Supporting Information

Synthesis of vinyl, alkyl-substituted chiral acrylates via Krische iridium complex-catalysed allylic phosphonation

Yuan-Yuan Zhang,[1,2,‡] Yi Deng,[1,2,‡] Kun Wei,[1] and Yu-Rong Yang*[,1]

[1]Key Laboratory of Phytochemistry and Natural Medicines, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, China;

[2]University of Chinese Academy of Sciences, Beijing 100049, China.

yangyurong@mail.kib.ac.cn

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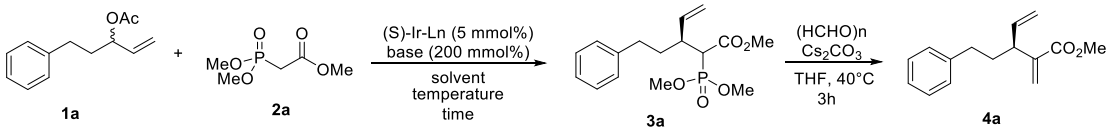
General information

Unless otherwise stated, all oxygen- or moisture-sensitive reactions were conducted in flame-dried glassware in an atmosphere of nitrogen. All solvents were purified and dried according to standard methods prior to use. The corresponding ligands (*S*)-Ir-Ligand and allylic acetate were prepared according to the reported procedure [1][2]. Trimethyl phosphonoacetate was purchased from commercial sources and was used without further purification.

Chromatographic purification of products was accomplished using forced-flow chromatography on 200-300 mesh silica gel. The TLC glass plates were performed on 0.20 mm or 1.0 mm (preparative) silica gel GF254 plates. Visualization was performed using ultraviolet light (254 nm) and potassium permanganate ($KMnO_4$) in water.

^1H NMR and ^{13}C NMR spectra were acquired on Bruker Avance III-400 spectrometer and Bruker Avance III-600MHz spectrometer (Bruker Corp., Germany); TMS was used as an internal standard. Chemical shifts were given in parts per million (ppm) with reference to residual solvent signals [^1H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.0)]. Peak multiplicities were recorded as follows: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet or unresolved, br: broad singlet. Infrared (IR) spectra were recorded on a Nicolet iS10 Fourier transform infrared (FT-IR) spectrometer (Thermo Scientific, United States) with KBr pellets and ATR ITX-DIAMOND. High-resolution mass spectral (HRMS) data were obtained at the mass spectrometry service operated at Agilent 6540 Q-TOF LC/MS spectrometer for electrospray ionization (ESI), electron Ionization (EI) and were reported as (*m/z*). Optical rotations were measured on an Automatic Polarimeter APVI-6W 91058. HPLC analysis was performed on an Agilent 1260 series system using Daicel chiralpak AD-H, OD-H, OJ-H, OC-H, and IC with *n*-hexane and *i*-PrOH as solvents.

Optimization of reaction conditions



General procedure: A pressure tube equipped with a magnetic stir bar was charged with (*S*)-Ir-Ligand (5 mmol%), base (200 mmol%), then dried solvent (0.5 M), trimethyl phosphonoacetate **2a** (200 mmol%) and corresponding allylic substrates **1a** (100 mmol%) were added. The tube was purged with argon for 1 minute and sealed with a PTFE-lined cap. Then, the tube was placed in an oil bath at the indicated temperature and stirred for the indicated period. After cooling to ambient temperature, the crude reaction mixture was directly subjected to flash column chromatography to obtain intermediate **3a**. The α-allylic phosphonate **3a** was then taken in a round-bottom flask and dissolved in THF (0.1 M), followed by the sequential addition of Cs2CO3 (3.0 equiv) and paraformaldehyde (6.0 equiv) under open-air. The resulting mixture was then stirred at 40 °C until TLC revealed the complete consumption of **3a** (~3 h). Then, the crude mixture was directly purified by silica-gel flash column chromatography to obtain **4a**.

1. Optimization of solvent

Standard conditions: Following general procedure, allylic acetate (100 mmol%), trimethyl phosphonoacetate (200 mmol%), (*S*)-Ir-tol-BINAP (5 mmol%), Cs_2CO_3 (200 mmol%), solvent (0.5 M), 50 °C, 24 h.

entry	solvent	yield(%)[a]	ee(%)[b]
1	DME	67	95
2	THF	32	90
3	Dioxane	5	93

[a]Two-step yield. [b]The *ee* value was determined by HPLC on the Daicel chiralpak OJ-H.

2. Optimization of base

Standard conditions: Following the general procedure, allylic acetate (100 mmol%), trimethyl phosphonoacetate (200 mmol%), (*S*)-Ir-Tol-BINAP (5 mmol%), base (200 mmol%), DME (0.5 M), 50 °C, 24 h.

entry	base	T(°C)	ligand	yield(%)[a]	*ee*(%)[b]
1	Cs_2CO_3	50	(*S*)-Ir-tol-BINAP	67	95
2[c]	Cs_2CO_3	50	(*S*)-Ir-tol-BINAP	52	96
3[d]	Cs_2CO_3	50	(*S*)-Ir-tol-BINAP	62	96
4	K_2CO_3	50	(*S*)-Ir-tol-BINAP	n.r.	n.d.
5	K_3PO_4	50	(*S*)-Ir-tol-BINAP	48	96
6[e]	*t*-BuONa	50	(*S*)-Ir-tol-BINAP	28	n.d.
7	NaOAc	50	(*S*)-Ir-tol-BINAP	n.r.	n.d.

[a]Two-step yield. [b]The *ee* value was determined by HPLC on the Daicel chiralpak OJ-H. [c]Cs_2CO_3 was 1.5 eq. [d]Cs_2CO_3 was 1.5 eq, and the reaction time was 36 h. [e]The reaction time was 18 h, and the yield was only the first step of Ir-catalyzed allylic alkylation.

3. Optimization of ligand

Standard conditions: Following the general procedure, allylic acetate (100 mmol%), trimethyl phosphonoacetate (200 mmol%), (*S*)-Ir-Ligand (5 mmol%), Cs_2CO_3 (200 mmol%), DME (0.5 M), 50 °C, 40 h.

entry	ligand	yield(%)[a]	*ee*(%)[b]
1	(*S*)-Ir-tol-BINAP	61	94
2	(*S*)-Ir-Cl, OMe-BIPHEP	50	86
3	(*S*)-Ir-DM-BINAP	58	85
4	(*S*)-Ir-SEGPHOS	39	87
5	(*S*)-Ir-tol-SDP	19	21
6	(*S*)-Ir-DM-SEGPHOS	20	70

[a]Two-step yield. [b]The *ee* value was determined by HPLC on the Daicel chiralpak OJ-H.

4. Optimization of temperature

Standard conditions: Following general procedure, allylic acetate (100 mmol%), trimethyl phosphonoacetate (200 mmol%), (*S*)-Ir-tol-BINAP (5 mmol%), Cs_2CO_3 (200 mmol%), DME (0.5 M), 40 h.

entry	T(°C)	yield(%)[a]	*ee*(%)[b]
1	70	41	91
2	50	61	94
3	30	66	97

[a]Two-step yield. [b]The *ee* value was determined by HPLC on the Daicel chiralpak OJ-H.

5. Optimization of reaction time

Standard conditions: Following general procedure, allylic acetate (100 mmol%), trimethyl phosphonoacetate (200 mmol%), (*S*)-Ir-tol-BINAP (5 mmol%), Cs_2CO_3 (200 mmol%), DME (0.5 M), 50 °C.

entry	Time(h)	yield(%)[a]	*ee*(%)[b]
1	18	49	95
2	24	67	95
3	30	67	95
4	40	61	94
5[c]	60	90	96

[a]Two-step yield. [b]The *ee* value was determined by HPLC on the Daicel chiralpak OJ-H. [c]The reaction temperature was 30 °C.

6. The scale of reaction

Standard conditions: Following general procedure, allylic acetate (100 mmol%), trimethyl phosphonoacetate (200 mmol%), (*S*)-Ir-tol-BINAP (5 mmol%), Cs_2CO_3 (200 mmol%), DME (0.5 M), 30 °C, 60 h.

entry	Scale(mmol)	yield(%)[a]	*ee*(%)[b]
1	0.1	90	96
2	0.5	87	96
3	2.0	85	96

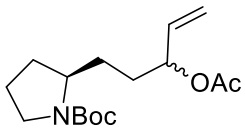
[a]Two-step yield. [b]The *ee* value was determined by HPLC on the Daicel chiralpak OJ-H.

Synthesis and characterization of substrates and products

General procedure for preparation of allylic acetates[1]

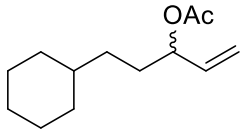
Vinyl magnesium bromide (1.0 M in THF, 3.6 mmol) was added dropwise to a solution of the corresponding aldehyde (3.0 mmol) in dry THF at 0 °C. The mixture was stirred at room temperature for 10 minutes, at which point triethylamine (6.0 mmol) and acetic anhydride (4.5 mmol) were added, and the reaction was stirred vigorously for 30 minutes. After water was added, the organic layer was extracted with diethyl ether. The combined organic layers were washed with 1N HCl and brine dried over Na2SO4, concentrated in vacuo, and then purified by silica gel column chromatography to afford the corresponding allylic acetates.

Characterization of allylic acetates



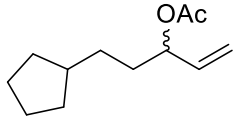
1e

$\mathbf{R_f}$ = 0.26 (petroleum ether/ethyl acetate 18/1). **^{1}H NMR** (400 MHz, CD_3OD contains 2% pyridine): δ 5.81 (ddd, J = 17.1, 10.5, 6.4 Hz, 1H), 5.41-5.05 (m, 3H), 3.52-3.15 (m, 3H), 2.04 (s, 3H), 2.00-1.54 (m, 8H), 1.45 (s, 9H) ppm. **^{13}C NMR** (100 MHz, CD_3OD contains 2% pyridine): δ 170.5, 155.0, 136.4, 115.6, 79.4, 74.7, 74.6, 45.9, 30.6, 30.2, 27.5 (overlap), 23.2, 22.6, 19.8 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{27}NO_4Na$ $[M+Na]^+$ 320.1832, found 320.1832.



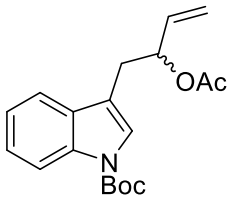
1f

$\mathbf{R_f}$ = 0.27 (petroleum ether/ethyl acetate 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.75 (ddd, J = 17.1, 10.5, 6.5 Hz, 1H), 5.38-4.95 (m, 3H), 2.04 (s, 3H), 1.88-1.46 (m, 7H), 1.41-1.01 (m, 6H), 0.89-0.81 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4, 136.7, 116.5, 75.2, 37.5, 33.3 (overlap), 32.6, 31.6, 26.6 (overlap), 26.3, 21.2 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{13}H_{22}O_2Na$ $[M+Na]^+$ 233.1512, found 233.1509.



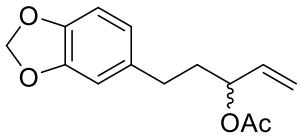
1g

R_f = 0.29 (petroleum ether/ethyl acetate 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.75 (ddd, J = 17.2, 10.5, 6.3 Hz, 1H), 5.37-4.99 (m, 3H), 2.03 (s, 3H), 1.84-1.67 (m, 3H), 1.65-1.53 (m, 4H), 1.50-1.40 (m, 2H), 1.30-1.35 (m, 2H), 1.11-0.90 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3, 136.7, 116.5, 75.0, 39.9, 33.4, 32.6, 32.6, 31.4, 25.1 (overlap), 21.2 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{12}H_{20}O_2Na$ $[M+Na]^+$ 219.1356, found 219.1355.



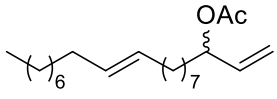
1k

R_f = 0.47 (petroleum ether/ethyl acetate 18/1). **^{1}H NMR** (400 MHz, CD_3OD): δ 8.11 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.42 (s, 1H), 7.36-7.20 (m, 2H), 5.86 (ddd, J = 17.0, 10.5, 6.2 Hz, 1H), 5.56-5.51 (m, 1H), 5.34-5.06 (m, 2H), 3.07 (dd, J = 14.5, 6.7 Hz, 1H), 2.96 (dd, J = 14.5, 6.7 Hz, 1H), 2.04 (s, 3H), 1.67 (s, 9H) ppm. **^{13}C NMR** (100 MHz, CD_3OD): δ 170.2, 149.7, 135.8, 134.1, 130.7, 124.3, 124.0, 122.4, 119.2, 117.2, 115.8, 115.2, 83.5, 74.1, 30.2, 28.2 (overlap), 21.3 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{19}H_{23}NO_4Na$ $[M+Na]^+$ 352.1519, found 352.1519.



1l

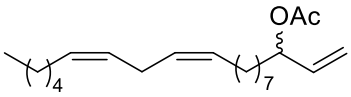
R_f = 0.28 (petroleum ether/ethyl acetate 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.72-6.47 (m, 3H), 5.91 (s, 2H), 5.79 (ddd, J = 17.2, 10.5, 6.3 Hz, 1H), 5.47-5.07 (m, 3H), 2.69-2.44 (m, 2H), 2.07 (s, 3H), 2.00-1.72 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3, 147.6, 145.7, 136.3, 135.1, 121.1, 116.9, 108.8, 108.2, 100.8, 74.2, 36.1, 31.2, 21.2 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{14}H_{16}O_4Na$ $[M+Na]^+$ 271.0941, found 271.0937.



1n

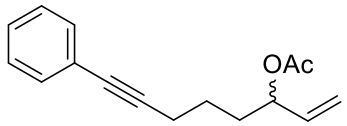
R_f = 0.30 (petroleum ether/ethyl acetate 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.77 (ddd, J = 17.1, 10.5, 6.4 Hz, 1H), 5.54-5.32 (m, 2H), 5.28-5.05 (m, 3H), 2.06 (s, 3H), 1.98-1.94 (m, 4H), 1.63-1.55 (m, 2H), 1.33-1.26 (m, 22H), 0.88 (t, J = 6.6 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.4, 136.7, 130.4, 130.2, 116.5, 74.9, 34.2, 32.6, 32.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3 (overlap), 29.2,

29.0, 25.1, 22.7, 21.2, 14.1 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{22}H_{40}O_2Na$ $[M+Na]^+$ 359.2921, found 359.2919.



1o

$\mathbf{R_f}$ = 0.30 (petroleum ether/ethyl acetate 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.76 (ddd, J = 17.1, 10.5, 6.4 Hz, 1H), 5.41-5.34 (m, 4H), 5.27-5.04 (m, 3H), 2.77 (t, J = 6.4 Hz, 2H), 2.07-2.03 (m, 7H), 1.66-1.57 (m, 2H), 1.51-1.18 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3, 136.6, 130.2, 130.1, 128.0, 127.9, 116.5, 74.8, 34.2 (overlap), 31.5(overlap), 29.6, 29.4, 29.3, 29.2, 27.2, 25.6, 25.0, 22.6, 21.2, 14.1 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{22}H_{38}O_2Na$ $[M+Na]^+$ 357.2764, found 357.2769.



1p

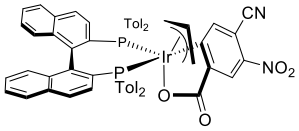
$\mathbf{R_f}$ = 0.51 (petroleum ether/ethyl acetate 18/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.36 (m, 2H), 7.27 (dd, J = 5.2, 2.0 Hz, 3H), 5.79 (ddd, J = 17.0, 10.5, 6.4 Hz, 1H), 5.44-4.90 (m, 3H), 2.43 (t, J = 7.0 Hz, 2H), 2.07 (s, 3H), 1.91-1.73 (m, 2H), 1.71-1.55 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 136.3, 131.6 (overlap), 128.2 (overlap), 127.6, 123.9, 116.8, 89.5, 81.1, 74.3, 33.3, 24.3, 21.2, 19.2 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{18}O_2Na$ $[M+Na]^+$ 265.1199, found 265.1199.

General procedure for preparation of (*S*)-Ir-Ligand[2]

The preparation of **(*S*)-Ir-Ligand** described previously by Prof. Michael J. Krische was modified as follows: To a mixture of $[Ir(cod)Cl]_2$ (100 mmol%), (*S*)-Ligand (200 mmol%), Cs_2CO_3 (400 mmol%), 4-CN-3-NO_2BzOH (400 mmol%) and allyl acetate (500 mmo%) in a sealed tube under argon atmosphere was added THF (0.05 M). The reaction mixture was stirred for 30 min at ambient temperature and heated for 1.5 h at 80 °C, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was filtered through a celite and washed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and subjected to column chromatography (CH_2Cl_2/Et_2O 10/1). The obtained gum-like product was dissolved in THF and precipitated upon the rapid addition of HPLC-grade hexanes. A yellow precipitate formed, which was collected by filtration and dried under vacuum.

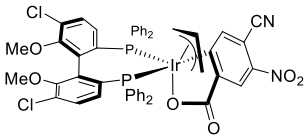
Preparation of (*rac*)-Ir-Ligand

The preparation of **(*rac*)-Ir-Ligand** was achieved by using the above procedure with **BIPHEP** to afford **(*rac*)-Ir-BIPHEP**.



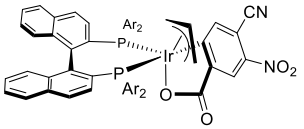
(*S*)-Ir-Tol-BINAP

cat-1



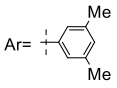
(*S*)-Ir-Cl, OMe-BIPHEP

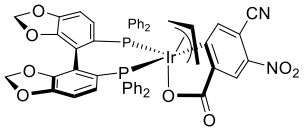
cat-2



(*S*)-Ir-DM-BINAP

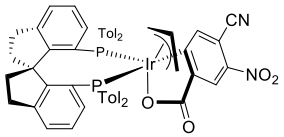
cat-3





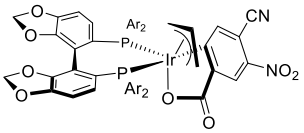
(*S*)-Ir-SEGPHOS

cat-4



(*S*)-Ir-Tol-SDP

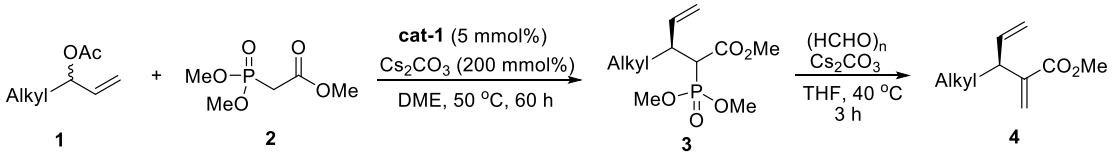
cat-5



(*S*)-Ir-DM-SEGPHOS

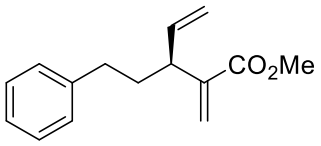
cat-6

General procedure for the enantioselective synthesis of skipped dienes



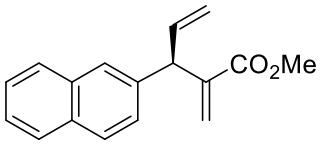
General procedure:

A pressure tube equipped with a magnetic stir bar was charged with (*S*)-Ir-tol-BINAP (5 mmol%), cesium carbonate (200 mmol%), then dried DME (0.5 M), trimethyl phosphonoacetate **2** (200 mmol%), allylic acetate **1** (100 mmol%) were added. The tube was purged with argon for 1 minute and sealed with a PTFE-lined cap. Then, the tube was placed in an oil bath at the indicated temperature and stirred for the indicated period. After cooling to ambient temperature, the crude reaction mixture was directly subjected to flash column chromatography to obtain intermediate **3**. The α-allylic phosphonate **3** was then taken in a round-bottom flask and dissolved in THF (0.1 M), followed by the sequential addition of Cs_2CO_3 (3.0 equiv) and paraformaldehyde (6.0 equiv) under open air. The resulting mixture was then stirred at 40 °C (an oil bath) until TLC revealed the complete consumption of **3**. Then, the crude mixture was directly purified by silica-gel flash column chromatography to obtain **4**.



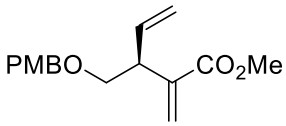
4a

$\mathbf{R}_f$ = 0.47 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 2H), 7.21-7.12 (m, 3H), 6.23 (s, 1H), 5.82 (ddd, *J* = 19.3, 9.7, 8.0 Hz, 1H), 5.58 (s, 1H), 5.26-4.98 (m, 2H), 3.74 (s, 3H), 3.28 (m, 1H), 2.66 (ddd, *J* = 13.7, 10.2, 5.7 Hz, 1H), 2.57 (ddd, *J* = 13.7, 10.1, 5.9 Hz, 1H), 1.92 (m, 1H), 1.82 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.4, 143.1, 142.1, 139.9, 128.4 (overlap), 128.3 (overlap), 125.8, 124.4, 115.8, 51.8, 44.7, 35.4, 33.7 ppm. **FT-IR** (KBr): 3083, 3063, 3026, 2979, 2952, 2858, 1755, 1738, 1641, 1603, 1454, 1435, 1298, 1265, 1246, 1199, 1153, 925, 748, 700 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{15}H_{19}O_2$ $[M+H]^+$ 231.1380, found 231.1380. $[\alpha]_D^{25.0}$ = +25.77 (*c* = 0.35, $CHCl_3$). **HPLC**: Daicel Chiralpak OJ, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, 20 °C, 210 nm; [t_1 (major) = 9.274 min, t_2 (minor) = 11.363 min], 96% *ee*.



4b

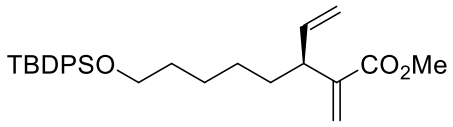
$\mathbf{R}_f$ = 0.41 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82-7.78 (m, 3H), 7.64 (s, 1H), 7.48-7.42 (m, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.43 (s, 1H), 6.18 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.65 (s, 1H), 5.24 (d, *J* = 10.2 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.85 (d, J = 6.7 Hz, 1H), 3.69 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.2, 142.4, 138.8, 138.2, 133.5, 132.4, 128.0, 127.8, 127.6, 127.2, 126.9, 126.5, 126.0, 125.6, 117.0, 52.0, 50.2 ppm. **FT-IR** (ATR ITX - DIAMOND): 3055, 2960, 2917, 2849, 2180, 2153, 1628, 1600, 1508, 1436, 1407, 1328, 1192, 953, 923, 859, 748 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{17}H_{16}O_2Na$ $[M+Na]^+$ 275.1043, found 275.1039. $[\alpha]_D^{24.9}$ = –79.27 (*c* = 0.74, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 99.2/0.8, 0.6 mL/min, 15 °C, 210 nm; [t_1 (major) = 11.768 min, t_2 (minor) = 12.350 min], 53% *ee*.



4c

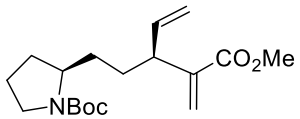
$\mathbf{R}_f$ = 0.39 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26-7.22 (m, 2H), 6.88-6.85 (m, 2H), 6.28 (s, 1H), 5.89 (ddd, *J* = 17.3, 10.2, 6.6 Hz, 1H), 5.62 (s, 1H), 5.15-5.10 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.63 (m, 1H), 3.58-3.52 (m, 2H) ppm. **^{13}C NMR** (100

MHz, $CDCl_3$): δ 167.2, 159.1, 140.3, 137.2, 130.4, 129.2 (overlap), 126.0, 116.6, 113.7 (overlap), 72.6, 71.5, 55.3, 51.9, 45.0 ppm. **FT-IR** (KBr): 2957, 1723, 1613, 1513, 1465, 1440, 1249, 1171, 1098, 1036, 922, 819 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{20}O_4Na$ $[M+Na]^+$ 299.1254, found 299.1250. $[\alpha]_D^{24.5}$ = +8.47 (*c* = 0.77, $CHCl_3$). **HPLC**: Daicel Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 96/4, 1.0 mL/min, 20 °C, 210 nm; [t_1 (major) = 24.546 min, t_2 (minor) = 28.643 min], 95% *ee*.



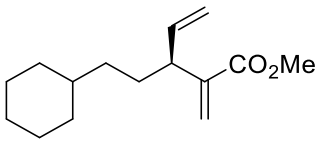
4d

$\mathbf{R_f}$ = 0.49 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69-7.66 (m, 4H), 7.43-7.37 (m, 6H), 6.20 (s, 1H), 5.77 (ddd, *J* = 17.7, 10.2, 8.0 Hz, 1H), 5.54 (s, 1H), 5.07-5.02 (m, 2H), 3.75 (s, 3H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.22 (m, 1H), 1.58-1.50 (m, 4H), 1.40-1.27 (m, 4H), 1.06 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.5, 143.4, 140.3, 135.6 (overlap), 134.2 (overlap), 129.5 (overlap), 127.6 (overlap), 124.1, 115.2, 63.9, 51.8, 44.9, 33.7, 32.5, 29.7, 27.2, 26.9 (overlap), 25.7, 19.2 ppm. **FT-IR** (KBr): 3072, 2932, 2858, 1724, 1625, 1430, 1256, 1192, 1147, 1110, 998, 917, 822, 740, 704, 613 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$ 473.2482, found 473.2476. $[\alpha]_D^{24.9}$ = +13.40 (*c* = 0.37, $CHCl_3$). **HPLC**: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99.5/0.5, 0.57 mL/min, 20 °C, 210 nm; [t_1 (major) = 9.240 min, t_2 (minor) = 10.072 min], 94% *ee*.



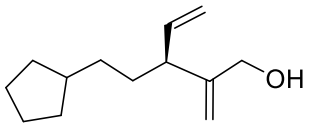
4e

$\mathbf{R_f}$ = 0.35 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, CD_3OD): δ 6.18 (s, 1H), 5.81 (ddd, *J* = 17.0, 10.3, 8.1 Hz, 1H), 5.61 (s, 1H), 5.07-5.02 (m, 2H), 3.73 (s, 3H), 3.37-3.26 (m, 3H), 3.19 (m, 1H), 1.93-1.77 (m, 4H), 1.76-1.64 (m, 2H), 1.63-1.53 (m, 2H), 1.44 (s, 9H) ppm. **^{13}C NMR** (150 MHz, CD_3OD): δ 168.8, 156.7, 144.9, 141.6, 125.2, 116.1, 80.9, 59.1, 52.5, 47.4, 46.8, 33.7, 31.8, 31.7, 29.0 (overlap), 24.1 ppm. **FT-IR** (KBr): 3083, 3063, 3026, 2979, 2952, 2858, 1755, 1738, 1641, 1603, 1454, 1435, 1298, 1265, 1246, 1199, 1153, 925, 748, 700 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{18}H_{29}NO_4Na$ $[M+Na]^+$ 346.1989, found 346.1990. $[\alpha]_D^{24.7}$ = –27.43 (*c* = 0.14, $CHCl_3$). **HPLC**: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99.3/0.7, 0.45 mL/min, 15 °C, 210 nm; [t_1 (major) = 19.455 min, t_2 (minor) = 20.926 min], 84% *ee*.



4f

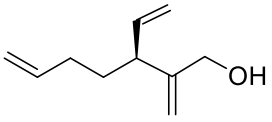
R_f = 0.59 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.19 (s, 1H), 5.70 (ddd, J = 17.3, 10.1, 7.7 Hz, 1H), 5.53 (s, 1H), 5.10-5.00 (m, 2H), 3.75 (s, 3H), 3.17 (m, 1H), 1.70-1.61 (m, 6H), 1.47 (m, 1H), 1.25-1.10 (m, 6H), 0.89-0.81 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.5, 143.5, 140.5, 124.1, 115.1, 51.8, 45.1, 37.7, 35.1, 33.4, 33.3, 31.0 (overlap), 26.7, 26.4 ppm. **FT-IR** (KBr): 2924, 2852, 1725, 1626, 1440, 1259, 1194, 1133, 999, 943, 916, 816 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{15}H_{24}O_2Na$ $[M+Na]^+$ 259.1669, found 259.1674. **$[\alpha]_D^{25.0}$** = +25.19 (*c* = 0.52, $CHCl_3$). **HPLC**: Daicel Chiralpak OC-H, *n*-hexane/*i*-PrOH = 99.6/0.4, 0.6 mL/min, 15 °C, 210 nm; [t_1 (major) = 16.852 min, t_2 (minor) = 18.954 min], 89% *ee*.



4g'

The compound **4g** was prepared according to the general procedure (50 °C oil bath, 60 h). The crude reaction mixture was purified on silica gel to afford **4g**, then **4g** was reduced by Dibal-H (1.5 M in toluene, 2.5 equiv) to obtain **4g'** as a colorless oil (petroleum ether/ethyl acetate 10/1).

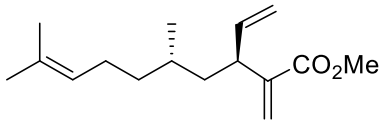
R_f = 0.36 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.69 (ddd, J = 17.9, 10.1, 8.2 Hz, 1H), 5.11 (s, 1H), 5.07-4.98 (m, 2H), 4.94 (s, 1H), 4.08 (s, 2H), 2.67 (m, 1H), 1.78-1.68 (m, 3H), 1.61-1.54 (m, 4H), 1.52-1.45 (m, 4H), 1.35-1.28 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.1, 141.5, 114.6, 109.3, 65.0, 47.6, 40.2, 33.9, 32.7, 32.6, 32.1, 29.7, 25.2 ppm. **FT-IR** (ATR ITX - DIAMOND): 3854, 3343, 2955, 2919, 2850, 2182, 2069, 2028, 2005, 1967, 1636, 1457, 1413, 1377, 1260, 1089, 1020, 911, 868, 797, 687 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{13}H_{23}O$ $[M+H]^+$ 195.1743, found 195.1739. **$[\alpha]_D^{25.0}$** = +51.16 (*c* = 0.50, $CHCl_3$). **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 99/1, 0.6 mL/min, 20 °C, 210 nm; [t_1 (major) = 22.287 min, t_2 (minor) = 23.502 min], 94% *ee*.



4h'

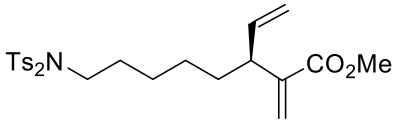
The compound **4h** was prepared according to the general procedure (50 °C oil bath, 60 h). The crude reaction mixture was purified on silica gel to afford **4h**, then **4h** was reduced by Dibal-H (1.5 M in toluene, 2.5 equiv) to obtain **4h'** as a colorless oil (petroleum ether/ethyl acetate 10/1).

R_f = 0.29 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.80 (ddd, J = 16.9, 10.3, 6.6 Hz, 1H), 5.68 (ddd, J = 17.1, 10.2, 8.3 Hz, 1H), 5.13-4.90 (m, 6H), 4.09 (s, 2H), 2.74 (m, 1H), 2.17-1.95 (m, 2H), 1.76-1.51 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.7, 141.0, 138.5, 115.1, 114.8, 109.6, 65.0, 46.6, 32.0, 31.4 ppm. **FT-IR** (ATR ITX - DIAMOND): 3329, 3077, 2963, 2927, 2855, 1640, 1413, 1260, 1091, 1019, 912, 863, 800, 701 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{10}H_{16}ONa$ $[M+Na]^+$ 175.1093, found 175.1098. **[α]**$_D^{25.0}$ = +48.40 (c = 0.45, $CHCl_3$). **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 97.7/2.3, 0.4 mL/min, 15 °C, 210 nm; [t_1 (major) = 23.319 min, t_2 (minor) = 24.105 min], 93% *ee*.



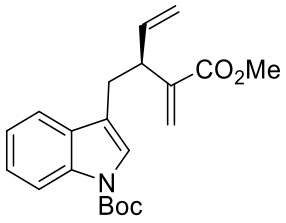
4i

R_f = 0.66 (petroleum ether/ethyl acetate 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.18 (s, 1H), 5.72 (ddd, J = 17.1, 10.2, 8.2 Hz, 1H), 5.54 (s, 1H), 5.10-5.02 (m, 3H), 3.75 (s, 3H), 3.38-3.32 (m, 1H), 2.00-1.91 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.53-1.43 (m, 2H), 1.33-1.28 (m, 2H), 1.15 (m, 1H), 0.89 (d, J = 6.3 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.5, 144.0, 140.2, 131.1, 124.8, 123.9, 115.4, 51.8, 42.5, 41.1, 37.5, 29.9, 25.7, 25.4, 19.1, 17.7 ppm. **FT-IR** (KBr): 2958, 2923, 2853, 1727, 1644, 1466, 1261, 1081 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{26}O_2Na$ $[M+Na]^+$ 273.1825, found 273.1820. **[α]**$_D^{24.4}$ = +17.00 (c = 0.60, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 96.6/0.4, 0.6 mL/min, 20 °C, 230 nm; [t_1 (minor) = 8.585 min, t_2 (major) = 9.107 min], 96% *ee*.



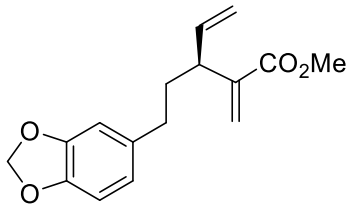
4j

R_f = 0.18 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 4H), 7.33 (d, J = 8.0 Hz, 4H), 6.19 (s, 1H), 5.74 (ddd, J = 17.6, 9.8, 8.0 Hz, 1H), 5.53 (s, 1H), 5.10-5.00 (m, 2H), 3.75 (s, 3H), 3.62 (t, J = 8.1 Hz, 2H), 3.19 (m, 1H), 2.45 (s, 6H), 1.68-1.62 (m, 2H), 1.56-1.38 (m, 2H), 1.25-1.20 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.4, 144.8, 143.3 (overlap), 140.1, 137.2 (overlap), 129.6 (overlap), 128.2 (overlap), 124.2, 115.3, 51.8, 49.3, 44.7, 33.4, 29.7, 26.7, 26.4, 21.7 (overlap) ppm. **FT-IR** (ATR ITX - DIAMOND): 3362, 2962, 2925, 2852, 1975, 1720, 1598, 1459, 1372, 1164, 867, 704, 663, 553 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{26}H_{33}NO_6S_2Na$ $[M+Na]^+$ 542.1642, found 542.1641. **[α]**$_D^{25.0}$ = +5.54 (c = 0.13, $CHCl_3$). **HPLC**: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99/1, 0.6 mL/min, 20 °C, 230 nm; [t_1 (major) = 12.175 min, t_2 (minor) = 12.982 min], 89% *ee*.



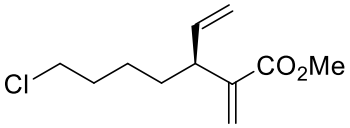
4k

$\mathbf{R}_f$ = 0.50 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.37-7.25 (m, 2H), 7.24-7.22 (m, 1H), 6.24 (s, 1H), 5.91 (ddd, J = 16.8, 10.5, 7.7 Hz, 1H), 5.62 (s, 1H), 5.13-4.93 (m, 2H), 3.78-3.71 (m, 4H), 3.04 (dd, J = 14.6, 8.4, 1H), 2.88 (dd, J = 14.6, 8.4 Hz, 1H), 1.67 (s, 9H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.2, 149.8, 142.6, 139.3, 135.4, 130.8, 125.2, 124.2, 123.5, 122.3, 119.1, 118.5, 116.0, 115.2, 83.4, 51.9, 44.8, 29.6, 28.2 (overlap) ppm. **FT-IR** (KBr): 2928, 1729, 1627, 1454, 1371, 1311, 1255, 1160, 1083, 1017, 920, 858, 817, 747 cm^{-1}. **HRMS** (ESI$^+$): *m/z* calcd for $C_{21}H_{25}NO_4Na$ $[M+Na]^+$ 378.1676, found 378.1678. $[\alpha]_D^{24.7}$ = +9.54 (c = 1.20, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 99.5/0.5, 0.5 mL/min, 15 °C, 210 nm; [t_1 (major) = 28.288 min, t_2 (minor) = 32.749 min], 92% *ee*.



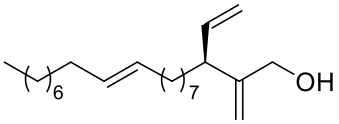
4l

$\mathbf{R}_f$ = 0.34 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.72 (d, J = 7.9 Hz, 1H), 6.66 (s, 1H), 6.61 (d, J = 7.9 Hz, 1H), 6.22 (s, 1H), 5.91 (s, 2H), 5.80 (ddd, J = 17.7, 9.8, 8.0 Hz, 1H), 5.57 (s, 1H), 5.11-5.06 (m, 2H), 3.75 (s, 3H), 3.26 (m, 1H), 2.58 (ddd, J = 13.9, 10.1, 6.3 Hz, 1H), 2.49 (ddd, J = 13.9, 10.0, 6.5 Hz, 1H), 1.92-1.83 (m, 1H), 1.81-1.72 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.4, 147.5, 145.6, 143.1, 139.9, 135.9, 124.4, 121.1, 115.8, 108.9, 108.1, 100.7, 51.8, 44.5, 35.6, 33.4 ppm. **FT-IR** (KBr): 2962, 2920, 1727, 1443, 1261, 1093, 1021, 865, 801, 703 cm^{-1}. **HRMS** (ESI$^+$): *m/z* calcd for $C_{16}H_{18}O_4Na$ $[M+Na]^+$ 297.1097, found 297.1092. $[\alpha]_D^{25.0}$ = +7.40 (c = 0.10, $CHCl_3$). **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, 20 °C, 210 nm; [t_1 (minor) = 9.940 min, t_2 (major) = 10.557 min], 91% *ee*.



4m

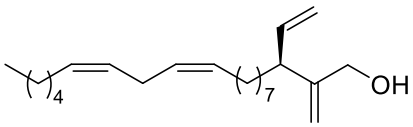
R_f = 0.48 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.21 (s, 1H), 5.77 (ddd, J = 17.0, 10.3, 8.0 Hz, 1H), 5.56 (s, 1H), 5.09-5.04 (m, 2H), 3.75 (s, 3H), 3.52 (t, J = 6.7 Hz, 2H), 3.23 (m, 1H), 1.82-1.74 (m, 2H), 1.64-1.36 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.4, 143.1, 139.9, 124.4, 115.6, 51.9, 44.9, 44.8, 32.9, 32.4, 24.7 ppm. **FT-IR** (KBr): 2929, 2859, 1723, 1626, 1438, 1256, 1194, 1138, 996, 947, 919, 818 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{11}H_{21}NClO_2$ $[M+NH_4]^+$ 234.1255, found 234.1258. **$[\alpha]_D^{24.5}$** = +29.20 (c = 1.07, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 99.5/0.5, 0.5 mL/min, 15 °C, 210 nm; [t_1 (major) = 11.663 min, t_2 (minor) = 12.278 min], 94% *ee*.



4n'

The compound **4n** was prepared according to the general procedure (50 °C oil bath, 60 h). The crude reaction mixture was purified on silica gel to afford **4n**, then **4n** was reduced by Dibal-H (1.5 M in toluene, 2.5 equiv) to obtain **4n'** as a colorless oil (petroleum ether/ethyl acetate 10/1).

