17}H_{33}O]^+$: 253.2)
IR (thin film, cm^{-1}): 3354, 2853, 1467, 1057, 930.



(*R*)-Octadeca-5,6-dienenitrile (34)
(*R*)-Heptadeca-4,5-dien-1-ol **32** (131 mg, 0.5 mmol) was dissolved in Et_2O (5 ml) and cooled to 0 °C. Triphenylphosphine (262 mg, 1 mmol) and DIAD (202 mg, 1 mmol) were added followed by the addition of acetone cyanohydrin **33** (85 mg, 1 mmol). The reaction mixture was allowed to stir at the same temperature for 1 h and warm up to room temperature. After 24 hours, the reaction mixture was flashed through a short pad of silica gel and the solvent was removed under vacuum. The crude product was purified by column chromatography with hexanes/EtOAc (50:1) to afford the pure product as a colorless oil.
Yield: 95 mg, 73%
$[\alpha]_D^{22}$ = –47.5 (c = 1.0, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (dddt, *J* = 6.5, 6.5, 6.4, 3.0 Hz, 1H), 5.05 (dddt, *J* = 6.4, 6.3, 6.3, 3.0 Hz, 1H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.16 – 2.10 (m, 2H), 2.01 – 1.94 (m, 2H), 1.82 – 1.74 (m, 2H), 1.38 (q, *J* = 7.3 Hz, 2H), 1.34 – 1.20 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 119.6, 92.3, 88.6, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.9, 27.6, 24.6, 22.7, 16.4, 14.1.
ESIMS found 262.2 (calculated for $[C_{18}H_{32}N]^+$: 262.2)
HRMS found 284.2364 (calculated for $[C_{18}H_{31}NNa]^+$: 284.2354)
IR (thin film, cm^{-1}): 2924, 2854, 2250, 1963, 1465, 880.



(*R*)-Octadeca-5,6-dienoic acid, laballenic acid (35)
(*R*)-Octadeca-5,6-dienenitrile **34** (115 mg, 0.44 mmol) was dissolved in EtOH (0.5 ml). To this solution was added a solution of NaOH (120 mg, 3 mmol) in H_2O (0.16 ml). The reaction mixture was stirred at 80 °C for 5 h. The reaction was acidified with HCl (2 M) to pH=1, and extracted with Et_2O (3 X 5 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude mixture was purified by column chromatography with hexanes/EtOAc/AcOH (100:10:0.1) to afford the pure product as a colorless oil with acidic smell.
Yield: 107 mg, 87%

$[\alpha]_D^{22}$ = –45.0 (c = 1.0, $CHCl_3$). In lit: **$[\alpha]_D^{29}$** = –42.7 (c = 0.96, $CHCl_3$).[39] **$[\alpha]_D^{27}$** = –50.6 (c = 1.025, $CHCl_3$).[40]
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 – 5.00 (m, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.04 (qd, *J* = 7.0, 2.9 Hz, 2H), 1.97 (qd, *J* = 6.9, 2.9 Hz, 2H), 1.75 (tt, *J* = 7.3, 7.3 Hz, 2H), 1.38 (tt, *J* = 7.1, 7.1 Hz, 2H), 1.34 – 1.21 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0, 179.9, 91.6, 89.6, 33.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 28.9, 28.2, 24.0, 22.7, 14.1.
ESIMS found 279.2 (calculated for $[C_{18}H_{31}O_2]^-$: 279.2)
HRMS found 279.2325 (calculated for $[C_{18}H_{31}O_2]^-$: 279.2324)
IR (thin film, cm^{-1}): 2923, 2854, 1710, 1457, 1254, 878.
All spectra were in agreement with reported data.[39-40]

3. Summary of Absolute Stereochemistry Determination for Allenols and Allyl Allenes
The absolute stereochemistry of allenols was determined unambiguously by direct comparison of the optical rotations of **6a**,[7] **6g**,[9] **6i**,[9] **6j**,[11] **6n**,[13] with those reported for the same compounds or their enantiomers.
The cyclized product **25** from **6a** also matched the reported optical information.[36]

The absolute stereochemistry of **23bS2** and **38** was confirmed by their NMR data and optical rotations compared to those that had been reported by Ma's group.[35] Therefore the absolute stereochemistry of crotyl allenes was decisively determined.
The optical rotation of laballenic acid **35**[39-40] confirmed the absolute stereochemistry of the corresponding allyl allene precursor **31**, and the absolute configuration of the remaining allyl allene products was determined by analogy.

The optical rotations of allenols and allyl allenes both match Lowe's rules.[33]

4. References

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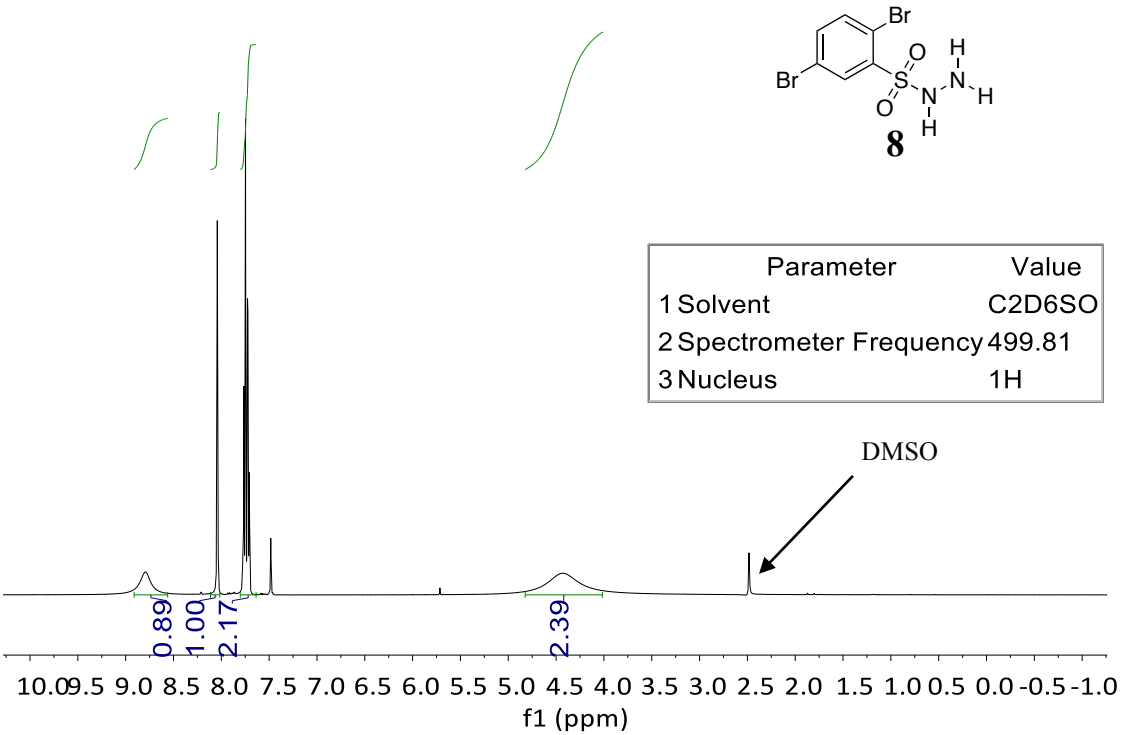
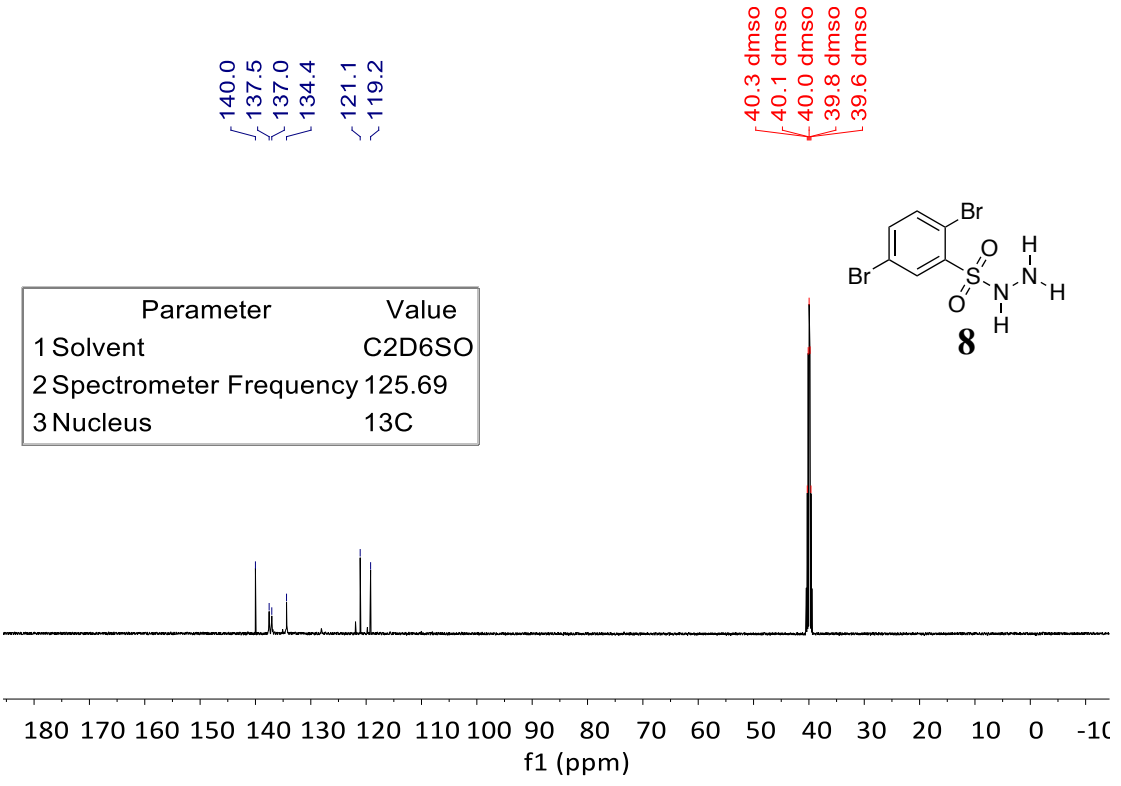
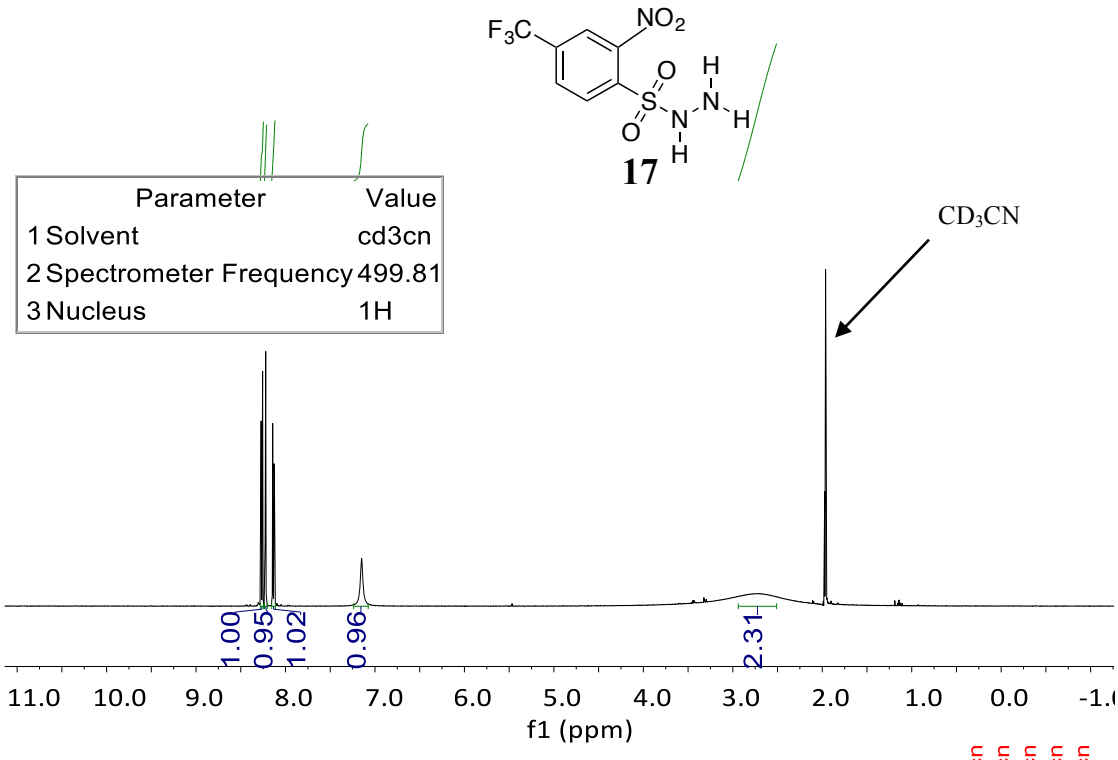
5. ^{1}H and ^{13}C NMR Spectra






F3C
NO2
O
S
N
H
H
O
17
Parameter Value
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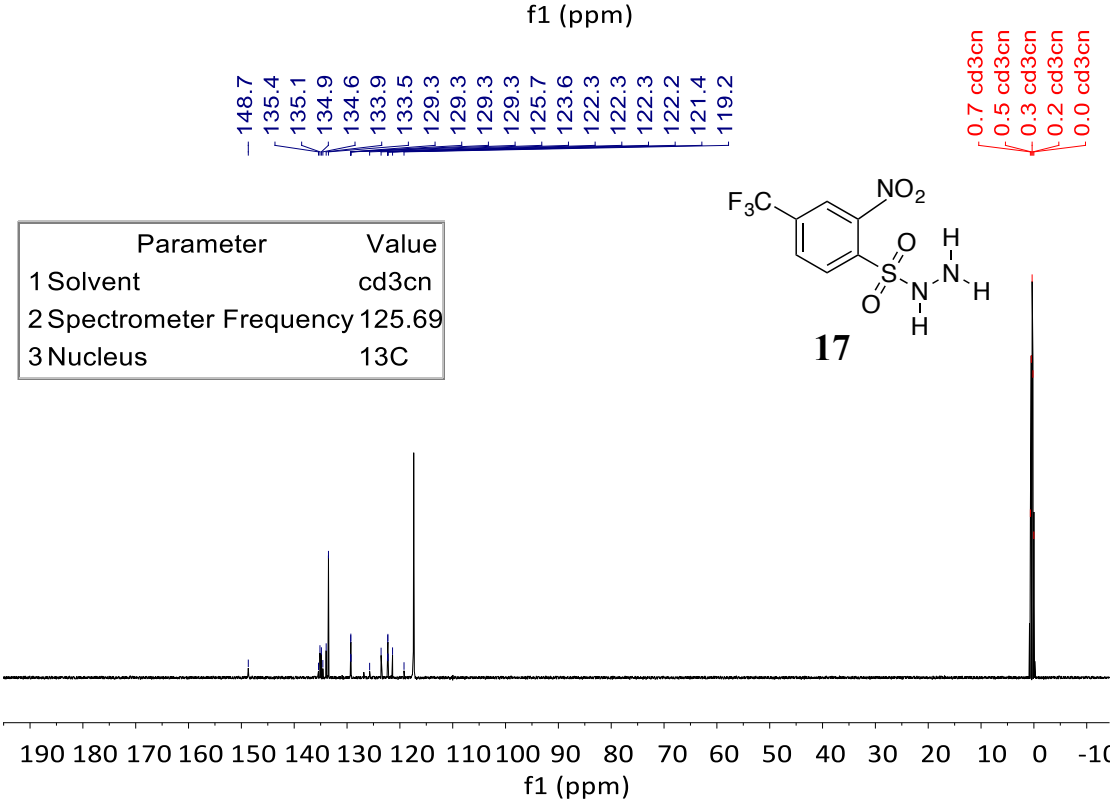
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CD3CN
1.00
0.95
1.02
0.96
2.31
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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135.4
135.1
134.9
134.6
133.9
133.5
129.3
129.3
129.3
129.3
125.7
123.6
122.3
122.3
122.3
122.2
121.4
119.2
0.7 cd3cn
0.5 cd3cn
0.3 cd3cn
0.2 cd3cn
0.0 cd3cn
F3C
NO2
O
S
N
H
H
O
17
Parameter Value
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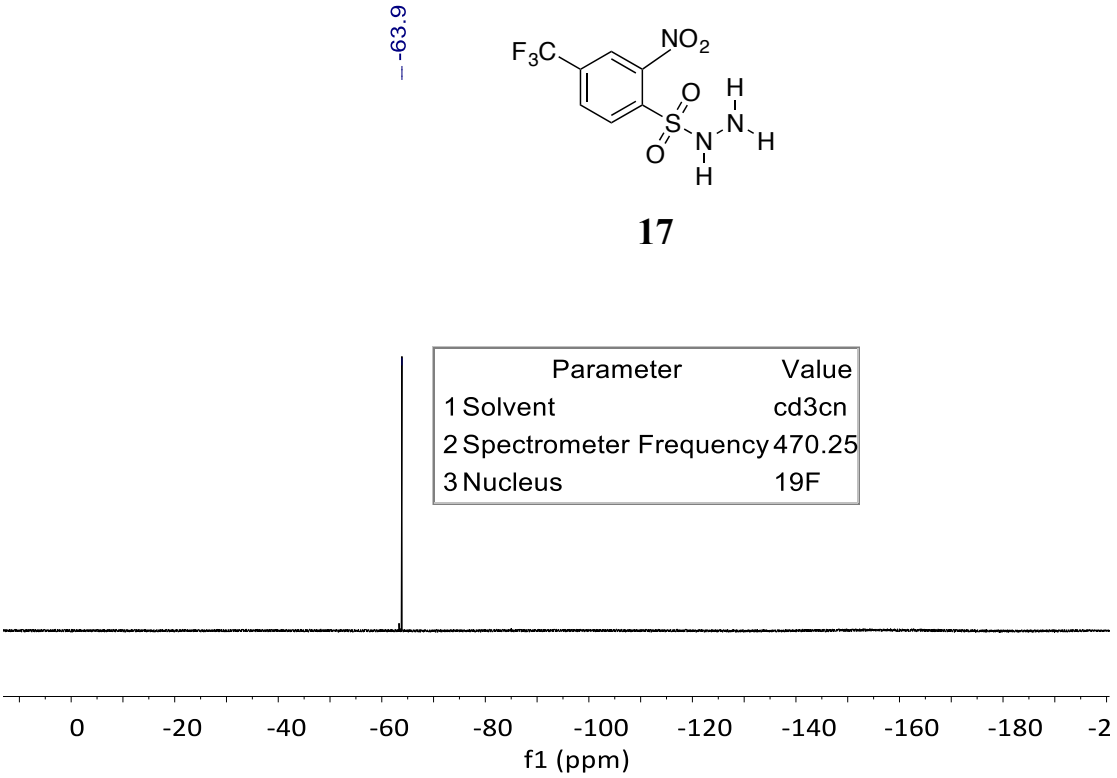
2 Spectrometer Frequency 125.69
3 Nucleus 13C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.9
F3C
NO2
O
S
O
N
H
H
N
H
Parameter
Value
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cd3cn
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470.25
3 Nucleus
19F
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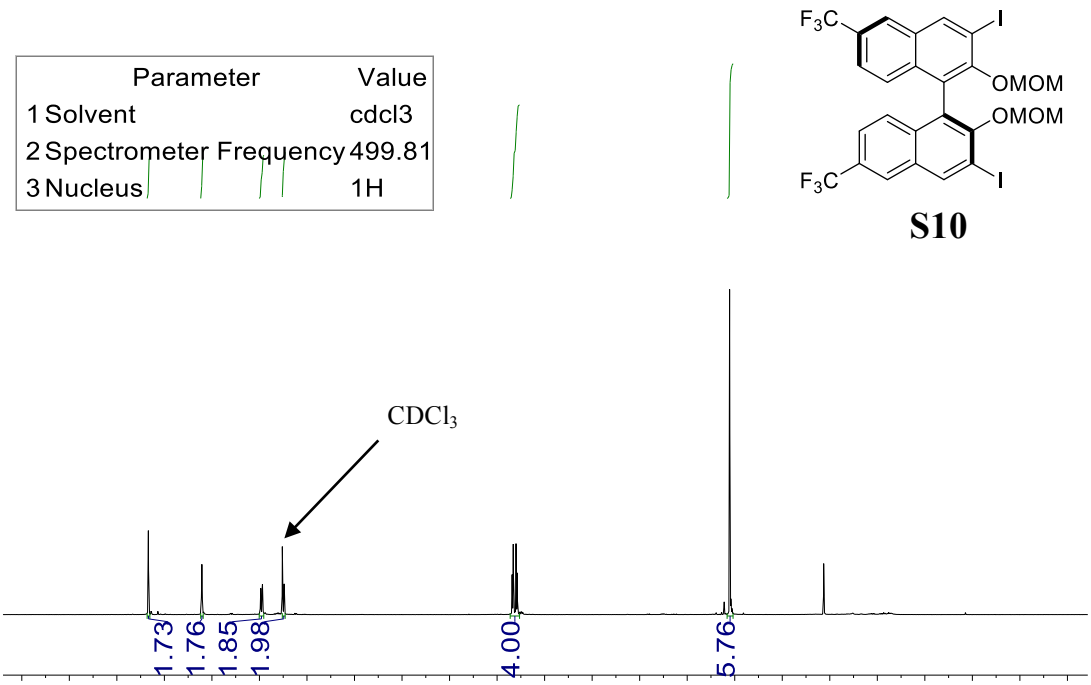
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

17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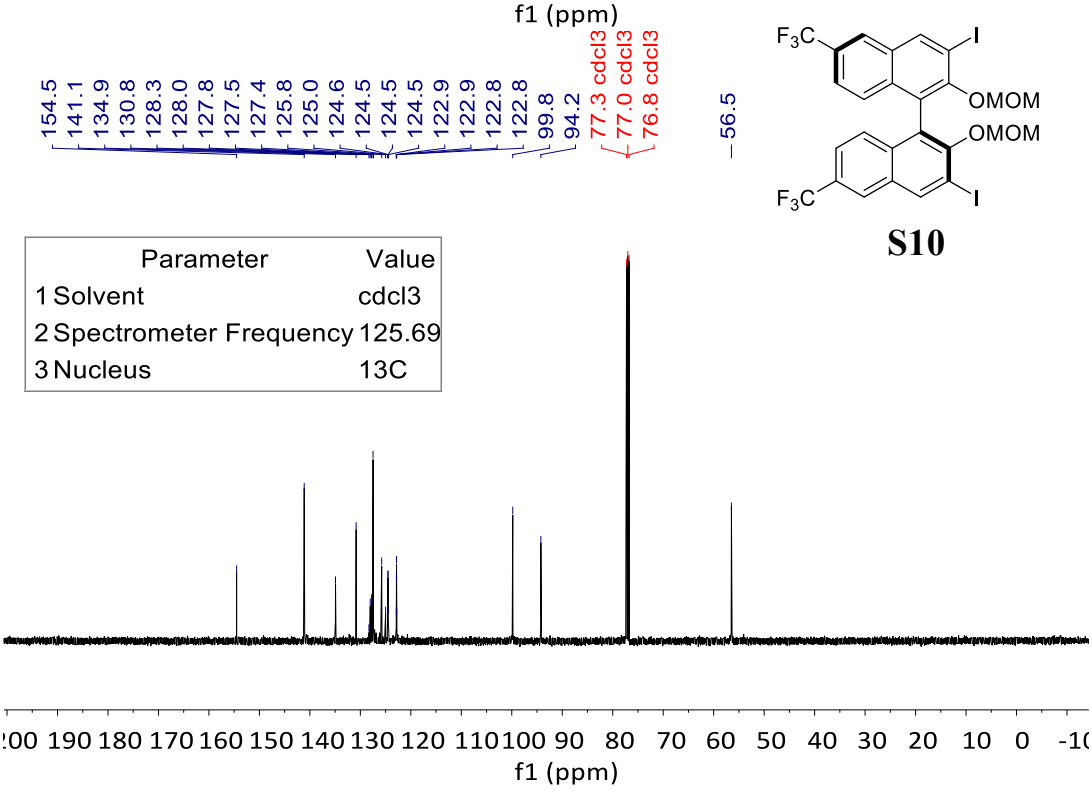
F3C
I
OMOM
OMOM
F3C
I
S10
CDCl3
1.73
1.76
1.85
1.98
4.00
5.76
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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141.1
134.9
130.8
128.3
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127.8
127.5
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125.8
125.0
124.6
124.5
124.5
124.5
122.9
122.9
122.8
122.8
99.8
94.2
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
56.5
F3C
I
OMOM
OMOM
F3C
I
S10
Parameter Value
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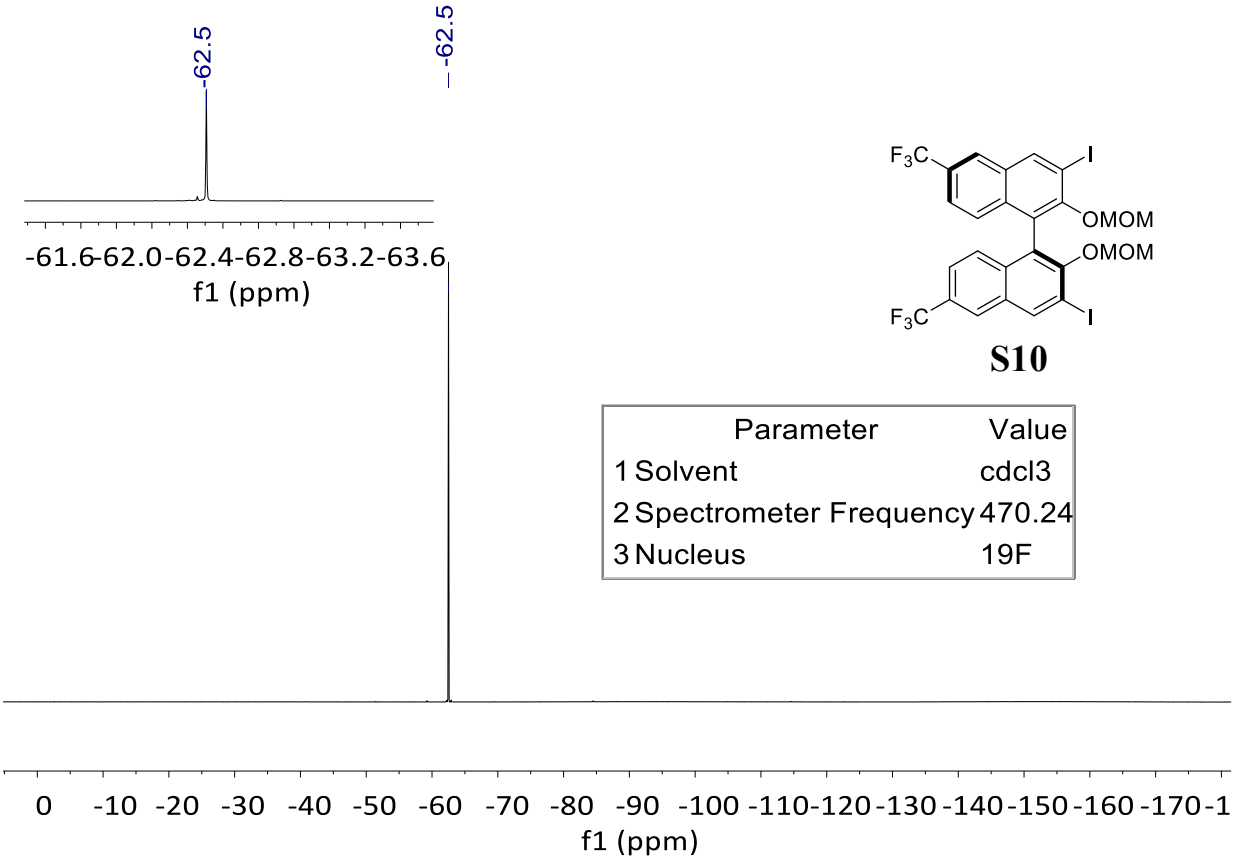
2 Spectrometer Frequency 125.69
3 Nucleus 13C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



S10

	Parameter	Value
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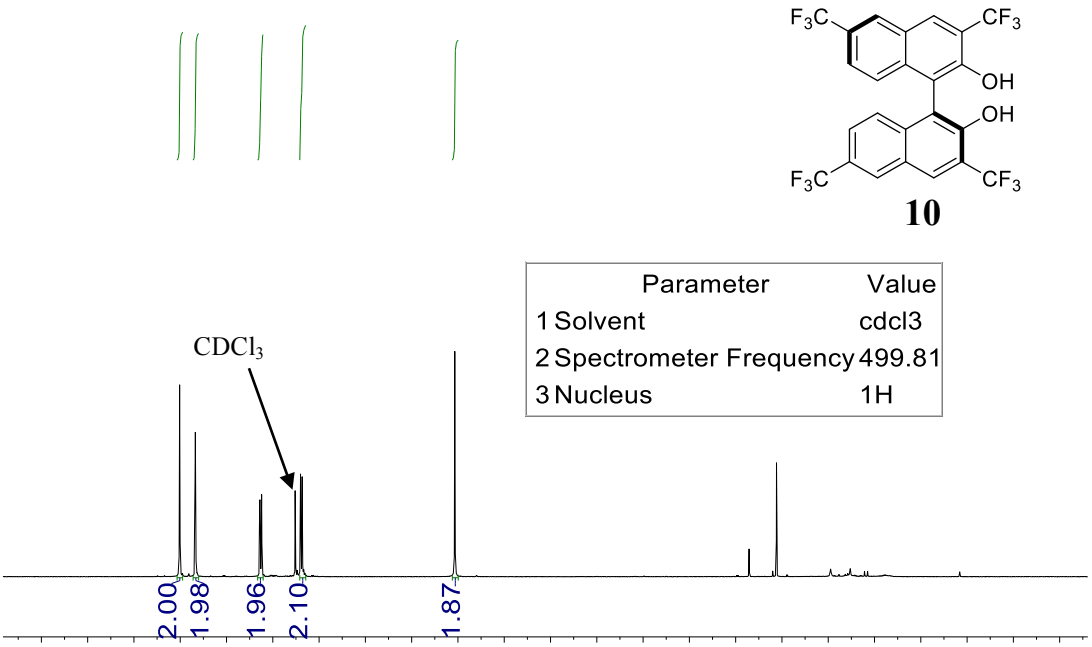
3	Nucleus	19F


F3C
CF3
OH
OH
F3C
CF3
10
Parameter Value
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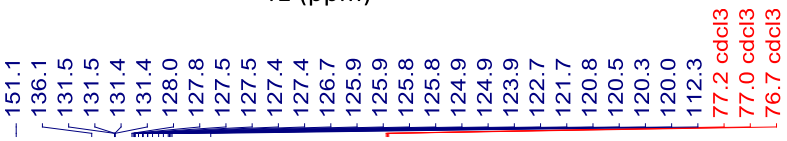
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
2.00
1.98
1.96
2.10
1.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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136.1
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131.5
131.4
131.4
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127.8
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127.5
127.4
127.4
126.7
125.9
125.9
125.8
125.8
124.9
124.9
123.9
122.7
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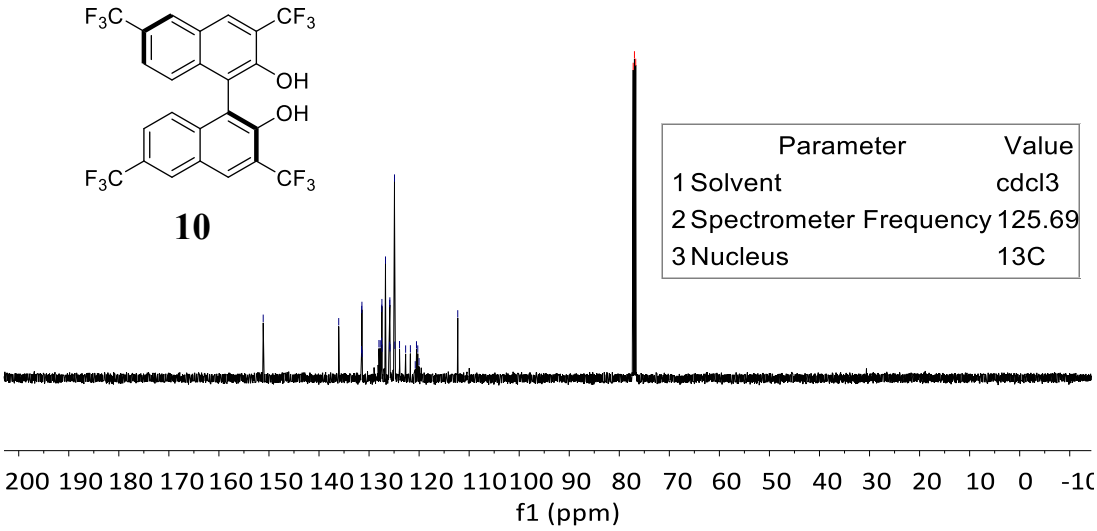
120.8
120.5
120.3
120.0
112.3
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3


F3C
CF3
OH
OH
F3C
CF3
10
Parameter Value
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2 Spectrometer Frequency 125.69
3 Nucleus 13C
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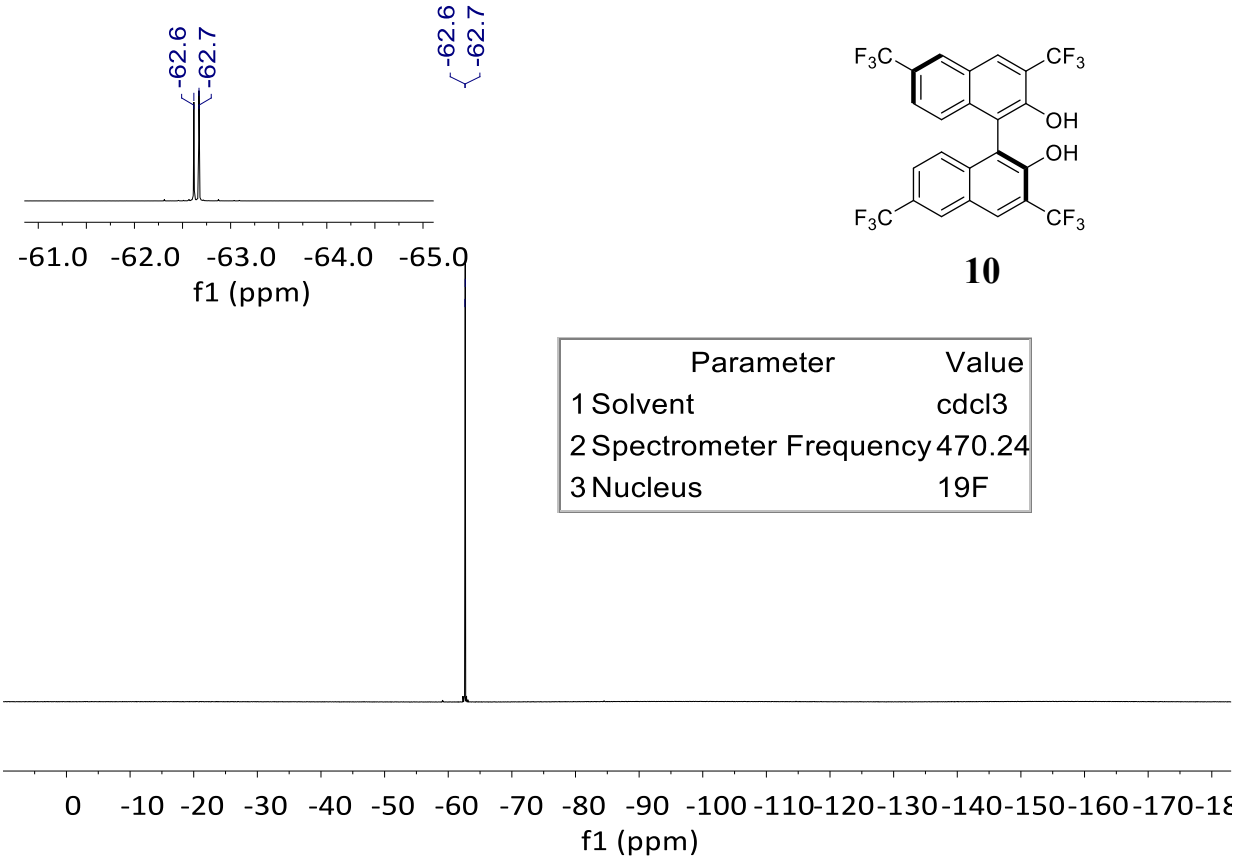
f1 (ppm)


-62.6
-62.7
-62.6
-62.7
-61.0 -62.0 -63.0 -64.0 -65.0
f1 (ppm)
F3C
CF3
OH
OH
F3C
CF3
10
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 470.24
3 Nucleus 19F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -18
f1 (ppm)

Parameter	Value
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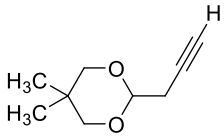
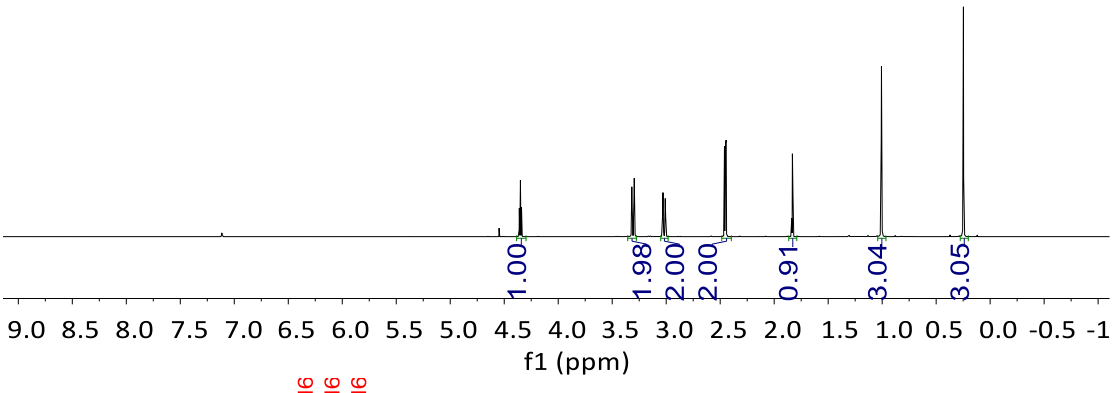
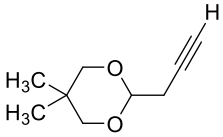
2 Spectrometer Frequency	499.81
3 Nucleus	1H

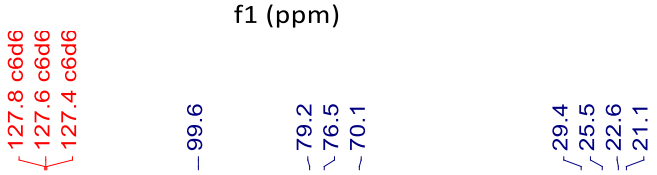


S1l





S1l



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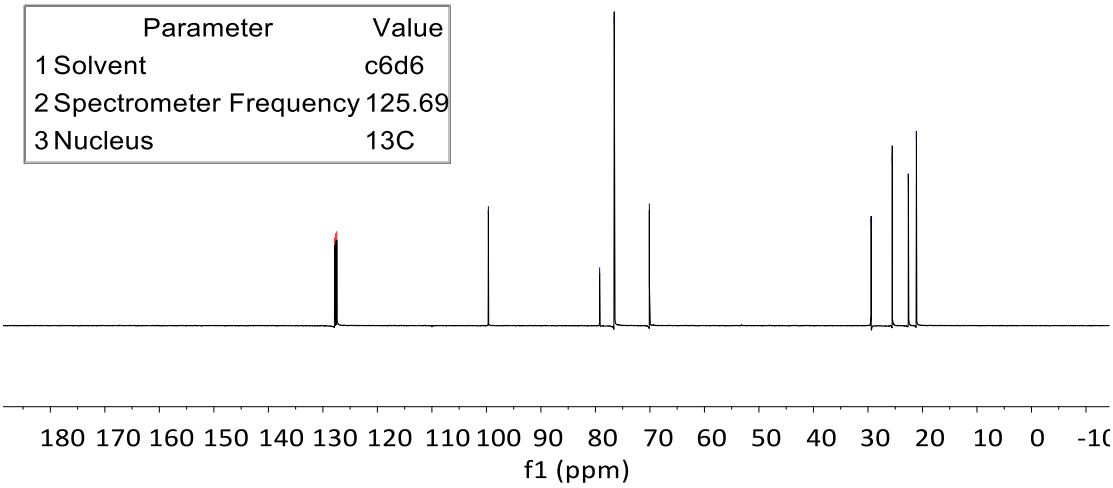
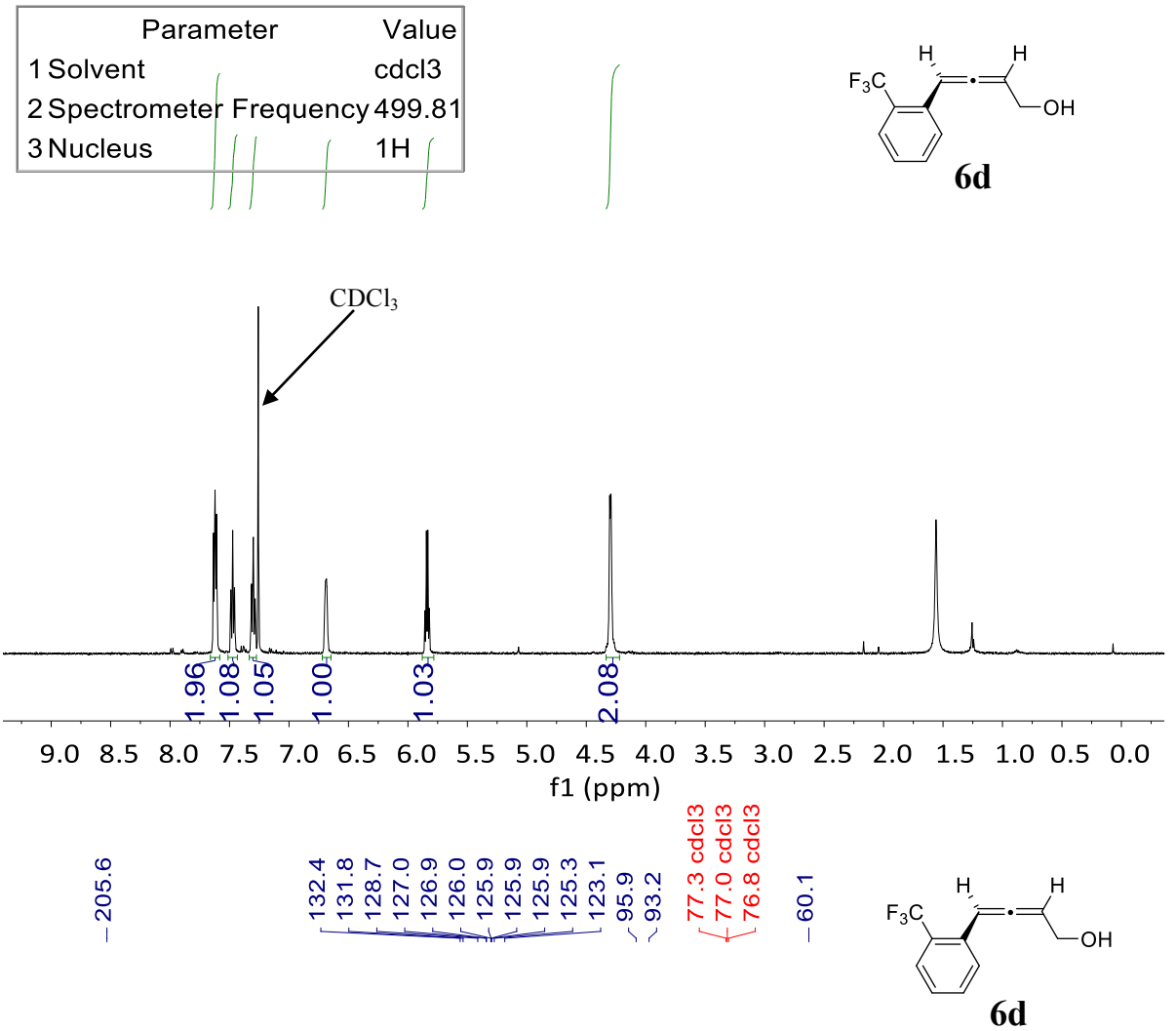
3 Nucleus	13C

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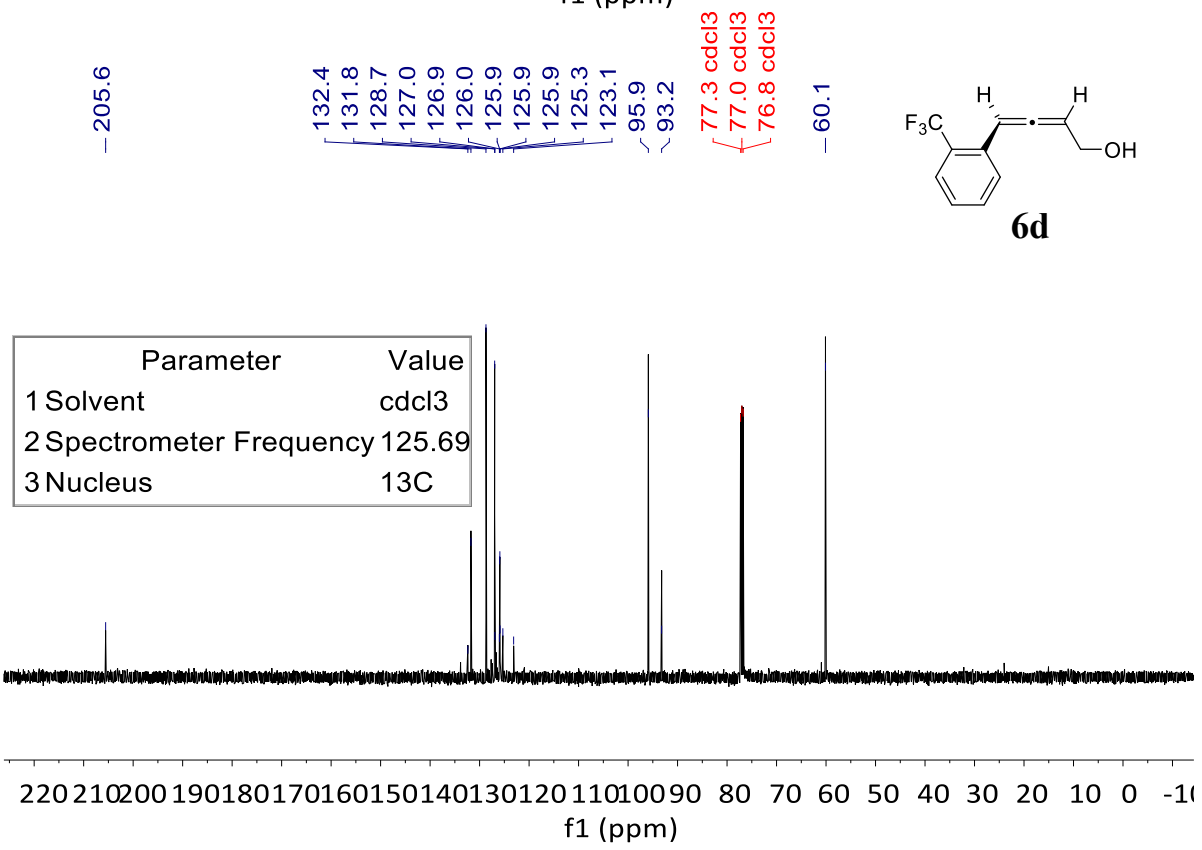
CDCl3
1.96
1.08
1.05
1.00
1.03
2.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
6d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132.4
131.8
128.7
127.0
126.9
126.0
125.9
125.9
125.9
125.3
123.1
95.9
93.2
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
60.1
6d

Parameter Value
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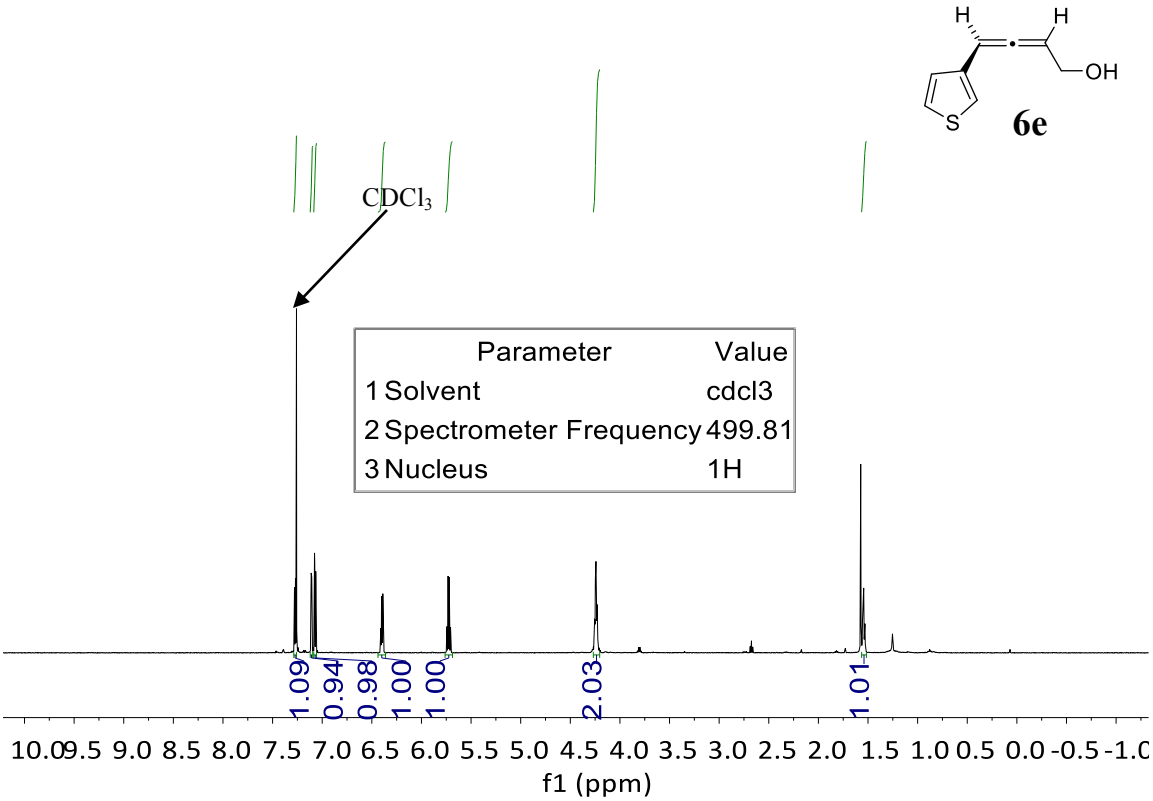
2 Spectrometer Frequency 125.69
3 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6e
CDCl3
Parameter Value
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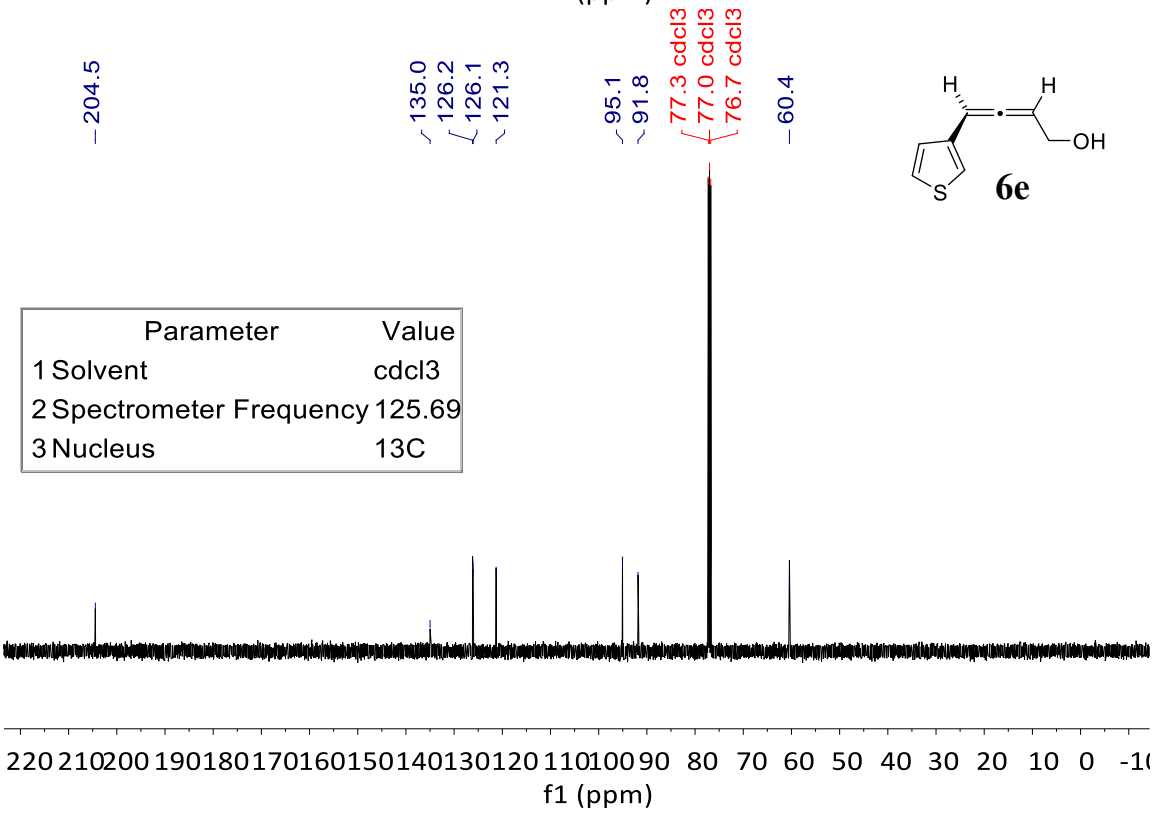
0.94
0.98
1.00
1.00
2.03
1.01
f1 (ppm)


204.5
135.0
126.2
126.1
121.3
95.1
91.8
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
60.4
6e
Parameter Value
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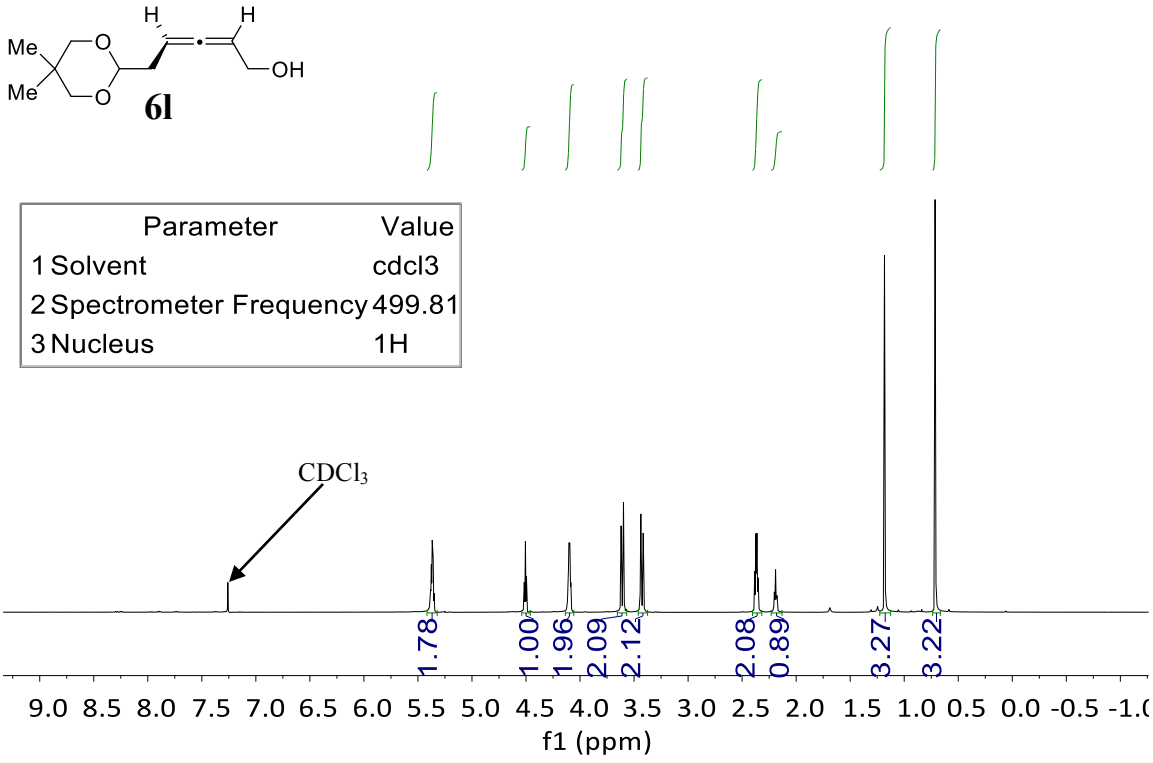
2 Spectrometer Frequency 125.69
3 Nucleus 13C
f1 (ppm)


