Iterative Synthesis of Stereodefined Polyacetals and their Domino-Coates-Claisen Rearrangement

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Supporting information

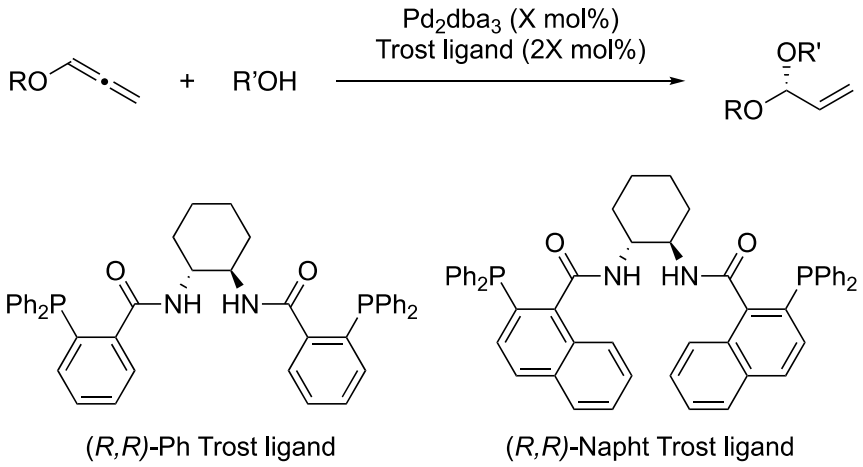
1. General experimental details

Unless stated otherwise, reactions were conducted in flame-dried glassware under an argon atmosphere. Et_2O and THF were dried using a Pure-Solv® Solvent Purification System (Innovative Technology©). DCM and DCE were distilled from CaH_2. Toluene was distilled from sodium and benzophenone. All other commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm), visualized by exposure to UV light (254 nm) or staining with anisaldehyde or potassium permanganate. Column chromatography was performed using Fluka silica gel 60 Å (40- 63 μm, 230-400 mesh). ^{1}H-NMR spectra were recorded on Bruker spectrometers (AVIII 400 and AVIII 300) and are reported relative to deuterated solvent signals. Chemical shifts are reported in parts per million (ppm) with respect to the residual $CHCl_3$ solvent signal in $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.36). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were obtained at the mass spectrometry facility at the Technion.

2. Stereochemical assignment

Stereocontrol in the Pd-catalyzed hydroalkoxylation is assigned based on precedents from Rhee[1] and Overman[2], which determined the configuration of analogous products through correlation and X-ray crystallography, respectively.
The stereoselectivity of Claisen rearrangements is extensively documented to align with chair-like transition states.[3] Our previous study on the Coates-Claisen rearrangement is in line with this model, as confirmed by a total synthesis of the natural product isoneomatatabiol.[4] The stereochemistry of the rearrangement products in this study are assigned analogously. This is further confirmed by the relative configuration of product **41** (see section 7).

3. General procedure for the Pd-catalyzed hydroalkoxylation of alkoxyallenes



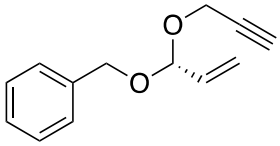
Pd_2dba_3 and Trost ligand (or dppp for racemic and stereorandom samples) were dissolved in toluene or dichloromethane (0.5M in alkoxyallene). The alcohol partner was added (1.5 equiv. for allyl and propargyl alcohol, 1.1 equiv. for aryl vinyl carbinols), followed by alkoxyallene. Conversion was monitored by TLC, (acetal products typically display lower R_f values by 0.2-0.3 compared to the alkoxyallene starting materials). Upon complete consumption of the alkoxyallene, the solvent was removed in vacuo and the crude mixture was purified by column chromatography on silica gel (diethylether/petroleum ether).

Note: the originally developed procedure by Rhee[1] requires the addition of triethylamine (0.1 or 1.5 equiv.). While the use of triethylamine led to clear yellow-green reaction mixtures, rather than dark mixtures without triethylamine, its omission did not lead to detectably worse reaction performance.

Single acetals

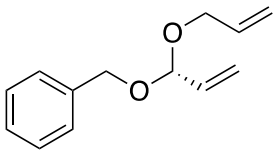
From benzyloxyallene (**1**).[5]

(*S*)-(((1-(prop-2-yn-1-yloxy)allyl)oxy)methyl)benzene **2**



(*R*,*R*)-Napht Trost L (4 mol% Pd) in DCM at 0°C for 5 hours.
Column chromatography with 1% diethylether in petroleum ether.
87% yield (17.6 g, 87 mmol on 100 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.89 (ddd, *J* = 17.5, 10.6, 4.7 Hz, 1H), 5.51 (dt, *J* = 17.4, 1.4 Hz, 1H), 5.38 (dt, *J* = 10.6, 1.3 Hz, 1H), 5.24 – 5.18 (m, 1H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.32 – 4.17 (m, 2H), 2.43 (t, *J* = 2.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.95, 134.32, 128.56, 127.93, 127.82, 119.65, 99.96, 79.87, 74.32, 67.69, 52.67.
HRMS (APCI): m/z calculated for $C_{13}H_{15}O_2$ $[M+H]^+$: 203.1072, found 203.1065.
HPLC (DAICEL OB-H, 10/90 isopropanol/hexane, 1.0 mL/min, 220 nm, tR_1= 9.5 min, tR_2= 12.4 min): **98/02 *er***

(*S*)-(((1-(allyloxy)allyl)oxy)methyl)benzene **3**

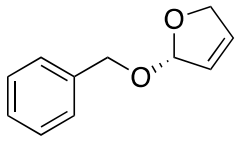


(*R*,*R*)-Napht Trost L (4 mol% Pd) in DCM at 0°C for 5 hours.
Column chromatography with 1% diethylether in petroleum ether.
96% yield (1.95 g, 9.64 mmol on 10 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.92 (m, 2H), 5.48 (dt, *J* = 17.4, 1.5 Hz, 1H), 5.35 (dt, *J* = 10.7, 1.4 Hz, 1H), 5.30 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.18 (dq, *J* = 10.4, 1.5 Hz, 1H), 5.08 (dt, *J* = 4.8, 1.2 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.15 (ddt, *J* = 12.9, 5.4, 1.5 Hz, 1H), 4.05 (ddt, *J* = 12.8, 5.7, 1.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.25, 135.06, 134.63, 128.53, 127.92, 127.73, 119.01, 117.04, 100.45, 67.18, 66.39.
HRMS (APCI): m/z calculated for $C_{13}H_{15}O_2$ $[M-H]^+$: 203.1072, found 203.1046.

The corresponding RCM product was used to determine **3**'s enantiopurity:

3 (102 mg, 0.5 mmol) was added to a solution of Grubbs' second generation catalyst (2.5 mol%) in dichloromethane (0.1M in **3**, 5 mL). The mixture was allowed to stir at ambient temperature overnight and was then purified by column chromatography on silica gel, eluting with 2-5% diethylether in petroleum ether.

(*S*)-2-(benzyloxy)-2,5-dihydrofuran **SI-1**

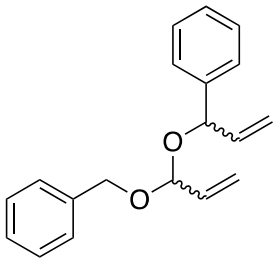


85% yield (75 mg, 0.42 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 6.29 (dq, *J* = 6.0, 1.4 Hz, 1H), 5.97 (dq, *J* = 4.6, 1.2 Hz, 1H), 5.85 (dtd, *J* = 6.1, 2.5, 1.1 Hz, 1H), 4.82 – 4.71 (m, 2H), 4.65 – 4.54 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.32, 132.31, 128.52, 128.04, 127.72, 126.12, 108.20, 74.67, 68.94.

The spectra are in line with previous reports.[6]

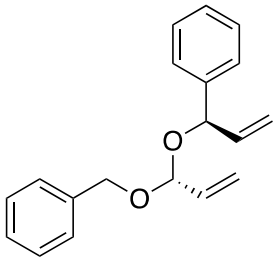
HPLC (DAICEL OB-H, 10/90 isopropanol/hexane, 1.0 mL/min, 220 nm, tR_1= 15.0 min, tR_2= 22.2 min): **99/01 *er***

(1-((1-(benzyloxy)allyl)oxy)allyl)benzene **SI-2**



dppp (10 mol% Pd) in DCM at rt for 1 hour.
Column chromatography with 1-1.5% diethylether in petroleum ether.
60% yield (502 mg, 1.8 mmol on 3 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 10H), 6.09 – 5.86 (m, 2H), 5.47 (ddt, *J* = 20.6, 17.4, 1.4 Hz, 1H), 5.38 – 5.11 (m, 4H), 5.02 (dt, *J* = 4.8, 1.2 Hz, 1H), 4.62 – 4.41 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.14, 140.65, 139.08, 138.38, 138.30, 135.28, 135.24, 128.60, 128.55, 128.51, 128.46, 127.99, 127.97, 127.87, 127.73, 127.69, 127.65, 127.36, 127.03, 118.87, 118.84, 117.03, 115.80, 99.01, 98.98, 78.52, 78.28, 66.52.
HRMS (TOF-ESI): m/z calculated for $C_{19}H_{19}O_2$ $[M-H]^+$: 279.1385, found 279.1389.

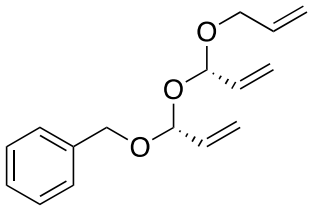
((*R*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)benzene **4**



(*R*,*R*)-Ph Trost L (10 mol% Pd) in PhMe at 40°C rt for 2 hours.
Column chromatography with 1-1.5% diethylether in petroleum ether.
69% yield (581 mg, 2.1 mmol on 3 mmol scale)
95/5 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 10H), 6.03 (ddd, *J* = 16.8, 10.3, 6.1 Hz, 1H), 5.93 (ddd, *J* = 17.4, 10.6, 4.8 Hz, 1H), 5.45 (dt, *J* = 17.4, 1.5 Hz, 1H), 5.32 (dt, *J* = 10.5, 1.4 Hz, 1H), 5.26 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.22 – 5.14 (m, 2H), 5.02 (dd, *J* = 4.7, 1.4 Hz, 1H), 4.58 – 4.49 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.65, 139.08, 138.38, 135.24, 128.60, 128.51, 128.00, 127.88, 127.69, 127.36, 118.85, 115.81, 98.98, 78.28, 66.53.
HRMS (TOF-ESI): m/z calculated for $C_{19}H_{19}O_2$ $[M-H]^+$: 279.1385, found 279.1381.

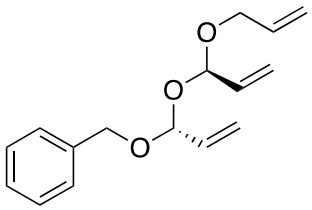
Double acetals

((((*R*)-1-(((*S*)-1-(allyloxy)allyl)oxy)allyl)oxy)methyl)benzene **10**



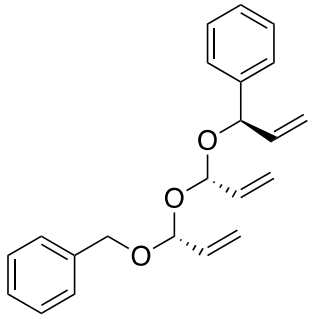
(*R*,*R*)-Napht Trost L (2 mol% Pd) in PhMe at 40°C for 1 hour.
Column chromatography with 0.8-1.5% diethylether in petroleum ether.
98% yield (1.04 g, 4 mmol on 4.1 mmol scale)
>98/2 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 4H), 5.91 (dddd, *J* = 18.1, 13.1, 10.5, 5.4 Hz, 3H), 5.43 (d, *J* = 17.4 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 5.35 – 5.23 (m, 3H), 5.21 – 5.10 (m, 3H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.16 (dd, *J* = 12.9, 5.4 Hz, 1H), 4.11 – 4.02 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.97, 135.06, 135.02, 134.37, 128.40, 127.80, 127.64, 118.52, 118.48, 116.94, 98.82, 98.65, 67.73, 66.91.
HRMS (APCI): m/z calculated for $C_{16}H_{19}O_3$ $[M-H]^+$: 259.1334, found 259.1338.

((((*R*)-1-(((*R*)-1-(allyloxy)allyl)oxy)allyl)oxy)methyl)benzene **11**



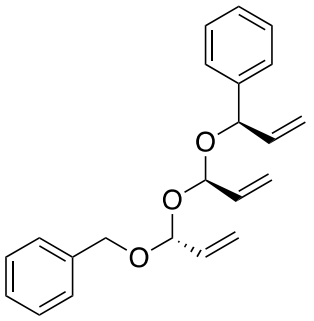
(*S*,*S*)-Napht Trost L (2 mol% Pd) in PhMe at 40°C for 1 hour.
Column chromatography with 0.8-1.5% diethylether in petroleum ether.
92% yield (960 mg, 3.7 mmol on 4 mmol scale)
>98/2 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.01 – 5.82 (m, 3H), 5.54 – 5.41 (m, 2H), 5.38 – 5.21 (m, 6H), 5.15 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.07 (dd, *J* = 12.7, 5.4 Hz, 1H), 4.00 (dd, *J* = 12.8, 5.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.15, 135.03, 135.01, 134.55, 128.53, 127.88, 127.74, 118.87, 118.73, 117.01, 98.59, 98.50, 66.87, 66.10.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1491, found 261.1490.

((*R*)-1-(((*S*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)oxy)allyl)benzene **12**



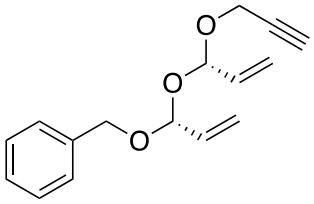
(*R*,*R*)-Napht Trost L (6 mol% Pd) in PhMe at 40°C for 12 hours.
Column chromatography with 0.9-1.5% diethylether in petroleum ether.
86% yield (1.02 g, 3 mmol on 3.5 mmol scale)
>98/2 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 11H), 6.03 – 5.84 (m, 3H), 5.42 (dt, *J* = 17.4, 1.3 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.27 – 5.08 (m, 6H), 5.02 (d, *J* = 5.8 Hz, 1H), 4.60 – 4.48 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 138.89, 138.05, 135.34, 135.15, 128.61, 128.46, 127.92, 127.87, 127.68, 127.36, 118.70, 118.24, 116.12, 98.13, 97.83, 78.72, 67.45.
HRMS (TOF-ESI): m/z calculated for $C_{22}H_{24}O_3Na$ $[M+Na]^+$: 359.1623, found 359.1595.

((*R*)-1-(((*R*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)oxy)allyl)benzene **13**



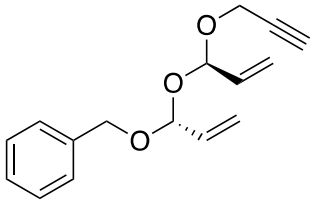
(*S*,*S*)-Napht Trost L (6 mol% Pd) in PhMe at 40°C for 12 hours.
Column chromatography with 0.9-1.5% diethylether in petroleum ether.
93% yield (1.09 g, 3.2 mmol on 3.5 mmol scale)
>98/2 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 11H), 6.03 – 5.84 (m, 3H), 5.42 (dt, *J* = 17.4, 1.3 Hz, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.27 – 5.08 (m, 6H), 5.02 (d, *J* = 5.8 Hz, 1H), 4.60 – 4.48 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.97, 138.70, 138.15, 135.48, 135.02, 128.54, 128.43, 127.76, 127.72, 127.60, 127.02, 118.88, 118.34, 116.76, 98.58, 97.89, 78.89, 66.77.
HRMS (APCI): m/z calculated for $C_{22}H_{24}O_3Na$ $[M+Na]^+$: 359.1623, found 359.1620.

((((*R*)-1-(((*S*)-1-(prop-2-yn-1-yloxy)allyl)oxy)allyl)oxy)methyl)benzene **14**



(*R*,*R*)-Napht Trost L (2 mol% Pd) in PhMe at 40°C for 1 hour.
Column chromatography with 0.9-1.5% diethylether in petroleum ether.
96% yield (3.5 g, 13.5 mmol on 14.1 mmol scale)
94/6 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.91 (dddd, *J* = 22.8, 17.3, 10.5, 5.4 Hz, 2H), 5.43 (ddt, *J* = 17.4, 8.8, 1.3 Hz, 2H), 5.33 (ddt, *J* = 10.6, 2.7, 1.2 Hz, 2H), 5.26 (dd, *J* = 5.4, 1.1 Hz, 1H), 5.18 (dt, *J* = 5.5, 1.1 Hz, 1H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.31 (dd, *J* = 15.7, 2.4 Hz, 1H), 4.22 (dd, *J* = 15.8, 2.5 Hz, 1H), 2.41 (t, *J* = 2.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.95, 134.93, 134.41, 128.52, 127.98, 127.79, 119.29, 118.91, 99.21, 98.14, 79.76, 74.50, 68.17, 53.29.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{18}O_3Na$ $[M+Na]^+$: 281.1154, found 281.1149.

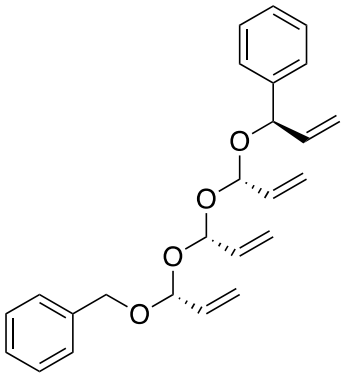
((((*R*)-1-(((*R*)-1-(prop-2-yn-1-yloxy)allyl)oxy)allyl)oxy)methyl)benzene **15**



(*S*,*S*)-Napht Trost L (2 mol% Pd) in PhMe at 40°C for 1 hour.
Column chromatography with 0.9-1.5% diethylether in petroleum ether.
96% yield (5.22 g, 20.2 mmol on 21 mmol scale)
95/5 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.91 (dddd, *J* = 22.7, 17.4, 10.7, 4.8 Hz, 2H), 5.51 (ddd, *J* = 17.4, 4.2, 2.0 Hz, 2H), 5.42 – 5.32 (m, 5H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.26 – 4.12 (m, 2H), 2.39 (t, *J* = 2.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.04, 134.78, 134.32, 128.55, 127.87, 127.78, 119.40, 119.05, 99.03, 98.14, 79.72, 74.49, 67.08, 52.56.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{18}O_3Na$ $[M+Na]^+$: 281.1154, found 281.1156.

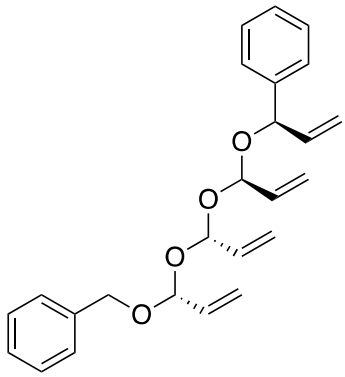
Triple acetals

(3*R*,5*R*,7*S*,9*R*)-1,9-diphenyl-3,5,7-trivinyl-2,4,6,8-tetraoxaundec-10-ene **18**



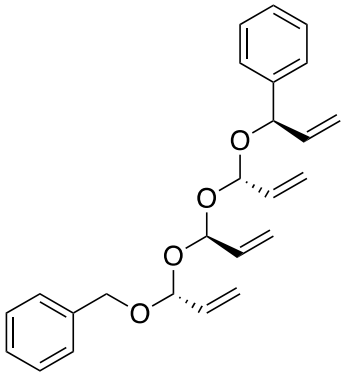
(*R*,*R*)-Napht Trost L (6 mol% Pd) in PhMe at 40°C for 4 hours.
Column chromatography with 1.6-2% diethylether in petroleum ether.
81% yield (2 g, 5.1 mmol on 6.3 mmol scale)
>98/2 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 12H), 6.03 – 5.78 (m, 4H), 5.40 – 5.09 (m, 12H), 5.03 (d, *J* = 5.8 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.59, 138.86, 138.12, 135.06, 134.94, 128.59, 128.43, 127.87, 127.80, 127.63, 127.37, 118.87, 118.51, 118.43, 116.23, 98.22, 97.71, 96.23, 78.54, 67.34.
HRMS (TOF-ESI): m/z calculated for $C_{25}H_{28}O_4Na$ $[M+Na]^+$: 415.1885, found 415.1889.

(3*R*,5*R*,7*R*,9*R*)-1,9-diphenyl-3,5,7-trivinyl-2,4,6,8-tetraoxaundec-10-ene **19**



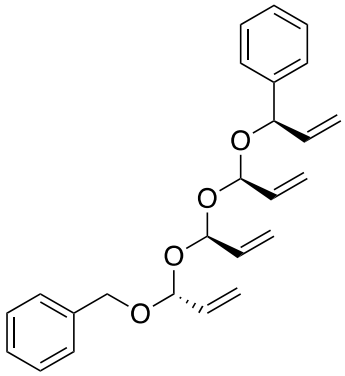
(*S*,*S*)-Napht Trost L (6 mol% Pd) in PhMe at 40°C for 4 hours.
Column chromatography with 1.6-2% diethylether in petroleum ether.
83% yield (746 mg, 1.9 mmol on 2.3 mmol scale)
92/8 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 11H), 5.87 (dddd, *J* = 33.3, 17.2, 10.9, 5.0 Hz, 4H), 5.47 – 5.04 (m, 12H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.12, 138.81, 138.12, 135.32, 135.23, 134.99, 128.51, 128.45, 127.89, 127.71, 127.66, 127.02, 118.80, 118.48, 118.36, 116.64, 98.18, 98.13, 97.13, 78.58, 67.21.
HRMS (TOF-ESI): m/z calculated for $C_{25}H_{28}O_4Na$ $[M+Na]^+$: 415.1885, found 415.1879.

(3*R*,5*S*,7*S*,9*R*)-1,9-diphenyl-3,5,7-trivinyl-2,4,6,8-tetraoxaundec-10-ene **20**



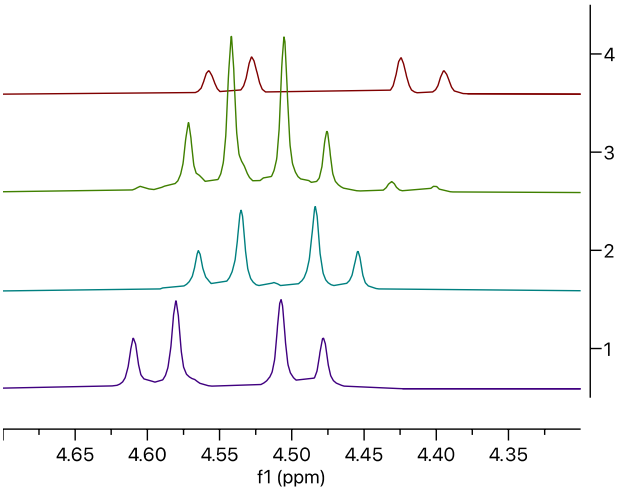
(*R*,*R*)-Napht Trost L (6 mol% Pd) in PhMe at 40°C for 4 hours.
Column chromatography with 1.6-2% diethylether in petroleum ether.
82% yield (767 mg, 2 mmol on 2.4 mmol scale)
92/8 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 12H), 5.99 – 5.79 (m, 4H), 5.48 (d, *J* = 17.4 Hz, 1H), 5.38 – 5.06 (m, 12H), 4.55 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.70, 139.01, 138.13, 135.39, 135.17, 134.82, 128.59, 128.49, 127.88, 127.79, 127.69, 127.27, 119.18, 118.60, 118.05, 116.10, 98.73, 98.26, 97.31, 78.31, 66.54.
HRMS (TOF-ESI): m/z calculated for $C_{25}H_{28}O_4Na$ $[M+Na]^+$: 415.1885, found 415.1877.

(3*R*,5*S*,7*R*,9*R*)-1,9-diphenyl-3,5,7-trivinyl-2,4,6,8-tetraoxaundec-10-ene **21**



(*S*,*S*)-Napht Trost L (6 mol% Pd) in PhMe at 40°C for 4 hours.
Column chromatography with 1.6-2% diethylether in petroleum ether.
80% yield (744 mg, 1.9 mmol on 2.4 mmol scale)
>98/2 *dr*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 12H), 5.87 (dddd, *J* = 28.3, 17.9, 10.6, 6.0 Hz, 4H), 5.49 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.41 (dd, *J* = 4.8, 1.2 Hz, 1H), 5.37 (dt, *J* = 6.5, 1.3 Hz, 1H), 5.32 (dt, *J* = 6.2, 1.3 Hz, 1H), 5.28 (ddt, *J* = 8.1, 5.4, 1.1 Hz, 3H), 5.19 (dt, *J* = 10.3, 1.3 Hz, 1H), 5.16 – 5.00 (m, 4H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ
HRMS (TOF-ESI): m/z calculated for $C_{25}H_{28}O_4Na$ $[M+Na]^+$: 415.1885, found 415.1888.

Benzyl CH_2 region of the ^{1}H-NMR spectrum. Top to bottom: **18**, **19**, **20**, **21**



4. General procedure for the *t*-BuOK-mediated isomerization of propargyl acetals

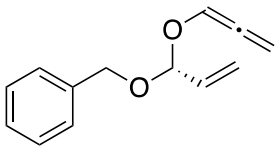
The appropriate propargyl acetal was dissolved in dry THF (1M in acetal). 1M *t*-BuOK in THF (1 equiv.) was added and the reaction was allowed to stir at room temperature for 3 hours. Diethylether and water were then added, and the aqueous phase was extracted thrice with diethylether. The combined organic fractions were dried on sodium sulfate and concentrated in vacuo (note: the rotavap water bath was maintained at 30°C to minimize premature rearrangement).
The crude allenyl acetal was purified by column chromatography on silica gel neutralized with 1% triethylamine in petroleum ether and packed in a column cooled with ice-water through a cooling jacket.

Note 1: the purified products can be stored in the freezer for several days without detectable levels of Claisen rearrangement, but were usually subjected to hydroalkoxylation immediately.

Note 2: conversion typically plateaus around 85%. Unreacted propargyl acetal can be recovered by chromatography or separated following the next hydroalkoxylation step.

Single acetal 5

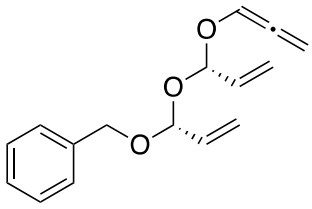
(*R*)-(((1-(propa-1,2-dien-1-yloxy)allyl)oxy)methyl)benzene **5**



Column chromatography on an ice-water-cooled column with 1/1.5/97.5 triethylamine/diethylether/petroleum ether.
67% yield (3.37 g, 16.7 mmol on 24.7 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 4H), 6.73 (t, *J* = 6.0 Hz, 1H), 5.92 (ddd, *J* = 17.4, 10.6, 4.6 Hz, 1H), 5.49 (dt, *J* = 17.4, 1.3 Hz, 1H), 5.43 – 5.32 (m, 3H), 5.28 (dt, *J* = 4.7, 1.3 Hz, 1H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.72, 137.61, 134.20, 128.55, 128.07, 127.91, 119.53, 117.02, 100.30, 89.56, 68.54.

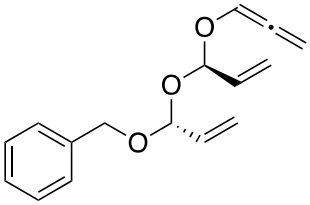
Double acetals

((((*R*)-1-(((*S*)-1-(propa-1,2-dien-1-yloxy)allyl)oxy)allyl)oxy)methyl)benzene **16**



Column chromatography on an ice-water-cooled column with 1/2/97 triethylamine/diethylether/petroleum ether.
82% yield (1.62 g, 6.3 mmol on 7.7 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.69 (t, *J* = 6.0 Hz, 1H), 5.92 (dddd, *J* = 17.3, 10.5, 5.3, 1.6 Hz, 2H), 5.47 (dt, *J* = 9.2, 1.3 Hz, 1H), 5.42 (dt, *J* = 9.3, 1.2 Hz, 1H), 5.40 – 5.30 (m, 5H), 5.21 (dt, *J* = 5.4, 1.1 Hz, 1H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.63, 138.01, 134.66, 134.16, 128.55, 127.90, 127.81, 119.27, 119.26, 117.13, 98.66, 97.82, 89.75, 67.09.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{18}O_3Na$ $[M+Na]^+$: 281.1154, found 281.1156.

((((*R*)-1-(((*R*)-1-(propa-1,2-dien-1-yloxy)allyl)oxy)allyl)oxy)methyl)benzene **17**



Column chromatography on an ice-water-cooled column with 1/2/97 Et_3N/Et_2O/petroleum ether.
83% yield (1.3 g, 5 mmol on 6 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 4H), 6.66 (t, *J* = 6.0 Hz, 1H), 5.92 (dddd, *J* = 17.3, 10.6, 7.8, 4.8 Hz, 2H), 5.57 – 5.43 (m, 3H), 5.43 – 5.29 (m, 5H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.63, 138.01, 134.66, 134.16, 128.55, 127.90, 127.81, 119.27, 119.26, 117.13, 98.66, 97.82, 89.75, 67.09.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{18}O_3Na$ $[M+Na]^+$: 281.1154, found 281.1165.

5. Ir-initiated Coates-Claisen rearrangement

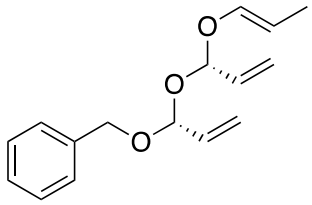
General procedure for the Ir-catalyzed isomerization of allyl acetals and subsequent Coates-Claisen rearrangement

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (5 mol%), tricyclohexylphosphine (15 mol%) and 1,5-cyclooctadiene iridium chloride dimer (2.5 mol%) were stirred for 1 minute at room temperature before dichloromethane (0.2M in acetal) was added. Upon complete dissolution of the solids (resulting in an orange-reddish solution), hydrogen gas was bubbled through the solution for three minutes using a balloon attached to an oven-dried reusable needle.
The resulting mixture was degassed by four freeze-pump-thaw cycles, followed by addition of the neat allyl acetal. Conversion was monitored by TLC (the isomerized acetals typically have R_f values higher by 0.2-0.3 than the starting allyl acetals). Upon consumption of the allyl acetal (usually 30-60 minutes), the solvent was removed in vacuo and the residue was used directly for the ensuing Claisen rearrangement.

Magnesium bromide diethyl etherate (2 equiv.) dissolved in dry diethylether (0.05M in acetal). $LiAlH_4$ (2 equiv. for monoacetals, 3 equiv. for double acetals) was then added, followed by the crude isomerized acetal. The mixture was allowed to stir at ambient temperature for 24 hours. Upon complete consumption of the isomerized acetal, as detected by TLC (alcohol products are significantly more polar than isomerized acetals, there are typically minor impurities visible in similar R_f to the isomerized acetal starting material), the mixture was cooled to 0°C and water (1 mL per g $LiAlH_4$) was carefully added, followed by 15% NaOH (1 mL per g $LiAlH_4$) and more water (3 mL per g $LiAlH_4$). The mixture was stirred vigorously at ambient temperature for 15 minutes, and was then filtered on a pad of celite, washed with ethyl acetate. The solvents were removed in vacuo and the crude mixture was purified by column chromatography on silica gel.

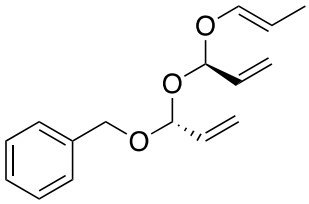
Isomerized acetals

((((*R*)-1-(((*S*)-1-(((*E*)-prop-1-en-1-yl)oxy)allyl)oxy)allyl)oxy)methyl)benzene **26**



Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.40 – 7.27 (m, 5H), 6.26 (d, *J* = 12.3 Hz, 1H), 5.90 (ddt, *J* = 15.5, 10.0, 4.8 Hz, 2H), 5.44 (d, *J* = 17.3 Hz, 2H), 5.33 (d, *J* = 10.6 Hz, 2H), 5.26 (d, *J* = 4.9 Hz, 1H), 5.19 (d, *J* = 5.4 Hz, 1H), 5.07 (dq, *J* = 13.4, 6.9 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 1.57 – 1.51 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.79, 134.80, 134.54, 128.51, 127.98, 127.82, 119.01, 104.15, 99.69, 98.28, 68.53, 12.61.

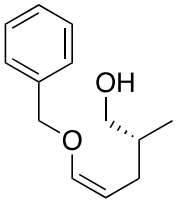
((((*R*)-1-(((*R*)-1-(((*E*)-prop-1-en-1-yl)oxy)allyl)oxy)allyl)oxy)methyl)benzene **SI-3**



Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.20 (dq, *J* = 12.1, 1.6 Hz, 1H), 5.90 (dddd, *J* = 17.0, 12.4, 10.5, 4.8 Hz, 2H), 5.57 – 5.40 (m, 3H), 5.39 – 5.28 (m, 3H), 5.05 (dq, *J* = 12.2, 6.8 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 1.52 (dd, *J* = 6.9, 1.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.84, 138.02, 134.66, 134.50, 128.56, 127.93, 127.81, 119.25, 119.00, 104.18, 98.26, 97.94, 67.13, 12.58.

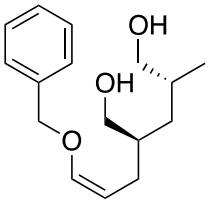
Claisen-reduction products

(*R*,*Z*)-5-(benzyloxy)-2-methylpent-4-en-1-ol **23**



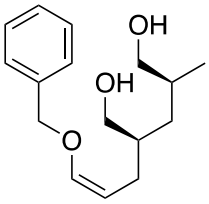
72% yield (74 mg, 0.36 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 6H), 6.12 (dt, *J* = 6.3, 1.2 Hz, 1H), 4.80 (s, 2H), 4.44 (td, *J* = 8.0, 6.2 Hz, 1H), 3.44 (ddq, *J* = 17.1, 11.3, 5.7 Hz, 2H), 2.14 (ddd, *J* = 7.9, 6.4, 1.3 Hz, 2H), 1.94 (t, *J* = 6.4 Hz, 1H), 1.79 – 1.64 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.71, 137.38, 128.71, 128.18, 127.62, 105.06, 73.94, 67.17, 35.73, 27.16, 16.68.
HRMS (APCI): m/z calculated for $C_{13}H_{17}O$ [M-OH]$^+$: 189.1279, found 189.1259.
HPLC (DAICEL OB-H, 5/95 isopropanol/hexane, 0.5 mL/min, 250 nm, tR_1= 19.2 min, tR_2= 21.1 min): **96/4 *er***

(2*S*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diol **27**



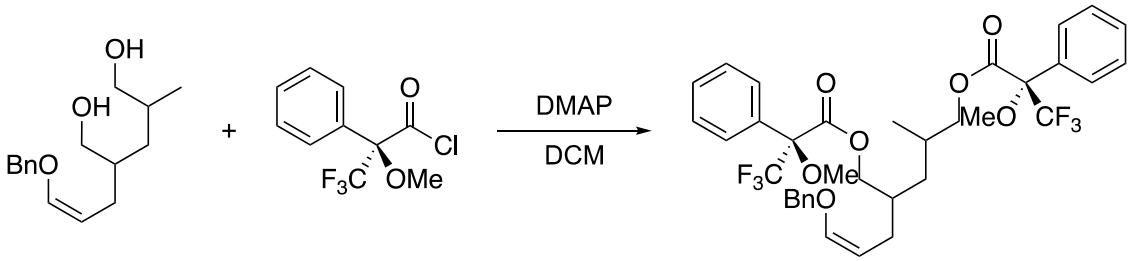
From 10.
50% yield (66 mg, 0.25 mmol on 0.5 mmol scale)
>98/2 *dr*, >98/2 *Z*/*E*, 93/7 *er* (Mosher analysis, see below)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.12 (d, *J* = 6.2 Hz, 1H), 4.79 (s, 2H), 4.42 (td, *J* = 8.0, 6.2 Hz, 1H), 3.42 (m, 4H), 2.62 (bs, 1H), 2.31 – 2.14 (m, 2H), 2.08 (dt, *J* = 14.6, 7.8 Hz, 1H), 1.82 – 1.63 (m, 2H), 1.33 (ddd, *J* = 13.7, 8.4, 5.3 Hz, 1H), 1.08 (ddd, *J* = 13.9, 8.5, 5.5 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.00, 137.18, 128.75, 128.30, 127.72, 104.60, 74.05, 68.75, 65.65, 37.72, 34.34, 33.14, 24.50, 16.89.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{24}O_3Na$ [M+Na]$^+$: 287.1623, found 287.1626.

(2*S*,4*S*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diol **29**



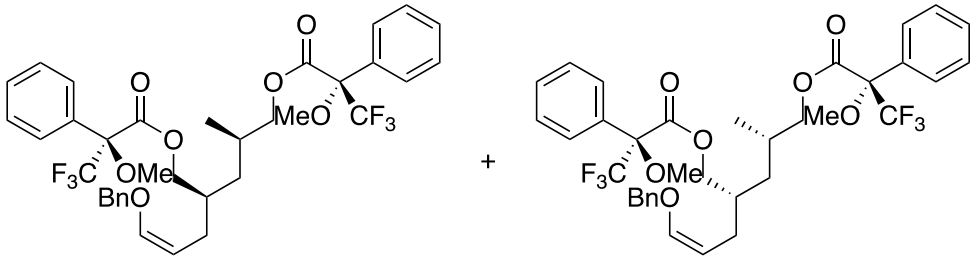
From 11.
48% yield (63 mg, 0.24 mmol on 0.5 mmol scale)
>98/2 *dr*, 11/1 *Z*/*E*, 90/10 *er* (Mosher analysis, see below)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 6.17 – 6.10 (m, 1H), 4.80 (s, 2H), 4.44 (td, *J* = 8.1, 6.2 Hz, 1H), 3.58 – 3.39 (m, 4H), 2.22 – 2.11 (m, 2H), 1.79 – 1.59 (m, 5H), 1.45 (ddd, *J* = 14.0, 8.2, 5.9 Hz, 1H), 1.02 (ddd, *J* = 13.9, 8.2, 5.8 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.90, 137.22, 128.74, 128.27, 127.70, 104.98, 74.03, 68.50, 64.44, 37.86, 34.67, 33.37, 26.08, 17.26.
HRMS (TOF-ESI): m/z calculated for $C_{16}H_{24}O_3Na$ [M+Na]$^+$: 287.1623, found 287.1622.

Mosher analysis of 27 and 29



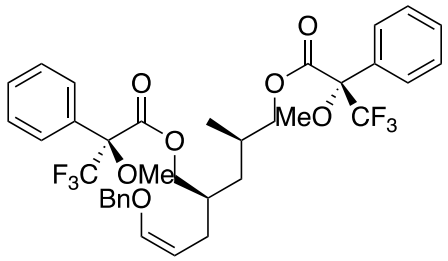
(*R*)-(–)-Mosher acyl chloride (10.5 mg, 2.2 equiv.) was added to a stirred solution of diol (5 mg, 19μmol) and DMAP (7 mg, 3 equiv.) in dichloromethane (0.5 mL). The mixture was allowed to stir at ambient temperature for two hours. The mixture was then purified by column chromatography on silica gel (using a Pasteur pipette), eluting with 5-10% ethyl acetate in petroleum ether.

(2*S*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diyl (2*S*,2'*S*)-bis(3,3,3-trifluoro-2-methoxy-2-phenylpropanoate) + (2*R*,4*S*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diyl (2*S*,2'*S*)-bis(3,3,3-trifluoro-2-methoxy-2-phenylpropanoate) **SI-4**



From racemic 27 (prepared from a stereorandom double acetal, followed by separation of the diastereomers by column chromatography).
76% yield (10 mg, 14 μmol on 19 μmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dq, *J* = 7.8, 2.4 Hz, 4H), 7.42 – 7.27 (m, 12H), 6.07 (tt, *J* = 6.3, 1.3 Hz, 1H), 4.74 (d, *J* = 1.8 Hz, 2H), 4.30 – 4.22 (m, 2H), 4.20 (dd, *J* = 10.9, 5.3 Hz, 0H), 4.16 – 4.10 (m, 1H), 4.10 – 4.03 (m, 1H), 4.01 (dd, *J* = 10.9, 6.4 Hz, 1H), 3.51 (tt, *J* = 4.1, 1.2 Hz, 6H), 2.17 – 1.97 (m, 2H), 1.97 – 1.77 (m, 2H), 1.32 – 1.19 (m, 2H), 1.09 (dddd, *J* = 14.1, 8.0, 5.7, 2.1 Hz, 1H), 0.82 (dd, *J* = 6.7, 1.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.77, 146.58, 137.54, 132.41, 129.75, 128.64, 128.55, 128.10, 127.55, 127.47, 103.24, 103.08, 73.86, 71.30, 69.27, 69.08, 55.53, 35.09, 34.63, 29.82, 25.19, 25.01, 20.14, 16.86, 16.77, 1.16.

(2*S*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diyl (2*S*,2'*S*)-bis(3,3,3-trifluoro-2-methoxy-2-phenylpropanoate) **SI-5**



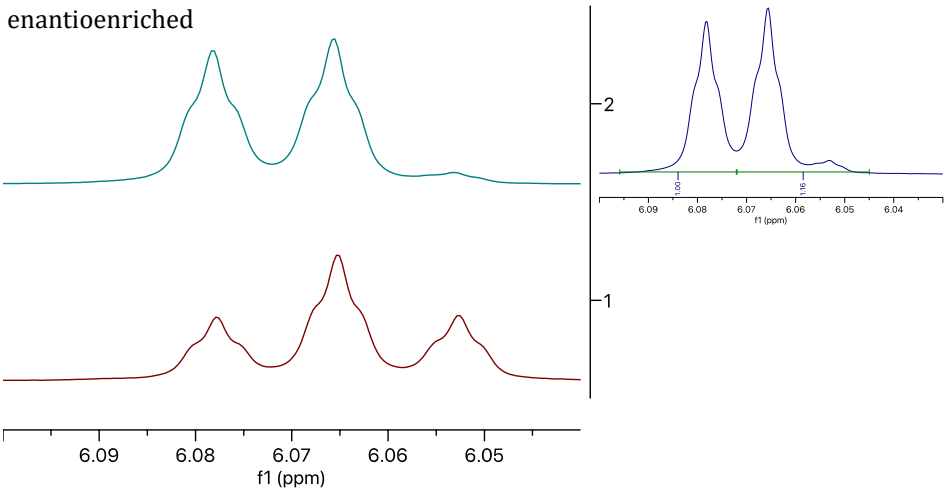
From enantioenriched 27.
98% yield (13 mg, 18.7 μmol on 19 μmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dq, *J* = 8.0, 2.5 Hz, 4H), 7.42 – 7.27 (m, 12H), 6.07 (dd, *J* = 6.2, 1.3 Hz, 1H), 4.75 (d, *J* = 1.2 Hz, 2H), 4.30 – 4.24 (m, 2H), 4.11 – 4.02 (m, 3H), 3.51 (dt, *J* = 4.0, 1.2 Hz, 7H), 2.14 – 2.00 (m, 2H), 1.91 (dp, *J* = 8.5, 6.3 Hz, 1H), 1.82 (tq, *J* = 7.5, 5.6 Hz, 1H), 1.31 – 1.22 (m, 1H), 1.09 (ddd, *J* = 14.1, 8.5, 5.9 Hz, 1H), 0.82 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.77, 146.58, 137.54, 132.39, 129.76, 129.73, 128.65, 128.57, 128.55, 128.11, 127.56, 127.47, 103.25, 73.87, 71.31, 69.08, 55.53, 35.12, 34.57, 29.82, 25.20, 16.87, 1.17.

Analysis of *er*(**27**) according to the ^{1}H-NMR spectra:

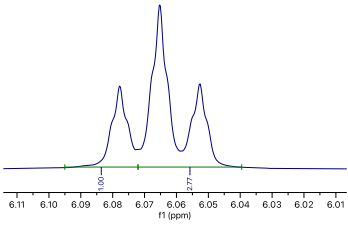
Assuming that the two enol ether doublets are symmetrical, and that integrating halfway through the left-hand doublet should represent half of the peak area, the *er* can be calculated as: $\%_{major\ enantiomer} = \frac{2area_{left}}{area_{left} + area_{right}} = \frac{2}{2.16} = 0.926$

er=93/7

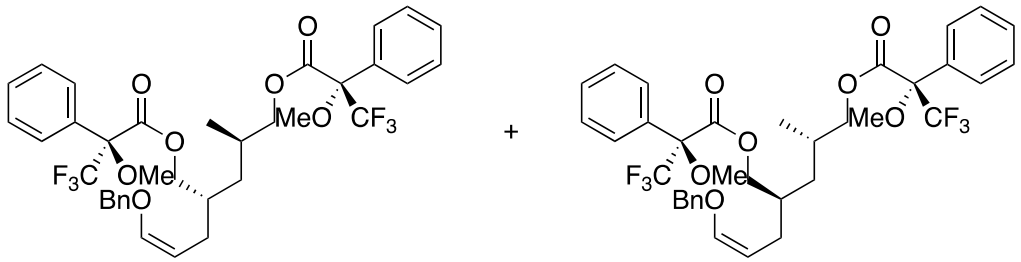
enantioenriched



racemate

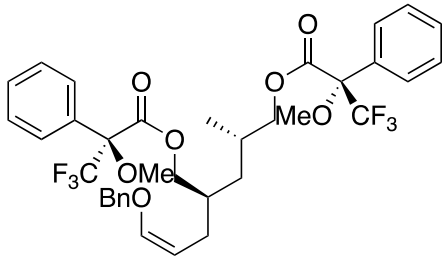


(2*R*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diyl (2*S*,2'*S*)-bis(3,3,3-trifluoro-2-methoxy-2-phenylpropanoate) + (2*S*,4*S*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diyl (2*S*,2'*S*)-bis(3,3,3-trifluoro-2-methoxy-2-phenylpropanoate) **SI-6**



From racemic 29 (prepared from a stereorandom double acetal, followed by separation of the diastereomers by column chromatography).
98% yield (13 mg, 18.7 μmol on 19 μmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 10H), 7.43 – 7.26 (m, 25H), 6.08 (ddt, *J* = 5.9, 4.4, 1.3 Hz, 2H), 4.75 (s, 4H), 4.27 (qd, *J* = 7.7, 6.2 Hz, 2H), 4.21 – 3.98 (m, 8H), 3.91 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.51 (dtd, *J* = 8.6, 2.4, 1.2 Hz, 15H), 2.21 – 2.01 (m, 4H), 1.85 (m, 4H), 1.27 – 1.06 (m, 6H), 0.90 – 0.80 (m, 7H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 146.54, 137.54, 132.41, 129.76, 128.65, 128.61, 128.57, 128.55, 128.11, 127.55, 127.45, 124.90, 122.04, 116.41, 103.49, 103.37, 84.87, 84.59, 73.87, 71.22, 68.82, 68.57, 55.55, 35.02, 34.65, 29.97, 29.86, 26.23, 17.15, 17.10, 1.17.

(2*S*,4*S*)-2-((*Z*)-3-(benzyloxy)allyl)-4-methylpentane-1,5-diyl (2*S*,2'*S*)-bis(3,3,3-trifluoro-2-methoxy-2-phenylpropanoate) **SI-7**



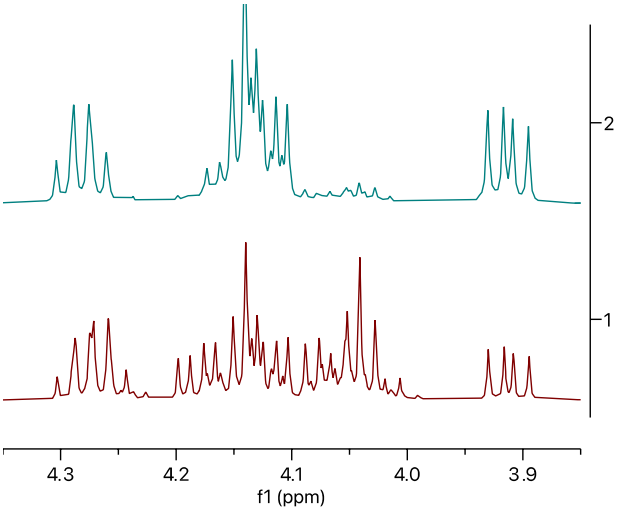
From enantioenriched 29.
91% yield (12 mg, 17 μmol on 19 μmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 5H), 7.44 – 7.26 (m, 13H), 6.08 (dt, *J* = 6.3, 1.2 Hz, 1H), 4.75 (s, 2H), 4.28 (td, *J* = 7.7, 6.3 Hz, 1H), 4.18 – 4.09 (m, 3H), 3.91 (dd, *J* = 10.7, 6.8 Hz, 1H), 3.58 – 3.48 (m, 7H), 2.21 – 2.12 (m, 1H), 2.06 (dddd, *J* = 14.5, 7.4, 6.0, 1.4 Hz, 1H), 1.85 (m, 2H), 1.31 – 1.17 (m, 2H), 1.12 (ddd, *J* = 14.3, 8.5, 6.3 Hz, 1H), 0.84 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 146.51, 137.50, 132.40, 129.73, 129.69, 128.62, 128.56, 128.53, 128.51, 128.08, 127.52, 127.40, 124.87, 103.45, 73.84, 71.28, 68.53, 55.52, 35.04, 34.61, 29.83, 26.19, 17.06, 1.13.

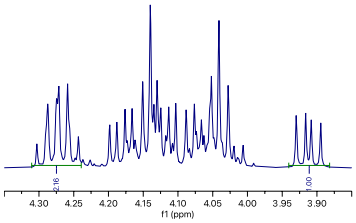
Analysis of *er*(**29**) according to the ^{1}H-NMR spectra:

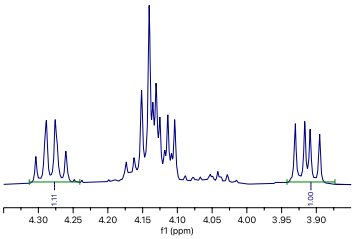
Assuming that the left-hand peak represents one enol ether proton of each diastereomeric Mosher ester, and that the right-hand dd represents one diastereotopic -OC$\mathbf{H}_2$ proton of the major diastereomer:

$$\%_{major\ enantiomer}=\frac{area_{right}}{area_{left}}=1/1.11=0.9$$

er=90/10







6. *t*-BuOK-initiated Coates-Claisen rearrangement

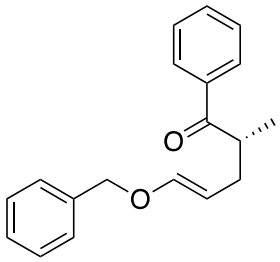
General procedure for the *t*-BuOK-mediated isomerization of branched allyl acetals and subsequent Coates-Claisen rearrangement

The appropriate branched allyl acetal was dissolved in THF (1M in acetal) and the mixture was cooled to 0°C. *t*-BuOK in THF (1M, 3 equiv.) was added dropwise and the mixture was allowed to stir at 0°C until complete consumption of the starting acetal was observed by TLC (isomerized acetals are typically 0.1 units higher in R_f than the starting materials). Diethylether and water were then added, and the aqueous phase was extracted thrice with more diethylether. The combined organic fractions were dried on Na_2SO_4 and concentrated in vacuo. The crude isomerized acetal was dissolved in diethylether (0.2 M) and was left standing in a sealed vial at 25°C for ca. 24 hours until complete Claisen rearrangement observed (ketone products 0.5 units lower in R_f compared to allyl acetal starting material).

Magnesium bromide diethyl etherate (2 equiv.) dissolved in dry diethylether (0.05M in acetal). $LiAlH_4$ (3 equiv. for double acetals and 4 equiv. for triple acetals) was then added, followed by the crude isomerized and rearranged acetal. The mixture was allowed to stir at ambient temperature for 24-48 hours. Upon complete consumption of the reduced ketone (aliquot taken 5 minutes after addition), as detected by TLC, the mixture was cooled to 0°C and water (1 mL per g $LiAlH_4$) was carefully added, followed by 15% NaOH (1 mL per g $LiAlH_4$) and more water (3 mL per g $LiAlH_4$). The mixture was stirred vigorously at ambient temperature for 15 minutes, and was then filtered on a pad of celite, washed with ethyl acetate. The solvents were removed in vacuo and the crude mixture was purified by column chromatography on silica gel.

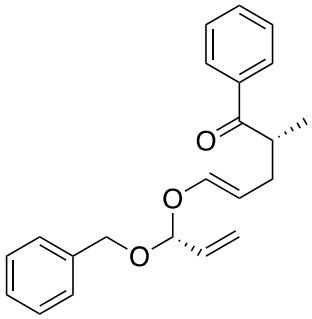
Isomerization-thermal rearrangement products

(*R*,*E*)-5-(benzyloxy)-2-methyl-1-phenylpent-4-en-1-one **26**



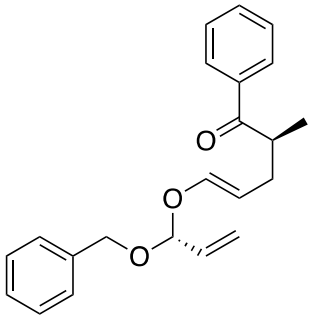
63% yield (88 mg, 0.31 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.61 – 7.52 (m, 1H), 7.51 – 7.42 (m, 2H), 7.32 (tdd, *J* = 9.9, 5.8, 4.4 Hz, 5H), 6.34 (dt, *J* = 12.6, 1.2 Hz, 1H), 4.83 (dt, *J* = 12.5, 7.7 Hz, 1H), 4.66 (s, 2H), 3.46 (m, 1H), 2.42 (dddd, *J* = 13.9, 7.5, 6.4, 1.2 Hz, 1H), 2.08 (dddd, *J* = 14.0, 8.0, 6.9, 1.1 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.14, 147.61, 137.19, 136.82, 132.99, 128.76, 128.60, 128.43, 127.99, 127.65, 101.97, 71.24, 41.90, 32.01, 17.09.
HRMS (APCI): m/z calculated for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1536, found 281.1554.
HPLC (DAICEL OB-H, 10/90 isopropanol/hexane, 1.0 mL/min, 220 nm, tR_1= 14.2 min, tR_2= 20.6 min): **89/11 *er***.