R_f = 0.42 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.68 (ddd, J = 17.8, 10.1, 8.2 Hz, 1H), 5.38 (t, J = 3.8 Hz, 2H), 5.10 (s, 1H), 5.07-4.98 (m, 2H), 4.94 (s, 1H), 4.08 (s, 2H), 2.69 (m, 1H), 1.98-1.94 (m, 4H), 1.55-1.45 (m, 2H), 1.32-1.26 (m, 22H), 0.88 (t, J = 6.6 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.1, 141.4, 130.4, 130.3, 114.7, 109.3, 65.0, 47.4, 32.9, 32.6, 32.6, 31.9, 29.7, 29.6(overlap), 29.5, 29.4, 29.3, 29.2, 29.1, 27.4, 22.7, 14.1 ppm. **FT-IR** (ATR ITX - DIAMOND): 3319, 2925, 2854, 2150, 1636, 1465, 1027, 966, 911, 722 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{23}H_{42}ONa$ $[M+Na]^+$ 357.3128, found 357.3132. **$[\alpha]_D^{25.9}$** = +35.82 (c = 0.57, $CHCl_3$). **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 99.3/0.7, 0.4 mL/min, 15 °C, 210 nm; [t_1 (major) = 22.937 min, t_2 (minor) = 23.681 min], 80% *ee*.

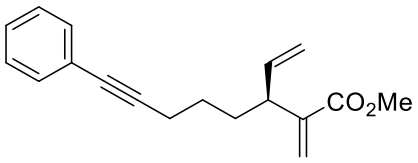


4o'

The compound **4o** was prepared according to the general procedure (50 °C oil bath, 60 h). The crude reaction mixture was purified on silica gel to afford **4o**, then **4o** was reduced by Dibal-H (1.5 M in toluene, 2.5 equiv) to obtain **4o'** as a colorless oil (petroleum ether/ethyl acetate 10/1).

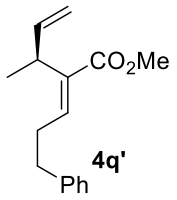
R_f = 0.39 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.68 (ddd, J = 17.7, 10.1, 8.2 Hz, 1H), 5.41-5.30 (m, 4H), 5.11 (s, 1H), 5.07-4.98 (m, 2H), 4.94 (s, 1H), 4.08 (s, 2H), 2.77 (t, J = 6.5 Hz, 2H), 2.69 (m, 1H), 2.07-2.02 (m, 4H), 1.60-1.42 (m, 4H), 1.36-1.25 (m, 14H), 0.89 (t, J = 6.7 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.1, 141.4, 130.2, 130.1, 128.0,

127.9, 114.7, 109.3, 65.0, 47.4, 32.9, 31.5, 29.7, 29.6, 29.5, 29.4, 29.3, 27.4, 27.3, 27.2, 25.6, 22.6, 14.1 ppm. **FT-IR** (ATR ITX - DIAMOND): 3327, 3077, 3009, 2927, 2855, 2180, 2150, 2008, 1635, 1465, 1260, 1024, 912, 799, 731 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{23}H_{40}ONa$ $[M+Na]^+$ 355.2971, found 355.2969. $[\alpha]_D^{25.6}$ = +35.45 (*c* = 0.73, $CHCl_3$). **HPLC**: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 99.3/0.7, 0.4 mL/min, 15 °C, 210 nm; [t_1 (major) = 25.383 min, t_2 (minor) = 26.351 min], 93% *ee*.



4p

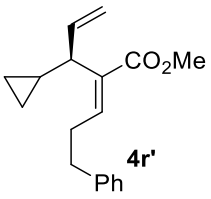
$\mathbf{R}_f$ = 0.43 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.36 (m, 2H), 7.28-7.26 (m, 3H), 6.23 (s, 1H), 5.79 (ddd, *J* = 17.7, 10.2, 7.9 Hz, 1H), 5.59 (s, 1H), 5.16-5.02 (m, 2H), 3.75 (s, 3H), 3.29 (m, 1H), 2.41 (t, *J* = 6.9 Hz, 2H), 1.81-1.54 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.4, 143.1, 140.0, 131.5, 128.2 (overlap), 127.5 (overlap), 124.4, 124.0, 115.5, 89.9, 80.8, 51.8, 44.5, 32.8, 26.6, 19.3 ppm. **FT-IR** (ATR ITX - DIAMOND): 3409, 3081, 2864, 2031, 1956, 1625, 1599, 1490, 1437, 1193, 1111, 1071, 999, 947, 917, 818, 692 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{18}H_{20}O_2Na$ $[M+Na]^+$ 291.1356, found 291.1354. $[\alpha]_D^{25.0}$ = +24.95 (*c* = 1.33, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 99.5/0.5, 0.5 mL/min, 15 °C, 210 nm; [t_1 (major) = 12.588 min, t_2 (minor) = 13.312 min], 91% *ee*.



4q'

The compound was prepared according to the general procedure (50 °C oil bath, 60 h). Then **3q** was reacted with Phenylpropyl aldehyde (1.5 equiv) in the presence of sodium hydride (2.5 equiv) at 0 °C for 4 h to afford **4q'** (petroleum ether/ethyl acetate 40/1) as a colorless oil.

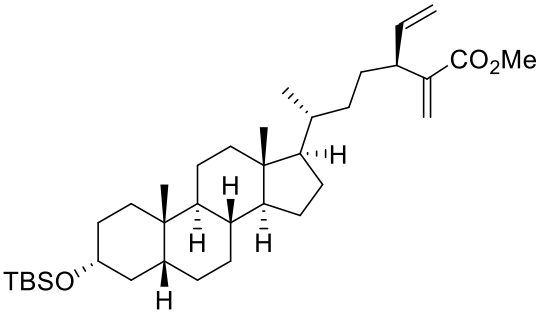
$\mathbf{R}_f$ = 0.41 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.20-7.17 (m, 3H), 5.85-5.75 (m, 2H), 5.04-4.98 (m, 2H), 3.72 (s, 3H), 3.31-3.24 (m, 1H), 2.75-2.62 (m, 4H), 1.14 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.3, 146.0, 141.5, 137.8, 136.6, 128.5 (overlap), 128.3 (overlap), 125.9, 113.8, 51.3, 40.3, 35.7, 31.4, 18.9 ppm. **FT-IR** (KBr): 2962, 2919, 2851, 1727, 1261, 1093, 1021, 865, 801, 701 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{20}O_2Na$ $[M+Na]^+$ 267.1356, found 267.1360. $[\alpha]_D^{24.8}$ = –8.00 (*c* = 0.10, $CHCl_3$). **HPLC**: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99.6/0.4, 0.62 mL/min, 15 °C, 210 nm; [t_1 (major) = 26.802 min, t_2 (minor) = 28.639 min], 98% *ee*.



4r'

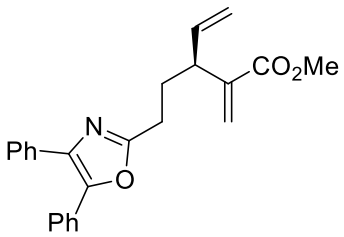
The compound was prepared according to the general procedure (50 °C oil bath, 60 h). Then **3r** was reacted with Phenylpropyl aldehyde (1.5 equiv) in the presence of sodium hydride (2.5 equiv) at 0 °C for 4 h to afford **4r'** (petroleum ether/ethyl acetate 40/1) as a colorless oil.

$\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.20-7.16 (m, 3H), 5.98 (t, J = 7.1 Hz, 1H), 5.83 (ddd, J = 17.2, 10.3, 6.9 Hz, 1H), 5.09-5.00 (m, 2H), 3.71 (s, 3H), 2.77-2.65 (m, 4H), 2.38 (t, J = 8.1 Hz, 1H), 0.85 (m, 1H), 0.54 (ddd, J = 10.4, 7.9, 2.7 Hz, 1H), 0.46 (ddd, J = 10.3, 7.9, 2.8 Hz, 1H), 0.17-0.11 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.8, 141.5, 139.6, 138.3, 135.4, 128.5 (overlap), 128.3 (overlap), 125.9, 114.8, 51.4, 51.2, 35.7, 31.4, 14.2, 4.6, 4.0 ppm. **FT-IR** (KBr): 2957, 2925, 2854, 1719, 1457, 1260, 1087, 1018, 799 cm^{-1}. **HRMS** (ESI$^+$): *m/z* calcd for $C_{18}H_{23}O_2$ $[M+H]^+$ 271.1693, found 271.1691. $[\alpha]_D^{24.3}$ = +11.40 (c = 0.10, $CHCl_3$). **HPLC**: Daicel Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 99.2/0.8, 0.20 mL/min, 20 °C, 230 nm; [t_1 (minor) = 12.531 min, t_2 (major) = 13.047 min], 96% *ee*.



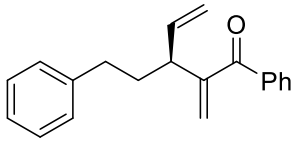
4s

$\mathbf{R}_f$ = 0.61 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.18 (s, 1H), 5.74 (ddd, J = 16.8, 10.3, 8.1 Hz, 1H), 5.54 (s, 1H), 5.07-5.02 (m, 2H), 3.75 (s, 3H), 3.56 (m, 1H), 3.16 (td, J = 8.1, 5.6 Hz, 1H), 1.94 (m, 1H), 1.85-1.71 (m, 4H), 1.58-1.52 (m, 3H), 1.46-1.44 (m, 2H), 1.42-1.31 (m, 8H), 1.26-1.17 (m, 3H), 1.14 (m, 1H), 1.10-1.02 (m, 6H), 0.89 (s, 15H), 0.62 (s, 3H), 0.05 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.6, 143.7, 140.3, 123.9, 115.3, 72.9, 56.4, 56.2, 51.8, 45.1, 42.7, 42.3, 40.2, 40.1, 36.9, 35.9, 35.6, 35.5, 34.6, 33.5, 31.0, 30.2, 28.3, 27.3, 26.4, 26.0 (overlap), 24.2, 23.4, 20.8, 18.6, 18.4, 12.0, -4.6 (overlap) ppm. **FT-IR** (KBr): 2960, 2944, 2926, 2854, 1468, 1369, 1261, 1093, 1021, 950, 908, 870, 835, 803, 773 cm^{-1}. **HRMS** (ESI$^+$): *m/z* calcd for $C_{36}H_{62}O_3SiNa$ $[M+Na]^+$ 593.4360, found 593.4363. $[\alpha]_D^{25.0}$ = +38.46 (c = 0.26, $CHCl_3$). ^{1}H NMR analysis of the product **4s** showed the dr > 40:1. **m.p.** 64-66 °C.



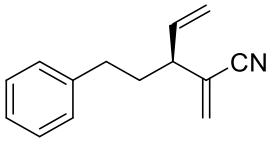
4t

R_f = 0.41 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76-7.49 (m, 4H), 7.42-7.25 (m, 6H), 6.27 (s, 1H), 5.84 (ddd, *J* = 17.7, 10.2, 8.0 Hz, 1H), 5.64 (s, 1H), 5.25-4.92 (m, 2H), 3.74 (s, 3H), 3.40 (q, *J* = 7.6 Hz, 1H), 2.95-2.75 (m, 2H), 2.29-1.98 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.1, 163.1, 145.1, 142.4, 139.1, 135.1, 132.6, 129.1, 128.6 (overlap), 128.5 (overlap), 128.3, 128.0 (overlap), 127.9 (overlap), 126.4, 124.9, 116.3, 51.9, 44.7, 30.8, 26.3 ppm. **FT-IR** (KBr): 3060, 1722, 1625, 1605, 1572, 1502, 1484, 1441, 1258, 1195, 1142, 1060, 1025, 993, 961, 919, 818, 764, 695 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{24}H_{24}NO_3$ $[M+H]^+$ 374.1751, found 374.1758. $[\alpha]_D^{20.0}$ = +10.39 (*c* = 0.77, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 1.00 mL/min, 25 °C, 210 nm; [t_1 (minor) = 7.636 min, t_2 (major) = 8.442 min], 94% *ee*.



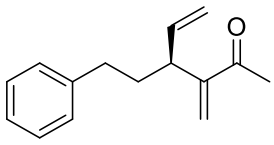
4u

R_f = 0.45 (petroleum ether/ethyl acetate 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81-7.71 (m, 2H), 7.57-7.50 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34-7.23 (m, 2H), 7.20-7.10 (m, 3H), 5.95-5.83 (m, 1H), 5.82 (s, 1H), 5.62 (s, 1H), 5.28-5.03 (m, 2H), 3.52 (td, *J* = 8.4, 5.7 Hz, 1H), 2.80-2.67 (m, 1H), 2.66-2.55 (m, 1H), 2.03-1.93 (m, 1H), 1.92-1.80 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.0, 150.5, 142.1, 139.5, 137.9, 132.4, 129.6 (overlap), 128.4 (overlap), 128.4 (overlap), 128.2 (overlap), 125.8, 124.4, 116.3, 45.1, 35.3, 33.8 ppm. **FT-IR** (KBr): 3062, 3026, 2927, 1658, 1598, 1495, 1450, 1411, 1266, 1160, 981, 921, 750, 699 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{20}H_{21}O$ $[M+H]^+$ 277.1587, found 277.1592. $[\alpha]_D^{25.0}$ = +24.53 (*c* = 0.19, $CHCl_3$). **HPLC**: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 99/1, 1.00 mL/min, 25 °C, 210 nm; [t_1 (major) = 8.009 min, t_2 (minor) = 8.557 min], 89% *ee*.



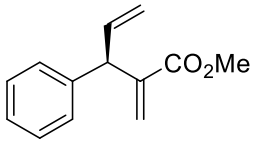
4v

R_f = 0.42 (petroleum ether/ethyl acetate 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 2H), 7.24-7.13 (m, 3H), 5.91 (s, 1H), 5.86-5.70 (m, 2H), 5.40-5.06 (m, 2H), 2.90 (q, J = 7.5 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.06-1.94 (m, 1H), 1.93-1.80 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.0, 137.0, 130.3, 128.5 (overlap), 128.4 (overlap), 126.1, 126.1, 117.7 (overlap), 47.7, 34.2, 33.0 ppm. **FT-IR** (KBr): 3084, 3028, 2926, 2859, 2222, 1604, 1496, 1454, 993, 930, 751, 700 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{14}H_{16}N$ $[M+H]^+$ 198.1277, found 198.1276. **$[\alpha]_D^{25.0}$** = +5.32 (c = 0.65, $CHCl_3$). **HPLC**: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99.3/0.7, 1.00 mL/min, 25 °C, 210 nm; [t_1 (major) = 12.367 min, t_2 (minor) = 14.028 min], 94% *ee*.



4w

R_f = 0.58 (petroleum ether/ethyl acetate 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.25 (m, 2H), 7.20-7.10 (m, 3H), 6.08 (s, 1H), 5.85-5.72 (m, 2H), 5.12-5.00 (m, 2H), 3.43 (q, J = 7.5 Hz, 1H), 2.70-2.58 (m, 1H), 2.57-2.45 (m, 1H), 2.32 (s, 3H), 1.86-1.74 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.1, 151.5, 142.2, 140.3, 128.4 (overlap), 128.4 (overlap), 125.8, 124.7, 115.5, 42.8, 35.8, 33.8, 26.3 ppm. **FT-IR** (KBr): 3082, 3027, 2928, 1679, 1637, 1496, 1454, 1362, 1257, 917, 750, 700 cm^{-1}. **HRMS** (ESI^+): *m/z* calcd for $C_{15}H_{19}O[M+H]^+$ 215.1430, found 215.1434. **$[\alpha]_D^{25.0}$** = +11.86 (c = 0.29, $CHCl_3$). **HPLC**: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 99/1, 0.50 mL/min, 20 °C, 210 nm; [t_1 (major) = 15.370 min, t_2 (minor) = 16.305 min], 91% *ee*.

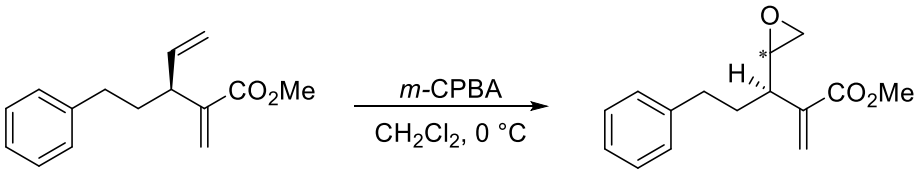


4x

R_f = 0.50 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.26 (m, 2H), 7.25-7.12 (m, 3H), 6.35 (s, 1H), 6.09 (ddd, J = 17.1, 10.2, 6.8 Hz, 1H), 5.57 (s, 1H), 5.17 (d, J = 10.2 Hz, 1H), 4.94 (d, J = 17.1 Hz, 1H), 4.66 (d, J = 6.8 Hz, 1H), 3.67 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.2, 142.5, 140.7, 138.9, 128.5 (overlap), 128.4 (overlap), 126.7, 126.3, 116.7, 52.0, 50.2 ppm. **HRMS** (EI): *m/z* calcd for $C_{13}H_{14}O_2$ $[M]^+$ 202.0988, found 202.0986. **$[\alpha]_D^{20.0}$** = –76.96 (c = 0.65, $CHCl_3$). **HPLC**: Daicel Chiralpak OJ-H, *n*-hexane/*i*-PrOH = 70/30, 0.5 mL/min, 20 °C, 230 nm; [t1 (major) 16.851 min, t2 (minor) = 20.059 min], 70% *ee*. Literature[3] $[\alpha]_D$ +98.1 (c 0.5 $CHCl_3$) for an enantiomerically enriched sample of **ent-4x** with 90% ee.

Derivatizations of products

methyl (*R*)-2-methylene-3-((*S*)-oxiran-2-yl)-5-phenylpentanoate (5)

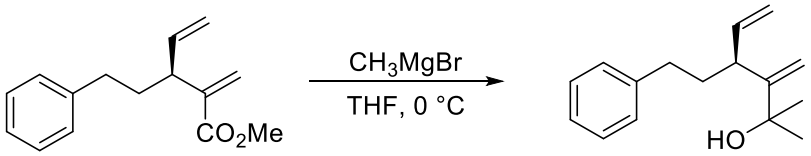


4a **5**

In an oven and vacuum-dried 10 mL round-bottom flask, **4a** (23 mg, 0.1 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (1 mL, 0.1 M) and cooled to 0 °C. Then, the solution was added *m*-CPBA (60.4 mg, 3.5 equiv) and the resulting suspension was stirred at room temperature for 12 h. Then, the reaction mixture was quenched with saturated aqueous Na2S2O3 (3 mL), the organic phase was separated from the aqueous phase, and the aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic phase was washed with saturated aqueous NaHCO3 (3 mL) and brine, dried over anhydrous Na2SO4, and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel flash column chromatography (petroleum ether/ethyl acetate 20/1) to obtain **5** as a colorless oil (16 mg, 65%). ^{1}H NMR analysis of product **5** showed the *dr* = 1.85:1.

R$_f$ = 0.19 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34-7.22 (m, 3H), 7.20-7.14 (m, 5H), 6.35 (s, 1H), 6.34 (s, 1H), 5.70 (s, 1H), 5.67 (s, 1H), 3.77 (s, 5H), 3.16 (ddd, *J* = 6.7, 3.9, 2.7 Hz, 1H), 3.02 (ddd, *J* = 6.6, 4.1, 2.6 Hz, 1H), 2.79 (m, 1H), 2.71 (m, 1H), 2.68-2.61 (m, 3H), 2.55-2.52 (m, 2H), 2.50 (m, 1H), 2.45 (m, 1H), 2.11(m, 1H), 2.02-1.84 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.2, 167.1, 141.8, 141.6, 140.1, 139.6, 128.4 (overlap), 128.4 (overlap), 128.4 (overlap), 128.3 (overlap), 126.9, 126.2, 126.0, 125.9, 55.2, 53.9, 52.1, 52.0, 47.0, 46.0, 44.0, 43.6, 33.6, 33.5, 33.4, 32.6 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{15}H_{18}O_3Na$ $[M+Na]^+$ 269.1148, found 269.1146.

(*S*)-2-methyl-3-methylene-4-phenethylhex-5-en-2-ol (6)



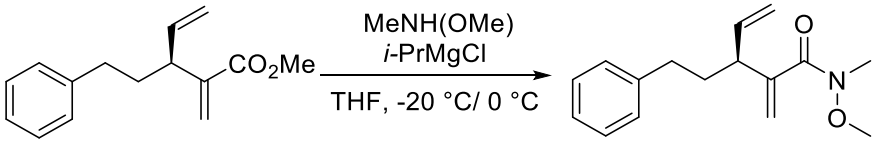
4a **6**

In a dried round bottom flask, **4a** (23 mg, 0.1 mmol, 1.0 equiv) was added, followed by dry THF (0.5 mL, 0.2 M) under an N_2 atmosphere. The solution was cooled to 0 °C using ice bath. To the cooled mixture, MeMgBr (1 M solution in THF, 0.23 mL, 0.23 mmol, 2.3 equiv) was

added dropwise. Then, the reaction was allowed to warm to room temperature and stirred for 15 hours. The reaction was then poured into saturated aqueous NH_4Cl (2 mL) and extracted three times with EtOAc (3 x 5 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated, and purified via silica gel chromatography (petroleum ether/ethyl acetate 10/1) to afford the compound **6** as a colorless oil (16 mg, 72%).

$\mathbf{R}_f$ = 0.33 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.26 (m, 2H), 7.18-7.08 (m, 3H), 5.74 (ddd, J = 17.3, 10.3, 8.3 Hz, 1H), 5.24 (s, 1H), 5.15-4.96 (m, 2H), 4.90 (s, 1H), 2.95 (m, 1H), 2.67 (dt, J = 15.1, 8.0 Hz, 1H), 2.57 (dt, J = 15.1, 7.7 Hz, 1H), 1.87-1.81 (m, 2H), 1.32 (s, 3H), 1.31 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.3, 143.4, 142.3, 128.4 (overlap), 128.3 (overlap), 125.8, 114.2, 107.8, 73.9, 44.4, 38.0, 33.9, 29.1, 29.1 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{22}ONa$ $[M+Na]^+$ 253.1563, found 253.1565. $[\alpha]_D^{25.0}$ = +40.7 (c = 0.57, $CHCl_3$).

(*S*)-*N*-methoxy-*N*-methyl-2-methylene-3-phenethylpent-4-enamide (7)

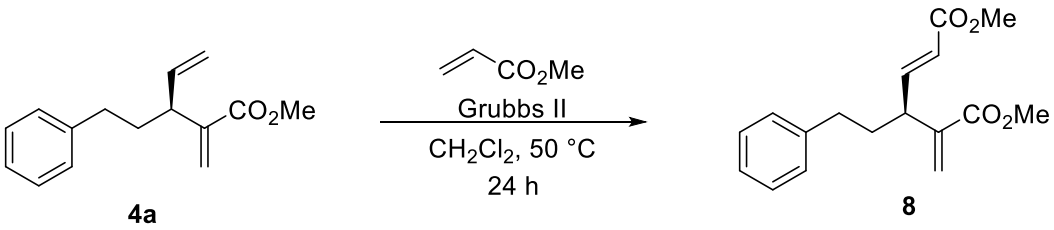


4a **7**

A solution of *i*-PrMgCl (2.0 M in THF, 0.1 mL, 0.2 mmol, 2.5 equiv) was added dropwise to a solution of **4a** (18 mg, 0.08 mmol, 1.0 equiv) and MeNH(OMe)·HCl (8 mg, 0.096 mmol, 1.2 equiv) in dry THF (0.2 mL, 0.4 M) at –20 ℃ under N_2 atmosphere. The mixture was warmed slowly to 0 ℃ and stirred at 0 ℃ for 12 h. The reaction was then quenched with saturated aqueous NH_4Cl (2 mL), and the mixture was extracted with EtOAc (3 x 5 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and filtered. The resulting solution was concentrated *in vacuo*. Purification with column chromatography of the crude residue (petroleum ether/ethyl acetate 5/1) afforded the compound **7** as a colorless oil (12 mg, 60%).

$\mathbf{R}_f$ = 0.14 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 2H), 7.19-7.15 (m, 3H), 5.75 (m, 1H), 5.34 (s, 1H), 5.27 (s, 1H), 5.21-5.03 (m, 2H), 3.62 (s, 3H), 3.22 (s, 3H), 3.14 (m, 1H), 2.70 (ddd, J = 15.2, 10.3, 5.7 Hz, 1H), 2.58 (ddd, J = 15.2, 10.7, 5.2 Hz, 1H), 2.00-1.91 (m, 1H), 1.82-1.73 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.8, 146.9, 142.2, 139.2, 128.5 (overlap), 128.3 (overlap), 125.8, 116.7, 115.3, 61.1, 46.7, 34.7, 33.5, 29.7 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{16}H_{22}NO_2$ $[M+H]^+$ 260.1645, found 260.1648. $[\alpha]_D^{25.0}$ = +20.61 (c = 0.33, $CHCl_3$).

dimethyl (*S*, *E*)-5-methylene-4-phenethylhex-2-enedioate (8)

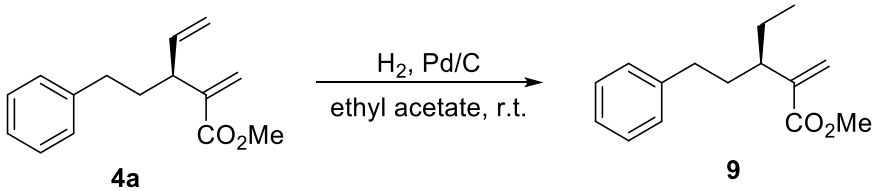


4a **8**

In a dried 10 mL 2-neck round-bottom flask equipped with a reflux condenser, **4a** (11.5 mg, 0.05 mmol, 1.0 equiv) and Grubbs II (2.2 mg, 0.05 equiv) were taken in 2.5 mL of dry CH_2Cl_2 under argon and the resulting solution was heated to 50 °C. Then methyl acrylate (45 μL, 10.0 equiv) was added at once, and the resulting mixture was stirred at 50 °C for 24 h. Subsequently, the solvent was evaporated to obtain a yellow residue. The residue was purified by silica-gel flash column chromatography (petroleum ether/ethyl acetate 10/1) to obtain **8** as a colorless oil (8.4 mg, 58%).

$\mathbf{R}_f$ = 0.28 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 (t, J = 7.4 Hz, 2H), 7.21-7.14 (m, 3H), 6.95 (dd, J = 15.7, 8.3 Hz, 1H), 6.32 (s, 1H), 5.87 (d, J = 15.7 Hz, 1H), 5.64 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.45 (q, J = 7.7 Hz, 1H), 2.72-2.48 (m, 2H), 2.06-1.83 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.9, 166.7, 149.7, 141.3, 141.2, 128.4 (overlap), 128.3 (overlap), 126.0, 126.0, 121.8, 52.1, 51.6, 43.1, 34.9, 33.5 ppm. **HRMS** (ESI^+): *m/z* calcd for $C_{17}H_{21}O_4$ $[M+H]^+$ 289.1434, found 289.1433. $[\alpha]_D^{23.8}$ = +39.67 (c = 1.79, $CHCl_3$).

methyl (*R*)-3-ethyl-2-methylene-5-phenylpentanoate (9)



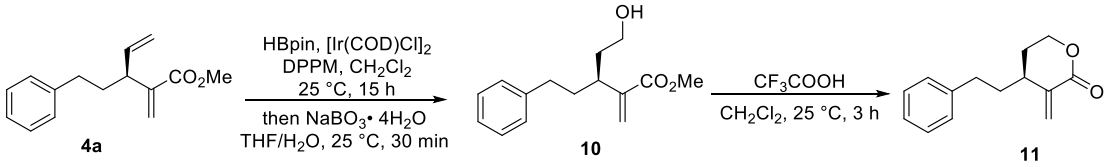
4a **9**

Compound **4a** (10 mg, 0.044 mmol, 1.0 equiv) was dissolved in dried ethyl acetate (440 μL, 0.1 M), and 10% Pd/C (2.3 mg, 0.05 equiv) was added. The reaction mixture was sparged with hydrogen and then stirred under hydrogen (1 atm) for 10 min at room temperature. The mixture was then filtered through a celite pad and washed with ethyl acetate. The filtrate was concentrated in *vacuo,* and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 20/1) to afford **9** as a colorless oil (6.5 mg, 65%).

$\mathbf{R}_f$ = 0.51 (petroleum ether/ethyl acetate 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26 (t, J = 7.4 Hz, 2H), 7.16 (t, J = 7.4 Hz, 3H), 6.27 (s, 1H), 5.53 (s, 1H), 3.76 (s, 3H), 2.57-2.51 (m, 3H), 1.80 (q, J = 7.8 Hz, 2H), 1.58-1.51 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.0, 143.4, 142.6, 128.3 (overlap), 128.2 (overlap), 125.7, 124.6, 51.8, 42.3, 35.7,

33.6, 27.0, 11.5 ppm. **HRMS** (ESI$^+$): *m/z* calcd for $C_{15}H_{21}O_2$ $[M+H]^+$ 233.1536, found 233.1535. $[\alpha]_D^{23.9} = -9.14$ (*c* = 0.58, $CHCl_3$).

(*S*)-3-methylene-4-phenethyltetrahydro-2*H*-pyran-2-one (11)



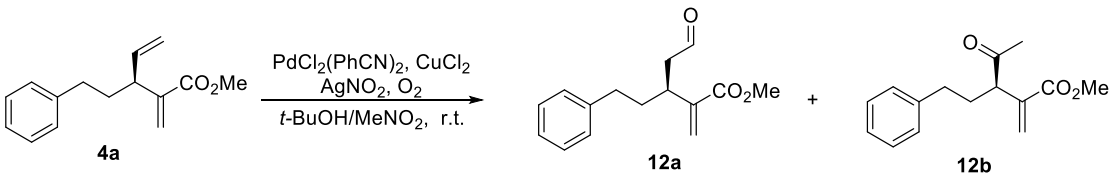
Step 1: In an oven and vacuum-dried 10 mL round-bottom flask, **4a** (23 mg, 0.1 mmol, 1.0 equiv) was taken along with $[Ir(COD)Cl]_2$ (2.2 mg, 3.2 mmol %), and DPPM (2.5 mg, 6.4 mmol %) under a positive argon pressure. Then 1.5 mL of dry CH_2Cl_2 was added to it, followed by the addition of HBpin (48 µL, 3.3 equiv), and the resulting solution was stirred at 25 °C for 15 h. Upon completion, the reaction mixture was concentrated under reduced pressure, and the residue was directly dissolved in 1.5 mL of (1:1) THF/H_2O. Then, $NaBO_3 \cdot 4H_2O$ (92.3 mg, 6.0 equiv) was added to the reaction mixture, and the resulting suspension was stirred at 25 °C for 30 mins. Upon completion, the reaction was quenched with 1 mL of saturated NH_4Cl solution and diluted with 1.5 mL of CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted with (2 x 3 mL) of CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get a yellow oil. The residue was purified by silica-gel flash column chromatography (petroleum ether/ethyl acetate 3/1) to obtain **10** as a colorless oil (22 mg, 89%).

Step 2: In an oven-dried 10 mL round-bottom flask, **10** (22 mg, 0.089 mmol, 1.0 equiv) was taken in 4 mL of dry CH_2Cl_2 under a positive argon pressure. To this, trifluoroacetic acid (88 µL, 13.0 equiv) was added, and the reaction mixture was stirred at 25 °C for 3 h. Upon completion, the reaction was quenched with 6 mL of saturated $NaHCO_3$ solution and diluted with CH_2Cl_2. The organic layer was separated, and the aqueous phase was extracted with (2 x 8 mL) of CH_2Cl_2. Combined organic layers were washed with brine (8 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (petroleum ether/ethyl acetate 5/1) to obtain **11** as a white solid (14 mg, 70%). **m.p.** 72-73 °C.

11: $\mathbf{R_f}$ = 0.45 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 2H), 7.23-7.17 (m, 3H), 6.46 (s, 1H), 5.60 (s, 1H), 4.46 (ddd, *J* = 10.9, 6.6, 4.0 Hz, 1H), 4.28 (ddd, *J* = 10.9, 6.6, 4.0 Hz, 1H), 2.75-2.61 (m, 3H), 2.17-2.10 (m, 1H), 2.01-1.92 (m, 1H), 1.84-1.73 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.2, 138.9, 128.6 (overlap), 128.3

(overlap), 127.5, 126.2, 67.0, 36.9, 35.8, 32.7, 28.1 ppm. **HRMS** (ESI$^+$): *m/z* calcd for $C_{14}H_{17}O_2$ $[M+H]^+$ 217.1223, found 217.1218. $[\alpha]_D^{23.6}$ = +32.31 (*c* = 0.13, $CHCl_3$).

Methyl (*S*)-2-methylene-5-oxo-3-phenethylpentanoate (12a) and methyl (*R*)-3-acetyl-2-methylene-5-phenylpentanoate (12b)

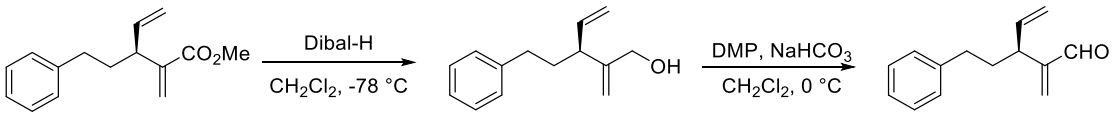


In a dried 10 mL round-bottom flask, $PdCl_2(PhCN)_2$ (4.6 mg, 0.012 mmol, 0.12 equiv), $CuCl_2$ (1.7 mg, 0.012 mmol, 0.12 equiv), $AgNO_2$ (0.93 mg, 0.006 mmol, 0.06 equiv) were added. The round-bottom flask was evacuated and backfilled with an O_2 balloon. To this, **4a** (23 mg, 0.1 mmol, 1.0 equiv) was added as a solution in 2 mL of (16:1) t-BuOH/CH3NO2 under positive oxygen pressure. The reaction mixture was then stirred at room temperature for 66 h under a balloon of O_2. Then the reaction mixture was diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (petroleum ether/ethyl acetate 20/1) to obtain **12a** and **12b** as a colorless oil (**11**: 11 mg, 45%; **12**: 10 mg, 40%).

12a: R_f = 0.25 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (t, *J* = 2.0 Hz, 1H), 7.29-7.25 (m, 2H), 7.21-7.09 (m, 3H), 6.31 (s, 1H), 5.64 (s, 1H), 3.77 (s, 3H), 3.20 (m, 1H), 2.76-2.64 (m, 2H), 2.63-2.52 (m, 2H), 1.93 (ddt, *J* = 15.1, 8.9, 4.3 Hz, 1H), 1.82 (ddt, *J* = 15.1, 9.0, 4.5 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 167.0, 141.9, 141.5, 128.4 (overlap), 128.3 (overlap), 126.2, 126.0, 52.0, 48.4, 35.6, 35.6, 33.4 ppm. **HRMS** (ESI$^+$): *m/z* calcd for $C_{15}H_{19}O_3$ $[M+H]^+$ 247.1329, found 247.1331. $[\alpha]_D^{25.0}$ = –5.39 (*c* = 0.66, $CHCl_3$).

12b: R_f = 0.36 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.23-7.12 (m, 3H), 6.41 (s, 1H), 5.70 (s, 1H), 3.78 (s, 3H), 3.64 (t, *J* = 7.2 Hz, 1H), 2.77-2.44 (m, 2H), 2.28-2.18 (m, 1H), 2.15 (s, 3H), 1.91-1.82 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.3, 166.9, 141.3, 138.5, 128.4 (overlap), 128.4 (overlap), 127.6, 126.1, 53.3, 52.3, 33.5, 31.9, 29.2 ppm. **HRMS** (ESI$^+$): *m/z* calcd for $C_{15}H_{18}O_3Na$ $[M+Na]^+$ 269.1148, found 269.1147. $[\alpha]_D^{25.0}$ = –30.95 (*c* = 0.46, $CHCl_3$).

(*S*)-2-methylene-3-phenethylpent-4-enal (14)



4a **13** **14**

Step 1: To a solution of **4a** (23 mg, 0.1 mmol, 1.0 equiv) in dry CH_2Cl_2 (0.5 mL, 0.2 M) was added dropwise diisobutylaluminum hydride (Dibal-H, 1.5 M in toluene, 0.16 mmol, 0.11 mL, 2.0 equiv) via syringe at −78 °C. The reaction was stirred at −78 °C for 30 min before it was diluted with ethyl ether and quenched with 5 mL of icy cold Rochelles salt (saturated Na/K tartrate). The mixture was allowed to room temperature and stirred for 30 min. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3 x 3 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash-column chromatography on silica gel (petroleum ether/ethyl acetate 5/1) to afford **13** as a colorless oil (20 mg, 95%).

Step 2: To a solution of **13** (20 mg, 0.1mmol, 1.0 equiv) in CH_2Cl_2 (3 ml, 0.03 M) was added $NaHCO_3$ (17 mg, 0.2 mmol, 2.0 equiv) and Dess-Martin periodinane (49 mg, 0.15 mmol, 1.5 equiv) at 0 °C, then the reaction mixture was stirred at room temperature until the alcohol had disappeared thoroughly monitored by TLC. The reaction was then quenched with saturated aqueous $NaHCO_3$ (1 mL) and saturated aqueous $Na_2S_2O_3$ (1 mL). The mixture was allowed to stir at room temperature until the layers were separated. Then, the aqueous layer was extracted with ethyl acetate (3 x 5 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash-column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) to afford **14** as a colorless oil (19 mg, 95%).

14: $\mathbf{R}_f$ = 0.41 (petroleum ether/ethyl acetate 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.2-7.25 (m, 2H), 7.21-7.12 (m, 3H), 6.27 (s, 1H), 6.06 (s, 1H), 5.81 (ddd, J = 17.6, 9.8, 8.0 Hz, 1H), 5.31-4.91 (m, 2H), 3.31 (m, 1H), 2.64 (ddd, J = 13.8, 10.3, 5.7 Hz, 1H), 2.53 (ddd, J = 13.8, 10.1, 6.0 Hz, 1H), 1.91-1.80 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 152.4, 141.9, 139.2, 134.2, 128.4 (overlap), 125.9, 116.0, 41.4, 35.2, 33.7 ppm. **HRMS** (ESI^-): *m/z* calcd for $C_{14}H_{15}O$ $[M-H]^-$ 199.1128, found 199.1132. $[\alpha]_D^{25.0}$ = +7.45 (c = 0.11, $CHCl_3$).

References

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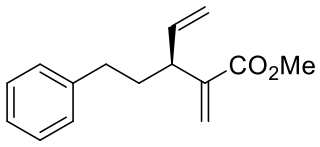
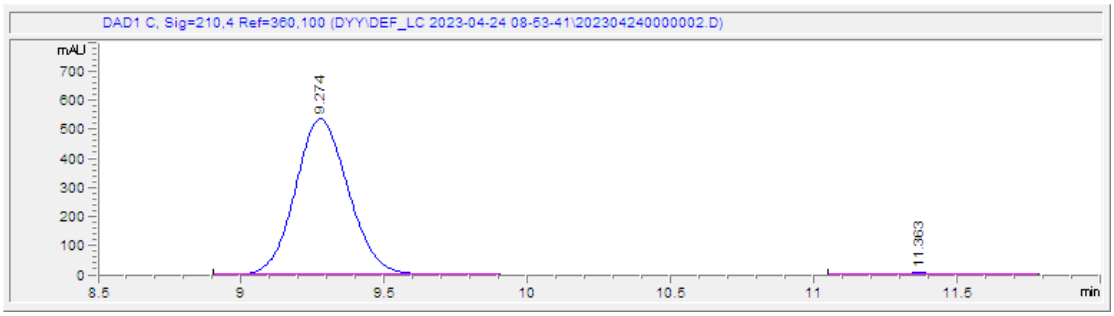
2. Han, S. B.; Han, H.; Krische, M. J. Diastereo- and Enantioselective anti-Alkoxyallylation Employing Allylic gem-Dicarboxylates as Allyl Donors via Iridium-Catalyzed Transfer Hydrogenation. *J. Am. Chem. Soc.* **2010**, *132*, 1760-1761.
3. Xu, Q.-L.; Dai, L.-X.; You, S.-L. Iridium-catalyzed enantioselective allylic alkylation of methyl 2-(4-nitrophenylsulfonyl)acetate and subsequent transformations. *Adv. Synth. Catal.* **2012**, *354*, 2275-2282.