Me
Me
O
O
H
H
OH
6l
Parameter Value
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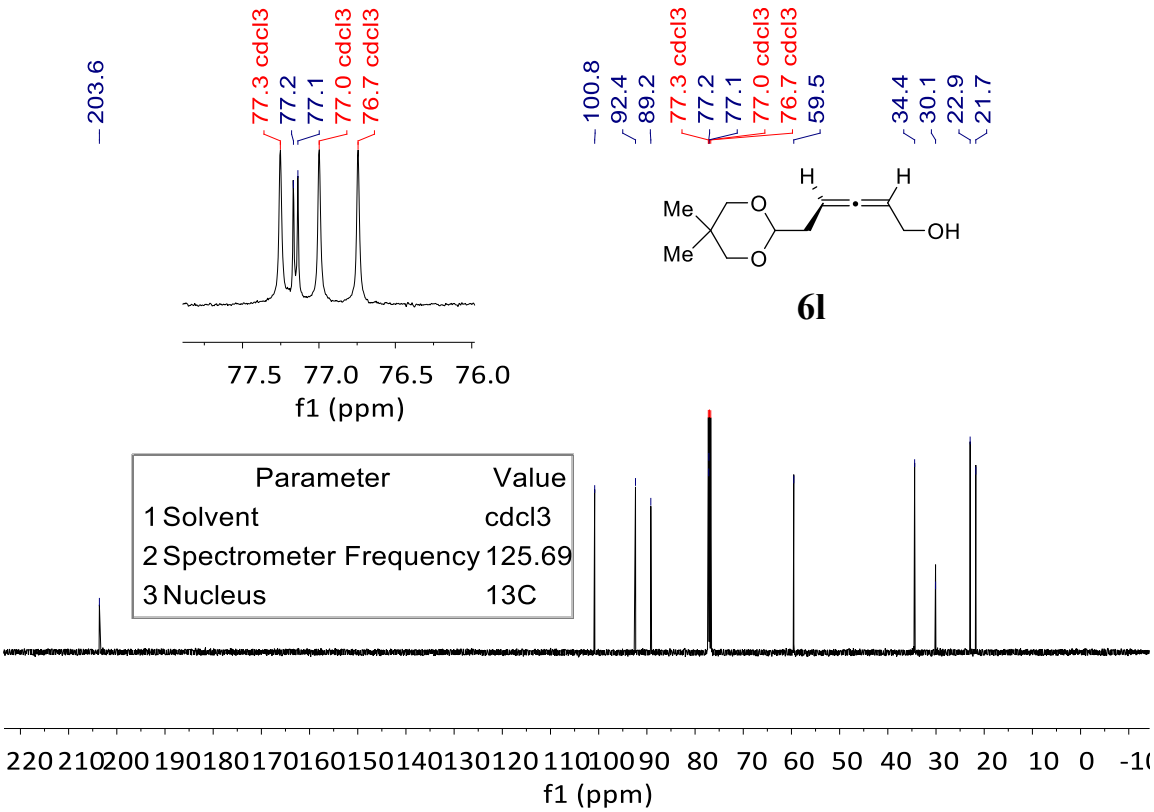
CDCl3
1.78
1.00
1.96
2.09
2.12
2.08
0.89
3.27
3.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


203.6
77.3 cdcl3
77.2
77.1
77.0 cdcl3
76.7 cdcl3
77.5 77.0 76.5 76.0
f1 (ppm)
100.8
92.4
89.2
59.5
34.4
30.1
22.9
21.7
Me
Me
O
O
H
H
OH
6l
Parameter Value
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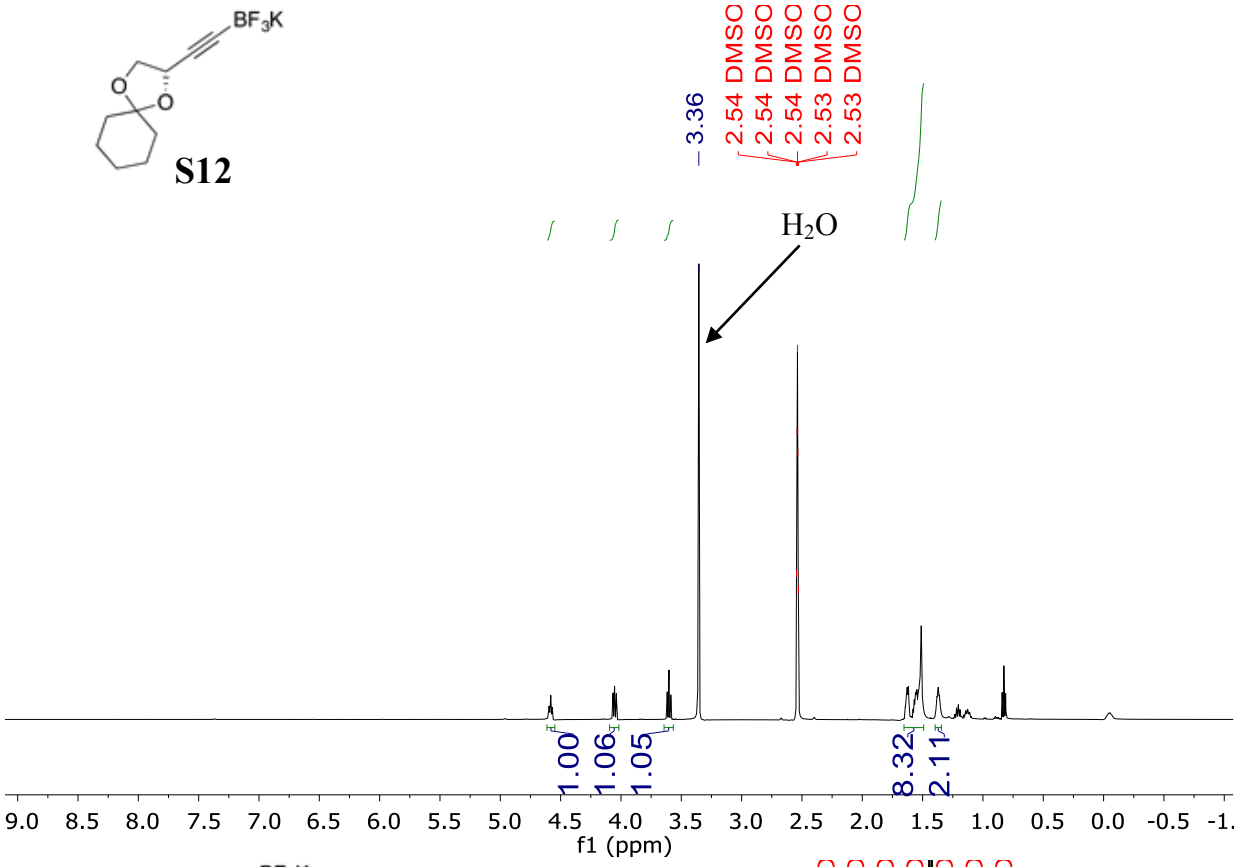
2 Spectrometer Frequency 125.69
3 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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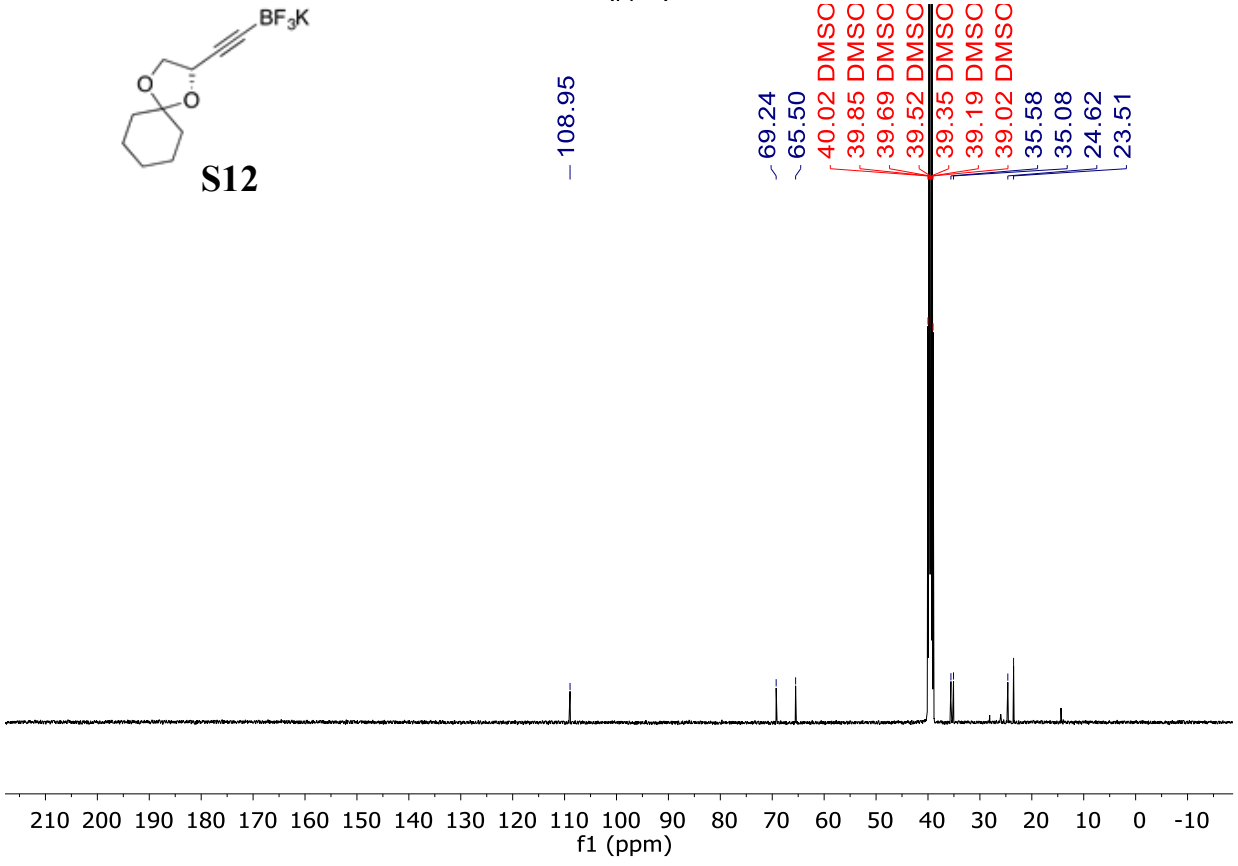
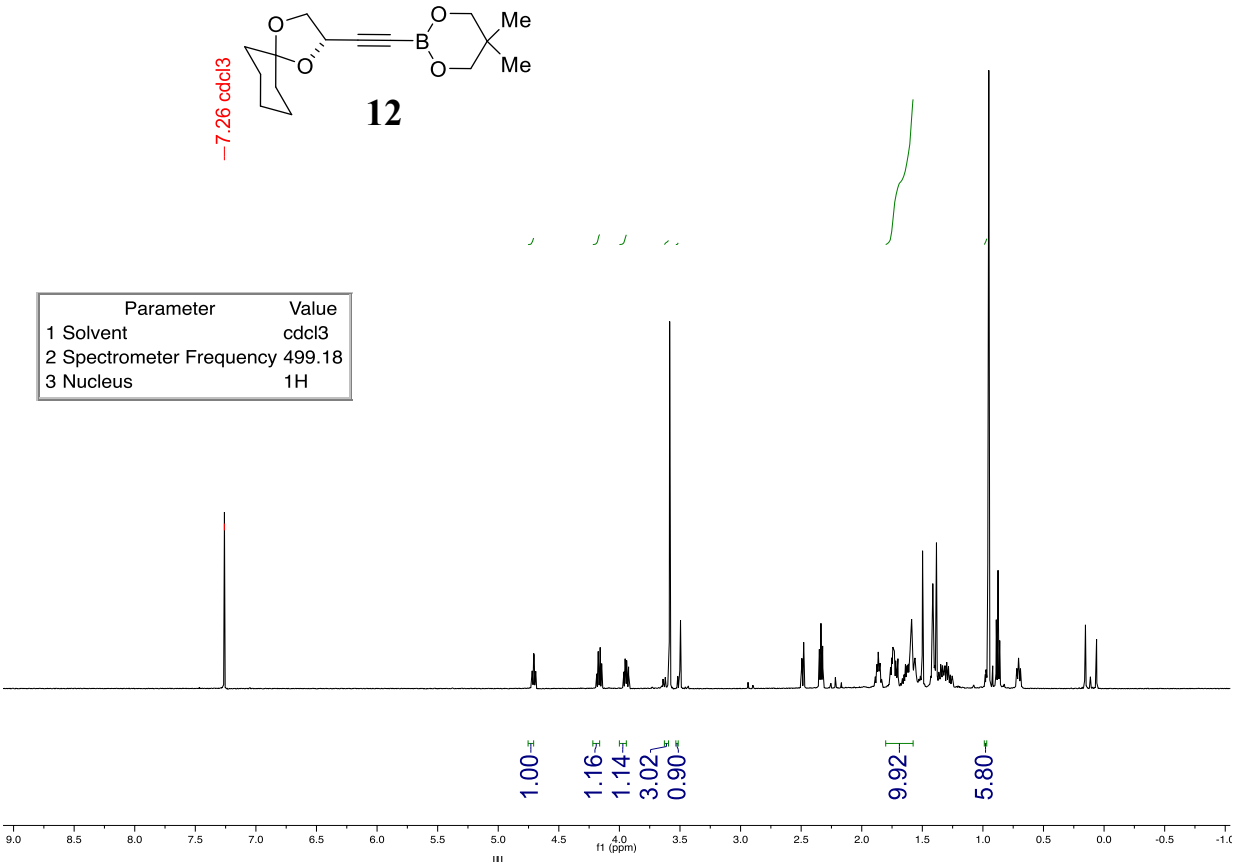
S12
3.36
2.54 DMSO
2.54 DMSO
2.54 DMSO
2.53 DMSO
2.53 DMSO
H2O
1.00
1.06
1.05
8.32
2.11
f1 (ppm)


BF3K
S12
108.95
69.24
65.50
40.02 DMSO
39.85 DMSO
39.69 DMSO
39.52 DMSO
39.35 DMSO
39.19 DMSO
39.02 DMSO
35.58
35.08
24.62
23.51
f1 (ppm)


12
7.26 cdcl3
Parameter Value
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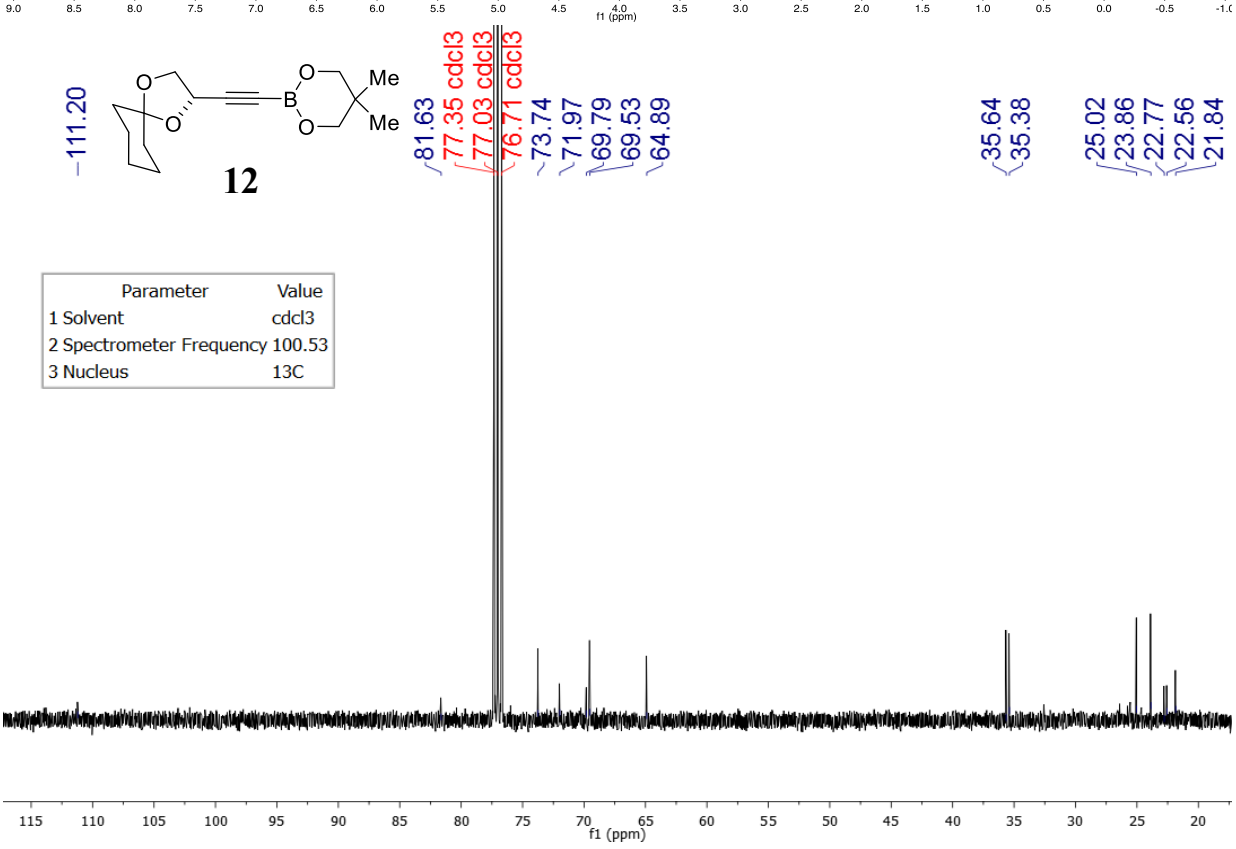
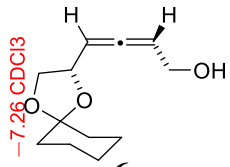
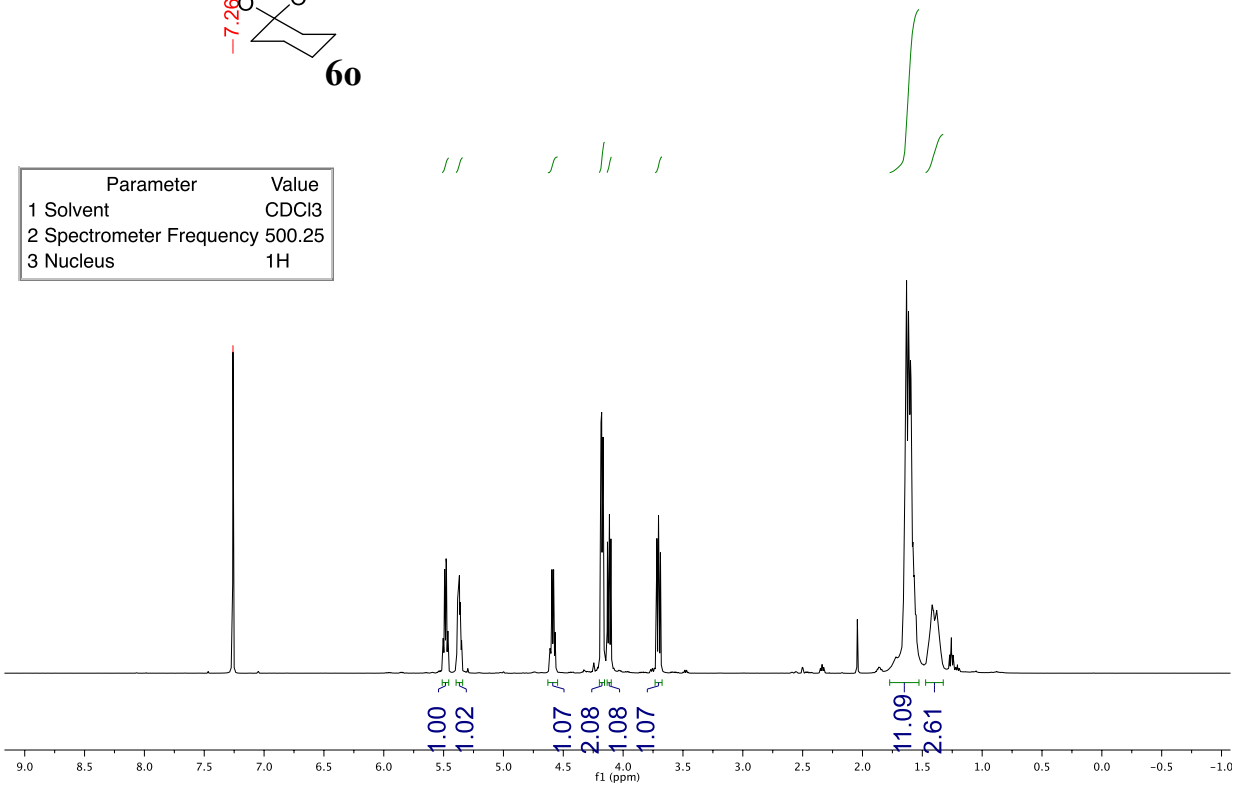
1.16
1.14
3.02
0.90
9.92
5.80
f1 (ppm)


12
111.20
81.63
77.35 cdcl3
77.03 cdcl3
76.71 cdcl3
73.74
71.97
69.79
69.53
64.89
35.64
35.38
25.02
23.86
22.77
22.56
21.84
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 100.53
3 Nucleus 13C
f1 (ppm)

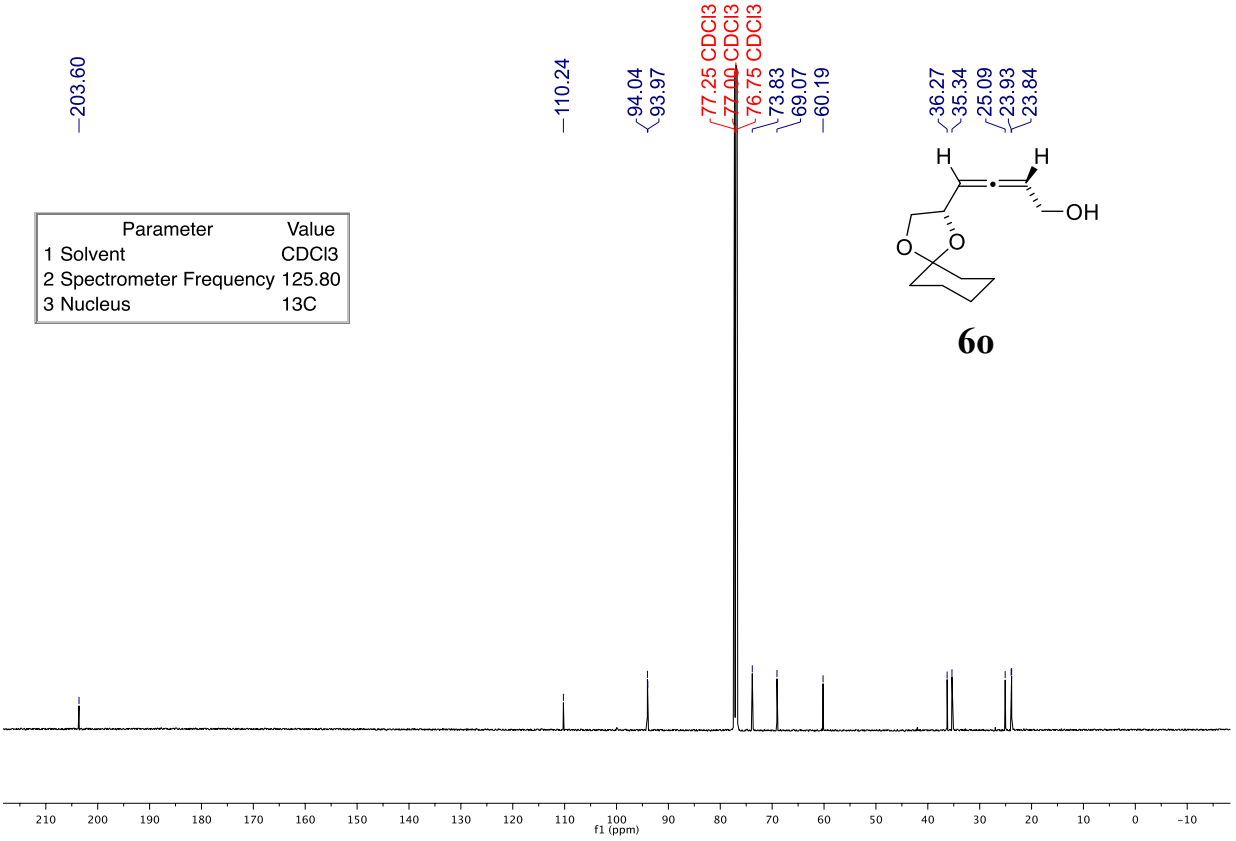


6o

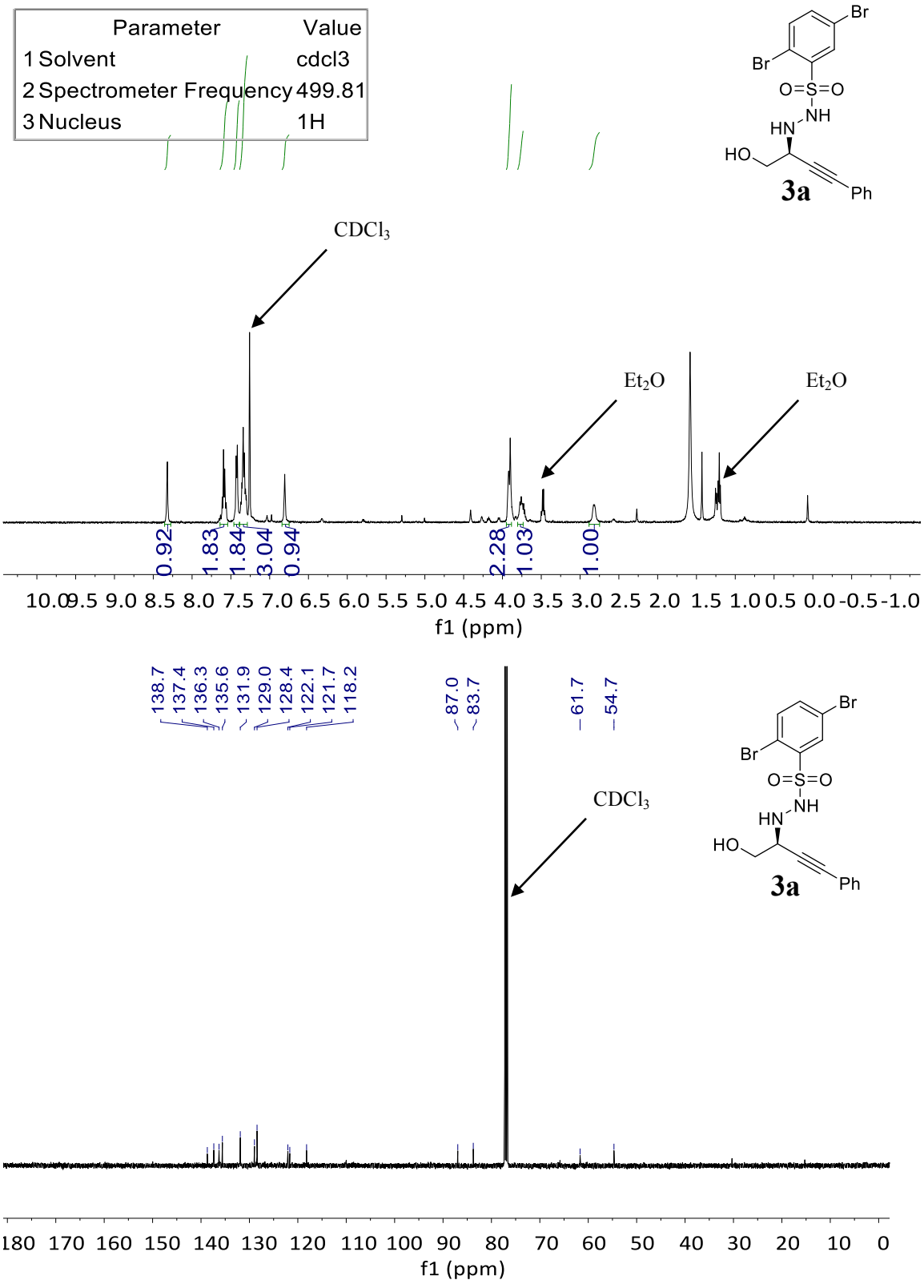
Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	500.25
3 Nucleus	1H

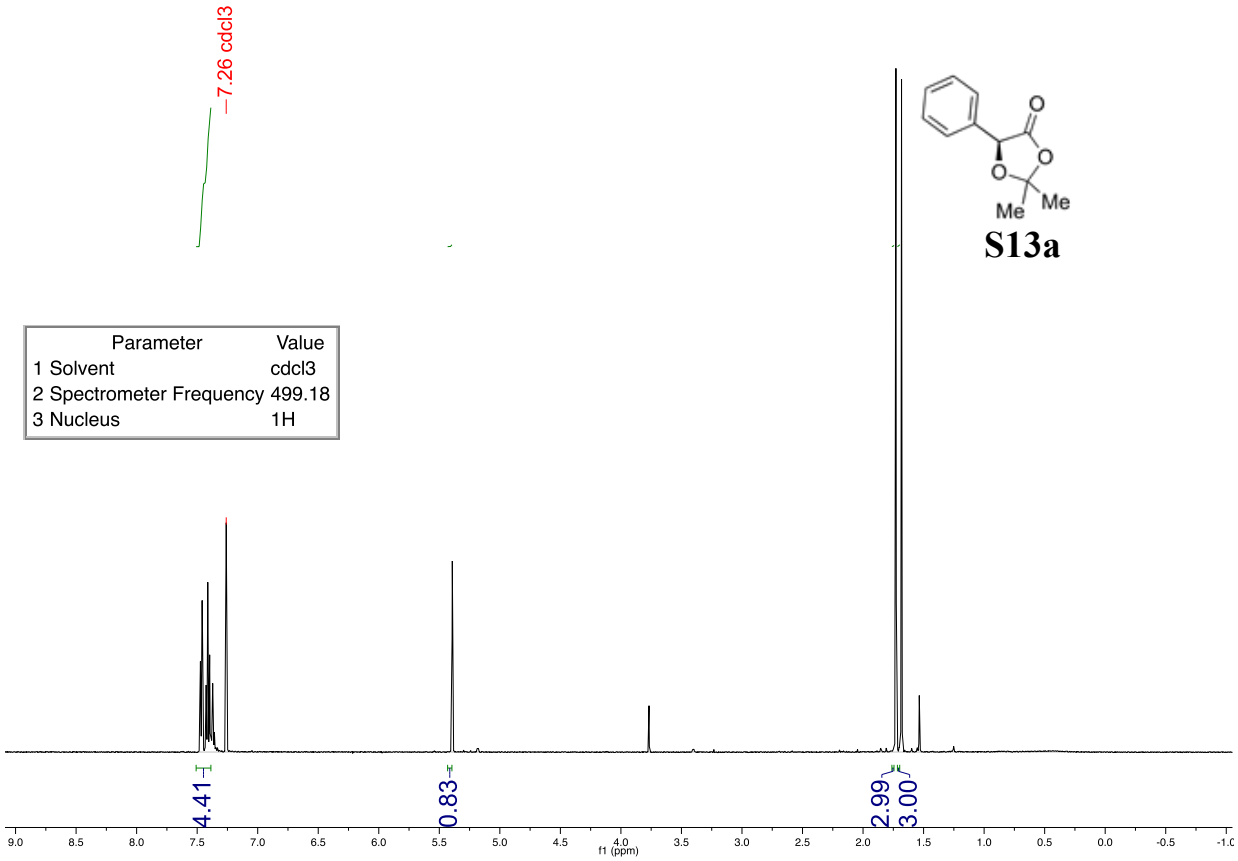


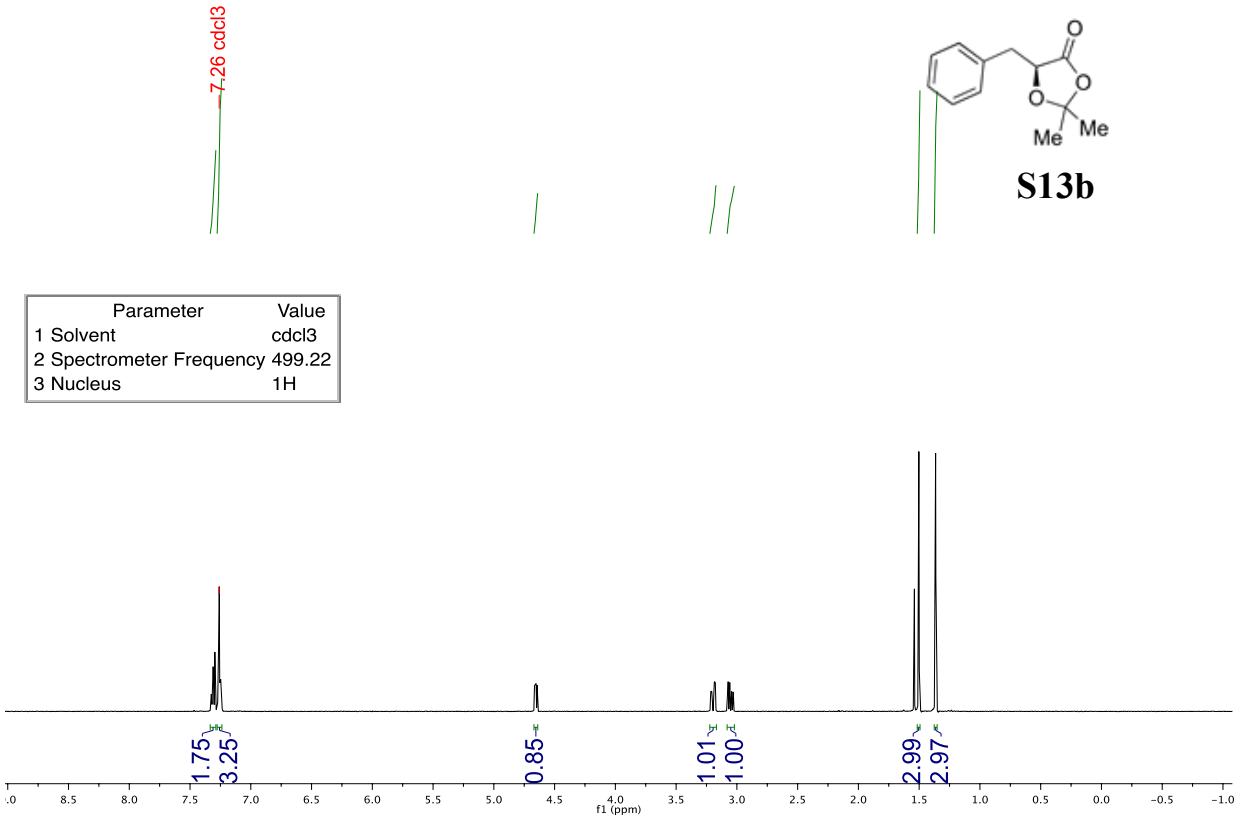
Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	125.80
3 Nucleus	13C

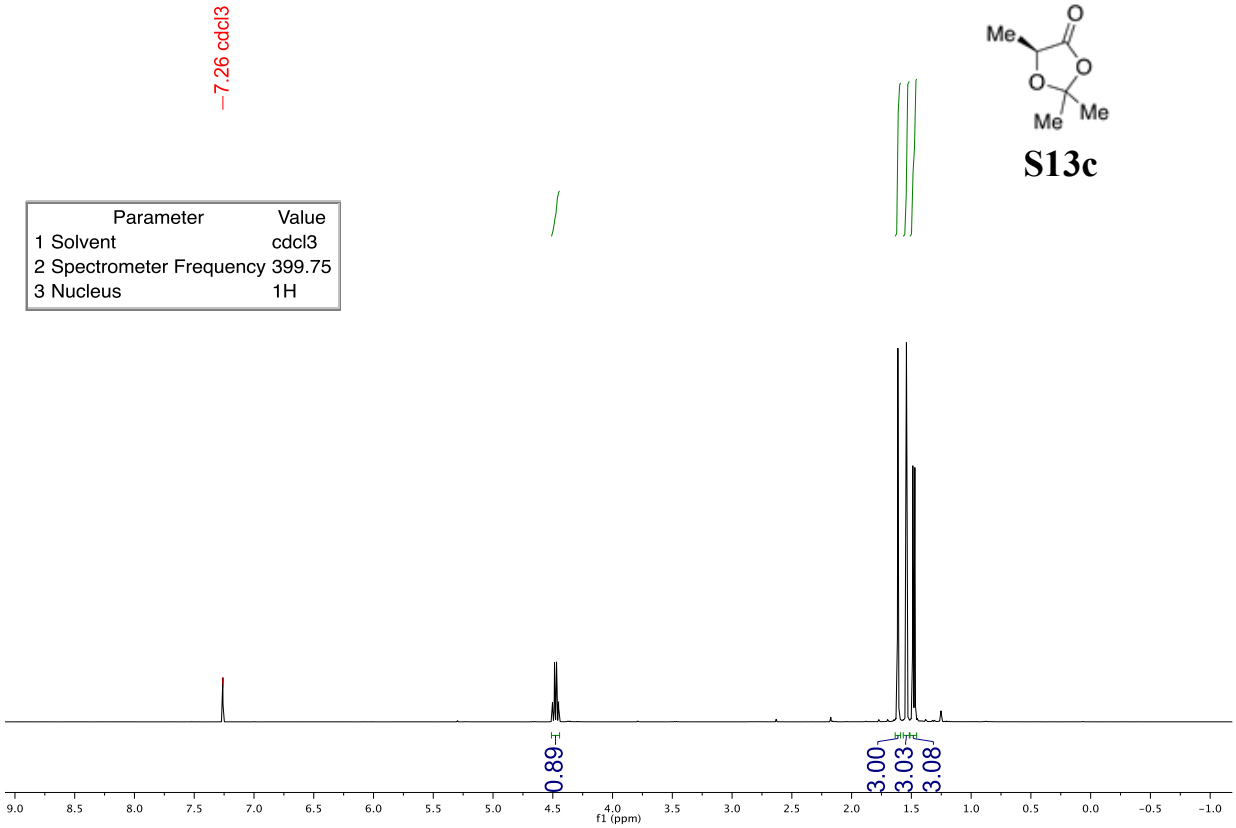


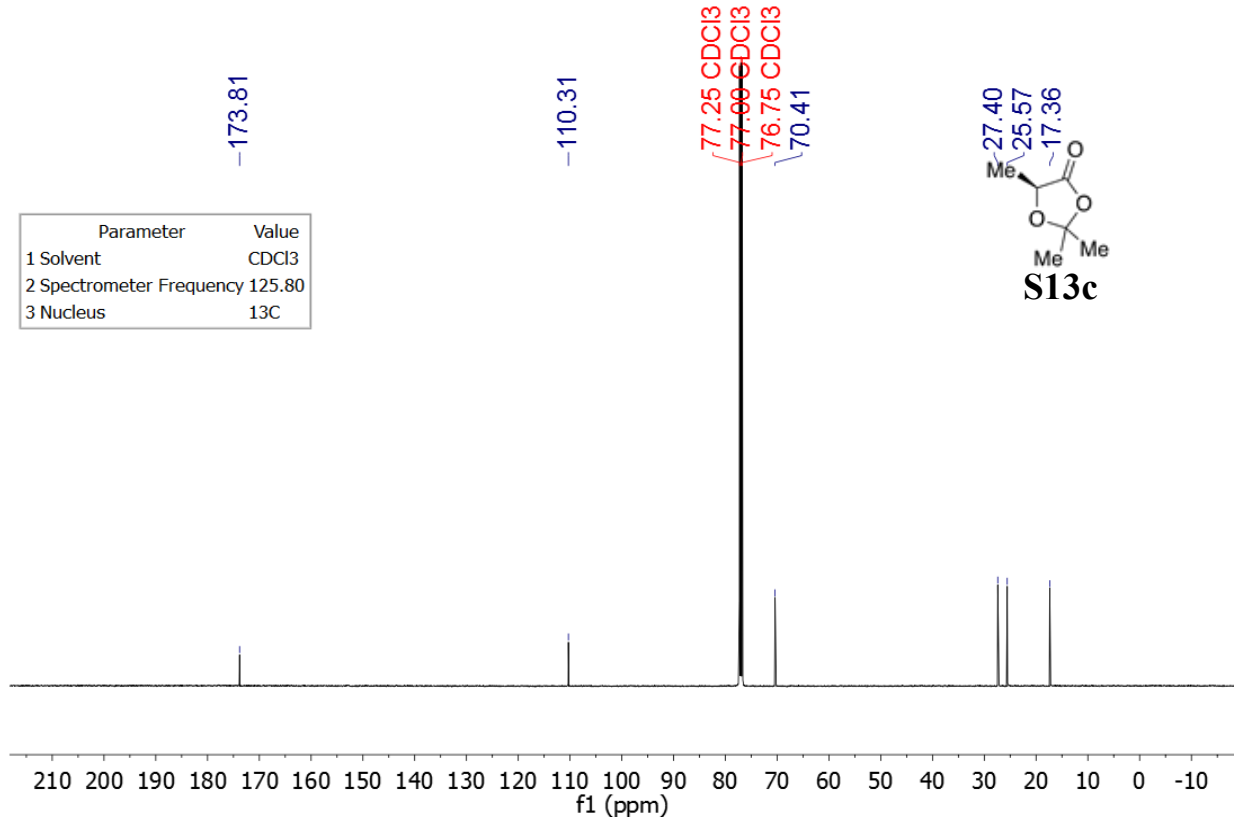
6o

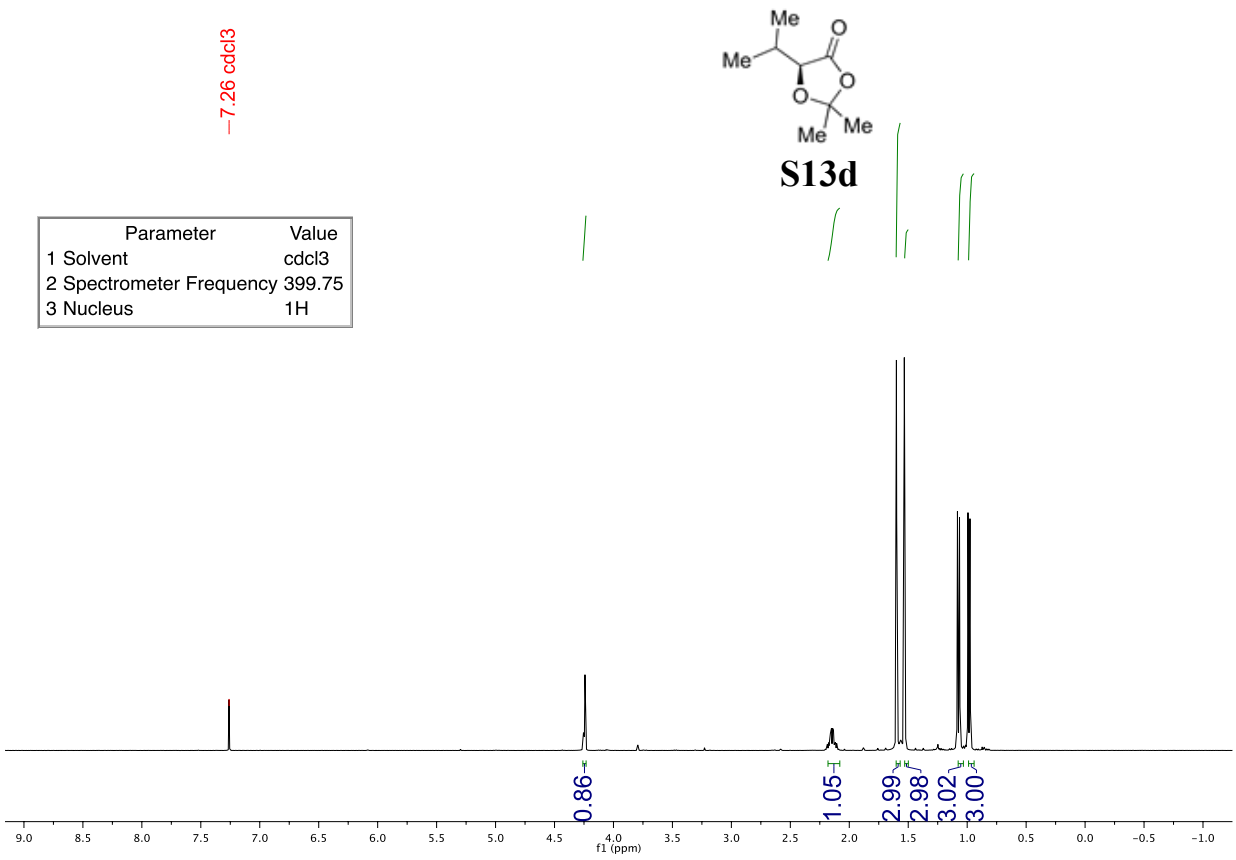

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
Br
Br
O=S=O
NH
HN
HO
Ph
3a
CDCl3
Et2O
Et2O
0.92
1.83
1.84
3.04
0.94
2.28
1.03
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
138.7
137.4
136.3
135.6
131.9
129.0
128.4
122.1
121.7
118.2
87.0
83.7
61.7
54.7
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

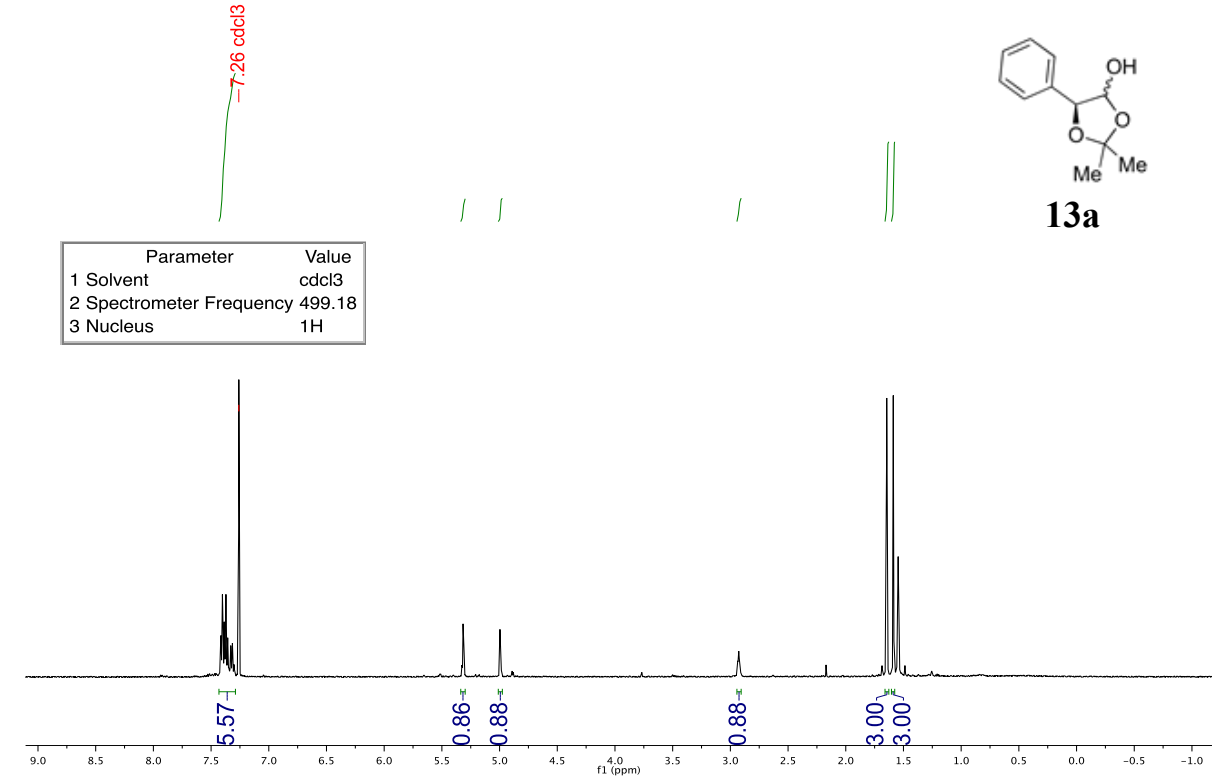

7.26 cdcl3
Me
Me
S13a
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.18
3 Nucleus 1H
4.41
0.83
2.99
3.00
f1 (ppm)

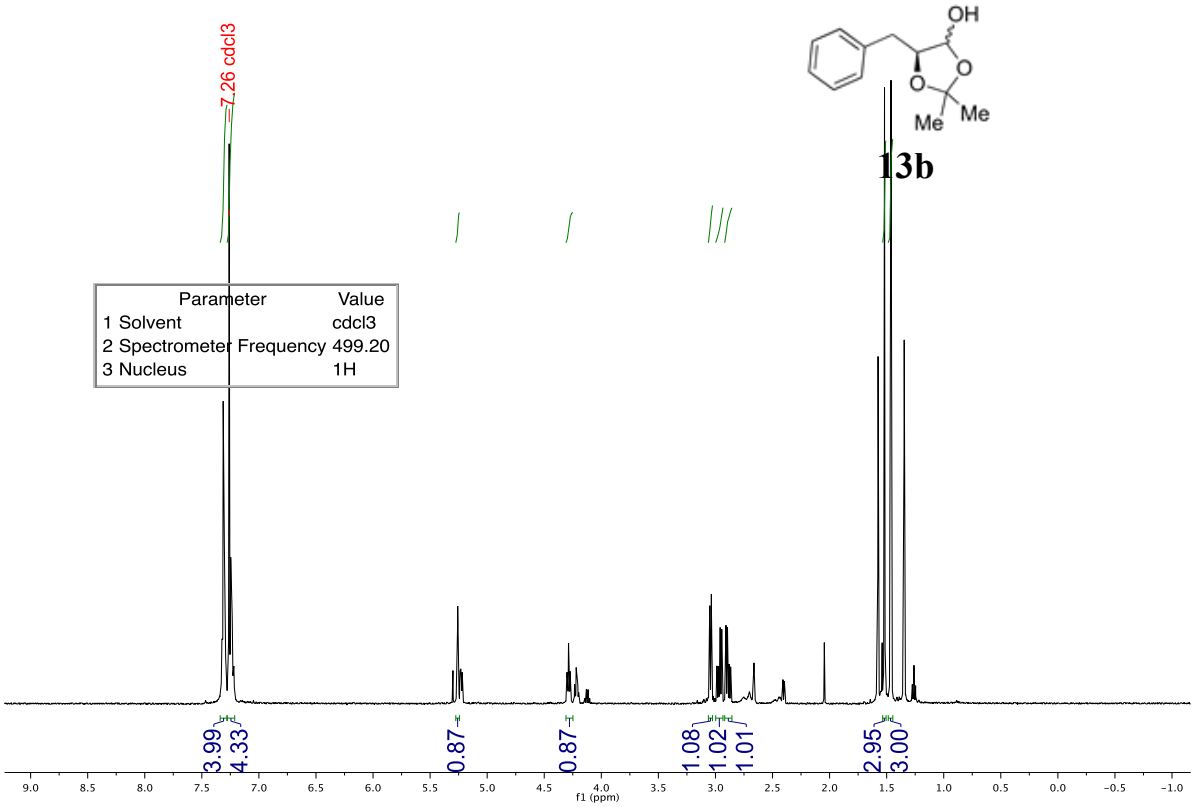

7.26 cdcl3
Me
Me
S13b
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.22
3 Nucleus 1H
1.75
3.25
0.85
1.01
1.00
2.99
2.97
f1 (ppm)

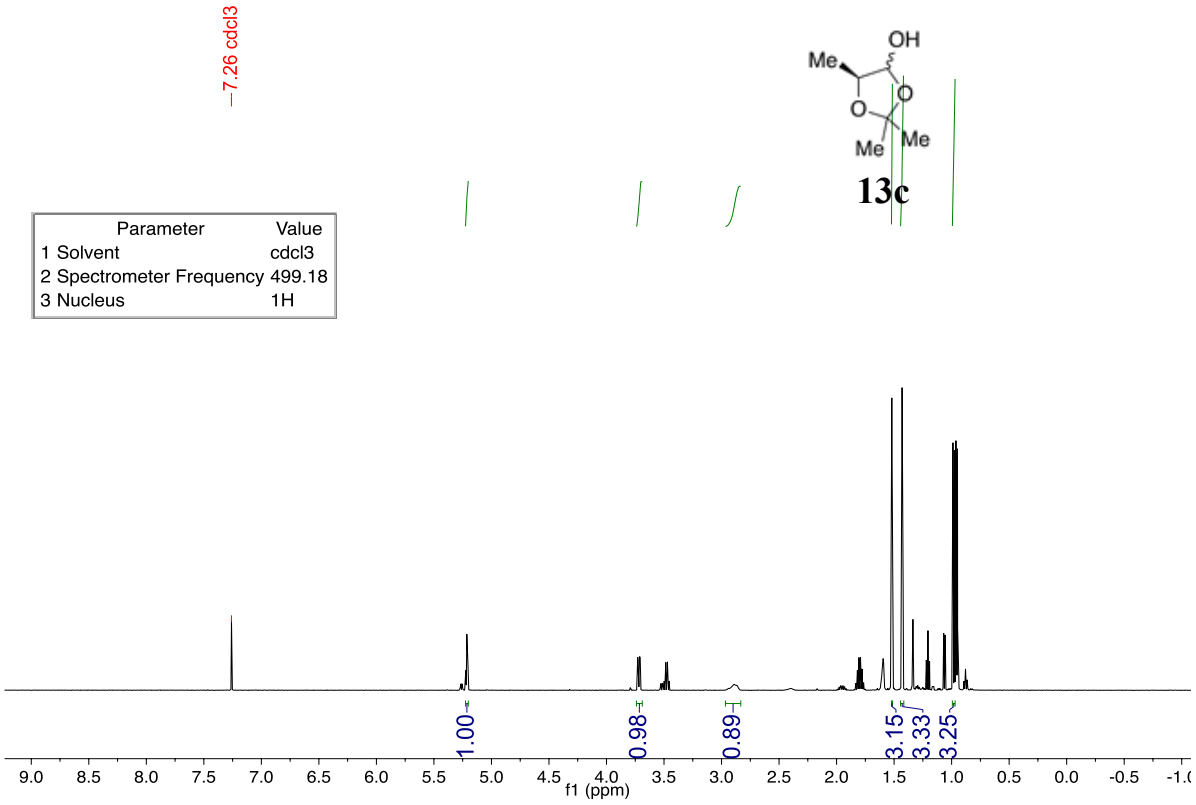

7.26 cdcl3
Me
O
O
O
Me
Me
S13c
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 399.75
3 Nucleus 1H
0.89
3.00
3.03
3.08
f1 (ppm)

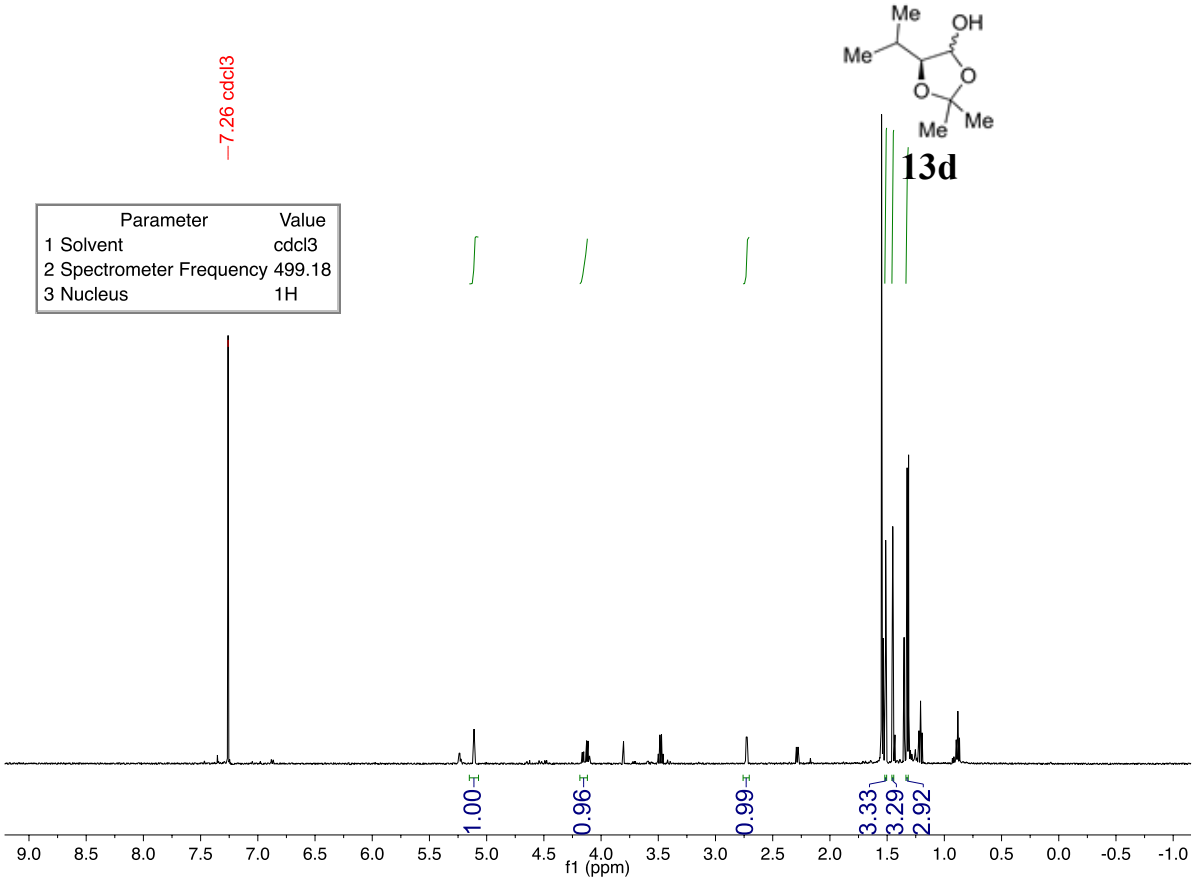

173.81
110.31
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
70.41
27.40
25.57
17.36
Me
O
O
O
Me
Me
S13c
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 125.80
3 Nucleus 13C
f1 (ppm)