(*R*,*E*)-5-(((*R*)-1-(benzyloxy)allyl)oxy)-2-methyl-1-phenylpent-4-en-1-one **31**



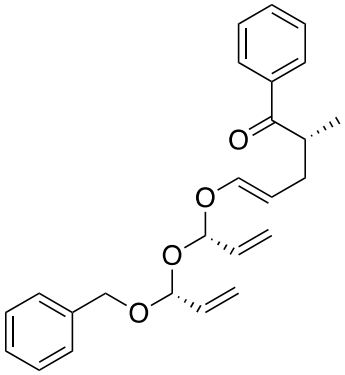
From 13.
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.59 – 7.51 (m, 1H), 7.45 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.37 – 7.27 (m, 4H), 6.31 (dd, *J* = 12.3, 1.3 Hz, 1H), 5.85 (ddd, *J* = 17.4, 10.7, 4.4 Hz, 1H), 5.45 (dt, *J* = 17.4, 1.4 Hz, 1H), 5.33 (dt, *J* = 10.6, 1.4 Hz, 1H), 5.18 (dt, *J* = 4.4, 1.3 Hz, 1H), 5.07 (dt, *J* = 12.3, 7.8 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 3.53 – 3.39 (m, 1H), 2.41 (dddd, *J* = 13.8, 7.5, 6.2, 1.3 Hz, 1H), 2.14 – 2.01 (m, 1H), 1.19 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.01, 142.99, 137.56, 136.75, 134.24, 128.77, 128.56, 128.43, 128.06, 127.92, 119.48, 106.20, 100.49, 68.14, 41.59, 31.86, 17.08.

(*S*,*E*)-5-(((*R*)-1-(benzyloxy)allyl)oxy)-2-methyl-1-phenylpent-4-en-1-one **SI-8**



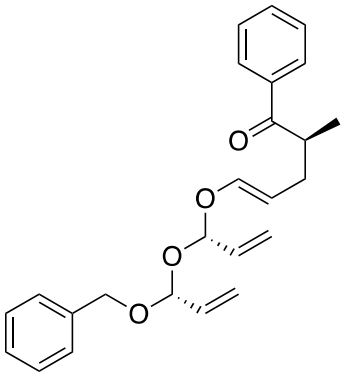
From 14.
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.41 (m, 2H), 7.38 – 7.27 (m, 5H), 6.31 (dt, *J* = 12.2, 1.2 Hz, 1H), 5.85 (ddd, *J* = 17.4, 10.7, 4.4 Hz, 1H), 5.45 (dt, *J* = 17.4, 1.4 Hz, 1H), 5.33 (dt, *J* = 10.8, 1.4 Hz, 1H), 5.18 (dt, *J* = 4.4, 1.3 Hz, 1H), 5.07 (dt, *J* = 12.3, 7.8 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 3.46 (h, *J* = 7.0 Hz, 1H), 2.41 (dddd, *J* = 13.9, 7.6, 6.3, 1.3 Hz, 1H), 2.07 (dddd, *J* = 14.1, 8.2, 7.1, 1.2 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.03, 143.06, 137.55, 136.76, 134.25, 133.00, 128.76, 128.55, 128.42, 128.06, 127.91, 119.46, 106.17, 100.55, 68.18, 41.57, 31.87, 17.12.

(*R*,*E*)-5-(((*S*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)oxy)-2-methyl-1-phenylpent-4-en-1-one **SI-9**



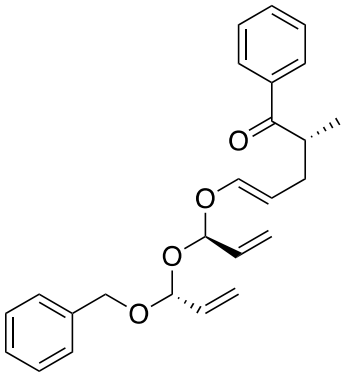
From 18.
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.59 – 7.50 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 3H), 7.37 – 7.27 (m, 4H), 6.29 (d, *J* = 12.3 Hz, 1H), 5.86 (dddd, *J* = 17.4, 10.5, 8.7, 5.1 Hz, 2H), 5.40 (dq, *J* = 17.2, 1.3 Hz, 2H), 5.30 (dt, *J* = 10.4, 1.2 Hz, 2H), 5.25 (d, *J* = 4.8 Hz, 1H), 5.15 (d, *J* = 5.4 Hz, 1H), 5.02 (dt, *J* = 12.2, 7.7 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 3.41 (p, *J* = 6.7 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.04 (dt, *J* = 14.7, 7.7 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.93, 149.15, 143.02, 134.72, 134.31, 133.01, 128.76, 128.52, 128.41, 127.96, 127.80, 106.28, 99.74, 98.15, 68.63, 41.57, 31.76, 17.13.

(*S*,*E*)-5-(((*S*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)oxy)-2-methyl-1-phenylpent-4-en-1-one **SI-10**



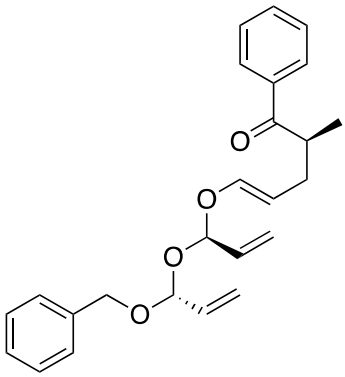
From 19.
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 7.0, 1.4 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.44 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.35 – 7.27 (m, 8H), 6.28 (dt, *J* = 12.3, 1.2 Hz, 1H), 5.86 (dddd, *J* = 17.4, 10.5, 8.0, 5.1 Hz, 2H), 5.40 (dt, *J* = 17.3, 1.3 Hz, 2H), 5.30 (ddt, *J* = 10.4, 2.5, 1.2 Hz, 2H), 5.25 (d, *J* = 4.8 Hz, 1H), 5.15 (dt, *J* = 5.4, 1.1 Hz, 1H), 5.02 (dt, *J* = 12.3, 7.8 Hz, 1H), 4.74 – 4.68 (m, 1H), 4.58 – 4.52 (m, 1H), 3.42 (h, *J* = 6.8 Hz, 1H), 2.39 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.04 (dt, *J* = 14.7, 7.7 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.94, 143.05, 137.86, 136.71, 134.72, 134.33, 133.00, 128.76, 128.51, 128.41, 127.94, 127.80, 119.12, 119.03, 106.26, 99.76, 98.20, 68.60, 41.55, 31.80, 17.16.

(*R*,*E*)-5-(((*R*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)oxy)-2-methyl-1-phenylpent-4-en-1-one **SI-11**



From 20.
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.45 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.37 – 7.27 (m, 4H), 6.23 (d, *J* = 12.2 Hz, 1H), 5.86 (tdd, *J* = 17.5, 10.6, 4.4 Hz, 2H), 5.53 – 5.39 (m, 3H), 5.36 – 5.26 (m, 3H), 5.01 (dt, *J* = 12.3, 7.8 Hz, 1H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 3.42 (h, *J* = 6.8 Hz, 1H), 2.43 – 2.31 (m, 1H), 2.02 (dt, *J* = 14.7, 7.8 Hz, 1H), 1.16 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.96, 143.00, 137.98, 136.72, 134.57, 134.26, 133.00, 128.75, 128.57, 128.41, 127.89, 127.82, 119.25, 119.15, 106.33, 98.34, 97.93, 67.15, 41.53, 31.77, 17.09.

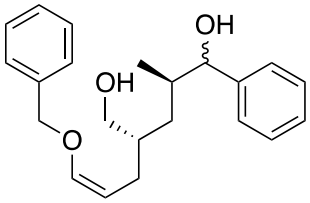
(*S*,*E*)-5-(((*R*)-1-(((*R*)-1-(benzyloxy)allyl)oxy)allyl)oxy)-2-methyl-1-phenylpent-4-en-1-one **SI-12**



From 21.
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.59 – 7.51 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 5H), 6.23 (d, *J* = 12.2 Hz, 1H), 5.95 – 5.77 (m, 2H), 5.53 – 5.38 (m, 3H), 5.37 – 5.26 (m, 3H), 5.00 (dt, *J* = 12.2, 7.8 Hz, 1H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 3.42 (q, *J* = 6.8 Hz, 1H), 2.37 (dt, *J* = 14.0, 6.9 Hz, 1H), 2.03 (dt, *J* = 14.7, 7.7 Hz, 1H), 1.16 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.01, 137.98, 134.57, 134.27, 133.00, 128.76, 128.57, 128.41, 127.89, 119.29, 119.14, 111.44, 106.33, 98.34, 97.92, 67.14, 41.54, 31.77, 17.10.

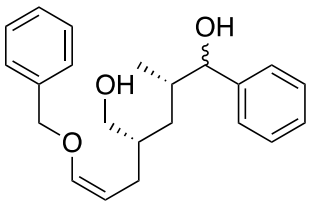
Claisen-reduction products

(2*R*,4*S*)-4-((*Z*)-3-(benzyloxy)allyl)-2-methyl-1-phenylpentane-1,5-diol **32**



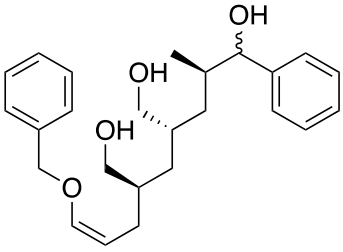
From 12.
91% yield (155 mg, 0.455 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 12H), 6.12 (d, *J* = 6.2 Hz, 1H), 4.79 (d, *J* = 4.3 Hz, 2H), 4.70 – 4.57 (m, 1H), 4.49 – 4.32 (m, 2H), 3.61 – 3.34 (m, 3H), 2.29 – 2.11 (m, 2H), 2.09 – 1.81 (m, 3H), 1.80 – 1.61 (m, 2H), 1.51 – 1.39 (m, 0H), 1.21 (t, *J* = 7.0 Hz, 1H), 1.06 (tdd, *J* = 12.8, 8.9, 4.9 Hz, 1H), 0.86 (d, *J* = 6.7 Hz, 1H), 0.73 (d, *J* = 6.8 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.91, 145.83, 128.73, 128.36, 128.30, 127.67, 127.32, 126.86, 126.39, 105.23, 104.92, 79.72, 74.01, 66.01, 64.18, 42.09, 38.36, 38.12, 37.97, 37.75, 34.56, 34.42, 26.74, 26.15, 16.68, 15.43, 14.65.
HRMS (APCI): m/z calculated for $C_{22}H_{27}O_2$ $[M\text{-}OH]^+$: 323.2006, found 323.1999.

(2*S*,4*S*)-4-((*Z*)-3-(benzyloxy)allyl)-2-methyl-1-phenylpentane-1,5-diol **33**



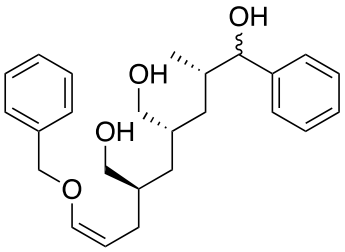
From 13.
83% yield (142 mg, 0.42 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 15.0, 9.1 Hz, 10H), 6.10 (dd, *J* = 10.4, 6.2 Hz, 1H), 4.79 (d, *J* = 4.4 Hz, 2H), 4.64 – 4.20 (m, 2H), 3.58 – 3.28 (m, 3H), 2.35 – 2.11 (m, 2H), 2.10 – 1.81 (m, 3H), 1.72 (d, *J* = 13.2 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 2H), 1.07 (dddd, *J* = 18.5, 13.7, 9.5, 4.4 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 1H), 0.76 (d, *J* = 6.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.94, 143.60, 137.15, 128.75, 128.34, 128.27, 127.71, 127.59, 127.44, 126.79, 126.56, 104.42, 79.52, 78.55, 74.02, 66.02, 65.85, 37.96, 37.90, 37.57, 33.81, 33.23, 23.95, 16.42, 15.42, 14.81.
HRMS (APCI): m/z calculated for $C_{22}H_{27}O_2$ $[M\text{-}OH]^+$: 323.2006, found 323.1999.

(2*R*,4*S*,6*S*)-6-((*Z*)-3-(benzyloxy)allyl)-4-(hydroxymethyl)-2-methyl-1-phenylheptane-1,7-diol **34**



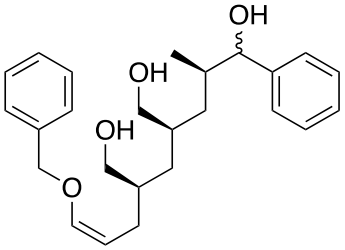
From 18.
64% yield (127 mg, 0.32 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 11H), 6.14 – 6.06 (m, 1H), 4.77 (d, *J* = 3.4 Hz, 2H), 4.58 (dd, *J* = 11.5, 3.9 Hz, 1H), 4.46 – 4.30 (m, 1H), 3.44 (tp, *J* = 16.0, 5.4 Hz, 4H), 3.13 (s, 1H), 2.73 (s, 1H), 2.20 – 2.01 (m, 2H), 1.89 (dq, *J* = 16.8, 8.7 Hz, 1H), 1.62 (ddq, *J* = 23.7, 12.0, 6.0 Hz, 2H), 1.50 – 1.39 (m, 1H), 1.21 (tddd, *J* = 27.4, 21.2, 11.0, 7.0 Hz, 2H), 0.96 (ddd, *J* = 13.8, 8.5, 5.1 Hz, 0H), 0.83 (t, *J* = 7.0 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 145.79, 145.74, 143.74, 143.65, 143.42, 137.22, 137.19, 128.67, 128.58, 128.32, 128.28, 128.19, 128.16, 128.12, 127.66, 127.63, 127.61, 127.52, 127.15, 126.87, 126.84, 126.50, 126.45, 126.42, 105.05, 104.97, 104.79, 80.10, 79.60, 73.91, 66.47, 66.29, 65.51, 65.30, 65.18, 64.94, 64.78, 38.10, 37.81, 37.64, 37.53, 37.41, 37.35, 37.28, 35.83, 35.76, 35.65, 35.45, 35.17, 35.11, 34.83, 34.57, 33.84, 33.57, 32.77, 29.78, 25.99, 25.78, 25.41, 25.11, 17.23, 17.03, 15.16, 15.00, 14.81.
HRMS (APCI): m/z calculated for $C_{25}H_{35}O_4$ $[M+H]^+$: 399.2530, found 399.3269.

(2*S*,4*S*,6*S*)-6-((*Z*)-3-(benzyloxy)allyl)-4-(hydroxymethyl)-2-methyl-1-phenylheptane-1,7-diol **35**



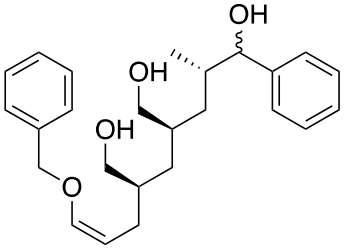
From 19.
62% yield (124 mg, 0.32 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 8H), 6.13 (ddt, *J* = 6.4, 4.3, 1.2 Hz, 1H), 4.79 (d, *J* = 3.6 Hz, 2H), 4.57 (d, *J* = 5.3 Hz, 1H), 4.47 – 4.36 (m, 1H), 3.60 – 3.38 (m, 3H), 2.24 – 2.04 (m, 2H), 1.94 (dt, *J* = 11.9, 7.2 Hz, 1H), 1.83 – 1.52 (m, 2H), 1.39 – 1.06 (m, 3H), 0.89 (dd, *J* = 6.8, 2.3 Hz, 2H), 0.80 – 0.70 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.94, 145.90, 143.65, 137.19, 128.75, 128.42, 128.30, 127.72, 127.38, 126.84, 126.51, 104.92, 104.88, 79.80, 77.92, 74.04, 66.64, 66.00, 65.12, 64.93, 37.84, 37.51, 37.34, 35.92, 35.78, 35.36, 34.96, 32.60, 25.91, 17.32, 15.41, 15.19.
HRMS (APCI): m/z calculated for $C_{25}H_{35}O_4$ $[M+H]^+$: 399.2530, found 399.2521.

(2*R*,4*R*,6*S*)-6-((*Z*)-3-(benzyloxy)allyl)-4-(hydroxymethyl)-2-methyl-1-phenylheptane-1,7-diol **36**



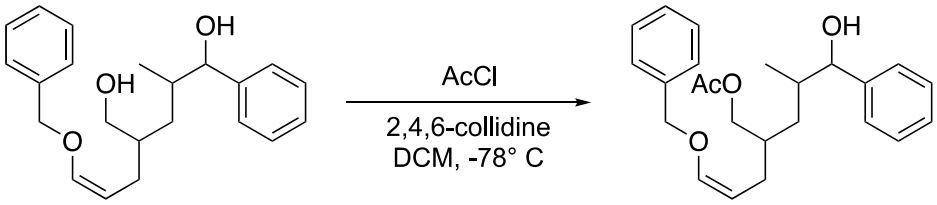
From 20.
78% yield (155 mg, 0.39 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 9H), 6.13 (dt, *J* = 6.2, 1.2 Hz, 1H), 4.79 (d, *J* = 1.9 Hz, 2H), 4.48 – 4.32 (m, 2H), 3.61 – 3.41 (m, 4H), 2.25 – 2.04 (m, 2H), 1.93 (qd, *J* = 7.2, 3.6 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.65 (ddd, *J* = 11.9, 8.2, 3.7 Hz, 1H), 1.58 (s, 1H), 1.31 – 1.12 (m, 2H), 0.89 (dd, *J* = 6.7, 2.0 Hz, 0H), 0.74 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.97, 143.66, 137.24, 128.73, 128.40, 128.25, 127.68, 126.83, 104.78, 79.76, 74.00, 66.51, 66.00, 65.52, 38.20, 37.33, 35.83, 35.39, 32.49, 25.42, 17.15, 15.41.
HRMS (APCI): m/z calculated for $C_{25}H_{35}O_4$ $[M+H]^+$: 399.2530, found 399.2511.

(2*S*,4*R*,6*S*)-6-((*Z*)-3-(benzyloxy)allyl)-4-(hydroxymethyl)-2-methyl-1-phenylheptane-1,7-diol **37**

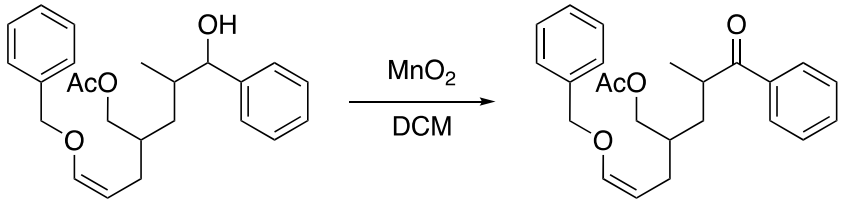


From 21.
73% yield (146 mg, 0.37 mmol on 0.5 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 9H), 6.13 (dt, *J* = 6.2, 1.3 Hz, 1H), 4.79 (d, *J* = 3.2 Hz, 2H), 4.58 (d, *J* = 5.2 Hz, 0H), 4.42 (tt, *J* = 8.0, 5.9 Hz, 1H), 4.33 (d, *J* = 7.7 Hz, 1H), 3.61 – 3.41 (m, 3H), 2.43 (s, 2H), 2.24 – 2.04 (m, 1H), 2.01 – 1.84 (m, 1H), 1.84 – 1.73 (m, 0H), 1.73 – 1.56 (m, 3H), 1.56 – 1.35 (m, 1H), 1.18 – 0.95 (m, 2H), 0.88 (d, *J* = 6.7 Hz, 1H), 0.71 (d, *J* = 6.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.94, 145.89, 137.23, 128.73, 128.44, 128.30, 128.24, 127.67, 127.40, 126.82, 126.54, 104.93, 104.83, 80.06, 77.76, 74.01, 73.99, 66.00, 64.99, 38.04, 37.92, 37.73, 35.25, 35.11, 34.05, 33.82, 25.70, 17.12, 15.42, 15.25.
HRMS (APCI): m/z calculated for $C_{25}H_{35}O_4$ $[M+H]^+$: 399.2530, found 399.3345.

Derivatization of the rearrangement products

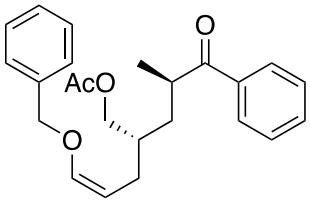


According to a procedure by Yamamoto.[7] The purified polyol products were dissolved in distilled dichloromethane (0.1 M). Freshly distilled 2,4,6-collidine (2 equiv. for diols, 3 equiv. for triols) was added, and the mixture was cooled to -78°C. Freshly distilled acetyl chloride (1.1 equiv. for diols, 2.2 equiv. for triols) was added dropwise, and the mixture was allowed to stir for three hours. Upon complete consumption of the starting polyol, the mixture was poured into 1M aqueous HCl/diethylether. The aqueous phase was extracted thrice with diethylether and the combined organic fractions were dried over sodium sulfate and concentrated in vacuo.



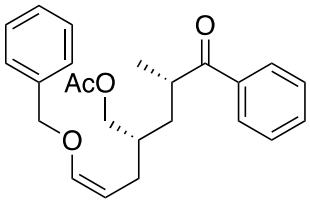
The crude acetates were dissolved in dichloromethane (0.1M) and homemade manganese dioxide[8] (10 weight equivalents) was added. The mixture was allowed to stir until complete consumption of the alcohol was observed by TLC (typically 4 hours). The mixture was filtered on a pad of celite washed with more dichloromethane, and the solvent was removed in vacuo. The crude mixture was purified by column chromatography on silica gel.

(*S*,*Z*)-5-(benzyloxy)-2-((*R*)-2-methyl-3-oxo-3-phenylpropyl)pent-4-en-1-yl acetate **SI-13**



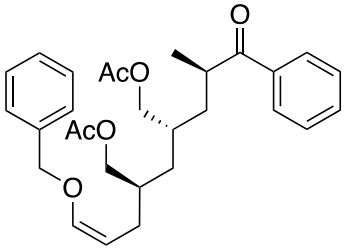
From 32.
52% yield over two steps (55 mg, 0.145 mmol on 0.28 mmol scale)
89/11 *dr* (*Z*), 1/4.3 *E*/*Z*
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.89 (m, 3H), 7.61 – 7.38 (m, 4H), 7.38 – 7.27 (m, 6H), 6.09 (dt, *J* = 6.2, 1.3 Hz, 1H), 4.76 (s, 2H), 4.36 – 4.29 (m, 1H), 4.03 (h, J = 5.7 Hz, 2H), 3.64 (p, *J* = 7.0 Hz, 1H), 2.22 (dddd, *J* = 14.6, 8.0, 6.7, 1.3 Hz, 1H), 2.11 (dddd, *J* = 14.4, 7.2, 5.7, 1.4 Hz, 1H), 1.99 (s, 3H), 1.95 – 1.86 (m, 2H), 1.84 – 1.76 (m, 1H), 1.46 – 1.34 (m, 1H), 1.17 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.09, 171.31, 146.28, 137.60, 136.56, 132.97, 128.72, 128.59, 128.37, 128.01, 127.49, 103.78, 73.80, 66.76, 38.05, 35.71, 34.89, 25.89, 21.00, 18.11.
HRMS (APCI): m/z calculated for $C_{24}H_{29}O_4$ $[M+H]^+$: 381.2060, found 381.2068.

(*S*,*Z*)-5-(benzyloxy)-2-((*S*)-2-methyl-3-oxo-3-phenylpropyl)pent-4-en-1-yl acetate **SI-14**



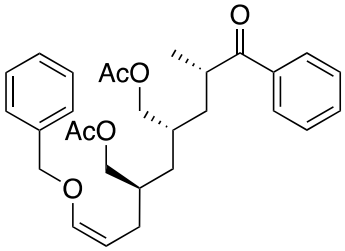
From 33.
45% yield over two steps (51 mg, 0.134 mmol on 0.3 mmol scale)
80/20 *dr* (*Z*), 1/6.7 *E*/*Z*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 3H), 7.57 – 7.51 (m, 1H), 7.46 – 7.41 (m, 2H), 7.37 – 7.27 (m, 6H), 4.77 (s, 2H), 4.39 (td, *J* = 7.6, 6.2 Hz, 1H), 4.05 – 3.98 (m, 1H), 3.90 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.65 (qd, *J* = 7.0, 2.8 Hz, 1H), 2.21 (dddd, *J* = 7.8, 6.6, 3.0, 1.4 Hz, 2H), 1.91 (s, 3H), 1.89 – 1.77 (m, 2H), 1.48 – 1.39 (m, 1H), 1.18 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.19, 171.32, 146.28, 137.66, 136.57, 133.03, 128.78, 128.61, 128.43, 128.01, 127.46, 103.99, 73.81, 67.27, 38.04, 35.71, 35.04, 25.76, 20.96, 18.15.
HRMS (APCI): m/z calculated for $C_{24}H_{29}O_4$ $[M+H]^+$: 381.2060, found 381.2074.

(2*S*,4*S*)-2-((*Z*)-3-(benzyloxy)allyl)-4-((*S*)-2-methyl-3-oxo-3-phenylpropyl)pentane-1,5-diyl diacetate **SI-15**



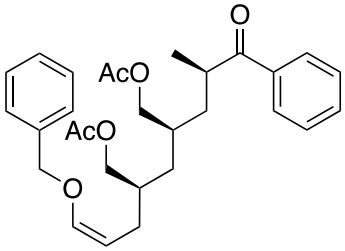
From 34
45% yield over two steps (27 mg, 0.056 mmol on 0.125 mmol scale)
43/44/45/46= 72/18/10/0 (*Z*), 1/6.4 *E*/*Z*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 3H), 7.60 – 7.52 (m, 2H), 7.51 – 7.42 (m, 3H), 7.39 – 7.26 (m, 7H), 6.09 (dq, J = 6.3, 1.3 Hz, 1H), 4.77 (s, 2H), 4.31 (td, *J* = 7.7, 6.3 Hz, 1H), 4.07 – 3.84 (m, 6H), 3.66 – 3.51 (m, 1H), 2.21 – 2.09 (m, 3H), 2.00 (d, *J* = 2.1 Hz, 3H), 1.92 (d, *J* = 1.1 Hz, 3H), 1.91 – 1.74 (m, 3H), 1.44 – 1.21 (m, 4H), 1.18 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.87, 171.32, 146.32, 137.63, 136.35, 133.15, 128.83, 128.61, 128.39, 128.05, 127.51, 127.45, 103.73, 73.81, 67.01, 66.87, 38.13, 35.54, 35.06, 33.91, 32.79, 25.75, 21.04, 20.96, 17.57.
HRMS (APCI): m/z calculated for $C_{29}H_{37}O_6$ $[M+H]^+$: 481.2585, found 481.2558.

(2*S*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-((*R*)-2-methyl-3-oxo-3-phenylpropyl)pentane-1,5-diyl diacetate **SI-16**



From 35
45% yield over two steps (59 mg, 0.123 mmol on 0.271 mmol scale)
44/43/45/46= 83/17/0/0 (*Z*), 1/5.3 *E*/*Z*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.43 (m, 2H), 7.39 – 7.26 (m, 5H), 6.08 (dt, *J* = 6.3, 1.3 Hz, 1H), 4.75 (s, 2H), 4.34 (td, *J* = 7.6, 6.3 Hz, 1H), 4.08 – 3.83 (m, 4H), 3.68 – 3.53 (m, 1H), 2.24 – 2.11 (m, 2H), 2.00 (s, 3H), 1.92 (s, 3H), 1.90 – 1.85 (m, 1H), 1.78 (q, *J* = 6.0 Hz, 1H), 1.44 – 1.34 (m, 1H), 1.30 (t, *J* = 7.0 Hz, 2H), 1.21 – 1.16 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.84, 171.35, 171.26, 146.29, 137.72, 136.65, 133.13, 104.02, 73.78, 67.53, 67.14, 38.17, 36.01, 35.21, 33.90, 33.21, 25.99, 21.06, 20.94, 18.84.
HRMS (APCI): m/z calculated for $C_{29}H_{37}O_6$ $[M+H]^+$: 481.2585, found 481.2597.

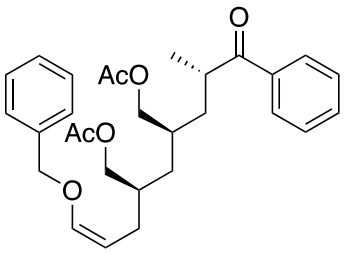
(2*S*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-((*S*)-2-methyl-3-oxo-3-phenylpropyl)pentane-1,5-diyl diacetate **SI-17**



From 36
40% yield over two steps (42 mg, 0.087 mmol on 0.218 mmol scale)
45/43/44/46= 82/0/0/18 (*Z*), 1/3.5 *E*/*Z*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dq, *J* = 7.1, 1.6 Hz, 3H), 7.60 – 7.51 (m, 1H), 7.50 – 7.41 (m, 3H), 7.39 – 7.27 (m, 6H), 6.10 (dt, *J* = 6.2, 1.3 Hz, 1H), 4.77 (s, 2H), 4.36 (td, *J* = 7.6, 6.2 Hz, 1H), 4.07 – 3.84 (m, 5H), 3.68 – 3.52 (m, 1H), 2.20 – 2.14 (m, 2H), 2.13 – 2.01 (m, 2H), 1.99 (d, *J* = 2.8 Hz, 3H), 1.93 (s, 3H), 1.92 – 1.83 (m, 1H), 1.78 (p, *J* = 6.1 Hz, 1H), 1.42 – 1.23 (m, 3H), 1.18 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.86, 171.27, 146.33, 137.71, 136.61, 133.14, 128.85, 128.62, 128.41, 128.02, 127.49, 104.01, 73.82, 67.37, 67.17, 38.17, 36.20, 35.27, 33.85, 33.19, 25.82, 21.05, 20.94, 18.86.
HRMS (APCI): m/z calculated for $C_{29}H_{37}O_6$ $[M+H]^+$: 481.2585, found 481.2607.

(2*S*,4*R*)-2-((*Z*)-3-(benzyloxy)allyl)-4-((*R*)-2-methyl-3-oxo-3-phenylpropyl)pentane-1,5-diyl diacetate **SI-18**

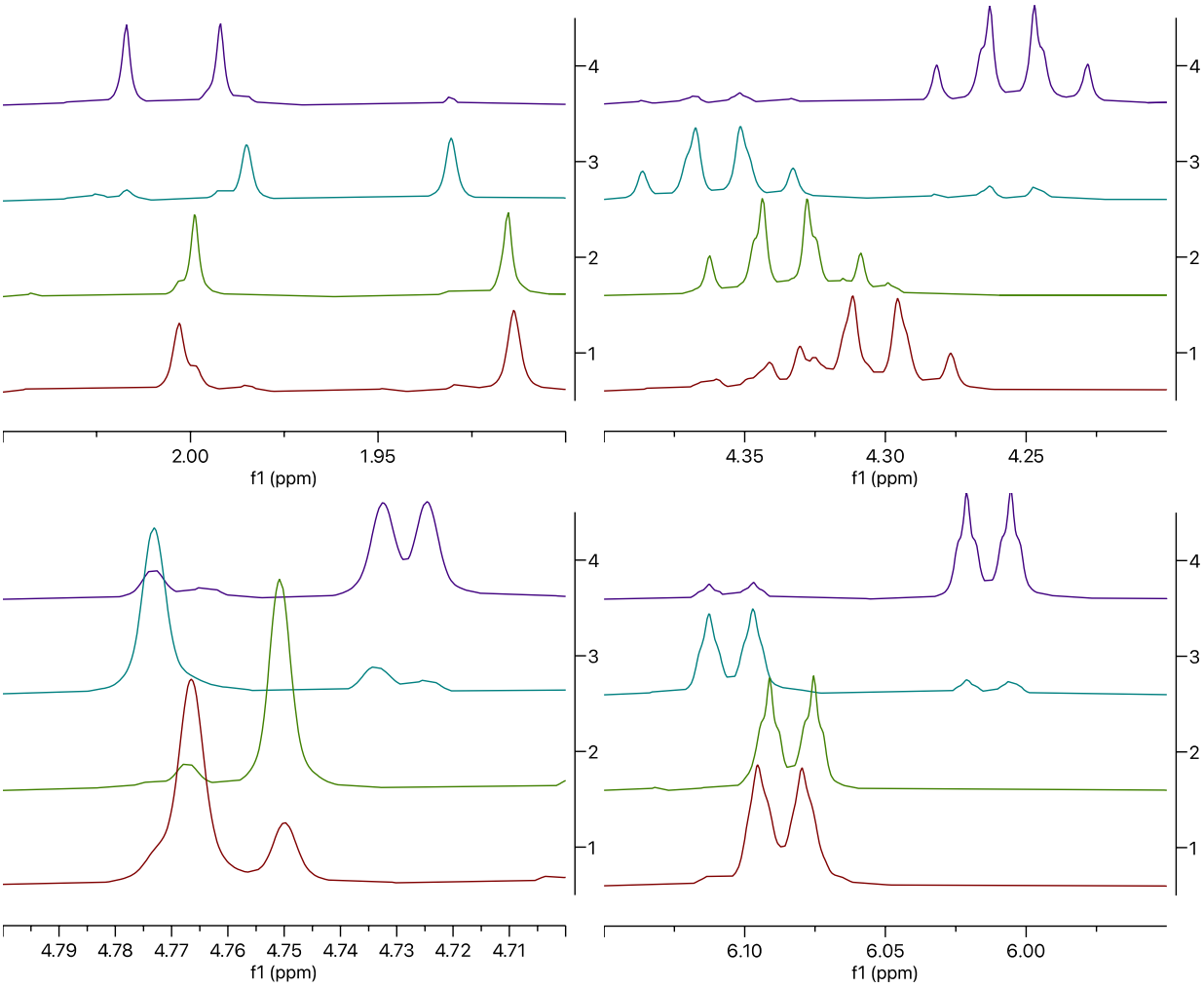


From 37
61% yield over two steps (85 mg, 0.177 mmol on 0.291 mmol scale)
46/43/44/45= 85/0/0/15 (*Z*), 1/5.7 *E*/*Z*
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.60 – 7.50 (m, 1H), 7.50 – 7.41 (m, 2H), 7.39 – 7.27 (m, 5H), 6.01 (dt, *J* = 6.3, 1.3 Hz, 1H), 4.73 (d, *J* = 3.2 Hz, 2H), 4.25 (td, *J* = 7.6, 6.2 Hz, 1H), 4.03 (d, *J* = 4.3 Hz, 2H), 3.93 (qd, *J* = 11.0, 5.7 Hz, 2H), 3.66 – 3.51 (m, 1H), 2.20 – 2.05 (m, 2H), 2.02 (s, 3H), 1.99 (s, 4H), 1.82 (ddt, *J* = 30.6, 12.7, 6.0 Hz, 3H), 1.44 – 1.32 (m, 2H), 1.27 – 1.21 (m, 1H), 1.19 (d, *J* = 6.9 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.86, 171.31, 171.27, 146.34, 137.68, 136.45, 133.12, 128.82, 128.61, 128.42, 128.02, 127.47, 103.73, 73.77, 67.14, 66.69, 38.17, 35.85, 35.24, 33.94, 32.94, 25.72, 21.04, 21.02, 17.70.
HRMS (APCI): m/z calculated for $C_{29}H_{37}O_6$ $[M+H]^+$: 481.2585, found 481.2583.

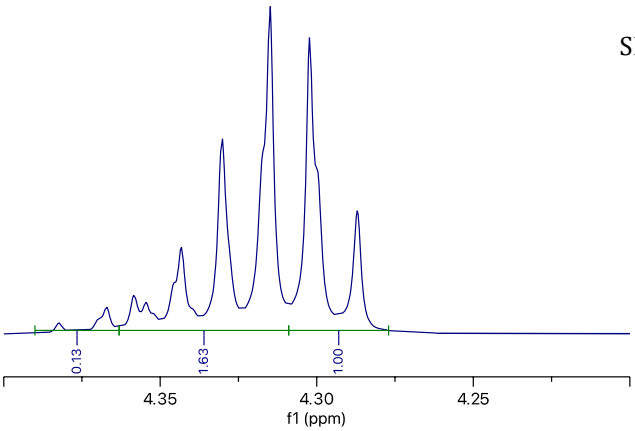
Stereochemical analysis of SI-15-18

The ^{1}H-NMR spectra of the three diastereomers **SI-15-18** are complex, but there were several relatively well-resolved regions usable for determining their diastereomeric ratios.

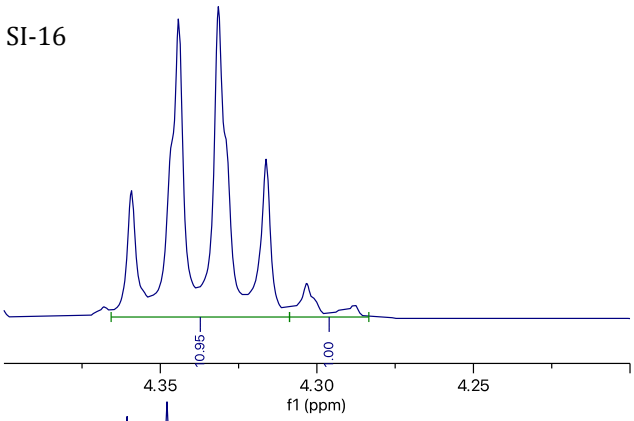
Order of stacked spectra from top to bottom: **SI-18**, **SI-17**, **SI-16**, **SI-15**.
Top left: acetate methyl protons.
Top right: enol ether proton (alkyl side).
Bottom left: benzyl methylene protons.
Bottom right: enol ether proton (benzyloxy side).



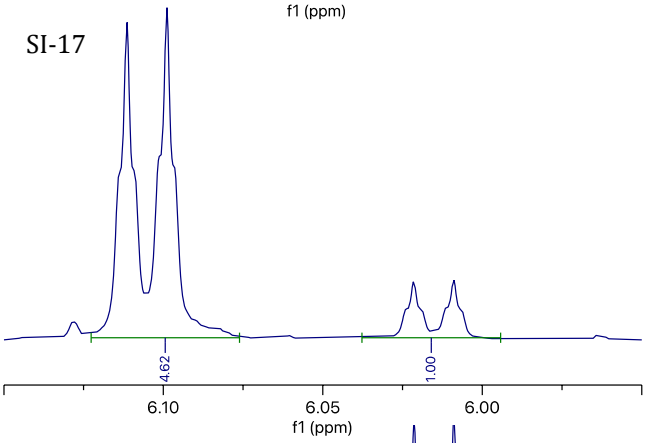
SI-15



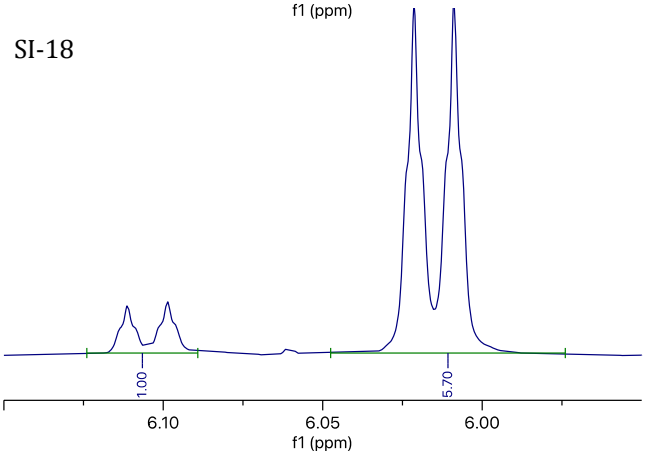
SI-16



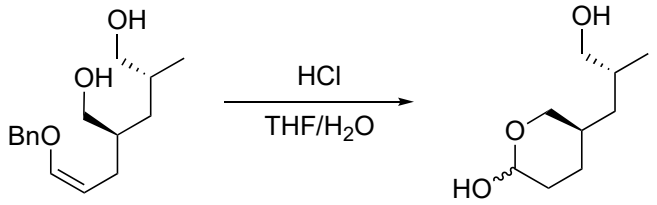
SI-17



SI-18



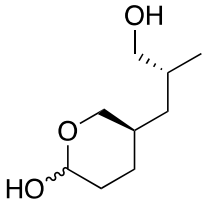
7. Application to the formal synthesis of deoxypropionates



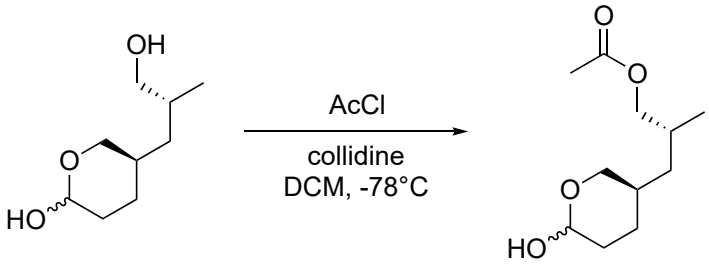
28 **29**

27 (386 mg, 1.46 mmol) was dissolved in 3 mL of THF and 3 mL of 3M aqueous HCl was added. The mixture was stirred at ambient temperature for 3 hours and was then added to diethylether and water. The aqueous phase was extracted thrice with diethylether. The combined organic fractions were dried on sodium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel, eluting with 80-100% ethyl acetate in petroleum ether.

(5*R*)-5-((*R*)-3-hydroxy-2-methylpropyl)tetrahydro-2H-pyran-2-ol **38**



49% yield (124 mg, 0.71 mmol on 1.46 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (d, *J* = 3.4 Hz, 1H), 4.70 (s, 1H), 3.94 (d, *J* = 11.6 Hz, 1H), 3.65 (t, *J* = 10.5 Hz, 1H), 3.57 – 3.40 (m, 8H), 3.17 (t, *J* = 10.8 Hz, 1H), 2.83 (s, 1H), 2.43 (s, 1H), 1.96 – 1.86 (m, 2H), 1.79 – 1.60 (m, 1H), 1.55 – 1.33 (m, 1H), 1.34 – 1.23 (m, 2H), 1.22 – 1.06 (m, 3H), 0.98 (ddd, *J* = 13.5, 8.6, 5.5 Hz, 1H), 0.93 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 96.37, 71.35, 68.63, 65.82, 35.67, 34.98, 32.90, 32.64, 32.57, 32.40, 32.26, 29.87, 28.19, 23.96, 16.78, 16.70, 15.42.

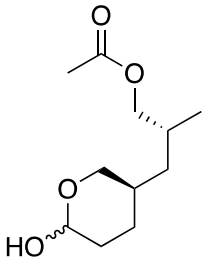


38 **39**

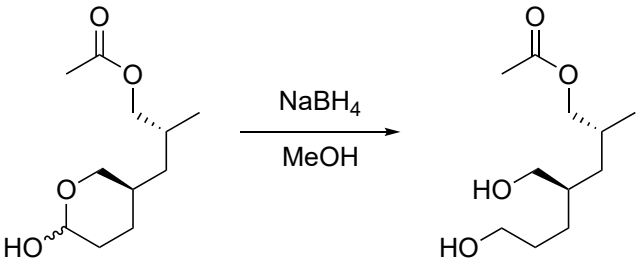
According to a procedure by Yamamoto.[4] **38** (82 mg, 0.47 mmol) was dissolved in 5 mL of freshly distilled dichloromethane. Freshly distilled 2,4,6-collidine (2 equiv., 114 mg, 125 µl) was added, and the mixture was cooled to -78°C. Freshly distilled acetyl chloride (1.5 equiv., 55 mg, 50 µl) was added, and the mixture was allowed to stir for three hours. Upon complete consumption of **38**, the mixture was poured into 1M aqueous HCl/diethylether. The aqueous phase was extracted thrice with diethylether and the combined organic fractions were dried over sodium sulfate and concentrated in vacuo.

Crude **39** was used as is for the next step.

(2*R*)-3-((3*R*)-6-hydroxytetrahydro-2H-pyran-3-yl)-2-methylpropyl acetate **39**



Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (dd, *J* = 7.8, 2.6 Hz, 0H), 5.14 (d, *J* = 2.9 Hz, 1H), 4.67 (dd, *J* = 8.9, 2.1 Hz, 1H), 3.98 (d, *J* = 28.7 Hz, 3H), 3.86 (dtdt, *J* = 16.3, 11.0, 5.7, 2.1 Hz, 5H), 3.62 (t, *J* = 10.5 Hz, 1H), 3.52 – 3.39 (m, 2H), 3.27 (dd, *J* = 11.6, 8.5 Hz, 0H), 3.12 (t, *J* = 10.8 Hz, 1H), 2.02 (d, *J* = 1.5 Hz, 8H), 1.93 – 1.52 (m, 9H), 1.52 – 1.31 (m, 2H), 1.31 – 0.92 (m, 5H), 0.88 (d, *J* = 6.6 Hz, 8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.97, 171.39, 171.35, 169.81, 96.28, 94.03, 91.79, 70.93, 70.33, 69.62, 69.54, 65.90, 65.46, 35.93, 35.77, 35.14, 34.62, 32.46, 32.41, 32.23, 32.10, 31.48, 30.36, 29.83, 29.74, 29.40, 29.29, 28.19, 28.01, 26.25, 23.85, 22.22, 21.22, 20.98, 20.81, 16.94, 16.90, 16.86, 15.27, 1.06.

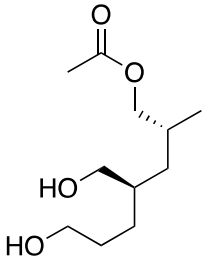


39 **40**

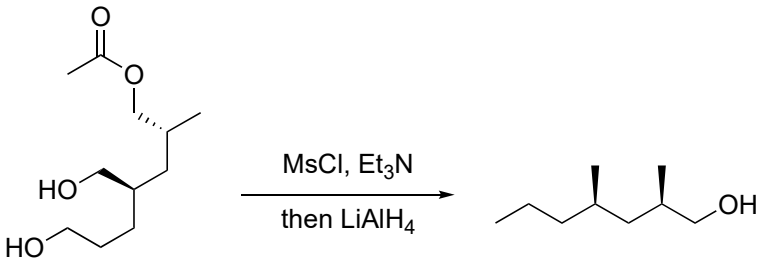
Crude **39** was dissolved in methanol (5 mL). Sodium borohydride (21 mg, 0.56 mmol, 1.2 equiv.) was added and the mixture was stirred at ambient temperature for three hours, until complete consumption of **39** was observed by TLC. The mixture was added into diethylether and water. The aqueous phase was extracted thrice with diethylether and the combined organic fractions were dried over sodium sulfate and concentrated in vacuo.

Crude **40** was used as is for the next step.

(2*R*,4*R*)-7-hydroxy-4-(hydroxymethyl)-2-methylheptyl acetate **40**



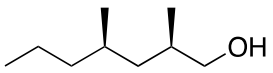
Crude
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 – 3.76 (m, 2H), 3.65 – 3.57 (m, 2H), 3.51 (qd, *J* = 10.8, 5.5 Hz, 2H), 2.71 (s, 3H), 2.03 (s, 4H), 1.86 (tt, *J* = 12.5, 6.4 Hz, 1H), 1.65 – 1.47 (m, 3H), 1.46 – 1.21 (m, 4H), 1.14 (ddd, *J* = 14.1, 8.2, 6.2 Hz, 1H), 0.90 (dd, *J* = 8.9, 5.5 Hz, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.54, 69.69, 65.43, 62.90, 37.40, 35.18, 30.08, 29.28, 26.78, 21.05, 17.36.



40 **41**

40 was dissolved in 3 mL of freshly distilled dichloromethane. Triethylamine (4 equiv., 11 mg, 76 μl) was added, and the mixture was cooled to 0°C. Methanesulfonyl chloride (4 equiv., 132 mg, 181 μl) was added, and the mixture was allowed to warm to ambient temperature and stir for two hours. Upon complete consumption of **40**, the mixture was poured added into water and dichloromethane. The aqueous phase was extracted thrice with dichloromethane and the combined organic fractions were dried over sodium sulfate and concentrated in vacuo.
The crude mesylate was dissolved in dry THF (3 mL). The solution was cooled to 0°C and $LiAlH_4$ (5 equiv. 62 mg) was added. The mixture was allowed to stir at ambient temperature for five hours.
The mixture was cooled to 0°C and water (60 μl) was carefully added, followed by 15% NaOH (60 μl) and more water (180 μl). The mixture was stirred vigorously at ambient temperature for 15 minutes, and was then filtered on a pad of celite, washed with diethylether. The solvents were removed in vacuo and the crude mixture was purified by column chromatography on silica gel, eluting with 10-20% diethylether in pentane.

(2*R*,4*R*)-2,4-dimethylheptan-1-ol **41**



32% yield over two steps (15 mg, 0.1 mmol on 0.3 mmol scale)
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 – 3.49 (m, 1H), 3.43 – 3.32 (m, 1H), 1.80 – 1.64 (m, 1H), 1.57 – 1.44 (m, 1H), 1.41 – 1.23 (m, 5H), 1.04 (tdd, *J* = 12.6, 5.9, 3.3 Hz, 1H), 0.97 – 0.81 (m, 10H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 68.56, 41.19, 39.10, 33.25, 29.91, 20.46, 20.07, 17.43, 14.53.