HPLC data



4a



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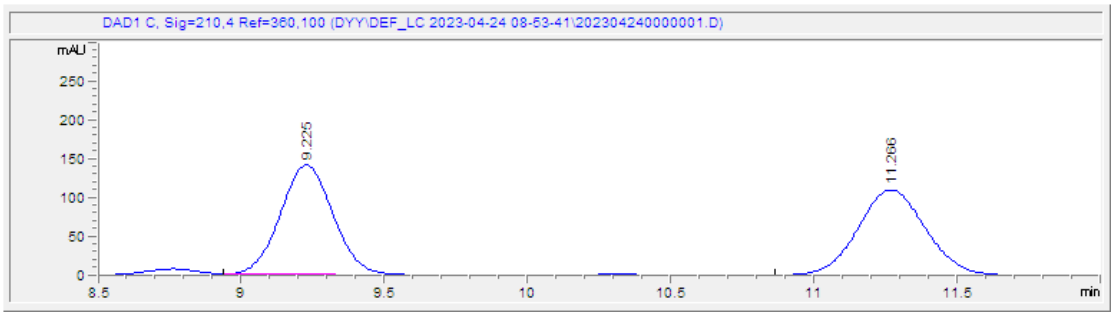

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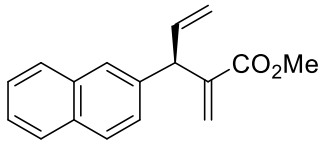
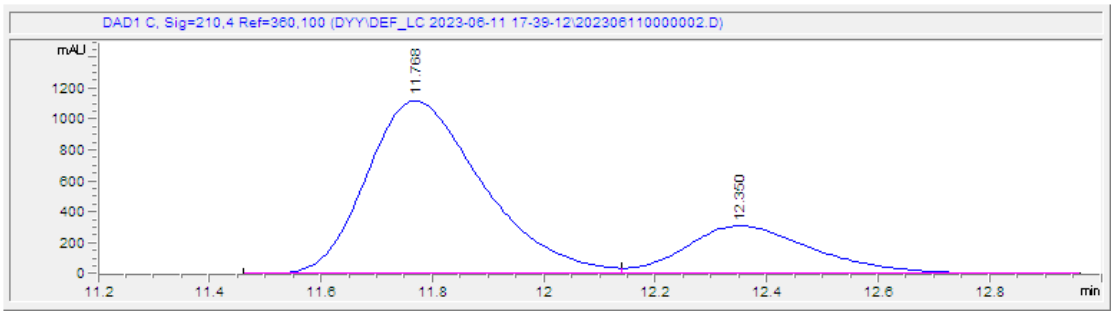


4b



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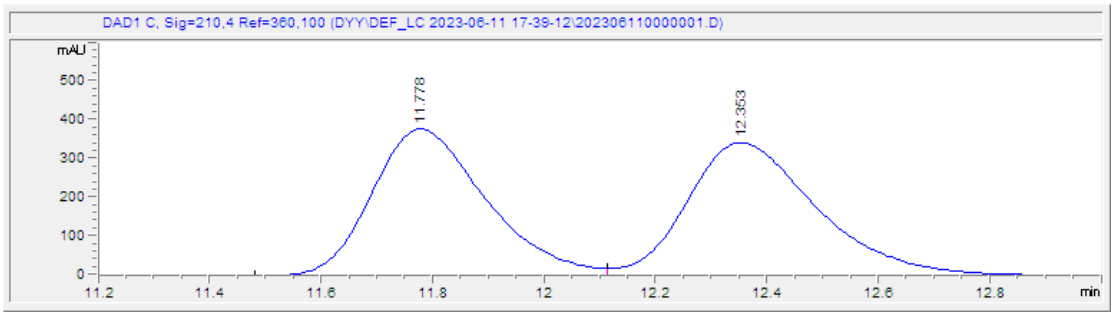
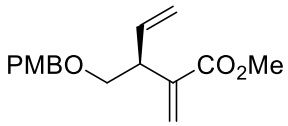
2	12.35	5062.1	312.3	0.2451	23.643	0.688

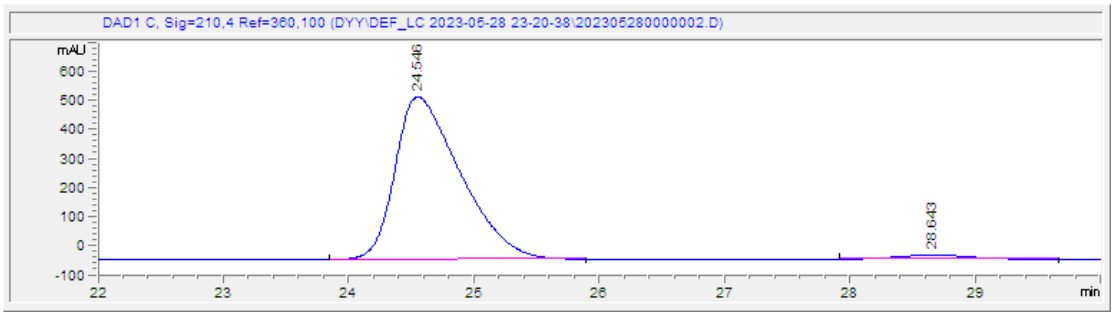
Racemic 4b:



#	Time	Area	Height	Width	Area%	Symmetry
1	11.778	5404.9	379.1	0.2163	49.288	0.711
2	12.353	5561.1	343.9	0.2447	50.712	0.68

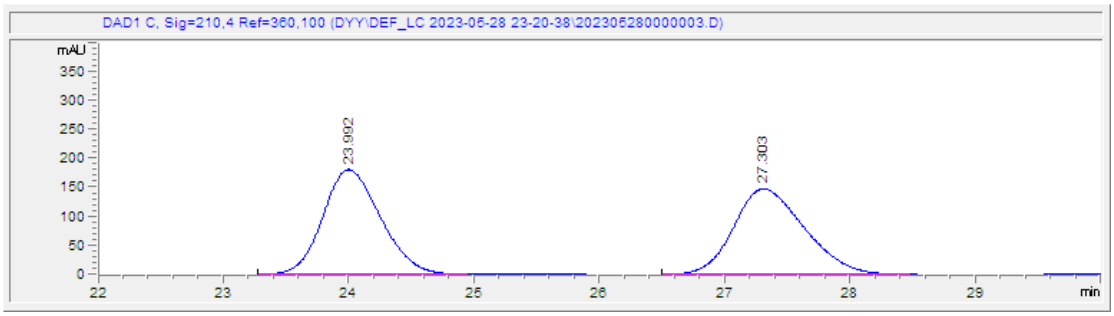


4c

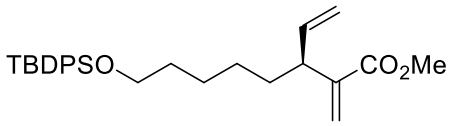


#	Time	Area	Height	Width	Area%	Symmetry
1	24.546	20226.8	558.8	0.5443	97.383	0.511
2	28.643	543.6	14.2	0.5388	2.617	0.963

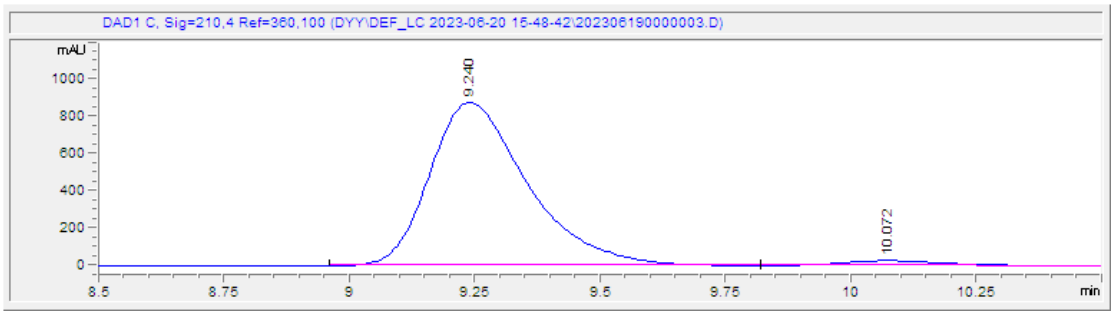
Racemic 4c:



#	Time	Area	Height	Width	Area%	Symmetry
1	23.992	5798.8	180.8	0.4923	49.828	0.776
2	27.303	5839	148	0.6041	50.172	0.713

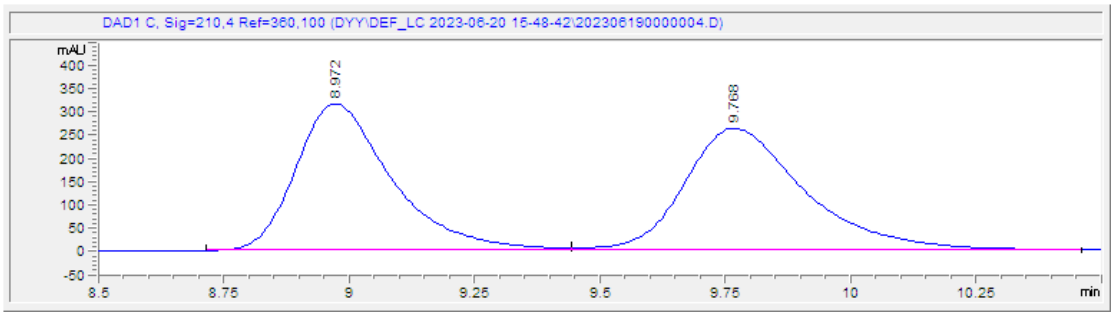


4d

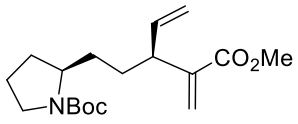


#	Time	Area	Height	Width	Area%	Symmetry
1	9.24	11959	878.9	0.2067	96.537	0.648
2	10.072	429	27.7	0.2306	3.463	0.692

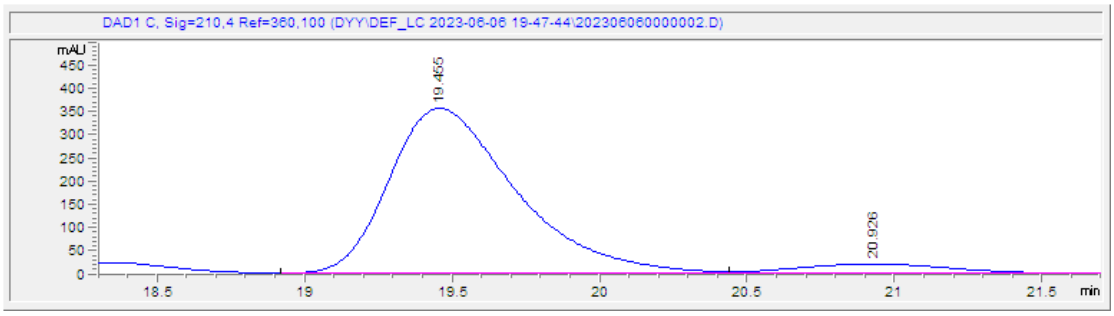
Racemic 4d:



#	Time	Area	Height	Width	Area%	Symmetry
1	8.972	4214.3	315.4	0.1999	48.776	0.644
2	9.768	4425.9	262.4	0.2528	51.224	0.667

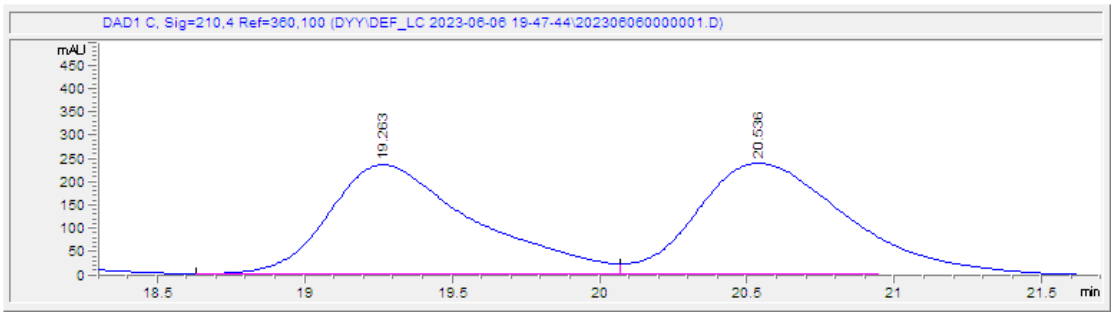


4e

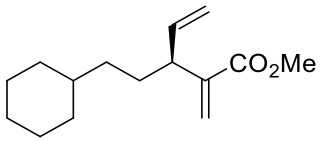


#	Time	Area	Height	Width	Area%	Symmetry
1	19.455	10719.4	356.6	0.4567	92.675	0.614
2	20.926	847.3	21.6	0.5987	7.325	0.867

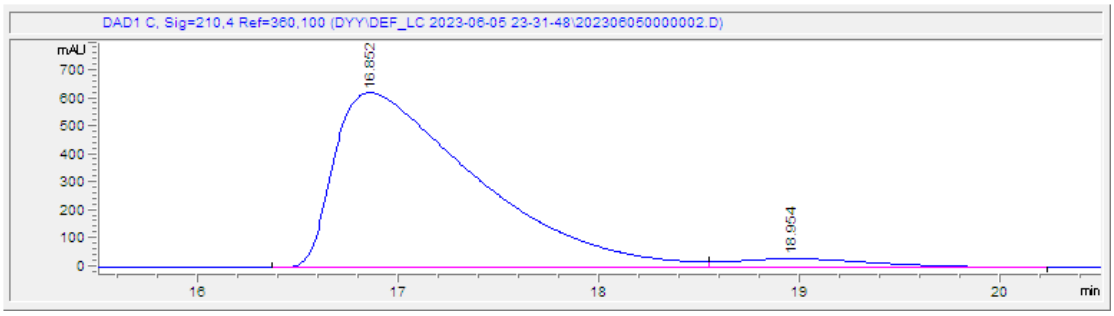
Racemic 4e:



#	Time	Area	Height	Width	Area%	Symmetry
1	19.263	8221	236.5	0.5036	48.765	0.559
2	20.536	8637.5	240.2	0.5495	51.235	0.654

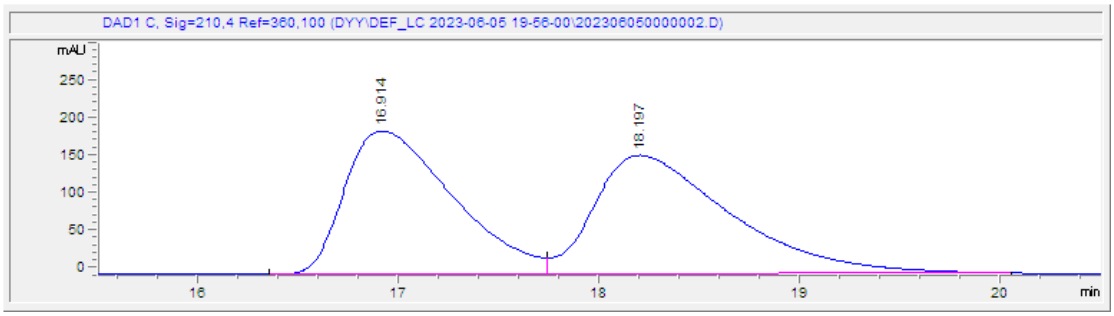


4f

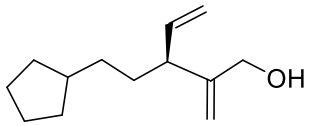


#	Time	Area	Height	Width	Area%	Symmetry
1	16.852	30994	626.1	0.7295	95.040	0.305
2	18.954	1617.5	32	0.7268	4.960	0.645

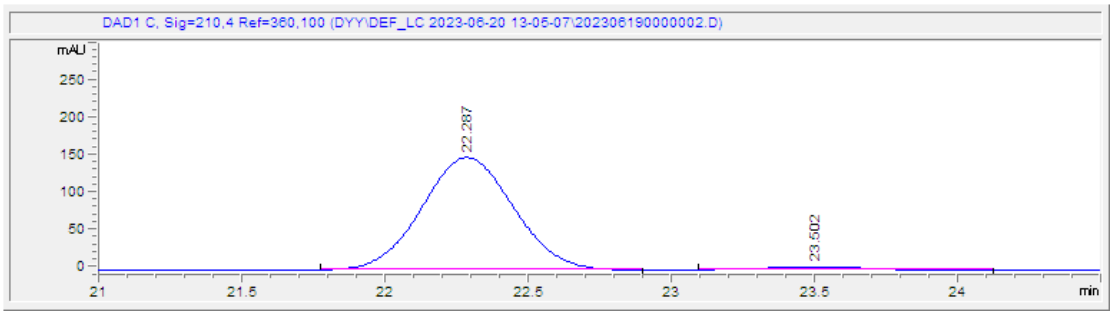
Racemic 4f:



#	Time	Area	Height	Width	Area%	Symmetry
1	16.914	7157.5	190.8	0.5816	48.850	0.502
2	18.197	7494.6	157.9	0.7098	51.150	0.466

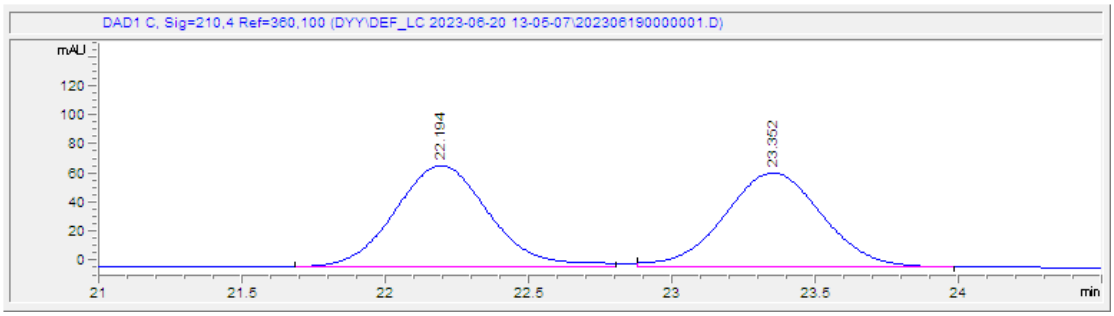


4g'

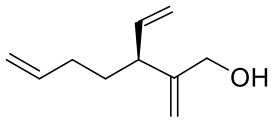


#	Time	Area	Height	Width	Area%	Symmetry
1	22.287	3346.1	150	0.3482	97.230	0.945
2	23.502	95.3	4.2	0.3587	2.770	1.075

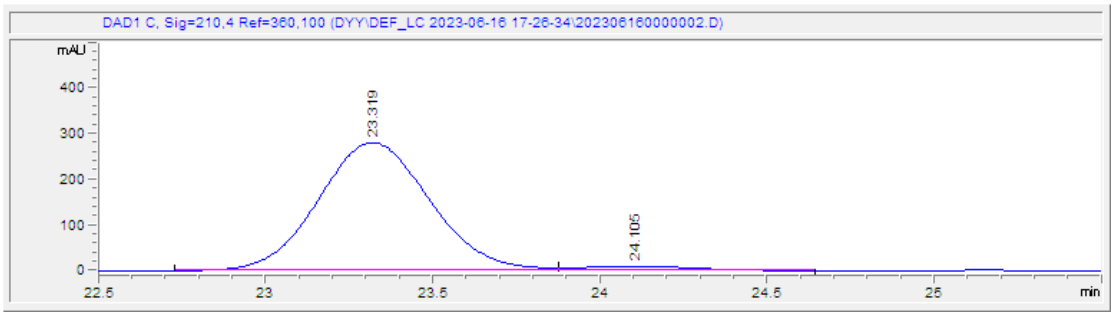
Racemic 4g':



#	Time	Area	Height	Width	Area%	Symmetry
1	22.194	1611	69.7	0.3577	50.969	0.907
2	23.352	1549.8	64.7	0.3733	49.031	0.974

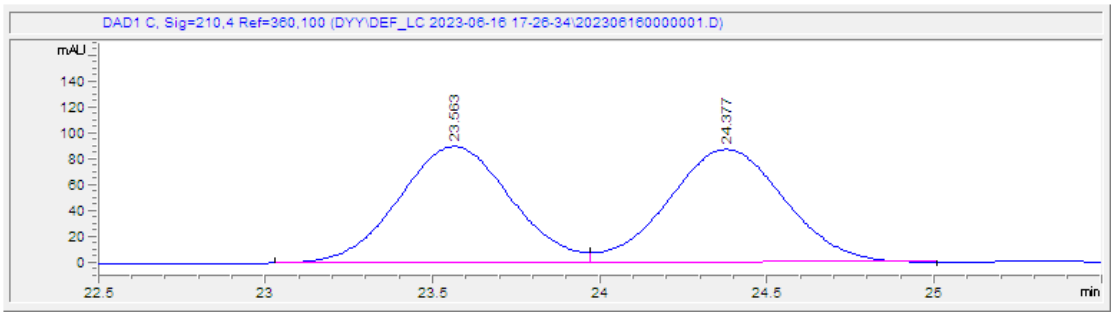


4h'

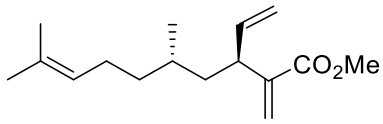


#	Time	Area	Height	Width	Area%	Symmetry
1	23.319	6545.3	280.3	0.3644	96.526	0.909
2	24.105	235.6	9.6	0.3661	3.474	0.838

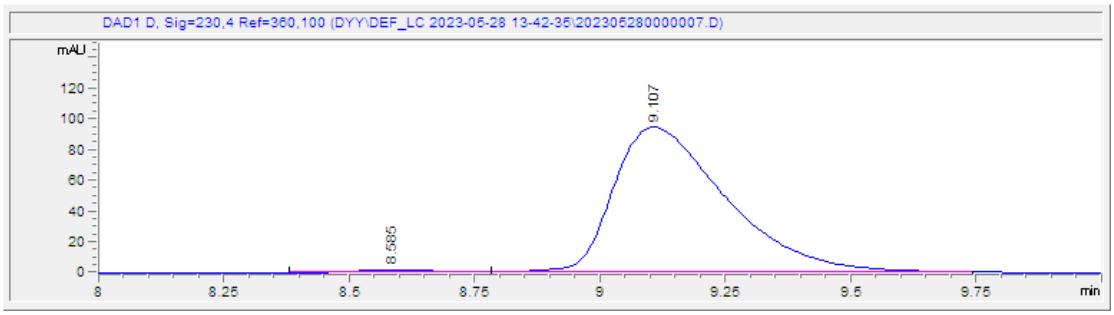
Racemic 4h':



#	Time	Area	Height	Width	Area%	Symmetry
1	23.563	2105	90	0.3628	49.817	0.952
2	24.377	2120.5	87.3	0.3772	50.183	0.972

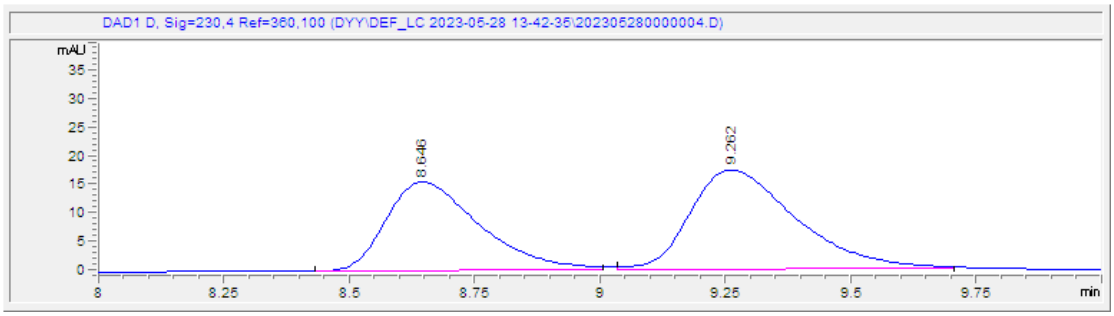


4i

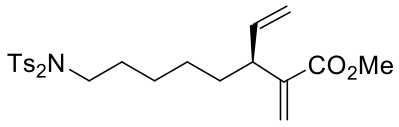


#	Time	Area	Height	Width	Area%	Symmetry
1	8.585	22.7	1.8	0.1948	1.500	0.704
2	9.107	1489	94.6	0.2376	98.500	0.524

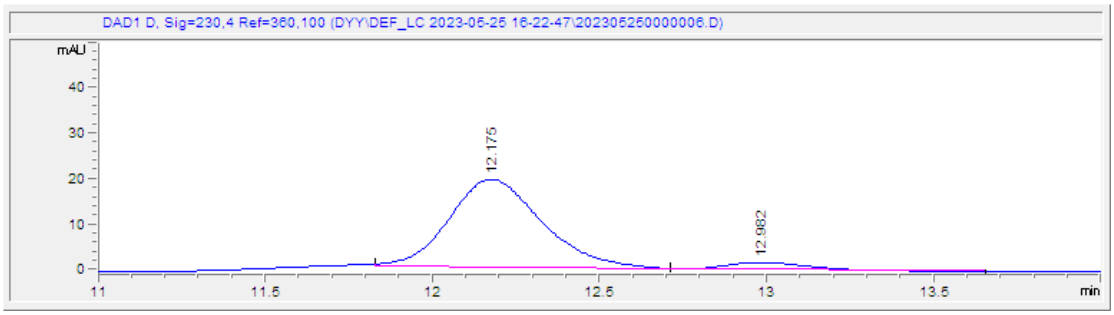
Racemic 4i:



#	Time	Area	Height	Width	Area%	Symmetry
1	8.646	204.1	15.6	0.1983	43.917	0.588
2	9.262	260.6	17.6	0.2248	56.083	0.599

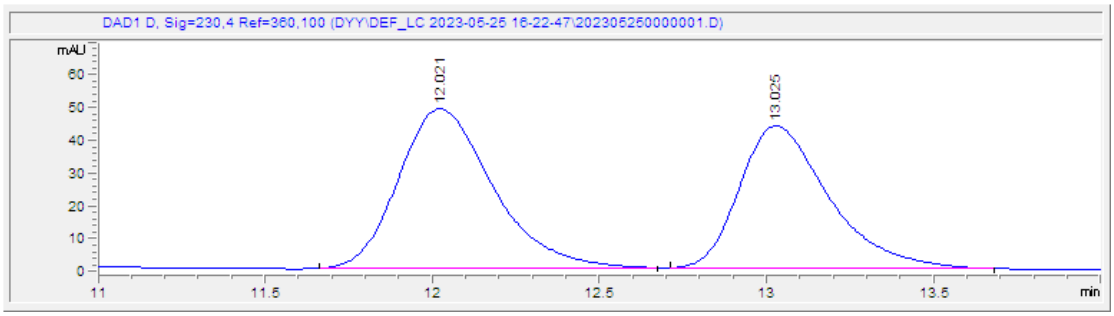


4j

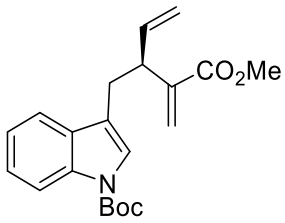


#	Time	Area	Height	Width	Area%	Symmetry
1	12.175	374	19.3	0.2981	93.599	0.798
2	12.982	25.6	1.6	0.2481	6.401	0.729

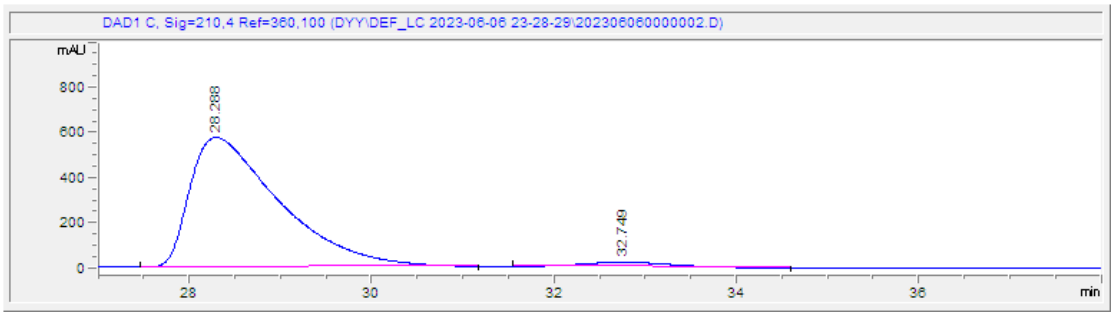
Racemic 4j:



#	Time	Area	Height	Width	Area%	Symmetry
1	12.021	965.7	48.8	0.3031	54.128	0.741
2	13.025	818.4	43.6	0.2848	45.872	0.645

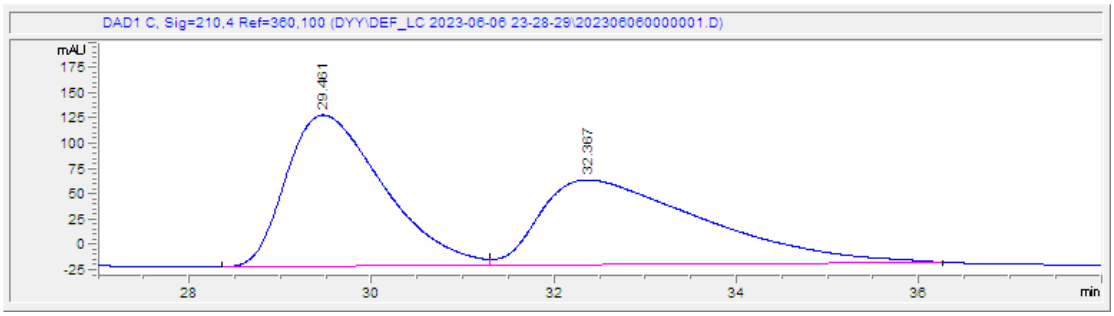


4k

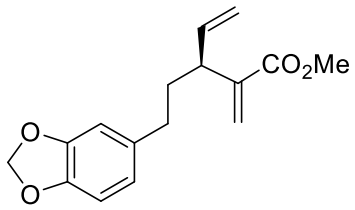


#	Time	Area	Height	Width	Area%	Symmetry
1	28.288	39187.8	573.7	0.9989	96.202	0.384
2	32.749	1546.9	21.9	0.9415	3.798	0.814

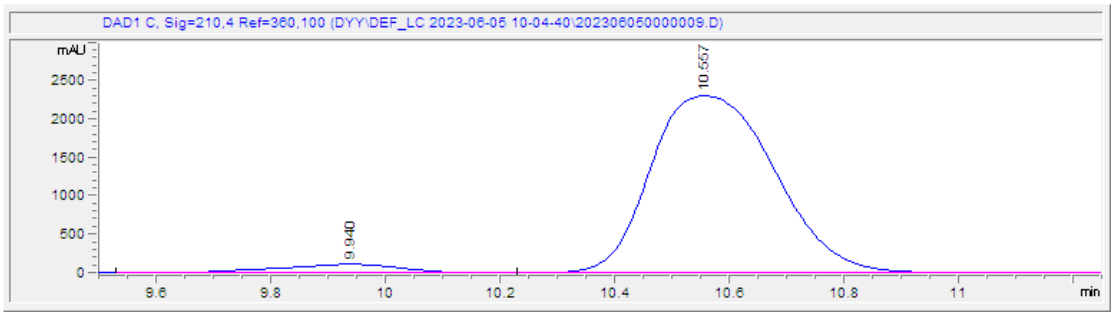
Racemic 4k:



#	Time	Area	Height	Width	Area%	Symmetry
1	29.461	11112.9	149.8	1.1236	51.272	0.584
2	32.367	10561.6	84.1	1.7346	48.728	0.388

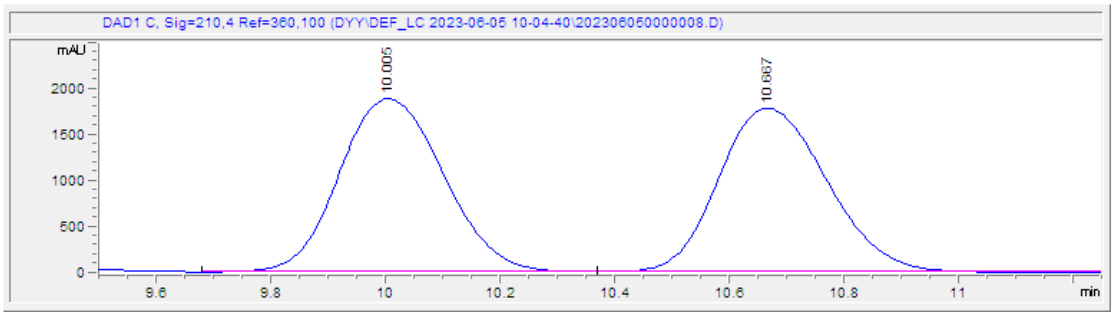


4l

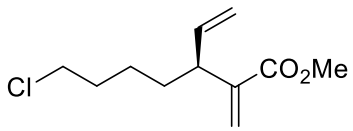


#	Time	Area	Height	Width	Area%	Symmetry
1	9.94	1717.2	113.9	0.2179	4.717	1.477
2	10.557	34685.2	2304.5	0.2416	95.283	0.733

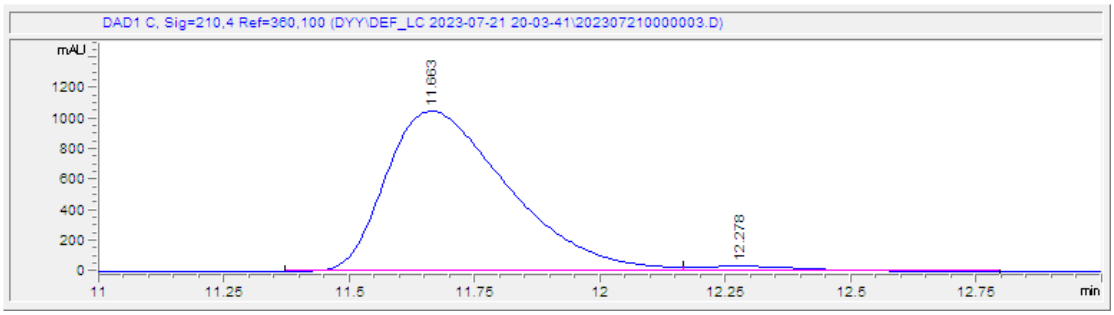
Racemic 4l:



#	Time	Area	Height	Width	Area%	Symmetry
1	10.005	24058.3	1883.5	0.203	50.425	0.853
2	10.667	23653.1	1779.9	0.209	49.575	0.79

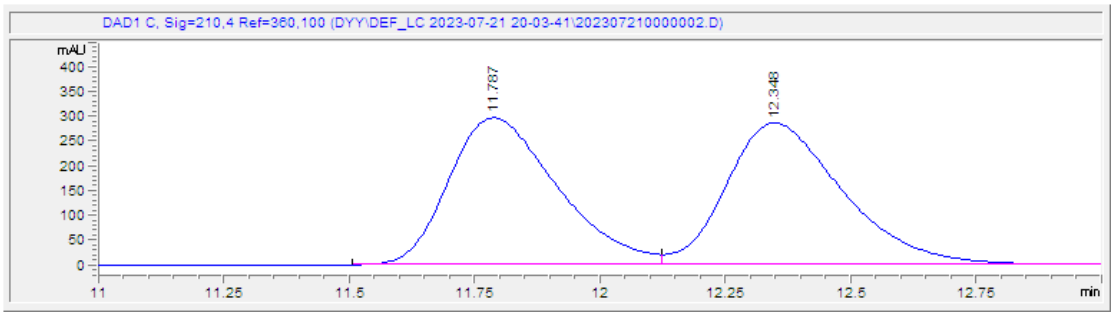


4m

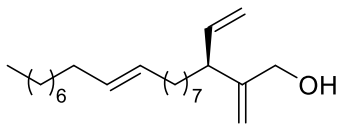


#	Time	Area	Height	Width	Area%	Symmetry
1	11.663	17870.1	1048.9	0.2628	97.212	0.545
2	12.278	512.5	33.2	0.2281	2.788	0.589

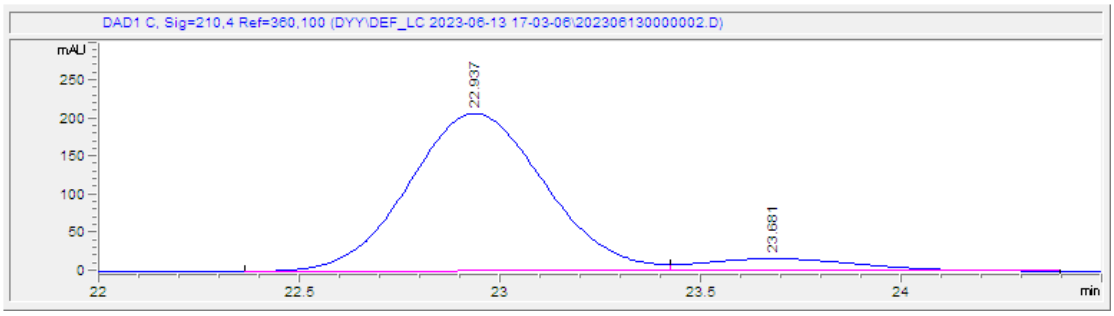
Racemic 4m:



#	Time	Area	Height	Width	Area%	Symmetry
1	11.787	4467.2	296.4	0.2298	49.136	0.659
2	12.348	4624.2	285.4	0.247	50.864	0.67

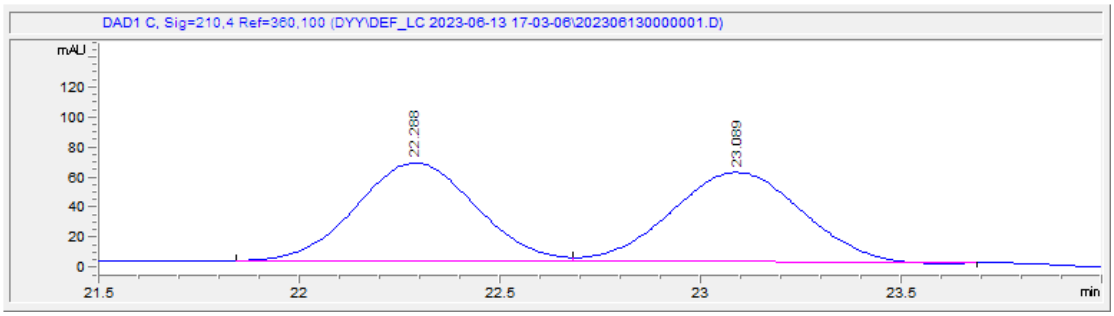


4n'

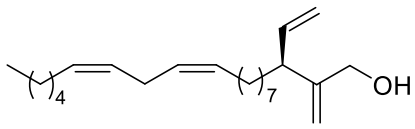


#	Time	Area	Height	Width	Area%	Symmetry
1	22.937	4926.7	207.6	0.3708	91.475	0.911
2	23.681	459.1	16.7	0.4039	8.525	0.755

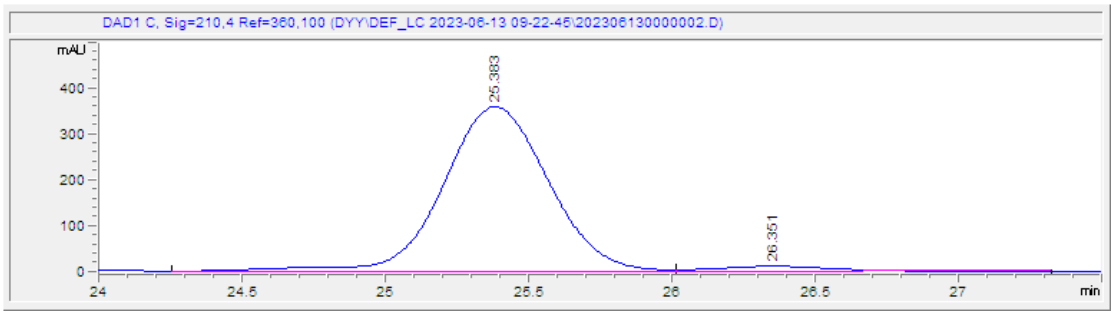
Racemic 4n':