7.26 cdcl3
Me
Me
O
O
O
Me
Me
S13d
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 399.75
3 Nucleus 1H
0.86
1.05
2.99
2.98
3.02
3.00
f1 (ppm)


7.26 cdcl3
OH
O
O
Me
Me
13a
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.18
3 Nucleus 1H
5.57
0.86
0.88
0.88
3.00
3.00
f1 (ppm)

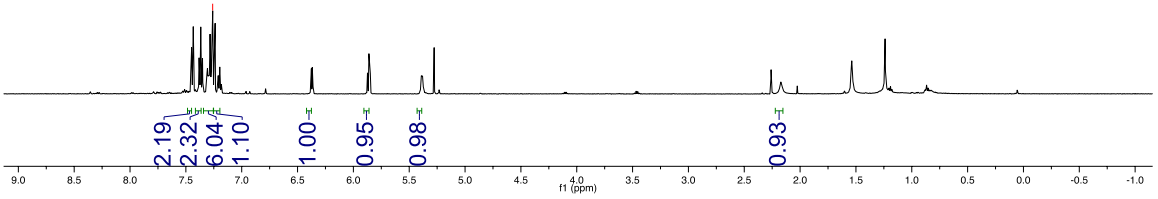

7.26 cdcl3
OH
O
O
Me
Me
13b
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.20
3 Nucleus 1H
3.99
4.33
0.87
0.87
1.08
1.02
1.01
2.95
3.00
f1 (ppm)

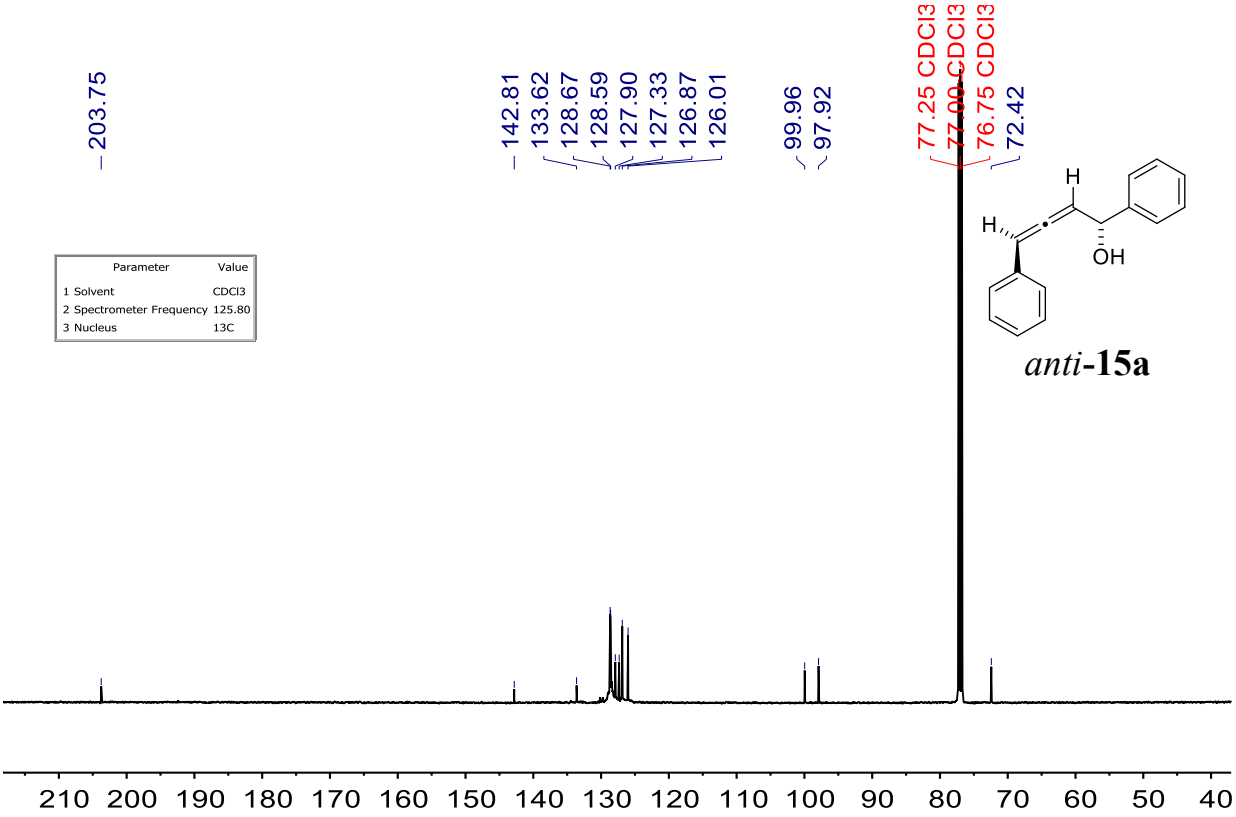

7.26 cdcl3
OH
Me
O
O
Me
Me
13c
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.18
3 Nucleus 1H
1.00
0.98
0.89
3.15
3.33
3.25
f1 (ppm)


7.26 cdcl3
Me
OH
Me
O
O
Me
Me
13d
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.18
3 Nucleus 1H
1.00
0.96
0.99
3.33
3.29
2.92
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)

anti-**15a**

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.18
3 Nucleus	1H



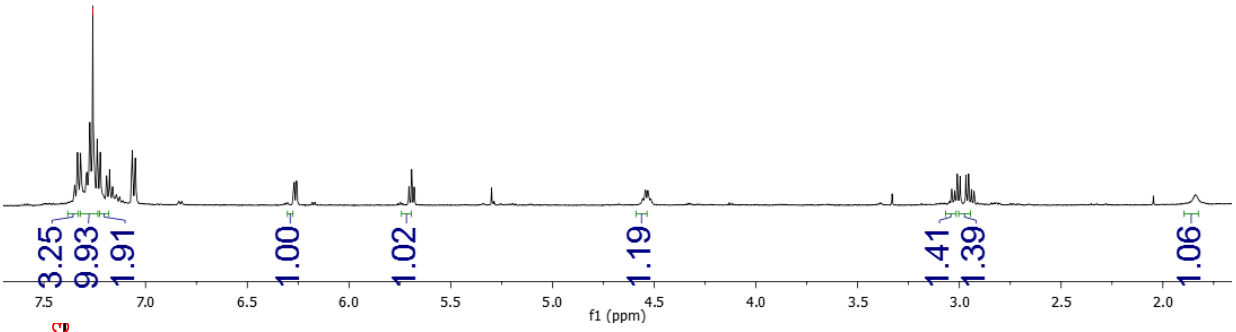


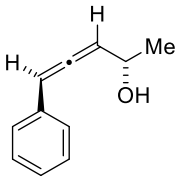
Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	125.80
3 Nucleus	13C

anti-**15a**

anti-**15b**

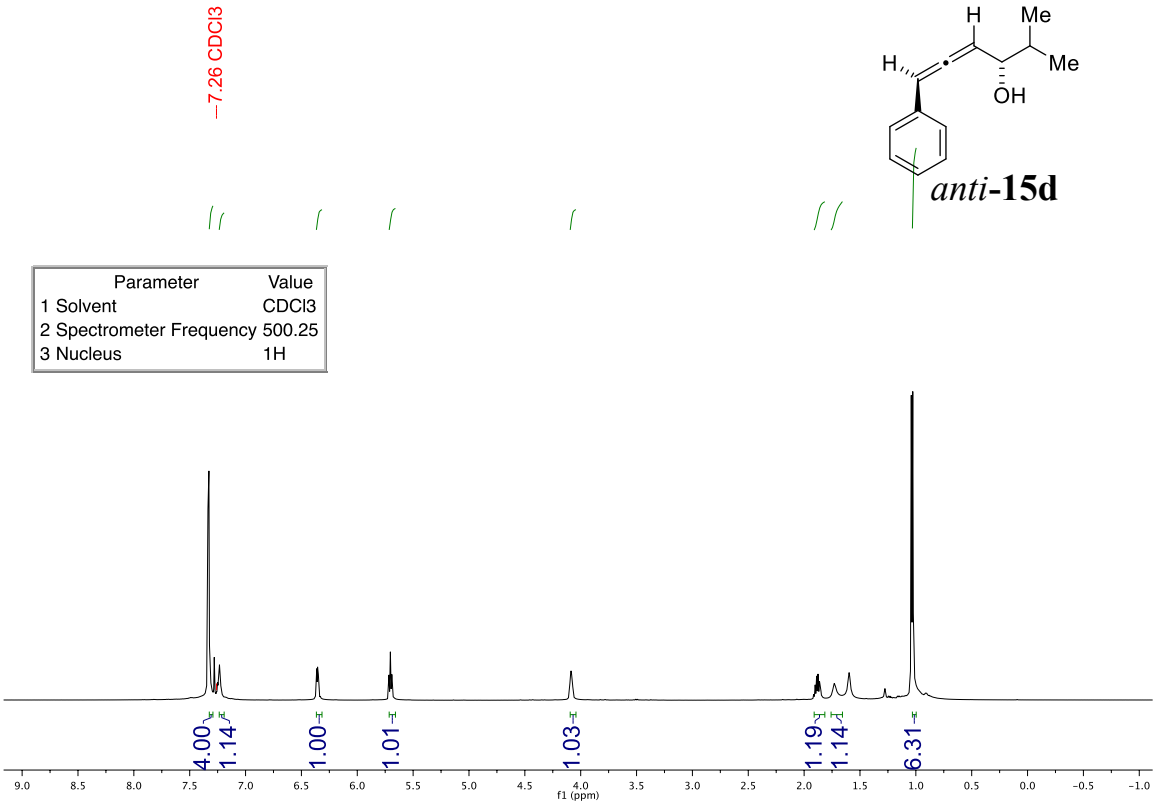
	Parameter	Value
1	Solvent	cdcl3
2	Spectrometer Frequency	499.18
3	Nucleus	1H

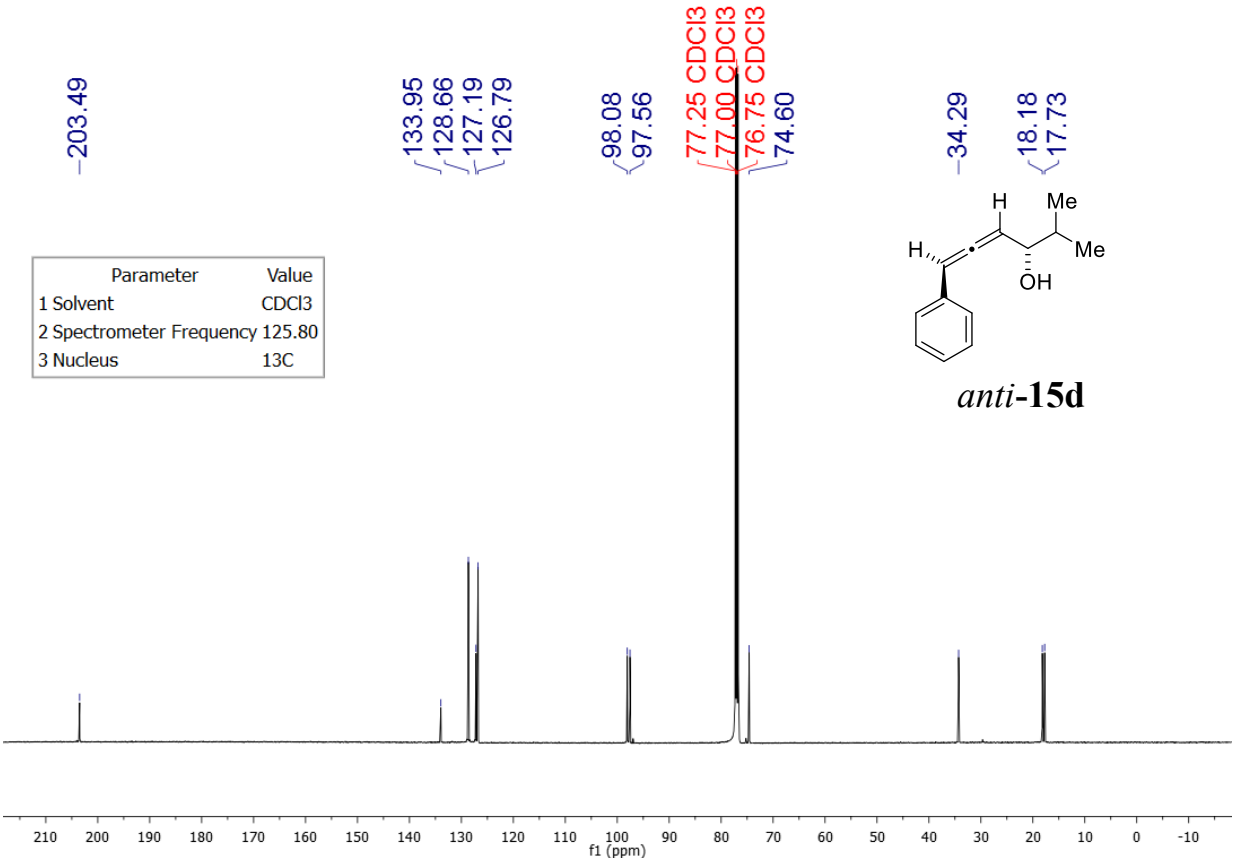


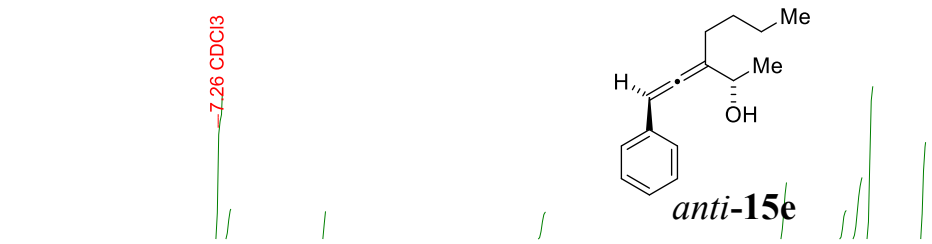


anti-**15c**

	Parameter	Value
1	Solvent	CDCl3
2	Spectrometer Frequency	500.25
3	Nucleus	1H

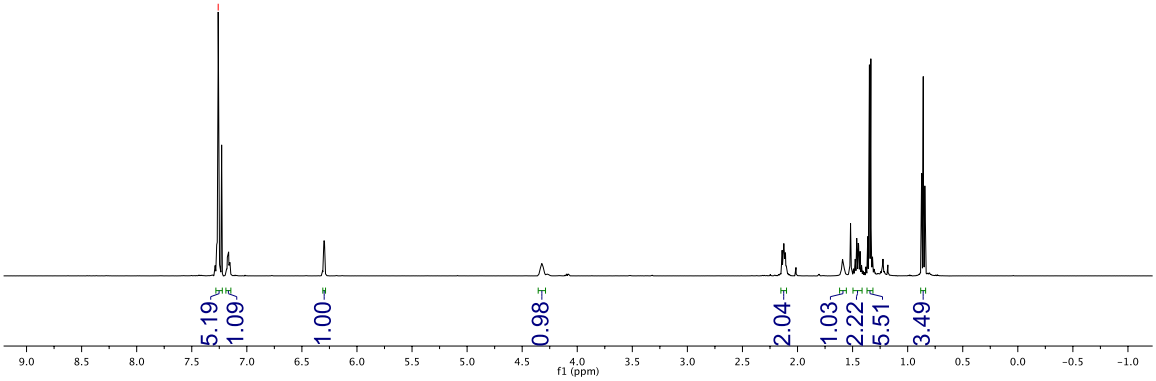

7.26 CDCl3
H
Me
H
Me
OH
anti-15d
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 500.25
3 Nucleus 1H
4.00
1.14
1.00
1.01
1.03
1.19
1.14
6.31
f1 (ppm)

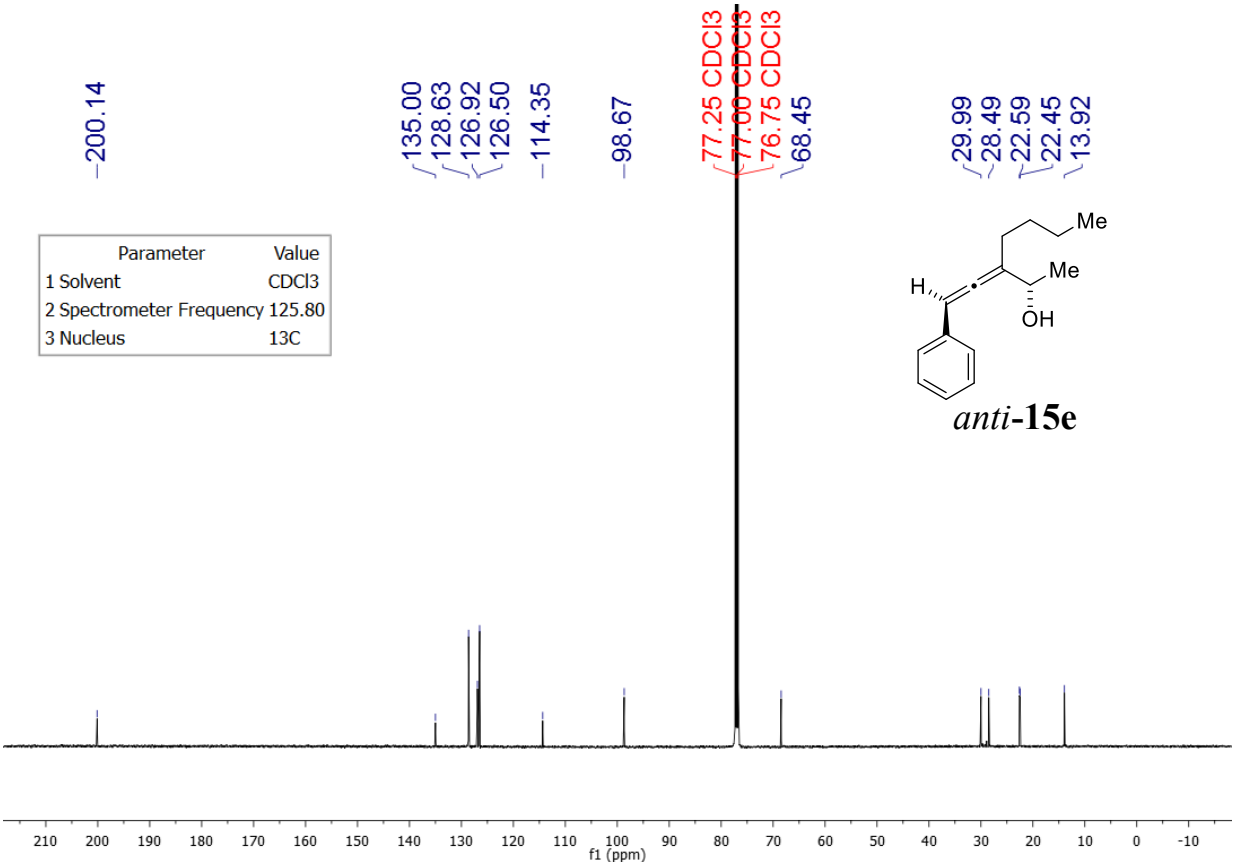

203.49
133.95
128.66
127.19
126.79
98.08
97.56
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
74.60
34.29
18.18
17.73
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 125.80
3 Nucleus 13C
H
Me
H
Me
OH
anti-15d
f1 (ppm)



anti-**15e**

Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	500.25
3 Nucleus	1H

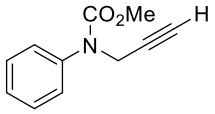




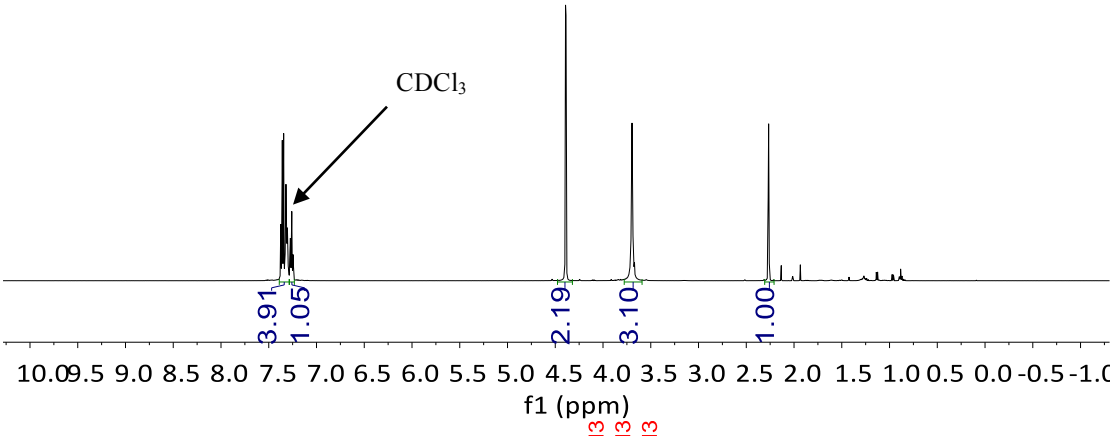
Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	125.80
3 Nucleus	13C

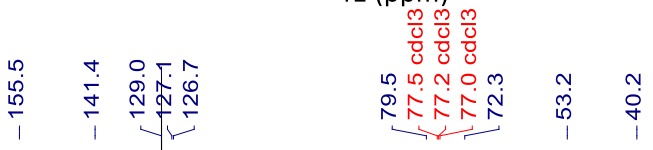
anti-**15e**

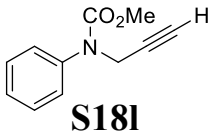
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



S18l

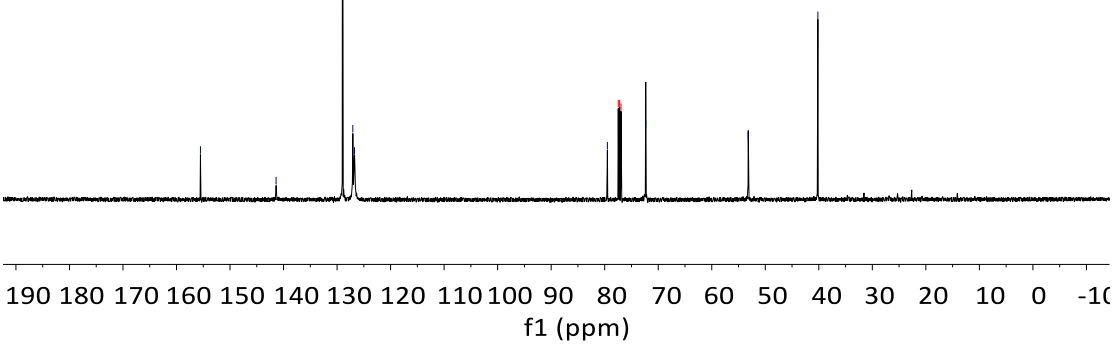




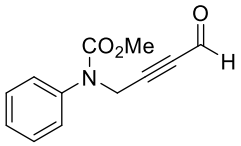


S18l

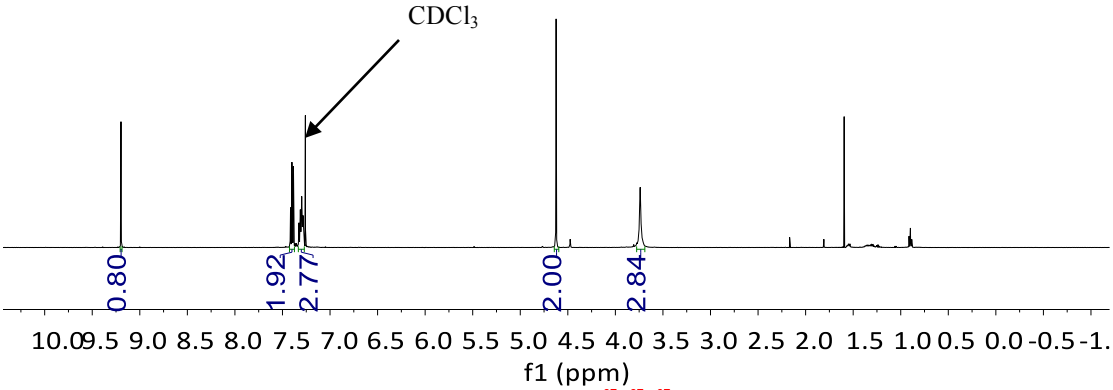
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

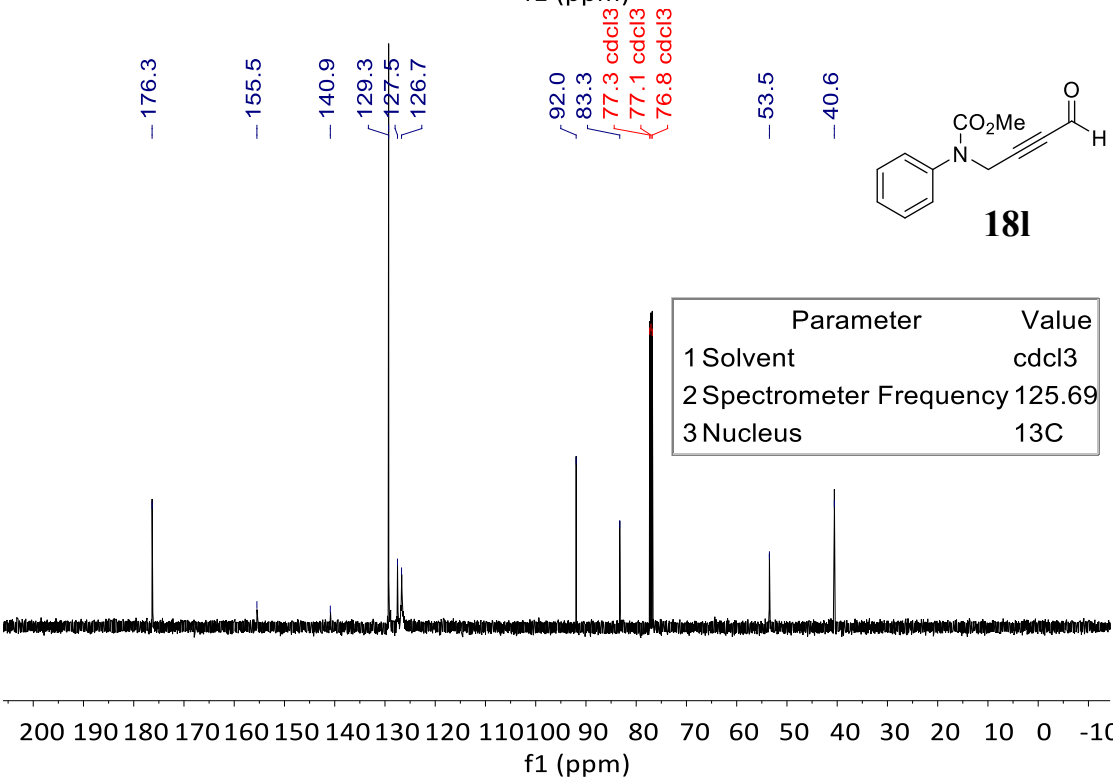


Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



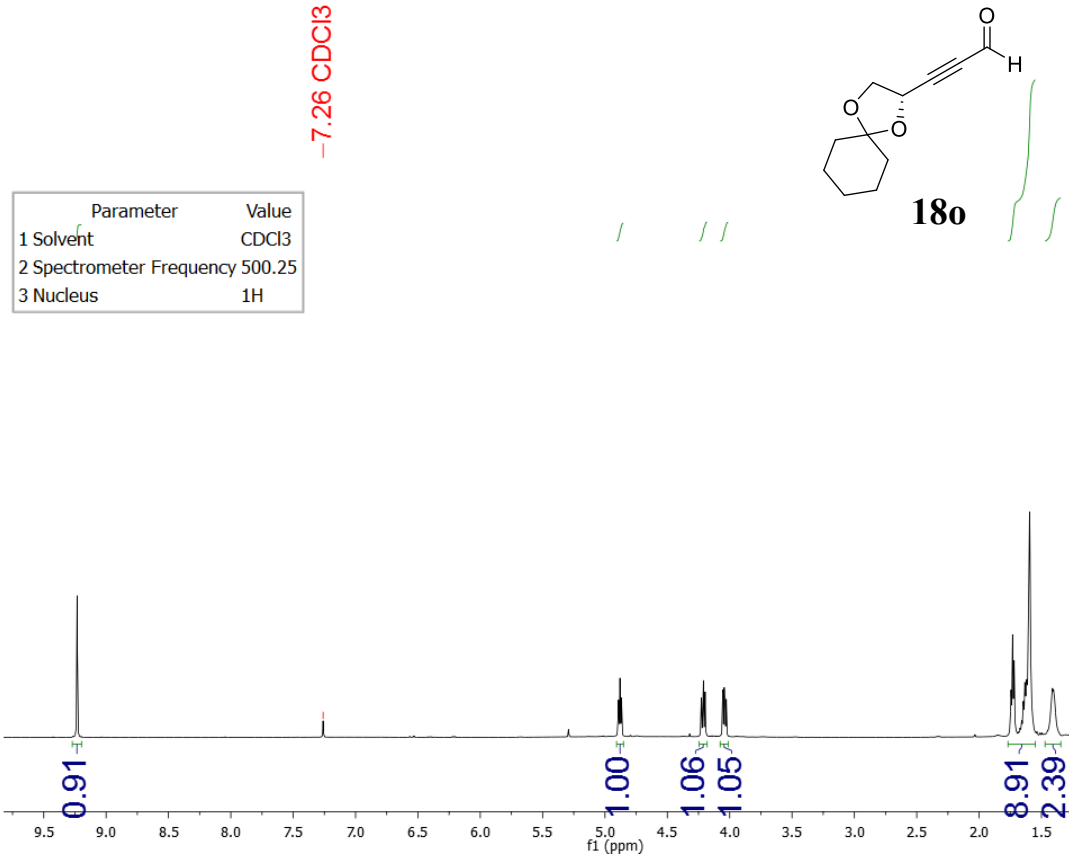
18l

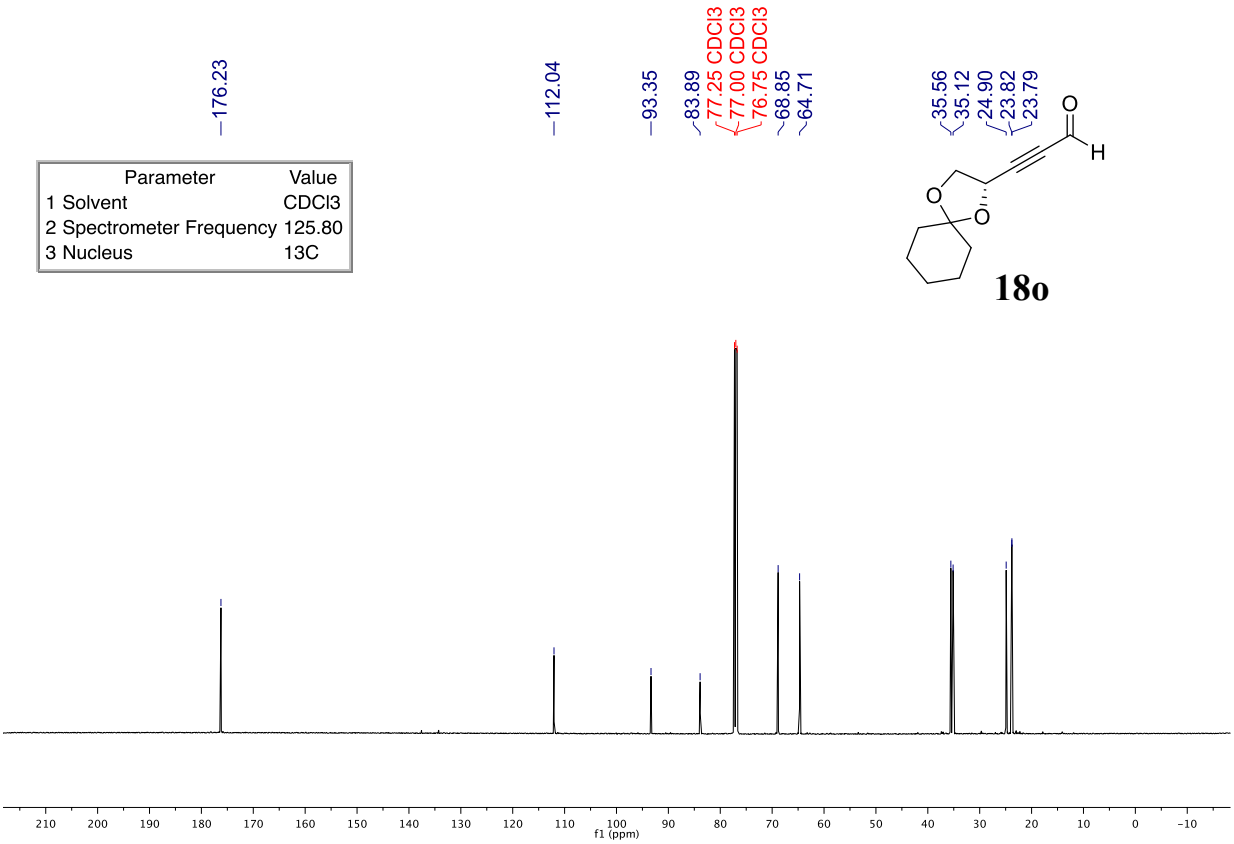


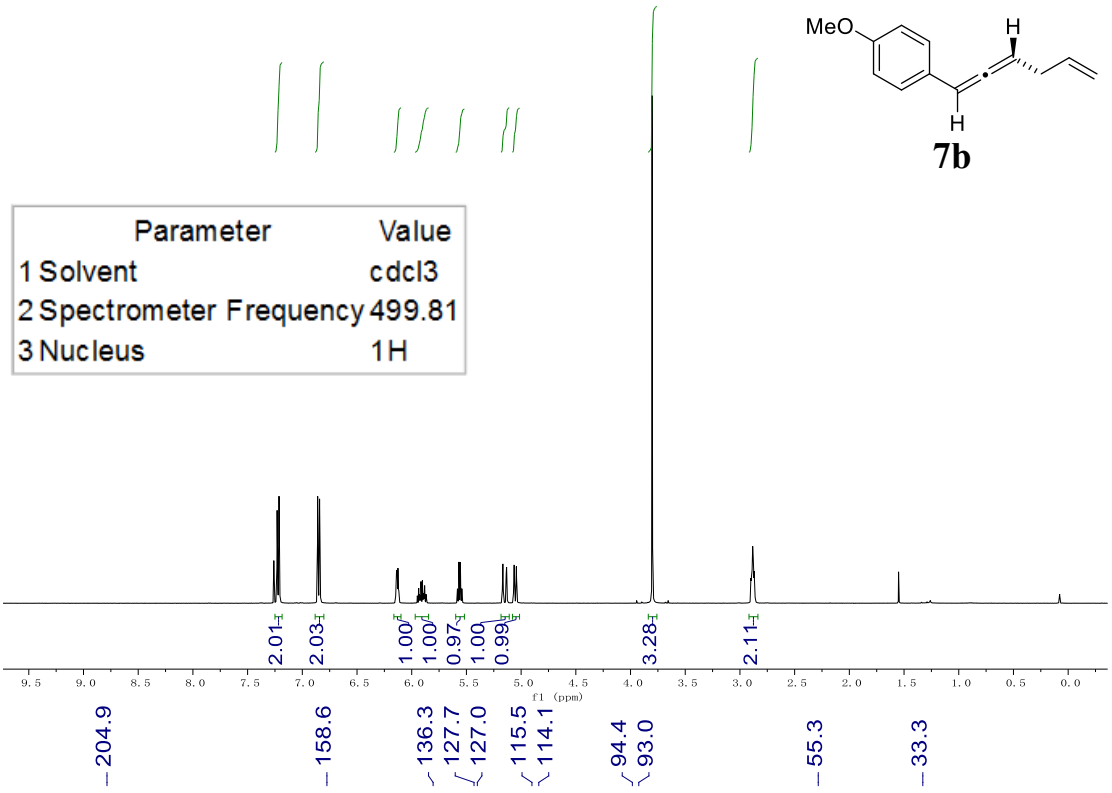


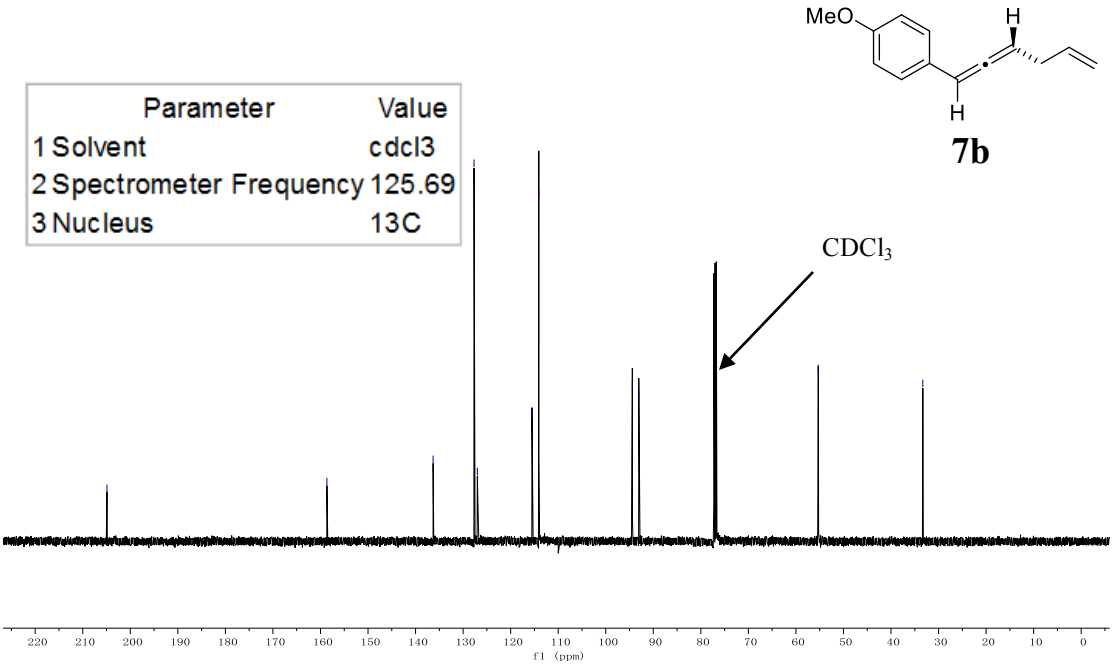
18l

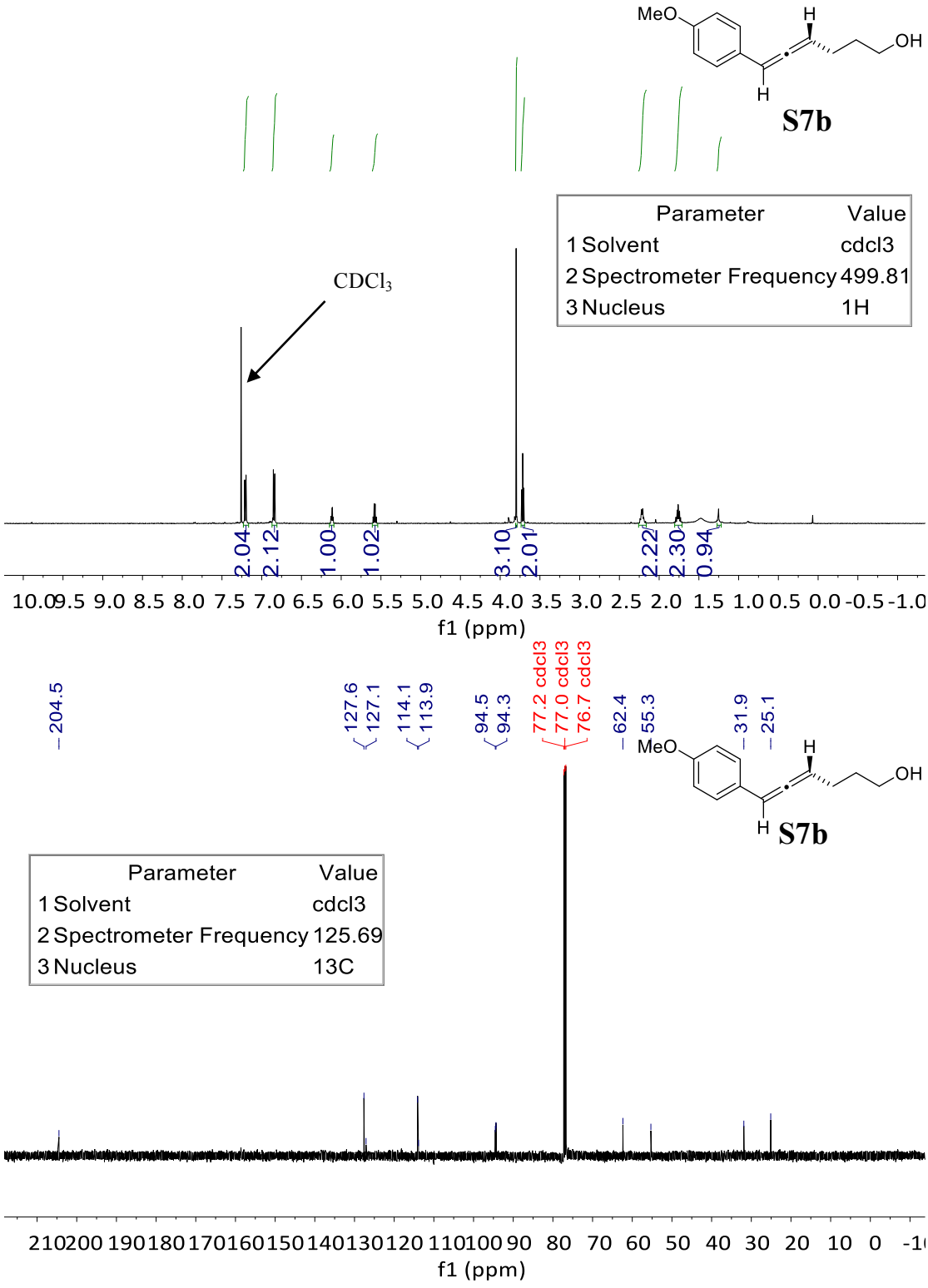
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

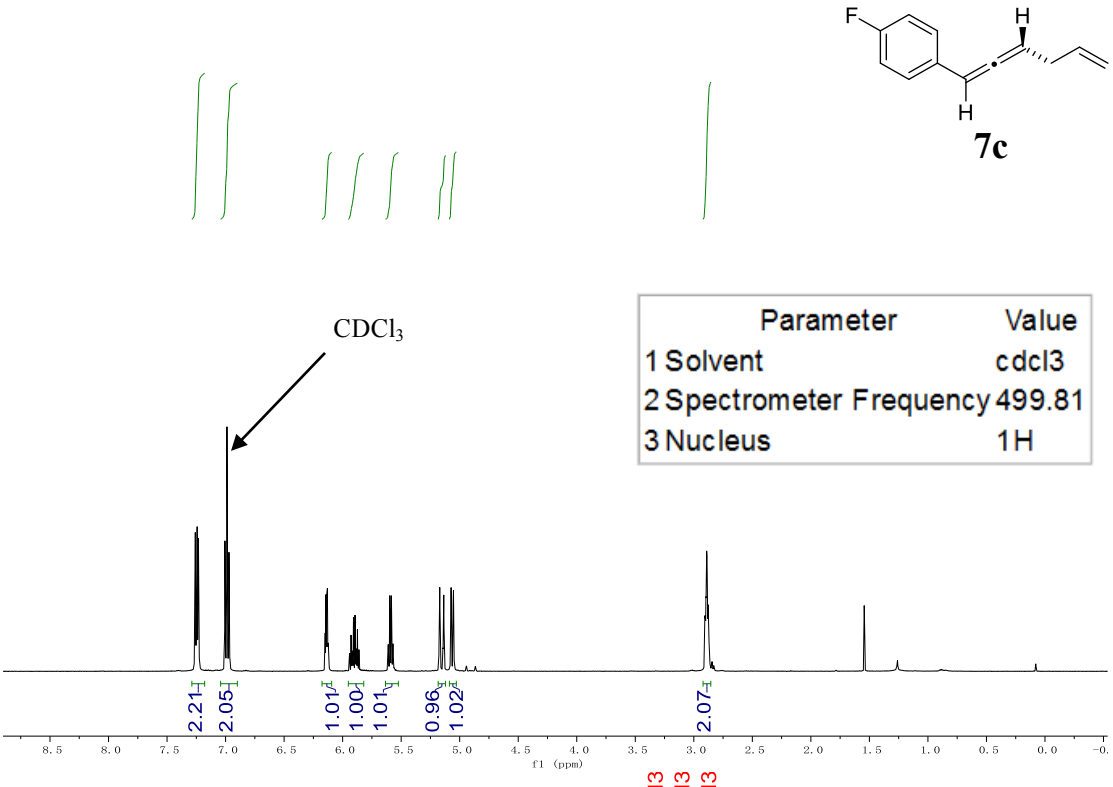

7.26 CDCl3
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 500.25
3 Nucleus 1H
18o
0.91
1.00
1.06
1.05
8.91
2.39
f1 (ppm)

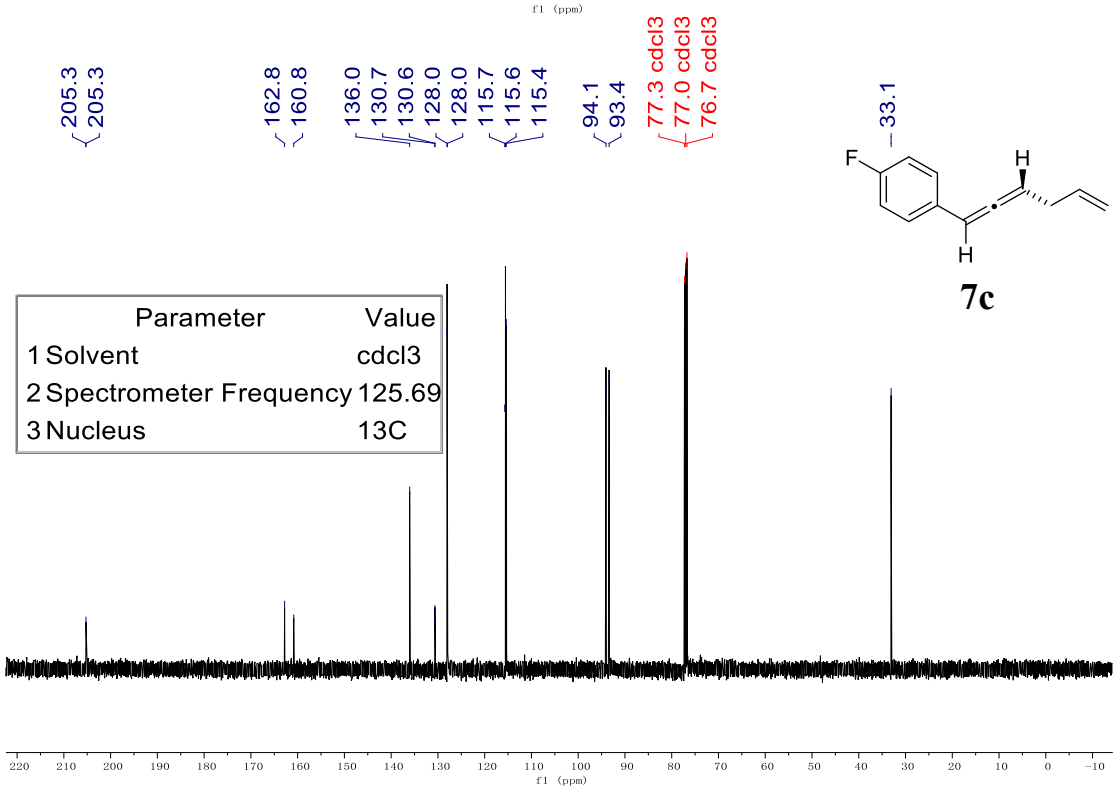

176.23
112.04
93.35
83.89
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
68.85
64.71
35.56
35.12
24.90
23.82
23.79
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 125.80
3 Nucleus 13C
18o
f1 (ppm)


MeO
H
H
7b
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
2.01
2.03
1.00
1.00
0.97
1.00
0.99
3.28
2.11
f1 (ppm)
204.9
158.6
136.3
127.7
127.0
115.5
114.1
94.4
93.0
55.3
33.3


MeO
H
H
7b
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
CDCl3
f1 (ppm)

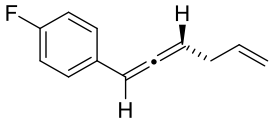

MeO
H
OH
H
S7b
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
2.04
2.12
1.00
1.02
3.10
2.01
2.22
2.30
0.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
204.5
127.6
127.1
114.1
113.9
94.5
94.3
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3
62.4
55.3
31.9
25.1
MeO
H
OH
H
S7b
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
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)


F
H
H
7c
CDCl3
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
2.21
2.05
1.01
1.00
1.01
0.96
1.02
2.07
f1 (ppm)

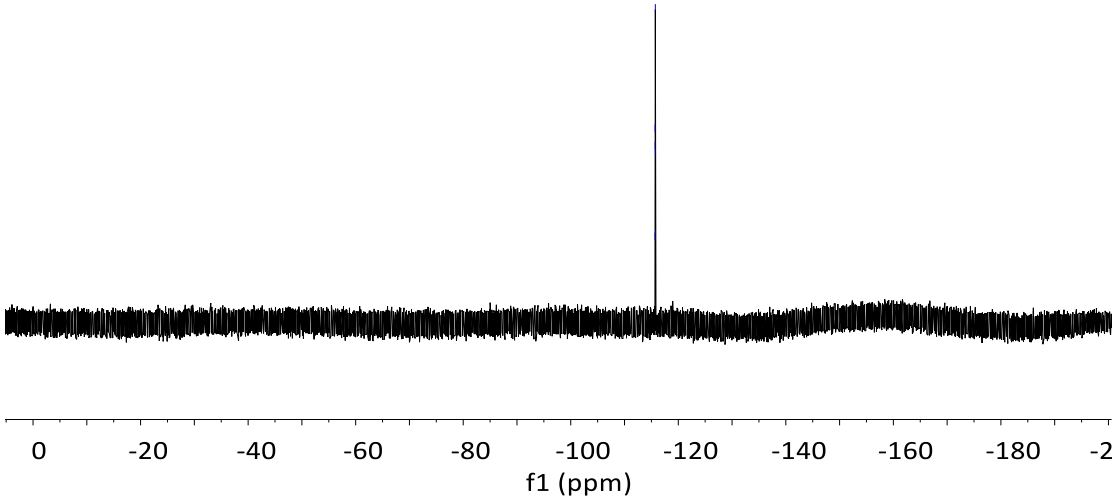

205.3
205.3
162.8
160.8
136.0
130.7
130.6
128.0
128.0
115.7
115.6
115.4
94.1
93.4
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
33.1
F
H
H
7c
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
f1 (ppm)

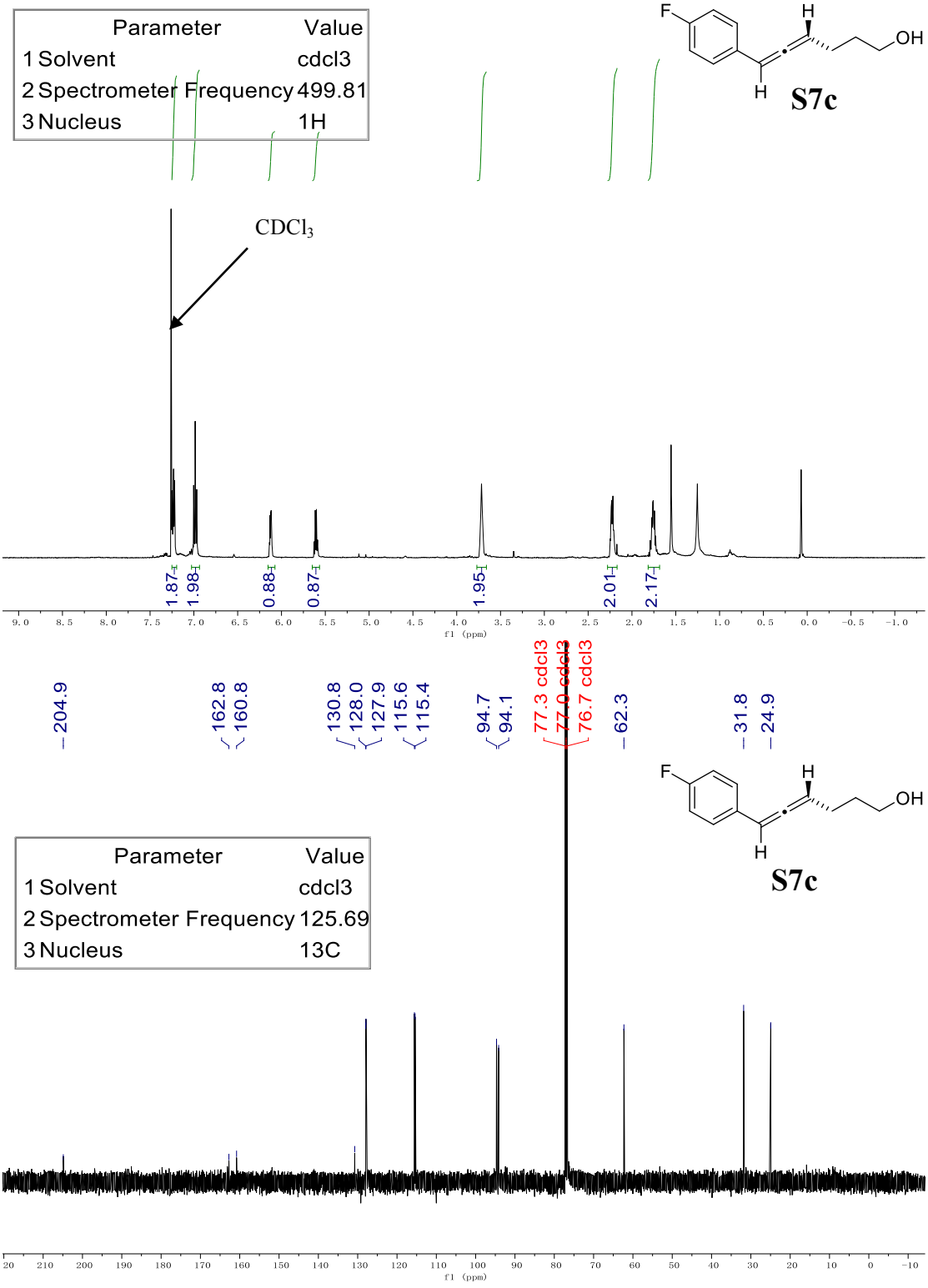
	Parameter	Value
1	Solvent	cdcl3
2	Spectrometer Frequency	470.24
3	Nucleus	19F

-115.7
-115.7
-115.7
-115.7
-115.7
-115.7
-115.8



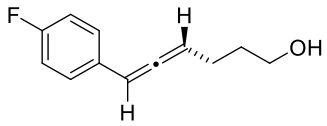
7c



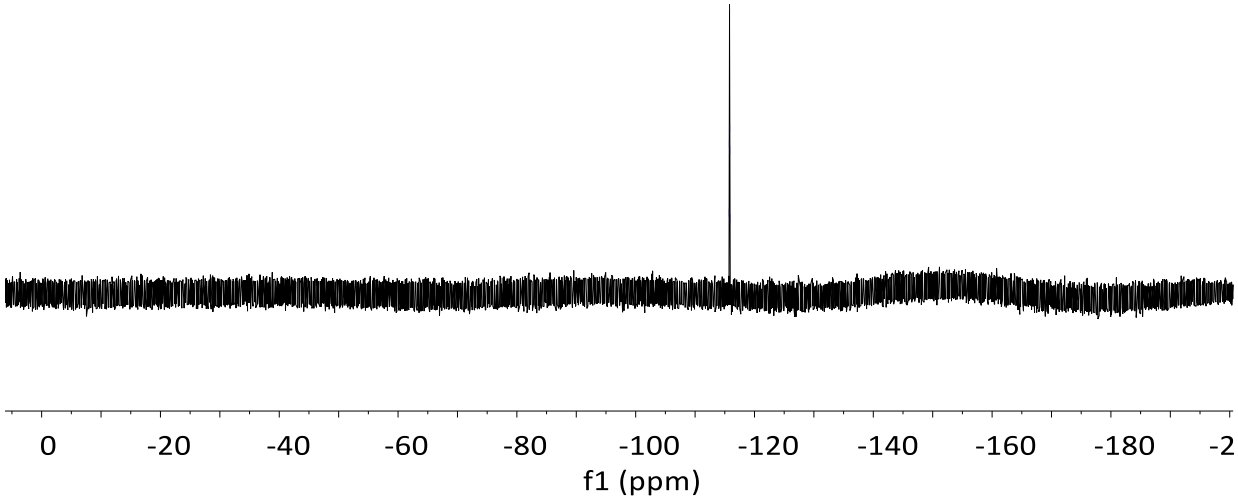

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
F
H
OH
H
S7c
CDCl3
1.87
1.98
0.88
0.87
1.95
2.01
2.17
f1 (ppm)
204.9
162.8
160.8
130.8
128.0
127.9
115.6
115.4
94.7
94.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
62.3
31.8
24.9
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
F
H
OH
H
S7c
f1 (ppm)