The spectra are in line with previous reports.[9]

8. References

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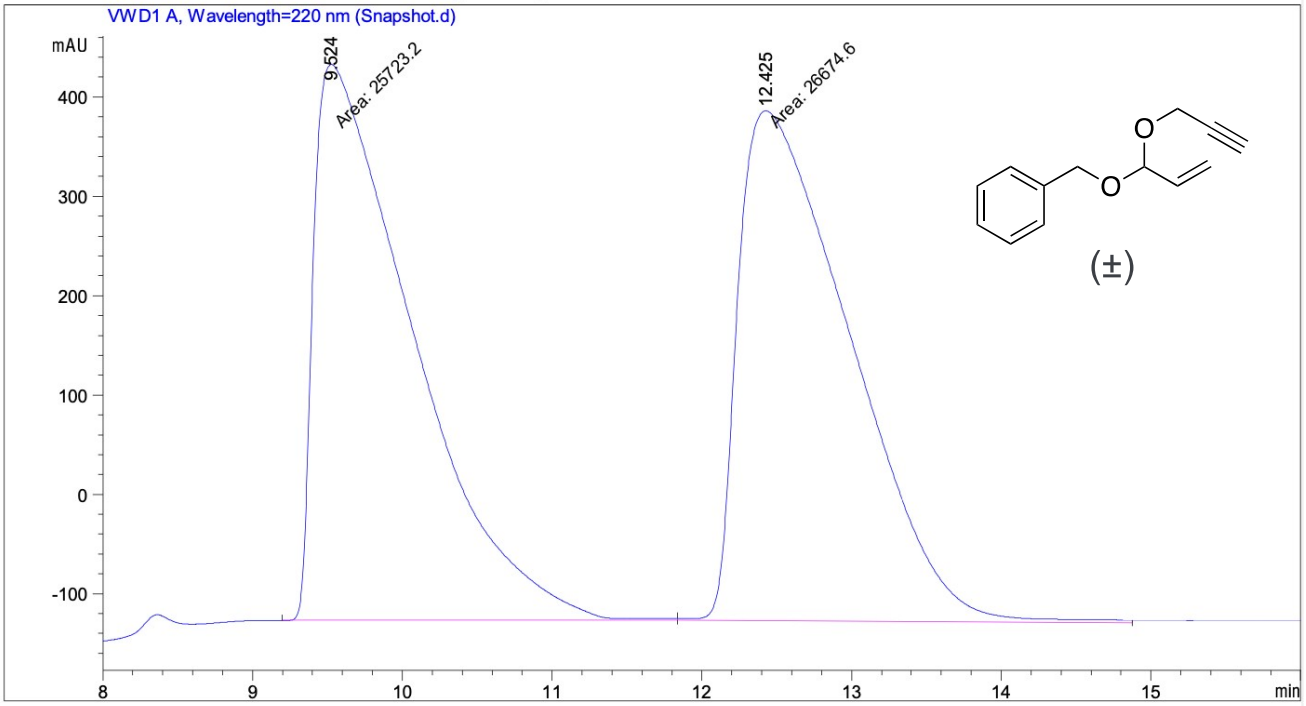
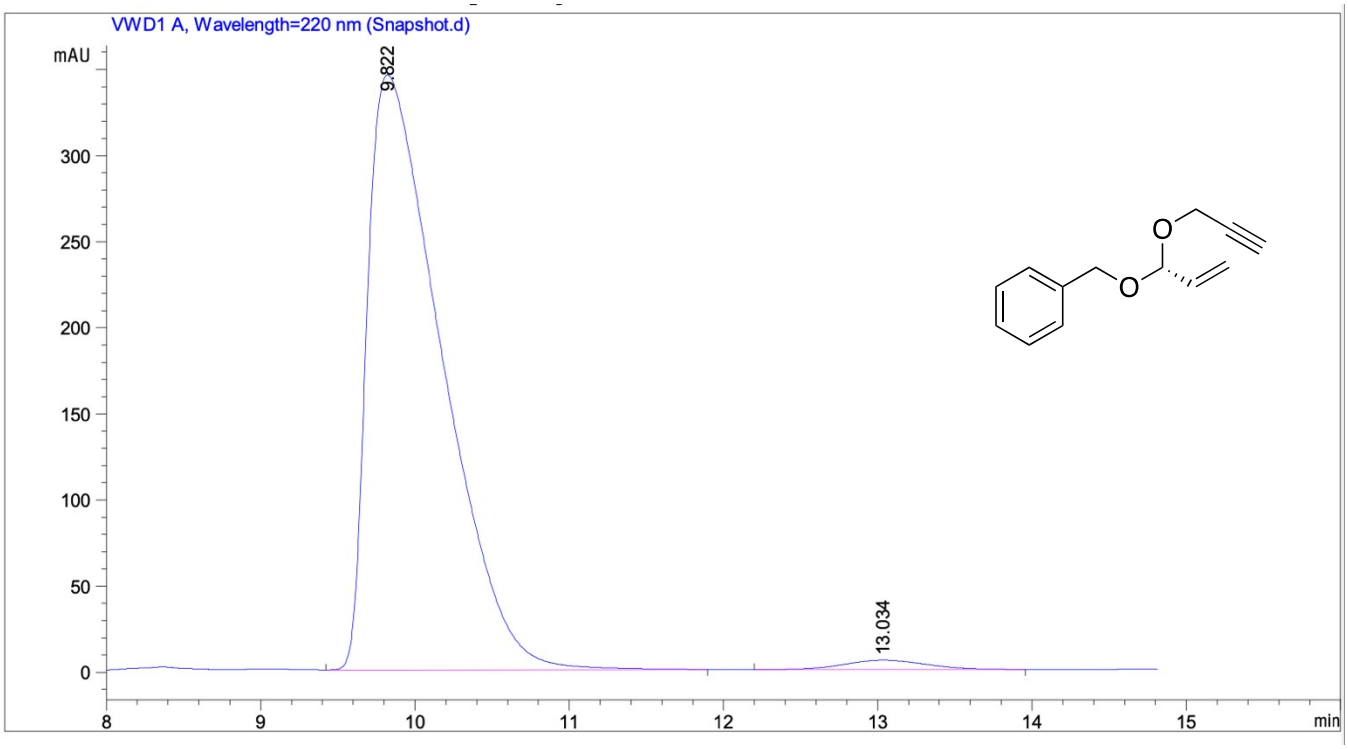
8. HPLC chromatograms

2



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.524	MM	0.7662	2.57232e4	559.50867	49.0922
2	12.425	MM	0.8661	2.66746e4	513.31543	50.9078



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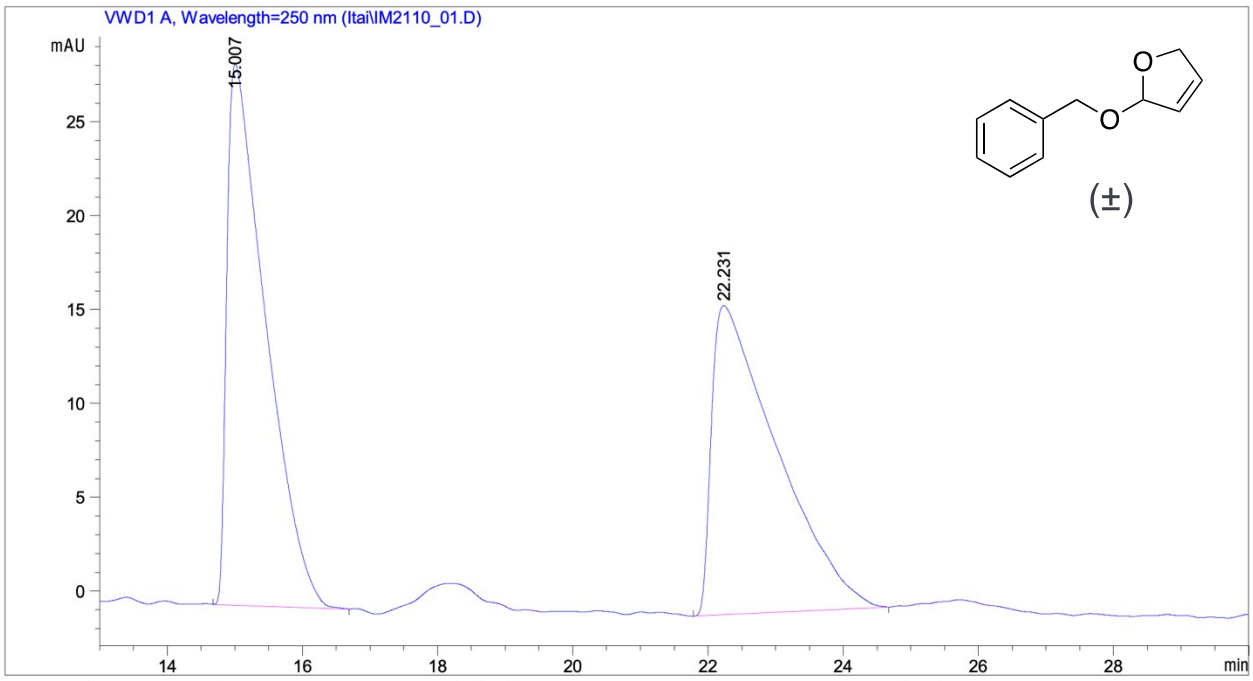
1	9.822	BB	0.5115	1.14776e4	345.55566	98.2894
2	13.034	BB	0.5685	199.75226	5.40039	1.7106

SI-1



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.007	BB	0.5610	1146.12085	28.81851	50.9006
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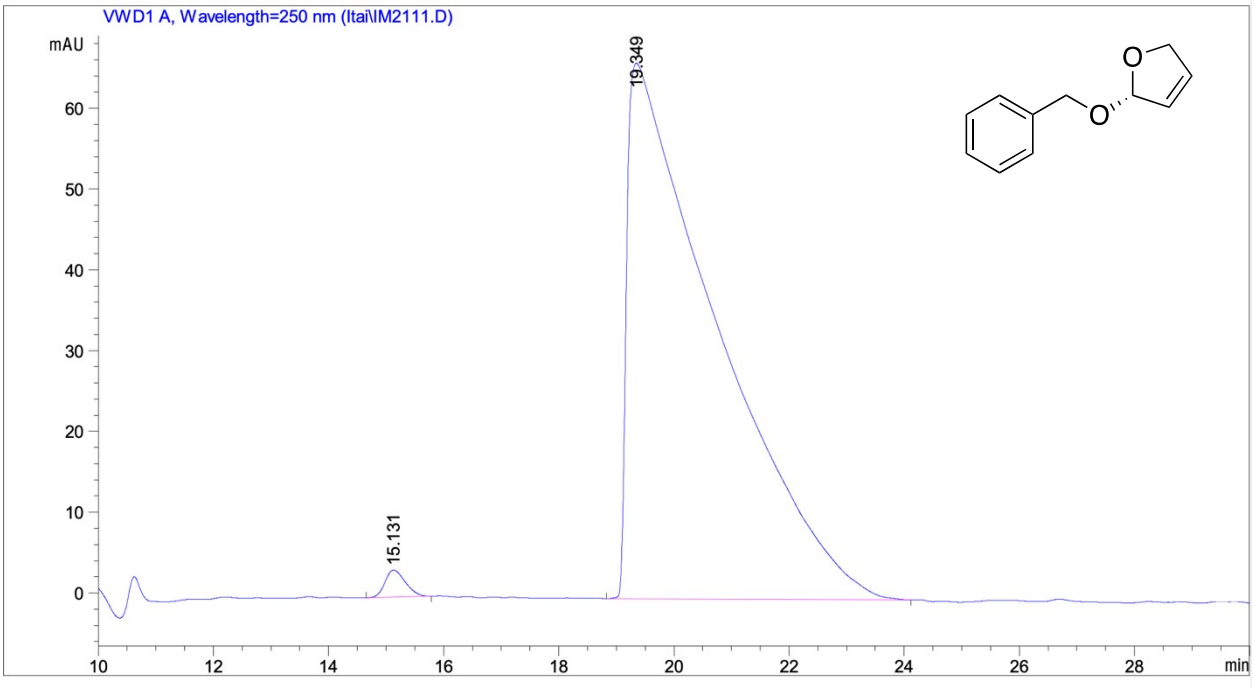
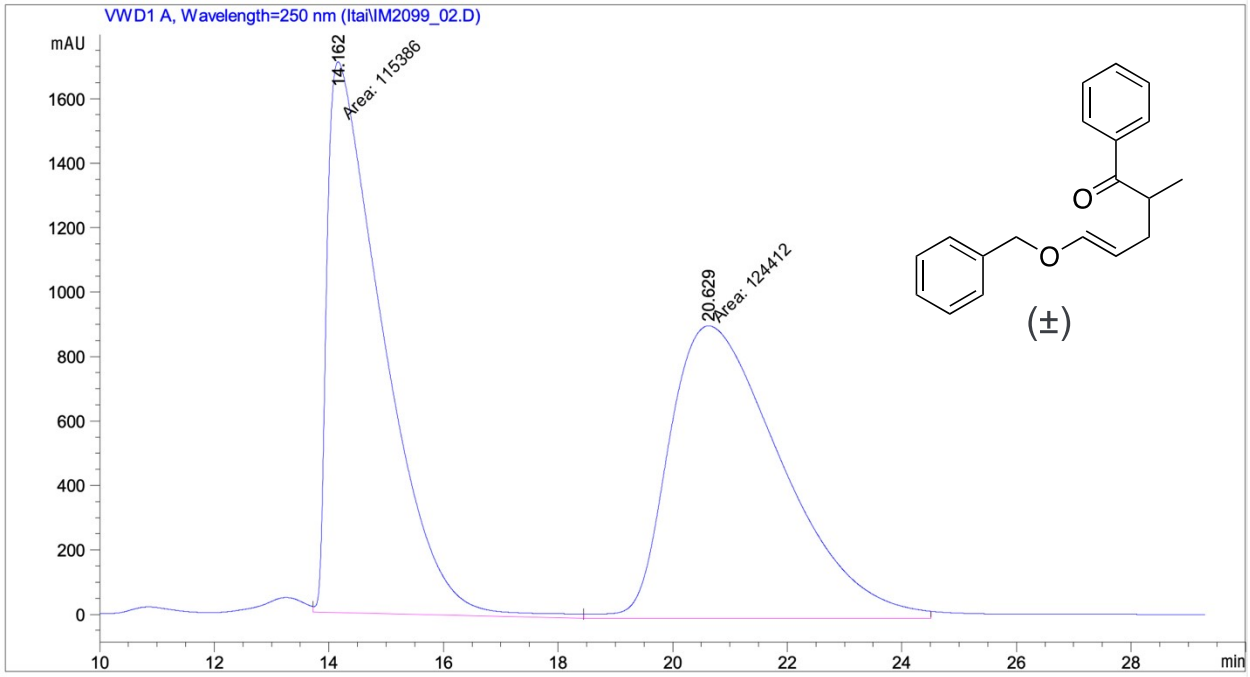
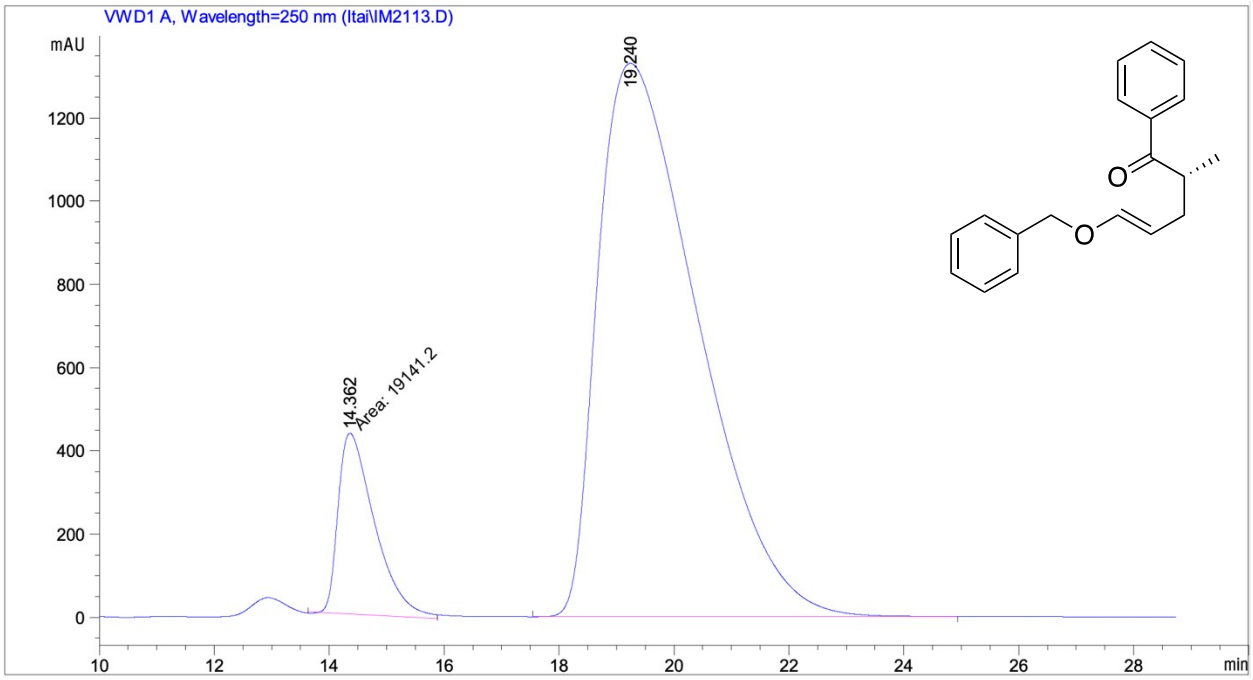


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.131	BB	0.3738	82.90036	3.36106	1.1429
2	19.349	BB	1.3927	7170.77246	66.30893	98.8571

25



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.162	MM	1.1252	1.15386e5	1709.13489	48.1179
2	20.629	MM	2.2845	1.24412e5	907.66797	51.8821



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1	14.362	MM	0.7343	1.91412e4	434.45169	10.6644
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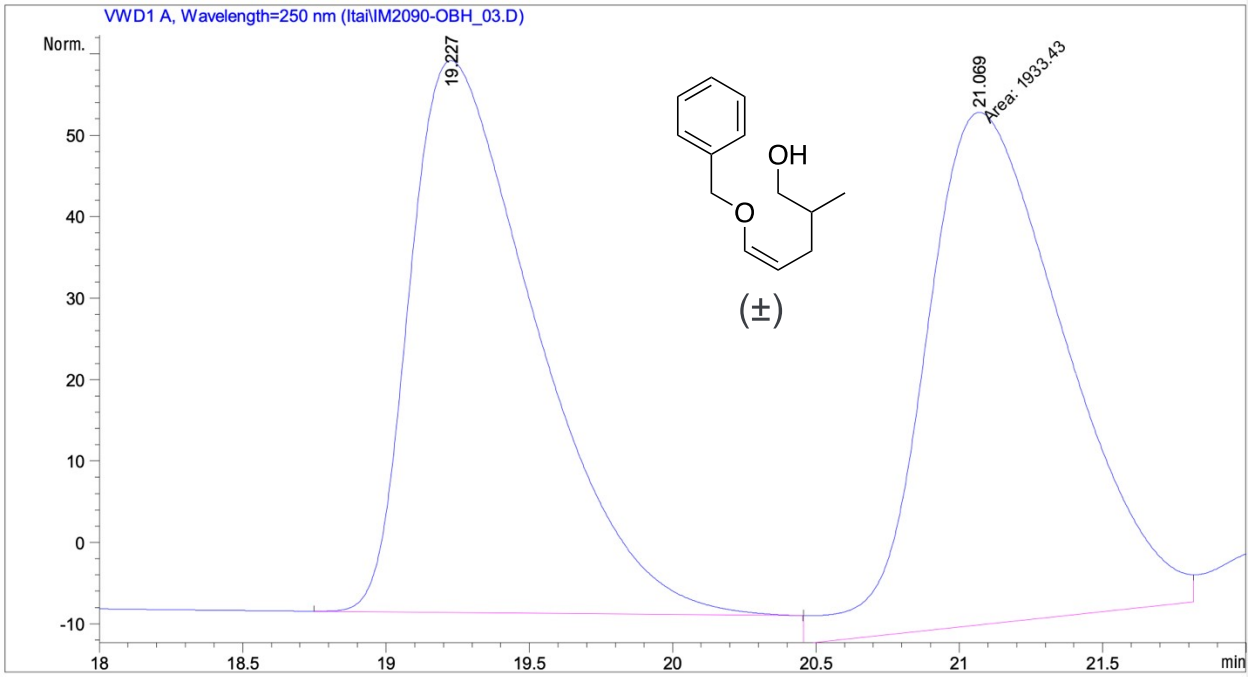
23



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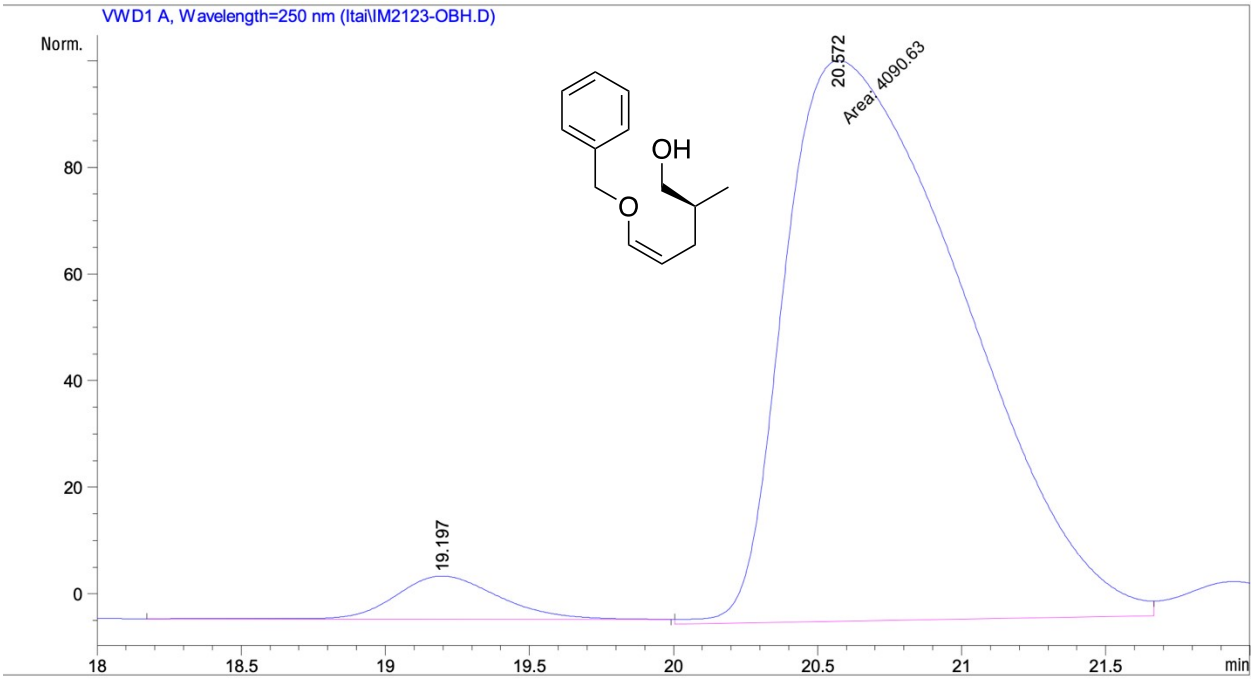

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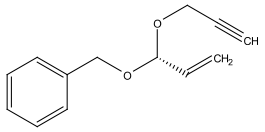
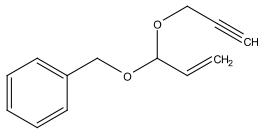
1	19.197	VB R	0.3801	179.58498	7.27345	4.2055
2	20.572	MM	0.7177	4090.62915	94.98782	95.7945

9. NMR spectra



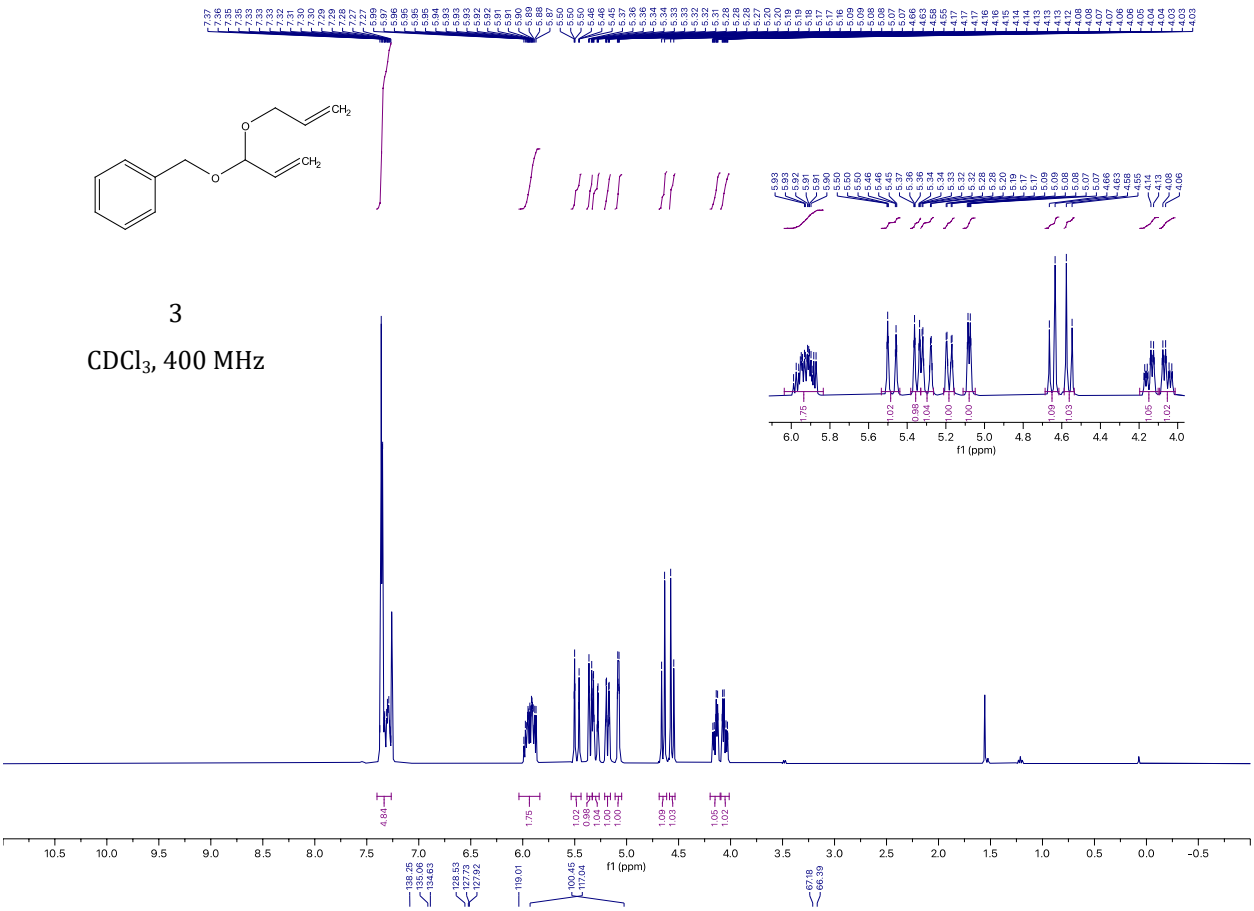
2

$CDCl_3$, 400 MHz



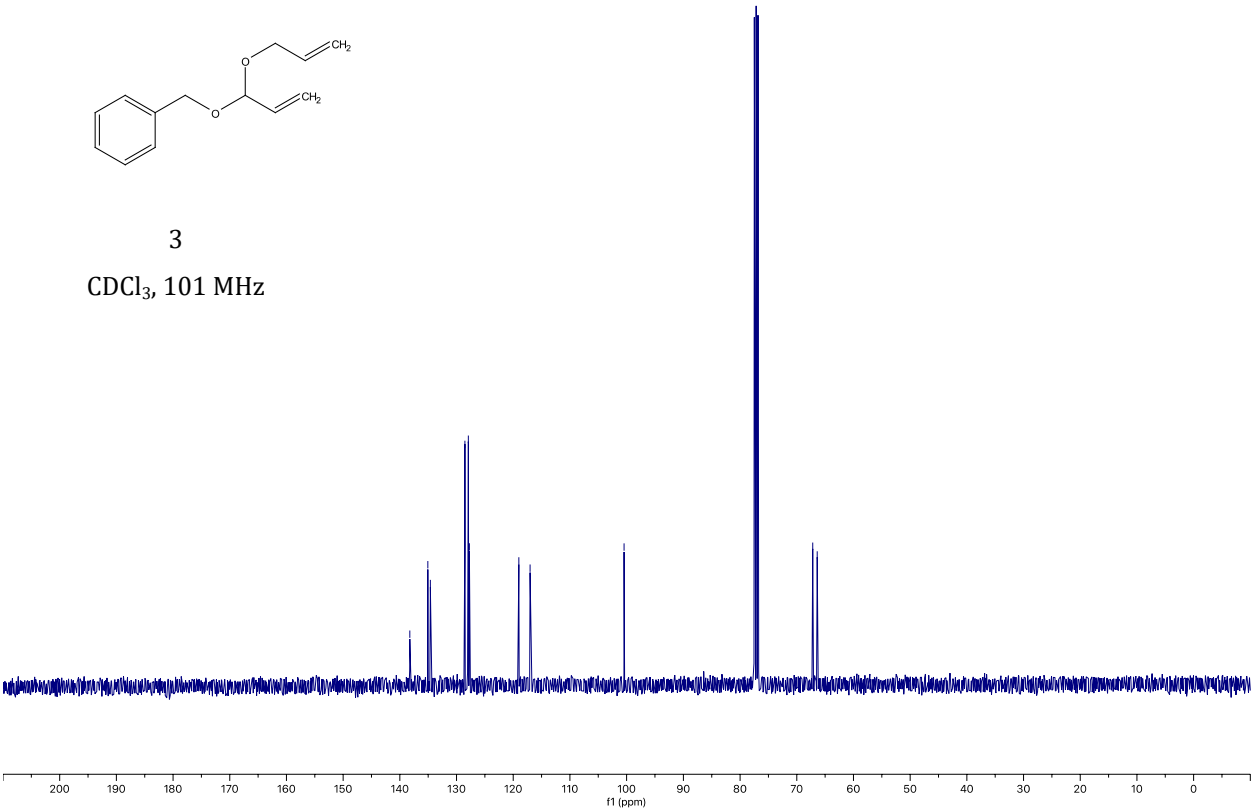
2

$CDCl_3$, 101 MHz



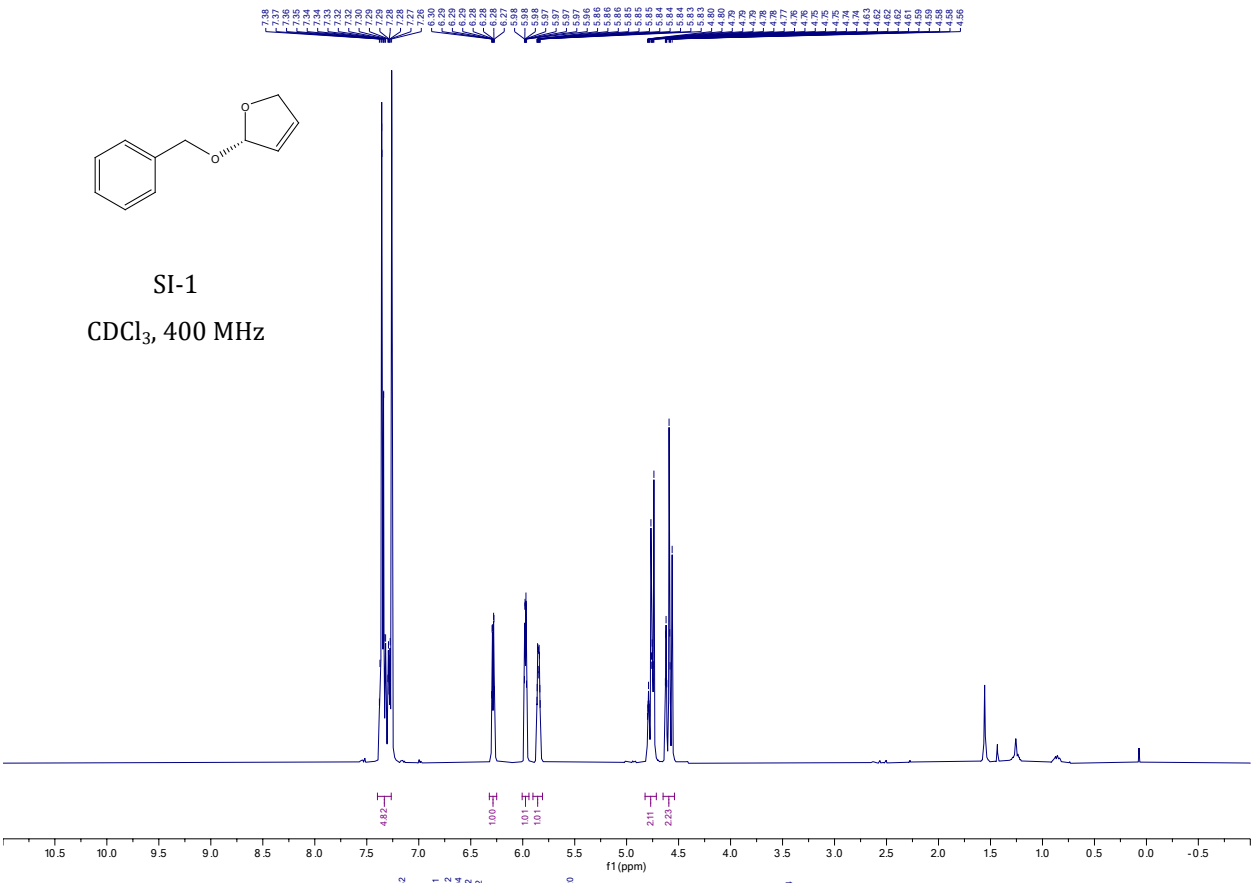
3

$CDCl_3$, 400 MHz



3

$CDCl_3$, 101 MHz



SI-1

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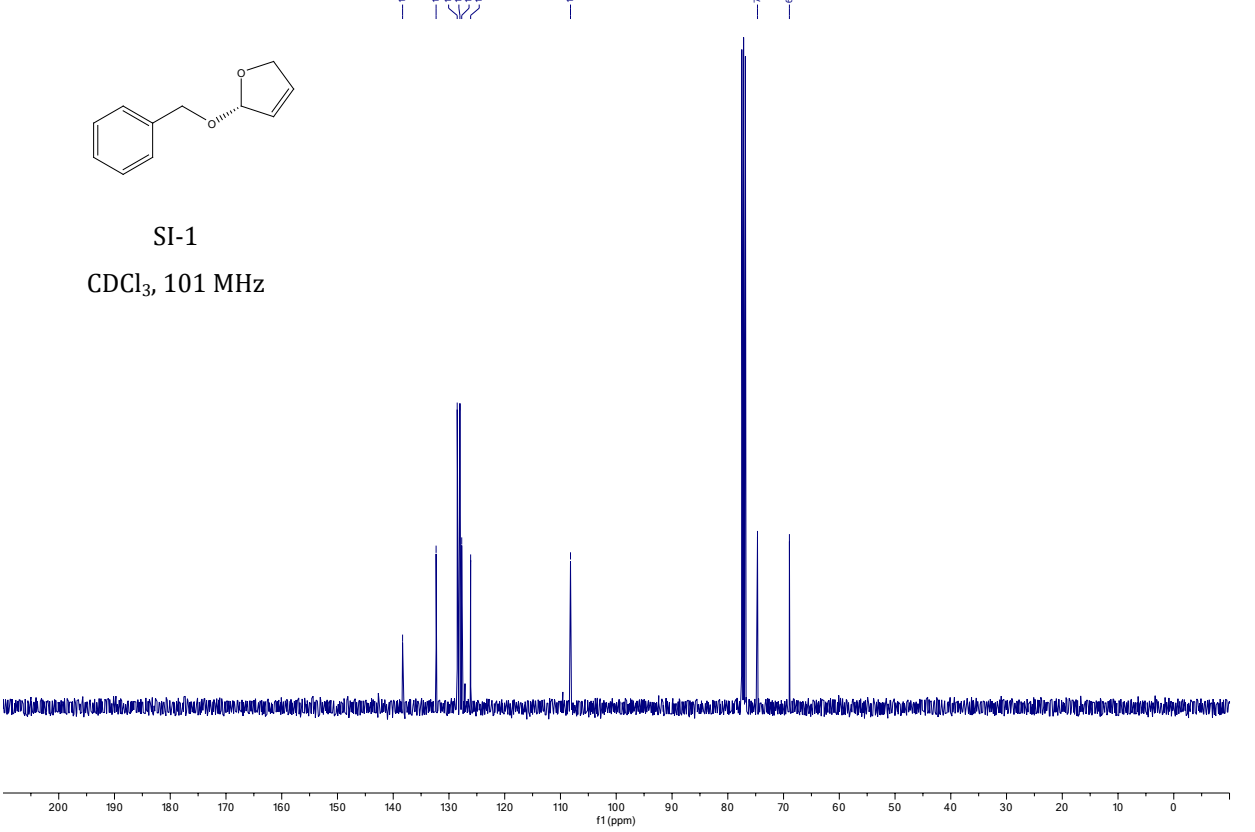

SI-1

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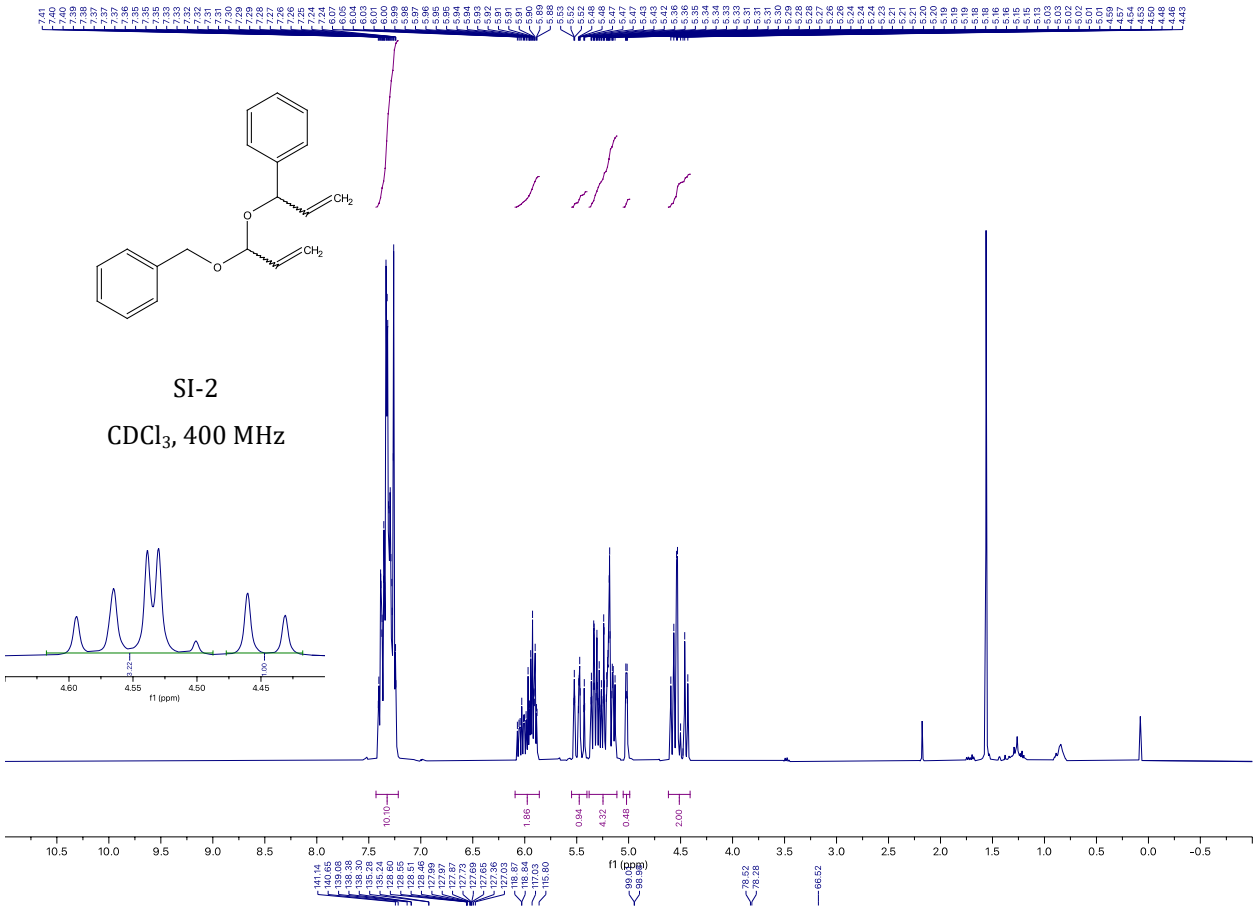

SI-2

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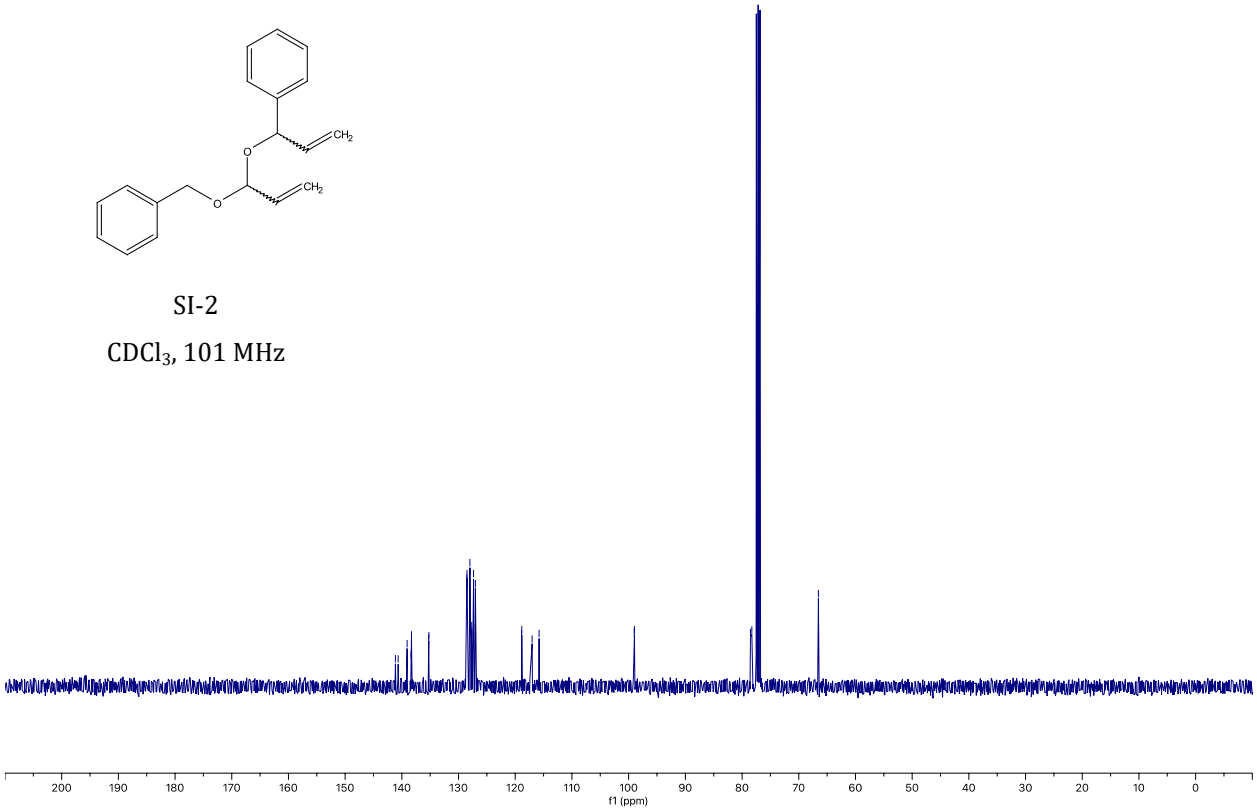

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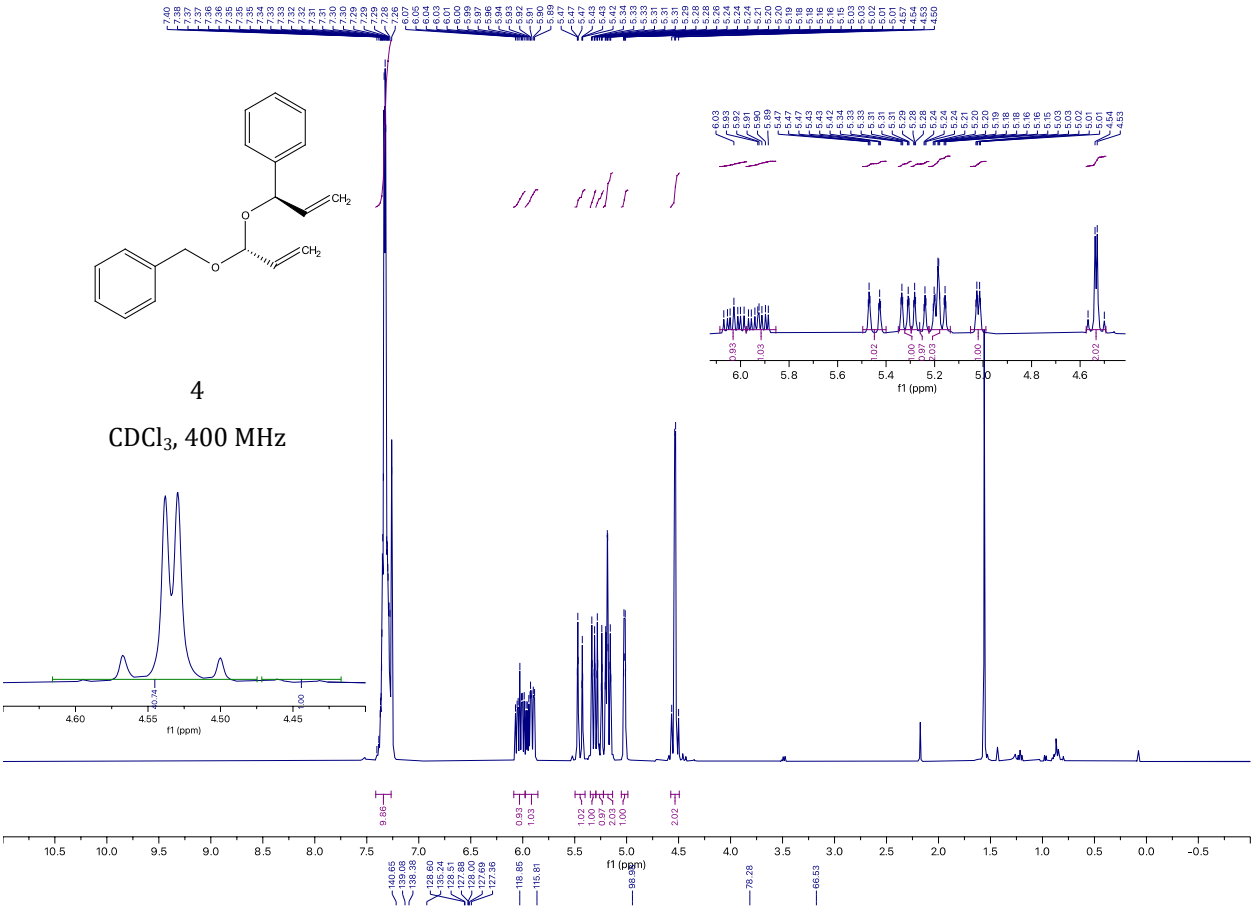

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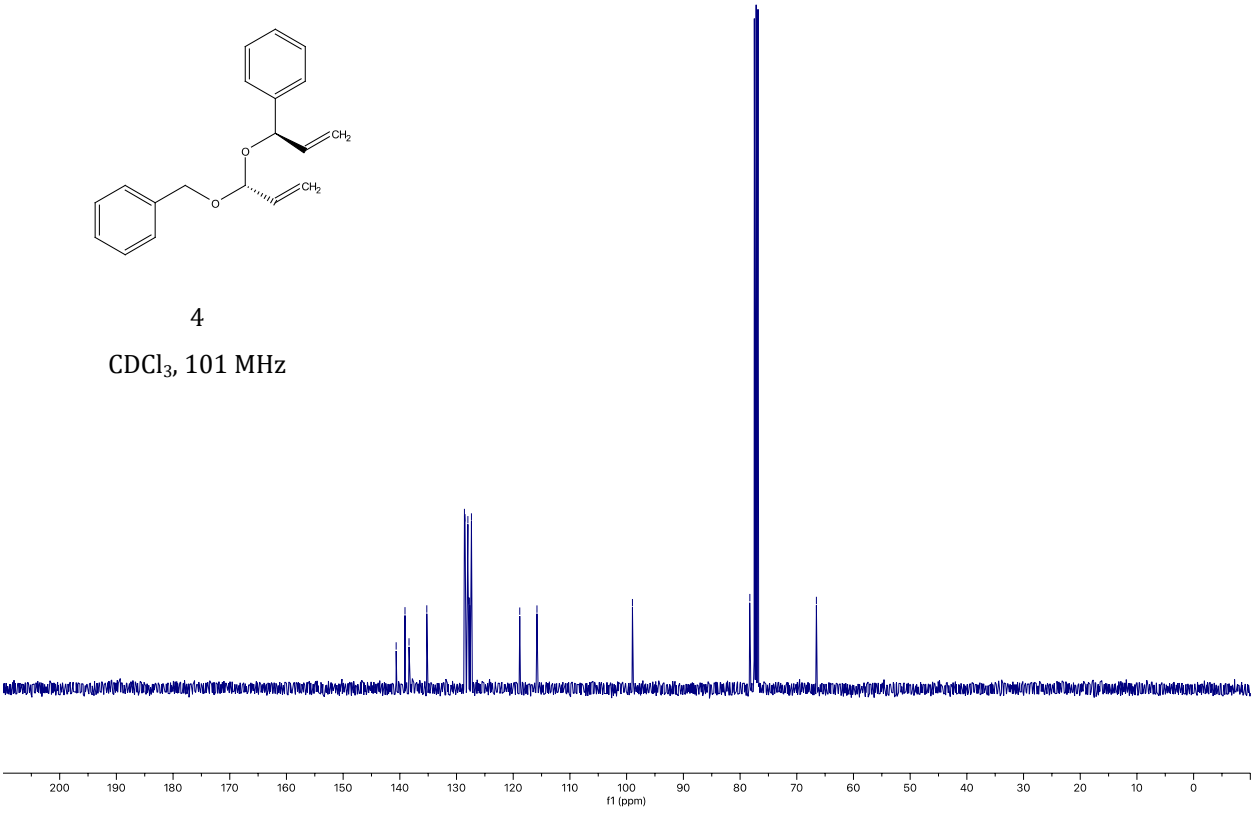

4

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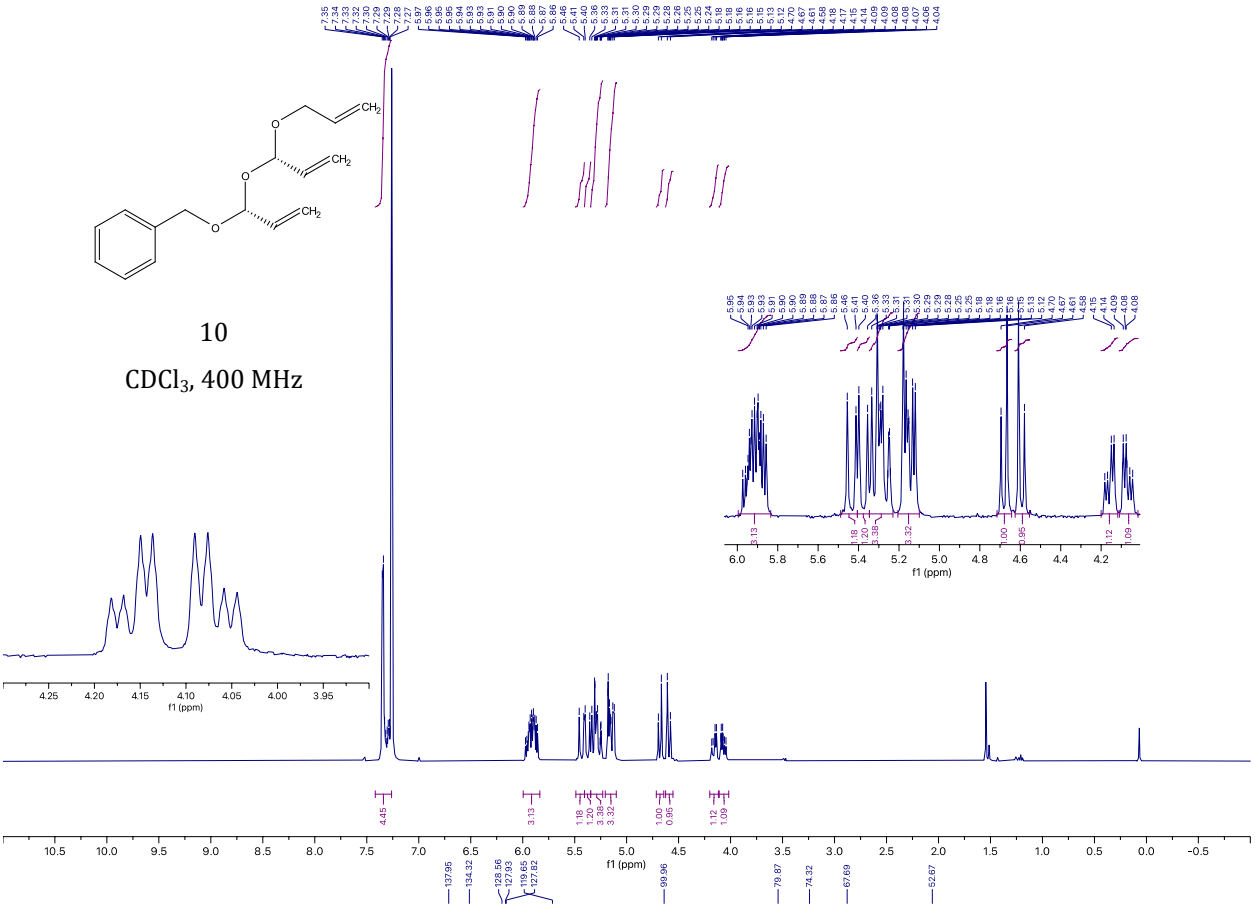

10

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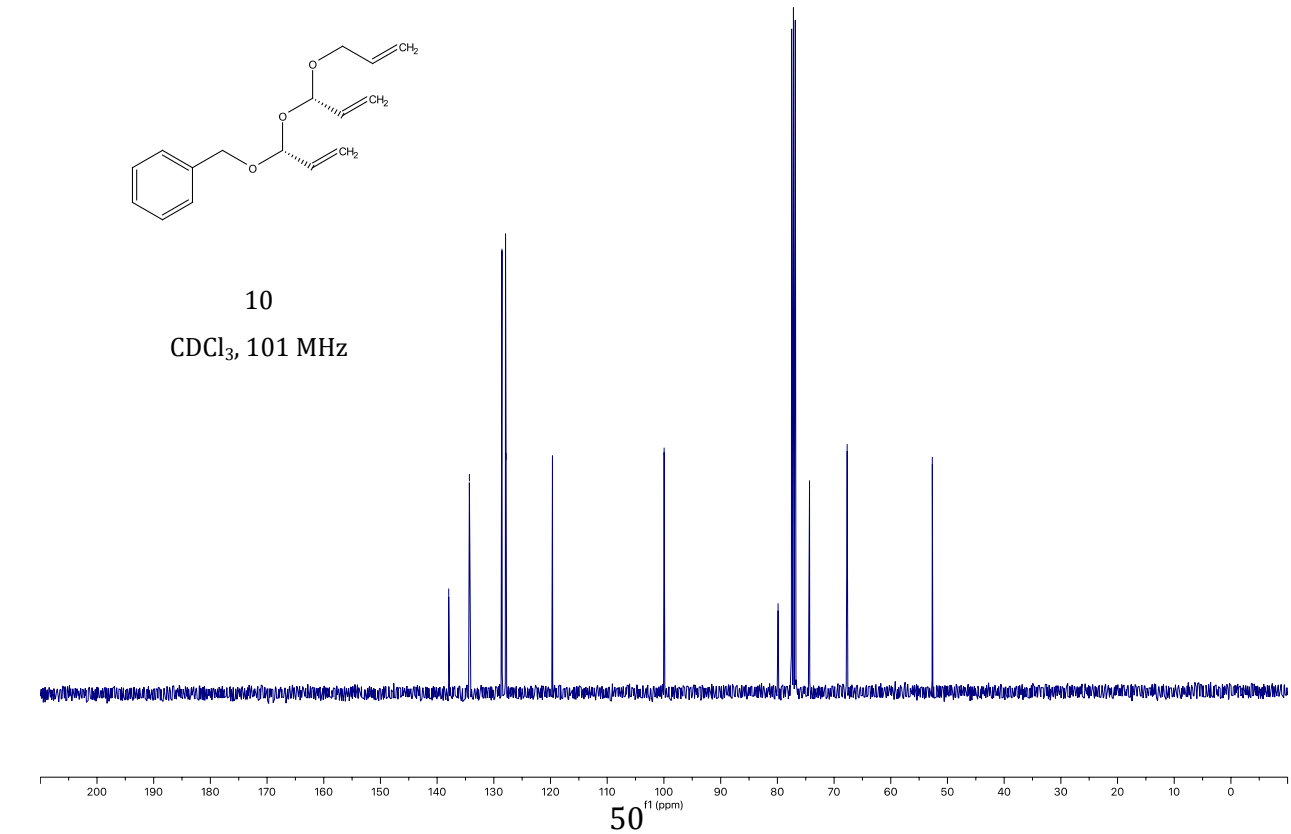