#	Time	Area	Height	Width	Area%	Symmetry
1	22.288	1370.5	65.6	0.3259	50.198	0.945
2	23.089	1359.7	59.9	0.355	49.802	0.988

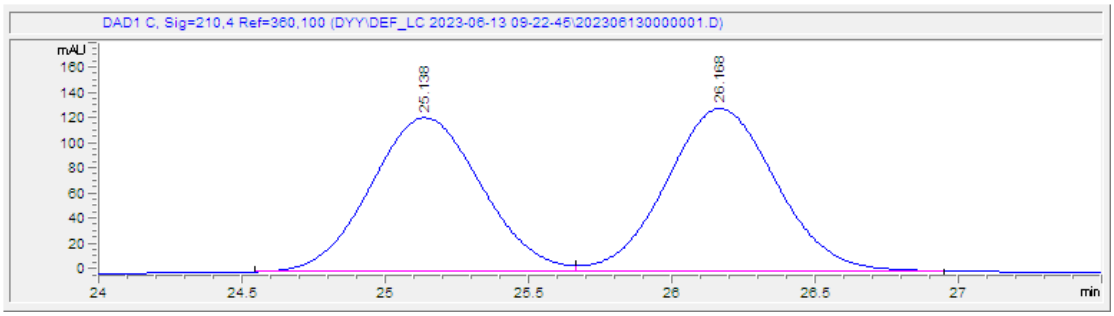


4o'

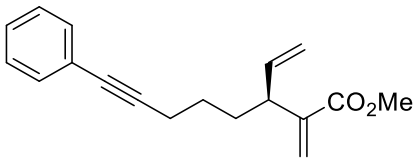


#	Time	Area	Height	Width	Area%	Symmetry
1	25.383	9240.5	358.5	0.3987	96.395	0.973
2	26.351	345.5	11.6	0.4436	3.605	0.796

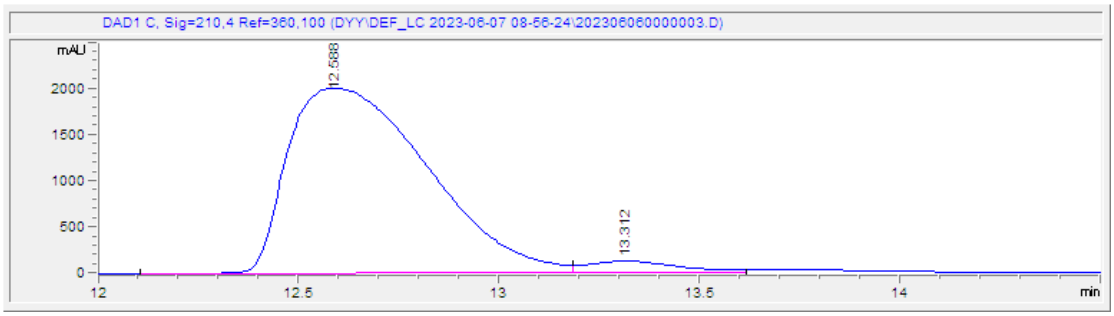
Racemic 4o':



#	Time	Area	Height	Width	Area%	Symmetry
1	25.138	3323	122.7	0.424	48.833	0.936
2	26.168	3481.8	129.8	0.417	51.167	0.933

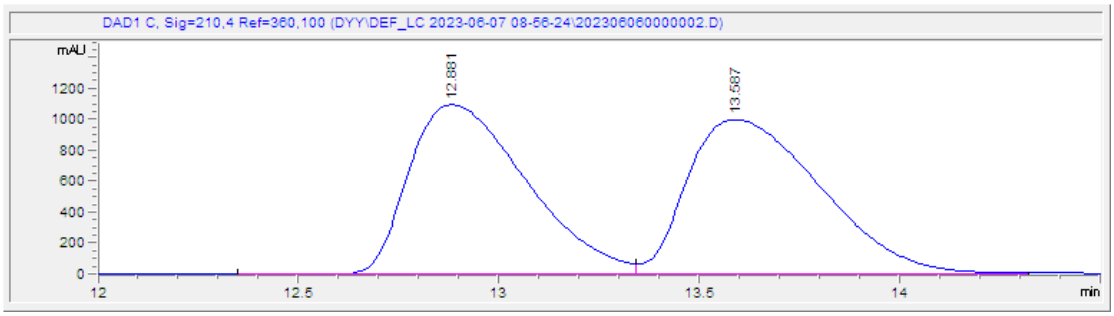


4p

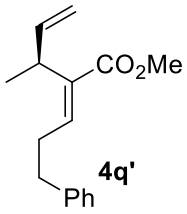


#	Time	Area	Height	Width	Area%	Symmetry
1	12.588	48975.6	2010.9	0.3961	95.486	0.468
2	13.312	2315.3	137.8	0.2421	4.514	0.583

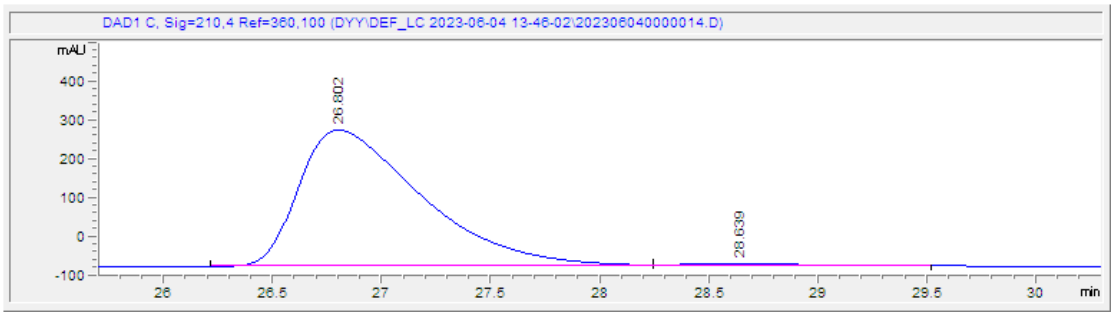
Racemic 4p:



#	Time	Area	Height	Width	Area%	Symmetry
1	12.881	22494.3	1099.3	0.3247	49.085	0.557
2	13.587	23333.2	1003.2	0.3754	50.915	0.535

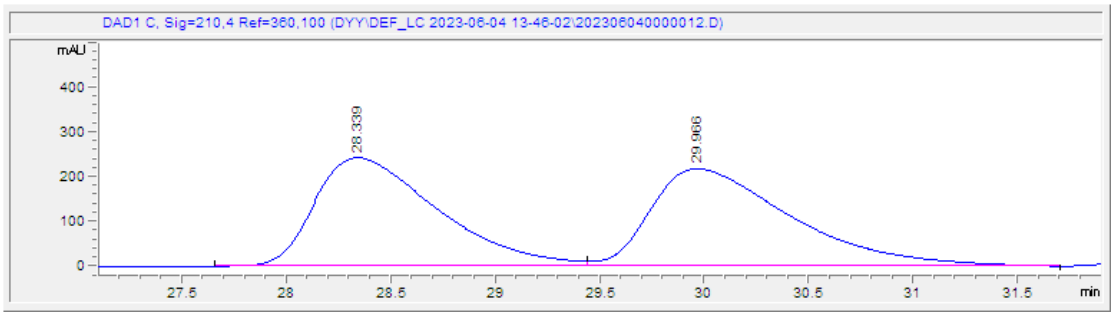


4q'

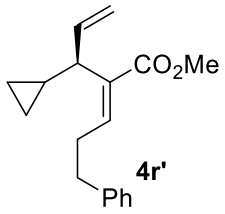


#	Time	Area	Height	Width	Area%	Symmetry
1	26.802	13832.2	351.2	0.5955	98.172	0.449
2	28.639	257.5	6.7	0.5589	1.828	0.876

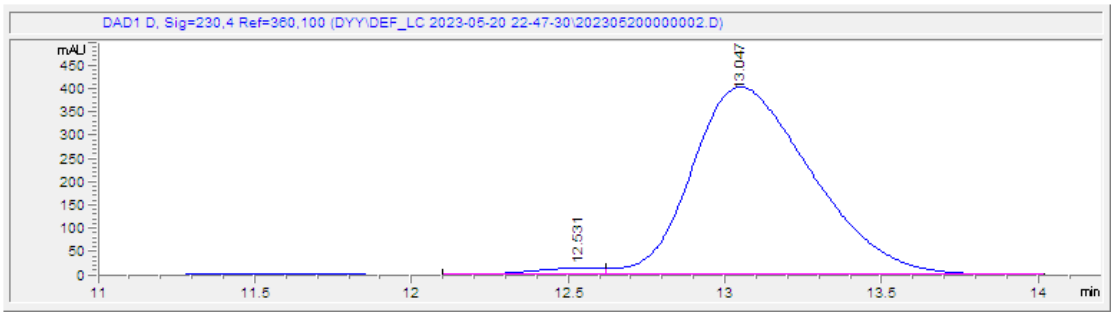
Racemic 4q':



#	Time	Area	Height	Width	Area%	Symmetry
1	28.339	9975.6	242.7	0.6274	49.314	0.503
2	29.966	10253.3	217.9	0.7169	50.686	0.471

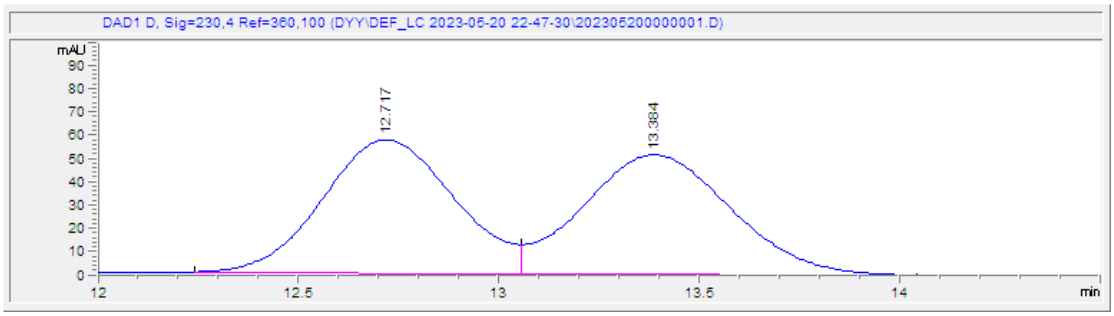


4r'

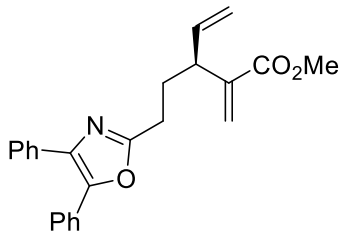


#	Time	Area	Height	Width	Area%	Symmetry
1	12.531	224.8	14.2	0.2449	2.049	2.176
2	13.047	10747.1	403.3	0.4109	97.951	0.65

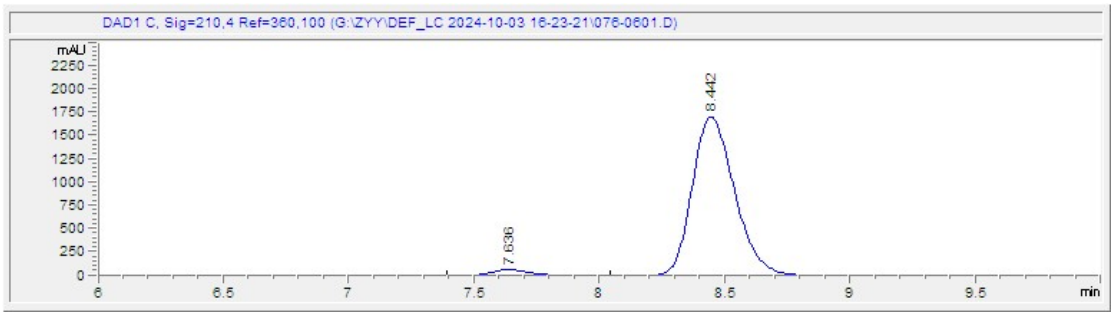
Racemic 4r':



#	Time	Area	Height	Width	Area%	Symmetry
1	12.717	1317	57.4	0.3557	49.914	0.918
2	13.384	1321.5	51.4	0.396	50.086	0.888

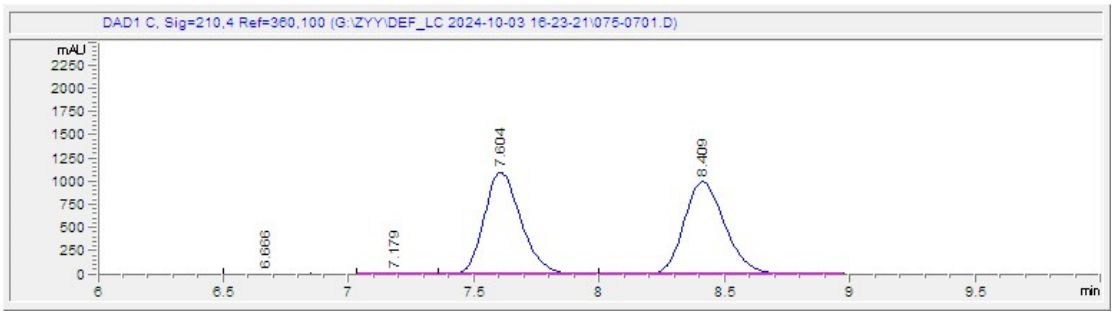


4t

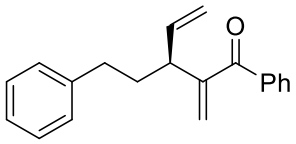


#	Time	Area	Height	Width	Area%	Symmetry
1	7.636	644.8	62	0.1594	3.132	0.818
2	8.442	19946.2	1699.7	0.1829	96.868	0.756

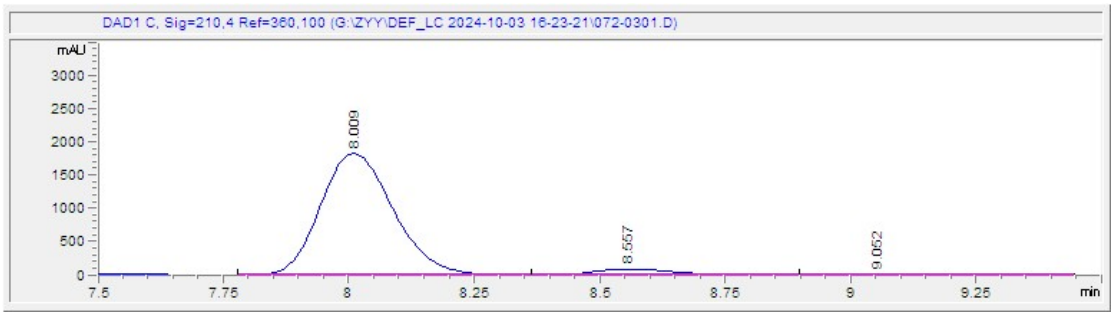
Racemic 4t:



#	Time	Area	Height	Width	Area%	Symmetry
1	7.604	11266.4	1104.2	0.157	49.765	0.769
2	8.409	11372.7	1000.9	0.1746	50.235	0.79

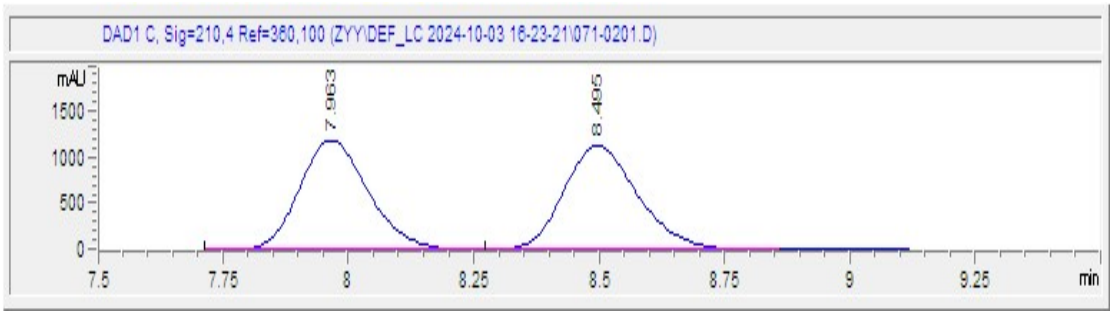


4u

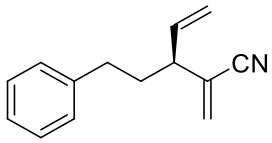


#	Time	Area	Height	Width	Area%	Symmetry
1	8.009	18561.1	1827	0.1585	94.474	0.804
2	8.557	1085.6	95.8	0.1703	5.526	0.72

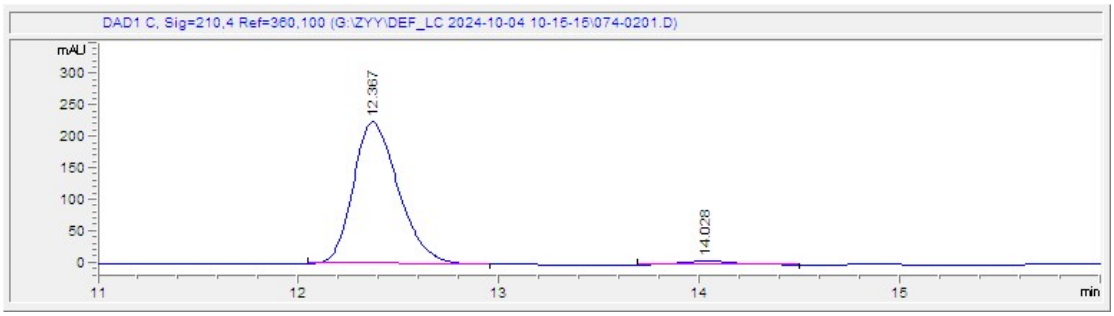
Racemic 4u:



#	Time	Area	Height	Width	Area%	Symmetry
1	7.963	11519.7	1199.4	0.1481	49.361	0.798
2	8.495	11817.8	1135.9	0.1594	50.639	0.774

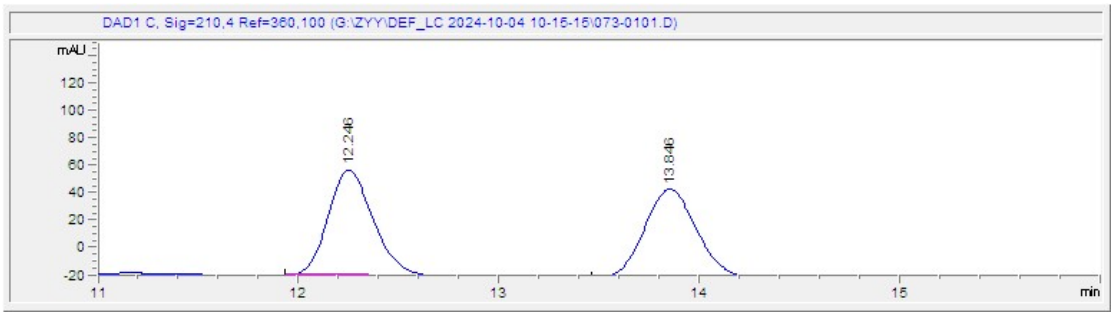


4v

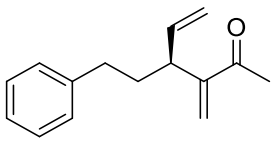


#	Time	Area	Height	Width	Area%	Symmetry
1	12.367	3544.6	225.7	0.2412	97.260	0.729
2	14.028	99.9	5.7	0.2739	2.740	0.873

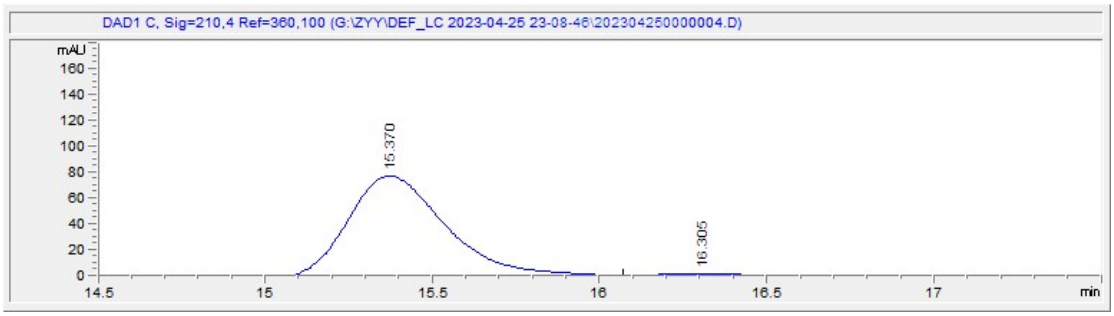
Racemic 4v:



#	Time	Area	Height	Width	Area%	Symmetry
1	12.246	1211.2	77.1	0.2433	50.997	0.786
2	13.846	1163.8	64.7	0.282	49.003	0.894

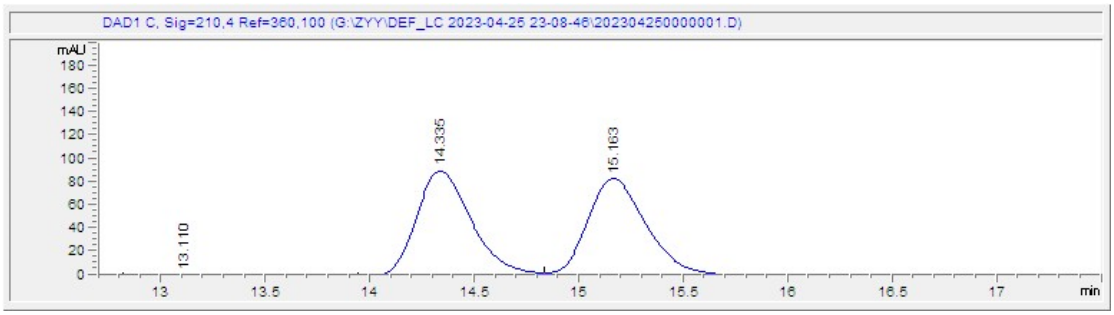


4w

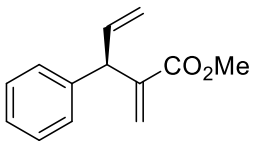


#	Time	Area	Height	Width	Area%	Symmetry
1	15.37	1706.7	80.1	0.3227	95.277	0.685
2	16.305	84.6	3.3	0.3392	4.723	0.865

Racemic 4w:



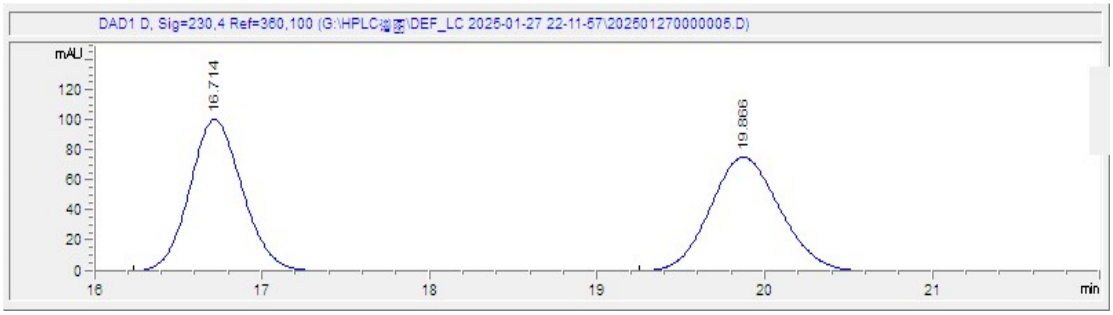
#	Time	Area	Height	Width	Area%	Symmetry
1	14.335	1751.8	92	0.2901	50.342	0.713
2	15.163	1728	85.4	0.31	49.658	0.727



4x

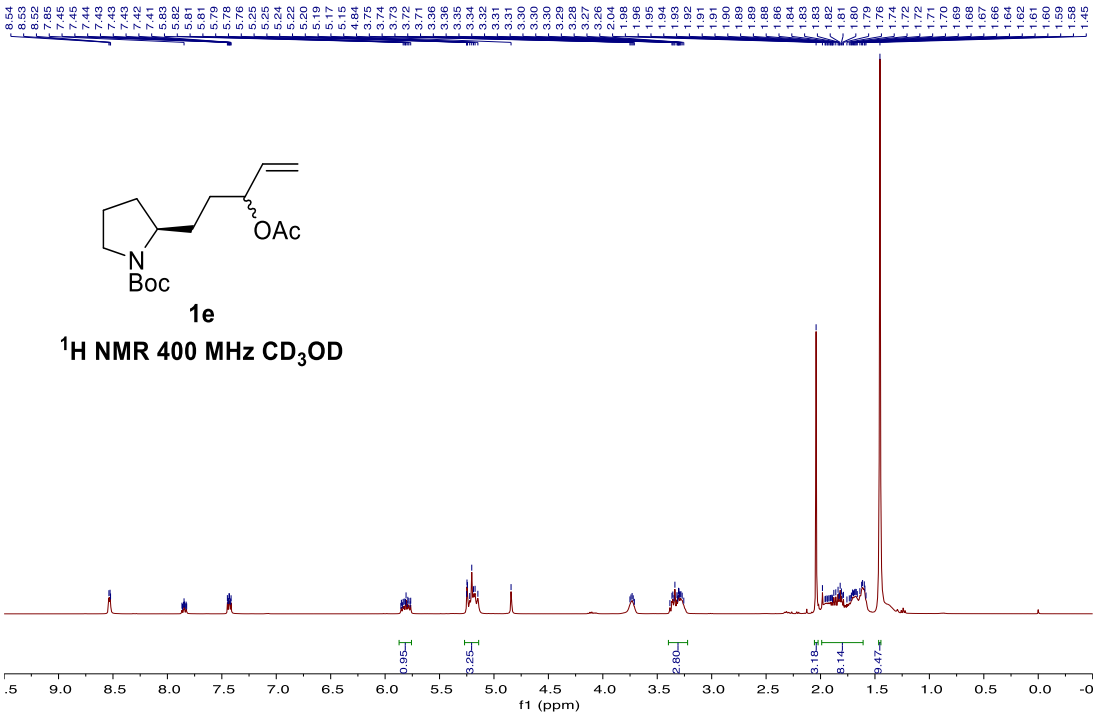
#	Time	Area	Height	Width	Area%	Symmetry
1	16.851	3773	171.8	0.3363	85.147	0.775
2	20.059	658.2	23.4	0.4342	14.853	0.941

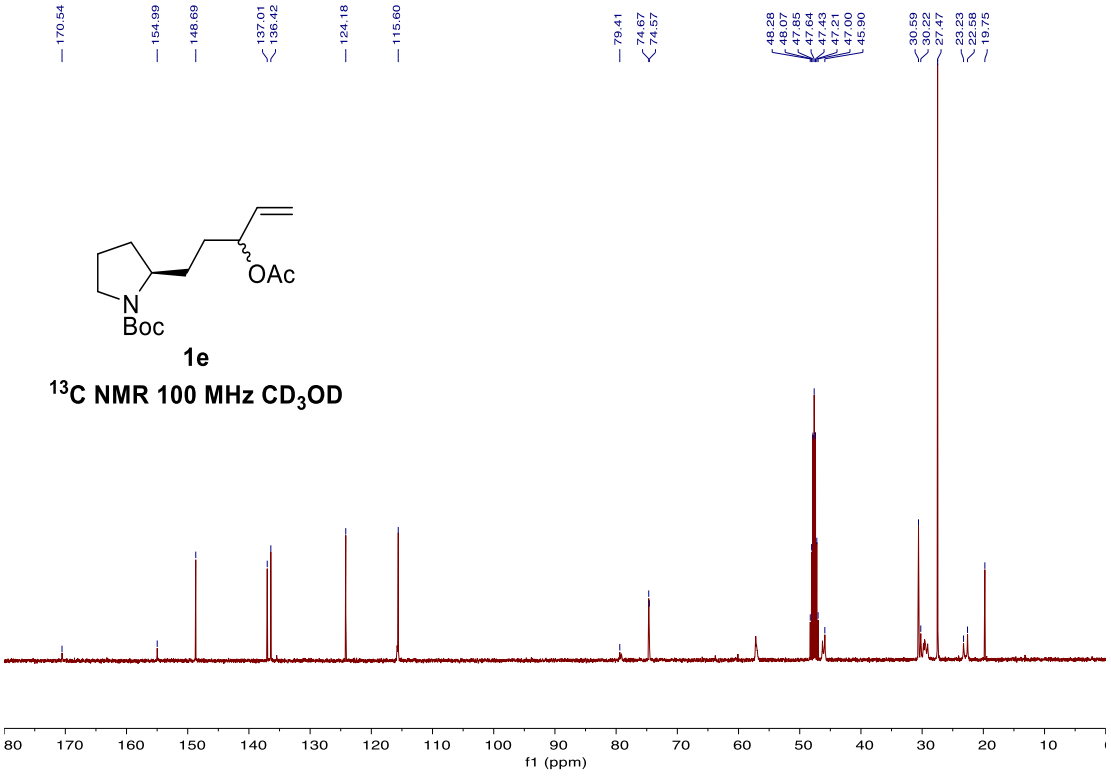
Racemic

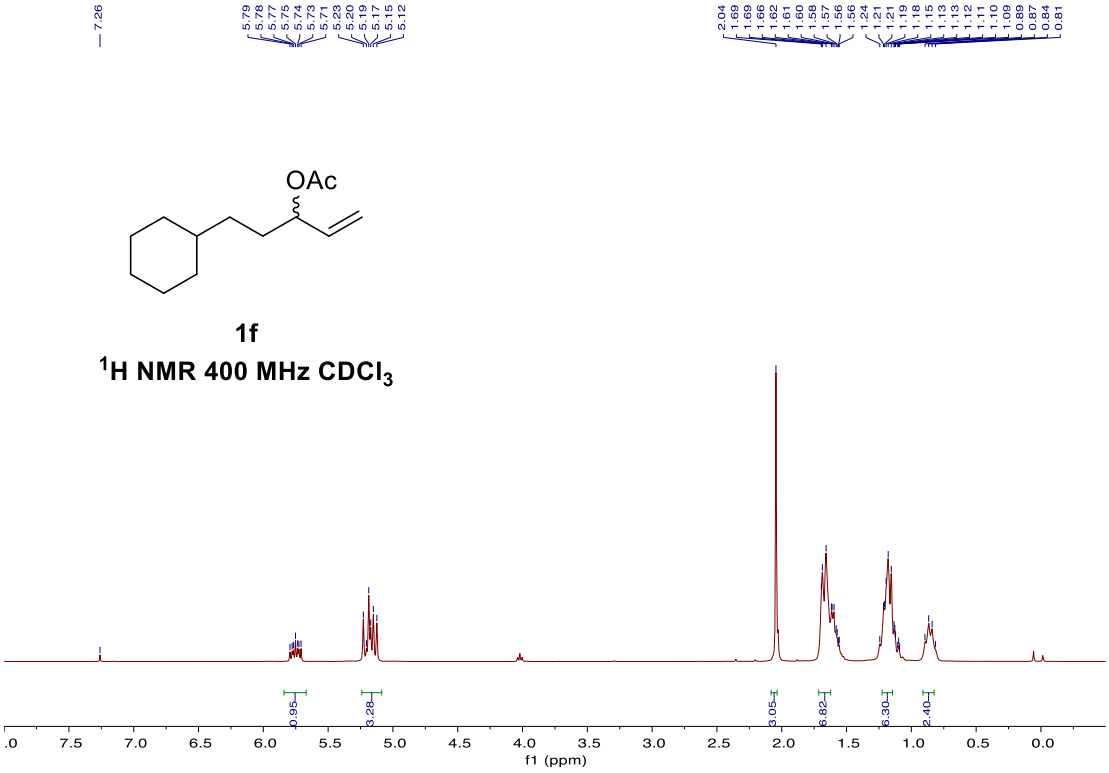


#	Time	Area	Height	Width	Area%	Symmetry
1	16.714	2211.3	101.2	0.3368	50.019	0.865
2	19.866	2209.6	76.1	0.4487	49.981	0.866

NMR spectra

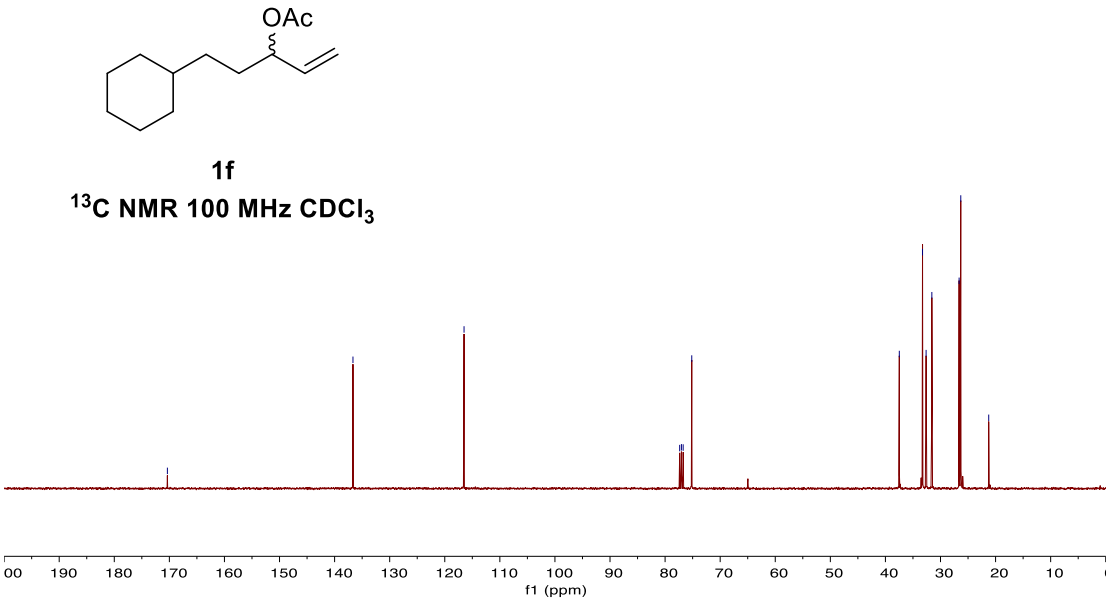

OAc
N
Boc
1e
^{1}H NMR 400 MHz CD_3OD
f1 (ppm)


OAc
N
Boc
1e
^{13}C NMR 100 MHz CD_3OD
f1 (ppm)