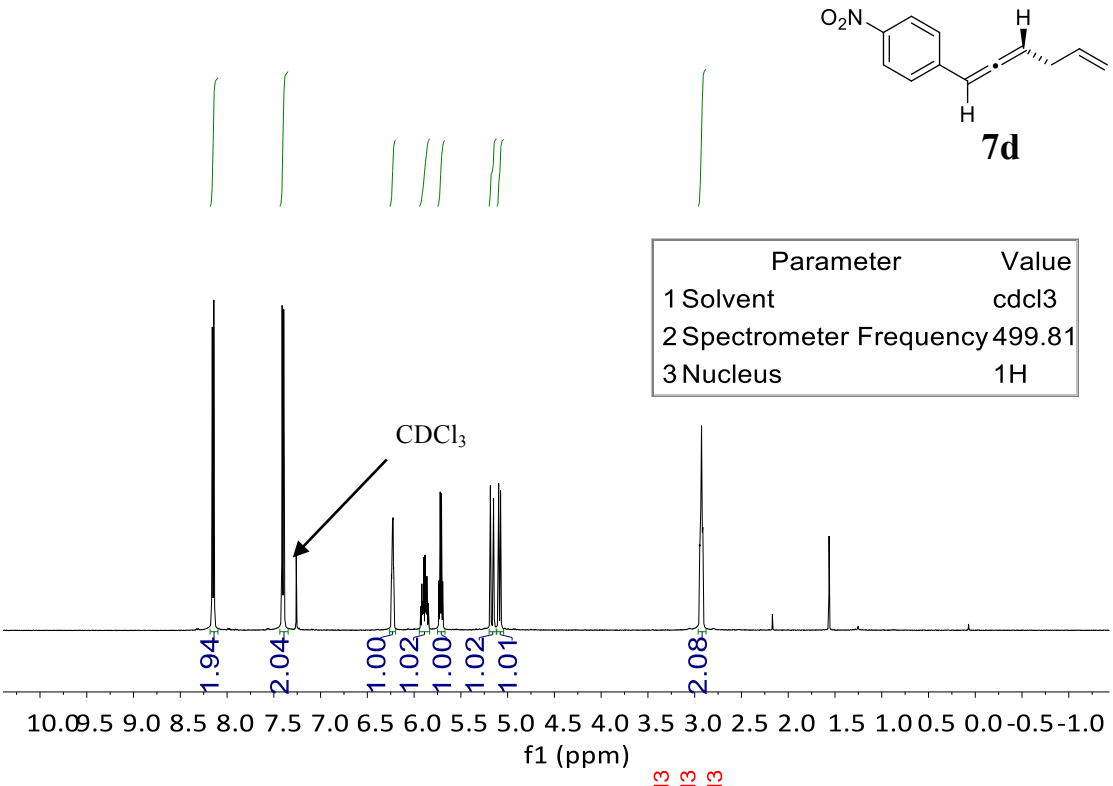
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	470.24
3 Nucleus	19F

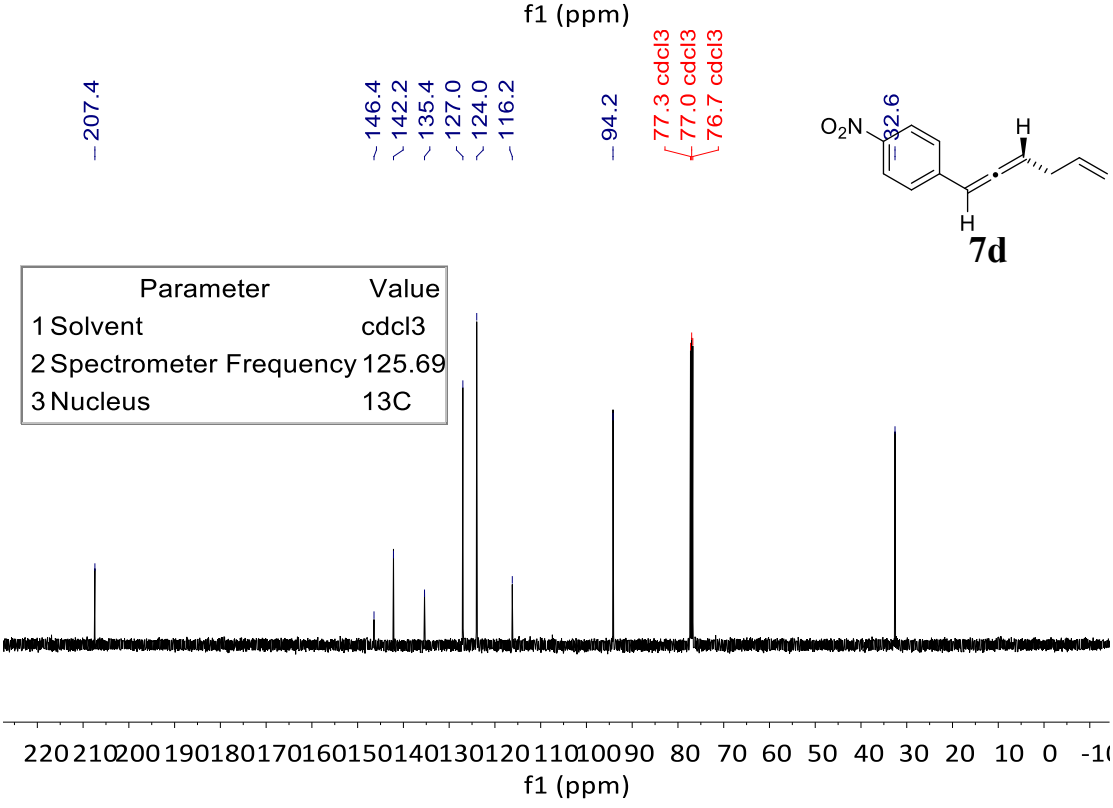
-115.8
-115.8
-115.8
-115.8
-115.8
-115.8
-115.8

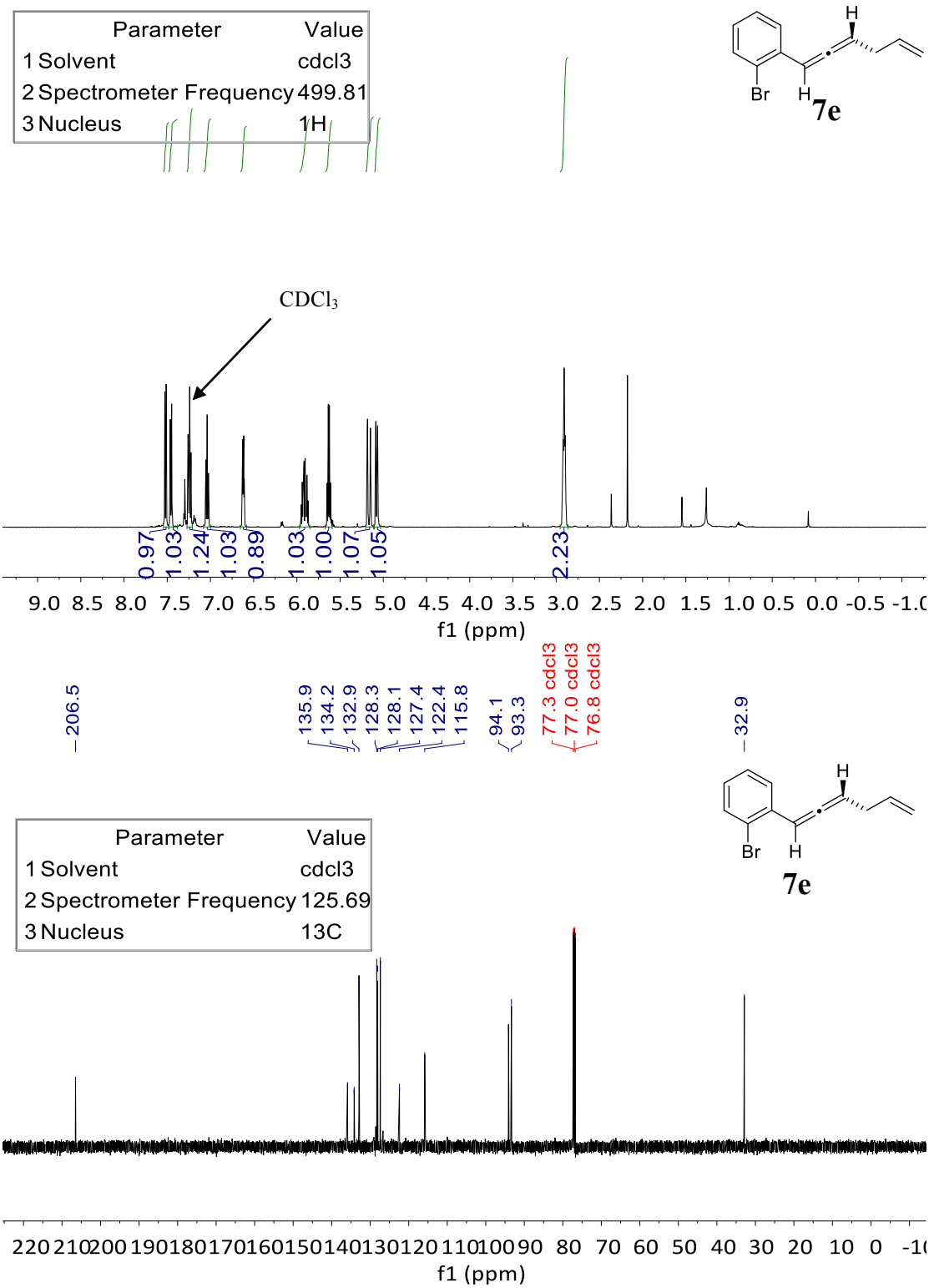


S7c

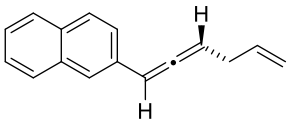



O2N
H
H
7d
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
1.94
2.04
1.00
1.02
1.00
1.02
1.01
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

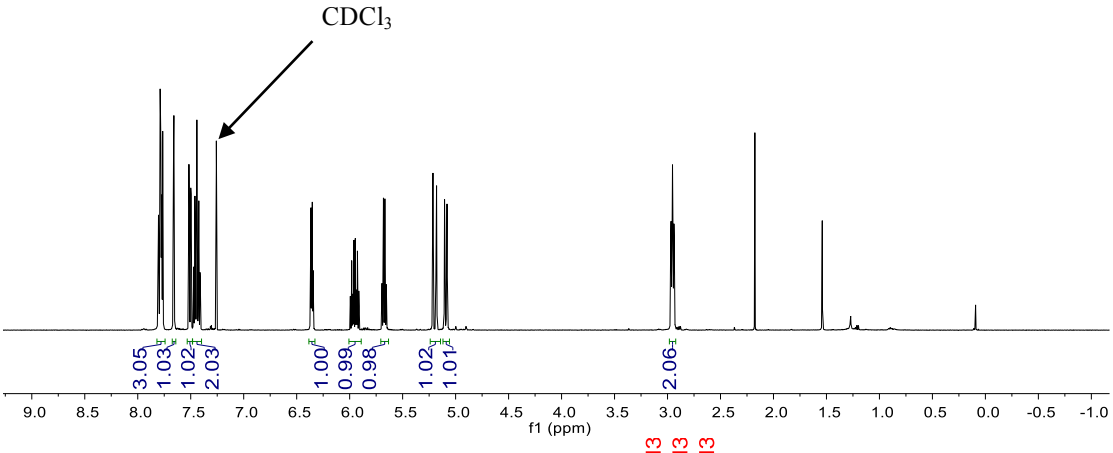

207.4
146.4
142.2
135.4
127.0
124.0
116.2
94.2
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
82.6
O2N
H
H
7d
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

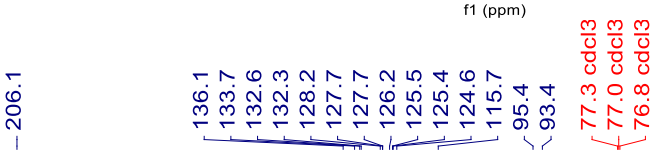

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
Br
H
7e
CDCl3
0.97
1.03
1.24
1.03
0.89
1.03
1.00
1.07
1.05
2.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
206.5
135.9
134.2
132.9
128.3
128.1
127.4
122.4
115.8
94.1
93.3
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
32.9
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
Br
H
7e
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)

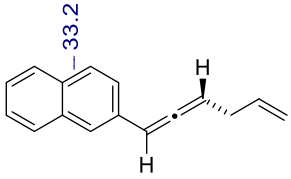
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



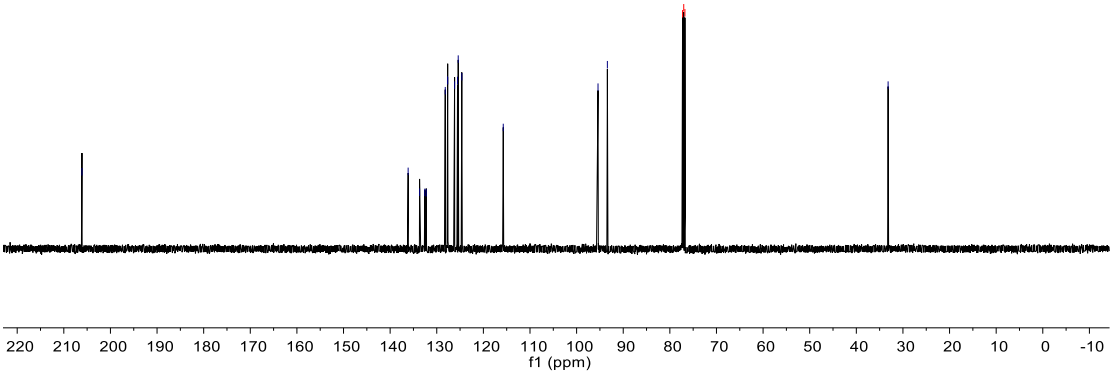
7f





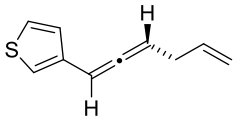


Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

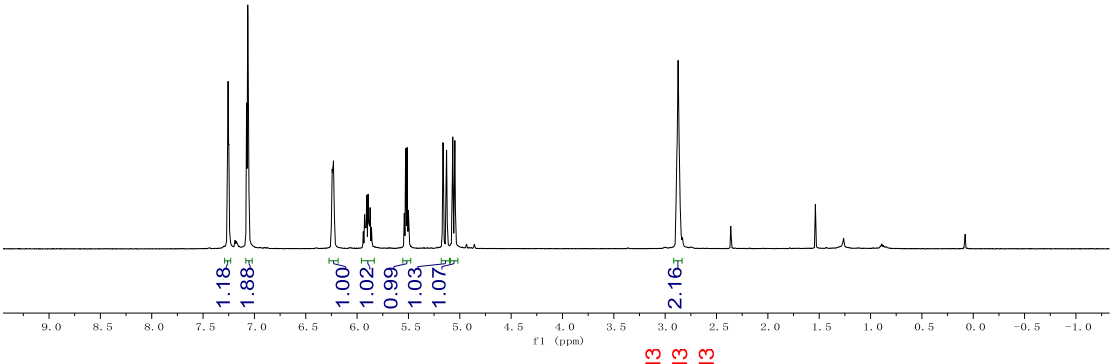


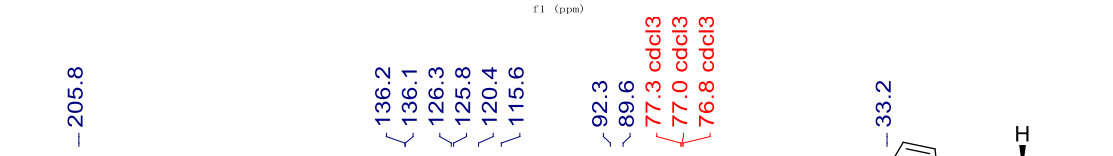
7f

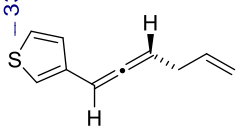
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



7g

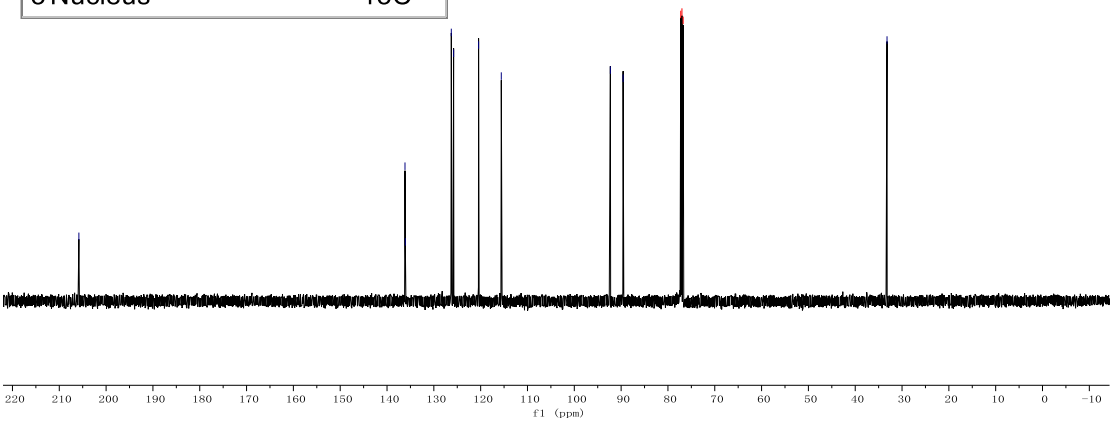




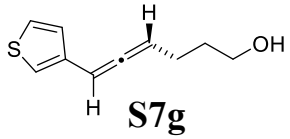


7g

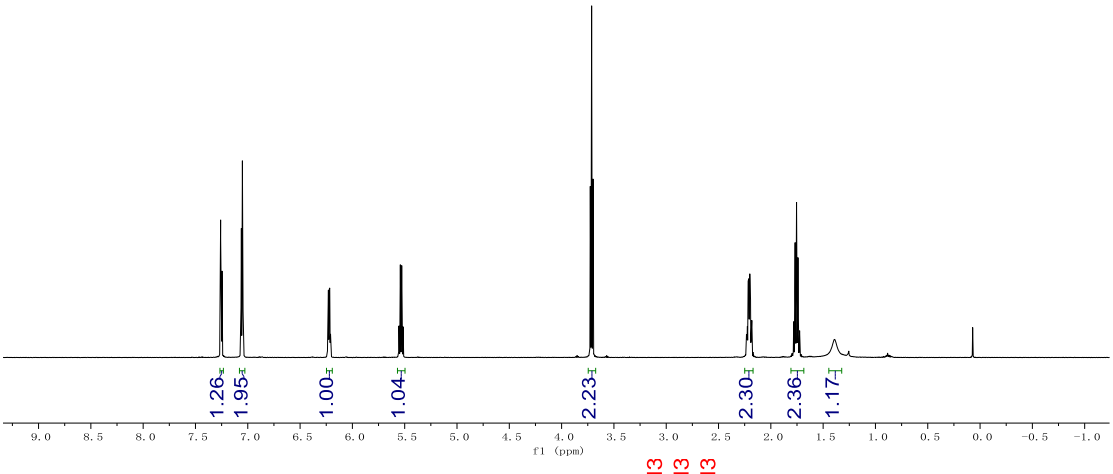
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

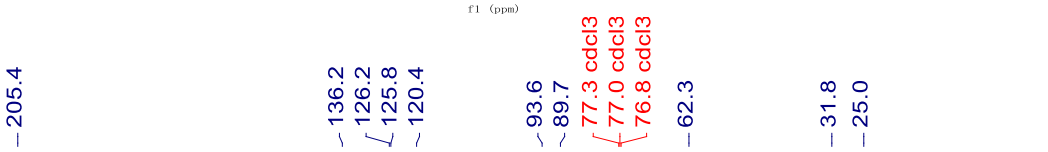


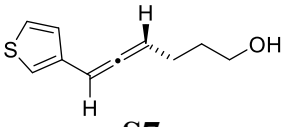
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



S7g

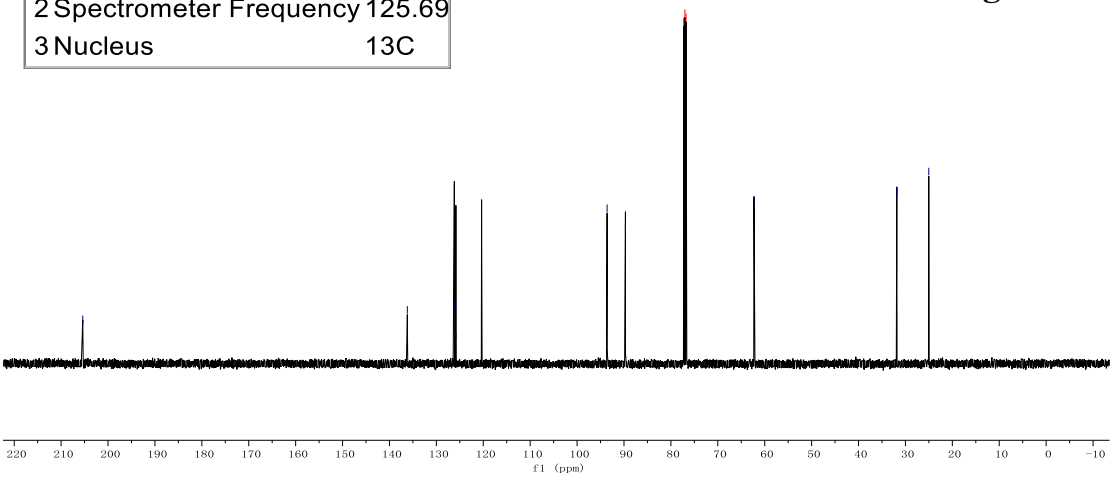


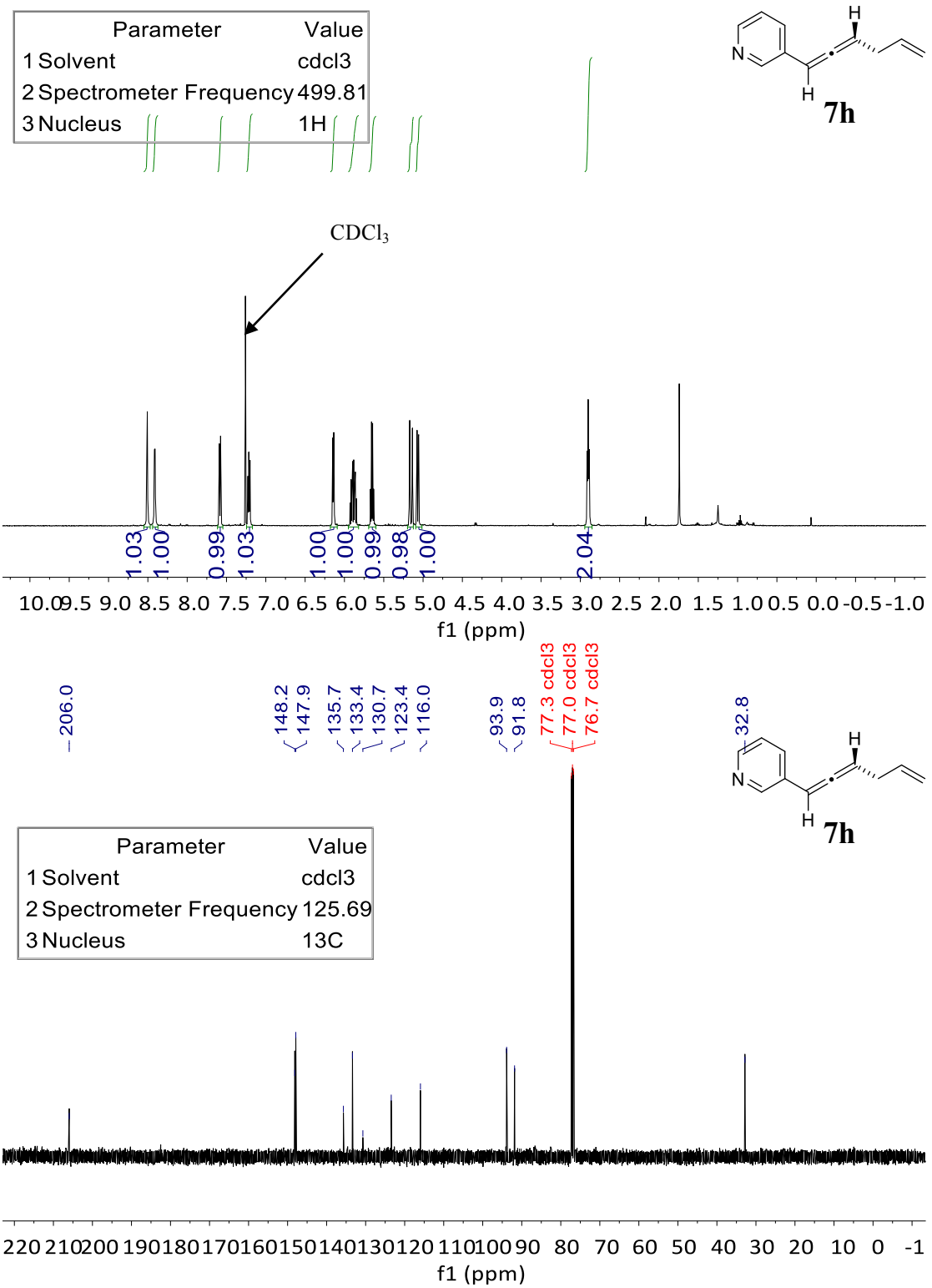


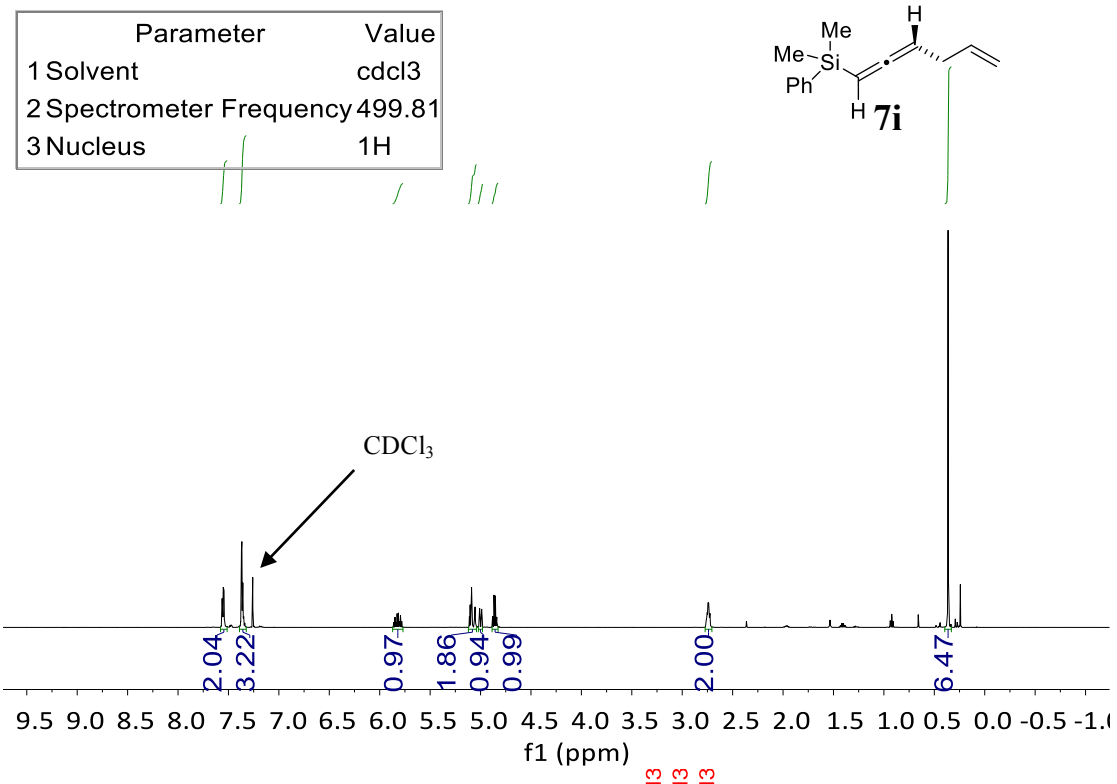


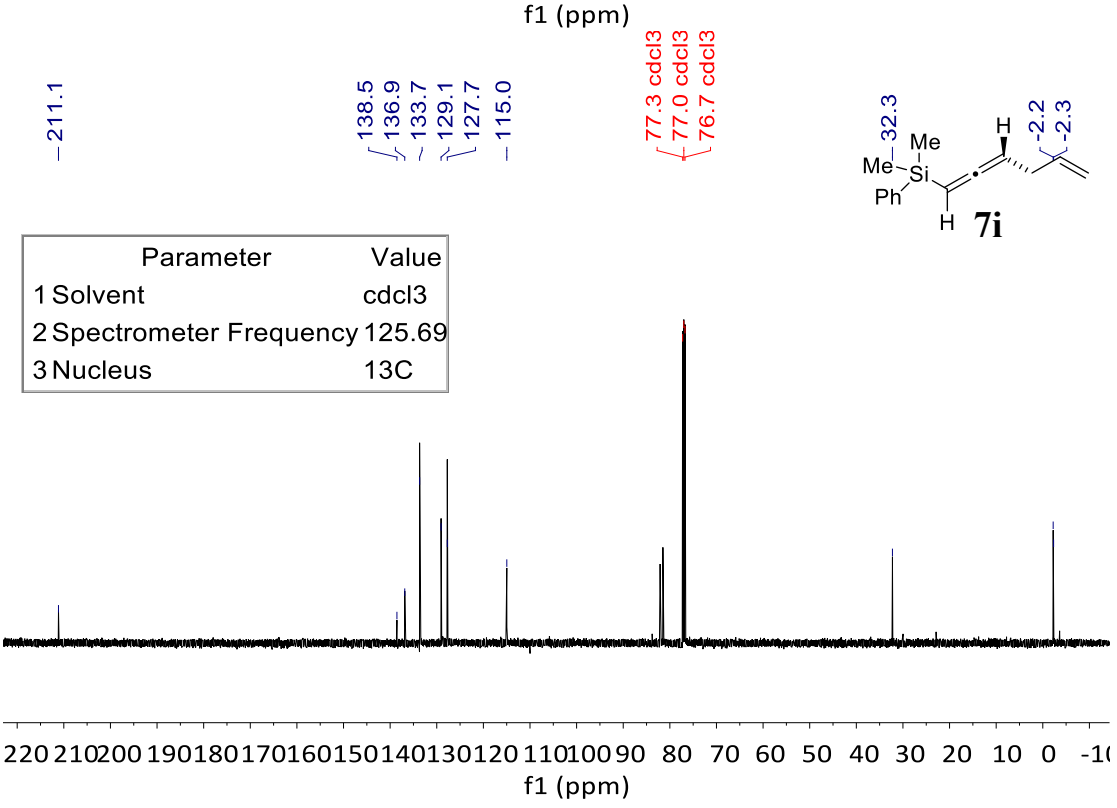
S7g

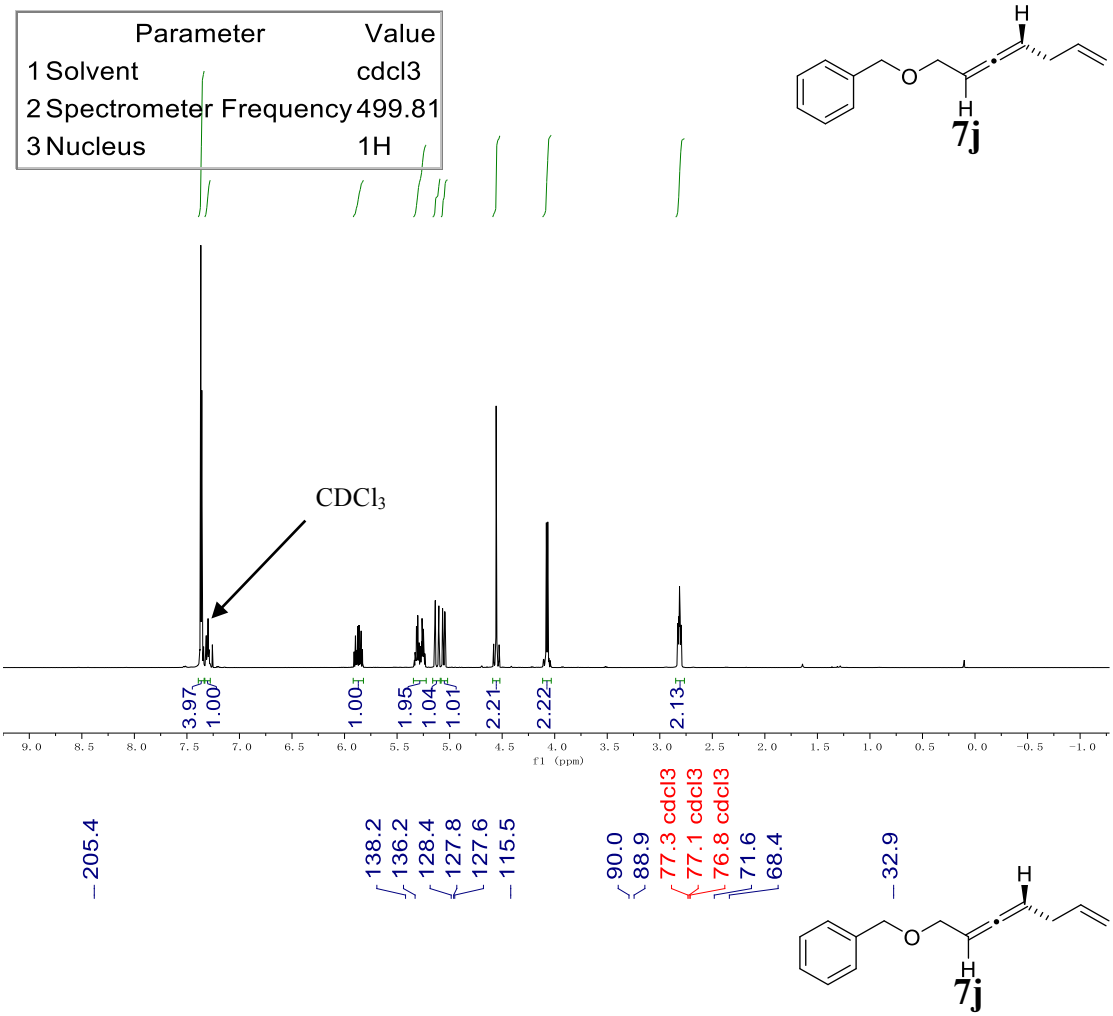
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

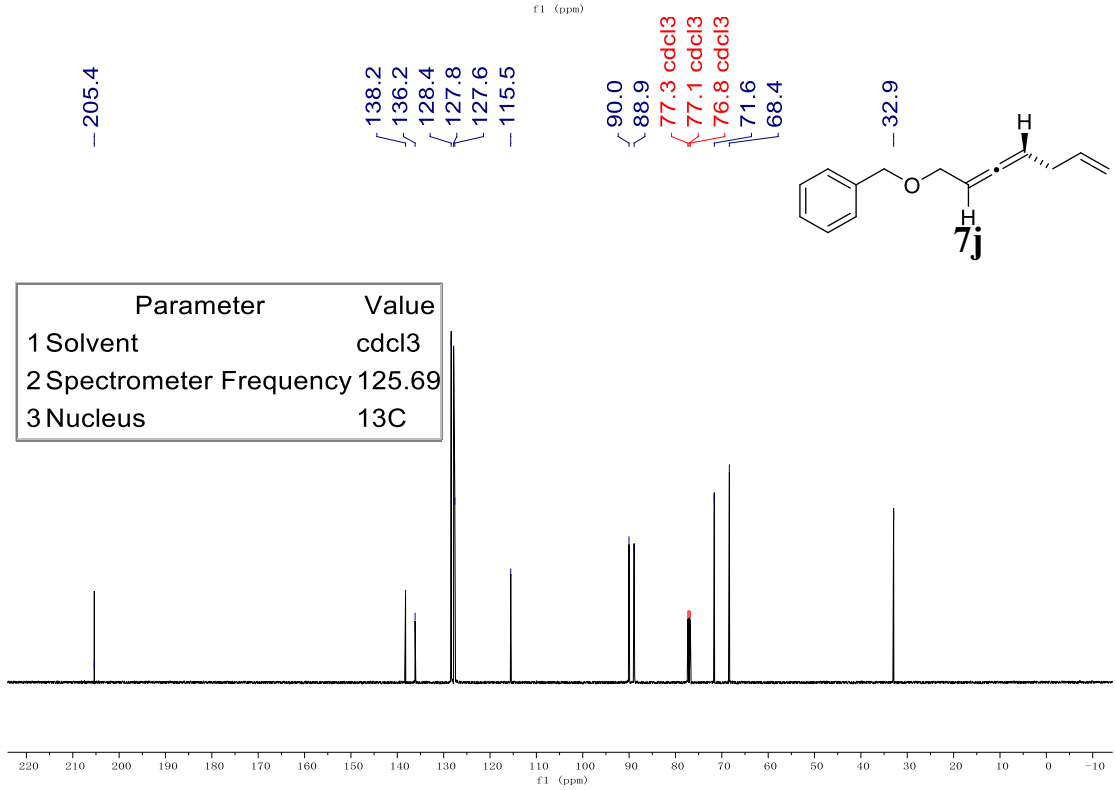


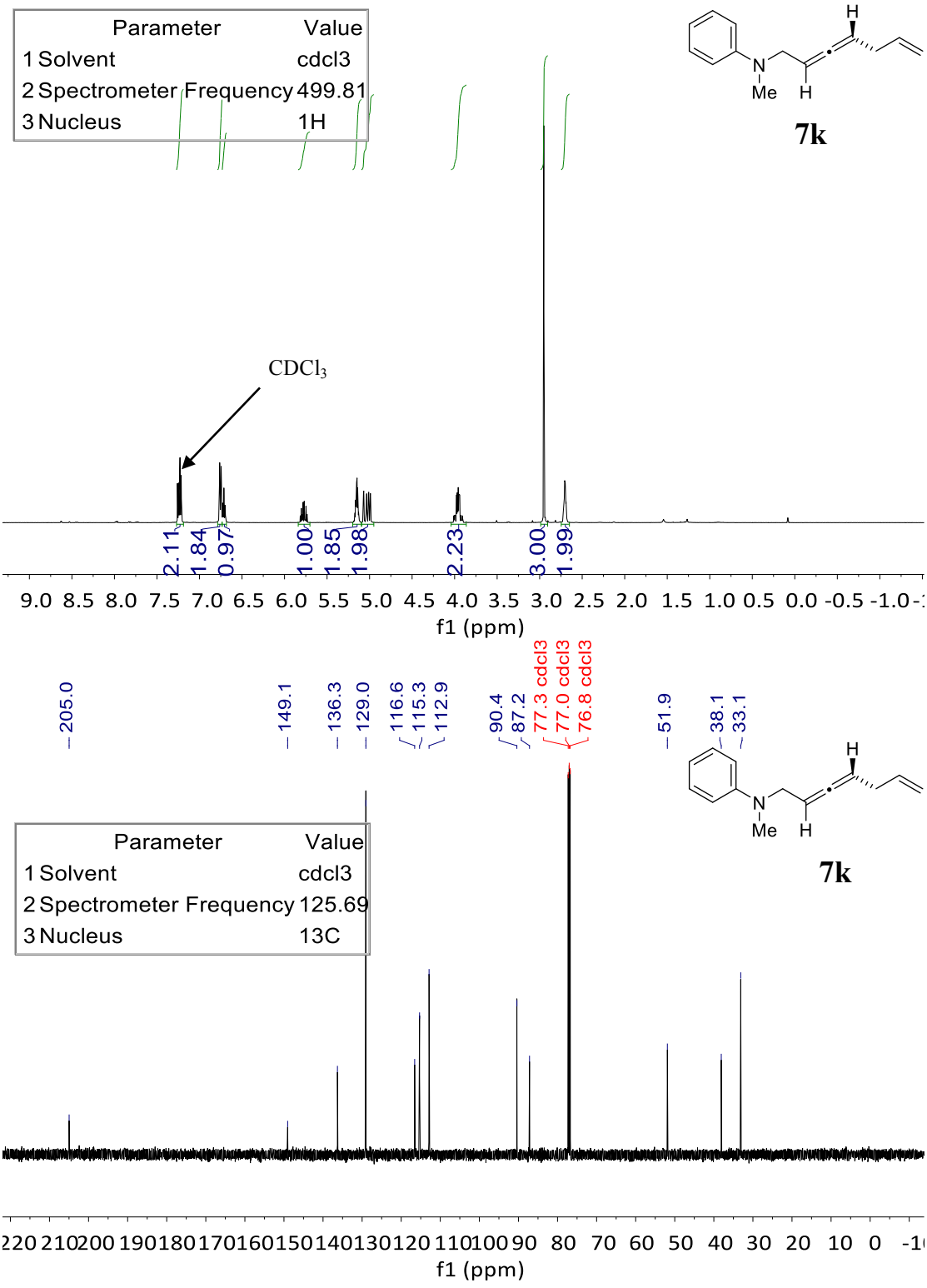

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
1.03
1.00
0.99
1.03
1.00
1.00
0.99
0.98
1.00
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
7h
206.0
148.2
147.9
135.7
133.4
130.7
123.4
116.0
93.9
91.8
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
32.8
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)
7h

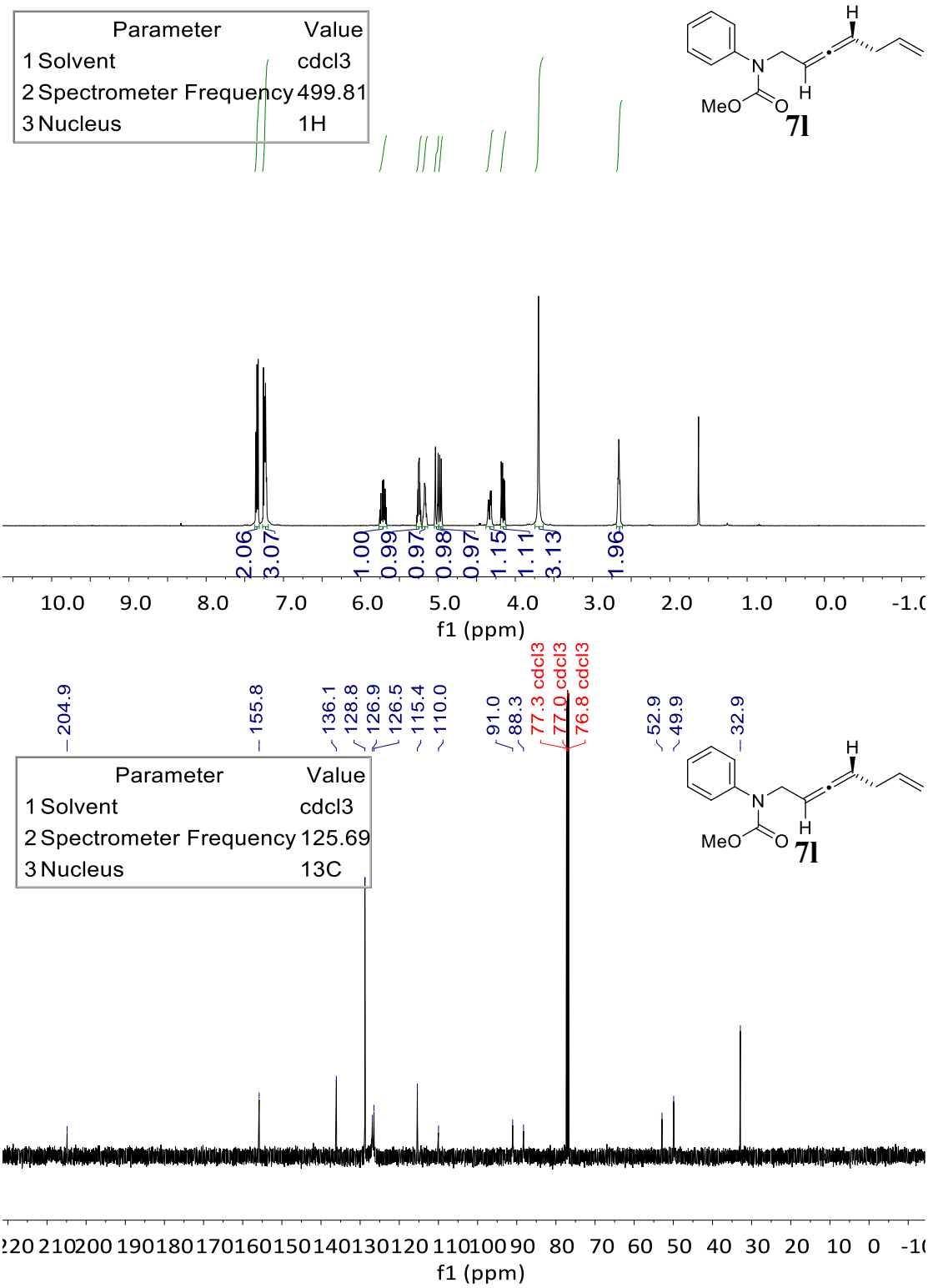

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
Me
Me
Si
Ph
H
H
7i
CDCl3
2.04
3.22
0.97
1.86
0.94
0.99
2.00
6.47
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

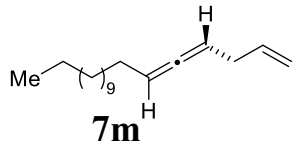

211.1
138.5
136.9
133.7
129.1
127.7
115.0
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
32.3
-2.2
-2.3
Me
Me
Si
Ph
H
H
7i
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
7j
CDCl3
3.97
1.00
1.00
1.95
1.04
1.01
2.21
2.22
2.13
f1 (ppm)


205.4
138.2
136.2
128.4
127.8
127.6
115.5
90.0
88.9
77.3 cdcl3
77.1 cdcl3
76.8 cdcl3
71.6
68.4
32.9
7j
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
f1 (ppm)

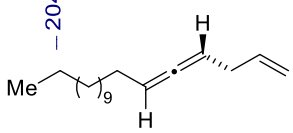

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
2.11
1.84
0.97
1.00
1.85
1.98
2.23
3.00
1.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
7k
205.0
149.1
136.3
129.0
116.6
115.3
112.9
90.4
87.2
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
51.9
38.1
33.1
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
7k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
MeO
O
N
H
H
7l
2.06
3.07
1.00
0.99
0.97
0.98
0.97
1.15
1.11
3.13
1.96
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
204.9
155.8
136.1
128.8
126.9
126.5
115.4
110.0
91.0
88.3
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
52.9
49.9
32.9
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
MeO
O
N
H
H
7l
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



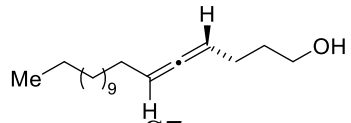
7m

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



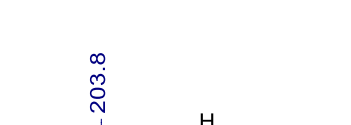
7m

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C



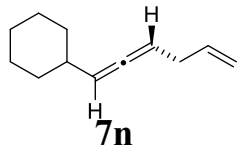
S7m

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



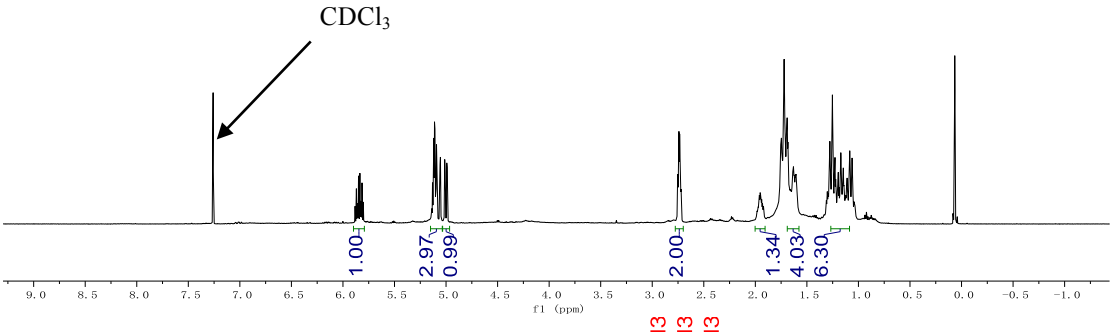
S7m

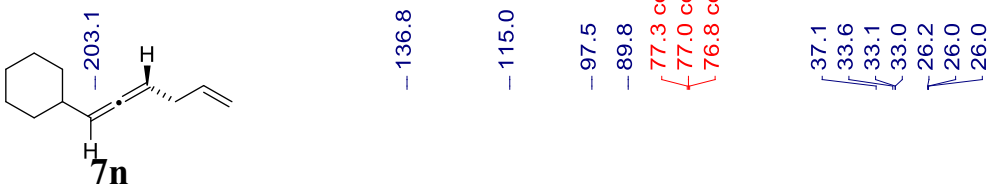
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C



7n

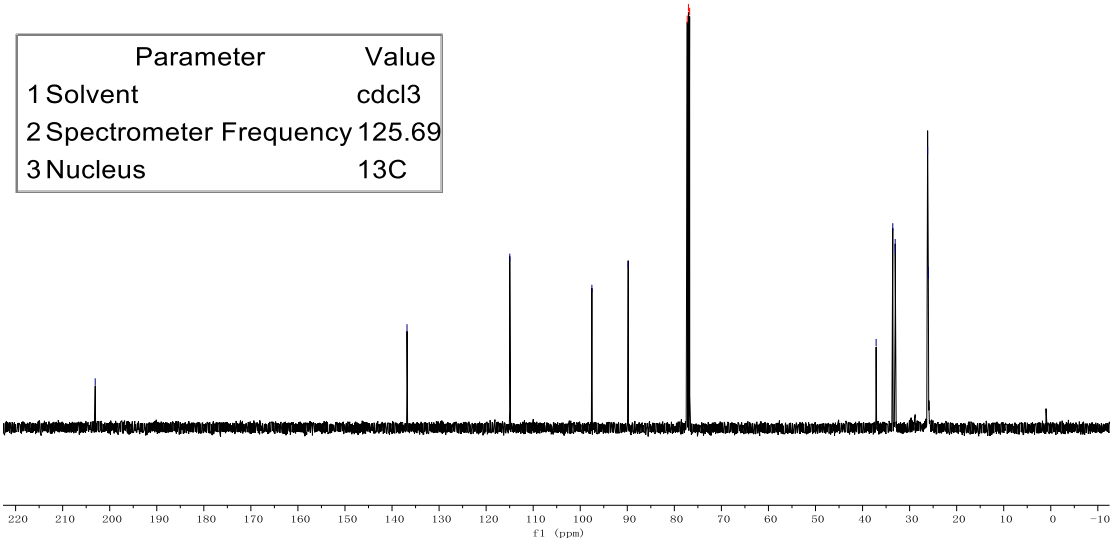
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H

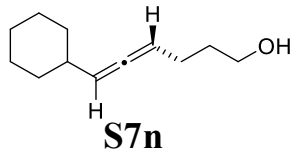




7n

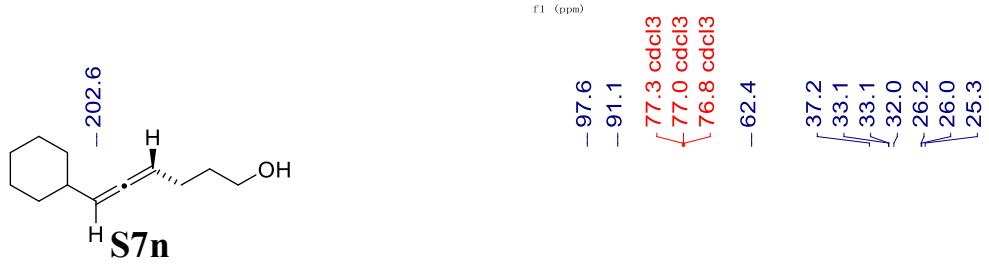
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C





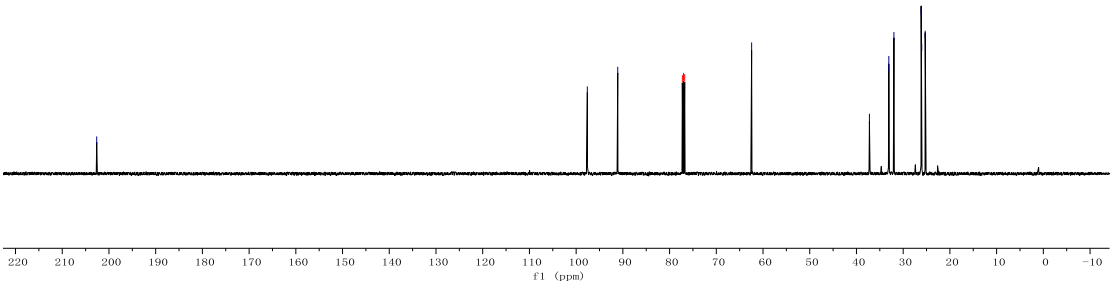
S7n

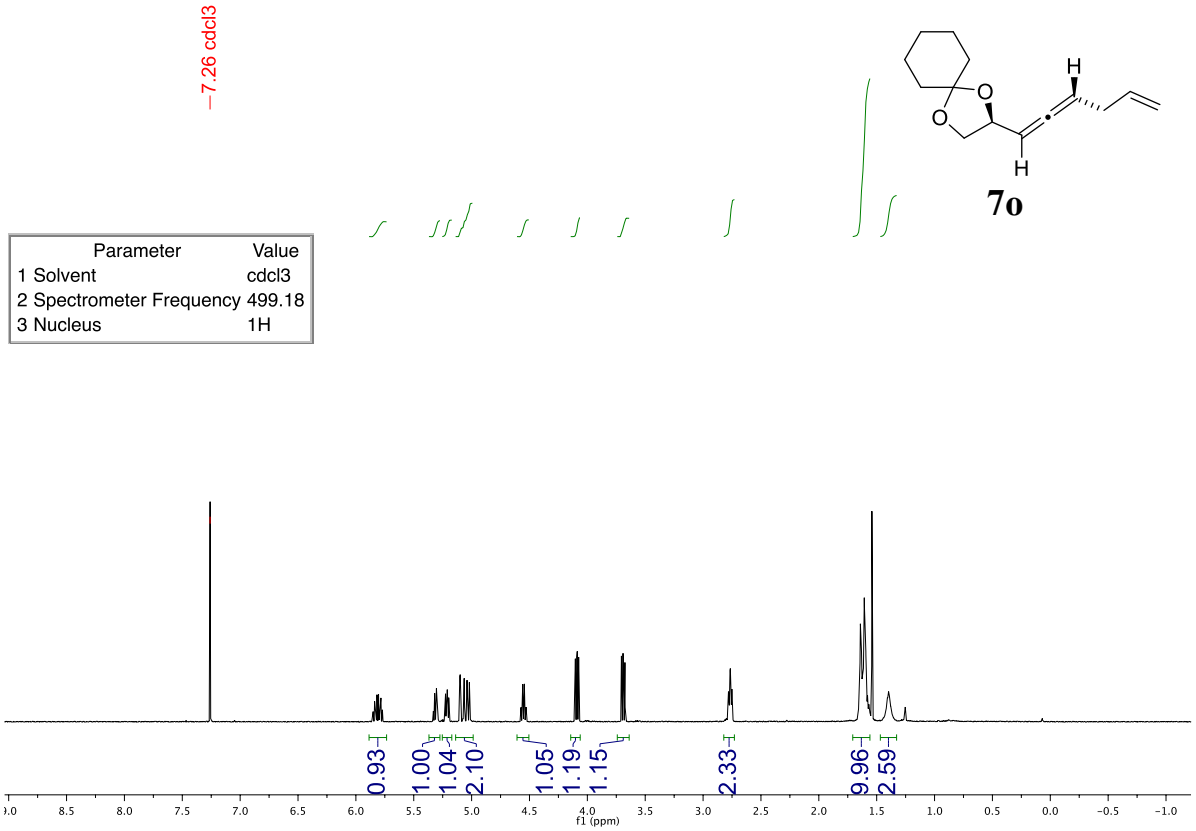
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H