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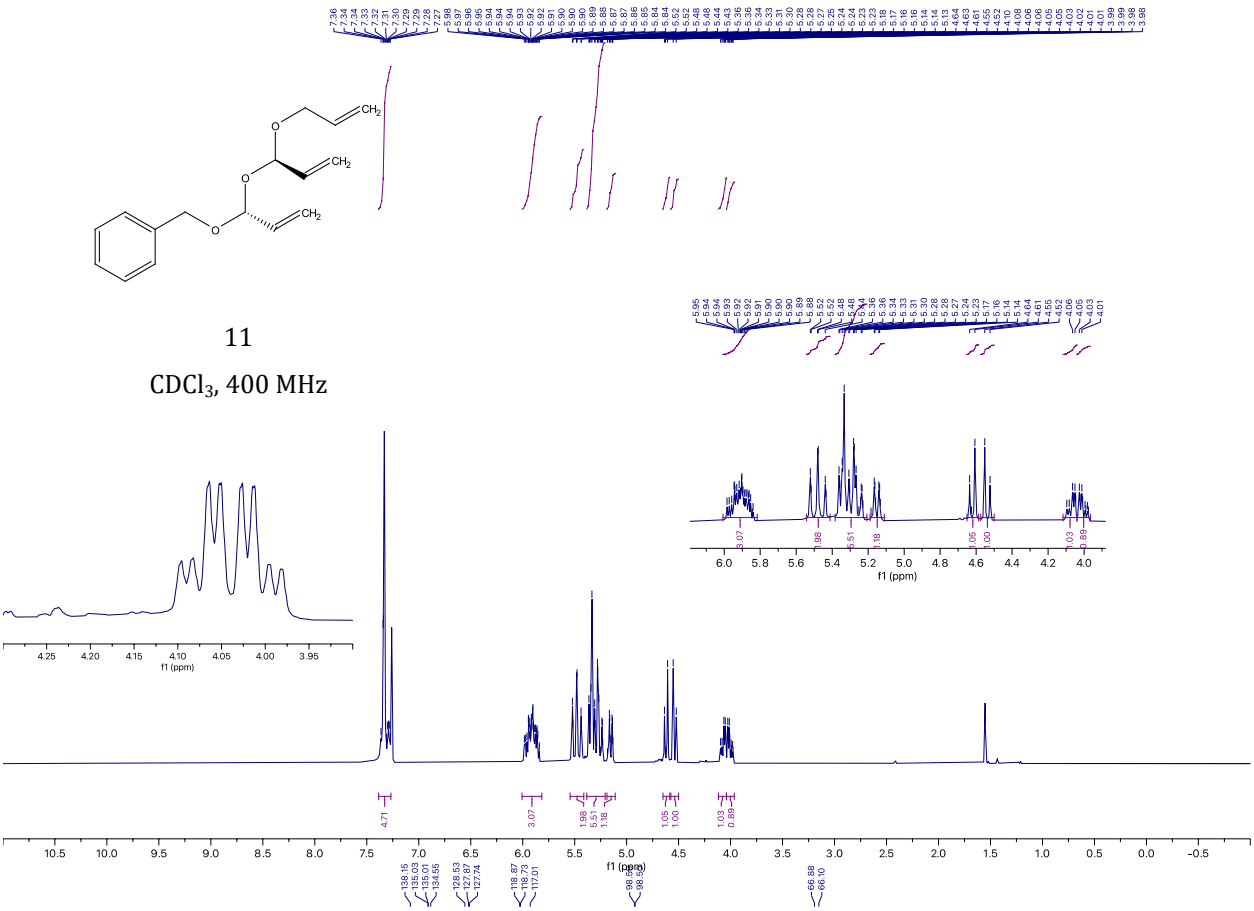

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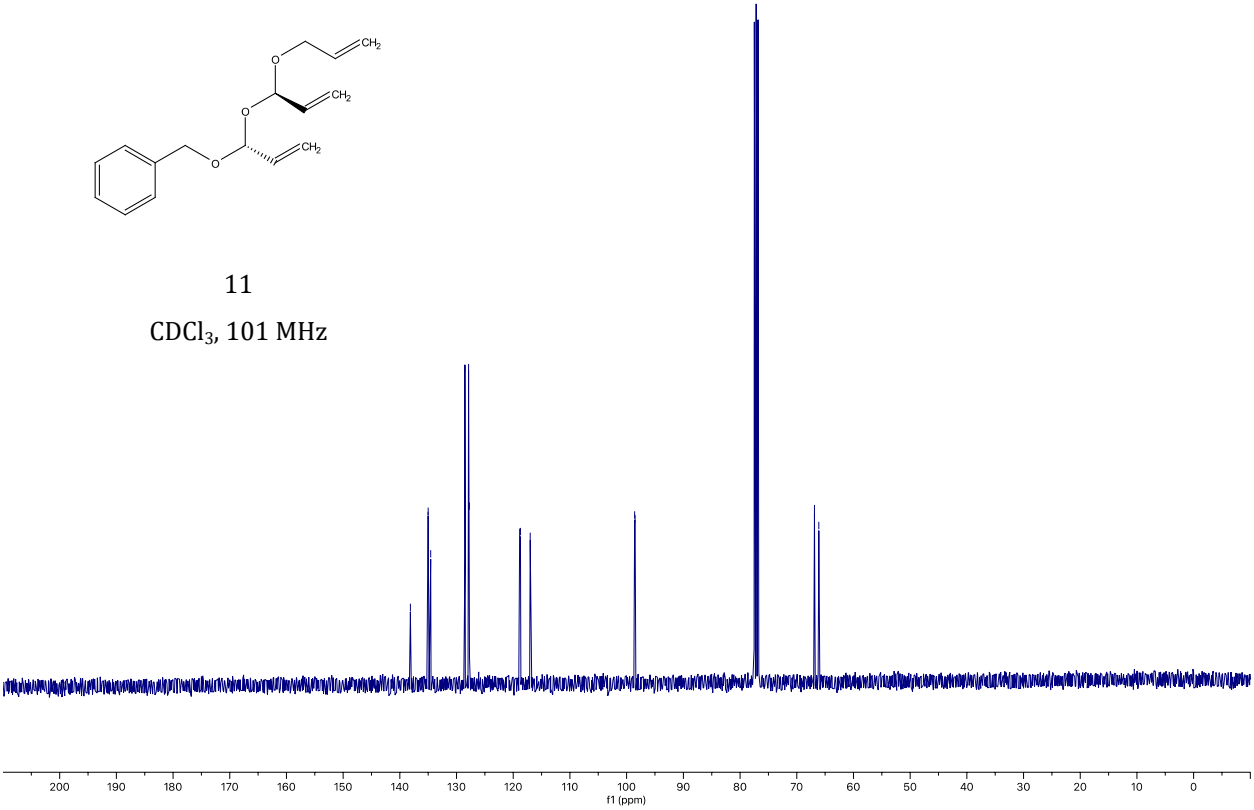

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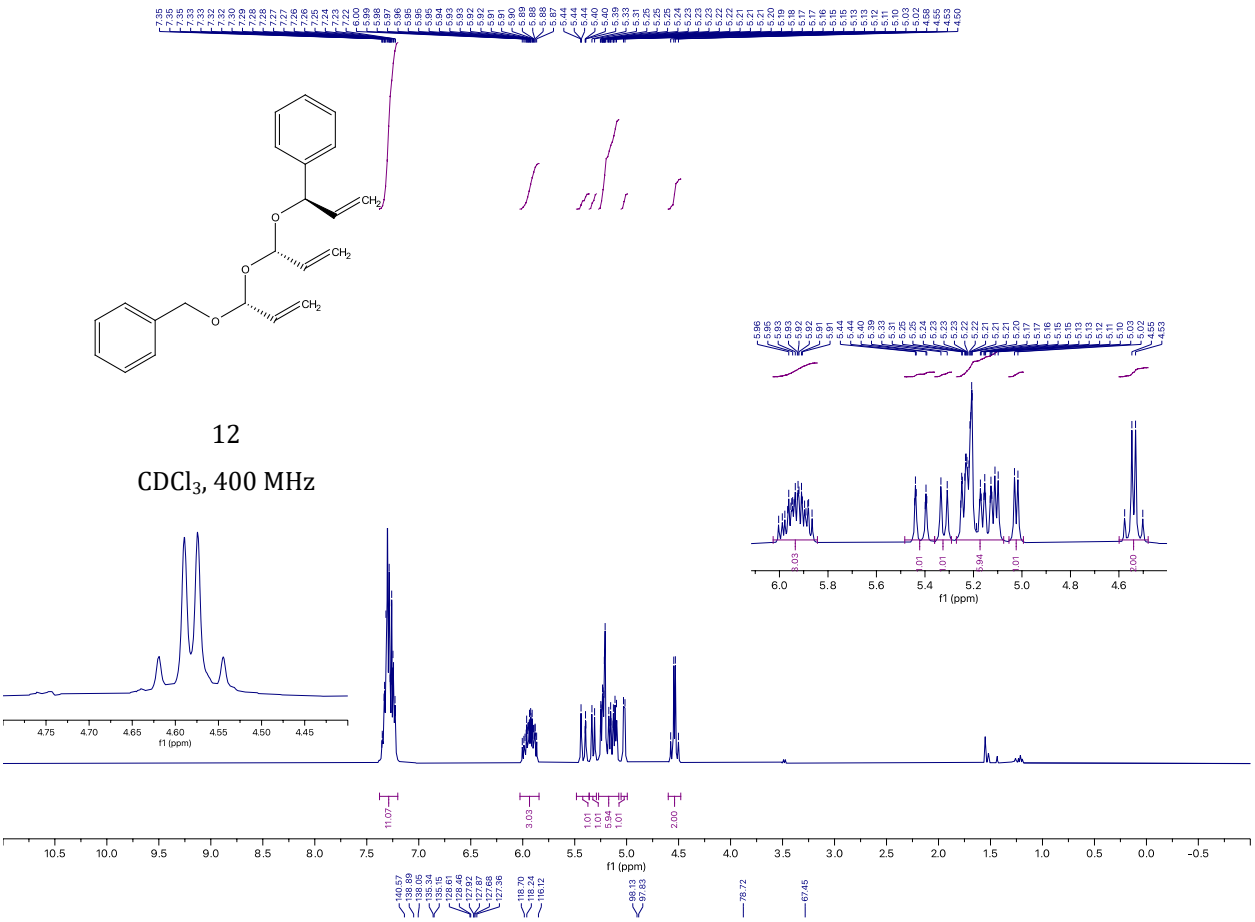

12

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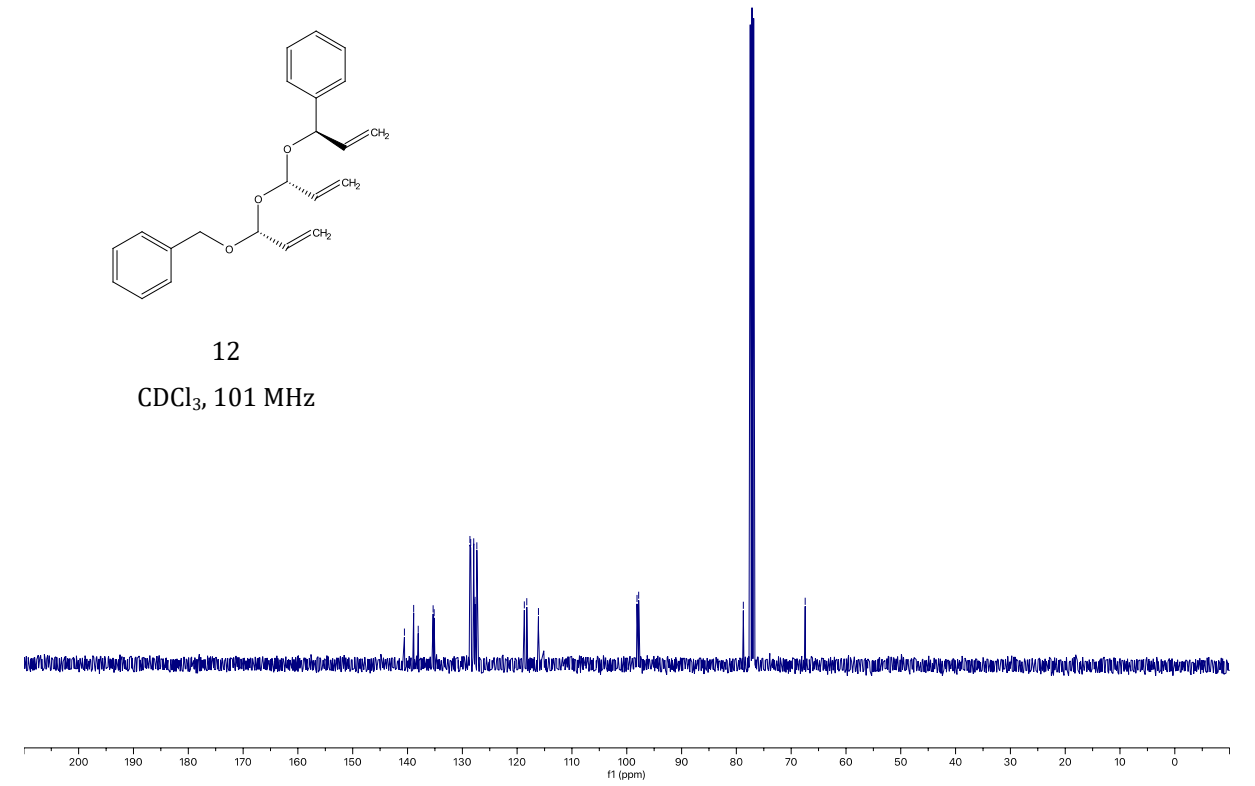

12

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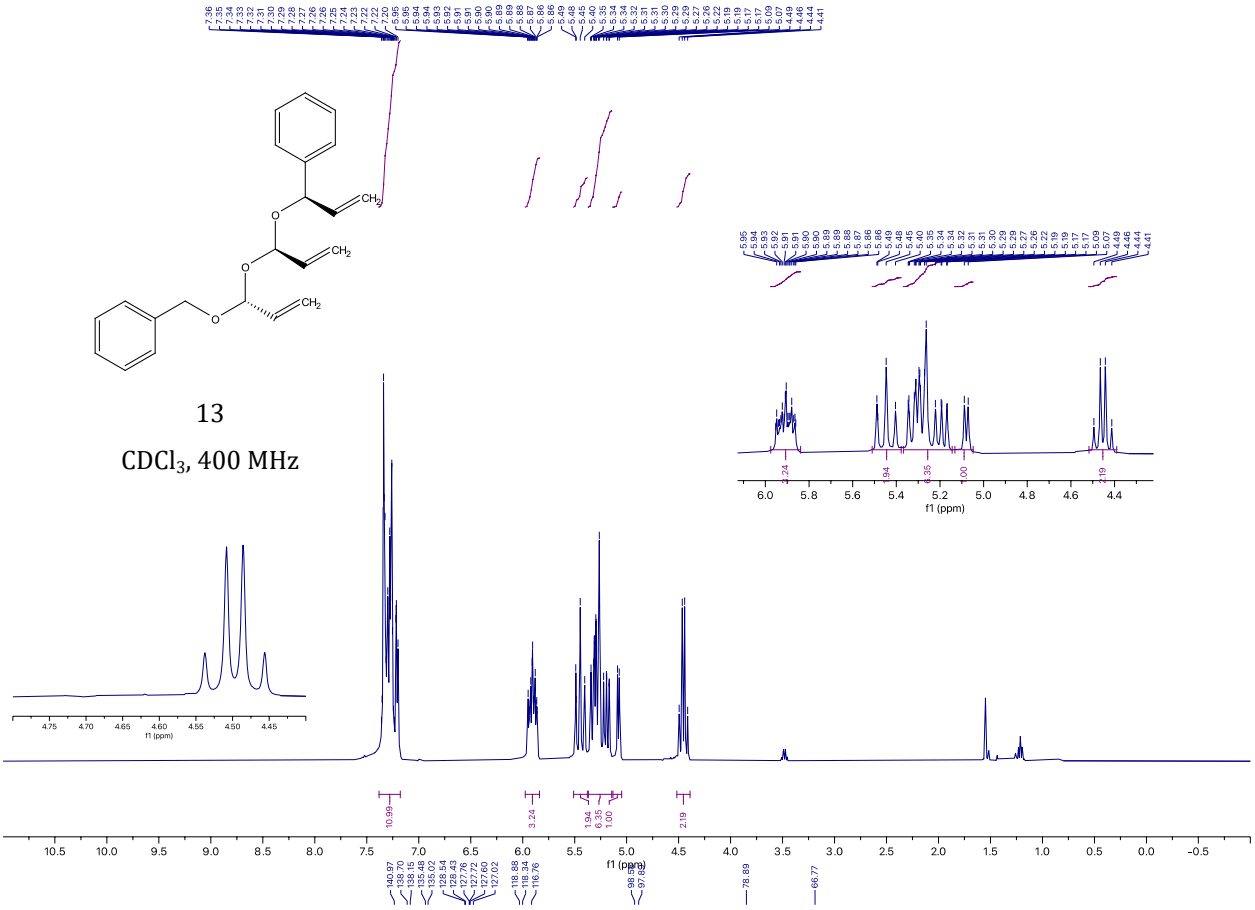

13

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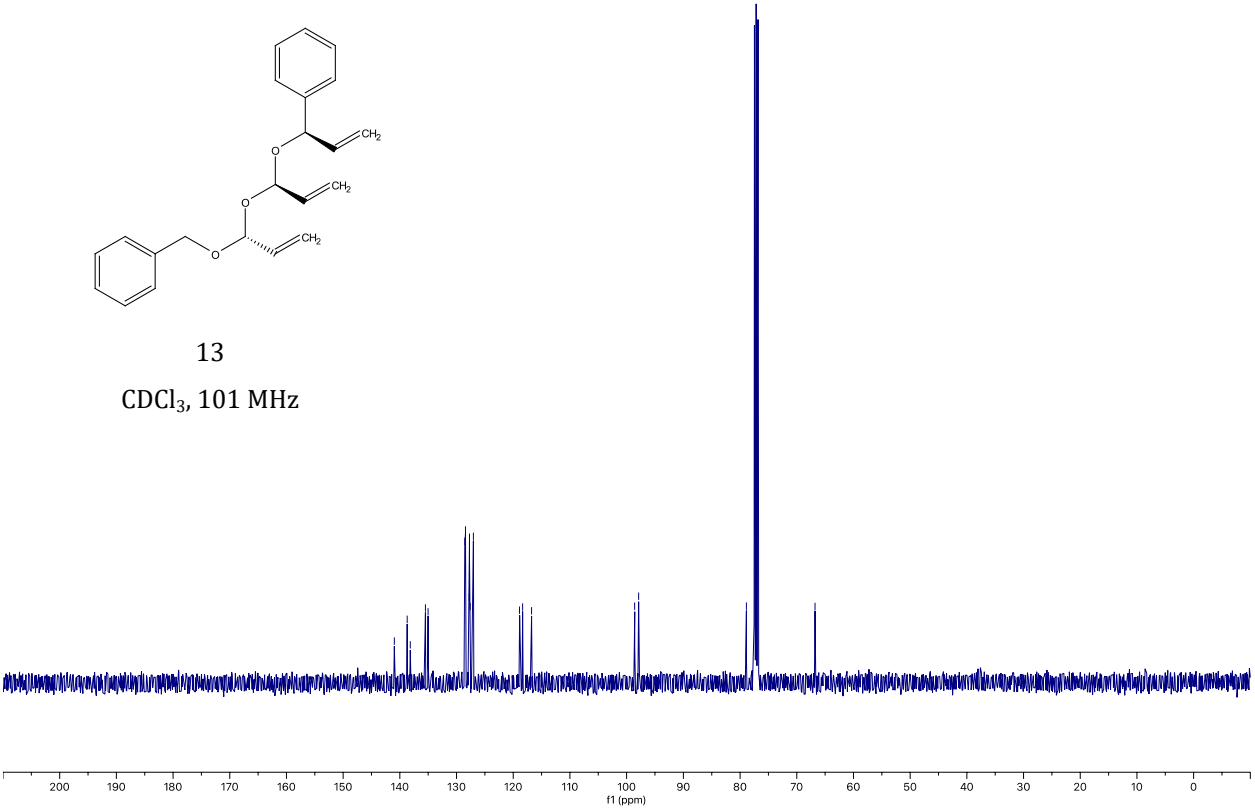

13

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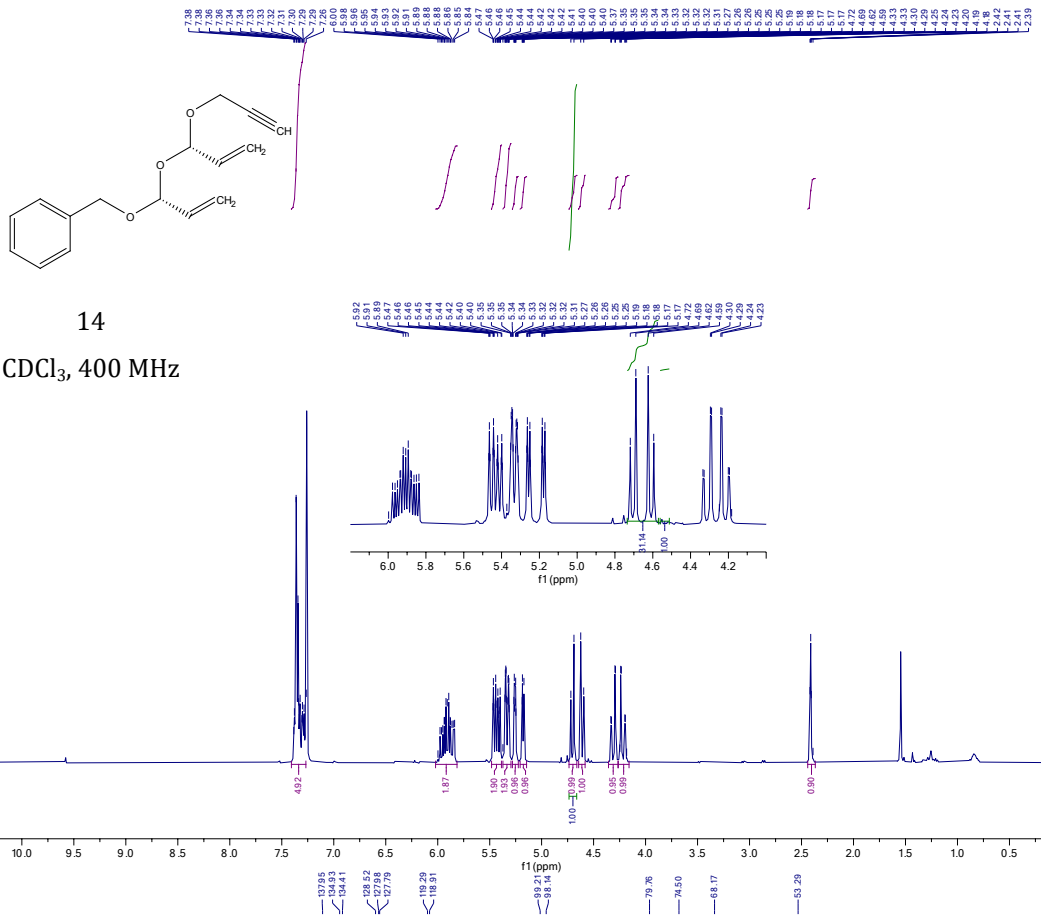
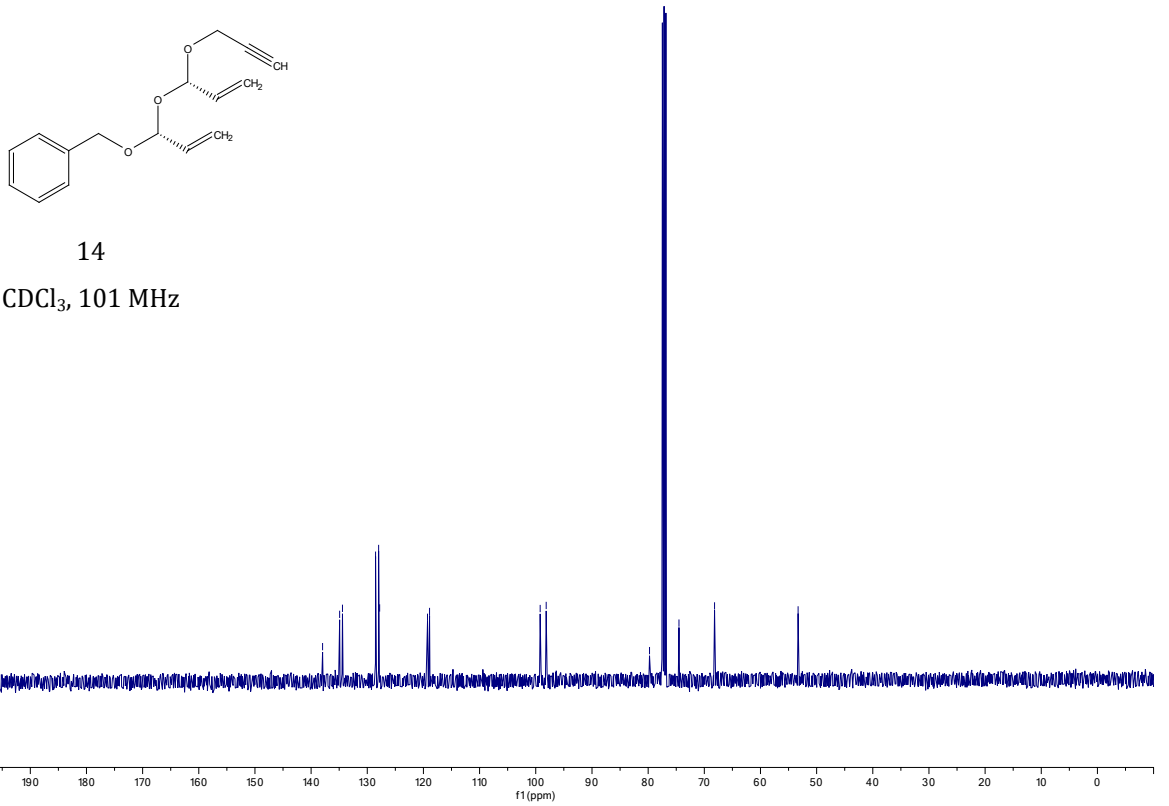