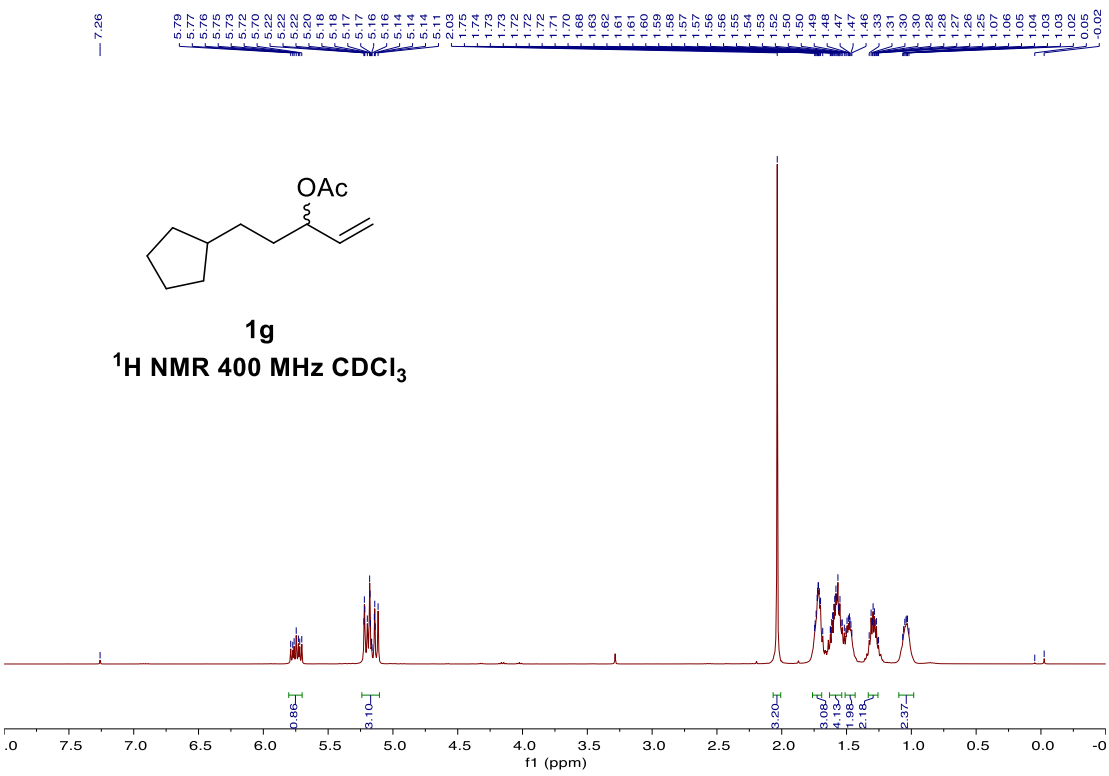
1f

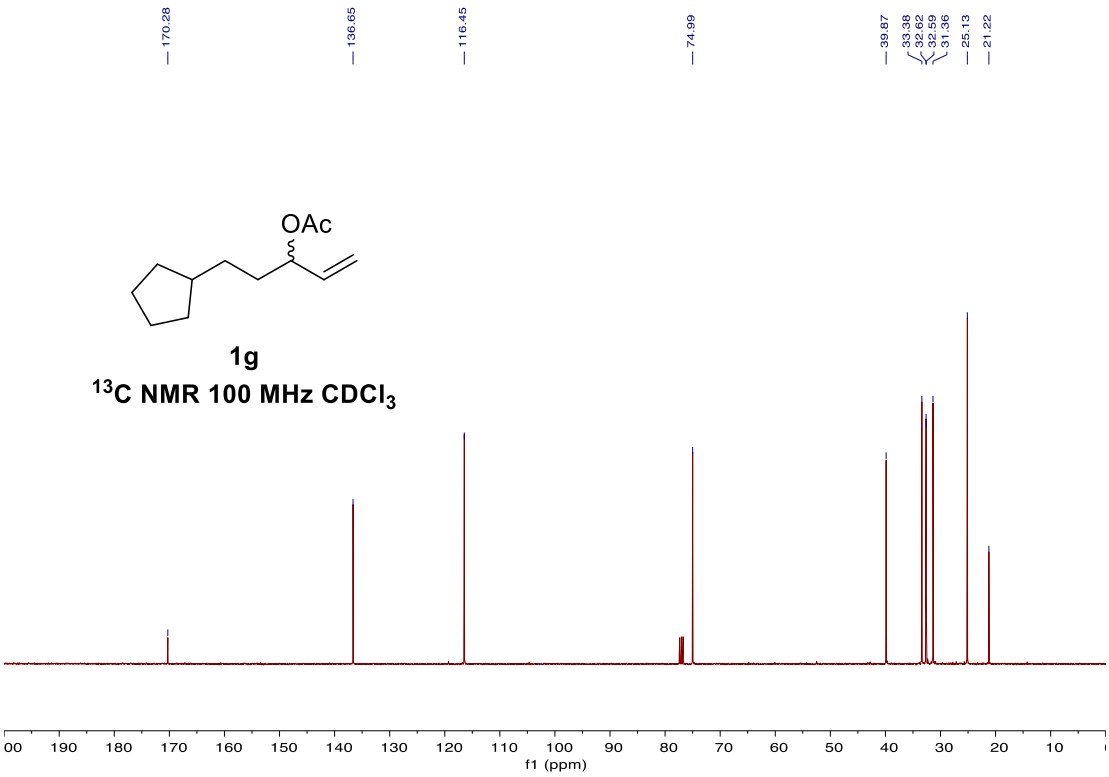
^{1}H NMR 400 MHz $CDCl_3$

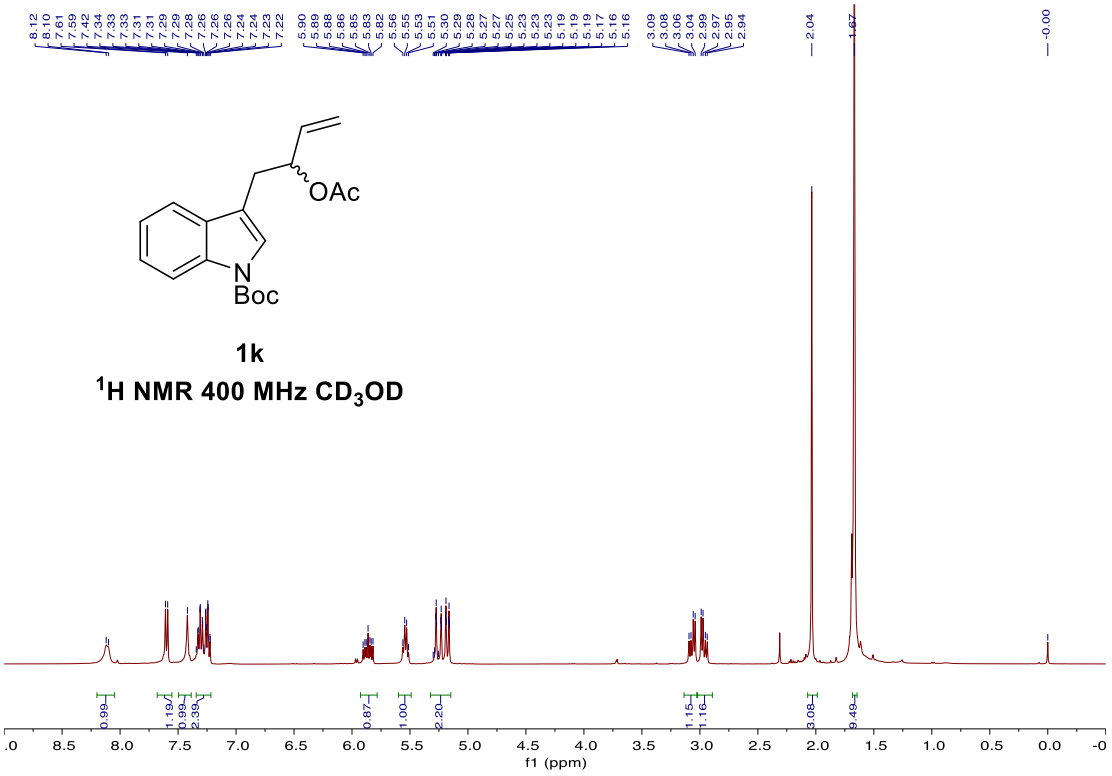


1f

^{13}C NMR 100 MHz $CDCl_3$

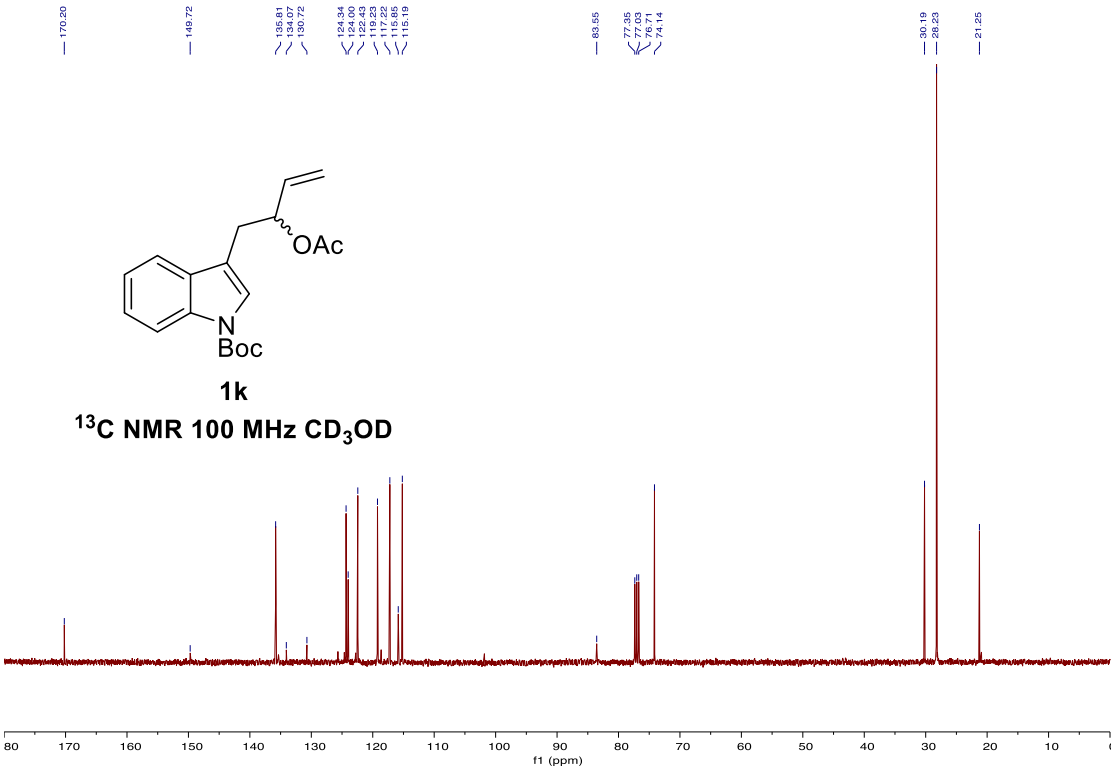

OAc
1g
1H NMR 400 MHz CDCl3
f1 (ppm)


OAc
1g
13C NMR 100 MHz CDCl3
f1 (ppm)



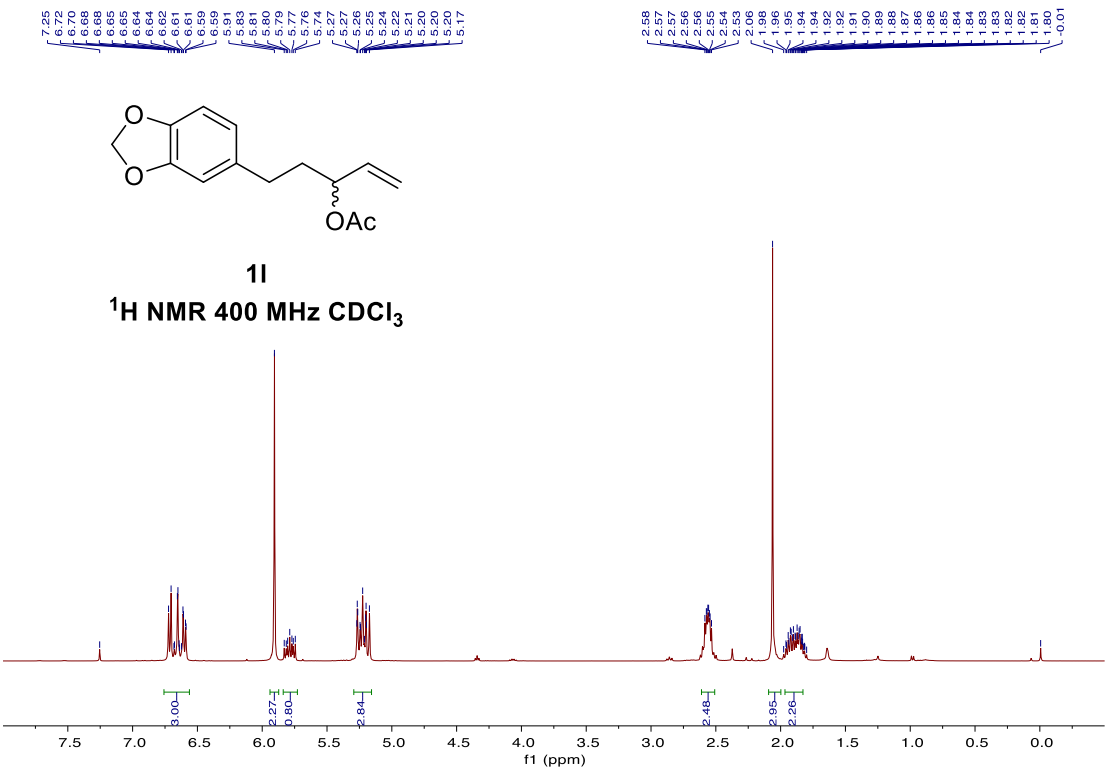
1k

^{1}H NMR 400 MHz CD_3OD



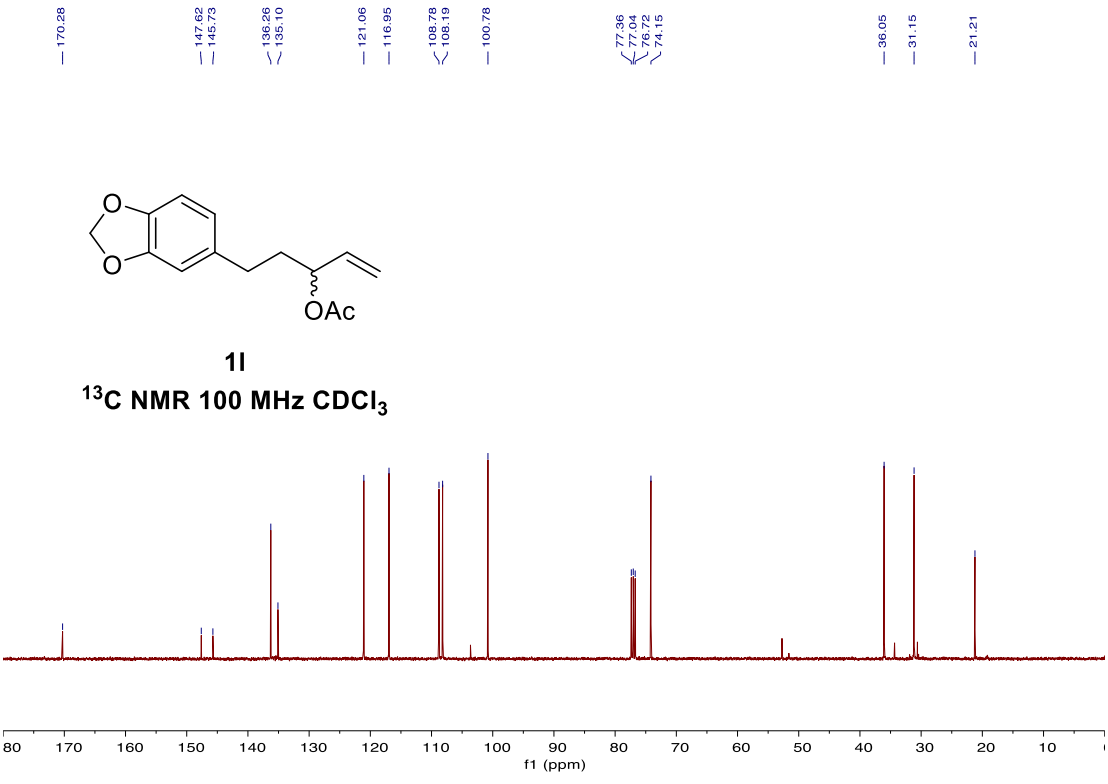
1k

^{13}C NMR 100 MHz CD_3OD



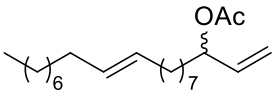
1l

^{1}H NMR 400 MHz $CDCl_3$



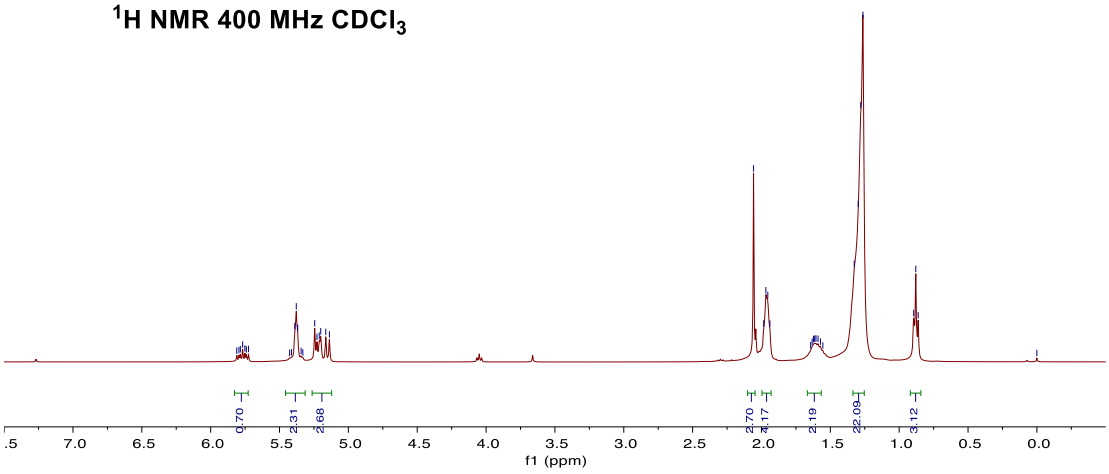
1l

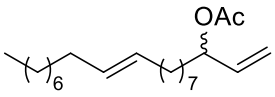
^{13}C NMR 100 MHz $CDCl_3$



1n

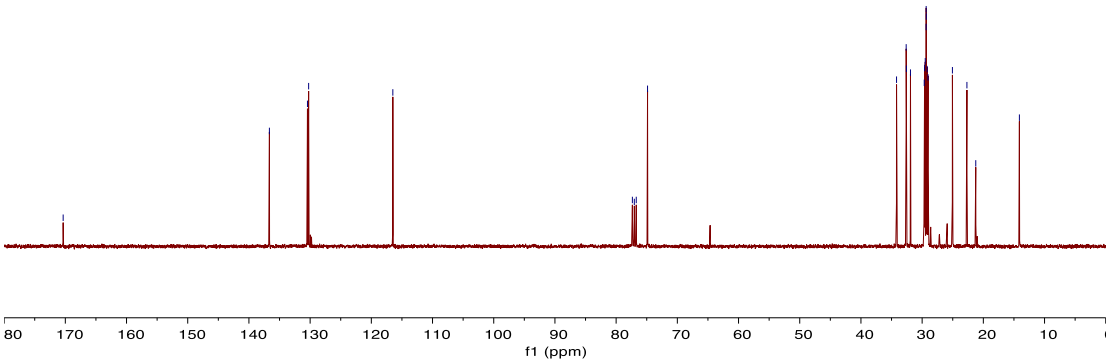
^{1}H NMR 400 MHz $CDCl_3$

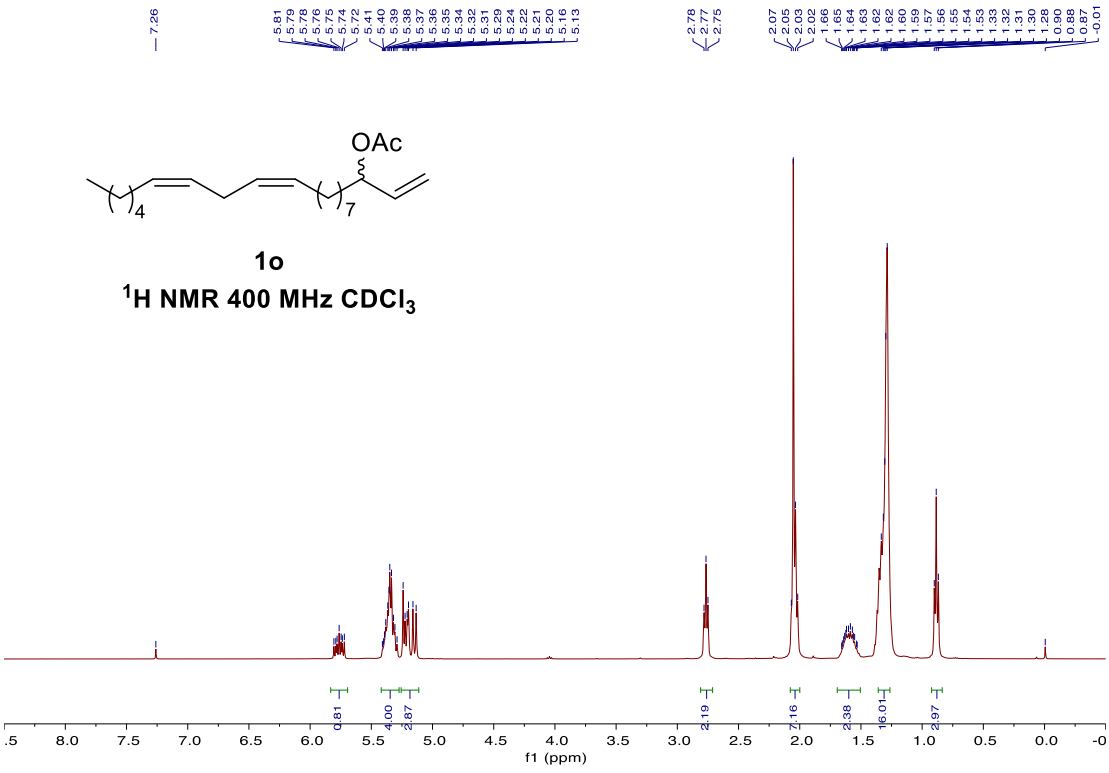


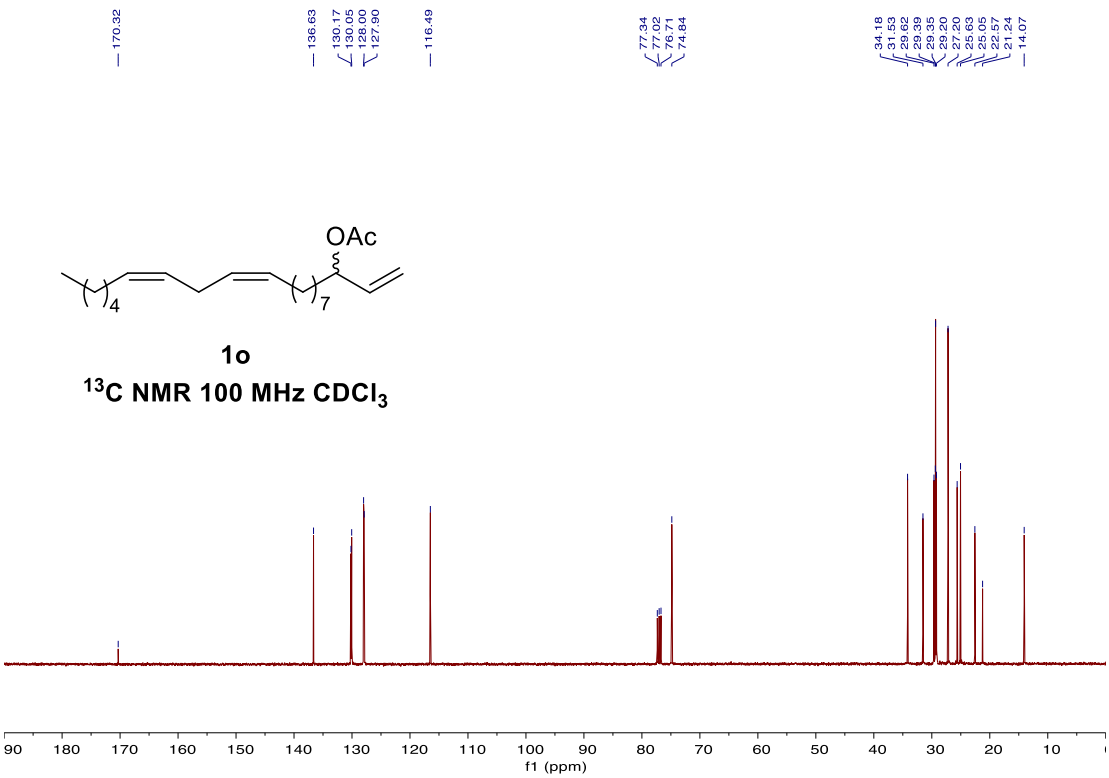


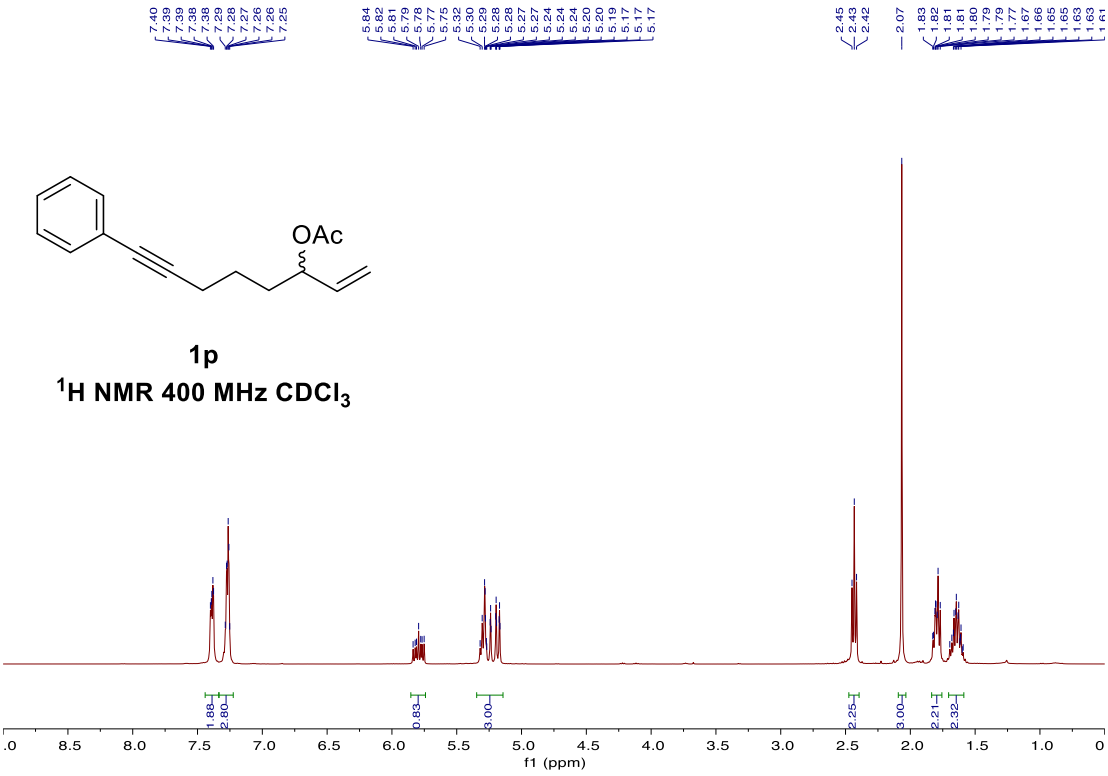
1n

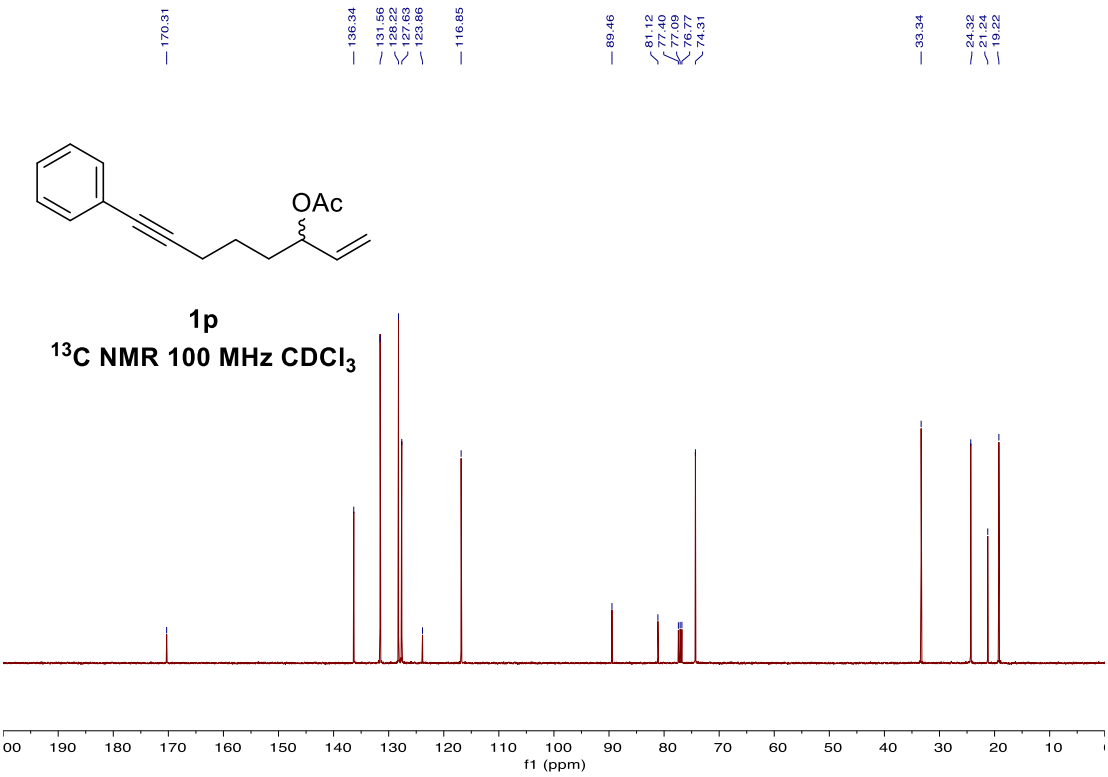
^{13}C NMR 100 MHz $CDCl_3$

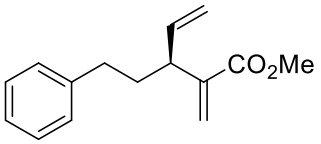



OAc
4
7
1o
1H NMR 400 MHz CDCl3
f1 (ppm)


OAc
4
7
1o
13C NMR 100 MHz CDCl3
f1 (ppm)

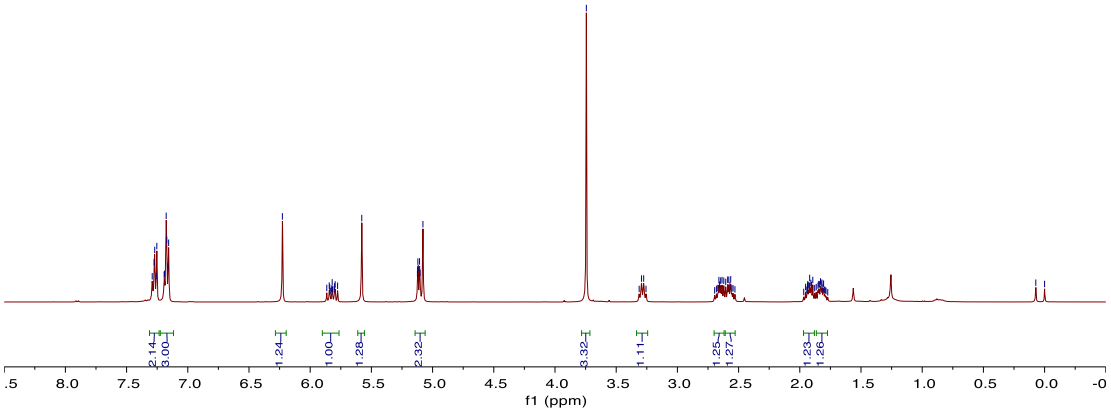

OAc
1p
1H NMR 400 MHz CDCl3
f1 (ppm)

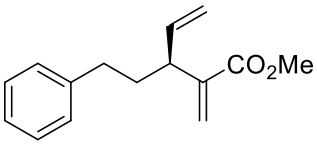

OAc
1p
13C NMR 100 MHz CDCl3
f1 (ppm)