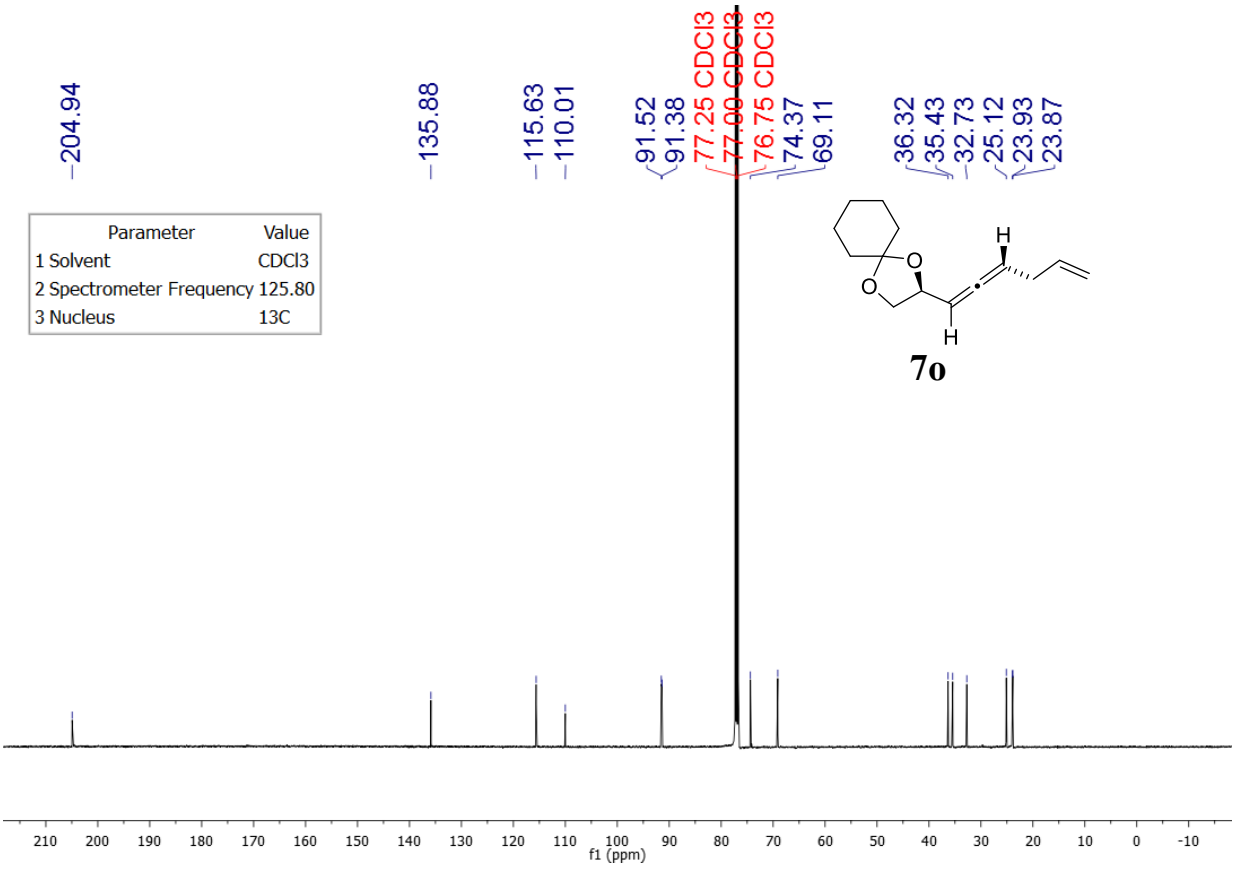


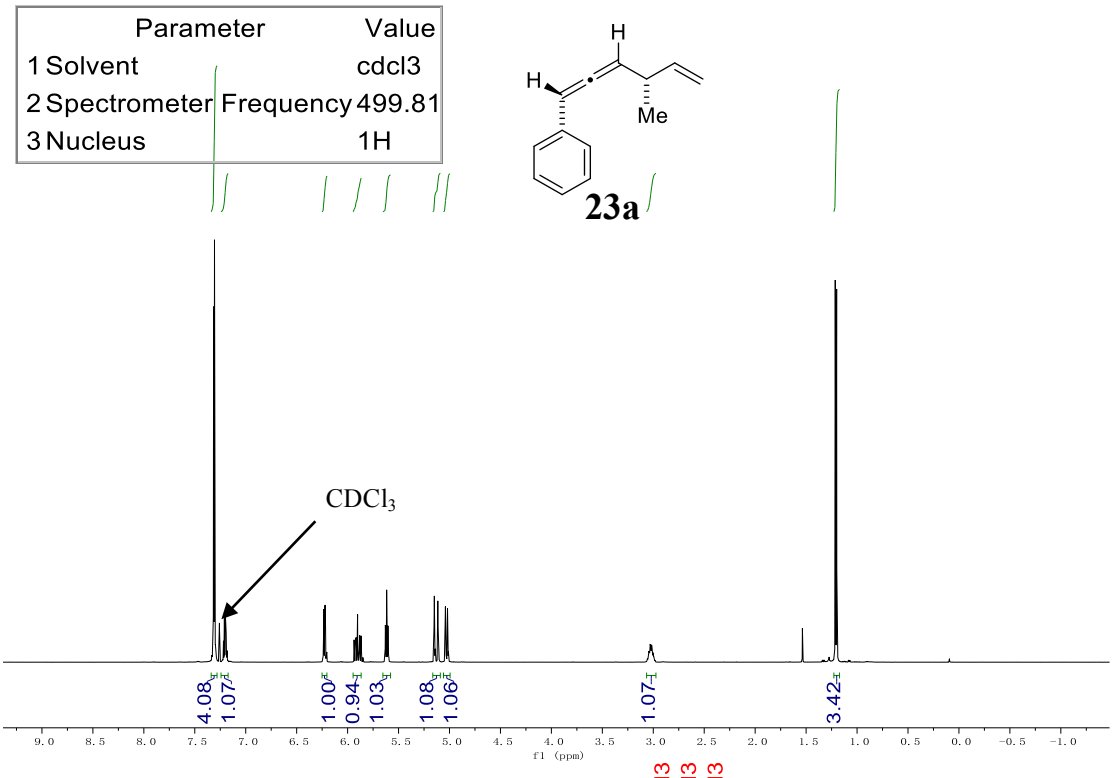
S7n

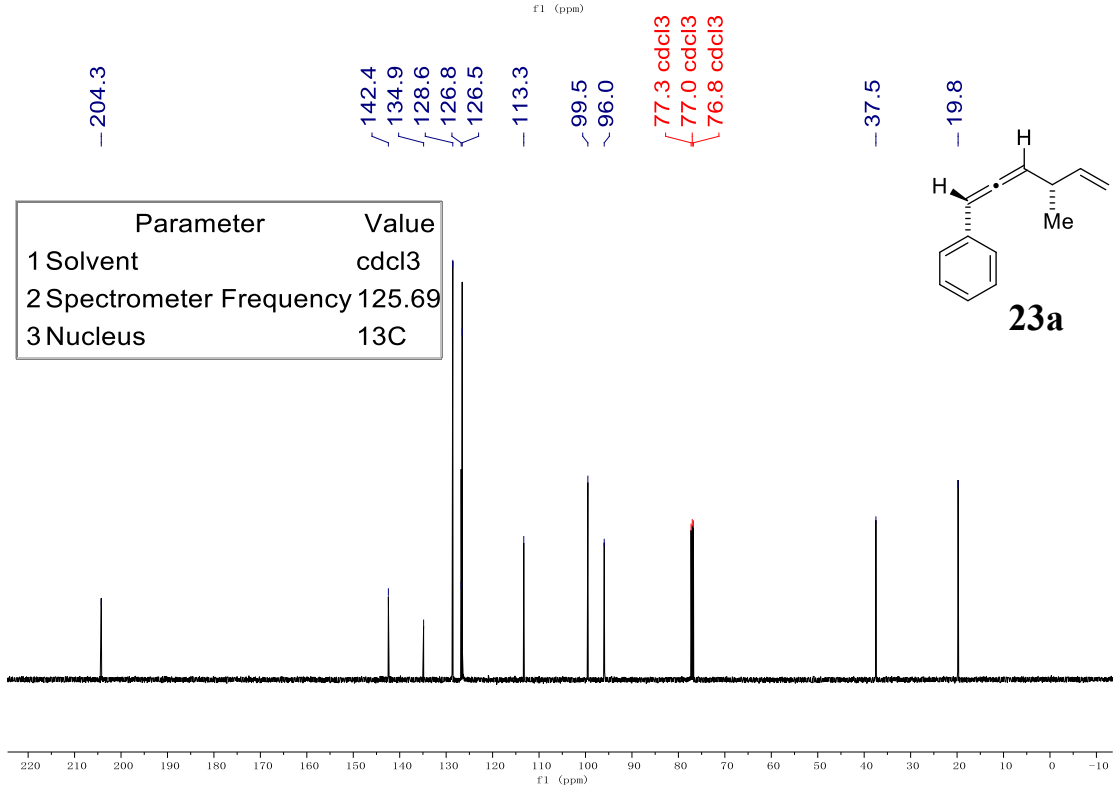
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

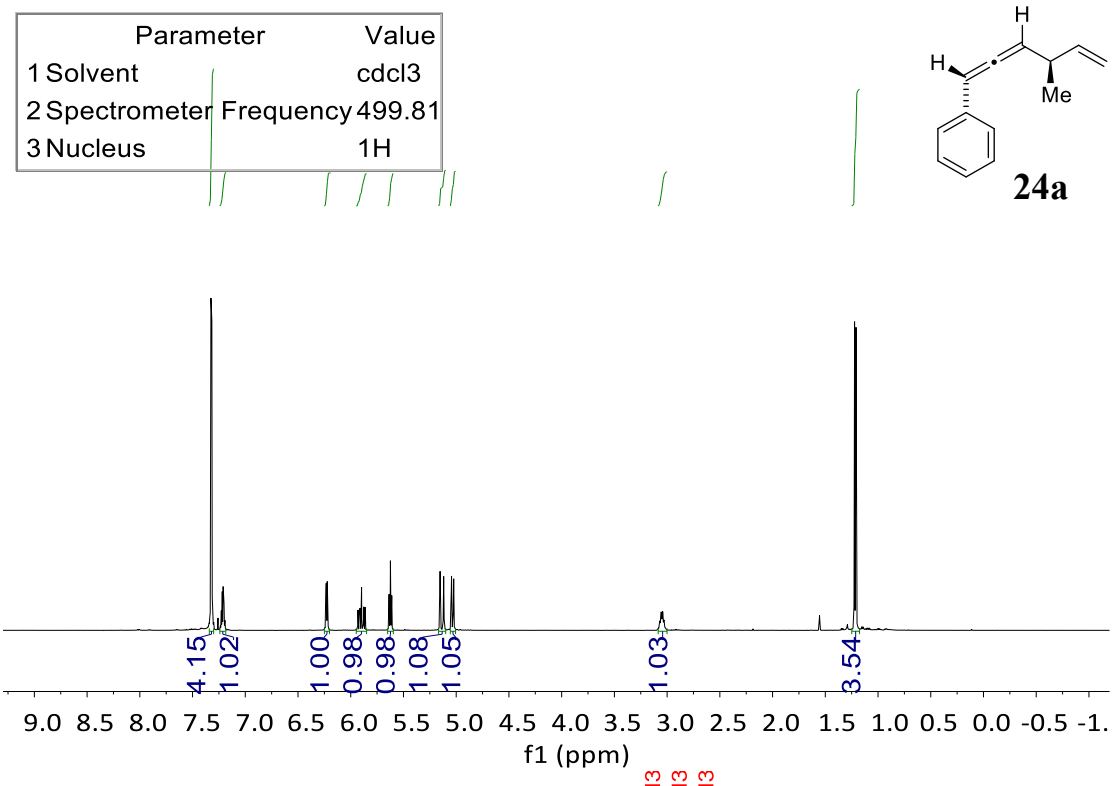


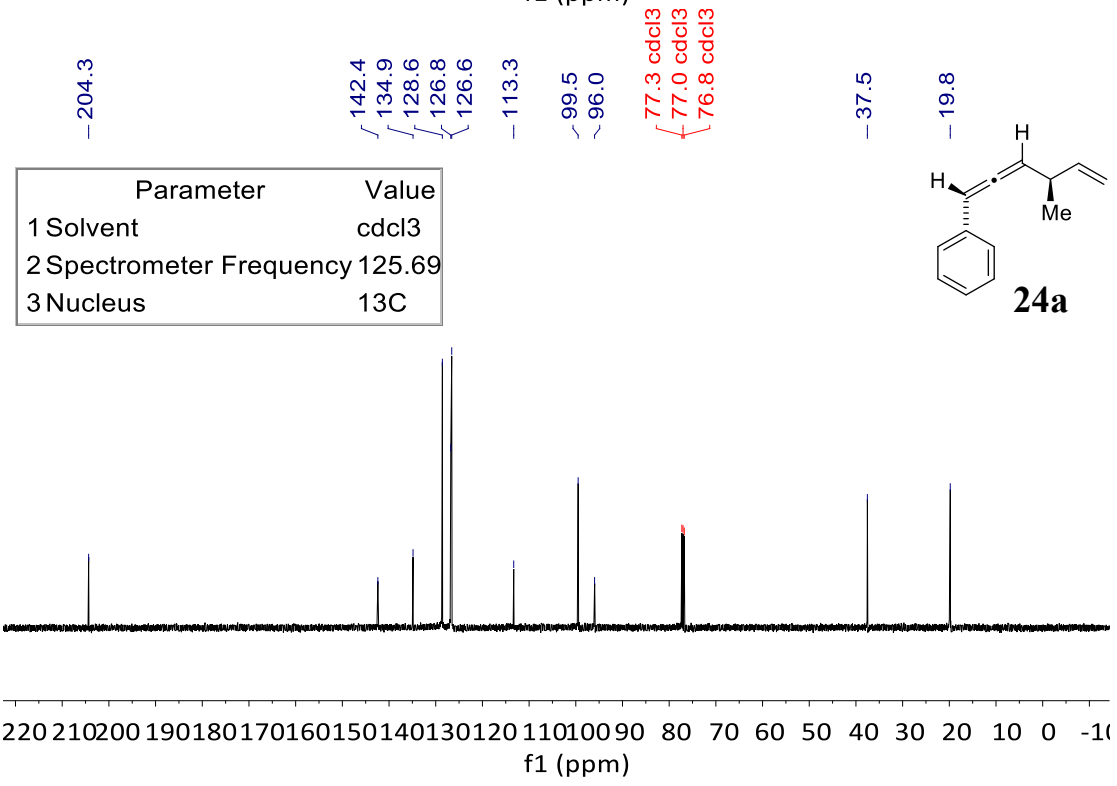

7.26 cdcl3
H
O
O
H
7o
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.18
3 Nucleus 1H
0.93
1.00
1.04
2.10
1.05
1.19
1.15
2.33
9.96
2.59
f1 (ppm)

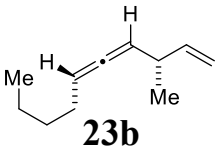

204.94
135.88
115.63
110.01
91.52
91.38
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
74.37
69.11
36.32
35.43
32.73
25.12
23.93
23.87
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 125.80
3 Nucleus 13C
H
O
O
H
7o
f1 (ppm)


Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
H
H
Me
23a
CDCl3
4.08
1.07
1.00
0.94
1.03
1.08
1.06
1.07
3.42
f1 (ppm)


204.3
142.4
134.9
128.6
126.8
126.5
113.3
99.5
96.0
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
37.5
19.8
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
H
H
Me
23a
f1 (ppm)

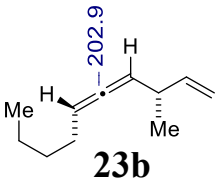

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
H
H
Me
24a
4.15
1.02
1.00
0.98
0.98
1.08
1.05
1.03
3.54
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


204.3
142.4
134.9
128.6
126.8
126.6
113.3
99.5
96.0
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
37.5
19.8
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
H
H
Me
24a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

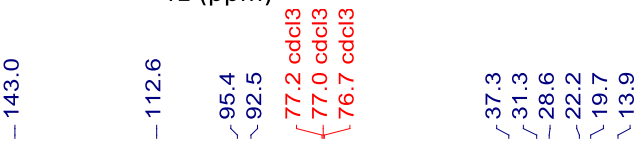


23b

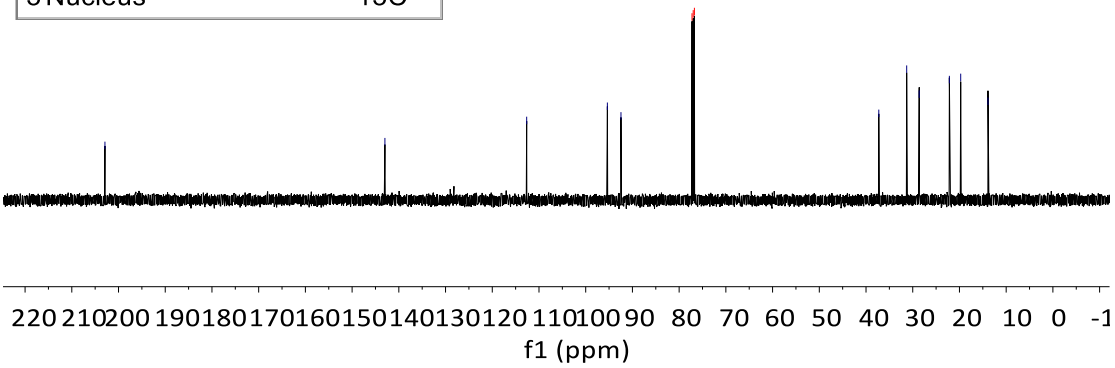
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H

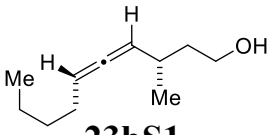


23b



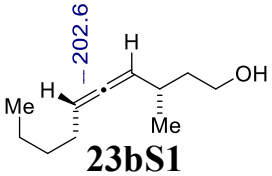
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C




H
OH
H
Me
Me

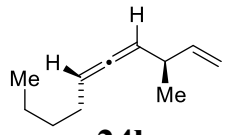
23bS1

Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
1.00
0.98
1.94
1.17
2.24
2.43
4.27
3.23
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 -0.5 -1.0
f1 (ppm)


202.6
H
OH
H
Me
Me

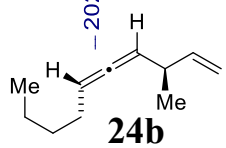
23bS1

96.4
92.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
61.2
39.8
31.3
30.4
28.7
22.2
20.7
13.9
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
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)



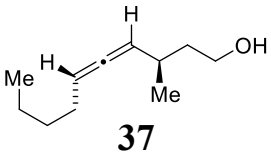
24b

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H



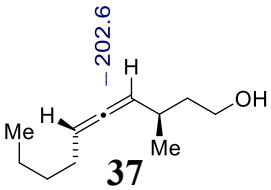
24b

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C



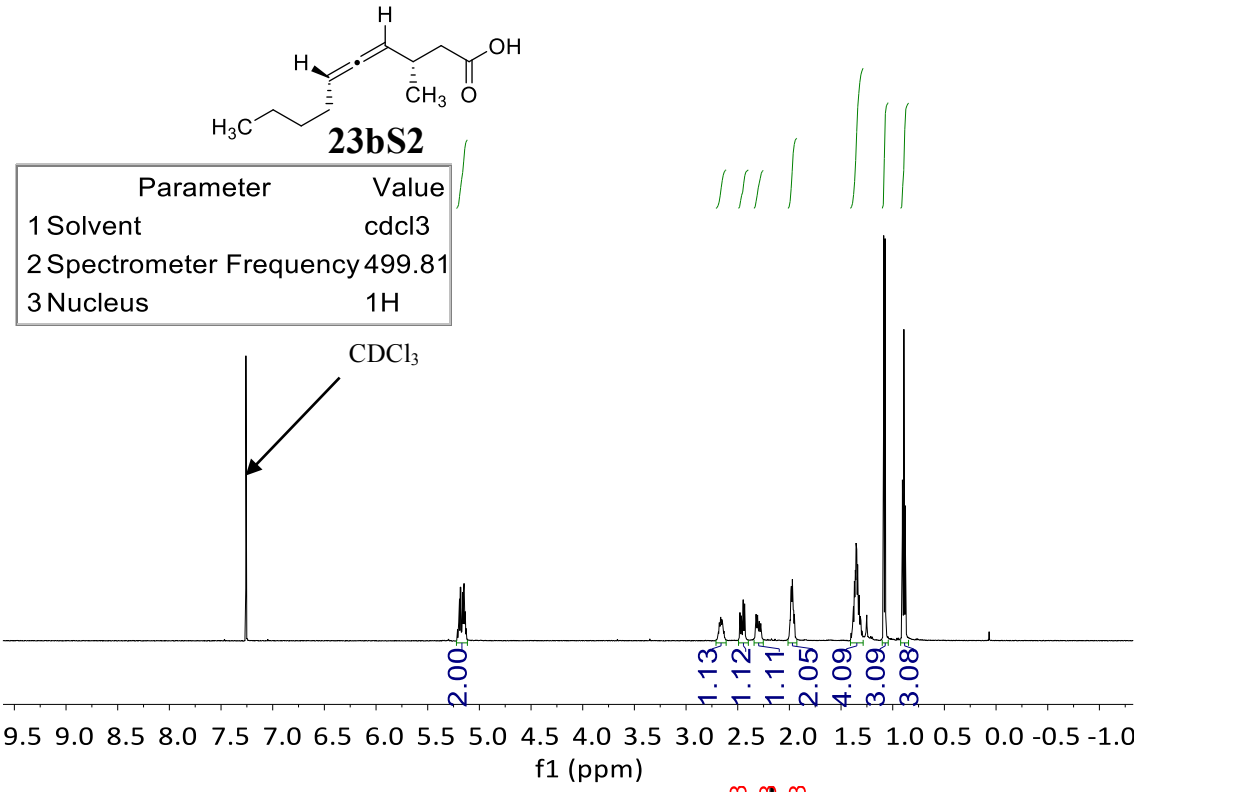
37

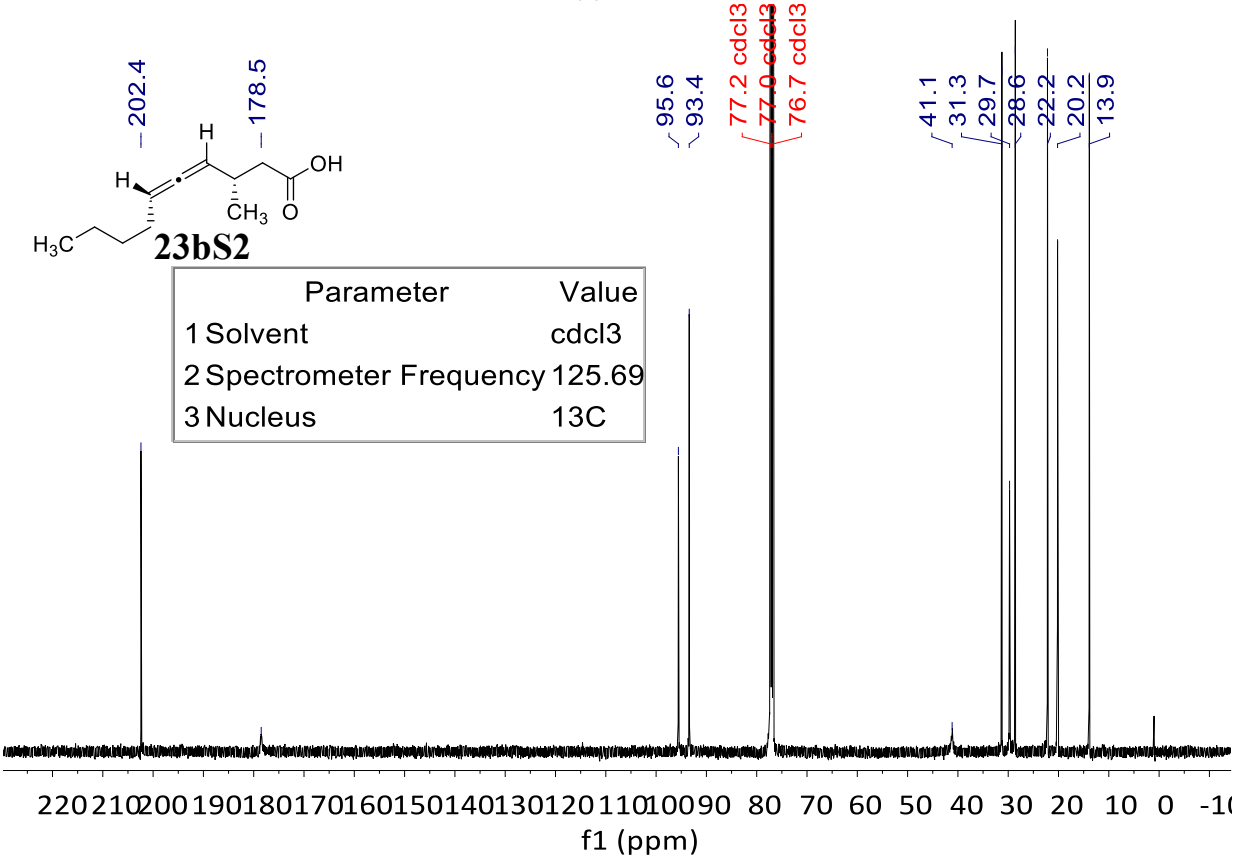
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H

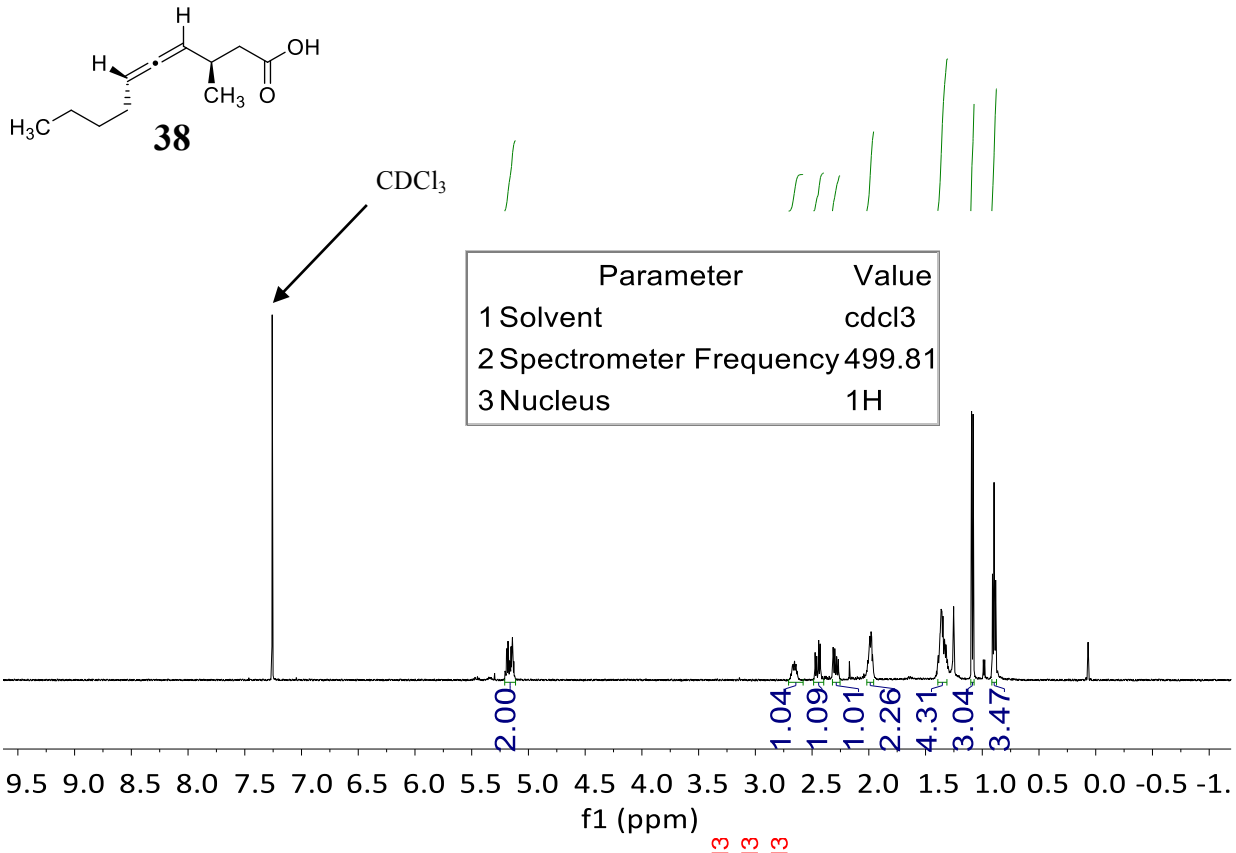


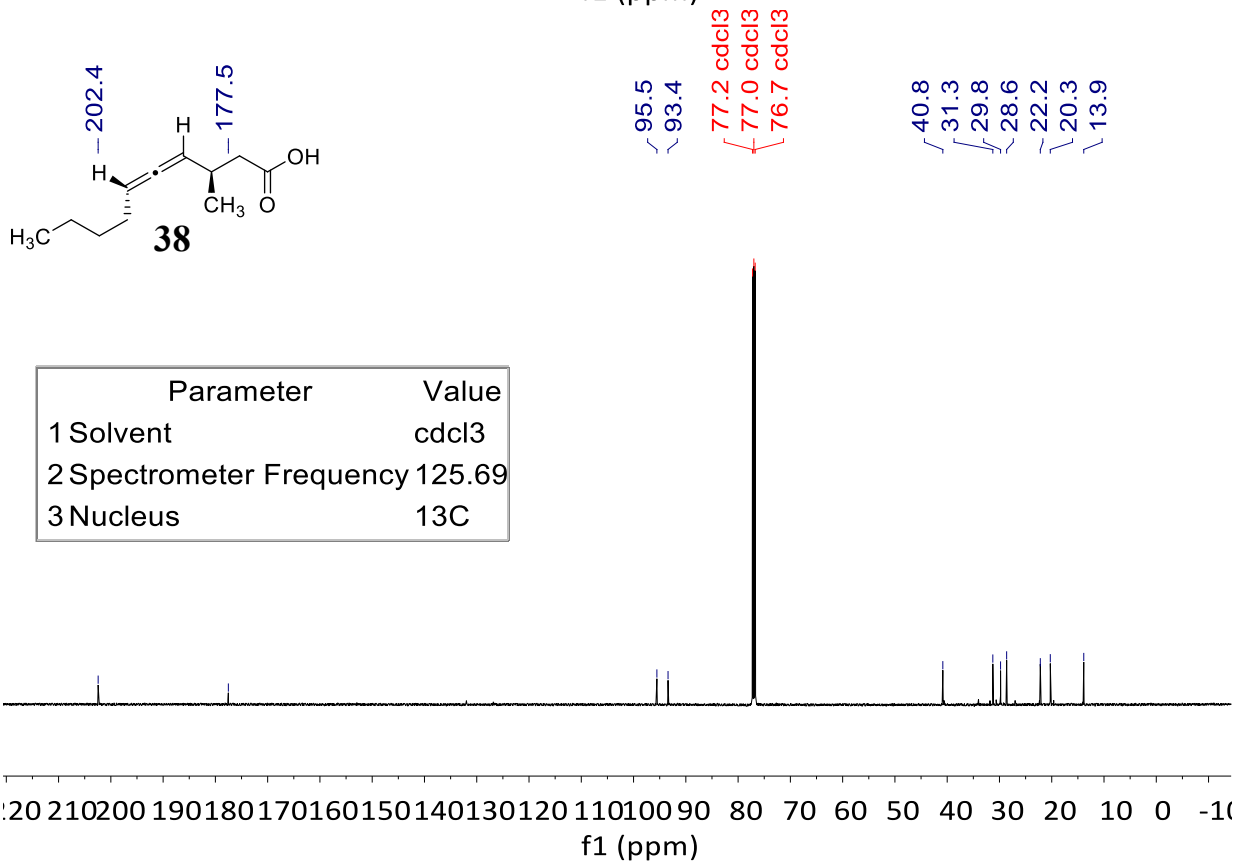
37

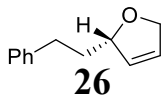
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C


23bS2
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
2.00
1.13
1.12
1.11
2.05
4.09
3.09
3.08
f1 (ppm)


202.4
178.5
23bS2
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
95.6
93.4
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3
41.1
31.3
29.7
28.6
22.2
20.2
13.9
f1 (ppm)

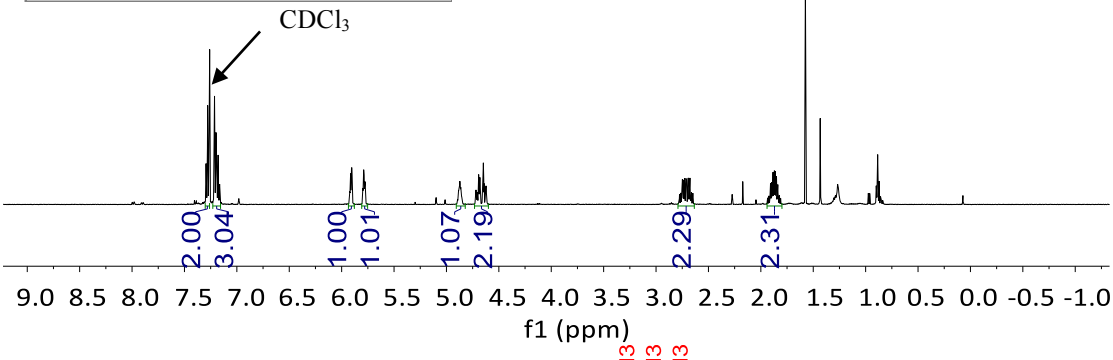

38
CDCl3
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
2.00
1.04
1.09
1.01
2.26
4.31
3.04
3.47
f1 (ppm)

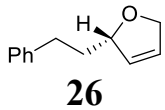

38
202.4
177.5
95.5
93.4
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3
40.8
31.3
29.8
28.6
22.2
20.3
13.9
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
f1 (ppm)



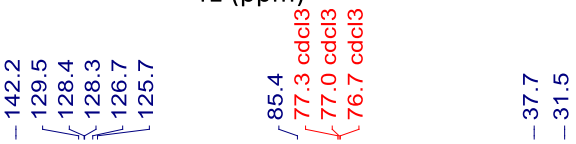
26

Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H

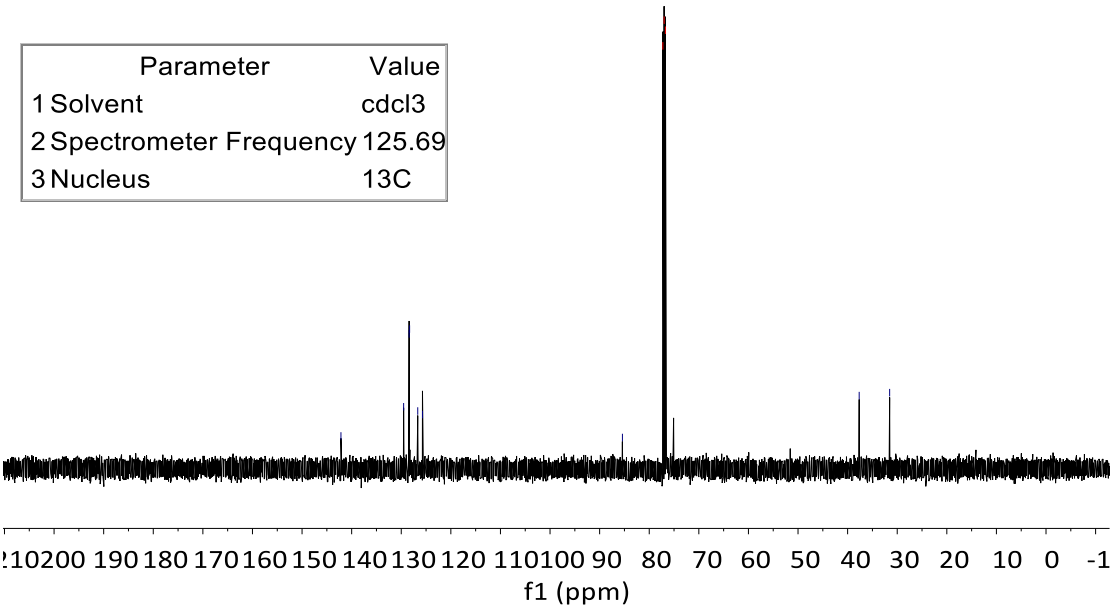


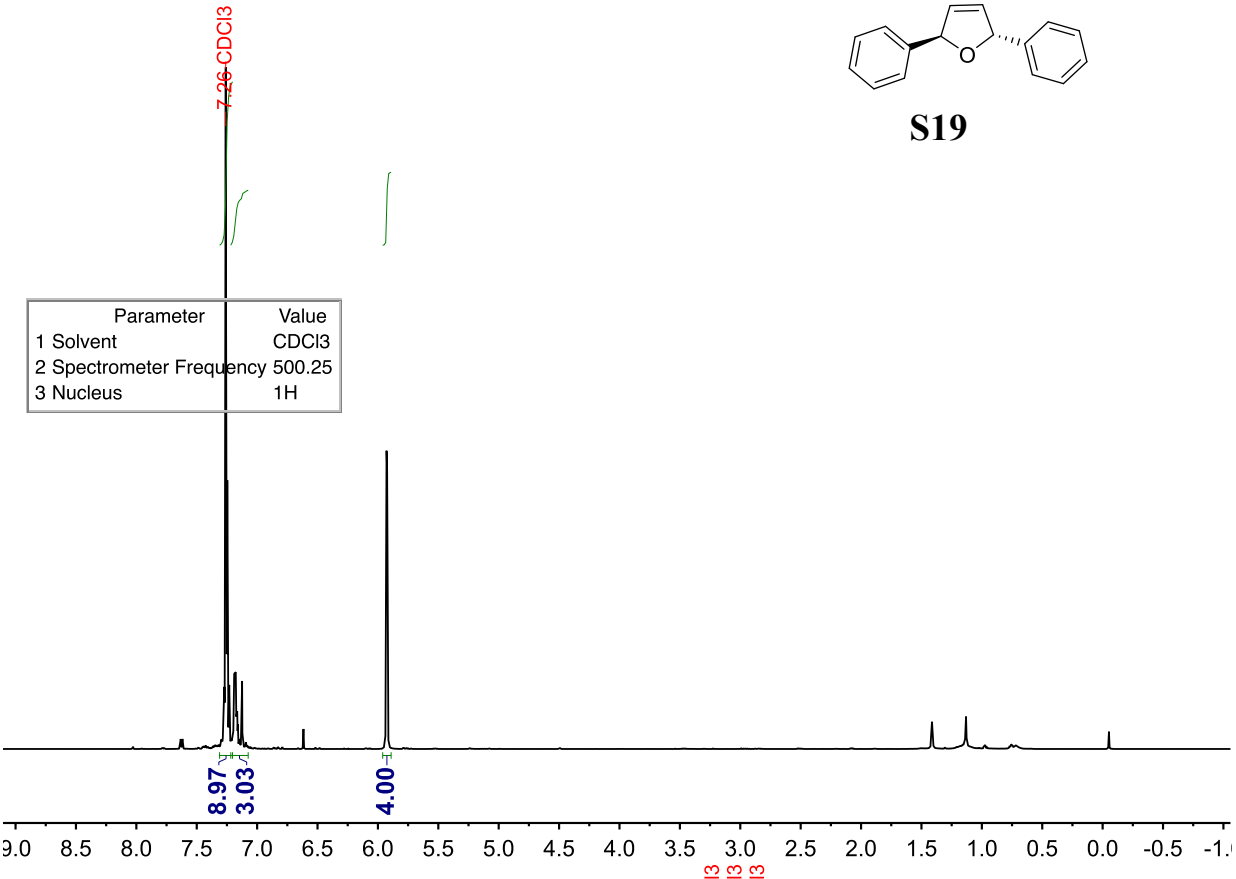


26

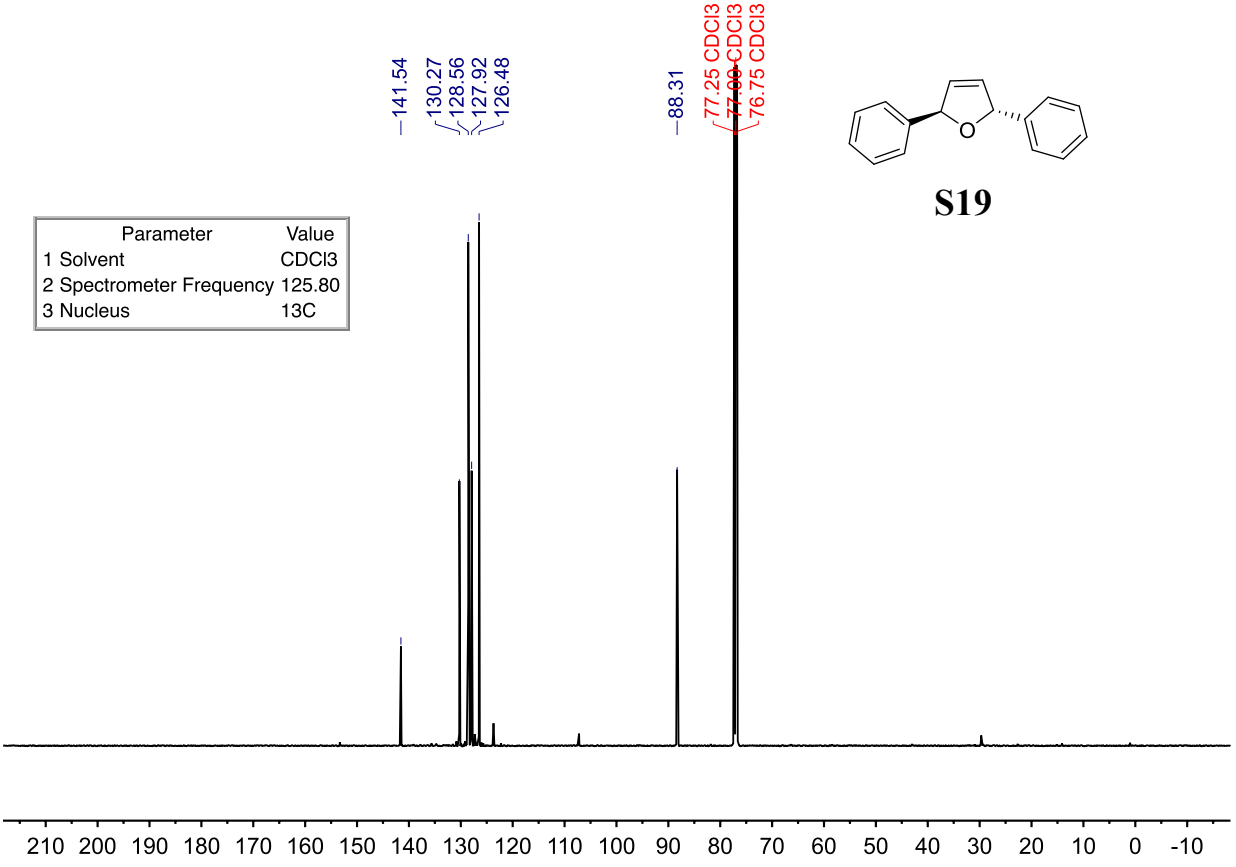


Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C

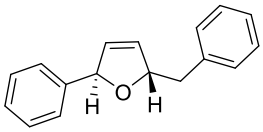



7.26 CDCl3
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 500.25
3 Nucleus 1H
8.97
3.03
4.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

S19

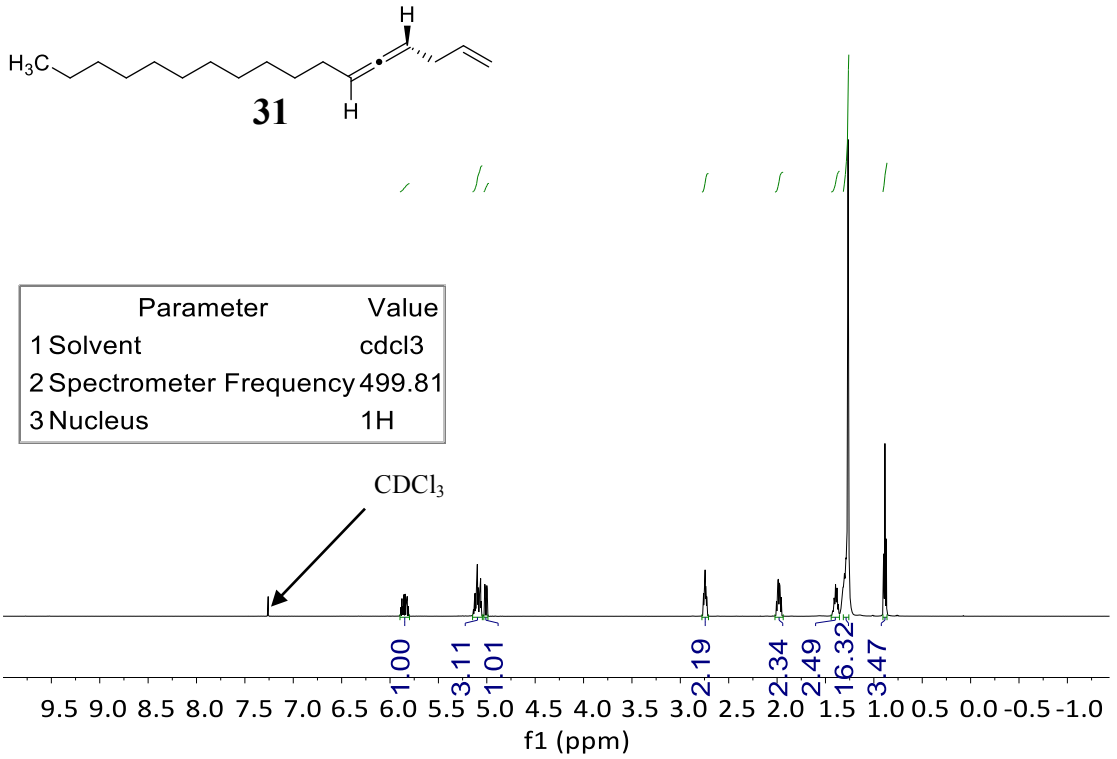

141.54
130.27
128.56
127.92
126.48
88.31
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 125.80
3 Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

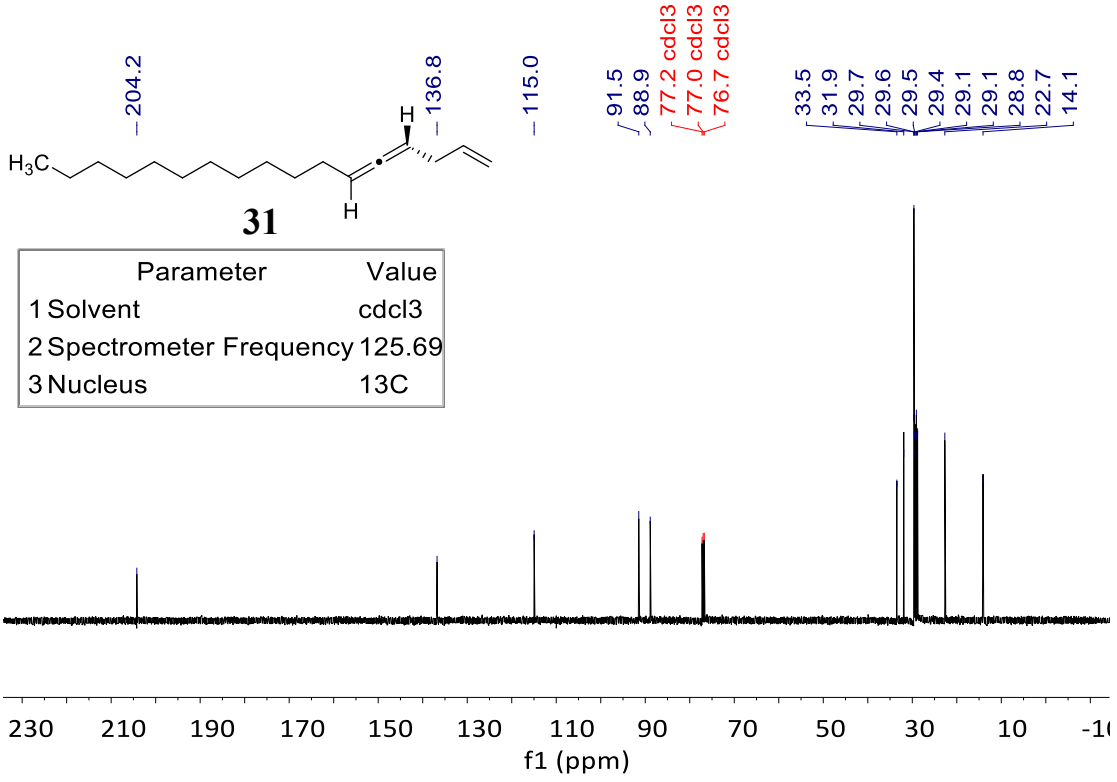
S19

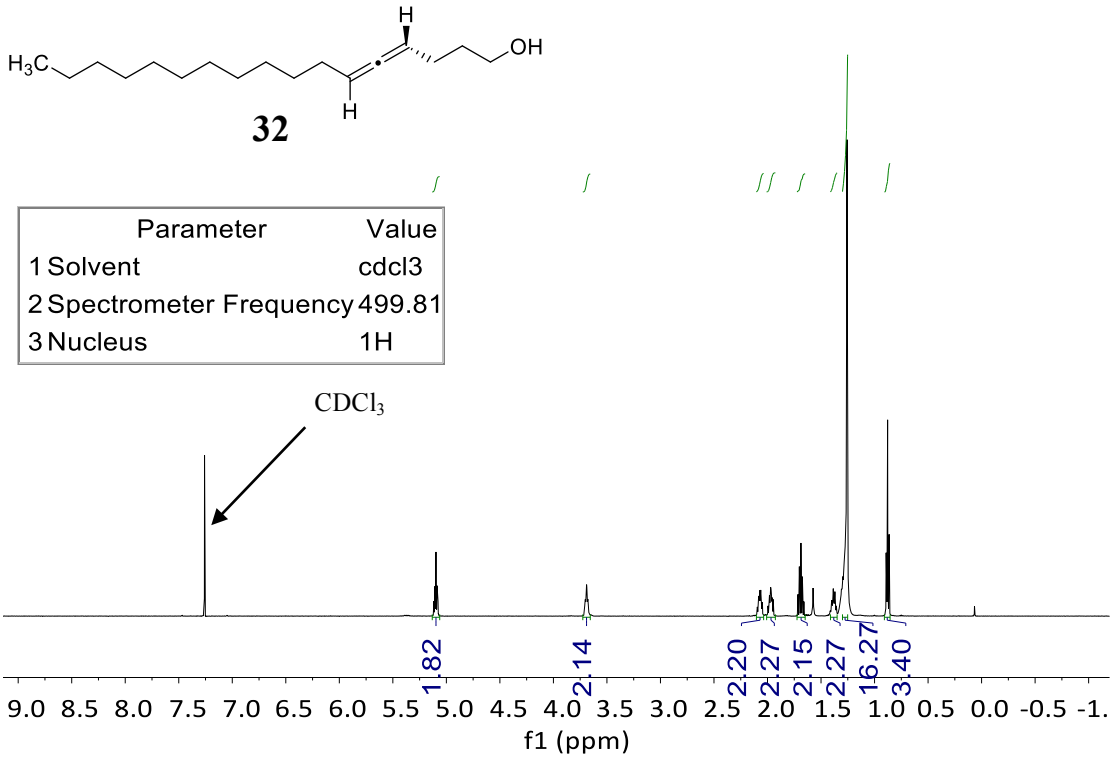


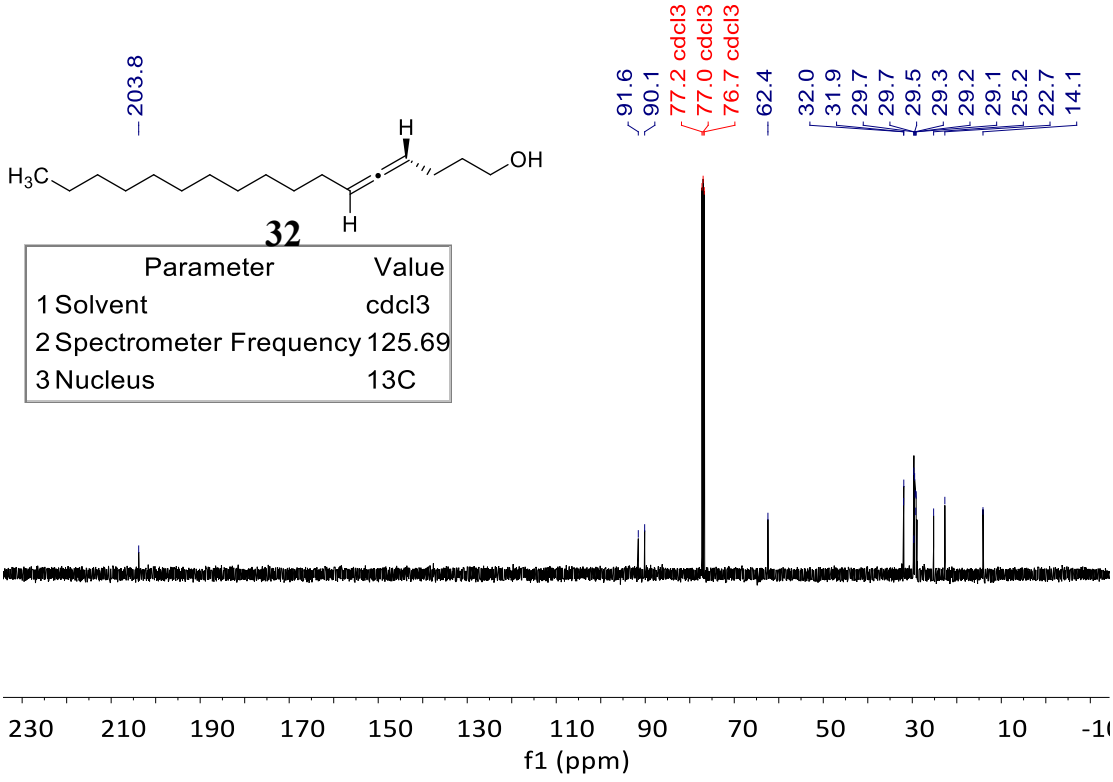
29

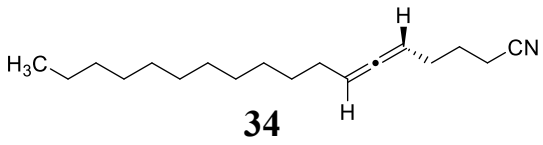
7.26 cdcl3
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.26
3 Nucleus 1H
11.12
1.00
0.99
0.99
1.04
1.17
1.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


H
H3C
H
31
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
1.00
3.11
1.01
2.19
2.34
2.49
16.32
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)


204.2
136.8
115.0
91.5
88.9
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3
33.5
31.9
29.7
29.6
29.5
29.4
29.1
29.1
28.8
22.7
14.1
H
H3C
H
31
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
230 210 190 170 150 130 110 90 70 50 30 10
f1 (ppm)

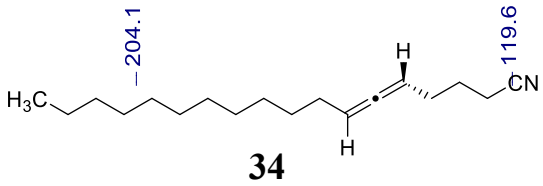

H
H3C
OH
H
32
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
1.82
2.14
2.20
2.27
2.15
2.27
16.27
3.40
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


203.8
91.6
90.1
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3
62.4
32.0
31.9
29.7
29.7
29.5
29.3
29.2
29.1
25.2
22.7
14.1
H
H3C
OH
H
32
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
230 210 190 170 150 130 110 90 70 50 30 10
f1 (ppm)

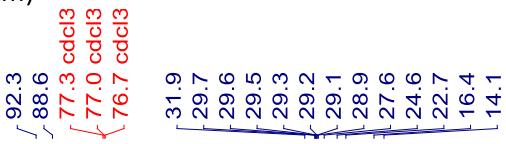


34

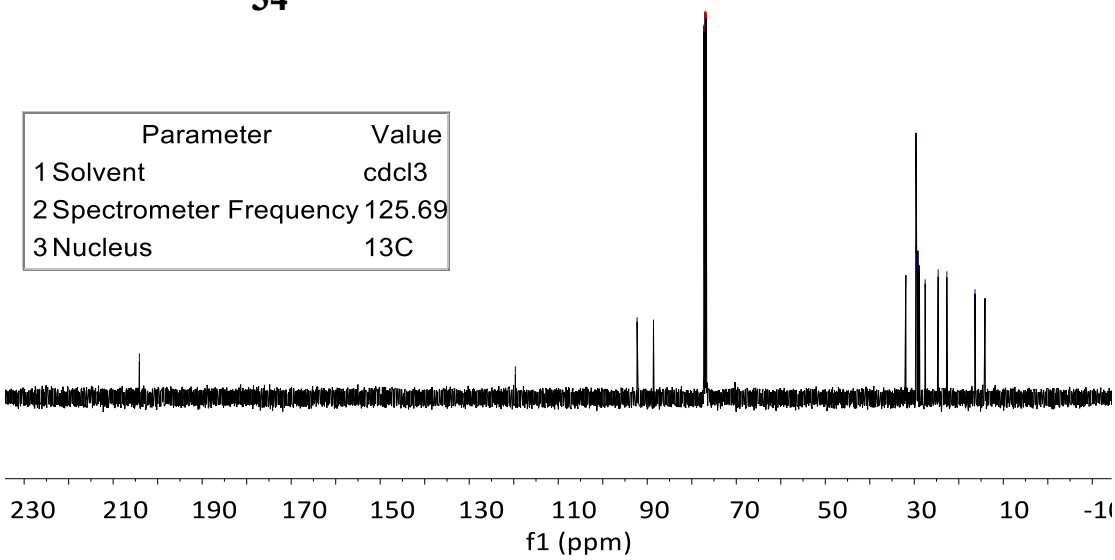
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	499.81
3 Nucleus	1H