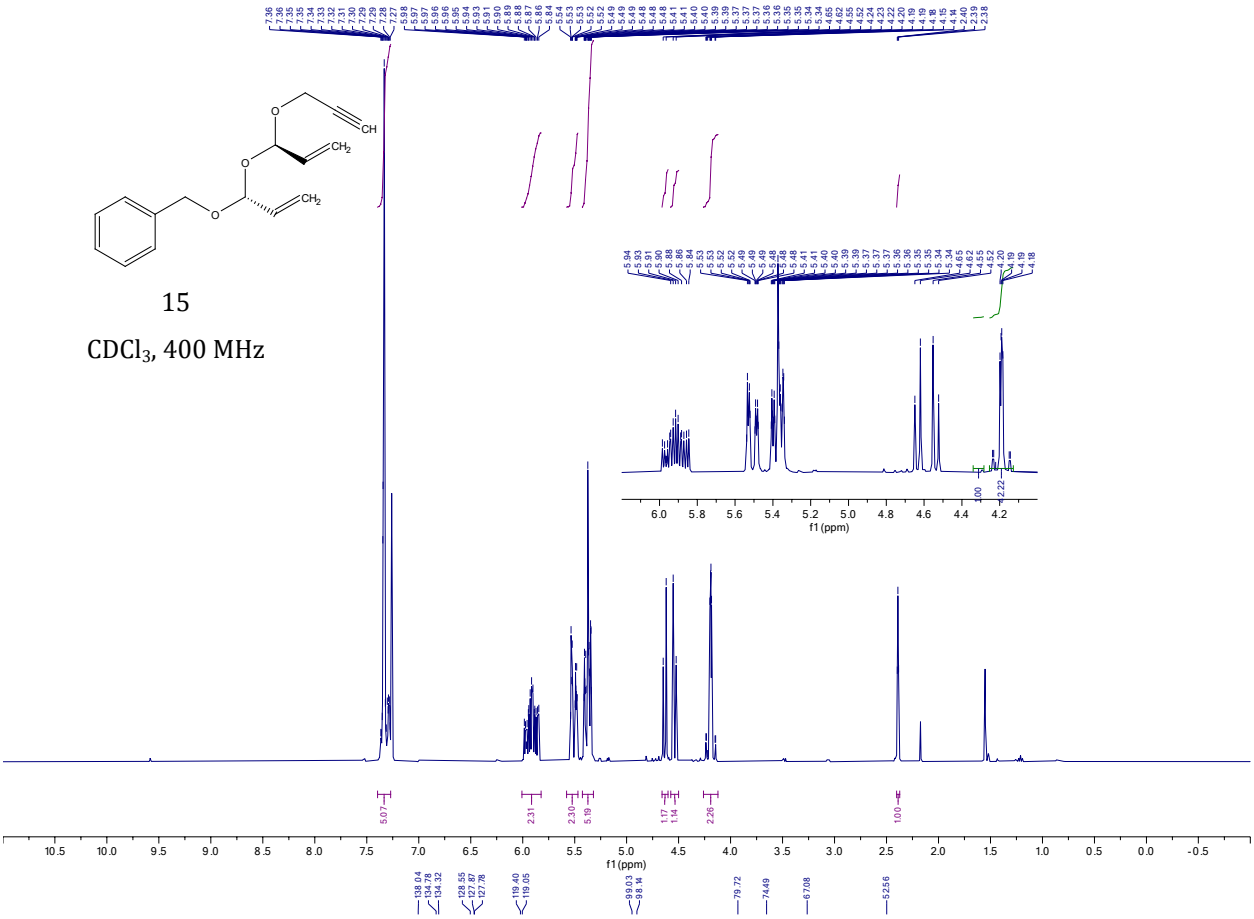
14

$CDCl_3$, 400 MHz



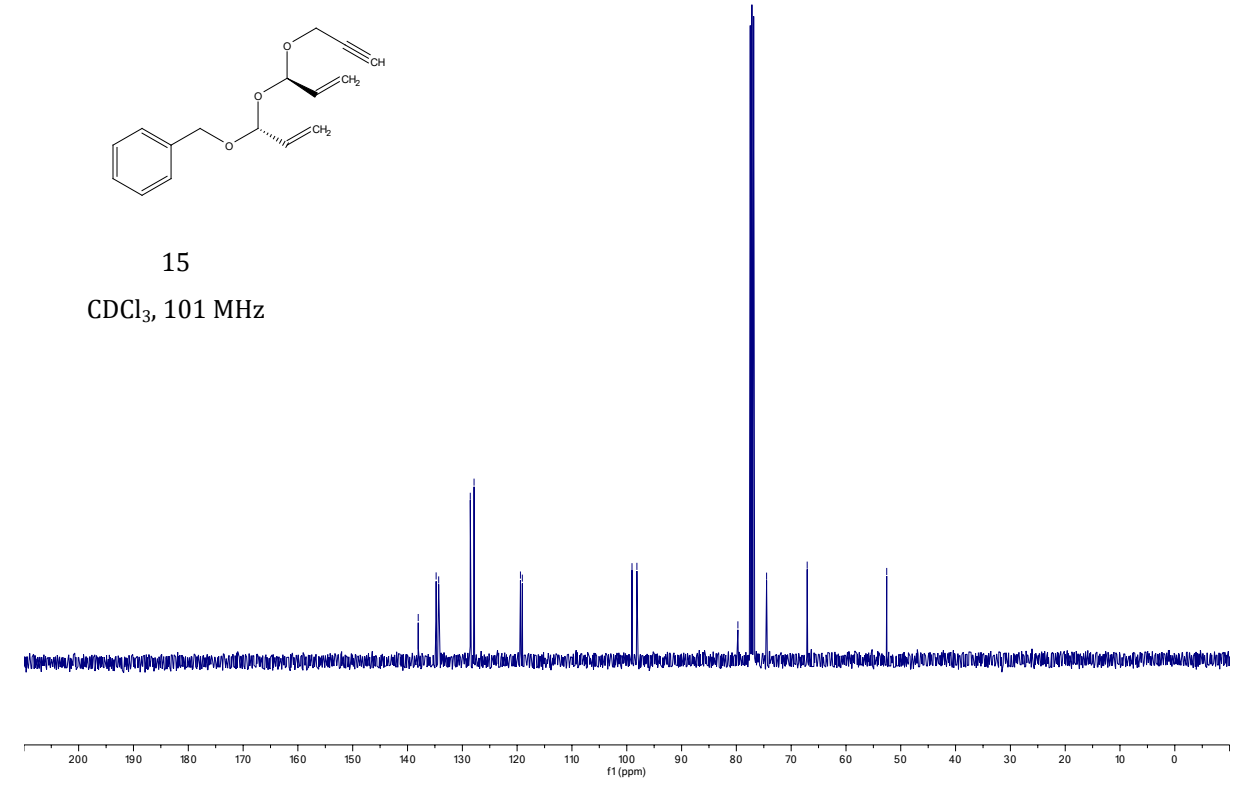
14

$CDCl_3$, 101 MHz



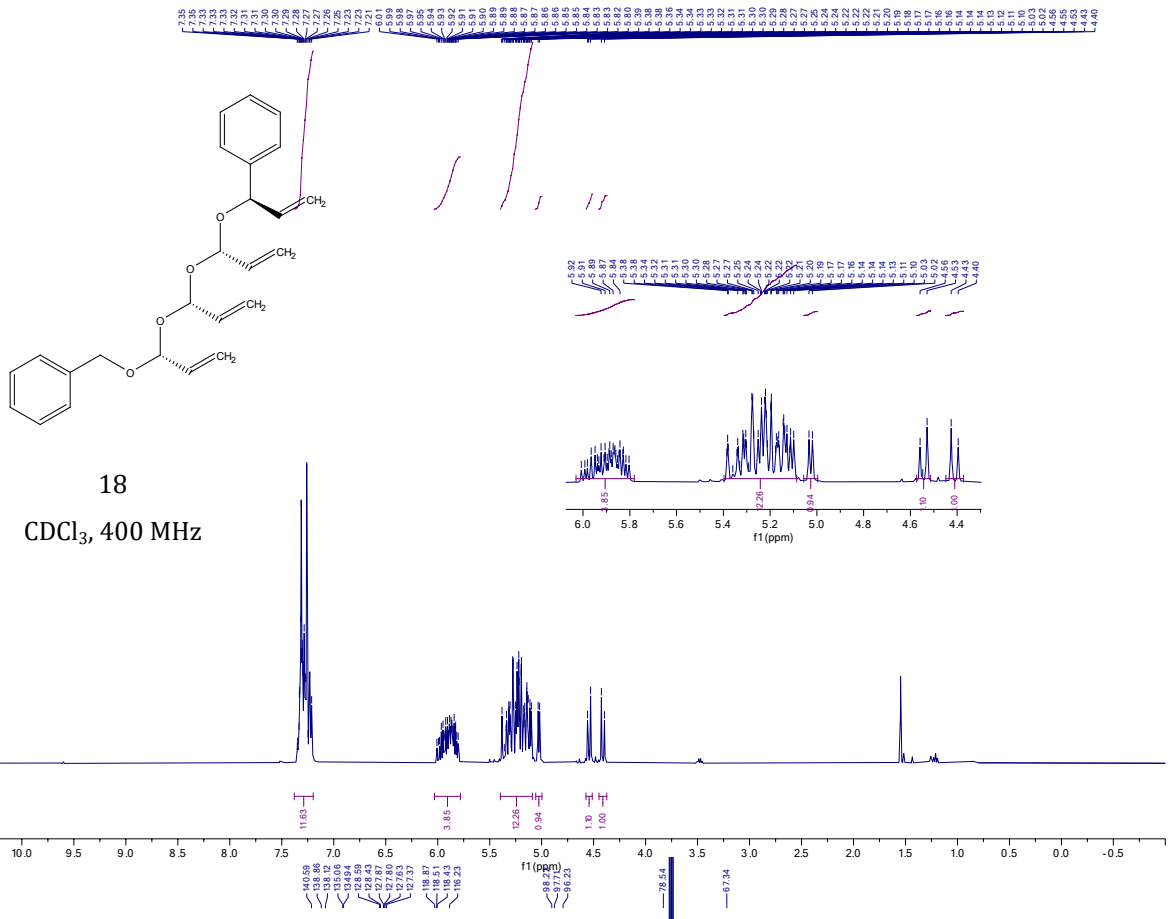
15

$CDCl_3$, 400 MHz



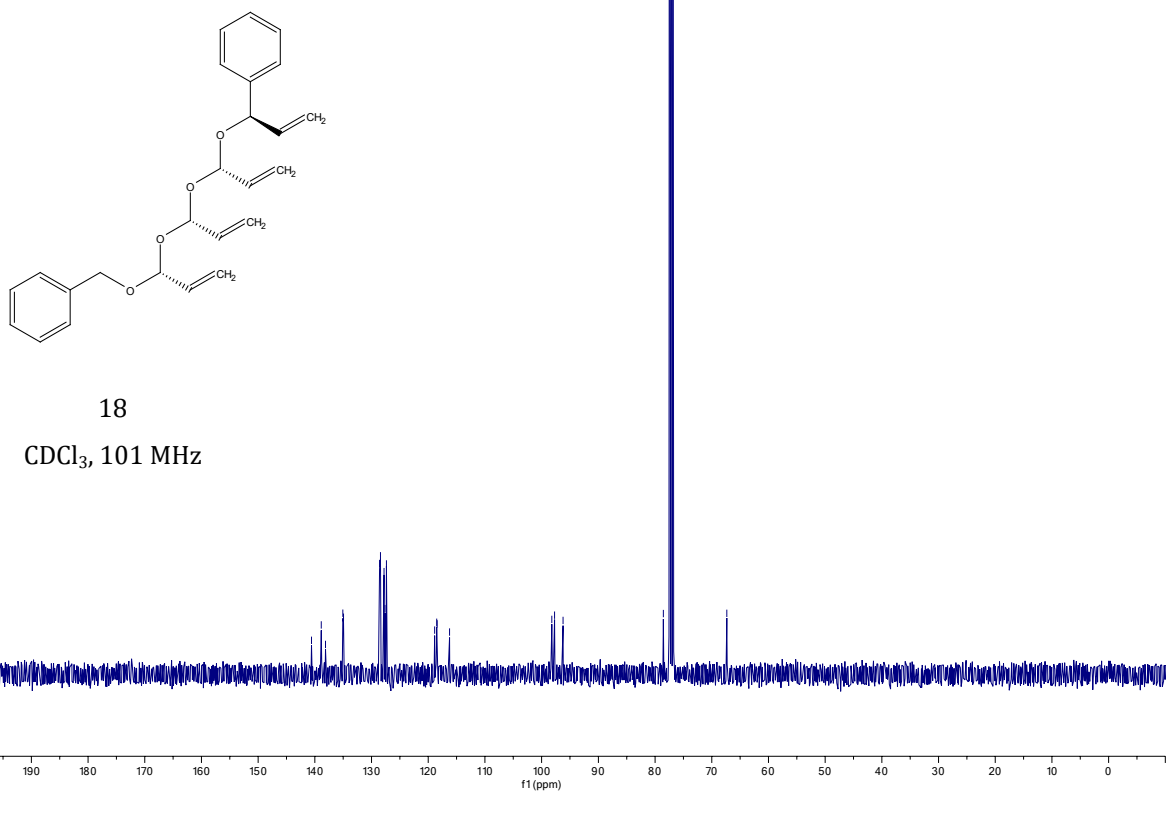
15

$CDCl_3$, 101 MHz



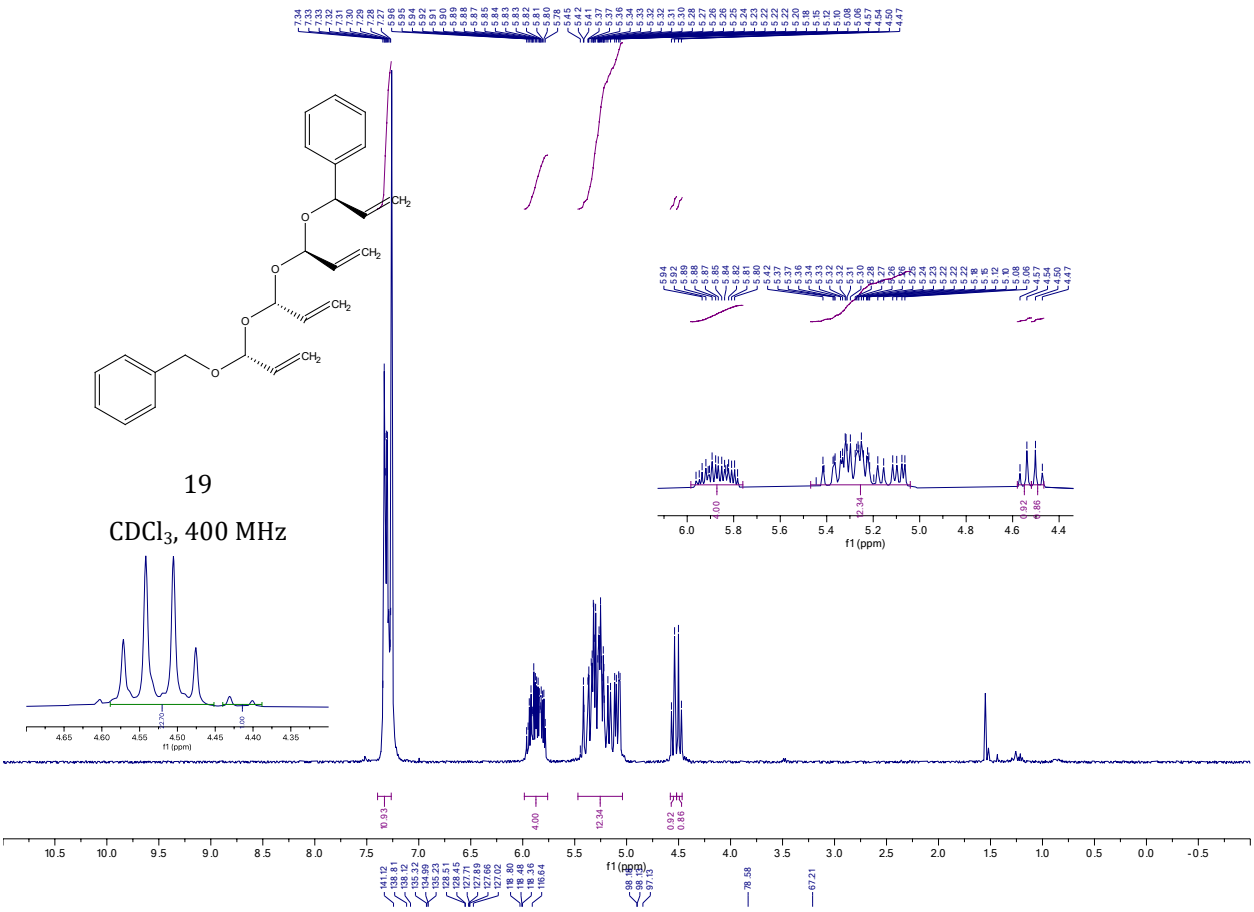
18

$CDCl_3$, 400 MHz



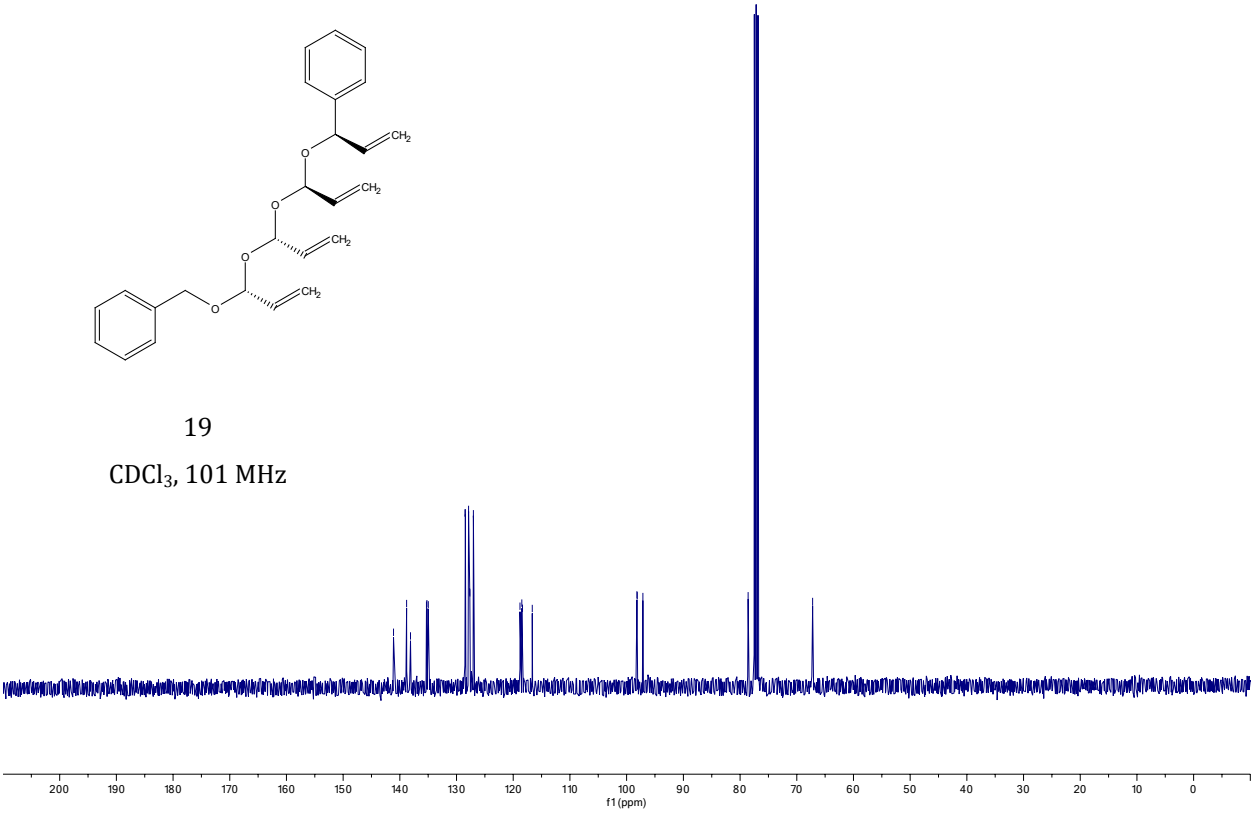
18

$CDCl_3$, 101 MHz



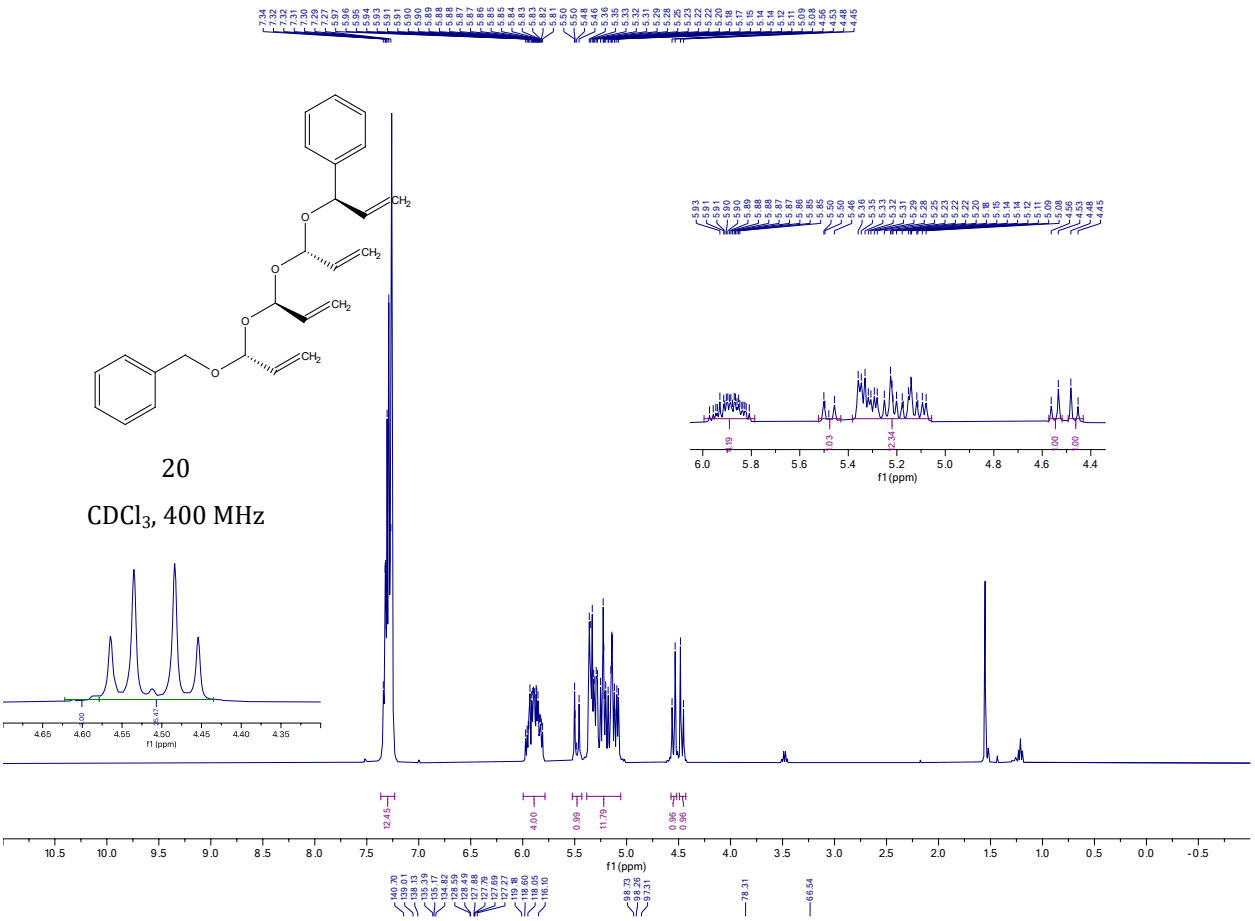
19

$CDCl_3$, 400 MHz



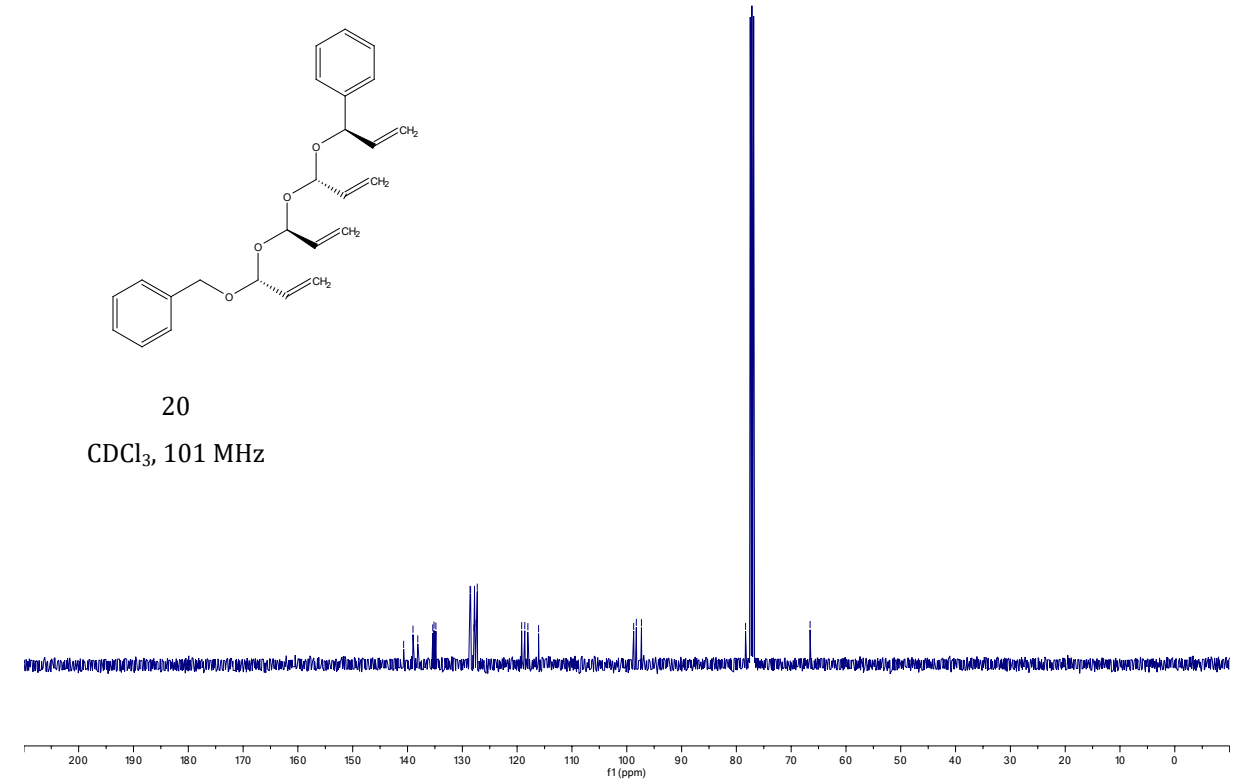
19

$CDCl_3$, 101 MHz



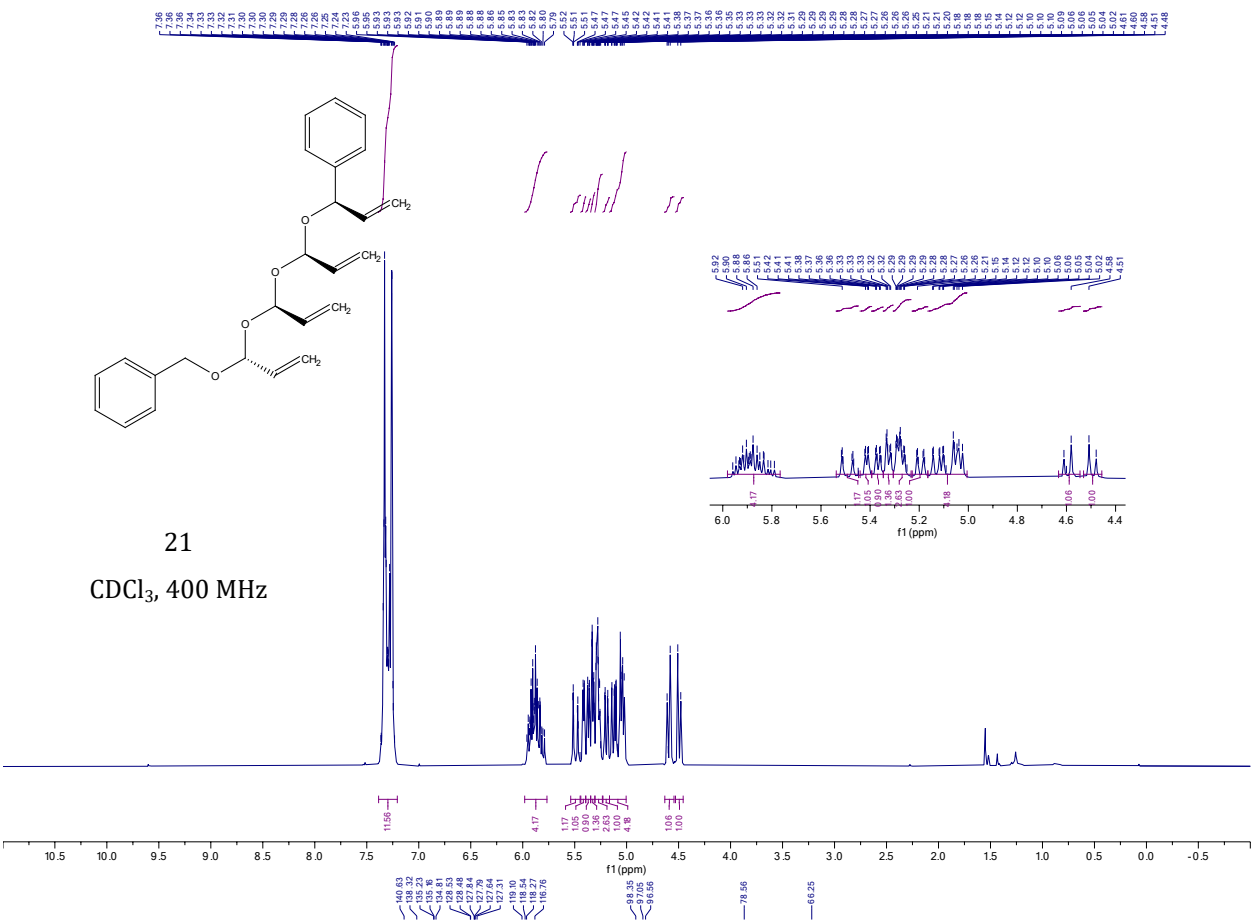
20

$CDCl_3$, 400 MHz



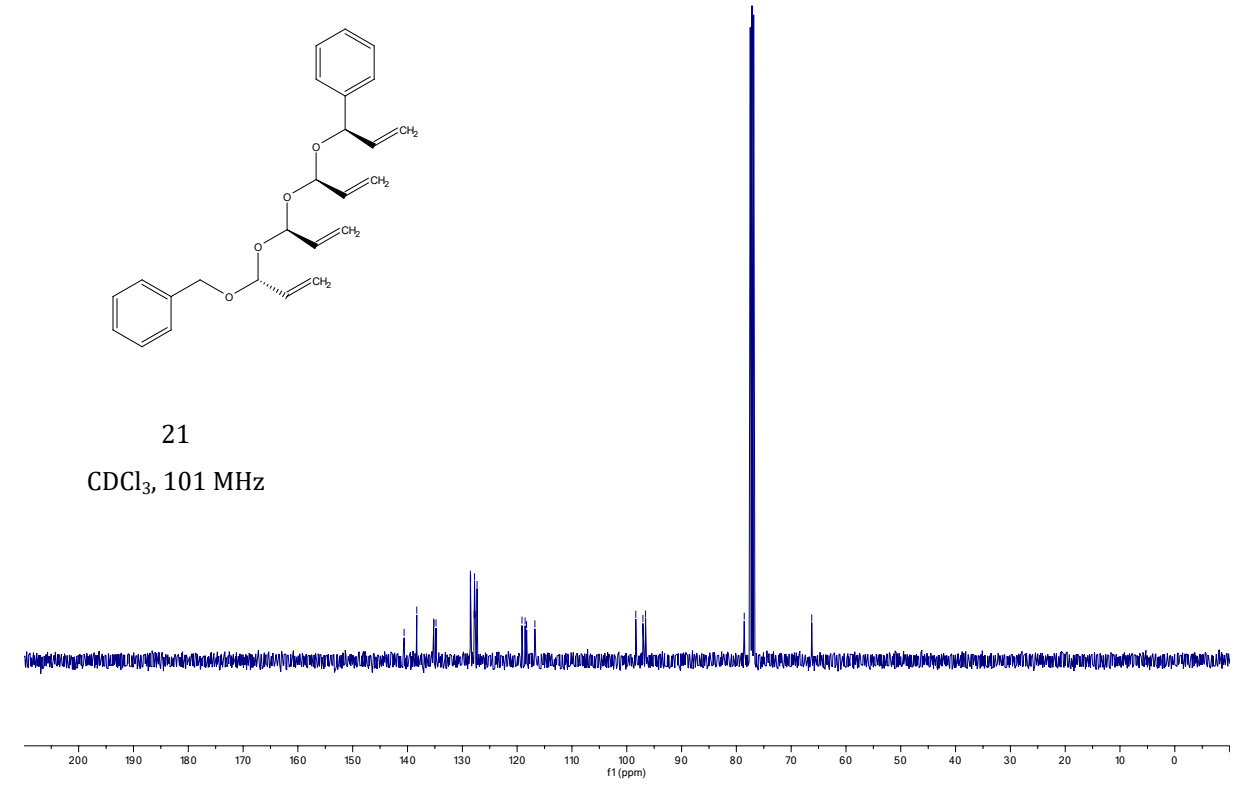
20

$CDCl_3$, 101 MHz



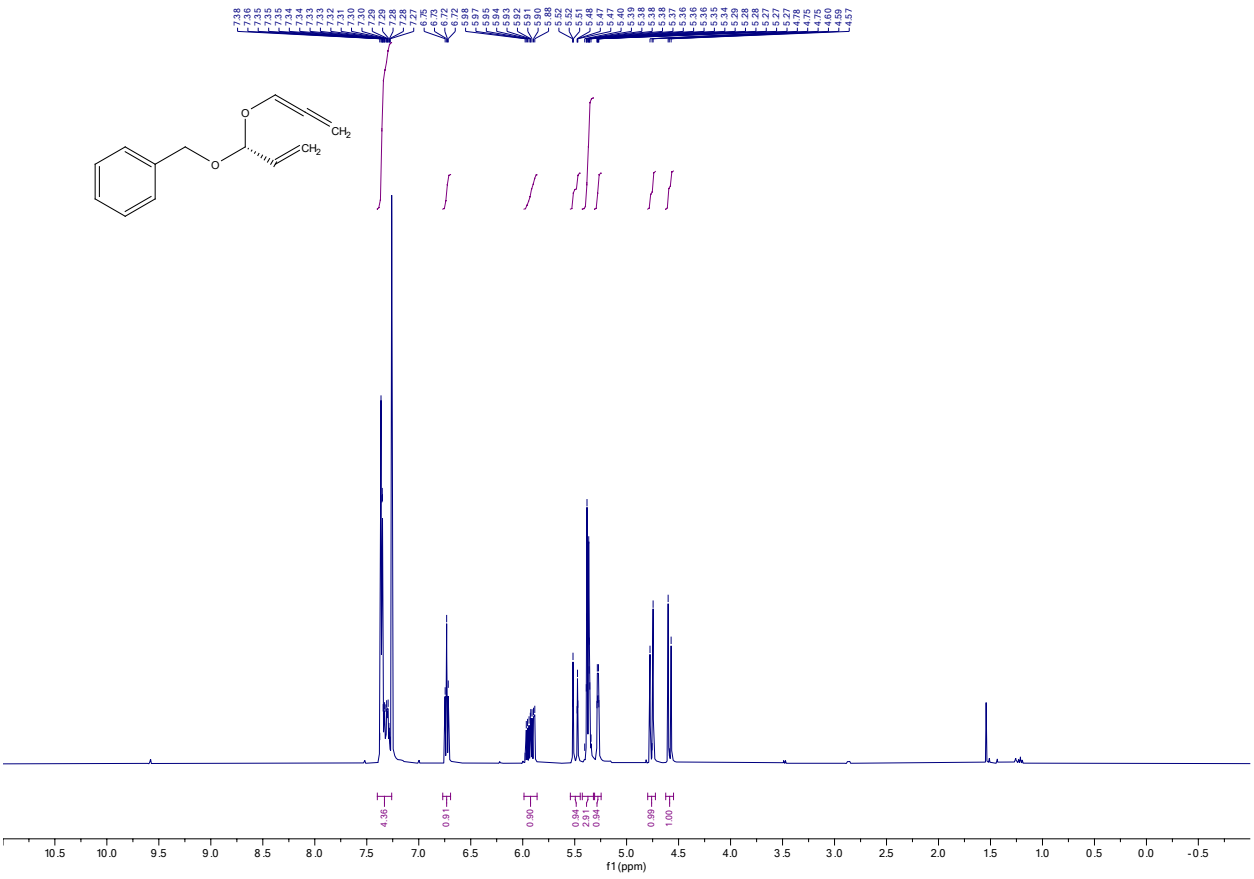
21

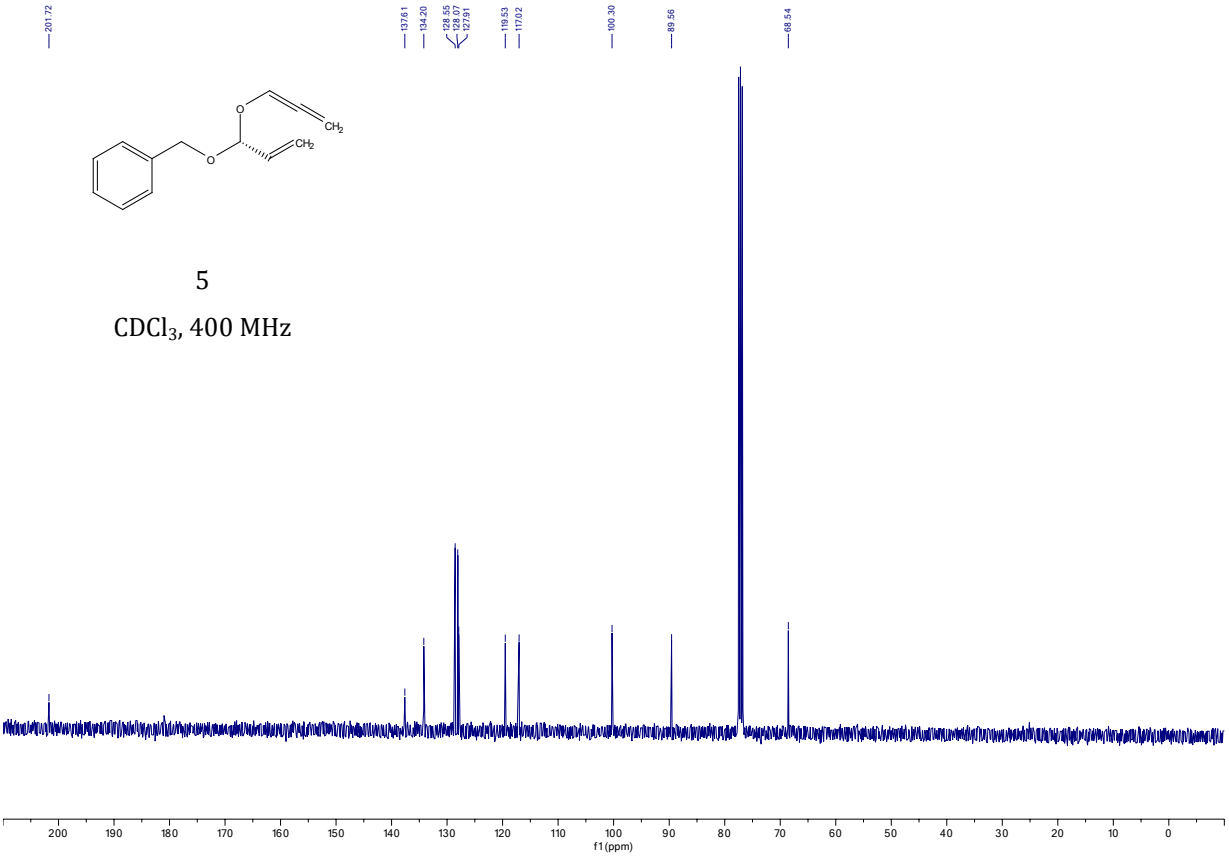
$CDCl_3$, 400 MHz



21

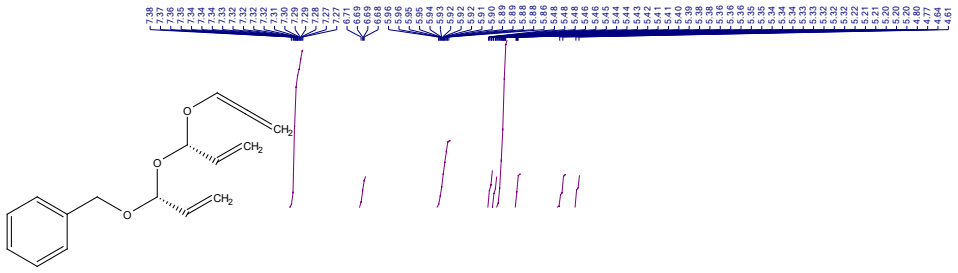
$CDCl_3$, 101 MHz





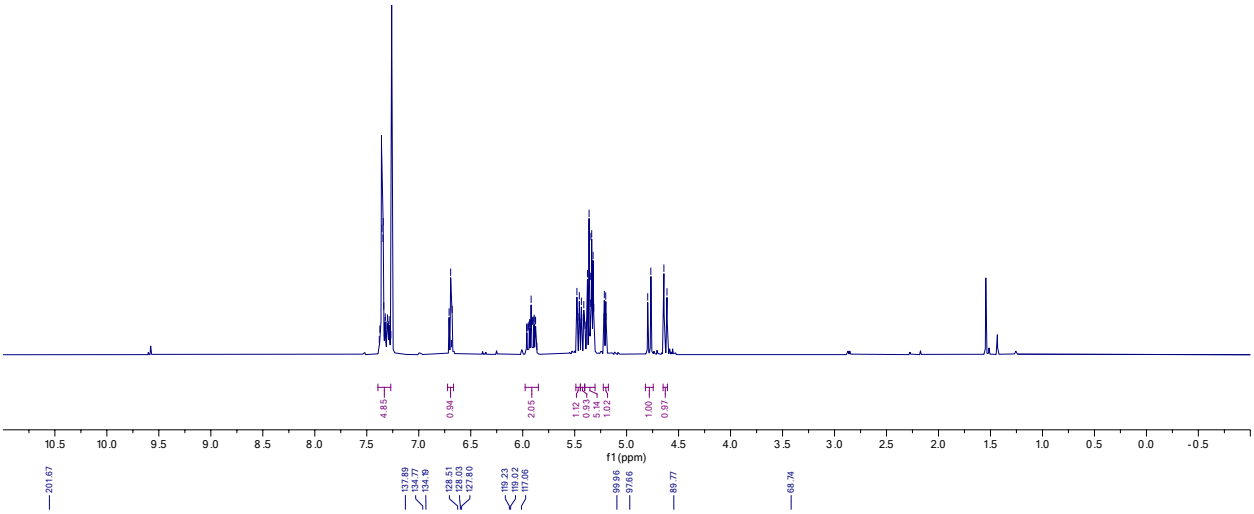
5

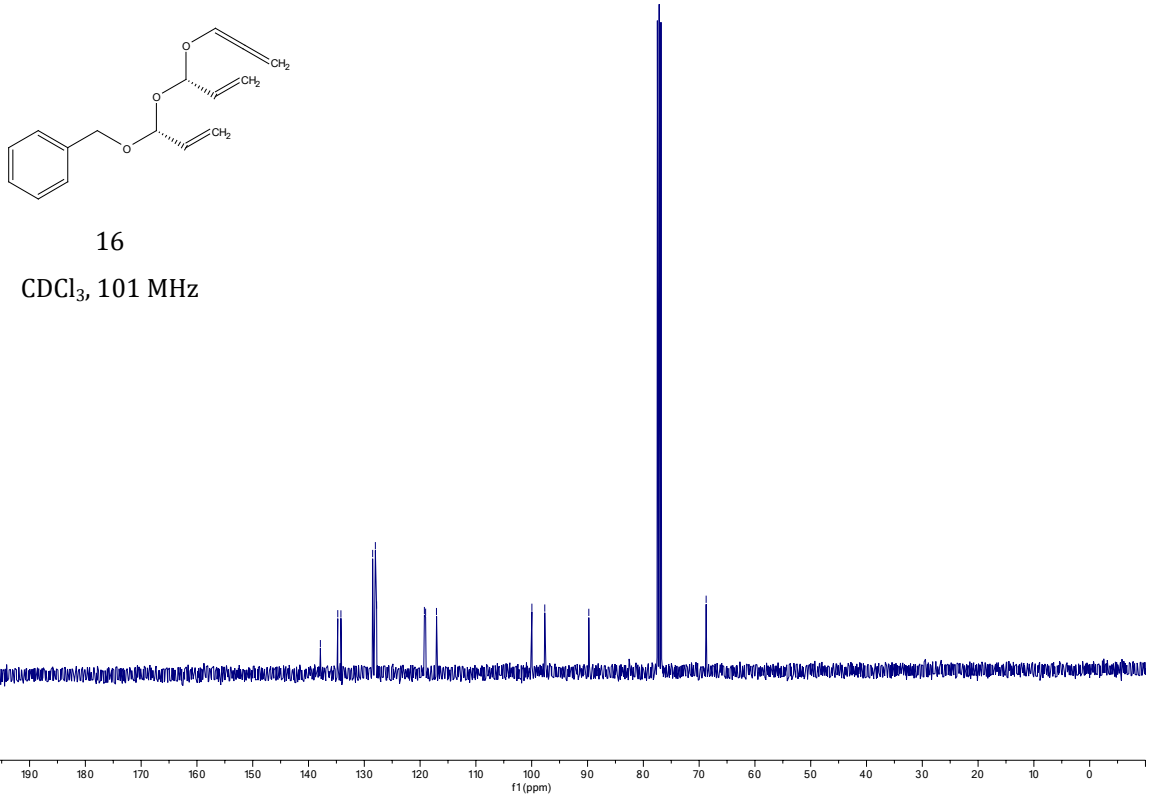
$CDCl_3$, 400 MHz



16

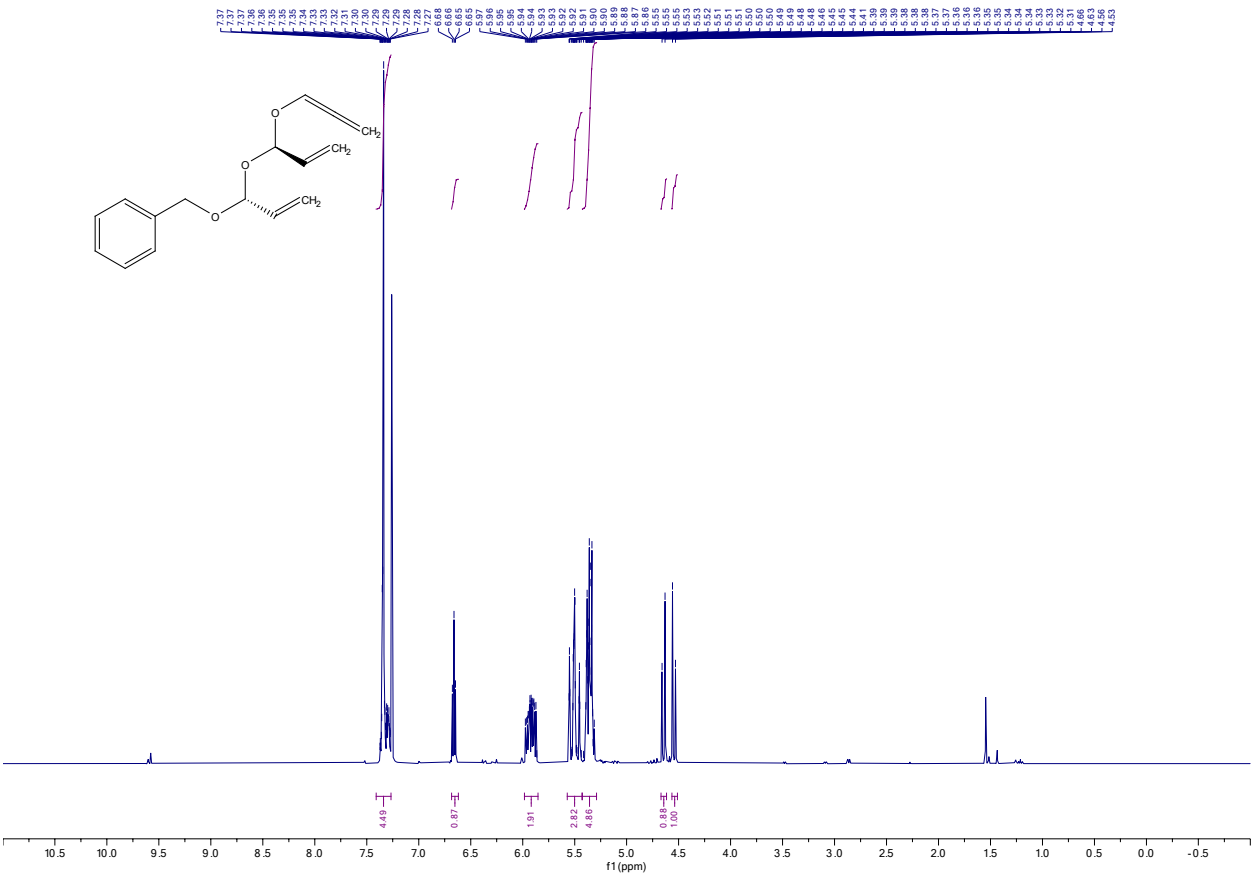
$CDCl_3$, 400 MHz

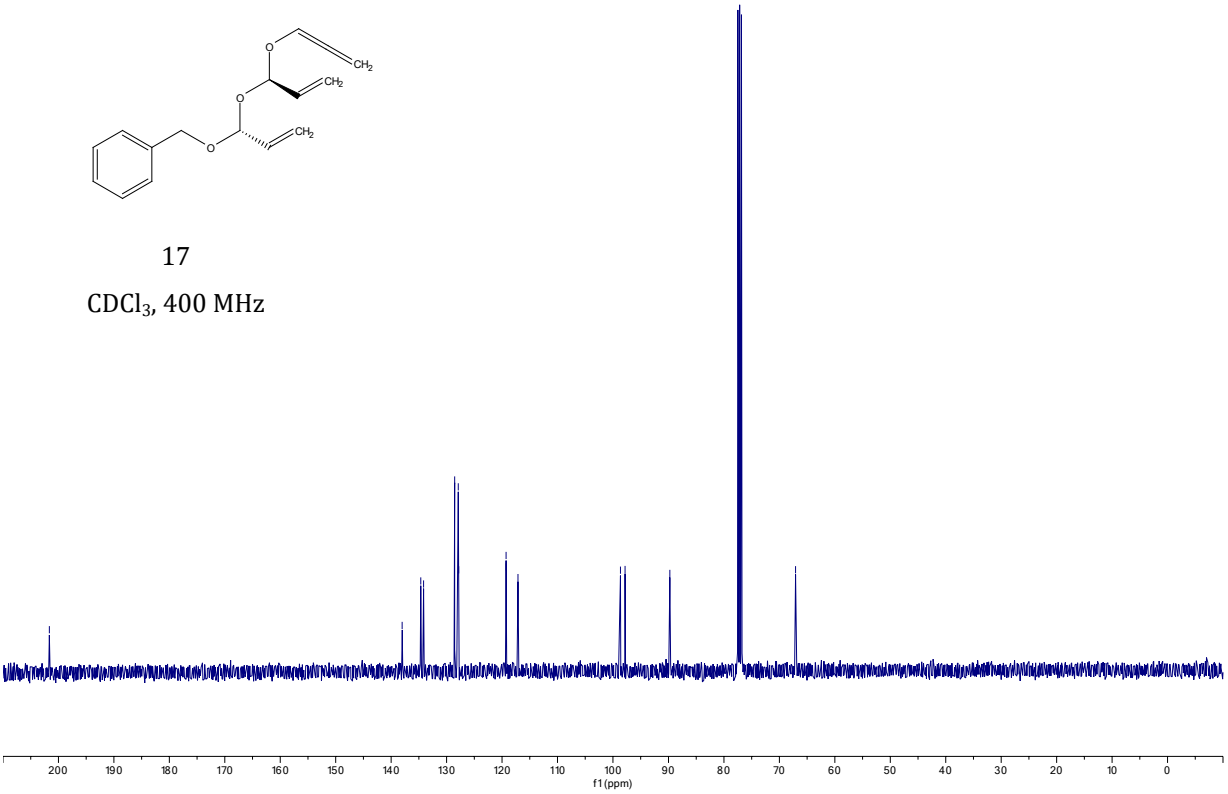




16

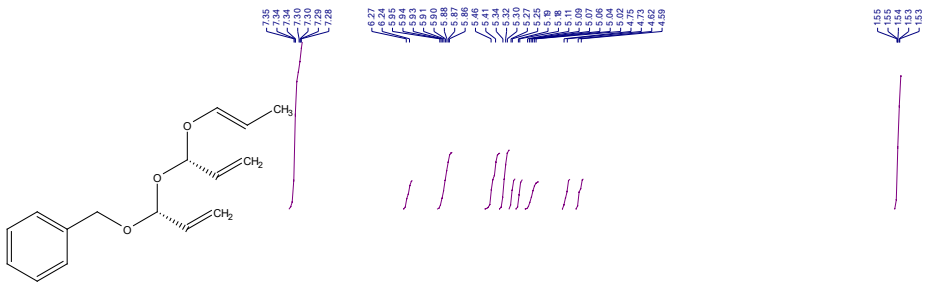
$CDCl_3$, 101 MHz





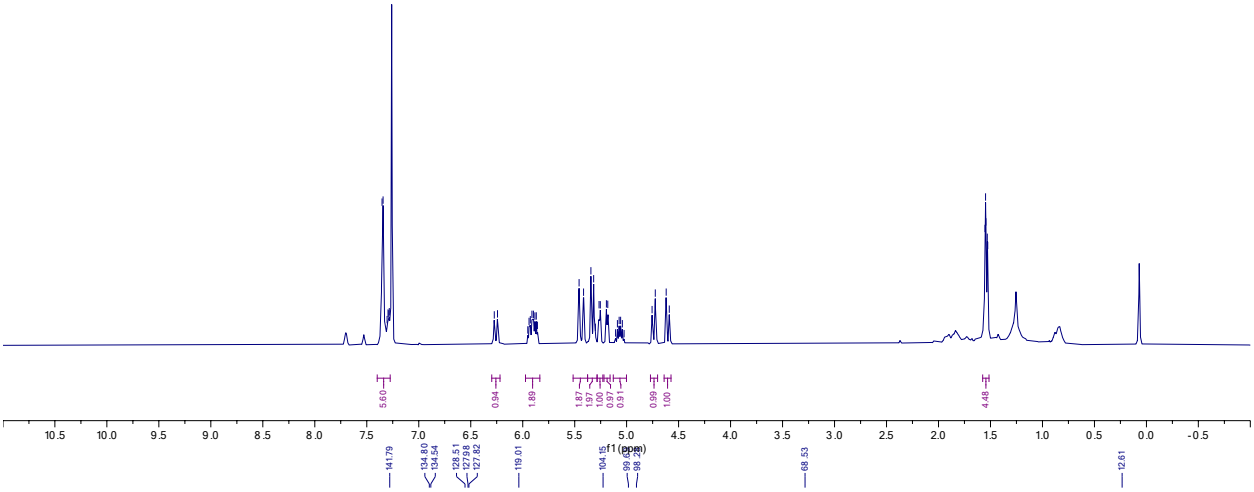
17

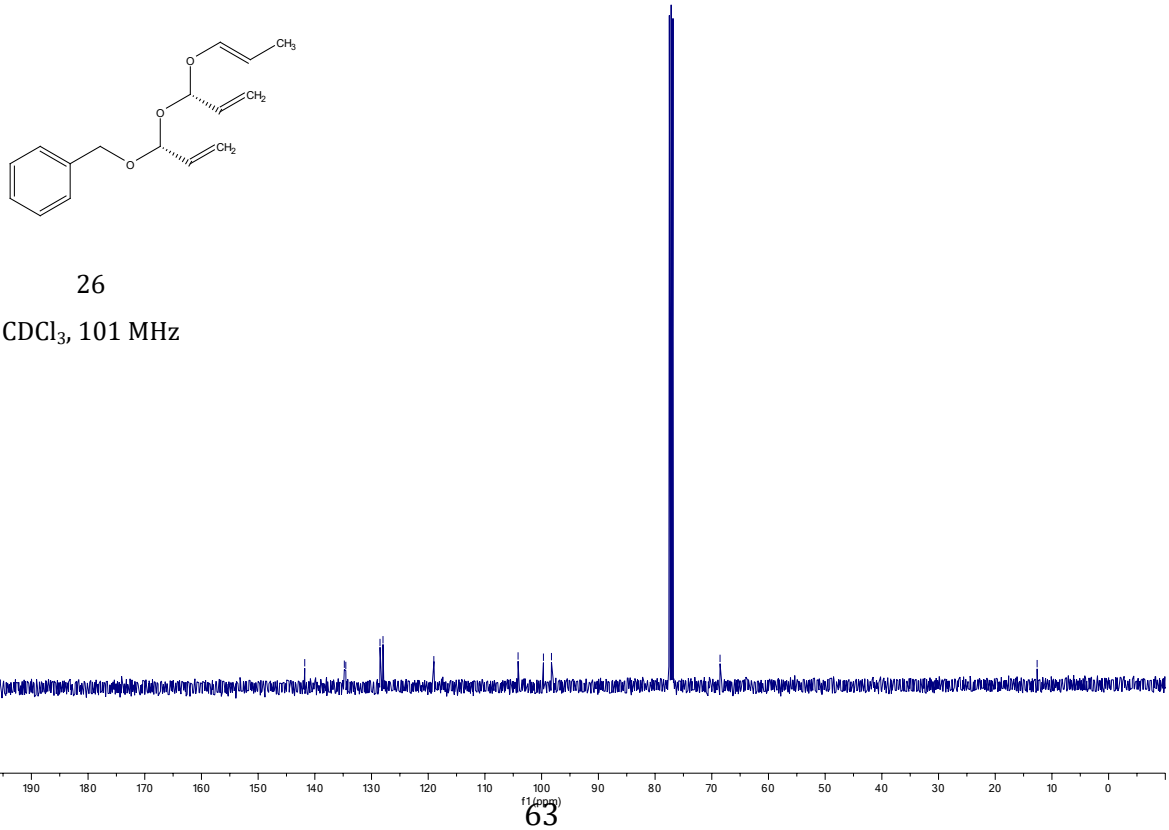
$CDCl_3$, 400 MHz



26

$CDCl_3$, 400 MHz



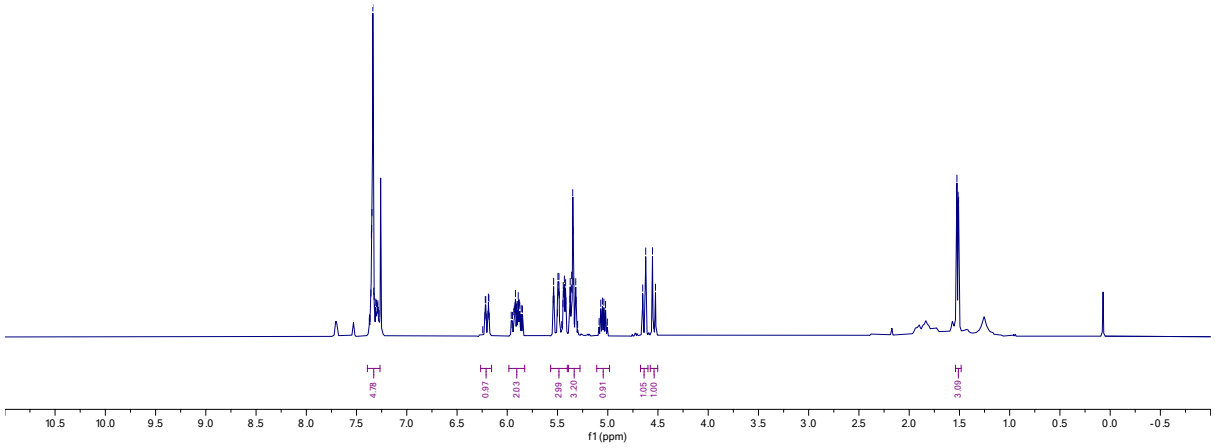