4a

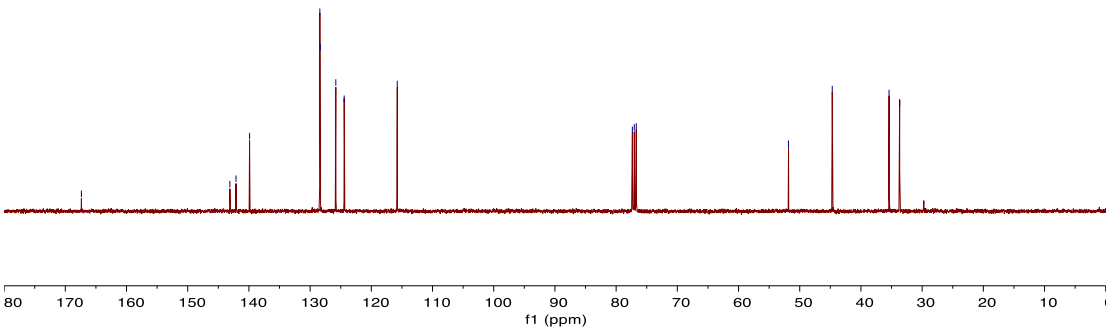
^{1}H NMR 400 MHz $CDCl_3$

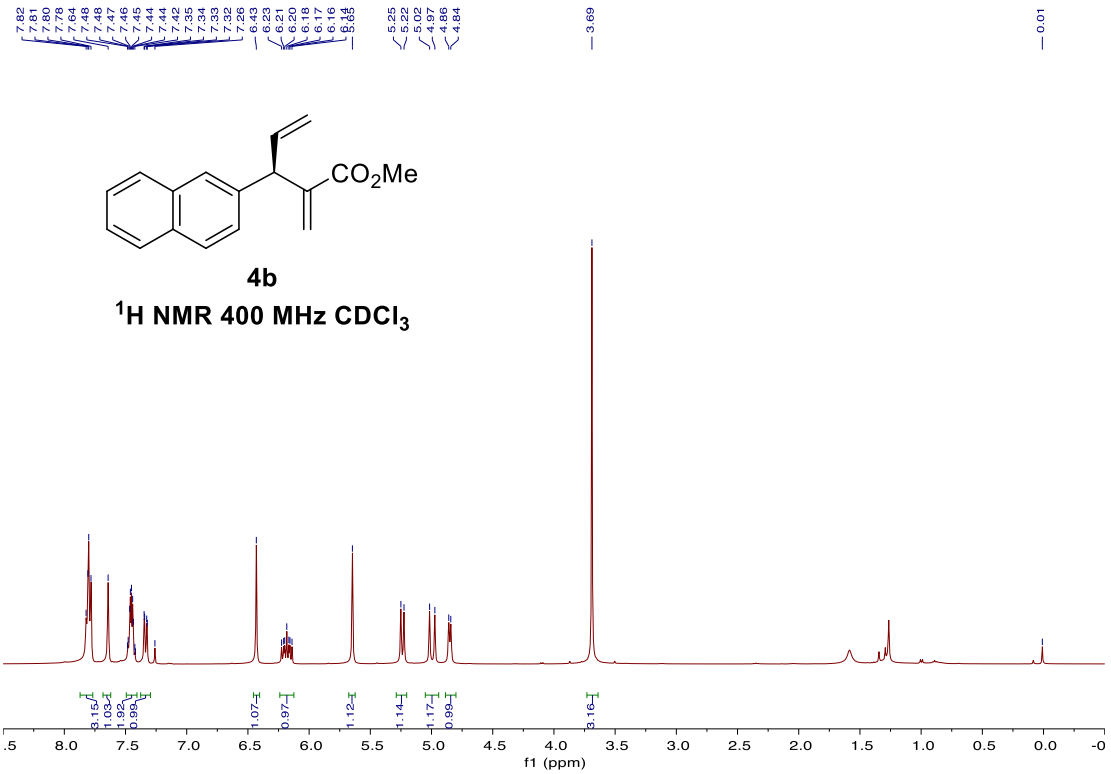




4a

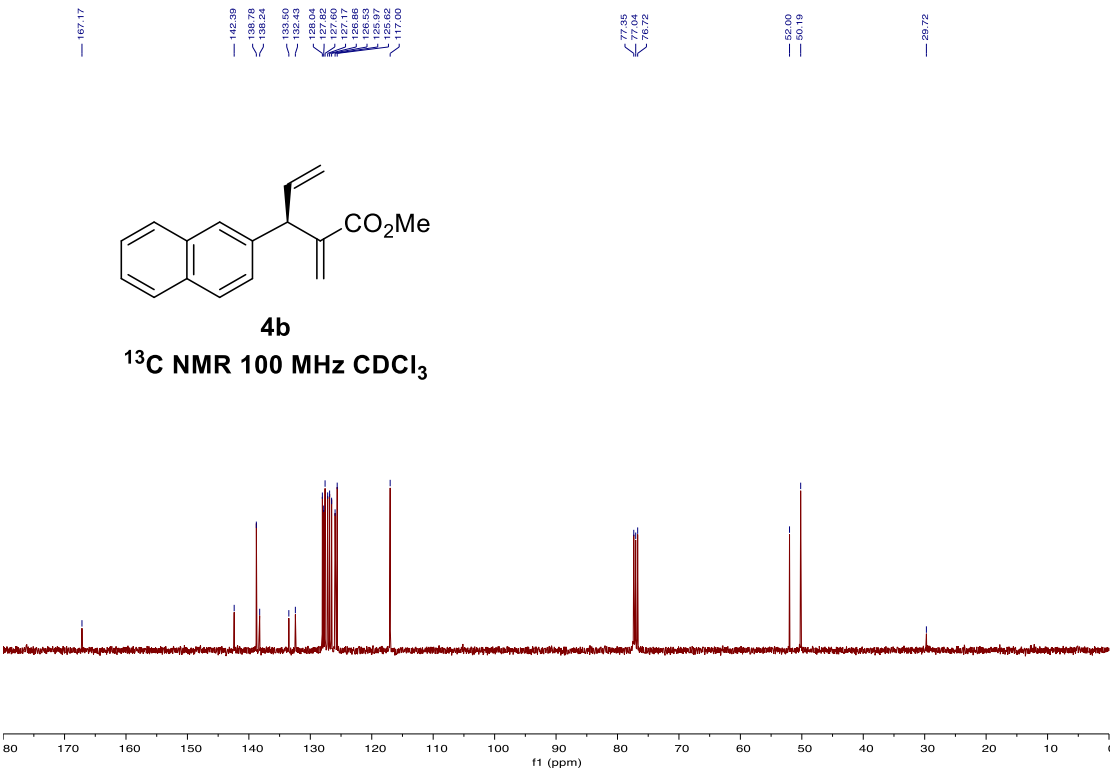
^{13}C NMR 100 MHz $CDCl_3$





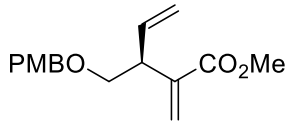
4b

^{1}H NMR 400 MHz $CDCl_3$



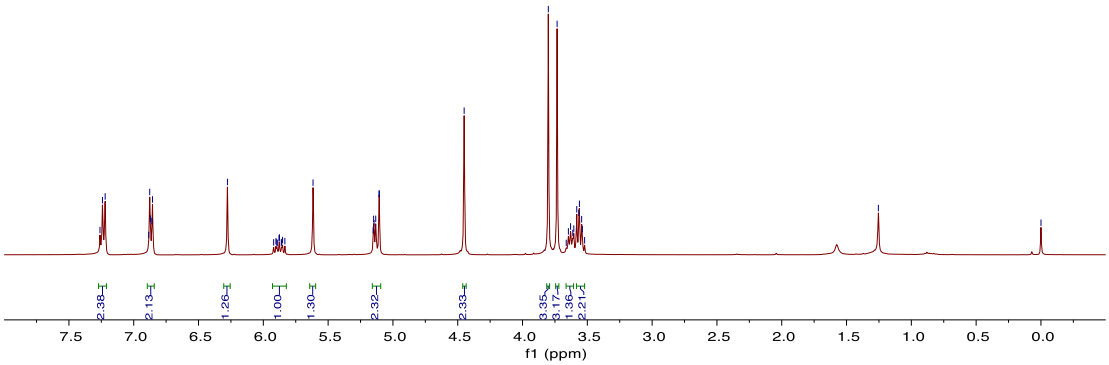
4b

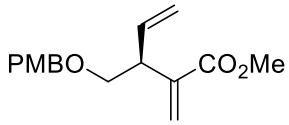
^{13}C NMR 100 MHz $CDCl_3$



4c

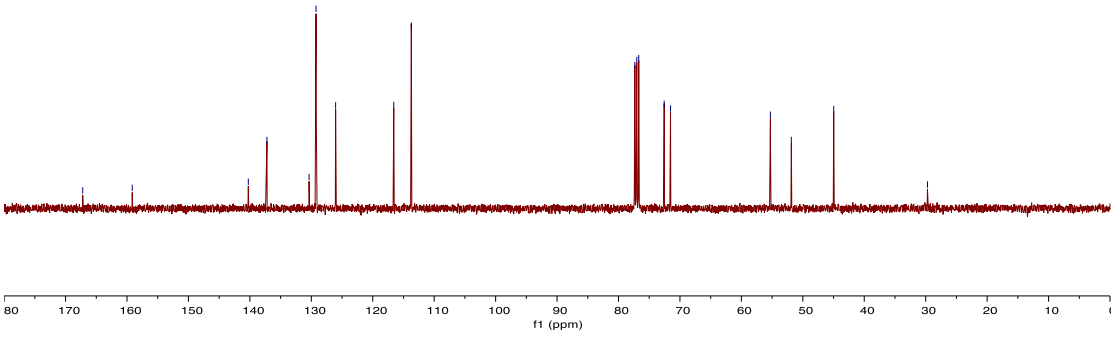
^{1}H NMR 400 MHz $CDCl_3$

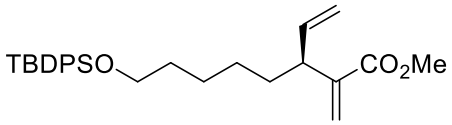




4c

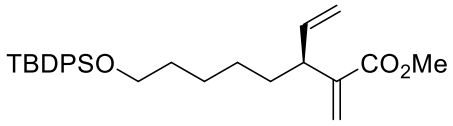
^{13}C NMR 100 MHz $CDCl_3$





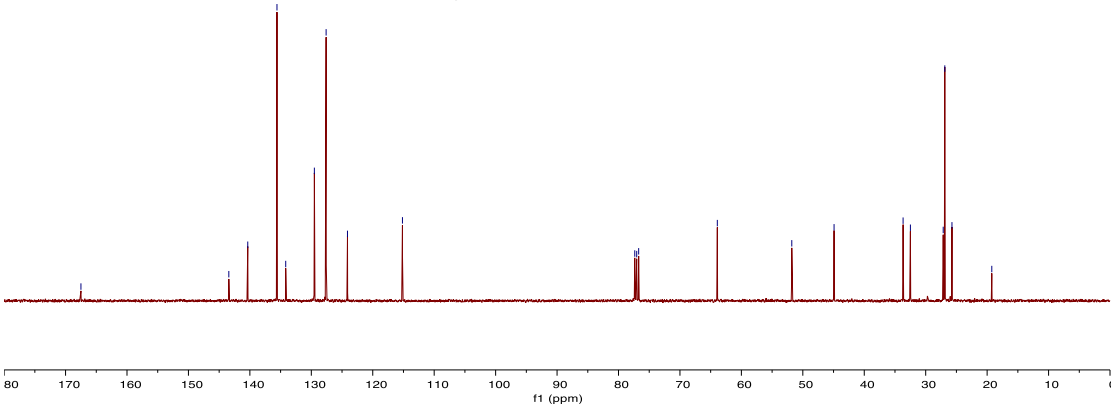
4d

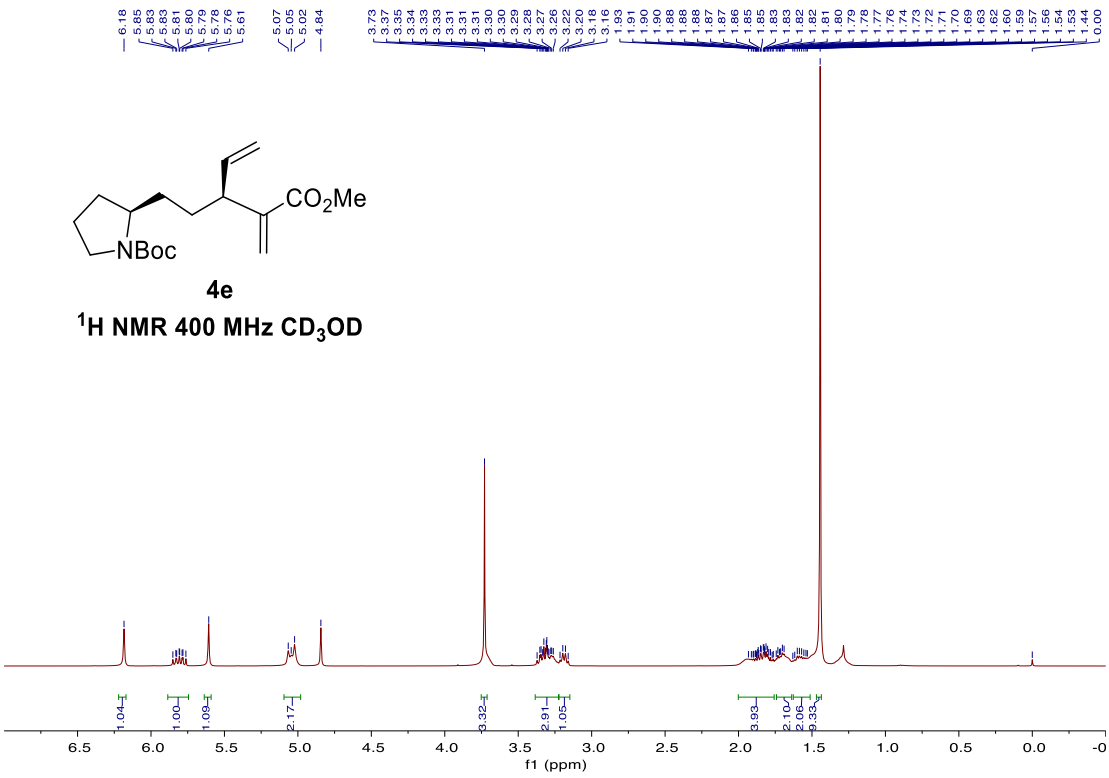
^{1}H NMR 400 MHz $CDCl_3$



4d

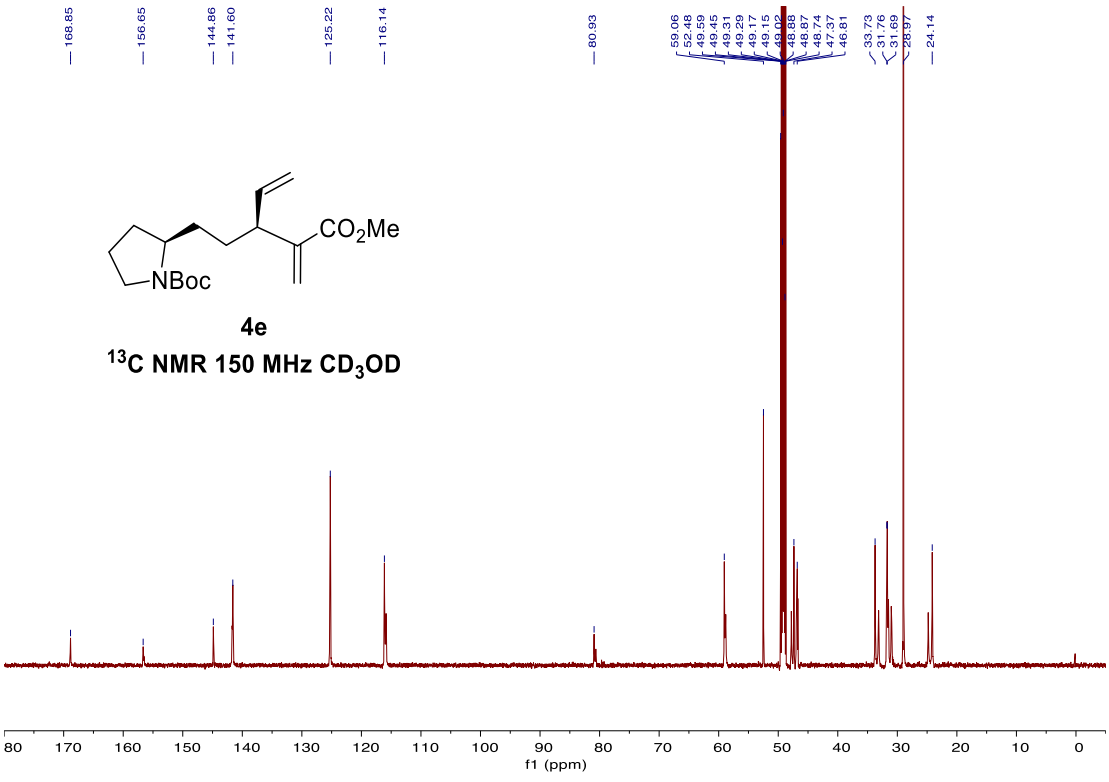
^{13}C NMR 100 MHz $CDCl_3$





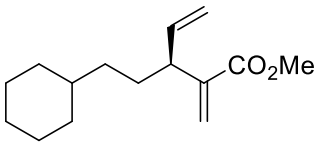
4e

^{1}H NMR 400 MHz CD_3OD



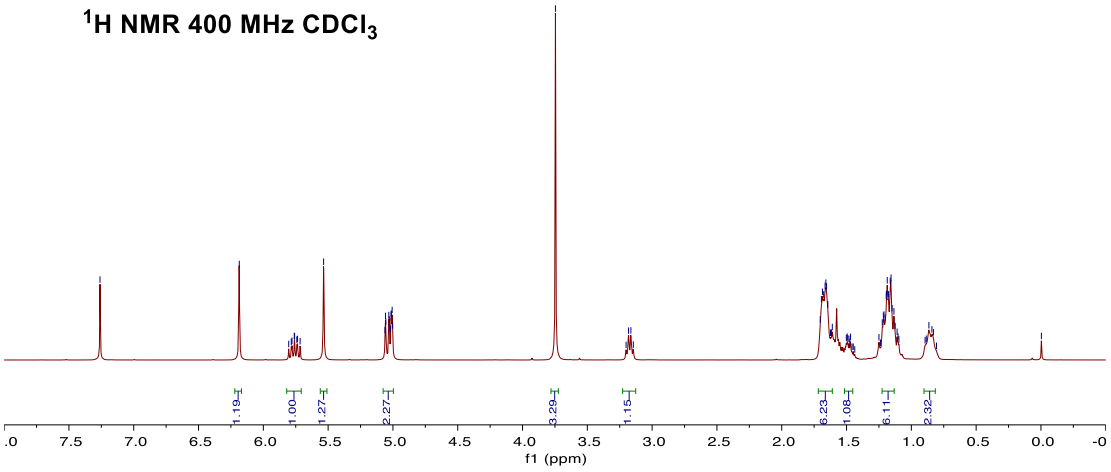
4e

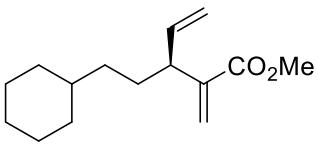
^{13}C NMR 150 MHz CD_3OD



4f

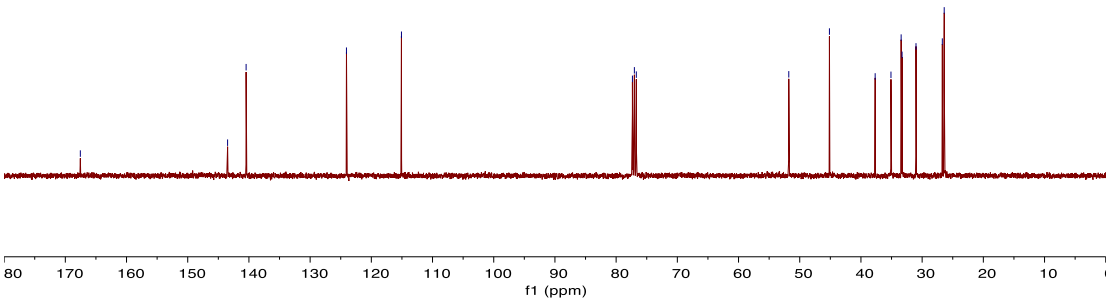
^{1}H NMR 400 MHz $CDCl_3$

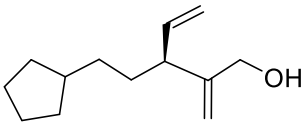




4f

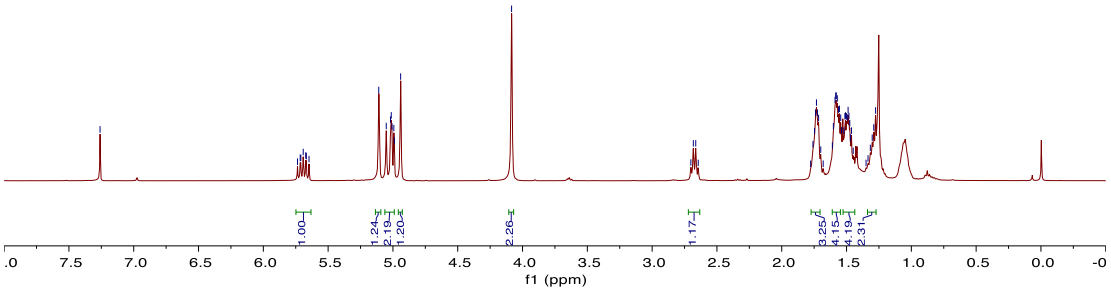
^{13}C NMR 100 MHz $CDCl_3$

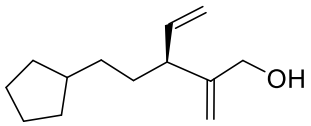




4g'

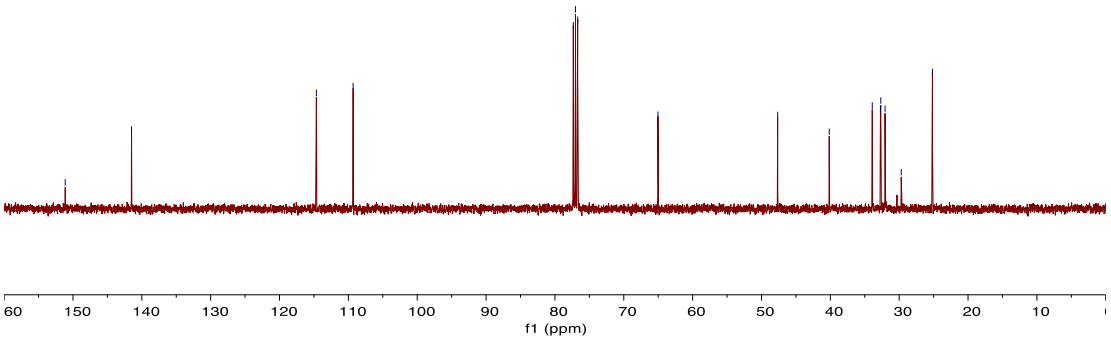
^{1}H NMR 400 MHz $CDCl_3$

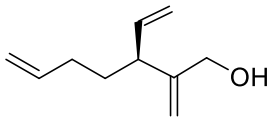




4g'

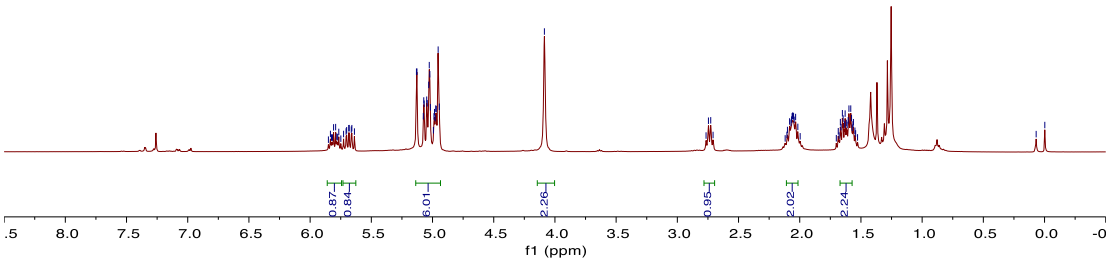
^{13}C NMR 100 MHz $CDCl_3$

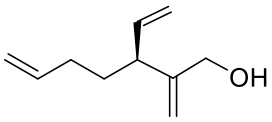




4h'

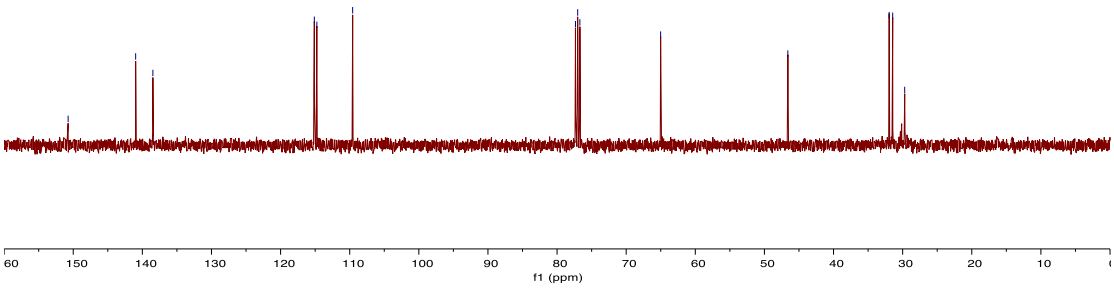
^{1}H NMR 400 MHz $CDCl_3$

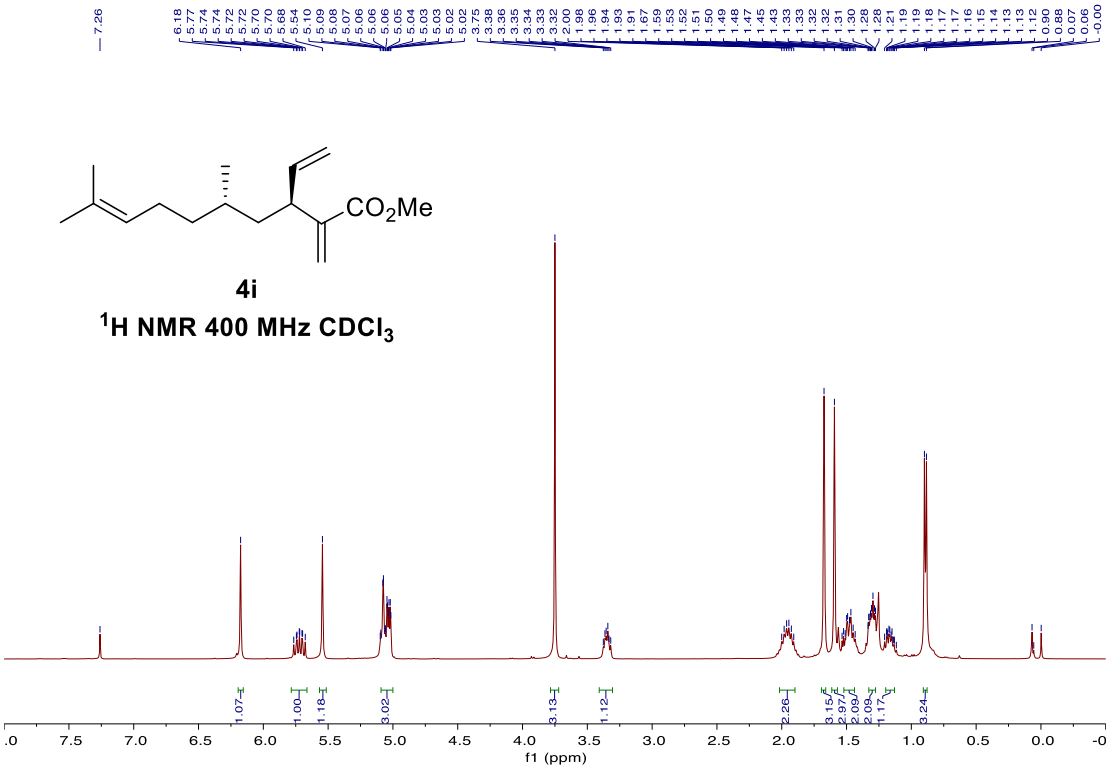


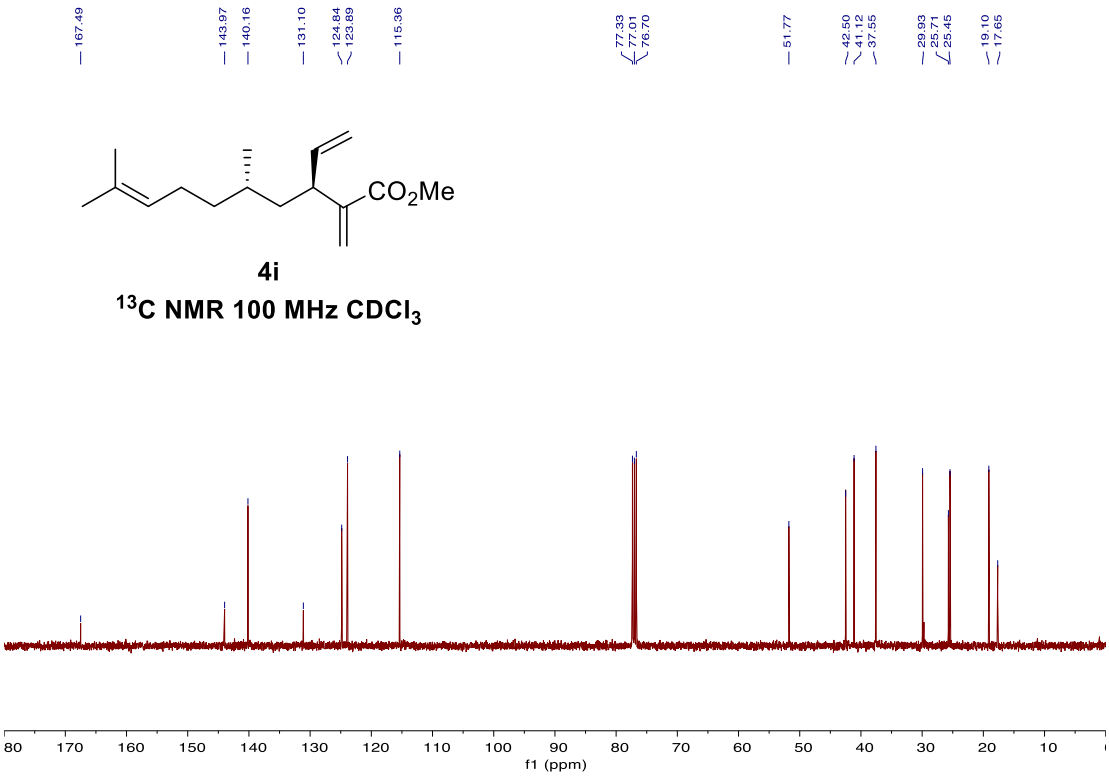


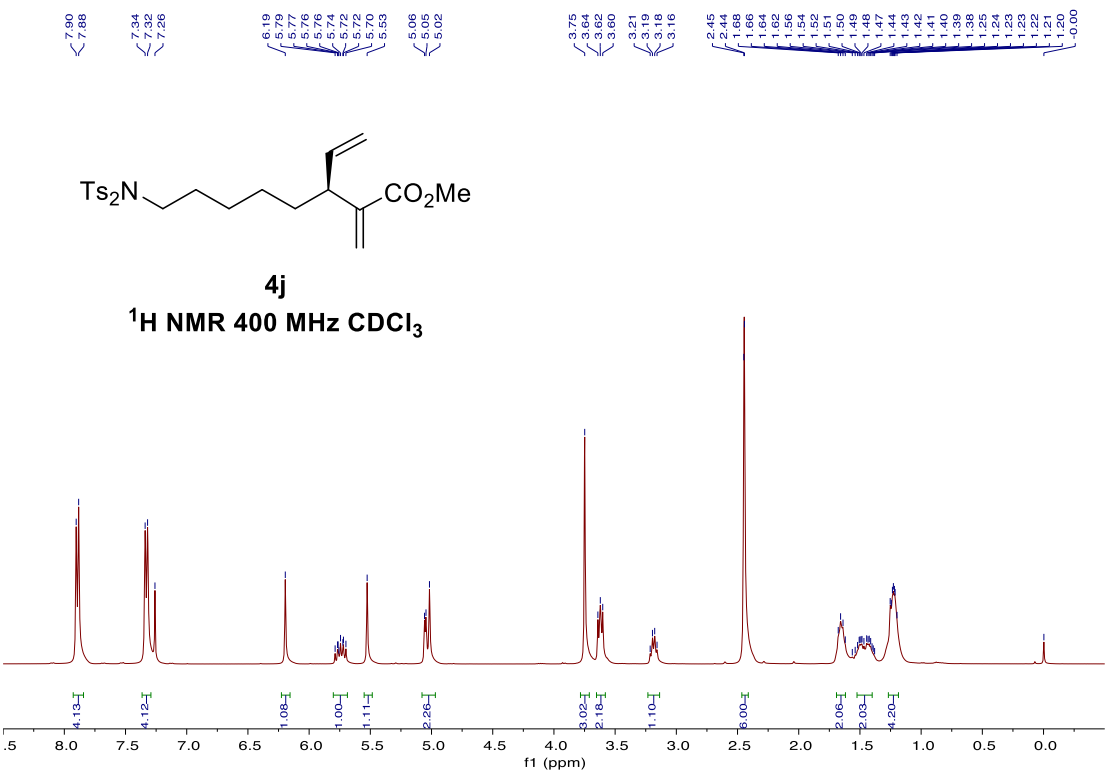
4h'

^{13}C NMR 100 MHz $CDCl_3$



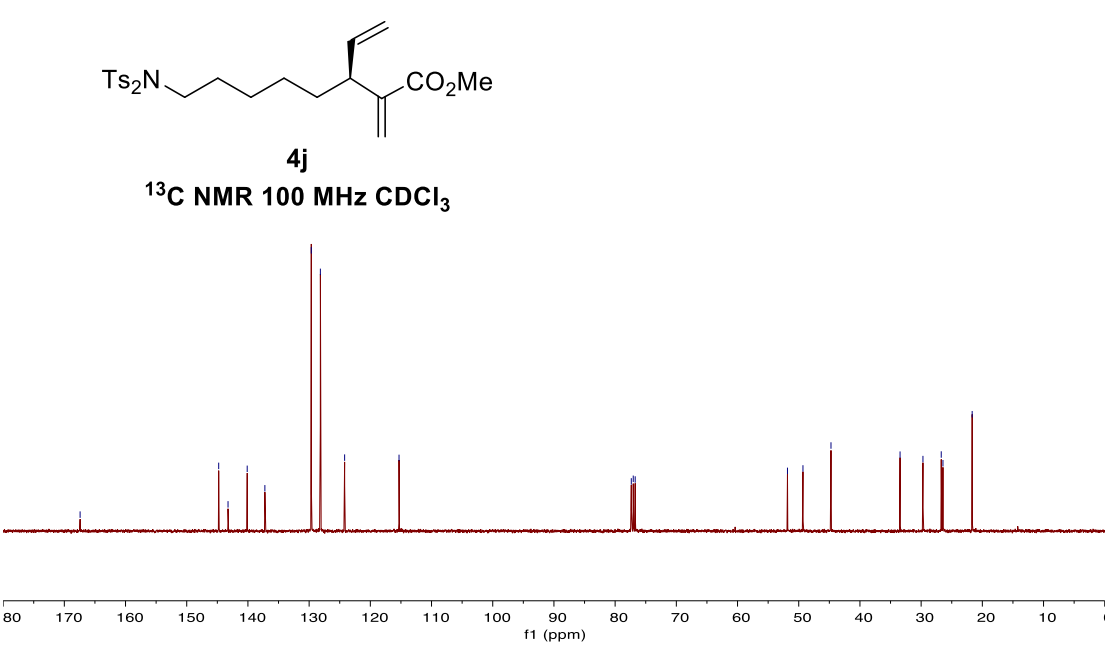

CO2Me
4i
1H NMR 400 MHz CDCl3
f1 (ppm)


CO2Me
4i
13C NMR 100 MHz CDCl3
f1 (ppm)