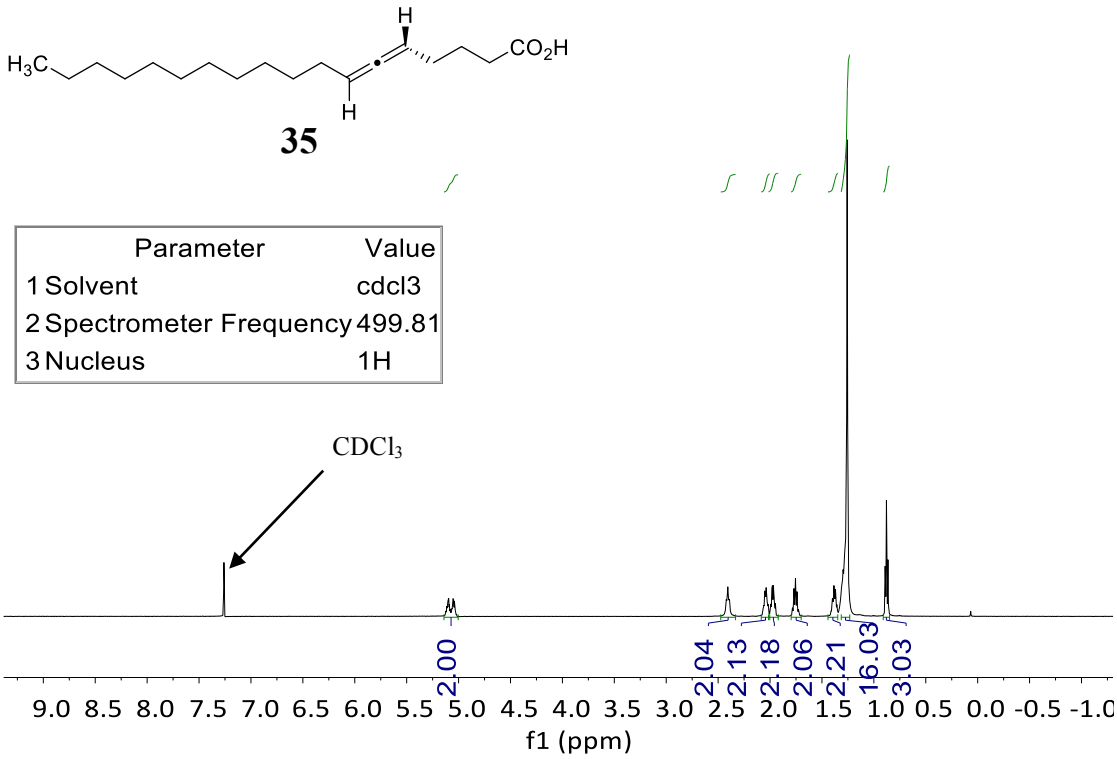


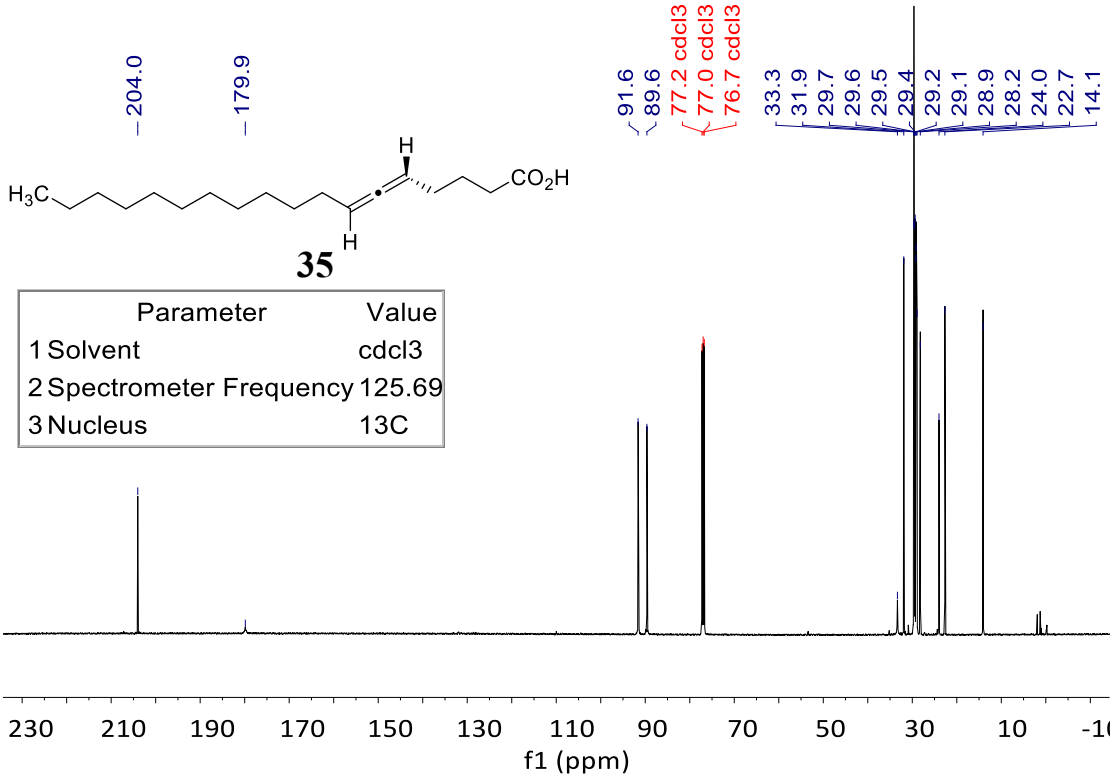
34



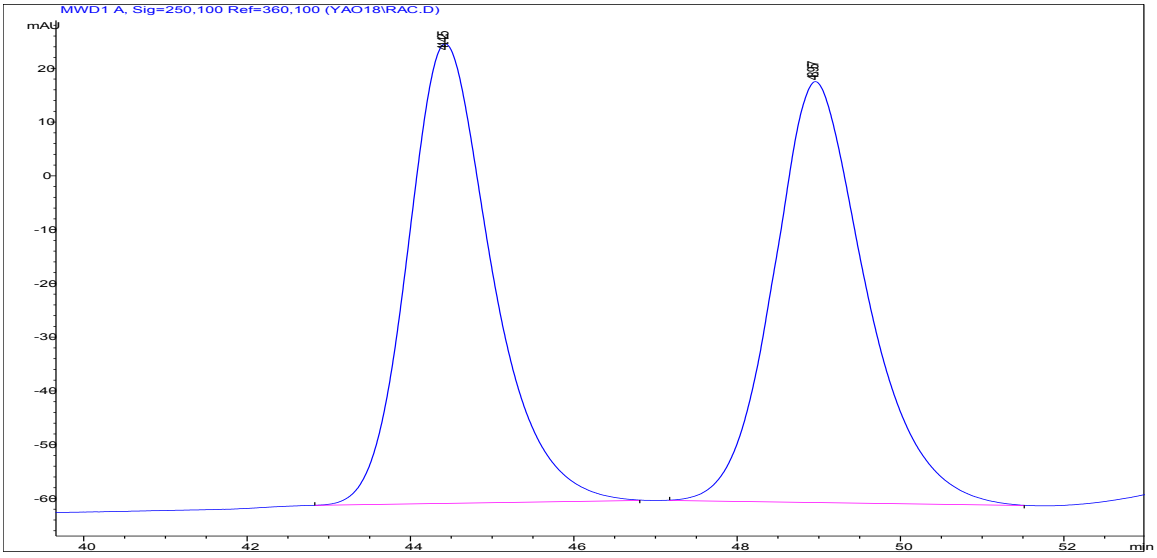
Parameter	Value
1 Solvent	cdcl3
2 Spectrometer Frequency	125.69
3 Nucleus	13C



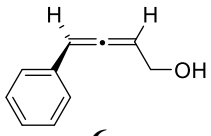

H
H3C
CO2H
H
35
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 499.81
3 Nucleus 1H
CDCl3
2.00
2.04
2.13
2.18
2.06
2.21
16.03
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


204.0
179.9
91.6
89.6
77.2 cdcl3
77.0 cdcl3
76.7 cdcl3
33.3
31.9
29.7
29.6
29.5
29.4
29.2
29.1
28.9
28.2
24.0
22.7
14.1
H
H3C
CO2H
H
35
Parameter Value
1 Solvent cdcl3
2 Spectrometer Frequency 125.69
3 Nucleus 13C
230 210 190 170 150 130 110 90 70 50 30 10
f1 (ppm)

6. HPLC Traces for Enantiomeric Excess Determination

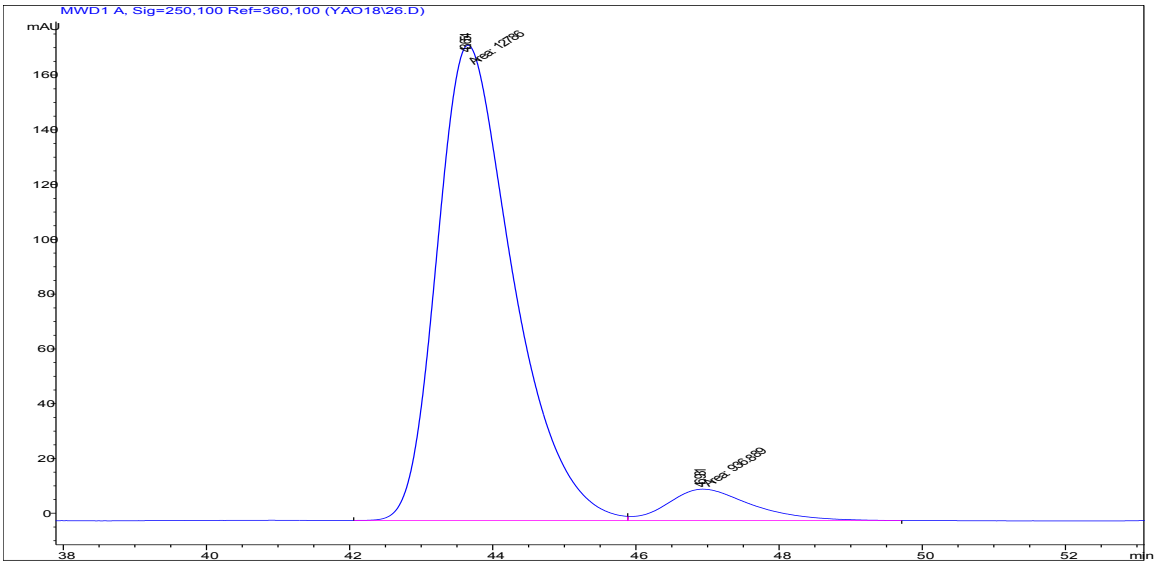


Signal 1: MWD1 A, Sig=250,100 Ref=360,100



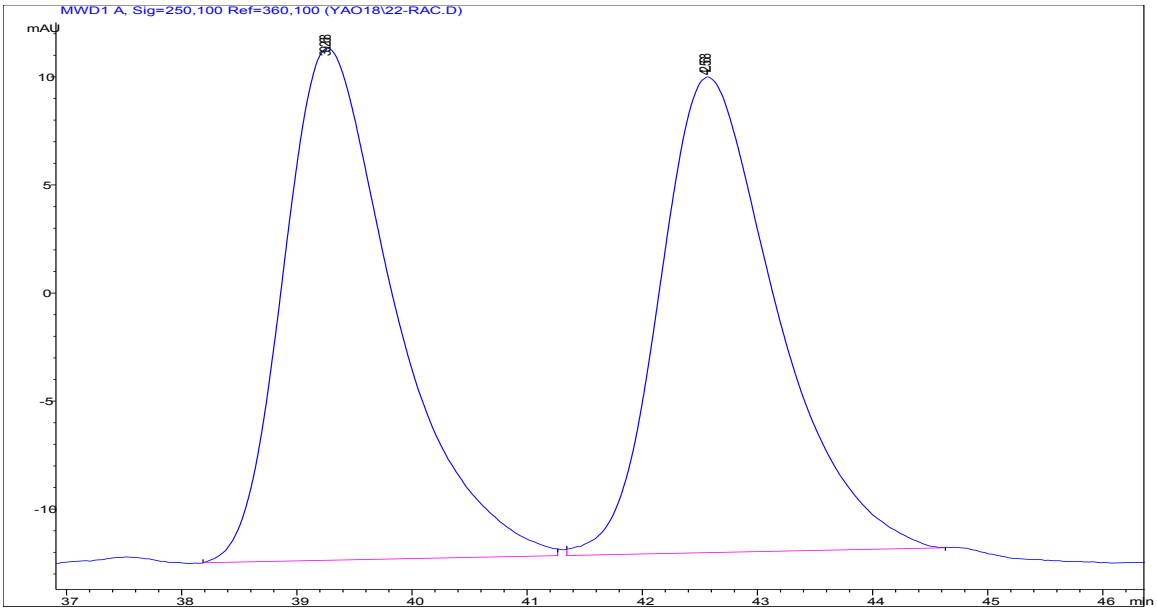
6a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.425	BB	1.0617	6123.25830	85.48061	49.7261
2	48.957	BB	1.1346	6190.71826	78.28782	50.2739
Totals :				1.23140e4	163.76842	

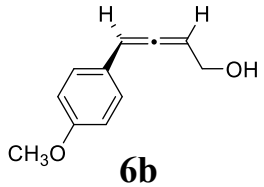


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.654	MF	1.2283	1.27860e4	173.49753	93.1728
2	46.931	FM	1.3604	936.88940	11.47831	6.8272
Totals :				1.37229e4	184.97584	

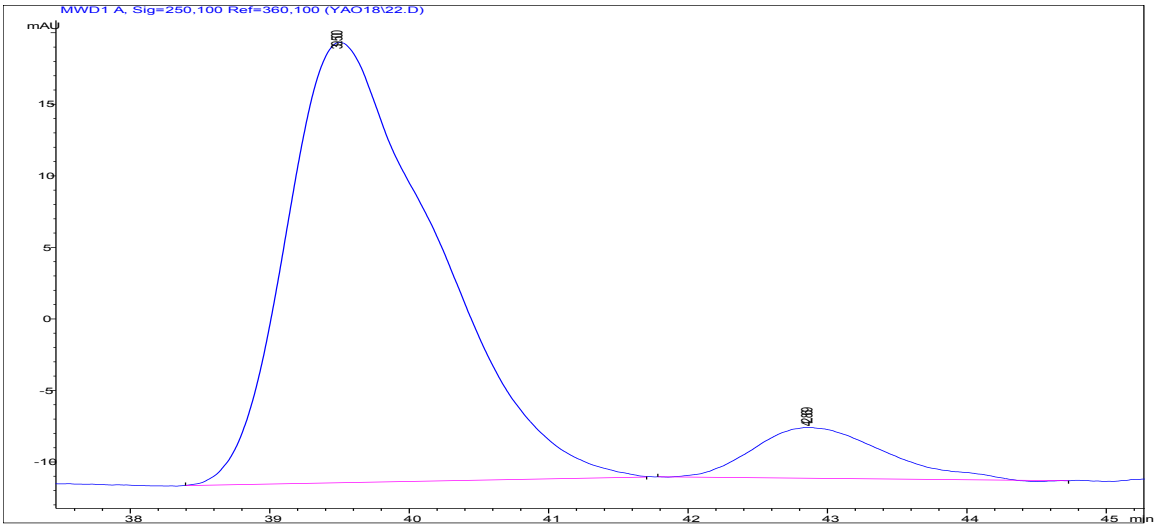


Signal 1: MWD1 A, Sig=250,100 Ref=360,100



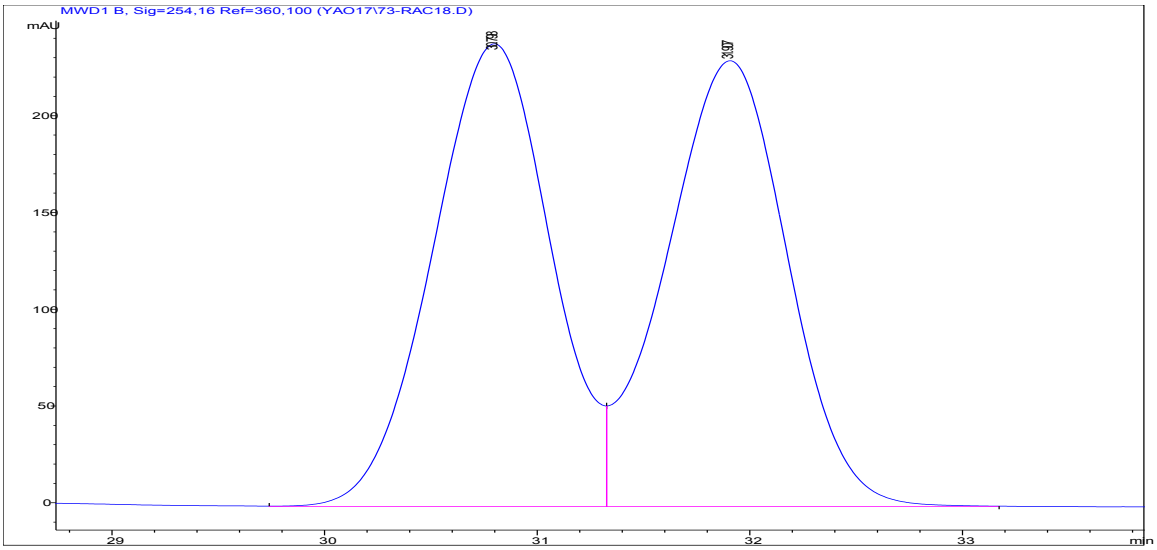
6b

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.268	PB	0.9427	1589.81372	23.69629	50.6876
2	42.568	BB	0.8619	1546.68115	22.00929	49.3124
Totals :				3136.49487	45.70558	

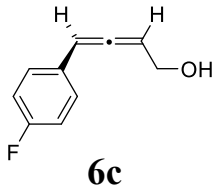


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.500	BB	1.0270	2287.01050	30.77516	90.7920
2	42.869	BP	0.7732	231.94621	3.55491	9.2080
Totals :				2518.95671	34.33006	

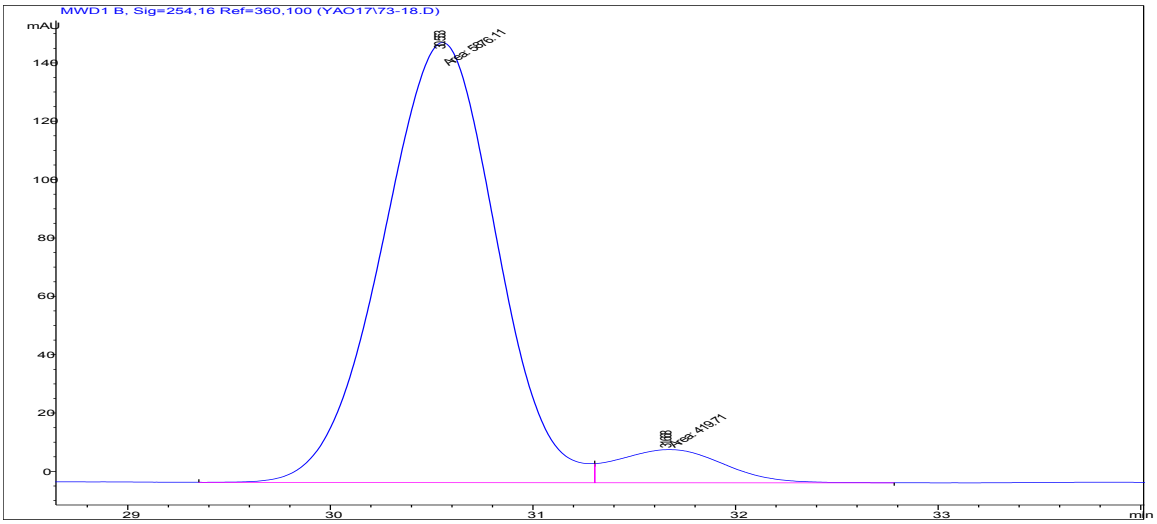


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



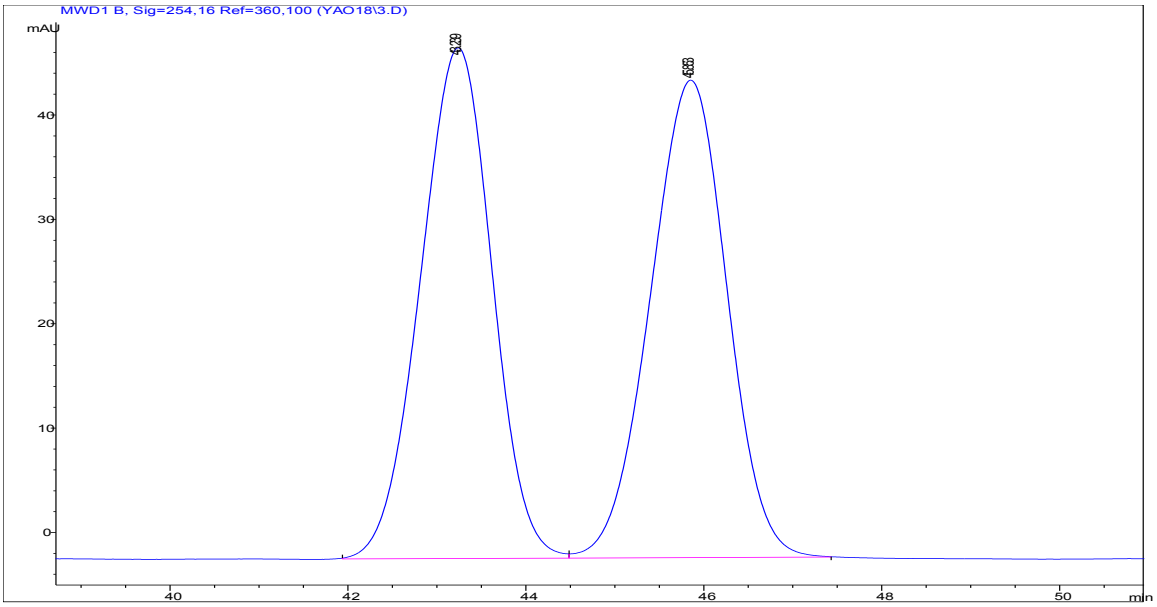
6c

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.798	VV	0.5964	9231.63477	239.11053	50.1566
2	31.907	VB	0.6147	9173.98047	230.32614	49.8434
Totals :				1.84056e4	469.43668	

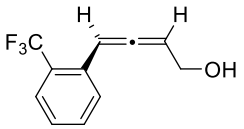


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.553	MF	0.6493	5876.10938	150.83855	93.3335
2	31.668	FM	0.6153	419.71033	11.36878	6.6665
Totals :				6295.81970	162.20732	

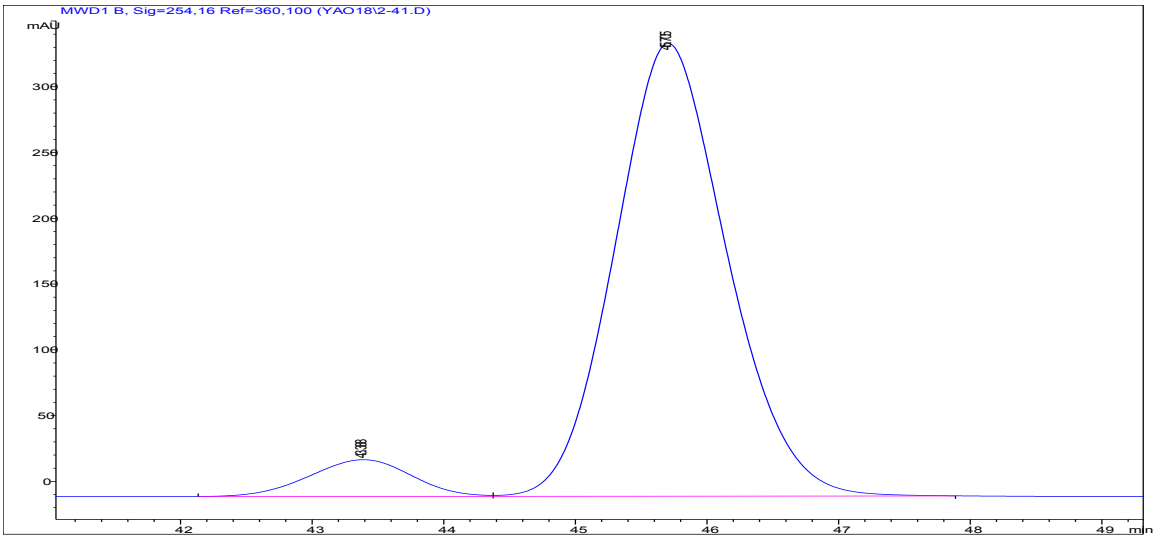


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



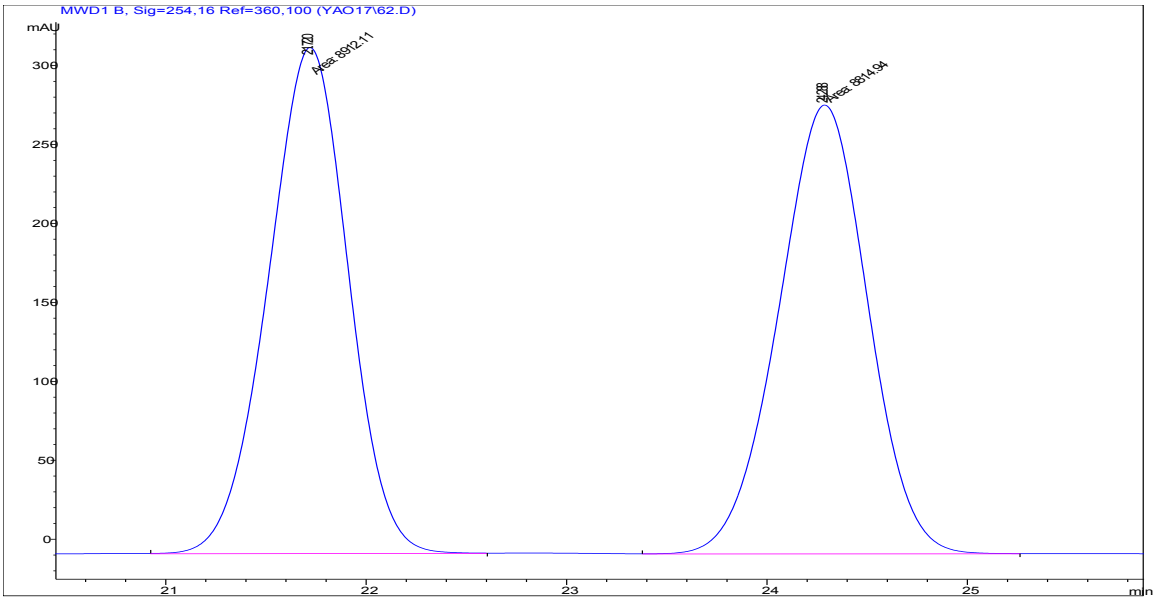
6d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.239	BV	0.8754	2731.17944	48.91761	49.9265
2	45.853	VB	0.9227	2739.22192	45.74107	50.0735
Totals :				5470.40137	94.65868	

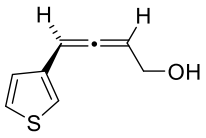


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.388	BV	0.8341	1513.86182	27.94063	6.9265
2	45.705	VB	0.9033	2.03423e4	344.29584	93.0735
Totals :				2.18562e4	372.23647	

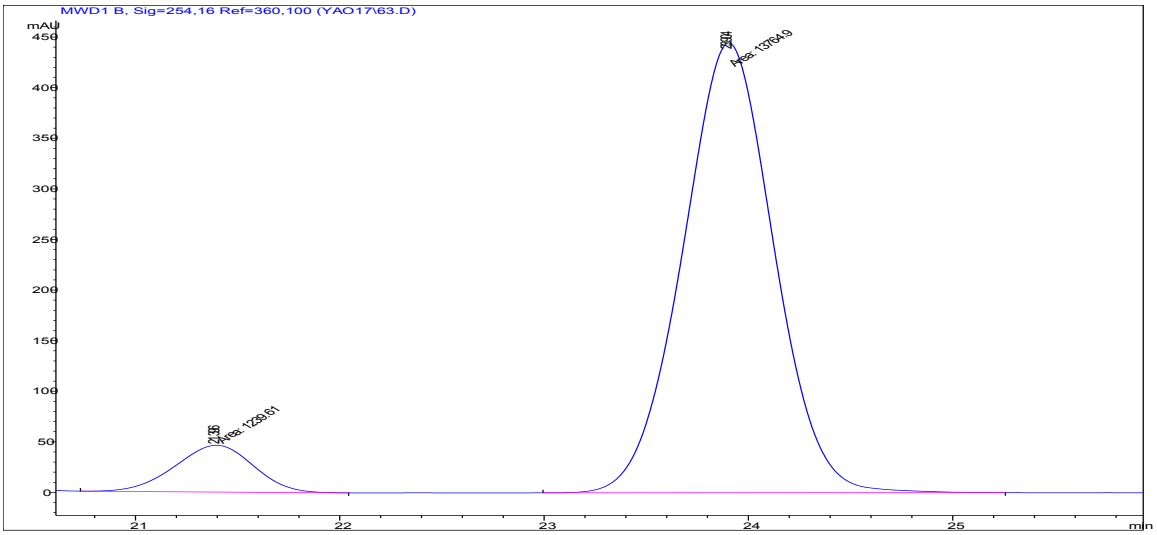


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



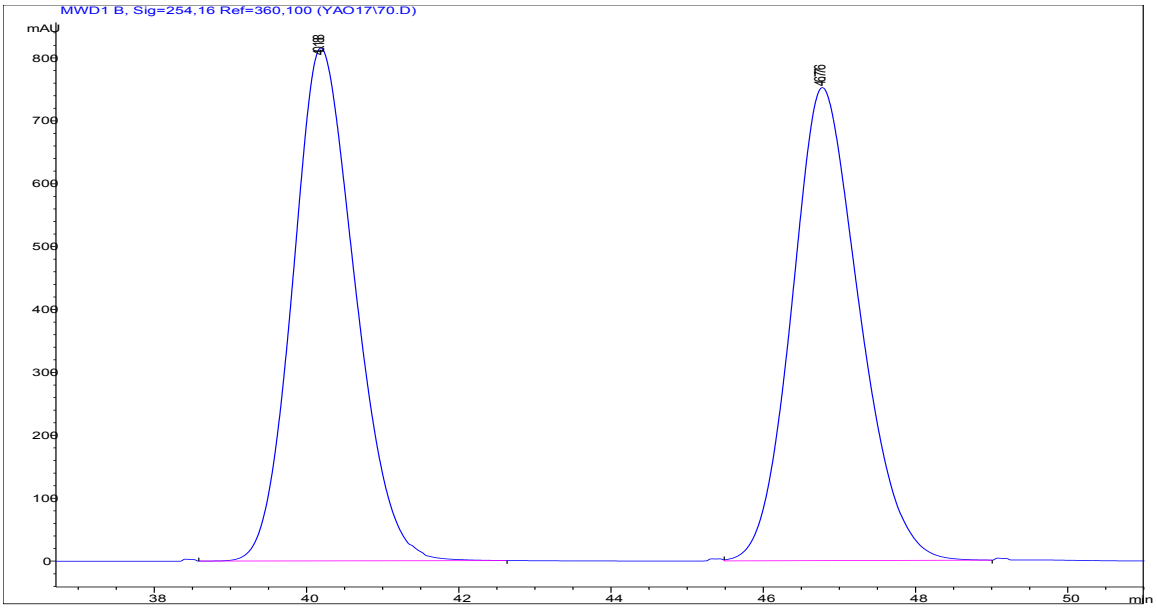
6e

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.720	MM	0.4634	8912.11328	320.55563	50.2741
2	24.288	MM	0.5168	8814.94434	284.26099	49.7259
Totals :				1.77271e4	604.81662	

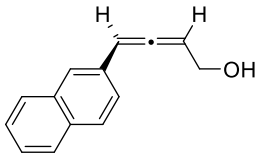


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.396	MM	0.4464	1239.60657	46.28024	8.2615
2	23.904	MM	0.5162	1.37649e4	444.45715	91.7385
Totals :				1.50046e4	490.73739	

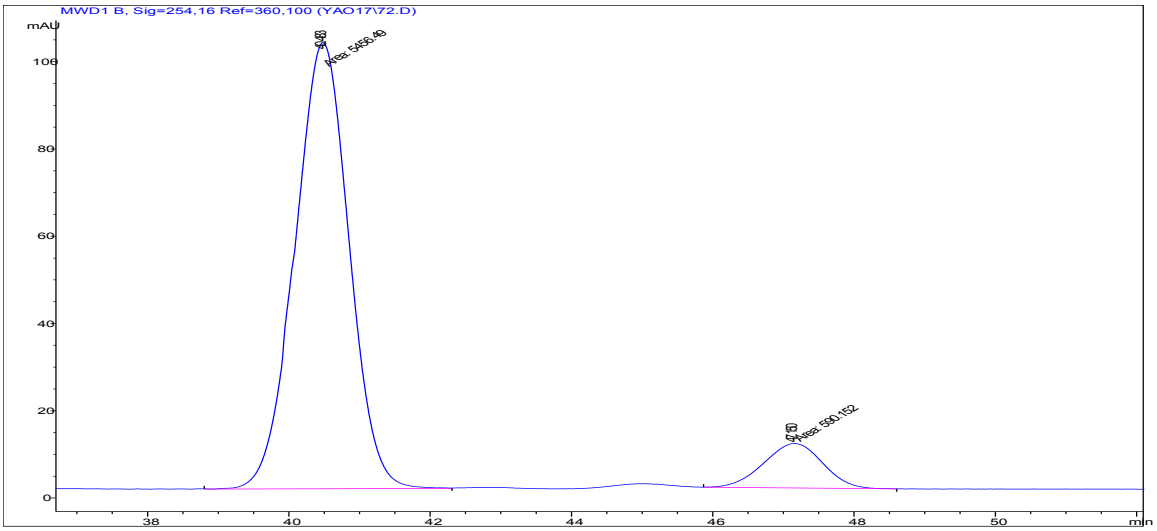


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



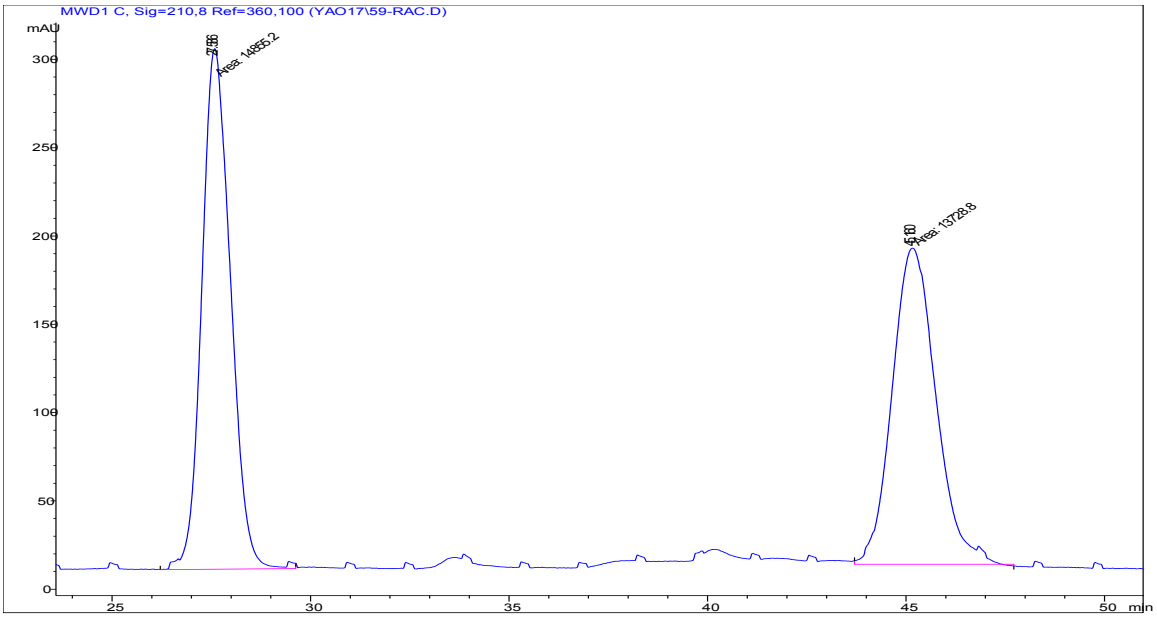
6f

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.188	VB	0.8526	4.64582e4	815.50146	50.0745
2	46.776	VP	0.9386	4.63200e4	752.05536	49.9255
Totals :				9.27782e4	1567.55682	

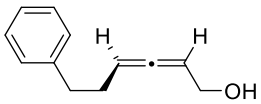


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.483	MM	0.8895	5456.49365	102.23568	90.2400
2	47.150	MM	0.9648	590.15155	10.19430	9.7600
Totals :				6046.64520	112.42998	

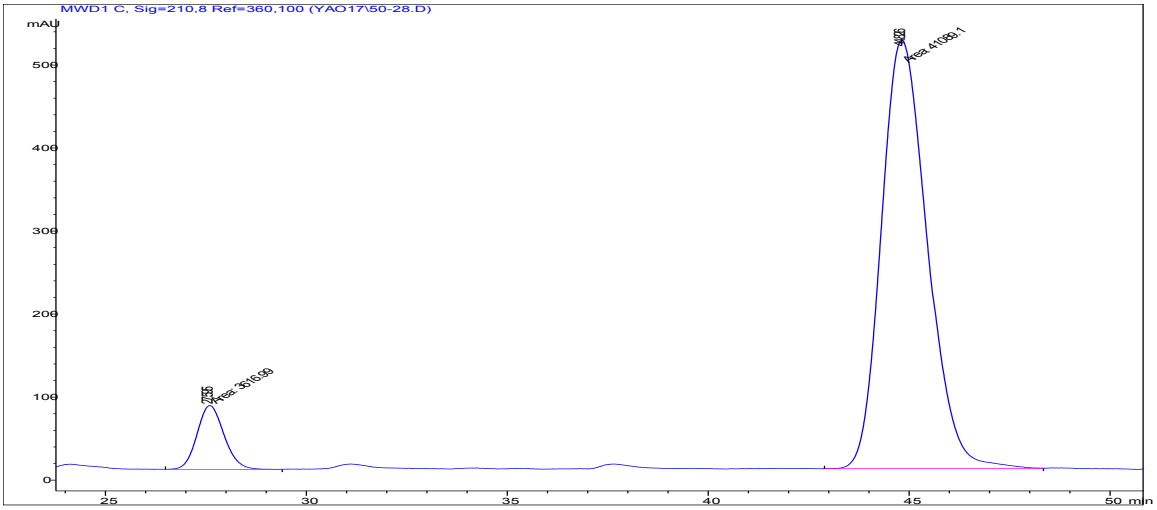


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



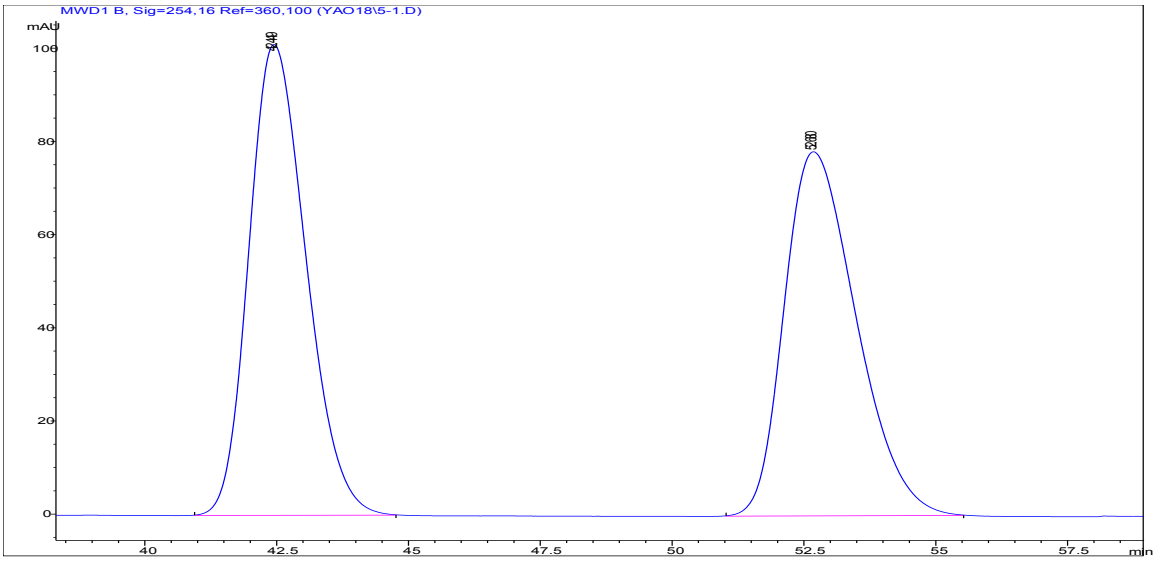
6g

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.586	MM	0.8398	1.48552e4	294.81522	51.9704
2	45.160	MM	1.2787	1.37288e4	178.94424	48.0296
Totals :				2.85839e4	473.75946	

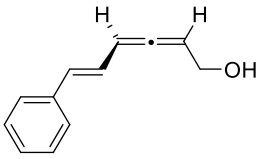


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.595	MM	0.7817	3616.99487	77.11399	8.0906
2	44.826	MM	1.3273	4.10891e4	515.93872	91.9094
Totals :				4.47061e4	593.05271	

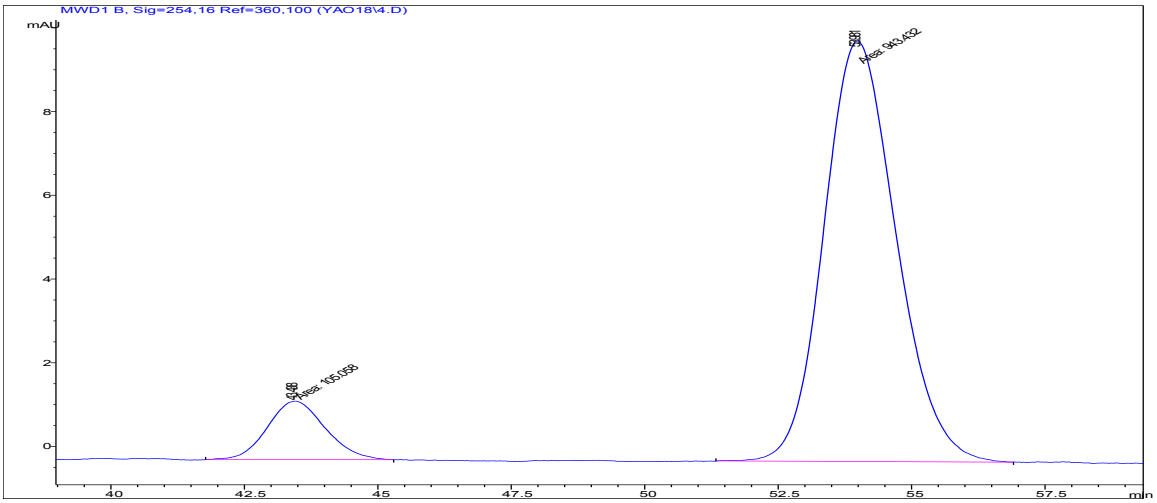


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



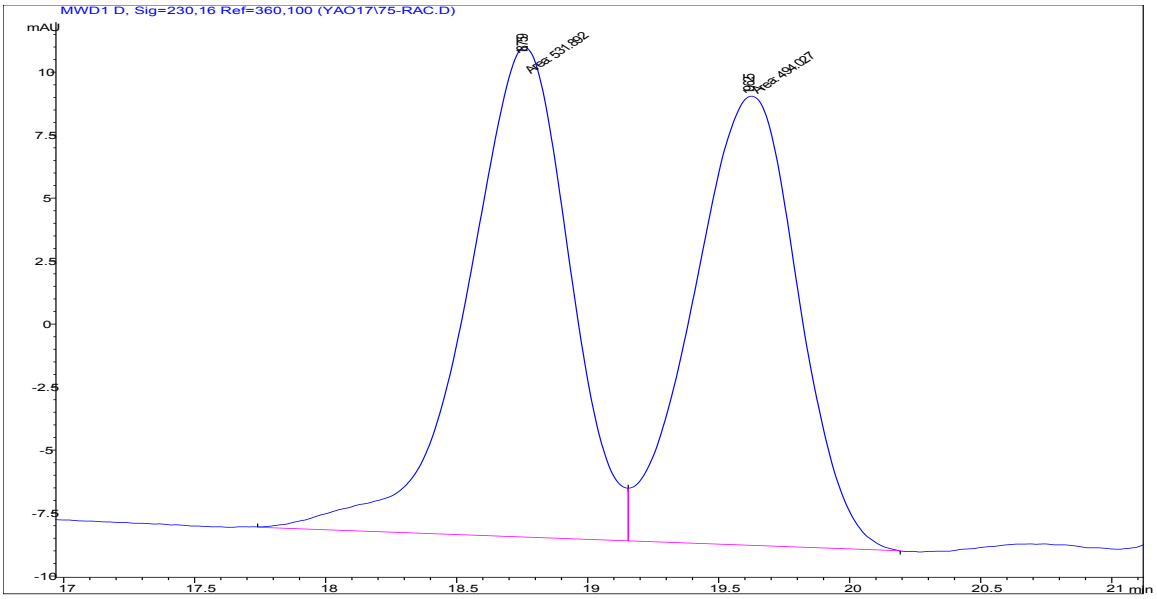
6h

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.449	BB	1.1259	7617.34766	101.00359	50.6764
2	52.680	BB	1.4192	7413.99902	78.11987	49.3236
Totals :				1.50313e4	179.12346	



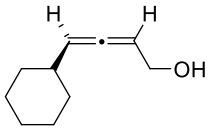
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.438	MM	1.2537	105.05833	1.39660	10.0200
2	53.981	MM	1.5653	943.43237	10.04545	89.9800
Totals :				1048.49070	11.44204	

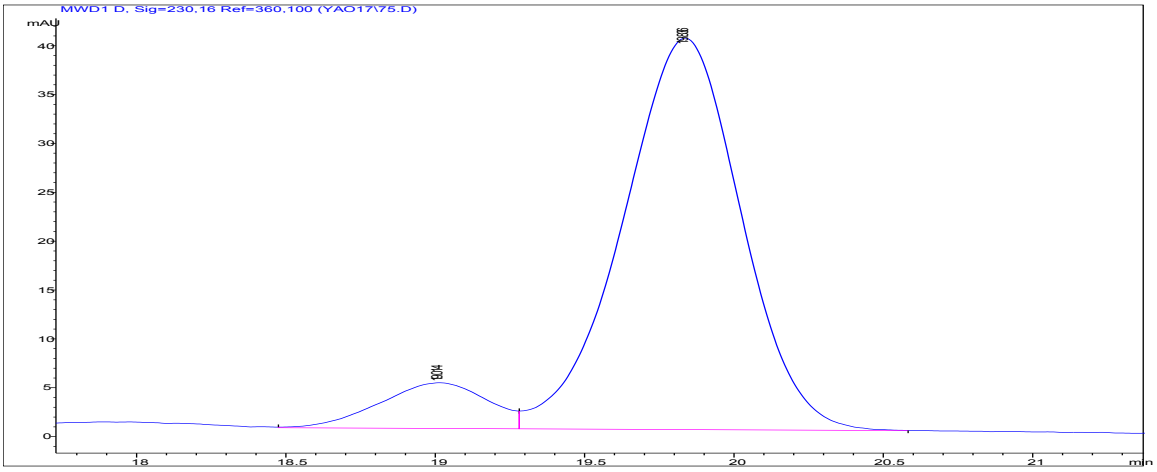


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.759	MF	0.4559	531.89172	19.44322	51.8454
2	19.625	FM	0.4618	494.02719	17.83003	48.1546
Totals :				1025.91891	37.27325	

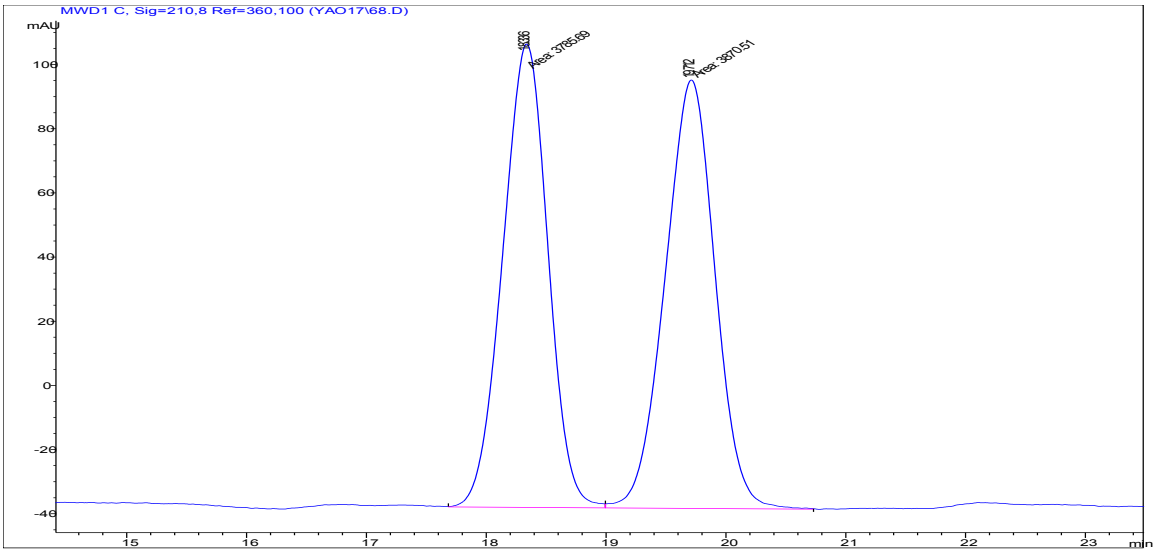


6i

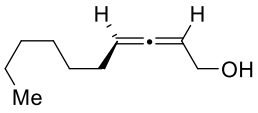


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.014	VV	0.3566	117.23238	4.67478	9.6295
2	19.836	VB	0.4264	1100.19128	40.06168	90.3705
Totals :				1217.42367	44.73646	

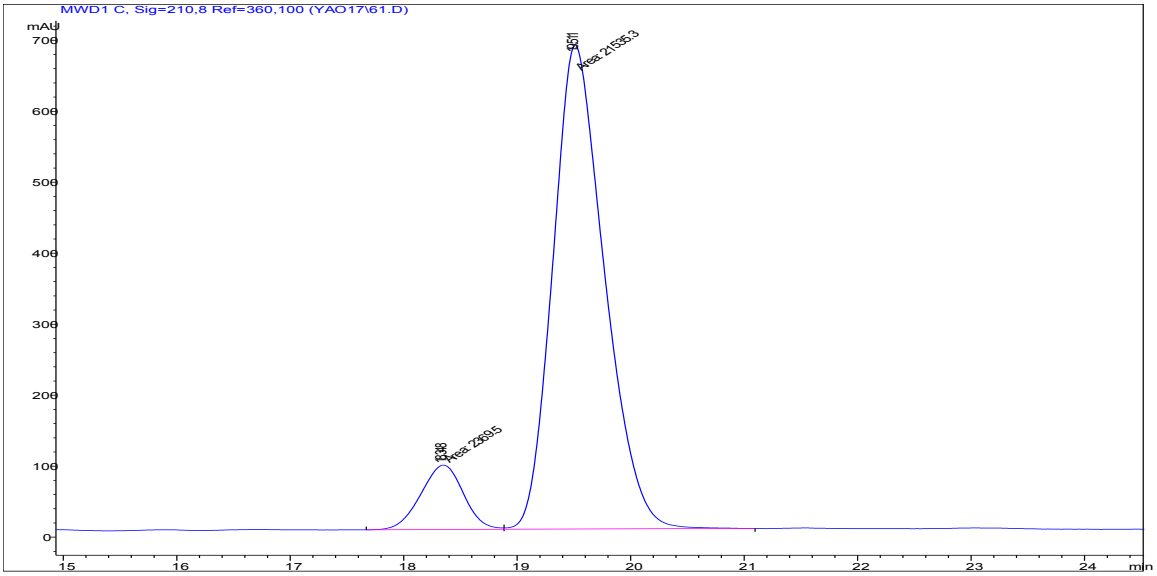


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



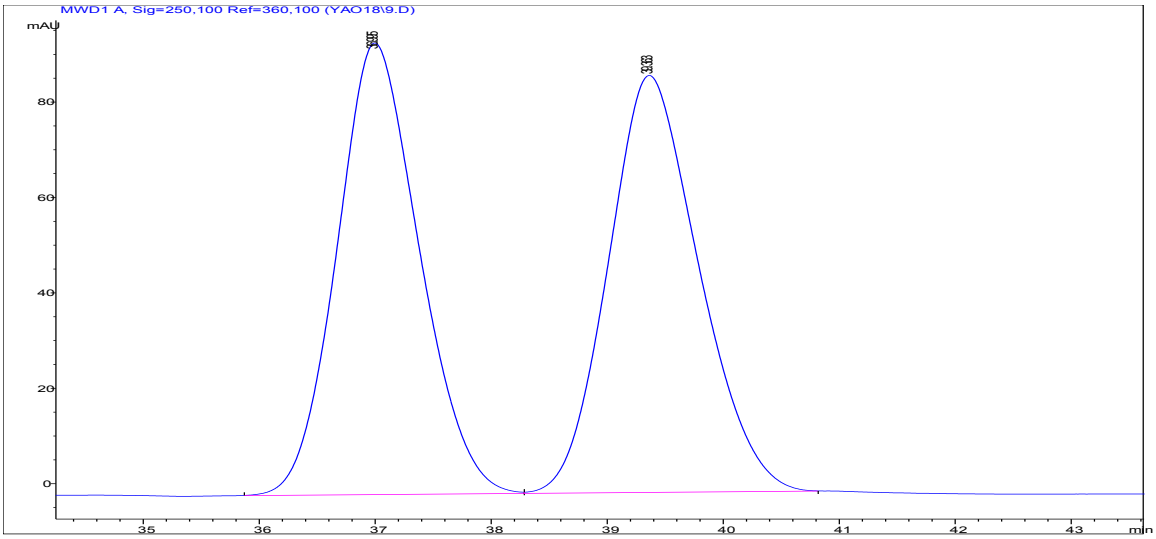
6j

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.336	MF	0.4368	3785.69141	144.43956	49.4461
2	19.712	FM	0.4830	3870.51025	133.54718	50.5539
Totals :				7656.20166	277.98674	



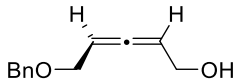
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.348	MF	0.4351	2369.49561	90.75724	9.9122
2	19.511	FM	0.5263	2.15353e4	681.97656	90.0878
Totals :				2.39048e4	772.73380	

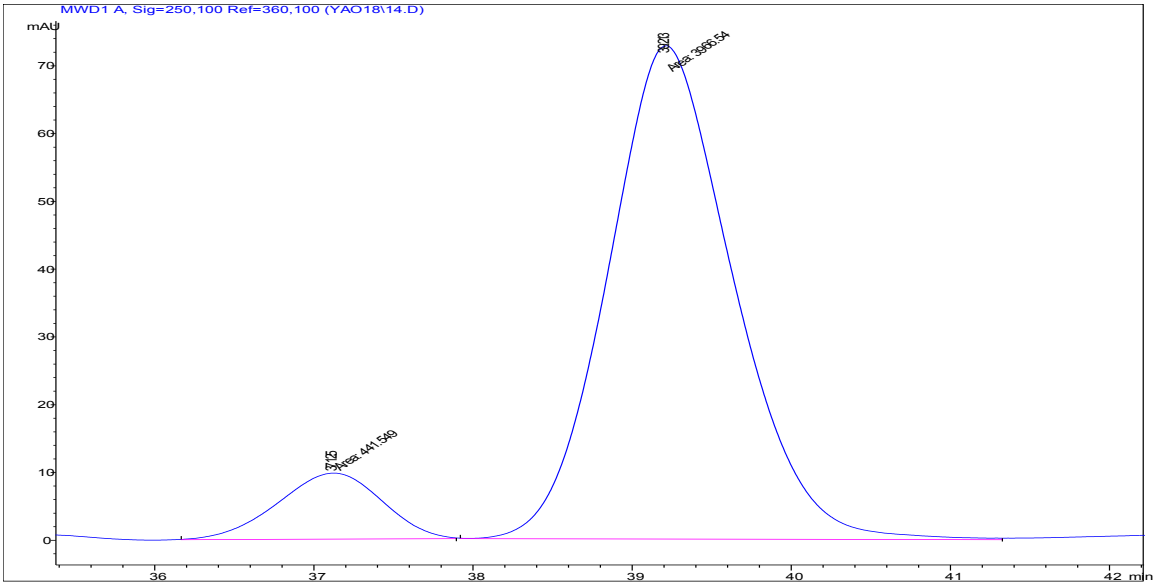


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.995	BV	0.7269	4664.57129	94.66388	49.6491
2	39.363	VB	0.7895	4730.50146	87.39897	50.3509
Totals :				9395.07275	182.06285	