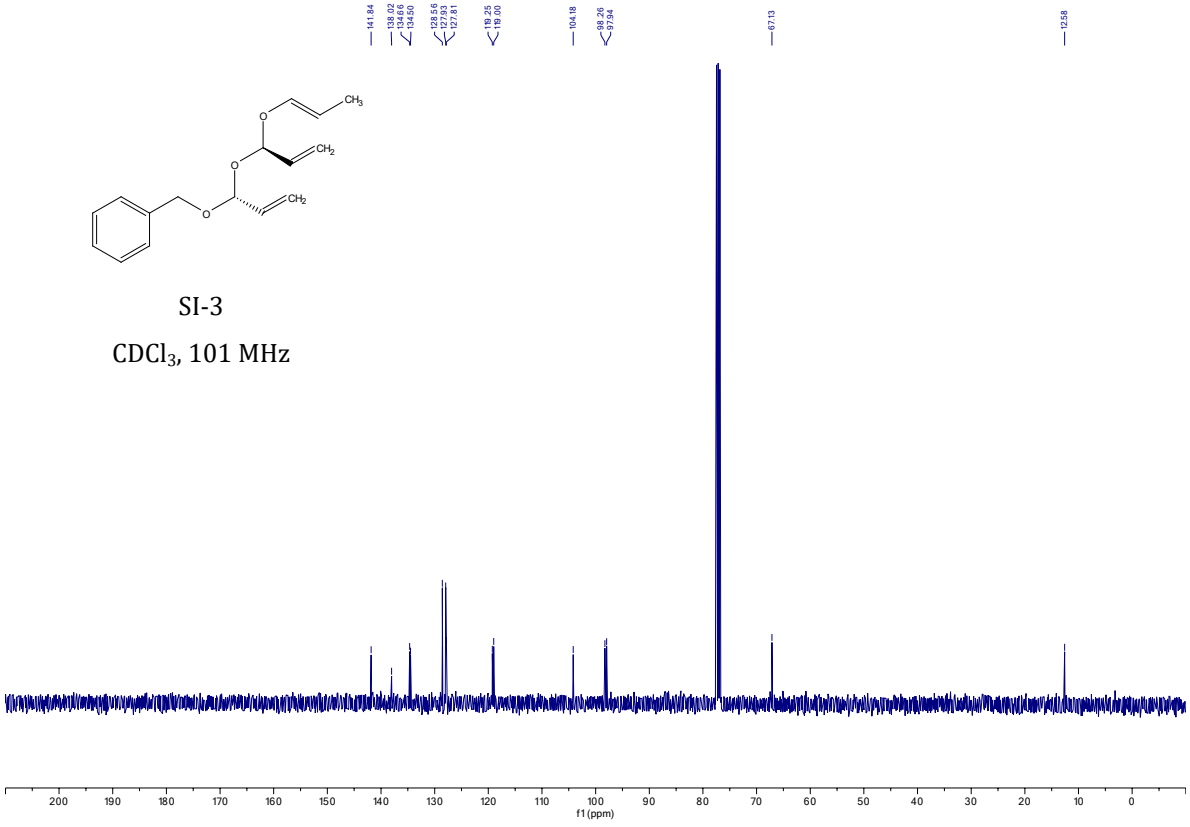
26

$CDCl_3$, 101 MHz

SI-3

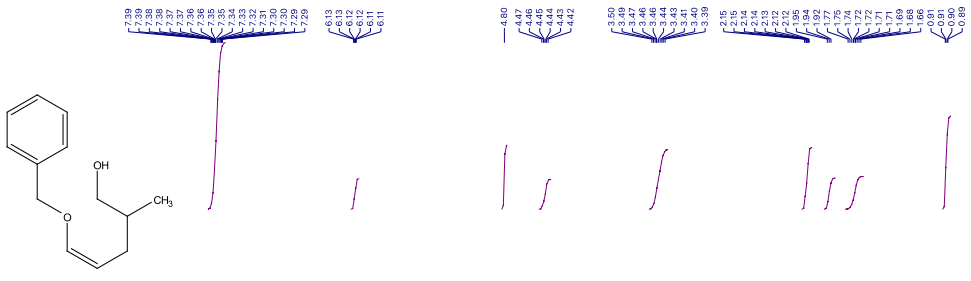
$CDCl_3$, 400 MHz





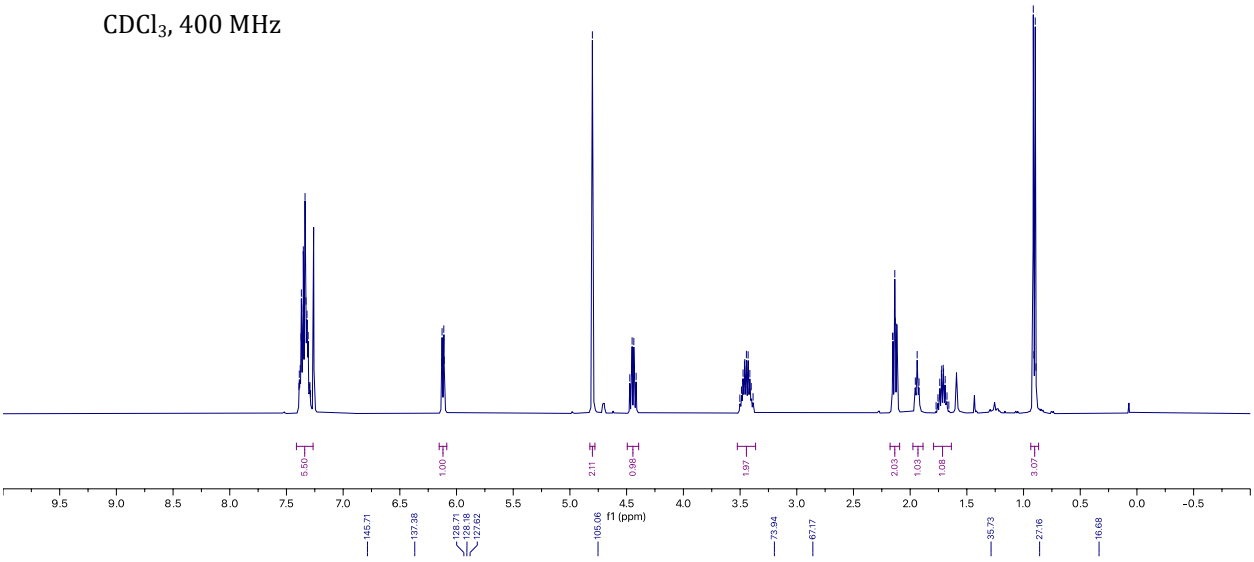
SI-3

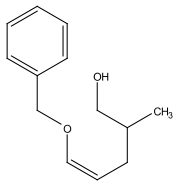
$CDCl_3$, 101 MHz



23

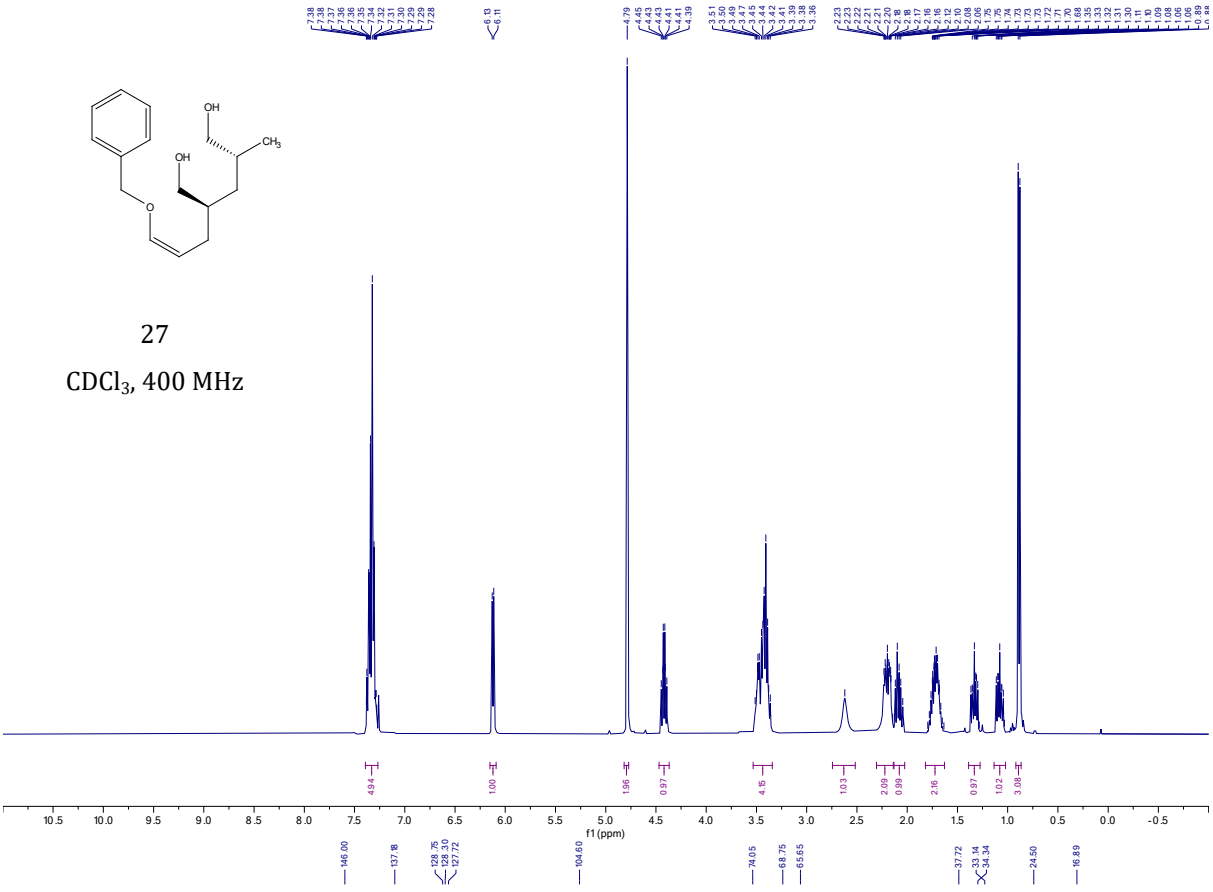
$CDCl_3$, 400 MHz





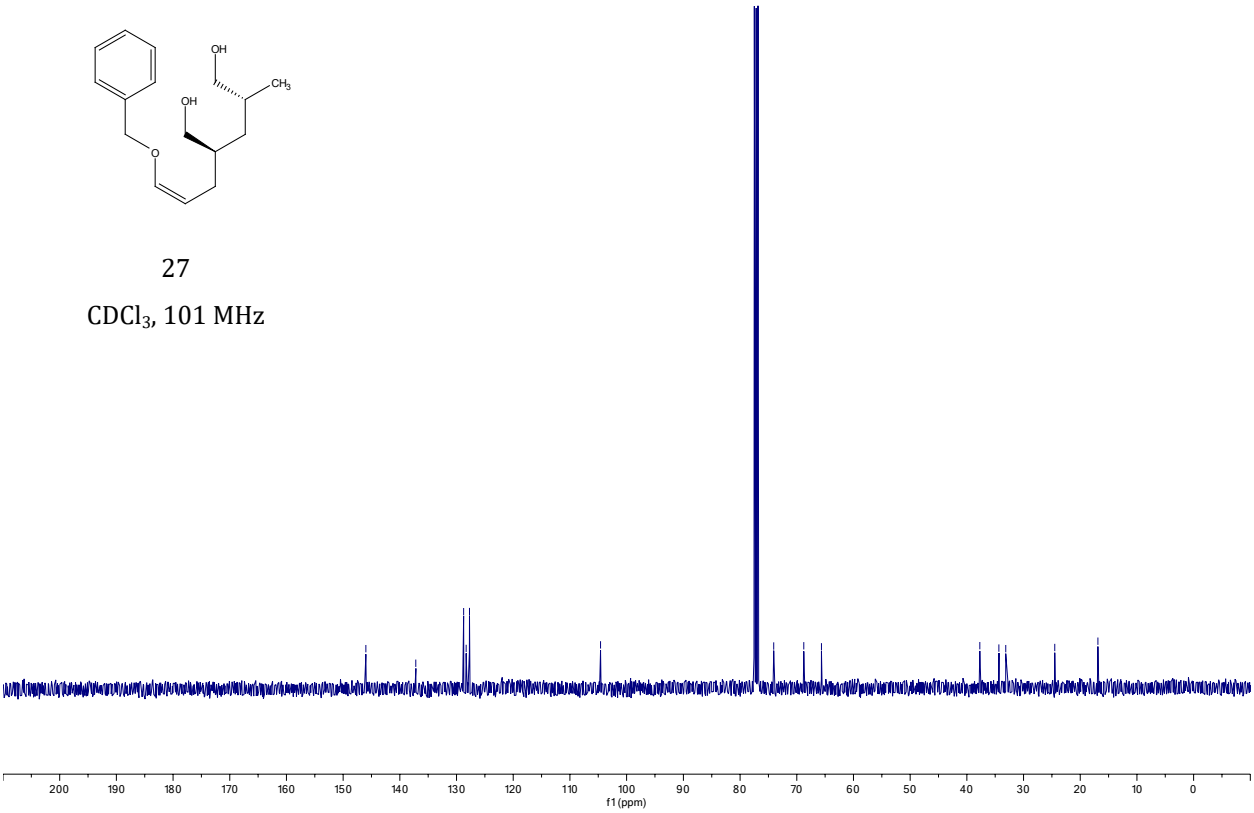
23

$CDCl_3$, 101 MHz



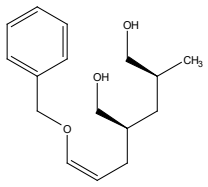
27

$CDCl_3$, 400 MHz



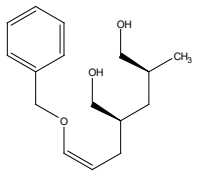
27

$CDCl_3$, 101 MHz



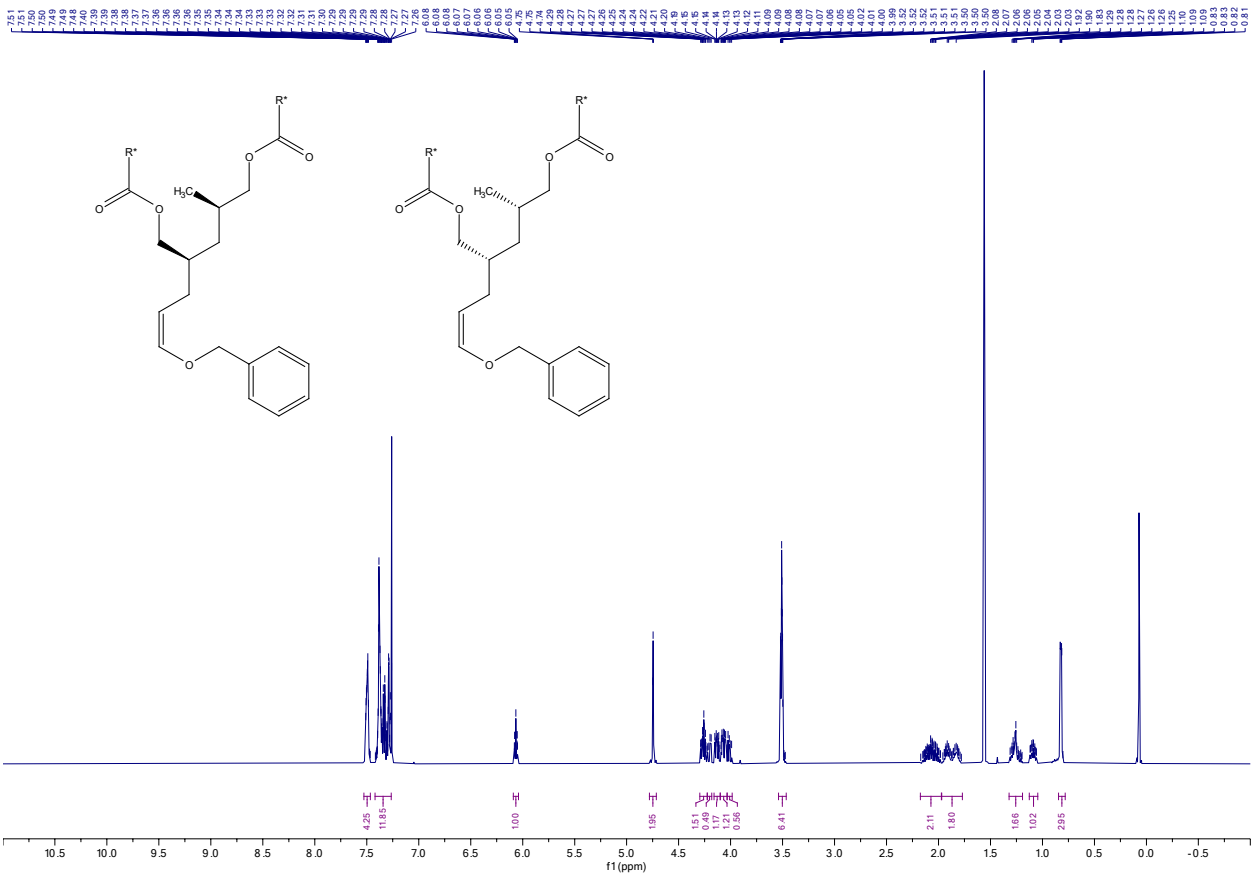
29

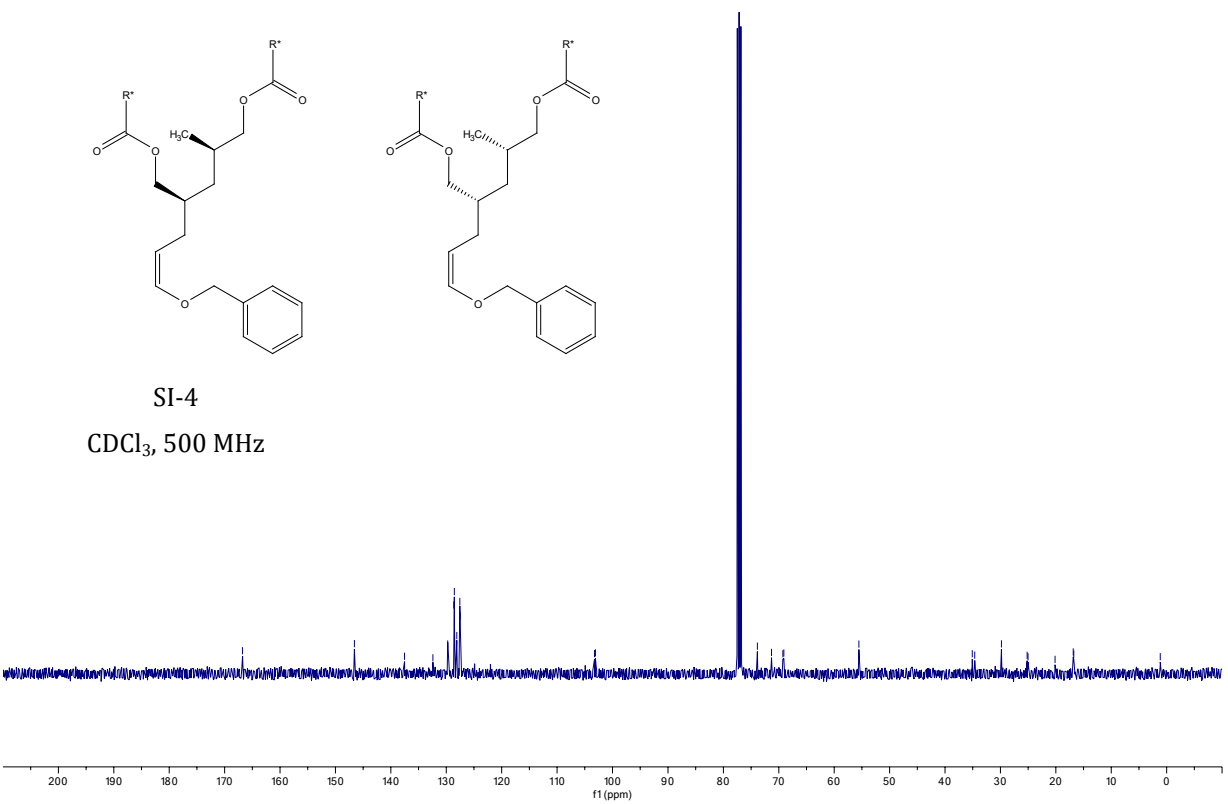
$CDCl_3$, 400 MHz



29

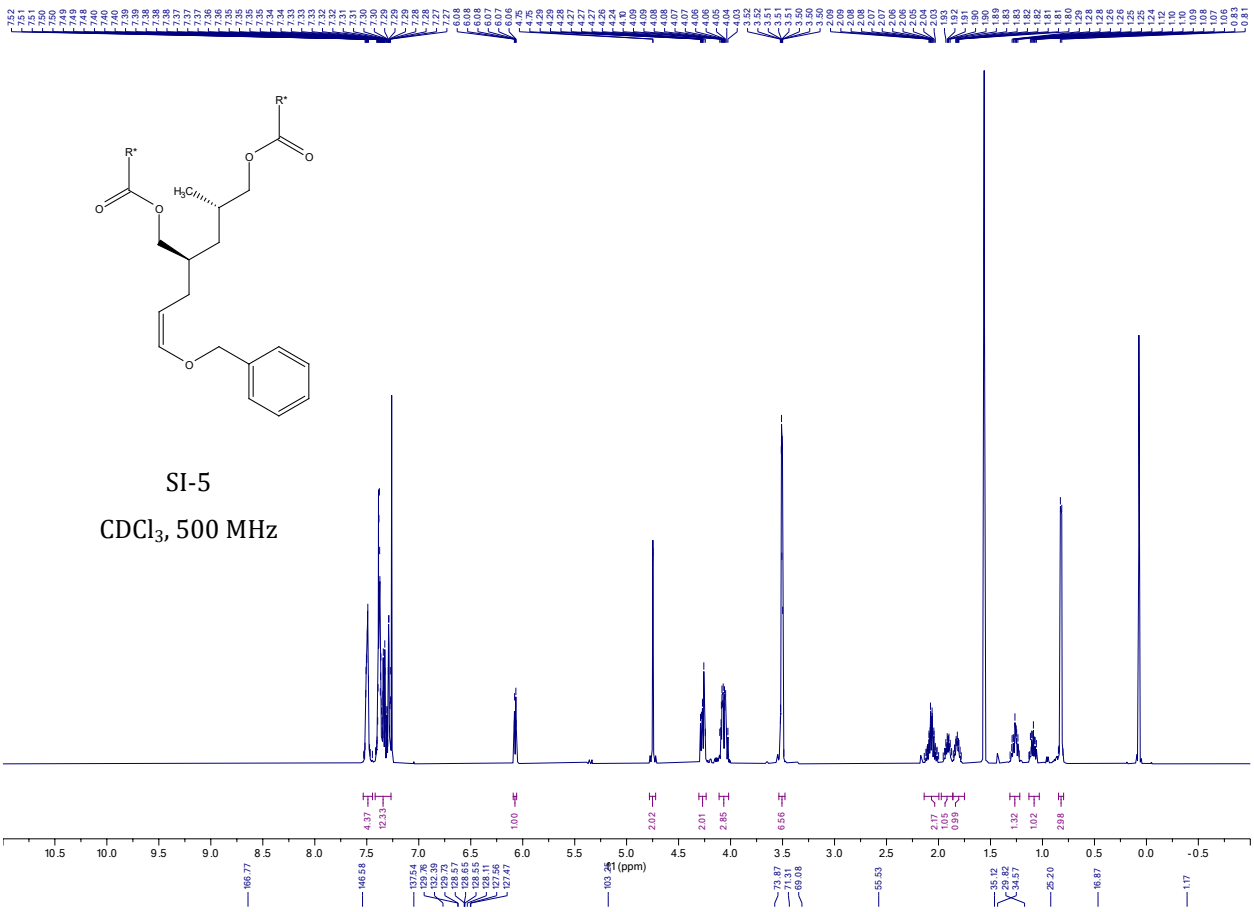
$CDCl_3$, 101 MHz

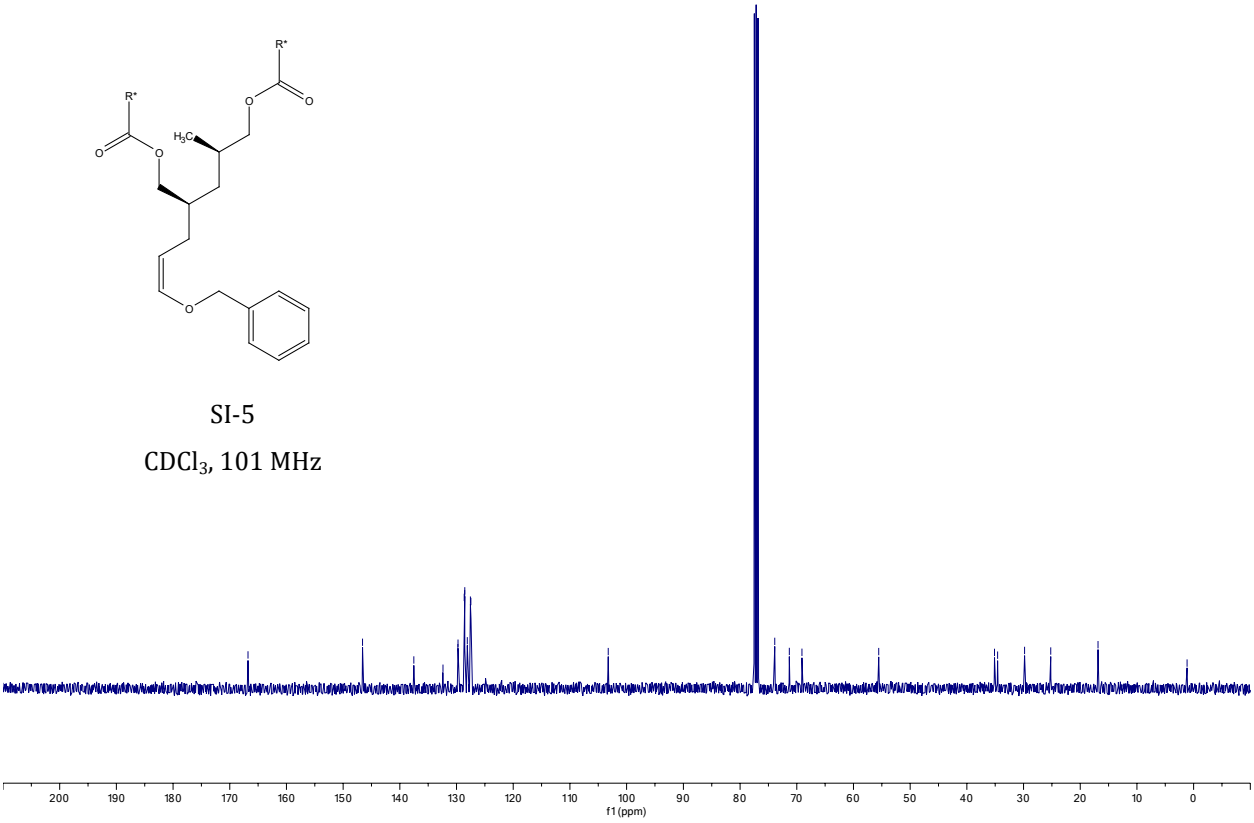


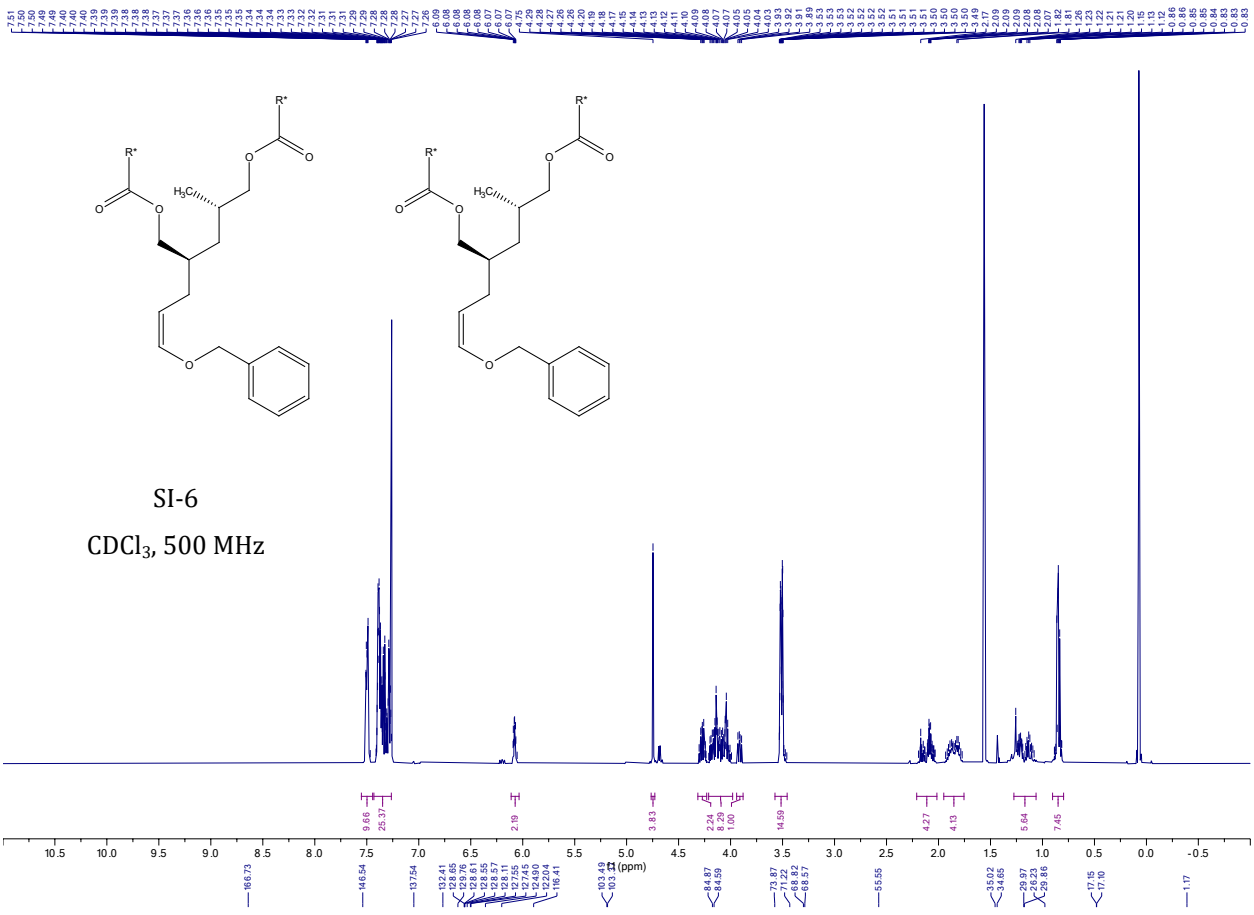


SI-4

$CDCl_3$, 500 MHz

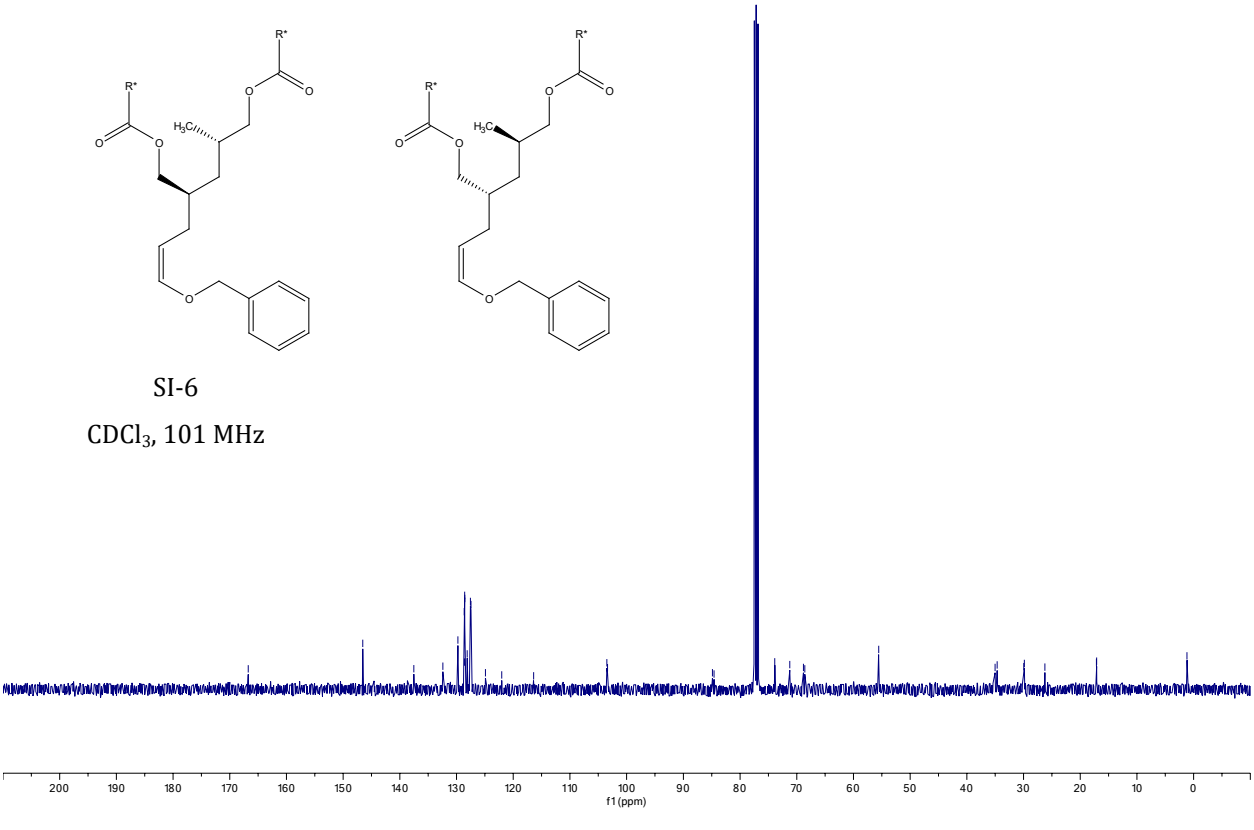

R*
R*
O
O
O
O
O
H3C
SI-5
CDCl3, 500 MHz
f1 (ppm)


R*
R*
O
O
O
O
O
H3C
SI-5
CDCl3, 101 MHz
f1 (ppm)



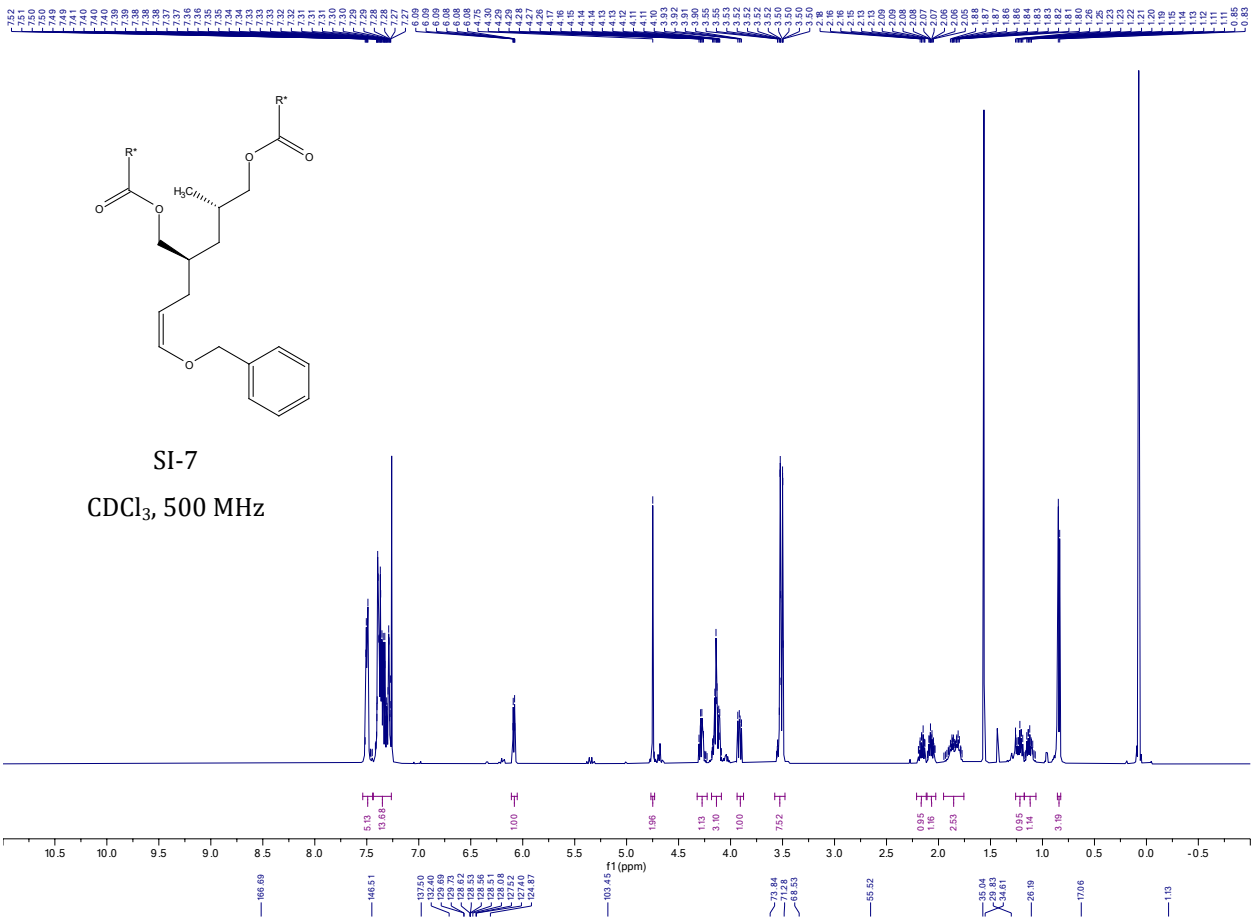
SI-6

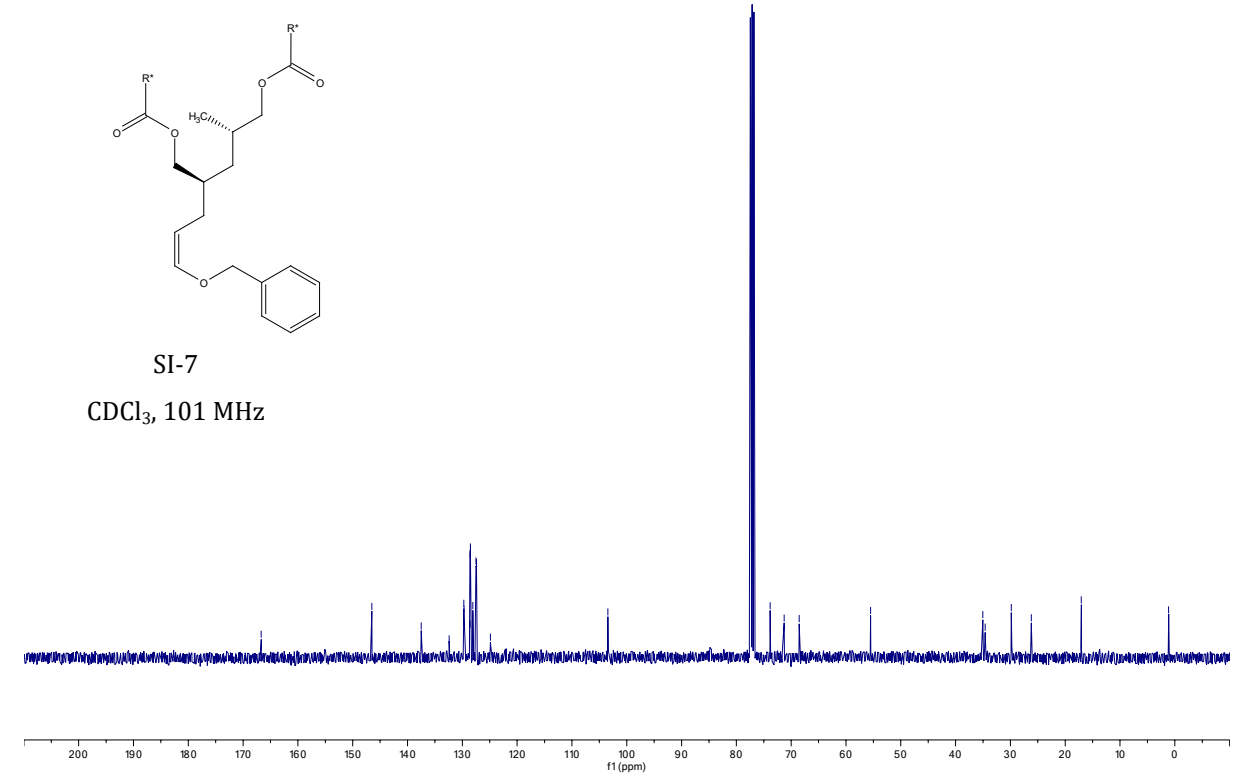
$CDCl_3$, 500 MHz

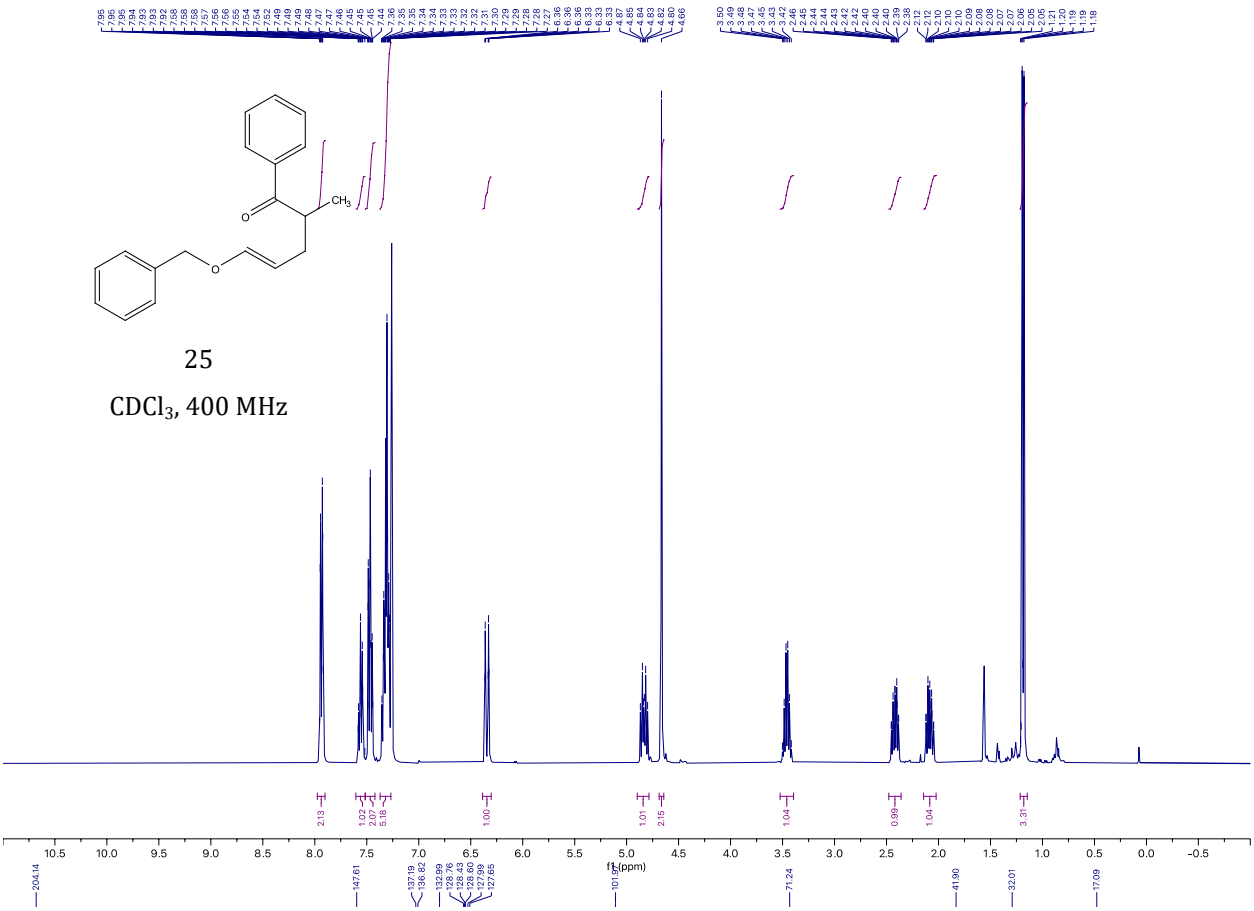


SI-6

$CDCl_3$, 101 MHz

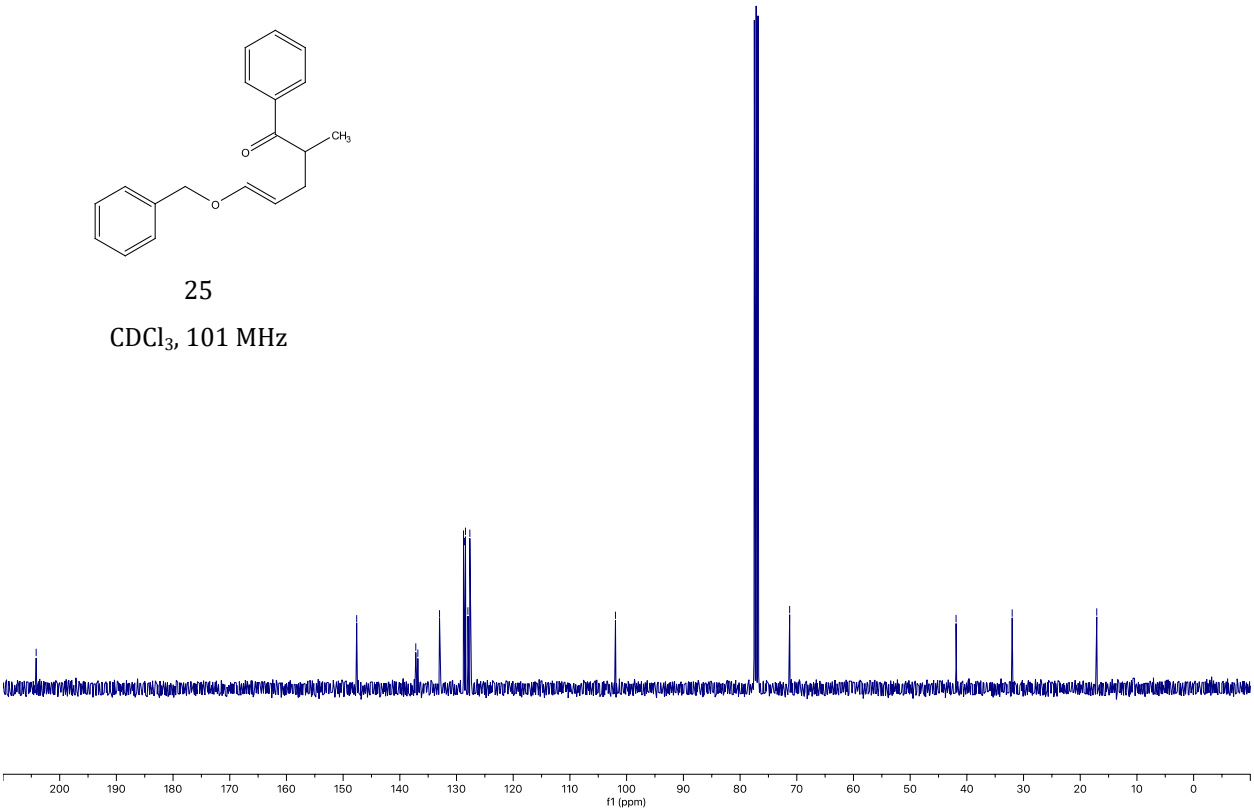

R*
R*
O
O
O
O
O
H3C
SI-7
CDCl3, 500 MHz
f1 (ppm)


R*
R*
O
O
O
O
O
H3C
SI-7
CDCl3, 101 MHz
f1 (ppm)