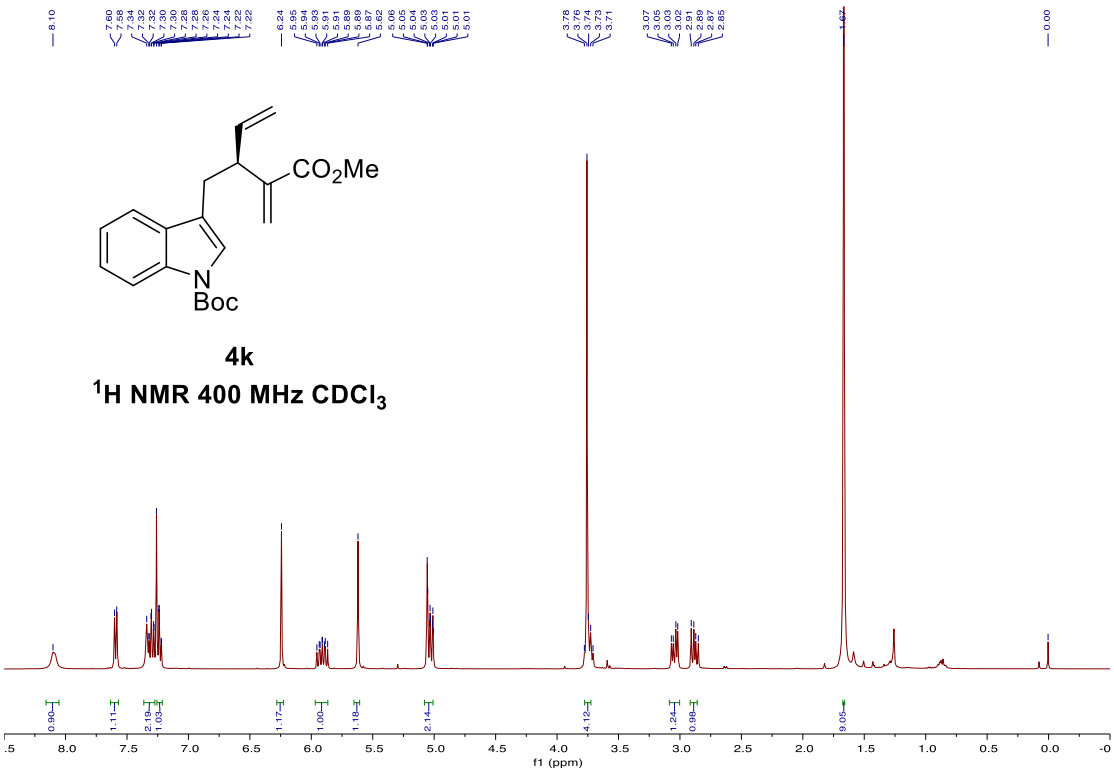
4j

^{1}H NMR 400 MHz $CDCl_3$



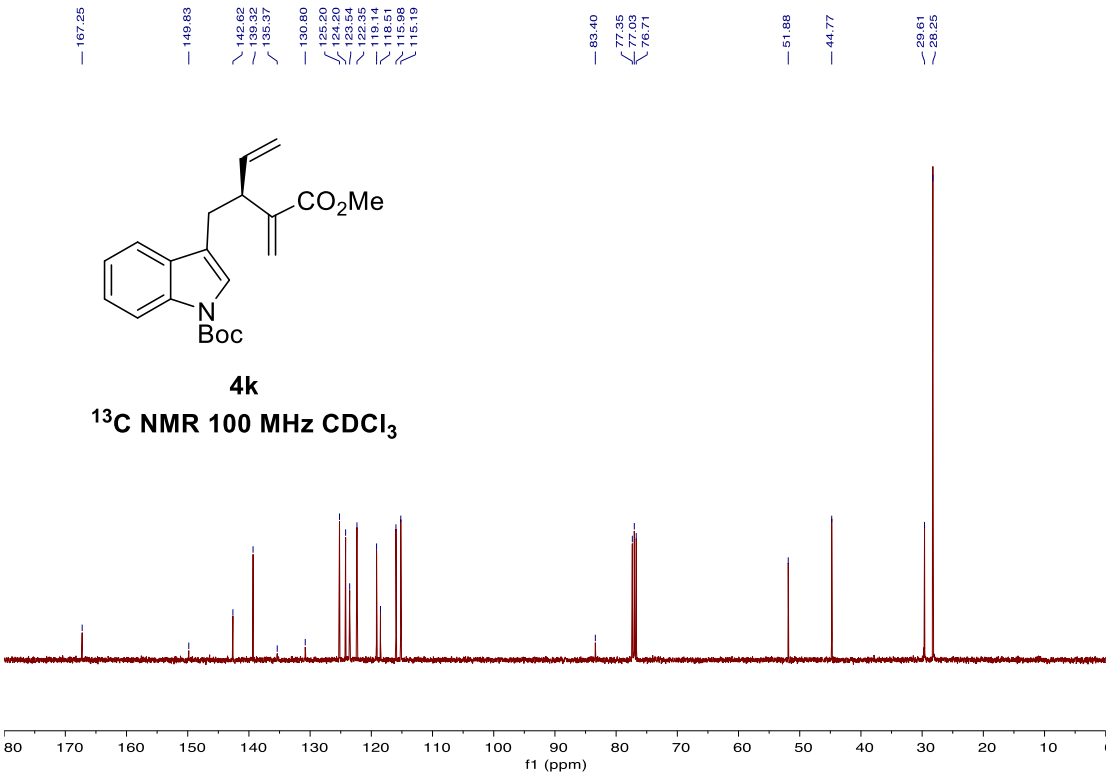
4j

^{13}C NMR 100 MHz $CDCl_3$



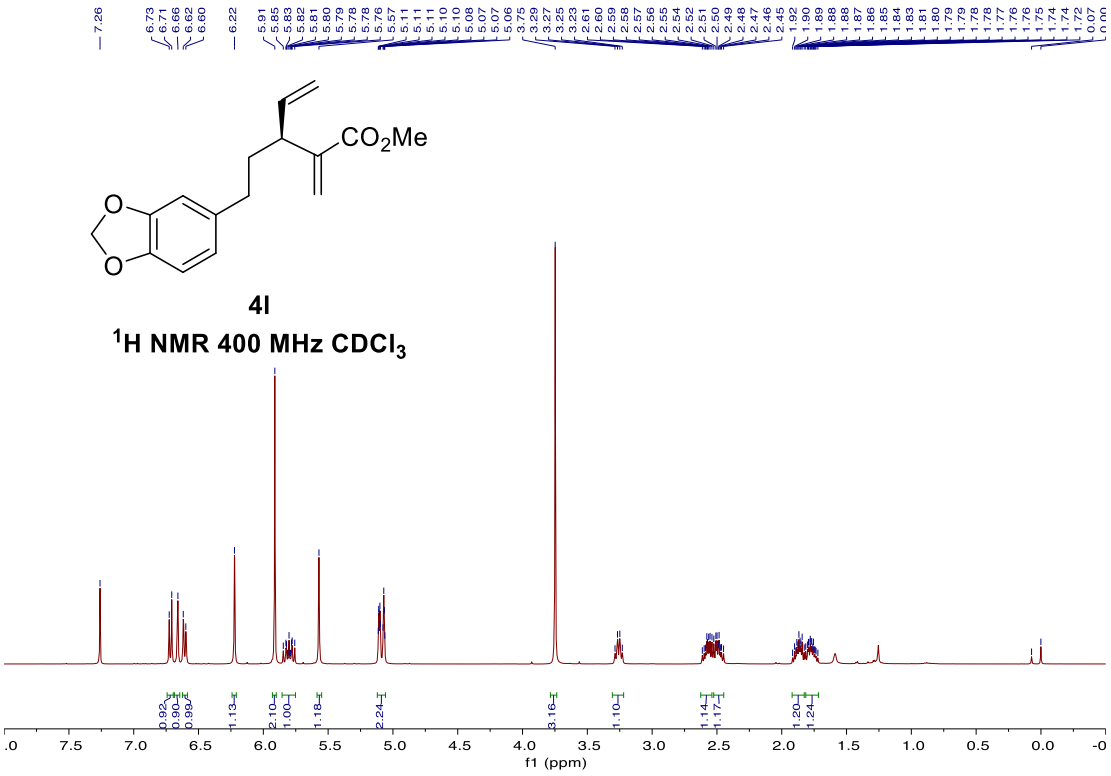
4k

^{1}H NMR 400 MHz $CDCl_3$



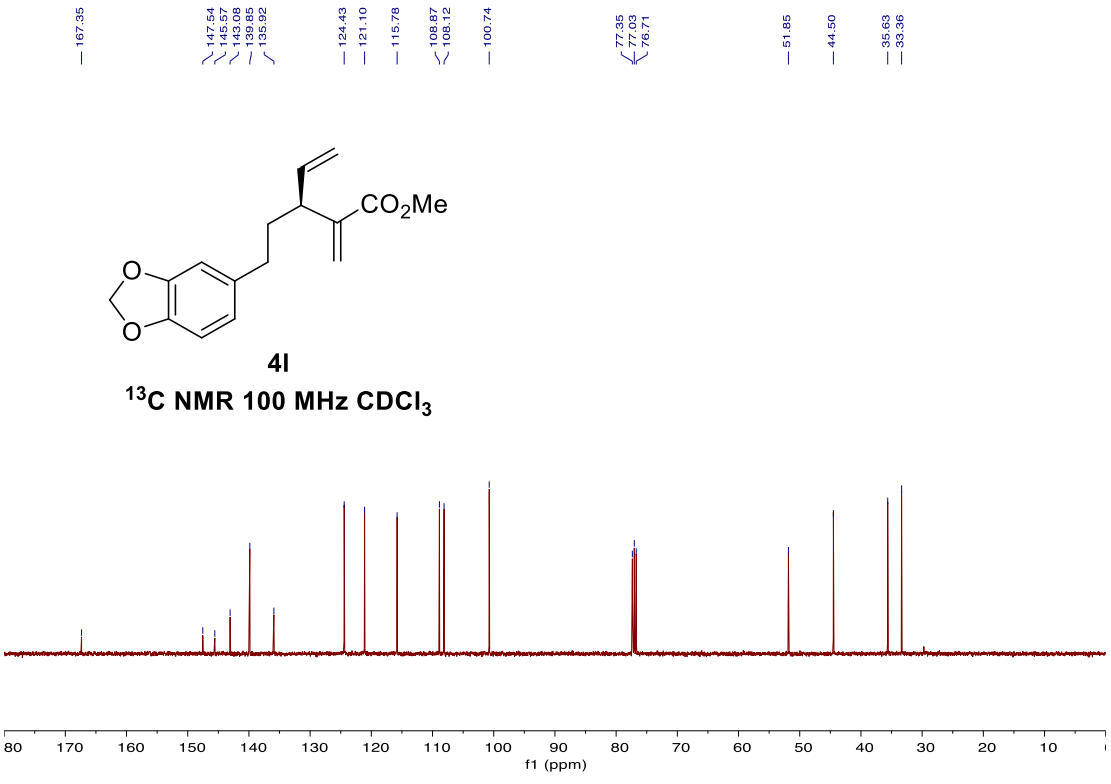
4k

^{13}C NMR 100 MHz $CDCl_3$



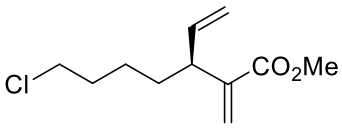
4l

^{1}H NMR 400 MHz $CDCl_3$



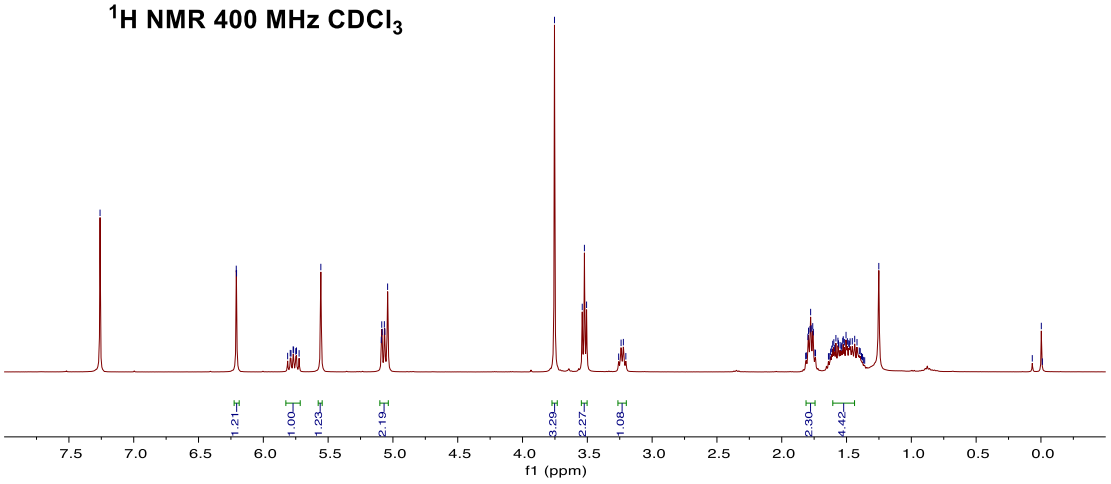
4l

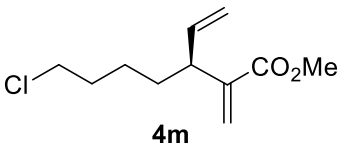
^{13}C NMR 100 MHz $CDCl_3$



4m

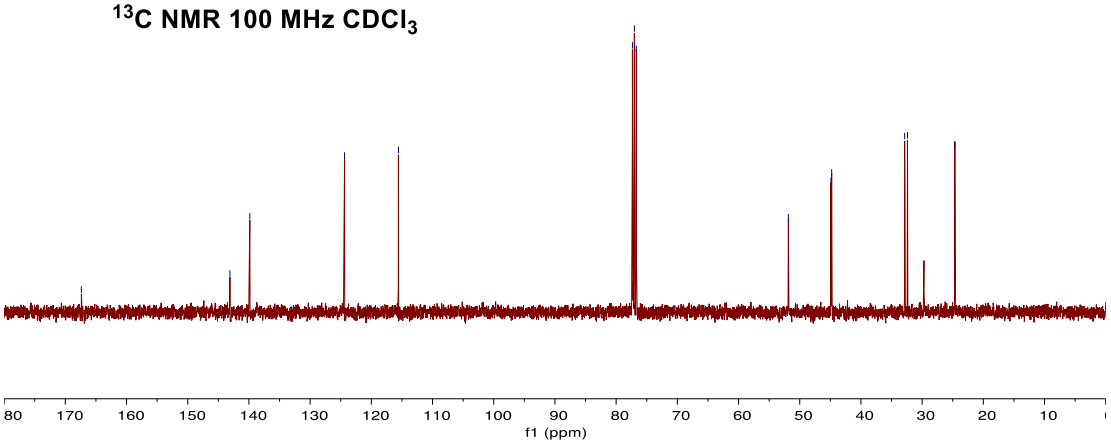
^{1}H NMR 400 MHz $CDCl_3$

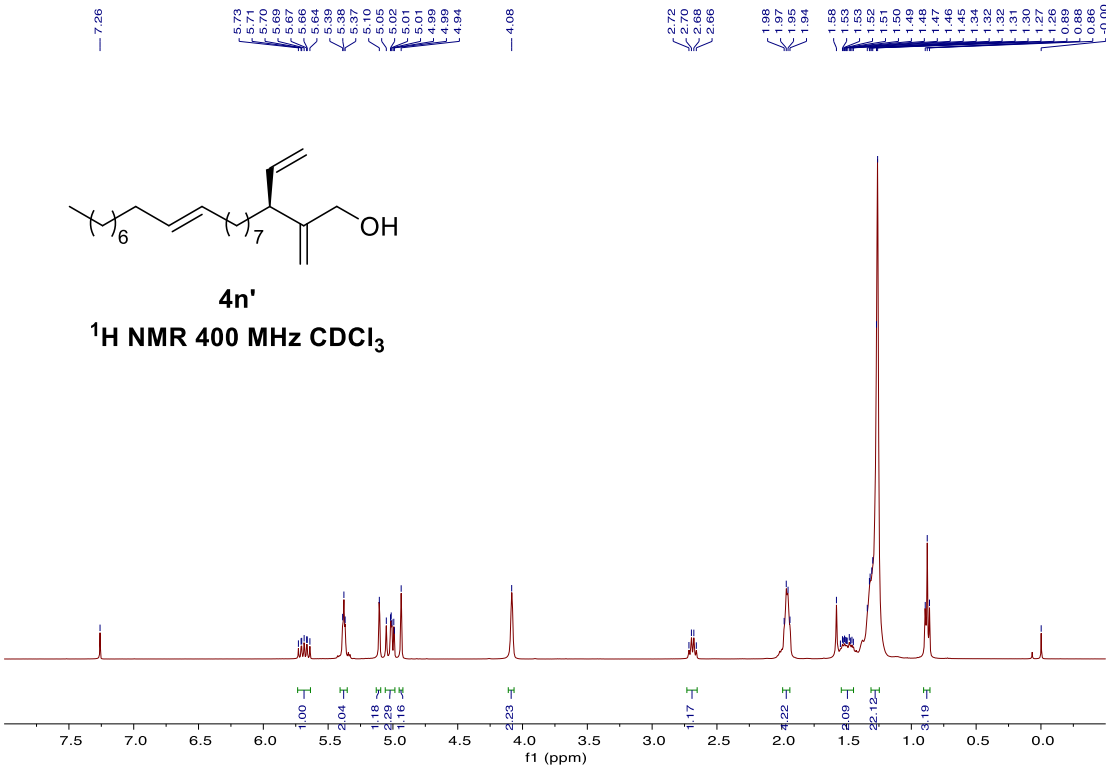




4m

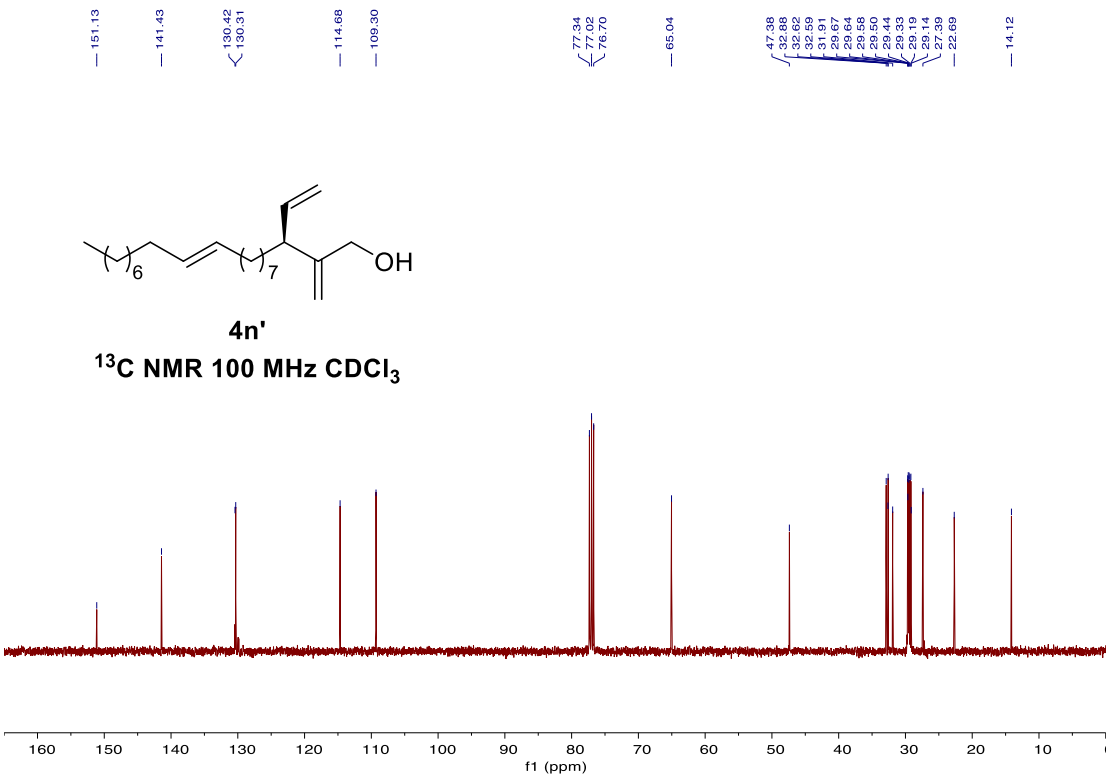
^{13}C NMR 100 MHz $CDCl_3$





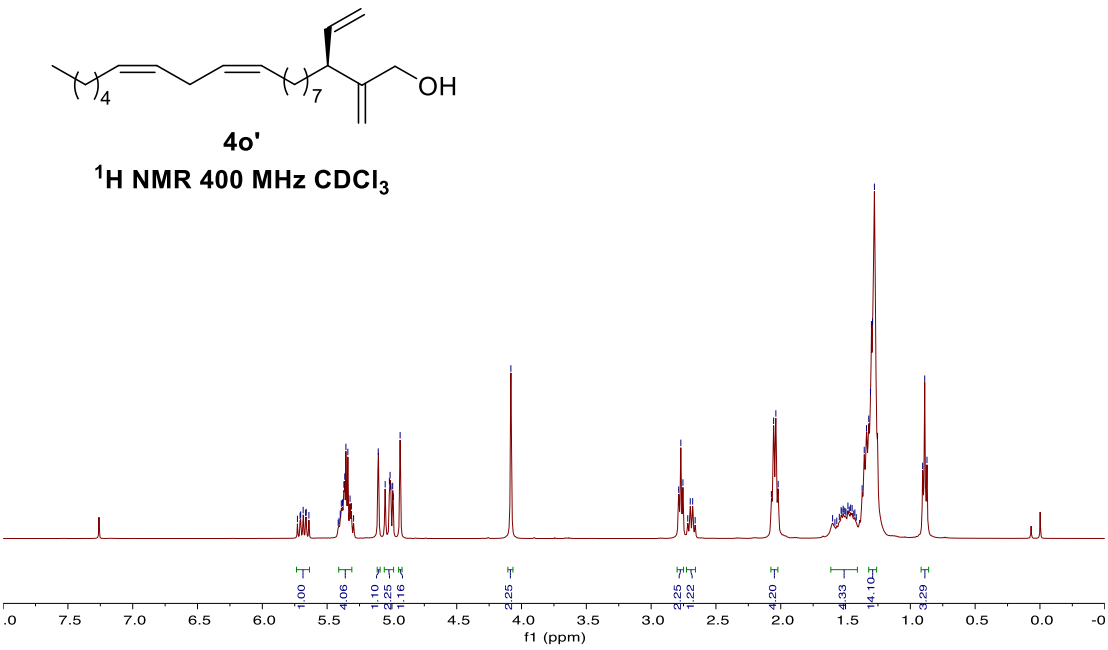
4n'

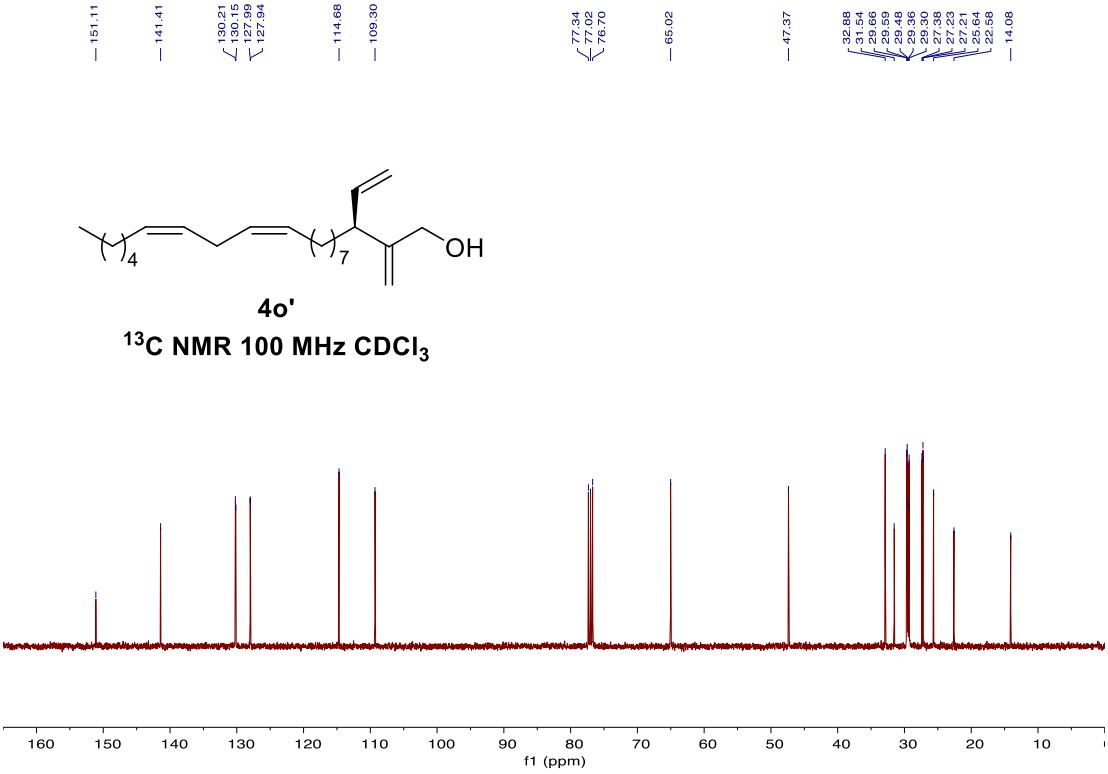
^{1}H NMR 400 MHz $CDCl_3$

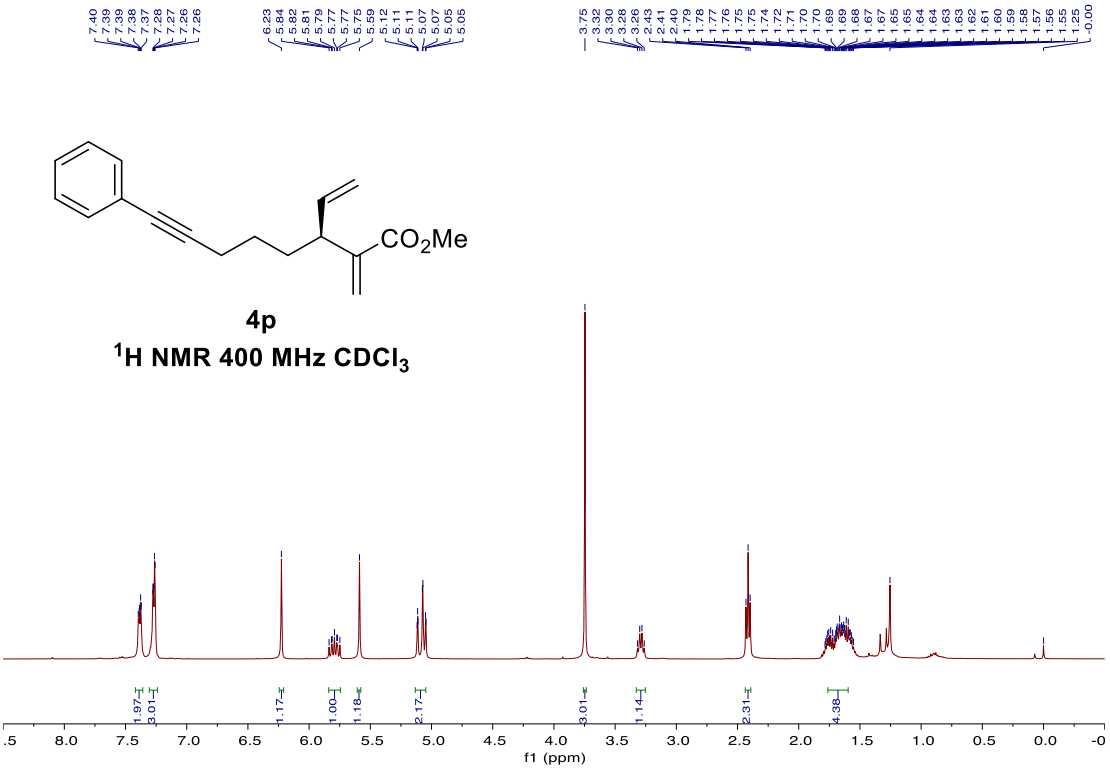


4n'

^{13}C NMR 100 MHz $CDCl_3$

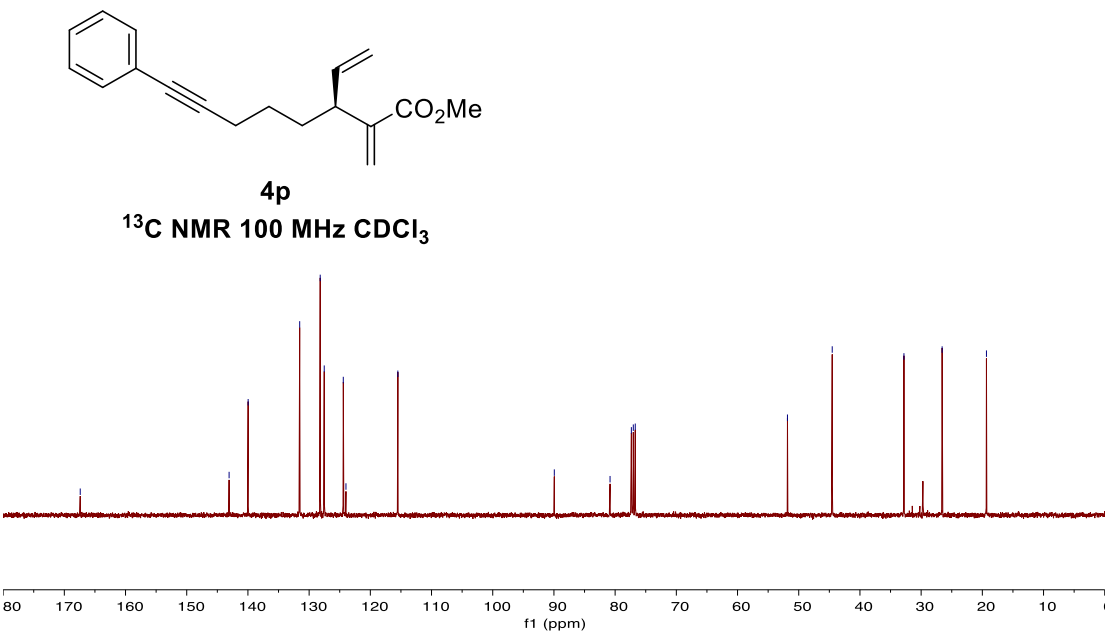

OH
4o'
1H NMR 400 MHz CDCl3
f1 (ppm)


OH
4o'
13C NMR 100 MHz CDCl3
f1 (ppm)



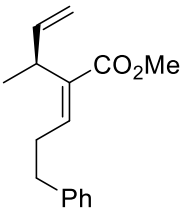
4p

^{1}H NMR 400 MHz $CDCl_3$



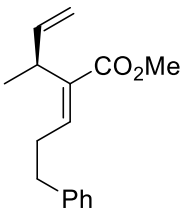
4p

^{13}C NMR 100 MHz $CDCl_3$



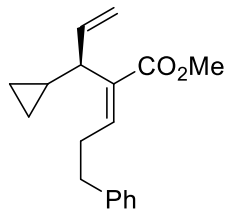
4q'

^{1}H NMR 400 MHz $CDCl_3$



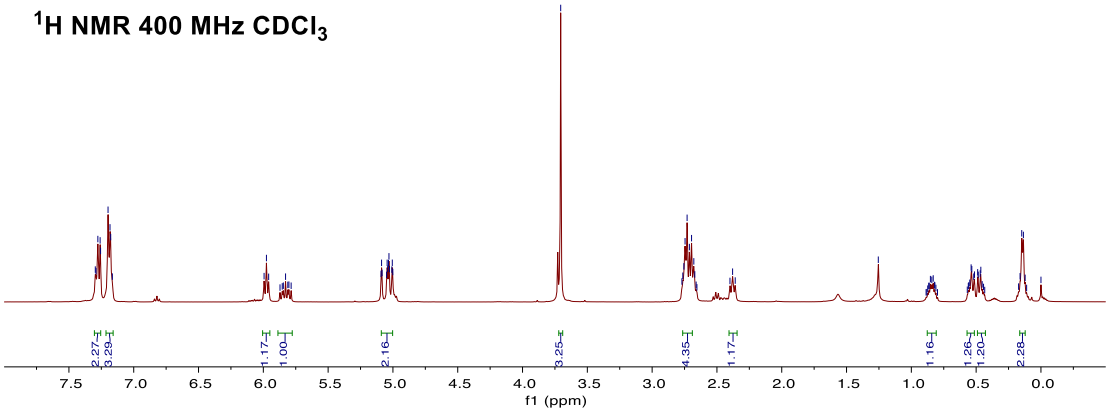
4q'

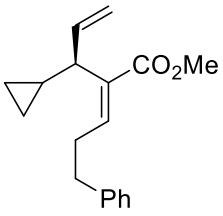
^{13}C NMR 100 MHz $CDCl_3$



4r'

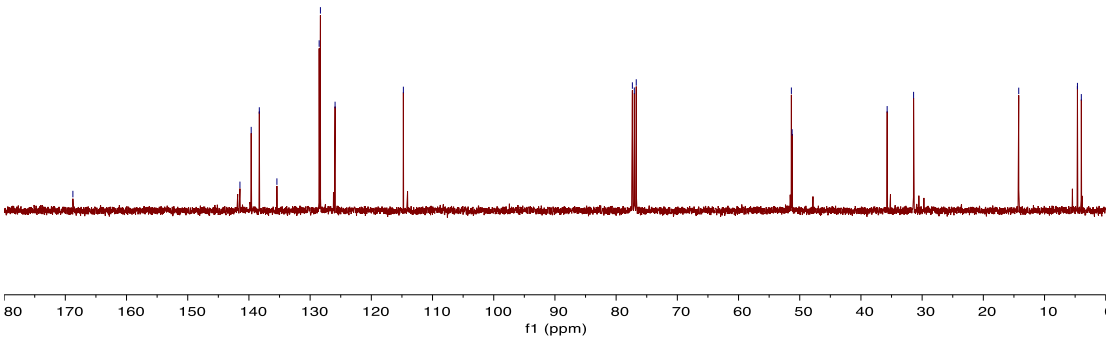
^{1}H NMR 400 MHz $CDCl_3$

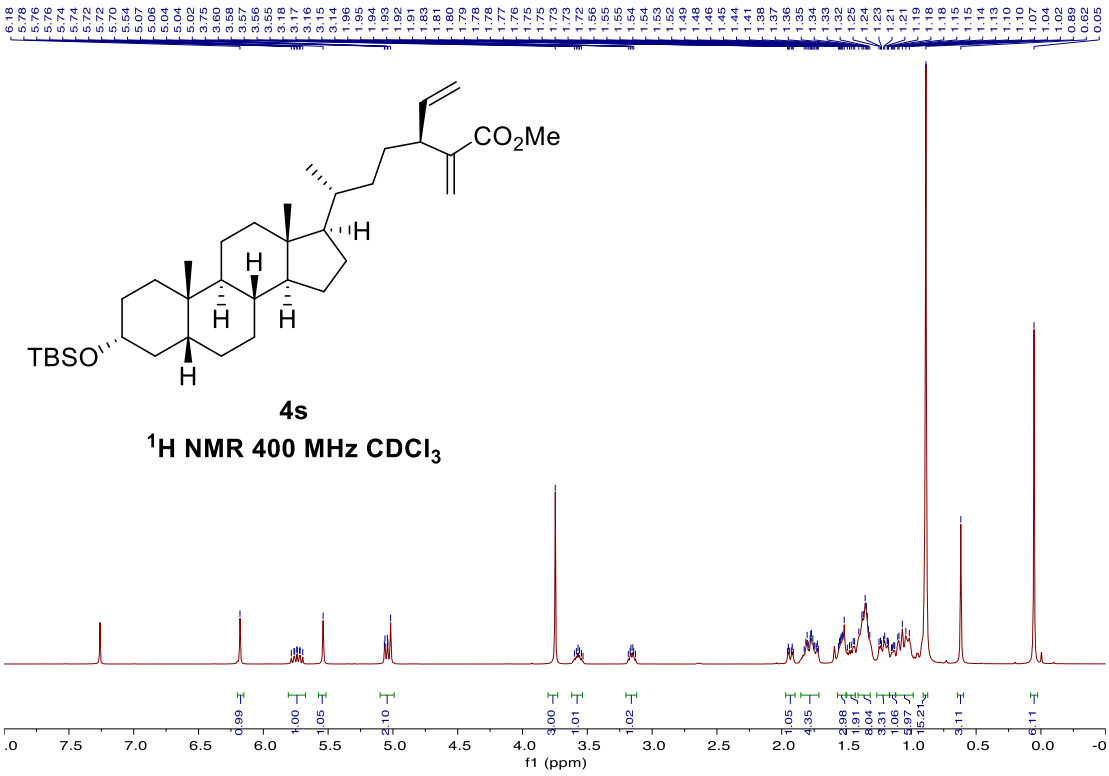


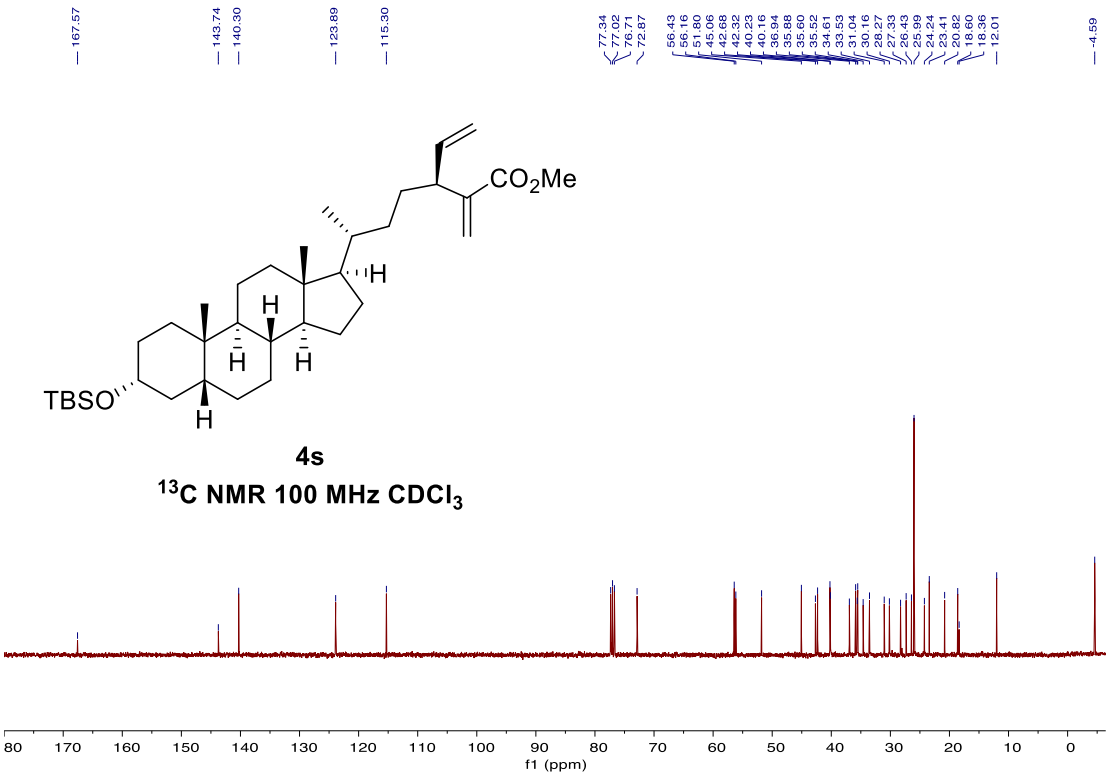


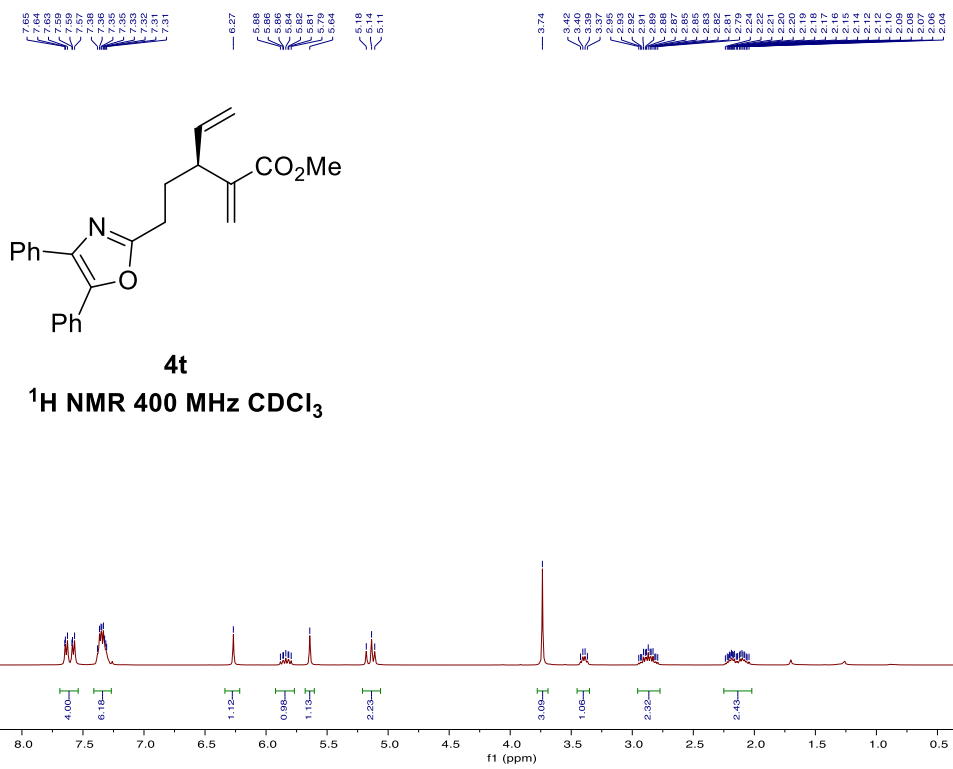
4r'

^{13}C NMR 100 MHz $CDCl_3$



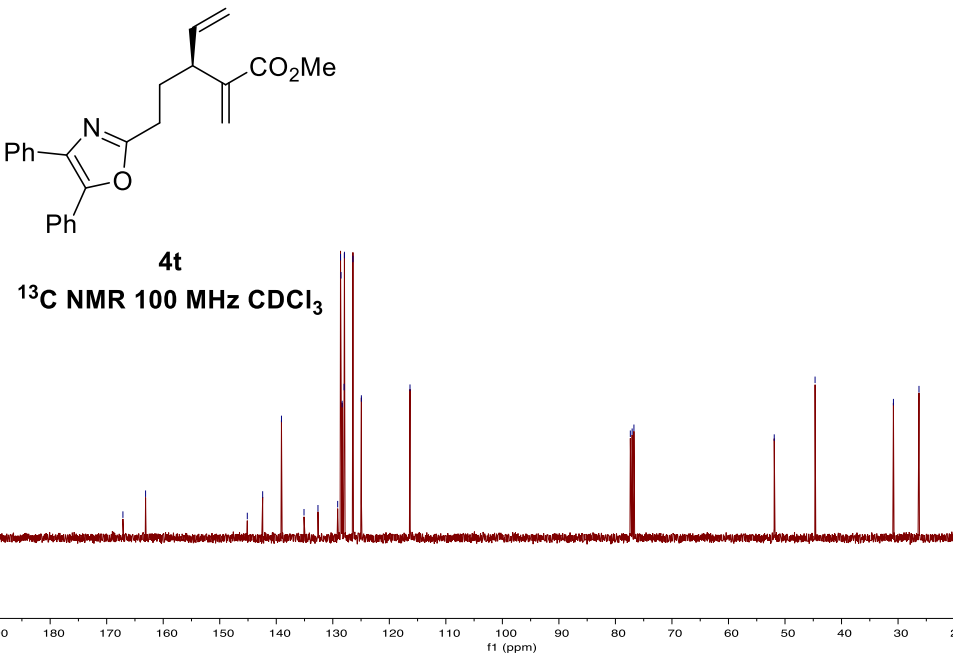

CO2Me
TBSO
H
4s
1H NMR 400 MHz CDCl3
f1 (ppm)


CO2Me
TBSO
H
4s
13C NMR 100 MHz CDCl3
f1 (ppm)



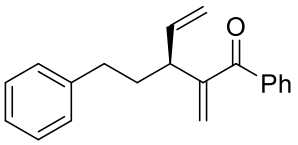
4t

^{1}H NMR 400 MHz $CDCl_3$



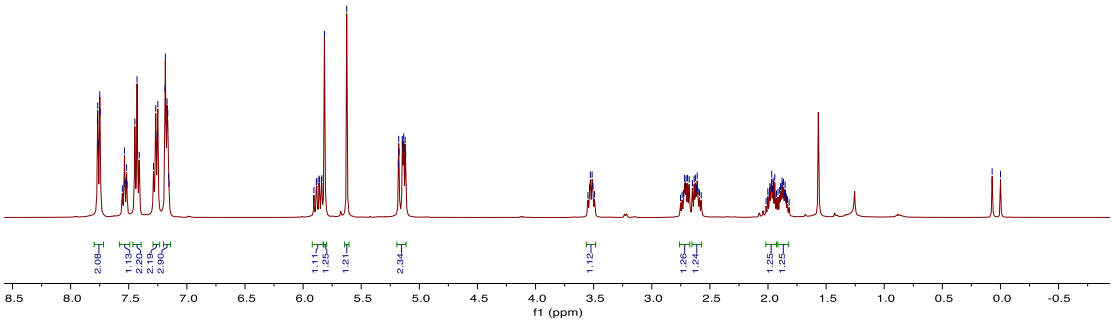
4t

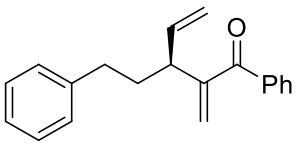
^{13}C NMR 100 MHz $CDCl_3$



4u

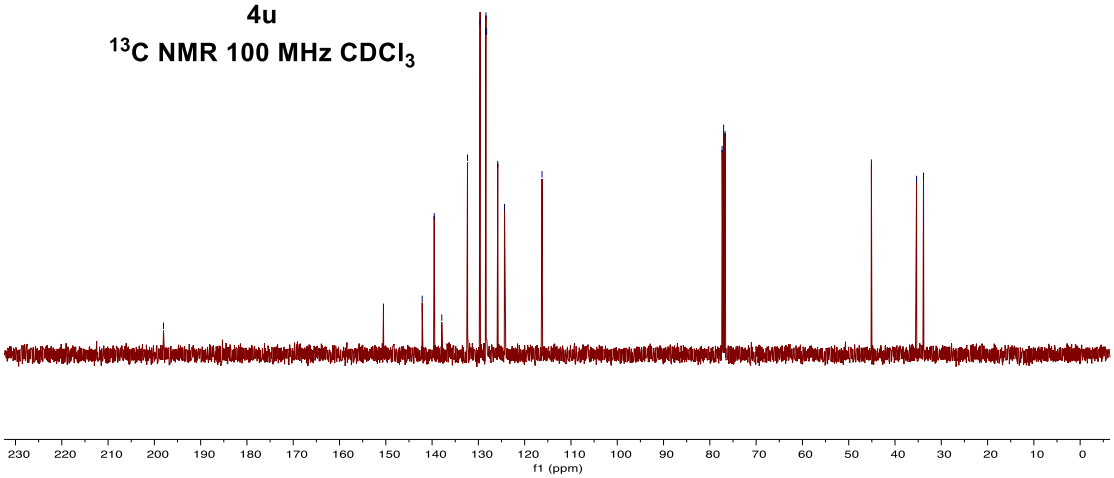
^{1}H NMR 400 MHz $CDCl_3$

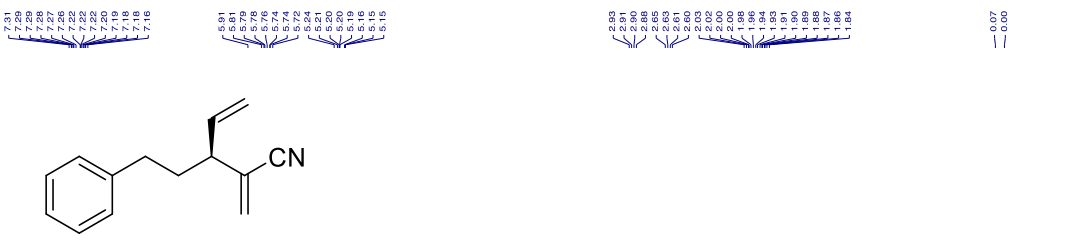




4u

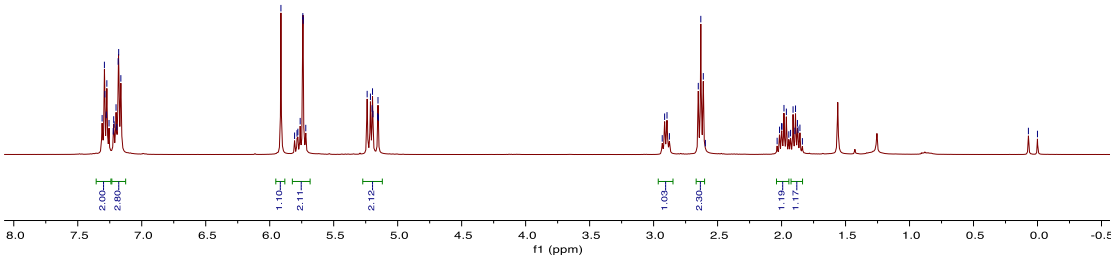
^{13}C NMR 100 MHz $CDCl_3$

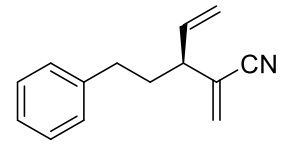




4v

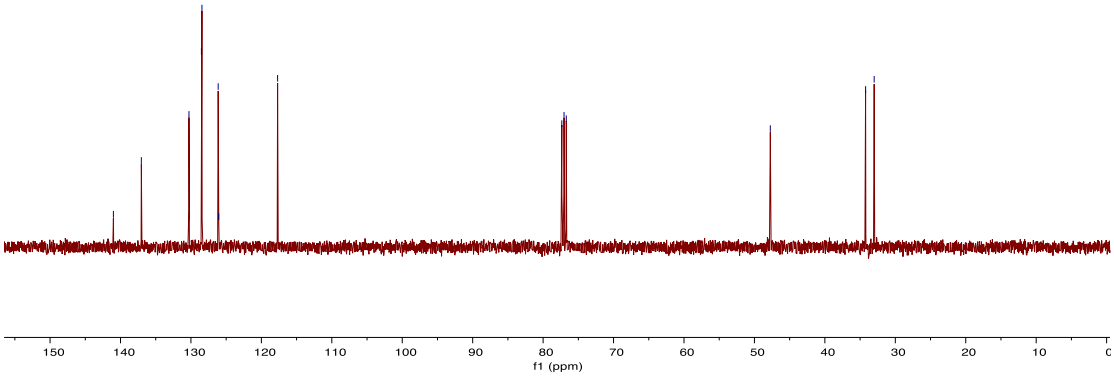
^{1}H NMR 400 MHz $CDCl_3$

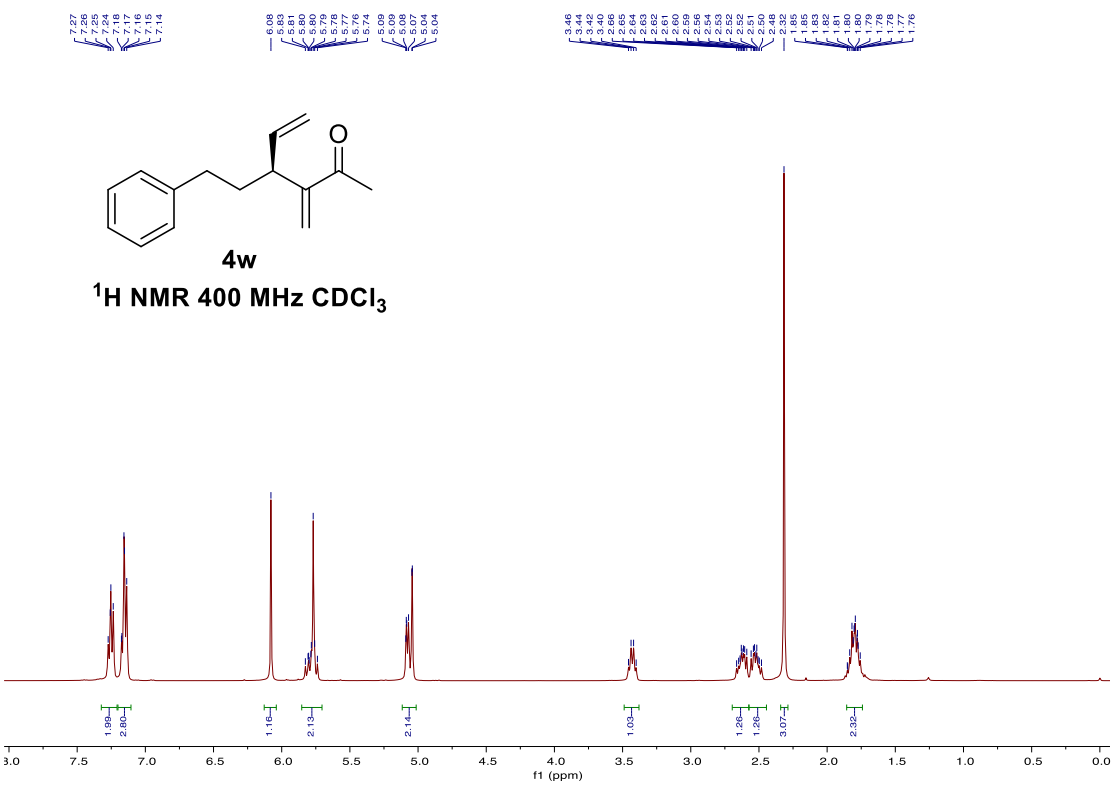


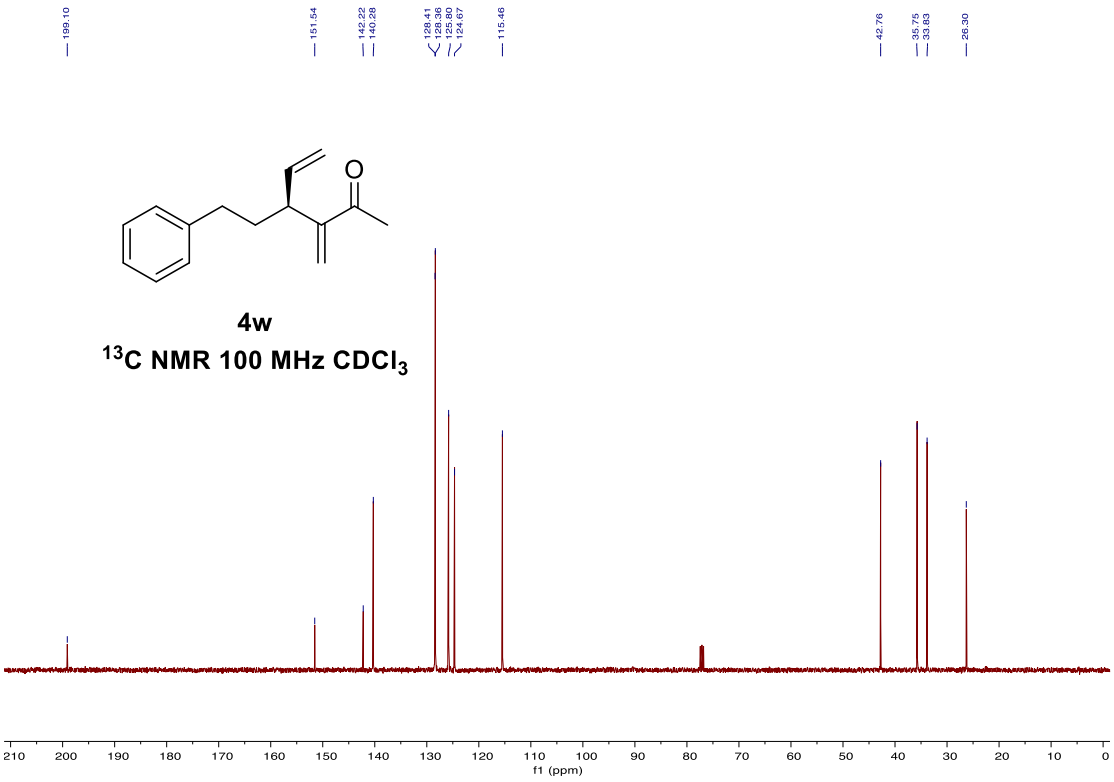


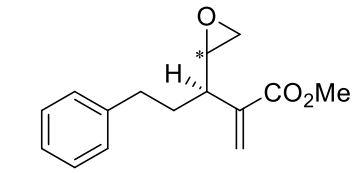
4v

^{13}C NMR 100 MHz $CDCl_3$



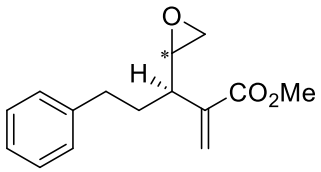

4w
1H NMR 400 MHz CDCl3
f1 (ppm)