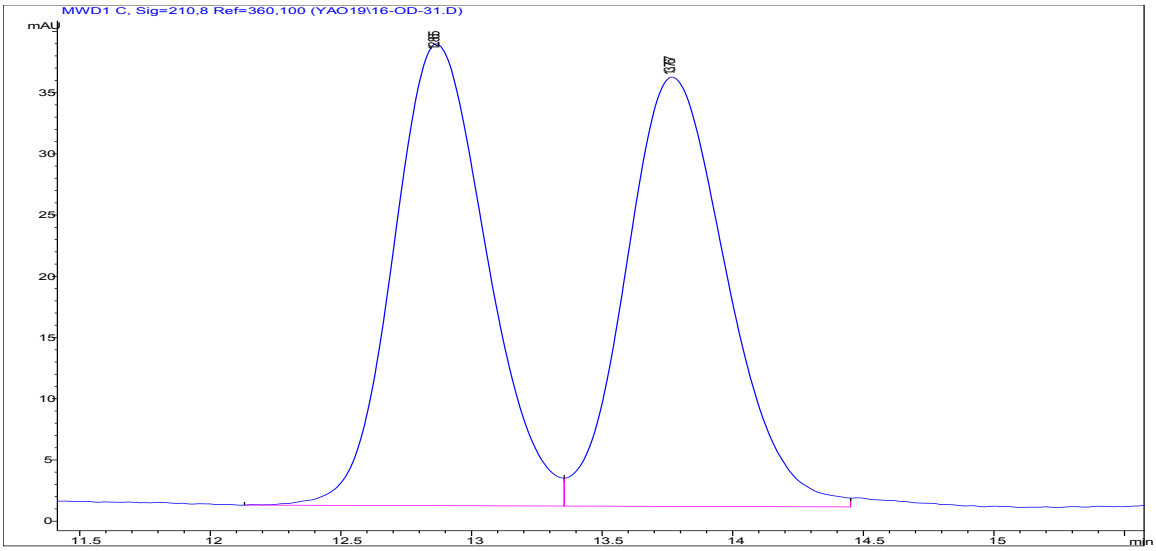


6k



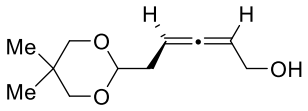
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.125	MM	0.7558	441.54852	9.73720	10.0168
2	39.213	MM	0.9084	3966.54126	72.77692	89.9832
Totals :				4408.08978	82.51411	

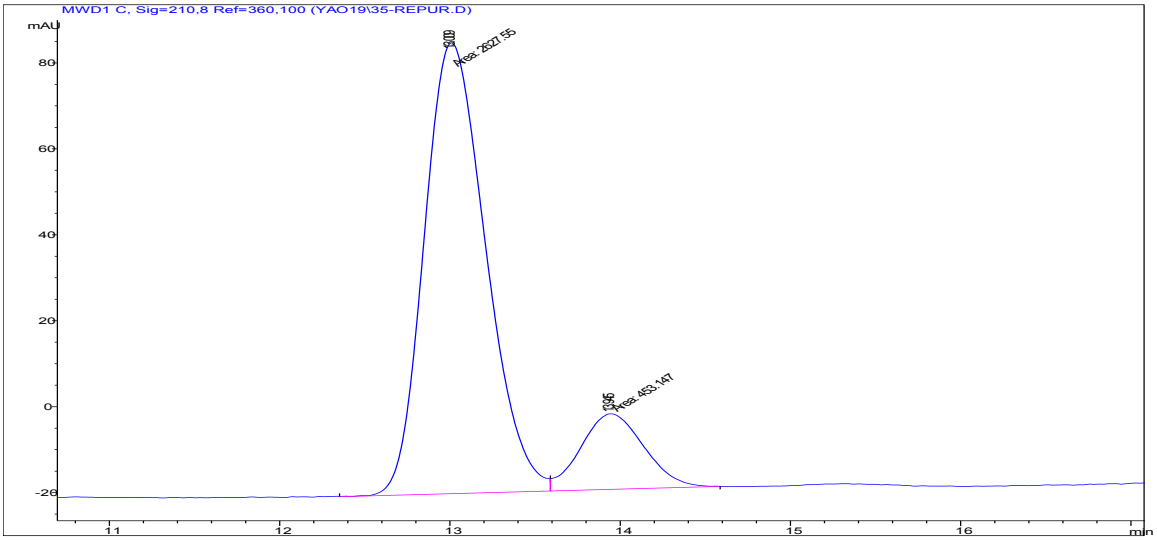


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.865	PV	0.3912	934.88318	37.71471	49.9179
2	13.767	VV	0.4141	937.95966	35.05968	50.0821
Totals :				1872.84283	72.77439	

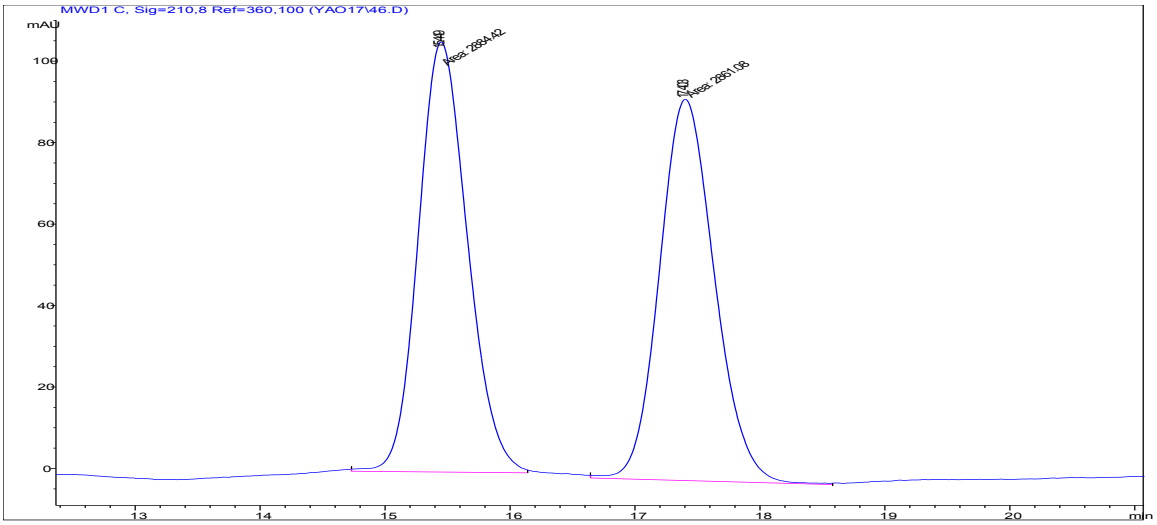


6l

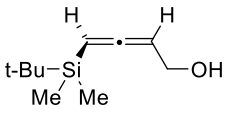


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.009	MF	0.4175	2627.55298	104.89553	85.2908
2	13.945	FM	0.4292	453.14676	17.59686	14.7092
Totals :				3080.69974	122.49239	

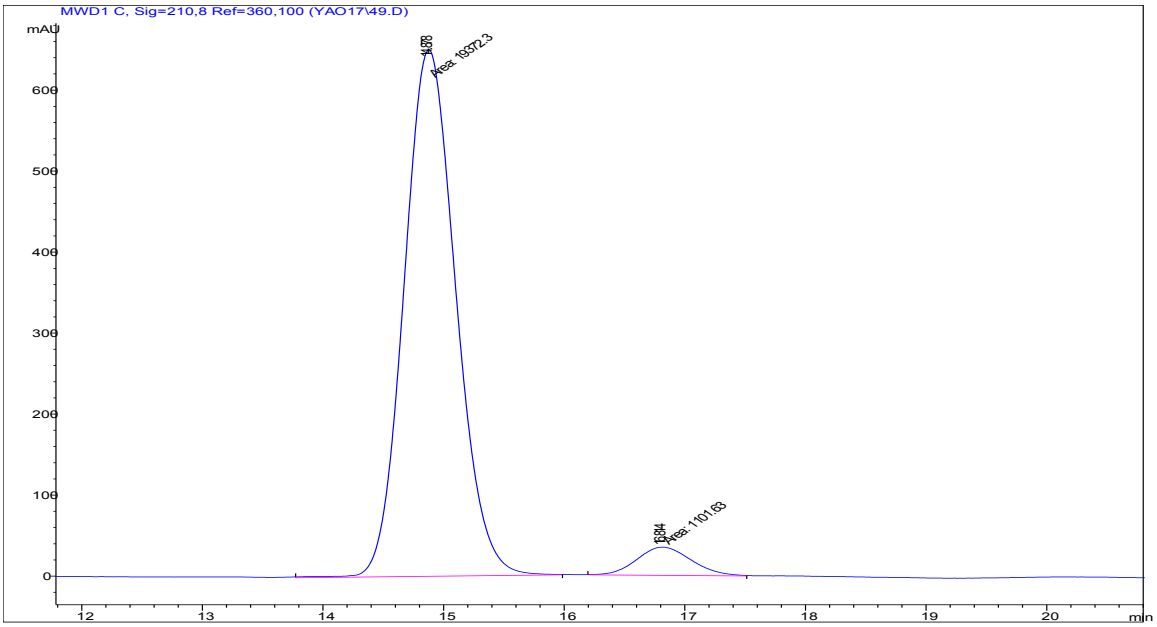


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



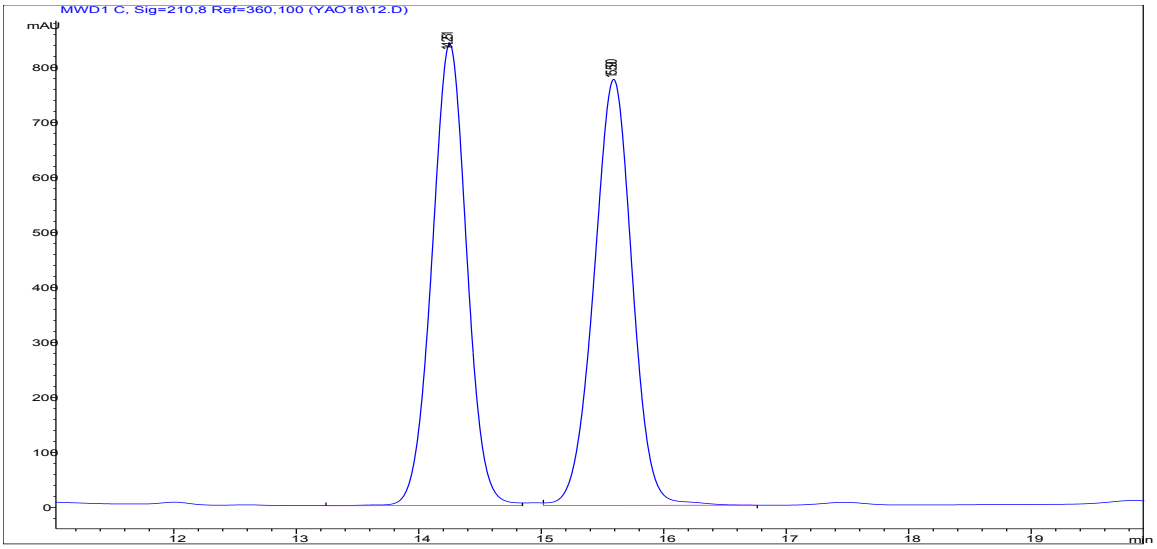
6m

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.449	MM	0.4552	2884.41772	105.60197	50.2031
2	17.403	MM	0.5095	2861.07910	93.58549	49.7969
Totals :				5745.49683	199.18746	



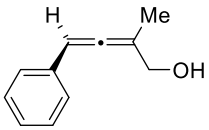
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.878	MM	0.4965	1.93723e4	650.30615	94.6194
2	16.814	MM	0.5256	1101.62573	34.93325	5.3806
Totals :				2.04740e4	685.23940	

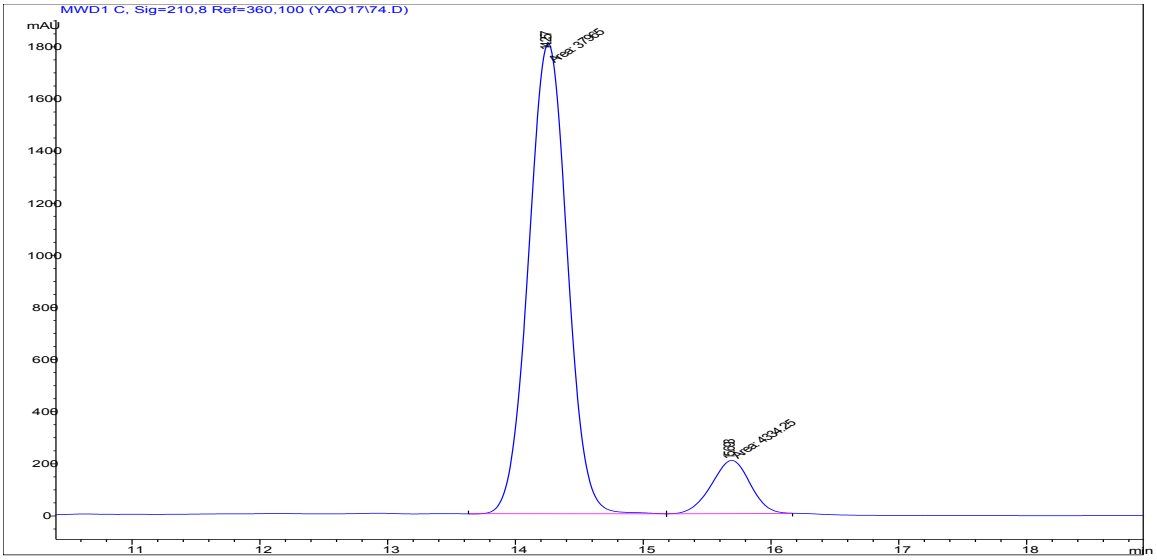


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.251	VV	0.3025	1.65874e4	839.48456	49.6502
2	15.590	VB	0.3334	1.68211e4	774.41156	50.3498
Totals :				3.34085e4	1613.89612	

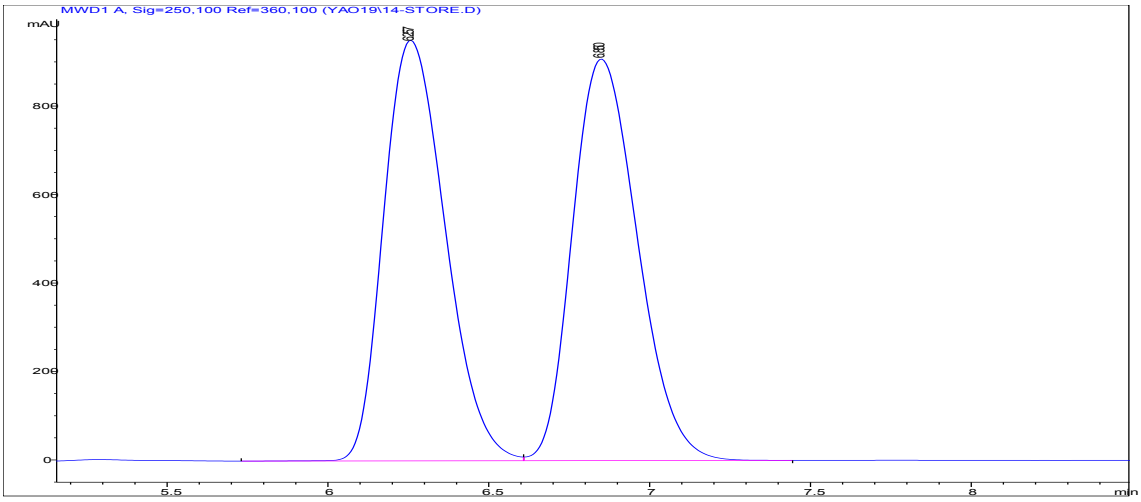


6n



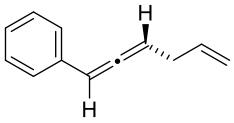
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.257	MM	0.3506	3.79650e4	1804.73767	89.7534
2	15.693	MM	0.3535	4334.24658	204.35019	10.2466
Totals :				4.22992e4	2009.08786	

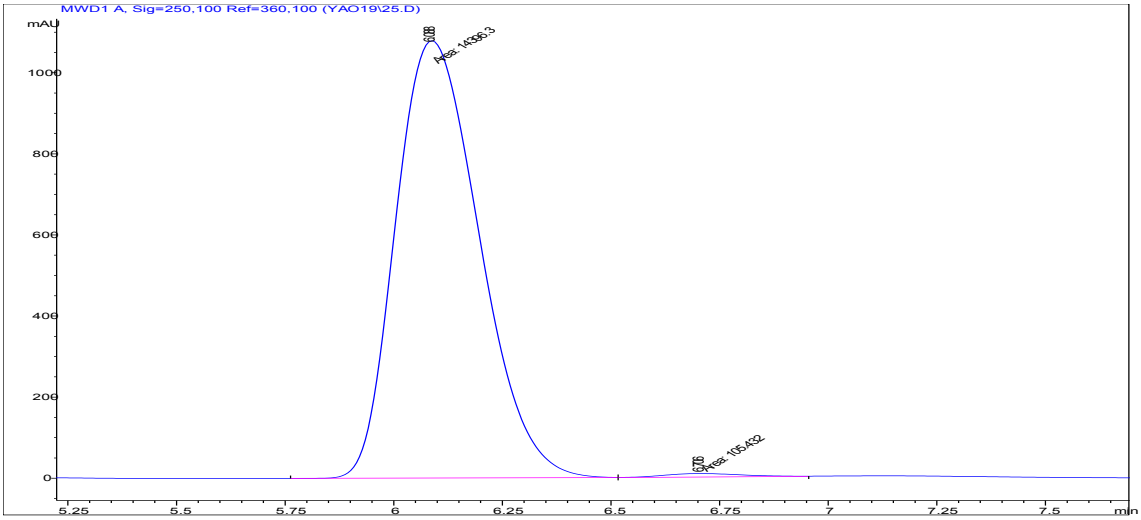


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.257	VV	0.2115	1.26719e4	951.03210	49.8235
2	6.850	VB	0.2220	1.27616e4	907.89984	50.1765
Totals :				2.54335e4	1858.93195	

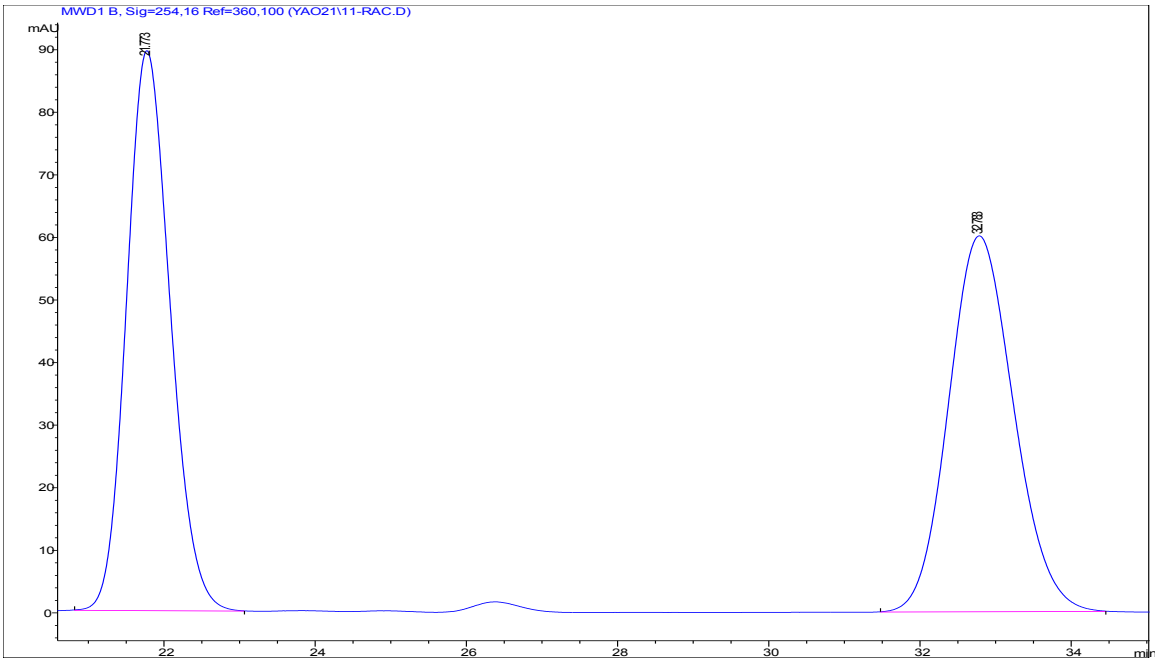


7a



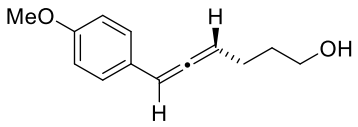
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.088	MM	0.2224	1.43963e4	1078.87366	99.2730
2	6.706	MM	0.2043	105.43246	8.60119	0.7270
Totals :				1.45017e4	1087.47484	

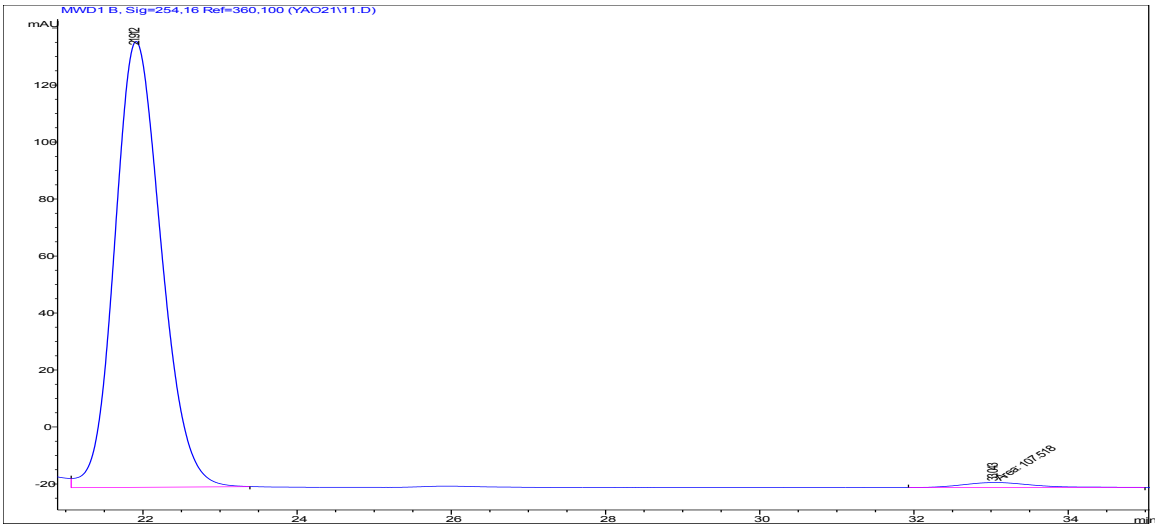


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.773	BB	0.6223	3592.52222	89.49754	50.0242
2	32.783	BB	0.9149	3589.04053	60.08356	49.9758
Totals :				7181.56274	149.58110	

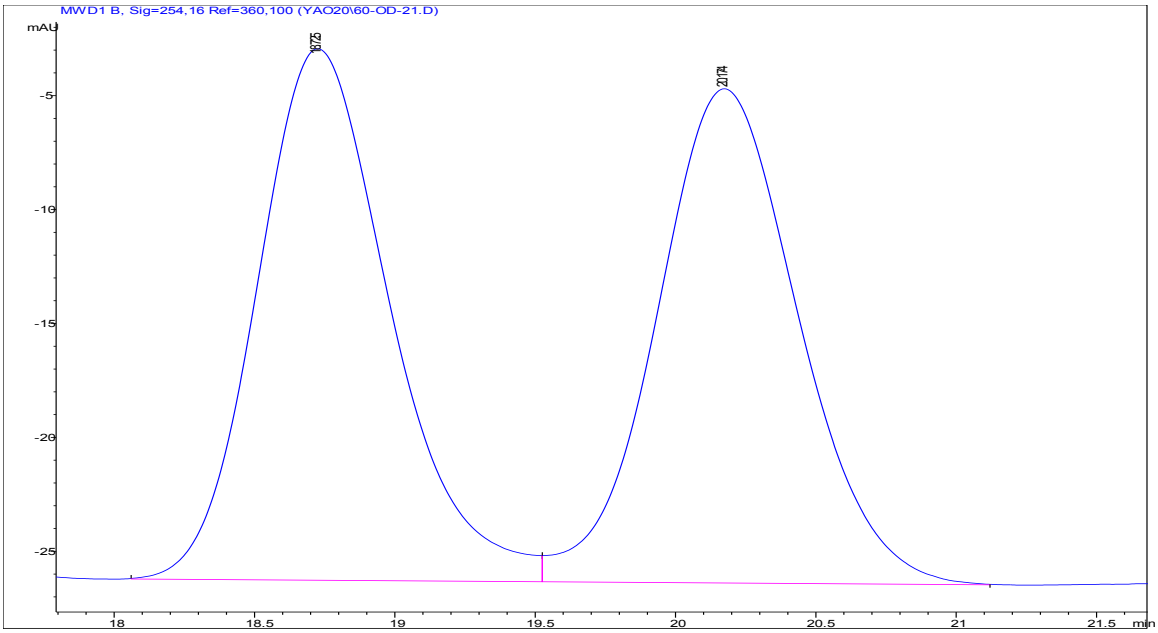


S7b



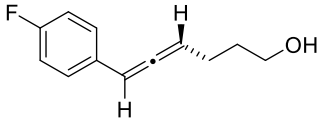
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.912	VB	0.6473	6562.77930	156.49417	98.3881
2	33.043	MM	1.0262	107.51844	1.74614	1.6119
Totals :				6670.29774	158.24032	

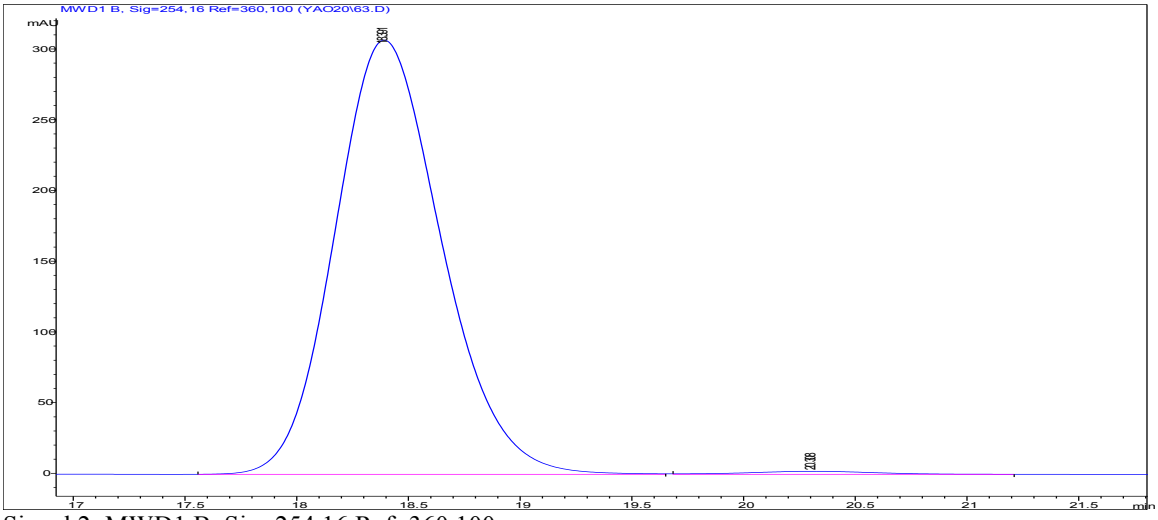


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.725	BV	0.5064	764.85852	23.33280	50.1838
2	20.174	VB	0.5423	759.25659	21.69337	49.8162
Totals :				1524.11511	45.02617	

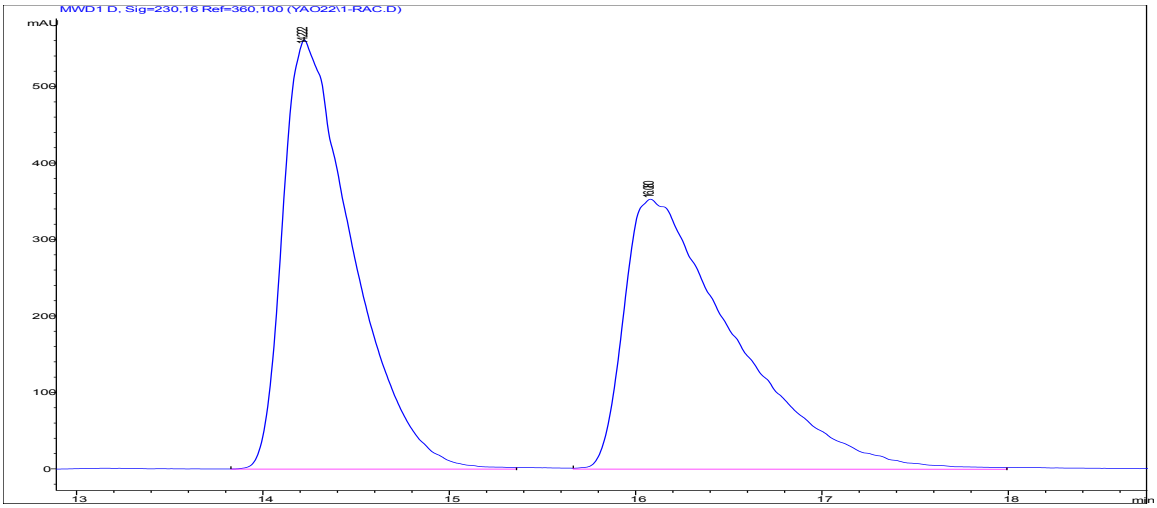


S7c



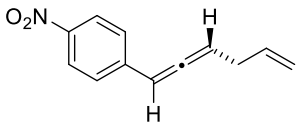
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.391	BB	0.5153	1.01933e4	307.01639	99.1788
2	20.308	BB	0.5158	84.40445	2.15095	0.8212
Totals :				1.02777e4	309.16734	

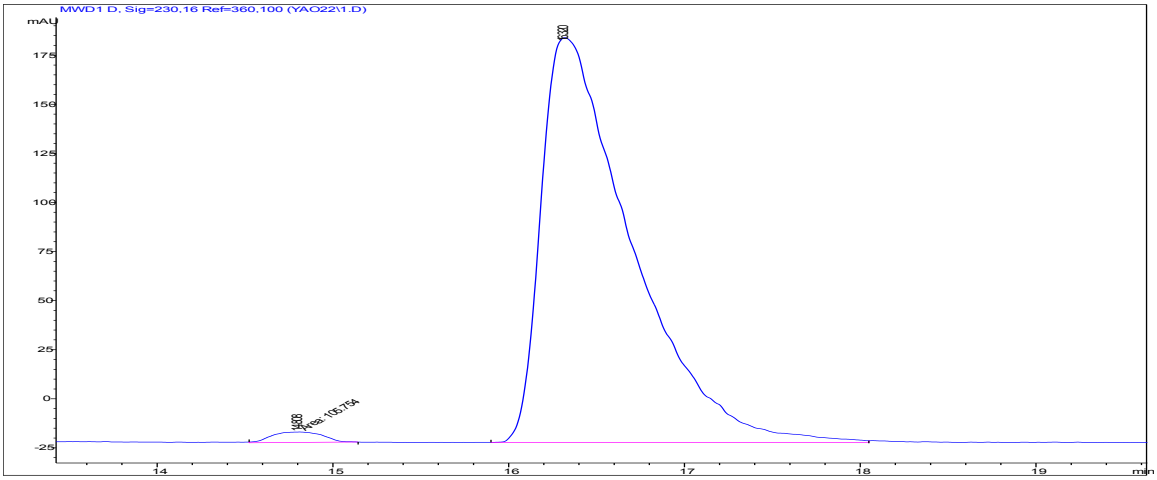


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.222	VV	0.3199	1.46301e4	561.61340	50.2835
2	16.080	VV	0.4940	1.44652e4	353.08664	49.7165
Totals :				2.90953e4	914.70004	

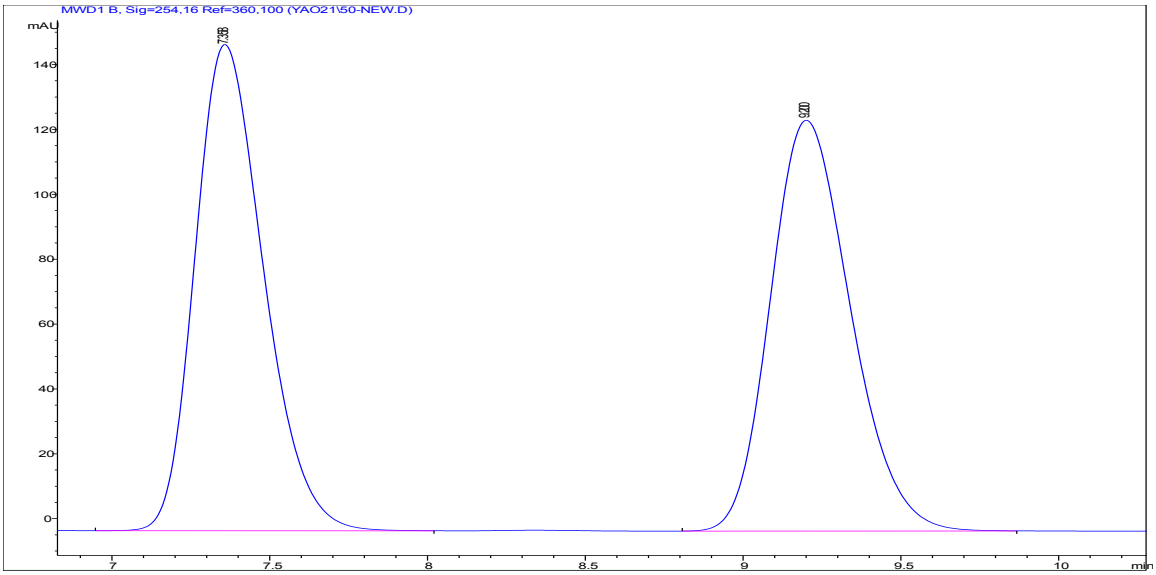


7d

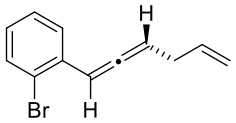


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.808	MM	0.3344	105.75404	5.27122	1.4140
2	16.320	VV	0.4909	7373.18750	206.31596	98.5860
Totals :				7478.94154	211.58718	

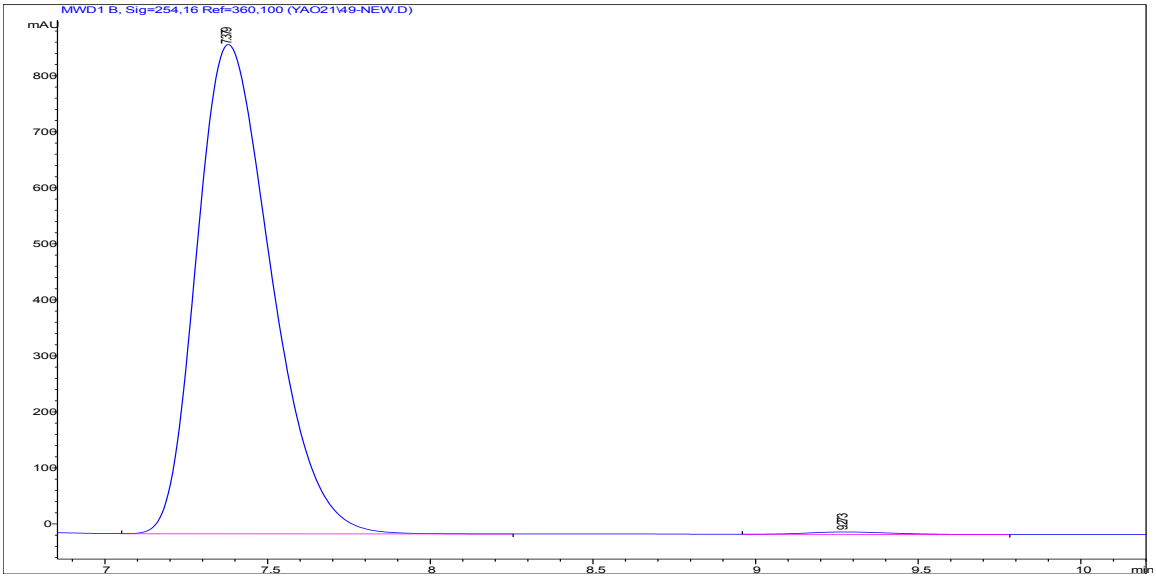


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



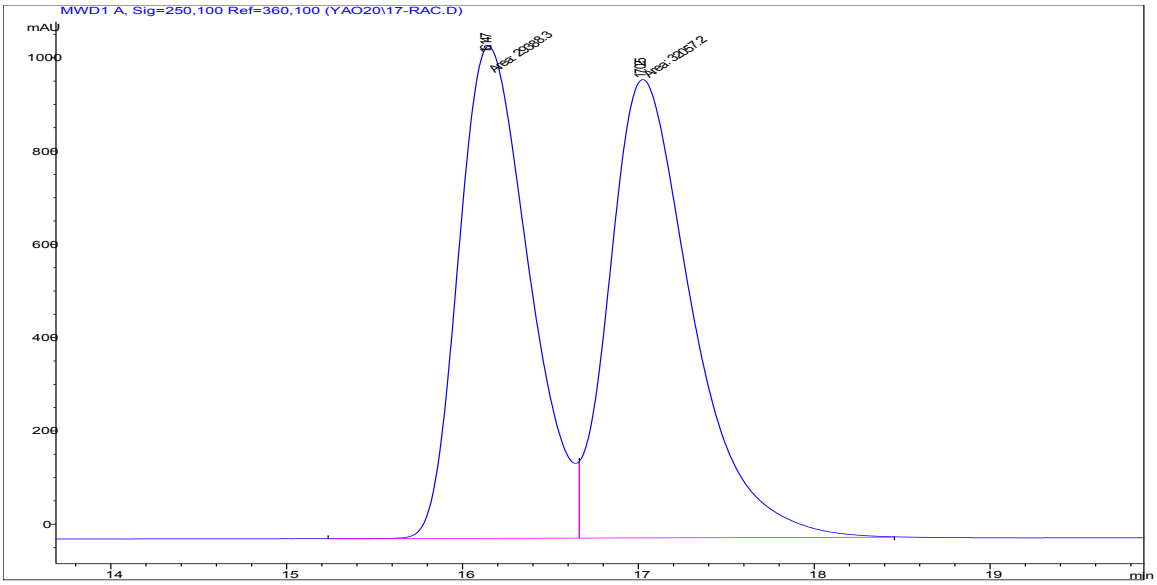
7e

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.358	VB	0.2345	2268.17944	149.96297	50.3140
2	9.200	BB	0.2763	2239.86938	126.67419	49.6860
Totals :				4508.04883	276.63716	

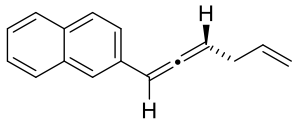


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.379	VP	0.2477	1.39069e4	873.65680	99.4693
2	9.273	BP	0.2707	74.19672	4.22903	0.5307
Totals :				1.39811e4	877.88583	

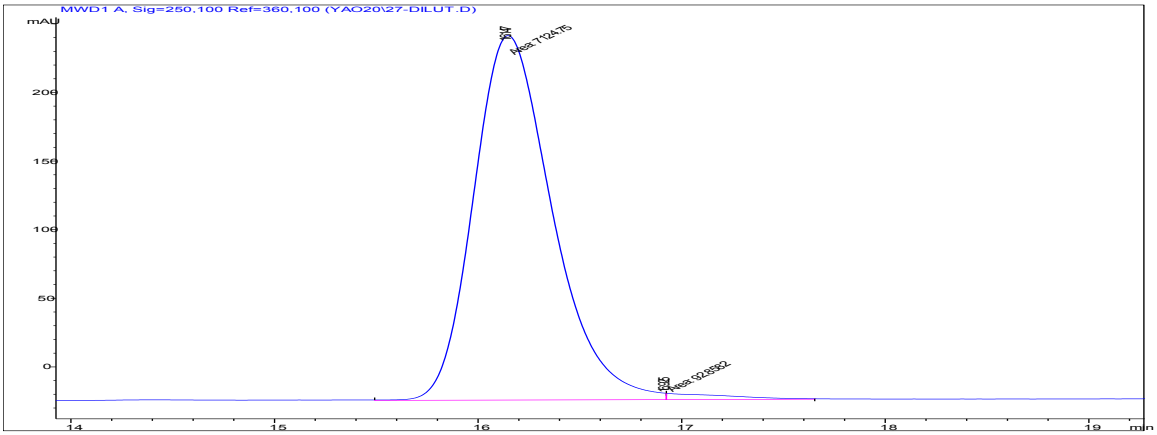


Signal 1: MWD1 A, Sig=250,100 Ref=360,100



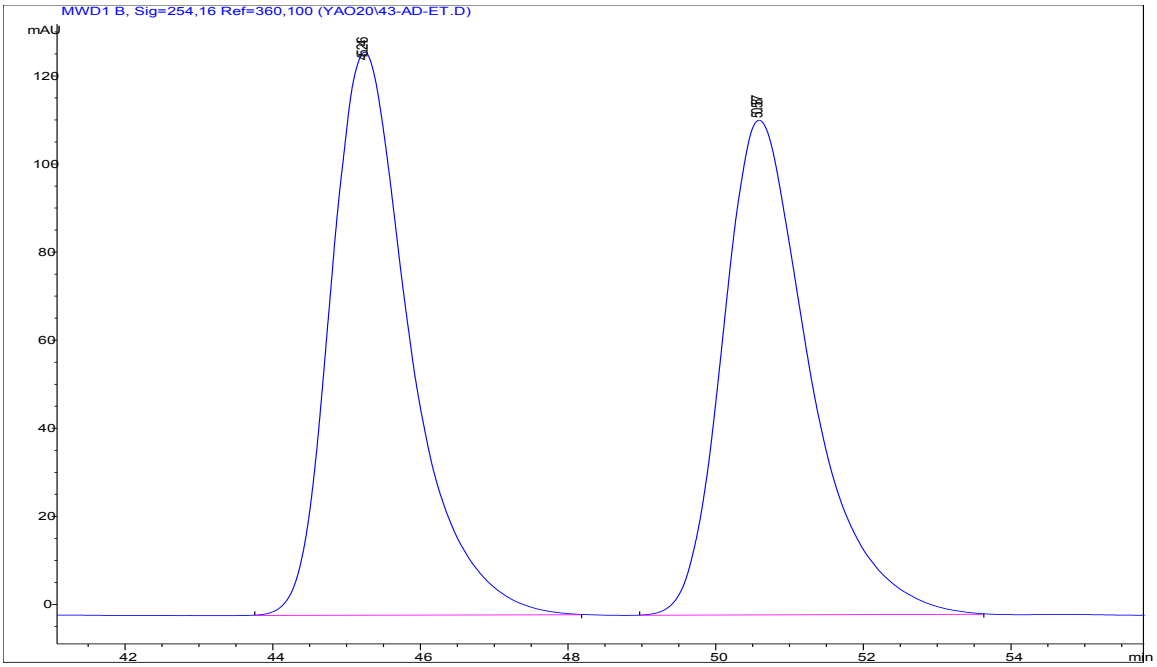
7f

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.147	MF	0.4642	2.93883e4	1055.14380	47.8283
2	17.025	FM	0.5436	3.20572e4	982.77771	52.1717
Totals :				6.14455e4	2037.92151	



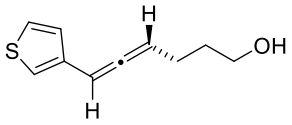
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.147	MF	0.4470	7124.74658	265.67194	98.7134
2	16.925	FM	0.3361	92.85820	4.60466	1.2866
Totals :				7217.60478	270.27660	

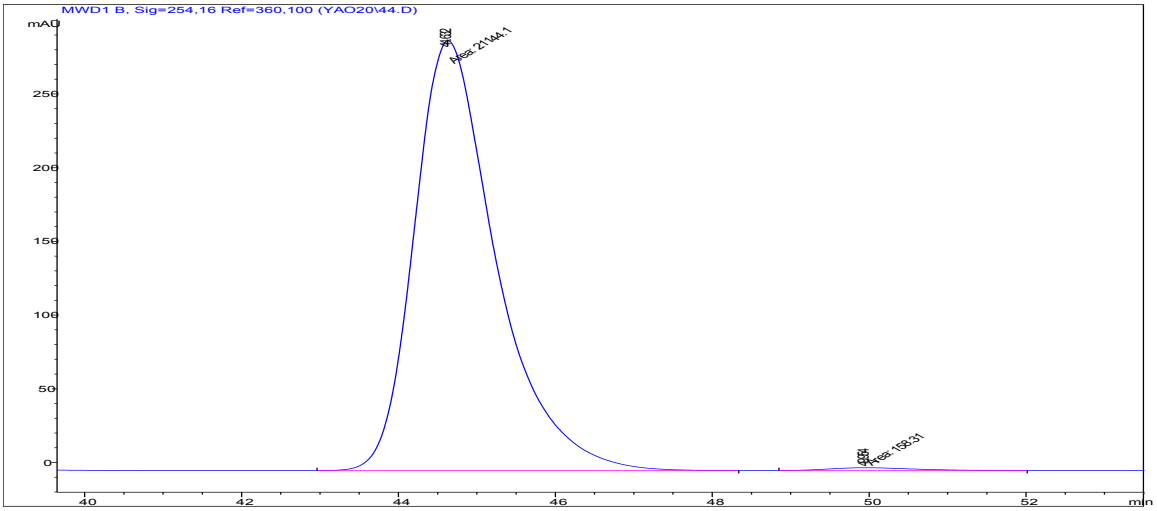


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.246	BB	1.0746	9559.47070	127.81477	50.9275
2	50.587	BB	1.2408	9211.27930	112.31322	49.0725
Totals :				1.87708e4	240.12799	

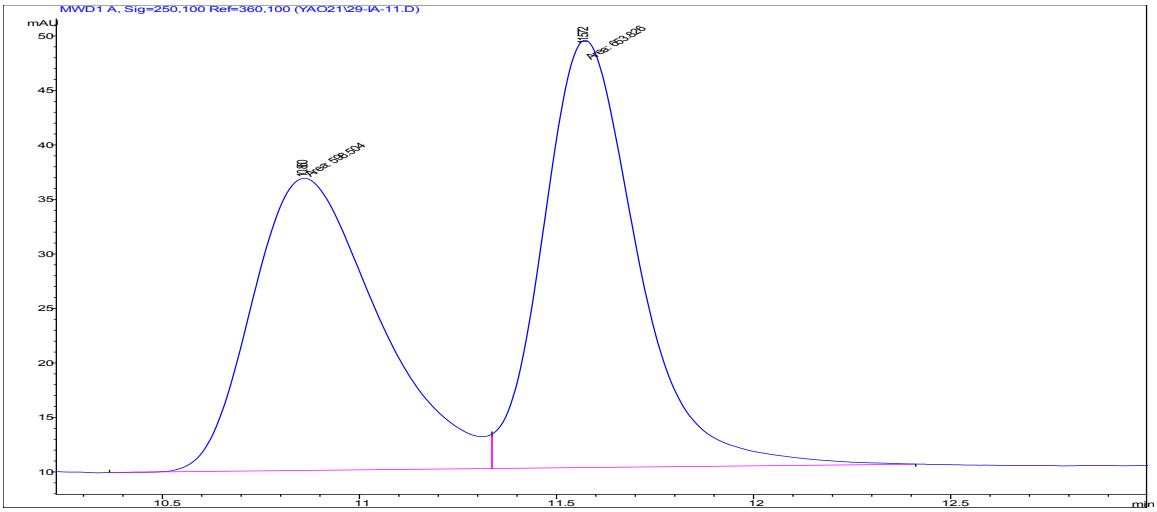


S7g

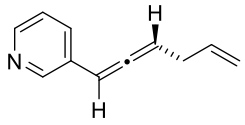


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.632	MM	1.2082	2.11441e4	291.68411	99.2568
2	49.954	MM	1.3190	158.31035	2.00036	0.7432
Totals :				2.13024e4	293.68447	

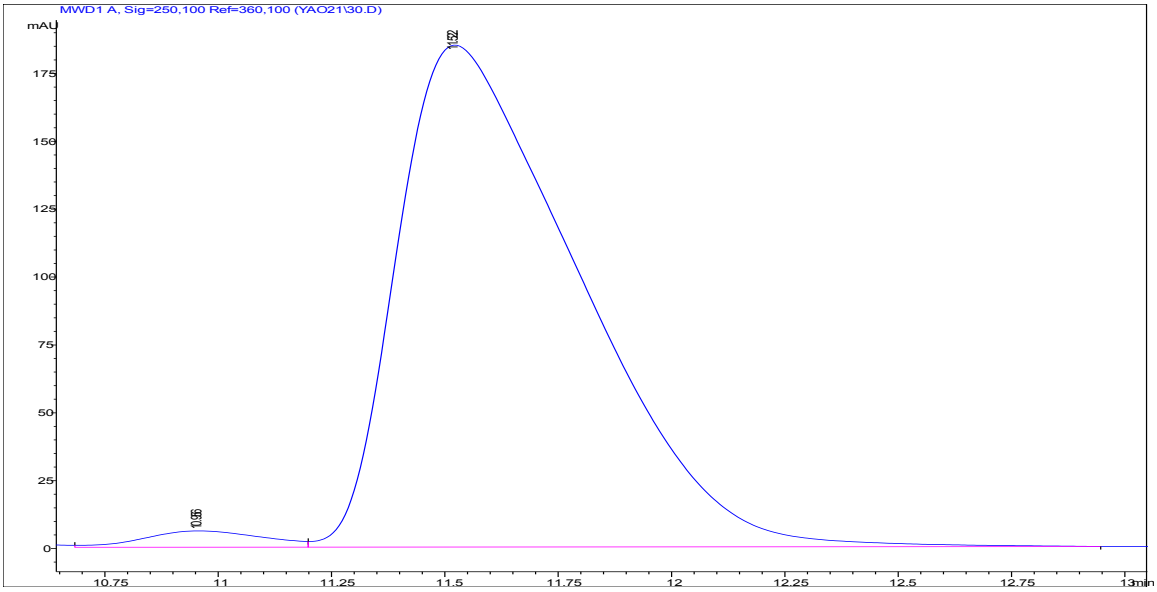


Signal 1: MWD1 A, Sig=250,100 Ref=360,100



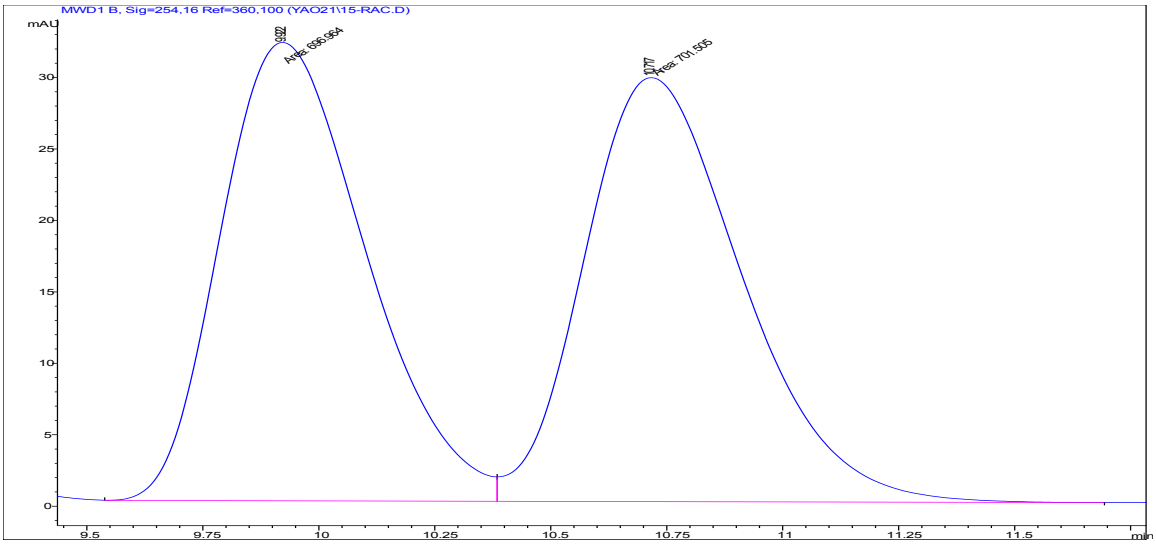
7h

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.860	MF	0.3721	598.50427	26.80676	47.7913
2	11.572	FM	0.2778	653.82581	39.22197	52.2087
Totals :				1252.33008	66.02874	

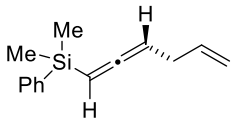


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.956	VV	0.2740	109.08604	6.00417	2.0786
2	11.522	VB	0.4083	5138.98145	184.88509	97.9214
Totals :				5248.06749	190.88926	

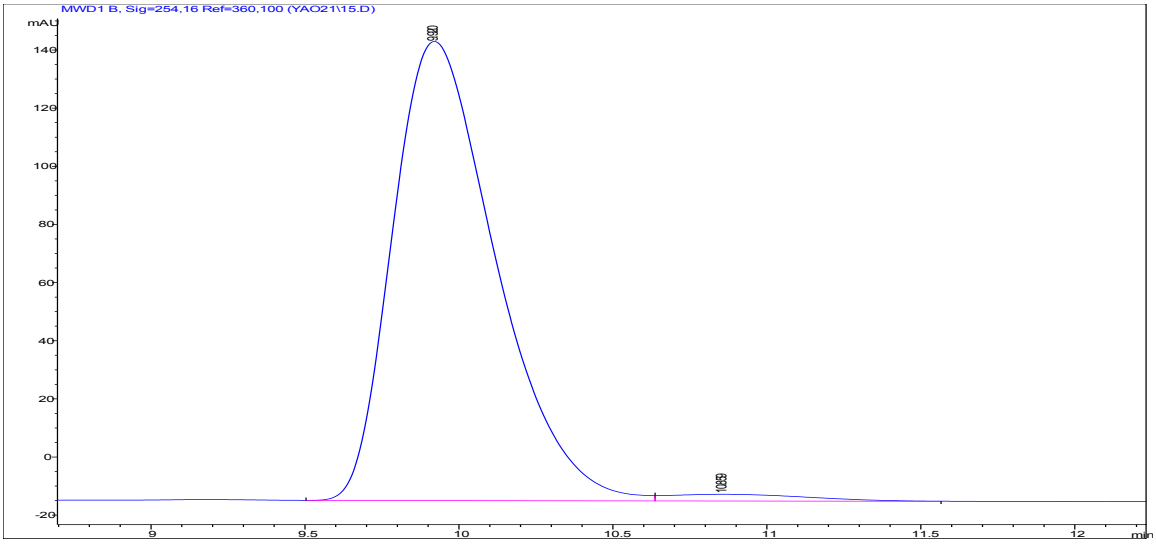


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



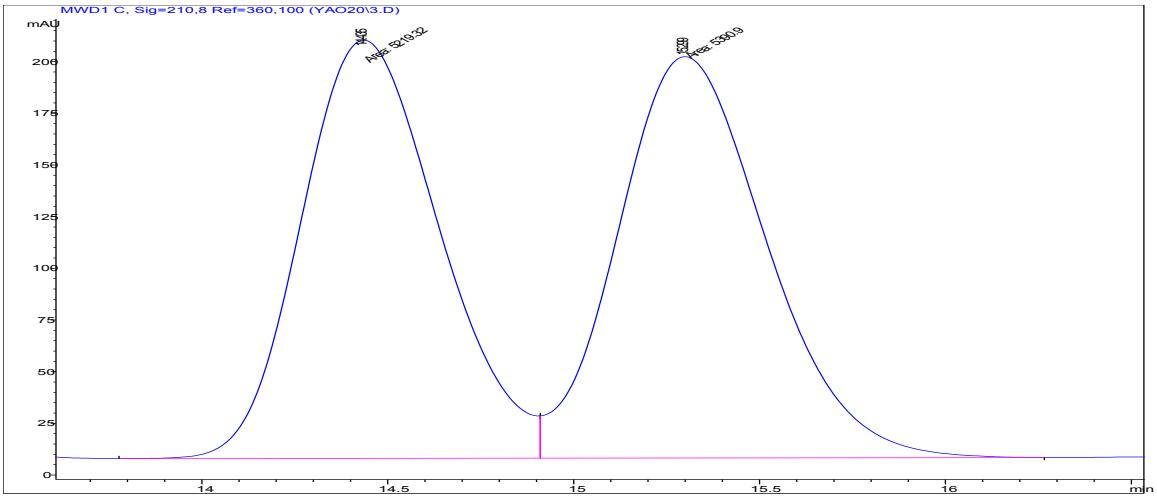
7i

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.922	MF	0.3621	696.96429	32.08057	49.8376
2	10.717	FM	0.3941	701.50549	29.66974	50.1624
Totals :				1398.46979	61.75031	



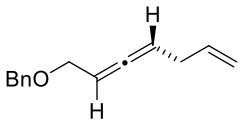
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.920	VV	0.3637	3677.83496	157.94389	98.0815
2	10.859	VB	0.3822	71.94076	2.30454	1.9185
Totals :				3749.77572	160.24843	