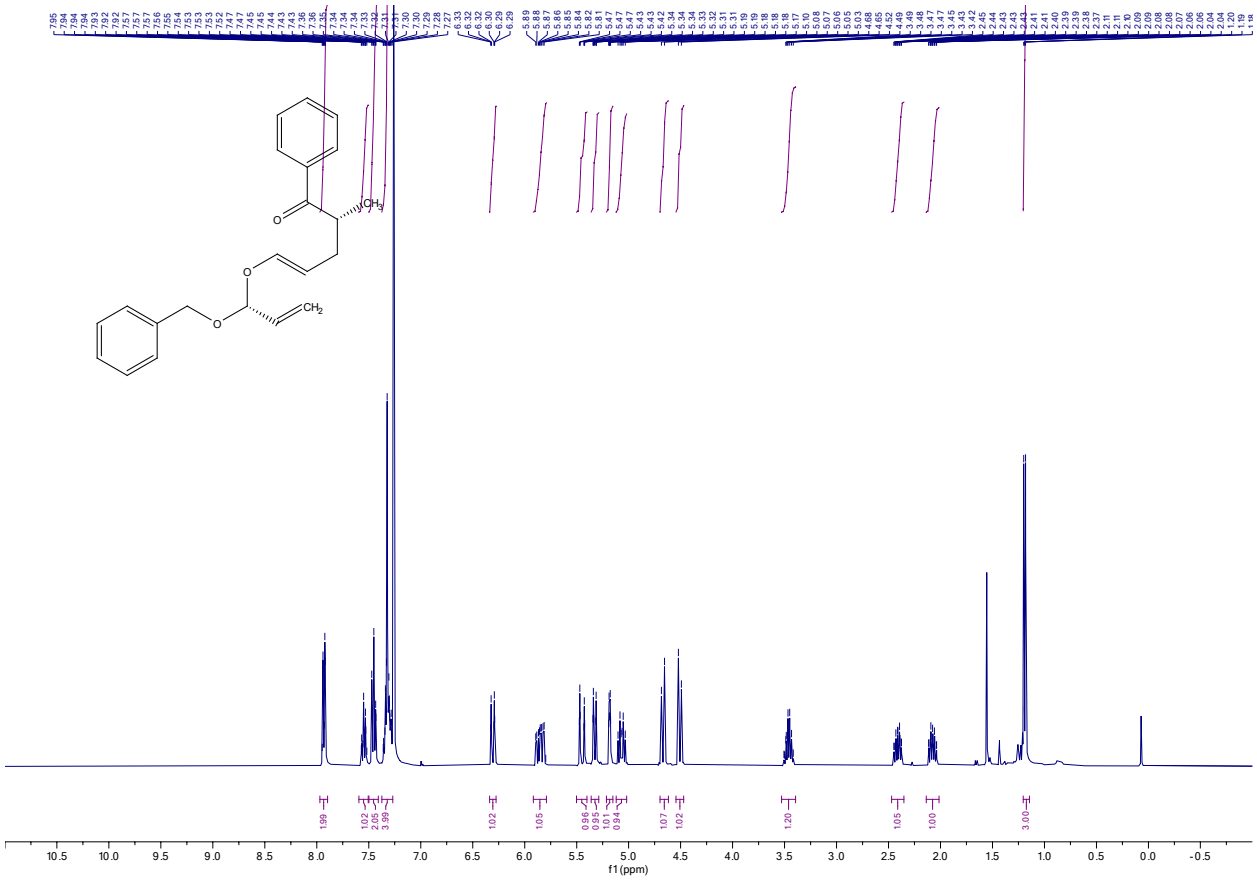
25

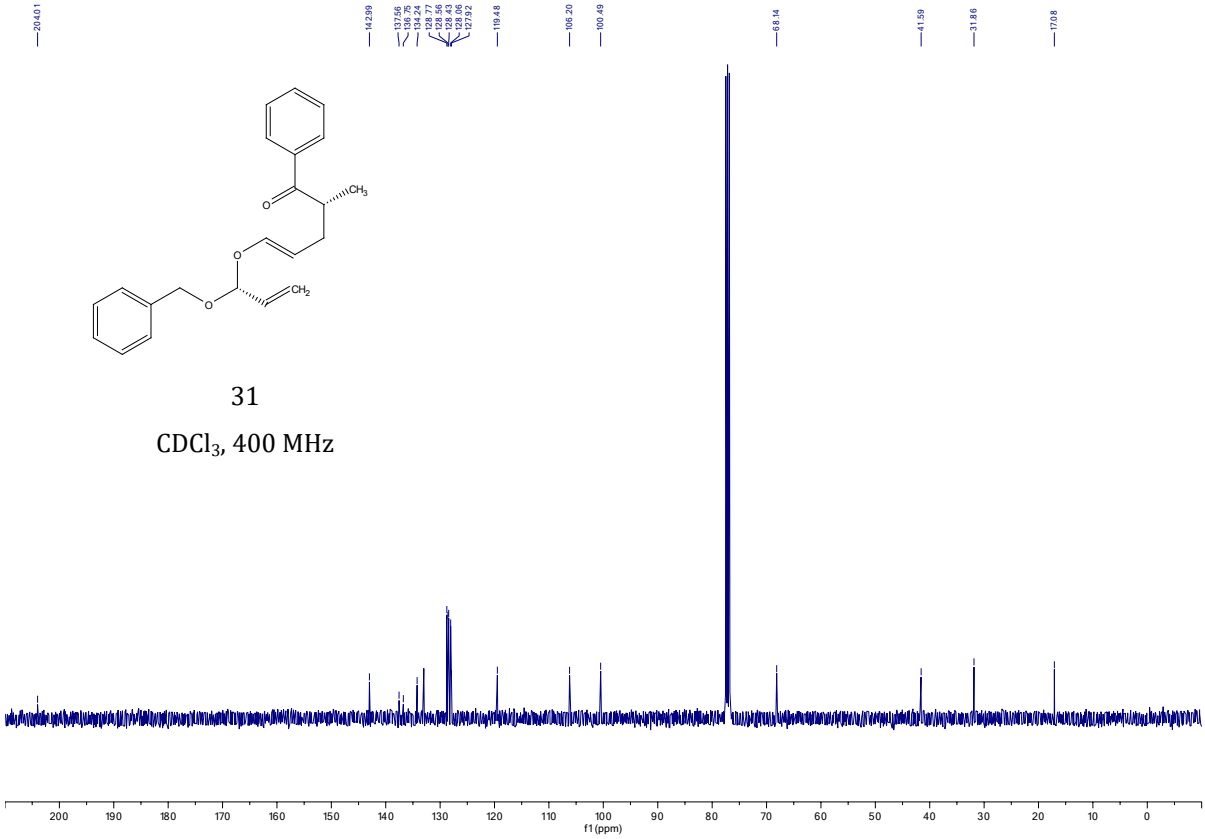
$CDCl_3$, 400 MHz



25

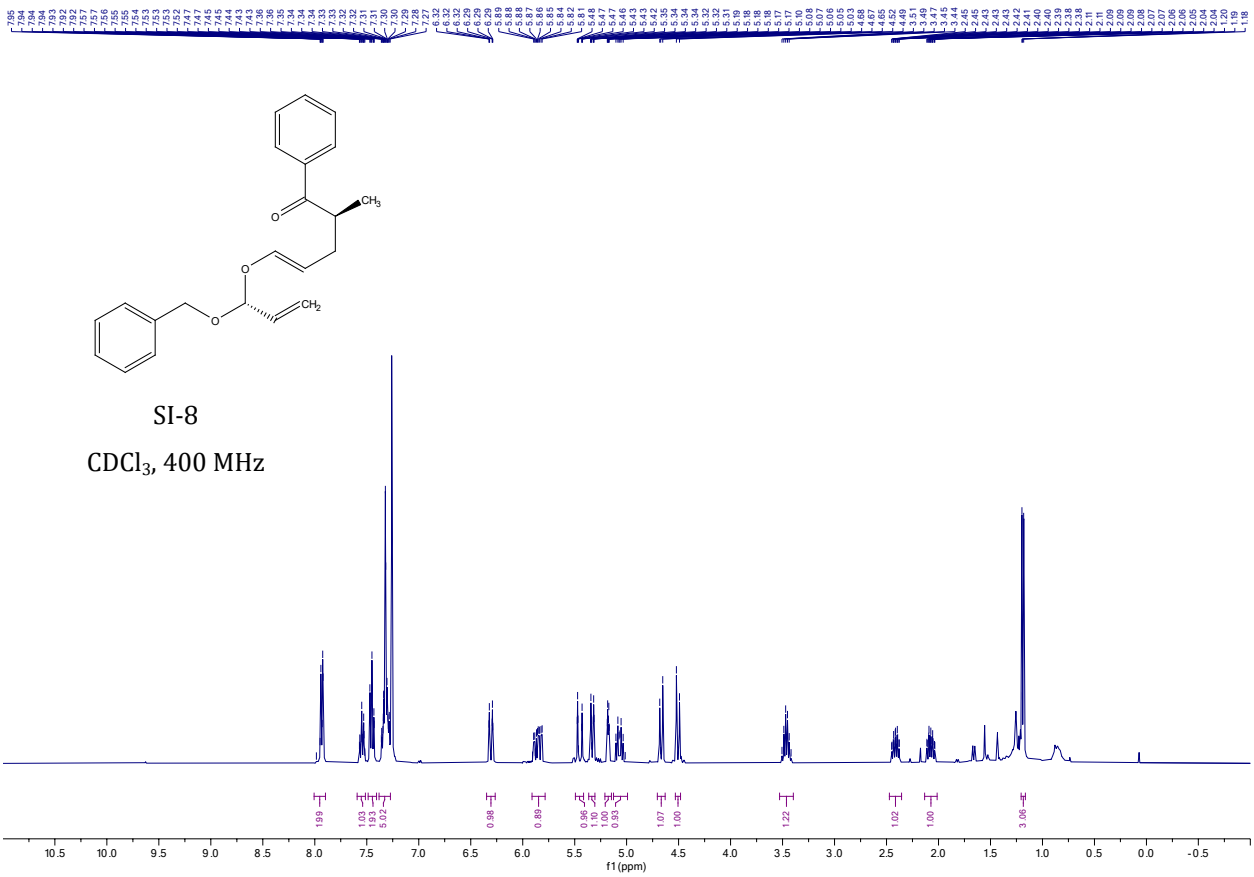
$CDCl_3$, 101 MHz





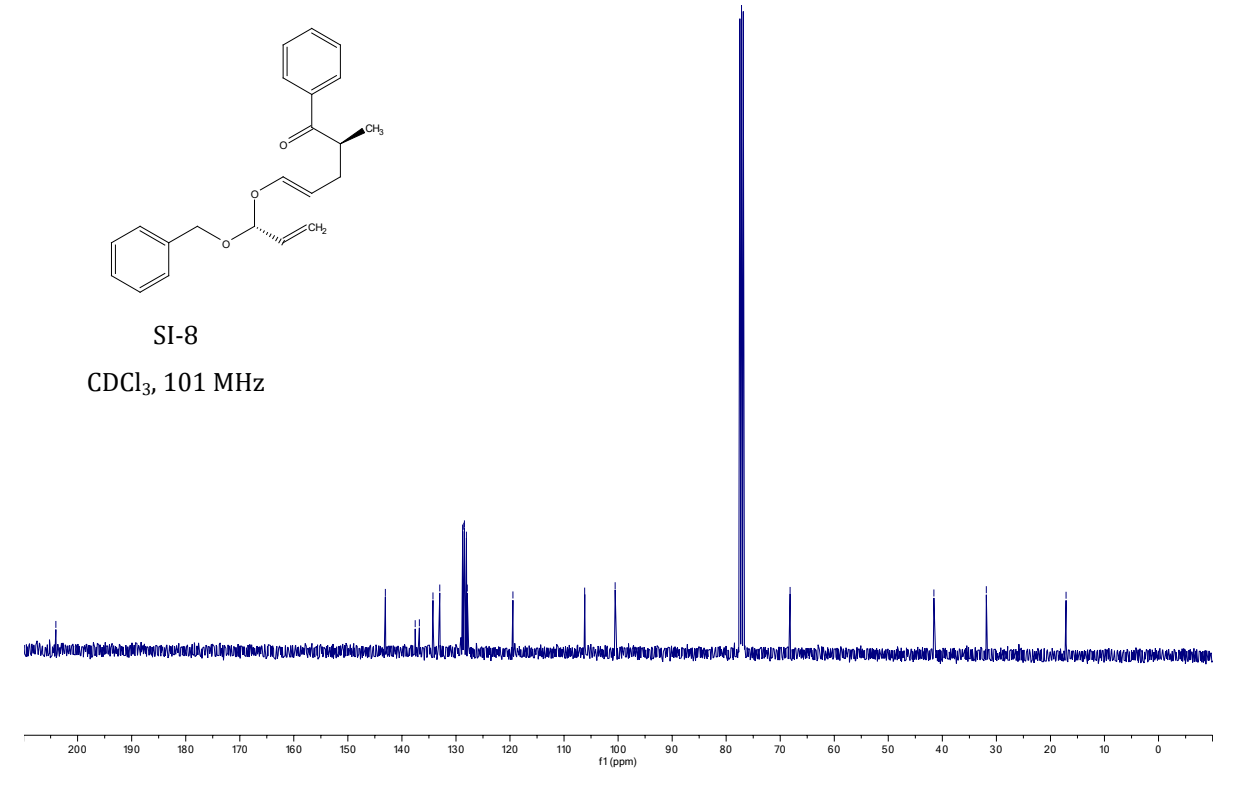
31

$CDCl_3$, 400 MHz



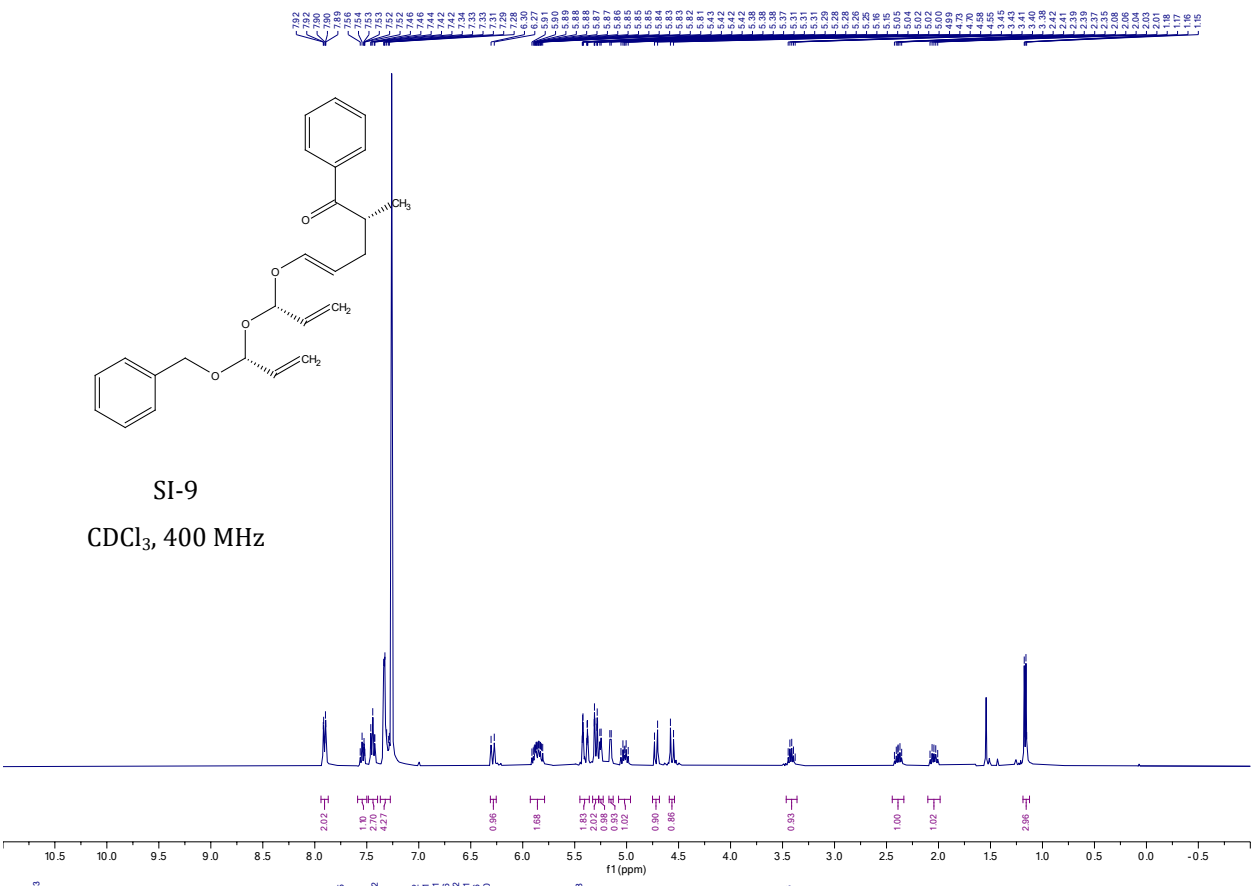
SI-8

$CDCl_3$, 400 MHz



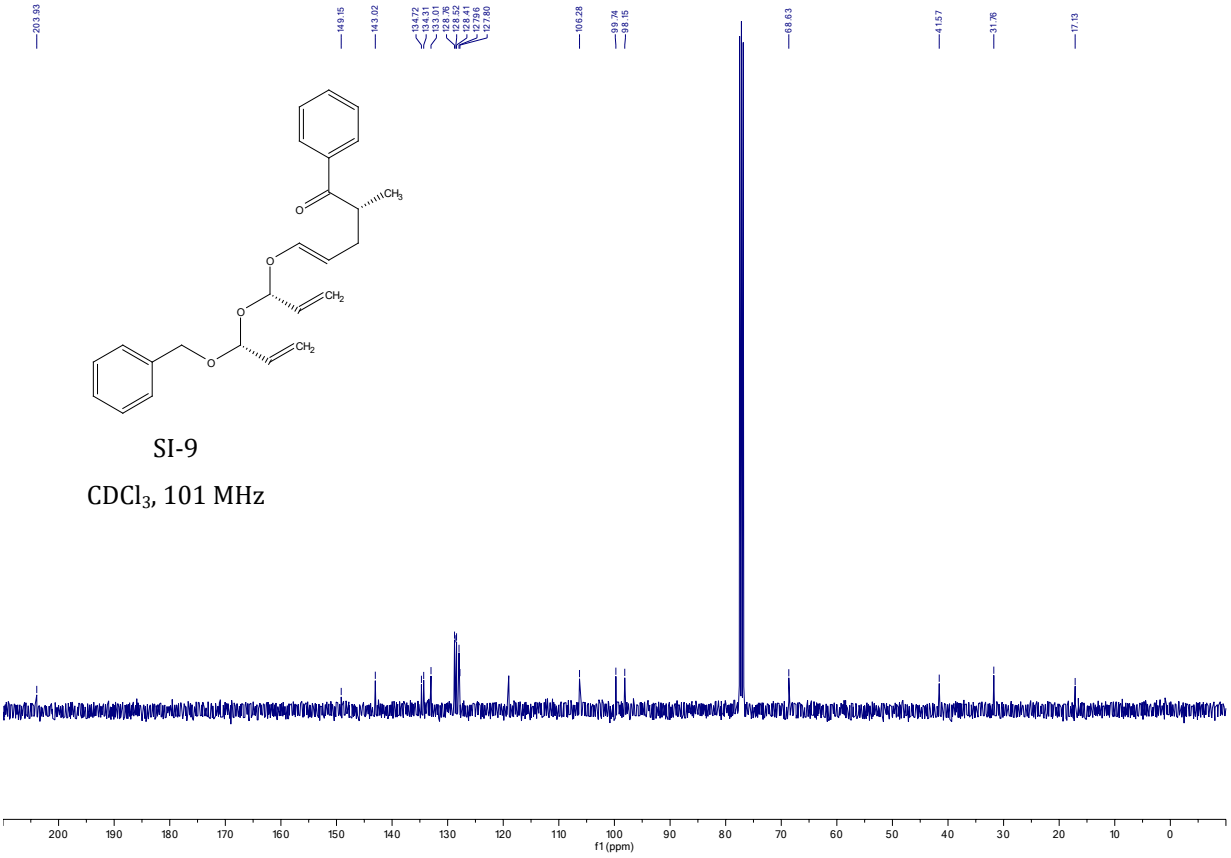
SI-8

$CDCl_3$, 101 MHz



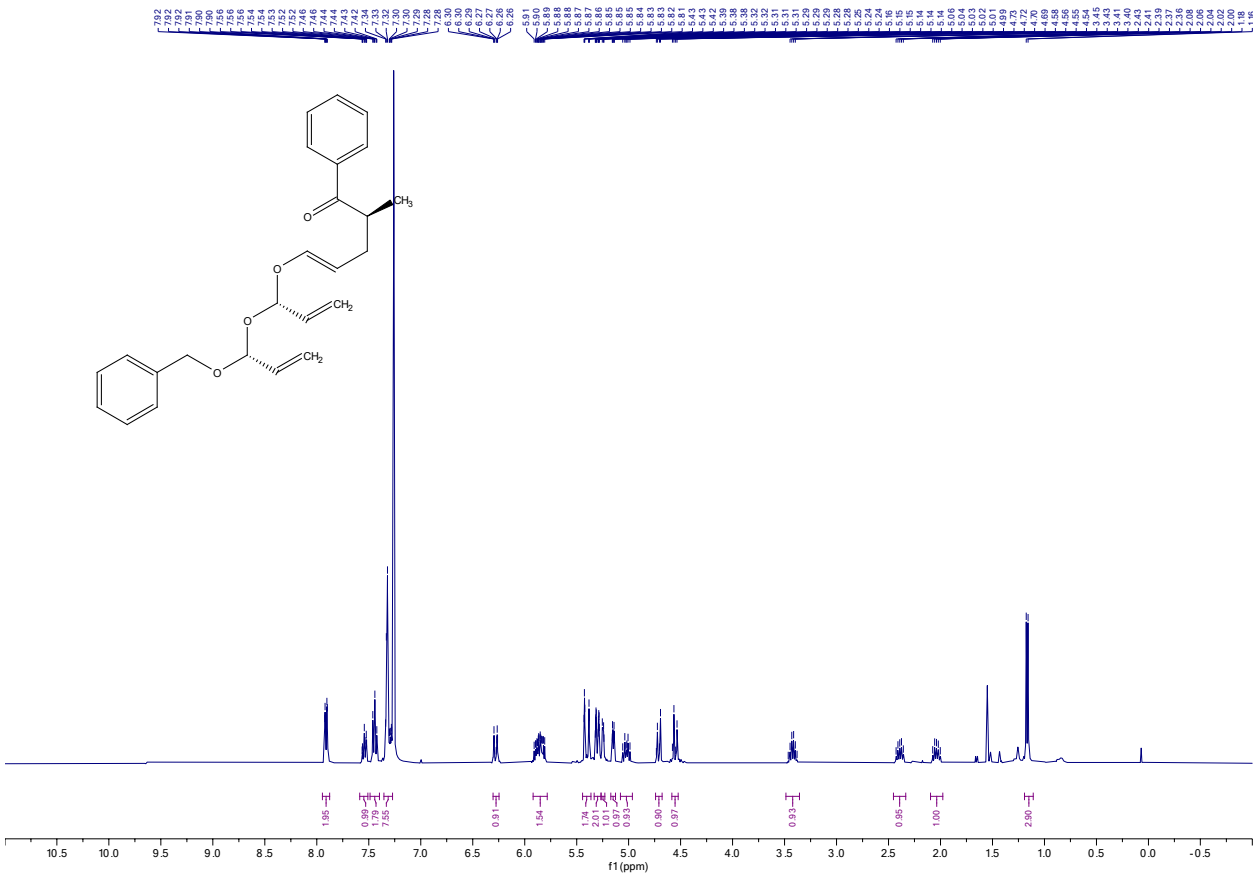
SI-9

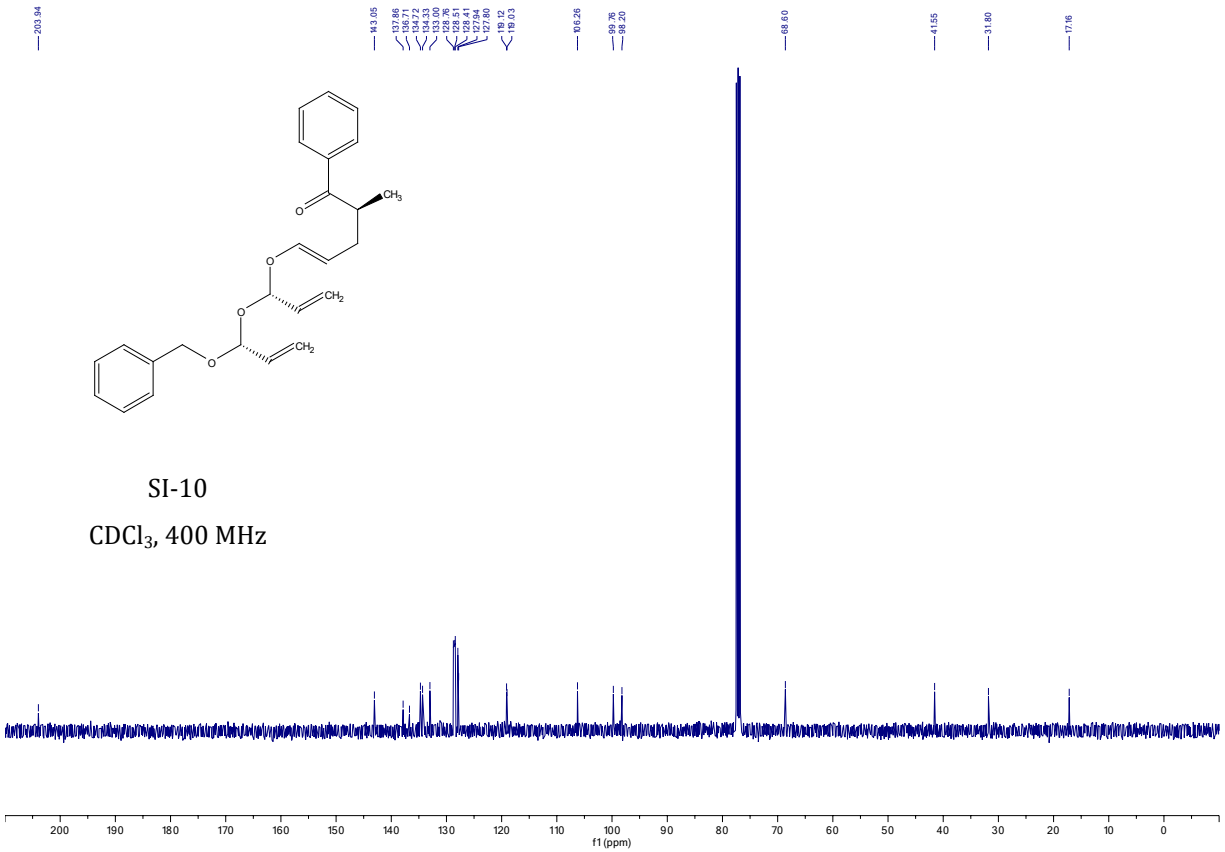
$CDCl_3$, 400 MHz



SI-9

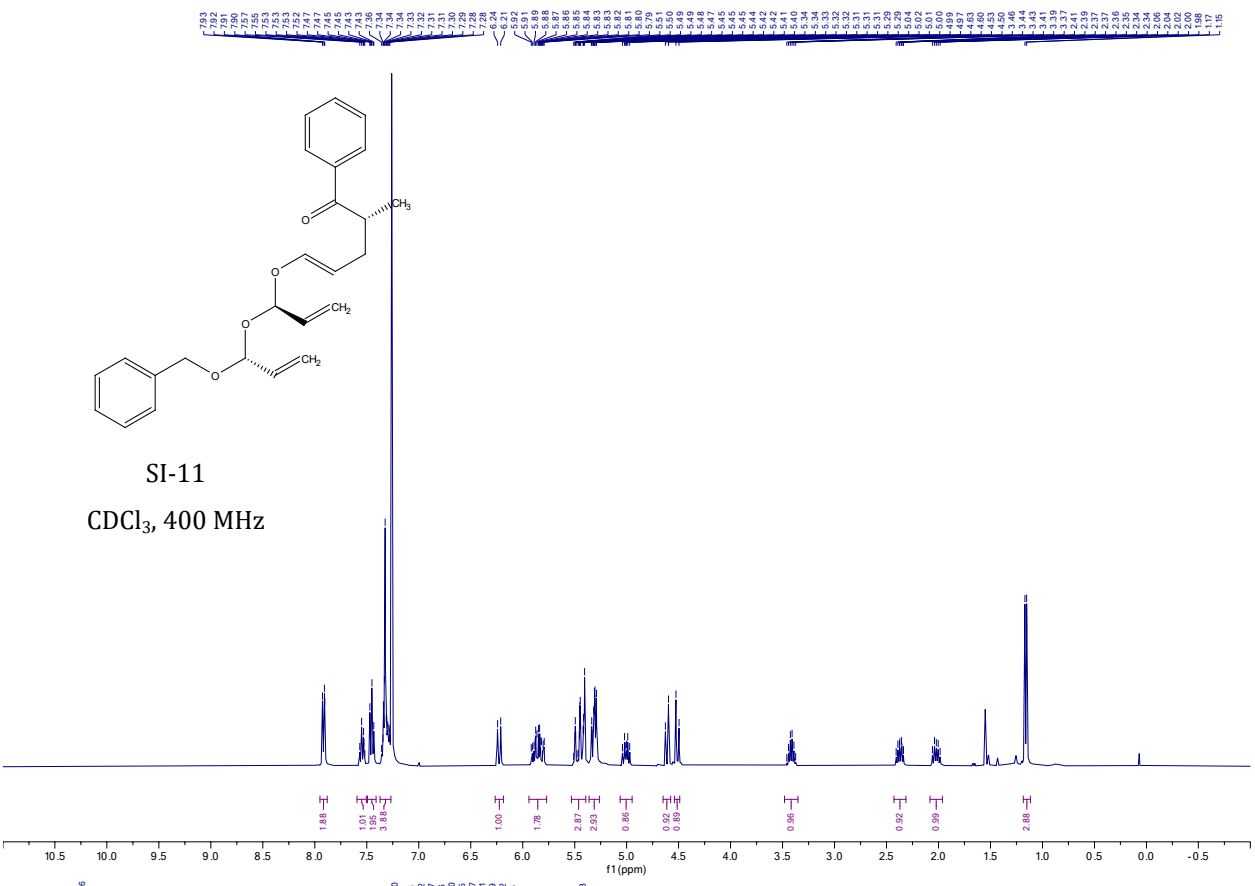
$CDCl_3$, 101 MHz





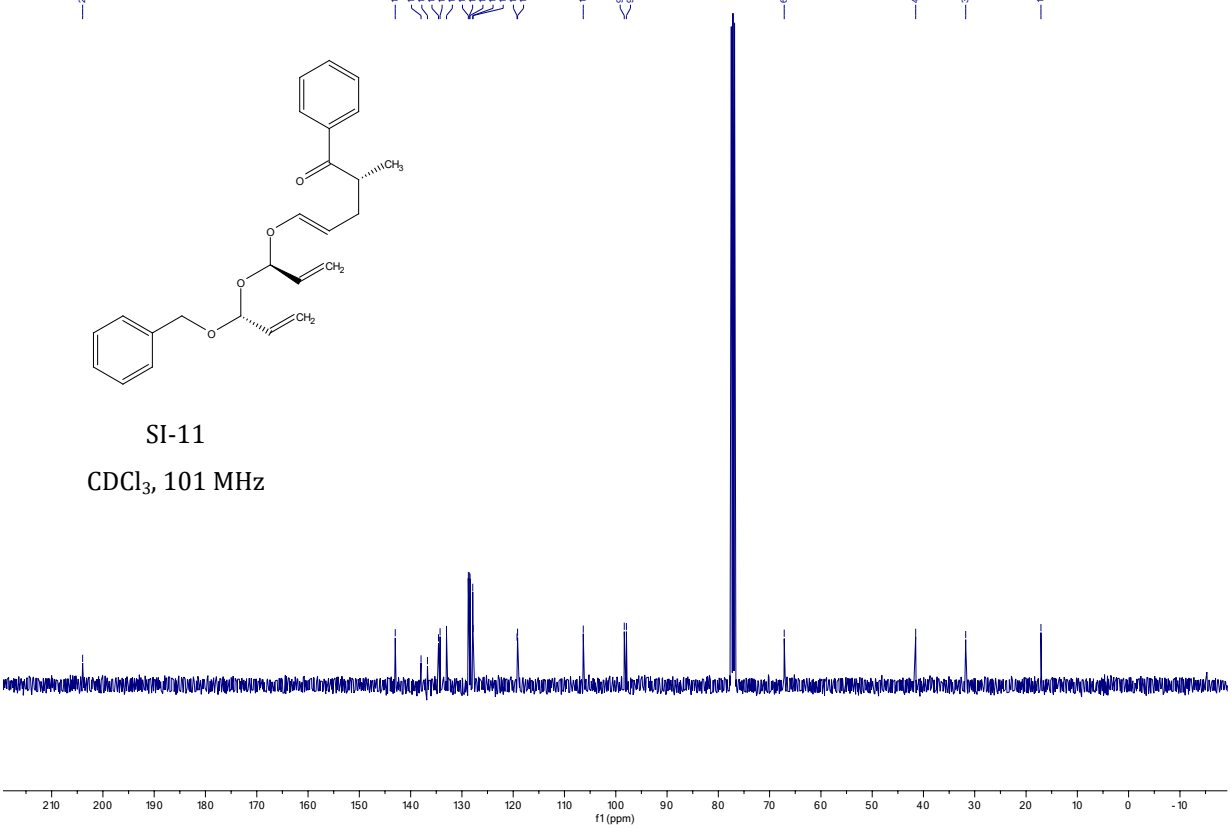
SI-10

$CDCl_3$, 400 MHz



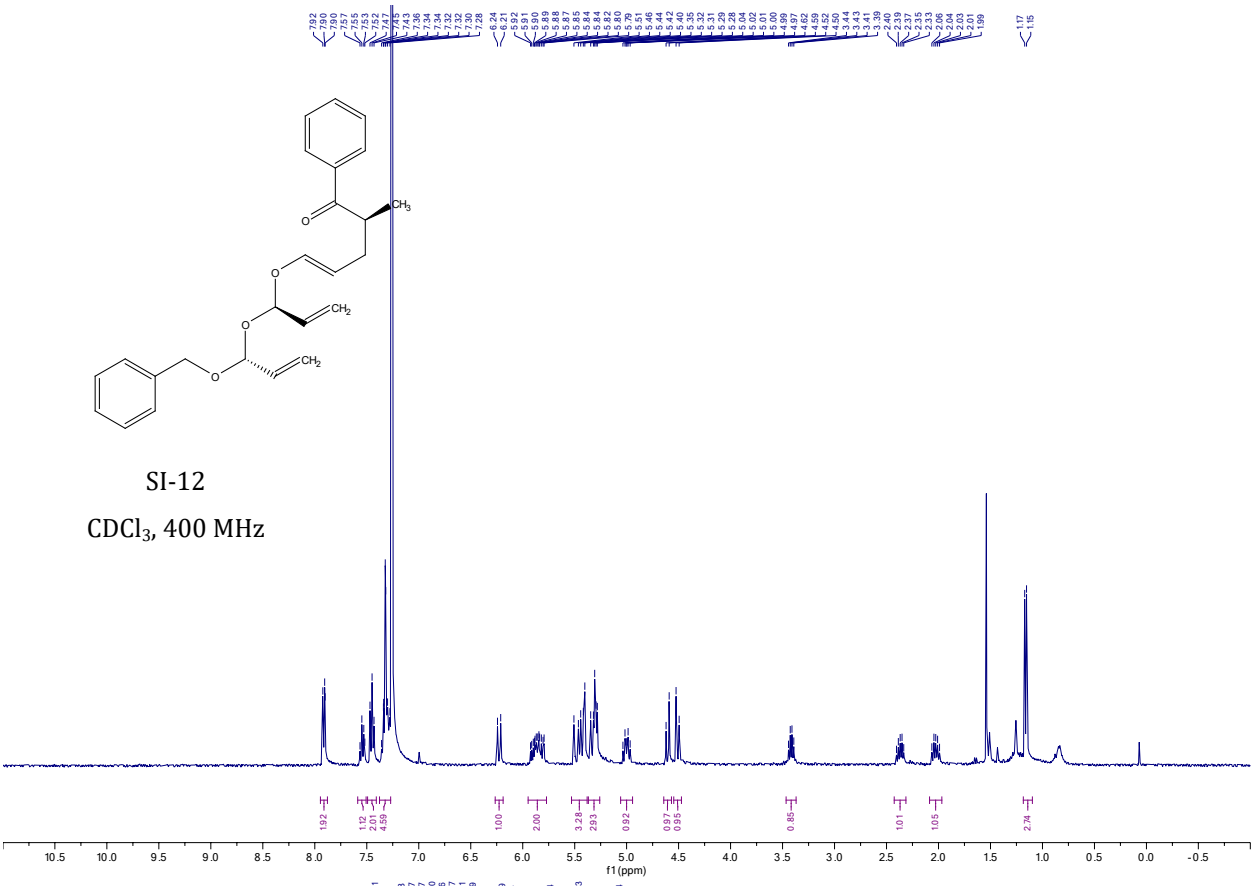
SI-11

$CDCl_3$, 400 MHz



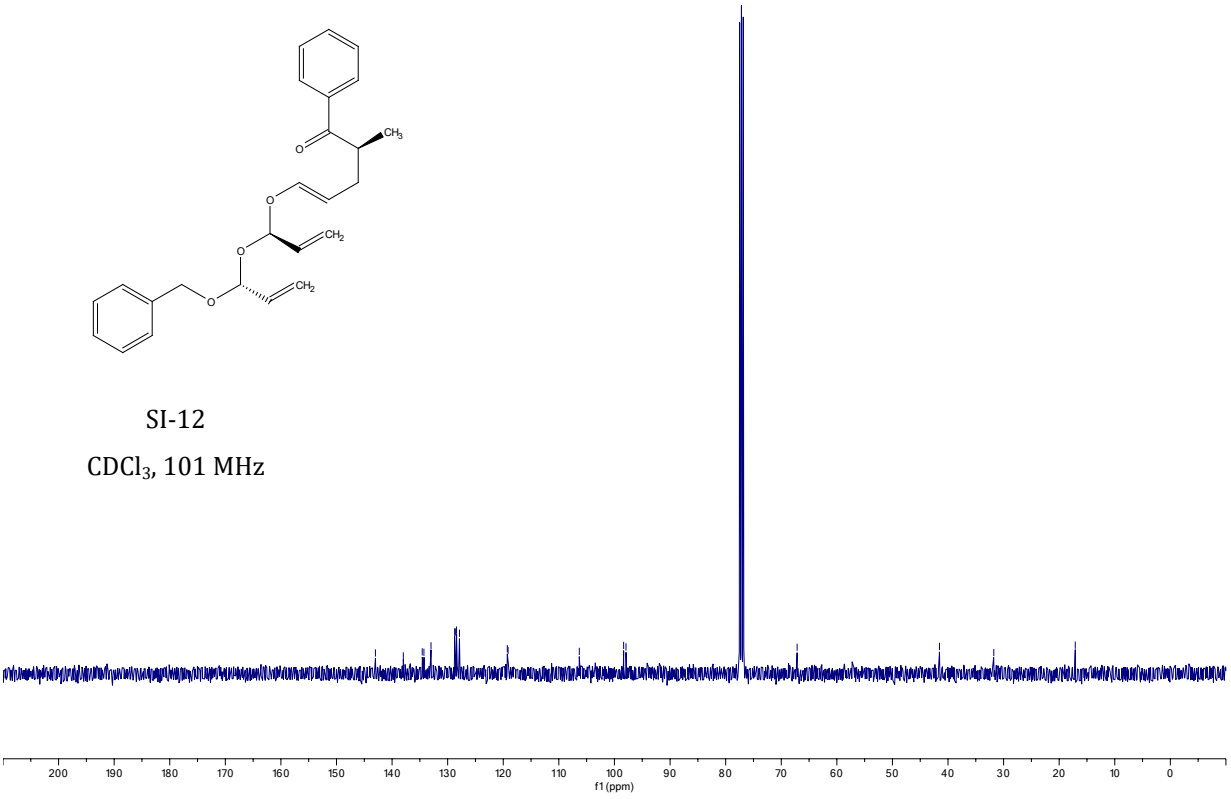
SI-11

$CDCl_3$, 101 MHz



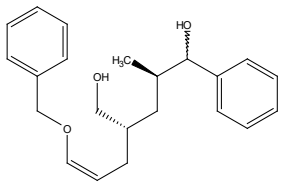
SI-12

$CDCl_3$, 400 MHz



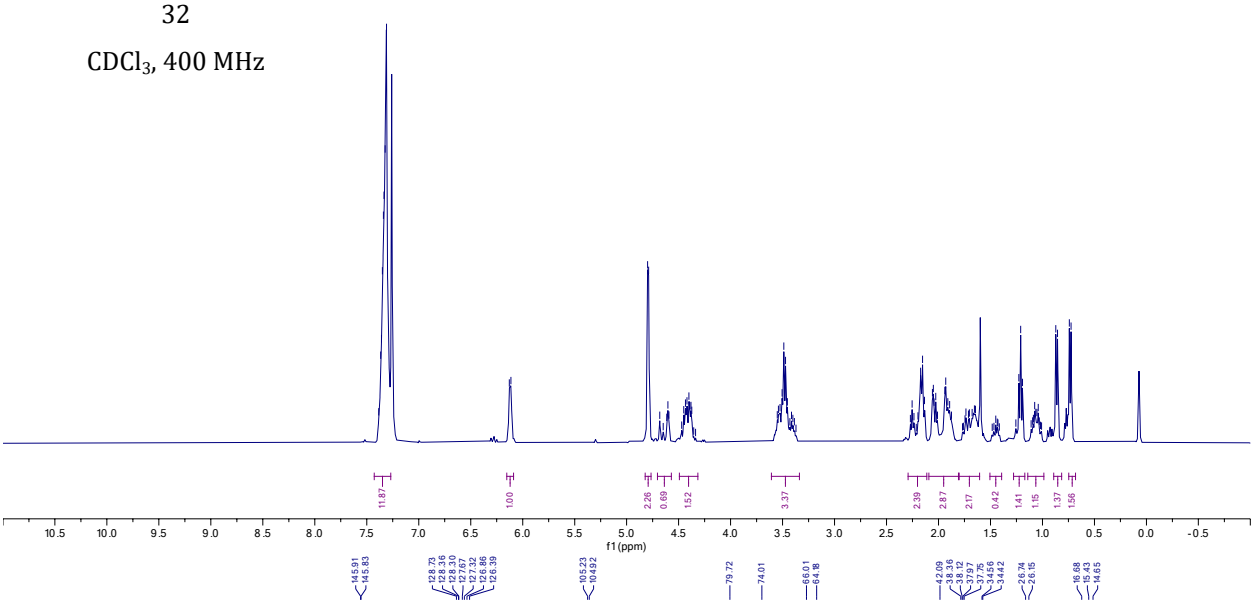
SI-12

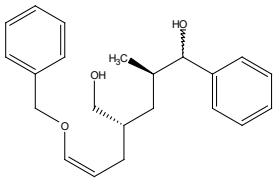
$CDCl_3$, 101 MHz



32

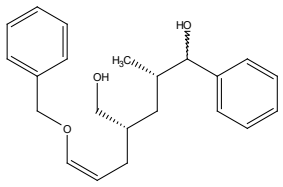
$CDCl_3$, 400 MHz





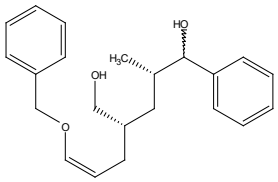
32

$CDCl_3$, 101 MHz



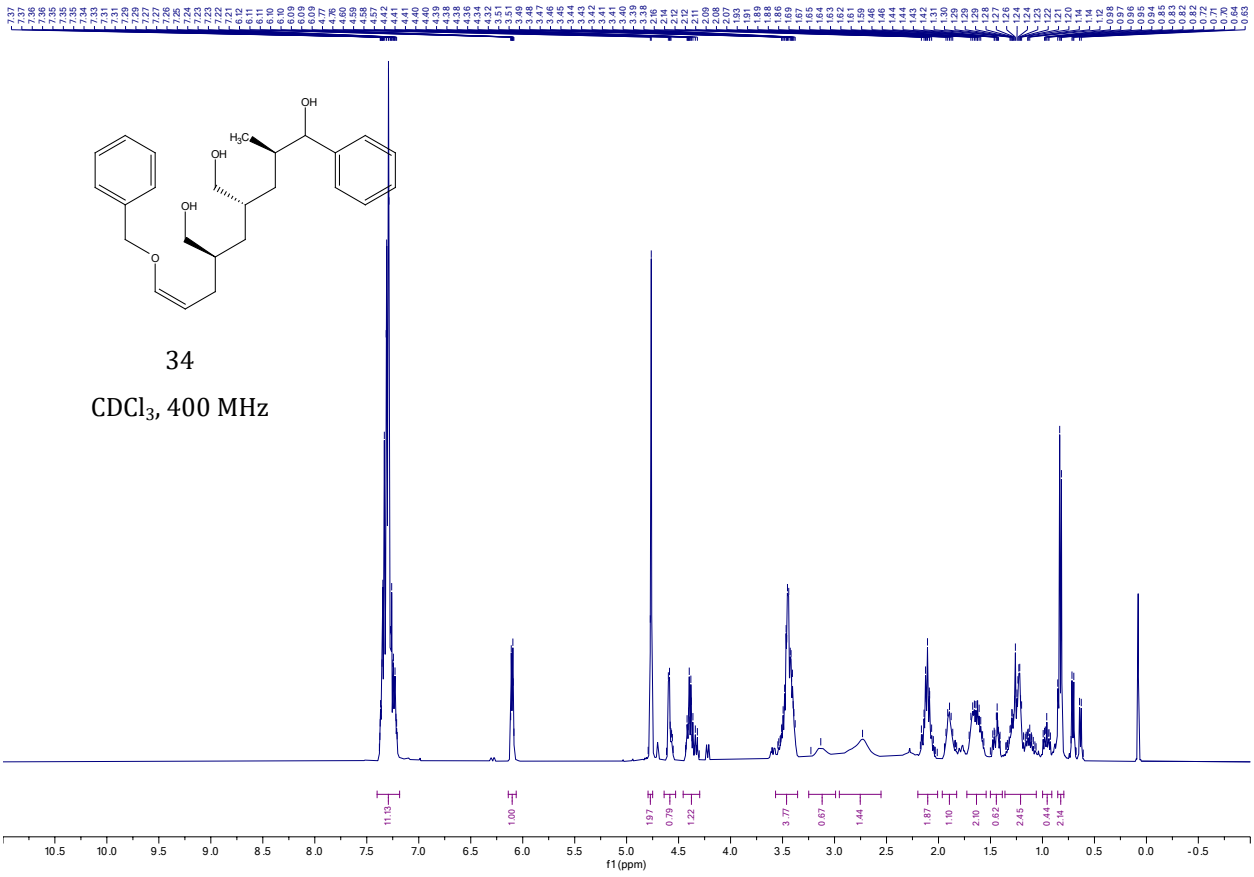
33

$CDCl_3$, 400 MHz



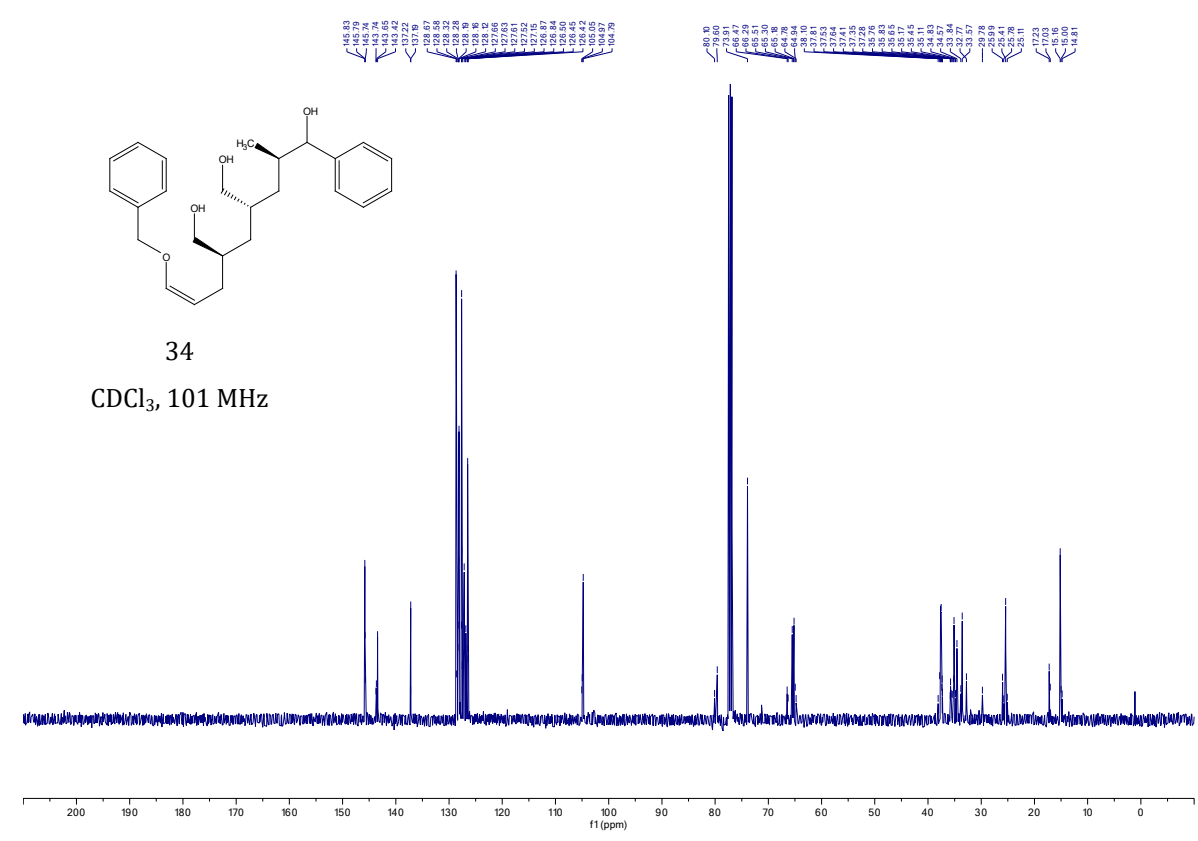
33

$CDCl_3$, 101 MHz



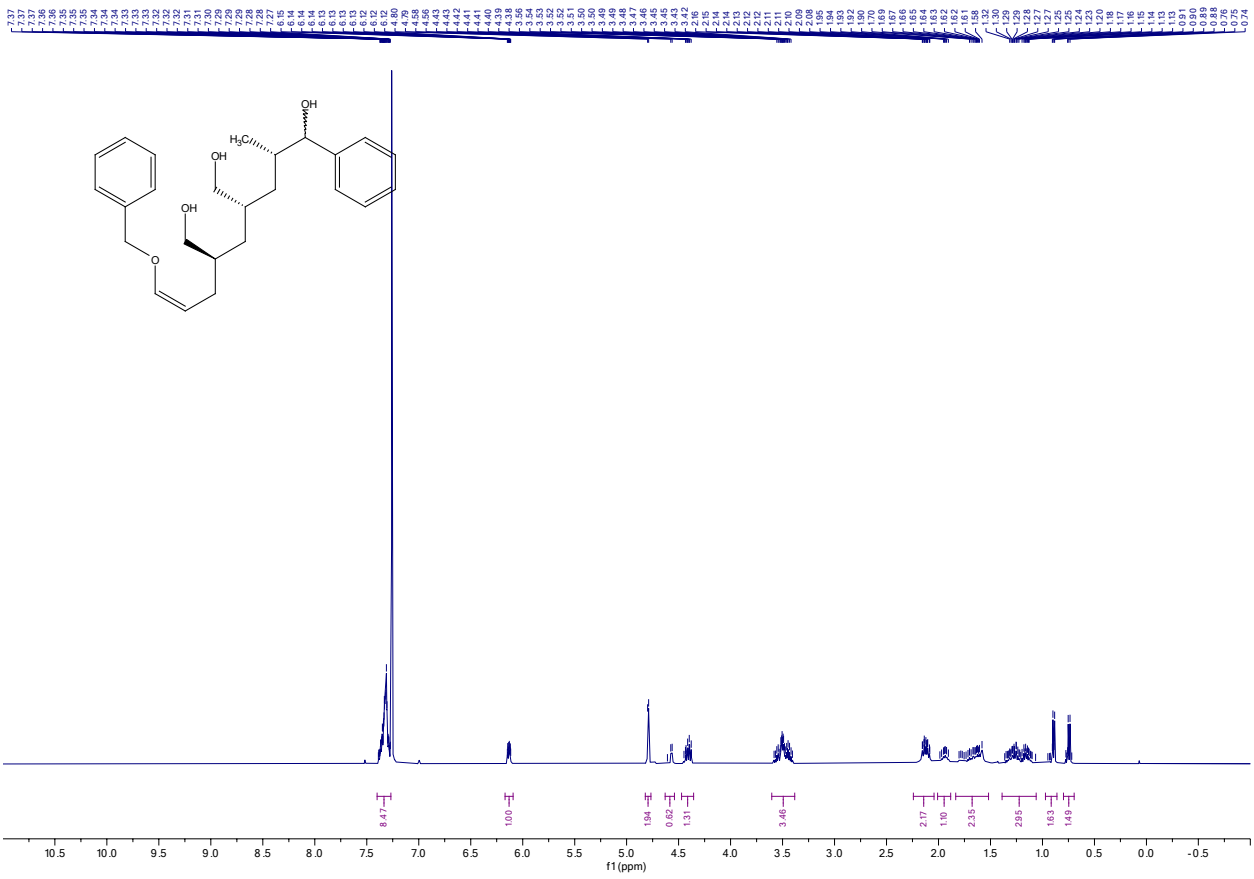
34

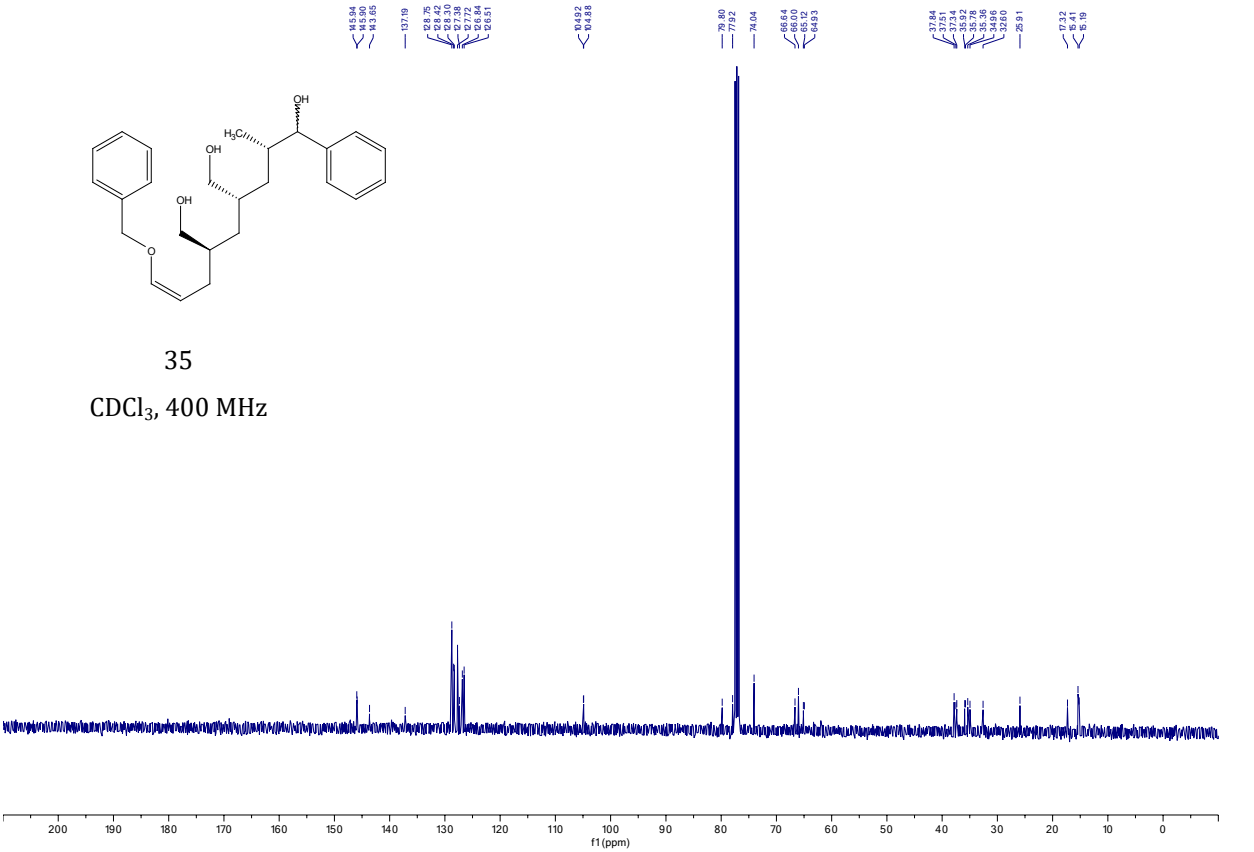
$CDCl_3$, 400 MHz



34

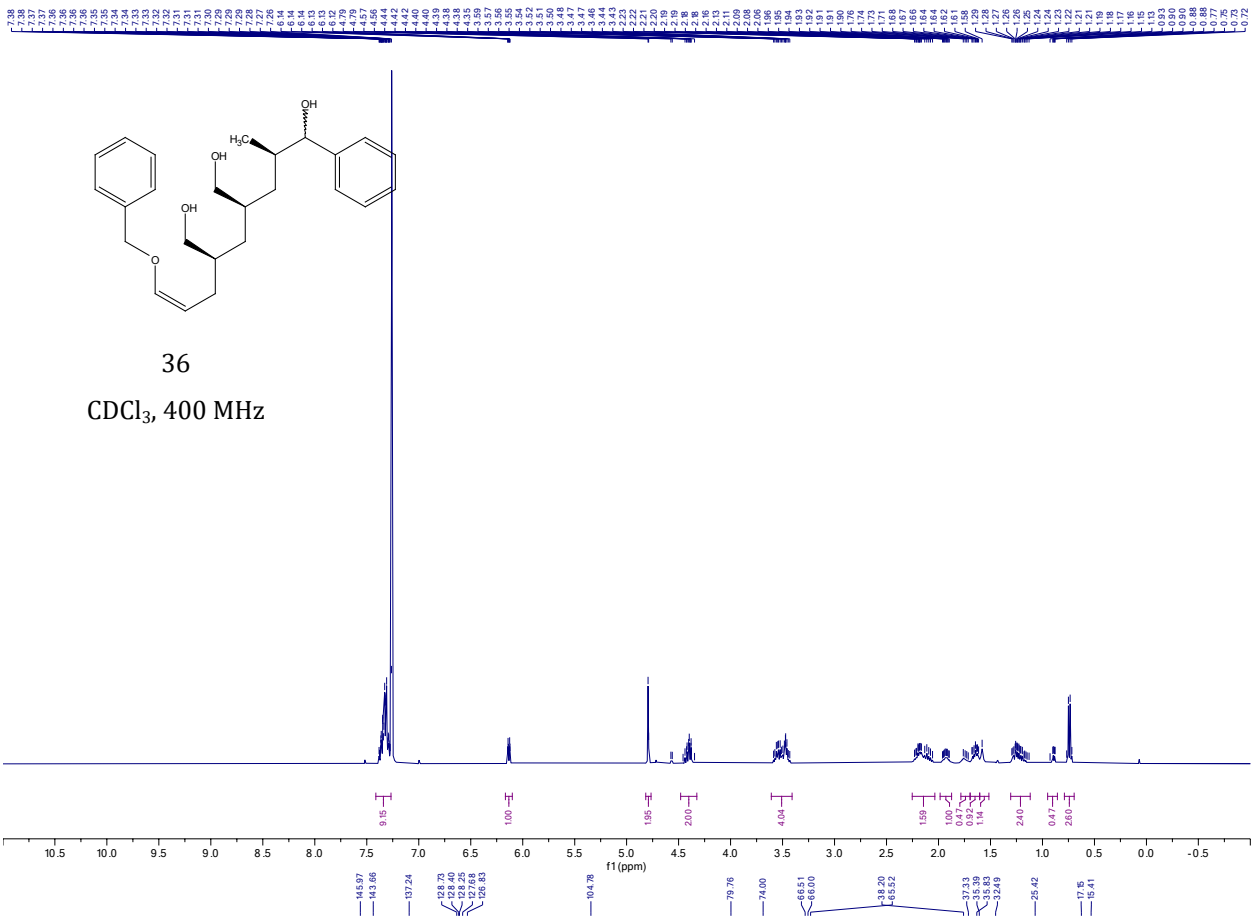
$CDCl_3$, 101 MHz





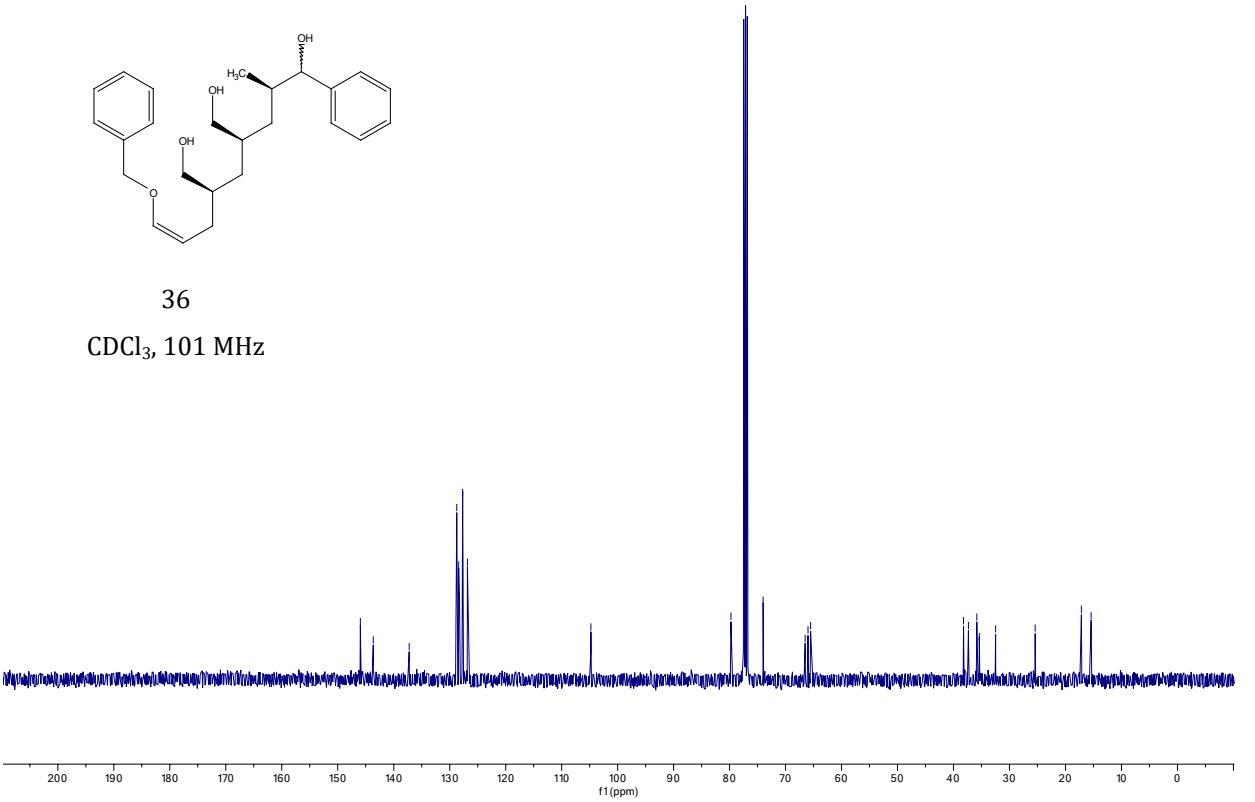
35

$CDCl_3$, 400 MHz