4w
13C NMR 100 MHz CDCl3
f1 (ppm)



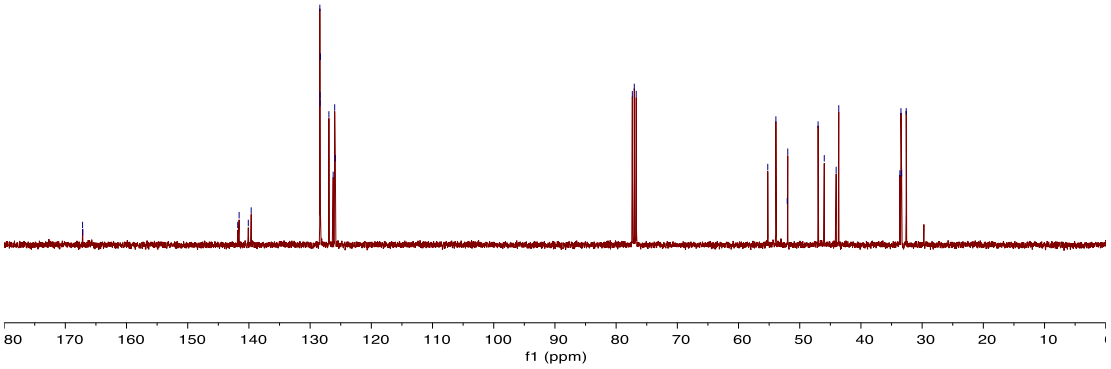
5

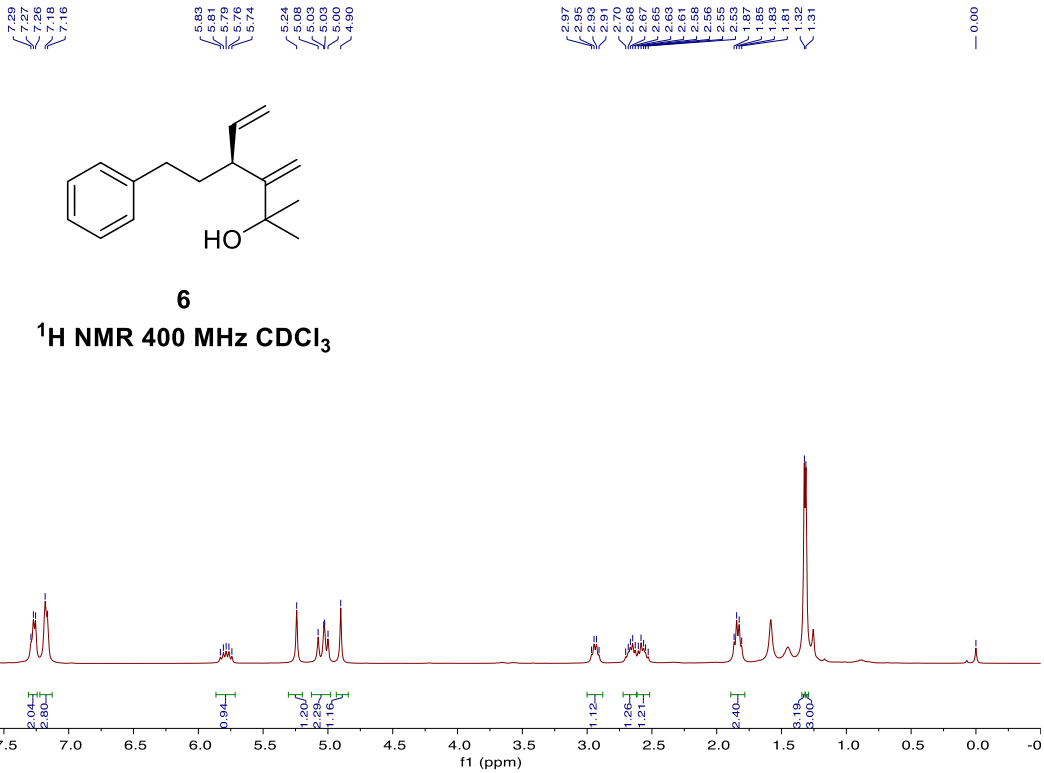
^{1}H NMR 400 MHz $CDCl_3$



5

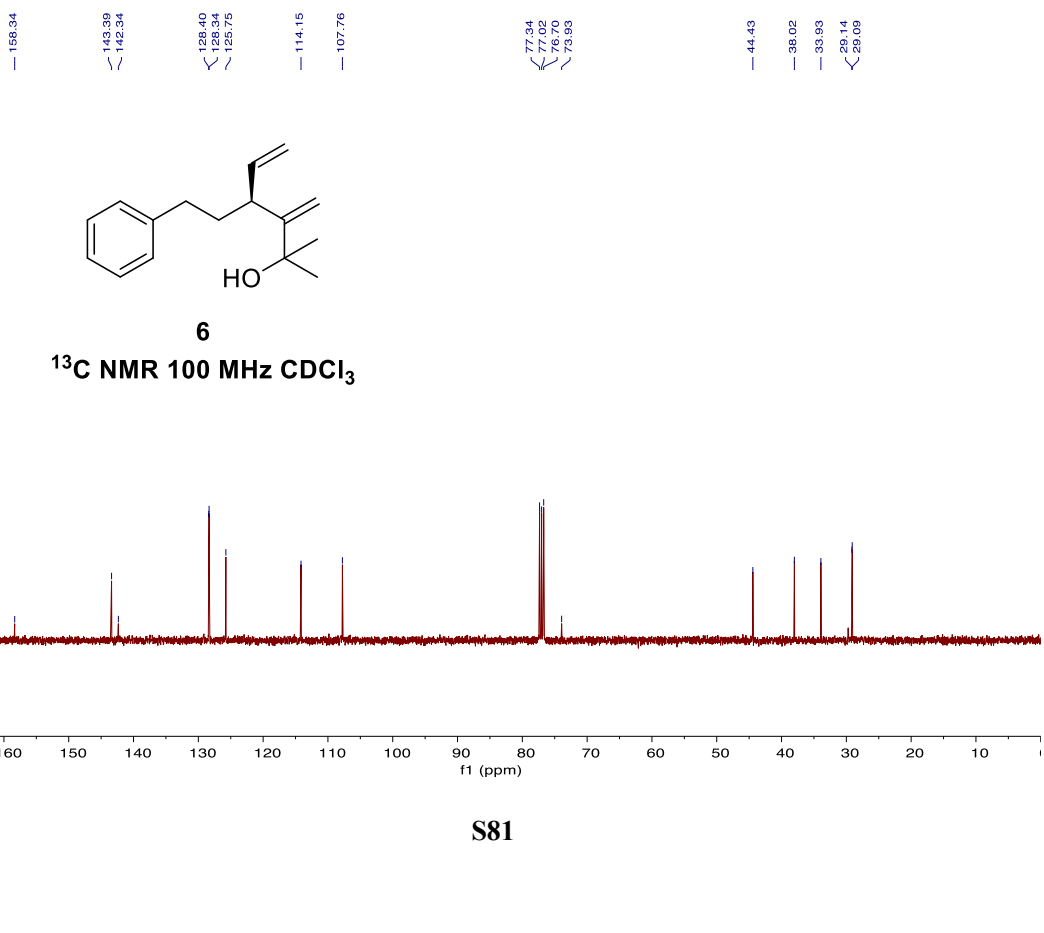
^{13}C NMR 100 MHz $CDCl_3$





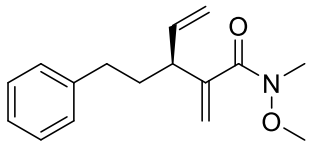
6

^{1}H NMR 400 MHz $CDCl_3$



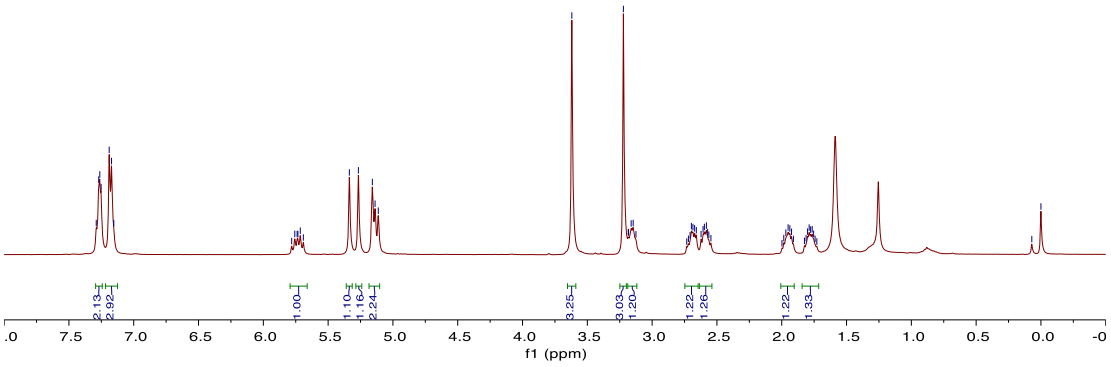
6

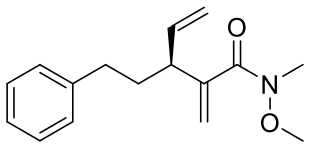
^{13}C NMR 100 MHz $CDCl_3$



7

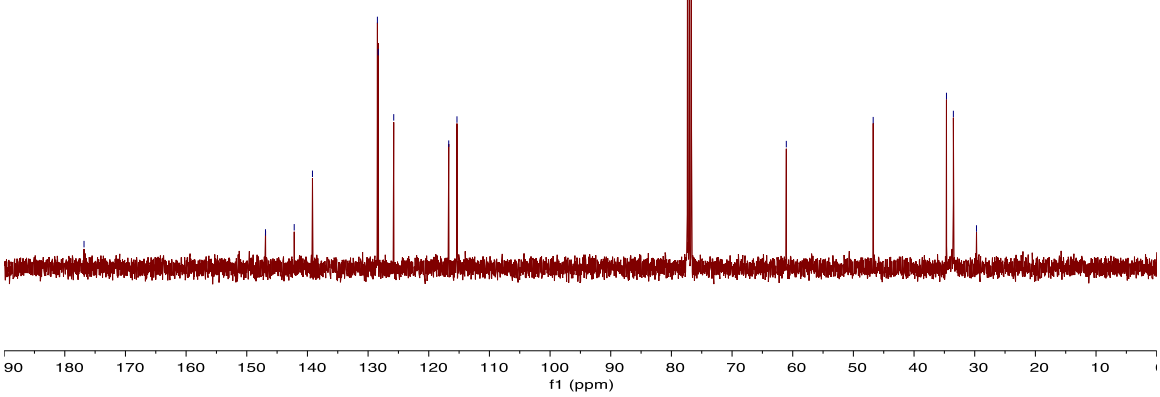
^{1}H NMR 400 MHz $CDCl_3$

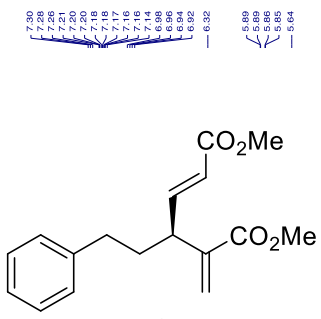




7

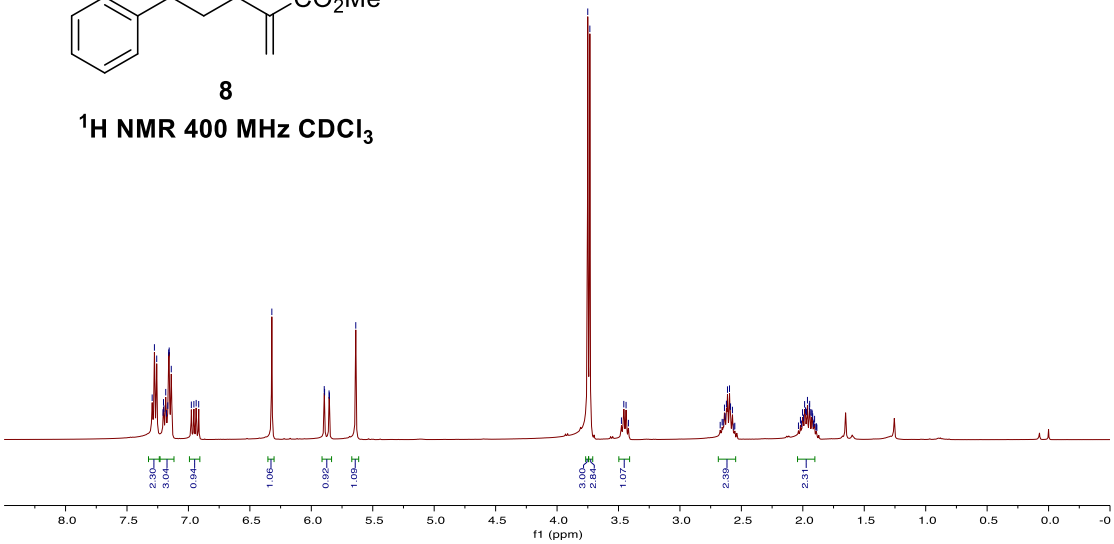
^{13}C NMR 100 MHz $CDCl_3$

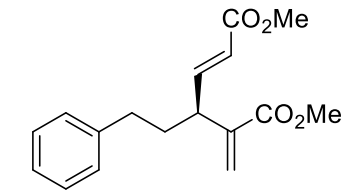




8

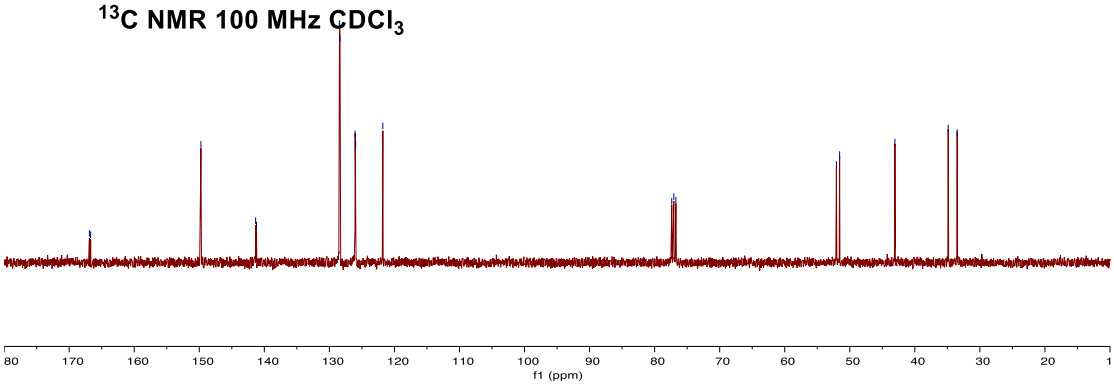
^{1}H NMR 400 MHz $CDCl_3$

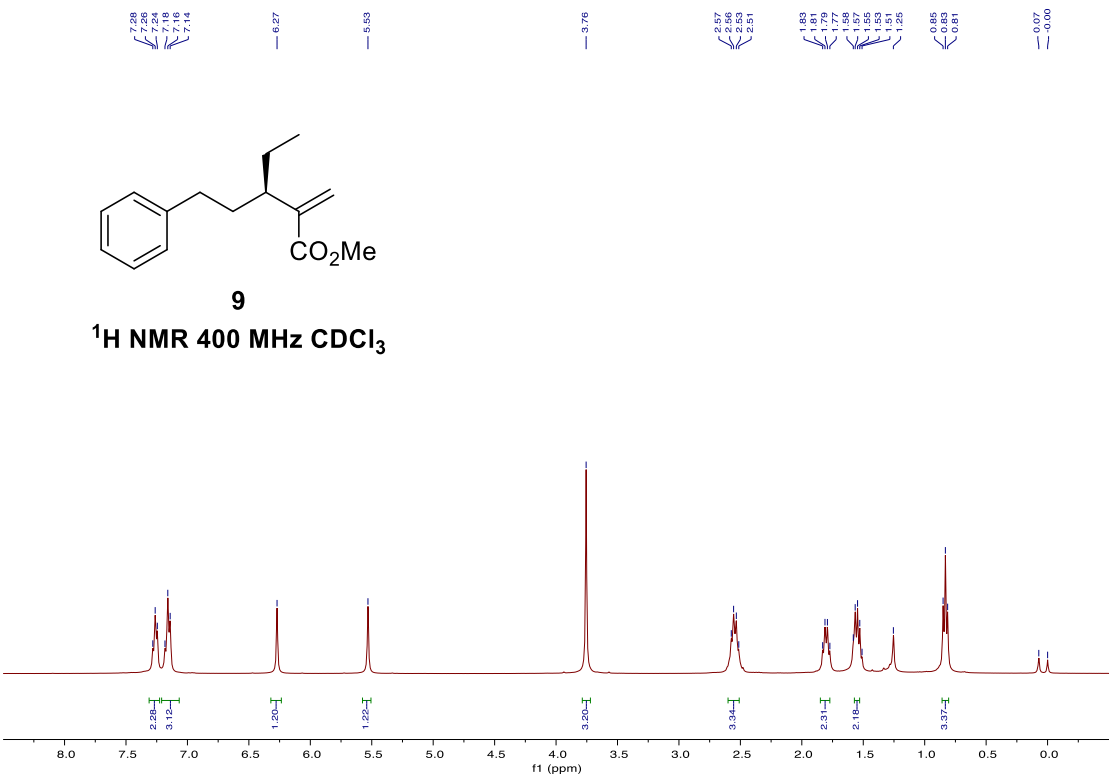




8

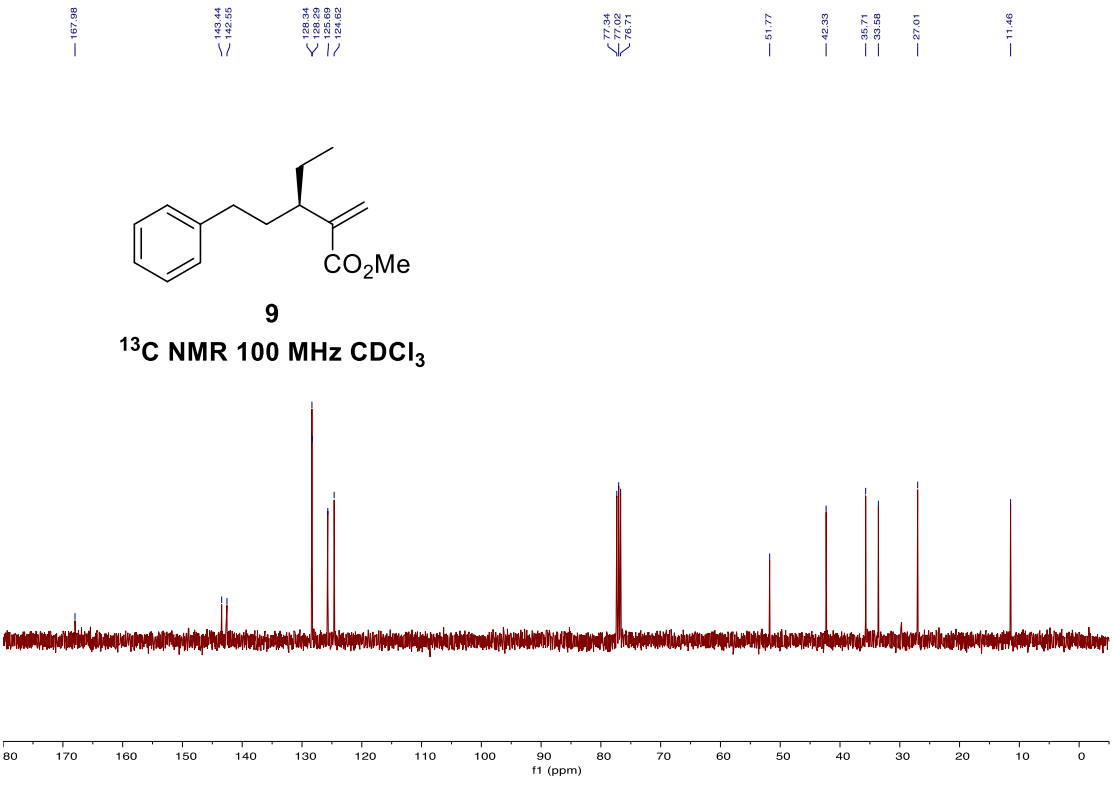
^{13}C NMR 100 MHz $CDCl_3$





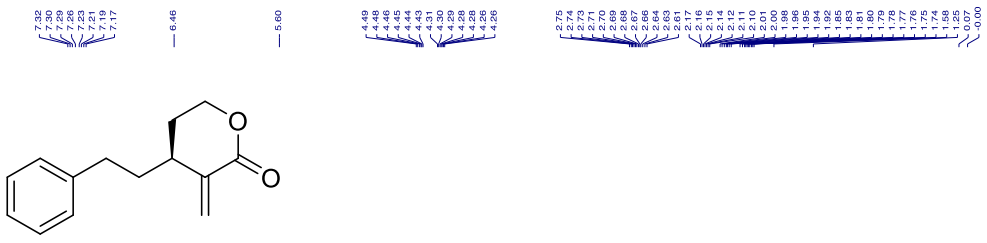
9

^{1}H NMR 400 MHz $CDCl_3$



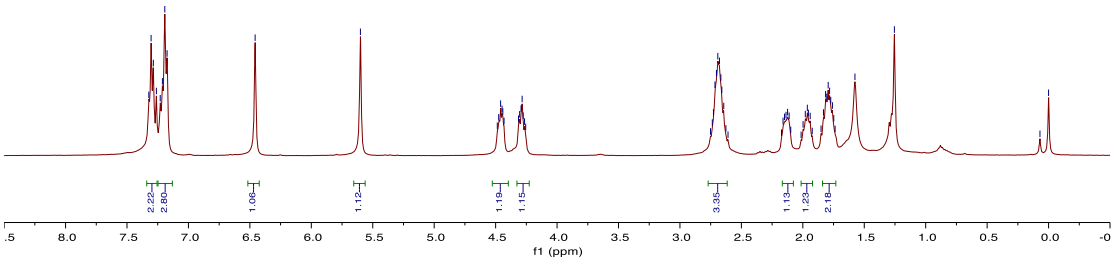
9

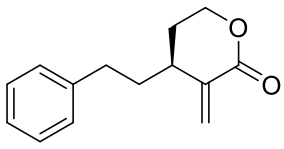
^{13}C NMR 100 MHz $CDCl_3$



11

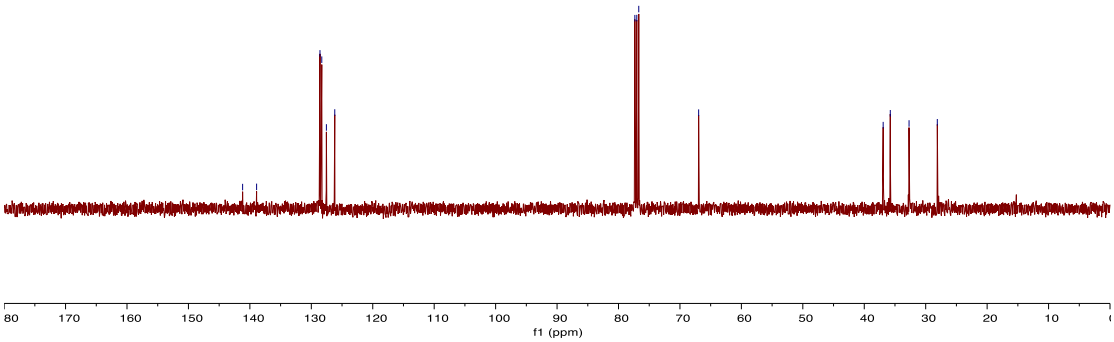
^{1}H NMR 400 MHz $CDCl_3$

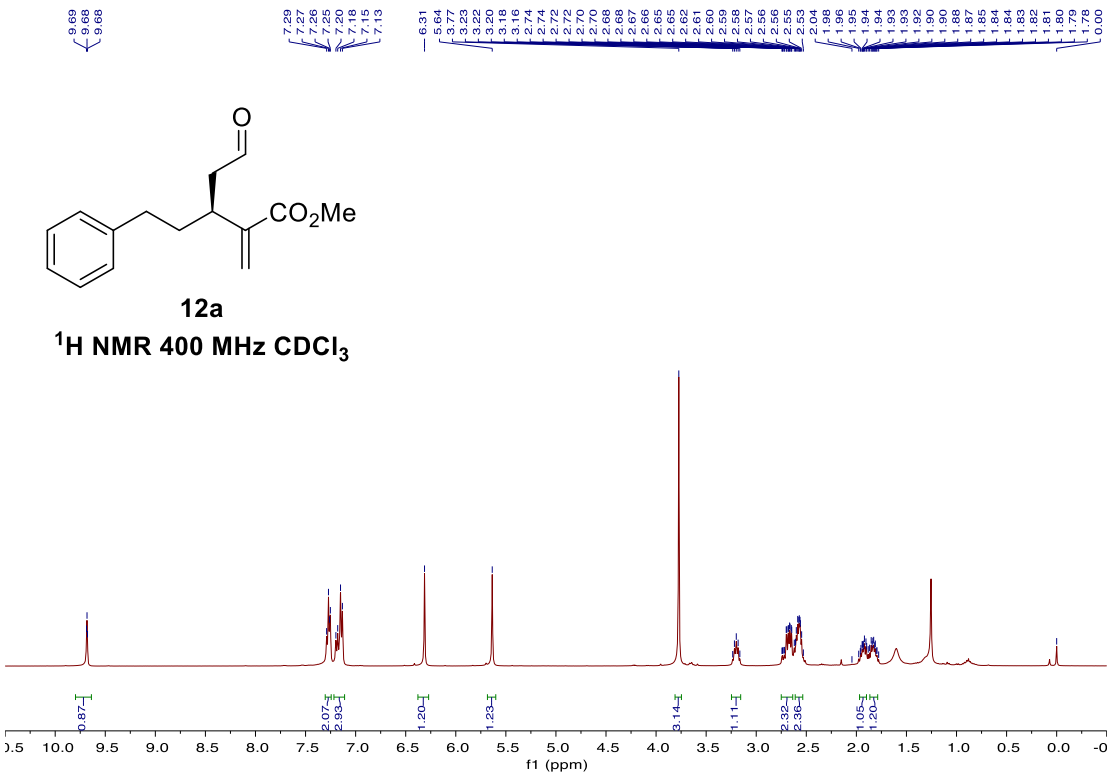




11

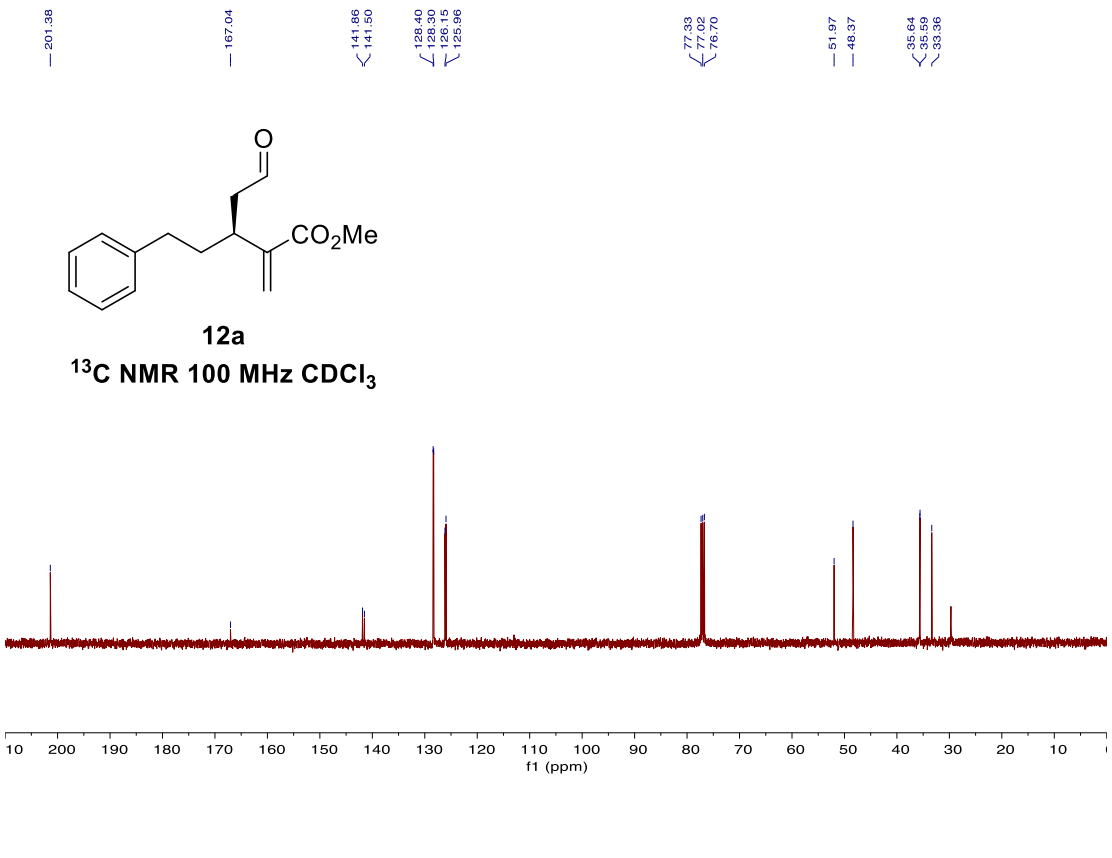
^{13}C NMR 100 MHz $CDCl_3$





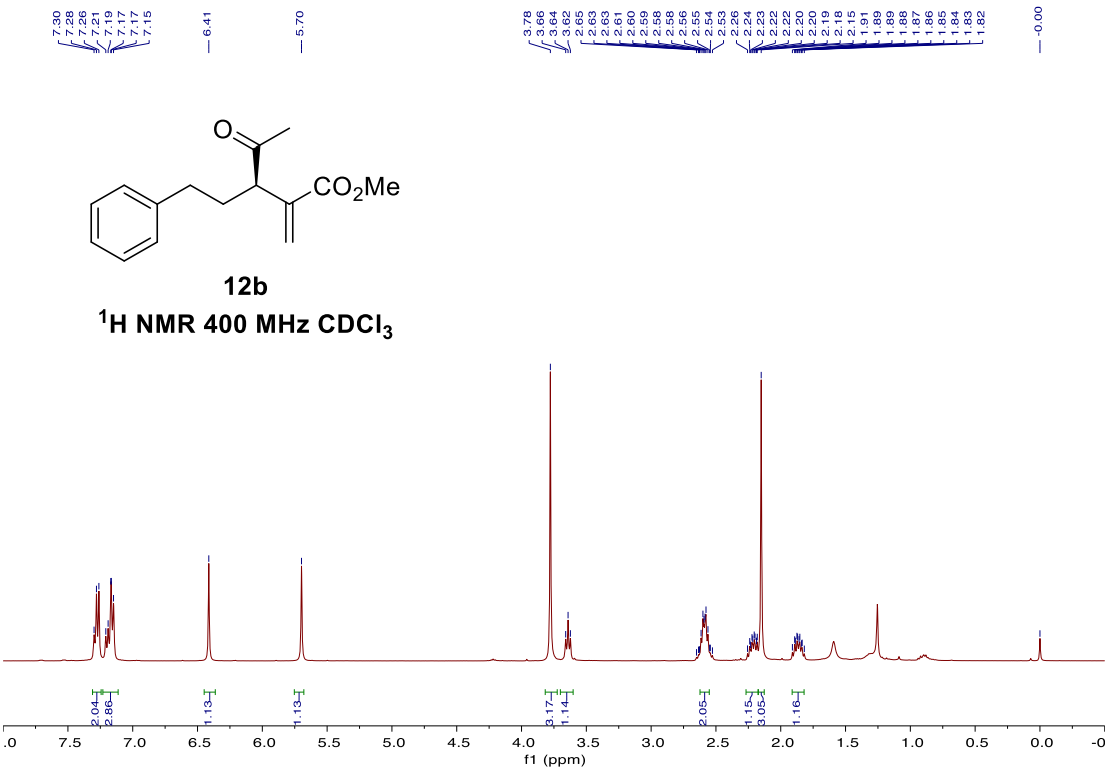
12a

^{1}H NMR 400 MHz $CDCl_3$



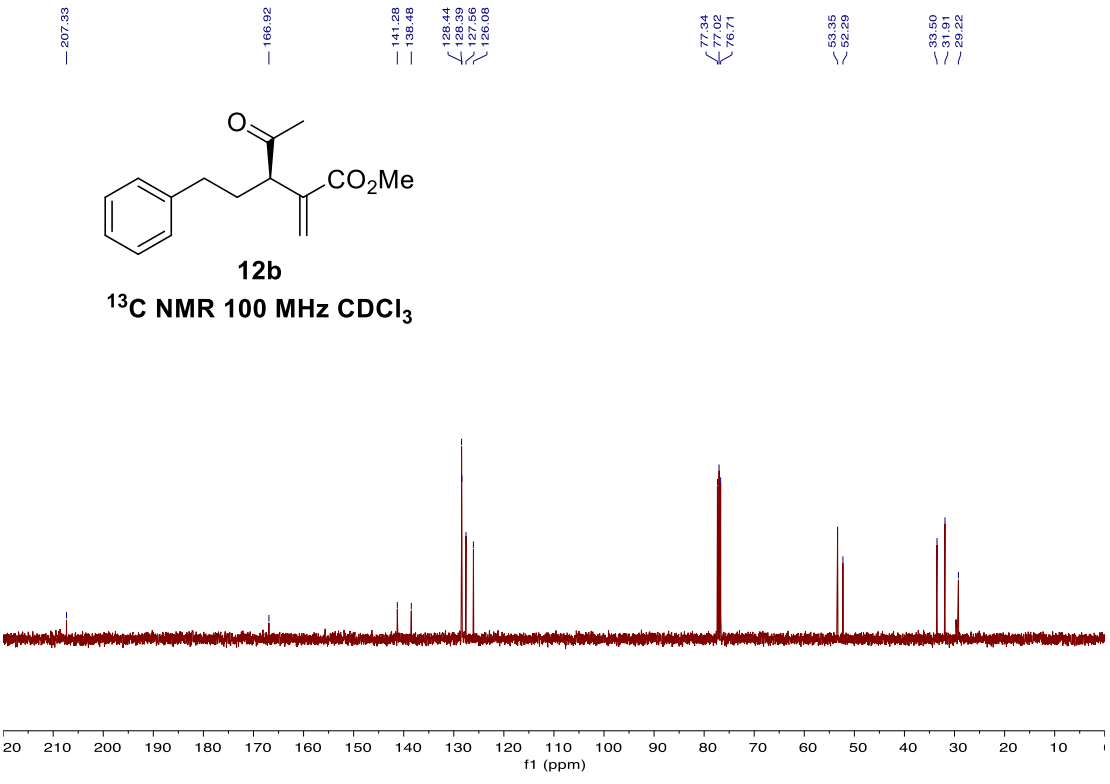
12a

^{13}C NMR 100 MHz $CDCl_3$



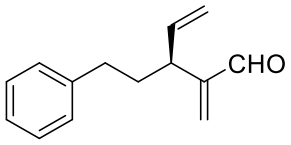
12b

^{1}H NMR 400 MHz $CDCl_3$



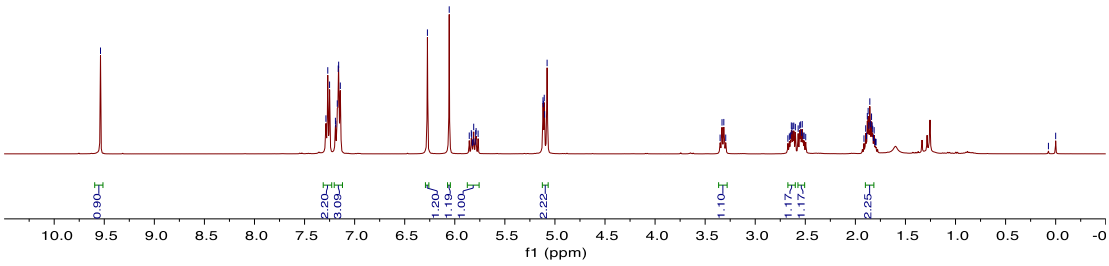
12b

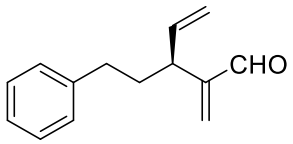
^{13}C NMR 100 MHz $CDCl_3$



14

^{1}H NMR 400 MHz $CDCl_3$





14

^{13}C NMR 100 MHz $CDCl_3$