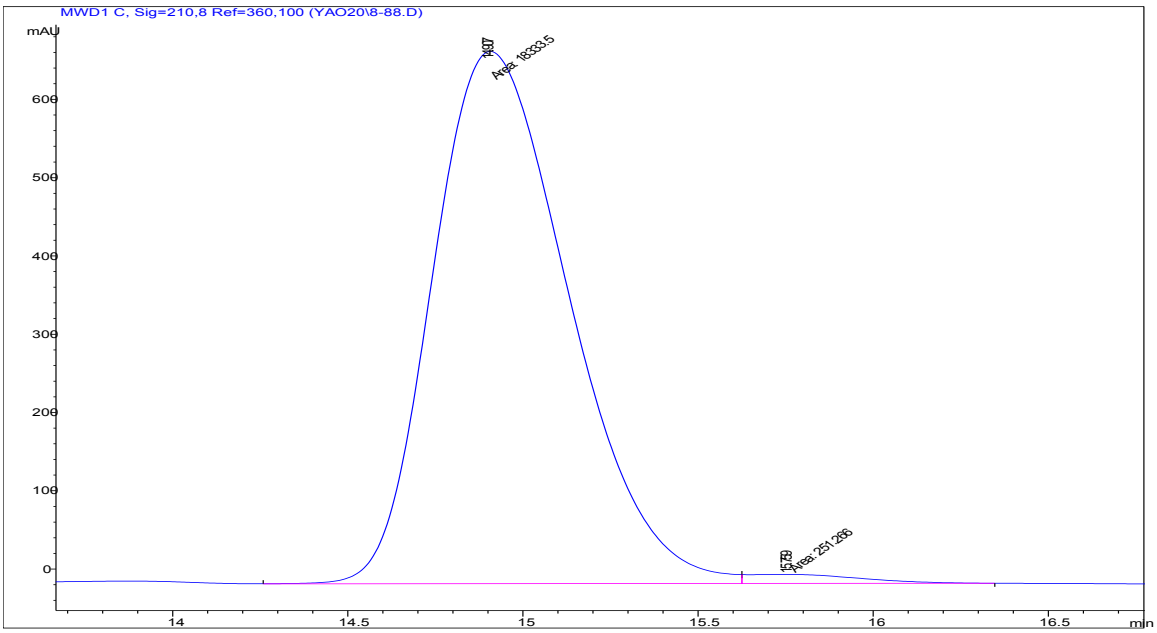


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.435	MF	0.4298	5219.31787	202.38109	49.1914
2	15.299	FM	0.4627	5390.89844	194.17436	50.8086
Totals :				1.06102e4	396.55545	

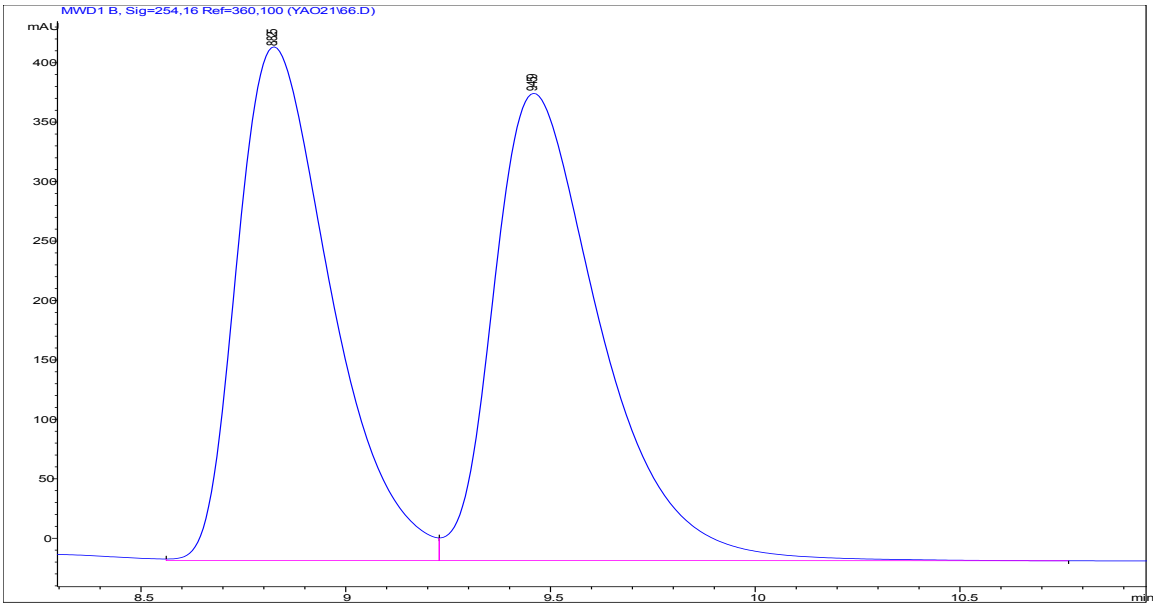


7j



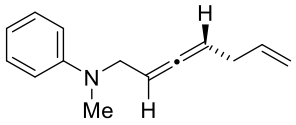
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.907	MF	0.4493	1.83335e4	680.11548	98.6480
2	15.759	FM	0.3634	251.26598	11.52379	1.3520
Totals :				1.85848e4	691.63927	

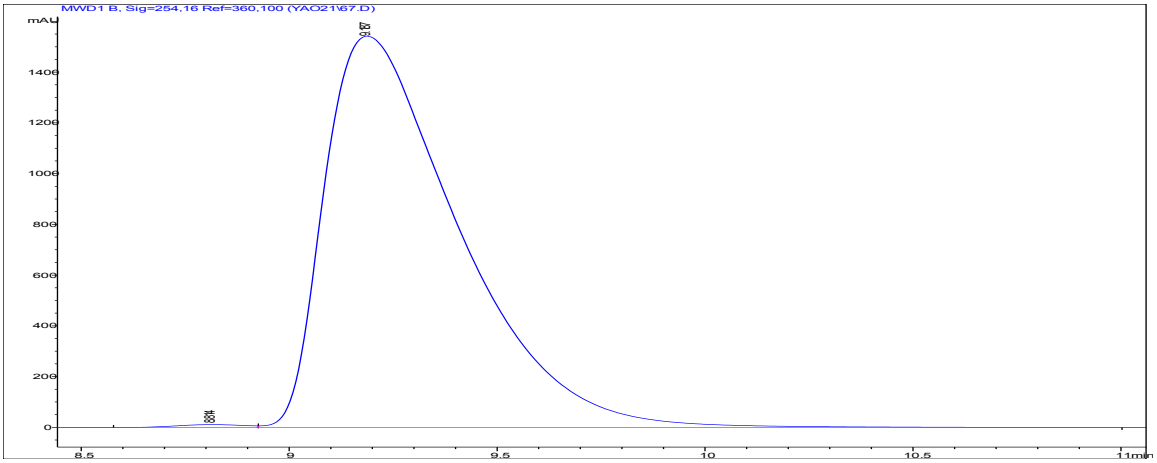


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.825	VV	0.2461	6892.05127	432.06876	49.1223
2	9.459	VB	0.2759	7138.33105	393.07870	50.8777
Totals :				1.40304e4	825.14746	

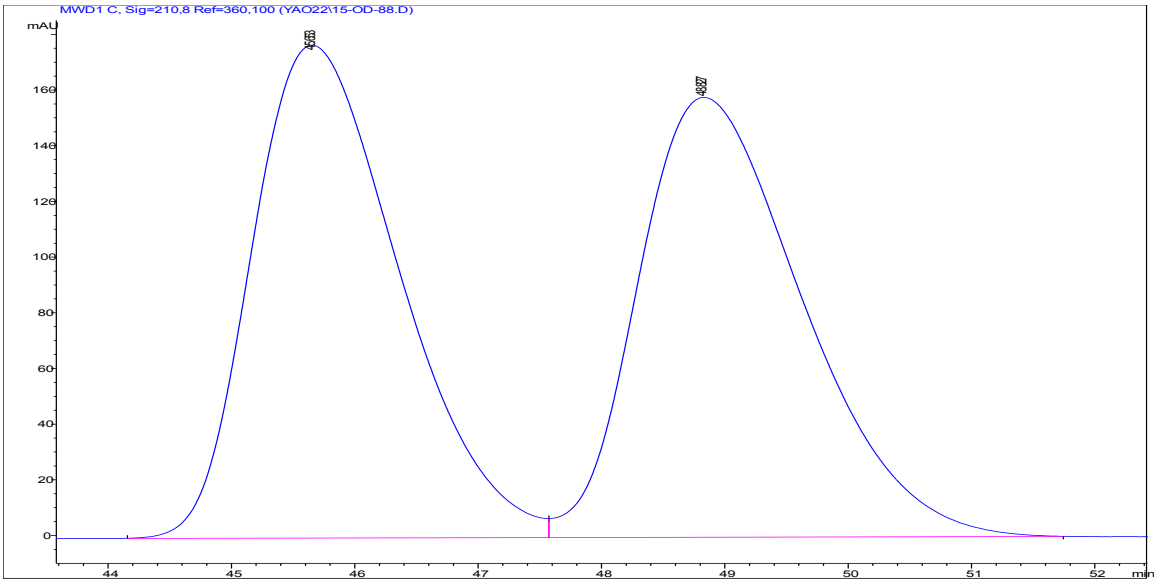


7k

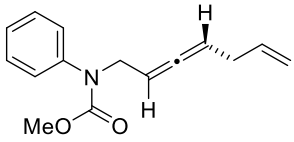


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.814	VV	0.1824	132.84184	11.53262	0.3823
2	9.187	VB	0.3317	3.46116e4	1542.96179	99.6177
Totals :				3.47444e4	1554.49441	

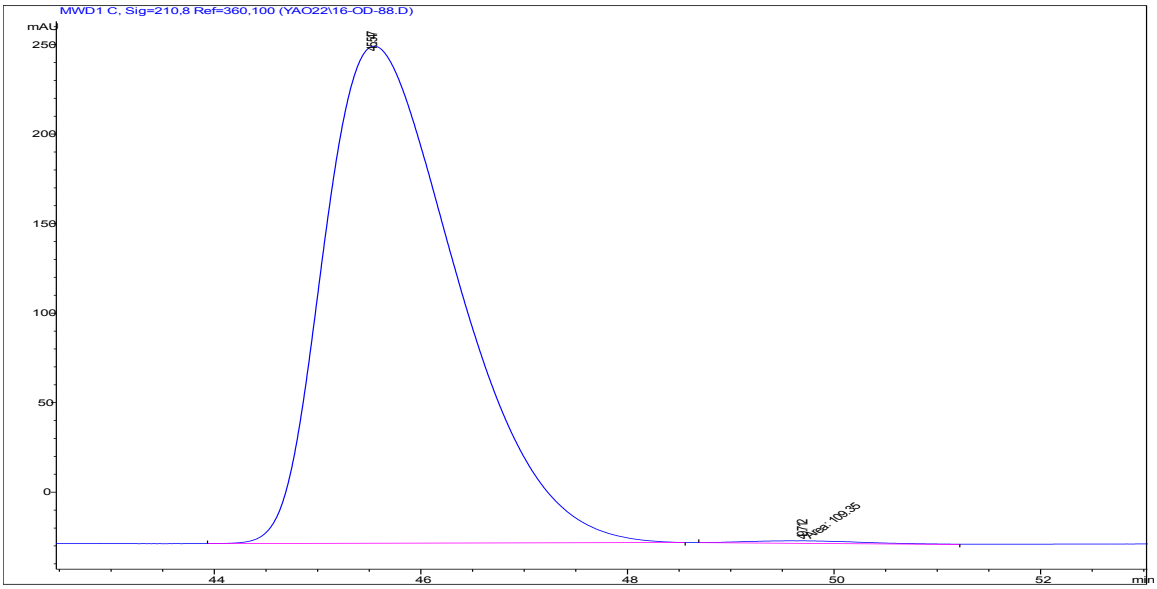


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



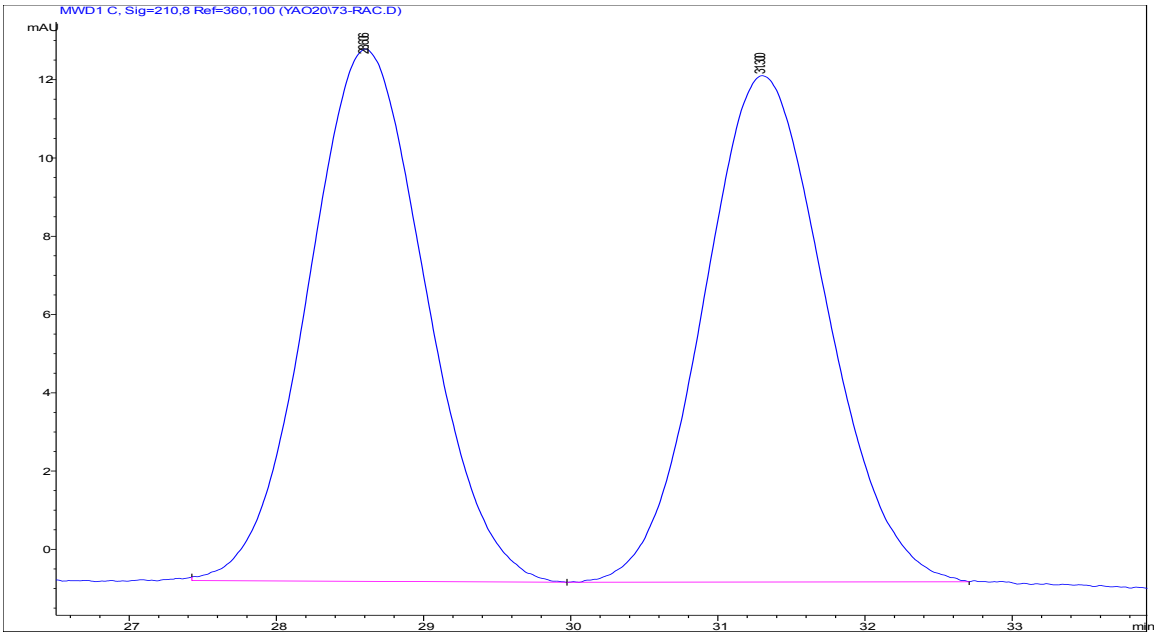
7l

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.653	BV	1.2073	1.46786e4	177.04016	50.1230
2	48.827	VB	1.3625	1.46066e4	158.01196	49.8770
Totals :				2.92853e4	335.05212	

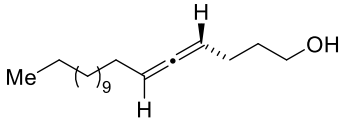


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

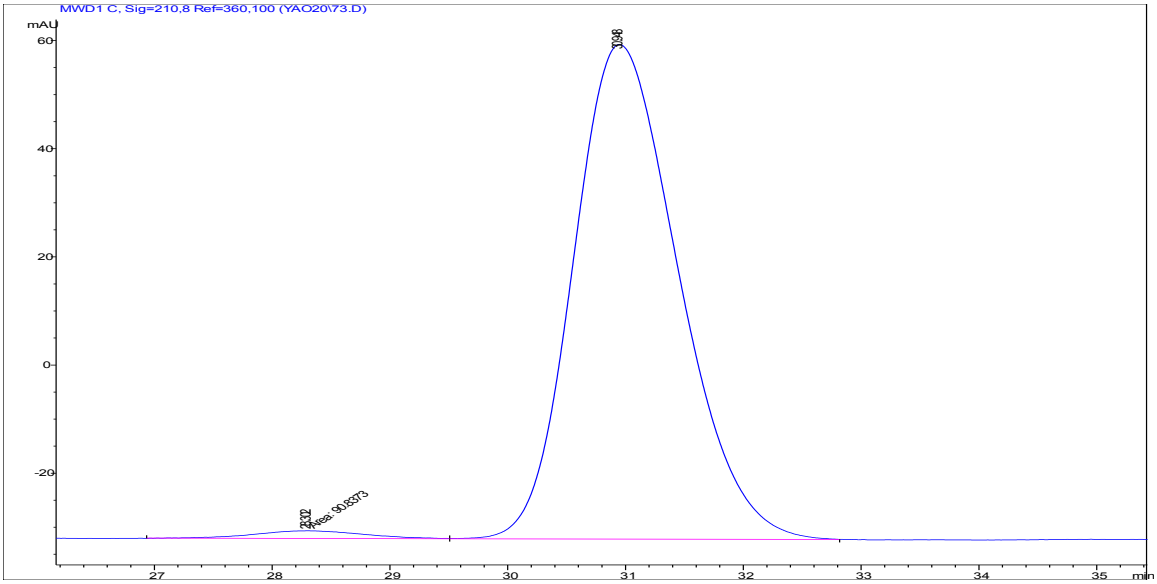
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.547	BB	1.3380	2.47968e4	277.64362	99.5610
2	49.712	MM	1.2803	109.34953	1.42350	0.4390
Totals :				2.49062e4	279.06711	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.606	BP	0.7122	753.59131	13.60506	50.1497
2	31.300	VV	0.6875	749.09137	12.93819	49.8503
Totals :				1502.68268	26.54325	

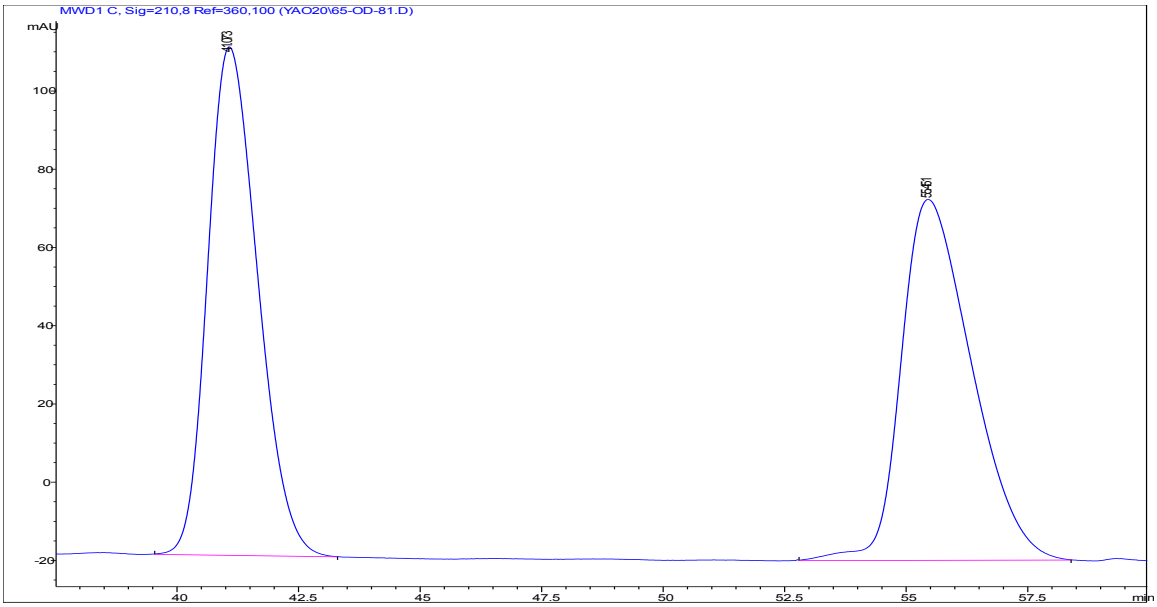


S7m



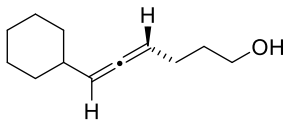
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.302	MM	1.0558	90.83733	1.43388	1.5843
2	30.948	VB	0.9454	5642.61475	91.50510	98.4157
Totals :				5733.45207	92.93897	

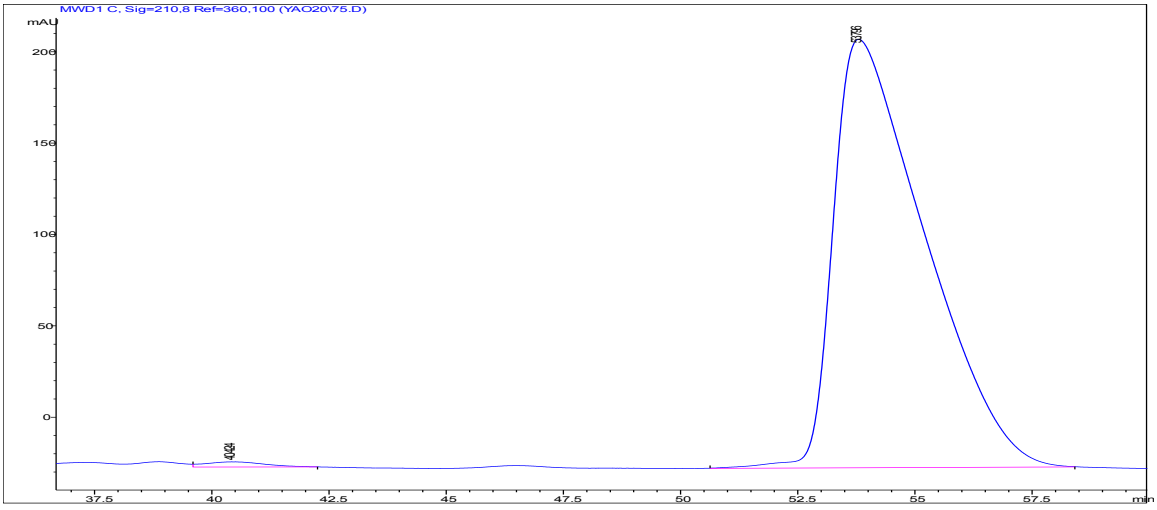


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.073	BB	1.1010	9302.50684	129.98210	50.0732
2	55.451	VB	1.4112	9275.30566	92.23551	49.9268
Totals :				1.85778e4	222.21761	

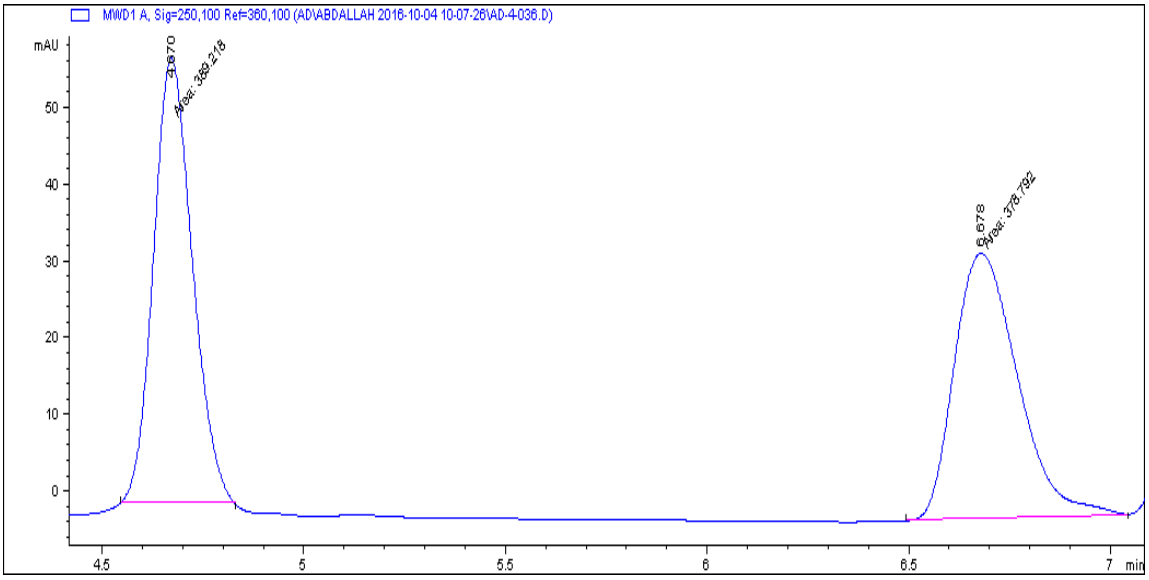


S7n

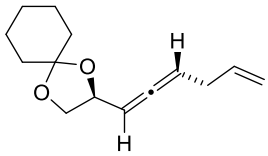


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.424	VB	1.0311	249.30116	2.83738	0.7788
2	53.796	BB	1.8265	3.17606e4	234.44470	99.2212
Totals :				3.20099e4	237.28209	

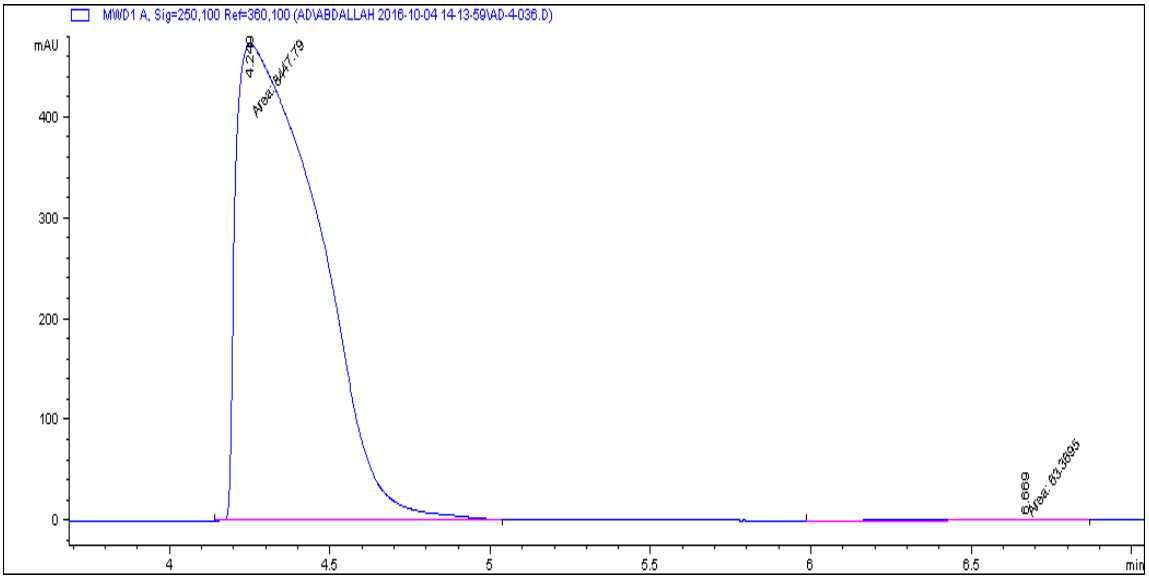


Signal 1: MWD1 A, Sig=250,100 Ref=360,100



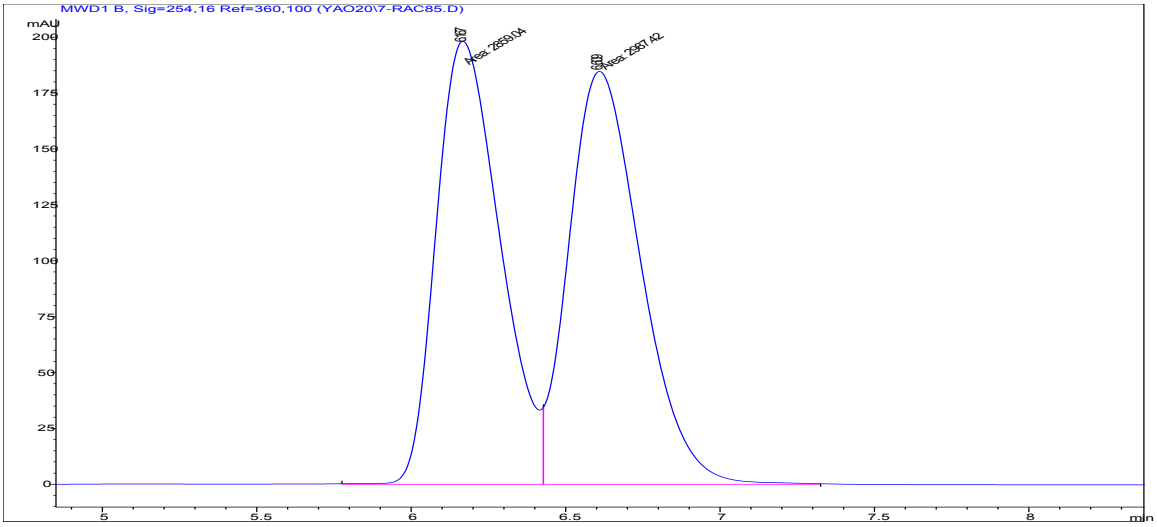
7o

Peak #	RetTime [min]	Type	Width [mAU*s]	Area [mAU]	Height [mAU]	Area %
1	4.670	MM	0.1120	389.21753	57.93702	50.6788
2	6.678	MM	0.1826	378.79153	78.28782	49.3212
Totals :				768.00906	92.51422	

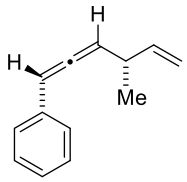


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [mAU*s]	Area [mAU]	Height [mAU]	Area %
1	4.249	MM	0.2976	8447.79492	473.10165	99.2555
2	6.669	MM	0.9822	63.36955	1.07535	0.7445
Totals :				8511.16447	474.17700	

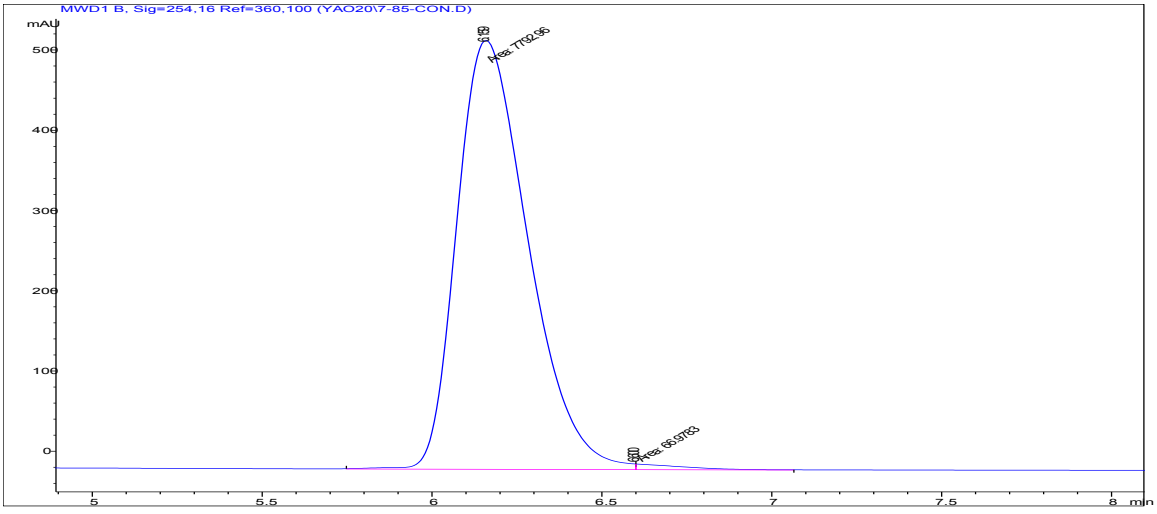


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



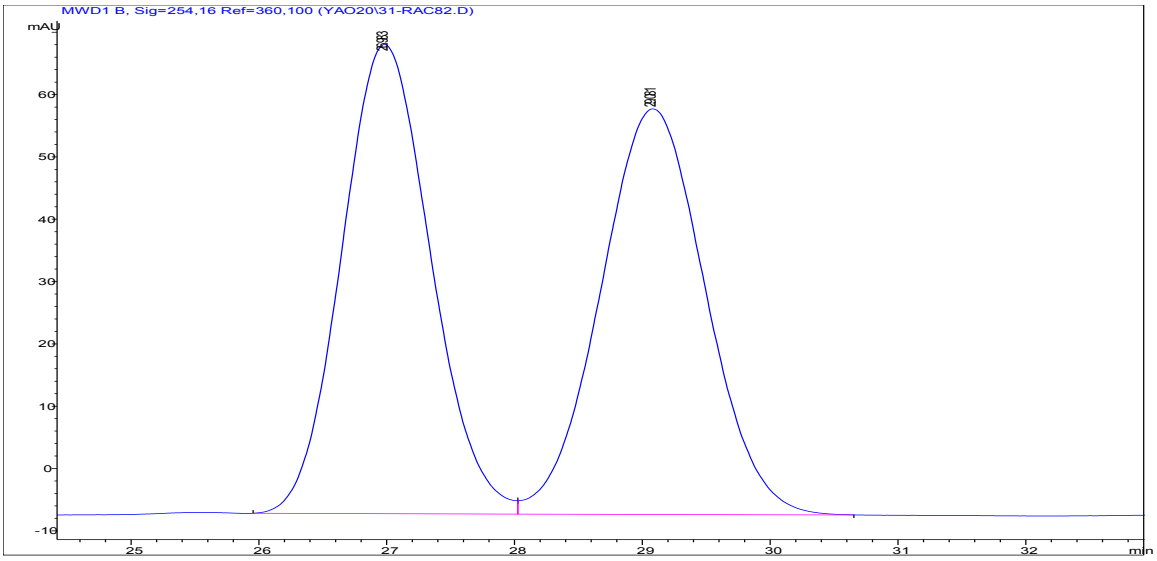
23a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.167	MF	0.2403	2859.03613	198.30685	48.9020
2	6.609	FM	0.2695	2987.41968	184.75233	51.0980
Totals :				5846.45581	383.05919	

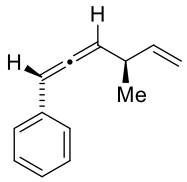


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.159	MF	0.2429	7792.95996	534.67914	99.1479
2	6.600	FM	0.1582	66.97829	7.05811	0.8521
Totals :				7859.93825	541.73725	

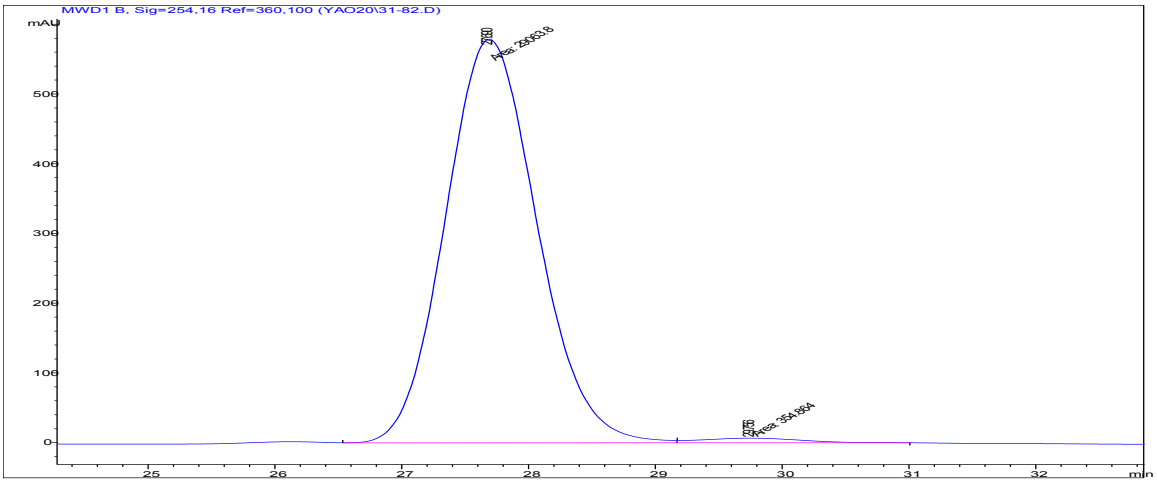


Signal 2: MWD1 B, Sig=254,16 Ref=360,100



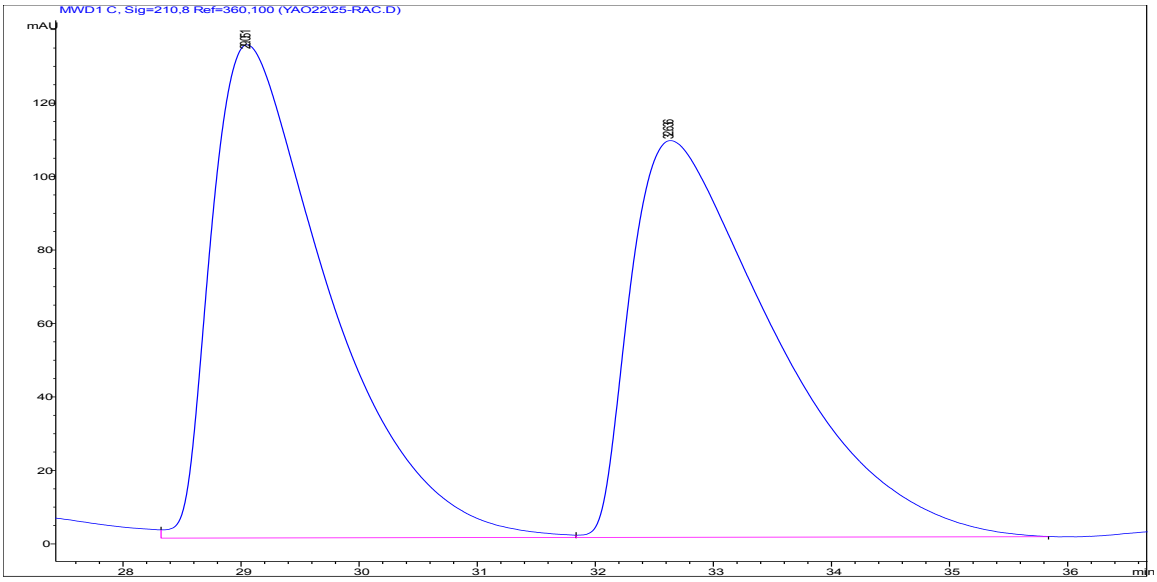
24a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.983	BV	0.7082	3640.75757	75.28212	49.5958
2	29.081	VB	0.8073	3700.09692	65.07899	50.4042
Totals :				7340.85449	140.36111	



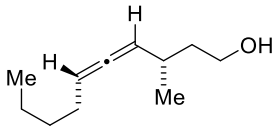
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.690	MF	0.8367	2.90638e4	578.90973	98.7937
2	29.756	FM	0.8905	354.86429	6.64148	1.2063
Totals :				2.94186e4	585.55121	

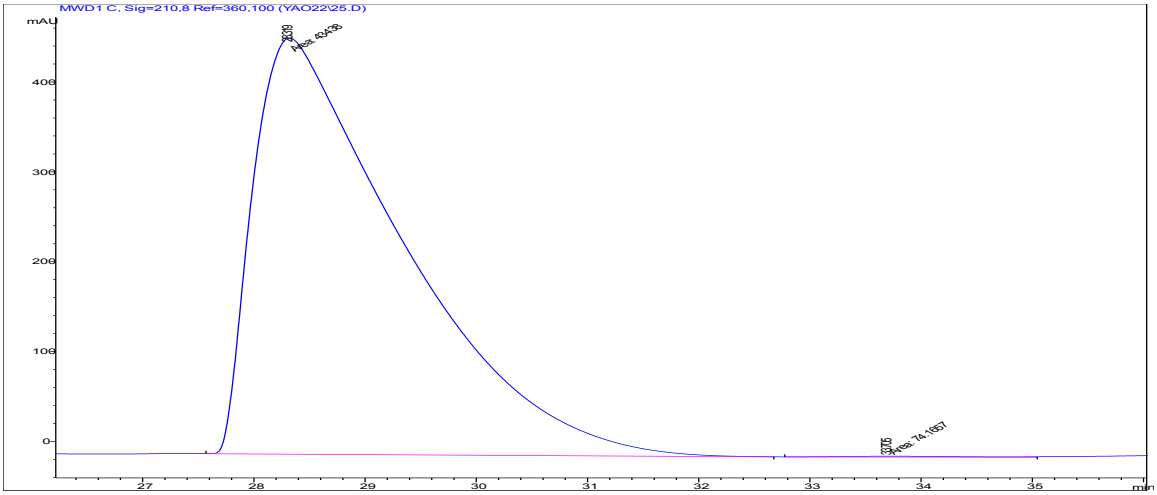


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.051	VV	1.0020	9274.04004	134.23459	50.3345
2	32.636	VB	1.1764	9150.77148	108.01012	49.6655
Totals :			1.84248e4	242.24471		

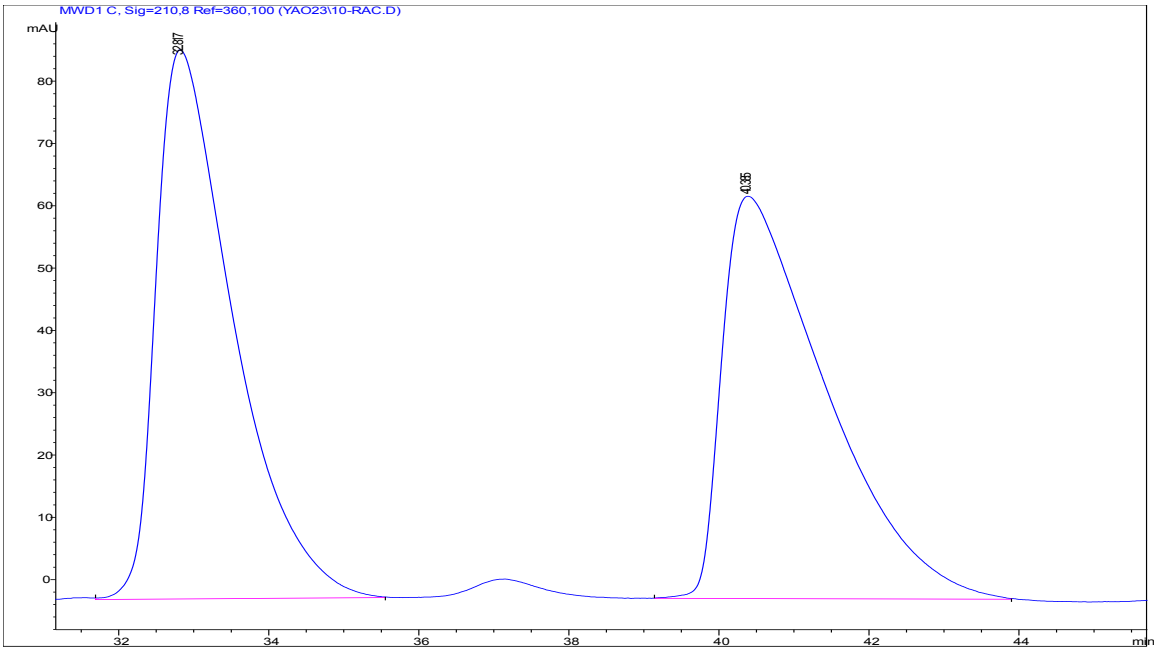


23bS1

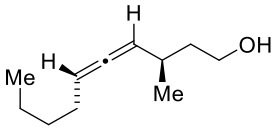


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.319	MM	1.5627	4.34380e4	463.28732	99.8296
2	33.705	MM	1.2395	74.16568	9.97235e-1	0.1704
Totals :			4.35121e4	464.28456		

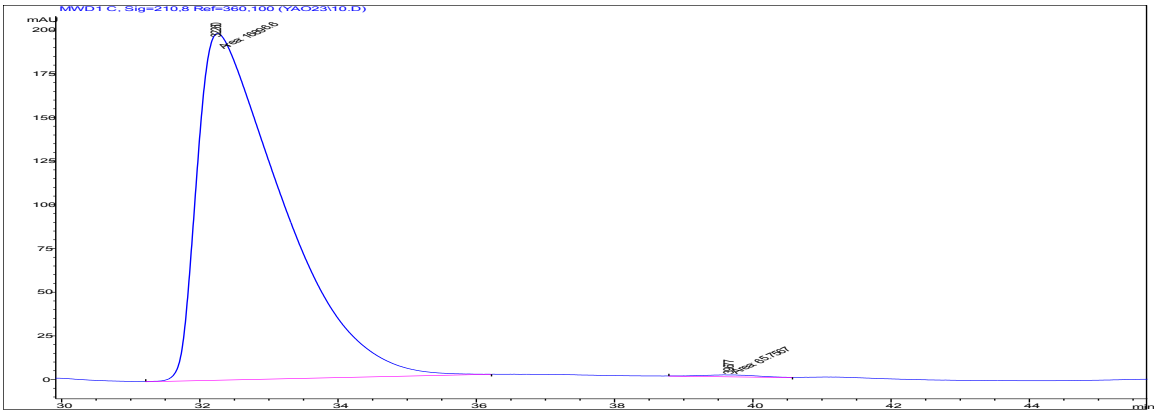


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



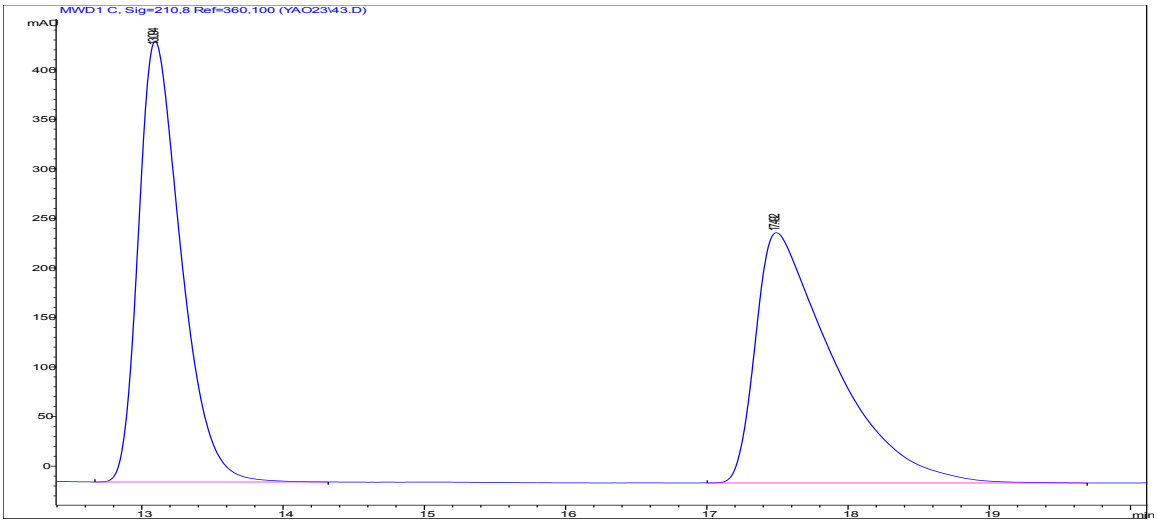
37

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.817	VB	1.0170	6308.98682	88.14474	50.3866
2	40.385	BB	1.3166	6212.16943	64.56104	49.6134
Totals :				1.25212e4	152.70578	

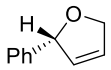


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.260	MM	1.4188	1.68966e4	198.48203	99.6123
2	39.677	MM	0.9670	65.75671	1.13334	0.3877
Totals :				1.69623e4	199.61536	

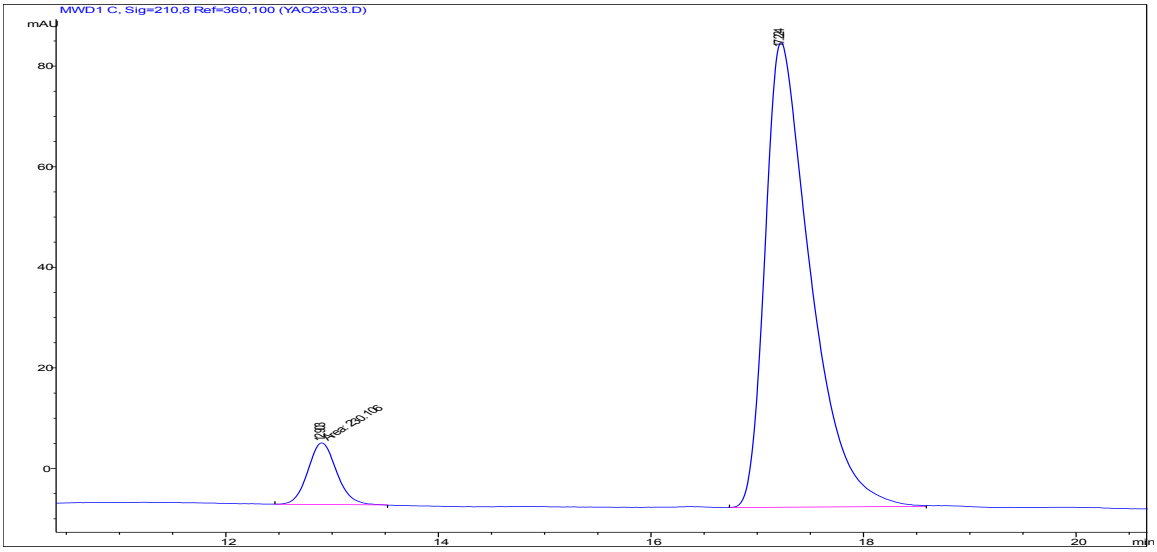


Signal 3: MWD1 C, Sig=210,8 Ref=360,100



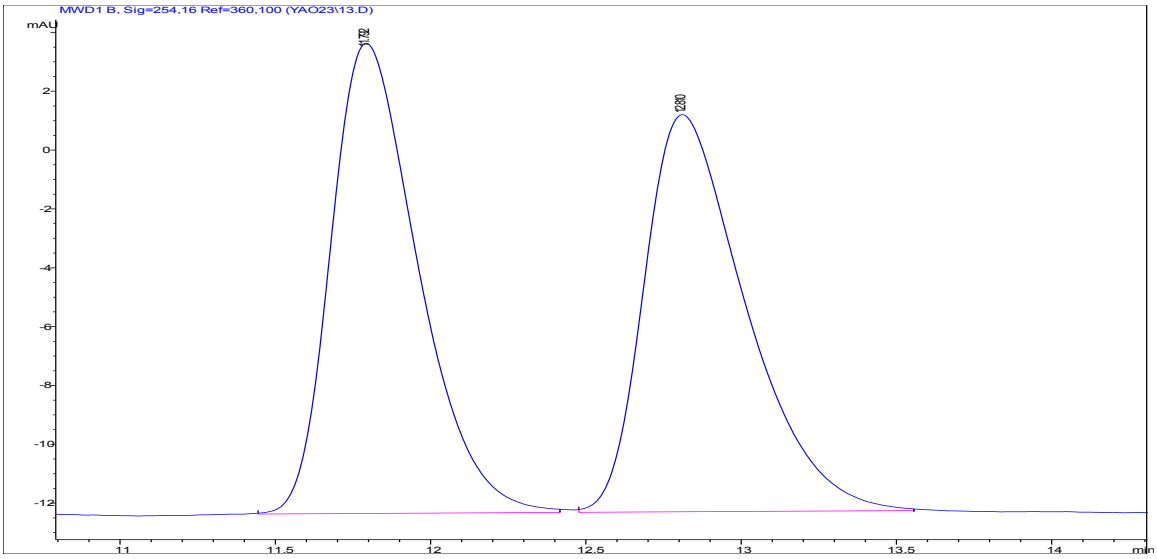
25

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.094	VB	0.3188	9337.34863	444.97882	49.2448
2	17.492	VB	0.5446	9623.74023	252.50923	50.7552
Totals :				1.89611e4	697.48805	



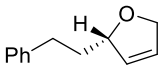
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.903	MM	0.3132	230.10577	12.24614	7.7157
2	17.224	PB	0.4415	2752.19360	92.39245	92.2843
Totals :				2982.29938	104.63859	

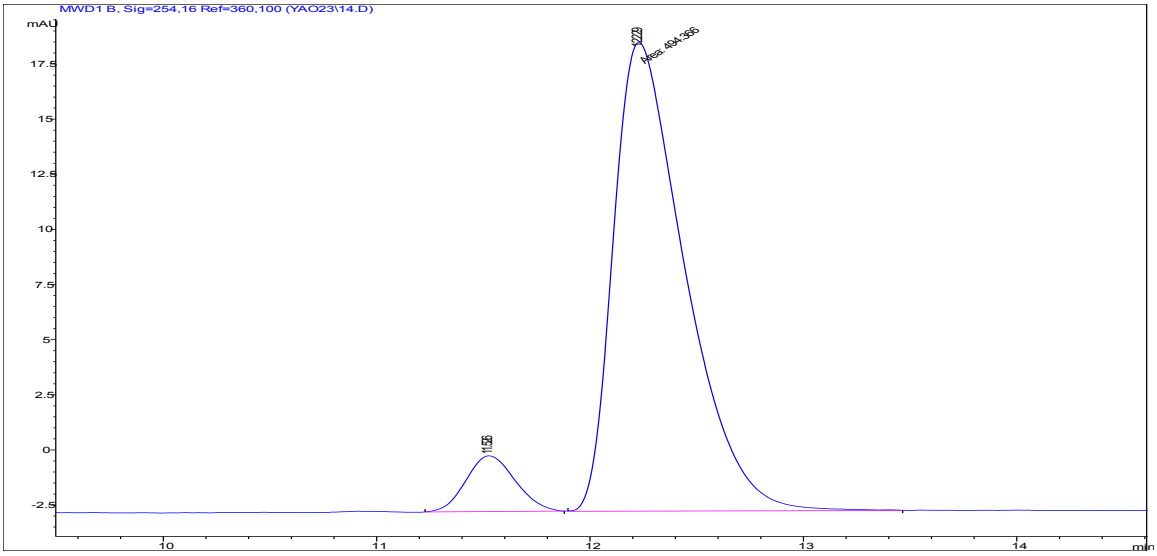


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.792	BB	0.2996	311.73242	15.98258	50.4548
2	12.810	BB	0.3446	306.11273	13.49895	49.5452
Totals :				617.84515	29.48153	

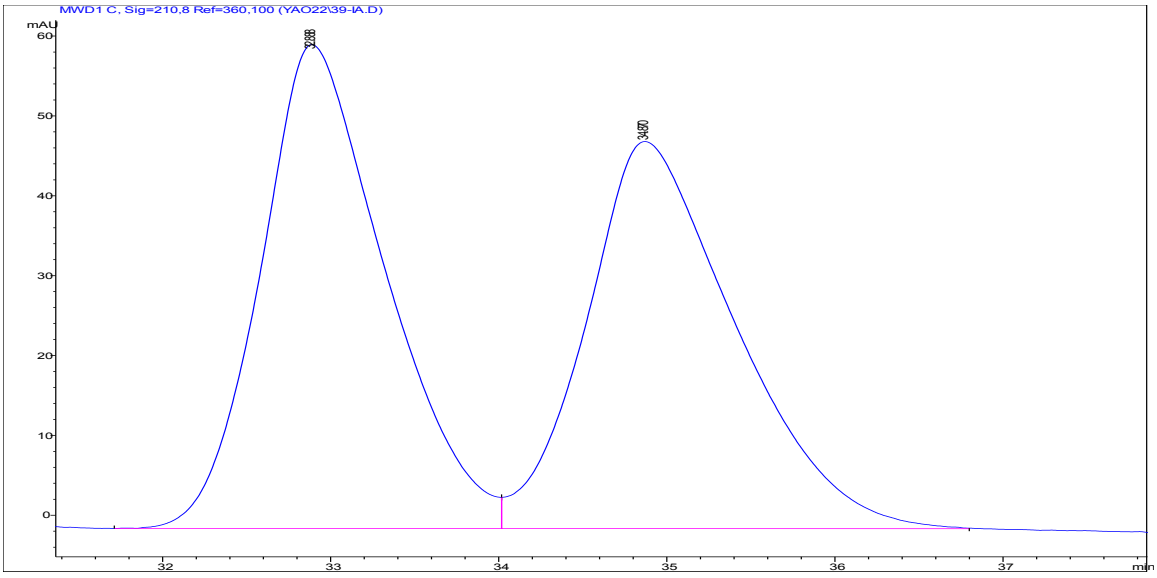


26



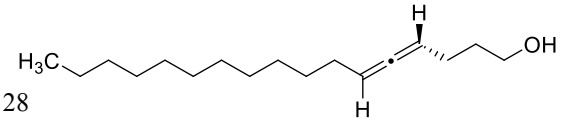
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.526	BP	0.2465	40.38449	2.52653	7.5520
2	12.229	MM	0.3876	494.36609	21.25785	92.4480
Totals :				534.75058	23.78438	

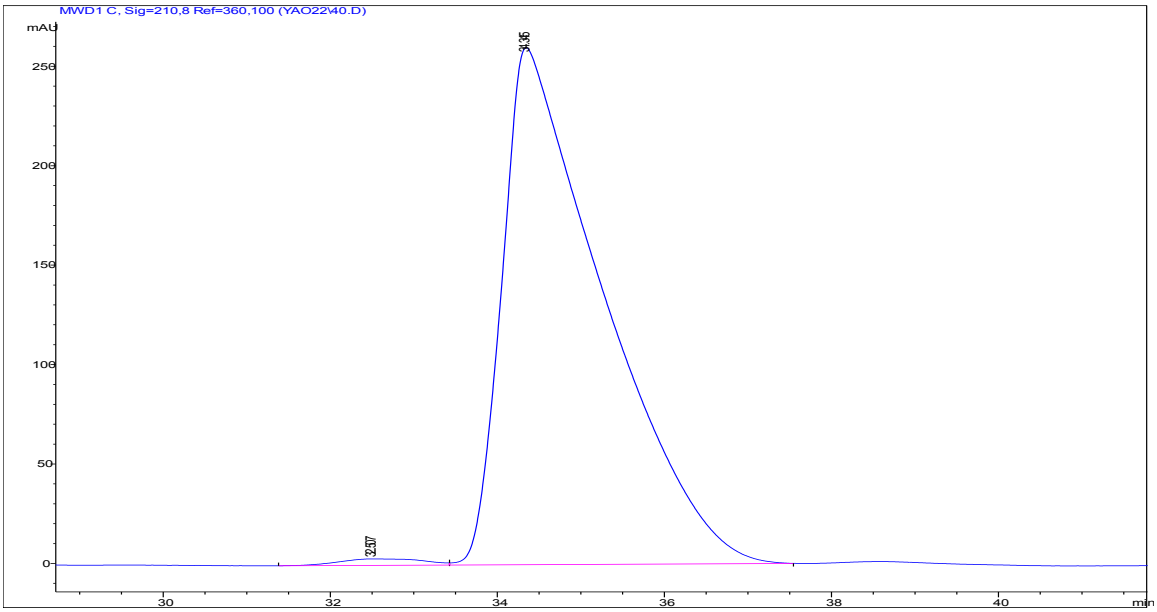


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.888	VV	0.7343	3128.99512	60.60584	51.1128
2	34.870	VB	0.8483	2992.74438	48.47647	48.8872
Totals :				6121.73950	109.08231	



32



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.507	PV	0.8162	226.18513	3.25690	1.0226
2	34.345	VB	1.1085	2.18925e4	259.96841	98.9774
Totals :				2.21187e4	263.22532	