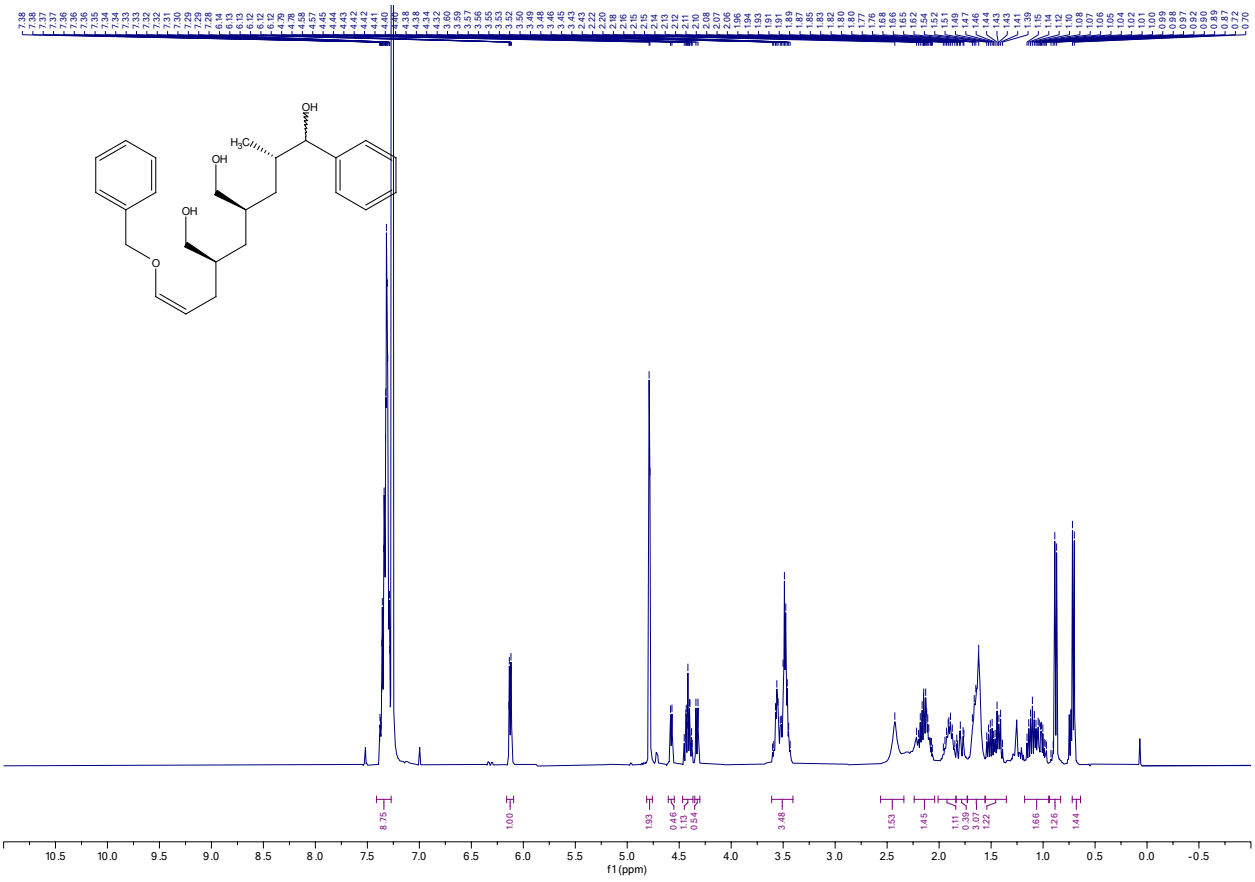
36

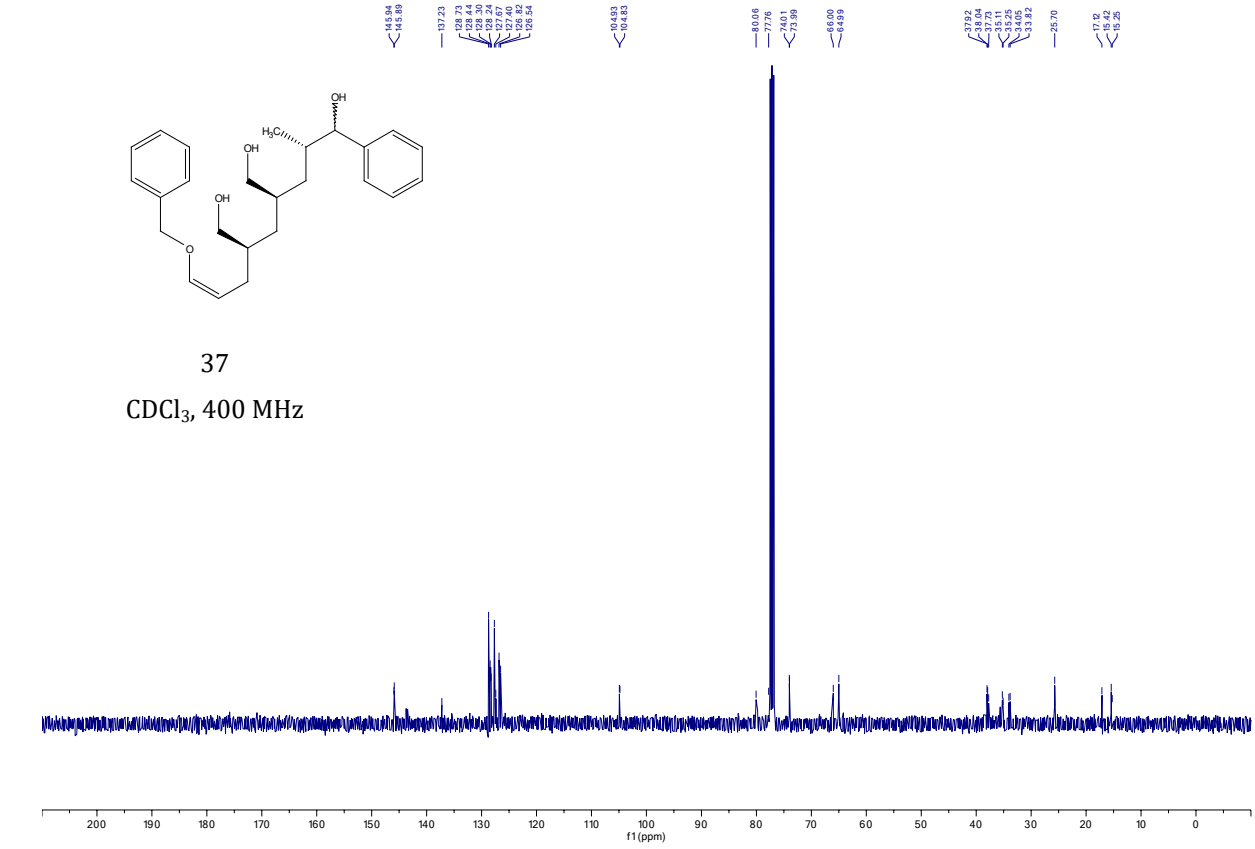
$CDCl_3$, 400 MHz



36

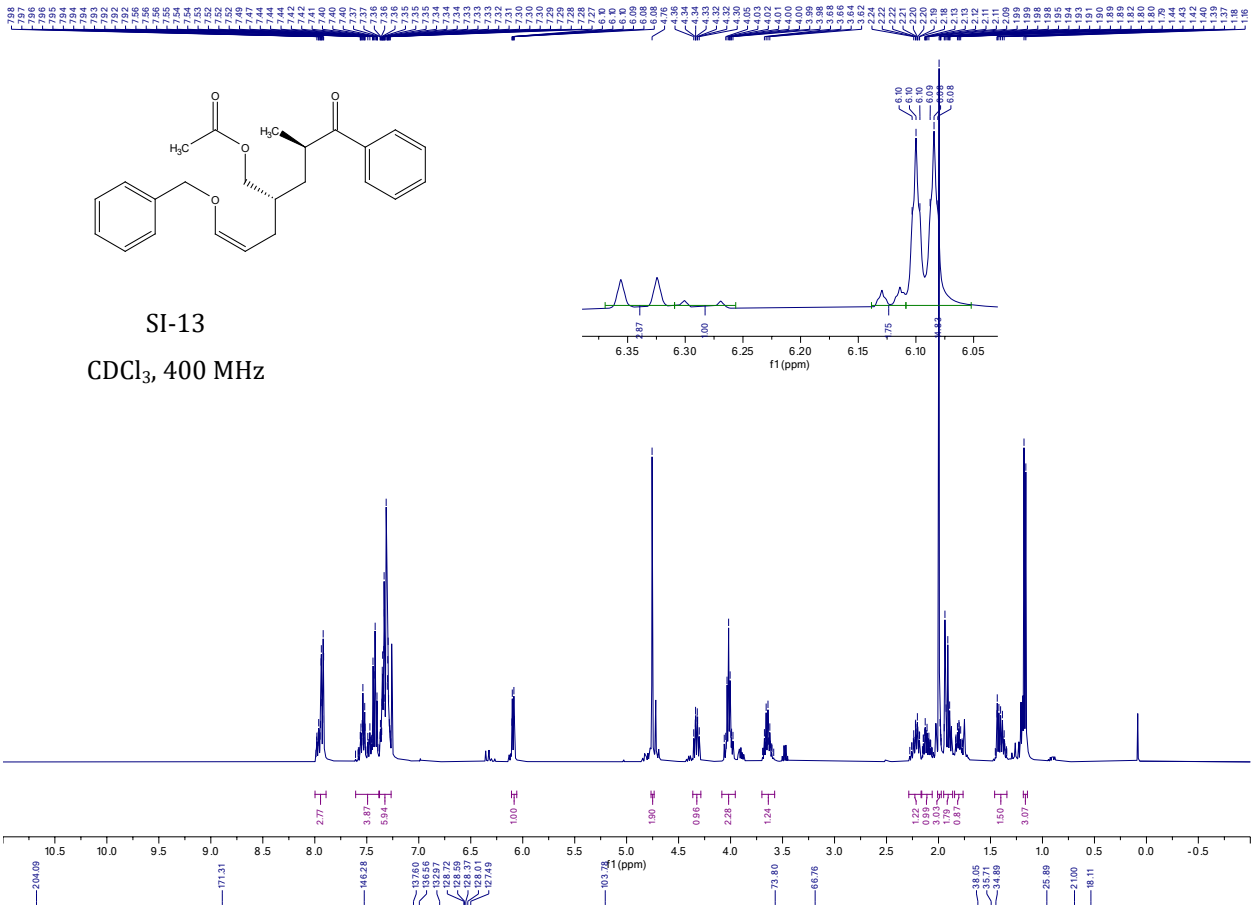
$CDCl_3$, 101 MHz





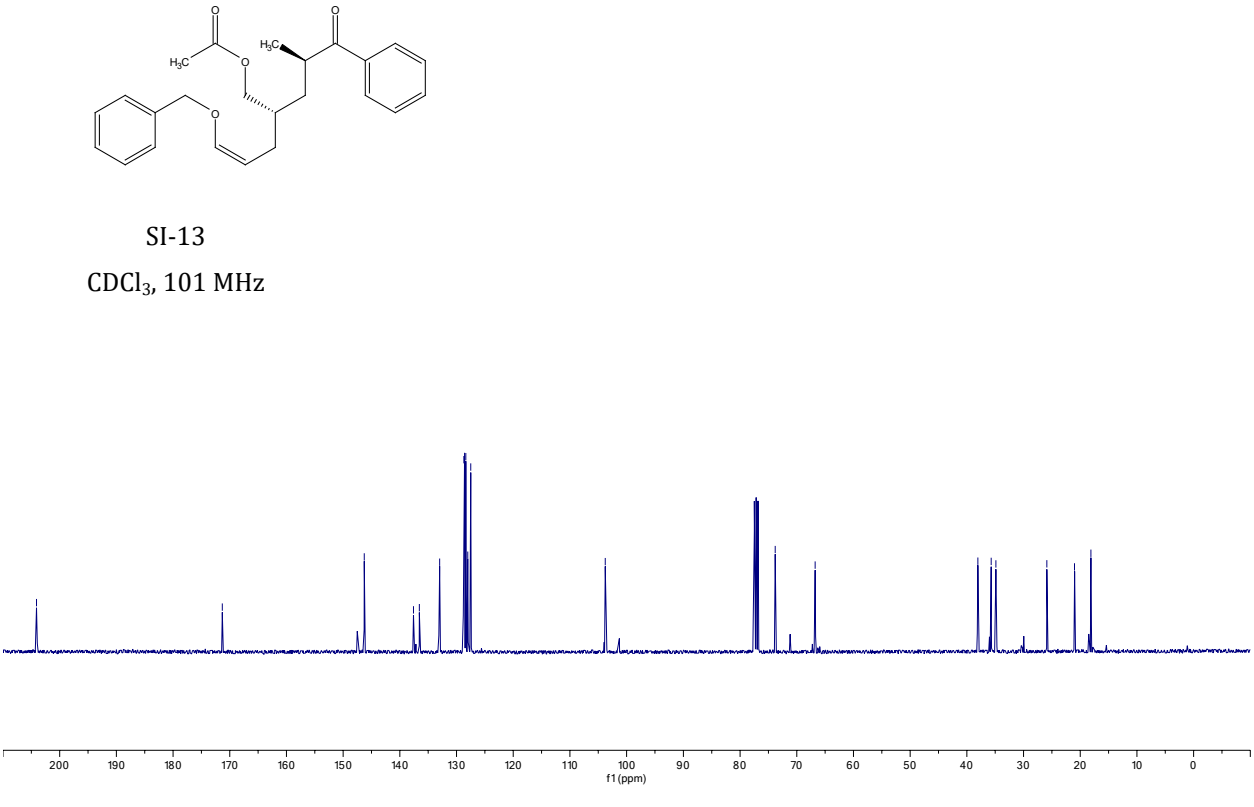
37

$CDCl_3$, 400 MHz



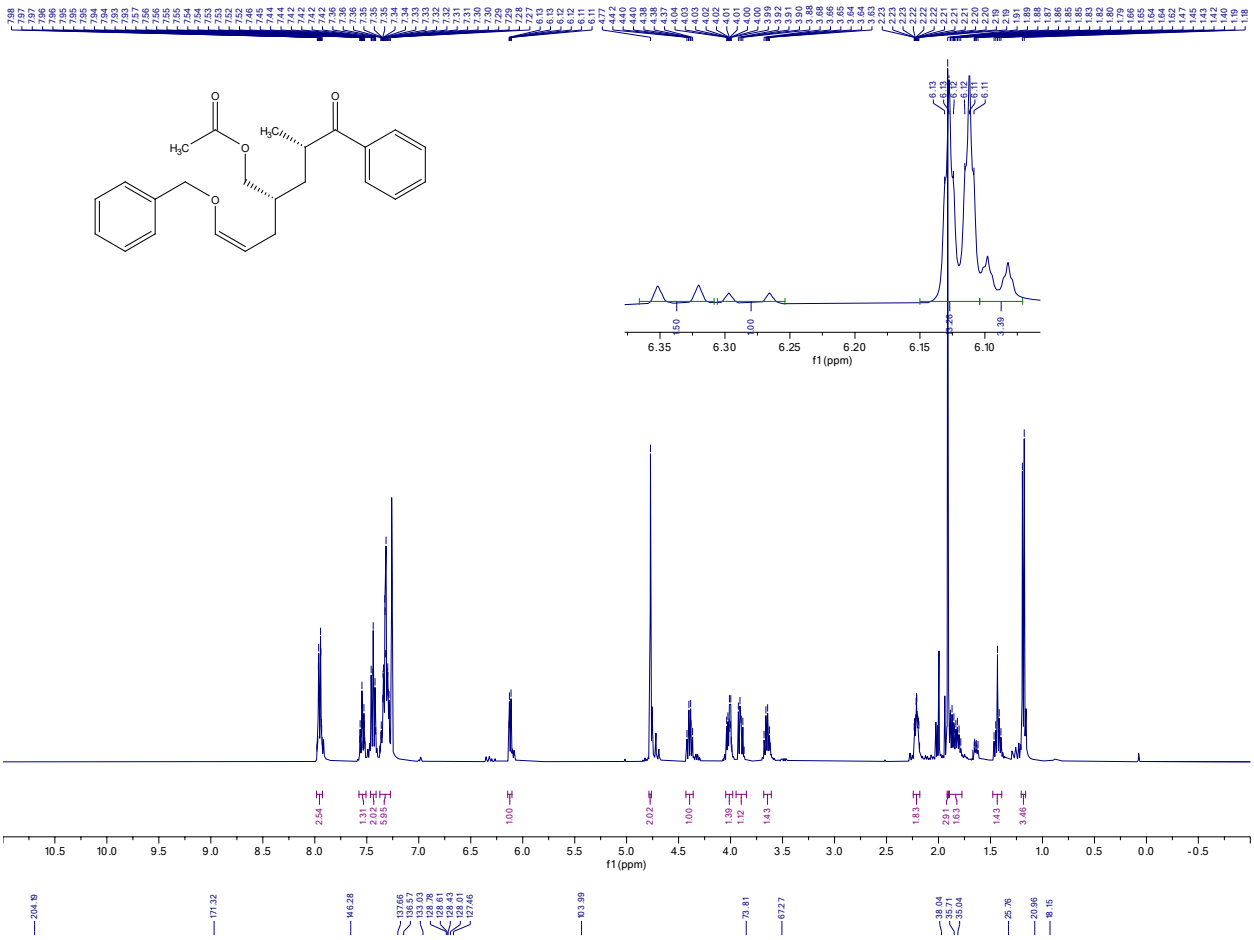
SI-13

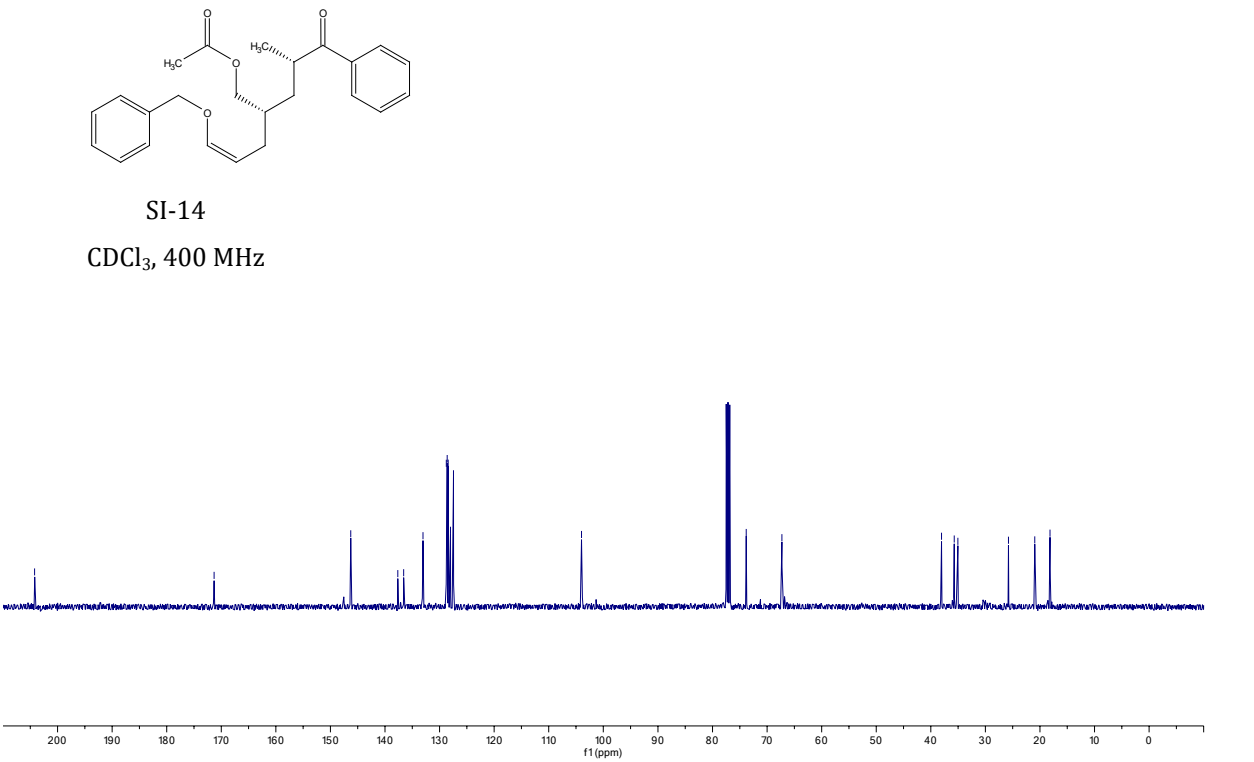
$CDCl_3$, 400 MHz



SI-13

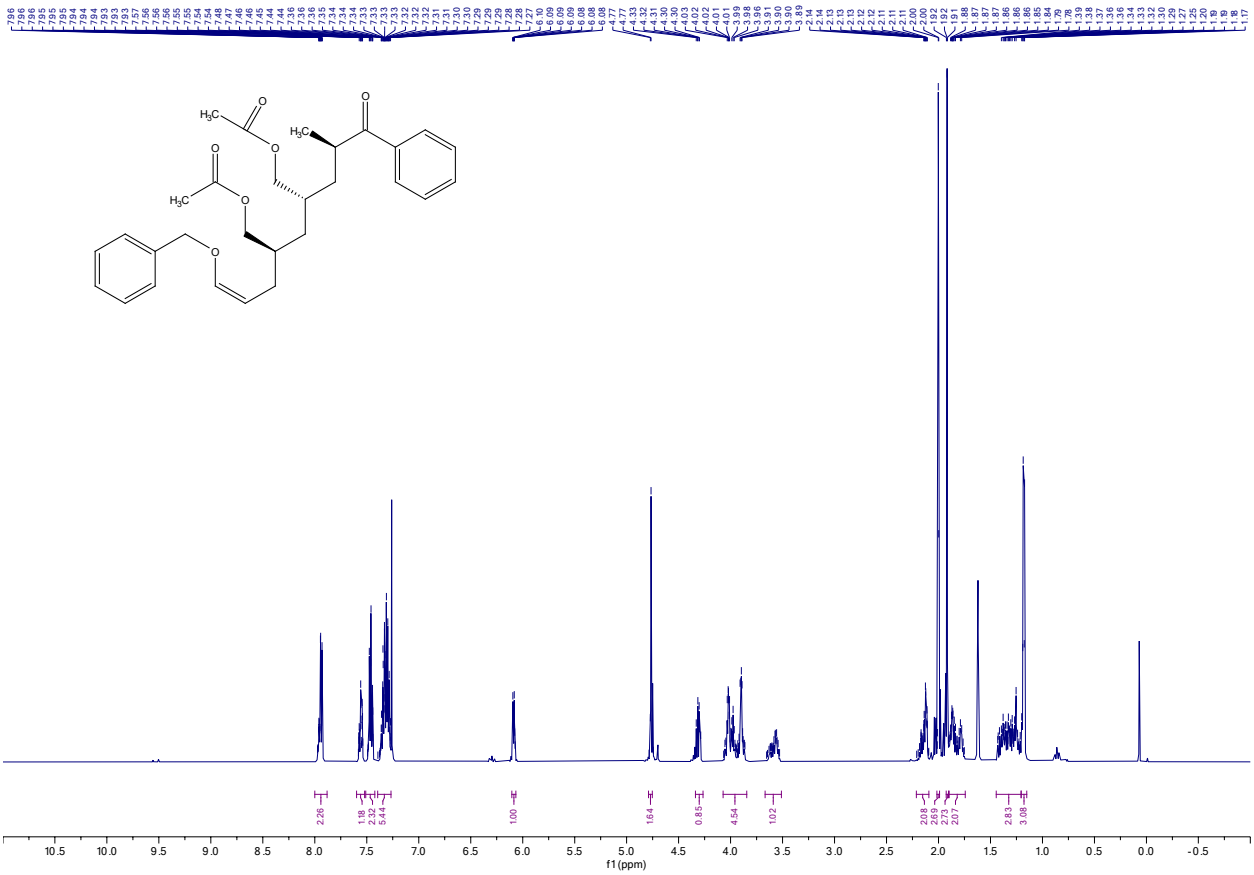
$CDCl_3$, 101 MHz

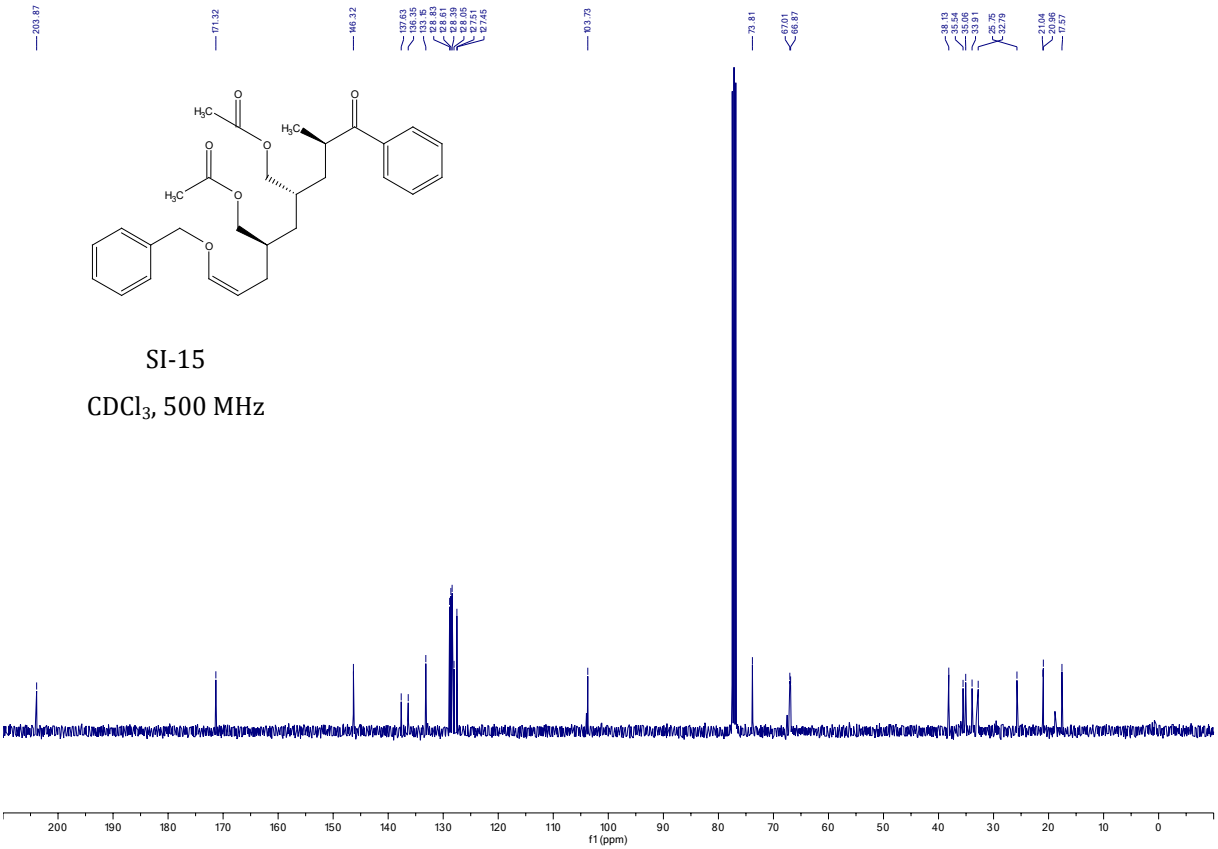




SI-14

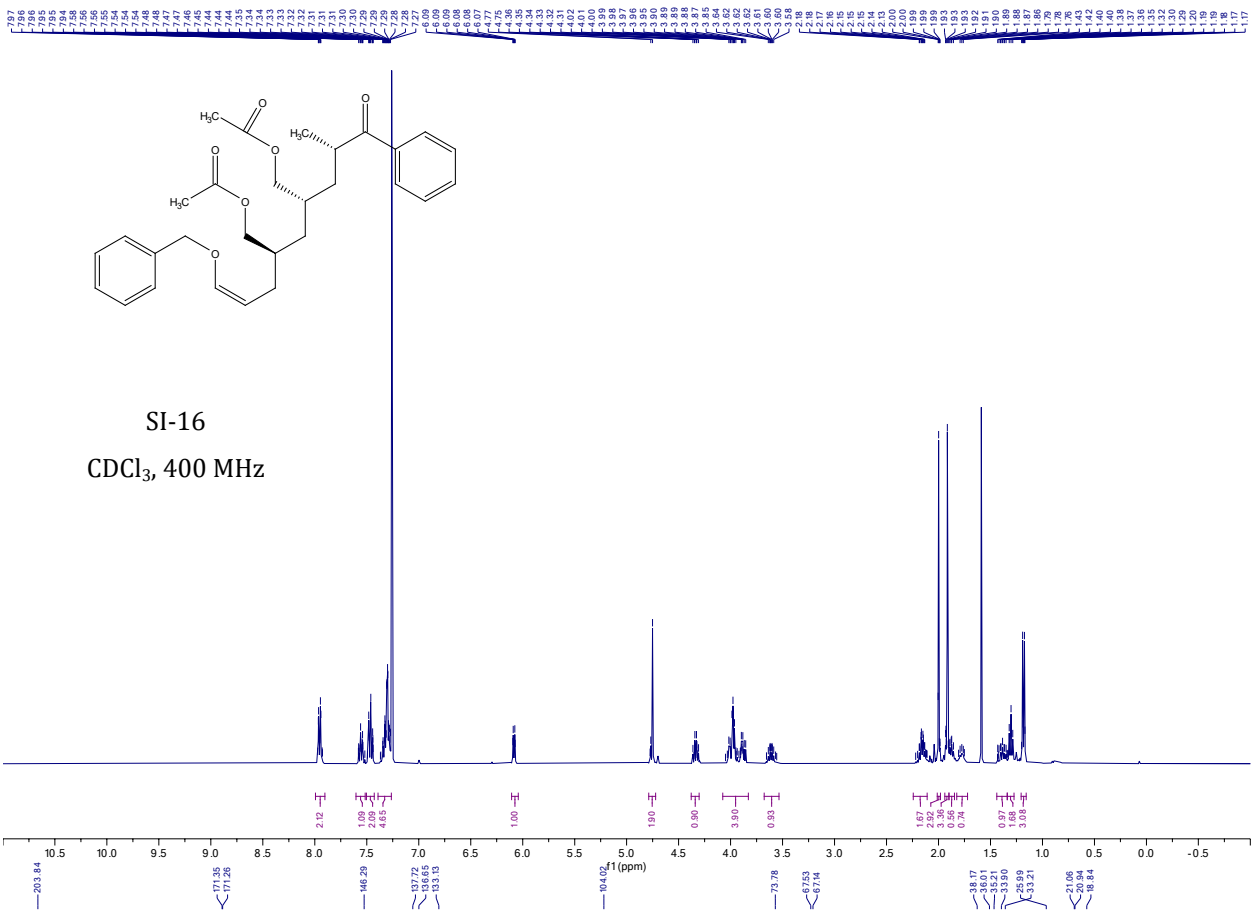
$CDCl_3$, 400 MHz





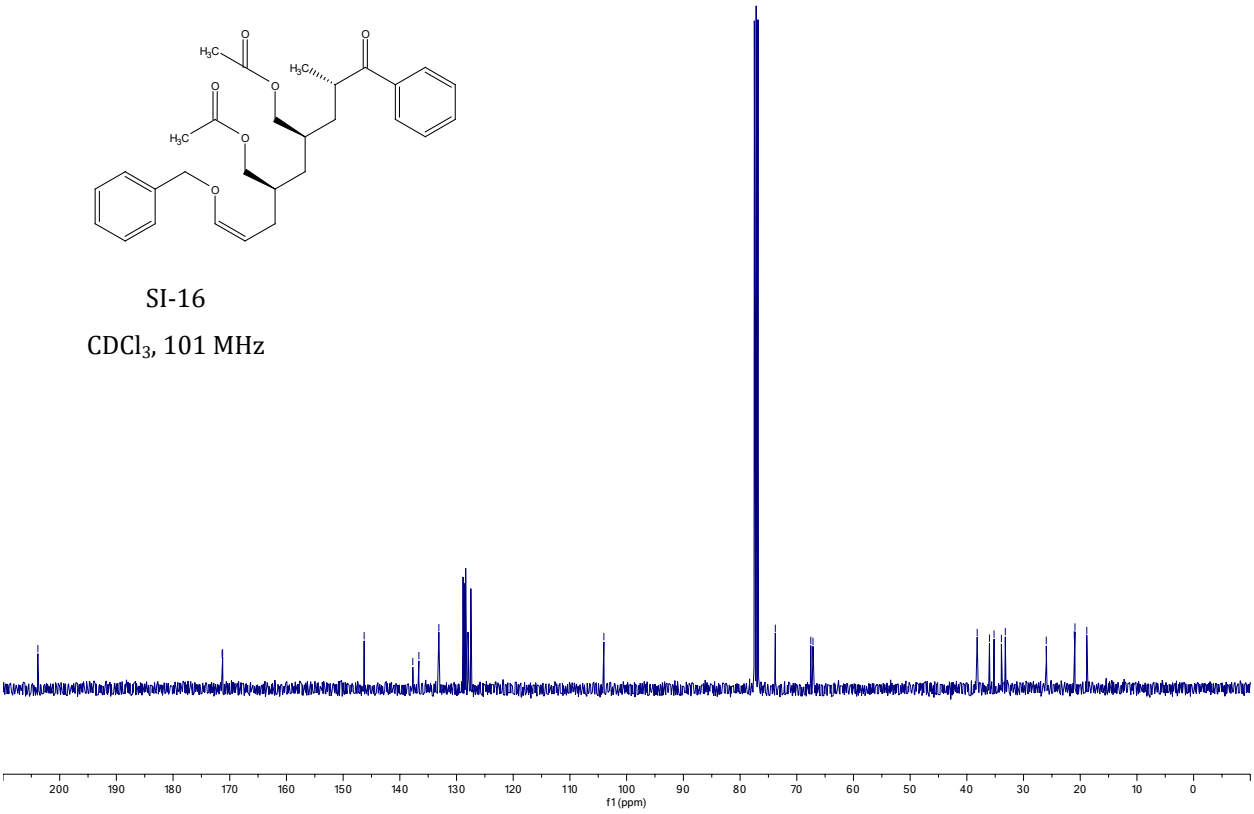
SI-15

$CDCl_3$, 500 MHz



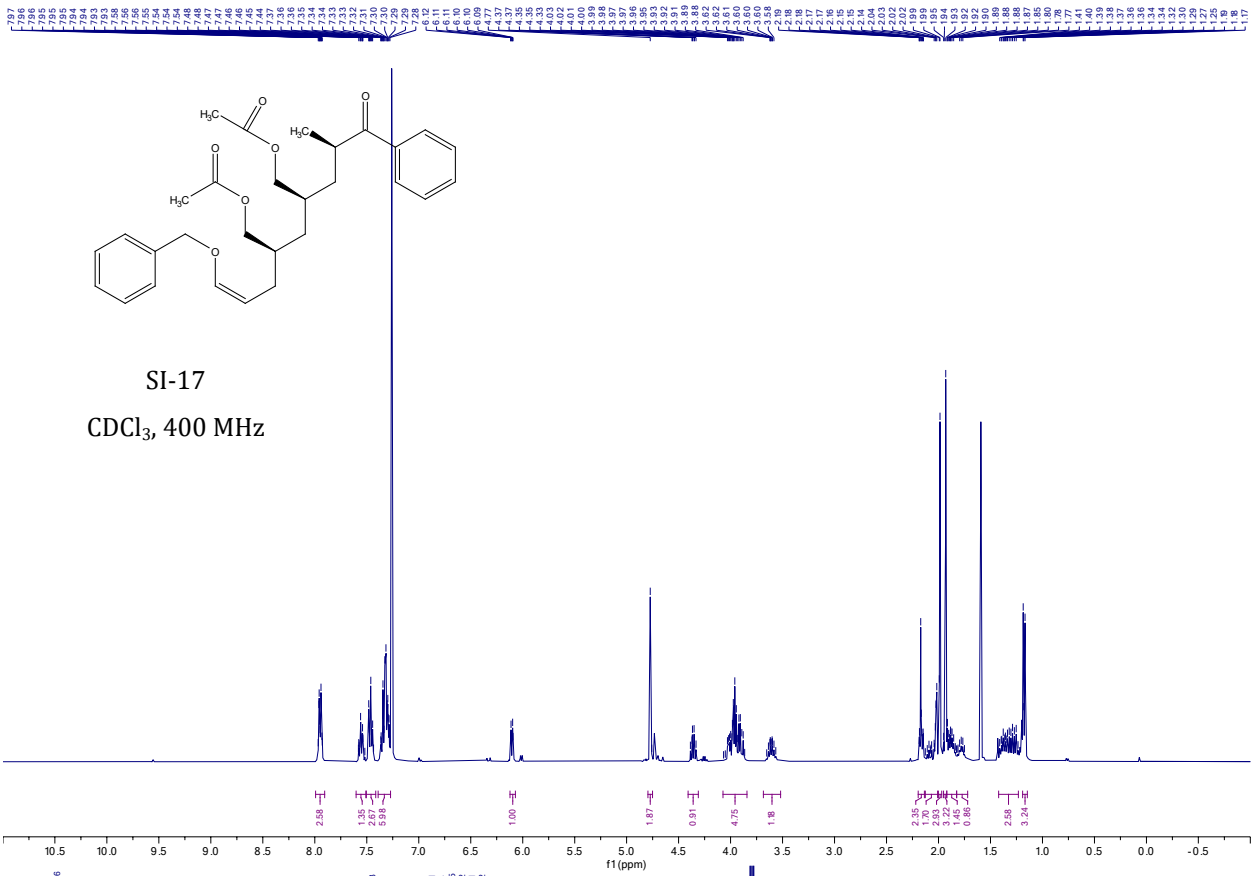
SI-16

$CDCl_3$, 400 MHz



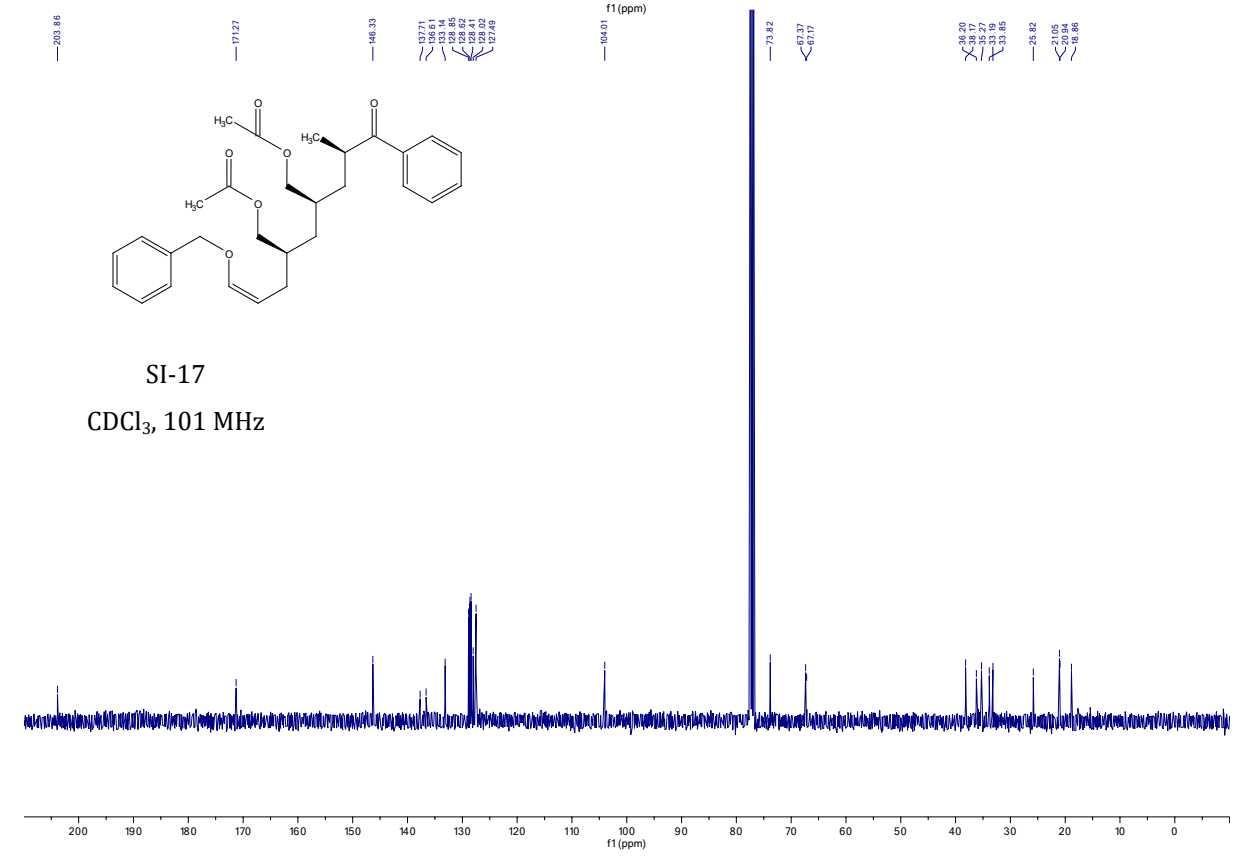
SI-16

$CDCl_3$, 101 MHz



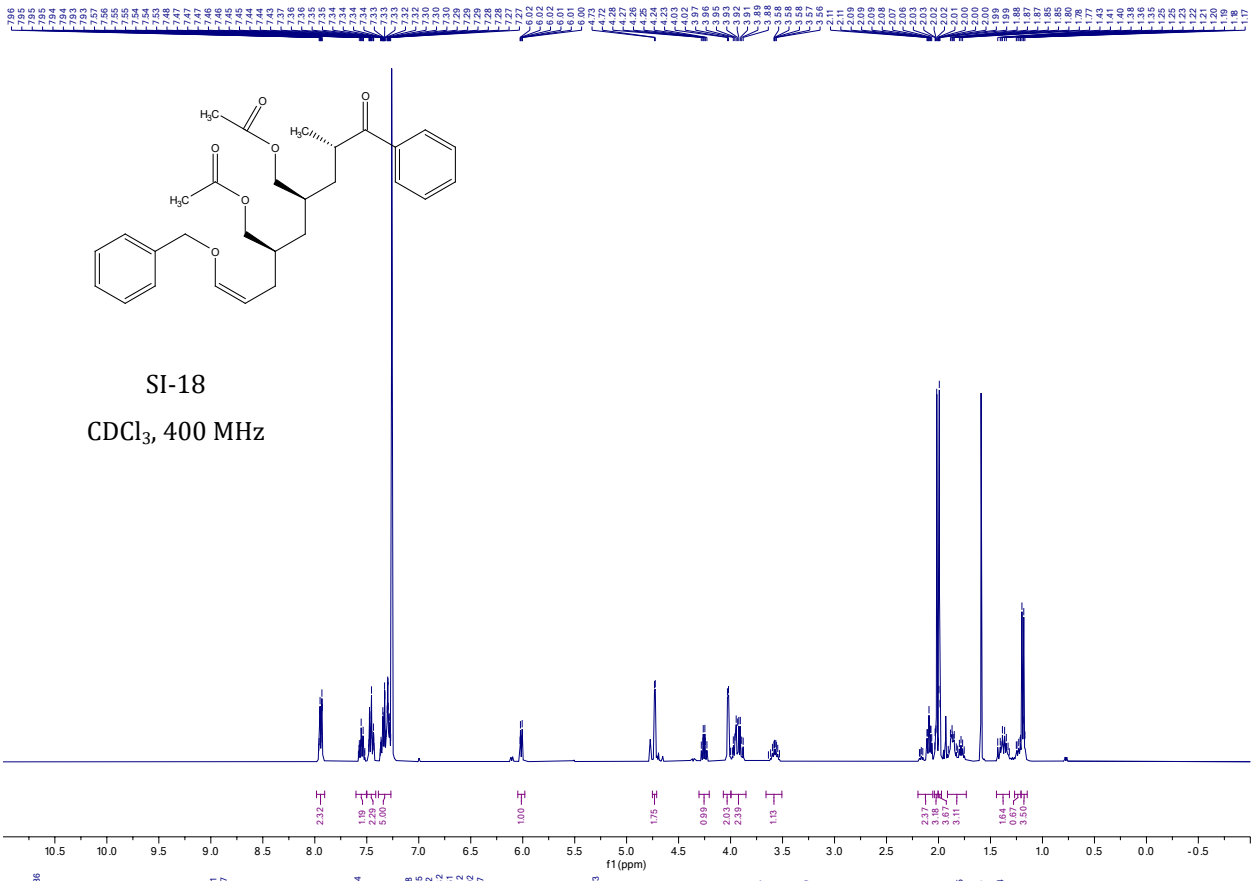
SI-17

$CDCl_3$, 400 MHz



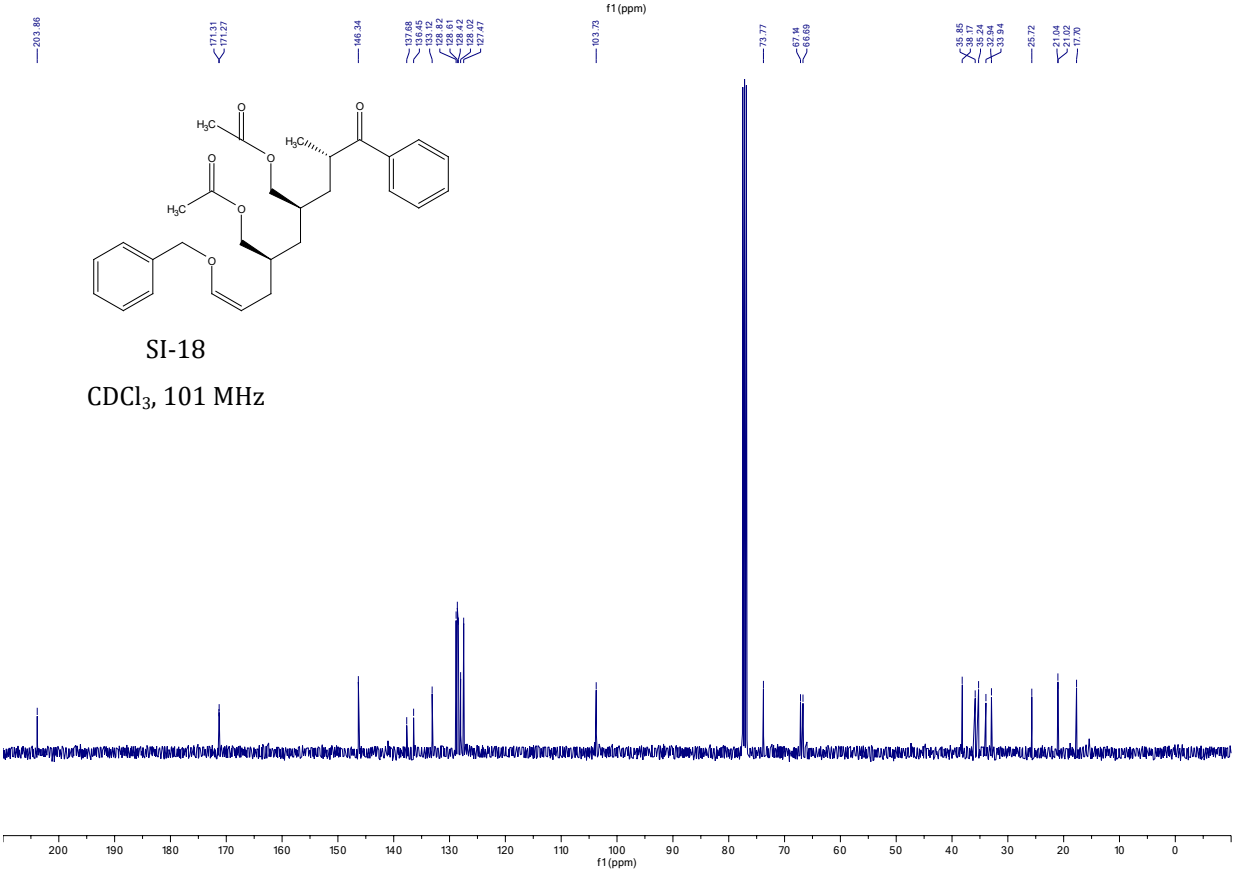
SI-17

$CDCl_3$, 101 MHz



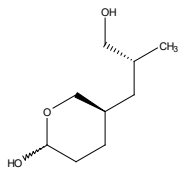
SI-18

$CDCl_3$, 400 MHz



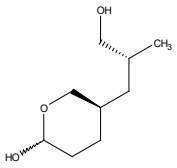
SI-18

$CDCl_3$, 101 MHz



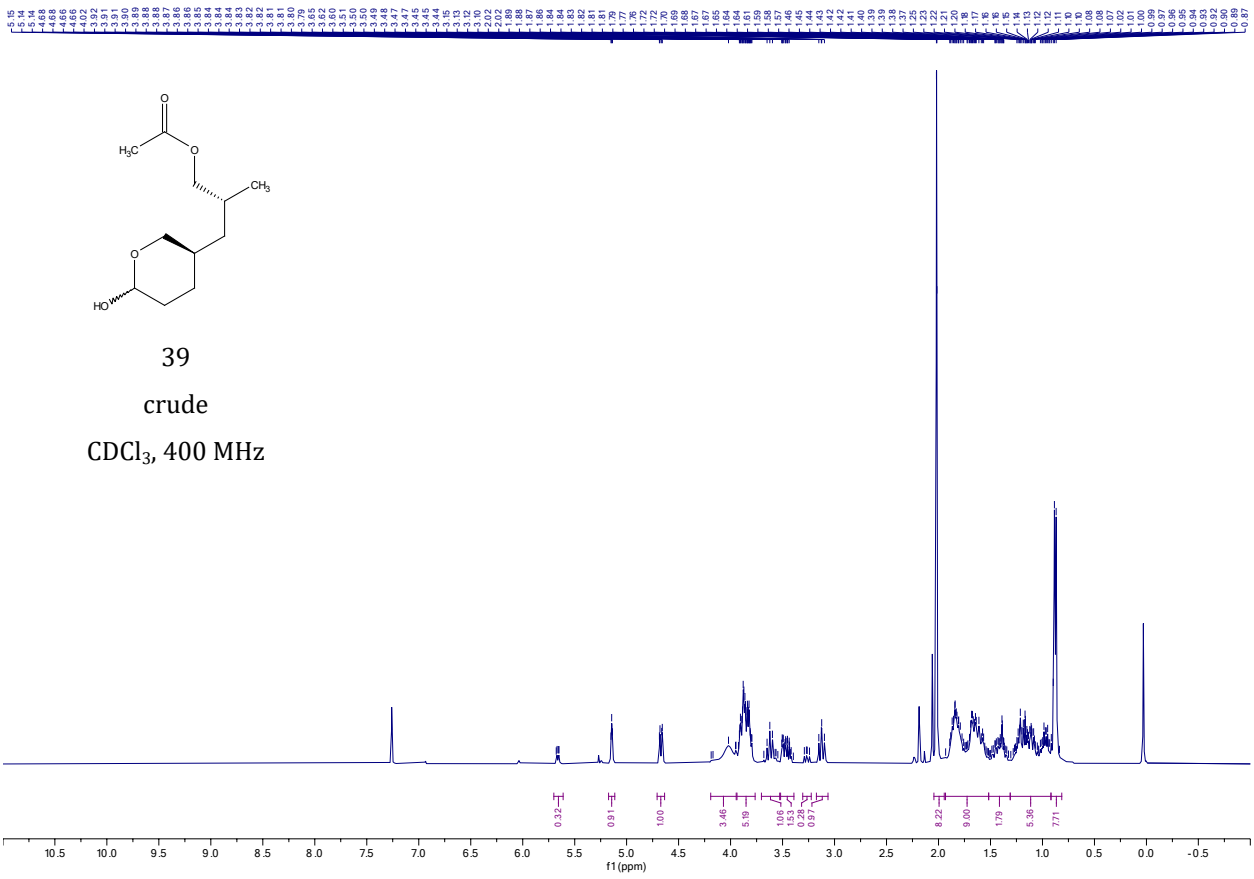
38

$CDCl_3$, 400 MHz



38

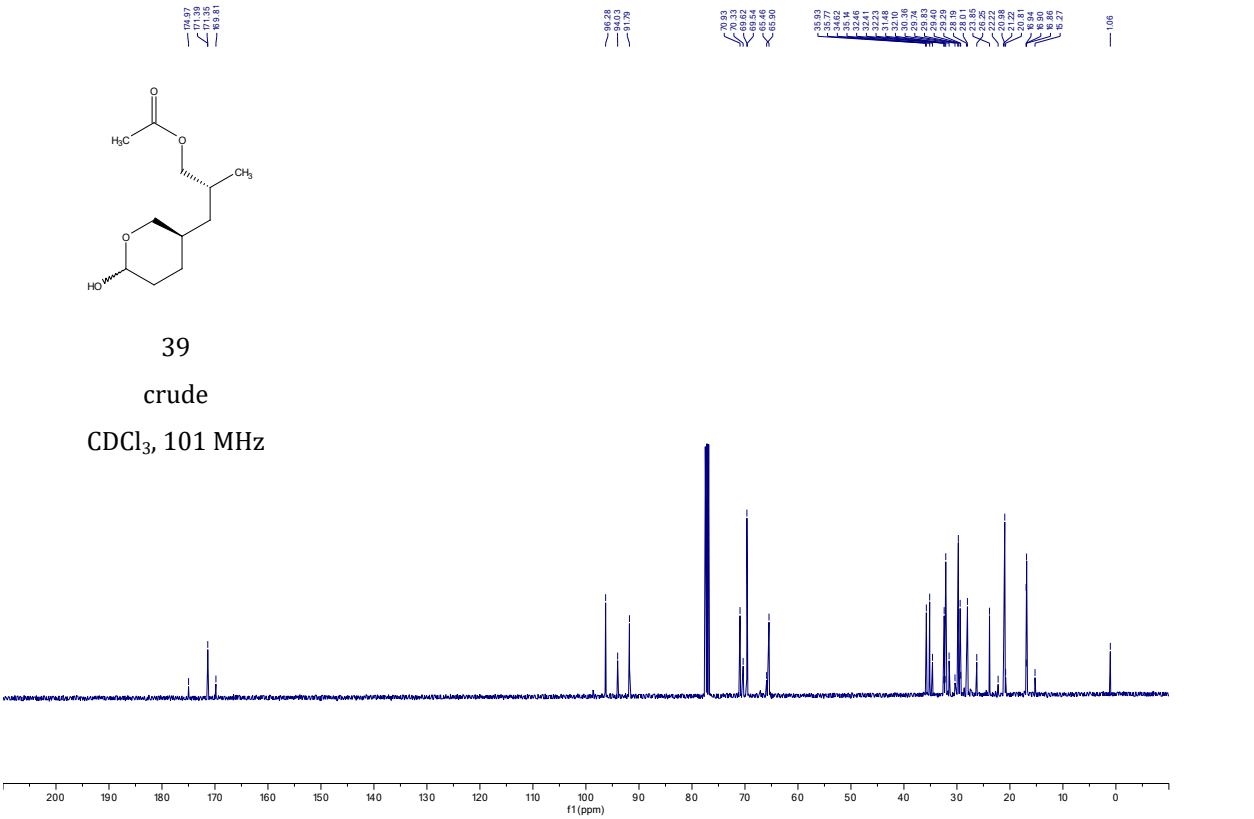
$CDCl_3$, 101 MHz



39

crude

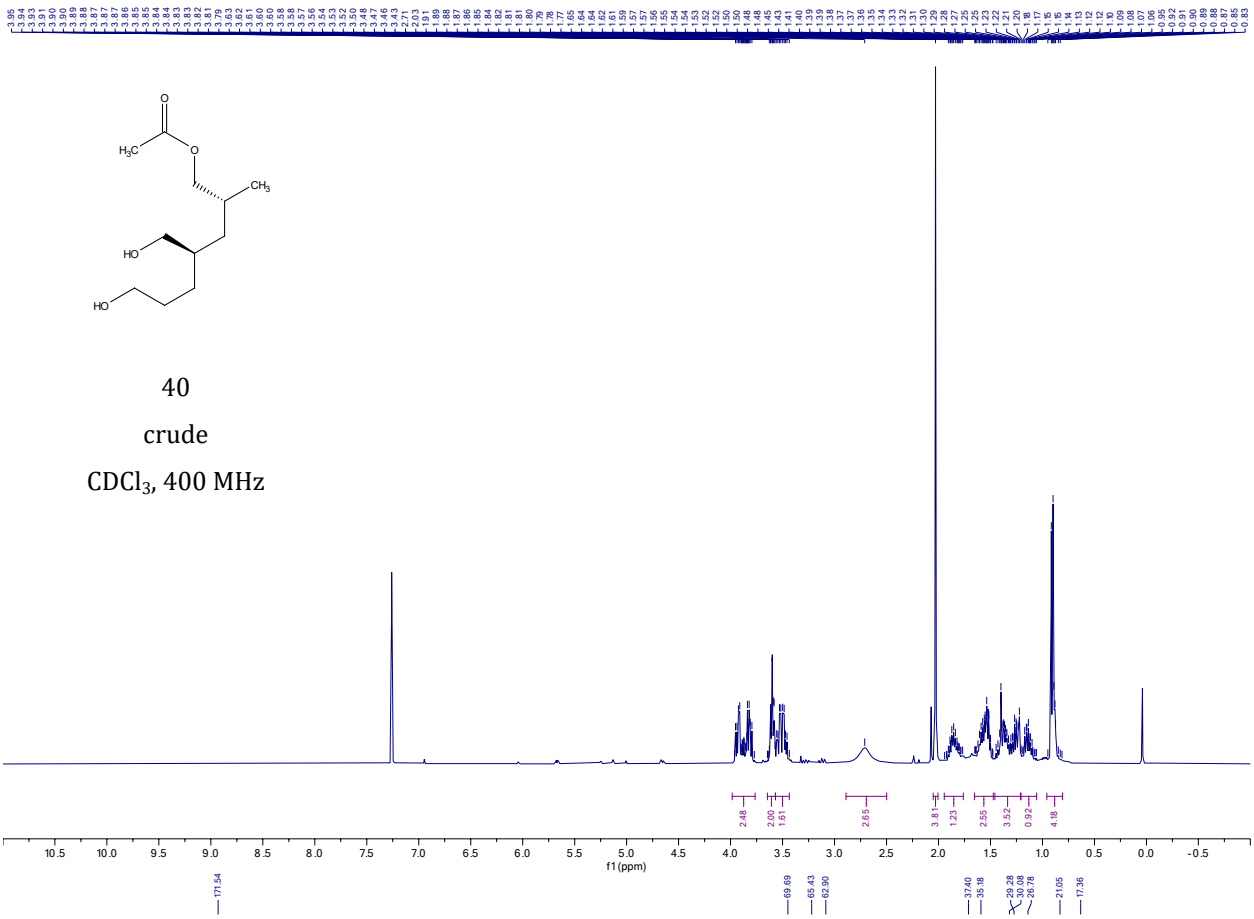
$CDCl_3$, 400 MHz



39

crude

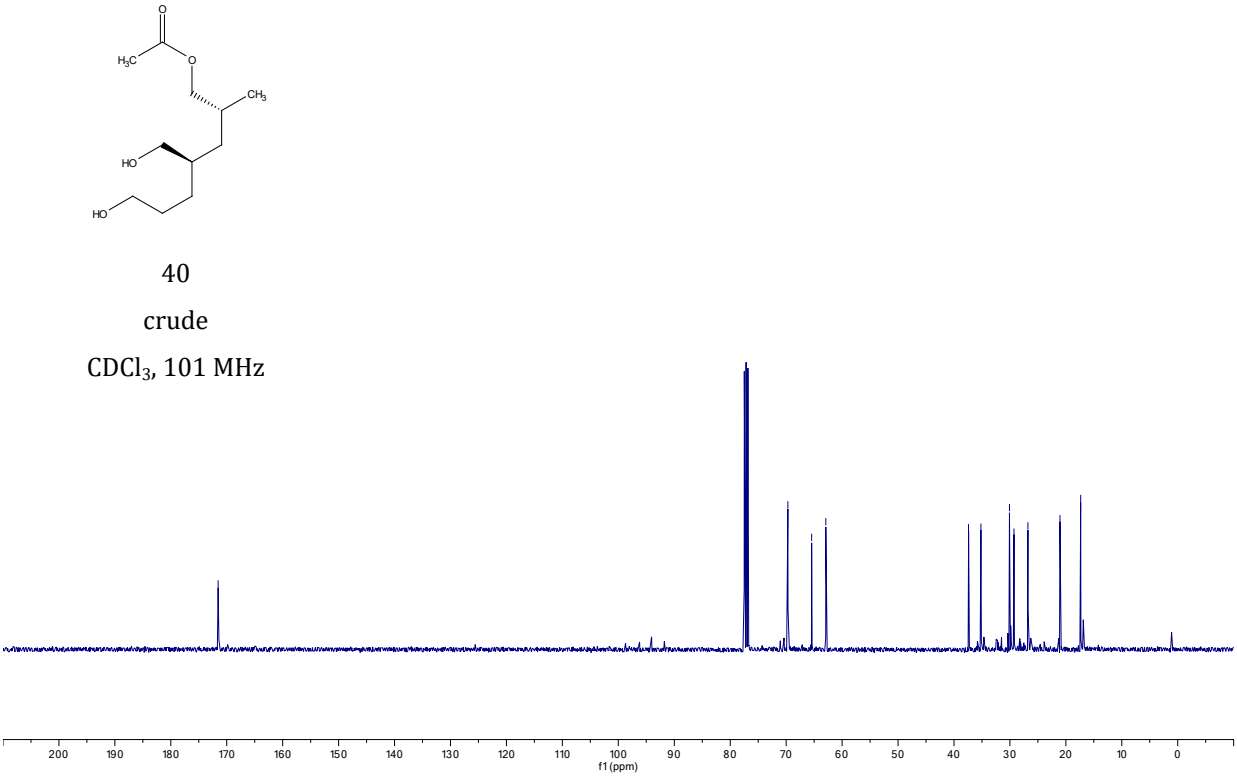
$CDCl_3$, 101 MHz



40

crude

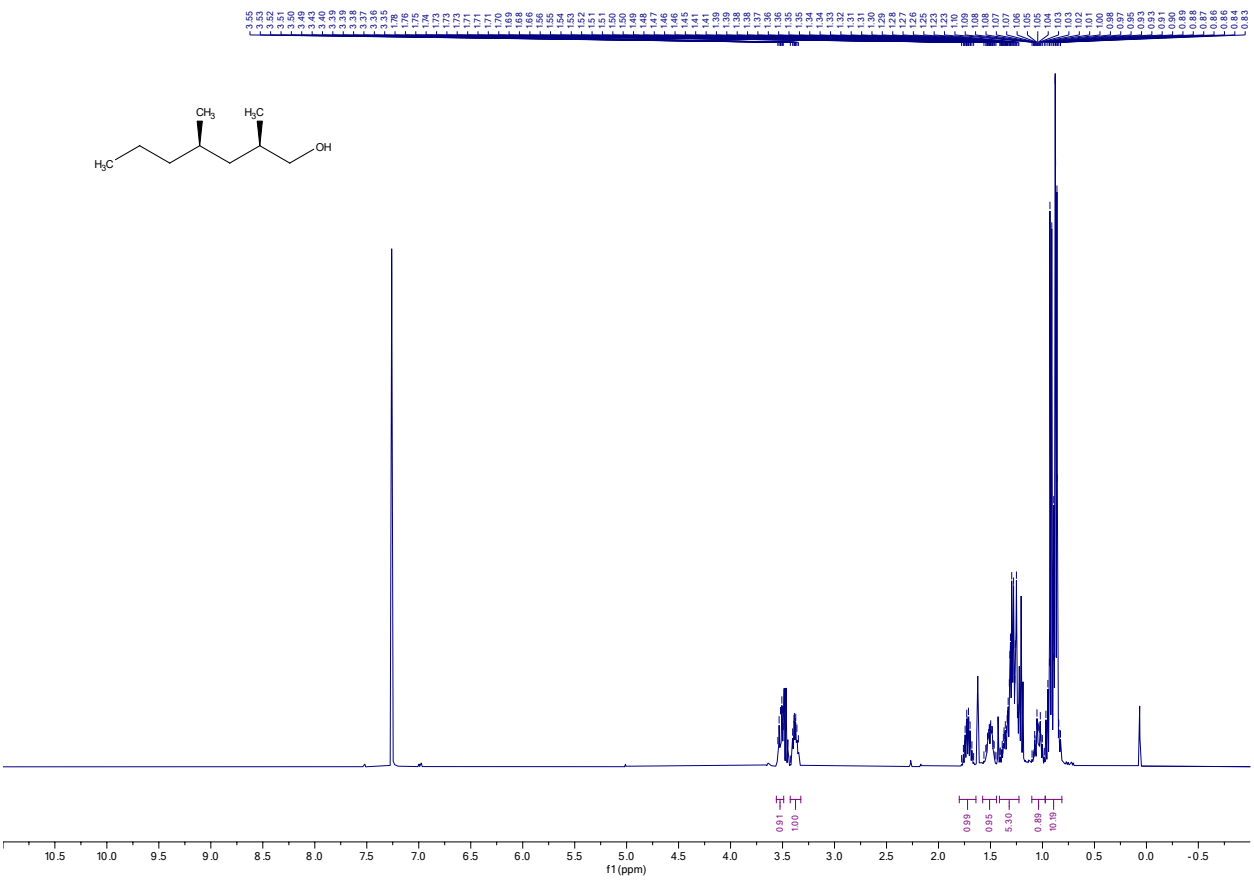
$CDCl_3$, 400 MHz

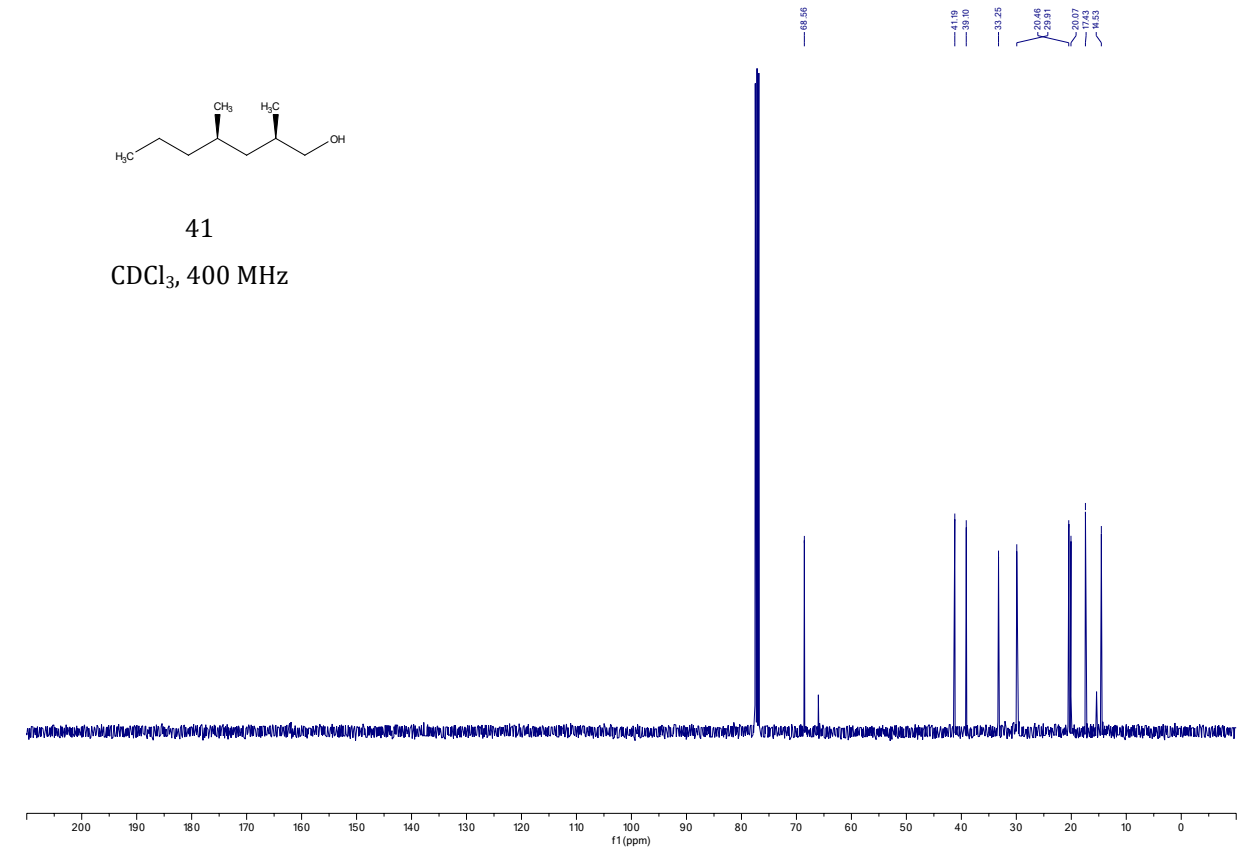


40

crude

$CDCl_3$, 101 MHz





41

$CDCl_3$, 400 MHz